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Nutrient Cycling in Terrestrial Ecosystems

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Nutrient Cycling in Terrestrial Ecosystems

With 55 Figures

Springer

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Preface

Food production will need to keep increasing substantially to meet the demands of the world's population, which is projected to increase to 8 billion people within the next two decades. Current levels of food production will require doubling by 2030, not only because of the sheer magnitude of the population increase, but also due to increased expectations in many countries as regards diet quality and quantity. This required increase in food production will place significant pressure on existing food-producing ecosystems as well as on their surrounding environments.

Environmental concerns, including conservation of natural ecosystems as well as sustainability of managed ecosystems in agriculture, horticulture, forestry and similar economic activities, have attracted increasing attention around the world in recent decades. A principle that is paramount in ensuring the health and sustainability of ecosystems is nutrient cycling in the soil–water–microbe–plant–animal continuum. Nutrient cycling in the majority of food- and fibre-producing ecosystems depends on the addition of fertilisers. However, most fertilisers are produced from natural minerals, which represent a finite resource. While predictions on how much time we have before such resources run out differ substantially depending on underlying assumptions, we can conclude that for some nutrients (e.g. phosphorus) estimates about longevity of economically viable mineral sources are in terms of decades rather than centuries. Hence, a knowledge of cycling of nutrients in the environment is essential in our attempts to efficiently utilise the finite resources of our planet.

Nutrient Cycling in Terrestrial Ecosystems covers important aspects of nutrient cycling at two different scales: (1) on a small scale and more fundamental scientific level, to present the current state of understanding of processes involved in cycling of nutrients from organic matter and other sources; and (2) at a large (whole-ecosystem) scale, describing cycling of nutrients and relevant impacts in situ as well as in the surrounding environment. The first part of the book covers cycling of carbon (Chapter 1), nitrogen (Chapter 2), phosphorus and sulphur (Chapter 3) and micronutrients (Chapter 4), paying particular attention to the role of root exudates (Chapter 5) and rhizosphere microorganisms (Chapter 6) in facilitating nutrient cycling. In the second part of the book, the authors cover nutrient cycling from the standpoint of the complexity of various ecosystems, emphasising cropping systems (Chapter 7), pastures (Chapter 8), natural grass-

lands (Chapter 9), arid lands (Chapter 10), tundras (Chapter 11) and forests (Chapter 12). Finally, Chapter 13, on modelling of nutrient cycling, integrates available knowledge on fundamental processes as well as on how these processes interact at the ecosystem level.

In covering a range of scales, and in emphasising the multidisciplinary approaches essential to increasing the understanding of the underlying processes and devising practical approaches for maintaining healthy nutrient cycling in native and sustainable managed ecosystems, this book will support scientists and practitioners alike, as well as demonstrating that improving sustainable economic output from managed ecosystems and conservation of natural ecosystems are inseperably linked.

All chapters have been reviewed according to the standards of international scientific journals. We would like to thank the authors for patiently revising the chapters, sometimes repeatedly, to meet these high standards. We would also like to express our thanks to the Editor-in-Chief, Prof. Ajit Varma, and to Jutta Lindenborn of Springer for their dedication, patience and diligence in the production of this book.

Adelaide and Perth   *Petra Marschner*
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Abbreviations

AM	arbuscular mycorrhiza
AM	arbuscular mycorrhizal fungi
ARA	acetylene reduction assay
BNF	biological N fixation
CEC	cation-exchange capacity
DNRA	dissimilatory reduction of NO_3^- to $NH4^+$
DOC	dissolved organic carbon
DON	dissolved organic N
DON	Dissolved organic nitrogen
DON	Dissolved organic nitrogen
DTPA	Diethylenetriaminepentaacetic acid
EDDHA	Ethylenediamine di(o-hydroxyphenylacetic acid)
EDTA	ethylene diaminetetraaminoacetate
FAME	Fatty Acid Methyl Ester
Ggt	*Gaeumannomyces graminis var. tritici*
HUM	humified organic materials
IBP	International Biological Programme
IHP	inositol hexakisphosphate
IOM	inert organic materials
IPCC	Intergovernmental Panel on Climate Change
LCO	lipo-chito-oligosacharide
LMW	low-molecular-weight
MAT	Mean Annual Temperature
MIT	mineralisation-immobilisation turnover
MIT	mineralisation-immobilisation turnover
MIT	mineralisation-immobilisation turnover
Mt	million tonnes
NA	nicotianamine
NAAT	nicotianamine-aminotransferase
NPP	net primary productivity
NUMALEC	Nutrient Management Legislation in European Countries
OM	organic matter
PGPR	Plant growth-promoting rhizosphere microorganism
PLFA	phospholipid fatty acids

PS	Phytosiderophores
PS	phytosiderophores
RPM	resistant plant materials
SIR	substrate induced respiration
SOC	Soil organic carbon
SOM	soil organic matter
SOM	soil organic matter
SON	soluble organic N
TNSC	total nonstructural carbohydrates
VA	vesicular arbuscular
VOC	volatile organic compounds
VOC	volatile organic compounds
XANES	X-ray absorption near-edge structure spectroscopy

1 Composition and Cycling of Organic Carbon in Soil

Jeffrey A. Baldock

1.1
Introduction

Soil organic carbon (SOC) represents a significant reservoir of carbon within the global carbon cycle that has been estimated to account for 1,200–1,550 Pg C to a depth of 1 m and for 2370–2450 Pg C to a depth of 2 m (Eswaran et al. 1995; Lal 2004a). Comparative estimates of organic C contained in living biomass (560 Pg) and atmospheric CO_2-C (760 Pg) (Lal 2004a) indicate that variations in the size of the SOC store could significantly alter atmospheric CO_2-C concentrations. A 5% shift in the amount of SOC stored in the 0–2 m soil profile has the potential to alter atmospheric CO_2-C by up to 16%.

Land-use change can induce emission or sequestration of carbon depending on a range of soil and environmental properties and land management practices. Carbon sequestration in soils is a slow process but may offer the most efficient natural strategy for offsetting increased atmospheric CO_2-C concentrations induced by fossil fuel burning and conversion of natural terrestrial systems to agriculture (Lal 2004a; Metting et al. 1999; Post et al. 1999). It has been suggested that, over the next century, improved land management strategies could sequester up to 150 Pg CO_2-C (Houghton 1995; Lal 2004b; Lal et al. 1998); however, considerable uncertainty exists in such estimates because of an inability to accurately predict the total carbon sequestration potential of soils. Improving our understanding of SOC cycling processes and how these are affected by land management practices will be important to defining future opportunities for carbon sequestration in soils.

In addition to its importance in the global carbon cycle, SOC contributes positively to a range of biological, physical and chemical properties important to defining the potential productivity of a soil (Baldock and Skjemstad 1999;

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Reeves 1997). SOC provides the energy essential to biological processes and, when considered in combination with its associated nutrients (N, P and S), can contribute to the resilience of soil/plant systems. Soil physical properties influenced by SOC content include soil structural form and stability, water retention, and thermal properties. SOC also contributes to defining the cation exchange and buffer capacities of soils. The amount and form of SOC required to make significant contributions to these soil properties varies with the property being considered and the soil type (Baldock and Skjemstad 1999). For example, more carbon may be required to maintain the structural stability of a sandy-loam soil than in a self-mulching clay, yet in terms of provision of energy or nutrient mineralisation, more SOC may be required in the clay-rich soil. Likewise, pieces of plant debris with a high C/N ratio (>40) are likely to have a different effect on net nutrient mineralisation during decomposition processes than well decomposed materials with a low C/N ratio (<40).

Understanding the dynamics of SOC, both in its entirety and its various components, and the influence of environmental and soil properties is essential to adequately characterise the effects of management and land use on fluxes of carbon and soil productivity. In this chapter, the composition of SOC and the factors that define the biological stability and cycling of SOC will be examined. Given this scope, it would not be possible to present an exhaustive review of all relevant studies. Instead, the objective of this chapter was to identify the major soil and environmental properties and processes that influence SOC cycling and provide references that can act as a starting point for further exploration of the concepts presented.

1.2
Composition of Soil Organic Carbon

SOC exists as a heterogeneous mixture of a wide range of organic materials, including individual simple molecules (amino acids, monomeric sugars, etc.), polymeric molecules (e.g. cellulose, protein, lignin, etc.), and pieces of plant and microbial residues composed of a mixture of simple and polymeric molecules bound together into recognisable cellular structures. Plant and microbial residues represent the major parent material from which SOC is formed. The chemical composition of these residues has been reviewed by Kögel-Knabner (2002). Each molecular form of SOC can exist along a continuum from fresh unaltered materials through to materials whose chemical composition has been significantly altered by decomposition processes. In this chapter the term SOC is hereafter used to refer to the entire organic fraction of soils, and various SOC components are defined as delineated by Baldock and Nelson (2000).

Given the compositional variability of SOC, different components of SOC will accumulate or be lost at different rates depending on their accessibility to

decomposition and/or biological stabilisation. Changes in SOC content with time therefore represent the weighted average change in contents of all SOC components. Radiocarbon dating (e.g. Anderson and Paul 1984) and isotopic labelling (e.g. Ladd et al. 1981) experiments clearly demonstrated that different components of SOC turn over at different rates. A variety of chemical and physical fractionation procedures has been developed in an attempt to isolate and characterise relatively "homogeneous" fractions of SOC that exhibit different biological stability.

1.2.1
Chemical Fractionation of SOC

Early attempts at fractionating SOC were chemically based and involved the use of alkaline extraction followed by acidic precipitation (Muller 1887). This fractionation scheme continues to be used to partition SOC into fractions referred to as humic acids, fulvic acids and humin on the basis of solubility in alkaline and then acidic solutions. Radiocarbon dating of SOC in a chernozem revealed that humin and humic acid fractions were older and the fulvic acid fraction was younger than intact SOC (Campbell et al. 1967). Given the mode of extraction and isolation of humic materials from soil and the potential for a variety of inter- and intra-molecular interactions to occur after acidifying alkaline extraction solutions, the probability of mixing older and younger organic species during extraction is high, and complete segregation on an age basis can not be expected.

A second form of chemical fractionation uses various extraction or degradative methodologies considered to be "selective" for given molecular components. Such methodologies are used to identify fractions of SOC with different susceptibilities towards mineralisation based on differences in chemical recalcitrance. Hydrolysis with 6 M HCl or methanesulfonic acid can be used to quantify the proportion of SOC associated with proteins, amino acids and amino sugars (Appuhn et al. 2004; Friedel and Scheller 2002; Martens and Loeffelmann 2003). Hydrolysis with sulphuric acid has been used to quantify the fraction of SOC attributable to carbohydrate structures (Martens and Loeffelmann 2002; Rovira and Vallejo 2000). The proportion of lignin in SOC has been quantified using a variety of methods that attempt to either isolate the intact lignin molecule (Tuomela et al. 2000) or quantify the monomeric species released (Chefetz et al. 2002; Leifeld and Kögel-Knabner 2005). A range of organic solvent extraction techniques have been developed to quantify the amount of lipid and lipid-like carbon in soils (Poulenard et al. 2004; Rumpel et al. 2004).

Although these molecular extraction or degradation methods are capable of identifying relative differences between different samples of SOC, due to incomplete extraction and non-selective action, absolute quantities should be considered as approximate. This issue is well exemplified by the work of Preston et

al. (1997), where a combination of extraction and degradation techniques were used in a "proximate" analysis procedure to fractionate carbon associated with various types of litter. ^{13}C NMR spectroscopy clearly demonstrated that the Klason lignin fraction contained significant amounts of non-lignin carbon.

Chemical fractionation procedures have also been used to allocate SOC to labile and recalcitrant fractions without attempting to define molecular composition. Two examples are the use of HCl hydrolysis and permanganate oxidation. In HCl hydrolysis, carbon retained in the residue after hydrolysis is considered recalcitrant, whilst carbon contained in the hydrolysate is considered labile. This was substantiated by radiocarbon dating HCl hydrolysis residues of 65 surface and subsurface soils (Leavitt et al. 1996). SOC in the hydrolysis residues was older than that present in the non-hydrolysed soils by an average of 1,800 years. A similar result was obtained by Paul et al. (2001), where hydrolysis residues were found to be 1,340 years older on average than total SOC in surface soils and 5,584 years older in subsoils. It is important to recognise that different biomolecules have different susceptibilities to acid hydrolysis, and the presence of acid hydrolysis resistant biomolecules, such as lignin, may lead to hydrolysis residues having younger radiocarbon ages.

Quantification of the proportion of SOC oxidised in permanganate solutions of increasing concentration has also been used to define fractions of SOC with different labilities (Blair et al. 1995). Permanganate concentrations of 0.033, 0.167 and 0.333 mM have typically been employed under the assumption that more labile fractions of SOC are oxidised at lower permanganate concentrations. The existence of strong correlations between the amounts of SOC oxidised at each permanganate concentration and between permanganate-oxidisable carbon and total SOC (Lefroy et al. 1993) question the selectivity of this approach towards identifying differentially labile SOC components (Blair et al. 1995; Mendham et al. 2002). It has also been shown that permanganate-oxidisable SOC had little relation to the labile pool of SOC respired over a 96-day incubation period (Mendham et al. 2002). These results, when considered with the absence of a clear definition of the chemical nature of SOC components attacked by each permanganate solution, limit the utility of this technique in helping to delineate biologically labile and recalcitrant fractions of SOC.

1.2.2
Physical Fractionation of SOC

The majority of organic carbon input to soils is in the form of plant residues. As these residues decompose and become mixed into mineral soil layers, particle size is reduced and the potential for interaction with soil minerals increases. Methods that fractionate SOC on the basis of particle size and density can therefore be used to isolate components of SOC that have different turnover times (Christensen 1996a, 2001). A prerequisite to separating SOC into primary parti-

cles with different sizes or densities is complete dispersion. To minimise chemical alteration, inclusion of strong acid, alkali or chemical oxidant pre-treatments is avoided, and a combination of sodium saturation and physical dispersion methods is used (Skjemstad et al. 2004). Initial approaches to SOC fractionation tended to complete the dispersion process first in the fractionation scheme (Baldock et al. 1992). However, Golchin et al. (1994a) and Amelung amd Zech (1999) showed that recovery of coarse particulate organic matter decreased with increasing sonification time or energy and resulted in a redistribution of carbon into finer particle size classes.

To avoid a redistribution of coarse SOC into finer size classes, it is now recommended that a two-step process be followed (Amelung and Zech 1999). In the first step, the free particulate SOC is removed either prior to dispersion or subsequent to minimal dispersion in which the integrity of soil aggregates is maintained. A second more vigorous dispersion treatment is then used to release pieces of SOC occluded within soil aggregates and SOC adsorbed onto mineral surfaces. In its simplest form this approach results in the isolation of three forms of SOC: (1) free pieces of organic residue found between soil particles and aggregates (inter-aggregate SOC), (2) occluded pieces of organic residue found within aggregations of soil particles (intra-aggregate SOC), and (3) organic matter strongly bound to mineral particle surfaces (mineral-associated SOC).

The rate of turnover of SOC found in different particle size classes has been examined using $\Delta^{14}C$ measurements. Trumbore and Zheng (1996) determined the $\Delta^{14}C$ content of 2,000–63 µm, 63–2 µm and <2 µm fractions of soils. After normalisation of the $\Delta^{14}C$ values to those measured for the 2,000–63 µm fraction (Fig. 1.1a), relative changes associated with decreases in particle size ranged from a depletion (in sample BS-7) through to an enrichment (in sample NS-13) of ^{14}C, suggesting that the age of SOC can either increase or decrease in progressing from coarse to fine particles. Schöning et al. (2005) measured the percentage of modern carbon in the Ah horizons of Luvisols, Leptosols and Phaeozems under a European beech (*Fagus silvatica* L.) forest and found a consistent trend of decreasing amounts of modern SOC with decreasing particle size (Fig. 1.1b).

Kahle et al. (2003) used $\Delta^{13}C$ and $\Delta^{14}C$ measurements to assess the extent of decomposition and turnover times of SOC associated with fine (<0.2 µm) and coarse (0.2–2 µm) clay fractions of illitic soils. Fine clay organic carbon was more enriched with ^{13}C and ^{14}C, suggesting a greater extent of microbial processing but a shorter turnover time than coarse clay organic carbon. Enrichments in ^{13}C and a decrease in C/N ratio with decreasing particle size were also observed by Amelung et al. (1999). The general lack of consistency with respect to changes in ^{13}C and ^{14}C enrichment with decreasing particle size suggests that different processes of SOC stabilisation operate in different soils and that relatively young SOC may be stabilised against mineralisation.

The application of density fractionation, either independently or combined with particle size fractionation methods, has also been used to isolate and characterise SOC fractions with different labilities. Trumbore and Zheng (1996)

(a)

(b)
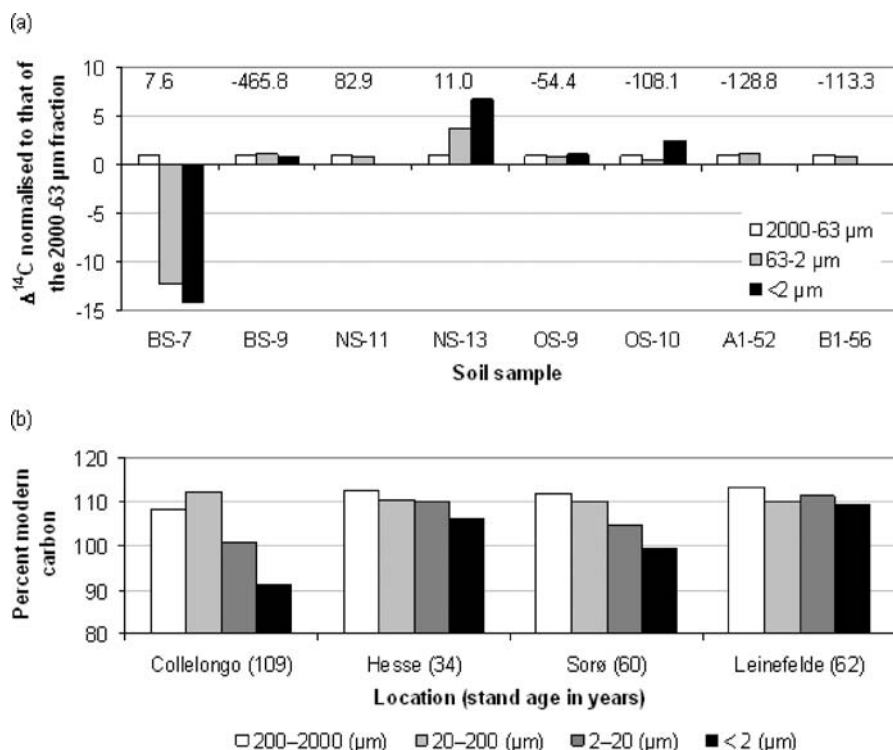
Fig. 1.1 a Relative change in $\Delta^{14}C$ value of organic carbon associated with 2,000-63 μm, 63-2 μm and <2 μm particle size fractions isolated from eight different soil samples after normalisation against the $\Delta^{14}C$ value of the 2,000-63 μm fraction (Trumbore and Zheng 1996). Values given above bars associated with each soil sample present the $\Delta^{14}C$ value obtained for the 2,000-63 μm fractions. **b** Changes in the percentage of modern soil organic carbon (SOC) associated with particle size fractions obtained from soil under beech (*Fagus sylvatica* L.) forests (Schöning et al. 2005)

found that SOC in dense soil fractions (>2.0 g cm^{-3}) was more depleted in ^{14}C and therefore older than that found in less dense fractions (<2.0 g cm^{-3}). John et al. (2005) determined the $\Delta^{13}C$ of four density fractions isolated from silty soils under maize: (1) free particulate organic matter <1.6 g cm^{-3} (fSOM$_{<1.6}$), (2) light occluded particulate organic matter <1.6 g cm^{-3} (oSOM$_{<1.6}$), (3) dense occluded particulate organic matter 1.6–2.0 g cm^{-3} (oSOM$_{1.6-2.0}$) and (4) mineral-associated soil organic matter >2 g cm^{-3} (mSOM$_{>2.0}$) and then calculated the mean age of the C in each pool (Table 1.1). The decreasing C/N ratio measured in progressing from the fSOM$_{<1.6}$ through to the mSOM$_{>2.0}$ fractions was suggested to indicate an increase in the degree of degradation and humification. The mean age of SOC in these fractions and the values obtained for percent modern carbon (Rethemeyer et al. 2005) did not follow the same trend, suggesting that the oldest carbon in a soil may not be the most decomposed.

Table 1.1 Properties of the organic matter associated with soil density fractions isolated from the surface soil of a maize trial at Rotthalmünster (John et al. 2005; Rethemeyer et al. 2005). *SOC* Soil organic carbon

Density fraction[a]	% of SOC	C/N ratio	$\Delta^{13}C$ (‰)	Mean age[b] (years)	Modern C[c] (%)
$fSOM_{<1.6}$	4.1	19	−17.3	22	103
$oSOM_{<1.6}$	1.0	19	−23.9	83	98
$oSOM_{1.6–2.0}$	8.1	13	−22.0	49	103
$mSOM_{>2.0}$	86.8	7.5	−22.1	63	103

[a] $fPOM_{<1.6}$: free particulate organic matter <1.6 g cm^{-3}, $oPOM_{<1.6}$: light occluded particulate organic matter <1.6 g cm^{-3}, $oPOM_{1.6–2.0}$: dense occluded particulate organic matter 1.6–2.0 g cm^{-3}, $mOM_{>2.0}$: mineral-associated soil organic matter >2 g cm^{-3}
[b] Mean ages were calculated from changes in carbon content and $\Delta^{13}C$ (John et al. 2005)
[c] Percent modern carbon data was calculated from $^{14}C/^{12}C$ ratios with 100 pMC = 1950 AD (Rethemeyer et al. 2005)

Baisden et al. (2002) measured C/N ratios, $\Delta^{13}C$, $\Delta^{15}N$, and $^{14}C/^{12}C$ of soil organic matter isolated in free particulate organic matter ($fSOM_{<1.6}$), three density fractions of occluded organic matter ($oSOM_{<1.6}$, $oSOM_{1.6–1.85}$, $oSCO_{1.85–2.2}$) and mineral-associated organic matter ($mSOM_{>2.2}$) from soils of different ages. Generally, C/N ratios decreased and $\Delta^{13}C$ and $\Delta^{15}N$ values increased in progressing from the $fSOM_{<1.6}$ through to the $mSOM_{>2.2}$ fractions irrespective of soil age, indicating an increase in extent of decomposition with increasing density. In the young soil (<200,000 years), these changes were not associated with an increase in $\Delta^{14}C$-derived residence times other than for the $fSOM_{<1.6}$ fractions that were much younger. However, a progressive increase in $\Delta^{14}C$-derived residence times with increasing density and extent of decomposition was noted for the oldest soil (1–3 million years).

Swanston et al. (2005) used a simpler density fractionation scheme to isolate three types of SOC ($fSOM_{<1.7}$, $oSOM_{<1.7}$ and $mSOM_{>1.7}$) from a forest soil receiving vegetative residues inadvertently labelled with ^{14}C and an unlabelled near-background site. The occluded fraction of Swanston et al. (2005) represents the sum of the occluded fractions differentiated by John et al. (2005) and Baisden et al. (2002). Changes in C/N ratio and $\Delta^{14}C$ values at the unlabelled background site were consistent with those measured by Baisden et al. (2002), with the exception of a higher C/N ratio in the occluded SOC fraction. Differences in SOC content, C/N ratio and $\Delta^{14}C$ of the fractions isolated from the ^{14}C-labelled soil indicated that free particulate SOC was the most active fraction and also most responsive to C inputs subsequent to the labelling event. The occluded particulate SOC fraction appeared to be less dynamic with a minimal entry of ^{14}C since the labelling event. Based on ^{13}C NMR analyses (Golchin et al. 1994a; Poirier et al. 2005; Sohi et al. 2001, 2005), occluded SOC is more degraded compared to free

particulate SOC; however, this is not consistent with the higher C/N ratios measured by Swanston et al. (2005). Such high C/N ratios would be consistent with the presence of a significant amount of charcoal C, which could mask the entry of new labelled ^{14}C into this pool based on Δ^{14}C measurements alone. A significant movement of new labelled ^{14}C into the dense mineral-associated SOC fraction was also measured. The depleted ^{14}C signature of this dense fraction at the near-background control site suggested that, at the ^{14}C labelled site, the dense fraction consisted of at least two different pools of SOC: a fast cycling pool and an older, more stable, pool. The presence of a labile pool of carbon within the dense mineral-associated SOC fraction is supported by the lack of a difference in rate of carbon respiration from free particulate and dense mineral-associated SOC over the first 120 days of an incubation study (Swanston et al. 2002).

Irrespective of whether fractionations of SOC are completed on the basis of particle size, density, or a combination thereof, it is essential that any potential for redistribution of SOC amongst the fractions is minimised. It is evident that, although general trends of increasing extent of decomposition and age are associated with decreasing particle size and increasing density, significant perturbations to these sequences may occur. Protection of young chemically labile organic carbon against biological attack through interactions with soil mineral components, and the presence of relatively inert and potentially old charcoal may account for at least a portion of these perturbations. Combining assessments of chemical composition with measures of isotopic composition and SOC age would be most instructive in elucidating the mechanisms responsible for quantifying the cycling of organic carbon in soils.

1.3
Consistency between SOC Fractionation Methods and Pools of SOC in Simulation Models

SOC simulation models [e.g. Rothamsted (Jenkinson et al. 1987), Century (Parton et al. 1987) and APSIM (McCown et al. 1996)] are used to predict the influence of management and climate change on fluxes and stocks of soil carbon. Most SOC simulation models are based on a series of conceptual SOC pools with rapid (annual), moderate (decadal) and slow (millennial) rates of turnover. Although such models have been used successfully to simulate changes in total SOC contents, their ability to identify the underlying mechanism(s) accounting for SOC change is weak and difficult to test. Developing a capability to replace the conceptual pools of SOC found in models with measurable pools offers several advantages: (1) internal verification of appropriate allocations of SOC to pools, (2) greater mechanistic understanding of the implication of management and environment on the components of SOC most affected, and (3) improved confidence in simulation outcomes. Most attempts to define measurable frac-

tions of SOC that can be incorporated into simulation models have focused on the use of physical fractionation techniques. A suitable fractionation procedure should be capable of isolating and quantifying the allocation of SOC to pools that differ significantly in biological availability.

Christensen (1996b) proposed a revised model structure that included measurements of water-soluble SOC (readily decomposable), SOC associated with microbial biomass, light-fraction SOC (free pieces of plant residue not associated with mineral particles or aggregates), intra-aggregate SOC (particulate organic materials contained within aggregates), inert SOC (dominated by charcoal) and SOC associated with mineral surfaces. Sohi et al. (2001) proposed a simpler scheme that isolated only three fractions: free (fSOM$_{<1.7}$), intra-aggregate (oSOM$_{<1.7}$) and mineral-associated (mSOM$_{>1.7}$). In subsequent studies (Poirier et al. 2005; Sohi et al. 2005), the 1.7 g cm^{-3} density solution used in the fractionation process was replaced by a 1.8 g cm^{-3} solution. On the basis of differences in chemical composition defined by a range of spectroscopic and wet chemical oxidation techniques, Sohi et al. (2005) and Poirier et al. (2005) suggested that the biological reactivity of each SOC density fraction would differ and that the proposed method of density fractionation could form a basis for measurable SOC fractions in simulation models. However, biological availability of carbon in each fraction was not assessed. In addition, no attempt was made to substitute the measurable pools of C into a working carbon simulation model to demonstrate the utility of this proposal.

SOC simulation models often contain an "inert" pool of carbon that does not actively cycle. The cross polarisation ^{13}C NMR spectra presented for the occluded fractions of SOC isolated by density fractionation (Poirier et al. 2005; Sohi et al. 2001, 2005) all contained significant signal intensity in the aryl-C chemical shift region, especially the occluded intra-aggregate SOC fraction of the silty clay loam (Sohi et al. 2001). The distribution of aryl-C signal intensity in the occluded SOC fractions was consistent with that noted for charcoal derived from wood and for charcoal found in soils (Baldock and Smernik 2002; Skjemstad et al. 1999b, 2002), indicating a variable contribution of charcoal carbon to these fractions. It is also important to note that ^{13}C NMR spectra acquired using a cross polarisation analysis detect <50% of the total charcoal C present in a sample (Baldock and Smernik 2002). Actual contributions of charcoal C to the density fractions may therefore be much greater than indicated by the presented ^{13}C NMR spectra.

Skjemstad et al. (1999b) devised a method of estimating the charcoal carbon content of soils by correcting cross polarisation ^{13}C NMR spectra obtained after a photo-oxidation process for the presence of lignin and low cross polarisation NMR observability. A significant amount of charcoal found in soils has a small particle size (<53 μm) (Skjemstad et al. 1998). The potential therefore exists for charcoal to move vertically and accumulate at certain depths in the soil profile, and to move laterally and accumulate in zones of deposition within a landscape. Charcoal carbon has been found to account for 0–60% of the SOC found in Australian, German and American soils, and no relationship has been found to

exist between total SOC content and the proportion of charcoal carbon present (Schmidt et al. 1999, 2001; Skjemstad et al. 1996, 1998, 1999a, 1999b, 2002). Pieces of charcoal selectively removed from soil and not associated with soil minerals have radiocarbon ages equivalent to or greater than soil humin fractions (Pressenda et al. 1996). High recalcitrance of charcoal carbon to biological mineralisation has been demonstrated (Baldock and Smernik 2002), although priming with glucose has also enhanced mineralisation of a portion of charcoal carbon (Hamer et al. 2004). If variable quantities of charcoal exist in density fractions, as suggested by the NMR spectra presented by Sohi et al. (Poirier et al. 2005; Sohi et al. 2001, 2005), the usefulness of these fractions as measured surrogates for inclusion in carbon simulation models will be limited due to variation in the biological reactivity of the fractions.

Skjemstad et al. (1996) proposed a three-component fractionation scheme to identify measurable SOC fractions that avoids issues associated with redistribution of carbon during dispersion and fractionation and allocation of appropriate proportions of SOC to the most recalcitrant charcoal-rich pool (Fig. 1.2). The fractions isolated included: free particulate SOC (>53 μm particles), humus (<53 μm particles – charcoal carbon) and charcoal carbon (<53 μm particles from which non-charcoal carbon was removed using a photo-oxidation proce-
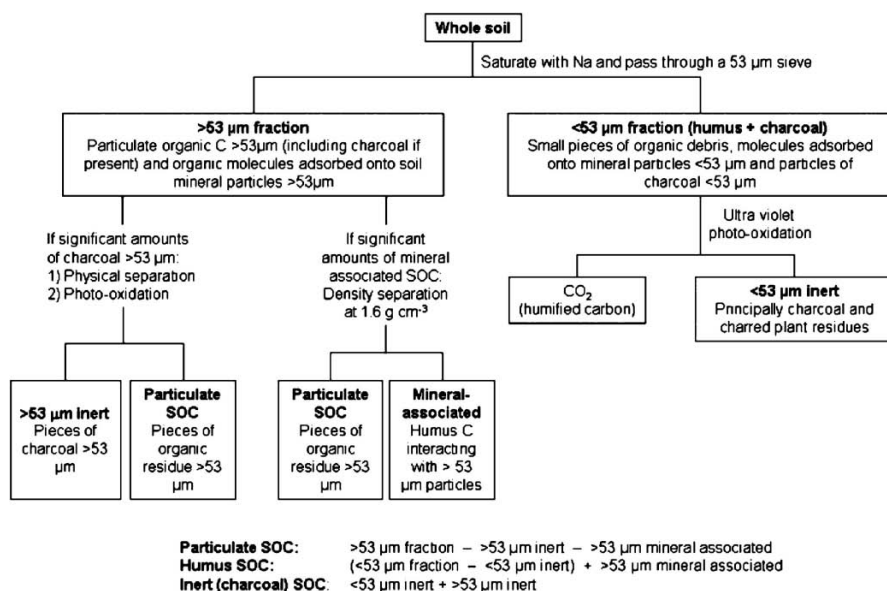
Fig. 1.2 Methodology used to isolate measurable SOC fractions that define the allocation of carbon to charcoal and minimise the potential for carbon redistribution during the fractionation process

dure). By first removing the large pieces of plant residue in the free particulate fraction and aggregating all soil particles <53 μm into one single fraction, any redistribution of C between soil particles <53 μm has no consequence on allocation of C to this fraction. Two issues that must be assessed when using this approach are the inclusion of large pieces of charcoal and organic carbon adsorbed to large mineral particles in the >53 μm fraction. The importance of both of these issues can be rapidly assessed by examining the >53 μm fraction under a light microscope. If a contribution from large particles of charcoal is present, this can be accounted for by physical removal or photo-oxidation. Where a significant amount of carbon is associated with >53 μm mineral particles, a density fractionation process using a solution of 1.6 g cm^{-3} can be used to separate the free particulate material from the mineral-associated humus material (Fig. 1.2).

Skjemstad et al. (2004) assessed the suitability of substituting the fractions identified in Fig. 1.2 for several of the conceptual pools included in version 26.3 of the Rothamsted soil carbon simulation model (RothC). A schematic representation of the pools and flows of carbon in the Rothamsted model is presented in Fig. 1.3. The resistant plant materials (RPM), humified organic materials (HUM) and inert organic materials (IOM) pools in the Rothamsted model were substituted with the >53 μm particulate SOC, humus SOC and inert SOC fractions, respectively. Changes in total SOC content and allocation to the pools were simulated for soils collected from two long-term field studies. Initial SOC content and allocation of C to the fractions was defined by applying the fractionation methodology to archived soil samples collected at the start of the studies. Model performance was assessed by comparing simulated changes in total
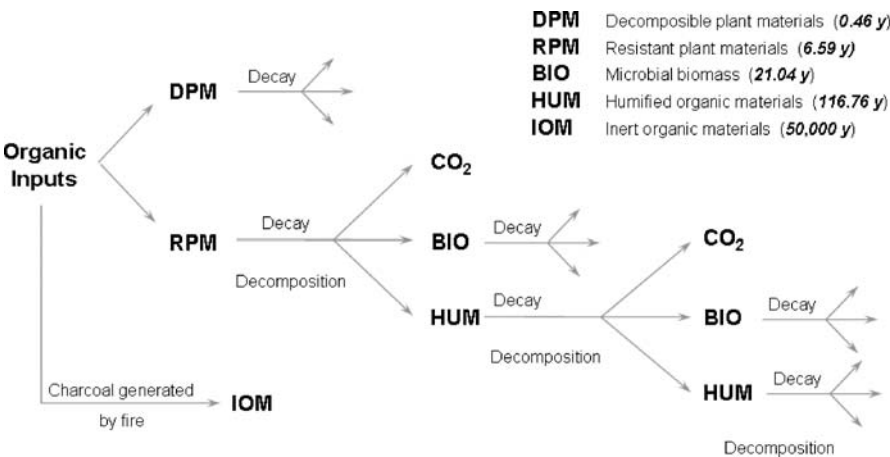
Fig. 1.3 Pool structure and flows of carbon in the Rothamsted SOC simulation model (modified from Jenkinson et al. (1987)
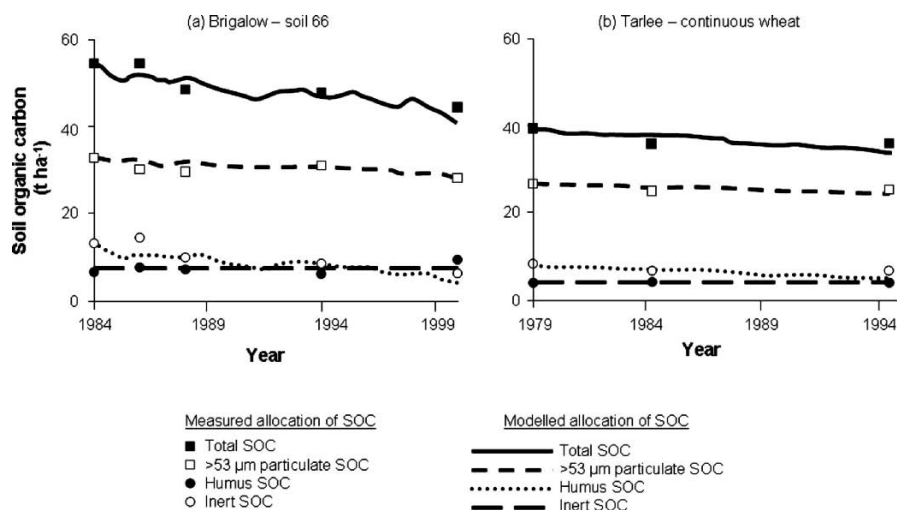
Fig. 1.4 Comparison of simulated (*lines*) and measured (*points*) total SOC contents and allocation of carbon to measurable SOC fractions at the (**a**) Brigalow and (**b**) Tarlee field sites (modified from Skjemstad et al. 2004)

SOC content and allocation of carbon to the pools with values measured on soils archived throughout the duration of the field studies. Without any modification to RothC, reasonable agreement was obtained for both total SOC and allocation of carbon to the fractions; however, improvements in agreement were obtained by decreasing the rate of decomposition of the particulate SOC pool (RPM in Rothamsted notation) from 0.30 $year^{-1}$ to 0.15 $year^{-1}$ (Fig. 1.4). Given the variation in environment, soil type, and rotation composition examined, it was concluded that, at least for Australian environmental conditions, the conceptual pools of carbon within the RothC soil carbon simulation model could be replaced with measurable fractions based on the methodology developed by Skjemstad et al. (1996). The potential for "modelling the measurable" (Christensen 1996b; Magid et al. 1996) appears to be a valid next step in simulating SOC dynamics. The challenge is to define the most appropriate set of fractions and, while several different procedures have been proposed, only that proposed by Skjemstad et al. (2004) has been successfully incorporated into a working SOC simulation model.

1.4
Factors Controlling SOC Contents

The organic carbon content attained by a soil is a function of the balance between the rate of carbon deposition and the rate of carbon loss. The magnitude and direction of changes in the amount of SOC found in a soil can be represented by a mass-balance equation (Eq. 1).

$$\Delta SOC = C_A - C_L - C_E - C_M \tag{1}$$

In Eq. 1, ΔSOC represents the net change in the amount of SOC over a specified time in response to the addition of an amount of organic carbon, C_A, and the concomitant losses due to leaching of dissolved organic carbon (DOC) out of the soil profile, C_L, lateral movement due to erosion, C_E, and mineralisation, C_M.

Unless external sources of carbon are applied, carbon inputs are controlled by net primary productivity (NPP) originating from photosynthesis in the soil/plant ecosystem. NPP represents the difference between total C uptake by plant photosynthesis and C loss via plant respiration. Recent estimates of NPP for various forest, prairie and agricultural ecosystems are presented in Table 1.2. Forested systems tended to have NPP values >350 g C m^{-2} year^{-1}, with the exception of those located in northern Canada where NPP values were estimated to be >200 g C m^{-2} year^{-1}. With the exception of the two maize systems examined (Brye et al. 2002), prairie and agricultural systems had lower NPP values than forests. When grain removal is included, actual returns of residue to the soil/plant system are significantly lower than NPP. For cereal crops such as wheat, an NPP of 134 g C m^{-2} year^{-1} for each Mg ha^{-1} of grain harvested is derived, assuming a harvest index of 0.50 g grain g^{-1} shoot dry matter, an allocation of photosynthate below ground of 0.67 g shoot g^{-1} total plant and a shoot and root dry matter carbon content of 45%. However, the actual return of carbon after accounting for harvested grain decreases to 89 g C m^{-2} year^{-1} for each Mg ha^{-1} of grain harvested. On the basis of these calculations, annual inputs of carbon to agricultural soils should generally be >80 g C m^{-2} year^{-1}.

Leaching of DOC and lateral transfers of SOC in eroded material contribute to carbon loss. Whether these processes result in a net increase or decrease in the amount of SOC stored at a landscape scale remains debatable. If leached DOC is adsorbed to mineral particles deep in the soil profile, or eroding SOC accumulates in local depressions, SOC leaching and erosion may result in net increases in carbon storage.

Measured fluxes of DOC through surface soil layers (0–20 cm) in a range of ecosystems are typically greater than those through subsurface (20–100 cm) soil layers, suggesting a reduction in DOC flux as it passes through the soil (Neff and Asner 2001). Fluxes of DOC through the surface organic horizons of temperate forest ecosystems vary between 10 and 40 g DOC m^{-2} year^{-1}, with significant

Table 1.2 Recent estimates of net primary productivity (NPP) for forest, prairie and agricultural systems

Ecosystem	NPP (g C m^{-2} year^{-1})[a]	Reference
Oregon coast range forest (USA)	950	Van Tuyl et al. 2005
Oregon west cascades forest (USA)	700	
Oregon east cascades forest (USA)	370	
Pine/spruce mixed forest (Sweden)	810	Lagergren et al. 2005
Boreal forests	280±160	Pregitzer and Euskirchen 2004
Temperate forests	710±350	
Tropical forests	830±520	
Unfertilised tropical forest (Hawaii, USA)	1,050	Giardina et al. 2003
Fertilised tropical forest (Hawaii, USA)	1,110	
Old-growth *Pseudotsuga-Tsuga* forest	597 (453–741)	Harmon et al. 2004
Boreal forest (Finland and Sweden)	563 (252–1,426)	Zheng et al. 2004
Boreal black spruce 12–20 years after fire (Canada)	(332–521)	Bond-Lamberty et al. 2004
Deciduous forests (Japan)	(880–1,410)	Tateno et al. 2004
Deciduous forests (USA)	(350–460)	Jenkins et al. 2001

Table 1.2 (continued)

Ecosystem	NPP (g C m^{-2} year^{-1})[a]	Reference
Cheatgrass grown on prairie soil in an Eco-cell	490	Verburg et al. 2004
Maize (no fertiliser) (USA)	620	Brye et al. 2002
N-fertilised maize (USA)	1,040	
Restored tallgrass prairie (USA)	260	
Conifer forest (Canadian average)	210	Liu et al. 2002
Mixed forest (Canadian average)	385	
Deciduous forest (Canadian average)	440	
Cropland (Canadian average)	280	
Grassland (Canadian average)	150	

[a]Values in parentheses represent the range of observed values

attenuations to 1–10 g DOC m^{-2} year^{-1} through the soil C horizon (Michalzik et al. 2001). DOC fluxes through C horizons are thought to be indicative of DOC export from a soil. Consistent with DOC flux data presented by Michalzik et al. (2001), Hope et al. (1994) suggested that DOC fluxes from terrestrial ecosystems range from 1–10 g C m^{-2} year^{-1} based on river DOC fluxes. Reductions in DOC flux on passage through mineral soils are a general observation and can be attributed to adsorption of DOC onto soil minerals or DOC mineralisation.

Differential adsorption of DOC onto soil minerals in two adjacent catchments with similar vegetation but different geological origins was proposed to account for the large differences in DOC concentration in catchment drainage water (Nelson et al. 1993). DOC sorption capacity was shown to vary significantly with soil depth, mineralogy and organic C content (Guggenberger and Kaiser 2003). Surface mineral horizons rich in organic carbon had little capacity to adsorb additional DOC (1–2 g DOC m^{-2}) compared to iron- and aluminium-rich B horizons (often >150 g DOC m^{-2}). Such measurements suggest that attenuation of DOC flux with increasing depth is most likely dominated by mineralisation in the organic-rich surface horizons and then by adsorption reactions in iron- and aluminium-rich B horizons. Given that the fluxes of DOC exiting soil profiles are small when compared to estimates of NPP (Table 1.2), DOC fluxes are generally not included in carbon balance calculations over short time-scales. However, the process of DOC formation, vertical movement and potential accumulation at depth can contribute significantly over long time-scales.

Erosion by wind and water preferentially moves light and fine fractions of a soil. Specific SOC components have a low density (e.g. POC), are associated with fine silt and clay particles (e.g. humus), and/or are concentrated near the soil surface. Preferential erosion of SOC can be demonstrated by expressing the organic carbon content of the eroding sediment as a function of the organic carbon content of the soil from which the sediment was derived. Such enrichment ratios are typically >1 and are often as large as 5 (Lal 2003). Depletion of SOC due to erosion can be significant. Ritchie et al. (2005) found that SOC content was significantly correlated with erosion/deposition rates and noted reductions in SOC content from 3.4% to 2.4% and from 1.6% to 1.3% in eroded zones of two agricultural fields. Fenton et al. (2005) measured reductions in SOC content from 3.6% to 1.8% for till soils and 3.7% to 2.0% for loess soils in Iowa in progressing from slightly to severely eroded soils. SOC losses of this magnitude are likely to be greater than losses associated with mineralisation, and demonstrate the dramatic, but typically localised, impact that erosion can have on SOC content.

Eroded SOC may move into riverine, estuarine or marine environments, where it can be mineralised by aquatic organisms or stored in sediments. It has been suggested that erosion and subsequent protection of eroded carbon by burial in landscape depressions and aquatic sediments can account for a sequestration of 0.6–1.5 Gt C year^{-1} (Lal 2005; Smith et al. 2001; Stallard 1998). Long-term storage (geological time-scales) of eroded organic carbon due to burial in terrestrial or aquatic environments could account for a significant carbon sink,

provided that vegetation can re-establish itself and SOC values can be returned to their original values on eroded sites.

The final term of the potential components of SOC loss identified in Eq. 1 is the mineralisation of SOC to carbon dioxide, C_M. Given that the time and spatially averaged fluxes of DOC and eroded SOC are small relative to NPP (Table 1.2), the loss of carbon from a soil must be dominated by mineralisation during decomposition. The terms "decomposition" and "mineralisation" are often used interchangeably to describe the process of converting organic carbon to carbon dioxide. Although it is correct to describe the release of carbon dioxide from biological respiration as mineralisation, decomposition refers to the removal of a given carbon substrate. Thus, decomposition represents the sum of the processes of mineralisation, alteration and assimilation (Eq. 2).

$$C_D = C_M + C_{Alt} + C_{Ass} \tag{2}$$

C_D represents the amount of carbon decomposed and C_M, C_{Alt} and C_{Ass} represent the losses of initial substrate organic carbon associated with mineralisation, alteration and assimilation, respectively. Alteration occurs when the chemical composition of an organic substrate is changed so that the remaining organic carbon is no longer identical to that present in the initial substrate. Such changes can occur due to an incomplete or partial enzymatic attack of a substrate. Assimilation refers to the retention of substrate carbon by decomposer organisms as they synthesise cellular materials during growth. As a result, the extent to which SOC is mineralised or decomposed can differ significantly, with carbon losses due to mineralisation generally being lower than the amount of carbon decomposed.

A variety of mechanisms exist to protect SOC from mineralisation. Sollins et al. (1996) presented a conceptual model that proposed the existence of three mechanisms to account for the formation of biologically stable SOC: selective enrichment, chemical stabilisation and physical stabilisation. Baldock et al. (2004) suggested that the biological stability of organic materials in soils can be expressed as a function of three controlling factors and an interaction between a set of ecosystem properties (Eq. 3). The three controlling factors define whether a particular organic molecule can be used by the decomposer community. An interaction between ecosystem properties and the duration of exposure to conditions conducive to decomposition define the rate of utilisation.

$$\begin{array}{l} \text{Biological} \\ \text{stability of} \\ \text{organic C} \end{array} = f \left(\begin{array}{l} \text{Biochemical} \\ \text{recalcitrance} \end{array}, \begin{array}{l} \text{Biological} \\ \text{capability} \\ \text{and} \\ \text{capacity} \end{array}, \begin{array}{l} \text{Physical} \\ \text{mechanisms} \\ \text{of} \\ \text{protection} \end{array}, \begin{array}{l} \text{Ecosystem} \\ \text{properties} \\ \text{influencing} \\ \text{mineralisation} \\ \text{rate} \end{array} \times \begin{array}{l} \text{Duration} \\ \text{of} \\ \text{exposure} \end{array} \right)$$

$$\tag{3}$$

The controlling factors in Eq. 3 are similar to those proposed by Sollins et al. (1996). Biochemical recalcitrance equates to selective enrichment. Physical mechanisms of protection include both the chemical and physical stabilisation mechanisms proposed by Sollins et al. (1996). The additional factor added by Baldock et al. (2004) describes the biological capability and capacity of the decomposer community.

1.5
Biochemical Recalcitrance

Plant residues represent the dominant input and thus the primary source of organic carbon into or onto soils (Kögel-Knabner 2002). However, organic molecules synthesised by the soil decomposer community (fauna and microorganisms) create a secondary source of decomposable organic carbon once decomposition of plant residues is initiated. Despite a large diversity in origin and physical form, the majority of primary and secondary sources of organic carbon can be allocated to discrete classes of biomolecules, including polysaccharides (e.g. cellulose, hemicellulose, chitin and peptidoglycan), protein, lipid/aliphatic materials (e.g. fatty acids, waxes, cutin, suberin and terpenoids), and lignin. The chemical composition of each of these classes of biomolecules in terrestrial ecosystems has been reviewed by Kögel-Knabner (2002).

The biochemical recalcitrance of each type of biomolecules present in decomposing residues is defined by the strength of intra- and inter-molecular bonds, the degree of polymerisation and regularity of structural units in polymers, and the content of aromatic and aliphatic functional groups (Baldock et al. 1997b; Gleixner et al. 2001). Mineralisation rates and extent of decomposition decrease in progressing from simple and monomeric molecules, to larger polymeric molecules and to plant residues that can be viewed as complex mixtures of a variety of polymeric molecules (Fig. 1.5). The presence of a relationship between biological stability and plant residue composition has been demonstrated in many studies (e.g. Agren and Bosatta 1996; Cortez et al. 1996; Edmonds and Thomas 1995) and led to the development of indices that define the susceptibility of organic substrates to decomposition based on chemical composition. The most widely accepted indices of biological stability include N concentration, C:N ratio, lignin and/or polyphenol concentration, and lignin (and/or polyphenol)/nitrogen ratios (Heal et al. 1997). Various organic condensation reactions between potentially labile organic precursor molecules have also been proposed to enhance the biological stability of SOC (e.g. the non-enzymatic browning reaction that occurs between carbohydrate and amino groups to form hydroxymethylfurfurals). The contribution that the products of such reactions make to SOC contents has not been clearly established.

    A requirement to selectively define the influence of chemical composition on biological stability of SOC is the exclusion of potential contributions made by the other controlling factors. Under natural conditions it is very difficult to find such a situation. The closest systems to this ideal behaviour would be forest litter layers and peat devoid of mineral particles. However, the requirement for the presence of a decomposer community having both the capability and capacity to degrade organic materials may still be questioned. Baldock et al. (1997b) reviewed the chemical changes associated with the decomposition of organic materials in such systems. In virtually all instances, concomitant with an increase in the extent of decomposition were a decrease in O-alkyl C and an increased in alkyl C. Variations in aryl C content were not found to be consistent with measures of the extent of decomposition. This may be attributable to variations in the activity of lignin-degrading fungi across the various environments from which samples were derived. The more hydrophobic behaviour of alkyl-dominated organic materials, and a preservation of the more highly cross-linked rigid alkyl components of plant residues have been proposed to account for the biological stability of alkyl C in soils (Kögel-Knabner et al. 1992a, 1992b). Hwang and Druffel (2003) also reported an enhanced biological stability of cross-linked alkyl materials relative to protein, polysaccharide or simple lipid materials in marine environments.
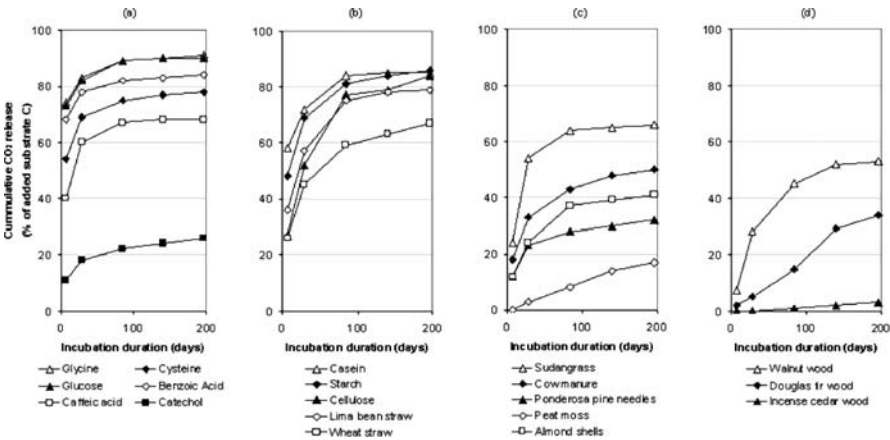
Fig. 1.5 Proportion of substrate C mineralised during incubation in Greenfield sandy loam for (**a**) monomers, (**b**) polymers and complex mixtures of polymers originating from different types of (**c**) plant litter and (**d**) wood (Martin and Haider 1986)

1.6
Biological Capability and Capacity for Degrading Organic Materials

The biological capability of a population of decomposer organisms is defined by the genes responsible for producing the enzymes required for degradation to occur. As the diversity of degradative enzymes produced by a decomposer community increases, so does its biological capability. However, a diverse range of enzymes targeting a narrow range of molecular compositions would not provide a significant biological capability. For example, if the genes required to produce enzymes capable of degrading lignin were absent from a community, biological capability would be reduced even if a wide range of other degradative enzymes were being produced. The extent of expression of the genes (amount of enzymes produced) is not described by biological capability, but rather by biological capacity as discussed below.

An important consideration when examining biological capability is the size scale being examined. Biological capability can be described at scales ranging from individual organisms (micro to macro) through to colonies of individual species, communities of mixed species, and ecosystems composed of a variety of decomposer communities. As the size scale being considered increases, biological capability will also increase. At the ecosystem scale, where many different communities may exist in different niches, biological capability will be greatest. An ecosystem with a high biological capability will contain all the genes necessary to produce the enzymes required to decompose the various types of organic matter that enter the ecosystem, even though these capabilities may reside within a range of organisms operating across a range of size scales. As the size scale decreases, the potential for absence of any single degradative capability increases. In the absence of a degradative capability, an accumulation of a particular type of organic material would be expected.

The influence of biological capability for degradation is well demonstrated by the chemical changes associated with decomposition of a single species of wood (*Eucryphia cordifolia*) by a white-rot fungus (*Ganoderma australe*) and a brown-rot fungus (unidentified) (Martínez et al. 1991). Incubation of the wood with the brown-rot fungus resulted in a 62% mass loss and a residue dominated by lignin; whereas the white-rot fungus produced a 79% mass loss and a residue devoid of lignin and dominated by carbohydrate. The wood/brown-rot system therefore exhibited a decreased biological capability relative to the wood/white-rot system due to its reduced capability to degrade lignin as effectively. The biological capability of a decomposer community may therefore be influenced by an interaction between the species of organisms present and the nature of the organic materials added.

The ability of a decomposer community to use an organic material can be defined as its biological capacity, i.e. the magnitude of expression of the biological capability of the decomposer community. Biological capacity does not

define whether or not a particular organic substrate can be used by the decomposer community but rather the rate at which the substrate is used. In many natural ecosystems, it is possible that the biological capability exists, but is not expressed, or its expression is reduced by some factor limiting the activity of individual decomposer organisms or interactions between individuals in the decomposer community.

Several methodologies exist that can provide information pertaining to the biological capability and capacity of decomposer communities and how these properties are altered by environmental parameters or management practices. Substrate utilisation profiles based on Biolog plates (e.g. Bucher and Lanyon 2005) or micro-respirometry (e.g. Campbell et al. 2003) can be used to assess the potential degradative capabilities of decomposer communities. Extraction and analysis of soil-derived DNA, RNA or phospholipid fatty acids (PLFA) can provide an indication of the genetic diversity and structure of soil microbial communities (Crecchio et al. 2004; Widmer et al. 2001). A variety of indices and multivariate statistical techniques can be used with these techniques to quantify the influence of environmental and soil properties on the capability and capacity of the decomposer community. Influences of vegetation (forest versus cultivated) (De Fede et al. 2001), soil type (Banu et al. 2004; Schutter and Dick 2000), soil horizons (De Fede et al. 2001), the presence of living roots (Baudoin et al. 2002), crop rotation (Bending et al. 2004; Crecchio et al. 2004), and application of manure and inorganic fertilisers (Bucher and Lanyon 2005) have been noted. The combined application of DNA, PLFA and Biolog methods to different soils revealed that each method gave reproducible but different results (Widmer et al. 2001), suggesting that the use of these methodologies in isolation should be avoided if a representative assessment of microbial community structure is desired.

1.7
Physical Mechanisms of Protection

Interactions between organic materials and mineral particles are common. The potential for such interactions to occur increases as the surface area of reactive minerals and the presence of multivalent cations increases. A decreased solubility due to formation of complexes with multivalent cations, adsorption onto mineral surfaces, burial within aggregations of mineral particles, and burial within biochemically recalcitrant biomolecules have all been proposed to protect SOC from mineralisation (Baldock et al. 2004).

Addition of divalent Ca^{2+} to soils has been shown to reduce the mineralisation of SOC (Muneer and Oades 1989a). Protection of SOC against biological attack has also been observed in the presence of Fe^{3+} and Al^{3+} cations and amorphous Fe and Al minerals, with the effects attributed to Al being greater than

those attributed to Fe (Boudot et al. 1989; Juste 1975). An important role of Al is also demonstrated by the typically high SOC contents of allophonic soils and reductions in SOC mineralisation on addition of allophane to soils (Boudot et al. 1988, 1989; Zunino et al. 1982), indicating the protective effect that Al-containing minerals may have on SOC. In addition to the direct effect of multivalent cation complexation, surface adsorption reactions may also be of significance. Clay-size layered silicates, and oxides and hydroxides of Fe and Al provide large surface areas with a capacity to adsorb organic materials. Many studies have identified positive correlations between SOC and clay content (e.g. Ladd et al. 1985) and the amount of residual substrate C retained in a soil after a period of decomposition (e.g. Amato and Ladd 1992; Ladd et al. 1985). In similar studies where mineralisation of carbon from soils with widely differing mineralogies was assessed, the extent of protection offered by minerals was better described by variations in surface area than by clay content (Saggar et al. 1996). Surface area and mineralogy have also been identified as important variables defining organic carbon protection mechanisms in marine sediments (Mayer 1994).

The architectural arrangement of pores and particles can also influence the biological stability of SOC. All organic materials are located in the pore space as discrete particles or molecules adsorbed to surfaces, and must be broken into molecular units <600 Da to allow passage across microbial cell walls (Weiss et al. 1991). The majority of decomposition activity therefore occurs outside of microbial cells and depends on the ability of exoenzymes to diffuse to their target and hydrolysed products to diffuse back. Architectures that result in significant portions of total pore space existing in pores <0.5 μm in diameter will limit microbial activity since microorganisms are not able to enter such pores (van Veen and Kuikman 1990). With increasing clay content, the fraction of total porosity found in pores <0.5 μm increases, resulting in protection of any organic materials associated with particles in these pores. Clay particles have also been observed to encapsulate particles or patches of organic material (Baldock 2002) and isolate organic materials from the decomposer community. At a larger size scale, the formation of aggregates around pieces of plant debris can also limit SOC mineralisation. Since intra-aggregate pores are more often filled with water than inter-aggregate pores, and the diffusion of oxygen is 10^4 times slower through water than air, organic material trapped inside aggregates tends to be less decomposed than that found on aggregate exteriors (Amelung and Zech 1996). Sextone et al. (1985) showed that the interior of aggregates could be anaerobic under well-aerated bulk soil conditions. The presence of organic cores within aggregates (Golchin et al. 1997) will enhance these effects by increasing the biological oxygen demand within the aggregate interior.

Encapsulation of labile biomolecules (proteins) by recalcitrant biomolecules (algaenan) has been proposed as a mechanism of enhancing biological stability (Knicker and Hatcher 1997, 2001). Studies using solid-state ^{15}N NMR to characterise the nature of organic nitrogen in algaenan acquired from a ^{15}N-labelled mixed culture of algae (Knicker et al. 1996) and from *Scenedesmus communis* (Derenne et al. 1993) have shown that the nitrogen contained in these materials

is dominantly found in amide structures typical of protein. The ability of this amide material to survive HCl hydrolysis was suggested to provide evidence for the protection of protein during decomposition.

1.8
Rate Modifiers and Duration of Exposure

Ecosystem properties (e.g. temperature, oxygen status, etc.) exert control on the biological capacity of an ecosystem to decompose organic matter. Rather than altering the potential for a decomposer community to degrade organic matter, these properties govern the rate at which biological processes proceed. Ecosystem properties considered most important to defining the biological capacity of soil decomposer communities include temperature and availability of oxygen and water. Various studies have reported negative correlations between SOC content and temperature and positive correlations between SOC and precipitation (Burke et al. 1989; Parton et al. 1987). As a result, this discussion of rate modifiers and duration of exposure will be limited to the effects of temperature and availability of oxygen and water. Other factors that may impact on defining biological capacity include sufficiency of nutrient supply, presence of readily available organic substrates and predator/prey relationships (Baldock et al. 2004). Soil management practices can also alter rates of SOC mineralisation through their influence on the level of plant residue inputs, exposure of physically protected SOC via cultivation, modification of soil temperature and water status and alteration of soil nutrient status. Paustian et al. (1997) and Johnson et al. (Johnson and Curtis 2001; Johnson et al. 2002) comprehensively reviewed the influence of agricultural and forest management on SOC levels, respectively.

Studies defining the influence of temperature on carbon mineralisation have used a variety of organic materials, including well-defined single substrates, plant residues with differing chemical composition, and soil organic materials. Increases in carbon mineralisation with increasing temperature are nearly always described by an exponential function, but discussion remains as to which exponential formulation is best (Lloyd and Taylor 1994). Fierer et al. (2005) used the formulation presented by Lloyd and Taylor (1994) (Eq. 4).

$$y_T = B \times e^{kT}$$

(4)

Where y_T is the decomposition rate at any given temperature (in μg CO_2-C g^{-1} soil h^{-1}), T is temperature in °C and B and k are exponential fit parameters. Fierer et al. (2005) used the value of B as an overall indicator of substrate quality (availability and lability). Temperature sensitivity of carbon mineralisation is often defined using Q_{10} values – the average increase in respiration rate for a

10 °C increase in temperature – and can be calculated according to Eq. 5 using the value of k derived in Eq. 4.

$$Q_{10} = e^{10k}$$

(5)

Before examining the results derived from specific studies, it is important to recognise the impact that compositional variability may have on measurements of temperature sensitivity. Both chemical complexity and heterogeneity increase in progressing from well-defined single substrates through to SOC. Measurements of temperature sensitivity in more complex systems therefore provide a weighted average value defined by the content and temperature sensitivity of all components. In addition, when working with soils, biological availability of SOC or particular fractions may be significantly altered by physical protection mechanisms. Fierer et al. (2005) observed an increase in the temperature sensitivity of carbon mineralisation (increased Q_{10}) within decreasing substrate quality for different individual organic compounds, plant litter types, and litter at different stages of decomposition. Similar findings of increased temperature sensitivity of C mineralisation with decreasing quality of plant residues were obtained by Hobbie (1996) and O'Connell (1990), and for SOC by Mikan et al. (2002) and Fierer et al. (2003).

When comparing Q_{10} values across different studies, it is important to examine the experimental conditions used. Of particular importance is the duration over which measurements of carbon mineralisation are made. As the measurement duration increases, the potential for substrate depletion and conversion of substrate carbon into other compounds with different mineralisation potentials (higher or lower) increases. Thus, the most accurate estimates of Q_{10} for a given organic substrate are obtained with shorter incubation durations. Q_{10} values measured by Ferrier et al. (2005) over 24-h incubations across the temperature range of 10–30 °C varied between 2.0 and 3.0 for seven organic compounds and between 2.0 and 3.4 for a variety of plant residues. Ladd et al. (1985) showed that rates of carbon mineralisation from ^{14}C-labelled substrates doubled with successive increases in mean annual temperature of 8–9 °C (Q_{10} ~2.5), and Kätterer et al. (1998) found that a Q_{10} value of 2 was appropriate over the temperature range of 5–35 °C for SOC mineralisation. Q_{10} values obtained for various litters have also been shown to display a strong dependence on incubation temperature, with Q_{10} values of 8, 4.5 and 2.5 being obtained at temperatures of 0 °C, 10 °C and 20 °C, respectively (Kirschbaum 1995).

Adequate quantities of available water and oxygen are required to optimise the processes of decomposition and mineralisation. Given that the total amount of pore space and the pore size distribution of the soil matrix control water and oxygen availability, these soil architectural properties exert a control over decomposition and mineralisation. An optimum air-filled porosity exists at which processes of organic carbon decomposition and mineralisation will be maximised for a given soil. Changes in the pore size distribution towards a greater

proportion of large pores, such as in progressing from a clay to sand, are accompanied by higher rates of carbon mineralisation at equivalent values of air-filled porosity (Franzluebbers 1999). Franzluebbers (1999) also showed that reducing total porosity by compression induced reductions in C mineralisation at all levels of air-filled porosity and shifted the air-filled porosity at which C mineralisation was maximised. Schjønning et al. (1999) and Thomsen et al. (1999) reported that the degradability of soil carbon was better correlated with water-holding capacity and volumetric water content than with clay content.

To completely define the role of temperature and availability of oxygen and water on biological capacity, an assessment of the duration of exposure to conditions conducive to decomposition is also required. Indices such as growing-degree days or heat units have been used extensively in agronomic studies to study and predict the progression of crop development (e.g. Stewart et al. 1998). The concept of oxygen exposure time has been used in marine systems to examine preservation mechanisms in sediments (Gélinas et al. 2001; Hedges and Keil 1995). In studies of SOC cycling, thermal time indices have been used to characterise the decomposition of various organic residues. Rahn and Lillywhite (2002) found that the decomposition of 13 different vegetable crop residues exhibiting a range in C/N ratio and lignin content could be described by a single exponential equation based on thermal time (degree days above 0 °C). Curtin and Fraser (2003) observed that the percentage of wheat straw remaining in litter bags buried in soil in four different years was well related to cumulative degree-days (day degrees above 0 °C). The application of oxygen exposure time to the study of SOC dynamics is more limited than in marine sediments, but may be useful in differentiating SOC cycling processes in soils that experience different frequencies and durations of water-logging.

1.9
Conceptual Model of the Role of Stabilising Mechanisms in Defining Chemical Structure

Baldock et al. (1992) presented a conceptual model describing the progressive alteration of SOC chemistry with increasing extent of oxidative decomposition (grey region of Fig. 1.6). Two assumptions included in this model were: (1) biological availability of SOC is controlled by biochemical recalcitrance (i.e. biological stability increases in the order protein<cellulose<lignin<lipid carbon), and (2) the decomposer community has both the capability and capacity to degrade all organic materials present. Baldock et al. (2004) subsequently amended the model to account for the controlling factors and rate modifiers identified in Eq. 3. These controlling factors and rate modifiers have the potential to protect SOC found in chemical structures normally susceptible to rapid mineralisation. Schöning et al. (2005) determined the ^{14}C abundance and chemical composition
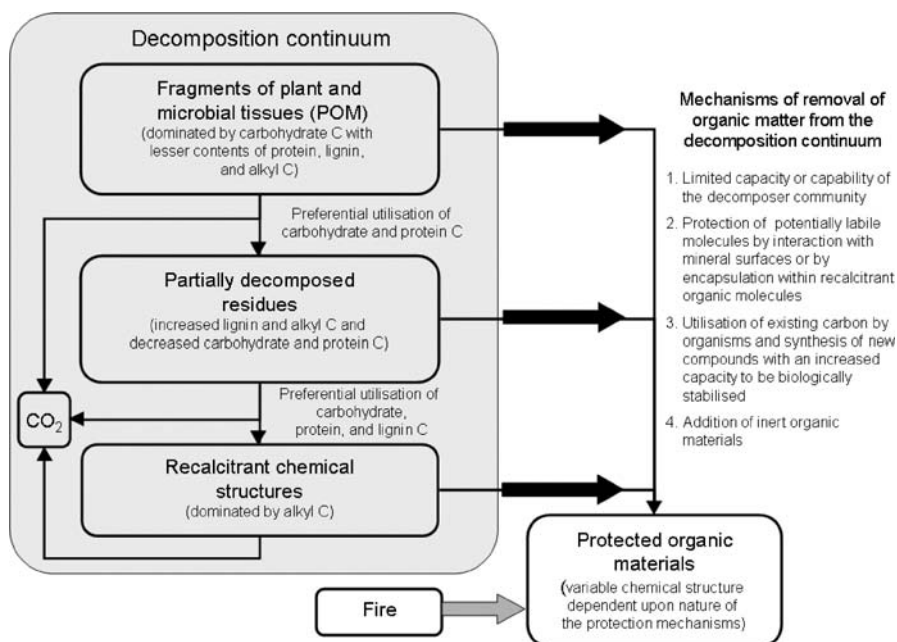
Fig. 1.6 Conceptual model describing the influence of the presence of protection mechanisms on the chemistry of soil organic matter Baldock et al. (2004)

of SOC found in particle size fractions. Measurements of ^{14}C suggested that association with the clay fraction resulted in a specific stabilisation of potentially labile O/N-alkyl C (polysaccharides and proteins) and alkyl C (aliphatic structures), but not on aryl C. Quantification of residence times of molecular components of SOC from bulk soils using differences in the $\Delta^{13}C$ values of pyrolysis products (Gleixner et al. 2002) also revealed a high life-time for N-containing organic compounds (amino acids, proteins and chitin) and polysaccharides, supporting the existence of mechanisms that protect these typically labile structures. Thus, the existence of significant quantities of SOC with chemical structures considered to be biologically labile does not necessarily correlate with a high potential for decomposition or mineralisation. As indicated by Baldock et al. (2004), improved understanding of carbon release from soils will require the development of a means of quantifying the mechanisms operating to stabilise potentially labile organic carbon as well as the controls that define the magnitude of transfer from labile to protected forms of SOC (i.e. the transfer of carbon associated with the black arrows in Fig. 1.6). In addition, an assessment of the total protective capacity of soils and the permanence of the protection offered to biologically labile forms of carbon is required.

1.10
Conclusions

Organic carbon exists in soils in a large variety of forms with variable chemical composition and extents of decomposition. Many fractionation procedures based on the chemical and physical properties of SOC have been developed in an effort to isolate relatively homogeneous pools of carbon with different turnover times. Whilst most of these procedures can theoretically be used to allocate SOC to potentially more labile and less labile fractions, only Skjemstad et al. (2004) have demonstrated the capability and utility of incorporating measurable fractions of SOC into a computer simulation model. Whether carbon accumulates or is lost from soil in response to management or disturbance is defined by the balance between carbon inputs and losses. Inputs are governed by NPP, which can vary significantly across ecosystems. Losses are defined by the biological stability of the organic materials. A range of factors including biochemical recalcitrance, biological capability and capacity, physical protection and soil environmental conditions define the biological stability of SOC. The presence of mechanisms capable of stabilising SOC against microbial attack can reduce rates of SOC turnover and stabilise SOC found in organic structures that would normally be considered labile on the basis of their chemical composition. Although a general continuum of changing chemistry with increasing extent of decomposition exists, these characteristic changes can be significantly perturbed where protection mechanisms are operative. Under such conditions, consistency between SOC chemistry, age and lability may not follow the typical trends, and preservation/protection of potentially labile forms of SOC may result.

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2 The Nitrogen Cycle in Terrestrial Ecosystems

Ann McNeill, Murray Unkovich

2.1
Introduction

The terrestrial nitrogen (N) cycle comprises soil, plant and animal pools that contain relatively small quantities of biologically active N, in comparison to the large pools of relatively inert N in the lithosphere and atmosphere, but that nevertheless exert a substantial influence on the dynamics of the global biogeochemical N cycle. After carbon (ca. 400 g kg^{-1}) and oxygen (ca. 450 g kg^{-1}), N is the next most abundant element in plant dry matter, typically 10–30 g kg^{-1}. It is a key component of plant amino and nucleic acids, and chlorophyll, and is usually acquired by plants in greater quantity from the soil than any other element. Plant N provides the basis for the dietary N (protein) of all animals, including humans.

In this chapter we will describe how N cycles through the soil-plant-animal continuum within terrestrial ecosystems, and how N may be added (inputs) or removed (losses) from these ecosystems. The cycling occurs via decomposition of organic matter in soil, which then provides available N for plant and microbial uptake. Nitrogen subsequently returns to the soil organic N pool following plant or microbial death or via dung or urine from grazing animals. Decomposition of organic matter is mediated by the microbial biomass (Fig. 2.1), which, despite being a very small N pool within soil organic matter, has long been recognised as a critical nutrient pool, with the living microbial biomass providing the enzymes for decomposition and the dead microbial biomass representing a labile pool of soil N. Human activities exert enormous influences on the turnover and cycling of N within terrestrial agroecosystems.

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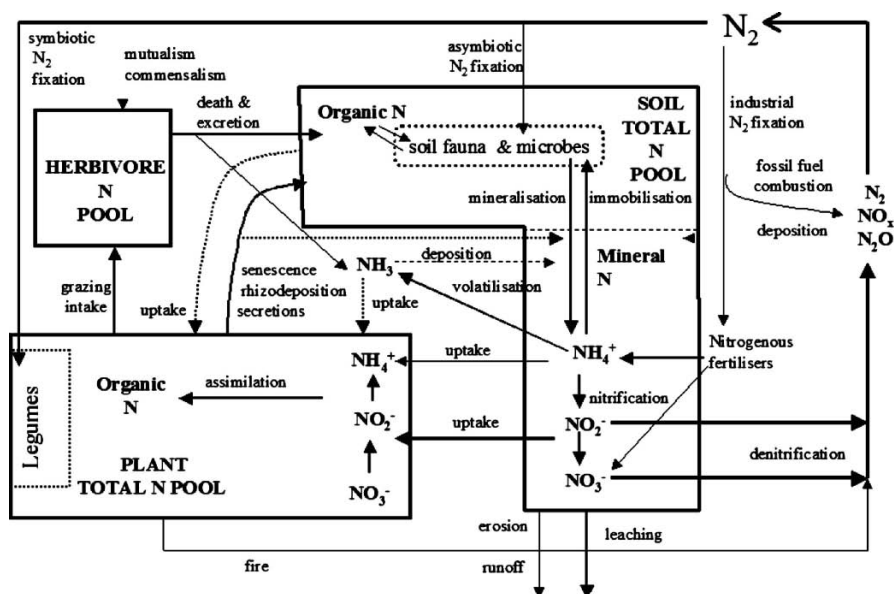
Fig. 2.1 Important pools, processes and fluxes of N in natural and managed terrestrial ecosystems

Major inputs to the terrestrial N cycle occur naturally via biological fixation and by wet and dry deposition (Fig. 2.1), with comparatively minor amounts fixed by lightning (Galloway et al. 1995). Humans have a direct impact on N inputs to terrestrial systems in several ways: (1) by the industrial fixation of N, mainly into manufactured N fertilisers, (2) by increasing the productivity and area sown with N_2-fixing legume crops and pastures, and (3) by use of the inter-nal-combustion engine (Jenkinson 2001). It is estimated that human activity has resulted in a doubling of the fixation of "unreactive" N_2 from the atmosphere to biologically "reactive" forms on land (Vitousek et al. 1997). This has fuelled an increase in biomass productivity and provided the protein needed to feed a global population of 6 billion people consuming around 25 million tonnes N per year (Jenkinson 2001).

Losses of inorganic and organic N from terrestrial systems to the atmosphere or hydrosphere can occur in liquid, solid or gaseous phases. Nitrate (NO_3), dis-solved organic N and soluble organic N can be lost by leaching (Fig. 2.1). Off-site transport of organic and mineral N occurs due to wind and water erosion, and formation of aerosols. Whilst most deliberate inputs of N are localised, the mobility of reactive N means that the influence can spread regionally and even globally (Vitousek et al. 1997). Thus, increased N availability in the biosphere contributes to many contemporary environmental problems (Galloway et al. 2003).

This chapter focuses on recent research concerning the pools and fluxes involved in the major chemical and biological transformations of N in terrestrial ecosystems (Fig. 2.1). Plant N uptake in natural and managed ecosystems, removal of N in harvested produce, and the contribution of grazing animals to internal N transfer will be discussed. Inputs of N to the soil and biosphere from symbiotic and non-symbiotic N_2 fixation, atmospheric deposition and N fertilisers, as well as the processes involved in losses of N from terrestrial ecosystems will also be described.

2.2
N Transfers within the Terrestrial N Cycle

2.2.1
Decomposition, Mineralisation-Immobilisation Turnover, and Nitrification

The largest N pool (tonnes ha^{-1}) in the plant root zone is in the soil organic matter, but this is mostly unavailable to plants. However, this organic N may be released (mineralised) to form plant-available or mineral N (kg ha^{-1}). Organic matter decomposition is a complex process that occurs, to differing extents, with newly added plant residues (above- and below-ground), animal waste products, root exudates and rhizodeposits as well as various existing or "native" soil organic matter pools (see also Chapter 1 by Baldock, this volume). This results in a continuum of organic materials of varying ages, stages of decay and degrees of recalcitrance. Decomposition is mediated largely by soil biota and results ultimately in release of nutrients in mineral form and loss of C from the soil as CO_2 via respiration. Initial detritus comminution and litter breakdown are dominated by the actions of macro- and meso-fauna (Wardle and Lavelle 1997) with subsequent decomposition by microflora, chiefly fungi and bacteria. The microbial biomass – the living part of the soil organic matter – has a pivotal role in the soil N cycle (Fig. 2.1) and was aptly described by Jenkinson (1990) as "the eye of the needle through which virtually all nutrients must pass". The continuous transfer of mineral N into organic materials via incorporation of N into soil microbial biomass, and the subsequent release of that immobilised N back into the soluble mineral N pool is known as "mineralisation-immobilisation turnover" or MIT (Jansson and Persson 1982). MIT is considered to play a dominant role in the availability of N for plants and microbes in natural ecosystems and, in the absence of substantial recent mineral fertiliser inputs, also in managed ecosystems.

Gross N mineralisation in soil results in the release of ammonium (NH_4^+) or ammonia (NH_3) by non-specific heterotrophic soil micro-organisms under aerobic and anaerobic conditions. The bulk of N mineralisation occurs in the

biologically active surface soil (0–5 cm) that contains most of the dead and decomposing plant and animal litter. The process of gross N immobilisation involves microbial assimilation of NH_4^+ (Recous et al. 1988) and, to a lesser extent, NO_3^- (Recous et al. 1990). It is also known that the microbial biomass may immobilise N by utilising low-molecular-weight N-containing organic compounds such as amino acids from soil organic matter (Barraclough 1997). Indeed, as much as 40% of N in complex substrates such as plant residues may be incorporated directly into microbial biomass without passing through the soil NH_4^+ pool (Barraclough et al. 1998). Ammonium can also be immobilised non-biologically by fixation in clay lattices or adsorption to organic matter, which can reduce both the NH_4^+ concentration in soil solution and feedback to microbial utilisation.

It has proved far easier to measure the net effect in soils of MIT, rather than gross immobilisation or mineralisation, by simply analysing temporal changes in inorganic N over defined periods (weeks or months), whilst minimising or taking into account losses or gains. The available approaches range from laboratory incubations to large-scale field studies (Jarvis et al. 1996). Edaphic and climatic influences on net N mineralisation or immobilisation are well documented (Haynes 1986b; Kumar and Goh 2000) with the effects of specific soil characteristics and residue composition having been recently reviewed (Cabrera et al. 2005). Other recent comprehensive reviews summarise the effects of environmental variables and agricultural management practices on soil N dynamics and MIT (Kumar and Goh 2000; Martens 2000; Silgram and Shepherd 1999).

Ammonium in soil may be oxidised via nitrite (NO_2^-) to NO_3^- at a rate regulated primarily by availability of NH_4^+. The process of nitrification and the factors regulating it are detailed by Haynes (1986a). Nitrification can be autotrophic or heterotrophic (Wood 1990). The relatively small number of microbial species involved results in nitrification being greatly influenced by edaphic factors such as pH, moisture, temperature and aeration. Autotrophic nitrification is considered to predominate in agricultural soils (Tortoso and Hutchinson 1990). Evidence for heterotrophic nitrification in soils is limited mostly to acidic and organic matter-rich forest soils where autotrophic nitrification can be inhibited (e.g. Pedersen et al. 1999), although recent research has demonstrated the occurrence of heterotrophic nitrification in a fertilised agricultural soil (Bateman and Baggs 2005). Nitrification is spatially heterogenous – a result of a high degree of spatial compartmentalisation of NH_4^+ production and consumption sites. This, coupled with diffusional constraints between microsites, controls the nitrification rate (Bramley and White 1991). Recent studies have highlighted that net nitrification rates strongly underestimate gross nitrification rates in such systems because of the magnitude of microbial immobilisation (Stark and Hart 1997; Verchot et al. 2001). Overall, nitrification still remains poorly understood in many soils (Jarvis et al. 1996).

2.2.2
Plant Uptake of Soil N

Plants may acquire N from the soil as NH_4^+ (Chaillou and Lamaze 1997), NO_3^- or NO_2^- (Darwinkel 1975), or in simple organic forms (Lipson and Monson 1998). The latter may be particularly important for native plants in some organic-matter-rich environments (Chapin 1995). The physiology and ecology of NH_4^+ and NO_3^- nutrition is well understood for many agroecosystems (Haynes 1986c), but much less so for natural ecosystems. The concentration of N in plant dry matter of herbaceous plants is typically 10–20 g kg^{-1} for grasses and forbs, and 20–30 g kg^{-1} for legumes, and tends to be higher in younger tissues. For woody plants, the concentration of N varies with plant parts, typically being ≤5 g kg^{-1} for woody tissue and ≤20 g kg^{-1} for leaves. The N concentration of plant roots has been far less investigated than that of shoots but is typically at the lower end of the range recorded for the above-ground parts.

Plant uptake of NH_4^+ and NO_3^- is a function of the concentrations of NH_4^+ and NO_3^- in the soil solution, root distribution, soil water content and plant growth rate. Plant growth rate is more important under conditions of high N supply, whereas mineral N concentration and root distribution are critical under N-limiting conditions. Ammonium and NO_3^- may reach the root surface in mass flow with soil water by diffusion or via root extension. Since NH_4^+ readily adsorbs to soil cation exchange sites, mass flow and diffusion of NH_4^+ are lower than those of NO_3^-. Whilst some plant species may show a preference for NH_4^+ or NO_3^- uptake, the significance of this for plant N uptake at the field level is usually far less than the above-mentioned factors, especially in agroecosystems.

Once absorbed by plants, it is generally thought that NH_4^+ must be assimilated into amino acids to avoid NH_4^+ toxicity (Brugiere et al. 1997), although recent evidence indicates that some NH_4^+ may be translocated within the plant (Schjoerring et al. 2002). Ammonium assimilation occurs in the plant root, the first product of assimilation being glutamine ($C_5H_{10}N_2O_3$), which is readily transported within the plant or converted to a range of other amino acids and proteins.

Nitrate is usually not toxic to plants and can be transported to the shoot before assimilation, stored in vacuoles for later reduction, and, in some cases, used for osmotic adjustment (Millard 1988). The enzyme responsible for NO_3^- assimilation in plants (nitrate reductase) is synthesised in response to NO_3^- uptake. Assimilation of NO_3^- by plants involves the reduction of NO_3^- to NO_2^-, the reduction of NO_2^- to NH_4^+ by nitrite reductase (another inducible enzyme), and then incorporation of NH_4^+ into glutamine as per NH_4^+ assimilation. Nitrate uptake is therefore energetically more demanding than NH_4^+ assimilation. As in soils, NO_2^- is a transitory intermediate in plants. More detailed discussion of plant NH_4^+ and NO_3^- uptake and assimilation can be found in Morot-Gaudry (2001).

The significance of organic forms of N to plant nutrition is only now being thoroughly investigated. Acquisition of N by plants via vesicular-arbuscular

(VA) mycorrhizal associations is an important process, particularly in naturally N-deficient ecosystems. Read and Perez-Moreno (2003) have recently reviewed this topic and note that a key element of the effectiveness of such systems is the unique extracellular enzymes produced by the fungal partners that are able to "unlock" otherwise unavailable nutrients. Organic N uptake is likely to be of less importance in the absence of VA mycorrhizal associations or specialised root structures (Turnbull et al. 1996). Ectomycorrhizal associations are not effective in increasing plant uptake of organic N. Simple amino acids are the most likely form of organic N to be taken up by plants (Nasholm et al. 2000). Conditions favouring increased organic N uptake include low soil mineral N concentration, environmental conditions conducive to turnover of soil microbial biomass and release of cell contents (Lipson and Monson 1998), and reduced competition with soil microbes (Lipson and Nasholm 2001).

Total amounts of N taken up by plants are a reflection of ecosystem productivity and N supply. In highly productive agroecosystems, total N uptake by crops may be high, as much as 450 kg ha^{-1} year^{-1} for irrigated wheat under ideal conditions (Sinclair and Bai 1997), equating to 15 kg N per tonne crop dry matter, whereas in low rainfall (<300 mm per annum) environments, N uptake by cereals is generally less than 100 kg ha^{-1} year^{-1}. For most grain crops >50% of plant N is removed in the grain at harvest. In unmanaged ecosystems (not subject to fire), most of the N in plant material is eventually returned to the soil surface as litter (with the amount of N varying enormously depending on the ecosystem), or via excreta of grazing animals. There is a paucity of data for plant or crop root N accumulation and, thus, it is difficult to accurately quantify total return of N as plant residues.

2.2.3
Herbivores and N Transfers

Grazing animals exert a substantial direct influence on N cycling in ecosystems as most of the N ingested in plant material is returned to the soil in highly concentrated patches as urine and dung, providing nutrient-rich sites that can have positive and negative influences on subsequent plant growth and other terrestrial N cycling processes. Indirect effects of grazing on the N cycle can also occur as plants are defoliated, changing their internal N economies and N dynamics in the rhizosphere, as well as impacting on plant community structure.

Of the dietary N consumed by domestic ruminant herbivores, less than 30% is retained as live weight gain, milk or wool, the remainder being excreted as urine or dung (Whitehead 1995). Some of the factors influencing the proportion of dietary N excreted and its partition between urine and dung include dry matter intake, the N concentration of the diet, and climate. Since both urine and dung tend to supply N well in excess of immediate plant demands they often lead to N losses and/or alter plant N uptake and metabolism.

The size and frequency of urination and defaecation events varies between animals, and across animal species, resulting in heterogeneous redistribution of N within the soil-plant system. Furthermore, the chemical composition of the excreta, and in particular the C:N ratio of dung, contributes to variation in the quantity and availability of the recycled N.

Urea generally accounts for 60–90% of total N in urine, with the remainder chiefly as allantoin and hippuric acid, other amino acids, and traces of ammonia. Urine is therefore a source of highly labile N that is rapidly available for plants and microbes. It can also solubilise soil C and further stimulate microbial activity (Monaghan and Barraclough 1993). Thus, the presence of grazing herbivores has been shown to directly enhance soil microbial activity, N mineralisation and N availability within natural (Frank et al. 2000) and managed soil–plant systems (Frank et al. 2000; Jarvis 2000).

Most of the N in cattle, sheep and pig dung is present as insoluble organic forms; about 45–65% is amino N, 5% is nucleic acids and 3% is ammonia, with the remainder consisting of partially degraded compounds and N bound in fibre. The concentration of N in the dung of cattle or sheep grazing grass–clover pasture is usually in the range 12–40 g/kg dry matter (Whitehead 1995), with similar values reported for rabbit and vole dung (Baaker et al. 2004). The extent to which dung influences N transfers within the soil–plant system of various ecosystems, particularly under field conditions, is poorly understood (Jarvis 2000). Where dung pats are large (e.g. for cattle), the vegetation underneath the pats may die, and much of the N remains in the soil for months or years or may be leached (Haynes and Williams 1993) before being taken up by plants (Williams and Haynes 1995). The return of the N to soils in dung and urine patches can be localised on a larger scale where animals rest or "camp", or where they spend long periods drinking or feeding, and thus there can be N depletion in some areas and N build-up in others (Haynes and Williams 1999).

Selective grazing by herbivores can alter the species composition of ecosystems and affect the quantity and quality of N inputs in litter. Indeed, complete exclusion of herbivores from an ecosystem causes marked changes in the quantity of N stored in plant shoots, and in the balance between plant types e.g. grasses, forbs and legumes (Chaneton et al. 1996). Furthermore, ungrazed shoot material left to senesce tends to decompose relatively slowly compared to dung and urine. As defoliation by herbivores reduces the rate of photosynthesis and the N demand of plant shoots, it can influence internal transfers within the plant and increase leakiness and death/turnover of roots (Dawson et al. 2000). Also, in legumes, the reduced carbohydrate supply to nodules following defoliation reduces N fixation. Effects of herbivory on plant biomass and, to a limited extent, below-ground functions have been well defined, but only recently has attention focussed on understanding the link between plant physiological responses to foliar herbivory and below-ground N cycling (Bardgett et al. 1998). Trampling by herbivores, as well as potentially enhancing plant litter N turnover, can indirectly influence biological transformations of soil N by causing soil physical conditions that impact on soil water content, aeration and temperature.

Some burrowing herbivores increase aeration of soil, which may stimulate N mineralisation and N turnover.

In ecosystems where animals are removed from grazing areas, N is transferred to yards and housing as manures and urine. In intensively managed pasture/forage agroecosystems, the shoot N from grassland pastures can be removed, conserved as hay or silage and fed either in the same enterprise or off-site to herbivores that are kept in concentrated animal feeding lots. Large amounts of excreta accumulated in confined animal systems are usually applied back on to agricultural land. A discussion of N balances in such systems can be found in Whitehead (1995).

2.3
Inputs of Nitrogen to Terrestrial Ecosystems

The principal points of entry for N into terrestrial ecosystems are through the fixation of atmospheric N_2 to NH_3 via biological or industrial processes, and through deposition of dust (dry deposition) or in rain (wet deposition). The relative importance of these processes depends on the extent of direct human intervention in the N cycle and the extent of atmospheric pollution. In some ecosystems, significant N inputs can come from animals; one such example (Erskine et al. 1998) is found in sub-Antarctic islands where bird guano provides the major N input to the ecosystem. Increased inputs of N to terrestrial ecosystems have resulted in increased fluxes of N to the atmosphere (see section 2.4 on N losses), resulting in increased deposition of N (Vitousek et al. 1997).

2.3.1
Nitrogen Fixation

Nitrogen bonded to carbon (organic N), hydrogen (NH_3, NH_4^+) or oxygen (NO_x, NO_3^-, N_2O) is termed "reactive" N because it is available for biological assimilation or transformation. The source of all reactive N in terrestrial ecosystems is the relatively inert N_2 gas that makes up approximately 78% of the atmosphere. Conversion of this N_2 to reactive forms of N is termed N fixation, and this may occur via biological or industrial means and in lightning. The relative importance of these processes to the global N cycle has changed during the Earth's history (Leigh 2004), with lightning being initially very important, followed by biological nitrogen fixation (BNF) and, much more recently, by industrial fixation and fossil fuel combustion. Recent global N budgets estimate that inputs of fixed N to terrestrial ecosystems now total around 160 million tonnes N per year; 40 from BNF, 98 from industrial fixation (mainly N fertilisers), 22 from

combustion of fossil fuels for energy generation and less than 10 from lightning (Galloway et al. 1995).

2.3.1.1
Biological Nitrogen Fixation

About 90 genera of specialised microorganisms (diazotrophs) have the enzyme complex nitrogenase to reduce N_2 to $2NH_3$ (Eq. 1) in the process known as BNF (Dilworth and Glenn 1991). These organisms exist as free-living entities, but some are also able to live in close association with plants, from which the plants may benefit. Yet others can also form complex symbioses where the plants sequester the bulk of the N_2 fixed by the bacteria, in exchange for a carbon (energy) source. Such symbioses range from cyanobacteria with lichens, *Azolla* and cycads, a range of genera collectively known as "rhizobia" that form symbioses, largely within root nodules on annual and perennial legumes, and the actinomycete *Frankia* in the root nodules of some non-legumes such as *Casuarina*

Table 2.1 Examples of some N_2-fixing bacteria and some of the possible plant symbiotic partners [see Sprent and Sprent (1990) and Sprent (2001) for a full discussion]

Bacterial group	Microsymbionts	Some possible host plant genera
Actinomycetes	*Frankia*	*Alnus*, *Casuarina*, *Myrica*, *Gymnostoma*
Cyanobacteria	*Nostoc, Anabaena*	Cycads, most lichens and *Azolla*
Eubacteria (symbiotic)	*Azorhizobium, Bradyrhizobium, Mesorhizobium, Rhizobium*	Woody perennial legumes – *Acacia*, *Calliandra*, *Chamaecrista*, *Erythrina*, *Leucaena*, *Robinia*
	Sinorhizobium	Herbaceous legume species – *Arachis*, *Cicer*, *Glycine*, *Lotus*, *Lupinus*, *Medicago*, *Pisum*, *Trifolium*, *Vicia*
	Blastobacter, Burkholderia, Devosia, Ralstonia	See Chen et al. 2003
Eubacteria (asymbiotic)	*Acetobacter, Azospirillum, Beijerinckia, Herbaspirillum, Klebsiella, Pseudomonas*	See James 2000

and *Alnus*. There are also a few curious associations where N_2 fixers establish symbioses with animals (e.g. ruminants and termites). The principal N_2-fixing bacteria are listed in Table 2.1, along with some of the possible host plants. The legume and *Azolla* symbioses are of substantial economic importance in agriculture. Investigations into endo- or epiphytic N_2-fixing associations between grass species, and heterotrophic or cyanobacteria, are yet to provide unequivocal evidence for truly symbiotic BNF (James 2000).

A basic stoichiometry for BNF is given below (Eq. 1), with the ATP consumption reflecting the large energy expenditure required, the amount of which varies from ca. 20 to >100 g C per gram N for free living diazotrophs (Zuberer 1999), 3–7 g C per gram N fixed for crop legume systems (Pate and Layzell 1990) and >8 g C per gram N fixed for other natural terrestrial symbiotic systems (Vitousek et al. 2002).

$$N_2 + 16ATP + 8e^- + 8H^+ \rightarrow 2NH_3 + H_2 + 16ADP + 6Pi \tag{1}$$
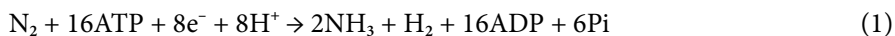
Quantities of N_2 fixed vary depending on the N_2-fixing system in question, but in general free-living and associative N_2 fixers tend to fix less N than symbiotic systems in plants, where the host may supply the microsymbiont with carbon (energy) and better protect the nitrogenase enzyme from deactivation by oxygen (Dilworth and Glenn 1991).

Both NH_4^+ and NO_3^- in soils suppress BNF. Hence, where there is sufficient mineral N to meet plant N demand, both the establishment of the symbiosis and BNF will be strongly reduced. This dynamic equilibrium is illustrated in a glasshouse study in sand culture (Fig. 2.2). In the absence of mineral N, all legume N is necessarily sourced from N_2 fixation. As NO_3^- supply is increased to 10 mM, nodulation is initially reduced and then eventually completely inhibited, along with N_2 fixation.

Development of crop and forage legumes for agriculture has resulted in these systems being both the best studied and having the most productive N_2-fixing systems. Legumes in agroecosystems are best grown following non-legume crops, which deplete soil mineral N, thus providing ideal conditions for the establishment of nodulation. For annual agricultural crops, BNF is estimated to range from an average of 250 kg N ha^{-1} for soybean to 57 kg N ha^{-1} for chickpea, although much higher and lower values are often recorded (Unkovich and Pate 2000). Relatively few studies account for fixed N accumulated in roots, and hence total inputs of fixed N may often be underestimated (McNeill et al. 1997). In semi-arid climates, productivity of perennial forage plants such as lucerne (*Medicago sativa*) or white clover (*Trifolium repens*) and hence BNF (75–150 kg N ha^{-1}year^{-1}) may be limited by rainfall, whereas under irrigated or high rainfall conditions BNF may reach 200–400 kg N ha^{-1} year^{-1} (Whitehead 1995). In woody, perennial shrub or tree agriculture BNF maxima of 550–600 kg N ha^{-1} year^{-1} have been recorded (Unkovich and Pate 2000), although 100–200 kg N ha^{-1} year^{-1} is more typical (Peoples et al. 1995). Another important BNF symbiosis in agriculture is that of the aquatic fern *Azolla* with a
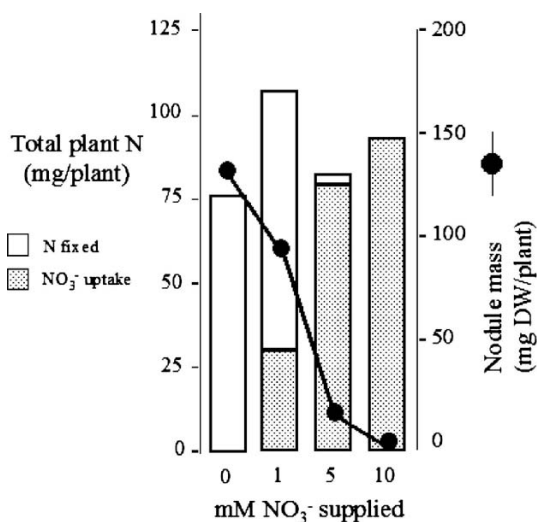
Fig. 2.2 Nodulation and N_2 fixation in *Medicago truncatula* (barrel medic) as a function of NO_3 supply in a pot study (M. Unkovich, unpublished)

range of cyanobacteria, which together typically fix around 30 kg N ha^{-1} $year^{-1}$ in flooded rice paddies (Roger 1997).

Reliable estimates of BNF in natural ecosystems are few, due to particular difficulties with measurement of BNF in these situations (Vitousek et al. 2002). Whilst legumes may dominate some natural ecosystems, BNF tends to be lower than in productive agricultural systems. At the top end of the range, dense stands of red alder (*Alnus rubra*) in symbiosis with *Frankia* may fix 50–150 kg N ha^{-1} $year^{-1}$, and regenerating forest stands of black locust (*Robinia pseudoacacia*) 35–300 kg N ha^{-1} $year^{-1}$ (Adams 2003). However, BNF for symbiotic legumes and other associations in unmanaged ecosystems is more typically less than 100 kg N ha^{-1} $year^{-1}$. Cyanobacteria in lichen within old-growth forests may fix 3–5 kg N ha^{-1} $year^{-1}$ (Rai et al. 2000), with cycads in forests 19 kg N ha^{-1} $year^{-1}$ (Halliday and Pate 1976), and in soil crusts and soils in arid regions typically 1–10 kg N ha^{-1} $year^{-1}$, but with maxima of 41 kg N ha^{-1} $year^{-1}$ (Vitousek et al. 2002). More work is required to improve the understanding and quantification of BNF in natural ecosystems.

2.3.1.2
Industrial Nitrogen Fixation

The development of cost-effective industrial N_2 fixation via the Haber-Bosch process is easily one of the twentieth century's greatest advances (Smil 1997).

The process (Eq. 2) is very energy demanding, and today some factories lie idle due to a shortage of natural gas. The Haber-Bosch N_2 fixation process generates H_2 from natural gas and water, and then combines the H_2 with N_2 from the atmosphere at ca. 600°C and $\leq 10^6$ kPa to produce NH_3 in the presence of a catalyst.

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad \text{then} \quad N_2 + 3H_2 \leftrightarrow 2NH_3 \tag{2}$$
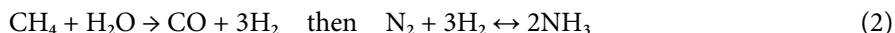
Currently, production of some 90 million tonnes per annum of manufactured fertiliser N approximates N inputs to global agricultural systems. In many industrialised countries inputs of N from manufactured fertilisers now exceed estimated inputs from BNF (e.g. Xing and Zhu 2002). The main fertiliser N consumers (IFA 2005) are China (25% of world consumption), North America (16%), central and western Europe (15%) and India (12%). Cereals (wheat, barley and rice, sorghum and maize) receive a high proportion of the fertiliser N, with significant amounts also being applied to fruit and vegetables in China and the United States, sugar cane and cotton in India, and grasslands in Europe (FAO 1999).

Urea $[CO(NH_2)_2]$, the cheapest N fertiliser to produce and one that is relatively easy to transport and handle, accounts for some 75% of total fertiliser N produced. Ammonium nitrate (ca. 16%), ammonium sulphate (ca. 5%) and calcium ammonium nitrate (ca. 4%) are other important N fertiliser compounds. Whilst urea can be a very cost-effective way of applying N to soils for crops and pastures (Bacon 1994), it has the disadvantage that much of it can be lost to the atmosphere from the soil surface as NH_3 gas under alkaline conditions.

Most fertiliser is applied to soils, but in some intensively managed systems fluid fertiliser can be applied directly to crop foliage or with irrigation (termed fertigation). Regardless of the fertiliser type, only a portion (20–50%) of N applied to soils is taken up by the crops to which it is applied; the remainder is available for MIT, and gaseous and leaching losses, dependent on management, edaphic and climatic factors. Such losses can be reduced, but not eliminated, by judicious management.

2.3.2
Nitrogen Deposition

The main forms of N that are returned to the earth from the atmosphere through deposition processes are NH_4^+, NH_3 and NO_3^-. Organic N deposition, in the form of amine aerosols, organic nitrates and particulate N (dust, pollen, bacteria) in the atmosphere, may make up ca. 30% of N deposited in some ecosystems (Neff et al. 2002).

Ammonia released to the atmosphere tends to return to the plant–soil system relatively rapidly. It can increase the N content of nearby vegetation, but at high concentrations may result in adverse effects such as leaf burn (Asman et

al. 1998; Krupa 2003). However, the bulk of atmospheric NH_3 is converted to NH_4^+, consuming some of the atmospheric acidity produced by human activities (Schlesinger and Hartley 1992). Fine-particle ammonium aerosols formed in the atmosphere have a lifetime of 1–15 days (Anderson et al. 2003). They can travel long distances and cause problems at a regional scale, impacting on air quality and through wet deposition. Ammonium and NO_3^- are returned mostly through wet deposition in rainfall, and NH_3, NO_2^- and particulate N as dry deposition. Since considerable amounts of N may be deposited on leaves and subsequently picked up by rain in canopy throughfall (Beier and Gundersen 1989; van Breemen and van Dijk 1988), N deposition to soils tends to be higher in forests than in many other ecosystems. However, whilst many canopies add N to throughfall, some crop canopies may absorb N by foliar uptake (Bohme et al. 2003; Farquhar et al. 1980; Gessler et al. 2000). Deposition may be relatively greater at higher altitudes (Pitcairn et al. 1995), and adjacent to urban areas (Kirchner et al. 2005). A review of long-term (1853–1996) studies of N deposition at Rothamsted in the United Kingdom indicated that N loads in rainfall (wet deposition) rose from 4 kg ha^{-1} year^{-1} (NH_4^+ 1 kg, NO_3^- 3 kg) in 1855 to 18 kg ha^{-1} year^{-1} (NH_4^+ 8 kg, NO_3^- 10 kg) in 1980, but declined to 4 (NH_4^+) and 5 (NO_3^-) kg ha^{-1} year^{-1} thereafter. Total N deposition to cereal crops in the United Kingdom was estimated to be 45 kg ha^{-1} year^{-1} (Goulding et al. 1998). Average contemporary total N deposition across the entire area of the United Kingdom was estimated at 25 kg ha^{-1} year^{-1}, attributed not only to dry deposition, but also to organic N deposition. In other regions of the world where inputs of N to the atmosphere are smaller and where rainfall and ecosystem productivity are lower, deposition is predominantly as dust, and rates are likely to be <5 kg ha^{-1} year^{-1} (Littmann 1997).

Although there is still some uncertainty about the impact of N deposition on forest ecology (Binkley and Hogberg 1997; Bredemeier et al. 1998; Engvild 1998), there is general agreement that chronic N additions should be minimised (Vitousek et al. 1997). Ferm (1998) reported that critical annual loads to prevent N saturation in Europe, where deposition is greatest, were 5–20 kg ha^{-1} year^{-1} for deciduous forests and 3–15 kg ha^{-1} year^{-1} for coniferous forests. For native grasslands, critical values are 3–10 kg N ha^{-1} year^{-1}. If NO_x is oxidised it can return to terrestrial ecosystems as HNO_3 or acid rain, and this has serious implications for soil and atmospheric chemistry (Kennedy 1996). Reductions in N deposition have been observed recently in some parts of the world, probably due to lower inputs from combustion (Butler et al. 2005).

2.4
N Losses

The major pathways for N loss from terrestrial ecosystems to the atmosphere or hydrosphere are (1) ammonia volatilisation, (2) gaseous emissions of nitrous

oxide (N_2O), nitric oxide (NO) and nitrogen dioxide (NO_2) collectively termed NO_x, and dinitrogen (N_2), (3) leaching of nitrate, and (4) off-site transport of organic or inorganic N by wind and water erosion. These N losses can reduce ecosystem productivity and N storage of the ecosystem from which they occur. They may also, as mentioned earlier, indirectly affect adjacent ecosystems.

2.4.1
Ammonia Volatilisation

The key reactions involved in exchange of ammonia from the soil to the atmosphere in terrestrial ecosystems can be represented as follows:

$$\text{Absorbed} \ \ NH_4^+ \leftrightarrow NH_{4(solution)}^+ \leftrightarrow NH_{3\,(solution)} \leftrightarrow NH_{3\,(gas)} \leftrightarrow NH_{3\,(gas\,in\,atm)} \tag{3}$$
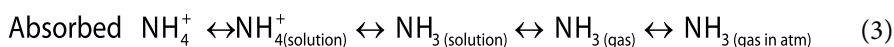
Ammonium is present in soil either as the free NH_4^+ ion or physically absorbed to soil particles or to organic matter. Ammonia volatilisation may occur where free ammonia is present near the surface, and increases with pH and temperature. Plants represent both a source and a sink for ammonia, although it is often considered that ammonia is emitted from agricultural systems while semi-arid natural ecosystems act as sinks (Sommer et al. 2004). However, emission is dependent on a number of factors, including the leaf NH_3 compensation point, plant age and N content (Asman et al. 1998; Wetselaar and Farquhar 1980). The extent to which ammonia uptake occurs (Denmead et al. 1976; Nemitz et al. 2000) is unclear, and therefore net impacts of ammonia emissions on agroecosystem N balances can be difficult to determine (Schjoerring and Mattsson 2001).

Following the excretion of urine and faeces by grazing animals, a proportion of the N (ca 10% for dung and 4–55% for urine) hydrolyses to ammonium and, due to concomitant production of bicarbonate, rapidly deprotonates to NH_3. Thus, on exposure to the atmosphere, volatilisation of NH_3 from these animal wastes occurs relatively rapidly (hours–days), although total NH_3 loss is related to a range of environmental and management factors (Bolan et al. 2004; Chambers et al. 1997; Misselbrook et al. 2000; Oenema et al. 2001; Sommer and Hutchings 1997; Terman 1979).

Ammonia volatilisation is responsible for large and significant losses of N from ammonium and urea fertilisers (Sommer et al. 2004). Losses may reach 50% of N applied to rainfed agricultural ecosystems, particularly on alkaline soils, and as much as 80% in flooded systems (Freney 1997b). As NH_3 needs to be in contact with the surface of the soil before it can be lost to the atmosphere, injection, drilling or incorporation rather than surface application of N fertiliser reduces losses (Mosier 2001).

Emissions from agricultural animal excreta and losses during the application of manufactured fertilisers are estimated to be the most important sources

of atmospheric NH_3 (Ferm 1998; Mosier 2001), together contributing 57% of the estimated annual global output (Olivier et al. 1998). Losses from burning biomass, including savanna, deforestation and bio-fuels, are considered to contribute about 12% of the total global budget (Schlesinger and Hartley 1992), similar to that from the oceans. Many sources of NH_3 are not well characterised; hence, the variation associated with most estimates of NH_3 emission is quite large (Olivier et al. 1998).

2.4.2
Processes Producing Gaseous Oxides of Nitrogen and N_2

2.4.2.1
Biological Denitrification

Biological denitrification (Fig. 2.3, pathway 2) is the reduction of one or both of the ionic nitrogen oxides (NO_3^- and NO_2^-) to the gaseous oxides (NO and N_2O), which may themselves be further reduced to N_2 (Knowles 1982). The general pathway is shown below (Firestone 1982):

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2 \tag{4}$$
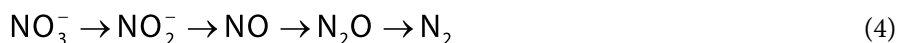
The dominant organisms responsible for denitrification are heterotrophic bacteria (Payne 1981) and fungi (Shoun et al. 1992) that can utilise N oxides as terminal electron acceptors and organic C as electron donors under restricted
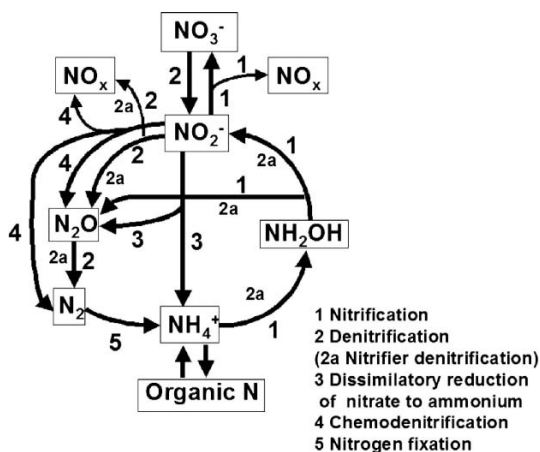
Fig. 2.3 Major N transformation processes influencing production of N_2O, N_2 and NO_x in soils (adapted from Stevens and Laughlin 1998)

oxygen availability. Many denitrifying bacteria are chemoheterotrophic, using NO_3^- as the primary electron acceptor to obtain energy from organic compounds, whereas some are autotrophic and obtain energy by using nitrate for oxidation of inorganic compounds. There is evidence that aerobic denitrification by bacteria capable of NO_3^- respiration in the presence of oxygen may be significant in both natural and managed ecosystems (Patureau et al. 2000).

Edaphic and management factors that influence denitrification have been discussed recently by Bolan et al. (2004). Briefly, denitrification is promoted by high availability of organic C and NO_3^--N, a low rate of oxygen diffusion associated with high soil moisture content or compaction, or an increase in soil pH or temperature. A recent review of data for agricultural and forest soils around the world (Barton et al. 1999) identified a wide range in measured annual N loss from denitrification (0–239 kg N ha^{-1} $year^{-1}$). However, most annual rates were fairly low with a mean of 2 kg N ha^{-1} $year^{-1}$ for forest soils and 13 kg N ha^{-1} $year^{-1}$ for agricultural soils.

Current field methodologies for measuring N_2O emissions make it difficult to distinguish between losses from the soil and the plant, and data is mainly reported either for bare soil or for soil–plant systems. Direct emission of N_2O from plants has been reported in forest, grassland and crop ecosystems (Pihlatie et al. 2005) but requires further research. Overall, the literature indicates that N_2O emissions are generally greater and more variable from agricultural systems than from uncultivated land or natural ecosystems (Freney 1997a). The highest rates of denitrification can be expected from agroecosystems where management increases soil nitrate availability (e.g. N fertilisers, animal excreta, legumes and crop residues), and are exacerbated under irrigation. The losses can represent up to 7% of fertiliser N applied (Freney 1997a) and can range from 0.1% to 18% of the N deposited as dung and urine on grazed pastures (Mosier et al. 1998; Oenema et al. 2001). However, the data are mostly from temperate regions and losses from sub-tropical and tropical ecosystems may be greater. The range of management practices currently available to increase plant N-use efficiency from fertilisers and applied manures has the potential to reduce losses of N_2O, although direct evidence is still required (Dalal et al. 2003). Nitrification inhibitors can reduce emissions of N_2O from soil, but problems with persistence due to hydrolysis, sorption to soil colloids or volatilisation reduce their effectiveness and few are commercially available (Freney 1997b). Denitrification to N_2 is effective in returning excess reactive N to the relatively stable atmospheric N_2 pool.

2.4.2.2
Chemodenitrification

Nitrate is not subject solely to biological denitrification, but can also be chemically denitrified (Fig. 2.3, pathway 4) by non-enzymatic pathways under fully aerobic conditions (Paul and Clark 1989). Chemodenitrification describes various chemical reactions of NO_2^- ions within soil that result in the emission of

N_2, NO, NO_2 and sometimes N_2O (Nelson 1982). It is potentially significant in soils at pH<5 and in any soil under situations conducive to NO_2^- accumulation; for example, in alkaline soils treated with acid hydrolysing fertilisers, in urine patches, during biological denitrification in soils receiving high NO_3^- inputs, and in unfrozen water of freezing soils (Chalk and Smith 1983). However, in terms of contributions to total emissions of N_2O from agricultural lands, chemodenitrification is currently considered relatively minor (Bremner 1997).

2.4.2.3
Nitrification

Until relatively recently, biological denitrification under anaerobic conditions was considered the major source of N_2O from soils, although the potential for N_2O release during nitrification was known (Blackmer and Bremner 1978). Recent research has shown that both autotrophic and heterotrophic nitrification can also contribute to N_2O production in soils and, under certain conditions, may be more dominant than denitrification (Abbasi and Adams 2000; Bateman and Baggs 2005). It is highly probable that nitrification and denitrification take place simultaneously since many soils contain a mosaic of aerobic and anaerobic zones (Smith 1980). The processes can be considered coupled where NO_2^- and NO_3^- produced by nitrification (Fig. 2.3, pathway 1) are subsequently utilised by denitrifiers (Fig. 2.3, pathway 2). Nitrite does not usually persist for long in soil, since in well-aerated unfertilised soils the autotrophic oxidation of NO_2^- to NO_3^- generally proceeds at a faster rate than the conversion of NH_4^+ to NO_2^-, thus keeping the concentration of NO_2^- low (<1 $\mu g\ g^{-1}$). However, there is a single group of nitrifying organisms called autotrophic ammonia oxidisers that oxidise NH_4^+ to NO_2^- and subsequently reduce NO_2^- to N_2O and N_2 (Fig. 2.3, pathway 2a). The importance of this process, called nitrifier denitrification (Poth and Focht 1985), to gaseous N losses from terrestrial ecosystems is currently unclear, with measured amounts varying from insignificant to about 30% of the total N_2O produced (Wrage et al. 2001).

2.4.2.4
Dissimilatory Reduction of NO_3^- to NH_4^+

The presence of fermentative bacteria in soils and sediments that can carry out dissimilatory reduction of NO_3^- to NH_4^+ [dissimilatory reduction of NO_3^- to NH_4^+ (DNRA), Fig. 2.3, pathway 3] has been known for some time (Buresh and Patrick 1978). These bacteria are also capable of reducing NO_2^- to N_2O, whilst they may not be able to convert N_2O to N_2. Strongly reduced soil conditions such as those in flooded soils, with readily available carbon and low oxygen, as well as NO_3^- limitation, appear to favour DNRA, although both denitrification and

DNRA can occur simultaneously (Stevens and Laughlin 1998). The extent and significance of DNRA in relation to gaseous N loss from soils is relatively unknown. Reports suggest that the process accounts for 1–5% of NO_3^- reduction in anaerobic agricultural soils without exogenous addition of C, although a value of 15% was recently reported (Yin et al. 2002).

2.4.2.5
NO_x Production

Nitric oxide may be produced from soil during nitrification, biological denitrification and chemodenitrification (Fig. 2.3, pathways 1, 2, 4), with the magnitude of emission dependent on the rate of these processes, and on soil properties that regulate gaseous diffusion. Since NO can be readily oxidised to NO_2 and absorbed by leaves, the presence of a plant canopy may reduce the amounts entering the atmosphere. The edaphic and management factors affecting NO_x emission from soils are discussed in detail by Skiba et al. (1997), and are similar to those influencing N_2O emissions. Whilst the largest source of NO_x is fossil fuel combustion, about 7.7 million tonnes N per annum are estimated to be contributed by biomass burning, including savanna and crop residue fires, deforestation and biofuels (Olivier et al. 1998).

There is great uncertainty concerning the extent of NO_x emissions from soil; reported values range from 0.1 to 11 kg N ha year^{-1}, and vary within and between ecosystems (Davidson and Kingerlee 1997). Thus, global estimates range from 5 to 20 million tonnes per annum, leading to conflicting perceptions about the importance of NO_x derived from soil (Matson 1997). It is generally agreed that soil emissions are larger in situations where availability of N is high, as occurs with soil disturbance, addition of inorganic or organic fertiliser and under grazing animals. Mitigation options for N_2O, discussed above, should equally contribute to reducing NO_x emissions.

2.4.3
Leaching

Since the particle surfaces in most soils in temperate regions are negatively charged, the anion NO_3^- is not retained and can relatively easily be leached down the soil profile beyond the plant root zone, and into the groundwater. The processes involved in NO_3^- leaching, and the climatic and edaphic factors affecting it, are well described (e.g. Addiscott 1991; Cameron and Haynes 1986; Follett et al. 1991). The two major determinants of NO_3^- leaching are the quantity of water passing through the soil profile and the concentration of NO_3^- in the soil at that time. Thus NO_3^- leaching occurs whenever NO_3^- accumulation in the soil profile coincides with, or is followed by, a period of high drainage. Ecosystem

disturbances caused by fire, harvest, fallowing, cultivation, and grazing tend to increase the potential for NO_3^- leaching in both natural and agricultural systems. This is largely due to an accumulation of NO_3^- in the soil resulting from an uncoupling of the intrinsically linked processes of mineralisation and plant N uptake, together with increased drainage caused by an imbalance in the hydrologic cycle. There has also been concern expressed recently that N saturation of some mature forest systems by N deposition may result in an enhanced potential for NO_3^- leaching (Fenn et al. 1998) as well as losses of organic N.

Reported quantities of NO_3^--N leached vary enormously within similar ecosystems and even more widely between different ecosystems, depending largely on climate and management factors (Di and Cameron 2002; Fillery 2001; McNeill et al. 2005). Overall, leaching is exacerbated on light sandy soils and under irrigation, and tends to be much larger in agricultural ecosystems that are frequently disturbed, and where N inputs from fertilisers, legumes or animal manures are high. A recent review of temperate agroecosystems concluded that, in general, the potential for NO_3^- leaching was least in forests, increasing in the order cut grasslands < grazed pastures < arable cropping < ploughed pastures, and was highest for intensive vegetable production systems (Di and Cameron 2002). However, there are management techniques that can be used to avoid or minimise high risk leaching situations, in particular, selection of the most suitable type and amount of fertiliser N or animal wastes, careful timing of N application, ploughing at a time that avoids significant drainage or mineralisation events, and use of cover crops and irrigation scheduling have also proved successful. The efficacy of measures such as residue retention, minimum or zero tillage, improved stock management, precision farming and nitrification inhibitors are still debatable.

The extent and scale of losses of organic N via leaching in natural and managed terrestrial ecosystems is still relatively unknown. Significant amounts of dissolved organic N (0.1–5 mg l^{-1}) have been measured in forest and agricultural soils as well as large amounts of water-extractable organic N (10–30 kg ha^{-1}) in agricultural soils (see references in Chantigny 2003; Murphy et al. 2000). The limited data suggests that much of the N lost by leaching is in the form of these dissolved organic compounds, both from unpolluted, undisturbed forests (Perakis and Hedin 2002; Siemens and Kaupenjohann 2002) and from arable agricultural soils (Murphy et al. 2000). However, despite acknowledgement that these losses may comprise a significant part of the terrestrial N cycle, there is a paucity of quantitative information on the sources, cycling and fate of labile organic N, as well as on the influence of changes in land management.

2.4.4
Erosion

Wind erosion transports N attached to soil particles or bound in organic matter, particularly in semi-arid and arid regions with periodic high wind veloci-

ties. Losses of terrestrial N by wind erosion have not been widely quantified (Delgado 2002), although significant redistribution or loss of organic matter following erosion has been measured (Gregorich et al. 1998). The potential for soil erosion by water occurs whenever rainfall strikes bare soil or where water flows over unprotected soils and causes detachment, transport and deposition of soil particles. Water erosion is particularly pronounced for soluble N (including nitrate and some dissolved organic N compounds) and for ammonium and organic N associated with the fine soil fractions (Follett and Delgado 2002). The detailed processes involved in erosion and surface run-off as well as the environmental and management factors influencing the likely scale of associated N losses are discussed in some detail by Cameron and Haynes (1986), and have been recently summarised by Delgado (2002).

Both wind and water erosion are generally accelerated by severe ecosystem disturbances that remove vegetation and expose soil, such as fire (Certini 2005). The potential for N loss via erosion has often been exacerbated by ploughing, clear-felling, overgrazing, irrigation, mining and construction. The dissolved N concentration in surface run-off from conservation or no-till fields can be higher than for conventional tillage (McDowell and McGregor 1984) possibly due to the residues decomposing at the soil surface, although the total amount of water running off is likely to be less in stubble retention systems.

Erosion may simply constitute a transfer of N from one part of the terrestrial ecosystem to another with associated positive or negative impacts at the local or regional scale. However, in many instances the N is lost from the terrestrial system to streams, rivers and lakes and oceans, either as inorganic N or as dissolved or particulate organic N, and can cause deleterious N imbalances in these ecosystems (Vitousek et al. 1997). It has been estimated that globally 20 million tonnes of dissolved N and 20 million tonnes of particulate N, largely derived from anthropogenic sources, are transported by rivers to coastal systems annually (Galloway et al. 1995).

2.5
Conclusions

Inputs of N to terrestrial ecosystems have increased dramatically over the past 50–100 years. Estimates of industrial fixation based on fertiliser N use and fossil fuel combustion are relatively easily calculated, but accurate estimates of BNF remain more elusive. Despite great advances in measurement techniques, particularly using stable isotope ^{15}N technology, most BNF estimates are hampered by the paucity of data regarding quantities of fixed N accumulated belowground. Estimates for asymbiotic and associative N fixation are also scarce, with basic knowledge of mechanisms and processes lacking. Some of the N transfer and loss mechanisms, such as MIT, nitrification, ammonia volatilisation and NO_3^- leaching are relatively well defined at the process level. On the other hand,

the complex nature of processes governing the emission of gaseous N oxides and N_2 causes difficulties in defining mechanisms, as well as identifying the source of such losses and the quantities of N involved. N deposition appears to be highly related to human activities, but requires more data to evaluate its impact on a global scale. The role of dissolved and soluble organic N in transfer and loss processes has only relatively recently been fully acknowledged and further research is needed to determine the important sources and sinks of this labile N component in the N cycle of terrestrial ecosystems.

The spatial heterogeneity of all these soil-based processes presents a limitation to scaling up at even the local level, let alone at the regional or global scale. This difficulty has been addressed in some instances by using large scale measurements, for example monitoring of gaseous outputs or leaching losses from catchment zones, but relatively few studies have done this. Determining the fluxes through some of these processes at the local, regional and global scale remains an ongoing challenge. In the case of some processes, such as MIT or nitrification, reliable models that can extrapolate from the micro-scale will be invaluable, but will require extensive soil and landscape characterisation for input as well as further understanding of soil micro-structure and its influence on biological processes (see Chapter 13 by de Willigen et al., this volume).

The environmental impacts of excess N, as well as the increasing costs of N fertiliser production and use, are beginning to force land managers to consider reducing N inputs in some parts of the world. Many countries have government policies aimed at reducing adverse effects associated with increased terrestrial N cycling. The pertinent question is whether current rates of terrestrial N cycling need to be maintained in order to sustain future global protein supplies. It is anticipated that with improved understanding of the N cycle at a range of scales, N inputs may decrease, or should at least be better managed so that N is used much more efficiently within production systems and reduce the impacts of excessive N input to terrestrial and aquatic ecosystems. In addition to reducing inputs, efforts to increase denitrification through to N_2 might also prove useful in reducing some of the negative impacts of excess reactive N in terrestrial ecosystems.

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3 Phosphorus and Sulphur Cycling in Terrestrial Ecosystems

Else K. Bünemann*, Leo M. Condron

3.1
Introduction

3.1.1
Forms and Amounts of Phosphorus and Sulphur in Terrestrial Ecosystems

Phosphorus (P) and sulphur (S) are essential elements for all living cells. Among the biomolecules that contain P are nucleic acids (DNA and RNA), phospholipids, sugar phosphates (e.g. glucose-6-phosphate) and molecules with an energy-rich pyrophosphate bond (e.g. ATP), whereas S is contained in two amino acids (cysteine and methionine) and various coenzymes, vitamins and sulpholipids. The forms, amounts, transformation processes and cycling rates of the two elements in terrestrial ecosystems are usually studied either from an agronomic point of view, i.e. from the perspective of imminent deficiencies, since both elements are major plant nutrients and therefore essential to achieve sufficient crop yields, or from an environmental point of view, where a surplus of these elements in ecosystems may lead to eutrophication or even direct toxicity effects in the case of S.

Major global reservoirs of P and S are the oceans and the lithosphere, while less than 1% of both elements are found in the three main compartments of terrestrial ecosystems, i.e. the atmosphere, plant biomass and the soil (Stevenson and Cole 1999). In the atmosphere, P is negligible, as phosphine gas (PH_3) oc-

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curs only under highly reducing conditions. Relatively small amounts of S are found in the atmosphere: hydrogen sulphide (H2S) and organic S gases are produced by anaerobic bacteria, while sulphur dioxide (SO2) is a product of industrial combustion, microbial oxidation and volcanic activity, with anthropogenic S emissions representing about 55% of total S inputs into the atmosphere (Zhao et al. 1996). Recent work has shown that dimethyl-sulphide produced by marine algae is another major source of S in the atmosphere (Kelly and Murrell 1999). The role of sulphate aerosols over the oceans in cloud formation and albedo (reflectance of solar radiation) is currently being investigated in the context of global warming (Satheesh and Moorthy 2005).

The concentrations of P and S in plant biomass are quite similar (usually $1–5\,g\,kg^{-1}$ dry matter), and above-ground P and S amount to about 10–$100\,kg\,ha^{-1}$ in most ecosystems. In plant tissues, S is mainly in C-bonded forms such as amino acids, while about one-half of the P in plants is present as nucleic acids, followed by phospholipids and monoesters. Concentrations of P and S in natural soils range between 100 and $1{,}000\,mg\,kg^{-1}$, which is equivalent to about $200–2{,}000\,kg\,ha^{-1}$ in the top 20 cm. Concentrations of P in fertilised agricultural as well as some volcanic soils can be considerably higher. In soils, P is
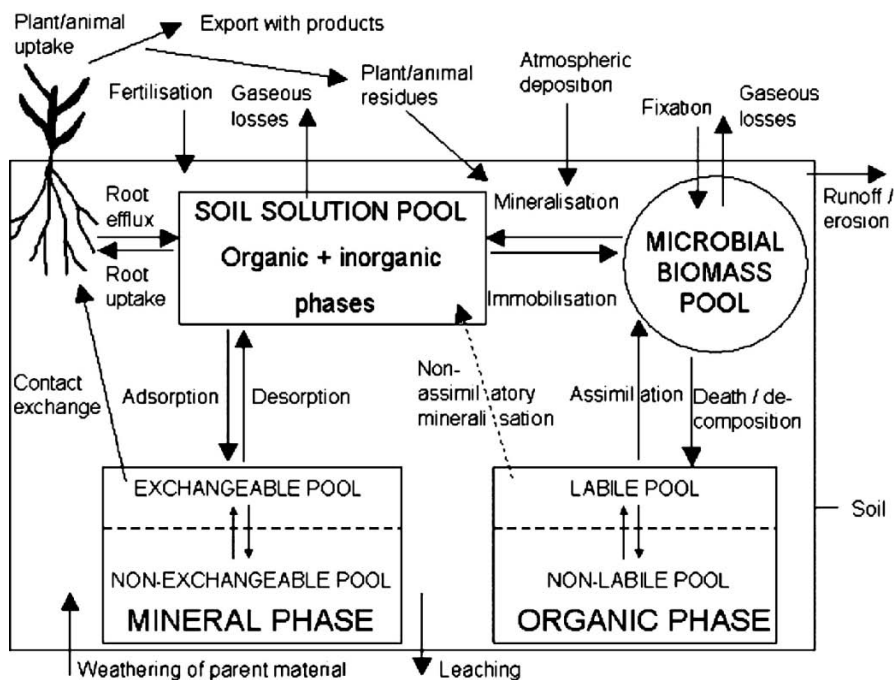
Fig. 3.1 Schematic presentation of nutrient cycling in terrestrial systems (modified after McLaughlin et al. 1999)

found largely in its oxidised state as orthophosphate, whereas S exists in several oxidation states, e.g. –2 for sulphides (S^{2-}), 0 for elemental sulphur ($S°$), +4 for sulphites (SO_3^{2-}) and +6 for sulphates (SO_4^{2-}).

The most labile pool of P and S in soil is the soil solution, followed by the microbial biomass, exchangeable inorganic pools, and labile organic P and S (Fig. 3.1). The mineral phase of P consists of primary and secondary minerals, mainly calcium, iron and aluminium phosphates, while inorganic S is present predominantly as aluminium sulphates, pyrite (FeS_2) and gypsum ($CaSO_4$). The proportion of soil organic P ranges from 20 to 80% of total P, while in most soils 80% or more of total S is in organic form. The mineral phase is thus much more important for P, although in highly weathered soils, more than 50% of total S may be adsorbed to mineral surfaces (Krouse et al. 1996). However, sorption of phosphate groups is generally stronger. This applies in particular to some organic P compounds, such as inositol hexakisphosphate (IHP) with six phosphate groups, three of which may become sorbed onto iron and aluminium oxides and clays (Celi and Barberis 2004). When sorbed, IHP is less available to microorganisms than orthophosphate or glucose-6-phosphate (Shang et al. 1996). The reduced decomposition may be the main reason why extractable organic P is often dominated by inositol phosphates (Magid et al. 1996). Soil organic S is often present in approximately equal proportions of ester sulphate S and C-bonded S, although the proportion of ester sulphate S usually increases with depth (Zhao et al. 1996).

3.1.2
Cycling of Phosphorus and Sulphur in Terrestrial Ecosystems

The cycling of P and S in terrestrial ecosystems is illustrated in Fig. 3.1. Without plants or soil organisms, fluxes in the soil would be small, since the chemical equilibrium between different forms of P and S would be disturbed only by abiotic effects, such as moisture and temperature fluctuations, as well as through atmospheric inputs and leaching losses. The microbial biomass has long been recognised as the driving force in soil organic P dynamics. Plant uptake and microbial immobilisation have also great potential to disturb the equilibria of inorganic nutrients. In the case of S, microorganisms promote not only immobilisation and mineralisation, but also oxidation and reduction processes. The soil fauna is less important as a nutrient pool but increases the turnover of the microbial biomass by grazing and predation.

Of the four input pathways into the soil (atmospheric deposition, weathering of parent material, fertilisation, plant and animal residues), atmospheric deposition is often the main source of S, with annual inputs of >80 kg S ha^{-1} close to industrial sources (Krouse et al. 1996). In more remote areas, atmospheric input of S is in the range of 2–15 kg ha^{-1} $year^{-1}$. Atmospheric deposition of P is generally negligible. Weathering of parent material contributes variable amounts

of P and S. In highly weathered soils, the primary P mineral apatite has been transformed completely into various secondary P minerals (Walker and Syers 1976). Some parent materials are a significant source of S, e.g. pyrite-rich shales (Krouse et al. 1996).

Mineral P fertilisers have increased total P contents in the agricultural soils of industrialised countries (Fairhurst et al. 1999), but application is still lagging behind in developing countries. The use of chemical S fertilisers is becoming more widespread in recent years due to reduced inputs of S from the atmosphere and little or no S contamination of high-purity NPK fertilisers (Zhao et al. 1996). Elemental S fertiliser is oxidised to SO_4^{2-} by soil microorganisms, with slow rates observed under cold, dry conditions (Krouse et al. 1996).

Leaching losses of S are often equivalent to atmospheric S inputs (Mitchell et al. 1992), while annual P loss from soil in subsurface drainage and by overland flow is commonly less than 1 kg ha^{-1} (Condron 2004). For example, in a long-term fertiliser experiment in a grazed pasture in Australia, 7% of P applied as superphosphate was unaccounted for in the top 43 cm after 17 years, compared to 60% in the case of S (McCaskill and Cayley 2000). Gaseous losses of S from agro- or forest ecosystems are usually in the range of 0.1–3 kg ha^{-1} year^{-1} (Zhao et al. 1996).

Processes of soil P cycling have been described in detail by several researchers (e.g. Frossard et al. 1995, 2000), whereas Zhao et al. (1996) gave a comprehensive overview of the turnover of soil organic S. The dynamics of soil organic P in natural and agricultural ecosystems have been reviewed by Magid et al. (1996), while recent reviews of the dynamics of S in different ecosystems include those by Mitchell et al. (1992) for forest ecosystems, Nguyen and Goh (1994) for grazed grasslands and Janzen and Ellert (1998) for agroecosystems in general.

3.1.3
Chapter Aims

In this chapter, the cycling of P and S in terrestrial ecosystems is described, with the main focus on processes occurring in aerobic soils. Since our knowledge is always determined by the available methods, we first describe a range of analytical methods, including some recent developments, and give a short overview of experimental approaches. We then present three case studies of P and S cycling chosen to represent different scales, ranging from laboratory incubations to elucidate processes of mineralisation and immobilisation, to two field applications, namely the use of stable isotopes to trace S dynamics, and changes in soil P and S cycling associated with land use change from grazed pasture to short-rotation plantation forest. Rather than trying to review all aspects of P and S cycling, these examples were chosen to represent successful applications of appropriate methodology to elucidate processes of P and S cycling in terrestrial ecosystems.

3.2
Methods and Approaches to Study Phosphorus and Sulphur Cycling

3.2.1
Analytical Methods

3.2.1.1
Total P and S and Sequential Fractionation Schemes

Total P and S in soils are usually determined by fusion with Na_2CO_3 or wet digestion methods followed by determination of phosphate and sulphate or H_2S by colorimetry or inductively coupled plasma atomic emission spectrometry (Kuo 1996; Tabatabai 1992). In the case of plant materials, dry ashing procedures are often sufficient to convert all organic P into the extractable inorganic form, whereas this method cannot be used for S since organic S is lost as SO_2. For S, dry combustion in a LECO S analyser followed by infrared detection of SO_2 is a convenient and precise alternative to wet chemical methods (Tabatabai 1992).

Chemical extraction schemes have been widely used for the characterisation of both P and S in soils (Fig. 3.2). For P, sequential extraction allows a partitioning into inorganic (P_i) and organic (P_o) P pools with different extractability. Alkaline extractants are thought to remove Al- and Fe-bound P, whereas acids render Ca-bound P extractable. In the original fractionation scheme (Hedley et al. 1982), soil is sequentially extracted with an anion exchange resin, 0.5 M $NaHCO_3$, 0.1 M NaOH (before and after sonication) and 1 M HCl, followed by digestion of the soil residue with concentrated H_2SO_4 and H_2O_2. Because this residual P fraction still contained 20–60% of total P (P_t) and often a significant proportion of P_o, Tiessen and Moir (1993) added another extraction step with concentrated HCl to the scheme (and removed the sonication step). Except for the 1 M HCl extracts, which contain only P_i associated with Ca, all extracts contain both P_i and P_o. The indirect determination of P_o as the difference between P_t and P_i constitutes a source of variation and error. For example, P_i in $NaHCO_3$ and NaOH extracts is determined after acid precipitation of organic matter. An overestimation of P_o can, however, occur when P_i associated with Fe or Al hydroxides precipitates together with organic matter (Tiessen and Moir 1993). Although it is important to realise the limitations of such chemical extraction schemes, they have rendered useful information in many studies, especially for the comparison of different treatments on the same soil type.

For decades, total soil P_o has been determined as the increase in acid-extractable inorganic P after destruction of organic matter by high temperature ignition (Saunders and Williams 1955). This method relies on a complete extraction
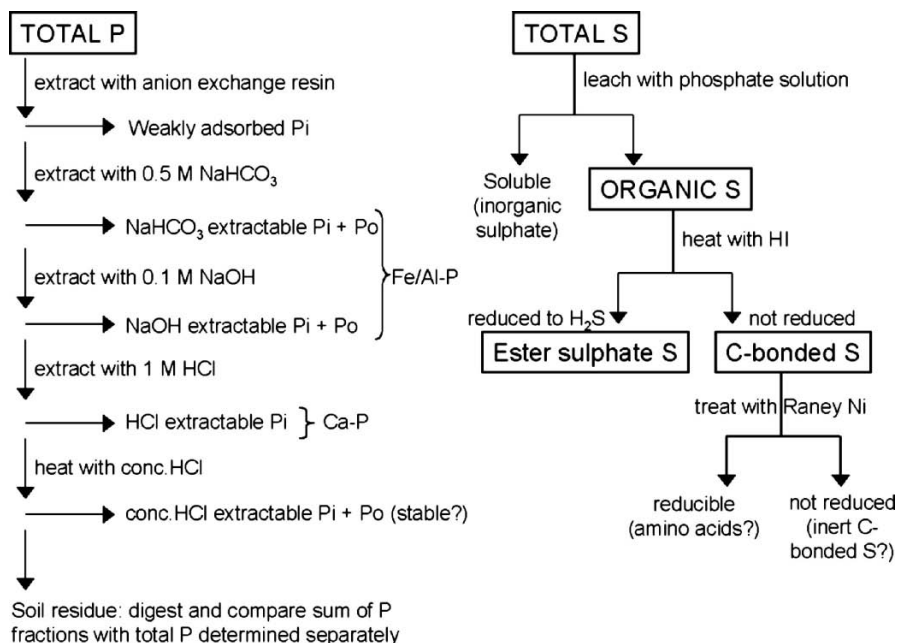
Fig. 3.2 Sequential fractionation schemes for P and S (modified after Stevenson and Cole 1999; Tiessen and Moir 1993). *Pi* Inorganic P, *Po* organic P

of P_o; it is assumed that the P_i solubility does not change during ignition, which is often not the case. For this reason, the ignition method was reported to overestimate soil P_o in highly weathered soils (Condron et al. 1990), as compared to two methods for estimating total P_o with various sequential alkali and acid extractions (Anderson 1960; Bowman 1989).

Chemical fractionation of S allows the differentiation of total S into inorganic S and organic S with or without C-bonds. The distinction is possible because hydriodic acid (HI) reduces only S that is not directly bonded to C, such as organic ester sulphate (–C–O–S–) and sulphamate (–C–N–S–). The sample is thus first leached with phosphate solution to remove adsorbed inorganic S by displacement, and subsequently reacted with HI. The remaining C-bonded S can be further separated into Raney-Ni reducible S, which is thought to consist mainly of amino acid-S, and a chemically unreactive fraction of presumably C-bonded S (Zhao et al. 1996). It is important to realise that total organic S is determined indirectly, i.e. by the difference between total and inorganic S (Tabatabai 1992).

3.2.1.2
Microbial P and S

The soil microbial biomass is widely recognised as a sink and source of nutrients and has often been found to provide a sensitive indicator of land use changes. Nutrients held in the microbial biomass are usually determined by fumigation-extraction methods, in which the biomass is killed during fumigation with cell-lysing agents such as chloroform or hexanol and subsequently extracted. The difference in nutrients extractable from a fumigated and a non-fumigated sub-sample provides an estimate of nutrients held in the biomass that can be corrected for incomplete recovery of the nutrient due to sorption or due to incomplete release and extractability from the soil.

Methods to determine microbial P have recently been reviewed by Oberson and Joner (2005). The most widely used protocols involve fumigation with chloroform followed by extraction with 0.5 M $NaHCO_3$ solution (Brookes et al. 1982), or liquid fumigation with chloroform or hexanol in the presence of an anion-exchange resin membrane (Kouno et al. 1995). Microbial S is usually determined by fumigation with chloroform followed by extraction with 0.01 M $CaCl_2$ or 0.1 M $NaHCO_3$ (Saggar et al. 1981).

3.2.1.3
Spectroscopic Methods

Non-invasive spectroscopic methods could potentially overcome some of the problems associated with chemical extraction of soil P and S. Nuclear magnetic resonance (NMR) spectroscopy is a powerful technique with which to analyse the chemical forms of P in any material since the resonating ^{31}P nucleus of P has 100% natural abundance. Since only nuclei with odd numbers of neutrons plus protons have magnetic properties, NMR cannot be used for ^{32}S. Problems associated with ^{31}P NMR spectroscopy of soils are the relatively low P concentrations and the association of P with paramagnetic ions such as Fe and Mn (Cade-Menun 2004). Spectral resolution tends to be poor in solid-state ^{31}P NMR. For this reason, much more detailed information on the chemical composition of soil P has been obtained with solution ^{31}P NMR. For solution ^{31}P NMR, P needs to be extracted, which may lead to errors due to incomplete and potentially disproportionate extraction of P, and potential changes of P forms during extraction.

Despite the above shortcomings, the continued development and application of solution ^{31}P NMR have contributed significantly to an improved understanding of the nature and dynamics of soil organic P in particular (Condron et al. 1997; Preston 1996). In recent years, solution ^{31}P NMR of soils has been dramatically improved by the proposition of a standard extractant (0.25 M NaOH–0.05 M Na-EDTA) and confirmation of peak assignments for a wide range of P

compounds likely to be present in soil (Turner et al. 2003b). Accordingly, Turner et al. (2003a) demonstrated that it was possible to quantitatively determine the following forms of P in soil with solution ^{31}P NMR: orthophosphate, pyrophosphate, polyphosphates, orthophosphate monoesters, orthophosphate diesters, DNA-P, phospholipids and phosphonates. In a further significant development, it has been shown that detailed convolution of the monoester region of ^{31}P NMR spectrum enables quantitative determination of individual IHP isomers, including *myo*-IHP and *scyllo*-IHP (Turner et al. 2003c; Turner and Richardson 2004). The application of this improved methodology will undoubtedly contribute to further advances in our understanding of soil organic P turnover and bioavailability in natural and managed ecosystems.

For S, synchrotron-based K-edge X-ray absorption near-edge structure spectroscopy (XANES) has recently been used to identify S oxidation states in humic substances (Xia et al. 1998), showing a dominance of reduced organic S species in aquatic humic substances and a dominance of the most oxidised S species in soil humic substances. Solomon et al. (2003) recorded spectra for clay and silt size particles as well as freeze-dried extracts of humic substances from the same samples. Even though high background noise precluded quantification of S species in the soil fractions, major absorption bands were similar for the spectra of soil fractions and extracts; XANES was thus considered to provide a characteristic fingerprint of S in mineral soils. Sulphonate-S was found to be dominant in extracts from the clay fraction, whereas ester sulphate dominated extracts from the silt fractions. Correlation with wet chemical fractions was rather poor and S speciation by XANES appeared to provide more useful information on the impact of land use changes. Prietzel et al. (2003) combined X-ray transmission and S fluorescence images to assess the spatial distribution of S species on soil particles with a resolution in the range of a few hundred nanometres.

Further progress in non-invasive spectroscopic methods for both P and S is expected to give new and better insight into some of the unresolved questions of the chemical composition of P and S in soils.

3.2.1.4
Enzyme Lability

Mineralisation of organic P and S in soil is controlled to a large extent by the activities of extracellular phosphatase and sulphatase enzymes released by plant roots and microorganisms (Speir and Ross 1978). There is, however, some evidence that plant enzymes, especially those that are not naturally secreted into soil, lose most or all of their activity when added to soil, in contrast to similar enzymes of microbial origin (Ganeshamurthy and Nielsen 1990; Quiquampoix and Mousain 2005).

The activity of phosphomonoesterases ('acid' and 'alkaline' phosphatase) in soils has been studied extensively, mainly using an assay that measures phosphatase activity based on the release of *p*-nitrophenol from the artificial substrate

p-nitrophenyl phosphate (Tabatabai 1994). For arylsulphatases, a similar assay uses *p*-nitrophenyl sulphate as substrate. Such assays have generally revealed a close correlation of enzyme activities to contents of soil organic matter and microbial biomass (e.g. Dick et al. 1988; Klose and Tabatabai 1999), although both phosphatase and sulphatase activities can be repressed by high P and S availability (e.g. Colvan et al. 2001). Enzyme activity against an artificial substrate must, however, be viewed as a potential activity and can not be translated into actual reaction rates, since enzyme activity against natural substrates and in soil rather than under assay conditions will be different. For example, nearly complete hydrolysis of *p*-nitrophenyl sulphate was achieved by an immobilised sulphatase, while under similar conditions only about 20% of ester sulphates extracted from soil were hydrolysed (Lou and Warman 1994).

In recent years, addition of purified enzymes to soil solution and other soil extracts has increasingly been used for the biochemical characterisation of organic P and S. For example, during incubation of filtered soil solution from a peaty soil without enzyme addition, the proportion of molybdate-reactive (inorganic) P in the solution increased from 13% to 44%, pointing to the activity of native phosphatases, while an additional 10% of total P in solution was hydrolysed after addition of acid phosphatase (Shand and Smith 1997).

Commercial phytase with activity against a broad spectrum of organic compounds hydrolysed 12% of water-extractable organic P (Hayes et al. 2000). Three times more organic P was extracted from the same soil with 0.05 M citric acid, and a greater proportion was enzyme-labile (80%). This was attributed to the chelating properties of citric acid, which is interesting in the context of citrate exudation by plant roots (see also Chapter 5 by Neumann, this volume). The specificity of various phosphatase enzymes (alkaline phosphatase, phosphodiesterase and phytase) was used by Turner et al. (2002) to classify water-extractable molybdate-unreactive P into orthophosphate monoesters, diesters and IHP. In the case of S, Lou and Warman (1992) extracted soil organic matter with a chelating resin and incubated it with sulphatase. Between 2 and 12% of HI-acid-reducible S extracted from three Podzols was hydrolysed within the 2-h incubation period.

The above examples provide information on the biochemical stability of organic P and S compounds in solution, which is an important step forward from chemical approaches that do not necessarily indicate biological availability. Even though it would be valuable to expand this type of analysis into assessing the hydrolysis of organic P and S by added enzymes in the presence of the soil matrix, there are several limitations to such an approach: (1) the potential sorption of hydrolysed product onto the soil solid phase, especially in the case of P, (2) soil type- and pH-specific loss of enzyme activity upon addition to soil (George et al. 2005), and (3) incongruence of pH optima of enzyme activity and soil pH, complicating the comparison between soil types. In addition, there is some indication that, in most cases, the availability of substrate rather than enzyme activity is the rate-limiting step for mineralisation (Ganeshamurthy and Nielsen 1990).

3.2.1.5
Stable Isotopes

Since ^{31}P has 100% natural abundance, the use of stable isotopes in the study of nutrient cycles is an option only for S. There are four naturally occurring stable isotopes of S that differ greatly in their common abundances: ^{32}S (95.02%), ^{33}S (0.75%), ^{34}S (4.21%) and ^{36}S (0.02%). Due to higher abundances and sensitivity problems, stable isotope studies of S cycling have been limited to using the ratio of ^{34}S to ^{32}S ($\delta^{34}S$ values) as a tool to trace S sources and transformations (Krouse et al. 1996). In addition, the oxygen isotope composition of sulphate ($\delta^{18}O$ of SO_4^{2-}) depends on the process of sulphate formation. This has been used in a study of S cycling in two catchments in the Black Forest, Germany, to differentiate sulphate from precipitation and from mineralisation of C-bonded S (Mayer et al. 1995).

The isotopic composition can be determined on total S or on extractable forms of S. Provided that extraction and ionisation are not accompanied by isotope fractionation, the variation in $\delta^{34}S$ values can be attributed to the source of a given S compound, e.g. atmospheric deposition, weathering of parent material, or biological pathways. Isotope fractionation during biological transformations is, however, not yet well understood, except for preferential uptake of ^{34}S during dissimilatory sulphate reduction under anaerobic conditions (Krouse et al. 1996). In addition to examining the natural abundance of S compounds in ecosystems, ^{34}S-enriched compounds can be applied as tracers. For example, Eriksen (1996) applied 600–1,300 kg S ha^{-1} as a liquid desulphurisation product with a $\delta^{34}S$ signature of +0.57‰ over 5 years to a rotation at two sites in Denmark. Even though total organic S in the topsoil (0–20 cm) did not change, the isotopic soil S composition of around +6‰ shifted by 1.5–2.1 δ units towards the fertiliser δ value. The amount of soil S derived from the fertiliser was calculated and corrected for the increase in inorganic S due to fertilisation. The resulting estimate of about 30% of soil organic S having been derived from the fertiliser within 5 years may be too high due to uneven labelling of inorganic and organic S, but nevertheless it gives an interesting indication of the turnover of soil organic S due to mineralisation-immobilisation processes in the field.

3.2.1.6
Radioisotopes

Of the two radioisotopes that are available for P, ^{32}P with a half-life of 14.3 days, is less expensive and thus more widely used than ^{33}P with a half life of 25.4 days. Both isotopes emit β-radiation during radioactive decay, but the energy emitted is considerably lower for ^{33}P (0.25 MeV) than for ^{32}P (1.71 MeV). Even though less protective measures have to be taken in the handling of ^{33}P, its detection

requires the addition of a scintillant, whereas ^{32}P can be detected by Cerenkov counting, albeit with a lower efficiency. The sulphur radioisotope ^{35}S has a half-life of 87.4 days, emitting a low β-radiation of 0.167 MeV (L'Annunziata 1987).

Radioisotopes of P are commonly used to estimate pools of isotopically exchangeable inorganic P in soils (Fardeau 1996; Frossard et al. 1994; Frossard and Sinaj 1997; Hamon et al. 2002), either by determining the removal of added isotope from the soil solution (E-values), or by determining the specific activity of plants grown in labelled soil (L-values). The disappearance of added isotope within the first minute after addition has been found to give a good indication of P sorption (Frossard et al. 1993), and a similar approach has been used to estimate S sorption (Vannier et al. 1993).

Radioisotopes have also been used to measure rates of biological P and S cycling. Isotopic dilution methods have been developed to measure gross P and S mineralisation (Di et al. 2000; Nziguheba et al. 2005; Oehl et al. 2001b). Labelling of soil to follow microbially mediated transformations of P and S has been particularly successful. Results from such studies are summarised in Sect. 3.3.1. In all cases, the great sensitivity with which the radioisotope can be detected allows determination of fluxes between pools rather than the size and chemical composition of a given pool.

3.2.1.7
Physical Fractionation

The physical fractionation of soil organic matter into different particle-size fractions has greatly aided the development of concepts of soil organic matter dynamics (Tiessen et al. 1984) and led to the successful modelling of carbon turnover based on measurable C pools (Skjemstad et al. 2004; see also Chapter 1 by Baldock, this volume). Unprotected soil organic matter is measured as the light fraction based on density fractionation, or as particulate organic matter based on size fractionation (Six et al. 2002). The various nutrients contained in unprotected soil organic matter can contribute substantially to crop nutrient uptake. This has been shown for N and P in agroforestry systems in the tropics (Phiri et al. 2001; Smestad et al. 2002; Vanlauwe et al. 1999), but may also apply to other elements such as S and different climatic conditions.

Physical rather than chemical fractionation of soil organic matter and associated nutrients may thus be an important technique to improve our understanding of nutrient cycling. For example, the isolation of particulate organic matter in a decomposition study of two plant residues (*Sorghum bicolor* and *Crotalaria juncea*) added to an Ultisol and an Alfisol suggested that most of the P in particulate organic matter was of microbial rather than plant origin (Salas et al. 2003). Eriksen et al. (1995a) extracted S with a mild chemical extractant after subjecting the soil sample to different intensities of ultrasonic dispersion and could thus subdivide organic S into non-protected, protected and insoluble organic S. Turnover of protected organic S was slow, as deduced from the low

incorporation of ^{35}S into this fraction (Eriksen et al. 1995b). Measurable P and S pools based on physical fractionation techniques may thus eventually improve existing models of nutrient cycling. Interestingly, the dynamics of P and S may be partly controlled by factors other than those controlling C and N (Amelung et al. 1998; McGill and Cole 1981).

3.2.2
Experimental Approaches

Analytical methods have to be combined with sound experimental approaches in order to meet the objectives of a given study. The choice of experimental approach thereby depends greatly on the scale of the investigation, i.e. whether studying a specific process or nutrient cycling in a given system. Laboratory incubation experiments as well as glasshouse experiments have been used successfully to elucidate some of the processes in soil P and S cycling as well as plant–soil interactions. Examples of such studies are given in Sect. 3.3.1. Repeated soil sampling in the field during the course of the year can provide evidence on the temporal variation and drivers of P and S cycling. For example, both climatic variables and plant litter inputs influenced microbial P cycling in the study by Chen et al. (2003a) described in Sect. 3.3.3.

Since it is often difficult to detect changes in soil P fractions against natural and analytical variation, long-term soil P dynamics are usually deduced from comparison of P fractions on the same soil type under different land-use or management, in long-term field experiments or in chronosequences of pastures and woody vegetation of various ages. For S, an interesting example of following long-term dynamics with the use of stable isotopes is given in Sect. 3.3.2. Paired site comparisons of adjacent grassland and forest plots form the basis for the studies on grassland to forest conversion summarised in Sect. 3.3.3.

3.3
Examples of Phosphorus and Sulphur Cycling at Different Scales

3.3.1
Microbial Immobilisation and Mineralisation Processes

Patterns and processes of microbial immobilisation and mineralisation of P and S have been studied primarily in incubation and pot experiments, although some field studies have also been conducted. In this section, the main focus is

on the similarity and differences in immobilisation-mineralisation processes for P and S, including a discussion of radioisotope methods.

Microbial immobilisation of P and S (as opposed to the physico-chemical reactions of sorption and precipitation, which remove P and S from the soil solution) can be deduced from a decrease in phosphate and sulphate in the soil solution and/or measured as an increase of P and S in the microbial biomass. In the absence of net changes, the incorporation of radioisotopes into the microbial biomass has been used to determine rates of microbial immobilisation. Numerous studies have shown that microbial uptake of P and S is governed mainly by C availability. For example, the recovery of ^{35}S in the microbial biomass of six soils 3 days after labelling increased from 0–14% without glucose to 17–44% after addition of 2 g glucose-C kg^{-1} soil (O'Donnell et al. 1994). Likewise, glucose additions of 3 g kg^{-1} increased the recovery of ^{33}P in the microbial biomass from 8% to 66% (Oehl et al. 2001a). In both studies, the increase of stable and radioactive elements in the microbial biomass was mirrored by a decrease of element and tracer extractable with 0.01 M CaCl$_2$ for S or H$_2$O for P, but this decrease could not entirely account for the microbial nutrient uptake. In the case of P, phosphate in the soil solution, which is in equilibrium with other inorganic P pools, is likely to be the main source of rapid microbial P uptake, while for S, a priming effect of glucose additions on soil organic S was reported (O'Donnell et al. 1994). Methodological problems in estimating amounts of total and radioactive P and S in the microbial biomass due to incomplete extraction, applied correction factors and heterogeneous labelling of the microbial biomass may, however, also be involved whenever the increase in nutrient content of the biomass is not entirely reflected in the decrease in the extractable nutrient.

Interestingly, the threshold for C substrates to affect P and S immobilisation may be much lower than the relatively large C additions frequently used in laboratory incubations. For example, Vong et al. (2003) observed increased immobilisation of ^{35}S after addition of C as organic acids or glucose already for rates from 80 mg C kg^{-1} soil onwards. In the same soil sampled under rape, barley and fallow, microbial immobilisation of ^{35}S was positively related to hot-water-soluble organic C, which ranged between 300 and 450 mg C kg^{-1} soil (Dedourge et al. 2003). Small inputs of labile C, e.g. from root exudates and root turnover, thus appear to be the main driver of microbial immobilisation. This is in agreement with observations by de Nobili et al. (2001) of microbial activity being triggered by trace concentrations of glucose, amino acids and root exudates. The addition of inorganic nutrients, on the other hand, often has little effect on microbial immobilisation. For example, microbial P did not change after addition of inorganic P in laboratory incubations (Chauhan et al. 1979) or in the field (Bünemann et al. 2004b). Microbial S may, however, be more sensitive to S additions, since the total inorganic S in soil is often only a minute fraction of total S. In forest soils, sulphate inputs have increased aerobic respiration and the formation of soil organic S (Autry and Fitzgerald 1993).

After cell death, microbially immobilised P and S can either be re-mineralised or incorporated into soil organic P and S. Early work by Freney et al. (1971) showed negligible incorporation of ^{35}S into soil organic S in autoclaved

soils as opposed to a steady increase in ^{35}S into organic S fractions over time in non-sterile soils, providing evidence for the role of microorganisms in the formation of organic S compounds in soils. Ghani et al. (1993b) demonstrated the increasing incorporation of ^{35}S into organic S during 120 days of incubation, which was greatly increased by glucose additions, with some re-mineralisation of newly formed ^{35}S-labelled organic S observed in the later part of the experiment. Leaching of the labelled soils from the above study after different times of incubation suggested that newly formed organic S became more recalcitrant over time (Ghani et al. 1993a).

Since inorganic S can be leached easily from incubated soils, leaving only organic S behind, studying the incorporation of ^{35}S into organic S is analytically less challenging than studying the incorporation of ^{32}P or ^{33}P into organic P where a separation of inorganic and organic P is required for each chemically extracted fraction. The fact that amounts of organic P increased after repeated additions of cellulose has, however, produced some evidence for the microbial formation of organic P (Chauhan et al. 1981). More recent studies combining sequential P fractionation and carrier-free labelling with ^{33}P found up to 20% of the label in organic fractions after 2 weeks in an Oxisol from Colombia (Bühler et al. 2002), and up to 5% in organic P plus 8% in the microbial biomass after 51 days in a Ferralsol from Kenya (Bünemann et al. 2004c).

A potential problem with studies using ^{35}S lies in the loss of S compounds to the atmosphere. Recoveries of added ^{35}S were, however, close to 100% during 4 months of incubation (Ghani et al. 1993b). Likewise, negligible atmospheric losses of S of 0.2, 0.5 and 3.4% were observed after addition of sewage sludges, manures and plant material to soil, respectively, which were attributed to microbial degradation of methionine and cysteine (Banwart and Bremner 1976). For P, ongoing isotopic exchange causes the radioactive P tracer to move into more resistant fractions over time, leading to a continuing decrease in the specific activity of labile inorganic P fractions (Bühler et al. 2002; Bünemann et al. 2004c), whereas for S, in most soils such a decrease would be attributed solely to mineralisation of unlabelled organic S.

Since immobilisation and mineralisation occur at the same time, there is a need to distinguish between gross and net mineralisation. Net mineralisation can be measured by extraction or leaching of soil after different times of incubation, unless sorption of the end product (phosphate or sulphate) prevents this approach. For P, measuring net mineralisation is thus rarely an option. For S, both closed incubation systems (with extractions before and after the chosen incubation period) and open incubation systems (with periodic leaching of the same soil column) have been used. Cumulative S mineralisation is typically several times higher in open incubation systems (Maynard et al. 1983; Pamidi et al. 2001) because the end product is frequently removed and thus cannot be immobilised and utilised by the microbial biomass. The presence of plants in closed incubation systems can likewise increase net S mineralisation due to uptake of sulphate by the plant (Maynard et al. 1985).

Gross mineralisation rates of P and S can be assessed only with the use of isotopic dilution methods (Di et al. 2000; Nziguheba et al. 2005; Oehl et al. 2001b,

2004). Net transformation rates of S are measurable, and the additional information obtained from isotopic dilution may not always be worthwhile, especially in view of the costs, labour and potential errors connected with the use of isotopes. This is in agreement with the considerations of Murphy et al. (2003) for N. For P, daily gross mineralisation rates of 1.4–2.5 mg P kg^{-1} soil measured in Swiss agricultural soils amounted to about 10% of available inorganic P (Oehl et al. 2004), suggesting a limited contribution of basal mineralisation to the supply of plant-available inorganic P.

Recent work has tackled mineralisation processes from the microbial side, thus beginning to elucidate the role of specific microorganisms. For example, Kahnert et al. (2002) induced mutagenesis in *Pseudomonas putida* and isolated a mutant (S-313) that, in contrast to the parent strain, was unable to grow with aryl- or alkyl-sulphate esters as the sole S source, but grew normally with sulphonates and sulphate. Survival of this mutant in agricultural and grassland soils was lower than that of the parent strain, pointing at sulphate esters as an important S source for microorganisms in the soil environment. Several mutants of *P. putida* were subsequently tested for their potential to promote tomato growth (Kertesz and Mirleau 2004). Both the wild type and the sulphatase-deficient mutant described above increased the dry matter of tomatoes grown in unsterilised compost compared to the non-inoculated control, suggesting that the ability to utilise sulphate esters was not related to the plant growth-promoting effect. Two other mutant strains that were unable to use aryl- and/or alkyl-sulphonates did not show the growth stimulation that was observed with the wild type, pointing towards the microbial mobilisation of sulphonates by the wild type and subsequent uptake by the plants.

For P, comparable work has been done by Richardson and Hadobas (1997) who isolated *Pseudomonas* strains that were able to grow on IHP as their sole source of C and P. Inoculation of several pasture grasses and legumes with this specific isolate or a culture of total soil microorganisms improved growth and P uptake of plants grown in sand-vermiculite amended with IHP as the sole P source (Richardson et al. 2001). Well-characterised microbial strains thus have great potential as a tool to elucidate the role of microorganisms in nutrient transformation processes in soils. More specifically, this applies also to the symbiosis of mycorrhizal fungi and plants that has been shown to improve plant uptake of P and other nutrients (Godbold 1999).

When discussing mineralisation processes in this section, we have focussed on the basal mineralisation of soil organic matter, i.e. in the absence of recently added plant material. It is important to realise that the initial release of P and S from plant residues can proceed very rapidly (Wu et al. 1993), since a large proportion of P and S in plant residues can be present as inorganic phosphate and sulphate. This rapid release is then often followed by immobilisation of nutrients into the plant residues (Salas et al. 2003). Plant residues can thus be considered primarily as a C substrate, and the soluble C is particularly important for the early patterns of immobilisation and mineralisation processes (Bünemann et al. 2004a). Therefore, P dynamics after addition of a P source to the soil differ considerably depending on the form in which P is added. For example, when the

Table 3.1. Relative distribution of fertiliser and plant residue P (in percentage of the amount applied) in a Ferralsol under a maize-legume fallow rotation as concluded from the recovery of ^{33}P in the various pools after 51 days of incubation (modified after Bünemann 2003). *Pi* Inorganic P, *Po* organic P

^{33}P-labeled P source[a]	Recovery of applied ^{33}P (%) in:				
	Available P_i	Microbial P	NaOH-P_i	NaOH-P_o	Not extracted
Plant residue	2	15	56	12	15
Inorganic P	5	5	64	6	20

[a]Added at 6 mg P kg^{-1} soil

same amount of P (6 mg kg^{-1} soil) was added to a highly weathered soil from Kenya, either as a plant residue or as inorganic P, the recovery in inorganic pools was greater in the case of added inorganic P, while a greater proportion of P applied with the plant residue was recovered in microbial and organic P pools (Table 3.1). This illustrates that as the turnover of C in a system increases, e.g. through plant residue addition, the biological processes of immobilisation and mineralisation will increasingly determine the availability of P.

3.3.2
Impact of Anthropogenic Sulphur Deposition on Sulphur Cycling as Revealed by Stable Isotope Techniques

The unique record of archived soil and plant samples from the long-term field experiments in Rothamsted, England, has been used to investigate the impact of anthropogenic SO$_2$ emissions on S cycling in arable and grassland ecosystems (Knights et al. 2000; Zhao et al. 1998, 2003). Herbage samples from a non-fertilised control plot of a grassland experiment (Zhao et al. 1998) showed constant P concentrations between 1856 and 1996, whereas S concentrations peaked around 1970 (Fig. 3.3). At the same time, δ^{34}S decreased strongly, with the minimum around 1970 being 10 δ units lower than the initial value in 1856. The isotopic S signature of pre-industrial herbage was estimated to have been about +10‰, whereas anthropogenic S has a signature of –10‰ to –12‰ (Zhao et al. 1998). The contribution of anthropogenic S to grass S uptake was estimated to have increased from 6% in 1863 to 52% in 1972, followed by a decrease to 30% in 1995.

Total S in the topsoil of the unfertilised control plot remained constant, but its δ^{34}S signature decreased by up to 4 δ units (Fig. 3.4). By 1996, approximately 30% of total S had been derived from anthropogenic SO$_2$ emissions (Zhao et al. 1998). A similar estimate of 28% of topsoil S derived from anthropogenic
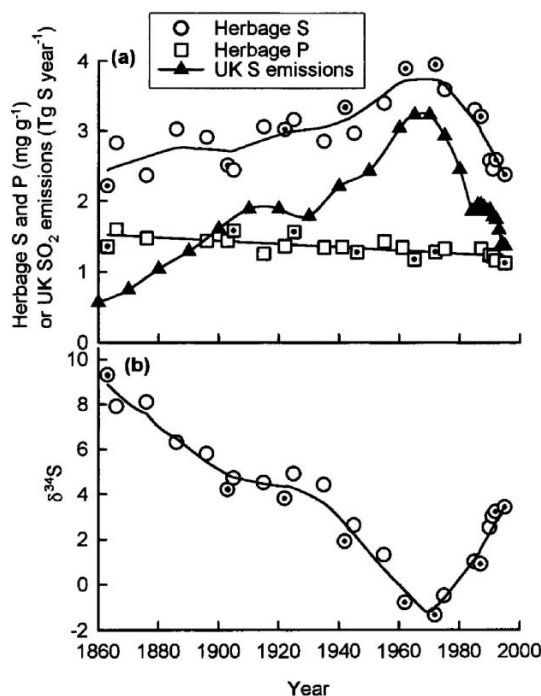
Fig. 3.3 Changes in total annual emissions of SO_2 in the United Kingdom and the concentrations of herbage S and P (**a**) and herbage $\delta^{34}S$ (**b**) in an unfertilised grassland plot at Rothamsted (UK). Symbols with a *dot* represent composite samples, and those without a dot represent single year samples. Reprinted with permission from Zhao et al. (1998). Copyright (1998) American Chemical Society, Washinton DC
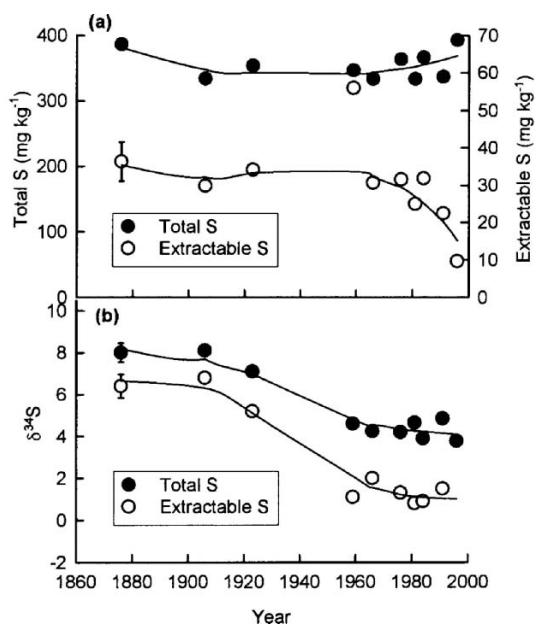
Fig. 3.4 Changes in the concentrations of total and extractable S in the topsoils (**a**) and soil $\delta^{34}S$ (**b**) in an unfertilised grassland plot at Rothamsted, UK. Reprinted with permission from Zhao et al. (1998). Copyright (1998) American Chemical Society, Washinton

deposition was made for a non-fertilised arable control plot with stable organic S content since 1865, as compared to 40% of soil S derived from the atmosphere for a woodland and a grassland plot in which organic C and S accumulation occurred (Knights et al. 2000). With anthropogenic S deposition used as a tracer, these studies thus provide important information on the sources of plant S uptake as well as on the turnover of soil organic S.

3.4
Changes in Phosphorus and Sulphur Cycling Following Afforestation of Grassland

Recent large-scale afforestation of pastoral farmland in New Zealand represents a major land use change with significant impacts on the cycling and availability of soil P and S. Currently 15.5 million ha in New Zealand are utilised for agriculture, horticulture and plantation forestry. Since large-scale European settlement after 1840, most of this area (12 million ha) is under extensive pastoral farming (sheep and beef) on hill country and mountain slopes. A significant accumulation of organic matter and associated nutrients (N, P, S) occurred in these soils as a consequence of inputs of P and S fertilisers (Kemp et al. 1999).

Following the abrupt removal of all product and input subsidies in 1985, sheep numbers decreased dramatically from over 70 million to less than 45 million by 2000, while over the same period the area under short-rotation plantation forestry [20–40 years, mainly radiata pine (*Pinus radiata*)] doubled from 0.9 to 1.8 million ha (ca. 12% of the productive land area). Most of the recently established forests have been planted on hill and high country areas developed under pastoral farming.

Table 3.2. Mean concentrations ($mg\ kg^{-1}$) of organic P and organic S determined in adjacent soils under grassland and recently established plantation forest in New Zealand

	Depth (cm)	Grassland	Forest	Source
Organic P				
	0–10	700	592	Condron et al. 1996
	0–10	474	370	Chen et al. 2000
Organic S				
	0–10	504	408	Chen et al. 2001
	0–12	526	378	Groenendijk et al. 2002

A number of field studies have been carried out in New Zealand over the past 15 years to investigate and quantify the effects of grassland afforestation on soil properties and processes (e.g. Alfredsson et al. 1998; Chen et al. 2000, 2003a; Condron et al. 1996; Condron and Newman 1998; Davis and Lang 1991; Yeates et al. 1997). These unreplicated experiments involved comparison of soil in adjacent areas under grassland and recently established forest (commonly <20 years old) that had not received inputs of fertiliser since forest establishment. The findings of these studies have consistently demonstrated that levels of organic matter and associated nutrients (N, P and S) were generally significantly lower in mineral soil under recently established forest compared with grassland. Data from a total of 51 paired-site comparison studies on a range of soil types in different environments revealed that decreases in organic C under forest compared with grassland ranged from 3 to 47% (Davis and Condron 2002). The average decrease in topsoil (0–10 cm) organic C during the 20 years following establishment was 10%. Comparable field data show that concentrations of organic P in mineral soil (0–10 cm) have decreased by 15–22% under recently established forest compared with grassland (Chen et al. 2000; Condron et al. 1996; Davis 1994; Davis and Lang 1991), while concentrations of soil organic S under forest soils were 19–28% lower than adjacent soils under grassland (Chen et al. 2001; Groenendijk et al. 2002) (Table 3.2). Belton et al. (1995) reported that concentrations of plant-available P were 2–4 times higher in a range of soils under pine forest compared with adjacent grassland. Similarly, data for plant-available sulphate-S show that average concentrations increased from 7 mg kg^{-1} under grassland to 26 mg kg^{-1} under adjacent forest, with concentrations of sulphate-S being consistently higher under forest than grassland at all soil depths (Chen et al. 2001; Groenendijk et al. 2002).

The findings described above clearly indicate that increased mineralisation of organic P and S occurred under recently established forest compared with adjacent grassland. Short-term studies carried out under glasshouse conditions confirmed increased mineralisation of soil organic P under radiata pine (Chen et al. 2003b; Condron et al. 1996; Davis 1995). For example, Chen et al. (2003b) showed that concentrations of organic P in 15 grassland soils were consistently and significantly lower (6–20%) after only 40 weeks growth of radiata pine compared with perennial ryegrass (*Lolium perenne*). A related study showed that concentrations of orthophosphate monoesters were consistently lower in soils under pine (103–480 mg P kg^{-1}) than under ryegrass (122–679 mg P kg^{-1}) (Chen et al. 2004). Hence, these compounds were available for uptake by radiata pine, but the ability of ryegrass to utilise them was limited. Interestingly, the identification and quantification of *myo*-IHP using ^{31}P NMR indicated that mineralisation of this compound accounted for between 19% and 100% of the total mineralisation of orthophosphate monoester organic P during the 10-month growth of radiata pine in most soils.

Data from a variety of field experiments revealed that, despite increased mineralisation of organic P and S, levels of microbial biomass P and S were consistently and significantly lower in soils under forest compared with grassland (Chen et al. 2000, 2001; Ross et al. 1999; Yeates and Saggar 1998; Yeates et al.

1997). Furthermore, it was also demonstrated that activities of the extracellular enzymes responsible for organic P and S mineralisation (phosphomonoesterase, phosphodiesterase and arylsulphatase) were significantly lower in mineral soil (0–30 cm) under forest compared with adjacent grassland (Chen et al. 2000, 2001).

A detailed investigation of temporal changes in various P parameters under adjacent forest and grassland found that seasonal variations in soil P were broadly similar under forest and grassland, and rates of organic P mineralisation increased during spring and summer in response to plant P demand, whereas organic P accumulated during late autumn and winter (Chen et al. 2003a). It was concluded that plant P requirements were satisfied by P release from leaf litter inputs in the forest system and from root litter inputs under grassland, which was consistent with data on fine root mass from the same site (Chen et al. 2000). However, the data also revealed that, despite the fact that levels of microbial biomass C and P were lower in the forest than grassland soil, the calculated annual rate of P flux through the microbial biomass was 16 kg P ha^{-1} in the forest soil compared with 14 kg P ha^{-1} in the grassland soil.

It is also possible that the apparent increases in organic P and S mineralisation evident in soil under forest compared with grassland may be attributed, at least partly, to differences in the amounts, forms and spatial and temporal distribution of above- and below-ground organic matter and nutrients. For example, Chen et al. (2000) showed that, despite a decrease in organic C in the mineral soil (0–30 cm), the total quantity of organic C in the soil profile was substantially greater under forest (137 t ha^{-1}) compared with grassland (124 t ha^{-1}). Forest litter contains significant quantities of inorganic, organic and microbial P and S (Chen et al. 2001, 2003a; Groenendijk et al. 2002), which can make a significant contribution to plant requirements (Attiwill and Adams 1993). Continued comminution of surface litter organic matter might account for the observation that levels of organic C in mineral soils were similar under forest and grassland after 20 years (Davis and Condron 2002).

It is clear from the above that the change in land use from grazed pasture to plantation forest had a rapid and significant impact on the nature, distribution and dynamics of soil P and S. Investigation of this phenomenon has and will continue to provide a template for advancing our understanding of the key properties and processes that determine the turnover, bioavailability and mobility of P and S in the soil environment.

3.5
Conclusions

The findings described and discussed in this chapter clearly demonstrate that the biogeochemical cycling of P and S are important in determining the productivity of terrestrial ecosystems. The long-term sustainability of agroecosystems

depends on continued inputs of P and S as well as sound management of soil P and S in order to maximise cycling rates and to avoid losses from the system. Despite significant advances in recent years, there is an ongoing need for research to be carried out in the following areas to further improve our understanding of aspects of P and S cycling in terrestrial ecosystems:

1. Chemical nature, turnover and associated bioavailability of soil organic P and S, especially in intensively managed agroecosystems. This will require the use and continued development of techniques such as ^{31}P NMR, XANES and other spectroscopic methods, together with determination of the effects of land use and management on rates of organic P and S mineralisation in soil.

2. Quantities and dynamics of microbial biomass P and S in soil, which will involve using a combination of appropriate isotopic labelling and molecular biology techniques. This includes a better understanding of the role of specific groups of microorganisms, both free-living and in symbiosis with plants.

3. Role and function of extracellular hydrolase enzymes in the dynamics of organic P and S, and associated interactions between the cycling of organic C and organic P and S in soil.

4. Potential impacts of climate change on the nature, dynamics and bioavailability of inorganic and organic forms of P and S in the soil-plant system.

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4 Cycling of Micronutrients in Terrestrial Ecosystems

Zed Rengel

4.1
Introduction

Plants require eight micronutrients for normal growth and development: Fe, Mn, Zn, B, Cu, Mo, Ni and Cl. Through their involvement in various enzymes and other physiologically active molecules, micronutrients are important for gene expression; biosynthesis of proteins, nucleic acids, growth substances, chlorophyll and secondary metabolites; metabolism of carbohydrates and lipids; stress tolerance, etc. Micronutrients are also involved in structural and functional integrity of membranes and other cellular components (Rengel 2003).

Millions of hectares of arable land in the world have low availability of micronutrients (White and Zasoski 1999). On such soils, growth and yields of crops and pastures are reduced (e.g. Cakmak et al. 1996), and supplementation with micronutrients in the form of fertilisers or organic amendments may increase crop growth.

Food production in most countries results in depletion of soil nutrient reserves. Calculations for macronutrients show a world average depletion (in kg ha^{-1} year^{-1}) of 12 for N, 5 for P and 20 for K (Sheldrick et al. 2002). Unfortunately, similar budgets are not available for micronutrients; however, offtake of micronutrients is generally small, and the total amounts in soils may be sufficient for a large number of crops (potentially hundreds to thousands) (e.g. Graham 1984).

Voluminous literature exists on cycling of macronutrients in agroecosystems (e.g. Edmeades 2003; Goulding et al. 2000; Ikpe and Powell 2002) and even more so in forest ecosystems (e.g. Attiwill and Adams 1993; Johnson et al. 2000; Ohte et al. 2001). However, considerably less knowledge exists on the dynamics of

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micronutrients in managed and native ecosystems, and how various inorganic and organic inputs influence micronutrient cycling. Hence, this review will concentrate on micronutrient cycling, especially of Cu, Fe, Mn and Zn.

4.2
Spatial Considerations in Micronutrient Cycling

Soils with low levels of plant-available micronutrients occur in various climatic regions world-wide, especially in regions of Mediterranean climate (Takkar and Walker 1993). Often, micronutrient deficiency is linked to soils of high pH, resulting in low availability of micronutrients (Welch 1995; White and Zasoski 1999). Crops grown on such soils suffer from Cu, Fe, Mn or Zn deficiency, or a combination of various micronutrient deficiencies (Sillanpää and Vlek 1985).

Solubility of micronutrients is controlled largely by pH and the redox potential. For every unit increase in pH, solubility decreases from 100-fold (for divalent metals such as Zn, Cu and Mn) to 1,000-fold (for trivalent Fe) (Rengel 2001). Given that the primary effect of liming of soil is to increase pH, micronutrient deficiencies become more severe when soils are amended with lime (e.g. Verma and Minhas 1987). Thus, micronutrient fertilisers should be applied to ameliorate micronutrient deficiencies associated with lime application (Mortvedt 1994).

4.2.1
Recycling Nutrients from Deep Soil Layers

Nutrients taken up by deep roots are transported into the above-ground parts and re-deposited on the soil surface through litterfall, stemflow or throughfall. Theoretically, such a mechanism may be especially significant in soils where deep layers contain substantial micronutrient reserves, and for plants that have deep roots. In contrast to native vegetation (especially forests), which is generally deep-rooted, crops have variable rooting depth. For example, the root depth of three species of vegetables grown under identical conditions varied from 0.6 m (sweet corn, *Zea mays*) to 1.3 m (carrot, *Daucus carota*) to >2.4 m (cauliflower, *Brassica oleracea* convar. *capitata*) (Kristensen and Thorup-Kristensen 2004).

Interestingly, continuous NPK fertilisation in a 25-year long trial on an Inceptisol in India did not alter micronutrient availability in the topsoil, whereas the non-fertilised control showed decreased micronutrient availability (Selvi et al. 2002). One possible explanation for these results is that stronger plant growth elicited by NPK fertilisation resulted in recycling of micronutrients from deeper soil layers into the topsoil, thus maintaining the micronutrient status of the topsoil.

4.2.2
Off-Site Impact

An off-site impact of micronutrients in native and managed ecosystems is expected to be minimal because micronutrients become bound to soil particles quite effectively, preventing their movement off site. However, there is little data to shed more light on such a hypothesis.

Off-site transport of micronutrients (especially Zn and Cu) following application of sewage sludge on land has been reported. In such situations of heavy loading of land with micronutrients, their transport off-site was substantial (Burton et al. 2003; Loch et al. 1995), especially when organo-metal complexes were taken into account (Burton et al. 2003).

4.3
Micronutrient Cycling in Agroecosystems

Around the world, most farming is reliant on chemical fertilisers to grow crops efficiently. However, understanding the cycle of nutrients and the amount of nutrients removed in grain and crop residues is essential for nutrient budgeting and fertilisation for the following season. Any perturbations in nutrient status, such as larger than usual nutrient removals, or problems with root growth and function, can cause nutrient deficiency and yield losses. Particular attention in this respect needs to be paid to micronutrients because inorganic fertilisation generally means adding N, P and K. Increased yields achieved by such fertilisation may accelerate micronutrient removal from agroecosystems, causing imbalance in nutrient cycling. For example, after 30 years of continuous inorganic NPK fertilisation in an acid red loam soil in India, the soil contents of Zn, Mn and Cu decreased (Lal and Mathur 1989).

Micronutrient supplementation can be provided not just by inorganic fertilisers, but also by addition of various sources of organic matter (manures, sewage sludge, crop residues, etc.). In addition, biofertilisers are being increasingly used to enhance macro- and micro-nutrient (especially Zn) cycling in managed ecosystems (e.g. Hafeez et al. 2002). Finally, crop and variety selection plays an important role in enhancing micronutrient cycling.

4.3.1
Fertilisers

Macronutrient fertilisers are commonly used to compensate for removal of nutrients in harvest products, whereas micronutrient fertilisers are used less regu-

larly. Often, attention to micronutrient fertilisers is paid only in extreme cases [e.g. 90-mile desert in South Australia, which was brought to agricultural production after introduction of fertilisers, especially Zn and Cu (Marshall 1972; Tiver 1988)] with micronutrient deficiency frequently going unrecognised or untreated for long periods of time (e.g. Zn deficiency in Central Anatolia, Turkey, see Cakmak et al. 1996). Micronutrient fertilisers can be applied to soil or foliarly.

4.3.1.1
Soil Application of Fertilisers

Micronutrients are usually added to soil as inorganic fertilisers. For Zn, the most common fertiliser form is sulphate ($ZnSO_4$) (23–55% Zn, depending on the water content). Other forms used as fertilisers include (percentage of Zn indicated in parentheses) the Zn-ammonia complex (10%), Zn-nitrate (22%), Zn-oxide (50–80%), Zn-oxysulphate (40–55%), Zn-carbonate (52–56%), Zn-chloride (48–50%), and organics, such as lignosulphonate (5–8%) and synthetic chelates [with ethylene diaminetetraaminoacetate (EDTA), 14% Zn; with HEDTA and NTA, 9% Zn]. In addition, macronutrient fertilisers (such as di-ammonium phosphate, superphosphate, nitrophosphate) supplemented with Zn or containing natural Zn impurities (e.g. superphosphate) are good sources of Zn, at least for rice (*Oryza sativa*) (Savithri et al. 1999a). For more details on various forms of other micronutrient fertilisers as well as on the chemical and physical characteristics of interactions between these fertilisers and soil, readers are referred to the literature (e.g. Shuman 1998).

Sulphate salts of Cu, Zn or Mn added to soil are a good source of Cu, Zn or Mn for crops, e.g. rice (Dhaliwal and Chahal 1996; Purakayastha and Chhonkar 2001; Savithri et al. 1999a; Swarup 1983), wheat (*Triticum aestivum*) (Dhaliwal and Chahal 1996; Gupta 1986), a range of pasture species (Gupta 1986), etc. Manganese sulphate (28% Mn) is at least 2-fold more effective than Mn oxide (78% Mn) in supplying Mn to wheat grown on alkaline soils (Brennan and Bolland 2004c).

In contrast to other inorganic micronutrient fertilisers such as Zn (Lawrence et al. 2001; Loss et al. 2003), Cu (Brennan and Bolland 2004a) and Mn (Brennan and Bolland 2004c), soil application of inorganic Fe fertilisers (e.g. Fe-sulphate) to Fe-deficient soils is usually ineffective because of quick conversion of Fe into the plant-unavailable Fe^{3+} form. Hence, Fe sulphate is generally more effective as a foliar spray than as a soil amendment (e.g. Sadana and Nayyar 2000). Alternatively, soil application of synthetic Fe-chelates is usually effective in correcting Fe deficiency, but may be expensive (Alvarez-Fernandez et al. 2002; Matocha 1984; Wallace and Wallace 1982). However, relatively small amounts of Fe chelates may be sufficient, e.g. in the case of FeEDDHA (Fe ethylenediamine-N,N'-dihydroxyphenylacetate), because utilisation of native soil Fe can be facilitated (e.g. by sorghum, *Sorghum bicolor*, Anderson and Khattari 1984).

Humic substances can increase effectiveness of FeEDDHA in providing Fe to plants grown on calcareous soils (Sanchez-Sanchez et al. 2002).

Micronutrient fertilisers may not need to be applied every season or to every crop in the rotation (cf. Rengel et al. 1999). Indeed, if micronutrient fertilisers are applied repeatedly in substantial amounts, they may accumulate in soil, with residual micronutrients supplying most (if not all) of the plant needs. Nevertheless, supplementation of superphosphate with a range of micronutrients (Cu, Zn, Mo) has been a standard practice in southern Australia for decades.

4.3.1.2
Foliar Application of Fertilisers

Plants can absorb soluble compounds and gases through their leaves, a phenomenon that has been utilised for delivering plant nutrients by foliar sprays (for a review, see Kannan 1990). Application of foliar sprays implies that nutrients will be absorbed and exported from the point of application (leaf) to the point of utilisation (usually growing tissues). The leaf cuticle is the first major obstacle in that chain of events. For Fe, Zn and Mn applied as either chelates or sulphate salts, extensive fixation by the cuticle occurred at the point of application (Ferrandon and Chamel 1988). Foliar absorption of these three elements was lower from chelates than sulphates, but translocation within the plant was greater when chelated forms were applied. Overall, chelates are more effective than sulphates (Wallace and Wallace 1982), but the relative effectiveness of the two sources may depend on the stage of crop development (Brennan 1991).

Effective crop nutrition via foliar supply of micronutrients implies good phloem transport of nutrients out of sprayed leaves and into other growing tissues (particularly roots and fruiting bodies). For micronutrients poorly mobile in phloem (e.g. Fe), roots may remain deficient and function poorly even when above-ground parts are supplied sufficient foliar Fe. In contrast to Fe, foliarly applied ^{65}Zn was easily mobile from the wheat leaf where it was applied and was transported all the way to the root tips as well as into the leaves above the point of application (Haslett et al. 2001). Zinc applied to one side of a split-root system was also effectively transported to the other (non-fertilised) part; all these findings suggest good mobility of Zn in wheat phloem.

4.3.2
Biofertilisers

Biofertilisers are microbial inoculants or microbially converted organic materials used to provide nutrients to plants. To date, most biofertilisers have been developed and used primarily to supply N and P to plants, and relatively little is known about their usefulness for supplying micronutrients. However, there is an

opportunity to develop biofertilisers that could be used specifically to increase the bioavailability of micronutrients to plants (cf. Douds et al. 2005; Kumar et al. 2005; Pragati et al. 2004). In particular, various strains of *Pseudomonas fluorescens* are known to solubilise Zn-phosphate (e.g. strain 3a isolated from a forest soil, Di Simine et al. 1999), or reduce plant unavailable Mn^{4+} or Mn^{3+} to plant available Mn^{2+} (e.g. Rengel et al. 1996).

4.3.2.1
Siderophores

Almost all microorganisms in nature synthesise and release metal-chelating compounds called siderophores in response to Fe deficiency (e.g. Johnston 2004). Siderophores accumulate at higher concentrations in the rhizosphere than in the bulk soil, and are effective in providing Fe to some plants when supplied at concentrations similar to synthetic Fe chelates such as EDTA or EDDHA (Wang et al. 1993). Siderophores are easily degraded by microorganisms, thus accumulating only temporarily at sites of high microbial activity at the root apices or at sites of lateral root emergence (Crowley and Rengel 1999). Large-scale commercial applications of siderophores as biofertilisers are yet to be reported.

4.3.2.2
Mycorrhiza

Mycorrhiza are naturally occurring associations between certain soil fungi and plant roots in which the fungi colonise the root tissue, but also act as extensions of the plant root system in which the hyphae external to the root absorb and transport water and various nutrients (Jeffries et al. 2003; Read and Perez-Moreno 2003). In experiments examining plant responses to mycorrhizal inoculation, mycorrhizal plants normally contain significantly higher levels of P and various micronutrients, most notably Zn and Cu (e.g. Mohammad et al. 2003; Ortas et al. 2002; Purakayastha and Chhonkar 2001; Rubio et al. 2002). This effect may be due partly to the enhanced vigour of mycorrhizal plants, but mycorrhizal hyphae have also been shown to take up and transport metals to the roots, where they are absorbed and translocated to the plant shoot. The contribution of mycorrhiza to total Zn and Cu uptake is estimated at approximately 50% in clover (see Marschner 1995), and 25% in maize (Kothari et al. 1991). Conversely, Mn uptake is decreased in some mycorrhizal plants, presumably due to a decrease in populations of Mn reducing/solubilising bacteria in the rhizosphere of mycorrhizal roots (Kothari et al. 1991).

Opportunities for increasing plant micronutrient uptake by mycorrhizal inoculation depend on whether or not there is low abundance of indigenous mycorrhizal fungi that can effectively colonise plants, and the soil conditions, which

control the level of mycorrhizal colonisation. In Australia, a condition known as long-fallow disorder, in which fields are kept unplanted and weed-free for more than 10 months, results in a decline of mycorrhizal propagules, causing Zn deficiency in wheat following the fallow. In this case, inoculation with mycorrhizal fungi has been beneficial in enhancing Zn uptake (Thompson 1990).

4.3.3
Crop Residues

Stubble, straw, chaff and other above-ground crop parts as well as roots below ground represent crop residues. The nutrient content of various crop parts may vary depending on nutrient supply and environmental factors as well as crop physiological characteristics, particularly nutrient remobilisation from vegetative tissues into developing grains.

Remobilisation of micronutrients from vegetative tissues into developing grains can influence nutrient cycling in the ecosystem, but little is known about mechanisms governing such remobilisation (e.g. see Haslett et al. 2001; Pearson and Rengel 1994; Schmidke and Stephan 1995; Welch 1995). Iron has low mobility in the phloem; less than 20% of Fe contained in vegetative tissues was remobilised to the grain (Miller et al. 1993). Similarly, Mn remobilisation from wheat leaves and stems into grain is poor (Pearson and Rengel 1994). In

Table 4.1 Concentration and total amount of micronutrients partitioned in grain and straw in wheat and canola grown in southern Australia. Data from Schultz and French (1978), and unpublished data from various sources (Bhupinderpal-Singh; B. Bowden; Z. Rengel). Yield was estimated at 2 t ha^{-1} and 1.5 t ha^{-1} for wheat and canola, respectively, plus corresponding straw (4 t ha^{-1} for wheat and 3.75 t ha^{-1} for canola). For calculating total amount of nutrients per hectare, a point in the middle of the concentration range was chosen

Nutrient	Wheat		Canola	
	Grain	Straw	Grain	Straw
Concentration of nutrients (g t^{-1})				
Copper	4–13	3–12	2–8	2–7
Iron	20–80	70–100		22–26
Manganese	19–56	16–78	27–34	8–14
Zinc	8–32	3–27	35–43	7–11
Amount of nutrients (g ha^{-1})				
Copper	17	30	8	17
Iron	100	340		90
Manganese	74	188	45	41
Zinc	40	60	59	34

Table 4.2 Concentration and total amount of micronutrients partitioned in grain of various crops grown in India. Data from Phillips (2004). Yield estimates were (in t ha^{-1}): wheat 3.0, canola 3.0, rice 5.0 and maize 4.0

	Wheat	Canola	Rice	Maize
Amount of nutrients (g ha^{-1})				
Copper	43	17	20	20
Iron	380	150	810	120
Manganese	12	90	60	36
Zinc	180	50	215	60

contrast, Zn is remobilised from old wheat leaves, especially the flag leaf, into developing grains to a considerable extent (Pearson and Rengel 1994). Copper can be loaded into the leaf phloem when applied as a foliar spray (see Graham and Nambiar 1981), but can be remobilised from old wheat leaves only if premature senescence was induced (Hill et al. 1979).

In southern Australia, wheat grain, on average, has lower concentrations of Zn and higher concentrations of Cu and Mn compared with canola grain (Schultz and French 1978) (see also Table 4.1). However, taking into account both grain and straw, similar amounts of Zn are removed from soil by wheat and canola, whereas more Cu and Mn are removed from soil by wheat than a canola crop. In India, more Fe and Zn is contained in rice grain than in wheat, canola and maize (Phillips 2004) (see also Table 4.2). Most Cu was removed in grain of wheat and most Mn in canola grain. Budgeting micronutrient removal is essential to optimise fertilisation and nutrient cycling in agroecosystems.

4.3.3.1
Crop Residue Management

Farmers use a number of different crop residue management techniques. In Australia, farmers harvest crops either directly or swath them before harvest, with trash behind the harvester being either spread or maintained in concentrated rows. Stubble/crop residues can be grazed or burnt. The options chosen by farmers depend on the type of machinery available, the soil erodability, the cost, and the nutritional effects on the following crop. However, nutritional effects in relation to stubble management options in Australia are poorly characterised at present, making it difficult for farmers to balance nutritional issues with the pros and cons of disease and weed control measures, the ease of seeding and harvesting as well as with sustainability issues, including acidification, soil wettability and erosion control.

Canola (*Brassica napus*) is known as a voracious scavenger of nutrients. It has an extensive root system, with a large surface area of contact with soil. Hence, canola is efficient in taking up soil nutrients, particularly immobile nutrients

Table 4.3 Field trials in five regions in the wheat belt of Western Australia. Rotation: cereals after canola. Fertilisation treatments were cross-plotted on the canola windrows from the preceding season (modified from Brennan et al. 2000)

Region	Holt Rock	Kukerin		East Hyden	Darkan	South York
Crop	Wheat	Wheat	Barley	Wheat	Wheat	Wheat
	Tops Z45	Tops	Tops	Tops Z53	Grain	Grain
Treatment	Ratio of off-windrow to on-windrow yield					
None	0.33	0.25	0.31	0.43	0.55	0.40
Complete macro- and micro-nutri- ent fertilisation	0.57	0.40	0.46	0.52	0.70	0.78
Complete –Cu	–	0.64	0.32	0.65	0.73	0.73
Complete –Zn	0.67	0.37	0.39	0.56	0.67	0.73
Complete –Mn	0.75	0.42	0.34	0.47	0.66	0.78
Complete –Mo	0.53	0.49	0.32	0.47	0.64	0.73

such as K, P, Cu, Zn and Mn (Brennan 1997; Brennan and Bolland 2001, 2004d; Grant and Bailey 1993) and accumulating them in tissues.

In Western Australia, canola is generally swathed into windrows prior to harvest to reduce the amount of seed lost as a result of seedpod shattering. Swathing can condense a 10-m-wide area of canola into a 1.5-m strip. This practice transfers the nutrients taken up by the whole crop into strips covering about 15% of the field (Bowden et al. 1999). If any nutrient was marginal in supply before cropping with canola, it can become deficient off the windrow, causing poor growth in subsequent crops (Bowden et al. 1999; Brennan et al. 2000) (Table 4.3).

Complete fertilisation restored some of the yield lost in off-windrow areas due to nutrient re-distribution (Table 4.3), but this restoration was incomplete, suggesting a poor soil fertility status even after fertilisation. Omission of micronutrients from the complete fertilisation was particularly damaging for barley at Kukerin in the wheat belt of Western Australia.

4.3.3.2
Dynamics of Crop Residue Decomposition and Nutrient Release

The dynamics of decomposition of organic matter is paramount in determining the rate of nutrient cycling (see also Chapter 1 by Baldock, this volume). Agricultural measures that enhance organic matter decomposition tend to intensify nutrient cycling in the short term, but this may not be sustained over long periods without adequate inputs of organic matter to continue fuelling decomposition processes (Tiessen et al. 2001). For example, ploughing as opposed to

no-till and stubble mulching decreased organic matter content as well as soil Zn, Mn, Fe and Cu in long-term (16 years) field trials in Western Nebraska (Follett and Peterson 1988).

Crop residue decomposition is a result of the activity of a variety of soil microorganisms (Dalal 1998; Marschner et al. 2003). The rate of crop residue and other organic matter decomposition is greatly dependent on the C:N ratio of the material and the supply of energy to microorganisms (Nicolardot et al. 2001). During residue decomposition, a number of processes occur simultaneously: (1) an increase in microbial biomass causing temporary nutrient immobilisation, (2) an increase in the amounts of nutrients coming into the system from decomposing crop residues, and (3) changes in pH, other soil chemical and physical factors, etc. (e.g. Trinsoutrot et al. 2000). Soil microbial populations grow rapidly during decomposition of crop residues, taking up (immobilising) a significant proportion of nutrients (e.g. Marschner et al. 2003; Stockdale 2000), and hence decreasing availability of these nutrients to crops. These nutrients become available again upon decline of the microbial biomass.

Nutrients can be released from crop residues by mechanisms other than decomposition, e.g. some soluble salts crystallise on the surface of crop residues and can be washed off with minimal rainfall. Salts could also migrate to the surface of residues in the process of wetting and drying following minor rainfall events. Quantitative data to illustrate these processes are generally lacking. Preliminary research in the author's laboratory indicates that some macronutrients (e.g. K and S) can be leached from crop residues very effectively, whereas micronutrients generally leach to a small extent.

4.3.3.3
Burning

Burning crop residues causes the total loss of N and loss of a large proportion of S to the air through oxidation. Metal nutrients are converted into oxides and to a lesser extent carbonate forms. Knowledge of the chemical changes in nutrient forms during the burning process is limited, especially for micronutrients. Ash is a good source of K, P, Ca and Mg as well as Cu, Zn, Mn, Na and Si. The ash has a liming and salting effect, but its main effect is boosting the nutrient supply (Abdul et al. 2004; Du Preez et al. 2001).

Burning organic residues in shifting cultivation (slash-and-burn) resulted in increased total content of most cationic micronutrients in soil (Abdul et al. 2004), whereas concentrations of plant-available Fe, Cu and Zn decreased and those of Mn increased (Venkatesh et al. 2003). After 11–12 years of different tillage and residue management treatments in a semi-arid Plinthosol in South Africa, available Zn increased in the straw burning vs the non-burning treatment as well as under conservation vs conventional tillage (Du Preez et al. 2001). Copper and Zn are leached slowly from ash, but erosion of ash can cause large losses from the burnt system (Abdul et al. 2004; Menzies and Gillman 2003).

Table 4.4 The effect of burning windrowed canola residues on availability of soil micronutrients as illustrated by wheat tissue concentrations (shoots at the booting stage) as well as accumulation in grain. Field trial at Varley (Western Australia) (modified from Bowden et al. 1999)

	Shoot concentrations (mg kg^{-1})			Nutrient removal in grain (g ha^{-1})		
	Burnt[a]	Off-windrow[b]	Ratio burnt/ off-windrow	Burnt	Off-windrow	Ratio burnt/ off-windrow
Cu	2.3	2.0	1.15	6	2	3.00
Zn	11	10	1.10	33	11	3.00
Mn	141	102	1.38	443	121	3.66
Yield (t ha^{-1})				3.14	1.19	2.66

[a]Burnt windrow
[b]Inter-row between windrows

Burning windrowed canola residues resulted in slightly higher concentrations of Cu, Zn and Mn in wheat shoots, but substantially greater accumulation of these micronutrients in grain (Table 4.4). Accumulation of micronutrients in the grain was greater than the increase in grain yield, suggesting that the increased off-take from burnt windrows was due to higher grain concentrations as well as higher grain yield.

4.3.4
Manures, Composts and Other Organic Amendments

Manures, composts and other organic fertilisers represent good sources of micronutrients (e.g. Shuman and McCracken 1999; Warman 1990b). Indeed, while continuous application of inorganic NPK fertilisers in cassava production resulted in a decrease of available Zn and Cu in soil (Ultisol in Kerala, India), application of farm-yard manure caused an increase in the soil content of Zn, Cu, Fe and Mn (Kabeerathumma et al. 1993; Santra et al. 1999; Selvi et al. 2002). Similarly, in a rice-wheat rotation, use of farmyard manure and green manure maintained the available fraction of soil micronutrients (Fe, Zn, Cu and Mn) compared to the same rotation fertilised with inorganic NPK fertilisers alone (Kumar and Yadav 1995). However, supplying micronutrients via manures (e.g. cattle, pig and poultry manure, Warman 1990a) may not always result in increased soil or plant micronutrient content, depending on the particular soil-crop system (e.g. Chitdeshwari and Krishnasamy 1998; Kabeerathumma et al. 1993; Selvi et al. 2002; Warman and Cooper 2000).

Nutrient balances are under considerable pressure in pastures grown for hay because export of nutrients is especially large and requires adequate inputs to prevent decline in soil nutrient content (e.g. Ledgard 2001). Replacement of nutrients taken out in hay can be either via inorganic or organic fertilisers.

Chicken broiler litter may be a significant source of macro- and micronutrients. For example, use of this manure resulted in increased soil concentrations of extractable cationic micronutrients of between 1.6 (Mn) and 7.5 (Cu) times in bermudagrass (*Cynodon dactylon*) grown for hay in Georgia in the United States (Franzluebbers et al. 2004).

Given that *Azolla* can accumulate Zn when grown in polluted waters (Nirupama et al. 1996), *Azolla* might also be supplied ('loaded') with Zn during growth in non-polluted water to provide a slow-release, organic Zn 'fertiliser' during its decomposition (Anju and Sudhir 2005). Similarly, organic waste and recycled plant materials enriched with Fe or Zn are useful for micronutrient fertilisation of a variety of crops (Garcia-Mina et al. 1995; Kiemnec et al. 1990; Matocha 1984).

4.3.4.1
Availability of Soil Micronutrients in Soil Treated with Organic Amendments

Soil organic matter amendments influence the availability of micronutrients to plants. With Fe, which is present largely as insoluble Fe(III)-oxides, organic matter can increase its solubility through the effect on the soil redox potential (see review by Lindsay 1991). During decomposition of organic matter and respiration by soil microflora, electrons are generated, which result in a lowered soil redox potential and the reduction of insoluble Fe(III) to highly soluble Fe(II). Fulvic acid formed during organic matter decomposition and siderophores produced by microorganisms also increase Fe solubility and its availability to plants. On the other hand, metals such as Cu and Ni are tightly bound by soil organic matter, becoming less available in organic matter-amended soils.

Addition of organic matter causes a shift in the pool of extractable, bioavailable Zn (Mandal and Mandal 1987), which is temporarily immobilised into the soil organic matter (Tagwira et al. 1992). Immobilisation of Zn and other micronutrients by the microbial biomass can also occur during the initial stages of organic matter decomposition.

Decomposition of organic matter under submerged conditions results in a lower soil redox potential and elevated Fe and Mn solubility. These metals are thought to competitively inhibit Zn uptake (Rengel 1999); moreover, Fe may cause precipitation of soluble Zn as franklinite ($ZnFe_2O_4$) (Sajwan and Lindsay 1986).

Organic matter in manures, sludges and other soil amendments can effectively chelate micronutrients. Hence, adding inorganic fertilisers to manures may provide a superior source of micronutrients, e.g. in Zn-deficient rice-growing soils (Chitdeshwari and Krishnasamy 1998; Savithri et al. 1999a), a rice-wheat rotation (Kulandaivel et al. 2004), etc. This strategy has proved particularly useful in augmenting the Zn nutrition of dryland rice fertilised either with poultry or cattle manure (see Rengel et al. 1999), in which $ZnSO_4$ mixed with

these manures was more effective at fertilising rice and maize than $ZnSO_4$ alone. Presumably, the inorganic Zn is complexed by fulvic acid and other organic acids generated during the decomposition of organic materials, which increases its solubility and bioavailability to plants. In addition, farmyard manure may increase availability of native non-labile soil micronutrients, e.g. by increasing the concentration of amorphous oxide-bound Fe and Mn at the expense of residual and non-extractable Fe and Mn in savanna (Agbenin 2003).

4.3.4.2
Green Manure

Green manure can be an effective source of micronutrients for a range of crops. However, potential negative allelopathic effects on crops may need to be monitored (cf. Ohno 2001). Green material produced by plants such as *Azolla microphylla*, sunn hemp (*Crotalaria juncea*) and other *Crotalaria* sp. cowpea (*Vigna unguiculata*), water hyacinth (*Eichhornia crassipes*), *Sesbania* sp., *Leucaena* sp., *Calotropis* sp., *Tephrosia* sp., *Gliricidia* sp., and others, are used (e.g. Dhaliwal and Chahal 1996; Hegarningsih et al. 1991; Mandal et al. 1997; Mishra et al. 2004; Sadana and Nayyar 2000; Savithri et al. 1999b). These green materials increase availability of cationic micronutrients in soil (Dhaliwal and Chahal 1996; Mishra et al. 2004; Santra et al. 1999), and hence decrease the need for inorganic micronutrient fertilisers. However, the quality of green manuring material (e.g. C:N ratio, micronutrient content, etc.) is important in determining the effectiveness in supplying micronutrients and increasing crop yields. For example, *Sesbania* was better than wheat straw in supplying micronutrients to rice (Mishra et al. 2004), whereas *Leucaena leucocephala* accumulated more Fe and Mn than *Acacia tortilis* (Mehari et al. 2005).

Green manures may increase use-efficiency of inorganic micronutrient fertilisers added, e.g. Zn (Savithri et al. 1999), etc. However, flooding of rice soils may result in a negative effect of green manuring on availability of Zn and Cu (Mandal et al. 1997). In contrast, availability of Mn can be increased due to a decrease in pH and pE (Sadana et al. 1990) or due to a more intensely reducing environment even when the pH of acidic soil increases due to flooding (Porter et al. 2004).

4.3.5
Contribution of Livestock to Micronutrient Cycling on Grazed Pastures

Grazed pastures receive uneven deposition of animal urine and excreta, causing substantial temporal and spatial variability in nutrient loadings. Although a

large body of literature exists on the contribution of urine and excreta to N (e.g. Bolan et al. 2004) and other macronutrient cycling (Carran and Theobald 2000), little is known about how urine and excreta deposition influences micronutrient cycling in grazed pastures (Wilkinson and Mays 1979). Such research is urgently required, especially in the light of livestock being identified as a potential micronutrient vehicle for improving human nutrition through consumption of meat and dairy products (Muller and Krawinkel 2005).

4.3.6
Crop and Variety Selection

Crop rotations appropriate for a particular region and climate may have numerous advantages in terms of increasing availability of micronutrients or selectively utilising different soil micronutrient pools (e.g. Fe, Cu and Zn; Karlen et al. 1994). The beneficial effects of crop rotations include improved soil chemical and physical fertility, reduced weed infestation and disease reduction .

Different crop species will have different micronutrient requirements and will differ in micronutrient density in various crop parts (e.g. harvested grain vs residues) when grown under similar conditions (Rengel 1999, 2001; Rengel and Marschner 2005). This knowledge can be utilised in managing nutrient cycling in agroecosystems.

Field pea (*Pisum sativum*) was less effective than spring wheat in utilising fertiliser Cu added to alkaline soils (Brennan and Bolland 2004b). In contrast, canola, white lupin (*Lupinus albus*) and durum wheat (*Triticum durum*) were all more effective than spring wheat in taking up fertiliser Cu and producing a greater yield when grown on alkaline soils (Brennan and Bolland 2004a).

The optimal rates of inorganic Zn fertilisers may vary by an order of magnitude depending on the soil-crop system (Savithri et al. 1999). For grain legumes grown on alkaline soils in Western Australia, Zn is the trace element most likely to be deficient because it becomes less available to plants with an increase in soil pH (Loss et al. 2003). Although grain legumes have a higher Zn requirement than cereals, they tend to produce lower yields, thus the amount of Zn removed in the grain (and needing to be replaced in soil) are likely to be similar (cf. Rengel 2002).

With increasing ZnO application (0–2 kg ha^{-1}), yield of faba beans (*Vicia faba*) increased almost 2-fold and that of field pea about 30% (Fig. 4.1). No response to Zn was recorded for chickpea *(Cicer arietinum)* (Loss et al. 2003). Organic acid anions excreted by chickpea roots (e.g. Wouterlood et al. 2005) as well as intense acidification of the rhizosphere under certain conditions (Neumann and Römheld 1999) may increase Zn availability (Khan et al. 2000).
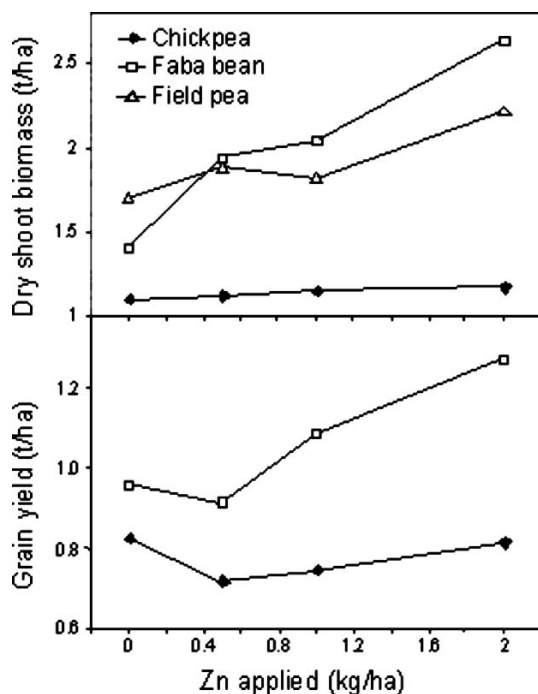
Fig. 4.1 Dry vegetative biomass (14 weeks after sowing) and grain yield responses of grain legumes to Zn application on a brown gravelly loam at Calingiri, Western Australia (pH=6.0) (modified from Loss et al. 2003)

4.4
Micronutrient Cycling in Forest Ecosystems

Nutrient cycling in forests has been studied for more than 100 years (Attiwill and Adams 1993; see also Chapter 12 by Adams, this volume). However, there is limited information on micronutrient cycling, with most attention being traditionally devoted to N and P.

Different forests systems vary substantially in nutrient cycling and nutrient dynamics, even when grown adjacent to each other, e.g. red alder (*Alnus rubra*) and Douglas fir (*Pseudotsuga menziesii*) in Washington State (USA) (Turner et al. 1976). Fir forests have slow nutrient cycling and may therefore be nutrient-stressed. Work in California has shown that the Mn concentration in the bark and wood of red fir (*Abies magnifica*) can increase over a 3–17 year period, even though the total amount of Mn in the forest system remained the same (in the wood) or increased slightly (in the bark) (McColl and Powers 2003).

Plantations are becoming an increasingly important source of timber for various purposes. They are perceived as a more desirable environmental solution than logging of natural (especially old-growth) forest. Hence, plantations (particularly short-term rotations) are managed as intensive systems and receive substantial nutrient input in the form of fertilisers.

4.4.1
Litterfall, Stemflow and Throughfall

4.4.1.1
Litterfall

The relative proportion between wood and leaf production in forests of differing latitudes changes from leaf production being about one-third of wood production in high latitudes to being about 30% higher than wood production in tropical forests (Jordan 1985). These differences in the proportion of plant parts are reflected in a differential amount and quality of litterfall.

The biomass of litterfall was 684–737 g dw m^{-2} year^{-1} in the subtropical forest on the northern Okinawa Island (Japan) (Xu et al. 2003) or 640 g dw m^{-2} year^{-1} in the subtropical eucalypt forest in south-eastern Queensland (Australia) (Rogers and Westman 1977). The amount of leaf litter may be around two-thirds of the total litterfall (Xu et al. 2003), but the proportion of wood (such as twigs and branches) in litterfall may increase as the forest stand ages (Turner et al. 1976).

The concentration of Cu and Mn was higher in leaves, whereas that of Zn was higher in wood and that of Fe higher in bark than in the other components of the litter accumulated on the eucalypt forest floor (Rogers and Westman 1977)

Table 4.5 Micronutrients in the litter accumulated in subtropical eucalypt forest floor litter (North Stradbroke Island, Queensland, Australia). The predominant species were *Eucalyptus signata* (46% of the total foliar cover) and *Eucalyptus umbra* (20%) (data modified from Rogers and Westman 1977)

Component	Cu	Fe	Mn	Zn
Concentration (mg kg^{-1} dw)				
Wood	5	250	58	17
Bark	5	410	43	9
Leaves	8	385	74	10
Residue	4	550	58	12
Nutrient pools (mg dw m^{-2})				
Wood	4.3	218	50	15
Bark	4.4	363	37	7.6
Leaves	4.0	193	3.7	5.0
Residue	1.8	247	26	5.4

(see also Table 4.5), indicating the complexity of micronutrient cycling in forest ecosystems. Combining the concentration in litter components and the absolute amounts of these litter proportions, it became clear that wood is the biggest pool of Mn and Zn in litter, in contrast to Fe, which was present mostly in bark. Copper did not show any specific pattern of distribution among wood, leaves and bark in the litter accumulated on the eucalypt forest floor (Table 4.5).

In the subtropical eucalypt forest in south-eastern Queensland, the total litter accumulating on the forest floor amounted to 2.7 kg m^{-2}, with an estimated litter half-life of 2.9 years, suggesting a relatively slow decomposition (Rogers and Westman 1977). Among the four micronutrients discussed in this review, Cu appeared to be the only one easily lost from eucalypt leaves placed on the forest floor (Table 4.6). Hence, cycling of most micronutrients is relatively slow.

In chestnut (*Castanea sativa*) and oak (*Quercus pyrenaica*) in western Spain, the largest absolute amount of micronutrients returning to the soil in litterfall was found for Mn, followed by Fe, Zn and Cu (Gallardo et al. 1998b). However, when throughfall was considered, Mn and Fe were returned to soil through both litter and throughfall, whereas Zn and Cu were returned to soil almost exclusively through leaching from the canopy by rainfall. Cycling of Fe was impeded because litterfall decay appeared to partially immobilise Fe in the soil (Gallardo et al. 1998a).

In a mixed forest of overstorey quaking aspen (*Populus tremuloides*) and understorey sugar maple (*Acer saccharum*), between 40% and 60% of nutrients were retained in the perennial biomass, whereas the rest remained in the leaves and appeared in the litterfall. However, regarding micronutrients in particular, translocation out of leaves was of little importance for Fe, and did not appear to be important at all for Zn (Pastor and Bockheim 1984). In contrast, in Australian Banksia woodland and other forest ecosystems grown on impoverished sands

Table 4.6 Micronutrients (in mg kg^{-1}) retained in leaves of two eucalypt species over time (branches were cut and placed on the forest floor) (data modified from Rogers and Westman 1977)

Micronu-trient	Fresh	After 6 months	After 13 months	After 18 months	Litter
E. signata					
Cu	29	6	6	6	11
Fe	146	129	130	143	110
Mn	95	98	112	79	160
Zn	12	12	11	12	7
E. umbra					
Cu	28	5	16	6	11
Fe	192	700	416	163	88
Mn	57	108	72	66	104
Zn	13	14	29	15	11

where micronutrient availability is extremely low, substantial re-translocation of micronutrients occurs from leaves into seeds of species of the family Proteaceae (Kuo et al. 1982). This is an important mechanism of ensuring adequate micronutrient supply for young seedlings and impacts profoundly on micronutrient cycling in the litterfall.

The variation in Mn concentration in plant leaves can be enormous: in a survey of native species in south-western Australia, a range from 4 μg Mn g^{-1} dry matter (in *Oxylobium capitatum*, Fabaceae) to 2,180 μg Mn g^{-1} dry matter (in *Phyla nodiflora*, Verbenaceae) was found (Foulds 1993). In contrast, the standard values for sufficient tissue Mn to allow 90% of maximum growth in crop plants are within 25–35 μg g^{-1} dry matter, and can be as low as 11 μg Mn g^{-1} dry matter for the youngest emerged blades of wheat (see Rengel 2000). Thus, some plant species have the capacity to take up Mn at high rates, apparently higher than their physiological requirement. The mechanisms underlying these high uptake rates are especially puzzling when species like *Banksia attenuata*, and a number of species from the family Proteaceae, accumulate Mn to over 300 μg g^{-1} dry matter, while growing on soil that is considered deficient in plant-available Mn (<2 μg Mn g^{-1} soil in DTPA extract) (Foulds 1993).

Some eucalypt subgenera also have an exceptional capacity to accumulate Mn, i.e. concentrations of Mn in the leaves, stem and bark of symphyomyrts are consistently greater than those in monocalypts, even though it does not appear that availability of Mn governs the distribution of eucalypt subgenera in these ecosystems (Hill et al. 2001). The concentration of Mn in eucalypts may be as high as 800 μg g^{-1} in green leaf-fall and up to 2,800 μg g^{-1} in leaves of glasshouse-grown seedlings, i.e. well within the toxic range for annual crop plants (Hill et al. 2001).

White-rot fungi require Mn as a structural component of lignin peroxidase (Kern 1989; Perie and Gold 1991), an enzyme involved in the decomposition of lignin. Hence, relatively high Mn concentrations are maintained in decomposing bark and wood (McColl and Powers 2003).

4.4.1.2
Throughfall

Throughfall generally represents an important pathway for returning nutrients to soil and thus fuelling the soil-plant cycling of nutrients in forest stands. Leaching from leaves and washing-off of leaf exudates, together with solutes deposited on the foliage after evaporation of intercepted rainfall and the dry-deposited materials all contribute to the concentration of solutes in the throughfall (Tobon et al. 2004). However, the contribution of throughfall to translocating Mn, Fe and other micronutrients to soil is relatively small compared with macronutrients SO_4, K, NO_3 and NH_4. Hence, litterfall is by far the biggest contributor to nutrient input into the forest floor despite the substantial nutrient enrichment in rainfall as it passes through the canopy (Tobon et al. 2004).

Nevertheless, there are examples of throughfall representing an important input of micronutrients. In a lowland rain forest, the largest proportion of Zn reaching the forest floor was in throughfall washing Zn from leaves and branches. In contrast, for Fe, Mn and Cu, leaf litter was the greatest contributor transferring these micronutrients to the forest floor. Stemflow, wood and reproductive litter contributed only small quantities of micronutrients to the forest floor (Muoghalu 2003).

4.4.2
Burning

The nutritional effects of burning litter accumulated on the forest floor will depend on the burn intensity (temperature and duration). While low-intensity fires may result in an increase in nutrient availability, severe fires may cause significant losses of nutrients through volatilisation, ash entrapment in smoke columns, leaching and erosion (Certini 2005; Neary et al. 1999). Immediate changes in exchangeable soil cations occur upon burning of organic material due to solubilisation of cations from ash (Khanna et al. 1996).

Forest burning results in formation of oxide forms of many nutrients, with hydrolysis of these oxides contributing to a pH increase and potentially deleterious effects on the availability of cationic micronutrients (Ballard 2000). However, in a *Pinus pinaster* forest in Spain, burning caused an increase in total as well as available Mn; the latter may be due to an increased proportion of easily reducible Mn forms (Gonzalez Parra et al. 1996). Copper leaches more easily than Zn from the ash of branches and trunks of tropical forest (Menzies and Gillman 2003).

4.4.3
Organic Amendments

Various sources of wastewater can be used in irrigation of plantations. In addition to supplying macronutrients, such wastewater may be a good source of cationic micronutrients. For example, municipal wastewater allowed river gum (*Eucalyptus camaldulensis*) trees to accumulate more Fe, Zn, Cu and Mn than trees irrigated with clean water (Singh and Bhati 2003). Effluent from meatworks represented a significant micronutrient source for bluegum (*Eucalyptus globulus*), with 67 kg Mn having accumulated in the biomass per hectare during a 3-year period (Guo et al. 2002). However, caution should be exercised regarding the source of effluent and concentration of micronutrients applied because excessive accumulation of Fe, Zn, Cu and Mn occurred in *E. camaldulensis* and *Acacia niloti* trees irrigated with effluent from a steel industry, even when diluted with other types of effluent (Singh and Madhulika 2003).

4.4.4
Fertilisers

Fertilisation is a standard silviculture practice (Adegbidi et al. 2005), especially fertilisation with N in coniferous forests (e.g. Chappell et al. 1991; van den Burg 1991). Micronutrient fertilisation is practised in specific situations, such as reforestation of healthlands in the southern Netherlands, where Cu deficiency is common (van den Burg 1991). Eucalypts frequently suffer from micronutrient disorders that need to be remedied by fertilisation (Dell et al. 2002). About 10,000 ha of predominantly coniferous plantations in Australia are fertilised with micronutrients, mainly Cu and Zn (Turner 1983).

4.5
Conclusions

With increasing costs and environmental considerations associated with fertiliser use, managing nutrient cycling for maximum benefit is an important component of agroecosystems and intensively managed forest ecosystems. In most agroecosystems, greater removal than input of micronutrients is unlikely to result in micronutrient deficiencies over relatively short time-frames. However, in agroecosystems grown on infertile soils (e.g. in southern and south-western Australia) micronutrient cycling needs to be considered to ensure an adequate supply of micronutrients to crops even on a short-time scale.

Given that most inorganic micronutrient fertilisers are relatively cheap, are required only in small amounts, and are easily mixed with macronutrient fertilisers for application, and that various organic fertilisers (farmyard manure, green manure, etc.) or crop residues may be a good source of available micronutrients, an adequate supply of micronutrients should be achievable even in extensive agriculture.

In most forest ecosystems litterfall and throughfall represent excellent sources of micronutrients in balance with growth processes. However, fertilisation with micronutrients may be required in plantations and other forest ecosystems where removal of biomass and thus micronutrients occurs regularly.

4.6
Future Research

Remobilisation of micronutrients from vegetative parts prior to senescence and/or fall needs to be characterised together with loading of micronutrients into

grains because this is what determines the fraction of plant micronutrients that either enters into nutrient cycling in situ (due to litterfall) or is taken off-site through harvest (e.g. grain).

Mechanisms governing micronutrient release from crop residues (by leaching as well as decomposition of organic matter) need to be elucidated.

Nutrient cycling in the soil-plant-microbe system may be altered by increasing CO_2 concentrations (e.g. in wheat, uptake and shoot accumulation of Mn were increased similarly to P, K and Mg, whereas uptake of Fe and Zn was unaltered; Fangmeier et al. 1997). With CO_2 concentrations in the atmosphere continuing to increase, it is likely that the effect on nutrient cycling will become even more pronounced. Further research into understanding the effects of increasing CO_2 concentration on nutrient cycling is warranted.

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5 Root Exudates and Nutrient Cycling

Günter Neumann

5.1
Introduction

In addition to their role as organs for anchorage in soil, soil exploitation, and uptake of water and nutrients, plant roots can modify the physico-chemical conditions in the surrounding soil via alterations of root activity. The soil volume that is directly or indirectly influenced by the activity of plant roots is called the rhizosphere (Hinsinger 1998). As early as the beginning of the last century, the German phytopathologist Lorenz Hiltner (1904) recognised that the rhizosphere, as the interface between the soil matrix, plant roots and soil microorganisms, plays a critical role in nutrient cycling in ecosystems. Root-induced physico-chemical changes in the rhizosphere are major determinants of the plant availability of nutrients and toxic elements in soils. Organic compounds released from plant roots as rhizodeposits can have a direct impact on the solubility of mineral elements or can indirectly influence turnover and availability of nutrients by interaction with soil micro-organisms. Thus, rhizodeposition is a key factor determining fluxes and pool sizes of mineral nutrients in ecosystems.

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5.2
Root Exudates and Organic Rhizodeposition

5.2.1
Rhizodeposition – Definition and Quantity

In higher plants, a substantial proportion (20–60%) of carbon fixed during photosynthesis can be translocated below ground (Grayston et al. 1996; Kuzyakov and Domanski 2000). Depending on root activity, 15–60% of this carbon fraction is used for root respiration and is finally released as CO_2 (Lambers et al. 2002). Of the assimilates translocated below ground, up to 70% in perennials and up to 40% in annual plants enter the soil as organic rhizodeposition, corresponding to 800–4,500 kg carbon ha^{-1} year^{-1} (Kuzyakov and Domanski 2000; Lynch and Whipps 1990). This is associated with a concomitant input of nitrogen ranging between 15 and 60 kg ha^{-1} year^{-1} (Hooker et al. 2000).

Rhizodeposition comprises lysates of sloughed-off cells and tissues resulting from root turnover [up to 50% of carbon translocated below ground (Grayston et al. 1996)], and root exudates released from intact root cells (Fig. 5.1). Root exudates can be further subdivided into (1) diffusates – organic compounds
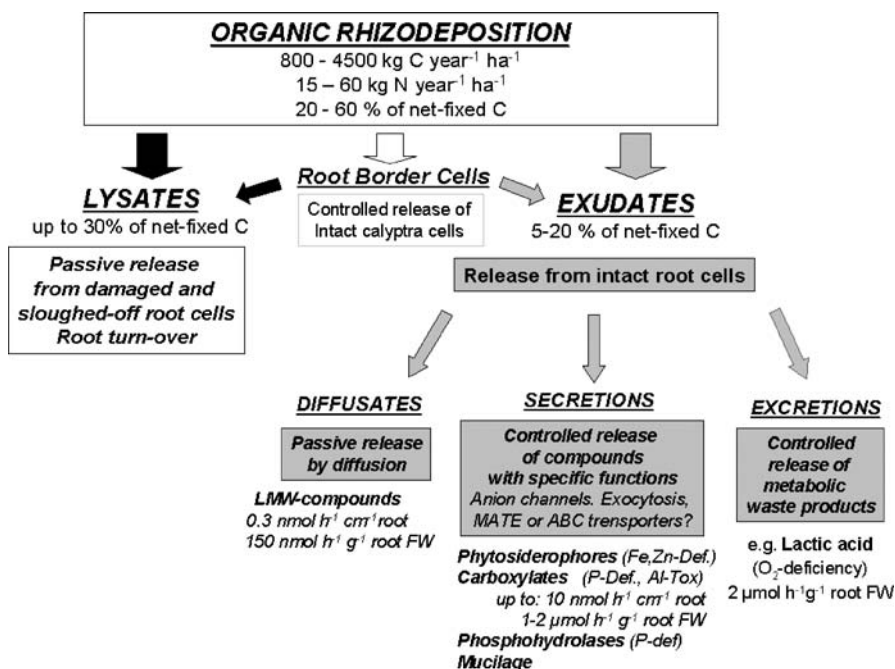

Fig. 5.1 Classification, quantities and release mechanisms of organic rhizodeposition

continuously lost from plant roots by diffusion, (2) root excretions released as metabolic waste products, or (3) secretions with special functions in nutrient mobilisation, detoxification, plant-microbial signalling and defense reactions (Neumann and Römheld 2000; Werner 2000). Root exudates may comprise 5–10% of the net fixed carbon in soil-grown plants (Jones et al. 2004). The controlled liberation of so-called root border cells, released as living root cells from the root cap (Hawes et al. 2000), also contributes to rhizodeposition to some extent. However, the related carbon input has been calculated to account only for 1–2% compared with the carbon fraction released as root exudates (Nguyen 2003).

The outstanding importance of the rhizosphere for cycling of carbon and nutrients in soils is illustrated by the fact that organic rhizodeposition, which can account for 30–40% of the total soil organic matter input, is released into the rhizosphere soil, which comprises only 2–3% of the total soil volume (Grayston et al. 1996).

5.2.2
Release Mechanisms

Every soluble compound present in root cells in contact with soil may be subject to loss to the rhizosphere; accordingly, a wide range of different substances has been detected in rhizodeposits (Table 5.1). However, there is also evidence suggesting the presence of mechanisms for controlled release of organic compounds in plant roots as the controlled extrusion of (1) waste products and (2) compounds with specific functions in the rhizosphere.

5.2.2.1
Diffusion

As a consequence of rhizosphere microbial turnover and sorption to the soil matrix, a large concentration gradient in low-molecular-weight (LMW) organic solutes usually exists between the cytosol of epidermal root cells (millimolar range) and the rhizosphere (micromolar range). This gradient promotes outward diffusion, particularly of LMW compounds such as sugars, carboxylates, amino acids and phenolics (Fig. 5.1), whereas diffusion is limited for polymers such as proteins, polysaccharides and nucleic acids.

Release rates of diffusates are determined by both membrane permeability and the size and polarity of the exuded compounds. Proton extrusion via plasmalemma H^+ ATPase and the large K^+ diffusion potential create an outward-positive electrochemical potential gradient across the plasma membrane. This promotes outward-diffusion of carboxylates and amino acids that are negatively charged at the slightly alkaline cytosolic pH (ranging between 7.1 and 7.4; Jones

Table 5.1 Root exudates with impact on nutrient cycling

Compounds	Reported functions
	Nutritional functions
Low molecular weight sugars, amino acids, carboxylic acids	Readily available sources of carbon and nitrogen for microorganisms (in case of carboxylates availability reduced by adsorption processes)
	Plant nutrient acquisition
Citrate, oxalate, malate, malonate, piscidic acid, phytosiderophores	Mobilization of P, Fe, Zn, Mn, by metal chelation
Phenolics, malate, citrate	Mobilization of Fe, Mn, by contact reduction
Root-secretory phosphohydrolases	Mobilization and retrieval of P from organic P esters
Phenol-carboxylic acids, Flavonoids, malate, mucilage	Chemo-attraction of N_2-fixing microorganisms
Flavones, flavanones, isoflavones	Nod-gene inducers and resistance-inducers against phytoalexins in symbiotic N_2 fixation
Flavonoids, sugars, amino acids	Signal functions in establishment of mycorrhizal associations
Invertase	Carbon supply to mycorrhizal fungi
	Protective functions
Citrate, oxalate, malate, phenolics, mucilage, secretory proteins	Detoxification of Al_3^+ by complexation
Malate, citrate	Increased intracellular accumulation and exudation in response to bicarbonate toxicity
Mucilage	Protection of the root meristem, improved root-soil contact, increased water-holding capacity by inclusion of soil particles (rhizosheaths, mucigel)
Isoflavonoids, quinones, hydroquinines, saponins, chitinase, root border cells	Phytoalexins, defense against of pathogens, parasites and competitors

1998). Based on diffusion experiments with synthetic membrane vesicles artificially loaded with labelled LMW compounds, a rate of diffusion-mediated basal root exudation has been calculated as approximately 0.3 nmol h^{-1} cm^{-1} root length or 150 nmol h^{-1} g^{-1} root fresh weight (Jones 1998; Jones et al. 1994). This fits well with release rates of LMW compounds, which range between 0.5 and 0.9 nmol h^{-1} cm^{-1} root length for apical root zones of various plant species in hydroponics with sufficient nutrient supply (Neumann and Römheld 2000).

Particularly intense root exudation is frequently observed in apical root zones (1–2 cm distance from the root tip), where microbial density is lower than in older parts of the roots (Neumann and Römheld 2002). This emphasises the importance of considering spatial variation in exudation along the root for quantitative measurements. Assuming root elongation rates of 1–2 cm per day, the average residence time of apical root zones with the highest rates of exudation in a given soil compartment would barely exceed 12–24 h. Based on a volume of 30 μl – calculated for the rhizosphere soil solution at a distance of 1 mm from the surface of a 1-cm apical root segment (Bar-Yosef 1991) – diffusion-mediated exudation of LMW compounds in apical root zones may therefore account for an approximate concentration of 300–2,000 μM, accumulating over a time period of 12–24 h. With half-lives between 1 and 5 h as a result of microbial degradation of sugars, amino acids and organic acids (Jones et al. 2003), as well as sorption to the soil matrix are taken into account, this leads to a concentration of 1–50 μM for LMW compounds frequently reported in rhizosphere soil solution (Jones et al. 2003). In older root zones with higher microbial densities, a higher contribution of lysates from sloughed-off cells and tissues, and of microbial metabolites released into the rhizosphere soil solution may be expected.

5.2.2.2
Retrieval Mechanisms

A possible mechanism to counteract the continuous, diffusion-mediated release of organic carbon and nitrogen from plant roots is the expression of transporters for active ATPase-coupled uptake of LMW organic compounds. Amino acid transporters for direct acquisition of organic nitrogen were first described in plants adapted to arctic tundras, where mineralisation may be delayed (Chapin et al. 1993). Meanwhile, transporters mediating uptake of small peptides, amino acids and LMW sugars by plant roots have been identified in a large number of different plant species (Fischer et al. 1998; Steiner et al. 1994; Xia and Saglio 1988). Amino acid and peptide transporters frequently show enhanced expression under limited N supply (Nazoa et al. 2003; Persson and Nashölm 2002), suggesting a function in N acquisition but also in retrieval of organic N lost by plant roots via rhizodeposition (Jones et al. 2005), which can account for 20–30% of the total N assimilation during the growth period (Janzen 1990).

When photosynthesis is reduced under certain stress conditions, such as nutrient deficiency, drought or oxidative damage, sugar supply may be a limiting factor for plant growth. Re-uptake of sugars lost by diffusion may be a strategy to minimise losses of carbon. The expression of retrieval mechanisms for LMW sugars in plant roots (Xia and Saglio 1988) may also enable plants to control microbial colonisation at the rhizoplane and in the rhizosphere by modifying the supply of easily available carbohydrates (Jones et al. 2004).

Up to 90% retrieval of amino acids and sugars released from plant roots has been demonstrated in hydroponic culture (Darrah 1996; Jones and Darrah 1993). However, the contribution of retrieval mechanisms to N and C uptake under field conditions remains to be established (Jones et al. 2005).

Interestingly, no active retrieval mechanisms have so far been identified for organic acids, which are usually present in the rhizosphere as carboxylates. Particularly the di- and tricarboxylate anions, such as malate, fumarate, oxalate, malonate, citrate and aconitate, as major carboxylates released from plant roots (Jones et al 2004; Neumann and Römheld 2000), frequently exhibit rapid and intense adsorption to the soil matrix, while sorption of sugars, amino acids and monocarboxylates is weak (Jones et al. 2004). Therefore, the energy investment for re-mobilisation and subsequent uptake of carboxylates against the inside-negative membrane potential of root cells may be much higher than the gain of energy derived from retrieval of carbon from carboxylates. Moreover, carboxylates with metal-chelating properties have been implicated in mobilisation of sparingly soluble nutrients (Neumann and Römheld 2002), and efficient mobilisation frequently requires high concentrations of carboxylates in the rhizosphere (see Sect. 5.3).

5.2.2.3
Controlled Release Mechanisms

In contrast to diffusion-mediated losses of LMW organic substances from plant roots, there are also indications for the controlled release into the rhizosphere of organic compounds with specific functions. Polymers, such as root mucilage or ecto-enzymes (e.g. root-secretory phosphohydrolases) are usually released by vesicle transport via exocytosis (Fig. 5.1). Secretory processes involved in exocytosis depend strongly on intracellular and extracellular Ca^{2+} levels (Battey and Blackbourn 1993; Battey et al. 1999).

Mucilage is a gelatinous uronic acid polysaccharide with a high capacity for water uptake. The resultant swelling protects the root meristem, improves root-soil contact by inclusion of soil particles, and plays a role in attracting associative N_2-fixing rhizobacteria (Neumann and Römheld 2002). Biosynthesis and secretion occur in the hyper-secretory cells of the root cap, which are subsequently released as root border cells by a genetically controlled mechanism (Hawes et

al. 2000). Root border cells embedded in a layer of mucilage are viable for up to 1 week without direct root contact. Mucigel, which includes root mucilage, border cells, soil particles and microorganisms, is translocated during root growth to older, more basal root zones.

Root-induced mobilisation of sparingly soluble nutrients (e.g. P, Fe and Zn) or exclusion of toxic elements (e.g. Al^{3+}) by LMW organic metal chelators requires: (1) the release of specific compounds with high stability constants for the respective metal complexes (e.g. citrate, malate, oxalate, malonate, phytosiderophores) in the root zones with the highest activity in nutrient uptake (e.g. apical root zones), and (2) accumulation of the organic ligand in the rhizosphere, with millimolar concentrations reported for rhizosphere soil solutions (Jones 1998; Neumann and Römheld 2000, 2002). This stresses the importance of specific transport mechanisms to mediate root exudation of organic metal chelators in sufficient quantities (Fig. 5.1).

Using patch-clamp approaches and inhibitor studies, anion channels responsible for Al-induced exudation of malate and citrate that confer Al-tolerance to cultivars of maize and wheat have recently been identified (Kollmeier et al. 2001; Pineros and Kochian 2001; Zhang et al. 2001). Anion channels, which have also been implicated in exudation of citrate in cluster roots of *Lupinus albus* (Neumann et al. 1999; Zhang et al. 2004), are responsible for mobilisation of sparingly soluble Fe- and Al-phosphates, and are involved in release of Fe- and Zn-mobilising phytosiderophores in graminaceous plant species (Sakaguchi et al. 1999). Anion channels facilitate outward diffusion of specific carboxylates along the steep electrochemical potential gradient at the plasma membrane. To maintain charge balance, the release of carboxylate anions via anion channels seems to be coupled with increased release of protons via plasma membrane H^+-ATPase, or increased K^+ extrusion by K^+ channels and possibly also release of other cations (Kania et al. 2001; Ryan et al. 1995a; Sakaguchi et al. 1999; Yan et al. 2002; Zhu et al. 2005).

Much less is known about the release mechanisms from plant roots of secondary plant metabolites, such as phenylpropanoids, flavonoids, terpenoids and alkaloids, which have specific functions in plant-microbial signalling and feeding deterrence, as well as anti-microbial and allelopathic interactions. The large number of different compounds with specific functions in the rhizosphere obviously requires control of root exudation. The cytotoxicity of many secondary plant metabolites prevents accumulation in the cytosol; hence, biosynthesis frequently occurs at the endoplasmic reticulum with subsequent storage in vesicles or vacuoles (Facchini 2001; Walker et al. 2003; Winkel-Shirley 2001). Therefore, vesicle transport may be responsible for release of secondary metabolites by plant roots (Gagnon 1992; Walker et al. 2003). However, members of transporter families involved in detoxification and vacuolar compartmentation of pathogen toxins, agrochemicals (e.g. pesticides) and plant-borne flavonoids (MATE/ABC transporters) are also possible candidates for regulating root exudation of secondary plant metabolites (Brown et al. 1999; Martinoia et al. 2002).

5.2.3
Rhizodeposition as Affected by External Factors

Release of organic compounds from plant roots can be affected by a wide range of external factors. Stress conditions that impact on membrane permeability usually stimulate organic rhizodeposition and include temperature extremes (Rovira 1959; Vancura 1967), mechanical impedance of the substrate (Boeuf-Tremblay et al. 1995; Groleau-Renaud et al. 1998), drought (Reid 1974; Tesche 1974), the presence of toxic elements and low pH of the soil solution (Costa et al. 1997; Kochian 1995; Römheld and Marschner 1983), nutrient deficiency (Marschner 1998; Neumann and Römheld 2000), oxidative damage, the presence of toxic microbial metabolites (Meharg and Kilham 1995; Phillips et al. 2004; Sacchi et al. 2000), and impairment of retrieval mechanisms (Jones and Darrah 1993; Sacchi et al. 2000).

Apart from stress conditions affecting membrane integrity, rhizodeposition can also be influenced by factors modulating the physiological activity of plant cells. Light intensity may have an impact on rhizodeposition by regulating the photosynthetic carbon supply to the roots. This may explain the stimulation of phytosiderophore release in roots of barley and wheat under Fe and Zn limitation with increasing light intensities (Cakmak et al. 1998), with diurnal variations in root exudation during the light period (Marschner et al. 1987; Tagaki et al. 1984; Watt and Evans 1999). Similarly, elevated atmospheric CO_2 concentrations increase the below-ground translocation of carbohydrates (Rogers et al. 1994) by stimulating photosynthetic CO_2 assimilation. Enhanced carbon supply to the roots may thereby affect the quantity and composition of rhizodeposition (Wasaki et al. 2005). Controlled secretion of compounds with specific functions in the rhizosphere depends on metabolic energy. Therefore, root-zone temperature can affect root exudation by determining the speed of metabolic reactions. For example, phytosiderophore release in Fe-deficient barley decreases upon decreasing the temperature from 30 °C to 5 °C (Kissel 1987).

5.3
Root Exudates and Chemical Mobilisation of Nutrients

Less than 20% of the topsoil is explored by plant roots within a growing season. Nutrients that reach the root surface mainly by diffusion (e.g. P, K, NH_4^+ and most micronutrients) are rapidly depleted in the rhizosphere soil solution by root uptake (Kuchenbuch and Jungk 1984; Römheld 1998), Diffusion-based release from the soil solid phase is frequently too slow to match plant demands for mineral nutrients with limited solubility (Marschner 1995) and thus requires additional adaptations of higher plants for nutrient acquisition. Apart from adaptive changes in root morphology and mycorrhizal colonisation to increase

the spatial availability of nutrients, plant roots are able to modify the chemistry of the rhizosphere to increase the solubility of nutrients. Chemical strategies for nutrient mobilisation include root-induced modifications of pH and redox potential in the rhizosphere, expression of high-affinity uptake systems, and release of nutrient-mobilising root exudates or hydrolytic enzymes.

Increased rhizodeposition has been reported as a response to wide range of nutrient limitations, such as deficiencies in P, Ca, K, Fe or Zn (Cakmak and Marschner 1988; Kraffczyk et al. 1984; Neumann and Römheld 2000; Ratnayake et al. 1978). Under conditions of severe nutrient deficiency, this increased rhizodeposition may be attributed mainly to impairment of membrane integrity (Cakmak and Marschner 1988; Ratnayake et al. 1978). However, at least in some cases, there are indications for a controlled release of specific compounds that can mobilise sparingly soluble nutrients in the rhizosphere as an adaptive response (Neumann and Römheld 2002) increasing the competitiveness of plants in ecosystems.

5.3.1
Phosphorus Mobilisation by Carboxylates

As an example of an extremely efficient strategy towards chemical mobilisation of nutrients in the rhizosphere, the formation of so-called "cluster roots" is characteristic mainly of members of the Proteaceae and Casuarinaceae families and for several leguminous plant species adapted to habitats of extremely low soil fertility (Fig. 5.2). Cluster roots are characterised by a large number of closely spaced, tertiary lateral rootlets with limited growth (3–5 mm long, 50–1,000 rootlets cm^{-1} root axis) and are densely covered with root hairs (Dinkelaker et al. 1995).

Cluster roots have been identified as the sites of intense exudation of carboxylates, phenolics, protons, and root secretory acid phosphatases in amounts sufficient to mediate not only the mobilisation of sparingly soluble soil P sources but also co-mobilisation of Mn, Zn, Fe and Mo (Dinkelaker et al. 1989, 1995; Gardener et al. 1983; Gerke et al. 1994; Tesfamariam et al. 2005). Mobilisation studies with a wide range of different soils suggest that at least millimolar concentrations of carboxylates with high stability constants for metal complexation (e.g. citrate, oxalate and malonate) are required in the extraction solution to liberate significant quantities of P from sparingly soluble Al-/Fe- and Ca-phosphates (Fig. 5.3) by mechanisms of ligand exchange or dissolution of P sorption sites (Jones 1998; Neumann and Römheld 2002). This is equivalent to rhizosphere concentrations >5–10 µmol carboxylate anions per gram rhizosphere soil (Amann and Amberger 1988; Gerke et al. 1994, 2000). Carboxylate concentrations of 47–55 µmol g^{-1} rhizosphere soil have been reported for cluster roots (Dinkelaker et al. 1989; Gerke et al. 1994).

In this context, the high density of lateral rootlets (and root hairs) contributes to accumulation of root exudates in the rhizosphere by providing an increased
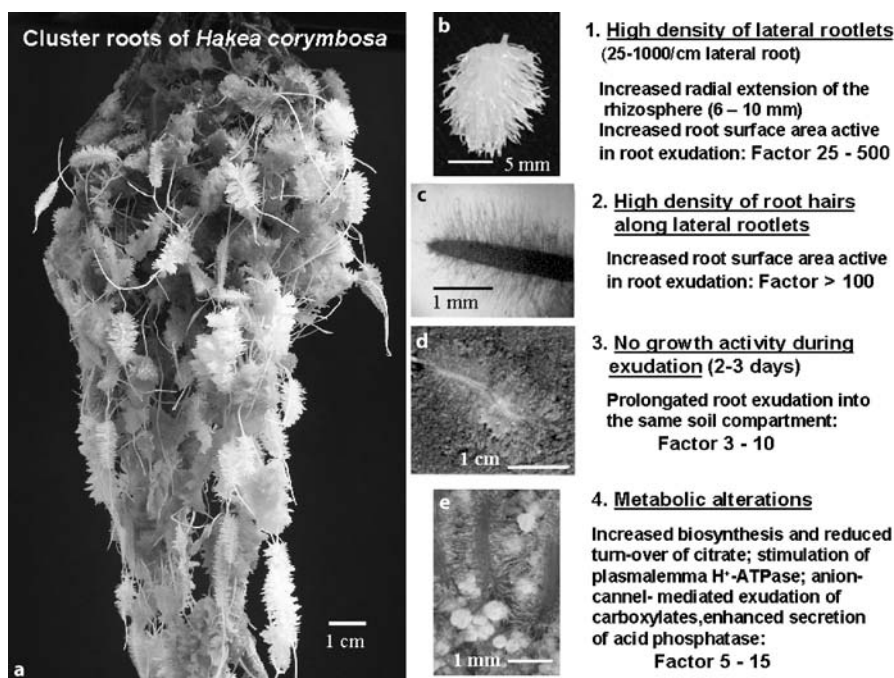
Fig. 5.2a–e Contribution of morphological and physiological characteristics to root exudation in cluster roots. **a** Cluster roots of *Hakea corymbosa*. **b** Dense spacing of lateral rootlets in individual root clusters of Hakea corymbosa. **c** Intense proliferation of root hairs along lateral rootlets of cluster roots of Lupinus albus. **d** Mature root cluster without growth activity of *Hakea undulata* in soil culture. **e** Precipitation of Ca-citrate after citrate release from root clusters of Lupinus albus grown on a calcareous Loess subsoil

root surface area with secretory activity. Assuming an average length of 5 mm per rootlet, and a density of 50–1,000 rootlets per centimetre of cluster root axis, carboxylate exudation may increase by a factor of 25–500 compared with normal lateral roots (Fig. 5.2). Even higher values can be expected due to the high density of root hairs potentially involved in root exudation, which increase the surface area more than 100-fold (Vance et al. 2003). Moreover, in contrast to normal lateral roots, mature cluster roots with the highest secretory potential exhibit no growth activity (Watt and Evans 1999) and root exudates can therefore be released over an extended period of time (2–3 days) into the same volume of rhizosphere soil. The prolonged secretory activity of cluster roots into the same soil compartment may further increase the accumulation of root exudates in the rhizosphere by a factor of approximately 3 to 10 compared with normal lateral roots (Fig. 5.2).
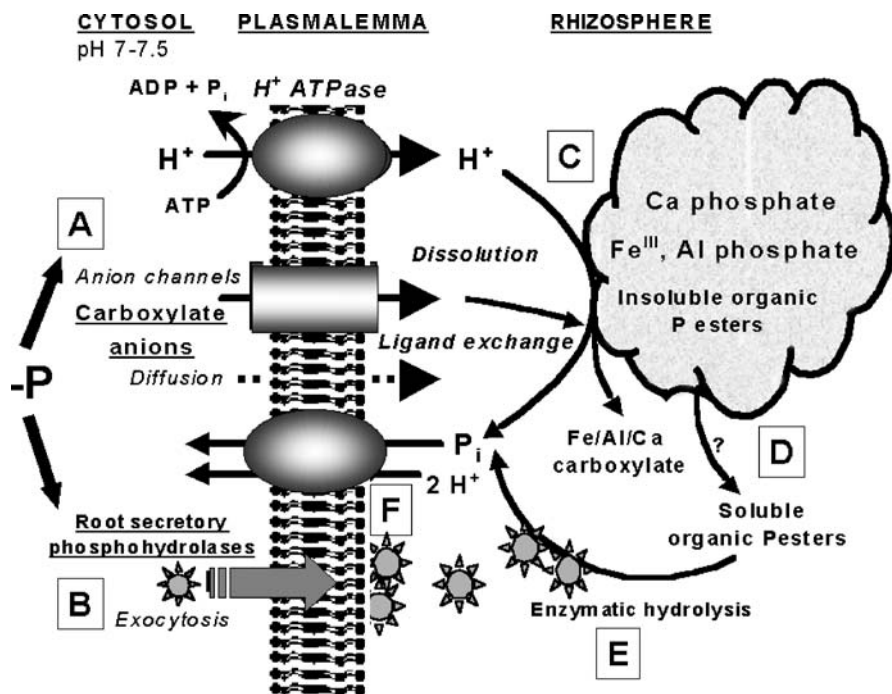
Fig. 5.3 Model for the role of root exudates in chemical P mobilisation in the rhizosphere. *A* Phosphorus deficiency-induced secretion of carboxylates by anion channels with concomitant H$^+$ extrusion (*A*) and of root-secretory acid phosphatase (*B*). *C* Dissolution of acid soluble Ca-P by root-induced H$^+$ release and displacement of phosphate anions from anion sorption sites (Fe/Al/Ca) at the soil matrix by carboxylates. *D* Displacement of organic P esters from anion sorption sites at the soil matrix by carboxylates. *E* Enzymatic hydrolysis of organic P esters in the soil solution by the activity of phosphatases released by roots and microorganisms. *F* Root uptake of mobilised inorganic P via H$^+$ cotransport by P transporters

Additionally, various modifications of cluster root metabolism have been identified recently in relation to increased accumulation and release of root exudates involved in nutrient mobilisation. These changes include increased biosynthesis, reduced turnover and release of citrate into the rhizosphere, activation of ion channels for carboxylate exudation (Kania et al. 2001; Neumann et al. 1999; Zhang et al. 2004), increased activity of plasma membrane H$^+$-ATPase for proton extrusion (Kania et al. 2001; Yan et al. 2002), increased production and exudation of phenolics (Dinkelaker et al. 1995; Neumann et al. 2000; Weisskopf et al. 2005), and increased expression and release of root-secretory acid phosphatases (Gilbert et al. 1999; Neumann et al. 1999; Wasaki et al. 1999).

In cluster roots of *Lupinus albus*, these metabolic alterations may increase root exudation of carboxylates by a factor of approximately 5 to 15 compared with normal lateral roots (Fig. 5.2). The intense exudation of metal-chelating

carboxylates in cluster-rooted plant species, which are usually not colonised by mycorrhizal fungi, comprises 5–25 % of the assimilated carbon (Dinkelaker et al. 1989; Pate et al. 2001). This seems to be an extraordinarily high loss of carbon, but resembles the carbon investments in various mycotrophic plant species for maintaining mycorrhizal associations as an alternative strategy for nutrient acquisition (Lambers et al. 1998). Moreover, non-photosynthetic, anaplerotic CO_2 fixation in cluster roots via phosphoenolpyruvate carboxylase can contribute up to 30% of the exuded carbon (Johnson et al. 1996), and respiratory carbon losses are reduced by down-regulation of citrate turnover (Kania et al. 2003; Kihara et al. 2003; Johnson et al. 1994).

Rapid pH changes resulting from activation of plasma membrane H^+-ATPase (Kania et al. 2001; Yan et al. 2002) and increased release of phenolics during the period of highest secretory activity (Dinkelaker et al. 1995; Neumann et al. 2000) may counteract rapid microbial degradation of P-mobilising carboxylates, which normally have a half-life of 1–5 h in rhizosphere soil (Jones 1998; Jones et al. 2003). Changes in secretory activity during cluster root development lead to distinct alterations in rhizosphere microbial community structure (Marschner et al. 2002; Wasaki et al. 2005)

In summary, the available data suggest that the function of cluster roots for chemical P mobilisation in soils is determined by alterations in root morphology and root metabolism. Skene (2000) postulated that, along with mycorrhizae and N_2-fixing nodules, cluster roots may be regarded as a third major adaptation for nutrient acquisition in terrestrial vascular sporophytes.

Carboxylate exudation as a mechanism for P mobilisation has also been discussed for a range of other plant species, such as rape, chickpea, pigeon pea, buckwheat and others (Ae et al. 1993; Hoffland et al. 1989; Neumann and Römheld 1999). However, in many cases, it is still a matter of debate whether the measured rates of carboxylate exudation from single roots are sufficient to mediate significant P solubilisation in soils (Jones et al. 2003) or whether it can even be regarded as an adaptation to P limitation (Otani and Ae 2001; Wouterlood et al. 2004).

Pronounced accumulation of LMW carboxylate metal complexes is also found in coniferous forest soils of the northern hemisphere and has been implicated not only in P mobilisation but also in podzolisation and weathering of mineral soils and rocks (Jongmans et al. 1997; Lundstrom et al. 2000; Pate et al. 2001; van Breemen et al. 2000). These carboxylates may be mainly of fungal origin because intense carboxylate exudation has been demonstrated for saprophytic, pathogenic, and also some ectomycorrhizal fungi (Casarin et al. 2003; Dutton and Evans 1996; Gadd 1999).

5.3.2
Root Secretory Phosphohydrolases

Another widespread response of higher plants to P limitation is the enhanced expression and release of root-secretory phosphohydrolases – specific isoforms of acid phosphatase with a pH optimum in the slightly acidic range (Gilbert et al. 1999; Wasaki et al. 1999). Large variations in phosphatase release exist between different plant species and cultivars (Li et al. 1997; Römer et al. 1995). Additionally, phytase, nuclease, pyrophosphatase, apyrase and alkaline phosphatase activities have been detected in the rhizosphere (Neumann and Römheld 2000). These extracellular phosphohydrolases can originate from plant roots and soil microorganisms. Wasaki et al. (2005) demonstrated that acid phosphatase activity in the rhizosphere of cluster roots in *Lupinus albus* was predominantly of plant origin.

Phosphohydrolases in soils mediate the mineralisation of various organic soil P forms, which can comprise 30–80% of total soil P, thereby providing a significant proportion of plant-available P in natural ecosystems (Richardson et al. 2005) (see also Chapter 3 by Bünemann and Condron, this volume). Given that there is no evidence for direct uptake of organic P by plant roots in significant amounts, the increased release of root-secretory phosphohydrolases may be a response to P limitation (Fig. 5.3). In nutrient solution or sand culture, plants can utilise organic P to a similar extent as inorganic P. However, in many cases organic P utilisation is limited in soil-grown plants (Adams and Pate 1992; Hübel and Beck 1993). This may be attributed to the low mobility of organic P forms in many soils, limited by adsorption and precipitation processes similar to those for inorganic P.

Solubility of phytate (myo-inositol hexakisphosphate), a major storage form of P in plants, is particularly low in soils because up to six negatively charged phosphate residues can interact with cationic sorption sites in the soil matrix. Moreover, root-secretory acid phosphatases exhibit only limited hydrolytic activity towards phytates, and the release of specific phytases seems to be more abundant in microorganisms than in plants (Richardson et al. 2005). The limited availability of phytates for enzymatic hydrolysis may explain why phytates are the dominant organic P fraction in many soils, whereas sugar, lipid or nucleotide phosphates exhibit higher solubility and thus higher rates of mineralisation by enzymes released from plants and microorganisms (Richardson et al. 2005). Root exudation of carboxylates, such as citrate and oxalate, in sufficient quantities appears to enhance the solubility not only of inorganic P but also of organic soil P forms (Fig. 5.2), which would subsequently be available for hydrolysis by phosphohydrolases in the rhizosphere (Beißner 1997; Hens et al. 2003; Neumann and Römheld 2000; Otani and Ae 1999).

Once released into the rhizosphere, secretory phosphohydrolases may be subject to adsorption and inactivation on clay minerals and organo-mineral associations (Rao et al. 1996), and a substantial proportion of enzyme activity

remains immobilised at the root cell wall or in the mucilage layer (Dinkelaker et al. 1997). Similar to organic N (Janzen 1990, Jones et al. 2005), organic P may be passively lost from plant roots. Therefore, root-secretory phosphohydrolases may have an additional role in retrieval of organic P at the root surface (Lefebvre et al. 1990).

5.3.3
Mobilisation of Iron and Micronutrients by Phytosiderophores

Phytosiderophores (PS) represent a group of LMW metal chelators released from roots of graminaceous plant species in response to iron (Fe) and zinc (Zn) limitation (Tagaki 1976; Zhang et al. 1989) [see also Chapters 4 (Rengel) and 6 (Marschner), this volume]. Low solubility of Fe and other micronutrients (Zn, Mn and Cu) is widespread, particularly in neutral and alkaline soils. Phytosiderophores are non-proteinogenic, tricarboxylic amino acids (mugineic acids) with a high capacity to form stable chelates with Fe^{3+} even at soil pH >7. Phytosidero-
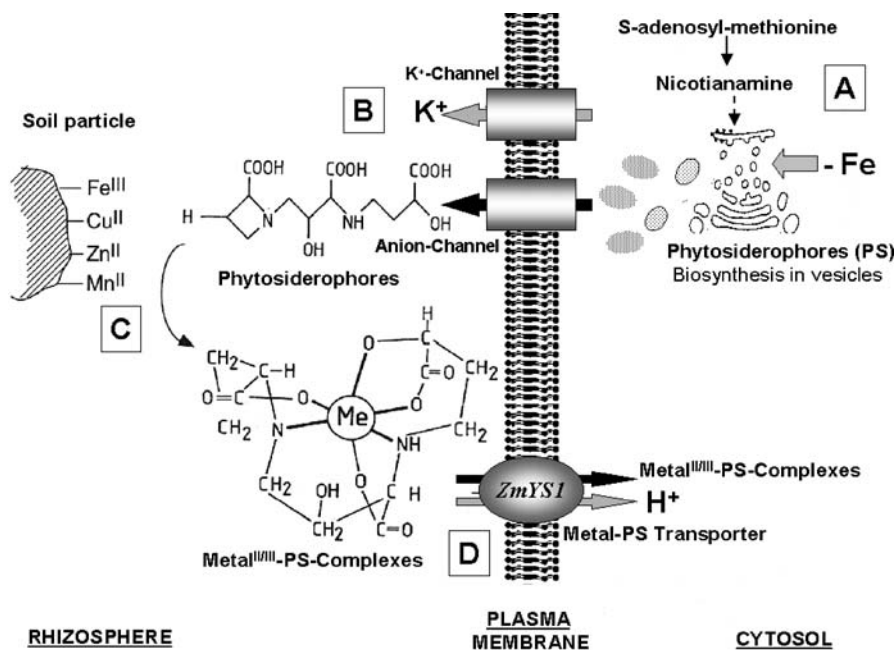
Fig. 5.4 Model for the role of phytosiderophores (PS) in chemical mobilisation of Fe and trace metals in the rhizosphere of graminaceous plants. *A* Iron deficiency-induced biosynthesis of PS from adenosylmethionine in vesicles of the root tissue. *B* Secretion of PS via anion channels with co-transport of K^+. *C* Mobilisation of Fe and trace metals in the rhizosphere by complexation with PS. *D* Transport of metal-PS complexes to the root surface and subsequent uptake by a metal-PS transporter with H^+ co-transport

phores can also mediate the mobilisation of significant amounts of Zn, Mn, Cu (Treeby et al. 1989) and even Cd and Ni (Awad and Römheld 2000; Shenker et al. 2000) in calcareous soils (Fig. 5.4). Tolerance of graminaceous plant species to Fe and Zn deficiency was found to be roughly related to the amount of PS released in response to Fe and Zn starvation (Hopkins et al. 1998; Marschner 1998).

High release rates of PS are frequently found in cereals adapted to the calcareous soils of the "fertile crescent" in the Middle East, such as barley, rye, bread wheat, oats and their wild ancestors. In contrast, rice, maize, sorghum or millet, as plant species originating from the humid tropics with an abundance of acid soils not limited in Fe availability, are usually much less efficient in PS release and more susceptible to Fe deficiency chlorosis. However, considerable genotypic variation in Fe and Zn tolerance can exist within cultivars of single plant species (Erenoglu et al. 1996; Kawai et al. 1988), suggesting that PS exudation is not the only mechanism determining Fe and Zn efficiency (Rengel and Römheld 2000).

Secretion of PS appears to be regulated by the intracellular Fe level (Walter et al. 1995a). Biosynthesis of PS in root tissue increases before appearance of Fe chlorosis as a visible symptom of Fe limitation (Tagaki 1984). Phytosiderophores are trans-amination and hydroxylation products of nicotianamine (NA), which is derived from S-adenosyl methionine (Ma and Nomoto 1996; Ma et al. 1995) and has ubiquitous functions as an intracellular metal chelator in higher plants (Pich et al. 1994). In barley, PS biosynthesis seems to occur in large storage vesicles of the endoplasmic reticulum, which appear in a diurnal rhythm in epidermal cells of apical root zones prior to a pulse of intense PS release after onset of the light period (Negishi et al. 2002; Nishizawa and Mori, 1987). However, the exudation process of PS anions is probably mediated by an anion channel (Fig. 5.4), associated with co-transport of K^+ (Neumann and Römheld 2000; Sakaguchi et al. 1999). Similar to the localised exudation of carboxylates in cluster-rooted plant species, the temporal and spatial concentration of intense PS exudation in apical root zones where microbial density is low, may be a strategy to counteract microbial degradation and unspecific adsorption of PS in the rhizosphere, and may lead to millimolar concentrations of PS in the rhizosphere soil solution (Römheld 1991; Tagaki et al. 1984). Accordingly, the slow continuous release of PS observed in sorghum and maize was able to overcome Fe deficiency in axenic culture, but not after inoculation of the culture medium with rhizosphere microorganisms due to the consequent rapid biodegradation of PS (von Wirén et al. 1993, 1995). For a more detailed discussion of the interactions between phytosiderophores and microbial siderophores, the reader is referred to Chapter 6 (Marschner, this volume).

Uptake of Fe mobilised by PS occurs as the intact FeIII-PS complex (Fig. 5.4) associated with H^+ co-transport (Schaaf et al. 2004) and is mediated by a specific transport system (*ZmYS1*) (Curie et al. 2001). Root uptake also occurs to a lesser extent for PS complexes with Cu, Zn and Co (Fig. 5.4), but may still be sufficient to match the comparatively lower demand of plants for these micronutrients (Gries et al. 1998). It is still unclear whether PS exudation under micronutrient

deficiency is a specific response. In Zn-deficient bread wheat, intense PS exudation is attributed to an impaired Fe metabolism in response to Zn limitation (Rengel and Graham 1996; Walter et al. 1994). Accordingly, up-regulation of ZmYS1 in maize was induced by Fe deficiency, but not by limiting the supply of other micronutrients such as Zn, Mn or Cu (Roberts et al. 2004; Schaaf et al. 2004). In contrast, Gries et al. (1998) suggested PS release in *Hordelymus europaeus* L. as a specific response to Cu deficiency.

The controlled uptake of organic metal complexes appears to be a unique feature of graminaceous plant species because uptake of mineral nutrients in higher plants usually occurs in the free ionic form. In contrast, chelation of metals frequently acts as an exclusion mechanism to avoid toxicity (see Sect. 5.4.1). In non-graminaceous plant species, organic metal complexes are dissociated by root-induced modifications of pH and redox potential prior to uptake of the free metal ion (Neumann and Römheld 2002). Root exudates such as phenolics and malate and citrate (Godo and Reisenauer 1980; Olsen et al. 1981; Römheld 1987), as well as fulvic acids and humic acids derived from decomposed organic matter (Pandeya et al. 1998; Pinton et al. 1998), may be involved in contact reduction and transport of Fe and Mn to the root surface.

5.4
Protective Functions of Root Exudates Against Abiotic Stress

Maintenance or even stimulation of root growth is of critical importance not only for water uptake and responses to nutrient limitation (particularly N, P and Fe) (Neumann and Römheld 2002), but also for exploitation of nutrient-rich patches in soils (Drew 1975; Hodge et al. 1999). Impairment of root growth can be induced by various stress factors, such as aluminium (Al) toxicity in acid soils, bicarbonate toxicity in calcareous soils, salinity, drought, hypoxia, toxic microbial metabolites and pathogen attack. In many cases, root exudates appear to be involved in stress responses to alleviate inhibitory effects on root growth and thereby on plant nutrient acquisition.

5.4.1
Aluminium Toxicity

At soil pH levels below 5.0, solubilisation of mononuclear Al species increases dramatically (Fig. 5.5) and can limit root growth by cytotoxic effects at the zone of transition between cell division and cell elongation in root apices (Kollmeier et al. 2000; Rengel 1996). There is increasing evidence that Al complexation by organic metal chelators released in these apical root zones
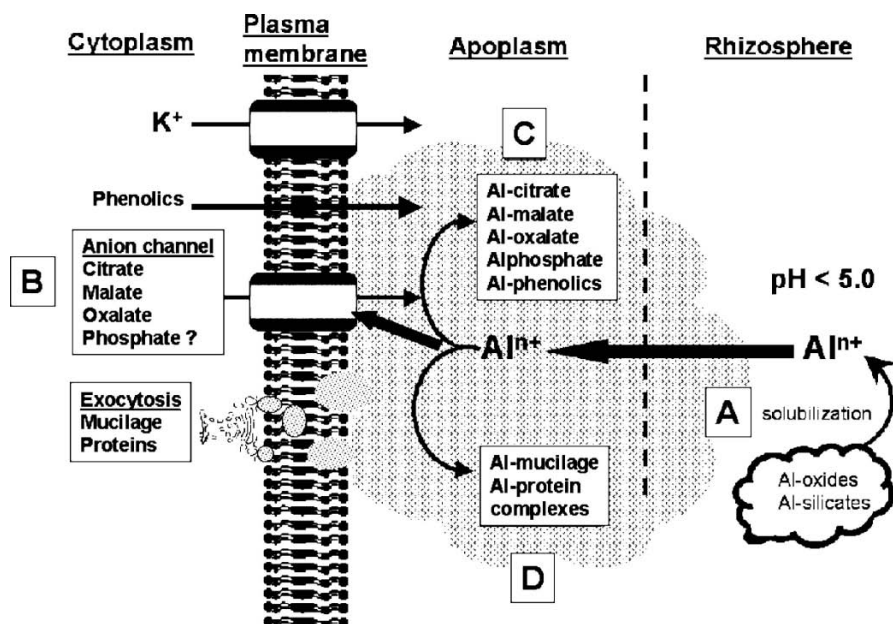
Fig. 5.5 Model for root-induced aluminium (Al) detoxification by secretion of organic Al chela-tors. *A* Solubilisation of toxic Al^{n+} species in acid mineral soils at pH <5.0. *B* Aluminium-induced activation of anion channels in the Al-sensitive apical root zones. Release of organic Al-chelators. Detoxification of Al^{n+} by complexation with low molecular weight (LMW) chelators (*C*) with pro-teins and mucilage (*D*)

(Fig. 5.5) represents a widespread mechanism for Al detoxification in higher plants, but considerable variation exists within plant species and cultivars. Stable Al complexes are formed with citrate, oxalate, tartrate and, to a lesser extent, also with malate and various phenolics (Ryan et al. 2001). Accordingly, Al-induced root exudation of citrate, malate and oxalate has been reported for various Al-tolerant plant species and cultivars such as wheat, maize, rye, com-mon bean, potato, rape, buckwheat, taro and others (Neumann and Römheld 2000).

Formation of Al-carboxylate complexes prevents Al uptake by plant roots and the detrimental effects induced by unspecific interactions of free cationic Al forms with binding sites at the root apoplast and the plasma membrane (Ko-chian 1995; Rengel 1996). Trapping of Al by carboxylate exudation probably oc-curs in the apoplastic space (Fig. 5.5) since Al concentrations and binding sites for carboxylates in the rhizosphere soil would easily exceed the exudation ca-pacity of plant roots. The level of Al tolerance in plant species and cultivars ap-pears to be related to the amount of exuded carboxylates (Pellet et al. 1995; Ryan et al. 1995a), but also to the ability to maintain the release of carboxylates over extended time periods (Zheng et al. 1998). In Al-resistant wheat cultivars, chan-

nel-mediated malate exudation occurs almost instantaneously after exposure to Al (Zhang et al. 2001; see Sect. 5.2.2). In other plant species (e.g. soybean, rye and potato), release of citrate in response to Al treatment is preceded by a lag phase of several hours associated with modifications of organic acid metabolism (Li et al. 2000; Ma 2000). Charge balance is maintained by a concomitant release of K^+ through a K^+ channel (Ryan et al. 1997).

In many Al-resistant plant species, carboxylate release rates in response to Al are comparable to the intense pulses of citrate exudation in cluster roots of P-deficient *Lupinus albus* or the release of PS in Fe-deficient barley, but the response to Al toxicity occurs much more rapidly (Neumann and Römheld 2000; Ryan et al. 2001). The highly localised exudation pattern – restricted to the Al-sensitive zone of the root apex (Kollmeier et al. 2000) – prevents excessive losses of carbon. Aluminium tolerance in different plant species and cultivars is, however, not always correlated with Al-induced carboxylate exudation (Pineros et al. 2005), suggesting the presence of additional mechanisms involved in the expression of Al resistance. Apart from the well-documented intracellular detoxification of Al (Kochian 1995; Rengel 1996), increased rhizosphere pH and constitutive or Al-induced secretion of other Al-binding compounds, such as phosphate, phenolics, polypeptides, hydroxamates and root mucilage (Fig. 5.5) have also been implicated in alleviation of Al stress (Basu et al. 1999; Heim et al. 1999; Horst et al. 1982; Poschenrieder et al. 2005).

5.4.2
Drought Stress

About 50% of the Earth's land surface is located in arid or semi-arid climate zones, and periods of drought are also common in temperate climates. Moderate water limitation can lead to a stimulation of root growth, probably reflecting a stress response to lower availability of nutrients with declining water potential. In contrast, more severe drought stress inhibits root growth due to the higher mechanical impedance of the soil (Russel 1977). Additional factors include drought-induced nutrient deficiencies and limited carbon supply to the roots as a consequence of reduced photosynthesis due to ABA-mediated closure of stomata to minimise transpiration. In dry soils, root mucilage secretion can be stimulated in response to the increased soil-mechanical impedance, with protective functions for the root meristem during penetration of drought-hardened soils (Vivanco et al. 2002). Mucilage can improve root-soil contact by inclusion and aggregation of soil particles (McCully 1999), thereby facilitating nutrient uptake in dry soils (Nambiar 1976).

Possible functions of phosphatidylcholine surfactants in root mucilages for P mobilisation, inhibition of nitrification and modification of soil water retention have been discussed by Read et al. (2003). A direct function of mucilage as a lubricant seems unlikely because no water retention capacity can be demonstrated at water potentials below zero (McCully 1999). However, mucilage

translocated during root elongation to more basal parts of the root can form so-called rhizosheaths by inclusion of adhering soil particles, covering the root surface (Huang et al. 1993; McCully 1999). Shrinking of mucilage with declining water potentials leads to a tighter association of soil particles within the rhizosheaths and can thereby reduce water losses from the root by approximately 30% (Huang et al. 1993).

5.4.3
Bicarbonate Stress

High bicarbonate concentrations are a well-documented stress factor in calcareous soils (Lee 1998), limiting the availability of nutrients (particularly Fe, Zn, Mn and P) by increasing the soil buffering capacity and inhibiting root growth, due to direct rhizotoxic effects (Lee 1998). Detrimental effects on root growth have been related to excessive intracellular carboxylate accumulation, particularly in the apical root zones, reaching malate and citrate concentrations of 30–70 μmol g^{-1} root fresh weight. In contrast, root growth of bicarbonate-tolerant plant species is not affected, and in fact can even be stimulated, in response to bicarbonate treatments (Hajiboland 2000; Hajiboland et al. 2003; Lee 1998; Yang et al. 1994).

Bicarbonate-tolerant genotypes of rice exhibit lower intracellular concentrations and higher root exudation of carboxylates, associated with higher shoot concentrations of Zn and Fe, which are major limiting nutrients in calcareous soils (Hajiboland 2000; Yang et al. 1993, 1994). These findings suggest root exudation of carboxylates as a mechanism of detoxification, maintaining root growth under high external concentrations of bicarbonate. Moreover, bicarbonate-induced carboxylate exudation may also contribute to mobilisation of sparingly soluble nutrients, such as P, Fe, Zn and Mn, in calcareous soils. Accordingly, Ström et al. (1994) reported higher exudation rates of carboxylates in various calcicole plant species in comparison with calcifuge plants as a possible mechanism for improved acquisition of nutrients in calcareous soils.

5.5
Root Exudates and Plant-Microbe Interactions

Since populations of free-living soil microorganisms are strongly carbon limited (Wardle 1992), rhizosphere carbon input from plant roots via rhizodeposition is the driving force for the well-documented "rhizosphere effect", which stimulates microbial growth and activity in close proximity to plant roots (Hiltner 1904; Semenov et al. 1999). This holds true for fungal and bacterial populations, but also for subsequent microfaunal grazers, such as protozoa and free-living nematodes (Bonkowski 2004). Increased microbial activity in the rhizosphere

can promote competition between microbes and plants for limiting mineral nutrients such as N, P, Fe and Mn (Crowley 2000; Rengel et al. 1996; Stevenson and Cole 1999). On the other hand, microorganisms can also increase availability of nutrients to plants. This is particularly evident in beneficial symbiotic interactions, such as mycorrhizal associations (critically important for acquisition of P, N and Zn in more than 90% of terrestrial plants), and in symbiotic and associative interactions with N_2-fixing bacteria (Vance 2002), but also in processes of N mineralisation, such as bacterial nitrification (Sylvia et al. 1999) and liberation of N sequestered in rhizosphere microorganisms by microfaunal grazers (Bonkowski 2004). These aspects are discussed in more detail in Chapter 6 (Marschner, this volume).

Apart from serving as a source of carbon and nitrogen for rhizosphere microorganisms, root exudates can also have important functions as signalling compounds in plant-microbial cross-talk. Secondary plant metabolites such as phenolics, terpenoids or alkaloids are frequently involved in such signalling. Probably the best investigated example of this phenomenon is the release of phenolic compounds from the roots of leguminous plants as signals for the establishment of the legume-Rhizobium symbiosis, which can provide an input of 10–350 kg N ha^{-1} $season^{-1}$ by fixation atmospheric N_2 (Vance 2002). Simple phenolics, such as cinnamic and coumaric acids, can induce a strong chemotactic response in attracting Rhizobia to the root surface. Certain flavonoids (flavones, flavanones, isoflavones) derived from these simple phenolics, are responsible for the activation of a transcription factor of the rhizobial *nodD* gene and have optimum concentrations of 10^{-4}–10^{-7} M (nod gene inducers). The activated transcription factor induces the biosynthesis of specific lipo-chito-oligosacharides (LCOs), which act as bacterial signals for induction of changes in the root morphology of the host plant involved in the infection process, such as root hair curling and cell division of the nodule meristem in the root cortex (Vance 2002). At lower concentrations (10^{-9} M) at some distance from the root surface, some of these flavonoids can also induce chemotaxis (Squartini 2000). An additional function of flavonoids released from host roots is the induction of *Rhizobia* resistance to plant defence mechanisms, e.g. release of phytoalexins (Werner 2000). Release of nod-gene inducers is stimulated by the presence of *Rhizobia*, and the availability of these flavonoids in the rhizosphere can limit nodulation (Werner 2000). Although the molecular events involved in the infection process of the rhizobial micro-symbiont are well-characterised, surprisingly little is known concerning the release mechanisms of signals originating from roots of the host plant, which obviously require highly coordinated regulation in space and time (see Sect. 5.2.2).

Root exudation also appears to be an important determinant of root colonisation by associative diazotrophic (N_2) fixing bacteria such as *Azospirillum* sp. or *Enterobacter* sp., which are abundant in the rhizosphere, at the rhizoplane, and even in the apoplast of the root cortex, particularly in graminaceous C4 plant species (Boddey and Döbereiner 1988). Chemotaxis of *Azospirillum* by mucilage polysaccharides has been reported by Mandimba et al. (1986). *Azospirillum* strains preferentially use malate, which is a major carboxylate in root

exudates (Neumann and Römheld 1999), as a carbon source (Alexander and Zuberer 1989). The role of N_2 fixation in N cycling is discussed in Chapter 2 (McNeill and Uncovich, this volume).

Root exudates have also been implicated in the establishment of ecto- and endo-mycorrhizal associations. As in legume-*Rhizobium* symbiosis, flavonoid and strigolactones have been discussed as possible signalling compounds, but there are also contradictory reports; hence, the nature of root exudates and the related mechanisms remain unclear (Akiyama et al. 2005; Jones et al. 2004).

In addition to these examples of a role for root exudates in microbial interactions supporting plant nutrient acquisition, there are also indications for functions in interactions with pathogens, parasites and plant competitors: Seed, and root, exudates and their rhizosphere metabolites, can stimulate spore germination of fungal pathogens, seed germination of parasitic weeds, and can attract fungal and bacterial pathogens, parasitic nematodes and weeds (Fate et al. 1990; Katan 2002; Koltai et al. 2002). In many cases these are unspecific reactions in response to the presence of easily available carbon sources, such as volatile compounds (CO_2, acetaldehyde, ethanol, ethane etc.) in the rhizosphere (Katan 2002; Koltai et al. 2002), but there are also examples of host-specific interactions, e.g. alkyl-, and alkenyl-l-cysteine sulfoxides released from *Allium* roots are metabolised in the rhizosphere to volatile thiols and sulphides, which are able to activate dormant sclerotia of the *Allium*-pathogenic fungus *Sclerotium cepivorum* (Cooley-Smith and Cooke 1971). Oligosaccharides and lectins released from the roots of host plants are discussed as host-specific chemo-attractants for plant-pathogenic nematodes (Koltai et al. 2002), while a specific dihydroquinone released from the roots of *Sorghum bicolor* stimulates seed germination of *Striga*, a parasitic weed, which uses *Sorghum* as a host plant (Fate et al. 1990). On the other hand, as an example of an allelopathic interaction, dihydroquinone is readily oxidised in the rhizosphere to the more stable quinine and sorgoleone, which strongly inhibit growth of competing plants (Rasmussen et al. 1992).

Root exudates can also have protective functions against pathogens: avenacoside B is a glucosylated saponin present in the epidermal root cells of black oat (*Avena nuda*), from where it is released into the rhizosphere in significant amounts. Enzymatic hydrolysis of the glucose moiety converts avenacoside B to the fungitoxic saponin avenacin, which causes membrane disintegration in the infecting fungus. This has been discussed as a tolerance mechanism against infection by *Gaeumannomyces graminis* (Osbourn 1996). Shikonin naphtoquinones in roots and root exudates of *Lithospermum erythrorhizon* exhibit inhibitory activity against various fungal and bacterial soil pathogens, such as *Pseudomonas solanacearum*, *Phytium ultimum* and *Phytium aphanidermatum* (Flores et al. 1999).

Chitinase and β-1-3-glucanase, which mediate enzymatic hydrolysis of fungal cell walls, appear to be secreted into the rhizosphere by cluster roots of *Lupinus albus* (Neumann et al. 2000; Wasaki et al. 2005; Weiskopf et al. 2005). In addition to constitutive mechanisms of pathogen resistance, a wide range of compounds with antibiotic activity, so-called phytoalexins, are synthesised in

response to pathogen attack. Some of these compounds, such as the isoflavonoid phytoalexin glyceollin in soybean, are also released as root exudates (Werner 2000). Root border cells, liberated from the root cap in many plant species, are able to attract pathogenic nematodes and fungal zoospores, but also suppress fungal growth and sporulation by release of as yet unknown compounds. This is discussed as a potential mechanism to protect the root meristem against pathogen attack (Gunawardena et al. 2005; Hawes et al. 2000).

5.6
Knowledge-Gaps and Perspectives

Most of our knowledge of the effects of root exudation on nutrient cycling originates from model experiments with mini-rhizotrons (Fig. 5.6) or even hydroponic culture, whereas direct investigations under field conditions are rare, with conclusions frequently being based on correlation of field observations with results obtained from model experiments or even on model experiments only. There is an obvious lack of non-destructive methodological approaches that would allow the identification and quantification of root exudates with high spatial resolution in different root zones and their differentiation from microbial metabolites under field conditions. Micro-sampling techniques in combination with miniaturised analytical methods (e.g. use of microprobes for specific compounds, reporter bacteria, micro-suction cups, sorption media applied to the root surface, capillary electrophoresis, chromatography chip technologies, tracer techniques, image analysis and video-densitometry) can facilitate non-destructive measurements of rhizosphere processes. However, under field conditions, robust routine methods for processing large sample numbers are required to account for heterogeneity and variability in the field. A major limiting factor also arises from the sampling process itself: even rhizobox, or root-window approaches (Smit et al. 2000) employed for in situ sampling along soil-grown roots with minimal disturbance are not necessarily identical with natural growth conditions. Moreover, the majority of investigations have been carried out with crop plants, and studies at the ecosystem level considering wild plant species, genotypic differences and plant communities are only just emerging.

Despite the obvious importance of rhizodeposits for the availability of nutrients in soils, the lack of knowledge concerning the composition, pool sizes, fluxes, origin and binding forms of organic compounds in the rhizosphere of field-grown plants limits the integration of this factor into models of nutrient cycling in ecosystems.

It is also important to consider the possibility of synergistic or antagonistic effects of simultaneous chemical and biological processes in the rhizosphere. Examples of this might include the potential effects of root-induced pH changes, the release of phenolic compounds and chitinase counteracting micro-
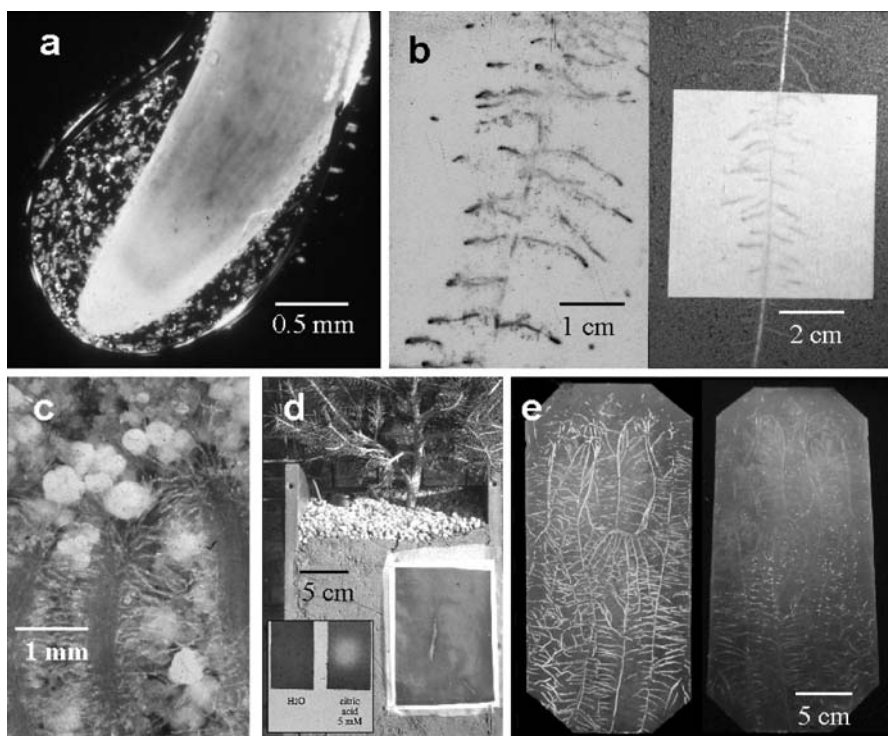
Fig. 5.6a–e Visualisation of root exudation. **a** Mucilage with root border cells released from a root tip of maize in hydroponic culture. **b** In situ activity staining of acid phosphatase along soil-grown maize roots by surface application of filter papers soaked with naphthyl phosphate/Fast red TR as artificial substrate. **c** Precipitation of Ca-citrate after citrate release from root clusters of *Lupinus albus* grown on a calcareous loess subsoil. **d** In situ detection of Al complexation in the rhizosphere of soil-grown Norway spruce by exchange chelation with a red Al-aluminon complex supplied in agar onto the root surface. **e** UV visualisation of blue-fluorescent phenolics in the rhizosphere of soil-grown *Phaseolus vulgaris* collection with nylon membranes applied to the root surface for 20 h

bial degradation of root exudates involved in nutrient mobilisation (Dinkelaker et al. 1995; Wasaki et al. 2005; Weisskopf et al. 2005), increased availability of organic P forms for root secretory phosphohydrolases via concomitant release of carboxylates (Neumann and Römheld 2000), or the effects of rhizosphere pH and redox potential on metal complexation with organic ligands. Despite the widespread occurrence of mycorrhizal associations in higher plants, the potential impact of mycorrhiza on the various processes involving root exudation have not been widely investigated.

Elucidation of the mechanisms regulating root exudation at the physiological and genetic level is a major challenge. A detailed understanding of the regulatory processes is a prerequisite for directed manipulation of the soil-root interface aimed at improving the efficiency of nutrient acquisition in plants, im-

proving resistance to adverse soil chemical conditions, or designing plants for phytoremediation and phytomining. Recent advances in this direction include improved Fe acquisition in rice via over-expression of the barley gene encoding nicotianamine-aminotransferase (NAAT) – a key enzyme in PS biosynthesis (Takahashi et al. 2001). However, similar approaches to increase root exudation of citrate in various plant species by over-expression of citrate synthase gave rise to contradictory results (Delhaize et al. 2001; De La Fuente et al. 1997; Lopez-Bucio et al. 2000). These findings suggest that up-regulation of metabolic pathways involved in biosynthesis of root exudates may not be sufficient to increase exudation in all cases.

Expression of the gene encoding the anion channel responsible for Al-induced root exudation of malate in Al-tolerant wheat (*ALMT1*), also conferred Al tolerance to Al-sensitive rice, barley and cell cultures of tobacco (Sasaki et al. 2004; Delhaize et al. 2004). Phosphorus acquisition from phytate by *Arabidopsis* and *Trifolium subterraneum* grown on agar medium was significantly increased by heterologous expression of a gene encoding a secretory phytase from *Aspergillus niger*. However, this effect was markedly reduced in soil, probably due to strong fixation of phytate in soils (Richardson et al. 2001, 2005). Apart from presenting promising approaches for the bioengineering of root exudation, these examples illustrate the obvious gap between basic research and rhizosphere management under field conditions.

A better understanding of the functions and the behaviour of root exudates in the rhizosphere may also allow more directed selection or breeding of plant genotypes adapted to adverse soil conditions (Ryan et al. 1995b), as well as approaches for improved rhizosphere management in crop rotations and inter-cropping systems (Khalil et al. 2000; Zuo et al. 2000, 2004).

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6 Plant-Microbe Interactions in the Rhizosphere and Nutrient Cycling

Petra Marschner

6.1
Introduction

Microbial communities carry out fundamental processes that contribute to nutrient cycling, plant growth and root health. Microorganisms play a key role in nutrient cycling because they (1) decompose organic material (plant residues and soil organic matter) and release inorganic nutrients that can then be taken up by plants; (2) affect nutrient availability by solubilisation, chelation, oxidation and reduction; (3) store nutrients in, and release nutrients from, the microbial biomass; and (4) affect plant growth by release of stimulating or inhibiting substances. Microorganisms in the rhizosphere – the soil surrounding the root – are of particular importance for plant nutrient uptake and growth because of their vicinity to the roots. Via their effect on plants, rhizosphere microorganisms influence the composition and amount of residues returned to the soil.

This chapter presents an overview of the colonisation of the rhizosphere by microorganisms and the role of rhizosphere microorganisms in N, P, Fe and Mn cycling. Mycorrhiza are included because of their importance for nutrient uptake by plants, but are considered quite distinct from rhizosphere microorganisms because they form a symbiosis with plants. The chapter ends with a section on plant growth-promoting microorganisms, which enhance plant growth through a wide range of mechanisms, and a brief introduction to the rhizosphere priming effect.

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6.2
Colonisation of the Rhizosphere by Microorganisms

Rhizosphere communities are influenced by soil and plant factors. Soils have distinct microbial communities (species composition and relative abundance of different species; Carelli et al. 2000; Gelsomino et al. 1999) that result from different physical and chemical soil characteristics (e.g. soil texture, nutrient and organic matter content, and pH) and environmental factors such as climate and vegetation. Rhizosphere microbial communities are a subset of the soil microbial community; therefore, they too are influenced by the chemical and physical properties of the soil. However, the structure of rhizosphere communities differs from that in the bulk soil (Berg et al. 2002; Foster 1986; Gomes et al. 2001; Marilley and Aragno 1999), which is a clear indication that plants strongly influence the microbial populations on their roots.

The rhizosphere communities of different plant species growing in the same soil are often distinct (Ibekwe and Kennedy 1998; Marschner et al. 2001b). Plants may even have similar microbial community structures when grown in different soils (Grayston et al. 1998; Miethling et al. 2000). However, it has also been shown that different plant species growing in the same soil may have a similar rhizosphere microbial community structure, indicating that, in some cases, the influence of the soil may be greater than that of the plant (Buyer et al. 1999; Latour et al. 1999). It is unclear which factors are responsible for the relative importance of plant and soil factors in shaping of the microbial community structure in the rhizosphere. Plant age appears to be important, with species effects becoming more pronounced during plant development (Gomes et al. 2003; Marschner et al. 2001a). For example, lucerne cultivar-specific effects on *Sinorhizobium meliloti* populations became more important than soil effects as the plants matured (Carelli et al. 2000).

Among rhizosphere microbial ecologists, there is currently a consensus that community structure in the rhizosphere is strongly influenced by root exudate amount and composition because microbial species differ in their ability to metabolise, and compete for, different carbon sources. Between 1% and 25% of the net photosynthesis can be deposited in the rhizosphere as soluble compounds or in form of sloughed-off cells (Merbach et al. 1999) (see also Chapter 5 by Neumann, this volume); 40–80% of this carbon is respired by microorganisms, whereas the remaining 20–60% is incorporated into the microbial biomass, adsorbed to soil particles or converted into soil organic matter (Haller and Stolp 1985; Merbach et al. 1999).

The microbial biomass can be regarded as a transient nutrient pool with turnover rates ranging from hours to weeks (Butler et al. 2004). Upon cell death, nutrients are released and can be taken up by plant roots or other microorganisms. The extent to which nutrients will become available to plants will be determined largely by the turnover and growth rate of the microbial biomass in the rhizosphere. Another important factor is the nutrient demand of the microbial

biomass. Generally, microorganisms have lower C/N and C/P ratio than plants (C/N in microbial biomass ≈10, in plants >20; C/P microbial biomass ≈30, in plants 300; Stevenson and Cole 1999). If C is readily available, the demand of the microbial biomass for N, P and other nutrients will determine whether nutrients are released (when supply exceeds demand) or immobilised in the microbial biomass (when supply equals, or is lower than, demand).

A wide range of factors have been shown to affect root exudation, including plant genotype (Grayston et al. 1998; Rengel 1997; Rovira 1959), plant age (Martin 1971; Van Veen et al. 1991), nutritional status (Fan et al. 2001; Hoffland 1992; Liljeroth et al. 1990) and colonisation by mycorrhizal fungi (Marschner et al. 1997; Po and Cumming 1997) (see also Chapter 5 by Neumann, this volume). A large proportion of the carbon is in the form of water-soluble substances such as sugars, organic acid anions and amino acids, which are rapidly degraded by microorganisms in the rhizosphere; the half-life of organic acid anions and amino acids in soil is only a few hours (Jones and Darrah 1994; Jones and Hodge 1999). However, organic acid anions, such as citrate, may be strongly adsorbed onto soil components, which reduces their availability to soil microorganisms and hence their mineralisation (Jones and Edwards 1998). Besides serving as a carbon source for microorganisms, root exudates also play an important role in nutrient release via chelation and desorption of poorly soluble nutrients such as P and Fe (see also Chapter 5 by Neumann, this volume).

The microbial biomass may comprise up to 36% of root dry weight (Whipps and Lynch 1983) and usually comprises species with high growth rates and relatively high nutrient requirements, such as pseudomonads (Marilley and Aragno 1999). However, the view of the rhizosphere as a habitat with large amounts of readily available C sources has been challenged (Whipps and Lynch 1983). As an increasing number of rhizosphere microbial species is identified, it becomes clear that some of them do not conform to the traditional view of fast-growing rhizosphere microorganisms, but rather have a wide range of growth strategies (Gomes et al. 2001; Mansfeld-Giese et al. 2002; Smalla et al. 2001).

Certain compounds in root exudates can have a selective influence on rhizosphere microorganisms by repelling some species and increasing the competitive ability of others (Geurts and Franssen 1996). A well-known example of such signalling substances are the flavonoids released by legumes, which attract rhizobia (Sheng and Citovsky 1996; Zhu et al. 1997).

As the root tip grows through the soil, microorganisms in its path will be the first colonisers. Root exudates are released primarily in the zone of elongation behind the root tips (Hoffland et al. 1989; Marschner et al. 1997; Römheld 1991) (see Chapter 5 by Neumann, this volume). The abundance of root exudates attracts soil microorganisms; however, during rapid root growth, this zone is colonised only sparsely by soil microorganisms because the initial cell density is low. Root exudates are used for microbial growth and metabolism, leading to a rapid increase in microbial density in the root hair zone. Along older root parts, the primary substrates for microbial growth include cellulose and other recalcitrant cell wall materials from sloughed-off root cortex tissues.

Consequently, microbial growth and density are lower in older root parts than in the zone of elongation. The differences in type and quantity of carbon available in different root zones not only influence microbial growth, but also select for distinct rhizosphere community structures (Marschner et al. 2001b; Yang and Crowley 2000).

6.3
Nitrogen Cycling

6.3.1
Nitrogen Mineralisation

Soil microorganisms play a key role in N mineralisation (Table 6.1, see also Chapter 2 by McNeill and Uncovich, this volume). A wide range of microorganisms is capable of decomposing proteins into amino acids and converting amino acids into NH_4^+ (ammonification). Nitrification, which results in the formation of NO_3^-, is carried out by a few specialists, predominantly *Nitrosomas* and *Nitrobacter* sp. (Sylvia et al. 1999). Plants can take up NH_4^+ and NO_3^-, but nitrification occurs rapidly in most soils; therefore, NO_3^- is the main N source of plants (Marschner 1995). Nitrification can subsequently lead to N loss via leaching and denitrification, with the latter being carried out predominantly by anaerobic bacteria (Sylvia et al. 1999).

The microbial biomass can compete with plants for N (Stevenson and Cole 1999). At high C/N ratios, which are often found in the rhizosphere because roots exude predominantly sugars and carboxylic acid anions, net N immobilisation occurs, whereas N mineralisation dominates at low C/N ratios (Parkin et al. 2002; Stevenson and Cole 1999). Grazing by protozoa can increase N mineralisation, N release from the microbial biomass and N uptake by plants (Kuikman and Van Veen 1989; Parkin et al. 2002). This may be particularly pronounced in the rhizosphere because protozoa are attracted by the high bacterial density and hence grazing is more intense.

N mineralisation is higher in the rhizosphere than in the bulk soil because of the release of easily decomposable substrates (Parkin et al. 2002). The presence of plants can also increase denitrification rates (Qian et al. 1997), probably due to respiration by roots and microbial biomass, which creates anaerobic microsites in the rhizosphere.

Ammonia-oxidising bacteria have been shown to form biofilms on the root surface of rice; the community structure of ammonia oxidisers varies among rice cultivars (Briones et al. 2003). These bacteria, being in intimate contact with roots, could play an important role in the N nutrition of plants. Nitrate produced in the biofilms could be taken up directly by roots.

Table 6.1 Examples of microbial genera affecting P, N, Fe and Mn availability, and plant growth-promoting rhizobacteria

P solubilisers	
Bradyrhizobium, Rhizobium	Antoun et al. 1998
Gordonia	Hoberg et al. 2005
Enterobacter	Kim et al. 1997b
Rahella	Kim et al. 1997a
Panthoea	Deubel et al. 2000
Pseudomonas	Deubel et al. 2000; Hoberg et al. 2005
Aspergillus, *Penicillium*, *Trichoderma*	Barthakur 1978
Bacillus	Sahin et al. 2004
Phytase producers	
Pseudomonas	Richardson and Hadobas 1997
Aspergillus	Hayes et al. 2000
Aspergillus, *Emmericella*, *Penicillum*	Yadav and Tarafdar 2003
Telephora, *Suillus* (ectomycorrhizal fungi)	Colpaert et al. 1997
N₂ fixers in non-legumes	
Azoarcus	Egener et al. 1998
Azospirillum	Bashan and Dubrovsky 1996; Martin et al. 1989
Azotobacter	Bagyaraj and Menge 1978
Panthoea	Ruppel et al. 1992
Pseudomonas, *Bacillus*	Rozycki et al. 1999
Bacillus	Sahin et al. 2004
N mineralisation	
Nitrosomonas	Briones et al. 2003
Nitrospira	Avrahami et al. 2002; Baeckman et al. 2003
Siderophores	
Bradyrhizobium	Antoun et al. 1998
Pseudomonas	Bakker et al. 1988; Bar-Ness et al. 1991; De Weger et al. 1986; Sharma et al. 2003
Ericoid mycorrhizal fungi	Schuler and Haselwandter 1988
Ectomycorrhizal fungi	Szaniszlo et al. 1981
Rhizopus	Yehuda et al. 2000

Table 6.1 (continued)

Mn reducers	
Ectomycorrhizal fungi	Cairney and Ashford 1989
Pseudomonas	Marschner et al. 1991
Mn oxidisers	
Arthrobacter	Bromfield and David 1976
Gaeumannomyces	Rengel et al. 1998; Wilhelm et al. 1990
Plant growth promotion	
Azospirillum	Martin et al. 1989; Russo et al. 2005
Bacillus	Chanway and Holl 1991; Ryu et al. 2005
Panthoea	Hoeflich and Ruppel 1994
Sinorhizobium	Galleguillos et al. 2000
Pseudomonas	Dey et al. 2004; Hoeflich et al. 1995; Iswandi et al. 1987; Kloepper and Schroth 1981; Wang et al. 2005

6.3.2
Dinitrogen Fixation

The density of free-living N_2-fixers such as *Azospirillum* sp. is higher in the rhizosphere than in the bulk soil (Assmus et al. 1995). N_2-fixers may contribute to N uptake by non-legumes in N-deficient soils. However, N_2 fixation requires a high amount of energy; therefore, due to the intense competition for root exudates in the rhizosphere, the contribution of free-living N_2-fixers to plant N uptake is probably small. A special case is endophytic N_2 fixation in sugar cane. *Azospirillum* sp. enter the roots of sugar cane and colonise the vascular system of roots and stems, where they are thought to fix substantial amounts of N (Boddey et al. 2003).

The importance of rhizobia to N uptake of legumes will not be discussed in this chapter because they are only transient rhizosphere microorganisms. After entering the roots and nodule formation, they are spatially separated from the microorganisms in the rhizosphere. Rhizobia ecology is distinct from that of the rhizosphere microorganisms. For further information on symbiotic N_2 fixation and Rhizobia, the reader is referred to Chapter 2 by McNeill and Uncovich (this volume) and other recent reviews (Broughton et al. 2003; Hardarson and Atkins 2003).

6.4
Phosphorus Cycling

Although the total amount of P in the soil may be high, it is present mainly in forms that are unavailable to plants and microoganisms. The availability of applied P to crop plants is often low because more than 80% of added P is immobilised due to adsorption, precipitation, or conversion to organic forms (Schachtman et al. 1998). Organic P, predominantly phytic acid, may represent up to 80% of total soil P (see also Chapter 3 by Bünemann and Condron, this volume).

As a response to the low P availability in soil, organisms have evolved different strategies to increase P uptake. Under P deficiency, plants may increase the soil volume exploited by increasing root growth and root hair length, or by decreasing root diameter (Föhse and Jungk 1983). Plants and microorganisms can increase the solubility of inorganic P by releasing protons, OH^- or CO_2, and organic acid anions such as citrate, malate and oxalate. Organic acid anions increase solubility of inorganic P by ligand exchange and dissolution of P-sorbing Fe-/Al-oxides and hydroxides (Banik and Dey 1983; Gerke et al. 1994; Hoffland 1992; Neumann et al. 1999).

The importance of organic acid anions released by plant roots for P solubilisation has been questioned because of their rapid decomposition in the rhizosphere (Jones 1998). However, organic acid anions may still be effective if released at the root tip, where the density of microorganisms is low, or if exudation occurs in intense bursts as in cluster roots (Neumann et al. 2000) (see also Chapter 5 by Neumann, this volume).

A large number of soil microorganisms have the capacity to solubilise sparingly soluble P in vitro (Table 6.1) (Banik and Dey 1983; Whitelaw et al. 1999). In several pot and field experiments, inoculation with P-solubilising microorganisms resulted in increased P uptake and growth (Gerretsen 1948; Kumar and Narula 1999; Kundu and Gaur 1980). Often, a combination of microorganisms with different characteristics, such as P solubilisers combined with N_2-fixers or with arbuscular mycorrhizal fungi (AM) fungi, is superior to inoculation with P solubilisers alone (Kundu and Gaur 1980; Toro et al. 1997). However, the effectiveness of inoculants will depend on the capacity of the strain to colonise the rhizosphere and maintain a high activity. A number of traits have been identified that are important for rhizosphere competence of inoculated strains, including motility, high growth rate, ability to synthesise amino acids and vitamin B1, ability to utilise organic acids and certain cell surface proteins, as well as rapid adjustment to changing conditions (Lugtenberg and Dekkers 1999).

Organic P is not immediately available to plants or microorganisms. Phosphatases are enzymes released by roots and microorganisms that mineralise organic P. They are classified into mono-, di- and tri-esterases and polyphosphatases based on the organic P compounds they cleave (Tabatabai 1982).

Phytate, the dominant form of organic P in soils, is a poor P source for plants grown under sterile conditions because plant roots have low extracellular phytase activity (Richardson et al. 2001). Microorganisms, on the other hand, excrete phytase (Table 6.1) (Richardson and Hadobas 1997), which may play an important role in plant P uptake from phytate (Richardson et al. 2001). However, the effectiveness of phytase in soil is unclear because (1) phytate is adsorbed to Fe/Al oxides, thus strongly reducing its availability, and (2) phytase is rapidly adsorbed to soil particles leading to decreased activity (George et al. 2005).

In the rhizosphere, plant and microbial solubilisation and mineralisation processes occur simultaneously. Mineralisation/solubilisation dominate at low soil C/P ratios, whereas immobilisation (uptake of P by the microbial biomass) exceeds mineralisation/solubilisation at high C/P ratios (He et al. 1997). The mobilised P can be taken up by plants or microorganisms. Thus, plants and microorganisms compete for P. It has been hypothesised that an active microbial biomass with a high turnover rate can rapidly take up added P, but may also represent a slow and constant source of available P through decomposition of dead microbial cells (Oberson et al. 2001; Seeling and Zasoski 1993). The amount of added P that ends up in the biomass depends on the form of P added to soil, with 23% from inorganic P and 68% from P added as residues taken up and stored in the microbial biomass (McLaughlin et al. 1988). It should be noted that P in plant residues consists not only of organic P, but that 30–50% of total P in plant residues can be in inorganic form (Kwabiah et al. 2003). Seeling and Zasoski (1993) suggested that P uptake by the microbial biomass could be beneficial for plants because it would decrease P fixation by maintaining low inorganic P concentrations in the soil solution.

6.5
Iron Cycling

The total Fe content in soil is relatively high, but its availability to organisms is low in aerated soils because the prevalent form (Fe^{3+}) is poorly soluble. Plants and microorganisms have developed mechanisms to increase Fe uptake (Marschner 1995) [see also Chapters 4 (Rengel) and 5 (Neumann), this volume]. In plants, two different strategies in response to Fe deficiency are evident. Strategy I plants (dicots and non-graminaceous monocots) release organic acid anions that chelate Fe. Iron solubility is also increased by decreasing the rhizosphere pH, and Fe uptake is enhanced by an increased reducing capacity of the roots ($Fe^{3+} \rightarrow Fe^{2+}$). Additionally, root morphology and histology may change (root tip swelling, increased root branching, more root hairs, formation of rhizodermal transfer cells, etc.). Strategy II plants (Poaceae, formerly Graminaceae) release phytosiderophores (PS) that chelate Fe^{3+}. PS are non-proteinogenic amino acids

(Marschner 1995) with high specificity for certain metals. Iron is taken up in the chelated form as Fe-PS by a specific uptake system that is activated under Fe deficiency (Römheld 1991; Von Wiren et al. 1993). PS are released for only a few hours per day at the root tip (Römheld 1991). The rate of PS release is positively related to Fe efficiency of grass species (Römheld 1991).

Under Fe deficiency stress, microorganisms release organic acid anions or siderophores that chelate Fe^{3+}. After movement of the ferrated chelate to the cell surface, Fe^{3+} is reduced either outside or within the cell (Neilands 1984). Microorganisms produce a range of siderophores, e.g. ferrichromes in fungi, and enterobactin, pyoverdine and ferrioxamines in bacteria (Table 6.1). A given species may produce one or several siderophores and can have the capacity to take up not only its own siderophores, but also those of other species (Raaijmakers et al. 1995).

Bacterial siderophores are usually poor Fe sources for both monocot and dicot plants (Bar-Ness et al. 1992; Crowley et al. 1992; Walter et al. 1994). However, in some cases microbial siderophores have alleviated Fe deficiency-induced chlorosis in dicots (Jurkevitch et al. 1988; Sharma et al. 2003; Wang et al. 1993; Yehuda et al. 2000). On the other hand, plant-derived Fe-PS complexes appear to be a good Fe source for bacteria (Jurkevitch et al. 1993; Marschner and Crowley 1998).

The interactions between different Fe chelators are a function of the affinity of the chelators towards Fe and their relative concentration. Compared with PS, bacterial siderophores such as pyoverdine have a higher affinity towards Fe (Yehuda et al. 1996). If siderophore and PS are present at similar concentrations, Fe is preferentially bound to the siderophore; siderophores may even remove Fe from Fe-PS. In contrast to many bacterial siderophores, rhizoferrin from the fungus *Rhizopus arrhizus* has only a slightly higher affinity for Fe compared with PS. Rhizoferrin is a good Fe source for barley, probably because of exchange of Fe from rhizoferrin to PS (Yehuda et al. 1996).

Not only the affinity of the chelators for Fe is important, but also their relative concentration (Yehuda et al. 1996). The diurnal rhythm of PS release by grasses results in a high concentration of PS at the root tips at certain times of the day (Crowley and Gries 1994). Under such conditions, PS may be efficient Fe chelators that could even remove Fe from bacterial siderophores. A high rate of PS release also increases their effectiveness against rapid degradation by microorganisms (Von Wiren et al. 1995).

With respect to Fe, microorganisms appear to be highly competitive compared to plant roots (Fig. 6.1). Microorganisms produce chelators with high affinity to Fe, can utilise Fe chelated by plant-derived chelators and decompose plant-derived chelators. Plants on the other hand, have only a limited capacity to utilise Fe chelated by microbial siderophores. However, a spatially and temporally restricted high release rate of Fe-chelating substances will improve the competitiveness of the plants.
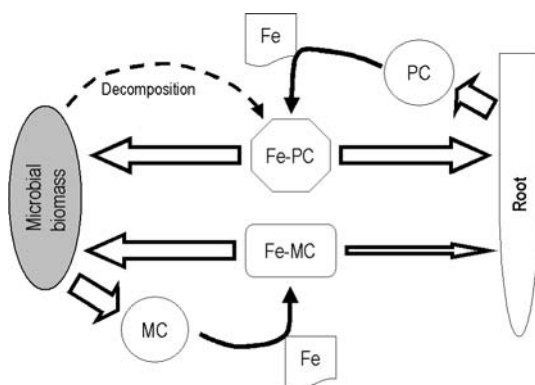
Fig. 6.1 Interactions between roots and rhizosphere microorganisms for iron. The thickness of the arrows towards roots and microorganisms indicates the rate of uptake. Roots and microorganisms release chelating substances: *PC* plant chelators, *MC* microbial chelators. Iron chelated by PC is easily taken up by plants and microorganisms whereas Fe chelated by MC is poorly available to plants. Microorganisms can reduce the effectiveness of PC by decomposing them

6.6
Manganese Cycling

Millions of hectares of arable land worldwide are deficient in Mn (Welch 1995). Only the reduced form of Mn (Mn^{2+}) is available to plants, while its oxidised form (Mn^{4+}) is unavailable. Oxidation is biological, whereas reduction can be either biological or chemical (Ghiorse 1988) (see also Chapter 4 by Rengel, this volume).

Crop plant genotypes differ in sensitivity to Mn deficiency, and rhizosphere microorganisms may play an important role in these genotypic differences (Rengel 1997). Under Mn-deficient conditions, the density of Mn reducers is higher in the rhizosphere of Mn-efficient than Mn-inefficient wheat (Rengel et al. 1996) and oat (Timonin 1946) genotypes (Table 6.1).

There is a complex interaction between Mn and the take-all fungus *Gaeumannomyces graminis var. tritici* (Ggt). Lignin accumulation in the cell walls is an important mechanism to prevent the spread of pathogens in plant tissues, and Mn is important in lignin synthesis. Mn-deficient roots have lower lignin contents and are more susceptible to Ggt (Wilhelm et al. 1990). Increased Mn availability increases the lignin content of roots and decreases the number of lesions caused by Ggt (Rengel et al. 1993). Interestingly, Ggt is a strong Mn oxidiser and thus decreases Mn availability. The fungus is inhibited by high Mn availability (Wilhelm et al. 1990) and it has been shown that Mn reducers can reduce the growth of Ggt (Marschner et al. 1991).

6.7
Mycorrhiza

Mycorrhizal fungi form a mutually beneficial symbiosis with most terrestrial plants (Smith and Read 1997). They play an important role in nutrient cycling. In this chapter, only the most important aspects will be discussed. For a more extensive discussion on mycorrhiza, the reader is referred to reviews in the literature (Barker et al. 1998; Koide and Dickie 2002).

The roots of most plant species, including the majority of crop plants, are colonised by arbuscular mycorrhizal fungi (AM). Trees, on the other hand are colonised mainly by ectomycorrhizal fungi. Other forms include ericaceous and orchid mycorrhiza. In this chapter we focus on the former two types.

The host plant supplies C to the fungus, and the fungus enhances the capacity of the plant to take up poorly available nutrients, particularly P. The fungi colonise the roots and fungal hyphae grow into the surrounding soil beyond the P depletion zone created by the roots. The hyphae increase the soil volume exploited (Li et al. 1991) and have access to pores that are too small for roots. They increase mineralisation of organic P by releasing phosphatases (Tarafdar and Marschner 1994). Mycorrhizal colonisation can improve trace element uptake (Cu, Zn) under deficient conditions, but may also alleviate heavy metal or Al toxicity (Cumming and Weinstein 1990; George et al. 1994).

Ectomycorrhizal and ericoid mycorrhizal fungi can play an important role in N cycling. It has been shown that they can utilise organic N sources (Abuzinadah and Read 1986b; Stribley and Read 1980). Plants colonised by ectomycorrhizal fungi grow well with organic N as the sole N source, whereas un-colonised controls grow poorly (Abuzinadah and Read 1986a). This capacity of mycorrhizal fungi to directly utilise organic N sources has implications for nutrient cycling because it would short-circuit the N cycle and reduce the dependence of the plant on heterotrophic microorganisms.

Some ectomycorrhizal fungi form extensive hyphal mats close to the soil surface. These mats differ in chemical and biological properties from non-mat soil, including higher availability of nutrients and higher microbial biomass and activity (Entry et al. 1991, 1992).

Mycorrhizal colonisation may also influence root exudation and microbial community structure in the rhizosphere, which will in turn affect nutrient cycling. AM colonisation has been shown to decrease root exudation (Dixon et al. 1989; Graham et al. 1981; Marschner et al. 1997), although some reports have shown no effect on exudation (Azaizeh et al. 1995). Mycorrhizal colonisation affects root exudate composition (Marschner et al. 1997; Po and Cumming 1997) and carbohydrate metabolism in the roots (Buwalda and Goh 1982; Shachar-Hill et al. 1995). Mycorrhizal fungi themselves may release exudates that selectively influence the microorganisms in the rhizosphere. Examples include the release of organic acid anions by ectomycorrhizal fungi (Duchesne et al. 1989) or glomalin by AM fungi (Rillig et al. 2002).

AM colonisation affects the distribution of bacteria on roots, resulting in a greater spatial variability of bacterial distribution on AM roots compared with non-AM roots (Christensen and Jakobsen 1993). AM colonisation can either increase the population density of bacteria in the rhizosphere (Andrade et al. 1998a; Bagyaraj and Menge 1978), have no effect on bacterial density (Andrade et al. 1997; Meyer and Linderman 1986; Olsson et al. 1996), or decrease bacterial density (Ames et al. 1984; Christensen and Jakobsen 1993). These apparently contradictory findings may be due to AM fungal species-specific interactions (Marschner and Baumann 2003; Marschner and Crowley 1996; Secilia and Bagyaraj 1987). AM colonisation can change the bacterial community structure in the rhizosphere by stimulating the population density of certain bacterial species or functional groups, while depressing others (Andrade et al. 1997; Meyer and Linderman 1986; Posta et al. 1994; Secilia and Bagyaraj 1987; Wamberg et al. 2003).

In many studies it has been shown that the population density of Gram-negative bacteria (Posta et al. 1994; Secilia and Bagyaraj 1987) and actinomycetes (Bagyaraj and Menge 1978) is increased in the rhizosphere of AM roots. AM colonisation may increase the population density of Mn-reducers in the rhizosphere, thus increasing Mn availability to the plants and increasing plant Mn uptake (Kothari et al. 1991; Posta et al. 1994). On the other hand, AM may also alleviate Mn toxicity (Bethlenfalvay and Franson 1989). A complex interaction between AM colonisation and Mn was reported recently; AM colonisation increased Mn toxicity in the early stages of growth of soybean, but AM later alleviated Mn toxicity; AM plants had greater shoot dry weight and lower Mn concentration than non-mycorrhizal plants (Nogueira et al. 2004). This suggests that the interactions between AM and Mn reducers/oxidisers may change during plant development.

AM colonisation can also affect microorganisms involved in N mineralisation in soil. The population density of autotrophic ammonia oxidisers was higher, while those of ammonifiers and nitrifiers was lower in pot cultures of *Glomus mosseae* and *Glomus fasciculatum* than in non-mycorrhizal pot cultures (Amoralazcano et al. 1998). On the other hand, there are reports that AM colonisation has no effect on bacterial community composition (Mansfeld-Giese et al. 2002; Olsson et al. 1996; Soederberg et al. 2002). As mentioned above, these contrasting results indicate that the effect may be fungal species-specific (Marschner and Baumann 2003; Marschner and Crowley 1996; Marschner et al. 2001a), or plant species-specific (Vancura et al. 1989). This is supported by a recent study, which showed complex interactions of plant and AM fungal species on the bacterial community composition in the rhizosphere (Marschner and Timonen 2004). Mycorrhizal fungi can also influence nutrient cycling indirectly by enhancing soil aggregation, creating more favourable conditions for soil microorganisms and roots (Andrade et al. 1998b).

6.8
Plant Growth-Promoting Rhizosphere Microorganisms

Plant growth-promoting rhizosphere microorganisms (PGPRs), are a heterogenous group of microorganisms that stimulate plant growth by various mechanisms, including P solubilisation (Sahin et al. 2004), N_2 fixation (Mirza et al. 2001), plant hormone production (Russo et al. 2005; Ryu et al. 2005), pathogen suppression (antibiotics, siderophores) (Dey et al. 2004; Kumar et al. 2005) and/or stimulation of other beneficial microorganisms such as N_2-fixers or mycorrhizal fungi (Table 6.1). A given strain will often exhibit a number of the above-mentioned traits (De Weger et al. 1995; Dey et al. 2004; Höflich et al. 1992; Shishido and Chanway 1999). Recently, it was shown that PGPRs cause substantial changes in gene expression in plants, including genes involved in metabolism and signal transduction (Wang et al. 2005). PGPRs enhance nutrient cycling by improving plant growth and nutrient uptake as well as by increasing the amount of plant residues returned to the soil.

The success of an introduced PGPR is based on successful colonisation of the rhizosphere. For such colonisation, certain traits are important, including motility and growth rate to match root growth, attachment to the root surface (e.g. by polysaccharides), capacity to utilise root exudates, synthesis of amino acids, and high competitive ability towards other microorganisms (Chin et al. 2000; De Weger et al. 1995). In order to be effective, PGPRs need to express their plant growth-promoting traits in the rhizosphere.

Another group of PGPRs may improve plant growth indirectly. An example is mycorrhiza helper bacteria (bacteria isolated from ectomycorrhizal roots have been shown to enhance mycorrhizal colonisation and growth of trees) (Becker et al. 1999; Duponnois and Garbaye 1991; Garbaye 1994; Poole et al. 2001). Co-inoculation with P-solubilising bacteria can increase AM colonisation and P uptake by plants (Toro et al. 1997).

6.9
Rhizosphere Priming Effect

"Priming effect" is the strong short-term change in the turnover of soil organic matter (SOM) induced either by addition of compounds to the soil or by soil disturbance (Hamer and Marschner 2002; Kuzyakov 2002; Kuzyakov et al. 2000). A positive priming effect occurs when easily available root exudates increase the activity and density of rhizosphere microorganisms. Negative priming effects may be found if root exudates have an inhibitory effect on microorganisms (Fu and Cheng 2002). The presence of roots can increase SOM turnover (Personeni

et al. 2005). Root-induced changes in SOM decomposition rate affect nutrient cycling because they influence nutrient availability and thus nutrient uptake by plants.

Despite a positive priming effect of root exudates, plants tend to increase SOM content in the long-term. As plants age, root exudation decreases and rhizodeposits are more recalcitrant because a large proportion of the root systems consists of older roots; in addition, dead roots contribute to SOM (Kuzyakov 2002).

6.10
Conclusions

The rhizosphere plays an important role in nutrient cycling (Fig. 6.2). Stimulated by root exudates, microbial processes such as mineralisation, N_2 fixation, and solubilisation of P and Fe are increased in the rhizosphere compared to soil not influenced by roots. On the other hand, nutrient immobilisation by the microbial biomass may decrease nutrient availability to plants. However, over the long-term, the microbial biomass in the rhizosphere represents a labile nutrient source if the turnover rate is high and not all nutrients released by dying microorganisms are taken up by active biomass. More studies are needed to understand competition between plants and microorganisms in the rhizosphere and how this interaction is modulated by plant genotype and microbial community composition.
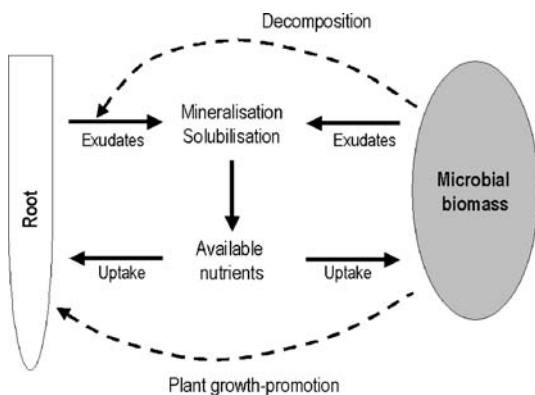

Fig. 6.2 Interactions between rhizosphere microorganisms and plant roots for nutrients. Plant roots and microorganisms release compounds that increase nutrient availability. The nutrients can then be taken up by microorganisms and roots. Rhizosphere microorganisms can reduce the effectiveness of root-derived compounds by decomposition. Plant growth-promoting rhizobacteria usually exhibit a number of properties that increase plant growth

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7 The Role of Crop Residues in Improving Soil Fertility

Bhupinderpal-Singh, Zed Rengel

7.1
Introduction

Soil fertility is a measure of the ability of soil to sustain satisfactory crop growth in the long-term, and can be determined by physical, chemical and biological processes intrinsically linked to soil organic matter content and quality (Fig. 7.1). Given that a decrease in soil fertility is a major constraint to productivity, investing in practices leading to soil fertility enhancement is likely to generate large returns (Syers 1997). In recent years, increased concerns for healthy food production and environmental quality, and increased emphasis on sustaining the productive capacity of soils, have raised interest in the maintenance and improvement of soil organic matter through appropriate land use and management practices (Loveland and Webb 2003; Puget and Lal 2005; Whitbread et al. 2003).

Crop residues are an important source of organic matter that can be returned to soil for nutrient recycling, and to improve soil physical, chemical and biological properties (Kumar and Goh 2000). Globally, the total crop residue production is estimated at 3.8 billion tons per year, of which 74% are from cereals, 8% from legumes, 3% from oil crops, 10% from sugar crops and 5% from tubers (Lal 2005). Besides C, crop residues contain all mineral nutrients, the content of which varies among crop species depending on the fertility of the soil (Table 7.1). These residues should be returned to the soil, and should be spread uni-

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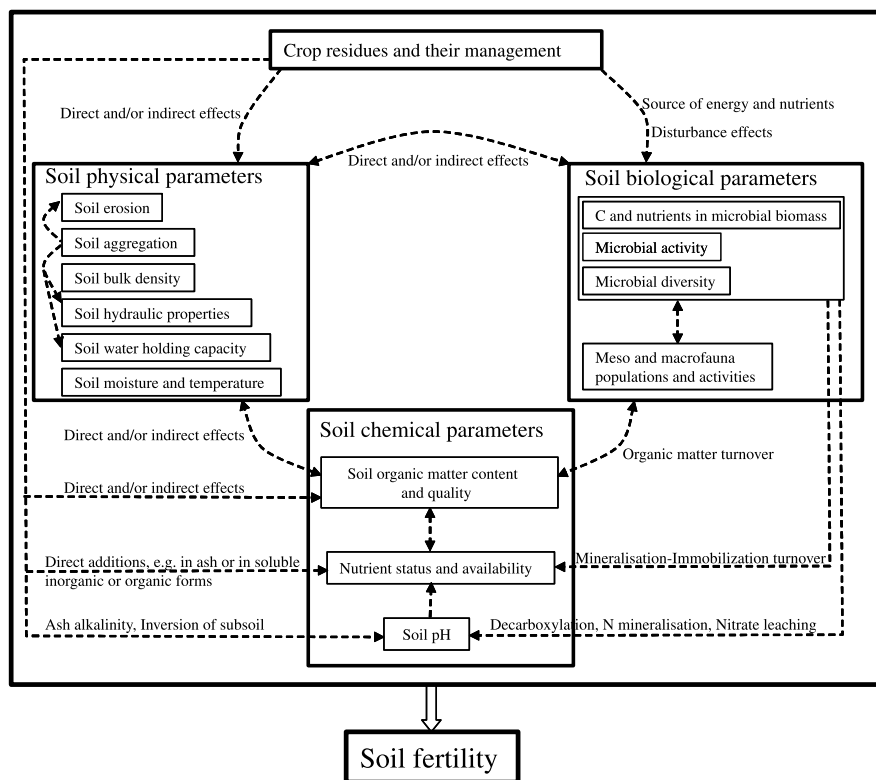E-mail: bp.singh@sf.nsw.gov.au

Fig. 7.1 Effects of crop residues and their management on physical, chemical and biological parameters of soil quality and overall soil fertility

formly over an entire field to prevent impoverishment of nutrients and organic C in the soil (Brennan et al. 2004; Lal 2005). It is, however, difficult to predict how much of the nutrients in the residue will become available to crops during a given time because of the complex processes governing residue decomposition and nutrient release (see Fig. 7.2). In addition, the nature of crop residues and their management can significantly affect the amount of nutrients available for subsequent crops as well as the content and quality of soil organic matter (Kumar and Goh 2000; Yadvinder-Singh et al. 2005).

Effective management of crop residues in the field should conserve soil and its resources with minimal adverse effects on the environment (Conteh et al. 1998; Kumar and Goh 2000; Puget and Lal 2005; Yadvinder-Singh et al. 2005). After harvesting crops, crop residues can be (1) left on the soil surface, (2) swathed and concentrated in windrows, (3) incorporated into soil, and/or (4) burnt prior to tillage or seedbed preparation. Crop residues that are partially
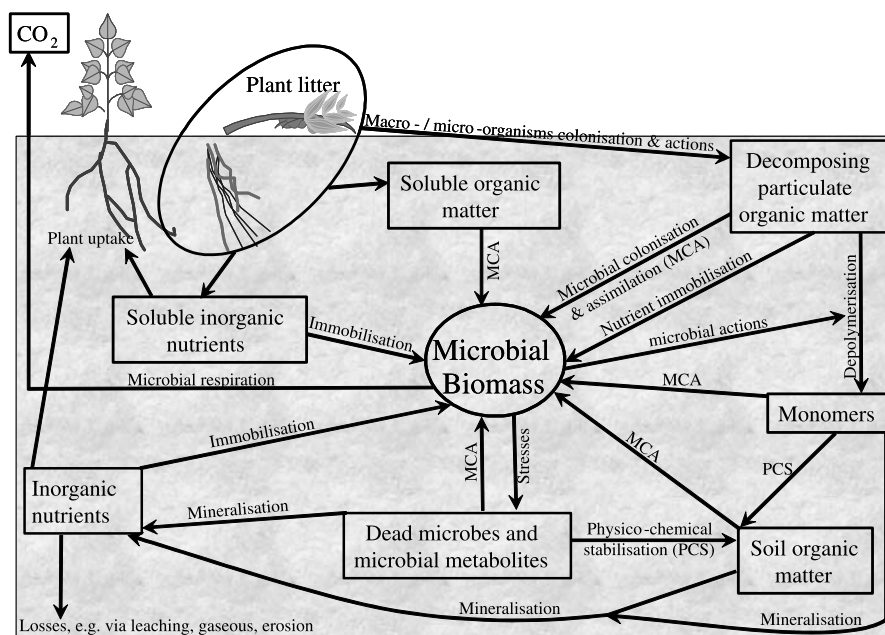
Fig. 7.2 Conceptual flow of C and other nutrients in agroecosystems following addition of crop residues to soil

Table 7.1 Contents of nutrients in some crop residues

Crop residues	kg tonne^{-1} (dry matter)						Source
	N	P	K	S	Ca	Mg	
Canola-1[a]	3.8	0.6	8.6	0.9	4.6	1.2	Bhupinderpal-Singh
Canola-2[a]	8.2	0.6	7.2	0.9	5.2	1.3	(unpublished data)
Lupin	7.8	0.3	9.3	2.8	3.4	2.7	
Wheat	3.0	0.2	7.8	0.6	1.2	1.1	
Oat	5.9	0.6	23.3	1.1	1.4	0.5	Fraser and Francis 1996
Barley	4.6	0.4	14.3	1.4	2.6	0.8	

[a]Canola residues originated from two different fields: Canola-1 from a non-N fertilised plot and Canola-2 from an N-fertilised plot

or wholly removed from field can be used as mulches, composts, industrial raw material, household fuel, biofuel for off-setting fossil fuel emissions or fodder for animals (thereby returning residues to the field as animal wastes) (Lal 2005; Smil 1999). Tillage options range from (1) no-till, (2) chisel, disk, or sweep till

(minimum tillage), to (3) several passes by mouldboard plough or disc plough (conventional tillage) (Alvarez 2005; Heenan et al. 2004; Salinas-Garcia et al. 2001).

Retaining sufficient amounts of harvested crop residues on the soil surface (providing at least ca. 30% cover) together with no-till, or partial incorporation in soil by minimal tillage (conservation tillage) decreases wind and water erosion (Lal 2005; Unger and McCalla 1980). Residue addition to soil in conventional or conservation tillage systems may also have positive effects on organic matter level and quality in soil (Alvarez 2005). However, there are conflicting reports on the rate and degree of organic matter accumulation associated with returning crop residues to soil, due mainly to differences in climate, soil type, residue quality, and depth of sampling (Alvarez 2005; Kumar and Goh 2000; Prasad and Power 1991). Moreover, the effects of residue return to soil and associated tillage on soil physical, chemical and biological properties occur concurrently and hence are difficult to separate from each other (Chan et al. 2003). Chan et al. (2002) have shown that 80% of changes in soil C levels under cropping were attributable to tillage (conservation vs conventional) and 20% to residue management (stubble retained vs burnt). Besides breaking residues into smaller pieces and mixing them with soil (Summerell and Burgess 1989), tillage can mechanically break soil aggregates and expose the protected organic material to microbial decomposers, thus leading to faster losses of soil C (Bhupinderpal-Singh et al. 2004).

Burning crop residues is usually done in an attempt to obtain a seedbed that is easy to work (i.e. improved tillage efficiency), to minimise impediment to the growth of a new crop, to reduce diseases where crop residues serve as a host for pathogens, and to control weeds and insects (Smil 1999). Repeated removal of residues by burning can, however, cause significant environmental problems and land degradation and residue burning is therefore controversial. Unlike grassland and forest ecosystems (González-Pérez et al. 2004; Raison 1979), there is only limited information on the effects of crop residue burning on soil properties in agro-ecosystems, thus leaving open questions about the validity of this practice (Rasmussen and Rohde 1988).

This chapter reviews the role of different crop residue management practices as well as the quantity and quality of crop residues in governing the chemical, physical, and biological parameters of soil quality, which are closely linked to each other with respect to overall soil fertility (Fig. 7.1). A better understanding of these aspects of soil fertility will help maximise the beneficial effects of crop residues on agricultural soils (such as minimising soil degradation, increasing soil fertility through build-up of soil organic matter, thereby sustaining plant productivity), and minimise the negative effects (such as immobilisation of nutrients, leaching and run-off losses of nutrients, erosion, and impeding of sowing operations), thereby contributing directly to the sustainability of crop-production systems.

7.2
Effects of Crop Residue Management
on Soil Chemical Properties

7.2.1
Soil Organic Matter

7.2.1.1
Dynamics of Soil Organic Matter and its Pools

Total organic C as a measure of soil organic matter content can vary depending on soil type and management (Alvarez 2005; Lal 2005; Loveland and Webb 2003). However, monitoring changes in soil organic matter may be constrained by the difficulty in detecting small changes occurring over relatively short time periods against a large and variable background of existing soil organic matter (Pankhurst et al. 2002; Rasmussen and Collins 1991). Separation of organic matter in soil into pools of discrete sizes, specific bioavailability and turnover rates can provide detailed information on the dynamic changes in soil organic matter content and quality after addition of crop residues (Conteh et al. 1998; Magid et al. 1997; Wang et al. 2004b) (see also Chapter 1 by Baldock, this volume).

Small but relatively labile pools of soil organic matter would respond more quickly to changes in crop residue management than larger, more recalcitrant, pools. For example, significant increases in the amount of light C fraction were found after 3 years of residue incorporation compared with burning treatments; this pool made the greatest contribution to changes in total soil organic C during the period studied (Conteh et al. 1998). However, for long-term response (~three decades), changes in heavy fraction C ($>1.6 \, \text{g cm}^{-3}$) are the prevalent factor in determining changes in total organic C caused by differences in farming practices (Wang et al. 2004b). Crop residue burning decreased the relatively stable pool of organic matter associated with silt and clay aggregates of $<53 \, \mu\text{m}$ in size, whereas tillage preferentially reduced particulate organic matter ($>53 \, \mu\text{m}$) (Chan et al. 2002).

Continued losses of organic matter from agricultural soils have detrimental implications for the global CO_2 balance and soil quality in general, and organic matter pools that change over the short term could provide early indications of such losses and changes in soil quality. Additionally, the relatively labile components of soil organic matter play an important role in short-term nutrient turnover (Bhupinderpal-Singh et al. 2004; Chan et al. 2002) and short-term soil aggregate stabilisation (Chan et al. 2002; Roper and Gupta 1995; Tisdall and Oades 1982). The less-labile organic matter plays an important role in long-lasting stabilisation of soil aggregates (Chan et al. 2002; Piccolo and

Mbagwu 1999). Thus, crop residue management practices that cause a loss of less-labile organic matter (e.g. organic matter associated with soil particles of <53 μm) can significantly enhance breakdown of soil macro- and micro-aggregates to much smaller sizes (e.g. Chan et al. 2002) and thus decrease soil structural stability.

Returning crop residue to soil, in contrast to its removal or burning, has been shown to increase the organic matter content of topsoil in many long-term field experiments, especially where N was also applied and rainfall was >500 mm (Alvarez 2005; Chan et al. 2003; Heenan et al. 2004; Salines-Garcia et al. 2001; Wang et al. 2004b). Many such studies in Europe and the United States have shown that approximately a decade or two may be required for soil C content to increase to a new equilibrium after favourable changes in crop residue management (e.g. no-till, stubble retained and N application) (Alvarez 2005; Paustian et al. 1997; Puget and Lal 2005; Smith et al. 1998). This observation contrasts with those from tropical regions (such as in Australia and Asia), where more than two decades may be required for soil C to reach a new equilibrium after favourable changes in management (Heenan et al. 1995, 2004; Wang et al. 2004b; Yadvinder-Singh et al. 2005). The reasons for this inconsistency in the rate of soil C accumulation may be due to differences in the climatic conditions in these regions (e.g. dry and warm vs wet and cold climate), and in local edaphic conditions, crop rotation systems, and crop yield causing further differences in
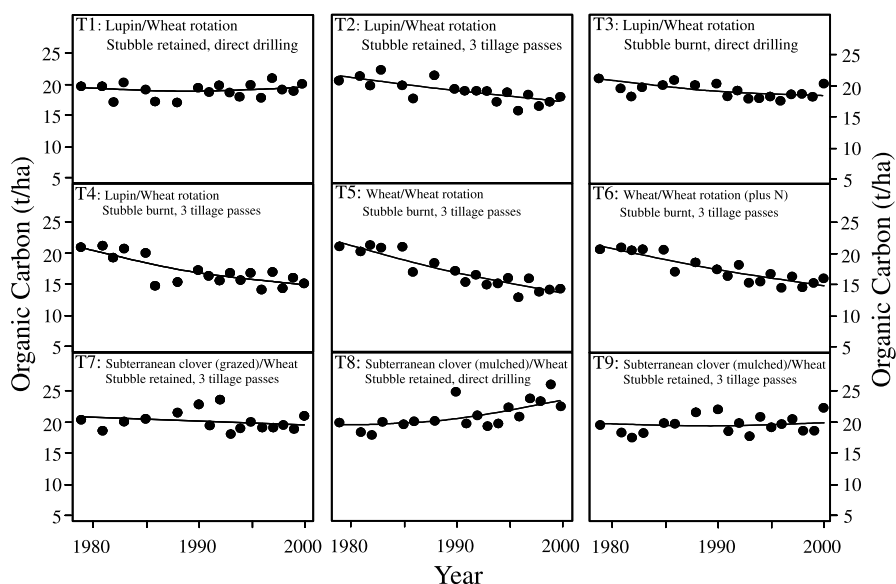

Fig. 7.3 Changes in soil organic C for different rotation, tillage and stubble management treatments (*T1–T9*) over 21 years on a red earth, a Chromic Luvisol, at Wagga Wagga (New South Wales, Australia). *Lines* represent fitted models (reprinted from Heenan et al. 2004, with permission from Elsevier, Amsterdam)

the amount of crop residues that are returned to the soil (Alvarez 2005; Chan et al. 2003; Franzluebbers and Steiner 2002; Wang et al. 2004b). Nevertheless, long-term studies are useful in testing the effectiveness of farming practices in determining the direction of change in soil organic matter and associated soil properties (Chan et al. 2003). For example, Heenan et al. (1995) found either a decrease or no significant change in soil organic C after 14 years of various combinations of crop rotations, tillage and residue management practices on a red earth, a Chromic Luvisol, in Australia. The soil C levels under a direct-drilled and stubble retained treatment in the subterranean clover/wheat rotation (treatment T8, Fig. 7.3) were thought to have reached a state near equilibrium in the first 14 years (Heenan et al. 1995). However, a significant gain in soil organic C was observed in this treatment (T8) over the next 7 years (Fig. 7.3), possibly due to greater crop residue input during this time (Heenan et al. 2004) in combination with a reduction in soil C loss, which was also observed in other direct-drill treatments (Fig. 7.3, treatments T1 and T3). These studies emphasise the need for long-term studies to correctly interpret management effects.

7.2.1.2
Factors Governing Decomposition and Status of Organic Matter in Soil

The quantity and quality of crop residues (including physical characteristics such as residue size as well as chemical composition) and their placement, edaphic factors, and physico-chemical environment have variable and interactive influences on soil organic matter content (Paustian et al. 1997; Puget and Lal 2005; Swift et al. 1979; Schomberg et al. 1994). Incorporation, or retention near the soil surface by conservation tillage, of low quality crop residues (e.g. wheat) with high C:N ratio and high ligno-cellulose content may cause greater increases in soil organic C than a low C:N ratio residue (such as green manure), which is likely to be due to the higher percentage of low quality residues being transformed into soil organic matter (Beri et al. 1995). However, accumulation of soil organic matter is often less related to quality than to quantity of crop residues (Voroney et al. 1989), suggesting that soil organic matter formation may be a function of accumulation of recalcitrant decomposition products (Gleixner 2005).

Conservation tillage often results in greater increases of organic C near the soil surface than at greater depths (Rasmussen and Collins 1991; Salinas-Garcia et al. 2001). Such increases in soil organic C in conservation-tillage systems as opposed to conventional tillage can be attributed to poor residue-soil contact, which reduces decomposition of structural plant constituents through delayed colonisation by microbes (Henriksen and Breland 2002) and reduced availability of nutrients to microbes colonising the surface residue (Beare 1997), greater fluctuations in surface temperature and moisture, and reduced soil disturbance, thereby promoting aggregate formation followed by protection of organic mat-

ter within aggregates (Six et al. 1999, 2000). Tillage breaks up residues into smaller particles, mixes them with soil to greater depths, and thereby exposes a greater residue surface area to microbial attack (Summerell and Burgess 1989). However, decomposition of high quality residues (e.g. legume residues with low C:N ratio) may be unaffected by placement (on the surface or mixed with soil) (Henriksen and Breland 2002).

Compiling the data from several long-term field studies, Paustian et al. (1997) found in most cases an increase in C content under no-till compared with conventional tillage, with the rate of increase in organic C being higher in heavy than in light soils, most likely due to physical protection of organic matter by clay and silt (Hassink 1997). More recently, Puget and Lal (2005) analysed 56 paired experiments of no-till versus conventional tillage and found that no-till had a positive effect on C sequestration, at 330 kg C ha^{-1} year^{-1} on average, with the greatest positive effect observed in cropping systems with high residue inputs. However, the effect of no-till on soil organic C stock was highly variable and dependent on site-specific pedo-climatic conditions (Puget and Lal 2005).

Residue management practices can interact with the type of tillage and N-fertiliser application. For example, intensive tillage operations can decrease organic C in soil regardless of whether residue is retained or burnt (Heenan et al. 2004). Nitrogen application can enhance above- and below-ground biomass productivity, alter C cycling, and hence indirectly affect the rate of change in soil organic C (Alvarez 2005; Heenan et al. 1995, 2004; Paustian et al. 1997; Wang et al. 2004a).

7.2.1.3
Effect of Crop Residue Burning on Soil Organic Matter

Information on the effect of crop residue burning on soil organic matter content and quality is scarce; variable effects are often reported depending on the degree to which crop residues are burnt, the temperature and time of burning, the depth of sampling, and tillage practices (Biederbeck et al. 1980; Chan et al. 2002; Graham et al. 2002; Rasmussen et al. 1980; Prasad and Power 1991). One reason for the inconsistent effects on soil organic C levels found in different studies may be the incomplete burning of crop residues, which leave behind charred and relatively recalcitrant C forms that are less good an energy source for microorganisms than fresh or biologically decomposed plant materials (González-Pérez et al. 2004; Rasmussen and Parton 1994). Over time, this recalcitrant C may be accumulated (also partly due to decreased microbial biomass and activity after burning, see below) and may still be detected in soil analysis as soil organic matter. However, by being biologically and chemically stable, the burnt residues may not constitute a pool of soil C that facilitates microbial activity (González-Pérez et al. 2004); thus, it is likely that burning crop residues changes the quality more than the quantity of organic matter in soil (Kumar and Goh 2000).

7.2.2
Nutrient Status and Availability in Soil

Crop residues contain nutrients (Table 7.1) that may not be readily available for crop use; indeed, a significant proportion of organically bound nutrients have to undergo biological processes [mineralisation-immobilisation turnover (MIT)] before becoming available to plants (Bhupinderpal-Singh et al. 2006; Jensen 1994; Salas et al. 2003). A conceptual flow of C and nutrients in agro-ecosystems following addition of crop residues in soil is presented in Fig. 7.2. Upon return to soil, crop residues are readily colonised by a range of macro- and micro-organisms, thereby initiating decomposition and mineralisation of crop residues and the organic nutrients contained within them. Carbon and nutrients in decomposing organic matter and in soil are assimilated/immobilised by the growing microbial biomass. Over time, the decomposing crop residues (including dead microorganisms) are converted to simpler monomers, which can be further assimilated by microorganisms, or physically and chemically (i.e. due to their recalcitrance to decomposition) stabilised in soil, thereby forming soil organic matter (Fig. 7.2). Nutrients in excess of microbial demand are released into the soil (mineralisation). Mineralisation–immobilisation processes in soil occur simultaneously, and the rate at which nutrients are available from decomposing organic materials for plant uptake (and for leaching or volatilisation) depends on the net balance between these two processes (Myers et al. 1994).

Crop residues may contain some plant nutrients in a soluble inorganic form (e.g. K^+, SO_4^{2-}), or associated with readily mineralisable organic constituents (e.g. amino- and protein-bound S and phosphate esters) (Bhupinderpal-Singh et al. 2006; Salas et al. 2003; Wu et al. 1993). Such nutrients are readily released/mineralised and immobilised in microbial biomass upon return of crop residues to soil (Fig. 7.2). In addition, soluble salts could crystallise on the surface of residues after they absorb moisture and can be washed off into soil with minimal rainfall input (S. Collins, personal communication). Nutrients that are released into the soil from crop residues and are not readily immobilised by microorganisms, or taken up by plants, may become unavailable through fixation onto soil particles or lost via leaching, volatilisation and/or soil erosion.

7.2.2.1
Crop Residue Quality in Relation to Nutrient Availability

Manipulation of crop residue quality, particularly N, lignin and polyphenol concentration, may alter decomposition dynamics and is hence a potentially important way to manage N supply in relation to crop demand, thereby improving N-use efficiency (Handayanto et al. 1997; Myers et al. 1997; Whitbread et al. 2003). Easily decomposable plant residues, such as high-N leaf residues from lucerne, medics, pea and clover, can be mineralised relatively quickly. Non-legume crop

residues (such as wheat, barley, maize, canola, rice, sorghum, sugarcane) with high C:N ratio and/or lignin content may require application of fertiliser-N to meet microbial N requirements and thus facilitate decomposition. However, high lignin (and/or polyphenol) content may interact with soil or plant residue N, suppressing N availability (Bending and Turner 1999; Wang et al. 2004a) due to formation of recalcitrant organic N forms.

Addition of crop residues with a wide range of C-to-nutrient ratios to soil can cause initial immobilisation of nutrients (N, P, S) by microorganisms (Bhupinderpal-Singh et al. 2006; Graham et al. 2002; Salas et al. 2003; Wu et al. 1993). Microbial immobilisation of nutrients may temporarily decrease their availability to plants by conserving substantial amounts in slowly available organic forms, thereby preventing nutrient losses, for example by leaching of mobile nutrients (NO_3^-, SO_4^{2-}), volatilisation of N (Williamson and Johnson 1994) or fixation of phosphate by soil. However, nutrients immobilised by the microbial biomass can increase the nutrient-supplying potential of soil through the turnover of microbial biomass with time (Singh et al. 1989).

7.2.2.2
Nutrient Distribution in Soil

Repeated deposition of crop residues on the soil surface can cause a gradient in nutrient distribution with depth; for example, conservation tillage causes greater accumulation of inorganic and organic P near the surface compared with conventional tillage (Du Preez et al. 2001; Salinas-Garcia et al. 2001; Weil et al. 1988). The differences in P distribution between tillage treatments usually diminish with depth; however, deep incorporation of residues may result in high P content at greater depths compared with the surface layer (Salinas-Garcia et al. 2001).

Possible reasons for the differences in stratification of P with depth between conservation and conventional tillage are: (1) decreased contact of organic P fractions in crop residues with soil in conservation tillage systems (Follett and Peterson 1988), and (2) greater organic matter content in conservation- compared with conventional-tillage may increase inorganic P availability by saturating P adsorption sites on soil colloids (Schomberg et al. 1994). Similarly, total and inorganic soil N (ammonium + nitrate) in the surface soil can be significantly affected by tillage practices; with conservation tillage generally resulting in greater total and inorganic N than conventional tillage (Salinas-Garcia et al. 2001).

7.2.2.3
Nutrient Losses

There are some important differences in nutrient losses (especially N via volatilisation of NH_3, denitrification and leaching) when residues are left on the surface

in conservation tillage systems versus incorporation by conventional tillage, or burning. For example, conservation tillage will lead to higher soil organic matter content, higher soil water content and improved infiltration rate (Puget and Lal 2005). Consequently, crop residues with high decomposition rates (especially N-rich residues) may show increased losses of N through denitrification and leaching (Kumar and Goh 2000; Schomberg et al. 1994). Further, N immobilisation can be of greater magnitude and of longer duration in surface-located compared with incorporated crop residues with a relatively high C:N ratio (Schomberg et al. 1994). However, on the positive side, retaining residues on the surface through conservation tillage is important in reducing P losses, as this practice alleviates runoff and erosion losses (Basic et al. 2004; Lal 2005). Mixing residues with soil by tillage usually enhances their decomposition (see above), but soil cultivation during a fallow period or before planting the next crop could result in nitrate leaching or denitrification during rainy periods, or uptake by weeds (Salinas-Garcia et al. 2001).

A significant proportion of total plant K (ca. 80%) is usually located in residues. Thus the magnitude of K export from the field upon residue removal is likely to be quite high, and K deficiency may develop in crops grown on land where residues are removed (Du Preez et al. 1991; Whitbread et al. 2003). In Western Australia, Brennan et al. (2004) found increases in soil-extractable K under burnt swaths of windrowed canola residues compared with off-windrow areas. The K redistribution due to windrowing of crop residues is one of the main causes of poor growth off-windrow (K depletion) and good growth on-windrow (K enrichment) of subsequent cereal crops (Brennan et al. 2004). Similarly, incorporation of rice or wheat residues significantly increased the available K content in soil, but the increases were small relative to the amount of K contained in the residues, probably because of leaching of residue K in highly permeable coarse-textured soils (Yadvinder-Singh et al. 2004). Potassium is not present in plant tissues in any organic structures, therefore its release from residues is not dependent on residue decomposition. Hence, rain would wash K out of the residue and, at a time when there is no crop demand, would expose K to leaching losses in coarse-textured soils. This further highlights the need for residue management aimed at synchronising nutrient release from residues and nutrient uptake by subsequent crops.

7.2.2.4
Crop Residue Burning and Nutrient Cycling

Burning of residues is arguably the quickest way of releasing nutrients tied-up in crop residues, but can result in volatilisation loss of appreciable quantities of N, S, and, to some extent, P or even K at very high temperatures (Biederbeck et al. 1980; Boerner 1982; Raison 1979; Sharma and Mishra 2001). Nitrogen in organic matter is particularly sensitive to burning due to its low temperature of volatilisation (ca. 200 °C), but inorganic N tends to increase, becoming more

available in the soil surface after burning (Biederbeck et al. 1980; Raison 1979). This may be because of decreased microbial immobilisation of N resulting from a decrease in microbial activity and biomass following burning events (Biederbeck et al. 1980; Hoyle et al. 2006), and also due to deterioration in the quality of organic matter remaining after burning (González-Pérez et al. 2004). Similarly, following burning events, immobilisation of nutrients such as S and P by microorganisms would be expected to be reduced.

In situations where rapid microbial immobilisation of nutrients released from high C-to-nutrient ratio residues decreases their short-term availability (Bhupinderpal-Singh et al. 2006; Ocio et al. 1991), the reduction in nutrient immobilisation following residue burning could be useful for subsequent crops. In addition, significant proportions of P and K remain in the ash left on the soil surface (i.e. fertilisation effect) (Brennan et al. 2004; Du Preez et al. 2001; Kumar and Goh 2000; Yadvinder-Singh et al. 2005) because these nutrients are volatilised only at temperatures higher than those normally reached during burning of crop residues (Biederbeck et al. 1980; Rasmussen et al. 1986). Thus, the magnitude of nutrient loss during burning is influenced by the quality of residue burned and the intensity of the fire (Raison 1979). The nutrients (e.g. P, K) left in the ash are highly soluble (Khanna et al. 1996) and thus are readily available for crop uptake, as well as being prone to leaching, particularly because burning decreases the organic matter content and exchange capacity of surface soils (Raison 1979). As an indirect effect, the physical transport of nutrients off site can be related to fire intensity. Convective transport of ash varies from 1% in low intensity fires to 11% in high intensity fires (Neary et al. 1999).

7.2.3
Soil pH

Soil pH plays a major role in governing nutrient availability to plants. Increased use of fertiliser N in cropping systems, inclusion of legume crops in crop rotation and continuous cultivation over many years have resulted in the development of acidic soils in many parts of the world, including Australia and New Zealand (Bolan and Hedley 2003; Tang and Rengel 2003).

The addition of plant materials to soil can cause soil pH to increase, decrease or remain unchanged (Bessho and Bell 1992; Yan et al. 1996; Tang and Yu 1999; Xu et al. 2002, 2006). Often, there is an initial increase in pH over the first 1 or 2 months of residue decomposition followed by a decline (Bessho and Bell 1992; Hoyt and Turner 1975; Marschner and Noble 2000; Yan et al. 1996). The direction and extent of soil pH change depends on the concentrations of excess base cations, organic anions and N in plant materials, the initial pH level of the soil (Tang and Yu 1999; Xu and Coventry 2003), ammonification of plant residue-N, nitrification of ammonium, and leaching of nitrate-N (Xu et al. 2002). The magnitude of the change in soil pH also varies depending on plant residue application rate and the buffering capacity of the soil (Haynes and Mokolobate

2001; Noble et al. 1996). Generally, increases in soil pH following plant residue addition occur when initial soil pH values are lower than those of plant residues or when the amended soil is acidic (Pocknee and Sumner 1997; Tang and Yu 1999). In soils with pH values greater than those of residues (neutral or alkaline soils), added plant materials can decrease soil pH (Tang and Yu 1999).

The major causes of soil pH increase when plant residues are returned to soil are (1) decarboxylation of organic anions causing consumption of protons and release of OH^-, (2) specific adsorption of organic molecules produced during decomposition onto Al and Fe hydrous oxides with the consequent release of OH^- ions, and (3) high concentration of excess base cations such as Ca, Mg, Na (or ash alkalinity) in plants (Haynes and Mokolobate 2001; Tang and Rengel 2003; Wong and Swift 2003; Xu and Coventry 2003, Xu et al. 2002). Ammonification of residue-N (causing consumption of H^+) may not increase soil pH if accompanied by strong nitrification (causing release of $2H^+$) (Haynes and Mokolobate 2001).

Excess base cation content or ash alkalinity determines the liming potential of plant materials (Noble et al. 1996; Pocknee and Sumner 1997; Tang et al. 1999; Tang and Rengel 2003); this causes a longer-term pH increase following a similar, but transient, increase in pH as a result of ammonification (Wong and Swift 2003). The rate of ammonification of organic N depends on the C:N and lignin:N (or lignin+polyphenol:N) ratios of plant materials (Wong and Swift 2003). The capacity of different plant species to accumulate organic anions (e.g. legumes accumulate greater amounts than grasses) (Mengel and Steffens 1982) will have a strong effect on the magnitude of changes in soil pH upon residue incorporation into soil (Bessho and Bell 1992; Tang et al. 1999; Xu and Coventry 2003; Yan and Schubert 2000). Burnt plant residues add ash alkalinity directly into the soil as Ca, Mg, K and Na oxides, hydroxides and carbonates (Kumar and Goh 2000; Xu et al. 2002) and can be an effective source of soluble alkalinity that can move rapidly down the soil profile to ameliorate soil acidity (Brennan et al. 2004; Raison 1979; Yan and Schubert 2000).

In field experiments, it may be difficult to single out changes in soil pH due to residue management alone because of the small direct effect on soil pH, as soil pH change can also be influenced by lime or fertiliser application, crop rotation, or tillage (Schomberg et al. 1994; Xu et al. 2002). The effect of crop residue management and tillage practices on soil pH can often be more pronounced in the surface soil (e.g. 0–10 cm depth) than at greater depths (Chan et al. 1992; Xu et al. 2002). Conventional tillage can decrease soil pH considerably compared with direct drilling; this may be due to mixing of the soil, with more acidic deep soil layers rich in exchangeable aluminium being brought up to nearer the surface (Chan et al. 1992). Furthermore, N_2 fixation via inclusion of legumes (e.g. lupin) in crop rotation and N fertilisation can substantially decrease soil pH, whereas such decreases can be at least partially offset where crop residue is burnt or retained (Xu et al. 2002). Compared with conventional tillage, no-till or minimum tillage treatment can maintain a significantly higher level of exchangeable Ca due to the indirect effect on increased exchange capacity associated with higher organic matter content and/or decreased erosion (Schomberg et al. 1994). Moreover, soil pH can be higher upon residue burning than if resi-

dues are retained (Chan et al. 1992). Recently, Brennan et al. (2004) found an increase in soil pH (of 0.3–0.8 units), and a decrease in extractable aluminium (of 1–6 mg kg^{-1}), in parts of the field where canola was windrowed, trashed and residues burnt compared with off-windrow areas. These changes in pH and Al are likely to contribute to waves of good wheat and barley growth on windrows and poor growth off-windrows on acidic sandy soils following burning of windrowed canola residues.

7.3
Effects of Crop Residue Management on Soil Physical Properties

7.3.1
Soil Temperature

Crop residue management can cause significant changes in soil temperature by affecting radiant energy balance (Horton et al. 1994). Crop residue cover on the soil surface provides an insulation effect, which varies depending on the amount and thickness of residue cover (Unger 1978). Further, bare soil (residue removed) dries more rapidly than mulched soil after rainfall or irrigation (Bristow 1988). In wet conditions, the insulating properties of surface residue cover cause a decrease in temperature and temperature fluctuations, compared with bare soil (Bristow 1988; Horton et al. 1994; Unger 1978).

Burning plant residues can cause significant changes in soil temperature, depending on parameters such as thickness of the organic layer, fire duration and intensity, soil moisture, soil texture, soil mineralogy and organic matter content (González-Pérez et al. 2004; Raison 1979). Forest fire events can be of much longer duration and the burn temperatures can be higher (up to 1,000 °C) compared with crop residue burns (<500 °C for <10–15 min at most) (Biederbeck et al. 1980; Rasmussen et al. 1986). Maximum air temperatures may not occur near the soil surface but at a variable height above the point of burn (Rasmussen et al. 1986). Changes in soil surface temperature are highly variable (120–400 °C) depending on the extent of burning. Moreover, heat from crop residue burning seldom reaches more than 1–2.5 cm below the soil surface (Biederbeck et al. 1980; Rasmussen et al. 1986).

Heat transfer in soil occurs mainly by thermal conductance, with conductivity increasing with moisture content; thus, heating of dry soil can cause a greater rise in surface temperatures, but less penetration of heat, compared with moist soil (Raison 1979). Transfer of heat to different depths in soil after fire events is perhaps the main mechanism by which burning differentially affects physical, chemical and biological soil properties (Biederbeck et al. 1980; Valzano et al. 1997).

7.3.2
Soil Moisture

Crop residues placed on the soil surface reduce water loss by evaporation due to their mulching effect (Munawar et al. 1990). Thus, one of the major advantages associated with conservation tillage systems where residue is retained (compared with conventional tillage or system in which residues are burnt) is the greater availability of soil water, especially in years with low rainfall (Chan and Heenan 1996), thus leading to its popularity in rain-fed agriculture in semi-arid climates (Bescansa et al. 2005). Even in soils in colder regions (Canada), Diiwu et al. (1998) found higher available water content under direct drilling versus conventional tillage. According to Bescansa et al. (2005), the higher soil water content found under conservation tillage than under conventional tillage cannot be attributed solely to the mulching effect of residues, but may also be due to the absence of the effect of mild fires and fires of shorter duration on existing soil moisture and other related soil physical properties (Valzano et al. 1997). However, the other potential factor (in addition to the mulching effect) resulting in higher soil water and available water content may be the favourable changes in pore-size distribution in untilled or minimum-tilled soil compared with conventionally cultivated soil (Bescansa et al. 2005; Chan et al. 2003).

7.3.3
Soil Hydraulic Conductivity and Infiltration

High saturated hydraulic conductivity is important for transporting water from the soil surface to deeper layers during rainfall or irrigation, thereby decreasing runoff/erosion and improving soil aeration in the upper part of the profile. Significantly higher hydraulic conductivity and surface infiltration rates were measured where residues were left on the surface in no-till/minimum-tillage compared with where residues were burnt or removed (Chan and Heenan 1993; Valzano et al. 1997; Zeleke et al. 2004). These effects of crop residues in conservation tillage are likely to be the result of increased soil organic matter content, macro- and total-porosity and/or pore continuity, proportion of microaggregates and aggregate stability, and, on the other hand, decreased bulk density (Chan et al. 2003). Unsaturated hydraulic conductivity is important for water movement to roots as the soil dries; it may also be improved by increasing soil organic matter content (Khaleel et al. 1981).

In the case of residue burning, soil hydraulic properties can be adversely affected by decreased soil porosity (Biederbeck et al. 1980; Chan and Heenan 1993), possibly due to blockage of soil macropores by fine ash particles (Valzano et al. 1997).

7.3.4
Soil Bulk Density and Porosity

Increasing soil organic matter content through continuous return of crop residues to soil may decrease bulk density (Shaver et al. 2002; Zeleke et al. 2004), as a result of 'dilution' of the dense mineral fraction of soil. Roseberg and McCoy (1992) found that tillage increased total porosity, but that macropores (pores that allow rapid infiltration) decreased in number, stability and continuity compared with the no-till soil. Dao (1996) found that conventional tillage initially decreased bulk density, probably by loosening the soil and thus temporarily forming macropores at the beginning of the season (Karunatilake and van Es 2002), but no-till had a lower bulk density than conventional methods by the end of the growing season because of its positive effect on soil organic matter content and soil aggregation (see below).

Zeleka et al. (2004) found a significant decrease in bulk density, an increase in macro- plus meso-porosity, and a decrease in penetration and shear resistance in systems where maize residues were incorporated annually over 3 years than where residues were removed. This is probably due to the increased organic matter input and reduced exposure of the soil to raindrop impact, which can cause soil compaction (Mapa et al. 1986). Removal of crop residues by burning can also increase soil bulk density (Biederbeck et al. 1980) by altering soil structure and decreasing organic matter levels, but inconsistent effects of burning residues on soil bulk density are also reported (Bescansa et al. 2005; Biederbeck et al. 1980; Valzano et al. 1997).

7.3.5
Soil Aggregation and Soil Structure

Soil organic matter binds soil particles into aggregates. Thus, any changes in organic matter content in soil due to crop residue management will affect formation and stabilisation of soil aggregates and consequently soil structural stability (Graham et al. 2002; Loveland and Webb 2003; Paustian et al. 1997; Six et al. 1999, 2000). Easily decomposable plant residues (e.g. legume residues) provide transient aggregate-stabilising agents, whereas slow decomposable residues (e.g. cereals) provide longer-lasting aggregate-stabilising agents (Elliott and Lynch 1984; Loveland and Webb 2003). Fungal hyphae and extracellular polysaccharides are capable of linking soil particles together (Beare et al. 1997; Puget et al. 1999; Tisdall and Oades 1982), and are found in greater densities in conservation tillage than in conventional tillage systems (Frey et al. 1999; Prove et al. 1990). Total organic matter in soil is usually less well correlated with aggregate stability as opposed to the content of labile organic matter, such as particulate

organic C (Chan et al. 2002; Loveland and Webb 2003; Tisdall and Oades 1982). Furthermore, the soil concentration of glomalin, a glycoprotein produced by arbuscular mycorrhizal fungi, correlates well with the percentage of s (Rillig et al. 2002).

Conventional tillage generally reduces aggregation and increases turnover (i.e. rate of formation and degradation) of macroaggregates compared with conservation tillage, thereby resulting in an overall loss of protected organic C in soil (Six et al. 1999, 2000; Tisdall and Oades 1982; Wright and Hons 2004). According to Six et al. (1999), a slower turnover rate of macroaggregates in conservation tillage compared with conventional tillage leads to a faster rate of new microaggregate formation within macroaggregates and greater stabilisation of new organic matter (mineral-associated C and intra-aggregate particulate organic matter) in these new microaggregates.

Burning crop residues can significantly decrease the content of soil polysaccharides and the percentage of water-stable aggregates compared with residue-retained systems (Biederbeck et al. 1980; Dormaar et al. 1979), thereby increasing the susceptibility of the soil to water erosion (see below). In a study by Valzano et al. (1997), low-intensity fire had no effect on soil aggregate stability or clay dispersion in comparison with the unburnt treatment, which was probably due to a lack of differences in moisture and organic C content between burnt and unburnt plots in their study.

7.3.6
Soil Erosion

Application of crop residues to soil minimises soil surface erosion (Michels et al. 1995) because a surface cover protects soil aggregates from raindrop impact. Thus, compared to tillage, no-tillage can effectively conserve soils, especially on sloping land (Basic et al. 2004). Increased soil aggregate and structural stability under conservation tillage systems can also reduce soil erosion (Graham et al. 2002; Paustian et al. 1997; Six et al. 1999, 2000). Retaining increasing amounts of crop residues on the soil surface may decrease soil loss caused by wind erosion (Michels et al. 1995).

The amount of crop residues necessary to control soil erosion will depend on soil erodibility, rainfall erosivity, terrain characteristics, tillage and crop management practices (Basic et al. 2004; Lindstrom et al. 1990). Some studies have suggested that crop residues can be partially removed for other purposes (e.g. for biofuel production) if soil erosion control is the only objective of residue retention (Nelson 2002; Sheehan et al. 2004). However, Lal (2005) argued that even a partial removal (30–40%) of crop residues could exacerbate the soil erosion hazard, deplete soil organic carbon, and accentuate emission of CO_2 and other greenhouse gases from the soil.

7.3.7
Water Repellence of Soil

Accumulation of significant amounts of organic carbon can induce water repellency in soil (Harper et al. 2000). This could be of concern in conservation tillage systems as these usually lead to the accumulation of organic matter at, and immediately under, the soil surface (Chan 1992). Cultivation can decrease water repellence by both mixing and enhancing mineralisation of organic matter (Chan 1992). For duplex soils (i.e. sand over clay), deep cultivation may increase the clay content of the topsoil by mixing clayey materials from deeper soil layers, thereby reducing water repellence (Harper et al. 2000). Water repellence can also be a function of the type of soil organic matter (Capriel et al. 1995). Water-repellent alkyl C plays an important role in longer-lasting stabilisation of soil aggregates (Piccolo and Mbagwu 1999) and hence in sequestration of C in soil.

   Intense burns may induce or enhance water repellency in soils by inducing the movement of hydrophobic substances in plant residues deeper into the soil profile (DeBano et al. 1976), where they then coat soil particles or aggregates, thereby leading to a decline in soil hydraulic properties due to formation of a discrete water-repellent soil layer (García-Corona et al. 2004; Savage 1974). Water-repellent soil layers can be formed at fire temperatures between 176 and 288 °C and are destroyed at >288 °C (Neary et al. 1999). Valzano et al. (1997) did not find fire-induced water repellence and thus ruled it out as a factor affecting soil hydraulic properties. This is probably because burning of crop residues does not usually generate sufficiently high temperatures for the formation of a water-repellent soil layer (Biederbeck et al. 1980; Valzano et al. 1997). Hence, the observation that burning of crop residues did not affect a range of physical and chemical properties was not surprising (Biederbeck et al. 1980).

7.4
Effects of Crop Residue Management on Soil Biological Properties

The way crop residues are managed on agricultural fields can significantly affect biomass, activity, and composition of micro- and macro-organisms and their functions by altering the supply of carbon and other nutrients, and the physico-chemical characteristics of the soil environment (Kumar and Goh 2000; Roper and Gupta 1995). Microorganisms include bacteria, fungi, algae and protozoa; mesofauna include nematodes; and macrofauna include earthworms, arthropods and termites (Roper and Gupta 1995). In this section, we provide a brief overview of the responses of soil biota to crop residue management practices with particular emphasis on microbial biomass, activity, and microbial commu-

nity structure, composition and function. Detailed reviews on the effect of plant residue management on soil biota and soil biological properties can be found elsewhere (Cochran et al. 1994; Holland 2004; Pankhurst et al. 1997; Roper and Gupta 1995).

7.4.1
Soil Microorganisms

7.4.1.1
Microbial Properties as Sensitive Indicators of Soil Health

Microbial biomass represents only a small proportion (1–5%) of the total C, N, S and P pool of organic matter in arable soils (Balota et al. 2003; Brookes et al. 1984; Chapman 1997; Wu et al. 1993). However, microorganisms are key players in the decomposition of organic residues and thus in cycling of N, S and P (Balota et al. 2003; Pankhurst et al. 1997). Microorganisms can also act as direct sources and sinks for nutrients (Singh et al. 1989), with gross turnover time of microbial biomass C and N estimated at 1–2 years (Jenkinson and Ladd 1981). Because microorganisms are a living component, with a high surface-to-volume ratio, they respond more rapidly to changing soil conditions than the soil organic matter as a whole. In some instances, changes in microbial biomass or activity caused by changes in crop residue management precede detectable changes in soil physical and chemical properties (Graham et al. 2002; Gupta et al. 1994; Kushwaha et al. 2000; Pankhurst et al. 1995, 2002; Spedding et al. 2004). In addition to their effect on nutrient cycling, microorganisms affect the physical properties of the soil by producing extracellular polysaccharides and other cellular debris involved in maintaining soil structure by acting as cementing agents that stabilise soil aggregates (Puget et al. 1999; Rice et al. 2004).

For many of the above characteristics, a change in the microbial biomass provides an early sign of soil fertility, with biomass increase indicating improvement, whereas a biomass decrease suggests soil degradation (Kushwaha et al. 2000; Pankhurst et al. 1995; Syers 1997). However, microbial biomass measurements using traditional methods (fumigation-extraction, fumigation-incubation) provide no information about qualitative community-level changes (e.g. fungal-to-bacterial ratio, biodiversity, occurrence of key species) and do not indicate the activity of microorganisms in soil. Fatty acid methyl ester (FAME) analysis can be used to assess microbial community structure, whereas soil respiration (basal respiration or substrate induced respiration (SIR) provides information about microbial activity (Beare 1997; Frey et al. 1999; Spedding et al. 2004).

Microbial properties of the surface soil (microbial C and N, respiration, metabolic quotient, and the ratio of fungal-to-bacterial fatty acids) can respond within 1–3 years to changes in crop residue management in warm climates (e.g.

Gupta et al. 1994; Kushwaha et al. 2000; Pankhurst et al. 2002). Some studies from high altitude locations, however, found slower (>4 years) or no response of microbial properties to changes in management (Carter and Rennie 1982; Cochran et al. 1989), indicating that, in addition to crop residue management and tillage practices, local/regional climatic conditions can also play a role in governing soil microbial properties (Cochran et al. 1994).

Conservation tillage generally leads to increased soil organic matter (see Sect. 7.2.1), microbial biomass, and microbial activity near the soil surface (Balota et al. 2003; Gupta et al. 1994; Roper and Gupta 1995; Spedding et al. 2004). In contrast, incorporation of crop residues into soil by tillage can result in a more even distribution of microbial substrates and associated nutrients throughout the ploughed layer (Gupta et al. 1994; Holland and Coleman 1987; Salinas-Garcia et al. 2001; Spedding et al. 2004). Crop residue removal causes significant decreases in soil microbial biomass compared with residue retention (Salinas-Garcia et al. 2001). Conservation tillage, in contrast to conventional tillage systems, sustains significantly higher microbial biomass C in the long term, and increases the proportion of microbial biomass C in total soil organic C (Balota et al. 2003). The wider microbial C:N and C:P ratios recorded under no-till than under conventional tillage (Balota et al. 2003) suggest preferential growth of fungi rather than bacteria under reduced soil disturbance (Wardle 1995).

7.4.1.2
Functional Groups of Microorganisms

Different tillage and residue management practices influence the diversity of soil biota and therefore alter nutrient cycling in soils (Frey et al. 1999; Lee and Pankhurst 1992; Roper and Gupta 1995; Spedding et al. 2004). Tillage leads to the development of soil microbial communities dominated by aerobic microorganisms with high metabolic rates, typically bacteria, whereas, under conservation practices, plant residues left at or near the soil surface encourage fungal growth and temporary immobilisation of nutrients (Balota et al. 2003; Beare et al. 1997; Frey et al. 1999; Pankhurst et al. 2002). Fungal-to-bacterial ratios are usually greater (3:1 versus 1:1) under residue retained/no-till systems than under residue burned/removed and cultivated systems (Roper and Gupta 1995), because there is less damage to fungal hyphae due to little soil disturbance. Rice et al. (2004) argued that greater fungal density would contribute to the high C sequestration usually noticed in conservation tillage systems because of the higher C-use efficiency of fungi compared to bacteria.

Besides responding to crop residue management practices, the populations of various functional groups of soil microorganisms (e.g. nitrifying and denitrifying bacteria, aerobic and anaerobic bacteria, cellulolytic bacteria and fungi) can fluctuate greatly in response to biotic and abiotic soil factors (Cochran et al.

1994; Drijber et al. 2000; Feng et al. 2003; Lee and Pankhurst 1992; Pankhurst et al. 1995). For example, increases in numbers of denitrifying bacteria occur due to greater C addition from residue retention as well as the greater soil water content under this management (Doran 1980). Changes in biomass, activity, and composition of microbial populations in response to changes in residue management practices are most pronounced during a fallow period or at the start of the growing season (Drijber et al. 2000; Feng et al. 2003). During a crop growth period, root C input from the standing crop and associated changes in soil environmental conditions may confound interpretation of the effect of tillage/residue management alone on soil microbial parameters. A better understanding of how management systems, crop root inputs, and the resulting biotic and abiotic changes in soil conditions, influence soil biological parameters will determine their usefulness as indicators of soil health (Feng et al. 2003; Pankhurst et al. 1995).

Soils with residues retained and no-till management contain higher densities of bacterial- and fungal-feeding protozoa and nematodes than residue-burnt or residue-incorporated soils (Hendrix et al. 1986; Pankhurst et al. 1995; Roper and Gupta 1995). By altering the proportion of fungal-to-bacterial biomass in soil and modifying the soil environment, residue management practices may indirectly affect the numbers of protozoa and nematodes feeding on bacteria or fungi (Cochran et al. 1994; Roper and Gupta 1995).

7.4.1.3
Crop Residue Quality and Microbial Populations

The quality of crop residues returned to soil can influence microbial populations and their composition (Wardle and Lavelle 1997). For example, lupin residue favoured development of higher numbers of cellulolytic bacteria, whereas cereal straw supported greater numbers of cellulolytic fungi (Eitminaviciute et al. 1976), probably due to the greater ability of fungi to decompose residues with low N content (Burns 1982). Furthermore, crop residues containing mainly easily decomposable compounds and less lignin may favour rapid colonisation by species of "sugar" fungi (Griffiths et al. 1999; Salas et al. 2003), in addition to greater colonisation by bacteria (Cookson et al. 1998). Repeated addition of residues (especially with high lignin-to-N ratio) may allow prior conditioning of soil microbial community to specific residue types or to their recalcitrant chemical constituents. For example, Cookson et al. (1998) reported greater residue-induced microbial activity, residue decomposition rates, and higher densities of bacteria and fungi on newly added wheat residues recovered after 90 days from field plots that had been managed previously by incorporation of wheat straw for up to 3 years compared with plots where wheat straw had been burnt or removed.

7.4.1.4
Effect of Burning of Crop Residues on Microbial Properties

Burning or removal of residues can decrease microbial biomass and microbial activity (measured as basal soil respiration) compared with soils where crop residues are returned to the soil (Biederbeck et al. 1980; Gupta et al. 1994; Hoyle et al. 2006; Rasmussen et al. 1980). Microbial activity in soil would decrease due to rapid removal of substrates upon burning, especially the labile organic fractions (Biederbeck et al. 1980; Val'kov et al. 1996). The remaining burnt organic residues may not be a suitable energy source for microorganisms because of increased chemical recalcitrance (González-Pérez et al. 2004).

In general, bacteria are more tolerant to heat than fungi (Dunn et al. 1979; Raison 1979). During burning events, soil microorganisms (non-spore forming fungi and some bacteria) exposed to temperatures of 70 °C (for 10 min duration) can be killed; temperatures above 127 °C sterilise soil (Raison 1979). Therefore, the extent of microbial death will depend on the intensity and duration of burning. In the short-term, crop residue burns can cause a drastic reduction in soil microbial biomass (Biederbeck et al. 1980; Val'kov et al. 1996), but may temporarily increase soil respiration rates (microbial activity) above those at unburnt sites, primarily due to the immediate availability of labile substrates from the dead microorganisms (Biederbeck et al. 1980). A single straw burn resulted in immediate decreases in fungal and bacterial densities of 95% and 70%, respectively, in the top 1 cm of soil, but there was no effect of burning on microflora at a depth of 1–4 cm (Biederbeck et al. 1980). In repeatedly burnt sites, Biederbeck et al. (1980) found permanent decreases in bacterial density (by >50%) and biological activity in the top 2.5 cm of soil compared with sites where straw was incorporated; however, the fungal density appeared to recover with time.

7.4.2
Soil Meso- and Macro-fauna

Meso- and macro-fauna play a prominent role in organic matter decomposition and nutrient cycling through indirect effects such as comminuting crop residues, their mixing with soil, and grazing on decomposers (Cochran et al. 1994). Populations of soil microarthropods such as collembolas feeding on fungi (Pankhurst et al. 1995), mites (House and Parmelle 1985) and earthworms (Chan and Heenan 1995; Doube et al. 1994; House and Parmelle 1985; Pankhurst et al. 1995) can be higher under no-till and/or residue-retained systems compared with conventional cultivation. Moreover, standing stubble versus residues in close contact with soil can affect the numbers, size and biomass of macroorganisms such as earthworms (Doube et al. 1994).

Crop residue quality may have different effects on soil faunal populations (Van Vliet et al. 2000; Wardle and Lavelle 1997). Hendrikson (1990) found that

earthworms prefer plant material with a low C:N ratio and low lignin (polyphenol) content. In a field study using lupin or wheat residues placed in litterbags on soil surface, Van Vliet et al. (2000) found that soil fauna (microarthropods) colonised lupin residues earlier than wheat residues, and prostigmatic mites were found in higher numbers on wheat residues, whereas collembolas were the most abundant microarthropods on lupin residues.

Burning crop residues can adversely affect the density and activity of macro-organisms (Doube et al. 1994). Val'kov et al. (1996) found an immediate decrease in the density of soil fauna (mites, collembola) in the topsoil following burning of barley residues. Doube et al. (1994) reported smaller adult earthworms, a lower density of cocoons, and a lower mean number of cocoons per adult in plots where crop residue was burnt compared with direct-drilled unburnt plots.

7.5
Conclusions

Considerable quantities of fertilisers can be saved by returning nutrients stored in crop residues, which need to be managed in synchronisation with crop demand and also to minimise leaching. Retention of crop residues on the soil surface (e.g. in conservation tillage systems) not only reduces runoff and soil erosion, but also improves soil physical characteristics (such as hydraulic properties and soil aggregation) and increases soil organic matter content, especially in the surface layer. Additionally, increases in soil microbial biomass and activity following crop residues addition can improve the nutrient-supplying capacity of soil and reduce nutrient losses. Incorporation of crop residues by conventional means (e.g. tillage) may enhance organic matter decomposition compared with conservation tillage systems, thereby making nutrients prone to losses (via leaching, volatilisation and denitrification), if release of nutrients is not matched with crop demand.

Short-term laboratory and field studies may have shown the potential of crop residues in ameliorating soil acidity; burning of crop residues can be more effective for this than other modes of residue management because burnt crop residues can directly (and rapidly) add ash alkalinity to soil from the oxidation of organic anions in residues. Burning of crop residues could also increase nutrient supply in the short term through decreasing microbial biomass and activity, thereby decreasing nutrient immobilisation. However, long-term burning of crop residues can accelerate soil erosion, adversely affect soil physical conditions, and enhance losses of soil organic matter and associated nutrients. The extent of such adverse effects will depend on the intensity and duration of crop residue burning and the soil properties.

Crop residue management practices and the quality and quantity of crop residues returned affect soil fertility through a series of chemical, physical and biological changes in the soil. Reliable indicators of changes in soil quality that

correlate well with critical aspects of soil physical, chemical and biological fertility could provide the basis for developing sustainable crop residue management strategies. For example, the dynamics of labile fractions of soil organic matter and changes in the composition and function of microbial populations could provide an early indication of changes in soil quality as a result of variation in crop residue management. However, labile pools may be too sensitive to other factors critical for productivity (such as environmental conditions) to allow changes to be ascribed solely to soil management.

Long-term studies are needed to evaluate sustainability of particular management practices, as increases in soil organic matter content and improvement of many other soil properties may become evident only after several decades, depending upon local climatic and edaphic conditions. Such long-term field studies, especially in warmer regions of the world, should be established and maintained at sites carefully selected for variations in temperature, moisture, soil mineralogy and agricultural residue management representing different cropping systems across regions.

In actual field situations, a complex array of interactions between soils, crop inputs, climate and types of management exists; therefore, accurate predictions of the effect of crop residue management on soil fertility and, ultimately, plant productivity will be possible through the development of realistic process-based simulation models. Controlled laboratory studies and many field studies have provided useful information on the effect of a range of plant (residue quality and quantity), soil (texture, soil moisture and temperature, nutrient availability), and management (tillage, management of crop residues) factors on soil organic matter, nutrient cycling (especially N), pH, and many biological and physical parameters of soil fertility. To make better use of information from controlled studies in simulation models, future studies should focus on the interactive influence of driving factors on various soil properties, with emphasis on further exploration of linkages between measured soil fertility parameters (see also Chapter 13 by de Willigen et al., this volume). Similar research initiatives should also be undertaken for nutrients other than N (such as P, S and micronutrients), for which there is only limited information. Only then will the potential benefits of crop residues for amelioration of degrading soil fertility be fully realised.

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8 Nutrient Cycling Budgets in Managed Pastures

David Scholefield, Elaine Jewkes, Roland Bol

8.1
Introduction

About 53 million km², or 40% of the Earth's land surface is grassland, containing about one-third of the global stock of terrestrial C. Grasslands are ecosystems where the dominant vegetation component is comprised of herbaceous species, with less than 10% tree cover (Jones and Donnelly 2004). Grasslands are either natural vegetation (e.g. the steppes of central Asia and prairies of North America) or anthropogenic in origin (e.g. north-western and central Europe, New Zealand, parts of North and South America and Australia). Grasslands are heavily relied upon for food and forage production, and about one-third of world milk and beef production occurs on grassland managed solely for these purposes (Conant et al. 2001).

It is predicted that over the next 30 years or so, global food production will need to rise by about 60% to feed the world population of 8,000 million and to meet an increased preference for meat and milk products (FAO 2005). Much of this increase is expected to come from developing countries in a so-called 'livestock revolution', where demand for meat and milk is growing much faster than in the developed countries (Delgado 2005; Sims et al. 2005). Thus, by 2020, it has been calculated that developing countries will consume 72 million tonnes (Mt) more meat and 152 Mt more milk per year compared to 2002/2003, whereas in the developed countries only 9 Mt and 18 Mt more meat and milk, respectively, will be consumed. A substantial proportion of this increased demand will be

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met by ruminant production. The extra productivity required in the developing countries will be achieved by increased inputs of nutrients to pastures and to support the growth of feed crops, increased efficiency of nutrient use and, to a lesser extent, increased area of managed agricultural land (FAO 2003).

Unfortunately however, as the inputs of nutrients to pasture and crop plants are increased, the efficiency with which they are used generally decreases. Consequently, in the developed countries, particularly on dairy farms in many regions of Western Europe, the United States, Australasia and Japan, the pursuit of the highest economically sustainable yields has resulted in increased incidence of losses of nutrient elements to drainage waters and to the atmosphere at levels considered detrimental to the environment. Nutrient enrichment of surface waters, especially with nitrogen (N) and phosphorus (P) compounds is found to cause eutrophication and a reduction in biological diversity, while increased emission of ammonia (NH_3) leads to acidification and nutrient enrichment of sensitive terrestrial and aquatic ecosystems. Emissions of carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O) enhance the greenhouse effect and, in the case of N_2O, destroy stratospheric ozone (O_3). Thus, productive grasslands are no longer thought of as environmentally benign, especially where high stocking rates are employed and the storage and disposal of large amounts of manures are necessary.

Much research has been conducted during the last 20 years in order to understand the complex mechanisms underlying the cycles of the main nutrient elements C, N, P, K, and S, and their interactions in controlling the economic and environmental sustainability of grassland farming systems. Many approaches to assess and compare nutrient-use efficiency and the sustainability of systems have been developed, ranging from the synthesis and use of detailed mathematical models to simple diagnostic tests of the nutrient content of soil, plant and animal components. The nutrient input-output budget has been identified as one of the most useful of these approaches. It is clear from the recent literature (e.g. Oenema et al. 2003; see also Chapter 13 by de Willigen et al., this volume) that budgets are being calculated and used for a number of purposes, from creating awareness about efficiency of nutrient use, to forming the basis of definition and implementation of environmental policy through legislation (Schröder et al. 2003).

In this chapter, we review the literature on nutrient budgets (Sects. 8.1, 8.2) and establish what a budget can tell us about nutrient flows in pasture systems. In doing so, we consider the efficiencies of nutrient flows through the various components of the pasture system (Sect. 8.3) and the general effects of management and site conditions on these efficiencies (Sect. 8.4). Through analysis of nutrient surplus data for some typical European pasture systems, we draw general conclusions about the potential of budget keeping to help achieve more sustainable pasture systems. In this context, the effects of the scale of the budget, the use of multiple nutrient budgets and, alternatively, the application of other systems diagnostics and nutrient cycling models are discussed. We also examine whether it is possible to identify sustainable systems from nutrient budgets alone, and if not, what ancillary information is required (Sect. 8.5) Finally, we

identify knowledge gaps and point to the future uses that nutrient budgets may have (Sect. 8.6).

8.2
Developments in Nutrient Budget Keeping

8.2.1
Nitrogen

Early research was mostly fragmented, with researchers and research groups concentrating on single nutrients and specific areas of expertise involving single system components and processes. In Europe, understanding the N cycle in grassland systems has been the focus of the largest research effort. Although this began with generation of the N fertiliser-yield response curves under cutting, on experimental plots with a range of sites and conditions (e.g. Morrison et al. 1980; Vellinga and Andre 1999), it was not until inclusion of the grazing animals and technical developments enabling field-scale assessment of N loss processes (e.g. Jarvis et al. 1989; Ryden 1986; Steenvoorden et al. 1986) that conceptual mass-balance models of the N flows through the whole system could be assembled (Field and Ball 1982; Long and Hall 1987). This advance led to the development of dynamic, predictive models, responsive to a range of N inputs and site conditions (e.g. NCYCLE – Scholefield et al. 1991; GRASMOD – van der Ven 1992; OVERSEER – Wheeler et al. 2003; see also Rotz et al. 2005). These models have enabled the efficiency of N-use in pasture systems to be thoroughly investigated.

Many potential strategies of improving the efficiency of N flows in pasture systems have now been identified (Scholefield 2004). These include improving the efficiency of flows through the different components by changing their inherent properties and the quality of inputs to them, tactical application of N inputs, application of nitrification inhibitors, balancing all nutrients and close-coupling to an arable cropping rotation in a mixed system. Because of the wide diversity of pasture systems, wide ranges of climates, weather patterns and the variability in farm management strategies, there is also a need to develop and apply 'real-time' assessment tools and tests of N-use efficiency on the farm. These could be termed 'integrating diagnostics' and include farmer-friendly tests for soil and plant N (Farruggia et al. 2004) and the calculation of annual N budgets. Such diagnostics may have the potential to enable short and longer-term audit of actual and potential N-use efficiency of the pasture to be made by the farmer to trigger management changes towards improved efficiency and compliance with indices of sustainability. Some, such as budget keeping, also provide a convenient vehicle for implementation of legislation on nutrient use by the policy maker (Schröder et al. 2003).

8.2.2
Phosphorus

In Western Europe, our understanding of the P cycle in pastures has lagged behind that of N, and it is only recently that mass balances for temperate systems have been assembled (Haygarth et al. 1998). However, in other grassland regions of the world, such as Australasia, where for many years P (not N) has been the dominant fertiliser input, both P availability for plant growth (e.g. Mackay et al. 1980) and P transport into surface waters (Sharpley and Syers 1976) have been well-studied since the 1970s. With the more recent work of Sharpley's group in the Unites States and Haygarth in the United Kingdom, the mechanisms determining P flows through the main system components and out either into saleable products or the aqueous environment have been better elucidated. However, the mass balance of P alone (unlike that of N) is not very useful for indicating fluxes and losses because of the diverse range of sources of plant-available P, the complexities of the mobilisation-immobilisation reactions and the high dependency of P transport 'events' on chance combinations of conditions. Nevertheless, at the river basin scale, export coefficient-based models have been developed and used successfully for predicting P loads in surface waters (Johnes 1996). Moreover, P balances are being assembled as a means of indicating potential for P loss and as a basis for legislation implementation (The MINAS system, Hanegraaf and Jan den Boer 2003).

8.2.3
Carbon

The fixation of C as CO_2 by plants provides the chemical energy and building materials for all life on earth but, despite its overwhelming importance, the C cycle in grazed pastures has not yet been accurately quantified, and simplified whole system C budgets and balances have only recently been compiled (e.g. Soussana et al. 2004). The C cycle in managed pastures has been researched for several reasons. The ability of a soil to supply nutrients, store water, release greenhouse gases, modify pollutants, resist physical degradation and produce crops is strongly affected by the quality and quantity of organic matter (OM) it contains (Carter 2001). However, the earlier focus was on the role of the pasture phase in ley-arable farming as a means to build-up soil OM for conferring structural stability (Tisdale and Oades 1980) and fertility for exploitation in subsequent arable cropping (Clement and Williams 1967; Scholefield and Smith 1996). Tyson et al. (1990) indicated that the potential for build-up of organic C under temperate pasture is considerable, with a mean annual accumulation under grazed grass/white clover pasture on a sandy loam soil of 1.0 t C ha^{-1} over the first 10 years.

A second focus has been the effects of grazing management on net canopy photosynthetic rate and consequent sward production (e.g. Baron et al. 2002;

Conant et al. 2003; King et al. 1984; Wilsey et al. 2002). The predominant current focus is assessment of the potential of grasslands to sequester atmospheric C to offset climate change (Follett and Schuman 2005; Franzluebbers 2005; Lynch et al. 2005; Rees et al. 2005; Smith 2004; Soussana et al. 2004). This involves consideration of not only the C balance itself, but also the potential impacts of the system (and system changes to bring about any increased C sequestration) on net fluxes of the greenhouse gases N_2O and CH_4 (Scholefield et al. 2005a; Smith et al. 2001). It is clear from this that the C cycle is intimately linked with those of the other nutrient elements, particularly the N cycle, such that for mechanistic interpretation of transformations and flows in one cycle, analogous information about the other is essential, a fact well recognised by modellers (e.g. The Hurley Pasture Model – Thornley and Verberne 1989; and DNDC − Li et al. 1992). There will be a limit to the effectiveness of the mere cross-referencing of budgets, however, and evidence is mounting that the chemical nature of the C compounds in pools and transfers will be required to explain some differences between the performances of systems relative to sustainability criteria defined by elemental nutrient budgets alone (McNeill et al. 2005).

8.2.4
Potassium

Much less attention has been paid to the cycles of K and S and of micronutrients compared with those of N, P and C. Potassium has recently been recognised as the 'forgotten nutrient element' (Oborn et al 2005), despite its strong biochemical linkage with N in the plant (Nowakowski and Byers 1972). Certainly, K fertiliser application rates to pastures in most European countries have been reducing steadily during the last 20 years (Oborn et al. 2005), as farmers have sought to economise inputs as a means to maintain incomes. Potassium reserves in clay soils may be enormous, yet, despite leaching losses being generally quite small (e.g. Alfaro et al. 2003), limited K supply from slow rates of mineral weathering and strong fixation on exchange sites must be supplemented by inorganic fertiliser to maintain the levels of herbage production required in intensive livestock systems. Fertiliser input to maintain K balance is even more important on sandy and OM-rich soils, where mineral reserves and exchange reservoirs are lower and leaching may be greater. In situations where fertiliser application is restricted either due to cost, for example in developing countries, or due to policy as with organic livestock production (Cuttle and Bowling 1999; Watson et al. 2002), K supply can become critical to the sustainability of the system. On the other hand, over-supply of K fertilisers to a grazed pasture on K-rich soil can lead to luxury uptake by the forage plant and depression of Ca and Mg capture by the animal, with consequent negative effects on animal health.

The value of calculating and applying K budgets to avoid under- or over-supply and in relation to optimising the efficiency of N use has been pointed out in several recent reviews (Kayser and Isselstein 2005; Oborn et al. 2005). Williams

and Haynes (1992) report modelled K losses from New Zealand pastures, calculated using a simple mass-balance approach, and concluded that a great proportion of total losses was due directly to the dairy cow through product removal, transfer of excreta to unproductive areas and preferential flow of urine to below rooting depth. Their model provided the basis for K fertiliser recommendations. Another method of calculating long-term trends in K budgets was reported by Garwood et al. (1999), who correlated survey data of fertiliser practice with agricultural statistics from the national census to compile a 29-year run of annual K surplus values for United Kingdom grassland systems.

8.2.5
Sulphur

Sulphur is a constituent of proteins and is involved in the biochemistry of electron transport. Sulphur deficiency can be a problem in situations with high N input on sandy soils, because leaching losses as SO_4^{2-} can be high (Close and Woods 1986; Till and May 1971). Much early work on the agronomy of S use in pasture systems was conducted in Australasia (Till and May 1971); annual S budgets for sheep systems were compiled as early as the 1960s in New Zealand (Williams and Haynes 1992), and in the 1980s in the United Kingdom (Bristow and Garwood 1984). These budgets demonstrated the impacts of grazing animals on increasing S losses from the system and the need to balance these losses with fertiliser inputs to avoid forage yield reductions. Several forms of S fertiliser have been used for this purpose throughout the world, including elemental S, reduced organic forms and sulphate, but in the industrial areas of Western Europe, until recently, much of the S requirement of forage plants has been met from atmospheric deposition from the emissions from burning fossil fuels. Now that this source has been much reduced in response to environmental pressures, the S budget will regain its former importance as a guide for maintenance of forage yields through application of S fertilisers.

Since the realisation that S deficiency, especially on sandy soils, can drastically reduce the efficiency with which N is used in grassland (Brown et al. 2000), farmers and fertiliser companies alike have become much more aware of the need to maintain soil S status, and S-containing N fertilisers have recently been formulated. In addition, there are several important interactions of S with other nutrients that may take place within one or several of the key system components (soil, plant and animal). These include, for example, interactions with Cu and Se (Murphy and Quirke 1997) affecting animal health, with P sorption-desorption and lime on certain soil types (Bolan and Rajan 1993; Pardo and Guadalix 1990) and with C in mineralisation of S from manures (e.g. Williams and Haynes 1993). There are two deleterious environmental impacts related to S cycling and the pasture S budget. One is the well-known acidification of streams and lakes due to deposition of SO_2^- from upwind industrial point sources and due to leaching from acid sulphate soils after disturbance (e.g. Powell and Mar-

tens 2005). The other is less well appreciated: the newly discovered substantial emissions of dimethyl sulphide from the breath and slurry of dairy cattle (Hobbs et al. 2004). This compound is a potent acidic particle-former and is involved in the formation and destruction of tropospheric O_3.

8.2.6
Other Nutrients

Recognition by agricultural scientists of the importance of Mg, Ca and Cl and the micronutrients Fe, Mn, Zn, Cu, B, Mo, Ni, Co, I and Se for plant and animal health and growth rate was reported in the literature during the early years of the last century (cited in e.g. Donald and Prescott 1975). An appropriate model for 'sustainable' nutrient management within a whole pasture system was (and still is) provided by the response of the organism (plant or animal) to incremental additions of an essential micronutrient: too little and growth is retarded; just sufficient and growth is optimal; but excess may lead to death from toxic effects. However, few micronutrient budgets have been calculated for intensive European pasture systems (Goodlass et al. 2003; see also Chapter 4 by Rengel, this volume), except for specific purposes (Haygarth et al. 1991). Most concerns about maintaining micronutrients in positive balance have been expressed from countries with inherently deficient soils, such as Australia and New Zealand (see Donald and Prescott 1975) and for extensive (Khan et al. 2004), organic, and 'biodynamic' systems (e.g. Condron et al. 2000). Micronutrient budgets are difficult to interpret due to the many interactions between micronutrients themselves (e.g. Mo-induced Cu deficiency in animals) and with macronutrients (e.g. Mg interaction with P). In addition, there are many other factors that cause variability through space and time in the plant availability of any given micronutrient supplied at a given rate to the soil (Condron et al. 2000; Fageria et al 2002). These include reactions with soil colloids (clays and organic matter), ingestion of soil by grazing animals, sward botanical composition, diet selection, soil temperature and pH. Consequently, large differences in uptake due to management, plant species and location (Hopkins et al. 1994) have been reported. A further consideration with micronutrient cycling is the quality of the animal product and its potential effects on human health. These can be either negative (high accumulations of Cd, Cu, Cr and Co: e.g. Brekken and Steinnes 2004; Sivertsen and Plassen 2004) or positive (raised Se, Fe and I levels in milk and meat; Knowles et al. 2004).

8.2.7
Nutrient Budget Methods

Figure 8.1 represents the main routes of nutrient input, transport, transformation and loss in, within, and from a pasture system. At least three types of nu-
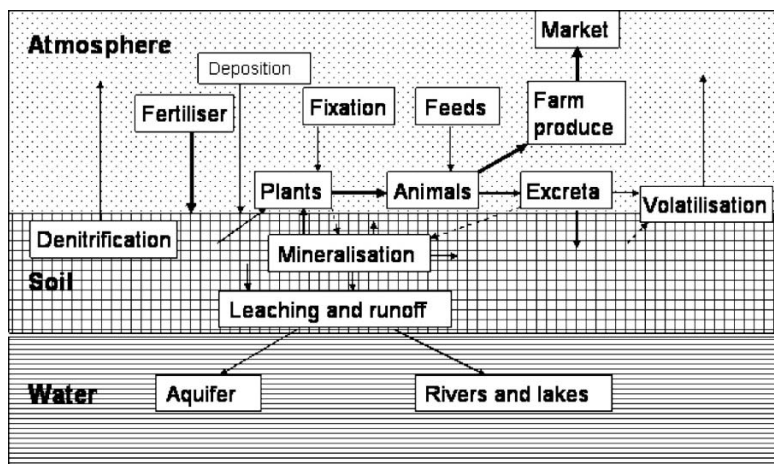
Fig. 8.1 Flow diagram of the nutrient cycle in managed pastures at the farm scale

trient budget methods have been used and the differences relate to the scale of the system being considered, the detail of the budget and/or its boundary conditions. These are 'farm-gate', 'soil surface' and 'soil system' budgets. The 'farm-gate' budget accounts for all nutrients entering and leaving the farm by the gate, with any internal transformations and losses to the environment left unaccounted for. The 'soil surface' budget records all nutrients entering the soil as inputs and leaving in crops. The soil systems budget records all those nutrient inputs transformations and losses represented in Fig. 8.1 (Oenema et al. 2003, see also Chapter 13 by de Willigen et al., this volume). The most commonly used budget for on-farm nutrient accounting is the farm-gate budget and, even though the soil system budget has been similarly applied (e.g. Sacco et al. 2003), the farm-gate budget is more commonly used in research and modelling.

Goodlass et al. (2003) identified over 50 European farm accounting systems, of which the great majority covered nutrients: N, P and K in 13 cases, N and P in 12 cases, N only in 9 cases and P only in 4 cases. Most of these systems were developed to help reduce environmental impacts and 41% of the dairy farmers using nutrient budget keeping considered it to have had a positive effect, in contrast to the 18% who reported that it had a negative or no effect. Many indicators of nutrient use can be generated from the budget (see e.g. Jarvis 1999; Schröder et al. 2003), but the most common is the farm-gate budget, or simply, inputs minus outputs across the farm gate. Inputs will normally be greater than outputs (farm-gate surplus); the greater this difference, the poorer the efficiency of nutrient use.

All indicators of nutrient use need careful interpretation with relation to scale. For example, the nutrient surplus can be expressed per unit of area, of output or of input, and each can indicate subtly different information about environmen-

tal impact, the farmer's management skills and the effects of external supplies of feed and exports of manures (Schröder et al. 2003). While nutrient budgets have been used successfully at scales greater than the field and farm (e.g. Sacco et al. 2003; Woli et al. 2002), accounting correctly within a defined temporal scale is also important to the interpretation of nutrient cycling information (Cuttle and Jarvis 2005).

Perhaps the most significant application of a nutrient balance sheet approach to regulate nutrient use in agriculture has been the Dutch mineral accounting system (MINAS), designed to reduce N and P losses. Under MINAS, the maximum allowable N surplus on Dutch dairy farms has been reduced stepwise each year from 324 kg N ha^{-1} in the late 1990s to values of 140–180 kg N ha^{-1} in 2003 (depending on soil type), to enable the nitrate concentration in ground water to be maintained at <50 mg NO$_3$ l^{-1}. Similar stepwise reductions in P surplus have been legislated for, and failure to meet reduction targets has incurred financial penalties. The development and implementation of this system have been supported by dedicated research and development programmes centred around the De Marke experimental dairy farm (Aarts et al. 2000a, 2000b) and the Cows & Opportunities project (den Boer and Vergeer 2001).

Schröder et al. (2003) reviewed the application of nutrient balance approaches to improving the efficiency of nutrient use and reducing nutrient losses. They concluded that balances do not reveal the nature and magnitude of losses, nor do they, in themselves, provide sufficient information to improve the efficiency of nutrient use. We now explore this contention by considering the efficiency of nutrient transfer through the various pasture system components.

8.3
Relationships of Nutrient Budgets to Efficiency of Nutrient Use

8.3.1
Nutrient Supply to the Soil and Nutrient Availability

The rate of supply and plant-availability of nutrients in soils are the most important factors determining the sustainability of a pasture system. These define soil fertility for plant yield and, to a large extent, determine the potential for deleterious environmental impact due to losses to water and air. The temporal and spatial scales of supply and demand are often mismatched and this impairs efficiency of capture by the plant. Also, the plant must compete with soil microorganisms for nutrients and any physico-chemical processes either immobilising nutrients or transporting them out of the 'system'. Thus, it would be surprising if the efficiency of plant uptake of available nutrients could be 100%. Never-
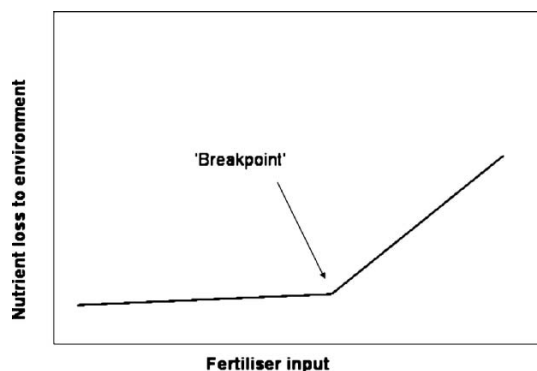
Fig. 8.2 The hypothetical 'breakpoint' in the relationship between supply of plant available N or P in the soil and losses to drainage water

theless, there is a long-held general opinion by some scientists, farm advisors and environmental legislators that this inefficiency is due to poor nutrient management and that it is feasible, by improving management, to perfectly match supply with demand from the plant, such that no losses occur. Hand-in-hand with this notion is the model that the plant always gets first pick at any available nutrient molecule until its demand is met, giving rise to a 'break-point' in a flat nutrient input-losses relationship, where supply exceeds demand (Fig. 8.2). This whole way of thinking about nutrient-use efficiency has been the basis for fertiliser recommendation schemes for agriculture (e.g. RB209; MAFF 2000) and, through extrapolation, has given rise to the analogous assumptions concerning whole system nutrient balances, that minimum or zero surplus is the target to achieve sustainability.

There is some evidence for the flat nutrient supply-losses relationship in N supply to arable crops and for P supply more generally (McDowell et al. 2001). However, it turns out that for grazed pastures, the higher the mean rate of supply of N, the lower the efficiency of capture by the plant roots. Figure 8.3 shows the mean proportion of annual flux of inorganic N through the soil pool that is captured by the plant, a mixed ryegrass/*Agrostis*/*Poa*/*Holcus* permanent grass sward, under grazing by beef cattle.

There are several mechanisms controlling nutrient supply in soils to plants. The dominant ones are: (1) application of inorganic and organic (manures, composts and sludges) fertilisers; (2) mineralisation from several organic pools – old, humified organic matter, exudates from plant roots, senescent plant material, manures and composts; (3) deposition from the atmosphere; (4) excretal returns from grazing animals; (5) desorption from sites of fixation on clays and other colloids; (6) transport in water draining to site; (7) fixation (of N) by legumes.
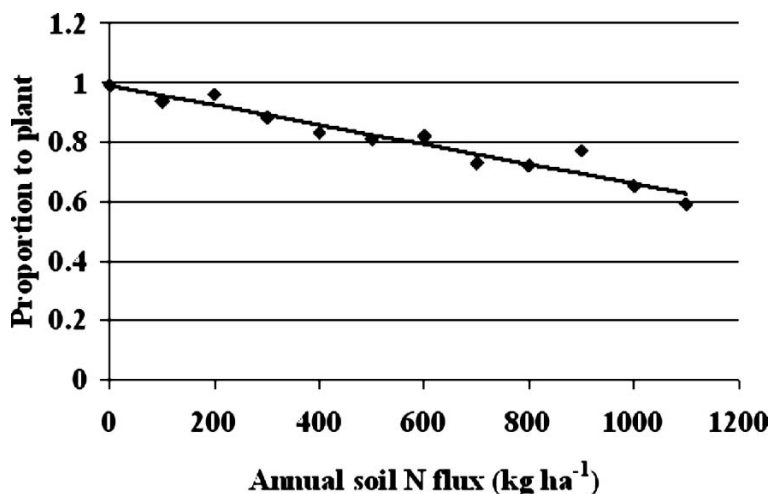
Fig. 8.3 Experimentally derived relationship between the total annual supply of mineral N in the soil from all sources and the proportion of N taken up by the whole plant in a continuously grazed beef pasture (after Scholefield et al. 1991)

The temporal rate and spatial distribution of supply by each mechanism are likely to be different for each nutrient and at any given moment, and are unlikely to match perfectly the requirements of the growing plant. These nutrient requirements will also vary in time and space with the physiological and developmental state of the plant, with light intensity and with changing soil conditions due to management and weather patterns. With N, for example, it has been ascertained that a different response curve can be identified for every month of the growing season (Brown et al. 2005), with uptake in May (the most efficient month in the United Kingdom) and March being 87% and 47% efficient, respectively, for grass swards supplied with 150 kg N ha^{-1} month^{-1} (Fig. 8.4).

This has important consequences for the effects of grazing management on nutrient-use efficiency and highlights one of the strong potential linkages between farm management decisions based on economic considerations (e.g. making better use of grazed rather than conserved or bought-in forages for example) and environmental impacts.

Some of the main soil biological processes of mineralisation, immobilisation, nitrification and denitrification undertaken by bacteria and fungi (see also Chapter 2 by McNeill and Unkovich, this volume), as well as macrofauna that give rise to heterogeneity in nutrient supply, are dependent not only upon temperature and moisture, but also on a supply of labile C to fuel the process. It is this function that, especially in low-intensity pasture systems, can act to moderate or buffer the high potential mismatch between nutrient supply and plant requirements. Senescence of, and exudates from, plants localise nutrient supply
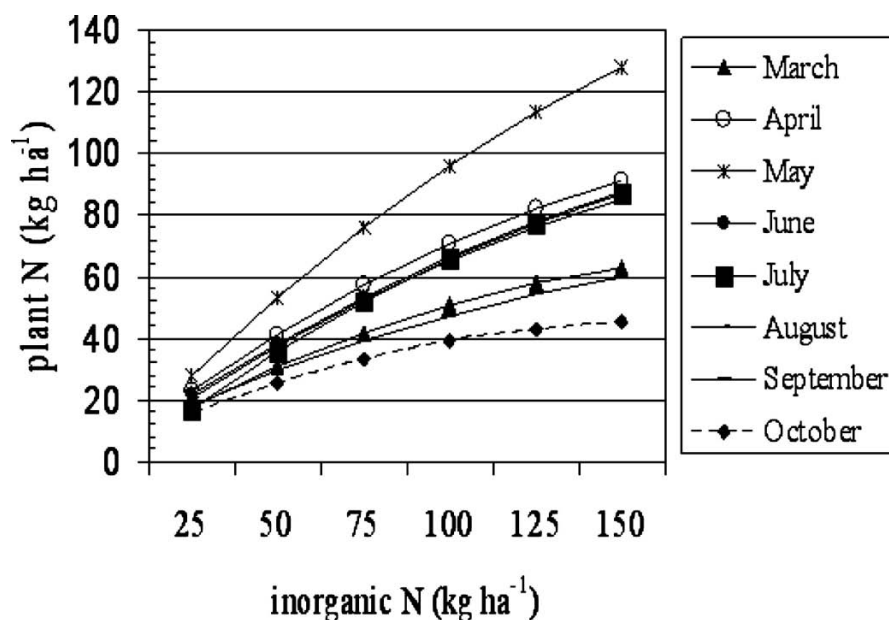
Fig. 8.4 Curves relating N taken up by the whole plant to total supply of mineral N in the soil during different months, derived from cut-plot data reported by Morrison et al. (1980) after Brown et al. (2005)

from mineralisation around plant roots. Beetles, earthworms and other macro-fauna act to more evenly distribute and mineralise the nutrients from applied manures and excreta throughout the rhizosphere. In high-intensity systems this moderating function of targeted C supply on nutrient availability is most probably nullified by the effects of inorganic fertiliser application.

The model of efficiency of nutrient use (Fig. 8.5) can be scrutinised in order to identify potential management practices for improvements in efficiency. It also indicates the potential for each plant to exert control over its own micro-environment and thereby engineer a more optimal supply of nutrients in time and space. Such a model also allows explanation of the effects of intensity of nutrient input on above- and below-ground biodiversity; with reducing availability of nutrients, plants are able to exert increasing control over their own nutrient supplies relative to that of their neighbours (Scholefield 2003).

Imbalance between nutrients can be very important to overall nutrient use efficiency. Brown et al. (2000) showed that correction of S deficiency in a sandy soil greatly reduced nitrate leaching and increased herbage yield with high levels of N fertiliser applied, but had little effect at more moderate levels of N input.

It is important to consider the temporal and spatial scales over which this variability in nutrient availability to plants and mismatches between supply and
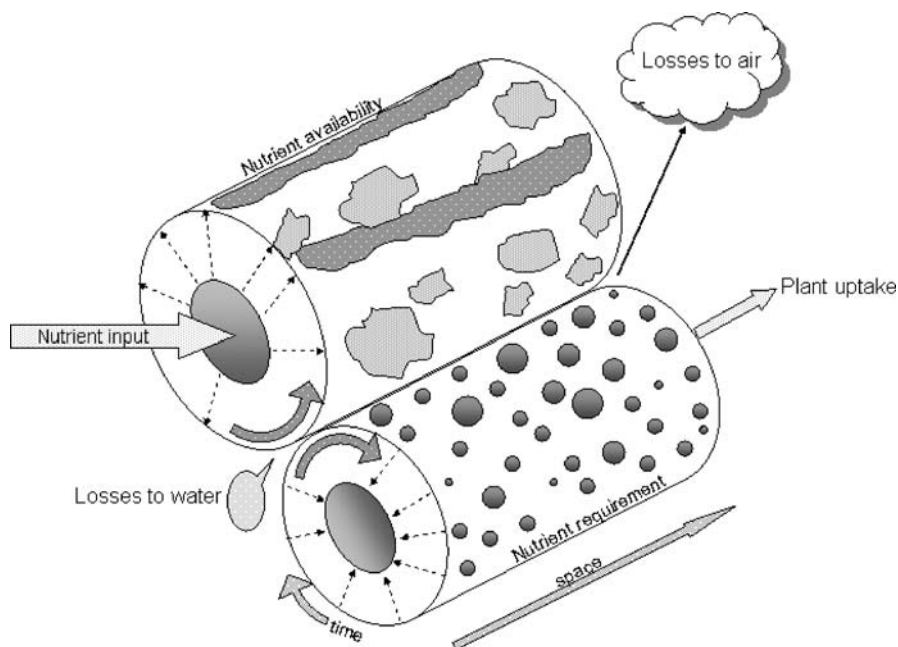
Fig. 8.5 'Mangle' model of nutrient use efficiency by the plant. The top roller controls soil supply of plant available nutrient, giving rise to spatially (*lengthwise*) and temporally (*circumferential*) variable patches of nutrient at different concentrations. This drives the bottom roller (plant uptake), which has holes or sinks for nutrients that are again spatially and temporally variable and of different strengths. Nutrient use efficiency is determined by the degree of coincidence between supply (*patches*) and requirements (*holes*), such that nutrients are lost through being squeezed out of the mangle where coincidence is lacking, upwards to the atmosphere, and downwards to the aqueous environment

requirements operates. We generally consider rather long temporal scales, typically from 1 year down to 1 month when, for example, considering fertiliser requirements for grazing and cutting cycles. Plant requirement for nutrients is driven by light intensity and duration, and supply from the soil is controlled by temperature and water content. Therefore, we should expect mismatch between requirement and supply rates to be manifested at this temporal scale. Indeed, at finer temporal scale still, solution culture studies in controlled environments have demonstrated strong diurnal variation in uptake of nitrate-N, ammonium-N and K (MacDuff et al. 1997). The authors of this latter study conclude that it is highly probable that 'sink strength' for nutrients varies diurnally during vegetative growth of grasses, although not necessarily synchronously for different nutrients. We are currently beginning to appreciate that many of the processes giving rise to nutrient loss also exhibit strong diurnal effects, both with gaseous emission (Hatch et al. 2005) and nutrients in water bodies (Scholefield et al. 2005a).

Grasses employ compensatory mechanisms to reduce the impacts of short term mismatches between nutrient supply and requirement by including the capacity for luxury uptake (of N) and enhanced dark period uptake following nutrient starvation during the light period. Despite this, early solution culture work showed that compensation for intermittent deprivation of *Lolium* plants of nitrate-N was insufficient over the longer term to maintain shoot growth rate the same as that of plants continuously supplied with the same nitrate concentration.

As with the temporal scale, the spatial scale that we generally consider nutrient supply (as manures and fertilisers) and requirement to operate at, is greater than the scale at which the controlling mechanisms act, which is the soil aggregate-plant root interface. Excretal returns (dung and urine) from grazing livestock give rise to inefficient nutrient use (Cuttle et al. 2001), not so much because of the relatively fine spatial scale of input, but because of the high nutrient concentrations applied at that scale. Other mechanisms of spatial mismatch include topographic features giving rise to variation in soil water content, transport down slopes and camping of cattle around water supplies. Precision applications of fertilisers and manures would be one way of correcting these and, although spectral imaging methods are being applied as part of intelligent nutrient metering technology, this is being used only with highly profitable crops.

In order to calculate the efficiency of uptake of any particular nutrient by the plant, the amounts made available by all mechanisms must be determined and summed and the amount taken up by the whole plant over the same time period quantified. Neither of these quantities is readily measured directly. The first can be estimated only by the use of models and the second needs assessment of the flux of nutrients passing into (and through) the whole plant (shoots and non-harvestable roots and stubble, plus that from all plant fractions passing to death, exudation and decay during the period). This has been achieved only for N and C under relatively few sets of conditions by the use of isotope tracers and models (Avice et al. 1996; Parsons et al. 1991; Scholefield et al. 1991; Soussana et al. 2004). Consequently, the amounts of nutrients harvested in herbage relative to the amounts applied in fertilisers has been used as a surrogate for nutrient-use efficiency, giving rise to errors and misconceptions. Nevertheless, the nutrient offtake is a useful value in the calculation of the efficiency of nutrient capture by the animal.

Through photosynthesis, plants use CO_2 from the atmosphere to build their plant biomass. In grassland systems this assimilated plant biomass C can directly enter the soil, either as above-ground litter or root-derived material (e.g. root death and rhizodeposition) (Brady and Weil 1999; Jones and Donelly 2004). About one-third to one-half of photosynthate is allocated below ground, of which 10–15% is used for root growth and maintenance. The remainder is exuded into the rhizosphere, which supports the soil microbial community (see also Chapter 5 by Neumann, this volume). However, a significant but variable proportion of plant material in grassland is consumed by herbivores and then enters the soil C pool indirectly through animal excretion (Bol et al. 2004a, 2004b; Dungait et al. 2005). Furthermore, a considerable amount of additional

C materials (e.g. manures or composted materials) are applied to grassland soil only after variable lengths of storage and processing (Bol et al. 2003a, 2003b). The wide diversity of C inputs between systems can give rise to large differences in soil C content and ultimately in soil organic matter (SOM), and hence lead to totally different grassland soil C dynamics even on similar soils.

The SOM has a large part to play in controlling the availability of mineral nutrients for plant uptake. SOM encompasses all the organic components present in the soil: living flora and fauna, fresh debris and readily decomposable material, and 'humic' substances resistant to degradation (see also Chapter 1 by Baldock, this volume). Many different compounds are present in SOM, ranging from labile sugars, amino acids and volatile fatty acids to more complex and recalcitrant fractions comprising polysaccharides, lignins and polyphenols. Each fraction contains and/or is associated with macro- and micro-nutrients to different degrees, and the rate of turnover of these fractions determines nutrient availability. However, a significant proportion of SOM is either biochemically recalcitrant or is physically protected from degradation in soil micropores.

The long-term action of soil organisms in grassland systems, combined with the effects of climate, inherent soil properties and land management leads to 'visual' differences in the soil with depth, i.e. the soil profile (Bol et al. 1999). These visual differences have been utilised as a basis of soil classification but, more specifically, they could also be thought of as a visualisation of the long term budget record for C and possibly other nutrients. For example, the Andosols of Japan and other volcanic regions are classified according to well-defined visual patterns of organic C banding. However, little attention has been paid to these records as a means of assessing ancient C budgets under different land uses and climatic regimes.

8.3.2
Nutrient Flows through the Plant

The pattern of nutrient uptake and herbage production throughout the growing season is determined by the physiology of the plant, its frequency of defoliation by cutting or grazing and ambient conditions of temperature, soil water and light. These factors control the rates of incorporation of the different nutrients into the major plant fractions (leaf, shoot, root, stolon, stubble etc.), herbage removal by cutting, grazing and pest attack, rhizodeposition and the death and decay of these parts, returning the various organic fractions back to the soil for mineralisation by microorganisms. Accurate assessment of gross nutrient flows through the plant is very difficult to achieve (Jones and Donelly 2004), due to the fact that the above processes tend to occur concurrently, which 'snapshot' analyses of plant parts cannot account for. Any re-mobilisation of nutrients among these parts (e.g. Clark 1977) between the snapshots will add to error in assessment. Nevertheless, some progress with assessment of gross C and N flows in temperate C3 grassland has been made by the combined use of mass balance

principles and isotopic tracers (e.g. Hansson and Petersson 1989; Parsons et al. 1983, 1991). Simple calculations and assumptions about C loss through respiration and about C:N ratios in the various fractions result in values for annual gross photosynthetic C uptake of 16,720 kg ha^{-1} and for gross annual N uptake of 667 kg ha^{-1}. These values can be larger or smaller depending on the ecosystem. Little analogous information is available for other nutrients except for very specific instances.

However, it can be appreciated from the limited data above that plant nutrient throughput can be much greater than that typically represented by input-output budgets, and it is the efficiency of nutrient flow through the plant that impacts most on the efficiency of the whole system. The offtake of nutrients in harvested herbage is known with much greater certainty, with the N content of the harvested herbage of C3 grasses ranging typically between 15 and 45 g kg^{-1} dry matter, depending on N input and the physiological state of the sward. The contents of P, K and S of herbage from both grasses and legume species in temperate C3 grassland normally lie within the ranges 2.1–4.2, 18–30 and 2.7–4.0 g kg^{-1} dry matter, respectively (Scholefield and Oenema 1999). For comparison, in C4 grasses the nutrient contents are within the same range but tend to be at a lower value, particularly for N and K, for the same level of input and herbage yield (Robinson 1996).

A typical composition of green plant materials (adapted from Brady and Weil 1999) is cellulose 45%, lignin 20%, hemicellulose 18%, proteins, 8%, starch and sugars 5%, fats and waxes 2% and polyphenols 2%. The quantity and quality of plant litter input will vary in grasslands due to removal by grazing or mowing for hay and silage, or addition by application of a wide range of soil improvers and fertilisers, including animal manures. This, in turn, will affect rates of decomposition and the balance between mineralisation and immobilisation [see also Chapters 1 (Baldock) and 2 (McNeill and Unkovich), this volume].

8.3.3
Nutrient Flows through the Herbivore

Ruminants are rather inefficient at incorporating nutrients ingested in herbage into milk or meat, and this transfer is the most inefficient of the whole nutrient cycle. The proportion of N in diet that is incorporated by beef animals varies typically between 10 and 20%, while that incorporated into milk by dairy cows varies between 15 and 30%, depending on the quality of the feed, feeding management and the genetics of the animal. Efficiency of P and K incorporation is typically 35 and 12%, respectively (Haynes and Williams 1993). This leads to the return of excreta rich in N and K relative to that taken up by the plant. The efficiency of incorporation of N can be increased by optimising the ratio of degradable protein to energy in the rumen to minimise ammonia production and loss in urine. Other strategies include the 'protection' of dietary protein with more resistant fractions such as condensed tannins as in *Lotus* species for

example (Min et al. 2003). It is becoming apparent, however, that dietary manipulations for better nutrient capture will also have important consequences for CH_4 emission from the animal.

Grazing animals can have large effects on the distribution of nutrients due to selection of specific sward components (e.g. Rutter 2004; Tallowin and Brookman 1988), rejection of herbage from unpalatable areas, and enhanced excretion around water troughs, trees and shelter features (Ledgard et al. 1982; Peterson et al. 1956; Richards and Wolton 1976). Diet selection has recently been observed to have diurnal trends, with both cattle and sheep showing a 70% partial preference for clover when presented with a mixed white clover/ryegrass sward, but with this preference being exhibited more during mornings (Rutter et al. 2004).

8.3.4
Excretal Returns

While grazing livestock return dung and urine to the soil, the stored manures (slurry, dairy washings, compost and dung) produced on the farm together with other organic composts and sludges produced externally are applied additionally, also in spatially and temporally heterogeneous patterns. In the developed countries, particularly Western Europe and Japan, large amounts of organic manures are applied to grassland, and export of organic manures and the nutrients contained therein to arable land and to biogas plants is increasing. On the other hand, in tropical and sub-tropical regions, manures from animals and humans are considered to be valuable resources, rather than as nutrient-replete waste materials and are often the only means of redressing soil nutrient and OM depletion. Additions of organic manures increase SOM content (Sommerfeldt and Chang 1985) resulting in improved soil structure, increased soil animal biodiversity and soil microbial biomass. While the storage and application to land of slurries, manures and composts gives rise to direct and indirect losses of nutrients to the environment, it is only the net imports and exports of these on and off the farm that are accounted for in the farm nutrient budget.

In 1996, global nutrient excretion by livestock was estimated at 94, 21 and 67 Mt of N, P and K, respectively, with 60% contributed by cattle (Sheldrick et al. 2003). However, only 34, 8.8 and 23 Mt of N, P and K, respectively, were recovered as manure; as fractions of nutrient inputs, this represented 14%, 25% and 20%, respectively, demonstrating a large potential for better manure management to reduce nutrient losses in storage and upon application. Carbon inputs via excretal returns are substantial with, for example, ca. 1.4 t C ha^{-1} supplied by cows grazing at 700 cow days ha^{-1}, which is equivalent to 23 t on the 6.4% of the grazed area receiving excreta (Whitehead 1986).

Excretal returns by animals are hot spots for enhanced nutrient losses, especially N and P. Urine patches give rise to ammonia and nitrous oxide emissions during dry and wet weather, respectively, and to leaching of nitrate and P compounds if deposited immediately prior to the rainy season. Although

much is known about the composition of dung in terms of NPK availability (e.g. MacDiarmid and Watkins 1972), there is little specific knowledge about the major organic components of this ubiquitous material and their fate in the soil post-deposition.

The breakdown of dung pats in the field is an extremely variable process (Lovell and Jarvis 1996), corresponding to the various mechanisms of decomposition. Time taken for 75% of dung to disappear ranges between 32 and 450 days (Dickinson et al. 1981). The initial quality of the dung, especially the water content, influences decomposition rates (Weeda 1967). Season and weather, particularly rainfall, have major effects on the rate of decomposition (Dickinson and Craig 1990). In warm, dry weather, the formation of a crust retards decomposition, and radiant heat absorbed by the dung warms the soil beneath the pat causing changes in soil processes (Dickinson et al. 1981). Invertebrates break up and remove material from dung (Underhay and Dickinson 1978), though Dickinson et al. (1981) found that earthworms were not significant in dung decomposition, which may be due to the anti-parasitic pharmaceuticals excreted in faeces.

In many intensive livestock farming regions, large volumes of liquid cattle slurry, rather than solid manure, have to be stored and disposed of to land. Both storage and land application provide opportunities for nutrient losses, particularly of N via ammonia volatilisation and denitrification and of P via mobilisation and transport to watercourses. Cattle slurry contains 1.0–4.0, 0.26–0.87, and 1.5–3.8 N, P and K kg m^{-3} respectively, of fresh weight, but only <50% of the N and P is available immediately for crop uptake (MAFF 2000).

Haygarth et al. (1998) reported the annual inputs to soil for a typical United Kingdom dairy farm were 32, 16 and 10 kg P ha^{-1} for slurry+farmyard manure, fertiliser and direct excretal returns from grazing animals, respectively. However, the latter are distributed unevenly, leading to highly localised high P inputs ('hotspots') equivalent to ca. 150 kg P ha^{-1} at conventional stocking rate and grazing intensity (Whitehead 1986).

Stable isotope tracer techniques allow sources of respired CO_2 to be identified and products of slurries and manures to be quantified. Using such methodologies, Bol et al. (2003b) showed that slurry incorporation into soil strongly increased soil CO_2 respiration compared to the unamended soil. The ^{13}C natural abundance tracer technique was used to determine that slurry incorporation induced a priming effect, i.e. additional release of soil-derived C, which was most pronounced in a Pelostagnogley (highest C content). The majority of respired soil-derived C (>70%) was primed C. This study also indicated that the environmental benefit from potential reductions in ammonia volatilisation following slurry injection to grasslands might be offset by enhanced loss of primed soil C (i.e. pollution swapping).

The application of human sewage and sewage-derived sludges to productive land is now becoming more prevalent in developed countries as legislation limits other methods of disposal, such as dumping at sea. However, many countries now ban the application of untreated sludges to food crops and grassland, but

application to biomass fuel crops may still be permitted. Anaerobic digestion and heat treatments are used to destroy pathogens and the efficiency of these treatments determines the method of application to land and the target land use permitted (e.g. Safe Sludge Matrix 2001). The nutrients applied in sludge include N, P and a range of micronutrients as well as organic C, but the amounts can be very variable depending on source and pre-treatment. Thus, the N and P contents of treated sludges can be rather low (<5 and <1 g kg^{-1}, respectively), while the heavy metal contents can approach toxic levels (e.g. 230 and 370 mg kg^{-1} for Zn and Pb, respectively; Safe Sludge Matrix 2001).

8.3.5
Outputs and Losses

The main nutrient output routes from grassland systems are within food products (milk, meat and wool), as gaseous compounds emitted to the atmosphere (NH_3, N_2O, NO_x, N_2, CH_4, CO_2 and volatile organic compounds, VOCs) and as inorganic ions (NO_3^-, NH_4^+, NO_2^-, PO_4^{3-}, SO_4^{2-} and HCO_3^-), dissolved organic compounds (proteins, amino acids, sugars, humic materials and fatty acids) as well as colloids and particulate materials transported in drainage water. Other less-used output routes include as timber in silvo-pastoral systems, in dry soil, dust and pollen blown by the wind, in manures and composts exported for application elsewhere and in excreta from animals and as animal bodies (vertebrate and invertebrate) travelling 'outside' of the system. An output route likely to become more important however, particularly in Europe, is as energy crops such as *Miscanthus* and oilseed rape (*Brassica napus* L.) for industrial processing.

Nutrient outputs as constituents of food products are normally small relative to inputs in intensive systems operating under temperate conditions, but become progressively larger (relative to inputs) with reducing intensity and under warmer and wetter conditions. Thus, N in milk ranges as high as about 100 kg ha^{-1} from high input systems operating in temperate regions (see Moorby et al. 2003), but this may account for only 20% of the N input. Fractions of N inputs incorporated into food are even smaller for intensive beef and sheep systems. Phosphorus outputs in milk from a similarly intensive dairy system are about 15 kg ha^{-1} (Haygarth et al. 1998), and K outputs have been estimated at between 0.6 and 2.9 kg ha^{-1} for low and high intensity beef systems, respectively (Alfaro et al. 2003).

Losses of nutrients via volatilisation are only relevant for N and C in terms of significant mass balance effects, but even the low rates of volatilisation of organic S (e.g. dimethyl sulphide) and P (phosphine) compounds, may have significance environmentally. A key N loss pathway is the volatilisation of NH_3, which takes place mainly from urine patches, dung, urea fertiliser, stored and applied slurry, and from senescent plant tissues (Whitehead 1995) (see also Chapter 2 by McNeill and Unkovich, this volume). Losses from intensively grazed pasture can be

as high as 63 kg N ha^{-1} (Ledgard et al. 1996), while losses from surface-applied slurry can be as high as 94 kg N ha^{-1} (Pain et al. 1998).

Nitrogen losses from the soil via denitrification may also be high, when excess NO_3^- is present under warm, wet conditions. The main products of denitrification are N_2O and N_2 and thus, while the total N loss is important in terms of N-use efficiency, it is the N_2O emission that is environmentally important. Nitrous oxide is also a product of nitrification, which occurs in more aerobic conditions, and so attempts to correlate emissions from denitrification with the known driving variables have had little success under field conditions (Jarvis et al. 1991; Skiba et al. 1994). Emissions are sporadic and event-driven, with high spatial variability in the field (Kelliher et al. 2002), so that accurate assessment of annual N losses at the field and coarser scales has proved very difficult to achieve. Annual N losses through denitrification in New Zealand pasture soils ranged from 15 to 63 kg ha^{-1}, depending on management intensity and sward composition (Ledgard et al. 1996). Annual losses as N_2O via both denitrification and nitrification are rarely greater than 2 kg N ha^{-1}. A relationship suggested by Bouwman (1996) between annual emission of N_2O-N and percentage of fertiliser N applied to a field of 1.25% is now accepted by many European countries as a basis of calculating emissions for inventory purposes.

Whether or not grassland is considered to be 'CO$_2$ neutral' depends on many factors, including the initial soil C content and the subsequent intensity of management, which, in turn, determine whether C inputs are greater or smaller than C respired through mineralisation (Loiseau and Soussana 1999; Soussana et al. 2004). Changing from intensive to moderate N inputs in temperate grasslands could result in C sequestration of 0.3–0.5 t N ha^{-1} year^{-1} (Fig. 8.6). However, the recent claims by Keppler et al. (2006) that tropical forests and grasslands could emit 46–169 Tg CH_4 year^{-1} globally, will need to be verified and, if true, considered together with the net CO_2 budget on a common 'Global Warming Potential' basis.

Many nutrients can be lost from grasslands through transport in drainage waters. The most important losses are N as NO_3^-, NO_2^-, NH_4^+ and in combination with organic compounds; P in many inorganic, organic and particulate forms; S as SO_4^{2-}; metals (K^+, Mg^{2+}, Ca^{2+}) as cations and C in soluble and particulate organic forms (in combination with N and P). Annual losses of NO_3^- depend on many factors (Scholefield et al. 1993) and can range between 10–13 kg N ha^{-1} for upland sheep-grazed systems (Cuttle et al. 1996) and 338 kg N ha^{-1} for intensive double cropping systems on sandy soils in Portugal (Trindade et al. 1997). Losses of P at 1–2 kg P ha^{-1} are much smaller (Hawkins and Scholefield 1996; Haygarth et al. 1998; Smith et al. 1995), but nevertheless have an important environmental impact on water quality. Losses of S are highly interactive with those of N (Brown et al. 2000), but rarely exceed 40 kg ha^{-1} (Garwood and Tyson 1973; Nguyen and Goh 1993), although 25% of ^{35}S-labeled SO_4^{2-} applied in sheep urine was leached after 41 days from a New Zealand pasture in winter (Williams and Haynes 1993). Losses of K from moderately intensive temperate grasslands were as great as 31 kg ha^{-1}. Losses of other alkali metal cations (Na^+,
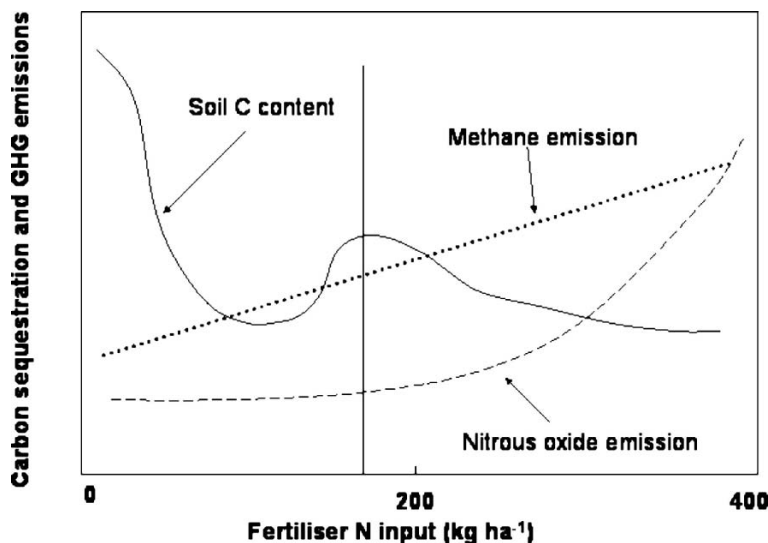
Fig. 8.6 Modelled relationships (after Soussana et al. 2004 and Scholefield et al. 2005a) between the input of N to a temperate pasture system and the soil C content at 'equilibrium', the emissions of methane from stock and emissions of nitrous oxide from the soil. These show an intermediate value of N input (ca. 175 kg N ha^{-1}) at which the global warming potential of a productive pasture would be minimal

Ca^{2+} and Mg^{2+}) can be variable depending on soil type, hydrological regime and the need to balance anions.

There have been few assessments of losses of dissolved organic C in drainage waters from productive grasslands, but McTiernan et al. (2001) observed losses during a 2-month winter drainage period of 42–118 kg C ha^{-1}, which were considerably greater than previously measured losses (e.g. 108 kg C ha^{-1} year^{-1} from a Swiss grassland; Hagedorn et al. 2000).

Losses of micronutrients via leaching have rarely been evaluated and most studies have considered micronutrients from the toxicological aspect rather than from the budgetary standpoint (e.g. Carey et al. 1996; Ozturk et al. 2004).

8.4
Effects of Management and Site Conditions

The factors known to have major influence on efficiency of nutrient use, nutrient budgets and surpluses can be classified as either site factors or management factors. Site factors include weather/climate and soil conditions such as those

conferred by texture and drainage status. These factors can be important but may not be generally exploitable for improving efficiency and achieving sustainability because they cannot be modified in the short term. Management factors include the level of nutrient input, the proportion of the year the animals are either grazing or being fed indoors, the type and quality of diet fed, the type of animal and the methods of manure storage and disposal to land. Site and management factors are not independent, however, as for example soil fertility is strongly influenced by the intensity of management, as well as climate, while soil water content determines plant yield and the length of the grazing period. Management factor specifications are generally determined by site factors and by the pertaining economic situation.

Both farm management and site conditions can have potentially large effects on nutrient flows through each of the system components (soil, plant, animal and excreta), as discussed earlier in this chapter. The level of nutrient input (from all sources) determines the intensity of management and, broadly, the efficiency of nutrient use and amounts lost to the environment. However, at every level of nutrient input, the efficiency of nutrient use can be modified by the methods and timings of those inputs (particularly of manures) and other site and management factors.

Much research effort has been aimed at identifying and implementing management strategies for improving the efficiency of N flows through each individual system component, using both experimental (e.g. the De Marke experiment, Aarts et al. 2000a; the Rowden farmlets, Laws et al. 2000) and systems synthesis/modelling approaches (e.g. Cuttle and Jarvis 2005; Jarvis et al. 1996). These include use of tactical fertiliser addition (Brown et al. 2005), use of better manure storage and land application methods (Webb et al. 2005), optimisation of the proportions of grass, clover and maize grown and fed for improved capture of dietary protein-N by the ruminant (Jarvis et al. 1996) and inclusion of phytase enzyme with diet to improve P availability to livestock (Huff et al. 1998). Implementation of several of these 'single factor' strategies together in the same system may not necessarily result in whole system benefits equal to the sum of those conferred by each strategy implemented alone because of interactions and antagonisms between them. Moreover, the phenomenon of 'pollution swapping', whereby one nutrient loss pathway is substituted for another (e.g. Monteny et al. 2006) has to be considered when evaluating potential benefits from nutrient control strategies. These kinds of effects will become even more complex and difficult to predict as nutrients other than N and climate change scenarios are considered. Novel modelling approaches will be required to examine this complexity (e.g. del Prado et al. 2006; Scholefield et al. 2005b).

The view that the spatial separation of arable cropping from animal production systems in agriculture is partly responsible for our present problems with poor efficiency of nutrient use is currently gaining ground, particularly in Europe. Advocates of a return to mixed farming emphasise the close coupling of nutrient transfers that is made possible by this method (e.g. Watson et al.

2005), but pay little attention to the differences in site factors, which were partly responsible for evolution of traditional mixed farms into single enterprise systems. Despite the theoretical advantages for more efficient nutrient transfers, nutrient use efficiency values of mixed farms tend to be intermediate between those of arable and livestock (Leach et al. 2004; Scholefield and Smith 1996; Watson et al. 2005).

Organic livestock farming is another example of a farm management system that has been seen as potentially more nutrient efficient and hence more sustainable than the analogous conventional system. Recent reviews of evidence tend to uphold this supposition (Condron et al. 2000; Watson et al. 2002), although comparisons were not always made at equal levels of output. Where this has been taken into account, however (Cuttle et al. 1998), there is little difference between the two management types in, for example, N losses, despite N sources being dominated by (1) fixation with organic and (2) mineral fertiliser with conventional production. Where organic products command higher prices, there is no doubt that the organic system can be more sustainable because the lower levels of production and (nutrient losses) typical of legume-based systems can be economically viable.

It might be supposed that, because nutrient flows, balances and surpluses are controlled by different combinations of site and management factors, sets of such nutrient data characteristic of the different ethnic cultures and special site conditions from managed pastures around the world would exist. Although there are extremes exemplified by, on the one hand, the nutrient-poor, low input, grazing/browsing system practised in many tropical and sub-tropical regions and, on the other hand, the intensive, nutrient-rich, concentrate- and fertiliser-dependent, housed system practiced in developed temperate countries, there are few other marked differences assignable to location. This is partly because the efficiencies of nutrient use by the different pasture plants and animals are rather similar at similar levels of nutrient availability and under similar soil moisture regimes. Indeed, the almost ubiquitous reliance on one or two species of forage grass and legume and one breed of dairy cow has served to obscure any differences within the temperate dairy production systems. However, there is a tremendously large range of nutrient use indicator values within each regional system type around the globe and this serves also to thwart attempts to characterise regional nutrient use. This large range could be due to the fact that wide variability in site factors within each region exist, and also to the unique approaches taken by individual farmers to seek economic sustainability. Consequently, in the remaining part of this chapter we have chosen to introduce and discuss concepts that offer a general understanding of the relationships between nutrient use efficiency, budgets, surpluses, and the sustainability of our managed pastures, rather than embark upon a regional analysis.

8.5
Nutrient Surpluses for some Typical European Pasture Systems and their Interpretation

One important end-point of assembling a farm-gate nutrient budget is to calculate the nutrient balance or surplus. Surpluses (inputs–outputs through the 'farm gate') can then be compared on several different bases and for different objectives, such as (1) for different farms with the same basic management within the same region, country or globally; (2) for the same farm, over years; in response to changes in management and with weather patterns; and (3) between farms with different managements across a region, country or globally. The first basis of comparison allows assessment of the variation in nutrient use due to site factors (e.g. soil and climate) in addition to error in applying and assessing the budget and the effects of coarser scale externalities, such as differences in product values (Schröder et al. 2003). The second basis allows assessment of the effects of implementation of nutrient management legislation over time. The third basis may allow the identification of farm managements that confer better efficiency of nutrient use when operating at the same level of animal product output and/or profit margin. All this assumes that reducing the nutrient surplus (N and/or P) will make the farm more sustainable and that transition to certain site factor-management combinations may enable any such reductions to, in turn, reduce nutrient losses rather than economic productivity. The latter has some support from model-based studies (e.g. Jarvis et al. 1996), but the mere presence of a high level of variation in measured nutrient surplus values from any coherent class of livestock farms (e.g. Jarvis 1999 reported N surplus values ranging between 63–667 kg ha^{-1} for some dairy farms in southwest England) does not necessarily indicate potential for derivation of general routes for achieving sustainability through analysis of the variability. This is because farmers strive to maximise profitability and not output per se and so a small surplus in one economically viable situation may not be at all profitable on the adjacent farm. Secondly, variability can be dominated by accounting errors, bias, imprecise nutrient management and local weather effects, which may not be generally exploitable in strategies to confer sustainability (Oenema et al. 2003).

To illustrate these points, we present data collected as part of the European NUMALEC (Nutrient Management Legislation in European Countries) study (De Clerq et al. 2001). Typical N and P farm-gate balances for dairy systems of many European countries ranged between 36–316 kg N ha^{-1} and 3–33 kg P ha^{-1}, respectively. Figures 8.7 and 8.8 show the relationships of these N and P surpluses, respectively, with nutrient in product (surrogate for level of productivity) and efficiency of nutrient use (% of input incorporated into animal product).

For N, the greater the surplus, the greater the production level, but the smaller the efficiency of N use. Similar, but weaker trends were found for P. These trends reflect and are analogous to that in Fig. 8.3 depicting the reduction in efficiency of N capture by the plant with increasing N supply. Similar relationships show-
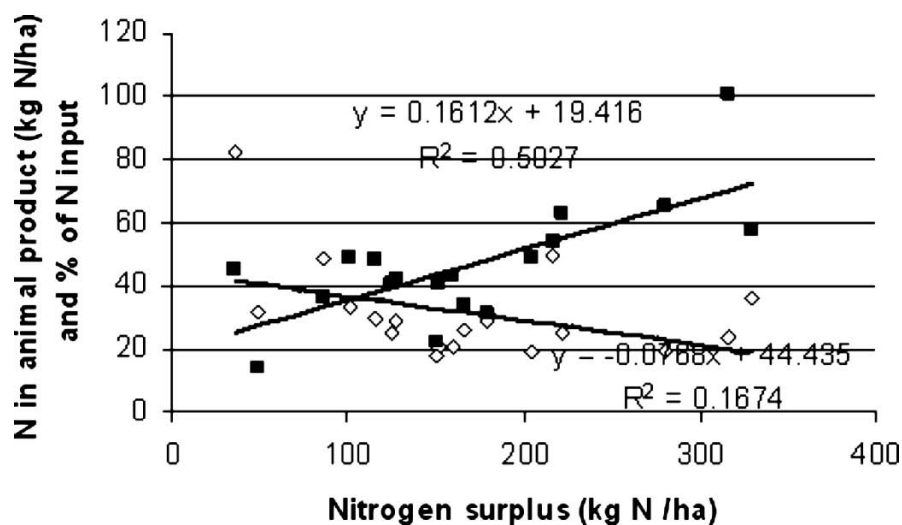
Fig. 8.7 Relationship of farm-gate N surplus calculated for European countries (Nutrient Management Legislation in European Countries – NUMALEC) with productivity (*solid squares*) and N use efficiency (*open diamonds*)
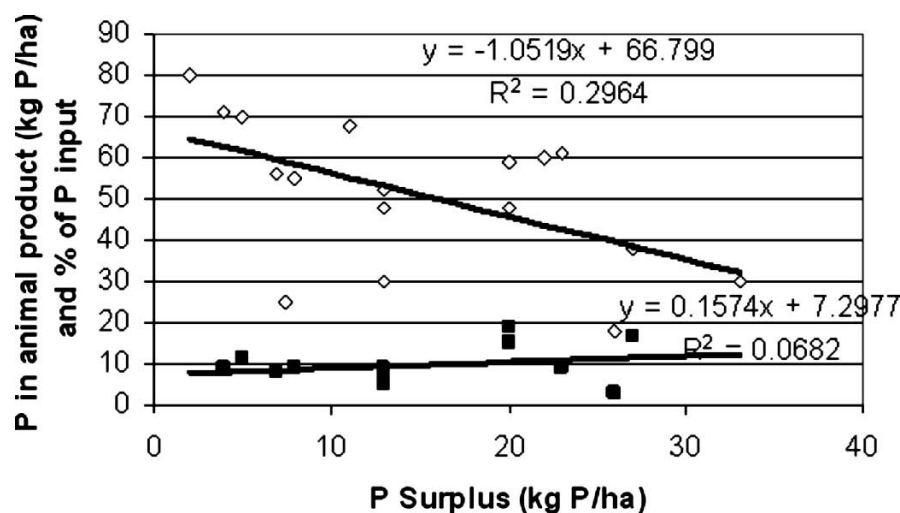
Fig. 8.8 Relationship of farm-gate P surplus calculated for European countries (NUMALEC) with productivity (*solid squares*) and P use efficiency (*open diamonds*)

ing increasing N loss with increasing N surplus have been derived at farm scale (e.g. Fraters et al. 1998) and at coarser scales (Lord et al. 2002). However, in most cases the values of N loss were calculated using models rather than being measured. Salo and Tutola (2006) concluded from experimental data alone that annual farm-gate N balances were not reliable indicators of N leaching in Finland, although a Japanese study at the drainage basin scale gave more confidence to the correlation (Woli et al. 2002). However, it seems that, in general, reducing the surplus of N or P is likely to reduce the productivity of a farm (Børsting et al. 2003), increase efficiency of nutrient use, and reduce environmental impact. Whether these three effects can confer sustainability depends on (1) whether the variability in the relationships is due to real site and/or management factors, (2) whether maximum productivity is coincident with maximum profitability, and (3) whether there is 'overlap' between the range of the values of nutrient surplus where the farm is economically and environmentally sustainable.

Figure 8.9 depicts situations in which reducing N surplus from a value A, which is only economically viable, to a value B, which in the first case, would confer sustainability (as B is in an overlap position), whereas in the second case it would not as there is no overlap. It should also be remembered that the positions of the economic and environmental sustainability boundaries are arbitrary and largely independent of each other. Thus, the economic boundary is determined by site conditions, commodity price structures, market forces and, ultimately, by political decisions, whereas the environmental boundary is determined by legislation in response to the public desire for clean water and air and a biologically diverse and attractive countryside.

The positions of the boundaries and the values of the nutrient surplus range will be different for each country in the world and will each be changing, according to site factors (climate and soil) and economic and environmental pressures, and how these are reacted to politically. However, for most productive grassland farming in Europe, Australasia, Japan, China and North America, it is likely that any overlap between the economic and environmental boundaries (in Fig. 8.8) will be small and currently reducing, as environmental constraints become more stringent and prices for meat and milk are reduced. However, in resource-poor regions such as West Africa, the N and P budget farm-gate balances are commonly in deficit (e.g. Manlay et al. 2004). Here, organic resource allocation dominates economic viability and hence the position of the economic boundary in relation to the surplus.

In a review of N-use efficiency in African livestock systems, Rufino et al. (2006) revealed a wide range of efficiencies of transfer through the main system components. Such 'partial N cycling' efficiencies had ranges of 46–121%, 6–99%, 30–87% and 3–73% for the 'livestock', 'manure handling', 'manure storage' and 'soil and crop conversion' components, respectively. They concluded that although livestock and manures were the main sources of inefficiency in N use, this could be improved by better management.

What proportion of a farm-gate nutrient surplus is lost in non-productive outputs, to water or the atmosphere, is determined by a combination of both
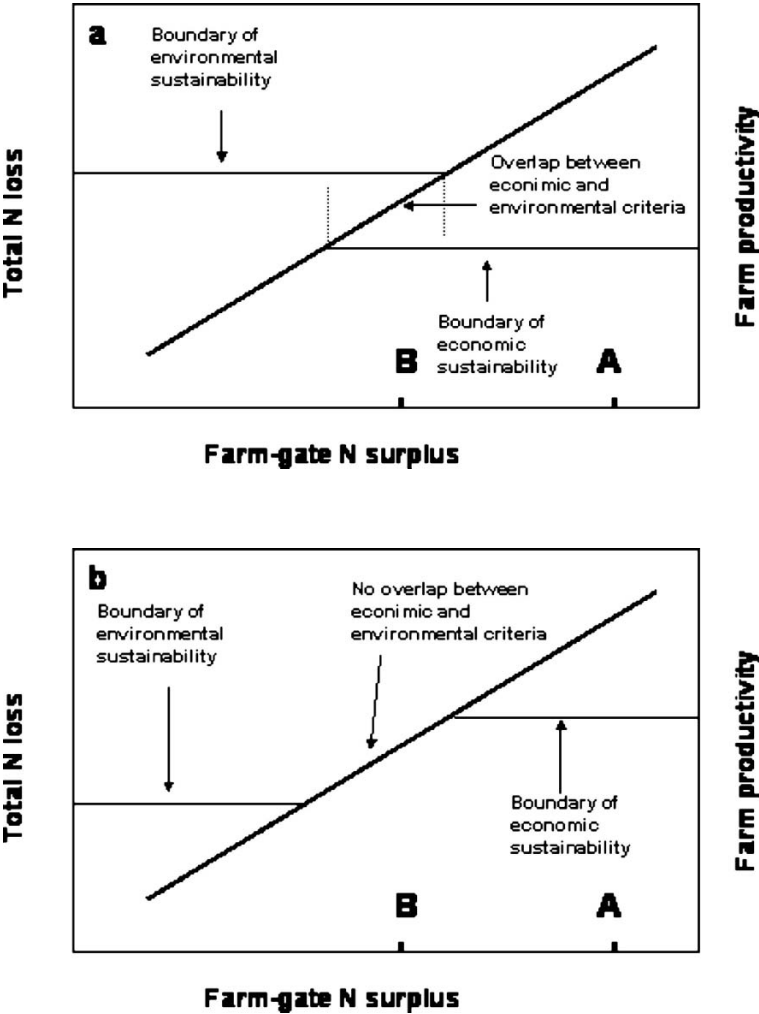
Fig. 8.9 Hypothetical relationships between farm-gate N surplus with farm productivity and N losses showing (**a**) scope and (**b**) no scope for achieving sustainability by reducing surplus from positions *A* to *B*, due to (**a**) overlap and (**b**) no overlap between economic and environmental boundaries

site and management factors. Thus, a high proportion of a large surplus would be lost under conditions favouring rapid mineralisation and leaching (high soil aeration, high temperature and rainfall, old permanent pasture), whereas a smaller proportion of a small surplus would be lost under similar conditions (Scholefield et al. 1988, 1991). This can be explained by considering the rates at which nutrients from different sources cycle within the whole system. Under

conditions whereby nutrient turnover rates are rapid and a large proportion of available nutrients are derived from mineralisation and (in the case of N and C) from fixation, efficiency of nutrient use can sometimes seem relatively high from budgetary information, as the proportion of total inputs from fertiliser and feeds is small. Under such conditions, however, losses can also be high, with the 'soil surface' surplus rendered small or even negative. Jarvis and Ledgard (2002) compared NH_3 emissions on typical dairy farm systems in the United Kingdom and New Zealand and showed that although N losses via NH_3 volatilisation were smaller in New Zealand, N inputs and farm-gate N surplus were also substantially smaller for similar levels of output. Other studies (e.g. de Klein and Ledgard 2001; Ledgard et al. 1996) have indicated that in the North Island pastures of New Zealand, milk production can be as great per hectare as from northern European intensive dairy systems, with less N input, but that N losses per unit of production are rather similar. In other words, the New Zealand system is apparently more efficient, since a greater proportion of the input is incorporated into products, but the two systems have roughly equal environmental impacts.

Another important consideration in the interpretation and use of nutrient budgets is that of scale, both temporal and spatial, as mentioned earlier in relation to nutrient inputs. The shorter the temporal scale, the greater will be the inaccuracies in the budget due to boundary effects and the effects of variations in weather. However, it must also be borne in mind that farming systems are continuously being modified, and so minimising these sources of error will not necessarily be possible. On the other hand, the greater the spatial scale of the budget, the greater the potential uncertainty in the data available; hence, going from field to farm scale (e.g. Jarvis et al. 1996) and from farm to river basin scale (e.g. Woli et al. 2002) gives rise to increasing degrees of uncertainty in relationships between budget surpluses and other parameters (see also Chapter 13 by de Willigen et al., this volume). It seems therefore that the best source of data on which to base ideas about the benefits and limitations of nutrient budgets might be the long-term field or 'farmlet' experiment.

Further progress with the derivation and use of suitable nutrient budget information/data is dependent on being able to assess the scope for exploitation of the variability in budget surplus datasets for achieving economic and environmental sustainability. This assessment can be done in several ways: examination and analysis of farm budget data (Jarvis 1999); using system synthesis approaches to calculate nutrient-use efficiency benefits of a range of managements (e.g. Jarvis et al. 1996) or a combination of the two (Cuttle and Jarvis 2005). The objective is to derive suitable 'indicators' of nutrient-use efficiency and to normalise the data for either equal economic or equal environmental performance. Such indicators include 'litres of milk per kilogram nutrient applied', 'surplus nutrient per volume of milk produced' (Jarvis 1999) and nutrient losses per gross margin (Jewkes et al. 2004). Normalisation can be achieved through regression analysis (e.g. Scheringer 2003) and/or bi-plot and cluster analysis using the relevant variables.
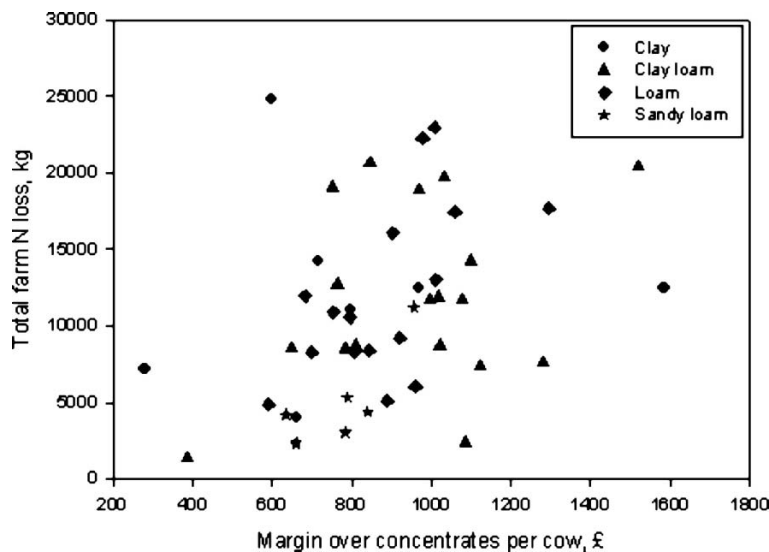
Fig. 8.10 Scatter plot showing variability of calculated N losses (kg) with farm profit (margin over concentrates) for a sample of dairy farms in southwest England: effects of soil type

In Fig. 8.10 we show the scatter plots of a set of N balance indicators that indicate the degree of variability across a number of typical dairy farms in the United Kingdom and the contribution to that variability from site factors, in this case soil type (after Jewkes et al. 2004). In this particular case, there are no readily discernible major influences of this site factor on the variability (degree of scatter) in the plot, due possibly to the effects of soil texture on N losses to water and N losses to the atmosphere nullifying one another.

As discussed in this chapter, much of the published information on nutrient budgets to achieve better management of pasture systems is for N and P, with little reference to the flows of other nutrients or energy. Such additional information could be useful for aiding the interpretation of N and P budgets and surpluses, in relation to assessing the scope for achieving sustainability. For example, much better efficiency of N and P use might be expected by replenishment of K, S and Mg supplies. Whether efficient use of support energy (e.g. fuel use on farm and to transport inputs and products) and minimal dissipation of photosynthetic energy can be linked to efficiency of nutrient mass flows has not been generally established, but the concepts hold promise. For example, White et al. (1983) showed that, of the animal production systems (dairy, beef and sheep) in the United Kingdom, milk production was the most efficient in terms of support energy per unit of output energy and protein and also in

terms of energy and protein per hectare. Support energy could be reduced by substituting bought-in concentrates by home-grown forage and N fertilisers by legume-fixed N. These concepts were taken further in a systems-synthesis approach to investigating the impacts of implementing various N loss mitigation strategies on dairy farms (Jarvis et al. 1996) in which reductions in N loss were linked with changes in support energy and emissions of greenhouse gases. Such integrated approaches combining analysis of nutrient budget and surplus data together with nutrient loss, greenhouse gas emissions and energy exchange data would seem to constitute a way of identifying the blueprints of sustainable systems for a range of site conditions and economic situations, as advocated by Oborn et al. (2003). These kinds of analyses will probably be best conducted within modelling frameworks (e.g. Brown et al. 2005; Cuttle and Jarvis, 2005; McDowell et al. 2005; van der Meer and van der Putten 1995), which can then be more conveniently integrated with socio-economic aspects (the third 'pillar' of sustainability) such as transport (Pretty et al. 2005; Stephens et al. 2003), external costs (Pretty et al. 2000) and the 'value' of the landscape (e.g. O'Leary et al. 2004; Stephens et al. 2003). Simple indicators incorporating all such sustainability information can then be derived from modelled and empirical data and used to compare and improve the nutrient flows and budgets of different pasture systems.

Global scale nutrient transport in food and fertiliser to centres of population and food production is becoming an increasingly important issue as the world population grows and the developed countries introduce more comprehensive and stringent environmental limitations to nutrient input and management. The eutrophication of coastal waters surrounding a densely populated, developing country due to loss of nutrients imported in human food, livestock feeds and fertiliser from other parts of the globe may be within the environmental limits tolerated in that country. In contrast, many of the developed countries are in danger of passing such strict environmental legislation that economic food production in those countries will be made increasingly less feasible, despite the implementation of the most effective strategies for optimal nutrient-use efficiency.

The derivation and use of national nutrient and energy budgets for the different food production and consumption sectors will be required in order to track global nutrient transfers. Whether or not nutrient emissions to the environment become further polarised across the globe will depend on (1) the effectiveness of policies based on nutrient balances at all scales; (2) to what degree they can be integrated with policies on energy use, food traceability, climate change and population dynamics; (3) the political and economic intricacies of global food markets and trade; and (4) the desire for a pristine home environment.

8.6
Conclusions

Nutrient budgets, particularly those of N and P are being used increasingly to assess the fertility and potential environmental impact of managed pastures throughout the world. In nutrient-poor and/or infertile regions, budgets can help farmers to conserve valuable nutrient stocks and organic matter reserves to reduce the risk of crop failure and famine. In the developed countries, the farm-gate nutrient budget has been regarded as one of the most practical and effective way of basing and implementing environmental legislation. It has been generally assumed that reduction in annual farm-gate N and P surpluses will enable both economic and environmental sustainability to be achieved by exploitation of the high variability in nutrient surpluses commonly measured on livestock farms in every region. However, we have not yet firmly established how much of this variability in any given dataset can be exploited for this objective (through e.g. integration of specific crop and animal managements and implementation of strategies for improved nutrient use efficiency) relative to that proportion due to intractable site factors, i.e. error and non-steady-state effects. A range of nutrient-use indicators has been developed and applied to help solve this problem through quantitative linkage of the economic and environmental performances of livestock farms. These performance values change with the spatial and temporal scales under consideration. Additional help with interpretation of the causes of the variability in N and P nutrient budgets and nutrient-use indicators could be provided by integration with relevant budgets for C, other nutrients and energy using models, but this will require a major research initiative to obtain the concerted data.

Notwithstanding the high variability found in farm-gate N and P surpluses and the scope indicated by this for achieving sustainability, it must be remembered that both the economic and environmental boundaries to achieving sustainability are transient and arbitrary. Moreover, the general trends with reducing surpluses reduce productivity as well as reducing losses to the environment. Whether sustainability is feasible will depend on whether a range of surplus values over which both criteria are satisfied exist. In many developed countries the implementation of ever more stringent environmental legislation is reducing this possibility, and mainstream livestock production is threatened. Transfer of nutrients across the globe from net food producer to net consumer will therefore become an increasingly important issue as localised nutrient emissions are balanced with the need to 'feed the nation' Many of the nutrient accounting methods developed for farm-scale situations may then be invaluable for application at the national scale, at which socio-economic and political factors will have considerably more importance.

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9 Natural Grasslands – a Case Study in Greece

Z. Koukoura

9.1
Introduction

The climate in the area surrounding the Mediterranean is characterised by the alternation of a rainy season in the cold months with a dry season in the warm months. Optimal moisture and temperature optima often do not coincide, although there are numerous spatial and temporal variations. The topography, soils and vegetation of the Mediterranean areas are also variable. Most of the area is covered by hills and mountains, resulting in a very rugged and highly dissected landscape. Soils are very variable, but the majority have been derived from calcareous formations. The soils are relatively shallow, slightly acidic (mean pH 5.6), with low concentrations of carbon (14 mg kg^{-1}), nitrogen (14 mg kg^{-1}), and phosphorus (17 mg kg^{-1}).

Grasslands cover 693,000 km^2 of the European Mediterranean region. Grassland vegetation has high species richness with over 500 species (Talamucci and Chaulet 1989). In dry and semi-dry areas the dominant species are annuals, whereas in sub-humid and humid areas perennial species dominate. The most important grass species are C$_3$ plants belonging to several genera such as *Bromus*, *Avena*, *Festuca*, *Lolium*, *Dactylis*, *Stipa*, etc., but there are also grasses of the C$_4$ group such as *Cynodon dactylon*, *Hyparrhenia hitra*, *Andropogon* spp., etc., which are less dominant and of inferior quality compared to the former group. The majority of Greek grasslands are dominated by perennial species that are either C$_4$ grasses, such as *Hypparrhenia hirta*, *Dichanthium ischaenum* and *Chrysopogon gryllus*, or C$_3$ grasses such as *Festuca* spp., *Bromus* spp and, *Brachypodium* spp. The former grassland sub-type with warm-season grasses is distributed in the low elevation zone (up to 800 m altitude) where the summers are long and dry, whereas the

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latter sub-type is found in the high elevation zone (above 800 m altitude) with short summers and occasional rainfall (Papanastasis 1981, 1982).

In these grasslands, annual and perennial legumes are the most important groups of forbs and include several species of *Trifolium*, *Medicago*, *Lotus*, *Astragalus*, *Vicia* and *Onobrychis*.

Grassland productivity is relatively low and has a strong seasonal and inter-annual variability. Seasonal growth results in two feed gaps, a short one in winter and a long one in summer. Annual growth may vary 2- to 3-fold between dry and wet years. The seasonal growth of herbage is related to soil moisture, air temperature and radiation (Cereti et al. 1987; Gutman 1978; Koukoura and Papanastasis 1997). In dry and semi-dry areas in Greece, annual production is usually below 1,500 kg ha^{-1}, while in sub-humid and humid areas it may reach 3,000–4,000 kg ha^{-1}. These differences are also reflected in altitude zonation, with the lower altitudes having lower production than the higher altitudes (Papanastasis 1982).

The majority of grasslands in the Mediterranean are overgrazed, with serious consequences to their productivity and sustainability. Visible signs of grassland degradation are a dense network of trails made by grazing animals, the presence or dominance of various weedy species, and soil erosion in extreme cases. Several studies have shown that moderate grazing of Greek grasslands is the key factor in maintaining their productivity, biodiversity and environmental value (Papanastasis and Koukoura 1992; Tsiouvaras et al. 1998).

9.2
Biomass Loss during Decomposition of Plant Residues

Litter decomposition is important for maintaining the productivity of grassland ecosystems because it controls nutrient cycling and humus formation as well as the availability of nutrients required for plant growth. Mason (1977) distinguished three basic processes of decomposition, namely biological action, weathering and leaching. Key factors affecting decomposition are: the decomposer community, litter quality and the physical and chemical characteristics of the environment (Berg and McClaugherty 1989; Hooper and Vitousek 1998; Kalburji et al. 1998; Koukoura 1998; Koukoura et al. 2003; Moretto et al. 2001; Rose et al. 2002; Swift et al. 1979).

In Mediterranean semi-arid grasslands that are species-rich, decomposition rates of litter differ because of interspecific variation in leaf or culm litter quality. Decomposition rates may also vary across sites because soil physical and chemical characteristics and meteorological conditions influence the abundance of soil microorganisms necessary for litter decomposition (Galantini et al. 1992).

Relatively few studies have examined plant species effects on rates of litter decomposition and nutrient availability in semi-arid grasslands (Burke et al.

1989; Kalburtji et al. 1998; Koukoura et al. 2003; Vinton and Burke 1995). In the semi-arid environment, the abundance of soil micro-fauna depends on soil organic carbon content and soil texture (Garcia and Hernandez 1996; Noble et al. 1996). The decomposition rate of soil organic matter or any litter substrate is defined by the feeding microbial populations, i.e. microbial production-to-assimilation ratio, microbial growth rate, and efficiency during decomposition in a given soil (Bosatta and Agren 1991). Litter decomposition studies have not shown consistent effects of plant species diversity on decomposition rates (Blair et al. 1990; Elliot et al. 1993; Fyles and Fyles 1993; Hart et al. 1993; Klemmedson 1991). Four recent studies have specifically examined the effect of litter diversity on decomposition (Bardget and Shine 1999; Finzi and Canham 1998; Wardle et al. 1997) and found that biodiversity itself was not a significant determinant of decomposition rate. Kalburtji et al. (1998) suggest that litter decomposition in a Mediterranean grassland is related more to soil characteristics and rainfall conditions (low decomposition in acidic soils with low soil water content and dry weather conditions) than to differences among plant species. In contrast, Bardgett and Shine (1999) studied six herbaceous species and found that increased litter diversity corresponded to increased litter decomposition and increased efficiency of soil biological processes.

The changes (x) in mass and nutrient content of decomposing litter, as percentages of their initial quality (x_0) at time T are well described by the equation cited by Olson (1963) and Swift et al. (1979):

$$x/x_0 = e^{-kt}$$

where x_0 is the initial % weight, e the natural log constant, and k the rate constant. Two methods of comparison are used for the constant k. In the first method, k values of each parameter between plant parts of each species are compared by using a t-test. In the second, the ranking order of k values of the various examined parameters between plant parts of the species are compared by using the Spearman rank correlation coefficient (Steel and Torrie 1980). Aber and Melillo (1980, 1982) suggested a model to calculate the amount of nutrients immobilised per gram litter and this is used to regress the percentage remaining litter mass against the nutrient concentration in the remaining litter. From the slope (b) and the intercept (a) of the linear regression and the initial nutrient concentration of the litter (Nu_o), the amount of nutrient immobilised (Nu_i, milligrams of immobilised nutrient per gram litter) is calculated as:

$$Nu_i = [(a^2/-4b) - 100\ N_{u0}]/10$$

The percentage of litter mass remaining (M_r) at the point at which immobilisation changes to mineralisation is described by the equation $M_r = a/2$. The effects of plant species on nutrient cycling is determined by the nutrient release rates from the litter, the total amount of litter produced per unit area and the immobilisation capacity (Chapin 1991).

9.3
Effect of Residue Composition on Decomposition Rates

Koukoura (1998) and Koukoura et al. (2003) studied the changes (x) in cellulose, lignin, total nonstructural carbohydrates, cell walls and total N, P, K and Ca content of decomposing litter of the perennial grasses *C. gryllus*, *D. ischaemum*, *Festuca ovina* and the annual legume *Trifolium purpureum* (Tables 9.1, 9.2, 9.3). These species cover almost 72% of the soil in a semi-arid Greek grassland. The total leaf litter loss of these species during the decomposition process varied from 46 to 49% after 12 months and reached up to 65–73% after 24 months. The rate of litter mass loss of stems was significantly lower than that of leaves. The decomposition constants (k values) for all species and plant parts are shown in Table 9.4.

Lignin, cellulose and total nonstructural carbohydrates (TNSC) were examined with regard to their effect on the decomposition rate of *C. gryllus* and *D. ischaemum* (C_4), and *F. ovina* and *T. purpureum* (C_3) (Tables 9.5, 9.6, 9.7). Differences were found even among species using the same photosynthetic pathway. The litter of *C. gryllus* had the highest lignin and cellulose content and appeared

Table 9.1 Plant species present at the end of spring 1987 in the study site

Plant species	Cover (%)
Grasses	
Bromus tectorum	2.01
Chrysopogon gryllus	29.28
Dichanthium ischaemum	8.27
Festuca ovina	32.31
Phleum phleoides	4.03
Vulpia myuros	3.01
Legumes	
Astragalus austriacus	3.84
Coronilla varia	4.04
Trifolium purpureum	2.15
Vicia craca	4.03
Trifolium subterraneum	3.01
Forbs	
Rumex acetosela	2.01
Potentilla recta	2.01

Table 9.2 Decomposition constants (*k* values) for all species and plant parts were calculated from the weight losses during the first and second year using the formula $x/x_0 = e^{-kt}$ (Olson 1963)

Species		Decomposition constants (*k*) g^{-1}	
	Plant part	First year	Second year
D. ischaemum	Leaves	0.59	0.37
	Culms	0.34	0.22
C. gryllus	Leaves	0.51	0.31
	Culms	0.28	0.19
F. ovina	Leaves	0.56	0.35
	Culms	0.32	0.20

Table 9.3 Cell wall content (%) of species litter during the decomposition process

Plant species	Initial content (%)		First year content (%)		Second year content(%)	
	Leaves	Culms	Leaves	Culms	Leaves	Culms
D. ischae-mum	59.6	74.5	53.6	69.8	50.0	63.4
C. gryllus	68.7	79.3	63.5	78.2	58.5	71.5
F. ovina	65.2	77.3	58.7	73.4	56.0	66.6

Table 9.4 C/N ratios for all species and plant parts during the experimental period

Species	Plant part					
	Initial		12 months		24 months	
	Leaves	Culms	Leaves	Culms	Leaves	Culms
D. ischaemum	35.5	59.2	27.3	46.2	20.2	34.7
C. gryllus	30.1	76.5	21.9	65.3	17	46
F. ovina	36.2	80.1	28.2	63.6	21.1	40.6

Table 9.5 Lignin content (%) of species litter during the decomposition process

Plant species	Initial content (%)		First year content (%)		Second year content (%)	
	Leaves	Culms	Leaves	Culms	Leaves	Culms
D. ischae-mum	27.32	29.3	24.0	28.97	23.6	25.6
C. gryllus	31.30	32.30	30.0	32.31	28.6	30.1
F. ovina	29.2	31.7	27.5	29.5	27.0	28.4

Table 9.6 Cellulose content (%) of species litter during the decomposition process

Plant species	Initial content (%)		First year content (%)		Second year content (%)	
	Leaves	Culms	Leaves	Culms	Leaves	Culms
D. ischaemum	32.2	45.2	29.5	40.8	26.4	37.8
C. gryllus	37.40	47.0	33.5	45.9	29.9	41.4
F. ovina	36.0	45.6	31.2	43.7	28.2	38.2

Table 9.7 Total non structural carbohydrate (TWSC) concentration (mg g^{-1}) of species litter during the decomposition process

Plant species	Initial concentration (mg/g)		First year concentration (mg g^{-1})		Second year concentration (mg g^{-1})	
	Leaves	Culms	Leaves	Culms	Leaves	Culms
D. ischaemum	254.5	238.5	142.2	138.3	97.88	71.2
C. gryllus	226.2	216.4	121.4	114.1	76.2	56.3
F. ovina	248.2	225.5	130.9	127.3	89.7	65.7

to be more resistant to decay than *D. ischaemum, F. ovina* and *T. purpureum*. According to Chapin (1991), differences in litter quality may be due to interspecific differences in the response of plants to nutrient supply, as well as differences in nutrient translocation and nutrient leaching from senescent plant parts after changes in nutrient supply. These differences influence actual litter decay, which is also affected by plant part and "litterbag" type (soil fauna effect). The smaller the mesh-size of the litterbag, the slower the decomposition rate because only smaller soil fauna has access to the litter.

There is evidence for the importance of tannins in controlling rates of litter decomposition. After initial loss of various components, decomposition rates decrease and organic matter becomes more resistant to decomposition. Minder-

Table 9.8 Tannin concentration (mg g^{-1}) of species litter during the decomposition process

Plant species	Initial tannin concentration mg g^{-1}		First year tannin concentration mg g^{-1}	
	Leaves	Culms	Leaves	Culms
D. ischaemum	12.9	17.1	27.3	30.17
C. gryllus	15.7	19.3	35.1	38
F. ovina	14.7	18.5	32.35	33.9

man (1968) found that decomposition of litter in the field did not equal the sum of the decay rates of its individual components. Clark and Paul (1970) showed that this could be overcome by correcting data for individual components to allow for re-synthesis of secondary metabolites that were relatively resistant to decomposition.

Tannins with slow decomposition rates may originate from the litter itself or be synthesised by microbes. Tannins determine the rates of litter decomposition, their effects being influenced by the pH of the litter and the soil nutrient status. In the later stages of decomposition, humic materials, which also contain tannins, can influence decomposition. It has been shown that the action of microbial proteolytic enzymes can be inhibited or stimulated by humic acids. From the study of Koukoura (1998) in semi-arid grassland (Table 9.8), it is obvious that *C. gryllus* had a higher tannin content than other species by the end of the first year. As a result of its higher lignin, cellulose and tannin content, the litter of *Chrysopogon gryllus* was more resistant to decay than that of *D. ischaemum* and *F. ovina*.

A negative relationship was also found between decomposition rates and litter lignin and cellulose content. Swift et al. (1979), Pastor et al. (1987), Chapin (1995), Hobbie (1996) and Aerts and De Caluwe (1997) found that decomposition proceeds rapidly in materials high in N and low in lignin and other polyphenolic compounds. In many cases, plant species from infertile soil produce litter that is more difficult to decompose than litter from fertile soil because they generally have higher C/N ratios and higher concentrations of decay-resistant plant compounds (Field et al. 1992).

Differences in decomposition rate among different plant parts (leaves and stems) can be related to differences in allocation of metabolic products among plant parts and the differences between growing seasons. Allocation of these products differs between C_3 and C_4 plant species. In semi-arid grassland, the soil receives a high proportion of litter from species with high lignin and cellulose concentrations that decompose slowly. Thus, one may postulate that the concentration of lignin and other slowly decomposable compounds influences the rate of litter decomposition and nutrient release. This hypothesis is in agreement with the results of Koukoura et al. (2003), who showed a positive relationship

between C content and decomposition rate, which probably reflects the negative relationship between C and lignin ($r=-0.39$, $P=0.1$) and lignin and total non-structural carbohydrates ($r=-0.48$, $P=0.05$). The negative relationship between lignin content and decomposition rate largely reflects the positive relationship between lignin and cellulose contents ($r=0.71$, $P=0.0022$).

More similarities were found in the k values for the two dominant species *C. gryllus* and *F. ovina*, which produce above-ground litter with low decomposition rates and high concentrations of lignin and cellulose. The slow decomposition rate also means that nutrients released from their litter will be available over a long period.

Kosmidou and Koukoura (Kosmidou and Z. Koukoura, unpublished data) found that the total loss of root litter from the initial weight varied from 39% to 59% for *D. ischaemum* and from 36% to 58% for *C. gryllus*. Root residues of the two C_4 species were decomposed with lower rates than leaf residues. Lohmus and Ivask (1995) found that the root system loss of *Picea abies* in Estonia varied from 21% to 33% during the first year.

Perennial grasses have significantly higher root biomass and significantly lower root N content than cool-season annuals (Hooper 1998), suggesting greater potential for N immobilisation (Wedin and Tilman 1990). Large quantities of readily decomposable litter could lead to higher microbial growth and higher immobilisation.

9.4
Mineralisation and Immobilisation of Nutrients

Litter quality and decomposition rates are also defined by litter content of N, P, K and Ca. Gosz et al. (1973) observed an increase in nutrients such as N, K and Ca during decomposition of plant materials; they suggested that nutrient accumulation may be attributed mainly to microbial activity (Chen and Stark 2000). The effects of litter quality on litter microbial immobilisation are not clear. More recalcitrant litter may lead to greater microbial N demand and higher immobilisation of N (Aber and Melillo 1982; Melillo et al. 1982). Litter content of N, P, K and Ca of the species *C. gryllus*, *D. ischaemum*, *F. ovina* and *T. purpureum* in a semi-arid grassland were positively related to decomposition rate (Koukoura et al. 2003).

After 12 months, the leaf nitrogen content increased, relative to the initial N content, by 5.7%, 19.3% and 4.2% for *D. ischaemum*, *C. gryllus* and *F. ovina*, respectively, and decreased by 4.8% for *T. purpureum*. After 24 months the initial N content was increased by 14% for *D. ischaemum*, 27% for *C. gryllus*, 118% for *F. ovina* and decreased by 16% for *T. purpureum*. This indicates that N accumulation occurred during the entire decomposition period for grass species. N accumulation decreased in the following order *C. gryllus* > *D. ischaemum*

> *F. ovina*. In contrast, N release was observed for legume species during the entire decomposition period. An increase in N content was observed over a 12- to 24-months period during decomposition of culms. The N content of root litter of *D. ischaemum* and *C. gryllus* was reduced during the first year and was higher for *D. ischaemum* than that for *C. gryllus*. Fahey (1983) has stated that an increase in N content during the early stages of litter decomposition is common, presumably resulting from N transfer by saprophytic fungi. In a semi-arid grassland, Kalburtji et al. (1998) found an increase in nitrogen content during the first year in the leaf litter of *Dactylis glomerata* and *Vicia villosa*, probably due either to import from an external source or to N fixation. Nitrogen immobilisation is important because it prevents loss of this readily available nutrient, especially during winter months with high rainfall. Mary et al. (1996) summarised the results of different incubation studies that indicated that the amount of N immobilisation is favoured by large amounts of mineral N present in the soil. In contrast, low mineral N concentrations decrease decomposition of plant residues but do not stop it completely.

The N immobilisation potential associated with the decomposition of most plant residues must be compared to N availability in the soil layers where residues are incorporated. The immobilisation potential may be high, and is often higher than available mineral N. Therefore, plant residue decomposition may frequently be controlled by N. Under limiting N conditions, decomposition is slowed, and takes place over a long period of time.

The rate of N loss is associated with the C/N ratio of the soil and the litter. At the start of decomposition, the litter C/N ratio is usually higher than that of the soil, decreasing with time and becoming similar to the C/N ratio of the soil. In the experiments of Kalburtji et al. (1998) in semi-arid grasslands, C/N ratios were 8.9 for soil, 39 for *Dactylis glomerata* and 44 for *Vicia villosa* at a neutral site. The corresponding values at an acidic site were 7, 70 and 45, respectively. The higher C/N ratio of *D. glomerata* at the acidic than the neutral site is probably due to the lower soil N concentration at the acidic compared with the neutral site. *V. villosa*, as a legume species, was not influenced by soil N concentration, and the C/N ratio of *V. villosa* litter did not differ between the two sites. The C/N ratio of litter of both species decreased with time, but remained higher than in the soil.

According to Gosz et al. (1973), litter N in forest soils is immobilised at C/N ratios greater than 20 to 30, and is released or mineralised at lower ratios. In the study by Kalburtji et al. (1998) N mineralisation was found at C/N ratios higher than 20–30, probably due to differences in climatic conditions and litter components (forest litter contains branches and leaves, whereas annual plant litter contains mainly leaves and stems).

Koukoura (1998) found relatively lower C/N ratios (<23) for the species *Chrysopogon gryllus, Dichanthium ischaemum and Festuca ovina* at the end of the second year of the decomposition period. The initial soil C/N ratio was 10. This provided evidence that mineralisation had occurred. Phosphorus and K were also released during the first and second years, with significant differences

among species (*C. gryllus* > *D. ischaemum* > *F. ovina* > *T. purpureum*), whereas Ca was accumulated.

The release of P and K from litter of the grass *Dactylis glomerata* and the legumes *Vicia villosa* and *Lotus corniculatus* was studied by Kalburtji et al. (1998). The rate of P and K release was lower at the neutral site than at the acidic site. This suggests that soil acidity combined with wet environmental conditions facilitated the release of P and K. Pomeroy (1970) stated that nutrient ratios such as the N/P ratio are important. The initial N/P ratios of three grass species in the study by Koukoura (1998) were 14, 17 and 19 for *Dichanthium ischaemum, Chrysopogon gryllus* and *Festuca ovina,* respectively, changing to 20 for *D. ischaemum* and *C. gryllus* and 22 for *F. ovina* at the end of the first 12 months and to 21 for all three species during the subsequent 12 months. Similarly, Gosz et al. (1973) found that the N/P ratio of plant material tended to stabilise with time.

9.5
Conclusions

Plant residues and their decomposition play an important role in the long-term fertility of grasslands. Plant residue decomposition provides nutrients, but is also a source of soil organic matter, thereby promoting water infiltration and, by thermally insulating the soil surface, moderating soil temperature and limiting evaporation from the soil.

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10 Dryland Ecosystems

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10.1
Introduction

Drylands occupy approximately 40% of the Earth's land surface and have low inputs of mean annual precipitation (P) relative to mean annual potential evapotranspirational (ET) losses (Millennium Ecosystem Assessment 2005). The United Nations Educational, Scientific and Cultural Organization (UNESCO 1979) proposed the following classification scheme for drylands: hyper-arid zone (P/ET <0.03), arid zone (P/ET 0.03–0.20), semi-arid zone (P/ET 0.20–0.05) and subhumid zone (P/ET 050–0.75). The majority of studies summarised in this chapter were conducted in arid and semi-arid zones with mean annual precipitation ≤300 mm.

The low precipitation and high temperature regimes characteristic of dryland regions result in low annual rates of organic matter decomposition, nutrient cycling and primary productivity (Noy-Meir 1973). While biogeochemical fluxes are small in drylands over the course of a year, relative to temperate or tropical ecosystems, "hot spots" or "hot moments" of biological activity occur, initiating pulses of nutrient flow. These patches or events of biological activity are driven by rainfall and linked to movement of water across the landscape (Belnap et al. 2005). The high degree of spatial and temporal variability in rainfall and associated biological activity that drive nutrient cycling in dryland ecosystems complicate efforts to compile annual nutrient budgets for these ecosystems. Never-

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theless, nutrient budgets are useful tools to identify gaps in current knowledge of dryland biogeochemical cycles.

10.2
Nitrogen Cycle

10.2.1
Nitrogen Inputs from Biological Fixation

Nitrogen (N) as it occurs in the atmosphere cannot be used by vascular plants or other eukaryotic organisms as a nutrient source. Gaseous dinitrogen (N_2) must be reduced or "fixed" to ammonia (NH_3) by either lightning or prokaryotic organisms (e.g. eubacteria and cyanobacteria). These organisms can be found free-living in soils as autotrophs or heterotrophs, lichenised by fungi, or as symbionts with some species of vascular plant (see also Chapter 2 by McNeill and Uncovich, this volume).

Nitrogen fixation rates in dryland ecosystems have long been assumed to be low due to high temperatures and low soil moisture, providing less than optimal conditions for N fixation to occur. This assumption has been supported by using a mass balance approach to identify levels of ecosystem N inputs; biogeochemical model results suggest that soil N levels may be fully accounted for by atmospheric N deposition alone, resulting in little or no inputs via fixation in dryland ecosystems (see CENTURY results in Cleveland et al. 1999). In contrast, field measurements of N fixation can be quite high when conditions are optimal. The length of time over which optimal conditions occur within a year, however, is limited, resulting in low N_2 fixation annually. This will be a recurring theme throughout this chapter. In this section, we review the knowledge of N_2-fixing organisms and rates in dryland ecosystems and outline the major uncertainties in estimating N_2 fixation in these ecosystems.

Many species of cyanobacteria found in drylands fix N_2 (e.g. *Nostoc*, *Scytonema* and *Schizothrix*). These species can be free-living within the soil, as epiphytes on the surface of lichens, mosses and vascular plants (Belnap 2003), or as part of soil lichens. Much of the research on N_2 fixation in dryland ecosystems has focused on cyanobacteria present in biological soil crusts (Tables 10.1, 10.2, 10.3). Heterotrophic bacteria can also fix N_2 in bulk soil and in the root zone of plants (Table 10.4). The most well-known genera, *Azotobacter*, *Clostridium*, *Azospirillum*, *Streptomyces* and *Spirilla* occur worldwide (West 1991); however, most reported values of N_2 fixation by heterotrophic bacteria are extremely low. Heterotrophic soil bacteria can also live inside the cyanobacteria sheath. In these cases, the heterotrophs often scavenge oxygen, thereby creating anaerobic microzones and thus facilitating N_2 fixation in the cyanobacteria. The hetero-

Table 10.1 Nitrogen fixation estimates for biological soil crusts in United States drylands

Location	Crust type	Converted rates (nmol cm^{-2} h^{-1})	Laboratory/field	Incubation conditions	Reference
Chihuahuan Desert	Cyanobacteria-lichen	0.001	Laboratory	12 h, 25°C	Hartley and Schlesinger 2002
	Microcoleus, Nostoc, Scytonema	0.5–1.5	Laboratory	1 h, 24°C	Yeager et al. 2004
Colorado Plateau	*Microcoleus, Nostoc, Scytonema, Collema*	0.002–0.98	Laboratory	4 h, 26°C	Belnap 1996, 1999, 2002; Evans and Belnap 1999; Belnap et al. 2004
		0.3–1.0	Field	1 h, 32°C	Barger 2003
	Microcoleus, Nostoc-Scytonema	0.2, 2.0	Laboratory	1 h, 24°C	Yeager et al. 2004
		0.7, 4.8	Laboratory	No data	Johnson et al. 2005
		11–12	Laboratory	96–144 h, 23°C	Jeffries et al. 1992
Great Basin Desert	*Microcoleus, Nostoc, Scytonema, Collema*	0.3–5.4	Laboratory	24 h, 21°C	Terry and Burns 1987
		11–21	Laboratory	23°C	Skujins and Klubek 1978
		22–27; 141–178	Field; laboratory	18–20°C; 12 h, 26°C	Rychert and Skujins 1974
Mojave Desert	Cyanobacteria-lichen	1.2–3.3	Laboratory	24 h, 30°C	Billings et al. 2003
Sonoran Desert	Cyanobacteria-lichen	6.4, 11	Laboratory	48 h, 5–30°C	Eskew and Ting 1978
	Cyanobacteria	12, 18	Laboratory	520 days	Mayland et al. 1966[a]
	Cyanobacteria	78	Laboratory	38°C	MacGregor and Johnson 1971

[a]Mayland et al. 1966 used ^{15}N to estimate nitrogen fixation; all other studies used the acetylene reduction assay (ARA)

Table 10.2 Nitrogen fixation estimates for biological soil crusts in drylands in Africa and the Middle East [a]

Location	Crust type	Converted rates (nmol cm^{-2} h^{-1})	Laboratory/ field	Incubation time/ temperature	Reference
Kalahari Desert, Botswana	Light cyanobacteria	60	Laboratory	9–22 days at 27.5°C	Skarpe and Henriksson 1987
	Nostoc–Scytonema	680			
Maasai Mara, Kenya, 45 sites	Cyanobacteria	0.1–12	Laboratory	4 h at 26°C	J. Belnap, unpublished data
Sahel Desert, Niger	Cyanobacteria	3.5–4.2	Laboratory	2–163 h at 30°C	Issa et al. 2001

[a] All Studies used ARA

Table 10.3 Nitrogen fixation estimates for free-living *Nostoc commune* sheets in dryland ecosystems [a]

Location	Crust type	Converted rates (nmol cm^{-2} h^{-1})	Laboratory/field	Incubation time/ Temperature	Reference
Chihuahuan Desert, USA	*N. commune* sheets	8.2	Laboratory	4 h at 26 °C	Barger 2003
Chihuahuan Desert, USA	*N. commune* sheets	44.6	Laboratory	4 h at 26 °C	J. Belnap, unpublished data
Inner Mongolia, China	*N. commune* sheets	2.8	In situ field	4 h at 26 °C	J. Belnap, unpublished data
Vestfold Hills, Antarctica	*N. commune* sheets	0–5.0	Field	2 h at –20 to 10 °C, throughout summer	Davey and Marchant 1983

[a] All Studies used ARA

Table 10.4 Heterotrophic nitrogen fixation estimates for dryland ecosystems [a]

Location	Vegetation	Converted rates	Laboratory/field	Incubation time/Temperature	Reference
Mojave desert, USA	*Larrea tridentata, Lycium* spp., *Pleuraphis rigida*	0.3–1.9 nmol cm^{-2} h^{-1}	Laboratory, glucose added	24 h at 30°C	Billings et al. 2003
Great Basin Desert, USA	*Artemisia*	27.6 ng N (g soil)$^{-1}$ h^{-1}	Laboratory	21 days at 22°C, in the dark	Klubek and Skujins 1980
	Ceratoides	21.4 ng N (g soil)$^{-1}$ h^{-1}			
	Atriplex	34.7 ng N (g soil)$^{-1}$ h^{-1}			
Egypt	Non- or low saline soils	17–19 mg N (100 ml)$^{-1}$	Laboratory	7 days at 30°C	Mahmoud et al. 1978
	Saline alkaline soils				
	Moderate-strongly saline	13 mg N (100 ml)$^{-1}$			

[a] All Studies used ARA

trophs also fix N_2 themselves. Such a relationship has been demonstrated for the cyanobacteria *Microcoleus vaginatus* (Steppe et al. 1996).

Many dryland plants have root nodules containing N_2-fixing bacteria or actinomycetes. The bacteria found in leguminous plants are either *Rhizobium* or *Bradyrhizobium* spp. (Farnsworth et al. 1976; Whitford 2002). In arid and semi-arid ecosystems, the main N_2-fixing plant species include the shrubs *Acacia*, *Prosopis*, *Pterocarpus* and *Pericopsis* and the herbaceous *Lupinus*, *Dalea*, *Astragalus* and *Lotus*. Many non-leguminous dryland plants also have nodules. These nodules are most often occupied by the actinomycete *Frankia.* These plant families include, but are not limited to Asteraceae, Scrophulariaceae, Zygophyllaceae, Poaceae, Cactaceae, Krameriaceae, Casuarinaceae, Rosaceae and Rhamnaceae (Farnsworth et al. 1976; Redell et al. 1991).

Estimates of biological soil crust and heterotrophic N_2 fixation measured by the acetylene reduction assay (ARA) are highly variable, ranging from 0 to 680 nmol C_2H_4 cm^{-2} h^{-1} (Tables 10.1, 10.2). Although these rates differ by several orders of magnitude, approximately 85% of the reported acetylene reduction rates were <20 nmol cm^{-2} h^{-1}. There are few reported values for symbiotic N fixers in unamended non-agricultural dryland soils due to the difficulty in measuring in situ N fixation rates. However, N inputs by symbiotic N fixers may be quite high. Rundel et al. (1982) estimated that *Prosopis* woodlands in the Sonoran Desert fixed N_2 at rates of 25–30 kg ha^{-1} $year^{-1}$. There are several factors that may contribute to the large range of N_2 fixation rates reported in the literature. In this next section, we review key factors that influence measurements of N_2 fixation in dryland ecosystems and provide suggestions on how to standardise N_2 fixation methodology for future studies.

10.2.1.1
Methodological Considerations

A basic understanding of N_2 fixation methodology is essential to the interpretation of this body of work Researchers estimate N_2 fixation by measuring the incorporation of $^{15}N_2$ into the soil directly, or by measuring nitrogenase activity using the acetylene (C_2H_2) reduction assay (ARA). In the latter case, ARA rates must then be converted back to an estimate of the amount of N_2 fixed. Although most studies report nitrogenase activity, and not actual N_2 fixation, we use these terms interchangeably throughout this chapter. Most studies use the theoretical ratio of 3:1 to convert from ethylene (C_2H_4) produced to N_2 fixed (six electrons are required for N_2 reduction, but only two electrons for the reduction of C_2H_2). However, there are many conditions that alter this theoretical ratio. Values from 3 to 4 appear to hold for lichens and N_2-fixing plants; however, values for free-living soil cyanobacteria range from 0.1 to 6.1 and can change seasonally (reviewed in Belnap 2001a, 2001b). There is no information on conversion ratios for heterotrophic N_2 fixation. Since conversion ratios may be flexible, ARA must be calibrated with $^{15}N_2$ for each site and organism of interest if ARA is to be used effectively as an estimate of N_2 fixation.

10.2.1.2
Environmental Controls on Cyanobacterial N₂ Fixation

Environmental conditions experienced by the organisms before and during the measurements, although often not reported and seldom standardised, strongly influence N_2 fixation rates. In addition, nitrogenase activity is not linear through time, resulting in N_2 fixation rates that may vary depending on incubation time. Here, we review the environmental controls of cyanobacterial N_2 fixation.

Cyanobacteria and bacteria are physiologically active only when water is available; consequently, N_2 fixation is controlled primarily by moisture (Kershaw 1985; Nash 1996). Liquid water is required for carbon (C) fixation in cyanobacteria (Lange 2003) and, because N_2 fixation requires the products of photosynthesis, availability of water also ultimately determines the amount of N_2 fixed. Most dryland soil cyanolichens require a water content of at least 80% dry weight for initiation of net C fixation activity (Lange et al. 1998). Moisture needed to initiate and optimise N_2 fixation varies widely among species, ranging from 6% of dry weight to total saturation (reviewed in Belnap 2003). Nitrogenase activity in *Microcoleus-Collema* soil communities, common in dryland ecosystems, drops rapidly at soil water potentials below –0.33 kPa, with a 50% reduction by –100 kPa (Rychert et al. 1978).

Time from initial wetting to the initiation of C and N_2 fixation is critical in drylands, as high temperatures can cause soils to dry so rapidly that organisms may be unable to accumulate the C needed to support N_2 fixation activities. Upon rewetting, nitrogenase activity generally does not begin for 10–60 min, depending on the species and past and current environmental conditions. Time to maximal fixation ranges from 1 to 36 h (reviewed in Belnap 2003). Time since the last wetting event can also influence time to nitrogenase activity initiation (Dodds et al. 1995; Kershaw and Dzikowski 1977). The lag time between wetting and nitrogenase activity probably reflects the amount of C, nitrogenase enzymes, and ATP in the cell.

Nitrogen fixation rates are also limited by temperature extremes. Most nitrogenase activity occurs at –5 °C to 30 °C, with the optimum at 20–28 °C for most drylands (e.g. Lange et al. 1997, 1998). Minimum air temperatures for nitrogenase activity have been recorded at –7.6°C (Horne 1972), although some species show no activity at 0 °C (Isichei 1980). Freezing can damage nitrogenase and thus substantially reduce nitrogenase activity (Scherer et al. 1984). Low temperatures can reduce photosynthetic rates and thus reduce available ATP and reductant pools, creating a lag time after freezing before N_2 fixation is initiated (Kershaw 1985). Once above the minimum temperature for a species, N_2 fixation rates show a strong, positive response to increasing air temperature until an upper limit is reached, after which rates quickly decline.

Light optima vary among species and places, depending on the distribution and concentrations of photosynthetic and UV-screening pigments, soil characteristics, and the distribution of cyanobacteria within the substrate, colony, or thallus (e.g. Dodds et al. 1995; Garcia-Pichel and Belnap 1996). Light levels required for maximum nitrogenase activity in cyanobacteria are generally low

(100–150 μmol m^{-2} s^{-1} photosynthetically active photon flux density; Garcia-Pichel and Belnap 1996). Below this level, nitrogenase activity is greatly reduced, presumably due to a lack of photosynthetic products to support N$_2$ fixation (Kershaw 1985). Although depression of N$_2$ fixation at high light levels has been reported (e.g. Rychert et al. 1978), high temperatures and low moisture content could also explain these results.

Soil properties such as pH, salinity and nutrient content in drylands vary with topographic position or management practices. Dryland soils in low lying areas tend to be more alkaline and saline compared to up-slope soils (James et al. 2004). Intensive irrigation and fertilisation in agricultural dryland soils increase salt and nutrient contents. All of these factors influence N$_2$ fixation rates. Growth and nitrogenase activity in soil cyanobacteria are greatest above pH 7 (Brock 1973), although some depression of nitrogenase activity has been seen at pH 8–10 (Granhall 1970). Depression of nitrogenase activity at high pH may be due to lower P availability in Ca-rich soils (Lajtha and Schlesinger 1988b; see Sect. 10.3.2), whereas depression of nitrogenase activity at low pH is likely due to reduced photosynthetic capacity (Shapiro 1973) or reduced concentration of nitrogenase enzymes (Stewart et al. 1977).

Salinity effects on nitrogenase activity in dryland soils are not studied frequently and show mixed results. In Utah, N$_2$-fixing cyanobacteria preferred soils with high electrical conductivity (70 dS m^{-1}; Anderson et al. 1982). In contrast, experimental addition of NaCl to cyanobacterial lichen crusts in the Chihuahuan desert inhibited nitrogenase activity (Delwiche and Wijler 1956).

Nutrient effects on nitrogenase activity vary in dryland ecosystems depending on the element. Elevated soil ammonium (NH$_4^+$) depresses nitrogenase activity, whereas mixed results have been obtained with elevated nitrate (NO$_3^-$). NH$_4$NO$_3$ amendments inhibited nitrogenase activity in cyanobacterial lichen crusts in the Chihuahuan desert (Hartley et al. 2002). Phosphorus and potassium additions can stimulate cyanobacterial nitrogenase activity, perhaps through a stimulation of ATP synthesis (e.g. Dodds et al. 1995). Low amounts of zinc (Zn), cobalt (Co), molybdenum (Mo) and iron (Fe) can stimulate cyanobacterial nitrogenase activity, whereas high levels of the same have adverse effects (e.g. Granhall 1981; Dodds et al. 1995). Field studies did not demonstrate a positive effect of P or micronutrients (Mo, Fe or Co) on Chihuahuan Desert cyanobacterial crusts (Hartley et al. 2002). The absence of enhancement by P or Mo may occur because these elements bind to Ca in CaCO$_3$-rich soils, making them unavailable to microbes or plants (Kabata-Pendias and Pendias 1992).

10.2.1.3
Environmental Controls on Heterotrophic N$_2$ Fixation

Heterotrophic N$_2$ fixation in dryland ecosystems is influenced by soil temperature, moisture, pH and carbon (Rychert et al. 1978; West and Skujins 1978); however, very few studies have been done on these influences. Experiments show

that heterotrophic nitrogenase activity increases with glucose additions, suggesting that carbon sources are essential (Billings et al. 2003; Rychert et al. 1978). Klubek and Skujins (1980) reported a 15–60% increase in nitrogenase activity in Great Basin desert soils supplemented with 2% glucose. Glucose additions boosted nitrogenase activity in Chihuahuan desert soil crusts, presumably due to heterotrophic activity (Hartley et al. 2002). Because heterotrophic N_2 fixers rely on external C sources, it is expected that most heterotrophic fixation takes place close to or within surface autotrophic organisms and in rhizosphere of vascular plants (Rychert et al. 1978; West and Skujins 1978). Binet (1981), Mahmoud et al. (1978), and Stewart (1966) report that optimal heterotrophic N_2 fixation requires a soil temperature of 28 °C, soil moisture >10%, a pH of 6.5–09.5, low salinity (<0.8 g NaCl kg^{-1} for non-salt-tolerant isolates, <1 g kg^{-1} for salt-tolerant isolates), and low soil N. Suppression of N_2 fixation by plant leachates (exudates) was observed by Rychert et al. (1978), and this may be due to suppression of both heterotrophic and autotrophic fixers. Plant root exudates have also been shown to reduce growth of *Azotobacter* and *Rhizobium* (Rice 1964).

10.2.1.4

Environmental Controls on Higher Plant N_2 Fixation

There is limited information on the environmental controls of symbiotic N_2 fixation in drylands. Binet (1978) reports that *Rhizobium* nodule formation on *Zygophyllum* is favoured by low soil moisture and high soil temperatures, but no specific values were given. Nodule formation is limited when soil pH and N levels are high (Pepper and Upchurch 1991; Zahran 1999). Stress from high salt (EC >7.5 dS m^{-1}), high temperature (>40 °C), high pH (>9), or high water deficit reduces nitrogenase activity (Pepper and Upchurch 1991). Species that commonly nodulate in other environments do not always do so under dryland conditions (Virginia et al. 1992; West and Skujins 1978); even with nodules, nitrogenase activity rates are low, as soils underneath leguminous shrubs often are not higher in nitrogen than soils underneath non-leguminous shrubs (Garcia-Moya and McKell 1970; West 1991). It appears that only *Prosopis glandulosa*, and then only when its roots can reach permanent water, fixes appreciable amounts of N in dryland ecosystems (Pepper and Upchurch 1991; West 1991). In addition, legumes are rare or even absent in most dryland areas (West and Skujins 1978), being generally concentrated in a few specific habitats.

Similarly to the rhizobia, the nodulation, growth, and N_2 fixation of *Frankia* are reduced by high soil N, high temperatures (>30 °C), high water stress (–0.5 to –0.8 MPa), high salt (>100 mM), pH (>7), and low levels of soil nutrients other than N (e.g. Fe, Mn, Cu and Zn) (Redell et al. 1991). However, there are few studies on a small number of species, and thus it is difficult to assess the importance of *Frankia* associations in drylands.

Overall, any study of N_2 fixation at the very minimum should closely document the environmental conditions (i.e. moisture, temperature, light, soil char-

acteristics) at which the measurements were taken. If N_2 fixation rates are to be scaled to an annual estimate, measurements must be collected across a range of moisture and temperature regimes in order to allow more accurate estimation of the actual input.

10.2.1.5
Species Considerations

Rates of N_2 fixation vary widely among species of free-living cyanobacteria and cyanolichens; for example, *Microcoleus vaginatus* has lower nitrogenase activity rates than *Nostoc–Scytonema* combinations, and free-living *Nostoc* has lower rates than lichenised *Nostoc* (in *Collema*; Table 10.1). As few studies report the proportion of the different cyanobacterial species present or the biomass/cover of cyanobacteria or lichens in the test material; it is therefore impossible to directly compare reported rates.

10.2.2
Nitrogen Losses

10.2.2.1
Nitrogen Gas Losses

During the last two decades, advances in measuring trace N gases such as nitric oxide (NO) nitrous oxide (N_2O) and dinitrogen (N_2) from soils have resulted in an ever-widening body of literature on N gas loss from a range of ecosystems. Few of these studies have been conducted in dryland ecosystems (Davidson and Kingerlee 1997). Due to the importance of these gases in atmospheric chemistry, most research in trace N gas production has focused on identifying the major terrestrial sources of NO and N_2O (Davidson and Kingerlee 1997). An understanding of pathways of N loss in drylands may be critical to identifying the processes that underlie losses of soil fertility associated with desertification.

Becaux very little research effort has focused on trace N gas production from dryland soils, it begs the question, based on what we know of controls of nitrification and denitrification processes, whether dryland soils could be a major source of trace N gases. In a review of NO losses from a range of ecosystems, tropical dry forest ecosystems were a major source of NO globally (Davidson and Kingerlee 1997), which suggests that trace N gas losses from aridland ecosystems may also be significant.

NO, N_2O and N_2 are produced in soil via microbially mediated pathways in nitrification and denitrification (see also Chapter 2 by McNeill and Uncovich, this volume). In nitrification, both NO and N_2O production may occur in the

oxidation of NH_4 to NO_3^- along a two step pathway (NH_4^+ to NO_2^-, NO_2^- to NO_3^-). Primary controls of nitrification rates are availability of NH_4^+ and O_2 partial pressure, soil pH, soil moisture, and soil temperature (Firestone and Davidson 1989; Paul and Clark 1996).

NH_4^+ availability in dryland soils is low relative to other ecosystems. Along a precipitation gradient in South America, Austin and Sala (2002) showed that NH_4^+ availability was more than 100-fold higher in a *Northofagus* forest soils as compared to desert scrub soils. Although soil NH_4^+ concentrations are low, environmental factors such as temperature and moisture may favour nitrification of the available NH_4^+ pool.

Optimum temperatures for denitrification range between 30 and 35 °C, temperatures common in dryland soils during the warmer months. Saturated soil conditions limit diffusion of O_2 into soils, which is essential for nitrifiers, therefore the generally low moisture content in dryland soils should favour nitrification. Ammonium: NO_3^- ratios in dryland soils are often <1 (Barger et al. 2006; Hartley and Schlesinger 2000; Mummey et al. 1997), which suggests that available NH_4^+ is rapidly nitrified.

Denitrification is the biological process that occurs under reducing conditions where NO_3^- is used by denitrifying bacteria (primarily heterotrophic bacteria) in the absence of O_2 as an electron acceptor (see also Chapter 2 by McNeill and Uncovich, this volume). NO_3^- is converted to NO, N_2O and N_2 along a reduction pathway. Factors regulating denitrification rates are low O_2 partial pressure, available NO_3^- to serve as an oxidant, and organic C as an energy source for heterotrophic bacteria (Williams et al. 1992). Previously, it was thought that denitrification in dryland ecosystems would be low because anaerobic conditions should rarely occur in arid environments. However, the presence of anaerobic microsites within dryland soils is not as rare as previously believed. Garcia-Pichel and Belnap (1996) reported oxygen levels near zero in the surface 4 mm of a biological soil crust. A large portion of the microbial community resides in the top few millimetres of dryland soils; thus, a pulse in microbial activity after a rain event may quickly reduce soil oxygen levels.

Denitrification rates reported from several western United States drylands are highly variable ranging from 0.65 to 322 ng N_2O-N m^{-2} s^{-1}, with an average of 55 ng N_2O-N m^{-2} s^{-1} (Table 10.5). The upper end of these short-term dentrification rates is comparable to those observed in forest and agricultural soils (Barton et al. 1999; Ullah et al. 2005). Much of the variability in published rates may be attributed to experimental design. Across studies, denitrification rates were positively correlated with the amount of water added, with the simulated rain event explaining 99% of the variability in denitrification rates (Fig. 10.1). The simulated rain event of 31 mm used by Schlesinger and Peterjohn (1991) is in the range of a 10-year precipitation event for these sites (http://hdsc.nsw. noaa.gov/hdsc/pfds/) and far higher than the typical summer rain event, which is generally less than 2 mm. As a result, soil moisture values that rarely occur in these soils were used to generate estimates of annual denitrification rates, which may have resulted in overestimation of denitrification from these soils.
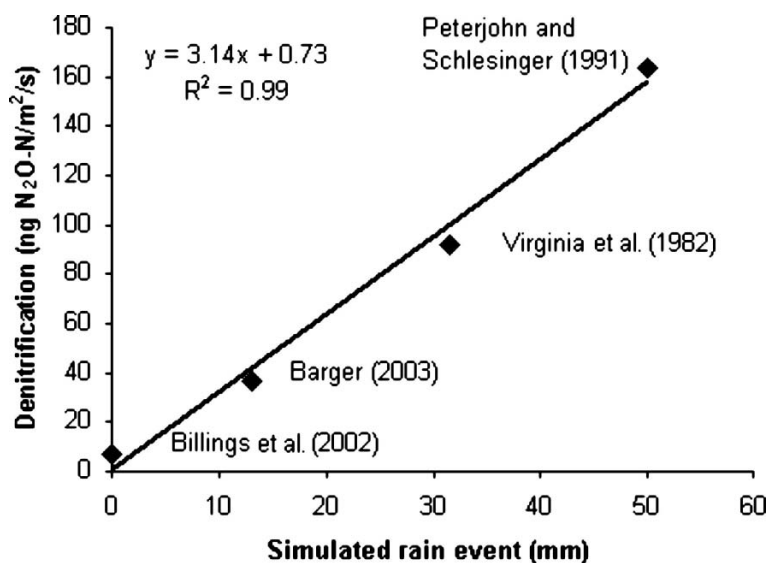
Fig. 10.1 Denitrification rates as a function of simulated rain event. The amount of water added in the simulated rain event explained 99% of the variability in denitrification across four desert sites

Table 10.5 Denitrification N losses from desert soils

Location	Vegetation	Rates (ng N m^{-2} s^{-1})	Rates (kg N ha^{-1} year^{-1})	Reference
Chihuahuan Desert, USA	*Bouteloua eriopoda* grassland, *Larrea tridentata* shrubland, playa grassland	92	7.2	Peterjohn and Schlesinger 1991
Colorado Plateau, USA	Biological soil crust	38	0.7	Barger 2003
Great Basin Desert, USA	Salt desert shrub	–	19	West and Skujins 1977
Mojave Desert, USA	Desert scrub	2	–	Billings et al. 2002
Sonoran Desert, USA	*Prosopis*	322	–	Virginia et al. 1982
	Interspace	6		

The first effort to create an annual N gas loss budget for a desert ecosystem was conducted during the US/International Biological Program Desert Biome effort in the 1970s. These early estimates of annual N gas loss were high, i.e. 20 kg N ha^{-1}, of which 19 kg N ha^{-1} year^{-1} was attributed to denitrification (West and Skujins 1977), rates that are comparable to fertilised agricultural and forested ecosystems (Barton et al. 1999; Davidson and Kingerlee 1997). More recent experiments have shown that annual N gas loss from dryland soils is far lower than early estimates, which may be partially explained by differences in methodology. Denitrification rates from soils were estimated from a laboratory ^{15}N addition study of decaying biological soil crusts maintained at high moisture contents. Over a 10-week period 75% of the added ^{15}N was not recovered, which was then assumed to have been lost via denitrification. Estimates of annual N_2 fixation by biological soil crusts in this study were 25 kg N ha^{-1} year^{-1} Of the N fixed by biological soil crusts, 75% was assumed to be lost via denitrification based on the laboratory incubations, yielding an annual denitrification rate of 19 kg N ha^{-1} year^{-1} (West and Skujins 1977). However, the laboratory conditions under which the biological soil crusts were incubated optimised N_2 fixation rates in these soil crusts, most likely resulting in an overestimation of denitrification rates.

Three of the five studies listed in Table 10.5 scaled up short-term denitrification rates to an annual loss rate. Estimates of annual N loss rates via denitrification were highly variable, which may have been due to a number of factors. The study by Barger (2003) was conducted on biological soil crusts in plant interspaces. Plant interspaces tend to have lower denitrification rates relative to soils beneath plants (Billings et al. 2002; Virginia et al. 1982), resulting in lower annual N loss estimates Annual N gas loss via denitrification from a Chihuahuan desert site was high, with estimates of denitrification at 7.2 kg N ha^{-1} year^{-1} (Schlesinger and Peterjohn 1991). In scaling to an annual denitrification loss rate in this study, the assumption was made that soils were wet for 3 months or approximately 90 days per year. However, soil moisture data collected over a 3-year period near Canyonlands National Park on the Colorado Plateau showed that soils only maintain adequate soil moisture for microbial activity (>1% volumetric water content) for approximately 10 days during the summer monsoon (J. Belnap, unpublished data). Although the largest proportion of annual precipitation falls during the summer in the Chihuahuan Desert, one would not expect the number of hours available for denitrification from soils to be 9-fold higher in the Chihuahuan desert compared to the Colorado Plateau. Thus, denitrification rates from the Peterjohn and Schlesinger (1991) study most likely overestimate annual losses.

Nitrous oxide fluxes from dryland soils ranged from –1.6 to 7.3 ng N_2O-N m^{-2} s^{-1}, much lower than denitrification rates, which suggests that a large proportion of the N gas loss in denitrification is lost as N_2 and not N_2O (Table 10.6). In the study by Barger (2003), denitrification rates (N_2O + N_2) were 30-fold higher than N_2O losses alone, which further supports the idea that much of N gas being lost is in the form of N_2. In the studies that estimated annual N_2O losses, rates ranged from 0.15 to 0.48 kg N_2O-N ha^{-1} year^{-1}.

Table 10.6 Nitrous oxide emissions from desert soils

Location	Vegetation	Rates (ng N m^{-2} s^{-1})	Rates (kg N ha^{-1} year^{-1})	Water addition	Reference
Colorado Plateau, USA	Biological soil crusts	1.2	–	Yes	Barger 2003
Great Basin, USA	*Artemisia* shrub-steppe	7.0	0.15	Yes	Mummey et al 1994
	Artemisia shrub-steppe	1.5	0.48	Yes	Mummey et al. 1997
Mojave Desert, USA	*Larrea-Ambrosia-Lycium* scrub	0.51	–	No	Billings et al. 2002
	Larrea-Ambrosia-Lycium scrub	0.001–13	–	Yes	Schaeffer et al. 2003
Sonoran Desert, USA	*Syderoxylon* spp., *Larrea tridenta-ta, Parkinson aculeate* overstory	–1.6–7.3	0.40	No	Guilbault and Matthias 1998

Table 10.7 Nitric oxide emissions from desert soils

Location	Vegetation	NO-N (ng N m^{-2} s^{-1})	NO-N (kg N ha^{-1} year^{-1})	Water addition	Reference
Chihuahuan Desert, USA	Grassland	3.0	0.15–0.38	Yes	Hartley and Schlesinger 2000
	Shrubland	0.3			
	Creosote	3.4			
	Tarbush	1.7			
Colorado Plateau, USA	Biological soil crust	4.4	0.02–0.16	Yes	Barger et al. 2006

There have been few published studies of NO loss from dryland ecosystems. Of the two studies listed in Table 10.7, NO loss rates after a simulated rain event ranged from 0.3 to 4.4 ng NO-N m^{-2} s^{-1}. When scaled to an annual loss rate, NO losses were similar to N_2O losses and in the range of 0.02 to 0.38 kg N ha^{-1} $year^{-1}$ In the Barger et al. (2005) study, NO fluxes were measured only from biological soil crust communities in plant interspaces, which partially explains the lower rates compared to Hartley and Schlesinger (2000), where NO fluxes were measured in a variety of plant communities. Although NO losses may be due to both nitrification and denitrification processes, losses from arid soils are more often associated with nitrification (Hartley and Schlesinger 2000; Martin et al. 2003; Smart et al. 1999). In a study of NO fluxes in a creosotebush community in the Chihuahuan desert, net nitrification rate explained 89% of the variability in NO fluxes, and fluxes were controlled by soil moisture and NH_4^+ availability (Hartley and Schlesinger 2000).

Ammonia (NH_3) volatilisation occurs with the deprotonisation of NH_4^+ and subsequent formation of NH_3 gas (see also Chapter 2 by McNeill and Uncovich, this volume). Unlike N gas loss in denitrification and nitrification pathways, NH_3 volatilisation is not a microbially mediated N loss pathway, thus temperature and moisture have less impact on NH_3 volatilisation rates. Dryland soils, however, do provide optimal conditions for ammonia volatilisation, since rates are positively correlated with soil pH, $CaCO_3$ and total salt content, but negatively correlated with organic matter content, cation-exchange capacity (CEC) and clay content (Duan and Hongland 2000). The range of ammonia volatilisation rates from dryland soils are similar to N gas losses as NO and N_2O and range from 0.06 to 2.2 ng NH_3-N m^{-2} s^{-1} (Table 10.8).

Although NH_3 volatilisation rates from dryland soils were in the same range as NO and N_2O losses, there is reason to believe that these rates are strongly underestimated due to problems with current methods used to measure NH_3 volatilisation from soils. In all of the studies listed in Table 10.8, a static chamber method was used to measure the amount of NH_3 volatilised from soils. In this method, a soil sample is placed in a sealed container along with a vial of strong acid that captures the volatilised the NH_3 In contrast, the dynamic chamber actively pumps chamber gases through the acid trap. In a study that calibrated the dynamic chamber method against the static method, only 5% of the NH_3 volatilised was captured using the static method as compared to the dynamic method (Frank and Zhang 1997). As a result, studies based solely on the static chamber method may result in vastly underestimated NH_3 volatilisation rates.

10.2.2.2
Nitrogen Leaching Loss

Nitrogen leaching losses have long been thought to be an insignificant N loss pathway in dryland ecosystems (Peterjohn and Schlesinger 1990; West and

Skujins 1977) due to low mean annual precipitation, which limits water and associated element movement to deeper soil layers. Not surprisingly, most of the work on leaching of N compounds through the soil profile has been conducted in irrigated agricultural systems and regions such as tropical and temperate forests that receive plentiful rainfall. However, a recent study examining nitrate (NO_3^-) reservoirs across several deserts in the western United States showed that the vertical flux of NO_3^- in dryland soils may be higher than previously believed. Estimates of NO_3^- leaching from surface soils to sub-soils were in the range of 0.09 to 1.17 kg NO_3^--N ha^{-1} year^{-1} (Table 10.9, Walvoord et al. 2003). These rates were highly variable across different deserts, which may be attributed to differences in climate, vegetation type, land use history, and soil type (Walvoord et

Table 10.8 Ammonia loss from dryland soils

Location	Vegetation	Rates (ng NH$_3$-N m^{-2} s^{-1})	Rates (kg NH$_3$-N ha^{-1} year^{-1})	Water addition	Reference
Chihua-huan Des-ert, USA	Grassland	0.64	–	Yes	Schlesinger and Peter-john 1991
	Shrubland				
	Playa				
Colorado Plateau, USA	Biological soil crust	0.2	–	Yes	Evans and Jo-hansen 1999
	Bare soil	0.06	–		
	Biological soil crust	2.2	–	Yes	Barger 2003
Great Basin, USA	*Artemisia* shrub-steppe	–	1.0	Yes	West and Skujins 1977
Mojave Desert, USA	Desert scrub	2.0	–	No	Schaeffer et al. 2003
	Desert scrub	1.3	–	No	Billings et al. 2002

Table 10.9 Nitrate leaching to subsoils (to 1 m depth) in three desert environments (Walvoord et al. 2003)

Site	NO_3^- flux (kg ha^{-1} year^{-1})
Mojave Desert, USA	0.09–1.17
Chihuahuan Desert, USA	0.02
Sonoran Desert, USA	0.13–0.76

al. 2003). These estimates also do not include other forms of dissolved N such as organic N, which often make up a large fraction of the dissolved N flux (Hedin et al. 1995; Oyarzún 2004; Pregitzer 2004). As a result, N leaching losses to deeper soils in these regions may be largely underestimated.

10.2.2.3

Erosional Losses of Nitrogen

Nitrogen may be lost during water erosion as dissolved N in runoff and N bound to eroded sediments. Runoff amount is determined by soil infiltration capacity, which is affected by soil porosity and residence time of water on the soil surface. Sediment yield in water erosion is affected by energy of incoming rainfall or rainfall intensity.

Total dissolved N losses in rainfall simulation experiments ranged from 0.11 to 1.17 mg N m^{-2} min^{-1} (Table 10.10). Dissolved organic nitrogen (DON) made up a large proportion of the total N flux, ranging from 40% to 78%. Interestingly, the range in total dissolved N loss did not vary strongly across sites even though there were large differences in experimental conditions. Of these studies, only one reported sediment-bound N losses, which ranged from 0.06 to 0.63 g N m^{-2} min^{-1} from biological soil crusts (Barger et al. 2006). Sediment-bound N in this study was ≥98% of the total N flux (dissolved + sediment).

Estimating annual N losses in water erosion is difficult due to the low frequency of natural runoff events in dryland environments. In some sites several years may pass without generating a runoff event. As a result, there is very little data available on annual N loss from natural precipitation events for dryland ecosystems. Thus, the available data on N loss in water erosion were generated in rainfall simulation experiments. Where a number of factors, such as size of rainfall simulation plot and intensity and duration of the simulated rain events affect N loss calculations.

The spatial scale of the study will often determine whether a net loss or accumulation of N is observed. For example, in a study of N in runoff with a natural precipitation event at the watershed scale at a Sonoran desert site, Fisher and Grimm (1985) reported net N accumulation (N inputs in rainfall exceeded outputs in runoff) (Table 10.11). However, all small plot studies listed in Table 10.10 exhibited net N loss (N outputs exceed inputs). Wilcox et al. (2003) examined runoff and erosion dynamics at several spatial scales in a semi-arid woodland and showed that runoff decreased by 50-fold from the microplot (1–3 m^2) to the hillslope (2,000 m^2) scale. Patterns in erosion losses in that same study were similar to runoff dynamics. Sediment losses from the microplot scale ranged from 1,000 to 4,000 kg ha^{-1}, but decreased to <100 kg ha^{-1} at the hillslope scale. Thus, small plot studies are more likely to represent nutrient redistribution within the watershed rather than a net loss of N from the watershed.

Rainfall intensity of a simulated rain event also impacts N loss in runoff and sediments. In rainfall simulation experiments conducted in a California grass-

Table 10.10 Dissolved N losses in water erosion from rainfall simulation experiments. *DON* Dissolved organic nitrogen

Site	Vegetation	NH_4^+ (mg m^{-2} min^{-1})	NO_3^- (mg m^{-2} min^{-1})	Inorganic N (mg m^{-2} min^{-1})	DON (mg m^{-2} min^{-1})	Total dissolved N (mg m^{-2} min^{-1})	Plot size (m^2)	Rainfall intensity/duration	Reference
Colorado Plateau, USA	Dark crust	0.03	−0.002	0.014	0.15	0.19	0.5	228 mm h^{-1} 10 min	Barger et al. 2006
	Light crust	−0.01	0.03	0.02	0.07	0.11			
Chihuahuan Desert, USA	Grassland	Not reported	Not reported	0.42	0.55	0.98	2.0	90 mm h^{-1}	Schlesinger et al. 1999
	Shrubland			0.33	0.42	0.76		30 min	
	Intershrub			0.18	0.41	0.59			
Chihuahuan Desert, USA	Mesquite-nabkha	0.08	0.08	0.16	0.22	0.54	1.0	144 mm h^{-1}	Parsons et al. 2003
	Interdune	0.06	0.24	0.30	0.87	1.17		15 min	

Table 10.11 Dissolved N losses in water erosion from natural precipitation events

Site	Vegetation	NH_4^+ (kg N ha^{-1} year^{-1})	NO_3^- (kg N ha^{-1} year^{-1})	Inorganic N (kg N ha^{-1} year^{-1})	DON (kg N ha^{-1} year^{-1})	Plot size	Reference
Chihuahuan Desert, USA	Creosotebush	0.10	0.41	0.51	0.06	4 m^2	Schlesinger et al. 2000
	Grassland	0.08	0.05	0.13	0.03		
Sonoran Desert, USA	Lower Sonoran desert scrub	−0.02	−0.08	−0.10	−0.008	Watershed	Fisher and Grimm 1985

land, Fierer and Gabet (2002) showed that sediment N loss increased linearly with increasing rainfall intensity. The relationship between dissolved N in runoff and rainfall intensity was less clear in this study. Nitrate loss increased with increasing rainfall intensity, but no relationship existed between rainfall intensity and NH_4^+ and organic N loss. Of the three studies listed in Table 10.10, rainfall intensities range from 90 to 228 mm h^{-1}, but there was no clear relationship between dissolved N flux and rainfall intensity across the studies.

The duration of simulated rainfall also affects calculations of N loss in water erosion. In many rainfall simulation experiments, rainfall intensity must be high in order to generate runoff and to obtain a steady-state runoff rate. Using precipitation frequency estimates for the site, investigators are able to choose over what time period to calculate N losses. For example, in Schlesinger et al. (1999), N losses were calculated over a 30-min rainfall simulation at an hourly intensity of 90 mm. Over the 30-min period 45 mm was applied, which, according to precipitation frequency estimates, occurs every 50–100 years in this region (Precipitation Frequency Data Server, http://hdsc.nws.noaa.gov/hdsc/pfds/). If investigators were interested in N losses in a 5-year precipitation event, then calculations would be done over the first 10 min of the precipitation event. These, calculations over different time periods of a rainfall simulation may yield different information on N loss and how it relates to precipitation frequency data for a given site.

10.2.2.4
Aeolian Losses

Arid and semiarid systems typically have sparse and variable cover. Due to the size and connectivity of unvegetated gaps in these regions, abiotic transport processes are able to move nutrient-rich sediments. Short-distance transport of nutrients by wind and water is an important factor in the development of islands of fertility common in drylands, especially from bare interspaces to nearby subcanopy areas (Okin et al. 2001b; Schlesinger et al. 1990). Long-range transport of sediments and their associated nutrients can lead to the overall loss of nutrients from the landscape (Leys and McTainsh 1994; Schlesinger et al. 1996; Schlesinger et al. 2000).

Aeolian transport can account for observed redistribution and losses of nutrients from the soil surface, as well as disrupt nutrient cycling in deserts in other ways. Aeolian transport is initiated when the wind shear velocity exceeds the threshold shear velocity. The threshold of particle transport in the absence of vegetation, the soil erodibility, can be impacted by several factors such as soil texture (Alfaro and Gomes 2001; Leys and McTainsh 1996), mineralogy (Gillette 1997) and moisture (Ravi and D'Odorico 2005). Above the threshold shear velocity, three aeolian transport processes observed by Bagnold (1941) govern the fundamental erosion and movement of mineral dust aerosols: suspension, saltation and creep.

Saltation is initiated when the lift provided by wind exceeds the forces of gravity and cohesion holding the particle to the surface (Cornelis and Gabriels 2003). The most efficient saltators, those with the lowest threshold shear velocity, have a diameter of about 70 μm, but most saltation sized particles are 50 to 500 μm (Raupach and Lu 2004). Due to their size, saltation-sized particles have low surface area. As a result, they likely have low concentration of adsorbed plant-available inorganic nutrients. Particles that are ejected from the surface are entrained by saltation bombardment. Larger particles move by creep when they are nudged by impacting saltators.

Saltating sediments carry the bulk of the kinetic energy and momentum flux in aeolian transport. As a result, saltation has an important effect on vegetation in areas undergoing wind erosion. The abrasion and damage of plant tissue within the saltation layer, usually less than 1 m above the surface, can be a critical control on plant productivity and longevity. Cleugh et al. (1998) have reviewed the mechanical impacts of sandblasting for crops. Okin et al. (2001a) observed that, even for endemic shrub species, sandblasting can destroy cambium, strip leaves, and bury plants. This physical damage likely results in diminished net primary productivity and high mortality of young plants while their soft tissue is within the saltation layer (Okin and Gillette 2001). Thus, though saltation particles are themselves poor in plant-available nutrients, they can disrupt nutrient cycling in drylands by reducing the growth and establishment rates of plants, thus reducing the amount of organic matter (C, N and P) added to the soil in litter.

Saltation also leads to the emission of suspended material, dust, by sandblasting the surface (Alfaro and Gomes 2001; Gillette et al. 1997). Saltating particles bombard the surface, imparting kinetic energy to small particles that cannot be ejected by aerodynamic forces alone (i.e. particles with diameter <50 mm). Small mineral particles ejected in this way have high surface area and therefore high cation- and anion-exchange capacities. Low-density particles composed of organic material from the decomposition of plant litter are also ejected from the surface by this mechanism. In addition to having high CEC, these organic particles are also long-term reservoirs of organic nutrients.

The loss of nutrient-rich mineral and organic particles by dust emission has important consequences for the fertility of arid regions (Leys and McTainsh 1994). Okin et al. (2001a, 2001b) have shown that aeolian transport can lead to a reduction of nearly two-thirds of plant-available N and P on the 10-year timescale. More recent results from field experiments have supported this estimate and shown that this effect, when coupled with the removal of grasses, may be an important mechanism in the conversion of grasslands to shrublands observed throughout the world's drylands (Li and Okin 2004; J. Li et al. manuscript submitted).

Because plants serve as a barrier for wind and aeolian sediment flow, vegetation canopies can serve as the loci of deposition in partially vegetated areas. Coarse-grained particles travel short distances and therefore are often moved from plant interspaces to adjacent regions underneath plant canopies. Fine-grained particles that are suspended in the wind can also be intercepted by plant

canopies and deposited within the plant canopy (Okin et al. 2006). Thus, transport and emission from interspaces likely leads to the depletion of soil nutrients in these areas, whereas deposition within canopies of wind-transported material likely contributes to the accumulation of nutrients here. This redistribution of nutrients is vital in the formation and maintenance of islands of fertility in dryland ecosystems.

10.2.3
Summary of N Budgets in Dryland Ecosystems

To date, efforts to close N budgets in dryland ecosystems have met with very little success, due primarily to the spatial and temporal variability in N pools and fluxes. Not surprisingly, in this review of N fluxes the results were highly variable across dryland sites and are strongly influenced by experimental conditions. Most experiments reviewed in this section were conducted in the laboratory under optimal conditions or in the field with water added to capture the short-term fluxes of N, which in many cases were comparable to rates observed in forested and agricultural ecosystems. Great care must be taken in scaling these results up to an annual flux. In drylands, there are very limited periods within a year when these optimal conditions occur, especially for the microbially mediated processes. For example, we know from studies on the Colorado Plateau that conditions for N gas loss are optimal during only 9–25 days each year (Barger et al. 2005). As a result, in future experiments of N cycling in drylands it is critical to couple N fluxes to measured data on soil moisture and temperature throughout the year in order to constrain an annual N budget. Problems also arise when processes do not occur on an annual basis. For example, runoff events are extremely episodic, and N loss in water erosion may only occur once every few years. Thus, rainfall simulation experiments must be coupled with data on rainfall intensity data to adequately estimate N losses in water erosion. Overall, this review suggests that dryland soils have a high potential to fix or lose N, and short-term rates can be extremely high but scaling these rates to estimate annual fluxes remains a challenge.

10.3
Phosphorus

Several studies report P as limiting to plants in drylands Schlesinger et al. (1990) in the Chihuahuan Desert. In a lab experiment, Lajtha and Schlesinger (1988b) observed that *Larrea tridentata* seedlings grown in the highest P treatment produced more biomass, had higher P concentrations in roots and whole seedlings, higher total uptake of N and P, and higher final root and shoot N and P contents

than plants grown in the lower P treatments. In the same study, *L. tridentata* seedlings grown in soils amended with $CaCO_3$ had higher root:shoot and tissue N:P ratios, and lower specific absorption rates of P than control plants without $CaCO_3$, which suggests that $CaCO_3$ reduces P availability.

10.3.1
Phosphorus Inputs

Weathering of primary minerals such as apatite is the major source of phosphorus in soils (see also Chapter 3 by Bünemann and Condron, this volume). Data on chemical weathering rates of P are sparse for terrestrial ecosystems, but published values from temperate ecosystems range from 0.01 to 1 kg P ha^{-1} year^{-1} (Newman 1995; no dryland estimates listed). Rock weathering rates are estimated using a mass balance approach on a catchment scale (Schlesinger 1997). This method has limited applications in dryland ecosystems; for example, inputs or losses of elements other than P by erosion or weathering can affect the estimate of the relative percentage of P in the remaining material (Lajtha and Schlesinger 1988a).

Phosphorus inputs from the atmosphere are assumed to be negligible; however, organic and inorganic P can be added as wet and dry deposition, i.e. deposited in rainfall or in particulate form. Methodological challenges associated with measurements of atmospheric P deposition are described in Newman (1995). In this review of terrestrial ecosystems, total inputs of P in wet or wet+dry deposition ranged from 0.07 to 1.2 kg ha^{-1} year^{-1}; however, none of these studies were from dryland ecosystems. Using global dust deposition models, Okin et al. (2004) have estimated global P deposition in desert dust. Estimates of dust-borne P deposition rates for drylands vary over several orders of magnitude depending on proximity to the world's largest dust sources in North Africa, the Middle East and northernwestern China.

10.3.2
Geochemical and Biological Controls on Phosphorus Availability

Because of the geological origin of P in terrestrial ecosystems and the fact that secondary minerals in soils regulate P availability, P is considered to be geochemically controlled. As parent material weathers chemically and soil forms, P is leached and lost from the system or it may remain in the soil in either occluded, non-occluded or organic fractions of the total P pool (Walker and Syers 1976; see also Chapter 3 by Bünemann and Condron, this volume). Non-occluded P is bound to hydroxides of Al and Fe or $CaCO_3$. The presence of these secondary minerals in dryland soils, $CaCO_3$ in particular, strongly influences availability of P (Cross and Schlesinger 2001; Lajtha and Bloomer 1988). The

above model of P weathering was developed for soils derived from igneous rock. Neff et al. (2006) propose that in dryland soils derived from sedimentary rock, the majority of P weathers from Fe and Al oxide forms rather than primary minerals. Fe oxide minerals appear to regulate P availability more than Ca in some areas near Canyonlands National Park (Utah; Neff et al. 2006).

Erosional losses of P are important in arid and semiarid regions. Okin et al. (2001b) have shown that wind erosion can dramatically reduce the concentration of plant-available P in surface soils. Runoff studies (Schlesinger et al. 1999, 2000) have shown that runoff is not a significant cause of P loss from soils.

The extent to which P remains available for uptake by organisms depends on soil chemical properties, which in turn are determined by the degree of weathering, soil development and erosion. In aridisols with an argyllic (clay-rich) A horizon, phosphorus sorbs to Fe- and Al-oxides and precipitates out of solution as $AlPO_4 \cdot 2H_2O$ and $FePO_4 \cdot 2H_2O$ as soil pH falls below ~ 6.0–6.5. Below the argyllic A horizon or at the surface if the argyllic horizon has eroded, P binds to calcium (Ca) and precipitates out of solution as $Ca_3(PO_4)_2$ as the pH rises above 7.0 (Lindsay and Vlek 1977). High levels of Ca^{2+} and HCO_3^- can reduce or prevent the dissolution of carbonate and Ca-P compounds, making P unavailable. Phosphorus can also complex with other elements (e.g. Mn or Zn).

The predominance of geochemical controls has been documented in drylands around the world. In an analysis of a soil chronosequence in the Chihuahuan Desert (New Mexico), Lajtha and Schlesinger (1988a) found negligible accumulation of organic P, but increasing inorganic P storage in calcium carbonate layers. Integrated over time, dryland vegetation appears not to conserve and store P as other ecosystems do. Even direct inputs of organic P do not increase inorganic P availability. Soil column experiments showed negligible net P mineralisation rates even in moist Kalahari Desert soils amended with cattle dung (Dougill et al. 1998). The authors suggest that microbial immobilisation or inorganic fixation of P to minerals occurs in these relatively Ca- and Fe-rich soils.

A few studies suggest that biological processes exert strong local influences on P availability. Leaf P in wild populations of an indigenous Kalahari desert tree *Vangueria infausta* increased with both the percentage of arbuscular mycorrhizal (AM) colonisation of roots and the P concentration in the soil (Bohrer et al. 2001). *V. infausta* seedlings inoculated with local strains of AM fungi depleted soil mineral P concentrations and increased seedling size (Bohrer et al. 2003). The mechanism used by mycorrhizal fungi to mediate P uptake for its desert hosts is not yet understood. Ectomycorrhizal and arbuscular mycorrhizal fungi occur throughout aridlands in the United States (Great Basin, Southern California deserts; Allen et al. 1996) but, unlike their counterparts in forest ecosystems, these symbionts do not appear to produce oxalate or phosphatase that could facilitate P uptake by their desert hosts (Jurinak et al. 1986).

Climate can interact with biotic processes to affect P availability in dryland ecosystems. The rate of H_2CO_3 formation in soil is partially controlled by soil water content and the solubility of CO_2 in water (Krauskopf and Bird 1995). Solubility of CO_2 in soil solution increases in cold temperatures. Because both abiotic CO_2 solubility and biotic CO_2 production vary relative to soil tempera-

ture and soil moisture, but in the opposite direction to each other, maximum H_2CO_3 production occurs with increasing soil temperature and decreasing soil moisture (Seastedt and Knapp 1993). Assuming most P in these soils is present as $CaHPO_4^-$, P availability should also be highest at this maximum as $CaHPO_4^-$ is solubilised by H_2CO_3 in favour of the formation of $CaCO_3$. This scenario is supported by several studies. *Bromus* shows high levels of winter root growth when soils are cold and moist (Harris 1967). Under the above scenario, winter would be the time when P would be most available in dryland soils. Root growth would also contribute respiratory CO_2, facilitating the acquisition of carbonate-bound nutrients. In situ resin bags near our Colorado Plateau sites also show an increase in soil P availability during cold, moist conditions found in winter (Miller 2000). *Bromus* growth rates were greatest at these sites in winter, and were positively correlated with P/Ca and inversely correlated with above-ground N and P. Lajtha and Schlesinger (1988b) also found that in situ resin bag P concentrations peaked in cool winter conditions in the Chihuahuan desert. Magid and Nielsen (1992) showed that laboratory extractions performed at 4 °C recovered significantly more P than those at 25 °C. In general, lower diffusion rates at lower temperatures partially counteract the increase in available soil P. However, the situation may be different in calcareous soils, as diffusion rates may actually increase with decreasing temperatures (but above freezing), as H_2CO_3 generation facilitates carbonate dissolution and the transition of solid-phase P to solution-phase P (Jungk and Claassen 1997).

10.4
Other Nutrient Cycles

Potassium (K) is an essential nutrient for plants. Plants require a fairly large quantity of K and can often use more than is available in soils (Troeh and Thompson 1993). Most K is derived from the micas muscovite and biotite, the feldspars orthoclase and microcline, and evaporative deposits found in dryland climates (Day and Ludeke 1993; Troeh and Thompson 1993). In soil, K generally occurs in mineral structures or as hydrated ions either in solution or adsorbed onto the negatively charged sites on clays and organic matter. Hydrated K ions are the same size as ammonium ions and held with about the same strength, whereas they are weakly held relative to calcium (Ca) and magnesium (Mg) ions. Therefore, K ions are readily exchangeable. Plant roots can easily obtain K if they reach the adsorption site; however, K moves very slowly through soils. Potassium is more soluble in calcareous than non-calcareous soils, due to the effect of carbonic acid in the calcareous soils. It is also more easily exchanged with other cations in calcareous soils compared to non-calcareous soils. In general, K is not easily leached from soils, even over long periods of time, due to K fixation and sorption to the cation-exchange sites in soils. In drylands, K accumulates at

the surface due to upward transport by plants and accumulation of K in plant litter (Jobbàgy and Jackson 2001; Schlesinger and Pilmanis 1998; and references therein). Higher K concentrations in surface soils are also attributed to illite deposition in aeolian materials (Singer 1989).

Most K in soils is in a non-exchangeable form, with only about 1% occurring in an exchangeable form. The transformations of non-available K to available K forms are facilitated by wet-dry, freeze-thaw, and warming-cooling cycles that accelerate mineral weathering. However, high soil moisture and freezing temperatures occur only rarely in dryland regions, which results in low rates of weathering and K transformations. Despite the importance of K to plants and the low transformation rates and thus availability in drylands soils, there have been only a few studies on how K may influence vascular plant distribution or productivity in these regions.

Crooke and Knight (1962) and Scott and Billings (1964) were the first to note that dryland soils with high K/Mg ratios were dominated by annual plants, whereas soils with a low K/Mg ratio were dominated by perennial plants. Harner and Harper (1973), Pederson and Harper (1979), and Woodward et al. (1984) all corroborated these earlier findings. Crooke and Knight (1962) and Gray et al. (1953) found that K uptake by plants was highly correlated with plant root CEC and that annual plants, especially grasses, generally had higher root CECs than perennial plants. Annual grasses have also been found to have higher tissue concentrations of K than adjacent native perennial plants (Blank et al. 2002), as well as higher root CECs (Belnap et al. 2006). This may also indicate that annual grasses have a higher requirement for K than native perennial plants (Tilman 1982). Belnap et al. (2006) found that annual grasses in south-east Utah are found only in soils with higher K, K/Mg and K/Ca. Traditionally, agriculture has regarded soils with less than 140 mg kg^{-1} of available K to be deficient in K. However, this standard may be too high, with K deficiency occurring at less than 70 mg kg^{-1} (Leigh and Storey 1991). If the standard of 70 mg K kg^{-1} is used, many soils in western United States drylands are K limited (Belnap et al. 2006).

There are several reasons why K may be important to dryland plants. Osmoregulation in plants is mediated by K (e.g. Mäser et al. 2002; Wang et al. 2002). The high Na levels of many dryland soils can be toxic to many plants, and there are multiple studies showing that K ameliorates Na toxicity in plants (e.g. Mäser et al. 2002) as well as in other organisms such as bacteria (e.g. Kraegeloh and Kunte 2002). The preferential transport of K over Na is especially pronounced in actively photosynthesising organs such as young leaves and developing seeds (Wang et al. 2002). The extent to which plants utilise K to avoid Na stress varies among species (Mäser et al. 2002). In addition, K has been implicated in plant adaptation to water stress (Xu et al. 2002). Multiple studies support the observations that high levels of Mg and Ca can restrict plant uptake of K in both the laboratory and the field (Epstein 1961; Sinanis et al. 2003).

Calcium (Ca) concentrations in dryland soils are generally sufficiently high not to limit plant productivity. Calcium generally occurs in the minerals apatite, plagioclase and hornblende. Because minerals that contain Ca can weather rela-

tively quickly, Ca is subject to leaching. Dryland soils generally have very high levels of Ca, reaching more than 5% of the soil by weight and occupying 75–85% of the CEC sites (Troeh and Thompson 1993). Hydrated Ca ions are relatively small polyvalent ions; thus, they tend to preferentially occupy CEC sites, making Ca less bioavailable than other cations that are held less strongly. The high levels of Ca in dryland soils can have a profound influence on the availability of other nutrients. Excess Ca precipitates as Ca carbonate at the soil depth to which most precipitation infiltrates; this layer can harden (called caliche or calcrete) and block plant roots and water flow. Calcium carbonate is an effective pH buffer maintaining alkaline conditions; however, Ca can bind with other soil nutrients, such as P, Mn, Zn and Mg, making these unavailable to organisms (Troeh and Thompson 1993). In addition, the polyvalent Ca can swamp CEC sites in plant roots. Therefore, the ratio of Ca to other cations can influence plant productivity (Barber 1995; Lajtha and Schlesinger 1988b). Under cold conditions Ca carbonate solubility in water is high (Krauskopf and Bird 1995) and thus these bonds may be broken or weakened when soils are cold and wet.

Magnesium (Mg) is found in igneous rocks, associated with the ferro-magnesium minerals such as olivine, inosilicates and biotite micas. It is also an important component of the sedimentary rock dolomite. Magnesium-containing minerals tend to be relatively easily weathered, and thus soils are depleted of Mg faster than of K or Ca. The Mg ion is much smaller than the Ca ion, being more similar in size to K, and, as with Na and K, is less strongly held to CEC sites than Ca. Generally, Mg occupies 12–18% of the CEC sites. Both Mg and Ca ions are more likely found on CEC sites than in solution. Dryland soils with an excess of Mg (occupying 40–60% of the CEC sites and having a Ca/Mg ratio <1) have sparse plant cover and high erodibility (Burt et al. 2001). Fertiliser trials show that Mg ions interact strongly with other cations, especially the monovalent K and Na, due to the preferential adsorption of the polyvalent Mg ion. Therefore, similar to Ca, the ratio of Mg to other cations can influence plant productivity (see Sect. 10.4).

Sodium (Na) is considered a non-essential element, but is beneficial in small amounts. Sodium levels in soil are almost always sufficient for plant growth. Sodium ions are less tightly held to soil particles than K, Ca or Mg. Therefore, Na is more easily leached from soil than the other cations. However, in dryland soils, low amounts of precipitation limit the amount of downward leaching. In addition, salts (mostly Na salts) move upwards in the soil due to capillary action when the soil surface is drier than underlying layers, forming a white crust on the surface that is almost exclusively sodium chloride (Troeh and Thompson 1993). Thus, much of the alkalinity of dryland soils is due to the presence of Na. The large amount of Na often found in dryland soils can damage soil structure and reduce plant productivity. Many dryland plants have active mechanisms to handle excess soil Na, such as extruding salt onto the leaf surface or storing Na in cell vacuoles to prevent interference with processes in the cytoplasm (Whitford 2002).

Sulphur (S) is an essential plant nutrient. Sulphur is similar to nitrogen in that it occurs in a gaseous and solid form, it is unavailable to plants in its elemental form, and its most common bioavailable form, SO_4^{2-}, is an anion easily leached from the soil (see also Chapter 3 by Bünemann and Condron, this volume). Similarly to N, a considerable amount of S can be added to the soil via rain and the breakdown of organic matter. The presence of Ca limits the solubility of S; thus S generally has low mobility in dryland soils. On the other hand, high pH soils generally have a low anion exchange capacity, and thus anions such as SO_4^{2-} are more easily leached than in soils with lower pH (Troeh and Thompson 1993). Lack of precipitation in dryland regions results in limited overall leaching and dryland soils often have high concentrations of dissolved sulphates. Gypsum ($CaSO_4$) is common in dryland regions. In addition to occurring in surface soils, it often accumulates just below or in the Ca carbonate layer. Gypsum influences plant distribution in the Mojave Desert (Meyer 1986), due primarily to soil physical factors such as the tendency of indurated surfaces to inhibit seedling establishment, rather than nutrient chemistry.

Most copper (Cu) found in soils is associated with organic matter, but can also be held by cation exchange or bound in Fe-Cu oxides. The cation exchange bond is stronger than that of Ca, making Cu relatively immobile. High pH, calcareous and/or Fe-rich coarse soils, typical soils of dryland areas, have inherently low concentrations of available Cu (Alloway and Tills 1984). Jarrell and Virginia (1989) postulated that Cu may limit plant productivity in dryland regions. Copper deficiency has been linked to suppressed N_2 fixation in vascular plant-*Rhizobium* associations (Cartwright and Hallsworth 1970), and may also limit N_2 fixation for N_2-fixing lichens. As discussed in the section on N above, soil lichens can be the dominant source of N for many dryland ecosystems. Therefore, low available Cu may have large implications for plant productivity in these regions.

Most iron (Fe) is found in igneous rocks in the ferrous (Fe^{2+}) form. However, Fe can also be found as the highly insoluble ferric Fe (Fe^{3+}) form. Both forms of Fe are less soluble in high pH soils compared to low pH soils; thus, Fe availability is low in calcareous soils. Low temperature also reduces the solubility of Fe compounds (Troeh and Thompson 1993). Iron oxides can adsorb P, making them both unavailable to organisms. The formation of Fe phosphate reduces Fe solubility, so the presence of P can reduce Fe availability. Because Fe and Mn are chemically similar, they can be antagonistic. Similarly, high levels of Zn or Cu can also result in Fe deficiencies (Day and Ludeke 1993), as these other micronutrients can act as oxidising agents to convert ferrous to ferric Fe. Iron deficiencies are much more common in dryland regions with high pH soils than in soils with lower pH. Hunter et al. (1980), Nelson and Jolley (1989) and Wallace (1989) all suggest that Fe may limit plant productivity in drylands.

Manganese (Mn) is derived mostly from widespread igneous inosilicate minerals. Concentrations of total Mn in dryland soils can be so high that Mn nodules are found in lower soil horizons (Yaalon et al. 1972). In contrast, exchangeable, available Mn is often low, due to its low solubility in alkaline soils. The

availability of Mn is also reduced with high levels of Na, K, Fe, Cu or Zn (Day and Ludeke 1993). As mentioned above, Mn and Fe have a similar structure, and thus compete with each other. Because many dryland soils contain high levels of Na and Fe, Mn deficiency may be quite common. Bowker et al. (2006) reported that Mn deficiency controls the distribution of the common N_2-fixing lichen *Collema tenax* in the western United States. Therefore, as with Cu, limitation by Mn may reduce N input into dryland ecosystems, thus reducing plant productivity. Belnap et al. (2006) have shown that exotic annual grasses prefer soils high in Mn in cool western deserts in the United States. Cramer and Nowak (1992) report that the addition of Mn stimulates growth in annual grasses, whereas others have noted that Mn deficiency may limit plant productivity in drylands (Jaurequi and Reisenauer 1982; Marschner 1995; B. Blank, personal communication). These studies indicate that Mn may play a large role in dryland ecosystems, which warrants further investigation.

Zinc (Zn) is derived mostly from rock minerals. Total Zn concentrations in soils is generally high, but very little Zn is found in solution, especially in soils with a pH above 6 (Troeh and Thompson 1993). Above a pH of 8.4, Zn can precipitate. Carbonates can also adsorb Zn. Therefore, available Zn in dryland soils is generally low in the western United States (Jarrell and Virginia 1989), and this deficiency is likely common throughout dryland regions of the globe, limiting plant productivity (Hacisalihoglu and Kochian 2003; Jarrell and Virginia 1989; Jaurequi and Reisenauer 1982; Killingbeck 1989; Marschner 1997). Belnap et al. (2006) found that high levels of Zn suppressed annual grass occurrence, which may result from the formation of low solubility of Zn phosphates or the interference of high Zn with P uptake by plants (Sharma et al. 1968). Zinc uptake can also be reduced by high levels of soil Mn, as it is similar in size to Zn and can compete for carrier molecules in the root cells. The solubility and plant uptake of Zn is also reduced in cool soils.

10.5
Conclusions

This chapter reviews a large number of studies on dryland nutrient cycling, many of which were conducted in the western United States. Despite the multitude of studies on nutrient fluxes and stocks, few dryland regions are studied intensively enough to permit the compilation of nutrient budgets even for essential macronutrients like N and P. Nutrients are lost from drylands in wind and water erosion and become unavailable when secondary minerals bind nutrients in soils. Human activity can accelerate nutrient losses; for example, livestock grazing reduces vegetation cover, which leads to more rapid erosion. Satellite imagery documents climate-driven trends in dryland primary productivity and reveals large-scale transport of dust into oceans and other continents, but more

work is needed to quantify the magnitude of nutrient exports. Because nutrient fluxes are highly variable in space and time, more intensive measurements are needed to compile annual budgets and thereby track long-term trends in the nutrient status of dryland ecosystems.

Acknowledgments

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11 Nutrient Cycling in the Tundra

Sari Stark

11.1
Introduction

The term tundra is generally applied to treeless areas that are situated beyond the climatic limit for tree growth. This definition can denote both regions of high latitude north or south of the tree line (i.e. arctic/Antarctic or polar tundra), or high altitude belts above the natural tree line in all climatic zones (i.e. alpine tundra). Arctic and alpine tundras have many similarities, but also great differences. This chapter describes the processes of carbon (C) and nutrient cycling in arctic or arctic-alpine tundra, the latter referring to high elevation belts in the boreal region above 60 ºN. The majority of this area is located in northern parts of Russia, North America and Scandinavia. For a comprehensive description of tundra systems, see Wielgolaski (1997).

Microbial and biological processes that govern soil nutrient cycling operate at different rates depending on a number of environmental factors. In arctic or arctic-alpine tundra systems, these processes are generally slower than in most other ecosystems due to low soil temperature, short growing season, strong seasonal fluctuations and sometimes also the occurrence of permafrost. Furthermore, slow-growing plants with high contents of lignin and phenolic secondary compounds often dominate tundra vegetation. Tundra nutrient cycling is thus limited by the recalcitrant nature of the plant residues. Since the deglaciation of the region after the last Ice Age ca. 3,000–8,000 years ago, organic matter decomposition has been slower than primary production, resulting in the accumulation of organic matter in tundra soils. In contrast to most tropical ecosystems, where the bulk of the organic matter is in the living biomass, a considerable portion of the C in tundra ecosystems is in the non-living part of the system, i.e. in the litter and soil.

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Due to the imbalance between production and decomposition of organic matter, arctic tundra is a strong sink for C and, consequently, it represents a significant reservoir of C even at the global scale. It is estimated that tundra soils contain 11% of the world's soil C pool (Melillo et al. 1990).

Research conducted during the 'Tundra Biome' project of the International Biological Programme (IBP) forms the basis of our understanding of microbial ecology and soil nutrient cycling in tundra systems. During the last two decades, much research has focused on the potential effects of global climate change, which is expected to bring about considerable changes in the arctic and subarctic climate. The expected increase in mean temperatures in tundra systems has raised concerns about whether global change will enhance organic matter decomposition of tundra systems and turn these long-term C sinks into C sources, thus contributing to the increase in atmospheric CO_2 concentrations (Oechel et al. 1993).

Although tundra systems are characterised by slow nutrient cycling, the differences in CO_2 production and nutrient mineralisation between contrasting plant communities are relatively large. This variation is related to differences in e.g. precipitation, evaporation, topography, and organic matter quality (Giblin et al. 1991; Nadelhoffer et al. 1991; Schmidt et al. 1999).

The slow release of plant-available nutrients is the primary factor controlling plant productivity in tundra systems. Evidence for this comes from numerous studies that show strong responses of the plant biomass to mineral nutrient addition (Chapin and Shaver 1996; Grellmann 2002; Jonasson et al. 1996, 1999a). The accumulation of organic matter and low plant biomass lead to a situation where the soil microorganisms immobilise a considerable proportion of the ecosystem nutrient pool (Jonasson et al. 2001). In tundras, microbial immobilisation of nutrients may often exceed mineralisation from the organic matter. Because of the low availability of inorganic nutrients, many arctic plants have the ability to assimilate nutrients in simple organic form (Kielland 1994). Dissolved organic nitrogen (DON) is considered to be even more important for soil nutrient cycling than inorganic forms of nitrogen (Jones and Kielland 2002).

Several reviews on tundra nutrient cycling are available in the literature (see Jonasson et al. 2001; Nadelhoffer et al. 1992; Robinson 2002; Robinson and Wookey 1997; Van Cleve and Alexander 1981). The finding that organic nutrient sources may play an important role in ecosystem nutrient cycling has considerably changed our views on tundra nutrient cycling. Our concepts of tundra nutrient cycling are currently going through a phase of rapid development, and this is likely to continue into the future. In this chapter the characteristics of soil nutrient cycles in tundra systems are discussed in the light of the recent literature, and the most important research questions that remain to be answered are highlighted.

11.2
Components of Tundra Nutrient Cycling

11.2.1
Mineralisation, Nitrification, Denitrification, and N Fixation

Organic matter has accumulated in tundra systems for several millennia, resulting in high organic N stocks. Plant nutrient availability is limited by the rate at which nutrients are released from the stocks of plant litter and soil organic matter. Van Cleve and Alexander (1981) estimated that nitrogen mineralisation in tundra systems is only 0.4–1.3% of the total soil N, whereas the analogous range in temperate systems is 3–7%. According to our present understanding, the nutrient pool available for plants and soil microorganisms may consist of either inorganic or soluble organic sources (Schimel and Bennett 2004). Saprotrophic fungi are the primary decomposers of organic matter in the tundra, and the fungal species composition is very similar to that in temperate latitudes. However, fungal isolates from tundras have often been found to be adapted to low temperatures (Robinson and Wookey 1997).

In contrast to temperate forests or agricultural soils (Table 11.1), nitrate concentrations in tundra soils are often negligible, and nitrification is not considered an important component of the N cycle in tundra soils (Gersper et al. 1980; Giblin et al. 1991; Hartley et al. 1999) (see also Chapter 2 by McNeill and Uncovich, this volume). Low nitrification is due to the low mean temperature and low pH of tundra soils, which limit the activity of nitrifying microorganisms. Furthermore, nitrifying bacteria generally appear to compete poorly for ammonium with heterotrophic microbes under conditions of severe nutrient limitation (Giblin et al. 1991; Schimel et al. 1996). However, Giblin et al. (1991) found that nitrification accounted for about one-half of the N mineralised in moist tussock tundra, whereas there was no evidence of nitrification in dry heaths of wet sedge tundra. Chapin (1996) found higher nitrification and denitrification

Table 11.1 Processes of N cycling in the tundra in comparison with boreal and temperate forests

	Tundras	Boreal forests	Temperate forests
Ammonification	Low/absent	Low	Moderate
Nitrification	Negligible	Low/negligible	Low
Denitrification	Negligible	Low	Low
N fixation	Moderate	Moderate	High
Organic N uptake by plants and microorganisms	High	High	Moderate

rates in a drier hummock site compared with a willow-herb hummock. Thus, although nitrification is generally considered to be low in tundra systems, its importance in the nutrient cycle may vary considerably between ecosystems. Denitrification has rarely been studied in tundra systems (Chapin 1996; Gersper et al. 1980). Denitrification in tundra soils is limited by the low availability of nitrate as a substrate for the process, although anoxic conditions necessary for denitrification may occur in waterlogged tundra sites (Chapin 1996). Due to the low availability of nitrate, N losses through denitrification in tundra systems are probably small and are likely to be relatively insignificant for the total N budget of these systems.

N input through the process of microbial N_2 fixation seems to be important in the tundra nutrient budget. In some tundra systems it has been estimated that N_2 fixation is responsible for about one-half of the external annual N input, with precipitation and snowmelt accounting for the remainder (Chapin and Bledsoe 1992). In tundra systems, N_2-fixing organisms are associated with mosses in wet areas and with lichens in drier areas, whereas free-living N_2-fixing bacteria are relatively uncommon (Robinson and Wookey 1997; Van Cleve and Alexander 1981). Symbiotic bacteria in association with legumes or other higher plants are usually of minor importance in arctic environments, but may be important locally (Chapin and Bledsoe 1992). Relatively few studies have measured both N inputs and losses through biotic and abiotic processes, and more attention should be paid to measuring total nutrient budgets of tundra systems to improve our understanding of these important ecosystems.

11.2.2
Microbial Turnover and Mineralisation-Immobilisation Dynamics in Tundra Nutrient Cycles

One of the most distinctive features of tundra nutrient cycling is that mineralisation of macronutrients such as N and P may be negative during the growing season (Giblin et al. 1991; Nadelhoffer et al. 1991; Schmidt et al. 1999; Stark et al. 2002). Negative rates of net mineralisation indicate that the microbial immobilisation of nutrients outweighs the gross mineralisation. Hence, inorganic nutrient concentrations decrease over time. The phenomenon of microbial net immobilisation instead of net mineralisation has stimulated much discussion about its implications for plant nutrient availability, and the role of microbial immobilisation of nutrients is one of the key issues in studies on tundra nutrient cycling. The discrepancy between plant nutrient uptake and levels of net mineralisation may indicate that inorganic nutrients are available for plants only at times when the microbial biomass declines, or that the uptake of organic nutrients may be more important for tundra plants than that of inorganic nutrients (Jonasson et al. 2001).

A relatively high proportion of ecosystem nutrients is immobilised in the microbial biomass in tundra systems. Jonasson et al. (1999a) calculated that, in

an arctic tundra heath, 19% and 2.5% of the total ecosystem C pool was in the plant and microbial biomass, respectively. For comparison, 10% and 6.5% of the total ecosystem N pool were immobilised in plants and soil microorganisms, respectively. For P, the corresponding proportions were 11% and 30%. Hence, the C and N pools in plants were about 8 and 1.5 times the corresponding pools in soil microorganisms, while the proportion in the plant P pool was only one-third of the microbial P pool. In tundra soils, soil microorganisms appear to be serious competitors of plants for nutrients, especially during periods of rapid increase in microbial biomass. Conversely, even a small reduction in the soil microbial biomass could lead to a substantial increase in plant-available nutrients. In a greenhouse experiment, Schmidt et al. (1997a) demonstrated the ability of soil microorganisms to retain nutrients, thus making them unavailable to plants, by showing that sterilising arctic soil considerably enhanced plant growth because it released the microbially bound nutrients.

The ability of soil microorganisms to immobilise nutrients in tundra soils is, at least to some extent, regulated by the availability of C (Michelsen et al. 1999; Schmidt et al. 1997b). Net mineralisation represents the balance between gross mineralisation and immobilisation, and C limitation often results in ammonium being present in excess of microbial demand. Glucose addition to arctic-alpine tundra soils enhanced microbial C availability and subsequent microbial immobilisation of nutrients (Michelsen et al. 1995), resulting in significantly decreased plant nutrient availability and growth (Schmidt et al. 1997b). The feedbacks mechanisms that influence the availability of labile C substrates to microbes, such as plant root exudation and recently deposited plant residues, may therefore play an important role in microbial immobilisation–mobilisation dynamics. Although, as a result of thousands of years of accumulation, C is abundant in tundra soils, microbial C availability may be limited by poor C quality. The majority of C in soil organic matter consists of large molecules of polyphenols that are generally poorly decomposed compared to soluble carbohydrates. Tundra lichen heaths with poor organic matter quality may show net N mineralisation whereas ecosystems with more easily decomposed plant species show net N immobilisation (Cheng et al. 1998; Giblin et al. 1991; Stark et al. 2002).

11.2.3
Can Plants Compete with Soil Microorganisms for Nutrients in Tundra Soils?

Despite the finding that soil microorganisms immobilise considerable amounts of nutrients in tundra systems, several studies indicate that plants are more efficient than expected in acquiring soil nutrients. In a fertilisation experiment in alpine tundra, Fisk and Schmidt (1996) showed that nutrient addition did not increase microbial N during the growing season, but did so after plant senescence. In the experiment of Jonasson et al. (1999b) in an arctic ecosystem,

fertilisation alone did not affect resource distribution between plants and microbes. However, when combined with shading, which reduced plant growth and sink strength for nutrient uptake, fertilisation increased microbial N. In a subarctic meadow, fertilisation considerably enhanced plant growth, but did not affect microbial N immobilisation, even when the plants were subjected to intense artificial clipping (Stark and Kytöviita 2006). These studies, conducted in different types of tundra systems, show that plants can compete efficiently for nutrients with soil microorganisms, especially when the nutrients are added in inorganic form.

Schmidt et al. (2002) compared microbial N immobilisation in root-free soil and in soil to which roots had access. They showed that even though the microorganisms immobilised large amounts of nutrients in the root-free soil, the same high immobilisation was not observed in the soil to which roots had access. In the rooted soil, the nutrient content of the microbial biomass remained constant or declined over the growing season. Thus, plants were able to obtain considerable amounts of nutrients during the growing season despite the presence of soil microbes, but soil microbes were only able to do so in the absence of plants. This experiment unequivocally demonstrated that plants in tundra systems are able to limit the nutrient acquisition of soil microorganisms. In the long-term, soil microorganisms may not compete with plants for nutrients because nutrients are immobilised in plant roots for longer periods than in soil microorganisms (Hodge et al. 2000).

The observation that plants can effectively assimilate nutrients at times when mineralisation measurements show microbial net nutrient immobilisation has raised concerns about whether the buried bag method or other means of soil incubation in describing N mobilisation from organic matter is a good indicator of net N mineralisation in tundra soils (Eno 1960; see also Jonasson et al. 2001; Schimel and Bennett 2004; Schmidt et al. 2002). Measuring gross N mineralisation and immobilisation using the ^{15}N isotope dilution method (Davidson et al. 1991; Hart et al. 1994) could provide a powerful tool for analysing N processes in tundra soils. However, Fierer et al. (2001) calculated that a significant proportion of the gross mineralisation measured by the isotope dilution technique may in fact correspond to internal cycling of N in the microbial biomass rather than release of N from soil organic matter.

Jonasson et al. (2004) modified the buried bag method by incubating soil with litter and plants, using an indirect measurement of the sum of soil inorganic N pools and the N in the new plant biomass as an index of nutrient mobilisation. Their study showed that in the absence of plant roots, such as is the case in incubations for measuring N mineralisation, nutrient mobilisation was significantly lower than in the presence of plants or both litter and plants. To date, there is reasonably good evidence to conclude that mineralisation measured during soil incubation does not reflect the availability of nutrients for plant uptake.

The problem of the significance of microbial immobilisation–mineralisation dynamics for plant nutrient availability in tundra systems is not yet completely resolved. Soil microorganisms immobilise a considerable proportion of the nutrients in an ecosystem (Jonasson et al. 1999a; Schmidt et al. 1997b). However,

plant nutrient uptake does not appear to be susceptible to competition with microbial immobilisation of nutrients. In contrast, plants can even limit the nutrient uptake of soil microorganisms (Schmidt et al. 2002). Moreover, the temporal variation in the concentrations of inorganic nutrients in tundra soils appears to be determined by the phenological patterns of plants (Weintraub and Schimel 2005). The hypothesis that soil nutrients would be available for plants only during times of microbial biomass decline is thus no longer valid. Although added nutrients may be taken up by the microbial biomass in the short term (Nordin et al. 2004), a greater proportion is taken up by plants rather than the microbial biomass in the longer term (Fisk and Schmidt 1996; Stark and Grellmann 2002; Stark and Kytöviita 2006).

11.2.4
Organic Nutrient Sources

The low rate of net nitrogen mineralisation has traditionally been considered to represent a major bottleneck in the flux of N and plant productivity in both boreal and tundra systems. The observation that arctic, alpine and boreal plants can acquire amino acids directly has focused attention on the role of soluble organic soil N in plant nutrition and nutrient cycling (Chapin et al. 1993; Lipson and Monson 1998; Näsholm et al. 1998). Moreover, it was shown in permafrost-dominated taiga soils that dissolved organic N constitutes a larger proportion of the soluble N flux than inorganic forms of N (Jones and Kielland 2002). At present, nutrient availability for plants and soil microorganisms in N-poor systems, such as tundras, is considered to be driven more by the degradation of N-containing polymers to amino acids, amino sugars and nucleic acids, than by mineralisation of soluble organic N into inorganic N (Schimel and Bennett 2004). Surprisingly, however, no study to date has reliably quantified the proportion of nutrients taken up by plants in tundra systems in inorganic or in organic forms.

The availability of soluble organic nutrients to plants may, to a large extent, be limited by the C quality of the soluble organic pools. DON can generally be separated into two distinct pools: soluble and recalcitrant (Jones et al. 2004). The soluble organic N pool comprises amino acids and proteins, which have an extremely rapid turnover rate. In permafrost-dominated taiga soils, free amino acids formed about 10–20% (Jones and Kielland 2002) and in arctic tundra sites 1–6% (Weintraub and Schimel 2005) of the soil DON pool. The remaining DON is formed by a recalcitrant fraction originating from microbial by-products, which are associated with phenols and have a slow turnover rate. Thus, a large proportion of the soluble N retained in the soil organic matter may be present in a form that is not plant-available (Jones et al. 2004). For example, in subarctic grasslands, DON constituted a larger N pool than the microbial N throughout the growing season, suggesting that the bulk of soil DON was not directly utilisable by soil microorganisms or plants (Stark and Kytöviita 2006). If

the major proportion of ecosystem nutrients is bound in the stable soil organic matter as phenolic and humic materials, the factors that control degradation of this recalcitrant organic matter may ultimately control the availability of nutrients to tundra plants and soil microorganisms.

Nutrient acquisition by tundra plants occurs primarily through mycorrhizal symbiosis. The dominant heath plants are Ericaceae, which form a symbiosis with ericoid mycorrhizal fungi, which can degrade organic compounds and thus liberate and acquire nutrients bound in organic matter (Bending and Read 1996). Besides plant nutrient uptake, mycorrhizal fungi thus play an important role in the mineralisation of nutrients in the soil. However, new methods have to be developed before the relative significance of mycorrhizal fungi in nutrient mineralisation can be quantified.

In contrast to what could be predicted in nutrient-poor ecosystems such as tundras, many plants in the high arctic are non-mycorrhizal. Arctic floras are dominated by non-mycorrhizal plants or by plants with limited mycorrhizal colonisation (Bledsoe et al. 1990; Kohn and Stasovski 1990). The rarity of mycorrhizas in the high arctic has been explained by an assumption that plants in the high arctic are C-limited and thus cannot afford to spend C on mycorrhizas (Väre et al. 1997). Alternatively, Kytöviita (2005) hypothesised that the low occurrence of mycorrhizal symbioses at high latitudes could be caused by impaired fungal performance in harsh climatic conditions. Arctic ecosystems are still relatively young on an evolutionary timescale, and the arbuscular mycorrhizal fungi that colonise the majority of plant species may still be poorly adapted to low temperatures.

11.3
Factors Affecting the Rate of Nutrient Cycling in Tundras

11.3.1
Regulation of Decomposition and Mineralisation by Soil Temperature During the Growing Season

The low soil temperatures in arctic tundra ecosystems limit microbially mediated processes of organic matter decomposition and soil nutrient cycling and, as these ecosystems will be subjected to a climatic change within the next century, the temperature-limitation of tundra nutrient cycling has recently received considerable attention. The expected increase in temperature in the arctic tundra is 2–4 °C in summer and 1–5 °C in winter. However, the change will not be uniform throughout the arctic tundra. In some areas temperatures have risen during the last few decades, but other areas may even experience cooling (Heal

et al. 1998). Furthermore, we do not know to what extent changes in air temperature will lead to changes in soil temperature (Robinson 2002). Increases in temperature and the length of the growing season are expected to increase plant growth and change the distribution of plant species. However, due to the strong nutrient limitation of plant productivity in tundra ecosystems, any temperature-mediated changes in soil nutrient cycling would have considerable feedback on plant growth and productivity. This may have even more important consequences on the structure and functioning of the tundra ecosystems than the direct effects of temperature increase on plant performance (Hobbie and Chapin 1998; Robinson 2002).

Despite the obvious temperature limitation of soil microbial processes in tundra systems, there are several factors that complicate the simple prediction that increased temperature will enhance nutrient cycling in tundra systems (Robinson 2002). Firstly, studies on the temperature dependence of microbial activity in tundra litter and soil show contrasting results. In the study by Hobbie (1996), decomposition of litter of arctic plants was significantly higher at 10 °C compared to incubation at 4 °C. Nadelhoffer et al. (1991) reported that microbial CO_2-C release in arctic soils was insensitive to the temperature fluctuations normally encountered in tundra soils, but was increased between 9 °C and 15 °C. In the study by Schmidt et al. (1999), soil respiration was insensitive to warming below 15 °C, and increased only when temperature rose above 15 °C.

Organic substances of different decomposability may respond differently to temperature increases, which could explain the differences in the temperature dependence of litter and organic matter decomposition. In a broad range of tundra soils, temperature sensitivity decreased after the most easily degradable organic matter near the soil surface had been decomposed (Christensen et al. 1999). Their results indicate that, when the decomposition process has proceeded to a level where only slowly decomposable substances remain, decomposition is no longer sensitive to changes in temperature. Hence, the slowly decomposable organic reservoirs that have accumulated in tundra systems since the last glaciation would be relatively insensitive to global temperature changes. This conclusion is in line with results concerning the temperature dependence of litter decomposition in boreal forests. Berg et al. (1993) found that the lignin concentration in chemically identical Scots pine needle litter incubated under different climatic conditions increased faster when the climatic conditions promoted a higher initial rate of mass loss. They concluded that enhanced soil temperatures stimulate the decomposition of easily decomposable substrates in litter, thus enhancing accumulation of the recalcitrant substrates in the litter.

In contrast to the studies mentioned above, Hobbie (1996) and Fierer et al. (2005) reported that litter decomposition became more sensitive to increased temperatures as the overall quality of the litter organic C declined. This was true regardless of whether the differences in C quality were due to inherent differences in litter chemistry or to differences in the extent of decomposition (Fierer et al. 2005). The same appeared to be true in organic soil from tundra systems, in which the temperature dependence tended to decrease with increasing soil organic matter quality (Mikan et al. 2002). The enzymatic reactions required to

metabolise structurally complex, low-quality C substrates should have higher net activation energy than reactions metabolising simple C substrates, resulting in higher temperature dependence of decomposition of recalcitrant substrates (Bosatta and Ågren 1999). The temperature dependence of litter and soil organic matter decomposition may be different (Fierer et al. 2005), but the interactions between C quality and the temperature dependence of decomposition require further investigation. Nevertheless, it seems likely that the effect of temperature on the microbial release of C varies among ecosystem types (Schmidt et al. 1999).

Another interesting point in studies on temperature control is that the response of soil C cycling to soil temperature differs from that of N cycling (Hobbie 1996; Moorhead and Reynolds 1993; Oechel et al. 1997). There may be a poor relationship between an increase in temperature and net N mineralisation because of the important role of microbial N immobilisation in net N mineralisation. No direct correlation was found between temperature and net mineralisation in arctic tundra heath because a temperature-induced increase in gross mineralised nutrients can either lead to nutrient immobilisation in the microbes or to nutrient release to the soil inorganic pool (Schmidt et al. 1999). To understand the temperature dependence of nutrient mineralisation and plant nutrient availability, it is therefore essential to understand microbial immobilisation-mineralisation dynamics.

Studies on the effects of experimental warming of tundra soils do not show consistent enhancement of net N mineralisation at higher soil temperatures. Hartley et al. (1999) found that soil warming stimulated soil N cycling during the first 2–3 years of treatment, but that it had no detectable effects on plant growth or soil N cycling after 5 years. There seems to be a flush of mineralisation after a temperature increase, after which net N mineralisation returns to its former level or even decreases (Hartley et al. 1999; Jonasson et al. 1993). Elevated soil temperatures and the subsequent increase in microbial activity may deplete the soil organic matter of readily decomposable C during the first years of warming, which would lower the substrate quality in the warmed plots and, consequently, reduce N mineralisation in the long term (Hartley et al. 1999). The question remains as to whether the changing climate will affect the stocks of recalcitrant soil organic matter, or if the stable organic matter is insensitive to increases in the activity of soil microorganisms.

11.3.2
The Significance of Soil Temperatures Outside the Growing Season

In tundra systems, the processes of decomposition and nutrient mineralisation continue throughout the year. Microbial activity continues at temperatures well below zero (Clein and Schimel 1995). In fact, a major proportion of the decomposition in arctic and subarctic systems occurs during the winter (Hobbie 1996;

Moore 1984). Although organic matter decomposition may be slow, the decomposition during the winter may still constitute a significant proportion of the total decomposition because the winters are very long. Winter temperatures are thus important for the outcome of the global climate change in ecosystem processes (Oechel et al. 1997). For example, thicker snow cover during the winter as a result of global warming can have considerable effects on tundra nutrient dynamics (Schimel et al. 2004).

Microbial processes taking place around 0 °C have interested researchers because of the diurnal temperature fluctuations, especially during the spring and autumn. Freeze-thaw events may release nutrients from the microbial biomass and, through this, be major drivers of nutrient mobilisation in tundra systems (Lipson et al. 1999; Schimel and Clein 1996). There are often distinct shifts in the microbial community structure between the summer and the winter, and the window of nutrient release after the snow melt, when protein is released from the winter microbial biomass before the summer biomass has built up, may be the key period for plant nutrient uptake (see Lipson et al. 1999). It was hypothesised that a large proportion of P uptake by tundra plants might occur during the period when soil microorganisms are still dormant and do not immobilise the nutrients (Chapin et al. 1978).

After freeze-thaw events there is a significant flush of microbial respiration, most probably because soil microorganisms that die during the event form an easily decomposable and nutrient-rich substrate for the surviving microorganisms (Herrman and Witter 2002; Schimel and Clein 1996). This effect, however, seems to be relatively short-lived and, after repeated freeze-thaw events, the release of microbial C and N may even decrease (Schimel and Clein 1996). The pool of easily decomposable material that becomes available after freeze-thaw cycles may be relatively limited (Herrman and Witter 2002) and, over the long term, the response may be negative because of the reduction in the size of the microbial biomass decomposing the soil organic matter (Schimel and Clein 1996). Although a flush of soluble C was found after freezing and thawing, there was no significant release of N because of net N immobilisation by the surviving microorganisms that utilised the readily available C (Larsen et al. 2002).

Some studies indicate that the microbial community in tundra soils is relatively resistant to freezing. The study by Grogan et al. (2004) showed no immediate effects of freeze-thaw cycles on microbial biomass and respiration, suggesting that the microbial communities were relatively resistant to the freezing regimes used in the experiment and that nutrient release from lysed microbes may have been limited. Slow freezing does not appear to be particularly lethal to soil microbes, and thus substantial microbial death is unlikely to occur in situ (Lipson et al. 2000). Schmidt et al. (1999) found no evidence of microbial death during the winter in the Fennoscandian tundra, and soil microorganisms even continued to immobilise nutrients during the winter. The effects of freeze-thaw cycles may thus strongly depend on the number of cycles, the duration of the freezing period, and the minimum temperature (Grogan et al. 2004). The significance of microbial biomass fluctuations during the winter and the summer

may vary between ecosystems, and high winter nutrient release from microbial biomass cannot be considered to be characteristic of all tundra ecosystems (Schmidt et al. 1999).

Interestingly, the net mineralisation rates in tundra soils are often negative during the summer, but positive during the winter, which means a shift from immobilisation during the growing season to mineralisation during the cold season (Giblin et al. 1991; Hobbie and Chapin 1996). Schimel et al. (2004) hypothesised that soil microbial substrate-use patterns differ substantially between frozen and thawed soils. In thawed soils, microorganisms utilise the C-rich material in plant litter and soil organic matter, but in frozen soils the soil microorganisms shift to recycling N-rich microbial biomass and small labile compounds that might remain available in water films (Clein and Schimel 1995; Schimel et al. 2004).

Schimel et al. (2004) demonstrated the importance of winter soil temperatures for microbial processes and immobilisation-mineralisation dynamics in arctic tundra communities in an experiment in which they increased the depth of the snow cover during the winter. Increased snow depth during the winter considerably enhanced winter soil temperatures, microbial activity and net N mineralisation. After 5 years, the enhanced soil temperatures during the winter also influenced the nutrient dynamics during the growing season; whereas the untreated plots showed net N immobilisation in the summer, the snow-treated plots showed net N mineralisation. Schimel et al. (2004) concluded that, because low soil temperatures limited soil microbial activity during the winter, the system with low snow cover was limited by nutrient availability, resulting in a strong immobilisation potential of microbial biomass. At higher winter soil temperatures as a result of thicker snow cover, microbial activity and nutrient release are enhanced, thus easing nutrient limitation. The recognition of the importance of winter temperatures for tundra nutrient dynamics during the following growing season is likely to inspire more research in the future. For instance, snow accumulation patterns as a result of topography may have a more significant role in tundra nutrient cycling than previously thought.

11.3.3
Feedback Mechanisms between Soil Nutrients and Organic Matter Decomposition

Although plant growth in tundra ecosystems is considered to be strongly nutrient-limited, soil microorganisms are considered to be limited more by C than by other nutrients. Glucose addition strongly increases microbial biomass and respiration (Michelsen et al. 1995; Schmidt et al. 2000) and enhances microbial respiration even in soil that is immobilising N (Vance and Chapin 2001). In the review by Hobbie et al. (2002), it was concluded that microbial activity in arctic and boreal soils appears to be limited mainly by poor C quality rather than by low N availability; increased concentration of inorganic N is thus unlikely to stimulate organic matter decomposition. This conclusion is supported by two

factors. Firstly, the decomposition of soil organic matter can be reduced by N, because N inhibits the enzymes that are responsible for the degradation of lignin-like compounds, and because N compounds react with humus break-down products to form recalcitrant compounds (Berg 2000). Secondly, because the net energy gain from degrading polyphenols is low, phenol-degrading organisms require extra energy in the form of easily decomposable substrates (Paul and Clark 1996). Hence, the degradation of recalcitrant and phenolic organic matter is limited by the availability of labile C.

In contrast, Schimel and Weintraub (2003) presented a hypothesis that soil organic matter degradation is regulated by nutrient availability. They argued that, in tundra soils, synthesis of exoenzymes responsible for degrading C- and N-containing substances is limited by soil nutrient availability, because the shortage of resources available for microbes limits exoenzyme synthesis. Enhanced nutrient availability would thus accelerate the breakdown of soil organic matter, because the microbes could then increase their production of exoenzymes degrading C-substances. Their model suggested that, in cases of C-limitation, glucose addition should increase growth respiration, but, in cases of N-limitation, glucose addition increases waste respiration through overflow metabolism. Therefore, an increase in microbial respiration after glucose addition cannot be used as evidence of microbial C limitation.

Since plants compete with decomposing microorganisms for nutrients, they have in fact been shown to retard litter decomposition (Moorhead et al. 1998) or soil respiration (Jonasson et al. 2004). The hypotheses of microbial limitations in tundra soils need to be critically tested in the future in order to improve our understanding of the factors regulating organic matter decomposition in tundra soils.

11.3.4
Mammalian Herbivores and Nutrient Cycling in the Tundra

Mammalian herbivores have a considerable effect on the structure of tundra plant communities (Chapin 1980; Grellmann 2002; McKendrick et al. 1980; Post and Klein 1996; Van der Wal et al. 2001). However, few studies have been carried out on the subsequent effects on tundra nutrient cycling. Herbivores often selectively consume more palatable and decomposable plant species, thus increasing the proportion of less decomposable species in the plant community. This reduces the quality of the organic matter and, consequently, retards soil nutrient cycling (Grime et al. 1996; Pastor and Naiman 1992; Ritchie et al. 1998). In other cases, herbivores enhance the quality of decomposing material and thus the rate of nutrient cycling in the soil by increasing the nutrient content of plants through induced compensatory growth (Frank and Groffman 1998; McNaughton 1985). The shift in plant species composition may therefore have either positive or negative effects on nutrient turnover rates, depending on whether the plant community changes towards less or more decomposable

plant species (Chapin 1991; Augustine and McNaughton 1998). Consequently, herbivores may have either positive or negative effects on ecosystem productivity (Augustine and McNaughton 1998; Chapin 1991; Hobbie 1992; Milchunas and Lauenroth 1993).

11.3.4.1

Which Factors Determine the Effect of Mammalian Herbivores on Tundra Nutrient Cycling?

It has been hypothesised that herbivory enhances soil nutrient cycling if nutrient availability is high, and retards it if nutrient availability is low (Chapin 1991). The underlying mechanism is the grazing-mediated shift in the vegetation. In nutrient-rich conditions, herbivores cause a shift in plant species composition toward fast-growing plants that respond to herbivory by compensatory growth, which increases plant nutrient uptake and nutrient concentrations in plant tissue. These plant species are also easily decomposable, and thus have an accelerating effect on nutrient turnover (Chapin 1991). In nutrient-poor conditions, on the other hand, herbivory favours grazing-resistant plant species that have prolific C-based defence mechanisms and slow decomposition rates, which indirectly reduce nutrient turnover rates (Bryant et al. 1991; Jefferies et al. 1994). A reduction in nutrient availability further favours slow-growing, nutrient-poor plant species because they are the best competitors for nutrients under nutrient-deficient conditions. Therefore, herbivory constitutes a feedback mechanism that either increases or reduces the rate of nutrient cycling and plant productivity (Hobbie 1992).

This hypothesis of the differential effects of herbivory according to soil nutrient availability was tested in northernmost Fennoscandia by comparing the effects of reindeer (*Rangifer tarandus* L.) grazing on soil nutrient cycling in tundra systems at different levels of nutrient availability. In oceanic, nutrient-rich tundra heaths, grazing enhanced microbial respiration, while in continental, nutrient-poor tundra heaths, grazing had no effects on microbial respiration, indicating that poor C quality constrained the microbial decomposition activity (Stark et al. 2002), thus supporting the hypothesis of Chapin (1991). However, N mineralisation rates and concentrations of microbial N were higher in the grazed areas in both nutrient-poor and nutrient-rich study areas. In another experiment, where nutrient availability was manipulated by experimental fertilisation, herbivory by reindeer and small rodents reduced microbial respiration rates and had a negative impact on soil N pools in both unfertilised and fertilised tundra heath (Stark and Grellmann 2002). At the same time, the proportion of graminoids in the vegetation in relation to dwarf shrubs decreased (Grellmann 2002). The evidence therefore does not support differential effects of herbivores in low-productive and high-productive systems.

The effects of grazing on nutrient cycling seem to depend more on the grazing intensity than on nutrient availability (Fig. 11.1). The processes of soil nutri-
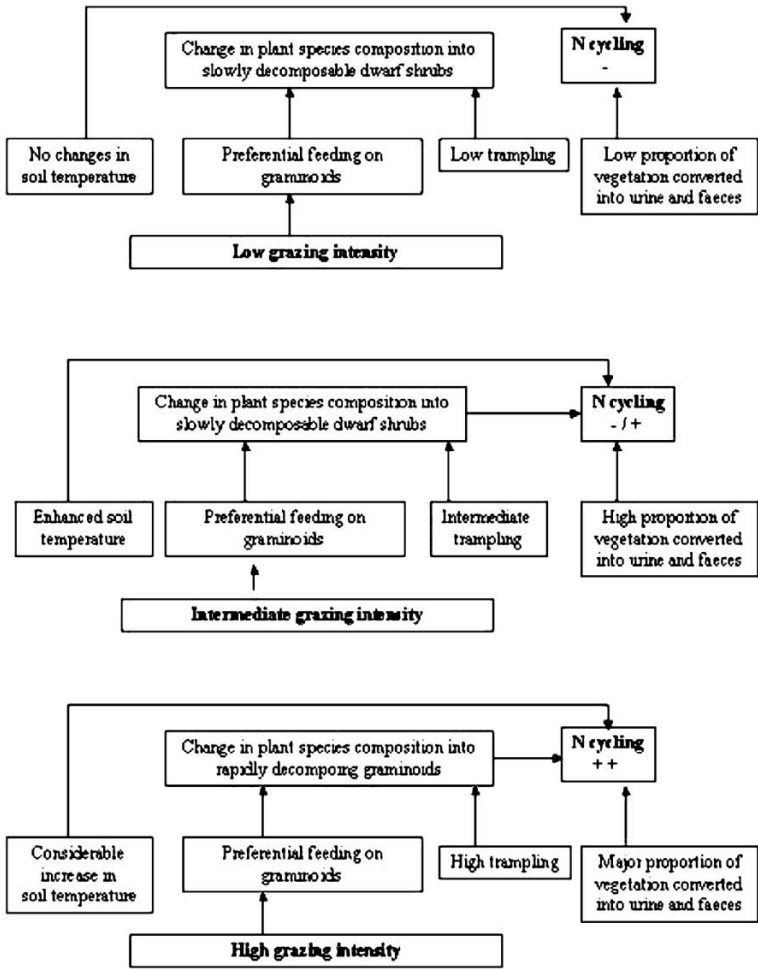
Fig. 11.1 Feedback mechanisms by which grazing intensity determines the effect of herbivores on soil nutrient cycling in tundra ecosystems

ent cycling were enhanced to a greater extent at high than at moderate grazing intensity (Olofsson et al. 2004). It would appear that the disturbance to vegetation caused by herbivores has to be strong enough to break up the dominance of dwarf shrubs in the vegetation in order to initiate a positive feedback loop on soil nutrient cycling. Graminoids gain from heavy grazing in relation to dwarf shrubs because of their higher tolerance to grazing (Chapin et al. 1986), and their greater capacity to exploit increased soil nutrient availability (Grellmann 2002; McKendrick et al. 1980). Graminoids produce rapidly decomposing litter, and their increasing proportion in the vegetation therefore enhances soil C and

nutrient cycling. Moreover, if herbivores convert a significant proportion of the vegetation into urine and faeces, then they also fertilise the soil and enhance N cycling in tundra soil (Stark et al. 2002; Van der Wal et al. 2004). Overall, the establishment of graminoids in the vegetation creates a feed-back effect in which the distribution of plant species is both cause and effect in soil nutrient cycling.

Although herbivores appear more likely to stimulate nitrogen cycling in tundra systems than in boreal forests (Pastor et al. 1993; Stark et al. 2003), herbivores have mixed effects on nutrient cycling in tundra systems. The effect of grazers on nutrient cycling is determined by a combination of three factors: (1) enhancement of growth of graminoids with nutrient-rich and rapidly decaying litter, (2) conversion of plant biomass into urine and faeces, and (3) changes in the soil microclimate, i.e. increased soil temperatures that enhance decomposition. Nitrogen cycling is enhanced to the greatest extent when all three processes operate in concert, as in the heavily grazed reindeer summer ranges. However, in the moderately grazed summer ranges (Olofsson et al. 2004) or in the winter tundra range (Stark et al. 2002) the stimulation of nitrogen availability is less pronounced because the vegetation remains dominated by dwarf shrubs. However, the fertilisation effect by urine and faeces may in many cases be strong enough to ensure that the net effect of grazing on soil N cycling is positive (Stark et al. 2002). At low grazing intensity, such as in migratory corridors, reindeer decrease N availability because they do not remain long enough to deposit sufficient amounts of urine and faeces; the vegetation remains dominated by dwarf shrubs, and the preference of graminoids in the diet may even decrease their proportion in the vegetation (Stark and Grellmann 2002). The variable impact of herbivores on nutrient cycling in tundra systems may have implications for the ecosystem-level diversity of tundra systems. If grazing reinforces spatial patterns of nutrient availability, it may increase spatial variation in the vegetation and plant productivity in the same way as proposed by McNaughton (1985) in savannah systems.

11.3.4.2
Did the Disappearance of Mega-Herbivores Change Tundra Nutrient Cycling?

During the last glaciation, the tundra in the area around the Bering Sea was a complex mosaic of steppe and polar desert, and mega-herbivore grazers dominated the vertebrate herbivore fauna. However, early in the Holocene warming, there was a rapid shift in vegetation to dominance by shrub birch over large proportions of the area, which probably contributed significantly to the extinction of mega-herbivore grazers (Jeffries and Bryant 1995). Zimov et al. (1995), however, proposed the so-called keystone herbivore hypothesis, which states that large mammalian herbivores kept large areas of the continents in the form of a shrub steppe during the Pleistocene. This is because they reduced moss cover and enhanced graminoids in the tundra vegetation, at the same time enhancing

soil nutrient cycling. They hypothesised that climate change in the late Pleisto-
cene does not explain the shift in the vegetation from productive steppe to un-
productive dwarf-shrub tundra, but rather that the extinction of large mammals
through human hunting was the primary reason for the shift in vegetation.

Studies conducted by Olofsson et al. (2004) and Van der Wal et al. (2004)
show that herbivores in tundra systems can cause changes in vegetation and
soil microbial activity similar to those proposed by Zimov et al (1995). More-
over, Olofsson et al. (2004) reported that the shift in vegetation considerably in-
creases the time period in the growing season during which the soil temperature
is above 10 °C. Therefore, the influence of herbivores on soil nutrient cycling in
tundra systems may also be due to their ability to alter abiotic factors (Mulder
1999). Herbivore effects in European and Asian tundra are influenced by the
domestication of reindeer, which has increased the grazing intensity (Oksanen
and Virtanen 1995). It is thus unknown whether the natural population density
of reindeer – limited by lichen availability during the winter – would be high
enough to break the dominance of dwarf shrubs and cause a shift to grami-
noids in arctic-alpine tundra (Olofsson et al. 2004), or to break the dominance
of mosses in high tundra (Van Der Wal et al. 2004). These interactions should
be studied more closely in the North American tundra, where the population of
caribou is closer to natural levels.

As a result of their influence on plant production, microbial activity and soil
nutrient cycling, mammalian herbivores may also affect the tundra C balance
(Kryazhimskii and Danilov 2000; Olofsson et al. 2004). Mammalian herbivores
can increase the ecosystem pool of soil organic C because they enhance the pro-
duction of root litter (Franzluebbers et al. 2000; Molvar et al. 1993; Olofsson et
al. 2004). Although the regulators of the tundra C balance are currently studied
extensively within the framework of global climate change, the effects of herbi-
vores on the C balance in the present-day and future tundra climate remain to
be determined.

11.4
Conclusions

Tundra nutrient cycling is characterised by a low rate of nutrient mineralisation
and high rates of microbial nutrient immobilisation, which are the consequence
of low soil temperatures and high stocks of recalcitrant organic matter in these
systems. The utilisation of organic nutrient sources by both plants and soil mi-
croorganisms is thought to constitute the major component of nutrient cycling
in the tundra; organic nutrients play an important role in plant nutrient uptake.
However, improved methods need to be developed to reliably quantify the pools
and fluxes of inorganic and organic nutrient sources. Studies on the regulatory
effect of temperature and organic matter quality on decomposition and miner-

alisation processes have resulted in several new hypotheses on tundra nutrient cycling. Experimental testing of these hypotheses is likely to contribute significantly to a better understanding of these ecosystems in the future.

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12 Nutrient Cycling in Forests and Heathlands: an Ecosystem Perspective from the Water-Limited South

Mark A. Adams

12.1
Introduction

Nutrient cycling in forests and to a lesser extent, in heathlands, has been regularly and thoroughly reviewed, especially in the past 15 or so years. For example, there have been numerous major projects, conferences and meetings focused on nutrient cycling in forests since 1990 (e.g. Boyle and Powers 2001; Nilsson et al. 1995; Schultze et al. 2000). These compendia are complemented by nutrient cycling contributions to more broadly based meetings (e.g. to Press et al. 1999). Seminal texts on biogeochemistry such as that by Schlesinger (1997) are essential reading and deal with forests, woodlands, shrublands and heathlands in varying detail. More recent works by Melillo et al. (2003), Schultze et al. (2001) and Vitousek (2005) are focused on biogeochemistry and global change. Even encyclopaedic treatments of aspects of nutrient cycling in forests are now available (e.g. Burley et al. 2005; Evans 2001).

For heathlands, there are fewer syntheses. Much of the extensive work on wet heathlands in Europe has been summarised in papers by Aerts, Berendse and co-workers (e.g. Aerts 1990, 1999; Berendse et al. 1989, 1994). Similarly, the review by Aerts and Chapin (2000) drew heavily on studies of heath and taiga vegetation. Overwhelmingly, these works are written from a 'northern' perspective, or at best from a north and tropical perspective.

Attiwill and Leeper (1987) provided the first in-depth treatment of nutrient cycling in forests from a 'southern' perspective. More recently, the text on eucalypt nutrition by Attiwill and Adams (1996) provides several comprehensive treatments of nutrient cycling in a range of eucalypt forests.

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In 1993 we noted that possible nutrient limitations, especially phosphorus limitation, were important themes that had developed from studies of nutrient cycling (Attiwill and Adams 1993). In part, these themes developed as a result of concerns about nutrient removal from ecosystems caused by forest harvesting and/or fire, as well as nutrient requirements and balance for plant growth (e.g. as indicated by 'Redfield ratios', Redfield 1958), and the effects of time on soils (e.g. Walker and Syers 1976). These themes have become more central as concerns about global change have increased (e.g. Archer et al. 2001; Vitousek and Field 2001) and as scientists make many observations of increases in plant growth and carbon fixation in controlled, high CO_2 environments.

It is possible that nutrient limitations to growth could become more common across landscapes under a higher CO_2 environment, and there is thus even more reason to study nutrient cycling in forests and related ecosystems. For example, Lloyd et al. (2001) modelled the availability of soil phosphorus under a high CO_2 environment, albeit in an analysis limited to moist tropical forests. Somewhat surprisingly, their modelling suggested that phosphorus availability could increase to match the increase in rates of carbon fixation, due largely to an unexplained positive effect of increased soil carbon content resulting in the release of previously adsorbed phosphorus. This modelled outcome provides some support for an earlier, more general suggestion by Gifford et al. (1996) that, in a high CO_2 world, more of the less labile forms of phosphorus may be brought into circulation. These and other studies have emphasised, as did earlier concerns about logging and fire, the importance of improving our understanding of nutrient cycling in forests and heathlands.

Much of the 'northern' literature has a bias towards ecosystems where water and phosphorus are usually at least adequate for growth of many species and where, as a result of pollution, nitrogen availability may be in excess of plant demand. Even though that viewpoint is changing (e.g. Wassen et al. 2005), the view from the 'south' has always been different (e.g. Adams et al. 2004). For much of the Australian continent, for example, rates of evaporation are far in excess of rates of precipitation. Only on the continental fringe, and then only in small areas, does precipitation approach or exceed evaporation. Large areas of the African continent are dominated by similar, obviously water-limited, ecosystems. These continents also share an abundance of geologically and geomorphically old and thus highly weathered landscapes – landscapes that are more widespread in the southern hemisphere continents than they are in Europe or on the North American continent.

While it is obvious that fire goes hand-in-hand with either long-term or seasonal shortages of water in many of the world's natural ecosystems (or at least it did prior to European intervention), a far harder task is to unravel the role of fire in putative nutrient limitations or its interaction with global change (including nutrient enrichment, changes in CO_2 or in temperature and water regimes), via nutrient cycling and availability. The 're-discovery' of fire as an essential element of the global change research agenda for forests and heathlands is more than timely – it ought never to have been forgotten.

This chapter is not intended to duplicate the focus on more specific soil and plant processes found in other chapters in this volume [e.g. Chapters 1 (Baldock), 2 (McNeill and Unkovich), 3 (Bünemann and Condron) and 4 (Rengel)]. Rather, it attempts to bring together, at the ecosystem scale, some of the current knowledge of nutrient cycling in 'southern' forests and heathlands. Hopefully it enunciates strong reasons for developing a better understanding of the interaction of fire and global change with all aspects of nutrient cycling in water-limited forests and heathlands. Nutrient cycling in forests and heathlands is a huge topic that could not possibly be covered in a single chapter. Hence, in addition to providing an overview of the major pools and fluxes, this chapter focuses on N and P and several key questions:

- What are the key controls on nitrogen cycling in forests and heathlands?
- Phosphorus limitation – real or incidental to water limitations?
- Are southern forests and heathlands different to those in the north or in the tropics?

12.2
Internal Cycles of N and P

12.2.1
Ratios of Nutrients in Forest and Heathland Plants – are they Useful?

One of the most salient features of nutrient elements in plants is the relatively narrow ranges in the ratios of one element to another. These ratios, sometimes known as Redfield ratios after the pioneer of stoichiometric analysis in marine systems (Redfield 1958), remain widely discussed (e.g. Vitousek and Howarth 1991), with several recent regional and global treatments (Han et al. 2005; Kerkhoff and Enquist 2006; McGroddy et al. 2004; Reich and Oleksyn 2004). These syntheses have done much to provide strong guiding relationships for forests in particular, and, to a lesser extent, heathlands. Combined, these syntheses show that: (1) the N:P ratio of foliage increases with mean annual temperature (i.e. toward the equator, Reich and Oleksyn 2004, see Fig. 12.1, lines a–c); (2) the N:P ratio of total plant mass is invariant to changes in plant size (across three orders of magnitude in plant size; Kerkhoff and Enquist 2006); and (3) because productivity is allometrically related with biomass (or phytomass), productivity per unit N or P actually declines with increasing biomass (Kerkhoff and Enquist 2006). In other words, at a global scale, trees produce less biomass per unit N or P than the small shrubs that dominate heathlands.

Within these overarching relationships, there remains considerable room for variation – both within communities and between functional types. For exam-
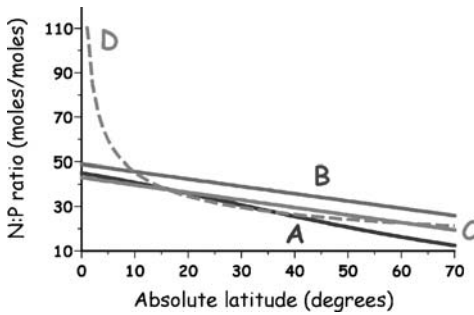
Fig. 12.1 Global patterns in N:P ratios in green foliage and leaf litter (from Hedin 2004)

ple, Kerkoff and Enquist (2006) point out that some of the reduction in productivity in forests (relative to other life forms) is due to small trees having almost zero carbon gain when growing under a canopy of larger individuals. Foresters often refer to these as 'suppressed' trees and they are widespread in Australian eucalypt forests. Kerkoff and Enquist (2006) also highlighted the more general case of dominant species or individuals in a community that can often access more resources than sub-dominant species/individuals, leading to considerable within-site variation in productivity per unit nutrient.

The slope of the N:P relationship in the global data set (e.g. Fig. 12.1) used by Reich and Oleksyn (2004) was less for conifers and angiosperm shrubs than for angiosperm trees or grasses and herbs. Similarly, at any concentration of P, concentrations of N were always least in conifers amongst the functional groups. Reich and Oleksyn discussed the previously made suggestions of 'break points' that act as indices of N or P limitation. This idea, which has been around for some time (e.g. Aerts and Chapin 2000; Koerselman and Meuleman 1996), arose from similar observations that within functional groups (e.g. heathland plants and trees), N:P ratios were clustered around a mean of roughly 15. Based on analysis of data from studies in wetlands, Koerselman and Meuleman (1996) concluded that plant growth was limited by P when N:P >16 and by N when N:P <14.

The work of Reich and Oleksyn (2004) refines this idea according to their observed patterns in N:P with changes in mean annual temperature (MAT), "… if it applied equally to all species types, would suggest a potential transition from P- to N-limitation at <25 °C, 20 °C, 15 °C and 12 °C for coniferous trees, herbs, grasses and angiosperm woody plants, respectively." These patterns seemingly owe much to the distribution of soils, especially soils of different age, on a global scale. The older soils common to the tropics are also highly weathered (as a result of greater rainfall and MAT) and seemingly lack P. Soils elsewhere are less weathered and are generally N-limited.

What do these global patterns look like at more local and possibly more practically useful scales? Using plantations of *Eucalyptus nitens* as an example where genotypic variation in physiology has been greatly reduced (Fig. 12.2), we see
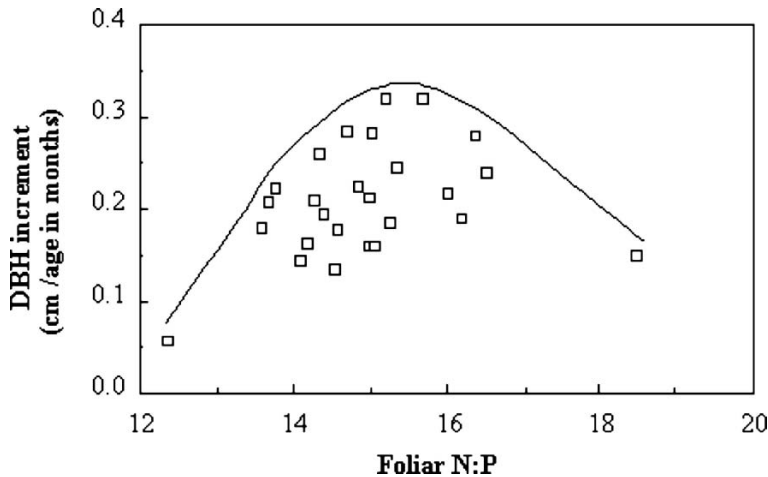
Fig. 12.2 N:P ratios in foliage of *Eucalyptus nitens* sampled from 35 plantations in southern Australia (after Judd et al. 1996)

evidence of the 'break-point' ideas. The N:P ratios in foliage from more than 25 plantations were clustered around a mean close to 15, and were clearly related to growth. Due to the strength and reliability of this relationship it has been proposed as a basis for decision-making about fertiliser needs by forestry companies (e.g. Schönau and Herbert 1982, 1983). Likewise, re-examination of data from a study of over 60 species from a range of arid heathlands and woodlands in Western Australia, Keay and Bettenay (1969) showed that of the 69 species investigated, 56 species had N:P ratios >16, often >>16, suggesting P limitation. Any wider analysis, including more Australian and overseas examples suggests the same – dominance of heathlands by plants with N:P >>16 and therefore P-limited. Unfortunately, some syntheses (e.g. Güsewell 2004) lack sufficient coverage of the Australian literature (e.g. the major data set collated by Judd et al. 1996) and as a result promote a somewhat different view.

12.2.2
Australian Case Study 1

A useful case study to illustrate several of the features of nutrient cycling combines heathlands with heathy woodlands and shrublands in a near-coast environment in south-east Australia (Taranto 2003). This study was conducted on a landscape dominated by duplex soils with sandy A horizons over heavy clay B horizons. Across the prevailing topography, which corresponds closely to water availability, there are clearly distinct communities. The tops of hills are communities of heathy woodlands, the mid-slopes are heathlands, and the valley

Table 12.1 Mean N:P ratios in foliage for selected dominant genera in three heathy communities at Anglesea, coastal southern Victoria. Also shown for each community are the mean proportional withdrawals of N and P during leaf senescence. See text for further details of the communities

Genus	Bald hills heathland		Heathy woodland		Closed shrubland	
	Mean (SE)	n	Mean (SE)	n	Mean(SE)	n
Eucalyptus	27 (0.7)	36	29 (0.9)	45	–	–
Gahnia	37 (1.3)	36	37 (1.8)	35	36 (1.4)	33
Leptospermum	28 (1.0)	40	28 (0.6)	35	33 (1.0)	43
Melaleuca	–	–	–	–	40 (1.0)	35
Resorption of N (%)	58		57		53	
Resorption of P (%)	92		87		80	

bottoms are closed shrublands. A range of parameters were compared among the three communities, using wherever possible the same species as the basis for comparison (Table 12.1). Hence, identical species of *Eucalyptus* (tree) and *Leptospermum* (heath) and *Gahnia* (sedge/herb) were common in the first two communities and *Eucalyptus* was replaced by *Melaleuca* in the closed shrubland. There are two clear points: first, all dominant species exhibited N:P ratios well in excess of 16, as has been shown for other heathland and heathy woodland ecosystems in Australia. Secondly, the lowest N:P ratios were observed for emergent trees; a clear expression of within-community variation in N:P caused by large individuals within a small-stature community – the big trees have better access to resources than the small shrubs and herbaceous species (Kerkhoff and Enquist 2006). Given the generally low nutrient status of soil supporting heathland plants in Australia and elsewhere, N:P ratios >>16 are consistent with the long-held hypothesis that low P status is a feature of heathlands.

12.2.3
Nutrient Remobilisation and Nutrient-Use Efficiency

In Fig. 12.1, we see another feature that provides a link to the topic of nutrient remobilisation and internal cycling. In addition to foliar N:P, McGroddy et al. (2004) also synthesised the N:P data for litterfall from forests. While much of the data (Fig. 12.1, Line d) show that the ratios of N:P are maintained as foliage senesces (i.e. the slope of the line is much the same as for Lines a–c) and that both N and P are withdrawn from green leaves in equal proportions, the situation changes as we move close to the tropics, with far more P than N being retained within the plant rather than shed in litterfall. Litterfall thus becomes poorer in P and has increasing N:P.

The general topic – nutrient resorption and re-use – is again contentious owing mainly to the methods of calculation of how much of any nutrient is withdrawn from foliage (or fine roots) prior to abscission. Errors in calculation, usually underestimates, arise principally from lack of consideration of all processes that contribute to losses of nutrients from foliage (e.g. leaching, herbivory and resorption; Aerts and Chapin 2000). Simple approaches (e.g. Chapin 1980) consider only the changes in concentration in nutrients between green foliage and leaf litter, ignoring the many other variables, including changes in mass. It has been shown that the underestimate that would have been produced using a simple approach can vary from as little as 3% to more than 25% depending on element (e.g. Luyssaert et al. 2005; Van Heerwaarden et al. 2003). The situation is worse for wet temperate deciduous forests than for ecosystems like many of those in Australia, where losses of leaf mass, C and nutrients via leaching and in situ decomposition in the canopy are greatly limited by the association of peak litterfall with the summer drought.

12.2.4
Australian Case Study 2

As an example, we might again consider the case study of coastal heathlands and heathy woodlands (Table 12.1; Taranto 2003). Using a simple method of calculation, withdrawal of N and P were similar for all communities. There was no obvious species dependency. Very clear is the far greater withdrawal of P – up to 90% of the P content of green foliage had been removed by the time leaves were shed as litter – than of N (removal averaged around 55%), in accordance with the patterns noted by Hedin (2004) for P-poor ecosystems.

12.2.5
N and P Uptake

Our understanding of N and P uptake by trees and heaths has undergone a revolution in recent years, with particular emphasis on the roles of mycorrhizal fungi and specific structures such as cluster roots. Much was summarised by Read and Perez-Moreno (2003), and more recently by Lambers and Colmer (2005). Amongst the many advances, there are a few worthy of special comment. First, the Proteaceae and other cluster-root forming species have long been noted as being highly sensitive to P supply (e.g. Handreck 1997) – so much so that many species are killed by even small additions of P fertiliser. Similar traits have been recorded for other species, genera and functional types endemic to low-nutrient soils in Australia and South Africa (e.g. Thomson and Leishman 2004; Witkowski 1991). Recently, considerable differences in capacity to regulate P

uptake have been demonstrated among paraphyletic, cluster-root-producing species that dominate heathlands in south-western Australia (Shane et al. 2004; Shane and Lambers 2006). This research has been linked with the ecology of species that differ only very slightly (a few grams per kilogram) in P status in a region noted for its diversity. Secondly, a wide range of fungi and plants, including cluster-root-producing species, have the ability to modify/solubilise/hydrolyse organic compounds in the rhizosphere (Adams et al. 2002; Chen et al. 2002; George et al. 2006; Marschner et al. 2005; Read and Perez-Moreno 2003). Thirdly, it is now confirmed that simple organic N is a potential source for trees and shrubs for a range of genera, including Australian native trees (e.g. Warren 2006), South African and Australian proteaceous shrubs (Hawkins et al. 2005; Schmidt and Stewart 1999; Schmidt et al. 2003) and most likely a considerable range of Australian heaths (e.g. Bell and Pate 1996).

These are important developments, yet must still be judged for significance in the context of the overall cycles of nutrients. Soil processes dominate the availability of N and P for native trees and shrubs, and plants influence soils via their inputs of organic matter both from above (leaf litterfall) and within (exudates, fine roots). For example, in relation to organic N uptake, Jones et al. (2005) noted that we still lack "evidence demonstrating this as a major plant N acquisition pathway". The same applies to organic P – the more likely scenario is that plant adaptations, including cluster roots (e.g. Adams et al. 2002), produce exudates that help solubilise and/or hydrolyse soil P (both organic and inorganic) at or close to the root surface. Most of the P taken up is in inorganic form. These points are dealt with further in the section on external cycles of nutrients.

12.2.6
Ammonium / Organic N Uptake – a Point of Difference to Herbaceous Species – and their Interaction with Water

Authors of even recent texts on plant and tree physiology (e.g. Buchanan et al. 2002; Heldt 1997; Kozlowski and Pallardy 1997) give little attention to the ammonium nutrition of woody plants in natural ecosystems. The lack of attention is all the more surprising given the decades-old and detailed knowledge of: (1) dominance of ammonium in plant-available nitrogen in forests and heathlands, (2) patterns of uptake and preference of ammonium over nitrate exhibited by woody plants (e.g. Kronzucker et al. 1997; see also Garnett et al. 2001, 2003 for studies on eucalypts), and (3) the significance of mycorrhizal symbioses, which allows woody plants to compete effectively with soil micro-organisms for immobile ions like ammonium. Instead, nitrate captures attention in forests and heathlands as a 'pollutant' of drainage waters and a sign of excessive N inputs (e.g. Aber et al. 2003; Goodale et al. 2003; see also special 2005 issue of Water, Air and Soil Pollution).

As noted above, the last 10 or so years has also seen the 'discovery' of simple forms of organic N, mainly amino acids, as sources of N for forests and especially for heathlands. Both the ability to degrade complex polymers (such as protein) and the ability to take up the products of that degradation (amino acids) provide significant advantages to mycorrhizal plants in competition with soil micro-organisms. From a plant perspective, however, ammonium and amino N are equally suitable. Uptake of either is energetically cheaper than nitrate. Herein perhaps, lies one of the great differences between woody and herbaceous plants. The ability to take up and use ammonium and amino N saves woody plants a significant proportion (>30% by some estimates) of their reserves of carbon and energy-reserves that would otherwise be spent on nitrate reduction (e.g. Buchannan et al. 2002). In water-limited ecosystems, this saving could well be even more significant. Plants that must wait for and use water to transport nitrate to the root surface are clearly at a disadvantage to those that can decompose complex polymers in situ or that can compete strongly for adsorbed ammonium to obtain their N.

12.3
External Cycles of N and P in Forests and Heathlands

It is well documented that global patterns in forest litterfall (and thus in nutrient cycling) mirror those of productivity – greatest in the wet tropics (e.g. mean for evergreen tropical species > 7 t ha^{-1} year^{-1}; Scurlock and Olsen 2003) and least in arid and boreal zones (e.g. ~2 t ha^{-1} year^{-1} for needle-leaved conifers; Scurlock and Olsen 2003) where either water availability or temperatures or both are extreme. Notwithstanding the difficulties in accessing litterfall data and cautionary notes about the quality of this data, especially from the tropics (e.g. Clark et al. 2001), the available data sets (e.g. from the Oak Ridge National Laboratory, see Scurlock and Olsen 2003; Scurlock et al. 1999; http://www.daac.ornl.gov/VEGETATION/vegetation_collections.html; or from Ecological Archives, http://esapubs.org/archive/archive.htm) have expanded rapidly in recent years owing to the now pressing need to better understand the relationships between net primary production and nutrient cycling.

Perhaps less well appreciated are the patterns of temporal and spatial variability that accompany large-scale productivity gradients. Figure 12.3 illustrates the changes in litterfall with productivity, as well as the spatial variability in litterfall, for a set of eucalypt forests in southern Australia. Apart from the expected positive relationship between litterfall and productivity, there is an inverse relationship between a measure of spatial variability (the co-efficient of variation) and productivity. This inverse relationship is readily observed in patterns of distribution of dominant trees and is due to an overriding water limitation – as
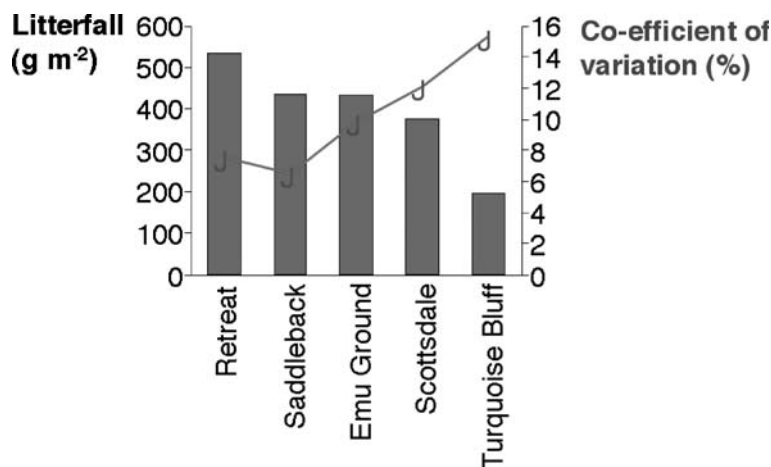
Fig. 12.3 Litterfall and the spatial variability in litterfall for eucalypt forests in northern Tasmania. Data were re-calculated from Adams and Attiwill (1991)

water becomes more and more scarce, both spatially and temporally, the trees in forests and woodlands become more widely spaced. The relationship between productivity and litterfall on the one hand, and spatial variability on the other, has yet to be fully explored, but offers considerable promise for use as a measure of impact because the variance is sometimes easier – and cheaper – to assess than the mean. Casual observation suggests that similar relationships exist for heathlands and grasslands – as water-limited productivity declines, spatial variability in productivity increases.

Below-ground, the inputs of carbon via root turnover are very difficult to quantify. Beyond making generalisations such as "proportionally, more carbon is allocated below-ground during dry periods" (e.g. Schenk and Jackson 2002), there is little we can say definitively about root turnover. Consequently, attempts to synthesise and model data for forests (e.g. Li et al. 2003) and heathlands generally fail to find the strong predictive relationships so readily generated for above-ground inputs. For example, Gill and Jackson (2000) summarised almost 200 studies of root turnover around the world and found only temperature to be a significant predictor of root turnover on a global scale. Even then it was only a moderately good predictor for grasslands ($r^2 = 0.48$) and shrublands ($r^2 = 0.55$); relations with root turnover in forests were weak ($r^2 = 0.17$). Gill and Jackson (2000) found other predictors (e.g. rainfall) were useful at smaller scales, but concluded that existing patterns of root turnover and climate were not particularly useful under future, possibly changed, climate conditions.

12.3.1
Soil Processes – N

Once on top of the soil or in it, plant organic matter contributes to the 'bottleneck' (sensu Chapman et al. 2006) or, alternatively, the key source of control in the N (and P) cycle. Although the focus of attention may shift from time to time, for example to rates of input and output as a result of concerns about excessive N inputs from the atmosphere (e.g. Aber et al. 2003; MacDonald et al. 2002), the central role of soil organic matter remains clear. This conceptual model has withstood the test of time.

While a model of the major soil N processes that contribute to making organic N once again available to plants can be drawn in any number of formats (see also Chapter 2 by McNeill and Uncovich, this volume), here I use a format (Fig. 12.4) from recent work by Cookson et al. (2006) that builds in turn on the knowledge gained during the 1980s and 1990s as synthesised by Schimel and Bennett (2004) and Chapman et al. (2006). The major evolution in thinking, from that of Jansson some 50 years earlier (see Attiwill and Leeper 1987), is the insertion of depolymerisation as a major and rate-regulating step between N in soil organic matter and plant-available N. Whereas we once thought conversion of simple organic N forms to ammonium (=mineralisation) controlled the overall flow of N from organic matter to forms available to plants, there is growing evidence that depolymerisation (e.g. of proteins to amino acids, of other more complex molecules to simpler constituents) regulates the overall process. This conceptual shift, after more than 50 years of little change, naturally throws up further questions. However, it is strongly supported by numerous lines of evidence, not the least being the aforementioned increase in our knowledge of the ability of plants to acquire simple forms of organic N.

One challenge is to understand the influence of root inputs of C, N and P. In contrast to the pronounced resorption of nutrients before leaf fall, resulting in
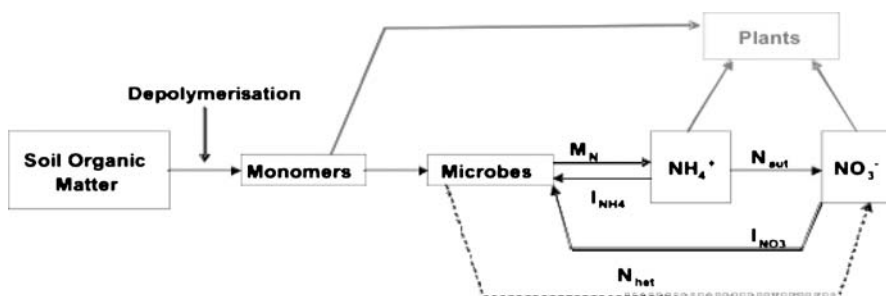
Fig. 12.4 Conceptual nitrogen cycling model. NH_4^+ Ammonium pool, NO_3^- nitrate pool, M_n organic N mineralization, N_{aut} autotrophic nitrification, N_{het} heterotrophic nitrification, I_{NH4} ammonium immobilization, I_{NO3} nitrate immobilization. After Cookson et al. (2006)

C-rich, nutrient-poor inputs from above-ground biomass to soil surfaces, available evidence suggests little nutrient resorption from the fine roots. Roots are also well-known for their exudation, both passive and active, of a wide range of carbon-based compounds, including sugars, sugar alcohols and amino acids (see also Chapter 5 by Neumann, this volume). Jones et al. (2005) recently suggested that at least part of observed amino acid uptake by roots was a means of retrieving amino compounds previously lost by exudation. The distinctions between additions of non-labile leaf litter of high C:N (or C:P) to the soil surface and highly labile root exudates, are particularly important and can lead to sometimes seemingly contradictory results. For example, Knops et al. (2002) highlighted below-ground inputs (carbon exudates, root turnover) as potential negative feedbacks to productivity (through slower mineralisation and/or enhanced immobilisation), at least for grasslands. Nevertheless, in some semi-arid grasslands, the processes that make N available to plants (including depolymerisation, mineralisation, nitrification) can be limited by lack of above-ground inputs of C as well as by N (Cookson et al. 2006). On the other hand, Monson et al. (2006) recently observed that in high altitude pine forests in Colorado, sugar alcohols accumulate in roots, where they serve to protect root cells against freezing. These same compounds are released into the soil early during the following thaw and help to kick-start soil respiration (Monson et al. 2006; Scott-Denton et al. 2006) and, presumably, other microbially dominated processes like nitrogen mineralisation. Hence, while input of litter to the soil surface usually favours immobilisation of N until sufficient carbon can be respired to allow mineralisation, below-ground inputs can produce rather more variable results, depending on the nature of the organic matter and whether it is an exudate or due to root sloughing.

It appears likely that woody plants distribute a much smaller proportion of their total annual carbon to either root exudation or root turnover than some grasslands, e.g. during drought. In addition, there is usually a substantial buffer to above-ground inputs of carbon to forest soils in the form of a litter layer that moderates plant-driven changes (e.g. temporal increases or reductions in leaf litterfall). Consequently, in heathlands and forests, feedbacks to productivity via soil processes are likely to be at least delayed if not obscured (e.g. Knops et al. 2002) by the buffer of leaf litterfall and litter layers.

12.3.2
Patterns in Nitrogen Availability and Processes

Notwithstanding our improved knowledge of organic N uptake and the role of depolymerisation, there are some remarkable patterns that underpin more traditional views of soil N processes and that provide predictive power. The most remarkable is the C:N ratio of soils. Figure 12.5 provides a summary of the influence of soil C:N for forests in Australia and Europe. Clearly, nitrification and attendant processes (denitrification and nitrate leaching) can be predicted on
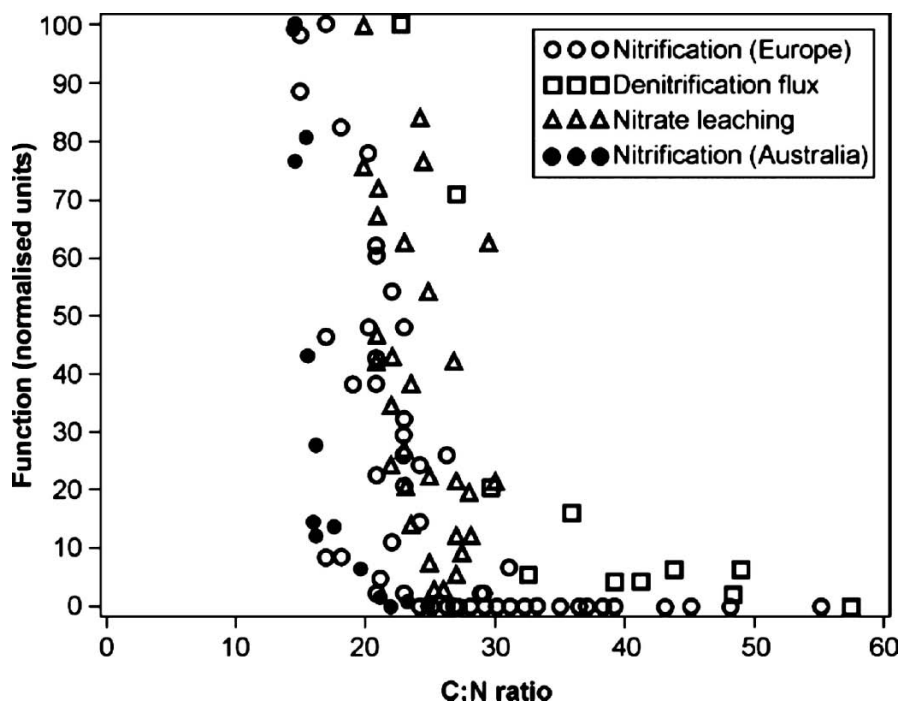
Fig. 12.5 Nitrogen cycling functions (normalised units) plotted against the C:N ratio of forest floor/litter layer. o Nitrate production in humus samples from northwestern German forest soils (100=68.1 mg kg^{-1}); □ nitrogen oxide fluxes (N$_2$O and NO) from humid wet and semi-deciduous dry tropical forests soils in Peurto Rico (100=14.5 ng N cm^{-2} h^{-1}); Δ nitrate leaching (100=40 kg N ha^{-1} year^{-1}) of forest floor at 33 temperate forest sites (two broadleaf and the rest coniferous) in Europe from the Element Cycling and Output-fluxes in Forest Ecosystems in Europe (ECOFEE) database; • nitrification (100=0.25 µg g^{-1} day^{-1}) in a range of Australian forest soils. After Adams et al. (2004)

the basis of soil C:N. When C:N ratios are low (<20), nitrification and attendant processes dominate rates of nitrogen transformation. When C:N ratios are high (>25), they rapidly decline in influence and other factors (e.g. moisture, temperature) exert more control. Many soils have C:N between these two values; hence, both the quality of the soil (e.g. its C:N) and edaphic factors exert some control.

The strength of the C:N influence is remarkable for its generality. As a further example, Lovett et al. (2002) found that watershed C:N strongly influences nitrate export from forested watersheds – the first such demonstration for North America. Owing to the observed strong influence of species composition on C:N (negative for sugar maple and white ash, positive for red oak and red maple), they suggested that changes in species composition by whatever means could have a significant influence on the capacity of watershed to retain N. These data

are also "a compelling example of how tree species can affect important eco-system characteristics and processes at both the stand and watershed scales" (Lovett et al. 2002).

In Australian forests, species also have marked effects on soil and litter chemistry (Table 12.2). Using a series of experiments with the same tree species planted some 40 years ago, we can see conclusively that establishment of exotic eucalypts caused a reduction in C:N in total litter, leaf litter, fine litter fragments and surface soils. Soil C:N was strongly related to the C:N of fine fragments (r^2 =0.66). In many instances, there were highly significant differences among species, notwithstanding an obvious influence of site (which we could not test for). These results also counter the uninformed opinion that planting of trees

Table 12.2 C/N ratio of total litter, eucalypt leaves, fine fragments and surface soils for five exotic and one endemic eucalypt species grown for ~40 years in three common gardens (that spanned about 2° of latitude and mean annual temperature) in south-west Western Australia. Reference species were *Eucalyptus diversicolor* at Walpole and Pemberton and *Eucalyptus marginata* at Dwellingup. The effects of species was highly significant ($P < 0.01$) for most attributes across all sites. Mean values for soil C:N for each site are also given (Stillwell and Adams, unpublished data)

Site and species	Total	Leaf	Fragments <10 mm	Soil (0–5 cm depth)
Dwellingup				26.5
E. maculata	166.8	90.7	64.5	24.5
E. microcorys	150.1	87.9	56.5	20.9
E. pilularis	165.9	119.0	72.7	23.8
E. resinifera	148.6	109.5	60.6	29.3
E. viminalis	166.0	104.7	61.9	28.2
Reference	190.8	121.8	73.9	32.2
Pemberton				19.5
E. maculata	120.9	70.8	39.3	20.0
E. microcorys	117.7	70.6	49.9	17.9
E. pilularis	133.0	82.5	54.3	20.7
E. resinifera	120.6	77.9	40.9	15.0
E. viminalis	118.0	79.7	59.0	25.7
Reference	131.4	90.9	43.9	18.0
Walpole				14.6
E. maculata	128.5	73.3	47.8	13.6
E. microcorys	124.7	76.6	33.7	15.0
E. pilularis	120.4	100.1	49.7	13.9
E. resinifera	121.6	83.1	41.0	15.7
E. viminalis	89.2	49.6	41.0	12.7
Reference	141.8	94.3	54.0	17.0

may impoverish or make soils somehow less fertile. Curiously, the data also conform to the general pattern whereby exotic species typically increase N availability (Ehrenfeld 2003), even though in this case it is eucalypt replacing eucalypt.

12.3.3
Soil Processes – P

The most marked among soil P processes in southern hemisphere forests and heathlands is the commonly low concentrations of total P as a result of the age of parent materials. While the general patterns in soil P fractions have been known for decades (e.g. Attiwill and Leeper 1987; Walker and Syers 1976), recent studies have highlighted biotic aspects of the P cycle, and it is here that plants and micro-organisms play a role similar to that in the N cycle.

For example, P cycling via litterfall serves to enhance the pools of labile organic P in soils, at least over the periods between major fires or other disturbances. Polglase et al. (1992) provided a clear example from an age sequence of mountain ash forests (Fig. 12.6). In jarrah forests in Western Australia, the ac-
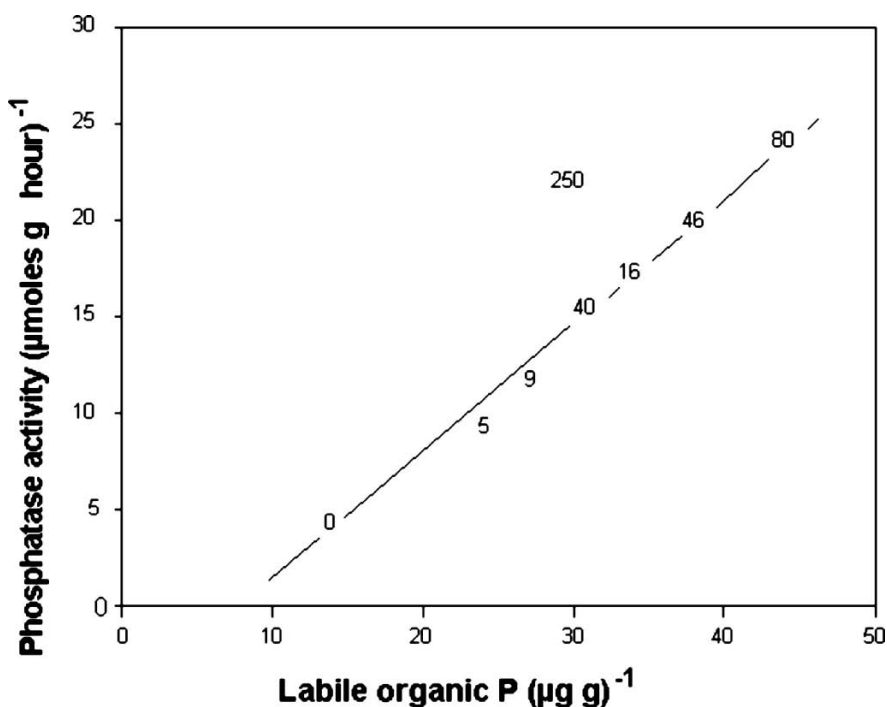
Fig. 12.6 The relationship between the activity of phosphomonoesterase and labile organic phosphorus (extracted in 0.5 N NaHCO3) in an age-sequence of *Eucalyptus regnans* forests in Victoria (after Polglase et al. 1992)
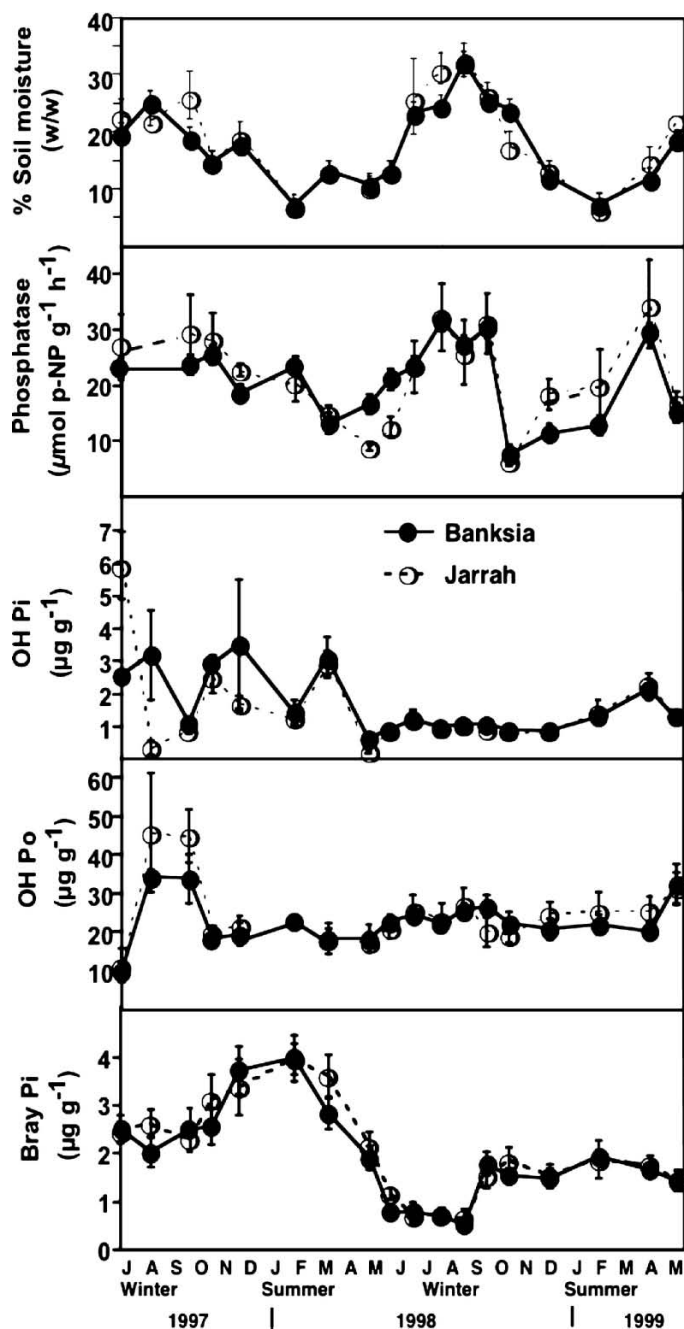
Fig. 12.7 Seasonal changes in soil moisture, acid phosphatase activity and P fractions in jarrah (*Eucalyptus marginata*) forest soil where *Banksia grandis* is present (jarrah + banksia) and absent (jarrah). Data for 0–5 cm depth only (after Grierson and Adams 2000)

tivity of phosphatase enzymes and labile organic P fractions were clearly related to climatic conditions and to the presence or absence of the major understorey species, *Banksia ornata* (Fig. 12.7), which was, in turn, related to fire regime (Grierson and Adams 2000).

Chronosequence studies (Wardle et al. 2004) highlighted the role of P limitation (e.g. Richardson et al. 2004, 2005) in collapse, or potential collapse, of forests without stand-replacing disturbances that serve to refresh and renew P supplies in the soil (and frequently stimulate N_2 fixation). These studies include Australian and New Zealand examples. The concerning aspect of this work is that we know so little of the ecologically relevant disturbance history of southern forests and heathlands (hundreds to thousands of years) and, despite some studies, so little of the detail of P cycling as influenced by parent materials, species and climate.

Instead, much attention has been focused on anthropogenic disturbance as a cause of potential losses of P and N (e.g. in fuel reduction fires) via deliberate burning. Despite some criticism (e.g. Kitayama 2005), Wardle et al. (2004) have proposed a hypothesis that rings true for many Australian ecosystems – vanishingly small pools of P in soils are locked away over time in occluded forms in soil or in plant biomass. This is discussed further in the next section.

12.4
Fire and Nutrient Cycling

Bond et al. (2005) recently drew attention to the role of fire in plant community distribution at the global scale. At around the same time, Mouillot and Field (2005) prepared a global fire map and fire history as a "first approximation for questions about the consequences of historical changes in fire for the global carbon budget". These latter authors noted the strong decline in area of temperate forest burnt annually during the twentieth century – a decline that was particularly pronounced for South American and Australian temperate forests. They also noted that there was some evidence of a reversal of this pattern in the closing years of the century. While Bond et al. (2005) and Mouillot and Field (2005) drew attention to the interaction of fire and future climates for biomass and carbon, the implications of these changes for nutrient cycling are too significant to be ignored.

Perhaps the most significant is the redistribution of nutrient elements and changes in their relative abundance (or stoichiometry) in ecosystems. As demonstrated by Hungate et al. (2003b), many biological processes in ecosystems have little effect on the stoichiometry (e.g. C:N, N:P, C:P, etc) of the major nutrient elements, whereas fires change those ratios substantially owing to the differing volatility of elements. In particular, fires greatly narrow the ratio of available N to available P owing to the far greater volatilisation temperature of P. Legumi-

nous species play a crucial role in promoting regrowth after fire by replacement of lost N.

The processes of nutrient loss, translocation and replacement are of great significance to diversity and productivity in Australia and other fire-prone, water-limited environments. For example, 10 years ago we noted for southern Australian heathlands that "over- or under-use of fire will significantly alter soil nutrient pools and availability and these changes may alter species composition and productivity" (Adams et al. 1994) – a conclusion supported by the work of Shane and colleagues (Shane and Lambers 2006; Shane et al. 2004). Likewise, Witkowski (1989) noted for Fynbos *Protea* spp.: "… the ratio of plant available nitrogen to phosphorus may be at least as important, in determining the range of species, as the absolute amounts of available N and P". Returning to the thesis advanced by Wardle et al. (2004), that reductions in P availability and cycling are inevitable without disturbance and are accompanied by losses of species diversity and productivity, we can recognise immediately that this situation gets worse with soil age, and that much of Australia and Africa is dominated by very old soils. Simply put, if the interval between fires increases, as a result of management and policy, we can expect to see losses of diversity and productivity. Indeed, there are many examples of changes in species composition and of losses of diversity in normally fire-prone heathlands as a result of changes in fire regime.

The debate about fire regime and the nutrient status of forests and heathlands has become of practical as well as of academic interest. For example, McIntosh et al. (2005) contrasted Australian and New Zealand forest soils and concluded that fires may play a significant role in the physical development of texture-contrast soils (which are common in lower rainfall areas) because "fire will encourage clay eluviation". These authors endorsed a previously advocated "feedback mechanism" [as proposed by Bowman et al. (1986) and Jackson (2000) for sedgelands] that "a fire-prone ecosystem proceeds irreversibly down a pathway of incremental nutrient loss and increasing susceptibility to further fires, because the decreasing nutrient status of the ecosystem encourages fire-tolerant forest communities" (see Fig. 12.8). On the other hand, Jurskis and colleagues (e.g. Jurskis 2000, 2005, Jurskis and Turner 2002) have been strident in their calls for restoration of more frequent low-intensity fire as a solution to many of the instances of tree and forest decline throughout southern Australia, which they attribute to a build-up of nutrients, especially N (see Fig. 12.8). Curiously, this could just as easily be an imbalance in N and P availability – too much N, too little P. These two hypotheses are drawn with that of Wardle et al. (2004) in Fig. 12.8. Whilst not ruling out any single hypothesis, there is little evidence to support suggestions that fire-tolerant forest communities are of low nutrient status. Here though, efforts to test such ideas are often stymied by confounding of water and nutrient status – many dry (and fire-prone) forests are also nutrient-poor. On the other hand, many if not all of the southern eucalypt forests – even the most productive and 'nutrient-rich' – require fire for regeneration. The
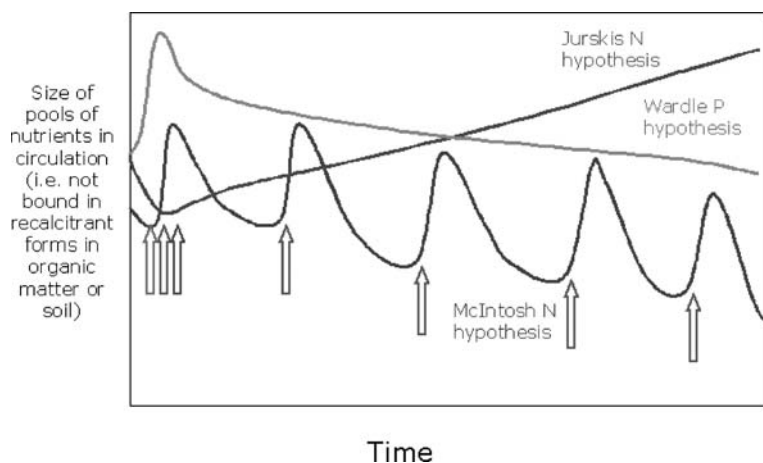
Fig. 12.8 Conceptual models of testable hypotheses regarding the influence of disturbance, mainly fire, on the availability of N and P. Models are the author's representations of suggestions by McIntosh et al. (2005), Jurskis (2000, 2005), and Wardle et al. (2004). *Arrows* Fires

weight of global evidence sits firmly on the side of widening N:P ratios without fire as the cause of large, even wholesale changes in diversity (e.g. change from grassland to heathland or forest) and productivity.

In all of the above, water and water availability play a major role. The dry heathlands common in the southern hemisphere are obviously more fire-prone than the extensively studied, wet heathlands of Europe and other parts of the northern hemisphere. It is frequently difficult to apply nutrient cycling knowledge generated from studies in the north to the south without including an assessment of the effects of fire. The same is true for drier forests – fires are integral to nutrient cycling. It is somewhat ironic that in Australia, as well as in Europe and North America, current interest, even controversy, about fire regimes stems in part from reduced rainfall in many areas over the past 10–15 years. In a study of Mediterranean oak stands, drought produced negative impacts for P cycling (e.g. Sardans and Peñuelas 2004; Fig. 12.9) that are likely to exacerbate losses of P from the active pools. Chief among these effects was a substantial increase in the increase of P in litter layers (as a result of leaf shedding), and a reduction in canopy P (from the same cause). Enhanced additions of organic P to litter layers can take many years to filter back to the active pools of P owing to extensive P immobilisation in organic matter in soils, and litter already poor in P.

Reductions in rainfall, irrespective of whether a short- or long-term change, increase both the risk of bushfire and the reluctance of authorities to use fire deliberately to control fuel loads and, possibly, maintain ecosystem characteristics such as nutrient cycling and species diversity and abundance.
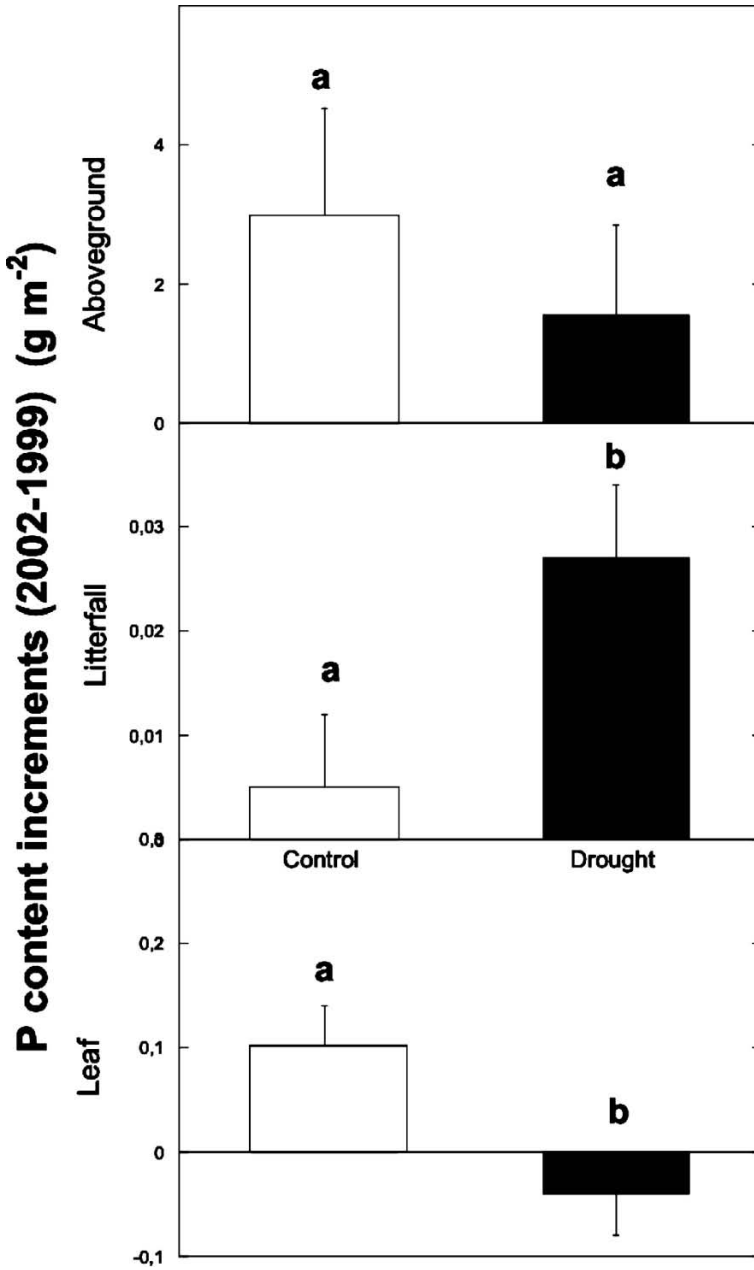
Fig. 12.9 Effects of drought on changes in P content in biomass, litterfall and canopy foliage in a stand of Mediterranean oaks. From Sardans and Peñuelas (2004)

12.5
Climate Change and Nutrient Cycling

The role of nutrients in modifying the capacity of forests and heathlands to adapt to a world of higher CO_2 concentrations and changes in temperature, rainfall and evaporation serves as an illustration of the utility of ratios. In their *Third Assessment Report*, the Intergovernmental Panel on Climate Change (IPCC) suggested that the then best-available process-based models of productivity indicated that terrestrial ecosystems, especially forests, could take up between 22% and 57% of expected CO_2 anthropogenic emissions. However, these models did not include N cycling. Hungate et al. (2003a) used the known C:N ratios in trees (~200), wood (~500), and soils (~15) to calculate, using the same models, the amounts of 'extra' N that would be required to synthesise biomass and soil C. They then calculated how much extra N might be available as a result of pollution or biological N_2 fixation. Finally, they calculated the shortfall between the amounts of N required and that likely to be available. Globally, those shortfalls ranged up to 37×10^{15} g N. Even allowing all the simulated increase in tree carbon to accumulate in the wood, reduced the amount of N required only slightly (owing to the small absolute change in amounts of N) and the shortfall. Changes to the soil C: N ratio were considered unlikely to result in additional N being made available due to the negative feedback between C:N ratio and rates of mineralisation (see also below and Fig. 12.5).

The point Hungate et al. (2003a) made was that failure to take nutrient cycling into account would likely result in an over-estimation of the capacity of terrestrial ecosystems to take up CO_2. This situation also depends on fire frequency (Hungate et al. 2003b). While Hungate et al. (2003a) made reasonable provision for biological N_2 fixation, Dan Binkley and colleagues (e.g. Binkley 2005; Binkley et al. 2000; Kaye et al. 2000; Resh et al. 2002) have shown that introduction or invasions, or even 'natural expansions', of N_2-fixing trees can produce "massive changes in soil N cycling" (Binkley 2005). There remains a possibility that increases in atmospheric concentrations of CO_2, particularly if accompanied by changes to climate and fire regimes, may result in changed abundance of N_2-fixing species that could significantly increase soil carbon storage and lower soil C: N ratios. Binkley (2005) also noted that rates of cycling of P always seem to be greater under N_2-fixing species – thereby solving another problem of the large requirement for P by biological N_2 fixation and possible future P-limitations. Incidentally, it is only for those ecosystems with an abundance of biological N_2 fixation that we have significant evidence of changes in species or changing edaphic conditions bringing less labile forms of phosphorus into active circulation, in support of suggestions by Gifford et al. (1996).

12.6
Conclusions

Vitousek (2005) posed the rhetorical question as to how N limitation could ever develop in a world where biological N_2 fixation is abundant. Perhaps the view from the south provides an answer – fire. Without fire it is hard to imagine that most sclerophyllous Australian forests and heathlands would ever be truly N limited – but with fire it seems axiomatic that they can be, or at least could be. However, the evidence collated here argues strongly, even strenuously, that shortages of plant-available P dictate much of the nature of nutrient cycling in Australian forests and heathlands, which often exhibit extremes of observed global ranges in key measures of nutrient efficiency and productivity. Fortunately, it seems that, in some cases, if the supplies of P are too low for one species, there is another species better able to make use of what there is. Eventually, though, there are very few species that can cope with vanishingly small supplies of P, and ecosystems both stagnate and become rather species-poor. There are already many such examples in Australia. Fire is essential to refresh P-cycling, species diversity and productivity. This suggestion supports the arguments put forward by Körner (2003) in the sense that rather than focus on limitation, we should focus on changes in resource availability as producing new sets of conditions that favour one species or community over another.

In keeping with previous arguments (Adams 1996), I propose that it is and will remain fire – including frequency and severity – that plays the major role in delineating boundaries between eucalypt communities as well as many of the different features of their nutrient cycles, including N and P availability and the ability to cope with other aspects of global change (high CO_2, changes in water availability). Fire plays a similar defining role for the distribution and species composition of heathlands (and related vegetation types, e.g. Adams et al. 1994; Manders 1990) and their nutrient cycles. How fire frequency is affected by global change in much of the south will probably be through soil moisture, a function of site water balances and a direct influence on nutrient availability, especially P availability. The recent and important contributions from Bond et al. (2005) and Mouillot and Field (2005), highlighting the neglecting of fire from global change scenarios and from the mindsets of land managers, serves to reinforce the tentativeness of predictions of climate-driven changes in distribution of community types and species as well as productivity and carbon sequestration. This is a truly southern view.

Acknowledgements

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13 Modelling Nitrogen and Phosphorus Cycling in Agricultural Systems at Field and Regional Scales

Peter de Willigen, Oene Oenema, Wim de Vries

13.1
Introduction

Models evolve together with the evolution of our notion and perception of reality. Models can be narratives, graphical or mathematical descriptions, or computer simulations. More than two millennia ago, Chinese and Greek philosophers already had the notion that the environment was composed of the interacting elements earth, air, water, life and metals, but the complex relationships between these factors could only be understood after the birth of modern chemistry, at the end of the eighteenth century. The chemist Justus von Liebig (1803–1873) played an important role in unravelling how plants acquire nutrients from soil, air and water, but other chemists and microbiologists in the eighteenth and nineteenth centuries also contributed to improving the understanding of nutrient cycling processes (Smil 2001). Since that time, numerous (long-term) field experiments have been carried out to test Liebig's mineral theory and its modifications. For over a century and a half, dose-response experiments have addressed one or more of the following five basic questions (Van Noordwijk 1999): (1) to what extent do nutrients limit crop yield and quality?; (2) what is the quantity of nutrients supplied by the soil?; (3) what constitutes an effective fertiliser?; (4) how much fertiliser should be applied?; and (5) what are the environmental consequences of fertiliser use?

With the increased availability of computers, increases in labour costs, and the increased awareness of the complexities involved in nutrient cycling as a

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result of spatial and temporal heterogeneity, computer simulation models have become increasingly important, replacing, to some extent, long-term field experiments. For the nitrogen (N) cycle, Clark (1981) distinguished four stages of model development, namely (1) the process diagram stage, showing the connection between the possible biogeochemical transformation processes for a nutrient; (2) the process and compartmental stage, showing the flow and transformation of a nutrient between various sites or compartments; (3) the budgeted flows and compartmental stage, with quantified pools and flows; and (4) the simulation stage, i.e. the representation of the 'real' world via a computer model. Clark (1981) noted that published process diagrams show great similarity and durability in the literature, but that compartmental and ecosystem diagrams and simulation models tend to be highly individual and to show a great propensity for change. Hence, whereas nutrient transformation processes are considered to be ubiquitous, and there appears to be a common notion about these processes, (agro)ecosystems are notoriously diverse, with great differences in the relative importance of compartments and the transfer of nutrients between compartments.

The early simulation models of the 1970s and 1980s – the so-called research models – focussed on increasing an understanding of the mechanisms of nutrient cycling and testing of ideas and hypotheses, e.g. Beek and Frissel 1973; DeCoursey et al. 1989; Dutt et al. 1972. A range of applications, including quantification of nutrient flows and losses, scenario and policy analyses, and management guidance, has evolved. Such applications of simulation models are increasingly used as discussion- and decision-support tools by policy makers, managers and farmers. Along with their increased use, there is also a continuing debate over how correct and appropriate such models are as well as over the reliability and accuracy of their results. This ongoing debate fuels model improvement, testing and comparison. The increased use of nutrient modelling tools in policy and management decision-making also reflects increased concerns in today's society about nutrient losses from agro-ecosystems and their role in environmental sustainability.

This chapter deals with computer models simulating nutrient cycles in (agro)ecosystems. We limit the discussion to models simulating the cycling of nitrogen (N) and phosphorus (P), because these nutrients have the largest influence on crop production and the environment, although aspects of the carbon (C) cycle that are relevant for these cycles are also discussed. With respect to spatial scale, we restrict this chapter to plot-scale models and regional models because these models (with some modifications) are usually also the core of models at catchment level (plot-scale models) and at national, continental or even global levels (regional models). Models dealing with nutrient cycling in farming systems, the agricultural sector, and food chains in natural ecosystems and human societies are special cases and are not discussed here. For further information on these topics, the reader is referred to McCown (2005) and references therein.

Hence, the emphasis in this chapter is on dynamic, mechanistic models at the field and regional scale. For each scale, the basic characteristics of three simulation models are described and compared. Since there are already many papers describing/comparing different N and P models, the focus of this chapter is problems that arise when going from plot scale to regional scale. We first discuss N and P cycling processes and scaling issues (from point to field scale and from plot to regional scale), followed by an overview of the similarities and differences of a selection of N and P cycling models (three at plot scale and three at the regional scale). We end with a discussion on validation, upscaling, desirable future developments and integrated modelling.

13.2
N and P Cycling Processes and their Modelling

Figure 3.1 in Chapter 3 (Bünemann and Condron, this volume) shows schematically the pools and fluxes involved in a nutrient cycle in a terrestrial system (see also Chapter 2 by McNeill and Uncovich, this volume). With some exceptions, the processes shown apply to the cycling of N and P in the soil. For N, there is no weathering of parent material. Furthermore, soil exchange processes between the solid and dissolved phase are limited to NH_4 adsorption/fixation.

The greatest pool of N in the soil–plant–atmosphere system is that in the atmosphere, comprising about 70% of the N in the biosphere. This is converted into forms available (nitrate, ammonia, ammonium) for plants and microbes by natural processes – oxidation by lightning, biological fixation by e.g. legumes – and by industrial fixation.

Most of the N in soil is in organic form, originating from plant production (litterfall, decaying roots, crop residues), dung, and, in the case of agricultural soils, manure. Through mineralisation by the microbial biomass, organic N can be transformed into inorganic forms, in the first instance ammonium, which is then converted into nitrite and ultimately nitrate (nitrification). On the other hand, inorganic forms of N can be incorporated into newly formed biomass (immobilisation). The central role of mineralisation and microbial immobilisation in the N cycle are highlighted in Chapter 2 (McNeill and Uncovich, this volume). Nitrite and nitrate can be reduced by microorganisms into gaseous forms (N_2O and NO) and eventually N_2 (denitrification). Viewed on the scale of a plot, all these processes can occur simultaneously, but on the micro (point) scale some processes require conditions (e.g. availability of oxygen) that preclude the appearance of others.

In contrast to the N cycle, gaseous losses, deposition and biological fixation are absent or negligible in the P cycle (for details, see Chapter 3 by Bünemann and Condron, this volume). Other differences from N cycling include the strong

adsorption of P in soil, the slow immobilisation of adsorbed P in a non-exchangeable pool, and the release of P from weathering. Other processes, such as mineralisation and immobilisation proceed in essentially the same way as in the N cycle. The same applies for leaching and runoff; in the case of P, the transport of P sorbed to the surfaces of colloidal particles is particularly important (Jarvis et al. 1999; McGechan et al. 2002).

Modelling of the N and C cycle has a long history. De Wit (1974) pointed to the work of von Wulfen in the early nineteenth century, which was a precursor to the work of Henin and Dupuis (1945) and later Kortleven (1963) on the cycling of organic matter. The real growth of models started in the computer era. Early examples are the models of Dutt et al. (1972) and Beek and Frissel (1973). Nowadays, such models abound – many books and papers discuss N sources, pools and processes in agriculture, and losses from agriculture to the environment (e.g. Burt et al. 1993; Follett and Hatfield 2001; Mosier et al. 2004; Smil 2001; Wolf et al. 2005), and many of these studies are based on models.

There are fewer P models. Frossard et al. (1995) gave an overview of seven models of the P cycle for various ecosystems. Sharpley et al. (1995) did the same for models aimed at simulation of transfer of P from terrestrial to aquatic ecosystems. Grobbelaar and House (1995) mention some modelling work for the P cycle in aquatic ecosystems.

Some papers focus on the comparison of models; examples are De Willigen and Neeteson (1985), De Willigen (1991), Diekkrüger et al. (1995), Lewis and McGechan (2002), Liwang Ma and Shaffer (2001), McGechan and Wu (2001).

Addiscott et al. (1991) compared the performance of various models simulating nitrate leaching. Frolking et al. (1998) compared models simulating nitrous oxide emissions. The results indicate that most models do a reasonable job, but there are often significant differences between measured and modelled emissions, suggesting that such models do not capture satisfactorily all variations in nature.

13.3
Scaling Issues

One of the common characteristics of environmental problems such as nutrient leaching is that they operate across many spatial scales, from local, through regional, national and continental, to the global scale. In this context, regional models generally pertain to areas of 1–1,000 km² (catchment areas, rural regions, different terrestrial ecosystems). Wolf et al. (2005) gave an overview of some models on the regional scale. Scaling problems are discussed in numerous papers and books (e.g. Bierkens et al. 2000; Heuvelink and Pebesma 1999; Pachepsky and Radcliffe 2003; Refsgaard et al. 1999).

Within the framework of the modelling process, there is already the problem that the point scale at which processes take place is often different from the scale

at which observations take place, thus providing an average value on the field or plot scale. Upscaling from point scale to field scale may not always be valid. Additionally, as pointed out earlier, field scale processes may occur simultaneously, although they may preclude each other on the point scale.

Regarding the model scale, Bouma et al. (1998) state that many biogeochemical models developed on a plot scale may also be used at larger spatial scales. However, this may cause problems (cf. Heuvelink 1998a):

- The relative importance of a process or sub-process may vary with scale. A particular process may be negligible at larger spatial and temporal scales, e.g. unsaturated preferential flow (Blöschl and Sivapalan 1995).
- At small scales, e.g. at those of intensively monitored plots, data availability can often support the demand of complex models. At larger spatial scales data may be only sparsely available, requiring model input data to be derived from generic data sources such as maps and pedo-transfer functions (cf. De Vries 1994).
- Moving from a smaller towards a larger scale is generally accompanied by an increase in the level of aggregation. Usually, the model input data become some kind of average of point values within a large spatial unit or 'block'. This may require adaptation of the model (cf. Heuvelink 1998a).

It is imperative that the spatial and temporal scales addressed in a model take these issues into account. In this context, the relationship between modelling objectives and scaling issues should also be addressed. When the aim of the model is to provide insight into system behaviour, generate hypotheses and direct further investigations (research models), it is important to develop detailed process-oriented mechanistic models that can generally (partly) be tested only at plot scale. When the aim is, for example, to help policy makers in designing or evaluating environmental policies (management models), requiring application at the regional to national scale, it is generally more appropriate to develop more simple process-oriented models including empirical relationships. This is because of the general parameterisation problem that arises from applying a detailed plot scale model at a larger spatial scale.

The more parameters a model contains, the less likely it is that they can be derived either directly from available data or indirectly by using relationships with environmental data. Especially at large spatial scales, many model parameters cannot be measured directly or determined at all. In addition, when particular parameters can be obtained only by calibration, an explicit allocation of an optimal parameterisation to each individual parameter is often impossible (identification problems). Consequently, there is a trade-off between scale and model complexity.

Sometimes, complex plot-scale models are applied directly to a large temporal and spatial scale. Examples are the application of the STONE model (cf. Boers et al. 1995), which describes, amongst other things, the fate of nitrate in agricultural soils at a national scale (Wolf et al. 2003), or the DNDC model (Li et al. 2000) describing the exchange of greenhouse gases in agricultural soils at a national to continental scale (Kesik et al. 2005). This may cause large parameter

errors as few of the required data are available at larger spatial scales. One possibility is to simplify the model description in such a way that the temporal and spatial resolution is comparable to the resolution of the data. During such a simplification of processes, model results must remain reliable. The reliability can be determined by comparing results from the simplified model and the original model on a plot scale using long-term observation data to gain insight into the loss of reliability at that scale (e.g. Van der Salm et al. 1995).

Different approaches can thus be followed when developing and applying models on a regional scale (Refsgaard et al. 1999), ranging from simple models with semi-empirical process description (e.g. Arnold and Williams 1995; Beasley et al. 1980; De Vries et al. 2003; Johnes 1996; Knisel and Williams 1995; Leonard et al. 1987; Young et al. 1995) to complex models with mechanistic process description such as RZWQM (DeCoursey et al. 1989, 1992), DAISY (Hansen et al. 1991) and WAVE (Vanclooster et al. 1994, 1995; Vereecken et al. 1991).

When a model is applied on a regional, national or even continental scale, it is likely that, as the complexity of the model increases, descriptive (model) errors decrease but parameter errors increase. The aim is to choose a level of complexity that minimises the total prediction error in large-scale environmental applications. In theory, there is an optimal level of model complexity, i.e. a point at which the degree of model complexity (in terms of number of state variables) matches the data resolution and quality, leading to maximal knowledge gain about the modelled system (Janssen 1998; Jørgensen 1992).

Since environmental systems are regarded as complex, "…increased complexity in models is often interpreted as evidence of closer approximation to reality" (Oreskes 2000). However, Janssen (1998) pointed out that "…a model should be made no more complex than can be supported by the available brains, computers and data". In order to obtain more reliable results, a theoretical justification for the use of model simplification can be obtained by uncertainty analyses (cf. Hettelingh 1989; Janssen 1994; Heuvelink 1998b; Hornberger et al. 1986).

13.4
Models at Plot Scale

Models at plot scale vary from simple models dealing with a specific process within the nutrient cycle (e.g. leaching in a period where microbiological transformations do not play a role) to complex models describing "all" relevant processes. Here we describe three plot scale models, namely ANIMO, DAISY and MACRO. References for the models are given below. These three models were developed more than 10 years ago, and have been updated regularly. They are well documented, have been tested several times and used in several studies on model comparison.

13.4.1
ANIMO

13.4.1.1
Description

ANIMO is a one-dimensional mechanistic and deterministic model at field scale for calculating the cycling of C, N and P in soils and N and P emissions to ground and surface waters. It was first developed in the mid-1980s and has been updated regularly since then (e.g. Groenendijk and Kroes 1999; Rijtema et al. 1999; Groenendijk et al. 2005; Kroes and Roelsma 1998; Wolf et al. 2005). The following description is taken mainly from Wolf et al. (2005). The relevant parts of the model are: (1) the organic C cycle, (2) the N cycle, and (3) the P cycle. In the organic C cycle, the following processes are described: (a) application of various organic materials; (b) decomposition of fresh organic materials in soils and transformation to humus; (c) turnover of humus. The organic part of the N and the P cycle in the soil runs largely parallel to the organic C cycle.

In the inorganic part of the N cycle, the following processes are described: (a) addition of mineral N in fertilisers and N precipitation; (b) ammonium-N volatilisation; (c) ammonium sorption; (d) nitrification of ammonium; (e) denitrification; and (f) N uptake by crop. Groenendijk and Kroes (1999) and Vinten (1999) gave a more detailed description of the C and N cycling within the ANIMO model. A number of ANIMO applications for modelling N leaching are given by Hack-ten Broeke (2001), Hack-ten Broeke and De Groot (1998) and Vinten (1999).

In the inorganic part of the P cycle the following processes are described: (a) addition of mineral P in organic and inorganic fertilisers; (b) P sorption; (c) P precipitation; (d) P uptake by crop. Groenendijk and Kroes (1999) gave a detailed description of P cycling within the ANIMO model. An application of ANIMO for modelling P leaching is given by Schoumans and Groenendijk (2000).

Transport of solutes is described by the convection-dispersion equation. Fluxes of water are not calculated in ANIMO, but have to be simulated prior to the ANIMO calculations with another model called SWAP (Van Dam 2000).

13.4.1.2
Validation

ANIMO had been tested a number of times, usually with reasonable to good results. Groenendijk and Kroes (1999) gave examples for different land use and transport of nitrate and phosphate (Fig. 13.1). Other examples on N leaching
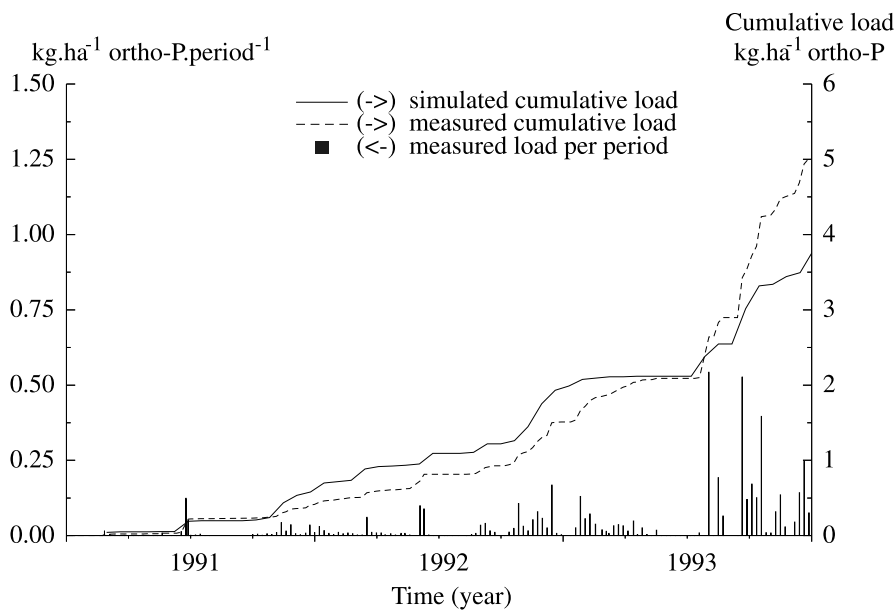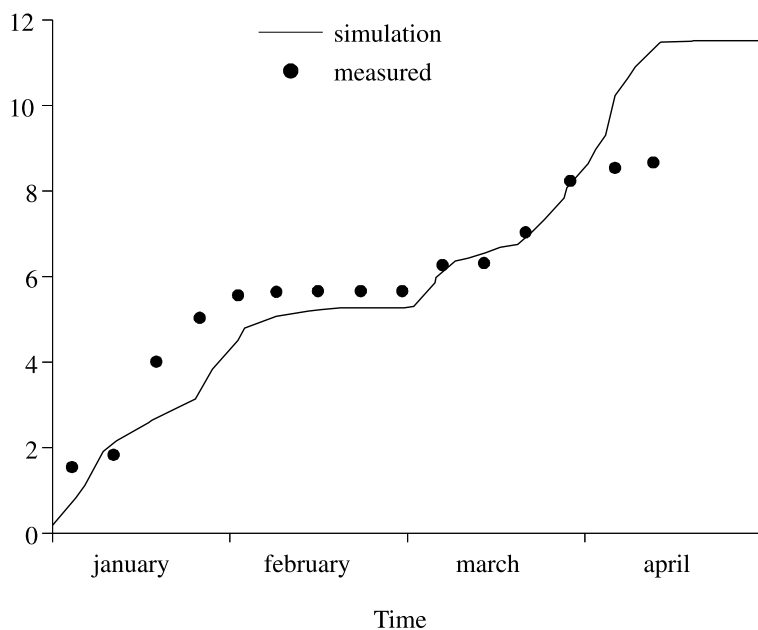
Fig. 13.1 Observed and ANIMO-simulated cumulative discharge of (**a**) nitrate from a field covered by a mixtures of grass and clover over the period January–April 1994 (*points* observed, *line* simulated) and (**b**) ortho-P to ditches in grassland experiments (from Wolf et al. 2003)

are found in Wolf et al. (2005). The model has been subjected to a number of reviews and model comparisons (de Willigen 1991; Lewis and McGechan 2002; McGechan and Lewis 2002; Reiniger et al. 1990; Silgram and Schoumans 2004; Wu and McGechan 1998).

13.4.2
DAISY

13.4.2.1
Description

The soil-plant-atmosphere system model DAISY is a deterministic, one-dimensional, mechanistic model for the simulation of crop production and water and N balance in the root zone. The model includes sub-models for evapotranspiration, soil water dynamics based on the Richard's equation, water uptake by plants, soil temperature, soil mineral N dynamics based on the convection-dispersion equation, N uptake by plants and N transformation in the soil. N transformations simulated by the model are mineralisation-immobilisation turnover (MIT), nitrification and denitrification. In addition, the model includes a module for agricultural management practice. The model is described in detail elsewhere (Hansen et al. 1990, 1991; Petersen et al. 1995).

13.4.2.2
Validation

The model has been validated in a number of studies (De Willigen 1991; Diekkrüger et al. 1995; Jensen et al. 1994; Smith et al. 1997; Vereecken et al. 1991). Hansen et al. (2001) gave an overview of the performance of the model in simulation of crop growth, N uptake and N leaching and conclude that good results are achieved. Figure 13.2 shows an example of a successful validation of simulated spatial and temporal variation of soil nitrate concentrations obtained with DAISY on measurements in a coarse sandy soil in Jyndevad, Denmark. The spatial variation is based on the measured spatial variability in soil water retention and hydraulic conductivity at the plot scale. In their comparison of 19 models, Diekkrüger et al. (1995) remark that DAISY was the only model to simulate "…all main processes, such as water dynamics, plant growth, and N dynamics, with the same quality; the others were only able to partially reproduce the measured dynamics".
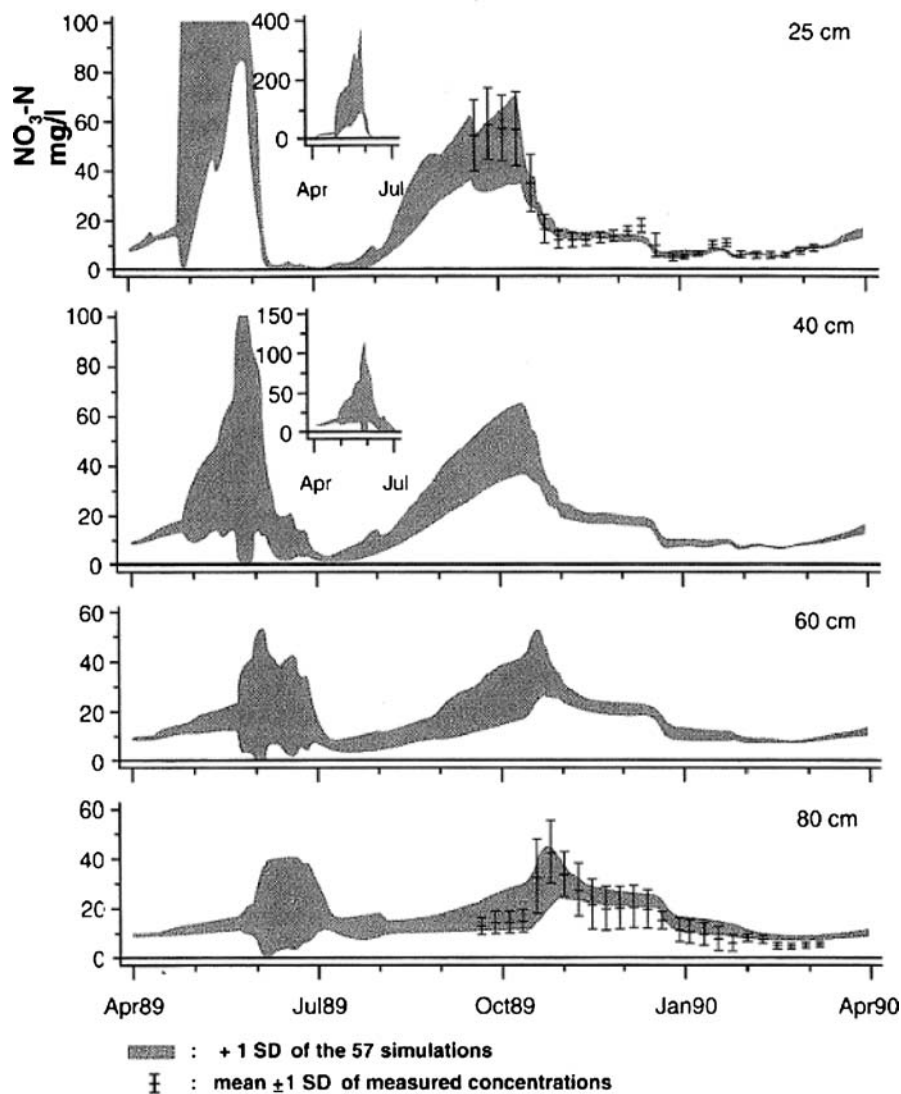
Fig. 13.2 Comparison of the spatial and temporal variability in measured and DAISY-simulated NO_3-N concentrations (mg l^{-1}) in a coarse sandy soil in Jyndevad, Denmark (from Djurhuus et al. 1999)

13.4.3
MACRO

13.4.3.1
Description

MACRO is a one-dimensional model that describes transient water flow and solute transport in a layered soil. It considers two types of soil pores: micropores where water and solute transport are governed by the Richard's equation and convection-dispersion, and macropores where water flow is gravity-driven and solute transport is by convection only. Jarvis and Larsson (1998) provided a detailed description. Originally (Jarvis 1994), the model dealt only with soluble contaminants (mainly pesticides, e.g. Larsson and Jarvis 1999a), but it has also been used to calculate nitrate leaching (Larsson and Jarvis 1999b). Jarvis et al. (1999) extended the model so that particle mobilisation at the soil surface by the impact of rain and subsequent transport of soil particles through macropores, as well as filtering of the particles by micro- and macro-pores could be computed.

McGechan et al. (2002) parameterised MACRO so that leaching of P attached to colloids could be simulated. They considered two sources of production of colloids: firstly by impact of rain, and secondly – as the main source of colloids – applied slurry. Inorganic P is subject to two sorption reactions in the soil matrix. One, given by a Freundlich isotherm, proceeds so fast that instantaneous equilibrium between dissolved and adsorbed P can be assumed. The slow reaction is completely irreversible and proceeds according to a pseudo first-order reaction, with the rate coefficient being a function of time. The sorption on colloids is given by a linear isotherm, the ratio between adsorbed P and P in solution is constant.

13.4.3.2
Validation

McGechan et al. (2002) used the model to calculate P flows to field drains following slurry application at two sites and found reasonable-to-good agreement between model results and measurements (Fig. 13.3). The peak in P leaching following slurry application was well reproduced and was, according to the model, due almost entirely to transport of colloid-sorbed P. Because the filtration parameters and the adsorption coefficient of the slurry colloids could not be measured these had to be calibrated, thus the model was not validated in the proper sense. Nonetheless, it could mimic the measurements well, and so supported the supposition that transport of P sorbed onto colloids is an important mechanism in P leaching.
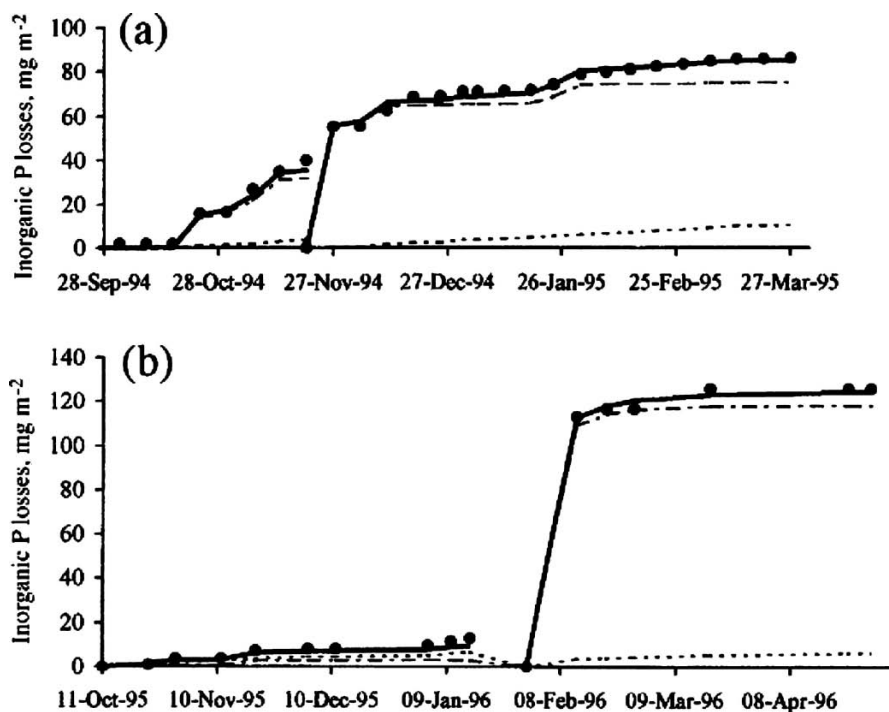
Fig. 13.3 Cumulative P flows to field drains measured and calculated with MACRO, following slurry spreading at a grassland site in Dumfries (Scotland, UK) from the start of each simulation period (1 October) and from slurry application date (**a** 21 November 1994, **b** 31 January 1996). *Points* Measured total inorganic P, *solid lines* simulated total inorganic P, *dotted lines* simulated colloid-sorbed inorganic P, *dashed lines* simulated dissolved inorganic P (from McGechan et al. 2002)

13.4.4
Comparison of Models

Models can be compared in various ways. One possibility is to concentrate on the comparison of the formulation of certain processes in the models and analyse the consequences for results. An example of comparisons of N models is the paper by Wu and McGechan (1998), who reviewed four European models, including ANIMO and DAISY. Liwang Ma and Shaffer (2001) did the same for nine US models, and McGechan and Wu (2001) extended their 1998 study to six European models.

Another way of comparing models is to investigate the models with respect to their performance when run with the same set of input data and then compare the results with measurements. For the N cycle this has been done by (e.g.) De Willigen and Neeteson (1985; 6 models), De Willigen (1991; 14 models), Diekkrüger et al. (1995; 19 models), Kersebaum et al. (2006; 18 models). The

Table 13.1 Simulated results of the components of the nitrogen balance in a wheat experiment over the growing season from the models DAISY and ANIMO

	DAISY	ANIMO
Fertilisation	110	110
Mineralisation	51	112
Denitrification	17	85
Plant uptake	170	176
Leaching	2	0
Change in storage	−23	−26

latter authors note that especially the microbial turnover processes of C and N are still not sufficiently understood.

Both ANIMO and DAISY were used in a comparison of simulation models of the N cycle in the soil-crop system (de Willigen 1991). The models were run with the same data set, derived from fertilisation trials with winter wheat in the Netherlands. The two models yielded similar results with respect to the water balance. Also, the calculated N uptake and change of storage of N in soil were similar. However, other components of the N balance, i.e. mineralisation and especially denitrification, differed substantially (Table 13.1).

In both models, mineralisation is calculated as a consequence of decomposition of organic matter by the microbial biomass and incorporation of N into newly formed biomass. Decomposition proceeds as a first-order process in both models, but the number of pools is different. DAISY divides the native organic matter into dead organic matter and biomass, each of which consists of two subpools. In ANIMO, all soil organic matter is regarded as a single pool. Also, the number of pools in the added organic matter (manure, crop residues) is different in both models. This leads to differences in calculated mineralisation.

Potential denitrification in DAISY is proportional to the production rate of CO_2, which is released during the decomposition of organic matter. The potential denitrification rate is corrected by multiplying it by a factor taking into account the oxygen status of the soil, as measured by the degree of water saturation. The actual denitrification rate is a function of potential denitrification rate and the rate at which the nitrate in soil becomes available for denitrification. ANIMO – at least in the version discussed here – calculates the oxygen status of the soil by considering vertical and horizontal diffusion of oxygen as driven by oxygen consumption. In this way the fraction of anaerobic soil can be estimated. Denitrification in the anaerobic part is calculated as the potential denitrification, which is, as in DAISY, proportional to the production rate of CO_2. However, the proportionality factor in ANIMO is five times that in DAISY, which explains, at least in part, the difference in calculated denitrification.

Lewis and McGechan (2002) compared four field-scale models of the P cycle: ANIMO, GLEAMS, DAYCENT and MACRO. The comparison concerned the model concepts and the equations used to describe the different processes. In

an appraisal of the strength and weaknesses of the models, they concluded that in future a hybrid version of the models should be developed: "Such a model is likely to include a description of both soluble and particulate P flow through micropores and macropores as in the MACRO model framework, combined with a full representation of the C/N/P cycle as described by GLEAMS, with manure and slurry components as described by ANIMO, and plant residue decay equations taken from the DAYCENT model. Finally, the overland flow and erosion losses should be represented by components from the GLEAMS model."

To our knowledge, a comparison of performance of P models when run with the same set of input data has not yet been conducted.

13.5
Models at Regional Scale

To illustrate the various possibilities of model up-scaling, three regional models will be discussed: a simple empirical model (INITIATOR); the so-called Johnes model, which also uses a simplified approach; and finally the STONE model, which is based on mechanistic models. As stated above, it is possible to apply a complex, plot-scale model directly to a large temporal and spatial scale, but another option is to use more simplified model approaches and compare the results of these simpler models to those of complex models on plots at various scales and with various observations. STONE and INITIATOR are examples of the first and second approaches, respectively. We thus selected these two models for discussion.

13.5.1
STONE

13.5.1.1
Description

STONE consists of a chain of models and can be characterised as follows: (1) developed specifically for support of environmental policy development and evaluation; (2) applicable at national and regional scales; (3) input data on land characteristics are spatially distributed; (4) chain of models incorporating first an optimisation model (CLEAN2; Mooren and Hoogervorst 1993; Van Tol et al. 2001) for calculating the distribution of inorganic fertilisers and animal manure over the Netherlands and the resulting N and P input to soils, second a meta-model (SRM) for calculating N deposition from the air, and third, a mechanistic deterministic model (ANIMO, see Sect. 2.2) for calculating N and P emissions;

(5) ANIMO calculations done on a grid of 250×250 m with a time step of 1 day; (6) detailed spatial schematisation for ANIMO calculations: 6,405 unique land units in the Netherlands that differ with respect to hydrological and drainage characteristics, land use, soil type, soil chemical characteristics and climate; (7) soil hydrological data are imported from separate calculations with SWAP (Van Dam 2000).

Due to the relatively coarse spatial and temporal resolution of input data, manure distribution and atmospheric deposition, results from STONE are preferably interpreted for mean nutrient fluxes and concentrations of larger spatial units (at least 250 km²) and for more than 1 year.

13.5.1.2
Validation and Application

Validation: Results from the STONE system have been compared with observed data to analyse plausibility (Overbeek et al. 2001, 2002). The STONE results concerning (1) N concentrations in shallow ground water, and (2) N and P con-
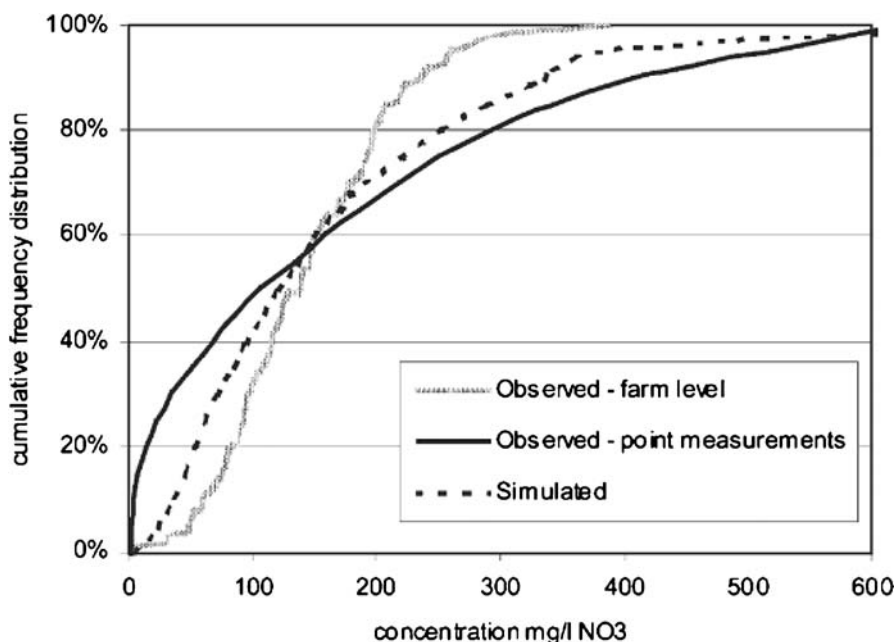
Fig. 13.4 Comparison of frequency distributions of with STONE simulated and measured N concentrations in shallow groundwater at 140 different farms in the Netherlands (from Wolf et al. 2003)

centrations in fluxes to surface waters were analysed. The measured N concentrations in shallow ground water were taken from measurements at 140 different farms. Comparison of frequency distributions and of mean and median values showed a good correspondence with those of the measurements (Fig. 13.4). N and P concentrations in fluxes to surface waters were compared with a data set of measured N and P concentrations in surface waters in agricultural areas in the Netherlands. The STONE results were ca. 50% higher than the measured N and P concentrations, which Wolf et al. (2003) considered as acceptable.

Application: STONE has been applied to evaluate different scenarios for target N and P surpluses in agriculture in the Netherlands (Schoumans et al. 2002; Wolf et al. 2005).

13.5.2
INITIATOR

13.5.2.1
Description

The model INITIATOR (Integrated NITrogen Impact Assessment Tool On a Regional scale) was developed by De Vries et al. (2003). It calculates the excess of total N input over total N output:

$$N_{ex} = N_{in} - N_{im} - N_{em} - N_{de} - N_{up} \tag{1}$$

where N_{ex} is excess N, N_{in} total N input, N_{im} net immobilisation (immobilisation – mineralisation), N_{em} emission of ammonia, N_{up} uptake by plants and N_{de} losses by denitrification. Total N input is the sum of five components:

$$N_{in} = N_{in,am} + N_{in,g} + N_{in,f} + N_{dep} + N_{fix} \tag{2}$$

where $N_{in,am}$ is input of N in manure, $N_{in,g}$ input of N due to deposition of dung and urine by grazing animals, $N_{in,f}$ amount of applied fertiliser, N_{dep} nitrogen deposition, and N_{fix} biological N_2 fixation. All these components are input to the model, i.e. not calculated but given values prior to the calculations. The output components are calculated from the input values. The equations used are, with the exception of that for N uptake and immobilisation, all of a simple first order nature. The parameters were derived from literature data, results from more detailed model calculations, and from expert judgement.

The model was parameterised for various land use forms (grassland, maize and arable land) and soil types (sand, loess, clay and peat) and drainage classes (well drained, moderately drained and poorly drained). INITIATOR can also
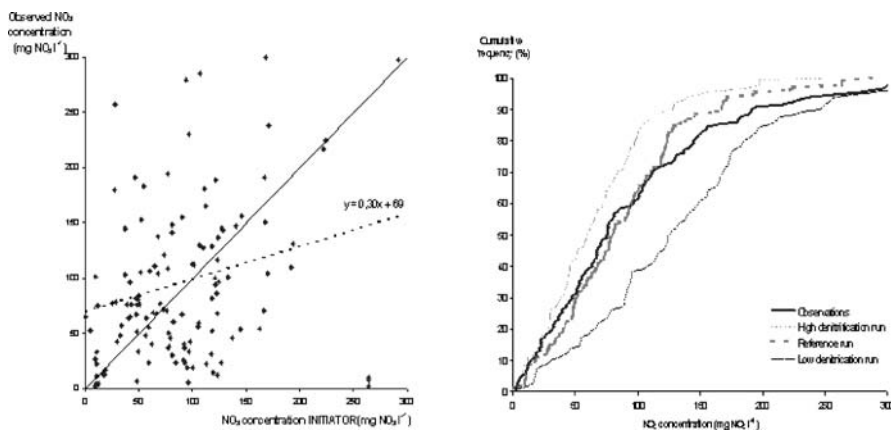
Fig. 13.5 Comparison between observed nitrate concentration (mg NO3 l^{-1}) and concentrations calculated with INITIATOR for 130 sampling locations on sandy soils throughout the Netherlands, using a X–Y plot *(left)* and a cumulative distribution function (CDF) *(right)*. The CDF also shows the results for a run with either low or high denitrification rate constants

make calculations for non-agricultural soils where the input of manure and fertiliser is zero.

13.5.2.2
Validation and Application

Validation: The INITIATOR model was validated on measured nitrate concentrations in ground water from a Dutch manure monitoring network (Kros et al. 2005). This monitoring network consists of 250 farms distributed across the whole of the Netherlands. For the validation, farm-averaged observations during the period April 1998 to February 2001 were used. At each monitoring point, the available farm-specific input data, such as soil type, crop type, manure and fertiliser use, were included. When compared to observations from the national monitoring network, the NO$_3$ concentrations calculated by INITIATOR were lower for all soil types. The deviation found was greatest for clay soils (about 65% lower than observations) and smallest for sandy soils (about 10%). Most likely, this was due to an over-estimation of the reference denitrification rate used in the model, since the NO$_3$ concentration is very sensitive to the denitrification rate parameter, which is difficult to estimate correctly (Kros et al. 2005).

Application: INITIATOR was used to estimate the uncertainties in the flows of N within and out of agricultural and non-agricultural soils in the Netherlands (De Vries et al. 2003). For agricultural land, 6,400 plots with unique combinations of land use, soil type and hydrology were distinguished. For non-agricultural land, a grid classification similar to that used in STONE was used.

The uncertainty was quantified by means of a Monte Carlo analysis. The 90% confidence range for the fluxes of N compounds to air, groundwater and surface water from all agricultural land (in Gg N year^{-1}) ranged between 102 and 194 for ammonia emission, between 18 and 51 for N_2O emissions, between 32 and 108 for NO_3 inflow to groundwater, and between 2 and 38 for N inflow to surface water. The calculated average N fluxes are comparable to those presented in Kroeze et al. (2003), who summarised literature data for the year 1995. The INITIATOR model has also been applied to calculate maximum N application rates and to assess the effects of various changes in agricultural structure and farming practices on N fluxes in the Netherlands (De Vries et al. 2001a, 2001b). Recently, the model was extended to include phosphate and heavy metal behaviour in soils (De Vries et al. 2005).

13.5.3
The Johnes Model

13.5.3.1
Description

The Johnes model uses an export coefficient approach and was developed to predict the loss of N and P from a complex catchment to its drainage system. The total nutrient load transported by a water body at any point along its length is predicted as the sum of the loss or 'export' of N and P from each nutrient source within the catchment. The loss of a nutrient is the sum of the export coefficients for the relevant nutrient sources, e.g. sewage systems, arable land, grassland, cattle, poultry, etc. The model requires information about: (1) the area and spatial location of each land use type on a field-by-field basis, the application rates of fertiliser to each, and the number of each livestock type on each farm; and (2) the rates of input of N and P to the catchment from atmospheric sources, the number of people in the catchment and the type and degree of sewage treatment before discharge to the aquatic environment. In order to calibrate and validate the model data, the actual nutrient loads in the catchment should be known.

13.5.3.2
Validation

The model has been applied to two catchments in the United Kingdom (Windrush and Slapton), with areas of 363 km² and 46 km², respectively. A sensitivity analysis was carried out to find which exports most strongly determine the loads. Part of the data collected was then used to calibrate the corresponding export coefficients. Using these adapted coefficients, the model was validated with data not

used for calibration. In the case of Windrush, the predicted N and P loading of the catchment slightly overestimated the observed loading, with a mean error of 7.4% and 4.3%, respectively (see also Fig. 13.6). For Slapton, the corresponding figures were 7.5% and 3.3% (underestimation), respectively. The small deviation from the actual data implies that the model could be used to investigate the consequences of different catchment management strategies for nutrient loadings.
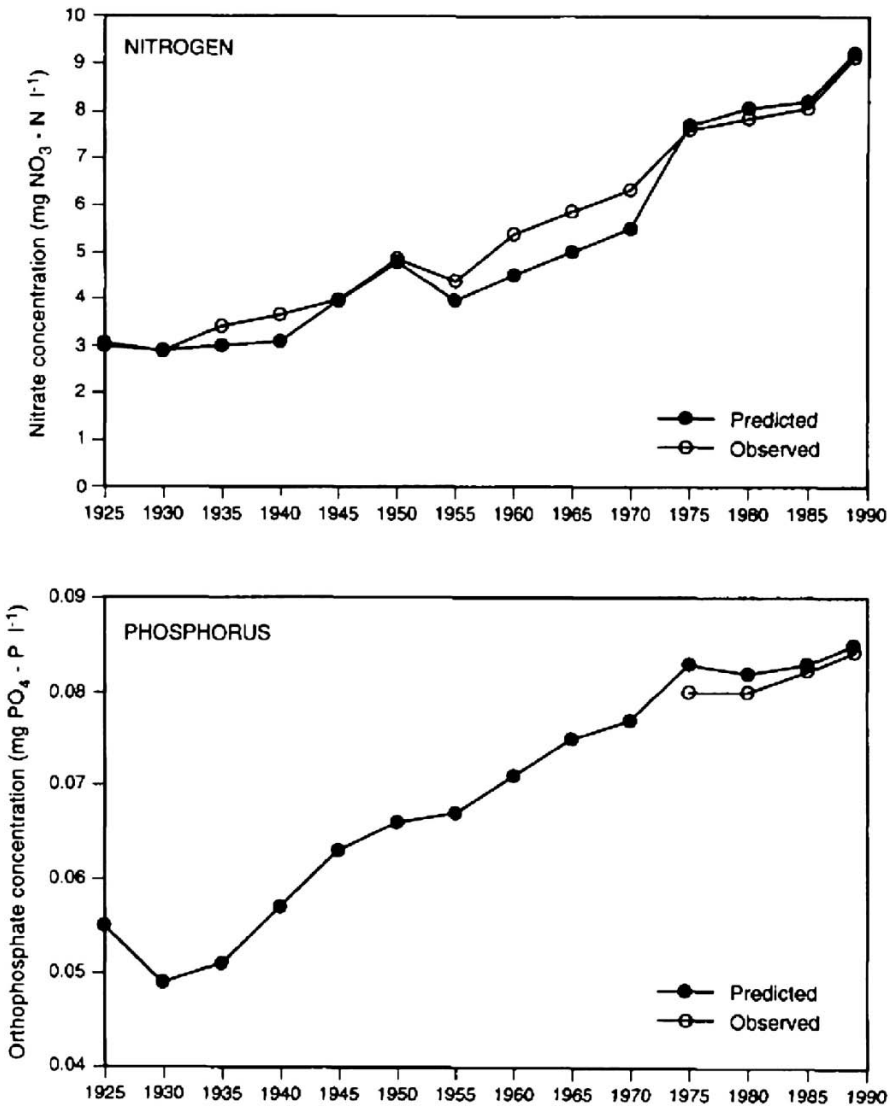
Fig. 13.6 Observed and Johnes-model-simulated N and P concentrations in the river Windrush in the period 1925–1989 (from Johnes 1996)

13.5.4
Comparison of Models

In contrast to plot-scale models, a comparison of models at regional scale has apparently not yet been conducted. However, in the European Union project Euroharp, nine models for the regional scale were selected and tested with data from three catchment areas (in Norway, England and Italy). The results are due to be published towards the end of 2006.

The results of the evaluation by STONE of different scenarios offer the possibility to compare the predictions of STONE with those of INITIATOR using the same input (by fertilisation, deposition and manure application). Kros et al. (2005) thus compared nitrate concentrations in ground water in the Netherlands as calculated with INITIATOR with results calculated with STONE. Both models were run with the same N input. The results show that concentrations calculated with INITIATOR are quite comparable with those from STONE (Fig. 13.7). STONE and INITIATOR were also compared with respect to annual leaching and denitrification and N uptake by the crop as a function of N input for maize on well-drained and moderately well-drained sandy soil. Figures 13.8 and 13.9 show the results for annual N leaching and denitrification, respectively. The relationships between input and denitrification and input and leaching as calculated by INITIATOR are linear, as is to be expected. However, it is striking that the relationships calculated by STONE are also linear. This suggests that
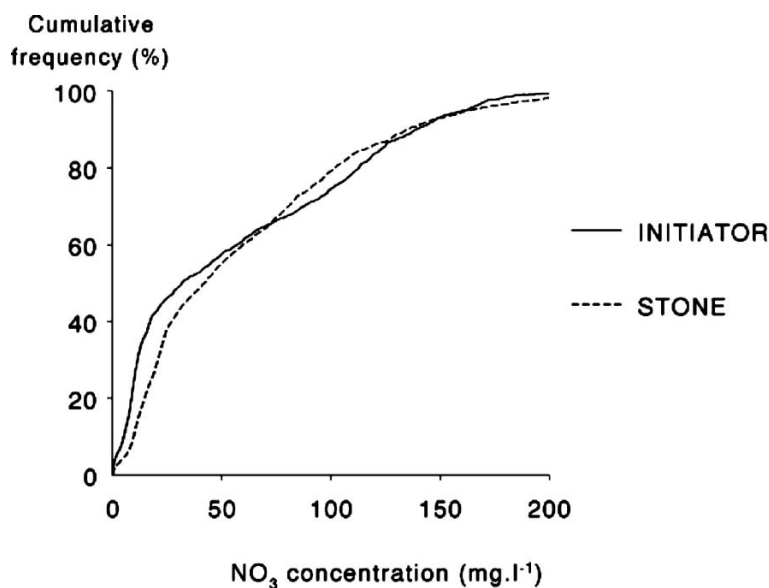
Fig. 13.7 Cumulative distribution functions of the NO_3 concentration (mg NO_3 l^{-1}) for more than 6,000 plots in the Netherlands for the year 2000 as calculated with STONE and INITIATOR
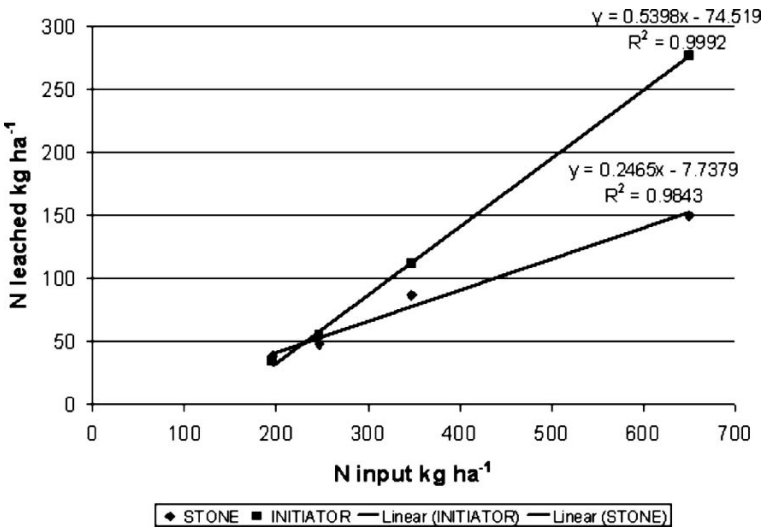
Fig. 13.8 Nitrogen leached as a function of nitrogen input (as the sum of fertilisation, manure application and deposition) for maize on a dry sandy soil, calculated with STONE and with INITIATOR
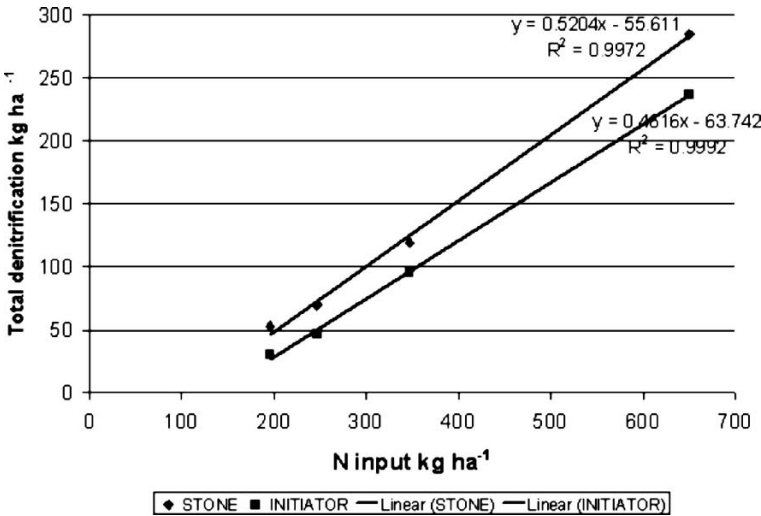
Fig. 13.9 Denitrification as a function of nitrogen input (as the sum of fertilisation, manure application and deposition) for maize on a dry sandy soil, calculated with STONE and with INITIATOR

it is possible to simplify STONE along the lines of INITIATOR. A model like INITIATOR is, thanks to its simplicity, considerably more transparent and easy to use than a complex model like STONE. On the other hand, the nature of the formulations used in INITIATOR make extrapolation to situations beyond those used for derivation of the equations difficult.

13.6
Conclusions

13.6.1
Future Developments in Modelling

We believe that, as a research tool, further development of the most promising quantitative process-based mechanistic plot-scale models with a high degree of process knowledge, spatial (horizontal and vertical) and temporal resolution is still useful. However, this should be done in combination with testing (calibrating/validating) the models on detailed data of nutrient fluxes with high time-resolution that are gathered at sites, most preferably with and without experimental manipulation. In this context calibration (where necessary) implies minimising the difference between observations and model results by adapting poorly defined model parameters, whereas validation includes the comparison of model results with other independent, high-resolution data sets. The validation status of promising models should be increased to make them useful for general purpose applications. Furthermore, more research is needed with respect to upscaling of models from plot scale to regional (up to continental) scale. Finally, we propose that more integrated models, comprising not only the dynamics of C, N and P, but also those of heavy metals and major agricultural greenhouse gases (e.g. nitrous oxide and methane) should be developed. Each of these aspects is discussed in more detail below.

13.6.2
Validation

Models are useful tools with which to quantify nutrient flows and losses in response to different scenarios and, as such, valuable for policy analyses and management guidance. One of the key questions as to the use of models is: Which model is best suited to do the job? This, obviously, depends on the job itself and the targets the user has set. However, even for a given situation, it would be difficult to find objective criteria to justify the choice of a model. A prerequisite

would be that the model to be used is well validated. But, when can a model be considered to be well validated? Is validation possible at all (see discussion by Oreskes et al. 1994)? Rijkiel (1996) argues that models can indeed be validated sufficiently for pragmatic purposes, and we share his view. We strongly agree with Diekkrüger et al. (1995), who stated that "…considering the amount of published models it seems that it is much easier to develop a new model than verifying or validating existing computer codes. This is mainly due to the fact that laboratory and field measurements necessary for model verification are expensive and that it is easier to obtain money for model development than for experiments".

A continuous flow of new models is no longer justified. Instead, more emphasis should be placed on verification/validation and model comparison to identify the most promising models. The remark by Diekkrüger et al. (1995) in their comparison of 19 models that "…DAISY was the only model to simulate all main processes … with the same quality" is an example of such identification. As stated before, the validation status of promising models, such as those presented in this overview, should be increased to make them useful for general purpose applications.

13.6.3
Up-Scaling

Models developed for the plot scale can be applied at regional and even continental scale by running the model for various combinations of land use, soil type, hydrological conditions etc. and then aggregating the results as is done for example with the ANIMO model in the Netherlands. The problem, however, is that the large amount of data required in detailed models is simply not available, thus generic data have to be used, potentially reducing the precision of those models at larger scales. Their validation status at the plot scale does not imply that they are suitable for larger scales, and may give a false appearance of accuracy.

One approach for upscaling is model simplification in order to match data demands and data availability (e.g. Van der Salm et al. 1995). This can be done either by simplification of plot-scale models or by use of empirical relationships based on available datasets or on results of detailed plot-scale models. To assess the possible loss of model adequacy, the performance of regional-scale models and site-scale models can be compared at the regional scale (regions/countries with a high amount of inventory data). The errors inflicted by poor input data while using detailed data-demanding models and more simplified models can be further investigated by comparing model outputs from both types of model obtained in data-poor and data-rich situations (e.g. model the same study area using national data and then the more general European data).

13.6.4
Integrated Models

In reality, every process influences every other process to a certain degree. In building a model, one has to decide which processes can be neglected and which processes are essential for the purpose of the model. When considering a period of a year or more, it is essential to couple the N and P cycle to the C cycle and crop growth. Hence, an appropriate description of the C cycle is a prerequisite for a model of N and P cycling. As the supply of mineral N strongly determines the growth of the crop and therefore its demand for P, a field-scale model meant to be used over a rather long period should ideally consider the C, N and P cycles simultaneously.

In many countries, measures to control problems related to animal manure inputs are directed more and more towards integrating different environmental impacts, including ammonia emission, emission of greenhouse gases [mainly nitrous oxide (N_2O) and methane (CH_4)], nitrate leaching to ground water and runoff of N, phosphate and heavy metals to surface water. Insight into all these environmental impacts requires an integrated model, such as INITIATOR2 (De Vries et al. 2005). In this model, the interactions between e.g. heavy metal concentration and the mineralisation of C, N, and phosphate as well as the interaction between denitrification and N_2O emission are included.

The aim of integrated models is to obtain information on the effectiveness of policies aimed at the simultaneous reduction of all relevant element fluxes (nutrients and contaminants) to atmosphere, ground water and surface water. As such, we believe that further development of integrated models is of great importance for policy and management.

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