

Chapter 7

Nutrient Leaching

J. LEHMANN¹ AND G. SCHROTH²

¹College of Agriculture and Life Sciences, Department of Crop and Soil Sciences, Cornell University, 909 Bradfield Hall, Ithaca, NY 14853, USA; ²Biological Dynamics of Forest Fragments Project, National Institute for Research in the Amazon (INPA), CP 478, 69011-970 Manaus, AM, Brazil

7.1 Synopsis

Nutrient leaching is the downward movement of dissolved nutrients in the soil profile with percolating water. Nutrients that are leached below the rooting zone of the vegetation are at least temporarily lost from the system, although they may be recycled if roots grow deeper. Leached nutrients may contribute to groundwater contamination in regions with intensive agriculture. Nitrate leaching is also a significant source of soil acidification. In humid climates, some nutrient leaching occurs even under natural vegetation, but agricultural activities can greatly increase leaching losses (Havlin *et al.*, 1999).

Soil and climatic factors that influence nutrient leaching

In general, water transport below the rooting zone requires that the soil water content exceeds field capacity and the water balance is positive, which means that water inputs with rainfall (and irrigation) exceed evapotranspiration. Therefore, nutrient losses through leaching are generally higher in humid than in dry climates (Havlin *et al.*, 1999). In certain soils, however, water can infiltrate into the subsoil through continuous vertical macropores when the bulk soil is dry. This is especially important in cracking clay soils (Vertisols) at the onset of the rainy season (Smaling and Bouma, 1992). Macropores are also created by faunal activity and root growth. They only conduct water under conditions of heavy

rainfall or irrigation, under other conditions they are filled with air. Macropore or bypass flow may increase nutrient leaching following the surface application of fertilizers, because a solution with high nutrient concentration then infiltrates rapidly into the soil with little contact with the soil matrix. On the other hand, macropore flow may also protect nutrients present in smaller soil pores from being leached by rapidly channelling away surplus water (Cameron and Haynes, 1986; van Noordwijk *et al.*, 1991b).

Soils with high water infiltration rates and low nutrient retention capacity, such as sandy soils and well-structured ferrallitic soils with low-activity clays and low organic matter contents, are particularly conducive to nutrient leaching (von Uexküll, 1986). Some nutrients are easily leached from organic soils (see below). Subsoil acidity also tends to increase nutrient leaching by restricting the rooting depth of sensitive plants (see Section 5.6).

In the subsoil of many tropical soils the mobility of nitrate and other anions decreases because of increasingly positive net charge and, therefore, anion retention by soil minerals, and this increases the probability that these ions are eventually taken up by deep-rooting plants (see Box 8.1 on p. 171). It is, therefore, important to distinguish between nutrient leaching within the soil profile, from the topsoil into the subsoil, leading to temporary nutrient loss, and leaching beyond the rooting zone of deep-rooting plants, into the groundwater, leading to permanent nutrient loss.

Susceptibility of different nutrients to leaching

The leaching risk for a nutrient increases with its mobility in the soil. Among nutrient anions, nitrate is particularly easily leached because it shows negligible interaction with the negatively charged matrix of most topsoils and is, therefore, very mobile in the soil (see Section 5.2). Nitrification rates are variable in tropical soils, but can be sufficiently high to make nitrate the dominating form of mineral nitrogen even in acid soils (Robertson, 1989; Schroth *et al.*, 1999a). As a consequence, leaching may contribute significantly to negative nitrogen balances of agricultural systems (Smaling *et al.*, 1993). In seasonal climates, nitrate is also particularly exposed to leaching because a mineralization flush of organic nitrogen that causes release of large quantities of nitrate in the topsoil often occurs when dry soil is rewetted at the onset of the rainy season, at a time when crops have not yet been sown or are still small (Birch, 1960).

A mineralization flush at rewetting of dry soil has also been reported for sulphur (Havlin *et al.*, 1999). Sulphate is also readily leached from surface soils, the losses being highest in soils dominated by monovalent cations (potassium, sodium) and lowest in soils with high amounts of

aluminium (Havlin *et al.*, 1999) (see Section 5.4). Dissolved organic sulphur contributed between 18 and 86% of total dissolved sulphur at 2 m depth in an agroforestry system in central Amazonia (J. Lehmann, unpublished data).

In contrast to nitrate and sulphate, phosphate is immobile in most soils because of precipitation and adsorption to mineral surfaces, and leaching is therefore negligible, except in certain very sandy and organic soils (Wild, 1988) (see Section 5.3). Dissolved organic phosphorus forms are more mobile in soil than phosphate (Havlin *et al.*, 1999). Phosphorus may also be lost if surface soil particles are eroded in runoff (see Section 17.1).

The percolating soil solution that carries nutrients down the soil profile is necessarily electrically neutral; therefore, anions are leached together with equivalent amounts of cations. In most soils, the cations most likely to be leached are calcium and magnesium. In West African savanna soils, close relationships between the combined concentration of Ca and Mg and that of nitrate in the soil solution below the crop rooting zone have been reported, pointing to the role of fluxes of nitrate, and to a lesser extent chloride, as factors controlling calcium and magnesium leaching in these soils (Pieri, 1989). In sandy soils, considerable amounts of magnesium can be leached after applications of potassium chloride or potassium sulphate fertilizers (Havlin *et al.*, 1999). Potassium is usually leached in much smaller quantities than calcium and magnesium even when applied as fertilizer and was not related to nitrate fluxes in the aforementioned studies in West Africa (Pieri, 1989). However, significant potassium leaching may occur in sandy and organic soils and in high-rainfall areas (Malavolta, 1985; Havlin *et al.*, 1999). Among the micronutrients, manganese and boron are susceptible to leaching in certain soils (Havlin *et al.*, 1999).

Management practices that reduce nutrient leaching

A number of agricultural practices reduce nutrient losses through leaching by increasing the synchrony and synlocation of nutrient uptake by the vegetation with nutrient supply from soil, mineral fertilizers and organic materials (see Section 6.1). These include:

- early sowing of crops at the onset of the rainy season in savanna climates to make use of the mineralization flush of nitrogen upon rewetting of the soil (Myers *et al.*, 1994);
- rapid installation of a vegetation cover after forest or fallow clearing to avoid nutrient losses from bare soil (Webster and Wilson, 1980; von Uexküll, 1986);
- applying fertilizers (especially nitrogen) in several small applications during the cropping season rather than all at once; and

- placing fertilizer at the zone of maximum root activity of tree crops (IAEA, 1975; Havlin *et al.*, 1999).

Leaching of nutrients from organic sources

Of particular relevance for agroforestry is the efficient management of nutrients in organic materials, including biomass and manure, for increased crop uptake and reduced leaching losses (see also Chapter 6). Nutrient release from organic sources is generally more difficult to predict than from mineral fertilizers and so developing practices to counteract leaching is particularly important. Nutrients are often released from organic sources at a time when there is little crop uptake and consequently more opportunity for leaching. Although leaching losses of nutrients from organic sources comparable to or even higher than from mineral sources have been reported (Havlin *et al.*, 1999), other results show lower leaching of nutrients from biomass than from mineral fertilizer. Snoeck (1995) applied ^{15}N -enriched urea or biomass from either *Leucaena leucocephala* or *Desmodium intortum* that was also enriched with ^{15}N to coffee plants on an Oxisol in Burundi and measured the distribution of the nitrogen in undecomposed biomass, coffee plants and soil after 1 year. Almost half of the urea nitrogen was lost from the system, presumably by leaching below 30 cm soil depth, but most of the nitrogen released from biomass was retained in the topsoil (Fig. 7.1). Lehmann *et al.* (1999c) found that sorghum (*Sorghum bicolor*) took up more nitrogen from labelled ammonium sulphate than from *Acacia saligna* leaves in a runoff agroforestry system in northern Kenya. Much of the fertilizer nitrogen that was not taken up by the crop was lost from the system by leaching or volatilization, whereas 99% of the biomass nitrogen was recovered in soil and crop at the end of the cropping season. This highlights the important point that labile nutrients are both more vulnerable to leaching and more readily taken up by crops, so in some circumstances farmers may tolerate higher leaching losses from mineral fertilizers because the short-term nutrient uptake by crops and crop yields may also be greater than from organic nutrient sources. Mechanisms responsible for lower leaching losses from biomass than from mineral sources include:

- slower nutrient release, which is especially important when relatively large quantities of nutrients are applied at a time, as in the latter study, and
- stimulation of microbial growth in the soil by organic nutrient sources, leading to temporary immobilization of nutrients in the microbial biomass.

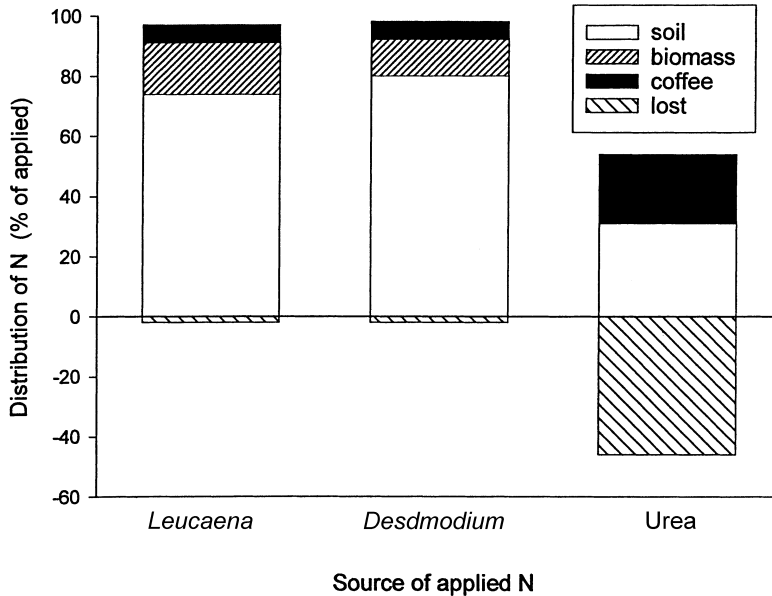


Fig. 7.1. Distribution of ^{15}N -labelled nitrogen 1 year after application to coffee (*Coffea arabica*) plants as urea or biomass of *Leucaena leucocephala* or *Desmodium intortum* on an Oxisol in Burundi. Total quantities applied were 9.2 g per plant of urea-N vs. 34.4 g per plant of *Leucaena*-N (1225 g biomass with 2.81% N) and 20.5 g per plant of *Desmodium*-N (682 g biomass with 3.01% N). Note that absolute quantities of nitrogen taken up from urea and *Leucaena* biomass were similar (2.1 g per plant); differences in percentage uptake resulted from different quantities applied. Nitrogen uptake from *Desmodium* biomass was 1.2 g per plant (after Snoeck, 1995).

Effect of trees on nutrient leaching

One of the central hypotheses of agroforestry is that the continuous or intermittent presence of trees in land-use systems can increase the efficiency with which nutrients are retained in the soil-plant system and transformed into biomass and harvested products instead of being lost by leaching (Young, 1997). This hypothesis has been confirmed in a limited number of studies. Seyfried and Rao (1991) measured lower nutrient concentrations in the soil solution and calculated lower nutrient leaching in a multistrata agroforestry system with cocoa, banana and *Cordia alliodora* than in a maize monocrop in Costa Rica. Horst (1995) reported lower nitrate concentrations in the soil solution and consequently less leaching under hedgerow intercropping with *Leucaena leucocephala* and annual food crops than in the agricultural control treatments in southern Benin.

Lehmann *et al.* (1999a) measured lower nutrient leaching under an *Acacia saligna*–sorghum intercrop than under pure sorghum with runoff irrigation in northern Kenya.

Several mechanisms may contribute to reduced nutrient leaching under agroforestry compared with agricultural monocrops. Through increased litter, mulch and root production, agroforestry practices may contribute to increased soil organic matter levels and therefore increased cation exchange capacity and nutrient retention (see Chapter 4). Also, trees may create macropores with their roots or through the stimulation of macrofaunal activity (see Chapter 16), and this may help to channel surplus water through the soil with limited contact with nutrients in the soil matrix (bypass flow, see above and Chapters 10 and 11). These tree effects are desirable in both fallow rotations and simultaneous agroforestry systems. Furthermore, water uptake by trees may reduce water infiltration and, therefore, nutrient leaching. Lower soil water contents in agroforestry plots than in agricultural controls have often been reported (Malik and Sharma, 1990; Rao *et al.*, 1998). Trees may also reduce nutrient concentrations in the percolating soil solution through nutrient uptake (Horst, 1995). Reduction of nutrient leaching by trees through uptake of water or nutrients is only desirable in fallow systems and in tree–crop associations during periods when no crops are present, such as before sowing and after the harvest of annual crops. When both trees and crops are present in a field at the same time, water and nutrient uptake by trees may reduce nutrient leaching, but may also cause yield depressions of the crops through competition. These conflicting effects of trees in simultaneous agroforestry systems are apparently one reason why agroforestry associations such as hedgerow intercropping have often been successful in maintaining soil fertility at higher levels than agricultural controls, but have not improved crop yield (Rao *et al.*, 1998) (see also Chapter 5).

The safety-net hypothesis proposes that it is possible to achieve reduced nutrient leaching without increased root competition between trees and crops (van Noordwijk *et al.*, 1996). The hypothetical safety net for leached nutrients is formed by trees that possess few superficial roots, but whose deep roots spread laterally below the rooting zone of associated, shallow-rooting crops. Here, in the subsoil, they intercept nutrients and water, thereby reducing nutrient leaching without being associated with too much competition with the crops in the topsoil. The safety-net concept is an idealization that guides the search for tree species that exhibit a high degree of niche differentiation with crops in that they have relatively uncompetitive root systems in surface soil, but are sufficiently deep-rooting to acquire relevant amounts of subsoil resources. Utilization of subsoil nitrogen by a deep-rooting, uncompetitive tree species, *Peltophorum dasyrrhachis*, in association with groundnut on an Ultisol in Sumatra has

been demonstrated, where the tree obtained more than 40% of its nitrogen from below the crop rooting zone (Rowe *et al.*, 1999). Further support for the hypothesis comes from the observation of stratified root systems of associated plant species in different natural and artificial ecosystems, which develop either because the vertical root distribution of associated species responds differently to soil and climatic factors, or because the root system of one species avoids competition from the other species through increased growth in the subsoil (Schroth, 1999). However, a clear experimental demonstration of a safety-net effect in terms of lower nutrient leaching in agroforestry than in agricultural systems that is not offset by competition for water and nutrients in the topsoil is still lacking.

Another way in which agroforestry (or intercropping) techniques can reduce nutrient leaching is by optimizing the spatial patterns of nutrient use in tree crop plantations. If tree crops are planted at final spacing, they often take several years to fully occupy the soil with their root systems, and during this time nutrients released from the soil, a cover crop or decomposing residues from the previous vegetation may be leached in the spaces between the tree crop plants unless these are occupied by suitable intercrops, shade trees or spontaneous vegetation. Nitrate leaching in the spaces between 5-year-old widely spaced tree crops (peach palm – *Bactris gasipaes*, cupuaçu – *Theobroma grandiflorum*, Brazil nut – *Bertholletia excelsa* and annatto – *Bixa orellana*) has been reported from an Amazonian Oxisol, indicating the presence of surplus nutrients and water that could be used for additional crop production (Schroth *et al.*, 1999a). On a similar soil, the nitrate distribution in the soil under a 15-year-old oil palm plantation indicated that interplanting with shade-tolerant crops may still have been viable at this age (see Fig. 8.1 on p. 170). Similarly, in mature plantations of coconut (*Cocos nucifera*) significant quantities of light, water and nutrients may not be captured by the tree crops and so can be utilized by intercrops without reducing tree crop yield (Mialet-Serra *et al.*, 2001). The potential of tree crop-based agroforestry systems to reduce nutrient leaching has been discussed in more detail by Schroth *et al.* (2001b).

In contrast to simultaneous tree–crop associations, fallow systems rely on the rapid development of deep roots of the fallow trees to intercept nutrients in the subsoil which were leached during the previous cropping phase (see Chapter 8). Modelling results suggest that, under high-leaching conditions and for very mobile nutrients such as nitrate, fallows may not be effective in recycling leached nutrients; instead, the permanent presence of tree roots as in simultaneous systems would be necessary to intercept these nutrients before they are leached too deep into the subsoil (van Noordwijk, 1989). As discussed in Box 8.1 on p. 171, anion retention in the subsoil of many tropical soils increases the potential for intermittent fallows with deep-rooting trees to recycle leached nitrate, suggesting that leaching losses could be reduced at a lower competition cost than with

permanent tree–crop associations. Experimental comparisons of simultaneous and sequential agroforestry systems under different pedoclimatic conditions with respect to nutrient cycling and overall productivity would be required to confirm this.

7.2 Methods for Soil Solution Composition

The soil solution comprises the soil water and the inorganic and organic substances that it contains. Nutrient leaching can be determined from the quantity and composition of the soil solution that percolates to depths greater than the rooting depth of the plant species present. Depending on the respective research question, the collection of soil solution may be necessary either below the rooting zone of an annual crop, which could be anything from a few decimetres to a few metres deep, or below the rooting zone of a tree, which may be many metres deep. For technical reasons, solution sampling below the deepest roots of agroforestry trees is often not feasible. However, measurements of the soil solution composition and nutrient leaching at different depths under crops and trees may still provide valuable information on the ability of the plant species to capture nutrients from the percolating solution in the subsoil.

There are three approaches to the measurement of nutrient leaching through the collection and analysis of soil solution (Fig. 7.2).

- Solution samples are collected and leaching is estimated from the concentration of dissolved nutrients and the movement of the solution in the soil, which is measured separately. Suction cups are the most common tools for soil solution sampling. A more recent development, the tensionic sampler, allows soil solution measurements without application of suction due to diffusion of solutes through a porous cup

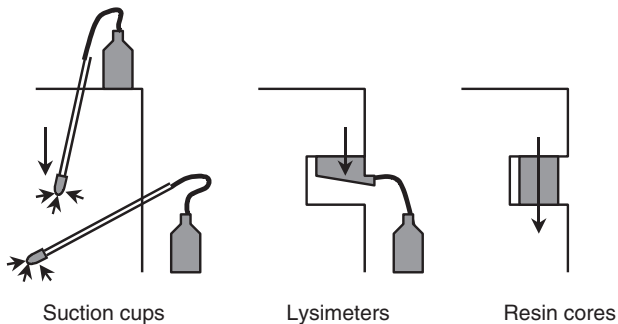


Fig. 7.2. Schematic depiction of the installation of suction cups, lysimeters and resin cores. The arrows indicate the direction of solution movement through the soil and into the collectors.

into the sampling device. As no suction is applied, the same device can be used for tensiometer readings (Moutonnet *et al.*, 1993). Alternative methods include the extraction of solution from field-moist soil by centrifugation or displacement with different immiscible liquids, but these techniques require destructive soil sampling for every solution measurement and are thus not suitable for determining cumulative nutrient losses during longer time intervals. Examples from agroforestry experimentation using suction cups and a water balance for leaching measurements include Seyfried and Rao (1991), Kühne (1993) and Lehmann *et al.* (1999a).

- The percolating solution is collected in lysimeters with a defined collection area, so that the downward flux of the solution can be determined from the collected sample volume, which is also used for nutrient analysis. A principal difference exists between tension lysimeters (including suction plates) and free-draining lysimeters. An agroforestry application of the latter technique is described by Santana and Cabala-Rosand (1982).
- The percolating solution passes through a sampler with a defined area, in which nutrients are retained on an ion-exchange resin; in this method the percolating water volume does not need to be measured. This inexpensive and simple technique is still under development. Agroforestry applications include Hagedorn *et al.* (1997) and Lehmann *et al.* (1999b).

Suction cups

Suction cups are fine-porous filters that are closed at one end and mounted on a rigid or flexible tube at the other end. The dimensions of the cups vary in general between 3 and 60 cm in length and between 0.5 and 10 cm in diameter. The soil solution is sucked through the cups and into a collection bottle by applying a vacuum, either temporarily or continuously. The vacuum applied to suction cups has to be adjusted in order to sample only the most mobile water, although it needs to be strong enough to gather enough soil solution for analysis. This can be a problem in very clayey soils. Battery-powered pumps can continuously keep the vacuum at the desired level. Where the soil water content shows pronounced fluctuations during the sampling, periodic adjustments of the applied vacuum may be necessary. Self-regulating devices are now available, which measure the soil water suction and automatically adjust the applied vacuum.

Suction cups are well suited for studies of short-term fluctuations and small-scale variability of soil solution chemistry, because the solution can be collected at short time intervals, and even the installation of a large

number of cups at depths of several metres causes little disturbance in a plot. Shortcomings of suction cups are that the mobile soil solution is not adequately sampled in most cases and that the collected solution cannot be related to a defined soil volume or infiltration area (Grossmann and Udluft, 1991). Preferential water flow through macropores may constitute the majority of the percolating solution, but its infiltration is often too rapid to be sampled with suction cups. Failure to sample the initial mobile soil water after rewetting may result in large errors in estimates of leaching, as this water may be enriched with nutrients (Lord and Shepherd, 1993). The suction cup technique may yield reliable data in sandy, unstructured soils (Webster *et al.*, 1993), whereas clayey and well-structured soils may pose considerable difficulties.

Various materials are used for the cups, which differ in their purpose and applicability. Cups made from P80 ceramic material with a pore diameter of about 1 μm are frequently used because of their low price. In these cups, however, significant amounts of phosphate and dissolved organic matter may be retained in the material. If organic compounds are of interest, therefore, the suction cups have to be conditioned for a long time in the soil being studied. More inert materials for phosphorus sampling include Teflon, glass, polytetrafluoroethene (PTFE)/quartz or cellulose acetate fibres (Dorrance *et al.*, 1991; Beier and Hansen, 1992). Pretreatment of the cups with dilute hydrochloric acid, followed by distilled water, before installation is generally necessary (Angle *et al.*, 1991; Beier and Hansen, 1992). This also eliminates problems with aluminium desorption from P80 cups. The glues connecting the cups with shafts may leak organic substances but contamination problems can be avoided by reducing the contact zone of solution and glue or by using glue-free suction cups. The installation should be done well in advance of the intended measurements to allow for chemical equilibration of the cups with the surrounding soil and to let the soil settle after the installation (Lord and Shepherd, 1993; Webster *et al.*, 1993).

To avoid microbial transformations, the collected solution should be frequently removed from the collection bottles and should be either analysed immediately or deep-frozen (Angle *et al.*, 1991). In practice, the solution often remains in the collection bottles in the field (dark bottles are preferred to prevent the growth of algae) or in the suction cups for a few hours or days before it is collected. Chemicals can be added to the bottles to inhibit microbial activity, such as chloroform or various acids. These additions, however, may interfere with the intended measurements of pH, certain colorimetric reactions, and dissolved organic matter. Alternatively, the solution can be collected without preservation and be digested prior to the analysis of elements that could be affected by microbial growth (especially nitrogen and phosphorus). In this case, only total fluxes of these nutrients are determined without specifying the chemical compounds.

Collection of the solution from several samplers in the same bottle or pooling of collected solution prior to analysis are common practices to obtain more representative samples without increasing the number of analyses. However, pooling may increase the risk of losing the whole sample if one cup produces contaminated solution. It is thus advisable to analyse samples from all individual cups at the beginning of a measurement programme.

When installing the cups, care has to be taken to avoid preferential water flow along the shafts by sealing with clay or rubber discs. At shallow depths, the cups are often installed at an angle to the soil surface. At greater depths, they may be installed horizontally from a soil pit. After long-term use, the connectors and tubings of the suction cups may show signs of ageing and not hold the vacuum any more. Termites and ants may destroy plastic tubes, and polyethylene materials are also susceptible to light damage. In soils rich in dispersible clay, the cup pores can become clogged after prolonged use, in which case the cups have to be replaced.

Lysimeters

Lysimeters as defined here are horizontally installed trays that capture percolating soil water. Discussions of the technique can be found in Dorrance *et al.* (1991), Barbee and Brown (1986) and Russell and Ewel (1985). Free-draining lysimeters are open at the top and rely on gravity for collecting the percolating solution (Jordan, 1968). In contrast, tension lysimeters (or suction plates) consist of porous materials similar to those used in suction cups with a sealed bottom, to which a vacuum is applied. This vacuum should ideally resemble the matrix potential of the underlying soil so that the water percolation is not influenced by the sampler. Unlike suction cups, lysimeters can also sample macropore flow.

Free-draining lysimeters have been found to yield more soil solution than suction cups in clayey soils (Barbee and Brown, 1986). However, they will still underestimate percolation because the soil water has to overcome the soil matrix potential to enter the collector, and in finely textured soil with weak soil structure no water at all may be collected. The sampling technique may also influence the solution chemistry. For example, free-draining lysimeters were found to yield solution from a wetting front later and with higher calcium and potassium concentrations than suction cups, which collected a solution with higher nitrogen and magnesium concentrations (Marques *et al.*, 1996). In an unstructured soil, similar results for both methods have been obtained (Webster *et al.*, 1993).

In experiments with annual crops or before tree planting, lysimeters can be installed from the soil surface below the plough layer. For greater installation depths and with an established tree root system, the installation

has to be carried out from the side using a soil pit. Special care has to be taken to ensure a good contact between the lysimeter and the overlying soil (Barbee and Brown, 1986). The same rules as for suction cups apply to selection and pretreatment of the porous material and preservation of the collected solution.

Resin cores

Resin cores are cylinders filled with ion-exchange resin and installed in the soil in a way that allows water percolation (Schnabel, 1983). Nutrients in the percolating solution are adsorbed to the resin and can be extracted after the core has been removed. Similarly to lysimeters, resin cores have a defined surface area, so that a time integral of nutrient leaching per unit area is obtained. Depending on the leaching rate and the construction of the cores, they can be left in the soil for periods as long as 6–12 months. Disadvantages of this technique are that collection of the resin is destructive and that short-term leaching events are not detected due to the integrative nature of the measurement.

The cores usually have a length and diameter of 5–20 cm and can be built from PVC tubing. The water flux through the cores relative to the surrounding soil and hence the validity of the results will strongly depend on the similarity between resin cores and soil with respect to water permeability at different water contents. To increase the similarity of hydraulic properties between cores and soil, the resin should be mixed with acid-washed sand or soil (Hagedorn *et al.*, 1997). Even with such precautions, it may be difficult to determine absolute leaching losses in finely textured soils. The collection efficiency of resin cores can be checked by tracer experiments using chloride.

Commercially available exchange resins used for water purification can be used in the cores since they show low blank values and high recovery rates for nitrate, ammonium, phosphate and basic cations. However, the resin properties should be checked in preliminary adsorption experiments. Dissolved organic matter and organic nutrients are often difficult to determine with this method, because inexpensive resins may bleed organic compounds and the necessary quantities of analytical resins may not be affordable (Lehmann *et al.*, 2001d).

At the end of the measurement period, the resin cores are recovered and the resin is extracted with KCl or CaCl₂ solution, depending on the nutrients to be analysed. The cores are cut and different resin layers extracted separately to make sure that the nutrient load of the percolated solution did not exceed the exchange capacity of the resin. The lowest layer may contain a large portion of nutrients derived from capillary rise and should be excluded from the calculation of nutrient leaching.

Resin cores should not be confused with resin bags, which are placed in the soil to obtain a time-integral of the availability of certain nutrients without an intention to measure nutrient leaching (Binkley, 1984).

7.3 Tracer Methods for Nutrient Leaching

Several different approaches exist for employing tracers to measure nutrient leaching. Their suitability depends on experimental objectives. First, it depends on the source of the nutrients whose leaching is being assessed. These may be derived from precipitation, nutrient mineralization in the topsoil, mineral fertilizer or organic materials such as prunings or manure. The source of the nutrient will determine the chemical form in which the tracer is best applied, for example, as a component of a mulch material or as a mineral fertilizer. Secondly, the choice of method will be influenced by the question as to which of the various processes that determine nutrient leaching need to be considered in the experiment. For example, different methods would be applicable if there were only interest in water percolation as influenced by the availability of water and the infiltration rate of the soil than if it were also necessary to understand nutrient uptake by plants.

There are two different approaches to the measurement of nutrient leaching with tracers:

- measuring the content of the tracer in the soil to a certain depth, comparing the recovered quantity with the amount that was applied (or measured in the same soil volume at an earlier date) and considering the difference as leached (for nitrate profiles see Box 8.1 on p. 171); and
- measuring the amount of tracer that passes through a certain soil depth (such as the maximum rooting depth of a crop) with the techniques described in Section 7.2.

A large number of different tracers exist, which can be classified as either:

- radioactive isotopes (e.g. ^{32}P , ^{33}P , ^{35}S);
- stable isotopes (e.g. ^{15}N , ^{34}S); or
- other tracers (e.g. strontium, lithium, rubidium, bromide or chloride).

Radioisotopes and stable isotopes allow use of the same nutrient for which the leaching is to be determined without significantly changing its concentration in the soil. Non-isotopic tracers can simulate the behaviour of certain chemically related nutrients in soil, for example, chloride and bromide can be used for nitrate, strontium for calcium, and rubidium and lithium for potassium (see also Section 8.2). However, higher amounts of

the tracers may have to be used to be detectable because of the low sensitivity of the analyses or sometimes the high amount of the substance already present in the environment. If nutrient leaching from organic sources or the effect of nutrient uptake by plants on nutrient leaching is to be studied, only radioactive or stable isotopes of nutrient elements can be used, because only these possess similar properties during decomposition and microbial transformation to the nutrient of interest. However, radioisotopes will in many cases be considered too dangerous for a field assessment of nutrient leaching, leaving stable isotopes as the only option.

Tracers can be applied to the soil in mineral form or in organic materials such as mulch, litter, compost or manure. In the latter case, the substrate has to be labelled beforehand. This can be done by supplying the tracer to a plant whose litter or biomass is to be used in the experiment and collecting the respective materials after some weeks. The application method depends on the objectives. Labelled fertilizer will usually be applied in the same manner as unlabelled fertilizer. If the emphasis of the study is on the assessment of the nutrient transport in the soil rather than the release from a certain nutrient source, the tracer is best applied in solution, which can be applied more evenly than solid materials such as fertilizer. A simple hand-sprayer or electric pump can be used to spray a known amount of the dissolved tracer on a defined area. The amount to be applied will depend on the amount already present in the soil and the duration of the experiment. For example, ^{15}N can be applied at a dose of 1 g m^{-2} to be detectable even after several months in cropping systems with trees.

If the purpose of the study is to examine nutrient leaching after fertilization, large amounts of nutrients are usually applied to the soil. This may cause pool substitution of the tracer with native soil nutrients, as reviewed for nitrogen isotopes by Jenkinson *et al.* (1985). As a result, more unlabelled soil nitrogen may be leached with fertilization using a labelled nitrogen source than without, and total nitrogen leaching as affected by fertilization may, therefore, be underestimated. Only by measuring total nutrient losses together with tracer losses can the extent of the added nitrogen effect be determined and conclusions drawn about the leaching of applied and native soil nitrogen.

Non-isotopic tracers are useful as long as nutrient uptake by plants does not need to be considered. For example, nutrient leaching at the onset of the rains before crop planting has been studied with bromide as a tracer in an East African Vertisol (Sticksel *et al.*, 1996). Walker *et al.* (1991) used the chloride content of wet deposition for measuring groundwater recharge as affected by land-use change in semiarid Australia. Also, hydrogen isotopes can be used to monitor water movements in soil (Münnich, 1983). However, in the presence of vegetation, these tracers

would only reflect the effect of plant water uptake on leaching, but not the effect of actual nutrient uptake by plants from the percolating soil solution. Such data can be combined with measurements of nutrient concentrations in the soil solution (see Section 7.2) to determine nutrient leaching.

The tracers can be retrieved for the analysis by collecting the soil solution (see Section 7.2), extracting the soil with a salt solution or a dilute acid (see section for the respective element in Chapter 5) or, in the case of nitrogen, be analysed directly by dry combustion of the soil (Barrie *et al.*, 1995).

Nitrogen occurs in the soil solution mainly as nitrate, ammonium and dissolved organic nitrogen (see Section 5.2). These nitrogen forms differ in their behaviour with respect to:

- the soil matrix in terms of their adsorption and diffusion;
- soil microorganisms in terms of nitrification, denitrification and mineralization; and
- plant uptake.

The analysis of ^{15}N is mostly done after the combustion of the entire soil sample. If separate analyses of the different nitrogen forms are of interest for the study, the sample has to be fractionated before the ^{15}N analysis. The separate analyses of nitrate- ^{15}N and ammonium- ^{15}N , for example, in soil solution samples or KCl extracts, is possible after steam distillation (Bremner and Edwards, 1965; Buresh *et al.*, 1982) or diffusion (Brooks *et al.*, 1989). The distillates are freeze-dried or dried by diffusion. The dried samples can be directly analysed by isotope mass spectrometry. Distillation is more laborious and expensive than diffusion and subject to a higher analytical error since cross-contamination can easily occur. Several ways of reducing this problem have been discussed by Mulvaney (1986) and Mulvaney *et al.* (1994).

In certain ecosystems, a large proportion of the total nitrogen in solution can be in an organic form, and it may then be interesting to consider organic nitrogen forms in leaching studies. The amount of ^{15}N in organic form can be obtained by subtracting the inorganic ^{15}N (ammonium + nitrate ^{15}N) from the total ^{15}N in the soil solution. Further fractionation into hydrophilic and hydrophobic organic nitrogen is also possible (Qualls and Haines, 1991).

7.4 Dyes as Tracers for Preferential Flow Paths

Water infiltration and nutrient movements in soil are strongly influenced by macropores (see Section 7.1). The macroporosity of soil can be influenced by tree roots and burrowing soil animals, whose activity may be favoured by the presence of tree litter (see Section 10.1). Laboratory

and field procedures for measuring soil porosity and water infiltration are discussed in Sections 10.4 and 11.4. Dyes are useful for staining flow pathways in the soil, so that these can be analysed in relation to other characteristics, such as the distribution of roots, faunal structures (van Noordwijk *et al.*, 1993b) or soil microbial properties (Bundt *et al.*, 2001). A disadvantage is that the infiltration of dyes is often limited to a few decimetres from the depth of application. Dyes that have been successfully used include rhodamine-B (Douglas, 1986), acid-red 1 (Ghodrati and Jury, 1990), methylene blue (van Noordwijk *et al.*, 1991b) and brilliant blue (Bundt *et al.*, 2001). Van Ommen *et al.* (1988, 1989) detected preferential flow paths in soil to 70 cm depth by infiltrating a solution of iodine, which does not interact much with the matrix of most soils. The iodine is transformed into a coloured complex after treating the exposed soil with starch and Cl_2 . Dyes can be applied in the field by spraying on the soil surface, or through metal rings or bore holes as in infiltration measurements (see Section 11.4). Flow paths are evaluated in vertical trenches and/or by successively removing horizontal soil layers (Ghodrati and Jury, 1990).