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Ecosystem Nutrient Balance and Dynamics

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Introduction

Many attempts at balancing ecosystem-level nutrient budgets have been made in the past few decades using a variety of approaches, and for a variety of different purposes. Relatively simple mass balance equations have been used at the level of the watershed that might comprise single forested ecosystems (e.g., Binkley et al. 1982; Stohlgren et al. 1991; Likens and Bormann 1995; Hedin et al. 1995; Stottlemyer and Troendle 1992), or at the level of a larger-scale region (e.g., Gold 1990; Frink 1991; Jaworski et al. 1992; Howarth et al. 1996; Valiela et al. 1997) that might include different land uses and nutrient inputs. These budgets have been developed with varying efforts at measuring, or modeling, internal processes of nutrient retention and release.

The whole-ecosystem-level budget has a variety of purposes, including:

1. directly testing mechanistic models and understanding processes that control nutrient retention, turnover, and leaching in a field setting;
2. estimating processes by difference that are difficult to measure directly (such as weathering), or to test measurement methods for complex processes when the measurement techniques are called into question (such as dry deposition inputs, nitrogen fixation, or denitrification);
3. understanding controls on regional water quality;
4. in an experimental setting, understanding responses to watershed perturbations such as harvest, fire, or anthropogenic pollutant deposition (e.g., Likens et al. 1978; Pardo et al. 1995);
5. assessing the potential for long-term depletions in critical nutrient pools, such as cation stocks in forests affected by acidic deposition (e.g., Federer et al. 1989; Likens et al. 1996).

Each specific purpose may require a unique level of analysis and detail of measurement.

Often the lack of balance in an ecosystem budget has proven far more interesting than a budget that has balanced. For example, Bormann et al. (1977) found a higher rate of nitrogen (N) storage (as accumulation in biomass) plus loss (as streamwater) in the Hubbard Brook, NH, watershed than they found in inputs of N measured as bulk deposition. At the time, they suggested that the imbalance was probably due to unmeasured N_2 fixation. Thus the imbalance led to a testable hypothesis that directed future research, and later measurements showed that fixation inputs were unlikely to correct the imbalance. Only a portion of the imbalance could be corrected by improved methods of measuring atmospheric inputs such as dry deposition. However, when the imbalance was compared with the mass of N in the soil pool (7200 kg ha^{-1}), it became clear that a fluctuation of 0.5% in this pool would dwarf the budget imbalance, and thus much of the N uptake by vegetation probably came from a small net change in the mineral soil. This study showed the difficulty in comparing relatively well-quantified external fluxes with poorly quantified and considerably larger internal fluxes, and showed the importance of examining the common assumption of ecosystem steady state.

In this chapter I will review some of the basic methods and problems of creating whole-ecosystem nutrient budgets, including budgets at the whole-watershed scale, at the smaller plot or landscape scale, and in systems without readily measurable hydrologic outflows, as well as uses of nitrogen-15 (^{15}N) tracer techniques to follow N in ecosystems. I will focus primarily on forested ecosystems, as there is relatively little data in other vegetation types at the watershed level (but see Dodds et al. (1996) for an analysis of tallgrass prairie watersheds).

Input–Output Ecosystem Budgets at the Watershed Scale

The most basic input–output budget for a forested catchment can be constructed by comparing measured atmospheric inputs to fluvial outputs for a watershed that meets the requirement of having relatively impermeable bedrock. Geochemists have used input–output budgets for decades to estimate weathering rates and mechanisms, generally assuming that biota have little effect on the cations measured in streamflow (e.g., Miller and Drever 1977; Johnson et al. 1968). However, ecosystem ecologists are generally more interested in those nutrient ions that have substantial interactions with both vegetation and the microbial community, making specific process-level inferences from input–output budgets alone more challenging. Using N as an example, lower outputs of N in streamwater than was input via atmospheric deposition could be attributed to microbial immobilization, losses to the atmosphere, uptake and storage in vegetation and soil organic matter, or a combination of several of these processes (Fig. 16.1). On the other hand, a simple input–output budget may find its greatest use in providing an independent check of the measurement of internal processes, such as dry deposition inputs (discussed below).

The interpretation of an input–output budget certainly requires some knowledge of internal forest characteristics. Time since stand initiation (Vitousek and Reiners 1975; Emmett et al. 1993; Lepistö et al. 1995; Pardo et al. 1995), fire history (Chorover et al. 1994; Grier 1975; Bayley and Schindler 1991), weathering rate and chemistry (Johnson et al. 1968; Reynolds and Johnson 1972; Miller and Drever 1977; Anderson 1988), and land use (McDowell et al. 1995) may all exert strong control over streamwater concentrations of nutrient ions, and these are often not controlled for in studies attempting to understand patterns of ecosystem nutrient retention. For example, attempts to find patterns of streamwater or soil solution output relating to pollutant deposition in N-saturated ecosystems have had mixed results (Johnson 1992; Tietema et

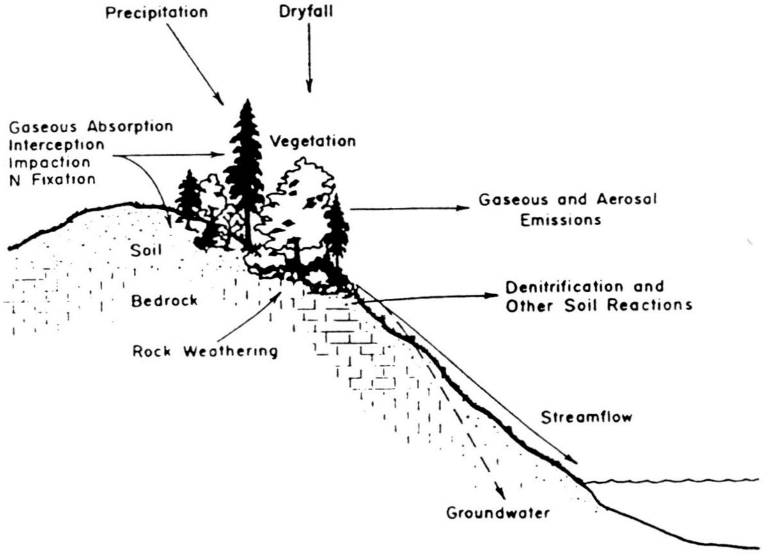

FIGURE 16.1. Major inputs and outputs of elements to a terrestrial watershed. (From Waring and Schlesinger [1985].)

al. 1995; Gundersen 1995; Dise and Wright 1995) in part due to internal differences among ecosystems that now are only beginning to be explored with more detailed process-level work on internal cycles and characteristics. Ecosystems may not be in steady state, or storage may not be constant from year to year; in these cases, caution must be taken in interpreting input–output budgets.

Atmospheric Inputs

One of the central concerns in obtaining an accurate input–output budget is errors associated with measurements of both the atmospheric inputs and the hydrologic outputs. Concerns with the different methods of estimating atmospheric deposition to a forested or otherwise complex watershed terrain are briefly outlined here and reviewed thoroughly in Rustad et al. (1994) and Lovett et al (1997). Further details and discussion of the available measurement techniques are given in Chapter 17. Most reports in the literature have used either wet-only deposition or else bulk deposition to measure total atmospheric inputs to an ecosystem. With the realization that dry and occult deposition may provide substantial percentages of the total inputs of specific elements, various techniques were developed to measure or model dry inputs, none of which have been generally accepted. Direct measurement techniques such as deposition to surrogate collectors have known inherent errors, as natural vegetation surfaces cannot be replicated or even modeled accurately. Current methodologies that use models and inferential techniques are strongly debated (Hicks et al. 1980, 1986, 1991). Inferential techniques include the use of towers, met stations, and surrogate surfaces and filters (see Chapter 17), and thus are expensive and require a high level of technical expertise compared with other techniques. Because no direct measurement of total deposition to a canopy has been found, these models cannot be independently verified, although as the models are refined and more catchment level budgets are constructed as secondary estimates of inputs, these techniques may prove to be the most sound. However, canopy type and structure, topographic exposure, elevation, and slope orientation all affect deposition inputs by wet, dry, and cloud water, making it difficult to determine deposition inputs to a complex terrain from a single collector at a field station (Lovett et al. 1997).

Some authors have used throughfall as a surrogate for deposition, as it is an integrator of dry, cloud, and wet deposition that actually reaches the vegetation, and a network of throughfall collectors over a large and variable landscape is more feasible than a large array of the more expensive deposition collectors (e.g., Gundersen 1995). However, although canopy uptake and leaching may be minimal for ions such as sulfate (SO_4^{2-}), sodium (Na^+) or chloride (Cl^-), they are significant processes for ions such as nitrate (NO_3^-) and ammonium (NH_4^+) (e.g. Lindberg et al. 1986; Friedland et al. 1991; Lovett et al. 1996) making throughfall estimates of total deposition less accurate. These processes may also vary among sites and vegetation types, depending on total rainfall and evergreen/deciduous differences, making simple corrections inaccurate. However, across a range of forest types and background N deposition rates at low elevations, Lovett and Lindberg (1993) calculated a reasonably constant net canopy N uptake of 16% of inputs ($r^2 = 0.89$), which has been used as a correction factor for throughfall estimates in similar sites. When an array of deposition collectors is not feasible, applying such corrections factors to other estimates of input may be the most accurate technique, with the understanding that changes in vegetation type, potential inputs from cloud water, etc., will certainly make the estimates less accurate.

Although no one method to determine atmospheric deposition to an ecosystem has received complete acceptance by the scientific community, studies that have calculated a catchment mass balance may offer an independent test for different methods of estimating dry deposition of various ions. For example, Hultberg and Grennfelt (1992) found good agreement between throughfall estimates of salt dry deposition and dry deposition calculated from a watershed mass balance. Rustad et al. (1994), however, found much higher estimates of dry deposition inputs of SO_4 and Cl from a catchment budget than from measured throughfall and canopy mass balance calculations. They suggested that the discrepancy was due to an error in their throughfall calculation, as occasional (and thus not sampled) superdominant conifers in the mixed hardwood and conifer forests at their study site in Maine could be extremely efficient scavengers of dry and occult deposition. Lovett et al. (1992) also found that estimates of sulfur (S) deposition at Hubbard Brook were significantly higher using the catchment mass balance method compared to throughfall or inferential measurements. Similarly, Shepard et al. (1989) found that estimates of dry deposition inputs of S provided by a catchment level budget were significantly higher than estimates by regressions applied to wet-only deposition or models of atmospheric concentrations of S coupled to deposition velocities. Thus, although throughfall measures of dry deposition have the advantage of being relatively inexpensive and easy, they may underestimate true deposition. Although it is not clear which measurement technique is more accurate, the catchment budget can provide either verification of an independent measure or else evidence that a particular measurement approach is in error.

Stream Outputs

The classic small watershed approach to ecosystem budgets ideally uses long-term data from gauged streams as the major output measurement (Likens 1985). Techniques for sampling streams for representative seasonal and annual estimates of hydrology and nutrient flux can be found in Likens et al. (1977) and Stottlemyer (1987). A detailed discussion of stream gaging sites and types of stations can be found in Reinhart and Pierce (1964). Methods for accurate and precise hydrologic sampling are necessarily site- and climate-specific, and thus few set rules apply. Flumes might be needed for steep slopes where high sediment yields are common, while V-notch weirs are more accurate in systems without high sediment loads. While some sites use proportional, automatic samplers for collecting stream water, other sites such as Hubbard Brook have found that weekly grab samples are equally as accurate in their ecosystems (W. Martin, personal communication). A detailed analysis of sampling frequency requirements in different catchment types for accurate representation can be found in Semkin et al. (1994).

Multiple years of data are critical to reduce the chance that input–output budgets are biased by hydrologic and climatic variability (Williams and Melack 1997a), as the retention of nutrients within the ecosystem can change with variations in the hydrologic (Lajtha et al. 1995, Seely et al. 1998) or temperature regime (Mitchell et al. 1996). However, even long-term data cannot accurately determine climatic links to variations in stream water chemistry, and thus a paired, or replicated, watershed approach is a preferred goal if manipulative experiments are to be performed. Clearly, finding or measuring a control, or reference, watershed is not always possible, although most long-term ecological research (LTER) sites with watersheds make some attempt at replication. Experiments involving effects of forest harvest, sewage sludge disposal, or experiments within the stream ecosystems at the Hubbard Brook Experimental Forest provide some of the best examples of this approach. More often, a single control and a single manipulated watershed are measured, limiting true statistical power (Chorover et al. 1994) although differences might be large enough to be convincing even without much replication (e.g. Kahl et al. 1993). Paired-catchment data can be augmented with pre- and postdisturbance comparisons, but there is always the possibility that interannual variability could be falsely interpreted as an effect of the manipulation (Williams and Melack 1997b). Local "control" watersheds cannot, of course, serve as controls for the analysis of regional disturbances, such as climate change or increased anthropogenic deposition of nutrients or pollutants. In these cases, large regional assessments can be performed (e.g., Stoddard 1994) or else annual discharge-concentration relationships can be separated into trajectories of time, discharge, and ion concentration to determine processes that regulate streamwater concentrations (Williams and Melack 1997a). Due to funding and time constraints, however, most watershed studies are performed without much replication or over long time spans, and thus cannot reliably address biogeochemical trends.

Because stream water chemistry integrates many processes over a large spatial scale and often over a large and poorly understood time scale, it is difficult and often misleading to directly relate stream water chemistry to processes within the forest stand. However, most watershed budgets have attempted to attribute differences in inputs and outputs to retention processes within the terrestrial ecosystem. Denitrification of N leached from the terrestrial ecosystem can be significant, variable, and high. depending on the presence and characteristics of a forest riparian zone, groundwater dynamics, and/or in-stream processing (Billen et al. 1991). Tietema and Verstraten (1991), for example, found that while streamwater N losses were only 21% of extremely high atmospheric inputs of N to an acid forest ecosystem in the Netherlands, 83% of the amount "retained" by the ecosystem was actually denitrified. A literature compilation by Hill (1996) found that denitrification of subsurface water inputs from agricultural and unsewered residential land uses through riparian zones ranged from 55 to 94% and were dependent on hydrologic flow paths and residence times. In an analysis of tallgrass prairie watersheds, Dodds et al. (1996) found that denitrification and ammonia volatilization were a large percentage of N inputs, and noted that large watersheds had a greater amount of time to immobilize or to denitrify N inputs than smaller watersheds, causing stream water concentrations of N to be lower. Holmes et al. (1996) also found stream water outputs to be a poor measure of N exports from the terrestrial ecosystem, and that denitrification was related to stream order and to organic inputs.

Although the simplest answer to this problem might be to directly measure denitrification losses as part of the internal cycling of N, the measurement of actual denitrification rates (rather than denitrification potentials) is fraught with difficulties. Denitrification is extremely variable in the terrestrial landscape, and is dependent on landscape position (Farrell et al. 1996; Groffman and Tiedje 1989) and the presence of rare "hot spots" (Christensen et al. 1990; Parkin 1987). Perhaps more importantly, the most common method for measuring denitrification, the acetylene blockage technique, has been called into question in recent years in both oxic and anoxic soils and sediments (Seitzinger et al. 1993; Bollmann and Conrad 1997) as acetylene appears to scavenge intermediate nitric oxide, and also blocks autotrophic nitrification and thus does not measuring coupled nitrification–denitrification. Although more complex methodologies are being developed for both terrestrial and aquatic soils and sediments, including N_2 flux and ^{15}N isotope pairing methods (cf. Nielsen et al. 1997; Joye et al. 1996; LaMontagne and Valiela 1995; Scholefield et al. 1997; Seitzinger et al. 1993; Van Luijn et al. 1996), no one technique has been accepted. Also, most denitrification at the watershed scale may take place primarily in riparian forest, stream, or lake sediments, and thus capturing the spatial scale of denitrification is extremely difficult.

Burns (1998) pointed out that denitrification was only one of many aquatic and in-stream processes that could reduce nutrient concentrations in streams. In his study of the Neversink River (Catskill Mountains, NY), diurnal variations in stream NO_3^- levels of up to 30% were consistent with uptake by photoautotrophs during daylight hours, and that both biological uptake and denitrification were important processes reducing stream NO_3^- over a reach by up to 29%. Clearly, stream NO_3^- concentrations integrate both terrestrial and aquatic retention processes. However, Burns (1998) points out the failure of many models of watershed response to atmospheric N deposition to acknowledge aquatic and in-stream processes, because many attribute all retention to terrestrial processes.

Other Budget Approaches

Johnson and Van Hook (1989) discussed some of the advantages and disadvantages of the watershed-level versus the stand-level approach to nutrient balance studies. Advantages of the watershed approach include little site disturbance and the fact that the system is viewed as a unit. Disadvantages include the fact that fluxes in the soil are rarely accounted for, and the requirement of impermeable bedrock is rarely met. The stand-level approach allows investigators to examine aboveground nutrient cycling, and has the advantages of reduced heterogeneity, estimates of within-soil processes, and a decoupling from aquatic processes (if that is a goal). Outputs can be measured using lysimeters, which have some decided disadvantages, including problems with interpreting the pool of soil water sampled and obtaining an accurate estimate of water flux.

Stand-Level Budgets Using Lysimetry

Ecosystem budgets have been conducted at scales smaller than the watershed in a variety of ways. Often when stream sampling is impossible or impractical, or unnecessary for the hypothesis being tested, a stand-level approach can be used, and ecosystem outputs can be estimated using lysimeters, or soil water collectors (e.g., Binkley et al. 1992; Joslin et al. 1992; Joslin and Wolfe 1992; Johnson and Lindberg 1992; Mitchell et al. 1992; Likens et al. 1994; Johnson 1995). Lysimetry has been used in experimental settings where the experiments, such as fertilization with N, are performed on stands smaller than a watershed (e.g., Currie et al. 1996; Christ et al. 1995; Rustad et al. 1996; Magill et al. 1997; Gundersen 1998 and other nitrogen saturation experiment (NITREX) sites). In these studies, streamwater outputs would integrate over too large an area, making the fertilization signal hard to detect, and riparian or in-stream denitrification and processing could also confound results. Lysimetry is also used when streams are not present (e.g., Lajtha et al. 1995) due to high infiltration rates. Lysimetry is perhaps most appropriate when the soil solution per se needs to be measured in studies of the terrestrial part of a watershed. For example, questions concerning the role of plant uptake versus soil sorption in watershed-level studies of nutrient retention might best be answered using lysimeters so that confounding effects of stream or riparian zone denitrification are omitted. However, due to variable and significant in-stream processing of some nutrients such as N, lysimeter results should be used cautiously for predictions of stream or drinking water quality.

The term lysimeter has had several meanings in the soil science literature; for the purpose of this chapter, a lysimeter is a sampler, inserted into the soil, that collects in situ soil solution water. Lysimeters collect water either with (tension) or without (zero-tension) applied tension to extract water. Tension lysimeters are generally smaller and relatively easy to install. They are most commonly made of ceramic or Teflon and glass mixes with a fine pore size to filter the soil solution before it is extracted. In theory, tension can be applied to match that of the soil water moving via gravitational or matric flow, and thus these lysimeters should collect water from the soil matrix as well as saturated, or macropore flow. Zero-tension lysimeters (ZTLs) can only collect saturated flow, although this is, presumably, the majority of water flow through the soil. These are constructed to have significantly larger collection areas than tension lysimeters, whose collection area is not easily measured, and thus ZTLs have the advantage of sampling a known, potentially quite wide area. Because ZTLs should be relatively large, they are inserted into the soil via a soil pit adjacent to the soil column that is under investigation.

There are advantages and disadvantages to each type of lysimeter (summarized in Lajtha et al. 1999, along with a general description of purchasing or constructing different types of lysimeters). Zero-tension lysimeters are more difficult to install and cause more disturbance to a site, especially if they are to be installed at depth. They tend to collect significantly less soil water at depth, and thus investigators have generally restricted the use of ZTLs to surface horizons. A number of studies have compared concentrations of elements collected by these different types of lysimeters, and summaries can be found in Litaor (1988), Marques et al. (1996), and Lajtha et al. (1999). Although several studies have found that soil solutions collected with tension lysimeters had higher concentrations of many ions, as one would expect since they should collect a more tightly bound fraction of soil water, this varied a great deal depending on the ion examined and the site. In general, there have not been clear patterns of differences between lysimeter types across the many studies, although nitrate appears to often be elevated in tension versus zero-tension lysimeters.

Lysimeters collect soil solution, and thus are not, per se, flux measurements of ecosystem losses. Even ZTLs only collect a variable fraction of total solution flux. Measurements of solute concentration must be coupled with a water-balance model in order to calculate fluxes below the rooting zone. It is likely that this calculation introduces one of the larger errors in lysimetry; it is certainly easier to directly measure stream hydrology and water chemistry than to model water flux. Coupled ecosystem and hydrologic models must, of course, be customized to each site, and require significant knowledge about the climatology of the site (e.g., PnET-II [Aber et al. 1995], WaVES [Dawes and Hatton 1993]). Chloride and bromide have been used as inert tracers through ecosystems as a way of bypassing modeling water flux, although the Cl^- method has recently been called into question (Chorover et al. 1994).

It is critical to realize that there are few reasons to believe that soil solution leachates would or should match patterns of stream water chemistry. In theory, lysimeters placed below the rooting zone of an ecosystem collect soil water that would otherwise leach from the system, and can no longer be affected by vegetation. In fact, significant denitrification, adsorption, and immobilization can take place in deep mineral soil (Qualls and Haines 1992). Several studies have examined both streamwater chemistry at the watershed scale and within-site soil solution chemistry with lysimeters (e.g., Sollins and McCorison 1981; Johnson et al. 1995; Fenn et al. 1996; Adams et al. 1997) although direct comparisons are rare. At one site in the Hubbard Brook Experimental Forest, long-term means of nitrate concentrations collected from the Bs horizon by lysimeters were higher than those found in streamwater, but differences were small (Fig. 16.2). There were no differences in dissolved organic carbon (DOC) concentrations, suggesting that the lysimeters represented streamwater fairly accurately, and that few removal processes operated below the Bs horizon. Similarly, Adams et al. (1997) measured both soil solution concentrations at different

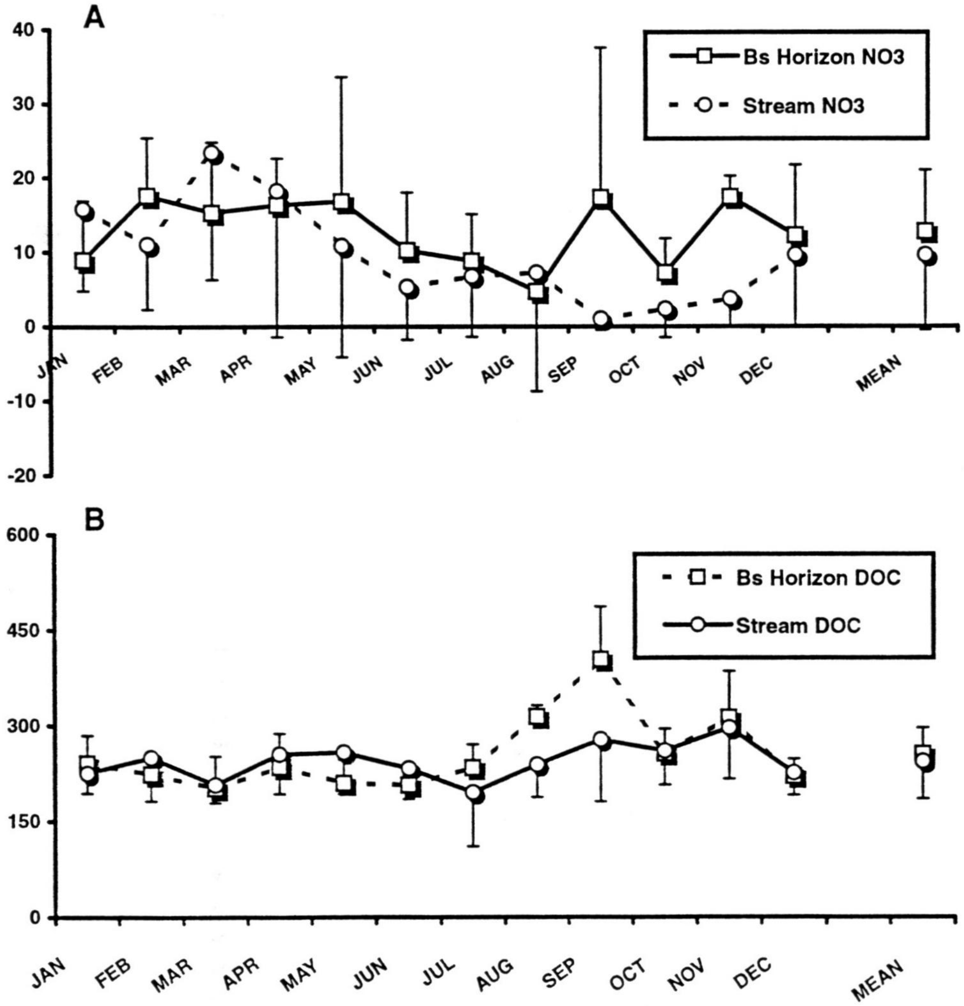

FIGURE 16.2. Long term (1984–1995) mean (± SD) monthly concentrations (μmol liter^{-1}) of nitrate and dissolved organic carbon in lower soil water (below the Bs horizon, measured using tension lysimetry) and in streamwater at the low elevation hardwood site (600 m) at the Hubbard Brook Experimental Forest, NH (Driscoll, unpublished data).

soil depths in zero-tension lysimeters and stream concentrations after fertilization in the Fernow Experimental Forest, West Virginia. C horizon soil solution concentrations of most elements appeared comparable to stream concentrations. Because soil solution concentrations declined with depth, soil solution concentrations from below the B horizon were higher than stream concentrations. This has implications for lysimetry studies, as many experiments have installed lysimeters below the B horizon, with the justification that the majority of roots rarely extend below the B horizon. Both the soil solution and stream water responded similarly to fertilization, although trends appeared more clearly in the stream water data. As part of the NITREX study, Kjonaas et al. (1998) compared plot-scale lysimetry and whole-catchment N export data both before and after N fertilization of a small catchment in Sweden. Although N losses measured using tension lysimeters were higher before N fertilization, losses at the plot and watershed scales were similar after fertilization. Curiously, although plot-scale lysimeters collected more dissolved organic nitrogen (DON), catchment-level runoff data showed greater dissolved inorganic nitrogen (DIN) levels, perhaps simply due to differences between the plot with installed lysimeters and the rest of the catchment. Finally, Seely et al. (1998) compared concentrations of different N species in lysimeters placed below the rooting zone in sandy soils and in groundwater outputs directly below the sites (Fig. 16.3). Concentrations of all N species declined with passage to groundwater, but the attenuation of DON was greater than the attenuation of either NO_3^- or NH_4^+, and the decline in DON in these soils below the rooting zone, and thus below a zone of any significant organic matter accumulation, was greater than the attenuation seen in upper mineral and organic zones. Although DON is generally the predominant form of N leaching from most forested watersheds (Hedin et al. 1995; Sollins and McCorison 1981; Johnson and Lindberg 1992), clearly budgets of DON and thus N will differ markedly depending on the output measurement used.

Such differences in the estimate of ecosystem outputs need to be noted in literature compilations, although many data syntheses, such as the European ECOFEE and ENSF compilations, have combined studies that use both lysimeter and stream water measures of output N (Gundersen 1995, Dise and Wright 1995). Studies of N saturation often address the question of eutrophication of surface or drinking water; clearly in these cases stream water outputs are the critical variable (e.g., Murdoch and Stoddard 1992; Stoddard 1994, Baron et al. 1994). Other studies of N saturation potential at the watershed level also analyze stream outputs (Durka et al. 1994; Hedin et al. 1995; Lepistö et al. 1995; Nodvin et al. 1995), and many conclusions about the relationship between N inputs and outputs, and current N saturation models (i.e. Aber 1992) have been made. Many studies, such as the European NITREX study or the U.S. Integrated Forest Study (IFS) network, measured losses of N compounds from either fertilized or unfertilized plots via lysimeters (Johnson and Lindberg 1992; Aber et al. 1993; Tietema et al. 1995; Gundersen and Rasmussen 1995; Kjonaas et al. 1998) and also draw conclusions about the relationship between N leaching and anthropogenic N loading. Because systematic errors can be introduced when merging results from these different types of ecosystem budgets, it will be important to keep leaching estimates separated by collection method.

Monolith Lysimetry and Sandbox Experiments

A completely different approach to the element mass-balance budget is to create an artificial ecosystem under field conditions. Isolated pits filled either with native soil or sand and variously instrumented to measure leaching losses have been used for decades in soil and agricultural research (e.g., Young et al. 1996) and are variously referred to as monolith lysimeters, weighing lysimeters, unconfined lysimeters, or sandboxes. These microecosystems can allow for a nearly complete budgeting of inputs and outputs. In the San Dimas lysimeter experiment (San Dimas Experimental Forest, Glendora, CA) (Ulery et al. 1995; Quideau et al. 1996), large earthen-walled pits were filled in 1937 with homogenized soil material that was sampled and archived at each 7.5 cm depth, and planted into different monocultures. These have been used for studies of weathering under different species, soil aggregate stability, and changes in soil C, N, and exchangeable cations over time, but these were not equipped to measure complete input and output budgets.

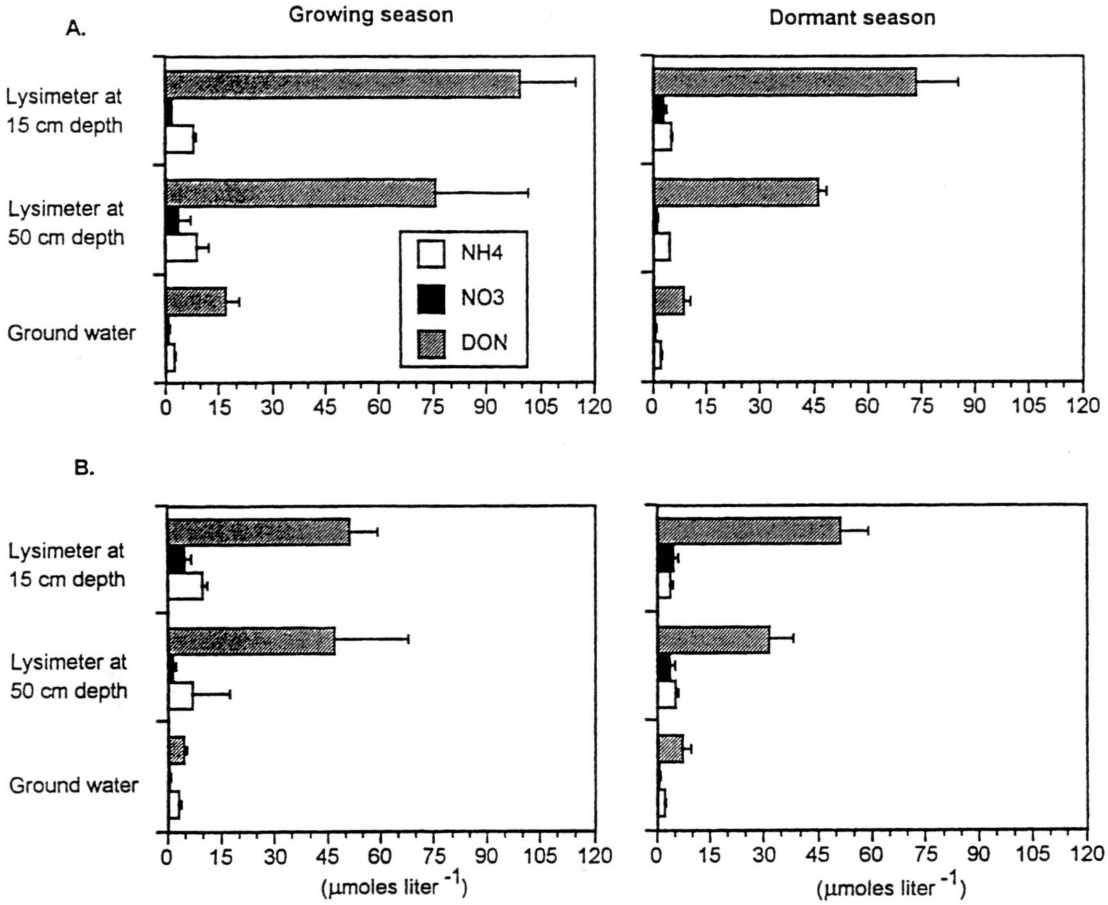

FIGURE 16.3. Mean concentrations of N species captured in zero-tension lysimeters and measured in groundwater during the growing season (April 15 to October 15) and dormant season (October 16 to April 14) over a 2-year period in a forested watershed developed on sandy substrates, Waquoit Bay, Cape Cod, MA. Values for two sites with different soil textures are shown: A, fine sand and B, loamy sand. (Redrawn from Seely et al. [1998].)

The Hubbard Brook "sandbox" experiment (Bormann et al. 1987; Bormann et al. 1993), was created in 1982 specifically to calculate complete plot-level element budgets. Large monolith lysimeters were dug to a depth of 1.5 m, lined with reinforced membranes on the sides and outfitted with bottom drains to measure output solution chemistry, filled with screened glacial outwash sand and 5 cm of topsoil, and planted with seeds or seedlings of known N content. Here an experimental ecosystem was created under field conditions where, in theory, all inputs and outputs could be measured. Even in these carefully controlled ecosystems, though, a balanced budget could not be made; pine sandboxes had an unexplained input of 54 kg N ha^{-1} yr^{-1} (Bormann et al. 1993). The authors argued against dry deposition inputs at this order of magnitude, and suggested that associative rhizosphere N_2 fixation could account for this imbalance. Although they measured rates of acetylene reduction in low-O_2 chambers in pitch and red pine rhizospheres, they declined to convert these direct measurements into annual or per-unit-area values of N_2 fixation, citing the uncertain ratio of C_2H_4 fixed to N_2 fixed and unknown O_2 concentrations in the actual rhizospheres. Thus rapid associative fixation could not be independently measured, and other studies of associative fixation have uniformly measured rates of <1 kg N ha^{-1} yr^{-1} (Kapustka and Dubois 1987; Grant and Binkley 1987; Silvester 1989; Binkley 1996).

These studies suggest that a controlled, artificial ecosystem with known boundaries can yield important information about nutrient cycling processes that cannot be determined from the larger-scale whole-ecosystem budget approach where spatial variability is high and many processes cannot be measured at a spatially explicit scale. However, these experiments are expensive, are rarely replicated (San Dimas was not replicated by species), and take several decades before the first meaningful analyses can be made. The artificial nature of fill soil may have a large effect on process rates, making extrapolations to undisturbed ecosystems difficult. The small scale of the mesocosms also pose some limitations on interpretation, just as plot-scale studies cannot always be representative of ecosystem-level dynamics. Although the measured output from these mesocosms quite accurately represent the true outputs, only a narrow portion of an ecosystem is measured, as deep soil, groundwater, and riparian dynamics are not measured.

Nitrogen-15 Studies at the Ecosystem Scale

Because the watershed budget approach cannot trace internal movement or storage of ions, various authors through the years have used isotopes to follow the fate of ecologically relevant elements. The use of phosphorus-32 (^{32}P) or other radioactive tracers in large-scale experiments in natural terrestrial systems is not common (but see Caldwell et al. 1985), but ^{15}N has been added to natural ecosystems in a large number of studies either as enriched fertilizer (Mead and Pritchett 1975; Broadbent and Carleton 1978; Nadelhoffer et al. 1995; Koopmans et al. 1996; Jordan et al. 1997; Nadelhoffer et al. 1998b; Tietema et al. 1998, to name a few) or at background, throughfall input concentrations (White and Howes 1994; Stams et al. 1991; Koopmans et al. 1996; Buchmann et al. 1995, 1996; Seely and Lajtha 1997; Nadelhoffer et al. 1998a). Unfortunately, less than a handful have used ^{15}N at background throughfall input levels and have traced movement over long time periods and in a number of ecosystem pools, including output pools such as deep lysimeters.

Buchmann et al. (1995, 1996) used ^{15}N as a tracer at background levels in the Fichtelgebirge, Germany. Because there was a 20% decrease in the recovery of both $^{15}NO_3$ and $^{15}NH_4$ tracer after 15 months, they estimated that this reflected the amount of loss from the system via leaching. The highest retention of ^{15}N was in organic soil horizons, followed by mineral soils, uptake by understory herbs, and uptake by overstory trees. Quite similar patterns have since been seen in many other studies with ^{15}N tracer additions, where input–output budget studies alone could not have measured the retention rates in these different pools. Similarly Koopmans et al. (1996), using quite low as well as fertilizer levels of ^{15}N addition in N-saturated sites in the Netherlands, budgeted the added N into vegetation uptake, soil retention, and leaching losses, and found more uptake of label by trees in a Douglas fir site than in a Scots pine site. Seely and Lajtha (1997) added ^{15}N to throughfall to trace seasonal differences in N retention in a coastal watershed in the United States and to examine soil texture effects on N retention, and found patterns similar to those of Buchmann et al. (1995), but with much higher leaching losses.

Other studies using background levels of ^{15}N for other purposes, such as estimating nitrification rates, have not measured many internal pools, but have measured leaching losses of label (e.g., Stams et al. 1991). Similarly, Hart et al. (1993) compared the fate of deposited N in a grassland and a plantation forest using background-level ^{15}N tracer, but because the purpose of the experiment was to analyze internal N processes, the plot sizes used were too small to make ecosystem-level budgets. However, they were able to identify important retention mechanisms in the soils examined, and found that the grassland retained significantly more of the deposited N than the forest. In most of these studies the recovery of ^{15}N was relatively high initially, often close to 100%, but declined with time, suggesting that there might be a very real time limitation on following these experiments.

Other studies have used tracers in both reference and fertilized plots; such complete cross-system studies allow researchers to evaluate retention mechanisms under different fertilizer and climate regimes. Nadelhoffer et al. (1998a) added ^{15}N to both reference and chronically fertilized stands at the Harvard Forest, Massachusetts, and found that tree uptake increased with fertilization; this pattern was not, however, observed by Tietema et al. (1998) in a series of lightly (3 to 6 kg N ha^{-1} yr^{-1}) to more heavily (20 to 91 kg N ha^{-1} yr^{-1}) fertilized NITREX sites. In this latter study, the percentage of ^{15}N applied that was taken up by trees (10 to 42%) after 1 year did not appear to be related to total fertilizer addition, although the efficiency of retention by organic soil horizons (11 to 47%) decreased with N addition as loss to leaching (0 to 50%) increased with N additions.

Labeled tracers have the advantage of allowing the researcher to trace the movement of an element through a plot-level ecosystem. However, there are several disadvantages to these techniques. Most studies have added tracer directly to the forest floor, thus ignoring canopy interactions. The size of the plots that can be used is necessarily small, as tracers tend to be expensive and, in the case of radioactive tracers, dangerous to use in levels that can leach out of the system. Another problem is the time course of study. Most studies can follow added label for a year or two at most due to the decreasing recovery of the tracer. Preston and Mead (1995) followed labeled litter for 7.5 years and found stabilization of the label after 3 years, but also found a low recovery (under 20%) with time. In contrast, White and Howes (1994) found 40% of added label remaining after 7 years in a salt marsh. Yet because so much of added N is immobilized in soil organic matter, this N could become available for uptake by vegetation or else lost from the system via leaching or denitrification at a later date, and thus these processes will be underestimated in short-term studies. Because there is continuous exchange between mineral and organic bound N-forms in soils, the label will begin to behave like the bulk of soil N (Knicker et al. 1997). However, with further refinement and perhaps through the use of models to track the further fate of label, these techniques will certainly add to the arsenal of methods that can be used in the calculation of ecosystem-level elemental budgets.

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