Some Perspectives of the Major Biogeochemical Cycles Edited by Gene E. Likens © 1981 SCOPE

# CHAPTER 6

# Interactions Between Major Biogeochemical Cycles in Terrestrial Ecosystems\*

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#### ABSTRACT

Best approximations at present would suggest that global cycles of carbon, sulphur, nitrogen, and phosphorus have been altered by human activity. However, little quantitative information exists on the interplay between the individual biogeochemical cycles of elements in terrestrial ecosystems. Because of man's potential to modify major biogeochemical cycles, such information is badly needed. Interactive effects may outweigh effects measured in terms of individual elements.

Boundary conditions generally have been ignored in attempts to quantify the flux and cycling of water and chemical elements for terrestrial ecosystems. Watershed (catchment) areas are convenient, functional units of the landscape for such studies.

Relative to watersheds, the hydrologic cycle assumes paramount importance through its effect on all other biogeochemical cycles; e.g. by regulating the timing and amount of inputs of chemicals in precipitation, and loss of dissolved and particulate substances by erosion, in runoff, or deep seepage. In turn, transpiration by plants affects the hydrologic cycle, thereby reducing the loss of nutrients from a drainage area.

\*This is a contribution to the Hubbard Brook Ecosystem Study. Financial support was provided by the National Science Foundation. We appreciate a critical review and comments from B. Peterson. Likewise, acid precipitation, an anthropogenic manifestation of the sulphur and nitrogen cycles, increases the flux of aluminium, phosphorus, calcium, etc., (in or from soils) and may decrease the flux of carbon by inhibiting photosynthesis and decomposition of organic matter. Conversely, as plant nutrients, the nitrogen and sulphur contained in acid precipitation may stimulate primary productivity and decomposition in some ecosystems, and thus enhance the flux of carbon in terrestrial ecosystems. Such interplay between cycles is undoubtedly common, but the quantitative effects are essentially unknown.

Biogeochemical cycles can also be altered indirectly through effects of haze, ozone, smog,  $CO_2$ , and dust on climate. In this regard, the carbon cycle is often crucial for interactions between cycles because of the pivotal role of photosynthesis and decomposition.

Comparative studies or experimental manipulations of entire ecosystems are costly and difficult, but the results are very informative. Such studies provide quantitative data on changes in flux and reveal linkages between cycles that are needed to advance the state-of-the-art and to elucidate mechanisms of interaction.

#### **6.1 INTRODUCTION**

To date most of the attention relative to biogeochemical cycles has been given to fluxes and mass balances ('budgets') of individual elements such as carbon, nitrogen, sulphur, and phosphorus. Feedback or synergistic type interactions between the cycles of the various elements has received little serious attention (cf. Bolin, 1976; Lerman, *et al.*, 1977). It is technically difficult to monitor and quantify the various fluxes, standing stocks, and processes regulating these parameters for only one element, let alone to study various cycles interacting together within an ecosystem or planetary context. Nevertheless, interactions exist and we shall attempt to point to some of them here. Our examples will be largely drawn from experience in temperate, humid, forested ecosystems.

#### 6.2 TERRESTRIAL ECOSYSTEMS

A critical conceptual consideration in evaluating biogeochemical cycles for terrestrial ecosystems is scale. What are the boundaries of a forest or grassland? Obviously quantitative determinations of fluxes, mass balances, or interactions cannot be made without establishing boundaries, but such pragmatic edges of a terrestrial ecosystem are usually established for the convenience of the investigation rather than to delimit integral functional units.

Lakes, streams, or islands appear to have obvious boundaries—but do they? What are the boundaries? How are they affected during periods of flooding or drought? Aquatic invertebrates may be found many metres below the sediment-water interface or horizontally beyond the banks of the stream and 'beneath' the terrestrial ecosystem (e.g. Hynes, 1974). Where then are the boundaries? Terrestrial landscapes often have political, climatic, topographic, vegetational, or other boundaries. Are these in any way functional boundaries?

The size of 'ecosystems' studied in the past has ranged from plots only a few metres in area to the entire planetary surface. Experimental scale has a profound effect on the theoretical context of a functional ecosystem. Larger systems, for example a global one, tend to be 'closed' with respect to mass. As such they may be in a time-invariant state (equilibrium) or a time-dependent state (disequilibrium). In contrast smaller ecosystems tend to be 'open' with respect to mass and may be in a steady-state mode (time invariant) or a non-steady-state mode (time dependent). Our comprehension of the processes operating within an ecosystem (Johnson, 1971) are thus framed by the state of the boundaries for the system (open versus closed) and the reaction pathways (reversible versus irreversible).

Because of their immense theoretical value, thermodynamic parameters (e.g. equilibrium constants, solubility products, phase diagrams) are occasionally used to describe certain natural processes. Implicit in such attempts, however, is that the field conditions must conform to the exacting conditions required by the thermodynamic considerations. More often than not, however, the necessary conditions for thermodynamic equilibrium are not met in the field, and thermal kinetic theory, or some approximation thereof, is required. Kinetic theory represents a reliable body of knowledge equally as powerful as thermodynamics and perhaps more applicable to natural processes.

Clearly it is much easier to make quantitative measurements of the process rates in smaller ecosystems, but do such areas exhibit all of the functional properties of a larger system? What are the critical functional properties? What are the linkages with other systems that affect these properties? Such questions are rarely addressed by ecologists or geochemists.

The error limits associated with measurements of rate processes within very large ecosystems may be so great as to compromise any real understanding of the biogeochemistry of these systems. The problem of signal-to-noise ratios are rarely addressed when reporting estimates of rates for processes in ecosystems.

In our biogeochemical studies of the Hubbard Brook Experimental Forest in the White Mountains of New Hampshire (cf. Likens *et al.*, 1977; Bormann and Likens 1979), we sought a solution to some of these problems by utilizing rather small, discrete watershed (catchment) ecosystems. We looked for units of the landscape that could be isolated on the basis of flowing water in the system. Because water is such an important vector for chemical flux and cycling in natural forested ecosystems, watershed (phreatic) divides would appear to form both functional and reasonable boundaries, amenable to quantitative analysis (Bormann and Likens, 1967; Likens and Bormann, 1972; Likens *et al.*, 1977; Bormann and Likens, 1979). Our model (Figure 6.1) accounts for the quantitative movement of matter across the boundaries of such a watershed ecosystem by the three principal vectors—meteorologic (movement by atmospheric forces), geologic (movement by alluvial or colluvial forces) and biologic (movement by animals). We consider the release and storage of materials inside the boundaries, for example by weathering, or biomass accumulation and release, as internal features of the ecosystem rather than input/output



Figure 6.1 A model depicting nutrient relationships in a terrestrial ecosystem. Inputs and outputs to the ecosystem are moved by meteorologic, geologic, and biologic vectors (Bormann and Likens, 1967; Likens and Bormann, 1972). Major sites of accumulation and major exchange pathways within the ecosystem are shown. Nutrients that, because they have no prominent gaseous phase, continually cycle within the boundaries of the ecosystem between the available nutrient, organic matter, and primary and secondary mineral components tend to form an intrasystem cycle. Fluxes across the ecosystem's boundaries link individual ecosystems with the remainder of the biosphere (after Likens *et al.*, 1977)

fluxes but in any event they must be quantitatively accounted for in the bookkeeping of mass balance determinations. All of these vectors and transformations must be carefully considered in quantitative evaluations of biogeochemical cycles. However, surprising deficiencies occur in many evaluations of mass balances for large-scale systems. For example, it is frequently assumed that biological uptake and release of nutrients are in balance (steady state) over a yearly cycle, when this condition probably rarely exists in present-day, man-disturbed landscapes. If biological storage and release do not approach steady state, then errors in mass balance calculations or interpretations can result from simple measurements of inputs in precipitation and outputs in stream water (cf. Likens *et al.*, 1977). To effectively study single cycles or interactions between cycles, it is imperative to use well-defined systems and to make no unwarranted assumptions about the developmental state of the ecosystem. Quantitative studies of watershed ecosystems can provide a conceptual basis for the use and management of landscapes (O'Sullivan, 1979).

# **6.3 CYCLE INTERACTIONS**

It is important to learn at what points the major biogeochemical cycles interact and how these linkages are affected by disturbance. For example, a general question might be-How sensitive is the nitrogen cycle to changes in the sulphur cycle and what are the most sensitive or diagnostic linkages between these two cycles? More specifically it might be asked-How does sulphuric acid in rainfall affect nitrification in the soil, the base exchange capacity, or mineralization activities or microorganisms? Little is known about the answers to such questions, but it is highly likely that as human stress on the natural environment increases, effects on individual biogeochemical cycles will reverberate throughout the system and affect all of the other interlinked cycles. The composite end result may be more important to the overall function of a natural system than an analysis of any single cycle would indicate. It is not clear to us how to obtain such complex answers on a global scale. On the scale of watersheds, however, it is possible by judicious comparative studies or experimental manipulations to elucidate mechanisms, reaction rates, and interactions. Insights may be obtained not only from the results of experimentally imposed disturbance, but it is also possible to 'relax' or remove a pre-existing stress on an ecosystem; e.g. reduce the pollution in a stream or stop the cultivation of a field, and observe the recovery of the system. On a global scale some stress 'experiments' are in process, e.g. increased CO2 in the atmosphere, acid rain from combustion of fossil fuels, and accelerated use of nitrogenous fertilizers, but unfortunately these alterations were not planned as experiments and the 'controlled replicates' are difficult or impossible to construct. Under these circumstances it is difficult to quantify the effects on individual cycles, let alone complex interactions between cycles. As a result, scientists frequently have resorted to smaller, more manageable systems and/or simulation models with the hope of extrapolating these results to a global scale. At this point, in the development of such information,



Figure 6.2 Relationship between streamflow and gross output of cations during 1963 to 1974 at the Hubbard Brook Experimental Forest (after Likens et al., 1977)

however, global valuations of individual biogeochemical cycles are at the very best only rough approximations.

#### 6.3.1 Hydrologic Cycle

Water is perhaps the most important linkage mechanism for chemical elements in terrestrial ecosystems. The hydrologic cycle affects other biogeochemical cycles in numerous (direct and indirect) ways. Water acts as a solvent, carrier, catalyst and reagent in many ecosystem reactions and processes. The flux of nutrients into and through many terrestrial ecosystems is largely dependent on the amount and temporal distribution of rain and snow and the chemical content of this water. For example, in an extreme case, Art et al., (1974) found for a coastal terrestrial ecosystem on Long Island, New York, that all of the inputs of calcium, magnesium, sodium, and potassium came from bulk precipitation and deposition of sea spray. Smaller but significant amounts of these nutrients are added to natural ecosystems in bulk precipitation at greater distances from the ocean (cf. Likens et al., 1977). Likewise, losses of major nutrients are usually a function of the amount of water draining from an area (Figure 6.2). In this regard, water lost by transpiration, which is an indirect function of the carbon cycle via photosynthesis, is not available for drainage and thereby transpiration serves to reduce the dissolved nutrient flux out



Figure 6.3 Relationship among precipitation, streamflow, and evapotranspiration for the Hubbard Brook Experimental Forest during 1965 to 1974. Transpiration accounts for the majority of the annual evapotranspiration water loss for this humid forest ecosystem (after Likens *et al.*, 1977)

of the system. For example, at the Hubbard Brook Experimental Forest, on average, some 38 per cent of the annual precipitation is lost as evapotranspiration each year (Figure 6.3).

The amount of available water affects the rate of primary production (carbon cycle) in terrestrial ecosystems (e.g. Leith, 1973) and, hence, the rate of uptake and storage of nutrients in biomass. It also plays a major role in the regulation of the processes of throughfall, leaching, decomposition, and mineralization which are integral parts of all nutrient cycles in humid regions.

Water is the primary agent of erosion and transport in humid regions (cf. Bormann *et al.*, 1974; Dunne and Leopold, 1978; Leopold *et al.*, 1964). The downstream transport of particulate matter constitutes an important loss in terrestrial ecosystems, particularly for relatively insoluble elements such as phosphorus, iron, and lead. A major biogeochemical aspect of erosion is related to the removal of exchange surfaces, since not only does this result in the loss of available nutrients, but loss of exchange surfaces can greatly alter the capacity of the system to regulate nutrient cycles and to recover from disturbance. The regulation of the hydrologic cycle and, therefore, erosion is dependent on the developmental phase of the terrestrial ecosystem (cf. Bormann and Likens, 1979), and may be drastically changed by disturbance, man-made or otherwise.

It is noteworthy that where knowledge of hydrologic fluxes is uncertain, associated chemical element budgets are also poorly known. Semi-arid and arid ecosystems exemplify this condition. It is difficult at best to deal quantitatively with the biogeochemistry of ecosystems where the hydrologic budget is unknown, unreliable or ephemeral.

In summary, it is difficult to exaggerate the importance of the water cycle with regard to practically every aspect of biogeochemistry. Massive irrigation works, diversions of major river systems, large-scale cloud seeding, major impoundments and deforestation or urbanization of catchment areas are all examples of man's conscious or unconscious efforts in manipulating the hydrologic cycle. All of the above have well-documented effects in dislocating or disturbing the biogeochemical activity within the affected area. Perhaps the ultimate hydrologic trauma, however, occurs when the hydrologic cycle switches from a 'normal' mode to an 'ice age' mode. Can man's influence on the  $CO_2$  balance, atmospheric dust and photochemical smog, and albedo of the earth bring about this most profound and dramatic interaction of all?

#### 6.3.2 Carbon Cycle

The carbon cycle often regulates interactions between various other biogeochemical cycles because of its pivotal role through photosynthesis and decomposition. For example, if ecosystem production exceeds decomposition then storage of nutrients would occur as biomass accumulates. If decomposition predominated, then nutrients would be released from the decaying organic matter. It must be realized, however, that these are generalized responses, since actual uptake and mineralization rates will be dependent on behaviour of different vegetational and chemical species, or both (e.g. Gosz *et al.*, 1973; Gosz, 1981).

Nutrient release through decomposition of leaf tissue in the Hubbard Brook Experimental Forest is influenced by critical carbon to element or element to phosphorus ratios (Gosz *et al.*, 1973). Once the critical C:N, C:P, etc., ratio is attained, mineralization occurs. Threshold ratios may exist for other elements and thereby control their mineralization rates in decomposing organic matter. Thus the presence of one nutrient can affect the availability of another through this type of biogeochemical interaction.

Currently a great amount of attention is being focused on the carbon cycle because of increasing concentrations of  $CO_2$  in the atmosphere from the combustion of fossil fuels and the resulting potential for climatic change (cf. Anonymous, 1977). Spatially, terrestrial ecosystems are quite heterogenous, i.e. some areas store carbon while others lose it. Globally, however, it is thought that terrestrial ecosystems are a net source of carbon for the atmosphere (see Olson *et al.*, 1978; Bolin,

	С	:	Ν	:	S	:	P
Global <sup>1</sup>							
Fossil fuel emissions	9300	:	36	:	130	:	1
Land plants	790	:	7.6	:	3.1	:	1
Ocean plants	129	:	12	:	2.9	:	1
Soil humus	54	:	3	:	1.2	:	1
Hubbard Brook Experimen	tal Forest						
Leaf material <sup>2</sup>	268	:	13	:	1	:	1
Total living biomass <sup>3</sup>	821	:	6	:	0.6	:	1
Forest floor	358	:	16.5	:	1.6	:	1
Precipitation	775	:	162	:	317	:	1
Runoff	615	:	200	:	800	:	1

Table 6.1 Elemental Ratios (by weight) for Major Nutrients

<sup>1</sup>Modified from Delwiche and Likens (1977); amount of phosphorus in land plants decreased 4fold and ratios adjusted accordingly;

<sup>2</sup>weighted for species composition;

<sup>3</sup>weighted for above and below ground materials of different species.

1977; Woodwell *et al.*, 1978). Although the amounts and assumptions underlying this flux are disputed (e.g. Broecker *et al.*, 1979). Moreover, the prevailing wisdom, although not certain either, is that elevated levels of  $CO_2$  in the atmosphere have not, in turn, stimulated terrestrial photosynthesis on a global scale (cf. Woodwell *et al.*, 1978). If net global ecosystem production were enhanced, then storage of nitrogen, phosphorus, and other nutrients in the accumulating biomass would be increased accordingly and transpiration also might be altered.

The so-called 'Redfield ratio' for content of carbon, nitrogen and phosphorus in organic material is widely quoted and used in 'megacalculations' for ecosystem and global budgets. This atomic ratio for C:N:P or 106:16:1 (weight ratio of 40:7:1) was based on analysis of marine plankton (Redfield, 1958; Redfield *et al.*, 1963). Ratios for terrestrial ecosystems, dead organic matter, or global systems may differ widely from the values for marine plankton (Table 6.1), and it is not appropriate to use the Redfield ratio generally for terrestrial ecosystems. The fact that the ratios are different is not at all surprising since the terrestrial plants have a much greater proportion of carbon (cellulose) stored in structural tissues (e.g. wood). Even 'ocean plants' (Table 6.1) have a different ratio than that proposed by Redfield because macrophytes and attached algae are included.

Redfield (1958) argued convincingly that organisms controlled the proportion of inorganic nitrogen and phosphorus in the sea. Furthermore, he proposed strong interaction between these two elements which resulted in a net equilibrium and fixed C:N:P ratio in marine organisms. The same argument can be made for terrestrial systems even though the C:N:P ratios are significantly different from those found in the sea. According to Redfield's arguments, phosphorus is the '... master

# Some Perspectives of the Major Biogeochemical Cycles

element which controls the availability of the others,' because it is present in lowest supply at the earth's surface relative to carbon, nitrogen, and oxygen. This relatively simple relationship, however, does not necessarily hold for terrestrial ecosystems where nitrogen, water, and other factors frequently limit growth (e.g. Waring and Franklin, 1979).

Simulation models of forest growth may give insight into the effects of vegetation disturbance or effects of accelerated plant growth on biogeochemical cycles (e.g. Botkin *et al.*, 1973; Shugart and West, 1977). For example, simulation suggests that catastrophic losses of major tree species (e.g. blights of chestnut, hemlock from the hardwood forests of the eastern USA) would affect biogeochemical cycles in a variety of ways, e.g. via uptake, release and differential storage of nutrients, gaseous exchange, impaction of aerosols, etc. The carbon cycle would be temporarily affected by such changes, as would be the flux and cycling of N, P, S, and other nutrients.

Harvesting of forest products by clearcutting provides an example of how various cycles may be affected through their linkages. Immediately following clearcutting of northern hardwoods in the northeastern USA, photosynthesis would be reduced and decomposition would be increased. As a result, transpiration would be increased; inventories, accumulation and release of all elements in biomass would be altered depending on the type of harvest and developmental stage of the ecosystem. Nitrification would be accelerated and there would be increased loss of calcium, magnesium, potassium, sodium, nitrate, phosphate, and hydrogen ion and decreased loss of sulphate in stream water (cf. Bormann and Likens, 1979).

Another aspect that should be considered here is the developmental stage of the forest ecosystem (cf. Bormann and Likens, 1979). Carbon flux might be greater for young forests in early stages of development, but impaction of sulphurous, nitrogenous, and phosphorus aerosols probably would be less because the architecture (impaction surface) of the forest would not be fully developed. The effects of ecosystem development and dramatic or subtle shifts in species composition on biogeochemical cycles and their interaction are areas worthy of detailed study (cf. Bormann and Likens, 1979; Gorham *et al.*, 1979).

# 6.3.3 Sulphur Cycle

Apparently, human activity, mainly through the combustion of fossil fuels, has altered the global sulphur cycle relatively more than for any of the other major elements (Table 6.2). One current estimate suggests that some 65 Tg of gaseous S are emitted to the atmosphere each year by anthropogenic activities, whereas only about 40 Tg-S yr<sup>-1</sup> are contributed by natural sources (see also Chapters 3 and 4). A manifestation of this alteration is the widespread phenomenon of acid precipitation in Europe and North America (e.g. Likens, 1976; Likens *et al.*, 1972, 1979). Acid precipitation is defined as rain and snow that has a pH of less than 5.6. The cause is strong acids (sulphuric and nitric) originating as combustion products (SO<sub>x</sub>,

	Carbon	Sulphur	Nitrogen	
	(Tg)	(Tg)	(Tg)	
Natural Anthropogenic (combustion of fossil fuels)	$\begin{array}{c} \sim 75 \times 10^3 \\ 5 \times 10^3 \end{array}$	~ 40 65	~ 210 18	

Table 6.2. Annual Gaseous Emissions to the Atmosphere (based on Delwiche and Likens, 1977; Granat *et al.*, 1976; Svensson and Söderlund, 1976)

 $NO_x$ ) from fossil fuels. Annual pH values of precipitation average between 4.0 and 4.5 over large areas of western Europe and eastern North America and pH values in the twos and threes are not uncommon for individual storms (Figure 6.4).



Figure 6.4 Distribution of acid precipitation in North America and Europe. Areas designated 10, 20, and 30 × receive 10, 20, and 30 times more acid in precipitation than expected if the pH were 5.6 (after Likens and Butler, 1981)

As rainwater falls through the canopy of a forest, its chemistry is markedly altered (cf. Likens *et al.*, 1977). These changes suggest both an effect on the various biogeochemical cycles by the vegetation and an effect on the vegetation itself (carbon cycle) by the rainfall. Highly acidic precipitation may reduce the primary productivity of terrestrial ecosystems through a variety of mechanisms (direct toxicity, leaching of nutrients from foliage, stress, etc.). As a result the carbon cycle

## Some Perspectives of the Major Biogeochemical Cycles

would be affected, and nutrient uptake from the soil as well as accumulation of elements in biomass would be reduced. Conversely, there is evidence that the rate of decomposition also might be slowed as a result of acid precipitation, perhaps having a secondary effect on productivity through a reduction in nutrient supply. Sulphur (and particularly nitrogen and phosphorus) compounds in precipitation may increase productivity if these nutrients are limiting in natural systems, and such increased productivity would alter the uptake, storage, and release of other mineral nutrients. Leaching of nutrients from the leaves could affect predator/prey relations, thereby altering the capacity of the vegetation to resist herbivores or pathogens. In turn, production, nutrient uptake, storage and release, etc., could change.

The potential interaction of the sulphur cycle, via acid precipitation, with other biogeochemical cycles is great. For example, if soil pH were lowered, absorption of ammonia would be enhanced and vice versa (e.g. Allison, 1973). Acid precipitation enhances the solubility and leaching of aluminium and other major cations (Ca, Mg, Na, K) from the soil (cf. Likens *et al.*, 1977; Johnson, 1979). A variety of other elements are also involved with these reactions including dissolved organic carbon, phosphorus, silicon, and fluorine compounds (Driscoll, 1980) thereby affecting their cycles through dissolution, leaching, and redeposition. The linkage between the sulphur-aluminium-phosphorus cycles requires careful study relative to interactions between biogeochemical cycles and their alterations by humans.

A revealing case study is the effect on chemical weathering when acid rain is imposed on the landscape. As seen in the Hubbard Brook Experimental Forest (Johnson, 1979) and in the Adirondack Mountains of New York State (Driscoll, 1980), the intrusion of acid rain into the weathering process has disrupted what is believed to be the normal chemical processes. The strong mineral acids of acid rain appear to have displaced weak acids such as  $H_2 CO_3$ , which ordinarily cause weathering of mineral substrates. No indications of carbonic acid reactions (carbonation) are evident in the headwater drainage streams from either area. Furthermore, the acid rain dissolves and mobilizes  $Al^{3+}$  from the soil zone, where usually it is deposited. The acidified, aluminium-rich drainage waters from these chemical reactions are toxic to fish in downstream waters (Driscoll *et al.*, 1980). Ironically, the acid rain may not itself kill fish, but one of its neutralization products ( $Al^{3+}$ ) does. This illustrates how a perturbation in one cycle, in this case the sulphur cycle, in one part of an ecosystem, can propagate through the system with unexpected and sometimes undesirable results.

Another dimension of this problem concerns the effect of acid rain on chemical weathering rate. Studies by Granat *et al.* (1976) suggest that acid rain is accelerating chemical weathering rates substantially, perhaps even doubling the normal rate globally. The assumption is that the effects of acid rain are superimposed upon preexisting reactions, so that the effect is additive. On the other hand, Johnson (1979) believes that, 'no excessive chemical weathering activity can be attributed to acid rain over the northeastern United States,' because of a displacement of the weak acid activity by the strong acids. These contradictory views illustrate the diffi-

culty of comparing global estimates and assumptions with data from discrete ecosystems.

Sulphurous aerosols from human activity can result in increased haziness (e.g. Husar *et al.*, 1979) which, in turn, can affect climate and plant productivity (and all the associated biogeochemical cycles). There is evidence that atmospheric haziness is increasing in the arctic as well as in industrialized areas of the world. Thus, the sulphur cycle could have an affect on the albedo, heat budget, and ultimately the climate of the earth.

The transport and deposition of metals such as zinc, copper, lead, cadmium, etc., from industrial pollution sources has been shown to depress vegetation growth and decomposition rates in forest litter (e.g. Rühling, and Tyler, 1973; Jordan, 1975). Concentrations of some of these metals in rain and snow is surprisingly high and significant accumulation is occurring in remote forested ecosystems of the northeastern USA (Galloway and Likens, 1979; Siccama and Smith, 1978). Thus, it is likely that important feedbacks are occurring between these metal cycles, acid precipitation, and other cycles such as N, S, and P through effects on productivity and decomposition.

Pollution standards or regulations probably show the greatest weakness in using the single factor or single-cycle approach. For example, atmospheric sulphur standards might be based on the role of sulphur in acid precipitation. However, acid precipitation also is the result of atmospheric nitrogen oxides, chlorides, ammonia, metallic bases, etc. Hence control of the acid precipitation problem requires simultaneous consideration of all of these elements and their interactions.

## 6.3.4 Nitrogen Cycle

Annually some 40 Tg of N are fixed commercially as agricultural fertilizer (Delwiche and Likens, 1977). There has been appreciable concern about the role of this fertilizer in the eutrophication of aquatic ecosystems (e.g. Kohl et al., 1971), and whether gaseous losses from the soil would be enhanced and thereby produce atmospheric imbalances (e.g. McElroy et al., 1977; Crutzen and Ehhalt, 1977; Council for Agricultural Science and Technology, 1976; Hutchinson and Mosier, 1979). E. Lemon and co-workers (personal communication) at Cornell University have found that the vegetational uptake of gaseous  $NH_3$  may serve as a balancing mechanism for levels of ammonia in the atmosphere. Apparently agricultural vegetation can release NH<sub>3</sub> when ambient atmospheric concentrations are low, and absorb it when gaseous concentrations are high. In fact, the uptake rate is accelerated at higher concentrations. Lemon has suggested that if nitrogen were limiting to photosynthesis, then losses of  $NH_3-N$  (from fertilizer as well as naturally-fixed N) in one area could stimulate net production by plants in another area via the mechanism described above and thus influence the storage of atmospheric  $CO_2$  in living and dead biomass. In turn, all other major nutrients would be affected proportionally by the changing levels of photosynthetic and decomposition activity.



Figure 6.5 Annual nitrate concentrations in precipitation in the northeastern USA (after Likens and Bormann, 1980)

Biologically significant amounts of nitrogen are added to terrestrial ecosystems each year in rain and snow. At various locations in the eastern USA annual inputs in precipitation range between 6 and 10 kg-N ha<sup>-1</sup> (Likens *et al.*, 1977; Likens, 1972). Wet deposition values in industrialized Europe may be even greater (Söderlund, 1977). Such inputs have increased significantly during the last decade in both the eastern USA (Figure 6.5) and western Europe (e.g. Likens, 1976). There is no quantitative evidence as yet whether these increased inputs have had a significant effect on plant productivity or decomposition in natural ecosystems.

An interesting, but as yet unexplained, finding from the Hubbard Brook Ecosystem Study is the relationship between  $NO_3$  and  $SO_4^2$ ; in drainage water (cf. Likens *et al.*, 1970). In a recently deforested watershed, it was found that the concentration of  $NO_3$  in stream water was inversely proportional to the concentration of  $SO_4^{2-}$ , to a minimum value of  $SO_4^{2-}$  (~ 3 mg litre<sup>-1</sup>) which approximated the concentration in ambient precipitation (Figure 6.6). A similar but less pronounced relationship was observed in stream water draining from forested watersheds (Figure 6.7).

# 6.3.5 Phosphorus Cycle

As discussed above, phosphorus is frequently limiting to plant growth in natural ecosystems. As such the interactions with other biogeochemical cycles, particularly carbon, are obvious.

In most natural ecosystems where budgetary information is available, the input of phosphorus via bulk precipitation exceeds the losses in drainage waters (Likens *et al.*, 1977). This finding would imply that the biomass in these diverse ecosystems is not in steady state and that organic matter was accumulating, or that phosphorus was stored geochemically in the soil. At Hubbard Brook the ratio of annual storage



Figure 6.6 Relationship between nitrate and sulphate concentrations in stream water from a deforested watershed of the Hubbard Brook Experimental Forest. Nitrate values less than 25 mg litre<sup>-1</sup> show the transition period between forested and deforested conditions (after Likens *et al.*, 1970)

in the biomass to input was higher for phosphorus than for any other nutrient in this forested ecosystem (Table 6.3). Any stimulation of net ecosystem production by additions of phosphorus would correspondingly affect many, if not all, of the other elemental cycles.

The origin of phosphorus in rain and snow is largely unknown. Some phosphorus may originate from terrestrial dust swept into the atmosphere, but there are indications that concentrations are higher in rain and snow adjacent to urban and industrial centres.

An excess of phosphorus in aquatic ecosystems usually results in eutrophication (cf. Schindler, chapter 7). However, it is an open question as to how much of this phosphorus originates from fertilizer, applied to adjacent terrestrial ecosystems. In general, forested ecosystems lose smaller amounts of phosphorus in drainage waters than cultivated or urbanized areas, but with disturbance, levels in stream water generally increase (cf. Likens and Bormann, 1974). Also more phosphorus is typically lost in drainage from areas with sedimentary rocks and fertile soil other factors being similar (Dillon and Kirchner, 1975). Much of the phosphorus in surface waters adjacent to urbanized areas comes from the industrial and domestic use of detergents containing phosphorus, and from sewage.



Figure 6.7 Relationship between nitrate and sulphate concentrations in stream water from forested watersheds of the Hubbard Brook Experimental Forest during October to May of 1964 to 1974 (after Likens et al., 1977)

Table 6.3 Annual Input/Output and Fate of Nutrients in the Hubbard Brook Experimental Forest. Values in %

Element	Source			
	Meteorologic input	Weathering release	Annual storage/input	Annual output/storage
Na	22	78	2	4400
S	96	4	10	880
Mg	15	85	22	370
Ca	9	91	41	146
K	11	89	76	39
N	100	<1	81	24
Р	1*	99*	99*	0.7

\*Estimated

Appreciable amounts of carbon and nitrogen are lost to the atmosphere when natural ecosystems are burned, but it is not known how much phosphorus is lost in this way.

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#### 6.4 SUMMARY

Terrestrial cycles of water and all nutrients, including carbon, nitrogen, sulphur, and phosphorus, have been altered by man through such activities as combustion of fossil fuels, application of agricultural fertilizers and pesticides, deforestation, erosion, and irrigation. However, quantitative data are so deficient that it is difficult to determine how much the cycles of these elements have been affected, particularly on a global scale. There is almost no useful quantitative information on interaction between global cycles, but we suspect that interactive effects may outweigh individual effects that we know for single elements.

Not only is there interaction between cycles, but also between systems. It is unrealistic to consider terrestrial systems or cycles in isolation from adjacent aquatic and atmospheric systems and cycles.

Comparative studies or experimental manipulations of entire ecosystems are costly and difficult, but the results can provide quantitative data on processes and reaction rates for biogeochemical cycles, and for interactions between cycles. Quantitative data on flux as well as information on linkages between cycles are needed in a variety of ecosystem types to elucidate mechanisms of interaction and to advance the state of the art. We believe there is a need to establish international technical working groups, primarily concerned with the measurement and prediction of interactions between global cycles. This effort should be an important part of any overall evaluation of the effects of human activities of the global environment.

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109

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# Some Perspectives of the Major Biogeochemical Cycles

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