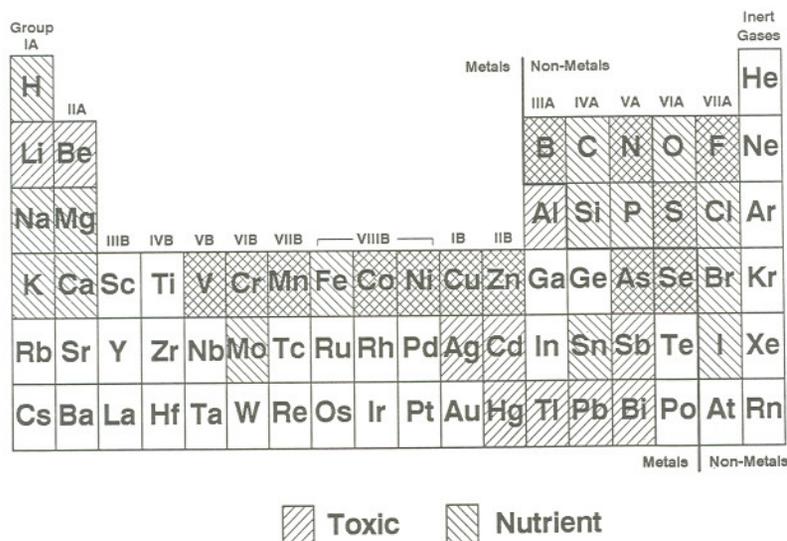


# 13 Trace Metals Speciation and Cycling

CHARLES T. DRISCOLL, JAMES K. OTTON AND ÅKE IVERFELDT

## 13.1 INTRODUCTION

Trace metals are important elements in the biogeochemistry of forest and aquatic ecosystems. Many trace metals are required micronutrients for plant or animal life (Figure 13.1; Bohn *et al.*, 1979). At very low concentrations or availability, organisms may show nutrient deficiencies of certain trace metals (Simkiss and Taylor, 1989). Anthropogenic activities, such as mining, fossil fuel combustion or industrial processes, have greatly altered the biogeochemical cycles of trace metals and enhanced their bioavailability (Garrels *et al.*, 1975). At elevated concentrations or



**Figure 13.1** Periodic table showing which elements are required for plant and/or animal life, and which elements can be toxic to plant and/or animal life. Some elements are nutrients at low concentrations and toxic at high concentrations. An arbitrary division between metals and non-metals is given.

availability, certain trace metals may be toxic (Figure 13.1). Indeed, many metals are required by organisms but can have deleterious effects at high concentrations (e.g. Cr, Cu, Ni, Se). The objectives of this chapter are to provide some background information on the environmental chemistry of trace metals; to describe four case studies of trace metal cycling (the Hg cycle at Lake Gårdsjön, Sweden; the Pb and Al cycles at the Hubbard Brook Experimental Forest (HBEF), New Hampshire, USA; and the U cycle at Flodelle Creek in the state of Washington, USA); and to provide some recommendations for future research on the biogeochemistry of trace metals.

There is considerable interest in the biogeochemistry of trace metals in forest ecosystems and interconnected aquatic ecosystems. Atmospheric deposition may serve as an important pathway of trace metal influx to forest ecosystems (Reiners *et al.*, 1975; Siccama and Smith, 1978; Smith and Siccama, 1981; Johnson *et al.*, 1982). Data on concentrations of certain trace metals in precipitation for a variety of areas are summarized in Table 13.1. These data show a wide range of concentrations, however in general, precipitation exhibits higher concentrations in more heavily populated and industrialized areas than remote regions. Elevation and vegetation characteristics are particularly important in metal deposition due to increased concentrations in cloud and fog water, relative to bulk precipitation (Reiners *et al.*, 1975; Johnson *et al.*, 1982; Ross and Lindberg, this volume, Chapter 3). Atmospheric deposition has been reported to be an important component of the total ecosystem input of certain trace metals (e.g. Cd, Cu, Pb, Zn; Heinrichs and Mayer, 1980; Troutman and Peters, 1982; Smith *et al.*, 1986; Steinnes, 1987).

For other trace metals (e.g. Al, Fe, Mn), atmospheric deposition may be a less important source than internal release (e.g. weathering, mineralization, desorption from soil/sediment surfaces). Acidic atmospheric deposition may facilitate leaching of trace metals in acid-sensitive regions and adversely impact surface water quality (Heinrichs and Mayer, 1977; Miller *et al.*, 1983). These effects are particularly evident at high elevations due to increased amounts of precipitation and the scavenging of acidic aerosols by coniferous canopies (Lovett *et al.*, 1982; Ross and Lindberg, this volume, Chapter 3), as well as shallow soils which show limited neutralization of acid inputs (Driscoll *et al.*, 1988).

Trace metals can be immobilized within the forest floor by adsorption (Gosz *et al.*, 1976; Swanson and Johnson, 1980; Friedland and Johnson, 1985). Conversely, soluble organic acids from leaf leachate or mineralization of soil organic matter may form aqueous complexes with trace metals, facilitating transport to the lower mineral soil or to surface water (Perdue *et al.*, 1976; Turner *et al.*, 1985). The mineral soil may serve as a trace metal sink through adsorption and precipitation reactions or as a trace metal source through desorption and dissolution reactions (Bogges, 1977; Driscoll *et al.*, 1988). Finally, forest vegetation may assimilate trace metals and facilitate cycling through canopy leaching, or decomposition of leaf and root litter (Reiners *et al.*, 1975; Likens *et al.*, 1977; Whittaker *et al.*, 1979).

**Table 13.1** Examples of concentrations of trace metals in precipitation at various sites. Note that concentrations are generally higher in industrialized areas and lower in remote regions

	Greenland <sup>a</sup>	Enewetak <sup>b</sup>	Washington State <sup>c</sup>	Bermuda <sup>d</sup>	S. Sweden <sup>e</sup>	N. Sweden <sup>e</sup>	SE USA <sup>f</sup>	Deleware <sup>g</sup>	N. Ontario <sup>h</sup>	SW Ontario <sup>i</sup>
Cd	0.013	0.002	0.012	0.06	0.13	0.041	0.04–0.25	0.18	0.09	0.16
Cu	0.05	0.013	0.14	0.66	2.3	0.85		0.68	1.3	1.4
Fe			9.8		27.0	9.8				
Mn		0.012	0.49	0.27	2.5	1.7	1.3–3.2	1.4	2.7	4.7
Pb	0.12	<0.04	0.15	0.77	3.8	1.8	3.2–5.6	3.0	2.3	7.0
Zn	0.3	0.05	0.99	1.15	10.0	4.1	4.9–10	6.4	4.0	9.0
Cr					0.16	0.064				
Ni				0.17	0.44	0.13		0.79	0.17	0.9
V		0.018		0.096	1.2	0.27		0.67	0.096	1.0

<sup>a</sup>Davidson *et al.*, 1982; mean.

<sup>b</sup>Arimoto *et al.*, 1985; mean.

<sup>c</sup>Vong *et al.*, 1988; volume weighted mean.

<sup>d</sup>Jickells *et al.*, 1984; volume weighted mean.

<sup>e</sup>Ross, 1990; annual volume weight mean.

<sup>f</sup>Lindberg and Turner, 1988; annual volume weight mean.

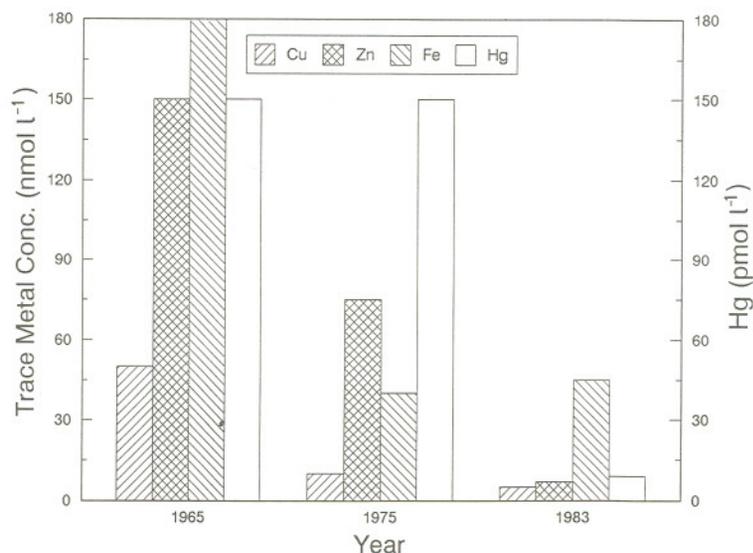
<sup>g</sup>Church *et al.*, 1984; annual volume weight mean.

<sup>h</sup>OME, 1985; volume weight mean.

<sup>i</sup>Chan *et al.*, 1982; annual volume weight mean.

The small watershed approach is an effective tool to facilitate understanding the transport and cycling of trace metals in forest ecosystems, and subsequent effects on surface waters. However, care must be exercised in the collection and analysis of samples for trace metals. Many values of trace metal concentrations reported in the literature are in error because of contamination (Barrie *et al.*, 1987). This problem is illustrated in values reported in the literature for mean oceanic concentrations of selected trace metals (Figure 13.2; Fitzgerald and Watras, 1989). The decline in trace metal concentrations in seawater since the 1960s is not due to any environmental trend, but rather occurs by minimizing sample contamination. The determination of accurate concentrations of ultratrace metals is difficult because of many sources of contamination. Contamination may arise from sample collectors, the collection process, sample containers, sample storage, sample processing (e.g. filtration, centrifugation), reagents used in the analysis, as well as the actual analysis of samples.

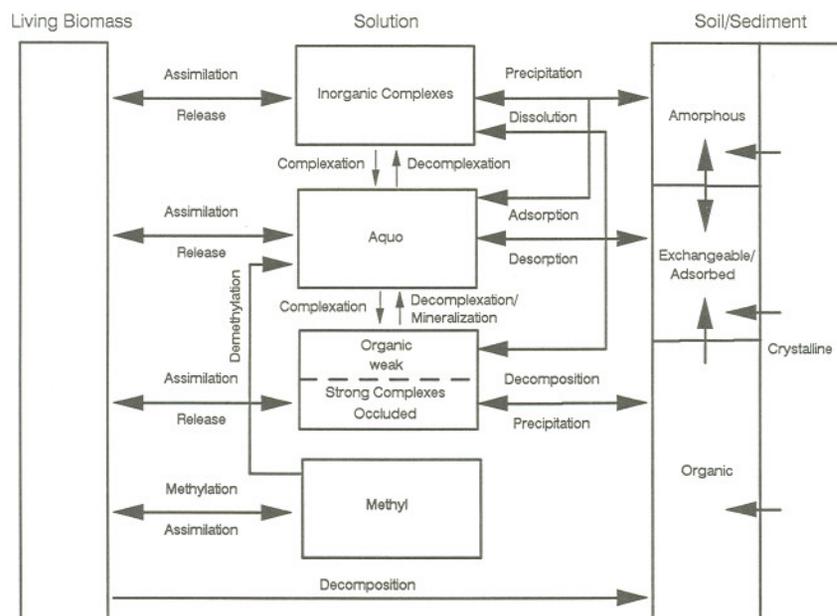
The geochemistry and bioavailability of trace metals are strongly influenced by speciation. Trace metals can exhibit a variety of aqueous and particulate species (Figure 13.3). Within the aqueous environment, metals can associate with a range of ligands to form complexes. These include water (aquo complexes),  $\text{OH}^-$  (hydroxo complexes), other inorganic ligands (e.g.  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{F}^{T-}$ ; Table 13.2) and organic ligands. Trace metals can be mobilized/immobilized from solid



**Figure 13.2** Mean oceanic concentrations of selected trace metals reported in the literature (after Fitzgerald and Watras, 1989; reproduced by permission of Elsevier Science Publishers BV). It is evident that concentrations of these metals have declined in recent years. The reason for this decline is not due to reduced concentrations, but rather improvement in the determination of detection limits.

phases. These may include suspended particles, soil and sediments. Solid–solution interactions of trace metals occur through adsorption/desorption reactions on organic or mineral functional groups or direct precipitation/dissolution reactions. Solid phase metals may be associated with surface functional groups, hydroxide, carbonate or sulphide minerals (in amorphous or crystalline forms) or organic matter (Tessier *et al.*, 1979). Finally, biota may alter the cycling of trace metals through uptake by assimilation or surface adsorption, and release by mineralization, methylation or desorption reactions.

Interactions between trace metals and organisms are of particular interest in environmental chemistry because of potential nutrient deficiencies and toxicity (Simkiss and Taylor, 1989). Unfortunately, mechanisms of trace metal bioavailability vary from organism to organism and metal to metal. Moreover, a detailed understanding of metal–organism interactions is only available for a few systems. In general, there are two mechanisms by which trace metals can be assimilated by organisms (Figure 13.4). Ionic species may form surface complexes with carrier proteins used in active transport and be transported across cellular membranes. Non-ionic species may be transported across biological membranes by passive diffusion. An understanding of the speciation of trace metals is critical to an evaluation of bioavailability.



**Figure 13.3** Conceptual diagram illustrating the pools and transfers of trace metals in the environment. Note that not all pools and transfers illustrated here are important for all metals, rather the significance of individual forms and pathways varies from metal to metal.

**Table 13.2** Predominant inorganic species and solid phases regulating aqueous concentrations for selected trace metals in aquatic systems (after Morel 1983)

---

*Ba*  
 $Ba^{2+}$   
 $BaSO_4(s)$ ,  $BaCO_3(s)$

*Cr*  
 $Cr(OH)_2^+$ ,  $Cr(OH)_3$ ,  $Cr(OH)_4^-$ ,  $HCrO_4^-$ ,  $CrO_4^{2-}$ ,  $Cr(OH)_3(s)$

*Al*  
 $Al(OH)_3$ ,  $Al(OH)_4^-$ ,  $AlF^{2+}$ ,  $AlF_2^+$   
 $Al(OH)_3(s)$ ,  $Al_2O_3(s)$ ,  $Al_2Si_2O_5(OH)_4(s)$ , Al-silicates

*Fe*  
 $Fe^{2+}$ ,  $FeCl^+$ ,  $FeSO_4$ ,  $Fe(OH)_2^+$ ,  $Fe(OH)_4^-$   
 $FeS(s)$ ,  $FeS_2(s)$ ,  $FeCO_3(s)$ ,  $Fe(OH)_3(s)$ ,  $Fe_2O_3(s)$ ,  $Fe_3O_4(s)$ ,  $FePO_4(s)$ ,  
 $Fe_3(PO_4)_2(s)$ , Fe-silicates

*Mn*  
 $Mn^{2+}$ ,  $MnCl^+$   
 $MnS(s)$ ,  $MnCO_3(s)$ ,  $Mn(OH)_2(s)$ ,  $MnO_2(s)$

*Co*  
 $Co^{2+}$ ,  $CoCl^+$ ,  $CoSO_4$   
 $CoS(s)$ ,  $Co(OH)_2(s)$ ,  $CoCO_3(s)$ ,  $Co(OH)_3(s)$

*Ni*  
 $Ni^{2+}$ ,  $NiCl^+$ ,  $NiSO_4$ ,  $NiS(s)$ ,  $Ni(OH)_2(s)$

*Cu*  
 $Cu^{2+}$ ,  $CuCO_3$ ,  $CuOH^+$   
 $CuS(s)$ ,  $CuFeS_2(s)$ ,  $Cu_2CO_3(OH)_2(s)$ ,  $Cu_3(CO_3)_2(OH)_2(s)$ ,  $Cu(OH)_2(s)$ ,  
 $CuO(s)$

*Zn*  
 $Zn^{2+}$ ,  $ZnCl^+$ ,  $ZnSO_4$ ,  $ZnOH^+$ ,  $ZnCO_3$ ,  $ZnS$   
 $ZnS(s)$ ,  $ZnCO_3(s)$ ,  $ZnSiO_3(s)$

*Pb*  
 $Pb^{2+}$ ,  $PbCl^+$ ,  $PbCl_2$ ,  $PbCl_3^-$ ,  $PbOH^+$ ,  $PbCO_3$   
 $PbS(s)$ ,  $PbCO_3(s)$ ,  $Pb(OH)_2(s)$ ,  $PbO_2$

*Hg*  
 $Hg^{2+}$ ,  $HgCl^+$ ,  $HgCl_2$ ,  $HgCl_3^-$ ,  $HgOHCl$ ,  $Hg(OH)_2$ ,  $HgS_2^{2-}$ ,  $HgOHS^-$   
 $HgS(s)$ ,  $Hg(liq)$ ,  $Hg(OH)_2(s)$

*Cd*  
 $Cd^{2+}$ ,  $CdCl^+$ ,  $CdCl_2$ ,  $CdCl_3^-$ ,  $CdOH^+$ ,  $CdS$ ,  $CdHS^+$ ,  $Cd(HS)_2$ ,  $Cd(HS)_3^-$ ,  
 $Cd(HS)_4^{2-}$   
 $Cd(s)$ ,  $CdCO_3(s)$ ,  $Cd(OH)_2(s)$

*Ag*  
 $Ag^+$ ,  $AgCl$ ,  $AgCl_2^-$ ,  $AgS^-$ ,  $AgHS$ ,  $AgHS_2^{2-}$ ,  $Ag(HS)_2^-$   
 $Ag_2S(s)$ ,  $AgCl(s)$ ,  $AgBr(s)$

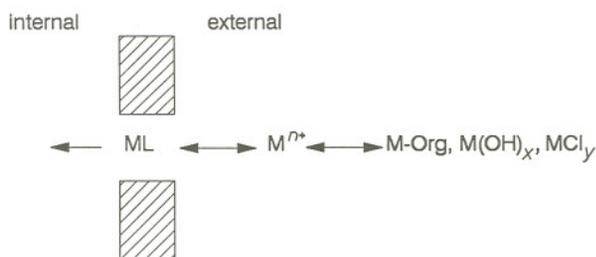
---

## Uptake of Dissolved Metals

### Uptake rate Membrane permeable M complex

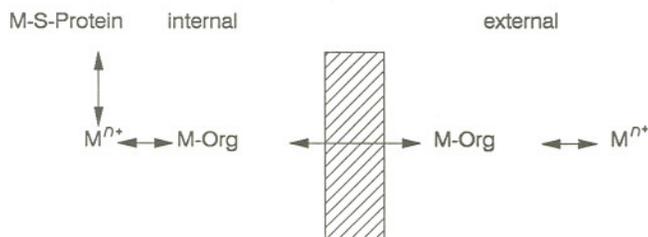
(a) Nutrient metal uptake systems

- Ligand associated with facilitated transport system (L), complexes metal for transport.
- $M^{n+}$  can be "mistaken" for nutrient metals, e.g. Zn, Mn.



(b) Passive diffusion through membrane

- Membrane permeable species diffuse passively through plasma membrane.
- Neutral species (e.g. M-Org) may be most permeable.



**Figure 13.4** Conceptual diagram illustrating the mechanisms of trace metal assimilation by organisms. Two mechanisms are thought to be important: (a) facilitated transport and (b) passive diffusion. Ionic metals may be "mistaken" for nutrient metals allowing transport via protein ligands complex in the facilitated transport system. Neutral species probably occurring as metal-organics may diffuse passively through the plasma membrane.

In general, it is difficult to assess the speciation of trace metals. Our understanding of complexation reactions with inorganic ligands is, for the most part, good because of the availability of high quality thermodynamic data and the widespread application of chemical equilibrium models (Jenne, 1979; Ball *et al.*, 1980; Morel, 1983). While complexation with organic ligands is recognized as being important in trace metal speciation in freshwaters, little direct information is available.

Thermodynamic data are available to describe complexation of trace metals with well-defined organic ligands (e.g. amino acids, citrate, oxalate, salicylate), but concentrations of these solutes are generally low and they are readily oxidized in the natural environment (Smith, 1976; Morel, 1983; Thurman, 1985; Stevenson and Fitch, 1986). Of more importance are polycarboxylic aromatic humic and fulvic acids (Thurman, 1985). However, these materials are poorly characterized with respect to  $H^+$  and metal-binding reactions. As an alternative, investigators have attempted to measure directly the inorganic/organic speciation of trace metals in solution by a number of operationally defined techniques. These approaches include size exclusion (dialysis, ultrafiltration), charge separation (ion exchange chromatography), chemical reactivity (use of complexing agents, anodic stripping voltammetry) and direct measurements such as using ion selective electrodes. Only rarely have determinations of chemical speciation been verified by independent measurements (e.g. Driscoll, 1984; McAvoy *et al.*, 1992).

The speciation of solid phase trace metals is often an important consideration in biogeochemical studies. The distinction between aqueous and particulate metal concentrations is not trivial. For example, Kennedy *et al.* (1974) found that the measured concentration of "dissolved" Al, Fe, Mn and Ti decreased with pore size used in filtration. Note that the distinction between "dissolved" and "particulate" trace metals is always operational, because very small particles pass through the filter regardless of the pore size used. Several investigators have developed selective extraction techniques to determine the "speciation" of trace metals associated with solid phase materials (Tessier *et al.*, 1979; Shannon and White, 1991). Like aqueous speciation measurements, these are operationally defined.

## 13.2 CASE STUDIES—MERCURY, LEAD, ALUMINIUM AND URANIUM

### 13.2.1 HG CYCLING AT LAKE GÅRDSJÖN

#### 13.2.1.1 Site description and approach

The Lake Gårdsjön research area (58°04'N, 12°03'E) is located in southwestern Sweden, in a region receiving elevated deposition of acidity and mercury deposition (Grennfelt *et al.*, 1985; Hultberg and Grennfelt, 1992; Iverfeldt, 1991a,b). In 1987, an investigation was initiated on the biogeochemistry of Hg in forested catchments. This study initially included a reference watershed (F1 3.6 ha) and was later expanded to include two smaller catchments (G1 0.6 ha and G2 0.5 ha; Iverfeldt, 1991b). The catchments G1 and G2 have a southwest aspect and therefore, due to prevailing winds, receive higher inputs of atmospheric deposition than the reference catchment (F1). The climate is relatively humid and marine. The soils are shallow podzols (Olsson *et al.*, 1985) and are underlain by granitic bedrock. Lake Gårdsjön is a remote oligotrophic lake, which is representative of the region.

Initial work has focused on quantifying concentrations and transport of methyl Hg ( $Hg_m$ ) and total Hg ( $Hg_t$ ) in surface runoff from the reference (F1) catchment. Collection of precipitation and throughfall event samples was initiated at the end of 1987. For a period of about one year, various operationally defined Hg fractions, as well as  $Hg_m$  and  $Hg_t$  were measured. Detailed descriptions of sampling equipment and procedures for collection of Hg samples are given elsewhere (Lee and Hultberg, 1990; Lee and Iverfeldt, 1991; Iverfeldt, 1991b). The analytical methods used in this investigation have been reported previously (Lee, 1987; Lee and Mowrer, 1989; Lee and Hultberg, 1990; Iverfeldt, 1988, 1991a,b). In this case study, concentrations of Hg and to some extent  $Hg_m$  in precipitation, throughfall, litterfall and surface waters are presented and discussed relative to values recently reported in the literature. Moreover, fluxes and pools of Hg in the Lake Gårdsjön catchment are summarized.

### 13.2.1.2 Results and discussion of the Hg cycle

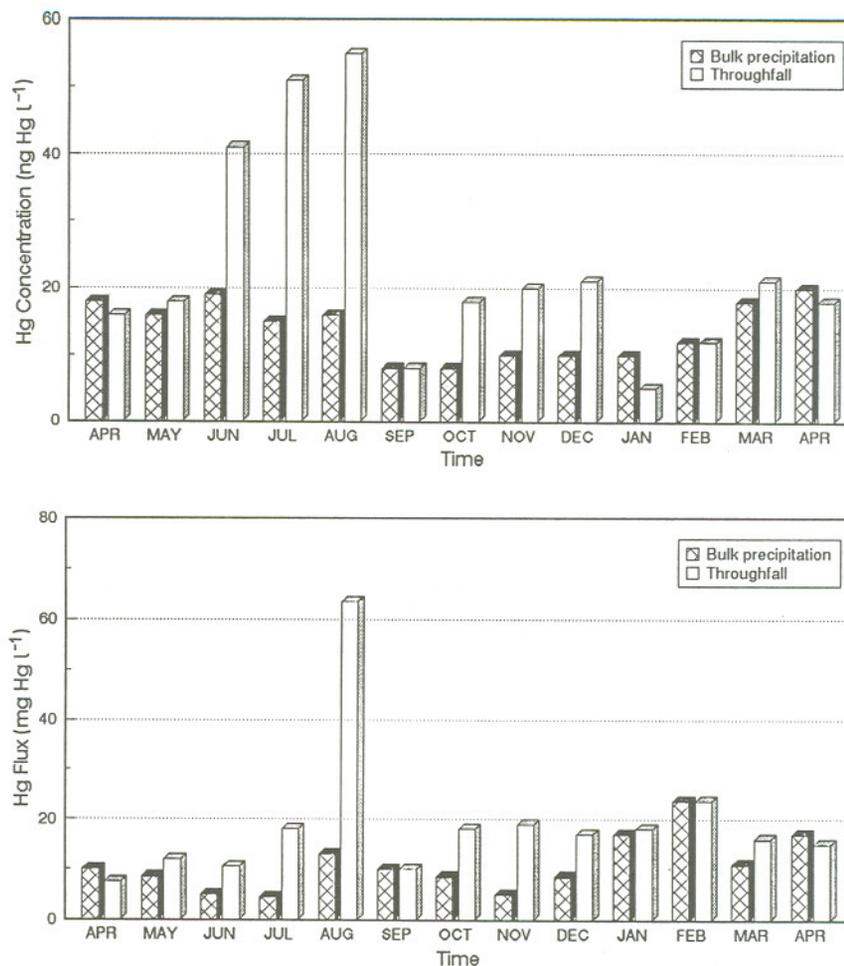
In 1989–1990, throughfall inputs of  $Hg_t$  to catchments G1 and G2 at the Lake Gårdsjön research area varied between 6.4 and 63.4 mg Hg ha<sup>-1</sup> month<sup>-1</sup> over a 13-month period (Iverfeldt, 1991b; Figure 13.5). During the same period, the monthly fluxes of  $Hg_t$  in bulk precipitation were found in the range 3.8 to 23.2 mg Hg<sub>t</sub> ha<sup>-1</sup> month<sup>-1</sup> (Figure 13.5). Concentrations of  $Hg_t$  in the forest canopy throughfall water showed a seasonal variation with the highest values during May to December (i.e. more or less during the growing season; Figure 13.5). In the bulk deposition, concentrations of  $Hg_t$  occurred during February to June (Figure 13.5). Assuming the difference between throughfall and bulk deposition measurements (net removal) can be used to estimate inputs of dry deposition, the results suggest that the annual dry deposition of  $Hg_t$  to a spruce stand in throughfall water can be 50% of the wet deposition, about 0.06 compared to 0.12 g Hg ha<sup>-1</sup> year<sup>-1</sup>, respectively, in this area (Iverfeldt, 1991b; Figure 13.5).

The deposition of  $Hg_m$  to the Gårdsjön area can be estimated from measurements in bulk precipitation and throughfall event samples collected in 1988 (Lee and Iverfeldt, 1991). No significant difference was found between the  $Hg_m$  flux in bulk deposition and throughfall (0.0023 compared to 0.0024 g ha<sup>-1</sup> year<sup>-1</sup>), suggesting that methylation/demethylation does not occur in the canopy.

It is assumed that the flux of  $Hg_t$  to the forest floor can be quantified by throughfall and litter fall inputs, although there is considerable uncertainty in these estimates (Iverfeldt, 1991b). The total  $Hg_t$  flux to the forest floor of the catchments in the Lake Gårdsjön area was of the order 0.4 g Hg<sub>t</sub> ha<sup>-1</sup> year<sup>-1</sup> (Figure 13.6).

Very few data exist on the uptake of Hg by vegetation. A net uptake of Hg by the above-ground biomass is assumed to be close to zero for Lake Gårdsjön watersheds (Iverfeldt, 1991b). No measurements of the net  $Hg_t$  uptake by the below-ground biomass have been conducted at this area.

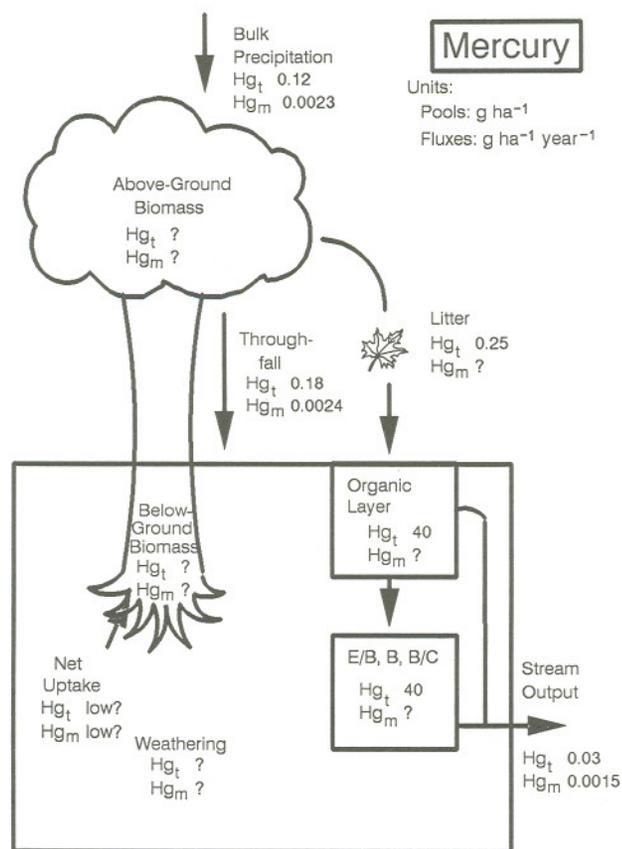
The  $Hg_t$  pool for the Gårdsjön area can be estimated from other studies (Aastrup *et al.*, 1991). The amount of  $Hg_t$  in the organic layer was about 40 g ha<sup>-1</sup>. The



**Figure 13.5** (a) Throughfall and bulk precipitation fluxes of  $Hg_t$  to the Lake Gårdsjön area, 1989/90. (b) Seasonal variation in the  $Hg_t$  concentration in throughfall and bulk precipitation in the Lake Gårdsjön area, 1989/90. Reproduced from Inverfeldt, 1991 by permission of Kluwer Academic Publishers.

mineral soil horizons (E/B, B, B/C) also contained about  $40 \text{ g ha}^{-1}$ , for a total soil pool of about  $80 \text{ g ha}^{-1}$ . For the Lake Gårdsjön research area, measurements of the  $Hg_m$  pool in soil have not yet been made.

Much of the  $Hg_t$  pool at Lake Gårdsjön watersheds was found in the upper part of the soil, which is rich in organic matter (Figure 13.6). This pattern is likely due to an elevated atmospheric deposition of  $Hg_t$  over an extended period and immobilization of Hg by organic functional groups and accumulation of organic matter as part of the soil-forming process (e.g. Aastrup *et al.*, 1991). The retention of Hg in the mor layer was almost complete due to the very strong association between



**Figure 13.6** Detailed budget of Hg for experimental forested catchments at the Lake Gårdsjön research area. Shown are fluxes and pools of total Hg ( $\text{Hg}_t$ ) and methyl Hg ( $\text{Hg}_m$ )

$\text{Hg}_t$  and humic substances (Aastrup *et al.*, 1991; Lee and Iverfeldt, 1991; Figure 13.6).

The  $\text{Hg}_t$  and  $\text{Hg}_m$  output from three catchments in the Lake Gårdsjön area are currently being studied. From preliminary analyses, the runoff export was about  $0.03 \text{ g Hg}_t \text{ ha}^{-1} \text{ year}^{-1}$ . This value lies within the range of  $0.008$  to  $0.059 \text{ g Hg ha}^{-1} \text{ year}^{-1}$ , derived from a number of catchment studies in Sweden (Johansson and Iverfeldt, 1991). The output of  $\text{Hg}_m$  from catchment F1 in the Lake Gårdsjön area has been reported (Lee and Hultberg, 1990) to be  $0.0015 \text{ g Hg ha}^{-1} \text{ year}^{-1}$ . This is substantially lower than the input to the catchments. There appear to be an ongoing net accumulation of  $\text{Hg}_m$  in the terrestrial ecosystem, similar to the pattern previously reported for  $\text{Hg}_t$  (e.g. Johansson and Iverfeldt, 1991). Thus, there is no evidence for the presence of methylation processes in the soil (Figure 13.6).

There exists evidence of a coupling between the  $Hg_t$  and  $Hg_m$  concentrations in surface runoff water (Lee and Iverfeldt, 1991). The concentration of  $Hg_m$  in surface runoff is of special interest, since this pathway is a major component of the total mercury loading to a lake (drainage lake). Moreover,  $Hg_m$  is the form of Hg that is enriched in the aquatic food web and subsequently transferred to the human population through fish consumption. A close correlation was found between the water colour (i.e. dissolved humic substances) and the concentration of  $Hg_m$  in surface runoff from small catchments, independent of the total pool of Hg in the soil mor layer (Lee and Hultberg, 1990; Lee and Iverfeldt, 1991). A similar empirical relationship was also evident between water colour and  $Hg_t$  (Iverfeldt and Johansson, 1988; Johansson and Iverfeldt, 1991; Lee and Iverfeldt, 1991). The marked co-variation between water colour and concentrations of  $Hg_m$  and  $Hg_t$ , supports the assumption that the transport of dissolved organic matter from the soil with drainage water is regulating the flux of  $Hg_m$  and  $Hg_t$  from the terrestrial to the aquatic ecosystem.

Given that the variation in the flux of dissolved organic carbon (DOC) in surface runoff water is the result of interrelated biological, geochemical and hydrological processes, periods of elevated concentrations of organic matter and  $Hg_t$  as well as  $Hg_m$  can be explained. High DOC concentrations observed during late summer and early autumn are likely the result of microbial decomposition of the soil organic material and subsequent release of organic solutes (e.g. dissolved fulvic and humic acids or colloidal organic forms). These materials strongly bind with  $Hg_t$  (or specifically  $Hg_m$  and other Hg forms) and thus facilitate their transport in drainage waters. Elevated  $Hg_m$  and  $Hg_t$  exports via streamwater were observed during periods of high groundwater stage and elevated surface runoff, especially when preceded by a long and dry summer period (Iverfeldt and Johansson, 1988; Lee and Hultberg, 1990). These observations suggests that export of Hg from the terrestrial ecosystem is enhanced by transport along shallow flowpaths.

A weak negative correlation between the ratio  $Hg_m/Hg_t$  and pH in surface runoff water may indicate a shift in mobility between methyl and non-methyl forms (Lee and Iverfeldt, 1991). If true, then decreases in pH caused by acidification processes may enhance the drainage output of  $Hg_m$ , without affecting the other forms of Hg. This pattern may occur because  $Hg_m$  is largely associated with low-molecular humic substances while inorganic Hg forms are largely associated with high-molecular humic materials (Lee and Iverfeldt, 1991). In theory, the output of  $Hg_m$  may shift following decreases in pH, if the composition of organic matter in surface runoff is altered in favour of more low-molecular humic fractions; even if the total amount of organic matter is unaffected.

### 13.2.2 THE Pb AND Al CYCLE AT HUBBARD BROOK, NH, USA

At the Hubbard Brook Experimental Forest in New Hampshire, the small watershed approach has been used to study element cycling since, 1963 (Likens *et al.*, 1977). By monitoring precipitation inputs and stream outputs from small water-

sheds that are essentially free of deep seepage, it is possible to construct accurate element balances. The precipitation and stream monitoring programme at Hubbard Brook has been supplemented by detailed studies of soil and soil solution chemistry, as well as forest floor and vegetation dynamics. The objective in this case study was to compile and summarize available information on the biogeochemistry of two trace metals, Pb and Al, for the HBEF.

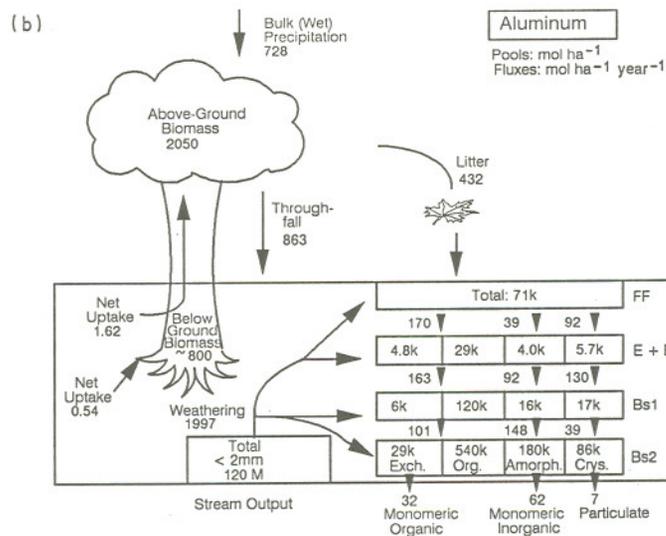
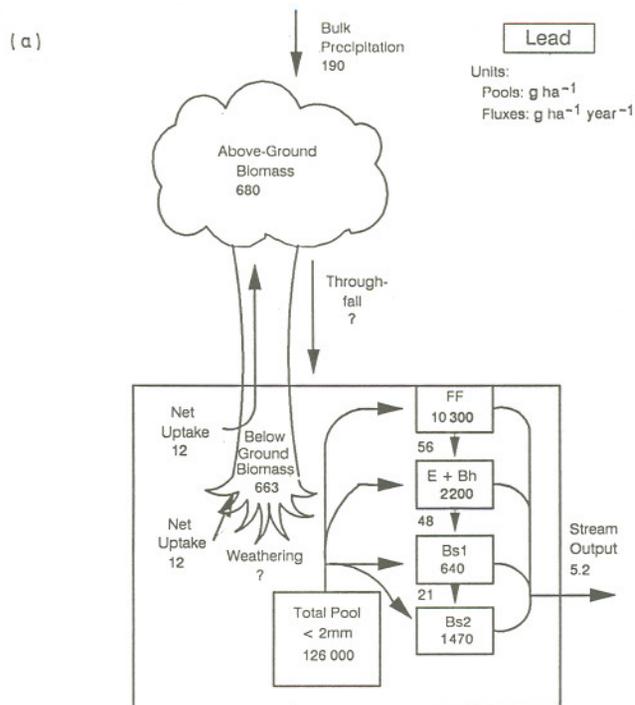
### 13.2.2.1 Site description and approach

The Hubbard Brook Experimental Forest (HBEF) is located in the White Mountains of New Hampshire (43°56'N, 71°45'W). This investigation was conducted in watershed 6 (W6), the biogeochemical reference watershed at Hubbard Brook (13.23 ha, elevation 546–791 m). The watershed has a southeasterly aspect and a slope of 20–30% (Likens *et al.*, 1977). Soils at the site are acidic, well-drained Spodosols (Haplorthods and Fragiorthods), with a well-drained organic layer (3–15 cm). They are underlain with variable depths of glacial till and impervious bedrock (Littleton formation; schist) (Likens *et al.*, 1977). Soils are shallow at high elevations and increase in depth with decreasing elevation (Lawrence *et al.*, 1986).

Climate at the HBEF is cool temperate, humid continental with mean July and January temperatures of 19°C and –9°C, respectively (at 450 m elevation). Mean annual precipitation is approximately  $1423 \pm 197$  mm (mean  $\pm$  std. dev.), with 25–33% of the total occurring as snow (Likens *et al.*, 1977; Federer *et al.*, 1990). Mean annual streamflow from W6 is  $896 \pm 213$  mm (Federer *et al.*, 1990).

Northern hardwood vegetation dominates most of W6, consisting of American beech (*Fagus grandifolia* Ehrh.), yellow birch (*Betula alleghaniensis* Britt.) and sugar maple (*Acer saccharum* Marsh.) from 500–730m. Coniferous vegetation, consisting primarily of red spruce (*Picea rubens* Sarg.) and balsam fir (*Abies balsamea* (L.) Mill) dominates at elevations above 730 m. The HBEF was logged between 1909–1917, and there is no evidence of recent fire (Bormann and Likens, 1979; Whittaker *et al.*, 1979).

This section is a summary of data from trace metal studies that have been conducted at the HBEF. Data collected include fluxes and concentrations of trace metals in bulk precipitation, streams (Smith and Siccama, 1981; Smith *et al.*, 1986), soil solutions (Fuller *et al.*, 1987; Driscoll *et al.*, 1988), forest floor (Smith and Siccama, 1981; Johnson, 1989), mineral soil (Johnson *et al.*, 1991) and vegetation (Whittaker *et al.*, 1979). Details of sampling and analytical methods for these studies are provided in the above papers. Trace metal biogeochemistry from these studies is summarized here through element budgets (Figure 13.7). Ecosystem element pools include: above- and below-ground vegetation biomass, the total forest floor content, exchangeable metals in E+Bh horizons (0–10 cm), Bs1 horizon (10–20 cm) and Bs2 horizon soil (>20 cm), and the total mineral soil pool (<2 mm size fraction). Ecosystem fluxes include bulk precipitation inputs, uptake by biomass, throughfall, solution fluxes through the Oa, Bh and Bs horizons and



stream outflow. Weathering fluxes are not determined directly, but are calculated as differences in the mass balance. In these calculations it is assumed that readily available soil element pools are at steady state.

### 13.2.2.2 Results and discussion of the Pb cycle

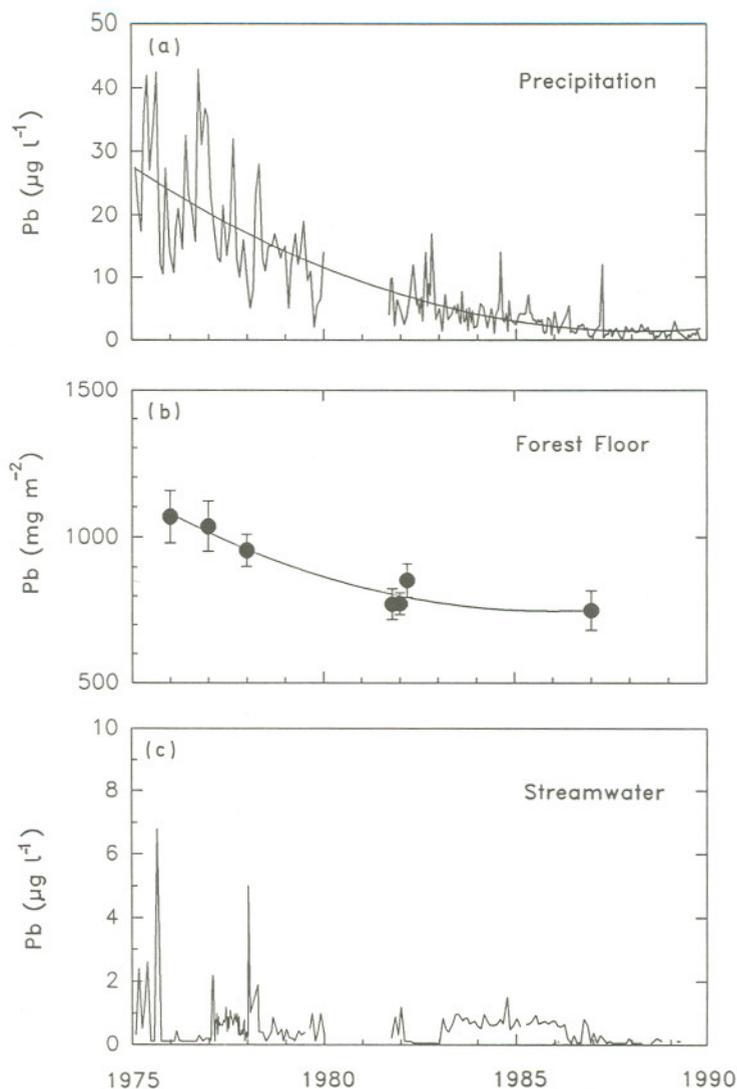
Smith and Siccama (1981) previously developed a Pb budget for Hubbard Brook. With additional data on soil (Johnson, 1989) and soil solution (Driscoll *et al.*, 1988) chemistry, it is possible to expand this analysis (Figure 13.7a). Atmospheric deposition of Pb has been declining since Pb was added to the precipitation monitoring programme at Hubbard Brook in 1975 (Smith and Siccama, 1981; Smith *et al.*, 1986; Figure 13.8a). This decline is consistent with the decreased use of leaded petrol over the same period (Smith *et al.*, 1986; US Environmental Protection Agency, 1984).

The mineral soil and forest floor were the major pools of Pb in the ecosystem (Figure 13.7a). Mineral soil pools (<2 mm size fraction) are generally the largest element pools for the HBEF (Likens *et al.*, 1977), however this includes relatively unreactive soil minerals. Deposition and accumulation of Pb in the forest floor have been the focus of a number of investigations (Johnson *et al.*, 1982; Smith and Siccama, 1981; Friedland *et al.*, 1984; Friedland and Johnson, 1985). At Hubbard Brook, much of the Pb entering the ecosystem from the atmosphere appears to be retained in the forest floor. Concentrations and fluxes of Pb in bulk deposition are much greater than in Oa horizon leachate. Solution concentrations and fluxes of Pb decrease through the soil profile (Driscoll *et al.*, 1988) and losses in streamwater are low. Driscoll *et al.* (1988) noted that there was a strong correlation between concentrations of Pb and dissolved organic carbon (DOC) in soil solutions and streamwater at Hubbard Brook. Moreover, Smith and Siccama (1981) showed that acid-extractable Pb concentrations were elevated in the forest floor (89 mg kg<sup>-1</sup>), low in the E horizon (5.2 mg kg<sup>-1</sup>), intermediate in the B horizon (12 mg kg<sup>-1</sup>) and low in the C horizon (8.7 mg kg<sup>-1</sup>). This pattern is consistent with decomposition and release of DOC from the forest floor, transport through the E horizon and deposition in the B horizon which occurs as part of soil development (the podzolization process). Mobilization and immobilization of Pb at Hubbard Brook appears to be associated with the dynamics of soil organic matter.

Pools and uptake of Pb in vegetation at Hubbard Brook were small. Lead is not a plant nutrient (Figure 13.1) and therefore it is not surprising that uptake was low.

---

**Figure 13.7** Detailed budgets for Pb (a) and Al (b) for the biogeochemical reference watershed at the Hubbard Brook Experimental Forest, NH. For the Al budget, soil pools include (left to right): exchangeable Al (KCl-extractable), organic Al (pyrophosphate-extractable), amorphous Al (oxalate-extractable), and crystalline Al (citrate-dithionate-bicarbonate-extractable).



**Figure 13.8** Temporal patterns of the concentration of Pb in the biogeochemical reference watershed at the Hubbard Brook Experimental Forest, NH: (a) bulk precipitation; (b) the forest floor; (c) streamwater.

The calculated weathering release for Pb at Hubbard Brook is negative ( $-174 \text{ g ha}^{-1} \text{ year}^{-1}$ ). This pattern is likely due to changes in mineral soil Pb pools over the study period. There has been marked decline in the Pb concentration of the forest floor; concurrently with decline in atmospheric inputs during the past 15 years (Figure 13.8b).

There has been some concern over the effects of elevated inputs of Pb to forest ecosystems (Reiners *et al.*, 1975; Johnson *et al.*, 1982; Smith and Siccama, 1981; Friedland and Johnson, 1985). These potential effects include leaching of Pb to surface waters (White and Driscoll, 1985), and mineralization and release of Pb in the forest floor following clearcutting disturbance (Smith and Siccama, 1981). Results from long-term monitoring at Hubbard Brook suggest that streamwater concentrations are very low (Figure 13.8c) and not a water quality concern (Smith and Siccama, 1981; Driscoll *et al.*, 1988). In addition, a study of Pb in soil solutions and streamwater following a commercial whole-tree harvest at Hubbard Brook showed that Pb was not released to drainage waters from clearcutting activities (Fuller *et al.*, 1988).

### 13.2.2.3 Results and discussion of the Al cycle

The Al cycle at Hubbard Brook is characterized by large internal pools (Figure 13.7b). Aluminium is the most abundant metallic element in the Earth's crust, so these pools largely occur as minerals and free Al fractions in soil. Soil Al fractions include exchangeable Al (KCl-extractable), organic Al (pyrophosphate-extractable), amorphous Al (oxalate-extractable) and crystalline Al (citrate-dithionate-bicarbonate extractable). Aluminium is not a plant nutrient (Figure 13.1) and therefore the rate of Al assimilation and cycling by vegetation is low.

At the HBEF, Al is characterized by mobilization from soil pools to drainage water. Drainage transport of Al occurs in three fractions: particulate Al, organic monomeric Al (organic complexes of Al) and inorganic monomeric Al (inorganic complexes of Al including aquo Al,  $\text{OH}^-$ ,  $\text{F}^-$  and  $\text{SO}_4^{2-}$  complexes). The speciation of dissolved Al is particularly significant because inorganic forms of Al are thought to be toxic to plants and aquatic organisms, while organic and particulate Al are not considered toxic (Driscoll *et al.*, 1980; Parker *et al.*, 1989). Precipitation and throughfall fluxes of Al were relatively low. This Al was largely in a particulate form and probably associated with wind-blown dust. Soil solutions draining the O horizon showed elevated fluxes and concentrations of organic and particulate Al, while concentrations and fluxes of inorganic monomeric Al were low. It seems likely that Al is largely mobilized from the forest floor by organic acid dissolution of soil minerals (April *et al.*, 1993). Minerals occur in the forest floor through the dust inputs and mixing of soil profiles due to falling of wind-thrown trees. Concentrations and fluxes of organic monomeric Al decreased as soil water passed through the mineral soil, coinciding with increases in pH. Immobilization of dissolved organic carbon (DOC) in the mineral soil also likely contributed to low streamwater concentrations and fluxes of organic monomeric Al. As concentrations and fluxes of organic monomeric Al declined within the soil profile, inorganic monomeric Al increased. It is not clear whether the source of inorganic monomeric Al is decomplexation of organic monomeric Al, dissolution of free Al in soil, or both processes. Inorganic monomeric Al was the dominant form of Al in Bs horizon drainage waters and streamwaters.

Patterns of Al concentration and speciation in drainage waters have implications for potential Al toxicity to plants and aquatic organisms. Aluminium occurred largely in the organic monomeric form in the upper soil horizons where the density of fine roots is greatest (Wood, 1980). Despite the low pH of the upper soil horizon, concentrations of aquo Al were low because of complexation by organic ligands. Since aquo Al is generally considered to be the toxic species of Al to plants (Parker *et al.*, 1989), one would assume the potential for Al toxicity to plants is low. However, Parker *et al.* (1989) reported that low molecular weight Al polymers are the most toxic form of Al to plants. Only recently has the existence of polymeric Al in natural soil waters been demonstrated (Hunter and Ross, 1991). The relevance of these species to Al toxicity to forest vegetation is not known. In W6 drainage waters (Figure 13.7b), polymeric Al, which would be included in the particulate fraction, showed the largest concentrations and fluxes in the upper soil horizons.

Elevated concentrations of inorganic monomeric Al in streamwater are potentially toxic to aquatic organisms. Elevated inputs of strong inorganic acids from atmospheric deposition in excess of the ability of the terrestrial environment to neutralize these inputs through the supply of basic cations, result in the release of inorganic monomeric Al and export to surface waters (Johnson *et al.*, 1981; Lawrence *et al.*, 1986). Significant concentrations of inorganic monomeric Al have only been reported in acid-sensitive waters that receive elevated inputs of strong inorganic acids (Driscoll *et al.*, 1988; Driscoll and Schecher, 1990). Concentrations of inorganic monomeric Al in W6 streamwater are well above concentrations reported to be toxic to fish ( $5 \mu\text{mol l}^{-1}$ ; Muniz and Leivestad, 1980; Mount and Marcus, 1989).

### 13.2.3 URANIUM CYCLE AT FLODELLE CREEK, WASHINGTON, USA

Under favourable climatic, geomorphic and geologic conditions, wetlands in watersheds are capable of storing significant quantities of trace elements. In order to evaluate the role of wetlands in moderating drainage water chemistry as well as the effects of wetland disturbance, the extent of trace metal storage and processes controlling immobilization must be quantified. To illustrate these issues, detailed geologic and geochemical studies are summarized of U in bedrock, soils, water, trees and valley-floor deposits in a small ( $4.2 \text{ km}^2$ ) catchment of the north fork of Flodelle Creek in northeastern Washington ( $48^{\circ}33'N$ ,  $117^{\circ}34'W$ ). Typically, U is leached from bedrock under well oxygenated conditions, accumulates in organic-rich areas under reducing conditions, and may be remobilized if  $O_2$  is introduced, such as from wetland disturbance (Garrels and Christ, 1965).

#### 13.2.3.1 Site description and approach

The catchment basin of the north fork of Flodelle Creek receives about 60–75 cm of precipitation each year. Topographic relief in the drainage is about 183 m and the slopes are generally 30–65%. The slopes are heavily forested, with douglas fir

(*Pseudotsuga menziesii*) occurring as the dominant species. The valley floor is vegetated with willow, alder, incense cedar, subalpine fir, and, in open areas, sedges, forbs and grasses. Bedrock in the drainage basin is a two-mica quartz monzonite that is fractured and faulted locally and is mostly covered on valley slopes by as much as 2m of sandy glacial till, thin volcanic ash and minor loess. Glacial till was deposited about 13 000–15 000 years BP. The till is composed mostly of the underlying quartz monzonite. Soils on the slopes are poorly developed, a thin (0–3 cm) organic horizon overlies a silt loam of variable thickness and a deeper sandy stony loam. Groundwater on the valley slopes moves along the base of the sandy till just above the till–bedrock contact and in fractures within the bedrock. Organic-rich sediments have accumulated in small wetlands, shallow beaver ponds, floodplains and stream channels along the valley floor, varying from about 1 m thick near the drainage divide to about 4 m thick in the lower part of the catchment basin. These sediments range from mucky peat (50–60 weight per cent organic matter) to clay, silt and sand of lesser organic content.

#### 13.2.3.2 Results and discussion of the U cycle

The major source of U in this catchment is the anomalously uraniferous bedrock ( $15.8 \pm 2.7 \text{ mg kg}^{-1}$ ; 13 samples), and the overlying till and volcanic ash. There is no evidence of significant atmospheric contributions of U to the catchment. Although minor amounts of U remain stored locally in the organic-rich soil horizon near springs on the hillslopes, and trace amounts are stored in trees, most of the U weathered from bedrock, till and ash, migrates downslope in shallow groundwater ( $17\text{--}320 \mu\text{g U l}^{-1}$ ) from which it is trapped and stored in the valley floor fill of the catchment basin, or it migrates out of the catchment basin in surface water. Uranium is entrapped primarily by adsorption on organic matter in the  $\text{U}^{6+}$  state in the highly permeable upper 1 m of the valley fill. Where the permeability of the valley fill is reduced by compaction, the sediment becomes isolated from groundwater and no longer immobilizes additional U.

Hydrologic data are insufficient to conduct a mass balance for U in this catchment. However, data for core and outcrop suggest that granitic bedrock has lost about  $10 \text{ mg U kg}^{-1}$  from weathering. Losses from till may be comparable since it is largely locally derived, and the U concentration of soil developed on till ( $4.8 \text{ mg U kg}^{-1}$ ) is comparable to weathered rock ( $5.9 \pm 4.2 \text{ mg U kg}^{-1}$ ). If the upper 2 m of till and bedrock have lost about  $10 \text{ mg U kg}^{-1}$  over the area of the catchment, then, assuming an average density of  $2.3 \text{ g cm}^{-3}$ , about 200 tonnes of U have been lost from bedrock since glaciation. This value is less than the estimated 500 tonnes of U stored in the valley floor. This calculation suggests that weathering of U from bedrock is deeper than the depth used in the calculations or that groundwater is leaching substantial quantities of U from deep bedrock fractures (Zielinski and Burruss, 1991). Moreover, it appears that a substantial portion of the U lost from bedrock, till and ash remains stored within the valley floor of the catchment.

The laboratory leaching studies suggest that U is loosely held on organic matter

within the sediment column. Disturbances to this system, such as acidification of drainage water, introduction of complexing agents or aeration could result in the remobilization of U and other metals from the organic-rich sediment and compromise the quality of local surface waters.

### 13.3 RECOMMENDATIONS FOR FUTURE RESEARCH

There have been very few ecosystem-level studies of trace metals. As a result, trace metal cycling in the environment is not well understood. This problem is the result of many factors, including difficulty in the accurate determination of trace metal concentrations due to contamination associated with sample collection, processing and analysis; limited understanding of the speciation of trace metals in aqueous and solid phases; limited understanding of the linkages between the cycling of trace metals and other element cycles; and the interaction of trace metals with terrestrial and aquatic organisms. As a result, the following recommendations have been made for future research activities:

1. Methods for determining the speciation of trace metals in solution and solid phases should be developed, improved and verified.
2. Stable and radioactive isotopes should be used to a greater extent in the study of trace metals in small catchments.
3. A better understanding of the processes controlling the aqueous concentrations of trace metals from solid phases should be obtained.
4. The role of dissolved organic carbon in regulating the concentration and transport of trace metals should be evaluated.
5. The role of the near-stream environment in regulating surface water concentrations of trace metals should be investigated.
6. A better understanding of the linkages between trace metals and biota should be developed.
7. Process-oriented models to predict the speciation, cycling and bioavailability of trace metals should be developed, applied and verified.
8. Laboratory, plot and ecosystem-level manipulations should be conducted to evaluate the biogeochemistry of trace metals.
9. Analysis of trace metals should be included in long-term monitoring programmes of small catchments.

### 13.4 REFERENCES

- Aastrup, M., Johnson, J., Bringmark, E., Bringmark, L. and Iverfeldt, Å. (1991) Occurrence and transport of mercury within a small catchment area. *Wat. Air Soil Poll.* **56**: 155–167.
- April, R., Keller, D. and Driscoll, C.T. (1993) Smectite and aluminum in Adirondack Spodosols. *Soil Sci.* (in review).

- Arimoto, R., Duce, R.A., Ray, B.J. and Uni, C.K. (1985) Atmospheric trace elements at Enewetak Atoll: 2. Transport to the ocean by wet and dry deposition. *J. Geophys. Res.* **D90**: 2391–2408.
- Ball, J.W., Nordstrom, D.K. and Jenne, E.A. (1980) *Additional and Revised Thermochemical Data for WATEQ-2 Computerized Model for Trace and Major Element Speciation, and Mineral Equilibria of Natural Waters*. US Geol. Survey Water Resource Investigations, Menlo Park, CA.
- Barrie, L.A., Lindberg, S.E., Chan, W.H., Ross, H.B., Arimoto, R. and Church, T.M. (1987) On the concentration of trace metals in precipitation. *Atmospheric Environment* **21**: 1133–1135.
- Bogges, W.R. (1977) Summary and conclusions. In *Lead in the Environment*. National Science Foundation, Washington, DC, pp. 267–272.
- Bohn, H., McNeal, B. and O'Connor, G. (1979) *Soil Chemistry*. Wiley-Interscience, New York.
- Bormann, F.H. and Likens, G.E. (1979) *Pattern and Process in a Forested Ecosystem*. Springer-Verlag, New York.
- Chan, W.H., Tang, A.J.S., Lusic, M.A., Vet, R.J. and Ro, C. (1982) An analysis of the impact of smelter emissions on precipitation quality and wet deposition in the Sudbury area: Sudbury environmental study event precipitation network results. SES 006/82, Ontario Ministry of Environment, Toronto, Ontario, Canada.
- Church, T.M., Tramontano, J.M., Scudlark, J.R., Jickells, T.D., Tokos, J.J. Jr, Knap, A.H. and Galloway, J.N. (1984) The wet deposition of trace metals to the western Atlantic Ocean at the mid-Atlantic coast and on Bermuda. *Atmospheric Environment* **17**: 1779–1786.
- Davidson, C.I., Chu, L., Grimm, T.C., Nasta, M.A. and Qamoos, M.P. (1982) Wet and dry deposition of trace metals onto the Greenland ice sheet. *Atmospheric Environment* **15**: 1429–1437.
- Driscoll, C.T. (1984) A procedure for the speciation of aqueous aluminum in dilute acidic waters. *Int. J. Environ. Anal. Chem.* **16**: 267–283.
- Driscoll, C.T. and Schecher, W.D. (1990) The chemistry of aluminum in the environment. *Environ. Geochem. Health* **12**: 28–49.
- Driscoll, C.T., Baker, J.P., Bisogni, J.J. and Schofield, C.L. (1980) Aluminum speciation and its effect on fish in dilute acidified waters. *Nature* **284**: 161.
- Driscoll, C.T., Fuller, R.D. and Simone, D.M. (1988) Longitudinal variations in trace metal concentrations in a northern forested ecosystem. *J. Environ. Qual.* **17**: 101–107.
- Federer, C.A., Flynn, L.D., Martin, C.W., Hornbeck, J.W. and Pierce, R.S. (1990) *Thirty Years of Hydrometeorologic Data at the Hubbard Brook Experimental Forest*. Gen. Tech. Rep. NE-141. US Dept. of Agriculture, Forest Service, Northeastern Forest Experiment Station, Radnor, PA, 44 pp.
- Fitzgerald, W.F. and Watras, C.J. (1989) Mercury in surficial waters of rural Wisconsin lakes. *Sci. Total Environ.* **87/88**: 223–232.
- Friedland, A.J. and Johnson, A.H. (1985) Lead distribution of fluxes in a high-elevation forest in northern Vermont. *J. Environ. Qual.* **14**: 332–336.
- Friedland, A.J., Johnson, A.H., Siccama, T.G. and Mader, D.L. (1984) Trace metal profiles in the forest floor of New England. *Soil Sci. Soc. Am. J.* **48**: 422.
- Fuller, R.D., Driscoll, C.T., Lawrence, G.B. and Nodvin, S.C. (1987) Processes regulating sulfate flux after whole-tree harvesting. *Nature* **325**: 707.
- Fuller, R.D., Simone, D.M. and Driscoll, C.T. (1988) Forest clearcutting and effects on trace metal concentrations: spatial patterns in soils solutions and streams. *Wat. Air Soil Poll.* **40**: 185.
- Garrels, R.M. and Christ, C.L. (1965) *Solution, Minerals and Equilibria*. Freeman, Cooper and Co., San Francisco, CA. 450 pp.

- Garrels, R.M., Mackenzie, F.T. and Hunt, C. (1975) *Chemical Cycles and the Global Environment*. William Kaufman, Inc., Los Altos, CA. 206 pp.
- Gosz, J.R., Likens, G.E. and Bormann, F.H. (1976) Organic matter and nutrient dynamics of the forest floor in the Hubbard Brook Forest. *Oecologia (Berl.)* **22**: 305–320.
- Grennfelt, P., Larsson, S., Leyton, P. and Olsson, B. (1985) Atmospheric deposition in the Lake Gårdsjön area, SW Sweden. *Ecol. Bull. (Stockholm)* **37**: 101–108.
- Heinrichs, N. and Mayer, R. (1977) Distribution and cycling of major and trace elements in two central European forest ecosystems. *J. Environ. Qual.* **6**: 402–407.
- Heinrichs, N. and Mayer, R. (1980) The role of forest vegetation in the biogeochemical cycle of heavy metals. *J. Environ. Qual.* **9**: 111–118.
- Hultberg, H. and Grennfelt, P. (1992) Sulphur and seasalt deposition as reflected by throughfall and runoff chemistry in forested catchments. *Environmental Pollution* **75**: 215–222.
- Hunter, D. and Ross, D.S. (1991) Evidence for a phytotoxic hydroxyl-aluminum polymer in organic soil horizons. *Science* **251**: 1056–1058.
- Iverfeldt, Å. (1988) Mercury in the Norwegian fjord Framvaren. *Mar. Chem.* **23**: 441–456.
- Iverfeldt, Å. (1991a) Occurrence and turnover of atmospheric mercury over the Nordic countries. *Wat. Air Soil Poll.* **56**: 251–265.
- Iverfeldt, Å. (1991b) Mercury in forest canopy throughfall water and its relation to atmospheric deposition. *Wat. Air Soil Poll.* **56**: 553–564.
- Iverfeldt, Å. and Johansson, K. (1988) Mercury in run-off water from small watersheds. *Verh. Internat. Verein. Limnol.* **23**: 1626–1632.
- Jenne, E.A. (Ed.) (1979) *Chemical Modeling in Aqueous Systems*. American Chemical Society Symposium Series 93. American Chemical Society, Washington, DC.
- Jickells, T.D., Knap, A.H. and Church, T.M. (1984) Trace metals in Bermuda rainwater. *J. Geophys. Res.* **D89**: 1423–1428.
- Johansson, K. and Iverfeldt, Å. (1991) Factors influencing the run off of mercury from small watersheds in Sweden. *Verh. Internat. Verein. Limnol.* **24**: 2200–2204.
- Johnson, A.H., Siccama, T.G. and Friedland, A.J. (1982) Spatial and temporal patterns of lead accumulation in the forest floor in the northeastern United States. *J. Environ. Qual.* **11**: 577.
- Johnson, C.E. (1989) The chemical and physical properties of a northern hardwood forest soil: harvesting effects, soil–tree relations and sample size determination. Ph.D. Dissertation, University of Pennsylvania, Philadelphia, PA.
- Johnson, C.E., Johnson, A.H. and Siccama, T.G. (1991) Whole-tree clear-cutting effects on exchangeable cations and soil acidity. *Soil Sci. Soc. Am. J.* **55**: 502–508.
- Johnson, N.M., Driscoll, C.T., Eaton, J.S., Likens, G.E. and McDowell, W.H. (1981) Acid rain, dissolved aluminum and chemical weathering at the Hubbard Brook Experimental Forest, New Hampshire. *Geochim. Cosmochim. Acta* **45**: 1421.
- Kennedy, V.C., Zellweger, G.W. and Jones, B.F. (1974) Filter pore-size effects on the analysis of Al, Fe, Mn and Ti in water. *Water Resour. Res.* **10**: 785–790.
- Lawrence, G.B., Fuller, R.D. and Driscoll, C.T. (1986) Spatial relationships of aluminum chemistry in the streams of the Hubbard Brook Experimental Forest, New Hampshire. *Biogeochemistry* **2**: 115–135.
- Lee, Y-H. (1987) Determination of methyl- and ethylmercury in natural waters of sub-nanogram per liter using SCF-adsorbent preconcentration procedure. *Int. J. Environ. Anal. Chem.* **29**: 263–276.
- Lee, Y-H. and Hultberg, H. (1990) Methylmercury in some Swedish surface waters. *Environ. Toxicol. Chem.* **9**: 833–841.
- Lee, Y-H. and Mowrer, J. (1989) Determination of methylmercury in natural waters at the sub-nanograms per litre level by capillary gas chromatography after adsorbent preconcentration. *Anal. Chim. Acta.* **221**: 259–268.

- Lee, Y.-H. and Iverfeldt, Å. (1991) Measurement of methylmercury and mercury in runoff, lake and rain waters. *Wat. Air Soil Poll.* **56**: 259–268.
- Likens, G.E., Bormann, F.H., Pierce, R.S., Eaton, J.S. and Johnson, N.M. (1977) *Biogeochemistry of a Forested Ecosystem*. Springer-Verlag, New York, 146 pp.
- Lindberg, S.E. and Turner, R.R. (1988) Factors influencing atmospheric deposition, stream export, and landscape accumulation of trace elements in four forested watersheds. *Water, Air, and Soil Pollution*. **39**: 123–156.
- Lovett, G.M., Reiners, W.A. and Olson, R.K. (1982) Cloud droplet deposition in subalpine balsam fir forests: hydrologic and chemical inputs. *Science* **218**: 1303–1304.
- McAvoy, D.C., Santore, R.C., Shosa, J.D. and Driscoll, C.T. (1992) A comparison between pyrocatechol violet and 8-hydroxyquinoline procedures for determining aluminium fractions. *Soil Sci. Soc. Am. J.* **56**: 449–455.
- Miller, W.J., McFee, W.W. and Kelly, J.M. (1983) Mobility and retention of heavy metals in sandy soils. *J. Environ. Qual.* **12**: 579.
- Morel, F.M.M. (1983) *Principles of Aquatic Chemistry*. John Wiley & Sons, New York. 446 pp.
- Mount, D.R. and Marcus, M.D. (Eds) (1989) *Physiologic, Toxicologic and Population Responses of Brook Trout to Acidification*. EPRI En-6238, Electric Power Research Institute, Palo Alto, CA.
- Muniz, I.P. and Leivestad, H. (1980) Acidification-effects on freshwater fish. In Drabløs, D. and Tollan, A. (Eds): *Ecological Impact of Acid Precipitation*. SNSF, Oslo.
- Olsson, B.L., Hallbäck, L., Johansson, S., Melkerud, P.-A., Nilsson, S.I. and Nilsson, T. (1985) The Lake Gårdsjön area—physiographical and biological features. *Ecol. Bull. (Stockholm)* **37**: 10–28.
- OME (1985) *Annual Statistics of Concentration and Deposition—Cumulative Precipitation Monitoring Network, 1983*. ARB-087-85-AQM. Ontario Ministry of the Environment, Air Resources Branch, Toronto, Ontario, Canada.
- Parker, D.R., Zelazny, L.W. and Kinraide, T.B. (1989) Chemical speciation and plant toxicity of aqueous aluminum. In Lewis, T. (Ed.): *Environmental Chemistry and Toxicology of Aluminum*. Lewis Publishers, Chelsea, MI, pp. 117–146.
- Perdue, E.M., Beck, K.C. and Reuter, J.H. (1976) Organic complexes of iron and aluminum in natural waters. *Nature* **260**: 418.
- Reiners, W.A., Marks, R.H. and Vitousek, P.M. (1975) Heavy metals in subalpine soils of New Hampshire. *Oikos* **26**: 264.
- Ross, H.B. (1990) Trace metal deposition in Sweden: insight gained from daily wet only collection. *Atmospheric Environment* **24A**: 1292–1938.
- Shannon, R.D. and White, J.R. (1992) The selectivity of a sequential extraction procedure for iron oxyhydroxides and sulfides. *Biogeochemistry* **14**: 193–208.
- Siccama, T.G. and Smith, W.H. (1978) Lead accumulation in a northern hardwood forest. *Environ. Sci. Technol.* **12**: 593–594.
- Simkiss, K. and Taylor, M.G. (1989) Metal fluxes across membranes of aquatic organisms. *Rev. Aquat. Sci.* **1**: 174–188.
- Smith, W.H. (1976) Character and significance of forest tree root exudates. *Ecology* **57**: 324–331.
- Smith, W.H. and Siccama, T.G. (1981) The Hubbard Brook ecosystem study: biogeochemistry of lead in a northern hardwood forest. *J. Environ. Qual.* **10**: 323.
- Smith, W.H., Siccama, T.G. and Clark, S. (1986) Atmospheric deposition of heavy metals and forest health: and overview including a ten year budget for the input/output of seven heavy metals to a northern hardwood forest. FWS-87-02. Virginia Polytechnic Institute and State Univ., Blacksburg, VA.
- Steinnes, E. (1987) Impact of long-range atmospheric transport of heavy metals to the terrestrial environment in Norway. In Hutchinson, T.C. and Meema, K.M. (Eds): *Lead,*

- Mercury, Cadmium and Arsenic in the Environment*. SCOPE 31. John Wiley & Sons, Chichester, UK, 384 pp.
- Stevenson, F.J. and Fitch, A. (1986) Chemistry of complexation of metal ions with soil solution organics. In Huang, P.M. and Schnitzer, M. (Eds): *Interactions of Soil Minerals with Natural Organics and Microbes*. Spec. Publ. No. 17. Soil Science Society of America, Madison, WI.
- Swanson, K.A. and Johnson, A.H. (1980) Trace metal budgets for a forested watershed in the New Jersey Pine Barrens. *Water Resour. Res.* **16**: 373.
- Tessier, A., Campbell, P.G.C. and Bisson, M. (1979) Sequential extraction procedure for the speciation of particulate trace metals. *Anal. Chem.* **51**: 844–851.
- Thurman, E.M. (1985) *Organic Geochemistry of Natural Waters*. Martinus Nijhoff/Dr W. Junk. Dordrecht. 497 pp.
- Troutman, D. and Peters, N. (1982) Deposition and transport of heavy metals in three lake basins affected by acid precipitation in the Adirondack Mountains, NY. In *Energy and Environmental Chemistry 2*. Ann Arbor Science, Boston, MA, pp. 33–60.
- Turner, R.S., Wang, D.W. and Johnson, A.H. (1985) Biogeochemistry of lead in McDonald's Branch Watershed, New Jersey Pine Barrens. *J. Environ. Qual.* **14**: 305.
- US Environmental Protection Agency (1984) *National Air Quality and Emission Trends Report 1982*. EPA-450/4-84-002. Research Triangle Park, NC.
- Vong, R., Hansson, H.C., Ross, H.B., Covert, D.S. and Charlson, R.J. (1988) Northeastern Pacific submicrometer aerosol and rainwater composition: a multivariate approach. *J. Geophys. Res.* **D93**: 1625–1637.
- White, J.R. and Driscoll, C.T. (1985) Lead cycling in an acidic Adirondack lake. *Environ. Sci. Technol.* **19**: 1182.
- Whittaker, R.H., Likens, G.E., Bormann, F.H., Eaton, J.S. and Siccama, T.G. (1979) The Hubbard Brook ecosystem study: forest nutrient cycling and element behavior. *Ecology* **60**: 203.
- Wood, T.E. (1980) Biological and chemical control of phosphorus cycling in a northern hardwood forest. Ph.D. Thesis, Yale University, 205 pp.
- Zielinski, R.A. and Burruss, R.C. (1991) Petrogenesis and geology history of a uranium source rock: a case study in northeastern Washington. *Applied Geochemistry* **6**: 597–612.