SOIL SOLUTION CHEMISTRY AND METAL BUDGETS OF SPRUCE FOREST ECOSYSTEMS IN S. SWEDEN

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Abstract. The fluxes of metals (Na, K, Ca, Mg, Fe, Mn, Al, Cu, Zn, Pb, Cd, Cr, and Ni) in two spruce forest soils in S. Sweden were quantified using the lysimeter technique. Amounts in precipitation (dry and wet), throughfall, litterfall and annual accumulation in biomass were also quantified, as well as stores in soil and biomass. The metal concentrations of the soil solutions varied greatly according to season. The leaching of some metals (Fe, Cu, Pb, Cr, and organic forms of Al) was associated with the leaching of organic matter. These complexes were leached from the A horizon in considerable amounts. They were precipitated in the upper B horizon and only small amounts were transported further downward. By contrast, the leaching of Na, Mg, Ca, Mn, Cd, Zn, Ni, and inorganic forms of Al increased with increasing soil depth. The concentrations of these metals also increased with increasing soil solution acidity. The highest concentrations were often found at the transition to the C horizon. The amounts of Na, K, Mg, Ca, Mn, Al, Zn, Cd, Cr, and Ni leached from the rooting zone were found to be larger than the amounts deposited from the atmosphere, the main source of these metals being the mineral soil. The reverse was true of Pb, Cu, and Fe, the sink being the upper part of the B horizon.

1. Introduction

Knowledge of mobility and budgets of metals in forest soils is of great concern to environmental research. The amounts of metals, especially those available in trace quantities, that are cycled through different compartments of the forest ecosystems are still not well known. This knowledge is necessary in estimating cycling rates and long-term effects of metals from atmospheric deposition and in natural soil pools. The prevailing soil acidification (Butzke, 1981; Falkengren-Grerup, 1986; Hallbäcken and Tamm, 1985) will increase the release and leachability of many elements in soil (Norton, 1977; Bergkvist, 1986), those of anthropogenic as well as those of natural origin.

In the biologically most active part of the soil (litter and mor layer), the biological activity has proved to be highly sensitive to heavy metal pollution (Tyler, 1972; 1976a; Rühling and Tyler, 1973). It is necessary to know the metal balances in this horizon to be able to estimate the risk for adverse effects on nutrient mineralization, maybe also on primary productivity.

It is also of great concern to study the loss of metals from the entire soil profile. Ulrich (1975) claimed that there was a risk of increased soil acidification inducing Mg deficiency in forest trees due to extensive loss from soil of that nutrient. Raisch (1983) found Mg and Zn deficiency to prevail in five spruce forests in the Black Forest, Southwest FRG (Federal Republic of Germany). There are indications of diminishing nutrient pools in northeast USA (Norton *et al.*, 1980), central Europe (Raisch, 1983) and south Scandinavia (Nilsson, 1985a).

Forest decline is tending to become a widespread phenomenon in Europe (see Breloh

and Dieterle, 1985, for the situation in FRG) and in northeast USA (Bruck, 1985). In parts of central Europe nutrient deficiency seems to be a main factor in forest decline (Zöttl, 1985; Zöttl and Huettl, 1985) and fertilization with e.g. Mg improved growth and vigour rapidly.

Soil acidification is also considered to increase soil solution concentration of Al and heavy metals to toxic levels for the tree roots (Ulrich, 1983a; Matzner and Murach, 1985). These authors claim that every hypothesis trying to explain the present forest decline must include root decline as a major symptom. When spruce seedlings were grown at Al concentrations comparable to those found on several occasions in soil solutions of this study, root and shoot growth declined significantly (Rost-Siebert, 1983; Hutchinson *et al.*, 1985). Allium exposed to solutions from the A horizon of the Värsjö soil reported in this paper showed a marked decrease in root elongation as Al concentration in soil solution increased. In the B horizon soil solution with a high Al content (5 to 15 mg L^{-1}) no root growth at all was observed (Berggren and Fiskesjö, 1986).

The objectives of this study on spruce forest ecosystems are to: (a) quantify the deposition and biomass cycling of metals (Na, K, Mg, Ca, Fe, Mn, Al, Cu, Zn, Cd, Pb, Cr, and Ni) and H^+; (b) quantify the net loss of metals; (c) quantify metal budgets in different soil horizons; (d) study the differences in concentration of metals, H^+ and soluble organic compounds in soil solution from the various soil horizons; and (e) study the release and re-precipitation of organic compounds in the soil.

2. Site Description

The two areas studied are mature mixed-coniferous forests situated in southwest Sweden. Their main tree species is Norway spruce (*Picea abies*); some Scots pine (*Pinus sylvestris*) also occurs, but it does not influence the studied plots.

The southern study area (Värsjö) is situated 130 km NNE Lund, south Sweden. The mature stand is mainly even-aged, the spruce being ca. 80 yr, younger trees occurring in openings. The vegetation of the forest floor is patchy. Areas dominated by the grass *Deschampsia flexuosa* alternate with areas dominated by the dwarfshrub *Vaccinium myrtillus*, the mosses *Ptilium crista-castrensis* and *Pleurozium schreberi* or areas devoid of vegetation surrounding the tree stems. No shrub layer is usually present. The stand is developed on a low hill of sandy glacial till, originating from siliceous rocks, poor in carbonates. It is partly surrounded by mires. The soil is generally very deep and freely drained. Arable land is absent within several km of the study area. The soil is an Fe podzol, with a 7 to 10 cm purely organic litter + mor horizon ($A_{00} + A_0$), a 5 to 12 cm greyish mineral horizon (A_2), and a 25 to 35 cm illuvial horizon (B). The vertical distribution of organic matter, clay content and pH of the soil profile are shown in Table I.

The northern study area (Gårdsjön) is situated within the catchment of lake Gårdsjön on the Swedish west coast, ca. 40 km N Göteborg. Two microcatchments (3.3 and 3.6 ha), delimited by low hills, are studied. They have a similar vegetation. Norway

TABLE I

Content of organic C and clay (% dw), pH–H$_2$O and pH–KCl of the two studied soils at Värsjö and Gårdsjön. Sampling period: September at Värsjö and April at Gårdsjön.

Soil horizon	Soil depth (cm)	Organic carbon		Clay		pH–H$_2$O		pH–KCl	
		Värsjö	Gårdsjön	Värsjö	Gårdsjön	Värsjö	Gårdsjön	Värsjö	Gårdsjön
A$_{00}$ + A$_0$	0– 5	48	50	1.1	0.9	3.6	3.7	2.8	2.8
A$_1$ + A$_2$	5–15	9	18	1.6	1.8	3.8	3.9	3.0	3.1
B$_1$	15–35	2.9	5.3	1.0	1.8	4.2	4.3	4.0	4.0
B$_2$	35–55	1.8	3.2	0.3	1.4	4.4	4.5	4.4	4.3

spruce dominates with Scots pine, though only spruce occurs on the plots studied. The forest is 70 to 80 yr old. The field and ground layer is mainly dominated by the same dwarf shrubs, mosses and lichens as at Värsjö. The area as a whole is dominated by mixed coniferous forest alternating with lakes, exposed bedrock and mires. Many hills delimit several microcatchments. The soil is generally very shallow. Depths of 50 cm or less are characteristic of more than 50% of the area. An Fe-humus podzol is the most common soil type, but an Fe podzol with less organic matter in the B horizon can be found on top of the hills. A distinct C horizon is often lacking, the lower part of the B horizon being in direct contact with the bedrock. The texture is dominated by fine sand and silt (Olsson *et al.*, 1985). The depths of the soil horizons are similar to those of the Värsjö soil. The content of organic matter and clay, and the pH in different soil horizons, are shown in Table I.

The areas studied were extensively utilized during the 19th century for grazing and, possibly, hay-making. Most of the ground, at least at Värsjö, was cleared from stones already prior to the 19th century, nowadays evidenced by scattered fences of stone and moss-covered stone-heaps. In the Värsjö area no sources of pollutants of any great importance to the deposition of acid or metals occur within 50 km of the area. The area fulfills the demands of a 'background' site of southwestern Sweden. In the Gårdsjön area local sources occur. As close as 10 km from the study site, there is a petrochemical industry at Stenungsund. Here, an oil-fired power plant was also in operation some 10 yr ago.

3. Climate and Weather Conditions

The influence of the Atlantic gives a maritime climate to the southwest part of Sweden. The most frequent winds are from the southwest. The main part of the precipitation sum of the year falls in late autumn and winter. Mean annual precipitation of the southern study area (Värsjö) is ca. 785 mm according to data from four meteorological stations within 15 km (Ellesson, 1985). In the northern study area (Gårdsjön) the mean annual precipitation sum is 730 mm according to data from four official meteorological stations within 60 km. However, the precipitation is highly influenced by altitude and orography,

being 700 to 1200 mm in the region as a whole. The yearly precipitation sums during the period of investigation were never below normal (at Värsjö: 842, 1049, and 994 mm during 1979, 1980, and 1981, respectively; at Gårdsjön: 1162, 1082, 1250, 1235, and 975 mm during 1980, 1981, 1982, 1983, and 1984, respectively) though differences between seasons were great; part of the summers of 1982, 1983, and 1984 were drier than normal.

The years 1979, 1980, and 1981 were cold, yearly mean, summer and winter temperatures being below normal. Warmer than normal were 1982, 1983, and 1984 with warm summers and autumns. The length of the growing season (mean daily air temperature $> 6\ °C$, at least 4 days in succession) ranges between 200 and 210 days in both areas.

The snow cover is not often stable throughout the winter. However, the four winters from 1978/1979 until 1981/1982 were characterized by a considerable snow cover (20 to 50 cm) of above-normal duration. The other winters during the study were closer to average. In a normal year, the run-off amounts to 300 to 400 mm, the mean annual evapotranspiration being ca. 60% of the precipitation sum.

4. Materials and Methods

4.1. INSTALLATION WORK AND FIELD SAMPLING

Lysimeters were constructed in plexiglass; the only other components used were an adhesive and a plastic net, both with insignificant traces of metals. Soil cores from places with freely drained soil were taken vertically from the surface. Steel cylinders of the same length and diameter as the lysimeters were used. The cores were transferred to the lysimeters with a minimum of disturbance and the whole units were replaced in their original positions, after two supporting plastic cylinders had been installed (Figure 1). Design and installation procedures were originally developed by Tyler (1981) who studied the leaching of several metals from the A horizon below a spruce plantation in southernmost Sweden.

The exact positions were chosen subjectively in such a way that certain criteria were fulfilled: (1) within the crown projection of spruce, (2) no direct influence from other tree species, (3) the ground vegetation as uniform as possible, usually without vegetation or with some mosses, (4) the lysimeters in each set kept as close together as possible.

Four different soil depths were chosen for each set of lysimeters. They represented approximately the $A_{00} + A_0$ horizons, including some moss vegetation (depth 0 to 5 cm), the A horizon including most of A_2 (depth 0 to 15 cm), the A horizon + the B_1 horizon (depth 0 to 35 cm) and finally the A horizon + most of the B horizon including B_2 (depth 0 to 55 cm).

The diameter of the lysimeters was 290 mm (0 to 5 and 0 to 15 cm) or 190 mm (0 to 35 and 0 to 55 cm). Two different sets of lysimeters were installed at Värsjö, and three at Gårdsjön. This makes two and three 'replicates', respectively, for each soil depth.

The lysimeters at Värsjö were installed in September 1978 (5, 15, and 35 cm) and in
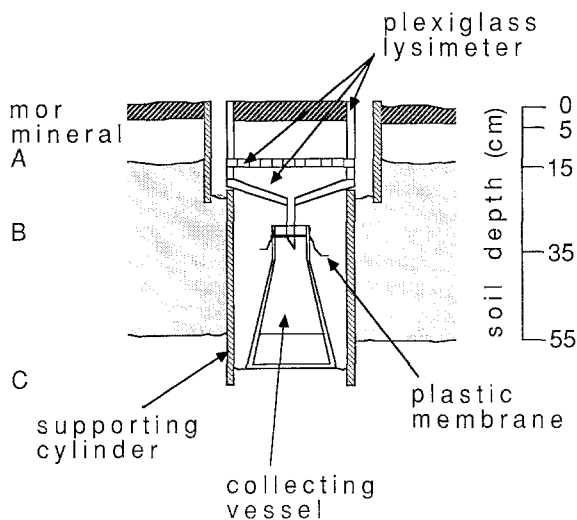
Fig. 1. Lysimeter installation, one of the four soil depths studied (15 cm, A horizon).

September 1979 (55 cm). Sampling started in October 1978 and 1979, respectively, and ceased in December 1981. The lysimeters at Gårdsjön were installed in April 1980. Sampling started in July 1980 and is at present (January 1986) continuing. Precipitation water percolating the soil cores was collected in Erlenmeyer flasks (Duran glass), which were sealed with a plastic membrane, through which the outlet tubes of the lysimeters could easily penetrate.

Open-field precipitation was collected at the Värsjö site in 4 plastic funnels (diam. 22 cm) placed on a 5 m tall mast, situated on a nearby bog, and connected to plastic bottles on the ground through silicon tubes. Throughfall water in the forest was collected in 10 systematically distributed plastic funnels (diam. 30 cm) connected to plastic bottles. Plastic nets in the bottom of these funnels trapped the litterfall which was also collected. During winter an equal number of plastic buckets was used (diam. 40 and 30 cm for open-field and throughfall, respectively). Polyethylene was used in all plastic equipment.

Percolates obtained and used for measurements and calculations were never turbid. To minimize the risk of the metal concentrations of the percolates being altered by the installation procedure, the first few samples were omitted. The collection interval was about 1 mo, shorter during periods of heavy rain and longer during periods when the soil was frozen or too dry. Samples of open-field precipitation, throughfall and litterfall were taken at the same time as the lysimeter percolates.

4.2. SAMPLE PRETREATMENT

All glassware and plastic material was acid cleaned before use. At least one blank in each series of six samples was handled through sample treatment and analysis. Water volume and pH were measured immediately after each collection. A small amount of

the percolate was stored at $-20\ °C$ for subsequent determination of dissolved organic carbon (DOC). Lysimeter percolates and open-field precipitation samples were treated separately; the throughfall water from each sampling occasion was made into 2 bulk samples. From each sample 1000 mL was taken (except when the amount was smaller) and transferred to a 2 L Erlenmeyer flask. The flask was sealed with a hood of fine-grained filter paper and placed in an evaporation cabinet at 105 °C until dry. The evaporation residue was treated with 10 mL HNO_3 (conc., anal. gr.) for total destruction of organic matter and converting the metals into a chemically uniform and soluble state. Remaining acid was evaporated to ca. 2 mL and the digestion residue diluted to 25 mL.

The needle litter from each sampling occasion was made into one bulk sample and dried at 35 °C to constant weight. Total dry weight was determined and 2.5 g were digested in a 250 mL Erlenmeyer flask in the same way as described for the evaporation residue. Tree biomass was sampled from 3 different trees at the Gårdsjön site (samples made available by Hallbäcken, Swedish University of Agricultural Sciences, Uppsala). Ca. 100 samples from different parts of the trees were digested as for the needle litter, and analyzed for metals.

Simultaneously with the lysimeter installation, four soil profiles around the lysimeter soil core were sampled at six levels (0 to 5, 5 to 15, 15 to 25, 25 to 35, 35 to 45, and 45 to 55 cm, area of sampling cylinder: $38\ cm^2$). All samples from the same level were pooled into a bulk sample. Total and extractable metal contents were determined.

The total contents of metals in the soil samples were determined by atomic absorption spectrophotometry (see Section 4.3), after treating 1 g dry wt. of soil with hot conc. $HNO_3 : HClO_4$ (4 : 1) for three days. Complexible heavy metals (Cu, Zn, Pb, Cd, Ni, and Cr) were determined after extraction of fresh soil (corresponding to 20 g dry wt.) with 100 mL 0.05 M Na-EDTA, against similarly prepared standards. This is regarded as an approximation of the secondary, non-lattice fractions. Acid ammonium acetate (pH 4.8; 1 M) extractable metals (Na, K, Ca, Mg, Fe, Mn, and Al) were determined, also against similarly prepared standards, after extraction of fresh soil (corresponding to 20 g dry wt.) with 200 mL of the extractant and subsequent evaporation and digestion of 100 mL of the extract as described for lysimeter solutions above; in this case the digestion residue was diluted to 50 mL. This could be regarded as an approximation of the exchangeable fractions. Soil pH was determined after extraction of fresh soil (corresponding to 5 g dry wt.) with 50 mL extractant, distilled water and 0.2 M KCl solution, respectively.

4.3. SAMPLE ANALYSIS

Thirteen metals were analyzed: Na, K, Ca, Mg, Fe, Mn, Al, Cu, Zn, Pb, Cd, Cr, and Ni. Furthermore, pH, organic matter (organic C) and clay content of soils were determined.

The following analytical methods were used. Metals were determined by acetylene-air flame atomic absorption spectro-photometry (Varian AA6) with recorder registration, unless otherwise stated: Na and K with 1000 ppm CsCl in solutions; Ca and Mg with

10 000 ppm $LaCl_3$ in solutions; Fe, Mn, Cu, Zn, and Cr (Cr with a surplus of acetylene), standard procedure; Al by acetylene-N_2O flame; Cd and Pb with H_2 background corrector; Ni by carbon-rod technique with H_2 background corrector and registration with curve area integrator and recorder; DOC in lysimeter solutions was determined by IR technique using a Beckman 915B carbon analyzer; pH was determined electrometrically at ca. 20 °C, using ca. 10 mL of the untreated waters or settled soil extracts; organic matter in soil samples was determined as percent organic C by IR technique using a LECO CR 12 carbon determinator; percent clay content was determined gravimetrically after sedimentation of soil samples in water and subsequent drying and ignition of subsamples taken after a fixed time interval and at a fixed depth in the water column.

5. Results

5.1. DATA PRESENTATION

Data are presented in the following ways: (1) Yearly means of the concentrations of metals, H^+ and DOC and pH, of precipitation water, throughfall water, soil solutions from various depths and stream water (run-off); (2) extractable and 'total' amounts of metals in the soils, and (at the Gårdsjön site) metal content in biomass; (3) metal budgets of ecosystems and soils.

Concentrations in solutions are calculated as $mg L^{-1}$ for DOC, Na, K, Ca, Mg, Fe, Mn, and Al as $\mu g L^{-1}$ for Cu, Zn, Pb, Cd, Cr, Ni and H^+. Metals in soils and biomass are calculated as $g m^{-2}$; the flow of metals between the compartments of the ecosystem as $g m^{-2} yr^{-1}$ and $mg m^{-2} yr^{-1}$, respectively.

5.2. GENERAL CONSIDERATIONS OF THE BUDGET CALCULATIONS

The term 'ecosystem budget' is used to indicate whether there is a net increase of the metal (positive budget; higher input than output) or a net decrease (negative budget; lower input than output) in the ecosystem as a whole (down to a soil depth of 55 cm). This is shown in Table V (calculated from data given in Figure 4 for the Värsjö forest and from Table III for the Gårdsjön forest). The ecosystem budget is considered positive if the wet and the dry deposition together are greater than the outflow below the rooting zone at 55 cm. Correspondingly, the budget is considered negative if the outflow is greater.

Amounts of water collected from the lysimeter soils are over-estimations of the actual situation, due to the use of lysimeter technique (root uptake by the trees is excluded). Therefore, water flows were estimated using a numerical model (Jansson and Halldin, 1980) based on assumed plant and soil properties. Transpiration from the forest was calculated with a Penman combination equation (Monteith, 1965) using a valve of 100 s m^{-1} for the surface resistance when soil water tensions were below 400 cm water. At higher tensions a reduction of transpiration took place. Soil properties, the water retention curve and the unsaturated conductivity function, were roughly estimated from

given textural composition. Driving variables to the model, air temperature, vapor pressure, wind speed and cloudiness, were taken from official national meteorological statistics (SMHI). In addition the most important driving variable, precipitation, was selected from a denser network of meteorological stations (Ellesson, 1985). Flux of water used in the calculations of the soil flux of metals at Värsjö was the simulated amounts of run-off water for the forest (precipitation at the four adjacent stations during 1980–1981 used in the model: 950–1050 mm yr^{-1}; run-off ('percolation') from the model: 470 mm yr^{-1}). At Gårdsjön the run-off measured in the microcatchments was used in the metal flux calculations of the soil at this site (precipitation in the study area during July 1980–September 1984: ca. 1200 mm yr^{-1}; run-off ('percolation'): 623 mm yr^{-1}). Data on run-off were obtained from another project (Johansson and Nilsson, 1985) for those microcatchments where the lysimeters were installed. In Figure 4 and Table III the flux of metals in the soils were calculated using run-off values.

5.3. CHEMICAL COMPOSITION OF THE WATER ON ITS WAY THROUGH THE ECOSYSTEM

Quite different concentrations of most metals were measured in open-field precipitation and in throughfall water, throughfall concentrations being higher, as a rule. The contribution from the tree crowns was considerable, in particular of Mn, K, Mg, and Ca (Figure 2). These elements have a rapid ecosystem cycling and/or a large proportion of dry deposition. Also certain heavy metals show significant augmentation from open-field precipitation to throughfall; Zn and Cd are two good examples of this pattern. However, Pb concentrations increase only slightly on the passage through the canopy.
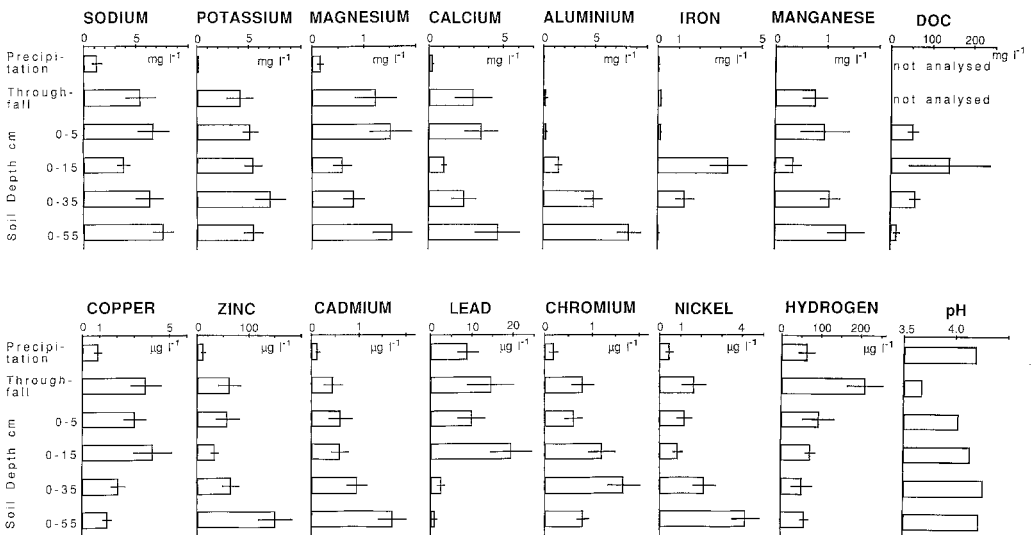

Fig. 2.   pH, concentration of metals, DOC and H^+ in precipitation, throughfall and soil solutions from different depths at Värsjö. Means from 2 yr (1980–1981) and 95% confidence limits; n = 19 (precipitation and throughfall) or 44 (soil solution).

The throughfall water was also enriched in H^+ compared to precipitation; the lowest pH of the water in the system was usually found in the throughfall. The yearly mean pH at Värsjö of open-field precipitation was 4.20, of throughfall 3.68; at Gårdsjön these figures were ca. 4.37 and 3.96, respectively, as calculated from Grennfelt et al. (1985).

When the throughfall water reached the soil surface and percolated the soil, the solution chemistry was, again, greatly altered. This is reflected by the change both in pH and in the contents of metals and DOC. The organic topsoil (upper 5 cm litter and mor layer) made the solution pH increase considerably. The yearly mean pH at Värsjö and Gårdsjön in soil solution at 5 cm was 4.03 and 4.09, respectively (Figures 2 and 3).
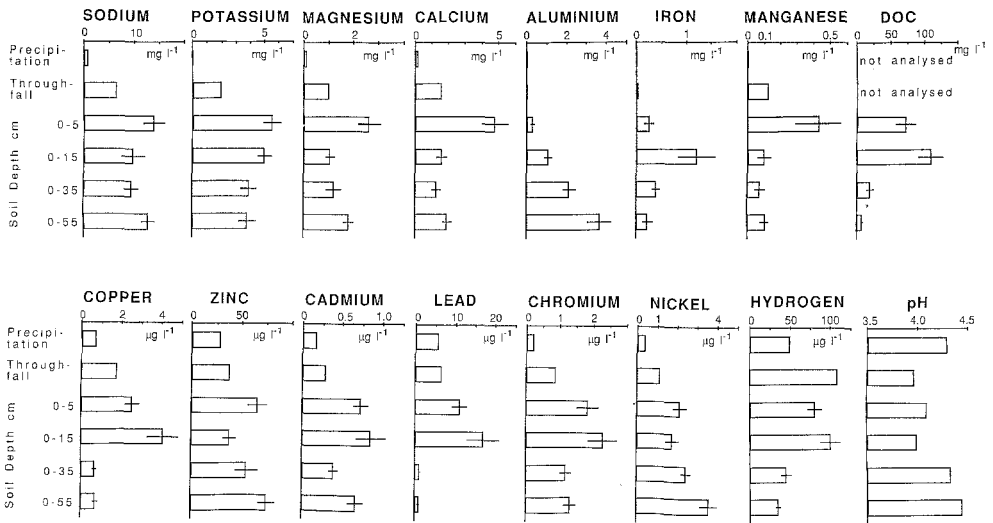

Fig. 3.   pH, concentration of metals, DOC and H^+ in precipitation, throughfall and soil solution at different depths at Gårdsjön. Precipitation and throughfall data calculated from Grahn and Rosén (1983), Grennfelt et al. (1985), and Hultberg (1985). Means from 4 yr (1980–1984) and 95% confidence limits for soil solution, $n = 90$.

At Värsjö the lowest soil solution pH was usually measured after passage of the organic horizon, and at Gårdsjön after passage of the mineral part of the A horizon, at 15 cm soil depth (mean pH 4.14 and 4.00 at Värsjö and Gårdsjön, respectively). The content of organic acids was here at its highest level. In the B_1 horizon, at 35 cm, the pH had increased (pH 4.27 and 4.34 at Värsjö and Gårdsjön, respectively); no significant increase was found after passage of the B_2 horizon, and the soil solution entering the C horizon must be considered unexpectedly acid (pH 4.23 and 4.45 at Värsjö and Gårdsjön, respectively).

The release of dissolved organic matter is considerable in the A horizon; at 15 cm soil depth the content as DOC of the soil solution is at its peak, 100 to 150 mg L^{-1} as yearly means. As the very dark brown-colored soil solution from the A horizon percolated the B horizon it became increasingly less brown-colored. Most of the

dissolved organic matter precipitated in the upper part of the B horizon (Figures 2 and 3). At 55 cm (lower B_2) very little organic matter was left in the solution, which was visibly uncolored at this soil depth; the content of DOC was still 10 to 15 mg L^{-1}, however.

Together with the organic matter almost all Pb and Fe disappeared from the solution in the B horizon, and so did part of the Cu and Cr. Organic species of Al also precipitated in the upper part of the B horizon together with the organic matter (Nilsson and Bergkvist, 1983). Aluminium in soil solutions from the lower B horizon originates mainly from the mineral soil of this horizon and ca. 80% of this is an inorganic species.

The concentrations of Al, Ni, and Zn continued to increase in the soil solution at least throughout the whole B horizon. At the Värsjö site this was also true of Mg, Ca, Mn, and Cd. At the Gårdsjön site, soil solution content of Mg, Ca, and Mn decreased through the A and B_1 horizons (down to 35 cm soil depth), but in B_2 (0 to 55 cm) these concentrations increased again, as was the case with Cd after an irregular pattern above in the soil. No data are available from the C horizon (below 55 cm).

The contents of metals in the small brook draining the study area at Värsjö were also measured during one year (September 1980–October 1981) (Table II). The Stream water was always colored brown by organic matter (however, no determination of the organic matter content was made). The contents of metals in run-off waters from the microcatchments of lake Gårdsjön, in ground water and in the lake itself are also listed.

TABLE II

Annual mean of metal concentrations and pH in brook waters, ground water and lake water (lake Gårdsjön). $\pm 95\%$ confidence limit in waters from the Värsjö site; $n = 8$

	Värsjö: brook	Ground water	Gårdsjön: brook[a]	Lake
pH	3.90 ± 0.08	–	4.15	–
DOC (mg L^{-1})	–	–	8.2	–
Na	5.97 ± 0.96	–	6.8	5.6
K	0.65 ± 0.17	–	0.61	0.61
Mg	1.81 ± 0.24	–	1.4	1.2
Ca	4.04 ± 0.91	–	1.3	1.7
Al	0.37 ± 0.03	1.7	0.8	0.3
Fe	1.71 ± 0.92	0.09	0.30	0.06
Mn	0.12 ± 0.07	0.07	0.06	0.14
Zn (μg L^{-1})	16.1 ± 2.77	33	21	16
Cu	1.18 ± 0.29	2.8	0.6	0.6
Cd	0.2 ± 0.06	0.2	0.2	0.1
Pb	1.19 ± 0.53	3.1	0.7	1.4
Cr	0.53 ± 0.28	1.1	0.6	0.2
Ni	0.49 ± 0.11	1.9	1.0	1.3

[a] From Grahn and Rosén (1983) except Na, K, Ca, Mg from Hultberg (1985) and pH and DOC from Persson and Broberg (1985).

There is little change in the soil solution content of Na, Ca, Mg, Cu, Cr, and Pb leaving the soil profile at 55 cm (Figures 2 and 3) on the way to the brook (Table II); this is also the case for Mn and Fe at the Gårdsjön site. In contrast, at Värsjö only about 10% of the content of K, Mn, Zn, Cd, and Ni was found in the brook compared to soil water concentrations at 55 cm depth; of Al only 5%. The elimination of these elements from the percolation water thus seems to take place mainly below 55 cm depth. The only significant increase in concentration between the lower B horizon and the brook at Värsjö was found for Fe.

At the Gårdsjön site about 15 to 25% of the soil solution content at 55 cm of K, Al, Zn, Cd, and Ni was found in the run-off water draining the microcatchments. In the lake water only Al, Fe, Zn, Cd, and Cr concentrations were significantly lowered compared to run-off. Manganese and Pb concentrations were higher in the lake; the concentrations of Na, K, Mg, Ca, Cu, and Ni did not differ between the brook and the lake.

5.4. ELEMENT DEPOSITION AND CYCLING

The mean annual input of metals with wet and dry deposition, canopy release, throughfall, litterfall, root uptake (only internal circulation) and loss of metals with percolation water during 2 yr are calculated for the Värsjö forest (Figure 4). Mean
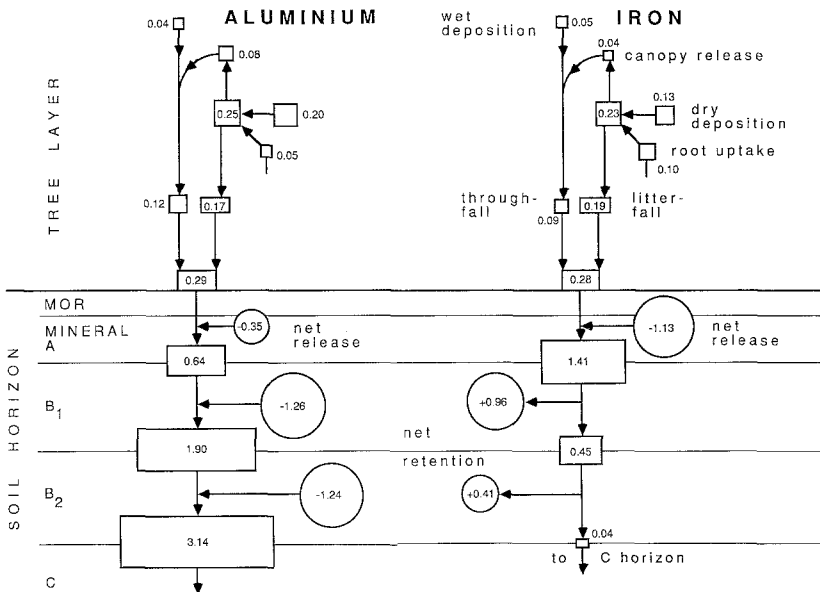

Fig. 4a

Fig. 4. Deposition and cycling of metals at Värsjö. Compartment size for each metal graph is proportional to the annual flow through plant cover and soil. (a) Al, Fe; (b) Ca, Mg; (c) Na, K and Mn; (d) Pb, Cu and Cr; (e) Zn, Cd and Ni. 1–c (g m^{-2} yr^{-1}), d–e (mg m^{-2} yr^{-1}). (Dry deposition from Wiman (1984, 1985b).

annual loss of metals with the percolation water is calculated for the Gårdsjön site, the measurement period being 4 yr. Soil fluxes are compared with input by wet and dry deposition and throughfall as well as litterfall and accumulation in biomass (Table III). Extractable and 'total' contents of metals in the soil at the two sites have been calculated, and at Gårdsjön also the biomass content of metals (Table IV).

TABLE III

Fluxes of metals (annual means) in different compartments of the Gårdsjön forest. Output from different soil horizo $\pm 95\%$ confidence limits; $n = 12$ (3 lysimeters at each soil depth × 4 years).

	Deposition				Soil solutions from (depth)			Acc. in biomass	
	Wet[a]	Dry[b]	Total	Through-fall[a]	15 cm	35 cm	55 cm	excl. yr shoots + needles	yr shoots + needles 'litterfall'
					(g m^{-2} yr^{-1})				
Na	0.85	3.2	4.05	4.29	6.01 ± 2.17	5.57 ± 0.91	7.67 ± 1.03	0.08	0.11
K	0.06	0.23	0.29	1.29	2.75 ± 0.76	2.10 ± 0.41	2.16 ± 0.70	0.53	1.47
Mg	0.12	0.52	0.64	0.66	0.78 ± 0.33	0.78 ± 0.34	1.15 ± 0.20	0.18	0.39
Ca-	0.17	0.13	0.30	1.02	0.97 ± 0.25	0.84 ± 0.30	1.15 ± 0.95	0.88	1.3
Al	0.02	0.20	0.22	0.05	0.56 ± 0.14	1.25 ± 0.46	2.15 ± 0.61	0.11	0.03
Fe	0.02	0.13	0.15	0.03	0.35 ± 0.17	0.24 ± 0.09	0.14 ± 0.16	0.09	0.02
Mn	0.002	0.007	0.009	0.09	0.06 ± 0.04	0.04 ± 0.01	0.07 ± 0.03	0.08	0.23
					(mg m^{-2} yr^{-1})				
Zn	31.8	1.3	33.1	28.3	21.0 ± 5.56	39.3 ± 15.9	45.6 ± 5.61	27	23
Cu	0.74	0.16	0.90	1.3	2.35 ± 1.25	0.56 ± 0.29	0.48 ± 0.11	1.3	1.2
Cd	0.19	0.13	0.32	0.22	0.45 ± 0.17	0.24 ± 0.11	0.42 ± 0.13	0.15	0.05
Pb	6.42	1.3	7.7	4.9	7.62 ± 2.95	1.12 ± 0.73	0.24 ± 0.11	3.4	0.9
Cr	0.25	0.05	0.3	0.65	1.10 ± 0.41	0.69 ± 0.28	0.83 ± 0.29	0.81	0.19
Ni	0.44	0.13	0.57	0.85	1.00 ± 0.27	1.48 ± 0.34	2.18 ± 0.63	1.4	0.8

[a] Na, K, Mg, and Ca (October 1980–September 1981) from Grennfelt et al. (1985); Fe, Mn, Al, Cu, Zn, Pb, Cd, Cr, ai Ni (October 1980–September 1981) from Grahn and Rosén (1983).
[b] From Wiman (1984, 1985b), except: Na and Mg, from Grennfelt et al. (1985).

The importance of 'wet' deposition (with precipitation funnels) to the ecosystem flux differs greatly among the metals (Figure 4 and Table III). Of the gross input of Mn to the forest floor (= throughfall + litterfall) in the spruce forest ecosystems, the contribution from precipitation was almost negligible. Also the supply of K and Ca from precipitation was very small, only a few percent of the amounts reaching the soil surface during a year.

The contributions from wet deposition to the forest floor of Na, Mg, and Al as well as of Fe, Ni, Cu, Zn (at Värsjö), and Cr are somewhat greater, about 10 to 30% of the gross input to the forest floor. Of Pb and Cd roughly 50% of the gross input is supplied in wet deposition, this being also true of Zn at Gårdsjön.

TABLE IV

Content of metals in the Värsjö soil and the Gårdsjön biomass and soil, $g\,m^{-2}$

Soil depth (cm)	Na	K	Mg	Ca	Al	Fe	Mn	Cu	Zn	Cd	Pb	Cr	Ni
Värsjö:													
Acid digestible ('total')													
0– 5	5	5	11	53	44	74	6	0.23	1.1	–	2.3	0.09	0.07
5–15	32	36	70	242	492	1260	28	0.22	2.5	–	2.1	0.3	0.13
15–35	60	106	232	674	3040	5010	87	0.60	6.7	–	2.9	1.2	0.45
35–55	115	228	526	1290	4830	5810	126	0.85	9.3	–	1.8	2.0	1.5
SOIL 0–55	212	375	839	2260	8410	12200	247	1.90	19.6	–	9.1	3.6	2.2
Extractable[a]													
0– 5	1.0	7.5	3.7	10	0.2	0.2	0.3	0.04	0.8	0.007	1.7	0.011	0.04
5–15	2.3	3.8	2.9	18	9	2.9	1.7	0.03	1.4	0.009	1.7	0.006	0.03
15–35	1.9	4.7	1.4	4.8	96	12	0.7	0.04	1.3	0.009	1.3	0.012	0.05
35–55	2.3	3.3	1.6	3.2	110	3.7	0.3	0.02	0.6	0.007	0.2	0.005	0.07
SOIL 0–55	7.5	19	9.6	36	215	19	3.0	0.13	4.1	0.032	4.9	0.034	0.19
Gårdsjön:													
Biomass	2.0	17	5.9	31	1.1	1.4	3.4	0.04	0.8	0.003	0.1	0.02	0.04
Acid digestible ('total')													
0– 5	6	16	12	206	33	38	2	0.2	1.2	–	1.9	0.24	0.09
5–15	34	50	67	400	579	741	9	0.3	4.2	–	2.9	0.40	0.16
15–35	121	309	437	1530	5530	7360	45	0.9	7.6	–	3.6	2.29	1.03
35–55	93	421	750	162	7340	6630	67	1.2	11.5	–	2.0	3.30	1.94
SOIL 0–55	254	796	1270	2300	13500	14800	123	2.6	24.4	–	10.4	6.23	3.22
Extractable[a]													
0– 5	4.3	7.8	6.9	13	0.4	0.1	1.1	0.04	0.7	0.009	1.5	0.009	0.04
5–15	5.7	6.7	8.6	46	0.8	1.5	0.6	0.05	1.1	0.02	2.0	0.01	0.05
15–35	7.2	7.1	1.7	3.7	140	22	0.1	0.06	1.9	0.01	0.9	0.03	0.07
35–55	5.5	6.4	0.5	2.9	160	4.2	0.1	0.04	1.6	0.006	0.3	0.01	0.06
SOIL 0–55	22.7	28.0	17.7	66	308	28	1.9	0.19	5.3	0.05	4.7	0.06	0.22

[a] Na-EDTA: Cu, Zn, Cd, Pb, Cr, Ni; Acid NH_4Ac: Na, K, Mg, Ca, Al, Fe, Mn.

The dry deposition of several metals to the Värsjö spruce forest was studied by Wiman (1984, 1985a). Dry deposition values in Figure 4 are yearly estimates from model-generated mean deposition rate over the first 850 m from upwind forest edge and inwards (Wiman, 1984, 1985b). The dry deposition of K and Mn was twice as high as the wet deposition, while the dry deposition of Ca was only about half of the wet deposition. The sum of dry and wet deposition of these metals was not sufficient to explain the gross input to the soil surface. Thus, cycling between soil and vegetation is of great importance to the ecosystem budget of these metals. The wet deposition of Cr, Pb, Ni, Zn, and Cu dominated over dry deposition, whereas the wet deposition of Fe was only half of it.

The Värsjö dry deposition estimations in Figure 4 were used also at Gårdsjön (Table III), except Na and Mg from the Gårdsjön site (Grennfelt et al., 1985). The
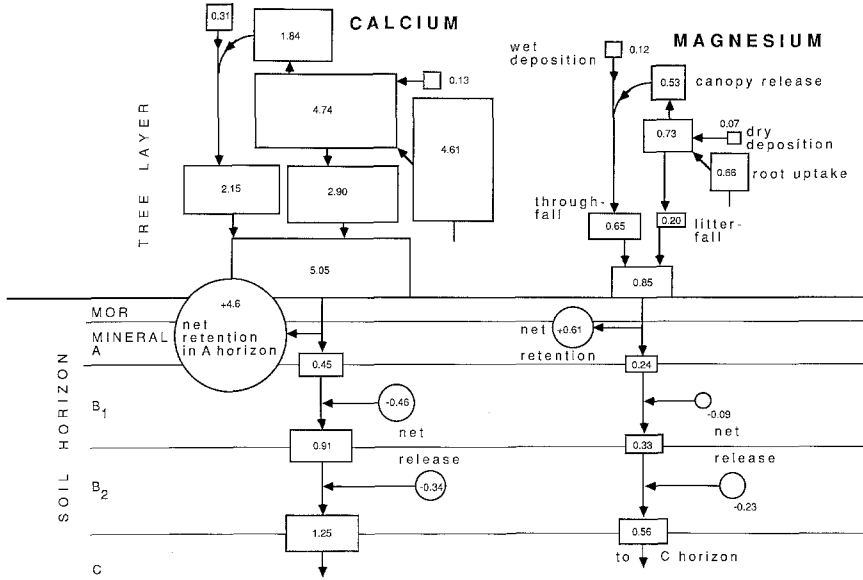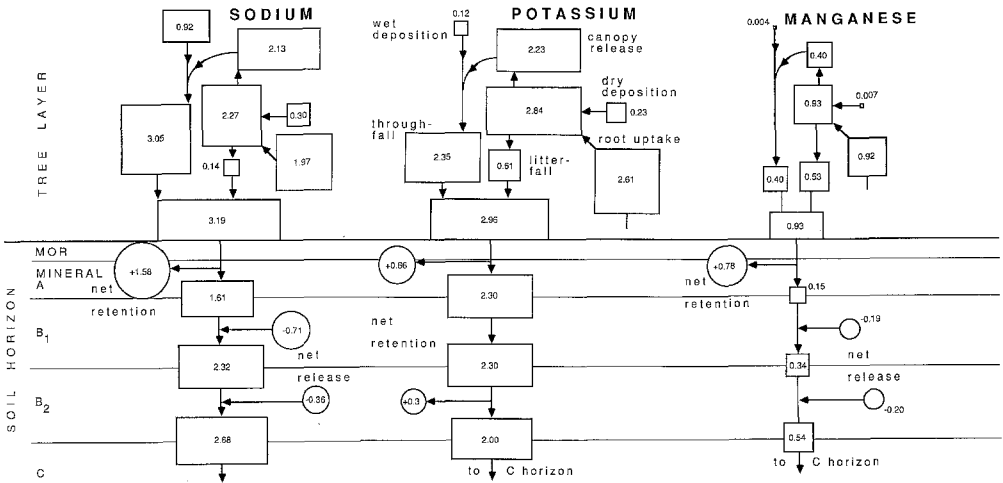
Fig. 4b

Fig. 4c

deposition rate of at least these two metals was much higher at Gårdsjön due to the greater maritime influence there. However, in estimations of ecosystem budgets for the Gårdsjön forest, values on dry deposition at Värsjö may be used, as the structure and density of the two forests are comparable, though anthropogenic and maritime influences on air masses differ.
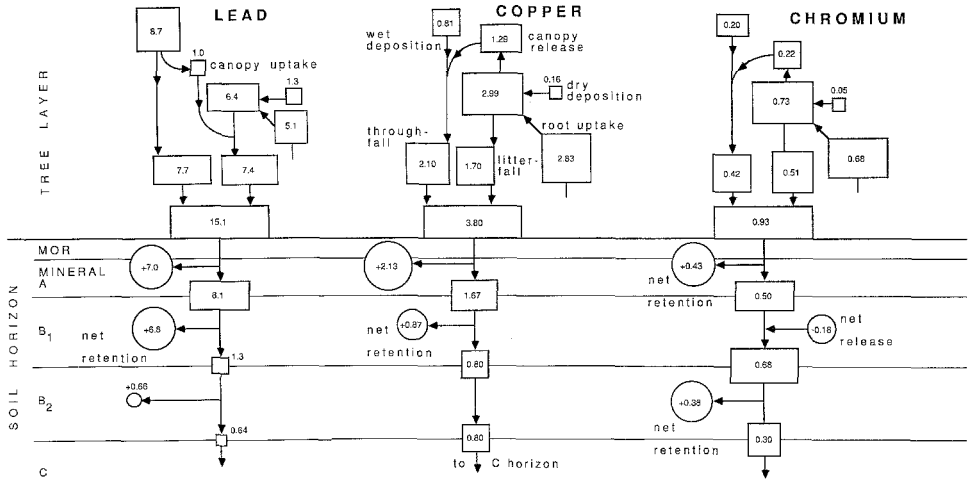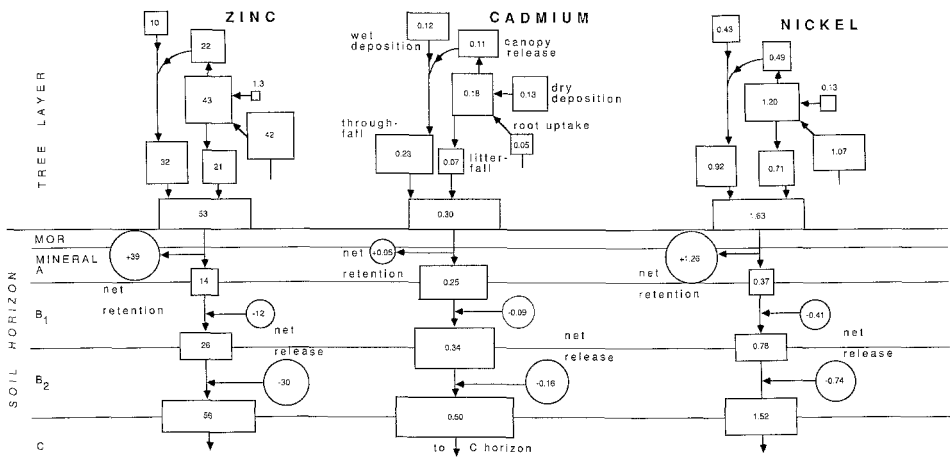
Fig. 4d

Fig. 4e

5.5. SOIL BUDGETS

Most metals, except Fe and Al, are to some extent accumulated in the A horizon of Värsjö (Figure 4). The A horizon at Gårdsjön is losing Fe, Al, Na, Cr, and Cd (Table III).

There is a net release of several metals from the B horizon at the two sites. This is true for Na, Mn, Mg, Ca, Al, Zn, Ni, and Cd. These metals have a negative budget in the entire mineral soil (15 to 55 cm), except Cd at Gårdsjön where input and output were of the same size (Figure 4, Tables III and V). The only metal with a net outflow throughout the A and the B horizons of the two sites was Al.

The net fluxes in the soil are usually of the same magnitude at the two sites (Table V).

TABLE V

Annual metal budgets of the two forests (in brackets the change in the soil pool of metals as % of current extractable amounts), '+' denotes an increase (gain) and '−' a decrease (loss). (Calculated from Figure 4 and Tables III and IV, no biomass accumulation assumed.)

	Mineral soil (B horizon)[a]		Ecosystem budget[b]		Catchment study at Gårdsjön[c]
	Värsjö	Gårdsjön	Värsjö	Gårdsjön	
			(g m^{-2} yr^{-1})		
Na	− 1.1 (25)	− 1.7 (13)	− 1.46(19)	− 3.6 (16)	− 0.14
K	+ 0.30(4)	+ 0.59(4)	− 1.7 (7)	− 1.9 (7)	+ 0.24
Mg	− 0.32(11)	− 0.37(17)	− 0.37(4)	− 0.51(3)	− 0.32
Ca	− 0.80(10)	− 0.18(3)	− 0.81(2)	− 0.85(1)	± 0
Al	− 2.5 (1)	− 1.6 (0.5)	− 2.9 (1)	− 1.93(0.6)	− 0.53
Fe	+ 1.4 (9)	+ 0.21(0.8)	+ 0.14(0.7)	+ 0.01(0.04)	− 0.17
Mn	− 0.39(39)	− 0.01(5)	− 0.53(18)	− 0.06(3)	− 0.04
			(mg m^{-2} yr^{-1})		
Zn	− 42 (2)	− 18 (0.5)	− 45 (1.1)	− 13 (0.2)	+ 16
Cu	+ 0.87(1.5)	+ 1.9 (1.9)	+ 0.17(0.1)	+ 0.42(0.2)	+ 0.43
Cd	− 0.25(2)	+ 0.03(0.2)	− 0.25(0.8)	− 0.10(0.2)	+ 0.09
Pb	+ 7.5 (0.5)	+ 7.4 (0.6)	+ 9.4 (0.2)	+ 7.5 (0.2)	+ 6.0
Cr	+ 0.20(1)	+ 0.27(0.7)	− 0.05(0.1)	− 0.53(0.9)	− 0.06
Ni	− 1.2 (1)	− 1.2 (0.9)	− 0.96(0.5)	− 1.6 (0.7)	− 0.18

[a] Input to 15 cm minus output from 55 cm soil depth.

[b] Total deposition (wet + dry) to the forest canopy minus output from 55 cm soil depth.

[c] From Hultberg (1985) (Na, K, Mg, Ca) and Grahn and Rosén (1983) (Al, Fe, Mn, Zn, Cu, Cd, Pb, Cr, Ni).

The annual net loss of Mg from the entire soil profile amounting to a few % of the currently exchangeable soil store, while the mineral soil is losing 10 to 15%. The loss of K is probably over-estimated by the use of the lysimeter technique. If the rapid root uptake for internal circulation indicated in Figure 4 and Table III were considered, the net flux of K from the soil would probably be reduced.

The spruce forest ecosystem at Värsjö is losing Na, K, Mg, Ca, Mn, Al, Zn, Cd, and Ni (negative ecosystem budgets) (Figure 4 and Table V); the soil release below the rooting zone exceeds the input by wet + dry deposition. Almost at balance is Cr, whereas Fe, Pb, and Cu are accumulating in the forest. Sodium, K, Mg, Ca, Al, Zn, Cd, Cr, and Ni are being lost from the ecosystem at Gårdsjön. A tendency to balance is encountered for Fe and Mn, whereas Pb and Cu are accumulating (Tables III and V). Only insignificant amounts of Pb (and Fe) leave the rooting zone.

6. Discussion

6.1. SOIL PROCESSES

It is evident from the study that the leachability in the soil differs greatly among metals. Generally, the metals demonstrate two distinct patterns of metal release from the spruce forest soils. As the organic matter in the mor layer is mineralized there is a release of soluble organic acids. These are transported through the A horizon with the percolating soil water. Iron, Al, Pb, Cu, and Cr are known to form stable complexes with dissolved organic acids (Himes and Barber, 1957; Stevenson, 1972, 1975, 1976; Verloo *et al.*, 1973; Cheshire *et al.*, 1977; Kirkham, 1977), and are transported through the soil in complexed form. The amounts of these metals released from the A horizon are mainly regulated by the dissolution of organic matter, as shown by Tyler (1981). A high biological activity in the mor layer favors the formation of dissolved organic acids and the release of these metals from soil. Maximum release was found in late summer and autumn, at high soil temperature and soil moisture. The seasonal and annual variability of metal concentrations in the soil solutions of different horizons was shown in two earlier papers (Bergkvist, 1983; Nilsson and Bergkvist, 1983).

This vertical transport of metal-organic complexes is a normal feature of the podzolization process. It is described as an acid dissolution of hydroxides and silicates of Al and Fe and a subsequent complex formation between these metals and dissolved organic acids. The dissolved complexes are believed to become gradually saturated by metals and to precipitate at zero charge (see, e.g., Petersen, 1976). As complexes many trace elements are transported in the soil with an organic Fe–Al complex and may be co-precipitated with this (Mitchell, 1964; Gomah and Sakhar, 1972; Bolter, 1974). Most of the organic matter, Fe, Pb, Cu, and Cr released from the A horizon was accumulated in the upper part of the B horizon.

Soil solution content of Al increases continuously through the B horizon, though this element would be expected to precipitate in the upper B horizon according to podzolization theory. In an earlier paper (Nilsson and Bergkvist, 1983) this was explained by the occurrence of at least two different Al species. Aluminium in the A horizon is almost totally organic; this species disappears gradually from the solution with depth as the soluble organic matter precipitates. Instead, an inorganic Al species appears and increases in concentration downward through the B horizon, constituting more than 80% of total Al at the transition to the C horizon. The observed high concentrations of mainly inorganic Al in soil solution (more than 40 mg L^{-1} on occasions) were claimed to be at least partly due to a high atmospheric deposition load of acidifying substances, where acid S compounds are one important constituent.

A constantly quite high soil solution acidity through the B horizon was shown in the study. Regulation of soil solution acidity was explained by the vertical distribution of DOC and the two Al forms (Nilsson and Bergkvist, 1983). Using H^+ as the dependent variable in a linear regression, DOC was the best predictor of soil acidity in the mor layer, organic Al species in the mineral A horizon and inorganic Al in the lower B horizon. Thus, acidity in the A horizon is likely to be regulated mainly by biological

ativity together with ion exchange and direct protolysis of dissolved organic acids; in the deep B horizon hydrolysis of Al is the main H^+ regulating process (cf. also Ulrich, 1983b). Nitrate was not included in the analytical program. However, the importance of a possibly increased nitrification, brought about by the lysimeter installation when cutting of the roots (cf. Likens *et al.*, 1970), must also be considered. The process of nitrification not only produces NO_3^- but also H^+ and may be an important controlling factor in determining the rate of cation exchange and metal solubilization in the soil. In catchment studies (Likens *et al.*, 1969, 1970) concentrations in stream-water of Mg, Ca, Al, K, and Na were all highly positively correlated with the concentration of NO_3^-. However, when Rasmussen (1986) compared soil solution chemistry in samples from different lysimeter-types, it was indicated that increased mineralization and nitrification in the soil was of minor importance in those acid forest sites. And during more than eight yr of studies with the type of lysimeter used in this study, no longterm trend in the flux of metals was observed. A fact contradicting that artifacts produced by the installation are of major importance.

   Soil solution from the deep B horizon contains only minor, though still appreciable, amounts of organic acids. Precipitation of the organic complexes requires dissolution of sufficient metals to cause a neutralization of the negative charge carried by the organic molecules. However, as podzolization proceeds, available Fe and Al will be removed from the upper soil layers, causing the B horizon to descend gradually. Some organic compounds probably require larger amounts of metals to become precipitated, and may even be leached out of the soil profile. When A horizon soil solutions from the Värsjö soil were leached through an anion-exchange resin (DEAE-Sephacel, Pharmacia; method described by Miles *et al.*, 1983) ca. 10% of the soluble organic compounds was not recovered (Berggren, 1986), indicating these compounds to be either neutral or to have a positive or only weak negative charge.

   The pattern of a gradual release of metals from the mineral soil and an increase in soil solution content of metals through the B horizon was characteristic for Al, Mg, Ca, Mn, Cd, Zn, and Ni; it was less characteristic for K. These metals are very susceptible to changes in soil acidity, as demonstrated by experimental acidification of lysimeter soils from the Värsjö forest (Bergkvist, 1986). The influence of accelerated soil acidification on the increased leachability of these metals is also shown in other studies (for references see Bergkvist, 1986). Even minor pH decreases in added extraction solutions increased the leaching of Zn, Cd, Ni, and Mn significantly from both metal-polluted and unpolluted mor layers according to a laboratory study (Tyler, 1978). These metals are readily extracted from soils by ion exchange (Andersson, 1977).

   Ion exchange was thought to be one of the factors determining the Ca and Mg concentrations in the B horizon soil solution, a probable second factor being mineral weathering (Nilsson and Bergkvist, 1983). Increased disintegration rates of organic complexes or chelates probably increase the solubility of many metals on soil acidification. It is known that many metal-organic complexes become less stable and more soluble at low soil pH (Schnitzer, 1968, 1969; Massey, 1972). However, complexes of Cu and Pb with humic substances are characterized by a very high stability, those of

Mn, Cd, and Zn by a comparatively low stability (Schnitzer and Skinner, 1967; Stevenson, 1976; Blomfield and Sanders, 1977). In the lower B horizon, however, organic complexes should play a minor role. Metal release from this horizon is mainly regulated by the mechanisms of ion exchange or mineral weathering.

6.2. INTERNAL CYCLING

Compared to atmospheric deposition internal cycling proved to be the wholly dominating source of K and Mn and the major source of Ca, Mg, and Zn input to the soil surface. These metal ions are readily taken up by the tree roots. A certain amount is accumulated in the biomass and temporarily taken out of the internal cycling. Well above half of the amounts of these metals taken up from the soil were recycled to the soil, either leached from the needles or returned as litterfall. Similar results were obtained by Nihlgård (1970, 1972).

A contrasting element is Pb, the internal cycling being small and deposition and mobility of organic matter determining the flux through the ecosystem. The needles absorb Pb from the atmosphere effectively: throughfall actually contains less Pb than open-field precipitation. Lindberg and Harriss (1981) also found internal cycling of Pb to be negligible and the input to the soil surface of Mn, Zn, and Cd mainly to be part of the internal cycling of these elements.

There are indications that the root uptake of certain metals is increased by accelerated soil acidification. The uptake of Rb by various organisms is usually greatly favored by a high soil acidity (Tyler, 1983). In a large number of beech forests in S. Sweden the concentrations of Mn, Rb, and Sr in young buds were positively well correlated to soil acidity (Tyler *et al.*, 1985), and in rhizomes and leaves of *Anemone nemorosa* this was also true of the concentrations of Cd, Mn, Rb, and Zn (Tyler, 1976b). At an increased availability metals could be expected to accumulate in vital parts of the ecosystem, such as growing organs and the organic top soil (Tyler, 1972). Effects on internal cycling may be expected in particular for mobile elements.

6.3. METAL BUDGETS

Run-off data on water flux from the two studied areas and concentrations in lysimeter solutions were used in calculations of the flux of elements through the soil. This introduces certain sources of error. The predictable close relationship between annual gross output of dissolved substances from the soil and total annual run-off (Likens *et al.*, 1977) may, however, justify the use of run-off volume in soil budget calculations. One source of error is that exclusion of viable tree roots from the lysimeter soils caused the soil solution concentrations to deviate to some extent from those *in situ*. This is particularly true of elements with a high potential of internal cycling, as they would readily be taken up by the tree roots. Examples are K and Mn, but also to a certain degree Ca, Mg, and Zn.

An attempt is made to estimate the rate at which the soil store of metals changes. The extractable stores of Mg and Mn are lost at a considerable rate from mineral soil and must be effectively resupplied from minerals to keep pace with the leaching; Ca, Zn, and

Ni are lost in minor quantities from the mineral soil. Evidently, there is a potential risk of a shortage to the plants of some elements known to be susceptible to the increases in soil acidity (Bergkvist, 1986) which are nowadays occurring in S. Scandinavia and Central Europe (Butzke, 1981; Falkengren-Grerup, 1985; Hallbäcken and Tamm, 1985). There is also a greatly negative budget in soil of the toxic cation Al; the budget of Cd is less negative. The prevailing large leaching in soil of certain metals could reasonably be regarded as a new phenomenon; this was proposed for Al in an earlier paper (Nilsson and Bergkvist, 1983).

A net increase in the mineral soil is evident for Fe, Cu, Pb, and Cr. In the soil the first sink for these metals is the organic topsoil (litter and mor layer). This soil horizon is often regarded as an almost permanent sink for Pb (Benninger *et al.*, 1975; Bowen, 1975; Siccama and Smith, 1978; Smith and Siccama, 1981). In the soils of this study a close relationship was shown between vertical transport of organic matter and Pb. Therefore, the uppermost B horizon seems to be the main sink for Pb in S. Swedish spruce podzols, though some Pb is transported even deeper.

6.4. COMPARISON WITH OTHER STUDIES

Metal budgets have been calculated for the whole microcatchments at Gårdsjön in which the lysimeters of this study are located (Grahn and Rosén, 1983; Hultberg, 1985; Nilsson, 1985b). The general picture from the two different approaches is that the calculated budgets of certain elements are more negative in the lysimeter study, though some elements also have different signs of the balance (Table VII). Sodium, Mg, Ca, Al, Cr, and Ni are lost in greater amounts from the soil profile than from the catchment as a whole, where Ca and Cr are almost at balance. Potassium, Zn, and Cd are lost from the soil but have a positive budget in the cachment as a whole. Manganese, Cu, and Pb correspond well in the different studies, the budget of Mn being slightly negative, that of Cu and Pb positive. Iron is being lost from the catchments as a whole while output from the lysimeter soils is balanced by input to the forest. The differences may partly be attributed to the different methods used: the lysimeters cover only the upper soil horizons of the catchment and the flux is studied at an early stage of transport through the ground. Input to groundwater is not considered in run-off studies, leading to an underestimation of ecosystem losses. Brook water has to a large extent passed through a freely drained soil profile, partly followed by an out-transport through soil layers rich in organic matter. Thus, these two budget approaches are not wholly comparable.

In Denmark, Rasmussen (1985) has used the same lysimeter technique as in this study. Acidity in precipitation is even a little higher at the Danish sites (Freiesleben, 1985). When three planted spruce stands were compared, soil solution concentrations of metals proved to be generally highest in the most acid soil, which was even more acid than the Värsjö soil. Metal concentrations in soil solution from the lower B horizon in this acid Danish soil were also higher than in the Swedish soils; the concentration of Cd was four times as high (ca. 8 to 10 μg L^{-1}) as at Värsjö (ca. 2 μg L^{-1}). Tyler (1981) used the same method in a study of the A horizon in a planted spruce forest in

S. Sweden. Acid input, soil acidity and soil solution concentrations of metals were generally the same as at Värsjö. In these poor, acid soils with a low buffering capacity to acid input, soil acidity must be regarded as the decisive factor in metal release.

In central Europe the problem of metal release and cycling in forest ecosystems has also aroused considerable interest, due to the severe forest decline during the last decade. Metal budgets are available from the heavily polluted Solling mountains (Seekamp, 1977; Heinrichs and Mayer, 1977, 1980). Soil solution concentrations of Al were higher in the Swedish soils whereas those of Zn, Cu, and Pb were much higher at Solling. There was a net accumulation in the Solling spruce forest soil of all elements entering the system with atmospheric deposition (except of Al and Mn) mainly due to a much higher deposition of most elements than in S. Sweden. The acidity of precipitation is also higher in the Solling area, pH in throughfall being ca. 3.4 as yearly mean (Mayer and Ulrich, 1977). Great differences in the mineral soil properties may also be of importance (a residual loess loam at Solling and a sandy-silty glacial till originating from siliceous rocks at the Swedish sites). The mineral soil was also shown to be a source of Ca, Mg, Mn, and Al in these studies (Matzner and Ulrich, 1981), as in a Calluna heath ecosystem (Matzner and Ulrich, 1980). In a Czechoslovakian spruce forest, in soil solutions from the B horizon even higher Al concentrations were found than in this study, ca. 20 mg L^{-1} as annual mean (Lochman, 1983).

Budget studies are also available from a forested watershed in the Black Forest, south FRG (Zöttl et al., 1979; Stahr et al., 1980; Trüby and Zöttl, 1984). The soil parent materials are periglacial solifluction layers and moraines derived from and covering the extremely acid Bärhalde granite. The research area (Bärhalde watershed) is very humid and cool but less polluted than the Solling mountains further north. The ecosystem showed positive budgets of Cd, Cu, Ni, Pb, and Zn, negative ones of Mn, Al, Fe, Ca, Mg, Na, and K. Percolating water leaving the subsoil at Bärhalde contains less metals than at Solling (25 to 50% of Pb and Cd; 10% of Cu), but the deposition input is also lower at Bärhalde. Nevertheless, the differences between the two FRG sites should be partly due to differences in humidity and soil properties. Element release below the rooting zone at Bärhalde is usually comparable to the acid Scandinavian soils for many elements, exceptions being Mn, Al, and Zn with a higher release rate from mineral soil in the Scandinavian studies.

The element turnover seems also to depend on vegetation type, as was shown in three adjacent stands, a spruce, a beech and a birch stand, having the same parent material (Bergkvist et al., 1985). Throughfall and soil solution were always most acid in the spruce stand, and concentration and flux of metals usually also highest. The birch soil had the highest pH and lowest concentrations and flow of metals. Aluminium concentration in input to the C horizon was 7, 3, and 1 mg L^{-1} as yearly mean for the spruce, beech and birch stands, respectively. Nihlgård (1971) showed that plantation of spruce on former beech forest land very rapidly initiated podzolization of the soil. Higher internal production of acids and a more effective trapping of acid aerosols from air in a spruce forest compared to a deciduous forest were regarded as responsible for the differences.

7. Conclusions

It may be concluded that:

(1) Lead, Cu, Fe, and Al are transported from the A horizon to the B horizon by soluble organic matter. Conditions favoring dissolution of organic compounds also favor this transport.

(2) Release of Na, Mg, Ca, Zn, and Cd from the A horizon will increase with increasing soil acidity. These elements are released throughout the soil profile and, usually, soil solution concentration continues to increase at least through the B horizon.

(3) The precipitation of Fe and Pb with organic matter in the upper B horizon is almost total. Organic forms of Al are also precipitated in the B horizon.

(4) An inorganic Al species will be released from the mineral soil and increase in concentration through the B horizon.

(5) The two forests studied are accumulating Fe, Cu, and Pb. At the Värsjö forest Cr is almost at balance, as is Mn at Gårdsjön.

(6) The two forests studied are losing significant quantities of Na, K, Mg, Ca, Al, Zn, Cd, and Ni. The Värsjö forest is also losing Mn and the Gårdsjön forest Cr.

Acknowledgments

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