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Liisa Ukonmaanaho

VANTAAN TUTKIMUSKESKUS – VANTAA RESEARCH CENTRE

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Supervisor:	Docent Michael Starr Finnish Forest Research Institute Vantaa Research Centre, Finland
Rewievers:	Docent Leena Finér Finnish Forest Research Institute Joensuu Research Centre, Finland
	Dr Martin Forsius Finnish Environment Institute, Finland
Opponent:	Dr Lage Bringmark Department of Environmental Assessment Swedish University of Agricultural Sciences Uppsala, Sweden
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Tämä kirja on painettu ympäristömerkin saaneelle paperille.

Abstract

The research was carried out in four catchment areas: Valkea-Kotinen, Hietajärvi, Pesosjärvi and Vuoskojärvi. The catchments are located in protected, conservation areas and there are no sources of air pollution nearby. The data has been collected as part of Finland's contribution to the UN-ECE International Cooperative Programme on Integrated Monitoring of Air Pollution Effects on Ecosystems. The aim of this thesis was to evaluate and assess the degree of interaction of long-range transported air pollutants (S, N, Ca, Mg, K, Na, Cd, Cu, Ni, Pb, Zn) with undisturbed, old growth forest ecosystems during the 1990s. The main emphasis is on comparing throughfall (TF), soil water (SW) and litterfall (LF) quality and quantity in relation to atmospheric deposition (BP). Uniquely, the data spans 10 years and has been collected using harmonized, internationally agreed methods and procedures.

Results showed that precipitation is strongly modified while passing through the canopy. The concentrations of major nutrients (with exception of N) and heavy metals generally increased in order BP<TF<SW. The canopy interaction was related to the tree species, tree density, canopy coverage and biomass. The greatest changes occurred in south Finland where air pollution was greatest. Litterfall amounts decreased northwards, reflecting a related climate and productivity gradient.

The acidity of BP, TF and SW generally decreased northward and this trend was reflected in decreasing SO_4 concentrations. A significant decline in the concentration of Pb in BP and TF over the study period was found. These decreases are well in line with the UN-ECE 1985, 1998 and 1999 protocols to decline acidified compounds and heavy metal emissions. Base cations showed only a slightly decreasing trend, although the bulk deposition of base cations has decreased significantly. The decrease in TF acidity has therefore been due to the decline in SO_2 emissions rather than an increase in neutralizing base cations deposition. In SW, decreasing trends in Ca, Mg and K were evident as well as SO_4 and H^+ at some of the plots and depths. However SO_4 concentrations at 15 cm depth at VK3 have significantly increased, which might indicate desorption of previously accumulated SO_4 stores. Nitrogen compounds did not show any remarkable trends in TF or SW.

Total deposition of SO_4 varied between 2–6.2 kg S ha^{-1} yr^{-1} and of inorganic N between 1–6 kg N ha^{-1} yr^{-1}. These are low compared to European levels. Annual total deposition loads of Cd, Cu, Ni, Pb and Zn were also considerably smaller than those reported.

Mass balance budgets at plot scale indicate that total deposition of H, N, S and most of heavy metals was greater at nearly all plots than SW leaching output from 40 cm depth. For base cations and Cd inputs were less than output in 40 cm. Budgets using TF+LF to describe the total input to the forest floor were, for most nutrients positive, i.e retention. The humus layer was important in the retention of total inputs for Ca, Mg, N and heavy metals. Sulphur was retained in the mineral soil, particularly in the B-horizon, where Al and Fe hydroxides have accumulated.

Current concentrations of heavy metals in the humus layer and surface water were below critical levels for toxicological effects. There was little concentration of heavy metals up the food chain; with most of the heavy metal deposition to the soil being retained in the upper soil. BP and TF deposition of SO_4, H^+ and N did not have a noticeable effect on forest health (canopy defoliation and discoloration), which was more determined by stand age and geographical location. The decline in air pollution deposition did not result in any systematic change in sensitive trunk epiphytes at these background sites, largely because the levels of air pollution have always been relatively low.

The value and importance of long-term integrated monitoring in the assessment and evaluation of the effects of atmospheric deposition on boreal forest ecosystems has been shown. At the present time forest condition in these background areas is satisfactory. The deposition of long-range transported pollutants has decreased and the risk for damage to forest ecosystem in general has therefore been reduced.

Keywords: forest ecology, concentration, fluxes, budgets, trends, nutrient cycle, long-range transported air pollution, integrated monitoring

Authors´s address: Liisa Ukonmaanaho, Finnish Forest Research Institute, Vantaa Research Centre, P.O. Box 18, FIN-01301Vantaa, Finland. FAX +358 9 8570 5569, e-mail: liisa.ukonmaanaho@metla.fi

List of original publications

This thesis is based on the following articles, which in the text will be referred to by their roman numerals.

I Ukonmaanaho, L., Starr, M. & Ruoho-Airola, T. 1998.Trends in sulfate, base cations and H^+ concentrations in bulk precipitation and throughfall at integrated monitoring sites in Finland 1989-1995. Water, Air, and Soil Pollution 105: 353-363.

II Ukonmaanaho, L., Starr, M., Hirvi, J.-P., Kokko, A., Lahermo, P., Mannio, J., Paukola, T., Ruoho-Airola, T. & Tanskanen, H. 1998. Heavy metal concentrations in various aqueous and biotic media in Finnish Integrated Monitoring catchments. Boreal Environment Research 3: 235-249.

III Ukonmaanaho, L. & Starr, M. 2001. The importance of leaching from litter collected in litterfall traps. Environmental Monitoring and Assessment, 66: 129-146.

IV Ukonmaanaho, L., Starr, M., Mannio, J. & Ruoho-Airola, T. 2001. Heavy metal budgets for two headwater forested catchments in background areas in Finland. Environmental Pollution 114/1: 63-73.

V Ukonmaanaho, L. & Starr, M. Major nutrients and acidity: trends and budgets over nine year period in four remote boreal stands in Finland (manuscript)

The author's contribution

Paper I: The paper was initiated and planned jointly with M. Starr and T. Ruoho-Airola. L. Ukonmaanaho was responsible for the preparing the first draft of the manuscript.
Paper II: The paper was initiated and jointly planned by L. Ukonmaanaho and M. Starr. Ukonmaanaho was responsible of data analysis and processing and wrote the first draft of paper with M. Starr. Other co-authors provided data and relevant text and assisted in the revision of the manuscript.
Paper III: The paper was initiated and planned jointly with M. Starr. Ukonmaanaho performed the data analyses and prepared the first draft of the data.
Paper IV: Ukonmaanaho initiated and jointly planned the paper with M. Starr. Ukonmaanaho was mainly responsible for plot scale budgets and M. Starr for the catchment scale budgets. Other co-authors provided data and comments, and assisted in the revision of the manuscript.
Paper V: Ukonmaanaho initiated the paper and performed the data analyses. M. Starr commented upon the paper.

Papers I-V: Ukonmaanaho was jointly responsible for coordinating the sample collection and laboratory analyses for data included in Papers I–V collected by the Finnish Forest Research Institute during 1989–1999.

List of used abbreviations

BD = bulk deposition
BP = bulk precipitation
CLRTAP = Convention on Long Range Transboundary Air Pollution
DL = detection limit
DOC = dissolved organic carbon
FC = foliage chemistry
FEI = Finnish Environment Institute
FIA = Flow Injection Analyzer
FL = foliar leaching
FMI = Finnish Meteorological Institute
EF = enrichment factory
GW = ground water
HJ = Hietajärvi
HJ1 = Hietajärvi, plot 1
HJ4 = Hietajärvi, plot 4
IBP = International Biological Programme
IC = High pressure Ion Chromatography
ICP forest = International Cooperative Programme on forest
ICP-AES = inductively coupled plasma emission spectrometry
ID = intercepted deposition
IFS = Integrated Forest Studies
IM = Integrated Monitoring
LC = lake chemistry
LECO CHN = LECO carbon-hydrogen-nitrogen analyzer
LF = litterfall
LFL = litterfall leaching
LFLgross = litterfall leaching + throughfall
LFLnet = LFLgross- throughfall
LFtot = litterfall+ LFLnet
LOEL = lowest observed effect level
MC = moss, *Pleurozium schreberi*
Metla = Finnish Forest Research Institute
NC = needle chemistry
PJ = Pesosjärvi
PJ2 = Pesosjärvi, plot 2
RW = stream water
SC = soil chemistry
SF = stemflow
SW = soil water
TD = total deposition
TF = throughfall
TF+LF = total input
UN ECE = United Nations Economic Commission for Europe
WATBAL = water balance model
VJ = Vuoskojärvi
VJ2 = Vuoskojärvi, plot 2
VJ3 = Vuoskojärvi, plot 3
VK =Valkea-Kotinen
VK3 = Valkea-Kotinen, plot 3

Contents

1. Introduction

1.1 Background

Anthropogenic emissions of air pollutants increased enormously during the last century. The increase was due to a combination of population growth and intensified industrialisation and the resulting deposition has had significant ecological consequences on the health and functioning of forest ecosystems.

Studies into the effects of atmospheric deposition on ecosystems started in the 1960's. The prevailing assumption at that time was that atmospheric deposition was an additional source of nutrients to ecosystems and therefore beneficial (Cole et al. 1968, Johnson et al. 1992). Later in the 1960's and 1970's forest damage was observed and attributed to the direct and indirect effects of acid deposition (Oden 1968, Cowling & Nilsson 1995). Studies indicated that acid deposition, far from being an additional source of nutrients, actually caused a net loss of nutrients from forest ecosystems and caused soil acidification (Oden 1968, Cowling 1982, Cowling & Nilsson 1995). The most pessimistic forecast predicted that forest growth would decline at a rate of 1.5 % per year as a result of the increased leaching of calcium from the soil (Engström et al. 1971). In addition to the loss of nutrients from the soil due to the effects of acid deposition, increased soil acidification may result in the mobilization of soil Al and potentially toxic heavy metals that are added due to the significant deposition loads of heavy metals (Nriagu 1990, Alloway 1995). The increased deposition of N compounds, which can cause soil eutrophication and nutrient imbalances, was also being considered a problem (Aber et al. 1989, NIVA 1996). More recently ozone formation in the troposphere has been shown to have detrimental effects on crops, forests and natural vegetation (NIVA 1996) and increased emissions of CO_2 and other potential greenhouse gases to cause changes in temperature and water regimes (Nilsson et al. 1995).

Today, as a result of many studies, we know much more about the effects of acid deposition and ecosystem processes, as well as how to measure changes in forest ecosystem functioning. However, the effects of air pollution on forest ecosystems are complex and often difficult to discern above the natural variation in the processes involved, and a long-term commitment to research is needed. One of the features of air pollution control has been the development of international agreements on the emissions of air pollutants such as the UN ECE's Convention on Long-Range Transboundary Air Pollution, CLRTAP (Bull & Fenech 2000, CLRTAP 2000). These agreements laid the basis for cuts in pollutants known to be damaging to the environment. For example, the 1985 UN ECE protocol on S emissions aimed at reducing emissions by at least 30 % by 1993 compared with 1980 levels. Finland's goal was to reduce S emissions to 121 000 t yr^{-1} by 2000. The 1998 Protocol of on Heavy Metals aimed at reducing Cd, Pb and Hg emissions below their levels in 1990 and the 1999 Protocol to Abate Acidification, Eutrophication and Ground Level Ozone has a target to cut S emissions by at least 63 %, NOx emissions by 41 % and ammonia by 17 % compared to 1990 levels (CLRTAP 2000). The success of such international agreements can only be verified by long-term, harmonised monitoring of the effects of reduced emissions on ecosystem functioning.

The impacts of atmospheric deposition on forest ecosystems can best be clarified by studying the state and changes in biogeochemical cycles (Fig. 1). Particles and gases of both biogenic and anthropogenic origin are emitted to the atmosphere and deposited to ecosystems as wet and dry deposition. Nutrients are returned to the soil for recycling via two major pathways: litterfall and throughfall. The throughfall pathway may include stemflow if it is important, as is the case with certain deciduous tree species, but it is often ignored in nutrient cycling studies. Forest canopies are effective receptors of airborne material delivered as both by wet and dry deposition processes,because of their reactivity and large surface area (Bredemeier 1988). In areas where the supply of nutrients from the soil by weathering is low precipitation is the main source of nutrients to the ecosystem and effective nutrient recycling is required to maintain productivity (Jordan 1980, Parker 1983). Litterfall supplies more matter to the forest floor than throughfall but the nutrients in litter have to be released through decomposition and mineralisation. The chemistry of the soil water reflects atmospheric inputs and a number of processes in the soil, including weathering, ion exchange, mineralisation and immobilisation (Ulrich 1983a). Knowledge about soil water chemistry is therefore particularly useful in assessing the ecological status of the soil, conditions for plant growth, and the potential leaching of substances to groundwater and surface waters. The relative sizes of the throughfall, stemflow, litterfall and soil water fluxes that define biogeochemical cycles depends upon several interacting factors, including levels of deposition, stand composition, structure and age, and soil type, and differ for each nutrient and with distribution and amount of rainfall (Parker 1983).

The value of nutrient cycling studies carried out in forest ecosystem is reflected by the many studies dealing with atmospheric deposition, canopy interaction, litterfall, decomposition and leaching. Important Finnish studies include those of Mälkönen (1974), Paavilainen (1980), Finér (1989, 1992), Helmisaari & Mälkönen (1989), Hyvärinen (1990) and Helmisaari (1995). Numerous national and international forest ecosystem nutrient cycling programs have been established, one of the best known being the *International Biological Programme* (IBP), which was established by the International Council of Scientific Studies in 1964 (Reichle 1981). It was the first integrated programme where ecologists throughout world agreed to investigate forest ecosystem structure and function using standard procedures in both native and managed forests in ways that they hoped would permit comparison and, eventually, a global synthesis (Reichle 1981). There have been other programs after IBP. One of the most significant in North America was the *Integrated Forest Studies* (IFS) (Johnson & Lindberg 1992).

In Finland, first national research programme that dealt with the impacts of air pollution on ecosystems, was the *Finnish Acidification Research Programme* (HAPRO 1985-1990) (Kauppi et al. 1990). The first long-term, integrated ecosystem monitoring programme was the *Integrated Monitoring* (IM) of small forested catchments, which started in the late 1980's and which forms the basis for this thesis. The Finnish IM programme is Finland's contribution

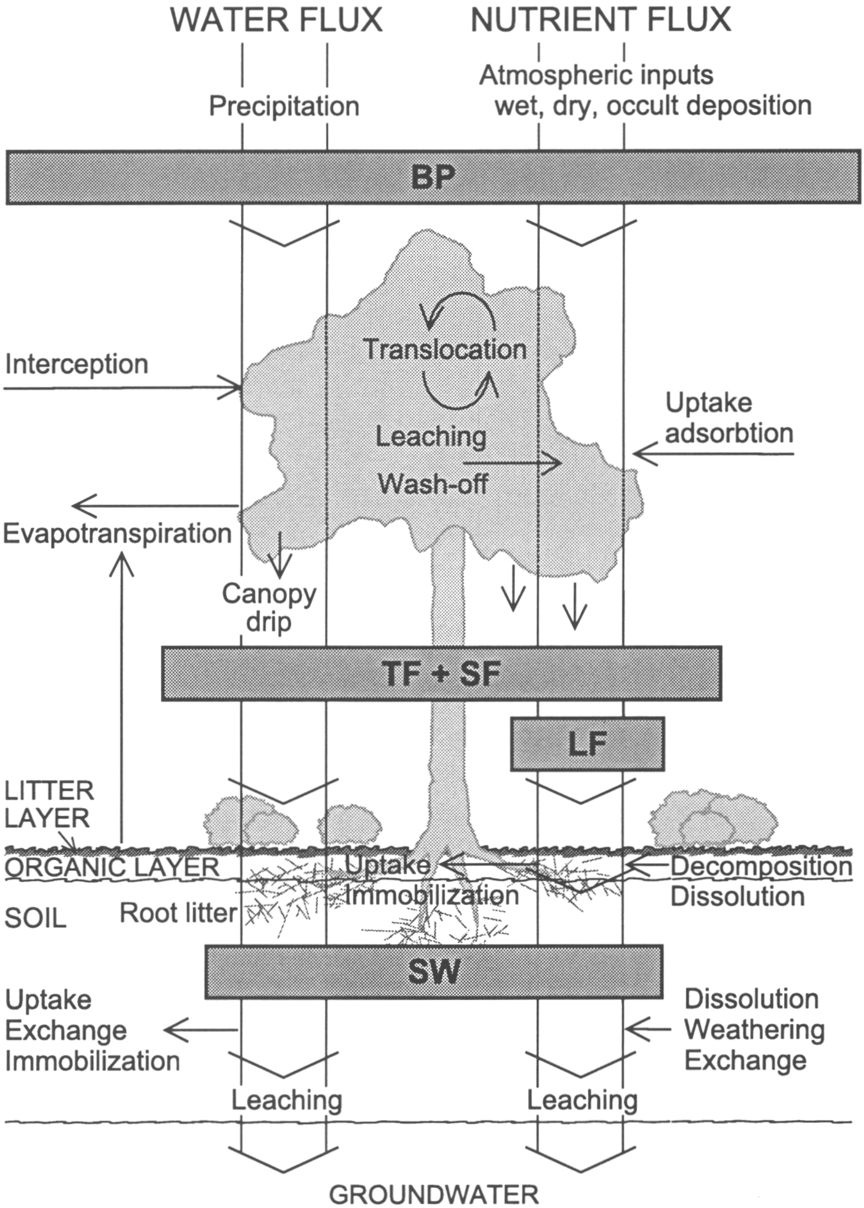


Figure 1. Water and nutrient fluxes in forest ecosystem. BP = bulk precipitation, TF = throughfall, SF = stemflow, LF = litterfall, SW = soil water.

to an part of an international ecosystem monitoring programme, the *International Cooperative Programme on Integrated Monitoring of Air Pollution Effects on Ecosystem*. This programme started in the mid of 1980's as a joint Nordic Council of Ministers project. From 1989 to 1991 it was run at a European scale as the *Pilot Programme on Integrated Monitoring of Air Pollution Effects on Ecosystems* under the auspices of United Nations Economic Commission for Europe (UN ECE). After a favourable evaluation in 1993, the programme became a permanent International Cooperative Programme of the UN ECE under the Convention on the Long-Range Transboundary Air Pollution (Bergström 1998).

The approach in the IM programme is to integrate physical, chemical and biological measurements of different ecosystem compartments simultaneously at the same location over time. In practise, the monitoring is divided into a number of compartmental subprogrammes that are linked by measurement of the same parameters (Manual for ... 1998). The stated aim of the UN ECE IM programme is '*to determine and predict state of ecosystems and their changes in a long-term perspective with respect to the regional variation and impact of air pollutants, especially nitrogen, sulphur and ozone, including effects on biota*' (Manual for... 1993), which was later extended to the '*effects of troposphere ozone, heavy metals and persistent organic substances*' (Manual for... 1998).

Finland contributes to the IM programme with data from four areas. Each area is a headwater catchment located in a national park or reserve and surrounded by an extensive area of forest. The effects of management, agriculture and traffic are therefore negligible and the only source of air pollution is from long-range transported emissions. The IM catchments therefore represent areas of boreal coniferous forest receiving background loads of air pollution and deposition. Although not regionally representative, they do provide an excellent early-warning system about changes in the environment and a means of verifying whether the international agreements on emission reductions have been successful or not.

1.2 Emissions of air pollutants

From an ecological point of view, air pollution may be defined '*a condition in which concentrations of substances in the air are elevated above typical background levels to the degree that they are measurable and have undesirable effects on organisms and/or ecosystems*' (Freedman 1995). When occurring at low levels, however, most of those same air pollutants are fertilizers to organisms. The most important air pollutants from the perspective of forest ecosystems are the acidifying and euthrophying S and N components of wet and dry deposition, heavy metal deposition, and gaseous sulphide dioxide (SO_2), ozone (O_3), hydrogen sulphide (H_2S), oxides of nitrogen (NO_x), ammonia (NH_3) and fluorides (particularly HF) (Manual for... 1998, Luttermann & Freedman 2000).

Air pollutants may originate from natural sources such as volcanoes and forest fires, as well as from large-scale anthropogenic emissions. Industrial processes, such as metal smelting and refining, and the production of energy through the burning of fossil fuels and the use of fossil-fuelled engines for transportation result in large emissions of S and N compounds, base cations, heavy metals and precursors for O_3 (Luttermann & Freedman 2000). Most anthropogenic sources emit air pollutants in the form of gases (SO_2, NO_x, NH_3) and only a minor part is in particulate form. In the atmosphere; SO_2, NO_x and NH_3 are subject to chemical transformation processes by oxidants such as H_2O_2, O_3 and OH^- radicals. Sulphate, nitrate and ammonium ions are formed during long-range transport, the residence time of which is several days enabling transport over long distances (Luttermann & Freedman 2000). Some metal particulates, e.g. Cu, Pb and Ni, are often associated with SO_2 emissions from metal smelters and deposited locally. However, long-range transport of heavy metals through the atmosphere can occur as soluble ionic forms. As a result, many regions of the world are exposed to air pollutants, even areas that are hundreds of kilometres away from the site of emission.

Emissions of SO_2 in Finland have decreased from 600,000 t y^{-1} in the 1970's to 99,000 t yr^{-1} in 1997 (Fig. 2a), whereas there has been little change in the emissions of nitrogen compounds (EMEP 2000). Most of the SO_2 emissions come from energy production and industrial processes (85,000 t in 1997), nearly half of the NO_x emissions from traffic (123,000 t in 1997) and most of the NH_3 emissions from agriculture (33,000 t in 1997) (EMEP 2000). The figures for Europe show a similar pattern.

Emissions of alkaline substances, including Ca, Mg, K and Na, are mostly due to soil dust, energy production, industrial processes, traffic and seawater. Of the anthropogenic sources, combustion of wood and dust raised by traffic are the biggest single sources in Finland (Anttila 1990). According to Anttila (1990), the emission of alkaline substances from industrial sources in 1987 was 63,000 t yr^{-1}, 10,000 t yr^{-1} from traffic and 260,000 t yr^{-1} from soil dust raised by vehicles.

Heavy metal emissions in Finland for 1990–1997 are shown in Figure 2b. The major sources of Cd, Cu, Pb and Zn are metallurgical processes and for Ni energy production and the use of oil fuel in industry (Jalkanen 2000). Gasoline use by cars was the primary source for Pb earlier, but after 1993 only unleaded gasoline has been used in Finland. According to Melanen et al. (1999) emissions of heavy metal particulates in 1997 are a third of what they were in the early 1990s due to the installation of sulphur removal systems.

1.3 Deposition

Atmospheric deposition is the process whereby precipitation (rain, snow, fog), particles, aerosols and gases move from the atmosphere to the earth's surface. Total deposition consists of wet, dry and, in some areas (e.g. mountain areas), fog and cloud (occult) deposition (Sigmon 1989). Particles in the atmosphere range from < 0.01 µm to > 100 µm. The mass of anthropogenic aerosols occurs in the 0.1–1 µm range (Ruijgrok et al. 1993). Particles > 20 µm are rapidly sedimentated and thus have a very short lifetime in the atmosphere and are important only in areas very close to the emitters (Ulrich et al. 1981).

Emissions can be transported within air masses over long distances, even thousands of kilometres, before they are eventually deposited. For example, 83 % of the S deposition in

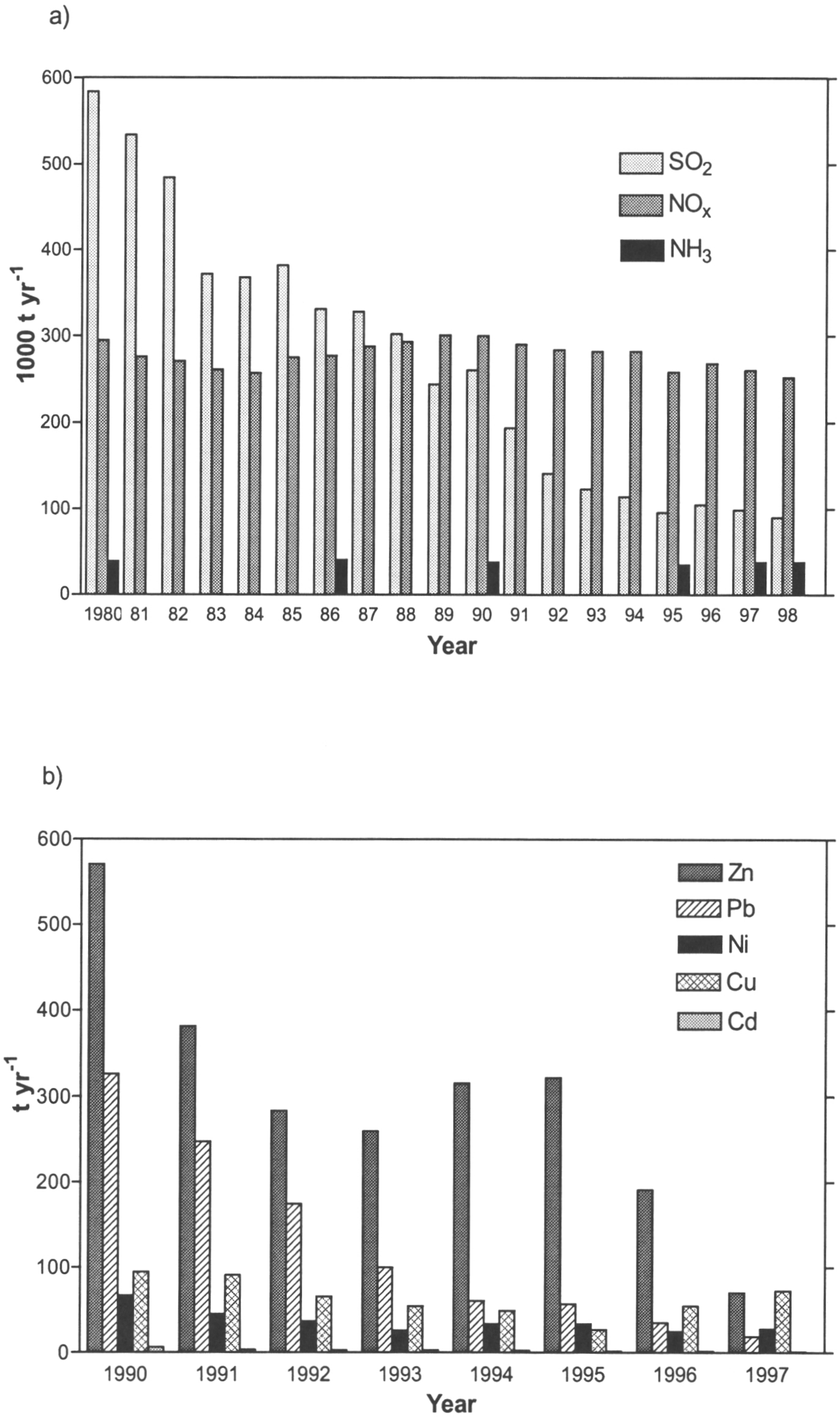


Figure 2. a) SO_2, NO_x and NH_3 emissions in Finland during 1980–1998 (EMEP 2000), b) Cd, Cu, Ni, Pb and Zn emissions in Finland during 1990–1997 (EMEP 2000).

Finland in 1998 came from cross border emissions (Tarrason 2000). Likewise the figure for Pb was 92 % and Cd 67 % in 1996 (Jalkanen 2000).

1.3.1 Wet deposition

Wet deposition includes deposition by rain or snow. Atmospheric pollutants are scavenged by cloud and precipitation droplets and subsequently delivered to the earth's surface as wet deposition (Erisman et al.1993). Falling droplets and snowflakes may also collect gases and particles in the air beneath the clouds and bring them to the earth's surface. These processes of scavenging and wash-out are important for water-soluble gases such as SO_2, NO_x, NH_3 and coarse particles (20–40 µm) but rather less effective for hydrophobic gases and fine particles (< 2 µm) (Lövblad & Westling 1989).

1.3.2 Dry deposition

Dry deposition includes sedimentation of particles, the impaction of aerosols onto surfaces and the absorption of gases (Matzner & Ulrich 1981). Aerosols (compounds of solid or liquid materials and gas dispersed in the air) can collide to form new aerosol particles that have a different dynamic and deposition behavior (Ulrich et al. 1981, Kulmala 1990). The deposition of SO_2 and NO_x is dominated by gases and aerosols while for base cations and heavy metals the sedimentation of larger particles is more important (Matzner & Ulrich 1981).

Gases and suspended particulates are effectively trapped by forest canopies and washed-off when it next rains (Parker 1983). This dry deposition is governed by the concentration in air and the degree of turbulence at the boundary layer, by the chemical and physical nature of the depositing substance and by the ability of the surfaces to capture or absorb gases and particles (Matzner & Ulrich 1981, Erisman et al. 1993). Therefore different tree species have different abilities to capture dry deposition; coniferous trees usually being more effective than deciduous in this respect.

Dry deposition can be divided into large particles (> 2 µm) and small and vapor particles (< 2 µm) reflecting a different chemical composition and physical properties affecting the deposition processes (Hummelshøj 1993). Small particles are generally formed by condensation and coagulation processes, and consist mainly of ammonium sulphates and nitrates, soot and organic compounds. The large particles are derived from the soil (silicate dust) and from the sea by wind, and are important in the deposition of base cations (Hummelshøj 1993).

Results from measurements and deposition modeling have shown that dry deposition in forest edges is considerably enhanced compared to deposition inside the stand (Ivens et al. 1988, Beier and Gundersen 1989). For an individual tree, dry deposition is believed to be highest at the top of the tree, because it is exposed to stronger winds, turbulence and higher air concentrations (Lovett & Lindberg 1992, Hansen 1996).

1.3.3 Cloud and fog (= occult) deposition

Deposition from cloud and fog water occurs via impaction and sedimentation similar to dry deposition (Lövblad & Westling 1989). The size of such droplets varies from 10–50 µm (Fowler 1984, Hicks et al. 1989). Cloud and fog water deposition usually contains higher concentrations of pollutants than found in precipitation (NAPAP 1987). Fog and cloud deposition will also be more important the longer the time the clouds and fog are present (Lövblad & Westling 1989). This type of deposition may contribute substantially to the total deposition in high mountain areas as well as in some valley and coastal locations (Fowler et al. 1991).

1.3.4 Open area deposition loads in Finland

Deposition (bulk) loads in Finland, and especially in the northern parts of the country, are low and clearly amongst the lowest in Europe (Hjellbrekke et al. 1997, Kulmala et al. 1998). Deposition is usually collected with bulk collectors (i.e. permanently open) situated in open area and collect wet and some dry deposition by sedimentation. The mean annual bulk deposition of sulphate in the open in south Finland during 1988–1996 varied between 3.0 and 5.0 kg S ha^{-1} yr^{-1} and in north Finland 0.5 and 1.0 kg S ha^{-1} yr^{-1} (Kulmala et al. 1998). The corresponding deposition of inorganic nitrogen (NO_3^- + NH_4^+) in southernmost Finland was about 6.0 kg N ha^{-1} y^{-1} and decreased northwards (Kulmala et al. 1998). Nitrogen deposition is approximately 30 % organic nitrogen and 70 % inorganic nitrogen, of which nitrate and ammonium are present in equal proportions (Järvinen and Vänni 1990). Calcium is the dominant base cation in open area deposition, varying from 0.11–2.5 kg ha^{-1} yr^{-1} over Finland (Kulmala et al. 1998). Heavy metal deposition in open areas located in background areas was 0.22–0.69 mg m^{-2} for Pb, 0.58–3.23 mg m^{-2} for Zn, 0.30–0.36 mg m^{-2} for Cu, 0.006–0.022 mg m^{-2} for Cd and for Ni 0.08–0.14 mg m^{-2} in 1999 (Leinonen 2000). In polluted areas, such as near the Harjavalta Cu-Ni smelter in southern Finland, the mean annual Cu deposition during 1993–1998 was 149 mg m^{-2} for Cu, 64 mg m^{-2} for Ni and 16.5 mg m^{-2} for Zn at a distance of 0.5 km from smelter (Derome 2000). At a distance of 8 km from the smelter the deposition of Cu was only 2.7 mg m^{-2}, 1.9 mg m^{-2} for Ni and 3.2 mg m^{-2} for Zn.

1.4 Deposition to the forest floor

1.4.1 Pathways and terminology

The pathways of precipitation as it moves through the forest ecosystem is depicted in Figure 1. As incoming precipitation passes through the forest canopy part is retained and evaporated back to the atmosphere. This fraction is referred to as interception loss. There is also interception and evaporation of snow as it builds up on tree branches and can be considerable (Kimmins 1987). The remainder of the precipitation that passes through the canopy (canopy drip) or through the gaps in the canopy and reaches the forest floor is termed throughfall (Parker 1983). That fraction which is collected by the canopy and runs down the branches and stem to reach the ground is termed stemflow (Parker 1983).

Throughfall is usually 90–60 % of precipitation depending on characteristics of stand (species, branch architecture etc.) (Parker 1983, Kimmins 1987). However, it can be over 100 % because of the unequal distribution of precipitation reaching the forest floor and through cloud or fog water intercepted by the canopy (Mahendrappa 1990). Previous studies in the Finnish IM areas (Starr & Ukonmaanaho 1994) showed that amount of throughfall correlated with stand basal area (r = -80) and crown cover (r = -0.81) (Fig. 3). The amount of stemflow varies among tree species. The architecture of the branches and whether they are predominately downward (e.g. spruce) or upward (e.g. beech) facing is particularly important (Parker 1983, Kimmins 1987). In Finnish forests stemflow has been shown to be < 2 % of open precipitation (Päivänen 1966). Stemflow in the IM plots included in this thesis has been shown to be < 0.2 % of precipitation (Starr 1995). Stemflow together with throughfall is sometimes referred as total throughfall (Parker 1983).

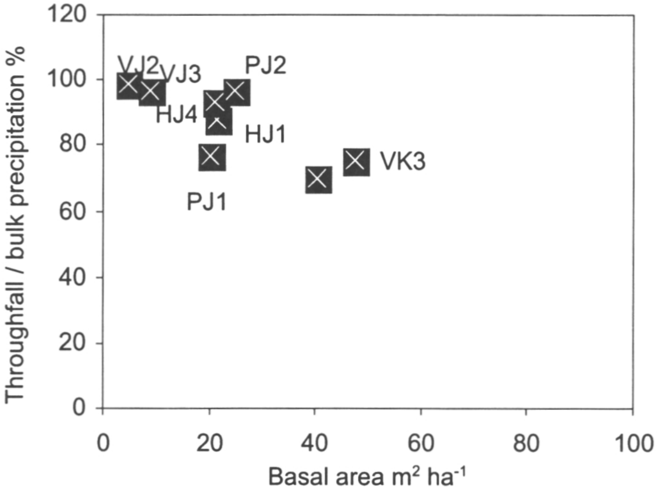
Both throughfall and stemflow reaching the forest floor is partly evaporated before it infiltrates into the soil to form soil water. Once in the soil, the water is consumed by plant roots, goes to storage in the soil or percolates to the groundwater. Infiltration into the forest floor is normally rapid because of the many large pores and the rough nature of the surface.

1.4.2 Throughfall and stemflow interaction with the canopy

Many studies have shown that rainwater passing through a forest canopy is enriched in some solutes and depleted in others (Tukey 1970, Parker 1983, Ulrich 1983b). The difference between deposition in the open and throughfall deposition is termed net throughfall (Parker 1983). To the extent that deposited material is washed from the canopy by the rain, the net throughfall flux provides information about the additional dry deposition intercepted by the canopy. For some solutes the precipitation is depleted so that throughfall concentrations are less than open bulk deposition. Any depletion that takes place in the canopy occurs through the adsorption and uptake (Tukey 1970, Cole & Rapp 1981, Hansen 1994). In addition epiphytic lichens have shown to be active absorbers e.g. of NO_3 and NH_4 in solution (Reiners and Olson 1984). If the throughfall collectors are situated underneath openings in the canopy, then the quality of the water collected can be expected to be more closer to open bulk deposition than to canopy drip.

Stemflow is usually more concentrated than throughfall. Stemflow quality is therefore strongly influenced by species. As the rainwater flows along the stem, it absorbs solutes and dry deposition captured by the surface of the bark (Parker 1983). Stemflow from aspen (*Populus tremula*) has been shown to be particularly concentrated compared to other tree species in Finland (Starr & Ukonmaanaho 1995a). A previous study in the Finnish IM areas (Ukonmaanaho 1977) showed that amount of stemflow deposition was the highest for Ca, 6 %, of total throughfall deposition. Stemflow, particularly in coniferous forests, has little importance at the stand scale but is important at the scale of individual trees. Stemflow is therefore not considered further.

Enrichment of throughfall takes place through the wash-off of dry deposition that a)



b)

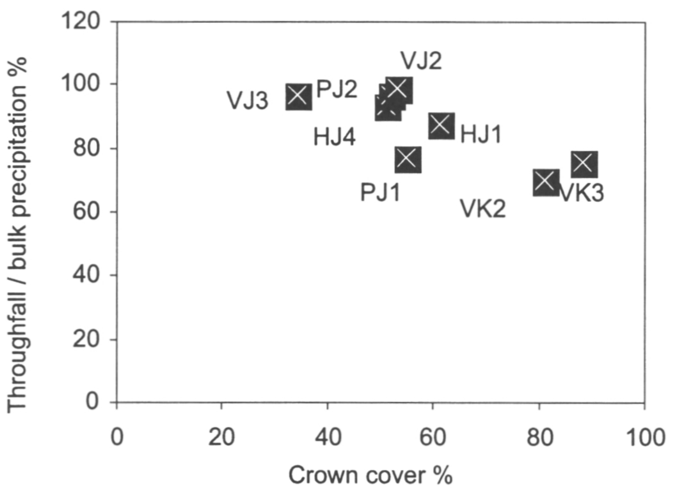


Figure 3. Relationship between the amount of throughfall (as percentage of rainfall) a) and basal area (r = -0.80, n = 8), b) and crown cover % (r = -0.81, n = 8). VK2 = Valkea-Kotinen plot 2, VK3 = Valkea-Kotinen plot 3, HJ1 = Hietajärvi plot 1, HJ4 = Hietajärvi plot 4, PJ1 = Pesosjärvi plot 1, PJ2 = Pesosjärvi plot 2, VJ2 = Vuoskojärvi plot 2, VJ3 = Vuoskojärvi plot 3.

accumulates between rainfall events and through foliar leaching. Foliar leaching occurs through the diffusion of ions from tissue solution and by cation exchange reactions with the rainwater passing over the leaf surfaces (Tukey 1970). In the cation exchange process, protons (H^+) in the rainwater, are typically exchanged for base cations from foliage (Miller et al. 1987). This forms an important acid buffering process by forests attached by acidic deposition (Ulrich 1983b). The relative importance of leaching versus wash-off differs among those solutes showing enrichment. Leaching can account for 10–80 % of the total return of base cations to the forest floor (Tukey 1970, Cole & Rapp 1981, Lovett & Schaefer 1992). While enrichment of sulphate (Parker 1983, Bredemeier 1988) and Pb (Bergkvist et al. 1989) is considered to be entirely due to wash-off of accumulated dry deposition.

The depletion of solutes in throughfall is due to uptake either by foliage or by canopy dwelling epiphytes and algae (Reiners and Olson 1984). Inorganic nitrogen, in particular, is taken up by the canopy, which helps alleviate the shortage of available N typical of boreal forest ecosystems (Mälkönen et al. 1990). In oligotrophic systems such as bog forests and rain forests, foliar uptake can be more important than soil uptake in the supply of nutrients (Parker 1983). Heavy metals can also be absorbed by foliage (Fergusson 1990), which may have a negative effect on growth.

1.4.3 Throughfall variability

A number of factors affect the degree of canopy interaction and therefore throughfall quality, including: the intensity and duration of the incident precipitation, the season, and the composition, structure and age of the stand.

Abrahamsen et al. (1976) showed that the amounts of nutrients leached from the canopy depended on precipitation pH. Therefore acidic deposition has been shown to accelerate the canopy leaching process (Lovett & Schaefer 1992). Fertilization (Matzner et al. 1983, Hansen 1994), abiotic stresses like drought and extreme temperatures (Tukey & Morgan 1963) have also been shown to lead to increased canopy leaching.

Precipitation experiments with loblolly pine (*Pinus taeda*) have indicated that base cation concentrations in throughfall decrease during rainfall (Lovett & Schaefer 1992). Studies have also shown that longer lasting rainfall events remove greater amount nutrients than the same amount of rainfall over shorter period of time (Tukey 1970).

Species composition and stand age have a considerable effect on canopy interaction with rainfall. Deciduous trees tend to loose more nutrients than conifers during the summer months but conifers continue to lose nutrients throughout the winter months (Tukey 1970). Thus Hyvärinen (1990) found that throughfall concentrations of several ions were higher for Norway spruce and Scots pine than for birch stands. Stevens et al. (1994) found that concentrations and fluxes of inorganic-N in throughfall both increase with tree age. Similar relationship for base cations has been shown by Helmisaari & Mälkönen (1989).

The degree of canopy interaction increases with variables describing the amount of above ground biomass such as height, breast height diameter, stem basal area and leaf area index (Päivänen 1966, Lindberg et al. 1989, Beier et al. 1993). Hansen (1995, 1996) found that while the amount of throughfall decreased down through the canopy and outwards from the trunks of Norway spruce stand, nutrient concentrations showed the opposite.

Canopy leaching tends to be greater at the end of the growing season, reaching a peak at senescence (Ulrich 1983b, Hansen 1994). This is a result of the decreased hydrophobicity of needles and increased amount of damaged tissue with needle age (Tukey 1970, Parker 1983).

Within and between stand variability in throughfall amount and quality has important implications for sampling. The number and siting of throughfall collectors, their size and form and the duration of the collection period will all affect the accuracy and precision of throughfall measurements (Kostelnik et al. 1989, Puckett 1991). A study in a Norway spruce forest by Starr & Ukonmaanaho (2000) indicated that 10–15 funnel type collectors would give weekly throughfall amounts and concentrations of H, Ca, K and total S to within 15–20 % of the true mean value with a confidence level of 95 %. For inorganic N, Na and Mg more collectors would be needed to secure the same level of accuracy and precision. The variability in throughfall measurements of snowfall is likely to be considerably higher than that for rainfall (Derome & Lindroos 2000). However logistical problems make snowfall collection more difficult and the number of collectors is usually less than used for sampling rainfall in most studies.

1.5 Soil water

Once the precipitation reaches the forest floor and infiltrates into the soil the quantity and quality of the water is further modified. The pH of the soil solution typically increases with soil depth as a result of proton buffering and neutralizing processes resulting in increased in concentrations of other cations. Other processes that modify soil water include: nutrient uptake, microbiological activity, adsorption/desorption, ion exchange and weathering (e.g. Ulrich et al. 1981, Seip 1983). Many of these processes are depicted in Figure 1.

The greatest changes in soil solution take place in the upper soil, particularly in the organic layer (Aber & Melillo 1991). Cation exchange, in which protons are adsorbed and other cations are released to the soil solution, in boreal forest soils is strongly related to their organic matter content and pH (Tamminen & Starr 1990). Changes in nutrient concentrations in the soil solution due to root uptake and microbial immobilization naturally reflect the distribution of roots and microbes in the soil, which are mainly in the humus layer (Gosz 1981). The capacity of organic matter to bind heavy metals results in the accumulation of heavy metal deposition in the humus layer (Bergkvist et al. 1989).

Concentrations of dissolved organic matter significantly increase after passage through the litter and humus layer. The dissociation of organic acids not only increase the acidity of the water entering the mineral soil but also dominate anion production in natural conditions (Reuss & Johnson 1986). These anions are able to accompany base cations leached from the dead organic matter and transport them into the mineral soil. As the water percolates deeper, protons are consumed by cation exchange and weathering reactions, resulting in the release of Al, Fe and base cations from the soil (Nissinen & Ilvesniemi 1990). The percolating organic matter is able to form soluble complexes with Al, Fe and heavy metals, making them leachable (Reuss & Johnson 1986). With increasing depth, the acidity of the percolate decreases and the solubility of Al, Fe and heavy metal organic complexes decrease such that they begin to accumulate (Reuss & Johnson 1986, Bergkvist 1987). Sulphate is a relatively mobile anion in the soil and is the form in which sulphur is taken up by plants. Sulphate ions are also adsorbed by amorphous Al and Fe oxides that have accumulated in the illuvial B-horizon of podzol (Karltun & Gustafsson 1993). This reaction is reversible and when the pH is increased, perhaps due to reduced S depositions, the concentration of sulphate in the soil solution can increase (Harrisson & Johnson 1992).

Soil water flow and chemistry tend to show considerable spatial variability due to the heterogeneity of soil. Soil water is also technically difficult to sample. It is usually sampled using suction or zero-tension lysimeters. Zero-tension lysimeters collect gravitational water whereas suction lysimeters collect both gravitational water and water held by the soil up to the tension applied to the lysimeter. The water balance of forest soils in Finland is such that most of the annual drainage takes place in spring during snowmelt (Soveri 1985). Most of the water entering the soil during the summer months goes to evapotranspiration and storage and there is little drainage (Starr 1985, 1999). The soil water at this time can often only be sampled by suction lysimeters. Installation of zero-tension lysimeters usually involves severing roots and disturbance of the soil, particularly in stony soils. Installation of suction cup lysimeters usually results in less disturbance but to work effectively there needs to be good contact with the soil matrix and there are often problems with poor installation. Although the effects of soil disturbance on the water quality should decline with time, the effects of plugging and interaction with cup material would tend to increase over time. Furthermore, the quality of water drawn with suction cup lysimeters varies with the material used to make the cup (Beier & Hansen 1992, Beier et al. 1992, Anderssen et al. 1999) and with sample volume drawn (Starr 1985).

1.6 Litterfall

Factors affecting litterfall production are related to climate and stand characteristics. In coniferous forests, the proportion of branches and bark in the litterfall increases with stand age, as does the number of cones (Mälkönen 1974, Flower-Ellis 1985, Finér 1996). Foliar litter constitutes the major part of litterfall to the ground. Deciduous forests loose most of their foliar biomass in the autumn, but 40 to 60 % of the total annual litterfall from conifers also occurs in September-October (Viro 1955, Mälkönen 1974). At the time of senescence, the concentrations of nutrients in foliage decrease. In the case of N and P, the decrease is due to retranslocation back into the trunk (Helmisaari 1992, Finér 1996), whereas the decrease in foliar K and Mg concentrations is mainly due to leaching (Aber & Melillo 1991). Calcium, in contrast, tends to accumulate in foliage up to the time of leaf fall. The role of litterfall in nutrient return is therefore more significant for Ca than for other nutrients.

In a study of 32 forests, including coniferous and deciduous forests, the annual return of N in litterfall averaged 83 % of the total return (litterfall + throughfall) to the forest floor (Cole & Rapp 1981). In contrast, the return of K in litterfall was only 41 % of the total return, the majority being returned via throughfall and stemflow. The return of Ca via litterfall was 71 % and for Mg, 60 %. Soluble organic compounds and mobile ions, such as K, are rapidly leached from litterfall but the more recalcitrant organic substances and associated mineral elements require microbial decomposition to make them available (Aber & Melillo 1991). Nutrients returned in throughfall are, in contrast, immediately available for uptake as they are nearly all in soluble form (Parker 1983). Annual fluxes of Ca and N in litterfall are greater than other nutrients regardless of forest type but the amounts vary among forest types, being less in boreal coniferous forests than in boreal deciduous forests (Cole and Rapp 1981).

1.7 Canopy and soil interaction with deposition

As already indicated, the interaction between air pollutants and forest ecosystems varies for pollutant and a whole range of factors, including: frequency of exposure, topography, soil type, seasonal weather pattern, species composition, age and structure of the stand and the cumulative effects of other environmental stress factors (Luttermann & Freedman 2000). It is therefore difficult to generalize the effects of air pollutants, particularly those of diffuse emissions such as S and N, in any particular region. However, in cases involving exposures to high concentrations of specific pollutants emitted by discrete point sources, it is often observed that damage is more severe close to the point source, and that it decreases in a more or less geometric fashion with increasing distance away from the source (e.g. Lindroos 1998, Nieminen et al. 1999, Derome 2000).

1.7.1 Major nutrients and acidity

In natural waters base cations (Ca, Mg, K) and Na exist primarily as cations, N as anions and cations (NO_3^-, NH_4^+) and S as anions (SO_4^{2-}). With the respection Na, all these elements are essential plant nutrients. The growth and productivity of boreal forest ecosystem is limited by the availability of N (e.g. Mälkönen 1990). Much of the sulphur deposited to forests is in the form of sulphuric acid (H^+ and SO_4^{2-} ions) or SO_2, which is easily adsorbed to wet substances and oxidised to H_2SO_4. Excess sulphur deposition may damage needles and leaves, cause soil acidification and lead to loss of base cations from the canopy, humus layer and rooting zone of plants (e.g. Lindberg & Lovett 1992, Lumme et al. 1995) and thus may cause nutrient deficiency. Soil acidification may result in increased concentrations of toxic aluminium and heavy metals in the soil solution. High ammonia deposition may enhance nitrification and NO_3 production may lead to increased base cation leaching (e.g. de Vries et al. 1995). Sustained high inputs of N may saturate previously nitrogen limited ecosystems, i.e. nitrogen availability exceeds the capacity of the plants and soil microbes to assimilate all the nitrogen, and lead to N leaching to the groundwater and surface waters (Ågren & Bosatta 1988, Aber et al. 1989). At lower levels of N deposition, the increased growth rate due to the fertilizing effect of N deposition may dilute the concentrations of other nutrients in the foliage, leading to nutrient imbalances (NIVA 1996). Of particular relevance to boreal forests is the risk of N deposition prolonging tree growth into late autumn when there is an increasing risk of frost damage (Aronsson 1980, Ferm et al. 1990).

The deposition of base cations, particularly Ca and Mg, decreases the acidifying effect of H^+ ions associated with the deposition of SO_4 and NO_3 (strong acid) anions (Hedin et al. 1994). The exchange of base cations from the foliage and soil by H^+ ions in acidic deposition may lead to net leaching loss of these nutrients from the ecosystem (e.g. Cronan et al. 1978, Berdén et al. 1987). If uptake does not keep pace with increased rate of foliar leaching, foliar cation concentration can decrease to defiency levels. The amount of base cation deposition is therefore important when considering the acidifying effects of sulphur and nitrogen deposition (Hedin et al. 1994). The removal of fly ash, rich in base cations, from power plant emissions would thus offset the benefits of reduced sulphur and nitric oxides emissions (Hedin et al. 1994, Jalkanen et al. 2000). The weathering of soil minerals represents an internal supply of base cations and thereby the ultimate acid buffering capacity of the soil (Van Breemen et al. 1983). If the deposition + weathering release of base cation can not keep pace with leaching losses there is soil acidification and the potential for decreased soil fertility and mobilization of toxic aluminium (Starr et al. 1998b).

1.7.2 Heavy metals

The atmospheric deposition of heavy metals is dominated by the dry deposition of aerosols and particulates (Lindberg et al. 1989, Fergusson 1990). Heavy metal deposition shows a strong affinity for adsorption to organic surfaces. Forest canopies are particularly effective in trapping such deposition because of the high adsorption surface area they present for interception (Lindberg & Turner 1988). Mosses, particularly *Pleurozium schreberi* and *Hylocomium splendens*, which take up water and elements through their entire surface from the atmosphere, are widely used as biomonitors of deposited airborne heavy metals (Berg et al. 1995, Økland 1999). The humus layer in coniferous forest ecosystems is also effective in retaining heavy metals, particularly Pb and Cu, through adsorption and complexation with organic matter (Tyler 1978, Bergkvist 1987, Bergkvist et al. 1989, Derome & Nieminen 1998).

The mobility and toxicity of heavy metals in soils is strongly related to the acidity and organic matter content (solid, suspended and soluble) (Adriano 1991, Fergusson 1990, Alloway 1995). In general, increasing acidity tends to increase the mobility of heavy metals. Furthermore, the proportion of free ionic forms of heavy metals, which are more toxic than organic complexed forms, is also pH dependent (Collins & Stozky 1989). The dependence of heavy metal mobility on acidity has been experimentally demonstrated in a number of simulated acidification studies (e.g. Tyler 1981, Bergkvist et al. 1989). There are several pH-dependent processes involved, including the physical disintegration of organic matter and increase in dissolved organic matter concentrations to which heavy metals are adsorbed, the association/dissociation and coagulation/flocculation of soluble organo-heavy metal complexes, adsorption by Al, Fe and Si oxides, and soil cation exchange and weathering (Fergusson 1990, Alloway 1995). Indeed, it has been suggested that an increase in the dissolution of heavy metals in soils related to acidic deposition has contributed to the forest decline observed in Europe, particularly in acid-sensitive terrains (Nriagu 1990).

Organo-metal complexes, are often more soluble than the metal themselves. Zinc, Ni and Cd are less strongly adsorbed by organic matter and the resulting soluble complexes are less stable than those with Pb and Cu (Bergkvist 1987). The mobility of Zn, Ni and Cd in soil, lake and stream water therefore tends to be strongly related to pH, while Pb and Cu fluxes tend to be more determined by organic matter considerations.

2. Aims of the study

The overall aim of this thesis is to evaluate and assess the degree of interaction of long-range transported air pollutants (S, N, Ca, Mg, K, Na, Cd, Cu, Ni, Pb, Zn) with undisturbed, old growth forest ecosystems during the 1990s. The main emphasis is on comparing throughfall, soil water and litterfall quality and quantity in relation to atmospheric deposition inputs rather than on the processes involved. In order to do this I have used bulk precipitation, throughfall, soil water and litterfall data collected from permanent plots in four catchments located south–north throughout Finland. The forest stands involved vary in composition and structure, and receive varying loads of long-range transported air pollution. The location of the catchments corresponds to a gradient of deposition loads that are related to both concentrations and amount of precipitation. This data is unique in that it covers 9 years of continuous monitoring of changes in precipitation as it moves downwards through the ecosystem at the same locations and using the same sampling and analytical methods. The period covered by the study, 1989–97, has seen major reductions in the emissions of acidic deposition primarily S. The specific aims are to:

- Describe and compare concentrations of SO_4, Ca, Mg, K, Na, NH_4, NO_3, total-N, and H in throughfall and soil water in relation to incoming deposition and stand characteristics.
- Determine if there has been any significant trend in the concentrations of SO_4, Ca, Mg, K, Na, NH_4, NO_3, total-N, and H in throughfall and soil water over the nine-year period, 1989-1997.
- Compare litterfall and throughfall as pathways for the transport of nutrients to the forest floor.
- Describe and compare the concentrations of heavy metals (Cd, Cu, Ni, Pb and Zn) in aquatic and biotic media, as well as to describe long-term trends.
- Describe and evaluate plot-scale mass balance budgets (inputs, outputs and internal fluxes) of SO_4, Ca, Mg, K, Na, NH_4, NO_3, N, S and H in each catchment and plot- and catchment-scale budgets of Cd, Cu, Ni, Pb and Zn at two of the catchments.

3. Material and methods

3.1 Study catchments and plots

The study has been carried out in four headwater catchments located at increasingly northerly latitudes (61º 14´ N – 69º 44´ N) throughout Finland: Valkea-Kotinen (VK, 0.3 km^2), Hietajärvi (HJ, 4.6 km^2), Pesosjärvi (PJ, 6.1 km^2) and Vuoskojärvi (VJ, 2.0 km^2) (Fig 4). The data has been collected as part of the UN ECE International Cooperative Programme on Integrated Monitoring (Manual for...1993, 1998).

Each catchment is situated in remote, forested and undisturbed conservation areas. Permanent monitoring plots were established in each catchment in 1988/89 and a number of monitoring subprogrammes have been continuously carried out since (Manual for...1993, 1998). The plots were laid out in the main forest types in each catchment and varied in size from 25x25 m to 40x40 m. They were situated on flat areas and are homogenous as possible with regard to soil morphology, ground vegetation and stand characteristics. The forests consist of old-growth stands composed of various proportions of Scots pine (*Pinus sylvestris* (L). Karst.), Norway spruce (*Picea abies* Karst.) and deciduous species (mainly *Betula* spp.). The catchments and plots are described in detail in Table 1, Bergström et al. 1995, and in the papers (I–V) included in this thesis.

The mean annual precipitation (1989–1997) during the study period was 619 mm VK, 614 mm HJ, 493 mm PJ, and 344 mm VJ (Kulmala et al. 1998, Leinonen 1999). Long-range transported emissions mainly originate, from Central and Eastern Europe. The St. Petersburg area and Estonian oil shale fueled power plants (Jalkanen 2000) are especially important in southern Finland. In north Finland, emissions from metal smelters in the Kola Peninsula, Russia, are important (Jaffe et al. 1995).

3.2 Sampling procedures and techniques

The sampling procedures and methods used follow those outlined in the Integrated Monitoring Manual (Manual for ...1998) and are described in each paper (I-V) and in Bergström et al. (1995). A summary of the monitoring subprogrammes, study areas, measured elements and sampling period in each paper is given in Table 2. The layout and design of the sampling is presented in Figure 5.

3.3 Pretreatment and chemical analyses

Within the Finnish IM programme, the Finnish Forest Research Institute (Metla) was responsible for the collection and analysis of the throughfall (TF), stemflow (SF), soil water (SW) and litterfall (LF) samples. The Finnish Meteorological Institute (FMI) was responsible for the collection and analysis of bulk precipitation (BP) samples (I-II, IV-V) and the Finnish Environment Institute (FEI) for the streamwater (RW) samples (II, IV). Sampling and analytical

Table 1. Description and characteristics of the study plots.

Catchment	Plot	Site type	Stem Volume m^3ha^{-1}	pine*	spruce†	deciduous‡	Mean height, m	Age of dominant trees (years)	Thickness of humus layer, mm	Soil type (FAO)	Bedrock
Valkea-Kotinen (VK)	2	Mtkg	406	3	87	10	16	145	n.a.	Terric histosol	mica gneiss
	3 (1)#	OMT	566	2	62	36	18	160	34	Dystric Cambisol	"
	11 (2)#	MT	568	0	71	29	18	160	65	Dystric Cambisol	"
Hietajärvi (HJ)	1 (1)#	EVT	189	81	0	19	9	165	63	Haplic Podzol	porphyritic granodiorites
	4 (2)#	EVT	258	86	0	14	16	155	37	Haplic podzol	"
Pesosjärvi (PJ)	1 (1)#	HMT	147	19	70	11	9	300	60	Carbic podzol	arkosic and sericite quartzites
	2 (2)#	HMT	164	5	85	10	9	250	35	Haplic podzol	"
Vuoskojärvi (VJ)	2 (1)#	SELiPIT	23	3	0	97	5	150	24	Haplic podzol	gneisses, amphibolites containing sulphide bearing minerals
	3 (2)#	lichen woodland	61	99	0	2	11	200	37	Haplic podzol	"

* Scots pine (*Pinus sylvestris*)
† Norway spruce (*Picea abies*)
‡ deciduous species (mainly Birch, *Betula spp.* and Aspen, *Populus tremula*; but Vuoskojärvi, Mountain birch, *B. pubescens spp. tortuosa*)
\# used plot number in paper III
n.a. no data

Table 2. A summary of monitoring subprogrammes, study areas, measured elements, methods and periods in each paper (I-V).

Paper	Subprogrammes	Catchments	Scale	Elements	Objectives	Period
I	BP, TF	VK, HJ, PJ, VJ	Plot	SO4-S, Ca, Mg, K, H	Concentrations, trends	1989–1995
II	BP, TF, SF, SW, GW, LC, RW, MC, NC, LF, SC, Ants, Shrew liver	VK, HJ, PJ, VJ	Catchment	Cd, Cu, Ni, Pb, Zn	Concentrations	1989–1996*
III	TF, LF	VK, HJ, PJ, VJ	Plot	Ca, Mg, K, Na, N, S	Concentrations, fluxes	1995 (August to September)
IV	BP, TF, SW, LF, SC, RW, LC	VK, HJ	Catchment and plot	Cd, Cu, Ni, Pb, Zn	Fluxes, input-output-budget	1994–1996
V	BP, TF, LF, SW	VK, HJ, PJ, VJ	Plot	H, Ca, Mg, K, Na, N, NO_3-N, NH_4-N, SO_4-S, S	Concentrations, trends, fluxes, input-output budget	1989–1997

*varies with subprogramme

methods used to collect data in other subprogrammes foliage chemistry (FC), moss chemistry (MC) and soil chemistry (SC) are described in the paper concerned.

The volumes of each throughfall, stemflow and soil water sample collected were recorded in the field by weighing. Throughfall samples were then bulked by plot and stemflow samples were bulked by species and plot. Soil water samples were not bulked for analyses. After air drying the litterfall samples were fractionated into 4 fractions: Scots pine needles, Norway spruce needles, leaves and the rest. The mass of each fraction was determined then recombined and bulked by plots. Throughfall, stemflow and soil water samples were stored in dark and cool (+4 °C) conditions until analysis began. The TF and SF samples were filtered before analysis (Schleicher & Schuell 589^2 filter paper); otherwise the analyses were performed on unfiltered standing samples. The air-dried LF samples were milled and wet digested (mixture of HNO_3 acid and H_2O_2).

The chemical parameters determined were those listed in the IM manual (Manual for...1993, 1998). Concentrations of NO_3 and SO_4 were analysed by high pressure ion chromatography (IC), NH_4 and total N by flow injection analyzer (FIA), and H^+ concentrations were calculated from pH measurements made potentiometrically using combined electrode. Concentrations of Ca, Mg, K, Na, S, Ni, Pb, Cu, Cd and Zn in the TF, SF, SW and LF samples were determined using inductively coupled plasma emission spectrometry (ICP-AES). The water samples were acidified with concentrated nitric acid (suprapure quality, 1:200 v/v) before analysis to promote desorption from the walls of the sample storage bottles. Concentrations of total N in LF were determined with a LECO CHN analyser. Details of the analytical methods and procedures used are documented in Jarva & Tervahauta (1993) and Ukonmaanaho (1996).

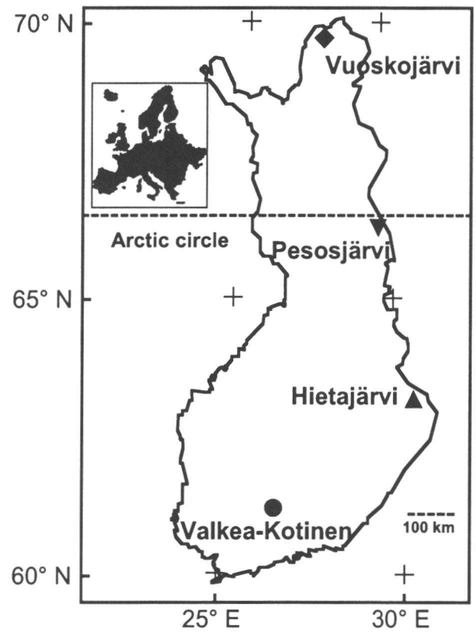


Figure 4. Location of the study catchments in Finland.

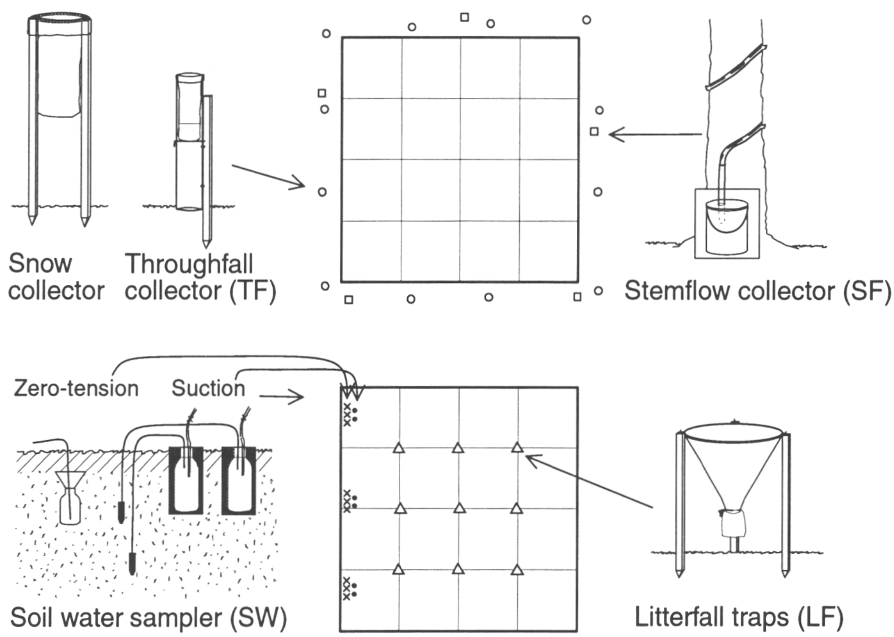


Figure 5. The layout of sampling at studied plots.

Concentrations of base cations and heavy metals in the BP and RW samples were analysed using inductively coupled plasma mass spectrometry (ICP-MS), NO_3, NH_4 and SO_4, by IC, and pH potentiometrically (Leinonen 2000).

The laboratories carrying out the analyses have continuous quality control programmes and regularly participate in national and international intercalibration exercises.

3.4 Calculation of total deposition

Permanently open collectors were used to collect precipitation over 1 week. This type of collector collects both wet and dry forms of deposition, i.e. bulk deposition. Permanently open collectors were also used to collect throughfall. Because of the interception of suspended dry deposition and chemical interaction in the canopy, throughfall does not correspond to total deposition to the forest floor for many elements. However, total deposition can be calculated using a combination of bulk and throughfall deposition data. The term *bulk precipitation* (BP) is used to refer to solute concentrations in the precipitation collected in the open area and the *bulk deposition* (BD) is used to refer to the flux of solutes associated with the bulk precipitation collected in the open area.

The so-called "throughfall method" to estimate total deposition is simple and widely used (Bredemeier 1988); (IV). The difference between the throughfall flux and open field bulk deposition (BD) flux is termed net throughfall. To the extent that dry deposited material is washed-off from the canopy by rain, the net throughfall flux below the canopy provides a measure of dry deposition. The net throughfall flux can partioned between interception deposition (ID) and a canopy sink/source component (±S) using sodium as an inert tracer. This is based on the assumption that Na shows insignificant interaction with the canopy. The calculations are as follows:

$TD_x = BD_x + ID_x$ x = element

$TF_x = BD_x + ID_x \pm S_x$

$ID_x = TF_x - BD_x$ x = Na

$(ID/BD)_{xpart} = (ID/BD)_{Na}$ xpart = Cd, Cu, Ni, Pb, Zn

$ID_{xpart} = (ID/BD)_{Na} * BD_{xpart}$

The method assumes a fixed relationship between wet and dry particles, and particles containing different elements are assumed to have the same median diameter as Na containing particles. Calcium, Mg and K can be assumed to be associated with the same sized particles as Na but this is probably not the case for other elements in deposition (Bredemeier 1988). The size of particles involved in the dry deposition of heavy metals captured by the canopy is unknown but it is expected to be relatively small because of the long-range transport involved. The throughfall method has therefore been used to estimate the TD loads of heavy metals (IV).

In paper V, sulphate was used as the inert tracer (Kubiznakova 1999). One of the studied catchments, Vuoskojärvi, is situated close to the sea and the use of Na (or Cl) as the tracer would give misleading results. Sulphate has not been shown to exhibit foliar exchange (uptake/

leaching); the SO_4 enrichment in throughfall being primarily the result of wash-off of accumulated dry deposition (Lindberg et al. 1986, Bredemeier 1988). The capture and filtration effect of the canopy was estimated using the sulphate enrichment canopy factor (EF). This factor is the ratio of throughfall (TF) sulphate flux to the open field bulk deposition (BD) sulphate flux:

$$EF = TF_{SO4} / BD_{SO4}$$
$$TD_x = EF * BD_x$$

3.5 Calculation of mass balance budgets and internal fluxes

In this thesis mass balance budgets at both the plot and catchments scale are presented. Input-output budgets for catchments containing lakes integrate the effects of both the terrestrial and aquatic parts of the catchment, while budgets at the plot-scale reflect only the terrestrial (canopy and soil) compartments. Mean annual input-output budgets were calculated for heavy metals both at plot and catchment-scales (IV) and at the plot-scale for major nutrients (V). Positive budget values indicate net retention (i.e. input > output) and negative values (i.e. input < output) net release.

3.5.1 Inputs

Inputs for the forested area of the catchments were calculated as the product of the average plot total deposition (TD) value and the area of catchment covered by forest. For the non-forested area, including the area of sparsely forested peatland and surface waters, inputs correspond to bulk deposition (BD) and were calculated as the product of the BD flux and the area of non-forested land in the catchment. Plot-scale inputs were the estimated total deposition flux values for the plot in question.

Differences between total deposition and throughfall are due to foliar exchange (uptake or foliar leaching). When TF < TD uptake of atmospheric inputs by the foliage is indicated, when TF > TD then foliar leaching (FL) is indicated (i.e. excretion from foliage, which is ultimately derived from the soil). The sum of FL and LF describes the amount of internal recycling between the soil and stand.

Total inputs to the forest floor were calculated as the sum of the throughfall and litterfall fluxes (i.e. TF+LF). Litterfall fluxes were calculated from elemental mass concentrations and the oven dry amounts of litterfall (mg m^{-2}). Although litterfall would include adsorbed atmospheric inputs this is considered negligible compared to amounts associated with the litter tissue and uptake from the soil (III).

3.5.2 Outputs

Catchment output fluxes (stream discharge) were calculated from streamwater (RW) concentrations and catchment runoff values (l s^{-1} km^{-2}). Monthly values were summed for the year and mean annual values calculated. Output fluxes for the plot-scale budgets were the leaching losses at 40 cm depth in the soil. Annual leaching fluxes were calculated as the product of measured annual mean SW concentration values (calculated from monthly volume-weighted concentrations at 35 cm depth) and modelled SW flux values at 40 cm depth. Monthly SW fluxes were modelled using a water balance model, WATBAL (Starr 1999), and summed to give annual values. Leaching fluxes from the humus layer (Hietajärvi only) and at 20 cm depth were also calculated. The fluxes from the humus layer at Hietajärvi were calculated from concentrations in zero-tension lysimeters and WATBAL hydrologic fluxes. The fluxes at 20 cm depth were calculated using the 15 cm depth suction lysimeter concentration data and WATBAL hydrologic fluxes at 20 cm depth.

3.6 Data handling and statistical analysis

In accordance with UN-ECE Integrated Monitoring Manual protocol (Manual for...1998) concentrations less than detection limit were substituted by a value equal to half the detection limit. The data was screened for gross outliers and any errors corrected. Gross outliers were rejected and given regression estimated values based on the concentration of other ions, if possible. Furthermore, TF samples with PO_4 concentrations >1 mg l^{-1} were rejected on the grounds of bird dropping contamination (Novo et al. 1992). Monthly mean values were calculated, volume weighted when possible. Statistical analyses were performed using the SYSTAT®, GraphPad PRISM™ and Quattro Pro© software packages.

Paper I: Bonferroni tests were used on TF and BP data to test for differences in mean concentrations between plots. Trends over the 7-year period were described using a LOWESS (locally weighted) smoothing curve fitted to the monthly data (GraphPad PRISM™). Significant long-term linear trends were analysed for using all the monthly values available and the non-parametric Seasonal-Kendall trend analysis procedure to calculate an estimate of the true slope of the linear trend (Hirsch et al. 1982, Gilbert 1987). This test may be used even though there are seasonal cycles and missing values.

Paper II: Because of positively skewed distributions, percentile summary statistics were used to describe concentration levels. The 50th percentile (median) describes average concentrations and the 95th percentile gives a reliable description of maximum concentrations. A log-normal distribution and maximum likelihood estimation procedure (Helsel 1990) was used to improve the accuracy of the percentiles for TF, SF and SW data because of samples with concentrations below detection limits. To determine whether monthly heavy metal concentrations in the aqueous media within each catchment were related to concentrations in BP, Spearman rank correlations were computed.

Paper III: The amount of nutrients leached from the litterfall collected in the LF traps were estimated. LFL_{gross} refers to the leachate collected from beneath the LF traps and includes nutrients derived from both throughfall passing through the LF traps and leaching from the litterfall itself. LFL_{net} refers to the nutrients leaching from the litterfall only (i.e., LFL_{gross}-TF). Total litterfall, LF_{tot}, is taken as the sum of LF and LFL_{net} and the total return of nutrients to the forest floor is given by the sum of TF and LF_{tot}.

Because of small sample sizes and non-normal distributions, non-parametric statistics were used. The Friedman statistic was used to test for pairwise differences between LFL_{gross} and TF concentrations and fluxes. Mann-Whitney and Kruskall-Wallis statistics were used to test for the significance of stand composition (Scots pine dominance vs. mixed) and regional effects, respectively, on the LFL_{net} fluxes.

Paper IV: Using a substitution value of half detection limit concentration with the relatively high detection limits of the equipment used would have resulted in too high SW and TF mean heavy metal concentration values, especially in the case Cd and Ni. A substitution value of zero was therefore used for values less than detection limit concentrations.

Paper V: The Friedman statistic was used to test for pairwise differences between plots in TF and SW concentrations. Linear trends were analysed using all the monthly values available and the non-parametric Seasonal-Kendall trend analysis procedure to calculate an estimate of the true slope of the linear trend (Hirsch et al. 1982, Gilbert 1987).

4. Results

4.1 Major nutrients and acidity (I,III,V)

4.1.1 Mean concentrations in bulk precipitation, throughfall and soil water (I,V)

Mean concentrations of H^+, SO_4 and sum of base cations (Ca+Mg+K) in bulk precipitation and throughfall during the period of 1989–1995 (I) and 1989–1997 (IV) are presented in Table 3. For each solute, TF concentrations were greater than BP concentration. The acidity of both BP and TF decreased northwards (i.e. increased pH) and mean values were generally lower for the 1989–1995 period than for the 1989–1997 period. The higher mean H^+ concentrations for the 1989–1997 period are probably because wintertime TF measurements were not made until winter 1994/1995. Sulphate and base cations showed a similar decreasing trend northwards and higher values for the 1989–1997 period. However, the mean of the sum of base cation concentrations in BP during both periods decreased northwards only as far as to Pesosjärvi and were then higher at Vuoskojärvi. A similar pattern was shown by TF, although not as clearly as for BP. The increase in the sum of base cation concentrations at Vuoskojärvi in both BP and TF is due to additional inputs of marine Mg derived from the nearby Arctic Ocean (Starr & Ukonmaanaho 1995b).

The mean concentrations of Ca, K, Mg, Na, NH_4, NO_3, total N, SO_4, total S and H in bulk precipitation, throughfall and soil water during 1989–1997 are presented in Table 2 (V). The values increased in the order: BP<TF<SW in case of Ca, Mg, Na and SO_4 concentrations. The increase in the case of throughfall is related to the capture and subsequent wash-off of dry deposition from the canopy but a number of possible processes may be involved in the case of SW, including: concentration effect due to water consumption (evapotranspiration), leaching

Table 3. Mean concentrations of H^+, SO_4-S and sum of base cations during the period 1989–1995 and 1989–1997 in bulk precipitation (BP) and throughfall (TF). (sd = standard deviation).

Catchment		H^+ µmol l^{-1}		SO_4-S µmol l^{-1}		Ca+Mg+K µmol$_{(+)}$$l^{-}$	
		1989-95	1989-97	1989-95	1989-97	1989-95	1989-97
Valkea-Kotinen	BP	30.3	35.6	18.7	21.9	12.5	14.6
	sd	(11.89)	(7.89)	(10.3)	(7.31)	(7.52)	(4.30)
	TF	34.15	38.0	48.3	57.7	125.0	150.8
	sd	(18.96)	(13.53)	(21.17)	(19.27)	(52.27)	(49.44)
Hietajärvi	BP	29.8	33.7	18.7	17.7	9.9	9.5
	sd	(11.62)	(5.37)	(8.4)	(5.90)	(6.24)	(2.90)
	TF	37.5	37.4	28.1	27.7	44.3	48.0
	sd	(23.1)	(8.44)	(16.85)	(9.24)	(33.5)	(24.80)
Pesosjärvi	BP	26.4	29.5	12.5	14.1	5.3	6.8
	sd	(11.45)	(4.84)	(6.9)	(4.71)	(2.64)	(2.05)
	TF	25.55	26.3	26.5	27.3	45.6	55.2
	sd	(16.04)	(9.20)	(21.3)	(9.11)	(27.56)	(31.26)
Vuoskojärvi	BP	22	24.2	12.5	14.2	10.3	17.9
	sd	(16.12)	(3.64)	(7.5)	(4.75)	(15.93)	(8.92)
	TF	23.7	25.5	21.85	22.3	58.9	55.9
	sd	(16.35)	(11.70)	(15.8)	(7.44)	(104.8)	(44.74)

from litterfall, mineralisation of organic matter, weathering and desorption and exchange reactions. Concentrations of NH_4 and NO_3 decreased in the order BP>TF> SW and reflects the shortage of available N typical in boreal forest ecosystems. Potassium concentrations were generally the highest in TF.

Within the soil, concentrations of K, total-N, S and acidity in soil solution tended to decrease with depth, while concentrations of Mg increased with depth at all plots. Changes in the concentrations of other solutes with depth were either unchanging or irregular. The buffering of acidity by the soil was observed as an increase in the pH (decrease H) of the soil water as it passed downwards through the soil. Ammonium and nitrate concentrations did not show any marked differences between depths. Calcium, Na and SO_4 concentrations were higher at 35 cm depth in Valkea-Kotinen and Vuoskojärvi, while higher at 15 cm depth at Hietajärvi and Pesosjärvi. Soil water leaving the humus layer was only collected at Hietajärvi. Solute concentrations in that water were always higher than those in BP, TF and SW at 15 and 35 cm depths.

4.1.2 Temporal trends (I, V)

4.1.2.1 Seasonality in TF quality (V)

Seasonal patterns in TF concentrations were observed during the period May 1994 to December 1997, when collection was continuous throughout the year (Fig. 6). Concentrations of H, Ca, Mg, Na, NO_3 and SO_4 generally peaked in the spring, which occurs later in northern plots. In contrast K concentrations peaked in the autumn, in relation foliar senescence and leaching. The seasonality in throughfall concentrations at northernmost plots (PJ2, VJ2 and VJ3) was, with the exception of H, SO_4 and K, rather subdued.

4.1.2.2 Long-term trends in bulk precipitation, throughfall and soil water quality (I, V)

Throughfall chemistry (I, V)

Over the period 1989–1995 monthly mean concentrations of SO_4 and H in both bulk precipitation and throughfall showed significant ($p < 0.05$) negative linear trends at three of the catchments, the exception being Vuoskojärvi (Table 4, I). Trends in throughfall over the longer period, 1989–1997, were examined in Table 3 (V) and they showed a continuation in the declining trends in H and SO_4 concentrations. At Valkea-Kotinen (plot 3), the slope estimate of the sulphate trend for TF indicates that SO_4 concentrations have decreased by 0.14 mg l^{-1} S yr^{-1}. At Hietajärvi (plots 1 and 4) the decrease was 0.1 mg l^{-1} S yr^{-1} and at Pesosjärvi (plot 2) 0.06 mg l^{-1} S yr^{-1} (Table 3, V). The acidity of TF at VK3 actually increased significantly over the study period.

The sum of base cation concentrations did not show a significant linear long-term (1989–1995) trend in either bulk precipitation or throughfall (I). In the period 1989–1997 (V) linear trends in throughfall were calculated for each base cation separately. Only Ca concentrations showed a decreasing trend, but only that for VK3 and HJ1 was significant (0.03 mg l^{-1} yr^{-1}). Sodium concentrations showed no trends other than a small but significant increasing trend (0.02 mg l^{-1} yr^{-1}) at VK3.

Trends in TF NO_3 concentrations at most plots decreased but only significantly at PJ2 (Table 3, V). Ammonium concentrations in TF at PJ2 also showed a significant decreasing linear trend but at the other plots the trend was for an increase. Throughfall total N concentrations, which have only been measured since 1994, showed a decreasing trend at all plots except in VK3.

Soil water (V)

In general the trends for soil water monthly solute concentrations (1989–1997) were rather similar to those for throughfall (Table 4, V). Sulphate concentrations decreased significantly at nearly all plots and depths, reflecting decreased atmospheric inputs to the soil. Concentrations of H^+ decreased significantly only at VJ3 at both depths and at HJ4 at 35 cm depth. However at VK3 acidity increased significantly at both depths and HJ1 at depth of 15 cm. Soil water

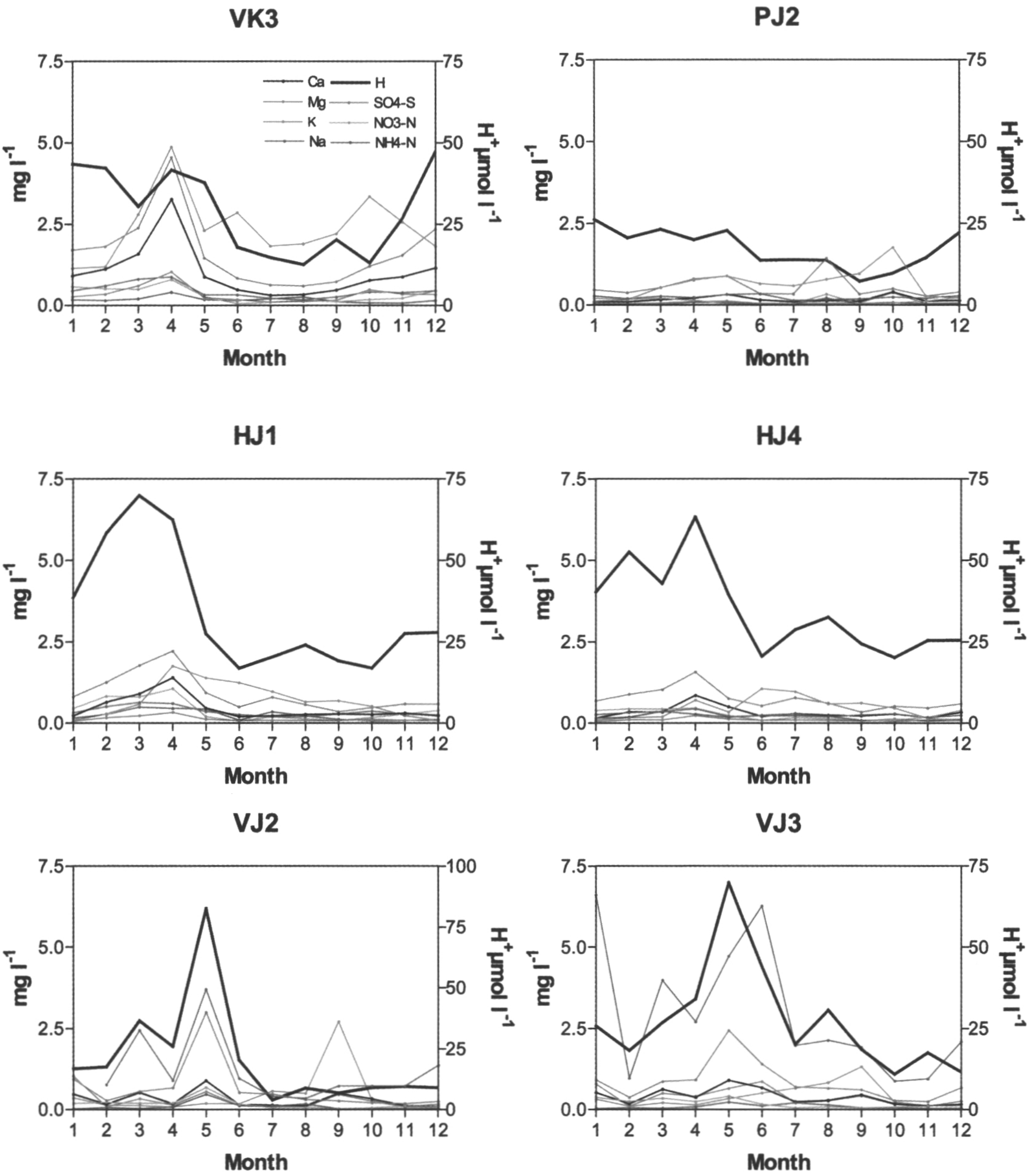


Figure 6. Average monthly throughfall concentrations (mg l⁻¹) in Ca, Mg, K, SO_4-S, NH_4-N,

concentrations of Ca, Mg and K decreased significantly at most of the plots and depths. Sodium concentrations increased significantly at VJ3 (15 cm depth), probably as a result of increased marine inputs. Inorganic N and total N concentrations showed few, small and inconsistent significant trends.

4.1.3 Fluxes and mass balance budgets (V)

4.1.3.1 Mean annual fluxes (V)

Mean annual fluxes of elements associated with bulk deposition, total deposition, throughfall, soil water and litterfall calculated for the period 1989–1997 are presented in Table 5 (V) and Figures 2a-f (V).

With the exception of Na and Mg, catchment fluxes were the highest at Valkea-Kotinen and decreased northwards. This reflects not only the same trend in solute concentrations but also in the amount of precipitation (Table 1, V) and distance of emission sources. The fluxes for Na and Mg were the highest at Vuoskojärvi, which is a result of proximity to the sea (within 100 km of the Arctic Ocean) and marine inputs of these elements. The north-south trend was less clear for SW fluxes, reflecting the importance of local soil factors in controlling soil water chemistry. The LF fluxes also decreased northwards, reflecting differences in stand density and species composition (Table 1, V).

4.1.3.2 Internal fluxes (V)

The foliar leaching (FL) is indicated when the flux ratio of TF to TD is > 1. Calcium, Mg, Na and particularly K exhibited foliar leaching, accounting for some 65 % or more of TF enrichment at each plot. Inorganic nitrogen compounds were retained in the canopy, as expected, except for NH_4 at VJ2.

Litterfall and foliar leaching fluxes form part of the ecosystem internal nutrient cycle and describe the return of nutrients from the above ground biomass to the forest floor. The magnitude and relative importance of the LF and FL pathways varied with nutrient and depended on geographic location, stand density and composition (Table 1, V). Results indicate that LF fluxes of Ca, Mg and N are greater than FL fluxes and vice verse for K, Na and S. The amount of recycled nutrients (LF+FL) returning to the forest floor (Fig. 2a-f, V) ranged between 2709 to 239 mg m^{-2} yr^{-1} for Ca, 430 to 71 mg m^{-2} yr^{-1} for Mg and 1358 to 125 mg m^{-2} yr^{-1} for K, inputs always being the lowest at VJ3 and the highest at VK3. Vuoskojärvi plot 3 is the northernmost plot with the lowest stand density; while VK3 is the southernmost plot with the highest stand density (Table 1, V).

4.1.3.3 Litterfall leaching losses (III)

Litterfall in the litterfall collectors is subject to washing and leaching by throughfall. This depletion may result in litterfall fluxes being underestimated. Conversely, microbial processes in the trapped litter may take-up nutrients from TF, which would be included in the LF flux. In

Paper III the results from a study to assess the possible importance of the leaching loss from litter in LF traps are presented.

For two months (August and September 1995) the flux of nutrients draining from the LF traps (which includes TF and any leaching from the litter material) was collected. The flux of nutrients associated with this litterfall leachate, LFL gross, was greater than the TF flux, which clearly indicates that nutrients were leached from or washed-off the litter collected in the LF traps. The contribution of this LF leachate component to the true LF flux (LF+LF leachate) was 91 % for Na, 51 % for S, 49 % for K, 13 % for Mg, 11 % for Ca, and 6 % for N when averaged across months. However, for one or the other months, the water draining from the LF traps had lower concentrations of some nutrients than in TF, indicating the trapped litter was retaining nutrients from the TF in these cases.

4.1.3.4 Mass balance budget (V)

Plot-scale annual total deposition inputs (TD) of H, NO_3 and NH_4 at all the plots and SO_4 at HJ1, HJ4, PJ2 and VJ3 plots were greater than output fluxes, i.e. leaching losses at depth of 40 cm (Table 5, V). Base cation inputs were less than outputs at all plots and SO_4 at VK3 and VJ2 plots. Comparing leaching outputs to total inputs to the forest floor (i.e TF+LF) showed that of Ca, Mg, K and N input were greater than outputs. The retention of total N by the soil was nearly 100 %, but 46–82 % for Ca, 9–70 % for Mg, 46–81 % for K, depending on plots. Sulphur retention by the soil only occurred at Hietajärvi (both plots) and there was a net leaching loss at other plots. There was a net leaching loss of Na at all plots except at VJ3.

At Hietajärvi, where SW from under the humus layer has been collected, showed that much of the total inputs (TF+LF) of Ca, Mg and N to the forest floor were retained in the humus layer. Although humus layer outputs of Na, K and S exceeded total inputs, retention subsequently took place in the mineral soil.

4.2 Heavy metals

4.2.1 Concentrations in deposition, soil, groundwater and surface waters (II)

The median concentration and variability of Cd, Cu, Ni and Pb in the various types of water studied decreased in the order: SW>TF, SF>BP, whereas the Zn concentrations were highest in SF (Table 3, II). The higher concentrations in stemflow and throughfall compared to bulk precipitation indicated the wash-off of intercepted dry deposition. Concentrations generally decreased in all water types and for all heavy metals from south to north. However, Cu and Ni concentrations in BP were the highest in the northernmost catchment, Vuoskojärvi, which is probably related to emissions from the Kola Peninsula (AMAP 1997). A relatively high median Cu concentration in SW at Vuoskojärvi was also seen. Median concentrations of Ni and Cu (TF and SF) and Pb (TF and SW) were higher at Pesosjärvi than at the other catchments.

Heavy metal concentrations in groundwater (GW), lake (LC) and stream water (RW) were similar and were also the lowest of the types of water monitored. This suggests that there was retention of heavy metals in the overburden below the soil and in lake sediments. Zinc and Pb concentrations in the surface waters (LC, RW) at Valkea-Kotinen were 3 to 9 times higher than those in the other catchments.

4.2.2 Concentrations in biota tissues (II)

Heavy metal concentrations in the *Pleurozium schreberi* moss (MC), current year Scots pine needles (NC), litterfall (LF), humus layer (SC), shrew liver and ants tissue are presented in Table 4 (II). For all media, Pb concentrations tended to decrease northwards, indicating that concentrations in biota were related to the deposition of Pb. Concentrations of Cd, Cu, Ni and Zn in different media (MC, NC, LF, SC, ants and shrew livers) were rather similar among catchments. Highest concentrations were at the southernmost catchment Valkea-Kotinen, except the highest Zn concentrations at Vuoskojärvi in NC and LF and Ni in MC.

4.2.3 Long-term trends (II)

Seasonal-Kendall trends fitted to monthly BP, TF and SW Cu concentration data for 1990–1999 indicated significant trends (decreasing) only in the case of SW 15 cm at Hietajärvi and in BP and TF at Pesosjärvi (Table 4). For Pb, there was a significant decreasing trend in BP at all catchments, in TF at three catchments and in SW at the two southerly catchments. For Zn, there was a significant decreasing trend in BP at Hietajärvi, but a significant increasing trend in TF at the southerly catchments. Concentrations of Zn in soil water showed a significant increasing trend at Valkea-Kotinen but a significant decreasing trend at Vuoskojärvi at 15 cm.

Only Pb and Zn concentrations in biota showed a trend (Fig. 3, II). Lead concentrations in mosses (MC), which are a reliable indicator of the atmospheric Pb deposition (Berg et al. 1995), indicated a near 50 % decrease from 1991 levels to 1996 levels at all catchments. However, the reduction in Pb deposition has had little effect on concentrations in LF, SC and NC, which have remained unchanged. Zinc concentrations in MC increased at Pesosjärvi (37 %) and Vuoskojärvi (31 %) over the period 1991–1996, while remaining the same at Valkea-Kotinen and Hietajärvi. Litterfall and humus layer Zn concentrations at Vuoskojärvi have also increased, but significantly only in the humus layer ($p = 0.004$). Zinc concentrations in NC, which were lower than in LF (Table 4, II), have remained unchanged at Vuoskojärvi and Pesosjärvi while decreasing at Valkea-Kotinen and Hietajärvi.

4.2.4 Fluxes and mass balance budgets (IV)

4.2.4.1 Plot-scale budgets (IV)

Plot scale input (TD) – output (SW) budgets for VK3, HJ1 and HJ4 are presented in Figures 2a-c (IV). Only Cd showed a consistent negative budget at all three plots, with leaching fluxes at 40 cm depth being two to threefold total deposition input fluxes. However, comparison of the leaching fluxes at 40 cm depth with total inputs to forest floor (TF+LF) indicate that, with

Table 4. Trace metal mean concentrations ($\mu g\ l^{-1}$) in bulk precipitation (BP, 1991-1999), throughfall (TF) and soil water (SW) at 15 cm and 35 cm depth, and the Seasonal-Kendall linear slope (trend) estimates ($\mu g\ l^{-1}\ yr^{-1}$) and associated probabilities during the 1990-1999.

Catchment		Cu $\mu g\ l^{-1}$	slope	p	Pb $\mu g\ l^{-1}$	slope	p	Zn $\mu g\ l^{-1}$	slope	p
Valkea-Kotinen	BP	1.4	-0.04	0.070	2.3	-0.20	0.000	6.3	-0.07	0.510
	TF	3.5	0.00	0.467	4.5	0.00	0.001	15.1	1.63	0.000
	SW15 cm	7.1	0.35	0.160	7.4	-0.08	0.000	40.2	4.03	0.001
	SW35cm	6.8	0.07	0.305	7.1	-0.06	0.001	21.3	1.26	0.005
Hietajärvi	BP	1.5	-0.03	0.063	1.9	-0.10	0.002	4.5	-0.12	0.019
	TF	5.2	0.00	0.183	3.0	0.00	0.043	11.6	1.19	0.003
	SW15 cm	7.5	-0.56	0.018	8.2	-0.01	0.067	44.9	1.47	0.132
	SW35 cm	7.3	-0.19	0.083	6.5	0.02	0.012	41.6	0.92	0.804
Pesosjärvi	BP	2.1	-0.07	0.003	1.4	-0.08	0.000	3.3	-0.10	0.030
	TF*	6.4	0.00	0.003	6.8	0.00	0.697	19.2	1.24	0.006
	SW15 cm*	10.6	-0.35	0.288	8.9	-0.58	0.193	39.4	-1.23	0.237
	SW35 cm*	6.3	-0.58	0.193	8.3	-0.65	0.252	18.9	-0.05	0.852
Vuoskojärvi	BP	3.3	-0.10	0.068	1.2	-0.04	0.012	2.9	0.00	0.777
	TF†	5.2	0.00	0.384	6.3	0.00	0.003	11.0	0.43	0.335
	SW15 cm‡	22.3	0.42	1.000	3.9	-0.11	0.100	72.6	-22.83	0.049
	SW35 cm	21.0	0.00	1.000	2.5	0.00	0.536	52.6	-3.22	0.575

* 1990-1998
† 1990-1997
‡ 1993-1997

exception of Ni at VK3, there was considerable retention in the soil (10–95 %). Comparison of the retention values with calculated internal fluxes (FL+LF) indicate that the retention was mainly in form of uptake and recycling in the case of Ni (HJ1 and HJ4), Cd and Cu. Assuming uptake of Pb does not take place, the retention of Pb took the form of accumulation in the soil. Throughfall fluxes of Cd and Cu were clearly greater than TD fluxes at all three plots, indicating foliar leaching of these metals. The LF flux of Zn indicates that litterfall is the major pathway by which Zn is recycled in forest ecosystems.

At Hietajärvi, where leaching from the humus layer has been determined, the level of retention of total inputs by the humus layer were > 50 % for each of the heavy metals at HJ4 and 26 % (Pb) to 65 % (Cu) at HJ1 (Fig. 2b-c, IV). Further retention of heavy metals took place in the mineral soil.

4.2.4.2 Catchment-scale budgets (IV)

Annual total deposition loads for Cd, Cu, Ni, Pb and Zn have been calculated for the Valkea-Kotinen and Hietajärvi catchment for the period 1994–96 (IV). The loads were low compared to polluted and temperate forest ecosystems (Lindberg & Turner 1988, Lindberg et al. 1989, Berg et al. 1996).

Catchment-scale input (TD) – (RW) output budgets are presented in Table 3 (IV). The budgets indicate that much of the atmospheric inputs of heavy metals were retained within the catchments. The relative of retention by the catchment ((TD-RW)/TD) was 77 % or more, except for Ni at Valkea-Kotinen where retention was only 54 %. For Pb and Cu, the retention was more than 94 %.

The amount of retention by the catchment terrestrial and lake compartments together with the calculated transport fluxes from the terrestrial part to the lake are included in Table 3 (IV). Retention in the terrestrial part of the catchment was greater than retention in lake sediments for all heavy metals; for Cu terrestrial retention was 97 % at VK and 94 % at HJ of the total retention in the catchment. The terrestrial retention of atmospheric inputs of Pb was 93 % of total catchment retention at VK and 74 % at HJ. Of the atmospheric input of Cu to the terrestrial area, < 2 % was transferred to the lake at both catchments. For Pb, the corresponding figure was 7 % at VK and 21 % at HJ.

5. Discussion

5.1 Levels and trends in concentrations of major nutrients and acidity (I,V)

The four Integrated Monitoring sites are situated along a north-south deposition gradient. The acidity of BP, TF and SW generally decreased northwards and this trend was reflected in decreasing SO_4 concentrations. Result indicate that the reduced SO_4 emissions throughout Europe have had a significant impact in reducing 'acid rain' pollution in Finland. Marine inputs of SO_4, Mg and especially Na from the nearby Arctic Ocean clearly affected the concentrations of these ions at Vuoskojärvi. Concentrations in SW were generally higher than TF and BP. Throughfall concentrations of Ca, Mg, K, Na and SO_4 were higher than BP, the result of foliar leaching or the wash-off of intercepted dry deposition. Inorganic nitrogen, NO_3 and NH_4, were taken up by the canopy, resulting in lower concentrations in TF compared to BP. Inorganic N concentrations were reduced further in the soil.

Concentrations of Ca, Mg, Na, SO_4, NO_3 and H in TF were higher during winter and in early spring although not as clearly at all plots (Fig. 6). BP also shows peak concentrations in winter and early spring (Ruoho-Airola et al. 2001) indicating that seasonal pattern in TF is mainly caused by seasonal patterns in emissions. However, the TF collectors in the wintertime also collect litterfall, which then can contaminate the snow samples upon melting. In addition high evaporation in springtime, especially in North Finland, could cause concentration effect of TF. The higher TF concentrations during wintertime accounts for the difference between the mean annual concentrations calculated for the 1989–95 and for the 1989–97 periods (Table 3). There was only wintertime sampling in the 1994/1995 winter in the first period. The seasonality in throughfall concentrations at the northernmost plots (PJ2, VJ2 and VJ3), with the exception of H, SO_4 and K, were rather subdued. The low seasonal variation in North of

Finland is also found in BP (Ruoho-Airola et al. 2001). Throughfall K concentrations peaked during the autumn at most of the plots, which is due to the foliar senescence (Ulrich 1983b).

Concentrations of SO_4 in TF were about double those in BP. Enrichment in TF is primarily the result of wash-off of intercepted dry deposition that accumulates between rainfall events (Lindberg & Lovett 1992). The concentration of SO_4 in SW increased with depth at Valkea-Kotinen and Vuoskojärvi. This increase is unlikely to be due to a concentration effect resulting from evaporation and storage changes since modelled water fluxes were similar at both depths. Desorption of previously retained SO_4 from deposition or the mineralization of organic S pools, however, may account for this increase (Harrisson & Johnson 1992, Mitchell 1992).

The trend analysis results showed that SO_4 concentrations in TF have significantly decreased during the 1990s at the 3 more southerly catchments. The linear slope of the trend was greatest at VK, the most southerly catchment, where air pollution has been the greatest. This is further evidence of a progressive reduction in the acidity and sulphate concentration in precipitation throughout most of Finland that has been observed during 1990s (Kulmala et al. 1998). The lack of significant decline in SO_4 concentrations at Vuoskojärvi in the north can be explained by the already low concentrations there and this SO_4 is mostly supplied from the nearby Arctic Ocean rather than being of anthropogenic origin. A decreasing trend in soil water SO_4 concentrations was also seen at plots, except VK3 depth of 35 cm. The decreasing trend was significant at both depths at HJ1 and VJ3. However, SW acidity has declined significantly only at VJ3 at both depths and HJ4 at depth of 35 cm.

The concentrations of Ca, Mg and K in precipitation as it passed through the ecosystem increased in the order: BP<TF<SW. The enrichment of TF in base cations, K in particular, is due to foliar leaching (FL). Calculating the FL flux as TF-TD when TF/TD > 1 (Table 5, V) shows that some 70 % or more of the Ca and Mg enrichment in TF is due to foliar leaching. For K, the figure was 90 % or more. Similar results have been presented by Lovett & Schaefer (1992). Potassium concentrations in SW were lower at 40 cm depth than at 20 cm indicating uptake. Similar reductions in K concentrations in soil water with depth have been found in different soil types in Europe (Farrell et al. 1994). Calcium, Mg and Na mean concentrations at 35 cm depth were similar or less than concentrations at 15 cm depth, also indicating uptake and cation exchange.

Trends in the TF concentrations of Ca, Mg and K were only slightly negative, being significantly negative only for Ca at VK3 and HJ1 (Table 3, V). A similar slight declining trend of base cation concentrations in BP at the IM sites has been reported by Ruoho-Airola et al. (1998). These results are contrast with those presented by Kulmala et al. (1998), who reports that regional decline in base cation concentrations in bulk precipitation has taken place during the 1990s. This decline has been attributed to the installation of dust removal systems in the oil shale power plants of Estonia and Russia (Jalkanen et al. 2000). Similar declining trends in BP base cations concentrations are reported for Europe and North America (Hedin et al. 1994). Nevertheless, there has been a declining trend in SW base cation concentrations at all plots and depths. If there has been no significant decline in the inputs of base cations in deposition, the decline in SW base cation concentrations may be related to the decline in the SO_4 deposition and SW concentrations. Since SO_4 in the SW would have served as an important accompanying anion for base cations (Singh et al. 1980), any reduction in SO_4 concentrations would lead to a reduction in base cation concentrations.

The acidity of precipitation also decreased with latitude and H^+ concentrations in TF were greater than in BP (Table 2, V) at all catchments except at Pesosjärvi. Many studies have found that the pH of TF coniferous forest is lower than that of precipitation (e.g. Parker 1983, Helmisaari & Mälkönen 1989, Hyvärinen 1990). The increase in the acidity of TF is due to leaching of organic acids and the release of H^+ in exchange for NH_4^+-ions at the needle surface (Tukey 1970, Cronan & Reiners 1983, Edmonds et al. 1991). The wash-off of SO_4 dry deposition from the canopy may also increase the acidity of TF. The decrease in soil water acidity with soil depth has been found in most studies (e.g. Helmisaari & Mälkönen 1989, Lindroos et al. 1995) and is related to various buffering and neutralisation processes in the soil (Binkley & Richter 1987, de Vries & Breeuwsma 1987). The decrease in SW acidity with depth is most clearly seen at HJ, where SW was collected from under humus layer in addition to 20 and 40 cm depths.

The pH of precipitation in Finland has increased overall by more than 0.2 pH units over the last 10 years (Leinonen et al. 2000). Proton concentrations in TF showed a decreasing trend at all plots over the 1989–1997 period, except VK3 (Table 3, V). This trend is clearly due to the observed decline in sulphate concentrations, but the degree of reduction depends also on the characteristics of stands. The increase in H^+ concentrations in TF at VK3 may be related to a proportionally greater reduction in Ca concentrations than SO_4 concentrations. The reduced SO_4 concentrations in SW may have been expected to result in decreased SW acidity. This was the case at most plots but not at VK3 and HJ1, where acidity significantly increased over time. This may be due to the declining trend of base cation concentrations at these plots. Nevertheless, the trend for declining acidity in BP, TF and SW at most plots is primarily due to the decline in SO_2 emissions and SO_4 depositions rather than an increase in base cations deposition.

Concentrations of inorganic N in TF were less than in BP at the two southern plots, indicating canopy uptake, but the difference disappeared northwards with concentrations of NH_4 in TF being actually greater than those in BP at PJ and VJ, indicating canopy release (Table 2, V). The canopy leaching of NH_4 at PJ and VJ may be due to a low demand for NH_4 by much old growth forests so far north (Edmonds et al. 1991). Soil water concentrations of NH_4 and NO_3 were lower than BP and TF, indicating efficient retention of NH_4 and NO_3 in the soil. Similar results have been reported by Piirainen et al. (1998). The shortage of available N (inorganic) in boreal coniferous forest is well known and the lower SW concentrations are considered to be due to uptake by roots and microbes.

The bulk deposition of inorganic nitrogen over Finland has reportedly decreased over the last 16 years (Kulmala et al. 1998). For NO_3 the reduction has been 20–40 % and even greater for NH_4 45–85 %. Such reductions, however, were not found in the TF collected of the IM plots, except at PJ2, where concentrations of inorganic N have significantly declined. Leinonen et al. (2000) also found the deposition of both NH_4 and NO_3 in the northernmost Finland to have increased during 1987–96, in the case of NH_4 by 30 % and slightly less for NO_3. No trend in SW in case of NO_3 or NH_4 concentrations was seen, except at VJ3, where NH_4 concentrations significantly decreased at both depths and at PJ2 at depth of 15 cm. The dominance of NO_3 over NH_4 in both BP and TF concentration (at least southern plots) and the low levels of nitrogen leaching from the soil all indicate that N deposition at these catchments does not have an acidifying effect on the soil (Van Breemen et al. 1983). Even though in contrast to bulk precipitation and throughfall NH_4 concentration in soil water was higher than NO_3.

5.2 Heavy metals concentrations and trends (II, IV)

Concentrations of heavy metals (Cd, Cu, Ni, Pb, Zn) in all the water types studied were generally low compared to temperate forest ecosystems (Bergkvist et al. 1989). Bulk precipitation concentrations were similar to those reported for six rural and remote sites in Norway in 1989–90 (Berg et al. 1994, Juntto 1997). Throughfall was generally enriched in heavy metals compared to BP. The concentrations of Pb and Zn in BP decreased northwards, reflecting the trend in the long-range atmospheric transport of these metals and local emissions. Local effects of geochemistry could also be observed, e.g. the relatively high Zn concentrations in SW at Vuoskojärvi compared to concentrations in BP.

The enrichment of Pb in TF must be due to the wash-off rather than foliar leaching since the internal cycling of Pb is negligible (Ulrich et al.1981, Bergkvist et al. 1989). For Zn and Cu however, the enrichment is probably due to foliar leaching since both elements are micro-nutrients and internally cycled (Alloway 1995). Zinc concentrations were particularly high in SF, as has also been found in other studies (Bergkvist et al. 1989). The high concentrations of Cu and Ni in BP at Vuoskojärvi are presumably related to emissions from the Cu-Ni smelters on the Kola Peninsula (AMAP 1997). However, the concentrations of Cu and Ni in the TF, SF or SW at Vuoskojärvi were not particularly higher than elsewhere. At Pesosjärvi median concentrations of Ni and Cu in TF and SF and Pb in TF and SW were higher than at the other catchments. In the case of Ni and Cu, the elevated concentrations might also be related to Kola Peninsula emissions. In the case of Pb the metallurgical complex at Kostamuskha situated 150 km southeast from Pesosjärvi might be related high Pb concentrations (Poikolainen 2000).

As throughout Europe (Renberg et al. 2000) Pb concentrations in BP have declined over the study period (Table 4). This reduction was also in TF and SW and is clearly a result of the use of nonleaded gasoline. Zinc concentrations in TF have increased, significantly at Hietajärvi and Pesosjärvi, even though no increase in BP concentrations could be seen. Soil water concentrations of Zn have remained unchanged at VK and HJ but decreased at PJ and VJ. This difference in SW trends for Zn between catchments may reflect ongoing adjustments in the cycling of Zn in response to changes in the acidity of deposition. Copper concentrations mostly show declining trends, which are significant in the case of SW at Hietajärvi and BP at Pesosjärvi.

The decline in Cu concentrations in BP and SW at Pesosjärvi are probably related to declining Cu emissions from Kostamuskha (Poikolainen 2000).

Decreases in moss (*Pleurozium schreberi*) concentrations of Pb corresponded to those in BP with nearly a 50 % decrease in concentration between 1991 and 1996 at all catchments. Zinc concentrations in the moss were greater in 1996 than in 1991, except at VK. Moss Zn concentrations are, however, a poor indicator of deposition because Zn is also micronutrient and recycled (Berg et al. 1995).

Concentrations of heavy metals in SW particularly for Pb decreased sharply with depth. Heavy metals are generally strongly adsorbed by organic matter (e.g. Schnitzer & Skinner 1967, Bergkvist 1987, Berkgvist et al. 1989), which also shows a strong depth gradient in forest soil (Tamminen & Starr 1990). Soil acidity is also an important factor in controlling the mobility and leaching of heavy metals particularly Cd in soils (Schnitzer & Skinner 1967). Soil acidity in forest soils typically increases with depth (Tamminen & Starr 1990).

5.3 Fluxes and mass balance budgets of major nutrients and heavy metals (III,IV,V)

5.3.1 Total deposition (V)

Deposition loads typically decreased northwards because of the decrease in precipitation amount and longer distance from emission sources (Table 1, V). The mean annual (1989–1997) total deposition of SO_4 decreased from 6.2 kg S ha^{-1} at Valkea-Kotinen to less than 2.0 kg S ha^{-1} at Vuoskojärvi. Similarly the total deposition of inorganic nitrogen decreased from 6.0 kg N ha^{-1} at Valkea-Kotinen to less than 1.0 kg N ha^{-1} at Vuoskojärvi. In Europe total deposition loads of S vary between 2–45 kg S ha^{-1} (EC-UN/ECE 1999). Total N loads in Central Europe during the 1990s was as high as 50 kg ha^{-1} y^{-1}, even 70 kg ha^{-1} yr^{-1} (Dise et al. 1998). The deposition loads of both N and S at the Finnish IM sites are therefore very low, particularly N. Only in the vicinity of fur farms has N deposition been shown to exceed over 10 kg ha^{-1} y^{-1} in Finland (Ferm et al. 1990). Changes in forest understorey vegetation may occur at N deposition loads of 15–20 kg ha^{-1} yr^{-1} and to have negative impacts on the tree health at 20–40 kg ha^{-1} yr^{-1} (EC-UN/ECE 1999). No negative impacts from N deposition are therefore to be expected at the Finnish IM areas. The total acidity (S+N compounds – base cations) of deposition varied between 9 $mol_{(c+)}$ ha^{-1} yr^{-1} at Vuoskojärvi to 200 $mol_{(c+)}$ ha^{-1} yr^{-1} at Valkea-Kotinen. The critical load of total acidity at which damage to forest ecosystems can be expected is between 1500-3000 $mol_{(c+)}$ ha^{-1} yr^{-1} (EC-UN/ECE 1999). Clearly, the total acidity load at the Finnish IM sites is far below critical load values.

5.3.2 Foliar leaching and wash-off (III,IV,V)

The LF flux primarily represents an internal flux related to nutrient uptake and cycling. However it also includes dry deposition collected by the needles and leaves while still part of the canopy. For Ca, Mg and N annual LF flux was greater than the TF flux and for K, Na and S annual TF flux was greater than LF flux. Other studies have found similar results (e.g. Helmisaari 1995, Gordon et al. 2000). Foliar leaching is also part of the internal flux of nutrients.

The relative importance of the LF and FL pathways varies with the mobility of the nutrient (Parker 1983). Of the combined LF+FL flux, about 51 % of K, 80 % of Na and 50 % of S was returned to the forest floor by canopy leaching. For the other nutrients the figure was less than 25 %.

For Ca, Mg, K, Na and S (Fig. 2a-f, V) TF fluxes of catchment were generally greater than the TD fluxes, indicating foliar leaching for these nutrients. Concentrations of TF and TD fluxes for heavy metals at VK3, HJ1 and HJ4 indicated foliar leaching in some cases, including Pb at VK3 (Fig. 2a-c, IV). Since the internal cycling of Pb in forest ecosystems is considered small or negligible (Bergkvist et al. 1989, Lindberg & Harriss 1981), foliar leaching of Pb seems unlikely. The apparent foliar leaching of Pb at VK3 may be related to the presence of Norway spruce in the stand. The Norway spruce in the stand at VK3 had a particularly a high number of needle age classes (up to 8 years) and it may be possible that Pb adsorbed onto the older needles during previous years, when Pb deposition was higher, may be enriching the current TF flux. This might also partly explain the higher LF flux of Pb at the Valkea-Kotinen plot, which was about fourfold that at the Hietajärvi plots. The results for Cd also indicate substantial foliar leaching. The potential foliar leaching of Cd is also indicated by larger TF fluxes compared to LF fluxes. Throughfall accounted for most of the total inputs of Cu to the forest floor (i.e.TF+LF) at Hietajärvi (86 % and 90 %) but only 51 % at Valkea-Kotinen. This would indicate that Cu is more easily mobilised from Scots pine canopies than from mixed Norway spruce-deciduous canopies. The relatively large LF flux of Zn, particularly at the VK3 plot, indicates substantial internal cycling of Zn. The foliage of deciduous trees, birch in particular, has considerably higher concentrations of Zn compared to coniferous trees (Berthelsen et al. 1995). The high proportion of birch in the stand at the Valkea-Kotinen plot may therefore partly explain the high Zn LF flux observed. The litterfall mass was also 2-3 times greater at the VK3 plot than at HJ1 and HJ4 plots. Nickel enrichment of throughfall has been reported for Swedish spruce forests (Bergkvist 1987) and Finnish Scots pine stands receiving Ni pollution from a nearby smelter (Derome & Nieminen 1998, Nieminen et al. 1999).

Comparing pathways is problematic because of sampling definition. For example, litterfall is affected by throughfall and throughfall by litterfall. In paper III the effect of including the leaching loss of nutrients from the litter with the solid litterfall was studied. If the LF leachate component was included, for K, S and Na litterfall became at least as important flux as the TF in the return of nutrients to the forest floor (Fig. 3, III). For Ca, Mg and N it made no difference if the litterfall leachate was included or not, litterfall was the more important pathway. The leaching loss of nutrients from the litterfall is usually not determined and relative importance of the litterfall and throughfall pathways may be affected. However, the net effect on the total return of nutrients to the forest floor can be expected to be zero, as overestimation of the TF flux would be compensated by an underestimation of the LF flux.

5.3.3 Mass balance budgets (IV, V)

Mass balance budgets have shown to be useful in assessing the fate of atmospheric pollutants (e.g Turner et al. 1985, Schut et al. 1986, White & Driscoll 1987, Bergkvist 1987, Dillon et al. 1988, Lindberg & Turner 1988, Johnson & Van Hook 1989, Aastrup et al. 1995, 1997, Forsius et al. 1995, Evans et al. 1997). Such budgets can identify the relative importance of various processes, including canopy interception, foliar leaching, uptake and nutrient cycling, ion exchange, weathering and leaching. The fate atmospheric inputs of major nutrients and heavy metals to the forest ecosystems studied was assessed by examining the difference between atmospheric inputs (TD) and leaching outputs at 40 cm depth. The role of the soil processes was assessed by comparing inputs to the soil (TF+LF) with the fluxes from beneath the humus layers (Hietajärvi plots only), 20 cm and 40 cm.

5.3.3.1 Total deposition inputs vs. soil leaching outputs (IV, V)

The leaching output of Ca, Mg, K and Na at 40 cm depth was greater than TD inputs (Table 5, V) indicating net release from the soil. These elements are important as major plant nutrients (excluding Na) and, as exchangeable cations and components of minerals, important in acid buffering and neutralization (Binkley & Richter 1987). Potassium and Na ions are held with weaker forces than Ca and Mg and therefore are more easily exchanged. The weathering release of base cations is not only an important acid neutralization mechanism but also the process by which soil fertility and cation exchange capacity is maintained (Van Breemen et al. 1984, Starr et al. 1998). The amount of leaching of Ca, Mg and K was clearly the greatest at Valkea-Kotinen (VK3) where the acid (H^+) load was also the greatest. The high Na soil leaching fluxes at Vuoskojärvi is clearly related to the high inputs of marine Na.

The output of H^+ ions at 40 cm depth was always less than the TD inputs; the consumption being related to the leaching of base cations as discussed above. The adsorption of SO_4 in the soil also results in a reduction in soil solution acidity. Leaching outputs of SO_4 were less than TD inputs, except at VK3, which showed a net leaching loss. A net release of SO_4 from the soil at Valkea-Kotinen may be evidence of ecosystem recovery from air pollution. Sulphate adsorption, related to the presence of amorphous Al and Fe oxides in the illuvial B-horizon (Karltun & Gustafsson 1993), is known to be reversible (Harrison & Johnson 1992). The pool of adsorbed sulphate would start to desorption and appear in leachate when the acid loading is reduced.

Retention of inorganic nitrogen in the soil is expected because biologically available N is in short supply in boreal forest ecosystems (Mälkönen et al. 1990). Nitrate retention was nearly 100 % and > 90 % for NH_4 except at VJ plots where it was 70 %. In the northernmost catchment, Vuoskojärvi, inputs and outputs were both considerably smaller than at other catchments. The lower retention of NH_4 at Vuoskojärvi may reflect a smaller demand for inorganic nitrogen in ecosystems so far north.

Sulphate and nitrate, as anions, are also important in controlling the leaching of cations since cations must be accompanied by anions (Singh et al. 1980). Although NO_3 ions are mobile, they are readily taken-up by roots and immobilized by microbes and the net NO_3 production and leaching in such soils is very low. Nitrate leaching therefore played little role in the leaching of base cations at the IM plots (Foster et al. 1989).

Retention of atmospheric inputs of heavy metals was only shown for Cu and Pb at HJ1 and HJ4 plots, Ni at HJ1 and Zn at VK3, otherwise the leaching fluxes of heavy metals were greater than atmospheric inputs. Cadmium had a negative budget at all three plots, with leaching fluxes at 40 cm depth being one to two times greater than total deposition inputs.

5.3.3.2 Total inputs to forest floor (TF+LF) vs soil leaching outputs (IV, V)

The sum of TF and LF constitutes the total input to the forest floor and includes both external (atmospheric) and internal (uptake from soil and recycling) sources. Litterfall represents a major pathway by which nutrients, particularly N, are taken up from the soil and are returned for recycling (Cole and Rapp 1981). However, the litterfall has to decompose before associated elements appear as ions in soil water. Throughfall, LF and SW fluxes from the humus layer (only at HJ1 and HJ4), 20 cm and 40 cm depths describe the fate and internal transfers of elements. Total S and N was used to calculate such budgets, because of the solid nature of the litterfall input. Besides inorganic forms, soluble organic forms of N and S are also important fluxes at these elements in BD, TF and SW. Unpublished data shows that 90 % of total S in BP is SO_4-S and 70 % of total N in BP is inorganic nitrogen.

Calculated budgets (Fig. 2a-c, IV and Fig. 2a-f, V) showed that, with the exception of S and Na and Ni at VK3 plot, leaching outputs at 40 cm were less than the total input flux to the forest floor. Averaged over all plots, 71 % of Ca, 46 % of Mg and 69 % of K total inputs to the forest floor had been retained compared to the leaching fluxes at 40 cm. In the case of N, the retention was nearly 100 %. At both Hietajärvi plots more than half of the total inputs of Cd, Cu and Zn had been retained compared to the leaching fluxes at 40 cm depth. The leaching of S was greater than total inputs, except at the HJ plots. In the northernmost plot, VJ2 and especially in VJ3, leaching of S was considerably higher compared to total inputs.

At Hietajärvi, where leaching fluxes from beneath the humus layer have been measured, the total inputs of most of the studied nutrients and heavy metals were retained in the humus layer. The exception were Na and K reflecting their high mobility, and S indicating a net mineralization of organic forms of S in the humus layer. Sodium and K are both mobile, but being a major nutrient there is much more demand for K than Na in the mineral soil. Potassium leaching from humus layer has also been reported by Helmisaari & Mälkönen (1989). The released K from the humus layer was, however, efficiently retained in the mineral soil. Sulphur released from the humus layer at the HJ plots, was also efficiently retained deeper in soil. Calcium, Mg and N tend to be retained in the humus layer where most of the fine roots are located (Helmisaari 1995). In this study over 56 % of N inputs were retained in the humus layer, the rest being almost totally immobilized in the surface layer of the mineral soil.

Comparison of the leaching fluxes at 20 cm and 40 cm depth generally indicate retention taking place in the 20–40 cm soil layer. This layer is comprised of the B-horizon, which is enriched in Al and Fe hydroxides (Karltun & Gustafsson 1993, Piirainen et al. 2001). These materials are known to be important in SO_4 adsorption and cation exchange and in accumulating percolating organic matter and any heavy metals with which it is complexed.

The budgets at Hietajärvi highlighted the major role of the humus layer in retaining heavy metals, particularly Pb and Cu, as shown in other studies (Tyler 1978, Turner et al. 1985, Bergkvist 1987, Bergkvist et al. 1989, Derome & Nieminen 1998). The retention of Pb by the humus layer, however, was less than expected, being 26 % (HJ1) and 54 % (HJ4). At 20 cm depth, 47 % of the total input of Pb to the forest floor had been retained at HJ1, 93 % at HJ4 and 57 % at the VK3. These results suggest that the upper mineral soil is as or more important in the retention of Pb as the humus layer. Bergkvist (1987) has also found the upper B-horizon of Podzols in southern Sweden to be the main sink for Pb in the soil rather than the humus layer. Over 60 % of Cu inputs were retained in the humus layer. Copper is known to readily form stable complexes with organic matter (Baker & Senft 1995). At VK3, Cu was apparently released from the 20–40 cm layer. It is unknown whether this release is through desorption or weathering. While there was retention of Zn inputs in the humus layer at plot HJ1 (39 %), there was a net leaching flux at HJ4 (11 %). The net leaching of Zn from the humus layer at HJ4 was presumably supplied through the decomposition of organic matter, although no significant difference in the decomposition of cellulose strips in the humus layer between these two plots has been detected (Kurka & Starr 1997, Kurka et al. 2000). Nevertheless, this released Zn was subsequently retained in the mineral soil. When comparing total inputs of Cu with leaching losses at 40 cm depth 85 % was retained at VK3, 56 % at HJ1 and 57 % at HJ4. Given that the LF flux of Zn was greater than the TF fluxes at all three plots, the retention was probably due to uptake and recycling. The budgets at Hietajärvi indicate that the humus layer retained over 50 % of the total inputs of Cd. Compared to other heavy metals, Cd is held less strongly hold by cation exchange forces and may be taken up by tree roots (Bergkvist et al. 1989) or lost to leaching (Andersson 1977, Borg & Johansson 1989). The retention of Ni by the humus layer was 75 % at HJ4 and 36 % at HJ1. Nickel, like Zn and Cu, is a micro-nutrient (Alloway 1995) and therefore subject to uptake and recycling. This was indicated by the relatively large internal recycling flux (FL+LF) of Ni at all three plots. There appeared to be a considerable release of Ni from the mineral soil. The net release was greater at the Valkea-Kotinen plot and may be due lower soil acidity compared to the Hietajärvi plots (Table 2, IV).

An overview of the fluxes of base cations, SO_4-S and N are presented in Figure 7. for each plot. The deposition fluxes are generally smaller than the biological cycling fluxes – litterfall and that included in the throughfall flux due to the canopy interaction. The fluxes also generally decrease northwards and are a reflection of the climatic condition, biological activity as well as levels of deposition.

5.3.3.3 Terrestrial vs. lake sediment retention of heavy metals (IV)

Heavy metal input-output budgets were calculated for the Hietajärvi and Valkea-Kotinen. Most of the retention of Cu, Pb, Zn, Cd and Ni was associated with the terrestrial part of the catchment (Table 3, IV). Retention in the terrestrial area may occur through adsorption in the canopy and soil, and accumulation in biomass. As the stands are old growth forests, the net increment growth can be considered to be low (Starr et al. 1998a) and therefore the net uptake of elements negligible. Assuming that the upland forested area of the catchments behaves as indicated by the plot-scale budgets (leaching fluxes > atmospheric inputs), most of the retention of heavy metals in the terrestrial part of the catchment must occur deeper than 40 cm in the upland soil (higher pH and reduced solubility) and/or in the organic soils (adsorption) located in the lowland zone. Organic soils are known to be important in the retention of heavy metals (Schut et al. 1986, Urban et al. 1987, LaZerte et al. 1989, Shotyk et al. 1997). There is a considerable amount of Histosols and histic soils in both catchments and this is probably the site for much of the terrestrial retention observed.

Of the total loading of heavy metals to Lake Valkea-Kotinen and Lake Iso-Hietajärvi, approximately two thirds or more of Cd, Ni, Pb and Zn was accounted for by terrestrial outputs, the remaining being direct atmospheric deposition inputs. For Cu, terrestrial loading accounted for only 13 % and 18 % of the total loading to the lakes at VK and HJ, respectively. Sedimentation of organo-metal complexes is the main process by which heavy metals are retained within lakes (Dillon et al. 1988, LaZerte et al. 1989, Verta et al. 1989). This process takes place in the deeper parts of the lake and occurs through the settling of suspended particles and the coagulation and flocculation of soluble organic complexes in response to decreases in pH. The relative importance of terrestrial and atmospheric loading to lakes is related to the proportion of land and water in the catchment. Schut et al. (1986) reported that a fifth of the total loading of Cu and Pb to two, relatively remote, Canadian lakes was from the terrestrial part of the catchment. Dillon et al. (1988) reported similar terrestrial output proportions of Ni and Zn to five polluted Canadian lakes. They also found a high proportion of terrestrial Cu, up to 83 % of total loading. Furthermore, exposed bedrock accounted for most of the terrestrial area of the catchments in the study by Dillon et al. (1988), and the high proportion of terrestrial inputs probably reflect the surface runoff of high atmospheric inputs. The high proportion of terrestrial inputs to lakes compared to direct atmospheric inputs in our study reflects the low levels of air pollution in our study areas. Runoff outputs at both catchments probably approximate terrestrial weathering fluxes.

5.4 Biological responses to changes in deposition (II)

The relationship between tree vitability (defoliation and discoloration) and deposition (BP and TF) at 19 plots, which included the VK3, HJ4, PJ2 and VJ3 plots, has been studied by Raitio et al. (1997). The degree of defoliation was < 20 % in most stands and discoloration < 10 %. There was no significant correlation between deposition (H^+, SO_4, total-N) and defoliation ($p > 0.1$), but the correlations were higher for the spruce stands. The correlation

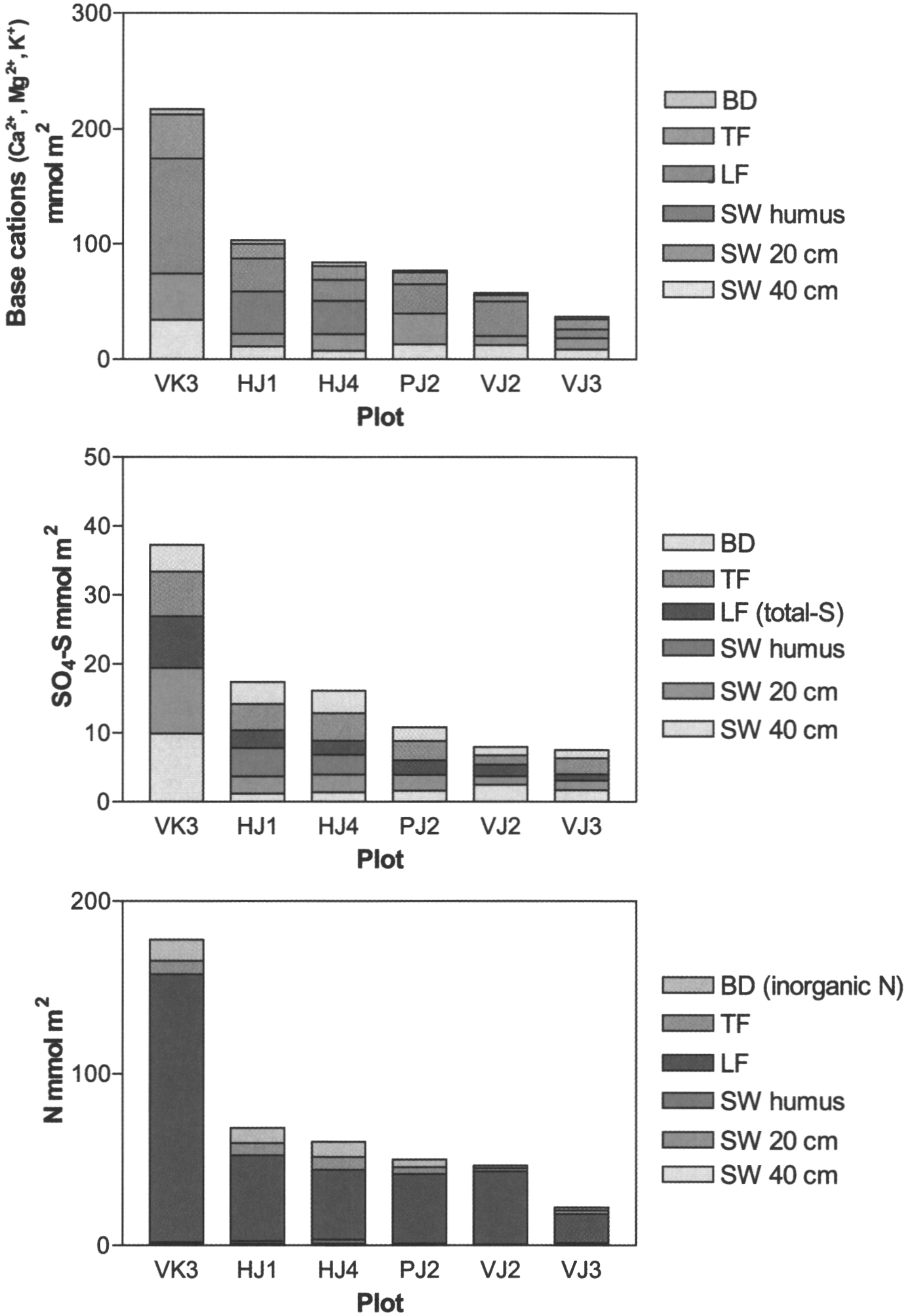


Figure 7. Annual amount of base cations, sulphate and N in bulk precipitation (BP), throughfall (TF), soil water (SW) in depth of 20 cm and 40 cm and litterfall (LF) in average during a period of 1989–1997 in studied plots.

between deposition and discoloration for the spruce plots was, however, nearly significant (p = 0.08). The results indicate that there may be weak relationship between deposition quality and defoliation/discoloration, but it was clear that age and geographical location are the main explanatory factors.

Epiphytic lichens have been widely used as biological indicators of air pollution. The response of trunk epiphytes at the Integrated Monitoring sites to BP concentrations has been reported by Kokko et al. (2001). Different indexes measuring the distribution, frequency and cover of lichens were used. Only in the southernmost catchment, Valkea-Kotinen, there was a small change in the epiphyte indexes that could be related to change in BP concentrations of SO_4 and H^+. Our unpublished results have also shown only a weak correlation between epiphyte index and stemflow concentrations of S and H^+. Farmer et al. (1991) reported rapid response (1 year) to changes in stemflow quality in two studied epiphytes *Lobaria pulmonaria* and *Isothecium myosuroides* in Northern England.

The bioaccumulation and potential toxicological impacts of heavy metal pollution of the Integrated Monitoring sites has also been made (II). The deposition to biota ratio of Pb concentration was calculated to describe the degree of bioaccumulation of Pb deposition. The ratios were calculated from the median concentration in the biotic media to the needles, litterfall, humus layer, moss (*Pleurozium schreberi*), ants and shrew liver concentrations. The concentrations of the heavy metals in mosses are known to be a good measure of pollution, particularly Pb (Berg et al. 1995, Berg & Steinnes 1997). The greatest degree of bioaccumulation (highest ratios) occured in the humus layer. This can be explained by the strong binding by the organic matter of Pb and the concentrating effect of decomposition. The ratio for needle (Scots pine) concentrations systematically increased northwards. However, it appears that there is little bioaccumulation of Pb up the food chain, however, ratios for ants and shrew livers were very low.

Tyler (1992) has presented critical concentrations values for heavy metals in humus (mor) layers for Swedish forests. These concentrations are the lowest at which a negative effect on microbiological activity has been found, so called lowest observed effect level (LOEL). LOEL values for Cd, Cu, Pb and Zn are: 3.5, 20, 150 and 300 mg kg^{-1} dry matter, respectively. The 95th percentile concentration values for the humus layer in this study were less than the LOEL values (II), indicating that present humus layer heavy metal concentrations in the IM catchments are not ecotoxicological to soil organisms.

The residence time of Pb and Cd in the humus layer at the Hietajärvi plots was calculated by dividing the heavy metal pool by the annual leaching flux (II). This calculation assumes that there would be no further atmospheric inputs and leaching fluxes would continue at current levels. Lead and Cd are potentially the most ecotoxicological of studied heavy metals and contents in the humus layer can be considered to be largely of anthropogenic origin. On this basis the pool of Pb would be depleted in 129 years and that of Cd in 22 years. Tyler (1978) calculated the time necessary for a 10 % decrease in humus layer concentrations at unpolluted Swedish sites of 6 years for Cd and 70–90 years for Pb assuming a throughfall pH of 4.2.

5.5 Validity and problems of long-term integrated monitoring approach

Long-term environmental monitoring has a substantial history in both biological and physical sciences. Monitoring has been defined as follows: '*Systematic observations of parameters related to a specific problem, designed to provide information on the characteristics of the problem and their changes with time*' (Spellerberg 1991). The aim of the Integrated Monitoring program was originally to determine and predict the state and change of terrestrial and fresh water ecosystems in a long-term perspective (Manual for...1993, 1998). This original aim has only partly come true. However, the data collected is probably the longest time series of integrated biogeochemical data for forest ecosystems in Finland. The data not only allows spatial comparison to be made across sites and media (waters, soil, vegetation etc.) but the time series are also long enough to allow time series analyses to be made. Finnish IM data including data presented in this thesis has been used in assessments of the effects of nitrogen and sulphur deposition on vegetation (Liu 1996), and the number of biogeochemical models such as MAGIC, SAFE, SMART were calibrated using data from the IM sites (e.g. Ahonen et al. 1998). Furthermore, IM data has shown that reduction in emissions of S, as a result of the UN ECE protocols, have clearly led to a reduction of S and acidic deposition to forest ecosystems.

Inconsistency of measurements as well as accuracy and precision is a serious problem in environmental monitoring. At the very least it throws doubt on the results and analyses and opens the door to criticism of any interpretation. At its worst it can invalidate analyses or produce completely spurious conclusions (Beard et al. 1999). To avoid these problems, all the used methods should be evaluated before starting to use them. In the IM programme has been, for example, studied precision and accuracy of throughfall collecting (Starr & Ukonmaanaho 2000), snow collecting has been evaluated by Derome & Lindroos (2000) as well as soil water collecting (Derome 2001); the only concern is that these studies have not been done in the beginning of the monitoring. In addition to reduce measurements inconsistency in monitoring there should be developed a detailed protocol for each measurements and analytical procedure. If method is changed during monitoring results should be statistically valid and can be related to other sites and personal should remain as same as possible. However used methods should be so flexible that new ideas and improvements are possible. In the case of long-term monitoring this is a small price to pay compared to the overall benefits.

As seen, the concentrations of many solutes in the remote, background IM areas are low. For example, concentrations of Cd and Ni in TF, SF and SW were often less than detection limit of the used equipment. The reliability of these data may therefore be uncertain. Most publications dealing with this fail to acknowledge the presence of 'less-thans' and how they have been dealt with. In Paper II a distributional method (Helsel 1990) was used to improve the percentile estimates of heavy metal concentrations in TF, SF and SW. In paper IV it was decided to use substitution value of zero for concentration values SW and TF samples as it was felt that 0.5* detection limit would still be too high.

To estimate the TD of major nutrients and heavy metals was used 'throughfall method'. It is common used method for estimating the total deposition of many elements in monitoring studies (e.g. Grennfelt et al. 1985, Lindberg et al. 1986, Beier 1991) but whether it is correct has often been questioned (e.g. Cape et al. 1987). Clearly for the components, which interact with the canopy (BD > TF) throughfall deposition is not equivalent to the total atmospheric deposition of these compounds. The method assumes that inert tracer (Na or SO_4) shows no interaction (removal or release) from the canopy and that the interception ratio of inert tracer (Na or SO_4) is similar to that of studied elements. The former assumption is generally accepted but we have no proof of the latter assumption. However, the size of particles involved in the dry deposition of heavy metals at our sites can be expected to be relatively small because of the long-range transport involved. Furthermore, the particle size of the intercepted dry deposition is known to be smaller than that of the dry deposition in bulk deposition, which is collected by sedimentation (Lindberg et al. 1989). The estimates of total deposition for different elements are therefore reasonable. Nevertheless the simplicity of the method and the general availability of the necessary deposition data greatly favor the method and the results give at least an approximation of total deposition.

In systematizing the ecosystem to pools and fluxes in order to be able to handle the inherent complexity, also have problems. The borders between conceptually defined compartments are sometimes difficult to preserve in measurements. For example distinction between LF and TF in practise is not exact: throughfall affects litterfall and vice versa (III). Nevertheless the total return of nutrients to the forest floor (i.e. TF+LF) can be expected to be correct, as the overestimation of the TF flux by litterfall leaching would be compensated by the underestimation of the LF flux leaching losses.

Finally, there is a problem of disturbance introduced by the monitoring procedure. For example, the vegetation may be disturbed by the presence of the sampling equipment and repeated visits to the site. It is only through long-term monitoring that real changes in the environment due to air pollution can detect above those due to natural variation, especially in relatively clean environments as those in this study. The time needed for a detectable trend to be observed is likely to vary with both substance and monitoring media. The BP, TF and SW trends presented were only possible to show with 9 years data; changes in vegetation or soil chemistry would require a much longer time.

Despite the raised problems, long-term integrated monitoring is important because only long-term monitoring can reveal the existence of trends, cycles and rare events (Lawton 1990). Long-term integrated monitoring provides essential information on how systems are changing and how fast and how the changes affect different media (Burt 1994).

6. Conclusions

Most of the used data in this PhD thesis are for the period 1989 to 1997. This period has probably seen the greatest reduction is S emissions that are feasible. Air pollution continues to be regarded as an important stress factor. However, the importance of atmospheric pollution varies regionally and its effects depend on site, stand and soil conditions. The effects of air pollution on forest ecosystems are therefore complex and difficult to isolate and quantify. A large number of other stress factors also influence forest condition and these should therefore be taken into consideration.

The results show that precipitation is strongly modified while passing through the canopy, even in remote sites receiving relatively low levels of air pollution. The concentrations of major nutrients, with the exception of N, generally increased in order: BP<TF<SW. The canopy interactions were related to the tree species, tree density, canopy coverage and biomass but the greatest changes occured in south Finland where air pollution was the greatest. Litterfall amounts decreased northwards, reflecting a climatic gradient in stand productivity. Litterfall was more important than throughfall as a pathway in the return to forest floor of most nutrients, except K and Na.

Total deposition of SO_4 varied between 2–6.2 kg S ha^{-1} yr^{-1}, of inorganic N between 1–6 kg N ha^{-1} yr^{-1}. These are low compared to European levels of S and N deposition. Also the amounts of acidified compounds (S and N corrected with base cations) were below the critical load levels. Heavy metal concentrations in deposition were low to compared European levels.

Significant declines in the concentrations of SO_4, H^+ and Pb in bulk precipitation and throughfall over the study period were found. These decreases are well in line with the UN-ECE 1985 Protocol to reduce S emissions (30 % compared to 1980), 1999 Protocol (63 % compared to 1990) and 1998 Protocol to reduce Pb emissions below levels in 1990. The effect of using unleaded gasoline from 1993 is shown in the reduction in Pb concentrations in BP and other media. However, because of the high degree of retention, it will take time before the effects of reduced deposition will become apparent in the soil pools. Trends in bulk precipitation were reflected in TF as well as in SW. The declining trend in Ca, Mg and Pb concentrations were more apparent in SW than in TF.

Mass balance budgets indicated that total deposition of H, N, S and heavy metals, were greater than leaching losses (SW) at a depth of 40 cm, indicating retention. For base cations and Cd inputs were less than outputs, indicating a net release of the elements from the soil. Mass balance budgets of total inputs (TF+LF) to the forest floor were positive for most elements, indicating retention. The humus layer was important in the retention of total inputs for Ca, Mg and N and heavy metals. Sulphur was retained in the mineral soil, particularly in the B-horizon, where Al and Fe hydroxides have accumulated. Catchment scale budgets also showed retention.

The results clearly show that 'acid rain' and its impacts on the soil have declined during the 1990s. This decline has been result of the marked reduction in SO_2 emissions taken place as a result of international agreements. However, the emissions of NO_x have largely remained same. There is therefore a need to continue monitoring under conditions of continued nitrogen deposition and recovery from sulphur deposition.

Current concentrations of heavy metals in the soil and surface water of these remote locations were below critical levels for toxicological effects. There was little concentration of heavy metals up the food chain; with most of the heavy metal deposition to the soil being retained in the upper soil. Bulk precipitation and throughfall deposition of SO_4, H^+ and N did not have noticeable effect on forest health (canopy defoliation and discoloration), which was more determined by stand age and geographical location. The decline in air pollution deposition did not result in a change in sensitive trunk epiphytes at these background sites, largely because the levels of air pollution have always been relatively low. These sites are therefore well suited to serving as background sites in which the ecosystem functioning and biogeochemistry of stressed system can be compared.

The value and importance of long-term integrated monitoring in the assessment and evaluation of the effects of atmospheric deposition on boreal forest ecosystems has been shown. At the present time forest condition in these background areas is satisfactory. The deposition of long-range transported pollutants has decreased and the risk for damage to forest ecosystem in general has therefore been reduced. However, the threat of other environmental problems e.g. climate change, increased O_3 formation and emissions of CO_2 and other greenhouse gases still exist.

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Live and learn !

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Paper I

Ukonmaanaho, L., Starr, M. & Ruoho-Airola, T. 1998. Trends in sulfate, base cations and H^+ concentrations in bulk precipitation and throughfall at Integrated Monitoring sites in Finland 1989–1995. Water, Air, and Soil Pollution 105: 353–363.

I

TRENDS IN SULFATE, BASE CATIONS AND H^+ CONCENTRATIONS IN BULK PRECIPITATION AND THROUGHFALL AT INTEGRATED MONITORING SITES IN FINLAND 1989-1995

LIISA UKONMAANAHO[1], MICHAEL STARR[1] and TUIJA RUOHO-AIROLA[2]

[1]Finnish Forest Research Institute, P.O. Box 18, FIN-01301 Vantaa, Finland
[2]Finnish Meteorological Institute, Sahaajankatu 22 E, FIN-00810 Helsinki, Finland

Abstract. Temporal trends in sulfate, base cation ($Ca^{2+} + Mg^{2+} + K^+$), and H^+ ion concentrations in bulk precipitation and throughfall samples collected over a seven year period (1989-95) in four forested catchments in Finland are presented. The catchments are in remote locations and span the boreal zone (61-69 °N). The stands represent old, undisturbed forests, and are composed of varying proportions of Scots pine, Norway spruce and deciduous species (mainly *Betula* spp.). Monthly SO_4^{2-}-S and H^+ ion concentrations in bulk precipitation averaged over the study period and catchments were: 18.7 µmol L^{-1} and 32.3 µmol L^{-1}. The corresponding values for throughfall were: 37.4 µmol L^{-1} and 32.4 µmol L^{-1}. Sulfate and H^+ ion concentrations in bulk precipitation and throughfall both showed negative linear trends, which were significant ($p < 0.05$) for the three southernmost catchments. Concentrations and trend slope decreased northwards (e.g., bulk precipitation SO_4^{2-}-S slope estimates: -1.6 to -1.0 µmol L^{-1} yr^{-1}). The decline was greater for throughfall than for bulk precipitation, indicating a proportionally greater reduction in dry deposition than wet. The sum of base cation concentrations averaged 12.1 $\mu mol_{(+)}$ L^{-1} in bulk precipitation and 83.1 $\mu mol_{(+)}$ L^{-1} in throughfall. There were no significant trends in the sum of base cations ($p > 0.05$). It is concluded that the reported reduction in S emissions over the study period has resulted in a significant reduction in the acidity and SO_4^{2-} concentration of bulk precipitation, and this reduction has has been reflected in throughfall concentrations. The greatest reduction has taken place in the southern part of the country.

Keywords: base cations, bulk precipitation chemistry, catchments, protons, sulfate, throughfall chemistry

1. Introduction

Emissions of SO_2 from Finland have declined progressively from their peak of about 600,000 t yr^{-1} in the 1970s to about 100,000 t yr^{-1} by the mid 1990s. This is well in line with the UN-ECE 1985 protocol to reduce S emissions by at least 30 % by 1993 compared with 1980 levels and Finland's goal of 121,000 t yr^{-1} by 2000. However, only about 22 % of the S deposition in Finland is derived from domestic sources (Tuovinen *et al.* 1990; Bernes, 1993).

Precipitation chemistry mainly consists of compounds of S and N, which have an acidifying effect, and base cations (Ca^{2+}, Mg^{2+}, K^+), which have a neutralizing effect. Differences in the composition of precipitation collected in the open and that collected under boreal forest canopies have been reported in many studies (e.g., Parker, 1983; Lindberg *et al.*, 1986, Helmisaari and Mälkönen, 1989; Hyvärinen, 1990; Edmonds *et al.*, 1991; Johnson and Lindberg, 1992; Lövblad *et al.*, 1994). These differences are due to interaction with the canopy (foliar uptake *vs.* leaching) and to additional dry deposition filtered out of the atmosphere by the canopy (interception) and subsequent wash-off. The difference between open and forest precipitation varies with chemical constituent as well as with the species composition and structure of the stand (Mahendrappa, 1983; Starr and Ukonmaanaho, 1995). Spruce stands are especially effective in trapping particles and certain gases (Bredemeier, 1988).

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The monitoring of throughfall and bulk precipitation has proved a useful means of assessing total deposition to forest ecosystems (Bredemeier, 1988; Forsius *et al.*, 1995; Hultberg and Grennfelt, 1992; Ivens *et al.*, 1990; Kallio and Kauppi, 1990). However, most throughfall and bulk precipitation studies have been carried out only for a few years and/or at single sites.

In this paper, we present some Finnish results from the throughfall and bulk precipitation subprograms of the UN-ECE International Cooperative Programme on Integrated Monitoring (ICP-IM) (EDC, 1993; Bergström *et al.*, 1995). The data cover a seven year period and are for eight stands, two in each of four catchments located throughout Finland. The ICP-IM program is an international ecosystem monitoring program, the overall objectives of which are to describe the present state of ecosystems and to monitor changes due to environmental change, particularly the influence of anthropogenic pollutants transported over long distances (EDC, 1993). To assess the levels of air pollution, we have decided to present concentration rather than deposition data because deposition fluxes in Finland are largely determined by the amount of precipitation, which shows a strong south-north gradient.

2. Materials and Methods

2.1. Catchments and Plots

The study was carried out at the four Finnish ICP-IM catchments: Valkea-Kotinen, Hietajärvi, Pesosjärvi and Vuoskojärvi (Table I). Bulk precipitation was collected in an open area and throughfall collected from two permanent plots located in each of the four catchments. The small forested catchments span the boreal coniferous phytogeographic zone and are situated in remote, protected, conservation areas (Table I). The forest in the catchments represent natural or semi-natural communities.

TABLE I
General features of the IM study catchments.

	Valkea-Kotinen	Hietajärvi	Pesosjärvi	Vuoskojärvi
Location	61° 14′ N	63° 09′ N	66° 17′ N	69° 44′ N
	25° 03′ E	30° 40′ E	29° 26′ E	26° 56′ E
Area, km^2	0.3	~~0.1~~ 4.6	6.1	2.0
Phytogeographic zone*	Southern boreal	Middle boreal	Northern boreal	Northern boreal
Climatic zone**	Humid continental	Continental subarctic	Continental subarctic	Continental subarctic
Annual mean temperature, °C	3.1	2.0	-0.5	-1.9
Annual mean precipitation, mm	618	592	571	395
Vegetation period (>5 °C), da	112	102	82	57

* Ahti *et al.* 1968; ** Köppen-Geiger classification

Permanent plots varying in size from 25 x 25 m to 40 x 40 m were established in each catchment. The plots are situated on flat to nearly flat surfaces in areas representative of the dominant forest site types in each catchment. The plots are as homogenous as possible with regard to soil morphology, ground vegetation and tree stand characteristics (Table II). The stands are composed of varying proportions of Scots pine (*Pinus sylvestris* L.), Norway spruce (*Picea abies* Karst.) and deciduous species (mainly *Betula* spp.), representing submesic heathland forests to lichen woodlands. For further details about the catchments and plots, see Bergström *et al.* (1995).

TABLE II
Characteristics of the throughfall study stands.

Catchment	Plot	Plot size, ha	Tree density ha^{-1}	Basal area $m^2\,ha^{-1}$	Mean height m	Stem volume $m^3\,ha^{-1}$	pine* %	spruce** %	deciduous† %	Canopy coverage %	dbh‡ cm	Age of dominant trees, years
Valkea-	2	0.16	1231	40	16	407	7	86	7	81	26.2	190
Kotinen	3	0.12	1433	48	17	531	4	54	41	88	26	155
Hietajärvi	1	0.16	1238	22	10	199	86	0	14	61	23.4	100
	4	0.16	519	21	15	228	91	0	9	51	30.3	230
Pesosjärvi	1	0.09	922	20	9	147	2	69	29	55	29.9	320
	2	0.12	1825	25	8	192	46	39	15	52	24	240
Vuoskojärvi	2	0.09	1789	5	4	16	3	0	97	53	8.4	150
	3	0.16	431	9	6	50	98	0	2	34	27.4	180

* Scots pine *(Pinus sylvestris)*

** Norway spruce *(Picea abies)*

† deciduous species (mainly Birch, *Betula spp.* and Aspen, *Populus tremula*; but at Vuoskojärvi, Mountain birch, *B.pubescens ssp. tortuosa)*

‡ breast height diameter, 1.3 m

2.2. Bulk Precipitation and Throughfall Collectors and Sampling

Three bulk precipitation collectors (NILU type) were placed in an open area at a height of 120 cm and such that the nearest trees did not shadow the collectors; the angle to the top of the trees was <45°. Samples were collected once a week throughout the year, but combined into monthly samples for each collector for analysis.

Throughfall collectors were placed systematically at 10 m intervals around the plots. Depending on plot size, there were 10 to 16 collectors per plot. Each collector used to collect rainfall consisted of an acid-washed polyethylene funnel (collecting surface = 308 cm^2) with a 2 cm high rim connected to an acid-washed polyethylene bottle (from 1994, a polyethylene bag) (Hyvärinen, 1990). Snow samples were collected only since winter 1994/95. The snow collectors, which replaced the rainfall collectors during the winter months (October-November to April-May), each consisted of a polyethylene bucket with a collector area is 491 cm^2. The volume of throughfall collected by each collector was recorded before being poured (after melting in the case of snow samples) into a common acid-washed polyethylene canister and a subsample was taken for analysis. The rainfall throughfall samples were collected weekly and snow throughfall samples monthly.

2.3. Sample Analysis

The samples were stored in dark and cool (+4 °C) conditions until analysis began. Concentrations of Ca^{2+}, Mg^{2+} and K^+ in bulk precipitation were determined using ion chromatography and in throughfall samples by using ICP-AES. Sulfate concentrations were determined by ion chromatography and H^+ concentrations were calculated from pH measurements made potentiometrically using a combined electrode. For further details, see Bergström *et al.* (1995).

2.4. Numerical Handling and Statistical Analysis

Throughfall samples with PO_4^{3-} ion concentrations >10.5 μmol L^{-1} (>1 mg L^{-1}) were rejected on the grounds of probable contamination of the whole sample chemistry from bird droppings (Novo *et al.*, 1992). Monthly volume weighted bulk precipitation values were calculated from the monthly values of the three parallel collectors. Monthly throughfall (rainfall) volume weighted concentrations were calculated from the weekly plot composite values.

Because the sampling of throughfall throughout the year did not start until 1994, the number of monthly observations for each catchment are less than the potential 84 (7 years x 12 months). Accordingly, the number of monthly throughfall observations ranged from 40 at Vuoskojärvi to 52 at Valkea-Kotinen.

The trend over the seven year period is shown as a LOWESS (locally weighted) curve fitted to the monthly data (GraphPad PRISM™) using an algorithm adapted from Chambers *et al.* (1993). Linear trends were analyzed using all the monthly values available and the non-parametric Seasonal-Kendall trend analysis procedure to calculate an estimate of the true slope of the linear trend (Hirsch *et al.*, 1982; Gilbert, 1987). This test may be used even though there are seasonal cycles and missing values.

3. Results

The monthly amount of throughfall was, as expected, strongly correlated to the amount of bulk precipitation (Valkea-Kotinen, r = 0.93; Hietajärvi, r = 0.93; Pesosjärvi, r = 0.94; Vuoskojärvi, r = 0.95). The amount of throughfall as a percentage of the amount of bulk precipitation (throughfall yield) for each catchment ranged from 86 to 90 %. In an earlier paper (Starr and Ukonmaanaho, 1994), we showed that the throughfall yield for the same plots was correlated to stand basal area (r = -0.80) and crown cover (r = -0.81).

The monthly SO_4^{2-}-S, sum of the base cations, and H^+ ion concentrations in bulk precipitation averaged over the study period and catchments were: 18.7 μmol L^{-1}, 12.1 $\mu mol_{(+)} L^{-1}$ and 32.3 μmol L^{-1}, respectively. The corresponding values for throughfall were: 37.4 μmol L^{-1}, 83.1 $\mu mol_{(+)} L^{-1}$ and 32.4 μmol L^{-1}.

3.1. Differences among Catchments and Plots

Mean monthly concentrations calculated for only those months common to all catchments are presented in Table III. By selecting values for the same common months only, the effects of seasonal (monthly) variability are reduced and geographic comparisons among the catchments can be made.

TABLE III

Monthly volume weighted mean concentrations and standard deviation of acidity (H^+), SO_4^{2-}-S and base cations ($Ca^{2+} + Mg^{2+} + K^+$) in bulk precipitation and throughfall. Values are only for those months common to all catchments during 1989-95 (n=36). Means within columns followed by the same letter (upper case for bulk precipitation,BP, and lower case for throughfall, TF) are significantly different by Bonferroni tests ($p < 0.05$).

Catchment	Plot	H^+, µmol L^{-1}		SO_4^{2-}-S, µmol L^{-1}		Base cations, µmol$_{(+)}$ L^{-1}	
		Mean	sd	Mean	sd	Mean	sd
Valkea-Kotinen	BP	30.3 A	11.89	18.7 AB	10.3	12.5 A	7.52
	TF 2	37.9 a	20.24	56.1 abcdef	25.0	141.8 abcdef	56.24
	TF 3	30.4 b	17.68	40.5 ghij	18.4	108.1 ghijk	48.30
Hietajärvi	BP	29.8	11.62	18.7 C	8.4	9.9	6.24
	TF 1	36.3 c	25.96	28.1 ak	20.3	48.7 ag	37.21
	TF 4	38.7 d	20.05	28.1 bg	13.4	39.9 bh	29.69
Pesosjärvi	BP	26.4	11.45	12.5 A	6.9	5.3 A	2.64
	TF 1	26.5	16.48	31.2 cl	17.5	63.5 c	39.44
	TF 2	24.6	15.60	21.8 dh	25.0	27.6 di	15.68
Vuoskojärvi	BP	22.0 A	16.12	12.5 BC	7.5	10.3	15.93
	TF 2	15.5 abcde	10.30	15.6 eikl	10.3	58.7 ej	139.53
	TF 3	31.9 e	22.40	28.1 fj	21.2	59.0 fk	70.08

The mean H^+ concentrations in bulk precipitation decreased northwards, but the only significant ($p < 0.05$) difference among catchment means was that between the northernmost and southernmost catchments (Vuoskojärvi and Valkea-Kotinen). Among the throughfall plots, only plot 2 at Vuoskojärvi was significantly different from any of the other throughfall plots.

Sulfate concentrations in bulk precipitation and throughfall showed the same latitudinal decrease as H^+ concentrations. The mean for Valkea-Kotinen was significantly different from the means for Pesosjärvi and Vuoskojärvi, and that for Hietajärvi was significantly different from that for Vuoskojärvi. Throughfall SO_4^{2-} means at Valkea-Kotinen were significantly greater than the means for the other, more northerly, throughfall plots.

The mean of the sum of base cation concentrations in bulk precipitation decreased northwards as far Pesosjärvi and then increased again at Vuoskojärvi. The means for Valkea-Kotinen and Pesosjärvi were significantly different. The same pattern was shown by the throughfall means, although not as clearly. The increase in the sum of base cation concentrations at Vuoskojärvi is due to additional inputs of marine Mg^{2+} derived from the nearby Arctic Ocean (Starr and Ukonmaanaho, 1995). The significantly greater bulk precipitation and throughfall sum of base cation means at Valkea-Kotinen are further evidence of greater anthropogenic base cation pollution (dry deposition) in the southwest of Finland (Tuovinen *et al.,* 1990).

3.2. TIME TRENDS

Monthly H^+, SO_4^{2-}, and sum of base cation concentrations for the seven year study period, together with the LOWESS smoother, are presented in Figures 1, 2 and 3, respectively. The corresponding Seasonal-Kendall linear slope estimates are presented in Table IV.

H^+ and SO_4^{2-} concentrations in both bulk precipitation and throughfall have significant ($p < 0.05$) negative linear trends at all catchments except Vuoskojärvi (where the slope estimates were not significantly different from zero). Thus, there has been a significant progressive reduction in the acidity and SO_4^{2-} concentration in precipitation throughout most of Finland over the period 1989-1995. Furthermore, the size of the slope estimate decreases northwards; showing that the reductions in acidity and sulphate concentrations have been the greatest in southern Finland where the concentrations have been the highest. Because bulk throughfall includes a fraction of dry deposition (filtered) that is not included in the bulk precipitation, the steeper decline in acidity and SO_4^{2-} concentrations registered for throughfall is presumably due to a proportionally greater reduction in the dry deposition of S than wet.

The sum of base cation concentrations did not show significant linear temporal trends ($p > 0.05$). The decrease in the acidity of bulk precipitation and throughfall therefore has been due to the decline in SO_4^{2-} concentrations rather than an increase in the neutralizing effect of base cations.

TABLE IV

Seasonal-Kendall estimates of true slope coefficients of linear trends for SO_4^{2-}-S (μmol L^{-1} yr^{-1}), H^+ (μmol L^{-1}yr^{-1}) and base cations ($Ca^{2+} + Mg^{2+} + K^+$, $\mu mol_{(+)}$ L^{-1} yr^{-1}) (ns= non significant, $p > 0.05$).

Catchment	Plot	SO_4^{2-}-S	H^+	Base cations
Valkea-Kotinen	BP	-1.6	-1.4	ns
	TF 2	-5.5	-6.3	ns
	TF 3	-5.4	-4.2	ns
Hietajärvi	BP	-1.7	-2.0	ns
	TF 1	-3.1	-3.0	ns
	TF 4	-3.1	-3.1	ns
Pesosjärvi	BP	-1.0	-1.4	ns
	TF 1	-3.4	-4.7	ns
	TF 2	-2.9	-2.1	ns
Vuoskojärvi	BP	ns	ns	ns
	TF 2	ns	-2.4	ns
	TF 3	ns	-4.5	ns

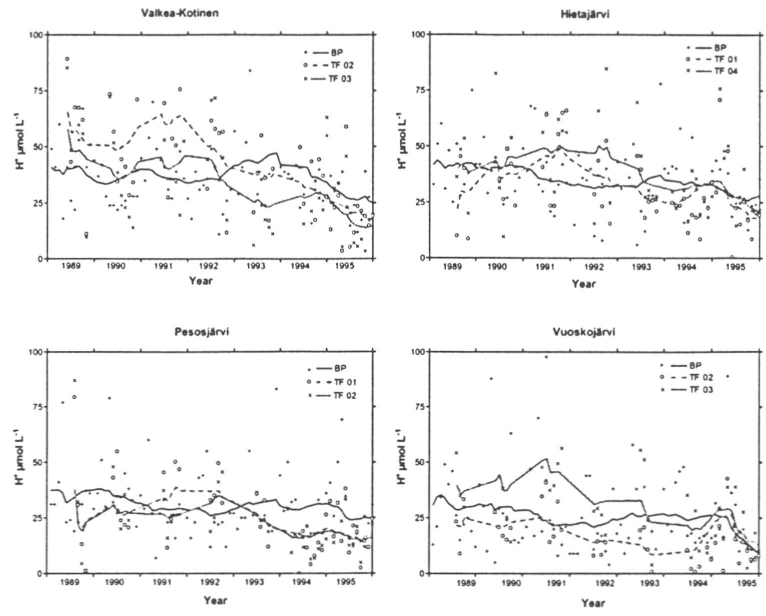

Fig. 1. Monthly H$^+$ ion concentrations in bulk precipitation (BP) and throughfall (TF) over ther period 1989-95 at each study catchment. For description of TF plots, see Table II. The lines are the LOWESS smoother.

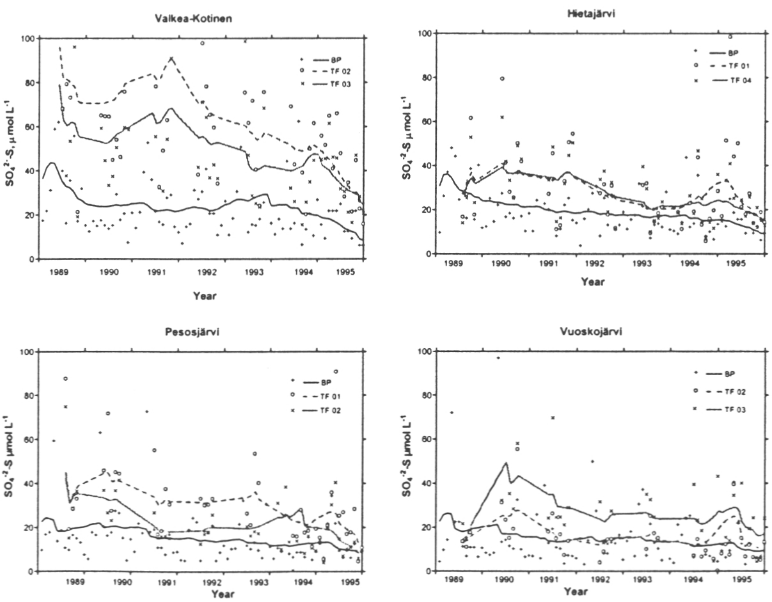

Fig. 2. Monthly SO_4^{2-} concentrations in bulk precipitation (BP) and throughfall (TF) over ther period 1989-95 at each study catchment. For description of TF plots, see Table II. The lines are the LOWESS smoother.

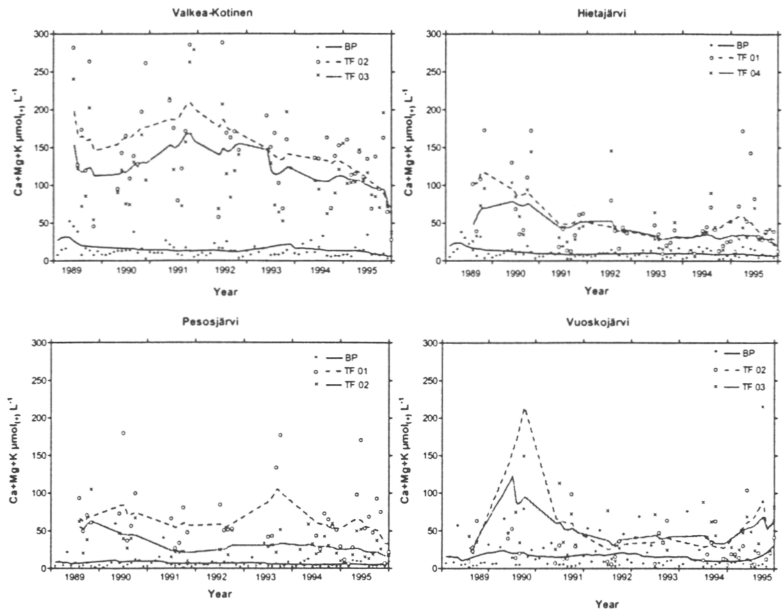

Fig 3. Monthly sum of base cations (Ca^{2+} + Mg^{2+} + K^{+}) concentrations in bulk precipitation (BP) and throughfall(TF) over ther period 1989-95 at each study catchment. For description of TF plots, see Table II. The lines are the LOWESS smoother.

4. Discussion

The open collectors used for bulk precipitation and throughfall collect wet and part of the dry deposition. The fraction of dry deposition collected in throughfall also includes that filtered by the forest canopy. Tuovinen *et al.* (1990) report that 10-30 % of the S collected by wet-only collectors is derived from dry deposition. However, in remote forested areas, such as our sites, this fraction can be expected to be less (Lindberg *et al.,* 1986).

Compared to bulk precipitation, H^{+} concentrations in the throughfall collected at those plots with a predominantly coniferous stand were slightly higher than for those stands with a significant deciduous tree species component (i.e., Valkea-Kotinen, TF3; Pesosjärvi, TF1 and TF2; Vuoskojärvi, TF2; see Table II). Cronan and Reiners (1983) also found that coniferous canopies tend to show a tendency toward net acidification of precipitation, indicating that acid interception rates are higher than the buffering capacity of canopy surfaces or dry deposited bases in coniferous stands. Further evidence of the effect of stand composition on throughfall chemistry is indicated by the difference between throughfall plots within catchment. The greatest difference between plots within catchment tended to be for those plots with the greatest difference in stand composition. Thus, the Vuoskojärvi plots showed the greatest difference in throughfall while the throughfall for the Hietajärvi plots were similar to each other.

Sulfate concentrations in throughfall were about double those in bulk precipitation (Table III). Because SO_4^{2-} shows little interaction with canopies (Bredemeier, 1988; Lindberg *et al.*, 1986), the SO_4^{2-} enrichment of thrughfall is primarily the result of wash-off of accumulated dry deposition (Lindberg and Lovett, 1992). The wash-off of deposited sea-salts from the canopy seems particularly important at the Vuoskojärvi catchment. The high concentrations of base cations in the bulk precipitation at the two southernmost catchments is probably related to shale burning in power stations in Estonia and the St. Petersburg region and the emission of base cation-rich aerosols (Anttila, 1990).

Even though the Seasonal-Kendall test can be used when there are missing values (Hirsch *et al.*, 1982; Gilbert, 1987), the number of throughfall observations was only about half of the 84 months making up the study period. This was primarily because snow sampling did not start until the 1994/95 winter. To test whether having a more complete data set changed our results we developed simple linear regression models of the form: TF = constant + BP for each plot to estimate snow throughfall SO_4^{2-} concentrations for those months with missing data. The models were based on the data for the two winters for which we had data. These models were all significant ($p < 0.05$) and had R^2 values ranging from 0.50 to 0.94. Using these data to make a complete data set, we then re-ran the Seasonal-Kendall test. The slope estimate was similar to that of the original run with missing data, although the negative trend for Vuoskojärvi became significant ($p < 0.05$). We therefore consider the trends shown by the original data with missing values (Table IV) to be valid.

5. Conclusions

Using bulk precipitation and throughfall collected over seven years (1989-1995) at four ·ated throughout Finland we have shown statistically significant reductions in the ncentrations of SO_4^{2-} and acidity (H^+ concentrations) in precipitation in southern :ntral Finland. These reductions have been the greatest in southern Finland where pollution concentrations have been the highest. Although there has been no significant reduction in bulk precipitation and throughfall SO_4^{2-} concentrations at the northernmost site, H^+ concentrations have been reduced significantly, as they have at all sites. The reduction in the acidity of precipitation has been due to the concurrent reduction in SO_4^{2-} concentrations, as base cations concentrations have not changed significantly over the study period.

Our results compliment the observed reduction in SO_2 emissions that has taken place over Europe over the last decade. They also validate the use of a long-term integrated monitoring programs to assess the success (or otherwise) of international agreements on air pollution abatement.

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Paper II

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II

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Heavy metal concentrations in various aqueous and biotic media in Finnish Integrated Monitoring catchments

Liisa Ukonmaanaho[1)], Michael Starr[1)], Juha-Pekka Hirvi[2)], Aira Kokko[2)], Pertti Lahermo[3)], Jaakko Mannio[2)], Tarja Paukola[3)], Tuija Ruoho-Airola[4)] and Heikki Tanskanen[3)]

[1)] *Finnish Forest Research Institute, P.O. Box 18, FIN-01301 Vantaa, Finland*
[2)] *Finnish Environment Institute, P.O. Box 140, FIN-00251 Helsinki, Finland*
[3)] *Geological Survey of Finland, P.O. Box 96, FIN-02151 Espoo, Finland*
[4)] *Finnish Meteorological Institute, P.O. Box 503, FIN-00101 Helsinki, Finland*

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Concentrations of Cd, Cu, Ni, Pb and Zn in various aqueous and biotic media in four small forested catchments located throughout Finland (61–70°N) are presented. The data has been collected (1989–96) as part of the UN-ECE Integrated Monitoring programme. Aqueous media included: bulk (open) precipitation, throughfall, stemflow, soil water, groundwater, and lake and stream waters. The biotic media included: moss (*Pleurozium schreberi*), needles (*Pinus sylvestris*), litterfall, humus layer, red wood ants (*Formica aquilonia* and *F. lugubris*), and common shrew (*Sorex areneus)* liver. In comparison to temperate ecosystems, the concentrations of each metal in all media were low. Levels and bioaccumulation of Cu and Zn were clearly affected by their role as micro-nutrients and, in the case of Zn at one of the catchments, by local lithological sources. Humus layer and surface water 95th percentile concentration values were below lowest effect values. Concentrations of Pb have significantly declined over the study period.

Introduction

As sulphur dioxide emissions and acidic deposition have declined over the last 1–2 decades, attention was increasingly turning towards the effects of nitrogen, and heavy metal deposition on forest and freshwater ecosystems (Tyler 1989, Adriano 1991, Alloway 1995). The environmental significance of heavy metals lies in their toxicity to organisms. Toxicity varies with heavy metal and depends on its speciation, concentration, exposure, and interaction with other solutes. Toxicity also varies between species and position in the food chain. Some heavy metals, e.g. copper and zinc, are needed in small amounts by organisms, only becoming toxic at elevated concentrations.

Heavy metal emissions to the atmosphere in Finland for 1990 were Cd: 4 t, Cu: 37 t, Ni: 71 t, Pb: 215 t and Zn: 143 t (Berdowski *et al.* 1997). The deposition (bulk) of heavy metals in Finland has only been systematically monitored since 1990 (Leinonen and Juntto 1991). Data for throughfall are available for a limited number of stands (Hyvärinen 1990), but virtually non-existent for stemflow. However, there is considerable data on heavy metal concentrations in mosses, lichens and bark (Lippo *et al.* 1995), which are widely used as bioindicators of atmospheric deposition (Tyler 1989, Steinnes 1995, Berthelsen *et al.* 1995, Berg *et al.* 1995, Berg and Steinnes 1997). Although mosses and lichens receive most of their nutrient supply from atmospheric deposition, their use as measures of deposition depends on the sampling location in relation to canopy cover and their capacity to retain elements, which varies with heavy metal (Berg *et al.* 1995, Steinnes 1995). Calibration of heavy metal concentrations in mosses collected from canopy openings with bulk deposition collected in the open shows that mosses are reliable bioindicators of the deposition for Pb and Cd but considerably less so for Cu, Zn and Ni (Berg *et al.* 1995, Ruoho-Airola *et al.* 1995). Repeated surveys of heavy metal concentrations in mosses for Northern Europe, including Finland, have been carried out at five year intervals since 1985 (Rühling *et al.* 1987, Rühling *et al.* 1992, Rühling *et al.* 1996). Areas of relatively high heavy metal deposition in Finland reflect local emission sources which are superimposed on a general pattern of decreased concentrations northwards. Comparison of the maps from 1985–95 indicate a clear decline in the deposition of several heavy metals over this period, Pb in particular. Moss Zn concentrations, however, have remained much the same.

A comprehensive regional study into the effects of air pollution from the Kola Peninsula Cu–Ni smelters was carried out in Finnish Lapland (Tikkanen and Niemelä 1995). The results showed that deposition of Cu and Ni decreased dramatically with distance westwards from the smelters. S‡y effects in Lapland were limited to the eastern border region, where concentrations in Scots pine needles and bark were higher. There was little measurable effect on the soil and soil water concentrations beyond 30 km westward from the smelters (Lindroos *et al.* 1996, Lindroos 1998).

Average heavy metal concentrations in forest soils in southern Finland were reported by Tamminen and Starr (1990). This study and a number of case studies (e.g., Helmisaari *et al.* 1995), indicate that much of the heavy metal deposition to forest ecosystems has accumulated in the humus layer. Thus, in spite of current reductions in deposition, the accumulation of heavy metals from the past can still exert an effect in the future. The duration of this effect will depend on the size of the pool and conditions affecting the mobility of heavy metals, which are strongly related to acidity and the mobility of organic matter (Bergkvist *et al.* 1989).

Maps of heavy metal concentrations in Finnish tills show that they are strongly determined by the geochemistry of the underlying bedrock (Koljonen 1992) and to the amount of fines (< 0.06 mm) in the deposit (Lintinen 1995, Tarvainen 1995). Concentrations of heavy metals in headwater lakes, streams, and groundwater show large regional differences, reflecting differences in bedrock geochemistry and catchment characteristics in the case of Cu and Ni and also deposition in the case of Pb and Cd (Lahermo *et al.* 1990, 1996, Mannio *et al.* 1993, Mannio *et al.* 1995, Tarvainen *et al.* 1997). Nevertheless, airborne heavy metals have accumulated in lake sediments, even in background areas; the mobility of which is also dependent on acidity and humic substances (Verta *et al.* 1990, Mannio *et al.* 1993, Mannio *et al.* 1995, Tenhola 1993).

Except for mosses and lichens, which are used as indicators of deposition heavy metal, data are much less available for biota than for the abiotic media. Lounamaa (1956) reported trace element concentrations in a wide range of plants in relation to concentrations in the underlying rocks and soil in Finland. Concentrations of the trace elements Cu and Zn in Scots pine and Norway spruce needles from repeated national surveys have been reported (Raitio 1994). There were no significant differences in concentrations between 1987, 1988 and 1989 samplings. Red wood ants (*Formica* spp.) and shrews (*Sorex* spp.) have been used as bioindicators of heavy metals in Finland because of their widespread distribution (Nuorteva 1990, Pankakoski *et al.* 1994, Heikura *et al.* 1997, Hirvi 1997). Heavy metal concentrations in aquatic plants and insects and in fish from acid and non-acid lakes were reported by Verta *et al.* (1990) and Iivonen *et al.* (1992). Concentrations, were poorly correlated to water and to sediment heavy metal concentrations, but were correlated to water acidity and dissolved humic substances, which are governed by the characteristics of the catchment rather than deposition loads.

A major problem in assessing the environmental impact of heavy metal pollution on forest ecosystems, however, is the lack of comparable and integrated data on ecosystems (Bergkvist *et al.* 1989). Most studies cover only one or two components of the ecosystem, and case studies have used different methods making comparison difficult. As a number of studies have shown, the best way of achieving integrated data is by studying the biogeochemistry of small catchments (e.g. Bergkvist 1987, Dillon *et al.* 1988, Johnson and Van Hook 1989, Lazerte *et al.* 1989, Johnson and Lindberg 1992, Kvindesland *et al.* 1994, Forsius *et al.* 1995, Aastrup *et al.* 1995 , 1997).

In this paper, we describe the levels of Cd, Cu, Ni, Pb and Zn in various aqueous and biotic media in four small forested catchments located in the southern, middle and northern (two) boreal zones in Finland. The catchments have been systematically monitored since 1989 as part of the UN-ECE International Cooperative Programme on Integrated Monitoring (IM) to monitor the effects of long-range transboundary air pollution on forest ecosystems (EDC 1993). The sampling and analytical protocols of the IM programme (EDC 1993) were followed for all media except the ant and shrew liver media. Geographic patterns, temporal changes, and bioaccumulation and toxicological implications are discussed. This is the first time such integrated data has been presented for Finland.

Material and methods

Integrated Monitoring catchments

The data were collected from the four Finnish IM catchments: Valkea-Kotinen, Hietajärvi, Pesosjärvi, and Vuoskojärvi (Table 1). The catchments are located in background areas, i.e. forested regions with little or no agriculture and no point sources of heavy metal air pollution within tens of kilometres (Fig. 1). Anthropogenic sources of heavy metals to such ecosystems are therefore considered to be due to long-range transported air pollution. For further information about nearest sources of atmospheric emissions see Ruoho-Airola *et al.* (1998). Typical of catchments in northern glaciated landscapes, the four catchments

Table 1. General characteristics of the IM study catchments.

	Valkea-Kotinen	Hietajärvi	Pesosjärvi	Vuoskojärvi
Latitude	61°14′N	63°09′N	66°17′N	69°44′N
Longitude	25°03′E	30°40′E	29°26′E	26°56′E
Catchment area, km^2	0.3	4.6	6.4	1.8
Forested area, ha	24	280	522	93
Surface water area, ha	6	124	62	19
Peatland area, ha	7	165	123	21
Elevation, m a.s.l (of lake)	156	165	256	145
Relative relief, m	40	49	44	105
Superficial deposit thickness, m	0–3	0–15	0–5	0–2
Annual mean temperature, °C	3.1	2.0	–0.5	–1.9
Annual mean precipitation, mm	618	592	571	395
Vegetation period (> 5 °C), d	112	102	82	57

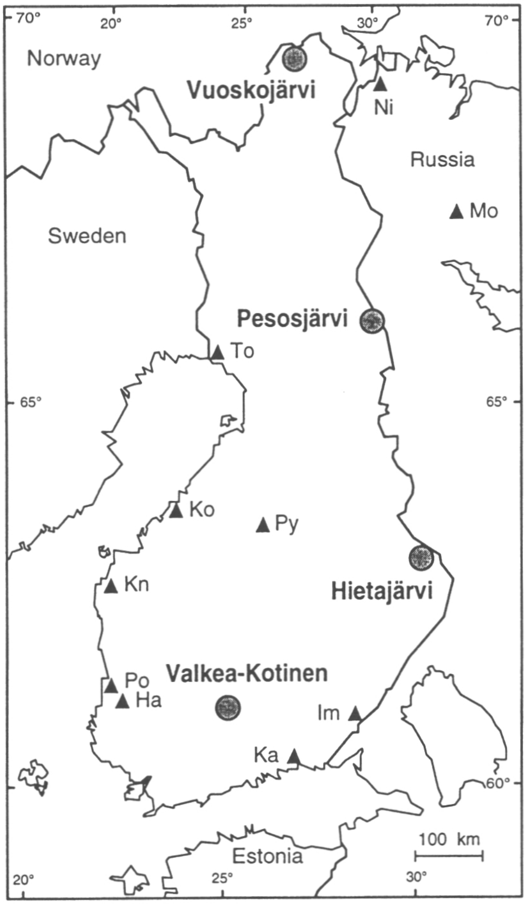

Fig. 1. Locations of IM catchments (circles) and some major point sources (triangles) for atmospheric heavy metal emissions. Ha = Harjavalta (Cu,Pb,Cd), Im = Imatra(Cr, Pb), Ka = Karhula (Cr), Kn = Korsnäs(Pb), Ko = Kokkola (Cd), Mo = Monchegorsk (Cu,Ni), Ni = Nikel (Ni), Po = Pori (Cu), Py = Pyhäsalmi mine (Zn,Cu), To = Tornio (Cr).

contain areas of forested upland, peatland and lake(s). A detailed description of the catchments is given in Bergström *et al.* (1995) but a brief description is given below.

The bedrock geology of the Valkea-Kotinen catchment is dominated by mica gneiss; that of Hietajärvi by porphyritic granodiorites; that of Pesosjärvi by arkosic and sericite quartzites contacted with greenstone bearing basaltic lavas, all bearing carbonate minerals; and that of Vuoskojärvi by gneisses (hornblende and feldspar types) and amphibolites containing sulphide bearing minerals.

The upland soils are Podzols or podzolic with a mor humus layer and developed on thin glacial or glacifluvial drift deposits. Some of the podzols of Valkea-Kotinen have transitions to Cambisols and all catchments have Leptosols and soils with lithic and rudic phases. The area of peatland (Histosols) varies from 2% (Vuoskojärvi) to 32% (Hietajärvi) of catchment area and are adjacent to or surround the lakes.

The forested parts of the catchments consist of old-growth (>100 years old) stands composed of varying proportions of Scots pine (*Pinus sylvestris* L.), Norway spruce (*Picea abies Karst.*), and deciduous species (mainly *Betula spp.*).

The surface water area varies from 10% (Pesosjärvi) to 27% (Hietajärvi) of catchment area. The Valkea-Kotinen catchment consists of a single small lake with a mean depth of ca. 3 m. Its waters are humic (TOC = 17 mg l^{-1}), and have exceptionally low pH (4.5) and alkalinity (– 40 μmol l^{-1}). The Hietajärvi catchment comprises a large lake, Iso Hietajärvi, with a mean depth of 3.6 m, and a number smaller lakes and ponds. The waters of Iso Hietajärvi are clear (TOC = 4.5 mg l^{-1}) with a pH of 6.2 and alkalinity of 75 μmol l^{-1}. The Pesosjärvi catchment also has one large lake (mean depth of 5 m) and four small lakes and ponds. Lake Pesosjärvi has clear waters (TOC = 5.2 mg l^{-1}) with a pH of 7.2 and exceptionally high alkalinity (460 μmol l^{-1}). Vuoskojärvi contains a single large, clear water (TOC = 3.7 mg l^{-1}) lake with a mean depth of 3 m, pH of 7.2 and alkalinity of 170 μmol l^{-1}. Chemistry values are median lake runoff values recorded during 1994–96.

Sampling

The following aqueous media were sampled: bulk precipitation (DC)[1)] throughfall (TF), stemflow (SF), soil water (SW), groundwater (GW), lake water (LC) and stream runoff (RW). The following biotic media have also been sampled: mosses (MC), needles (NC), litterfall (LF), humus layer (SC), and ants and shrew livers. The humus layer is included in the biotic media because it is derived from biomass and, like needles, litterfall, ants and shrews, is subject to biological uptake and bioaccumulation of heavy metals. Mosses were sampled as an indicator of deposition. Sam-

1) Abbreviations are those used in the UN-ECE Integrated Monitoring Manual (EDC 1993).

pling for TF, SF, NC, LF, and SC was carried out at 2–4 permanent plots located in homogeneous stands of the main habitat types in each catchment. A full description of the permanent plots is given in Bergström *et al.* (1995). Sampling procedures for all media except ants and shrews have been described in the UN–ECE Integrated Monitoring manual (EDC 1993) and Bergström *et al.* (1995), but are briefly described below.

Aqueous media

The bulk precipitation (DC) samples were collected with 2 parallel bulk (wet + dry) deposition collectors in an open area within the catchment. Throughfall (TF) was collected with bulk 12–16 collectors per plot (number depending on plot size) and stemflow (SF) with spiral collectors fitted to 2–8 pine trees per plot. The SF sampling of Scots pine at Valkea-Kotinen only started in 1992. The TF and SF samples were composited by plot for analysis. Soil water (SW) samples were collected with suction lysimeters using a vacuum of ca. 60 kPa. Only the data from lysimeters installed at 35 cm depth (i.e. below the zone of maximum illuviation and rooting) are reported in this paper. There were 3–6 lysimeters installed in each plot and the samples were analysed individually. Monthly TF (during snow-free period), SF and SW values are volume weighted values calculated from weekly values. The groundwater (GW) samples were taken from PVC tubes installed in Hietajärvi (5 locations) and in Pesosjärvi (1 location and from a spring). The other two catchments were unsuited to groundwater sampling. The GW samples were analysed individually. Lake chemistry (LC) samples were collected from the deepest parts of the lakes, at depths of 1, 3, and 5 m (mean value was used in this paper) in the case of Valkea-Kotinen and Hietajärvi, and 1 m in the case of Pesosjärvi. Runoff (RW) refers to samples taken from gauging weirs installed in the catchment outlet stream.

Biota

Only the needle chemistry (NC) data for Scots pine and for the current year's needles are presented in this paper. Each year, 2–3 shoots from the upper part of the canopy of five trees per plot were collected. The litterfall (LF) data refers to total (i.e. unfractionated) litterfall collected with six traps installed on each plot. A monthly composite sample from all the traps for each plot was analysed. The moss chemistry (MC) data refers to the heavy metal concentrations in *Pleurozium schreberi*. Samples were taken at 3–10 open (i.e. not under tree canopy) locations in each catchment and composited. Only the upper segment corresponding to the last 3 years' growth were analysed. For the humus layer (SC), four replicate samples of the Of + Oh layer were taken from each of the permanent plots. Each replicate was a composite of subsamples (one subsample from each 10 × 10 m subplot within each plot). The number of subsamples per replicate varied from 12 to 16, depending on plot size. The samples were taken using a stainless steel cylinder and placed in plastic bags. Specimens of red wood ants (*Formica aquilonia* and *F. lugubris*) were collected from nests located on hill tops in or near to the catchments in early May and September. Common shrew (*Sorex areneus*) specimens were trapped in May (adults) and September (juveniles) using a modified cone trap method (Pankakoski 1979).

Laboratory analysis

Analytical methods for most media were described in the UN-ECE Integrated Monitoring manual (EDC 1993) and Bergström *et al.* (1995), but are briefly presented in Table 2. Acid-washed equipment and polyethylene sample bottles were used throughout and samples acidified before analysis to promote desorption of metals from the walls of the sample storage bottles. The NC samples were not washed before analysis and therefore reported concentration values also include heavy metals absorbed to the surface of the needles. The shrews were dissected and samples of their livers taken for analysis. Concentrations of heavy and trace elements are often low, particularly in water samples, and values less than the detection limit (dl) frequently encountered. The detection limits of the different instruments used in this study are presented in Table 2. The detection limits with the ICP-ES instrument (ARL 3580) are high in

Table 2. Sampling frequency, analytical methods and detection limits used during the study (1989–1996) for aqueous media (μg l^{-1}) and biotic media (mg kg^{-1} dry matter).

Media°	Institute*	Sampling frequency	Analytical method §	Detection limit#				
				Cd	Cu	Ni	Pb	Zn
Aqueous media								
DC	FMI	monthly, from 6/1990	GAAS standing sample		0.10 (90–91)	1.00 (90–91)		0.50 (90–91)
			GAAS standing sample	0.005 (90–93)	0.30 (92–93)	0.50 (92–93)	0.20 (90–93)	0.20 (92–93)
			ICP-MS standing sample	0.006 (94–95)	0.04 (94–95)	0.04 (94–95)	0.03 (94–95)	0.10 (94–95)
			ICP-MS standing sample	0.005 (96)	0.01 (96)	0.01 (96)	0.01 (96)	0.05 (96)
TF	FFRI	weekly during snow-free period, also monthly during winter from 1995	ICP-ES filtered (8 μm)	2.0 (90–96)	5.0 (90–96)	18.0 (90–96)	25.0 (90–96)	2.0 (90–96)
SF,SW	FFRI	weekly in snow-free period	ICP-ES filtered (8 μm)	2.0 (90–96)	5.0 (90–96)	18.0 (90–96)	25.0 (90–96)	2.0 (90–96)
GW$	GSF	6–12 times/ year from 1993	ICP-MS standing sample	0.02 (93–96)	0.04 (93–96)	0.06 (93–96)	0.03 (93–96)	0.10 (93–96)
LC,RW	FEI	monthly from 1994	ICP-MS standing sample	0.03 (94–96)	0.07 (94–96)	0.04 (94–96)	0.03 (94–96)	0.3 (94–96)
Biotic media								
MC	FEI	1991†	ICP-ES ($HClO_4$-HNO_3)	0.2	0.2	0.2	2.0	0.2
		1996‡	ICP-MS (HNO_3)	0.01 (96)	0.01 (96)	0.20 (96)	0.02 (96)	3.00** (96)
NC	FFRI	yearly	ICP-ES (HNO_3-H_2O_2)	0.5 (90–96)	1.25 (90–96)	4.4 (90–96)	6.25 (90–96)	0.55 (90–96)
LF	FFRI	monthly during snow-free period	ICP-ES (HNO_3-H_2O_2)	0.5 (90–96)	1.25 (90–96)	4.4 (90–96)	6.25 (90–96)	0.55 (90–96)
SC	FFRI	1988/89, 1991/92, 1995	ICP-ES (dry ash+HCl)	0.1 (90–96)	0.25 (90–96)	0.89 (90–96)	1.25 (90–96)	0.11 (90–96)
Ants	FEI	twice annually, 1993–96	ICP-MS (HNO_3)	0.001 (93–96)	0.001 (93–96)	0.001 (93–96)	0.001 (93–96)	0.004 (93–96)
Shrew liver	FEI	twice annually, 1993–94	ICP-MS (HNO_3)	0.002 (93–94)	0.004 (93–94)	0.002 (93–94)	0.002 (93–94)	0.017 (93–94)

° *see* Material and methods for abbreviations
* FMI = Finnish Meteorological Institute, FFRI = Finnish Forest Research Institute, GSF = Geological Survey of Finland, FEI = Finnish Environment Institute
§ GAAS = Graphite atomic absorbtion spectrometry, ICP-MS = Inductively coupled plasma atomic mass spectrometry, ICP-ES = Inductively coupled plasma atomic emission spectrometry
# Years in parentheses
$ Only Hietajärvi and Pesosjärvi
† Digestions: Helsinki University; analysis: VTT, Technical Research Centre of Finland
‡ Digestions: Helsinki University; analysis: GSF
** ICP-ES

comparison with other (newer) instruments that were used.

All the analyses were performed in laboratories that have continuous quality control programmes and which regularly participate in national and international intercalibration exercises. For example, the FMI (Finnish Meteorological Institute) laboratory found mean relative differences from test samples of: Pb 4%, Cd 11%, Cu 6%, Zn 5%, and Ni 16%. Similar intercalibration exercises by the FFRI (Finnish Forest Research Institute) laboratory found mean relative differences from water test samples of: Pb 3%, Cd 3%, Cu 4%, Zn 3%, and Ni 7%.

Results

Spatial and temporal variability

Summary statistics describing the concentrations of the aqueous media are presented in Table 3 and for biotic media in Table 4. The 50th percentile (medians) is used to describe average concentrations and the 95th percentiles to give a reliable description of maximum concentrations for toxicological purposes.

Temporal changes in Pb and Zn concentrations in DC (mean annual), MC (1991 and 1996), LF (monthly) and SC (1989, 1991–92 and 1995)

Table 3. Heavy metal concentrations (μg l^{-1}) in the studied aqueous media reported for various percentiles.

Media*	n†	Cd			Cu			Ni			Pb			Zn		
		25th	50th	95th	25th	50th	95th	25th	50th	95th	25th	50th	95th	25th	50th	95th
Valkea-Kotinen																
DC	76	0.03	0.04	0.21	0.71	0.98	3.81	0.25	0.40	1.27	1.12	2.00	5.80	3.0	4.1	11.7
TF	175(91)	0.14	0.39	2.15	0.74	2.04	14.49	1.78	3.50	12.30	3.12	7.27	23.57	7.0	12.3	60.4
SF	25(17)	0.15	0.18	1.48	2.01	3.10	15.28	7.49	7.99	19.49	7.44	10.42	100.26	49.0	69.1	446.9
SW	42(17)	0.75	0.91	2.48	2.52	4.60	23.46	8.35	11.89	19.43	9.48	14.63	45.66	18.9	27.3	103.1
GW	0	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
LC	65	0.02	0.02	0.04	0.18	0.27	1.36	0.41	0.49	8.62	0.44	0.56	0.96	2.7	3.7	12.6
RW	35	0.02	0.02	0.05	0.16	0.20	0.84	0.40	0.46	4.26	0.48	0.60	1.04	2.2	3.8	11.0
Hietajärvi																
DC	79	0.02	0.03	0.14	0.60	1.00	4.06	0.25	0.31	0.60	0.9	1.42	3.70	2.4	3.3	9.3
TF	113(63)	0.36	0.48	1.37	1.42	1.77	32.55	2.27	2.95	11.19	5.81	7.88	22.45	4.5	6.7	23.3
SF	45(17)	0.25	0.43	1.70	1.73	2.58	22.94	9.54	9.84	19.87	5.51	8.54	81.50	27.7	42.5	99.7
SW	39(18)	0.67	0.88	2.87	1.75	4.17	25.80	6.82	8.82	11.95	10.32	13.27	44.65	7.2	13.8	35.8
GW	17	0.01	0.01	0.03	0.10	0.19	0.62	0.03	0.03	1.05	0.02	0.02	0.08	1.2	1.9	5.7
LC	73	0.02	0.02	0.02	0.08	0.11	0.34	0.09	0.11	0.19	0.05	0.07	0.97	0.4	0.6	3.5
RW	36	0.02	0.02	0.02	0.11	0.13	0.35	0.10	0.13	0.22	0.07	0.08	0.25	0.4	0.8	3.5
Pesosjärvi																
DC	77	0.02	0.03	0.09	0.82	1.20	5.52	0.25	0.35	1.41	0.60	1.00	3.32	1.5	2.3	7.6
TF	108(65)	0.12	0.66	2.72	0.21	2.75	28.15	4.09	5.37	12.91	1.98	9.75	35.50	4.5	7.0	61.3
SF	35(14)	0.01	0.03	1.27	1.26	4.89	16.06	10.57	10.90	11.69	0.99	1.83	55.35	28.0	48.3	219.0
SW	36(13)	0.35	0.54	2.52	2.75	3.72	12.42	8.14	9.18	10.19	4.46	14.91	25.49	10.0	12.1	30.9
GW	43	0.01	0.01	0.03	0.06	0.24	2.59	0.03	0.09	0.82	0.02	0.02	0.12	0.3	0.8	3.7
LC	14	0.02	0.02	0.02	0.66	0.75	1.62	0.43	0.54	0.86	0.06	0.08	1.08	0.7	1.5	3.6
RW	25	0.02	0.02	0.02	0.66	0.69	1.14	0.35	0.39	0.59	0.04	0.05	0.42	0.2	0.4	1.4
Vuoskojärvi																
DC	76	0.01	0.02	0.20	1.07	2.07	12.85	0.25	0.50	2.70	0.30	0.70	4.90	1.0	1.6	10.1
TF	103(60)	0.19	0.24	1.53	0.57	0.88	11.02	0.93	1.20	10.80	3.50	4.39	28.88	4.5	6.0	36.7
SF	32(13)	0.04	0.05	0.17	0.87	1.94	19.27	8.38	8.63	25.93	1.41	2.39	29.54	32.6	56.3	186.6
SW	35(13)	0.45	0.54	1.85	2.88	5.43	25.86	7.71	8.03	10.72	6.0	7.19	25.99	16.8	22.2	77.14
GW	0	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
LC	0	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
RW	5	0.02	0.02	0.02	0.41	0.48	2.51	0.15	0.16	0.20	0.05	0.05	0.18	0.9	1.5	34.9

* DC = bulk precipitation, TF = throughfall, SF = stemflow, SW = soil water, GW = groundwater, LC = lake water, RW = stream runoff.

† number of observations (for Ni in parentheses).

media over the study period are shown in Figs. 2 and 3. Besides representing a toxic element (Pb) and a micro-nutrient (Zn), the concentrations of these two elements were mostly above dl concentrations and therefore the percentiles are precise.

Influence of bulk precipitation

To determine whether the heavy metal concentrations in bulk precipitation had an affect on concentrations in the other aqueous media, Spearman rank correlations were computed using monthly data (Table 5). Since a delay in the response of ground and surface water concentrations to bulk precipitation concentrations maybe expected, correlations using delays of 1 and 2 months were also computed. Using this rather simplistic approach, a strong positive correlation is taken to indicate that DC exerts a determining influence. A weak or negative correlation indicates that other processes within the ecosystem, e.g. adsorption, ion exchange, nutrient cycling, weathering, and sedimentation, are determining heavy metal concentrations.

Bioaccumulation and toxicological assessment

Since most of the Pb in the ecosystem is from atmospheric deposition, biota:deposition concentration ratio should describe the degree of bioaccumulation of atmospheric Pb. We calculated such ratios using MC concentrations as an indicator of atmospheric Pb (Table 6). Median concentration values were used to calculate the ratios.

Discussion

In this paper we describe heavy metal concentrations in a range of aqueous and biotic media. We chose to present summary statistics in the form of

Table 4. Heavy metal concentrations (mg kg^{-1} dry matter) in the studied biotic media reported for various percentiles.

Media*	*n*	Cd			Cu			Ni			Pb			Zn		
		25th	50th	95th	25th	50th	95th	25th	50th	95th	25th	50th	95th	25th	50th	95th
Valkea-Kotinen																
MC	2	–	0.2	–	–	6.7	–	–	2.7	–	–	9.7	–	–	35.3	–
NC	78	0.3	0.3	0.3	2.3	2.6	4.5	n.a.†	n.a.	n.a.	3.3	3.4	3.5	34.8	40.5	64.2
LF	37	0.3	0.3	0.3	4.3	5.1	6.9	n.a.	n.a.	n.a.	4.3	6.5	9.8	55.2	65.8	107.3
SC‡	20	0.8	0.8	1.0	6.7	6.9	8.1	7.4	8.4	9.8	33.6	37.2	50.7	32.3	49.0	75.7
Ants	32	4.0	4.3	7.8	10.9	11.6	16.2	0.3	0.5	0.8	0.7	0.8	1.6	446.0	484.3	677.6
Shrew	40	1.4	2.7	6.2	18.1	19.3	22.5	0.1	0.1	0.3	0.5	0.9	1.6	64.4	67.8	79.0
Hietajärvi																
MC	2	–	0.1	–	–	5.0	–	–	1.9	–	–	5.7	–	–	23.8	–
NC	191	0.3	0.3	0.3	2.1	2.5	3.6	n.a.	n.a.	n.a.	3.3	3.4	3.4	34.4	39.8	57.0
LF	35	0.3	0.3	0.3	2.1	3.7	5.8	n.a.	n.a.	n.a.	3.3	3.4	4.7	45.9	52.5	75.0
SC‡	16	0.5	0.5	0.6	5.2	5.8	6.8	5.2	5.7	6.2	27.1	31.3	37.0	41.5	48.6	51.9
Pesosjärvi																
MC	2	–	0.1	–	–	5.2	–	–	2.2	–	–	3.7	–	–	21.6	–
NC	89	0.3	0.3	0.3	1.6	2.1	3.4	n.a.	n.a.	n.a.	3.3	3.4	3.4	29.3	33.4	44.1
LF	29	0.3	0.3	0.3	4.4	5.1	7.3	n.a.	n.a.	n.a.	3.3	3.4	5.0	60.2	66.0	105.3
SC‡	20	0.6	0.7	0.8	5.0	5.6	6.8	7.0	8.1	9.2	15.6	16.0	18.4	31.2	33.9	42.9
Ants	15	1.6	1.8	3.1	9.2	10.1	11.0	0.3	0.4	0.6	0.3	0.3	0.6	295.9	314.2	418.3
Shrew	45	0.5	0.9	3.0	17.4	18.7	26.1	0.1	0.1	0.6	0.1	0.1	0.3	60.2	63.5	72.2
Vuoskojärvi																
MC	2	–	0.1	–	–	5.9	–	–	3.5	–	–	2.6	–	–	23.7	–
NC	91	0.3	0.3	0.3	2.7	3.1	4.2	n.a	n.a	n.a.	3.3	3.4	3.4	37.7	40.8	51.5
LF	26	0.3	0.3	0.3	3.6	4.9	9.6	n.a	n.a	n.a.	3.3	3.4	4.6	55.1	77.1	147.7
SC‡	16	0.5	0.5	0.5	4.7	4.9	5.8	4.6	6.5	11.9	12.6	13.8	16.0	27.8	33.0	51.7
Ants	6	2.0	2.5	3.2	11.1	11.4	12.5	0.4	0.5	0.5	0.1	0.1	0.2	289.8	292.3	314.8

* MC = mosses, NC = needles, LF = litterfall, SC = humus layer
† n.a. data not available
‡ only 1989 data

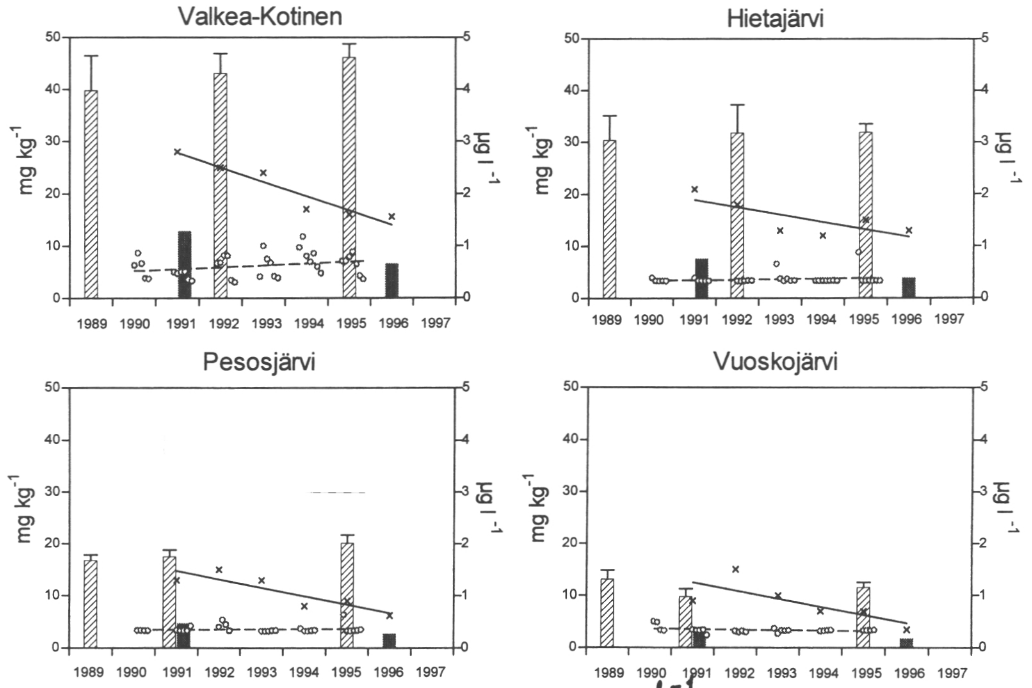

Fig. 2. Pb concentrations in bulk precipitation (mean annual DC in μg l^{-1} ~~g l^{-1}~~, crosses), litterfall (monthly LF in mg kg^{-1}, open circles), moss (MC in mg kg^{-1}, solid bar) and humus layer (SC in mg kg^{-1}, hatched bar). Lines are linear regression fits for DC and LF, and SC error bars are standard deviations.

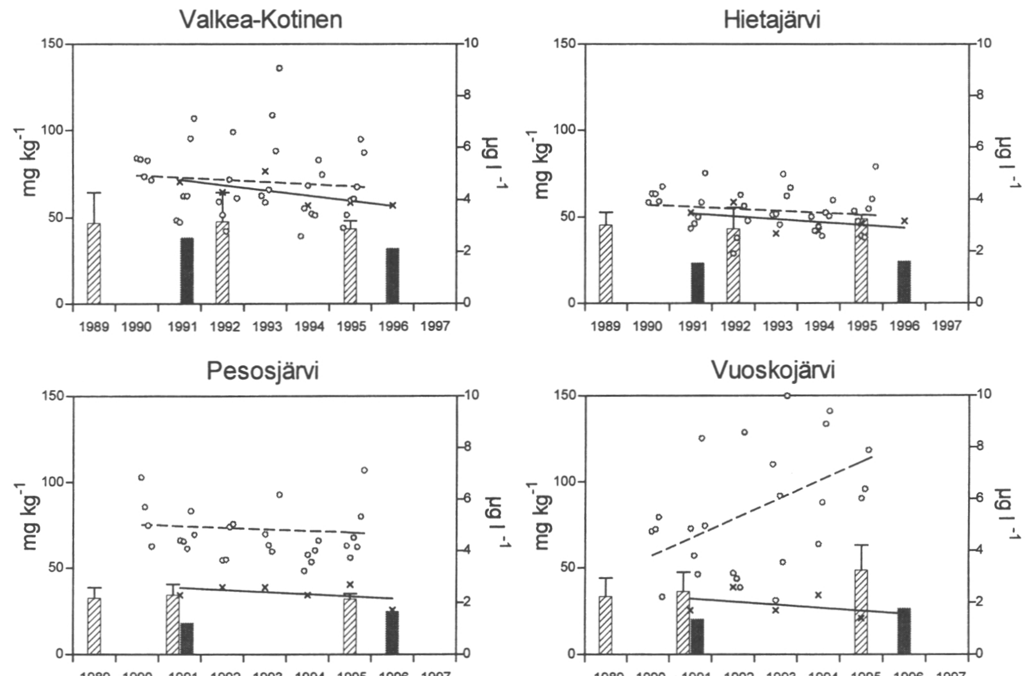

Fig. 3. Zn concentrations in bulk precipitation (mean annual DC in μg l^{-1} ~~g l^{-1}~~, crosses), litterfall (monthly LF in mg kg^{-1}, open circles), moss (MC in mg kg^{-1}, solid bar) and humus layer (SC in mg kg^{-1}, hatched bar). Lines are linear regression fits for DC and LF, and SC error bars are standard deviations.

percentiles rather than means and standard deviations because of the strong positive skewed distribution showed by the data. The percentiles also describe the frequency distribution of the data.

A simple substitution protocol (one-half of the dl) for handling values less than detection limit is given in the IM manual (EDC 1993). Data containing such substituted values is referred to as censored data and enables summary statistics (mean, standard deviation, percentiles, etc.) to be calculated. Censored data with substituted values can produce considerably biased mean and standard deviation values, however (Helsel and Cohn 1988, Porter *et al.* 1988, Helsel 1990). There may also be problems with percentile summary statistics. Depending on the number of ~~values~~ less than dl, the same substitute value will be given for increasing percentiles. This is seen, for example, in the case of Cd for GW and LC (Table 3). Although still providing valuable information (concentrations are not higher than dl), there is a lack of precision, particularly if the dl values are high. Because of the relatively high dl values of the instrument used for TF, SF and SW, we applied a maximum likelihood method using log-normal distributions to improve the precision of the percentile values for these media (Helsel 1990). With the exception of Cd, heavy metal concentrations in the biota were not affected by concentrations less than detection limits (Table 4).

Overall, the measured concentrations in the aqueous media in our boreal ecosystems in remote locations (Table 3) are low compared to those reported for temperate forest ecosystems (Bergkvist *et al.* 1989). Concentration values in our studies are also lower than those reported for two spruce forest ecosystems in southern and western Sweden (Bergkvist 1987). Bulk precipitation concentrations were similar to those reported for six rural and remote sites in Norway in 1989–90 (Berg *et al.* 1994, Juntto *et al.* 1997). Concentrations of Pb and Zn in bulk precipitation systematically decreased northwards, reflecting decreasing long–range atmospheric transport of these metals and also decreasing population densities. The highest concentrations of Cu and Ni in DC occurred at Vuoskojärvi, reflecting the influence of emissions from the Cu-Ni smelters on the Kola Peninsula. However, the higher Cu and Ni concentrations in DC at Vuoskojärvi were not reflected in higher concentrations in TF, SF, SW and RW compared to other catchments (Table 3).

Table 5. Spearman rank correlations between Zn concentrations in bulk deposition and other aqueous media for each catchment. Significant ($p < 0.05$) coefficients are indicated in bold.

Catchment	Aqueous media†											
	TF1*	TF2*	SF	SW	GW	GW_1‡	LC**	LC_1‡	LC_2‡	RW	RW_1‡	RW_2‡
Valkea-Kotinen	**0.385**	**0.384**	–0.059	–0.154			–0.014	0.047	**0.405**	–0.145	0.034	–0.034
Hietajärvi	**0.363**	**0.245**	0.269	0.068	0.142	–0.114	0.241	0.116	**0.397**	–0.040	–0.230	**0.525**
Pesosjärvi	–0.011	0.186	–0.018	0.257	0.118	0.062	–0.214	0.037	0.046	0.118	–0.080	0.070
Vuoskojärvi	**0.310**	**0.326**	0.110	0.081						–0.100	–0.100	–0.100

† TF = throughfall, SF = stemflow, SW = soil water, GW = groundwater, LC = lake water, RW = stream runoff.
* Throughfall reported for separate throughfall plots (stands).
** LC = 1 m depth samples only.
‡ Subscripts refer to delays of 1 and 2 months.

Table 6. Biota: moss median Pb concentration ratios at each catchment.

Media	Valkea-Kotinen	Hietajärvi	Pesosjärvi	Vuoskojärvi
Needles (NC)	0.35	0.59	0.91	1.31
Litterfall (LF)	0.67	0.59	0.91	1.30
Humus layer(SC)	3.82	5.51	4.31	5.37
Ants	0.08	–	0.08	0.04
Shrew livers	0.09	–	0.04	–

The relatively high Zn concentrations in soil water and runoff at Vuoskojärvi compared to concentrations in bulk precipitation (Table 3) is probably due to the weathering of hornblende and sulphide minerals in the drift deposit.

Comparison of monthly DC (corresponding to bulk precipitation to the canopy) and TF (below canopy precipitation) concentrations showed an enrichment of heavy metals in throughfall (Table 3). The mean monthly enrichment ratios (TF:DC) for Zn, Pb, Cu, Cd and Ni averaged across catchments were: 7, 17, 11, 33 and 18, respectively. These enrichment ratios increased northwards as far as Pesosjärvi, but were lower again at Vuoskojärvi. Throughfall enrichment arises through the washing-off of dry deposition and leaching from the canopy. Coniferous forest canopies are particularly efficient in trapping aerosols (Bergkvist *et al.* 1989), the form in which heavy metals are usually present in the air (Alloway 1995). The enrichment in TF Pb is primarily due to wash-off since the internal cycling of Pb is negligible (Lindberg and Harriss 1981, Alloway 1995). Lead in precipitation is known to occur in particulate form, whereas Cd and Cu are largerly dissolved (De Boer and Fortezza 1992). The water solubility of Zn aerosols, like Pb, is relatively low compared to Cd (and Cu) (Lindberg *et al.* 1989). Therefore, much of the Zn in precipitation can also be expected to be in particulate form. The enrichment of Zn and Cu in TF is partly due also to canopy leaching since both are micro-nutrients and internally cycled. Cadmium is also readily cycled (Bergkvist 1987, Lindberg *et al.* 1989). Zinc concentrations were particularly high in SF, as has been found in other studies (Bergkvist *et al.* 1989).

Concentrations of the heavy metals, particularly Pb, sharply decreased in water passing through the soil to groundwater (Table 3). A similar pattern was also shown for spruce forest ecosystems in southern and western Sweden (Bergkvist 1987). The monthly dilution ratios (SW:GW for those months in common) for Zn, Cu, Ni, Pb, and Cd averaged across Hietajärvi and Pesosjärvi catchments were: 11, 28, 97, 552 and 83, respectively. The influence of the humus layer and organic matter in the upper soil on heavy metal concentrations, particularly on Cu and Pb, and decreasing acidity with soil depth, particularly on Zn and Cd, in reducing leachability has been documented (Bergkvist *et al.* 1989). Since most heavy metals in soil solution exist as cations, they can be retained by cation exchange adsorption (Alloway 1995). The cation exchange capacity of upland soils such as those in our study, decreases with depth and is related to the amount and distribution of organic matter and clay (Tamminen and Starr 1990). Complexation with organic matter is also important in reducing the mobility of heavy metals in soils (Fergusson 1990, Alloway 1995). The effect of acidity on heavy metal mobilisation in soil is probably mainly regulated by the formation of water soluble organic complexes (Bergkvist 1986). Organic matter storage in Finnish forest soils is strongly related to productivity, which in turn, is largely determined by temperature, and therefore shows a clear decrease northwards (Kauppi *et al.* 1997, Liski and Westman 1997). Organic matter decomposition also strongly covariates with temperature and therefore shows a strong decline northwards (Kurka and Starr 1997). Lake water concentrations of heavy metals are also strongly influenced by acidity and humic matter (Mannio *et al.* 1993). Therefore, the area of peatland in the catchment and length of shoreline contact with peatland were found to be important factors explaining surface water heavy metal concentrations (Lazerte *et al.* 1989).

Spearman correlation coefficients analyses indicated that only Zn concentrations in aqueous media were dependent on bulk precipitation concentrations (Table 5). Monthly Zn concentrations in TF were significantly ($p < 0.05$) correlated to DC concentrations in each catchment with the exception of Pesosjärvi. However, the influence of DC on Zn concentrations disappeared as the water passed on further through the ecosystem. Zinc concentrations in the lake waters of Valkea-Kotinen and Hietajärvi and RW at Hietajärvi, however, had significant positive correlations with the Zn concentration of DC from two months before.

The annual mean Pb concentrations in DC at all catchments declined over the study period (Fig. 2). Testing whether the slope of the linear regression differed from zero gave p-values of 0.003, 0.078, 0.020 and 0.082 for Valkea-Kotinen, Hietajärvi, Pesojärvi and Vuoskojärvi, respectively. The decline was the largest for the most southerly catchment, Valkea-Kotinen (slope = –0.023). Moss lead concentrations, which are a reliable indicator of Pb deposition (Berg *et al.* 1995), indicate a near 50% decrease in deposition from 1991 levels to 1996 levels at all catchments (Fig. 2). However, the reduction in Pb deposition had little effect on Pb concentrations in litterfall. Needle Pb concentrations, which were similar to those in LF (Table 4), also remained unchanged. Lead concentrations in the humus layer showed significant ($p < 0.05$) differences between the sampling years at Pesosjärvi and Vuoskojärvi. However, the changes were not consistent with a decline over the study period. Annual mean Zn concentrations in DC did not significantly declined over the study period (Fig. 3). The probability of the linear slope of the relationship differing from zero varied from 0.126 (Valkea-Kotinen) to > 0.350 (others). The changes in the concentration of Zn in moss sampled in 1991 and 1996 were inconsistent among the catchments. Moss is a poor indicator of the bulk deposition of Zn because Zn is recycled as a micronutrient or leached (Berg *et al.* 1995). However, Zn concentrations in monthly litterfall at Vuoskojärvi significantly increased over the study period (slope = 0.923, $p = 0.01$). The mean Zn concentration in the humus layer at Vuoskojärvi was also significantly ($p < 0.05$) greater in 1995 than in 1989 (Fig. 3). The cause of these increases is unknown. There was no significant trend in needle Zn concentrations over the study period.

Lead concentrations in the biota tended to decrease northwards, indicating that Pb concentrations in biota are largely determined by atmospheric deposition (Table 4). Of the biotic media studied, the humus layer showed the greatest accumulation of atmospheric Pb (highest biota:moss ratios; Table 6). This can be explained by the well documented immobility of Pb in humus layers (e.g., Bergkvist 1989) and the concentrating effect of organic matter decomposition. The Pb biota:moss concentration ratio for ants and shrew livers were very low in comparison to the other biotic media, further indicating the low mobility of the atmospheric Pb deposition in the ecosystem. Copper and Ni concentrations in the biotic media at Vuoskojärvi were similar to or less than those at the other catchments (Table 4). This indicates that the Cu and Ni emissions from the Kola Peninsula had little or no effect on the biota at Vuoskojärvi.

Tyler (1992) presented heavy metal critical concentration values, so-called "lowest effective limit" (LOEL), for mor humus layers in Sweden. A LOEL value is the lowest concentration at which an effect was found, i.e. a negative influence on soil enzyme activity, soil respiration, nitrogen transformations, microflora, soil, and invertebrae. The LOEL values for Cd, Cu, Pb and Zn are: 3.5, 20, 150 and 300 mg kg^{-1} dry matter, respectively. The 95th percentile values for humus layer presented in Table 4 were less than these LOEL values, indicating that humus layer heavy metal concentrations in the IM catchments are not toxic to soil organisms.

Lithner (1989) has presented so-called "lowest known levels of effect" (LKE) concentrations for heavy metals in freshwaters at approximately neutral pH to identify toxic concentrations to aquatic organisms. The LKE values for Cd, Cu, Ni, Pb and Zn are: 0.15, 2, 25, 1.5 and 15 $\mu g\ l^{-1}$, respectively. Overall, our surface water (LC and RW) heavy metals concentrations were below the LKE values. Only at Hietajärvi, was one Cd value greater than the LKE Cd value, and the LC 95th percentile concentration for Pb at Valkea-Kotinen is close to the LKE Pb value. Otherwise, the 95th percentile concentrations in both Hietajärvi and Valkea-Kotinen were less than 50 percent of the LKE values. At Pesosjärvi, the 95th percentile concentrations of Cu are 60-80 percent of the LKE values. At Vuoskojärvi, the low number of LC samples taken do not allow a reliable comparison to LKE values to be made, but the single observations did exceed the LKE values for Cu and Zn.

Conclusions

The concentrations of Cd, Cu, Ni, Pb and Zn in various aqueous media in boreal ecosystems were low compared to those reported for temperate ecosystems. The decline in heavy metal concentrations as the precipitation passed through the ecosystem indicate that most of the heavy metal load in deposition is retained within the catchments. The sharp decline in heavy metal concentrations, particularly in the case of Pb, as the precipitation passed through the soil indicated the central role played by the humus layer in this retention. There is ample evidence from other studies to show that lake bottom sediments are also effective in retaining heavy metals. With the exception of Zn, heavy metal concentrations in deposition were not correlated with concentrations in the other aqueous media. This is concluded to be the result of interaction and retention as the water passes through the ecosystem. Zinc concentrations in throughfall and lake waters were correlated to bulk deposition concentrations, and this effect lagged by two months in the case of lake water. Soil water and runoff Zn concentrations at Vuoskojärvi were influenced by lithological sources of Zn.

Our results showed that the concentrations of Pb in bulk deposition have significantly declined over the study period (1989–1996). Since the IM catchments are located in background areas, this decline represents a decrease in the long-range transport of Pb. However, the reduction in Pb deposition has not yet significantly affected the levels of Pb in the ecosystem.

Current concentrations of the studied heavy metals in the humus layer and surface water were below critical levels for toxic effects. We consider that the concentration values we have presented can be used as background reference values.

Future studies will deal with the pools and fluxes of heavy metals within the IM catchments. This will enable us to quantify the amount and location of heavy metal retention in boreal ecosystems in Finland.

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Paper III

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III

THE IMPORTANCE OF LEACHING FROM LITTER COLLECTED IN LITTERFALL TRAPS

LIISA UKONMAANAHO* and MICHAEL STARR
Finnish Forest Research Institute, Vantaa Research Centre, Vantaa, Finland
(author for correspondence, e-mail: liisa@ukonmaanaho@metla.fi; fax: +358 985705569)*

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Abstract. Litterfall (LF) is usually collected by means of open traps. However, this litter will be subject to leaching by the throughfall which passes through the accumulated litter in the traps. The nutrients lost during this leaching are not taken into account in the calculation of LF nutrient fluxes. We report the results from a 2-month (August–September) study carried out in 8 northern coniferous forest stands to assess the possible importance of leaching from litter in LF traps. Compared to throughfall (TF), the litterfall leachate (LFL_{gross}), which includes a throughfall component, had significantly ($p < 0.05$) higher concentrations and fluxes of Ca, Mg, Na and S. The average net LFL (i.e., $LFL_{net} = LFL_{gross}$-TF) fluxes were 21 (Ca), 7 (Mg), 57 (K), 10 (Na), 10 (N), and 19 (S) mg m^{-2} mo^{-1}. LFL_{net} accounted for 42%, 37% and 50% of the LFL_{gross} flux, and for 91%, 51% and 49% of the total litterfall flux (i.e., LF + LFL_{net}) of Na, S and K, respectively. For Ca, Mg and N, the LFL_{net} flux accounted for 64%, 58% and 29% of the LFL_{gross} flux, and for < 14% of the total litterfall flux. Compared to TF, LF was the dominant return pathway for Ca, Mg and N to the forest floor regardless of whether LFL_{net} was included or not. However, for K and S, taking LFL_{net} into account determined whether TF or LF was the dominant pathway. TF remained the dominant pathway for Na even when LFL_{net} was included.

Keywords: fluxes, litter, nutrient cycling, Scots pine, throughfall

1. Introduction

In forest ecosystems, nutrients are returned to the soil for recycling via two major pathways: litterfall and throughfall fluxes. A third pathway, stemflow, is often of minor importance and is usually ignored in nutrient cycling studies. The relative size of these fluxes depends upon several factors, including the mobility of the nutrient in question, the distribution and amount of rainfall, stand composition and structure, and season.

In boreal coniferous forests, foliar litter constitutes the major part of the litterfall flux to the forest floor. The amount of branches and bark in the litterfall increases with stand age, as does the number of cones (Mälkönen, 1974; Flower-Ellis, 1985; Finér, 1996). Deciduous forests loose most of their foliar biomass in the autumn. However, 40 to 60% of the total annual litterfall from conifers also occurs in September–October (Viro, 1955; Mälkönen, 1974). At the time of senescence, the concentrations of nutrients in foliage decrease. In the case of N and P, the decrease

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is considerable due to retranslocation back into the trunk (Helmisaari, 1992; Finér, 1996), whereas the decrease in foliar K and Mg concentrations is mainly due to leaching and loss to throughfall and stemflow (Aber and Melillo, 1991). Calcium, in contrast, tends to accumulate in foliage up to the time of leaf fall. The role of litterfall in nutrient return is therefore more significant for calcium than for other nutrients (Cole and Rapp, 1981).

In a study of 32 forests (Cole and Rapp, 1981), the annual return of nitrogen in litterfall averaged 83% of the total return to the forest floor. In contrast, the return of potassium in litterfall was only 41% of the total return, the majority being returned via throughfall and stemflow. The return of calcium via litterfall was 71% and for magnesium, 60%. Although litterfall supplies more matter to the forest floor than throughfall, the nutrients in litter have to be released through decomposition and mineralization. The nutrients returned to the forest floor in throughfall are, in contrast, immediately available for uptake as they are nearly all in soluble form (Parker, 1983). Annual fluxes of Ca and N in litterfall are greater than other nutrients regardless of forest type but the amounts vary among forest types. For example, the annual litterfall return of Ca is 3.8 kg ha^{-1} in boreal coniferous forests but 35.5 kg ha^{-1} in boreal deciduous forests (Cole and Rapp, 1981). For nitrogen, the corresponding values are 2.9 and 20.2 kg ha^{-1} (Cole and Rapp, 1981).

Traditionally, litterfall is collected by means of open traps installed underneath the canopy but above the forest floor. The traps are periodically emptied, typically at monthly intervals. The litterfall that is collected during the sampling period is therefore subject to washing and leaching by throughfall. Although the litterfall leachate component will be included in the soil pool or soil water flux it is not recognised as being a component of litterfall in nutrient cycling studies. Similar to the interaction between deposition and the canopy and the production of throughfall, the passage of throughfall through the litterfall trap will include nutrients that are leached and washed off from the trapped litter as well as any additions (e.g., N fixation) and removals by free-living microbes within the litter (Aber and Melillo, 1991). However, the dominant effect of throughfall passing through the litter may be the removal of nutrients from the litter resulting in an underestimation of the true litterfall flux of nutrients to the forest floor.

In an earlier study (Starr and Ukonmaanaho, 1994), we compared the flux of nutrients to the forest floor via net canopy leaching (throughfall plus stemflow minus bulk deposition) and via litterfall (litter in traps) at a series of stands in Finland. These stands have now been monitored for ten years as part of an international long-term forest ecosystem monitoring programme, the UN ECE International Cooperative Programme on Integrated Monitoring (ICP IM Programme Centre, 1998). The protocol for litterfall (LF) sample collection (ICP IM Programme Centre, 1998) does not include the collection of litterfall leachate, as is also the case with most nutrient cycling studies. We therefore carried out a short-term experiment to assess whether the leaching of nutrients from the litter collected in litterfall traps was significant compared to the litter and throughfall fluxes in

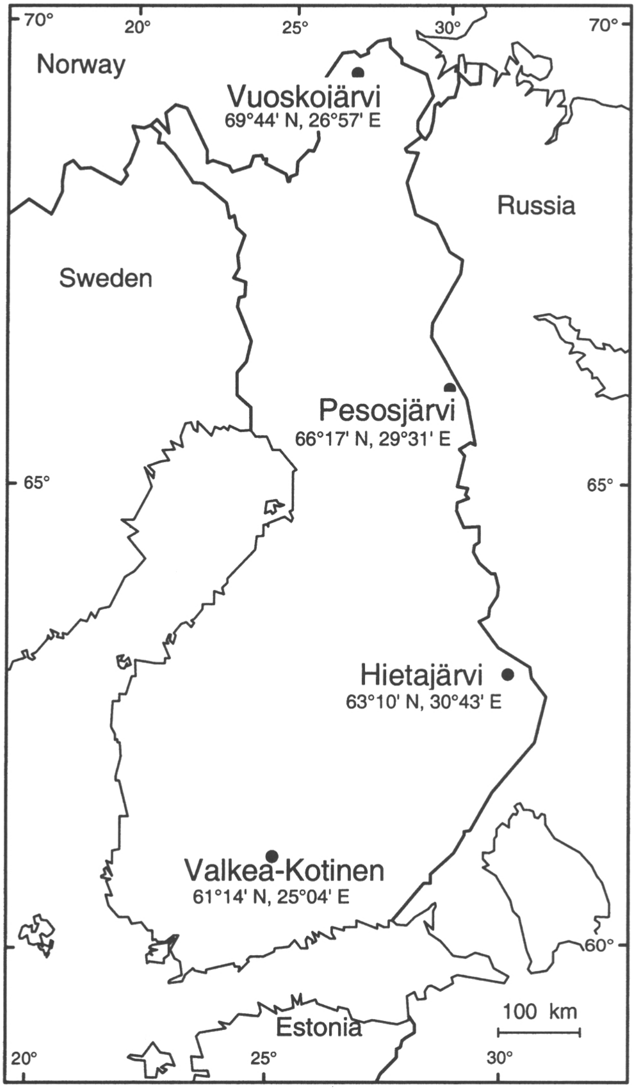

Figure 1. Map showing location of study site catchments.

these stands. We also sought to establish if the litterfall leachate flux differed in relation to stand composition (Scots pine *vs* mixed stands) and stand location (latitude). The intention was to highlight the possible underestimation of the nutrient fluxes associated with litterfall as determined in most nutrient cycling studies.

2. Materials and Methods

2.1. Site description

The study was carried out in four headwater catchments located at varying latitudes throughout Finland: Valkea-Kotinen (V-K), Hietajärvi (HJ), Pesosjärvi (PJ) and Vuoskojärvi (VJ) (Figure 1). These catchments are being monitored as part of the UN ECE International Cooperative Programme on Integrated Monitoring (Bergström *et al.*, 1995; ICP IM Programme Centre, 1998). All catchments are in protected conservation areas. In each catchment, permanent monitoring plots were established in 1988/89 at which a number of monitoring subprogrammes have been continuously carried out. Included in these subprogrammes are throughfall (TF) and litterfall (LF) subprogrammes. The plots were established in the main forest types in each catchment and varied in size from 25 × 25 m to 40 × 40 m. They are situated on flat sites and are as homogenous as possible with regard to soil morphology, ground vegetation and stand characteristics. The forests consist of old-growth stands composed of various proportions of Scots pine (*Pinus sylvestris* L.), Norway spruce (*Picea abies* karst.) and deciduous species (mainly *Betula spp.*) (Table I). The mean annual precipitation (1989–1996) for each catchment was 628 mm (V-K), 613 mm (HJ), 497 mm (PJ), and 351 mm (VJ) (Kulmala *et al.*, 1998).

2.2. Sample collection and analysis

The sampling protocol for the LF subprogramme consists of 6 traps set out in a systematic 10 × 10 m grid in the middle of each plot. The funnel-shaped traps have a collecting surface area of 0.5 m^2 and stand c.1.5 m above the forest floor (Figure 2). A cotton bag, attached to the bottom of the funnel, retains the litter sample. The bag is replaced with a clean bag at the beginning of each month.

The sampling protocol for the TF subprogramme consists of bulk collectors placed systematically at 10 m intervals around the plot. Depending on plot size, there are 12 to 16 collectors per plot. Each throughfall collector consists of an acid-washed polyethylene funnel (collecting surface = 308 cm^2) with a 2 cm high rim which drains into a polyethylene bag (Figure 2). A mesh was fitted into the neck of the funnel to prevent any litter that was collected from entering into the throughfall sample. The TF samples are collected weekly. Any litterfall that had accumulated in the TF funnel during the weekly collection interval was removed.

In order to investigate the possible importance of leaching from the LF sample in the field, leachate from the LF (LFL) was collected weekly over a two month period (August–September) 1995. LFL was collected from the litterfall traps by placing the cotton bag inside a plastic bag supported by a plastic bucket (Figure 2). The amount of precipitation, throughfall and litterfall for these months are presented in Table I. August and September together accounted for about a fifth of the precipitation in 1995 at each catchment. Compared to average (1989–1996) values, August 1995 precipitation at HJ, PJ and VJ catchments was wetter and at V-K

TABLE I

Stand characteristics, and precipitation, throughfall and litterfall fluxes for August and September 1995 for each study stand. Values in parentheses are the percentages of the annual flux

Catchment	Stand	Stem volume %				Precipitation, mm		Throughfall, mm		Litterfall, g m^{-2}	
		m^3ha^{-1}	pine[a]	spruce[b]	deciduous[c]	August	September	August	September	August	September
Valkea-Kotinen	1	566	2	62	36	50 (8)	60 (9)	4 (10)	50 (11)	26 (7)	27 (8)
	2	568	0	80	20			37 (9)	48 (12)	20 (5)	36 (8)
Hietajärvi	1	189	83	0	18	94 (16)	61 (11)	77 (22)	45 (13)	35 (22)	42 (27)
	2	228	94	0	7			79 (17)	48 (11)	25 (19)	31 (23)
Pesosjärvi	1	164	39	43	18	64 (13)	43 (9)	61 (13)	44 (9)	10 (10)	22 (9)
	2	191	37	41	23			61 (13)	44 (9)	12 (21)	28 (21)
Vuoskojärvi	1	23	3	0	97	69 (16)	9 (2)	66 (16)	10 (2)	7 (8)	80 (93)
	2	61	99	0	2			65 (15)	9 (2)	10 (34)	4 (14)

[a] Scots pine (*Pinus sylvestris*)
[b] Norway spruce (*Picea abies*)
[c] deciduous species (mainly Birch, *Betula spp.* and Aspen, *Populus tremula*; but at Vuoskojärvi, Mountain birch, *B.pubescens ssp. tortuosa*)

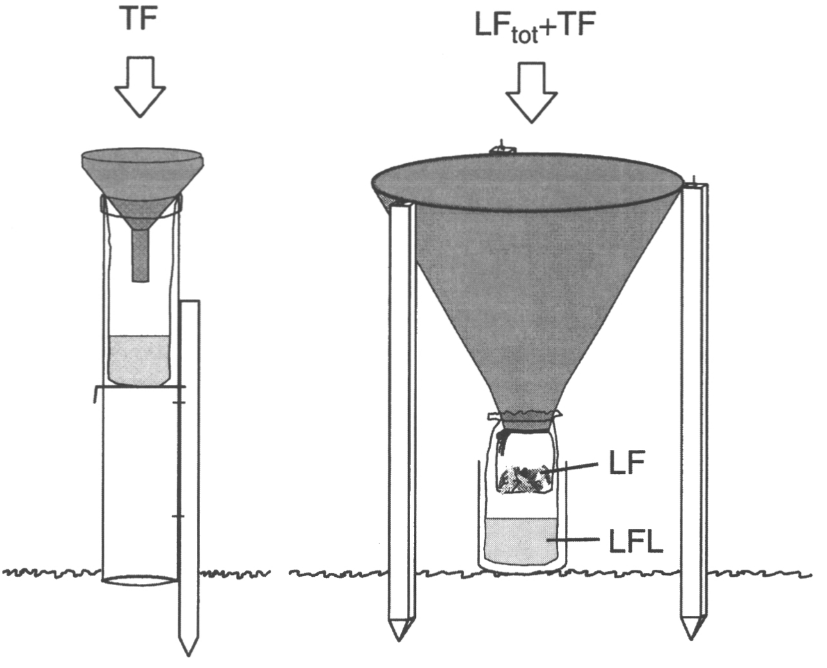

Figure 2. Design of the throughfall (TF, left) and litterfall (LF, right) collectors.

drier than average. September 1995 precipitation was similar to the average value at all catchments except VJ, which was particularly low in 1995. The amount of litterfall for August and September 1995 varied considerably among catchments, and also between months at VJ, reflecting differences in stand composition and season (Table I).

The TF and LFL samples were stored in dark and cool conditions (+ 4 °C) until they were analysed. To cut costs in recent years, the weekly throughfall samples have been combined (volume-weighted) into monthly samples by plot for analysis. This procedure was also followed in the case of the August–September 1995 samples. In the case of LFL, however, the weekly samples from each LF collector were analysed separately and the monthly mean volume-weighted concentration values calculated. Concentrations of K, Ca, Mg, Na, and S were determined with an ICP-AES analyser (ARL 3580). Total nitrogen concentrations were measured by flow-injection analysis and gas diffusion. The LF samples were dried at 40–60 °C for 24 h, weighed and then milled into a fine powder. For analysis, a subsample was digested in a mixture of nitric acid and hydrogen peroxide and concentrations of S, Ca, K, Mg and Na were determined using the same ICP-AES equipment. Total N was determined with a LECO CHN analyser.

2.3. Statistical Analyses

Since a fraction of the nutrients in LFL is derived from throughfall we have distinguished between gross litterfall leachate (LFL_{gross}) and net litterfall leachate (LFL_{net}). LFL_{gross} refers to the LFL collected in the field, which includes nutrients derived from both throughfall and the litterfall. LFL_{net} refers to the nutrients derived from the litterfall only (i.e., LFL_{gross}-TF). Total litterfall, LF_{tot}, is taken as the sum of LF and LFL_{net} and the total return of nutrients to the forest floor is given by the sum of TF and LF_{tot}.

Monthly nutrient fluxes were calculated as the product of the monthly TF or LFL concentration value and the monthly TF hydrological flux value. Because of the large volumes of water collected by the LF traps, the LFL collection bags overflowed on some occasions and the hydrological flux was therefore unreliable. Plotting LFL hydrological fluxes against TF hydrological fluxes for those weeks when the fluxes were greater than zero and the LFL fluxes reliable revealed a strong correlation ($r = 0.90$) and one that was close to a 1:1 relationship. We therefore consider the use of the TF hydrological flux to calculate the LFL nutrient fluxes to be justified.

For statistical analysis, the primary data consist of concentration and flux values for each of the two months and eight stands. Because of small sample sizes and non-normal distributions, non-parametric statistics were used. The Friedman statistic was used to test for pairwise differences between LFL_{gross} and TF concentrations and fluxes. We calculated Mann-Whitney and Kruskall-Wallis statistics to test for the significance of stand composition (Scots pine dominance *vs* mixed) and catchment latitude effects, respectively, on the LFL_{net} fluxes. All statistical analysis were performed using the SYSTAT® statistical package.

3. Results

3.1. Litterfall Leachate Quality and Fluxes

Nutrient concentrations in LFL_{gross} were generally greater than in TF (Table II). This indicates that nutrients were leached from the litterfall retained in the LF traps. Using the Friedman test, LFL_{gross} concentrations of all nutrients except nitrogen were shown to be significantly greater ($p < 0.05$) than TF concentrations for both months and stands within each catchment.

The monthly TF, LFL_{gross}, LFL_{net} and LF chemical fluxes (mg m^{-2}) for each stand are presented in Table III. The mean monthly LFL_{gross} flux for each nutrient was greater than the corresponding mean TF value, confirming that nutrients were leached from or washed off the litterfall collected in LF traps. The contribution of LFL_{net} to LF_{tot} for each nutrient, averaged across both months and all stands, was: 91% (Na), 51% (S), 49% (K), 13% (Mg), 11% (Ca) and 6% (N). However, the litterfall accumulating in the traps did take up nutrients from the percolating

TABLE II

Nutrient concentrations (mg l^{-1}) in throughfall (TF) and gross litterfall leachate (LFL_{gross})

Catchment	Stand	Month	Ca		Mg		K		Na		N		S	
			TF	LFL_{gross}	TF	LFL_{gross}	TF	LFL_{gross}	TF	LFL_{gross}	TF	LFL_{gross}	TF	LFL_{gross}
Valkea-	1	8	0.32	1.55	0.13	0.57	2.23	11.02	0.12	1.15	0.66	2.90	0.75	3.06
Kotinen	1	9	0.29	1.26	0.13	0.45	1.78	5.46	0.19	0.73	0.40	0.86	0.59	1.40
	2	8	0.68	1.78	0.18	0.59	3.03	9.98	0.18	0.99	1.07	2.55	1.17	3.17
	2	9	0.39	1.11	0.13	0.30	2.27	3.99	0.31	0.45	0.43	0.75	0.84	1.21
Hietajärvi	1	8	0.22	0.26	0.06	0.11	0.47	0.69	0.16	0.22	0.97	0.59	0.99	0.98
	1	9	0.25	0.54	0.05	0.20	0.83	1.10	0.28	0.30	0.44	0.36	0.62	0.79
	2	8	0.26	0.43	0.07	0.10	0.56	0.66	0.16	0.20	0.65	0.62	0.95	1.01
	2	9	0.22	0.40	0.05	0.13	0.94	0.75	0.25	0.28	0.32	0.40	0.55	0.64
Pesosjärvi	1	8	0.07	0.33	0.02	0.11	0.50	1.17	0.12	0.23	0.41	0.33	0.49	0.66
	1	9	0.13	0.78	0.06	0.32	1.01	1.57	0.17	0.76	0.14	0.48	0.36	0.91
	2	8	0.07	0.33	0.02	0.11	0.50	1.17	0.12	0.23	0.41	0.33	0.49	0.66
	2	9	0.13	0.78	0.06	0.32	1.01	1.57	0.17	0.76	0.14	0.48	0.36	0.91
Vuoskojärvi	1	8	0.10	0.30	0.05	0.12	0.47	0.65	0.18	0.46	0.45	0.42	0.48	0.52
	1	9	0.15	1.63	1.46	1.19	8.36	5.05	0.69	2.34	0.46	0.83	0.37	0.99
	2	8	1.46	0.28	0.12	0.11	0.64	0.47	1.00	0.57	0.51	0.40	0.71	0.51
	2	9	1.10	0.93	0.98	0.47	3.10	0.84	1.86	2.66	0.51	1.00	0.84	1.18
mean			0.37	0.79	0.22	0.32	1.73	2.88	0.37	0.77	0.50	0.83	0.66	1.16
sd			0.38	0.51	0.39	0.28	1.93	3.27	0.45	0.71	0.24	0.74	0.24	0.78
$X_r^{2,a}$				9.0		6.3		4.0		12.3		0.3		9.0
p[a]				0.003		0.012		0.046		< 0.001		0.617		0.003

[a] pairwise Friedman test statistic, H_0:LFL_{gross} = TF, H_1:$LFL_{gross} \neq$ TF

TABLE III

Throughfall (TF), gross litterfall leachate (LFL_{gross}), net litterfall leachate (LFL_{net}) and litterfall (LF) nutrient fluxes (mg m^{-2})

Catchment	Stand	Month	Ca				Mg			
			TF	LFL_{gross}	LFL_{net}	LF	TF	LFL_{gross}	LFL_{net}	LF
Valkea-	1	8	16	70	54	153	6	25	19	37
Kotinen	1	9	14	43	29	234	6	17	11	57
	2	8	25	68	43	123	7	22	15	20
	2	9	19	48	29	313	6	14	8	67
Hietajärvi	1	8	17	37	20	160	5	10	5	28
	1	9	12	21	9	229	3	7	4	42
	2	8	19	40	21	107	5	10	5	14
	2	9	11	8	–3	147	2	2	0	19
Pesosjärvi	1	8	4	45	41	43	1	17	16	6
	1	9	6	14	8	180	3	5	2	61
	2	8	4	41	37	59	1	18	17	13
	2	9	6	21	15	235	3	9	6	74
Vuosko-	1	8	7	23	16	30	3	9	6	9
järvi	1	9	15	23	8	646	15	18	3	270
	2	8	10	19	9	39	8	7	–1	7
	2	9	10	9	–1	20	9	4	–5	5
mean			12	33	21	170	5	12	7	46
sd			5.9	18.4	15.8	148.7	3.5	6.6	6.8	62.2
X_r^{2a}				9.0				6.3		
p^a				0.003				0.012		

[a] pairwise Friedman test statistic, H_0: LFL_{gross} = TF, H_1:$LFL_{gross} \neq$ TF.

throughfall during one or the other months, i.e. TF > LFL_{gross}, resulting in negative monthly LFL_{net} values (Table III). The LFL_{gross} flux values were significantly ($p < 0.05$) greater than the TF flux values for both months in the case of Na, S, Ca and Mg only. For N and K there was no statistically consistent difference between TF and LFL_{gross} flux values for both months. The litterfall in the traps was therefore sometimes a source and sometimes a sink for N and K.

3.2. Effect of Stand Composition and Latitude on Litterfall Leachate

The quality of litterfall is related to the species composition of the stand (e.g. Johansson, 1995), the amount of precipitation is related to latitude, and throughfall

TABLE III

Continued

Catchment	Stand	Month	K				Na			
			TF	LFL_{gross}	LFL_{net}	LF	TF	LFL_{gross}	LFL_{net}	LF
Valkea-	1	8	98	420	322	84	5	39	34	1.1
Kotinen	1	9	88	226	138	65	9	28	19	1.6
	2	8	113	316	203	52	7	31	24	0.5
	2	9	109	179	70	164	15	22	7	0.8
Hietajärvi	1	8	36	65	29	47	13	21	8	2.9
	1	9	38	24	–14	61	13	12	–1	2.3
	2	8	44	60	16	30	13	18	5	0.8
	2	9	45	11	–34	29	12	4	–8	0.8
Pesosjärvi	1	8	31	59	28	8	7	32	25	0.2
	1	9	44	68	24	52	7	16	9	0.3
	2	8	31	105	74	18	7	50	43	0.3
	2	9	44	144	100	89	7	18	11	0.8
Vuosko-	1	8	31	40	9	8	12	24	12	0.7
järvi	1	9	85	66	–19	245	7	14	7	3.6
	2	8	42	33	–9	5	65	32	–33	1.8
	2	9	27	8	–19	5	16	15	–1	1.7
mean			57	114	57	60	14	24	10	1.3
sd			29.4	113.7	92.3	62.2	13.7	11.1	17.0	0.96
X_r^{2a}				2.3				4.0		
p^a				0.134				0.046		

[a] pairwise Friedman test statistic, H_0: LFL_{gross} = TF, H_1:$LFL_{gross} \neq$ TF.

is related to both (e.g. Ukonmaanaho *et al.*, 1998). We therefore hypothesised that LFL_{net} would vary with stand composition and latitude.

To test for the influence of stand composition on the LFL_{net} fluxes, we classified the study stands as being either Scots pine-dominated (Scots pine accounting for > 80% stem volume) or mixed (Scots pine accounting for < 80% of stand volume) (Table I). The mixed stands therefore have a notable component of deciduous and/or Norway spruce. Using the Mann-Whitney test, a significant difference ($p < 0.051$) between the two stand composition types was found for each of the nutrients studied (Table IV). As previously shown (Table I, III), the Scots pine-dominated stands had smaller LFL_{net} fluxes than the mixed stands.

The effect of latitude on LFL_{net} fluxes was tested by looking at the differences between catchments using a Kruskal-Wallis test. For each nutrient, catchment had a significant ($p < 0.05$) effect on LFL_{net} (Table IV). LFL_{net} fluxes were generally

TABLE III

Continued

Catchment	Stand	Month	N				S			
			TF	LFL_{gross}	LFL_{net}	LF	TF	LFL_{gross}	LFL_{net}	LF
Valkea-	1	8	29	113	84	237	33	123	90	25
Kotinen	1	9	20	37	17	224	29	58	29	22
	2	8	40	95	55	212	44	102	58	24
	2	9	21	38	17	241	40	59	19	42
Hietajärvi	1	8	75	54	–21	129	77	94	17	17
	1	9	20	18	–2	155	28	35	7	19
	2	8	51	56	5	120	75	95	20	14
	2	9	15	6	–9	113	27	10	–17	14
Pesosjärvi	1	8	25	27	2	60	30	55	25	6
	1	9	6	11	5	109	16	23	7	13
	2	8	25	29	4	107	30	53	23	10
	2	9	6	13	7	178	16	32	16	18
Vuosko-	1	8	30	22	–8	66	32	41	9	5
järvi	1	9	4	8	4	597	4	5	1	49
	2	8	33	20	–13	48	46	38	–8	6
	2	9	5	6	1	20	7	8	1	2
mean			25	35	10	163	33	52	19	18
sd			18.1	30.4	25.2	130.3	19.7	34.4	24.6	12.4
X_r^{2a}				2.3				9.0		
p[a]				0.134				0.003		

[a] pairwise Friedman test statistic, H_0: LFL_{gross} = TF, H_1: $LFL_{gross} \neq$ TF.

greater in the southern catchments than in the northern catchments (Table III), and related to precipitation (Table I).

3.3. Comparison of Litterfall and Throughfall Nutrient Flux Pathways

The monthly litterfall and throughfall fluxes averaged across both months and eight stands are presented in Table V and the relative fluxes presented in Figure 3(a). Litterfall was the dominant pathway for Ca, Mg and N, accounting for about 80% of total return (LF_{tot} + TF). The LFL_{net} flux for these same nutrients accounted for 11%, 13% and 6%, respectively, of LF_{tot} (Figure 3(a)). Including the litterfall leachate flux with LF for these nutrients therefore had no effect on the relative importance of litterfall and throughfall as nutrient return pathways. Even though the leaching loss of nutrients from litterfall is not taken into account in forest

TABLE IV

Mann-Whitney test (U) to compare stand composition (Scots pine <80%> stand volume) and Kruskall-Wallis test (H) to compare latitude (catchment) effect on the net litterfall leachate (LFL_{net}) flux

	Ca	Mg	K	Na	N	S
Stand composition						
U	48.0	54.0	51.0	58.0	53.0	49.0
df	1	1	1	1	1	1
p	0.051	0.009	0.023	0.002	0.013	0.039
Latitude						
H	8.1	8.8	11.2	8.1	10.9	9.2
df	3	3	3	3	3	3
p	0.044	0.033	0.011	0.043	0.013	0.027

TABLE V

Mean monthly fluxes (mg m^{-2}) of litterfall (LF and LF_{tot}), litterfall leachate (LFL_{gross} and LFL_{net}) and throughfall (TF) for August-September (n = 16)

	Ca	Mg	K	Na	N	S
LF	170	46	60	1	163	18
LFL_{gross}	33	12	114	24	35	52
LFL_{net}	21	7	57	10	10	19
LF_{tot}	191	53	117	11	173	37
TF	12	5	57	14	25	33

LFL_{net}, = LFL_{gross}-TF, LF_{tot} = LF + LFL_{net}.

nutrient cycling studies, litterfall has been shown to be the dominant pathway for the return of these nutrients (Cole and Rapp, 1981).

For K, S and, in particular Na, the LFL_{net} flux was found to be an important fraction of the total litterfall flux, accounting for 49%, 51% and 91% of LF_{tot} for each nutrient, respectively (Figure 3(a)). Whether the LFL_{net} flux was included in the litterfall therefore determined whether litterfall or throughfall was the dominant pathway for the return of these nutrients. If LFL_{net} was not included in the litterfall flux, the litterfall pathway accounted for 51% (K), 35% (S) and 7% (Na) of the LF+TF return to the forest floor (Figure 3(b)). When LFL_{net} was included, the total litterfall flux accounted for 67% (K), 53% (S) and 44% (Na) of the total return

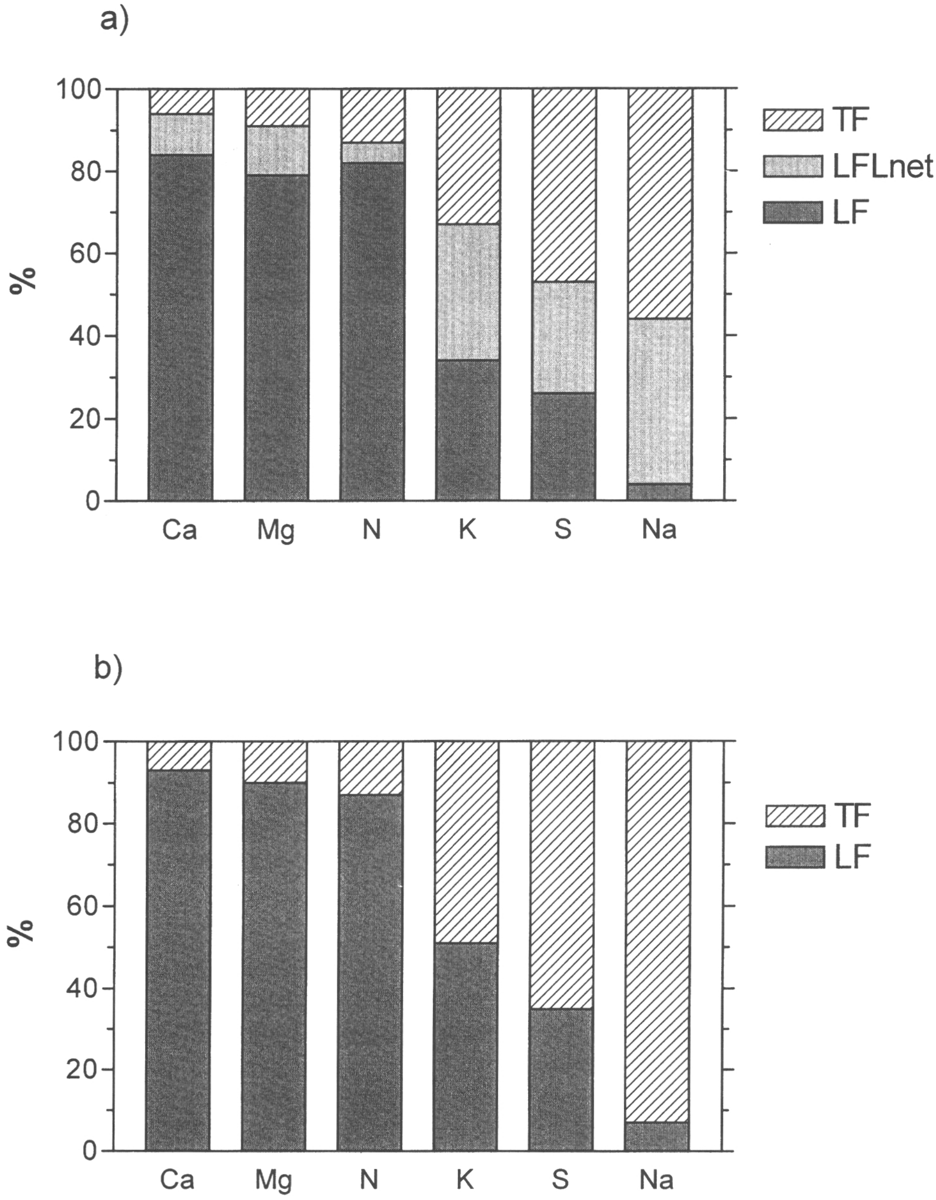

Figure 3. Relative amounts of nutrients in a) net litterfall leachate (LFL_{net}), litterfall (LF) and throughfall (TF) fluxes, and b) litterfall and throughfall.

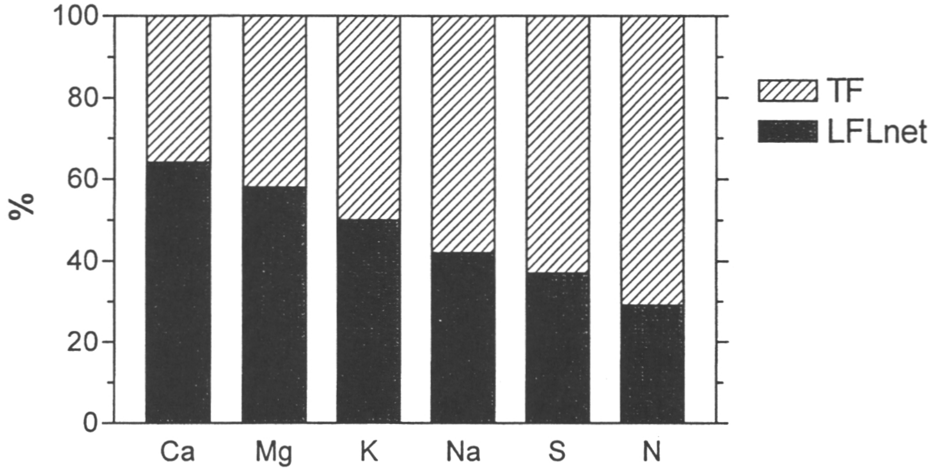

Figure 4. Relative amounts of nutrients in net litterfall leachate (LFL_{net}) and throughfall.

($LF+LFL_{net}$ + TF) to the forest floor. The results from many forest nutrient cycling studies have indicated that throughfall is the dominant return pathway for K, S and Na (Cole and Rapp, 1981). However, in these studies, the leaching of nutrients from the litterfall while in the traps has been ignored and the size of the litterfall flux therefore presumably underestimated.

The relative importance of the TF and LFL_{net} fluxes for each nutrient, i.e. the fluxes of nutrients that are in soluble form and readily available to the forest floor, are shown in Figure 4. In the case of Ca, Mg and K, it is seen that the LFL_{net} flux is as great or greater than the TF flux.

4. Discussion

In this study we investigated the importance of litterfall leachate, that is the loss of nutrients from the litterfall accumulating in litterfall traps, to the flux of nutrients to the forest floor via litterfall. The litterfall pathway with and without the litterfall leachate component was compared to the return of nutrients via throughfall.

In the case of K, S and Na, in particular, significant amounts were leached from the litterfall while in the traps (Table V and Figures 3(a)). The litterfall leachate contribution to total litterfall for Ca, Mg and N was < 14%. Potassium and Na are mobile elements, being easily leached from cells and washed off surfaces where they have accumulated as dry deposition. Sulphur is known to accumulate as dry deposition in forest canopies, particularly in coniferous forests (Miller and Miller, 1980; Cronan and Reiners, 1983). We have also observed a clear enrichment in throughfall sulphate concentrations compared to open bulk precipitation at the same study sites (Ukonmaanaho *et al.*, 1998). The washing off and dissolution of sulphur from the litter in the traps would explain the relatively high litterfall leachate sulphur fluxes we observed. Calcium and, to a lesser extent, also Mg in litter is less easily leached than Na and K because the former are components of cell walls. The release of these nutrients is therefore mainly dependent on the rate of decomposition of the litterfall fraction (Nordén, 1994). Therefore, litterfall for these nutrients continued to make up most of the total nutrient return to the forest floor (> 79%), even when the LFL_{net} component was excluded (Table III and Figure 3(a)).

Most N was returned to the forest floor as litterfall, as has generally been found in other litterfall studies (Cole and Rapp, 1981). We found that litterfall leaching accounted for only 5% of the total litterfall N flux, the remainder being in litterfall. In a study by Mahendrappa and Ogden (1973), the water-extractable fraction of total litterfall N for a black spruce stand (unfertilised, control plots) was 5%. Segal *et al.* (1990) reported higher annual litterfall leachate fluxes of inorganic N compared to throughfall for southern bottomland hardwood forests, but there was clear seasonal variability. Nitrogen retention and uptake by the canopy, resulting in negative net throughfall fluxes (throughfall minus open deposition), is typical for northern coniferous forests (e.g. Starr *et al.*, 1995; Dise *et al.*, 1998; Piirainen *et al.*, 1998). Similarily, we found that the litterfall that had accumulated in the litterfall traps took up N (and other nutrients) from the percolating throughfall in one or the other months in some stands. We consider this to be the result of uptake by microbes living in the litterfall accumulated in the traps (Segal, 1990; Lovett, 1992).

The nutrient contents of Scots pine needles are typically lower than those in Norway spruce needles and the leaves of deciduous trees (e.g. Johansson, 1995). Foliar nutrient contents also vary during the season due to nutrient uptake and internal retranslocation in preparation for over-wintering and prior to leaf fall in the autumn. The shedding of needles by coniferous trees also tends to peak in the autumn (Flower-Ellis, 1985; Helmisaari, 1992). Our study was carried out at a time (August–September) when retranslocation of nutrients from the foliage back into tree may have been active. This, together with monthly variability in precipitation, may also help explain the negative LFL_{net} values we observed. Nutrient contents in needles of differing age-classes also vary due to retranslocation (Helmisaari, 1992). For the same stands included in this study, we have shown that Scots pine needles contain less N and K than Norway spruce needles in the case of both current and one-year-old needles (Raitio *et al.*, 1995).

Nutrients returned to the forest floor in solution, i.e. throughfall and litterfall leachate, are immediately and directly available for uptake and recycling. In contrast, the availability of nutrients in litterfall is dependent on the rate of decomposition and mineralisation (Nordén, 1994). Our earlier studies revealed that the decomposition (weight loss) of cellulose strips placed on and in the forest floor of these study sites for one year ranged from 15% to 71%, and decreased with catchment latitude (Kurka and Starr, 1997). Compared to throughfall, the net litterfall leachate flux varied from 29% (N) to 64% (Ca) of the return of nutrients in solution (TF + LFL_{net}) and showed that litterfall leachate is an important nutrient pathway for Ca, Mg and K (Figure 4). In their black spruce study, Mahendrappa and Ogden (1973) found that the water-extractable fraction of N from litter was 13% of the throughfall N flux.

As hypothesized, significant differences in the LFL_{net} were found between stand composition types and latitude (Table IV). The LFL_{net} fluxes in the stands dominated by Scots pine were less than the fluxes from the mixed stands, at least for the months of August and September (Table III). The influence of stand composition reflects the effects of differing litter quality and abilities of canopies to interact with deposition, as discussed above, as well as species-related differences in the ease with which nutrients are leached from needles and leaves (Nykvist, 1963; Tukey, 1970). The effect of latitude is mainly the result of differences in amounts of precipitation, which in Finland decreases from south to north (Kulmala *et al.*, 1998).

5. Conclusions

When comparing litterfall and throughfall as nutrient return pathways, we found that litterfall was the dominant pathway for Ca, Mg and N, at least for the two months studied (August and September). This was the case whether the LFL_{net} flux was included in the litterfall flux or not. For K, S and Na, throughfall was the dominant pathway if only the litterfall flux was considered, as is the case in most nutrient cycling studies. However, if the litterfall leachate component was included, litterfall became at least as important as the throughfall nutrient return pathway. The leaching loss of nutrients from the litterfall accumulating in litterfall traps is not usually determined in nutrient cycling studies. Our results indicate that litterfall return of nutrients to the forest floor may thus be underestimated. Conversely, our results imply that throughfall fluxes in many nutrient cycling studies might be overestimated as a result of leaching from litterfall accumulating in the throughfall traps. This effect can be reduced by increasing the frequency of sample collection and removal of any accumulating litterfall. However, the net effect on the total return of nutrients to the forest floor (i.e., TF + LF) can be expected to be zero as the overestimation in the TF flux would be compensated by the underestimation of the LF flux. Nevertheless, when comparing the fluxes of these two pathways, the effect of litterfall leaching may be an important factor to consider.

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Paper IV

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IV

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Heavy metal budgets for two headwater forested catchments in background areas of Finland

L. Ukonmaanaho [a,*], M. Starr [a], J. Mannio [b], T. Ruoho-Airola [c]

[a]Finnish Forest Research Institute, Vantaa Research Centre, PO Box 18, FIN-01301 Vantaa, Finland
[b]Finnish Environment Institute, PO Box 140, FIN-00251 Helsinki, Finland
[c]Finnish Meteorological Institute, PO Box 503, FIN-00101 Helsinki, Finland

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"Capsule": *Plot (stand) and catchment mass balance budgets for heavy metals are provided for background sites in the boreal zone.*

Abstract

Mean annual (1994–1996) budgets for Cd, Cu, Ni, Pb and Zn at two background, forested catchments, VK and HJ, in Finland are presented. Budgets for plots (VK3, HJ1 and HJ4) included throughfall (TF), litterfall (LF) and soil leaching fluxes, and for catchments terrestrial retention and leaching and lake sedimentation fluxes. Total deposition (TD) loads were relatively low (Cd < 0.1, Cu < 2, Ni < 1, Pb < 3 and Zn < 5 mg m^{-2} $year^{-1}$) and that even in these areas almost half of the TD was in the form of dry deposition. Retention of TD within catchments was ⩾77% for all metals, except for Ni at VK (54%). For Cu and Pb, the retention was 94–97%. Most of the retention (74–97%) took place in the terrestrial part of the catchment, lake sedimentation accounting for the remainder. Plot-scale soil leaching fluxes at 40 cm of Cd, Cu (VK3) and Ni (VK3) were greater (⩾100%) than TD inputs. Most of the catchment retention must therefore have taken place either deeper in the soil or in the lowland peatland areas. The humus layer was particularly effective in retaining Cu and Cd (65–81% and 51–78% of total inputs to the forest floor (TF + LF)). The retention of Pb by the humus layer was less than expected (26–54% of TF + LF). Litterfall was a particularly important internal flux for Zn.

Keywords: Deposition; Fluxes; Input–output budgets; Litterfall; Sedimentation; Soil leaching

1. Introduction

While there is relatively much information available about the concentrations and fluxes of heavy metals in temperate forest ecosystems (see review by Bergkvist et al., 1989), there is less information about boreal coniferous ecosystems, particularly in background areas of heavy metal pollution.

It is known that the atmospheric deposition of heavy metals in polluted regions is dominated by dry deposition (Bergkvist et al., 1989; Lindberg et al., 1989; Fergusson, 1990). Coniferous forests are effective in trapping heavy metal aerosols because of the high adsorption surface area their canopies present for interception (Lindberg and Turner, 1988). Deposition loads of heavy metals to forested areas based on wet-only or bulk collectors placed in an open area therefore underestimate the total deposition load to the forest.

The humus layer of coniferous forest soils has often been found to be effective in retaining heavy metals, particularly Pb and Cu (Tyler, 1978; Bergkvist, 1987; Bergkvist et al., 1989; Derome and Nieminen, 1998). Zn, being less strongly adsorbed by organic matter and a plant nutrient subject to uptake and cycling, tends to show a weak depth-gradient in the soil and correlation with deposition (Andersson et al., 1991). Heavy metals are often associated with accessory minerals in acidic igneous rocks (Koljonen, 1992), which dominate in the boreal zone. The weathering of such minerals, perhaps induced by acidic deposition, would result in increased soil exchange and soil water concentrations of heavy metals. Cadmium although showing a strong atmospheric origin, like Pb, is more mobile because it is not so strongly adsorbed by organic matter. For those heavy metals that are essential nutrients (e.g. Cu and Zn), the

* Corresponding author. Fax: +358-9-85705-569.
E-mail address: liisa.ukonmaanaho@metla.fi (L. Ukonmaanaho).

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depletion of exchangeable stores in the soil induced by acidification may lead to reduced plant growth and microbial decomposition (Tyler, 1981; Bergkvist, 1986; Tyler et al., 1989).

Heavy metal concentrations in boreal lake water and sediments have been shown to be correlated with heavy metal and acidic deposition loads, lake water acidity and dissolved organic matter concentrations (Verta et al., 1990; Mannio et al., 1993, 1995).

Input–output (or mass balance) budgets are a useful means of describing the mobility, retention and flows of substances, including heavy metals, in the environment (e.g. Turner et al., 1985; Schut et al., 1986; Bergkvist, 1987; White and Driscoll, 1987; Dillon et al., 1988; Lindberg and Turner, 1988; Johnson and Van Hook, 1989; Aastrup et al., 1995, 1997). Most heavy metal input–output budgets have been calculated for whole catchments, which integrate the effects of the terrestrial and aquatic parts of the catchment. Budgets at the scale of the forest stand and soil, which may show a differing pattern of mobility and retention from that at the catchment-scale, are fewer.

In a recent paper we described the concentrations of heavy metals in the entire aquatic pathway (precipitation, throughfall, stemflow, soil water, ground water, lake and stream runoff) of four, forested headwater catchments in relatively remote background locations in Finland (Ukonmaanaho et al., 1998). The concentrations in a range of biotic media (mosses, humus layer, litterfall, needles, wood ants and vole livers) were also described. In this paper we describe the atmospheric inputs (bulk deposition from a forest opening and estimated total) and stream runoff (catchment) and soil leaching (plot) outputs for five heavy metals (Cd, Cu, Ni, Pb and Zn) at two of these catchments. In addition, we describe the internal sinks and sources associated with terrestrial area and lake of the catchments and with the canopy, humus layer, soil, litterfall and internal cycling of the forest stands. The aim was to give a comprehensive and integrated account of the biogeochemistry of the heavy metals, including the fate of atmospheric inputs, for such background sites in the boreal zone.

2. Material and methods

2.1. Site description

The study was carried out at the Valkea-Kotinen (VK) and Hietajärvi (HJ) catchments (Fig. 1). Both catchments are included in the network of UN-ECE International Cooperative Programme of Integrated Monitoring (IM) sites and have been monitored continuously since the end of the 1980s (Bergström et al., 1995; Bergström, 1998 and papers in same volume). Both are headwater catchments and, typical of northern glaciated landscapes, contain areas of forested upland, peatland, seepage lakes and ponds, and a discharge lake (Table 1). The catchment to lake (discharge) area ratio is 8.0 for Valkea-Kotinen and 5.6 for Hietajärvi (Lake Iso-Hietajärvi).

The catchments are situated in extensive forested regions in which there is no agriculture or sources of heavy metal emissions nearby. The wind mostly comes from the south (Sarkkula, 1995) bringing long-range transported air pollution from central Europe and countries bordering the southern coast of the Baltic Sea.

The forest at Valkea-Kotinen consists mainly of mixed stands of Norway spruce and deciduous species (birch and aspen) while the forest at Hietajärvi consists of Scots pine stands. Permanent plots (VK3, HJ1 and HJ4) for intensive monitoring have been established in stands representative of the most common forest types in each catchment. Some characteristics of the stands and soils at the plots for which the plot-scale budgets have been calculated are presented in Table 2.

The sampling and chemical analyses follow guidelines given in the IM Manual (IM Manual, 1998). Procedures are briefly described below; for further details see Bergström et al. (1995) and Ukonmaanaho et al. (1998).

2.2. Sampling and chemical analyses

2.2.1. Bulk deposition, throughfall, and litterfall

Bulk (i.e. wet + gravitational dry) deposition (BD) was collected monthly in an open area within each catchment using two NILU-type collectors (EMEP, 1991). Each collector has a collection area of 314 cm^2 and stood approximately 2 m above ground level.

Throughfall (TF) and litterfall (LF) were collected at the permanent plots. Throughfall was collected weekly during the snow-free period (May–November; 12–16 collectors per plot) and monthly during wintertime (6–8 collectors per plot). The collection area of each TF collector used during the snow-free period (funnels with a 2 cm high rim) was 308 cm^2 and stood c. 1.5 m above ground level. During winter, buckets with a collection area of 491 cm^2 were used. Acid-washed polyethylene plastic was used in the construction of all deposition collectors.

Litterfall was collected monthly during the snow-free period and once at the end of the winter using six traps per plot. The funnel-shaped traps were made of plastic coated Terylene fabric having a collection area of 0.5 m^2 and stood c. 1.5 m above ground level. The litterfall was collected into a replaceable cotton bag attached to the bottom of the LF trap.

2.2.2. Soil water and stream runoff

Soil water (SW) was collected during the snow-free period using suction cup and zero-tension lysimeters.

The suction lysimeters were installed at depths of 15 cm and 35 cm below the mineral soil surface (i.e. below the zone of maximum eluviation-illuviation and rooting). Three lysimeters were installed at each depth in each plot. The samples were drawn with vacuum of c. 60 kPa and collected into acid-washed glass bottles placed in a covered bucket dug into the soil to keep the samples cool and in the dark. The zero-tension lysimeters (three per plot) were installed underneath the humus layer (mor) at Hietajärvi only. Each had a collection area of 308 cm^2 and constructed of acid-washed polyethylene plastic. The sampling interval for both types of lysimeter was weekly, but depending on soil moisture conditions and functioning of the lysimeters, samples were not always available. Runoff water (RW) was sampled fortnightly or monthly from the outlet stream of the lake. Runoff was recorded at a gauging station fitted with a V-notch weir and a continuous water-stage recorder.

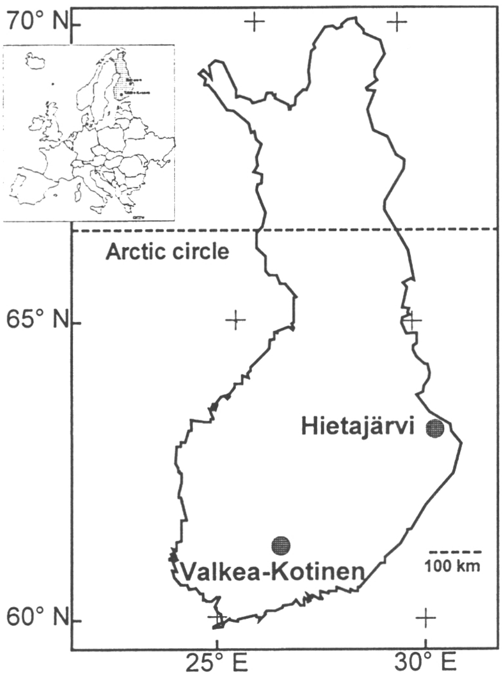

Fig. 1. Map showing location of the study catchments in Finland.

2.2.3. *Humus layer and soil*

Four replicate humus layer (Of + Oh) and soil (0–5, 5–20, 20–40 cm) samples were taken from each of the permanent plots. Each replicate was a composite of subsamples; one subsample from each 10×10 m subplot within each plot. The humus layer samples were taken volumetrically using a stainless steel cylinder (dia. 52 mm) and recording the thickness so that pools could be calculated. The mineral soil layers were sampled with a stainless steel auger. In addition, volumetric samples of each mineral soil layer were taken from a soil pit excavated at the side of the plot. These samples were used to determine the bulk density of the <2 mm (fine earth) fraction of the soil. The volume of stones in the soil was determined using Viro's rod penetration method (Tamminen and Starr, 1994). The pool of heavy metals in the fine earth fraction of each layer were calculated using heavy metal concentrations in the fine earth fraction, the bulk density of the fine earth fraction and the volume of stones in the bulk soil (m^3/m^3).

Table 1
General description and characteristics of the Valkea-Kotinen and Hietajärvi catchments

	Valkea-Kotinen	Hietajärvi
Latitude and longitude	61°14′ N, 25°04′ E	63°10′ N, 30°43′ E
Elevation (of lake), m a.s.l.	156	165
Relative relief (m)	40	49
Phytogeographic zone	Southern Boreal	Middle Boreal
Area (ha)	30	464
Forest covered (ha)	24	280
Main species	Picea abies	Pinus sylvestris
Age, years	155–190	100–230
Peatland (forested and open; ha)	7	165
Lake area (ha)	4	83
Runoff water chemistry, (pH)	4.5	6.2
TOC (mg l^{-1})	17	4.5
Alkalinity (μmol l^{-1})	−40	75
Mean annual temperature (°C)	3.1	2.0
Mean annual precipitation (mm)	618	592
Vegetation period (>5°C; days)	112	102
Bedrock geology	Mica gneiss	Porphyritic granodiorites
Surface deposit thickness (m)	0–3	0–15
Soil types	Histosols, Podzols with transitions to Cambisols	Histosols, Podzols and Leptosols

Table 2
General description and characteristics of the plots[a]

	VK3	HJ1	HJ4
Plot size (ha)	0.12	0.16	0.16
Stem volume (m^3ha^{-1})	566	189	228
Pine (%)	2	83	94
Spruce (%)	62	0	0
Deciduous (%)	36	18	7
Annual litterfall[b] ($g\ m^{-2}$)	306	141	117
Site type[c]	OMT	EVT	EVT
Soil type (FAO)	Dystric Cambisol	Haplic Podzol	Haplic Podzol
Parent material	Glacial (till)	Glaciofluvial (sorted)	Glaciofluvial (sorted)
Thickness of humus layer (Of+Oh; mm)	34	63	37
Soil pH_{H_2O}	4.1, 4.3, 4.6[d]	3.5, 4.4, 5.3, 5.7[e]	3.6, 4.5, 5.1, 5.5[e]
Soil Organic C (%)	39.0, 4.4, 3.0[d]	49.1, 1.8, 0.9, 0.3[e]	48.5, 0.8, 0.6, 0.2[e]
Annual soil water flux[b] (mm)			
Humus	241	303	308
Humus + 0–20 cm	245	281	286
Humus + 20–40 cm	200	269	282

[a] VK3, Valkea-Kotinen, plot 3; HJ1, Hietajärvi, plot 1; HJ4, Hietajärvi plot 4.
[b] mean, 1994–1996.
[c] OMT, Oxalis-Myrtillus type; EVT, Empetrum- Vaccinium type. See Cajander (1949) for description of site types.
[d] Humus, 0–5, 5–20 cm.
[e] Humus, 0–5, 5–20, 20–40 cm.

2.2.4. Chemical analyses

The Finnish Forest Research Institute (Metla) was responsible for the collection and analysis of the TF, SW, LF, humus layer and soil samples, the Finnish Meteorological Institute (FMI) for the BD samples, and the Finnish Environment Institute (FEI) for the RW samples. Heavy metal concentrations in the TF, SW and LF samples were determined using inductively coupled plasma emission spectrometry (ICP-AES) and in the BD and RW samples using inductively coupled plasma mass spectrometry (ICP-MS). The water samples were acidified with concentrated nitric acid (suprapure quality, 1:200 v/v) before analysis to promote desorption of metals from the walls of the sample storage bottles. The TF samples were filtered before analysis; otherwise the analyses were performed on unfiltered standing samples. The LF samples were air-dried, milled and wet digested (mixture of concentrated HNO_3 acid and H_2O_2). Humus layer and mineral soil samples were dry-ashed and the ash digested in concentrated HCl acid. Concentrations of heavy metals in the digest were determined using ICP-AES.

All the analyses have been performed in laboratories that have continuous quality control programmes and which regularly participate in national and international intercalibration exercises. Mean relative differences from test samples of 3% for Pb, 3% for Cd, 4% for Cu, 3% for Zn and 7% for Ni have been reported for Metla's laboratory and corresponding values of 4, 11, 6, 5, and 16%, respectively, for FMI's laboratory.

When BD, RW and LF samples had concentrations less than the detection limit, we substituted a value equal to half the detection limit. This is in accordance with the UN-ECE Integrated Monitoring Manual protocol (IM Manual, 1998). However, for SW and TF a substitution value of zero has been used. This was because we considered using a substitution value of half detection with the relatively high detection limits of the equipment used would have resulted in too high mean concentration values, especially in the case Cd and Ni.

2.3. Calculation and interpretation of fluxes

Mean annual fluxes for the period 1994–1996 were calculated. The total atmospheric inputs were estimates of total (wet+dry) deposition (TD). For the non-forested area, including the area of sparsely forested peatland and surface waters, TD corresponds to BD. For the forested area, the additional dry deposition intercepted by the canopy has to be taken into account (Hultberg, 1985; Lindberg et al., 1989). We have used a procedure described by Bredemeier (1988). Accordingly, TD is taken as the sum of BD and canopy interception (dry) deposition (ID). The ID values where calculated as the product of the ID/BD ratio for Na and the BD value of the heavy metal in question. The ID value for Na was calculated as the difference between TF[1] and BD values. For the forested area of the catchment, TD was calculated as the product of plot TD values

[1] In principle TF should be total throughfall, i.e. include stemflow. However, our earlier studies have shown that stemflow contributes less than 0.5 % of total throughfall (Starr, 1995). We have therefore ignored stemflow in this study.

(average of all plots in each catchment at which TF has been monitored, see Bergström et al., 1995) and the area of catchment covered by forest. Estimates of TD for the plot-scale budgets were made using the TF data from that particular plot. Total deposition for the non-forested area of the catchment was calculated as the product of BD values and the area of non-forested land in the catchment. Monthly values were summed to give annual values and the mean annual values calculated.

Catchment output values (stream discharge fluxes) were calculated from RW concentrations, catchment runoff (l s^{-1} km^{-2}) and catchment area. These values were summed for the year and a mean annual value calculated. Output values for the plot-scale budgets were the fluxes from the soil at 40 cm depth. Annual leaching fluxes were calculated as the product of measured annual mean SW concentration values (calculated from monthly volume-weighted concentrations at 35 cm depth) and modelled annual soil water flux values at 40 cm depth. Monthly soil water fluxes were modelled using a water balance model, WATBAL (Starr, 1999), and summed to give annual values. Leaching fluxes from the humus layer (Hietajärvi only) and at 20 cm depth (both catchments) were also calculated. The fluxes from the humus layer at Hietajärvi were calculated from concentrations in the zero-tension lysimeters and WATBAL hydrologic fluxes. The fluxes at 20 cm depth were calculated using the suction cup lysimeter data for 15 cm depth and WATBAL hydrologic fluxes at 20 cm depth.

Positive atmospheric input–output budgets (i.e. TD inputs > outputs) indicate retention of the atmospheric inputs within one or more of the pools (canopy, humus layer, soil, lake sediments) within the system. Balanced budgets (i.e. TD inputs = outputs) indicate that there is no net retention of inputs and that the system is in steady-state. Negative budgets (i.e. TD inputs < outputs) indicate that there is not only no retention of the atmospheric inputs but also that there is a release (depletion) from one or more of the pools within the system. Plot-scale budgets are presented for only one plot at Valkea-Kotinen because it was only at VK3 that both litterfall and soil water were collected.

Differences between TD and TF describe the interaction of atmospheric inputs with the canopy. When TF < TD retention of atmospheric inputs by the canopy is indicated, when TF > TD then foliar leaching (FL) is indicated (i.e. excretion from foliage, which is ultimately from the soil). The sum of FL and LF describes the amount of internal recycling between the soil and stand.

Total inputs to the forest floor were calculated as the sum of throughfall and litterfall fluxes (i.e. TF + LF). These inputs include the external atmospheric inputs as well as the internal flux associated with recycling (uptake from the soil, transfer to the needles, and foliar leaching) of heavy metals to the soil. Litterfall heavy metal fluxes were calculated from heavy metal concentrations and amounts of litterfall (mg m^{-2}). Although LF includes adsorbed atmospheric inputs it is usually considered to reflect an internal flux associated with uptake from the soil and recycling.

3. Results

3.1. *Catchment-scale budgets*

The catchment-scale atmospheric input–output budgets are presented in Table 3. The budgets indicate that much of the atmospheric inputs of the heavy metals were retained within the catchments. The relative amount of retention ((TD−RW)/TD) was 77% or more, except for Ni at Valkea-Kotinen where retention was only 54%. For Pb and Cu, the retention was more than 94%. However, with simple input–output budgets, it is not possible to specifically identify where in the catchment the retention is taking place — in the terrestrial part (forest or soil) or in the lake.

To estimate the relative importance of the terrestrial and lake components in the overall catchment retention we first calculated the amount of heavy metals lost to sedimentation in the lake bottom. This was done by multiplying annual sedimentation rates for each heavy metal by the sedimentation area of the lake. We used sedimentation rates reported for the end of the 1980s by Verta et al. (1989) for lake Valkea-Kotinen and by Simola (1988) and Simola et al. (1991) for lake Iso-Hietajärvi. The sedimentation areas, 0.7 ha for lake Valkea-Kotinen and 46 ha for lake Iso Hietajärvi, correspond to the area > 3 m deep. Estimates of the retention in the terrestrial part of the catchment were calculated as the difference between total catchment retention (as given by the atmospheric TD input–output budgets) and the loss to lake sediments as described above. The amounts of each heavy metal retained by the lake and in the terrestrial environment together with the amount transported from the terrestrial area to the lake (calculated as sedimentation plus catchment runoff losses minus deposition to lake) are included in Table 3.

3.2. *Plot-scale budgets*

All the appropriate fluxes describing the atmospheric inputs, internal transfers and leaching outputs from the plots are presented in Fig. 2a–c. Comparison of atmospheric inputs (TD) with leaching outputs (SW 40 cm depth) show that Cd has a negative budget at all three plots, with leaching fluxes being two to threefold TD fluxes. Cu and Pb budgets were positive at HJ1 and HJ4 but negative at VK3, while Zn budgets were negative at HJ1 and HJ4 but positive at VK3. The Ni budget for the VK3 plot was negative, slightly negative for HJ4

Table 3
Mean annual (1994–1996) input–output budgets, retention of atmospheric inputs and transfer of heavy metals in Valkea-Kotinen and Hietajärvi catchments

	Cd	Cu	Ni	Pb	Zn
Valkea-Kotinen					
Bulk deposition (mg m^{-2} year^{-1})	0.02	0.59	0.19	0.95	2.23
Total deposition (input; mg m^{-2} year^{-1})	0.04	1.06	0.35	1.74	4.12
Runoff water (output; mg m^{-2} year^{-1})	0.01	0.05	0.16	0.11	0.96
Output/input (%)	18	5	46	6	23
Retention (input–output) mg m^{-2} year^{-1})	0.03	1.01	0.19	1.63	3.16
Relative retention (input–output; %)	83	95	54	94	77
Deposition to terrestrial area (g year^{-1})	12	296	99	486	1156
Deposition to lake (g year^{-1})	1	22	7	36	84
Terrestrial retention (g year^{-1})	10	292	51	453	923
Lake retention (g year^{-1})	1	9	7	35	28
Terrestrial transfer to lake (g year^{-1})	2	3	48	33	233
Hietajärvi					
Bulk deposition (mg m^{-2})	0.02	0.55	0.17	0.80	1.82
Total deposition (input; mg m^{-2})	0.04	1.04	0.33	1.50	3.45
Runoff water (output; mg m^{-2})	0.01	0.06	0.05	0.05	0.45
Output/input (%)	20	6	16	3	13
Retention (input–output; mg m^{-2} year^{-1})	0.03	0.98	0.28	1.45	3.00
Relative retention (input–output/input; %)	80	94	84	97	87
Deposition to terrestrial area (g year^{-1})	162	4355	1370	6306	14480
Deposition to lake (g year^{-1})	17	458	144	661	1510
Terrestrial retention (g year^{-1})	n.a.[a]	4254	1085	5011	12101
Lake retention (g year^{-1})	n.a.	276	184	1748	1794
Terrestrial transfer to lake (g year^{-1})	n.a.	101	285	1295	2379

[a] n.a., not available.

and positive for HJ1. However, comparison of the leaching fluxes at 40 cm depth with total inputs to the forest floor (TF + LF) indicate that, with exception of Ni at VK3, there was considerable retention in the soil (10–95%). Comparison of the retention values with calculated internal cycling fluxes (FL + LF) indicate that the retention was in the form of uptake and recycling in the case of Ni (HJ1 and HJ4), Cd and Cu. Assuming uptake of Pb does not take place, the retention of Pb took the form of accumulation in the soil. Throughfall fluxes of Cd and Cu were clearly greater than TD fluxes at all three plots, indicating that foliar leaching of these metals is general. The LF flux of Zn indicates that litterfall is the major pathway by which Zn is recycled.

4. Discussion

4.1. Deposition

Our estimated annual total deposition loads of Cd, Cu, Ni, Pb, Zn to forest stands were similar to those reported for Sweden (Bergkvist et al., 1989) but considerably smaller than those reported for Central Europe (Berg et al., 1996) and eastern USA (Lindberg and Turner, 1988; Lindberg et al., 1989). Although the TD and BD loads of Cd, Cu and Ni were similar at all three stands that of Pb and Zn were somewhat higher in the more southerly catchment, Valkea-Kotinen. This reflects a general pattern of decreasing heavy metal deposition with increasing latitude observed in Finland (Lippo et al., 1995), which is related to similar trends in both the amount of precipitation and heavy metal concentrations (Ukonmaanaho et al., 1998).

The relatively large differences between TD and BD fluxes we observed at both catchments indicated that, even in such unpolluted areas, dry deposition formed almost half of the total deposition of heavy metals. The relative importance of dry deposition, however, was somewhat higher than reported for deciduous forests in the eastern USA (Lindberg et al., 1989) and for Norway spruce stands in Sweden (Bergkvist et al. 1989).

It is difficult to quantify the amount of additional dry deposition intercepted by tree canopies (Lindberg and Turner, 1988; Lövblad and Westling, 1989). The accuracy of the interception ratio method we used in estimating the total deposition of heavy metals is unknown. The method assumes that Na shows no interaction (removal or release) from the canopy and that the interception ratio of Na is similar to that of the heavy metals. The former assumption is generally accepted but we have no proof of the latter assumption. However, the size of particles involved in the dry deposition of heavy metals at our sites can be expected to be relatively small because

(a)

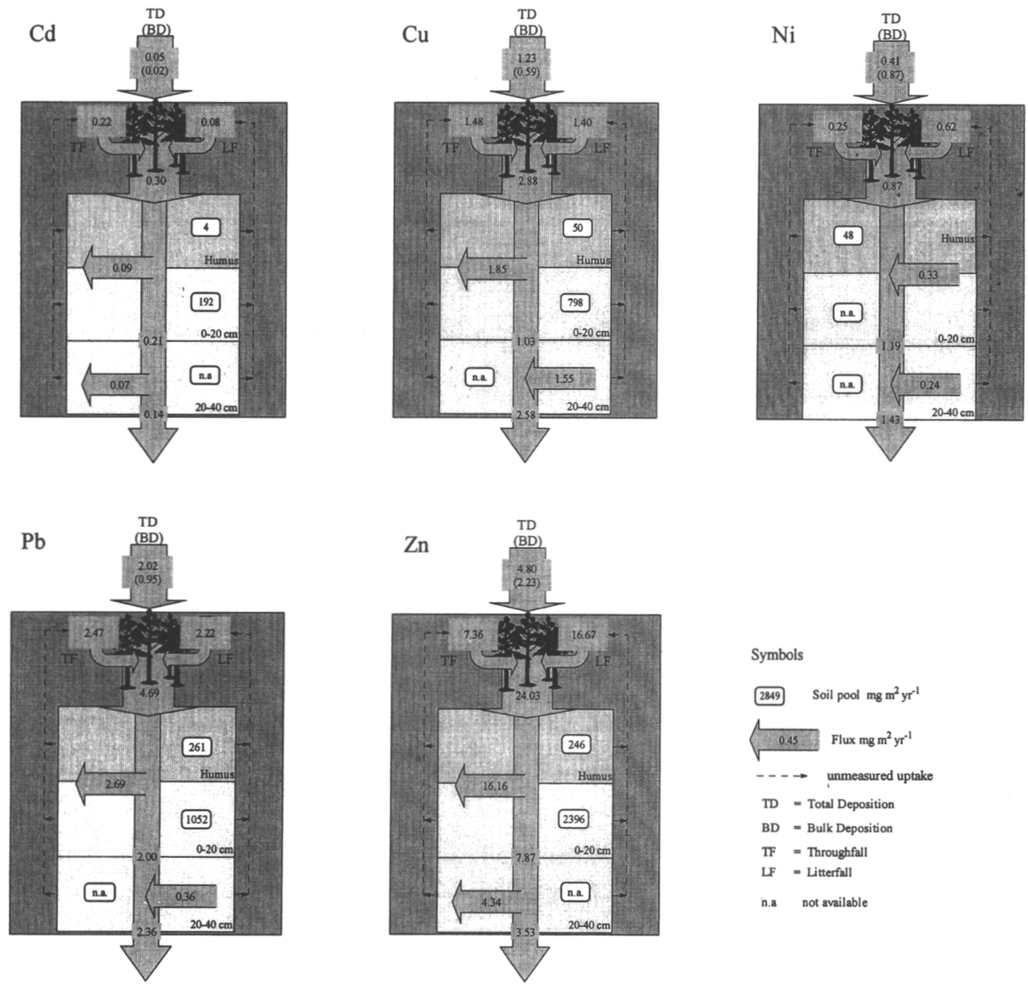

Fig. 2. (a) Plot (stand)-scale heavy metal mean annual (1994–1996) fluxes and input–output budgets for Valkea-Kotinen, plot 3 (b) Plot (stand)-scale heavy metal mean annual (1994–1996) fluxes and input-output budgets for Hietajärvi, plot ~~1~~ 4 (c) Plot (stand)-scale heavy metal mean annual (1994–1996) fluxes and input-output budgets for Hietajärvi, plot ~~1~~. 1

of the long-range transport involved. Furthermore, the particle size of the intercepted dry deposition is known to be smaller than that of the dry deposition in bulk deposition, which is collected by sedimentation (Lindberg et al., 1989). We therefore feel our estimates of heavy metal total deposition are reasonable.

4.2. Catchment-scale budgets

4.2.1. Atmospheric total inputs versus runoff outputs

Simple catchment input–output budgets showed that most of the atmospheric inputs of the five heavy metals studied were retained somewhere within the catchment (Table 3). Retention was the highest for Cu and Pb (>94%) and the lowest for Ni (54% at Valkea-Kotinen). Cd retention was about 80% at both catchments. Our catchment retention values tended to be higher than those reported by Schut et al. (1986) and Aastrup et al. (1995, 1997). However, these studies did not include dry deposition, which, as we have shown, forms a significant component of total deposition — even in remote sites. The study by Lindberg and Turner (1988) included dry deposition and our retention values were similar to theirs.

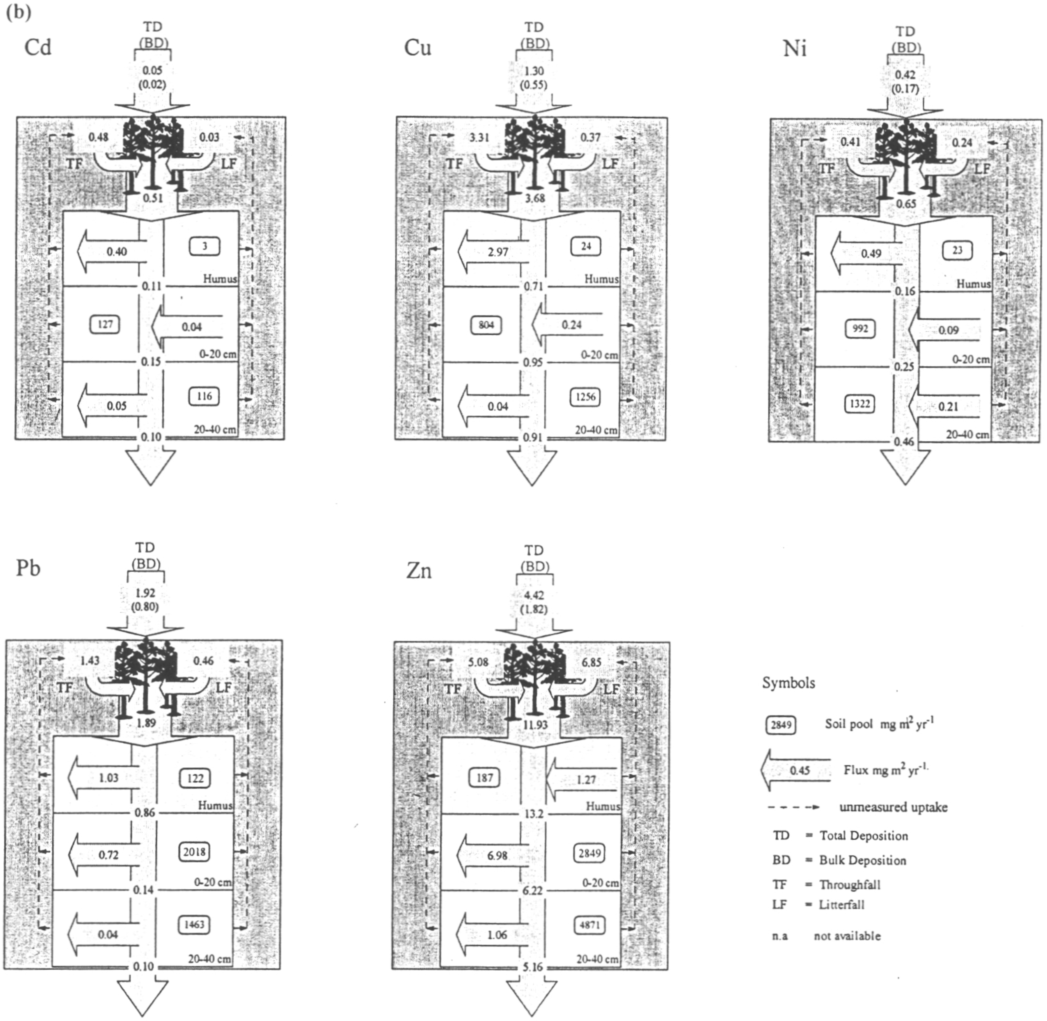

Fig. 2. (*continued*).

4.2.2. *Terrestrial versus lake sediment retention*

Most of the retention shown at the catchment-scale was associated with the terrestrial part of the catchment (Table 3). Nearly all the retention of Cu took place in the terrestrial area (97% VK and 94% HJ). Of the atmospheric input of Cu to the terrestrial area, $<2\%$ was transferred to the discharge lake in both catchments. The terrestrial retention of Pb accounted for a lower fraction of the total catchment retention than expected (93% at VK and 74% at HJ). Of the atmospheric load of Pb received by the terrestrial area, 7% at VK and 21% at HJ was transported to the lake. Retention in the terrestrial area includes adsorption in the canopy and soil and uptake and accumulation in biomass. As the stands at VK and HJ are old growth, the net increment growth can be considered low to zero (Starr et al., 1998). Retention of heavy metals in the biomass increment is therefore considered negligible.

Organic soils are known to be important in the retention of heavy metals (Schut et al., 1986; Urban et al., 1987; LaZerte et al., 1989; Shotyk et al., 1997). Assuming that the upland forested area of the catchments behaves as indicated by the plot-scale budgets (see later), most of the retention of heavy metals in the terrestrial part of the catchment must occur deeper than 40 cm in the upland soil (higher pH and reduced solubility) and/or in the organic soils (adsorption) located in the lowland zone. The drift deposits are relatively shallow,

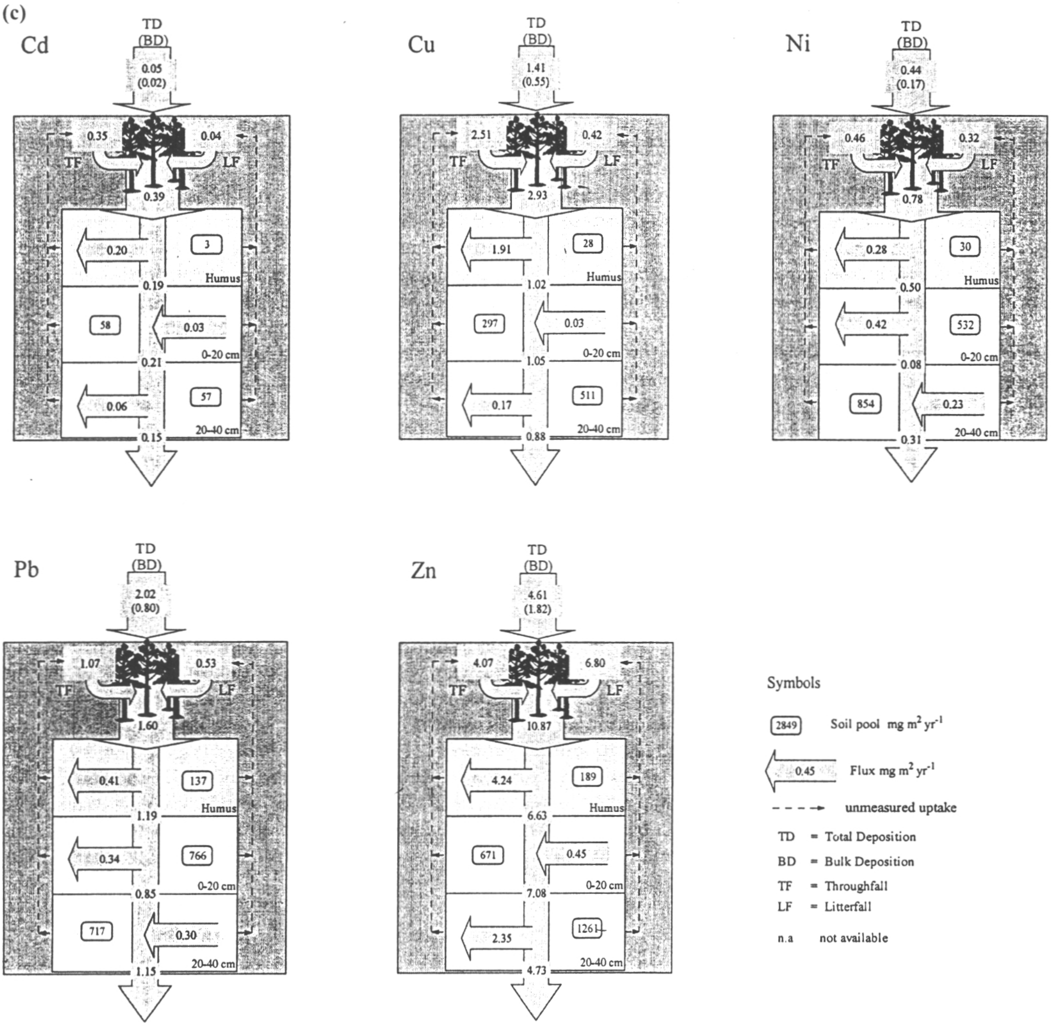

Fig. 2. (*continued*).

particularly at Valkea-Kotinen, and there is a considerable amount of Histosols and histic soils in both catchments. Given that terrestrial runoff would have to pass through these organic soils before reaching the lake, this is probably the site for much of the terrestrial retention observed.

Sedimentation of organo-metal complexes is the main process by which heavy metals are retained within lakes (Dillon et al., 1988; LaZerte et al., 1989; Verta et al., 1989). This process takes place in the deeper parts of the lake and occurs through the settling of suspended particles and the coagulation and flocculation of soluble organic complexes in response to decreases in pH. The relative importance of terrestrial and atmospheric loading to lakes is related to the proportion of land and water in the catchment. Of the total loading of heavy metals to Lake Valkea-Kotinen and Lake Iso-Hietajärvi, approximately two-thirds or more of Cd, Ni, Pb and Zn was accounted for by terrestrial outputs, the remaining being direct atmospheric deposition inputs. For Cu, terrestrial loading accounted for only 13 and 18% of the total loading to the lakes at VK and HJ, respectively. Schut et al. (1986) reported that a fifth of the total loading of Cu and Pb to two, relatively remote, Canadian lakes was from the terrestrial part of the catchment. Dillon et al. (1988) reported similar terrestrial output proportions of Ni and Zn to five polluted Canadian lakes to those we found at Valkea-Kotinen and Hietajärvi. They also found a high proportion of terrestrial Cu, up to 83% of total loading. The lakes in both Canadian studies had similar catchment to lake area ratios as Valkea-Kotinen and Hietajärvi, but the area of peatland was apparently small (although not reported). Furthermore, exposed bedrock accounted for most of the terrestrial area of the catchments in the study by Dillon et al. (1988), and the high proportion of terrestrial inputs probably reflect the surface runoff of high atmospheric inputs. The high proportion of terrestrial inputs to lakes compared to direct atmospheric inputs in our study reflects the low levels of air pollution in our study areas. Runoff outputs at both catchments probably approximate terrestrial weathering fluxes.

Except for Pb at Hietajärvi, there was relatively less retention of heavy metal inputs to the lake (atmospheric plus transfer from the terrestrial area of catchment) compared to the retention of atmospheric inputs to the terrestrial area at both catchments. Once in the lake, a higher proportion of the heavy metal inputs were lost to sediments in lake Iso-Hietajärvi compared with lake Valkea-Kotinen. The differences in the amount of sedimentation between the two lakes are presumably related to differences in their lake water chemistries (Table 1).

4.3. *Plot-scale budgets*

The role of the soil in controlling the retention or mobility of heavy metals in the upland areas of the catchment is indicated by the plot-scale budgets (Fig. 2a–c). Depending on the detail of such budgets, the importance of various processes in the canopy (foliar leaching, surface adsorption, wash-off, litterfall) and in the soil (root uptake and nutrient cycling, decomposition, weathering, soil adsorption/desorption and leaching) can be indicated.

4.3.1. *Atmospheric total inputs versus leaching outputs*

The difference between total deposition (TD) and the soil leaching fluxes from 40 cm depth indicate the amount of retention of atmospheric (external) inputs by the canopy (adsorption), vegetation (uptake and recycling) and soil. While these budgets were similar for the two plots at Hietajärvi they were different from the budgets at the Valkea-Kotinen plot. Retention of atmospheric inputs was only shown for Cu and Pb at both HJ1 and HJ4 plots, Ni at HJ1 and Zn at Valkea-Kotinen, otherwise the leaching fluxes were greater than the atmospheric inputs. Cd had a negative budget at all three plots, with leaching fluxes at 40 cm depth being one to two times greater than total deposition inputs. The interaction with the canopy and soil are discussed later.

4.3.2. *Total inputs to forest floor (TF+LF)*

Throughfall, litterfall and soil water fluxes from the humus layer (HJ1 and HJ4 plots only), 20 cm and 40 cm depths describe the fate and internal transfers of the heavy metals. The sum of throughfall and litterfall (TF+LF) constitutes the total inputs to the forest floor and includes both external (atmospheric) and internal (uptake from soil and recycling) sources. Compared to leaching flux at 40 cm depth our results showed that there was mainly retention of the heavy metals. Comparison of the amount of retention to the calculated internal recycling fluxes (i.e. FL+LF) indicated that most of the retention was accounted for by uptake and recycling rather than accumulation in the soil. Only in the case of Ni at the Valkea-Kotinen plot was the leaching loss at 40 cm greater than the total input flux to the forest floor. At both Hietajärvi plots more than half of the total inputs of Cd, Cu and Zn had been retained compared to the leaching fluxes at 40 cm depth. The retention Cd and Cu was proportionally less and that of Zn greater at the Valkea-Kotinen plot compared to the Hietajärvi plots.

The humus layer in coniferous forest ecosystems has often been found to be an effective sink for heavy metals, particularly Pb and Cu (Tyler, 1978; Turner et al., 1985; Bergkvist, 1987; Bergkvist et al., 1989; Derome and Nieminen, 1998). At Hietajärvi, where leaching fluxes from the humus layer have been measured, a major fraction of the total inputs to the forest floor of Cu was retained in the humus layer (HJ1 65%, HJ4 81%). Copper is known to readily form stable complexes with organic matter (Baker and Senft, 1995). It is unknown if the source of Cu in the soil 20–40 cm layer at Valkea-Kotinen, which results in there being a greater leaching flux at 40 cm depth than atmospheric inputs, was due to the mobilisation of adsorbed Cu or to weathering.

The retention of Pb by the humus layer, however, was less than expected. Only some 26% (HJ1) and 54% (HJ4) of the total input of Pb to the forest floor was retained by the humus layer. The lower degree of retention at HJ1 is difficult to explain. The humus layer was thicker at HJ1 (Table 2) and was therefore expected to have a higher retention capacity than HJ4. At 20 cm depth, 47% of the total input of Pb had been retained at HJ1, 93% at HJ4 and 57% at the Valkea-Kotinen plot. This indicates that the upper mineral soil is also important in the retention of Pb. Interestingly, Bergkvist (1987) found the upper B-horizon of Podzols in southern Sweden to be the main sink for Pb in the soil rather than the humus layer.

While there was retention of Zn in the humus layer at plot HJ1 (39%) the leaching flux from the humus layer at HJ4 was greater than the total input of Zn to the forest floor (11%). The additional Zn leaching from the humus layer at HJ4 was presumably supplied through the decomposition of organic matter, although no significant difference in the decomposition of cellulose strips on and in the humus layer between these two plots has been detected (Kurka and Starr, 1997; Kurka et al., 2000). Nevertheless, there was overall retention of Zn when comparing total inputs with leaching losses at 40 cm depth at all three plots (85% VK3, 56% HJ1 and 57% HJ4). Given that the litterfall flux of Zn was greater than the throughfall fluxes at all three plots, the retention was probably due to uptake and recycling.

The humus layer apparently retained over 50% of the total inputs of Cd to the forest floor at both Hietajärvi plots. Compared to other heavy metals, Cd is held less strongly in the soil by cation exchange and therefore relatively easily taken up by tree roots (Bergkvist et al., 1989) or lost to leaching (Andersson, 1977; Borg and Johansson, 1989). The retention of Ni by the humus layer was 75% at HJ4 and 36% at HJ1. Nickel is a micro-nutrient and therefore subject to uptake and recycling, and this was indicated by its internal recycling flux (FL + LF) at all three plots. There appeared to be a considerable release of Ni from the mineral soil, particularly at the Valkea-Kotinen plot. This might be related to the lower soil acidity at the Valkea-Kotinen plot compared with the Hietajärvi plots (Table 2) resulting in the mobilisation of soil Ni.

Compared with Cu, Zn and Ni, which are micronutrients and therefore taken up from the mineral soil and recycled as evidenced by the internal cycling fluxes (FL + LF), the pools of Pb and Cd in the humus layer can be considered to be largely anthropogenic and atmospheric in origin. We calculated the residence time of the pools of Pb and Cd in the humus layer at the Hietajärvi plots assuming that there would be no further atmospheric inputs and leaching fluxes would continue at current levels. The internal cycling of Cu, Ni and Zn would tend to maintain the humus layer pools longer than indicated by simply dividing the pool by the leaching flux. On this basis the pool of Pb would be depleted in about 129 years and that of Cd in about 22 years. Tyler (1978) calculated the time necessary for a 10% decrease in humus layer concentrations at unpolluted Swedish sites of 6 years for Cd and 70–90 years for Pb assuming a throughfall pH of 4.2.

4.3.3. *Foliar leaching versus litterfall*

At all three plots, but especially HJ1 and HJ4, TF fluxes of Cu were greater than TD fluxes, indicating foliar leaching. The results for Cd also indicate substantial foliar leaching and that throughfall is more important than litterfall in the return of Cd to the forest floor. Throughfall accounted for most of the total inputs of Cu to the forest floor (TF + LF) at Hietajärvi (86 and 90%) but only 51% at Valkea-Kotinen. This would indicate that Cu is more easily mobilised from Scots pine canopies than from mixed Norway spruce–deciduous canopies.

It is generally considered that the internal cycling of Pb in forest ecosystems is small or negligible (Lindberg and Harriss, 1981; Bergkvist et al., 1989). Assuming that foliar leaching of Pb is zero in our stands, TF theoretically should not be greater than TD. However, our results show that TF was greater (22%) than TD at the Valkea-Kotinen plot. This discrepancy between the measurements and the theory may be due to the presence of spruce in the stand and their high number of needle age classes (up to 8 years). It may be possible that Pb adsorbed onto the older needles during previous years, when Pb deposition was higher (Ukonmaanaho et al., 1998), may be enriching the current TF flux. This might also partly explain the higher LF flux of Pb at the Valkea-Kotinen plot, which was about fourfold that at the Hietajärvi plots.

The foliar leaching of Zn at HJ4 and VK3 and the relatively large LF flux of Zn, particularly at the VK3 plot, indicate substantial internal cycling of Zn. The LF flux of Zn at the Valkea-Kotinen plot is relatively large compared to the other Zn fluxes. The foliage of deciduous trees, birch in particular, has considerably higher concentrations of Zn compared to coniferous trees (Berthelsen et al., 1995). The high proportion of birch in the stand at the Valkea-Kotinen plot may therefore partly explain the high Zn LF flux observed. The litterfall mass was also 2-3 times greater at the VK3 plot than at HJ1 and HJ4 plots.

Throughfall fluxes of Ni at both Hietajärvi plots were similar to TD inputs, indicating Ni has little interaction with the canopy of Scots pine trees. At Valkea-Kotinen TF fluxes of Ni were clearly less than TD fluxes, indicating canopy retention and the possible role of Norway spruce or deciduous trees in this retention. Nickel enrichment of throughfall has been reported for Swedish spruce forests (Bergkvist, 1987) and Finnish Scots pine stands receiving Ni pollution from a nearby smelter (Derome and Nieminen, 1998; Nieminen et al., 1999).

5. Conclusions

The main conclusions from our study are summarized as follows:

1. Total deposition and bulk deposition fluxes of Cd, Cu, Ni, Pb and Zn were low in comparison to those reported for temperate forest ecosystems.
2. Estimates of total deposition indicated that dry deposition forms a major part of total deposition, even in remote, boreal, forested areas.
3. Runoff outputs of all five metals were less than atmospheric total inputs. The catchment retention of Cu and Pb was >90%. At least three quarters of the retention took place in the terrestrial part of the catchment, probably in the lowland organic soils, the remaining taking place through sedimentation in the lake.

4. Two thirds of the inputs of Cd, Ni, Pb and Zn to the discharge lakes was from the terrestrial part of the catchment, the remaining being directly from the atmosphere. For Cu, terrestrial outputs accounted for less than one quarter of total input to the lakes.
5. At the plot-scale, soil leaching fluxes at 40 cm depth of Cd, Cu (VK3) and Ni (VK3) were clearly greater ($\geqslant 100\%$) than total atmospheric inputs. Thus the terrestrial retention observed at the catchment-scale must have taken place either deeper in the upland soil or in the lowland peatland areas.
6. At the plot-scale, soil leaching fluxes at 40 cm depth of Pb were less than atmospheric total deposition inputs at two of the plots (43 and 95%) while approximately in balance at the third.
7. Total inputs (TF + LF) of heavy metals to the forest floor, which includes external, atmospheric and internal recycling components, compared to leaching losses (40 cm) showed retention in the soil (except Ni at one plot). Most of this retention appeared to be through uptake and recycling rather than accumulation in the soil.
8. The humus layer was important in the retention of atmospheric inputs of Cd, Cu and Ni, which were subsequently taken up and recycled. Atmospheric Pb inputs accumulated in the humus layer, but the retention was less than expected. The results concerning the retention of Zn by the humus layer were ambiguous.
9. Foliar leaching (TF−TD when TF > TD) was important in the recycling of Cd and Cu while litterfall (LF) accounted for most of the recycling flux of Zn to the forest floor. Lead adsorbed onto older Norway spruce needles enriched throughfall (TF) litterfall (LF) fluxes.

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Paper V

Ukonmaanaho, L. & Starr, M. Major nutrients and acidity: trends and budgets over nine year period in four remote boreal stands in Finland (manuscript).

V

Major nutrients and acidity: trends and budgets over nine year period in four remote boreal stands at Finland

Ukonmaanaho, Liisa & Starr, Michael
Finnish Forest Research Institute, Vantaa Research Centre, Jokiniemenkuja 1,
Box 18, FIN-01301 Vantaa

Abstract

Major nutrients and acidity was studied at four Integrated Monitoring catchments in Finland. Studied sites were located in along south-north deposition gradient. The quality and quantity of throughfall, and soil water, bulk precipitation and litterfall was calculated during 1989–1997. The results showed significant decline in SO_4 and H^+ concentrations. Mass balance budget showed that total deposition (input) was greater than outputs (soil water in depth of 40 cm) for NO_3, NH_4, H and S, indicating nutrient retention to the soil. On the contrary for Ca, Mg, K, Na at all plots and S at plots VK3 and VJ2 inputs were less than outputs indicating nutrient leaching. Internal mass balance budget showed that, humus layer is important in the retention of total inputs (TF+LF) for Ca, Mg and N. Sulphur retained in lower soil layers, indicating adsorption in the B horizon. Internal cycling indicated that most retention was accounted for by uptake and recycling than accumulating for soil.

1. Introduction

The deposition of air pollutants has been recognized as an important input to forest ecosystems, even in remote area, where most pollutants are transported over long distances. Forest vegetation is an effective receptor of airborne material delivered in both wet and dry forms because of the reactivity and large surface area of the canopy (e.g. Parker 1983, Ulrich 1983, Bredemeier 1988, Lindberg et al. 1989). Scavenging of these materials is largely a physical process that is influenced by wind speed and turbulence, particle size or droplet size and canopy surface characteristics related to tree size, density and species composition (e.g. Päivänen 1966, Cronan and Reiners 1983, Mahendrappa 1983, Lovett and Lindberg 1984). The forest floor, which includes the organic layer, is also effective in retaining deposition inputs. The soil solution may also reflect the atmospheric inputs but their influence becomes diluted by various processes in the soil including weathering, ion-exchange, adsorption/desorption, decomposition and immobilisation.

Acidic deposition is related to the amounts of acidifying substances, primarily S and N, and neutralizing substances base cations (Ca, Mg, K) and Na (Ulrich 1983). Sulphur, N and base cations are also essential plant nutrients. The growth and productivity of boreal forest ecosystem is limited by the availability of N (Mälkönen 1990). Changes in acidity (H^+), sulphur, nitrogen, hydrogen and base cation deposition can have a strong influence to organisms and processes in forest ecosystem. Acidic deposition may damage needles and leaves and lead to the loss of base cations from the foliage, the humus layer and rooting zone of plants (e.g. Lindberg and Lovett 1992, Lumme et al. 1995), resulting in possible nutrient deficiency for plants, soil acidification and generation of toxic concentrations of aluminum and heavy metals in soil solution. Excess nitrogen deposition may change the nutrient balance and regulation processes in coniferous trees and forest soil and lead to soil acidification (Grennfelt and Hultberg 1986, Aber et al. 1989). Sustained high inputs of N may saturate previously nitrogen limited ecosystems and lead to N leaching (Ågren and Bosatta 1988, Aber et al. 1989). The deposition of base cations decreases the acidifying effect of S and N deposition on forest soil by supplementing buffering reactions (Nissinen and Ilvesniemi 1990, de Vries et al. 1995). The beneficial effect of reducing the deposition of S and N would therefore be less if the deposition of base cations were also reduced (Hedin et al. 1994).

Emissions of SO_2 have decreased dramatically since 1970's. Finland's SO_2 emissions have decreased from some 600,000 t yr^{-1} to 99,000 t yr^{-1} in 1997 (EMEP 2000), most coming from energy production and industry. In contrast, emissions of NO_x and the deposition of N to European forests having actually increased (Dise and Wright 1995). Finnish emissions of NO_x were about 260,000 t yr^{-1} in 1997, nearly half coming from traffic. The figure for NH_3 emissions is 38,000 t^{-1} yr^{-1}, mostly coming from agriculture activities. Emissions of alkaline substances, primarily base cations, are mostly due to soil dust, energy production, industry, traffic and from seawater. Of the anthropogenic sources, combustion of wood and dust raised by traffic are the biggest single sources in Finland (Anttila 1990).

Deposition loads in Finland, especially in the northern parts of the country, are low (Hjellbrekke et al. 1997, Kulmala et al. 1998). Sulphate deposition in south Finland is 3.0–5.0 SO_4 kg S ha^{-1} yr^{-1} and in north Finland 0.5–1.0 SO_4 kg S ha^{-1} yr^{-1} (Kulmala et al 1998). The mean deposition of inorganic nitrogen (NO_3+NH_4) in open area in southernmost Finland during 1988–1996 was about 6.0 kg N ha^{-1} yr^{-1} (Kulmala et al 1998). A third of total N deposition in Finland has been shown to be organic N and other two thirds being nitrate and ammonium nitrogen in equal proportions (Järvinen and Vänni 1990). Calcium is the dominant cation in deposition, varying between 0.11–2.5 kg ha^{-1} yr^{-1} (Kulmala et al. 1998).

In this paper we present concentrations and fluxes of SO_4^{2-}, Ca^{2+}, Mg^{2+}, K^+, Na^+, NH_4^+, NO_3^-, total-N, H^+ and S in bulk precipitation, throughfall and soil water collected over a nine year period (1989–1997) in four sites in Finland. The input-output budget also include litterfall inputs. Such budgets are useful in studying the fate of atmospheric inputs and biogeochemical cycles of nutrients in forest ecosystem (e.g. Forsius et al. 1995, Evans et al. 1997, Ukonmaanaho et al. 2001). Furthermore, they can serve as an early warning system for the identification of ecological effects of anthropogenically-derived pollutants and for the verification (or otherwise) of emission reduction policies (Forsius et al. 1995).

2. Material and Methods

2.1. Description of sites

Permanent monitoring plots have been established in four Integrated Monitoring catchments (Bergström et al. 1995). Three of the catchments, Valkea-Kotinen (VK), Hietajärvi (HJ) and Pesosjärvi (PJ), are located in the boreal coniferous forest zone. The fourth catchment, Vuoskojärvi (VJ), is located in the northernmost part of Finland, in the subarctic zone (Fig. 1). Located in remote, protected conservation areas, the catchments have natural or semi-natural late succession communities (old growth forests).

Long-range transported air pollution from Central and Eastern Europe and from the St. Petersburg area and Baltic states are deposited in Finland (Jalkanen 2000). In north Finland emissions from the metal smelting industry on the Kola Peninsula are important (Jaffe et al. 1995).

The permanent plots varied in size from 25x25 m to 40x40 m and plots are situated on flat to nearly flat sites representative of the dominant forest types in each catchment. They are homogenous as possible regarding soil morphology, ground vegetation and tree stand characteristics. The forest types varied from submesic heaths to subartic lichen woodlands and the soils were podzols (or podzolic) with a mor surface organic layer developed on glacial or glaci-fluvial drift deposits (Table 1).

2.2. Sampling

Bulk precipitation (BP) has been collected in an opening in each catchment by the Finnish Meteorological Institute (Kulmala et al. 1998, Leinonen 2000). The term bulk precipitation (BP) is used to refer to solute concentrations in the precipitation collected in the open area, and the term bulk deposition (BD) is used to refer to the flux of solutes associated with the bulk precipitation.

Throughfall (TF) was collected with 12–16 polyethylene funnel-type collectors (collecting area = 308 cm^2) per plot (Table 1). The collectors were placed systematically at 10 m interval around plot. Samples were collected weekly during summertime and monthly during winter (winter collecting since 1995). During winter there were 6–8 snow collectors (collecting area = 1018 cm^2). Regular frosts precipitation fell as snow usually from November to April. Soil water (SW) was sampled with suction

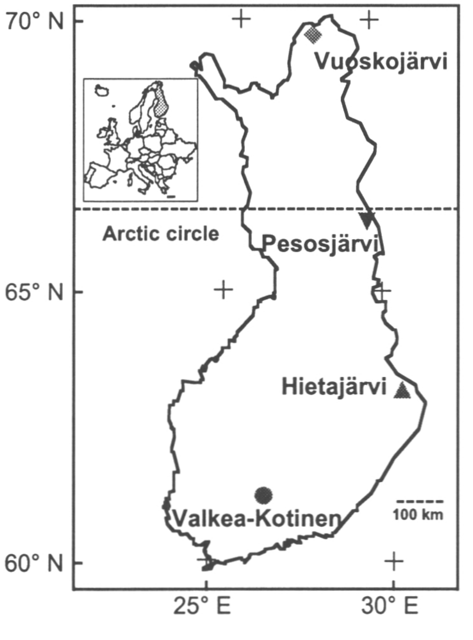


Fig. 1. Map showing location of the study catchments in Finland.

Table 1. Soil and stand and characteristics and annual mean precipitation (BP) (1989-97), throughfall (TF), soil water (SW) fluxes at various depths and mean annual litterfall (LF) (1990-97) for each studied plot.

Catchment	Plot	Soil	Stem	volume %			LF	BP	TF	SW#		
			m^3ha^{-1}	pine*	spruce†	deciduous‡	$g\ m^{-2}$	mm	mm	humus mm	20cm mm	40cm mm
Valkea-Kotinen	3	mor humus, podzolic cambisols	566	2	62	36	281	619	507	246	225	212
Hietajärvi	1	mor humus, haplic podzol	189	83	0	18	148	610	506	276	267	254
	4	-	228	94	0	7	115	610	548	280	254	260
Pesosjärvi	2	mor humus, haplic podzol	164	39	43	18	92	492	487	201	199	199
Vuoskojärvi	2	mor humus, haplic podzol	23	3	0	97	77	344	334	178	172	171
	3	-	61	99	0	2	52	344	326	178	172	170

* Scots pine (*Pinus sylvestris*)
† Norway spruce (*Picea abies*)
‡ deciduous species (mainly Birch, *Betula spp.* and Aspen, *Populus tremula*; but Vuoskojärvi, Mountain birch, *B. pubescens spp. tortuosa*)
# WATBAL modelled values (Starr 1999)

cup lysimeters (vacuum of ca. 60 kPa used) installed at depths of 15 cm and 35 cm below the mineral soil surface (i.e. below the zones of maximum illuviation and rooting respectively). In addition zero-tension lysimeters, consisting of a funnel (collecting area = 308 cm^2) fitted to a 2 L plastic bottle, were installed underneath the humus layer at Hietajärvi. Depth nests of the lysimeters were installed at three positions along one side of the plot. Samples were collected weekly during the snow-free period (usually May-October). Litterfall was collected using 6 funnel-shaped litterfall traps (collecting area = 0.5 m^2) placed in a systematic 10x10m grid in the middle of the each plot. Litterfall (LF) was collected monthly during the frost and snow free-period and once during at the end of winter.

2.3. Chemical analyses

The chemical analyses of bulk precipitation has been described by Leinonen 2000. Throughfall and soil water samples were stored in dark and cool (+4 °C) conditions until analysis began. Before analyses TF samples were filtered through using a Schleicher & Schuell 589^2 filter paper. Concentrations of NO_3^- and SO_4^+ were determined using high-pressure ion chromatography, NH_4^+ and total N by FIA, and H^+ concentrations were calculated from pH measurements made potentiometrically using a combined electrode. The litterfall samples were dried at 40–60 °C for 24 h, weighed and then milled into a fine powder. Concentration of total N was determined with a LECO CHN analyser. Concentrations of Ca, Mg, K, Na and total S in the TF, SW and LF samples were determined using inductively coupled plasma emission spectrometry (ICP-AES). Before ICP-analyses, the TF and SW samples were first acidified with concentrated nitric acid (supraquality, 1:200 v/v) to promote desorption of metals from the walls of the sample storage bottles. Subsamples of LF were wet digested in a mixture of HNO_3 acid and H_2O_2. Details of the analytical methods and procedures have been documented by Jarva and Tervahauta (1993) and Ukonmaanaho (1996).

2.4. Data handling and statistical analysis

Throughfall, soil water and litterfall concentration values were screened for gross outliers and any errors corrected. Remaining gross outliers were rejected or given regression estimates based on the relationships with other determinants if possible. Furthermore TF PO_4 concentrations > 1 mg l^{-1} were rejected onto grounds of that were contaminated with bird droppings (Novo et al. 1992).

Monthly TF fluxes (mg m^{-2}) were calculated by multiplying monthly volume weighted concentrations (mg l^{-1}) by the hydrological flux (mm). For years 1989–1994, missing TF winter values were substituted with BD values. Soil water fluxes were calculated by multiplying volume weighted SW concentrations by water balance modelled, hydrological fluxes (Starr 1999). Litterfall fluxes were calculated by multiplying elemental concentrations by litterfall mass fluxes.

Linear trends over nine years were analysed using all the monthly concentrations values available and the Seasonal-Kendall trend analysis procedure to calculate an estimate of the true slope of the linear trend (Hirsch et al. 1982, Gilbert 1987). This test may be used even though there are seasonal cycles and missing values. The data with missing value was tested using Seasonal-Kendall trend analyse in our earlier paper (Ukonmaanaho et al. 1998), conclusion was that data with some missing values is valid. The Friedman statistic was used to test for pairwise differences between plots in TF and SW concentrations. Non-parametric statistics were used because of non-normal distributions.

Total deposition was estimated using BD and TF sulphate measurements (Kubiznakova 1999). Sulphate shows little interaction with canopies and the ratio of TF to BD sulphate fluxes reflects the amount of dry deposition captured by the canopy (Bredemeier 1988, Lindberg et al. 1986). The enrichment factor for sulphate (EF) is used to multiply the bulk deposition (BD) of other substances to estimate total deposition (TD).

$$EF = TF_{SO4} / BD_{SO4} \qquad (1)$$

$$TD_x = EF * BD_x \qquad (2)$$

Input-output mass balance budgets were calculated using TD as inputs and leaching losses from 40 cm depths as outputs.

The difference between TD and TF reflects the interaction of atmospheric inputs with the canopy. When TF < TD flux, retention of atmospheric inputs by the canopy is indicated, conversely when TF > TD foliar leaching (FL) is indicated (i.e. excretion from foliage, which is ultimately from the soil). The sum of FL and LF is a measure of the internal recycling of nutrients between the soil and stand (uptake from the soil, transfer to the needles, foliar leaching and litterfall).

Total inputs to the forest floor, calculated as the sum of throughfall and litterfall fluxes (i.e. TF+LF), These inputs consist of both external atmospheric inputs and internal fluxes associated with nutrient recycling between the stand and the soil.

3. Results

3.1 BP, TF and SW concentrations and trends

Volume weighted mean solute concentrations during 1989–1997 were calculated by catchments and are shown in Table 2. At each catchment, the mean concentration and variability of Ca, Mg, Na and SO_4 increased in the order: BP<TF<SW. The enrichment of TF is related to the washing-off of dry deposition intercepted by the canopy. In the case of SW, enrichment is due to leaching from the organic layer, which is related to LF, ionic exchange reactions, dissolution and weathering processes in the soil, and to the concentration effect of evaporation. Ammonium and NO_3 concentrations, in contrast, decreased in the order BP>TF>SW. Lower concentrations in TF are due to canopy uptake, either by foliage or canopy dwelling epiphytes. Organic forms dominated total N in TF and SW. Total N is not routinely determined in BP but our recent (unpublished) results would indicate that organic N accounts for about 30 % of total N on average. This proportion compares with that reported Piirainen et al. (1998). In the case of K and H ions, the highest concentrations were associated with TF and are due to canopy leaching, wash-off and ion exchange reactions. Concentrations of H, K, total N and total S in soil water tended to decrease with depth, while concentrations of Mg increased with depth. Ammonium and NO_3 concentrations in SW did not show any consistent difference related to soil depths. Calcium, Na and SO_4 concentrations were higher in 35 cm depth at VK and VJ but higher at 15 cm depth at HJ and PJ.

Leachate from the organic layer was only collected at Hietajärvi. Compared to the SW collected of 15 and 35 cm depth organic layer leachate concentrations of all solutes, except inorganic forms of N, were always higher.

Seasonal-Kendall linear slope estimates by plots (Table 3) showed there were few trends in TF quality over the 1990s. Concentrations of SO_4 showed a significant ($p < 0.1$) decline as far north as Pesosjärvi plot 2 (PJ2). The greatest decline took place at Valkea-Kotinen, plot 3 (VK3), in the south, which confirms our findings reported for a shorter period (Ukonmaanaho et al. 1998). Since there were few significant trends in base cation concentrations, the significant decline in TF acidity (negative H^+ slope estimates) shown at all plots except VK3 is evidently the result of the reduced sulphate concentrations. The significant increase in TF H^+ concentrations at VK3 may be due to increase leaching of organic acids. However at Valkea-Kotinen, plot 3, hydrogen concentration increased significantly. Throughfall NH_4 and NO_3 concentrations have only significantly decreased at PJ2, which is Norway spruce dominated. Total nitrogen, which has only been analyzed since 1994, showed a significantly decreasing trend at HJ4, PJ2 and VJ2 plots.

Seasonal-Kendall linear trend slope estimates for SW concentrations are presented by plots in Table 4. Significant ($p < 0.1$) trends in SW sulphate concentrations were all negative, except at 35 cm depth at VK3 where SO_4 concentrations have significantly increased. In contrast to TF, SW concentrations of base cations have significantly decreased, the greatest decline taking place at VK3. The expected decrease in SW acidity related to reduced SO_4 concentrations appear to have been compensated at VK3 and HJ1 by base cations from SW displacing H^+ from the soil exchange sites (increased SW acidity). Inorganic N and total N concentrations showed few, small and inconsistent significant trends.

3.2. Fluxes and budgets

Mean annual BD, TD, TF, SW and LF fluxes are presented by plots in Table 5 and Figures 2a-f. Elemental fluxes in BD, TF and LF, with the exception of Na and Mg tend to decrease northwards. The fluxes for Na and Mg were the highest at the Vuoskojärvi plots, and are clearly the result of the proximity of the sea (< 100 km) showing importance of marine inputs for these elements. The decreasing trend northwards is largely related to the amount of precipitation, which also decreases northwards (Kulmala et al. 1998), but it is also dependent on the fact that major emission sources are far away. Geographic trends in SW fluxes were not so clear. The northwards decrease in LF elemental fluxes is largely related to the corresponding trend in the amounts of LF mass, which in turn is related to stand volume and productivity (Table 1).

The excess of TF above TD fluxes (Table 5) for Ca, Mg, K, and Na indicate foliar leaching. The amount of foliar leaching was proportionally the greatest for K and Na, which are both more mobile than the divalent cations, Ca and Mg. Inorganic nitrogen was retained in the canopy as generally found from boreal coniferous forests. For Ca, Mg and N LF flux was considerably greater than the FL flux. As much K and S are returned via foliar leaching as via litterfall. For Na as much as 80 % of the total return to the forest floor occurs via foliar leaching.

Soil leaching outputs of H^+ ions were considerably less and those of the base cations considerably more than corresponding atmospheric (TD) inputs, indicating a strong acid buffering response of the

Table 2. Volume weighted mean monthly bulk precipitation (BP), throughfall (TF), soil water (SW) solute concentrations (mg l^{-1}) during 1989–97 for studied catchments. Standard deviations in parenthesis. (n.d = no data).

Catchment	media	H^+	Ca^{2+}	Mg^{2+}	K^+	Na^+	SO_4-S	Total S	NO_3-N	NH_4-N	Total N
Valkea-Kotinen	BP	35.55	0.18	0.04	0.10	0.16	0.70	n.d	0.35	0.31	n.d
		(7.885)	(0.057)	(0.007)	(0.034)	(0.028)	(0.210)		(0.058)	(0.113)	
	TF	38.00	1.01	0.32	2.90	0.40	1.82	2.04	0.26	0.22	0.87
		(13.533)	(0.290)	(0.084)	(1.097)	(0.133)	(1.048)	(1.671)	(0.080)	(0.066)	(0.160)
	SW 15cm	15.73	2.82	1.02	1.71	1.36	3.53	5.95	0.01	0.05	1.14
		(9.122)	(1.250)	(0.412)	(1.382)	(0.446)	(1.249)	(3.467)	(0.005)	(0.053)	(0.684)
	SW 35cm	13.09	3.21	1.47	1.71	1.79	3.86	5.01	0.01	0.06	0.55
		(7.853)	(2.478)	(1.524)	(1.758)	(0.549)	(0.990)	(1.681)	(0.012)	(0.097)	(0.264)
Hietajärvi	BP	33.68	0.12	0.02	0.06	0.13	0.57	n.d	0.29	0.20	n.d
		(5.370)	(0.043)	(0.005)	(0.014)	(0.017)	(0.156)		(0.043)	(0.077)	
	TF	37.35	0.40	0.12	0.71	0.24	0.84	0.92	0.23	0.17	0.69
		(8.443)	(0.179)	(0.068)	(0.403)	(0.078)	(0.609)	(0.628)	(0.099)	(0.089)	(0.196)
	SW humus	106.43	1.68	0.30	1.93	0.65	1.22	2.12	0.02	0.11	1.15
		(29.628)	(0.597)	(0.066)	(1.483)	(0.535)	(0.758)	(0.977)	(0.014)	(0.136)	(0.271)
	SW 15 cm	12.26	0.69	0.21	0.53	0.92	0.77	1.60	0.01	0.03	0.39
		(11.927)	(0.326)	(0.112)	(0.280)	(0.260)	(0.379)	(1.297)	(0.011)	(0.020)	(0.208)
	SW 35 cm	2.51	0.63	0.23	0.44	0.90	0.47	1.22	0.01	0.03	0.34
		(2.198)	(0.383)	(0.158)	(0.285)	(0.282)	(0.201)	(0.875)	(0.000)	(0.024)	(0.260)
Pesosjärvi	BP	29.54	0.07	0.02	0.05	0.15	0.45	n.d	0.21	0.12	n.d
		(4.692)	(0.026)	(0.005)	(0.014)	(0.038)	(0.127)		0.030)	(0.040)	
	TF	26.33	0.32	0.11	1.18	0.36	0.82	0.89	0.12	0.16	0.43
		(9.198)	(0.182)	(0.053)	(0.697)	(0.371)	(0.790)	(0.736)	(0.056)	(0.139)	(0.220)
	SW 15 cm	2.14	1.76	0.55	0.81	1.07	0.94	9.21	0.01	0.04	0.92
		(1.917)	(2.226)	(0.203)	(0.645)	(0.742)	(0.461)	(21.687)	(0.002)	(0.020)	(0.948)
	SW 35 cm	0.97	1.10	0.56	0.35	0.87	0.83	1.65	0.01	0.03	0.44
		(1.302)	(0.525)	(0.256)	(0.280)	(0.218)	(0.330)	(0.743)	(0.000)	(0.016)	(0.258)
Vuoskojärvi	BP	24.15	0.11	0.13	0.08	1.03	0.46	n.d	0.15	0.08	n.d
		(3.644)	(0.042)	(0.072)	(0.037)	(0.613)	(0.084		(0.023)	(0.035)	
	TF	25.47	0.32	0.30	0.60	1.82	0.74	0.78	0.10	0.09	0.41
		(11.693)	(0.249)	(0.245)	(0.477)	(1.631)	(0.765)	(0.733)	(0.072)	(0.057)	(0.108)
	SW 15 cm	7.78	0.84	0.39	0.45	2.10	0.79	9.18	0.01	0.05	0.85
		(4.610)	(0.710)	(0.127)	(0.366)	(0.338)	(0.193)	(11.152)	(0.000)	(0.065)	(0.720)
	SW 35 cm	6.82	0.88	0.48	0.44	2.20	1.00	6.76	0.01	0.05	0.67
		(3.877)	(0.604)	(0.187	(0.477)	(0.522)	(0.476)	(7.332)	(0.000)	(0.069)	(0.560)

soil (Table 5). Sulphate leaching outputs were less than sulphate TD inputs, at all plots except VJ2 where inputs and outputs were nearly in balance and VK3 where outputs were considerably greater than inputs. Nitrate leaching outputs were less than 5 % and NH_4 outputs less than 10 % (VJ plots about 30 %) of TD inputs.

Table 3. Seasonal–Kendall slope estimates (mg l^{-1}, except for H^+ μmol l^{-1}) trends in throughfall monthly volume weighted concentrations 1989-97.

Plot		VK3	HJ1	HJ4	PJ2	VJ2	VJ3
mm	slope	-0.543	-0.002	0.200	1.275	-0.933	-0.433
	p						
H^+	slope	3.226	-2.269	-1.975	-2.423	-1.400	-0.715
	p	***	*	*	**	*	
SO_4-S	slope	-0.140	-0.090	-0.094	-0.057	-0.024	-0.021
	p	***	***	***	***		
Ca^{2+}	slope	-0.029	-0.030	-0.015	-0.010	0.006	0.004
	p	°	**				
Mg^{2+}	slope	-0.006	-0.003	-0.002	0.000	0.000	0.010
	p						
K^+	slope	0.035	-0.010	-0.013	0.009	0.000	0.000
	p						
Na^+	slope	0.016	0.010	0.005	0.000	0.021	0.084
	p	*					
NO_3-N	slope	-0.010	-0.006	-0.002	-0.010	0.000	0.000
	p				**		
NH_4-N	slope	0.002	0.002	0.000	-0.008	0.003	0.003
	p				*		
Total-N[#]	slope	0.046	-0.080	-0.067	-0.045	-0.070	-0.070
	p			*	*	*	

[#] years 1994-97
Significance levels: ° p < 0.1, * p < 0.05, ** p< 0.01, *** p < = 0.001

Comparing total inputs (TF+LF) to the forest floor (Figs. 2a-f) the leaching SW flux at 40 cm depth indicated retention of Ca, Mg, K and N at all plots. Na released from all plots, excluding VJ3, there was a net retention of Na. Sulphur also showed a net release all plots except both HJ plots. At Hietajärvi, where leachate from under the organic layer has been collected, a major part of the net retention of Ca, Mg and N took place in the organic layer (Figs. 2b-c).

Table 4. Seasonal-Kendall slope estimates (mg l^{-1}, except for H^+ µmol l^{-1}) for linear trends in soil water monthly volume weighted concentrations during 1989-97.

Plot		VK3		HJ1			HJ4			PJ2		VJ2[†]		VJ3	
Depth		15cm	35cm	humus	15cm	35cm	humus	15cm	35cm	15cm	35cm	15cm	35cm	15cm	35cm
mm	slope	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	p														
H^+	slope	3.035	2.982	5.958	3.926	0.116	17.980	-0.445	-0.180	-0.220	-0.011	-0.860	-1.692	-1.017	-0.940
	p	**	***		***		°		°					*	**
SO_4-S	slope	-0.366	0.207	-0.163	-0.069	-0.054	-0.110	-0.025	-0.037	-0.061	-0.050	-0.160	-0.067	-0.050	-0.050
	p	***	***	*	**	**	*				°			*	*
Ca^{2+}	slope	-0.223	-0.083	-0.210	-0.025	-0.094	-0.080	-0.045	0.015	-0.413	-0.151	-0.039	-0.160	-0.158	-0.078
	p	**	*	**	*	***				***	**		°	**	**
Mg^{2+}	slope	-0.120	-0.040	-0.017	-0.015	-0.030	-0.036	-0.020	0.005	-0.041	-0.034	-0.005	-0.070	-0.010	-0.010
	p	***	°		***	***	*	*	°	*	*		°		
K^+	slope	-0.250	-0.113	-0.755	-0.084	-0.071	-0.380	-0.050	0.030	-0.106	-0.061	-0.130	-0.093	-0.096	-0.036
	p	***	*	***	***	***	*			*	°	*		***	***
Na^+	slope	0.045	0.165	-0.040	0.018	0.010	-0.300	-0.050	0.024	-0.062	-0.037	0.065	0.053	0.090	0.006
	p		***					*		***	*			***	
NO_3-N	slope	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	p		*				*			°					
NH_4-N	slope	0.001	-0.002	-0.006	0.000	0.000	0.005	0.003	0.003	-0.006	0.025	0.000	0.000	-0.006	-0.008
	p									°				*	*
Total-N[‡]	slope	0.189	-0.027	0.008	0.089	0.074	-0.042	-0.053	0.173	-0.591	-0.081	-0.045	-0.097	-0.230	-0.074
	p				°	*			°					*	

[†] Years 1993-97
[‡] Years 1994-97
Significance levels: ° p < 0.1, * p < 0.05, ** p< 0.01, *** p < = 0.001

4. Discussion

4.1 Solution concentrations

In general, solute concentrations were the highest in the southernmost catchment, Valkea-Kotinen, and decreased northwards (Table 2). This trend was less clear for SW than for BP and TF due to interaction with soil and for SO_4, Mg, and especially Na, due to marine-derived inputs at Vuoskojärvi.

Compared to BP, TF had higher concentrations of base cations, especially K (Table 2), and SO_4 ions and lower concentrations of inorganic N (except NH_4 at PJ) (Table 2). Proton concentrations were slightly higher in TF, except at PJ where it was slightly lower than BP. Such canopy interaction has been observed in many studies (Helmisaari and Mälkönen 1989, Hyvärinen 1990).

In contrast to base cations and SO_4, the concentrations of NH_4 and NO_3 were less in TF than in BP, except in the case of NH_4 at Pesosjärvi and Vuoskojärvi. Both NH_4 and NO_3 are consumed in forest canopies, most likely direct uptake by the trees. This uptake of N in boreal coniferous forest is well known and reflects the shortage of available N (inorganic) in such ecosystems and their N limiting productivity (e.g. Mälkönen et al. 1990). Over 50 % of NH_4 deposition can be dry deposition origin in Finland (Tuovinen et al. 1990, Hyvärinen 1990). Sufficient amount of dry deposited NH_4, which exceed the canopy uptake, can explain canopy release at the PJ and VJ (Lindberg et al. 1990, Farrell et al. 1994) or that N fixation is occurring in the old-growth canopy as suggested by Edmonds et al. (1991).

Both BP and TF H^+ concentrations decreased northwards. Increased acidity in coniferous forest TF has been found in many studies e.g. Helmisaari and Mälkönen (1989), Schaefer et al. (1992). The increase has been attributed to the leaching of organic acids and exchange for NH_4^+ ions (Cronan and Reiners 1983, Helmisaari and Mälkönen 1989). Also the wash off of intercepted SO_4 from the canopy may increase the acidity of the TF. However, the increase in acidity at studied plots (except PJ) was relatively small and when comparing TF H^+ fluxes with TD fluxes (Table 5), TF fluxes were smaller indicating neutralization of acidity in the canopy. The increase in TF acidity is therefore probably also related to evaporative concentration effects.

Acid buffering and neutralization processes in forest soil (Van Breemen et al. 1984) normally result in an increase in SW pH as it moves down through the soil (e.g. Helmisaari and Mälkönen 1989, Lindroos et al. 1995). Increasing SW pH with depth was observed at all sites, especially at HJ, where SW was measured under humus layer in addition of 15 and 35 cm (Table 2). Soil water pH was noticeably higher at PJ than the other catchments. This is due to the presence of carbonates in the soil parent material (Tanskanen and Starr 1995).

Sulphate concentrations in SW increased with soil depth (Table 2) at Valkea-Kotinen and Vuoskojärvi. The increase in SO_4 concentrations with depth are unlikely to be concentration effect due to evapotranspiration and storage changes because modeled waterfluxes at both depths were similar (Table 1). The increased SO_4 concentration in soil water at deeper depth therefore is due to an additional of SO_4. This additional SO_4 could originate from the mineralization organic matter and/or desorption of

Table 5. Mean annual (1989-1997) input-output budgets in plots, H µmol m^{-2}, other elements mg m^{-2}.

	H	SO_4-S	Ca	Mg	K	Na	NO_3-N	NH_4-N
VK3								
Bulk Deposition	19653	372	85	20	53	90	188	169
Total Deposition	33583	620	143	33	91	155	324	279
Throughfall	17617	620	282	104	819	143	137	100
SW 40 cm	3048	955	560	271	279	421	2	19
TD-SW 40 cm	30535	-355	-418	-238	-188	-266	322	260
HJ1								
Bulk Deposition	18364	312	63	13	34	66	150	115
Total Deposition	21673	366	73	16	40	78	177	135
Throughfall	17214	366	140	40	222	105	137	89
SW 40 cm	647	115	189	72	107	279	3	9
TD-SW 40 cm	21026	252	-116	-56	-67	-201	174	129
HJ4								
Bulk Deposition	18364	312	63	13	34	66	150	115
Total Deposition	22790	385	77	16	42	82	186	142
Throughfall	20231	385	134	40	209	102	123	100
SW 40 cm	884	135	115	30	99	208	3	9
TD-SW 40 cm	22109	250	-38	-14	-57	-126	183	133
PJ2								
Bulk Deposition	12517	193	27	9	18	47	81	57
Total Deposition	17731	270	38	12	26	67	115	78
Throughfall	12196	270	68	27	220	85	68	52
SW 40 cm	119	159	224	106	97	147	2	7
TD-SW 40 cm	17613	111	-186	-93	-71	-81	113	71
VJ2								
Bulk Deposition	7070	116	21	21	16	169	36	19
Total Deposition	8000	131	24	24	18	193	40	21
Throughfall	5677	131	44	37	90	222	33	23
SW 40 cm	1622	239	152	87	152	355	2	6
TD-SW 40 cm	6378	-108	-128	-63	-134	-162	38	15
VJ3								
Bulk Deposition	7070	116	21	21	16	169	36	19
Total Deposition	13676	223	41	43	31	342	71	37
Throughfall	9553	223	81	84	107	684	34	28
SW 40 cm	959	166	153	78	45	410	2	12
TD-SW 40 cm	12717	57	-112	-35	-13	-68	70	25

SO_4 from the soil. Sulphate desorption may have occurred in response to lowered acid deposition inputs since soil SO_4 adsorption is reversible depending on pH (Harrisson and Johnson 1992). It might be also a sign that there is no additional sulphate absorption capacity left leading to leaching of SO_4 from upper layers (Mitchell 1992). There was also little depth related differences in SW sulphate concentrations at Hietajärvi and Pesosjärvi.

Calcium, Mg and Na mean concentrations at depth 35 cm were similar or less than concentrations at 15 cm depth. Potassium concentrations were lower in 35 cm depth than 15 cm, in spite of high K concentrations in TF. Although K is mobile, it is cycled efficiently within the ecosystem and concentrations decreased with depth (Farrell et al. 1994). Both NH_4 and NO_3 concentrations in SW were substantially lower than in BP and TF, indicating efficient retention by root and micro-organism uptake (Piirainen et al. 1998). Overall the dominance of NO_3 over NH_4 in both BP and TF concentrations and the low levels of nitrogen leaching from all plots indicate that the nitrogen at these catchments has not acidifying effect on soil (de Vries and Breeuwsma 1987).

4.2 Enrichment of TF and internal cycle

Enrichment of TF takes place through foliar leaching and/or the wash off of intercepted dry deposition. Comparing the TF, BD and TD fluxes it is possible to distinguish between these two processes. The difference between TF and TD describes the canopy interaction effect on TF. If the difference is negative, then canopy uptake is indicated, if the difference is positive then foliar leaching is indicated, and if there is no difference then there is no interaction. Because of the method used to calculate TD, TF fluxes of SO_4 are equal to TD fluxes, as SO_4 is assumed to show no interaction with the canopy (Lindberg et al. 1986). The enrichment in TF sulphate is entirely due to wash off of dry deposition intercepted between rainfall events. The difference between TF and BD, when positive, is due to wash off and/or FL. On this basis, foliar leaching accounted for 65 % or more of the TF enrichment of Ca and Mg, and 70–97 % of K (Table 5). For Na there was a small amount of canopy uptake at VK3 but TF enrichment at the other sites, was 30–70 % due to FL. Foliar leaching can take place through the diffusion of solutes from foliar tissues, which are added to the TF and through cation exchange reactions in which H^+ ions are exchanged for the base cations, a neutralisation process (Tukey 1970, Miller et al. 1987).

The LF flux primarily represents an internal flux related to nutrient uptake and cycling. However, it also includes dry deposition collected by the needles and leaves while still part of the canopy. For Ca, Mg and N annual LF flux was greater than the TF flux and for K, Na and S annual TF flux was greater than LF flux. Other studies have found similar results (e.g. Helmisaari 1995, Gordon et al. 2000).

Foliar leaching is also part of the internal flux of nutrients related to uptake and cycling, including also dry deposition component collected while still part of the canopy. The relative importance of the LF and FL pathways varies among nutrients (Parker 1983). For all elements inputs of FL+LF was greatest at the southernmost plot VK3, as a result of geographic location, stand density and tree species. Of the combined LF+FL flux about 51 % of K, and 50 % of S and about 80 % of Na is returned to the forest floor by foliar leaching, for the other nutrients less than 25 %. Both K and Na mobility is well known and SO_4 is the dominant mobile anion in forest canopy throughfall (Lindberg 1992). Need of Na is little for trees (Kramer and Kozlovski 1979) and the concentration e.g. in Scots pine needles is very low, $< 0.16\ \mu g\ l^{-1}$ (Raitio et al. 1995), therefore Na has only little interaction with canopy and as mobile cation it is easily leached. Other nutrients, which are more strongly bound to the canopy, are returned mainly by LF to the forest floor.

4.3 Trends

The trend analyses results showed a marked decrease in sulphate concentrations and acidity in TF during the 1990s, confirming our earlier findings (Ukonmaanaho et al. 1998). The decrease in SO_4 concentrations was greatest at VK3, the southernmost plot, and decreased northwards. Emissions of SO_2 have progressively declined during 1990s and are evidently responsible for the trends in TF SO_4

a)

b)

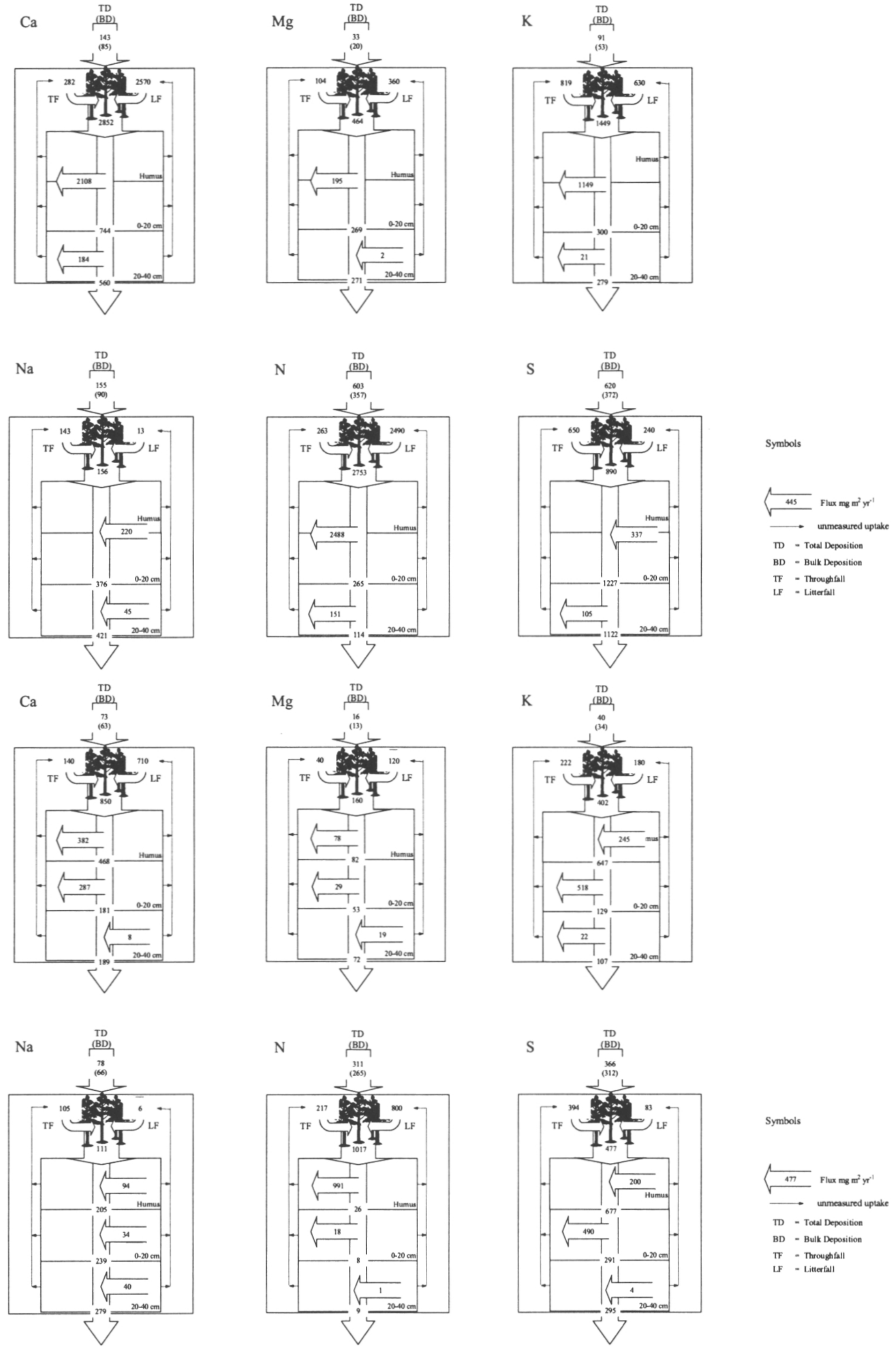


Fig. 2. (a) Plot-scale Ca, Mg, K, Na, N and S (for TD S = SO_4-S and N = NO_3-N+NH_4-N) mean annual (1989–1997) fluxes and input-output budgets for Valkea-Kotinen, plot 3, (b) Plot-scale Ca, Mg, K, Na, N and S (for TD S = SO_4-S and N = NO_3-N+NH_4-N) mean annual (1989–1997) fluxes and input-output budgets for Hietajärvi, plot 1.

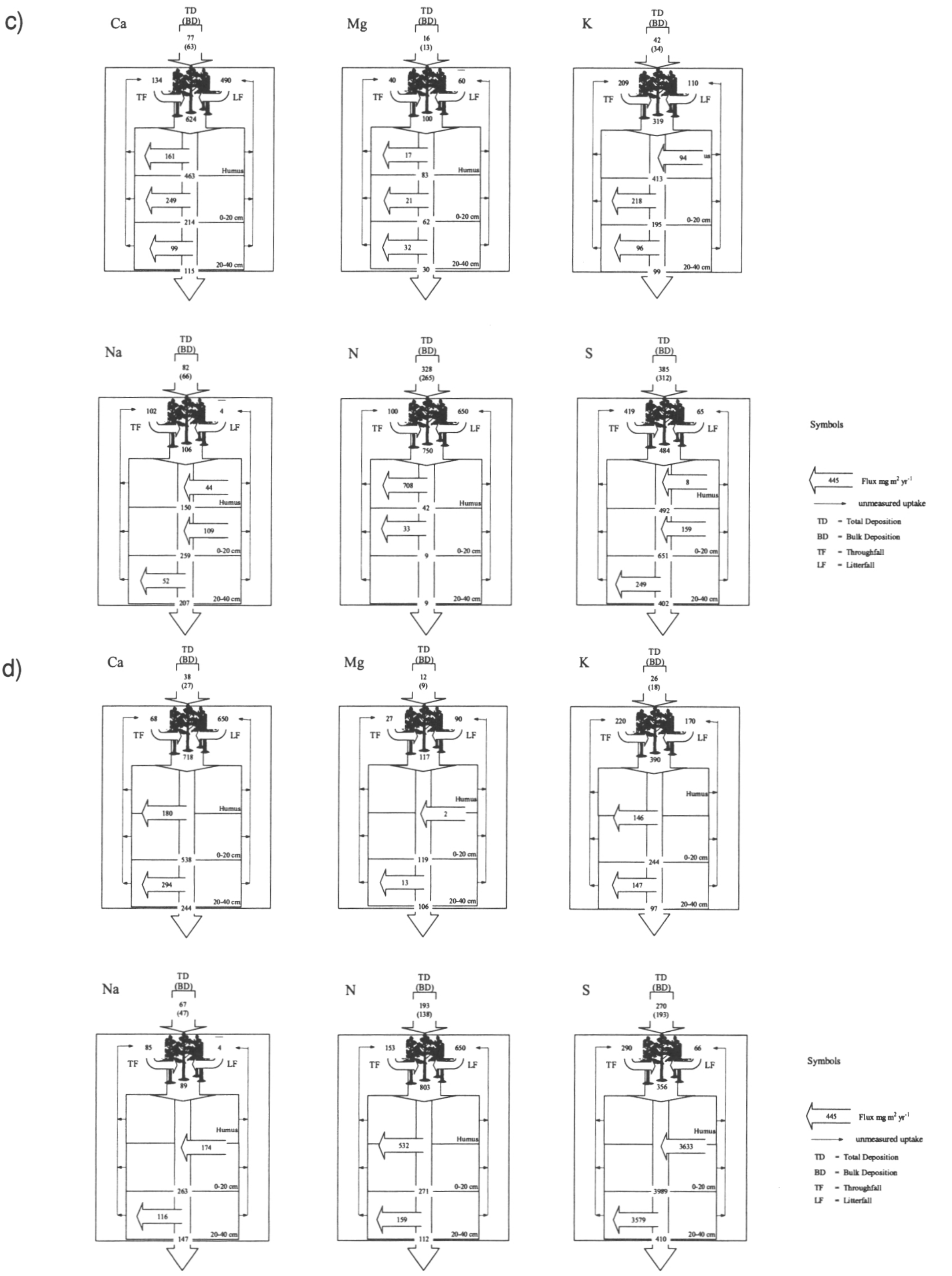
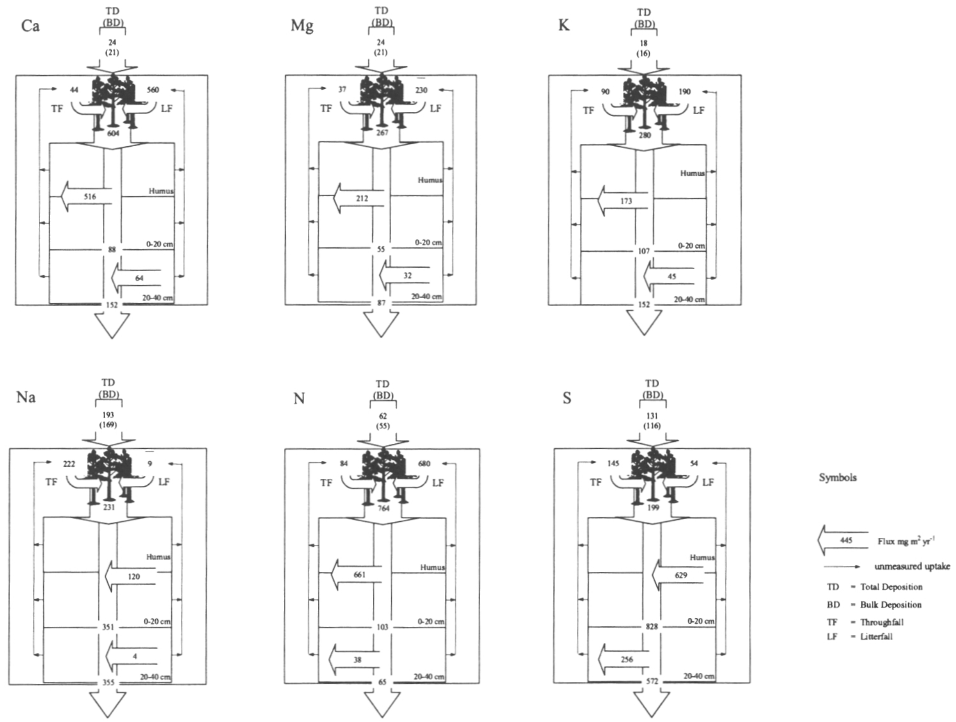


Fig. 2. ...continue (c) Plot-scale Ca, Mg, K, Na, N and S (for TD S = SO_4-S and N = NO_3-N+NH_4-N) mean annual (1989–1997) fluxes and input-output budgets for Hietajärvi, plot 4, (d) Plot-scale Ca, Mg, K, Na, N and S (for TD S = SO_4-S and N = NO_3-N+NH_4-N) mean annual (1989–1997) fluxes and input-output budgets for Pesosjärvi, plot 2.

e)



f)

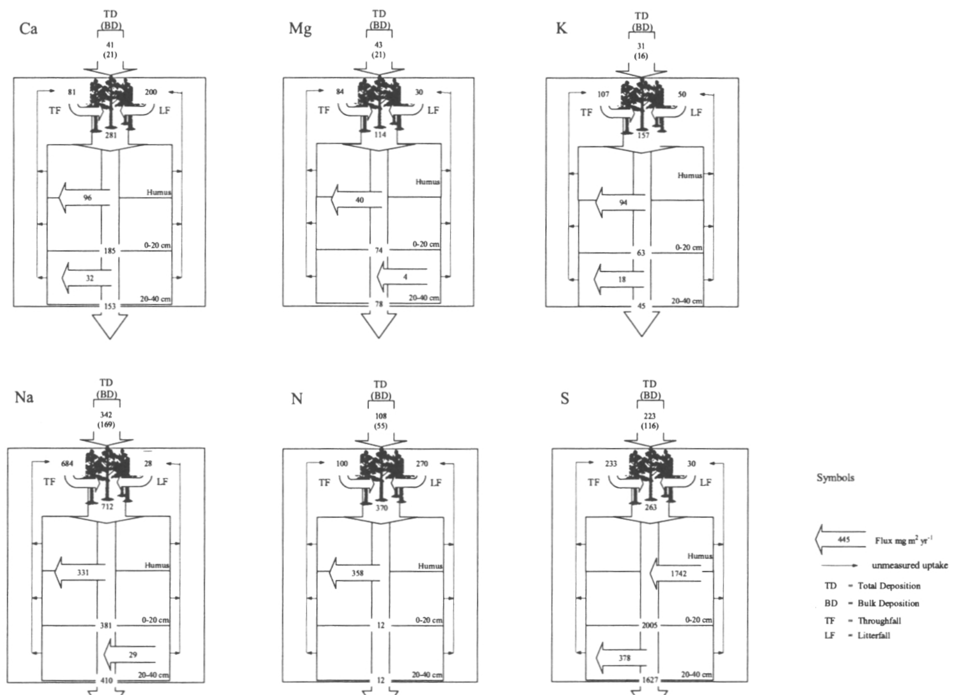


Fig. 2. ...continue (e) Plot-scale Ca, Mg, K, Na, N and S (for TD S = SO_4-S and N = NO_3-N+NH_4-N) mean annual (1989–1997) fluxes and input-output budgets for Vuoskojärvi, plot 2, (f) Plot-scale Ca, Mg, K, Na, N and S (for TD S = SO_4-S and N = NO_3-N+NH_4-N) mean annual (1989–1997) fluxes and input-output budgets for Vuoskojärvi, plot 3.

concentrations observed. According to Kulmala et al. (1998) bulk deposition of SO_4 has decreased 50–65 % during 1981–1996. There has been no significant change in TF SO_4 concentrations at VJ plots, which may be related to continuous inputs of marine origin. In SW a similar decreasing trend in SO_4 concentrations was seen, but the trend was significant in both depths only at VJ3 plots. The results showed that reduced SO_2 emissions have not only resulted in reduced deposition loads to forest ecosystems but that the reduction is also having an impact on soil. Sulphate concentrations at 35 cm depth at VK3 have significantly increased over the 1990s, which might indicate desorption of previously accumulated stores as a result of lowered H^+ inputs (Harrison and Johnson 1992). This recovery process could explain decreasing acidity of SW at HJ4, PJ2, VJ2 and VJ3 plots. The only significant decrease in SW acidity occured at VJ3.

Base cations (Ca, Mg, K) concentrations showed only slightly decreasing trend in TF, except significantly decreasing trend for Ca at VK3 and HJ1. Result confirms our earlier studies in which we calculated base cations as sum but we did not notice significant trend in concentrations (Ukonmaanaho et al. 1998). This may seem strange since base cation deposition in BD in Finland has been shown to have substantially decreased (Kulmala et al. 1998) as well Ca concentrations in BP at IM catchments according to Ruoho-Airola et al. (1998). The same reduction has been reported throughout Europe and North America (Hedin et al. 1994). Base cations concentrations in TF must therefore be maintained through intercepted dry deposition and foliar leaching. Declining trend of BP and TF base cation concentrations in south and southeast Finland might be due to the application of dust removal systems in oil shale power plants in Estonia and Russia, which have caused reductions of emissions of base cations (Jalkanen et al. 2000). Although there were only few significant trends in TF base cation concentrations, significant decreasing trends were seen in SW, indicating that the effect of reduced in bulk deposition loads is being transferred to the soil. On the other hand decline in SW base cation concentrations may be related to the decline in the SO_4 concentrations. Sulphate in the SW would have served as an important accompanying anion for base cations (Singh et al. 1980), any reduction in SO_4 concentrations would then lead to a reduction in base cation concentrations.

Trend analyses of TF showed for NO_3 declining trend at PJ2, which is significant, and at VK3 and HJ plots, which was not significant. There has been no change in NO_3 concentrations at VJ plots. The only significant declining trend for NH_4 was at PJ2, other plots trend was increasing. Concentrations of total N in TF have decreasing trend. Nitrogen concentrations in BP at two southernmost IM catchment (Ruoho-Airola et al. 1998) and in BD in Finland have decreased significantly; for NO_3 the reduction has been 20–40 % and for NH_4 45–85 % (Kulmala et al. 1998). However, according to Leinonen et al. (2000) deposition of NO_3 has slightly increased and NH_4 increased by 30 % at Kevo, which is situated close to VJ plots. Soil water concentrations of total-N have also been decreasing but only significantly at HJ1 (in 35 cm) and VJ2 (in 15 cm) plots.

4.4 Budgets

Atmospheric total deposition (TD) - soil water flux (SW)

Using of input-output budget for catchments has become an increasingly important means of assessing the sources, fate (i.e. loss to sinks or via transformations) and cycling of major nutrients (Dillon et al.

1988, Evans et al.1997). Used nutrient budget includes measurements from atmospheric inputs (precipitation + dry deposition) and in soil as SW (including weathering, the uptake of nutrients by the field and bottom layer vegetation, decomposition, soil adsorption/desorption and leaching). The long-term budget was measured as the difference between the nutrient input in TD (wet+dry deposition) and the output in SW depth of 40 cm (Table 5).

In general the leaching of Ca, Mg, K and Na through 40 cm mineral soil was greater than TD inputs (Table 5) indicating net release from the soil. These elements are important plant nutrients (excluding Na). Potassium and Na are very mobile and are easily leached from the canopy. Calcium and Mg are major cations on the soil cation exchange system and are exchanged for H^+ in percolating soil water. The acidity of infiltrating precipitation is also consumed in weathering, releasing base cations primary minerals (Starr et al. 1988). The amount of leaching of Ca, Mg and K was clearly the greatest at VK3, where acidic load was also greatest. Leaching of base cations is related to pH. According to Berkgvist (1987) especially Ca and Mg are very susceptible to changes in soil acidity, leaching more in low pH than high.

The output of other elements H, SO_4, NH_4, NO_3 was less than TD inputs. The sulphate and nitrate anions accompanying the H^+ in deposition play an important role in the leaching of base cations (Singh et al. 1980). Hydrogen deposition is mainly the result of chemical reactions in the atmosphere between water and sulphur dioxide (SO_2) and nitrogen oxides (NO_x) (Ulrich 1983). When hydrogen ions are entering to the soil, they can displace some of the base cations from the negatively charged exchange sites on soil particles, and the base cations pass into the soil solution (Van Breemen et al. 1984, Binkley and Richter 1987). Leaching of base cations might result acidification of the soil solid phase and alkalinisation of the soil solution. The output of H^+ ions at 40 cm depth was always less that the TD inputs. The consumption being related to the leaching of base cations discussed above.

The outputs of SO_4 at 40 cm depth were less than TD, except at VK3 and VJ2. At VK3 leaching loss was 57 % and at VJ2 21 %. Indicated leaching loss may be evidence of ecosystem recovery from air pollution sulphate adsorption, related to the presence of amorphous Al and Fe oxides in the illuvial B horizon (Karltun and Gustafsson 1993), which is known to be reversible (Harrison and Johnson 1992). The storage of soil sulphate resulting from atmospheric loading would start to desorption and appear in leachate. On the contrary it may indicate that there is less additional sulphate adsorption capacity (Mitchell 1992)

Retention of inorganic nitrogen in the soil is expected because available N is growth limiting nutrient in boreal forest ecosystems (Mälkönen et al. 1990). For NO_3 retention was nearly 100 % and for NH_4 > 90 %, except at VJ plots about 70 %. However in the northernmost plots inputs and outputs were considerably smaller than on the other plots. The lower retention of NH_4 at VJ plots may reflect lower uptake because smaller demand from ecosystems so far north. Also e.g. Helmisaari (1995) has found NH_4 leaching to the mineral soil in Scots pine forest at eastern Finland. Although NO_3 ions are mobile, they are readily taken-up from the soil by roots and microbes and net NO_3 production in such soils is very low. Leaching of NO_3 therefore played little role in the leaching of base cations (Foster et al. 1989).

Total inputs (TF+LF) to the forest floor – soil water flux

Because of the role nutrient cycling it is also necessary to study internal mass balance budget in soil. The sum of TF and LF constitutes the total inputs to the forest floor and includes both external (atmospheric) and internal (uptake from soil and recycling) sources. Litterfall represents a major pathway by which nutrients, particularly N, are taken up from the soil and are returned for recycling (Cole and Rapp 1981). However, LF has to decompose before associated elements appear as ions in soil water. Throughfall, LF and SW fluxes from the humus layer (only in HJ1 and HJ4), 20 cm and 40 cm depths describe the fate and internal transfers of the elements. Total S and N has used to calculate internal budget, because from LF has only measured total S and N. Our unpublished data shows that 90 % of total S in BP is SO_4 and 70 % of total N in BP is inorganic nitrogen.

At all plots in average 71 % Ca, 46 % of Mg and 69 % of K total inputs had been retained compared to the leaching fluxes at 40 cm depth mineral soil (Figs. 2a-f), indicating that total inputs (TF+LF) contained more of these nutrients as was lost in mineral soil leachate. In the case of N retention was nearly 100 %. In contrast, S and Na were leached in some amounts from 40 cm nearly at all plots. Leaching of S might indicate retention in the soil under 40 cm or that it is leaching to the groundwater. Adsorption of SO_4 in the soil mainly takes place in the B-horizon, where Al and Fe hydroxides have enriched (e.g. Karltun and Gustafsson 1993, Piirainen et al. 2001). In northernmost plot at VJ2 and especially at VJ3, leaching of S was considerably higher compared to total inputs.

At Hietajärvi plots (1 and 4), where leaching fluxes from humus layer have been measured, the major part of the nutrients of the total inputs were retained in humus layer, despite of Na, K and S (Figs. 2b,c). Releasing of K occurs through mineralization. Helmisaari and Mälkönen (1989) have also found leaching of K from humus layer. However K retained efficiently beneath of humus layer, probably through uptake by plants and microbes and cation exchange reactions. Released S in humus layer was most likely originated from mineralized organic sulphur. Total S was adsorbed in deeper part of the soil (20–40 cm) and some leached deeper soil profile. In studies of Helmisaari and Mälkönen (1989) sulphate was released in considerable amounts from humus layer. In turn in the study of Piirainen et al. (2001) SO_4 is retained in humus layer and probably taken up by plant roots and microbes in the humus (Strickland et al. 1986). However in the study of Piirainen et al. (2001) has not taken account LF flux. Sodium leaching indicates there is only little interaction in soil between Na and soil substances. The other base cations, Ca and Mg, retention mainly takes place in humus layer. Indicating that most of the elements in the soil are retained in humus layer or upper part of the mineral soil, where also major part of the roots is situated and which is biologically most active part of the soil. Similar result got also Berkgvist (1987) in his studies. Between 56–81 % of total N was retained in humus layer, being almost totally immobilized in the surface layer of the mineral soil, presumably because of uptake by the vegetation and micro-organisms.

In other plots, where fluxes from humus layer have not calculated, results were quite similar to HJ plots. Total S released upper part of the soil (humus + 20 cm soil) probably through mineralization and retained efficiently in layers between 20 and 40 cm. This indicates S adsorption in the B-horizon, where Al and Fe hydroxides have enriched (e.g. Karltun and Gustafsson 1993, Piirainen et al. 2001). However, S was also leached deeper in soil profile. Retention of Ca, Mg and K was greatest upper soil profile, including humus layer +20 cm mineral soil, indicating uptake and cation exchange. Retention of total N was similar as base cations, most retention taking place in humus layer and upper part of the mineral soil, indicating efficiently nitrogen uptake or immobilization. Sodium leached efficiently through 40 cm layer to deeper in soil.

Conclusions

The four studied catchments were situated along north-south deposition gradient. Nutrient concentrations and acidity generally decreased northwards. Mean concentration of base cations increased in the order: BP<TF<SW. This trend in enrichment in TF is related to foliar leaching and wash off, and in SW both TF and LF inputs and various processes in the soil. Nitrogen compounds NH_4 and NO_3 increased in order BP>TF>SW. Indicating uptake of nitrogen by canopy layer, by roots and micro-organisms. The dominance of NO_3 over NH_4 in both BP and TF concentration and the low levels of nitrogen leaching from the soil all indicate that the nitrogen at these catchment has not had an acidifying effect on the soil.

Trend analyses over nine year period indicated that there is marked decreased trend in SO_4 and H^+ concentrations in TF over the 1990s, which shows that reduced SO_2 emissions in Europe have had a significant impact in reducing 'acid rain' pollution. Base cations showed only slightly decreasing trend in TF, although bulk deposition of base cations has decreased significantly. The decrease in acidity of TF has therefore due to the decline in SO_2 emissions rather than an increase in neutralizing base cations deposition. In SW decreasing trend of Ca, Mg and K were evident as well as SO_4 and H^+ some of the plots and depths. However SO_4 at 15 cm depth at VK3 have significantly increased over the 1990s, which might indicate desorption of previously accumulated SO_4 stores. Nitrogen compounds did not have any remarkable trend in TF or SW. At all plots TF fluxes of Ca, Mg, K, Na and S were greater than TD fluxes indicating enrichment of TF.

Comparison of the amount of retention to the calculated internal fluxes indicated that most of the retention was accounted for by uptake and recycling than accumulating in the soil. For all elements inputs of FL+LF were greatest at the southernmost plot VK3, as a result of geographic location, stand density and tree species, which are related greater amount of LF flux to compared TF flux. Results indicate that most readily mobilized cations K and Na, and S are removed easily with canopy leaching; other nutrients, which are more strongly bound to the canopy, are returned mainly by LF to the forest floor.

Mass balance budget indicate that in plot scale, total deposition was for NO_3, NH_4, H and SO_4 greater than output (SW) from depth of 40 cm. For base cations inputs were less than output in 40 cm and sulphur at plots VK3 and VJ2. Because of role of nutrient cycling it was also studied internal mass balance budget ((TF+LF)- SW 40 cm), the input-output balances of most nutrients were positive, total inputs contained more of these nutrients as was lost in mineral leachate. The humus layer was important in the retention of total inputs for Ca, Mg and N, which they were subsequently taken up and recycled. Sulphur retained in the mineral soil, particularly in the B-horizon, where Al and Fe hydroxides have accumulated.

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