

**MOSSES, EPIPHYTIC LICHENS
AND TREE BARK AS
BIOMONITORS FOR AIR
POLLUTANTS –
SPECIFICALLY FOR HEAVY
METALS IN REGIONAL SURVEYS**

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Abstract

The thesis consists of regional forest condition studies, using different biomonitors. Heavy metal deposition was investigated in 1985–2000 on the basis of the heavy metal concentrations (As, Cd, Cr, Cu, Fe, Hg, Ni, Pb, V, Zn) in mosses in Finland. A comparison on the suitability of mosses, epiphytic lichens and pine bark as biomonitors of heavy metals was also carried. Bark was also used to study the dispersal of emissions from the Kola Peninsula into northern Finland. The occurrence of green algae on conifers in Finland was investigated in 1985 and 1995.

Regional and temporal differences were found in the heavy metal concentrations of mosses in Finland. The concentrations of most metals were the highest in southern Finland, and they decreased towards the north. Some of the major emission source had a noticeable effect on the Cu, Ni and Cr concentrations of mosses in the surroundings of the emission sources. The Pb, Cd and V concentrations decreased the most during the study period.

Mosses, lichens and bark gave a relatively similar result for heavy metal deposition in Finland. However, the comparisons indicated that mosses are better suited as biomonitors for regional surveys than epiphytic lichens, because the regional differences in heavy metal deposition were more readily reflected by concentrations in mosses than in lichens. Bark is relatively unsuitable for regional surveys due to the small range of variation in the concentrations.

Emissions from the Kola Peninsula had a clear effect on the sulphur and heavy metal concentrations of pine bark. The concentrations in bark were at very high levels close to the smelters, but they rapidly decreased on moving towards the west. The effects of emissions were still clearly visible in north-eastern Lapland.

There was strong increase in the abundance of green algae on conifers in southern and central Finland during the period 1985–1995. The increase is probably due to following factors: climate warming, and an increase in nitrogen and a decrease in sulphur in their habitats.

Half of each biomonitor sample collected in the surveys has been stored in the specimen bank at Paljakka. The storage of samples offers advantages for monitoring purposes. The availability of long-term sample series makes it possible to construct retrospective time series of the pollutants. The specimen bank is to be further developed in the future by establishing a reputation as a storage facility for samples related to forest ecosystems.

Keywords: atmospheric deposition, biomonitors, heavy metals, nitrogen, regional surveys, sulphur

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List of original publications

The thesis is based on the following original papers, which are referred to in the text by their Roman numerals:

- I Poikolainen J, Kubin E, Piispanen J & Karhu J (2004) Atmospheric heavy metal deposition in Finland 1985-2000 using mosses as bioindicators. *The Science of the Total Environment* 318: 171-185. Reprinted with permission from Elsevier.
- II Lippo H, Poikolainen J & Kubin E (1995) The use of moss, lichen and pine bark in the nationwide monitoring of atmospheric heavy metal deposition in Finland. *Water, Air, and Soil Pollution* 85(4): 2241-2246. Reprinted with permission from Springer.
- III Poikolainen J (1997) Sulphur and heavy metal concentrations in Scots pine bark in northern Finland and the Kola Peninsula. *Water, Air, and Soil Pollution* 93: 395-408. Reprinted with permission from Springer.
- IV Poikolainen J, Lippo H, Hongisto M, Kubin E, Mikkola K & Lindgren M (1998) On the abundance of epiphytic green algae in relation to the nitrogen concentrations of biomonitors and nitrogen deposition in Finland. *Environmental Pollution* 102: 85-92. Reprinted with permission from Elsevier.
- V Kubin E, Lippo H, Karhu J & Poikolainen J (1997) Environmental specimen banking of nationwide biomonitoring samples in Finland. *Chemosphere* 34(9/10): 1939-1944. Reprinted with permission from Elsevier.

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1 Introduction

1.1 Air quality research using biomonitors

All the chemical compounds or elements that are released into the atmosphere primarily as a result of human activities, and which can cause damage in living organisms, are considered air pollutants (Moriarty 1999). The majority of the heavy metals, and sulphur and nitrogen compounds that are considered pollutants originate from anthropogenic sources (Pitcairn *et al.* 1995, Whelpdale *et al.* 1998, Pacyna & Pacyna 2001). Natural sources of these compounds include volcanoes, forest fires, biological decomposition processes and the oceans (Nriagu 1989). The degree and extent to which emissions are spread depends on e.g., the type of emission source, composition of the emissions and the weather conditions. The majority of the emissions remain close to the source, but some can travel for thousands of kilometres. In general, sulphur and nitrogen compounds occur in the atmosphere in gaseous form, and heavy metals are attached to particles. Metals that have a density exceeding generally a value of 4.5 g/cm^3 are called heavy metals (Wittig 1993). However, use of the term has been criticised because the limit is artificial and there are no biological grounds for using the term (Hodson 2004).

Air quality can be monitored by measuring the pollutants directly in the air or in deposition, by constructing models depicting the spread of pollutants, or by using biomonitors (Markert *et al.* 2003). Direct measurements provide objective information about the level of pollutants, but they are expensive and there is a risk of contamination when determining low concentrations. The models provide information about extensive areas and they can be used to produce predictions of future air quality. However, their accuracy is dependent on the quality of the data used in constructing the models. Biomonitors provide information on both the quantity of pollutants and their effect on the occurrence and condition of biomonitors. Although the methods are fast and inexpensive, they only provide a relatively approximate picture of air quality and the deposition of pollutants.

The term bioindicator/biomonitor is used to refer to an organism, or a part of it, that depicts the occurrence of pollutants on the basis of specific symptoms, reactions, morphological changes or concentrations (Markert *et al.* 1997). There is considerable

variation in the use of the terms bioindicator and biomonitor, but *bioindicator* generally refers to all organisms that provide information on the environment or the quality of environmental changes, and *biomonitor* to organisms that provide quantitative information on the quality of the environment (Wittig 1993, Markert *et al.* 2003). Organisms can be classified according to the way in which the reaction is manifested: *reaction indicators*, which have a sensitive reaction to air pollutants and which are used especially in studying the effects of pollutants on species composition, and on physiological and ecological functioning, and *accumulation indicators* that readily accumulate a range of pollutants and are therefore used especially when monitoring the amount of pollutants and their distribution (Markert *et al.* 1997). Organisms can be further classified according to their origin into *passive biomonitors*, in which organisms that occur naturally in the study area are monitored, and *active biomonitors*, in which the organisms are brought into the research area under controlled conditions for a specific period of time (Markert *et al.* 2003).

A good accumulation indicator of air pollutants should meet the following requirements (Wittig 1993, Conti & Cecchetti 2001). It should accumulate pollutants from the air in the same way and to the same degree under different conditions. The pollutants should be easily measured and the measurements should provide information about the level of pollutant deposition. It should also indicate the risk limits caused by increasing levels of pollutants. The species of organism used should be common enough and be available for collection throughout the year in the same area. Its use should be based on standard sampling and analysis methods. In order to determine the state of the ecosystem in relation to the pollutant under study, the state of the ecosystem in the background area should also be known (Seaward 1995). The background level is usually considered to be the “natural” level at which emissions have as small an effect as possible (Conti & Cecchetti 2001). The background level of different pollutants varies between plant species. Mosses and lichens are considered to be the best plants for use as biomonitors of air pollutants (Rühling & Tyler 1968, Puckett 1988). Also the bark of trees has been used relatively extensively in investigating e.g., air quality in industrial and urban areas.

1.2 Factors that affect the element concentrations of mosses, lichen and bark

Mosses

Mosses are cryptogams that thrive in a humid climate. Ectohydric mosses have been used as biomonitors – in most cases terricolous bryophytes. They possess many properties that make them suitable for monitoring air pollutants (Onianwa 2001, Zechmeister *et al.* 2003a). These species obtain nutrients from wet and dry deposition and they do not have real roots. Nutrient uptake from the atmosphere is promoted by their weakly developed cuticle, large surface to weight ratio, and their habit of growing in groups. Other suitable properties include a slow growth rate, undeveloped vascular bundles, minimal morphological changes during the mosses’ lifetime, perenniality, wide distribution, ease

of sampling, and the possibility to determine concentrations in the annual growth segments.

Air pollutants are deposited on mosses in aqueous solution, in gaseous form or attached to particles. The accumulation of pollutants in mosses occurs through a number of different mechanisms: as layers of particles or entrapment on the surface of the cells, incorporation into the outer walls of the cells through ion exchange processes, and metabolically controlled passage into the cells (Brown & Bates 1990, Tyler 1990). The attachment of particles is affected e.g., by the size of the particles and the surface structure of the mosses. Ion exchange is a fast physiological-chemical process that is affected e.g., by the number and type of free cation exchange sites, the age of the cells and their reaction to desiccation, growing conditions, temperature, precipitation pH, composition of the pollutants and leaching (Tyler 1990, Brown & Brümelis 1996). In the ion exchange process, cations and anions become attached to functional organic groups in the cell walls among other things through chelation (Rao 1984).

The chemical composition of deposition has a large effect on the accumulation of pollutants, because the uptake efficiency of mosses for individual elements varies considerably (Berg *et al.* 1995). The uptake efficiency of the most common heavy metals follows mostly the order $Pb > Co, Cr > Cu, Cd, Mo, Ni, V > Zn > As$ (Zechmeister *et al.* 2003a). A high proportion of the pollutant load accumulates in mosses through wet deposition. The amount, duration and intensity of precipitation affect accumulation and leaching (Berg *et al.* 1995). The contribution of dry deposition increases on moving from humid to arid climates (Berg & Steinnes 1997b, Couto *et al.* 2004). There are considerable differences in the leaching of elements depending e.g., on whether they are bound to the cell walls or have accumulated on the surface of the mosses (Čeburnis & Valiulis 1999). Uptake efficiency is also affected by competition for free cation exchange sites; for instance, the presence of sea salts and acidic deposition has been found to have an effect on the absorption of metals by mosses (Gjengedal & Steinnes 1990). The type of vegetation and soil dust have also been reported to cause regional differences in uptake efficiency (Čeburnis *et al.* 1999). In general, the best correlation between the concentrations in mosses and in wet deposition have been found for elements (e.g., Pb, Cd, Co, Cu) that have a high uptake efficiency from wet deposition (Ross 1990, Berg *et al.* 1995).

In addition to air pollutants that originate from anthropologic sources, the concentrations in mosses are also affected by many “natural” factors associated with the morphological and physiological properties of the mosses, the site where the mosses are growing, and their immediate environment. There are natural differences in chemical composition between individual species and even between populations of the same species, between individuals with different growth and condition, and between the separate parts of individual mosses (Ross 1990, Thöni *et al.* 1996, Zechmeister *et al.* 2003b). Small amounts of nutrients may pass into the mosses from the substrate (Brown & Bates 1990, Økland *et al.* 1999), and nutrients can also be translocated from one part of the moss to another (Brümelis & Brown 1997). Mineral particles originating from soil and bedrock also increase e.g., the Fe, Cr, Al and Ti concentrations in areas which have a sparse vegetation, an arid climate or exposed mineral soil (Mäkinen 1994, Bargagli *et al.* 1995).

Other factors affecting the concentrations include stand throughfall and leaching from vegetation layers located above the mosses (Steinnes 1993), the nutrient status of the site (Pakarinen & Rinne 1979, Økland *et al.* 1999) and snowmelt water (Ford *et al.* 1995). The concentrations may also vary from one vegetation zone to another (De Caritat *et al.* 2001). The altitude may also have an effect (Zechmeister 1995, Gerdol *et al.* 2002), due e.g., to changes in the amount of precipitation, dust or biomass production. The sampling and measuring methods employed can also have a considerable influence on the analytical results in biomonitoring studies (Markert & Weckert 1989, Steinnes *et al.* 1993, Wolterbeek & Bode 1995). For example, the concentrations obtained in chemical analyses performed by e.g., AAS, ICP-AES or ICP-MS only depict the proportion of elements that dissolve in acid, while methods based on radiation techniques give the total concentration of each element in the material under study (Djingova & Kuleff 2000).

Lichens

Lichens are perennial cryptogams. They live on different types of substrate, usually on dry or nutrient-poor sites in boreal and sub-arctic regions (Nash 1996). The lichen species best suited as biomonitors are foliose and fruticose epiphytic lichens. Lichens consist of a symbiotic association of two organisms: the fungal component is usually an *Ascomycetes* fungus, and the algal component a green alga (*Chlorophyceae*) and/or blue-green alga (*Cyanobacteriae*). The fungal component is responsible for taking up water and minerals, and the algal component, which grows amidst the fungal mycelia, for photosynthesis. Most lichen species obtain their nutrients from wet and dry deposition (Martin & Coughtrey 1982, Garty 1993). They possess many of the same properties as mosses that make them suitable for monitoring purposes: the cuticle and vascular bundles are weakly developed, they do not have any real roots, they are slow-growing and long-lived, and they have an extremely broad distribution (Wolterbeek *et al.* 2003).

Lichens possess the same physiological-chemical mechanisms that affect the accumulation of air pollutants in mosses (Tyler 1989, Richardson 1995). The physiological processes affecting accumulation in lichens have been studied much more than for many other plants. Attempts have also been made to explain the accumulation processes with the aid of mathematical models (Reis *et al.* 1999). These studies have emphasised the significance of lichen morphology and physiology in the accumulation of elements (Brown 1991, Sloof & Wolterbeek 1991a). Clear differences in the accumulation of elements have been found between different lichen species and even different populations as a result of these morphological and physiological differences (Sloof 1995, Bennett & Wetmore 1999).

The sensitivity of lichen species to air pollutants varies. Most species are especially sensitive to SO₂, nitrogen and fluoride compounds and to ozone (Hawksworth & Rose 1970, Kovacs 1992). These compounds affect the condition of lichens and thus reduce the capacity of lichens to accumulate and absorb elements from the atmosphere. Heavy metals have also been found to affect e.g., the permeability of the cell membranes of lichens (Tyler 1989, Tarhanen *et al.* 1996). However, the detrimental effects of heavy metals on e.g., the occurrence of lichens usually only become apparent at high heavy metal concentrations (Van Dobben *et al.* 2001). Heavy metals have also been reported to increase a lack of water in the thallus (Nieboer *et al.* 1976). Air pollutants have a different effect on the fungal and on the algal partner. The algal partner has been reported to react

more sensitively e.g., to acidic deposition and heavy metals, and to show varying accumulation of metals depending on the acidity of precipitation (Demon *et al.* 1989, Tarhanen *et al.* 1999). Sporadic desiccation of lichens may also have an effect on the accumulation and absorption of elements (Puckett 1988). After a dry period, rainfall may result in appreciable washing off of particles and the exchange of cations bound on negatively charged exchange sites on the cell walls and plasma membranes of the cells (Bargagli 1998).

There are a considerable number of factors, associated with the site where lichens are growing, which may change the concentrations of pollutants in lichens (Brown 1991, Garty 2000). These factors are, in most cases, the same as those affecting mosses: quality of the deposition (form of occurrence, composition, pH), climate (composition of precipitation, temperature, wind, drought, length of the growing period) and local environmental factors (vegetation, quality of the substrate, stand throughfall and stemflow, dust derived from soil, altitude of area). On the other hand, throughfall and stemflow, which vary according to the type of canopy cover, have a greater effect on epiphytic lichens than on terricolous mosses (Barkman 1958, Rasmussen 1978). Nutrients and other elements may pass from the substrate into lichens (De Bruin & Hackenitz 1986, Bargagli 1990, Wolterbeek & Bode 1995).

Green algae

Green algae, mainly *Protococcus viridis*, are single-celled organisms, which live in symbiosis with lichens, among other things with *Scoliciosporum chlorococcum*. Their taxonomy is poorly known. Søchting (1997) has found that an algal crust on spruce needles consists of species belonging to the families *Protococcus* spp. (= *Desmococcus* spp.) and *Apatococcus* spp. Green algae occur on trees and other suitable substrata especially in the vicinity of various nitrogen sources (Göransson 1990, Søchting 1997). They obtain nutrients from wet and dry deposition like epiphytic lichens. They require also sufficient high temperature, high humidity and suitable light for their growth. Green algae have increased especially on Norway spruce needles and on tree trunks in recent years in the southern parts of Fennoscandia and in Central Europe (Peveling *et al.* 1992, Thomsen 1992, Poikolainen *et al.* 1998).

Tree bark

The outer bark of trees consists of the inner layer (*phloem*), the cork-forming layer (*phellogen*), and the outer layer (*rhytidom* or *phellem*) composed of dead cork cells (Srivastava 1964, Prance *et al.* 1993). This dead cork layer has usually been employed in biomonitor studies. The quality of bark varies according to the composition of the walls of the phellem and the thickness of the outer and inner bark layers. There are considerable differences in the chemical composition of the bark of different tree species (Barkman 1958). Bark is formed in layers, each new layer being formed below the old layer within a certain period of time, e.g., in Scots pine during a period of about two years (Schulz *et al.* 1999). The old surface layer is dead and no changes occur after it has been formed.

The accumulation of atmospheric pollutants in bark is purely a physiological-chemical process. The pollutants either accumulate passively on the surface of the bark surface or become absorbed through ion exchange processes in the outer parts of the dead cork layer

(Walkenhorst *et al.* 1993, Schulz *et al.* 1997). For example, sulphur accumulates in bark as sulphuric acid (H_2SO_4), most of which subsequently reacts with calcium to form gypsum (CaSO_4) (Kreiner 1986). The accumulation of heavy metals depends on the particle size and on the form in which the metals occur. They form compounds with other elements or occur in particles together with compounds of similar particle size. Heichel and Hankin (1972) reported already at the beginning of the 1970's that particles containing lead derived from traffic emissions in the US were mainly located on the surface or in the surface tissues of bark, and that their size ranged from 3 - 13 μm . Bark acidity has an effect on the concentrations of some heavy metals. For instance, Bates and Brown (1981) found a clear negative correlation between bark pH and the Fe concentration in a study on the occurrence of epiphytic lichens on oak and ash. They concluded that this is due to the increased mobility of Fe with decreasing bark pH.

There is no significant migration of elements from the bark surface through the cork tissue into the underlying wood, or vice versa (Trüby 1988, Schulz *et al.* 1997). Also the migration of heavy metals from the soil via the roots into the bark as it is being formed is also usually insignificant (Trüby 1988). On the other hand, heavy metals and other compounds may be carried by the wind from the soil to the bark surface. The surface structure of the bark has a considerable influence on passive accumulation on the surface of the bark. A coarse, rough surface more readily accumulates atmospheric pollutants than a smooth surface. The study carried out by Szopa and co-authors (1973) on lead concentrations along highways in the US indicated that the lead concentration in bark reacts rapidly to marked changes in lead concentrations in the atmosphere.

In addition to sulphur concentrations, the pH, buffering capacity and electric conductivity of bark can also be used as indicators of atmospheric SO_2 concentrations. Acidic pollutants reduce and alkaline pollutants increase the pH of bark. A clear dependence has been found between the pH and cation concentrations in bark (Farmer *et al.* 1991). When the pH of the bark is low, the amount of exchangeable cations is also low, and vice versa. In addition to pollutants, the pH is also affected by e.g., tree species, tree age and health, weather conditions, the substrate, and the thickness of the sample (Staxäng 1969, Grodzińska 1982). Owing to its lower acidity, the bark of deciduous trees is more sensitive to pH changes than that of conifers (Härtel & Grill 1972). The electrical conductivity of bark is mainly due to the presence of sulphate and other compounds (Kreiner & Härtel 1986). The sulphate concentration of bark has usually also been determined when the conductivity of bark has been used as an indicator (Härtel & Grill 1972). The bark of conifers is more suited to conductivity measurements than that of deciduous trees because the range of conductivity values of conifers is usually greater at the same site than that of deciduous trees (Kienzl 1978). In addition to pollutants, the conductivity of bark values is primarily affected by rainfall, high air humidity and sea salts (Kienzl & Härtel 1979, Poikolainen 1997).

Factors, in addition to atmospheric pollutants, that affect the chemical composition of tree bark are mainly the same as those for mosses and lichen, although the chemical reactions that occur in bark are somewhat different because bark is a non-living plant material. The concentrations in bark are mainly affected by bark quality, stand throughfall and stemflow (Staxäng 1969, Härtel 1982, Schulz *et al.* 1999). In general, the element concentrations in the bark of deciduous trees are much higher than those in coniferous bark (Rasmussen 1978). Even so, there can be considerable differences in concentrations

between conifers. For example, the zinc and manganese concentrations in Norway spruce bark are usually higher than those in Scots pine (Olsson 1978). The concentrations are highest in the surface layers of the outer bark, and decrease rapidly on moving towards the inner layers (Karandinos *et al.* 1985, Schulz *et al.* 1997). Variation in bark concentrations along the stem has also been reported (Barnes *et al.* 1976). Clear seasonal variation has been observed in the conductivity and sulphur concentrations of bark due, for instance, to weather factors and emission levels (Kienzl 1978). In a study carried out by Kosmus and Grill (1986) in Graz, Austria, the microclimate was found to have a significant effect on the amount of pollutant deposition and, through this, on bark concentrations.

No standard methods are available for sampling and analysing bark samples. The following points have to be taken into account when sampling bark: the location and number of sample trees, tree age and health, height of the sampling point on the tree stem, bark quality and sampling time (Staxäng 1969, Wolterbeek *et al.* 1996b, Schulz *et al.* 1997). In order to minimize the effect of variation between individual samples, bulked samples from a number of trees have been used in the analysis of bark samples (Kreiner & Härtel 1986, Huhn *et al.* 1995).

1.3 Use of mosses, lichens and bark as biomonitors specifically in regional surveys

Mosses

The use of mosses as biomonitors for atmospheric pollution became common after suitable methods for sampling and analysing mosses had been developed in Sweden (Rühling & Tyler 1968, Tyler 1970). Mosses have especially been used in regional heavy metal surveys. The first extensive survey was carried out in Scandinavia as early as the end of the 1960's (Rühling & Tyler 1973), and the first national surveys were carried out in Sweden, Norway and Denmark at the turn of the 1970's and 1980's (Steinnes 1977, Pilegaard *et al.* 1979, Rühling & Skärby 1979, Gydesen *et al.* 1983). During the 1980's the surveys expanded to cover all of the Nordic countries (Rühling *et al.* 1987, Rühling 1992) and, in the 1990's, to most of the countries in Europe (Rühling 1994, Rühling & Steinnes 1998, Buse *et al.* 2003). The results of many national surveys have been published during the last decade (Zechmeister 1994, 1997, Steinnes *et al.* 1994, 2001, Liiv *et al.* 1994, 2002, Kuik & Wolterbeek 1995, Markert *et al.* 1996a,b, Herpin *et al.* 1996, Berg & Steinnes 1997a, Čeburnis *et al.* 1997, Siewers & Herpin 1998, Sucharová & Suchara 1998, Galsomiès *et al.* 1999, Grodzińska *et al.* 1999, Gerdol *et al.* 2000, Fernández *et al.* 2000, 2002, Figueira *et al.* 2002, Schröder *et al.* 2002, Ötvös *et al.* 2003, Poikolainen *et al.* 2004a). The moss species most widely used in sampling have been *Hylocomium splendens* and *Pleurozium schreberi*, *Hypnum cupressiforme*, *Scleropodium purum* and *Brachythecium* sp. The purpose of the surveys has been to obtain information on the regional deposition of heavy metals, changes in deposition patterns, the long-distance spread of emissions, and local emission sources.

A considerable number of other regional studies on heavy metal and other element concentrations have been carried out using mosses, primarily in Europe (Ross 1990,

Mäkinen 1994, Äyräs *et al.* 1997, Reimann *et al.* 1997, 1998, 2001, Halleraker *et al.* 1998, Faus-Kessler *et al.* 1999, 2001, De Caritat *et al.* 2001, Grodzińska *et al.* 2003) and in North America (Groet 1976, Rinne & Barclay-Estrup 1980, Pott & Turpin 1998). Metal concentrations have also been investigated in so-called background areas (Carballeira *et al.* 2002), national parks (Grodzińska 1978, Wiersma *et al.* 1995), arctic areas (Ford *et al.* 1995, Riget *et al.* 2000) etc. Time series comparisons of moss concentrations have been carried out using e.g., herbarium samples (Pott & Turpin 1996, Herpin *et al.* 1997). In addition to national surveys, several regional surveys have also been carried out on element concentrations in forest and *Sphagnum* mosses in Finland (Pakarinen 1981a, Pakarinen *et al.* 1983, Rinne & Mäkinen 1988).

A considerable amount of research has been carried out in regional surveys e.g., on analysis and sampling methods (Steinnes *et al.* 1993, Wolterbeek & Bode 1995), the use of reference material (Steinnes *et al.* 1997), moss concentrations in relation to deposition levels (Berg & Steinnes 1997b, Reimann *et al.* 1999), other factors affecting concentrations (Zechmeister 1998, De Caritat *et al.* 2001, Fernández & Carballeira 2002), differences between moss species (Thöni *et al.* 1996, Halleraker *et al.* 1998), mosses as deposition accumulators in relation to other biomonitors (Bargagli *et al.* 2002), accumulation efficiency (Gjengedal & Steinnes 1990, Čeburnis *et al.* 1999), and analysis of the data (Schaug *et al.* 1990, Kuik & Wolterbeek 1995). Pollution indices have been calculated on the basis of the concentrations (Grodzińska *et al.* 1999), background area and contamination factor values (Fernandez *et al.* 2002), as well as absolute deposition values (Berg *et al.* 1995, Sucharová & Suchara 2004). Ever increasing attention has been focused on the effects of heavy metal deposition on human health (Wappelhorst *et al.* 2000, Wolterbeek 2002).

The use of mosses as accumulation indicators of nitrogen and sulphur in air quality monitoring has been relatively neglected. In general, nitrogen concentrations in mosses has been found to correlate rather well with the concentrations in rainwater (Baddeley *et al.* 1994, Pitcairn *et al.* 1995). Mosses have never been considered to be very good biomonitors for sulphur concentrations, although e.g., Pakarinen (1981b) reported that the sulphur concentrations in *Sphagnum* mosses correlate well with atmospheric SO₂ concentrations. The main reason for the poor biomonitoring value may be the fact that sulphur can damage plants in high concentrations (Äyräs *et al.* 1997). Relatively few extensive surveys have been carried out on the sulphur and nitrogen concentrations of mosses. Sulphur and nitrogen concentrations in mosses have usually been determined as a part of more comprehensive heavy metal and trace element analyses (Halleraker *et al.* 1998, Sucharová & Suchara 1998).

Lichens

Of the living organisms used as atmospheric indicators, lichens have been studied the most. Atmospheric pollutants have been known to have an effect on the occurrence of epiphytic lichens since the 19th century (Nylander 1866). The most work has been carried out on the effects of SO₂, either directly from the atmosphere or via the substrate, on the occurrence and abundance of epiphytic lichen, (Gilbert 1986, Farmer *et al.* 1991, Van Dobben *et al.* 2001). A range of air purity indices have been developed based on the occurrence of lichens (De Sloover & LeBlanc 1968). Several regional and even national surveys have been carried out on the relationship between the occurrence of epiphytic

lichen and atmospheric pollutants (Bruteig 1993, Van Dobben & De Bakker 1996, Poikolainen *et al.* 2000). Hundreds of studies have been published on the effects of sulphur dioxide, nitrogen compounds, ozone, heavy metals and other atmospheric pollutants on the morphology and physiology of lichens since the 1950's (see Nash & Wirth 1988, Richardson 1992, Garty 2000). These studies have primarily been experimental. Even in Finland these types of study have a long tradition (e.g., Huttunen 1975, Kauppi 1980).

Lichens have also been employed among other things as accumulation indicators of heavy metals (Nieboer *et al.* 1972, Freitas 1994) as well as sulphur and nitrogen compounds (Nimis *et al.* 1990, Søchting 1995) derived from industrial activities and power production in a countless number of studies carried out in the surroundings of emission sources. Tens of studies of this type have been performed also in Finland, e.g., in the surroundings of metal and steel works and smelters (Laaksovirta & Olkkonen 1977, Mukherjee & Nuorteva 1994), power plants (Nygård & Harju 1983), chlorine plants (Lodenius & Laaksovirta 1979), cement factories (Kortesharju & Kortesharju 1989) and pulp mills (Laaksovirta & Olkkonen 1979). The occurrence of heavy metals in urban areas has also been investigated using lichens (Kauppi & Halonen 1992, Bargagli *et al.* 1997) and along the highways (Laaksovirta *et al.* 1976, Martin & Coughtrey 1982). Lichens have been proven to be good accumulators of heavy metals, and that the concentrations correlate well with the concentrations measured in deposition. The concentrations have been very high near the emission sources, and they have decreased exponentially with increasing distance from the emission sources (Nieboer *et al.* 1972, Pilegaard 1979).

Lichens have not been used as accumulation indicators of atmospheric pollutants in extensive surveys to the same extent as mosses. National surveys have been carried out on heavy metals and micronutrient concentrations in lichens in e.g., Finland (Kubin 1990), the Netherlands (Sloof & Wolterbeek 1991b, 1993), Portugal (Reis *et al.* 1996, Freitas *et al.* 1999) and Slovenia (Jeran *et al.* 1996). Bruteig (1993) investigated the sulphur and nitrogen concentrations of *Hypogymnia physodes* on a national scale in Norway. Numerous regional surveys on epiphytic and terricolous lichens concentrations have been performed in different parts of the world. One of the first extensive surveys was the study on the element concentrations of 20 different lichen species in background areas of North-west Canada in the 1970's (Puckett & Finegan 1980). A number of regional time series comparisons have been carried out on the element concentrations of lichens (Walther *et al.* 1990, Bennett & Wetmore 1999). In many studies the concentration determinations have been combined with investigations on the occurrence of lichens (Herzig *et al.* 1989, Jeran *et al.* 2002).

In addition to Kubin's (1990) national survey, several other regional investigations have been made on sulphur, nitrogen and heavy metal concentrations in epiphytic lichens in Finland. The following have been investigated on a national scale: mercury concentrations of *Hypogymnia physodes* (Lodenius 1981), sulphur concentrations of epiphytic and terricolous lichens (Takala *et al.* 1985), the relationships between iron concentrations and titanium and sulphur concentrations (Takala *et al.* 1994), and sulphur isotopes (Takala *et al.* 1991). Regional studies have also been carried out on element concentrations in reindeer lichens on both mineral soils and ombrotrophic peatlands (Pakarinen *et al.* 1978, Pakarinen 1981b). One feature common to all these studies has

been the decrease in the concentrations of sulphur, nitrogen and most of the heavy metals studied on moving from southern to northern parts of Finland. Tens of smaller regional studies have been made on sulphur, nitrogen and heavy metal concentrations of epiphytic lichens in different parts of the Finland (Kauppi & Mikkonen 1980, Halonen *et al.* 1993, Jussila 2003). These studies have usually been carried out in connection with regional environmental surveys. The condition of lichens has usually also been evaluated, and biomonitors other than epiphytic lichen investigated.

Tree bark

It has for long been known that atmospheric sulphur and nitrogen compounds affect the acidity of bark and, as a result, affect the occurrence of epiphytic lichens (Barkman 1958). Ever since a correlation was reported between the pH of the bark of deciduous forest trees and sulphur deposition in Sweden during the 1960's (Skye 1968, Staxäng 1969), bark has been extensively used as an indicator of atmospheric SO₂ concentrations. Especially in Central Europe in the 1970's, the quality of air in urban areas was studied on the basis of the acidity, buffering capacity and sulphur concentration of bark. A clear correlation between bark pH and atmospheric SO₂ concentrations has, in general, been reported in most studies (Grodzińska 1971, Lötschert & Köhm 1973, Kienzl 1978). The effects of alkaline emissions on bark pH has also been investigated to some extent (Świeboda & Kalemba 1979, De Bakker 1989). The conductivity of bark also readily changes in response to atmospheric SO₂ concentrations. Härtel and Grill (1972) developed the "bark test", in which the conductivity and sulphate concentration of Norway spruce bark is determined. The test has been used extensively in Austria, e.g., in studies on air quality in urban areas (Kienzl 1978, Kosmus & Grill 1986). Similar studies have also been carried out to some extent elsewhere (Lötschert & Köhm 1977, Godoy *et al.* 1989, Suchara 1993). High correlation between bark sulphur concentrations and atmospheric SO₂ concentrations have also been reported (Johnsen & Søchting 1973, Punz & Schininger 1982).

pH, conductivity and sulphur concentration have rarely been used as a biomonitor for atmospheric SO₂ concentrations over large areas. Moser and co-authors (1993) carried out an air quality survey, based on the bark test mentioned earlier, in southern parts of Austria. The spreading of industrial emissions has been investigated on the basis of the sulphur concentration, pH and conductivity of bark e.g., in industrial areas in Germany (Stöcker & Huhn 1994) and in Northern Finland in an area affected by emissions from smelters on the neighbouring Kola Peninsula (Poikolainen 1997). A number of other regional surveys were carried out throughout the 1990's in Europe on micronutrient concentrations of bark, sulphur being one of the large number of elements determined (Wolterbeek *et al.* 1996b, Böhm *et al.* 1998, Schulz *et al.* 1999, 2000). Bark has also been used in regional surveys on isotopes of sulphur and nitrogen (Takala *et al.* 1991, Schulz *et al.* 2001).

Bark has also been used rather frequently in biomonitoring heavy metal emissions since the 1970's. It has primarily been used to survey the spread of heavy metal emissions from industry and traffic. Heavy metal emissions from industrial activities have been studied around emission point sources (Symeonides 1979, Kling *et al.* 1985, Kansanen & Venetvaara 1991), as well as in industrial areas (Türkan *et al.* 1995, Schulz *et al.* 1999). In studies on lead emissions from traffic, the lead concentration of bark has been found to

correlate well with e.g., traffic density (Hampp & Höll 1974, Ward *et al.* 1974, Laaksovirta *et al.* 1976), atmospheric CO concentrations, and negatively with the manganese concentration of bark (Lötschert & Köhm 1978). In some surveys performed in urban areas, the heavy metal concentrations of bark have been found to be higher in industrial areas and in city centres (Lötschert & Köhm 1978, Karandinos *et al.* 1985). The development of analytical techniques in recent years has meant that some elements that occur in bark in extremely low concentrations have also been studied. For instance, elements that are released into the atmosphere from traffic (Forget 1994), as well as radioactive elements (Bellis *et al.* 2000).

Tree bark has been used in some surveys of heavy metals and other elements on a national or regional scale (Herman 1992, Kuik & Wolterbeek 1994, Huhn *et al.* 1995, Lippo *et al.* 1995, Poikolainen 1997, Böhm *et al.* 1998). Takala and co-authors (1994) studied the relationship between iron concentrations and sulphur and titanium concentrations in Scots pine bark and lichens, and found that the iron concentrations of both lichens and bark correlated with the titanium concentrations. During the last decade, the use of bark for monitoring atmospheric pollutants has become a much more versatile tool. Statistical analyses have been used to determine, e.g., the source of the heavy metals and other pollutants in bark (Kuik & Wolterbeek 1994, Böhm *et al.* 1998). Models have even been used to calculate, on the basis of the element concentrations in pine bark, the level of sulphate, ammonium, nitrate, calcium and iron deposition in pine forests (Schulz *et al.* 1997). The temporal variation in the concentrations of heavy metals and a number of pollutants in tree bark has also been studied to some extent in industrial and background areas (Schulz *et al.* 1999). Satake and co-authors (1996) investigated the lead concentration in so-called "bark pockets", formed 186 - 255 years ago, in Japanese cedar (*Cryptomeria japonica*), and compared the concentrations with those in the same species in the 1990's.

The bark of over 40 different tree species has been used in biomonitoring studies in Europe. The most commonly used tree species are *Acer platanoides*, *Aesculus hippocastanum*, *Fraxinus excelsior*, *Quercus robur*, *Tilia cordata*, *Picea abies*, and *Pinus sylvestris*. Studies on the usefulness of different biomonitors have increased in Central Europe especially, where the high population density makes it difficult to obtain suitable biomonitors. As bark is usually readily available even in the most densely populated areas, it has been considered to be a useful biomonitor in e.g., urban areas. However, the more widespread use of bark as a biomonitor has been restricted by the lack of acceptable sampling and analysis methods.

2 Aims of the research

The main objective of the research was to investigate the deposition of air pollutants in Finland using different biomonitors, the changes occurring in deposition over time, and the effects of deposition on the abundance of green algae growing on conifers. Most of the studies have been carried out on the permanent sample plots of the National Forest Inventory (NFI), which were established between 1985 and 1986 to monitor forest condition. The heavy metal determinations on mosses are a part of the surveys covering almost all of the European countries, which were coordinated in 1990 and 1995 by the University of Lund in Sweden and, since 2000, by the ICP Vegetation programme. The studies on bark in northern Finland and on the Kola Peninsula, northwest Russia, are related to the "Lapland Forest Damage Project" which investigated the effects of emissions from the large Cu-Ni smelters on the Kola Peninsula on the health of forest ecosystems in Lapland. The most important objectives of the study were:

1. To investigate the deposition of the most common heavy metals in Finland on the basis of their concentrations in mosses (*Hylocomium splendens*, *Pleurozium schreberi*), the changes that took place in heavy metal deposition patterns during 1985 to 2000, and to identify the major emission sources (Publication **I**).
2. To compare the suitability of mosses (*Hylocomium splendens*, *Pleurozium schreberi*), epiphytic lichens (*Hypogymnia physodes*) and Scots pine bark as biomonitors of heavy metals on a national scale (Publication **II**).
3. To investigate, on the basis of the pH, electrical conductivity and sulphur and heavy metal concentrations in Scots pine bark, the dispersal of emissions from the large emission sources on the Kola Peninsula into northern Finland (Publication **III**).
4. To investigate the occurrence of green algae on conifers in Finland in relation to climatic and site factors, the nitrogen concentrations in biomonitors collected on the same sample plots, and the nitrogen deposition levels modelled for the same plots (Publication **IV**).
5. To investigate the importance of the long-term storage of bimonitor samples in regional surveys, improvements to the storage methods, and the possibilities of using the stored samples in joint studies (Publication **V**).

3 Material and methods

3.1 Study areas, observation and sampling

3.1.1 National heavy metal surveys using mosses, lichens and bark

Between the years 1985 and 1986 the Finnish Forest Research Institute (Metla) established a permanent sample plot network in connection with the 8th National Forest Inventory (NFI). The primary objective of establishing the sample plots was to monitor the changes taking place in the forests. In addition to changes in the trees and forest vegetation, forest health and vitality have also been monitored on the sample plots. This monitoring activities have involved the use of bioindicators such as heavy metal surveys on mosses, epiphytic lichens and pine bark (**I, II**), as well as surveys of the occurrence of epiphytic lichens on conifers (**IV**, Kuusinen *et al.* 1990, Poikolainen *et al.* 2000). The NFI sample plot network comprises a total of over 3 009 sample plots located throughout Finland (Fig. 1). The network consists of sample plot clusters located at fixed distances from each other (**I**).

Moss samples were collected from the sample plots in 1985, 1990, 1995 and 2000, lichen samples in 1985 and 1990, and bark samples in 1985 (**I, II**). The moss samples were collected according to the Nordic guidelines (Rühling *et al.* 1987, Kubin *et al.* 2000). The samples were taken on level ground in openings between the trees in order to ensure that neither throughfall nor soil water affect the element concentrations in the mosses. The size of the sampling area was approximately 50 m x 50 m. The principle moss species sampled was feather moss (*Hylocomium splendens*) or, if it was not present, red-stemmed feather moss (*Pleurozium scrobeberi*).

The lichen samples were collected from the dominant tree species at points located outside the actual sample plot (Kubin 1990). The principle species sampled was *Hypogymnia physodes* or, if it was not present in sufficient amounts, *Pseudevernia furfuracea* was collected in coastal areas and *Melanelia olivacea* in Northern Finland. Samples were taken at a height of ca. 1 - 2 m from ground level on at least 3 trees. In the

case of full-grown pines the sample was taken from the trunk, and in the case of saplings from the base of the dead lower branches. In the case of spruce the samples were collected from branches, and in the case of deciduous trees from the trunk and dead branch stubs.

The bark samples were collected from pine trees, located outside the actual sample plot, that represented the average age of the dominant tree species of the compartment (Reinikainen & Nousiainen 1985). Composite samples were taken from 3 trees at a height of 1 - 2 m around each trunk. Approximately equal amounts of sample were taken from each tree.

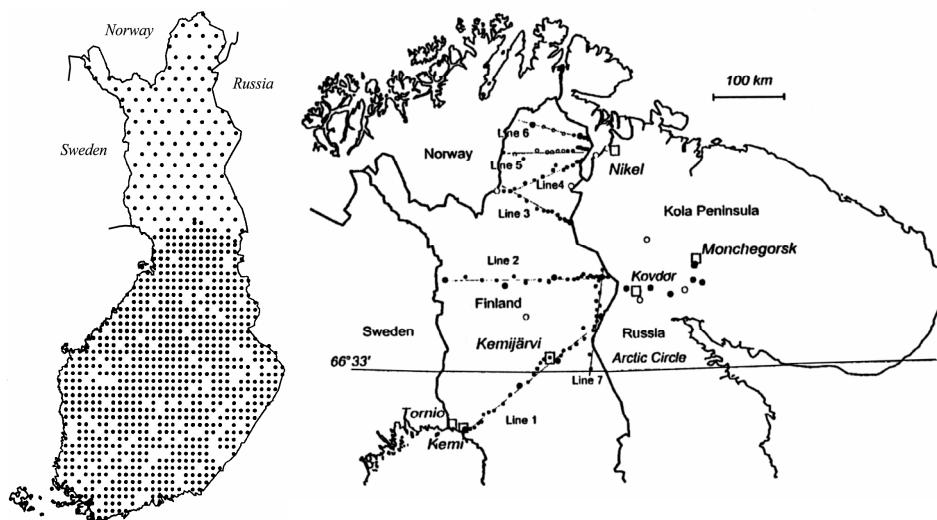


Fig. 1. Left: NFI permanent sample plots, right: Sample plots of the Lapland Forest Damage Project.

3.1.2 Regional studies on pine bark

One of the sub-projects ('The vitality of forest vegetation in Lapland, and changes in vitality since the 1950's) in the Lapland Forest Damage Project was centred on the effects of pollution emissions from the Kola Peninsula on sulphur and heavy metal concentrations in pine bark (Tikkanen & Niemelä 1995, III). The bark samples were collected in July 1991 from 110 sample plots located along six transects running across Lapland and from one transect close to the eastern border of Finland (Fig. 1). Six of the sample plots were situated on the Russian side, between Monchegorsk and the Finnish border. Composite samples were collected from around the trunk at breast height on five living pines. Sampling was performed in the same way as in the national bark study mentioned earlier.

3.1.3 National surveys on the abundance of green algae

The studies on green algae were associated with the national epiphytic lichen surveys on conifer trees carried out in 1985 and 1995 (Kuusinen *et al.* 1990, Poikolainen *et al.* 2000). The surveys were made on the same NFI permanent sample plot network as the heavy metal surveys using biomonitors. Thirteen different lichen species or families that commonly occur on conifers and are sensitive to atmospheric SO₂ concentrations were chosen for the surveys. *Scoliciosporum chlorococcum* and green algae represented resistant species in the survey. The occurrence and abundance of these organisms on conifers with respect to climatic and site factors, as well as to the nitrogen concentrations of biomonitors collected on the same plots and to nitrogen deposition levels modelled for the plots, were investigated in paper IV of this thesis. *Scoliciosporum chlorococcum* and green algae were considered as one entity in the surveys, even though green algae includes many species and the individual species behave to somewhat differently with respect to e.g., atmospheric sulphur and nitrogen concentrations.

3.2 Chemical analysis and other measurements

3.2.1 Element analysis of mosses, lichens and bark

In the national and regional surveys the moss, lichen and bark samples were first dried at a temperature of 35 °C and all the extraneous plant litter was removed. Annual shoots from the 3 years preceding the collection year were separated from the moss samples and a 3 mm thick surface layer was removed from the bark samples for analysis (I, II). The thallus of the lichens was used as such for analysis. Ca. 2 g of moss, lichen and bark from each sample plot were required for the analyses. The remainder of the samples were stored in the Paljakka environmental specimen bank for future requirements (V).

After separation and milling, the moss, lichen and bark samples were wet digested in a mixture of nitric acid and perchloric acid (HNO₃/HClO₄). The Cd, Cr, Cu, Fe, Ni, Pb, V, Zn and S concentrations were determined by inductively coupled plasma atomic emission spectrometry (ICP/AES). The total nitrogen concentration was determined using a modified micro-Kjeldahl method (Kubin & Siira 1980). The As concentration of moss samples collected in 1995 and 2000 was determined by graphite furnace atomic absorption spectrometry (GF-AAS) (Perämäki *et al.* 2000), and the Hg concentration by CV-AFS (Lippo *et al.* 1997). Commercial reference material was used as reference material, as well control material prepared from moss samples in the moss analyses (Steinnes *et al.* 1997). Determination of other elements (Al, Ca, Co, K, Mg, Mn, Na and Ti) is described in details in included papers (II, III).

3.2.2 *pH and electrical conductivity of bark samples*

For measuring electrical conductivity and pH, 1.5 grams of finely milled bark was mixed with 15 ml of deionised water and left to stand for 24 hours (III). Conductivity and pH were measured with a combined pH and conductivity meter (Radiometer PHM82 and CDM3).

3.2.3 *Estimation of the abundance of green algae*

The abundance of epiphytic lichens and green algae was estimated on the trunk and branches at a height of 0.5 - 2.0 m above ground level on the three dominant trees located closest to the mid-point of each plot in the NFI permanent sample plot network (IV). The abundance was estimated on a scale of 0 - 3, in which 0 = no lichens or green algae, 1 = small amounts, 2 = relatively abundant and 3 = abundant. Comparison of the abundance of lichens and green algae between 1985 and 1995 was performed on the same trees.

3.3 Statistical methods

The results of the national heavy metal surveys on mosses, lichen and bark are based on the values for individual clusters. An average value was calculated for each cluster for each of the heavy metals on the basis of the average of the sample plots in each cluster. This value was used in determining the average, minimum and maximum concentration values for the whole country. However, the cluster-wise value for bark was based on one sample collected from only one of the plots in a cluster.

The statistical significance of the differences between the heavy metal concentrations in the different years of the moss surveys, as well as for mosses, epiphytic lichens and bark, were determined using the Tukey test (I, II). In the studies of the Lapland Forest Damage Project a regression model was used to explain the sulphur and heavy metal concentrations in bark (III). The variables were the distance from the emission sources in Monchegorsk and Nikel, and the SO₂ dispersion model calculated for the area (Tuovinen *et al.* 1993).

The abundances of *Scoliciosporum chlorococcum* and green algae on the NFI sample plots were compared to the modelled values of NO_x, NH₄ and S deposition for the same plots (IV). The deposition values were calculated using the HILATAR model, developed by the Finnish Meteorological Institute (Hongisto 1998). The abundance of green algae was also compared to the nitrogen concentration of biomonitors, climatic parameters and site factors. The effective temperature sums for the sample plots were calculated using information from the weather stations of the Finnish Meteorological Institute (Meteorological yearbooks 1986-1995) and the model developed by Ojansuu and Henttonen (1983). The Spearman correlation test and the χ^2 test were used when comparing the abundance of green algae to the variables mentioned above (IV).

3.4 Compilation of the maps

Maps of the heavy metal and nitrogen concentrations in mosses for the whole country were made on the basis of the cluster-wise average values using the kriging interpolation technique (I, Krige 1951). Suitable colours were chosen for the maps and concentration classification in order to clearly illustrate changes in the heavy metals concentrations during the 1985 and 2000 study period. The same technique was used for the maps representing the abundance of green algae in 1985 and 1995, and also for the modelled NO_x and NH_4 deposition values for 1993.

3.5 Long term storage of the samples

Approximately half of the moss, lichen and bark samples collected from the NFI permanent sample plots and in regional studies have been used for the analyses, and the remaining part of the samples have been stored for future research purposes in the environmental specimen bank at Paljakka, Puolanka (V). All of Metla's dried plant samples that require long-term storage are lodged in the Paljakka environmental specimen bank. The floor area of the specimen bank is 770 m², of which ca. half is storage area. It also has premises for drying, pretreating and milling samples. The storage premises meet international standards. Special attention has been paid e.g., to fire safety in the construction of the sample bank. The temperature and humidity of the storage facilities is constantly monitored. Random tests are performed annually in order to prevent damage by pests and other damaging agents, e.g., mould, from affecting the samples.

The dried moss, lichen and bark samples are stored in paper bags in standard boxes in the individual storage rooms in the sample bank. The boxes are located on movable shelves that afford easy access to the samples for use in future research. Information about the samples is stored in the database. This includes e.g., information on sample species, sampling site, time of collection, and the location of the samples in the storage facility.

4 Results

4.1 Mosses, lichens and bark as biomonitors of air pollutants in national surveys

4.1.1 Mosses as heavy metal biomonitors

The heavy metals analysed in the national survey on mosses were divided into three groups on the basis of their concentrations (**I**). The first group included Pb, V and Cd. The concentrations of these metals were clearly the highest in southern Finland, and decreased gradually on moving from south to north with the lowest concentrations in northern Finland. The concentrations were also somewhat higher in western Finland compared to eastern Finland. The second group consists of Fe, Zn, Hg and As. Their concentrations also decreased from south to north, but the changes were considerably smaller and did not decrease as regularly as for Pb, V and Cd. The third group comprised Cu, Ni and Cr. The variation in the concentrations of these metals in background areas in different parts of the country were relatively small, but their concentrations were clearly elevated in the vicinity of a number of major local emission sources. However, there was a slight overall decrease in the concentrations of these metals on moving from south to north. The concentrations of Cu and Ni over an extensive area in southwest Finland were considerably affected by emissions from smelter at Harjavalta, and over an extensive area in northeast Lapland by the large Cu and Ni emissions from the smelters on the Kola Peninsula. Refined steel mill in Tornio had a considerable effect on Cr concentrations in southwest Lapland.

The concentrations of all of the heavy metals decreased during the monitoring period (**I**). The decrease in concentrations was, apart from that for Hg, statistically significant ($p < 0.0001$). The concentrations of Pb (78 %), V (70 %) and Cd (67 %) decreased the most. The decrease was clearly evident throughout Finland (also in background areas), but the decrease was relatively the greatest in southern Finland. Concentrations of the other heavy metals decreased to a considerably smaller extent: Cu 34 %, Fe 32 %, Zn 24 %, Ni

18 % and Cr 16 %. The concentrations of As and Hg decreased by 26 % and 10 %, respectively, from 1995, when they were first analysed in mosses, to 2000. The concentrations of Fe, Zn, As and Hg decreased throughout the country. The concentrations of Cu, Ni and Cr clearly decreased in the vicinity of the emission sources throughout the 1990's, but there was only a very small decrease in background areas. There was no clear decrease in concentrations in northeast-Lapland, in the vicinity of the Kola smelters.

All of the most important heavy metal emission sources in Finland and neighbouring areas were clearly distinguishable in the surveys (I). The Harjavalta and Kola smelters were clearly identified as emission sources of Cu and Ni. Smaller emission sources included the mines at Pyhäsalmi, Hitura and Outokumpu. The only significant emission source of Cr was the steel refinery in Tornio. The emission sources of Fe included the industrial plants in Raahe and Koverhar, of Zn the factories in Kokkola and Imatra, and of Zn, Hg and As the smelter in Kokkola. Identifying individual emission sources in southern Finland was much more difficult than in central or northern Finland owing to the higher concentrations in background areas in the south.

The highest concentrations of heavy metals occurred in the vicinity of the largest emission sources or in urban areas in southern Finland. The lowest concentrations occurred, in general, in mosses sampled in northwest Lapland. The highest and lowest concentrations of the individual heavy metals in the survey period between 1985 and 2000 were: As 1.07 - < 0.10 µg/g, Cd 1.46 - 0.01 µg/g, Cr 23.8 - < 0.05 µg/g, Cu 260 - 1.26 µg/g, Fe 3150 - 51 µg/g, Hg 0.180 - 0.014 µg/g, Ni 79.7 - 0.46 µg/g, Pb 49.9 - 0.65 µg/g, V 42.7 - 0.17 µg/g and Zn 137 - 11.5 µg/g. The highest concentrations usually occurred in the first survey, and the lowest in the last survey.

Significant correlation was found between the Cu and Ni concentrations in the material for the whole country in the 1985 and 2000 surveys, which indicates that they have the same emission sources (Table 1). A moderately good correlation was also found between the Pb, Cd and V concentrations in mosses. Lead concentrations correlated moderately also with the As, Hg and S concentrations. Pb, Cd, V, As, Hg and S are considered to be air pollutants that are readily subjected to long-distance dispersion. No correlation was found between e.g., Ni and V, even though both metals are frequently associated with emissions from the oil-refining industry.

Table 1. Correlation between heavy metals and sulphur concentrations in mosses in 1985 and 2000; r = correlation coefficient.

	As	Cd	Cr	Cu	Fe	Hg	Ni	Pb	S	V	Zn
<i>As 1985</i>	•	-	-	-	-	-	-	-	-	-	-
<i>As 2000</i>	•	-	-	-	-	-	-	-	-	-	-
<i>Cd 1985</i>	-	•	-	-	-	-	-	-	-	-	-
<i>Cd 2000</i>	0.326	•	-	-	-	-	-	-	-	-	-
<i>Cr 1985</i>	-	0.101	•	-	-	-	-	-	-	-	-
<i>Cr 2000</i>	0.288	0.198	•	-	-	-	-	-	-	-	-
<i>Cu 1985</i>	-	0.339	0.082	•	-	-	-	-	-	-	-
<i>Cu 2000</i>	0.365	0.358	0.097	•	-	-	-	-	-	-	-
<i>Fe 1985</i>	-	0.358	0.212	0.203	•	-	-	-	-	-	-
<i>Fe 2000</i>	0.585	0.277	0.500	0.267	•	-	-	-	-	-	-
<i>Hg 1985</i>	-	-	-	-	-	•	-	-	-	-	-
<i>Hg 2000</i>	0.450	0.399	0.246	0.310	0.381	•	-	-	-	-	-
<i>Ni 1985</i>	-	0.304	0.092	0.944	0.192	-	•	-	-	-	-
<i>Ni 2000</i>	0.326	0.235	0.094	0.815	0.130	0.161	•	-	-	-	-
<i>Pb 1985</i>	-	0.528	0.181	0.197	0.639	-	0.161	•	-	-	-
<i>Pb 2000</i>	0.512	0.616	0.262	0.341	0.499	0.575	0.155	•	-	-	-
<i>S 1985</i>	-	0.444	0.096	0.165	0.574	-	0.120	0.654	•	-	-
<i>S 2000</i>	-	-	-	-	-	-	-	-	•	-	-
<i>V 1985</i>	-	0.352	0.148	0.051	0.588	-	0.066	0.667	0.521	•	-
<i>V 2000</i>	0.507	0.427	0.450	0.215	0.811	0.353	0.081	0.743	-	•	-
<i>Zn 1985</i>	-	0.489	0.089	0.288	0.353	-	0.192	0.415	0.493	0.290	•
<i>Zn 2000</i>	0.409	0.576	0.172	0.247	0.360	0.495	0.065	0.571	-	0.477	•

4.1.2 Comparison of mosses, lichens and bark as biomonitors

Mosses, lichen and pine bark gave approximately the same result about heavy metal deposition (II). The concentrations of Pb, Cd, V, Fe and Zn in all three biomonitors were at their highest in southern Finland and decreased on moving northwards. The decrease in lichens and especially in bark, was less than that in mosses. The Cu and Ni emissions from the largest point sources, such as the smelters at Harjavalta and on the Kola Peninsula and the Cr emissions from the Tornio steel works, were clearly evident in all three biomonitors. However, the decrease in the sulphur concentration in bark along the south-north gradient was not as clear as that in mosses and lichens.

Mosses, lichens and bark accumulated the individual heavy metals in different ways. Lichens accumulated all the heavy metals more, when expressed on a dry weight basis, than mosses on the average, and clearly more than bark. The concentration of the individual heavy metals per dry weight in mosses varied from 36 to 91 % of that in lichens, and in bark from 17 % to 49 % of that in lichens (II). Lichens and mosses accumulated relatively more Fe, Ti and Cr than bark. Although lichens accumulated more heavy metals than mosses when calculated on a dry weight basis, the concentrations in

mosses were of more use than those in lichens for identifying emission sources. The concentrations of most of the heavy metals were of the same level or even higher in mosses close to the emission sources than in lichens, while in background areas the metal concentrations in lichens were, on the average, higher than those in mosses. In most cases it was more difficult to identify emissions sources on the basis of the concentrations in bark, and the variation in bark concentrations was smaller.

The metal concentrations in mosses are presented in Fig. 2 in relation to the corresponding concentrations in bark and in lichens. The first point always contains the mean of the 50 highest moss concentrations and the means of the corresponding concentrations for lichens and bark on the same plots. The next point contains the mean of the next 50 highest concentrations in mosses, and so on. The deviation of the concentrations of all the metals in lichens was to some extent smaller than that in mosses, and the deviation of the concentrations in bark considerable smaller than that in mosses and in lichens. The concentrations of Al, Fe, and Ti in mosses and lichens, which are metals usually associated with soil, were similar but, the cleaner the area, the greater were the differences in the concentrations of these metals. In the case of Cu, Ni and Cr, which are usually associated with point emission sources, the concentrations in mosses and lichens were very similar at high concentrations, but the differences between the metals increased at low concentrations. The situation was also relatively similar for Pb and S concentrations in mosses and lichens. In contrast, the level of and deviation in the Pb and S concentrations of bark were considerable smaller than for mosses and lichens. There were considerable differences between the Cd and Zn concentrations of the different biomonitors.

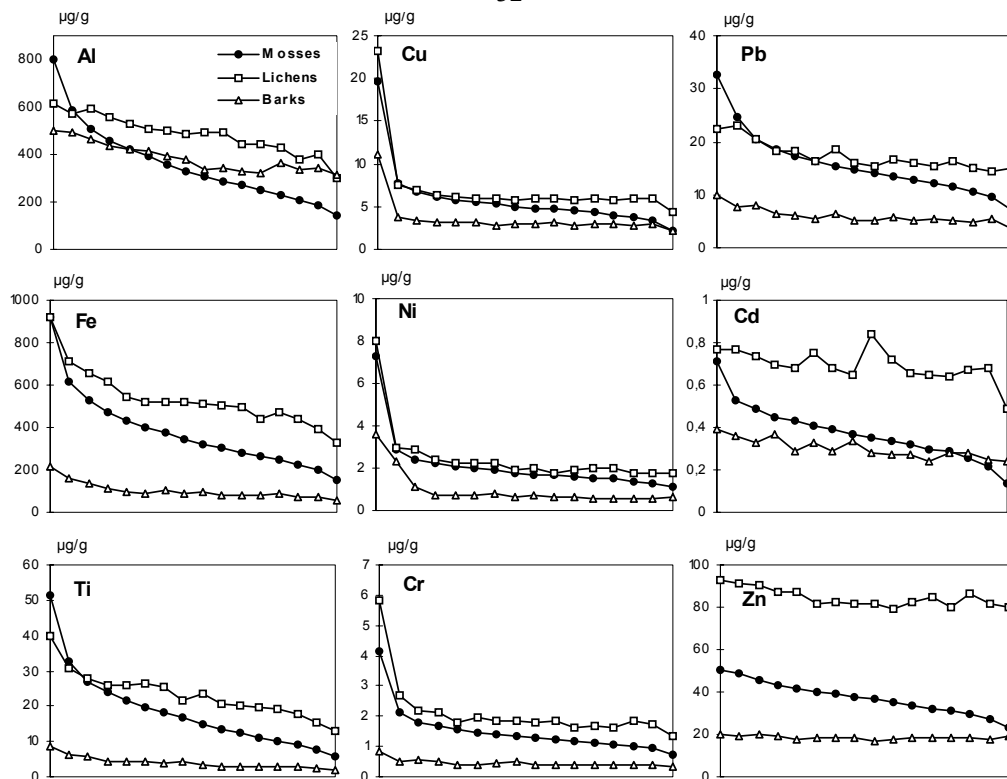


Fig. 2. The metal concentrations ($\mu\text{g/g}$) in mosses as the 50-plot mean from the largest to the smallest in relation to the same 50-plot means of corresponding concentrations in lichens and bark.

The concentrations of heavy metals estimated using different biomonitors correlated very variable with each other (Table 2). The best correlations between the concentrations in mosses and lichens were between Cu, Ni and Cr, between Ti and Fe, for mosses and bark between Cu, V, Ti and Fe, and for lichens and bark between Cu, Ti and Fe. The weakest correlations between concentrations in mosses and the two other biomonitors were between Pb, Cd and Zn, which are considered to be metals that are readily subjected to long-distance dispersal. The correlation between the Pb and Cd concentrations in the different bioindicators was surprisingly weak ($r < 0,400$). For S, too, the correlation between the concentrations in especially bark and the two other bioindicators was very small. The correlations appeared to be the strongest for those heavy metals that mainly remained in the vicinity of the emission sources (Cu, Ni, Cr, Fe), and weakest for those metals which are readily dispersed over relatively large distances from the emission sources (Pb, Cd, Zn). The correlations between the concentrations of macronutrients (Ca, K, Mg, N) in the different biomonitors were weak.

Table 2. Element concentrations ($\mu\text{g/g}$) and the correlation coefficients (r) between them in mosses, lichens and bark.

Element	Moss $\mu\text{g/g}$	Lichen $\mu\text{g/g}$	Bark $\mu\text{g/g}$	Moss/ Lichen	Moss/ Bark	Lichen/ Bark
Al	362 \pm 166	487 \pm 147	388 \pm 134	0.490	0.410	0.312
Fe	384 \pm 195	539 \pm 221	102 \pm 67	0.649	0.648	0.662
Ti	18.65 \pm 12.03	23.43 \pm 10.27	4.06 \pm 2.97	0.661	0.649	0.700
Cu	5.92 \pm 8.66	7.19 \pm 9.03	3.53 \pm 5.54	0.900	0.887	0.957
Ni	2.17 \pm 3.16	2.50 \pm 2.85	0.96 \pm 2.77	0.863	0.585	0.539
Cr	1.51 \pm 1.15	2.12 \pm 2.41	0.46 \pm 0.28	0.830	0.437	0.466
Pb	15.82 \pm 6.22	17.37 \pm 8.01	5.98 \pm 3.59	0.294	0.382	0.226
Cd	0.38 \pm 0.14	0.70 \pm 0.30	0.30 \pm 0.13	0.174	0.330	0.168
V	4.88 \pm 2.92	-	1.53 \pm 1.12	-	0.680	-
Zn	38.07 \pm 8.78	84.55 \pm 17.19	18.54 \pm 5.32	0.232	0.143	0.328
Ca	2353 \pm 475	3178 \pm 2908	3526 \pm 1096	0.067	0.030	0.093
K	4333 \pm 844	2684 \pm 574	212 \pm 51	0.210	-0.087	0.075
Mg	743 \pm 195	390 \pm 95	81 \pm 19	0.226	0.227	0.460
Mn	350 \pm 122	127 \pm 82	47 \pm 18	0.311	0.376	0.338
S	960 \pm 176	1082 \pm 249	373 \pm 71	0.489	0.187	0.216
N %	-	0.85 \pm 0.28	0.45 \pm 0.11	-	-	0.317

4.1.3 Abundance of green algae on conifers

In the national survey carried out on the NFI permanent sample plots in 1985, *Scoliciosporum chlorococcum* and green algae occurred on conifers only in southern and central Finland up to latitude 65° N (IV). Apart from in the Greater Helsinki area, they generally occurred on trees in low abundance only. There was a considerable increase in the abundance of *Scoliciosporum chlorococcum* and green algae in southern and central Finland between 1985-1995. In the 1995 survey they occurred widely on conifers in southern and central Finland, and the northernmost observations were made as far north as the Arctic Circle.

The occurrence of *Scoliciosporum chlorococcum* and green algae on the plots was investigated in relation to certain climatic and site factors, to the element concentrations in biomonitors sampled on the same plots, and to deposition data. In the 1995 survey, *Scoliciosporum chlorococcum* and green algae only occurred in areas where the effective temperature sum (threshold value +5 °C) was higher than 950 d.d. or in areas with an altitude below 250 m a.s.l. Their occurrence frequency was the greater, the more fertile the site type and the greater the stand basal area. Because *Scoliciosporum chlorococcum* and green algae favour nitrogen-rich sites, the abundance of these biomonitors was compared to the nitrogen concentrations of mosses, lichens and bark on the same plots. In 1985 data were available about the nitrogen concentrations of *Hypogymnia physodes* and pine bark, and in 1995 about the nitrogen concentration of mosses. The nitrogen concentration of lichens sampled in 1985 varied between 0.75-2.6 % (d.w.) and of bark

samples between 0.18-0.90 % (d.w.), and 1995 of mosses between 0.45-2.3 % (d.w.). The nitrogen concentration in all three biomonitors was the highest in southern Finland, and decreased gradually on moving northwards. In the 1985 lichens and algae occurred so sporadically and at low abundances that it was not possible to carry out a comparison between the nitrogen concentrations of the biomonitors. There was a weak correlation ($r = 0.54$; $p = 0.0001$) between the abundance of green algae and moss nitrogen concentrations in the 1995 survey. The abundance of green algae in 1995 was also compared to the deposition of NO_x , NH_4 and SO_2 modelled for the sample plots on the basis of deposition and weather data for 1993. Both nitrogen and sulphur deposition were the highest in southern Finland and gradually decreased on moving northwards. There was only a weak correlation ($r_1 = 0.47$; $r_2 = 0.44$; $r_3 = 0.44$; $p < 0.0001$) between the abundance of green algae and the modelled NO_x , NH_4 and SO_2 deposition levels.

Factors that were considered to have possibly affected the abundance of *Scoliciosporum chlorococcum* and green algae were an increase in nitrogen on their growing sites or climatic changes. Unfortunately it was not possible to obtain any results about the relationship between the abundance of algae and an increase in nitrogen on the plots because there were no data about the nitrogen concentrations of the same biomonitors in both survey years, nor about changes in deposition levels. On the other hand, the climate data showed that the annual mean temperature (+0.5 °C) and mean winter temperature (+0.8 °C) had risen during 1986-1995 in relation to the period 1930-1980. The years 1991-1995 were still warmer than average warmer than 1986-1990. The increase in temperature was also more distinct in southern than in northern Finland.

4.2 Pine bark as a biomonitor for air pollutants in regional surveys

4.2.1 Pine bark as a biomonitor for sulphur emissions

The sulphur concentration of the bark on the Lapland Forest Damage Project sample plots varied between 184-728 $\mu\text{g/g}$ (III). The highest concentrations were measured near to the large smelters at Monchegorsk on the Russian side of the border. The concentrations decreased rapidly with increasing distance to the emission sources on the Kola Peninsula at Nikel, Zapoljarny and Monchegorsk. In general, the sulphur concentration remained below 400 $\mu\text{g/g}$ in Finnish Lapland. The effects of sulphur emissions from the Kola smelters on the sulphur concentration of bark were reflected as a slight increase in concentrations in the Inari area and in the southern part of Lapland close to the eastern border. The lowest concentrations were measured in the western and central parts of Lapland.

The acidity (pH) and electrical conductivity of bark were also investigated in the project, mainly in relation to sulphur deposition. The pH of bark in the study area varied between 2.92 - 3.73. Sulphur emissions from the Kola smelters did not appear to have any clear effect on bark pH. The pH values were low near to the emission sources, but almost the same low values were found in central Lapland. The pH also varied considerably even between sample plots located close together. In contrast, the effects of

emissions from the Kola Peninsula were clearly reflected in the electrical conductivity values, which varied between 100-600 $\mu\text{S}/\text{cm}$ throughout the whole study area. The highest values occurred in eastern parts of Inari and at Monchegorsk. However, there was high between-plot variation in the conductivity values along the northernmost transect. The variation in western and central Lapland was small, and the conductivity values were generally close to or slightly below 200 $\mu\text{S}/\text{cm}$. The large variation on the northernmost sample plots was probably caused by the input of sea salt from the Arctic Ocean, because there was a clear increase in Na concentrations on the plots on moving towards the north. There was only a weak correlation between the sulphur concentration and pH of bark, as well as between the sulphur concentration and conductivity value.

4.2.2 Pine bark as a biomonitor of heavy metal emissions

The emissions of heavy metal from the smelters on the Kola Peninsula were clearly evident especially in the copper and nickel concentrations of bark over a wide area in north-eastern Lapland. The Cu and Ni concentrations of bark were very high close to Monchegorsk (Cu 867 $\mu\text{g}/\text{g}$, Ni 303 $\mu\text{g}/\text{g}$), but decreased rapidly on moving towards the west. However, the Cu and Ni concentrations at a distance of 100 km from Nikel and Monchegorsk (3 $\mu\text{g}/\text{g}$ and 1.5 $\mu\text{g}/\text{g}$) were still somewhat higher than in western Lapland, where the average values were 2.0 $\mu\text{g}/\text{g}$ and <1.0 $\mu\text{g}/\text{g}$, respectively. The Co, V, Ti and Fe concentrations of bark were also relatively high close to Monchegorsk, but decreased rapidly on moving towards the west, and in Finnish Lapland there were no clear signs that the smelters would have any effect on the concentrations of these metals in pine bark.

5 Discussion

5.1 The suitability of mosses, lichens and bark as biomonitors of air pollutants in regional surveys

Heavy metals

Mosses and lichens are the plants that most readily accumulate air pollutants (Rühling & Tyler 1971, Bargagli 1998). They function as biomonitors the best in conditions where the pollutant deposition level is low or moderate. They are either no longer present in the vicinity of large emission sources and in urban centres, or their condition is too poor for use as biomonitors (Folkeson & Andersson-Bringmark 1988, Salemaa *et al.* 2004). Tree bark, on the other hand, is usually available in severely polluted areas even (Kuik & Wolterbeek 1994).

The results obtained about the differences between mosses and lichens as accumulation indicators depend on the species used in the studies, on the type of emissions and environment in the studied area. Canopy throughfall and stem flow are the most important factors causing differences in the concentrations of heavy metals and other elements between ground mosses and epiphytic lichens growing at the same place (Rinne & Barclay-Estrup 1980, Steinnes 1993). Throughfall can have an especially strong effect on element concentrations in epiphytic lichens (Barkman 1958). The effect of throughfall on ground mosses varies according to whether the mosses are growing under or between the crowns. In biomonitoring studies, moss samples are collected in open areas between the crown canopies in order to minimise the effect of throughfall. The amount of throughfall and stemflow varies according to the type of tree crown (Rasmussen 1978). The crown canopy retains a part of the elements transported in free precipitation, but precipitation also leaches and washes off e.g., nutrients (Ca, K, Mg, Mn) from the canopy, which are subsequently absorbed from stemflow by epiphytic lichens.

There is also variation in the element concentrations in mosses and lichens, especially in arid areas where precipitation is concentrated in the winter period. The differences between the concentrations in mosses and epiphytic lichens in northern areas may also be

caused by the fact that epiphytic lichens are exposed to air pollutants throughout the year, while mosses are protected by the snow cover for almost half a year. More information is needed about the effects of throughfall and the other factors mentioned above on heavy metal concentrations in lichens and mosses.

The different morphological and physiological properties of mosses and lichens account partly for the differences in metal-uptake efficiency. The surface structure of mosses is different than that of lichens, and they also have a larger surface area to weight ratio. On the other hand, the surface of lichens is in most cases rougher and more porous than that of mosses. Many studies have shown, as in the Finnish surveys (II), that epiphytic lichens accumulate more heavy metals per dry weight than mosses (Steinnes 1977, Kuik & Wolterbeek 1995), but opposite results have also been reported (Folkesson 1979, Pilegaard *et al.* 1979). In the Finnish surveys (II) the accumulation of heavy metals per dry weight was the greater in epiphytic lichens than in mosses, the lower the deposition load. Similar results have also been reported in other studies (Kansanen & Venetvaara 1991, Steinnes 1993). The reason for this may be the difference in the uptake efficiency in different deposition conditions or the effect of throughfall on epiphytic lichens (Steinnes 1993). Lichens accumulate particularly heavy metals (Hg, Pb) that are volatile and which are continuously recirculated back into the atmosphere, more readily than mosses (Evans & Hutchinson 1996).

Many studies have also shown, that mosses accumulate dust more easily than lichens (Steinnes 1995, Reimann *et al.* 1999). In Finland, the metal concentrations in mosses were usually higher close to emission sources, and lower in background areas, than the corresponding concentrations in epiphytic lichens (II). Brown and Brümelis (1996) reported that the relative contribution of particulate material to the total concentrations in mosses increases near to emission sources, in arid areas and in agricultural areas. Especially in arid regions with a sparse vegetation cover, metals (Al, Cr, Fe, Ti) that originate from the soil accumulate more readily in mosses than in lichens (Loppi & Bonini 2000, Bargagli *et al.* 2002). However, there was no evidence of this phenomenon in the Finnish surveys (II) because the amount of dry deposition in Finland is relatively small (Berg *et al.* 2001) and the soil normally has a fully developed vegetation cover that effectively prevents the dispersion of soil dust.

Mosses and lichens seem to depict wet deposition in different ways. Laboratory tests have shown that cation exchange is a very fast process in *Hylocomium splendens*, and this has led to the conclusion that the concentrations measured in this species of moss reflect the effects of the composition of rainwater prior to sampling rather than the effects of long term accumulation (Brown & Brümelis 1996). Reimann and co-authors (1999) reported in their studies carried out on the Kola Peninsula, northwest Russia, that the concentrations of many of the elements in mosses were more closely related to the chemical composition of rainwater than to the annual deposition level, as reflected by terricolous lichens. Lichens are also more readily subjected to desiccation, and this can contribute to the differences in the accumulation of heavy metals between mosses and lichens (Bargagli 1998, Adamo *et al.* 2003). Snow melt water in northern latitudes may also have an effect on the accumulation of heavy metals in terricolous mosses (Ford *et al.* 1995, Reimann *et al.* 1999).

Comparing the concentrations in bark with those in mosses and lichens is difficult because the concentrations reported for bark are values determined using different

methods on a large number of different trees species growing in very different conditions. Despite this, tree bark usually appears to accumulate considerably smaller amounts of heavy metals per unit dry weight than mosses and lichens growing in the same conditions (Lötschert & Köhm 1978, Kling *et al.* 1985, Türkan *et al.* 1995). On the other hand, in some studies higher heavy metal concentrations have been reported for tree bark than from epiphytic lichens collected from the same tree (Laaksovirta *et al.* 1976, Kuik & Wolterbeek 1994, Loppi *et al.* 1997). Tree bark has been reported to reflect rather well the Pb emissions of traffic (Ward *et al.* 1974, Laaksovirta *et al.* 1976). In some studies pine bark has also proved to indicate, as well or even better, the dispersal of heavy metals from emission sources than the epiphytic lichens growing on the same trees (Kling *et al.* 1985, Kortesharju *et al.* 1989). However, the concentrations of heavy metals and the deviations in the concentrations in the Finnish surveys (II) covering the whole country were clearly smaller for pine bark than for mosses and epiphytic lichens. The bark concentrations did not depict the deposition of heavy metals as precisely as the concentrations in mosses and lichens. These conflicting results may be due e.g., stand throughfall and stemflow, which have a considerable effect on the concentrations of elements in tree bark (Staxäng 1969, Schulz *et al.* 1999). For instance, many studies have clearly shown that heavy metal concentrations in bark change on moving from the butt of the stem up to the crown (Barnes *et al.* 1976).

There is no clear-cut evidence to show that mosses and lichens would be better heavy metals biomonitors in regional surveys, because the results appear to vary from one place to another. However, the mechanisms through which mosses and lichens accumulate heavy metals are so different that they cannot be used to replace each another in regional surveys (Freitas *et al.* 1999, Bargagli *et al.* 2002). In Finnish conditions, mosses appear to be more suitable for regional surveys than epiphytic lichens. The differences between different parts of the country and the location of emission sources were expressed more clearly on the basis of mosses than of lichens (II). Standards are also available for the sampling and analysis of mosses, they are easy to sample, and the annual growth segments can be separated relatively easily. Wolterbeek and co-authors (1996a) also recommended the use of mosses because they more readily reflect local changes in heavy metal deposition. However, lichens may be better accumulation indicators than mosses in arid conditions. Based on the Finnish results (II, III), pine tree bark is not very suitable for extensive surveys due to the small differences in heavy metal concentrations. In contrast, however, it has been demonstrated in the Netherlands that the differences between mosses, epiphytic lichens and the bark of deciduous trees are not very large in relation to the deposition of atmospheric pollutants when the effect of dust on the concentrations has been eliminated by means of factorial analysis (Wolterbeek *et al.* 1996a). It would appear that bark is best suited for heavy metal emission surveys in urban and industrial areas where lichens and mosses are no longer present (II).

Sulphur

Mosses are not considered to be especially good biomonitors of atmospheric sulphur concentrations, although sulphur concentrations have been found to increase to high levels close to emission sources and to decrease with increasing distance from the emission sources (Mäkinen 1994, Äyräs *et al.* 1997). The reasons for their relatively poor bioindicator value may be that sulphur at high concentrations damages the plants and

changes their accumulation capacity (Äyräs *et al.* 1997). Active physiological processes in plants also control the uptake of sulphur (Moser *et al.* 1993). Because of their sensitivity, lichens are not suitable as biomonitors in areas with high atmospheric SO₂ concentrations. The relationships between the occurrence frequency of lichens and atmospheric SO₂ concentrations are complicated by the fact that nitrophytic and acidophytic species react differently to atmospheric NO_x and SO₂ concentrations (Van Dobben 1993).

The sulphur concentrations of lichens in the Finnish surveys were, on the average, somewhat higher than those in mosses, whereas the sulphur concentrations in bark were only one third of those in mosses and lichens when expressed on a dry weight basis (Kubin 1990, Poikolainen, unpublished). Salemaa and co-authors (2004) reported clearly higher S and N concentrations per dry weight in terricolous mosses in the Harjavalta area and background areas than in terricolous lichens.

Tree bark has been used relatively infrequently as a biomonitor for atmospheric SO₂ concentrations over extensive areas. The S concentration in bark has, in many studies, been found to correlate moderately well with sulphur deposition and atmospheric SO₂ concentrations, especially in areas with high sulphur deposition (Moser *et al.* 1993, Stöcker & Huhn 1994, Schulz *et al.* 1999). The sulphur concentration in bark has been found to follow clear seasonal variation in e.g., Central Europe, most probably due to both seasonal variation in emission levels and to variations in the residence time of sulphur in the atmosphere under different climatic conditions (Kienzl 1978, Kosmus & Grill 1986). In the national survey carried out in Finland between 1985 and 1986, the S concentration in pine bark did not, however, very well depict the sulphur deposition in different parts of the country (Poikolainen, unpublished). Neither were Wolterbeek and co-authors (1996b) able to find any significant correlation between sulphate concentrations and atmospheric SO₂ concentrations in a study on the effects of gaseous air pollutants on the concentrations in bark.

In a study (III) carried out on the dispersal of sulphur and heavy metals from the Kola smelters into Finnish Lapland, a combination of the S concentration, pH and electrical conductivity of bark better depicted the dispersal of sulphur emissions than the individual parameters alone. Bark's pH measurements are poorly suited for extensive areas because even the pH value of the same species bark can vary naturally e.g., according to rain amounts (Farmer *et al.* 1991). The use of bark pH is best suited to restricted areas where the emissions consist primarily of acidifying compounds (Staxäng 1969). The use of conductivity values in extensive surveys is complicated by the presence of e.g., sea salts, which increase the conductivity values (III). The main problem with conductivity is the large variation in the values even within the same area (Kienzl & Härtel 1979). Owing to the low costs, however, measuring the pH and conductivity of bark is a relatively easy and cheap method for obtaining preliminary information from an area affected by emissions and they can be used to supplement more detailed measurements (Grill *et al.* 1981).

5.2 How well do the measured heavy metal concentrations depict the deposition of metals in Finland?

The concentrations of the heavy metals in mosses in Finland are relatively low compared to the concentrations reported in other parts of Europe (Buse *et al.* 2003). The results for heavy metal concentrations in Finland (I) were in good agreement with the emission data (Melanen *et al.* 1999) and with the concentrations measured in precipitation and in the atmosphere (Jalkanen 2000, Leinonen 2001). A similar gradual decrease particularly in Pb, Cd, V and Zn concentrations on moving from the south towards the north has also been reported for the concentrations in precipitation (Ukonmaanaho *et al.* 1998, Leinonen 2001) and in studies carried out using different biomonitors (Pakarinen & Tolonen 1976, Lodenius 1981). In Sweden and Norway the concentrations of the above-mentioned heavy metals in mosses also gradually decrease from south to north (Steinnes *et al.* 2001, Buse *et al.* 2003).

The results indicating a decrease in heavy metal concentrations in mosses during the monitoring period (I) are also in agreement with heavy metal emissions and deposition measurements. Heavy metal emissions and depositions in Finland and other parts of Europe have decreased during the last decades (Jalkanen 2000, Pacyna & Pacyna 2001, UN/ECE 2002). A decrease in moss concentrations in Finland has been reported in studies with biomonitors carried out before 1985 (Rühling & Tyler 1973, Mäkinen 1983, Rinne & Mäkinen 1988). The results obtained in Finland are similar to those reported in other Nordic countries (Rühling *et al.* 1987, Buse *et al.* 2003), although only the Pb concentrations in mosses significantly decreased in Norway between 1995 and 2000 (Steinnes *et al.* 2001). The decrease in heavy metal concentrations in mosses in Finland is primarily due to the decrease in emissions of anthropogenic origin in Finland and neighbouring areas, because the other factors affecting concentrations in mosses have probably remained relatively constant in the sampling areas (I).

The concentrations measured in mosses are relative values and do not give empirical information about the actual deposition levels. According to Wolterbeek and co-authors (1996a), the concentrations in mosses depict the situation prevailing in the immediate vicinity of the mosses, irrespective of the origin of the heavy metals. No direct conclusions can be made necessarily on the basis of their concentrations about the deposition of heavy metals from anthropogenic sources. According to studies carried out in areas with conditions similar to those prevailing in Finland (Gydesen *et al.* 1983, Berg *et al.* 1995), however, the Pb concentrations in mosses have correlated well with the Pb concentrations in wet deposition. Relatively good correlations have also been obtained for V, Cd, Zn, Cu, Co and Mo, and in some cases also for As and Fe (Berg & Steinnes 1997b). In contrast, the concentrations of Cr, Mn and Ni have not usually correlated very well with the corresponding concentrations in wet deposition. Mosses are therefore not very well suited as biomonitors for Mn, and even less for Cr, Ni, As and Fe, in regional surveys. Despite the good correlations, there are still some reservations about the usability of Cd, Zn and Hg concentrations in mosses in regional surveys because many so-called secondary factors may also affect the concentrations of these metals (Steinnes & Andersson 1991, Økland *et al.* 1999, Reimann *et al.* 1999). Despite the rather weak

correlations for certain metals in mosses and wet deposition, the concentrations in mosses can still be used to depict their emissions at the local level (Rühling *et al.* 1987).

In order to obtain a more precise picture of heavy metal deposition on the basis of the results obtained with biomonitors, the concentrations obtained in some extensive surveys have been converted into absolute deposition values (Berg & Steinnes 1997b). This has been done by converting the moss concentrations to correspond to the wet deposition values at each sampling point. The absolute deposition values for the most common heavy metals (As, Cd, Fe, Ni, Pb, V) have been calculated for all the moss sampling sites of the Nordic Countries in the 1995 survey (Berg *et al.* 2003). The calculations for Finland were based on the same material as that presented in this thesis (I). The maps of the absolute deposition values were in good agreement with the maps calculated on the basis of the moss concentrations alone. Compared to the results from the Finnish Meteorological Institute's background stations (Leinonen 1997), the calculated deposition values appear to be quite high. Converting the values measured in biomonitors into deposition values is problematic because there is not enough information available about the factors affecting the concentrations in mosses (Wolterbeek *et al.* 2003). The reliability of calculated absolute values is also the lower, the higher the proportion of dry deposition out of total deposition (Berg *et al.* 2003).

The major emission sources in Finland were clearly visible on the basis of the heavy metal concentrations in mosses alone. Attempts have frequently been made in regional surveys with biomonitors to distinguish different emission sources, and even individual industrial plants, using statistical tests (Wolterbeek 2002). Corresponding tests have not been performed with material covering the whole country in the Finnish surveys. In a study using the same material, in which the concentrations of heavy metals that area readily dispersed over long distances were investigated in northern Finland, principal component analysis was, however, used to identify possible anthropogenic emission sources (Poikolainen *et al.* 2004b). This analysis showed that emissions from the Kola Peninsula have a major effect on Cu and Ni concentrations in mosses, and emissions from the industrial plants on the coast of the Gulf of Bothnia and traffic have an effect on the Cr, Pb and Cd concentrations in mosses in northern Finland.

Discussion about the use of biomonitors in regional surveys has centred especially on what is the effect of long-distance transport on the heavy metal concentrations in mosses. In Norway, statistical tests have shown that long-distance transport has a strong effect especially on the Pb, Cd, Hg, V, Zn, Mo and As concentrations in moss (Berg & Steinnes 1997a,b). However, some studies have suggested that the effects of anthropogenic emissions, and especially long-distance transport, on the element concentrations in mosses have usually been over-estimated in regional surveys, and that the effects of factors of local natural and anthropogenic origin have been underestimated (Pilegaard *et al.* 1979, Reimann *et al.* 1997). The evidence put forward to support this conclusion includes mass balance determinations associated with the transport of heavy metals (De Caritat *et al.* 1997), and the abrupt limits of the area affected by emissions from the smelters on the Kola Peninsula where the heavy metal concentrations in mosses approach the levels of background areas already at a distance of about 100 – 150 km from the emission source (Rinne & Mäkinen 1988, Reimann *et al.* 1999). It is not possible, without further study, to equivocally determine the contribution of long-distance transport to the heavy metal concentrations in mosses on the basis of the Finnish material (I). The

relatively regular decrease in the Pb, Cd and V concentrations also in the background areas appears to be a strong indicator of long-distance transport (**I**). A number of model calculations on the dispersal of heavy metals, based on emission data, deposition measurements and climatic factors, lend further support to this conclusion (Berg *et al.* 2001, Ilyin *et al.* 2002, 2003). In Norway the effect of elements derived from long-distance transport on concentrations in mosses has decreased, while the relative effect of soil factors has increased (Steinnes *et al.* 2001). A similar trend has also taken place in Finland.

The effect of soil factors on heavy metal concentrations in mosses is also a topic which has received considerable attention in heavy metal surveys. Mineral particles originating from soil and bedrock have been found to have an effect on the concentrations of Fe, Al, Ti and Cr especially in mosses (Berg & Steinnes 1997a, Fernández & Carballeira 2001). The effect is the greatest in arid climates and areas where there is a sparse vegetation cover or the mineral soil is otherwise exposed (Riget *et al.* 2000, Couto *et al.* 2004). The metal concentrations in moss samples collected from the permanent NFI sample plots in 1985-86 (**I**, **II**) have been compared to the corresponding concentrations in humus samples collected in 1986-89 from the same plots (Tamminen *et al.* 2004). Concentrations in both moss and humus layer samples were negatively correlated with latitude, except Mn, Cr and Ni, indicating an effect of deposition. However, heavy metal concentrations in the humus layer were relatively weakly but positively and statistically significantly correlated to the concentrations in mosses. In contrast, the direct effects of the mineral soil and the bedrock on the heavy metal concentrations are usually relatively small. The greenstone belt in Finnish Lapland has been suggested to have an effect on Cr concentrations in mosses (Äyräs *et al.* 1997). Ni concentrations in till in central Lapland has been also found to correlate with concentrations in mosses (Niskavaara & Lehmuspelto 1992). However, the effects are relatively small because no clear increase in Cr and Ni concentrations were found in the area in question in the national survey (**I**). In some areas there appears to be a relationship between the As concentrations in till soils and mosses (Reimann *et al.* 1997, Poikolainen & Piispanen 2004).

Mercury is a difficult metal from the point of view of surveys because it mainly occurs in the atmosphere in gaseous form (Schroeder & Munthe 1998). Gaseous Hg can be carried by the air masses for thousands of kilometres away from the emission sources, and remain in the atmosphere for periods of up to one year (Ilyin *et al.* 2003). Mercury returns from the atmosphere to the ground surface in dry and wet deposition, mainly in the oxidised form. Under certain conditions it can be converted into gaseous form and return to the atmosphere. The Hg concentrations in mosses in Finland are relatively low (**I**) and, as is the case in Norway (Steinnes *et al.* 2003), the differences in concentrations in different parts of the country are not large. No large differences were found in the Hg concentrations measured in the atmosphere during 1996-2001 between the southern and northern parts of Fennoscandia. In contrast, the Hg concentrations in wet deposition in the southern parts of the region have been considerably higher than those in the northern parts (Wängberg *et al.* 2002). It has been suggested that mosses are able to accumulate greater amounts of gaseous Hg in the cool climate in the northern parts of Fennoscandia, and that volatilization of Hg back into the atmosphere would be lower than that further to the south (Steinnes *et al.* 2003).

5.3 Problems with the use of bioindicators in nationwide surveys

Interpretation of the bioindication results is more difficult in regional surveys than in studies carried out in the vicinity of point emission sources. Finland is an ideal country for regional bioindication surveys because the differences in altitude are relatively small, almost the whole country is located within the boreal coniferous zone, and plant species suitable for surveys can be found growing throughout the country. However, Finland is a long country in the latitudinal direction and there is a clear climatic gradient running from the south of the country to the north. The deposition of air pollutants also decreases on moving from south to north. As many of the factors affecting the properties and concentrations in biomonitors along the same gradient, it is often difficult to determine which factors are the causes, and which the results, of the accumulation of air pollutants.

The climate in Finland becomes cooler on moving towards the north and, at the same time, there are changes in the vegetation cover. Mean annual precipitation is at its highest in southern Finland, and at its lowest in the northern parts of the country and in the coastal region of western Finland. The proportion of precipitation falling as snow increases towards the north. The amount, intensity and acidity of rainfall have an effect on the accumulation, mobility and leaching of elements in mosses (Berg & Steinnes 1997a, Pott & Turpin 1998). However, these factors probably do not cause any large differences between the element concentrations in mosses in Finland, because the differences in the amount and quality of precipitation in different parts of the country are not very large (Ukonmaanaho *et al.* 1998, Leinonen 2001). Most of the air pollutants deposited on mosses in Northern Europe are derived from wet deposition (Berg *et al.* 2003). The proportion of dry deposition increases slightly on moving northwards in Finland, but the change is so small that it probably has no effect on concentrations in mosses, apart from Hg (Steinnes *et al.* 2003).

The importance of weather conditions also became clearly apparent when interpreting the results concerning the occurrence and increase in abundance of green algae growing on trees between 1985 and 1995 in Finland (IV). A number of factors have probably simultaneously affected the increase in the abundance of green algae. Green algae thrives on nitrogen-rich sites (Søchting 1997). In contrast to sulphur and heavy metal emissions, nitrogen emissions have not decreased during the last 20 years, and in fact they have remained at approximately the same level (Erisman *et al.* 2003, Environment Statistic 2003). The pools of nitrogen in nature have increased and those of sulphur decreased, which is probably one of the reasons for the increase in abundance of green algae on trees trunks and branches (Søchting 1997). However, the main reason for the increase in abundance of algae might be the rise in the mean air temperature (Thomsen 1992, Liu Qinghong & Bråkenhielm 1995). Even the slightest rise in the mean temperature may have brought about an increase in the distribution area of green algae towards the north.

The growth of plants decreases on moving from the south towards the north in Finland. A decrease in growth means an increase in the amount of heavy metals accumulating per dry weight in mosses under the same deposition load (Zechmeister 1998, Gerdol *et al.* 2002). Relatively little variation has been reported in the growth rate of *Hylocomium splendens* in its main occurrence area, apart from arctic and alpine areas where its growth rate is low (Rühling 1985, Zechmeister 1998). In Central Europe,

Hylocomium splendens produces ca. 10 % more biomass per surface area than in Northern Europe, and *Pleurozium schreberi* up to 40 % more (Pakarinen & Rinne 1979, Rühling 1985). There are probably no major differences between the growth rate of mosses in different parts of the country. The air in northern Finland is more humid than that in the south, and this balances out the growth rate.

There are also differences in the quality and composition of the tree stands and ground vegetation between the southern and northern parts of the country, and this probably has an effect on e.g., throughfall, and subsequently on the concentrations in bark and epiphytic lichens especially. It has been suggested that changes in the vegetation cover have had an effect on heavy metal concentrations in mosses in northern Finland and north-west Russia (Reimann *et al.* 1997, De Caritat *et al.* 2001). In Finland, the amount of nutrients and pH in the organic layer of the soil decrease on moving northwards (Tamminen 2000). In Norway, Økland and co-authors (1999) reported that the Cd and Cu concentrations in mosses correlates with the nutrient status of the site and the pH of the organic layer. According to the Finnish surveys (**I**), however, these factors do not seem to have much effect on concentrations in mosses, because marked differences in the Cd and Cu concentrations in background areas between different parts of the country were no longer observed in the 2000 survey.

Finding a suitable, sufficiently common species for use as a biomonitor is usually problematic in extensive surveys. For example, in the pan-European heavy metal moss surveys, different moss species have been used as biomonitors in different parts of Europe (Buse *et al.* 2003). Two moss species (*Hylocomium splendens*, *Pleurozium schreberi*), that have somewhat different accumulation properties (Folkeson 1979, Halleraker *et al.* 1998), were used in the Finnish surveys (**I**, **II**). The use of correction factors in extensive surveys has been questioned because the concentrations in mosses vary so much from place to place (Wolterbeek *et al.* 1995). When moving hundreds of kilometres in a south-north direction, there may be changes in the physiological and morphological properties or behaviour of even the same moss species, thus causing the accumulation properties to change.

Many studies have shown that the element concentrations in mosses change with increasing altitude (Kral *et al.* 1989, Herman & Smidt 1994, Zechmeister 1995). The type of change seems to depend on how the factors (e.g., amount of precipitation, soil dust, growth) affecting mosses change with increasing altitude (Zechmeister 1995, Gerdol *et al.* 2002). In Finland, the variation in altitude does not appear to have remarkable effect on concentrations in biomonitors, because the altitude in most of the country is below 300 m a.s.l. (cf. however Mäkinen 1994). In the Finnish surveys (**II**), however, elevated Pb concentrations were found in lichens and bark in the hill region running to the northeast of the Gulf of Bothnia. Lead is presumably carried by the prevailing western winds from emission sources along the coast of the Gulf of Bothnia to the hill region, where the Pb is deposited on the mosses in precipitation.

5.4 The significance of sample storage in regional biomonitor studies

The unused portions of the moss, lichen and bark samples collected from the NFI permanent sample plots have been stored in the environmental specimen bank at Paljakka (V). Environmental specimen banks have been established for the long-term storage of representative environmental specimens (Iyengar & Subramanian 1997, Kettrup 2003). They are usually operated as a part of a larger environmental condition monitoring system that includes observation networks and database systems (Markert *et al.* 2003). Representative samples of ecological importance, e.g., soil, plants, and animal and human tissue, have been collected systematically from a range of different ecosystems. Such samples are generally stored frozen at very low temperatures. It is important that the samples are collected, prepared, stored and analysed in accordance with standard methods, and that the concentrations of both organic and inorganic compounds can be analysed on them (Emons *et al.* 1997, Aboal *et al.* 2001). They can be used to produce time series based on the analysis of the concentrations of e.g., toxic, carcinogen or elements that are essential for life. Such time series provide information on the current state of environment, and can also be used to predict future changes in the condition of the environment.

The Paljakka sample storage is not an environmental specimen bank in the general meaning of the term. Only dried plant samples are stored at Paljakka (V). The activities of the facility are based on the long-term storage of important material collected in a wide range of studies on the condition of the forest environment. Samples representing the longest time series extend from the 1960's up until the present day. The samples are used to facilitate joint research and academic theses. However, the Paljakka specimen bank is operated in accordance with many of the same principles as traditional environmental specimen banks. Strict operating instructions, which define e.g., the requirements set on the stored samples, have been drawn up for the storage of samples. The stored samples have been organised into a specimen bank, and information about the samples has been entered into the database. Reference material for the pan-European heavy metal moss surveys has also been prepared from moss samples in the Paljakka specimen bank (Steinnes *et al.* 1997). This reference material will also be used in the analysis of samples collected in the 2005 pan-European survey.

Permanent storage of the samples is of considerable advantage in heavy metal surveys. It is possible, already immediately after the samples have been analysed and the results checked, to reanalyse moss samples whose results do not appear to be correct or which differ from the expected values. Old samples can also be used to control whether the level of the analysis results of new surveys have changed, e.g., when new analysis methods are taken into use (Siewers & Herpin 1998). The accuracy of the analyses is increasing along with developments in instrumentation, and new elements that are found to be air pollutants can be analysed from biomonitor samples. In recent years, these elements have included metals in the platinum group and lanthanides (Markert *et al.* 2003, Ravindra *et al.* 2004). Platinum group metals are released into the atmosphere primarily from automobiles catalyzers (Djingova *et al.* 2003). The concentrations of platinum group metals in mosses are to be investigated in the future in connection with the national heavy metal surveys (I). Development of the analysis methods to be used in these studies has

already begun (Niemelä *et al.* 2004). Long-term sample series also make it possible to construct retrospective time series of these new pollutants.

The environmental specimen bank at Paljakka will, in the future, be further developed as a storage facility for forest environment samples that require long-term storage. The Paljakka specimen bank is acting as the example site in a project, which started in 2003, in which the operating principles for the long-term storage of environmental samples and their joint scientific use in Finland are being drawn up. The databases of the Paljakka specimen bank will be modernised and linked to more extensive databases (GBIF). The development of databases in the use of bioindicators has frequently been a popular topic in recent years. Wolterbeek (2002) proposed the development of a multidisciplinary programme that would collate data about all aspects associated with air pollutants. The more information there is available, the better will be the ecosystem-level models depicting the dispersal and effects of air pollutants.

6 Conclusions

The following conclusions can be made on the basis of the studies:

1. The regional differences in heavy metal deposition and the major heavy metal emission sources in Finland were clearly evident on the basis of the concentrations in mosses. The time series studies on moss concentrations indicated that the concentrations of all the studied heavy metals, and especially Pb, Cd and V, decreased significantly in Finland between 1985 and 2000. In future monitoring activities, however, the results should be used to determine, using different statistical tests, the proportion of heavy metals in mosses that are derived from anthropogenic sources especially.
2. Forest mosses (*Hylocomium splendens*, *Pleurozium schreberi*) are better suited to regional heavy metal surveys in Finland than epiphytic lichens (*Hypogymnia physodes*) and Scots pine bark. Mosses and epiphytic lichens accumulate air pollutants equally efficiently, but the concentrations in mosses more clearly indicate the emission sources and differences in heavy metal deposition than lichens and bark. Bark is not very suitable for regional surveys due to the clearly lower concentrations of heavy metals per dry weight, and the clearly smaller variation in concentrations than in mosses and lichens.
3. Sulphur emissions from the Kola Peninsula had a considerable effect on the sulphur concentrations and electrical conductivity of pine bark, but only a small effect on the pH close to the emission sources. Although the values decreased rapidly with increasing distance from the emission sources, the effect of sulphur emissions was still slightly visible in north-eastern Lapland on the Finnish side of the border. The sulphur concentrations, pH and conductivity values together gave a better overall picture of the long-distance transport of sulphur emissions from the Kola Peninsula into northern Finland than each parameter alone. The Cu and Ni concentrations in bark were also very high close to the emission sources, but they rapidly decreased to close to the background level along the Finnish border.
4. *Scoliciosporum chlorococcum* and green algae had become considerably more abundant in southern and central Finland during the period 1985-1995. Their distribution area had also increased towards the north: in 1985 they mainly occurred only in southern Finland, but in 1995 they were observed right up to the Arctic Circle.

The increase in the abundance of green algae is presumably due to a number of factors that have had a simultaneous effect: climate warming, and an increase in nitrogen and a decrease in sulphur in their habitats.

5. The environmental specimen bank at Paljakka, originally established as a storage facility for bioindicator samples collected in the national heavy metal surveys, has proved to be a vital part of the national forest health monitoring network. The long-term sample series in the sample bank will make it possible to construct, as new analysis methods are developed, retrospective time series of these new air pollutants. The specimen bank is to be further developed in the future by establishing a reputation as a storage facility for plant samples related to forest ecosystems, and by promoting the use of the samples in joint research.

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