# ASSESSING INDUSTRIAL POLLUTION BY MEANS OF ENVIRONMENTAL SAMPLES IN THE KEMI-TORNIO REGION

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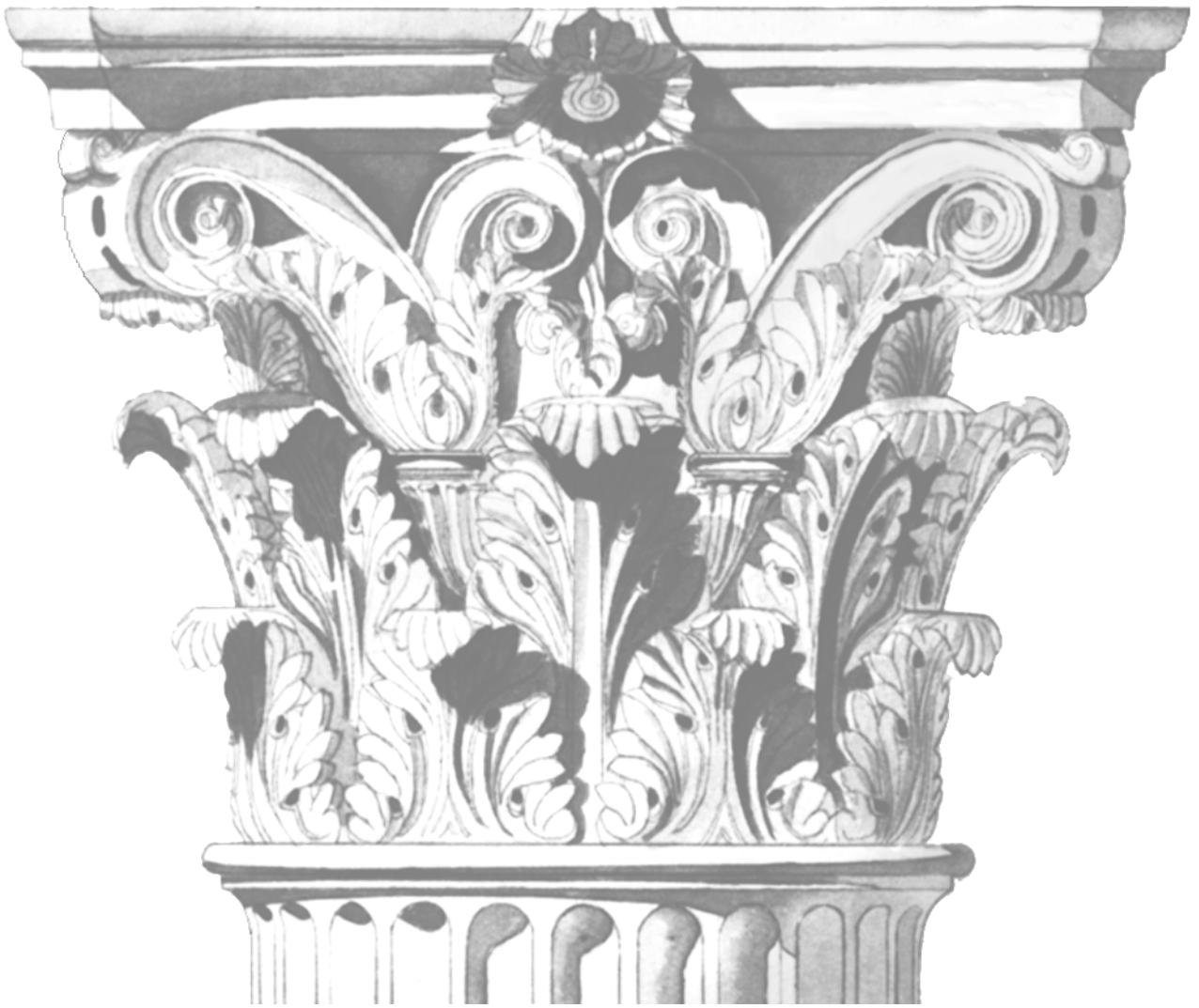

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***Abstract***

The results of the comparison of various dissolution methods for sulphur showed, that $HNO_3$ together with $H_2O_2$ gave more complete decomposition of organic components than $HNO_3$ alone. The acid procedure with a mixture of $HNO_3$+$H_2O_2$ slightly underestimated the S concentrations of plant material. The losses of sulphur were the highest in the dry ashing digestion procedure (HF(DAC)). The Leco combustion technique with infrared (IR) detection gave good precision and accuracy for sulphur. For the determination of heavy metals in plant materials, both the $HNO_3$ and $HNO_3$+$H_2O_2$ procedures were especially effective for determining Cr. However, the $HNO_3$+$HClO_4$ procedure gave lower results, and HF and HF(DAC) procedures greater values for Cr.

Sulphur accumulation in pine needles around the pulp and paper mills was clearly higher than other points in the Kemi area. For example, within a radius of about 1-1.5 km around the mills of Oy Metsä-Botnia Ab Kemi Mills, the sulphur concentrations for (C) and (C+1) needles were 28 % and 26 % higher than those in the corresponding background samples collected in Kuivaniemi at a distance about 25 km from Kemi. Pine needles do not appeared to be appropriate a method for monitoring the accumulation of Fe, Zn, V and Pb emitted from pulp and paper mills. However, the Ca concentrations in (C+1) needles in the vicinity of the Oy Metsä-Botnia Ab Kemi Mills was 48 % higher than the average Ca concentration calculated from all (C+1) needles; thus it is likely that part of the Ca in the needles is derived from the mills.

The regional distribution pattern of Cr and Ni in mosses in the Kemi-Tornio area in 2000 showed clearly that the most polluted area (Cr > 200 μg/g and Ni > 20 μg/g) appeared to lie within a few kilometres of the ferrochrome and stainless steel works of AvestaPolarit Stainless Oy. Within this area, the Cr concentrations in mosses were 4-13 times higher than those outside the urban area of Tornio. The area most polluted by the opencast chromium mining complex (Cr > 200 μg/g and Ni < 20 μg/g) appeared to be in the immediate vicinity of complex.

All the 95$^{th}$ percentile values for TSP (total suspended particles) in the mine area of AvestaPolarit Chrome Oy Kemi Mine were below the current Finnish air quality limit value of 300 μg/m$^3$. However, the 98$^{th}$ percentile value exceeded the Finnish air quality guideline value of 120 μg/m$^3$ at one monitoring site.

According to leaching studies, the sum of calculated annual airborne pollution impact of water-soluble fraction ($H_2O$) and environmentally mobile ($CH_3COONH_4$) fraction from the AvestaPolarit Chrome Oy Kemi Mine was Cr 1.2 kg, Fe 29 kg, Cu 63 kg, Ni 2.5 kg and Cd < 100 mg.

According to the homogeneity studies of heavy metal deposition on TSP filters, Cr, Ni, Cu and Fe were non-uniformly distributed over the glass fibre filters. The rsd values varied between 5.4-33.9 % for Cr, between 7.5-35.0 % for Ni, between 3.6-25.9 % for Cu, and between 6.6-19.9 % for Fe.

*Keywords:* air pollution, airborne particulate matter, bioindicators, dust, heavy metals, leaching, mining, pine needles, pulp and paper mills, sulphur, TSP

*"How little I know of this world*
*Deeds of men, cities, rivers,*
*Mountains, arid wastes,*
*Unknown creatures, unacquainted trees!*
*The great Earth teems*
*And I know merely a niche."*
Rabindranath Tagore, 1913

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Kemi, September 2002 Risto Pöykiö

# Abbreviations and definitions

| | |
|---|---|
| AAS | atomic absorption spectrometry |
| BAT | best available techniques |
| BCR CRM | Community Bureau of Reference, certified reference material |
| (C) needles | current-year needles |
| (C+1) needles | previous-year needles |
| CEN | European Committee for Standardization |
| $CH_3SH$ | methyl mercaptane |
| $(CH_3)_2S$ | methylsulphide |
| CRM | certified reference material |
| $d_{ae}$ | aerodynamic diameter |
| 3-D | three-dimensional |
| EDS | energy dispersive X-ray spectrometry |
| EFTEM | energy transmission electron microscopy |
| EIA | environmental impact assessment |
| FAAS | flame atomic absorption spectrometry |
| FPXRF | field portable X-ray fluorescence spectrometry |
| GFAAS | graphite furnace atomic absorption spectrometry |
| GPS | Global Positioning System |
| HC | hydrocarbons |
| hdw | hardwood |
| $H_2S$ | hydrogen sulphide |
| ICP-AES | inductively coupled plasma atomic emission spectrometry |
| ICP-MS | inductively coupled plasma mass spectrometry |
| IPPC | integrated pollution prevention and control (directive) |
| IR | infrared |
| ISO | International Organization for Standardization |
| KemiGis | computer-based geographic information system |
| lower-Q | lower quartile, *i.e.* the $25^{th}$ percentile (0.25) |
| LWC | Light Weight Coated |
| MVA | mega-volt-ampere; mega = $10^6$ |
| MWC | Medium Weight Coated |
| NAA | neutron activation analysis |

| | |
|---|---|
| PFA | perfluoroalkoxy |
| $PM_{10}$ | particulate matter < 10 µm in aerodynamic diameter |
| $PM_4$ | particulate matter < 4.0 µm in aerodynamic diameter |
| $PM_{2.5}$ | particulate matter < 2.5 µm in aerodynamic diameter |
| PTFE | polytetrafluoroethylene |
| Rsq | $R^2$ |
| RSD (rsd) | relative standard deviation |
| r.s. (%) | relative solubility |
| SEM | scanning electron microscopy |
| SFS | Finnish Standards Association SFS |
| SPSS | a commercial statistical computer program |
| SRM | standard reference material |
| stw | softwood |
| TEM | transmission electron microscopy |
| TRS | total reduced sulphur |
| TSP | total suspended particles |
| UNEP | United Nations Environment Program |
| USEPA | US, Environmental Protection Agency |
| upper-Q | upper quartile, *i.e.* the $75^{th}$ percentile (0.75) |
| WHO | World Health Organisation |
| VTT | Technical Research Centre of Finland |
| XRF | X-ray fluorescence spectrometry |

# List of original papers

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

I Pöykiö R, Torvela H, Perämäki P, Kuokkanen T & Rönkkömäki H (2000) Comparison of dissolution methods for multi-element analysis of some plant materials used as bioindicator of sulphur and heavy metal deposition determined by ICP-AES and ICP-MS. Analusis 28: 850–854.

II Pöykiö R & Torvela H (2001) Pine needles (*Pinus Sylvestris*) as a bioindicator of sulphur and heavy metal deposition in the area around a pulp and paper mill complex at Kemi, Northern Finland. Intern J Environ Anal Chem 79: 127–138.

III Pöykiö R, Tervaniemi O-M, Torvela H & Perämäki P (2001) Heavy metal accumulation in woodland moss (*Pleurozium Schreberi*) in the area around a chromium opencast mine at Kemi, and in the area around the ferrochrome and stainless steel works at Tornio, Northern Finland. Intern J Environ Anal Chem 81: 137–151.

IV Pöykiö R, Perämäki P, Bergström R, Kuokkanen T & Rönkkömäki H (2002) Assessment of the impact of opencast chrome mining on the ambient air concentrations of TSP, Cr, Ni and Pb around a mining complex in Northern Finland. Intern J Environ Anal Chem 82: 307–319.

V Pöykiö R, Perämäki P, Välimäki I & Kuokkanen T (2002) Estimation of environmental mobility of heavy metals using a sequential leaching for particulate material emitted from an opencast chrome mine complex. Anal Bioanal Chem 373: 190–194.

VI Pöykiö R, Perämäki P & Rönkkömäki H. The homogeneity of heavy metals deposition on glass fibre filters collected using a high-volume sampler in the vicinity of an opencast mine complex at Kemi, Northern Finland. Anal Bioanal Chem (submitted).

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In addition to the results and conclusions published in the 6 original articles mentioned above, some new conclusions and references are also presented. The summary of results in I has been represented in a poster at the Finnish Chemical Congress, Kemian Päivät-2000. The summary of results in IV and V has been represented in posters at the Finnish

Chemical Congress, Kemian Päivät-2000. In addition, the summary of results in IV has been represented in poster at the First Baltic Symposium on Environmental Chemistry Tartu, Estonia, in 2001.

# Contents

# 1 Introduction

## 1.1 Legislative basis for preventing pollution threats

Pollution is one the most serious of all environmental problems and, at its worst, poses a major threat to the health and well-being of millions of people and the global ecosystem. Pollution (contamination) is an inevitable and necessary part of life for most of the world´s population, especially those living in large communities and relying on technology and mechanized transport. Emission from industry, energy generation, and from road traffic have been responsible for the main local problems in past years (1–3).
The goal of environmental legislation is to prevent pollution of the air and consequential effects caused by industrial operations, energy generation, traffic *etc.*

In Finland, environmental legislation is of longer standing than environmental administration. The evolution of Finnish environmental legislation began in the 19$^{th}$ century, when the oldest act on nature conservation and environmental protection came into force. However, the Finnish Ministry of Environment was not founded until October 1, 1983 (4). A significant event in air pollution control in Finland occurred in 1982, when the first Air Pollution Control Act (5) came into force. Since then, air pollution control has developed rapidly; more knowledge on air pollution is continuously accumulating and new problems are being detected (5). In Finland, a new Environmental Protection Act (6) has been in force since 1.3.2000. It combines the environmental acts required to meet the requirements of Council Directive 96/61 EC of September 1996 concerning integrated pollution prevention and control (7).

The basic objective in the field of air pollution control is to restrict the concentration of pollutants in the ambient air to such levels as will not adversely affect the health, well-being or welfare of the community.

Finnish environmental legislation requires the operator to be aware of the amount and composition of their emissions, as well as of the efficiency of the purifying methods/ equipment used, and also of the impact on the environment caused by their operations. According to the Finnish Environmental Protection Act (6) and Degree (8), the operators of industrial processes and plants are generally obliged by their environmental permits to monitor the processes (operation monitoring), releases (emission monitoring) and impact of their operations on the environment (impact monitoring).

In the impact-monitoring procedures presupposed by the permit provisions laid down in the environmental permits approved by the competent authority of Lapland Regional Environmental Centre, pine needles (*Pinus Sylvestris*) are accepted as a bioindicator for sulphur deposition emitted from the Stora Enso Oyj Veitsiluoto Mills (9) and Oy Metsä-Botnia Ab Kemi Mills (10). Woodland moss (*Pleurozium Schreberi*) is accepted as a bioindicator for heavy metal deposition emitted from the AvestaPolarit Stainless Oy (11) and the AvestaPolarit Chrome Oy Kemi Mine (12). In addition, the determination of TSP in the air in the vicinity of the mining complex of the AvestaPolarit Chrome Oy Kemi Mine is laid down by the environmental permit provisions approved by the competent authority of Lapland Regional Environmental Centre.

By monitoring the environmental impact of point source pollution on the environment, authorities can foresee and prevent threats and risks before they become problems. The monitoring can be performed by a variety of methods, such as using plants as a bioindicator for air pollution assessment, fish as a bioindicator for effluents (13–15), computer modelling for both air pollution (16,17) and noise assessment (18,19), or even very high technology such as satellite images (20) for airborne or waterborne pollution. Environmental monitoring should involve the continuous or regular assessment of parameters depicting the state of the environment. It can also be used to measure and control the success of environmental policies (21).

In this context it is worth noting that, when the "environmental effects" of industrial activities are studied, the so-called basic methodology of natural sciences, *e.g.* chemistry and physics, are not the only environmental science that can be used. Määttänen (22) studied the environmental effects of Enocell Uimaharju pulp mill in North Karelia using the perspective of environmental geography (people´s attitudes, media *etc.*), and Marttila (23) mainly epidemiological methods (eye, respiratory and central nervous symptoms) on the health effects of pulp and paper mills in South Karelia.

Before carrying out an environmental investigation or any expansion in production, it is very important to document the normal state of the environment. This documentation can be done, for example, by carrying out intensive environmental studies on contaminant levels in the environment *e.g.* heavy metal concentrations in plants, by monitoring gaseous pollutant or particle concentrations in the air in the vicinity of pollutant sources and so on. The aim of this so-called environmental impact assessment (EIA) (24,25) is to determine what indirect and direct, both negative and positive, effects the project will have on the surrounding nature, society and industry. In the case of projects for which an actual environmental impact assessment is not required, there will be an environmental investigation, which conforms to the obligation to keep oneself posted on the environmental impact of a project and which focuses on known facts.

In these kinds of situation especially, but also in the normal operating state of industrial plants, there is a continuous need for efficient environmental research on the impact effects of industrial operations on the environment. There is no room for complacency, because natural processes responsible for the assimilation and detoxification of pollutants can be overloaded if the rate of pollutant emissions and transport is too high.

## 1.2 The use of plant bioindicators for determining the distribution pattern of aerial emissions

Point source pollution resulting from pulp and paper mills, mining, stainless steel works and from other kinds of industrial activities, *e.g.* municipal energy production, chemical works, and petrol storage, occur all over the world, often in some very remote regions. These point sources emit a range of gaseous and particle pollutants into the air depending on the process and the type of activities at point source (2).

Air pollution by gaseous compounds *e.g.* sulphur dioxide ($SO_2$), and total reduced sulphur compounds (TRS compounds) such as hydrogen sulphide ($H_2S$), methyl mercaptane ($CH_3SH$) and methylsulphides [$(CH_3)_2S$ and $(CH_3)_2S_2$], is released into the ambient air from pulp and paper mills (2,9–10,22–23).

Air pollution by heavy metals, such as Cr, Ni, Zn, Fe and Cd, are released into the ambient air from ferrochrome and stainless steel works and from metal-ferrous mining (2,11–12,26). Heavy metals are mainly emitted in the form of particulate material, and the distance that they are transported is, compared to gaseous pollutants, in general relatively short; the transport distance depends on factors connected with the production plant, such as the height of the stack and emission levels, as well as on the size of the particles (2,27). Air pollution from both local and distant sources impact the environment in the form of dry and wet deposition, and the spread of pollutants is dependent on the height they reach in the atmosphere, their particle size and on climatic factors (2).

Environmental bioindicators, such as pine needles, mosses, and lichens, represent a complementary tool for environmental monitoring systems, and could also overcome some of the shortcomings associated with the direct measurements of pollution. Biomonitoring – monitoring the state of the environment through the performance of living organisms (bioindicators) – directly depicts the impacts of environmental pollution on organisms, and can potentially detect the long-term exposure of a site to environmentally harmful chemicals. In addition, they also provide an overall picture of the impact of environmental factors that often cannot be detected by measuring even a wide range of physiochemical variables. Bioindicators can also be used to measure the cumulative impact of different types of environmental pressure, *e.g.* air pollution emitted from a range of emission sources (21,28–29).

### *1.2.1 Pine needles as a bioindicator*

Pine needles (*Pinus sylvestris*) have proved to be suitable air quality indicators for pollutants, especially for sulphur and heavy metals, in many studies such as the studies of Reimann *et al*. (30) in the vicinity of the nickel smelter and refinery at Monchegorsk, the Kola Peninsula, Russia, Manninen *et al*. (31) in the vicinity of the Neste oil refinery at Porvoo, Finland, and the Rautaruukki steel works at Raahe, Määttänen (22) in the area around a pulp and paper mill at Eno, and Huttunen *et al*. (32) in the vicinity of the pulp and paper mills at Oulu, Kemi and Valkeakoski, in order to clarify the effects of emissions from local point sources to needles, and in order to drawn up the pollution

maps needed to evaluate air pollution hazards. Spruce needles (*Picea abies*) have also been used as a bioindicator for sulphur and heavy metals in a number of studies, such as those carried out by Määttänen (22) in the area around a pulp and paper mill at Eno, and Tynnyrinen (33) in the vicinity of sulphuric acid, phosphoric acid, nitric acid and fertilizer plants and the areas around an apatite mine at Siilinjärvi. Nowadays, pine and spruce needles are widely used in Finland for biomonitoring purposes in areas around point sources, and the environmental authorities have accepted them as a bioindicator for sulphur and heavy metal deposition (*i.e.* impact monitoring).

### *1.2.2 Mosses as a bioindicator*

Mosses are very sensitive bioindicators of heavy metal contamination. Use of the moss technique for surveying atmospheric heavy metal deposition was developed in the late 1960s (34–35). The technique is based on the fact that mosses, especially the carpet-forming species, obtain most of their nutrients directly from rain water and from the deposition of air-borne particulate material. Two different species of moss, *Pleurozium schereberi* and *Hylocomium splendens,* are wide-spread, carpet-forming species that occur abundantly on acidic, organic substrates (mor) in coniferous forest throughout the Nordic countries. *Pleurozium schereberi* has been used in many studies for monitoring heavy metals in Scandinavia and in Europe (36–38). In addition, the Finnish Ministry of the Environment primarily recommends the use of *Pleurozium schreberi* as a bioindicator for heavy metal deposition, and secondarily the use of *Hylocomium splendens* (39).

Several international studies have shown that surveys of the metal concentration in mosses can be a valuable means of identifying sources of airborne pollution and of mapping metal deposition, such as in the area surrounding the Shallee silver mines in Ireland (40), in the vicinity of the steelworks at Frederiksvaerk area in Denmark (41), and in parts of the Kola Peninsula in the Russia Northern region (42). In Finland, mosses have been used as a bioindicator of heavy metals in the surrounding of point sources such as the pulp and paper mills of Enocell Oy in Northern Karelia (22), and Oy Metsä-Serla Ab Simpele Mills (43), in the vicinity of the Malmi crematorium (44), and in the Rovaniemi area around a district heating plant (38) for the assessment of sulphur and heavy metal deposition.

## 1.3 Physical characterization of airborne matter is important

Airborne particulate matter is one of the most important constituents of the atmosphere. Particulate pollutants consist of finely divided solids or liquids such as smoke, dust, fumes, mist, smog and sprays. Natural processes that emit particulate matter into the atmosphere include volcanic eruptions, geochemical sources, wind blown dust and soil and spray from marine source. Anthropogenic (man-made) sources include power plants,

traffic, agriculture, and various industrial activities such as mining and the metallurgical industries etc (2).

Airborne particulate matter is not a single pollutant, but rather a mixture of many subclasses of pollutants with each subclass containing a large number of different chemical species. Airborne particulate matter usually consists of discrete particles ranging in size from molecular clusters of 0.005 μm to coarse particles in the order of 100 μm, which is usually called TSP (total suspended particulate matter) (45). The European Committee for Standardization (CEN) used the following definition for TSP: "All particles surrounded by air in a given volume of air" (46).

Most metals in the atmosphere are associated with airborne particulate matter (47). The concentrations of metals in atmospheric particles (aerosols) are a function of their sources. This includes both the occurrence of the metals in combustion processes and their volatility, as well as their occurrence in crustal dust production and sea-spray generation (48). The physico-chemical properties, *i.e.* size fractions, possible occurrence of toxic minerals and /or metals and their concentrations are important factors for hygienists and analytical chemists in characterizing the possible health effects of airborne dust at workplaces (49).

Some elements such as Cr and Ni have a special relevance due to their potential carcinogenic impact (USEPA, 1987), and atmospheric levels of other elements such as Cd, Hg, Mn and Pb are also regulated by WHO (1987) owing to their high potential toxicity (50). However, according to Finnish Environmental Protection Act (6) and Degree (8) there are no air quality limit values for Cr and Ni.

### *1.3.1 Inhalable and respirable particulates*

Atmospheric particulate range < 10 μm ($PM_{10}$) is inhaled into the deeper respiratory tract, resulting in pathologies associated with aerosol pollution (46,49–51). For this reason, the US Environmental Protection Agency (USEPA) promulgated in 1984 an air quality standard for environmental particulate matter based on the measurements of $PM_{10}$ instead of total suspended particles (TSP) (50). The EU has also developed a new directive for the monitoring of $PM_{10}$ instead of TSP (52–53). In this context it is worth noting that $PM_{10}$ is only a fraction of TSP. No generally accepted conversion method has yet been devised for TSP and $PM_{10}$ which may, according to USEPA, constitute between 40–70 % of TSP (54–55), and according to Querol *et al*. (50) and Fang *et al*. (51) between 52–74 % and 35–89 %, respectively. However, according to EU directives (52) and the decision of the Finnish Council of State on air quality (53), of which the latter came into force in august 2001, the TSP concentration in the ambient air can be calculated from the $PM_{10}$ concentration (*i.e.* $TSP = 1.2 * PM_{10}$).

The particle size distribution is especially important in occupational health because it determines the regional deposition of inhaled aerosols in the different parts of the human respiratory tract. (46,49,56).

In human exposures by inhalation, three size-dependent particulate fractions are defined, which determine where penetration and deposition occur in the respiratory tract and a response is elicited. The inhalable fraction (aerodynamic diameter, $d_{ae} < 100$ μm) is

the fraction of total airborne particles that enters the body through the nose and/or mouth during breathing; it is relevant to health effects anywhere in the respiratory tract, such as rhinitis, nasal cancer and systemic effects. The inhalable fraction is sometimes called inspirable – the terms are equivalent (46). The thoracic fraction [corresponding to the mass fraction of total aerosol of 50 % at $d_{ae}$ = 10 µm (the $PM_{10}$ fraction) and of 1 % at $d_{ae}$ = 28 µm] is the inhaled particle component which penetrates into the lung (*i.e.* the whole region below the larynx) and is important for asthma, bronchitis and lung cancer. The respirable fraction [corresponding to the mass fractions of total aerosol of 50 % at $d_{ae}$ = 4 µm (the $PM_4$ fraction) and of 1 % at $d_{ae}$ = 10 µm] constitutes the inhaled particles that penetrate to the alveolar region of the lung (*i.e.* includes the respiratory bronchioles, the alveolar ducts and sacs) and is pertinent to the development of such chronic diseases as pneumoconiosis and emphysema (46,57).

In this context, it is worth noting that, within the context of environmental monitoring of industrial activities, lichens and mosses have been shown to trap micrometre-sized particles extracellularly at surface sites and in the interstitial spaces within the plant body (57,58).

### *1.3.2 Collection of airborne particles*

For the collection of airborne particles, so-called high-volume samplers ("Hi-vol") with an air flow in the range of between 60–90 $m^3$ h–1 (50,59–63), or so-called low-volume ("Low-vol") air samplers with an air flow of between 1–3 $m^3$ h–1 (64–65), have been widely used; the flow of air varies depending on the filter material and its flow resistance, and on the efficiency of the sampler (pump). The collection of suspended particulates can also be carried out with a beta-gauge sampling system on glass fibre filter tape (66). In addition, personal samplers with an air flow rate at a level of 2 L $min^{-1}$ (63,67–68) have been used, especially for exposure assessment, as well as a number of direct-reading instruments (56).

The methodology used for the determination of suspended particle concentration by "Hi-vol", "Low-vol" and personal samplers is usually based on gravimetric monitoring; the concentration of particles are determined by the net weight gain in dust on the filter subsequent to exposure to the appropriate sample of air. Beta-gauge sampling is based on the principle of beta radiation attenuation; the difference between the beta emissions measured on the unexposed filter (blank) and those on the collected sample is directly proportional to the mass of dust on the filter. In addition, the particulate sample collected using these sampling systems can be further analysed in a laboratory to determine the chemical and metal constitute of the particulate sample. For a more comprehensive review of direct –reading instruments for exposure assessment, see (56).

Various types of filter with different size and pore size have been used for the collection of particulate matter using "Hi-vol", "Low-vol" or personal samplers, *e.g.* Teflon membranes, polystyrene, cellulose acetate, polytetrafluoroethylene (PTFE) membranes, quartz, cellulose, cellulose ester, nitrocellulose, nylon, polystyrene, silver membranes, graphite, and glass fibre filters. However, although glass fibre filters usually contain high and variable levels of residual impurities, they are widely used in the high-

volume sampler because of their high collection efficiency and low flow resistance (69–70). For a more comprehensive review of filters, and sampling systems for airborne pollutants in the atmosphere, see (71–73).

### *1.3.3 The bioavailability of airborne particles*

Bioavailability is the degree of "environmental mobility and availability" of elements in aerosol samples once the aerosol is mixed directly into nature (74–80); the loosely bound fractions, *e.g.* water-soluble fraction and fraction leachable with ammonium acetate, are much more environmentally mobile than those associated with the silicate structure, *i.e.* leachable with a mixture of strong mineral acids. Thus, the loosely bound fractions are most likely to be released into aqueous solution after deposition on the surface of lakes, rives and soils, and are thus potentially bioavailable (47–48,74–80).

Another definition of bioavailability was formulated at the Winnipeg Ecotox Workshop in 1996: "the fraction of a substance that is available for absorption by an organism when considering a specific route of exposure". In certain cases it has been suggested that the word "absorption" be replaced by other terms such as "uptake" or "accumulation" (*e.g.* in the case of metal-ion uptake by cells, fish gill surfaces or plants) or even "deposition" or "intake" (*e.g.* inhalation of aerosols) (57). The chemical procedures for the determination of "bioavailability" of airborne particulate matter is presented later on this thesis.

### *1.3.4 The particle size distribution*

After sampling, the particle size distribution of airborne particulate matter can be determined by the Andreasen sedimentation method (49,81), as long as the dust can be quantitatively separated from the filter. In this method, the dust is recovered from the filter in an ultrasonic-bath using ethanol. However, the method is not suitable for use with glass fibre filters, because airborne particles penetrate into glass fibre filters, and thus cannot be separated from the filter matrix by shaking or by ultrasonic treatment; in addition, the glass fibre and dust form a slurry that disturbs the sedimentation. In this context it is worth mentioning that, the use of filters that dissolve in acetone [*e.g.* cellulose acetate and nylon filters (72)], or in other organic solvents [*e.g.* polystyrene filters dissolve in trichloroethylene (63)], or that can be destroyed by burning in alcohol [*e.g.* cellulose filters (72)], facilitates the particle size distribution and further analysis of the dust. After disposing of the filter, the residue consists of airborne particles only.

However, a high-volume sampling system equipped with a cascade impactor that separates the particulate matter during sampling has also been used (48,50,72,79–84). The particles can also be fractionated into different sizes during personal (individual) sampling by a cascade impactor (57).

## 1.4 Methods for the dissolution and analysis of environmental samples

### *1.4.1 Dissolution*

Most of the analytical methods used for trace element determination in environmental samples, such as plants, humus, organic stream sediments, mineral soil and sediments, require decomposition of the sample. Hence, when the analytical methods require dissolution of the sample, sample preparation (in addition to sampling) is the analysis step, that has the greatest effect on uncertainty of the final results (85,86). This is especially important in the determination of trace elements in plants, because plant materials are, as a rule, not homogeneous and they usually contain soil and/or mineral fractions, thus making them difficult to dissolve. Airborne particulate matter also presents a very complex matrix for analysis. It may contain a large number of elements of widely different concentrations, as well as variable amounts of organic material and silicate base dust (85,87).

During the last two decades great progress has been made in analytical instrumentation, but both sample preparation and sampling are still the major factors contributing to the uncertainty of the final results. To be effective, sample digestion methods must efficiently decompose the sample matrix so that the analytes of interest are completely released and solubilised, *i.e.* "total decomposition of the sample", and are in a form compatible with the analytical method of choice (88). The widely used sample decomposition procedures do not always ensure complete decomposition (85).

Nowadays a microwave oven is widely used for the total decomposition of environmental samples (88). There are many advantages in using microwave digestion for the decomposition of environmental samples, and include decreased digestion times, smaller amounts of acid required, reduced contamination during the digestion procedure, and the avoidance of using perchloric acid (89–90). For the determination of trace elements in environmental samples, *e.g.* plant materials and airborne particles, both the microwave assisted extraction (leaching) and total digestion techniques have been used for sample preparation (91–95). In addition, alkali fusion (64) with sodium carbonate and boric acid has been used especially for the decomposition of atmospheric particles containing chromium. The pressure bomb digestion method (69,96–97) has also been used.

In wet-chemical (wet-digestion) methods, hydrofluoric acid (HF) is needed for dissolution of the silicate matrix in airborne particles (96–97) and in plants (98–99). Usually HF is also needed for the total dissolution of glass fibre filters. However, one alternative method for the dissolution of airborne particulate matter on glass fibre filters is to leave the filter more or less intact. These techniques are usually based on leaching (extraction) procedures, such as for the determination of Pb in airborne particles by room-temperature ultrasonic extraction using $HNO_3$ and HCl (100–101). However, Cr cannot be extracted quantitatively by this method, and there is often the problem of high background values due to impurities in the filter materials, especially if glass fibre filters are used (101–103). In addition, depending on the type of filter, the filter can also be destroyed by burning or by ashing the filter as well as the plant material in a muffle

furnace or with a laser ashing device (104–106). Some filters can be dissolved in acetone or other organic solvents (63,72). More comprehensive reviews of the microwave digestion technique for the elemental analysis of a range of environmental samples are given in (88,91).

### *1.4.2 Determination of metals and sulphur*

After the sample has been decomposed and dissolved, the trace elements are usually determined by atomic absorption spectrometry (AAS) in flame mode (FAAS) or with a graphite furnace device (GFAAS), or by inductively coupled plasma atomic emission spectrometry (ICP-AES). Although AAS is still often used, simultaneous multielement analysis is not possible with this technique. Therefore ICP-AES has become a well established analytical tool for multi-element analysis. Low detection limits, a wide linear dynamic range, relative freedom from chemical interferences and, above all, its high sample throughput makes ICP-AES a powerful analytical tool for many applications. (107–108). A more comprehensive review of the applications of atomic spectrometry techniques for environmental analysis is given in (109).

Neutron activation analysis (NAA) (110–113) and especially X-ray fluorescence (XRF) (78,114–117) are often applied in trace elements determinations of plant and dust samples.

In this context it is worth noting that ongoing technological developments, particularly the recent ones in computer microchip and detector technology, have led to the design and production of battery-operated, field-portable X-ray fluorescence instruments (FPXRF) (118). These instruments have been successfully used for rapid, on-site characterization of Pb and other metals in workplace air samples collected on filters (119–120), as well as for the characterization of metals in contaminated soils for risk characterization, assessment and management (121–122). A more comprehensive review of the instrumentation and techniques, as well as the applications of X-ray spectrometry for environmental analysis, is given in (123).

### *1.4.3 Determination of sulphur*

In addition to the foregoing methods, total sulphur determination of plant material can be performed by on an Leco analyser (124–125), which utilizes a combustion technique (~ 1370 °C) with infrared (IR) detection for determination of the evolved sulphur dioxide. Ion chromatography (IC) is also a suitable method for the determination of total sulphur in plant materials. In this method, the sulphur species have to be oxidized to sulphate ($SO_4^{2-}$), for example in a Schöniger-type oxygen flask (126–129). This method, as well as other methods, [*e.g.* gravimetry (130), turdidimetry (131–132) and colorimetry (133)] for $SO_4^{2-}$ determination are described in (134).

## 1.5 Leaching and other techniques for the physico-chemical characterization of airborne particulate matter

### *1.5.1 Leaching*

Leaching is a procedure that is applied for the extraction of metals from environmental samples, *e.g.* soil, plants, airborne particles, sludge and wastes, and has become common term of EPA and in the environmental analytical field. Leaching is not total decomposition, and the leachable recoveries of analytes are generally lower than the total concentrations. Recoveries can only reach total values if an element is completely soluble in the leaching solvent. Leaching studies are often applied in assessing worst case environmental scenarios where components of the sample become soluble and mobile (135).

Two different approaches are usually applied in speciation studies: single and sequential leaching (extraction). In sequential leaching (extraction) procedures, chemical extractants of various types are applied to the sample, each successive treatment being more drastic in chemical action than the previous one (93).

### *1.5.2 Sequential leaching*

Sequential leaching has been used in many environmental studies on airborne particles. Dreetz *et al*. (47), Hlavay *et al*. (48,74), Lum *et al*. (76,77) and Varga *et al*. (78) used a sequential leaching procedure to determine the potential bioavailability and environmental mobility of airborne particulate matter collected in urban areas, and Querol *et al*. (50) for atmospheric particulates (TSP) derived from soil reclamation activities at the Donana mine area in Spain. Leaching procedures have also been used for partitioning heavy metals in soils contaminated by smelting (27,137–139) and mining activities (137–138,140), and in waste materials and metallurgical slags (140–141) for risk assessment. This is because, extractable rather than total element concentrations give better information on the potentially mobility of heavy metals and their bioavailability (47–48,74–80,142–143).

Although a large number of different methodological approaches have been developed and adapted to sequential extraction procedures for the speciation of trace metals, most of them mimic the basic method initially developed for sediments by Tessier *et al*. (143). Tessier *et al*. (143) applied it for the fractionation of metals into the following fractions: (i) exchangeable fraction, representing the most easily available metals, (ii) carbonate fraction, (iii) Fe, Mn and Al oxide fraction, (iv) organic matter fraction, and (v) residual fraction, tightly bound to the silicate matrix of the sample (142–143).

Hlavay *et al*. (48,74), who studied the distribution of trace elements in filter-collected aerosols at a large number of cities and towns, used sequential leaching for the fractionation of metals in urban particles into the following fractions: (i) the environmentally mobile fraction, *i.e.* leachable with ammonium acetate ($CH_3COONH_4$),

(ii) the fraction bound to carbonate and oxides, *i.e.* leachable with a mixture of hydroxylamine hydrochloride ($HONH_3Cl$) and acetic acid ($CH_3COOH$), and (iii) the fraction bound to silicates and organic matter (environmentally immobile), *i.e.* leachable with a mixture of nitric acid ($HNO_3$) and hydrofluoric acid (HF). However, some researchers (47,77–78,142) have estimated the water-soluble fraction first, and then fractions (i) – (iii) in the same way as Hlavay *et al*. (48,74).

### *1.5.3 Speciation*

From an environmental point of view, it is not the total metal concentrations in airborne particles which are of prime importance, but rather how easily the metals can be mobilized in the environment (47–48,74–80). Information on the chemical speciation of aerosols (particulate material /"dust") indicates the mobility of elements once the aerosol is mixed directly into natural waters or during scavenging of the aerosol by wet deposition. Sometimes it is also necessary to separate the different species of metals in airborne particles in order to clarify the adverse health effects to estimate the source and trends of air pollution, or to determine the carcinogenic fraction of airborne dust (57).

Cr(III) is a naturally occurring, essential element with a very low toxicity, but the inhalation of Cr(VI) is a health concern associated with chromite ore production and processing (*i.e.* anthropogenic sources), and is classified by the U.S. Environmental Protection Agency (EPA) as a human inhalation carcinogen (144). Thus, determination of the total Cr concentration does not provide sufficient information about possible health hazards. Hexavalent chromium, Cr(IV), is such a potential carcinogenic species that continuous monitoring is imposed in accordance with Directive 90/3941/EEC on exposure to carcinogenic substances. In occupational health, the OEL (Occupational Exposure Limits) for water-soluble and certain water-soluble compounds in indoor air is limited to 0.5 $mg/m^3$ for Cr, 0.5 $mg/m^3$ for Cr(III) and to 0.05 $mg/m^3$ for Cr(VI), which reflect the different toxicities of the species (145).

The analytical method for the determination of airborne Cr(VI) uses a triple impinger sampling train with impingers containing slightly alkaline (pH 8–9) sodium bicarbonate buffer solutions to ensure the valence stability of Cr(VI). The impinger solutions are analyzed using ion chromatography and visual absorption spectrometry (IC-VAS) methods (144).

In addition, the speciation of chromium ions in atmospheric precipitation has also recently been carried out using wet-only collectors for sampling, and ion-exchange (*i.e.* iminodiacetic acid ethylcellulose, IDAEC for Cr(III) chelating, and diethylamine ethylcellulose, DEAE for Cr(VI) chelating) together with GFAAS determination. (146).

Leaching methods (*e.g.* the benzene extraction) have been used for determination of the carcinogenic fraction of airborne dust (61–62,70,145). The most common extraction techniques for the speciation analysis of heavy metals in airborne particulates, soil and sediments are presented and briefly discussed in (147–148).

### *1.5.4 Morphological characterisation*

For the morphological characterisation (shape, size, roughness) of individual atmospheric particles, especially of asbestos, mineral fibres and quartz, a scanning electron microscope (SEM), transmission electron microscope (TEM), and a light microscope can be used (82,149–158), as well as quantitative determination of crystalline silica in respirable-size dust samples by infrared spectrophotometry (159).

# 2 The study area and sources of pollutants

## 2.1 The study area (I–VI)

The study was carried out in the vicinity of the town of Kemi (65º44´N, 24º35´E) and the town of Tornio (65º50´N, 24º8´E) on the Gulf of Bothnia, northern Finland. In 1999, Kemi had a population of about 24 500.

The industrial plants of Oy Metsä-Botnia Ab Kemi Mills, Stora Enso Oyj Veitsiluoto Mills and AvestaPolarit Chrome Oy Kemi mine (former name: Outokumpu Chrome Oy Kemi Mine) which are the largest pollutant sources, are located in the centre of the area.

Oy Metsä-Botnia Ab Kemi mills has two units, a chemical pulp mill and a board mill. The pulp mill produces 550 000 tonnes a year of bleached and unbleached pulps. The board mill produces 310 000 tonnes a year of different types of linerboard for use as raw material by the packaging industry. The sawmill produces 160 000 cubic metres of sawn timber a year. The annual production of Strora Enso Oyj Veitsiluoto Mills is 370 000 tonnes of bleached stw and hdw pulps, 455 000 tonnes of uncoated fine paper, 265 000 tonnes of sheet, 400 000 tonnes of coated paper (LWC and MWC), 200 000 cubic metres of sawn goods and 400 000 packaging pallets.

The AvestaPolarit Chrome Oy Kemi Mine is a large chromium ore deposit located about 7 km from Kemi. Present ore reserves are 70 million tonnes, and the estimated mineral resources 150 million tonnes. The mine produces approx. 1 million tonnes of chromite ore per year. At the same time, 8 million tonnes of waste rock are removed from the open-cast pits. Relatively hard, metallic, black oxide mineral of chromium and iron ($(Fe,Mg)(Cr,Al)_2O_4$) is the main economical important mineral of chromite. The ore also contains minor amounts of minerals such as magnetite ($Fe_3O_4$), ilmenite ($FeTiO_3$), hematite ($Fe_2O_3$), rutile ($TiO_2$), chalcopyrite ($CuFeS_2$) and millerite (NiS). The chromite content of the ore is about 65–70 %, the gangue minerals being talc ($Mg_3[Si_4O_{10}](OH)_2$), carbonate ($CO_3^{2-}$) and serpentine ($(Mg,Fe)_3[Si_2O_5](OH)_4$) (160–161, 169).

AvestaPolarit Stainless Oy (former name: Outokumpu Polarit Oy) is a large ferrochrome and stainless steel works located about 10 km from Tornio, and about 25 km from the AvestaPolarit Chrome Oy Kemi Mine, on a peninsula on the coast of the Gulf of Bothnia close to the Swedish border. The works have been producing ferrochrome and

stainless steel since 1968 and 1976, respectively. The process today consists of a steel belt sintering plant and two smelting furnaces. The annual output of the sintering unit is 400 000 tonnes of pellets, the transformer capacities of the smelting furnaces 40 and 70 MVA, and the total annual ferrochrome smelting capacity 250 000 tonnes.

## 2.2 Sources of pollutants (I–VI)

Air pollutants in the Kemi are a combination of the region´s own emissions and of long-distance transportation of pollutants. A cluster of pulp and paper mills using the sulphate method is located in Kemi. The paper mills release large amounts of sulphur dioxide ($SO_2$) and malodorous sulphur compounds, also called total reduced sulphur (TRS) compounds, such as hydrogen sulphide ($H_2S$), methyl mercaptane ($CH_3SH$), and methylsulphides ($(CH_3)_2S$ and $(CH_3)_2S_2$), into the ambient air. Malodorous sulphur compounds are typically measured as total reduced sulphur (TRS), and they are responsible for the so-called "pulp-mill-smell" during operation disturbances.

Total sulphur emissions ($SO_2$ + TRS) in Kemi have fallen considerably since 1980 following the extension of district heating and because the pulp mills have upgraded their processes (Fig 1).

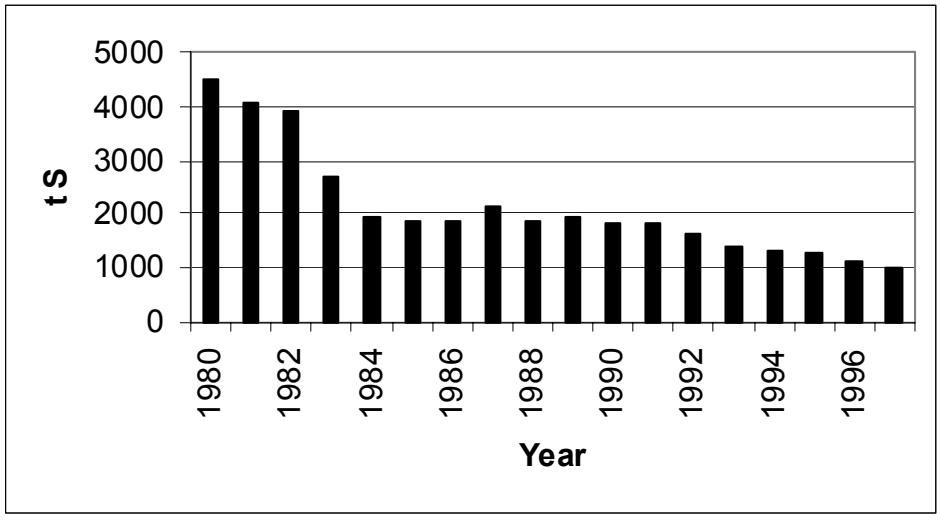


**Fig. 1. Total sulphur ($SO_2$ + TRS) emissions in Kemi during 1980–1998 (t S). (II)**

Other major constituents of local air pollution emitted from Oy Metsä-Botnia Ab, Stora Enso Oyj and AvestaPolarit Chrome Oy Kemi Mine are nitrogen compounds ($NO_x$; 2284 t ($NO_2$) in 1998), particles (397 t) and chlorine compounds ($Cl_{tot;}$ 23 t). Exhaust emissions from road traffic primarily consist of carbon monoxide (CO; 1849 t in 1996), hydrocarbons (HC; 300 t) and nitrogen compounds ($NO_x$; 667 t ($NO_2$)). Lead (Pb) is no longer a problem, because the petrol used by automobiles in Finland is unleaded. The

total VOC emissions in Kemi in 1998 were about 50 million tonnes, the main emission source being the oil and petrol storage at Ajos in south Kemi.

Air pollutants emitted from AvestaPolarit Chrome Oy Kemi Mine are derived from the various mining operations, such as crushing and enrichment plant, roads, piling stores, quarrying and random sources, as well as emissions from a thermal power station (5.6 t $SO_2$, 1.9 t $NO_x$ ($NO_2$)) and 0.9 t particles in 2000). The activities of the subcontractors operating in the mine area also make a contribution. Particle emissions from the industrial activities (thermal power plant + enrichment plant + crushing) were 2.9 t, which is only 6.0 % of the total particle emissions (47.9 t). The main particle emission sources (45 t) are the quarry, roads and stores, which account for about 94 % of the total particle emissions. The annual $SO_2$ and $NO_x$ emissions are estimated to have remained relatively constant for many years, but particle emissions from roads are estimated to vary depending on how frequently the roads are watered. There are no other heavy metal emission sources in the vicinity of the mining complex. The nearest industrial emission sources are the pulp and paper mills, Oy Metsä-Botnia Ab Kemi Mills and Stora Enso Oyj Veitsiluoto Mills, situated about 7 km away.

Annual emissions of heavy metals into the air from Oy Metsä-Botnia Ab and Stora Enso Oyj are about 12 kg for Cr, 75 kg for Ni and 40 kg for Zn, which are negligible compared to those emitted from the AvestaPolarit Stainless Oy and AvestaPolarit Chrome Oy Kemi Mine.

The estimated total particle and heavy metal (Cr, Ni and Zn) emissions into the air from the AvestaPolarit Stainless Oy and AvestaPolarit Chrome Oy Kemi Mine during the period 1990–1999 are given in Table 1.

*Table 1. Major air pollutants (t/a) emitted from the ferrochrome and stainless steel works of AvestaPolarit Stainless Oy, and from the opencast chromium mining complex of AvestaPolarit Chrome Oy Kemi Mine at Kemi during 1990–1999. (III)*

| Source | Emission | 1990 | 1995 | 1999 |
|---|---|---|---|---|
| AvestaPolarit Stainless Steel Oy | Particles | 260 | 132 | 229 |
| | Cr | 20 | 14.6 | 15.2 |
| | Ni | 1.7 | 2.2 | 5.3 |
| | Zn | 12 | 7.5 | 11.9 |
| AvestaPolarit Chrome Oy Kemi Mine | Particles | 38 | 52 | 42.7 |

Chromium emissions are mainly derived from the ferrochrome plant, and Ni and Zn emissions mainly from the steel mills. The total particle and heavy metal emissions are based on the emission measurements made by the plant. The total particle emissions, as well as the heavy metal emissions (Cr, Ni and Zn), vary from year to year owing to fluctuations in the use and composition of recycled material, in emissions related to process conditions and the efficiency of the dust removal processes and in the timing of sampling, uneven distribution of particles in the emissions etc (162); similar emission phenomena for metallurgical processes have also been reported by Derome (27) for the Harjavalta Cu-Ni smelter, SW Finland. The works, the AvestaPolarit Stainless Steel Oy, are by far the most important point sources of these heavy metals in Tornio and in northern Finland.

# 3 Aims of the study

This thesis is a summary of the results and conclusions published in 6 original articles (Appendices I–VI). The aims of the thesis are as follows:

- to compare a number of dissolution methods for the multi-element analysis of some plant materials used as bioindicators of sulphur and heavy metal deposition. An additional aim was to provide the authorities with the information required for assessing suitable dissolution methods for heavy metal determination in the plant materials used as bioindicators for sulphur and heavy metal deposition (I),
- to determine the sulphur concentrations in pine needles in order to assess the distribution patterns of aerial emissions emitted from the pulp and paper mill complex at Kemi and, to determine the element (Fe, Zn, Ca, V and Pb) concentrations in pine needles in order to assess metal accumulation in the area around the pulp and paper mill complex at Kemi (II),
- to determine the heavy metal concentrations (Cr, Ni and Zn) of mosses in the area around the chromium opencast mine at Kemi and around the ferrochrome and stainless steel works at Tornio in order to assess the aerial heavy metal distribution patterns of emissions from these point sources (III),
- to determine the TSP, Cr, Ni and Pb concentrations in the air in the vicinity of the mining complex of the AvestaPolarit Chrome Oy Kemi Mine, and to estimate the bioavailability and environmental mobility of heavy metals in TSP material (IV and V), and
- to study the distribution of heavy metals deposition on glass fibre filters collected using a high-volume sampler in order to clarify whether the heavy metals are homogeneously distributed on the filters or not (VI).

In addition, the aim of the list of references cited in this thesis is to form a database for all who require more information on the subject of this study, especially for the authorities who have to define the research methods to be used when studying the effects of industrial activities in natural environments.

# 4 Analytical procedures for sampling and trace element determination in environmental samples

## 4.1 Sampling and analysis of plant materials for the comparison of dissolution methods (I)

For the comparison of dissolution methods (Paper I), the pine needle (*Pinus sylvestris)* samples "Kemi" were collected in April 1999 in the area around the pulp and paper mill of Oy Metsä-Botnia Ab Kemi Mills at Kemi. Correspondingly, the pine needle (*Pinus sylvestris)* samples "Tornio" were collected in the vicinity of the ferrochrome and steel works of AvestaPolarit Stainless Oy at Tornio.

Reference materials BCR CRM 100 (Spruce Needles) and BCR CRM 101 (Beech Leaves) were commercial products prepared by The Commission of The European Communities (Bryssel), and reference material HUMH2 (Organic surface soil) prepared by the Finnish Forest Research Institute (Muhos).

For the determination of heavy metals and sulphur by ICP-AES or ICP-MS, the samples were digested with different acid mixtures using the US EPA method 3051 (163). For dissolution, 250 mg of plant sample was weighed into a microwave oven digestion vessel and 10 ml of 65 % $HNO_3$ (abbr. $HNO_3$) or 10 ml of 65 % $HNO_3$ + 2ml of 30 % $H_2O_2$ (abbr. $HNO_3$+$H_2O_2$) added. In the $HNO_3$+$HClO_4$ digestion procedure (abbr. $HNO_3$+$HClO_4$), the sample was first treated with 10 ml of 65 % $HNO_3$ + 3 ml of 40 % $HClO_4$ and, after evaporation to dryness, the residue was dissolved in 20 ml of 65 % $HNO_3$ and diluted to 50 ml with $H_2O$ (ultrapur). In the HF digestion procedure (abbr. HF), the sample was first digested with 10 ml of 65 % $HNO_3$ and 2 ml of 40 % HF was then added. All the dissolutions were performed with a computer controlled microwave oven. In the dry ashing digestion procedure [abbr. HF(DAC)], the sample was first ashed in a small crucible at 450 °C in a laboratory furnace, and the residue then dissolved in 10 ml of 65 % $HNO_3$ and 2 ml of 40 % HF.

For the sulphur determination by Leco, the dried and ground sample (0.20 g) was combusted with $V_2O_5$ as combustion accelerator in a stream (300 ml/min) of pure oxygen at 1350 °C for approximately 2 min. The evolved $SO_2$ was measured in an IR cell after removal of water vapour.

## 4.2 Sampling and analysis of pine needles for sulphur determination (II)

Scots pine (*Pinus sylvestris)* needles were collected in April 1999 at 29 sampling sites around a cluster of pulp and paper mills in the Kemi area (Fig. 2 in Paper II). Two background samples were collected in Kuivaniemi, about 25 km to the south from Kemi.

Sampling was carried out in April 1999 according to the standard SFS 5669 (164). The coordinates of the sampling sites were determined in the field by GPS. Needle samples were taken at heights of 4 to 7 m on three 50- to 100-year-old pines at each site. Needles were taken from different sides of the trees and combined into one sample. The current (C) and previous-year needles (C+1) were separated in the laboratory. The samples were stored in plastic bags in a freezer (–20 °C) before analysis.

The needles were dried at 40 °C for about 2 days until a constant weight was reached, and milled to pass through a 2 mm sieve. The samples (0.5 g) were digested with 10 ml of 65 % nitric acid in a pressure- and temperature-controlled microwave oven using US EPA method 3051 (162); this procedure was chosen because the local municipal environmental authorities approved the method. The concentrations of S, Fe, Zn, Ca, V and Pb were measured by ICP-AES. The analysis was validated by two certified samples NIST 1575 Pine Needles prepared by Michigan State University, East Lansing, MI, USA, and NIST 1573a Tomato Leaves prepared by Plant Analysis Laboratory, the Pennsylvania State University, University Oark, PA, USA.

## 4.3 Sampling and analysis of mosses for heavy metal determination (III)

Woodland moss (*Pleurozium schreberi)* samples were collected between 5.7.–14.7.2000 at 52 sampling sites in the Kemi-Tornio area. Extraneous plant material was removed from the mosses, and the unwashed samples were dried at 40 °C. Moss samples (2 g dry weight) were milled to pass through a 2 mm sieve and digested with a mixture of concentrated nitric and perchloric acids (4:1); this acid digestion procedure was chosen because it had also been used in the previous monitorings (165, 166). After digestion the solutions were diluted with distilled water and the concentrations of Cr, Ni and Zn determined by FAAS. The analysis was validated by a certified moss sample prepared by the University of Helsinki. Sampling and analysis were carried out according to the Finnish standard SFS 5671 (167).

## 4.4 Sampling and determination of total suspended particulate (TSP) material (IV)

The TSP samples were collected at monitoring stations MA1(Porasydänvarasto), MA2 (Konttori) and MA3 (Selkeytysallas) in the area of AvestaPolarit Chrome Oy Kemi Mine using a standard TSP high volume sampler at a height of 3 meter above ground level (59). The location of these sampling sites in the mine area are presented in IV, Fig. 1. The samples were collected simultaneously at each site on Sundays, Tuesdays and Thursdays between 2.1.–28.12.2000.

The sampling time was 24 hours. A total of 377 TSP samples were collected. The TSP samples were collected by drawing air through the sampler at a volumetric flow rate (104 $m^3\ h^{-1}$). The suspended particles were collected on glass fibre filters. Before insertion in the high volume samplers, the glass fibre filters were dried at 110° for 24 h until a constant weight was reached. The total mass of total suspended particulate (TSP) material on the filter was determined according to the standard SFS 3863 (59).

## 4.5 Sampling and analytical procedure for Cr, Ni and Pb determination in TSP material (IV)

The concentrations of Cr, Ni and Pb in ambient air at AvestaPolarit Chrome Oy Kemi Mine were analysed only at monitoring station MA2 (Konttori) because, according to the TSP measurements, this was the most polluted area and most of the anthropogenic activities were situated in the vicinity of this station. The location of monitoring station MA2 in the mine area is presented in IV, Fig. 1. The levels of heavy metals were analysed each month from the TSP filter with the largest amount (concentration) of TSP material, apart from September and October when the TSP filter with the second largest amount (concentration) was analysed.

The heavy metal concentrations in the TSP filters were analysed by GFAAS after decomposition of the 35 mm diameter discs by an alkali fusion procedure (64); this digestion procedure was chosen because it had been used in the previous study (168). The discs were cut from the TSP filters with a stainless steel circular cutter. The discs were digested with 2 ml of 40 % HF in a platinum dish and, after evaporation to dryness, the residue was heated for 4 min at 900 °C. The residue was then mixed with 1.5 g of sodium carbonate and 0.5 g of boric acid , and fused for 30 min at 950 °C over a Bunsen burner. After cooling, the fused sample was dissolved in 3 ml of distilled water and 3 ml of concentrated $HNO_3$. The solution was then diluted to 50 ml with distilled water. The blanks (unexposed filters) were digested simultaneously with the field samples. The analysis was validated by analysing the reference materials Marine Sediment PACS-2 prepared by the National Research Council of Canada, and Stream Sediment NCS DC 73309 prepared by the China National Centre.

## 4.6 Sampling and sequential leaching procedure for heavy metal determination in TSP material (V)

The TSP material was collected by the high volume method using a standard TSP high volume sampler (Wedding & Associates, Inc.) at a height of 3 meter above ground level (59). The TSP material was collected in February, April, June, August, November and December 2000 at monitoring station MA2 (Konttori), situated in the middle of the mining area (See Paper IV, Fig. 1). According to the TSP concentration in the air, this was the most polluted region in the mining area in 2000.

The sequential leaching procedure for heavy metal determination in TSP was carried out by cutting out 50 mm diameter discs from each of the TSP filters using a stainless steel cutter. The leaching experiments for the sampling filters and blanks in stage I were carried out according to the procedure of Szakova *et al*. (142), and in stages II–IV mainly according to the procedure of Hlavay *et al*. (48) as follows: (i) leaching stage I: water-soluble fraction ($H_2O$), (ii) leaching stage II: environmentally mobile fraction ($CH_3COONH_4$), (iii) leaching stage III: the fraction bound to carbonate and oxide ($HONH_3Cl$ + $CH_3COOH$), and (iv) leaching stage IV: fraction bound to silicate and organic matter, that is the environmentally immobile fraction ($HNO_3$ + HF + HCl).

The sequential leaching procedure was also applied to the certified reference materials VKI (QC Loam Soil A) and PACS-2 (Marine Sediments) to evaluate the accuracy and reproducibility of the leaching procedure. The heavy metals were determined by graphite furnace atomic absorption spectrometry (GFAAS) and flame atomic absorption spectrometry (FAAS).

## 4.7 Sampling and analysis of TSP filters for the homogeneity study (VI)

The homogeneity study is part of an air sampling program carried out in 2000 at AvestaPolarit Chrome Oy Kemi Mine (see paper IV). The TSP filters for the homogeneity study were collected in January, March, May, July, September and November at monitoring station MA2 (Konttori). A total of 6 filters were collected for the homogeneity study.

In order to test the homogeneity of heavy metal deposition on the glass fibre filter (Munktell MG 160, 203*254 mm, 75 g/$m^2$, Grycksbo, Sweden), 9 discs (35 mm) were cut from different parts (1–9) of each filter (A–F) (see Paper VI, Fig. 1). The discs were then digested in a microwave oven using a mixture of *aqua regia* (*i.e.* conc. $HNO_3$ and conc. HCl; 1:3) + HF acid according to the procedure of Bettinelli *et al*. (90), who reported good recoveries for Cr in samples containing chromite, *i.e.* NBS SRM 278 Obsidian Rock, NBS SRM 688 Basalt Rock, NBS SRM 1645 River Sediment and NBS SRM 1646 Marine Sediment. The heavy metals (Cr, Ni, Cu, Fe and Cd) in the total suspended particulate (TSP) material were analysed by ICP-AES or GFAAS.

# 5 Results and discussion

## 5.1 Biological samples (I–III)

### *5.1.1 Comparison of dissolution methods for sulphur and heavy metals analysis in plant materials (I)*

Biological samples consist of a complex mixture of carbohydrates, proteins and lipids. It is therefore necessary to decompose the organic matter and release the metals from the sample matrix. The majority of the digestion procedures used to date involve the initial use of strong oxidising agents, such as nitric acid, to decompose the organic matrix of the sample. Many elements are then liberated as soluble nitrate salts. Other acids can be employed to break down the sample matrix further, depending on the elements to be determined and the analysis technique chosen. The use of hydrofluoric acid is always necessary for the determination of a number of elements that are associated with siliceous minerals (88). Losses of trace elements during dissolution will affect the accuracy of the final results. There are number of possible loss mechanisms during sample decomposition, including gaseous evolution, absorption or adsorption onto surfaces, precipitation and the persistence of undissolved material (87).

According to the results obtained in I, Tables III and IV, the widely used acids or acid mixtures such as $HNO_3$+$H_2O_2$, $HNO_3$+$HClO_4$ or $HNO_3$ alone, or the dry ashing digestion procedure with HF used for the destruction of organic material, gave widely varying results for trace elements in plant materials. Thus, a careful choice of suitable digestion procedures for plant material is of great importance in order to ensure that correct results are obtained.

According to Table 2, which shows the results of sulphur analyses from I, Tables III and IV, the acid procedure with $HNO_3$ gave lower results for sulphur than the $HNO_3$+$H_2O_2$ procedure. Thus, our results correspond with those of another study which reported that a combination of an effective oxidizing agent, hydrogen peroxide ($H_2O_2$), and $HNO_3$ gives more complete decomposition of organic components than nitric acid alone (170).

*Table 2. Results (mg/kg) for sulphur (S) determination in certified samples BCR CRM 100, BCR CRM 101, HUMH2 and "Kemi" and "Tornio" pine needle samples using different digestion procedures. (n=3, except [(*)] for "Kemi" and "Tornio" pine needles where n=1). Analysis by ICP-AES [(a)] or Leco (IR combustion) method [(b)].(I)*

| Procedure | BCR CRM 100 | BCR CRM 101 | HUMH2 | "Kemi" | "Tornio" |
|---|---|---|---|---|---|
| Certified value | 2690 ± 40 | 1700 ± 40 | 1710 ± 100 | --- | --- |
| [(a)] $HNO_3$ | 2496.6 ± 5.7 | 1560.0 ± 20.0 | 1606 ± 28.8 | 920 [(*)] | 1090 [(*)] |
| [(a)] $HNO_3 + H_2O_2$ | 2616.6 ± 65.1 | 1646.6 ± 11.5 | 1653 ± 11.5 | 978 [(*)] | 1140 [(*)] |
| [(a)] $HNO_3 + HClO_4$ | 2240.0 ± 26.4 | 1400 ± 26.4 | 1543 ± 11.5 | 846 [(*)] | 994 [(*)] |
| [(a)] HF | 2986.6 ± 81.4 | 1993.3 ± 23.1 | 1870 ± 26.4 | 1290 [(*)] | 1510 [(*)] |
| [(a)] HF(DAC) | 1333.3 ± 40.4 | 771.0 ± 36.6 | 526 ± 17.4 | 359 [(*)] | 454 [(*)] |
| [(b)] Leco (Comb. + IR) | 2600 ± 80 | 1700 ± 20.8 | 1776.7 ± 15.3 | 1100 [(*)] | 1100 [(*)] |

BCR CRM 100 = Pine needles, BCR CRM 101 = Peach leaves, HUMH2 = Organic soil humus

According to our results, the digestion procedure with a mixture of $HNO_3$+$HClO_4$ slightly underestimated the S concentrations of plant materials. The low recoveries for sulphur using the $HNO_3$+$HClO_4$ procedure can, according to the studies of Randal *et al*. (171) on plant vegetative material (*i.e.*, pasture samples, rape, spinach and clover), be partly due to incomplete oxidation of sulphur.

In this context it is worth noting that gaseous losses of S can occur during the digestion of plant materials using $HNO_3$+$HClO_4$ in open vessels (171). According to the studies of Bethge (172) on wood and pulp samples, sulphur is lost in the form of sulphur dioxide ($SO_2$) and carbonyl sulphide ($CS_2$) during wet digestion with perchloric acid, but hydrogen sulphide ($H_2S$) was not detected.

According to Table 2, the losses of sulphur were the highest in the dry ashing digestion procedure (abbr. HF(DAC)) in the case of both reference samples BCR CRM 100, BCR CRM 101 and the "Kemi" and "Tornio" pine needle samples. This is obviously due to gaseous losses of sulphur at the high temperatures employed during ashing, and this phenomenon has also been reported by Huang *et al*. (170) and Randal *et al*. (171).

The results presented in Table 2 show that the Leco combustion technique with infrared (IR) detection gave good precision and accuracy for sulphur (S).The precision for sulphur in reference samples BCR CRM 100 and BCR CRM 101 and also in "Kemi" and "Tornio" pine needle samples were all within 1–3 %. In addition, Leco combustion gave excellent results for sulphur compared to the certified values in references materials BCR CRM 100, BCR CRM 101 and HUMH2.

Our results for Cr in reference material HUMH2 are listed in Table 3, and were originally presented in I, see Table IV. According to Table 3, both the $HNO_3$ and $HNO_3$+$H_2O_2$ procedures were especially effective for determining Cr in reference sample HUMH2 because the results for Cr agreed well with the certified value. However, the $HNO_3$+$HClO_4$ procedure gave lower result.

*Table 3. Results (mg/kg) for chromium (Cr) determination in certified sample HUMH2 and "Tornio" pine needle samples using different digestion methods. (n=3, expect [(*)] and for "Tornio" pine needles where n=1). Analysis by ICP-AES [(a)] or ICP-MS [(b)]. (I)*

| Procedure | HUMH2 | "Tornio" |
|---|---|---|
| Certified value | 4.46 ± 0.85 | --- |
| [(a)] $HNO_3$ | 4.6 ± 0.3 | 266 [(*)] |
| [(a)] $HNO_3 + H_2O_2$ | 4.4 ± 0.2 | 223 [(*)] |
| [(a)] $HNO_3 + HClO_4$ | 3.1 ± 0.1 | 75.6 |
| [(b)] HF | 7.5 [(*)] | 437 [(*)] |
| [(b)] HF(DAC) | 6.2 [(*)] | 426 [(*)] |

HUMH2 = Organic soil humus

Cary *et al*. (174) and Greenberg *et al*. (87) also reported a high deficit of Cr in plant materials with the $HNO_3$+$HClO_4$ procedure that they used. They attributed this to the formation and volatilization of chromyl chloride ($CrO_2Cl_2$) at a temperature of 116 °C during the acid digestion step. According to our results, the $HNO_3$+$HClO_4$ digestion procedure also gave a low result for Cr in the "Tornio" pine needles: values for Cr about 72 % and 66 % lower than the values with $HNO_3$ or $HNO_3$+$H_2O_2$, respectively.

However, in our study, the HF and HF(DAC) acid procedures gave 1.6 and 1.4 times greater Cr values for reference sample HUMH2 and the uncertified "Tornio" pine needle sample, respectively. The high Cr results for the HF and HF(DAC) procedures in the "Tornio" pine needle sample are probably due to the fact that the dust emitted from the ferrochrome and steel works of the AvestaPolarit Stainless Oy at Tornio contains FeO-$Cr_2O_3$, which is difficult to dissolve with other acid procedures (175). According to the results for Cr in reference material HUMH2, the values obtained with the HF and HF(DAC) procedures were also higher than those for the other procedures used. In this context it is worth noting that validation of the chemical analyses was performed using blanks, standard samples, and control moss samples, and it is therefore not likely that contamination by metals occurred during the analyses. However, if we compare the HF and HF(DAC) procedures with each other, the HF(DAC) procedure gave slightly lower values for Cr than the HF procedure, probably due to the volatilization of Cr at high temperatures during ashing (176–178).

According to the results in Paper IV (Table III) for the determination of Zn in reference material BCR CRM 101, both the HF and HF(DAC) digestion procedures gave values within the certified value. In contrast, the other procedures for Zn in BCR CRM 101 gave results lower than the certified values. According to the results in Paper IV (Table IV), the determination of Ni seemed to be less critical since a wide range of reagent combinations gave good results.

The low recovery for K in reference materials BCR CRM 100 and BCR CRM 101 with the $HNO_3$+$HClO_4$ procedure was also significant (see Paper I, Table III). A similar phenomenon has been reported in other studies, and is probably due to the formation of potassium perchlorate ($KClO_4$), which has a low solubility (173, 179). According to the results in Paper I (Table III), when the HF(DAC) digestion procedure was used for reference material BCR CRM 100, some K was evidently lost; this is probably due to volatilization at the high temperatures (99, 180).

### *5.1.2 Sulphur concentrations in pine needles (II)*

Sulphur accumulation in pine needles around the pulp and paper mills was clearly higher than that at other points in the Kemi area. The highest sulphur concentrations occurred in the northern part of Kemi in the vicinity Oy Metsä-Botnia Ab Kemi Mills, which is the main area affected by sulphur deposition derived from these mills (Fig. 2).

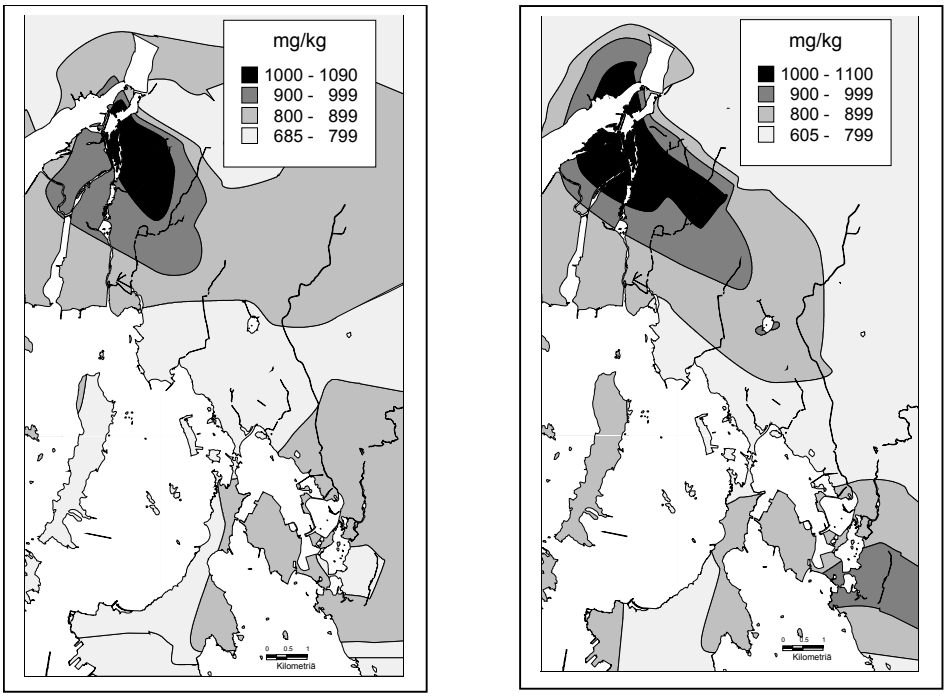


**Fig. 2. The dispersion pattern of sulphur in the (C) needles (left) and in the (C+1) needles (right) in 1999 at Kemi. (II)**

In 1999, the sulphur concentrations of pine needles varied between 699–1090 mg/kg in (C) needles and between 605–1100 mg/kg in (C+1) needles. The highest individual sulphur concentration (1090 mg/kg) in (C) needles occurred at sampling site 12 (Vilmilä), and the highest individual sulphur concentration (1100 mg/kg) in (C+1) needles at sampling site 10 (Sotisaari). These values were 46 % and 45 % higher than those in the corresponding background samples (C-needles: 746 mg/kg, C+1-needles: 759 mg/kg) collected in Kuivaniemi at a distance about 25 km from Kemi.

The average sulphur concentration calculated from pine needles collected at sampling sites 6 (Mäntylä), 9 (Vähäkuivanuorontie), 10 (Sotisaari), 12 (Vilmilä), 14 (Elijärventie) was 954 mg/kg for (C) needles and 953 mg/kg for (C+1) needles. These values are 28 % higher for (C) needles and about 26 % higher for (C+1) needles than those in the corresponding background samples collected in Kuivaniemi. Oy Metsä-Botnia Ab Kemi Mills and sampling points 6 (Mäntylä), 9 (Vähäkuivanuorontie), 10 (Sotisaari) and 12 (Vilmilä) are located inside the area where the sulphur concentration was between 1000–

1100 mg/kg (see also Fig 2 in II). Correspondingly, the average sulphur concentration of needles at sampling sites 6, 9, 10, 12 and 14, compared to the average sulphur concentration for needles at all sampling sites, was 11 % higher than the average sulphur concentration in (C) needles and 18 % higher than in (C+1) needles.

In the southern part of Kemi the impact of pollution from StroraEnso Oyj Veitsiluoto Mill was most clearly evident at sampling site 21 (Järppi) and at sampling site 22 (Hepola). However, the district heating plant in the vicinity of sampling site 22 (Hepola) probably also has an influence on the sulphur concentrations of needles at this sampling site. In conclusion, sulphur deposition and the accumulation of sulphur in pine needles around the pulp and paper mills were higher than at other points in the Kemi area. Thus our results are in good agreement with the studies of Määttänen (22) on the environmental effects of the pulp mills of Enocell Oy in North Karelia. Similar results have also been reported in many other studies using pine needles as a bioindicator for sulphur deposition in the areas surrounding point sources, such as Kekäläinen *et al*. (181) and Pesonen *et al*. (182).

In addition, the results of the needle sulphur survey carried out in 1999 also correspond well with the latest computer simulation study made in 2001 by the Finnish Meteorological Institute on the aerial distribution pattern of $SO_2$ and TRS in the area around the pulp and paper mills of Oy Metsä-Botnia Ab Kemi Mills (17). This model is based on the use of the UDM-FIM (Urban Dispersion Modelling System-Finnish Meteorological Institute) computer simulation program, which uses a Gaussian model to predict the dispersion of a plume in the vertical and horizontal directions (183). According to this simulation program, the modelled concentrations of $SO_2$ and TRS were the highest in the immediate vicinity of the mills, *i.e.* within a radius of 1–3 km around the mills of Oy Metsä-Botnia Ab Kemi Mills.

If we compare the results of the bioindicator study made in 1999 to those carried out earlier, *i.e.* in 1979 by Huttunen *et al*. (184) and in 1989 by Vanhatalo (185), there is a clear decreasing trend in the size of the sulphur dispersion area ($km^2$) during 1979–1999 (see Table 4). In 1979 and 1989 sulphur was determined by XRF, and in 1999 by ICP-AES.

*Table 4. Sulphur dispersion area ($km^2$) in Kemi during 1979–1999. (II)*

| Year | 900–1000 mg/kg | 1101–1300 mg/kg | 1301–1500 mg/kg |
|---|---|---|---|
| | $km^2$ | $km^2$ | $km^2$ |
| 1979 (C) | 34.8 | 18.8 | 12.5 |
| 1989 (C) | 48.8 | 14.0 | -- |
| 1999 (C) | 8.8 | -- | -- |
| 1979 (C+1) | 21.8 | 26.0 | 8.8 |
| 1989 (C+1) | 17.0 | 57.5 | 4.5 |
| 1999 (C+1) | 14.4 | -- | -- |

It is reasonable to suppose that this decreasing trend in the size of the sulphur dispersion area is due to decreased total sulphur emissions in the Kemi area during 1980–1998. The decreasing trends for the maximum and mean sulphur concentrations in needles also seem to be reasonable in the light of the decreased sulphur emissions (see Paper II, Fig. 1, Table III, Table IV). Thus, our results are similar to those reported for Oulu in the areas

around the pulp and paper mills works (186). In conclusion, although the total sulphur emissions in Kemi have decreased tremendously during the past two decades from a value of 4500 t (S) in 1980 to a value of 990 t (S) in 1998, pine needles still appear to be useful bioindicators for assessing the distribution patterns of aerial sulphur emissions derivated from the pulp and paper industry.

### *5.1.3 Concentrations of Fe, Zn, Ca, V and Pb in pine needles (II)*

The highest needle iron (Fe) concentrations occurred relatively close to the pulp and paper mills of Oy Metsä-Botnia Ab at sampling sites 6 (Mäntylä) and 12 (Vilmilä), and close to the mill of StoraEnso Oyj at sampling sites 51 (Rivinokka) and 52 (Haukkari). However, high values also occurred close to roads. It is thus highly likely that the high Fe concentrations are derived from dust from the surrounding land rather than from the mills. The fact that the highest results for zinc (Zn) occurred along roadsides and near roads also indicated that it is derived from the same sources as Fe.

High concentrations of calcium (Ca) occurred especially in needles collected in the northern part of Kemi in the vicinity of the Oy Metsä-Botnia Ab Kemi Mills. Thus it is likely that airborne pollutants from the Oy Metsä-Botnia Ab Kemi Mills have had a strong influence on needle Ca concentrations especially at sampling site 9 (Vähäkuivanuorontie), where the Ca concentration was 4960 mg/kg in (C+1) needles, as well as at sampling sites 10 (Sotisaari), 12 (Vilmilä), 15 (Ristikangas), 16 (Junko) and 32 (Lautiosaari). The Ca concentration in (C+1) needles at sampling site 9 (Vähäkuivanuoro) was 48 % higher than the average Ca concentration calculated from all (C+1) needles. Thus it is likely that Ca emissions, which are typical for pulp and paper mills, reached this sampling point located close to Oy Metsä-Botnia Kemi Mills, and that part of the Ca in the needles is derived from the mills.

According to Table 5, there is poor correlation between the concentrations of individual elements in (C+1) needles. The non-significant correlations are probably partly due to the extremely low emissions of heavy metals from the pulp and paper mills, and also due to the physiological properties of needles in accumulating metals (187).

*Table 5. The Kendall´s coefficients for the correlation between S, Fe, Zn, Ca, V and Pb in (C+1) pine needles in 1999, (n=29).*

| | S | Fe | Zn | Ca | V | Pb |
|---|---|---|---|---|---|---|
| S | 1.000 | 0.098 | 0.212 | – 0.145 | – 0.131 | -- |
| Fe | | 1.000 | 0.098 | 0.005 | – 0.201 | -- |
| Zn | | | 1.000 | 0.007 | 0.113 | -- |
| Ca | | | | 1.000 | 0.000 | -- |
| V | | | | | 1.000 | -- |
| Pb | | | | | | 1.000 |

However, although pine needles do not appear to be as appropriate a method for monitoring the deposition of heavy metals as mosses and lichens, Laaksovirta *et al*. (187) used the chemical analysis of pine needle as a method for monitoring the accumulation of

airborne pollutants emitted from pulp and paper mills at Valkeakoski, and Määttänen (22) in the areas around the pulp and paper mills of Enocell Oy in North Karelia (47).

In our study, the vanadium concentrations, which are a good indicator of fuel oil burning, were < 1 mg/kg at all the sampling sites, and the corresponding lead concentrations were < 5 mg/kg. Thus, needles did not readily accumulated these elements; this phenomenon has also been reported in another study (187). Therefore the low Pb concentrations in the needles is also partly due the fact that Pb emissions from traffic (0 t/1999) is no longer a problem, because nowadays the petrol used in cars in Finland is unleaded (188). However, even in the mid 1970s and mid 1980s, the average Pb concentrations in the Helsinki metropolis area were 22.8 mg/kg and 8.5 mg/kg in (C) and (C+1) needles, respectively (189).

### *5.1.4 Accumulation of Cr, Ni and Zn in mosses (III)*

The regional distribution patterns of Cr and Ni in mosses in the Kemi-Tornio area in 2000 showed clearly that the most polluted area (Cr > 200 µg/g and Ni > 20 µg/g) appears to lies within a few kilometres of the ferrochrome and stainless steel works of AvestaPolarit Stainless Steel Oy (see Paper III, Fig. 1). Within this area, the Cr concentrations in mosses were 4–13 times higher than those outside the urban area of Tornio. In 2000, the highest individual Cr concentration (2700 µg/g) occurred at a distance of 1.9 km from to the southeast from the works. Slightly polluted areas (Cr < 50 µg/g and Ni < 9.9 µg/g) were located farther away at a distance of about 12–14 km from the works.

The area most polluted by the opencast chromium mining complex of AvestaPolarit Chrome Oy Kemi Mine (Cr > 200 µg/g and Ni < 20 µg/g) appeared to be in the immediate vicinity of the complex. The slightly polluted area (5.0 µg/g < Ni < 9.9 µg/g) occurred within a radius of 2–6 km around the mining complex. However, there was a small anomaly to the south of the mining complex at Järppi, probably due to Ni emissions from local oil-burning sources.

According to Figure 3, the deposition and accumulation of Cr and Ni in mosses clearly decreased with increasing distance from the works. However, the Zn concentrations in mosses did not decrease with increasing distance from the pollution source (works). Thus, our results for Cr and Ni correspond to those obtained in another study carried out in the same area by Kansanen and Venetvaara (190) at the end of the 1980s.

The Zn concentrations were similar throughout the study area and there is therefore no distribution pattern at all for Zn. According to Rühling and Tyler, this phenomenon is probably due to the fact that the retention of Cr and Ni from atmospheric deposition by mosses is almost total, while that of Zn is relatively low; mosses have distinct accumulation rates for individual trace metals as a result of their physiological properties (34,191). Similar results have also been reported in other studies in which mosses were used as a bioindicator for heavy metal deposition (36, 38, 165, 192). Another possible explanation could be that metallic Zn has a relatively low boiling point (907 °C, as opposed to 2672 °C for Cr and 2730 °C for Ni), and a high proportion of the Zn emitted from the ferrochrome and stainless steel works of AvestaPolarit Stainless Oy is in the form of metal vapour. As a result, Zn emissions are likely to be spread over a great

distance (27). Differences in the translocation of heavy metals in the atmosphere have been reported in (2, 193).

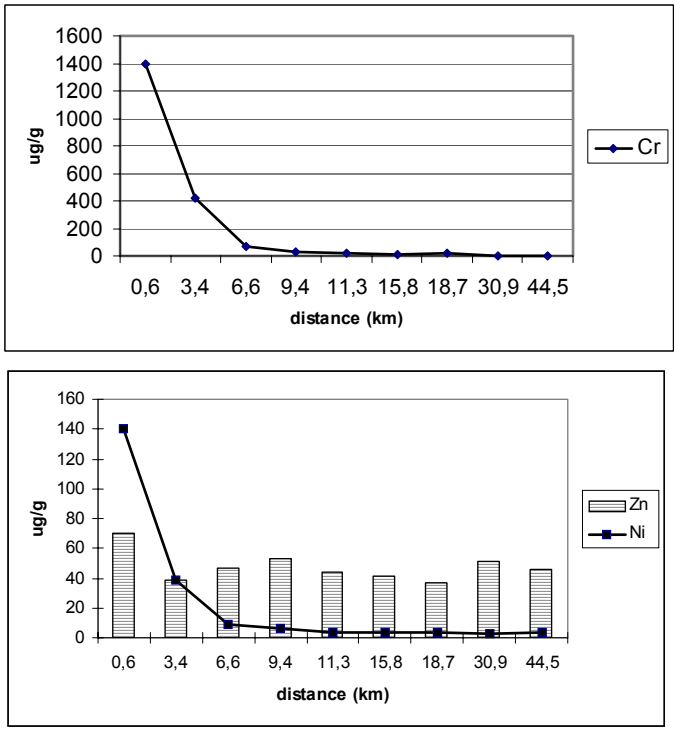


**Fig. 3. Heavy metal (Cr, Ni, Zn) concentrations (µg/g) in mosses at distances of 0.6–44.5 km (along the same straight line) to the north of the ferrochrome and stainless steel works of AvestaPolarit Stainless Oy in 2000. (III)**

Pilegaard (41) used transplanted lichens (*Hypogymnia Physodes*) for the biological monitoring of air pollution emitted from a Danish steelwork in Frederiksvaerk, and he reported low deposition of Zn on lichens; the lichens initially accumulated Zn, but they were not able to retain large amounts of Zn when deposition decreased. In addition, the "wash out" of heavy metals in mosses, lichens and needles as well as also sulphur in needles by water (*i.e.* rain or washing) has been reported in (28, 194–197).

The 3-D scatterplot results in Fig. 4 for Cr, Ni and Zn also partly support the finding that the highest Cr and Ni concentrations in mosses occurred close to the pollution sources (0.6–1.9 km and 0.6–3.5 km, respectively), but not for Zn, because the highest Zn concentration (78 µg/g) occurred at a distance of 12.3 km from the nearest pollution source (AvestaPolarit Chrome Oy Kemi Mine).

The 3-D scatterplots also illustrate that, although the heavy metal deposition emitted from both the ferrochrome and stainless steel works of AvestaPolarit Stainless Oy and the opencast chromium mining complex of AvestaPolarit Chrome Oy Kemi Mine overlap in many parts of the study area, the main deposition areas are close to the works and the mine.

The Kendall correlations in Table 6 show that Cr and Ni were highly correlated in mosses, thus indicating that they are originated from the same emission sources. Although the correlation between Zn and Cr and Ni was not very high, it is clear that the Zn deposition in the mosses was primarily derived from the ferrochrome and stainless steel works of AvestaPolarit Stainless Oy and the opencast chrome mine of AvestaPolarit Chrome Oy Kemi Mine, because the nearest point sources that emit significant amounts of these metals are located more than 150 km away.

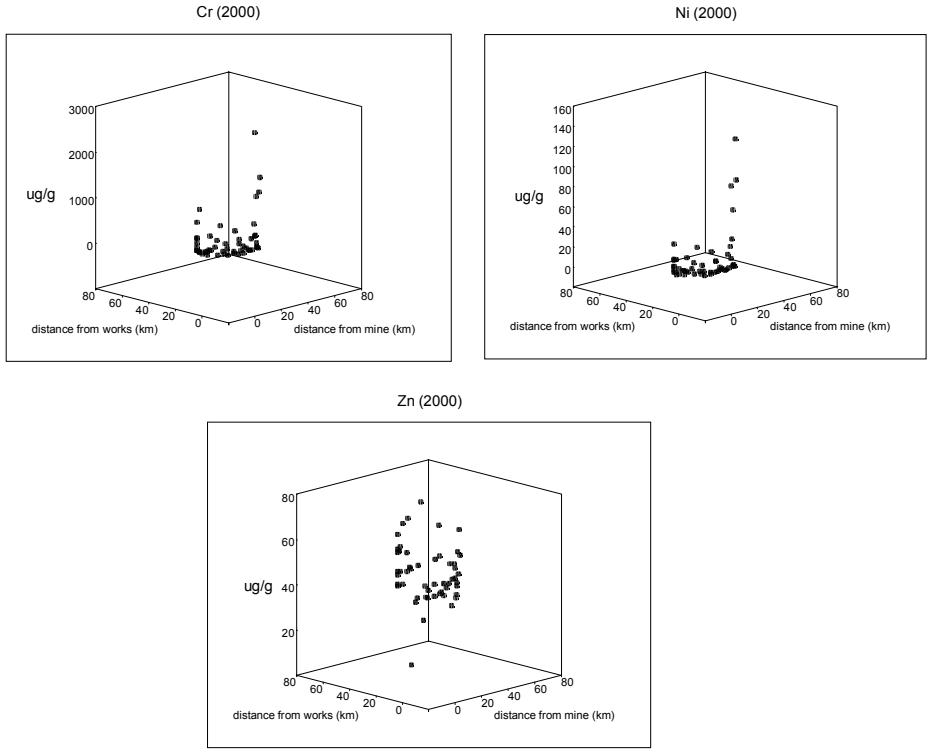


**Fig. 4. The 3-D scatterplots for Cr, Ni and Zn in 2000. (III)**

*Table 6. The Kendall´s cofficients for the correlation between Cr, Ni and Zn in the mosses in 2000, (n=52).(III)*

| | Cr | Ni | Zn |
|---|---|---|---|
| Cr | 1.000 | 0.728 (**) | 0.144 |
| Ni | 0.728 (**) | 1.000 | 0.199 (*) |
| Zn | 0.144 | 0.199 (*) | 1.000 |

(** correlation is significant at the 0.01 level (2-tailed); * correlation is significant at the 0.05 level (2-tailed).

According to the descriptive statistical results for the moss survey in 1990, 1995 and 2000 (Paper III, Table I and II), it can be concluded that the average Ni concentration (mean) in mosses has increased since 1990, which reflects the increased Ni emissions from the ferrochrome and stainless steel works during the same period. The Zn emissions

from works were at approximately the same level in 1990 and in 1999 but, according to our results, the average Zn concentration (mean) in mosses has decreased. However, the average Cr concentration (mean) for all the moss samples in 2000 was 2.2 times higher than the corresponding value in 1990 and 1995 even though the Cr emissions have decreased since 1990 from a value of 20 t to 15.2 t in 1999.

There are a large number of uncontrollable factors, *e.g.* weather parameters, such as wind direction and speed, precipitation, humidity, the uncontrolled spread of emissions, the composition and variations in the amount of emissions, and the efficiency of the dust removal processes, that cannot be "standardized" before sampling. All these factors may have an influence on the amounts of heavy metals emitted from point sources, and how they are spread and deposited after release from the point sources. Thus, these factors could partly explain why the average Cr concentrations (mean) in mosses have increased since 1990 even though the Cr emissions have decreased.

## 5.2 Airborne particulates and filters (IV–VI)

### *5.2.1 Concentrations of TSP, Cr, Ni and Pb in the ambient air in the mine area (IV)*

The results in Paper IV showed that opencast chromium mining operations by AvestaPolarit Chrome Oy Kemi Mine have had an adverse impact on the environment in the form of total suspended particulate (TSP) matter, referred to as "dust".

In 2000 all the 95$^{th}$ percentile values for TSP in the mine area were below the current Finnish air quality limit value of 300 µg/m$^3$ (73) at monitoring sites MA1, MA2 and MA3, but the 98$^{th}$ percentile value of 411.6 µg/m$^3$ at monitoring station MA2 exceeded the Finnish air quality guideline value of 120 µg/m$^3$ (73).

Our results show (see Paper IV, Table III and Fig. 2 and Fig. 3) that the highest daily TSP concentrations can occasionally reach relatively high values, since the highest individual daily TSP concentration was 1481 µg/m$^3$ at monitoring station MA2 in October. This value is exceptionally high compared to the other measurements, and was due a storm that lifted a substantial amount of particles into the air. Thus, our results correspond well with those of other studies carried out at the Jharia Coalfield mining area in India (61) and at the Donana mining area in Spain (50), where the highest TSP concentrations were between 900–1200 µg/m$^3$.

According to the our results (see Paper IV, Fig. 2 and Fig. 3), the TSP concentrations in the air varied considerably within short time intervals, *i.e.* day-to-day fluctuation (3–28.9.2000), as well as by the month (January – December in 2000).

The most reasonable explanation for the high summertime TSP values are the dust and particulate material emissions from the surrounding land, piling stores, and during loading; during the summer the land, piling stores and ore are not frozen, but they are in the winter. Because TSP and heavy metal concentrations in the air can vary considerably over short time intervals (day-to-day fluctuation), as well as monthly, TSP measurements

should be carried out as a long-term study in order to obtain reliable data about TSP concentrations in the air.

According to our results, the TSP concentrations in the air at monitoring stations MA1, MA2 and MA3 also seemed to be strongly dependent on the wind direction. According to Fig. 5, the TSP concentrations were higher than the annual means at monitoring station MA1 (mean 15.1 µg/m$^3$) when the wind direction was between 115–270°, at monitoring station MA2 (mean 80.2 µg/m$^3$) when the wind direction was between 30–240°, and at monitoring station MA3 (mean 11.0 µg/m$^3$) between 0–45° and 100–330°.

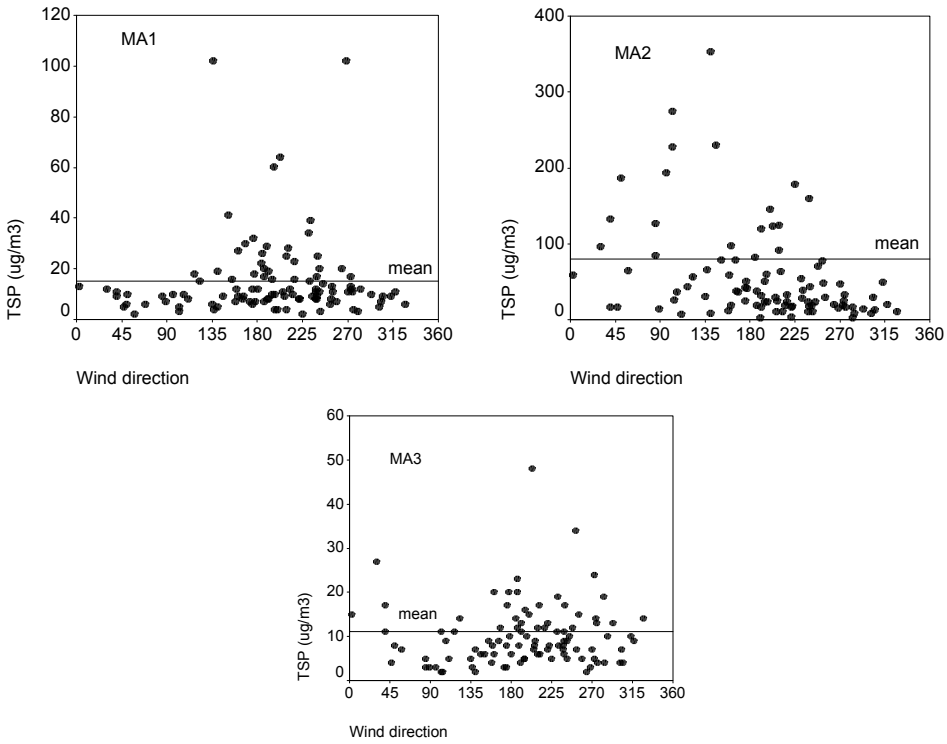


**Fig. 5. The correlation between TSP (µg/m$^3$) and wind direction at monitoring stations MA1 (Porasydänvarasto), MA2 (Konttori) and MA3 (Selkeytysallas) in 2000. (Mean = the annual mean). (IV)**

These results indicate that the dust emissions at monitoring station MA1 are most likely derived from a heap of mining spoil located at a distance of 300 meters from the station. The most likely dust source for TSP at monitoring station MA2 are the mineral piles at the enrichment plant and activities at the railway line where trains are loaded.

The heavy metal (Cr, Ni and Pb) concentrations were analysed only at monitoring station MA2 because, according to the TSP measurements (Paper IV, Table III and Fig. 2), this was the most polluted area and most of the anthropogenic activities were situated in the vicinity. In 2000, the Cr concentrations in ambient air varied between 0.65–48.2 µg/m$^3$ (average 17.9), the Ni concentrations between 0.05–1.4 µg/m$^3$ (average 0.52), and the Pb concentrations were all under 0.1 µg/m$^3$. It is not likely that that the Finnish air

quality limit value of 0.5 μg/m$^3$ (73) for Pb will be exceeded in the mine area at the current level of operations, because the highest Pb concentration in the air in mine area reached a maximum value of 0.09 μg/m$^3$. This is only 18 % of the air quality limit value.

Fig. 6 in paper IV shows the cross-correlation plots between the TSP and Cr, Ni and Pb concentrations in ambient air at monitoring station MA2 in 2000. The poorest correlation was between Pb and TSP ($R^2$ = 0.394). The data points indicate, that Pb in total suspended particles may have originated from at least two different emission sources, *i.e.* emissions from the quarrying and other mining operations, and emissions from dust caused by road traffic. However, it was not possible to distinguish between these two possible sources in this study. However, exhaust emissions from road traffic no longer contain Pb because the petrol used by automobiles and vehicles in Finland is unleaded (188). The correlations between the TSP and Cr and Ni clearly indicate that the Cr and Ni concentrations in the air are strongly correlated with the TSP concentration ($R^2$ = 0.842 and $R^2$ = 0.862, respectively).

In addition to the seasonal variation in TSP concentration, the seasonal variation in Cr concentrations (μg/m$^3$) in the air at monitoring station MA2 between January–December in 2000 also varied considerably from month to month (see Fig. 6); the lowest monthly value in 2000 was the Cr concentration of 0.65 μg/m$^3$ in January, and the highest the Cr concentration of 48.2 μg/m$^3$ in July.

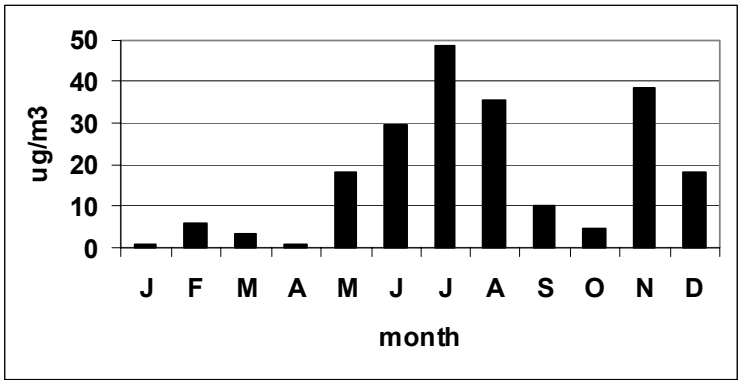


**Fig. 6. The ambient air concentration of Cr (μg/m$^3$) at monitoring station MA2 (Konttori) during January–December in 2000. (IV)**

If we compare the average Cr and Ni concentrations in ambient air (*i.e.* 17.9 μg/m$^3$ for Cr, and 0.52 μg/m$^3$ for Ni) at the mine area of AvestaPolarit Chrome Oy Kemi Mine with the forthcoming EU directive (50, 52–53) on $PM_{10}$ (20 μg/m$^3$ for Cr and 0.02 μg/m$^3$ for Ni, respectively) our results are very high. However, it should be noted that $PM_{10}$ is only a fraction of TSP.

Querol *et al*. (50) has also reported high ambient air, heavy metal concentrations for As, Pb and Cu during summertime especially (*i.e.* July–August). According to Infante *et al*. (84), high summertime values for ambient air heavy metals may be partly explained by climatic factors such as sea breezes, in which air particulates are thought to be rapidly mixed by wind action; this meteorological phenomenon is especially common during the summer on the coast of the Gulf of Bothnia. During this phenomenon the atmosphere is

unstable, and it has been reported to cause rapid vertical air movements. According to Ekholm *et al*. (165), this phenomenon is one cause of the rapid increase in the dust concentration in the ambient area in the mine area. The Finnish Meteorological Institute has also observed this phenomenon in studies on the aerial distribution pattern of malodorous sulphur compounds emitted from the pulp and paper mills located at Kemi (198).

In this context it is worth noting that the heavy metals concentrations in ambient air vary in different mine areas depending on the type of ore, operations, processes, weather conditions, and the location of the samplers. Therefore the results of different studies are not necessarily comparable with each other. Ghose *et al*. (146) reported Pb concentrations of between 0.4–6.6 μg/m$^3$, and Cr concentrations of between 0.004–0.08 μg/m$^3$ in ambient air near to a coal mine in India. Very high metal concentrations can also occur in the ambient air in mine areas. Querol *et al*. (50) reported exceptionally high maximum concentration for Pb (4.4 μg/m$^3$) in the Donana area (sulphide ore) in Spain. However, the maximum Cr concentration in their study was 0.07 μg/m$^3$, and the maximum Ni concentration 0.04 μg/m$^3$.

### *5.2.2 Estimation of the bioavailability and environmental mobility of heavy metals in TSP material (V)*

According to the results in Paper V (Table 2), Cr and Fe were the main leachable components of the heavy metals in TSP material emitted from the mining area of the AvestaPolarit Chrome Oy Kemi Mine. This result is reasonable considering that $((Fe,Mg))(Cr,Al)_2O_4$) is the chief mineral in the ore. However, Cr and Fe were clearly restricted to the environmentally immobile fraction (leaching stage IV), and thus do not have any direct impact on the environment. The very acidic mixture of hydroxylamine hydrochloride and acetic acid, ($HONH_3Cl + CH_3COOH$; pH = 1.16), in leaching stage III dissolved only a small proportion of the Cr, while a high proportion of the Fe, Cu and Ni were leached. The heavy metal concentrations obtained in fraction IV ($HNO_3$ + HF + HCl) were higher than those in fractions I–III for all the metals except Cu. Cd and Ni were mainly (50 % and 98 %, respectively) partitioned in the environmentally immobile fraction (leaching stage IV), although part of the Cd (29 %) also dissolved in ammonium acetate (leaching stage II).

The precision of the whole extraction procedure can be evaluated by verifying the results of replicate measurements. The data in Paper V (Table 2) show the results for two discs (d = 50 mm) cut from the same glass fibre filter (203*254 mm). The relative standard deviations were lowest for all the heavy metals in leaching stage IV: 0.54 % for Cr, 0.90 % for Fe, 4.96 % for Cu, 4.40 % for Ni and 1.66 % for Cd. Thus the reproducibility of the acid leaching procedure ($HNO_3$ + HF + HCl) was good for all the metals. The relative standard deviations were generally acceptable (< 13 %) for all the heavy metals in leaching stage I. The poorest reproducibilities occurred in leaching stage I ($H_2O$) for Cr (RSD of 35.5 %), and in leaching stage II ($CH_3COONH_4$) for Fe and Ni (RSDs of 54.2 % and 30.1 %, respectively). Lindberg *et al*. (79) reported similar

problems with poor reproducibility in the leaching of atmospheric particles, and Tessier *et al*. (143) in the extraction of sediments. In both studies this was attributed to differences in the particle size distribution of the samples. Lindberg *et al*. (79) also suggested that there are problems in maintaining a constant leachate chemistry from sample to sample.

The average amounts of metals in the water soluble fraction (*i.e.* leaching stage I) leached from a TSP sample with an average mass of 173 mg were Cr 3.6 µg, Fe 55 µg, Cu 19 µg, Ni 3 µg and Cd 0.1 µg. The corresponding values for the environmentally mobile fraction (*i.e.* leaching state II) were Cr 1 µg, Fe 53 µg, Cu 207 µg, Ni 6 µg and Cd 0.2 µg. The sum of water-soluble ($H_2O$) and environmentally mobile ($CH_3COONH_4$) metals was Cr 4.6 µg, Fe 103 µg, Cu 226 µg, Ni 9 µg and Cd 0.3 µg. Based on the total annual particle emissions from the AvestaPolarit Chrome Oy Kemi Mine (48 t), the calculated annual airborne pollution impact of water-soluble and environmentally mobile heavy metals is therefore Cr 1.2 kg (r.s. 1.2 %), Fe 29 kg (r.s. 30 %), Cu 63 kg (r.s. 66 %), Ni 2.5 kg (r.s. 2.6 %) and Cd < 100 mg (r.s. < 0.1 %). These amounts are theoretically released after deposition of the aerosols (particulate material) on the surface of lakes, rives, soil and plants, and are thus potentially bioavailable. However, the magnitude of the "bioavailable" and "environmentally mobile" fractions are strongly dependent on the physical and chemical properties of the "dust", *e.g.* the solubility, and chromite especially is known to be difficult to dissolve. The leaching studies represent an assessment of the worst case environmental scenarios in which the components of the sample become soluble and mobile (135).

Thus, the results of our leaching studies were in agreement with those obtained by Hlavay *et al*. (48) for the fractionation of Cr in urban particles at Tihany in Hungary, and by Dreetz *et al*. (47) at Oslo in Norway. Querol *et al*. (50) reported that only a minor portion of the Cr in atmospheric particulates collected in a sulphide ore mining area was leachable by $H_2O$ or by $CH_3COONH_4$. However, in another study carried out by Hlavay *et al*. (74) on the distribution of Cr in aerosol samples collected in the moderately polluted cities of Veszprém and Kabhegy in Hungary, Cr was also clearly partitioned into the environmentally mobile fraction (leaching state II; $CH_3COOHN_4$); the proportion of Cr in the environmentally mobile fraction in the two cities was 51 % and 44 %, respectively.

### *5.2.3 The homogeneity of heavy metal deposition on TSP filters (VI)*

The rsd values for Cr, Ni, Cu and Fe in paper VI (table 7) suggest that these heavy metals are not necessary uniformly distributed over the glass fibre filters. The rsd values between 9 discs cut from the same filter varied between 5.4–33.9 % for Cr, between 7.50–35.0 % for Ni, between 3.6–25.9 % for Cu, and between 6.6–19.9 % for Fe, depending on the sampling month. All the Cd concentrations in the TSP filters were very low, and it was therefore not possible to determinate the homogeneity or un-homogeneity of the deposition of Cd on the glass fibre filters.

Although the cause of the non-uniform distribution of elements on the filters was not determined, Zdrojewski *et al*. (199–200) reported that one explanation for this phenomenon in a study on Pb and Cd was that a high-volume sampler draws in air non-uniformly. Another reason might be the differences in the particle size distribution of the

metals. According to Zdrojewski *et al*. (199), one explanation could be the detachment of particulate matter during transit and storage.

However, although there is no exact criterion for the degree of homogeneity of heavy metal deposition on filters, Low *et al*. (201) and Dreetz *et al*. (47) considered heavy metal deposition to be homogeneous when the rsd for the element, calculated from different discs cut from the same filter, was < 15 %. The corresponding criterion value for rsd according to Wang *et al*. (69) was < 10%. Thus, if we compare the results in Paper VI (table 7) with the criteria of Low *et al*. (201), Dreetz *et al*. (47) and Wang *et al*. (69), it is apparent that the distributions of Cr, Ni, Cu and Fe across the glass fibre filters collected using a high-volume sampler were non-uniform. In conclusion, the non-uniform deposition of heavy metals in filters causes error in the calculated heavy metals concentrations of ambient air concentrations, and thus gives underestimated results for the impact monitoring (*i.e.* the quality of air) of point sources.

# 6 Conclusions

The results of the comparison of various dissolution methods for different elements (*i.e.* sulphur and metals) in plant materials used as bioindicators suggested that the widely used wet digestion techniques involving $HNO_3$, $HNO_3$–$HClO_4$, HF or HF(DAC) do not necessarily result in satisfactory dissolution of all the elements. The acid procedure with a mixture of $HNO_3$ and $HNO_3$–$HClO_4$ slightly underestimated the S concentrations of plant material. The losses of sulphur were the highest in the dry ashing digestion procedure [HF(DAC)].

For the determination of heavy metals, the wet digestion techniques involving $HNO_3$, $HNO_3$–$H_2O_2$ or $HNO_3$–$HClO_4$ sometimes underestimated the metal concentrations of plant material; good examples are the determination of Al, Ca and K in reference material BCR CRM 100. Thus stronger digestion conditions using even HF are sometimes required for the complete dissolution of the samples.

This study has provided rather comprehensive information about the effects of sulphur emissions emitted from the pulp and paper mill complex at Kemi (*i.e.* Stora Enso Oyj Veitsiluoto Mills and Oy Metsä-Botnia Ab Kemi Mills), and the heavy metal emissions emitted from the AvestaPolarit Chrome Oy Kemi Mine at Kemi, as well as from the ferrochrome and stainless steel works of the AvestaPolarit Stainless Oy at Tornio.

Sulphur accumulation in pine needles around the pulp and paper mills was clearly higher than other points in the Kemi area and in the background samples. For example, within a radius of about 1–1.5 km around the mills of Oy Metsä-Botnia Ab Kemi Mills, the sulphur concentrations for (C) and (C+1) needles were 28 % and 26 % higher than those in the corresponding background samples collected in Kuivaniemi at a distance about 25 km from Kemi. Pine needles do not appeared to be appropriate a method for monitoring the accumulation of Fe, Zn, V and Pb emitted from pulp and paper mills. However, the Ca concentrations in (C+1) needles in the vicinity of the Oy Metsä-Botnia Ab Kemi Mills was 48 % higher than the average Ca concentration calculated from all (C+1) needles; thus it is likely that part of the Ca in the needles is derived from the mills.

The regional distribution pattern of Cr and Ni in mosses in the Kemi-Tornio area in 2000 showed clearly that the most polluted area (Cr > 200 µg/g and Ni > 20 µg/g) appeared to lie within a few kilometres of the ferrochrome and stainless steel works of AvestaPolarit Stainless Oy. Within this area, the Cr concentrations in mosses were 4–13 times higher than those outside the urban area of Tornio. The area most polluted by the

opencast chromium mining complex (Cr > 200 µg/g and Ni < 20 µg/g) appeared to be in the immediate vicinity of complex. The deposition and accumulation of Cr and Ni in mosses clearly decreased with increasing distance from the point sources, but not for Zn. The Zn concentrations were similar throughout the study area and there is therefore no distribution pattern at all for Zn.

All the 95$^{th}$ percentile values for TSP (total suspended particles) in the mine area of AvestaPolarit Chrome Oy Kemi Mine were below the current Finnish air quality limit value of 300 µg/m$^3$. However, the 98$^{th}$ percentile value exceeded the Finnish air quality guideline value of 120 µg/m$^3$ at one monitoring site. The Cr concentrations in ambient air at mining area varied between 0.65–48.2 µg/m$^3$, the Ni concentrations between 0.05–1.4 µg/m$^3$, and the Pb concentrations were all under 0.1 µg/m$^3$.

According to leaching studies, the sum of calculated annual airborne pollution impact of water-soluble fraction ($H_2O$) and environmentally mobile ($CH_3COONH_4$) fraction from the AvestaPolarit Chrome Oy Kemi Mine was Cr 1.2 kg, Fe 29 kg, Cu 63 kg, Ni 2.5 kg and Cd < 100 mg. These amounts are released after deposition of the airborne pollution on the surface of lakes, soils and plants, and are thus potentially bioavailable.

According to the homogeneity studies of heavy metal deposition on TSP filters, Cr, Ni, Cu and Fe were non-uniformly distributed over the glass fibre filters. The rsd values varied between 5.4–33.9 % for Cr, between 7.5–35.0 % for Ni, between 3.6–25.9 % for Cu, and between 6.6–19.9 % for Fe.

# 7 Future research work

Future research work at the mine area should also concentrate on both $PM_{10}$ and $PM_{2.5}$ measurements and their heavy metal concentrations in the mine area. Such a study would provide information on the human exposure to those particle fractions that can possibly penetrate the lungs. The concentrations of asbestos and other mineral fibres should also be measured in order to gain information on possible human exposure in the mine area. In addition, occupational exposure measurements of airborne dust, fibrous minerals and crystalline silica, *e.g.* the particle size distribution of mineral phases and metals in dust, at different work-sites and in the underground mine gallery are necessary. Silicosis, the lung condition caused by the inhalation of respirable-size fine particles of crystalline silica, is a potential threat in mine works (49, 156, 202). In addition, limited evidence of the potential carcinogenic effect of silica dust has been reported (54, 203). The content of chromium(III) and chromium(VI) species, as well as the speciation of other metals in workplace air in the mine area and in the underground mine gallery, should be determined in order to assess the occupational risk for workers.

Future research work in the area around the ferrochrome and stainless steel works should focus on the concentration and fractions of heavy metals in the soil and in vegetables in order to provide information about the "contaminant" levels in the area around the works. Bioavailability and environmental mobility studies on heavy metals in the soil are also needed.

Future research work in the area around the pulp and paper mills at Kemi should concentrate on the effects of emissions of gaseous chlorine compounds on the forests, and on a questionnaire study (population panel); odour dispersion calculations and field inspections are primarily tools for measuring the odours, whereas population panels and questionnaires also give direct information about the degree of odour annoyance experienced by the residents.

All the future research work and mentioned above is related to the fields of air pollution or occupational exposure research. All these industrial plants represent a subject of many other fascinating research work in the other fields of "Green Chemistry" (204), for example sewage treatment studies, hazardous waste management, the use of landfills, recycling, and the use of so called BAT-techniques (205). In addition, the suitability of direct-reading instruments, *e.g.* field-portable X-ray fluorescence analysers, should be evaluated in obtaining information about the composition of mining samples, as well as for the determination of heavy metals in glass fibre filters.

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The aphorism by Rabindranath Tagore; The Nobel Prize in Literature in 1913.