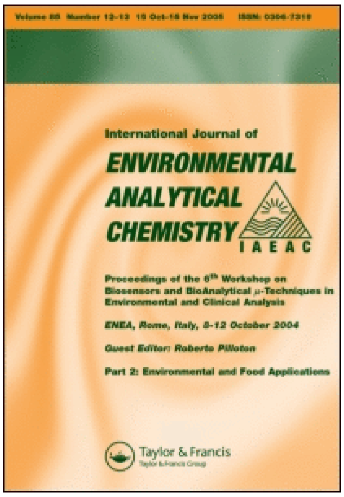

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Pine Needles (*Pinus Sylvestris*) as a Bioindicator of Sulphur and Heavy Metal Deposition in the Area Around a Pulp and Paper Mill Complex at Kemi, Northern Finland

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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

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The determination of sulphur and heavy metals in plants is an integral part of many environmental studies. Pine needles (*Pinus Sylvestris*) have proved to be suitable air quality indicators for pollutants, especially for sulphur. This study was carried out in the vicinity of Kemi, a town situated on the Gulf of Bothnia in northern Finland. An industrial complex comprising two pulp and paper mills is located in the centre of the area. Scots pine (*Pinus Sylvestris*) needles were collected from 29 sampling sites. The samples were dried, homogenized and digested with nitric acid. The concentrations of the elements S, Fe, Zn, Ca, V, and Pb were determined by ICP-AES. According to our results pine needles (*Pinus sylvestris*) appear to be an ideal bioindicator and sampling material for identifying and assessing atmospheric sulphur pollution derived from pulp and paper mills and can complement the information provided by plant mapping studies around pulp and paper mills.

Keywords: Foliar element analysis; environmental monitoring; heavy metals; airbone pollutants; pulp and paper mills

INTRODUCTION

Environmental monitoring involves 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. Bioindicators represent a complementary tool for environmental monitoring systems, and could also overcome some of the shortcomings associated with the direct measurements of pollution. Bioindicators directly depict the impacts of environmental pollution on organ-

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isms, 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. The determination of sulphur in plants and pine needles is an integral part of many environmental studies. Pine needles have proved to be suitable air quality indicators for pollutants, especially for sulphur. In Finland the sulphur concentration of *Pinus sylvestris* needles has been determined in several urban and rural environments, and numerous studies have shown correlations between the sulphur concentrations of pine needles and anthropogenic sources [1,2].

The use of pine needles as emission indicators around pulp and paper mills in Finland was first reported in the late 1960s [3]. In this study pine needles were collected from trees in the vicinity of a sulphite pulp mill and a district heating installation. In 1973 an attempt was made to assess the condition of trees before the construction of a new recovery boiler, and to clarify whether the pine needles had accumulated harmful amounts of sulphur in the vicinity of the sulphite pulp mill in Rauma, Finland. Analyses were made on needle samples collected at distances of 0,5 to 5 kilometres from the mill. Samples collected from the town of Lahti were used as comparison samples, because there are no pulp mills in Lahti. A method developed in collaboration with VTT for the determination of the total sulphur concentration was used. The procedure is based on X-ray fluorescence and has been found to be very suitable for determining large numbers of samples [4].

BACKGROUND AND OBJECTIVES

The Finnish Air Pollution Control Act and Decree has been in force since October 1982. Finnish environmental legislation requires the operator to be aware of the amount and composition of the emissions, and also of the impact on the environment caused by the operations. General requirements for monitoring, including biomonitoring, are determined by the information required by the authorities. Bioindicators, e.g. plants, directly depict the impact of environmental pollution on organisms and they can potentially detect long-term exposure of sites to environmental harmful chemicals. High concentrations of certain element in the needles may be the result of high emission levels. Nowadays bioindicators, e.g. pine needles, are widely used in Finland for biomonitoring purposes.

This study was based on a methodological investigation carried out in 1979 and 1989 in Kemi using *Pinus sylvestris* needles as the sampling material [5,6].

The aims of the study were: (i) to determine the sulphur content of needles, (ii) to compare the element concentrations in pine needles, and (iii) to produce easy-to-read maps of the regional sulphur distribution pattern for comparison with previous studies. This study is a part of a major project focusing on the effects of the forest industries on the environment in Finland.

EXPERIMENTAL

Study area and sources of pollution

The study was carried out in the town of Kemi (65°44′N, 24°35′E) on the Gulf of Bothnia, northern Finland. In 1999, Kemi had a population of about 24 500. Industrial plants of Oy Metsä-Botnia Ab Kemi Mills, StoraEnso Oyj Veitsiluoto Mills and Outokumpu Chrome 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 StroraEnso 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 Outokumpu Chrome Kemi Mine is a large chromium ore deposit. Present ore reserves are 70 million tonnes, and the estimated ore resources are 150 million tonnes. The main host rock of the ore is composed of talc-carbonate. The mine produces approx. 1 million tonnes of chromite ore a year. At the same time, 8 million tonnes of waste rock are removed from the open-cast pits.

Air pollutants in the area 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 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) depicted in Figure 1, have fallen considerably since 1980 following the extension of district heating and because the pulp mills have upgraded their processes. Other major forms of local air pollution, reported in Table I, are nitrogen compounds (NO_x), particles and chlorine compounds (Cl_{tot}). Exhaust emissions from road traffic, summarised in Table II, primarily consist of carbon monoxide (CO), hydrocarbons (HC) and nitrogen compounds (NO_x). Lead (Pb) is no longer a problem, because the petrol used by automobiles in Finland is unleaded [7]. The total VOC emissions in Kemi in 1998 were about 50 million tonnes, and the main emission source being the oil refinery at Ajos in south Kemi [8].

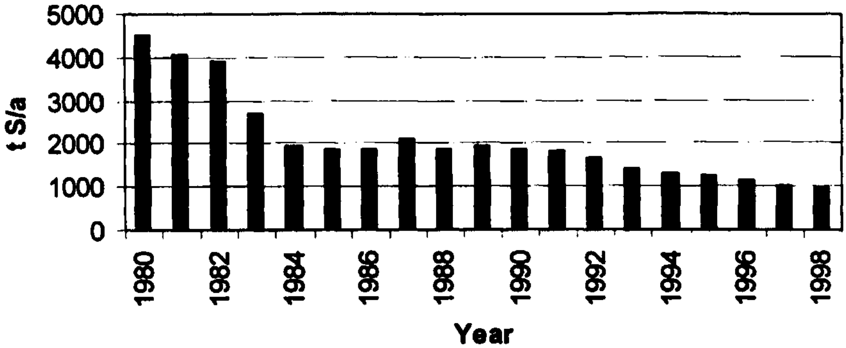

FIGURE 1 Total sulphur emissions in Kemi during 1980–1998 (t S/a)

TABLE I Major air pollutants and their sources in Kemi in 1998

Source	*SO_2 (t SO_2)*	*NO_x (t NO_2)*	*TRS (t S)*	*Particles (t)*	*Cl_{tot} (t)*
SE	780	954	330	72	13
MB	387	1328	74	277	10
OC	6	2	--	48	--
Total	1173	2284	404	397	23

Abbreviations: MB = Oy Metsä-Botnia Ab Kemi Mills, OC = Outokumpu Chrome Kemi Mine, SE = StoraEnso Oyj Veitsiluoto Mills.

TABLE II Emissions from road traffic in Kemi during 1987 and 1996 (t/a)

Year	*CO*	*HC*	*NO_x*	*Particles*	*SO_2*	*Pb*
1987	2238	372	622	65	51	1.7
1996	1849	300	667	41	6	--

Sampling and analysis

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

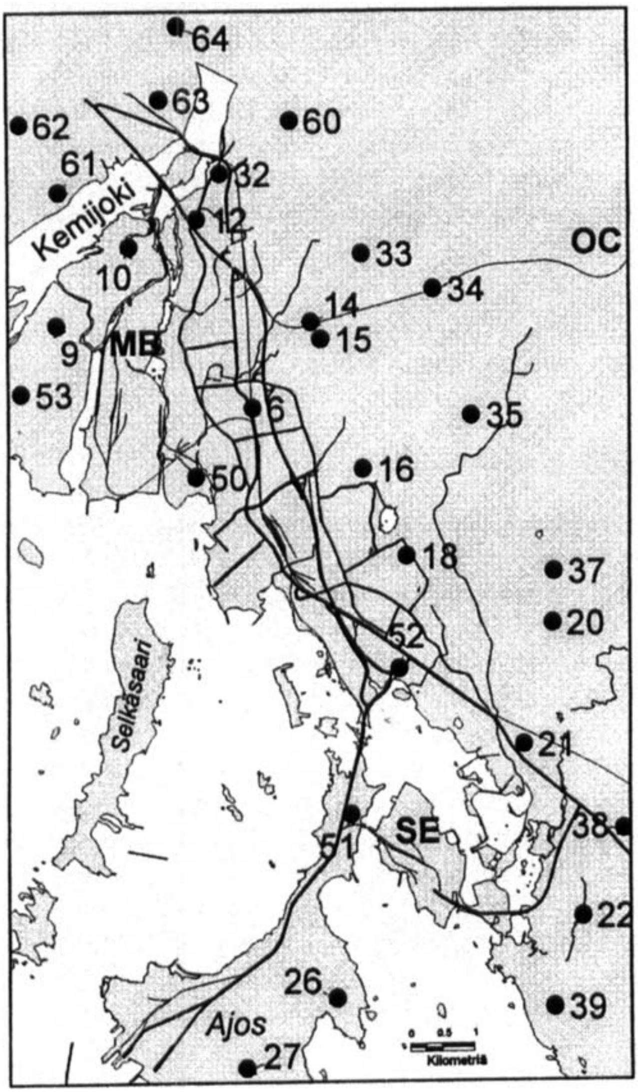

FIGURE 2 Sampling sites in the Kemi area in 1999. Abbreviations: MB = Oy Metsä-Botnia Ab Kemi Mills, OC = Outokumpu Chrome Kemi Mine, SE = StoraEnso Oyj Veitsiluoto Mills

Sampling was carried out in April 1999 according to the SFS 5669 standard. 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 and milled to pass through a 2 mm sieve. Samples (0.5 g) were digested with nitric acid (10 ml 65 % Riedel-de-Haen 30709 HNO_3lot. 82790) in a micro wave oven (CEM MARS-5) using US EPA method 3051. The concentrations of the elements S, Fe, Zn, Ca, V and Pb were measured by ICP-AES. The analysis was validated by monitoring the instrumental parameters and two certified samples (1575 Pine Needles and 1573a Tomato Leaves). All the chemical analyses were performed at The Geological Survey of Finland in Kuopio, Finland.

RESULTS AND DISCUSSION

Sulphur concentrations of needles

The average sulphur concentration in the current-year (C) needles was 828 mg/kg, with a standard deviation of 83.9 mg/kg and range 699–1090 mg/kg. The quartiles for (C) needle were lower-Q 777 mg/kg, median 811 mg/kg, upper-Q 877 mg/kg. The average sulphur concentration in the previous-year (C+1) needles was 835 mg/kg, with a standard deviation of 114.5 mg/kg and range 605- 1100 mg/kg. The quartiles for (C+1) needles were lower-Q 777 mg/kg, median 811 mg/kg, upper-Q 877 mg/kg. According to results, the sulphur concentrations differed significantly ($p<0.05$) among both the C and C+1 needles. In contrast, the differences between the sulphur concentrations of the C and C+1 needles were not statistically significant ($p<0.05$). According to Figures 3 and 4 the highest sulphur concentrations occurred in the vicinity of Oy Metsä-Botnia Ab Kemi Mills. The average sulphur concentration at sampling sites 6 (Mäntylä), 9 (Vähäkuivanuorontie), 10 (Sotisaari), 12 (Vilmilä) and 14 (Elijärventie) was 954 mg/kg for the (C) needles and 953 mg/kg for the (C+1) needles. These average sulphur concentrations are 28 % (C) and 30 % (C+1) higher than those in the corresponding background samples collected in Kuivaniemi.

If we compare the average sulphur concentration of sampling sites 6 (Mäntylä), 9 (Vähäkuivanuorontie), 10 (Sotisaari), 12 (Vilmilä) and 14 (Elijär-

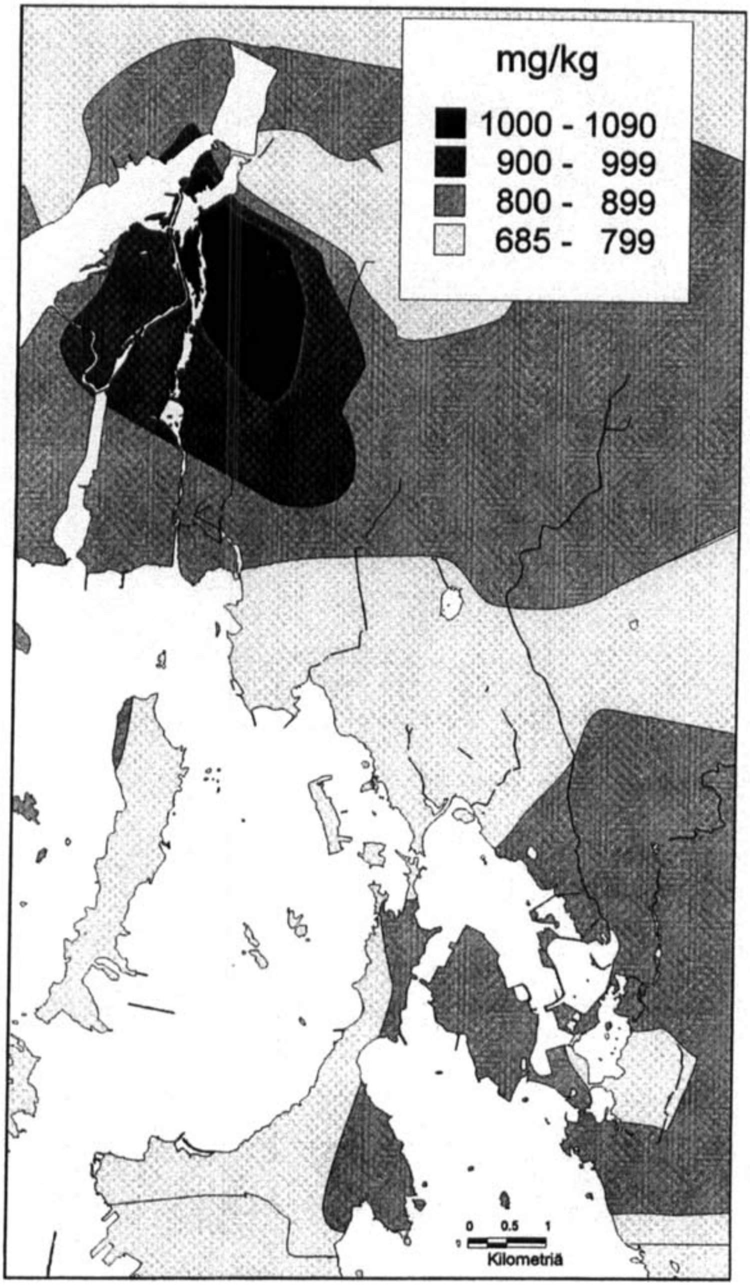

FIGURE 3 The dispersion pattern of sulphur in the (C) needles in 1999

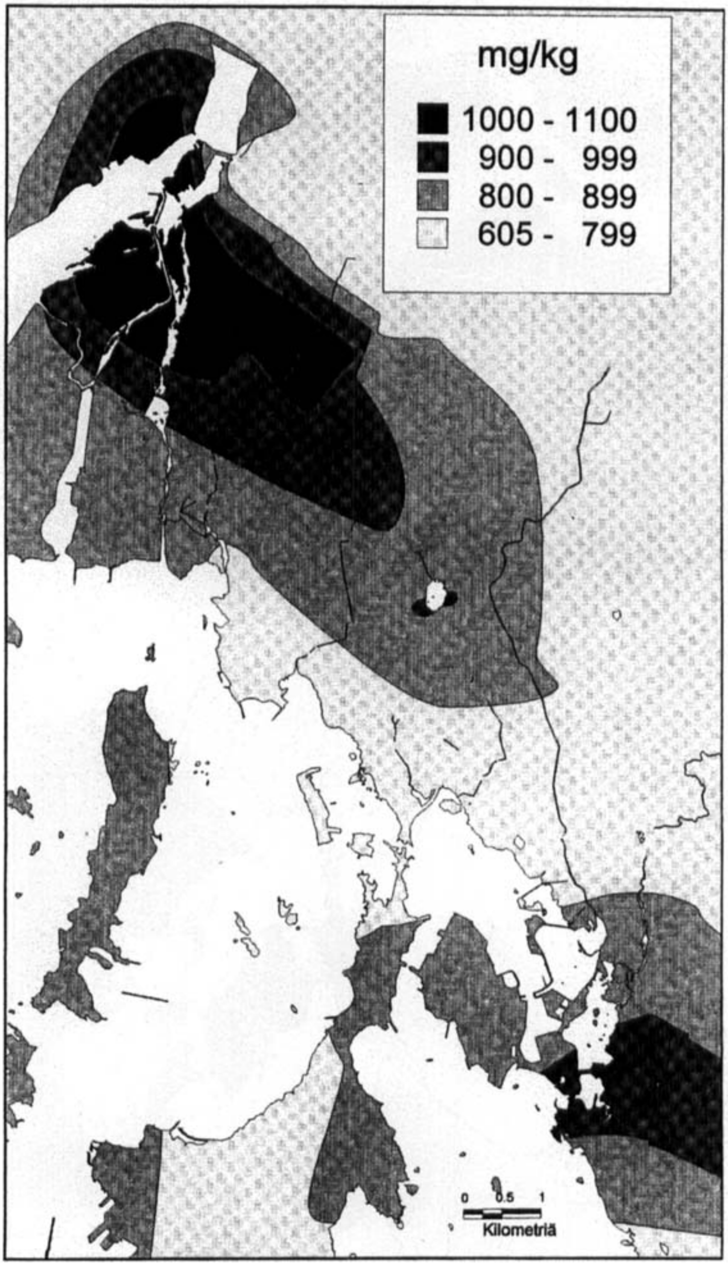

FIGURE 4 The dispersion pattern of sulphur in the (C+1) needles in 1999

ventie) to the average sulphur concentration for all needles, it is 11 % higher than the average sulphur concentration in (C) needles and 18 % higher than in (C+1) needles.

The highest individual sulphur concentration in (C) needles occurred at sampling site 6 (Mäntylä) 1090 mg/kg, which is 46 % higher than the corresponding value for Kuivaniemi. The highest individual sulphur concentration in (C+1) needles was at sampling site 14 (Elijärventie) 1020 mg/kg, which is 34 % higher than the corresponding value at Kuivaniemi.

In the southern part of Kemi the impact of pollution from StroraEnso Oyj Veitsiluoto Mill is most clearly evident at sampling site 21 (Järppi), and the impact of the district heating plant at sampling site 22 (Hepola). Before continuous air quality monitoring started in Kemi, we used mathematical dispersion models and computer simulations to depict the dispersion of sulphur and TSR compounds [9,10]. The dispersion of sulphur based on the needle analyses in this study is relatively similar to the modelled.

Both methods show that the sulphur accumulation in pine needles around the pulp and paper mills is clearly higher than at other points in the Kemi area. A similar phenomenon has also been reported in many other studies using pine needles as bioindicators [11–15] Compared the to the result of previously studies (See Table III), the minimum and maximum values have decreased during the period 1979–1999.

TABLE III Sulphur concentrations (mg/kg) in needles during 1979–1999

Year	*1979 (C)*	*1979 (C+1)*	*1989 (C)*	*1989 (C+1)*	*1999 (C)*	*1999 (C+1)*
Min	804	810	900	970	685	605
Max	1430	1420	1190	1520	1090	1100
Mean	1150	1145	1068	1220	828	835
Plots	13	13	13	13	29	29

If we compare the sulphur dispersion areas (km^2) of this study to those calculated from needles in previous studies (See Table IV), there has been a clear decreasing during 1979–1999.

The decrease in the sulphur dispersion (km^2) calculated from needle concentrations resembles that reported in another study [16].

TABLE IV Sulphur dispersion areas (km^2) in Kemi during 1979–1999

Year	*900–1000 mg/kg km^2*	*1101–1300 mg/kg km^2*	*1301–1500 mg/kg 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	--	--

Concentrations of other elements in needles

The concentrations of macronutrients and heavy metals in pine needles have not been measured in earlier studies around the pulp and paper mills in Kemi. The needle iron concentration varied between 37–123 mg/kg, and the average iron concentration was 59 mg/kg for (C) needles and 70 mg/kg for (C+1) needles. These average iron concentrations are 43 % (C) and 45 % (C+1) higher than the corresponding background values for samples collected in Kuivaniemi. The highest iron concentrations occurred at sampling sites 6 (Mäntylä), 12 (Vilmilä), 51 (Rivinokka), 52 (Haukkari), 63 (Kallijärvi) and 64 (Kokonkuja). Sampling sites 6 (Mäntylä), 12 (Vilmilä), 51 (Rivinokka) and 52 (Haukkari) are located relatively close to the mills, as well as roadsides, so it is highly likely that the high iron concentrations are derived from dust from surrounding land rather than mills, although fuel oil burning does emit iron containing particles.

The needle zinc concentration varied between 26–77 mg/kg. The variation is relatively small, and the highest concentrations clearly occurred in roadside environments and near roads, such as at like sampling site 38 (Taipaleenkylä), 51 (Rivinokka), 63 (Kallijärvi) and 64 (Kokonkuja). The results indicate that the zinc is derived from dust from the surrounding land.

The needle calcium concentration varied between 1450–4960 mg/kg, the average calcium concentration being 2144 mg/kg for (C) needles and 3348 mg/kg for (C+1) needles. The average calcium concentration in Kemi is 16 % (C) lower and 53 % (C+1) higher than corresponding values for samples from Kuivaniemi. The highest calcium concentrations occurred at sampling sites 9 (Vähäkuivanuorontie), 10 (Sotisaari), 12 (Vilmilä), 15 (Ristikangas), 16 (Junko) and 32 (Lautiosaari). The needle Ca concentration appears have been influenced by airborne pollutants from Oy Metsä-Botnia Ab Kemi Mills in northern parts of Kemi, especially at sampling site 9 (Vähäkuivanuorontie) where the calcium concentration in (C+1) needles was 4960 mg/kg, which is 48 % higher than average calcium concentration for all the (C+1) needles collected in Kemi. High concentrations of calcium, which is a typical pollutant from pulp and paper mills, have been recorded in many studies near factories emitting calcium [11,17,18].

The vanadium concentrations, which are a good indicator of fuel oil burning, were < 1 mg/kg at all the sampling sites. The lead concentrations at all the sampling sites were < 5 mg/kg.

CONCLUSIONS

The main atmospheric pollution sources in the Kemi area are municipal heating plants and pulp and paper mills, such as the Oy Metsä-Botnia Ab Kemi Mills and StoraEnso Oyj Veitsiluoto Mills, which emit heavy metals and gaseous sulphur compounds. The dispersion is very local and depends on the prevailing wind direction; usually between the south and southwest in Kemi. The dispersion also depends on the local relief. Pine needles *(Pinus sylvestris)* appear to still be an ideal bioindicator and sampling material for identifying and assessing atmospheric sulphur pollution derived from pulp and paper mills. Sampling is easy and inexpensive, and pine trees are easy to find in cultivated and densely populated areas in Kemi.

Sulphur emissions have decreased tremendously during 1980–1999. The most polluted areas appear to be in the vicinity of Oy Metsä-Botnia Ab Kemi Mills. Our results correspond to those reported in many other studies in which pine needles were used as bioindicators [4,5,6,11,19]. According to studies made by Finnish Meteorological Institute, the main reason for the high sulphur content in pine needles around pulp and paper mills are emissions from point sources that have low stacks and process malfunctions. Areas immediately downwind from a source with a low stack are usually the most polluted [10]. In the case of Oy Metsä-Botnia Ab Kemi Mills, there still are many point sources with a low stack and the typical "pulp-mill smell" is noticeable during operation malfunctions when the TRS concentration in ambient air has occasionally rather high.

The StoraEnso Oyj Veitsiluoto Mills are situated on an island, so the sampling density around this plant is not so dense as it is around Oy Metsä-Botnia Ab Kemi Mills. This may have some effects on the dispersion charts made by a computer-based geographic information system, KemiGis. The results show that pine needles can be used in the air pollution monitoring of sulphur compounds especially, and can complement the information provided by plant mapping studies around pulp and paper mills.

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