Scots Pine Needles as Bioindicators in Determining the Aerial Distribution Pattern of Sulphur Emissions around Industrial Plants

Risto Pöykiö, Jari Hietala, and Hannu Nurmesniemi

Abstract**—**In this study, the Scots pine (*Pinus sylvestris L.*) C needles (i.e. the current-year-needles) were used as bioindicators in determining the aerial distribution pattern of sulphur emissions around industrial point sources at Kemi, Northern Finland. The average sulphur concentration in the C needles was 897 mg/kg (d.w.), with a standard deviation of 118 mg/kg (d.w.) and range 740 – 1350 mg/kg (d.w.). According to results in this study, Scots pine needles (*Pinus sylvestris L.*) appear to be an ideal bioindicators for identifying atmospheric sulphur pollution derived from industrial plants and can complement the information provided by plant mapping studies around industrial plants.

Keywords**—**Emission, Sulphur, Scots Pine, *Pinus sylvestris*

I. INTRODUCTION

THE air pollution from local point sources and from distant diffuse sources impact the environment in the form of dry and wet deposition. The distance and area over which pollutant spread are dependent e.g. on the height they reach in the atmosphere and on climatic factors. Compared to gaseous compounds, the distance that particulate matter is transported, is generally 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 and density of the particles. Large particles are deposited relatively close to the emission sources, while smaller particles, aerosols and gaseous metallic compounds can be transported hundreds of kilometres through the atmosphere.

The term bioindicator/biomonitor is used to refer to an organism, or a part of it, that depicts the occurrence of pollutants on the basis of specific symptoms, reaction, morphological changes or concentrations. Biomonitoring, i.e. monitoring the state of the environment though the performance of living organisms (bioindicators), can be used to measure the cumulative impact of different types of environmental pressure, e.g. air pollution emitted from a range of emission sources. By monitoring the environmental impact of point-source pollution on the environment, the operators of industrial plants as well as environmental authorities can foresee and prevent threats and risks before they become a problem. Bioindicators directly depict the impact of environmental pollution on organisms, and can potentially quantity the long-term exposure of a site to potentially harmful, environmental contaminants, e.g. air pollutants [1].

Finnish environmental legislation requires that an operator is aware of the amount and composition of their emissions, as well as of the impact on the environment caused by their operations. According to the Finnish environmental legislation, the operators of industrial processes and plants are usually obliged by their environmental permits to monitor the processes (i.e. operation monitoring), releases (i.e. emission monitoring) and impact of their operations on the environment (i.e. impact monitoring).

Scots pine (*Pinus sylvestris L.*) is a widely distributed tree species in northern Europe, and its needles have proved to be suitable air quality indicators of the deposition of pollutants, especially of sulphur compounds [2, 3]. The use of pine needles as emission indicators around pulp and paper mills in Finland was first reported in the late 1960s [4]. Nowadays, Scots pine needles are widely used in Finland for biomonitoring purposes in areas around point sources, and the environmental authorities have accepted them as a bioindicator.

II. EXPERIMENTAL

A. The study area and pollution sources – the meteorological parameters

The study was carried out in the town of Kemi (65º44´N, 24º35´E) on the Gulf of Bothnia, Northern Finland (Figure 1). In 2008, Kemi had a population of about 22 400. Sulphur and particle emissions in the study area originate from the pulp and paper mills of Stora Enso Veitsiluoto Mill, from the pulp mill of Oy Metsä-Botnia Ab Kemi Mill, which is integrated with the lineboard mill registered under the name of M-Real Oyj, from the chromium mine of Outokumpu Chrome Kemi Mine Oy, from the municipal district heating plants of Kemin Energia Oy and Keminmaan Energia Oy, and from the port operations located on the Ajos peninsula. In 2008, the gaseous sulphur (SO_2 + TRS) emissions at Kemi were 485 tonnes, and the particulate matter emissions 124 tonnes. The sulphur

Risto Pöykiö (Ph.D.) is the Environmental Manager at the city of Kemi, FI 94100 Kemi, Finland (corresponding author to provide phone: +358-16-259 673; fax: +358-16-259 481; e-mail: risto.poykio@kemi.fi).

Jari Hietala (M.Sc.) is the Manager of Lapin Vesitutkimus Oy, FI 94100 Kemi, Finland.

Hannu Nurmesniemi (Ph.D.) is with the Stora Enso Oyj Veitsiluoto Mill, FI 94800 Kemi, Finland (e-mail: hannu.nurmesniemi@storaenso.com).

dioxide emissions from road traffic in Kemi are very low; in 2008 they were only about 0.7 t. More comprehensive review of the pollution sources and the development of gaseous and particulate matter emissions at the study area are given in our previous papers [5, 6].

Due to the proximity of the Gulf Stream, the typical average annual temperature in the region is between 1 and 3 °C, and the annual precipitation 450 – 550 mm with a relatively high proportion coming in the form of snow. Snow covers the study area for 150 – 200 days a year. According to the Figure 1, the prevailing winds during February 2008 – January 2009 were from the north (21 %), south (15.9 %) and from the south-west (13.4 %).

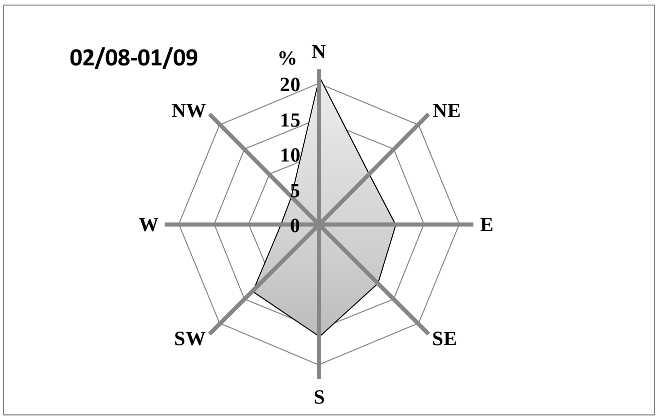

Fig. 1 A wind-rose of the study area during February 2008 – January 2009 [5].

A more comprehensive review of meteorological data in the study area during 2008 – 2009 and the long-term data (i.e. 1971-2000) of the Finnish Meteorological Institute on the monthly mean temperature and precipitation of the study area are given in our previous papers [5, 6].

B. Sampling and analyses

Scots pine (*Pinus sylvestris L.)* needles were collected at 29 sampling sites around industrial plants in the Kemi area (see Fig. 2). Two background sample was collected at Kuivaniemi, about 25 km to the south from Kemi (not shown in Fig. 1). The coordinates of the sampling sites were determined in the field by GPS (Garmin eTrex Venture CX). Sampling was carried out between 19 and 20 January 2009, according to the SFS 5669 standard [5, 6]. The current-year needle samples, i.e. C-needles, were taken at heights of 4 to 7 metres on pine of ages ranging between 50 to 100 years at each sampling site and 5 to 10 sample trees were randomly selected per sampling site.

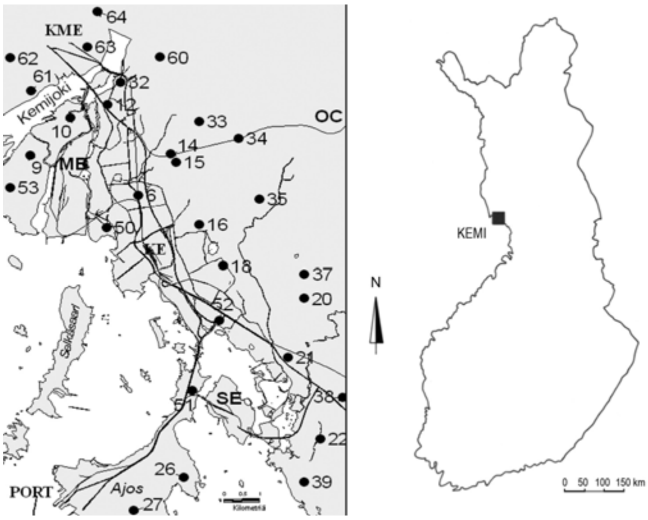

Fig. 2 Map of Finland showing the location of the sampling sites and industrial plants at Kemi in 2009 [5-7]

Note: Abbreviations in Figure 1: KE = Kemin Energia Oy, KME = Keminmaan Energia Oy, MB = Oy Metsä-Botnia Ab Kemi Mill (including M-Real Oyj), OC = Outokumpu Chrome Oy Kemi Mill, PORT = port of Ajos peninsula, SE = Stora Enso Oyj Veitsiluoto Mill.

After sampling, the C needles were combined to give one composite sample per site. The samples were stored in plastic bags in a freezer (-20°C) before analysis. The unwashed needles were dried at 40 °C until constant weight was reached, and then milled to pass through a 0.2 mm sieve. The samples (0.5 g) were digested with 10 mL of 65 % nitric acid (HNO_3) in a CEM Mars 5 micro-process controlled microwave-oven with using CEM HP 500 Teflon vessels (CEM Corp., Matthews, USA) in accordance with USEPA method 3051 [5-6]. The cooled solutions were transferred into 100 mL volumetric flasks and diluted to the mark with ultrapure water. The ultrapure water was generated by an Elgastat Maxima ion exchange water purification system (Elga Ltd., Bucks, England). All reagents and acids were suprapure or pro analysis quality. The concentrations of S, Na and Ca were measured with an inductively coupled plasma optical emission spectrometer (ICP-OES, Thermo Electron IRIS Intrepid II XDL, Franklin, USA).

III. RESULTS AND DISCUSSION

A. Sulphur concentrations in C needles at Kemi in 2009

The sulphur concentrations in the pine needles in the survey carried out at Kemi in 2009 are presented in Table 1.The average sulphur concentration in the C needles was 897 mg/kg (d.w.), with a standard deviation of 118 mg/kg (d.w.) and range 740 – 1350 mg/kg (d.w.). The highest (S ≥ 1000 mg/kg; d.w.) individual sulphur concentrations in C needles occurred at three sampling sites: site 10 (1350 mg/kg; d.w.), site 9 (1020 mg/kg; d.w.) and site 62 (1000 mg/kg; d.w.). These sites are all located in the northern part of the study area (see Fig. 2). The sulphur concentrations in C needles at these sampling sites were 39 - 88 % higher than the corresponding background value (720 mg/kg; d.w.). Sampling sites 9 and 10 are located in the immediate vicinity of Oy Metsä-Botnia Ab Kemi Mill (see Fig. 2). It is thus highly likely that the elevated sulphur concentrations in C needles at these sampling sites were primarily due to gaseous sulphur emissions from Oy Metsä-Botnia Ab Kemi Mill, as well as also to sulphate (SO_4) emissions from the mill, which are associated with particulate matter e.g. in the form of Na_2SO_4 [9-11]. However, gaseous sulphur emissions from the municipal district heating plant of Keminmaan Energia Oy may also extend to these sites.

TABLE I
SULPHUR CONCENTRATIONS IN CURRENT-YEAR (C) SCOTS PINE (PINUS SYLVESTRIS L.) NEEDLES AT KEMI AND IN THE BACKGROUND AREA AT KUIVANIEMI IN 2009

Sampling sites at Kemi (see Figure 2)	Sulphur (mg/kg; dry weight)
6	830
9	1020
10	1350
12	980
14	940
15	880
16	910
18	870
20	960
21	900
22	750
26	810
27	740
32	930
33	840
34	750
35	910
37	810
38	750
39	920
50	960
51	860
52	950
53	800
60	820
61	950
62	1000
63	950
64	870
Background (Kuivaniemi)	720

The moderately elevated sulphur concentrations (900 ≤ S ≤ 980 mg/kg; d.w.) in the C needles occurred at twelve sampling sites: site 12 (980 mg/kg; d.w), sites 20 and 50 (960 mg/kg; d.w.), sites 52, 61 and 63 (950 mg/kg), site 14 (940 mg/kg; d.w), site 32 (930 mg/kg; d.w.), site 39 (920 mg/kg; d.w.), site 16 and site 35 (910 mg/kg; d.w.), and site 21 (900 mg/kg; d.w.). The sulphur concentrations in C needles at these sampling sites were ca. 25 - 36 % higher than the corresponding background value (720 mg/kg; d.w.). Taking into account the location of emission point sources at Kemi (Fig. 2) we can conclude that the sulphur concentrations in C needles at sampling sites 12, 14, 32, 50, 61 and 63 are mainly due to gaseous sulphur and particle emissions from Oy Metsä-Botnia Ab Kemi mill and party also to the gaseous sulphur emissions from the municipal district heating plant of Keminmaan Energia Oy. In the southern part of the study area, the impact of pollutants from Stora Enso Oyj Veitsiluoto Mill was most clearly evident at sampling sites 52, 20, 21 and 39, which are located around the mill. Sulphur emissions from the municipal district heating plant of Kemin Energia Oy may also have accumulated in C needles collected at sampling sites 50, 16 and 6.

The slightly elevated sulphur concentrations (740 ≤ S ≤ 880 mg/kg; d.w.) occurred in the C needles at fourteen sampling sites: 15, 18, 64, 51, 33, 6, 60, 26, 37, 53, 22, 34, 38 and 27. These sites are located throughout the study area. The sulphur concentrations in C needles at these sampling sites were ca. 7 - 22 % higher than the corresponding background value (720 mg/kg; d.w.). Furthermore, at sampling sites 6 (830 mg/kg; d.w.), and 53 (800 mg/kg; d.w.), which are located in the immediate vicinity of the municipal district heating plant and the pulp and paper mill of Oy Metsä-Botnia Ab Kemi Mill, respectively, the sulphur concentrations in the C needles were relatively low, being only 11 – 15 % higher than the corresponding background value.

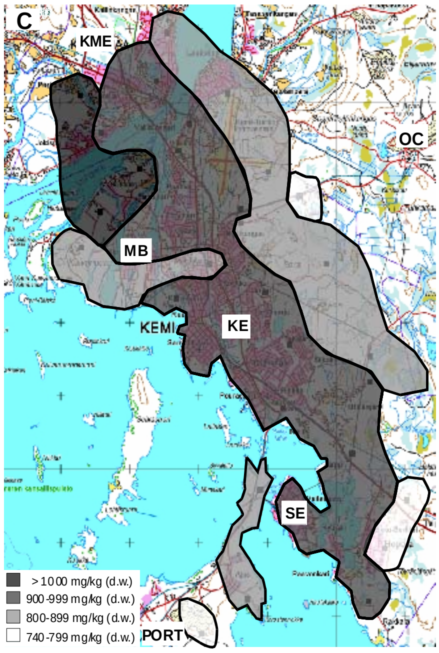

Fig. 3 Aerial distribution pattern of sulphur in C needles at Kemi, in 2009 [8].

In this context it is worth noting that, although sulphur in the form of sulphate (SO_4) is also a marine-derived ion [12], we can assume that almost all of the sulphur in the pine needles collected at Kemi is derived from emissions from local industrial plants. We have compared the sulphur concentrations in pine needles from the study area (i.e. Kemi) to those collected in a background area (i.e. Kuivaniemi) located at a distance about 25 km to the south from Kemi. Thus, we can eliminate the extremely small contribution of marine-derived sulphate from the sea because both areas are located on the Gulf of Bothnia, where the water in fact is only slightly brackish.

The aerial distribution pattern of sulphur in the C needles in this study (see Fig. 3) agree relatively well with our previous study [13], in which we determined the aerial distribution pattern of sulphur in the previous-year, i.e. C+1, needles. In both studies, the highest sulphur concentrations in the Scots pine *(Pinus sylvestris L)* needles we observed in the immediate or relatively close to the point sources. However, in this context it is worth to mention that, in this bioindicator study carried out at Kemi in 2009, the maximum sulphur concentration in the C needles (1350 mg/kg; d.w.; see Table 2) was higher than that in the C+1 needles (1070 mg/kg; d.w.; see Ref. 13). Furthermore, the sulphur concentration in the C needles (see Table 1) at sampling site 10 (1350 mg/kg; d.w.), 21 (900 mg/kg; d.w.), 33 (840 mg/kg, d.w.), 35 (910 mg/kg; d.w.), 39 (920 mg/kg, d.w.) and 61 (950 mg/kg; d.w.) were higher than those in the C+1 needles (see Ref. 8). Thus, our result is consistent with the findings of Rautio and Huttunen [3], and of Innes [14], who also reported that the sulphur concentration can be higher in the youngest needles compared to that in the older needles, even though sulphur concentrations have been found to increase with needle age. According to Rautio and Huttunen [3], one reason for this kind of phenomenon may be the relatively low precipitation, and hence low wet scavenging, which means that sulphur is primarily deposited as SO_2. Furthermore, according to Rautio and Huttunen [3], short-term SO_2 peaks from point-source emitters - which are common also at the pulp mills of Stora Enso Oyj and Oy Metsä-Botnia Ab Kemi Mills - may cause stomatal closure of the needles which, in turn, depresses gas exchange and thus also SO_2 uptake. Sulphur in a gaseous form (SO_2) is taken up most effectively by the youngest needles, which are also photosynthetically most active needles, and does not accumulate on the needles surface as needles age increases, unlike sulphur in the form of particulate matter [3]. According to Rautio et al. [15], this may be due to the fact that assimilation is highest in the C needles, because this also enhances gas exchange which, in turn, allows more SO_2 to enter through the stomata. Furthermore, according to Rautio et al. [15], the higher assimilation rate of the C needles also accelerates the transpiration stream, which could transport sulphur from the soil, thereby raising the sulphur concentrations in the C needles.

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