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HEAVY METAL ACCUMULATION IN WOODLAND MOSS *(PLEUROZZUM SCHREBERZ)* **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**

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Woodland moss *(Pleurozium schreberi?* samples were collected at **52** sampling sites around a chromium opencast mine and around a ferrochrome and stainless steels works. The samples were dried, homogenized and digested with a mixture of concentrated nitric and perchloric acids. The Cr, Ni and Zn concentrations in the moss samples were determined by **FAAS** in order to clarify the aerial distribution of heavy metals from both the opencast chromium mine and the ferrochrome and stainless steel works. This study, carried out in **2000,** compares the heavy metal (Cr, Ni, Zn) concentrations in mosses to the results of previous studies in **1995** and in **1990.** According to the results, the average Ni concentrations (mean) in mosses have increased since **1990** along with increased Ni emissions from point sources, but the average Cr concentrations (mean) in mosses have increased despite the decrease in Cr emissions from point sources have decreased. The results have been discussed from various point of view, as well as depicted out the low deposition of Zn on mosses.

Keywords: Mosses; Opencast chromium mining; Ferrochrome and stainless steel works; Heavy metals; Airborne pollutants

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INTRODUCTION

Air pollution by heavy metals from both local and distant sources impact the environment in the form of dry and wet deposition. Large particles are deposited close to the emission sources, while smaller particles (aerosols) and gaseous metallic compounds can be transported hundreds of kilometres through the air. The spread of pollutants from a point source is dependent on the wind direction. Metal aerosol pollutants (particles) remain suspended in the atmosphere for varying lengths of time depending on the size of the particles, the windspeed, relative humidity of the air and precipitation ^[1].

The value of the biological monitoring of air pollution by mosses has been proved in a large number of studies **[2-51.** Most mosses growing on the forest floor receive their nutrients only from dustfall and precipitation. Several studies have shown that surveys of the metal concentration in mosses can be a valuable means of identifying sources of airborne pollution and mapping the metal deposition $[6-8]$. 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 ^[9,10]. 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 schreberi* 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 schreberi* has been used in many studies for monitoring heavy metals in Scandinavia and in Europe **[11-141.** Assessment of environmental pollution by heavy metals in the vicinity **of** stainless steel and steel works or in the area around mines using especially *Pleurozium schreberi* as a bioindicator has been carried out in numerous studies **['s-lsl.**

Background and objectives

In order to obtain a more comprehensive picture of the phenomena occurring in the environment and to understand how human activities, in this case opencast chrome mining and a ferrochrome and stainless steel works, affect the environment, the environmental authorities have promoted a growing number of monitoring programs in which data are collected over wide areas and for extended periods. In Finland, a new Environmental Protection

Act has been in force since 1 March, 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 (IPPC) (Council Directive., 1996). In Finland, 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). The monitoring requirements presupposed by the permit provisions are laid down either in the environmental permits or in separate emission monitoring programmes approved by the competent authority.

This study is a part of the impact monitoring program of Outokumpu Chrome Kemi Mine Oy (current name AvestaPolarit Chrome Kemi Mine Oy) and Outokumpu Polarit Oy (current name AvestaPolarit Stainless Oy). The work provided an ideal opportunity to study the impact on the environment of opencast chromium mining prior to the planned expansion of chromite ore production at Outokumpu Chrome Kemi Mine Oy, and before the start of a planned increase in ferrochrome production at Outokumpu Polarit Oy. According to the environmental impact assessment (EIA) procedure, it is very important to document the normal state of the environment before carrying out an environmental investigation or any expansion in production ^[19].

This study was based on a methodological investigation carried out in 1990, 1995 and **2000** in Kemi and Tornio using *Pleurozium schreberi* moss as the sampling material. In environmental permits approved by the competent authority of the Lapland Regional Environmental Centre, *Pleurozium schreberi* is accepted as a bioindicator for heavy metal (Cr, Ni, Zn) deposition emitted from Outokumpu Chrome Kemi Mine Oy and Outokumpu Polarit Oy because it is wide-spread in the study area. In addition, the Finnish Ministry of the Environment primarily recommends the use of *Pleurozium schreberi* as a bioindicator for heavy metal deposition, and secondary the use of *Hylocomium splendens* ^[20]. According to environmental permits, the heavy metals Cr, Ni and Zn are to be analysed from mosses because they are the major metal pollutants emitted from these point sources. The aims of the study were (i) to determine the heavy metal (Cr, Ni, Zn) concentrations of mosses in the area around the chromium opencast mine at Kemi, and in the area around the ferrochrome and stainless steel works at Tornio, (ii) to produce easyto-read maps of the heavy metal distribution patterns for Cr and Ni, and (iii) to compare the results of previous heavy metal surveys based on mosses. This study is a part of a major project on the effects of the pulp and paper mills, and metal and mining industries on the environment in northern Finland, and on the use of plants as bioindicators of heavy metal deposition **[21-221.**

EXPERIMENTAL

Study area and pollution sources

The study area is situated on the Gulf of Bothnia, northern Finland, in the province of Lapland. There are two major heavy metal pollutant sources in the area, Outokumpu Chrome Kemi Mine Oy at Kemi $(65^{\circ}44' N, 24^{\circ}35' E)$ and Outokumpu Polarit **Oy** at Tornio (65"50'N, 24'8'E). The locations of the Outokumpu Chrome Kemi Mine **Oy** (abbrev. C) and the Outokumpu Polarit Oy (abbrev. P) in the study area are shown in Fig. 1.

The Outokumpu Chrome Kemi Mine Oy 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, 8million tonnes of waste rock are removed from the open-cast pits. Air pollutants emitted from Outokumpu Chrome Kemi Mine Oy are derived from the various mining operations, such as crushing and enrichment plant, roads, piling stores, quarrying and random sources and emissions from a thermal power station $(5.6 \text{ t } SO_2, 1.9 \text{ t } NO_x (NO_2)$ and 0.9t particles in 1999), as well as from the activities of the subcontractors operating in the mine area. The total particle emissions into the air from Outokumpu Chrome Kemi Mine Oy during the period 1990–1999 are given in Table I. It is worth noting that in 1999 the particle emissions from the process (thermal power plant + enrichment plant + cruching) were $2.7t$, which is only 6.3% of the total particle emissions (42.7t) from the opencast chrome mine of Outokumpu Chrome Kemi Mine Oy. The main emission sources (40t in 1999) were from the quarry, roads and stores, which account for about 93.7% of the total particle emissions of Outokumpu Chrome Kemi Mine Oy. The annual SO_2 and NO_x emissions have been estimated to be rather similar for many years, but the 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 Metsa-Botnia Ab Kemi Mills and Stora Enso Oyj Veitsiluoto Mills, situated about 7 km away, but they emit no Cr or Zn ^[21].

FIGURE 1 The dispersion pattern of Cr and Ni (µg/g) in 2000. P, the ferrochrome and **stainless steel works** of **Outokumpu Polarit Oy at Tornio. C, the opencast chromium mining complex of Outokumpu Chrome Kemi Mine Oy at Kemi.**

Outokumpu Polarit Oy is a large ferrochrome and stainless steel works located about lOkm from Tornio, and about 25km from Outokumpu Chrome Kemi Mine Oy, on a peninsula on the coast of the Gulf of Bothnia close of the Swedish border. The works have produced 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 400000 tonnes of pellets, the transformer capacities of the smelting furnaces **40** and **70MVA,** and the total annual ferrochrome smelting capacity 250000 tonnes. The estimated total particle and heavy metal (Cr, Ni and Zn) emissions into the air from Outokumpu Polarit Oy during the period 1992-1999 are given in Table I. Chromium emissions are mainly released 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 factory staff. The total particle emissions, as well as the heavy metal emissions (Cr, Ni and Zn), vary from year to years, owing to fluctuations in the use of recycled material, variation of emissions related to process conditions and the timing of sampling, uneven distribution of particles in emissions etc. The works are by far the most important point sources of these heavy metals in Tornio and in northern Finland.

Sampling and total heavy metal analysis of mosses

Woodland moss *(Pleurozium schreberi)* samples were collected between *5* July to 14 July 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 (2g dry weight) were milled to pass through a 2mm sieve and digested with a mixture of concentrated nitric and perchloric acids (4 : **1).** After digestion the solutions were diluted with distilled water and the concentrations of Cr, Ni and Zn determined by **AAS** in the flame mode (Perkin Elmer **31 10).** 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 SFS **5671** standard **[231.** The coordinates of the sampling sites were determined in the field by GPS.

Statistical methods

The statistical calculations as well as the 3-D scatterplots were made by SPSS 10.00 for Windows, and the dispersion patterns by a computerbased geography information system.

RESULTS AND DISCUSSION

The main purpose of the present study was to identify large-scale geographical variations in heavy metal deposition derived from the opencast chromium mining complex of Outokumpu Chrome Kemi Mine Oy at Kemi, and the ferrochrome and stainless steel works of Outokumpu Polarit Oy at Tornio, by analysing moss samples. In the environmental permits approved by the competent authority of the Lapland Regional Environmental Centre, *Pleurozium schreberi* is accepted as a bioindicator for heavy metal (Cr, Ni, Zn) deposition emitted from Outokumpu Chrome Kemi Mine Oy and Outokumpu Polarit Oy because it is wide-spread in the study area. According to the environmental permits, the heavy metals Cr, Ni and Zn are to be analysed from mosses because they are the major metal pollutants emitted from these point sources. In the interpretation of the results, it has to be kept in mind that both point sources emit Cr, Ni and Zn, and that the deposition areas partly overlap, especially along the coastline between Tornio and Kemi. For this reason the dispersion pattern of the heavy metal concentrations are presented as contours or isopleths (Fig. 1) and as 3-D scatterplots (Fig. 3).

Descriptive statistics for the moss analyses in 1990, 1995 and 2000 are given in Table 11. Compared to the results of the earlier studies [17,18], the average concentrations (means) of Cr and Ni in the moss samples have increased. A similar trend has also taken place in the upper-quartiles (Upper-Q; 75%) and maximum (max) values. In 2000 the Cr concentration of mosses varied between $2.3-2700 \mu g/g$, and the highest Cr concentrations **(1** 30@-2700 pg/g) were found in the most polluted area in the vicinity of the ferrochrome and stainless steel works. In 2000 the average Cr concentration (mean) was 201 μ g/g and the average Ni concentration (mean) 13 μ g/g, while in 1990 and in 1995 they were $87 \mu g/g$ and $90 \mu g/g$ for Cr and $9.0 \mu g/g$ and 7.7μ g/g for Ni, respectively. The highest Ni concentrations were also found in the vicinity of the ferrochrome and stainless steel works and in the vicinity of the chromium opencast mining complex.

| | Mean | SD | Lower- $Q(25%)$ | $Upper - Q (75%)$ | Min. | Max. |
|------|------|-----|-----------------|-------------------|------|------|
| Cr | | | | | | |
| 1990 | 87 | 217 | 9.0 | 44 | 3.0 | 1100 |
| 1995 | 90 | 206 | 9.0 | 57 | 3.0 | 1000 |
| 2000 | 201 | 509 | 6.4 | 66 | 2.3 | 2700 |
| Ni | | | | | | |
| 1990 | 9.0 | 18 | 2.5 | 6.2 | 1.4 | 120 |
| 1995 | 7.7 | 14 | 2.3 | 5.4 | 1.5 | 73 |
| 2000 | 13 | 27 | 2.4 | 8.7 | 1.6 | 140 |
| Zn | | | | | | |
| 1990 | 64 | 46 | 39 | 68 | 29 | 230 |
| 1995 | 100 | 36 | 81 | 120 | 44 | 210 |
| 2000 | 49 | 12 | 41 | 58 | 28 | 78 |

TABLE I1 Descriptive statistics for **moss analysis (pg/g) in 1990, 1995 and 2000. Total number of samples each year** = **52**

Chromium emissions from the ferrochrome and stainless steel works decreased from 1900 to 1995, and the Cr concentrations in mosses in the study area simultaneously increased (Table I and **11).** From 1995 to 1999 Cr emissions from the ferrochrome and stainless steel works increased, and the Cr concentrations in mosses in the study area have correspondingly increased. On the other hand, Ni emissions from the ferrochrome and stainless steel works and the Ni concentrations in mosses have also increased since 1992. It is worth noting that, although Zn emissions from the ferrochrome and stainless steel works have increased continuously since 1995, the Zn concentrations in mosses have decreased radically (see Tables I and **11).**

The regional distribution patterns of Cr and Ni in mosses in the Kemi-Tornio area in 2000 are shown as contours or isopleths in Fig. 1 according to the Finnish SFS 5671 standard **[231.** The individual sampling points and heavy metal concentrations at these points are not shown. There is no distribution pattern at all for Zn, because Zn levels throughout the study area were too similar. This result corresponds to that reported in other studies using mosses as bioindicators for Cr, Ni and Zn, and is probably due to the fact that the retention of Cr and Ni from atmospheric deposition is almost total, while that of Zn is relatively low $[9-11]$. According to these studies, mosses have distinct sorption/retention rates for individual trace metals that are based on their physiological properties.

According to the data analysis and Figs. 1-3 the Cr and Ni concentrations in mosses generally decreased with increasing distance from the emission source. According to Fig. 1 the area most polluted $(Cr > 200 \mu g/g$ and $Ni > 20 \mu g/g$) by the ferrochrome and stainless steel works appears to lie within a few kilometres from the works. Within this area, the Cr

FIGURE 2 The heavy metal (Cr, Ni, Zn) concentration (μ g/g) in mosses at distances of 0.6-**44.5 km (on the same straight line) to the north of the ferrochrome and stainless steel works of Outokumpu Polarit Oy in 2000.**

concentrations in mosses were 4-13 times higher than those outside the urban area of Tornio. Slightly polluted areas $(Cr < 50 \mu g/g$ and $Ni < 9.9 \,\mu g/g$) were located farther away. In 2000, the highest individual Cr concentration (2700 μ g/g) was located at the distance of 1.9 km from the factory to the southeast. According to the results for 1990 and 1995 [17,18], the Cr concentrations at this sampling point were $1100 \mu g/g$ and $220 \mu g/g$, respectively. The area most polluted by the opencast chromium mining complex $(Cr > 200 \mu g/g$ and $Ni < 20 \mu g/g$) appears to be in the immediate vicinity of the complex. The slightly polluted area $(5.0 \,\mu g/g \le$ $Ni < 9.9 \,\mu g/g$) occurred within a radius of 2–6 km around the mining

FIGURE 3 The 3-D scatterplots for Cr, Ni and Zn in 2000.

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distance from works (km)

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distance from mine (km)

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complex. One explanation for the small anomaly to the south of the mining complex in Fig. 1 might be Ni emissions from local oil-burning sources.

The heavy metal concentrations in mosses are depicted as a function of distance $(0.6-44.5 \text{ km})$ on the same straight line) to the north from the ferrochrome and stainless steel works of Outokumpu Polarit Oy in Fig. 2. As all these sampling sites are located at distances of 25–47 km from Outokumpu Chrome Kemi Mine Oy, it is not likely that the emissions from the mine area extend this far. According to the results, the deposition and accumulation of Cr and Ni in the mosses clearly decreased with increasing distance from the factory. Thus, our results correspond to those of an other study carried out in the same area by other researchers $[24]$. Figure 2 also shows an interesting feature associated with the deposition and accumulation of Zn in mosses. According to Fig. 2 the Zn concentrations in mosses did not decrease as the distance from the pollution source (works) increased. This phenomenon was similar throughout the study are and there is therefore no distribution pattern at all for Zn. According to Ruhling & Tyler [9,25], 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.

The 3-D scatterplots in Fig. 3 well illustrate that, although the heavy metal deposition emitted from both the ferrochrome and stainless steel works of Outokumpu Polarit Oy and the opencast chromium mining complex of Outokumpu Chrome Kemi Mine Oy overlap in many places in the study area, the main deposition areas are close to the works and the mine. The four highest individual Cr concentrations $(2700 \,\mu\text{g/g}, 1700 \,\mu\text{g/g})$ $1400 \,\mu g/g$ and $1300 \,\mu g/g$ respectively) were located at sampling sites within a distance of 0.6–1.9 km from the Outokumpu Polarit Oy, and within a distance of 21-25 km from the mine at Kemi. The Cr concentrations at these sampling sites were 6.5-13.4 times higher than the mean Cr concentration $(201 \mu g/g)$ in 2000. At these sampling sites, it is quite clear that most of the Cr deposition in this area is emitted from the ferrochrome and stainless steel works of Outokumpu Polarit Oy. The 5th highest individual Cr concentration $(1000 \mu g/g, 4.9$ times higher than the mean Cr concentration in 2000) occurred at sampling sites at a distance of 2.1 km from the mine district and 23 km from Outokumpu Polarit Oy. It is therefore rather clear that most of the Cr deposition in this area is emitted from the opencast chromium mine of Outokumpu Chrome Kemi Mine Oy.

According to the 3-D scatterplot (Fig. 3), the main deposition areas for Ni can also be estimated. The six highest individual Ni concentrations $(140 \,\mu g/g, 98 \,\mu g/g, 93 \,\mu g/g, 69 \,\mu g/g, 39 \,\mu g/g$ and $25 \,\mu g/g$ respectively) were located at sampling sites within a distance of 0.6-3.5km from the

| | Cr | Ni | Zn |
|-------------|-----------|-----------|----------|
| $_{\rm Cr}$ | 1.000 | $0.728**$ | 0.144 |
| Ni | $0.728**$ | 1.000 | $0.199*$ |
| Zn | 0.144 | $0.199*$ | 1.000 |

TABLE 111 The Kendall's coeficients for the correlation between Cr, Ni and Zn in the mosses in 2000.

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

"'correlation is significant at 0.01 level (2-tailed).

Outokumpu Polarit Oy, and within a distance of 21-25 km from the mine at Kemi. This clearly demonstrates that most of the Ni deposition in this area is derived from the chromium and stainless steel works. The Ni deposition inside this area was 1.9-10.7 times higher than the mean Ni concentration (13 μ g/g) in 2000. The 7th highest individual Ni concentration (19 μ g/g; 1.5 times higher than mean Ni concentration in 2000) was located at sampling sites a distance of 2.1 km from the mine and at a distance of 19 km from Outokumpu Polarit Oy. It is therefore evident that most of the Ni deposition in this area is emitted from the opencast chromium mine of Outokumpu Chrome Kemi Mine Oy.

According to the 3-D scatterplot (Fig. 3), the highest individual Zn concentration (78 μ g/g) occurred at the sampling sites at a distance of 12.3 km from the mine and at a distance of 26 km from the ferrochrome and stainless steel works. The second highest Zn concentration $(75 \mu g/g)$ was located at a distances of 3.9 km and 19.5 km from the mine and the ferrochrome and stainless steel works, respectively. The 3rd highest Zn concentration $(72 \mu g/g)$ occurred at two sampling sites. The first was located at a distance of 4.3 km from the mine and at a distance of 23.8 km from the works, and the other at a distance of 15.6 km and 7.9 km from the mine and the works, respectively. The 3-D scatterplot results for Zn in Fig. 3 support the results depicted in Fig. 2, i.e. that Zn concentrations in mosses did not necessarily decrease with increasing distance from the pollution source. Finally, it should be noted, that the highest Cr and Ni concentrations in mosses occurred close to the pollution sources $(0.6-1.9 \text{ km} \text{ and } 0.6-3.5 \text{ km} \text{, respectively})$ tively), but not for Zn, because the highest Zn concentration $(78 \mu g/g)$ occurred at a distance of 12.3km from the nearest pollution source (Outokumpu Chrome Kemi Mine Oy).

The Kendall correlations between the elemental contents in mosses (see Table III) indicate that Cr and Ni are highly correlated ($R=0.728$). This result indicates that these two elements originated from the same emission sources in the study area [26]. Although the correlation between Zn and Cr and Ni was not very high $(R=0.144$ and $R=0.199$, respectively), it is clear that the Zn deposition in the mosses is primarily emitted from the ferrochrome and stainless steel works of Outokumpu Polarit Oy and from the opencast chrome mine of Outokumpu Chrome Kemi Mine Oy; the nearest point sources that emit significant amounts of Cr, Ni and Zn are located over 150 km away.

CONCLUSIONS

According to the heavy metal concentrations in the moss samples, the influence of opencast chromium mining by Outokumpu Chrome Kemi Mine Oy and the ferrochrome and stainless steel works of Outokumpu Polarit Oy is clearly visible in the Kemi-Tornio area. Relatively high concentrations of Cr especially, as well as some elevated Ni values, are still to be found at Tornio and along the northern coast of the Bay of Bothnia in northern Finland. The average Cr concentration (mean) in 2000 for all the moss samples was 2.2 times higher than the corresponding value in 1990 and in 1995. The average Ni concentration (mean) in 2000 for all the moss samples was **1.4** and 1.7 times higher than the corresponding value in 1990 and in 1995, respectively. For Zn the average concentration (mean) in 2000 was 0.7 and 0.5 times the corresponding values in 1990 and in 1995.

According to the results, it can be concluded that the average Ni concentration (mean) in mosses has increased since 1990, because Ni emissions from the ferrochrome and stainless steel works of Outokumpu Polarit Oy have also increased at the same time. The Zn emissions from Outokumpu Polarit Oy 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. This result may be partly due the fact that the retention of Zn from atmospheric deposition by mosses is relatively low $[9-11]$. Although many studies $[11-18]$ have shown that woodland moss (Pleurozium *schreberi)* is a useful bioindicator plant for monitoring the deposition of heavy metals like Cr and Ni and can complement the information provided by plant mapping studies, according to our results we are convinced that there are still some factors that cannot be take into account before sampling, and these factors have an influence on heavy metal deposition on mosses. In our study such factors include weather parameters such as precipitation, humidity and wind conditions, which have an influence on the spreading pattern of pollution from point sources and on the deposition of heavy metals on mosses. Operating malfunctions at the ferrochrome and stainless steel works of Outokumpu Polarit Oy, and variations in the use of recycled material, vary from year to year. The uncontrolled spread of dust after blasting at the mine has an effect on emissions and on the deposition of heavy metals on mosses. In addition, although SO_2 and NO_x emissions from the opencast chrome mine of Outokumpu Chrome Kemi Mine Oy have remained relatively constant over the years, particle emissions from the quarry, roads and stores vary. These uncontrollable factors could perhaps explain why the average Cr concentrations (means) in mosses have increased since 1990 eventhough the Cr emissions from point sources have decreased.

Finally, the present study shows, that long-term monitoring studies on contaminants based on moss sampling is a useful tool for clarify the aerial distribution of heavy metals from both the chromium opencast mine and the ferrochrome and stainless steel works. Only long time series can indicate the size of random, between year variation.

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