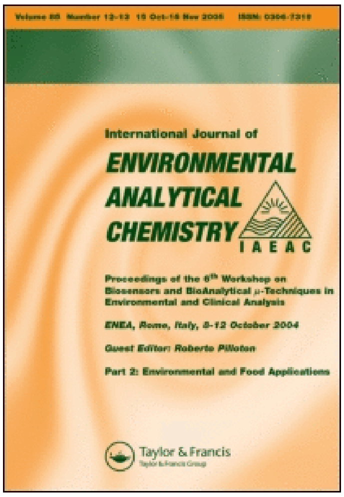

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The use of Scots pine (*Pinus sylvestris* L.) bark as a bioindicator for environmental pollution monitoring along two industrial gradients in the Kemi–Tornio area, northern Finland

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This paper describes the use of Scots pine (*Pinus sylvestris* L.) bark as a passive boindicator for environmental pollution monitoring in the immediate vicinity of the ferrochrome and stainless steel works of Outokumpu Stainless Oy at Tornio and of the opencast chromium mine of Outokumpu Chrome Oy Kemi Mine at Kemi, Northern Finland. According to the pollution factors (PF; i.e. the ratio of heavy metal concentrations in the bioindicators to those in the background area), the average Cr, Fe and Ni concentrations in bark samples around the works were 81, 7 and 5.9 times higher, respectively, compared with the levels in the background area. In the areas subjected to emissions from the mine, the PF values for Cr, Fe and Ni were 5.3, 12.4 and 3.0, respectively. In the vicinity of the works, the PF values followed the order Cr > Mo > Ni > Fe > Ti > Zn, but in the vicinity of the mine, the order Cr > Ti > Fe > Ni > Zn > Mo. In addition, two different microwave-assisted digestion procedures, i.e. a mixture of $HNO_3 + H_2O_2$, and a mixture of $HNO_3 + HCl + HF$, were compared for digestion of heavy metals (Ti, Cr, Fe, Ni, Zn and Mo) in Scots pine (*Pinus sylvestris* L.) bark samples. According to the results, the digestion procedures with a mixture of $HNO_3 + H_2O_2$, which is commonly used in bioindicator studies, underestimated heavy-metal concentrations in the bark samples. For the bark samples collected in the immediate vicinity of the point sources, which emit chromium in the chemical forms of $(Fe,Mg)(Cr,Al)_2O_4$ and $FeO\text{-}Cr_2O_4$, the digestion procedure with a mixture of $HNO_3 + HCl + HF$ gave 65%, 101% and 29% higher values for Ti, Cr and for Fe, respectively, than the digestion procedure with a mixture of $HNO_3 + H_2O_2$.

Keywords: Bark; Pollution factor; Ferrochrome and stainless steel works; Opencast chromium mine

1. Introduction

Heavy metals such as Cr, Ni, Zn, Fe and Cd are typically released into the ambient air from ferrochrome and stainless steel works. The heavy metals are mainly emitted in the

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form of particulate material, and the distance that they are transported is, in general, relatively short compared with that of gaseous pollutants; the transport distance of particles 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. Mining operations in general have an adverse impact on the environment. A substantial amount of particulate matter is generated and spread over wide areas during the individual mining operations, such as blasting, digging, crushing, screening, storing the intermediate and final products, packing, loading, unloading and the movement of vehicles along dusty roads. Air pollutants from both local and distant sources impact the environment in the form of dry and wet deposition [1].

Biomonitoring, i.e. monitoring the state of the environment through the condition 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 authorities can foresee and prevent threats and risks before they become a problem. Bioindicators directly depict the impacts of environmental pollution on organisms, and can potentially quantify 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 [2].

The bark accumulates airborne particulate matter derived from wet and dry deposition, and has thus been employed as a passive biomonitor of environmental contamination. Dry and wet depositions are intercepted and concentrated by the tree-bark crown, because of its large surface. The concentration profile of heavy metals in the bark decreases strongly from the bark to the wood core. Schulz *et al.* [3] reported that a significant concentration gradient of heavy metals has been found between bark at depths of 0.5 and 1.5 mm, with relatively low concentrations in deeper bark layers. According to Schulz *et al.* [3], this indicates that sampling the outer 2 mm of the bark layer will be sufficient to determine pollutants derived directly from the atmosphere. However, it is difficult to cut off bark samples of constant thickness. As a result, the bark samples suitable for chemical analysis have to be selected by hand. Bark flakes with a thickness greater than 2 mm, as well as barks samples overgrown with algae and lichen, must be avoided [3,4]. However, some studies have reported that, if present, epiphytic organisms (i.e. algae, lichens and mosses) can be removed with a synthetic hard brush [5,6]. For more comprehensive reviews of the element profiles in a piece of bark performed with a Laser ICP-MS, and of a survey of the heavy metal accumulation process in pine bark, see [3] and [7], respectively.

Tree bark has been used as a passive bioindicator for heavy metals in many environmental studies in the vicinity of metal smelters [4], iron and steel works [5], a cement plant [8], chemical and fertilizer plant [9], waste incinerator plant [10] and limestone quarry and plant [11]. Tree bark has also been used as an indicator for metal pollution emitted by traffic [12], as well as in the determination of isotope ratios, such as ^{206}Pb/^{207}Pb and ^{235}U/^{238}U emitted from a nuclear fuel fabrication plant [13,14]. In Finland, the Finnish Forest Research Institute has used Scots pine bark samples in the nationwide monitoring of atmospheric heavy-metal deposition [15]. In this context, it is worth noting that the Finnish Ministry of the Environment has accepted the use of tree bark as a bioindicator for biomonitoring metals accumulation [2].

1.1 *Background and aims of the study*

The main purpose of this study was to obtain information about heavy metal (Ti, Cr, Fe, Ni, Zn and Mo) concentrations in Scots pine bark (*Pinus sylvestris* L.) subjected to atmospheric pollution from the ferrochrome and stainless steel works of Outokumpu Stainless Oy at Tornio (former name AvestaPolarit Stainless Steel Works Oy) and from the chromium opencast mine of Outokumpu Chrome Oy Kemi Mine at Kemi (former name AvestaPolarit Chrome Oy Kemi Mine), northern Finland. In addition, the dissolution and decomposition efficiency of two different acid procedures, i.e. a mixture of $HNO_2 + H_2O_2$ and the mixture of $HNO_3 + HCl + HF$, to release elements in bark samples was also compared. The former mixture is commonly used in bioindicator studies, and the latter mixture is the USEPA procedure developed especially for the digestion of siliceous and other complex matrices [16].

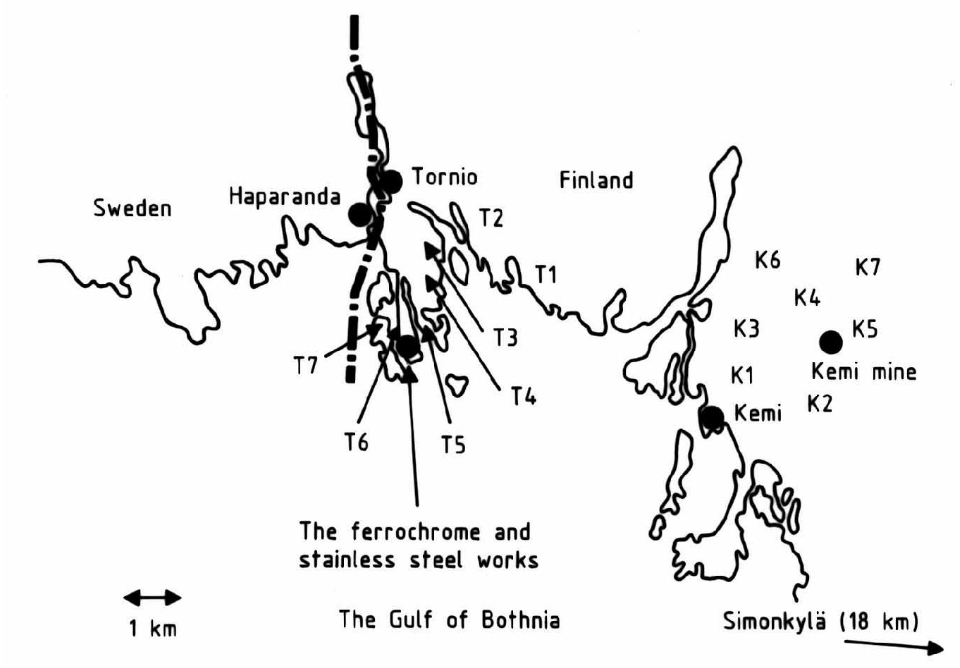
The heavy metals Cr, Ni, Zn, Ti and Mo were selected for analysis because, according to the European Community list ('a grey list' of dangerous substances), they are the elements considered to be of major priority concern [17]. These metals also occur in the major particles in airborne emissions from the ferrochrome and stainless steel works of Outokumpu Stainless Steel Oy and from the chromium opencast mine of Outokumpu Chrome Oy Kemi Mine [18]. The raw materials (i.e. ore and recycled materials) used in the ferrochrome and steel works also contain these elements [18]. It is therefore highly likely that these elements are spread into the environment together with the emissions. In this context, it is worth noting that, in the environmental permits approved by the competent authority of the Lapland Regional Environmental Centre, the heavy metals Cr, Ni and Zn are to be analysed from bioindicators in the study area because they are the major metal pollutants emitted from these point sources [19]. A more comprehensive review of the atmospheric heavy metal deposition in Finland during 1985–2000 is given in [20].

This study is a part of a major project focusing on the effects of industrial activities (i.e. pulp and paper mills, mine and stainless steel works) on the environment in the Kemi–Tornio region in northern Finland. Our previous studies have dealt with the use of bioindicators (pine needles) for determining the distribution pattern of aerial emissions emitted from pulp and paper mills in the same area [18,21]. In addition, earlier research has also focused on the ambient-air-quality measurements made in the opencast chromium mine area of Outokumpu Chrome Oy Kemi Mine [19], which is the largest chrome mine in Europe, as well as bioavailability (leaching) studies on the elements (Cr, Ni, Cu, Fe, Cd) present in airborne particles [22], and the sampling problems associated with the collection of particulate material using a high-volume sampler [23].

2. Experimental

2.1 *Study area and pollution sources*

The study was carried out in the vicinity of the town of Kemi (65° 44′ N, 24° 35′ E) and the town of Tornio (65° 50′ N, 24° 8′ E) on the Gulf of Bothnia, northern Finland. In 2003, Kemi and Tornio had populations of about 24 500 and 22 700, respectively. There are two major heavy-metal pollutant sources in the area: Outokumpu Chrome Oy Kemi Mine at Kemi, and Outokumpu Stainless Steel Works Oy at Tornio. The study area and the locations of the mine complex and works are shown in figure 1.



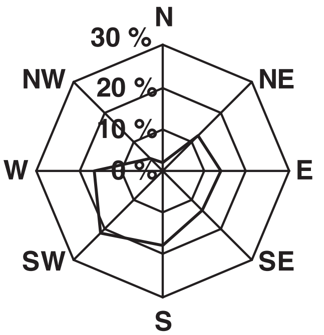


Figure 1. Sampling sites and the windrose in the Kemi–Tornio region on the Gulf of Bothnia, northern Finland. Background samples were collected at Simonkylä.

The Outokumpu Chrome Oy Kemi Mine is the largest chromium ore deposit in Europe and is 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. Metallic, black oxide mineral of chromite and iron ($(Fe,Mg)(Cr,Al)_2O_4$) is the main economically important chromite mineral produced at the mine. Outokumpu Stainless Steel Oy is a large ferrochrome and stainless steel works located about 10 km from Tornio, and about 25 km from the opencast mine, on a peninsula on the coast of the Gulf of Bothnia close to 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 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. The major emissions into the air are particles (229 t/year). Emissions of particles associated with the studied metals are estimated to be 15.2 t/year for Cr, 5.3 t/year for Ni and 11.9 t/year for Zn.

A detailed description of the flow charts of the production chain in the chromium opencast mine and the ferrochrome and stainless steel works is presented in Huvinen *et al.* [24], and of the study area in Pöykiö and Perämäki [18], and of the emissions from the Outokumpu Stainless Oy and Outokumpu Chrome Oy in Pöykiö *et al.* [19, 23].

2.2 *Sampling and sample pretreatment*

Scots pine bark (*Pinus sylvestris* L.) samples K1–K7 were collected on 11 October, and samples T1–T7 on 12 October 2003. The coordinates of the sampling sites were determined in the field by GPS (Garmin GPS 12). Sampling sites K1–K7 are located at Kemi (65° 44′ N, 24° 35′ E) and, according to the earlier moss survey [25], this area is the main deposition area of aerial emission (particulates) from the mining complex of the Outokumpu Chrome Oy Kemi Mine. Correspondingly, sampling sites T1–T7 are located at Tornio (65° 50′ N, 24° 8′ E), inside the main deposition area of atmospheric particulates from the ferrochrome and stainless steel works of the Outokumpu Stainless Steel Oy. Two background samples were also collected on 12 October at Simonkylä (65° 35′ N, 25° 5′ E), about 18 km from the mining area, and about 37 km from the works. The location of the sampling sites, and well as the location of the chromium opencast mine of Outokumpu Chrome Oy Kemi Mine and the ferrochrome and stainless steel works of Outokumpu Stainless Steel Oy in the Kemi–Tornio region are presented in figure 1.

Bark samples were taken with a steel knife from the loose, outermost layer (2 mm) of bark in the lichen-free part of the trunk. To avoid contamination, the steel knife was coated with self-adhesive plastic film, and disposable plastic gloves were worn by the collectors. Bark was sampled from all sides of the tree at a height of 1.5 m above the ground on six trees per sampling site [1]. Approximately the same amount of bark (0.2 L) was taken from each tree. Each tree was sampled twice (i.e. thin chips were cut off on all sides of the tree trunk; this procedure was repeated twice on the same sampling occasion). Sampling near roads and villages was avoided. The sample trees were selected in places where no obstacles (e.g. topography, other trees) prevented the free flow of air pollutants from the direction of the emission sources (i.e. from the stainless and steel works and from the mining complex). The forest in the region is typical of the boreal coniferous forest zone.

After sampling, the samples were stored in polyethylene bags in a refrigerator (+ 4° C) before pretreatment and analysis. The bark samples were dried for 18 h at a temperature of 105° C [12]. The bark was crushed and ground to a uniform particle size in a laboratory mill (IKA A 10) equipped with tungsten carbide blades. The mill was thoroughly cleaned and dried after each sample to avoid contamination.

2.3 *Instrumentation*

A sequential Pye Unicam 7000 inductively coupled-plasma optical emission spectrometer (ICP-OES; Unicam Analytical Systems, Cambridge, UK) was used for Fe determination at a wavelength of 259.94 nm. Other instrumental parameters for ICP-OES were: RF power, 1.3 kW; nebulizer gas pressure, 276 kPa; cooling gas flow, 15 L/min; sample uptake rate, 1.0 mL/min.

A Thermo Elemental X7 inductively coupled plasma mass spectrometer (ICP-MS; Thermo Elemental, Winsford, UK) was used for Cr, Ni, Zn, Ti and Mo determination. The instrumental parameters for ICP-MS were: RF power, 1.3 kW; nebulizer gas flow, 0.98 L/min; auxiliary gas flow, 0.85 L/min; cooling gas flow, 13.5 L/min. The analytical parameters of ICP-MS were: acquisition mode, peak jumping, simultaneous pulse count/analogue detector system; dwell time/isotope, 10 ms (^{52}Cr, ^{60}Ni, ^{66}Zn, ^{47}Ti and ^{95}Mo); number of repeats/sample, 3; points per peak, 1.

All the dissolutions were performed with a CEM Mars 5X (CEM Corp., Matthews, USA) microprocessor-controlled microwave oven using 12 closed CEM XP-1500 Teflon TFM vessels (CEM Corp) at a time. The microwave oven was equipped with temperature- and pressure-monitoring capabilities.

2.4 *Reagents, standards and the reference material*

The following reagents were used: 65% HNO_3 (suprapur, Merck, Darmstadt, Germany), 30% HCl (suprapur; Merck), 40% HF (suprapur; Merck), H_3BO_3 (p.a., Merck), AccuStandard INC ICP-MS tuning solution (Accutrace, Accustandard Inc., New Haven, USA) and argon gas (Messer, Krefeld, Germany). The water was made ultrapure by a Millipore Mill-Q Gradient (Millipore Corp., Billerica, USA) water-purification apparatus. The method's performance evaluation and optimization were obtained using a commercial reference material NIST SRM 1573a (Tomato Leaves). Commercial reference solutions of 1000 mg/L for Ti, Cr, Fe, Ni, Zn and Mo (Titrisol, Merck) were used for instrument calibrations.

2.5 *Digestion procedures*

To clarify whether the complete recovery of the elements in bark requires the use of HF, or whether the commonly used acid mixture of $HNO_3 + H_2O_2$ is sufficient, two digestion procedures were first compared using a certified reference material NIST SRM 1573a (Tomato Leaves), and a test sample 'Test 1', which was a combination of eight sub-samples (i.e. four sub-samples from around the ferrochrome and stainless steel works and four sub-samples from around the chromium opencast mine).

Sample digestion with a mixture of HNO_3 and H_2O_2 is commonly used in bioindicator studies [8,18,26]. However, in our laboratory, we regularly use 5 mL of HNO_3 and 3 mL of H_2O_2. The original procedure with this mixture was developed with a microwave oven having no temperature feedback control [18,26]. In this study, this procedure is assigned as an 'A'.

The digestion procedure B (9 mL conc. $HNO_3 + 2$ mL conc. $HCl + 0.1$ mL conc. HF) is based on the procedure of the US EPA 3052 standard for siliceous and organically based matrices [16]. In both procedures, 500 mg of sample was weighed in the microwave digestion vessel. Reagents were added, the vessels were closed, and 12 samples were heated at the same time in the microwave oven using optimized microwave programmes. The microwave programmes used were: procedure A (Stage 1:5 min at 126 W; Stage 2:12 min at 630 W) and procedure B (ramping at 5.5 min to 180° C and holding at 180° C for 9.5 min).

3. Results and discussion

3.1 *Comparison of digestion procedures*

The results of the two digestion procedures for certified reference material NIST SRM 1573a (Tomato Leaves), and for test sample 'Test 1' are shown in table 1. Because the real samples (e.g. bark samples) will differ in composition from that of the certified reference materials, the use of test sample 'Test 1' for comparison of the digestion procedures was considered reasonable.

The temperature and pressure profiles for digestion procedures A (5 mL conc. $HNO_3 + 3$ mL H_2O_2) and B (9 mL conc. $HNO_3 + 2$ mL conc. $HCl + 0.1$ mL conc. HF) are given in figure 2(A,B). It is worth noting that, in procedure A, the temperature rose to 177° C only at the end of the stage 2, while in procedure B, the temperature remained at 180° C for 9.5 min. Thus, the differences in the digestion temperatures/pressures provide one explanation for the lower recoveries obtained for some metals using procedure A.

According to the results in table 1, the digestion procedure with a mixture $HNO_3 + H_2O_2$ gave lower values for Ti, Cr, Fe and for Ni in reference material

Table 1. Means ($n = 4$) and standard deviations (±) of Ti, Cr, Fe, Ni, Zn and Mo determinations in reference sample NIST SRM 1573a (Tomato Leaves) and in the bark test sample 'Test 1' using two different digestion procedures (procedure A: 5 mL conc. $HNO_3 + 3$ mL H_2O_2 and procedure B : 9 mL conc. $HNO_3 + 2$ mL conc. $HCl + 0.1$ mL conc. HF; reaction profiles, see figure 2).[a]

Metal	Procedure	NIST SRM 1573a (mg/kg)	Recovery (%)	Test 1 (mg/kg)
Ti	Certified value	n.c.	–	n.c.
	$HNO_3 + H_2O_2$	10.6 ± 0.3[b]	–	35.8 ± 1.2[b]
	$HNO_3 + HCl + HF$	33.5 ± 2.1[b]	–	59.1 ± 1.4[b]
Cr	Certified value	1.99 ± 0.06	–	n.c.
	$HNO_3 + H_2O_2$	1.57 ± 0.03[b]	78.9	112 ± 8[b]
	$HNO_3 + HCl + HF$	1.78 ± 0.08[b]	89.4	225 ± 36[b]
Fe	Certified value	368 ± 7	–	n.c.
	$HNO_3 + H_2O_2$	303 ± 5[c]	82.3	888 ± 44[b]
	$HNO_3 + HCl + HF$	336 ± 17[c]	91.3	1148 ± 64[b]
Ni	Certified value	1.59 ± 0.07	–	n.c.
	$HNO_3 + H_2O_2$	1.66 ± 0.04[b]	104	26.7 ± 1.5[b]
	$HNO_3 + HCl + HF$	1.84 ± 0.06[c]	116	40.9 ± 1.6[b]
Zn	Certified value	30.9 ± 0.7	–	n.c.
	$HNO_3 + H_2O_2$	24.1 ± 0.4	78	54.5 ± 4.1
	$HNO_3 + HCl + HF$	22.9 ± 0.7	74.1	61.9 ± 4.7
Mo	Certified value	0.46	–	n.c.
	$HNO_3 + H_2O_2$	0.39 ± 0.01	84.8	5.95 ± 0.52[b]
	$HNO_3 + HCl + HF$	0.40 ± 0.01	86.9	7.35 ± 0.31[b]

[a] Results expressed on a dry-weight basis. n.c.: not certified; results in parentheses are non-certified values. [b] Results between digestion methods differ significantly according to the *t*-test ($p < 0.01$). [c] Results between digestion methods differ significantly according to the *t*-test ($p < 0.05$)[b].

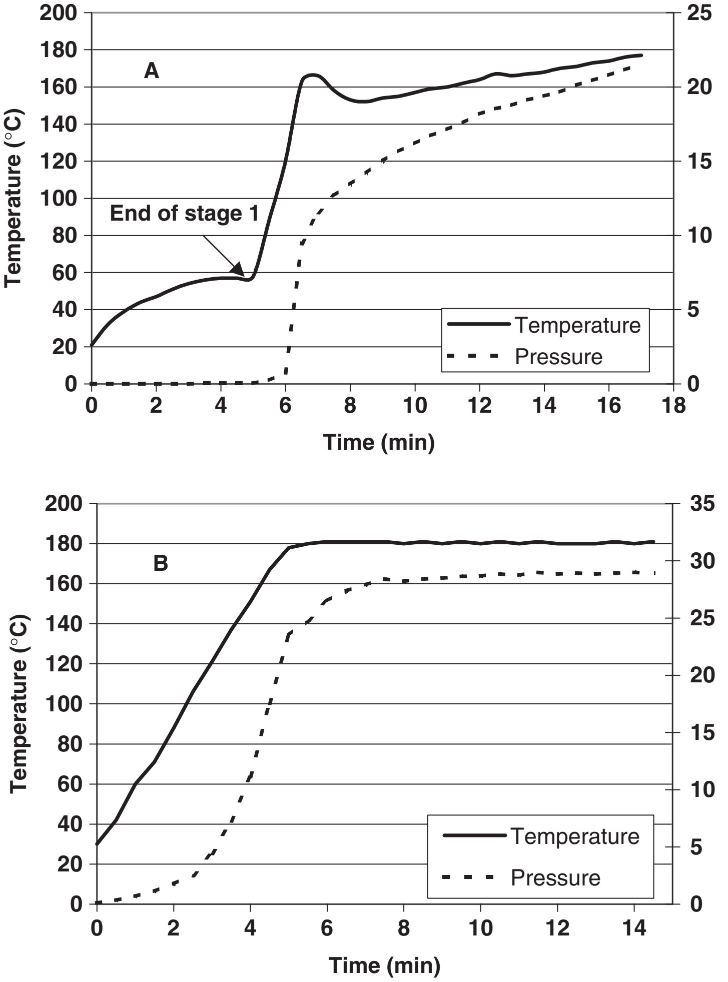


Figure 2. Microwave-assisted digestion reaction profiles for the A (5 mL conc. $HNO_3 + 3\,mL\,H_2O_2$) and B (9 mL conc. $HNO_3 + 2\,mL$ conc. $HCl + 0.1\,mL$ conc. HF) procedures.

NIST SRM 1573a (Tomato Leaves) than the procedure with a mixture of $HNO_3 + HCl + HF$. The low recoveries for Cr (78.9%) and Fe (82.3%) in reference material obtained with the mixture of $HNO_3 + H_2O_2$ is worth noting. This is probably due to the fact that this mixture, which is widely used in bioindicator studies especially, does not ensure complete dissolution of chromium from the sample matrix. Furthermore, according to the dissolution studies of plant material (i.e. NIST SRM 1547 Peach Leaves), carried out by Rodushkin *et al.* [27], incomplete analyte recoveries for heavy metals, and especially for Cr and Fe, may also be due to the presence of siliceous material in the matrix. Both Cr and Fe bind with the silicates in plant material, and it is therefore difficult to achieve full recovery from plant material.

The better recovery of heavy metals such as Ti, Cr, Fe and Ni in reference material with a mixture of $HNO_3 + HCl + HF$ than with a mixture of $HNO_3 + H_2O_2$ is most probably due to the complete decomposition and dissolution of the solid matrix by HF and HCl. There was no certified or even indicative value of Ti for reference material NIST SRM 1573a (Tomato Leaves) but, according to the results in table 1, the mixture of $HNO_3 + HCl + HF$ gave 216% higher value for Ti than the mixture of $HNO_3 + H_2O_2$. The Ti value for test sample 'Test 1' was correspondingly 65% higher. This is probably due to the low solubility of titanium compounds.

Although the actual heavy-metal concentrations in test bark sample 'Test 1' were not known, the data in table 1 provide information about the efficiency of the mixtures of $HNO_3 + H_2O_2$ and of $HNO_3 + HCl + HF$ to decompose and release heavy metals during microwave-oven digestion. In the determination of Ti, Cr, Fe, Ni, Zn and Mo, the mixture of $HNO_3 + HCl + HF$ gave 65%, 101%, 29%, 53%, 14% and 24% higher values, respectively, than the mixture of $HNO_3 + H_2O_2$. The lower recovery of Cr in test sample 'Test 1' with a mixture of $HNO_3 + H_2O_2$ is probably partly due to difficulties in dissolving the chromium in the sample matrix, since the dust emitted from the ferrochome and stainless steel works and from the chromium opencast mine contains $FeO\text{-}Cr_2O_3$ and $(Fe,Mg)(Cr,Al)_2O_4)$, respectively, which are difficult to solubilize without the use of HF. From the environmental point of view, this means that the bioavailability of Fe and Cr is low when these elements are associated with the above-mentioned minerals. Thus, our results agree with the findings of Huhn *et al.* [7] that oxides of these elements are generally difficult to dissolve.

The precision (repeatability) for the determination of different elements in NIST SRM 1573a (Tomato Leaves) employing the microwave-oven digestion was relatively satisfactory. After quadruple determinations, the RSD (%) values ranged between 1.7 and 6.3%. However, the determinations of Cr and Ni in test sample 'Test 1', had RSD values of 7.0–15% and 3.8–5.6%, respectively. These RSD (%) values were higher than the corresponding values of 1.7–4.3% for Cr and 2.6–3.4% for Ni determination in reference samples NIST SRM 1573a (Tomato Leaves). The lower precision (repeatability) for the determination of Cr and Ni in test sample 'Test 1' is probably due to the non-homogeneity of test sample 'Test 1', since it was a combination of sub-samples.

3.2 *Bark as bioindicator for heavy-metal deposition*

The concentrations of heavy metals (Ti, Cr, Fe, Ni, Zn and Mo) in bark samples, expressed on a dry weight (abbr. dw) basis, after microwave-assisted decomposition with digestion procedure B (9 mL conc. HNO_3 + 2 mL conc. HCl + 0.1 mL conc. HF; reaction profile see figure 2B) are presented in table 2. This mixture was chosen because the mixture of $HNO_3 + H_2O_2$ (i.e. procedure A) underestimated the heavy-metal concentrations in test bark sample 'Test 1'.

We have used the pollution factor (PF) as an overall indicator of anthropogenic inputs to the heavy metal budget of the biocollector samples. According to Cinar and Elik [28], the PF is determined as the ratio of heavy-metal concentrations in a contaminated area to those in unpolluted (background) areas. In some cases, the word 'pollution factor (PF)' has been replaced by another term such as 'bioindication index (BI)' [3]. However, the meaning and definition of PF and BI are the same.

At sampling site K5, which was located 1.6 km from the opencast chromium mine, the PF value for Cr was 28. The PF values at the other sampling sites around the chromium mine (sites K1–K4, K6, K7) were 6.5–12.5. This indicates that the opencast

Table 2. Mean and heavy metal (Ti, Cr, Fe, Ni, Zn and Mo) concentrations (dry weight; $n=1$) in bark using digestion procedure B (9 mL conc. HNO_3 + 2 mL conc. HCl + 0.1 mL conc. HF; reaction profile, see figure 2B) for samples collected at sampling sites K1–K7 around a chromium mine, and at sampling sites T1–T2 around the stainless steel works.

Site	Distance from the mine (km)	Distance from the works (km)	Ti (mg/kg)	Cr (mg/kg)	Fe (mg/kg)	Ni (mg/kg)	Zn (mg/kg)	Mo (mg/kg)
K1	2.7	20.1	14.1	27.8	269	5.2	63.0	0.2
K2	1.2	22.3	16.2	49.2	370	6.8	61.7	0.3
K3	2.8	30.1	93.2	42.7	1312	6.5	20.4	0.3
K4	2.6	21.7	26.5	36.5	396	4.3	18.3	0.2
K5	1.6	22.8	35.7	124	760	14.1	19.7	0.3
K6	2.9	22.3	127	53.9	1781	6.3	18.8	0.2
K7	4.1	24.4	29.0	38.6	494	5.4	25.8	0.2
T1	18.1	7.9	105	197	1150	17.4	43.9	3.8
T2	21.2	7.4	36.1	309	634	24.4	42.4	4.9
T3	22.7	5	86.3	717	2116	148	186	28.2
T4	22.5	2.7	61.0	314	798	34.8	39.3	10.6
T5	22.2	1.7	104	806	1614	52.4	52.5	10.8
T6	23.5	1.2	22.9	40.9	281	5.9	27.2	0.8
T7	24.8	1.7	41.8	57.5	497	6.3	29.3	0.8
Mean	–	–	57.1	201	891	24.1	46.3	4.4
Background	17.7	37.3	11.1	4.3	146	2.3	17.4	0.3

chromium mine has an adverse impact on the environment. The 'dust' (i.e. airborne particles) from the mining complex derived from individual mining operations, such as blasting, digging, crushing, screening, storing of intermediate and final products, loading, unloading and movement of vehicles along dusty roads, when a substantial amount of particulate matter was generated and spread over a wide areas.

The pollution factors indicate a high input of heavy metals, especially in the vicinity of the ferrochrome and stainless steel works of Outokumpu Stainless Steel Oy (sites T1–T7). The enrichment of Cr, with PF values of 9.5–187, was especially significant. According to the results in table 2, the highest Cr concentrations in bark samples occurred in the immediate vicinity (1.7 km) of the works at sampling site T5 (806 µg/kg; dw). Although sampling site T6 was the nearest to the works (1.2 km), the heavy-metal concentrations at this sampling site were not the highest for any of the elements. This is probably due to the dominant wind direction, which in the study area is from the southwest (see figure 1), and probably partly due to the height of the stacks, which means that areas immediately downwind of, and nearest to, the source are less affected by atmospheric (particle) pollution [17]. Thus, elevated concentrations in the bark samples do not necessarily occur near to the stack, but instead are downwind at a greater distance from the source.

According to the results in table 2, the Mo concentrations in bark samples at sampling sites T1–T5 (PF factors of 2.7–94), which are subjected to emission from the works, were clearly higher than those at the other sampling sites. The elevated Mo concentrations in bark in the vicinity of the works are probably partly due to the use of recycled materials, since stainless steel can have a molybdenum content of 2.0–2.5%. In contrast, the Mo concentrations of 0.2–0.3 mg/kg (PF factors of 0.2–1.0) recorded around the mining complex (sites K1–K7) indicate that there are no significant molybdenum emissions from the chromium opencast mine of Outokumpu Chrome Oy Kemi Mine.

It is interesting to note that the orders of the PF values for the heavy metals in the bark samples collected in the vicinity of the mine (K1–K2) and in the vicinity of the works (sites T1–T7) are different. The average PF values for sites K1–K7 around the mining complex were in the order: Cr (12.4) > Ti (7.7) > Fe (5.3) > Ni (3.0) > Zn (1.9) > Mo (0.6), whereas the average PF values for sites T1–T7 around the works were in the order: Cr (81.1) > Mo (28.5) > Ni (18.0) > Fe (7.0) > Ti (5.9) > Zn (3.5). The differences in the PF values of the individual heavy metals and the different order reflect the relative volume of particulate emissions (i.e. heavy metals) from the works and from the mine. The PF values of the heavy metals at each sampling site are considered suitable for use as an index of atmospheric pollution and heavy-metal deposition.

In addition, the high accumulation of Cr (PF values of 9.5–167) and the elevated Ti (PF values of 2.1–9.4) and Fe (PF values of 3.4–14.5) concentrations in bark in the vicinity of the ferrochrome and stainless steel works of Outokumpu Stainless Steel Oy are expected because the ore from the chromium opencast mine of Outokumpu Chrome Oy, used as a raw material in the metallurgical processes, contains minerals such as magnetite (Fe_3O_4), ilmenite ($FeTiO_3$), hematite (Fe_2O_3), rutile (TiO_3), which are minor minerals. However, the oxide mineral of chromium and iron ($(Fe,Mg)(Cr,Al)_2O_4$) is the major mineral used [18,19].

3.3 *Comparison with the results of other studies*

If we compare the heavy-metal concentrations in our bark sample (table 2) with those reported by the Finnish Forest Research Institute in the nationwide bark sampling network [15], our mean values for Cr (201 mg/kg; dw), Fe (891 mg/kg; dw) and Ni (24.1 mg/kg; dw) are 446, 8 and 22 times higher that the corresponding mean concentrations in bark for the 788 sampling sites systematically covering the whole of Finland. Thus, our results indicate that the industrial point sources of Outokumpu Stainless Steel works and opencast chromium mine of Outokumpu Chrome Oy Kemi Mine have a major impact on heavy-metal concentrations in Scots pine bark.

Although the heavy-metal concentrations, and especially the Cr and Ni concentrations, in bark in the study area are high compared with those for the background areas in Finland, the Ti and Fe concentrations in the study area (see table 2) are not exceptionally high compared with the values reported by Schulz *et al.* [3]. They reported the following maximum concentrations in Scots pine bark (*Pinus sylvestris* L.) samples from different polluted areas in northern, central and eastern Europe (i.e. in Germany, Norway, Poland and Russia): Ti 372 mg/kg (dw), Fe 4794 mg/kg (dw), Zn 189 mg/kg (dw) and Mo 4.70 mg/kg (dw).

4. Conclusions

According to the heavy-metal concentrations in the bark samples, the influence of the ferrochrome and stainless steel works of Outokumpu Stainless Steel Oy and chromium opencast mine of Outokumpu Chrome Oy Kemi Mine is clearly visible in the Kemi–Tornio region. The average pollution factors (PF) for heavy metals (Ti, Cr, Fe, Ni, Zn and Mo) in the immediate vicinity (1.2–7.9 km) of the works varied between 3.5

and 81.1, and in the immediate vicinity (1.2–4.1 km) of the mining complex between 0.2 and 26.1. The accumulation of Cr and Ti in the bark samples was clearly seen in the areas subjected to aerial emissions from the ferrochrome and stainless steel works and from the chromium opencast mine, respectively.

The wet-digestion technique involving a mixture of $HNO_3 + H_2O_2$, often used in bioindicator studies, underestimated especially the Ti and Cr concentrations in the bark samples. Although completely recoveries were not obtained for Cr and for Fe in reference material NIST SRM 1573a (Tomato Leaves), and perhaps also in the bark test sample, the US EPA digestion procedure with a mixture of $HNO_3 + HCl + HF$ gave better recoveries than the mixture of $HNO_3 + H_2O_2$. Slightly lower recoveries with both acid mixtures were expected since the dust emitted from the point sources of the chromium opencast mine of Outokumpu Chrome Oy Kemi Mine and from the ferrochrome and stainless steel works of Outokumpu Stainless Steel Oy contained chromite in the chemical forms $(Fe,Mg)(Cr,Al)_2O_4$ and $FeO\text{-}Cr_2O_3$, and these are difficult to dissolve.

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