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Fluoride in birch leaves, ground vegetation, litter and humus in the surroundings of a fertilizer plant and apatite mine in Siilinjärvi, eastern Finland

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Fluoride is one of the main emission components of the fertilizer plant and strip mine located at Siilinjärvi, in eastern Finland. The fluoride concentration of birch (*Betula pendula* Roth.) leaves, ground vegetation, litter layer and humus layer were determined in the surroundings of the plant and the mine to evaluate their validity as bioindicators of fluoride pollution. The highest fluoride concentrations were observed near the fertilizer plant, the strip mine or tailings impoundments in all studied materials. Highest total fluoride concentration was observed in the litter and humus layers where the fluoride has been accumulating over three decades. The fluoride concentration of both vegetation (birch leaves and ground vegetation) and soil organic horizon (litter and humus layers) can be regarded as good indicators of fluoride load but their role is quite different. Especially birch leaves, but also ground vegetation, can be used as indicators of annual or short time fluoride load and are available in repeated monitoring, whereas litter or humus layer reveal the long time accumulation of fluoride-containing fallout.

Introduction

The sources of fluoride for plant uptake are air, soil and water (Weinstein 1977, Davison 1982). In the air fluorides can occur in gaseous (principally HF, SiF_4) and particulate form. Both forms are deposited on leaf surfaces but gaseous fluoride is also taken up through stomata and is extremely phytotoxic (Weinstein 1977). The main natural sources of fluoride in soils are apatite, cryolite, fluorite or fluorospar and topaz (Pickering 1985). Fluoride is emitted mainly from mining and workings, fertilizer and other chemical industry and metal manufacturing. Fluoride pollution can be regarded as a local problem in a few places where these activities exist.

Our study area is situated around the fertilizer plant and the strip mine at Siilinjärvi, eastern Finland, where fluorides form an important part of the emissions. The fluoride concentration of Norway spruce (*Picea abies* (L.) Karst.) needles has been used several times for biomonitoring fluoride distribution in this area (Palomäki *et al*. 1992, Tynnyrinen *et al*. 1992, H. Kinnunen *et al*. unpubl. data), but there are only a few observations done on birches (Kärenlampi *et al*. 1982, Manninen 1993) and no attention has been paid to the fluoride concentration of the litter or humus layer. Although the fluoride emissions have been reduced notably in the 1990s the fluoride may still remain in the litter or humus layer for several decades.

In our earlier study (H. Kinnunen *et al*. unpubl. data), we concluded that needle fluoride concentration is a valid indicator for fluoride pollution even in the situation where emissions have been reduced. However, Norway spruce is not always the best indicator because in the vicinity of the sources the older spruces are sparse which restricts the number of monitoring sites. Birches (silver birch *Betula pendula* Roth., and pubescent birch *Betula pubescens* Ehrh.) have become the dominant species in our study area. The aim of this study was to test the suitability of fluoride concentration of birch leaves, ground vegetation and topsoil to indicate the fluoride pollution.

Table 1. Annual emissions (1000 kg a^{-1}), Kemira, Siilinjärvi site, eastern Finland. – = data not available.

Year	SO_2	NO_x	Fluoride	particles
1977	2047	–	3.5	–
1978	2442	477	2.0	–
1979	3382	801	3.0	–
1989	577	484	17.2	480
1990	513	111	15.6	89
1991	401	111	12.3	47
1992	591	202	11.4	32
1993	730	124	11.1	41
1994	779	297	14.1	42
1995	937	362	6.8	49
1996	775	175	6.7	67
1997	826	184	7.0	45
1998	1194	175	5.5	27
1999	1153	186	5.9	31
2000	1341	219	5.7	39

Materials and methods

Fertilizer plant

The fertilizer plant (Kemira, Siilinjärvi site) is located 25 km N of Kuopio (62°54´N, 27°40´E) in eastern Finland. Since 1969, the plant has produced compound fertilizers, sulphuric acid, phosphoric acid and nitric acid. The main pollutants emitted by the fertilizer plant are fluoride, SO_2 and NO_x (Table 1). The strip mine for apatite ore, situated 2–4 km NE of the factories, was opened in 1980 and it emits mineral dust. Other sources of impurities are the dusting from tailings impoundments and rock piles. The surface area of the impoundments is over 10 km^2. Tailings wastes consist of micas (mainly phlogopite, 75%), carbonates (20%) and apatite (< 2%). The fluoride emitted by the fertilizer plant is mostly in gaseous form and is more reactive than the fluoride emitted by the mine, which is bound to mineral dust, of which major fluoride sources are phlogopite mica $K_2Mg_6[Si_6(Al,Fe^{3+})_2](OH,F)_4$ and apatite $Ca_5[F(PO_4)_3]$ (Puustinen 1973, Palomäki *et al*. 1992).

Study area

The study area is located in the Siilinjärvi municipality, north of Kuopio in eastern Finland (Fig. 1). Quaternary deposits overlying the Precambrian bedrock mostly consist of basal meltout till and glaciofluvial sand and gravel. In valleys close to lakes surface sediments are lacustrine silt and clay sediments (Bargel *et al*. 1999). The main soil type in the forests is podzol classified for a typic haplocryod according the Soil Taxonomy (Räisänen 1996). Norway spruce, birches and other species of deciduous

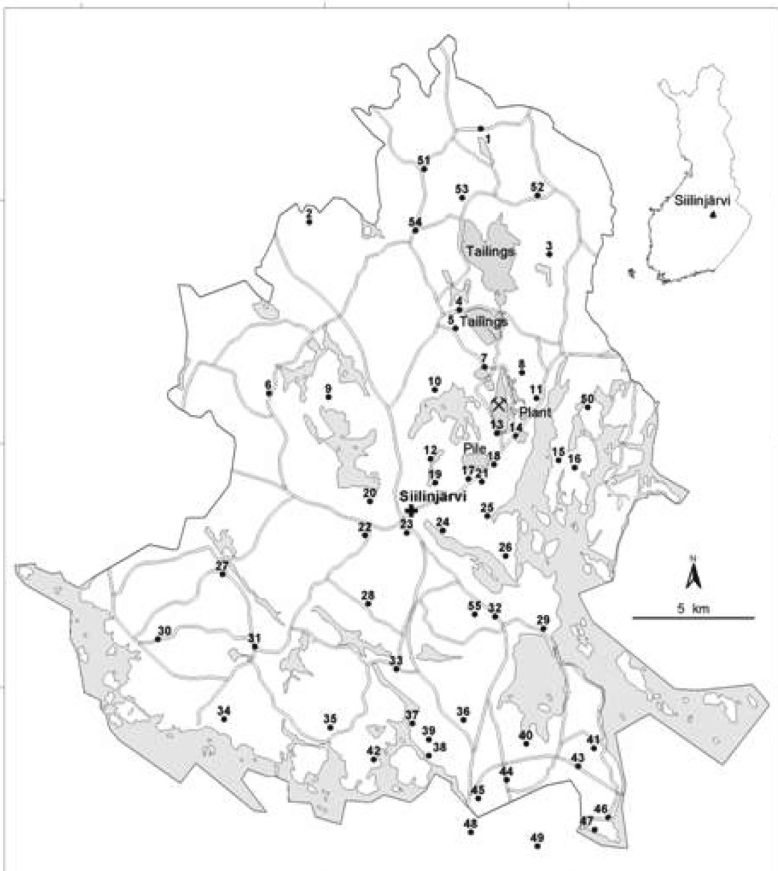

Fig. 1. Sampling plots in the Siilinjärvi study area, eastern Finland. The area of the Siilinjärvi fertilizer plant is located south-east of the apatite mine (east of the sample plot 14). The pile consists of gypsum wastes.

trees dominate local forests. Ground vegetation mainly consists of blueberry (*Vaccinium myrtillus* L.) and mosses (*Pleurozium schreberi* (Brid.) Mitt., *Hylocomium splendens* (Hedw.) B.S.G.). The prevailing winds in this area are south and south-west. Temperature and precipitation during the sampling period are given in Table 2.

Sampling

Altogether 55 sample plots were situated in the Siilinjärvi municipality (Fig. 1). These sample plots were selected because the same plots have been used earlier for biomonitoring the impact area of the fertilizer plant (STY Ympäristökonsultointi Oy 1993, H. Kinnunen *et al*. unpubl. data).

All samples were taken in the period of 17 July–3 August 2000. Surface samples were taken with a special core sampler with a diameter of 5.5 cm (Reimann *et al*. 1998). The thickness of the layer sampled varied between 10 and 15 cm. Layers of humus (lowest layer), litter (dead plant material) and living ground vegetation were separated to three separate paper bags, respectively, from the core sampler. Five sub-samples of each layer were taken at five plots of each sampling site having the surface area of 10 m × 10 m. The sampling plots were about 2–5 m far from trees (outside of canopies). For analysis, subsamples were combined and homogenized by sieving through a mesh.

From each sample plot, birch leaves were taken from five randomly selected trees, three branches of each (representing three different sides of the tree) with long pruning shears at the height of five–six meters. Samples from different trees and branches were combined to form one composite sample per plot. After sampling, the birch leaves were excised from the branches and placed in paper bags for transportation.

Chemical analysis

Samples (one composite sample/plot) of ground vegetation layer and birch leaves were dried at 40 °C and litter and humus layers were freeze-dried for 48 h and milled to fine powder before the chemical analysis.

From all samples, the fluoride was dissolved from the organic material with the microdiffusion method using perchloric acid in closed two-compartment plastic cells (Kari *et al*. 1976). About 50 mg of dry sample was weighed for each fluoride analysis in a microdiffusion cuvette. Diffusion was carried out overnight at 50 °C and the "diffused" hydrogen fluoride was collected in a small amount of NaOH. The remaining solution was then buffered with 5 M sodium acetate (pH 5.0) and the fluoride ion determined with the ion selective electrode (Radiometer, Model F1052F). The analyses and calibration were performed according to the Finnish standard SFS 5672 (Suomen standardoimisliitto (SFS) 1990).

Table 2. Mean, maximum (max) and minimum (min) temperatures (°C) and precipitation (mm) near the research area (Kuopio airport) during the sampling period in 2000 (Ilmastokatsaus 2000, Ilmatieteen laitos). – = data missing.

Month	Day	Temperature (°C)			Precipitation (mm)
		Mean	Max	Min	
July	17	19.0	23.3	14.8	0.4
	18	20.6	25.5	18.2	12.7
	19	18.9	22.7	16.2	8.3
	20	18.6	22.5	15.5	0.0
	21	19.6	23.8	15.2	0.2
	22	19.1	22.9	16.8	6.6
	23	18.6	20.4	17.7	0.4
	24	20.3	24.6	15.9	1.0
	25	14.4	23.4	12.3	0.4
	26	13.1	17.2	10.1	0.0
	27	13.9	19.0	9.9	–
	28	15.4	21.9	10.0	–
	29	17.9	23.5	11.4	–
	30	17.4	21.2	13.0	–
	31	17.4	20.0	15.0	3.5
August	1	16.1	18.6	15.2	6.2
	2	14.9	17.1	13.0	0.7
	3	14.8	17.8	12.8	1.0

Statistical analysis

The data were tested statistically with SPSS, using analysis of correlation (Spearman). The visualization of the distribution of fluoride was done with the Surfer program (Golden Software, Inc.).

Results

Fluoride concentration of the birch leaves

The fluoride concentration of birch leaves varied in the range < 5.0 to 45.0 μg g^{-1} (Table 3). The mean concentration was 13 μg g^{-1}. The fluoride concentration of birch leaf samples had a significant negative correlation with both the distance from the plant and distance from the mine (Table 3). Maximum fluoride concentration (45.0 μg g^{-1}) occurred at the sample plot 5 (locating 5.6 km northwest of the plant and 3.4 km from the mine) located close to a tailings impoundment (Fig. 2a and Table 3).

Table 3. The minimum (min), maximum (max) and mean (± S.D.) concentrations (μg g^{-1} dry mass) of fluoride in birch leaves, ground vegetation, litter and humus layer, at the Siilinjärvi study area, eastern Finland. The samples were taken in the end of July 2000. *r* = Spearman rank correlation coefficients for the relationship between the fluoride concentration and the distance from the fertilizer plant or strip mine, *n* = number of observations.

Fluoride concentration	*n*	Min	Max	Mean ± S.D.	Correlation (*r*)	
					Plant	Mine
Birch leaves	55	< 5.0	45.0	13.2 ± 8.79	–0.380**	–0.380**
Ground vegetation	55	7.7	127.7	37.9 ± 25.49	–0.411**	–0.411**
Litter layer	55	23.6	425.5	152.6 ± 111.05	–0.599**	–0.599**
Humus layer	55	33.5	357.3	139.3 ± 86.10	–0.498**	–0.498**

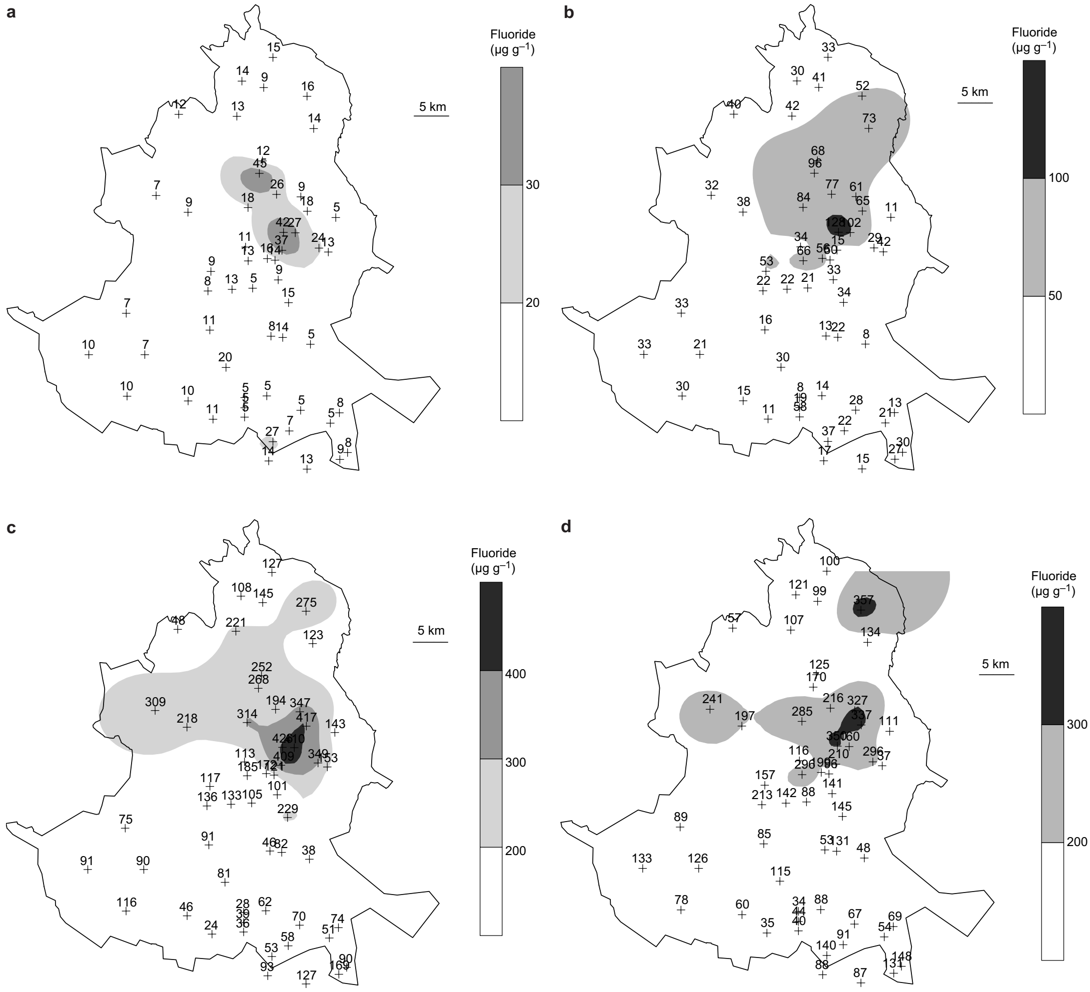

Fig. 2. The fluoride concentrations (μg g^{-1} dry mass) in (**a**) birch leaves, (**b**) ground vegetation, (**c**) litter layer, and (**d**) humus layer in the Siilinjärvi study area, eastern Finland.

Fluoride concentration of the ground vegetation layer

The mean concentration of fluoride was 37.9 μg g^{-1} in the ground vegetation layer (Table 3). At two sample plots (13 and 14), the concentration was extremely high (128 and 102 μg g^{-1}) (Fig. 2b). These sample plots were located within a distance of 0.8 and 1.6 km from the plant and the mine, respectively. As the comparison of Fig. 2a and b reveals, the highest fluoride concentrations in ground vegetation layer were found in the same areas as the highest concentrations of birch leaves. In addition, the ground layer vegetation showed slightly elevated fluoride concentration in a larger area than birch leaves extending to the surroundings of the mine tailings (Fig. 2b).

Fluoride concentration of litter and humus layers

In litter and humus (organic) layers, mean concentrations of fluoride were 153 μg g^{-1} and 139 μg g^{-1}, respectively (Table 3). The litter and humus layers had markedly higher fluoride concentrations than the ground vegetation layer and birch leaves. The highest fluoride concentration (426 μg g^{-1}) of the litter layer occurred at sample plot 13 located west and northwest of the plant and the mine (Fig. 2c). The highest fluoride concentration (357 μg g^{-1}) of the humus layer was measured at the sample plot 52 locating close to the tailings impoundment (Fig. 2d). The distribution patterns of fluoride in the litter and humus layer were almost equal (cf. Fig. 2c and d).

Moreover, there was a significant correlation between the fluoride concentrations of the litter and humus layers and the distance to the plant and the mine (Table 3). Litter and humus layers had extremely high fluoride concentrations in a somewhat wider area than birch leaves and ground vegetation (cf. Fig. 2). Despite that, the correlation coefficients for the concentrations between the sample materials showed to be significant as seen in Table 4.

Discussion

Silver birch is reported to be rather tolerant to fluoride, whereas Scots pine (*Pinus sylvestris* L.) and Norway spruce are fluoride-sensitive species (Weinstein 1977, Horntvedt 1997, Vike 1999). Vike and Håbjørg (1995) reported that clear leaf injury symptoms in Scots pine occur at fluoride concentration < 50 μg g^{-1} in dry mass, whereas pubescent birch, for example, showed corresponding symptoms at the concentration of 100 and 170 μg g^{-1}. In the uncontaminated area (background) of temperate climate, the mean fluoride concentration of leaves of most plant species is usually < 10 μg g^{-1} (World Health Organization 1984).

In this study, the fluoride concentrations of birch leaves were lower than the above critical concentrations for the injury symptoms. In 1978, the fluoride concentrations were 200 μg g^{-1} and 62.3 μg g^{-1} at a distance of 0.15 km and 1.2 km from the plant, respectively (Kärenlampi *et al.* 1982). In 1988, fluoride concentrations even as high as 1400 μg g^{-1} were detected (Manninen 1993). In 2000, fluoride concentrations of the birch leaves varied from < 5.0 μg g^{-1} to 45.0 μg g^{-1} being slightly higher than the fluoride concentration of Norway spruce needles (2.5–32.6 μg g^{-1}) analysed one year earlier (H. Kinnunen *et al.* unpubl. data). The decrease in the concentrations is due to the drop in fluoride emission from the plant starting from the year 1995 (Table 1).

In addition to the gaseous fluoride emission, the mineral dust in the mine area contains fluoride-bearing minerals (Palomäki *et al.* 1992). The impact of the dust is well seen at sample plots close to the tailings impoundments. The washing of the Norway spruce needles taken from dusty sample plots have decreased fluoride concentrations 25%–60% (Palomäki *et al.* 1992). Also Vike and Håbjørg (1995) reported that "wash off" by rainwater had an important impact on the fluoride concentration of silver birch and lilac (*Syringa vulgaris* L.). According to them, the "wash off" effect is one reason for the great variation between localities and years, and therefore suppressing the value of these species as biomonitors of fluoride.

In contrast to above, results of the present study suggest that birch leaves can be considered as good indicators for fluoride deposition as Norway spruce needles have been considered earlier (Horntvedt 1995, H. Kinnunen *et al.* unpubl. data). Furthermore, we conclude that birch leaves can be used as indicators of fluoride load of the current growing season, which enables the study on the annual variation. The accumulation period in spruce needles is longer, but depends, of course, on the age class of sampled needles.

The fluoride concentration of ground vegetation layer was distinctly lower than that of

Table 4. Spearman correlation coefficients of fluoride concentrations for birch leaves, and ground vegetation, litter and humus layers.

	Birch leaves	Ground vegetation	Litter layer	Humus layer
Birch leaves	–			
Ground vegetation	0.535**	–		
Litter layer	0.587**	0.597**	–	
Humus layer	0.545**	0.570**	0.796**	–

litter and humus layers. Beyer *et al*. (1987) have reported about four times higher fluoride concentration in the litter than ground vegetation layer. This is due to the fact that the litter and humus accumulate fluoride in long-term period, whereas the ground vegetation layer mainly contains fluoride emitted in one growing season. Therefore, ground vegetation layer is comparable to birch leaves as a short time accumulator even though mosses and shrubs may accumulate fluoride in a much longer period than one growing season.

The amount of fluoride adsorbed by soil varies with soil type and soil pH (Pickering 1985). According to Kylä-Setälä (1996), the natural fluoride concentration in soil is, on an average, 200 μg g^{-1} in Finland. Obviously, glacial sediments in the study area (Siilinjärvi) contain somewhat more fluoride bearing minerals, phlogopite and apatite due to the local bedrock geology (Puustinen 1971). Part of the soil fluoride (geogenic) is accumulated in humus and litter layer in long-term soil weathering processes and nutrient uptake. During podzolization F-bearing minerals apatite and mica are weathered in the topmost mineral soil layer, from which fluoride can accumulate via nutrient uptake and litterfall into the organic layer (cf. Räisänen 1996). In the uncontaminated area, concentrations of fluoride vary between 20 and 170 μg g^{-1} (southern parts of the study area in Fig. 2c and d). The range is suggested to represent the geogenic variation of fluoride in litter and humus layer in the Siilinjärvi area.

Geeson *et al*. (1998) have observed no significant relationship between the fluoride concentration in soil and plants. Our study, however, showed similar distribution patterns of fluoride in the vegetation and humus and litter layers close to the plant. In contrast, fluoride concentrations of humus and litter layer were elevated in the western part of the study area, whereas fluoride concentrations of ground vegetation layer and birch leaves were similar to the concentrations in the less contaminated area (background). In the western part of the study area, the source of the fluoride emission is mainly the dust (fluoride bearing mineral fines) from the tailings impoundments and the mine. Obviously, the dust accumulates more effectively on the litter and humus layer than vegetation, from which rainwater has washed it out.

With respect to the fluoride variation in the litter and humus layer in less contaminated area (southern part of the study area) we conclude that fluoride accumulation in the soil organic horizon occurs close to the plant and mine and its tailings impoundments. The influence of reduced emissions on the fluoride concentration of the humus layer cannot be estimated, since the fluoride concentration of the humus layer has not been analysed earlier in the Siilinjärvi area.

According to Reimann *et al*. (1998), the concentration of a pollutant in humus reflects rather long-term accumulation than the concentration in the vegetation. Also this study showed that the total fluoride concentration of litter and humus layers reflects the long-term fluoride deposition, even though the geogenic fluoride accumulation and adsorption capacity of pollutants in the organic soil layer vary greatly (Arnesen *et al*. 1995).

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