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Fluoride Content in Soil and Vegetation

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Until the war the production of aluminium was 75.000 tons per year and emission of fluorides 17 kilograms per ton. Gaseous fluorides, particularly hydrogen fluoride, are among the most phytotoxic air pollutants and have been a threat to vegetation on a local or regional scale in the highly industrialised countries (Klumpp, Domingos, and Klumpp, 1996). Relatively few studies have been directly concerned with the effects of fluoride-containing particles on plants, and it has been generally assumed that this form of airborne fluoride is much less phytotoxic than the gaseous. Most particulate fluorides (cryolite, calcium fluoride, sodium fluoride) are stable compounds that do not hydrolyze readily with vapour in the atmosphere. Therefore, their removal from the atmosphere is controlled by dry and wet deposition. Climatic conditions are important in determining the effects of deposited particulate emissions on plants and animals. Light rains may deposit fluorides from the atmosphere on vegetation whereas heavy rains may partially wash off fluoride dusts from vegetation to soil. In arid regions, the dusts may accumulate on vegetation and be ingested by grazing animals. In areas of heavy precipitation, plants may take up washed-off fluorides from the soil. It has been estimated that >90% of natural fluoride in soil is insoluble or tightly bound to soil particles. The mobility of fluorides in soil is enhanced if the solubility of fluorides is increased, either by increased acidity or by formation of soluble complexes.

The purpose of this study was to determine the accumulation of fluoride in two plant species (*Pinus halepensis* and *Olea europea*) and in the soil in the vicinity of aluminium reduction plant, which was destroyed during the aggression on Croatia 1991.

MATERIALS AND METHODS

Research was carried out during two seasons (spring and autumn) from 1996 to 2001. Samples were collected at distance range 0.43-4.50 km from the emission source (Kalinić, Vadjić, Hršak et al.,1997). The content of fluoride was measured in leaf samples and soil at five sites in polluted area, at one control vegetation site and two control soil sites in the control area. Distance (km) and direction of sampling sites from the emission source are shown in Table 1.

Leaf samples were picked one by one at a height of 1.5-2m from all sides of the tree. Because of aging accumulative effect all basal and terminal leaves were avoided. Attention must be paid to cut the samples at the same length because the fluoride content in the different parts of the plants varies (Vike and Håbjørg 1995, Giertych, De Temmerman, and Rachwal,1997). The mass concentration of fluoride in leaves was determined as sum of fluoride present as dust on the plant and fluoride in the plant. In this case the samples are not washed (Komers, 1976). The sample leaves were put into

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Table 1. Distance (km) and direction of sampling sites from the emmission source.

Sampling site	Distance	Direction
A	4.50	N-NW
B	0.43	NE
C	1.87	N
D	1.90	NW
E	2.33	W-SW
K	54.28	W
K1	38.65	N-NW

paper bags, dried in a drying oven at 105 °C (app. 15 hours), milled and analysed for fluoride by potentiometric method (NIOSH, 1977). The soil samples were collected at depth 0-10 cm (Hršak, Fugaš, and Vadjić, 2000) and dried at 105 °C. Ten grams of soil samples were shaken for 24 hours at the room temperature with 20 cm^3 of redistilled water. The fluoride concentrations in soil extract was determined by the potentiometric method (NIOSH, 1977, Arnesen, Abrahamsen, Sandvik et al.,1995).

RESULTS AND DISCUSSION

Table 2. Statistical parameters of measured mass concentrations of fluoride during the whole measuring period.

Statistical parameters	Soil (μg/g)		Olea europea (μg/g dw)		Pinus halepensis (μg/g dw)	
	Spring	Autumn	Spring	Autumn	Spring	Autumn
N	40	40	11	11	35	35
$C_{min.}$	0.63	0.31	2.1	0.8	2.1	1.8
$C_{max.}$	61.8	80.7	12.6	14.1	31.1	22.6
C	**10.6**	**11.7**	**5.71**	**5.72**	**11.9**	**9.5**
STD	12.6	15.77	2.96	4.07	7.84	5.20
SE	1.994	2.494	0.893	1.227	1.326	0.879
t	0.3418		0.0036		1,4310	
P	>>0.05		>>0.05		>>0.05	

N - number of samples
$C_{min.}$ - minimum value
$C_{max.}$ - maximum value

C - arithmetic means
STD - standard deviation
SE - standard error

The fluoride content in *Pinus halepensis* and *Olea europea* in different seasons is shown in Figures 1 and 2. The levels of fluoride in soil are shown in Figure 3 and average fluoride concentrations and difference between the measuring periods are shown in Table 2.

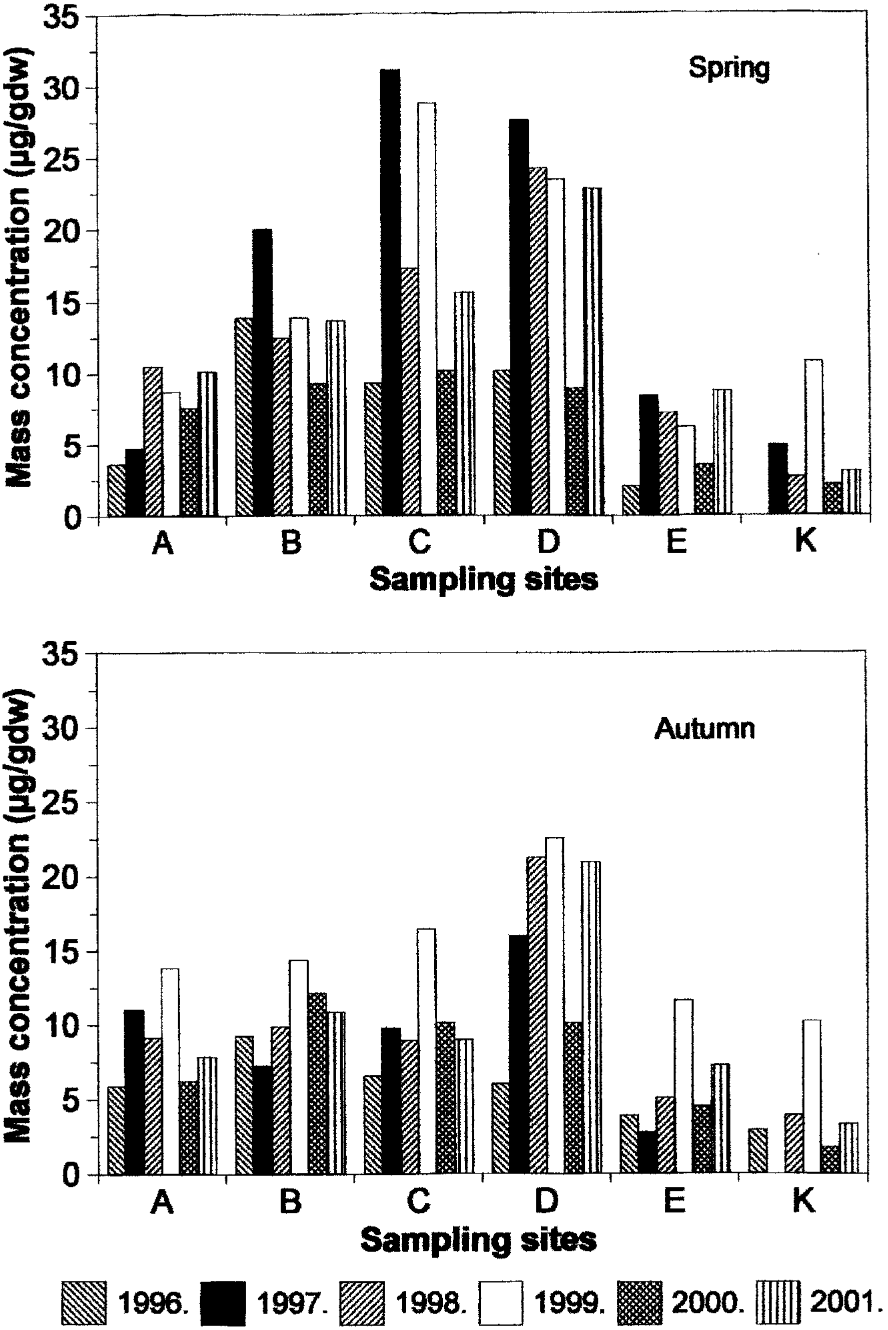

Figure 1. Fluoride in *Pinus halepensis*.

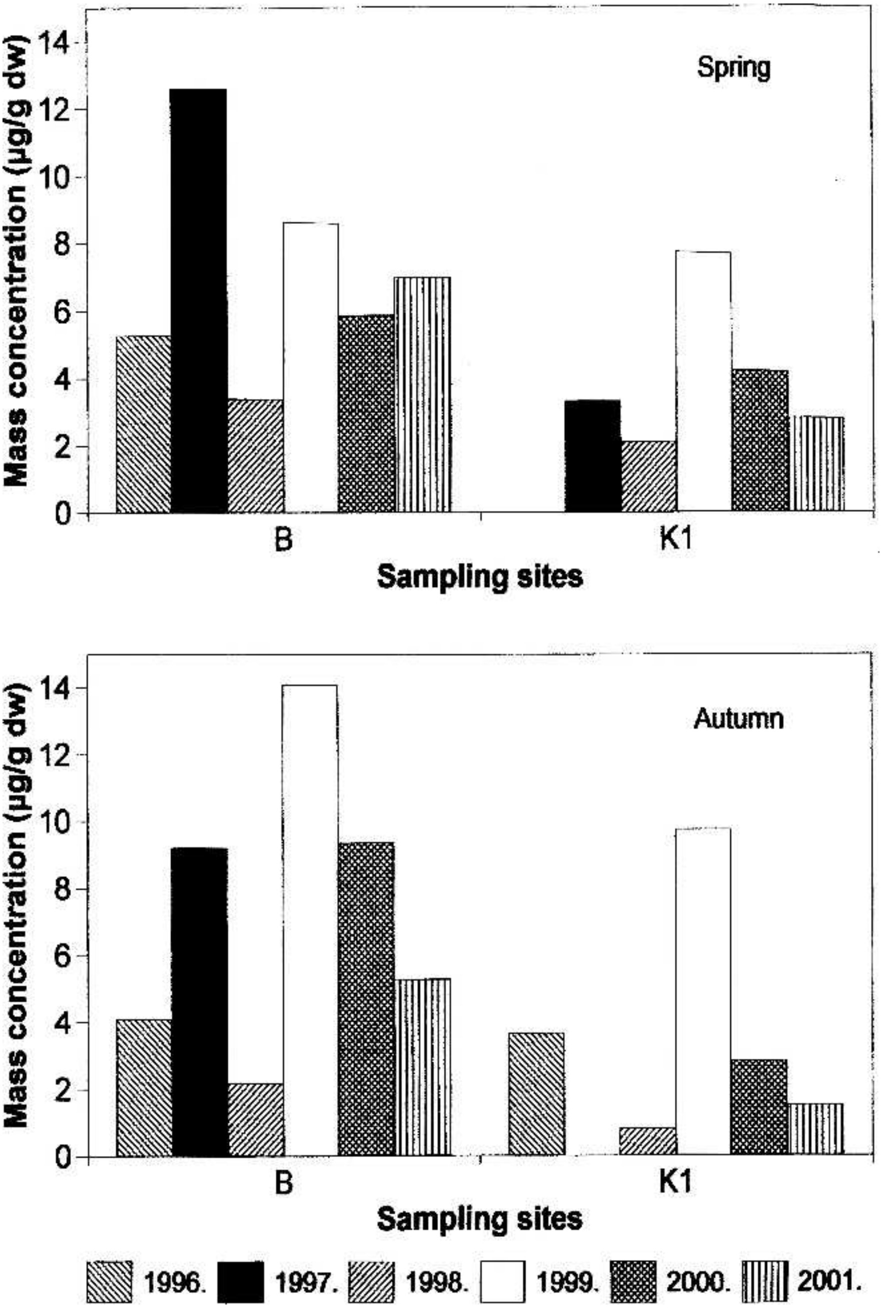

Figure 2. Fluoride in *Olea europea*.

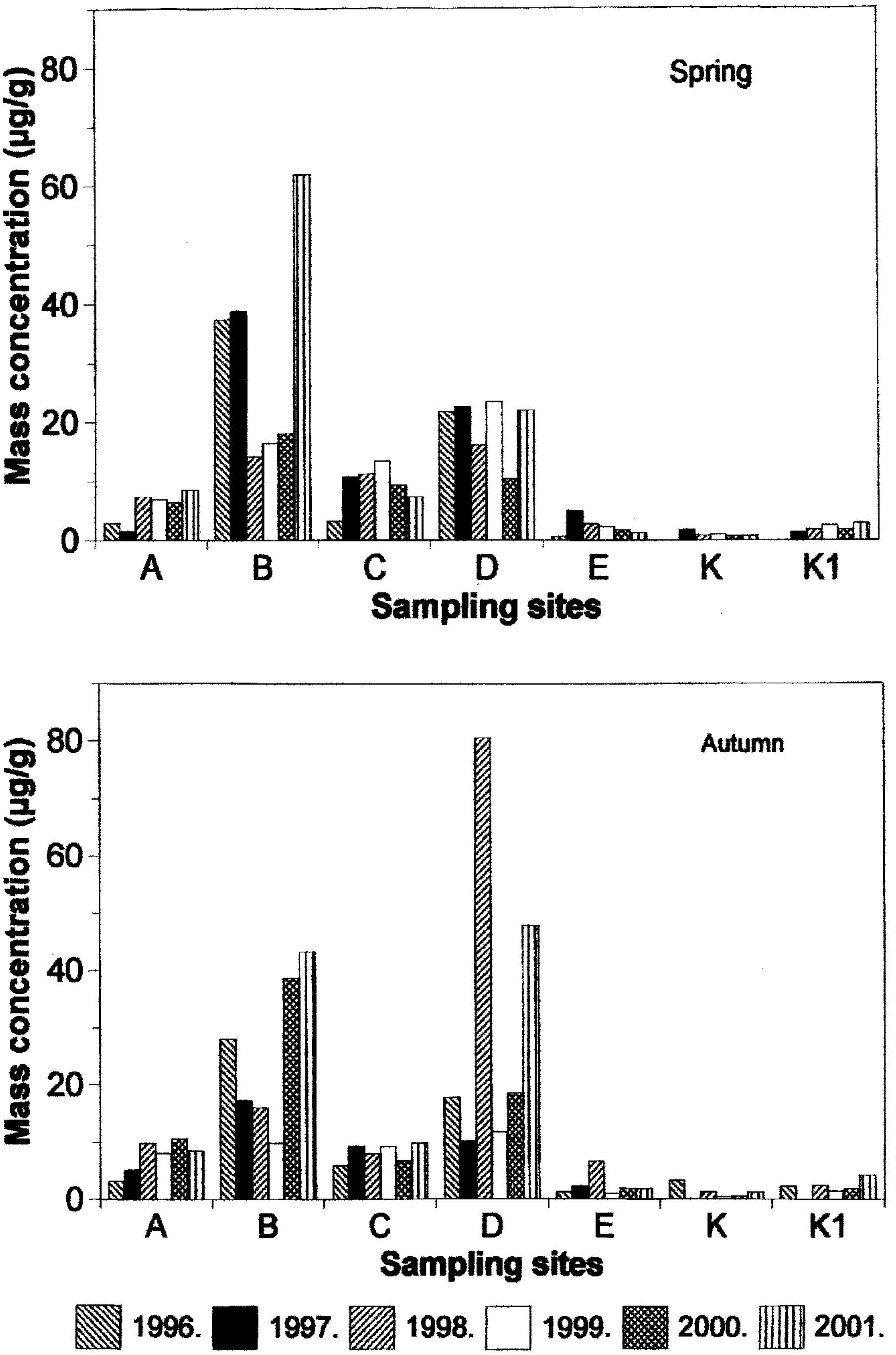

Figure 3. Fluoride in soil.

Statistical analysis showed that there were no significant differences in the fluoride content between springs and autumn for vegetation, neither for soil.

The normal fluoride content of leaves has been subject of considerable disagreement, but it generally ranges from 2 to 20 μg on a dry weight basis (NAS, 1971). It will vary with the species (and even the variety) of plant, the age of the leaf, characteristics of the soil, use of fertilizer, irrigation etc. (Zimmermann et al., 2000). This "background" fluoride is derived mostly from the soil, which normally contains from 20 to 500 μg/g. A comparison of the values obtained in this study with recommendations in the literature (WHO, 1971, Van der Eerden, 1991) fluoride concentrations were exceeded at seven samples of *Pinus halepensis* in the spring and three samples in the autumn. Mass concentrations of fluoride in *Olea europea* and in the soils were relatively low.

Both plant species used in the present study proved to be adequate bioindicators of airborne fluoride, as the dominating species in areas with high and long exposure to fluoride pollution. The monitoring of fluoride in the same species and in the soil at the same sampling sites has continued and the results will be compared.

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