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Effects of airborne fluoride on soil and vegetation

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This paper is dedicated to Alain Tressaud on the occasion of his winning the 2010 Award for Creative Work in Fluorine Chemistry given by the American Chemical Society.

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ABSTRACT

The study was initiated by the sudden uncontrolled release of airborne fluorides in 2005 into the environment from aluminium smelter factory that caused damage of vegetation. Samples of corn leaves and corn male flower heads with visible symptoms of fluoride intoxication had been collected in autumn 2005. Increased contents of total fluoride, which exceeded the maximum allowable content of fluorine in feeding stuffs, including meadow grass, were detected. During continuation of the study some commercially available herbal teas and plants used for preparing herbal teas infusions, collected in the field in 2010, were investigated to investigate possible uptake of fluoride from the soil. Nettle (*Urtica dioica*) has been found to be a promising passive bioindicator for monitoring phytotoxic effects of fluoride in the soil on the vegetation. Good correlation between labile free fluoride in the soil and total fluoride in the nettle has been found, while total fluoride in the soil, soil pH and the dominant wind direction were also proven as important factors influencing the uptake of fluoride by the nettle.

1. Introduction

Fluorine is widespread in the environment. To humans, plants and animals it is mainly available in the form of fluoride ion (F^-). Much attention devoted to fluorin(d)e research can be explained by its dual effect on human health. Fluorine is considered as an essential trace element due to the proven benefits of fluoride for dental health. Chronic uptakes of high amounts of fluoride can cause dental fluorosis in children, or even appearance of skeletal fluorosis in both, children or adults. Fluorine is not an essential element to plants and its essentiality for animals remains questionable [1]. Once taken up by the plants, fluoride enters into the entire food chain.

It is generally believed that most of airborne fluoride in fluoride polluted area is taken up through the stomata in the leaves and mainly accumulated in the tips and margins of the leaves [2,3]. The uptake depends not only on the concentration and composition of fluoride in ambient air and the duration of the exposure, but it also varies with the vegetation structure, plant species and growth conditions. Different plants have been suggested for active and passive biomonitoring of phytotoxic effects of airborne fluoride [4–6] and problems classifying plant species sensitivity to fluoride were discussed [7]. Information on the uptake of fluoride from contaminated soils, to which it enters in precipitation, dry deposition and through contaminated litter, is limited. Moreover, fluoride ion concentrations, controlled by inorganic constituents of the soil and soil pH, are of importance, when considering accumulation from the soil. The average of total fluoride contents ranges from about 100 to 600 mg kg^{-1} [7]. The minimum of fluorine solubility is at pH 6.0–6.5; the greater solubility of F under acidic conditions can be explained by the formation of AlF_x complexes, whereas under alkaline conditions by desorption of free F as a result of repulsion by the negatively charged surfaces [8]. Uptake of fluoride from the soil might occur, at least in some species. Examples of studied species include among others maple seedlings and orchard grass [2], clover and grasses [3], spinach [9] and onion [10]. Correlations between the atmospheric HF concentrations and the fluoride accumulation in plant leaves [11,12], and between free fluoride in the soil solution and of fluoride taken up by the plants have been observed [13]. The background concentrations of total fluoride in plants are usually lower than 10 mg kg^{-1} [7]. The maximum concentrations of heavy metals and fluoride in feeding stuffs, including meadow grass, are

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regulated with EU directives 2002/32/EC [14] and 2005/87/EC [15] concerning undesirable substances in animal feed.

Monitoring of highly phytotoxic airborne and particulate fluoride emitted from different anthropogenic sources of fluoride, which include coal-fired power plants, aluminium smelters, phosphate fertilizer plants, glass, brick, and tile works, and plastics factories remains, despite the growing importance of these activities in industrial countries and emerging economies, rather sporadic. The present study addresses the sudden, uncontrolled release of fluorine from aluminium smelter in Slovenia in autumn 2005, which resulted in the damage of the vegetation. First the approach to the inspection of the affected area conducted with the aim to examine the contents of fluorine in soil, corn leafs and corn male flower heads in the affected area and to compare them with the contents of fluorine in the same type of the samples taken in fluorine unburdened environment, is described. As second, plants used for preparing infusions of herbal teas were studied for the purpose of defining a possible bioindicator for passive biomonitoring of phytotoxic effects of fluoride on plants.

2. Materials and methods

2.1. Reagents

All reagents were of analytical grade and all solutions were prepared using double-distilled water. A 50% (w/w) solution and a 0.1 mol l^{-1} solution of sodium hydroxide (Merck) were prepared by dissolving the reagent pellets in water. A 0.050 mol l^{-1} working solution of NaF was prepared by dissolving NaF (Merck) in water and a (100.0 ± 0.5) mg l^{-1} standard solution of fluoride (Orion) was used to check the accuracy and precision of fluoride determination. For alkaline carbonate fusion, solid $NaKCO_3$ (Merck), for pyrohydrolytical decomposition solid WO_3 (Fluka) and for the acidification of samples, conc. H_2SO_4 (Merck) were used. Buffer solutions (pH = 4.00 and pH = 7.00), used for calibration of pH electrode, were prepared by dissolving the contents of capsules (Carlo Erba) in 100 ml volumetric flasks with water. A citrate buffer solution (CBS buffer) was prepared as reported previously [16].

The accuracy and precision of the methods employed were checked by the analysis of a standard reference material, SRM 2695 Fluoride in Vegetation, consisting of a standard with a high level and a standard with a low level of fluoride (National Institute of Standards and Technology) and of a certified reference material, BCR CRM 461, Fluorine in clay (Community Bureau of Reference Certified Reference Material).

2.2. Sample collection and preparation

Samples were collected in and out of the area of the dominant wind (south-west for this region) at different distances around the aluminium smelter (referred to as an emitter in the continuation). In autumn 2005 samples of top soil (0–20 cm), corn leafs and corn flowers heads were collected; the same type of samples were collected also in clean, with fluoride non-polluted area (control samples). Additionally, in autumn 2010 samples of herbs (without roots) used for preparing herbal teas infusions and samples of top soil (0–20 cm) were collected; as a control, samples of commercially available herbal teas were used. Samples have been dried on Teflon plates in the laboratory oven (Thermo, T 6) at 60 °C then ground and homogenized in agate ball mill. Samples of soil were additionally passed through 0.25 mm sieve.

The soil pH was determined after preparing soil slurry solution by mixing 30.0 g ($\pm$0.1 g) of soil with 30.0 g ($\pm$0.1 g) of water [17].

Samples for determination of free fluoride ion (F_f^-) in tea infusions were prepared by weighing 2 g ($\pm$0.05 mg) of tea into the filter bag (Tee-Filter Grösse 3, dm drogerie markt) and infusing the bag containing the tea with 100 ml of boiling water (1% (w/v) tea infusion). After t = 5 min the filter bag was removed and the infusion was cooled to room temperature.

2.3. Sample decomposition for determination of total fluoride

For determination of total fluoride (F_t) in plants material approximately 2 g ($\pm$0.05 mg) of sample was weighed into a 70 ml platinum dish and soaked with 1 ml of 50% (w/w) NaOH. After the sample had been evaporated to dryness in a sand bath, it was decomposed by fusion with 3 g of $KNaCO_3$ using a Bunsen burner and melted until a transparent melt with no solid remains was obtained. This was then cooled and quantitatively transferred to a 100 ml polyethylene volumetric flask. Before determining the fluoride content, the digestates were neutralized by addition of conc. H_2SO_4, acidified to pH 2–3 and diluted with water.

Samples of soil for determination of F_t were decomposed by weighing approximately 100 mg ($\pm$0.05 mg) of soil into a platinum crucible and mixing together with approximately 50 mg of WO_3 [18]. The crucible was inserted into the platinum reaction tube and heated for approximately 30 min at 1100 °C in the presence of a superheated water steam stream with a flow rate ranging from 0.5 to 1 ml min^{-1}. The distillate was collected into 20 ml of 0.1 mol l^{-1} NaOH in a 100 ml polyethylene flask. After the reaction was finished the flask was filled with water to the mark.

2.4. Determination of fluoride and pH

An Orion 960 autochemistry system with a temperature sensor and combined fluoride ion selective electrode (ISE) (Thermo Orion model 96-09) was used for the potentiometric determination of fluoride in prepared samples. Polyethylene flasks and beakers were used throughout.

The amount of F_t was determined, in the corresponding aliquot of the sample, to which 25 ml CBS was added and diluted with water to 50 ml, by the multiple known addition (MKA) technique. Adjustments made to the factory settings of the apparatus were the stability criteria of the electrode, which was set to be 1 mV min^{-1} (vs. a proposed 3 mV min^{-1}) and the constant increment, which was set to be 18 mV (vs. a proposed 10 mV). The memory effect of the electrode was minimized by soaking the electrode for t = 5 min in distilled water, blotted dry and then soaking for t = 5 min in sample solution before starting the program. The analysis was performed on at least duplicate sample portions. The amount of fluoride in each portion was measured in at least twice. The results reported were within the required ranges if: (1) results calculated after the first addition were similar to the result from the final addition; (2) the electrode slope was 59 ± 2 mV DEC^{-1}; (3) the level of precision was equal or better than the required 2%; (4) spike recovery was 100 ± 2%; and (5) no warning messages appeared. The amount of F_f^- in soils and herbal teas was determined as reported previously [19].

The digital voltmeter (Iskra pH-meter MA 5740) with a temperature sensor Pt 100 (Iskra) and combined pH glass electrode (ProMinent, Dulcotest PHEX-112-SE) calibrated at pH = 4.00 and pH = 7.00 was used for pH measurements.

3. Results and discussion

The MKA technique was selected as the technique of choice for determination of fluoride with fluoride ISE. A 0.050 M standard solution of NaF was used as a working standard solution. The accuracy and precision of the fluoride determinations was studied and the results of these experiments are presented in Table 1.

Table 1
Accuracy and precision of the determination of fluoride.

$C(F_f^-)_{theor.}$ (mg l^{-1})	Number (n)	$C(F_f^-)_{det.}$ (mg l^{-1})	$C(F_f^-)_{det.} - C(F_f^-)_{theor.}$ (mg l^{-1})	SD[a] (mg l^{-1})	RSD[b] (%)
0.100	4	0.110	0.010	0.003	2.87
0.200	5	0.211	0.011	0.004	1.80
0.400	3	0.415	0.015	0.007	1.76
1.000	3	1.000	0.000	0.018	1.75
2.000	5	2.039	0.039	0.013	0.65

[a] SD is the standard deviation.
[b] RSD is the relative standard deviation.

The results revealed good accuracy and precision of the method for determination of fluoride in solution using fluoride ISE. The method enables accurate and precise determination of fluoride in the directly prepared samples or decomposed samples containing at least 2 mg kg^{-1} of F_f^-. The contents of F_f^- in the samples of soil and herbal teas were determined according to the modified procedure, which enables determination of 0.013 mg l^{-1} of F_f^- [19]. The entire analytical procedure for determination of F_t in vegetation and of F_t in soil was then tested using certified reference materials – certified reference materials for determination of F_f^- in soil and vegetation are not available. The results of these analyses are presented in Table 2.

Good agreement between certified and reported values was observed for the samples of clay and vegetation. High accuracy and precision of the procedures for determination of F_t in samples of soil and vegetation were thus proven.

Samples of soil, corn leafs and flowers heads collected in the area of the dominant wind and contrary to dominant wind direction at the distance of about 500 m from the emitter and the same type of samples taken in clean area were then analyzed on the contents of F_t. The results of these determinations are presented in Table 3.

The results obtained revealed highly increased contents of F_t in male flower heads and corn leafs in the area around the emitter. In the direction of the dominant wind the contents were more than 100-fold higher, and in the area contrary to the dominant wind direction about 10-fold higher, than the background concentrations of fluorine in plants. These contents exceed the maximum allowable content of fluorine in feeding stuffs, including meadow grass [14,15]. The contents of F_t in the same type of samples taken in the clean, non-affected area were below background contents of F_t in plants. It is therefore possible to conclude that the increased contents of F_t in the area around the emitter can be ascribed to fluoride pollution. As to the soil it is not possible to claim, whether the differences in F_t contents are due to the natural variations of F_t in soils or due to the contamination with fluoride. Although the soil type supposed to be similar, it is nevertheless possible to observe that the soil in the direction of the dominant wind contains substantially higher contents of F_t than the soil contrary to the main wind direction. Quite lower F_t content, as opposed to polluted area, was determined in the soil from clean area.

In 2007, the primary aluminium production in potline B of the emitter was stopped, while the production in potline C is continuing. In the same year the company gained the Environmental permit for the operation of devices, which may cause pollution to a greater extent. The study was continued with the purpose of identifying possible bioindicator for passive biomonitoring of phytotoxic effects of fluoride on plants. The focus was put on the plants used for preparing herbal tea infusions. This type of plants is widely available and diverse samples not difficult to obtain. In order to identify possible plants that could uptake fluoride in larger quantities, F_t and F_f^- contents were first determined in some commercially available herbal teas. The results of these determinations are presented in Table 4.

Table 2
Results of determination of F_t in NIST SRM 2695 and BCR CRM 461 materials.

Sample	n	$w(F_t)_{certified}$ (mg kg^{-1})[a]	$w(F_t)_{det.}$ (mg kg^{-1})[b]
SRM 2695, High level	2	277 ± 27	280 ± 3
SRM 2695, Low level	2	64.0 ± 8.4	67 ± 2
CRM 461	2	568 ± 10	565 ± 5

[a] The uncertainties of the certified values are at 95% confidence intervals.
[b] Mean of two parallel determinations ± standard deviation of measurements.

Table 3
Results of determination of F_t in male flower heads, corn leafs, and soil in the area of the dominant wind and contrary to dominant wind direction in the surrounding of the emitter in the distance of approximately 500 m and in clean area.

Sample	$w(F_t)$ (mg kg^{-1})[a]			
	Area			
	n	Dominant wind	Contrary to dominant wind	Clean
Male flower heads	2	1392 ± 26	130 ± 6	8.0 ± 1.0
Corn leafs	2	159 ± 3	59 ± 2	6.0 ± 0.5
Soil	2	844 ± 33	614 ± 6	454 ± 11

[a] Mean of two parallel determinations ± standard deviation of measurements.

The results obtained (Table 4) showed that among investigated herbal teas, some contain higher concentrations of F_t, than the background contents in plants are. The highest contents, exceeding the background concentrations in plant materials were found in linden, peppermint, hibiscus, nettle, and chamomile herbal tea. The concentrations of F_f^- are dependent on the leaching of F_t into the tea infusions which ranges from about 12% in chamomile tea infusion to almost complete in elderberry tea infusion. The uptake of fluoride from infusions of herbal teas is from consumers' perspective negligible as herbal teas are usually prepared as 1% (w/v) tea infusions.

With the aim to investigate, whether plants used for preparing herbal teas infusions can contain larger amounts of fluoride, when sampled in the field, samples of plants and also top soil (0–20 cm) were taken in the area around the emitter, and in clean area (Razori, Smoleva, Ojstri vrh). As the sampling was conducted in

Table 4
Results of determination of F_t and F_f^- in some commercial herbal teas.

Type of herbal tea	n	$w(F_t)$ (mg kg^{-1})	n	$w(F_f^-)$ (mg kg^{-1})
Elderberry	3	3.7 ± 0.9	3	3.3 ± 1.0
Rosehip	2	5.5 ± 0.1	3	2.8 ± 1.0
Sage-1	2	8.9 ± 2.5	3	2.0 ± 0.6
Sage-2	3	9.0 ± 0.7	2	5.2 ± 0.9
Linden	2	10.7 ± 1.7	2	3.0 ± 0.5
Peppermint	2	12.2 ± 1.2	3	2.1 ± 0.8
Hibiscus	3	12.6 ± 0.5	2	4.0 ± 0.6
Nettle	2	15.7 ± 2.3	3	2.7 ± 0.7
Chamomile	2	28.9 ± 2.9	2	3.4 ± 0.8

Table 5
Sampling locations and the contents of F_t and F_f^- determined in plant materials and of F_t and F_f^- in soil and the soil pH.

Location	Air distance from emitter (km)	Wind factor	Plant	$w(F_t)_{plant}$ (mg kg^{-1})[a]	$w(F_f^-)_{plant}$ (mg kg^{-1})[a]	$w(F_t)_{soil}$ (mg kg^{-1})[a]	$w(F_f^-)_{soil}$ (mg kg^{-1})[a]	pH_{soil}[a]
(1) Forest, bees	1.61	1	Rosehip	5.6 ± 0.5	–	719 ± 31	3.5 ± 0.1	7.34 ± 0.04
(1) Forest, bees	1.61	1	Milfoil	7.0 ± 0.5	–	719 ± 31	3.5 ± 0.1	7.34 ± 0.04
(1) Forest, bees	1.61	1	Elderberry	9.0 ± 0.3	–	719 ± 31	3.5 ± 0.1	7.34 ± 0.04
(1) Forest, bees	1.61	1	Nettle	100.0 ± 1.9	7.2 ± 0.6	719 ± 31	3.5 ± 0.1	7.34 ± 0.04
(2) Storehouse	1.63	1	Nettle	70.5 ± 3.9	7.2 ± 1.7	859 ± 32	2.3 ± 0.3	5.72 ± 0.19
(3) Red mud	2.97	1	Rosehip	7.2 ± 0.1	–	1058 ± 70	4.0 ± 0.3	7.66 ± 0.04
(4) Hajdina	2.77	0.5	Milfoil	7.4 ± 0.5	–	528 ± 19	2.6 ± 0.1	7.74 ± 0.03
(4) Hajdina	2.77	0.5	Nettle	28.2 ± 2.0	2.1 ± 0.3	528 ± 19	2.6 ± 0.1	7.74 ± 0.03
(5) Kungota	3.47	0.5	Chamomile	10.0 ± 0.3	–	608 ± 28	1.2 ± 0.1	6.77 ± 0.06
(5) Kungota	3.47	0.5	Milfoil	6.1 ± 0.7	–	608 ± 28	1.2 ± 0.1	6.77 ± 0.06
(5) Kungota	3.47	0.5	Nettle	9.8 ± 1.0	2.8 ± 0.2	608 ± 28	1.2 ± 0.1	6.77 ± 0.06
(5) Kungota	3.47	0.5	St. John's Wort	3.2 ± 0.1	–	608 ± 28	1.2 ± 0.1	6.77 ± 0.06
(6) Polskava	12.09	0.5	St. John's Wort	7.8 ± 0.6	–	668 ± 18	2.2 ± 0.3	6.71 ± 0.01
(7) Razori	112	0	Nettle	13.0 ± 0.8	1.9 ± 0.4	451 ± 3	1.1 ± 0.0	7.36 ± 0.01
(8) Smoleva	127.35	0	Nettle	8.9 ± 1.7	2.6 ± 0.1	880 ± 17	0.8 ± 0.1	7.78 ± 0.03
(9) Ojstri vrh	130	0	Nettle	6.4 ± 1.4	3.3 ± 0.9	615 ± 14	1.1 ± 0.2	6.72 ± 0.11

[a] Mean of two parallel determinations ± standard deviation of measurements.

autumn, the diversity of sampled plants is not as wide as in the case of commercial teas.

In the plant samples F_t and F_f^- contents were determined, while in the samples of top soil F_t and labile F_f^- contents and pH were determined as correlation between fluoride in solution and of fluoride taken up by the plants has been reported in the literature [13]. Influence of the dominant wind was described by factor 1 for the areas in the dominant wind direction and with 0.5 for the opposite direction. Factor 0 was ascribed to the non-influenced, clean areas. Results of these analyses are presented in Table 5.

The data (Table 5) show that F_t determined in plants used for preparing herbal teas in the area around the emitter are generally lower than in the commercially available teas, with the F_t being equal or lower than 10 mg kg^{-1}. The only exception to this is common nettle (*Urtica dioica*), which is widely abundant plant, usually found in the countryside growing through the entire season. Nettle is used for preparing herbal tea infusions, as a part of diet and also as a medicine. It is easy to be found in the field and this is why the number of samples of the nettle is the highest. The F_t in the samples of nettle collected in the area of the main wind direction are considerably higher than contrary to the main direction, 70.5–100 mg kg^{-1} as opposed to 10–28 mg kg^{-1}. The nettle in the clean area contained F_t contents close to the background values of F_t in plants, 10 mg kg^{-1}. Results of the F_t and F_f^- determinations in the soil demonstrate that both F_t and F_f^- are higher in the area of the main wind, than contrary to this direction, although the soil type supposed to be the same. An increase in F_t and F_f^- contents with the distance from the source is observed. This is in accordance with Dässler and Grumbach [20], who were able to detect fluoride-containing gases emitted under very humid conditions at a distance of 1–2 km from the emitter, and reported that fluoride levels at a distance of 7–8 km from the source could be higher than in nearby zones. As to clean area it is evident that the contents of F_t are lower or comparable to the contents of F_t in the vicinity of the emitter but the contents of F_f^- are substantially lower. It is therefore possible to conclude that increased contents of F_f^- in soil from the area around the emitter, as compared to the clean area, are due to the fluorine emissions – pollution.

Table 6
Correlation coefficients between each pair of variables: $F_{t\ nettle}$, $F_{t\ soil}$, $F_f^-{}_{soil}$, pH, and wind.

	$w(F_t)_{nettle}$	$w(F_f^-)_{nettle}$	$w(F_t)_{soil}$	$w(F_f^-)_{soil}$	pH	Wind factor
$w(F_t)_{nettle}$	1					
$w(F_f^-)_{nettle}$	0.909	1				
$w(F_t)_{soil}$	0.373	0.574	1			
$w(F_f^-)_{soil}$	0.893	0.682	0.081	1		
pH	−0.265	−0.577	−0.305	−0.040	1	
Wind factor	0.885	0.838	0.342	0.848	−0.445	1

In order to evaluate the influence of each variable on the contents of F_t and F_f^- in common nettle correlation coefficients between each pair of variables determined during the study were calculated. The results are listed in Table 6.

The results (Table 6) indicate that the contents of F_t and of F_f^- in the nettle are highly dependent on the F_f^- content of soil and on the wind direction, while less expressed, but still of importance are influences of the F_t content of the soil and its pH. The correlation between other coefficients is low, with the exception of the wind correlating well with the $F_{t\ soil}$, $F_f^-{}_{soil}$, and wind direction.

As good correlation between the contents of F_t and of F_f^- in nettle and content of F_f^- in soil was observed, the contents of F_t and F_f^- determined in nettle were plotted against contents of F_f in soil and straight lines were fitted to the measured points by the least square method (Fig. 1).

As shown in Fig. 1, a straight line with relatively good R^2 for in-the-field conditions of the nettle growth with a value of 0.7962 was obtained when fitting the contents of F_t in nettle against the contents of F_f^- in the soil, while no relationship has been obtained for the dependence of the F_f^- contents of the nettle on the F_f^- contents of the soil.

The data were evaluated also by multiple regression analysis. The following dependency was obtained:

$$w(F_t)_{nettle} = -135.477 + 15.069w(F_f^-)_{nettle} - 0.034w(F_t)_{soil} + 16.977\,pH + 17.931\,wind \quad (1)$$

with R^2 = 0.9867 and R^2 adjusted for the number of measurements R^2(adj) = 0.9205.

Based on the results of linear regression and multiple regression analysis it is possible to conclude that the nettle is the plant, able to uptake free fluoride from the soil and to accumulate it. The most important factor influencing the uptake of free fluoride from the soil has been shown to be the content of labile or free fluoride F_f^- available in the soil. This is in agreement with the previously published results for some other plants [13]. In addition also the F_t contents of the soil, pH of the soil and wind factor seems to have an important impact on the contents of fluoride in the nettle. Additional experiments are however required to confirm these

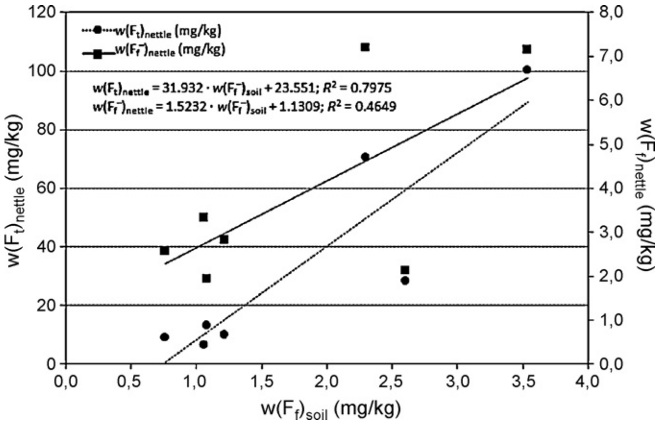

Fig. 1. The contents of F_t and of F_f^- determined in the nettle against the contents of F_f^- in soil and regression lines obtained by the least square method.

observations and to make statistical evaluation of the data on the uptake of fluoride by the nettle more reliable.

4. Conclusions

Signs of acute fluorine intoxication with airborne fluorides appeared on the vegetation around the aluminium smelter in Slovenia in autumn 2005. Increased contents of total fluoride were detected in the samples of corn and male corn heads. These contents exceeded the maximum allowable content of fluorine in feeding stuffs, including meadow grass. Higher contents of F_t found in the soil in the area in the wind direction as opposed to the contrary direction in the area around the emitter could be ascribed to pollution with airborne fluoride.

Different plants used for preparing herbal tea infusions (samples collected in the surroundings of aluminium smelter in 2010) and commercially available herbal teas were studied on the possible fluoride uptake from the soil. Nettle has been found to be a promising passive bioindicator for monitoring phytotoxic effects of fluoride present in the soil on plants. The uptake of fluoride was correlated to the contents of free fluoride present in the soil.

Nettle is widely used for preparing tea infusions and also represents an important part of the human nutrition. Therefore care should be taken, especially in the areas with high contents of F_f^- in the soil, on the possible too high intakes of fluoride with diet.

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