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FLUORINE CONTENT IN SOILS OF NORTHERN POMORAVLJE

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Abstract: Soil sampling was carried out in the Velika Morava river valley, covering the area from Velika Plana to the mouth of Morava to the Danube. The composite soil samples, representing alluvial soils (22 samples), cambisols (14) and smonitzas (4), were taken from plough layers, based on a regular square grid with intervals set at 5x5 km, covering total area of 100,000 ha. The total and available fluorine contents were determined in the soils samples. The highest average amount of total fluorine was found for alluvial soils (391 mg kg^{-1}), then for smonitzas (348 mg kg^{-1}) and the lowest one for cambisols (285 mg kg^{-1}). These amounts are within normal fluorine content for soils (150-400 mg kg^{-1}), although the maximum found levels were even about 500 mg kg^{-1}. The available fluorine content was very low (< 1 mg kg^{-1}), being mostly less than 0.2 % from its total amount, so it could be concluded that there was no danger from fluorine accumulation in the plants. Statistically significant correlation coefficient between total and available fluorine contents was not obtained. The total and available fluorine contents have mostly been in the correlation (with positive sign) with soil pH and the content of mechanical fraction silt+clay. Significant correlation coefficients between total fluorine content and the content of some heavy metals (Cr, Ni, Co, Cu, As) were also found, which indicated their mutual geochemical origin.

Key words: fluorine, content, total, available, soil.

Introduction

Fluorine is a typical litophilic element, mainly present in neutral (intermediate) and acid igneous rocks (850-1000 mg kg^{-1}). In surface sediments, it is mostly associated with clay fraction. There are not many stable fluorine minerals, among which, topaz – $Al_2(F,OH)_2SiO_4$ and fluorite – CaF_2 are widely distributed.

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Fluorine can replace hydroxyl ions in different minerals and, consequently, forms fluorapatite – $Ca_{10}(PO_4)_6F_2$, which is a common fluorine mineral in the sediments and soils. The same trend leads to an increase of its content in primary minerals (amphiboles and micas), as well as in clay minerals (ilits). Close relationship between fluorine and phosphate was observed at both primary and secondary minerals.

During the decomposition of igneous rocks, fluorine forms bonds with silicates, which leads to its high content in the residuum. Under natural conditions, fluorapatite and phosphorite have very low solubility, while cryolite – Na_3AlF_6 and similar minerals are easily soluble. Clays and phosphorite absorb fastly the soluble fluorine. Clay minerals, soil pH and Ca, P and Al concentrations in soil control fluorine content in a soil solution. Adsorption of fluorine in a soil is highest at acid and neutral reaction (pH=6-7).

Besides the principal fluorine containing mineral in a soil – fluorapatite, there are also other minerals, such as: CaF_2, AlF_3 and $Al_2(SiF_6)_2$. Fluorine can form complex ions with aluminum (AlF^{2+}, AlF_2^{+}, AlF_4^{-}), so it can control the activity of Al^{3+}-ions in a soil solution. Under ordinary conditions, fluorine has a low mobility in a soil and does not accumulate in upper soil horizons, especially in acid soils, where is more soluble and susceptible to greater leaching. Fluorine content in different soils is determined by its concentration in a parent material, while its distribution in soil profile depends on the rate of mineral decomposition, pH and content of the clay fraction (Omueti and Jones, 1980).

The average content of total fluorine for "world soils"amounts to 320 mg kg^{-1}. The lowest amounts are found in sandy soils in humid climate, while the highest ones are found in soils with high clay content and soils formed on igneous rocks. For most soils, the content of total fluorine ranges from 150 to 400 mg kg^{-1}, although the wider range is the characteristic of higher contents (Kabata-Pendias and Pendias, 1989). In the soils with high clay content total fluorine may exceed even 1000 mg kg^{-1}. In the areas with high fluorine content in a soil, an endemic disease – fluorosis has been recorded (Beljakova, 1977).

The aluminum smelters and factories of phosphatic fertilizers are some of the artificial sources of fluorine in a soil. There are, also, steel mills, industries of ceramics and glass, as well as coal combustion. Other possible sources are mineral fertilizers, sewage sludges, wastewaters and some pesticides. The fluorine from the artificial sources is easily soluble, but its greater portion fastly disappears from a soil solution due to bounding to some soil components: clay, Ca, P and Al, or due to leaching process in sandy soils (Kabata-Pendias and Pendias, 1989).

Airborne fumes of HF acid are the most dangerous consequence of soil contamination with fluorine. They may cause dissolution of clay and other silicates and their complexes with organic matter. That leads to destruction of soil structure and a decrease of humus content. As for plants, they poorly take up the soluble F^- -ions from soil solution. Concentration of fluorine in plants is frequently very low and has no correlation with its total content in a soil. Because of that, fluorine toxicity to animals and plants has not been recorded. But, there are records that airborne fumes of hydrogen fluoride damages the foliage of plants, which was especially observed in vine and fruits (Brewer,1966).

Up to today, there have not been any records of natural fluorine levels or its artificial inputs in our soils. For that reason, having the representative soil samples from the Velika Morava river valley, in which the content of different heavy metals (Jakovljevic et al., 1997) and selenium (Jakovljevic et al., 1995) have already been obtained, we decided to determine the total and available fluorine content in these soils.

Material and Method

Soil sampling was carried out in the Velika Morava river valley, covering the area from Velika Plana to the mouth of Morava to the Danube. The composite soil samples, which represent alluvial soils (22 samples), cambisols (14) and smonitzas (4), were taken from plough layers (0-20 cm), based on a regular square grid with intervals set at 5x5 km, according to the map 1:200 000.

The basic chemical soil properties, mechanical analysis and heavy metals content were determined by standard analytical methods.

The total fluorine content was determined by ion-selective electrode for F, after the decomposition of soil samples by fusion with NaOH in Ni crucibles, at 600 ^{0}C for 30 minutes. The fused samples (fusion cake) were dissolved with deionized water and mixed with TISAB buffer solution before electropotential measurement (McQuaker and Gurney, 1977).

The extraction with water (soil:water ratio 1:1, with occasional stirring, followed with vacuum pump filter method), was applied for the determination of available fluorine in the soil samples. In the filtrate aliquot, pH was adjusted with buffer solution and potentiometric measurement of fluorine content by ion-selective electrode was carried out.

The results obtained were statistically processed using STATISTICA for Windows 4.3b.

Results and Discussion

The basic chemical and physical soil properties are given in table 1. The analyzed chemical and physical soil properties show the wide variation range, especially in alluvial soil, as can be seen from the results obtained. It is evident that alluvial soils have higher humus, available phosphorus and available potassium content, comparing with cambisols. Content of mechanical fractions silt and clay and CEC are also higher in alluvial soils. These results have been more precisely discussed earlier (Jakovljevic et al., 1997), where total heavy metals content and the methods of their determination had also been given.

Tab. 1. – Chemical and physical properties of the investigated soils (mean, standard deviation and range)

Soil type	pH H_2O	pH nKCl	Humus (%)	Available (mg/100g) P_2O_5	Available (mg/100g) K_2O	CEC (meq/100 g)	Silt (%)	Clay (%)	Silt+Clay (%)
Alluvial soils (n=22)	7.06±0.63 5.80-8.30	5.80±0.67 4.50-7.10	3.19±0.37 2.57-4.03	17.8±13.9 1.4-60.0	30.1±6.9 19.4-53.0	36.9±5.8 27.4-54.1	27.9±6.4 16.6-43.0	42.5±7.1 33.7-64.9	70.4±8.6 58.3-89.1
Cambisols (n=14)	6.72±0.74 6.00-8.20	5.45±0.83 4.60-7.10	2.55±0.41 1.91-3.45	8.2±6.3 2.0-26.4	21.5±3.2 15.4-26.4	28.0±3.7 23.8-36.5	26.1±4.5 15.3-32.0	32.5±4.1 24.3-38.9	58.7±6.6 39.6-65.8
Smonitzas (n=4)	7.10±0.65 6.50	5.91±0.65 5.20-6.60	3.13±0.39 2.75-3.67	14.3±14.6 1.2-35.0	31.9±9.5 23.4-45.0	32.3±2.6 28.7-34.6	26.0±3.1 21.4-28.2	37.8±3.7 32.4-40.4	63.9±6.9 53.8-68.6
t-test Al. Vs Camb.	ns	ns	4.89**	2.63**	5.04**	5.06**	ns	4.75**	4.39**

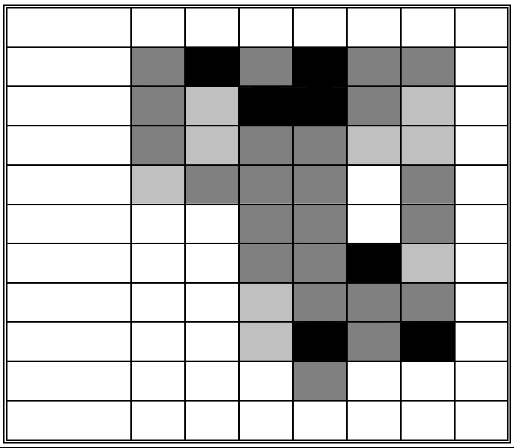
** - significant at 0.01 probability level
 * - significant at 0.05 probability level
ns – not statistically significant

Total and available fluorine contents in the investigated soil samples are given in table 2., while area distribution of total fluorine is given in figure 1. The highest average value of total fluorine content was found in alluvial soils (391 mg kg^{-1}), then in smonitzas (348 mg kg^{-1}) and the lowest one in cambisols (285 mg kg^{-1}). These values are within normal levels for soils (150-400 mg kg^{-1}). But, the maximum content of total fluorine in some alluvial and smonitzas samples have been almost 500 mg kg^{-1}. That is in agreement with literature data, since these soils have higher clay content, compared with cambisols.

Tab. 2. – Contents of total and available fluorine in Pomoravlje soils (mean, standard deviation and range)

Soil type and number of samples	Total F (mg kg^{-1})	Available F mg kg^{-1}	Available F % from total F
Alluvial soils (n=22)	390.9±78.4 273-514	0.31±0.17 0.09-0.93	0.08±0.03 0.02-0.19
Cambisols (n=14)	285.3±45.2 198-346	0.31±0.17 0.11-0.69	0.11±0.07 0.03-0.24
Smonitzas (n=4)	347.7±135.5 198-514	0.22±0.07 0.13-0.29	0.07±0.03 0.04-0.10
t-test Al.Vs Camb. Al. Vs Sm. Camb. Vs Sm.	4.56** ns ns	/	/

Much higher content of total fluorine in the alluvial samples, comparing with cambisols, corresponds to the higher content of some heavy metals, such as: Ni, Cr, Pb, Zn and As, in these soils (Jakovljevic et al., 1997). This may be a consequence of their mutual origin, since the same level of these elements could be found in a parent material on which investigated soils are formed. Namely, both heavy metals and fluorine may originate from mountains abundant with mineral ores, which contribute to the Velika Morava river basin (for example Rudnik mountain). The cambisols, formed on quite different parent material – loess, have lower both fluorine and heavy metals content. Significantly higher content of total fluorine in alluvial soils and smonitzas (formed on young and lower alluvial flats near the mainstream of Morava) can be seen in figure 1., which shows its spatial distribution.



Fluor (ppm)	198-235	235-287	287-388	388-462	462 - 514

Fig. 1. – Fluorine content and distribution in Pomoravlje soils

Much less difference between the investigated soils have been obtained for available fluorine content, which amounts from 0.1 to maximum 0.9 mg kg^{-1}, with average 0.2 and 0.3 mg kg^{-1}. When available fluorine is expressed in percentage from the total content, obtained values are even lower and are in the range from 0.02 to 0.24%, while average available fluorine content in relation to its total one ranges from 0.07 to 0.11%. Such low available fluorine content in the investigated soils confirms, as it was emphasized in the introduction, that different soils can bound soluble fluorine, so it is present mostly in a form of less soluble compounds. Also, fluorine availability is much more dependent on soil's capacity for its bounding than on total fluorine content. For that reason, statistically significant correlation coefficient between the total and available fluorine content has not been obtained.

Both total and available fluorine contents, being within its normal range for soils in the investigated soil samples, indicate its geochemical origin, without any form of artificial contamination. So, a danger from fluorine accumulation in plants or its toxicity to human and animals are not to be expected. The food produced in the investigated area is, in regard of fluorine content, unpolluted.

Correlation coefficients between the total and available fluorine contents obtained and the basic chemical and physical soil properties (table 3), as well as

Tab. 3. – Correlation coefficients between fluorine content (total and available) and basic chemical and physical soil properties

Soil type	pH H_2O	pH nKCl	Humus	Available P_2O_5	Available K_2O	CEC	Silt	Clay	Silt +Clay
				Alluvial soils					
Total F	0.62**	0.63**	ns	ns	ns	ns	ns	ns	0.56**
Avail. F	ns	ns	ns	ns	ns	ns	ns	ns	ns
				Cambisols					
Total F	ns	ns	ns	ns	ns	ns	0.78**	ns	0.66**
Avail. F	0.57*	0.59*	0.60*	ns	ns	0.53**	ns	ns	ns
				Smonitzas					
Total F	ns	ns	ns	ns	ns	ns	ns	ns	ns
Avail. F	ns	0.94*	ns	ns	ns	ns	ns	ns	ns

Tab. 4. – Correlation coefficients between total fluorine and total heavy metals contents in Pomoravlje soils

Heavy metals	Mn	Zn	Cu	Co	Cr	Pb	Ni	Cd	As	Hg
					Alluval soils					
Total F	ns	ns	0.46*	0.46*	0.61**	ns	0.42*	ns	ns	ns
					Cambisols					
Total F	ns	ns	ns	ns	-0.71**	ns	-0.63*	ns	ns	ns
					Smonitzas					
Total F	ns	ns	ns	ns	ns	ns	0.94*	ns	0.97*	ns

between the total fluorine content and heavy metals contents (table 4) may contribute to a better understanding of fluorine nature in the investigated soils. Statistically significant correlation coefficients were found for soil pH and, in some cases for silt+clay content, clay content, CEC and humus content. This is in agreement with the nature of fluorine in a soil, as was already mentioned in the introduction. Regarding correlations between fluorine and some heavy metals, the greatest number of positive coefficients has been obtained for alluvial soils (between total fluorine and Cr, Ni, Co, Cu and As), which may lead to a conclusion that these elements occur in the mutual metal associations and have mutual origin in the alluvial sediments from the Velika Morava river valley. Contrary to that, no positive coefficients were found for cambisols, while between the total fluorine and total Ni and Cr in this soil type statistically significant correlation coefficients have a negative sign. This confirms difference between origin and nature of fluorine in the alluvial soils and cambisols.

Conclusion

On the basis of the results shown, the following conclusions can be made:

The investigated alluvial soils and cambisols significantly differ regarding their total fluorine content. But, values obtained for both soil types are within normal fluorine levels for soils. So, danger from fluorine accumulation in plants does not exist, while the food produced in the investigated area is, in regard of fluorine content, unpolluted.

Significantly higher total fluorine content was found for the alluvial soils, in relation to cambisols, which is in agreement with the elevated content of some heavy metals (Cr, Ni, Co, Cu, As) in these soil samples. Composition of the parent material, which is greatly different from the loess on which cambisols have been formed, has the decisive influence on the higher fluorine and heavy metals contents in the alluvial soils. This leads to the conclusion that fluorine and heavy metals originate from the same mineral sediments from mountains (for example Rudnik) that contribute to the Velika Morava river basin.

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SADRŽAJ FLUORA U ZEMLJIŠTIMA SEVERNOG POMORAVLJA

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R e z i m e

U dolini reke Velike Morave, u delu od Velike Plane do njenog ušća u Dunav, uzeti su reprezentativni uzorci zemljišta iz orničnog sloja, po mreži kvadrata veličine 5x5 km. U njima su odredjeni ukupni i pristupačni sadržaji fluora. Istraživanjem su obuhvaćena aluvijalna zemljišta (22 uzorka), gajnjače (14) i smonice (4), što odgovara površini od 100. 000 ha.

Za ukupni fluor najviše srednje vrednosti su nadjene u aluvijumima (391 ppm), zatim u smonicama (348 ppm) i najmanje u gajnjačama (285 ppm). Ove vrednosti se nalaze u granicama normalnih sadržaja za zemljišta (150-400 ppm), mada se maksimalne vrednosti kreću i oko 500 ppm. Pristupačni sadržaj fluora je u ispitivanim zemljištima jako nizak (< 1 ppm), što najčešće čini ispod 0,2 % od ukupnog fluora, pa se može zaključiti da ne postoji opasnost od akumulacije fluora u biljkama koje se gaje na ispitivanom području. Nije nadjena korelativna veza ukupnog sa pristupačnim fluorom. Sadržaji ukupnog i pristupačnog fluora su najčešće bili u korelaciji (pozitivnoj) sa pH vrednošću zemljišta, i sadržajem frakcije prah+glina. Nadjene su i korelativne veze ukupnog fluora sa sadržajima nekih teških metala (Cr, Ni, Co, Cu, As), što ukazije na njihovo zajedničko geohemijsko poreklo.

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