CONTENT OF FLUORINE IN SOILS IN THE VICINITY OF ALUMINIUM PLANT IN PODGORICA

S. Blagojević, M. Jakovljević and Mirjana Radulović

Abstract: The purpose of this paper was to determine whether soils, located in the vicinity of the aluminium plant in Podgorica, are polluted with fluorine. For this purpose 60 soil samples (26 of brown and 34 of alluvial soil) were collected from two depths (0 to 20 and 20 to 40 cm). Total and available fluorine were determined by potentiometric method, after necessary preparations of soil samples for the analysis. It was found that in almost all soil samples the content of total fluorine was above 300 mg/kg – maximum permissible value for the content of this element in agricultural soils. Highest values were found on locations southwards of the aluminium plant. However, the content of available fluorine (soluble in water) in the soil samples is very low (average value is 0.70 mg/kg) indicating that major part of deposited fluorine had transformed itself into insoluble compounds like CaF₂.

Key words: fluorine, soils, aluminium plant.

Introduction

The content of total fluorine in normal soils is usually in the range from 150 to 400 mg/kg. Values that exceed 1000 mg/kg have been registered in some heavy clayey soils. Fluorine is usually present in soils in the form of the following minerals: fluorite - CaF₂; fluoroapatite - Ca₁₀(PO₄)₆F₂; cryolite - Na₃AlF₆. These minerals are sparingly soluble in water, so that only small amounts of F are taken up by plants.

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Artificial sources of soil pollution with fluorine are: aluminium smelters, phosphorus fertilizer factories, ceramic and glass industry, combustion of coal. This halogen element is also introduced into soil through the application of phosphorus fertilizers, sewage sludges and some pesticides.

The content and distribution of F in soils around aluminium plants was investigated in a number of papers published over the last ten years (Wenzel and Blum, 1992; Sarayev, 1993; Haidouti et al., 1993; Arnesen et al., 1995; Notcutt and Davies, 2000). The results obtained in these papers indicate that aluminium industry is an important source of soil contamination with fluorine. So, Arnesen et al. (1995) found that fluorine pollution of soil can be traced for more than 30 km from one of aluminium smelters in Norway.

The purpose of this paper was to determine whether soils located in the vicinity of aluminium plant in Podgorica (Montenegro) are polluted with fluorine. It is important to mention that no investigation of this kind has been conducted in our country.

Material and Methods

Representative soil samples were taken from a network of squares the position of which, in relation to aluminium plant, is presented in figures 1 and 2. The size of each square is 1.67x1.67 km. A total of 60 soil samples (26 of brown and 34 of alluvial soil) was collected from two depths (0 to 20 and 20 to 40 cm).

Total soil fluorine was determined by means of ion-selective electrode for F after fusion of the samples with NaOH (in Ni crucibles) at 600°C (McQuaker and Gurney, 1977).

The aforementioned electrode was also used for the determination of available soil fluorine. This was done after extraction of the soil samples with distilled water (Brewer, 1965).

Basic agrochemical properties and mechanical composition of the investigated soil samples were determined by standard methods of soil analysis.

The analytical data obtained were subjected to statistical analysis by means of the computer program STATISTICA for WINDOWS 4.3b.

Results and Discussion

The results of the determination of some important chemical and physical properties of the investigated soil samples are presented in table 1.

It can be seen that there is a wide variation in all investigated soil properties. So, for example, the content of CaCO₃ in the investigated samples ranged from 0 to 80%. These properties will not be commented, because the only purpose of their determination was to see their correlations with total and water-soluble soil fluorine.

Tab. 1. - Some chemical and physical properties of the investigated soil samples
Content of fluorine in soils in the vicinity of aluminium plant in Podgorica

<table>
<thead>
<tr>
<th>Property</th>
<th>Mean</th>
<th>Range</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH in H₂O</td>
<td>7.02</td>
<td>5.50-8.05</td>
<td>0.64</td>
</tr>
<tr>
<td>pH in 1M KCl</td>
<td>5.75</td>
<td>4.20-6.40</td>
<td>0.56</td>
</tr>
<tr>
<td>CaCO₃ (%)</td>
<td>14.73</td>
<td>0.00-80.00</td>
<td>18.60</td>
</tr>
<tr>
<td>humus (%)</td>
<td>2.87</td>
<td>0.77-5.66</td>
<td>1.06</td>
</tr>
<tr>
<td>available phosphorus (mg P₂O₅/100 g)</td>
<td>7.7</td>
<td>0.2-50.0</td>
<td>10.2</td>
</tr>
<tr>
<td>available potassium (mg K₂O/100 g)</td>
<td>14.2</td>
<td>5.8-50.0</td>
<td>8.00</td>
</tr>
<tr>
<td>sand (%)</td>
<td>52.19</td>
<td>29.05-76.25</td>
<td>11.82</td>
</tr>
<tr>
<td>silt (%)</td>
<td>33.29</td>
<td>17.43-51.97</td>
<td>8.23</td>
</tr>
<tr>
<td>clay (%)</td>
<td>14.52</td>
<td>5.28-30.88</td>
<td>5.85</td>
</tr>
<tr>
<td>silt + clay (%)</td>
<td>47.81</td>
<td>23.75-70.95</td>
<td>11.79</td>
</tr>
</tbody>
</table>

Spatial distribution of fluorine content in the soils is presented in figures 1 and 2.

Fig. 1. - Spatial distribution of fluorine in soil at the depth from 0-20 cm
Most of the investigated soil samples have values for total F content above 300 mg/kg, which is maximum permissible value for the content of this element in agricultural soils (Pravilnik, 1990). Highest values for total F content are noticed on locations within and southwards of the aluminium plant. This especially refers to soil layer from 0 to 20 cm. We suppose that this was caused by wind blowing from north to south. The results of other authors also indicate that soils in the vicinity of aluminium plants are polluted with fluorine. Haidouti et al. (1993) studied the effect of fluoride emissions from an aluminium plant in Greece on the concentration of fluoride in soils and vegetation. In soils total F concentrations ranged from 298 to 824 ppm, whilst in controls the values were from 95 to 109 ppm.

Data for the content of total and available fluorine in the investigated soil samples were subjected to statistical analysis. The results of this analysis are shown in table 2. Statistical significance of difference between mean values for fluorine content was evaluated for the two soil types and two depths (0-20 and 20-
40 cm). This was done by means of a t-test for independent and dependent samples, respectively.

### Table 2: Statistical analysis of data on the content of total and available fluorine in the investigated soil samples

<table>
<thead>
<tr>
<th></th>
<th>Number of samples</th>
<th>Range</th>
<th>Mean</th>
<th>Standard deviation</th>
<th>Significance of difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total F (ppm)</td>
<td>60</td>
<td>217-696</td>
<td>427</td>
<td>92</td>
<td>-</td>
</tr>
<tr>
<td>Available F</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(ppm)</td>
<td>60</td>
<td>0.06-2.67</td>
<td>0.70</td>
<td>0.52</td>
<td>-</td>
</tr>
<tr>
<td>Available F</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(in % of total)</td>
<td>60</td>
<td>0.013-0.575</td>
<td>0.167</td>
<td>0.124</td>
<td>-</td>
</tr>
<tr>
<td>Total F (ppm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a) brown soil</td>
<td>26</td>
<td>271-696</td>
<td>464</td>
<td>118</td>
<td>a-b **</td>
</tr>
<tr>
<td>b) alluvial soil</td>
<td>34</td>
<td>312-519</td>
<td>398</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>c) 0-20 cm</td>
<td>30</td>
<td>271-696</td>
<td>434</td>
<td>106</td>
<td>c-d /</td>
</tr>
<tr>
<td>d) 20-40 cm</td>
<td>30</td>
<td>284-638</td>
<td>420</td>
<td>75</td>
<td></td>
</tr>
<tr>
<td>Available F</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(ppm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a) brown soil</td>
<td>26</td>
<td>0.06-2.67</td>
<td>0.53</td>
<td>0.59</td>
<td>a-b *</td>
</tr>
<tr>
<td>b) alluvial soil</td>
<td>34</td>
<td>0.16-2.15</td>
<td>0.82</td>
<td>0.44</td>
<td></td>
</tr>
<tr>
<td>c) 0-20 cm</td>
<td>30</td>
<td>0.13-2.67</td>
<td>0.82</td>
<td>0.57</td>
<td>c-d *</td>
</tr>
<tr>
<td>d) 20-40 cm</td>
<td>30</td>
<td>0.06-2.15</td>
<td>0.58</td>
<td>0.46</td>
<td></td>
</tr>
</tbody>
</table>

* statistically significant at the 0.05 probability level
** statistically significant at the 0.01 probability level
/ not significant

It can be seen from the table that there is a very wide variation in the content of available (water soluble) F. Namely, the lowest value is 0.06 and the highest 2.67 mg/kg. These values are lower than the ones which Grewal and Dahiya (1992) found for the soils of different agroclimatic zones of the Haryana state in India. They found a mean value of 4.19 mg/kg for the entire state. The results presented in table 2 indicate that available F presents only a very small part of total soil fluorine. The mean value for its content (in % of total F) is 0.17. This fact indicates that most of fluorine that comes from the aluminium plant is present in nearby soils in sparingly soluble forms such as CaF₂. This is especially valid for calcareous soils. It is known (Kabata-Pendias and Pendias, 1989) that reduced mobility of F in calcareous soils occurs due to formation of weakly soluble CaF₂ and complexes of F with iron, aluminium and silicon. Most of the soil samples that we studied were calcareous with CaCO₃ content ranging from 1 to 80%.

When two soil types and two depths are compared, the following can be said. Brown soil contains, on average, more total F and less water-soluble form of this
Both differences are statistically significant. The two depths differ significantly with respect to the content of water-soluble F. More water-soluble F is present in the first soil layer (from 0-20 cm). The layer from 0-20 cm contains, on average, more total F but the difference is not statistically significant. Šarayev (1993), who studied F content in the soils of the Minusinsk lowland (Russia) in the zone of action of an aluminium plant, found an increase in the amount of fluorine in the upper part (5 cm) of the soil profile. Our results indicate that there is atmospheric deposition of F on to the surface of soils in the vicinity of aluminium plant in Podgorica. The investigated soils have naturally high contents of fluorine, so that the effects of this pollution are less pronounced than the results of the mentioned authors.

Correlation coefficients between fluorine content (total and available) and some important chemical and physical soil properties were calculated. The results are presented in table 3.

<table>
<thead>
<tr>
<th>Property</th>
<th>Total F</th>
<th>Available F</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH in H₂O</td>
<td>0.06</td>
<td>0.26*</td>
</tr>
<tr>
<td>pH in 1M KCl</td>
<td>0.11</td>
<td>0.30*</td>
</tr>
<tr>
<td>CaCO₃ (%)</td>
<td>-0.22</td>
<td>0.30*</td>
</tr>
<tr>
<td>humus (%)</td>
<td>0.31*</td>
<td>0.32*</td>
</tr>
<tr>
<td>available phosphorus</td>
<td>-0.12</td>
<td>0.12</td>
</tr>
<tr>
<td>available potassium</td>
<td>0.13</td>
<td>-0.01</td>
</tr>
<tr>
<td>total F</td>
<td>-</td>
<td>0.10</td>
</tr>
<tr>
<td>sand</td>
<td>-0.36*</td>
<td>0.29*</td>
</tr>
<tr>
<td>silt</td>
<td>0.28*</td>
<td>-0.21</td>
</tr>
<tr>
<td>clay</td>
<td>0.33*</td>
<td>-0.30*</td>
</tr>
<tr>
<td>silt + clay</td>
<td>0.36*</td>
<td>-0.29*</td>
</tr>
</tbody>
</table>

* statistically significant at the 0.05 probability level

It can be seen that there are significant correlations between total F content, on one side, and the contents of humus, sand, silt and clay, on the other side. However, the values for correlation coefficients are low. Significant and positive correlations were found between available F and soil pH (in water and 1M KCl) as well as the contents of CaCO₃, humus and sand. The obtained values for correlation coefficients are low, ranging from 0.26 to 0.32. It is interesting to note that there is no significant correlation between total and available fluorine.

**Conclusion**
On the basis of the results obtained, the following important conclusions can be drawn.

1. Most of the investigated soil samples have values for total fluorine above 300 mg/kg - maximum permissible value for the content of this element in agricultural soils. These soils have naturally high contents of fluorine.

2. Highest values were found on locations within and southwards of the aluminium plant, indicating the existence of artificial pollution of these soils with fluorine.

3. The content of available fluorine (soluble in water) in the soil samples is very low (average value is 0.70 mg/kg), indicating that major part of deposited fluorine had transformed itself into insoluble compounds like CaF$_2$.

4. Brown soil contains, on average, more total F and less water-soluble form of this element than alluvial soil. Both differences are statistically significant.

5. Correlation coefficients between fluorine content and some important chemical and physical soil properties have low values.

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SADRŽAJ FLUORA U ZEMLJIŠTIMA U BLIZINI ALUMINIJUMSKOG KOMBINATA U PODGORICI

S. Blagojević, M. Jakovljević i Mirjana Radulović

Rezime

Cilj ovog rada je bio da utvrdi da li su zemljišta, koja se nalaze u blizini aluminijumskog kombinata u Podgorici, zagadjena fluorom. U tu svrhu prikupljeno je 60 uzoraka zemljišta (26 uzoraka smedjeg i 34 uzorka aluvijalnog) i to sa dve dubine (0 do 20 i 20 do 40 cm). U prikupljenim uzorcima zemljišta određen je sadržaj ukupnog i pristupačnog fluora. Za ovo je korišćena potenciometrijska metoda sa fluoridnom jon-selektivnom elektrodom. Utvrđeno je da je kod većine ispitivanih uzoraka zemljišta sadržaj ukupnog fluora iznad 300 mg/kg – maksimalno dozvoljene vrednosti za sadržaj ovog elementa u poljoprivrednim zemljištima. Najveće vrednosti su nadjene na lokacijama južno od aluminijumskog kombinata. Medjutim, sadržaj pristupačnog fluora (rastvorljivog u vodi) u uzorcima zemljišta je vrlo mali (prosječna vrednost je 0,70 mg/kg), što znači da se najveći deo dospelog fluora transformisao u teško rastvorljiva jedinjenja kao što je CaF₂. Koeficijenti korelacije izmedju sadržaja fluora i nekih važnih hemijskih i fizičkih osobina zemljišta imaju male vrednosti.


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