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Concentrations of Heavy Metals in NPK Fertilizers Imported in Serbia

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SUMMARY

Concentrations of Pb, Cd, Cu and Mn in sixteen NPK fertilizers imported and widely used in Serbia were determined by flame atomic absorption spectrometry (AAS). The results show that contents of heavy metals varied significantly in different fertilizers depending on N:P:K ratio and fertilizer origin. Pb and Cd contents in water solution of fertilizers occurred at low ranges: 2.0-3.1 and 0.03-1.56 mg/kg, respectively. An NPK (15:15:15) fertilizer from Romania was found to contain the highest concentration of Pb and Cd as impurities. Cu content, ranging from 7.1 to 974.7 mg/kg, was the highest in coloured fertilizers from Hungary, the Netherlands and Greece. Mn value in a Hungarian NPK product (10:10:20) exceeds the average Mn value in soil.

The data indicate variable contents of heavy metals in fertilizers, some of which are significantly higher than natural concentrations in soil, which suggests that they need to be continuously monitored.

Keywords: Heavy metals; NPK fertilizers; Flame atomic absorption spectrometry

INTRODUCTION

Adding fertilizers to soil and plants is a common agricultural practice aimed at improving soil fertility and plant production. The FAO in Rome warned in 2005 that Serbia might become dependent on food imports. Enlarged food production volume begins by increasing crop yields through the use of higher amounts of fertilizers. Although fertilizers are predominantly beneficial in terms of plant production, they may also be potentially harmful as substances contaminating soil and both groundwater and surface waters.

Fertilizers usually get insufficiently purified in the manufacturing process and therefore often contain various levels of impurities, including heavy metals, depending on the quality of raw materials used for their production. As a result of accumulation of heavy metals in soil, groundwater and plants, toxic effects of these elements can become very harmful (Jagodin et al., 1991; Gupta and Gupta, 1998). Pb and Cd, for instance,

belong to a group of very toxic metals that can disturb metabolic processes (Travis and Haddock, 1980; Boeckx, 1986). On the other hand, Cu and Mn are essential elements for plants and living organisms generally, but should their concentrations exceed the respective average concentrations in soil, plants would uptake high amounts of these metals through the root system and so become harmful (Clark et al., 1981; Savage et al., 1981).

A high input of fertilizers in soil, particularly NPK, which in Serbia totals some 300-600 kg of the main components per ha of soil cultivated, i.e. 600-800.000 tons annually, may cause excessive additions of heavy metals in soil through the impurities of raw materials (Raven and Loeppert, 1997; Chen et al., 2006).

In Serbia, many fertilizer manufactures have closed down over the past decades. In addition, the leading manufacturer HIP-Azotara in Pančevo, which puts several NPK fertilizer products on the market, has recently sustained severe damages. We are therefore forced to import mineral fertilizers from various European and other countries.

Imported fertilizers tend to be of poor quality and are often delivered without appropriate quality control certificates. Despite the fact that heavy metal concentrations in fertilizers have been limited in several European countries, all fertilizers used in Serbia are still not being analysed for heavy metal contents in compliance with Standard Regulatives.

In this work, Pb, Cd, Cu and Mn concentrations in sixteen commercial NPK fertilizers of different types and origins were determined. The results obtained provided a basis for an assessment of risks from heavy metal toxicity in representative European and one American samples.

MATERIAL AND METHODS

Pb, Cd, Cu and Mn concentrations in inorganic NPK fertilizers were investigated by flame atomic absorption spectrometry (SpectrAA 220 – Varian) in oxidizing air-acetylene flame, under optimal conditions (Table 1). Nebulization rate was 5 mL/min in all measurements.

Sixteen commercial NPK fertilizers with different N:P:K ratios were analysed. The samples, originating from different countries, were: two Austrian samples (15:15:15), two Croatian (10:30:20 and 15:15:15), one Greek (19:9:27), two Hungarian (10:10:20 and 14:11:25), two Romanian (15:12:15 and 15:15:15), two Russian (16:13:16 and 16:16:16), four products from the Netherlands (18:11:18, 15:9:9, 16:15:25 and 12:13:12), and one American (15:11:29) NPK fertilizer.

The fertilizer samples were homogenized and grounded well in a blender. After drying at 105°C for 2 hours, an amount of about 1 g of each sample was dissolved in 100 mL of deionised water and the solutions were heated at 95°C for 30 minutes. After cooling at room temperature, the solutions were filtered with Milipore filters, in 50 mL volumetric flasks. The residues were washed by deionised water.

The same procedure was performed for fertilizer extraction with acetic solutions at pH 4.0 and 4.5. The choice of a solution was made upon the known fact that soils in Serbia are predominantly neutral to medium acid.

All reagents used in the experiments were of analytical grade and were checked for possible trace metal contamination. Deionized water was used in preparing stock solutions.

Table1. Instrumental parameters during Pb, Cd, Cu and Mn determination by flame AAS
Tabela 1. Instrumentalni parametri tokom određivanja Pb, Cd, Cu i Mn metodom plamene AAS

Instrumental parameters Instrumentalni parametri	Pb	Cd	Cu	Mn
Wavelength Talasna dužina (nm)	217.0	228.8	324.7	279.5
Lamp current Struja lampe (mA)	5.0	4.0	7.0	5.0
Slit width Širina otvora (nm)	1.0	0.5	0.5	0.2
Working range Radni opseg standarda (mg/kg)	0.1-0.5	0.01-0.08	1-5	1-6

RESULTS AND DISCUSSION

Pb concentrations in sixteen fertilizer samples analysed are presented in Table 2. It shows that in seven samples, i.e. both Austrian, three Dutch, one Hungarian (14:11:25) and one Russian (16:13:16), Pb was not detected. In the remaining samples, extracted in water solution, Pb was found in concentrations ranging from 2.0 to 3.1 mg/kg. The lowest contents of Pb were found in a Croatian (15:15:15) and the second Hungarian (10:10:20) NPK samples, while the highest were detected in Romanian and Russian samples. Interestingly, Pb contents in two NPK fertilizer products of the same origin (from Romania), 15:12:15 and 15:15:15, differed greatly. In the sample with the higher P content, Pb concentration was higher. This positive correlation was not dectected in all cases, i.e. in several other samples, such as those from Croatia (10:30:20), Hungary (14:11:25) and Russia (16:13:16), Pb was not found at all, which means that the raw materials used for preparing the series were of better quality.

As expected, Pb contents in the investigated samples were higher in acid solutions. In acetic buffer solution at pH 4.0 the detected values were on a scale from 8.5 to 11.1 mg Pb/kg. At pH 4.5, Pb concentration was the highest in one of the NPK samples from the Netherlands (6.4 mg Pb/kg).

Cadmium was detected in almost all of the analysed fertilizers and the levels in water solutions varied from 0.03 to 1.56 mg Cd/kg (Table 3). Considering the two NPK samples from Romania, Cd was found in higher concentration in the sample with higher P percentage, similar to the Pb content in the same samples. The data additionally confirm that contaminated raw materials were used for producing these samples.

The mean value of Cd concentrations is about 1.44 mg Cd/kg fertilizer which means that about 650 mg Cd per hectar is put into neutral soil annually. As Cd readily leaches through deeper soil layers, getting into groundwater and then to surface waters, the risk of contamination with fertilizers rich in Cd increases rapidly, especially in more acid soils.

Copper contents in the analysed samples are presented in Table 4. Evidently, the levels of this metal in the examined fertilizers, extracted in water and acid solutions, are highly variable depending on fertilizer type and origin. Cu values were found to vary on a large scale from 4.04 (in water solution) to 974.70 mg/kg (at pH 4.0) in one of the Hungarian samples, which is more than 240 times. The explanation for this considerable range is that some mixed fertilizers, such as the NPK samples from Greece, the Netherlands and Hungary, belong to a group of coloured mixed fertilizers in which copper sulfate was used as a colouring additive. Attention should be paid to the uncoloured NPK 14:11:25 sample from Hungary, which contained more than 90 mg Cu/kg.

Table 2. Pb concentrations in NPK fertilizers (mg/kg)
Tabela 2. Koncentracija Pb u NPK đubrivima (mg/kg)

Sample No. Br. uzorka	NPK fertilizer NPK đubrivo	Origin Poreklo	In water U vodi	At pH 4.5 Na pH 4,5	At pH 4.0 Na pH 4,0
1	15:15:15	Austria	nd	nd	nd
2	15:15:15	Austria	nd	nd	nd
3	10:30:20	Croatia	nd	nd	nd
4	15:15:15	Croatia	2.0	3.6	8.6
5	19:9:27	Greece	2.4	4.0	11.1
6	10:10:20	Hungary	2.0	5.2	8.5
7	14:11:25	Hungary	nd	nd	nd
8	15:12:15	Romania	2.6	4.2	9.9
9	15:15:15	Romania	3.1	4.4	10.7
10	16:13:16	Russia	nd	nd	nd
11	16:16:16	Russia	3.1	5.3	9.6
12	12:13:12	The Netherlands	nd	nd	nd
13	15:9:9	The Netherlands	nd	nd	nd
14	16:15:25	The Netherlands	nd	nd	nd
15	18:11:18	The Netherlands	2.4	6.4	10.5
16	15:11:29	USA	2.3	3.5	9.5

Table 3. Cd concentrations in NPK fertilizers (mg/kg)
Tabela 3. Koncentracija Cd u NPK đubrivima (mg/kg)

Sample No. Br. uzorka	NPK fertilizer NPK đubrivo	Origin Poreklo	In water U vodi	At pH 4.5 Na pH 4,5	At pH 4.0 Na pH 4,0
1	15:15:15	Austria	0.62	3.12	3.44
2	15:15:15	Austria	1.38	3.25	3.76
3	10:30:20	Croatia	1.56	2.53	2.62
4	15:15:15	Croatia	0.15	0.20	0.31
5	19:9:27	Greece	0.03	0.10	0.22
6	10:10:20	Hungary	0.30	0.35	0.42
7	14:11:25	Hungary	nd	nd	nd
8	15:12:15	Romania	0.10	0.17	0.27
9	15:15:15	Romania	0.24	0.46	0.50
10	16:13:16	Russia	nd	nd	nd
11	16:16:16	Russia	0.10	0.15	0.20
12	12:13:12	The Netherlands	0.10	0.20	0.40
13	15:9:9	The Netherlands	nd	nd	nd
14	16:15:25	The Netherlands	nd	nd	nd
15	18:11:18	The Netherlands	0.20	0.26	0.33
16	15:11:29	USA	0.30	0.35	0.41

Copper contents in nine NPK fertilizers is less than 30 mg/kg, which is satisfactory because the maximum allowed concentration for copper in soil and drinking water are 100 mg/kg and 0.1 mg/L, respectively (OGRS, 1994).

By using coloured mixed fertilizers, soil will accumulate more rapidly with the element used as a colouring reagent, so the application of coloured mineral fertilizers should be heavily restricted. The mean value of copper concentration in air-dried soil samples permissible by our Official Gazette is 50 mg/kg, which is sig-

Table 4. Cu concentrations in NPK fertilizers (mg/kg)
Tabela 4. Koncentracija Cu u NPK đubrivima (mg/kg)

Sample No. Br. uzorka	NPK fertilizer NPK đubrivo	Origin Poreklo	In water U vodi	At pH 4.5 Na pH 4,5	At pH 4.0 Na pH 4,0
1	15:15:15	Austria	10.93	13.26	18.62
2	15:15:15	Austria	8.70	11.05	16.18
3	10:30:20	Croatia	15.56	20.15	24.43
4	15:15:15	Croatia	7.08	10.02	13.01
5	19:9:27	Greece*	125.2	128.64	161.2
6	10:10:20	Hungary*	449.0	851.2	974.70
7	14:11:25	Hungary	91.55	98.45	112.06
8	15:12:15	Romania	13.53	14.57	17.62
9	15:15:15	Romania	9.20	10.6	14.30
10	16:13:16	Russia	4.04	8.39	11.74
11	16:16:16	Russia	23.15	30.76	36.33
12	12:13:12	The Netherlands*	206.49	208.94	209.81
13	15:9:9	The Netherlands*	376.85	456.66	609.97
14	16:15:25	The Netherlands*	185.50	201.73	239.43
15	18:11:18	The Netherlands*	215.87	218.32	227.33
16	15:11:29	USA	10.93	13.26	18.62

* Mixed fertilizers with copper sulfate as colouring additive
* Mešana đubriva sa dodatim bakar-sulfatom kao sredstvom za bojenje

nificantly lower than the concentrations determined in samples (OGRS, 1994).

The data shown in Table 4 also indicate that lower pH enables better solution capacity of copper, as expected, which is especially important for soils with lower pH.

Mn levels in the fertilizers investigated cover the widest range (Table 5). Concentrations of this potentially toxic metal vary from 8.75 (Austrian 15:15:15 sample) to 5236.65 mg Mn/kg of fertilizer (Hungarian 10:10:20 sample) in water solution. The reason for such a high variability in concentrations is the composition of raw materials used for fertilizers products. Hence, attention should also be directed to the quality of raw materials in order to prevent highly toxic concentrations. The extremely high Mn level of 9569.71 mg Mn/kg in a Hungarian NPK (10:10:20) sample extracted in a buffer at pH 4.0 is more than ten times higher than the average Mn level that can be found in soil (about 800 mg/kg). This value must be significantly lowered by rigorously controlling the manufacturing process of fertilizers.

Data acquired in this study of Pb, Cd, Cu and Mn contents in mineral NPK fertilizers imported in Serbia show considerable variation in their concentrations in water and acid solutions. Heavy metal concentrations exceeding the average values for normal soils can be very harmful. This is important particularly in terms of a need to use greater quantities of fertilizers in crops grown on neutral and acid soils, as it is often the case in our country.

These variable contents of Pb, Cd, Cu and Mn suggest that fertilizer chemical characterisation should be carried out on a regular basis in order to minimize persistent contamination of soils, surface and groundwaters and the biosphere in general.

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Table 5. Mn concentrations in NPK fertilizers (mg/kg)
Tabela 5. Koncentracija Mn u NPK đubrivima (mg/kg)

Sample No. Br. uzorka	NPK fertilizer NPK đubrivo	Origin Poreklo	In water U vodi	At pH 4.5 Na pH 4,5	At pH 4.0 Na pH 4,0
1	15:15:15	Austria	18.57	34.01	38.62
2	15:15:15	Austria	8.75	9.80	10.46
3	10:30:20	Croatia	64.17	72.44	74.43
4	15:15:15	Croatia	9.03	14.82	23.95
5	19:9:27	Greece	125.20	128.64	161.27
6	10:10:20	Hungary	5236.65	7099.00	9569.71
7	14:11:25	Hungary	751.72	759.86	828.71
8	15:12:15	Romania	13.53	14.57	17.62
9	15:15:15	Romania	9.20	10.60	14.30
10	16:13:16	Russia	52.20	58.22	61.94
11	16:16:16	Russia	125.64	128.61	219.14
12	12:13:12	The Netherlands	565.47	566.52	600.52
13	15:9:9	The Netherlands	228.32	485.27	554.83
14	16:15:25	The Netherlands	450.11	513.60	548.94
15	18:11:18	The Netherlands	590.51	646.75	720.14
16	15:11:29	USA	10.93	13.26	18.62

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Koncentracije teških metala u uvoznim NPK đubrivima u Srbiji

REZIME

Koncentracije Pb, Cd, Cu i Mn u šesnaest uvoznih NPK đubriva, koja se najčešće koriste u Srbiji, su određene metodom plamene atomske apsorpcione spektrometrije. Dobijeni rezultati pokazuju da sadržaj teških metala u uzorcima različitih đubriva značajno varira, što zavisi od odnosa N:P:K u ispitivanim uzorcima đubriva, kao i od samog porekla đubriva.

Koncentracije Pb i Cd su u uskom intervalu: 2,0-3,1, odnosno 0,03-1,56 mg/kg, respektivno. NPK đubrivo (15:15:15) uveženo iz Rumunije sadrži veoma visoke koncentracije Pb i Cd, koji se nalaze kao nečistoće u sirovinama za dobijanje ovog đubriva. Sadržaj Cu varira u znatno većem opsegu: od 7,1 do 974,7 mg/kg, jer je nekim mešanim đubrivima dodat bakar-sulfat kao sredstvo za bojenje. Najveći sadržaj Cu je nađen u obojenim, mešanim NPK đubrivima poreklom iz Mađarske, Grčke i Holandije, i prevazilazi vrednost maksimalno dozvoljene koncentracije Cu koja se može naći u zemljištu. Sadržaj Mn u mađarskom NPK đubrivu (10:10:20) je veći od prosečnog sadržaja Mn u zemljištu čak deset puta.

Ovi podaci ukazuju da je neophodno permanentno kontrolisati sadržaj teških metala u uvoznim đubrivima, u cilju smanjenja zagađenosti zemljišta, podzemnih i površinskih voda.

Ključne reči: Teški metali; NPK đubriva; plamena atomska apsorpciona spektrometrija