HEAVY METALS IN RELATION TO SOIL – FODDER – MILK

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Abstract

As the route of heavy metals in nature has a circular course, the consequences of their effects have great influence both on surroundings and people's health. The transport of heavy metals in relation to soil – fodder – milk was determined through concentration of lead, cadmium and zinc. Samples of soil and plants raised on it and used as fodder were analysed as well as milk samples taken from cows which were fed on that fodder. Samples were taken in certain time period and concentration values were statistically processed and correlated.
Key words: soil, fodder, milk, heavy metals.

Introduction

Because of their toxicity, long survival time, accumulation in nature and circular course in biosphere, heavy metals take a particular place among contaminants. According to previously pointed characteristics, especially accumulation in nature, the limits of heavy metals in environment are very strict, and the emission sources control severe with the tendency to achieve the level of so-called zero emission.
Heavy metals enter food chain mainly through plants. Mechanism of collecting, distribution, concentration and effects of heavy metals in plants cannot be generalized for the reason that they are exposed to heavy metals from air water and soil [1,2,3]. An increased content of heavy metals in soil can lead to their depositing in plant tissues, inhibit or block their physiological functions or make them unusable for nutrition. The soil with a low organic matter content is accessible to lead, cadmium and zinc absorption. By increasing oxygen characteristics of environment, absorption of elements except lead is increased too, which is probably related to undissolubility of Pb^{2+} salts such as $PbSO_4$. It means that, except lead, metal absorption is significantly lower in wet and reduction conditions [3]. Heavy metals are introduced into animals and human organisms through plants. Mammary glands in cows are the most physiologically active part and therefore the input and output of heavy metals in their organisms are clearly reflected through milk. Monitoring the route of heavy metals in relation soil-fodder-milk is important since the consequences of their activity have a great impact on both environment and people's health [4,5]. For these reasons, monitoring the route of heavy metals in the region of Kikinda (Vojvodina, Serbia and Montenegro) besides scientific has public interest as well

considering that this is an agrarian area with developed both metal and building material industries. However, favourable condition for such investigation is that there was a closed eco system in the region of Kikinda which was found ideal for monitoring the heavy metals transport, since the fodder produced on this soil was used on the cattle farm.

Method and material

Soil and fodder samples were collected in the area around Kikinda in the period from 1996 to 1997 from the plowed land on which fodder crops used on the cattle farm were raised. Milk was sampled on the cattle farm immediately after milking.

Soil samples, from a plowed layer (0-30 cm depth), were collected diagonally from the irrigated fields cultivated by cattle-feeding plants. Average sample was prepared by mixing five different samples. The weighed portion of 1 g of previously powdered and dried soil was transferred into a distillation flask. It was covered by 10 ml of concentrated HNO_3 and heated for 30 min. Then, additional 10 ml HNO_3 were added and the mixture boiled under reflux. When the residue became bright, 10 ml 6N HCl were added and the heating repeated. After heating, the solution was diluted with 20 ml of water, filtered into a 50 ml volumetric flask and made up to volume [6,7].

Fodder was sampled from the analysed soil. Average samples from which an amount was weighed for analysis was made by mixing six samples. Weighed portion of 1 g previously dried at 105^0C and powdered plant soaked in a glass with 10 ml concentrated HNO_3 and allowed for ten hours. It was heated until red vapor appeared. After cooling, 2-4 ml 70% $HClO_4$ were added, the mixture evaporated again, and the residue washed with deionised water, into a 50 ml vessel [6,7]. Milk was sampled immediately after milking on the farms supplying the Kikinda dairy. The samples were taken 8 times per month. 10 ml milk was used for each analysis. The dish was transferred into a furnace and heated to white ash at 450 ^{o}C for 12 h. If the ash was not white, 0.5 ml concentrated HNO_3 was added and the suspension evaporated to dryness, returned to the furnace and heated for about 1 h. After mineralisation, 1 ml 10% HCl was added, the solution filtrated to a 5 ml vessel and made up to volume using 1% HCl [6,7].

After the preparation of samples, Cd (228.3 nm), Zn (213.9 nm) and Pb (283,3) were determined by graphite furnace or flame atomic absorption spectrometry respectively (PERKIN-ELMER Model 5000, HGA-400). All the measurements were performed according to the general procedure described by the manufacturer.

In the statistic processing of data, methods of central tendency (arithmetic mean and standard deviation) were used and the level of statistic importance was determined (student T-test).

Results and discussion

The results obtained by analysis of soil, fodder and milk samples are evident in tables 1,2 and 3. Values of cadmium concentration in the investigation period ranged from 0,031 to 0,976 μg/g. Maximum limited values allowed by law for cadmium concentration in soil is 3 μg/g, so it may be concluded that investigated soils are not yet threatened by pollution from this element [8]. Considering that pH values of investigated soil samples existed in alkali medium it is supposed that cadmium in the investigated soil occurs as oxides, carbonates and phosphates.

Lead concentration in the investigation period ranged from 22,5 to 66,6 μg/g. Since the concentration of lead above 100 μg/g is an indicator for lead contaminated soil, it may be concluded that investigated soils are not lead contaminated above maximum allowed concentration (MAC) [8].

Zinc concentration in the investigation period ranged from 48,7 to 499 μg/g. It is important to stress that 21% of the analysed samples exceeded limited allowed values by law (300ppm) in 1996 and 2% in 1997 [8].

Cadmium concentration in fodder samples ranged from 0,022 to 0,131 μg/g. Since MAC for cadmium in fodder is 0,5 μg/g, it is necessary to stress that none of the values exceeded the allowed concentration [9].

Lead concentration in fodder samples ranged from 0,480 to 4,342 μg/g. Allowed MAC of 10 μg/g by law for lead in fodder means that there were no values above MAC [9].

Zinc concentration in fodder samples during the investigation period ranged from 10,74 to 278,9 μg/g, which is far more below allowed level (MAC 2000 μg/g) [9].

Cadmium concentration in analysed milk samples ranged from 0,001 to 0,016 μg/L. As MAC value for cadmium concentration in milk is 0 010 μg/L, it is essential to stress that in 1996, 32,3% and in 1997, 26% of samples exceeded the allowed value[10].

Lead concentration in milk samples ranged from 0,002 to 0,223 μg/L. MAC value for lead concentration in milk is 0,1 μg/L, therefore it should be pointed out that 26% of the samples in 1996 and 39,6% in 1997 exceeded MAC value [10].

Zinc concentration in analysed milk samples ranged from 0,543 to 3,90 μg/g. The percentage of improper milk samples determined through zinc concentration was impossible to estimate since MAC values for zinc in milk were not yet standardised by existing regulations[10].

To determine the dependence of heavy metal concentration in media, it is essential to monitor trends of concentration changes in them in the investigation period. The decrease of cadmium concentration in soil (in the period 1996 to 1997) for the value of 30% was followed by the decrease of cadmium concentration of 17% in fodder, and of 13% in milk. This trend is significant and it can be stated that the decrease of cadmium concentration in soil leads to the decrease of cadmium concentration in fodder, but not to the same extend, which indicates that concentration level is affected by more than one factor.

The decrease of lead concentration in soil of 21% is followed by the increase of lead concentration in fodder for 5%, and for 11% in milk. This trend of increase is not significant but it may be stated that the increase of lead concentration in soil is followed by the increase of lead concentration in fodder.

The decrease of zinc concentration in soil for 30% is followed by the decrease of zinc concentration in fodder for 17 %, as well as in milk. It is essential to state that the level decrease of zinc concentration in relation soil- fodder- milk is significant and is followed by the same decrease trend of cadmium concentration on this relation.

Low percentage of lead increase in fodder in relation to the percentage of the increase in soil is probably the consequence of reduced mobility and absorption of lead in dry and oxygenous conditions, deficiency of alkali and alkali earth elements as well as the presence of Pb^{2+} salts. A higher percentage of absorption on the route fodder- milk in relation to the percentage of absorption on the route soil-fodder in acid medium in the stomach, for the extraction of lead, particularly lead dust, is very good (80- 90%) in HCl in the stomach fluids. A low calcium and magnesium diet increases heavy metals absorption [2,4].

Table 1.
Average concentration interval certainty of metals in soil per year

	Year	N	Mean	SD	95% CI
Cd (μg/g)	1996	51	0.158	0.124	0.122 - 0.197
p= 0.133	1997	51	0.120	0.129	0.084 - 0.156
Pb (μg/g)	1996	51	40.2	7.9	37.9 - 42.4
p<0.001	1997	51	49.9	8.9	47.3 - 52.4
Zn (μg/g)	1996	51	182	115	149 - 214
p<0.001	1997	51	135	79.4	112 - 157

Table 2.
Average concentration and interval certainty of metal in fodder per year

	year	N	mean	SD	95%CI
Cd-(μg/g)	1996	27	0,064	0,025	0,054 – 0,074
	1997	27	0,053	0,018	0,046 – 0,061
Pb (μg/g)	1996	27	2.04	0.98	1,65 - 2,42
	1997	27	2.11	0.69	1,84 – 2,39
Zn (μg/g)	1996	27	52.52	64.59	27,0 - 78,1
	1997	27	44.19	36.87	29,6 – 58,8

Table 3.
Average concentration and interval certainty of metal in milk per year

	year	N	Mean	SD	95% CI
Cd (μg/L)	1996	96	0.0077	0.0036	0,0070 – 0,0084
p=0.243	1997	96	0.0071	0.0032	0,0065 – 0,0078
Pb (μg/L)	1996	96	0.078	0.042	0,069 – 0,087
p=0.032	1997	96	0.089	0.046	0,079 – 0,098
Zn (μg/L)	1996	96	1.88	0.49	1,77 – 1,98
p<0.001	1997	96	1.64	0.42	1,56 – 1,74

Conclusion

Regardless of biogenesis of the soil, analises of the results of heavy metals concentration in chain soil-fodder-milk show that soil has a direct effect on concentration of heavy metals on this relation.

Decrease trend, i.e.concentration increase trend in this chain for cadmium and zinc are similar, but there are differences for lead on the route soil-fodder. It is possible that it is the consequence of soil composition and mobility of lead (Pb^{2+} salts).

Decrease levels of cadmium and zinc,and increase concentration level of lead in milk in relation to decrease levels, i.e.increase concentration level in fodder are probably the consequences of defect of certain elements in fodder (calcium, magnesium and iron) and metabolism, because lead is more intensively absorbed in acid medium with defect of these elements.

References

1. J. Webber: Trace metals in agriculture. *In* ”Effect of Heavy Metal Pollution on Plants” (N. W. Lepp, Ed.), Appl. Sci. Publ., **2**, 159-184, (1981).
2. E. Fergusson: The heavy elements: Chemistry, environmetal impact and health effects, Pergamon press, Oxford, pp. 461-551, (1990).
3. A. M. Ure, M. L. Berrow: The elemental constituents of soil. *In* ”Reporter, Environmental Chemistry” (H. J. M. Bowen, Ed.), Roy. Soc., **1**, 142-204, (1982).
4. R. P. Sharma: Soil-plant-animal distribution of cadmium in the environment. *In* ”Cadmium in the Environment” (J. O. Nriagu, Ed.), pp. 587-605. Wiley, New York, (1980).
5. B. Markert, K. Friese: Trace Elements – Their Distribution and Effects in the Environment (1st Ed.). Elsevier, Oxford, (2000).
6. P. Vinas, N. Campillo, L. Garcia, C. M. Hernandez: Slurry procedures for the determination of Cd and lead in cereal-based products using electrothermal atomic absorption spectrometry. Fresenius J. Anal. Chem., 349, 306-310, (1994).
7. Official Methods of Analysis of AOAC, Int., 16^{th} ed. Arlington, USA, (1997).
8. Yugoslav Regulations: “Maximum levels of hazardous and toxic materials in soil and irrigation water and methods for their determination”. Official Register of the Republic of Serbia, № 23/94 (in Serbian),(1994).
9. Yugoslav Regulations: “Maximum contaminant levels in animal feed”. Yugoslav Official Register, №. 2/90 (in Serbia), (1990).
10. Yugoslav Regulations: “Levels of pesticides, metals metalloids and other toxic contaminants, chemotherapeutics, anabolic and other substances present in food”. Official Register of FR Yugoslavia, №. 5/92 (in Serbia), (1992).