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CONTRIBUTIONS REGARDING HEAVY METALS FLOW WITHIN SOIL-PLANT-ANIMAL SYSTEM IN POLLUTED AREAS

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Within the areas polluted with heavy metals, on a low macro-elements content background, a highly unbalanced level of nutrients in soil and plants was registered. In Romania, this phenomenon was emphasised within the areas affected by emissions from non-ferrous metallurgical industry in the Copşa Mică, Baia Mare, and Zlatna cities. The pollution degree of soils, assessed on the basis of loading/pollution index values, shows a moderate-high pollution with Cd (Copşa Mică), Pb (Copşa Mică, Baia Mare), and Zn (Baia Mare), a moderate pollution with Cu, Pb, Zn (Zlatna) and Zn (Copşa Mică), a low-moderate pollution with Cd and Cu (Baia Mare), and a low pollution with Cd (Zlatna) and Cu (Copşa Mică). The quality of vegetation in the pastures and meadows within these areas is depreciated by the high content of heavy metals and the macro-nutrients deficiency. The ingestion of grass and soil loaded with heavy metals altered the animal health conditions, inducing saturnism cases with lethal end. The heavy metals contents of some organs and tissues of the affected animals (cattle, horses) are several tens of times higher than the maximum allowable limits (MAL). The transfer intensity of Cd and Pb from one environmental component to another is up to 18, 13 times, respectively, higher in the polluted areas, as compared to the non-polluted ones. Liming, along with organic and mineral fertilisation of soils, lead to the improvement of the balance of nutrients in soils and plants within pastures and meadows from areas polluted with heavy metals.

Key words: heavy metals, soil, plant, animal.

INTRODUCTION

Along the external flow of the chemical elements at the environmental level, some anomalous concentrations may occur, mostly generated by the anthropic activity accomplished unlike natural laws and environmental protection. Some of the most illustrative aspects of this phenomenon are presented by heavy metals. Mining and processing of ores in the metallurgical and chemical factories cause depositions variously loaded with such chemical elements, depending on their nature and with great, sometimes negative, effects on biota. The daily impact of the emissions from these metallurgical factories, reaching high intensity in the last decades, has determined a severe environmental pollution with heavy metals and sulphur oxides, having a major implication on animal and human health condition.

In Romania, three such polluted areas are known: Baia Mare and Zlatna, within the mining areas, where flotations and smelters were placed, and Copşa Mică, rich in natural gas, used for metallurgical processing.

This paper presents an estimate of heavy metals loading of soil, vegetation of the pastures and meadows in these three areas, and their influence upon nutrients balance in soil, plant, and animal. It represents a synthesis of some works performed in many years (Lăcătuşu et al., 1995, 1996, 1997*a*, *b*, 1998*b*).

MATERIALS AND METHODS

The field investigations have been carried out on pastures and meadows located within the areas affected by the emissions from factories and between 0.5 and 14 km far from the emission sources. Soil samples from A horizons (0-20 cm) and plant samples (aerial parts) have been collected. Also hair, milk and blood samples were collected from the cattle rearing within these areas, as well as samples of organs and bones from the slaughtered cattle.

To characterise the soils, the main soil physical and chemical properties have been determined (texture, pH, carbonates content, base saturation, contents of total nitrogen and mobile forms of phosphorus and potassium.

Total contents of heavy metals (Cd, Cu, Pb, and Zn) have been measured in hydrochloric solution obtained by digestion of soil samples in $HClO_4$-HNO_3 mixture. Mobile forms of these chemical elements have been extracted by an EDTA-CH_3COONH_4 solution at pH 7,0.

Heavy metals have also been determined in plant, water (within the Baia Mare area), and biological samples collected from animals. All heavy metals have been determined by means of atomic absorption spectrometry.

RESULTS AND DISCUSSIONS

The soil of pastures and meadows within the investigated areas is mostly represented by acid soils, as Albic Luvisols, Haplic Luvisols, Dystric Cambisols, Luvic Phaeozems. All these represent 44-100 per cent of the investigated pastures and meadows (Table 1). The rest of the soils is represented by slightly acid to slightly alkaline soils, such as Eutric Fluvisols and Eutric Regosols. The chemical properties of the soils from the last group induce a higher buffering capacity, being practically non-vulnerable to the impact of acid rains and heavy metals pollution. Unfortunately, the areas of such soils are smaller, they are practically missing in pastures and meadows within Baia Mare, but they are under 38 per cent within the Copşa Mică area, and about 56 per cent within the Zlatna area. As a result, it may be estimated that the soils of pastures and meadows within the Baia Mare area are very vulnerable to the impact of acid rains and heavy metals pollution, while the soils within the Copşa Mică and Zlatna areas have a moderate vulnerability.

All soils from these three areas have a specific feature: very low-low up to medium contents in macro-nutrients (Tables 1 and 2). This led to an unbalanced level with trace elements (heavy metals).

If the values of the statistical parameters concerning heavy metals contents of topsoil (A horizon) within the three investigated areas are compared (Table 3) significant differentiations are observed from one area to another and from one chemical element to another. Thus, cadmium abundance is maximum within the Copşa Mică area and much lower within the Baia Mare and Zlatna areas. The comparison with the maximum allowable limit (MAL) established by Kloke (1980) shows that, on an average, the Cd contents of soils within the Copşa Mică area exceed this level up to 2.3 times. On the other hand, the Cd pollution level of soils, established after values of loading/pollution index (Lăcătuşu, 1997), is medium-high in the Copşa Mică area, low-medium in the Baia Mare area, and low in the Zlatna area (Table 4).

Table 1

Main physical and chemical properties of soil (A horizon) in the pastures and meadows within the areas influenced by emissions from the metallurgical factories in the Copşa Mică, Baia Mare and Zlatna areas

Soil type RSCS (FAO/UNESCO)	Covering degree (% of investigated areas of pastures and meadows)	pH_{H_2O}	Base saturation	$C \times 1{,}72$	Nt	P_{AL}	K_{AL}	Textural class*
			%			mg.kg^{-1}		
Copşa Mică								
Regosol (Eutric Regosol)	38	7.72-8.06	33-65	1.90-3.30	0.11-0.18	5-22	132-218	ML
Argilluvial Brown Soil (Luvic Phaeozem)	62	5.30-6.21	45-68	2.10-3.90	0.10-0.14	6-18	98-175	CSL
Baia Mare								
Albic Luvisol (Albic Luvisol)	53	4.40-6.50	33-65	1.80-3.20	0.08-0.13	7-18	73-190	SSL-ML
Brown Luvic Soil (Haplic Luvisol)	15	4.80-4.90	42-52	1.52-4.39	0.12-0.20	6-15	79-173	SL
Acid Brown Soil (Dystric Cambisol)	14	4.30-5.10	18-30	2.46-3.79	0.07-0.15	9-21	102-204	MSL-SL
Argilluvial Brown Soil (Luvic Phaeozem)	18	4.70-5.70	19-49	2.70-4.76	0.13-0.24	10-30	114-187	SSL-SL
Zlatna								
Argilluvial Brown soil (Luvic Phaeozem)	24	4.30-5.90	33-79	2.40-3.71	0.10-0.22	8-20	93-127	ML
Acid Brown Soil (Dystric Cambisol)	10	4.70-5.00	36-54	1.42-3.21	0.08-0.27	6-18	101-195	MSL-ML
Eumezobazic Brown Soil (Eutric Cambisol)	10	5.20-7.10	58-96	1.71-2.93	0.10-0.19	9-23	120-223	MSL-CSL
Alluvial Soil (Eutric Fluvisol)	19	5.98-7.82	72-100	2.93-4.78	0.17-0.29	11-25	109-137	MSL-LC
Erodisol (Eutric Regosol)	17	5.40-8.00	67-100	1.03-2.00	0.07-0.18	10-19	83-175	MSL-MCL
Regosol (Eutric Regosol)	20	6.90-7.92	93-100	1.90-3.00	0.11-0.25	10-21	69-149	MSL-ML

* MSL – medium sandy loam; SSL – silty sandy loam; SL – silty loam; CSL – clay sandy loam; MCL – medium clay loam; LC – loamy clay

Table 2

Nitrogen, phosphorus and potassium supply of soils (A horizon) within the pastures and meadows from polluted areas

* vl – very low; l – low; m – medium; h – high

Soil type	Nt	P_{AL}	K_{AL}
Copşa Mică			
Eutric Regosol	l*	vl - l	m
Luvic Phaeozem	l	vl - l	l
Baia Mare			
Albic Luvisol	vl - l	vl - l	l - m
Haplic Luvisol	l - m	vl - l	l - m
Dystric Cambisol	l - m	l - m	l - h
Luvic Phaeozem	m	l - m	l - m
Zlatna			
Luvic Phaeozem	l - m	vl - m	l
Dystric Cambisol	vl - m	vl - l	l - m
Eutric Cambisol	l - m	l - m	l - m
Eutric Fluvisol	m - h	l - m	l - m
Eutric Regosol	vl - m	l - ml	l - m

The second analysed element, copper, has the highest abundance in the Zlatna area, where, on an average, it exceeds only a little the MAL value (after Kloke). The soils within the other two areas (Copşa Mică and Baia Mare) have an average Cu content much lower (Table 3). According to the values of loading/pollution index, the soil within the Copşa Mică area is low polluted, the soil within the Baia Mare area is low-medium polluted, and the soil within the Zlatna area is medium polluted (Table 4).

Lead, the chemical element highly circulated in the non-ferrous metallurgical industry, is abundant in soils of the three areas. The values of the grouping centre parameters ($\bar{x}$, x_g, *Me*) exceed in all cases the MAL (100 $mg \cdot kg^{-1}$, after Kloke) (Table 3). At the same time, the values of the loading/pollution index show a medium-high level of soil pollution in the Copşa Mică and Baia Mare areas and a medium one in the Zlatna area (Table 4).

Finally, the last chemical element analysed, zinc, is present in soils of pastures and meadows within the three investigated areas at contrasting levels (Table 3). Thus, although the maximum determined values are higher then the MAL after Kloke, for all three areas, among the three average values only that characterising the Copşa Mică area is higher than this threshold. Zinc pollution level of soils from pastures and meadows is medium within the Copşa Mică and Zlatna areas and medium-high within the Baia Mare area (Table 4).

Table 3

Statistical parameters of total (t) and mobile (m) contents of heavy metals (Cd, Cu, Pb, Zn - mg.kg-1) in A horizon of soils under pastures and meadows within the areas affected by emissions from the metallurgical factories in the Copşa Mică (1), Baia Mare (2), and Zlatna (3) cities

Parameter	Cd						Cu						Pb						Zn					
	1		2		3		1		2		3		1		2		3		1		2		3	
	t	m	t	m	t	m	t	m	t	m	t	m	t	m	t	m	t	m	t	m	t	m	t	m
x_{min} *)	4.40	2.00	0.15	0.08	0.40	0.20	15	3	8	3	7	4	37	13	20	14	17	11	178	27	48	11		
x_{max} *)	11.90	6.00	2.95	2.50	14.00	6.30	127	18	72	39	1164	171	476	296	400	288	4162	2914	1819	410	598	197		
$\bar{x}$	6.90	4.00	1.36	1.05	1.50	0.60	39	7	30	13	106	42	171	84	184	89	223	107	539	167	188	62		
σ *)	2.50	1.00	0.55	0.70	1.60	0.50	40	6	15	11	145	163	158	98	94	62	98	79	576	126	153	38		
x_g *)	5.30	3.00	1.27	0.67	1.40	0.70	37	6	27	10	83	37	149	79	174	72	103	96	483	147	137	46		
Me *)	5.10	4.00	1.30	0.83	1.20	0.60	39	7	24	8	82	48	141	85	181	81	98	101	511	152	120	40		
MAL **)	3.00	1.00					100	8			100		100	18					300	43				
NC ***)	0.30						20						15						50					
Values ****) A	1.00						50						50						200					

*) x_{min} – minimum value, x_{max} – maximum value, $\bar{x}$ – arithmetic mean, σ – standard deviation, x_g – geometric mean, Me – median

**) Maximum allowable limit (MAL) after Kloke, 1980, for total (t) content, and after Lăcătuşu et al., 1987, 1993 for mobile (m) content

***) Normal content (NC), in Fiedler and Rösler (1988)

****) After Moen and Brugman (1987), in van Lynden (1997)

Taking into account the global abundance of heavy metals, and also the soil reaction, it is noticed that the most intensive solubilization of these elements in soil solution takes place in the Baia Mare area, because between 33 and 77 per cent of the total content is soluble in EDTA-CH_3COONH_4 solution, while the solubility interval specific to soils within the Copşa Mică and Zlatna areas is between 18 and 51 per cent.

Table 4

Heavy metals pollution level of soil within polluted areas, established after values of loading/pollution index (Lacatusu, 1998a)

Area	Cd	Cu	Pb	Zn
Copşa Mică	m - h	l	m - h	m
Baia Mare	l - m	l - m	m - h	m - h
Zlatna	l	m	m	m

* l – low; m – medium; h – high

The comparison of the average values of contents of soluble forms of heavy metals with maximum allowable limit values of these forms (Table 3) shows that these values are exceeded in the case of Cd for the soils within the Copşa Mică and Baia Mare areas, in the case of Cu for the soils within the Baia Mare and Zlatna areas, and in the case of Pb and Zn within all areas. The mobility degree of heavy metals indicates the present severity of pollution and its effect on the other environmental components: vegetation, waters, animals, and human beings.

The difference between the mobility of Cd and Pb is pointed out by the values of the fractions representative for the general abundance. Thus, 53 per cent and respectively 34 per cent of the total Cd content in soils within the Copşa Mică and Baia Mare areas belong to soil solution and exchangeable fraction, while only 20 per cent and 8 per cent, respectively, of the total Pb content belongs to these fractions. The differences are represented by the fractions bound by the organic matter, iron and manganese oxides and the residual fractions present in the crystalline structure of soil minerals (Fig. 1). These findings also reflect the suitable conditions of the physiological path transfer of the heavy metals from soil into plant.

From the viewpoint of species and their abundance, the vegetation within the three areas is similar (Table 5). Within the Copşa Mică area, the flora associations are represented by species as *Festuca rubra*, *Poa pratensis*, *Agrostis tenuis*, *Koeleria macrantha*. The fodder value and loading capacity with animals are moderate, the average fodder value being about 40 per cent, and the loading capacity 0.8 cow per hectare, excepting the pastures near the emission source, totally degraded pastures, where *Agropyron repens* is predominant and they are practically not grazed.

The flora associations of the pastures and meadows within the Baia Mare area are dominated by *Agrostis tenuis* and *Festuca rubra* species, sometimes associated with *Lolium perene* and *Trifolium sp.* The fodder value is, on an average, 53 per cent, the extremes being 27 and 81 per cent, and the loading capacity is 1.1 cow per hectare.

The pastures and meadows within the Zlatna area are characterised by flora associations including *Agrostis tenuis*, *Agropyron repens*, *Festuca rubra*, *Nardus stricta*, and sometimes *Trifolium repens*. The interval of the fodder value is larger, between 1 and 64 per cent, with an average value of 38 per cent and a loading capacity of 0.8 cow per hectare.

The nutritional value of vegetation of the pastures and meadows within the three areas is much diminished due to the high content of heavy metals in plant. Thus, by comparing the statistical parameters values (Table 6) it may be noticed that the vegetation within the Copşa Mică area has a Cd concentration exceeding even the phytotoxicity threshold and the average content is close to it. The Cd concentration in vegetation within the other areas is much lower, not reaching the toxicity threshold, but higher than the value normally measured in plants.

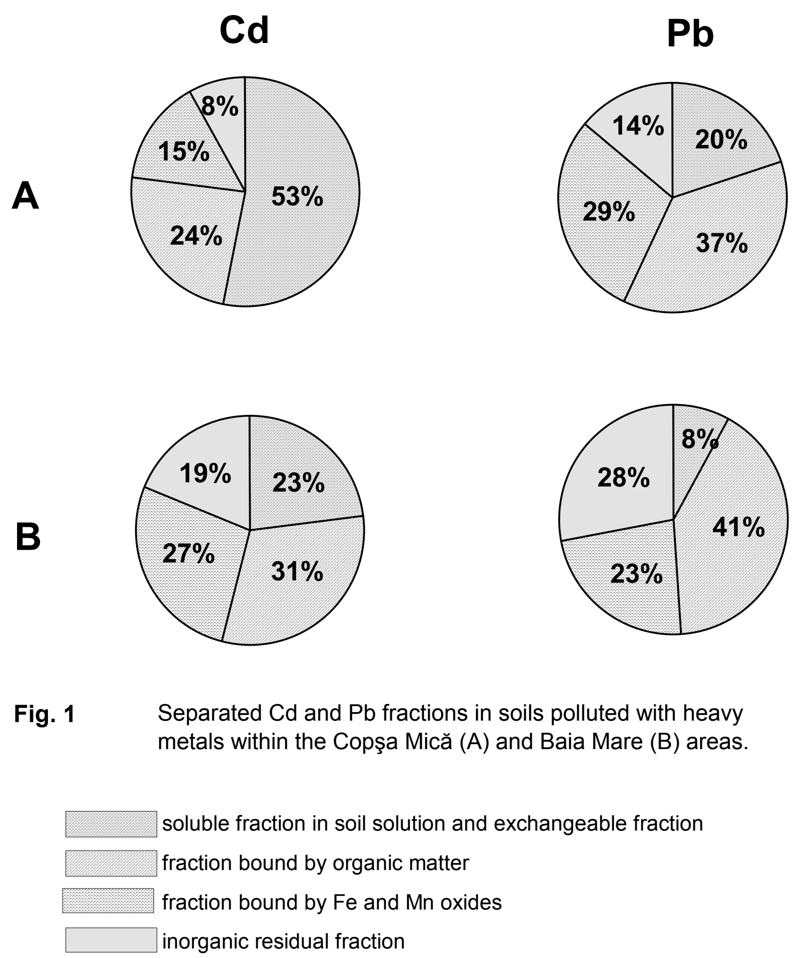

Fig. 1 Separated Cd and Pb fractions in soils polluted with heavy metals within the Copşa Mică (A) and Baia Mare (B) areas.

It should be specified that the analytical values obtained by this investigation represent the amount of both forms of the chemical elements: physiologically adsorbed and those deposited on the foliar system along with the dust from the atmosphere.

The data concerning Cu concentration lead to the conclusion that the vegetation within the Copşa Mică and Baia Mare areas has a normal concentration, excepting the maximum values of the distribution interval. On the contrary, the vegetation within the Zlatna area is characterised by high Cu contents, including the average values which belong to the toxicity interval, the right limit of the distribution interval being 7 times higher than the right limit of the normal content interval (Table 6).

The contents of plants are high, most of them over the normal range values, a large part of them belonging to the phytotoxicity range (Table 6).

The interval of Zn content is very large, between 23 and 1,006 $mg \cdot kg^{-1}$, a characteristic interval for the Zlatna area, but the average values of this interval are lower than those specific to the Copşa Mică area. Therefore, the vegetation within the Copşa Mică area has the highest Zn content, followed, in decreasing series, by the Zlatna and Baia Mare areas.

Table 5

Main features of pastures and meadows within polluted areas

Area	Flora Association	Fodder value %	Loading capacity (cow per hectare)
Copşa Mică	*Festuca rubra* *Poa pratensis* *Agrostis tenuis* *Koeleria macrantha* *Agropyron repens*	40	0.8
Baia Mare	*Agrostis tenuis* *Festuca rubra* *Lolium perene* *Trifolium sp.*	53	1.1
Zlatna	*Agrostis tenuis* *Agropyron repens* *Festuca rubra* *Nardus stricta* *Trifolium repens*	38	0.8

It may be concluded that the vegetation of the pastures and meadows within the Copşa Mică area has a high degree of loading with Cd, Pb, and Zn, that within the Zlatna area – with Cu, Pb, and Zn – and that within the Baia Mare area has a moderate loading with all four analysed elements. By comparison with the average contents and maximum values of normal content interval, it is noticed that the analysed vegetation samples contain up to 15 times more Cd, 17 times more Pb, 2.2 times more Cu, and 3.4 times more Zn.

Between the heavy metals contents of vegetation and soluble heavy metals contents of soil, directly proportional relations have been established, most of them being statistically ensured (Table 7).

The excessive heavy metals contents of vegetation, as a result of both the physiological absorption and deposition on the foliar system, added to the conditions of trace elements deficiency, causes strong nutritional disorders in plants, as well as in animals ingesting them.

The animal health is negatively influenced by the pollutants. The ingestion of plants nutritionally unbalanced due to the macro-nutrient deficiency (Table 8) and heavy metals excess, together with the swallowing of soil polluted with heavy metals, and, sometimes, the drinking of water contaminated with heavy metals and other organic and inorganic pollutants, highly contributes to the alteration of animal health condition in the mentioned areas. The air polluted with sulphur oxides and air-borne particles loaded with heavy metals also contributed to this phenomenon.

Table 6

Statistical parameters of Cd, Cu, Pb, and Zn contents (mg.kg-1) in the vegetation of pastures and meadows within the areas affected by emissions from the metallurgical factories in the Copşa Mică (1), Baia Mare (2), and Zlatna (3) cities, as compared to the normal contents (NC), phytotoxical values (PV), and normal cattle nutrition values (NCNV)

	Cd			Cu			Pb			Zn		
Parameter	1	2	3	1	2	3	1	2	3	1	2	3
x_{min} *	2.10	0.10	0.23	11	4	3	40	15	5	140	42	23
x_{max} *	6.30	2.00	2.41	25	80	145	211	338	1129	521	99	1006
$\bar{x}$	4.40	0.90	0.89	18	17	34	134	106	130	270	74	169
σ *	1.40	0.50	0.50	5	16	35	55	80	207	146	15	158
x_g *	3.80	0.70	0.80	19	14	23	130	97	107	259	81	127
Me*	4.70	0.80	0.85	16	13	17	121	88	86	150	75	114
NC **	0.20-0.30 (0.10-2.40)			5-15 (5-20)			6-8 (5-10)			16-80 (1-100)		
PV ***	5.00-30.00			20-100			30-300			100-400		
NCNV ****				5-10						20-100		

* x_{min} – minimum value, x_{max} – maximum value, $\bar{x}$ – arithmetic mean, σ – standard deviation x_g – geometric mean, Me – median

** After Fink (1968), Bergmann and Neubert (1976), Bergmann (1992), and, between brackets, values after Alloway and Ayres (1993)

*** after Alloway şi Ayres (1993)

**** after Miloş şi Drânceanu (1980)

Table 7

Values of correlation coefficients between the contents of heavy metals (soluble form in CH3COONH4-EDTA at pH 7.0) in soil and in vegetation of pastures and meadows within the Copşa Mică (1), Baia Mare (2), and Zlatna (3) areas

Cd			**Cu**			**Pb**			**Zn**		
1	2	3	1	2	3	1	2	3	1	2	3
0.632*	0.742*	0.592*	0.414	0.532 *	0.607 *	0.572 *	0.534 *	0.560 *	0.647 *	0.718 *	0.439

Table 8

Statistical parameters of N, P, K contents (%) in the vegetation of pastures and meadows within the areas affected by emissions from the metallurgical factories in the Copşa Mică (**1**), Baia Mare (**2**), and Zlatna (**3**) cities, as compared to normal contents (NC)

	N			P			K		
Parameter	1	2	3	1	2	3	1	2	3
x_{min}	1.04	0.93	1.14	0.12	0.09	0.07	0.52	1.09	1.32
x_{max}	2.43	2.74	2.57	0.42	0.36	0.49	2.12	2.40	2.70
$\bar{x}$	1.93	2.03	1.83	0.29	0.27	0.36	1.70	1.93	2.14
σ	0.46	0.59	0.64	0.10	0.09	0.12	0.50	0.32	0.59
NC*	2.5 – 3.5			0.35 – 0.80			1 – 3		

* After Fink (1969), Bergmann and Neubert (1976), Bergmann (1992)

Table 9

Statistical parameters of Cd, Cu, Pb, and Zn contents (mg.kg-1) in the vegetation of pastures and meadows within the areas affected by emissions from the metallurgical factories in the Copşa Mică (1), Baia Mare (2), and Zlatna (3) cities, as compared to the normal contents (NC), phyto-toxical values (PV), and normal cattle nutrition values (NCNV)

	Cd			Cu			Pb			Zn		
Parameter	1	2	3	1	2	3	1	2	3	1	2	3
x_{min} *	2.10	0.10	0.23	11	4	3	40	15	5	140	42	23
x_{max} *	6.30	2.00	2.41	25	80	145	211	338	1129	521	99	1006
$\bar{x}$	4.40	0.90	0.89	18	17	34	134	106	130	270	74	169
σ *	1.40	0.50	0.50	5	16	35	55	80	207	146	15	158
x_g *	3.80	0.70	0.80	19	14	23	130	97	107	259	81	127
Me*	4.70	0.80	0.85	16	13	17	121	88	86	150	75	114
NC **	0.20-0.30 (0.10-2.40)			5-15 (5-20)			6-8 (5-10)			16-80 (1-100)		
PV ***	5.00-30.00			20-100			30-300			100-400		
NCNV ****				5-10						20-100		

* x_{min} – minimum value, x_{max} – maximum value, $\bar{x}$ – arithmetic mean, σ – standard deviation x_g geometric mean, Me – median

** After Fink (1968), Bergmann and Neubert (1976), Bergmann (1992), and, between brackets, values after Alloway and Ayres (1993)

*** after Alloway şi Ayres (1993)

**** after Miloş şi Drânceanu (1980)

The synthetic epidemiological data emphasised the marasmus syndrome of the toxico-defficiency nature, hypotrepsia, gastro-intestinal affections, pulmonary affections (congestion, endema, bronchopneumonia); locally, cases of neoplasm and teratomas have been recorded.

The examination of metabolic profile emphasised the evolution of some cumulative chronic intoxication with cattle and horses, manifested by: hypogenerative aplastic anaemia, hypophosphoremia, secondary hypocupremia, hepato-renal and osteoarticulate disorders (decrease of haemoglobin and haematocryte, increase of activity of some hepatic enzymes, of alkaline serum phosphatase, leukopenia with lymphopenia. Hypocupremia occurs as a result of the interference of some sulphur compounds under conditions of not too high Cu contents, as in the cases within the Copşa Mică and Baia Mare areas.

Toxicological data, especially heavy metals determination, of the analysed samples have detected significant outrunning of MAL for all the four chemical elements measured in the main investigated organs and tissues (Table 9). Thus, Cd content in liver and kidney exceeds the MAL up to 25 times, 53 times respectively in the samples collected from animals within the Baia Mare and Copşa Mică areas. Significant outrunning has also been recorded in the case of Cu and Zn. Likewise, heavy metals have been detected in animal hair up to 34 times higher (Cd), 1.4 times higher (Cu), 1.3 times higher (Pb), and 1.2 times higher (Zn) than the values of MAL.

Table 10

Average content (g/l for blood serum and mg/kg for the other sample types) of heavy metals in biological samples collected from cattle within the Copşa Mică (1), Baia Mare (2), and Zlatna (3) areas as compared with the maximum allowable limits (MAL)*

	Cd				Cu				Pb				Zn			
Sample	1	2	3	MAL	1	2	3	MAL	1	2	3	MAL	1	2	3	MAL
Blood Serum			1.47	0.2	38	77	58	97	35	36	13	25	143	140	233	135
Liver	0.96	1.24		0.05	6.1	22		5	2.9	0.8		0.5	108	39		50
Kidney	7.16	2.67		0.05	4.2	5.1		5	2.4	1.3		0.5	38	24		50
Long Bone	1.7	1.35		0.14**	3.7	3.3		1.8	35	19		1.3 **	76	71		86**
Milk	0.03	0.004	0.08	0.01***		0.21	0.58	0.5***	0.25	0.34	0.53	0.10***	4.11	3.4	6.66	5***
Hair		0.1	0.34	0.01		8.7	11.5	8		8	6.4	6		140	150	130

*) In Ghergariu (1980)
**) Values of reference specific to animals within a non-polluted area
***) Written disposition of Ministry of Health for approving the Hygiene Standard on food production, processing, storing, preservation, transport and marketing (No. 611/April 3, 1998)

Cow milk proved to be an important marker for assessment of the cattle pollution degree. The analyses of the samples collected from the cows grazing within the three areas showed, on an average, up to 5.3 times more Pb and 3 times more Cd.

Finally, Cd content of the blood serum of cattle within the Copşa Mică area was 7.3 times higher than the MAL and Pb exceeds this value up to 1.4 times in the case of animals within the Baia Mare area.

The above presented data lead to the conclusion of an intense migration of heavy metals within the soil-plant-animal system. The Cd and Pb flow charts within the soil-plant-animal system are presented in Fig. 2 and 3. Their examination emphasises intensities of the Cd and Pb transfer from one enviromental component to another up to 18 times higher in the case of Cd and 13 times higher in the case of Pb within the polluted areas as compared to the non-polluted ones.

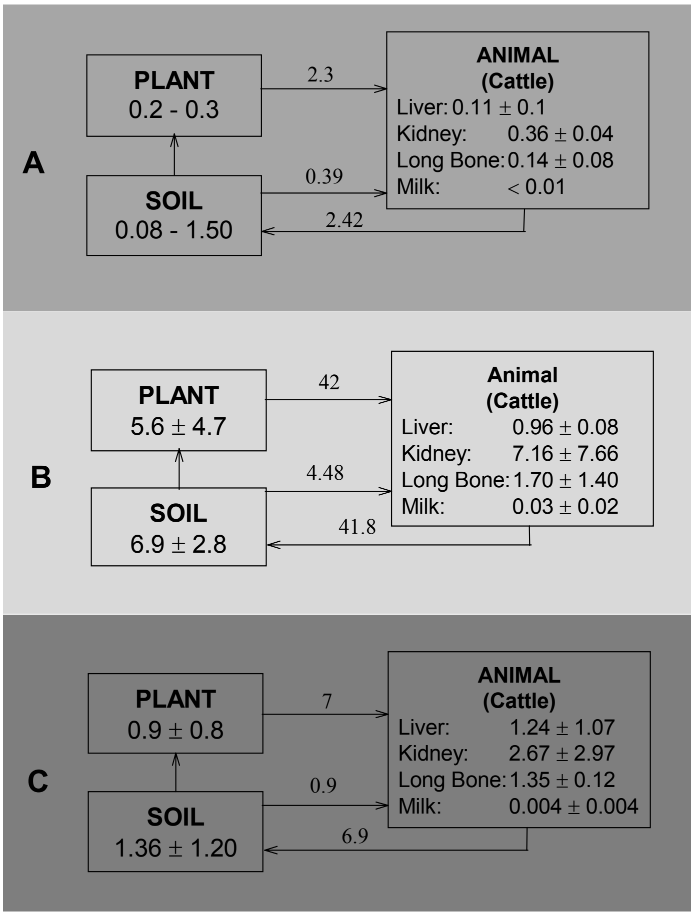

Fig. 2. Cd flow chart of soil-plant-animal system within a non-polluted area (A) and the Copşa Mică (B) and Baia Mare (C) polluted areas.
The units of measure are expressed by mg · kg^{-1} and mg · l^{-1} (milk). The transfer values from one environmental component to another are expressed by mg per day.

The daily impact of the emissions loaded with heavy metals, as well as their migration at high intensities from soil to plant, and from plant to animal, causes a chronic intoxication with heavy metals of animals, which leads to their number decrease and alteration of plant, animal, and human health within the areas influenced by the emissions from the factories processing the non-ferrous ores and extracting the non-ferrous metals.

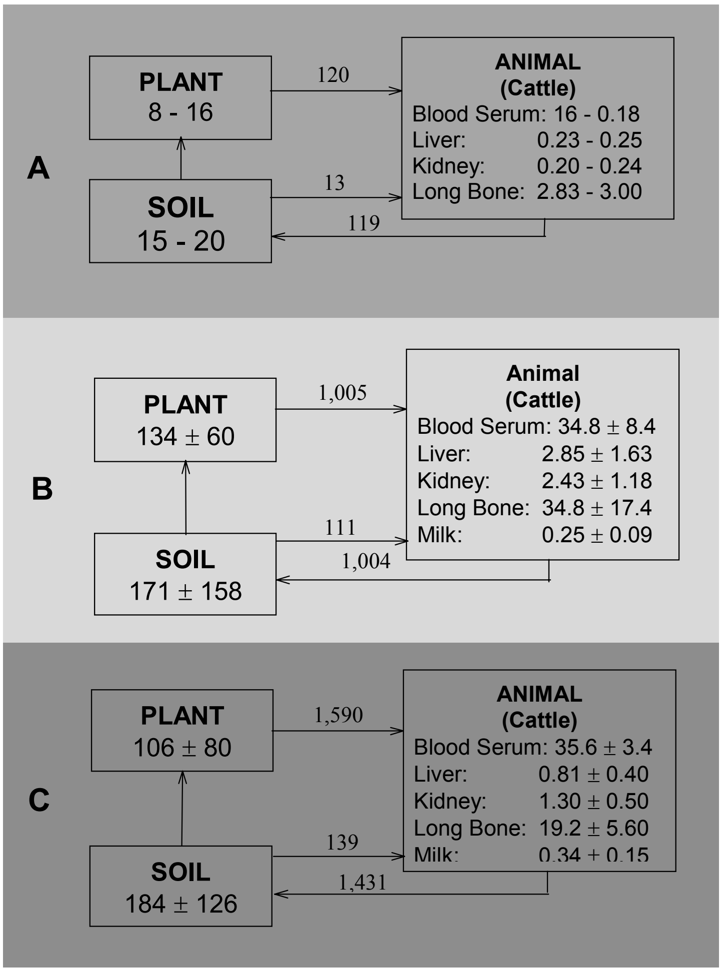

Fig. 3. Pb flow chart of soil-plant-animal system within a non-polluted area (A) and the Copşa Mică (B) and Baia Mare (C) polluted areas.

The units of measure are: $\mu \cdot l^{-1}$ for blood serum, $mg \cdot l^{-1}$ for milk and $mg \cdot kg^{-1}$ for the other sample types.
The transfer values from one environmental component to another are expressed by mg per day.

CONCLUSIONS

The soil cover of pastures and meadows from polluted areas includes acid soils, represented by Albic Luvisols, Haplic Luvisols, Dystric Cambisols, Luvic Phaeozems, and slightly acid to slightly alkaline soils, including Eutric Fluvisols and Eutric Regosols. The soils in the first group cover the whole Baia Mare area, 62 per cent of the Copşa Mică area and 44 per cent of the Zlatna area. The soils within the Baia Mare area are considered very vulnerable, while those within the Copşa Mică and Zlatna areas are moderately vulnerable.

Nitrogen, phosphorus, and potassium supply of soils is very low up to low in the Copşa Mică area and very low up to medium in the Baia Mare and Zlatna areas.

The pollution degree of soils, assessed on the basis of values of loading/pollution index shows a moderate-high pollution with Cd (Copşa Mică), Pb (Copşa Mică, Baia Mare), and Zn (Baia Mare), a moderate pollution with Cu, Pb, Zn (Zlatna) and Zn (Copşa Mică), a low-moderate pollution with Cd and Cu (Baia Mare) and a low pollution with Cd (Zlatna) and Cu (Copşa Mică).

The contents of nutrients in polluted soils with heavy metals is very unbalanced: a low content of macro-nutrients and a high content of micronutrients (heavy metals).

The vegetation within the Copşa Mică area has a high degree of loading with Cd, Pb, and Zn, that within the Baia Mare area has a moderate loading with all the four chemical elements, while the vegetation within the Zlatna area has a high loading level with Cu, Pb, and Zn. On a low macro-nutrients content background, a highly unbalanced level of nutrients in the vegetation has arose.

The ingestion of vegetation loaded with heavy metals, the swallowing, on pasture, of some amounts of soil polluted with heavy metals, and the possible drinking of polluted water, including the inhalation of air loaded with sulphur oxides and dust having a high content of heavy metals, caused animals saturnism, marasmus syndrome of toxico-deficiency nature, gastro-intestinal affections, pulmonary affections.

The analyses of organs (liver, kidney) samples from animals within the Copşa Mică and Baia Mare areas detected heavy metals contents exceeding MAL up to 53 times for Cd and 5.8 times for Pb. The analyses of hair samples detected 34 times Cd, 1.4 times Cu, 1.3 times Pb, and 1.2 times Zn more than MAL, respectively. The analysed milk samples showed, on an average, 8 times Cd, 5.3 times Pb, and 1.3 times Zn more than MAL. The Cd, Pb, and Zn concentrations in blood serum were also exceeded.

The transfer intensity of Cd and Pb from an environmental component to another is up to 18, 13 times, respectively, higher within the polluted areas as compared to the non-polluted ones.

Liming, along with organic and mineral fertilisation of soils, led to the improvement of the nutrients balance in soils and plants within the pastures and meadows from the areas polluted with heavy metals.

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U(VI) SORPTION FROM AQUEOUS SOLUTIONS ON NATURAL AND SYNTHETIC WAX

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The adsorbing properties of sorbents: beeswax, paraffin wax and polypropylenic wax were investigated for U(VI) concentration and separation from aqueous solutions. The optimum parameters which influence the equilibirum of the U(VI) sorption in the U(VI) sorbent-aqueous solution system, have been established: pH, concentration of the initial solution, sorbent amount, contact time were established. The study also developed a theoretical approach of the sorption process, involving identification of the model of the isotherm according to which sorption occurs. An optimum pH of 6.5-7.5 was established, and also a maximum sorption capacity – q_{max} *of 116.2* $mg.g^{-1}$ *for beeswax, of 115.6* $mg.g^{-1}$ *for paraffin wax and of 212.3* $mg.g^{-1}$*, respectively, for polypropylene wax. The values of the separation factor* R_L *and of constant* **b,** *calculated from the linearized form of the Langmuir isotherm, as well as the values of constants* K_F *and* **n,** *calculated from the linearized form of the Freundlich isotherm, indicate that - in the three systems – sorption is favourable and reversible, as due to the bonding affinity of sorbents' sites to U(VI). The ratio of adsorbed U(VI) increases with the increase in the concentration of the initial solution and with that of the sorbent amount, varying between 78.2 % – for polypropylenic wax – and 98.7 % – for beeswax. The FTIR spectra show that sorption on beeswax is a complex chemosorption process, involving cationic exchange and complexation, combined with physical adsorption while, for the rest of the systems exclusively surface adsorption and – possibly - superficial layer adsorption will occur.*

Key words: Uranium (VI), sorption, isotherms, beeswax, paraffin wax, polypropylene wax.

INTRODUCTION

Analysis and separation of the metallic ion species has always represented a problem of the hour. In recent years, when the environment came to have an ever-increasing, special impact, the identification, concentration and separation of the ions of the heavy metals, especially of the radioactive ones, represent a special concern for science.