DISTRIBUTION AND MOBILITY OF CADMIUM AND LEAD IN URBAN SOILS – CASE STUDY: IAŞI CITY – INDUSTRIAL ZONE

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In this study are presented the preliminary results regarding the distribution and migration of Cd and Pb in urban soils from industrial zone of Iaşi city. The studied soils are strong antropized and present radical modifications of lithology, mineralogy and chemistry. The Cd content varied between 0.09-1.36 μg/g, and the lead content between 25.83-186.73 μg/g. The experimental results have evidenced the existence of some abnormal distributions of cadmium and lead in studied soils, and association ways with soils components less characteristic for these metals, respectively. The characteristic for studied soils is high accumulation probability of Cd and Pb, as mobile species with high toxic potential.

Keywords: *urban soils; cadmium; lead, inter-phase distribution.*

The pollution of urban soils (*ss. Antrosoluri* [13, 14]) with heavy metals has a particular character, because these soils present significant modifications of lithology and chemical-mineralogical characteristics, in comparison with normal soils [16, 17, 18, 30]. The inter-phase distribution and heavy metals mobility in urban soils are conditioned by relative high number of factors which, in most cases, have atypical values and variations, and make very difficult the realization of some quantitative estimations and the establish of some explicit correlations. From practical point of view, the distribution and mobility of heavy metals in urban soils are analyzed on the basis of correlations between their contents (total, fix and mobile fractions) and some physic-chemical or geochemical parameters, which can be evaluated with a high accuracy or are more accessible for direct determinations [4, 5, 15, 16, 17].

The literature not offers univocal criteria for the differentiation between fix and mobile forms and between speciation forms of heavy metals in urban soils, respectively. The attribution of "fix" or "mobile" quality for a fraction from total content of a heavy metal is realized towards the analytical technique used for the metal determination [5, 21, 26, 30] or on the basis of some theoretical and semi-empirical considerations, derived from analogies, extrapolations and/or generalizations of some models or experimental data [15, 24, 29, 32]. Not always such interpretations determined concordant conclusions with the real behaviour of heavy metals in urban soils [12, 18, 22, 33]. According with most opinions, an acceptable estimation of heavy metals distribution and mobility in soils can be realized on the basis of data obtained by the application of sequential solid/liquid extraction. The "fix" or "mobile" quality is attributed to heavy metals in function of their extractability (levigability) in some extractants (solvents or aqueous solutions). On this basis is realized and the relative association of heavy metals with mineral and organic components of soil, and the estimation of speciation forms weight of these in a particular pedo-geochemical context, respectively [4, 5, 17, 21, 26].

The problems connected with distribution and migrations of heavy metals in urban soils have an important place in environment geochemistry studies due to the high toxicity of these metals and, on the other hand, due to scientific deficit from this domain. Cadmium and lead represent two from the most dangerous heavy metals, being included in A class of toxicity [1, 17, 25]. Cadmium and lead can appear in urban soils as a large variety of speciation forms, thus the way in which these metals can participate at inter-phase distribution processes are very different from a zone to other [1, 4, 16, 17, 20, 30].

In this paper are presented the results of preliminary studied regarding the distribution and mobility of cadmium and lead in urban soils from industrial zone of Iaşi city. The determination of fix and mobile fractions weight to total cadmium and lead contents, and the relative association of these with mineral and organic soil components respectively, was realized basis of experimental results obtained by sequential solid/liquid extraction and extraction in aqueous PEG-based two-phase systems. The experimental results have evidenced the existence of some abnormal distributions of cadmium and lead in studied soils, and association ways with soils components less characteristic for these metals, respectively. Characteristic for studied soils is high accumulation probability of cadmium and lead as mobile species with high toxic potential.

MATERIAL AND METHOD

1. Work samples. The soil samples were obtained from industrial zone of Iaşi city, from a perimeter situated on Tutora Bvd (IS.1 and IS.8 samples), by a distance of 3.2 km in SE direction. The samples were take at a dip between 0 and 20 cm, during of September – October 2005, the distance between samples being by 300 ÷ 500 m. All samples were dried in air (14 days) and then at 95°C, for 3 hours. After drying the samples were used for granulometric analysis, and then they were grinded until almost all material has the granulometric size less than 0.100 mm (*tab. 1*). The chemical analysis was done using average samples obtained from these granulometric fractions. The experimental strategy used in this study was detailed presented previous [11].

2. Physic-chemical analysis. For all soil samples have been determined: specific weight, pH, acid-basis buffering capacity, ionic exchange capacity, electric conductibility, clay minerals contents, carbonates, iron oxy-hydroxides and humus, total contents of cadmium and lead, and the weight of these heavy metals associated with the main organic and mineral components from soil, respectively. The procedure of soil samples preparation and study methodology of these have been presented in several previous studies [5, 7, 8, 9, 10, 11].

Table 1

Textural classification of studied soils samples and details of drawing points.

Texture	Class	Sample	Observation drawing points		
			Slope	Exposition	Hydrostatic level
Raw	Raw/ clay-sand	IS.8	0.5-1.0^{o}	S-SE	> 2.5 m; temporary
	Clay-sand	IS.10	2.0-2.5^{o}	E-SE	≈ 2.0 m; temporary
Medium	Clay-sand dust	IS.2	3.0-3.5^{0}	E-SE	> 3.0 m; temporary
	Medium clay	IS.5	2.0-2.5^{o}	E-NE	≈ 1.5 m; temporary
	Clay- medium sand	IS.9	1.0-1.5^{o}	S-SE	≈ 1.5 m; temporary
	Clay-sand dust	IS.13	3.5÷4.0^{o}	E-SE	≈ 2.0 m; permanent
Fine	Clay-media argyles	IS.1	4.0-5.0^{0}	E-SE	> 2.5 m; temporary
	Clay argyles	IS.3	1.0-1.5^{o}	E-NE	≈ 2.0 m; temporary
		IS.4	1.5÷2.0^{o}	E-NE	≈ 1.5 m; temporary
		IS.11	1.5-2.0^{o}	E-NE	≈ 1,5 m; temporary
		IS.14	2.0-2.5^{o}	E-SE	≈ 2.0 m; permanent
	Sand argyles	IS.6	2.5-3.0^{o}	E-SE	≈ 1.5 m; permanent
		IS.12	2.0-2.5^{o}	E-NE	≈ 2.0 m; permanent
	Dust argyles	IS.7	4.5-5.0^{o}	E-SE	> 3.0 m; temporary

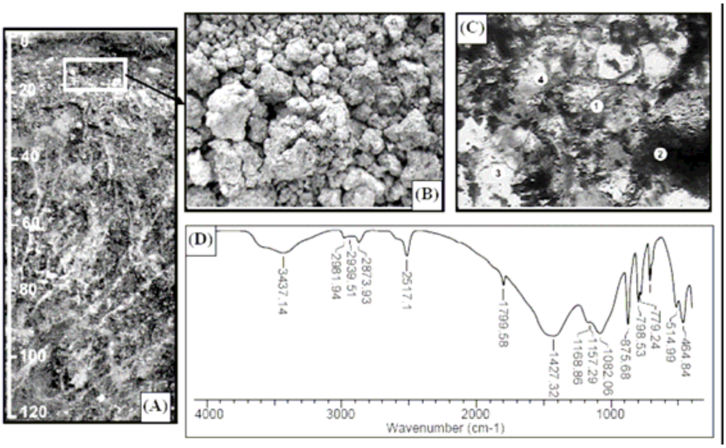

Figure 1. **The soil profile in drawing points IS.4 (soil with fine texture, clay-argyles) (A), drawing soil samples (5x) (B), microscopic image obtained from average sample (polarizate light, in thin section (400x) (C) IR adsorption spectra obtained on clay-humus fraction separated from soil sample (D). In figure (C): (1) complex formed between humus, clay minerals (montmorillonite ± kaolinite) and amorphous iron oxides and oxy-hydroxides; (2) humus associate with amorphous iron oxy-hydroxides; (3) deposition of amorphous silica; (4) aluminium-silica gel associated with clay minerals and iron oxy-hydroxides. The IR spectrum was obtained by KBr pellet method with a Bio-Rad Spectrometer [6].**

3. Determination of heavy metals contents from soil. The total content of Cd and Pb was determined by atomic absorption spectrometry (Perkin-Elmer 2380 atomic absorption spectrometer, mono-element lamp, air-acetylene flame, at 228 nm for Cd and 2833.3 nm for Pb) [5, 9, 10, 11, 21], after a complete weathering of samples with HNO_3, HF and H_2O_2. The separation of fix and mobile fractions of Cd and Pb was done by sequential solid/liquid extraction ad extraction in aqueous PEG-based two-phase systems: (**i**) extraction with 0.1 M $NaNO_3$ – easy exchanged cations (F. 1 fraction); (**ii**) extraction with 1 M CH_3-COONa (pH = 5), CH_3-COOH – cations bonded on carbonates phases (F. 2 fraction); (**iii**) extraction with 0.07 M $NH_2OH.HCl$, 4.5 M CH_3-COOH – cations bonded on Fe and /or Mn oxides (F. 3 fraction); (**iv**) extraction with 0.02 N HNO_3 and 30 %H_2O_2, 3 M CH_3-$COONH_4$ and 3.5 M HNO_3 – cations bonded on organic mater (F. 4 fraction); (**v**) dissolution with $HClO_4$ and HF – residual fraction (F. 5).

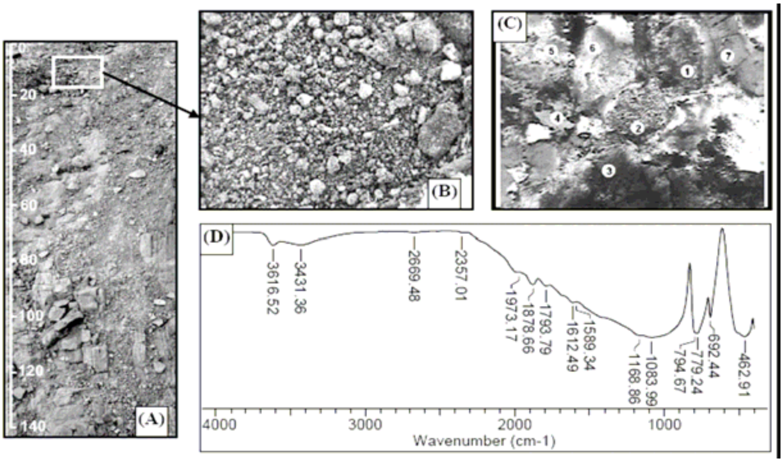

Figure 2. **The soil profile in drawing points IS.9 (soil with medium texture, medium dust argyles) (A), drawing soil samples (5x) (B), microscopic image obtained from average sample (polarizate light, in thin section (400x) (C) IR adsorption spectra obtained on clay-humus fraction separated from soil sample (D). In figure (C): (1) humus; (2) complex formed between humus, clay minerals (montmorillonite ± kaolinite) and amorphous iron oxy-hydroxides; (3) mixture of clay minerals; (4) deposition of iron oxy-hydroxides; (5) aluminium-silica gel associated with clay minerals, humus and iron oxy-hydroxides; (6) quartz; (7) feldspate.**

RESULTS AND DISCUSSION

1. General characteristics of studied soils. The pedological and physic-chemical of diagnostic characteristics (*tab.1, 2*) not permitted the classification of studied soil samples in one of the soil class characteristic of Iaşi city zone [3]. The frequent excavations and drillings (due to the constructions activities) and continuous adding of alohtone materials have determined radical changes of lithology, mineralogy and chemistry of these soils. According with SRTS 2003 [14] the studied soil samples can be classified in the antrosoil class with weak differentiated textural varieties (*fig. 3; tab. 1*).

The mineralogical composition of studied soil varied between large limits with important differences from a drawing point to other, as nature and contents of component minerals (*fig. 4*). The quantitative ratios between minerals component contents have an aleatory variation from a sample to other, without to can delimit a characteristic variation tendency for these. Under these conditions establish of some paragenesis and minerals associations for diagnostic are very difficult.

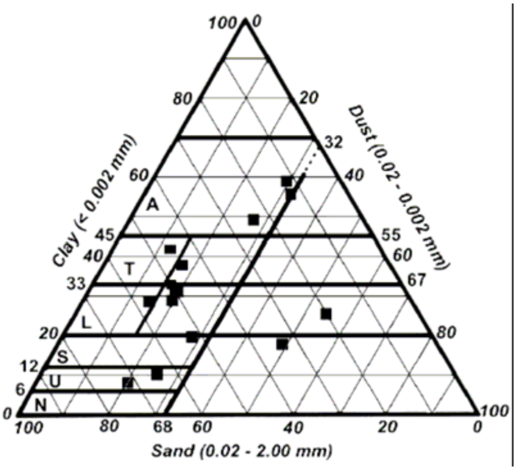

Figure 3. **The classification of studied soil samples after their texture: A – clay; T – clay-bearing; S – sand clay; U – Clay sand; N – sand [14].**

The clay minerals have a weight between 7.94-54.19 % (average: 29.48 %) and are represented by monthmorilonite, illite-hydromuscovite, kaolinite and halloysite. The weak correlations between clay minerals contents and another soil components, the microscopic and IR spectrometry studies (*figs. 1, 2, 5*) have indicate that in most part, the clay minerals have alohtone origins, not exist cert genetic connections between these and cannot be establish a characteristic distribution tendency of these (*fig. 4, 6*).

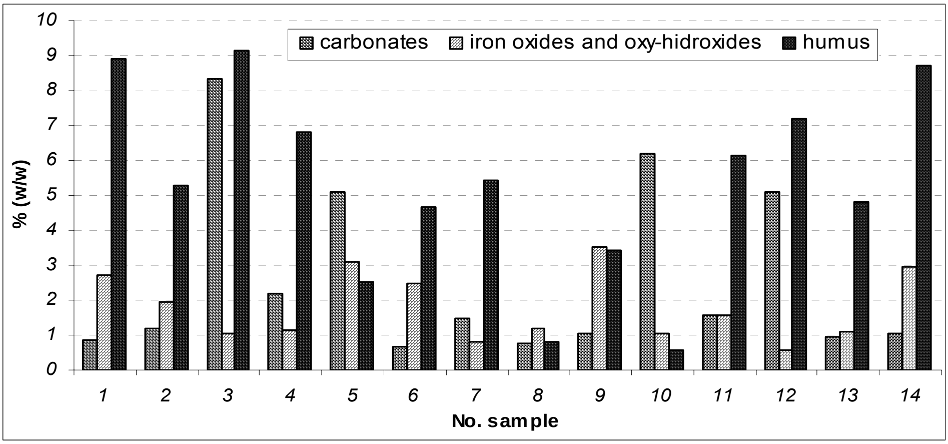

Figure 4. **The content of carbonates, humus, iron oxides and oxy-hydroxides of studied samples.**

The carbonates have a weight of 0.76-8.32 % (average: 2.60 %) (*fig. 4*), being represented by magnesium calcite, magnezite, dolomite, siderite, ankerite and several amorphous basic carbonates. The microscopic and IR spectrometry studies (*fig. 1, 2, 5*) have show that between carbonates only calcite, basic carbonates and partial ankerite have authigenic character. The observed basic carbonates are non-homogeneous mixtures, with amorphous aspect on calcite with carbonated, hydrated oxides and/or hydroxides of some minor elements co-precipitated on calcite.

Table 2

The physic-chemical characteristics of studied soil samples

Specification		Minimum	Maximum	Average
G.s.$^{(1)}$, g/cm^3		1.2677	1.5572	1.4383
pH(KCl)$^{(2)}$		5.28	8.30	6.67
$E_h^{(3)}$, Volts		0.109	0.640	0.348
pH(BC)$^{(4)}$		3.28	6.38	5.60
E.C$^{(5)}$, μS/cm		1.95	14.56	7.62
CSC$^{(6)}$; mechiv.g / 100 g dry soil	Na^+	0.18	3.20	1.33
	K^+	0.08	3.30	1.28
	Mg^{2+}	0.81	10.25	4.55
	Ca^{2+}	0.48	4.64	2.17
	H^+ (SH)	1.42	18.17	8.51
	T$^{(7)}$	6.77	33.26	17.91
SB$^{(8)}$		4.11	18.29	9.36
V$^{(9)}$, %		35.14	79.02	56.88

(1)Specific weight – determined by picnometric method. (2)Determined in KCl. (3)Redox potential. (4)Acid-basic buffering capacity. (5)Electrical conductibility. (6)Cationic exchange capacity. (7)Total cationic exchange capacity. (8)Sum of exchanged bases = Σ (Na^+, K^+, Ca^{2+}, Mg^{2+}). (9)Saturation in bases: V[%]=[SB/(SB+SH)]x100.

The iron oxides and oxy-hydroxides have a weight by 0.59-3.53 % (average: 1.80 %) (*fig. 4*), being represented by hematite, göethite, lepidocrocite, limonite, magnetite. With exception of magnetite, other iron oxides and oxy-hydroxides are in most cases by authigenic origin. The values of pH and redox potential (*tab. 2*) determined the iron occurrence in these minerals, predominant as Fe(III).

The humus content is relative low, his weight being by 0.56-9.15 % (average: 5.31 %) (*fig. 4*). The microscopic and IR spectrometry studies (*fig. 1, 2, 5*) have indicated that in studied soils, the humus was involve in intense processes of alteration and decomposition. A relative stabilization of this is realized by the formation of some complex associations with clay minerals, iron oxides and oxy-hydroxides ± amorphous silica or aluminium-silica gels.

In agreement with the contents of minerals and organic compounds, the ionic exchange capacities (average CTSC: 17.91 mechiv.g / 100 g soil) and the acid-basis buffering capacities (average: 5.60) have low values (*tab. 2*), which indicate a low re-adaptation capacity and a high vulnerability of these soils towards to the pollutants agents action. Under these conditions, the rapid and aleatory variations of pH and redox potential (0.109-0.605 volts) promoted the heavy metals accumulation in these soils. But, the sever modifications of lithology and chemical-mineralogical characteristics of urban soils imprint to the heavy metals distribution and migration processes a particular character.

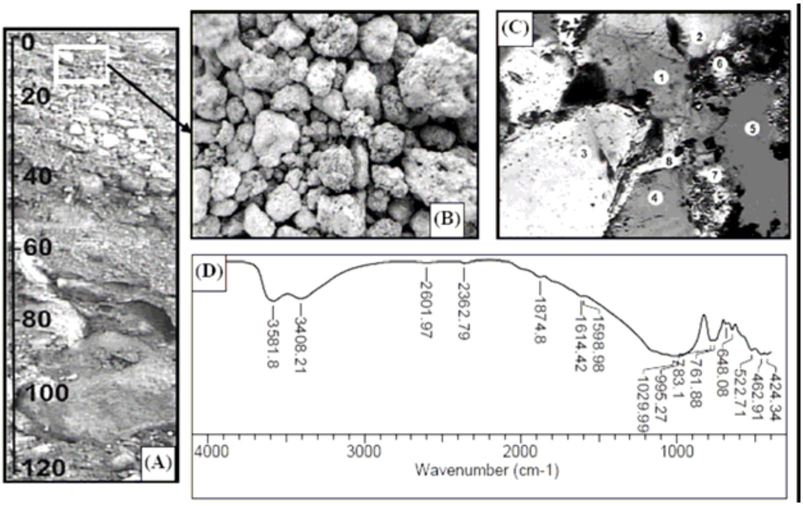

Figure 5. **The soil profile in drawing points IS.8 (soil with raw texture, raw clay dust) (A), drawing soil samples (5x) (B), microscopic image obtained from average sample (polarizate light, in thin section (450x) (C) IR adsorption spectra obtained on clay-humus fraction separated from soil sample (D). In figure (C): (1) iron oxides and oxy-hydroxides and caly minerals mixture; (2) quartz; (3) feldspate; (4) and (5) clay minerals in different alteration states; (6) complex formed between humus, clay minerals (montmorillonite ± kaolinite) and amorphous iron oxy-hydroxides; (7) amorphous silica; (8) association between aluminium-silica gel, humus and clay minerals.**

2. Cadmium and lead distribution in studied soils. In studied soils the cadmium concentration varied between 0.09-1.36 μg/g (average: 0.43 μg/g), only for three samples (IS.4, IS.10, IS.11) the values are higher than the normal values of cadmium concentration in soils. The lead concentration varied between 25.83-186.73 μg/g (average: 89.71 μg/g), but here the obtained values are higher than normal values of lead concentration in soils, for all samples. For none of studied soils samples the cadmium and lead contents are not over to values of alert concentrations. On the basis of these values the studied soils samples are situated in the unpolluted soils class and partial in the low polluted soils class, probable due to an accidental pollution. The presence of Cd and Pb in studied soils is recent and was realized by two mechanisms: (**i**) deposition from air soils and (**ii**) dissolution of some metallic components introduced in soil by specific industrial activities. These observations are sustained by the non-uniform way of Cd and Pb distribution in studied soils, evidenced by chemical analysis, IR spectrometry studies and correlations between Cd and Pb concentrations and main soil components, respectively. Similar observations have been noted and in other studies from urban soils pollution with heavy metals field [11, 17, 18, 30, 22, 33].

According with pH and redox potential values and chemical-mineralogical characteristics of studied soils (*fig. 7, 8; tab. 2*), the probable speciation forms of cadmium are: Cd^{2+}, $[Cd(OH)]^{+}$ and complexes with organic compounds, and for lead: Pb^{2+}, $[Pb(OH)]^{+}$, $Pb(OH)_{2(s)}$ and complexes with organic compounds. This means that the easy levigable fractions (F. 1) and those bonded by organic mater (F. 4) will have the predominant weight to the concentrations of these two metals in soils (*tab. 4, 5*).

Table 3

The Cd and Pb variation limits (total concentrations) in urban studied soils

Specification	Total; µg/g	F.1, %	F.2, %	F.3, %	F.4, %	F.5, %
Cadmium						
Minimum	0.09	19.20	3.19	3.97	30.16	2.62
Maximum	1.36	55.75	12.07	12.58	59.22	5.61
Average	0.43	36.40	3.48	8.08	48.21	1.97
Lead						
Minimum	25.83	13.71	4.33	2.19	25.93	1.86
Maximum	186.73	58.27	26.35	5.73	61.27	5.14
Average	89.71	36.97	12.07	2.29	45.11	2.97

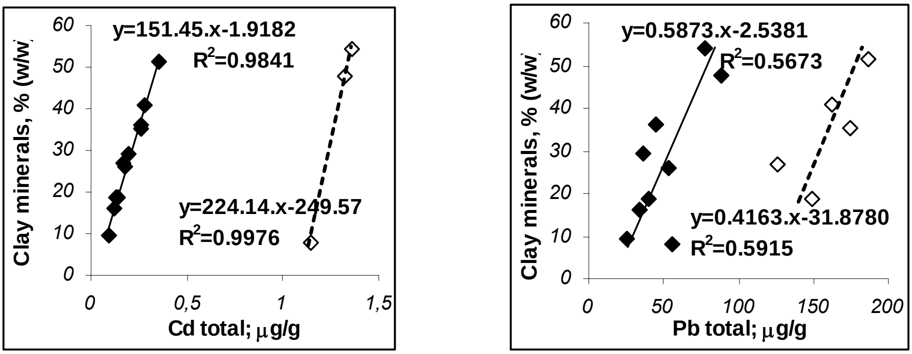

Figure 6. **The correlations between Cd and Pb concentrations and clay minerals content from studied soil samples. Both in case of cadmium and in case of lead the second correlation tendency corresponds to the samples where the total contents of these metals have high values**

Both, Cd and Pb concentration is positive correlated with the clay minerals content, and for both metals are evidenced two correlations tendencies (*fig. 6*). These indicate two fixation possibilities of the metals on clay minerals: (**i**) adsorption and/or ionic exchange - Cd^{2+} and $[Cd(OH)]^+$ species, and Pb^{2+} and $[Pb(OH)]^+$ species, respectively; (**ii**) complexation on clay-humus associations. In some studies, such correlations are attributed to the selectivity of Cd and Pb species towards to clay minerals type [2, 4, 17, 19, 23, 28, 31, 32]. In case of studied soils, for Cd such interpretation was not confirmed by chemical analysis, microscopic and IR spectrometry studies. In comparison with Cd, the lead manifests certain selectivity towards to clay minerals, being known his affinity for ilites. In general, Pb^{2+} and ionic hydoxi-complexes species are bonded on ilites and kaolinite by adsorption and on monthmorilonite predominant by ionic exchange [2, 16, 30, 31].

The ours studied cannot evidenced in an explicit way the selectivity of Pb binding on clay minerals. The chemical analysis, microscopic and IR spectrometry studies and the correlations between Pb concentration and clay minerals, and lead weight from F. 1 fraction and clay minerals respectively, (*fig. 9*) sustain only partial the previous observation. From our point of view, the interpretation of binding selectivity of heavy metals on clay minerals must be make with prudence, in special in case of urban soils and under concurrence conditions of inter-phase distribution processes.

Table 4

The cadmium distribution in studied soil samples (% from total content)

Sample	F.1	F.2	F.3	F.4	F.5
IS.1	34.16	n.d.	12.58	48.87	4.39
IS.2	29.27	n.d.	8.74	59.22	n.d
IS.3	43.90	12.07	4.27	35.66	4.1
IS.4	35.04	3.19	6.46	49.31	6.00
IS.5	41.80	6.73	9.18	40.15	n.d.
IS.6	34.10	n.d.	11.13	51.07	n.d.
IS.7	37.58	n.d.	4.77	54.68	n.d.
IS.8	27.82	n.d.	6.62	58.55	n.d.
IS.9	33.45	n.d.	13.74	51.08	n.d.
IS.10	19.20	9.72	8.55	56.92	5.61
IS.11	55.75	6.44	5.03	30.16	2.62
IS.12	41.39	10.64	3.97	42.29	n.d.
IS.13	43.90	n.d.	6.38	45.96	n.d.
IS.14	32.35	n.d.	11.71	51.03	4.91
Limits	*19.20-55.75*	*0.00-12.07*	*3.97-13.74*	*30.16-59.22*	*0.00-6.00*
Average	*36.40*	*8.13*	*8.08*	*48.21*	*4.60*

n.d. – undetermined; cadmium content is lower than detection limit of analysis method.

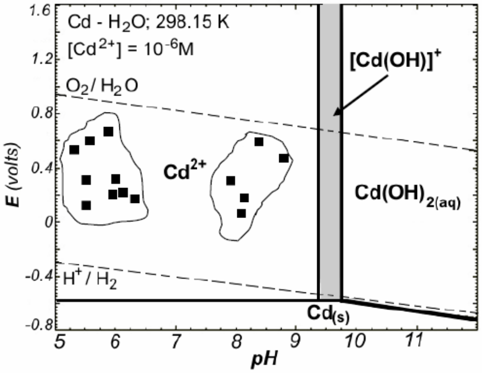

Figure 7. **The cadmium probable speciation forms in studied soil samples as function of pH and redox potential**

Towards to carbonates minerals, Cd not present correlations with cert geochemical signify. This indicate a low affinity of Cd for carbonates, and this observation is sustained by the low weight of F. 2 fraction at total Cd concentration (*tab. 4*). In case of lead, a good positive correlation with carbonates minerals is observed, which indicate a higher affinity of this for carbonates, in comparison with Cd. The weight of F 2 fraction at total Pb concentration is higher than in case of Cd. Under physic-chemical conditions of studied soils, Pb is fixed on carbonates minerals, probable by co-precipitation (as hydroxide or / and carbonates) (*fig. 8*). After that, Pb^{2+} can substitute isomorphic Ca^{2+} from carbonates network. By such mechanism the lead can be practical irreversible fixed and in significant quantities in urban soils.

Table 5

The lead distribution in studied soil samples (% from total content)

Sample	F.1	F.2	F.3	F.4	F.5
IS.1	35.79	5.08	2.92	53.71	2.50
IS.2	22.14	12.75	n.d.	60.78	2.85
IS.3	51.02	15.67	3.15	25.93	4.23
IS.4	47.60	6.44	2.81	39.55	3.60
IS.5	23.88	20.05	5.73	48.14	2.20
IS.6	13.71	15.79	4.09	61.27	5.14
IS.7	34.27	9.19	n.d.	50.62	4.70
IS.8	19.52	14.23	3.87	59.33	n.d.
IS.9	55.34	5.69	2.19	34.07	2.71
IS.10	17.81	26.35	5.05	48.29	2.50
IS.11	58.27	7.88	n.d.	29.65	3.12
IS.12	47.43	11.70	n.d.	39.01	1.86
IS.13	39.15	13.86	n.d.	42.91	2.90
IS.14	51.69	4.33	2.36	38.32	3.39
Limits	*13.71-58.27*	*4.33-26.35*	*0.00-5.73*	*25.93-61.27*	*0.00-5.14*
Average	*36.97*	*12.07*	*3.57*	*45.11*	*3.20*

n.d. – undetermined; lead content is lower than detection limit of analysis method.

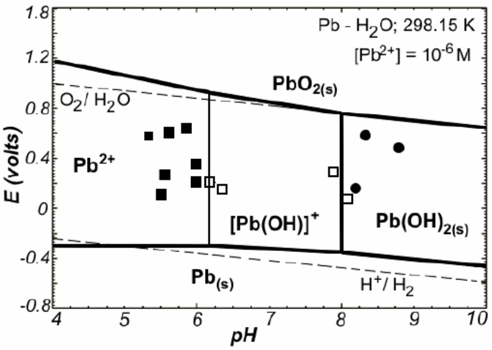

Figure 8. **The lead probable speciation forms in studied soil samples as function of pH and redox potential**.

Towards to iron oxides and oxy-hydroxides, the Cd and Pb concentrations not have correlations with cert geochemical importance, and the weight of F. 3 fraction at the concentration of the two metals have low values (*tab. 4, 5*). But, these results not indicate a weak affinity of Cd and Pb towards to iron oxides and oxy-hydroxides. Taking into account the physic-chemical and mineralogical characteristics of studied soils, is most probable the shutting of Cd and Pb fixation, due to the association of iron oxides and oxy-hydroxides with humus and clay minerals, in complexes with a relative high stability (*fig. 1, 2, 5*).

Towards to humus, the Cd and Pb concentrations are positive correlated, but the attribution to the geochemical significance is more difficult. For both metals can be distinguish two general correlations tendencies, which indicate two main fixation mechanisms of Cd and Pb on humus: (i) complexation (for low concentrations of Cd and Pb) - Cd^{2+} and $[Cd(OH)]^{+}$ species, and Pb^{2+} and $[Pb(OH)]^{+}$ respectively, (ii) adsorption (for high concentration of Cd and Pb) - $Cd(OH)_{2(aq)}$ and $Pb(OH)_{2(aq)}$ species. The high values of F. 4 fractions weight at Cd and Pb concentrations is due to the fixation of the two metals on humus by synergetic mechanism, induced by the humus association with iron oxy-hydroxides and clay minerals. In addition, the Cd and Pb fixation on such organic-minerals associations is very selective towards to the variations of physic-chemical conditions from soils.

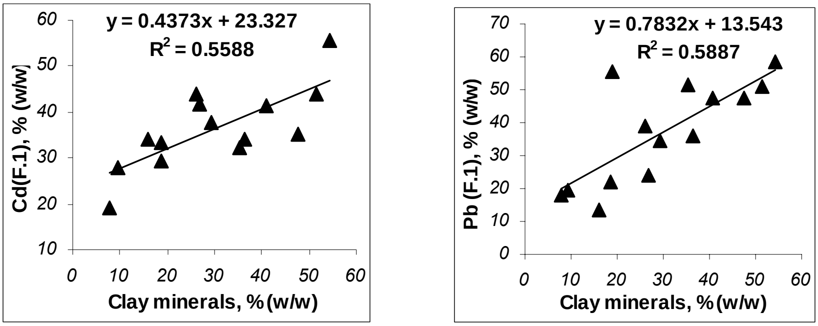

Figure 9. **The correlations between easy levigable fractions (F. 1) at total concentration of Cd and Pb and the content of clay minerals from studied soil samples.**

In case of studied soils, the weight of Cd and Pb fractions to the total concentration follows the order: F. 4 (fraction bonded on organic mater) > F. 1 (easy exchanged fraction) >> F. 2 (fraction bonded on carbonates minerals) > F. 5 (residual fraction) (*tab. 4, 5*). F. 1 and F. 4 fractions are predominant, for both Cd and Pb. The sum of these two fractions varied between 76.12-92.26 % (average: 84.61 %), in case of Cd, and between 66.10-90.01 % (average: 82.08 %), in case of Pb.

In comparison with Cd and Pb distribution in F. 1 and F. 4 fractions evidenced in “normal” soils (unmodified anthropic) [1, 13, 14, 16, 26], the values obtained in case of urban soils studied by as are significant higher. This behaviour of Cd and Pb in urban soils is probable due to the continuous perturbation of speciation equilibrium, as a consequence of aleatory variations of soils physic-chemical properties. These variation determined sever modifications of Cd and Pb inter-phases distribution, which are traduced by the levigation of these metals from some mineral phases (in special carbonates, iron oxides and oxy-hydroxides, etc.) and their passing in soil solution (as ionic forms and / or colloidal associations). From soil solution, the Cd and Pb levigated species are temporary fixed on clay minerals, which determined an abnormal increasing of F. 1 and F. 4 fraction weight.

The experimental data have evidenced n interesting particularity of Cd and Pb fractions bonded on clay minerals (F. 1) and organic compounds (F. 4). Practical, these fractions are composed by two parts: (i) one which correspond to normal distribution of Cd and Pb – where Cd and Pb are strong and selective bonded on the two soil component (strong chemisorptions and superficial complexation); (ii) another one which correspond to the “excess” of Cd and Pb towards to normal distributions – this is determined by Cd and Pb levigated from destabilized soil components and which are weak and non-selective fixed (by physical adsorptions). Chemical analysis, microscopic and IR spectrometry studies (*tab. 4, 5; fig. 1, 2, 5*) have confirmed the existence, on clay minerals and organic compounds from studied soils, both of Cd and Pb species, strong bonded (by chemisorptions and / or superficial complexation) and hard extractible, and of Cd and Pb species, weak bonded (most probable by labile colloidal associations) which can be relative easy extracted.

Table 6

The fixation ways and relative affinities of Cd and Pb toward to studied soils components

Mechanism	Adsorption	Ionic exchange	Complexation	Co-precipitation
Cd	Cl.Min. ≈ Hum. >> FeOx > Carb.	Hum. > Cl.Min. >> FeOx> Carb.	Hum. >> FeOx >> Cl.Min.	FeOx > Carb. >> Cl.Min.
Fraction	*Mobile fraction (levigable) of total Cd*		*Fix fraction (residual) of total Cd*	
Pb	Cl.Min. > Hum. > Carb. >> FeOx	Cl.Min. ≈ Hum. >Carb.>> FeOX	Hum. >> FeOx > Cl.Min.	Carb. >> FeOx >> Cl.Min.
Fraction	*Mobile fraction (levigable) of total Pb*		*Fix fraction (residual) of total Pb*	

Cl.Min – clay minerals; Hum. – humus; FeOx – iron oxides and oxy-hydrozides; Carb. - carbonates.

The weight of residual fraction (F. 5), both for Cd and for Pb, has low values. The association of this fraction with different mineral and organic components from urban soils is uncertain and disputed. In our opinion, an important contribution to the F. 5 fractions have the species of these two metals associated with low soluble compounds formed “in situ” (basic salts, oxides, hydroxides, carbonates, etc.). The chemical and physic-chemical analyses realized on residual fractions have evidenced the presence of Cd and Pb basic carbonates, in all samples.

The evidenced tendencies, for Cd and Pb, are predominant accumulative, but the distribution of these are inmost part abnormal towards to chemical-mineralogical characteristics of studied soils. Through and in other papers have been underlined similar behaviour of Cd and Pb in urban soils [11, 18, 22, 25, 27, 29, 33], in this moment cannot be formulated hypothesis with a general character. Cert, is the fact that in urban soils almost all heavy metals have particular distributions, different of normal distribution observed in another soils types.

The association way estimation of Cd and Pb with urban soils components and of mobility of these two metals respectively, on the basis of experimental results obtained by sequential solid/liquid extraction, generated several practical problems: (**i**) concordance between geochemical and analytical conceptions about notions of “fix” and “mobile” component; (**ii**) the association relevance of chemical elements with mineral phases, realized on the basis of the data obtained by sequential solid/liquid extraction and the real significations of those associations; (**iii**) practical possibilities for realization of a selective sequential solid/liquid extraction towards to components mineral phases of soils.

CONCLUSIONS

1. The urban soils from investigated perimeter are strong anthropized, and have radical modifications of lithology, mineralogy and chemistry. The pedological and physic-chemical diagnostic characteristics not permit an exact classification of samples in none of soils class characteristic for Iaşi city zone.

2. The mineralogical composition of studied soils varied in relative large limits. The quantitative ratios between mineral components have an aleatory variation, without to can delimit a characteristic variation tendency. Under these conditions, establish of some paragenesis and minerals associations for diagnostic, is very difficult.

3. In studied soils the Cd concentration varied between 0.09-1.36 μg/g, and the Pb concentration between 25.83-186.73 μg/g. In general, Cd and Pb concentration are positive correlated with the contents of clay minerals, carbonates, iron oxides and oxy-hydroxides and humus, but not all these correlations have cert geochemical significations.

4. In case of studied soils, the weight of Cd and Pb fractions to the total concentration follows the order: F. 4 (fraction bonded on organic mater) > F. 1 (easy exchanged fraction) >> F. 2 (fraction bonded on carbonates minerals) > F. 5 (residual fraction). F. 1 and F. 4 fractions are predominant, for both Cd and Pb. In comparison with Cd and Pb distribution in F. 1 and F. 4 fractions from unmodified anthropic soils, the values obtained in case of studied urban soils are significant higher.

5. In studied urban soils, Cd and Pb have generally abnormal distributions and association ways less characteristics for these metals with soil components. Characteristic for these soils is the high accumulation probability of Cd and Pb as mobile species with high toxic potential. Sever modifications of lithology and chemical-mineralogical characteristics of urban soils determined that the heavy metals distribution and migration processes to have a particular character.

REFERENCES

1. Alloway, B.J., Tills, A.R., Morgan, H., 1985 - *The speciation and avaiability of cadmium and lead in polluted soils*. In: D.D.Hemphill (ed.), *Trace Substances in Environmental health*, pp. 187-201. University of Missouri, Columbia, MO.
2. Altin, O., Ozbelge, O.H., Dogu, T., 1999 - *Effect of pH, flow rate and concentration on the sorption Pb and Cd on montmorillonite: I. Experimental*. J. Chem. Technol. Biotechnol., 74, 1131-1138.
3. Barbu, N., Ungureanu, Al. (coord.), 1987 - *Geografia Municipiului Iaşi*. Ed. Universității „Al.I.Cuza" Iaşi.
4. Bourg, A.C.M., 1995 - *Speciation of Heavy Metals in Soils and Groundwater and Implications for Their Natural and Provoked Mobility*. In: W.Salomons, U.Föstner and P.Mader (Eds.), *Heavy Metals. Problems and Solutions*, p. 19-32 Springer, Berlin.

5. Bulgariu, D., Bulgariu, L., Pui, A., 2004 - *The extraction and the determination of cadmium from geological samples (I)*, Anal. Univ. „Al.I.Cuza" Iaşi, s. Geologie, XLIX-L, 31-44.
6. Bulgariu, D., 2005 - *Procesul de zeolitizare a tufurilor vulcanice din România (vol. I)*, Ed. Universităţii "Al.I.Cuza" Iaşi.
7. Bulgariu, D., Rusu, C. (coord.), 2005 - *Metode instrumentale de analiză în geoştiinţe*. Vol. I: *Prelevarea probelor. Sampling*. Casa Editorială Demiurg, Iaşi.
8. Bulgariu, D., Rusu, C., Bulgariu, L., 2005 - *The pH Determination in Heterogeneous Solid / Aqueous Solution System. (I) Applications In Analytical Geochemistry*, Anal. Şt. Univ. Oradea, fac. Chimie, XII, p. 37-52.
9. Bulgariu, D., Rusu, C., Bulgariu, L., 2006 - *The impact of heavy metals pollution on the buffering and ionic exchange capacity of soils*. Universitatea de Ştiinţe Agricole şi Medicină Veterinară Iaşi, Lucrări Ştiinţifice – vol. 49, seria Agronomie, 47 – 62.
10. Bulgariu, L., 2006 - *Extracţia cu solvenţi a unor ioni metalici toxici* (teză de doctorat). Univ. Tehnică „Gh. Asachi" Iaşi, Facultatea de Chimie Industrială.
11. Bulgariu, L., Bulgariu, D., Robu, B., Macovenu, M., 2007 - *The impact of urbane soils pollution with heavy metals (cadmiu and lead) – case study: industrial zone, Iasi city*. Annals of West University of Timişoara, series Chemistry (in press).
12. Davies, J.A., Fuller, C., Cook, A.D., 1987 - *A model for trace metal sorption processes of the calcite surface: Adsorption of* Cd^{2+} *and subsequent solid solution formation*. Geochim. Cosmochim. Acta, 51, 1477-1490.
13. Filopov, F., 2005 - *Pedologie*. Ed. „Ion Ionescu de la Brad", Iaşi, p. 421.
14. Florea, N., Munteanu, I., 2003 - *Sistemul Român de Taxonomie a Solurilor*. Ed. ESTFALIA, Bucureşti.
15. Holm, P.E., Rootzén, H., Borggaard ,O.K., Christensen, T., 2003 - *Correlation of Cadmium Distribution Cofficients to Soil Characteristics*. J. Environ. Qual., 32, 138-145.
16. Kabata-Pendias, A., Pendias, H., 1992 - *Trace Elements in Soils and Plants* (2nd Edition). CRC Press Inc., Boca Raton, Florida.
17. Kabata-Pendias, H., 1995 - *Agricultural Problems Related to Excessive Trace Metal Contents of Soils*. In: W.Salomons, U.Föstner and P.Mader (Eds.), *Heavy Metals. Problems and Solutions*, p. 3-19, Springer, Berlin.
18. Kelly, J., Thornton, J., Simpson, P.R., 1996 - *Urban geochemistry: a study of the heavy metal content of soils in traditionally industrial and non-industrial areas of Britain*. Appl. Geochem., 11, 363-370.
19. 35. Liu, A., Gonzales, R.D., 1999 - *Adsorption / desorption in a system consisting of humic acid, heavy metals and clay minerals*. J. Colloid. Interface Sci., 218, p. 225-232
20. McBride, M.B., Sauvé, S., Hendershot, W., 1997 - *Solubility control of Cu, Zn, Cd, and Pb in contaminated soils*. Eur. J. Soil Sci., 48, 337-346.
21. Mester, Z., Cremisini, C., Ghiara, E., Morabito, R., 1998 - *Comparison of two sequential extraction procedures for metal fractionation in sediment samples*. Anal. Chim. Acta, 359: 133-142.
22. Möller, A., Müller, H.W., Abdulah,, A., Abdelgaward G., Uterman, J., 2005 - *Urban soil pollution in Damascus, Syria: concentrations and patterns of heavy metals in the soils of the Damascus Ghouta*. Geoderma, 14, 63-71.
23. Naidu, R., Kookana, R.S., Sumner, M.E., Harter, R.D., Tiller, K.G., 1997 - *Cadmium sorption and transport in variable charge soils: A review*. J. Environ. Qual., 26, 602-617.
24. Panizovkii, A.A., Mironenko, E.V., 2001 - *Mechanisms of lead (II) sorption in soils*. Euras. Soil Sci., 34, 371-381.
25. Ross, S.M. (ed.), 1994 - *Toxic Metals in Soil-Plant Systems*. Wiley, New York.
26. Sahuquillo, A., Rigol, A., Rauret, G., 2003 - *Overview of the use of leaching / extraction tests for risk assessment of trace metals in contaminated soils and sediments*, Trends in Analytical Chemistry, 22 (3): 152-159.

27. Sánchez-Camazano, M., Sánchez-Martin, M.J., Lorenzo, L.F., 1994 - *The content and distribution of cadmium in soils as influenced by the soil properties*. Sci. Total Environ., 156, 183-190.
28. Schindler, P.W., Furst, B., Dick, R., Wolf, P.U., 1976 - *Ligand properties of surface silanol groups. I. Surface complex with* Fe^{2+}, Cu^{2+}, Cd^{2+} *and* Pb^{2+}. J. Colloid. Interface Sci., 55, p. 469-475.
29. Smits, J.G.S., Rooiji, N.M., 1995 - *Mathematical Modeling for Assessment of Soil Pollution*. In: W.Salomons, U.Föstner and P.Mader (Eds.), *Heavy Metals. Problems and Solutions*, p. 101-118, Springer, Berlin
30. Thornton, J., 1991 - *Metal contamination of soils in urban areas*. In: P.Bullock, P.J.Gregory (Eds.), *Soils in Urban Environment*, Blackwell, Oxford, pp. 47-75.
31. Tiller, K.G., Greth, J., Brummer, G., 1984 - *The relative affinities of Cd, Ni, and Zn for different clay fractions and goethite*. Geoderma, 34, p. 17-35.
32. Wen, X., Du, Q., Tang, H., 1998 - *Surface complexation model for the heavy metal adsorption on natural sediment*. Environ. Sci. Technol., 32, 870-875.
33. Wilcke, W., Müller, S., Kanchanakool, N., Zech, W., 1998 - *Urban soil contamination in Bangkok: havy metal and aluminium partitioning in topsoils*. Geoderma, 86, 211-229.