POLISH JOURNAL OF SOIL SCIENCE
VOL. XLVIII/1 2015 PL ISSN 0079-2985

DOI: 10.17951/pjss/2015.48.1.31

Soil Chemistry

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THE CONTENT OF TOTAL CADMIUM AND ITS FRACTIONS IN ARABLE LAND OF THE PODLASIE PROVINCE**

Abstract. The aim of this study was estimation of total cadmium content and its fractional composition in arable soils, depending on their physicochemical properties. The research material consisted of samples taken from arable soil in 81 points within then Podlasie Province. The content of total cadmium in soils and its fractional composition was determined with the BCR method. It was found that the total content of cadmium was typical for uncontaminated soils and ranged from 0.11 to 1.59 mg kg^{-1}. The percentage of acid in the soluble and exchangeable fraction fluctuated at around 10% on average. The reducible fraction comprised about 20% and oxidizable fraction 26%, on average. Most of the cadmium was in the residual fraction. The factors that influenced the fractional composition of cadmium were determined. For the very light and light soils it was mainly the content of magnesium and pH, while for medium soils it was the organic carbon and magnesium content, content of soil fraction <0.02 mm, as well as the percentage of Cd in reducible fraction. [1]

The main source of contamination of cultivated plants with heavy metals (in areas free from meaningful sources of air pollution) is the soil, and their content is dependent on the concentration in the parent rock, pedogenesis [9], as well as the type of fertilizer used and the method of application. The behavior of heavy metals in the soil-plant system is dependent on chemical speciation and distribution of chemical forms of metals in soil [1, 17]. This, in turn, influences the availability and mobility of these metals in the soil. Fractions of heavy metals that are water soluble and exchangeable are considered the most mobile,

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**The studies were financed by the Ministry of Science and Higher Education, Poland under the grant No. NN310375539.

thus the most bioavailable as compared to other metal fractions in the soil [7, 21]. The bioavailability of elements contained in soil is dependent on pH, redox conditions, granulometric composition, organic matter and hydroxides of Fe, Mn and Al content, microorganisms, interactions between elements, the form of element occurrence and its ability to translocate from the solid phase to liquid phase within the soil. The uptake of elements by plants through chemical compounds from the soil solution is also related to some factors connected with the plant itself.

Cadmium is one of the most mobile metals in soils. It occurs in nature in zinc ores, as mineral greenockite (CdS) and in lead ores, as otavite ($CdCO_3$). Among sedimentary rocks, the highest amounts of cadmium can be found in shales (0.22 mg kg^{-1} on average). In the case of igneous rock, most cadmium is contained in alkaline rocks (0.13 mg kg^{-1} on average) [2].

In the Podlasie Province there is 96.91% of arable soils with natural heavy metal content, the first degree contamination pertain to 3.06% of soils and the second degree contamination occurs only in the case of 0.03% of soils. The higher degree of contamination does not occur [18]. Cadmium is taken up through roots and leaves, although it is not essential for plant development. The plants easily absorb this element from all the parts of environment (soil, water, air) [19].

The sequential extraction is one of the methods for evaluating the status of metals in the soil. Hence, the study on the content of cadmium and its fractions (using the BCR method) in arable soils was conducted. The influence of soil properties on the percentage of Cd fractions as compared to the total content was also estimated.

MATERIAL AND METHODS

The research material consisted of samples taken from arable soil in 81 points of Podlasie Province. Each point was located on mineral soil used as arable land, without external sources of contamination like roads or industrial plants. The samples were collected from the arable layer (0–30 cm) after plant harvest. Maize was cultivated in 14 points, cereals in 53 points, rape in 2 points, buckwheat in 2 points and grass in the rest of the sampling points. Basic physicochemical properties of soil samples there were determined: granulometric composition by Cassagrande's method with Proszynski's modification, organic carbon content by Tiurin's and pH in 1 mol· dm^{-3} KCl solution by the potentiometric method (2.5:1 v/m). Available phosphorus and potassium were determined by the Egner-Riehm method, and magnesium levels were determined in the soils by the Schachtschabel method (Table 1). Based on the percentage of soil fraction < 0.02 mm, soils were divided into two groups: very light (0–10%) and light (11–20%) textured as well as medium (21–35%) textured soils (referred to in the text as very light, light and medium). Heavy soil was not taken into account, because this type does not occur in the Podlasie Province. The total cadmium content was determined, after previous digestion in *aqua regia*, by means of the GFAAS technique using a Varian AA-100 apparatus.

TABLE 1. PHYSICOCHEMICAL PROPERTIES OF SOILS

Soils	Value	pH	C_{org} [g kg^{-1}]	Available P [mg P_2O_5 kg^{-1}]	Available K [mg K_2O kg^{-1}]	Available Mg [mg 100g^{-1}]	Content of soil fraction <0.02 mm [%]	Total content of Cd [mg kg^{-1}]
Very light and light textured n = 35	min-max	4.0–7.6	8–37	43–440	25–290	0.7–15.0	4–19	0.11–1.54
	$\bar{x}$	5.3	18	155	107	4.7	12	0.48
Medium textured n = 46	min-max	4.1–7.8	7–42	22–420	32–484	1.7–22.6	21–28	0.22–1.59
	$\bar{x}$	6.1	24	137	132	9.7	22	0.56

A modified BCR method with an ultrasonic probe (Sonics VCX 130) was used to evaluate fractional composition of Cd in soil samples. Extraction included four stages:

1. Acid in the soluble and exchangeable fraction (fraction I) – 1g of soil in 100cm^3 centrifuge tube with 40 cm^3 of 0.11 mol·dm^{-3} acetic acid was sonicated for 7 minutes (power – 20W) at a temperature of 22±5 ºC. Then, the mixture was centrifuged for 20 minutes at 3000g. The extract was separated for analysis. The residue with 20 cm^3 of deionized water was sonicated for 5 minutes (power – 20W) and centrifuged for 20 minutes at 3000 g. Water was discarded.

2. Reducible fraction, bound to Fe/Mn oxides (fraction II) – to the residue from the first step was added 40 cm^3 of 0,5 mol·dm^{-3} hydroxylamine hydrochloride fresh solution, pH 1.5, and sonicated for 7 minutes (power – 20W) at a temperature of 22±5 ºC. Then, the mixture was centrifuged for 20 minutes at 3000g. The extract was separated for analysis. The residue was rinsed with deionized water, like in the first step.

3. Oxidizable fraction, bound to organic matter (fraction III) – to the residue from the second step was added 20 cm^3 of 30% hydrogen peroxide and sonicated for 2 minutes (power – 20W) at a temperature of 22±5 ºC. Then, the volume of H_2O_2 was reduced to approx. 1 cm^3 using a water bath. To the moist residue was added 50 cm^3 of 1 mol dm^{-3} ammonium acetate and sonicated for 6 min. (power – 20W) at a temperature of 22±5 ºC. Then, the mixture was centrifuged for 20 minutes at 3000g. The extract was separated for analysis. The residue was rinsed with deionized water, like in the previous steps.

4. Residual fraction (fraction IV) – the residue from the third step was extracted using concentrated HNO_3 with the addition of 30% H_2O_2. The extract was separated for analysis.

The content of the studied element in fractions was determined by means of the GFAAS technique using a Varian AA-100 apparatus. The percentage share of individual fractions in the total content of cadmium was calculated. Pearson correlation coefficients between all sets of data were calculated. It was assumed that they are significant above 0.65 or below – 0.65. Since the correlation coefficients were non-significant, canonical factor analysis was made. Based on this analysis for both groups of soil, factors that influenced fractional composition of cadmium were determined.

RESULTS AND DISCUSSION

The majority of Podlasie Province soils belong to uncontaminated soils. The studied soils from the first group (very light and light) contained 0.48 mg kg^{-1} of total cadmium on average and from the second group 0.56 mg kg^{-1} Cd. Among 35 soils of the first group the cadmium content was higher than 1 mg kg^{-1} only in two samples. This was a similar case in the second group. According to Mocek [13] the average cadmium content in Polish arable soils amounted to 0.21 mg kg^{-1} with a range of 0.03 to 1.35 mg kg^{-1}.

Cadmium in the studied soils was mainly bound to the residual fraction and its percentage amounted to about 40% (Fig. 1–3). Many authors have stated the same results before [7, 6, 10, 15]. The high summary content of Cd in other fractions (above 50%, as compared to total content) extracted from analyzed soils has confirmed its large mobility in soils. These fractions have different phytoavailability [7, 8, 14, 16]. Biernacka and Małuszyński [4], investigating unpolluted soils over six years, have stated that 61.6% of Cd, as compared to total content, was bonded to fractions available and potentially available for plants (exchangeable, acid soluble, reducible and oxidizable fraction). Similar results are presented by Broos *et al.* [5] based on the study on soils with anthropogenic pollution. According to these authors, the labile cadmium pool (i.e. easily undergoes a mobilization under changes of environmental conditions) generally did not exceed 50% of total content.

The soil properties influenced the percentage of Cd content in particular fractions. Fraction III in very light and light soils (Fig. 1) contained more (31.5%) cadmium than in medium soils (20.1%). The percentage of Cd in fraction II was similar in both soil groups. Fraction I accumulated more cadmium in the case of medium soils. The literature [3, 11, 12, 20] often states that mobility of metals, including cadmium, increases with soil acidification. Obtained results confirmed that opinion (Fig. 2). The percentage of Cd in fraction I was the highest (above 13% of total content) in very acidic soils ($pH < 4.5$). In the case of fraction II the increase of Cd content from 15.7% for acidic soils (pH 4.6–5.5) to 25.3% for alkaline soils (pH > 7.2) was observed. The average Cd percentage was higher by about 8% than in fraction I. The percentage of Cd in fraction III was similar in acidic soils and considerably less in neutral and alkaline soils, but higher than in fraction II by about 10% in acidic and neutral soils and lower by about 10% in alkaline soils. The distribution of Cd in available and potentially available fractions can be explained by the occurrence of different compounds that are susceptible to changes based on pH. Cadmium forms different complex ions (e.g. $CdOH^+$, $CdCl^-$, $CdHCO_3^-$) and organic chelates. In soil solutions with neutral and slightly alkaline reactions, the cadmium occurs commonly as a free ion. In alkaline conditions, poorly soluble cadmium carbonates and phosphates precipitate [10].

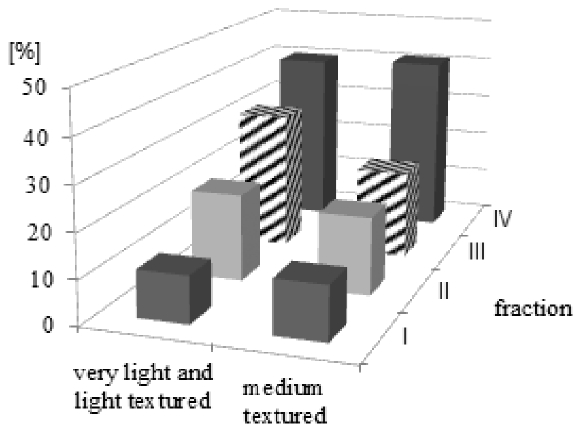

Fig. 1. Percentage of cadmium fractions in total content in soils depending on the agronomical category.

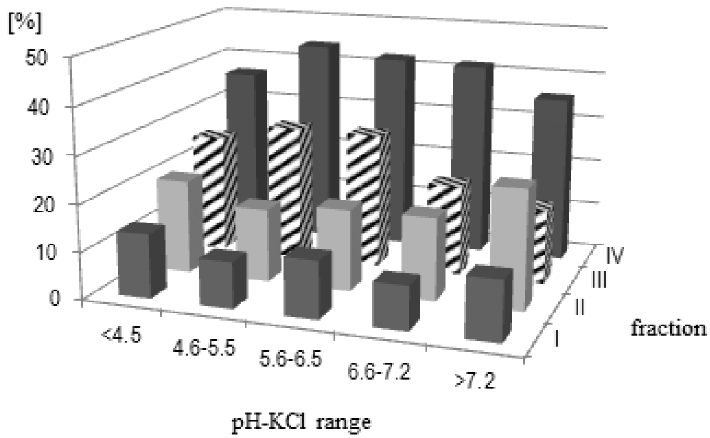

Fig. 2. Percentage of cadmium fractions in total content in soils depending on the soil pH.

The distribution of cadmium between particular fractions depending on the content of organic carbon is shown in Fig. 3. It was found that an increase of carbon content caused a drop in percentage of Cd in fraction I from 20% to 5%. In the case of fraction II the opposite trend occurred. In soils with a carbon content less than 10 mg kg^{-1} the percentage share of cadmium in this fraction was 15.6% and in soils with the content of carbon above 40 mg kg^{-1} it doubled. The percentage of fraction III in soils with a lower carbon content was high and exceeded 30%, but the percentage of the residual fraction did not exceed 40%. In soils where the content of carbon was higher than 20 mg kg^{-1}, the percentage share of Cd in fraction III was lowered, but more cadmium was in the residual fraction.

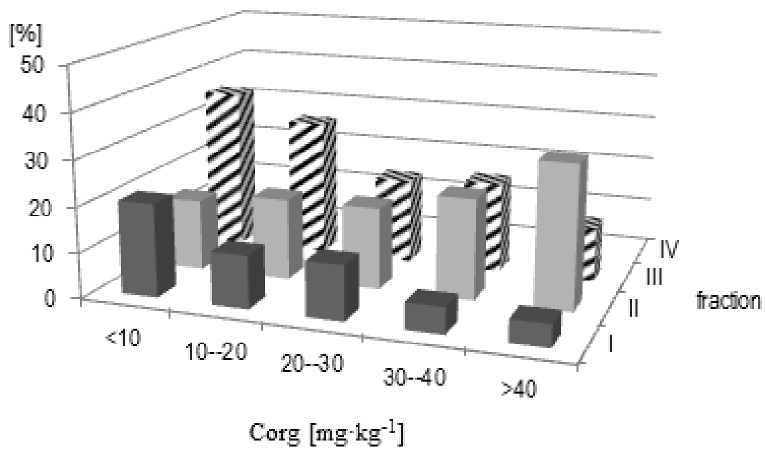

Fig. 3. Percentage of cadmium fractions in total content in soils depending on the content of organic carbon.

Based on the obtained results it's hard to clearly evaluate the influence of soil properties on the distribution of cadmium between fractions. The factor analysis that was made in the studied soils has allowed for the determination of the amount of factors and their influence on the percentage of cadmium in fractions as compared to the total content. It was conducted for both soil groups using the principal component analysis with varimax standardized rotation of factors. Variables characterized by factor loading with modulus equal or greater than 0.65 were considered as significantly influencing a particular factor. Based on this analysis, the set of four factors that were uncorrelated with each other was established. These factors explained about 70.24% of the changes in environment of medium soils (Table 2). According to the assumptions of factor analysis, the remaining factors explain to a lesser extent the changes in the studied system.

Factor 1 explained about 25.99% of the changes and mainly consisted of the following variables: the content of organic carbon and available magnesium, percentage of Cd in the fraction bound to Fe/Mn oxides as well as content of soil fraction <0.02 mm. It should also be pointed out that factor loadings can be interpreted as correlation coefficients between particular variables and the factor that explains the changes in the soil environment. According to this assumption it can be stated that all the variables significantly influencing the structure of factor 1 were positively correlated with it. Factor 2 explained about 18.67% of the changes in the studied soil environment and its structure was significantly influenced by the content of available phosphorus. This variable (P_2O_5) was positively correlated with factor 2. Factor 3 explained about 14.76% of the changes in the soil environment. Its structure was influenced in the highest degree by the percentage of Cd in fraction I, which was negatively correlated with the discussed factor. In contrast, factor 4 was related to changes of cadmium content in fraction 4. Similarly, like in the case of factor 3, this variable was negatively correlated with factor 4.

TABLE 2. FACTOR ANALYSIS OF CADMIUM FRACTION CONTENTS IN MEDIUM TEXTURED SOILS

Variable	Factor 1	Factor 2	Factor 3	Factor 4
pH	0.471722	0.495948	-0.528248	-0.119523
C_{org}	**0.869272**	-0.165352	-0.080930	0.095929
P_2O_5	0.105331	**0.870432**	-0.032039	-0.036448
K_2O	-0.058454	0.634006	0.307952	0.360030
Mg	**0.738873**	0.338247	0.116249	0.071196
Content of soil fraction <0.02mm	**0.721653**	0.094416	0.156718	-0.089266
Fraction I	-0.251588	-0.101048	**-0.840811**	0.126565
Fraction II	**0.652678**	-0.293653	-0.533949	0.019848
Fraction III	-0.220288	0.440170	0.253919	-0.547077
Fraction IV	0.041756	-0.143408	0.008559	**-0.773940**
Initial value	2.598939	1.867005	1.476143	1.082164
Share	0.259894	0.186700	0.147614	0.108216

The analysis for very light and light soils (Table 3) has allowed for the determination of a set of five factors that explained about 79.98% of changes of the soil environment. Factor 1 explained about 19.18% of the changes and mainly consisted of pH and the content of magnesium in studied soils. Factor 2 has clarified about 18.02% of changes in the studied soil environment. Its structure was significantly influenced in the highest degree by the content of cadmium in fraction II, which was positively correlated with factor 2 and by the content of Cd in fraction III (which was negatively correlated with the discussed factor). Factor 3 explained about 15.75% of changes in the soil environment. The factor structure in this case was dependent at most on the cadmium content in fraction IV, which was positively correlated with factor 3. Factor 4 was mostly connected to the changes of phosphorus and soil fraction content <0.02 mm. Factor 5 was related to the content of organic carbon.

TABLE 3. FACTOR ANALYSIS OF CADMIUM FRACTION CONTENTS IN VERY LIGHT AND LIGHT TEXTURED SOILS

Variable	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
pH	**0.725323**	0.112196	0.038625	0.041023	0.022425
C_{org}	0.137672	0.040884	0.051842	-0.042513	**0.924891**
P_2O_5	0.374736	0.216070	0.106814	**-0.831433**	0.001238
K_2O	0.616415	-0.262047	0.031346	-0.405619	-0.104617
Mg	**0.816509**	-0.106543	-0.123262	0.069742	0.384442
Content of soil fraction <0.02mm	0.428414	0.163942	0.018707	**0.774840**	-0.126920
Fraction I	0.030340	0.272246	-0.635140	0.261968	-0.395424
Fraction II	-0.005966	**0.833806**	-0.324886	-0.198227	0.047924
Fraction III	0.040782	**-0.865692**	-0.344749	-0.184231	0.044417
Fraction IV	0.004199	0.122283	**0.956724**	0.033191	-0.066912
Initial value	1.918303	1.701569	1.575241	1.607502	1.195884
Share	0.191830	0.170157	0.157524	0.160750	0.119588

CONCLUSIONS

1. The content of cadmium was typical for unpolluted arable land and varied over a wide range.
2. Most cadmium was found in the residual fraction (in both soil groups its percentage share amounted to about 40%). Its percentage in other fractions was differentiated by properties of the studied soils.
3. The distribution of cadmium between fractions was influenced by many properties of soils, which were correlated negatively or positively with each other (these are mainly the content of organic carbon, available magnesium and phosphorus).

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ZAWARTOŚĆ KADMU OGÓLNEGO I JEGO FRAKCJI W GLEBACH GRUNTÓW ORNYCH PODLASIA

Celem pracy było określenie zawartości ogólnej kadmu i jego składu frakcyjnego w glebach ornych w zależności od ich właściwości fizykochemicznych. Badania wykonano w oparciu o 81 próbek gleb uprawnych pobranych w woj. podlaskim. Określono w nich zawartość ogólną kadmu i jego skład frakcyjny metodą BCR. Zawartość ogólna kadmu była typowa dla gleb niezanieczyszczonych i wahała się w przedziale od 0,11 do 1,59 mg kg^{-1}. Udział kadmu we frakcji rozpuszczalnej w kwasach i wymienialnej wynosił średnio około 10%, we frakcji redukowalnej średnio około 20% i we frakcji utlenialnej średnio 26%. Najwięcej kadmu zgromadziła frakcja rezydualna. Określono czynniki, które wpływały na dystrybucję kadmu pomiędzy frakcjami. W przypadku gleb bardzo lekkich i lekkich największy wpływ miała zawartość magnezu i pH, a w przypadku gleb średnich zawartość magnezu, węgla organicznego, frakcji spławianych i udział procentowy kadmu we frakcji redukowalnej.