Time factor influence on soil heavy metal concentration in relation to soil contamination assessment

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Abstract: The aim of this study was to investigate the dynamics of changes in the metal concentrations in the soils contaminated with Cd, Pb, and Zn during a 5 year period. Additionally the purpose included assessment of the suitability of 1 M HCl to control soil contamination with heavy metals compared to using of aqua regia method. The study was conducted in concrete-framed microplots, filled with two soils (sandy and silty), which were artificially co-contaminated with Cd, Pb and Zn. There was a gradual decrease in these concentrations during the 5 year period. The concentrations of the metals extracted with 1 M HCl were very similar to the total concentrations. After 5 years of research, the topsoil had the smallest decrease in Pb concentration, which for the sandy, and silty soils was, respectively, by 7% and 9% in relation to the initial value. The concentrations of Cd and Zn decreased by up to about 35% in the sandy soil and by about 20% in the silty soil. Sandy soil contamination with metals poses a potentially higher threat to humans and the environment than silty soil contamination. Therefore, the examination of the sandy soils contamination, as well as of the groundwater occurring in these areas, should be carried out at least once for 5 years. It has been shown that the analytical method using aqua regia can be replaced by 1 M HCl method to track changes of metals concentration in the soil, that occur over time period.

Introduction

Heavy metals belong to class of substances that can pose a threat to human health and the deterioration of the environment (Shirkhanloo et al. 2015). Metals get into the air and then into the soil, mainly as a result of the combustion of fuels in the, power industry, as well as in the local heating furnaces. Metallurgy, the transportation as well as incineration of waste and trash, represent other source. Also the management of municipal sewage sludge in agriculture leads to contamination of soils with heavy metals.

There are several approaches to monitoring soil contamination with heavy metals such as chemical, geophysical, and biological techniques. Chemical techniques allow for the identification of each metals and determination of their concentration in the soil using instruments, such as atomic absorption spectrometer, or mass spectrometer, after prior metal extraction from the soil sample. Geophysical techniques are applicable to examine changes in physical properties of the soil and can address problems in large soil contamination areas. They are not invasive, but not useful for identifying individual metals. Biological techniques use organisms as indicators of soil contamination, to monitor or predict changes in soil contaminant concentrations over time (Markowicz et al. 2016).

The results of many studies have shown that the concentration of heavy metals in the soil varies over time.

These changes may be caused by fluctuations in metal emission, connected with reduction or intensification of industrial activity, transport, waste incineration and application of sewage sludge as a fertilizer. Numerous research studies based on monitoring have been devoted to tracking trends in spatial and temporal changes in the concentration of heavy metals and other trace elements in soils, caused by the abovementioned actions (Onweremadu et al. 2007, Li et al. 2009, Vilavert et al. 2012, Aelion et al. 2014, Meyer et al. 2014). The concentration of heavy metals in the soil may vary within a certain period of time, not only due to changes in the metal deposition, but also because of chemical and microbiological transformations in the soil, leading to increased mobility of metals and their leaching. Many authors have studied seasonal changes in the concentrations of mobile and bioavailable metal forms in the soil (Fendorf et al. 2004, Fernandez et al. 2007, Shikhova 2008, Owoade et al. 2014, Stanislawska-Glubiak and Korzeniowska 2018). The dynamics of these changes depended on the physicochemical properties of the soil and on weather parameters, mainly rainfall. Onweremadu et al. (2007) recorded a higher variation of metal concentration in the soil during the rainy season as compared with the dry season. Moreover, some authors observed the infiltration of mobile metal forms into the deeper layers of the soil (Fernandez et al. 2007, Li et al. 2009), which indicated the possibility of their

entry into aqueous systems, with the simultaneous reduction of the total metal concentration in the topsoil.

Current developments in soil contamination monitoring include increased efficiency of soil contaminant extraction processes that improve contaminant recovery, development of laboratory instrumentation with enhanced detection limits or ease of use.

Usually the assessment of soil contamination with metals is carried out on the basis of the so-called total concentration, which is determined using strong acid as extractant like aqua regia, $HClO_4$ or HNO_3. These procedures, however, are complicated, time-consuming, and quite expensive. 1 M HCl is also a strong extractant, sometimes used to assess the deficiency in the soil of metals, for example copper and zinc, which are also micronutrients (Korzeniowska and Stanislawska-Glubiak 2015). Preliminary studies have shown that it can be used to evaluate the potential risk of heavy metals in contaminated areas (Stanislawska-Glubiak and Korzeniowska 2010).

Referring to the soil contamination monitoring, the aim of this study was to investigate the dynamics of changes in the metal concentrations in soils contaminated with Cd, Pb, and Zn during a 5 year period. Additionally, the purpose included assessment of the suitability of 1 M HCl to control soil contamination with heavy metals compared to using aqua regia method.

Materials and Methods

Microplot experiment

In the years 2009–2014, a microplot experiment was conducted in the system of complete randomization, in 4 replications at the Experimental Station in Pulawy (Eastern Poland). The study included concrete-framed microplots sized $1 \times 1.2 \times 1$ m, filled with two types of soils. The first one, further referred to as sandy soil (A), had the texture of sand. Another, further referred to as silty soil (B) was classified as silt loam. Both soils can be classified as soils with very low organic matter content.

Eight years before our studies, in 2001, both experimental soils were artificially contaminated. The soils were treated with oxide forms of Cd, Pb and Zn by thoroughly mixing them together with a layer of 0–20 cm. Soil A, after introducing pollutants, contained Cd-3.8, Pb-529, Zn 906 mg kg^{-1} in the layer of 0–20 cm, while Soil B – Cd-13.0, Pb-1048 and Zn-3436 mg·kg^{-1}. Metal concentration in the contaminated Soil A was several-fold lower than in Soil B, as the doses of the metals were adjusted to the type of soil in order to obtain a moderate degree of contamination according to Kabata-Pendias et al. (1993) classification. In this classification, the levels of the concentration of individual metals which defined the degree of soil contamination (weak, average, high and very high) differ depending on soil texture, organic matter content, and pH. Our studies performed in the years 2009–2014 aimed at observing temporal changes in the concentrations of Cd, Pb and Zn in the layers of 0–20 cm and 20–40 cm of sandy and silty soils. Physicochemical properties of the studied soils, as determined at the commencement of the studies, are presented in Table 1.

In the years 2001–2004, the microplots were covered with Italian ryegrass *(Lolium multiflorum),* while in the years 2005–2009, the soil was fallowed. In 2010 and 2011 willow (*Salix viminalis*) was grown on them, and in 2012 the soil was not cropped again, while in 2013 and 2014 maize was cultivated.

The experiment was set up under the conditions of open space, where the soil and test crops were subject to natural weather conditions. The total annual rainfall during the period of the study oscillated between 502–751 mm, while the long--term mean for the previous 15 years was 585 mm (Table 2) at the mean air temperature of 7.9°C.

Soil samples

In the autumn of 2001 soil samples were collected only from the layer of 0–20 cm. In the autumn of 2009, as well as after harvesting willow (2011) and maize (2013 and 2014), the samples were collected from two layers: topsoil (0–20 cm) and subsoil (20–40 cm). The samples from each plot were collected using an Eijkelkamp soil sampler of the diameter size equal 2.5 cm. Each sample from a given plot consisted of five subsamples.

Plant samples

In the first year of willow cultivation (2010) after growing, the total biomass of the aerial parts was cut from each plot. Leaves were separated from stems, and stems were cut into smaller pieces. In the second year (2011), stems were cut and roots dug up, while leaves were left on the plot.

Table 1. Soil physicochemical properties at the beginning of studies (2009)

Soil	Layer (cm)	Soil fraction (mm)			TOC g·kg^{-1}	pH	CEC cmol(+)·kg^{-1}
		2.0–0.05	0.05–0.002	<0.002			
		%					
Sandy	topsoil (0–20)	90	8	2	3.7	5.9	2.18
(A)	subsoil (20–40)	93	6	1	1.8	6.0	2.65
Silty	topsoil (0–20)	27	63	10	5.1	6.2	5.04
(B)	subsoil (20–40)	36	59	5	2.1	7.2	6.50

Table 2. Total annual precipitation in the region of the Experimental Station in Pulawy

1991–2008 mean	A year of the study					
	2009	2010	2011	2012	2013	2014
	precipitation (mm)					
585	662	649	681	751	502	503

Each year (2013 and 2014), maize was collected at the stage of harvest maturity by cutting the whole aerial part from each plot. This part was then divided into individual parts: ears and straw. Then, the ears were separated into cobs and grains. In both years, the roots were dug up.

The roots of willow and maize were carefully brushed off the soil and rinsed with water. All parts of the plants were weighed individually after drying in an oven at 60°C. Then they were ground into fine powder and thoroughly mixed. Samples for chemical analyses were taken from the obtained plant material of each part of the plant.

Chemical analyses

All the chemical analyses were performed in the Central Laboratory of the Institute of Soil Science and Plant Cultivation in Pulawy, certified by the Polish Centre of Accreditation (certificate no. AB 339) according to PN-EN ISO/IEC 175 17025.

The soils underwent the following determinations: texture, total organic carbon (TOC), soil pH, cation exchange capacity (CEC) and concentration of Cd, Pb, Zn. The texture was evaluated by aerometric method according to Casagrande's and Prószyński (PN-R-04033: 1998). Total organic carbon in soil (TOC) was determined by Tiurin's method using potassium dichromate (PN-ISO14235: 2003), pH was established potentiometrically in KCl solution (ISO10390), while cation exchange capacity (CEC) – using barium chloride solution, (ISO 11260) and flame atomic absorption spectrometry (FAAS).Total content of Cd, Pb and Zn in soil were determined by FAAS after mineralization in aqua regia. Additionally, metals were determined after the extraction with 1 M HCl (Gembarzewski and Korzeniowska 1990). The extractant was added to air-dry soil at a ratio of 10:1, and shaken for one hour in a rotational 'overhead' mixer (about 40 rotations per minute).

Heavy metals in plant samples were determined by the FAAS method, after prior dry ashing of the material in a muffle furnace at 500°C and digesting it with 20% nitric acid (PN-R-04014: 1991).

Metal uptake by plants

The reason of metals losses from the soil can be leaching or accumulation by plants. The loss of metals from the soil over the period of 2009–2014 caused by plants accumulation was calculated as the sum of uptake with yield of willow and maize.

The uptake of metals by individual plants was calculated according to the following formula:

$$Mup = Y \cdot MC$$

where: Mup – metals uptake per plot (mg·plot^{-1})
   Y – yield (kg·plot^{-1})
   MC – the concentration of metal (mg·kg^{-1})

The calculation included the following parts of plants: willow 2010 – leaves + stems; willow 2011 – stems + roots; maize 2013 and 2014 – straw + cobs + grain + roots.

Metals uptake per plot was expressed also as the metals uptake from a kilogram of the soil according to the formula:

$$Muk = \frac{Mup}{V \cdot D}$$

where: Muk – metals uptake from a kilogram of the soil (mg·kg^{-1})
   Mup – metals uptake per plot (mg·plot^{-1})
   V – volume of topsoil (1.2 m^2 × 0.4 m = 480 000 cm^3)
   D – bulk density of sandy/silty soil (respectively 1.3 g cm^{-3} and 1.7 g cm^{-3})

Results

Cadmium concentration

The total cadmium concentration determined by using aqua regia (Cd$_{ar}$) in the top layer (0–20 cm) of the sandy soil markedly decreased over time (Fig. 1).

After 5 years, the concentration of this element fell by 35% compared to its initial concentration (Table 3).

In the subsurface layer (20–40 cm) of the same soil, the initial concentration of Cd$_{ar}$ was 2-fold lower than in the topsoil, and it was relatively stable over time. In the silty soil with a 2-fold higher CEC than sandy soil, the changes of Cd$_{ar}$ concentration in the topsoil proceeded more mildly compared with the sandy soil (Fig. 1). The concentration of Cd$_{ar}$ after 5 years was lower by about 20% compared to the initial concentration (Table 3). In the subsoil, it remained at the same
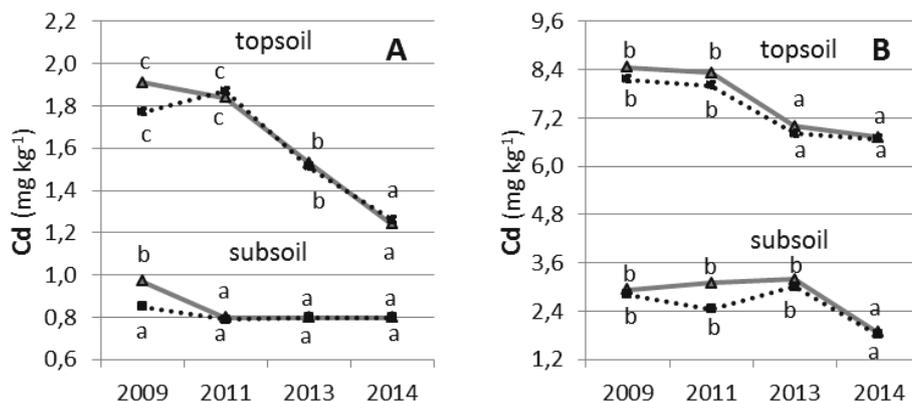

Fig. 1. The changes in the total cadmium concentration (——) and cadmium soluble in 1M HCl (·······) in sandy soil (A) and silty soil (B) in the layers of 0–20 cm (topsoil) and 20–40 cm (subsoil). The same letters, within the same line, stand for no significant differences between treatments by Tukey's test (P<0.05)

level, and only in the last year, it decreased by as much as 36% compared with the initial concentration.

Lead concentration

The total lead concentration determined by using aqua regia (Pb_{ar}) in the top layer of the sandy soil decreased only in the last year of the study by 7% compared to the initial value (Fig. 2, Table 3).

At the same time, in the subsoil, Pb_{ar} concentration decreased in the consecutive years, while in the last year, it rose again to the level lower by 10% compared to the initial concentration.

In the top layer of the silty soil, we recorded a single increase in 2011 of Pb_{ar} concentration, while in other years Pb_{ar} concentration slightly decreased. In the subsoil, there was an inexplicable significant increase in the concentration of this metal in the subsequent years, as well as its 50% decrease in the last year of the studies compared to the initial level (Fig. 2, Table 3).

Zinc concentration

The total zinc concentration determined by using aqua regia (Zn_{ar}) in the top layer of the sandy soil decreased almost linearly with time (Fig. 3).

Table 3. The total concentration of metals in the soil at the beginning and the end of the five-year study

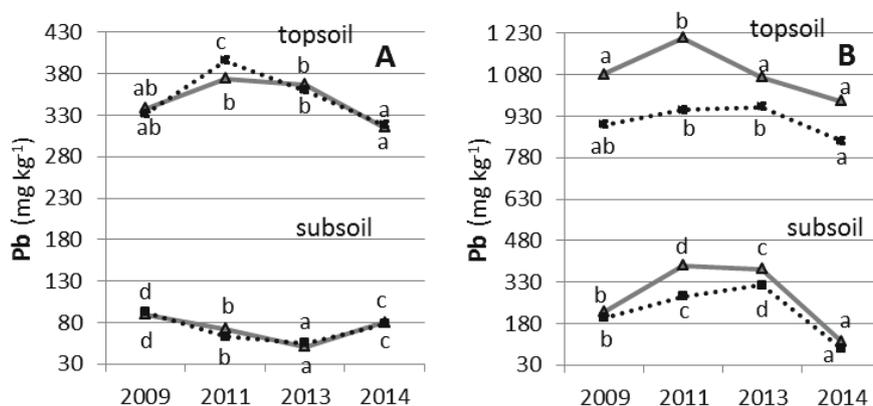| Soil	Layer (cm)	Cd			Pb			Zn		
		2009	2014	decrease %	2009	2014	decrease %	2009	2014	decrease %
		(mg·kg⁻¹)			(mg·kg⁻¹)			(mg·kg⁻¹)		
Sandy (A)	topsoil (0–20)	1.91	1.24	35	338	315	7	691	422	39
	subsoil (20–40)	0.97	0.8	18	89	80	10	430	352	18
Silty (B)	topsoil (0–20)	8.46	6.72	21	1083	986	9	3455	2770	20
	subsoil (20–40)	2.93	1.88	36	223	116	48	902	510	43

Fig. 2. The changes in the concentrations of total lead (——) and lead soluble in 1M HCl (·······) in sandy soil (A) and silty soil (B) in the layers of 0–20 cm (topsoil) and 20–40 cm (subsoil). The same letters, within the same line, stand for no significant differences between treatments by Tukey's test (P<0.05)

Fig. 3. The changes in total zinc concentration (——) and zinc soluble in 1M HCl (·······) in sandy soil (A) and silty soil (B) in the soil layers of 0–20 cm (topsoil) and 20–40 cm (subsoil). The same letters, within the same line, stand for no significant differences between treatments by Tukey's test (P<0.05)

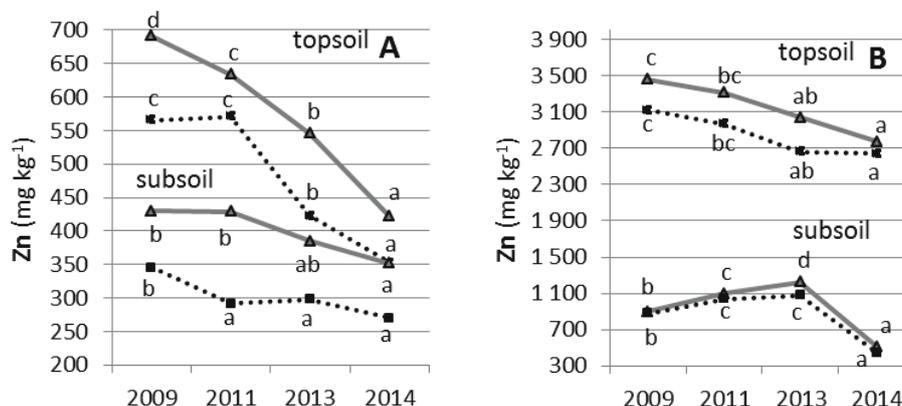After 5 years, the concentration lower by about 40% was recorded compared to the initial value (Table 3). In the subsoil, a similar declining trend was observed, while the final Zn_{ar} concentration was only by about 20% lower in relation to the initial one.

Temporal changes in the Zn_{ar} concentration in the top layer of the silty soil, similarly as in the sandy soil, were close to the linear, but with a much smaller slope (Fig. 3). The final concentration was only by 20% lower as compared to the initial one (Table 3). In the subsoil, the changes were less regular. Only in the last year, there was a 40% decrease in relation to the initial value.

Concentration of metals extracted with 1M HCl in the soil

Changes in the Cd_{HCl} concentration, which were observed over a 5-year period, both in the sandy soil and silty soil, showed a similar trend as the changes in the Cd_{ar} concentration. This indicates a very high correlation between the Cd concentration determined in aqua regia and in 1 M HCl solution (Fig. 1). In addition, the lines which showed temporal changes of both Cd forms, overlapped almost completely, and thus the level of their concentrations was very similar.

It was likewise in the case of both Pb forms in the sandy soil (Fig. 2). In the silty soil, however, although the temporal changes of Pb_{HCl} concentration showed an analogous trend as Pb_{ar}, Pb_{HCl} concentration was by about 10–20% lower compared to Pb_{ar} (Fig. 2).

In the case of zinc in the sandy soil, some discrepancies were found between the Zn_{ar} and Zn_{HCl}, both as regards the course of lines characterizing temporal changes, and the level of the concentration of this element. These concentrations differed in the range of 10–30%. (Fig. 3). In the silty soil,

however, the changes in the concentrations of both forms of Zn overlapped to a greater extent than in the case of the sandy soil, and the level of Zn_{HCl} concentration was by only 2–12% lower than the level of Zn_{ar} (Fig. 3).

Changes of soil pH

At the start of our research, sandy soil had a slightly lower pH in the layer of 0–20 cm than silty soil, amounting to, respectively, 5.9 and 6.2, while in the subsurface layer, there was a higher difference between the two soils (Table 4).

The value of pH in the subsoil was 6.0 for the sandy soil and 7.3 for the silty one. Generally in the period of 5 years, higher changes of pH occurred in the sandy soil compared to the silty one, especially in the layer of 0–20 cm. At the end of the studies, sandy soil became more acid compared to its initial state. Soil pH decreased by 0.7 and 0.4 units, respectively, in the top and subsoil. In the silty soil, pH decreased only by 0.4 and 0.2 units.

Metal uptake by plants

Metal uptake by test plants depended on a metal, soil type, plant species, and in the case of maize – also on a year of cultivation (Table 5).

During the period of the research, the plants accumulated the metals in the following order: Zn> Pb> Cd. On silty soil, the total removal of Cd per plot was about 12-fold larger, while of Zn and Pb – 2-fold larger compared to the sandy one. Generally, however, the loss of metals from the soil over a period of 5 years, caused by their uptake by plants, was very small – to 1.78 mg·kg⁻¹ for the sandy soil and to 3.10 mg·kg⁻¹ for the silty soil. These are completely insignificant quantities in confrontation with the total loss of metals from the soil shown in Table 3.

Table 4. Changes of soil pH during five-year period

Soil	Layer (cm)	A year of the study			
		2009	2011	2013	2014
Sandy (A)	topsoil (0–20)	5.9	5.8	5.5	5.2
	subsoil (20–40)	6.0	5.9	5.7	5.6
Silty (B)	topsoil (0–20)	6.2	6.1	5.9	5.8
	subsoil (20–40)	7.3	7.3	7.2	7.1

Table 5. Metal uptake from the soil by the test plants.

Year	Sandy soil			Silty soil		
	Pb	Cd	Zn	Pb	Cd	Zn
	mg plot⁻¹					
2010	0.04	0.04	7.01	0.36	1.76	56.6
2011	0.14	0.02	2.64	18.8	11.0	631.0
2013	14.1	0.29	226.0	12.0	1.00	332.0
2014	37.6	1.20	874.0	79.1	6.79	1501.0
Total (mg·plot⁻¹)	51.9	1.6	1109.7	110.3	20.6	2520.6
Total (mg·kg⁻¹)*	0.08	0.00	1.78	0.15	0.05	3.10

* The amount of metals accumulated by the plants from one plot was converted into one kilogram of soil for a layer of 0–40 cm

Discussion

Metal leaching from the soil is closely related to the climate, and especially to the level of rainfall and evapotranspiration, which depend on meteorological factors (temperature, humidity, radiation, solar energy, wind), as well as soil (texture) and plant factors (species, stage of development, stand density). High levels of rainfall, especially at not very high temperature air, promote the leaching of metals from the soil and their entry into the groundwater system, which poses environmental threat. In dry climates, however, with small amounts of rainfall and a high level of evapotranspiration, metal leaching from the soil is limited. Our studies concerned moderate climate zone, with an average annual air temperature in the range of 0°C to 10° C and precipitation occurring at different times of the year and being distributed relatively uniformly throughout the year. In the area of the microplot experiment, rainfall ranged from 502 to 751 mm per year, and the average annual temperature was 7.9°C. In this condition rainfall exceeding evaporation promoted the leaching of metal ions into the soil profile, which resulted in the gradual decrease of the total concentration of Cd, Pb and Zn in the soils over the 5-year period.

Metal leaching from the soil is caused, on the one hand, by climate factors, while on the other hand, by soil properties which determine the mobility or immobility of metals in the soil. The main mechanisms which control retention and mobility of heavy metals in the soil include: cation exchange, surface adsorption, chelation with solid organic matter and precipitation. According to Matos et al. (2001), the mobility and retention of metals such as Cd and Zn are strongly influence by cation exchange, while in the case of Cu and Pb – also the concentration organic matter. The formation of complex compounds and chelates, as well as the phenomenon of precipitation may play a significant role in the transport of Cu and Pb. The mechanisms controlling metal mobility are mostly determined by soil properties such as CEC, soil pH and the concentration and type of soil organic matter (Kabata-Pendias 2001). In these studies, the changes of the metal concentrations in the soil depended on its type. Metal concentration was more stable over time and less varied in the silty soil compared to the sandy one. It can be attributed to the fact that silty soil had a two-fold higher CEC value and higher TOC concentration than the sandy one. A relatively large immobilization capacity of the silty soil limited metal leaching, which resulted in smaller changes of metal concentrations compared to those observed in the sandy soil.

The tested soil differed in terms of pH value, especially in their subsurface layers. In comparison with the sandy soil, silty soil was characterized by a higher pH, the level of which did not diminish considerably over the period of 5 years, while sandy soil underwent gradual acidification. It also contributed to a more intensive leaching of metals and major changes of their concentrations in the sandy soil than in the silty soil. Dijkstra et al. (2004) based on modelling study showed a strong relationship between the concentration of metals leached from contaminated soils and pH value. The authors observed V-shaped leaching curves as the function of pH. At low pH, the heavy metals sorption in the solid phase of soil was weaker than at neutral pH, which resulted in an increase of their concentration in the soil solution. At neutral to weakly alkaline pH, their concentration in the soil solution and leaching was reduced due to deprotonation of the surface sites and favourable surface charge of oxide minerals and organic matter. At alkaline pH values, sorption to the solid phase is reduced again. These authors claim that increasing pH values cause the intensification of the complexation of metals with dissolved organic matter (DOM) due to the growing concentration of DOM in the solution phase. Jing et al. (2004) found that in the pH range of 6–12, Pb leaching is low due to adsorption and precipitation.

The changes in metal concentrations in the soil depended on the type of metal and the interaction between them. Specific properties of metals determine the strength of their sorption into the soil and their susceptibility to leaching. In column leaching experiment with the use of the sequential extraction procedure, Ash et al. (2015) found that Fe/Mn oxides (reducible) and organic matter fraction (oxidisable) are the most important for Cd retention, while the largest amounts of Pb were retained by oxidisable and residual fractions, and leaching of this metal occurred mostly in the reducible fraction. A higher seasonal variability of Cd concentration in the soil in comparison with Pb was recorded by Onweremadu et al. (2007).

The mobility of metals in the soil is to some extent determined also by their interactions. Due to the effect of competition among metals for adsorption places, metal immobilization is more effective from the single-element solution than from multi-element solution (Markiewicz-Patkowska et al. 2005). The fact that in our studies, the soil was contaminated with three metals, surely was of importance for the intensity of their individual leaching potential. In both our experimental soils, the leaching rate of metals was recorded in the following order: Zn>Cd>Pb.

The obtained results were to some extent confirmed by the work of Cao et al. (2013). These authors, under simulated landfill and rainfall conditions, found that the leachability of Pb, Cu and Zn followed the order Zn>Cu>Pb. A higher metal leaching occurred in soil with low organic carbon content and clay than in soil with high organic carbon content and clay.

In our studies, major changes in the concentration of metal occurred in the top layer compared to the subsurface layer of the sandy soil. The decrease in the metal concentration in the topsoil was most probably due to the migration of mobile forms to the subsoil, which systematically reduced the total amount of these metals in the topsoil. At the same time, migration occurred also from the subsoil into the deeper soil profiles. Changes in metal concentrations in the subsoil resulted from metal leaching into lower layers and a simultaneous subsoil enrichment with metals transferred from the topsoil. The phenomenon of metal leaching, even down to the depth of 80 cm, was confirmed by the studies of Fernandez et al. (2007). According to some authors, metal concentration in the soil solution, and thus its mobility is controlled by total metal concentration of the soil solid phase (Badawy et al. 2002, Kabala et al 2014). Nowack et al. (2010) reported that in the soil contaminated with Zn, Cd and Pb, the amount of soluble forms of these metals increased together with the increase of their total concentration. Our studies confirmed it only in the case of Cd and Zn in the sandy soil.

Several authors emphasize the impact of plants on the leaching of soil components. In the soil covered with vegetation, water conditions change, which has been already mentioned above, determine the mobility of metals in soils and their susceptibility to leaching. Nowack et al. (2010) and Chandra et al. (2014) suggest that plant activity kept the metals in a more soluble form, and that the vegetation has an effect on metal availability. In our research, it was difficult to clearly determine the effect of willow and maize on changes of metal concentration in the soil due to their leaching, as there were no comparable treatments without plants. However, the amounts of metals uptaken by these plants from the soil over the period of 5 years did not have a significant impact on their total concentration in the soil or on the changes observed. Antonkiewicz et al. (2017) found that during 6 years energy plants recovered only a small percentage of heavy metals from the sewage sludge applying to the soil.

An additional issue is the suitability of 1 M HCl to the evaluation of soil contamination with heavy metals. We do not mean the use of the extractant to evaluate the current mobility and phytoavailability of metals. The concentration of metals in the soil, determined in 1 M HCl does not decrease with increasing soil pH, while the phytoavailability of metals clearly decreases with the increase of this parameter (Karczewska 2002, Korzeniowska and Stanislawska-Glubiak 2015). Therefore, in this paper, we evaluate the usefulness of 1 M HCl method to replace burdensome and relatively costly procedure involving aqua regia. Such an approach is presented also in other research where the authors confirm the suitability of 1 M HCl to assess the degree of soil contamination with heavy metals (Allen 1993, Chowdhury et al. 2010, Stanislawska-Glubiak and Korzeniowska 2010, Korzeniowska and Stanisławska-Glubiak 2017).

In these studies, Cd and Pb in the sandy soil, determined in 1 M HCl turned out to be comparable to those determined in aqua regia, while in the case of Zn, the convergence of the results for aqua regia and 1 M HCl was not so high. It is possible that 1 M HCl did not extract Zn from all soil fractions. Kashem et al. (2007) found in the soils whose texture varied from sand to sandy loam, 1 M HCl extracted most of the non-residual and part of residual fraction of Cd, Cu and Pb, while it did not extract Zn from its organic and residual forms. On the basis of a sequential analysis in four contaminated and four non-contaminated soils, these authors showed that 1 M HCl extracted the largest proportion of Cd (79 to 96% of total), Cu (61 to 83%), Pb (51 to 99%) and Zn (23 to 52%). Extractability of metals using 1 M HCl was higher in the contaminated soils than the non-contaminated soils. The studies of Sienkiewicz-Cholewa et al. (2011) showed that in the sandy soil the higher the level of Zn contamination, the closer the concentration of this metal determined in 1 M HCl was to the aqua regia concentration. At the highest level of Zn contamination, Zn concentration determined in 1 M HCl accounted for 98% of the total concentration.

In our study, we found very similar levels of metals in 1 M HCl and in aqua regia. Only in some cases the metal concentration in 1 M HCl was 10–30% lower than in aqua regia. This involved Zn on sandy soil and Pb on silty soil. However, the course of the lines illustrating the temporal changes in concentration of all the metals determined in 1 M HCl for both soils was very similar in comparison to aqua regia. A similar course of lines demonstrates a high correlation between the two methods. This suggests that a less expensive and easier extraction of 1 M HCl compared to the aqua regia method is sufficient to evaluate the changes of metals in the soil. This is especially true for sandy soils with low organic matter. The lower metal level in 1 M HCl than in aqua regia does not indicate the inability of 1 M HCl to assess the contamination but simply requires different permissible limits of metal concentration in the soil. Kashem et al. (2007) report that the use of 1 M HCl may be recommended for the first screening of soils contaminated with heavy metals.

Conclusions

The soils contaminated with heavy metals should be systematically monitored in order to assess the risk to human health and the environment. Due to the changes in the level of total metals concentrations in the soil, which occur over time, the degree of risk to the environment varied also. In these studies, the dynamics and trends of changes in metal concentrations during 5 years depended on the sorption capacity of the soils, the type of metal, and a soil layer. In general, larger changes in metal concentrations were observed in the sandy soil than in the silty soil, especially in its top layer. Sandy soil contamination with metals poses a potentially higher threat to humans and the environment than silty soil contamination. Therefore, the examination of the sandy soils contamination, as well as of the groundwater occurring in these areas, should be carried out at least once for 5 years, and even more often.

Among all the tested metals, the weakest dynamics of changes in the sandy soil and in the top layer of silty soil in the period of 5 years was recorded for Pb. This indicates a lesser threat to human health and environment from this metal compared with Zn and Cd.

Due to the need for frequent monitoring of sandy soils contamination, the aqua regia method can be replaced by a less expensive, easier and equally effective 1M HCl method. It has been shown the usefulness of 1M HCl to track changes in Cd, Pb and Zn concentration in soil as a result of gradual leaching of these metals deep into the soil profile.

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Wpływ czynnika czasowego na zawartość metali ciężkich w glebie w aspekcie oceny zanieczyszczenia gleby

Streszczenie: Celem pracy było zbadanie dynamiki zmian zawartości metali w glebach zanieczyszczonych Cd, Pb i Zn w okresie 5-letnim. Dodatkowym celem była ocena przydatności 1 M HCl do kontroli stanu zanieczyszczenia gleby tymi metalami w porównaniu z metodą z użyciem wody królewskiej. Doświadczenie przeprowadzono w obetonowanych mikropoletkach wypełnionych dwoma glebami (piaskową i pyłową), które zostały symulacyjnie skażone Cd, Pb i Zn. Stwierdzono stopniowe obniżanie się zawartości tych metali w glebie wraz z upływem czasu, przy czym zawartości te, oznaczone po ekstrakcji metali z gleby 1 M HCl, były bardzo podobne do zawartości całkowitych oznaczonych z użyciem wody królewskiej. Po 5 latach badań górna warstwa gleby (0–20 cm) wykazywała spadek koncentracji Pb, który w glebie piaskowej i pyłowej wynosił odpowiednio 7% i 9% w stosunku do wartości początkowej. Zawartości Cd i Zn obniżyły się o około 35% w glebie piaskowej i 20% w pyłowej. Badania wykazały, że gleba piaskowa zanieczyszczona metalami stwarza większe potencjalne zagrożenie dla ludzi i środowiska, niż zanieczyszczona gleba pyłowa. Dlatego kontrola zanieczyszczonych gleb piaskowych, jak również wód podziemnych znajdujących się na tym obszarze, powinna być prowadzona co najmniej raz na 5 lat. Wykazano, że w celu śledzenia zmian zawartości badanych metali w glebie, jakie następują w danym okresie czasu, metodę analityczną z użyciem wody królewskiej można zastąpić tańszą i łatwiejszą metodą z użyciem1 M HCl.