Original Research

Toxic Metal Distribution in Rural and Urban Soil Samples Affected by Industry and Traffic

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Abstract

There is a worldwide growing concern about soil pollution by a wide range of contaminants due to their increased accumulation caused by expeditious industrial and urban development in recent decades. This issue is of special interest because of the danger toxic metals may pose to food quality and human health when they enter the food chain.

The present study was undertaken to determine the impact of industrial activities and traffic emissions on metal concentrations in soil samples and the waste product phosphogypsum. The major goal of the work was to assess the influence of different pollution sources resulting in changes in the composition of soil samples collected from Łódź city (central Poland, urban area) and the outskirts of Gdańsk city (northern Poland, rural area affected by industry). In context, knowledge of the natural (background) values in soils is of critical importance in order to evaluate human activity contribution. For that reason we have investigated soil samples taken from potentially uncontaminated sites as well (Lagiewniki Forest, central Poland). Analysis of metals was performed with inductively coupled plasma mass spectrometry, ICP-TOF-MS (Cd, Cr, Cu, Ni and Pb) and a mercury analyzer (Hg). The observed differences in studied metal concentrations in soil samples were a consequence of various degrees of anthropogenic activities on study areas. In general, the concentration of the measured metals tends to increase with the decline of the distance from the pollution source. The study compared relatively low levels of metals in urban soil collected from park areas in the center of Łódź with samples taken in the close vicinity of a phosphogypsum dump from a rural site affected by industrial activity. Total content of toxic metals turned out to be lower than the concentrations reported in the literature data for non-polluted and contaminated soils. Additionally, the application of OptiMass 8000 software allowed a comparison of full mass spectra of all investigated samples, which makes it possible to evaluate the qualitative variations among samples collected from affected forest, urban or rural-industrial areas.

Keywords: ICP-TOF-MS, Mercury Analyzer, soil contamination, toxic metals

Introduction

During the last few decades we are witnessing an increasing influence of anthropogenic factors on content of metals in soils and plants [1]. Human activities have dramatically changed the balance and biochemical and geological cycles of many heavy metals [2]. Although different means of evaluation of heavy metal loads and exposure in the environment are available, it is generally accepted that one of the effective ways of identification and determination of environmental contamination is soil sample analysis [3]. An assessment of the environmental risk caused by soil contamination is especially important for agricultural as well as non-cultivated areas due the fact that metals potentially

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harmful to human health persist in soils for a relatively long time and may transfer into the food chain in considerable amounts [2].

Recently, an increasing concern about the studies of quality of soil and wastes endangered to dust deposition coming from industrial and urban activities is observed. However, until now little has been known about the exact mechanism of penetration of heavy metals into soil and the way they are released. It could be partly attributed to the complex nature of soils. The differences in metal content can be connected with composition, texture variations, oxidation/reduction and adsorption/desorption processes, physical transport or sorting in addition to anthropogenic metal input [4]. We should also take into account the fact that metals can be associated with soil in different ways and strengths, which makes the analysis more complicated.

A lot of studies dealing with heavy metals inputs to soil of different industrial origins such as smelters, mining or cement factories have been carried out [5-9]. Based on their results, some danger areas in Europe have been identified. The so-called hot spot places in Central and Eastern Europe connected with heavy metal contamination include the Katowicie region (Poland), the Donetzk area (Ukraine), the Kuznetzk area (Russia), and North Bohemian and the Sokolow Brown-Coal Basins (Czech Republic) [10]. For example, one of the most polluted regions related to acidification of soil is Turoszów area (territory of Poland-Czech-German border). The open pit lignite mining and as well as the closeness of dump containing sulphur and carbon are the main factors responsible for very strong acidification (pH 1.8-3.8) [11].

The most common industrial soil pollutants are strictly connected with mining, smelting, refining of metals, processing industries, combustion of fossil fuels, waste or road traffic. They are introduced into the soil as wet or dry deposition [1, 12, 13]. The city environment create a mosaic of soils with different levels and origins of pollutants [2]. As an example, heavy traffic is responsible for emitting primarily Pb, Cd, Ni, Cu and Zn [1, 12]. Burning of fossil fuel is the main source of V, Ni, Hg, Se and Sn, while smelters mainly account for As, Cd, Cu and Zn emissions. On the other hand, the major source of agricultural soil contamination is recognized as atmospheric deposition and usage of fertilizers, pesticides, manure or municipal and industrial sewage sludges [1]. Present agricultural industry extorts the use of fertilizers in order to ensure an increase in production. During fertilizer production some waste products are created and mostly stockpiled afterwards [14, 15]. One of the by-products formed is phosphogypsum. Its composition is strongly affected by parent rock material, reagents used and process applied. The main ingredient is gypsum (95-98%), but it also contains some amount of impurities including fluorine, heavy metals and radionuclides [15, 16]. Therefore, soil can potentially be exposed to an excessive amount of toxic substances coming from localized as well as diffuse sources [13]. Emitted contaminants from the phosphogypsum disposal site containing toxic elements may be transported over a long distance before their deposition and distributed over a territory far away from the pollution source [14, 15]. However, the main threat to human health concerning soil pollution is incorporation of contaminants into the food chain in a comparatively easy way by dust ingestion, dermal contact or breathing [17].

The present work is part of an investigation aimed at analysis of the potential impact of various sources of air pollution on the territory of Łódź region and Wislinka/near Gdańsk (the surroundings of a phosphate waste disposal site) on ambient environment and humans.

The main goal of the study described here was to determine the level of chosen toxic elements (Cd, Cr, Cu, Pb and Ni) in soil and waste product samples collected from areas affected by industrial and urban pollution and to evaluate whether the studied soil samples meet legal requirements. The analysis of trace elements (including heavy metals) in soil samples seems to be crucial in order to assess a possible source of its contamination and to evaluate the potential hazards to inhabitants living in the closest neighborhood of polluted areas. The obtained quantitative results were compared with literature data values. Moreover, the additional qualitative elemental comparison based on mass spectral fingerprinting was made for all measured samples using advanced software. An attempt was also made to check the existence of a possible inter-element relation for two research areas using Pearson's test. Other objectives of the work were to assess the natural (background) concentrations of studied elements in soil collected from an uncontaminated area of Lagiewniki Forest (Łódź region) and to confirm the most probable sources of pollution of studied elements. The obtained results can be especially helpful in better understanding of the direct impact of anthropogenic activity on the adjacent environment and its components, leading to an increase of toxic metal accumulation and in predicting the potential risk to the environment and human health.

Materials and Methods

The analyzed material consists of samples of: soil and phosphogypsum (stored at a disposal place, including material taken from the fresh, older and recutivated part of the dump) collected in 2006. Soil samples were taken from two regions: Łódź (sampling sites mainly located near high-density traffic roads, in the surroundings of power plants in Łódź: EC-2, EC-3 and EC-4 and close to the Łódź-Kaliska railway Station) and Gdańsk, (samples collected close to a phosphate fertilizer waste disposal place located on the outskirts of the city).

Three big power plants and several smaller plants not equipped with sufficient ash removal installations are located in a comparatively small area of Łódź. Moreover, many households still use their own heating systems, but without any ash disposal devices. In addition, air particulate matter released from traffic makes a large contribution to total anthropogenic emissions. It is partly caused by the fact that the main south-north highway goes through the heart of Łódź [18, 19].

The village of Wislinka, a typical rural area, has been affected by industrial activity since 1969, when the phosphogypsum by-product began to be stockpiled in this small suburb of Gdańsk near the city border. To date, over 15 million tones of phosphogypsum have been dumped into an area of 26 ha. The wastes contain up to 5% of many impurities, including heavy metals, fluorine and radionuclides. The main danger for the local community is connected with the possible dusting process and penetration of toxic substances into human body by dust ingestion, dermal contact or breathing [20-22]. Maps of two cites under investigation are placed in Fig. 1 [23] and Fig. 2 [24]. In order to assess natural variations in levels of toxic elements in soil, it seems to be crucial to evaluate trace element concentrations in background areas. So as a reference place Lagiewniki Forest in Łódź was chosen. It is one of the biggest forest areas in Central Europe located within a city.

Soil samples were taken in open areas and after thorough mixing air-dried in laboratory at ambient temperature. Each sample consisted of four sub-samples collected and then mixed together to obtain a representative sample for a given sampling point as recommended by Biasioli et al. [13]. Afterward, soil material was ground in a porcelain mortar and sieved through a screen with a mesh diameter of 0.2 mm according to a procedure described elsewhere [1, 25-29]. Samples in Łódź were collected from urban parks in 22 measurement points situated at least 100 m away from roadsides and in the case of Wislinka from 8 sampling sites up to 600 m from the large phosphate industry waste disposal site in northern and eastern directions. All material was sampled at a depth of 0-20 cm [13, 25, 26, 29] with the exception of older phosphogypsum, which was taken from a deeper part of the dump. This surface soil analysis seems to be the most reasonable for a better assessment of potential health risks connected with toxic metal air pollution to local residents. The highest values are mostly recorded in the topsoil as a consequence of metals accumulation from the atmosphere to a depth of about 10-15 cm [30, 31].

A Milestone MLS-1200 MEGA microwave oven system was applied for mineralization of samples with a mixture of concentrated nitric and hydrochloric acids (1:3, [2, 13, 25]). An analysis of mercury was performed with Mercury Analyzer SP-3D, Nippon Instrument Corporation. Inductively coupled plasma mass spectrometry with time-of-flight analyzer, ICP-ToF-MS OptiMass 8000, GBC, was used for analysis of the following isotopes: ^{52}Cr, ^{60}Ni, ^{63}Cu, ^{111}Cd, ^{208}Pb. Operating parameters of ICP-TOF-MS are shown in Table 1. Three repetitions were made for each sample and the relative standard deviation (RSD) did not exceed 5% in any case.

Moreover, the additional qualitative elemental comparison based on mass spectral fingerprinting was made for all measured samples using OptiMass 9500 advanced software. Realized half-quantitative analysis revealed significant differences in the composition of studied samples for a selected region of mass spectra presenting strontium

Table 1. Operating conditions for the ICP-TOF-MS instrument, OptiMass 8000, GBC.

Acguisition time [s]	5
Nebulizer flow [l/min]	0.80
Plasma flow [l/min]	10.0
Auxiliary flow [l/min]	1.00
Set power [W]	1.200
Skimmer [V]	-1.500
Extraction [V]	-1.100
Multiplier gain [V]	3.080
Pushout plate [V]	708
Pushout grid [V]	-570
Reflectron [V]	702
Pump speed [rpm]	10.0

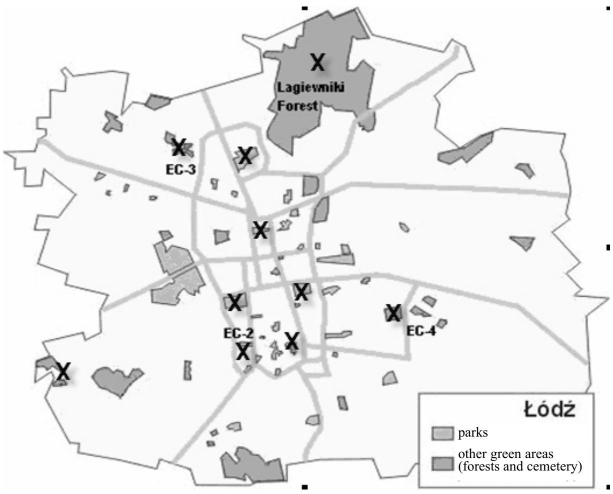

Fig. 1. A map of Łódź with three power plants and the reference site-Lagiewniki Forest marked; all sampling areas are indicated as crossbars [23].

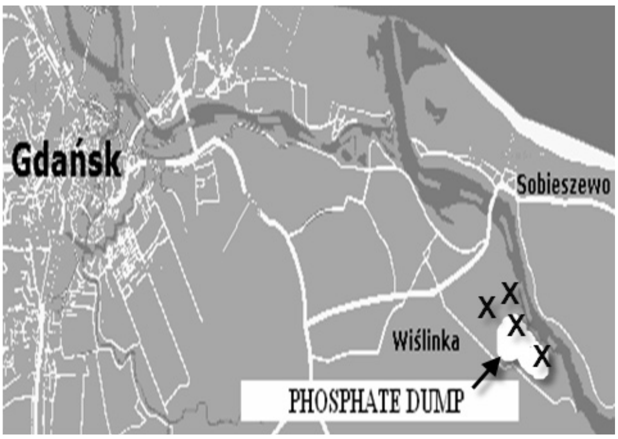

Fig. 2. The map of phosphate dump in Wislinka/near Gdańsk, sampling areas are indicated as crossbars [24].

Table 2. Results from the measurements of certificate reference material of IAEA-Soil-7 [mg kg^{-1}] (U-uncertainty).

Method/ Element		Certificate value ± U	Obtained result ± RSD	Recovery [%]
ICP-MS	Cd [mg/kg]	0.105 ± 0.013	0.100 ± 0.003	95.24
ICP-MS	Cr [mg/kg]	58 ± 2	62 ± 1.95	106.9
ICP-MS	Cu [mg/kg]	19 ± 1	18 ± 0.52	94.74
ICP-MS	Ni [mg/kg]	26 ± 1	28 ± 0.89	107.7
ICP-MS	Pb [mg/kg]	22 ± 2	21 ± 0.41	95.45
Mercury Analyzer	Hg [mg/kg]	0.033 ± 0.004	0.031 ± 0.002	93.94

Table 3. Average content of investigated metals in soil and phosphogypsum samples collected from Łódź and Wislinka city [mg kg^{-1}], in relation to statutory limits [33]; values for industrial areas are given in brackets.

Element	Statutory limits	Average content in soil from Łódź/ range	Average content in soil form Wislinka/ range	Average content in phosphogypsum form Wislinka/ range
Cd	4 (10)	0.42 (0.06-2.04)	1.20 (0.15 ÷ 3.61)	4.85 (0.11 ÷ 54.0)
Cr	150 (380)	25.5 (5.95-57.5)	16.6 (3.7 ÷ 38.7)	14.7 (1.40 ÷ 78.5)
Cu	150 (200)	17.8 (3.69-68.5)	8.60 (2.30 ÷ 47.2)	14.4 (0.91 ÷ 128)
Ni	100 (210)	9.92 (3.80-16.4)	5.56 (2.41 ÷ 22.9)	7.95 (2.25 ÷ 34.2)
Pb	100 (200)	50.6 (6.50-102)	19.3 (5.33 ÷ 44.8)	22.2 (0.80 ÷ 149)
Hg	2 (10)	0.11 (0.01-0.24)	0.05 (0.01 ÷ 0.26)	0.07 (0.02 ÷ 2.81)

(^{86}Sr, ^{87}Sr, ^{88}Sr), silver (^{107}Ag, ^{109}Ag), cadmium (^{110}Cd, ^{111}Cd, ^{112}Cd, ^{113}Cd, ^{114}Cd), barium (^{136}Ba, ^{137}Ba, ^{138}Ba), lanthanum (^{139}La), cerium (^{140}Ce), wolfram (^{182}W, ^{183}W, ^{184}W, ^{186}W) and lead (^{206}Pb, ^{207}Pb, ^{208}Pb) isotopes. As the demand for an environmental analysis has grown, computer technology has made analytical equipment more powerful and easy to operate. The continuous development of techniques including plasma as the ion source has coerced solutions in an increasing number of applications of software. Using the advanced fingerprinting software of OptiMass 9500 ICP-TOF-MS, we were able to assess qualitative variations for materials coming from places with different states of environmental pollution. The OptiMass 9500 fingerprinting software allows the user to load in a series of spectra simultaneously and then select a "reference" spectrum and a "compare" spectrum. A chi-squared fit is then calculated for a selected mass region of the two spectra and we can easily observe a correlation or total lack of relationship among the investigated samples. This comparison is achieved by application of a statistical algorithm that compares a test spectrum to a known spectrum.

Quality control of applied methods was based on the analysis of a certificate reference material of Soil NCS ZC 73001 (approved by the China National Analysis Center for Iron and Steel) and good agreement was achieved. Certified values and obtained results are compared and gathered in Table 2.

Results and Discussion

The content of elements of rural soils and their chemical composition differ from the urban ones by the fact that they are in general less affected by anthropogenic impact. This influence is oftentimes reflected by a low degree of contamination [13]. In order to investigate the potential variations in content of metals, the results from a rural area of Wislinka were compared with element concentrations in soil samples collected from the urban area of Łódź city.

Waste phosphogypsum is connected with technology of a wet-process of phosphoric acid. It is still a problem that requires a right solution. The composition of phosphogypsum varies depending on the phosphate rock source, differences in the production process of acid or the age of phosphogypsum. Phosphogypsum primarily contains $CaSO_4{\cdot}2H_2O$. However, it also includes amounts of impurities such as fluoride, heavy metals and radionuclides that are dangerous to the environment and humans [16, 32].

Table 3 shows the mean values and ranges of chosen elements determined in soil and phosphogypsum samples in relation to the statutory limits included in the Regulation of the Minister of Environmental Protection [33]. Generally, studied elements exhibited a characteristic distribution – their concentration increased as the distance form the pollution source decreased. The results for the soils of Łódź indicated that the combustion processes in power plant and domestic fireplaces together with vehicle exhausts were mainly responsible for metal pollution because the data showed that the highest concentrations of metals were recorded in soil collected in the vicinity of three power plants, near high-density traffic roads and in the older part of town where homes are not equipped with central heating. However, further analyses of lead isotope ratios are required in order to identify the main source of pollution in studied measurement points. The Pb isotopic composition makes it possible to distinguish lead sources and estimate their individual contributions. Lead ores display isotopic signatures that mainly relate to the original composition as well as the age of the ore bodies, thus the anthropogenic emissions of Pb reflect the isotopic composition of mentioned ores [34].

As we suspected, the lowest level of metals among all investigated samples was observed in soil taken from our reference place (Lagiewniki Forest). The obtained values for this sampling site were within the ranges treated as background ones recorded in other related studies for samples collected from uncontaminated areas [10, 11, 25, 35, 36]. On the other hand, the concentrations of elements in soil samples taken from Lagiewniki Forest were considerably lower than those proposed by Taylor et al. [37] that refer to the contents of metals in the Earth's crust and serve as reference values.

A comparison of element concentrations in soils taken from the urban area of Łódź with the material collected at sampling sites located farther from the stockpile revealed that urban samples were in general enriched much more in studied metals than rural ones. The values obtained in this study for the measured metals in soil samples from Łódź indicated that they can be classified as generally unpolluted, with the exception of lead. For this heavy metal, studied soil samples can range from uncontaminated to moderately contaminated with Pb. In remaining cases the determined content of elements did not exceed the Polish statutory limits [38] (Table 3). The values presented for Wislinka area show that the soils in general do not demonstrate significant pollution with studied metals, but there are some places where the concentration of metals is considerable and exceeds levels typically found in urban regions.

Results gathered for Łódź city were lower than reported in literature for other urban areas in Poland [2] as well as for farming soils affected by industry [39] and in the world [13]. For instance, a high amount of heavy metals was recorded in the central part of Katowice, Poland. Lead concentrations in the 0-20 cm soil layer ranged from 13 to 5,000 mg kg^{-1} (mean 202 mg kg^{-1}) and cadmium from 0.46 to 52 (mean 6.7 mg kg^{-1}) [40]. These extremely high levels of heavy metals are caused by the presence of approximately 200 industrial plants on this territory, which are considered particularly harmful to the environment [11]. Furthermore, concentrations of measured toxic metals were comparable with those reported in other related studies performed in the surroundings of the phosphogypsum dump [41, 42] and in the farming soils of Suszec commune (southern Poland) affected by the Upper Silesia industrial region and local pollution sources such as coal mines and the Czech Republic's Trzyniec smelter [39]. The study of Szczepaniak et al., based on the analysis of substrates and products, waste by-product, grass and soil samples, demonstrated that there exists a direct impact of phosphatic fertilizer plant on the adjacent environment and discarded phosphogypsum as a continuous contamination source [14]. Generally, there are numerous studies that assess the impact of the phosphate waste disposal site in Wislinka [20-22, 41, 42] and phosphatic fertilizer plant "Fosfory S.A." [14] on the ambient environment, plants, animals and humans. However, no uniquivocal agreement about the influence of mentioned pollution sources has been achieved.

This study revealed as well that there is a correlation among samples collected from the same sampling site based on the qualitative analysis of mass spectra. The exemplary mass spectra showing a number of counts for chosen isotopes for two samples taken from the neighborhood of Łódź Kaliska Station are presented in Fig. 3. Calculated chi-squared for a mass region of the spectra was generally over 85%, which suggests a strong dependence on the measured samples.

In this work, in order to obtain information on the composition of stockpiled phosphogypsum we determined the content of metals in three kinds of waste-byproduct material and, for comparison purposes, in soil samples taken from five measurement sites in the vicinity of a dump. Figs. 4-8 show a number of counts for selected isotopes of chosen mass spectra regions for various studied samples. The results for soil analyses coming from the close neighborhood of a waste disposal site in Wislinka (rural area affected by industrial activity) were more or less comparable with the values obtained for the urban area of Łódź. As we sus-

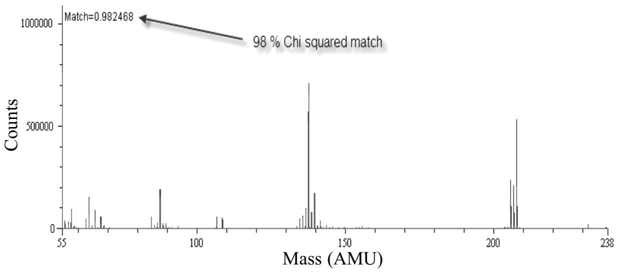

Fig. 3. The exemplary Chi squared for the soil samples collected from the same sampling site in Łódź (Łódź-Kaliska Station).

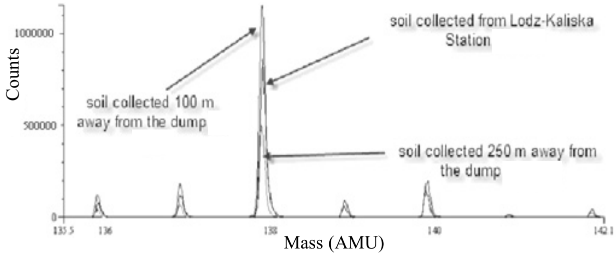

Fig. 4. Mass spectra presenting the comparison of the number of counts for selected regions showing barium (^{136}Ba, ^{137}Ba, ^{138}Ba), lanthanum (^{139}La), and cerium (^{140}Ce) isotopes between chosen soil samples collected from Łódź-Kaliska Station and Wislinka.

pected, values of metal concentrations in soils collected near the dump were in general higher than those observed for soil taken further from the phosphate waste deposal place or from Łódź (Fig. 4). Stored phosphogypsum in Wislinka originates from various types of phosphate rock material, including phosphorites from Tunis, Morocco or Togo [14].

The results of this paper are in general agreement with the characterization studies presented in the report about the assessment of soil and plant state in the phosphate dump influence area [41]. Moreover, the distinct increase in metal content in phosphogypsum during storage is clearly seen. Comparison of ranges and mean values obtained in our study for unrecultivated material with different literature data demonstrated that in general, concentrations of elements were similar to those reported by Acorena et al. [16] with the exception of Pb, for which the content of this element was much lower. The composition of waste product did not differ significantly from the values indicated in the work of Rutherford et al. [41]. However, our results considerably exceeded the average concentrations proposed by Conceição et al. [43]. These variations proved that the phosphate rock used plays a key role in the final product constitution. However, in our study the analysis of three samples of phosphogypsum (fresh, older and recultivated) undoubtedly proved that the highest concentrations of heavy metals in particular are observed for the part of phosphate waste deposal place treated with sewage sludge from the wastewater plant (Figs. 5, 6). Since 2001 the recultivation process using sewage sludge from the mechanical-biological treatment plant "Wschod" in Gdańsk has been applied only for some part of the phosphate waste deposal place. The major aim of activities is luxuriant vegetation expansion. Generally, metals like Cd, Cu, Hg, Pb, Zn, Cr and Ni can adsorb on the surface of soil profile and thus can accumulate in the plants [44]. The wastewater that flows to the treatment plant mainly consists of domestic and industrial sewage (from food production, gas, electrochemical and chemical processing). In the study of Kulbat et al. [45], the effectiveness of heavy metals removal in "Wschod" plant was discussed in the aspect of its possible application in land-farming. That study showed that average concentrations of seven analyzed metals (Zn, Cu, Pb, Cr, Ni, Cd, and Ag) in raw and excess sewage sludge did not exceed the obligatory Polish Regulations. After treatment, the metals concentrations met criteria presented in the Regulation of the Minister of Environmental Protection [38]. Concentrations of investigated metals in sludge decreased in the order as follows: Zn>Cu>Cr>Ag>Pb>Ni>Cd (for the primary sludge), and in the case of biological sludge Zn>Cu>Pb>Cr>Ag>Ni>Cd. Generally, the effectiveness of toxic metal removal was rather high, with the exception of cadmium [45]. That stays in agreement with our results,

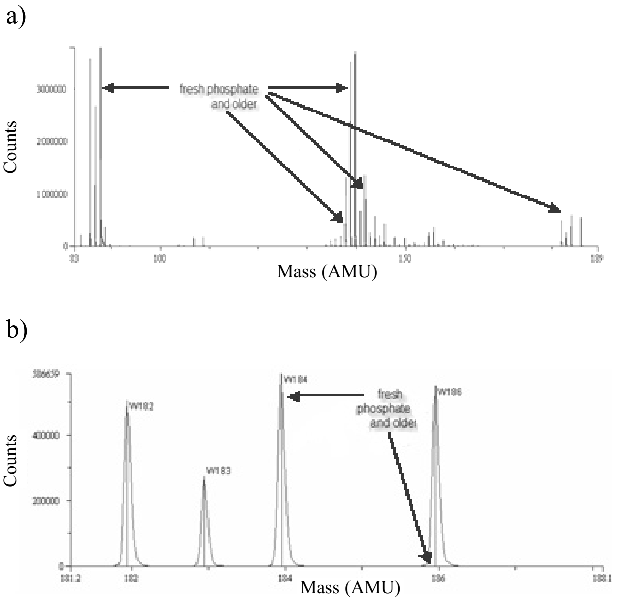

Fig. 5. Mass spectra showing the differences in the composition of fresh phosphogypsum and the older one for a selected region of mass spectra presenting e.g. barium (^{136}Ba, ^{137}Ba, ^{138}Ba), lanthanum (^{139}La), cerium (^{140}Ce) isotopes (a) and wolfram (182W, 183W, 184W, 186W) isotopes (b). The fresh phosphate in red generally contains more Sr, Ba, Ce, La (Fig. 5a) and W based on the number of counts (Fig. 5b).

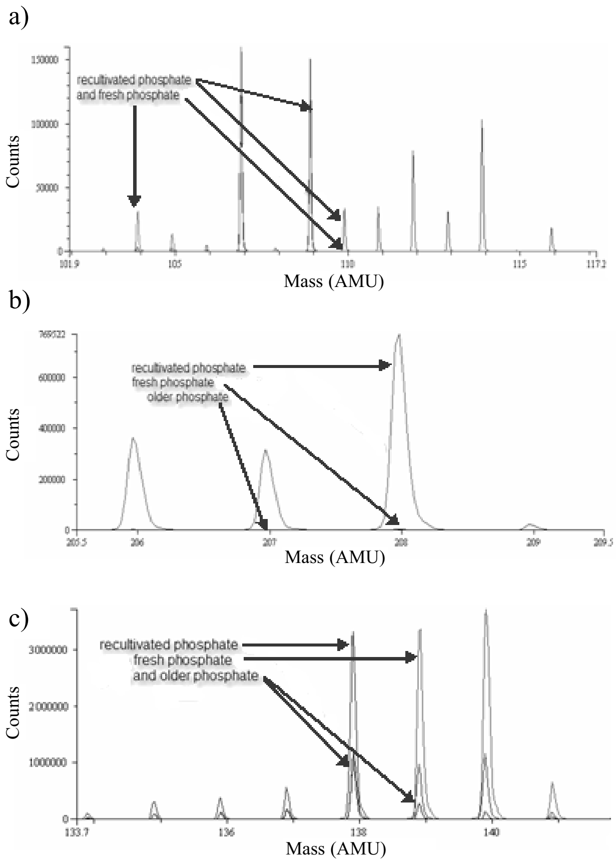

Fig. 6. Mass spectra showing the differences in the composition of recultivated, fresh and older phospogypsum for a selected region of mass spectra presenting e.g. silver (^{107}Ag, ^{109}Ag) and cadmium (^{110}Cd, ^{111}Cd, ^{112}Cd, ^{113}Cd, ^{114}Cd) isotopes (a); lead (^{206}Pb, ^{207}Pb, ^{208}Pb) isotopes (b) and strontium (^{86}Sr, ^{87}Sr, ^{88}Sr), barium (^{136}Ba, ^{137}Ba, ^{138}Ba), lanthanum (^{139}La), cerium (^{140}Ce) isotopes (c). Recultivated phosphate based on the number of counts contains for example much more Cd (Fig. 6a), Pb (Fig. 6b) and Ba (Fig. 6c).

Table 4. The average content of metals in cultivated, uncultivated soils and foot of dump based on literature data [mg kg^{-1}] [30].

Element	Soil	Range
Ni	Cultivated soil	30.57-31.22
	Uncultivated soil	31.63-35.15
	Foot of dump	34.67-37.09
Cd	Cultivated soil	1.21-1.26
	Uncultivated soil	0.94-0.98
	Foot of dump	2.99-10.39
Pb	Cultivated soil	33.51-36.00
	Uncultivated soil	39.04-39.33
	Foot of dump	87.90-293.20
Hg	Cultivated soil	0.080-0.089
	Uncultivated soil	0.094-0.104
	Foot of dump	1.175-1.500

Table 5. Pearson's coefficients among all analyzed soil and phosphogypsum samples collected from Wislinka [-].

r	Cr	Ni	Cu	Cd	Pb	Hg
Ni	0.47	-	-	-	-	-
Cu	0.99	0.34	-	-	-	-
Cd	0.87	0.14	0.93	-	-	-
Pb	0.99	0.47	0.98	0.87	-	-
Hg	0.99	0.25	0.99	0.93	0.96	-

because only for this metal was the elevated concentration, which exceeded the statutory limits, observed (Fig. 6.a., Table 4.). What is more, the values obtained for Cd were much higher than those recorded for dumps in other literature data [30] (Table 3). The authors [45] also suggested that while utilizing sludge in land-farming and other areas, the sanitary conditions and loads of metals in soils fertilized with wastewater should be considered. In other research the significant effects of applied sludge were observed. In sludge-treated soil the content of organic matter increased from 6.89% to 11.02%, while the concentrations of soluble metals reached values higher by 100-fold for cadmium, 20-fold for zinc and copper [46]. In other studies the background values were much lower than concentrations determined in soil exposed to anthropogenic origin. Additionally, the authors observed that element content decreased with depth, and the highest concentration corresponds to soil surfaces. It is a well-known fact that heavy metals coming from the atmosphere accumulate in the topsoil to a depth of 10-15 cm [31, 47]. Our results also showed a strong relationship between the depth and age of phosphorus due to their anthropogenic descent. Higher concentrations of toxic metals were noticed for fresh phosphate in contrast to older ones collected from the deeper part of the dump (Fig. 5). In the work of Ďurža, 1999 the level of heavy metals in the surroundings of dry refuse heap from the metallurgic plant located in eastern Slovakia, VSŽ, Košice, was investigated. The refuse heap is separated from the nearby village only by a road [30]. Table 4 shows the range of element concentration in soil and dump samples taken from the area of metallurgic plant based on the literature data. These results showed a higher amount of Ni and Pb compared to the content of these elements in our phosphate samples. However, concentrations of Cd and Hg for recultivated phosphate from Wislinka were much higher and exceeded statutory limits. What is more, for samples taken near the soil surface higher levels of metals were recorded. This stays in agreement with the previously mentioned literature data. In our case, generally higher values of exemplary Ba, Pb, and Cd were recorded in the recultivated part of the dump, in contrast to fresh and older phosphogypsum. On the other hand, the elements like Sr, Ce or W, which were determined to the highest extent, were noticed for fresh phosphate. As we suspected, the results recorded for three samples of phosphogypsum were much higher than the values for heavy metals determined in soil samples from Wislinka and Łódź (Figs. 7, 8).

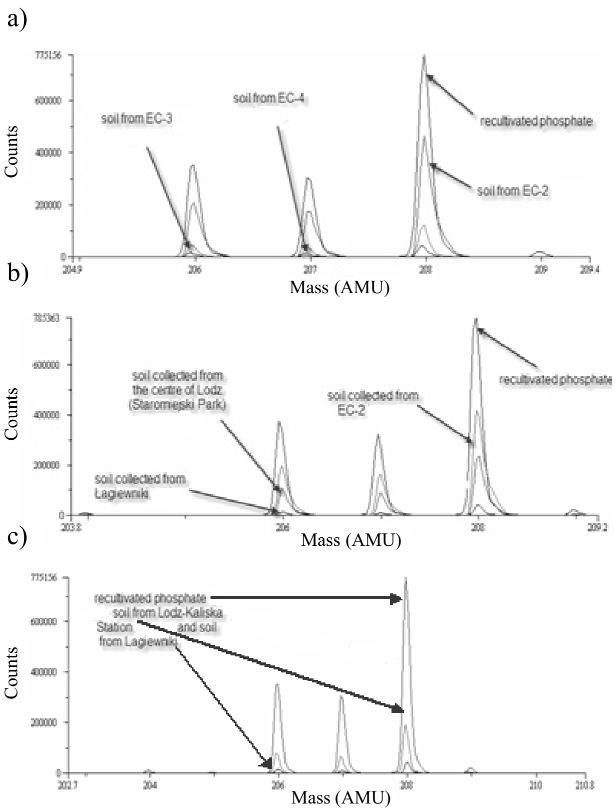

Fig. 7. The differences in the number of counts for lead isotopes (^{206}Pb, ^{207}Pb, ^{208}Pb) for samples collected from the recultivated part of phosphogypsum and chosen sampling sites in Łódź (a, b, c). Generally, the lowest number of counts for lead is recorded for control – Lagiewniki Forest and the highest for recultivated phosphate.

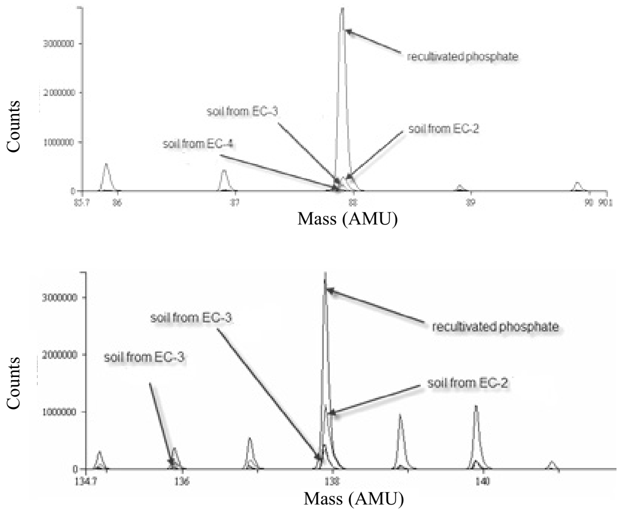

Fig. 8. The differences in the number of counts for strontium (^{86}Sr, ^{87}Sr, ^{88}Sr) (Fig. 8a), barium (^{136}Ba, ^{137}Ba, ^{138}Ba), lanthanum (^{139}La) and cerium (^{140}Ce) isotopes (Fig. 8b) for samples collected from the recultivated part of phosphogypsum and chosen sampling sites in Łódź. The highest number of counts of Sr, Ba, La and Ce was noticed for recultivated parts of phosphogypsum in contrast to soil samples taken from Łódź city.

We have also calculated Pearson's coefficients to check if any significant inter-element dependence in the samples collected from two sampling areas exist: Łódź and Wislinka. The correlation was assumed to be statistically significant at $p < 0.05$. In the case of the samples taken from Łódź territory, the strongest positive correlation was found for the pair of metals Cr-Cu (0.95) and between Cd and other elements (ranging 0.80-0.83) which can suggest the same origin of pollution by these metals. The coefficients for each pair of metals was not so high, which could be caused by the fact that in studied measurement sites have a varied contribution of pollution sources to levels of metals. Some sampling sites were exposed to three different, main pollution sources: heavy traffic, emissions from power plants and household heating systems while the others are mostly by automotive activity. The opposite situation is observed for samples collected from Wislinka, affected generally by the major contamination source-phosphate waste deposal site. In many cases the correlation coefficient was close to value 1, which could insinuate a considerable input of the deposition of particles derived from phosphate fertilizer waste disposal site on the sub-surface layer. Table 5 presents coefficients for a pair of metals determined in material taken from the Wislinka area. The strongest metal-metal relationship was noticed especially for the pair of elements: Cr-Cu, Cr-Pb, Cr-Hg, Cu-Pb, Cu-Hg and Pb-Hg (Table 5), while no statistically significant dependence was confirmed for Cr-Ni, Ni-Cu, Ni-Cd, Ni-Pb, and Ni-Hg. All things considered, there is evidence to suspect that Ni may have come from other strong sources of pollution not only the phosphate stockpile. The presence of Ni may be related to the process of burning of fossil fuels (oil or mixed fuels combustion in particular). Further studies are needed to establish if there is a relationship between the presence of Ni and V distribution because the joint occurrence of these two mentioned elements are treated as oil fingerprint [48].

Conclusions

Exposure to excessive amounts of heavy metals may be caused by elevated toxic element levels in different components of the environment polluted by compounds of industrial or traffic origin. Trace metal studies in soil are oftentimes required in order to assess a possible risk to humans and the environment, and prevent potential health and environmental hazards.

Based on obtained results, we can state that the soils of the urban area of central Łódź can be classified in general as non-polluted with a lower extent of metals, or moderately polluted. Soil samples from the nearest surroundings of a large phosphate industry waste disposal site and phosphogypsum materials taken from the rural territory of Wislinka demonstrated considerable pollution by studied metals. The results indicate that Wislinka has been affected by human activity, in particular connected with technology of wet-process phosphoric acid production leading to an increased accumulation of heavy metals in the closest neighborhood of a dump compared with the background levels (Lagiewniki). The highest recorded content of metals in the case of waste by-product was observed for the sample recultivated with sludge previously consisting of a high amount of heavy metals. The applied method of recultivation results in an increase in a significant amount of some toxic metals, Ba, Cd, Hg and Pb especially, on the part of the dump with unformed vegetation cover. However, an analysis of the mechanism of toxic metals migration into the dump profile, as well as the transfer of pollutants from phosphogypsum and sewage sludge directly to plants, requires further studies. This study also proved a versatile application of fingerprinting OptiMass 9500 software as a tool for comparison and identification of major contaminants of investigated samples.

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