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Analysis of long distance transport of pollutants in Lesser Poland area

Analiza transportu zanieczyszczeń na duże odległości na obszarze Małopolski

Mathieu Bonnet^[a], Witold Reczyński^[b], Małgorzata Jakubowska^[b]

[a] IUT University Institute of Technology, Biological Engineering, Environmental Engineering, 2 avenue Adolphe Chauvin 95302 Cergy-Pontoise, France

[b] AGH Akademia Górniczo-Hutnicza, Wydział Inżynierii Materiałowej i Ceramiki, al. Mickiewicza 30, 30-059 Kraków, Polska

1. Introduction

The environment undergoes quality changes mostly because of human activities. This is particularly the case of the city of Krakow. Indeed, the periphery of Krakow and the city itself was marked by a strong industrialization (including coal and metals mining, iron and aluminium smelters ect.). The city of Krakow is also subjected to long distance pollutants transport from the Silesia region localized to the West of the city. Considering, that predominant wind direction is North, North-West and West, winds transported aerosols containing heavy metals' particles to Krakow and spread them over a large area between Krakow and the point of emission. So we decided to study the concentration of heavy metals in two points. The first sampling was done in Olkusz. For over 50 years, in the vicinity of this city, lead and zinc ores were extracted. Sampling of soil was done in the industrial wastes heap (Pomorzany mine). The other three samples of the soil core were collected in the Nielepice Forest (an elevated area between Olkusz and Kraków).

Sequential extraction procedure was used to distinguish forms of metals (functional speciation) present in the analyzed soils samples [1, 2]. Two metals' fractions were obtained – ionic and carbonates forms (extracts A) and the elements in absorbed on Fe and Mn oxides and hydroxides. For quantitative determination of Fe, Mn, Mg and Zn atomic absorption spectrometry (AAS) flame technique was used, for K determination atomic emission spectrometry (AES) was applied. Differential pulse voltammetry (DPV) was used for quantitative determination of Pb.

The following scientific goals were set :

- Determination of metals (including heavy metals) and their forms in mine wastes and soil samples
- Determination of variability of the metal's concentrations in the soil core
- Determination of the metals' speciation in the analyzed material by means of the sequential extraction procedure.

2. Materials and methods

Using a spade the samples were collected into a polyethylene bags and transported to the laboratory. Locations of the waste heap (Olkusz – Pomorzany) and the soil core collection (Nielepice) are presented in **Fig. 1**. The sampling point at the industrial waste heap near Olkusz is shown in **Fig. 2**. The soil core sampling point in Nielepice is presented in **Fig. 3**.



Figure 1. Location of the sampling sites.



Figure 2. Sampling point near Olkusz.



Figure 3. Soil core sampling area.

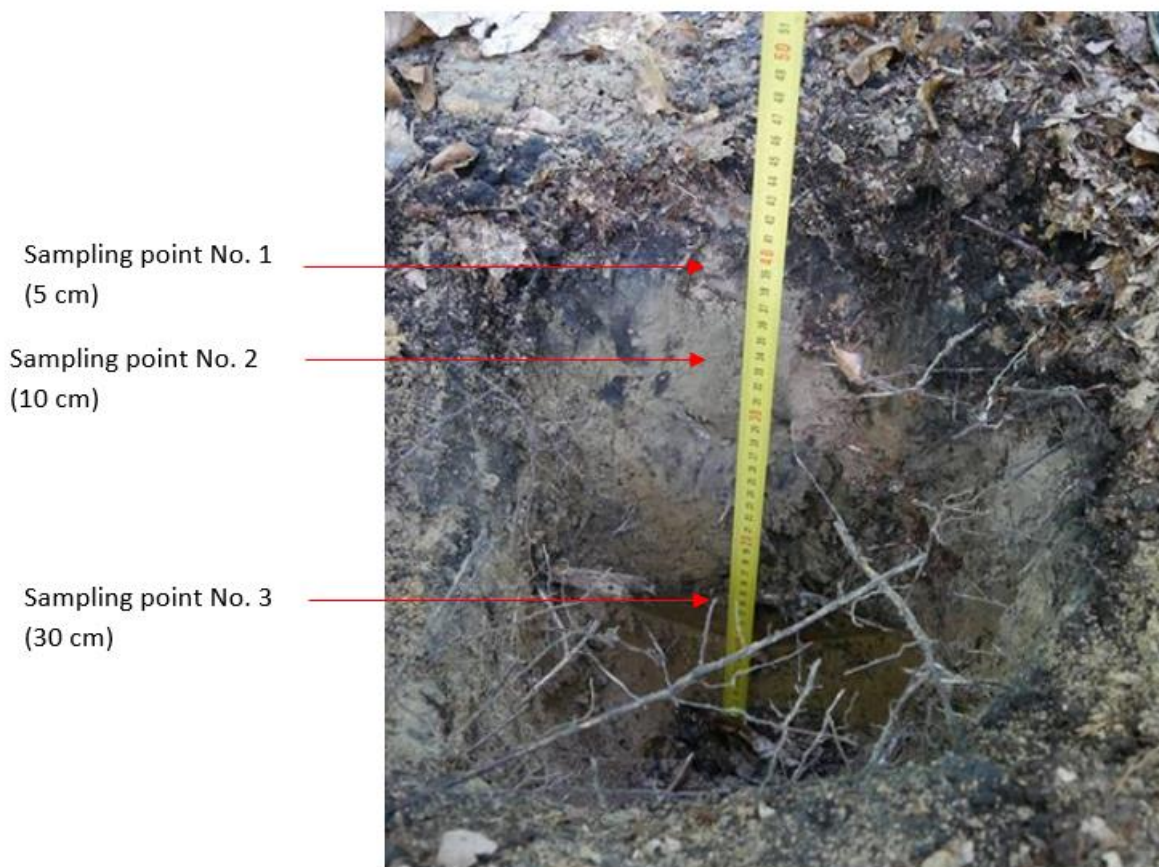


Figure 4. Picture showing the core samplings at different depths.

Sampling of the soil core was done in the Nielepiec forest. This forest is located 16 km east of Krakow (**Fig. 1**). The samples were taken at the same point but at different depths. **Sample No. 1** at 5 cm depth (top soil layer), **sample No. 2** was taken at 10 cm depth and finally **sample No. 3** was taken at 30 cm depth (**Fig. 4**).

Sample No. 4 was taken from the mining area of Olkusz, where a large mineral extraction occurred (**Fig. 2**). And more precisely in the waste zone of the mine where unused land has been accumulated.

2.1. Analytical procedure

The collected samples were dried to a constant weight for 24 hours at 100 °C, then grinded in an agalite mortar to obtain homogeneous, laboratory soil samples. Then, the modified sequential extraction procedure (Rauert et al., Sorin et al.) was applied to obtain the solutions for quantitative determinations of metals (**Fig. 5**).

For this, 1.00 gram of dry and homogeneous soil samples (1, 2, 3 and 4) were weight into a polyethylene Erlenmayer flasks. The procedure was executed in two replications. Then, 40 mL of Reagent A was added and shaken for 3 hours at 100 rpm and amplitude 5 (Laboratory Shaker ...). Afterwards, the suspension was transferred into the test tubes and centrifuged for 5 minutes at 2500 rpm. The supernatant was collected and marked accordingly. The remaining material was washed with double-distilled water, centrifuged and transferred back into the flasks. To the solid phase 40 mL of Reagent B was added. This suspension was then shaken for 2 hours at 100 rpm and amplitude 5. Then it was centrifuged for 5 minutes at 2500 rpm. The supernatant was collected and marked as solution B. The procedure was applied for all 4 samples, and the solutions were stored in the freezer till analysis.

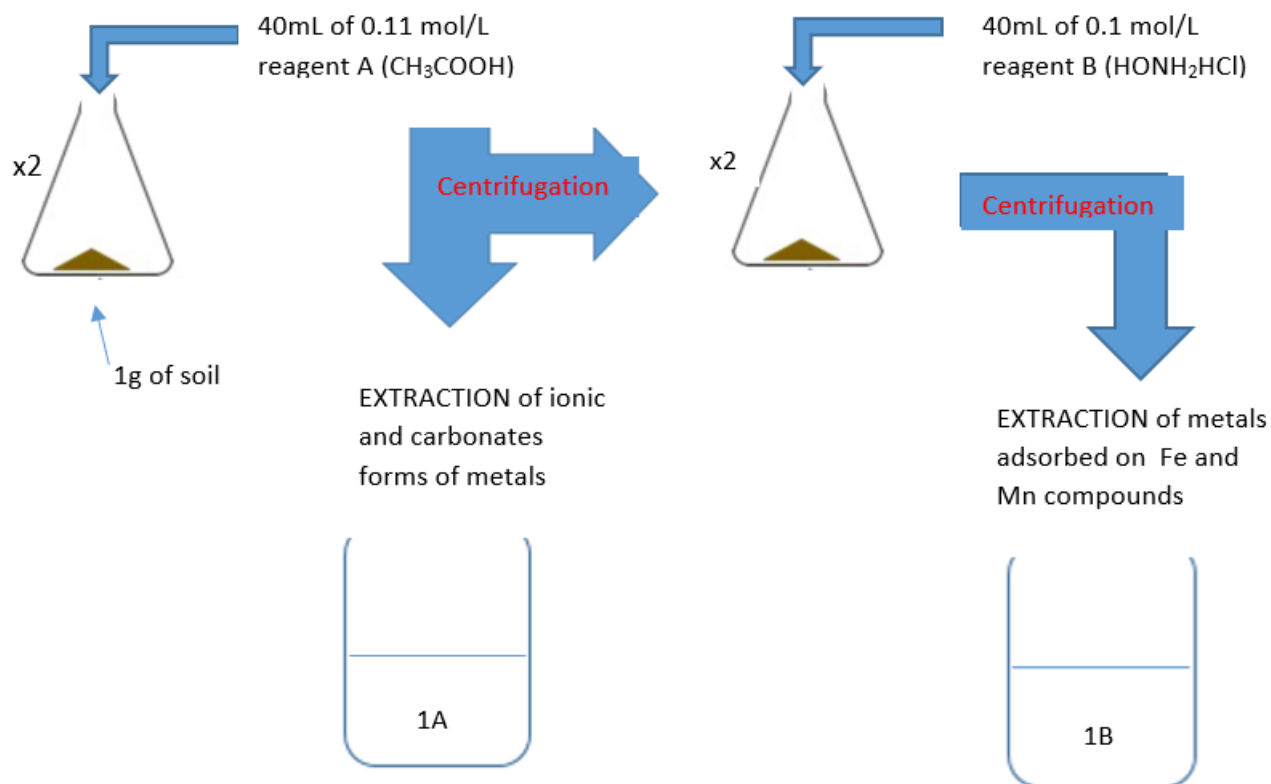


Figure 5. Scheme of the used sequential extraction procedure.

Atomic absorption spectrometry, flame technique was chosen for quantitative determination of Fe, Mn, Zn and Mg, while atomic emission spectrometry for determination of K. The Perkin Elmer AA spectrometer Model 3110 (USA) was used. In **Tab. 1** analytical parameters and calibration data are presented.

Table 1. Analytical parameters of metals' determination by means of AAS (Fe, Mn, Zn, Mg) and AES (K).

Parameter	Fe (mg/L)	Mn (mg/L)	Zn (mg/L)	Mg (mg/L)	K (mg/L)
Wavelength (nm)	248.3	279.5	213.9	285.2	766.5
Slit width (nm)	0.2	0.2	0.7	0.7	0.7

An Electrochemical Analyzer M161 with the electrode stand M161, both MTM-ANKO, made in Poland, were used for all voltammetric measurements. The classical three-electrode quartz cell, volume of 5 ml, consisting of the CGMDE type M164 (MTM-ANKO, made in Poland) with the surface area of 1.8 mm² as a working electrode, used in the hanging mercury drop electrode mode, a reference electrode Ag/AgCl/3M KCl and a platinum wire as an auxiliary electrode. All solution used for analyses were purged with argon. A magnetic Teflon-coated bar was used for stirring, approximately 600 rpm, during the accumulation period. Experiments were carried out at room temperature, approximately 24°C. The EAQt electrochemical analyzer software enabled electrochemical measurements, data acquisition, and advanced processing of the results.

For quantitative determination of lead the differential pulse voltammetry method was applied. In **Tab. 2**, measuring parameters are shown. Curves were recorded in 0.1 M KNO₃ and 5 µL of 7% HNO₃ was also added to the cell, which volume was 5 mL.

Table 2. Analytical parameters of Pb determination by means of DPV.

Parameter	Description
Voltammetry	DPV
Probing	Double
Working Electrode	CGMDE
Current range	100 nA
Measurement	Single
Ep (mV)	-700
Ek (mV)	-200
Estep (mV)	2
dE (mV)	50
tp (ms)	20
tw (ms)	20
td (ms)	500
Average	1
Mixer(s)	3
Points	250
Breaks	1
E of break (mV)	-700
t of break (s)	30
Setup	3 electrodes

3. Results

After performing the calibration for each element, the following results were obtained (**Tab. 3**). The highest concentrations of Fe (430.7 mg/L) was found in extract B of the sample 4 (industrial waste heap) near Olkusz. The same was true for the other analysed elements, with magnesium being the most abundant of all analysed elements (141 mg/l in extract A and 672.8 mg/L in extract B).

Relatively high concentrations of lead were also determined in the analysed extracts. The highest concentration was found in extract 4B (29.45 mg/L) and the lowest, below the detection limit in extract 4A (Table 4). Cadmium was not determined in the samples 1A-4A and 1B-4B, because concentration was below detection limit of the applied method.

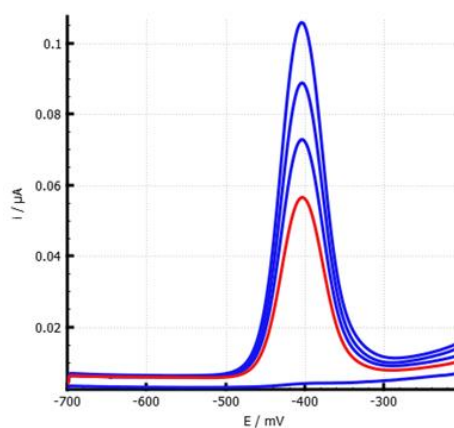
Table 3. Results of the elements quantitative determination in soil extracts.

	Fe (mg/L)	Mn (mg/L)	Zn (mg/L)	Mg (mg/L)	K (mg/L)
1A	1.49	0.68	0.12	1.05	3.52
% RSD	0.65	0.3	1.1	1.55	0.6
2A	1.94	0.40	0.09	0.56	2.23
% RSD	0.45	2.15	2.45	1.15	0.25
3A	2.13	0.12	0.51	0.27	0.86
% RSD	1.05	4.65	1.05	0.7	2
4A	0.22	0.04	0.03	141	3.00
% RSD	3	10.6	15.7	0.9	0.9
1B	30.5	0.31	0.18	0.80	0.98
% RSD	1.75	2.85	1.8	2.3	0.55
2B	1.27	0.06	0.07	0.12	0.43
% RSD	1.3	8.85	2.2	0.65	2.4
3B	10.4	0.24	0.09	0.62	0.50
% RSD	5.7	1.8	3.2	2.7	1.45
4B	430.7	33.6	135.5	672.8	12.1
% RSD	12.3	0.5	4.65	0.25	0.1

Table 4. Lead concentration in the soil extracts determined by means of DPV method.

Sample number	Pb ($\mu\text{g/L}$)	Sample number	Pb ($\mu\text{g/L}$)
1A	92 \pm 15	1B	241 \pm 88
2A	75 \pm 35	2B	60 \pm 26
3A	94 \pm 14	3B	284 \pm 053
4A	ND	4B	29450 \pm 2600

Fig. 6 and 7 present voltammograms recorded during determination of lead in the sample 4B.

**Figure 6.** Standard addition voltammetry for the sample 4B. Baseline and voltammograms of sample (red) and 3 standard addition of lead. Experimental curves.

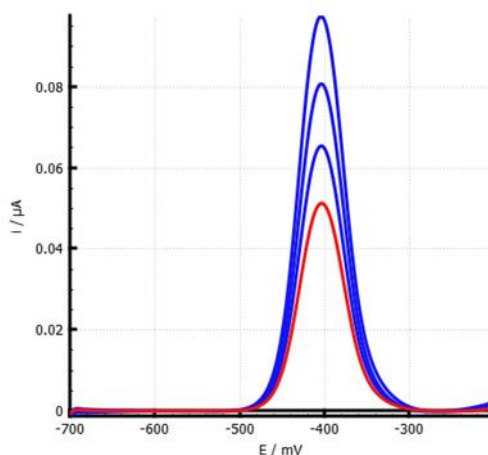


Figure 7. Standard addition voltammetry for the sample 4B. Baseline and voltammograms of sample (red) and 3 standard addition of lead. Curves after baseline subtraction by polynomial of 3rd approximation.

4. Discussion

4.1. Analytical assessment of the used methods (AAS, DPV)

DPV and AAS are methods of instrumental analysis. Indeed, it makes it possible to analyze and calculate concentration of an element in a liquid sample. However, these two methods remain different on some points. Each of them has advantages but also disadvantages. First of all, the AAS method allows relatively fast sample analysis: the analysis only takes few seconds. While for voltammetry, analysis of a single sample takes about 20 minutes. However, even if the method is more restrictive for time, it remains extremely sensitive. Indeed, the results we obtain are of the order of $\mu\text{g}\cdot\text{L}^{-1}$. While for the flame technique of AAS method, sensitivity does not exceed the order of $\text{mg}\cdot\text{L}^{-1}$. Finally, the most important point is that the AAS method allows us to analyze the elements in atomic form while the DPV method allows to analyze only the elements in ionic form.

4.2. Comparison of the samples in Nielepice and Olkusz

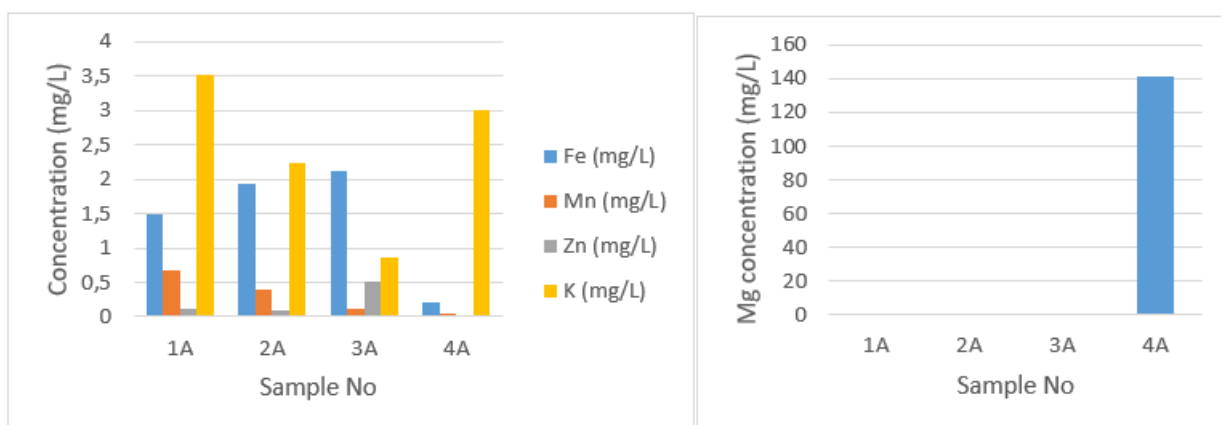


Figure 8. Histogram representing elements' concentrations in extracts A.

In **Fig. 8** a histogram showing the elements' concentrations in extracts A (ionic and carbonates forms of metals) is presented. Out of five studied elements, four namely Fe, Mn, Zn, Mg and K in A extracts form soil in both locations are of the same order of magnitude. Slight increasing tendency

down the soli core (samples 1, 2 and 3) is observed for Zn and Fe, while reversed tendency is noted for K and Mn. On the other hand concentrations of Mg in the samples from the Nielepice forest (in the whole profile) are over 100 times lower than in the A extract from the waste heap in Olkusz (**Tab. 3**).

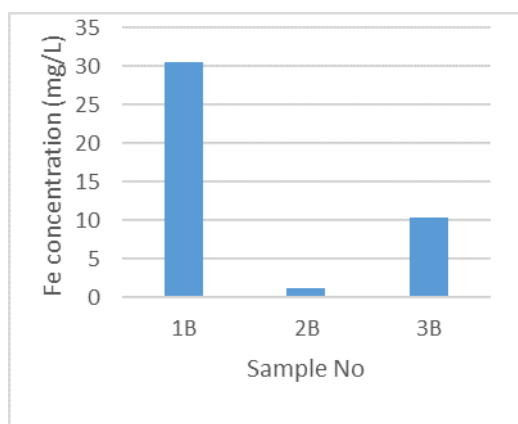


Figure 9. Elements concentrations in extracts B in the Nielepice forest soil core.

Concentrations of all analysed elements are the lowest in the middle layer of the profile. It can be seen (**Fig. 4**) that this layer of the profile is composed mainly of sand. As a result, low sorption properties of this layer can be expected (low concentrations of organic matter and minerals as well as low concentration of Fe – **Fig 9**). The highest concentrations of the examined elements were found in the top soil layer, rich in organic matter (**Tab. 3, Fig. 9**).

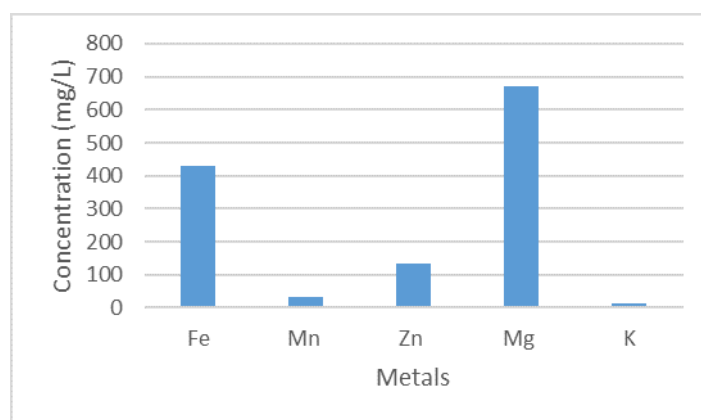


Figure 10. Metals concentrations in extract B from the soil sample collected in Olkusz.

In extracts B from the soil collected at the industrial waste heap in Olkusz, the highest was concentration of Mg, the lowest concentration of K (**Fig. 10**). Concentrations of the analysed elements was the highest in this sample comparing to soil samples from Nielepice. It is clearly the result of the soil origin. Waste heap was (and still is) formed as a collected overcap from the zinc and lead ores from the mine in Pomorzany. Thus, concentration of zinc is so high in this material (**Tab. 3**).

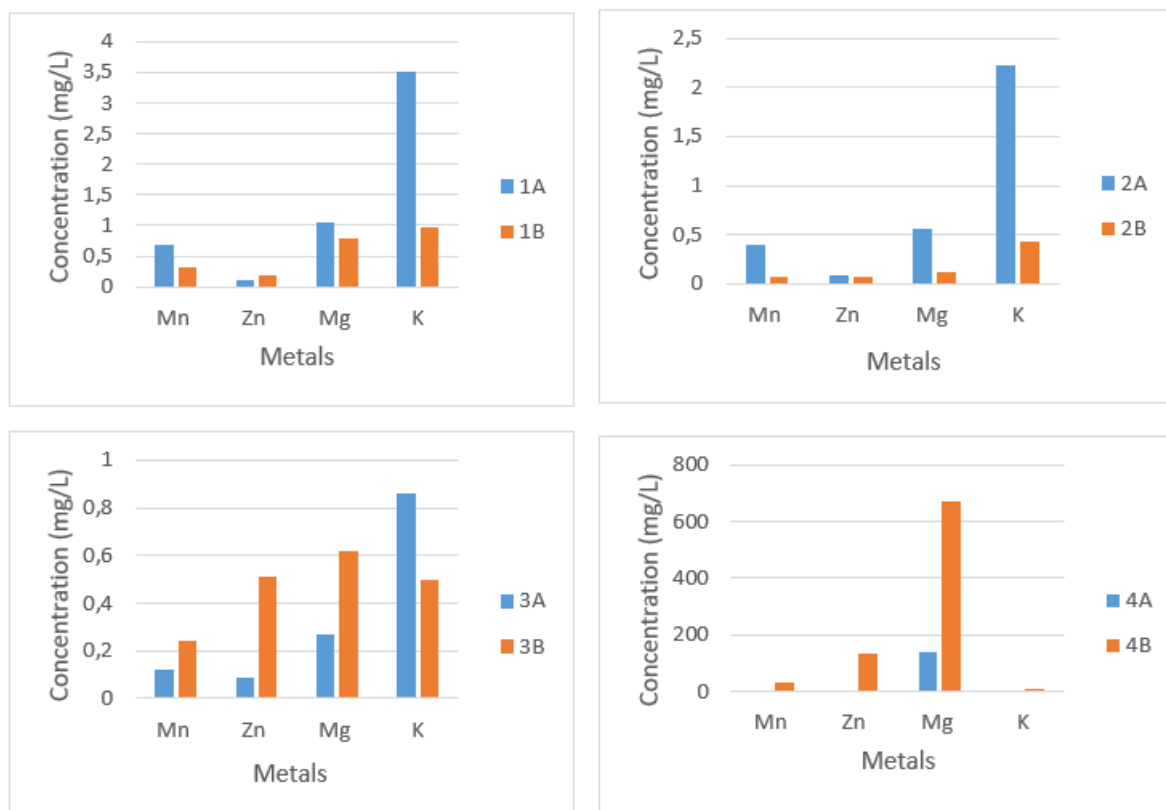


Figure 11. Comparison of Mn, Zn, Mg and K concentrations in extracts A and B.

Differences between metals' distribution in fractions A and B in the soil and wastes heap samples is clear and significant (Fig. 11). First, concentrations of all analysed elements are much higher in the material collected from the wastes heap – the rate reaching up to 1200 times for zinc and 1300 times for magnesium. Also, the analysed soil revealed (considering top and bottom layers of the core – rich in organic and clay materials) high sorption potential. The metals due to their chemical properties are distributed between the analysed fractions - the highest amount of Zn was adsorbed on Fe and Mn compounds of the top and bottom soil layers.

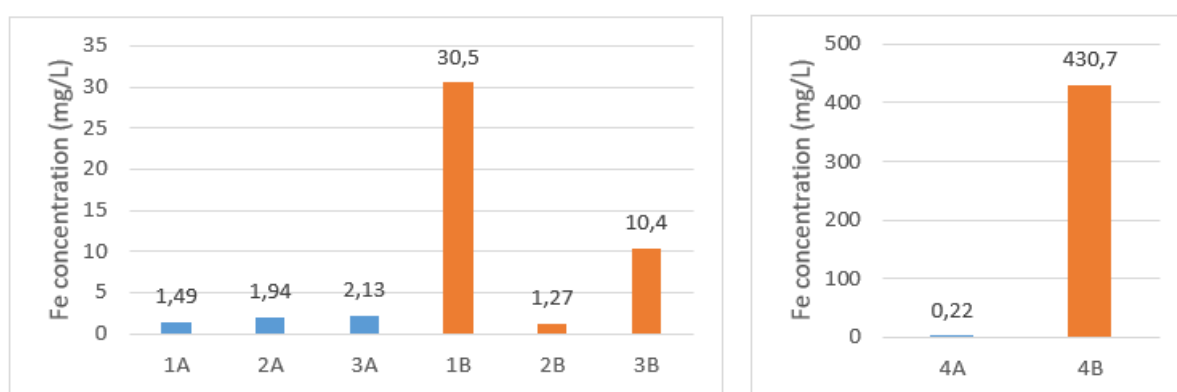


Figure 12. Comparison of Fe concentration in extracts A and B.

Iron in the sample collected from the waste heap practically does not exist in ionic form (extract A - 0.22 mg/L) but is abundant in oxidized forms (extract B - 430.7 mg/L) (Fig. 12). In the soil samples from Nielepice, despite the medium sand layer similar situation takes place – much higher fraction of the element is present in oxides and hydroxides than in ionic forms. As a result, accumulation of zinc in these layers takes place.

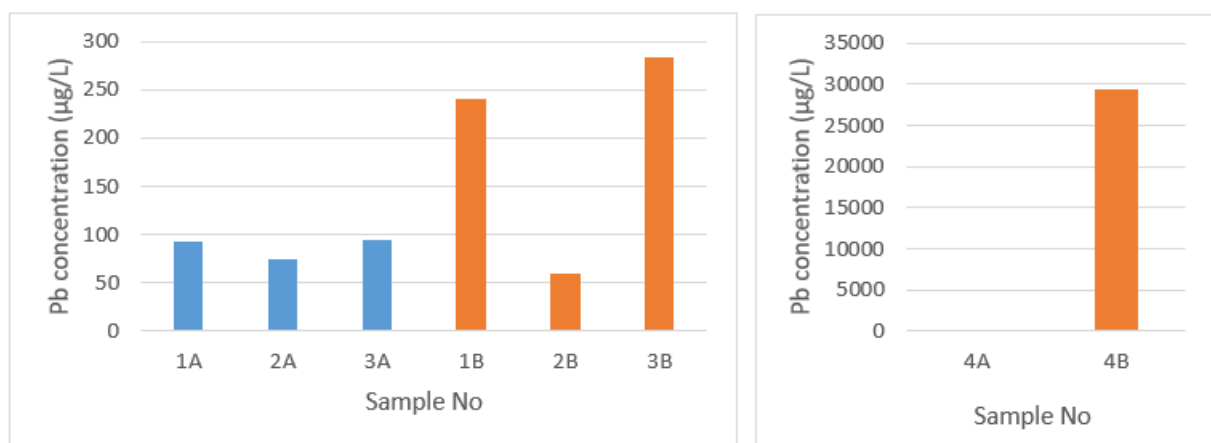


Figure 13. Comparison of Pb concentration in extracts A and B.

Lead in the soil samples is present in both forms (ionic or co-precipitated with Mg and Ca carbonates) and to much higher extend adsorbed on iron and manganese compounds (the same tendency as for Zn was observed in the soil core). In the wastes sample, extremely high concentration of lead was found in forms adsorbed on iron and manganese compounds (**Tab. 3, Fig. 13**).

5. Conclusions

The following facts have been established :

- The existing in the area mining and raw materials processing industry as well as localization of the waste heap leads to contamination of soils in the region.
- Use of the sequential extraction procedure for sample preparation allows analysis of the potential influence of heavy metals on the environment.
- The applied instrumental methods of analysis were adequate for the undertaken research task.

Literature

- [1] Rauret G., Lopez-Sanchez J.F., Sahuquillo A. Rubio R., Davidson C., Ure A., Quevauviller P., Improvement of the BCR three step sequential extraction procedure prior to the certification of new sediment and soil reference materials, *Journal of Environmental Monitoring*, no 1, 1999, pp. 57 - 61
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