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Assessment of elements mobility in anthropogenic layer of historical wastes related to glass production in Iżera Mountains (SW Poland)

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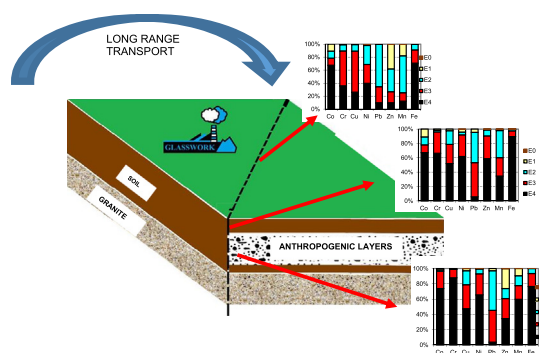
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HIGHLIGHTS

- In historical glass wastes Pb and Mn did not correlated with other PTEs and magnetic parameters.
- Magnetic parameters are helpful in understanding of the relationship of PTEs with various forms of iron.
- Up to 43% of Zn occurred in ionic form, associated with iron oxides only by surface adsorption forces.
- Considerable part of Ni, Co and Cu was associated with ferrimagnetic iron oxides in less mobile fractions.
- Some part of Zn, Ni, Co and Cu occurred also in the form of inclusions in aluminosilicates or was enclosed in glassy phases.

GRAPHICAL ABSTRACT



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ABSTRACT

A geophysical survey conducted in the remote forest glade, located in the Iżera Mountains (SW Poland), revealed the existence of an anthropogenic layer of historical glass wastes dumped in this area during the activity of a glass factory in the 18th and 19th centuries and domestic wastes dumped during the second part of the 20th century. The aim of the study was assessment of potential ecological risk related to the release of potentially toxic elements to the soil, groundwater and surface waters. The assessment was done on the base of classical geochemical analysis supported by calculation of environmental indices as well as on mobility of elements (leaching test and BCR sequential extraction). As an innovative aspect in the geostatistical interpretation of the data, some magnetic parameters (magnetic susceptibility- χ , χ /Fe ratio) were also used. It allowed for a better understanding of the relationship of PTEs with various forms of iron. The BCR sequential extraction found that among the PTEs, only Zn (up to 43%) was in a potentially mobile fraction probably occurring in ionic form, associated with iron oxides only by surface adsorption forces. The leaching has shown a slight increase in Zn and Cu content in the surface waters; however, it was not considered to be a real ecological threat because the pH of the waste material and soil cover is >6.0 and the scenario of a radical decrease in pH is rather unrealistic. The other PTEs were associated with more stable E2, E3 and E4 fractions. Zinc, similar to Ni, Co and Cu in waste samples, was highly correlated with magnetic parameters (χ and χ /Fe). It means that a considerable part of these metals was associated with ferrimagnetic iron oxides, although they can also occur in the form of inclusions in aluminosilicates and enclosed in glassy phases.

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1. Introduction

Former studies conducted in the mountain forest glade of Orle, located in the Western Sudetes (SW Poland), revealed the existence of anthropogenic layers of buried wastes consisting of slags, sinters, fragments of ceramics and ash, as well as sharp-edged sinters. These wastes are result of the ca. 100 years of glassworks activity in this area over the 18th and 19th centuries. The anthropogenic layer of historical wastes is partly mixed with modern bottom ashes and construction waste dumped here during the second part of the 20th century. The anthropogenic layer was detected by applying of soil magnetometry during the field survey in 2015, as the anthropogenic material has different magnetic properties than the natural geological background consisting of granites and gneisses. For this reason and also by using geophysical methods, it was possible to determine the depth of the buried waste layer as well as its spatial distribution in the forest glade. A geochemical study also revealed the high contents of Cu, Ni, Pb, Sn and Zn in the topsoil and subsoil samples taken in the area of magnetic anomaly (Zawadzki et al., 2016; Magiera et al., 2019).

Generally, ashes and slags, regardless of their source, contain elevated levels of potentially toxic elements (PTEs) that may pose a potential threat to soil and groundwater, especially during long time of storage (Parsons et al., 2001; Kierczak et al., 2009, 2013; Ettler et al., 2016; Schindler, 2014). The threat can be related to the leaching of elements to the ground and surface waters, especially if the anthropogenic wastes have a direct contact with streams, rivers or water reservoirs. In many cases, historical slags and wastes stored for tens and hundreds of years display even a lower residual content of potentially toxic elements (PTEs) compared to those observed in modern slags (Potysz et al., 2016) because the process of slow release of elements occurring in the first period after their deposit led to a decrease in their content. On the other hand, some authors have reported that, in slags, PTEs (mostly metals) were largely encased in droplets and remained protected by the glassy matrix, which was relatively resistant to weathering processes (Veselská and Majzlan, 2016).

The literature on the impact of pollutants emitted by glassworks on the soil environment is not very extensive; however, several studies based on currently active glassworks have been conducted in Europe (Giusti and Polo, 2002; Rampazzo et al., 2008; Rossini et al., 2010; Udatný et al., 2014). For example, centuries of glass-making activity revealed high levels of trace elements in marine waters, sediments and mussels around the Murano Island in Italy (Giusti and Zhang, 2002). The increased content of As, Cd, Pb and Zn in soils around glasswork or related glasswork dumps were also reported in the Czech Republic (Udatný et al., 2014) and Sweden (Jani and Hogland, 2017, 2018; Mutafela et al., 2020); however, the increased Pb content in soils around crystal glasswork in South-Eastern Sweden was earlier interpreted as natural geogenic enrichment (Zhang et al., 1999). Other studies conducted in South-Eastern Sweden reported the high content of a mobile fraction of Al, As, Fe and Pb in soils around an art glass factory as well as in leachates, where the concentrations was higher than the local guideline values for safe drinking water (Augustsson et al., 2016; Rai et al., 2019). This part of the country (Kalmar County) is regarded as one of the most contaminated spots in Sweden due to the 150 years of glasswork activity (Jani and Hogland, 2018). The negative effect of glasswork activity on soils and native flora has also been reported from India (Varun et al., 2012).

The Karlsthal glasswork on Orle glade in the Iżera Mts. (South-Western Poland) was founded in 1754, and in the beginning it produced white and coloured glass, chandeliers, retorts and pharmacy utensils, but there is lack of information about detailed production technology. From 1795, the Karlsthal glassworks started producing transparent crystal glass with a high lead oxide content. In some crystal and art glass, the weight content of Pb was up to 32% (Hynes et al., 2004). The production of crystal glass was associated with the emission of gases and dust containing lead compounds (e.g., cerussite-PbCO₃) and the

generation of solid waste (cullet, sinters, slags). Since the 1840s, the glasswork started the production of coloured glass, coloured with oxides of various metals. The Karlsthal glass was particularly known for the production of crystal and millefiori glass, as well as for adventure, purple and ruby glass. For the ruby glass production, copper oxides were used as colouring substances (Tichy, 1928). There is lack of information about technologies and colouring substances used in production of other kinds of glass.

This study aimed to investigate the level of pollution related to the anthropogenic layer of historical glasswork wastes mixed with much later bottom ash and domestic wastes, located on a remote mountain glade, and also to conduct an ecological assessment of potential ecological risk related to the release of potentially toxic elements to the soil, groundwater and surface waters. The assessment was done on the basis of conventional geochemical analysis of total elements content, supported by calculation of environmental indices as well as on mobility of elements (leaching test and sequential extraction). As an innovative aspect in the geostatistical interpretation of the data, some magnetic parameters were also used. It allowed for a better understanding of the relationship of PTEs with various forms of iron found in the studied waste and the adjacent soil layers.

2. Materials and methods

2.1. Study area and sampling procedure

The investigated historical wastes were found in the remote forest glade Orle located on the altitude of 840 m in the Iżera Mountains on the South-Western edge of Poland (Fig. 1). The eastern part of the glade cuts through Kamionek Creek, which is a tributary of the Iżera river. The wastes are located in the northern part of the glade, directly on the bank of the creek, forming an uncovered escarpment rising a few metres above the shore. The rest of the waste is under the soil cover with meadow vegetation. The area on the western bank of the Kamionek creek is generally flat but uneven, intersected by small hollows and dry channels as a result of gully erosions. Currently, only a tourist station consisting of four buildings is located in the glade, but in the past, from the middle of the 18th century until the end of the 19th century, the Karlsthal glassworks operated here, and a related settlement for ca. 100 glass workers was located in the glade (Süss-Karwiński, 2004). The natural soil of the glade is a shallow initial soil, which is formed on detritus of granite, which is the part of Iżera granite-gneisses complex (Różycka and Migoń, 2017).

Of the nine waste samples, four (G1, G2, G3, G7) were taken from a depth of 0.5 m using a manual soil borer, along the 100 m long section A-B (Figs. 1 and 2). Geoelectrical measurements were carried out in the same transect to precisely locate the anthropogenic waste layer (Magiera et al., 2019). The samples G1, G2 and G3 were collected between the 10th and 30th m of the profiles, whereas G7 was sampled between the 50th and 60th m of the same transect. Sample G8 was collected in the same point as G7 but from the depth of 1 m. Sample G9 consisted of large pieces of slags collected from layer of 0.5 m in point G9 (Fig. 2). Sample G4 contained the bottom sediment from Kamionek Creek near the escarpment, whereas G5 was collected from the surface on the foot of escarpment. G6 was collected from the surface of the escarpment on the bank of the creek. Also, 5 topsoil (0–5 cm) and 5 subsoil (10–20 cm) samples were collected from the soil that covers the waste layer. Additionally, five samples from C horizon of soil from the Orle glade were collected. They were used as the background for calculation of I_{geo} and PI indices. Also, four water samples from Kamionek Creek were collected in September in conditions of low-water flow: W1- upstream of the Orle glade, W2 and W3-near the escarpment, where the creek cuts through waste layer, W4-in the forest downstream of the Orle glade.

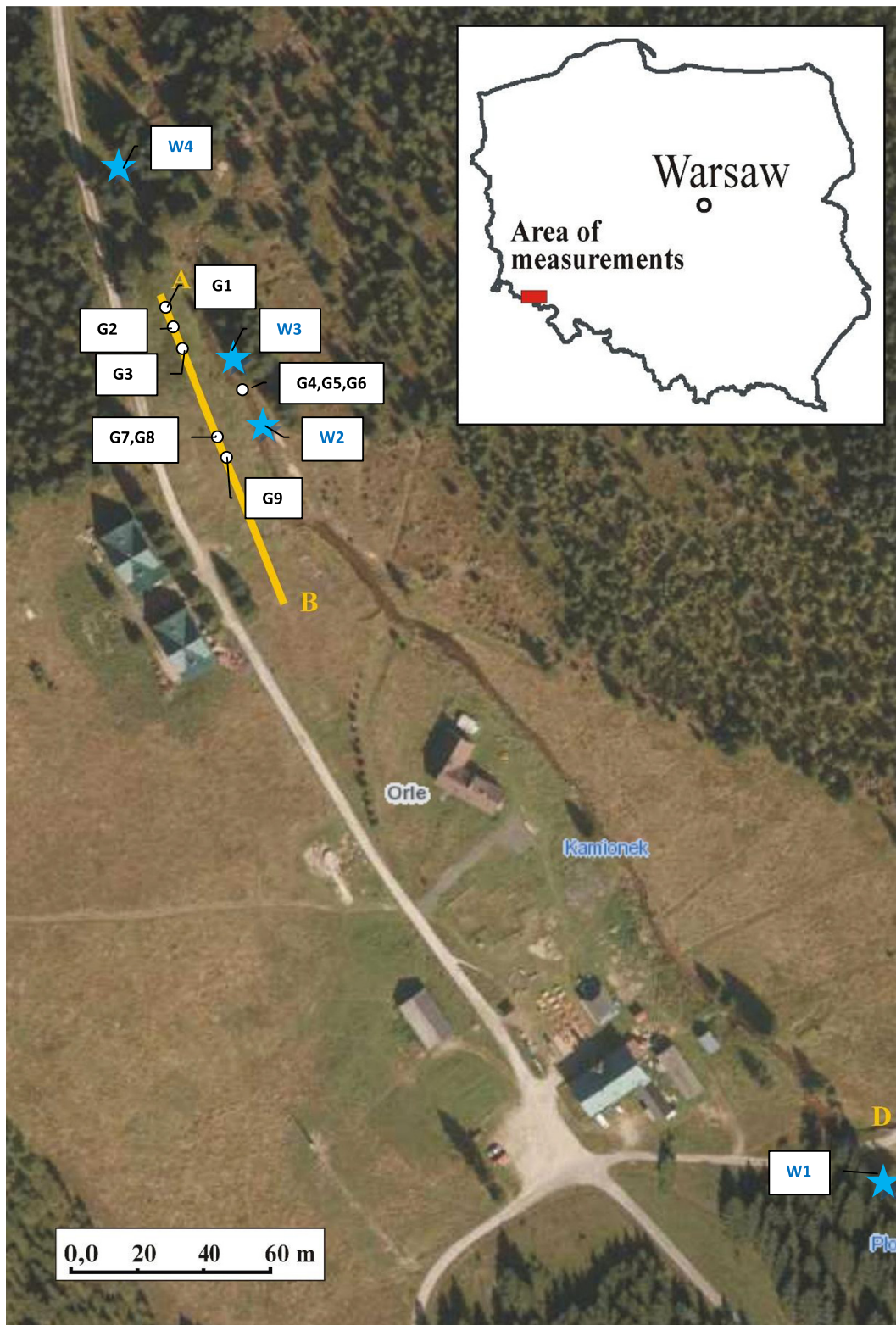


Fig. 1. The study area on the contour map of Poland, with detailed location of study area (transect A–B), sampling points and the objects of local infrastructure. Base map from “Google Earth Pro” (<https://www.google.com/intl/pl/earth/versions/#earth-pro>).

2.2. Geochemical measurements

Air dried samples collected from the topsoil, subsoil and C horizon and samples of anthropogenic waste material were sieved to <math><0.2\text{ mm}</math> fraction. The content of Fe, Mn and 17 PTEs (As, Cd, Co, Cr, Cu, Ga, Hg,

Mo, Ni, Pb, Rb, Se, Sn, Th, U, W and Zn) was determined after extraction in aqua regia. The extraction procedure was done according to the PN-ISO 11466 methodology. 3 g of sample was digested in 28 mL of aqua regia within 16 h in room temperature than boiling for 2 h. In case of determinations of metal contents in waste samples, the atomic absorption

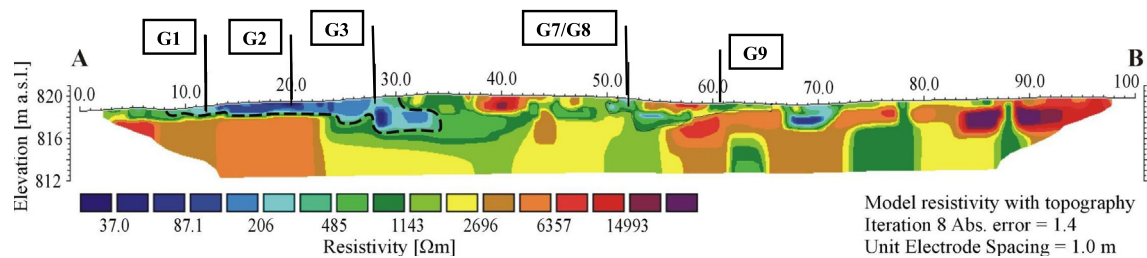


Fig. 2. Resistivity tomography profile (ERT) with marked location of samples collected along the profile. The location of anthropogenic material is marked by dash line. Anomaly around the 70th m of the profile is related to remains of old foundations latter used as bonfire place (Magiera et al., 2019).

spectrometry (AAS) technique was applied for Mn, Fe, Co, Cr, Cu, Ni, Pb and Zn. The measurement was conducted on a Perkin Elmer 1100 B apparatus at the chemical laboratory of the Institute of Environmental Engineering, Polish Academy of Sciences in Zabrze (Poland). For soil and water samples, the more precise ICP-MS technique was applied to measure Fe, Mn and 17 PTEs. The quality control procedures were conducted by using soil certified reference materials (NCS DC 73319, NCS DC 73323 and NCS DC 73325). The percentage recovery for the nine investigated elements ranged from 91 to 106%.

2.3. Mobility of PTE

2.3.1. Leaching test

The batch test with deionised water (H₂O batch test) was performed using the liquid:solid (L:S) ratio of 2:1 and 10:1 according to PN-EN 12457-1 (2006) and PN-EN 12457-2 (2006). The solid sample was shaken for 24 h in deionised water in an end-over-end shaker at 10 rpm. Then the liquid is separated by centrifugation for 20 min at 12,850g using a centrifuge with JA-20.1 rotor and a temperature control unit (AVANTI J 25, BECKMAN COULTER), and then supernatant was filtrated by 0.2- μ m filters (Millipore, Billerica, MA, USA) to remove the fine particles from the solution.

Analysis of Cr, Co, Cu, Fe, Mn, Ni, Pb and Zn content was measured by the ICP-OES (AVIO 200 spectrometer, Perkin Elmer) in the laboratory of the Institute of Environmental Engineering, Polish Academy of Sciences in Zabrze (Poland).

2.3.2. Sequential extraction procedure BCR

In order to determine the strength of the binding of Fe, Mn, Co, Cr Cu, Ni, Pb and Zn and their potential leachability and bioavailability, which can pose an environmental threat, the 3-step sequential chemical extraction procedure was used. It is modified procedure of sequential extraction proposed by the Community Bureau of Reference now known as the BCR sequential extraction method (Sutherland and Tack, 2002, 2003; Kaasalainen and Yli-Halla, 2003; Joksić et al., 2005). The procedure was preceded by a deionised water desorption test with water at the water to solid phase ratio of 10:1 (E0), and after completion of the sequential extraction procedure, the residual content of metals (E4) was determined.

Step 0 (E1): Loosely-bound fraction, metals mainly in pore solution. Use of deionised water at solid phase to water ratio 1:40 during 2 h in room temperature.

Step I (E1): It is so called “extractable fraction” or “acid exchangeable fraction” related to metal ions in mobile forms (exchangeable ions and bound to carbonates), obtained by application of 0.11 M CH₃COOH at pH 2.85, with solution ratio (solid to water ratio) 1:40 and contact time 16 h at room temperature.

Step II (E2): Easily reducible fraction related to metal ions in mobilisable forms bound to Fe and Mn oxides. In this step, 40 mL of 0.5 M NH₂OH·HCl adjusted to pH 1.5 with HNO₃ were added to the solid residue from the first step, and the flask was shaken for 16 h at laboratory temperature.

Step III (E3): Oxidisable fraction usually interpreted as a fraction connected with organic matter or/and sulphides. During this step, there were two times extractions using 10 mL of 8.8 M H₂O₂ acidified to pH 2–3 for 1 h at 85 °C each and then the sample was extracted with 1 M CH₃COONH₄ at pH 2.0, in room temperature at solid:solution ratio 1:50 and shaking time of 16 h.

Step IV (E4). The residual fraction was connected mostly with silicates or aluminosilicates. Digestion of residual fraction was performed with aqua regia 3HCl + HNO₃, after cooling to room temperature the digest filtered and diluted to 50 mL with 0.1 M HNO₃.

After each extraction step, separation was performed by centrifugation at 10,000 rpm for 10 min, and the supernatant was filtered using a 0.45 μ m syringe filter.

The metals concentration after each step were analysed with ICP-OES (AVIO 200 spectrometer, Perkin Elmer). Analytical grade reagents were used.

The modified BCR procedure differs from the original one in the higher concentration of hydroxylammonium chloride (NH₂OH·HCl) and lower pH of the reagent in E2 step, as well as an effect for release of Pb. It was observed that a modified reagent provides better attack on the iron oxyhydroxide phase, whereas the original reagent attacked only hydrous oxides of manganese. Additionally, Pb was not released from soil in the original BCR procedure until the residual (aqua regia) (Mossop and Davidson, 2003). The accuracy of the BCR SEP method was checked using Certified Reference Material CRM BCR 483 (IRMM), providing indicative values (only for Zn, not for Ba) for the concentrations of the solutions obtained from four steps of SEP and also the sum of these values.

2.4. Environmental indices

To assess the accumulation of PTEs in the waste and soil cover over the anthropogenic layer, two environmental indices that are commonly used in soil pollution study were calculated. The I_{geo} allows for the assessment of PTE soil contamination based on the ratio between the currently measured content of the PTEs (in topsoil, subsoil and the waste layer) and the content of the same elements in the bedrock or a specific geochemical background for metal (Kowalska et al., 2018; Müller, 1969).

I_{geo} is defined by the following equation:

$$I_{geo} = \log_2 (C_{EL}/1.5 C_{background})$$

where

C_{EL} - PTE's current content in the studied component of the environment (topsoil, subsoil and the waste layer).

C_{background} - content of PTE in the bedrock or reference geochemical background. In this case the content of element in C horizon of natural soil in Orle glade (outside the waste deposition area) were proposed as a background values.

1.5 - constant, allowing the analysis of fluctuations of PTE content as a result of natural processes.

The second calculated environmental index was Single Pollution Index (PI). The PI is helpful in the assessment of the most dangerous PTE among the studied elements (Gong et al., 2008; Kowalska et al., 2018).

$$PI = C/B_{\text{where}}$$

C - determined PTE content in the layer, and

B - content of PTE in the bedrock or reference geochemical background (C horizon of natural soil in Orle glade).

3. Results

3.1. Chemical analysis

The content of Fe, Mn and some PTEs in soil samples collected over the anthropogenic layer as well as from the C horizon of soils in the Orle glade outside of the anthropogenic layer is presented in Table 1. The iron content in organic and mineral horizons was not so high, between 1.0 and 1.8%, and was lower than in the geological background, where in some samples, Fe content was over 2.0% (Table 1). The manganese content was more variable, ranging in the organic horizon from 112 to 1512 mg/kg and in the mineral horizon from 167 to 815 mg/kg. A much smaller variability of Mn content was measured in the geological background, where its average content was 189 mg/kg. Compared to this value, a significant increase in the Mn content in the upper soil layer can be seen. In relation to the local geological background (C horizon), a high increase of Cu, Ni, Pb and Zn was observed in the soil cover over the anthropogenic layer. In the case of Cu, the mean content in organic horizon (25.68 mg/kg) is more than four times higher than the mean value in C horizon of Orle glade soil, whereas the maximum measured content in this horizon is over six times higher than the maximum background value. In the mineral horizon, the Cu variability is lower and the mean concentration is only two times higher than the background value. In turn, Zn showed higher mean and maximum contents in the mineral horizon (74.16 and 189.84 mg/kg, respectively) than in the organic one (67.16 and 110.88 mg/kg, respectively), where its increase was three times higher in relation to the geological background. The absolute Ni content in the topsoil is low (mean for organic 5.41 mg/kg and mean for mineral 7.17 mg/kg), but in relation to the local geological background (0.22 mg/kg), the concentration of Ni in the mineral soil horizon is over 30 times higher. Higher Ni content is observed in the mineral horizon than in the organic one. The opposite situation was found in

the case of Pb. Considerably higher mean contents of Pb were determined for the organic (130.37 mg/kg) compared to the mineral horizon (80.75 mg/kg). In relation to the value of the geological background, this means a 4.5 times increase in the organic horizon and 2.8 times in the mineral horizon. The maximum Pb content measured in organic horizon reached 322.18 mg/kg. Also, slightly increased content of As, Cd, Hg, Mo, Sn and W in the topsoil was observed; however, the absolute contents of these elements were not high. The contents of elements such as Co, Cr, Rb, Se, Th and U in both the organic and mineral horizons of topsoil were similar to those measured for the geological background.

The total content of Fe, Mn and PTEs in waste samples is given in Table 2. The total iron content in the waste samples was between 1.22 and 6.36%. The highest contents (>5.0%) were observed in the G1 sample collected from the 0.5 m depth and samples collected on the surface of escarpment. The lowest Fe content was detected in sample G7 collected in the central part of the A-B transect at the depth of 0.5. Definitely the highest manganese content was observed in the sample at point G7/G8, in the central part of the transect (2170 mg/kg at a depth of 0.5 and as much as 7450 at a depth of 1.0 m). In the same G8 sample taken from the 1.0 m depth, the highest Pb content (472 mg/kg) was detected. The lowest Mn and Pb content was detected in creek sediment and in samples collect from the escarpment (G4 and G6 in case of Mn and G4 and G5 in case of Pb). The total Zn content in the waste samples was between 83 mg/kg (in the creek sediment) and 1400 mg/kg in G7 (sample from 0.5 m depth of the central part of the transect). In addition to the highest Zn content, the G7 sample also had the highest Cu (247 mg/kg), Ni (216 mg/kg) and Co (80 mg/kg) contents. The lowest content of Cu (17 mg/kg and Co <20 mg/kg) was observed in G4 (creek sediment), whereas the lowest content of Ni was observed in G4, G8 and G9 (<25 mg/kg). The highest content of chromium (similar to Fe) was observed in sample G1, collected in the northern part of the A-B transect. The lowest content of Cr (<50 mg/kg) was detected in samples G2, G4, G6 and G8. Magnetic susceptibility of these samples is very diverse, from paramagnetic values ($\chi = 20 \times 10^{-8} \text{m}^3 \text{kg}^{-1}$) to high ferromagnetic $>1000 \times 10^{-8} \text{m}^3 \text{kg}^{-1}$ (samples G1 and G5) and even $2537 \times 10^{-8} \text{m}^3 \text{kg}^{-1}$ in sample G7 collected from the depth of 0.5 m in the central part of the transect. It is the same sample where the highest values of Pb and Mn were measured.

Results of the leaching test for the samples of waste material are presented in Table 3. Most of the investigated samples in aqueous solutions showed a neutral or slightly alkaline reaction in the pH range 6.6–7.9. A

Table 1

Descriptive statistics of the total concentration of Fe, Mn and potentially toxic elements (PTE) in soil over the anthropogenic layer of waste material and in the local geological background (C horizon outside the anthropogenic layer) as well as pH values for the samples collected on the Orle glade and surrounded forest.

| Element | Organic horizon 0–5 cm (mg/kg) n = 5 | | | Mineral horizon 10–20 cm (mg/kg) n = 5 | | | C horizon (mg/kg) n = 5 | | |
|-----------|--------------------------------------|------|--------|--|------|--------|-------------------------|------|--------|
| | Mean | Min. | Max. | Mean | Min. | Max. | Mean | Min. | Max. |
| Fe | 10,300 | 5060 | 16,000 | 11,700 | 6890 | 17,700 | 14,700 | 5870 | 23,700 |
| Mn | 657 | 112 | 1510 | 479 | 167 | 815 | 189 | 134 | 279 |
| As | 13.9 | 6.5 | 26.8 | 10.3 | 2.1 | 18.3 | 6.3 | 4.2 | 8.1 |
| Cd | 0.38 | 0.09 | 0.69 | 0.37 | 0.05 | 0.97 | 0.12 | 0.07 | 0.18 |
| Co | 2.4 | 1.5 | 3.6 | 3.9 | 1.9 | 7.6 | 2.2 | 1.2 | 3.7 |
| Cr | 16.6 | 8.3 | 26.3 | 16.8 | 4.5 | 31.1 | 20.8 | 14.0 | 27.1 |
| Cu | 25.7 | 9.6 | 58.7 | 15.3 | 6.7 | 31.5 | 6.1 | 3.3 | 9.7 |
| Ga | 7.4 | 5.3 | 9.9 | 7.2 | 4.6 | 8.0 | 10.1 | 9.4 | 10.7 |
| Hg | 0.31 | 0.02 | 0.96 | 0.17 | 0.00 | 0.39 | 0.08 | 0.04 | 0.17 |
| Mo | 0.47 | 0.31 | 0.59 | 0.42 | 0.10 | 0.71 | 0.22 | 0.13 | 0.43 |
| Ni | 5.4 | 3.8 | 7.2 | 8.4 | 3.1 | 16.7 | 0.2 | 0.1 | 0.4 |
| Pb | 130 | 22.7 | 322 | 80.8 | 13.0 | 189 | 28.3 | 17.4 | 68.9 |
| Rb | 39.7 | 28.7 | 50.9 | 40.7 | 35.8 | 50.6 | 56.7 | 46.8 | 75.5 |
| Se | 0.36 | 0.18 | 0.51 | 0.39 | 0.20 | 0.58 | 0.38 | 0.28 | 0.45 |
| Sn | 2.37 | 1.49 | 3.73 | 3.05 | 0.59 | 8.89 | 1.31 | 1.17 | 1.41 |
| Th | 13.5 | 11.8 | 15.8 | 15.1 | 12.6 | 17.6 | 16.0 | 14.8 | 16.8 |
| U | 4.8 | 3.5 | 6.2 | 6.1 | 3.6 | 13.0 | 5.9 | 4.2 | 9.7 |
| W | 0.19 | 0.04 | 0.61 | 0.19 | 0.03 | 0.38 | 0.05 | 0.01 | 0.12 |
| Zn | 67.2 | 32.2 | 111 | 74.2 | 31.1 | 190 | 25.5 | 19.5 | 38.3 |
| pH glade | 5.48 | 5.04 | 6.04 | 5.01 | 4.27 | 5.75 | 6.04 | 5.74 | 6.34 |
| pH forest | 4.59 | 4.43 | 5.22 | 4.29 | 4.27 | 4.50 | 5.51 | 4.72 | 6.31 |

Table 2
Content of Fe, Mn, some potentially toxic elements (PTE) and mass specific magnetic susceptibility (χ) of wastes used for sequential extraction procedure. Standard deviation in brackets.

| Sample | Fe % | Mn mg/kg | Co | Cr | Cu | Ni | Pb | Zn | χ $\times 10^{-8} \text{ m}^3/\text{kg}$ |
|--------|---------------------|--------------------|----------------|-----------------|-----------------|-----------------|------------------|-------------------|--|
| G1 | 6.36 (± 0.28) | 1250 (± 58) | 54 (± 2) | 137 (± 2) | 180 (± 6) | 129 (± 2) | 114 (± 2) | 952 (± 21) | 1006 (± 27) |
| G2 | 2.80 (± 0.07) | 1170 (± 19) | 21 (± 1) | 46 (± 1) | 47 (± 1) | 27 (± 1) | 105 (± 2) | 378 (± 7) | 263 (± 7) |
| G3 | 4.35 (± 0.15) | 1160 (± 22) | 22 (± 1) | 66 (± 2) | 116 (± 1) | 47 (± 3) | 100 (± 4) | 1230 (± 34) | 526 (± 14) |
| G4 | 3.08 (± 0.21) | 578 (± 16) | <20 | 46 (± 1) | 17 (± 1) | 22 (± 1) | 19 (± 1) | 83 (± 3) | 20 (± 1) |
| G5 | 6.22 (± 0.40) | 1160 (± 17) | 66 (± 2) | 142 (± 5) | 165 (± 1) | 170 (± 2) | 73 (± 3) | 435 (± 37) | 1056 (± 43) |
| G6 | 5.44 (± 0.25) | 653 (± 12) | <20 | 44 (± 1) | 132 (± 3) | 42 (± 1) | 192 (± 4) | 750 (± 23) | 501 (± 8) |
| G7 | 1.22 (± 0.04) | 2170 (± 50) | 80 (± 3) | 105 (± 2) | 247 (± 7) | 216 (± 6) | 149 (± 4) | 1400 (± 42) | 2537 (± 53) |
| G8 | 2.24 (± 0.10) | 7450 (± 253) | <20 | 38 (± 2) | 103 (± 3) | 19 (± 2) | 472 (± 13) | 607 (± 10) | 323 (± 5) |
| G9 | 2.90 (± 0.11) | 1250 (± 24) | <20 | 47 (± 1) | 60 (± 2) | 20 (± 1) | 227 (± 6) | 257 (± 4) | 138 (± 2) |

slightly acidic reaction pH 6.1–6.3 was found only in the sample of waste taken from a depth of 1 m (central part of transect A–B). The highest conductivity in water solution of waste samples was measured for all samples collected from the 0.5 m deep layer of anthropogenic material. It was in the range of 370–420 $\mu\text{S}/\text{cm}$ in S/L phase 1:2. The concentration of Cr, Co and Pb in leachates was below or close to the detection limit. In case of Pb, even in sample G8 with the highest total concentration of Pb (472 mg/kg) in leachate, its content was <1.0 $\mu\text{g}/\text{L}$. In sample G7, taken directly above G8 from the depth of 0.5 m, the Pb content was 6 $\mu\text{g}/\text{L}$. Slightly higher contents were observed in case of Ni (2–14 $\mu\text{g}/\text{L}$) and Cu (1–24 $\mu\text{g}/\text{L}$). In both cases, the highest contents were measured in sample G7, where the highest total content of these metals was also observed. In the same sample, the highest content of Zn (116 $\mu\text{g}/\text{L}$) was also detected. The content of Fe and Mn in leachates is variable. In S/L ratio 1:2, the measured concentrations of Fe and Mn were 38–722 $\mu\text{g}/\text{L}$ and 22–362 $\mu\text{g}/\text{L}$, respectively, whereas in S/L ratio 1:10, the concentrations were 21–474 $\mu\text{g}/\text{L}$ and 11–75 $\mu\text{g}/\text{L}$, respectively.

The content of PTEs in creek water was low. The highest concentrations were measured for Cu at 0.40–0.82 $\mu\text{g}/\text{L}$, Ni at 0.25–0.37 $\mu\text{g}/\text{L}$ and for Pb at 0.26–0.28 $\mu\text{g}/\text{L}$. For all elements except lead, a slight enrichment was observed at the place where the creek passed through the waste layer and further downstream. The Pb content was almost the same at all measurement points (Table 4).

Sequential extraction analysis revealed that most of the investigated elements (Co, Cr, Ni and Fe) in samples collected between the 10th and 30th m of the A-B transect at the depth of 0.5 m exhibit a similar pattern (Fig. 3). In case of Co, Cr and Ni, over 60% of these elements were associated with the residual fraction. In the case of Fe, over 80% was associated with the residual fraction. In sample G1, Zn was distributed almost

evenly between the E1, E2 and E3 fractions, but going south, the proportion of the “acid exchangeable fraction” (E1) fraction increased from 27% (sample G1) to almost 43% (sample G3), at the expense of fractions E2 and E3. The largest amount of Mn at G1 and G3 was bound in the E2 fraction (42% and 36%, respectively), although the sample of G3 was the same as the residual fraction (E4). In sample G2, however, over 50% of Mn was associated with the residual fraction. Similar differences between samples G1 and G3 on the one hand and G2 on the other can be seen in the Pb analysis. In samples G1 and G3, lead associated with the E2 fraction dominated (58% and 43%, respectively), while in the G2 sample, most Pb was associated with the E3 fraction, although the residual fraction share was also significant (41%). In samples G1 and G3, the share of Pb associated with the E3 fraction was 28 and 34%, respectively. The Pb and Cu content in the E0 and E1 fractions was marginal. Copper in sample G1 was evenly distributed into the E2 and E3 fractions (42 and 43%, respectively); in sample G2, the E3 fraction was definitely dominant (59%), and in sample G3, similar amounts of Cu were associated with the E3 and E4 fractions (44% each) (Fig. 3).

In samples G4, G5 and G6, the Co contents were evenly distributed into fractions E1, E2, E3 and E4. In the case of Cr, this occurred mainly in the residual fraction (>50%), although its share in the E3 fraction was also significant (between 27 and 44%) (Fig. 4). In the case of Cu in the bottom sediment from the creek (sample G4), it was mostly detected in both the G2 and G4 fraction (46 and 47%, respectively). In sample G5, taken from the surface at the foot of the escarpment, the Cu share in fractions E2, E3 and E4 was similar (36, 33 and 29%, respectively), and in sample G6, the E3 fraction was dominated (42%), although the fractions of E2 and E4 were also significant (23 and 30%, respectively). Nickel was evenly distributed between fractions E1, E2, E3 and E4 in samples G4 and G6, but in sample G5, >70% Ni was present

Table 3
Leaching of potentially toxic elements from waste samples collected in Orle glade. Test performed in two ratios of liquid phase to solid phase: S/L 1:2 and 1:10. Standard deviation in brackets.

| Sample | pH | conductivity $\mu\text{S}/\text{cm}$ | Co $\mu\text{g}/\text{L}$ | Cr | Cu | Fe | Mn | Ni | Pb | Zn | |
|--------|------|---|------------------------------|-------------------|------|--------------------|------------------|------------------|--------------------|-------------------|-----------------|
| G1 | 1:2 | 7.74 | 429 (± 12) | 4.3 (± 0.6) | <1.0 | 7.3 (± 0.6) | 50 (± 4) | 362 (± 16) | 7.3 (± 0.6) | <1.0 | 56 (± 4) |
| | 1:10 | 7.73 | 183 (± 5) | 1.7 (± 0.6) | <1.0 | 5.3 (± 0.6) | 98 (± 6) | 69 (± 8) | 5.3 (± 0.6) | 3.3 (± 0.6) | 31 (± 3) |
| G2 | 1:2 | 7.85 | 409 (± 11) | 1.3 (± 0.6) | <1.0 | 7.3 (± 0.6) | 68 (± 5) | 41 (± 5) | 6.0 (± 0.6) | <1.0 | 23 (± 2) |
| | 1:10 | 7.80 | 184 (± 6) | <1.0 | <1.0 | 5.3 (± 0.6) | 53 (± 4) | 13 (± 1) | 2.3 (± 0.6) | 3.3 (± 0.6) | 20 (± 2) |
| G3 | 1:2 | 7.93 | 38 (± 3) | 2.3 (± 0.6) | <1.0 | 10.2 (± 1.1) | 38 (± 3) | 22 (± 2) | 4.3 (± 0.6) | <1.0 | 21 (± 2) |
| | 1:10 | 7.71 | 140 (± 8) | 1.7 (± 0.6) | <1.0 | 6.3 (± 0.7) | 112 (± 9) | 14 (± 1) | 2.3 (± 0.6) | 2.3 (± 0.6) | 23 (± 2) |
| G4 | 1:2 | 6.78 | 103 (± 5) | 1.7 (± 0.6) | <1.0 | 25.0 (± 1.4) | 304 (± 13) | 50 (± 5) | 2.3 (± 0.6) | <1.0 | 20 (± 2) |
| | 1:10 | 6.34 | 32 (± 3) | 1.7 (± 0.6) | <1.0 | 11.5 (± 1.2) | 337 (± 15) | 35 (± 2) | 4.3 (± 0.6) | 4.3 (± 0.6) | 23 (± 2) |
| G5 | 1:2 | 7.35 | 156 (± 5) | 2.3 (± 0.6) | <1.0 | 18.5 (± 1.5) | 718 (± 21) | 52 (± 5) | 6.3 (± 0.6) | 4.7 (± 0.6) | 47 (± 4) |
| | 1:10 | 6.65 | 42 (± 4) | 1.7 (± 0.6) | <1.0 | 10.2 (± 0.8) | 473 (± 16) | 75 (± 6) | 7.6 (± 0.6) | 2.3 (± 0.6) | 42 (± 3) |
| G6 | 1:2 | 6.85 | 125 (± 6) | 1.7 (± 0.6) | <1.0 | 11.8 (± 0.9) | 745 (± 25) | 72 (± 6) | 7.3 (± 0.6) | 1.7 (± 0.6) | 65 (± 5) |
| | 1:10 | 6.85 | 54 (± 4) | 1.7 (± 0.6) | <1.0 | 6.2 (± 0.7) | 475 (± 18) | 13 (± 1) | 5.3 (± 0.6) | <1.0 | 39 (± 4) |
| G7 | 1:2 | 7.45 | 375 (± 9) | 1.7 (± 0.6) | <1.0 | 24.0 (± 2.5) | 418 (± 13) | 128 (± 11) | 12.3 (± 0.6) | 6.3 (± 0.6) | 117 (± 7) |
| | 1:10 | 7.12 | 119 (± 5) | 1.7 (± 0.6) | <1.0 | 21.0 (± 1.5) | 421 (± 14) | 35 (± 2) | 14.7 (± 0.6) | 2.3 (± 0.6) | 82 (± 5) |
| G8 | 1:2 | 6.12 | 65 (± 4) | 2.3 (± 0.6) | <1.0 | 2.7 (± 0.6) | 51 (± 4) | 223 (± 11) | 3.3 (± 0.6) | 1.3 (± 0.6) | 33 (± 3) |
| | 1:10 | 6.31 | 24 (± 3) | 1.7 (± 0.6) | <1.0 | 1.7 (± 0.6) | 21 (± 2) | 52 (± 4) | 4.3 (± 0.6) | <1.0 | 19 (± 2) |
| G9 | 1:2 | 7.69 | 196 (± 7) | 1.7 (± 0.6) | <1.0 | 6.3 (± 0.6) | 98 (± 5) | 25 (± 1) | 5.3 (± 0.6) | 2.3 (± 0.6) | 20 (± 2) |
| | 1:10 | 7.53 | 74 (± 5) | 1.7 (± 0.6) | <1.0 | 3.3 (± 0.6) | 82 (± 4) | 11 (± 1) | 2.3 (± 0.6) | <1.0 | 11 (± 1) |

Table 4

Content of potentially toxic elements in the water of Kamionek creek: W1 - above the Orle glade, W2 and W3 - near the escarpment, where the creek cuts through waste layer, W4 - in the forest below the Orle glade. Standard deviation in brackets.

| Sampling point | Co µg/L | Cr | Cu | Ni | Pb | Zn |
|----------------|----------------|--------------|--------------|--------------|--------------|-------|
| W1 | 0.021 (±0.002) | 0.11 (±0.03) | 0.40 (±0.04) | 0.25 (±0.05) | 0.27 (±0.03) | <0.25 |
| W2 | 0.025 (±0.002) | 0.15 (±0.03) | 0.72 (±0.08) | 0.37 (±0.08) | 0.25 (±0.03) | <0.25 |
| W3 | 0.036 (±0.004) | 0.16 (±0.04) | 0.53 (±0.06) | 0.30 (±0.06) | 0.28 (±0.03) | <0.25 |
| W4 | 0.032 (±0.003) | 0.15 (±0.03) | 0.82 (±0.09) | 0.30 (±0.06) | 0.26 (±0.03) | <0.25 |

in fraction E4. In case of Pb, the E2 fraction was definitely dominant (52 to 77%) in all three samples, with the remainder being associated with the E3 fraction. Pb's share in the remaining fractions was marginal. The remaining three metals (Zn, Mn and Fe) in sample G4 (sediment) were mostly associated with the residual fraction (62, 82 and 96%, respectively). In surface samples from the escarpment, Zn was more evenly distributed between fractions E1, E3 and E4. In the case of Mn,

the E5 fraction dominated in the G5 sample (38%), and the E3 dominated in the G6 sample (38%) (Fig. 4).

In samples G7, G8 and G9, collected from the central part of the A-B transect, most of Fe and Co was associated with the residual fraction (E4) (Fig. 5). The majority of Cr in samples G8 and G9 was also associated with the E4 fraction, but in sample G7, the E3 fraction predominated (54%) and the residual fraction was only 36%. In the case of Cu,

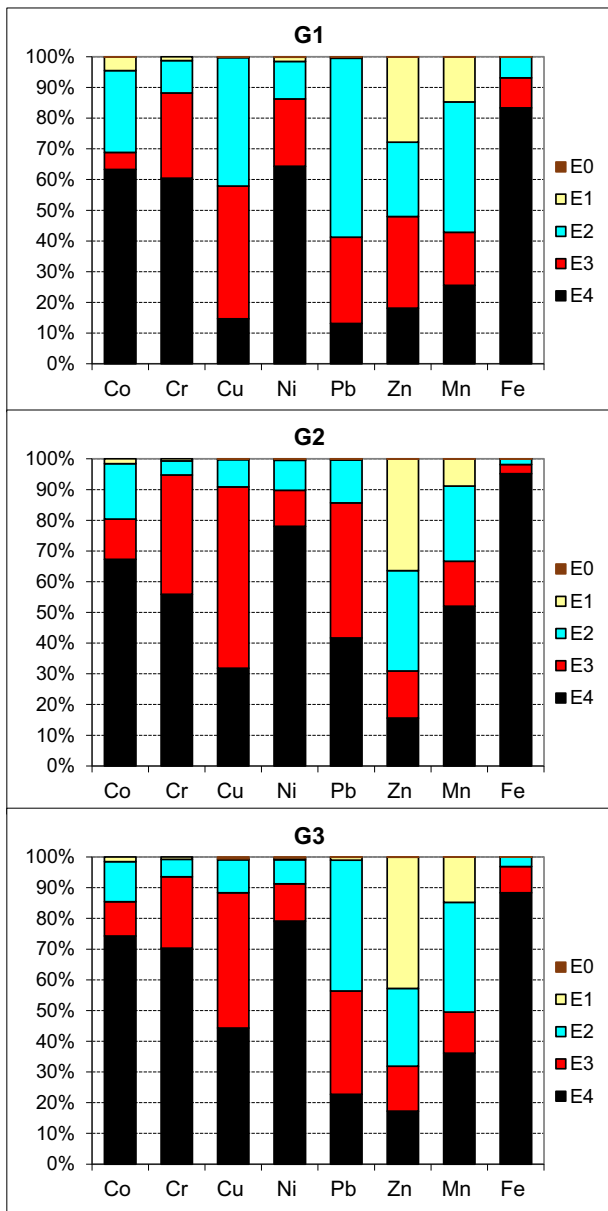


Fig. 3. Distribution of potentially toxic elements among the fractions E0–E4 in samples G1, G2 and G3 of anthropogenic waste materials collected in Orle glade from the depth of 0.5 m. between 10th and 30th m of A-B transect.

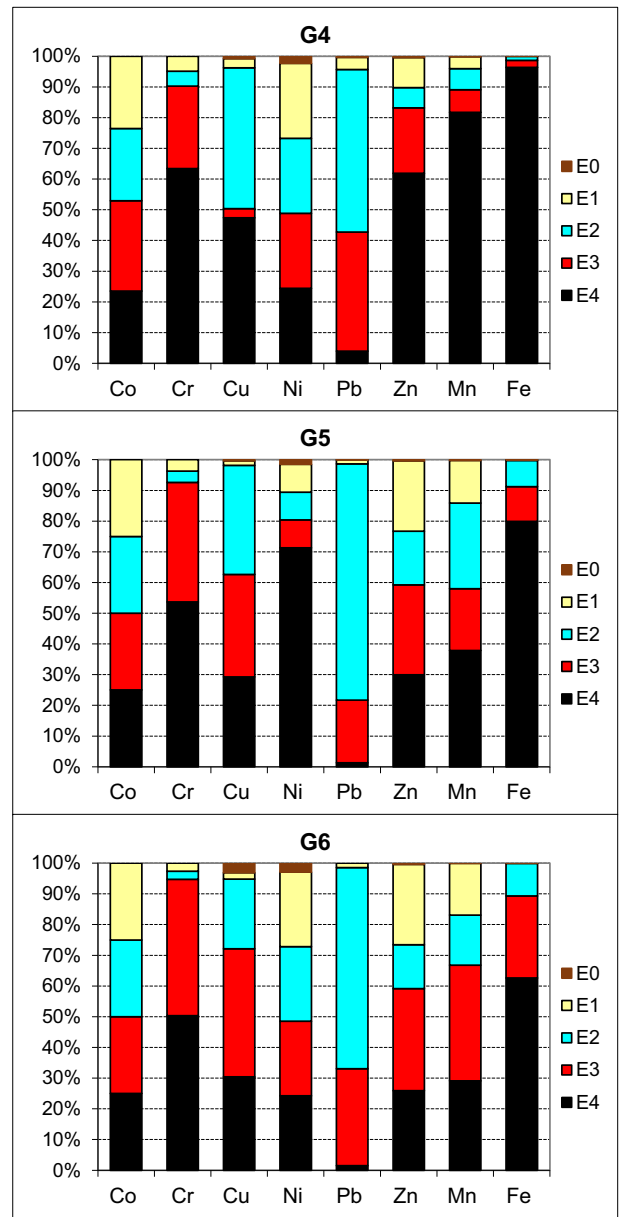


Fig. 4. Distribution of potentially toxic elements among the fractions E0–E4 in samples of anthropogenic waste materials collected in the Orle glade: G6 - sediment from the creek, G5- on the foot of escarpment, G6 from the surface of the escarpment.

in sample G7, the E3 fraction constituted as much as 63% and E4 only 26%. In samples G8 and G9, Cu (like Cr, Co and Fe) was mainly associated with the residual fraction (approx. 50%), however also fraction E3 constituted 25–30%. In samples G8 and G9, Ni was mainly found in the residual fraction, while in sample G7, it was evenly distributed in fractions E2, E3 and E4 (29, 29 and 40%, respectively). Lead behaved quite differently. In sample G7, 65% Pb was in the E2 fraction, and in samples G8 and G9, it was evenly distributed among the G2 and G3 fractions. About 90% of Pb was present in both of these fractions. Most of the Zn in sample G7 was associated with fractions E1 and E2 (38 and 35%, respectively), while in sample G8, taken from a depth of 1 m, >90% of Zn was associated with fraction E4 and E3 (32 and 59%, respectively). In sample G9, fractions E3 and E4 together also accounted for >60%, but the proportion of the E1 fraction was also significant (26%). In sample G7, Mn was mainly associated with the E2 fraction (57%), but the proportion of the E1 fraction (18%) is also significant. In sample G8, Mn is found mainly in three fractions: E2, E3 and E4 (38, 25 and 35%

respectively), and in the G9 sample, over 60% Mn is associated with the residual fraction (Fig. 5).

4. Discussion

The content of investigated PTEs in soil cover and anthropogenic layer in Orle glade was much lower than found in soils and glass waste samples around the Swedish glassworks (Jani and Hogland, 2018; Mutafela et al., 2020). Analyzing the total content of PTEs in the anthropogenic layer from Orle, which is a mixture of historical waste (ashes, slags and cullet after glass production, bottom ash and domestic wastes), shows that the potential threat to the soil and water environment can only be associated with lead and zinc (Table 2), the contents of which, in some samples, exceeded or were close to the threshold values set for forest, shrubland and wasteland soils at the level of 500 mg/kg for Pb and 1000 mg/kg for Zn (Regulations of the Minister of the Environment..., 2016). In samples G3 and G7 the concentrations of Zn were higher than the thresholds and in sample G1, the Zn content was close to this value. In sample G8 the Pb content (472 mg/kg) was also close to the threshold. The values of the geoaccumulation index calculated for Zn and Cu were similar (3.9 and 3.7, respectively) and are the highest among I_{geo} indexes calculated for the PTEs in the anthropogenic layer in relation to average values measured for the C horizon of the soil in Orle glade (excluding the area of waste location) (Table 5). Also, the pollution index values are the highest for these two metals (23.9 for Zn and 18.9 for Cu).

The maximal total concentration of Cu measured waste samples was detected in sample G7 (247 mg/kg), and it is only 72% of threshold value for soil (Table 2). The maximum content of Cu measured in soil in the Orle glade was <60 mg/kg, and it was detected for the organic horizon (Table 1). In the mineral horizons, the Cu content was lower (Table 1), and the same pattern was observed for the whole glade (Zawadzki et al., 2016). The content of Cu in topsoil is rather the result of airborne deposition from local sources (historical) and is a current effect of long range transport. In topsoil, Cu content is highly correlated with χ and contents of elements, such as As, Cd, Hg, Nb, Ni, Pb, Sb, Sn and Zn, usually considered as typical for airborne deposition (Strzyszczyk and Magiera, 1998; Magiera et al., 2006; Cao et al., 2015; Zawadzki et al., 2016). The same was found for the topsoil developed over the anthropogenic layer; Cu, Zn and Sn are highly correlated with χ values (Fig. 6) and are mostly connected with the same source.

In the case of copper, the anthropogenic layer seems to not be a real ecological threat. The Cu content in leachates was low, only in sample G7 at >20 $\mu\text{g/L}$ (Table 3). Also, in creek water, the content was low; however, a definite increase in Cu content can be seen near the waste escarpment and downstream. In most waste samples, Cu was associated with an easily reducible fraction, including potentially mobilisable ionic forms (E2) and oxidisable forms bounded with crystalline iron oxides (E3) (Figs. 3, 4 and 5). In all samples, except for stream sediment and the sample taken from depth 1.0 m, these fractions together account for 50 to 85%. Copper, similar to Ni, Co and Zn in waste samples was highly correlated with χ and χ/Fe (Table 6, Fig. 7) values; that means that a considerable part of these metals is associated with ferromagnetic iron oxides.

More problematic seems to be Zn, for which I_{geo} is equal to 3.9 and PI is 23.9 (Table 5) and its total content in waste samples is

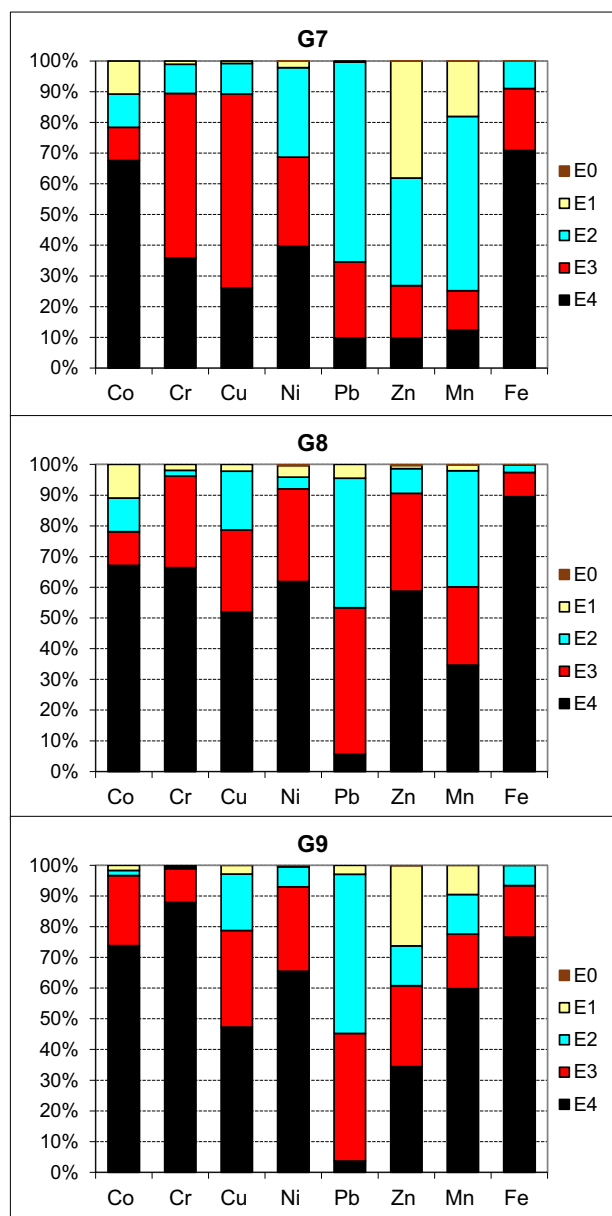


Fig. 5. Distribution of potentially toxic elements among the fractions E0–E4 in samples of anthropogenic waste materials collected in the Orle glade between 50th and 60th m of A-B transect: G7 - from the depth of 0.5 m; G8 - from the depth of 1.0 m; G9 - pieces of slags collected from layer of 0.5 m.

Table 5

Background values (Background) of elements (mg/kg) measured in C horizon of soils around Orle glade as well as geoaccumulation index (I_{geo}) and pollution index (PI) with values given as median of 9 waste samples.

| | Fe | Mn | Co | Cr | Cu | Ni | Pb | Zn | χ |
|------------|--------|-----|-----|------|------|-----|------|------|--------|
| Background | 14,700 | 188 | 2.2 | 22.7 | 6.1 | 5.3 | 28.3 | 25.5 | 12.6 |
| I_{geo} | 0.5 | 2.0 | 2.6 | 0.6 | 3.7 | 2.4 | 1.6 | 3.9 | 4.7 |
| PI | 2.1 | 6.2 | 9.2 | 2.3 | 18.9 | 7.9 | 4.7 | 23.9 | 39.7 |

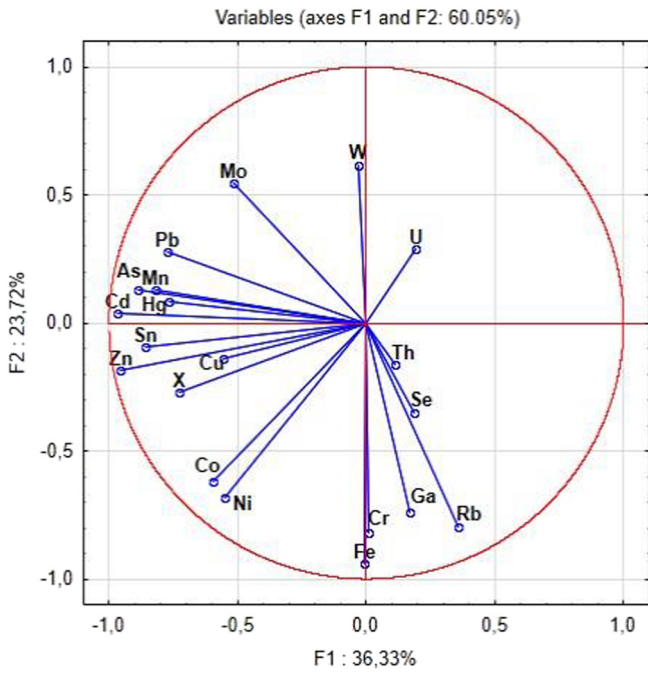


Fig. 6. Principal component analysis (PCA) of potentially toxic elements present in soils developed on anthropogenic layer of wastes in Orle glade.

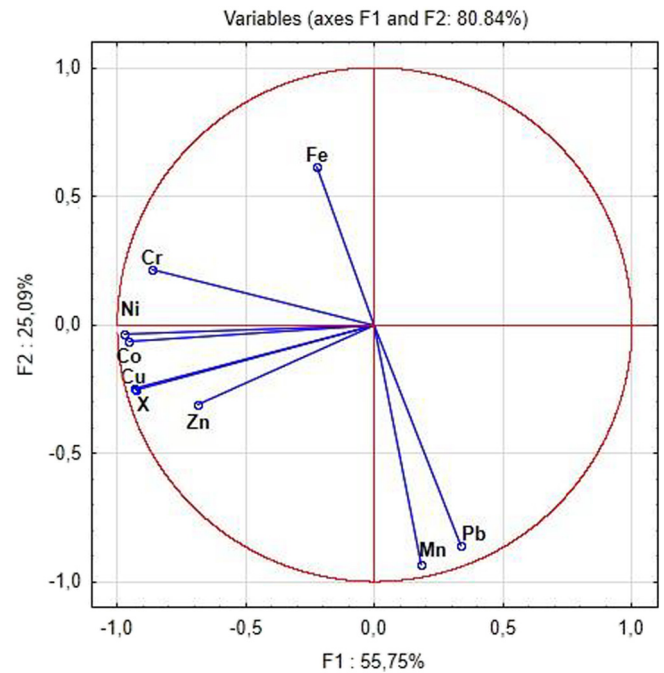


Fig. 7. Principal component analysis (PCA) of potentially toxic elements present in wastes forming the anthropogenic layer in Orle glade.

higher than other PTEs. In addition, Zn seems to be more mobile. Sequential analysis showed that although most of Zn in the examined waste, similar to Cu, is associated with the phases E2 and E3 (40–73%), the share of phase E1 is significant (18–43%) (Figs. 3, 4 and 5). This means that a considerable part of Zn is associated with the acid exchangeable fraction, which can be extracted even by weak organic acids. In practice, a decrease of soil pH can release larger amounts of Zn into environment. A leaching test in distilled water at pH 6.1–7.9 showed Zn content in leachate from 20 to 65 µg/L, and this metal was the third largest element after iron and manganese in the leachate (Table 3). Currently, the process is not active, as in Kamionek Creek water the Zn content was very low (Table 4), but the increased concentration of Zn in the place where the creek is passing through the waste escarpment was visible. Udatný et al. (2014) have found in soils around the glasswork in Ore Mountains (Czech Republic) that Zn represented a medium environmental risk in the upper horizons (litter and A) and a high risk in the B horizon under the beech forest stand.

Zinc shows lower coefficients of correlation with χ value in comparison to Cu (Table 6, Fig. 7), and probably a significant part of this element occurs in the ionic form, associated with iron oxides only by surface adsorption forces. In topsoil, the main source of Zn is surely airborne deposition (Fig. 6); however, the Zn content in soil cover over the

anthropogenic layer increases downward, and the waste material can also be the source of this metal in the mineral horizon.

The total content of Pb in only one waste sample (G8) was close to the threshold value, and other measured concentrations were much lower (73–227 mg/kg) (Table 2). Also, the I_{geo} and PI factors were relatively low (1.6 and 4.7, respectively), indicating that pollution by Pb in the anthropogenic layer was rather low. This is the opposite situation to what was found in the topsoil, where the Pb content was the highest of all investigated PTEs. The average Pb content within the investigated area exceeded 130 mg/kg, and the maximum values exceed 300 mg/kg (Table 1). However, within the entire Orle glade, the Pb content in individual samples even exceeded the threshold value reaching 600 mg/kg (Zawadzki et al., 2016). In the mineral horizon, the content was considerably lower. This means that the environmental threat related to the Pb is the effect of historical airborne deposition rather than historical waste storage. This high deposition may be related to the operation of the historical Karlsthal glassworks in Orle glade or the generally high deposition of heavy metals in the entire Izera Mts. as a result of long-range transport from the so-called “Black Triangle” area, which is the result of intense industrial activity within the last 100 years.

The surface of glass particles present in the anthropogenic layer may be subject to weathering due to permanent contact with moisture, CO₂, SO₂ and NO_x (Li et al., 2014). The weathering mechanism

Table 6
Correlation matrix of investigated waste samples (n = 9; correlation coefficients in bold are significant with p < 0.05).

| | Co | Cr | Cu | Fe | Mn | Ni | Pb | Zn | χ | %Fe in E2 + E3 | χ/Fe |
|----------------|-------|-------|-------|-------|-------|-------|-------|-------|--------|----------------|-----------|
| Co | | 0.63 | 0.90 | -0.34 | 0.67 | 0.99 | 0.38 | -0.12 | 0.84 | 0.93 | 0.68 |
| Cr | 0.63 | | 0.73 | 0.52 | -0.23 | 0.86 | -0.39 | 0.37 | 0.65 | 0.20 | 0.32 |
| Cu | 0.90 | 0.73 | | 0.17 | 0.07 | 0.89 | -0.18 | 0.80 | 0.91 | 0.61 | 0.72 |
| Fe | -0.34 | 0.52 | 0.17 | | -0.41 | 0.14 | -0.37 | -0.02 | -0.13 | 0.19 | -0.50 |
| Mn | 0.67 | -0.23 | 0.07 | -0.41 | | -0.13 | 0.98 | 0.08 | -0.01 | -0.18 | 0.08 |
| Ni | 0.99 | 0.86 | 0.89 | 0.14 | -0.13 | | -0.35 | 0.56 | 0.93 | 0.41 | 0.73 |
| Pb | 0.38 | -0.39 | -0.18 | -0.37 | 0.98 | -0.35 | | -0.15 | -0.25 | -0.31 | -0.13 |
| Zn | -0.12 | 0.37 | 0.80 | -0.02 | 0.08 | 0.56 | -0.15 | | 0.73 | 0.40 | 0.64 |
| χ | 0.84 | 0.65 | 0.91 | -0.13 | -0.01 | 0.93 | -0.25 | 0.73 | | 0.48 | 0.92 |
| %Fe in E2 + E3 | 0.93 | 0.20 | 0.61 | 0.19 | -0.18 | 0.41 | -0.31 | 0.40 | 0.48 | | 0.40 |
| χ/Fe | 0.68 | 0.32 | 0.72 | -0.50 | 0.08 | 0.73 | -0.13 | 0.64 | 0.92 | 0.40 | |

covers water adsorption by the glass surface, ion exchange of hydrogen ions mainly for alkali ions in the glass, followed by formation of particular hydroxides and, in the end, the production of a salt solution. The considerably increased concentration of these salts leads to extensive damage to the glass surface (Rebroš et al., 2006). The Pb and other metal ions leached from crystal glass waste may be bound by components of other wastes and/or Pb may precipitate in the hydroxycarbonates. Pb in the studied waste samples was extracted in the “reducible” (E2) and “oxidizable” (E3) fractions (58–97%), using strongly acidic extractants (pH near 1.5) of the BCR method. In surface samples collected on the escarpment, almost whole Pb (97%) was associated with these fractions. These results do not provide much information of the likely forms of Pb in the wastes and in the soils. The results of Tai et al. (2013) indicated that forms of Pb uptake with surface adsorption centres of solid phases or precipitated in hydroxycarbonate or phosphate minerals are bounded in the “reducible” fraction, and hydroxylamine hydrochloride (NH₂OH·HCl) extractant at very low pH has poor selectivity for the Pb forms. Moreover, low pH of NH₂OH·HCl rather than its reduction potential causes the release of Pb (Mossop and Davidson, 2003). Under long-term aging, in the solid phase and in presence of phosphorus and chloride ions, Pb can form stable lead phosphate, pyromorphite (Pb₅(PO₄)₃Cl), which is weakly susceptible to release. The other interesting fact is the lack of correlation between Pb and Fe contents as well as between Pb and magnetic parameters. This suggests that lead is not only associated with iron oxides (Table 6, Fig. 6). Mobility of Pb is much lower than Zn and Cu. In leachates, its content is very low and, in some cases, even below the detection limit (<1 µg/L). The maximum concentration 6 µg/L was observed in sample G7 with the highest total Pb content (Table 3). Also, the content of Pb in the creek water is low and stable upstream and downstream from the waste escarpment (Table 4). This is in agreement with finding of Augustsson et al. (2016), who stated relatively low source zone leachability of Pb, in spite of fact that he has measured, in samples of well water from South-Eastern Sweden, the Pb mean concentration of one order of magnitude higher. For this same region Rai et al. (2019) have found that <10% of Pb in the soil was found in the water-soluble leachates.

In waste material, Pb was strongly correlated with Mn ($r = 0.98$), and also, a positive correlation between these two metals was observed in the topsoil (Table 6, Fig. 6). This is not often observed in environmental pollution studies (Wang and Qin, 2006; Kapička et al., 2008; Duan et al., 2010; Naimi and Ayoubi, 2013; Bourliva et al., 2017; Rachwał et al., 2017a, 2017b). Usually, Mn is associated with geogenic sources, whereas Pb is controlled by factors related to pollution sources (Wang et al., 2005). The maximum Mn contents were detected in the same samples (G7 and G8), where the high Pb content was observed (Table 2). The I_{geo} and PI indices (2.0 and 6.2, respectively), calculated for Mn were even higher than for Pb (Table 5). In waste, Mn is also associated mostly with the E2 and E3 fractions (30–73%); however, unlike Pb, 18% of Mn is also associated with the acid exchangeable fraction (E1). This means that some part of Mn can be relatively easy to release to the environment. The leaching test revealed a considerable amount of Mn in leachates. In samples G1, G7 and G8, it was over 100 µg/L, but toxicity of manganese is relatively low and Mn is usually not considered among the PTEs (Håkanson, 1980; Mazurek et al., 2019).

The phenomena of such high correlation between Pb and Mn can be explained by the fact that lead oxides were used (and they are still use) in the production of crystal glass to improve refractive indices (Hynes et al., 2004) and Mn is one of the colouring agent in glass production. Depending on oxidation state, Mn is used to produce violet (Mn III) or yellow-brown (Mn II) glass (Srinivasarao and Veeraiah, 2001; Pant and Singh, 2014). There is no information on the technology used to manufacture glass at the Karlsthal glassworks in the 18th and 19th centuries, but both crystal glass and purple glass were among the basic products of the glassworks that can now be seen in local museums.

While the Pb and Mn compounds were used for glass production at the Karlsthal glassworks, the increased content of these elements also had to occur in both dust emissions and wastes from this source.

It is also necessary to mention the lack of correlation between Fe and the other parameters presented in Table 6, in particular, between Fe and magnetic parameters (χ and χ/Fe). According to the results of sequential analysis in waste samples, 62 to 95% of iron was associated with the residual fraction (F4) (Fig. 3.4 and 5) and, therefore, occurs mainly in aluminosilicates that have paramagnetic properties. Moreover, BCR extraction results indicated that that despite the use of NH₂OH·HCl with a higher concentration and a lower pH than in the original method, a high Fe content was found in E3. The results of the studies indicate that some Fe compounds are not extracted in E2.

The hydroxylamine hydrochloride reagent in nitric acid couldn't effectively dissolve the iron oxide phase, even after several consecutive extractions (Leermakers et al., 2019). Despite these limitations, the BCR procedure is a simple (3-step) method and allows for the determination of the mobility and bioavailability of the metals bound in soils. It should be remembered that the more degrees of extrusion, the greater the total error of the analysis because the concentration of metals in the leachate is calculated to the initial mass of the sample despite its change during the analysis due to dissolution of different fractions.

Ferromagnetic iron oxides, which are carriers of the magnetic signal, are mainly associated with the E2 and E3 fraction, although they can also occur in the form of inclusions in aluminosilicates and enclosed in glassy phases (this mainly applies to cullet, sinters and slags). In industrial dusts and fly ash, they are often found in silicate or aluminosilicate coatings (Magiera et al., 2011). As a result, magnetic particles can be scattered among different fractions of sequential analysis. The E2 and E3 fractions are mainly associated with amorphous and poorly crystalline forms of iron or in fine particles (maghemite, hydroxides), which usually have paramagnetic or antiferromagnetic properties. Hematite also exhibits antiferromagnetic properties. The metals associated with it, as well as with the fine-crystalline ferrimagnetic magnetite, should be released in the E3 fraction.

5. Conclusions

The investigated anthropogenic layer is currently not a considerable source of emission. Only Zn and Pb content in anthropogenic material was close to or slightly exceed the national threshold values for soil. Probably a significant part of Zn occurs in the ionic form, associated with iron oxides only by surface adsorption forces. However, Zn is not considered a very toxic element, and currently Zn leaching is not considered to be a real ecological threat. The increased Pb content do not pose an ecological risk as its mobility is much lower, and the BCR extraction revealed that most Pb is associated with fractions E2 and E3, which are rather stable in the soil environment. This shows that wastes from glass industry, including also production of lead glass can be relatively safely storage underground even if the total Pb content is close to or slightly exceed the threshold value for soil.

Zinc, similar to Ni, Co and Cu in waste samples, was highly correlated with magnetic parameters (χ and χ/Fe). This means that a considerable part of these metals is associated with ferrimagnetic iron oxides. The same was found for the topsoil developed over the anthropogenic layer; Cu, Zn and Sn are highly correlated with χ and these simple to measure magnetic parameters can be used as a tracers of their occurrence in the topsoil.

The application of some simply magnetic parameters is useful and should be used more often for the better understanding of results of sequential analysis. It should also be widely used for all buried anthropogenic layers containing materials produced at high temperatures (e.g. processing wastes, ashes, slags etc.). If high portion of the total iron is associated with the residual fraction, a correlation between Fe content and magnetic parameters is not observed, but high positive correlation coefficients can be observed between χ and some other elements (e.g. Cu,

Ni, Zn), as these elements are associated with ferromagnetic iron oxides produced during many high temperature technological processes. If the correlation between PTEs and Fe percentage associated with the sum of fractions E2 and E3 is slightly lower than for χ /Fe it suggests that ferromagnetic iron can also occur in the form of inclusions in aluminosilicates and/or enclosed in glassy phases. In this case, they will be associated with the residual fraction (usually paramagnetic) increasing their χ value. This is a specific situation that should be taken into account when analyzing glass waste and slags after glass production, as well as other anthropogenic materials containing a significant percentage of enamel. This is a specific situation that should be taken into account when analyzing glass waste and slags after glass production, as well as other anthropogenic materials containing a significant percentage of enamel.

CRedit authorship contribution statement

Tadeusz Magiera: Conceptualization, Project administration, Methodology, Writing – original draft. **Joanna Kyzioł-Komosińska**: Methodology, Validation. **Agnieszka Dzieniszewska**: Investigation, Formal analysis. **Małgorzata Wawer**: Formal analysis, Visualization. **Bogdan Żogała**: Investigation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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