Technology Critical Elements in industrial wastes as the source of soil contamination

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Abstract

The intensive development of industry, especially the mining and metallurgy, automotive and electrical industries, affects the increasing amount of Potentially Toxic Elements (PTE), including Technology Critical Elements (TCE) in the environment. This preliminary study focuses on the following TCE: Ga, Ge and Tl. The main thing they have in common is that they have not been much studied and the level of knowledge concerning the environmental impact of their use is quite slight. Additionally, content of more common PTE (As, Cd, Cu, Pb, Sb, Zn) was determined in order to discover some relationships between these both group.

Soil samples were collected from topsoil (0-5 cm) and subsoil (25-30 cm) in industrial area influenced by metallurgical slag dump and road traffic. Concentrations of elements were determined with High-Resolution Inductive Coupled Plasma-Mass Spectrometry (HR-ICP-MS) after HNO_3 microwave digestion. Results revealed that almost all studied elements were in higher amount in the topsoil suggesting the anthropogenic pollution as a source of their content in soil.

Keywords: potentially toxic elements, technology critical elements, magnetic susceptibility, topsoil, subsoil

1. Introduction

Since centuries, the growing population, urbanization, industrialization and traffic have influenced the natural cycles of PTE, which in the form of gaseous emission, aerosols, dusts and wastes contaminate the environment (Wong et al., 2006; Jabłońska-Czapla et al., 2014, 2015; Kulka and Gzyl, 2008; Magiera et al., 2011; Rachwał et al., 2017, 2018; Wawer et al., 2015). The method of soil magnetometry has been commonly used in soil contamination studies, due to the correlation found between magnetic susceptibility and the content (often excess) of metals/metalloids in soils (Zawadzki et al., 2015; Rachwał et al., 2017). As previous research has shown, it is a technique perfectly suitable for testing metals such as Cd, Cu, Pb and Zn in soil, and due to the correlation of these metals with TCE (Filella and Rodríguez-Murillo, 2017), this technique can be used as a new excellent tool for identifying TCE in soils.

2. Materials and Methods

Studies were carried out within a 1-km^2 area of arable land located near metallurgical dump in Silesia, the most industrialized and urbanized region of Poland. The objective of study was an assessment of the level of contamination by TCE and PTE as well as the relationships between TCE and PTE.

2.1. Magnetic susceptibility measurements

Magnetic susceptibility measurements of topsoil (κ) – a fast and easy proxy method – were carried out in order to preliminarily estimate soil condition. The MS2 Bartington meter equipped with MS2D loop sensor was used. Samples in the form of 30 cm length cores were collected from places with high magnetic susceptibility values, indicating high concentration of TCE and/or PTE. Soil cores were cut and samples from topsoil (0-5 cm) and subsoil (25-30 cm) were subjected for further analyses.

2.2. Geochemical analyses

Soil samples were treated with 50% v/v HNO_3, and after microwave digestion the contents of more common PTE (As, Cd, Cu, Pb, Sb, Zn) as well as chosen TCE: Ga, Ge and Tl were determined using High-Resolution Inductive Coupled Plasma-Mass Spectrometry (HR-ICP-MS). Quality Assurance and Quality Control (QA/QC) was verified against reagent blanks, repeating test, and certified reference material (Soil GBW-07408). Concentrations in the reagent blanks were below detection limits for all elements.

Afterwards, the basic statistical functions, Spearman correlation coefficients, and additionally factor analysis were applied (using Statistica 12 software; StatSoft) in order to analyze and interpret results and explain variations in the data.

3. Results

The preliminary field measurements show that above 80% of the studied area has κ values exceeding 100 ×

10^{-5} SI units. Higher values were observed for topsoil than for subsoil (mean: 173 and 120 × 10^{-8} m^3 kg^{-1}, respectively). In general, enhanced concentrations of most TCE and PTE are observed at 0–15 cm depth, decreasing toward the bottom end. This may suggest the influence of anthropogenic activity in this region and especially re-suspension from adjacent smelting slag dump.

Table 1. Mean values of TCE and PTE contents (in mg kg^{-1})

	Ga	Ge	Tl	As	Cd	Cu	Pb	Sb	Zn
Topsoil	5.6	1.0	1.0	18.2	12.9	22.0	454.2	0.2	1037.4
Subsoil	4.8	0.7	0.7	14.6	9.4	15.3	396.4	0.1	771.0

Correlation matrix of investigated elements indicates some relationships between them (Tab. 2, 3). Only Ga does not exhibit any significant correlation with another elements both in topsoil, and subsoil. In the topsoil, the highest significant correlation coefficients (0.88–0.95, Tab. 2) exhibits zinc with Ge, Tl, As, Cd and Cu. Germanium and Tl correlate well with all elements without Pb and Sb. Whereas in the subsoil, significant and relatively high correlation coefficients (0.77–0.99, Tab. 3) were observed in the case of all elements without Ga.

Table 2. Correlation matrix of investigated elements for topsoil (n = 11; correlation coefficients in bold are significant with $p < 0.05$)

	Ga	Ge	Tl	As	Cd	Cu	Pb	Sb	Zn
Ge	0.48								
Tl	0.42	**0.88**							
As	0.40	**0.80**	**0.93**						
Cd	0.09	**0.83**	**0.89**	**0.91**					
Cu	0.51	**0.96**	**0.91**	**0.88**	**0.84**				
Pb	-0.36	0.22	0.28	0.30	0.41	0.31			
Sb	-0.43	0.20	0.47	0.57	**0.64**	0.30	0.49		
Zn	0.32	**0.88**	**0.95**	**0.95**	**0.95**	**0.92**	0.35	0.52	
χ	0.33	**0.96**	**0.87**	**0.84**	**0.88**	**0.97**	0.39	0.39	**0.89**

Table 3. Correlation matrix of investigated elements for subsoil (n = 11; correlation coefficients in bold are significant with $p < 0.05$)

	Ga	Ge	Tl	As	Cd	Cu	Pb	Sb	Zn
Ge	0.69								
Tl	0.59	**0.91**							
As	0.59	**0.95**	**0.97**						
Cd	0.45	**0.86**	**0.97**	**0.97**					
Cu	0.61	**0.97**	**0.98**	**0.99**	**0.95**				
Pb	0.12	0.69	**0.80**	**0.77**	**0.81**	**0.80**			
Sb	0.29	**0.81**	**0.90**	**0.92**	**0.97**	**0.90**	**0.80**		
Zn	0.55	**0.91**	**0.99**	**0.99**	**0.99**	**0.97**	**0.79**	**0.92**	
χ	0.57	**0.98**	**0.94**	**0.97**	**0.92**	**0.99**	**0.79**	**0.90**	**0.93**

Results of factor analysis confirm two different sources of element load in the topsoil and subsoil as well. The first factor (explaining 69 and 86% of the variance for topsoil and subsoil, respectively) combines magnetic susceptibility and most individual elements (Ge, Tl, As, Cd, Cu, and Zn), i.e., variables mainly connected with the composition of the metallurgical dump. The second factor (19 and 10% of the variance for topsoil and subsoil, respectively) comprises Sb and Pb, which may be connected with traffic-related emissions.

4. Conclusions

The study revealed enhanced contents of PTE in the investigated area. The strong correlation stated between particular PTE (mainly As, Zn, Cu, Cd, Zn in topsoil and Tl, As, Cd, Cu, Pb, Sb, Zn in case of subsoil) and Ge and Tl indicates increasing concentration of TCE in areas polluted with heavy metals/metalloids. This preliminary study provides an introduction for further research on the occurrence and migration of selected TCE in soil in areas being under strong anthropogenic stress.

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