

# Identification by Geophysical/Geochemical Methods of the Areas Polluted by Anthropogenic Emission of Airborne Elements - a Case Study of City Park in the Vicinity of a Steel Plant, Southern Poland

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## Abstract

The recognition of a hazard to human health and the environment from the emissions of airborne pollutants resulted in the adoption of the Convention on Long-Range Transboundary Air Pollution (CLRTAP, 1979) and EMEP co-operative program. Extensive efforts have been undertaken to improve identification of soil contamination with airborne pollutants, in particular with potentially toxic elements (PTEs). An extremely useful, easy-to-use and reliable tool widely investigated for over two decades, is a geophysical method of screening soil pollution with PTEs by surface measurements of magnetic susceptibility  $\kappa$ . The extensive works on the method resulted in the development within the Polish-Norwegian IMPACT project (2014-2016) of an international standard ISO/CD 21226 (adoption procedure pending). Here, the use of this method is exemplified in a case study on assessment of soil pollution with PTEs in the city park area in the vicinity of a steel plant operating since 1976. The spatial distribution of magnetic susceptibility in the area indicated high pollution with PTEs in the whole area, with two centres of maximum  $\kappa$  values. These data were in conformity with concentrations of PTEs in soils in the area, in particular of Cd, Zn and Pb that occurred in concentrations posing threat to the environment.

**Keywords:** soil spatial pollution, airborne elements, magnetic susceptibility, steel plant emission, metal mobility

## 1. Introduction

Emissions of airborne potentially toxic elements (PTEs) from large industrial complexes contribute to the long-range airborne pollutant transport but also create environmental problems in the vicinity of an enterprise location. An extent of hazard to the environment is determined by the cumulative spatial dry and wet deposition during the entire history of enterprise operation, independently upon its current pollution control status. The adoption of the Convention on Long-Range Transboundary Air Pollution (CLRTAP, 1979) covered since 1981 by EMEP co-operative monitoring program, resulted in the intensification of efforts aimed at improving identification of soil contamination with airborne pollutants. Extensive

research conducted since 1990ties proved that some easily measurable geophysical parameters such as magnetic susceptibility (parameter directly related to concentration of magnetic particles in soil samples) can be used as environmental pollution indicators. Most of magnetic particles occurring in topsoil are of anthropogenic origin. Technogenic magnetic particles (TMPs) are generated in a wide variety of high temperature technological processes, where different iron minerals, present in raw materials, fuels and additives are transformed to highly magnetic iron oxides (Magiera et al. 2011). This feature makes possible using them as tracers of industrial pollution, as their presence, even in trace amounts, in soils can be easily detected by magnetic measurements. Magnetic susceptibility  $\kappa$  has been shown to be a reliable parameter for estimating dry and wet deposition of pollutants from industrial and urban sources (e.g. Magiera et al., 2007, 2011). Moreover, TMPs are known to serve as carriers of various pollutants such as trace metals and high correlation between Potentially Toxic Elements (PTEs) and magnetic parameters were observed (e.g. D'Emilio et al., 2007; Fürst et al., 2009; Zawadzki et al., 2009). It was found that TMPs and PTEs are enriched in uppermost 10 cm of forest soil (Of and Oh horizons), where the highest concentrations of trace metals are commonly observed (Zawadzki et al., 2007, 2009). Extensive works on the method resulted in the development within the Polish-Norwegian IMPACT project (2014-2016) of an international standard ISO/CD 21226 (adoption procedure pending). Here, the use of soil magnetometry for identification of anthropogenically polluted areas has been exemplified in the case study on the assessment of soil pollution with PTEs in the vicinity of the steel plant Arcelor Mittal Poland Complex operating since 1976 as Katowice Steel Plant.

## 2. Research object and methods

### 2.1 Studied area

The Steel Plant is the major source of pollutant emission in the ambient areas of Dąbrowa Górnicza City in Southern Poland for over three decades. For the study, an undisturbed area with a mixed stand located in the "Green" city park was selected.

## 2.2. Soil screening for PTEs

In the studied area, surface field measurements of volumetric magnetic susceptibility  $\kappa$  with the use of a portable MS2D Bartington loop sensor were performed in triplicate at the soil surface, after removal of organic sub-horizon O1. The spatial distribution of magnetic susceptibility has been presented as a 2D map prepared with the use of Surfer 8 program with kriging, based on mean  $\kappa$  values.

## 2.3. Soil sampling for geochemical analysis

From the map of magnetic susceptibility, points for soil sampling were selected, mostly in the range of  $\kappa$  values indicating high pollution with trace elements. From these points, soil for geochemical analysis was collected in triplicate.

## 2.4. Soil analysis

Soil samples were analyzed for basic parameters by standard methods used in soil analysis. Concentrations of trace elements in soil (dm) were determined with the use of microwave-assisted sample digestion in nitric acid according to EN 13656, and ICP-OES (Perkin-Elmer) analysis in accordance with EN ISO 11885:2009 for macrocomponents Ca, Mg, Na, K, Fe and trace elements Ba, Cd, Cr, Cu, Mn, Ni, Pb, Zn. Of these, Cd, Cr, Cu, Ni, Pb and Zn represent PTEs emitted along with ferrimagnetics from industrial emission sources and able to migrate with dust particles and aerosols for a long distances and fall at the earth surface as wet and dry deposition. The analyzed elements belong to the most common components of industrial emissions and are representative also for emitters occurring in the studied area. Element mobility and major chemical forms of binding in soil were assessed on the basis of 3-step BCR sequential extraction, that determine mobile and mobilizable forms of elements (Davidson et al., 1998; Sutherland and Tack, 2003).

## 3. Results and discussion

### 3.1. Spatial distribution of magnetic susceptibility in the studied area

Spatial distribution of magnetic susceptibility presented as 2D map developed on the basis of mean values of volumetric magnetic susceptibility (Fig. 1) showed occurrence in the predominant part of the studied area of magnetic anomaly in the  $\kappa$  range from  $100 \times 10^{-5}$ SI to  $190 \times 10^{-5}$ SI with two centers of maximum  $\kappa$  values ranging from  $170 \times 10^{-5}$ SI to  $190 \times 10^{-5}$ SI, which indicate high pollution with trace elements. In the whole area, no  $\kappa$  values  $<30 \times 10^{-5}$  indicating low pollution of soil with trace elements was detected. The southern part of the area showed  $\kappa$  values in the range from  $70 \times 10^{-5}$ SI to  $100 \times 10^{-5}$ SI that suggested elevated pollution level. Magnetic susceptibility in the central and northern part of the area, except aforementioned centers of magnetic anomalies, was at the level from  $100 \times 10^{-5}$ SI to  $150 \times 10^{-5}$ SI, also indicating high level of soil pollution with trace elements (Fig. 1).

### 3.2 Evaluation of the level and character of soil pollution with metals

On the basis of the magnetic susceptibility map, 10 points for soil sampling were selected, mostly indicating high pollution with trace metals (in the  $\kappa$  range from  $113 \times 10^{-5}$ SI to  $193 \times 10^{-5}$ SI). Only in one point (Tw 2)  $\kappa$  value could be placed within an elevated (moderate) pollution range. It was found that the analyzed soils represent acidic material (pH 5.27-6.07), oxidizing conditions (Eh 117-357 mV), el. conductivity in the range from 37.4 to 70.7  $\mu$ S/cm, organic matter in the range from 27.4 to 37.6 % wt, at relatively narrow range of soil quality parameters (Tab.1)

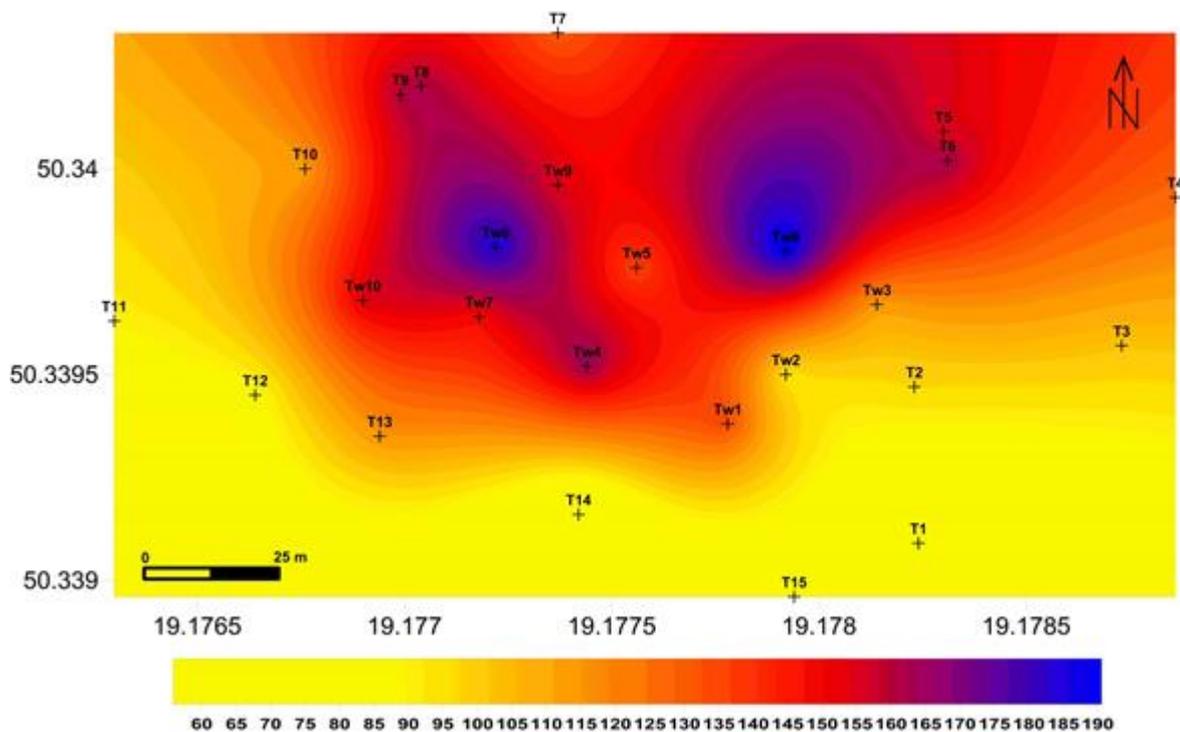
**Table 1:** Basic soil quality parameters

Material Parameters Samples	Soils <sup>*)</sup>			
	pH	Conductivity $\mu$ S/cm	Moisture % wt.	OM % wt.
<b>Tw1</b>	5.65	63.1	27.68	<b>27.43</b>
<b>Tw2</b>	<b>5.27</b>	47.7	33.96	36.23
<b>Tw3</b>	5.62	56.4	<b>35.48</b>	<b>37.58</b>
<b>Tw4</b>	5.63	<b>37.4</b>	30.61	35.56
<b>Tw5</b>	5.66	52.4	31.08	33.79
<b>Tw6</b>	5.50	67.4	35.77	32.50
<b>Tw7</b>	5.75	48.5	<b>27.01</b>	31.53
<b>Tw8</b>	5.54	40.8	32.36	31.30
<b>Tw9</b>	5.70	69.3	31.35	32.20
<b>Tw10</b>	<b>6.07</b>	<b>70.7</b>	34.06	27.59
<b>Mean</b>	5.64	55.4	31.94	32.58

<sup>\*)</sup> Minimum values are *italic*, Maximum values are **bold**

Contents of analyzed elements in soil showed good correlation with the magnetic susceptibility values. The lowest concentrations of the majority of trace elements, including typical components of industrial emissions and Fe, was found in the soil sample Tw2 – the only point with moderate  $\kappa$  value  $<100 \times 10^{-5}$ SI, while  $\kappa$  values in other points indicated high pollution with trace elements (Fig. 1, Tab. 2). The highest trace element concentrations (Ba, Co, Cr, Mg, Mn, Ni and Zn) were detected in the soil sample Tw 10, in the area of the highest magnetic susceptibility. Besides airborne elements able to long-range transport (Cr, Ni, Zn), emission comprise also elements that do not exhibit such properties (Ba, Co, Mn) and macrocomponents (K, Mg), due to the close proximity of the emission sources that are steel plant and its power plant fired by coal. The highest soil pollution level occurred with respect to Cd, Zn and Pb, while other elements, despite elevated contents compared to natural background concentrations, were close to the natural level and did not pose a risk to the environment. Observed high correlation of magnetic susceptibility and element concentrations in soil originated from, emissions and extensive works on the screening method resulted in the development within the Polish-Norwegian IMPACT project (2014-2016) of an international standard ISO/CD 21226 (adoption procedure pending). 3.3. Chemical forms and strength of metal binding in soil

Chemical forms and binding strength of elements in soil in the studied area showed high stability in the area, independent on the element concentrations (Fig. 2).



**Figure1.** Spatial distribution of volumetric magnetic susceptibility  $\kappa \times 10^{-5}$ [SI] in the studied area of a city park

**Table 2.** Concentrations of elements in the soils of the studied area in a city park affected with steel plant emission <sup>\*)</sup>

Elements	Tw 1	Tw 2	Tw 3	Tw 4	Tw 5	Tw 6	Tw 7	Tw 8	Tw 9	Tw 10
Ag	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25
Ba	380.6	310.6	315.6	430.6	430.6	295.6	425.6	370.6	408.1	<b>440.6</b>
Ca	5968	<i>3243</i>	<b>7918</b>	7418,1	7518	5693	6618	5368	7893	6618
<b>Cd</b>	22.56	<i>10.06</i>	15.56	24.81	25.31	16.31	<b>29.56</b>	18.56	24.81	24.56
Co	6.000	<i>1.500</i>	4.250	7.250	7.000	5.250	7.000	4.750	6.000	<b>8.750</b>
<b>Cr</b>	52.50	<i>47.25</i>	53.50	67.00	65.25	47.50	63.50	62.75	60.00	<b>87.00</b>
<b>Cu</b>	67.31	<i>55.06</i>	57.06	<b>100.6</b>	84.06	56.56	81.31	67.56	74.06	8756
Fe	33740	<i>22890</i>	23640	28240	24915	23065	29990	24915	25490	<b>34990</b>
K	2217	3240	2487	2042,3	2487	<i>1820</i>	2990	2865	2790	<b>4115</b>
Mg	1917	1590	1597	1702	1605	<i>1227</i>	1877	1937	1745	<b>2772</b>
Mn	451.8	<i>326.8</i>	406.8	586.8	556.8	479.3	571.8	394.3	474.3	<b>596.8</b>
Na	322.8	322.8	322.8	<b>452.8</b>	410.3	272.8	415.3	380.3	375.3	437.8
<b>Ni</b>	25.31	<i>18.31</i>	19.31	29.56	27.06	20.56	26.06	23.06	25.56	<b>32.06</b>
<b>Pb</b>	982,5	<i>737.5</i>	692.5	<b>1178</b>	1063	795.0	1093	812.5	967.5	1085
<b>Zn</b>	1753	<i>960.1</i>	1213	1805	1863	1275	1923	1228	1803	<b>2225</b>

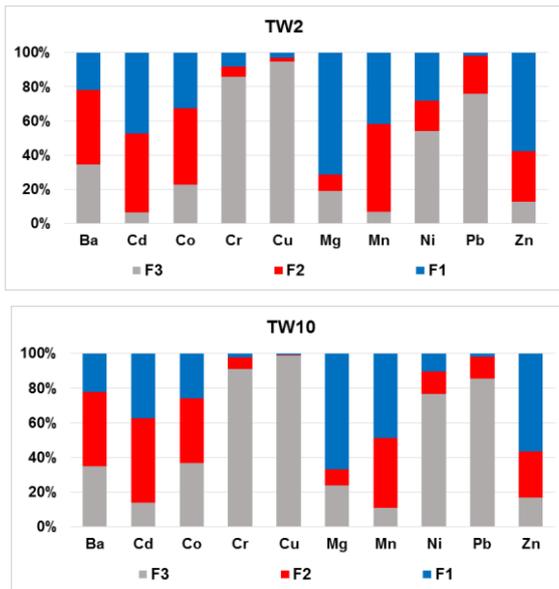
<sup>\*)</sup>Minimim values are *italic*; maximum values are **bold**

F1 – the most labile exchangeable and carbonate fraction; F2 – reducible fraction, bound onto amorphous Fe- and Mn-oxides; F3 – the most stable oxidizable fraction, bound onto organic matter and sulfides

Zn showed the highest enrichment in the studied area and the highest mobility. In the most mobile F1 fraction (ion exchangeable and carbonate forms, water and acid-extractable) was bound from 49 to 59% of the mobilizable Zn load. Share of F2 reducible fraction bound onto amorphous Fe- and Mn-oxides comprised from 27 to 37 % of Zn load, while the most stable F3 fraction was enriched with Zn by 13-17% wt. Cd belongs to the most toxic trace elements in the environment, and similarly to Zn, showed the highest enrichment in soils of the studied area. It also

displayed high mobility, however, a lesser amounts of Cd were bound in the most mobile F1 fraction (from 37 to 47%). The share of F2 fraction in Cd binding appeared to be predominant (42-54% wt.), while enrichment in the fraction of the highest binding strength was the lowest, generally <10% wt. (7-14%). Pb showed the highest enrichment in soils of the studied area, caused by the industrial emissions. However, its environmental behavior significantly differed from the mobile elements such as Zn and Cd. It showed high stability. The dominating Pb binding fraction was F3 that comprised from 76 to 86% wt. of Pb load. The share of Pb in the most labile F1 fraction was negligible (1.1-2.4% wt.), while enrichment in F2 fraction was also low (12-22% wt.). Despite low share of

the most labile F1 and reducible F2 fractions in Pb binding, due to high emission of Pb, the actual Pb load of high mobility in soil was as high as 7.6-19.4 mg Pb/kg, while 107-135 mg Pb/kg represented moderate mobility. Due to high toxicity and accumulation in living organisms, these loads should be considered as posing a high risk to the environment and human health. Other analyzed airborne elements (Cu, Ni and Cr) occurred in soils of the studied area in concentrations showing weak enrichment and domination of the strongly bound F3 fraction. Non-airborne elements (Co, Ba and Mn) also were not environmentally problematic, although were bound mostly in more labile fractions F2 and F1.



**Figure 2.** Binding strength and chemical fractionation of elements in the least (Tw2) and the highest polluted soils (Tw10)

#### 4. Conclusions

The study showed good conformity of magnetic susceptibility data with anomalies in trace element concentrations in soils of the area affected with the emission from iron metallurgical processes and coal-fired power generation. The highest accumulation in soils showed Cd, Zn and Pb, while other elements did not pose risk to the environment. Zn and Cd were bound predominantly in labile fractions F1>F2, whereas Pb was enriched in the stable F3 fraction. The chemical fractionation of metal binding showed high stability independently on the element concentrations in soils.

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