

ASSESSMENT OF HEAVY METAL CONTAMINATION OF SOILS IMPACTED BY A ZINC SMELTER ACTIVITY

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Abstract

Four metals (Cu, Zn, Pb and Cd) were assayed in soils within the impact zone of the Miasteczko Slaskie Zinc Smelter (southern Poland). The investigated area is afforested and has been subjected for a long time to intensive deposition of metal-bearing dusts. Soil pH_{KCl} varied broadly from very acidic ($\text{pH}_{\text{KCl}} = 3.4$) to slightly alkaline ($\text{pH}_{\text{KCl}} = 7.2$). Organic carbon (C_{org}) content fluctuated within a large range, i.e., 5.5 – 66.4 g kg^{-1} , whereas the cation exchange capacity (CEC) was in most cases markedly low (from 1.4 to 5.9 $\text{cmol}_{(+)}\text{kg}^{-1}$), with exception for two sites (C and D) exhibiting values of 26.8 and 15.1 $\text{cmol}_{(+)}\text{kg}^{-1}$, respectively. Total Zn, Pb and Cd contents exceeded manifold their respective levels in the Earth crust (reference value – RV) as well as those suggested as background levels for Poland (BLP). The assessment of the contamination of soils by these metals was undertaken on the basis of geoaccumulation indices (I_{geo}), contamination factors C_f^i and degrees of contamination (C_{deg}). The overall metal contamination represented practically two classes: low contamination for Cu; considerable to extreme contamination (in ascending order) for Zn, Cd, and Pb. The contribution (BLP-based assessment) of each metal to the degree of contamination index varied from 2.14 % (for Cu), via 26.33% (for Zn) to quite equally for Cd and Pb, both representing 35.22% and 36.32, respectively. It is worth pointing out that copper was the sole metal to threaten the least (Figure 1) the soils of the investigated ecosystem.

Key words: metallurgy, heavy metal contamination, index of geoaccumulation, contamination factor, degree of contamination.

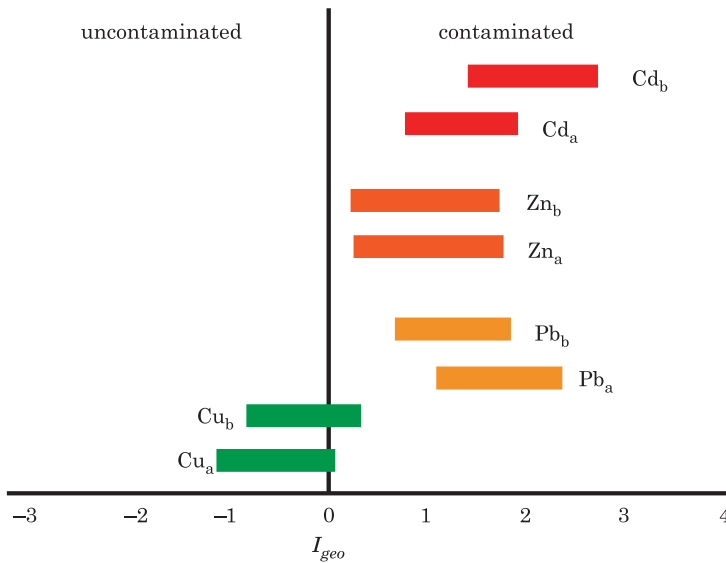


Fig. 1. Indices of geoaccumulation (I_{geo}) for metals within the impact zone of the Miasteczko Slaskie Zinc Smelter (footnotes a and b, see Table 2 and Table 3)

INTRODUCTION

The content of heavy metals in soils is a joint action of both natural processes and human activity, with a prevalence of anthropogenic sources (NRIAGU, PACYNA 1988, BAIZE, STERCKEMAN 2001). In many areas of Europe, soil is being irreversibly lost and degraded as a result of increasing and often conflicting demands from nearly all economic sectors. The combined action of these activities affects quality and limits many soil functions including the capacity to remove contaminant from the environment by filtration and adsorption. This capacity and the resilience of soil mean that damage is not perceived until it is far advanced. Significant increases in soil heavy metal content are generally found in lands under high industrial activity, where accumulation may be several times higher as compared to average content of uncontaminated lands (VAN LYNDEN 2000). Among the many heavy metals released from various products and processes, cadmium, lead and mercury are of great concern to human health because of their toxicity and potential to induce harmful effects at low concentrations and to bio(geo)accumulate. When assessing the persistence of soil contamination with heavy metals one should take into consideration that the half-life of cadmium ranges from 15 to 1,100 years as compared to lead, whose half-life may vary from 740 to 5,900 years depending on several biogeochemical factors. Therefore, due to such

a slow process of soil self-purification and the tendency of heavy metals to accumulate any assessment dealing with threats to the soil environment should consider the whole duration of their detrimental impact (FAGIEWICZ et al. 2006).

Several approaches have been used for evaluating the degree of heavy metals contamination in different ecosystems. They are commonly based on the amounts of metals extracted by applying specified soil tests or on the elaboration of phytotests, which are expected to confirm or not metal concentrations extracted by soil tests (KABATA-PENDIAS et al. 1993, GRZEBISZ et al. 1997, REIMANN et al. 2000).

Indices-based assessment of soils contamination by heavy metals seem to be a useful geochemical method, since it “shifts” from commonly reported concentrations of particular heavy metals into unitless parameters (DIATTA et al. 2003). Therefore the current work is intended to focus on indices, such as the index of geoaccumulation (I_{geo}), contamination factor (Cf) and degree of contamination (Cdeg.) for evaluating the potential contamination of soils impacted by the Miasteczko Slaskie Zinc Smelter activity.

Index of geoaccumulation (I_{geo})

This index enables the assessment of heavy metal contamination by comparing current and preindustrial metal contents. It was originally used for bottom sediments (MÜLLER 1969), but may be applied for assessing soil contamination on the basis of the following equation:

$$I_{geo} = \log_{10} \frac{C_n}{1.5 B_n} \quad (1)$$

where C_n is the measure concentration of the element n in the pelitic sediment fraction ($< 2 \mu\text{m}$) and B_n is the geochemical background value in the fossil argillaceous sediment (i.e., average shale). The constant 1.5 allows for involving natural fluctuations in the concentration of a given substance in the environment and very small anthropogenic influences. Six classes were suggested by MÜLLER (1981) as reported below:

Class	Value	Soil quality
0	$I_{geo} \leq 0$	practically uncontaminated
1	$0 < I_{geo} < 1$	uncontaminated to moderately contaminated
2	$1 < I_{geo} < 2$	moderately contaminated
3	$2 < I_{geo} < 3$	moderately to heavily contaminated
4	$3 < I_{geo} < 4$	heavily contaminated
5	$4 < I_{geo} < 5$	heavily to extremely contaminated

A modified method was applied in the current paper for the computations of the I_{geo} values and deals with the following details: C_n expresses the total concentration of a given metal in the surface layer of the tested soils, while B_n , the concentration of the same metal in the Earth's crust (i.e., Cu – 39; Zn – 67; Pb – 17 and Cd – 0.10 mg kg⁻¹) as reported by TAYLOR and McLENNAN (1995).

Contamination factor (C_f^i) and degree of contamination (C_{deg})

Soil contamination was also evaluated by using indices such as the contamination factor (C_f^i) and the degree of contamination (C_{deg}), (HAKANSON 1980), which were computed on the basis of the equation reported below:

$$C_f^i = \frac{C_{0-1}^i}{C_n^i} \quad (2)$$

where, C_{0-1}^i is the mean concentration of metals from at least five sampling sites and C_n^i is the preindustrial concentration of individual metals. A modification was done and consisted of using the concentration of metals in the Earth's crust as reference values (TAYLOR, McLENNAN 1995).

Four categories have been suggested by HAKANSON (1980) and represented the following ranges:

Contamination factor	Description
$C_f^i < 1$	low contamination factor
$1 \leq C_f^i < 3$	moderate contamination factor
$3 \leq C_f^i < 6$	considerable contamination factor
$6 \leq C_f^i$	very high contamination factor

Moreover it should be mentioned that C_f^i is a single-element index. The sum of C_f^i for all studied metals yields the so-called the contamination degree (C_{deg}) of the ecosystem and is represented by four classes as follows:

Contamination degree	Description
$C_{deg} < 8$	low degree of contamination
$8 \leq < C_{deg} 16$	moderate degree of contamination
$16 \leq < C_{deg} 32$	considerable degree of contamination
$32 \leq C_{deg}$	very high degree of contamination

MATERIALS AND METHODS

Location of the research area

The research area lays within the impact zone of the Miasteczko Slaskie Zinc Smelter, (N 51°41'03" and E 15°57'12", Poland) whose activity started since 1966. This zone is surrounded in the north, west and east by a large Lubliniec Forest complex, and in the south-east by the localities of Zyglin and Zygliniec, quarters of the Miasteczko Slaskie. A population of pine as part of artificial restoration, mainly of mixed forest, sporadically mixed wood grows in the impact zone. In the Miasteczko Slaskie region, the prevailing winds are from the south-westerly (21.4%) and westerly (18.7%) quarters, hence the pollution emitted by the Zinc Smelter creates the greatest threat to areas north-east and east of the Zinc Smelter.

Sample collection and analytical procedures

Five samples ordered like the five on a dice, with 15 m distance from the central point were collected (20 cm depth) at 8 selected sites (Table 1) on June 08, 2006. They were air-dried and sieved through a 1 mm polyethylene sieve before physical and chemical analysis. Prior to basic analyses soil samples were air-dried and crushed to pass through a 1 mm sieve. Granulometric composition was determined by the areometric method (GEE, BAUDER 1986) and organic carbon by the Walkly-Black method as reported by NELSON and SOMMERS (1996). Soil pH at soil/solution (water or 1 mol KCl dm⁻³) ratio of 1:2.5 was determined potentiometrically using a pH-meter. The cation exchange capacity (CEC) was obtained by summation of 1 mol KCl dm⁻³ extractable acidity and exchangeable alkaline cations (Ca²⁺, Mg²⁺, Na⁺ and K⁺) extracted by 1 mol CH₃COONH₄ dm⁻³ (pH 7.0) as described by THOMAS (1982). The total content of heavy metals was determined by using the *aqua regia* procedure (International Standard, 1995). All analyses were performed in duplication; computations and statistical evaluations were made by using the Excel[®] sheet.

Table 1

Selected physical and chemical properties of soils in the impact zone of the Miasteczko Slaskie Zinc Smelter (mean, $n = 5$)

Site*	Particles (g kg ⁻¹)		C _{org} (g kg ⁻¹)	EC** (μS cm ⁻¹)	pH		Ca cmol (+) kg ⁻¹	CEC***
	Silt	Clay			H ₂ O	1 mol KCl dm ⁻³		
A	90	90	5.5	34.7	6.7	5.7	1.0	1.4
B	150	90	9.1	41.6	6.2	4.9	1.4	1.8
C	490	260	15.5	189.0	7.6	7.2	24.1	26.8
D	240	260	20.0	128.5	7.5	7.0	13.3	15.1
E	270	130	11.2	68.3	6.3	5.6	4.3	5.4
F	290	80	7.5	72.3	6.8	6.0	4.9	5.9
G	410	90	31.1	65.7	6.0	4.6	2.2	2.9
H	180	60	66.4	134.6	4.7	3.4	1.8	2.5

* **A, B** – experimental area 500 and 1100 m ESE, respectively; **C** – Cynkowa Street, 100 m SE from the Zinc Smelter (Miasteczko Śląskie); **D** – Dworcowa Street, 500 m W from the Zinc Smelter (Miasteczko Śląskie); **E** – Brynicka Street, 500 m E from the Zinc Smelter (Zyglin); **F** – Sw. Marka Street, 1500 m SE from the Zinc Smelter (Zyglin); **G** – Zyglinska Street, 4500 m E from the Zinc Smelter (Brynica); **H** – Staromiejska Street, 6000 m E from the Zinc Smelter (Bibiela);

** Electrical Conductivity; *** Cation Exchange Capacity

RESULTS AND DISCUSSION

Soils within the impact zone of the Miasteczko Slaskie Zinc Smelter are characterized by significantly different physical and chemical properties summarized in Table 1. Soil reaction (pH) varied broadly from very acidic ($\text{pH}_{\text{KCl}} = 3.4$) at the site H to slightly alkaline ($\text{pH} = 7.2$) for soils of the site C. Organic carbon (C_{org}) content fluctuated within a large range, i.e., 5.5–66.4 g kg⁻¹, whereas the cation exchange capacity (CEC) was in most cases markedly low (from 1.4 to 5.9 cmol₍₊₎kg⁻¹, except for sites C and D with CEC values of 26.8 and 15.1 cmol₍₊₎kg⁻¹, respectively). The amount of silt and clay fractions reveals that investigated soils are preponderatingly sandy, *ca* 75% of soils exhibited silt + clay < 500 g kg⁻¹). Such soil texture may create a serious threat due to strengthened pollutants migration downward. The mean heavy metals content as reported in Table 2 showed significant variations related most specifically with both sites and type of metal. In the case of Zn, Pb and Cd, their levels exceeded *ca* 3 to 72 times; 13 to 176 times and 44 to 520 times, respectively, the reference values (RV) – Table 2, in opposite to Cu with 75% of its content

Table 2

Total (aqua regia) metal contents within the impact zone of the Miasteczko Slaskie Zinc Smelter, (mean \pm SD*, $n = 5$)

Site**	Cu	Zn	Pb	Cd
	mg kg ⁻¹			
A	5.15 \pm 0.45	614.50 \pm 30.43	404.15 \pm 46.96	5.75 \pm 1.16
B	5.40 \pm 1.29	368.50 \pm 39.47	542.15 \pm 61.44	5.05 \pm 1.08
C	69.60 \pm 12.40	4832.0 \pm 517.48	2986.0 \pm 147.88	52.00 \pm 5.82
D	56.55 \pm 9.69	1351.8 \pm 247.69	1009.65 \pm 95.60	16.35 \pm 2.45
E	6.60 \pm 0.80	246.0 \pm 31.10	352.15 \pm 14.65	5.52 \pm 0.38
F	6.20 \pm 1.36	649.0 \pm 88.56	226.95 \pm 12.34	5.05 \pm 0.84
G	5.00 \pm 0.40	202.0 \pm 7.62	288.10 \pm 24.04	4.50 \pm 0.47
H	5.95 \pm 0.86	240.0 \pm 31.42	446.15 \pm 30.35	4.35 \pm 0.78
Mean	20.06 \pm 3.40	1062.98 \pm 124.22	781.91 \pm 54.16	12.32 \pm 1.62
RV***	39.0	67.0	17.0	0.10
BLP****	17.5	75.0	40.0	0.65

*Standard deviation; **see Table 1; ***Reference value (TAYLOR, McLENNAN 1995);

****Background Level for Poland (KABATA-PENDIAS 1995)

not exceeding the RV. These orders of magnitude clearly show that cadmium is the most threatening heavy metal in the impact zone, followed by lead and zinc, respectively.

Copper

The mean Cu content in the study area amounted to 20.06 mg kg⁻¹ and was significantly lower than the reference value (RV = 39.0 mg kg⁻¹) reported by Taylor and McLennan, (1995) and slightly higher as compared to the background level (BLP), (mean value, *ca* 17.5 mg kg⁻¹) of the natural heavy metal content in the top layers of various soils in Poland (KABATA-PENDIAS 1995). On the other hand, the mean Cu content in soils in Poland is 6.7 mg kg⁻¹ (KABATA-PENDIAS, PENDIAS 2001), i.e., *ca* 3-times lower than the mean value obtained for the studied area.

Copper geoaccumulation indices ($Cu-I_{geo}$) calculated on the basis of the RV and BLP varied within ranges from -1.07 to 0.07 and from -0.72 to 0.42, indicating unambiguously a lack of contamination (Figure 1). This is in agreement with data reported by FAGIEWICZ et al. (2006), who pointed out significantly low Cu concentrations in dusts emitted by the Zinc Smelter. Both RV and BLP values used for assessing the $Cu-I_{geo}$ exhibited a quite similar contamination trend, which differed in range only. This is important in cases of delineating areas subjected to metal contamination

or pollution. The low contamination may be also related to Cu uptake by plants, a process leading to Cu depletion in the tested soils. However, copper depletion in soils could be induced by the elevated content of toxic bivalent metals (i.e., Zn, Pb and Cd) specifically “competing” with Cu for binding to soil particles as well as to organic matter (KABALA, SINGH 2001). This process may tend to increase Cu solubility and consequently its uptake by plants or leaching.

Zinc

Investigated soils exhibited a significantly high Zn level (mean content for the whole area is $1062.98 \text{ mg kg}^{-1}$, Table 2), which is higher than those reported for Norway, 62.0 mg kg^{-1} (STEINNES et al. 1997); the Baltic Countries, 53.8 mg kg^{-1} (REIMANN et al. 2000); for rural soils of Vietnam, 65.5 mg kg^{-1} (THUJ et al. 2000) and for forest soils of Switzerland, 60.0 mg kg^{-1} (BLASER et al. 2000). Zinc is an essential element, which is involved in plant metabolism. But at extremely high levels, it may impair – *via* toxicity - any biological growth (microorganisms and plants), hence the depletion process may not occur under conditions similar to those considered in the current study.

The calculated zinc geoaccumulation indices ($\text{Zn-}I_{geo}$) varied from 0.30 to 1.68 (for RV) and 0.25 to 1.63 (for BLP) as illustrated by the Figure 1. The reported ranges indicate that the relevant contamination state may be described as uncontaminated to moderately contaminated (MÜLLER 1981). Such “fair” $\text{Zn-}I_{geo}$ -based contamination state is partly related to both slightly high RV and BLP values as compared to Cu, whose values are lower. The fact that most soils exhibited markedly weak buffer mechanisms (CEC, Table 1), strengthens the assumption that a real contamination threat still exists, in spite of relatively low $\text{Zn-}I_{geo}$ indices.

Lead

Lead, in opposite to zinc, is by essence harmful for the biota. Natural attenuation processes – sorption, precipitation, retention creating suitable soil “sink” conditions for Pb, due to its high metal retention capacities (BORUVKA et al. 1997, KABALA, SINGH 2001), mostly control its transformation in soils. Therefore the persistence and (im)mobility of Pb should be dictated by the extent to which Pb is incorporated to soils. The mean Pb content of the studied area amounted for $781.91 \text{ mg kg}^{-1}$ (Table 2) and is *ca* 46 and 20 times higher than the RV and BLP values, respectively and 57 times higher as compared to the mean heavy metal content (i.e., 13.8 mg kg^{-1}) in Polish soils (KABATA-PENDIAS 2001).

Lead geoaccumulation indices indicated a contamination state, whose magnitude depended on the RV and BLP values exhibiting $\text{Pb-}I_{geo}$ indices in the ranges from 0.95 to 2.07 and 0.58 to 1.70, respectively as shown in the

Figure 1. These ranges fit the contamination class extending mostly from 0 to 2 and may be designated as uncontaminated to moderately contaminated (MÜLLER 1981). A similar contamination class was established for Zn, but with the specificity that $Zn-I_{geo}$ indices tended to shift more to the uncontaminated than contaminated class. The assessment of soils contamination on the basis of $Pb-I_{geo}$ indices does not reveal a serious concern and threat, even. Amounts reported in Table 2 represented significant contamination level, which implied that care should be taken to these areas, due to the harmful and detrimental effect of lead.

Cadmium

The mean cadmium content in the impact zone amounted to 12.32 mg kg^{-1} and was significantly higher than mean contents in soils of Poland (i.e., $< 0.05 \text{ mg kg}^{-1}$, LIS, PASIECZNA 1995 and 0.22 mg kg^{-1} , KABATA-PENDIAS 2001). The same applies for the RV and BLP values (Table 2), being exceeded *ca* 123 and 19 times, respectively. Such cadmium content is a matter of great concern since cadmium may exhibit toxicity properties at soils concentration above 3.0 mg kg^{-1} (BUCZKOWSKI et al. 2002). This supports the fact that the frequently suggested toxicity threshold values are relatively low, as shown just above.

Indices of Cd geoaccumulation ($Cd-I_{geo}$) indicated ranges extending from 1.46 to 2.54 and 0.64 to 1.72, accordingly to the BLP and RV values (Figure 1, Table 2). Contamination assessment based on these indices may create some discrepancies related to the establishment of a proper $Cd-I_{geo}$ class. Therefore it could be reasonable to group both classes into one with a range varying from 0.64 to 2.54, i.e., uncontaminated to moderately-heavily contaminated (MÜLLER 1981). Cadmium contamination of this area confirms data reported by FAGIEWICZ et al. (2006), that Cd, Zn and Pb displayed the highest levels relative to the background values. The high $Cd-I_{geo}$, is consistent with the findings of LIS and PASIECZNA (1995), who stated that soils in Upper Silesia are characterized by much higher cadmium content as compared to the whole area of Poland.

Copper, Zn, Pb and Cd contribution to soils contamination within the impact zone

The estimation of the overall contamination of investigated soils was carried out on the basis of the degree of contamination (C_{deg}) – Table 3. A detailed assessment was made throughout contamination factors (C_{f}), whose mean values allowed to classify soils accordingly to the RV and BLP values. Two classes (HAKANSON 1980) were operationally established, relatively to both values: low contamination for Cu, and considerable to extreme contamination for Zn, Pb and Cd, gradually. The BLP-based contamination assessment should be suggested in this case, due to the fact that this value has been

Table 3

Contamination factors and degrees for particular heavy metals within the impact zone of the Miasteczko Slaskie Zinc Smelter for RV and BLP values*

Metal	Contamination factor (range)		Mean	Share (%) of C_f^i to C_{deg}
$^x\text{Cu}_a$	C_f^i	0.13 – 1.78	0.51	0.27
$^y\text{Cu}_b$		0.29 – 3.98	1.15	2.14
Zn_a		3.01 – 72.12	15.87	8.57
Zn_b		2.69 – 64.43	14.17	26.33
Pb_a		13.35 – 175.65	45.99	24.83
Pb_b		5.67 – 74.65	19.55	36.32
Cd_a		43.50 – 520.0	123.22	66.54
Cd_b		6.92 – 80.0	18.96	35.22
Degree of contamination (a) [$C_{deg} = \sum(C_f^{Cu,Zn,Pb,Cd})$]		26.94 – 537.65	185.59	-
Degree of contamination (b)		6.90 – 119.08	53.83	

* details in Table 2; x and y: footnotes a and b refer to RV and BLP, respectively

intrinsically elaborated for Polish conditions. The re-evaluation of the degree of contamination on the basis of the BLP value gave similar contamination classes as those reported above. This rank confirmed the I_{geo} -based indices contamination assessment. Furthermore, the C_{deg} for mean heavy metal concentrations in the impact zone amounted to 53.83, which implied (HAKANSON 1980), that these soils were on the whole, considerably contaminated.

Cadmium and lead contributed the most to the degree of contamination index of the soils, with a share of 35.22 and 36.32%, respectively, followed by Zn, representing 26.33%. Copper, as reported throughout the current paper, was the sole metal to threaten the least (2.14%) the soils of the investigated ecosystem.

CONCLUSIONS AND STATEMENTS

The assessment of soils contamination throughout the application of the geoaccumulation index, contamination factor and degree has revealed that soils were differently contaminated by Cu, Zn, Pb and Cd. Metal contamination represented mostly two classes: low contamination for Cu and extremely high contamination for Zn, Cd, and Pb, in ascending order. It is

worth pointing out that copper, was the sole metal to threaten the least (2.14%) the soils of the investigated ecosystem. The impact zone is predominantly afforested; hence, the transfer of Pb, Cd, and Zn to the food chain is reduced enough. The great concern deals with the so-called forest fruits (bilberries, mushrooms), seasonally collected for sale or direct consumption (household). This topic is out of the scope of the paper.

REFERENCES

- BAIZE D., TERCHEMAN T. 2001. *Of the necessity of knowledge of the natural pedogeochemical background content in the evaluation of the contamination of soils by trace elements*. Sci. Total Environ., 264,127-139.
- BLASER P., ZIMMERMANN S., LUSTER J., SHOTYK W. 2000. *Critical examination of trace element enrichments and depletions in soils. As, Cr, Cu, Ni, Pb, and Zn in Swiss forest soils*. Sci. Total Environ., 249,257-280.
- BUCZKOWSKI R., KONDIJEWSKI I., SZYMANSKI T. 2002. *Methods for the remediation of soils contaminated by heavy metals*. Mikolaj Kopernik University Editions, Torun. First Edition, 110 p.
- BORUVKA L.S., KRISTOUFKOVA L., KOZAK J., HUAN WEI C. 1997. *Speciation of cadmium, lead and zinc in heavily polluted soils*. Rostliná Vyroba, 43: 187-192.
- DIATTA J.B., GRZEBISZ W., APOLINARSKA K. 2003. *A study of soil pollution by heavy metals in the city of Poznan (Poland) using Dandelion (Taraxacum officinale) as a bioindicator*. EJPAU, 6(2): 9 (<http://www.ejpau.media.pl>).
- FAGIEWICZ K., KOZACKI L., PRUS-GŁOWACKI W., CHUDZIŃSKA E., WOJNICKA-PÓLTORAK A. 2006. *Genetic-environmental controls of the tolerance of forest Trees to industrial pollution*. Archiv. Environ. Protect., 32(1): 73-88.
- GEE G.W., BAUDER J.W. 1986. *Particle size analysis*. In *Methods of Soil Analysis*. Part 1. *Physical and Mineralogical Methods*. KLUTE A. (ed) 2nd ed. Agron. Monogr. 9, ASA and SSSA, Madison, WI. p. 383-411.
- GRZEBISZ W., KOCIAŁKOWSKI W. Z., CHUDZIŃSKI B. 1997. *Copper geochemistry and availability in soils contaminated by a copper smelter*. J Geochem. Exploration, 58:301-307.
- HAKANSON L. 1980. *An ecological risk index for aquatic pollution control. A sedimentological approach*. Wat. Res., 14: 975-1001.
- International Standard. 1995. *Soil Quality – Extraction of trace elements soluble in aqua regia*. ISO 11466, Geneva.
- KABALA C., SINGH B.R. 2001. *Fractionation and mobility of copper, lead and zinc in soil profiles in the vicinity of a copper smelter*. J. Environ. Qual., 30: 485-492.
- KABATA-PENDIAS A. 1995. *Heavy metals in soils – issues in Central and Eastern Europe*. Int. Conf., Hamburg, 1: 20-27.
- KABATA-PENDIAS A. 2001. *Trace elements in soils and plants*, (3rd ed). CRC Press, 432 p.
- KABATA-PENDIAS A., MOTOWICKA-TERELAK, PIOTROWSKA M., TERELAK H., WITEK T. 1993. *Assessment of the level of contamination of soils and plants by heavy metals and sulphur*. IUNG, P-53, Pulawy, p. 5-14 (in Polish).
- LIS J., PASIECZNA A. 1995. *Geochemical Atlas of Upper Silesia*. Warsaw, PIG. (in Polish).
- MONTANERELLA L., OLAZABAL C., SELVARADJOU S.-K. 2004. *Reports of the Technical Working Groups Established under the Thematic Strategy for Soil Protection*. EUR 21319 EN/4., p. 493-654. Office for Official Publications of the European Communities, Luxemburg.

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- MÜLLER G. 1969. *Index of geoaccumulation in sediments of the Rhine River*. *Geojournal* 2: 108-118.
- MÜLLER G. 1981. *Die Schwermetallbelastung der Sedimenten des Neckars und Seiner Nebenflüsse*. *Chemiker-Zeitung*, 6: 157-164.
- NELSON D.W., SOMMERS L.E. 1996. *Total carbon, organic carbon and organic matter*. In: *Methods of soil analysis*. Part 3. *Chemical methods*. SPARKS D.L. (ed.) SSA Book Ser. 5. SSSA, Madison, WI. p. 961-1010.
- NRIAGU J.O., PACYNA J.M. 1988. *Quantitative assessment of worldwide contamination of air, water and soils by trace elements*. *Nature*, 333: 134-139.
- REIMANN C., SIEWERS U., TARVAINEN T., BITYUKOVA L. ERIKSSON J., GILUCIS A. 2000. *Baltic soil survey: Total concentrations of major and selected elements in arable soils from 10 countries around the Baltic Sea*. *Sci. Total Environ.*, 257: 155-170.
- STEINNES E., ALLEN R.O., PETERSEN H.M., RAMBAEK J.P., VARSKOG P. 1997. *Evidence of large-scale contamination of natural surface soils in Norway from long-range atmospheric transport*. *Sci. Total Environ.*, 205: 255-266.
- TAYLOR S.R., MCLENNAN S.M. 1995. *The geochemical evolution of the continental crust*. *Rev. Geophys.*, 33: 241-265.
- THUJ H.T.T., TOBSCHALL H.J., AN P.V. 2000. *Distribution of heavy metals in urban soils – a case study of Danang-Hoian Area (Vietnam)*. *Environ. Geol.*, 39: 603-610.
- THOMAS G.W. 1982. *Exchangeable cations*. In: *Methods of soil analysis*. PAGE A.L. et. al. (ed.) 2nd ed. *Agron. Monogr.* 9. ASA and SSSA, Madison, WI p. 159-164.
- VAN-CAMP L., BUJARRABAL B., GENTILE AR., JONES R.J.A., VAN LYNDEN G. W.J. 2000. *Soil degradation in Central and Eastern Europe. The assessment of human-induced degradation*. *FAO Report 2000/05 and ISRC*.