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Influence of land use pattern on changes in copper content in soils around a copper smelter, based on a 34-year monitoring cycle

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The concentration of trace elements in soils around the Glogów copper smelter has been continuously observed since opening the smelter in 1972. Permanent sampling sites are located at various directions and distances from the emission source. Soils are sampled every year in June, at a depth of 0–20 cm, in four replicates. Results from different sites are comparable only to a limited extent, as the smelter is situated on the boundary between a river valley and loess hills covered with soils varying both in texture and basic chemical properties. The total concentration of copper was determined after digesting a soil sample with aqua regia or concentrated perchloric acid. Analysis of a 34-year-long cycle revealed a significant initial increase in copper content, followed by its relative levelling out and a slow but continuous decrease typically observed in arable soils. By contrast, in soils afforested with poplars within the so-called "sanitary zone", a significant secondary rise in copper concentration was observed. Results of the long-term monitoring programme confirm a remarkable reduction in heavy metal emission from the smelter, the "phytoremediation" effect due to common cultivation of arable plants, as well as a secondary concentration of heavy metals captured from the air by fast-growing trees planted in the immediate vicinity of the smelter.

Key words: copper, soil monitoring, copper smelter, land use

INTRODUCTION

Toxic substances emitted by the industry and in particular those produced by the power generating sector and the non-ferrous metallurgy are intrinsically hostile to natural ecosystems and deteriorate the conditions of agricultural and forest production (Chlopecka et al., 1996; Heelmisaari et al., 1995; Kuo et al., 1983; Martley et al., 2004). One of the major ecological problems with regard to soils is the high concentration of heavy metals, since adverse effects of accumulated elements may take decades or even centuries to become manifest. Moreover, the mechanisms that halt or trigger their release are complex and still not entirely understood (Kabata-Pendias, Pendias, 1992).

In the south-west of Poland, the most important source of metal-containing dust emission is a mining and metallurgy industrial complex in which copper ores excavated from local deposits are being processed (Dobrzanski, Byrdziak, 1995). The heavy metal pollution levels of soils in the vicinity of Glogów and Legnica smelters have been repeatedly studied (Kabala, Singh, 2001, 2006; Karczewska, 1996; Karczewska et al., 1998). These works document the spatial distribution of soil contamination around smelters, the content of metals in soil profiles as well as the forms and solubility of metals. Little is known, however, about the time-dependent dynamics of trace element levels, despite the drastic change in smelter emissions and the type of land use in the vicinity of smelters (Szerszeń et al., 1993).

Nonetheless, long-term measurement cycles carried out on permanent observation surfaces can be vital for monitoring research in areas prone to degradation (Duijvenbooden, 1998; Mol et al., 1998; Wagner et al., 2001). Of particular value are measurement series carried out from the very moment when the pollution source starts to operate. In such cases, the type and the rate of environmental transformations caused by industrial facilities may be unequivocally determined (Kabata-Pendias, Pendias, 1992).

This paper aims to investigate the dynamics of total copper content in soils and seeks to point out the effect of change in the land use pattern on metal accumulation levels in topsoil. All this research is based on measurements carried out between 1972 and 2006 in the Glogów copper smelter area.

STUDY AREA AND METHODS

The Glogów copper smelter is part of a mining and metallurgy complex founded in 1959, which currently includes 4 mines, 3 ore enrichment plants (with two tailings ponds) and 3 smelters (Dobrzanski, Byzdziak, 1995). The complex has been producing approx. 400000 tons of copper annually, which initially involved large emissions of SO_2 and metal-containing dusts, but drastically reduced during the 1980s and 1990s in all the facilities of the complex (Fig. 1).

Permanent observation surfaces in the area of the smelter being opened were established in 1971–1972, located to the east and north- and south-east of the smelter, i.e. in the prevailing wind direction in the smelter area (Fig. 2). Initially, all the sampling points were situated on agricultural (arable) land. In early 1980s, the most contaminated soils within the so-called sanitary zone were planted with black poplar (*Populus nigra* L.) and black Italian poplar (*Populus euroamericana f. serotina* Hartig). Since that time, two observation surfaces have been covered with poplars (sites 1SE and 3NE), while the two others are still used for agriculture (sites 2SE and 4SE). Soil samples are collected in late spring or early summer (most often in June) from the depth of 0–20 cm. Periodically, samples are also taken from other soil horizons, which provides characteristics of metal content and forms in the entire profile (Kabała, Singh, 2001, 2006; Szerszeń et al., 1993). Representative samples for laboratory analyses (one composite sample for each monitoring site) are obtained by mixing at least 4 primary samples collected on a surface being monitored from points spaced at least 15–20 m apart.

As a standard, particle size distribution (by sieving and hydrometer method), organic carbon content (by oxidation with potassium dichromate), pH in distilled water and 1 M KCl (potentiometrically), and ECEC (as a sum of basic cations and exchangeable acidity) are determined for each soil sample (Van Reeuwijk, 2006). The total content of trace elements (in this study copper) was determined using flame atomic absorption spectroscopy (FAAS), after the samples had been digested with aqua regia (HCl : HNO_3 ratio 3 : 1) or with 70% $HClO_4$ (during the period 1991–2001). This temporary substitution of aqua regia with perchloric acid had no significant impact on recorded metal content levels. Since 1991, the quality of determination has been monitored using soil reference materials (SRM 2709,

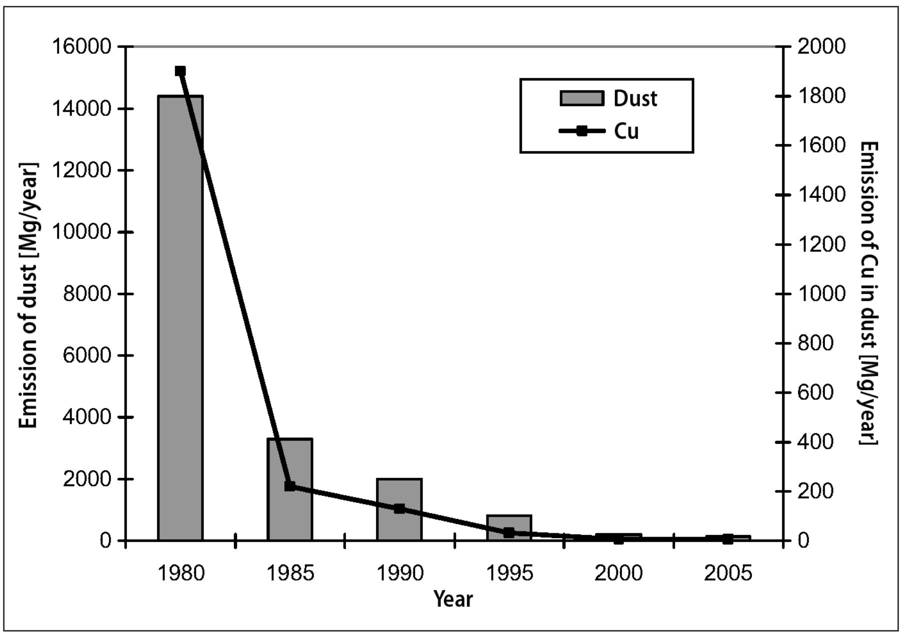

Fig. 1. Decrease of an industrial dust and copper emissions from the copper smelter near Glogów (SW Poland) between 1980 and 2005

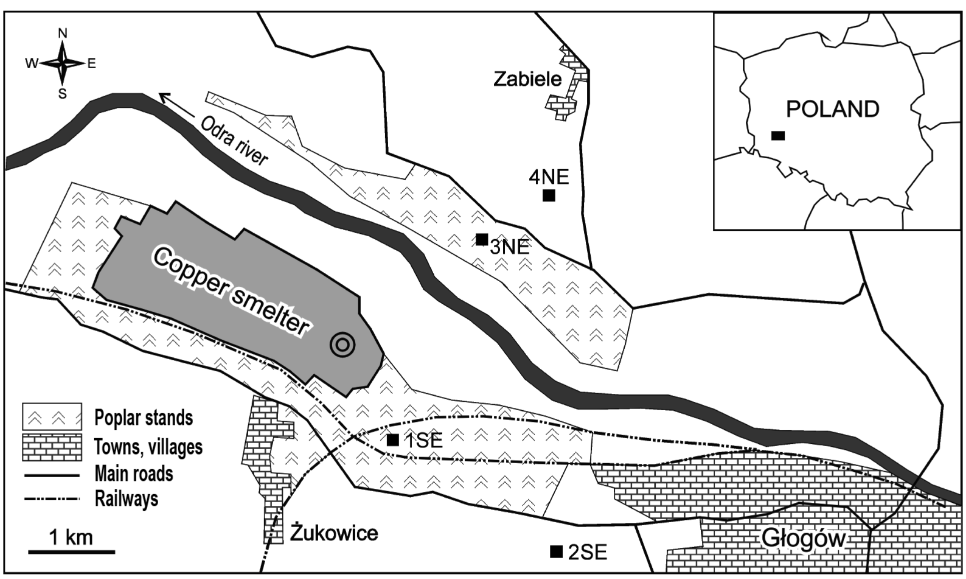

Fig. 2. Localization of the permanent soil-monitoring sites in the vicinity of the Glogów copper smelter

SRM 2711, RTH 912, RTH 953) with a certified total concentration of trace elements being analysed. Each analysis was made in duplicates, and the arithmetic mean was calculated if the difference between the results was no higher than 5%. If the difference exceeded 5%, additional subsample was analysed, and the mean content of metal was calculated from all three replicates.

RESULTS AND DISCUSSION

Soils around the smelter vary in terms of typology, have different textures and diversified physical and chemical properties. To some extent, this diversification limits the possibility of comparison of results from individual surfaces being monitored. The sampling sites to the south and south-east of the smelter (sites 1SE and 2SE) are *Luvisols* (World…, 2006). Here, topsoil texture is silt loam (according to the USDA classification), the reaction is neutral to slightly acid (pH ranging from 6.1 to 6.3), ECEC is relatively high, organic carbon content is medium-high (Table 1). To the north of the smelter, in the valley of the Odra river, alluvial soils prevail, the properties of which vary in either strip or mosaic pattern. The soil type of site 3NE is Brunic Arenosol (World…, 2006), its texture is sand (according to USDA), reaction is neutral and both organic carbon content and the ECEC value are relatively low (Table 1). The soil type of site 4NE is *Calcaric Cambisol* (World…, 2006). The other characteristics are as follows: loamy texture (according to USDA), neutral reaction, high organic carbon content and a very high ECEC in the plough layer (Table 1).

The opening of the Głogów smelter resulted in a rise in copper content at all observation sites (Figs. 3 and 4), but the growth rate and the maximum contamination level depended on the point location, i.e. on the distance and direction relative to the smelter. The maximum, over 7-fold, surge has been recorded at point 1SE, with an almost 4-fold rise at point 2SE. A strong increase in copper content was also recorded in the north-east direction, even as far as 3–4 km from the smelter. In the late 1970s and early 1980s, the copper content curve levels out or even starts to decrease (Table 2).

At point 2SE, a slow, almost uninterrupted decline of copper content has been observed since mid-1970s, with a constant (low) level value since mid-1990s (Fig. 3). Similarly, at point 4NE a decrease in copper concentration is recorded, although high yearly fluctuations hinder an unequivocal assessment of the actual speed of this phenomenon (Fig. 3). Oscillations occurring at

Table 1. **Texture and basic chemical properties of soils in the monitoring sites near the Glogów copper smelter**

Monitoring sites	Percentage of grain-size fractions (grain diameters in mm)							Organic carbon [%]	pH_{H_2O}	pH_{KCl}	ECEC [cmol (+) kg^{-1}]
	> 2	2–1	1–0.1	0.1–0.05	0.05–0.02	0.02–0.002	<0.002				
1SE 1.5 km SE	0	0	20	5.9	32	21	5	1.4	6.1	5.6	7.04
2SE 3.5 km SE	0	3	15	6.9	33	21	6	1.2	6.3	5.9	9.90
3NE 2.0 km NE	0	0	88	6.6	6	1	4	0.6	7.2	6.7	4.45
4NE 3.5 km NE	0	0	31	7.1	4	31	21	2.5	7.7	7.1	73.5

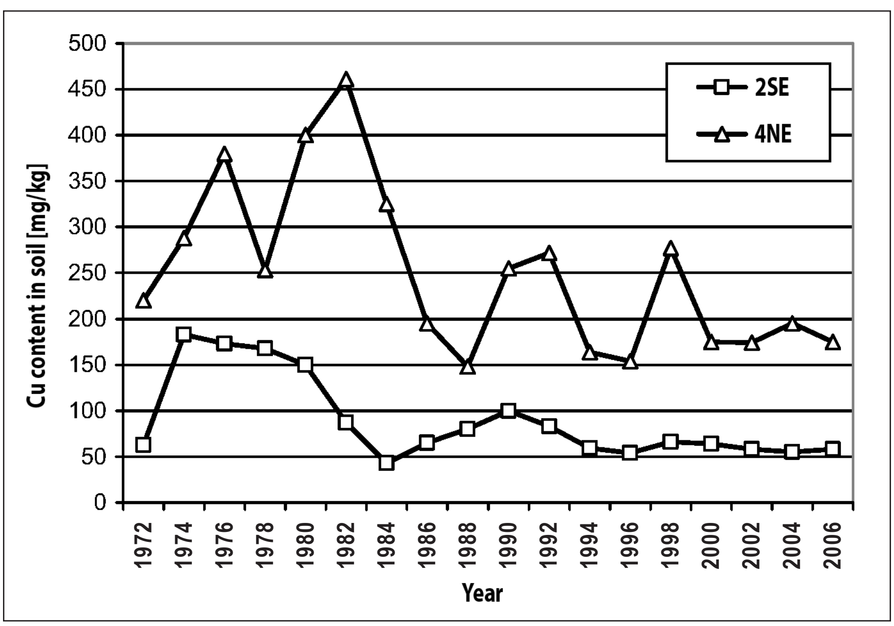

Fig. 3. Changes of copper concentration in soils used for crop production continuously between 1972 and 2006 (monitoring sites 2SE and 4NE)

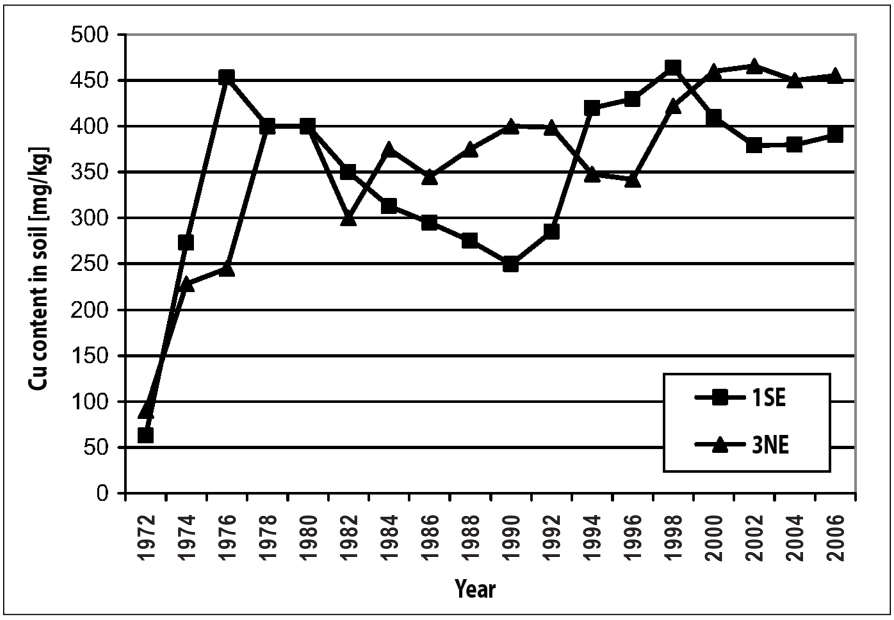

Fig. 4. Changes of copper concentration in soils afforested with poplar trees (monitoring sites 1SE and 3NE)

Table 2. **Total concentration of copper in surface horizons of soils in the monitoring sites near the Glogów copper smelter**

Year	1 SE 1.5 km SE	2 SE 3.5 km SE	3 NE 2.0 km NE	4 NE 3.5 km NE
	Cu concentration in soil [mg kg^{-1}]			
1972	62,5	63.0	90.0	220
1974	273	183	228	288
1976	453	173	245	380
1978	400	168	388	253
1980	401	150	395	400
1982	350	87.0	303	461
1984	313	43.0	375	325
1986	295	65.0	345	195
1988	275	80.0	375	148
1990	250	100	400	255
1992	285	83.0	399	272
1994	420	59.0	348	164
1996	430	54.0	342	154
1998	464	66.0	422	277
2000	410	64.0	460	175
2002	379	58.0	466	174
2004	380	55.0	450	195
2006	390	58.0	455	175

this point are most likely due to the exceptional variability of soil types in the Odra river valley. Points 2SE and 4NE are located on arable land which has been in uninterrupted agricultural use, i. e. was ploughed every year.

Sites 1SE and 3NE are located in the former sanitary zone of the smelter, on land withdrawn from agricultural use and planted with poplar in late 1970s / early 1980s. At point 1SE, a gradual decrease in copper content had been observed till early 1990s, with a subsequent levelling out (lasting several years) and a new increase from mid-1990s until today (Fig. 4). At point 3NE, after a period of strong upward trend (till the end of 1970s), the concentration of copper levelled out or dropped (insignificantly) in mid-1990s, to begin rising again starting from 1990s, similarly to point 1SE (Fig. 4).

A comparison of the direction of changes in copper content reveals the role of poplar plantations established around the smelter as a sanitary and soil-protection measure. It seems that a dense poplar stand, ten to twenty years old (currently over 25 years old) can contribute to a secondary rise in heavy metal concentration in topsoil in two ways:

1. The stand forms a mechanical barrier for contaminated air (also mist); a considerable amount of dust is retained by leaves from which it later comes to the forest floor and soil humic horizon.

2. Tree roots penetrate the soil profile much deeper than crops, taking up trace elements and carrying them to leaves which later fell down on the ground.

Both mechanisms may be summarized as "bioaccumulation". In contrast to arable land, the biomass (with a given content of metals) produced in a forest throughout the year is not removed from the ecosystem. This gradually leads to a concentration of heavy metals in topsoil.

In order to estimate the speed with which copper is being removed from the humic horizon of arable soils, the difference between recorded total concentrations was calculated over the overall measurement period. At point 4NE (highly contaminated loam soil), during 1982–2000 a drop in copper content of approx. 200 mg Cu kg^{-1} was recorded, yielding a yearly loss of 11 mg Cu kg^{-1}. At point 2SE (less contaminated silt loam soil), during 1976–1994 a drop of approx. 110 mg Cu kg^{-1} was measured, yielding 6 mg Cu kg^{-1} annually. In view of neutral soil reaction, the high ECEC and the totally opposite (increasing) trend in soils afforested with poplar, we are led to conclude that the principal reason for copper loss from plough layers of soils under analysis is not leaching into deeper soil horizons, but rather the intake by cultivated crops and removal from the ecosystem with harvested biomass (crops). Calculations being presented should not be considered as a strict pot experiment and may be challenged as being overestimated; nevertheless, they clearly indicate that provided the inflow of contaminants is halted, an intensive agricultural use (with maximum possible biomass removal) may be considered as a technique of "phytoremediation" of soils contaminated with copper.

CONCLUSIONS

Observations carried out over several years, which focused on the dynamics of copper content in soils around the Glogów copper smelter, lead to the following conclusions:

1. The concentration of heavy metals in topsoil has been approximately the same or reduced since 1980s, which confirms a lasting reduction in metal emissions from the smelter.

2. With little or no metal input from the atmosphere, metal concentrations in topsoil slowly but steadily decrease under the normal agricultural production.

3. In dense poplar stands around the smelter, a secondary rise of copper concentration in topsoil has been recorded. This is due to an intensified bioaccumulation by the canopy which retains part of atmospheric contamination.

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ŽEMĖS NAUDOJIMO POVEIKIS VARIO KIEKIUI DIRVOŽEMYJE ŠALIA VARIO LYDYKLOS PAGAL 34 METŲ STEBĖSENOS REZULTATUS

Santrauka

Sunkiųjų metalų kiekis dirvožemiuose šalia Glaguvo vario lydyklos stebėtas nuo jos atidarymo 1972 m. Pastovios dirvožemio tyrimo aikštelės išdėstytos skirtingomis kryptimis ir nuotoliais pagal įmonės emisijų sklaidą. Dirvožemio ėminiai imami kasmet birželį 0–20 cm gylyje keturiais pakartojimais. Dirvožemio varingumo tyrimo aikštelėse duomenų palyginimas yra ribotas, nes lydykla stovi tarp upelio slėnio ir liosiškų kalvų, padengtų nevienodos granuliometrinės ir cheminės sudėties dirvožemiais. Vario suminė koncentracija dirvožemyje nustatyta karališkosios degtinės („aqua regia") ar koncentruotos perchlorato rūgšties tirpikliuose. 34 metų stebėsena parodė, kad per pirmuosius kelerius gamyklos darbo metus dirvožemio varingumas ryškiai didėjo iki santykinio nusistovėjimo koncentracijos, kuri vėliau lėtai, bet nuolat mažėjo dirbamuose dirvožemiuose. Priešingai, lydyklos apsauginėje zonoje tuopomis apželdintuose dirvožemiuose vario koncentracija nuolat didėjo. Ilgalaikė stebėsenos programa parodė ryškų sunkiųjų metalų emisijos iš lydyklos mažėjimą, užteršto dirvožemio atstatymo kultūriniais augalais efektą, šalia gamyklos pasodintų sparčiai augančių medžių gebėjimą „pagauti" sunkiuosius metalus iš atmosferos ir su nuokritomis padidinti jų koncentraciją dirvožemyje.

Raktažodžiai: varis, dirvožemio stebėsena, vario lydykla, žemės naudojimas