

Agnieszka MEDYŃSKA¹ and Cezary KABAŁA¹

**HEAVY METALS CONCENTRATION
AND EXTRACTABILITY IN FOREST LITTERS
IN THE AREA IMPACTED
BY COPPER SMELTER NEAR LEGNICA**

**ZAWARTOŚĆ I ROZPUSTALNOŚĆ METALI CIĘŻKICH
W PRÓCHNICACH LEŚNYCH NA TERENACH ZDEGRADOWANYCH
PRZEZ HUTNICTWO MIEDZI**

Abstract: Three permanent study areas, each consisting of four sampling sites, located at distances of 500, 1500 and 2100 m from emission source, were established in poplar plantings surrounding a large copper smelter near the town Legnica in Lower Silesia region of SW Poland. Total content as well as water and acetic acid extractable contents of Cu, Zn, Fe, Ca and Mg were analyzed in samples of forest litter (ectohumus) collected in November 2007. The total content of Cu reached $9590 \text{ mg} \cdot \text{kg}^{-1}$, and Zn – $4020 \text{ mg} \cdot \text{kg}^{-1}$ d.m. in the site located 500 m away of smelter, and rapidly decreased with distance, while the content of Fe, Ca and Mg decreased insignificantly. Up to 0.5 % of total Cu and up to 1.2 % of total Zn was in water-extractable form, while $0.11 \text{ mol} \cdot \text{dm}^{-3}$ acetic acid released up to 7.2 % of Cu and 41 % of Zn, and more than 50 % of total Ca and Mg. Copper and zinc are immobilized in alkaline litter under poplar stands surrounding copper smelter, but any factor acidifying the litter may rapidly enhance solubility of accumulated heavy metals.

Keywords: heavy metals, solubility, extractability, copper industry, forest litter, soil pollution

The natural balance of the biogeochemical cycles has been considerably changed by the human activity causing enhanced mobilization of chemical elements in the environment as compared with the natural processes. Therefore, the essential processes of matter and energy cycling may become harmful [1]. Heavy metal accumulation in forest soil may effect nutrient cycling throughout the whole ecosystem by inhibiting litter decomposition and subsequently reducing the supply of nutrients released by mineralization [2]. Heavy metals can also have toxic effects on roots and mycorrhiza fungi resulting in seriously reduction of nutrient uptake [3]. Forest humus, which has a large cation binding capacity, and provides relatively stable bindings with most of elements or theirs compounds plays a significant role in trace element accumulation

¹ Institute of Soil Science and Environmental Protection, Wrocław University of Life and Environmental Sciences, ul. Grunwaldzka 53, 50–357 Wrocław, Poland, phone +48 71 320 5604, email: jagamedynska@yahoo.com, cezary.kabala@up.wroc.pl

[4–6] and in returning nutrients to the soil through decomposition [7]. The principal fate during litter decomposition and mineralization is rather well established only for limited number of forest environments, mainly unpolluted [8–11], while the dynamics of chemical elements in forest litter and soils contaminated with excessive amounts of heavy metals is still scarcely known [12–15].

The aim of the present work was to evaluate the potential risk of soil contamination by the determination of the total accumulation of trace metals in forest floor humus near large copper smelter Legnica (south-western Poland), and the potential mobility of metals as studied by water extracts from forest litter.

Material and methods

The Legnica copper smelter is a part of the mining and metallurgy complex founded in 1951, which currently includes 4 mines, 3 ore enrichment plants and 3 smelters [16]. The complex has been producing approximately 500 000 tons of copper annually, one fourth of that is produced in the Legnica smelter. Copper smelting was connected in the past with a large emission of metal-containing dust, significantly reduced during the 1980s and 1990s in all the facilities comprised in the complex [17]. Long-term copper smelting in the Legnica area has however resulted in an extensive soil contamination with number of trace elements.

Three permanent study sites, each consisting of four sampling points (“replicates”), were established in the poplar plantings surrounding the copper smelter near the town Legnica in Lower Silesia region of SW Poland. Study sites are located at distances of 500 m (Site 1), 1500 m (Site 2) and 2100 m (Site 3) north-west from emission source, within so-called “sanitary zone” surrounding the smelter (Fig. 1).

All three afforested sites are situated on similar soils, Cutanic Luvisols [18] developed of loess-like sediments, having a texture of silt loam and nearly neutral reaction in surface mineral soil horizons.

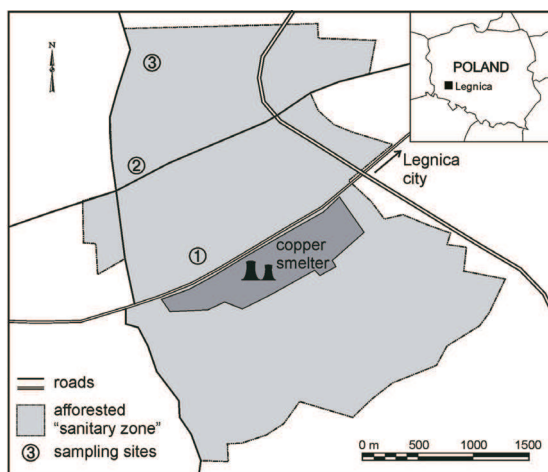


Fig. 1. Location of sampling sites near a copper smelter Legnica

The term “forest litter” used in this paper means all organic materials deposited at forest floor, including fresh litter (fresh leaves fall) and proper ectohumus, consisting of better decomposed plant residues. The overall thickness of sampled litters (including fresh fall) varied from 4–5 cm on Site 3 up to 8–10 cm on Site 1. Bulk samples of forest litter were collected in November 2007 in four replicates on each sampling site by using a steel cylinder (diameter 23 cm, sampling area 415 cm²). All replicates were stored and analyzed separately.

General aim of study was to assess the total content of elements stored in forest litter and the potential of elements leaching by determination of their extractability under actual environmental conditions. Distilled water was selected as a substitute of rain water washing the litter, and the 0.11 mol · dm⁻³ acetic acid was used as one of proposed substitutes of natural acidic excretions of plant roots and fungal hyphens [17]. Fresh samples of litter were weight, crumbled and mixed by hand. Dry mass of samples in 105 °C was than determined to establish the comparable amounts of litter in extraction mixtures. Water-extractable and acetic acid-extractable forms of elements were determined using the fresh litter samples extracted with distilled water or 0.11 mol · dm⁻³ acetic acid in a suspension 1:10 m/v (litter : liquid). The total content of elements was determined after sample digestion with *aqua regia* (HCl:HNO₃ ratio 3:1) using microwave oven (in high-pressure PTFE beakers). Measurement of metal concentration in water and acid extracts was made using the flame atomic absorption spectroscopy (FAAS). All extractions were made in two laboratory replicates of each sample. Quality of determination has been monitored using soil reference materials (NIST-1515, IAEA-V-10) with certified total content of trace elements being analysed.

The variability of litter properties and content of elements on particular sites was evaluated by use of Duncan’s multiple range test at $p < 0.05$.

Results and discussion

Although all forest litters were collected under the poplar stands of the same age, composition and canopy density, they significantly differed in thickness and mass of organic layer, as well as in the stage of decomposition. Forest litters collected on sites 2 and 3, located 1500 and 2100 m away from the smelter had at sampling time in November 2007 significantly smaller thickness and weight than the litters on site 1 located 500 m from the smelter (Table 1).

The difference in ectohumus thickness results not from higher biomass productivity in the stands near the smelter, but rather from reduced decomposition of leaves and their accumulation in thin compressed layers in successive years. Forest litters on sites 2 and 3 (1500 m and 2100 m away from the smelter) consisted mainly of freshly fallen leaves which confirms high rate of biomass decomposition in these areas.

All forest litters under examination have astonishingly high pH values, in a range of alkaline reaction in distilled water (Table 1) and very high total concentrations of calcium and magnesium, up to 2.9 % and 0.36 % of dry litter mass, respectively (Table 2).

Table 1

Characteristics of forest litter (ectohumus) on permanent study sites near the copper smelter Legnica

Parameter	Distance from the smelter [m]		
	500	1500	2100
Fresh mass of litter [$\text{g} \cdot \text{m}^{-2}$]	10.8* ^a 8.2–13.5**	4.6 ^b 1.2–6.4	4.9 ^b 3.9–5.8
Dry mass of litter [$\text{g} \cdot \text{m}^{-2}$]	4.0 ^a 3.0–4.9	1.6 ^b 0.4–2.5	1.6 ^b 1.3–1.9
pH _{H₂O} of litter (fresh mass)	6.9 ^a 6.6–7.2	7.0 ^a 6.8–7.1	6.9 ^a 6.3–7.3

Explanation: * – arithmetic mean, ** – range of results (minimum – maximum), ^{a, b, c} – homogeneous groups of Duncan's multiple range test (at $p < 0.05$).

Table 2

Total content of elements [$\text{mg} \cdot \text{kg}^{-1}$ d.m.] in forest litter (ectohumus) on permanent study sites near the copper smelter Legnica

Element	Distance from the smelter [m]		
	500	1500	2100
Cu	9160* ^a 8810–9590**	1282 ^b 1100–1450	472 ^c 303–610
Zn	2710 ^a 1680–4020	390 ^b 340–440	320 ^b 140–520
Fe	5565 ^a 3640–10160	2975 ^b 1600–3960	3460 ^b 2120–3540
Ca	22500 ^a 9600–29000	19300 ^a 12000–24400	21100 ^a 11000–27600
Mg	3045 ^a 2460–3340	3455 ^a 2780–3600	2055 ^b 1860–2440

Explanation: * – arithmetic mean, ** – range of results (minimum – maximum), ^{a, b, c} – homogeneous groups of Duncan's multiple range test (at $p < 0.05$).

Such properties of litters are evidences for pollution with alkaline dust emitted by smelter these days or in the recent past. Chemical composition of the dust emitted by the smelter was not determined, however, up to 11 % of total Ca and up to 12 % of total Mg amount in litter was found in water-extractable form (Table 3), which confirms that considerable part of these elements exists on plant residues as oxides easily soluble in water. Extraction with $0.11 \text{ mol} \cdot \text{dm}^{-3}$ acetic acid released 42–56 % of total Ca and 52–64 % of total Mg, indicating high potential solubility of calcium and magnesium compounds in litters in all three sites afforested with poplar trees around the copper smelter. Acetic acid-extractable forms may mobilize under any acidifying conditions, including acidic atmospheric precipitation, introduction of “acidifying” plant species, as birch, oak or coniferous trees, as well as an increasing activity of microorganisms in the rhizosphere.

Total contents of copper, zinc and iron (ie determined in *aqua regia*) in litter horizons in the surrounding of the copper smelter were much higher than found under

natural deciduous forests in central Europe [5, 6] reflecting negative influence of smelter activity on an adjacent environment. The content of copper in Site 1 (500 m away from smelter) reached nearly 1 % d.m. mass – $9160 \text{ mg} \cdot \text{kg}^{-1}$ (in average), and in Site 2 and Site 3 decreased to $1282 \text{ mg} \cdot \text{kg}^{-1}$ and $472 \text{ mg} \cdot \text{kg}^{-1}$ d.m., respectively (Table 2). Mean contents of copper in particular monitoring sites situated at increasing distance from the smelter differ (decrease) significantly that was confirmed with Duncan's multiple range test. Similarly, the highest content of zinc ($2710 \text{ mg} \cdot \text{kg}^{-1}$ d.m. on average) was found in the nearest surrounding of the smelter and significantly decreased with the distance, to $320\text{--}390 \text{ mg} \cdot \text{kg}^{-1}$ at $1500\text{--}2100$ m from the smelter. Total amount of copper and zinc in the litter on Site 1 (500 m from the smelter) was even twenty times, and nine times higher, respectively, than on Site 3 located 2100 m from the source of emission. Total content of iron was also significantly higher in the forest litter on Site 1 (mean value $5565 \text{ mg} \cdot \text{kg}^{-1}$ d.m.) than on Sites 2 and 3 ($2975 \text{ mg} \cdot \text{kg}^{-1}$ and $3460 \text{ mg} \cdot \text{kg}^{-1}$ d.m., respectively), but differences between studied areas were smaller than these found for copper and zinc.

Table 3

Concentration of water-extractable forms of elements [$\text{mg} \cdot \text{kg}^{-1}$ d.m.] in forest litter (ectohumus) on permanent study sites near the copper smelter Legnica

Element	Distance from the smelter [m]		
	500	1500	2100
Cu	12.0 ^{*a}	6.2 ^b	2.3 ^c
	9.8–15.2 ^{**}	4.2–8.6	0.6–5.1
Zn	7.1 ^a	4.6 ^b	2.2 ^c
	5.0–8.5	1.7–10.9	0.73–3.8
Fe	3.0 ^c	9.0 ^a	6.4 ^b
	0.9–4.3	2.5–13.8	4.2–7.7
Ca	2548 ^a	2125 ^a	1710 ^b
	850–4015	305–3257	1210–2624
Mg	142 ^a	268 ^b	254 ^b
	108–167	119–565	197–338

Explanation: * – arithmetic mean, ** – range of results (minimum – maximum), ^{a, b, c} – homogeneous groups of Duncan's multiple range test (at $p < 0.05$).

Extraction with use of distilled water released only 0.13–0.5 % of the total content of copper, however, due to the high total concentration of copper in litter, the amount of water-extractable copper in the litter was relatively high, in the range of 2.3 to $12.0 \text{ mg} \cdot \text{kg}^{-1}$ d.m. The amount of water-extractable zinc was similar to copper, in the range of 2.2 to $7.1 \text{ mg} \cdot \text{kg}^{-1}$ d.m., at relatively higher extractability in water (0.3–1.2 % of the total Zn amount). The amounts of the water-extractable copper and zinc decrease significantly with the increasing distance to the smelter (Table 3). The solubility of iron followed another rules, while the highest concentration of water-extractable iron was measured on Site 2 (1500 m to the smelter) – on average $9.0 \text{ mg} \cdot \text{kg}^{-1}$ d.m., and the lowest – ca $3.0 \text{ mg} \cdot \text{kg}^{-1}$ on Site 1 (500 m to the smelter). Relative extractability of iron

in distilled water was the least among studied elements, ranging from 0.05 to 0.3 % of the total iron content.

Extraction with $0.11 \text{ mol} \cdot \text{dm}^{-3}$ acetic acid, imitating natural root secretions, revealed significantly higher solubility of trace elements as compared with the extraction with distilled water (Table 4).

Table 4

Concentration of $0.11 \text{ mol} \cdot \text{dm}^{-3}$ acetic acid-extractable forms of elements [$\text{mg} \cdot \text{kg}^{-1}$ d.m.] in forest litter (ectohumus) on permanent study sites near the copper smelter Legnica

Element	Distance from the smelter [m]		
	500	1500	2100
Cu	677 ^{*a}	8.7 ^b	7.9 ^b
	171–1577 ^{**}	6.6–9.8	1.8–10.9
Zn	1116 ^a	117 ^b	101 ^b
	844–1460	101–140	31–131
Fe	10.7 ^a	13.0 ^a	10.8 ^a
	8.1–16.1	8.9–14.6	2.4–26.5
Ca	12690 ^a	8370 ^b	8820 ^b
	10650–15540	7350–9210	7500–10590
Mg	1747 ^a	1792 ^a	1319 ^b
	1577–1927	1584–2276	1200–1423

Explanation: * – arithmetic mean, ** – range of results (minimum – maximum), ^{a, b, c} – homogeneous groups of Duncan's multiple range test (at $p < 0.05$).

Copper concentration measured in acetic acid extracts on Site 1 (500 m to the smelter) reached values up to $1577 \text{ mg} \cdot \text{kg}^{-1}$ d.m. (on average $677 \text{ mg} \cdot \text{kg}^{-1}$), ie 7.2 % of the total content of copper in examined litters. Zinc concentration reached $1460 \text{ mg} \cdot \text{kg}^{-1}$ (on average $1116 \text{ mg} \cdot \text{kg}^{-1}$), ie about 41 % of the total Zn content in the litter. Such a large extractability of copper and zinc in acetic acid means that these metals occur in the examined litters as compounds easily soluble in acids – eg oxides and carbonates, rather than in stable complexes with organic matter. The amount of acetic acid-extractable copper decreases rapidly with the distance to the smelter, from $677 \text{ mg} \cdot \text{kg}^{-1}$ d.m. (on average) on Site 1 (500 m to the smelter) to $8.7 \text{ mg} \cdot \text{kg}^{-1}$ (on average) on Site 2 (1500 m to the smelter). The ratio of metal content (both copper and zinc) extracted with $0.11 \text{ mol} \cdot \text{dm}^{-3}$ acetic acid to those extracted with distilled water becomes narrower with the distance to the smelter (Fig. 2). On all sites the ratio is significantly wider for zinc than for copper, probably due to higher susceptibility of zinc compounds to acidic solutions. The amounts of iron extracted with $0.11 \text{ mol} \cdot \text{dm}^{-3}$ acetic acid were similar on all studied sites, in the range from 10.7 to $13.0 \text{ mg} \cdot \text{kg}^{-1}$, and were close to the amounts of water-extractable iron forms. Relative extractability of iron with acetic acid was on the level of 0.2–0.4 % of its total amount. Such a small solubility of iron confirms the strong binding of this element in insoluble compounds such as silicates, or in stable complexes with organic matter.

The results of the study show that organic horizons of the forest floor in an immediate surrounding of copper smelter near Legnica are strongly polluted with

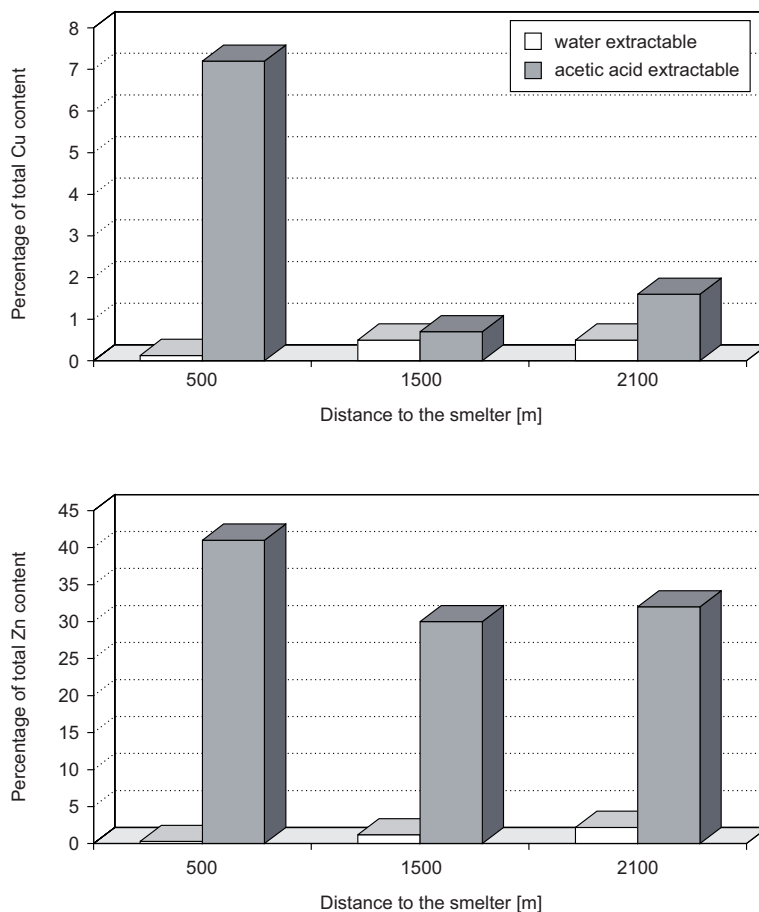


Fig. 2. Extractability of Cu and Zn (as a percentage of total content of the metals) in forest litter on permanent study sites near the copper smelter Legnica

copper and zinc, and, to a lesser extent, with iron. All these metals occur presently in relatively stable forms under alkaline reaction of the litter. Extraction with weak acids causes however large increase in solubility of examined metals, following the dissolution of calcium and magnesium compounds (oxides and/or carbonates). It means that organic horizons of forest floor may accumulate heavy metals from atmospheric pollution under specific conditions only. Any change in forest composition by an introduction of some deciduous or coniferous species, or the application of physiologically acidic fertilizers may lead to the acidification of forest litter and to the increase of solubility and mobility of previously accumulated heavy metals [2, 10, 11, 13]. Similar effect may cause natural rain precipitation correlated with reduction of alkaline dust emission from the smelter, as well as the raising of organic matter decomposition under decreasing litter contamination which follows the reduction of emission of metal-bearing industrial dusts [15].

Conclusions

1. Copper and zinc occur in highly contaminated and alkaline forest litters under poplar stands in the surrounding of copper smelter Legnica in relatively stable forms, weakly soluble in distilled water, that may extract only 0.13–0.50 % of total Cu and 0.3–1.2 % of total Zn content in forest litter.

2. Extraction with weak organic acid (as $0.11 \text{ mol} \cdot \text{dm}^{-3}$ acetic acid) releases up to $677 \text{ mg} \cdot \text{kg}^{-1}$ of copper (ie 7.2 % of the total Cu content in litter) and up to $1116 \text{ mg} \cdot \text{kg}^{-1}$ of zinc (ie 41 % of the total Zn content) from forest litter deposited in close surrounding of the smelter.

3. Any natural or anthropogenic changes in poplar stands, as mineral fertilization or introduction of coniferous tree species, that acidify the forest floor may significantly enhance solubility and mobility of metals accumulated presently in the ectohumus layer.

References

- [1] Knoepp J.D., Reynolds B.C. and Swank W.T.: *Forest Ecol. Manage.* 2005, **22**, 300–312.
- [2] Berg B., Ekbohm G., Soderstrom B. and Staaf H.: *Water Air Soil Pollut.* 1991, **59**, 165–177.
- [3] Derome J. and Nieminen T.: *Environ. Pollut.* 1998, **103**, 219–228.
- [4] Kabała C. and Szerszeń L.: *Water Air Soil Pollut.* 2002, **138**, 307–317.
- [5] Rusek A., Kabała C. and Drozdowska J.: *Roczn. Glebozn.* 2005, **56**, 137–146.
- [6] Suchara I. and Sucharova J.: *Water Air Soil Pollut.* 2002, **136**, 289–316.
- [7] Laskowski R., Niklińska M. and Maryański M.: *Ecology* 1995, **76**, 1393–1406.
- [8] Berg B.: *Scand. J. Forest Res.* 1986, **1**, 359–369.
- [9] DeSanto A.V., Fierro A., Berg B., Rutigliano F.A. and DeMarco A.: *Develop. Soil Sci.* 2002, **28**, 63–78.
- [10] Pohlman A.A. and McColl J.G.: *Soil Sci. Soc. Amer. J.* 1998, **52**, 265–271.
- [11] Tyler G.: *Forest Ecol. Manage.* 2005, **206**, 167–177.
- [12] Denaix L., Semlali M. R. and Huber R.: *5th Int. Conf. Biogeochem. Trace Elemen., Extend Abstr., ISTER, Wien 1995*, p. 938–939.
- [13] Heelmisaari H. S., Jerome J., Fritze H., Nieminen T., Palmgren P., Salemaa M. and Vanha-Majamaa I.: *Water Air Soil Poll.* 1995, **85**, 1727–1732.
- [14] Laskowski R., Niklińska M. and Maryański M.: *Water Air Soil Pollut.* 1995, **85**, 1759–1764.
- [15] McEnroe N.A. and Helmisaari H.S.: *Environ. Pollut.* 2001, **113**, 11–18.
- [16] Dobrzański J. and Byrdziak H.: *Zesz. Probl. Post. Nauk Roln.* 1995, **418**, 399–405.
- [17] Byrdziak H., Jędrzejewski J., Kierdel Z., Mizera A. and Nierzewska M.: *Environmental Protection – Bulletin 2002–2004. KGHM CUPRUM, Lubin, Poland 2005*, p. 1–170.
- [18] IUSS: *World Reference Base for Soil Resources. 2nd edition, World Soil Resources Reports 103, FAO, Rome 2006*, p. 1–122.
- [19] Rao C.R.M., Sahuquillo A. and Lopez Sanchez J.F.: *Water Air Soil Pollut.* 2008, **189**, 291–333.

ZAWARTOŚĆ I ROZPUSZCZALNOŚĆ METALI CIĘŻKICH W PRÓCHNICACH LEŚNYCH NA TERENACH ZDEGRADOWANYCH PRZEZ HUTNICTWO MIEDZI

Instytut Nauk o Glebie i Ochrony Środowiska
Uniwersytet Przyrodniczy we Wrocławiu

Abstrakt: Trzy stałe powierzchnie obserwacyjne, każda obejmująca po cztery punkty pobierania próbek, zlokalizowane w odległości 500, 1500 i 2100 m od źródła emisji zostały założone na obszarze zadrzewionym topolą wokół dużej huty miedzi w pobliżu Legnicy, w południowo-zachodniej Polsce. W próbkach próchnic nadkładowych pobranych w listopadzie 2007 r. analizowano całkowitą zawartość Cu, Zn, Fe, Ca i Mg oraz

zawartość form rozpuszczalnych w wodzie i $0,11 \text{ mol} \cdot \text{dm}^{-3}$ kwasie octowym. Całkowita zawartość miedzi w ściółce osiągała poziom $9590 \text{ mg} \cdot \text{kg}^{-1}$ suchej masy, a cynku – $4020 \text{ mg} \cdot \text{kg}^{-1}$ s.m. na powierzchni zlokalizowanej 500 m od huty i raptownie zmniejszała się wraz z odległością. Zawartość Fe, Ca i Mg w ściółkach również zmniejszała się wraz z odległością, lecz w znacznie mniejszym stopniu niż Cu i Zn. Do 0,5 % całkowitej zawartości Cu i do 1,2 % całkowitej zawartości Zn występowało w analizowanych ściółkach w formach rozpuszczalnych w wodzie destylowanej. $0,11 \text{ mol} \cdot \text{dm}^{-3}$ kwas octowy uwalniał nawet do 7,2 % całkowitej zawartości Cu i do 41 % całkowitej zawartości Zn oraz ponad 50 % całkowitej ilości Ca i Mg. Miedź i cynk są słabo rozpuszczalne w warunkach alkalicznego odczynu próchnic nadkładowych w drzewostanach topolowych, lecz jakichkolwiek naturalny lub antropogenny czynnik prowadzący do zakwaszenia ściółek może spowodować raptowny wzrost rozpuszczalności nagromadzonych metali ciężkich.

Słowa kluczowe: metale ciężkie, rozpuszczalność, przemysł miedziowy, ściółki leśne, zanieczyszczenie gleb