Speciation of Cu, Zn, and Pb in Soil Solutions Extracted from Strongly Polluted Soils Treated with Organic Materials

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Abstract

Five soils differently contaminated by emissions from copper smelters were treated with the organic materials lignite, compost, and sewage sludge. The concentrations of Cu, Zn, and Pb in soil solutions were measured after different incubation times within 30 days. Speciation of metals in soil solution was determined via modeling with Visual MinteQ. Soil amendment with all organic materials led to a temporary increase of Cu concentrations in soil solutions. Those effects and metal speciation in solutions were highly dependent on the kind of organic amendment that in particular affected pH and dissolved organic carbon concentrations in soils. Applying acidic lignite resulted in the release of free metal ions into the solution, while the application of immature compost led to the formation of metal complexes with soluble organic compounds. Soil amendment with limed, alkaline sewage sludge resulted in a strong increase in Cu concentrations in solutions due to the formation of ammine-Cu complexes. Principal component analysis confirmed that the main factors that determined solubility of metals in the experiment were pH and dissolved organic carbon concentrations in soil solutions. The strongest increase in metal solubility was observed directly after the application of amendments, and afterward the concentrations of metals in soil solutions started to decrease over time.

Keywords: contaminated soils, solubility, speciation, ammine-Cu complexes, dynamics

Introduction

Environmental risk caused by soil contamination with heavy metals is directly related to their transfer from solid phase into soil solution. Solubility of metals in contaminated soils, their phytoavailability, and toxic effects to biota depend on physical and chemical properties of soils – in particular soil texture, sorption capacity, pH, and organic matter content [1-2].

The strategies of soil remediation commonly used for large metal-contaminated areas are usually based on metals immobilization [3]. Various waste materials rich in organic matter may be used for this purpose, such as compost, sewage sludge, biochar, or lignite, as they have very high sorption capacity [4-8]. However, the use of non-stabilized organic fertilizers or biosolids, rich in dissolved organic carbon (DOC), can cause adverse effects in soils, and lead to increased solubility of metals [6, 9].

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Such effects were observed directly after the application of exogenous organic matter, and usually tended to wane with time, which is known as aging of contaminants [10]. The effects posed by metals onto soil biota depend on their speciation (ionic vs. complexed forms) in soil solution. Therefore, speciation studies are important from the standpoint of environmental risk assessment, as they provide an instrument for the prediction of metal fate and bioavailability [2, 11-12].

The aim of this study was to examine the changes in concentrations and speciation of Cu, Zn, and Pb in soil solutions acquired from soils contaminated by emissions from a copper smelter treated with organic materials commonly used as amendments in soil remediation: waste lignite, immature compost, and sewage sludge.

Experimental

Soil Material

Five large samples of topsoil (0-25 cm) material, each 250 kg, were collected from the surroundings of the Legnica Copper Smelter (Poland), highly contaminated with copper and other heavy metals [13-16]. Sampling sites were situated at different distances from the smelter so that the level of soil contamination varied considerably (Table 1). Soil material was air dried, homogenized, and sieved through a 10 mm sieve for incubation experiments in order to remove occasionally occurring large grains of gravel or artifacts. For laboratory analyses, soil samples were additionally sieved through a 2 mm sieve.

Basic soil properties were determined using the methods described by Tan [17]. Total concentrations of Cu, Zn, Pb, Ca, Mg, and K were measured by FAAS after digestion with concentrated $HClO_4$ in the open system with reflux. Total organic carbon (TOC) was determined by dry combustion (Ströhlein CS-MAT 5500) and total nitrogen using the Kjeldahl method. Water extracts of soils (m:v 1:10) were prepared for spectrofotometric determination of dissolved organic carbon DOC (Merck test 1.14878.0001) and extractable ammonium nitrogen [17].

Organic Amendments

Three kinds of organic amendments commonly used for greenery practice, horticulture, and land reclamation were used in the experiment: lignite LG, compost CO, and limed sewage sludge SS. Lignite was a granulated commercial product produced by the Turów Mine. Compost was a "ready-for-use" product produced from municipal green wastes in a two-stage process that involved three-day accelerated composting in a bioreactor followed by a three-week stabilization on heaps. Sewage sludge acquired from a municipal wastewater treatment plant in Wrocław was anaerobically digested and limed.

Incubation Experiment

Soils amended with organic materials (50 g per kg), as well as control soils (0) without amendments, were incubated in the 1 kg pots at constant moisture (85% of field water capacity). The samples of soil solution were collected repeatedly after 1, 2, 7, 14, and 30 days of incubation using MacroRhizon samplers supplied with 50 cm³ syringe plungers. Soil solution samples were filtered through 0.45 μm membrane filters, and the concentrations of metals, in particular Cu, Zn, and Pb, were determined by flame atomic absorption spectroscopy (FAAS). Soil solution pH was measured potentiometrically, $N-NH_4^+$ concentrations were determined with Nessler reagent [18], and DOC in soil solutions using Merck tests by spectrophotometric method [19] (as in soil extracts). For selected samples of soil solution, a more comprehensive analysis was performed to measure the concentrations

Table 1. Properties of soils and organic materials used in the experiment.

Materials		Distance from the smelter	Total concentrations in soils			TOC	pH	Concentrations in aqueous extracts (1:10, m:v), mg L⁻¹		Textural group	CEC
			Cu	Zn	Pb			DOC	N-NH₄		
		m	mg kg⁻¹			g kg⁻¹					cmol(+) kg⁻¹
Soils	1	150	5,180±150	368±13	1,148±49	9.0	7.38±0.01	85±5	16.2±0.08	SiL	19.5±1.7
	2	500	3,732±72	295±4.2	880±5	7.6	6.41±0.1	80±6	21.3±0.4	SiL	8.91±1.9
	3	880	1,686±140	174±15	862±26	13.0	5.22±0.04	180±18	17.1±0.02	SiL	16.6±2.7
	4	1070	531±18	94±2.2	156±2	6.6	7.00±0.05	140±9	28.5±0.5	SiL	11.8±1.6
	5	1300	301±12	79±1.5	93±7	9.3	7.15±0.07	160±12	14.6±0.08	SiL	19.3±1.2
Organic amendments	LG	-	4±0.2	8±0.4	4.2±0.3	620	4.54±0.05	16.5±2	300±24	n/d	39.2±3.7
	CO	-	267±3.6	89.7±2.3	34±1.8	240	6.73±0.08	273±21	250±15	n/d	73.3±4.6
	SS	-	121±2.5	319±4.8	29±1.6	280	9.61±0.03	4,230±203	7,000±90	n/d	58.5±5.6

n/d: not determined

of major cations Na$^+$, K$^+$, Ca^{2+}, and Mg^{2+} (determined by ICP-AES), and anions HCO$_3^-$, CO$_3^{2-}$, NO$_3$, Cl$^-$, and SO$_4^{2-}$ (determined by ion chromatography IC). The experiment was carried out in three replicates.

The concentrations of main components in soil solutions obtained from direct measurements were used to model metal speciation using the Visual MinteQ v. 3.1 program [20]. The Stockholm humic model (SHM) was applied as the one best fitting DOC properties. The data used for modeling were the means of measured parameters of three replicates.

The significance of differences between metal concentrations in the solutions obtained from different soils and various treatments after different incubation times was tested using Tukey's test carried out on normalized, log-transformed values. Complex relationships between the concentrations of metal species in solutions and other factors were analyzed using the principal component analysis (PCA) method and illustrated in related graphs using Statistica 12.0 software (StatSoft Inc.). A graphical presentation of variance analysis in figures was simplified so that only the values of standard deviation SD were shown as the error bars, to ensure the clearness of figures.

Results

The Properties of Soils and Organic Amendments

All five soils used in the experiment had texture similar to silt loams (soil texture was determined according to USDA classification; Table 1), and differed in the level of contamination. Copper concentrations in soils ranged from 301 to 5,180 mg kg^{-1}. Soils differed also in pH values, total organic carbon, and DOC concentrations, which was undoubtedly related to various characteristics of forest stands and various levels of litter decomposition.

Organic amendments used in the experiment differed greatly in their properties. Sewage sludge had a strongly alkaline reaction and the highest content of DOC and N-NH$_4^+$. Under such conditions, ammonium nitrogen

was easily transformed into gaseous ammonia. Compost indicated a relatively high DOC concentration at pH 6.73. Lignite contained small amounts of DOC and had high sorption capacity despite a relatively low pH. Lignite and compost contained negligible concentrations of Cu and Zn, and their application inconsiderably reduced soil concentrations of both metals due to the effect of dilution. A similar effect of Cu dilution was observed in SS-amended soils, while Zn concentrations in soil Nos. 2-5 increased slightly, as SS was rich in Zn [21]. This increase may, however, be considered negligible. The concentrations of Pb in all amendments were low, i.e., in the range 4.2-34 mg kg^{-1}.

Total Concentrations of Metals in Soil Solutions

The concentrations of metals in soil solutions depended mainly on the type of organic amendment and time of incubation (Figs 1-2). Graphical illustration of variance in Figs 1 and 2 was simplified so that only standard deviation values SD were presented as the error bars. Particularly high were the concentrations of Cu in soil solutions collected from SS-amended soils (Figs 1-2). The differences between amended and non-amended soils tended to decrease with time and only in the case of soils 2 and 4 amended with LG, CO, and SS did they remain significant after 30 days.

The highest concentrations of Cu were found in soil solutions of SS-amended soil Nos. 1 and 2, collected after two days of incubation (Figs 1-2; 632 and 669 mg L^{-1}, respectively). Copper concentrations in the solutions of soils amended with LG and CO were significantly lower; however, relatively intensive Cu desorption into solution occurred in LG-treated soils, particularly in soil No. 2. Soil amendment with CO caused an insignificant increase of copper concentrations in solutions collected from soils 4-5 compared to control treatments. In the case of soils 1-3 there was a significant increase of copper concentrations (Figs 1 and 2a).

Zinc and lead concentrations in soil solutions were apparently dependent on pH of soil solutions collected
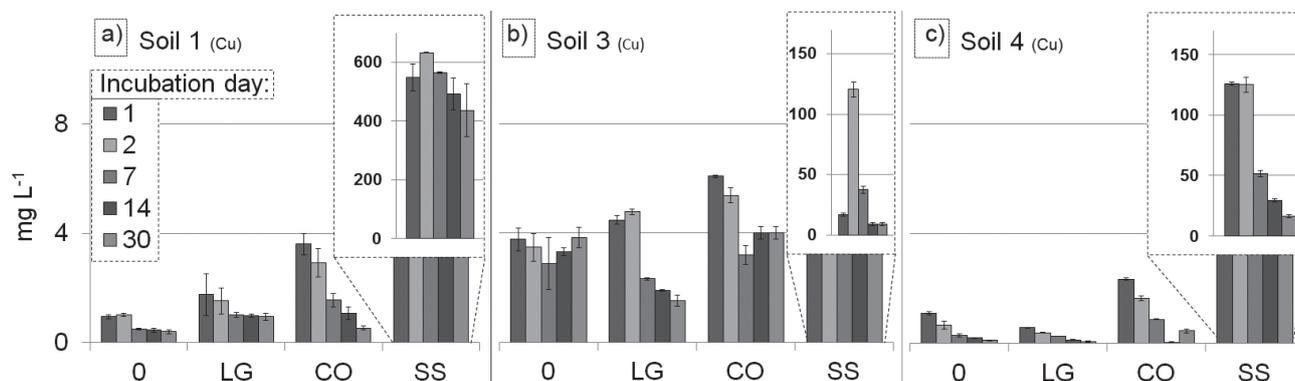

Fig. 1. Dynamics of copper concentrations (mg L^{-1}) in soil solutions acquired from soil Nos. 1 a), 3 b), and 4 c). Treatments: non-amended soils (0), soils treated with lignite (LG), compost (CO), and sewage sludge (SS). Error bars illustrate standard deviation SD.
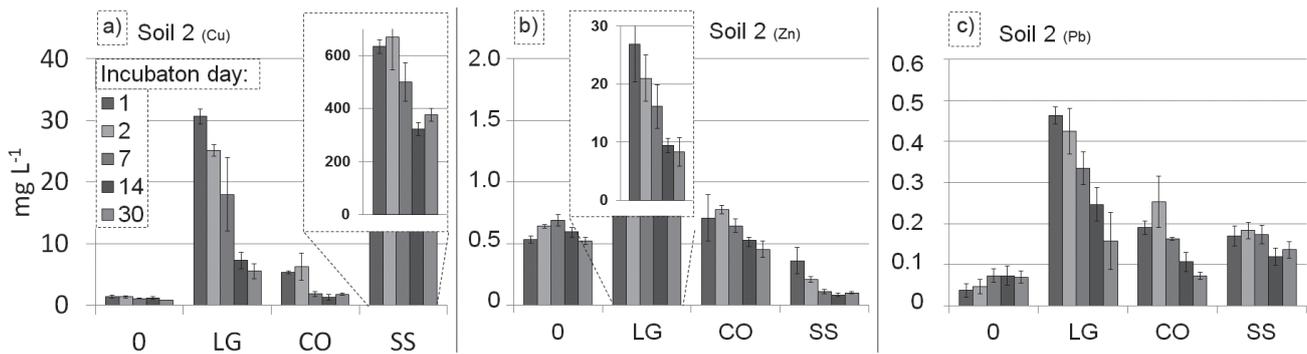
Fig. 2. Dynamics of copper a), zinc b), and lead c) concentrations (mg L^{-1}) in soil solutions acquired from soil No. 2 treatments: non-amended soil (0), soil treated with lignite (LG), compost (CO), and sewage sludge (SS). Error bars illustrate standard deviation SD.

Table 2. The percentage of various Cu, Zn, and Pb species in soil solutions collected on the second day of incubation from non-amended soils (0) and selected treatments. Data obtained from modeling with Visual MinteQ.

Species[a]	Soil No. 1				Soil No. 2		Soil No. 3		Soil No. 4		Soil No. 5	
	0	LG	CO	SS	0	LG	0	SS	0	CO	0	SS
Cu^{2+}	-	0.18	-	-	-	23.43	0.09	-	-	-	-	-
$CuOH^+$	-	-	-	-	-	1.45	-	-	-	-	-	-
$Cu_2(OH)_2^{+2}$	-	-	-	-	-	0.70	-	-	-	-	-	-
$Cu_3(OH)_4^{+2}$	-	-	-	-	-	0.03	-	-	-	-	-	-
$FA\text{-}Cu+2G(aq)$	-	-	-	-	-	0.09	0.02	-	-	-	-	-
$FA_2Cu(aq)$	68.7	82.0	64.9	0.3	64.2	42.9	90.3	7.72	77.4	57.5	70.0	1.21
$FACu^+(aq)$	0.17	1.52	0.09	-	0.49	28.5	7.05	-	0.2	0.03	0.10	-
$FA_2CuOH(aq)$	31	16.3	35	7.01	35.2	2.79	2.50	40.9	22.4	42.5	29.9	27.9
$Cu(NH_3)_4^{+2}$	-	-	-	86.0	-	-	-	40.9	-	-	-	66.2
$Cu(NH_3)_3^{+2}$	-	-	-	6.57	-	-	-	9.89	-	-	-	4.64
$Cu(NH_3)_2^{+2}$	-	-	-	0.1	-	-	-	0.47	-	-	-	0.05
Zn^{+2}	8.4	63.0	1.89	-	12.3	92.6	22.1	0.07	11.9	2.69	5.49	-
$ZnOH^+$	0.2	0.42	0.05	-	0.5	0.18	0.03	-	0.16	0.07	0.12	-
$Zn(OH)_2(aq)$	0.09	0.04	0.02	-	0.2	-	-	0.01	0.07	0.03	0.05	-
$FA\text{-}Zn+2G(aq)$	0.9	0.64	0.55	-	1.6	0.39	4.08	-	0.77	0.25	0.44	-
$FAZn^+(aq)$	17.8	18.4	12.9	-	25.6	6.59	63.4	0.68	17.6	7.26	10.9	-
$FA_2Zn(aq)$	72.6	17.5	84.5	0.34	59.8	0.25	10.4	13.9	69.5	89.7	83.0	0.64
$Zn(NH_3)_4^{+2}$	-	-	-	91.1	-	-	-	64.4	-	-	-	91.5
$Zn(NH_3)_3^{+2}$	-	-	-	8.17	-	-	-	18.3	-	-	-	7.57
$Zn(NH_3)_2^{+2}$	-	-	-	0.34	-	-	-	2.37	-	-	-	0.28
$ZnNH_3^{+2}$	-	-	-	0.02	-	-	-	0.37	-	-	-	0.01
Pb^{+2}	0.03	0.94	-	-	0.05	29.9	0.45	-	0.05	-	0.03	-
$PbOH^+$	0.02	0.17	-	-	0.05	1.47	0.02	-	0.02	-	-	-
$FA\text{-}Pb+2G(aq)$	-	-	-	-	-	0.13	0.08	-	-	-	-	-
$FAPb^+(aq)$	1.18	4.69	0.75	0.11	1.97	37.7	22.3	0.23	1.23	0.4	0.65	0.1
$FA_2Pb(aq)$	98.8	94.2	99.2	99.9	97.92	30.7	77.1	99.8	98.7	99.6	99.32	99.9

from treated soils. Zn solubility was strongly reduced in SS-treated soils. On the contrary, it increased significantly in LG-amended soil No. 2 (Figs 2b, 2c) and similarly in soil Nos. 1 and 3. Soil amendment with CO caused a slight increase in Zn concentrations in soil solutions compared to control, statistically significant only for soil Nos. 2 (Fig. 2b), 1, and 3. Solubility of Pb turned out to be much lower than that of Cu and Zn. Only trace concentrations of Pb (usually below 0.2 mg L^{-1}) were found in soil solutions. The largest increase of Pb solubility was observed in soil No. 2 after its amendment with LG (Fig. 2c).

Chelating properties of low molecular organic matter turned out to be the second factor, in addition to the pH of soil solution, that determined solubility of metals in soils. The concentrations of DOC in soil solutions differed greatly among the treatments. Soil amendment with those materials that contained large amounts of DOC, i.e., SS and CO, caused an increase of DOC concentrations in soil solutions. The highest DOC concentrations were present in soil solutions collected from SS-treated soils (4,030-8,010 mg L^{-1}). A statistically significant increase (even by six-fold) of DOC concentrations in solutions was also observed in CO-treated soils, while soil amendment with LG caused a decrease in solution DOC concentrations (except for soil No. 2).

It should be stressed that in all the treatments, metal concentrations in soil solutions decreased over time. A similar trend was also observed for DOC and pH values of soil solutions, except for DOC in soil solutions obtained from the most polluted soil No. 1.

Metal Speciation in Soil Solutions

The contributions of various species of metals in soil solutions (determined via modeling by MinteQ) did not differ significantly among non-amended soils (Table 2).

The forms of Cu, Zn, and Pb complexed with soluble organic compounds (featured in this paper as those bound to fulvic acids FA-Me$^+$ and FA$_2$Me) were predominant in solutions of non-amended soils, and their average contributions to total dissolved metals were as high as 98-99%, 55.5-96%, and 97-99%, respectively.

Soil amendment with compost did not significantly affect these speciation patterns, and metals complexed with organic compounds (FA-Me) were the predominant species in the solutions of CO-treated soils. However, their concentrations were higher than in soil solutions obtained from non-amended soils. Differently, soil treatment with lignite caused significant changes in metal speciation, i.e., a strong increase in contributions of ionic forms, particularly in soil solutions acquired from soils Nos. 1-3 (Table 2).

Speciation of Cu and Zn in soil solutions of SS-treated soils was also quite different from that in control treatments. Extraordinarily high were the contributions of ammine-metal complexes (Table 2), in particular in the solutions extracted from the most contaminated soils Nos. 1-3. The contributions of copper tetra-ammine complexes in total dissolved Cu reached values of 66-86%. The formation of easily soluble ammine-Cu complexes at high soil solutions pH and the presence of ammonia were responsible for extremely high concentrations of Cu in soil solutions of SS-treated soils (Figs 1-3). Similarly, although the predominant forms of Zn in soil solutions of SS-treated soils were tetra-ammine complexes, total concentrations of soluble Zn were lower compared to non-amended soils.

An additional characteristic feature of Cu speciation in soil solutions of control soils, as well as of LG and CO-amended soils, was relatively high contributions of mixed hydroxyl-organic complexes (FA$_2$CuOH$_{(aq)}$), present particularly at higher pH, i.e., in soil Nos. 1, 3, and 4 (Table 2).
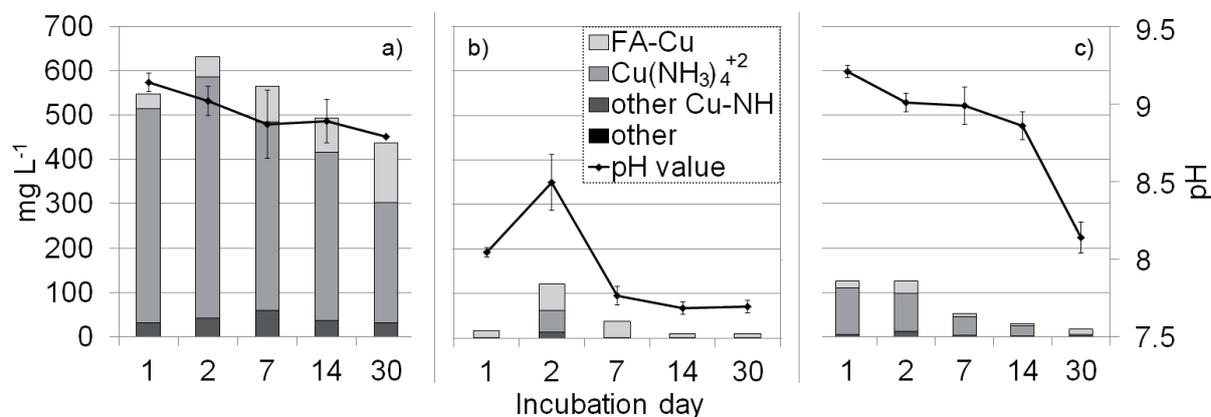

Fig. 3. The changes of Cu speciation (concentrations of the main Cu forms) in soil solutions during the incubation of SS-amended soil Nos. 1 a), 3b), and 4 c), as well as related pH values of soil solutions.
Explanations:
"Fa-Cu" stands for the sum of the following species: FA-Cu$^+$2G(aq), FA$_2$Cu(aq), FACu$^+$(aq), and FA$_2$CuOH(aq)
"other Cu-NH" stands for the sum of Cu(NH$_3$)$_3$$^{+2}$ and Cu(NH$_3$)$_2$$^{+2}$
"other" stands for the sum of CuOH$^+$, Cu$_2$(OH)$_2$$^{+2}$, and Cu$_3(OH)_4$$^{+2}$
Error bars illustrate standard deviation SD

Decreasing soil solution pH, observed in the course of the experiment in SS-treated soils, significantly affected the concentrations of ammine-Cu complexes $Cu(NH_3)_4^{2+}$ (Fig. 3), which decreased significantly over time. The importance of pH value of soil solutions for the formation of tetra-ammine Cu complexes is evident when comparing their concentrations in soil solutions obtained from SS-treated soil Nos. 3, 4 (Figs 3b and 3c), and 5.

Discussion

The release of metals from soil solid phase into solution and the patterns of their speciation in solutions apparently depended on numerous factors, the most important of which were soil solution pH value as well as the concentrations of DOC and ammonium-N in soil solution. These parameters tended to change with prolonged incubation time, causing changes in concentrations and forms of metals in soil solution. PCA analysis performed for the data obtained from the first two incubation days, both of non-amended soils (Fig. 4) and all the experimental treatments (Fig. 5), showed that total concentrations of Cu, Zn, and Pb in soils were of minor importance in determining their concentrations in soil solutions.

Total concentrations of copper and zinc in soil solutions were in non-amended soils primarily dependent on soil pH and DOC concentrations in soil solutions (Fig. 4). Many studies have documented a high affinity of copper, as well as zinc, to organic compounds [1, 11, 22-23]. In our study this affinity was reflected in high concentrations and high contributions of low molecular weight metal-organic complexes in soil solutions (Fig. 4). The solubility of Pb was much lower compared to Cu and Zn, despite its even stronger affinity to organic matter and very high contributions of FA-Pb species in solution. Generally low mobility of Pb in soils is a well-known fact as reported in numerous studies [1, 13].

Similarly to control soils, in those treated with organic amendments the solubility of metals was determined mainly by soil pH and DOC concentrations in soil solutions. However, the patterns of those relationships were contingent on the type of organic material and its particular interrelationships between pH and DOC. In the case of less polluted soils (Nos. 4 and 5), reduced concentrations of metals in soil solutions after LG-treatment should be assigned to a high sorption capacity of LG [5] coupled with reduced DOC concentrations in solutions (Fig. 1c) at neutral pH values. The opposite effect, i.e., increased concentrations of metals in soil solutions observed after CO-treatment, was associated with relatively high content of DOC, (2,730 mg kg^{-1}) in the compost used in the experiment. Increased solubility of Cu, Zn, and Pb caused mainly by their complexing with biosolids-derived DOC, has also been reported by several other authors [24-25].

An extremely high increase of copper concentrations in soil solutions after soil amendment with sewage sludge, as well as related rapid changes in Cu speciation, were associated with high concentrations of ammonium-nitrogen in sewage sludge. Although some other studies also reported increased solubility of copper in contaminated soils amended with alkaline waste materials such as sugar beet pulp, they did not reveal the mechanisms for this phenomenon in relation to copper speciation [26]. A characteristic dark blue color of solutions acquired from SS-treated Cu-contaminated soils confirmed the formation of specific ammine complexes at high pH: $Cu(NH_3)_4^{+2}$, $Cu(NH_3)_3^{+2}$, and $Cu(NH_3)_2^{+2}$. A high supply of ammonia and very high solubility of such complexes [27] were responsible for exceptionally high concentrations of Cu in soil solutions (up to 669 mg L^{-1}). The total content of Cu was the next significant factor that determined Cu concentrations in soil solutions obtained from SS-amended soils. The changes in speciation of Zn and Pb after soil amendment with SS were similar to those
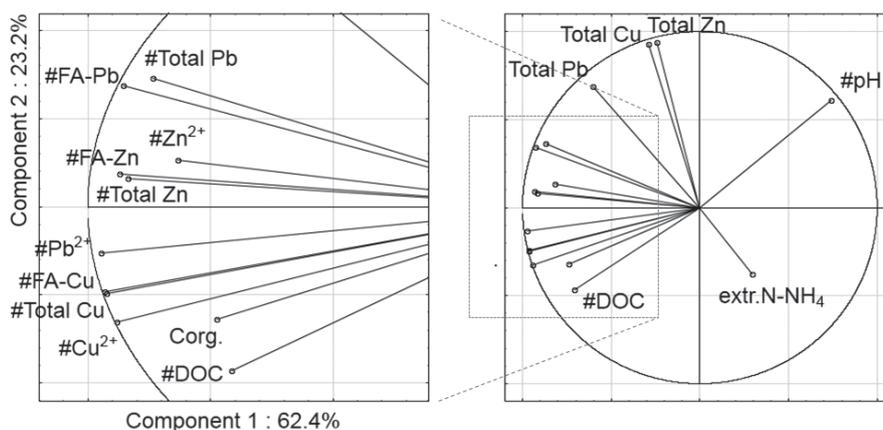

Fig. 4. PCA analysis of the variables illustrating speciation of Cu, Zn, and Pb in soil solutions obtained from non-amended soils during incubation (1, 2, 7, 14, and 30 days) as related to selected chemical properties of soils and soil solutions.
Explanations of symbols and abbreviations:
Total Cu, total Zn, Corg, etc, refer to soils; symbols preceded by "#" (e.g., #Cu, #pH, #DOC) refer to soil solutions.
The concentrations of Cu, Zn, and Pb species in soil solution: #FA-Cu: Cu complexed with DOC, #Cu^{2+}: ionic forms.

described for Cu, i.e., the ammine complexes of these metals were formed; however, this effect did not lead to increased concentrations of Zn and Pb in soil solutions, which is probably be explained by the relatively low solubility of those complexes.

The concentrations of Cu, Zn, and Pb in soil solution were particularly high within the first two days of incubation. Thereafter, they started to decrease in all the treatments and after a one-week incubation were significantly lower than in the first two incubation days, which was confirmed statistically for non-amended soils and LG and CO treatments. The decreasing trend over time may be attributed to hydrolysis of ionic species as well as all the processes referred to as aging of contaminants, for instance due to stabilization of organic matter. This effect was also associated with the pH value of soil solutions that tended to decrease as a result of buffering processes and microbiological activity (the release of CO_2 and organic acids). Another factor responsible for a decrease of metals solubility was a reduction of DOC concentrations in soil solutions, both due to the drop of pH and possible uptake of soluble organic compounds by microorganisms [10].

All the relationships discussed above were confirmed by PCA analysis. In the case of non-amended soils (Fig. 4), this analysis indicated that two components accounted for more than 85% of variation in the experimental results. Total concentrations of Cu and Zn in soil solutions of non-amended soils turned out to depend mainly on component 1 (62% of variation), which should probably be interpreted as an aggregate indicator of soil conditions – in particular soil pH and DOC. Component 2, of much lower importance (23%), was apparently related to total concentrations of metals in soils The solubility of metals in non-amended soils was strongly related to the concentrations of their particular species in soil solutions, i.e., metal complexes with low molecular organic acids (FA-metal forms) and also cationic forms (Fig. 4).

Similar patterns of metals speciation were reported from the field studies carried out in the research area [28]. In particular, a high contribution of metals (especially Cu) complexed with low molecular organic acids was proven to be characteristic for the forest soils of the research area [28]. It should be stressed, however, that two factors (pH and DOC in soils) apparently incorporated in principal component 1 were not clearly correlated with one another (R = 0.476). Therefore, there must have been an additional, unidentified factor that defined their relationships, undoubtedly associated with the type of organic matter originally present in soils.

In the case of soils treated with organic amendments (Fig. 5), the relationships between solubility of metals and soil or soil solution parameters were quite different from those described for non-amended soils. High concentrations of Cu in solutions were associated with FA-Cu, NH_4-Cu, and NH_4-Zn species, and corresponded with high pH values of soil solutions and high concentrations of DOC and ammonium ions, which has been indicated with grey area in the chart (Fig. 5). It should be stressed, however, that these parameters were first and foremost related to the type and properties of introduced organic matter. It is hence the properties of organic matter, and in particular its pH-related concentrations of DOC and N-NH_4, which should be interpreted as component 1 in PCA analysis, in control of soil capacity for complexing metals. It should also be stressed that the relationships between pH values and DOC concentrations in soil solutions of soils treated with organic matter were different from those typical for non-amended soils, and both these parameters were located in close proximity to one another in the PCA graph (Fig. 5).

Component 2 was apparently that associated with total concentrations of Zn and Pb in the solutions and their occurrence in cationic forms (another grey area). All other components of variance should be considered
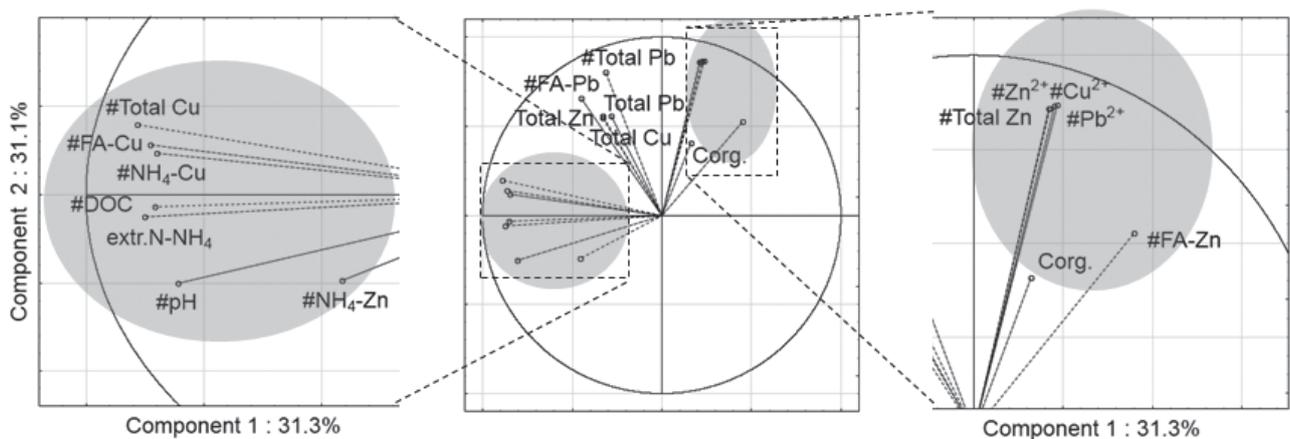

Fig. 5. PCA analysis of the variables illustrating speciation of Cu, Zn, and Pb as related to selected chemical properties of soils and soil solutions in all treatments (after first and second days of incubation). Two groups of interrelated factors are marked with grey color. Explanation of symbols and abbreviations:

Total Cu, total Zn, Corg, etc. refer to soils; symbols preceded by "#" (e.g., #Cu, #pH, #DOC) refer to soil solutions

The concentrations of Cu, Zn, and Pb species in soil solution: #FA-Cu: Cu complexed with DOC, #Cu^{2+}: ionic forms, #NH_4-Cu: ammine complexes

negligible, as each of them contributed to less than 5% of total variance in metal solubility.

PCA analyses, the results of which are presented in Figs 4 and 5, were performed using the analytical data from the first two days of incubation, where the effects of soil amendment with organic materials on metals mobilization were the strongest. A similar analysis based on the data from later stages of incubation (not shown in this paper) [21], indicated that the character of relationships between the main factors that governed metals solubility changed noticeably and became much more similar to the relationships presented for non-amended soils. This fact clearly corresponds with the aging of contaminants, i.e., the effects described earlier.

Conclusions

The pH of amended soils was confirmed to be a crucial factor that determines solubility of metals in polluted soils, the importance of which may be even greater than that of total soil concentrations of metals. At low pH, metals indicate increased solubility due to the release of their cationic forms or formation of complexes with DOC. At high pH and high concentration of ammonium nitrogen, copper solubility in polluted soils may also increase dramatically due to the formation of ammine-Cu complexes.

Based on this research, we can expect that various kinds of exogenic organic matter, rich in low molecular weight organic fractions with potential complexing capacity, may be – regardless of pH – responsible for the increasing solubility of metals in contaminated soils and the associated growth of environmental risk.

The considered application of alkaline organic waste materials rich in nitrogen, such as limed sewage sludge, to Cu-rich soils must be preceded by detailed studies focused on possible changes of pH-DOC relationships in soils and soil solutions, and the likely formation of highly soluble ammine-Cu compounds.

The strongest effects caused by soil amendment with organic materials and the related release of metals into soil solution are observed within the first few days after which soil conditions tend to stabilize and metal solubility decreases. Nevertheless, temporally increased metal concentrations in soil solutions should not be neglected, as they may have strong adverse effects on soil biota.

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