

Copper, Zinc, and Lead Fractions in Soils Long-Term Irrigated with Municipal Wastewater

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Long-term irrigation with municipal wastewater may lead, even in spite of intense farming, to an accumulation of organic matter, nutrient elements, and trace metals in soils. Excessive increases of heavy metals may pose a potential risk to the food chain and provoke restrictions for the further cultivation of sensitive crops. Copper (Cu), zinc (Zn), and lead (Pb) forms in soils under long-term irrigation (for 100–120 years) with treated wastewater of Wrocław were investigated by using selective seven-step sequential extraction (procedure of Zeien-Bruemmer) for partitioning the metals into operationally defined fractions, likely to be released in solution under various environmental conditions. The largest fraction of Cu, Pb, and particularly Zn in nonirrigated (control) soils was strongly bound in a residual form, while the percentage of exchangeable and the most labile fractions were negligible. Total concentration of metals in irrigated soils was elevated, and significant redistribution of metals among phases was observed. Percentages of residual fraction of Cu and Pb were no more than 25% (Zn < 40%), while significantly increased contribution of fractions occluded on iron (Fe) oxides and organically bound Cu. Exchangeable and readily mobile forms of Zn are predominant zinc fractions in soils irrigated with wastewater.

Keywords Mobility, sequential extraction, trace elements

Introduction

The reduced availability of water resources in several regions of Europe requires an efficient use of supply sources. Municipal (urban) wastewater, after initial treatment to minimize health hazards, may constitute an important resource for irrigation in areas characterized by intensive agriculture (Lin, Shacahr, and Banin 2004; Mapanda et al. 2005; Meli et al. 2002). Irrigation with municipal wastewater delivers to soil the considerable amounts of organic matter as well as macro- and micronutrients, which are in part currently taken by intensely growing plants, but in part are accumulated in soil (Singh et al. 2009; Wang et al. 2003). It is widely reported that long-term and/or intense treatment of the soil with urban wastewater or sewage sludge often results in increased concentrations of some phytotoxic trace metals in surface horizon of soils (Ahumada et al. 1999; Fitamo, Itana, and Olsson 2007; Lucho-Constantino et al. 2005; Mireles et al. 2004; Shomar, Muller, and Yahya 2005). The concentrations exceeding admissible level of metals in arable soils may

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pose a potential risk to the food chain and provoke restrictions for the cultivation of crops that are sensitive to or known to accumulate heavy metals.

Measurement of the total concentration of metals provides rather inadequate information on bioavailability or toxicity of metals (Kabata-Pendias 2001). An evaluation of total metal levels following a strong acid digestion of soil may be useful as a general indicator of contamination, but it provides little indication of metal's bioavailability, mobility, and reactivity in soils, particularly soils treated with wastewater, sludge, and other organic fertilizers (Baltreinaite, Sereviciene, and Paliulis 2009; Dudka and Chlopecka 1990; Han et al. 2000; Jakubus and Czekala 2001). Therefore, the speciation of metals in soil may help to assess the bioavailable metal fractions and the risk of mobilization of metals bound to particular soil constituents (Narwal and Singh 1998). Both single and sequential extraction methods are used in the study of the fate of environmental pollutants. Conceptually, specificity of single extractants can be improved by combining them into a series of sequential extractions. Residue from a first extraction is used for the second extraction and so on through a number of stages (Rao, Sahuquillo, and Lopez Sanchez 2008). Therefore, solid materials can be successively partitioned into specific fractions extracted selectively by using series of appropriate reagents (Tessier, Campbell, and Bisson 1979). Several procedures, varying in manipulative complexity, have been proposed for determining the speciation of metals (Rao, Sahuquillo, and Lopez Sanchez 2008). However, following increasing interest in an application of sequential extraction, several threats are distinguished: limited selectivity of the extractants, redistribution of elements among phases during extraction, and limited comparability of data obtained by several investigators (Ahnstrom and Parker 1999; Gworek and Mocek 2003). Also, the traditional system of the fractions classification may lead to some confusion, suggesting an unrealistic selectivity of the extractants used. The sequential separation of metal species is therefore defined on an operational basis and as such has been widely used in various environmental studies (Bacon and Davidson 2008).

Until now, several studies have been conducted on the total concentration and chemical forms of trace elements in soils irrigated with municipal wastewater. Reported periods of long-term irrigation vary generally between 10 and 50 years (Fitamo, Itana, and Olsson 2007; Lucho-Constantino et al. 2005; Mapanda et al. 2005; Mireles et al. 2004; Shomar, Muller, and Yahya 2005), and only single papers give information about effects of irrigation prolonged over 70 years (Wang et al. 2003). The objective of this study was to examine the concentration and chemical fractions of copper (Cu), zinc (Zn), and lead (Pb) in the surface layer of soils that have been irrigated with municipal wastewater for more than 100 years.

Materials and Methods

Irrigation with wastewater, an operational part of urban sewage treatment plant of the town of Wroclaw (southwestern Poland) started in 1881 on the initial area of 415 ha and was successively extended in years 1921–1934 to the present-day 1050 ha. Raw municipal sewages are initially cleaned in sedimentation ponds before their introduction on irrigation lodgings. Treated wastewater is applied by short-time flooding repeated twice per month (during the vegetation period). The load of municipal wastewater reached 5000 mm/year until 1998 and gradually decreased to about 2000 mm/year in 2004, after construction of a new central biological wastewater treatment plant.

The irrigation area is located within the administrative borders the town Wroclaw, in a regulated and drained section of the Odra River valley, generally protected from natural

flooding. The parent materials of soils are alluvial in origin, commonly sandy and loamy textured. Gleyic Cambisols (IUSS Working Group WRB 2007) prevail in soil cover of the area; however, Gleyic Phaeozems and Gleyic Arenosols locally occupy larger surfaces. Natural groundwater table is permanently lowered by drainage down to 0.7–2.0 m below ground level. Virtually all soils have redoximorphic mottling within profiles, but surface horizons are generally well drained and free of gleyic or stagnic properties (as defined by IUSS Working Group WRB 2007). Temperate type of regional climate is characterized by the mean annual temperature of about 8.5 °C, and the mean annual precipitation circulates around 580 mm. The irrigated area is under permanent agricultural use as grasslands moved two- or three-fold per year. Hay yielding is very variable, between 10 and 15 tons of dry matter per hectare, depending of soil properties, intensity of irrigation, and mowing frequency. The control sites (nonirrigated with wastewater) are located on grasslands in an immediate neighborhood.

The surface soil samples (0–15 cm) were collected in five locations (sites S1–S5) where application of municipal wastewater by flooding is being practiced for minimum 100 years. Two additional soil samples (sites S6 and S7) were collected on an adjacent area, not irrigated with wastewater, as controls. Each representative site sample was prepared by mixing 10 soil samples (collected around a central sampling point on each site) to overcome local soil variability.

Soil samples were air dried, ground, and passed through a stainless steel 2-mm sieve. Particle-size analysis was determined by sieve and hydrometer methods, following pretreatments to remove organic matter and chemical dispersion with sodium hexametaphosphate (Gee and Bauder 1986). Total organic carbon (C) was determined by dry combustion using an automatic apparatus CS-mat 5500 (Ströhlein, Germany). Soil pH was measured potentiometrically in 1:2.5 suspensions of soil and distilled water (Van Reeuwijk 2002). Total concentrations of Zn and Cu were measured by atomic absorption spectrophotometry (AAS), and Pb was determined by inductively coupled plasma (ICP-OE) in extracts obtained by digestion of soil samples with aqua-regia mixture (hydrochloric acid + nitric acid as 3 + 1) in a microwave oven (ISO 11466; ISO Geneva Switzerland). The quality of determinations has been monitored using soil reference materials (sample ID: SRM 2709, SRM 2711, RTH 912, RTH 953) with certified total concentration (“aqua-regia extractable”) of trace elements being analyzed.

Although the classical Tessier scheme and the standard BCR (European Community Bureau of Reference) scheme of sequential extraction are presently the most frequently used and adopted methods (Rao, Sahuquillo, and Lopez Sanchez 2008), the seven-step sequential extraction scheme of Zeien and Bruemmer (1989) was applied in this study to determine the fractions of metals [zinc (Zn), copper (Cu), lead (Pb), and additionally iron (Fe)]. A brief summary of the procedure is presented in Table 1. The sequential extraction of Zeien and Bruemmer (1989) enables more detailed partitioning of metals as compared to the BCR procedure, particularly among reducible fractions. It separates metals (i) easily reducible [bound to manganese (Mn) oxides], (ii) bound to amorphous Fe oxides, and (iii) bound to crystalline Fe oxides that may give useful information in soil under changing redox conditions (Naumeister, Krueger, and Schneider 1997), in detailed pedological studies (Lair, Gerzabek, and Haberhauer 2007; Wilcke and Kaupenjohann 1997) and in geochemical studies on freshly weathered materials (Kabala and Szerszen 2002; Schuwirth et al. 2007). Slightly acidified hydroxylamine hydrochloride releases metals mainly from amorphous Mn oxides phases with little attack on Fe oxide phases (Shuman 1982). Extraction in ammonium oxalate (at pH 3.0–3.25) in the dark has been widely used to dissolve Fe oxides and release bound trace metals. This step is placed after extraction of

Table 1
Summary of the sequential extraction for metal fractionation according to Zeien and Bruemmer (1989)

Fraction	Description	Extracting agent	pH	Reaction time and temperature
F1	mobile	1 M ammonium nitrate	not buffered	24 h, temp. 20 °C
F2	exchangeable	1 M ammonium acetate	6.0	24 h, temp. 20 °C
F3	Easily reducible/ bound to manganese oxides (MnOx bound)	1 M hydroxylammonium chloride (NH ₂ OH-HCl) + 1 M ammonium acetate	6.0	30 min, temp. 20 °C
F4	Oxidizable/ organically bound	0.025 M ammonium ethylenediaminetetraacetate (NH ₄ EDTA)	4.6	90 min, temp. 20 °C
F5	Reducible/occluded on amorphous iron oxides (amorphous FeOx bound)	0.2 M ammonium oxalate (in dark)	3.25	4 h, temp. 20 °C
F6	Reducible/occluded on crystalline iron oxides (crystalline FeOx bound)	0.2 M ammonium oxalate + 0.1 M ascorbic acid	3.25	30 min, temp. 96 ± 3 °C
F7	Residual	Aqua regia (conc. HCl + HNO ₃ , 3 + 1)	—	—

organically bound metals in the Zeien and Bruemmer procedure, as complexing capacity of oxalate may result in leaching of metals associated with organic matter. Although sodium dithionate (in combination with sodium citrate and sodium bicarbonate, DCB) has been widely used for the reduction of both crystalline and amorphous Fe oxide phases, it is little used for heavy-metal studies because of contamination of the dithionite and the possibility of precipitation of metal sulfides (Gibson and Farmer 1986). The solution of ammonium oxalate with ascorbic acid may be successfully used for dissolution of crystalline Fe oxides when it follows extraction of amorphous Fe oxides with ammonium oxalate (in the dark). It offers several advantages over the DCB reagent, because it can be achieved with a high degree of purity, and does not attack silicates (Rao, Sahuquillo, and Lopez Sanchez 2008; Shuman 1982). The Zeien–Bruemmer procedure replaces hydrogen peroxide with ethylenediaminetetraacetic acid (EDTA) for extraction of organically bound metals, placed between release of easily reducible and more readily reducible phases (Table 1). In some cases, oxalate produced during oxidation with hydrogen peroxide can attack Fe and Mn oxyhydroxides and release metals sorbed on clays (Rao, Sahuquillo, and Lopez Sanchez 2008). Other methodological advantages of the Zeien–Bruemmer procedure

is one-directional gradient of pH change during extraction and replacement of reagents bearing metallic cations with ammonium ion, which reduces possible interferences when the atomic absorption spectrophotometry (AAS) method is used for analysis of extracts.

All metal extractions in this study were carried out in triplicates. Concentrations of Cu, Zn and Fe in the soil extracts were determined by AAS, and concentrations of Pb by inductively coupled plasma (ICP-OE). Complete results of Cu, Zn, and Pb fractionation are presented in Tables 2–4, and the concentration of Fe released from amorphous oxide phase (Fe_{am}) and crystalline oxide phase (Fe_{cr}) is indicated in Table 5.

Necessary statistical calculations (arithmetic means, correlation coefficients, homogeneous groups by Duncan's multiple range test, etc.) have been carried out using the Statistica 8 software (Stat Soft Inc., Tulsa, Okla., USA).

Results and Discussion

Soil Properties

Soil textures are related to the alluvial origin of soil materials and range among sites from sand (site S1) and sandy loam (sites S2–S4) to loam (site S5), with clay contents ranging from 1 to 9%. The texture of soils in control sites (S6 and S7) is sandy loam (Table 5). Soil reaction is apparently less acidic in soils irrigated with municipal wastewater as compared to control soils, at pH_{H_2O} ranging from 5.3 to 7.2 in irrigated soils, and pH_{H_2O} 4.5 to 5.2 in nonirrigated grassland soils (Table 5). Organic C content varies considerably among sites from 8.9 to 36.0 g kg⁻¹ in a weak relation to soil texture. The difference between mean organic C contents in five irrigated and two control soils (23.2 and 22.4 g kg⁻¹, respectively) is not statistically significant.

Total Concentrations of Trace Elements

The ranges of metal concentration in soils irrigated with municipal wastewater were apparently wide (Table 5); however, Zn amounts were in all samples significantly greater (154.1–329.0 mg kg⁻¹) than concentrations of Cu (14.9–53.0 mg kg⁻¹) and Pb (18.1–34.0 mg kg⁻¹). Similar rule was found in control soils, however, on the considerably lower level of total concentration: Zn 39.4–72.4 mg kg⁻¹, Cu 20.4–23.0 mg kg⁻¹, and Pb 11.3–14.5 mg kg⁻¹ (Table 5). These data indicate significant enrichment of irrigated soils with trace elements, in particular with Zn. Highly elevated Zn content in soils irrigated with wastewater is often reported as important source of environmental and health risk (Mapanda et al. 2005; Wang et al. 2003; Fitamo, Itana and Olsson 2007; Usman and Ghallab 2006).

Total concentrations of Zn, Cu, and Pb in soils irrigated with wastewater are related to the content of clay, organic C and amorphous Fe oxides (Fe_{am}). Despite high values of the coefficients, the correlations are in general not significant, probably due to insufficient number of cases (Table 6). Apparent, but statistically not significant, correlations between clay content and organic C, as well as clay and Fe oxides (Fe_{am} in particular) were found. It may indicate that listed before correlations between metals and soil properties are, to some extent, secondary effects of sorption ability conditioned by soil texture.

Sequential Extraction of Trace Elements

Recovery of metals in sequential extraction ranges from 99 to 125%, indicating good agreement between sum of all fractions and the total concentration of a particular metal,

Table 2
Fractions of zinc (mg kg^{-1}) in soils irrigated with municipal wastewater (sites S1–S5) and nonirrigated (sites S6 and S7)

Sampling site	F1 mobile	F2 exchangeable	F3 easily reducible	F4 bound to organic	F5 bound to amorphous FeOx	F6 bound to crystalline FeOx	F7 bound to silicates	Sum F1÷F7	Recovery index ^a
S1	28.6	35.0	9.7	15.2	14.3	25.6	24.7	152.8	0.99
S2	21.5	37.9	18.2	23.4	29.7	27.1	53.6	211.4	1.04
S3	31.8	61.2	28.8	34.1	37.1	20.3	61.0	274.3	1.07
S4	11.4	6.0	6.4	9.6	26.7	37.8	70.2	168.1	1.03
S5	79.4	46.7	23.1	28.7	37.2	42.6	78.2	335.9	1.02
S6	0.2	0.9	2.1	2.1	1.4	2.4	32.4	41.5	1.05
S7	4.9	2.8	6.0	5.2	2.2	3.6	52.5	77.2	1.07

^aRecovery index: proportion of the sum of all fractions to the total concentration determined directly (by digestion with aqua regia).

Table 3
Fractions of copper (mg kg^{-1}) in soils irrigated with municipal wastewater (sites S1–S5) and nonirrigated (sites S6 and S7)

Sampling site	F1 mobile	F2 exchangeable	F3 easily reducible	F4 bound to organic	F5 bound to amorphous FeOx	F6 bound to crystalline FeOx	F7 bound to silicates	Sum F1÷F7	Recovery index ^a
S1	<0.1	0.6	0.2	5.9	4.7	2.2	3.5	17.1	1.15
S2	0.9	1.9	1.2	19.5	8.1	0.7	8.3	40.6	1.25
S3	1.3	3.9	2.3	27.8	11.3	0.9	9.5	57.0	1.08
S4	0.9	0.6	0.8	10.9	6.1	1.7	6.3	27.3	1.14
S5	1.1	0.8	0.9	15.2	9.6	2.3	10.4	40.3	1.14
S6	<0.1	0.1	0.1	7.0	5.3	1.9	9.5	23.9	1.17
S7	<0.1	<0.1	0.6	6.9	6.2	2.3	10.8	26.8	1.16

^aRecovery index: proportion of the sum of all fractions to the total concentration determined directly (by digestion with aqua regia).

Table 4
Fractions of lead (mg kg^{-1}) in soils irrigated with municipal wastewater (sites S1–S5) and nonirrigated (sites S6 and S7)

Sampling site	F1 mobile	F2 exchangeable	F3 easily reducible	F4 bound to organic	F5 bound to amorphous FeOx	F6 bound to crystalline FeOx	F7 bound to silicates	Sum F1÷F7	Recovery index ^a
S1	<0.1	1.6	2.4	3.1	4.3	2.8	2.3	16.5	1.18
S2	<0.1	0.5	1.6	5.2	6.1	2.9	4.6	20.9	1.15
S3	<0.1	0.7	1.8	4.6	6.2	2.5	6.2	22.0	1.11
S4	0.5	1.7	7.6	6.5	7.2	4.8	6.4	34.7	1.12
S5	0.5	3.0	14.2	5.8	3.1	3.5	6.8	36.9	1.08
S6	<0.1	0.1	1.2	3.4	3.5	2.4	6.0	16.6	1.14
S7	<0.1	<0.1	1.8	2.0	1.9	2.5	5.5	13.7	1.21

^aRecovery index: proportion of the sum of all fractions to the total concentration determined directly (by digestion with aqua regia).

Table 5
Selected properties of soils irrigated with municipal wastewater (sites S1–S5) and nonirrigated (sites S6 and S7)

Site	Grain-size (mm) distribution (%)			pH	Organic carbon (g kg ⁻¹)	Fe _{am} (g kg ⁻¹)	Fe _{cr} (g kg ⁻¹)	Total concentration (mg kg ⁻¹)			
	2.0–0.05	0.05–0.002	<0.002					Zn _t	Cu _t	Pb _t	
S1	98	1	1	6.2	8.9	0.8	4.4	154.1	14.9	13.1	
S2	73	22	7	5.6	19.3	4.1	17.8	203.2	32.6	18.1	
S3	73	20	7	6.1	36.0	4.2	18.8	255.6	53.0	19.8	
S4	67	29	4	7.2	22.1	5.1	5.1	163.3	24.0	31.1	
S5	54	37	9	5.3	29.5	4.9	3.4	329.0	35.5	34.0	
S6	72	18	10	4.5	20.8	4.6	4.9	39.4	20.4	14.5	
S7	64	21	15	5.2	23.9	8.1	8.4	72.4	23.0	11.3	
Mean	73.0a	21.8a	5.6a	6.1a	23.2a	3.8a	9.9a	221.0a	32.0a	23.2a	
S1–S5											
Mean	68.0a	19.5a	12.5b	4.9b	22.4a	6.4b	6.7b	55.9b	21.7b	12.9b	
S6–S7											

Notes.

Fe_{am}: iron in amorphous/poorly crystalline oxides (data from the sequential extraction, fraction F5).

Fe_{cr}: iron in crystalline oxides; amorphous oxides not involved (data from the sequential extraction, fraction F6).

Lowercase letters denote homogeneous groups of Duncan's multiple range test (differences between means significant at $P < 0.05$).

Table 6
Coefficients of correlations among total contents of Zn, Cu, and Pb and selected properties of soils irrigated with wastewater

	pH	Organic carbon	Fe _{am}	Fe _{cr}	Zn _t	Cu _t	Pb _t
Clay	-0.62	0.79	0.75	0.36	0.87	0.75	0.53
pH		-0.19	0.02	-0.21	-0.70	-0.33	0.06
Organic carbon			0.73	0.40	0.74	0.92*	0.49
Fe _{am}				0.17	0.50	0.54	0.80
Fe _{cr}					0.05	0.69	-0.45
Zn _t						0.65	0.53
Cu _t							0.14

*Correlation coefficient significant at $P < 0.05$.

measured directly (Tables 2–4). There was also good reproducibility between the three replications of the sequential fractionation (data not shown). These results are in agreement with Tessier, Campbell, and Bisson (1979), who concluded that the precision and accuracy of the sequential extraction procedure was inherently good, the limiting factor being the heterogeneity of the sample.

Zinc in control soils is predominately found in the residual fraction, strongly bound to silicates (68–78% of total Zn). In soils irrigated with wastewater only, from 16.2 to 41.8% of total Zn is in silicate-bound forms (Table 2, Figure 1), and the lowest percentage of residual fraction was found in sandy-textured soil (site S1). Zinc, in general, primarily exists in strong association with silicates in soils not irrigated or short-term irrigated with sewage wastewater (Fitamo, Itana, and Olsson 2007), and the transformation of Zn from residual fraction to easily labile forms clearly depends on the period of soil amendment (Lucho-Constantino et al. 2005). Amounts of Zn occluded on Fe oxides (sum of fractions F5 and F6) in control soils (sites S6 and S7) are greater than those organically complexed (fraction F4). Such pattern of Zn distribution (Zn residual > Zn reducible > Zn organically complexed) reported by Han et al. (2000) is probably typical in most uncontaminated soils (Narwal and Singh 1998). However, in soils irrigated with sewage wastewater, the content of Zn occluded on Fe oxides exceeds two- to four-fold the amount of Zn complexed by organic matter (Table 2). Zinc bound to Fe oxides forms up to 38.4% of total Zn (site S4), while Zn organically complexed forms maximally 12.4% of total Zn (site S3). Considerable amounts of Zn, in ranges from 36.7 to 48.1% of total Zn (43.4% on average), exist in the labile forms (fractions F1 mobile + F2 exchangeable + F3 easily reducible) in most amended soils. The proportion of labile forms is significantly lower in control soils—7.8% and 17.7% of total Zn—at sites S6 and S7, respectively. Labile forms are predominated by exchangeable F2 fraction (up to 23% of total Zn). Only at site S5 does the fraction F1 mobile apparently dominate, which individually forms 23.6% of total Zn. The labile fractions determine, in general, the total concentration of Zn in soils irrigated with wastewater. Lucho-Constantin et al. (2005) stated that even short-term irrigation with wastewater may result in significant increase of labile Zn fraction. Long-term use of sewage wastewater or sewage sludge may lead to significant accumulation of Zn in nonresidual fractions: oxidizable (Fitamo, Itana, and Olsson 2007) or exchangeable, reducible, and oxidizable as found by Usman and Ghallab (2006). Han et al. (2000) reported up to 47.3% of total Zn in the easily reducible oxide fraction in soils amended with sludge over a long

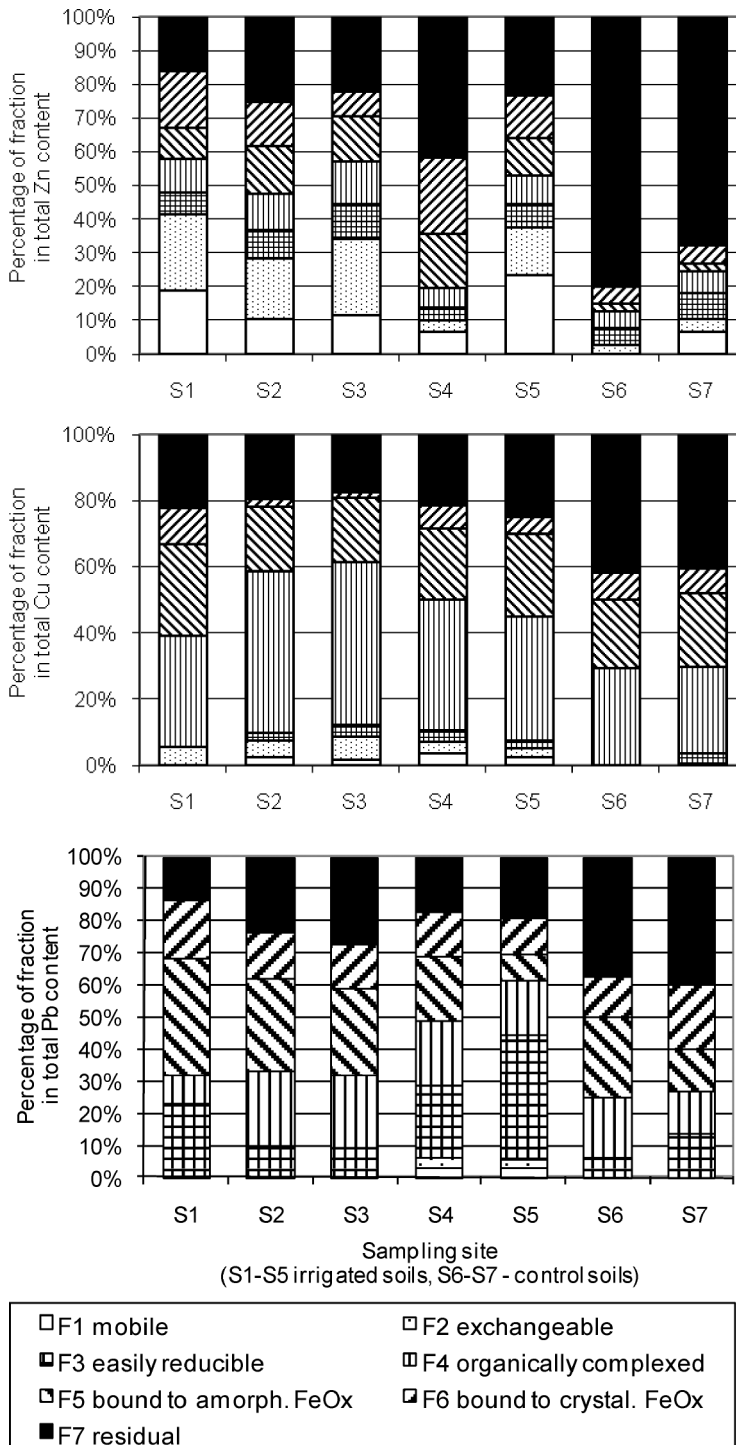


Figure 1. Relative contribution of Zn, Cu, and Pb fractions in soils irrigated with wastewater (sites S1–S5) and nonirrigated control soils (sites S6 and S7).

term. Ottosen, Hansen, and Jensen (2009) documented rapid desorption of Zn following little acidification of industrially polluted soils dominated by “mobile” (mainly exchangeable) forms on Zn. Therefore, the presented data suggest that Zn in soils under long-term irrigation with municipal wastewater is potentially bioavailable and mobile, which could pose threat for crops and groundwater quality.

Long-term irrigation of soils with wastewater has not resulted in drastic elevation of total Cu concentration in soils, nor essential rearrangement of Cu distribution among fractions. The largest amount of Cu is primarily strongly associated with silicates, but the proportion of Cu in residual fraction in control soils does not exceed 40.3% of total Cu (Figure 1). The content of silicate-bound Cu exists in most soils, both irrigated and non-irrigated, within a narrow range of 8–11 mg kg⁻¹, but the amount of Cu in nonresidual forms increased considerably in soils irrigated with wastewater, which resulted in a relative decrease of the proportion of metal bound in the residual fraction to 16.7–25.8% of total Cu (instead of 40% in control soils). The best visible effect of irrigation is the increase of an absolute amount of organically complexed Cu (Table 3). Although in control soils 25.7–39.4% of total Cu resides in organically bound fraction, in soils irrigated with wastewater up to 48.8% of total Cu exists in this form. Oxide-bound Cu is raised in irrigated soils only to a little extent, and thus the proportion of this fraction diminished slightly from 30.3–31.8% of total Cu in control soils to 21.7–29.6% in soils under irrigation. Copper bound to amorphous/poorly crystalline Fe oxides (fraction F5) predominates over Cu occluded on crystalline Fe oxides (fraction F6) in all soils. Long-term irrigation with wastewater resulted in formation of an easily soluble Cu pool, predominantly exchangeable, but their total percentage does not exceeded 10% of total Cu in any soil. The amount of easily labile fractions in control soils is negligible (Table 3). Little proportion of “labile” Cu and greater accumulation of the metal in organically complexed form are evidence of low mobility of Cu in soils irrigated with wastewater. Other authors report more often accumulation of Cu in the oxidizable fraction (organically bound) in soils under long-term irrigation with wastewater (Fitamo, Itana, and Olsson 2007) and amended with sludge (Han et al. 2000; Shrivastava and Banerjee 2004). However, in soils under short-term irrigation with sewage wastewater, the exchangeable fraction of Cu is preferentially raised (Usman and Ghallab 2006).

Lead primarily resides in the silicate-bound fraction that covers up to 40.1% of total Pb in nonirrigated soils (Figure 1). The reducible form is the second important Pb fraction primarily containing from 31.1 to 35.6% of total Pb (or even up to 45% if including Pb readily reducible/bound to Mn oxides). No significant predominance in Pb fixation of amorphous or crystalline oxides was found in nonirrigated soils. Furthermore, up to 20.1% of total Pb in the control soils is complexed by organic matter, and the amount of easily labile Pb forms is negligible (Table 4). The content of Pb in the residual fraction in soils irrigated with municipal wastewater is rather stable, on the level of 4.6–6.8 mg kg⁻¹ (with an exception of 2.3 mg kg⁻¹ in the sandy soil S1), and considerably higher are the amounts of Pb in nonsilicate associations: reducible (Fe-oxide-bound) and oxidizable (organically complexed). The Fe-oxide-bound fraction, on amorphous oxides in particular, containing from 34.6 to 45.6% of total Pb is the predominant form of Pb in soils under irrigation. Poorly crystalline Fe is generally considered a more active pool in the adsorption of trace elements, due in part to higher specific surface area compared to crystalline Fe oxides (Karczewska, Szerszen, and Kabala 1998). Furthermore, the large proportion of Pb in some soils, up to 38.5% of total Pb in site S5, exists in an easily reducible fraction (Figure 1). Finally, in soils under long-term irrigation with municipal wastewater, Pb accumulates preferentially in reducible fractions (bound to MnOx, amorphous and crystalline FeOx),

and those combined percentages may exceed 56% and 66% of total Pb in loamy and sandy soils, respectively. Similar strong affinity of Pb to the reducible fraction was found by Fitamo, Itana, and Olsson (2007) and Shrivastava and Banerjee (2004). The proportion of Pb in easily labile fractions (“mobile” and “exchangeable”) is negligible in all soils under investigation.

Conclusions

The present study indicates that long-term irrigation (more than 100 years) with initially treated municipal wastewater has resulted in an increase of the total levels of trace metals in soils, Zn in particular. The increases of Cu and Pb are usually found in less-soluble forms (Cu in oxidizable/organically bound fraction, Pb in reducible/bound to Fe oxides fractions), while Zn accumulates predominantly in easily soluble fractions. The patterns of metal distribution among operationally defined fractions in soils irrigated with treated municipal wastewater were found as follows:

- Zn: exchangeable + mobile > residual > reducible (FeOx-bound) > organically complexed > easily reducible (bound to MnOx);
 Cu: organically complexed >> reducible (FeOx-bound) > residual >> exchangeable + mobile > easily reducible; and
 Pb: reducible (FeOx-bound) >> residual = organically complexed > easily reducible >> exchangeable + mobile.

These data suggest that long-term irrigation with treated wastewater of the town of Wrocław did not contaminate soils with Pb and Cu. Metals accumulated in surface horizons have limited potential mobility and bioavailability and do not threaten food chain or groundwater quality. However, elevated total concentrations of Zn and predominance of easily soluble fractions could pose a risk to the groundwater quality and provoke the restrictions for the potential cultivation of crops that are known to accumulate heavy metals. The results indicate highly useful fractionation scheme by Zeien and Brummer (1989) to examine the main chemical associations of the metals in soils under irrigation. However, further investigation is recommended to explain the influence of seasonal reducing conditions on the forms, mobility, and bioavailability of trace metals in soils irrigated with urban wastewater.

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