

# Mobilisation of heavy metals in soils on a former sewage treatment farm.

By

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## Abstract

Soil solution composition in a sandy Anthrosol of a former sewage treatment farm was investigated over a four year period, starting 12 years after land application of sewage effluents had ceased. The heavy metal accumulations in the soils of the 1400 ha farm are characterized by a large spatial variability, with some "hot spots" of Cu, Zn and Cd reaching topsoil-concentrations of up to 1233, 3584 and 173 mg kg<sup>-1</sup>, respectively. The soil at the study plot is acidic (pH 4.8 in 0-38 cm) and has a negative pH-gradient with depth. Cd-, Cu- and Zn-concentrations in the soil solutions from 50, 100 and 180 cm are extremely high and showed a negative trend with time, especially at lower depths. For Zn and Cu, concentrations increased with depth, showing that no immobilization occurs in the subsoil due to the low pH and lack of mineral or organic sorption sites. From the temporal trends and depth gradients of nitrate and sulfate it is concluded, that topsoil acidification is due to intensive mineralisation and nitrification, whereas subsoil acidification appears to be caused by the oxidation of metal sulfides.

## Introduction

For a long time, land treatment of sewage effluents was a common practice in many countries such as Germany, Great Britain or Australia until a few years ago and still is practiced in some countries as an inexpensive and efficient method to decrease surface water pollution with nutrients and contaminants (Schirodo et al. 1986, Siebe & Fischer 1996). But as with the application of sewage sludge and other biosolids (McBride 1995), this can be associated with the accumulation of heavy metals and organic contaminants in the soils (Blume et al. 1980, Hoffmann et al. 1998). In agricultural soils, where pH is generally controlled by liming and where fresh sorption sites are regularly added with organic matter from biosolids or crop residues, the risk of heavy metal mobilisation for plant uptake or leaching is low (Williams 1984, McBride et al. 1997). But the role of soluble organic complexing agents is still unclear as they may increase heavy metal solubility even at neutral pH (McBride et al. 1997). Heavy metal mobilisation and the associated risks can therefore be expected to occur especially in soils with low pH and few sorption sites.

In the vicinity of Berlin, large areas have been used for the disposal of raw sewage effluents from 1870 up to the 1980s. Originally all fields were under agricultural use, thus utilizing the nutrients and the additional water (300-500 mm a<sup>-1</sup>) for crop production. Due to increasing sewage water production and the lack of treatment plants, in the early 1960s an area of about 1400 ha in the north of Berlin was converted to a pure sewage disposal fields, then receiving up to 11 000 mm a<sup>-1</sup> of untreated sewage effluents. This practice ended in 1985 and the area was graded, ploughed and afforested. Extensive soil surveys and analyses in the early 1990s showed high heavy metal concentrations in large parts of the area (Schlenter et al. 1996) and

thus initiated the present study, where the mobility and translocation of heavy metals with the soil solution was investigated.

### Materials and Methods

The study area is located in a rural area in the north of Berlin, about 20 km from the city center. Here, a ground moraine consisting of marl and loamy deposits is covered by 2-6 m of sandy glacial till from the Weichselian glaciation. Groundwater level is between 2 and 5 m depth. Natural soils found in the area are Cambisols and Podisols, but due to the long-term waste water irrigation and agricultural use, soils of the sewage farm are classified as Anthrosols and Regosols, depending on the accumulation of sludge-derived organic matter. The vegetation consists mainly of couch grass (*Agropyron repens*), since only few of the trees (mainly *Populus spec.*) planted in 1985 have survived. Average annual rainfall is 580 mm leading to a calculated groundwater recharge of 150-200 mm yr<sup>-1</sup>.

Heavy metal concentrations in the topsoil of the area are extremely variable and the different mean and median values shows that the distribution of the data is highly left-skewed (Tab. 1). This is caused by the former irrigation scheme, where several fields along a gentle slope were connected in a cascade. The raw sewage waters entered this cascade at the topmost position where the particulate organic components containing most of the heavy metals readily sedimented. Fields in lower slope positions thus received much lower organic matter and heavy metal loads.

**Tab. 1: Heavy metal concentrations (mg kg<sup>-1</sup>) in the topsoil (0-10 cm) of the former sewage treatment farm near Berlin (N = 298).**

	Cd	Cr	Cu	Ni	Pb	Zn
minimum	0,1	1	3	1	6	13
maximum	44,3	1850	876	285	452	3584
mean	4.4	210	73	14	74	225
median	2.0	128	49	9	59	153

The study plot is located within a former top-position field and some soil characteristics are listed in Tab. 2. The sandy material contains less than 2 % clay and silt in all horizons. The top 38 cm consist of a thoroughly mixed A-horizon and overly an old sludge layer with extremely high C<sub>org</sub>- and heavy metal concentrations. Below 45 cm depth, only C-material without any indications of pedogenesis is found and heavy metal concentrations are in the range of natural geogenic values (Blume et al. 1980). One important characteristic of the soil profile are the acidic conditions and the negative pH-gradient with depth. This is commonly found in the area and indicates strong top- and subsoil acidification processes since the termination of waste water application, when soil reaction was near neutral.

**Tab. 2: Characterisation of the Hortic Anthrosol from sandy glacial till.**

Depth [cm]	pH (CaCl <sub>2</sub> )	C <sub>org</sub> [g kg <sup>-1</sup> ]	CEC [mmol <sub>c</sub> kg <sup>-1</sup> ]	BS [%]	Cd	Cu [mg kg <sup>-1</sup> ]	Pb	Zn
0-38	4.8	61	100	48	18.0	247	452	874
-45	4.7	241	291	51	172.8	1232	562	2040
-110	4.4	3	18	26	1.7	20	7	61
-180	4.1	1	16	16	0.2	11	3	26

On a 10 m x 10 m study plot near the profile, ceramic suction cups were installed in 1993 in three depths (50, 100, 180 cm) with 12 replicates for each depth. Vacuum (-300 to -500 hPa)

was applied manually every two weeks and soil solution collected the next week. Samples were analyzed for pH with glass electrode, for cations (Ca, Mg, K, Na) and heavy metals (Cd, Cu, Zn, Pb) with flame and flameless AAS and for anions ( $\text{Cl}^-$ ,  $\text{NO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ) with ion chromatography. DOC was determined as  $\text{CO}_2$  with IRGA after combustion at  $450^\circ\text{C}$ .

### Results and Discussion

Table 3 summarizes the results of the soil solution analyses from 1993-1998. As shown by the large differences between minimum and maximum values for practically all parameters, the data is highly variable, both in time and space. Still, certain differences between depths and temporal trends are detectable, some of which are illustrated in Figures 1-4. As in the soil profile data (Tab. 2), the mean pH of the soil solution decreases with depth. This was most pronounced during the first two years (1994-1995) of measurement. In 1996, pH decreased in this depth and approached values of the soil solutions from 100 and 180 cm. In this context, the lowest pH-values of all solutions (pH 3.2) were recorded in 50 cm depth at some sampling dates in 1997.

**Tab 3: pH and element concentrations [ $\text{mg L}^{-1}$ ] in the soil solution from three depths of the study plot. Mean, maximum and minimum from 12 replicates of monthly samples from 1993 to 1997.**

		pH	DOC	$\text{NO}_3$	$\text{SO}_4$	Al	Cd	Zn	Cu
<b>mean</b>	50 cm	4.7	33	57	543	1.7	0.11	5.1	0.22
	100 cm	4.3	21	75	1167	6.5	0.11	20.4	0.42
	180 cm	4.1	21	146	1398	27.7	0.09	21.0	1.93
<b>min</b>	50 cm	3.2	7	1.3	0	0.2	0.01	0.1	0.01
	100 cm	3.6	10	2.2	147	0.6	0.00	0.4	0.03
	180 cm	3.6	10	10.2	39	1.6	0.01	1.1	0.07
<b>max</b>	50 cm	6.9	122	478	4360	6	0.67	79	2.22
	100 cm	5.7	85	978	2750	28	1.40	118	3.11
	180 cm	5.6	85	889	3070	93	0.38	68	8.30

Since external acid inputs are only moderate in the area (Marschner et al. 1998), internal acid production from mineralization processes must cause this pH-drop and the acidification of the profile. During nitrification, acid is produced and will contribute to soil acidification when leached below the rooting zone (Strebel et al. 1988). Evidence for this process is found in the nitrate concentrations which reached extremely high maximum values close to  $1000 \text{ mg L}^{-1}$  in 1994 in some suction cups from 100 and 180 cm depth (Fig. 1). Obviously, the organic matter from sewage residues with its narrow C:N-ratio of 10-12 is easily mineralized and the amount of nitrate released greatly exceeds plant demands. However, the decreasing nitrate concentrations in 180 cm since 1995 may indicate that easily mineralizable organic matter is depleted or that nitrification in the topsoil is reduced due to the lowered pH, so that the high concentrations in 1994 are only remnants of an earlier high nitrification activity.

The high sulfate concentrations occurring in the soil solutions can also be caused by intensive mineralisation of organic matter (Marschner 1993). However, the time course of  $\text{SO}_4$ -concentrations (Fig. 2) shows that concentrations are always much higher in 100 and 180 cm than in 50 cm, without any apparent time trend or seasonality. This concentration increase with depth can partly be caused by water uptake and sulfate discrimination by roots in the topsoil, as revealed by comparison with the conservative anion Cl that increases by roughly 50 % between 50 and 180 cm. However, the increase in sulfate concentrations with depth greatly exceeds this factor (Tab. 3, Fig. 2) and since it persists throughout the observation period it can not be caused by earlier sulfate-fluxes from the topsoil as with nitrate.

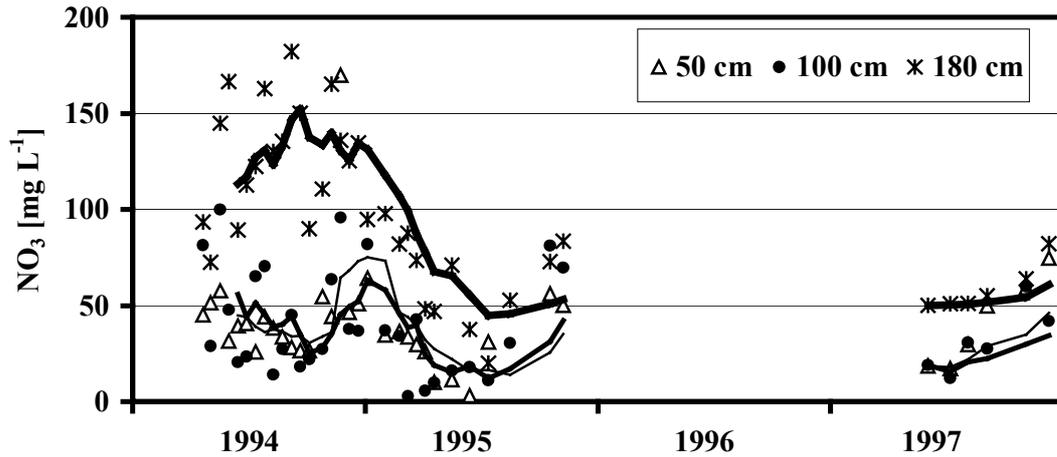


Fig. 1: Median nitrate concentrations in the soil solutions during the observation period from three depths. Lines represent moving averages of five data points. Data from Dec. 1995 - April 1997 is missing due to analytical problems.

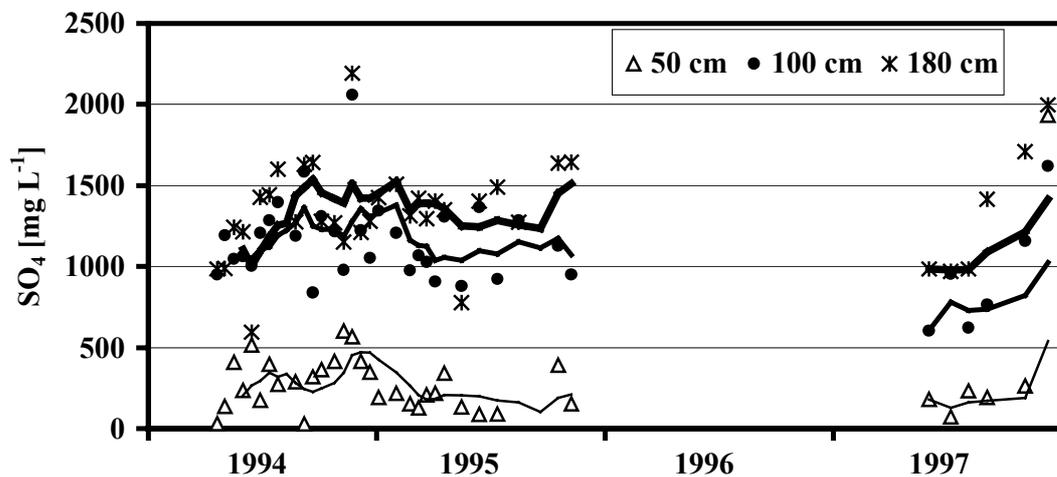


Fig. 2: Median sulfate concentrations in the soil solutions during the observation period from three depths. Lines represent moving averages of five data points. Data from Dec. 1995 - April 1997 is missing due to analytical problems.

We therefore conclude, that sulfate concentrations in the subsoil are controlled by either desorption processes or the dissolution of some mineral phase. Desorption is unlikely, since the subsoil is poor in Fe-oxides and organic matter and therefore provides only very few binding sites for anions. A mineral phase could be metal sulfides (such as FeS), that would have accumulated during waste water application, when groundwater tables were close to the surface and redox-conditions probably were highly anaerobic due to the continuous influx of easily degradable organic matter. The oxidation of these sulfides in response to falling groundwater tables would also explain the low pH-values of the subsoil, since sulfuric acid is produced during this reaction.

Another possible mineral phase as source for  $\text{SO}_4$  would be Al-hydroxo-sulfates, such as jurbanite, alunite and basalunite (Prenzel 1983). The dissolution of such minerals would also explain the elevated Al-concentrations in soil solutions from 100 and especially 180 cm depth (Tab. 3). However, these minerals rather form than dissolve under acidic conditions and high  $\text{SO}_4$ -concentrations. If they were the source of the elevated  $\text{SO}_4$ -concentrations, subsoil pH should have been lower and/or sulfate concentrations higher during waste water application, which is unlikely.

The concentrations of Cd, Zn and Cu are extremely high in all depths (Tab. 3), and greatly exceed the current test-values ("Prüfwerte") of the German soil protection law which calls for further risk assessment at soil solution concentrations above 0.005, 0.5 and 0.05 mg L<sup>-1</sup> for the three heavy metals, respectively (BBodschV 1999). Cd-concentrations are very similar in all depths (Tab. 3) and show no temporal or seasonal trends. They are correlated with Zn and Cu in all depths (R = 0.5 - 0.8) and correlated with pH in 50 cm (R = -0.38\*) and even closer in 180 cm (R = 0.57\*\*).

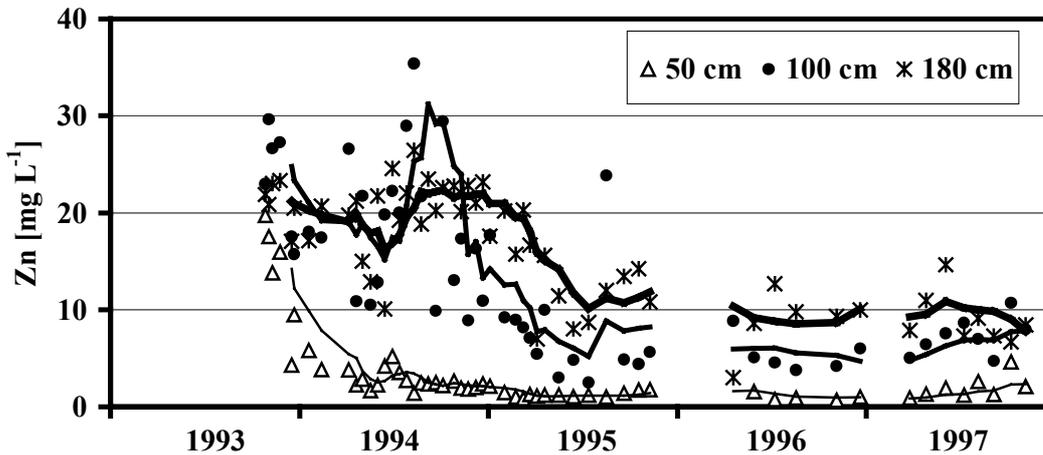


Fig. 3: Median zinc concentrations in the soil solutions during the observation period from three depths. Lines represent moving averages of five data points.

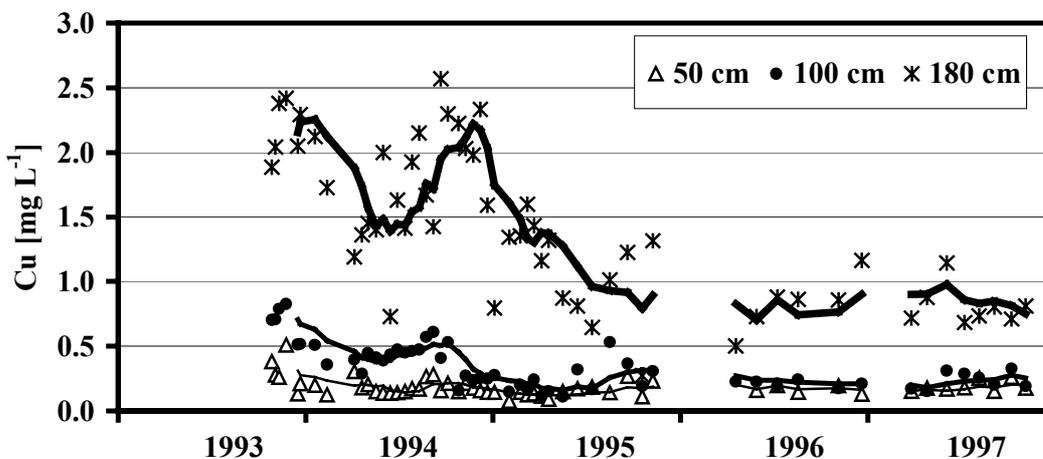


Fig. 4: Median copper concentrations in the soil solutions during the observation period from three depths. Lines represent moving averages of five data points.

In contrast, Zn-concentrations show a distinct differentiation with depth and time (Tab. 3, Fig. 3). When measurements started in late 1993, Zn-concentrations were around 20 mg L<sup>-1</sup> in all depths but in 50 cm declined within 6-8 months to median values below 5 mg L<sup>-1</sup>. About one year later, Zn-concentrations in the other two depths also decreased but remained 3-4 times higher than those of 50 cm until the end of the observation period. In 50 and 180 cm, Zn-concentrations correlate with pH, but the relationship is rather poor (R = -0.4 and -0.6 respectively).

Copper concentrations also decline with time, with the most pronounced changes occurring in 180 cm (Fig. 4), but they remain always higher than in 50 and 100 cm. In 100 cm, Cu-concentrations were initially higher than in 50 cm, but since 1995, no more differences are

observed. Cu-concentrations significantly correlate with pH only in 180 cm ( $R = -0.7$ ), and Cu is the only heavy metal that correlates with DOC ( $R = 0.5$  in 50 cm). Otherwise no significant relationships between solution parameters were identified.

The reasons for elevated Zn- and Cu-concentrations in 180 cm are still poorly understood. It appears, as if these derive from a source in the subsoil, although no heavy metal accumulations were found there (Tab. 2). Heavy metal containing minerals such as sulfides or Al-hydroxo-sulfates could however be present locally and thus control sulfate and heavy metal concentrations. On the other hand, elevated heavy metal concentrations could be only remnants of earlier mobilization phases and would then be leached further downward within the next years. From the calculations of the water budget this seems unlikely, since the annual groundwater recharge of 150-200 mm is sufficient to exchange the whole water-filled pore volume down to 200 cm. But recent experiments have shown, that infiltration can be very heterogeneous due to the hydrophobicity of the organic material in the topsoil (Hoffmann in prep.) so that certain soil volumes may not be percolated for long times.

In any case, the results show that the subsoil has no filtering ability for heavy metals mobilized in the topsoil. Countermeasures to reduce heavy metal mobility and downward movement can therefore only be directed towards immobilization in the topsoil. This is currently being tested in a 100 ha field test and remediation project by surface application and incorporation of  $5500 \text{ t ha}^{-1}$  of carbonaceous loamy marl (Boeken et al. 2000).

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Tab. 4: Composition of groundwater extracted from the capillary fringe in 360-380 cm depth on the study plot.

	<b>pH</b>	<b>DOC</b>	<b>NO<sub>3</sub></b>	<b>SO<sub>4</sub></b>	<b>Al</b>	<b>Cd</b>	<b>Zn</b>	<b>Cu</b>
Oct. 1993	4.5	ND	350	900	24.0	0.68	30.3	1.83
Apr. 1996	4.5	11	160	280	9.3	0.09	8.3	2.53
Jul. 1997	4.5	13	181	256	5.3	0.08	6.2	1.85
Jun. 1998	4.3	ND	ND	ND	4.4	ND	9.4	2.35