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DYNAMICS OF HEAVY METALS IN SOILS OF A REED BED SYSTEM

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Heavy metal balances of a reed bed system (soil pH > 7, carbonate content about 30%) continuously flooded with sewage during 5 years indicate that only Pb, Zn, Cd and Cu were partly stored in the soil. Strong reductive conditions, high sewage percolation and metal complexation with soluble organic compounds caused a considerable leaching of Fe, Mn, Ni and Cr from the soil and formation of amorphous iron oxides. The results indicate that continuously flooded reed bed systems with high percolation rates are not suitable for the elimination of heavy metals. Conversely, it should be possible to purify metal contaminated soils through percolation of sewage with low metal content.

KEY WORDS: Heavy metals, reed bed system, soil, sewage, redox potential, heavy metal complexation.

INTRODUCTION

Reed beds are regarded as low cost systems for purifying sewage in rural areas, aiming at a removal of C and N through microbial activity and plant-uptake, and storage of P and heavy metals through adsorption or precipitation within the soil.^{1–3}

This study aims to evaluate the capacity of a rural reed bed system in Austria for the elimination of heavy metals from sewage of different quality (raw sewage, settled sewage, biologically treated sewage). Therefore, we investigated changes in metal contents and speciation in the soil of a reed bed after a period of five years (1984–1989).

The main mechanism of heavy metal retention in soils is the adsorption on soil compounds, increasing with pH and the contents of organic matter, clay minerals and Fe-, Mn- and other oxides.⁴ The decrease of redox potential through flooding of soils^{5,6} causes changes of the metal solubility. Flooding of acid (pH 4.5–6.8) soils increased the contents of DTPA-soluble Fe- and Mn, and decreased those of DTPA-Cu and DTPA-Zn,⁷ whereas the contents of Fe²⁺ and Mn²⁺ in the solution of soils with high pH (6.4–8.0) increased.^{8,9} Sims and Patrick¹⁰ found greater amounts of Fe, Mn, Zn and Cu soluble with Na-acetate and pyrophosphate in flooded soils compared to well-aerated ones. Conversely, the amounts of Fe, Mn, Zn and Cu in the water- and oxalate-soluble fractions were greater in soils with high Eh.¹⁰

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The solubility of heavy metals generally is increased by complexation with soluble organic matter, exceeding inorganic equilibria.¹¹ Metal complexation by soluble organic matter increases with increasing pH¹² and with decreasing Eh.¹⁰ At very low Eh-values the formation of sulfides¹³ can favour the precipitation of heavy metal sulfides.¹⁴ Discontinuous flooding of soils with sewage increased total contents of heavy metals.¹⁵

As shown, mobility of heavy metals can decrease as well as increase through flooding of soils, depending on their physico-chemical characteristics. Therefore, no reliable prediction of heavy metal behaviour in the soil was possible when starting the reed bed system in 1984.

MATERIALS AND METHODS

Characteristics of the reed bed system

The experimental plant was installed in Mannersdorf/Leitha, Lower Austria, and planted with *Phragmites australis* in 1983.¹⁶ Figure 1 shows a plan of the experimental site.

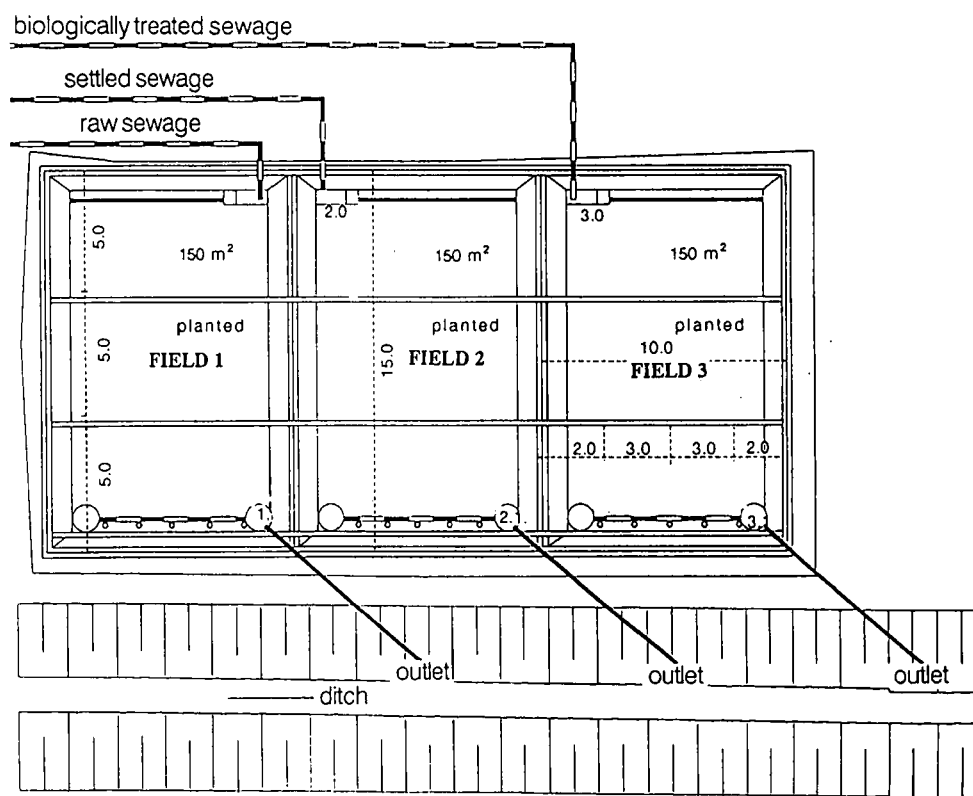


Figure 1 Plan of the experimental site.

The reed bed was divided into three fields (length 15 m, width 10 m, depth 0.9 m) onto which different kinds of sewage were applied since June 1984. Field 1 was fed with raw sewage, field 2 with settled sewage and field 3 with biologically treated sewage. The feed rates ranged from 30–50 mm day⁻¹, corresponding to sewage charges of 6000 l day⁻¹ field⁻¹ (field 1), 5850 l day⁻¹ field⁻¹ (field 2) and 4800 l day⁻¹ field⁻¹ (field 3), respectively. Each field was subdivided into 3 plots—plot 1 at the inlet, plot 2 in the middle and plot 3 at the outlet of the fields.¹⁶

In 1984 the soil texture was silty clay loam,¹⁷ the *k_f*-values ranged between 10⁻⁵ and 10⁻⁶ m s⁻¹.¹⁸ The bulk densities were 1100 kg m⁻³ (0–30 cm), 1200 kg m⁻³ (30–60 cm) and 1300 kg m⁻³ (60–90 cm).

Table 1 shows the chemical characteristics of the soils before starting the system in 1984. Due to the contents of clay, organic carbon and amorphous oxides of Fe and Mn, the high CEC as well as the high pH indicated a high adsorption capacity for heavy metals.¹² Facing the high content of CaCO₃, the precipitation of heavy metal carbonates was also thought to eliminate heavy metals from sewage.

Table 1 Chemical characteristics of the soils in the reed bed system (1984)

Field/plot	Depth cm	pH(CaCl ₂)	CaCO ₃ %	Fe _o ^a mg kg ⁻¹	Mn _o ^b mg kg ⁻¹	OC ^c %	CEC ^d mequ kg ⁻¹
1/1	0–30	6.6	35.6	7290	110	5.35	336
	30–60	6.8	32.0	5120	180	5.24	253
	60–90	6.9	28.1	3400	180	2.25	222
1/2	0–30	6.7	32.4	6770	150	4.51	295
	30–60	6.9	30.4	4990	190	4.79	315
	60–90	7.1	26.0	3720	230	2.19	234
1/3	0–30	6.5	33.5	5740	150	4.75	285
	30–60	6.7	31.2	4590	180	4.26	316
	60–90	6.8	27.5	3700	280	2.83	214
2/1	0–30	6.7	33.9	9190	130	6.11	252
	30–60	6.9	31.8	5140	200	5.39	312
	60–90	7.0	28.7	3310	140	3.13	189
2/2	0–30	6.8	32.2	7690	150	6.26	306
	30–60	7.0	28.3	4740	180	5.51	315
	60–90	7.1	24.3	3370	170	3.27	179
2/3	0–30	6.8	30.4	8590	150	5.93	319
	30–60	6.9	32.0	5740	160	4.42	315
	60–90	6.9	26.2	5770	160	3.19	169
3/1	0–30	6.6	32.7	8970	140	5.58	356
	30–60	6.8	31.0	5440	220	5.42	330
	60–90	7.1	25.0	3540	200	2.86	177
3/2	0–30	6.7	34.5	8270	150	5.60	304
	30–60	6.6	29.7	6270	240	5.48	303
	60–90	7.0	22.9	3970	240	3.05	261
3/3	0–30	6.6	31.6	9670	160	6.27	232
	30–60	6.8	30.2	5520	200	4.07	149
	60–90	7.1	22.9	3560	230	2.50	161

^a Ammonium oxalate soluble iron.

^b Ammonium oxalate soluble manganese.

^c Organic carbon.

^d Cation exchange capacity.

Analytical procedures

Soil samples were taken at three depth intervals (0–30 cm, 30–60 cm and 60–90 cm). For each plot 20 subsamples were mixed for laboratory analysis, air-dried and passed through a 2 mm sieve. Results were calculated on oven dry matter (105°C).

Bulk density was determined using 200 cm³ cores, pH in 0.01 M CaCl₂ (soil:solution ratio, 1:2.5) after 24 hours with ORION glass electrode, total carbon by dry combustion and IR-detection of CO₂, carbonate content by dissolution with 10% HCl and volumetric measurement of CO₂, organic carbon (OC) calculated by the difference of total carbon and carbonate carbon, CEC in 0.1 M BaCl₂ (soil:solution ratio 1:20) after 2 hours extraction, heavy metal contents in aqua regia¹⁹ and 0.05 M EDTA,²⁰ amorphous Fe- and Mn-oxides in ammonium oxalate.²¹

Elements were measured by plasma emission (DCP) or atomic absorption (AAS).

Calculation of heavy metal balances

Heavy metal balances were calculated for all depth intervals of each plot based on the changes of the heavy metal contents between 1984 and 1989 and summed up for the soil depth 0–90 cm, following the equation 1.

$$MB = (C_{1984} - C_{1989})BD0.3/1000 \quad (1)$$

where,

MB = heavy metal balance for the depth intervals 0–30 cm, 30–60 cm and 60–90 cm, respectively [g m⁻²]

C₁₉₈₄ and C₁₉₈₉ = heavy metal content for 1984 and 1989 [mg kg⁻¹]

BD = bulk density [kg m⁻³]

0.3 = thickness of the depth interval [m]

1000 = factor from mg kg⁻¹ to g kg⁻¹

RESULTS

Heavy metal contents in 1984

Heavy metal contents soluble by aqua regia and EDTA before starting the system in 1984 are shown in the Tables 2 and 3, indicating relatively high amounts of Cd, Cu and Zn. The contents of aqua regia soluble Zn, Pb and Cu are decreasing with depth (Table 2), corresponding to the decrease of organic carbon and iron oxides (Table 1). Ni and Cr soluble by aqua regia mainly show maxima in the middle layer 30–60 cm, whereas Cd, Fe and Mn show no consistent trend (Table 2). Depth distributions of the EDTA-extractable fractions are quite similar to those in aqua regia (Table 3).

Table 2 Heavy metal contents of the soils dissolved by aqua regia (1984)

Field/plot	Depth cm	Fe	Mn	Cd	Cu <i>mg kg⁻¹</i>	Cr	Ni	Pb	Zn
1/1	0-30	21381	338	1.25	160.5	30.7	30.0	58.5	181
	30-60	23231	428	1.80	76.5	35.6	52.0	25.5	120
	60-90	22931	464	1.60	26.9	35.9	39.3	5.5	74
1/2	0-30	22531	405	1.75	163.0	31.7	33.1	50.5	167
	30-60	22131	400	1.05	64.5	33.4	46.5	19.5	113
	60-90	22981	506	1.55	30.0	35.7	36.3	7.5	70
1/3	0-30	17781	373	1.80	162.0	30.8	32.0	51.5	167
	30-60	24281	413	2.10	82.0	39.0	53.5	35.0	125
	60-90	20431	583	1.70	27.5	35.2	41.8	5.5	71
2/1	0-30	22731	330	2.00	161.0	27.2	31.4	50.0	180
	30-60	20931	405	1.80	67.5	29.2	44.5	17.0	112
	60-90	21631	335	1.15	29.4	30.0	37.8	4.0	73
2/2	0-30	20131	345	1.95	114.0	28.7	35.1	53.0	200
	30-60	19631	382	1.50	52.5	31.7	49.5	15.5	113
	60-90	21781	333	1.75	28.9	29.3	37.4	6.0	72
2/3	0-30	22181	374	2.00	124.5	30.9	34.5	41.0	159
	30-60	20981	362	1.85	90.5	31.9	45.7	26.5	124
	60-90	21981	353	1.40	39.5	30.8	41.8	5.0	85
3/1	0-30	21631	333	1.85	153.5	30.0	35.0	60.5	192
	30-60	23281	430	1.80	71.0	32.9	50.0	23.5	121
	60-90	21231	332	1.50	29.2	31.1	40.4	11.0	72
3/2	0-30	22681	362	2.00	143.0	30.0	35.6	52.0	183
	30-60	23081	448	2.35	105.0	31.8	45.5	33.5	130
	60-90	21331	384	2.10	29.6	29.3	39.8	14.5	78
3/3	0-30	21481	330	1.90	166.0	27.9	35.5	56.0	164
	30-60	21281	377	2.45	82.0	30.0	44.0	30.0	111
	60-90	22731	328	2.10	30.1	31.1	39.6	29.0	69

Heavy metal balances of the differently treated fields

Table 4 shows the balances of Zn, Pb, Cd, Cu, Cr, Ni, Fe and Mn in different extracts after the 5 years period.

Aqua regia extractable Zn and Pb have been increased in each of the fields. Cd and Cu (aqua regia) show only slight increases in field 2 (Cu, Cd) and field 1 (Cd), and losses in the other fields. The balances of both metals decrease in the order of field 2 > field 1 > field 3. Cr, Ni, Mn and Fe show significant decreases in all three fields. Except of Fe, the highest decreases of these elements occurred in field 1 (Table 4).

The EDTA-soluble fractions (exchangeable and organically bound) of all elements increased significantly. The raises of EDTA-soluble Zn and Pb decrease in the order field 1 > field 2 > field 3, that of Cu, Cr, Mn and Fe in the order of field 2 > field 1 > field 3, whereas Cd- and Ni-balances show no significant differences between field 1 and 2 (Table 4). In addition, Table 4 shows an increase of ammonium oxalate soluble Fe and a decrease of Mn in the same extract.

Table 3 Heavy metal contents of the soils extracted by 0.05 M EDTA (1984)

Field/plot	Depth cm	Fe	Mn	Cd	Cu mg kg ⁻¹	Cr	Ni	Pb	Zn
1/1	0-30	254	30.8	0.20	49.1	1.5	2.9	30.3	45.0
	30-60	178	47.8	0.20	16.1	1.5	5.0	16.9	17.3
	60-90	193	89.2	0.10	4.6	1.5	3.5	10.5	5.0
1/2	0-30	196	31.3	0.20	47.0	1.4	2.7	24.7	33.0
	30-60	151	41.8	0.20	13.0	1.5	4.6	14.4	13.9
	60-90	233	94.5	0.10	4.7	1.6	3.5	10.5	5.3
1/3	0-30	208	28.9	0.20	48.6	1.4	2.6	25.5	37.0
	30-60	164	38.6	0.10	15.7	1.5	5.8	15.1	14.7
	60-90	208	80.8	0.10	5.7	1.5	4.4	10.5	5.5
2/1	0-30	319	33.8	0.20	54.7	1.5	3.8	28.8	43.0
	30-60	196	53.9	0.10	17.5	1.4	4.3	17.7	13.9
	60-90	183	56.7	0.10	5.4	1.4	3.7	10.8	5.2
2/2	0-30	214	26.9	0.20	27.5	1.4	3.4	26.0	58.7
	30-60	135	42.3	0.20	8.7	1.5	4.9	13.3	11.9
	60-90	160	54.5	0.10	4.8	1.4	4.3	9.9	5.3
2/3	0-30	279	40.3	0.40	37.8	1.5	3.2	23.7	35.4
	30-60	171	43.7	0.30	20.8	1.5	5.5	18.9	16.1
	60-90	200	60.3	0.20	8.2	1.6	5.1	12.4	7.7
3/1	0-30	224	29.4	0.30	45.4	1.6	3.2	28.2	47.8
	30-60	164	47.7	0.30	15.7	1.6	4.7	16.5	14.5
	60-90	162	55.1	0.20	6.0	1.5	4.7	11.6	5.6
3/2	0-30	223	37.4	0.40	43.7	1.6	3.8	26.1	43.9
	30-60	200	53.1	0.40	21.2	1.5	5.1	19.0	18.7
	60-90	223	75.5	0.30	7.5	1.6	6.0	13.6	7.7
3/3	0-30	218	24.8	0.40	47.4	1.5	3.4	24.2	38.3
	30-60	215	47.6	0.30	21.2	1.6	6.6	17.0	17.2
	60-90	236	81.2	0.20	6.0	1.6	5.0	12.0	6.7

Vertical distribution of metal balances in the reed bed soil

Figures 2 and 3 show the vertical distribution of the balances for Zn, Pb, Cd, Cu, Cr and Ni soluble in aqua regia and EDTA for each field, Figure 4 those for Fe and Mn in three extracts (aqua regia, ammonium oxalate, EDTA).

Aqua regia soluble Zn, Cu, Pb, and partly Cd and Ni were displaced into the subsoil (Figures 2 and 3). Only in field 1 (raw sewage) the balances of Cd and Zn show pronounced maxima in the layer 0-30 cm. Cr, Mn and Fe (aqua regia) were leached from all layers (0-90 cm).

In field 1, EDTA-soluble Zn and Pb were mainly increased within the topsoil 0-30 cm, in field 3 mainly in the subsoil 60-90 cm, and in field 2 in all three layers to a similar amount. Balances of EDTA-Cu show maxima in the middle layers of the first two fields and in the subsoil of field 3. On the other hand, balances of Ni- and Cd-extractable by EDTA in all fields increase with depth, whereas those of Cr, Fe and Mn show no consistent trends. The balances of ammonium oxalate soluble Fe show maxima in the topsoils 0-30 cm in the fields 1 and 2, and increase with depth in field 3. Ammonium oxalate soluble manganese was leached from all layers in each field.

Table 4 Field balances of metals extractable by aqua regia, EDTA and ammonium oxalate for the depth of 0–90 cm (1984–1989)

<i>Element</i>	<i>Field 1 raw sewage</i>	<i>Field 2 settled sewage</i>	<i>Field 3 biologically treated sewage</i>
<i>g 0, g m⁻³</i>			
Zn aqua regia	+ 52.6	+ 12.2	+ 0.97
EDTA	+ 4.5	+ 2.1	+ 1.1
Pb aqua regia	+ 18.9	+ 19.4	+ 4.0
EDTA	+ 2.3	+ 1.9	+ 1.3
Cd aqua regia	+ 0.49	+ 0.8	– 0.09
EDTA	+ 0.03	+ 0.03	+ 0.01
Cu aqua regia	– 4.9	+ 1.5	– 9.5
EDTA	+ 2.3	+ 2.6	+ 2.2
Cr aqua regia	– 8.9	– 1.1	– 3.1
EDTA	+ 0.02	+ 0.05	+ 0.02
Ni aqua regia	– 6.7	– 4.01	– 3.0
EDTA	+ 0.63	+ 0.63	+ 0.49
<i>kg 0, g m⁻³</i>			
Mn aqua regia	– 0.20	– 0.09	– 0.09
NH ₄ -oxalate	– 0.08	– 0.04	– 0.06
EDTA	+ 0.03	+ 0.04	+ 0.04
Fe aqua regia	– 4.3	– 2.8	– 4.4
NH ₄ -oxalate	+ 2.15	+ 1.8	+ 0.89
EDTA	+ 0.59	+ 0.63	+ 0.53

+ = gains, – = losses.

DISCUSSION

The positive field balances for Zn as well as the topsoil maximum in field 1 (raw sewage) indicate a significant input of Zn through sewage, due to corrosion of rain gutterings and tyre abrasion. Similarly, the increase of Pb and Cd is supposed to be caused by input of surface runoff from roads.²² In addition, the decrease of Zn-, Pb- and Cd-accumulation with the intensification of sewage pretreatment can be explained by the decreasing storage of solid organic compounds,²³ corresponding to a decreasing adsorption capacity for these metals⁴.

The leaching of Fe, Mn, Ni, Cr and Cu, indicated by their decrease in aqua regia (Table 4, Figures 2 and 3), is partly caused by the high, continuous percolation of sewage. The input rates of sewage, ranging between 14600 l m⁻² year⁻¹ (field 1) and 11680 l m⁻² year⁻¹ (field 3) exceed 15-fold those reported from the Braunschweig waste water irrigation area, where the contents of heavy metals increased.¹⁵ Moreover, the solubilization of Fe, Cr and Mn should be enhanced by reductive soil processes caused by flooding of the soil.^{9,24–27} Van Breemen²⁸ reports high solubility of Fe (up to 600 mg Fe²⁺ l⁻¹ soil solution) through flooding of soils during some weeks under laboratory conditions, thus supporting our results.

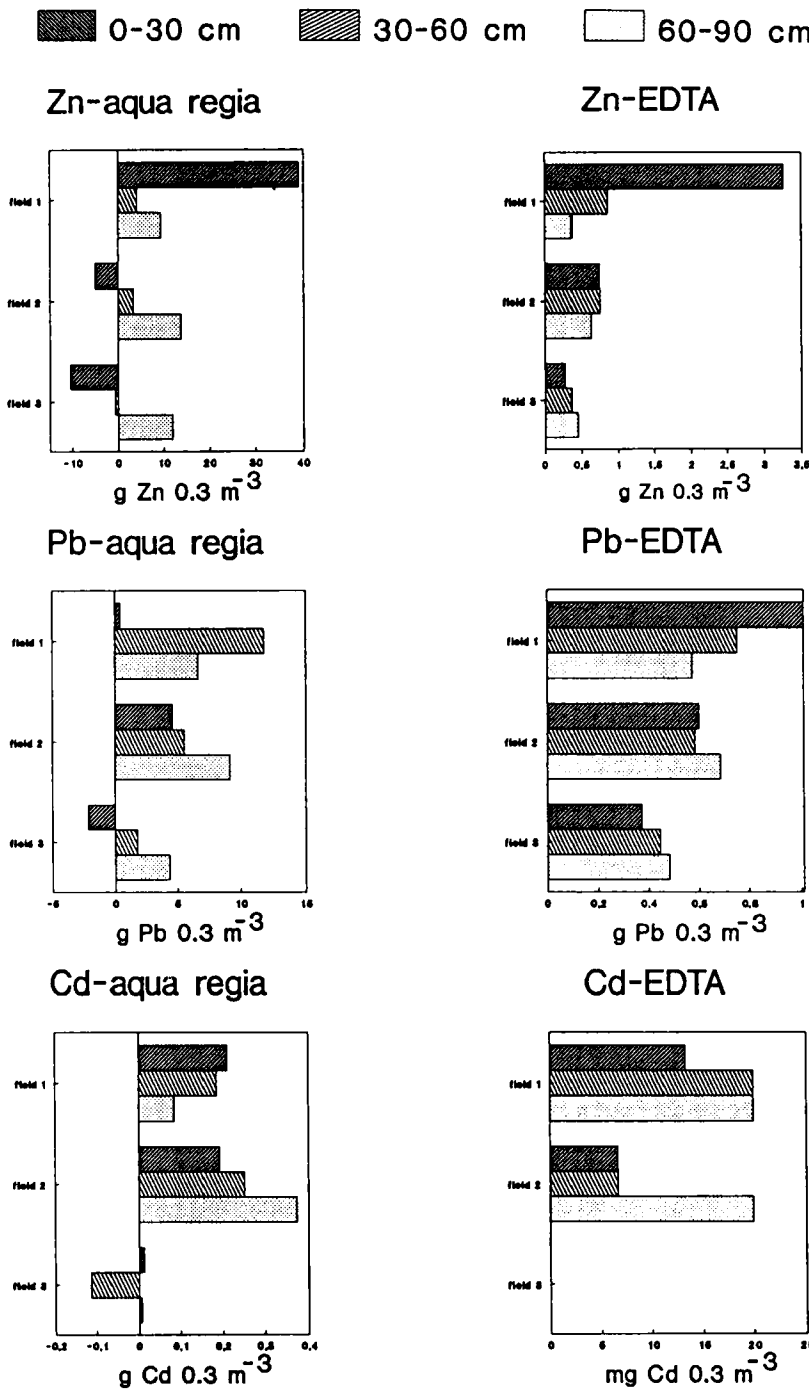


Figure 2 Vertical distribution of Zn-, Pb- and Cd- balances in the reed bed soil (soluble with aqua regia and EDTA).

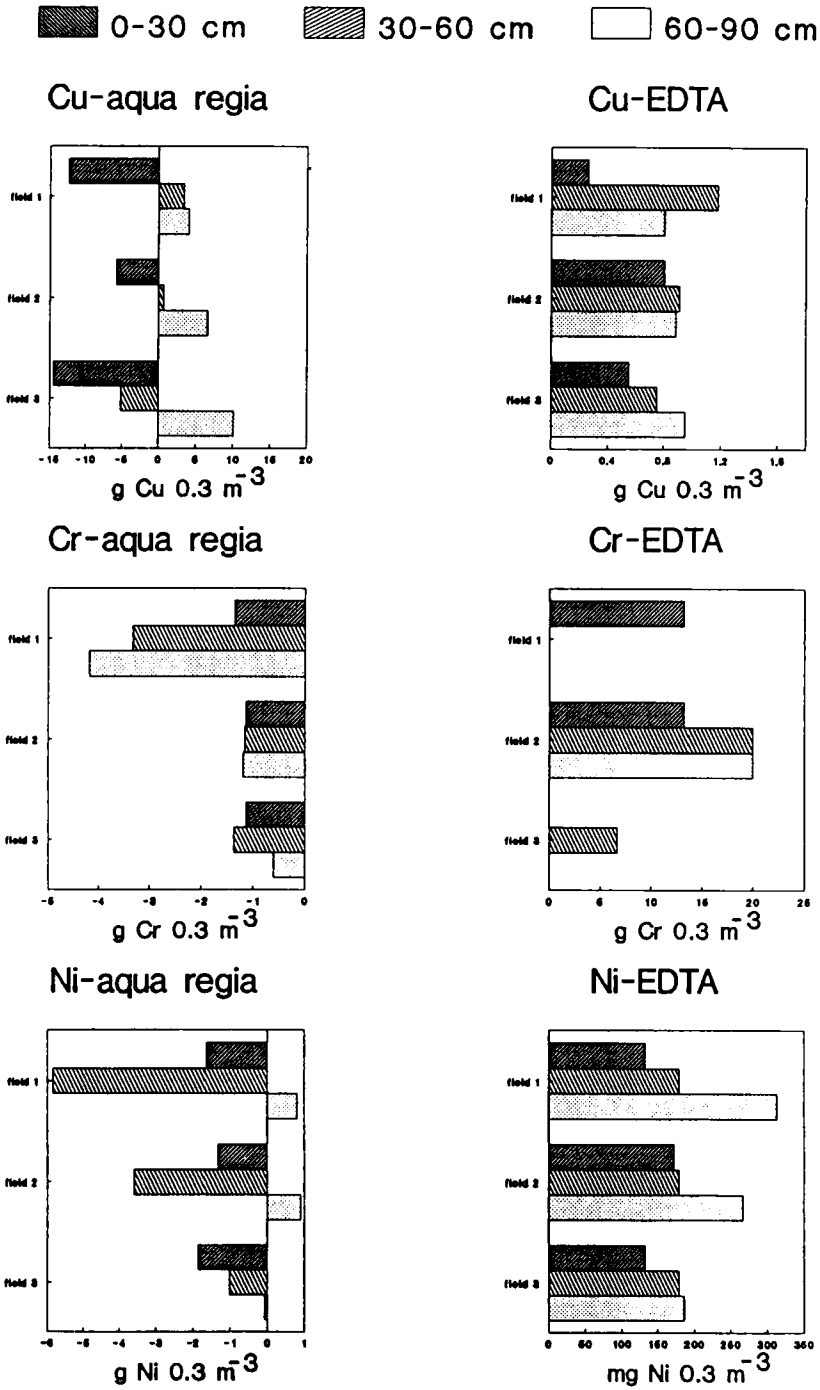


Figure 3 Vertical distribution of Cu-, Cr- and Zn- balances in the reed bed soil (soluble with aqua regia and EDTA).

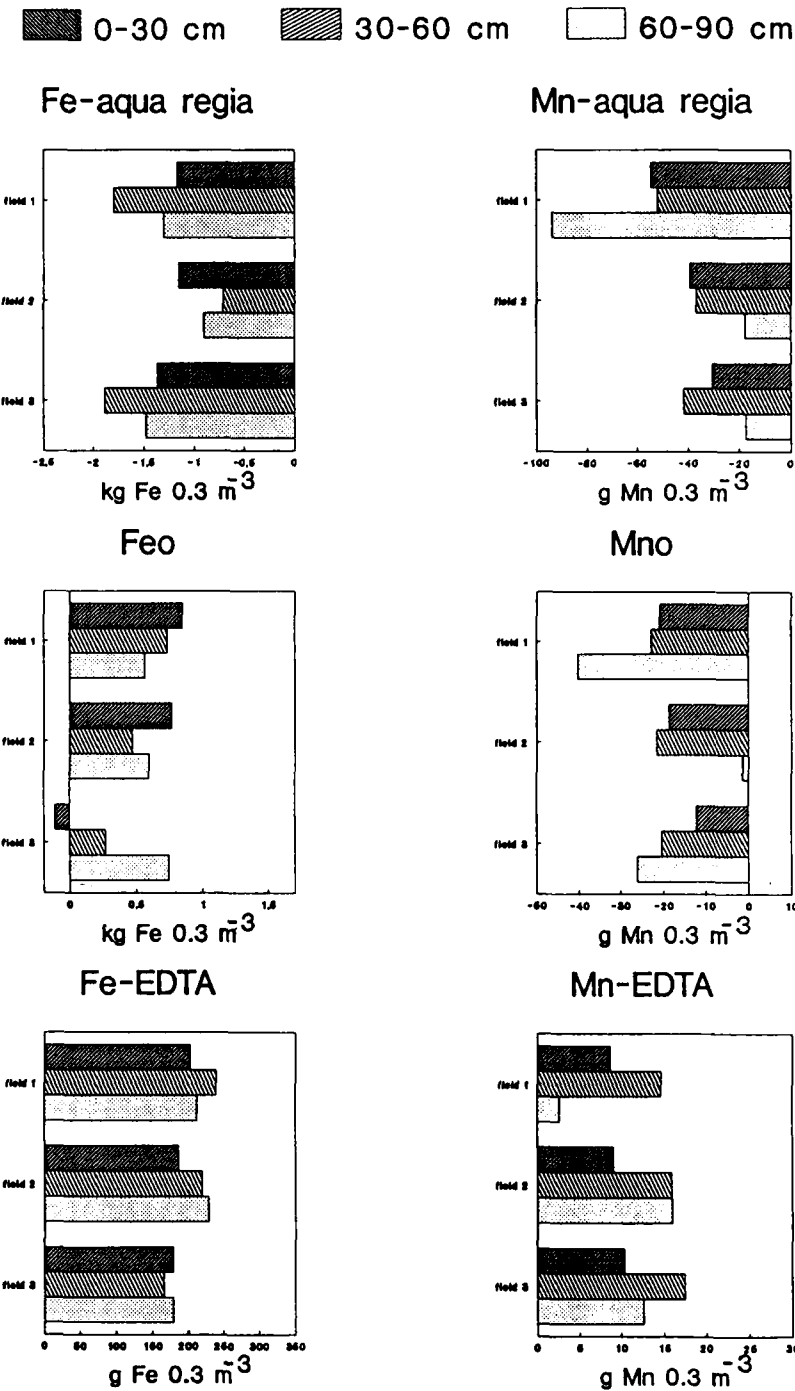


Figure 4 Vertical distribution of Fe- and Mn-balances in the reed bed soil (soluble with aqua regia, ammonium oxalate and EDTA).

The high losses of Mn, Ni, Cr and Cu in field 1 are probably due to their increased solubility through the complexation by organic ligands in the soil solution.^{8,12} This can be explained by the high input of organic compounds with raw sewage,²³ similar to the mobilization of metals by rice straw application onto paddy soils,⁶ or by the amendment of sewage sludge.²⁹ The low redox potential as well as the high pH (Table 1) favours metal complexation with organic compounds in the reed bed soil,^{10,12} also indicated by the significant increase of EDTA-soluble, organically bound fractions,^{7,10,30} compare Table 4.

In addition, the steady elimination of the dissolved metals with the sewage is thought to be essential for the high leaching rates.

Although the aqua regia soluble contents of most metals decreased, the EDTA-soluble fractions increased in all fields and layers, indicating a possible co-precipitation with inferred organic compounds (Table 4, Figures 2 and 3). These results combine well with the reported increase of organic Fe, Mn, Cu and Zn (pyrophosphate) through flooding of soils with high pH.¹⁰ Conversely, flooding of acid soils only caused an increase of organic Fe and Mn (DTPA), whereas Cu and Zn decreased.⁷

Despite the high losses of aqua regia soluble Fe in all 3 fields the contents of ammonium oxalate soluble Fe (Fe_0) increased significantly (Table 4), indicating the neoformation of amorphous Fe-oxides.³¹ The decrease of Fe_0 accumulation with the intensity of sewage pretreatment (field 1 > field 2 > field 3) gives evidence that the input of organic compounds might play a role in the precipitation of iron oxides.³¹

Conversely, amorphous Mn-oxides (MnO) were leached from all fields to a similar amount as aqua regia extractable Mn (Table 4). The excess of leaching over neoformation of Mn-oxides can be explained by the low content and the high solubility of manganese²⁶ as well as by the higher redox potential of the Mn(IV,III)/Mn(II) system^{26,32}.

CONCLUSION

The results indicate that continuous flooding of calcareous soils with sewage causes the leaching of metals, due to high percolation rates, strong reductive conditions and high amounts of complexing organic compounds in the sewage. Concurrently, neoformation of amorphous iron oxides as well as an increase of the EDTA-soluble, organically bound heavy metal fraction occurs.

Therefore, continuously flooded reed bed systems are not suitable for eliminating heavy metals from sewage. Conversely, it should be possible to purify soils contaminated with heavy metals by percolation with sewage of low metal content.

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