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FATE OF METALS AND HEAVY METALS IN CONSTRUCTED WETLANDS FOR SEPTAGE DEWATERING

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Abstract

An investigation was carried out into the fate and behaviour of metals and heavy metals contained in septage when applied to constructed wetlands for dewatering. Total metal contents in raw septage were determined, as well as their accumulation in the dewatered septage layer as the organic matter gradually decomposes. Metal availability was assessed by means of analysis of plant uptake by *Typha angustifolia,* as well as by single and sequential extraction techniques. Metal mobility was also assessed in terms of leachability.

It was found that most metal concentrations in septage are very low, except Zn. Upon organic matter decomposition, zinc accumulation will possibly exceed safe levels for reuse as fertilizer or soil amendment, as shown by the heating experiment. In the field, no significant accumulation is yet observed due to the limited degree of decomposition. Fifty to ninety percent of zinc was extracted by NH_4OA-EDTA solution, which means that Zn is readily available for plant uptake and for leaching. Both phenomena were observed. The high uptake of Cu and Zn caused a reduced uptake of essential elements such as Mn and Fe, which could possibly lead to deficiency symptoms.

Introduction

Septage dewatering in constructed wetlands offers a lot of advantages, ranging from technical reasons as the methodology is low-tech, but effective in obtaining a high dry matter content, to economical reasons, as it is generally cheap compared to conventional technologies and the resulting dried and humified septage may be resold as a prime organic fertilizer or soil amendment, to even ecological reasons as the wetlands may provide an interesting habitat for waterfowl and a green belt in urban areas (Nielsen, 1993, De Maeseneer, 1996, Liénard, 1995). Moreover, constructed wetlands have a long life-time.

The reuse as soil amendment or fertilizer offers good perspectives, provided that the dried septage meets the quality standards for reuse of sludge for agricultural purposes, as stipulated by the US EPA and many other national environmental government agencies. Loading of raw septage high in metal contents to constructed wetlands, will result in accumulation of these metals in the end product, the dried septage, as a result of the advanced mineralization it will undergo during the long retention time of several years. Whereas even persistent organic contaminants will eventually be decomposed, metals remain, as they don't easily leach out from polluted materials (Emmerich et al., 1982, Tack and Verloo, 1995). The fate of these accumulated metals is still unclear and contradicting theories have been formulated. One theory (He et. al., 1992, Teal and Paterson, 1993, Alloway, 1995) claims that upon organic matter decomposition or mineralization, the metals will become more mobile or available, as they cannot be longer tightly bound by the decreasing organic matter. Moreover, mineralization of organic matter may lower pH, which also increases metal mobility. Other researchers however, argue that upon mineralization, the metals will be accumulated as non-biodegradable organic complexes or will become occluded in insoluble precipitates (Emmerich et al., 1982).

Metal mobility is reflected in plant uptake, with phytotoxicity symptoms in extreme cases, and in metal leaching. These pathways cause metal redistribution and impacts on other environmental media such as contamination of groundwater and surface waters, as well as bioaccumulation in the food chain.

It was the purpose of this section of the research project on 'Septage Treatment in Constructed Wetlands and in Attached-Growth Waste Stabilization Ponds' to investigate the fate of septage borne metals and heavy metals in these treatment systems.

Experimental Set-up and Methodology

1. Monitoring program

In order to assess the fate of metals and heavy metals contained in septage, when treated in constructed wetlands for dewatering effectively, the following parameters were monitored troughout the project duration, with a different frequency:

1. total metal and heavy metal content in raw septage
2. total metal and heavy metal content in the dried septage layer
3. metal uptake in roots and leaves of *Typha angustifolia*
4. metal concentrations in the percolate
5. metal availability in dried septage
6. metal fractionation in dried septage

Metals in raw septage: replicate, composite samples of raw septage collected from different locations in Bangkok and Pathumthani were analysed for Cu, Zn, Mn, Fe, Cd, Pb, Ni and Cr for comparison. During the first phase of the project, the raw septage was analysed weekly during 6 weeks to determine average composition.

Metals in dried septage: composite dried septage samples were analysed after 6 months, 1 year and 1.5 years after sludge loading started. The samples were air-dried and ground to pass a 2 mm sieve before being analysed. Total metal contents were calculated in order to determine possible accumulation in the mineralized septage.

Metal uptake in roots, leaves and rhizomes: whole *Typha* plants were sampled before the septage loading started and at regular intervals thereafter (3 months, 6 months, 9 months, 15 months, 20 months). They were divided into composite leaf and root samples, washed with distilled water and dried at 70 C.

Metals in percolate: flow-proportionate, composite percolate samples were analysed for metals every 3 weeks during the first phase of the project, and every 3 months later on.

Metal availability in dried septage: metal availability in air-dried, ground and sieved dewatered septage samples was determined by means of a selective extraction technnique known to extract soluble and complexed metals, which are considered the most available metal fractions in solid media. The availability test was also performed on septage samples treated at 250 C for 5 hours, which simulated a progressed mineralization and gave an indication of changing metal availability upon decomposition.

Sequential extraction of metals in dried septage: this procedure allows the determination of the chemical form (or species) of the metal in the matrix, which in turn influences its behaviour in the environment and its mobilization capacity. Dried septage was sampled from wetlands 1 and 3, who are under a moisture regime of constant water table and of free drainage respectively. Samples were taken at 5-10 cm, 20 cm and 35 cm depth in the septage layer. A sequential extraction was performed on the fresh samples and Cu, Zn, Mn and Fe concentrations in the different fractions were determined. The results give an indication of changing metal fractionation upon decomposition.

2. Methods of analysis

Standard methods of analysis according to APHA (1985) were used for the determination of total solids, total volatile solids and total metal concentrations in raw septage and percolate. Total metal concentrations in dried septage and plant tissue samples were determined after digestion with a 2:1 HNO_3: $HClO_4$ acid mixture (Lisle et al., 1986). Available metals were extracted with a NH_4Oac-EDTA mixture, according to the method described by Cottenie et. al (1982). Metal fractionation was carried out following the sequential extraction procedure of Tessier et al. (1979). The sequential extraction procedure consecutively extracts metals that are (I) exchangeable, (II) bound to carbonates, (III) bound to Fe and Mn oxyhydroxides, (IV) bound to organic matter, and (V) residual.
The metals (Cu, Zn, Mn, Fe, Ni, Cr, Pb and Cd) were determined by using Flame Atomic Absorption Spectrophotometry (Hitachi model 8200), using external standards

in the same medium as the extractant. Aqueous metal concentrations found were then calculated on a dry weight basis for the solid samples.

Results and discussion

Metals in raw septage:

The metal concentrations found in different septage samples from Bangkok and Pathumthani are represented in Tables 1 and 2, on a liquid and dry basis respectively. The investigated samples were characterized by a very high variation of TS content (ranging between 3716 and 16830 mg/L) and heavy metal concentrations. The first 3 samples (Pathumthani, Nongkhaem and On-Nooch) have extremely low concentrations of all metals, a lot lower than the normal concentrations found in literature. Average concentrations found in septage in the U.S. for example, are 8.3, 27.4, 3.97, 191, 0.75, 0.27, 5.2 and 0.92 mg/L for Cu, Zn, Mn, Fe, Ni, Cd, Pb and Cr respectively. The lower values we found, can be explained by the relatively short residence period of septage in septic tanks in Thailand, which is about one year, compared to 2 to 5 years in for instance the United States (Teal and Peterson, 1993). Thus, for similar waste streams, the resistant organic compounds and heavy metals concentrate at relatively higher levels when the residence time is longer.

When these metal concentrations are compared with the ‘high quality pollutant concentration limits’ (US EPA) of 1500, 2800, 39, 300, 420 and 1200 mg/kg dry weight for Cu, Zn, Cd, Pb, Ni and Cr respectively, it can be concluded that septage contains very low concentrations of all of these metals, except for the sample from Chatuchak area that contains Zn in concentrations nearly reaching the limit. It is exactly this septage that is applied to the wetlands.

Table 1. Heavy metal concentrations in septage samples from Bangkok and Pathumthani (results on liquid base (mg/L)).

metal	sample			
	Pathum-thani	**Nongkhaem (Bangkok)**	**On-Nooch (Bangkok)**	**Chatuchak (Bangkok)**
Cu	0.08 (0.01)	0.45 (0.00)	3.02 (0.07)	6.00 (0.35)
Zn	0.34 (0.02)	1.93 (0.27)	0.40 (0.03)	63.75 (3.18)
Mn	0.33 (0.01)	0.74 (0.06)	4.03 (0.20)	6.92 (2.41)
Cd	0.013 (0.003)	0.008 (0.000)	0.026 (0.001)	0.066 (0.002)
Pb	0.14 (0.02)	0.02 (0.01)	0.08 (0.01)	0.55 (-)
Ni	0.02 (0.00)	0.06 (0.01)	0.40 (0.15)	0.52 (0.00)
Cr	n.d.	n.d.	0.13 (0.01)	0.04 (0.01)
Fe	11.70 (1.35)	4.31 (0.15)	n.m.	n.m.

n.d.: not detected, n.m.: not measured

Table 2. Heavy metal concentrations in septage samples from Bangkok and Pathumthani (results on dry base (mg/kg dry weight)).

metal	**sample**				
	Pathum-thani	**Nongkhaem (Bangkok)**	**On-Nooch (Bangkok)**	**Chatuchak (Bangkok)**	**average conc. phase 1**
Cu	22.7 (3.7)	56.0 (1.1)	180 (4)	259 (15)	289 (32)
Zn	69.5 (8.5)	245 (34)	23.7 (1.1)	2753 (137)	2085 (129)
Mn	87.9 (3.0)	94.2 (8.0)	239 (9)	299 (104)	356 (39)
Cd	3.46 (0.86)	1.06 (0.03)	1.55 (0.06)	2.86 (0.08)	2.79 (0.19)
Pb	38.4 (5.3)	2.01 (1.56)	4.43 (0.03)	23.5 (-)	6.85 (1.69)
Ni	6.50 (0.39)	6.97 (1.27)	23.8 (6.5)	22.6 (0.1)	21.5 (3.0)
Cr	n.d.	n.d.	7.61 (0.24)	15.9 (0.2)	20.1 (5.5)
Fe	3148 (362)	547 (19)	n.m.	n.m.	7235 (3733)

Metals in percolate

Cu, Zn, Mn, Ni, Cd, Pb and Cr concentrations in the percolate were monitored regularly throughout the project. They were generally very low and well below the industrial effluent standard set by the Thai government. When compared to the concentrations in the raw septage on a liquid basis, more than 90% of the metal loads were retained in the septage layer for most metals.

Interesting results were obtained when the different moisture regimes were applied during the second phase of the project. In wetland 1, a constant water table is maintained, in wetland 2 the drainage is retained for 2 days and released on the third, whereas wetland 3 is operated continuously with free drainage. The results of the metal analysis are shown in Table 3.

Table 3. Heavy metals in the percolate of the 3 wetlands (mg/L)

metal	**WL1**	**WL2**	**WL3**	**average**	**standard****	**standard***
Cu	0.025	0.132	0.216	0.124	< 2.0	0.1
Zn	0.24	2.95	7.15	-	< 5.0	1.0
Mn	0.91	0.42	0.67	0.67	< 5.0	1.0
Fe	1.12	1.11	1.45	1.23	-	-
Ni	0.049	0.053	0.029	0.044	< 1.0	0.1
Cr	0.0005	0.0033	0.0063	0.0033	< 0.25	0.05

Lead was not detected.

* standard: surface water quality criteria for class 3 (consumption and agricultural purposes) water (PCD, 1997)

**standard: industrial effluent standard (PCD, 1997)

Copper concentrations are similar to those observed during the first phase of the project, but Zn, Ni and to a more limited extent also Mn concentrations have increased. The standard for class 3 surface water is exceeded for Cu (exc. WL1) and

Zn. The Zn concentration in percolate from wetland 3 even exceeds the industrial effluent standard set by the Thai government, of 5 mg/L. Apparently, the filtering and sorption capacity of the gravel media seems to be deteriorating, possibly as a result of saturation of the sorption sites.

The observed lower concentrations of Cu and Zn in percolate of wetlands 1 and 2 with a standing water table, may be explained by the occurrence of anaerobic microsites, where the formed sulfides retain zinc and copper more effectively. Lower Mn concentrations with increased aeration (in wetlands 2 and 3), can be explained by the precipitation of Mn oxides in the prevailing aerobic conditions. The same should be observed for Fe, but is not so obvious from the obtained results.

Metal uptake by Typha angustifolia

Results of metal determination in roots and leaves of *Typha angustifolia* at different intervals during the project, are represented in Table 4. Few phytotoxicity data are available for aquatic macrophytes, but generally they are more resistant to heavy metal uptake than terrestrial plants (Besch, 1970, Mc Naughton et al., 1974, Taylor and Crowder, 1983).

In terrestrial plants, tissue concentrations of Zn higher than 150 to 200 mg/kg DW are phytotoxic (Mengel and Kirkby, 1987), resulting in a 25% yield decrease. Zinc concentrations in the roots of *Typha angustifolia* steadily increased during the course of septage loading and exceed these phytotoxic levels two- to threefold. Zinc is readily translocated to the leaves (Williams, 1975) and concentrations reach 100 mg/kg DW, which is also a lot higher than the background concentrations of 21.7 and 15.4 mg/kg DW as observed by Wells et al. (1980) and from *Typha angustifolia* in natural wetlands around AIT campus respectively. Williams (1975) mentioned phytoxic levels of 40 to 50 mg/kg DW in cereals. However, concentrations of up to 154 mg/kg DW have been observed in leaves of *Typha* spp. without signs of phytotoxicity (Mungur et al., 1995). Symptoms are reduced root growth, reduced leaf expansion followed by chlorosis and a reduced uptake of Fe and P. Reduced Fe uptake was indeed observed. Whereas normal concentrations of Fe in *Typha* are 5000 mg/kg DW (Kadlec and Knight, 1996), we observed consistently decreasing iron concentrations in roots and leaves during the course of the project. They declined from 1600 to 400 mg/kg DW and from 63 to 40 mg/kg DW in roots and leaves respectively.

The same steady decrease was also observed for manganese. In roots, concentrations declined from 1000 to 70 mg/kg DW after 20 months of septage loading, and in leaves, Mn decreased from 826 to 209 mg/kg DW. Normal concentrations reported range from 412 to 870 mg/kg DW (Boyd, 1970 and Mayer and Gorham, 1951, as cited by Taylor and Crowder, 1983).

Copper concentrations in *Typha angustifolia* increased from 10.2 to 41.8 mg/kg DW in roots and from 5.7 to maximum 8.9 mg/kg DW in leaves during the course of septage loading. Normal values for *Typha spp.* range from 3 to 48 mg/kg DW (cited by Taylor and Crowder, 1983). Elevated levels in roots reported are up to 265 mg/kg DW for *Typha* growing in heavily contaminated mining areas (Mungur et al., 1995, cited by Taylor and Crowder, 1983).

Table 4. Concentrations of heavy metals (mg/kg dry wt.) in roots and rhizomes of Typha latifolia at different intervals during the project..

metal	**ROOT**							**LEAF**						
	start	**3 months**	**6 months**	**9 monthsr**	**15 months**	**20 months**	**natural**	**start**	**3 months**	**6 months**	**9 months**	**15 months**	**20 months**	**natural**
Cu	10.2 (0.4)	18.4 (5.1)	19.8 (7.5)	38.5 (10.9)	41.8 (0.5)	33.9 (4.5)	9.0 (0.4)	5.71 (1.14)	5.32 (0.17)	2.55 (0.43)	8.91 (1.52)	5.30 (0.10)	7.71 (2.09)	3.28 (0.62)
Zn	58.2 (13.8)	202.7 (71.7)	144.0 (5.1)	545.0 (193.0)	613.0 (2.0)	593.5 (90.9)	63.9 (1.4)	34.2 (6.2)	45.8 (15.1)	25.2 (3.1)	49.0 (12.9)	101.0 (6.0)	63.8 (14.5)	15.4 (0.3)
Mn	1096.6 (46.9)	236.9 (110.9)	131.6 (36.2)	70.1 (24.8)	70.0 (1.1)	53.6 (7.4)	573.0 (23.0)	826.3 (99.3)	234.7 (110.9)	44-742	139.0 (24.0)	209.0 (6.0)	175.0 (48.0)	435.0 (13.1)
Fe	1607 (106)	1098 (32)	n.m.	n.m.	398 (31)	912 (278)	n.m.	54.5 (15.6)	62.6 (3.2)	n.m.	n.m.	40.1 (3.1)	38.8 (1.3)	n.m.
Ni	62.6 (20.5)	10.6 (2.9)*	8.4 (1.2)	8.7 (5.8)	n.d.	n.m.	12.5 (0.1)	n.d.	1.82 (0.47)	1.07 (0.23)	1.19-6.03	n.d.	n.m.	0.40 (0.26)
Cd	0.96 (0.49)	0.58 (0.09)	0.47 (0.13)	0.37 (0.33)	n.m.	n.m.	n.d.	0.05 (0.05)	0.23 (0.20)	n.d.	n.d.	n.m.	n.m.	n.d.
Cr	n.m.	n.m.	6.34 (1.74)	2.62 (1.29)	2.10 (1.91)	n.m.	6.69 (0.07)	n.m.	n.m.	1.81 (0.70)	0.25-1.89	0.71 (0.21)	n.m.	0.49 (0.09)
Pb	8.18 (3.46)	7.76 (2.55)	3.79 (1.39)	8.17 (3.81)	4.90 (0.15)	n.m.	4.56 (0.93)	n.m.	2.64 (0.42)	n.d.-0.44	n.d.-4.06	0.47 (0)	n.m.	0.33 (0.01)

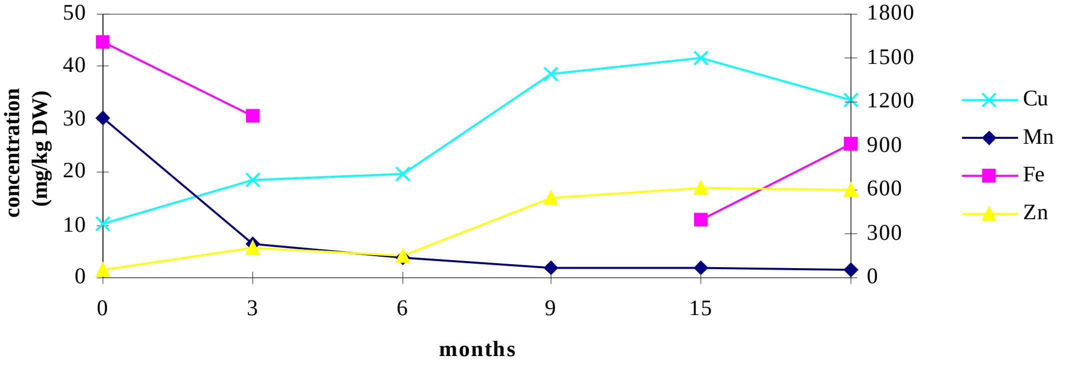
standard deviation between brackets
n.d.: not detected
n.m.: not measured

start: start of septage loading, after several months of feeding with stabilisation pond effluent
3, 6, 9, 15 and 20 months: time after sludge loading has started
natural: concentrations in *Typha angustifolia* growing in natural wetlands around AIT campus

In leaves, elevated levels of 5.0 to 12.7 mg/kg DW were found by De Maeseneer (1996) in constructed wetlands for sludge dewatering. The concentrations we observed are within this range. Evolution of Cu, Zn, Mn and Fe concentrations in roots and leaves of *Typha angustifolia* are represented graphically in figures 1 and 2. From these graphs, it can be more clearly seen that Zn and Cu concentrations seem to have reached an equilibrium.

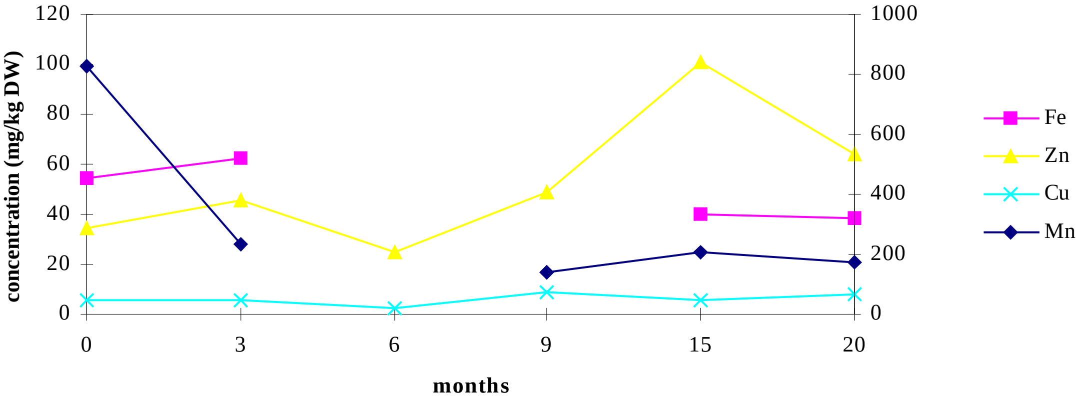
Strangely, concentrations of Ni, Cr, Pb and Cd in roots of *Typha angustifolia* steadily declined throughout the project. Concentrations in leaves showed a very high variability resulting from measurements near the detection limit, and no reliable conclusions can be drawn from them.

Fig 1. Evolution of metal concentrations in roots of Typha angustifolia during septage loading.



Note: for Cu, refer to Y1 axis, for other metals, refer to Y2 axis.

Fig 2. Evolution of metal concentrations in leaves of Typha angustifolia during septage loading.



Note: for Mn, refer to Y2 axis.

Metals in dried septage

Metal accumulation in the residual septage upon decomposition was assessed in the field, as well as by a laboratory experiment. The septage sampled at different depth represent increasing decomposition with depth, as the first septage layer dates from almost two years back. The laboratory experiment consisted of heating an oven-dry septage sample at 250 C for 5 hours, simulating advanced decomposition.

From field observations, no significant metal accumulation is yet found. The total metal contents in samples from three different depths, representing increased decomposition with increasing depth, did not differ statistically significant, as shown in Table 5. However, also the ash content, being an indicator for the degree of decomposition, does not increase significantly with depth. This leads us to the conclusion that over the septage loading period of almost 2 years, the septage has not mineralized substantially yet.

Table 5. Total metal (mg/kg DW) and ash content (% of TS) in dried septage cores from the wetland with constant water table (wet) and free drainage (drained) respectively.

	Cu		Zn		Mn		Fe		ash	
	wet	drain	wet	drain	wet	drain	wet	drain	wet	drain
Top	392[a]	323	2489	2570	353	323	7637	9076	24	30
Mid	377[a]	339	4016	2967	339	347	9306	12413	33	35
Bottom	349[a]	324	2900	2504	341	321	5936	8201	31	34

Upon heating, or organic matter decomposition, the metals became more concentrated in the remaining solids. However, the increase was not proportional for all metals and amounted to 20% for Cu, 72% for Zn, 40% for Mn, 13% for Fe, 43% for Ni and 56% for Cr. During the heat treatment, some metals may be more firmly incorporated in the crystal lattices than others, some of which can not be dissolved during the acid digestion procedure. In order to solubilize all metals and crystals, the use of HF is required.

Zinc concentrations in the heated sludge increased a lot, reaching up to 5300 mg/kg dry weight. This exceeds the US EPA standard for agricultural application of 2800 mg/kg. After the heat treatment, the organic matter content, as measured by further heating at 550°C, was still approximately 30%, which is similar to commonly applied stable city composts. From this fact, it can be concluded that heating the sludge at 250°C is not an irrealistic endpoint for estimating the final metal concentrations in the decomposed septage. Such high zinc concentrations can consequently be expected. However, it has to be kept in mind that the septage will eventually be applied on agricultural land at a dose of 1 to 10 tons per hectare per year, which would not lead to an unacceptable increase of the soil concentration. The US EPA guidelines for sludge reuse in agriculture, require that, in case Zn concentrations exceed 2800 mg/kg but are lower than the ceiling limit of 7500 mg/kg, the annual Zn load is restricted to 140 kg/ha.year with a cumulative pollutant loading rate of 2800 kg/ha. In case highly decomposed septage would be applied, containing 5.3 g/kg dry weight, a yearly application of 26.4 tons per hectare would still be acceptable. This is more than the normally applied dose. Applying a load of 10 ton/ha.year could thus be continued for about 50 years until the cumulative pollutant loading rate is reached.

For the other metals, even after far advanced organic matter decomposition, there is no danger that their concentrations would exceed the ‘high quality pollutant concentration limit’ (1500, 420 and 1200 mg/kg dry weight for Cu, Ni and Cr respectively).

Plant available metals and heavy metals

An availability test was performed on air-dry and on heat treated septage, in order to have an idea of the changing availability upon decomposition. The extractant used was NH_4OAc-EDTA, an extractant known to give a good indication of bioavailable metals, because it extracts exchangeable as well as some complexed metals from the solid medium (Cottenie et al., 1982). The results are again listed in Table 6 and 7.

Table 6. Total and available metals in the air-dry septage layer (mg/kg dry wt)

	WL1			**WL2**			**Average**		
metal	**Total**	**Extr.**	**% extr.**	**Total**	**extr.**	**% extr.**	**Total**	**Extr.**	**% extr.**
Cu	446	67	15	514	131	25	480	99	21
Zn	3288	2996	91	2886	2906	100	3087	2951	96
Mn	391	317	81	465	274	59	428	296	69
Fe	21845	4073	19	25926	5016	19	23886	4545	19
Ni	26.5	12.7	48	27.8	13.1	47	27.2	12.9	47
Cr	25.0	2.3	9.2	20.0	1.9	9.5	22.5	2.1	9.3

Even though we see that Mn is quite available for plant uptake, concentrations in plant tissues are below normal concentrations, so probably there is some interference from other metals, which prevents sufficient Mn to be adsorbed by the roots. It has been mentioned before that increased uptake of metals such as Zn, Cu may cause Mn and Fe deficiency (Taylor and Crowder, 1983).

The results of the availability test are according to the expectations. It is generally accepted that copper is strongly associated with organic matter and thus less available than zinc for instance (Emmerich et al., 1982), which is more soluble or less strongly adsorbed on exchange sites. Fe is less available because it is precipitated as hydrous oxides, which only dissolve under reducing conditions. The same would be expected of Mn, but apparently a large part of Mn remains available. Nickel is quite available in septage, which confirms Emmerich et al.’s (1982) findings that only Ni showed any appreciable percentage in the exchangeable form in air-dried sewage sludge. Chromium is least available, being largely associated with the crystalline phase.

Table 7. Total and available metals in the heat treated (250°C) septage (mg/kg dry weight)

	WL1			WL2			Average		
metal	**Total**	**Extr.**	**% extr.**	**Total**	**extr.**	**% extr.**	**Total**	**Extr.**	**% extr**
Cu	549	91	17	599	100	17	574	96	17
Zn	5156	2883	56	5459	2668	49	5308	2776	52
Mn	558	397	71	644	571	89	601	484	81
Fe	31311	2755	9	22822	2647	12	27077	2701	10
Ni	35.0	8.5	24	42.9	8.4	20	39.0	8.5	22
Cr	33.1	1.4	4.2	37.2	1.7	4.6	35.2	1.6	4.4

After the heating procedure, some metals became relatively less available, such as Zn, Fe, Ni and Cr. This is in accordance with the theory that upon decomposition of the organic matter, the bound metals will shift to the less available crystalline phase and non-degradable organic matter. However, in absolute figures, extractable zinc remains constant at approximately 2800 mg/kg DW. Mn on the other hand becomes more available, which is in accordance with the theory that the metals bound to organic matter will be solubilized upon decomposition (Teal and Paterson, 1993). For Cu, the bioavailability is not affected. Figures 3 to 8 compare extractable versus total metals in the air-dry and heated septage samples.

Fig. 3. Extractable versus total Cu in air-dry and heat-treated septage samples.

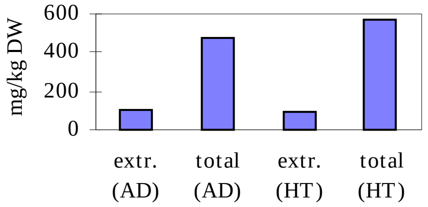


Fig. 4. Extractable versus total Zn in air-dry and heat-treated septage samples.

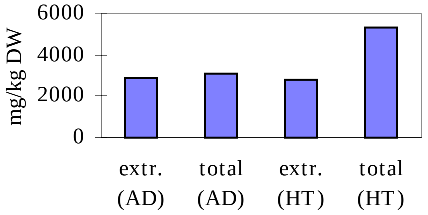


Fig. 5. Extractable and total Mn in air-dry and heat-treated septage samples.

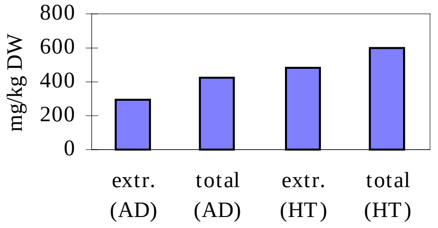


Fig. 5. Extractable and total Mn in air-dry and heat-treated septage samples.

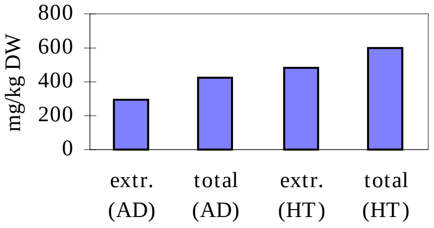


Fig. 7. Extractable versus total Ni in air-dry and heat-treated septage samples.

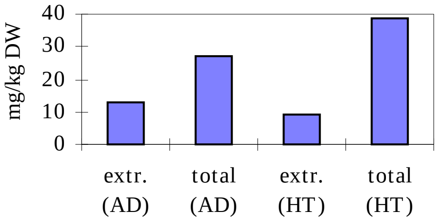
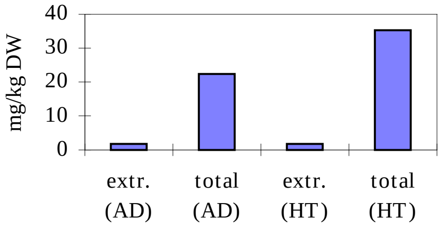


Fig. 8. Extractable versus total Cr in air-dry and heat-treated septage samples.



Note: AD = air-dry, HT = heat-treated

Metal fractionation in dried septage

The results of the sequential extraction procedure are represented in Figures 9 to12 for Cu, Zn, Mn and Fe respectively.

Copper is mainly found in the residual phase and bound to organic matter, as generally observed (Emmerich et al., 1982). Cu in the other phases is negligible. In wetland 1, under constant water logging, the residual copper increases with depth, whereas the organic bound copper decreases. In the wetland with free drainage, the copper fractionation remains stable over depth.

Zn is mainly bound to Fe and Mn oxides, but is also bound to carbonates and organic matter. Up to 10% of Zn is exchangeable in the wetland with constant water table, whereas it is almost 20% in the drained wetland. This causes the rather high Zn concentrations in the percolate, as observed and discussed previously. With increasing decomposition, or increasing depth, the organic bound Zn increases, whereas the carbonate bound Zn decreases. Exchangeable Zn and Zn bound to oxyhydroxides remain stable. In the wetland with constant water table, the residual zinc increases with depth, whereas it slightly decreases in the drained wetland.

Manganese is mainly found as oxides, as expected. In the wetland with constant water table, Mn oxides account for about 50% of total Mn, whereas in the drained wetland it is much higher, between 60 and 75%. This is the result of the better aeration and resulting Mn oxidation in the latter wetland. Manganese in phases I and II, the most available phases, is also higher in the wetland with constant water table, resulting in the higher percolate concentrations observed. With increasing depth, or increasing decomposition, the organic matter bound manganese gradually increases. In the wetland with constant water table, this increase is compensated by a decrease of manganese in phase II, whereas in the drained wetland it is due to a decrease in Mn oxides.

Iron is mainly found in the residual phase, as Fe oxides and bound to organic matter. Exchangeable Fe and Fe bound to carbonates or complexed (phase II) are negligible. Upon decomposition, this distribution remains stable in the drained wetland, whereas in the wetland with constant water table, the residual iron increases and the Fe oxides decrease, possibly due to the higher status of water saturation with increasing depth.

A general observation is that the metals extractable with NH_4OAc-EDTA are not in accordance with the sum of the most available fractions, I and II, extracted in the sequential extraction procedure. In most cases the ammonium acetate extract is higher, which was also observed by Tack and Verloo (1993). They also concluded that no extractant can really predict plant uptake, as apart from metal availability, also plant factors and environmental factors such as pH, play a role.

Fig. 9. Cu fractionation in dried septage in relation to depth and moisture regime.

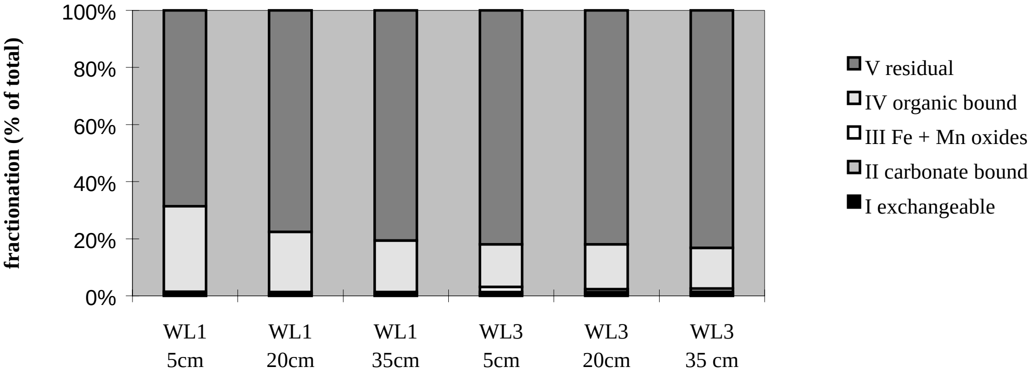


Fig. 10. Zn fractionation in dried septage in relation to depth and moisture regime.

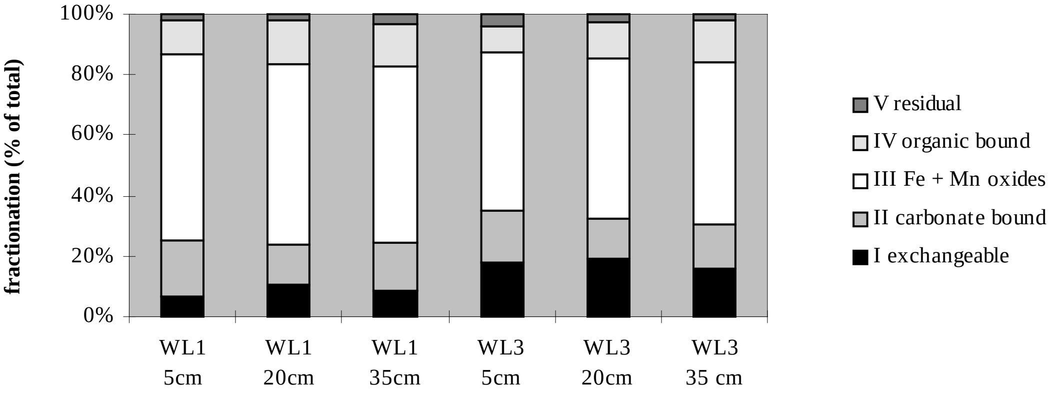


Fig 11. Mn fractionation in dried septage in relation to depth and moisture regime.

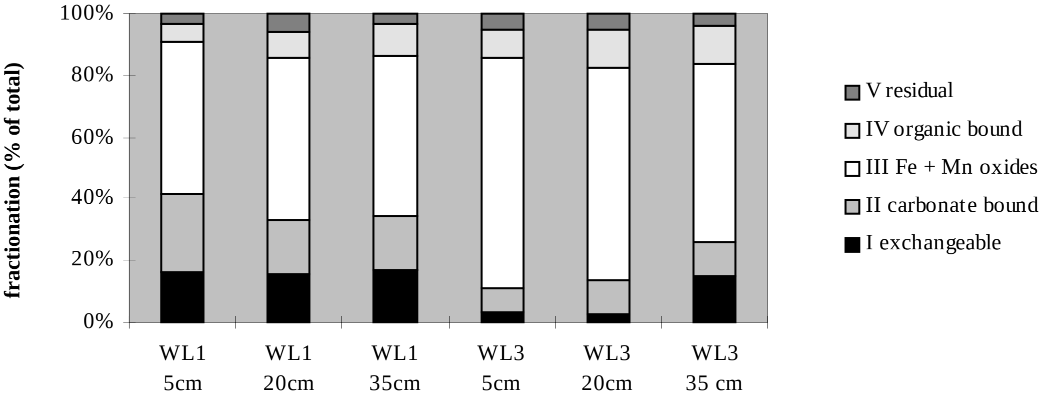
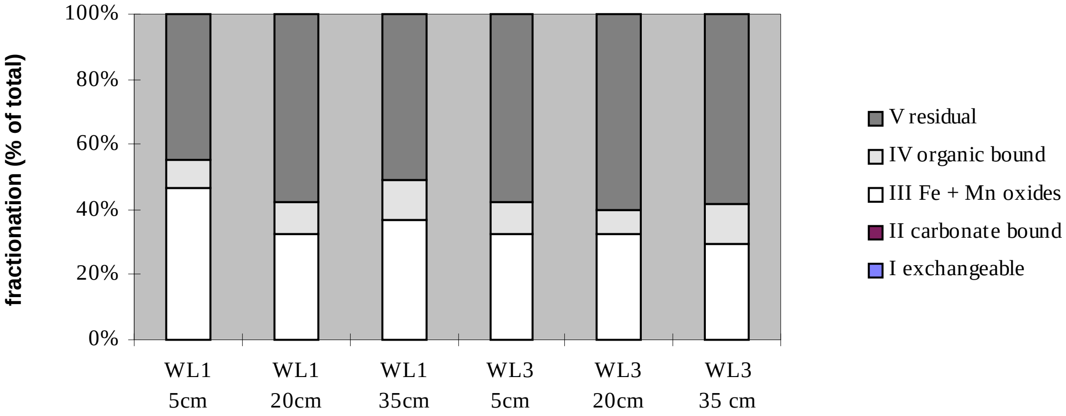


Fig. 12. Fe fractionation in dried septage in relation to depth and moisture regime.



WL 1: wetland with constant water table
WL3: wetland with free drainage

Conclusions

Whereas metal concentrations in septage are generally low, zinc was found at very high levels, nearly reaching the safe levels for unrestricted reuse as fertilizer. A laboratory experiment that simulated rapid decomposition showed that final Zn accumulation may reach over 5000 mg/kg DW at an organic matter content of 30% of total solids, which is an average content for stable city compost. As total concentrations do not give an indication of the metal availability and mobility to other environmental media, single and sequential extraction techniques were also applied. These confirmed the high availability of zinc, resulting in high plant uptake and leachability, which were observed in the field. Copper uptake also steadily increased during the course of septage loading, but not to phytotoxic levels, as copper is strongly bound to organic matter and consequently less available. The high Cu and Zn uptake clearly resulted in reduced Fe and Zn concentrations in tissues, which may possibly lead to deficiency symptoms.

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