

BEHAVIOUR OF HEAVY METALS IN SOIL BENEATH A LANDFILL; RESULTS OF MODEL EXPERIMENTS

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ABSTRACT

Column experiments were set up in order to study the behaviour of heavy metals from landfill leachate in the soil. Special attention was given to the influence of fatty acids in the leachate on the mobility of lead, copper, nickel and zinc. In addition the influence of the kind of soil material was investigated.

Of the six columns used in the experiments, three were percolated with synthetic landfill leachate and three with the same leachate without fatty acids.

In both cases the three columns contained sand, sand mixed with fine clay particles and sand mixed with large clay aggregates.

All experiments were carried out under anaerobic conditions. The soil solution of each column was periodically analysed.

At the end of the experiments, after 7 months, the soil was analysed for precipitates and adsorption of metals.

In the presence of fatty acids, breakthrough of respectively nickel, zinc and lead took place, whereas copper accumulated in the soil. In the absence of fatty acids precipitation and adsorption of the metals took place.

INTRODUCTION

As part of a research project on groundwater pollution, experiments with soil columns were carried out to simulate transport of pollutants in the field. The aim of these experiments was to obtain knowledge about the processes involved in the transport of pollutants from a landfill to soil and groundwater below it. In particular the influence of fatty acids on the mobility of heavy metals from the landfill was investigated.

At a landfill site in Ambt-Delden, The Netherlands, the presence of fatty acids coincided with large amounts of heavy metals in the leachate.

LITERATURE AND THEORY

Processes in the waste of a landfill

During decomposition of the organic waste in a landfill, a stage of anaerobic breakdown is reached, in which complex organic compounds are converted into volatile fatty acids. In the landfill Ambt-Delden, fatty acid concentrations up to 4 g/l were found in the percolate (Bannink, 1980). Characteristic for this stage are a pH decreasing to 5.5 - 6 and a decreasing redoxpotential.

In this stage high concentrations of heavy metals can be present in solution, because of complexation with fatty acids, and can be transported in the waste and the soil. In a landfill this stage can last from ½ tot 7 years (Hoeks, 1978), after which breakdown of fatty acids to methane dominates.

Transport and retention of heavy metals in the soil

Adsorption on colloidal surfaces plays a major role in the retention of heavy metal ions being transported in a soil matrix. These ions usually are present at very low concentrations in the soil solution. Under these circumstances adsorption of metal ions to clay minerals shows a very low reversibility because of preferential adsorption by chemical bond (Harmsen, 1977).

Also adsorption of heavy metal cations on soil organic matter, especially humic and fulvic acids, and on the oxides and hydroxides of Mn, Fe and Al is of chemical nature (Bar-Yosef et al., 1975).

Bruggenwert and Kamphorst (1979) conclude that there is little agreement in the literature about the order of preference for heavy metals.

Stevenson and Ardakani (1972) report that the preference sequence of complexation with fulvic acid is: Cu > Pb > Fe > Ni > Mn > Co > Zn > Mg. Sposito et al. (1976) report strong complexation of copper with the soil humic acid. Generally, mobility of copper in soils is reported to be very low.

Another retention process in the soil below a landfill is precipitation with sulphides and possibly carbonates. Concentrations of these anions are strongly dependent on pH and redoxpotential of the soil solution. Formation of sulphides is caused by sulphate reducing bacteria. Sulphate reduction takes place at redoxpotentials below - 100 mV (Postgate, 1979).

For the prediction of heavy metal behaviour in the soil, one has to know in what forms these metals are present in the soil solution. For equilibrium conditions Laqas and Harmsen (1980) conclude that in the presence of fatty acid concentration of 0.3 mol/l, a large percentage of the metal amount is present as monovalent positively charged, uncharged and negatively charged complexes. This severely reduces adsorption and precipitation of the metals as cations.

MATERIALS AND METHODS

Experimental set-up

Six percolation columns of grey polyethene, with a length of 140 cm and a diameter of 18 cm, were constructed.

Per column, five tappoints were inserted in the column wall, with a spacing of 20 cm. Each tappoint was connected to a perforated polyethene tube of 18 cm length, which penetrated into the column. The tubes were positioned alternatively perpendicular to each other.

The contents of the columns are indicated in table 1. All soil columns were watersaturated. The sand material was dune sand. The clay aggregates had a diameter of 2-4 cm. In columns 2-5 the sand/clay weight ratio was 10:1. Table 2 gives the relevant parameters of the soil components. The percolation rate was 1.6 cm.day^{-1} .

TABLE 1
Composition and percolation treatment of the six columns

Column nr.	1	2	3	4	5	6
Percolation liquid		Reference solution		Synthetic landfill leachate		
Soil material	Sand	Sand + Clay (fine)	Sand + Clay (aggregates)	Sand + Clay (aggregates)	Sand + Clay (fine)	Sand

TABLE 2
Parameters of the soil components used in the experiments

Parameter	Sand	Clay
Org. C	0.5%	0.1%
CaCO ₃	1.8%	12%
CEC (meq/100 g)	2	16
pH (KCl)	8.3	7.3
pH (H ₂ O)	8.5	8.0
M-number	240	
Sortinggrade	93	

TABLE 3

The composition of the synthetic landfill leachate and the reference solution

Component	Synthetic leachate mol/l	Reference solution mol/l
Acetic acid	0.17	
Propionic acid	0.05	
Butyric acid	0.11	
Valeric acid	0.12	
Ascorbic acid	0.01	0.01
Chloride	0.1	0.26
Sulphate	0.02	0.02
Total carbonate	0.003	0.003
Sodium	0.23	0.07
Potassium	0.05	0.02
Ammonium	0.17	0.04
Calcium	0.07	0.04
Magnesium	0.02	0.02
Iron	0.025	0.025
Manganese	0.001	0.001
Copper	0.001	0.001
Zinc	0.001	0.001
Lead	0.001	0.001
Nickel	0.001	0.001

Composition of the input solution

The composition of the percolation liquids used, is given in table 3. It was attempted to synthesize the leachate of the Ambt-Delden landfill as good as possible. The reference solution has the same heavy metal composition as the synthetic leachate but does not contain fatty acids.

In order to keep the redoxpotential of the solution low, ascorbic acid was added as a

redox buffer. Thus a redoxpotential of 150 mV was maintained in the solution, at a pH of 5.7.

The total fatty acid concentration in the synthetic leachate is about equal to that in real leachate. The Zn- and Mn-concentrations are comparable with those in real leachate; for the other metals the concentrations in real leachate are substantially lower. The reasons for this deviation were: to obtain measurable concentrations in the percolate and to be able to compare the behaviour of the metals.

Sampling and methods of analysis

Once per two weeks soil solution samples were taken from the tappoints and chemically analysed.

After 7 months, percolation was terminated and the soil material, drained to field capacity and subsequently frozen, was analysed. For this purpose the soil column was cut into cylindrical samples of 5 cm height.

In the columns with clay aggregates, sand and clay were sampled separately. In the laboratory the soluble salts and exchangeably adsorbed cations were extracted with a 0.5 molar BaCl_2 -solution, after which the precipitated and strongly adsorbed forms of the metals and other cations were extracted with 0.1 N HCl. In the extracts the metal concentrations were determined by atomic absorption spectroscopy. Precipitates in the soil were qualitatively analysed by X-ray diffraction and scanning electron microscopy (Bisdorn et al., 1981).

RESULTS AND DISCUSSION

The soil solution

The concentrations of lead and copper in the soil solution are presented in figure 1. The results for lead are similar to those for nickel and zinc. These three metals are retained by the soil when fatty acids are absent, whereas in the columns where synthetic landfill leachate was used, retention by the soil is less severe or absent. Copper deviates from this behaviour. It is retained in the upper 30 cm of the soil column, independent of the presence or absence of fatty acids. Complexation of the metal ions explains the mobility of the metals when fatty acids are present. Copper, complexed with low molecular organic acids, may become dismantled in contact with organic matter in the soil, to be subsequently complexed with the humus. The new complex must have a higher stability constant. Because the result is a high molecular complex, its mobility can be low (Bruggenwert and Kamphorst, 1979).

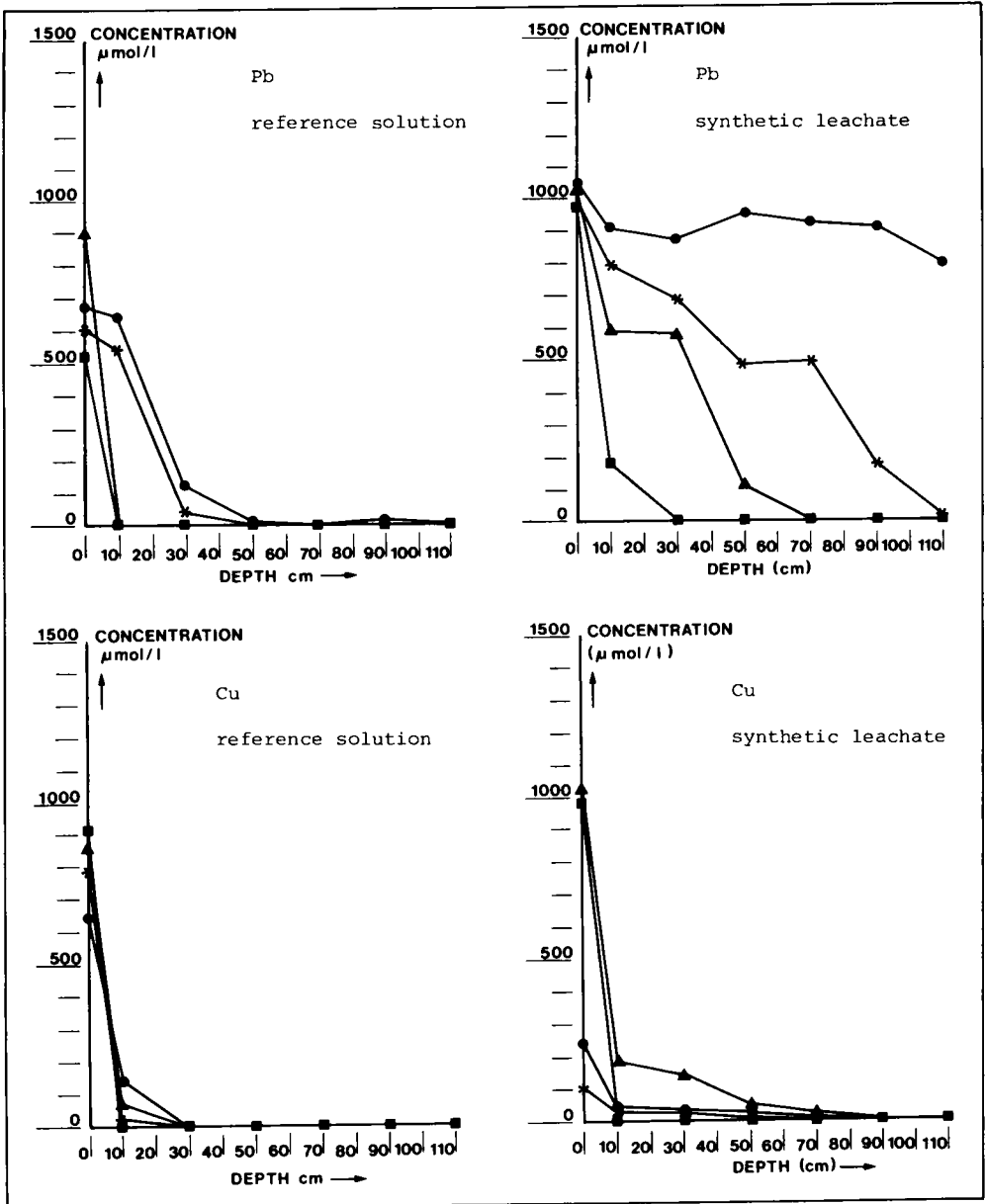


Fig. 1. Metal concentrations in the pore liquid of the columns with sand/fine clay mixture.

- percolation time = 2 weeks.
- ▲ " " = 4 weeks.
- * " " = 16 weeks.
- " " = 24 weeks.

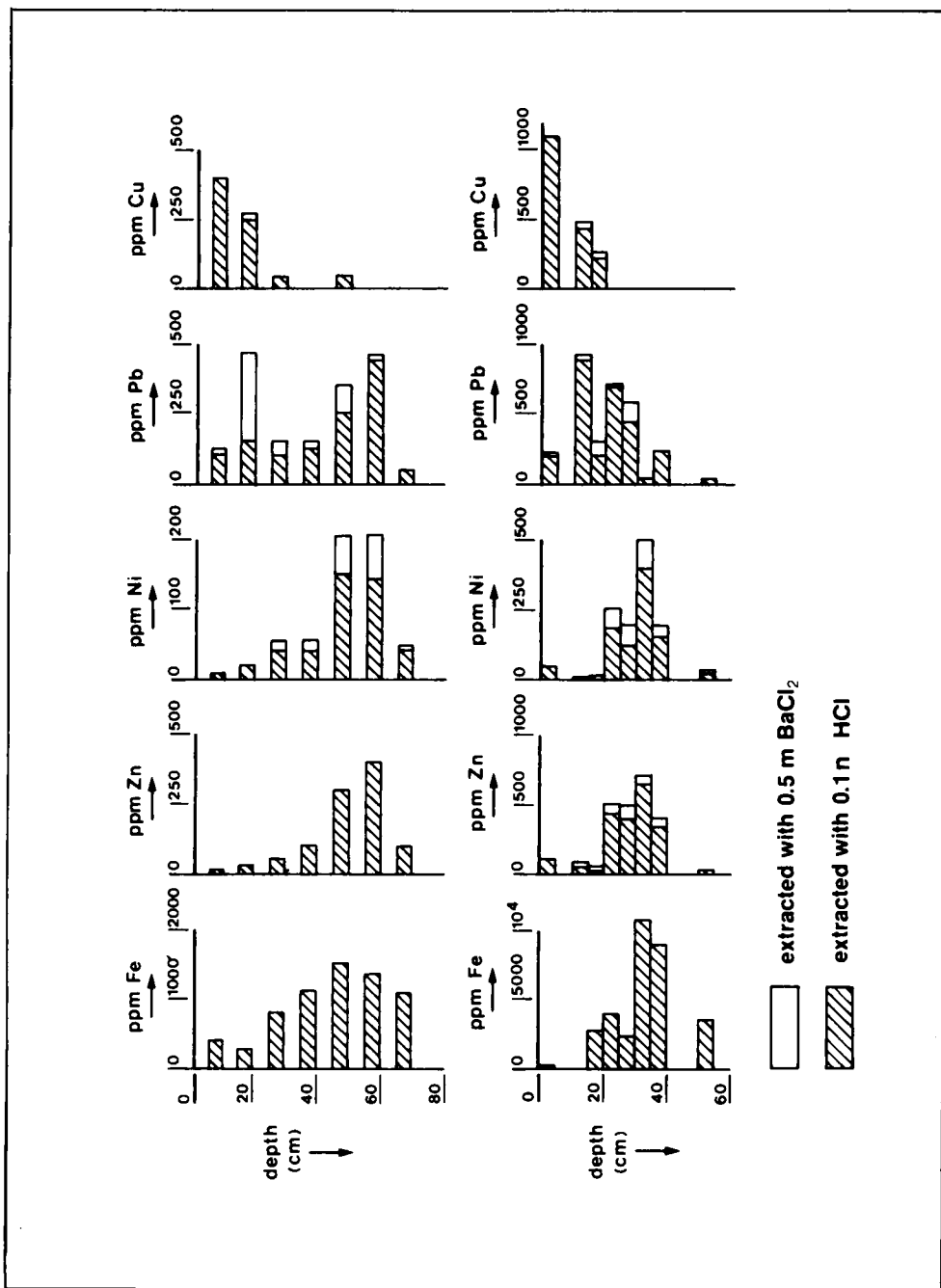


Fig. 2. Metal contents of the solid soil material versus depth in the column. Upper half: Column 1 (sand, percolated with the reference solution). Lower half: Column 2 (sand + fine clay, percolated with the reference solution).

Percolation with reference solution

Results of soil analyses at the end of percolation are presented in fig 2. for columns 1 and 2. It appears that:

- the sand/clay mixture is more effective than pure sand in the retention of heavy metals;
- retention of copper takes place immediately after the solution enters the column, that is, in the upper 30 cm of the soil;
- penetration depth of lead is intermediate between that of copper on the one hand and nickel and zinc on the other hand.

Black metalsulphide precipitates were found in columns 1-3, mainly in the depth range between 15 and 70 cm. This indicates that sulphate reducing bacteria could develop from a depth of 15 cm downward. Nickel and zinc, being predominantly present in this zone, were mainly retained by sulphide precipitation.

Lead was found both in the sulphide zone and above it. This indicates that it was retained both by precipitation and adsorption. Because copper could only be extracted by 0.1 N HCl and was found only above the sulfide zone, retention of copper was probably by preferential adsorption on the soil colloids. A relatively small part of the retention of each heavy metal was by exchangeable adsorption.

Percolation with synthetic landfill leachate

The breakthrough curves for lead, zinc and nickel in sand and fine clay are presented in fig. 3. The breakthrough curve for chloride did not significantly differ among the three columns. The low clay content apparently did not influence the dispersion, nor did anion exclusion play a role.

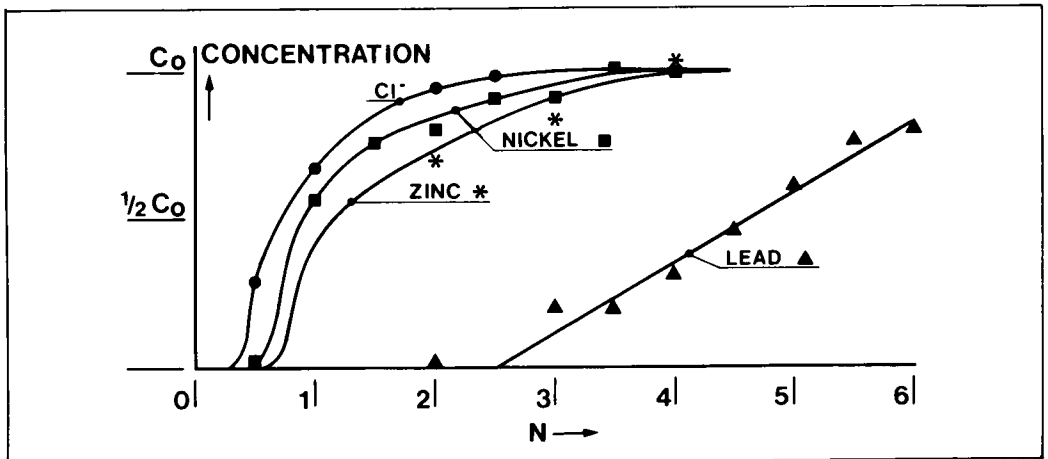


Fig. 3. Breakthrough curves for lead, zinc and nickel in column 5 (filled with sand + fine clay, percolated with synthetic landfill leachate) at a depth of 110 cm. C_0 (lead) = C_0 (nickel) = 1000 $\mu\text{mol/l}$; C_0 (chloride) = 170 mmol/l.

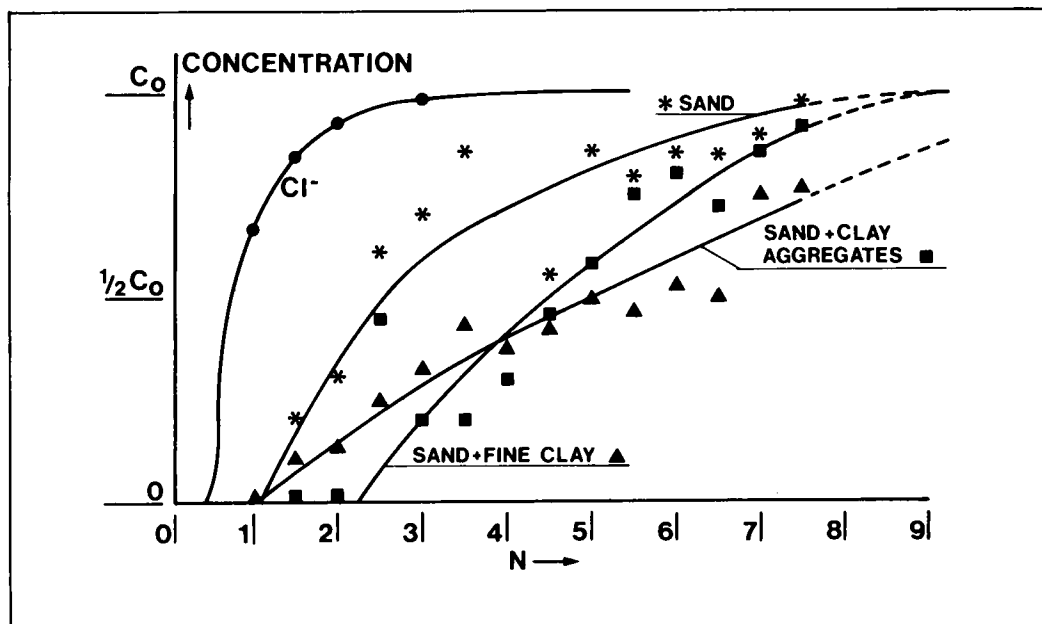


Fig. 4. Breakthrough curves for lead at a depth of 110 cm in the columns percolated with synthetic landfill leachate. C_0 (lead) = 1000 $\mu\text{mol/l}$; C_0 (chloride) = 170 mmol/l.

From the area between the chloride- and metalcurves one can compute for each metal how much has been retained in the column both by precipitation and adsorption. We may assume that in the columns with sand/clay mixture the same amounts of metal were precipitated and adsorbed on organic matter, as in the column with sand. Therefore the area in fig. 4 between the curves of the metal on sand and on the sand/clay mixture indicates the amount adsorbed on the clay material. In this way we computed that for the column with sand and fine clay a total amount of 29 mmol Pb, 6 mmol Zn and 4 mmol Ni was adsorbed on the clay. This order agrees with the order of increasing hydrated ionic radii. These radii determine the selectivity coefficients for reversible adsorption on the clay.

Fig. 4 very well illustrates the difference in retention by clay in fine particles and clay in aggregates. It appears that in the column with fine clay, adsorption takes place immediately. In the column with clay aggregates, adsorption on clay particles takes place too, but delayed, because the ions first have to diffuse from the pores in the sand matrix into the clay aggregates. This is why breakthrough occurs earlier, but the curve has a longer "tail".

Copper is not present in fig. 3 as it did not break through.

All results indicate that especially nickel and zinc and to a smaller degree lead are severely mobilized by the fatty acids.

Sulphides were not found in the columns percolated with synthetic landfill leachate, although the leachate contained a large amount of sulphate. Apparently sulphate reduction has not taken place. The presence of fatty acids may be a cause for this observation. An exact explanation cannot be given.

CONCLUSIONS

In the presence of fatty acids from landfill leachate, mobilization of zinc, nickel and lead in the soil takes place. Complexation of the metal cations and the absence of sulphides, explain this behaviour.

The presence of clay increases retention of the metals, even when they are largely complexed by fatty acids.

The breakthrough sequence of the metals in the landfill leachate, is respectively nickel, zinc, lead and copper. This agrees well with known adsorption properties of these metals.

It makes a substantial difference whether the clay material in the sand is finely divided or aggregated. Because of slow, but prolonged diffusion of ions towards and into the aggregates, before adsorption can take place, breakthrough starts relatively early, but it takes a long time before maximum effluent concentration is reached. In the absence of fatty acids, most of the metals Pb, Ni and Zn are retained by sulphide precipitation.

The behaviour of copper deviates substantially from that of the other metals. Copper is retained in the upper layer of the soil, no matter whether fatty acids are present or absent. This is probably due to preferential adsorption or complexation of copper on soil colloids.

The presence of fatty acids in a waste disposal site is not desirable as they cause transport of heavy metals from the waste disposal site into the soil and possibly to the groundwater table.

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