Effect of Liquid Animal Manure Application on the Solubilization of Heavy Metals from Soil

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EFFECT OF LIQUID ANIMAL MANURE APPLICATION ON THE SOLUBILIZATION OF HEAVY METALS FROM SOIL

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The effect of liquid animal manure on heavy metal solubilization in soil has been studied in the laboratory; three different types of experiments were carried out:

1) aerobic and anaerobic incubation of soil/manure mixtures

2) desorption of heavy metals from soil, as affected by manure liquid fraction

3) gel permeation chromatography of soil/manure aqueous extracts to identify components responsible for heavy metal solubilization.

All three different approaches showed that complexation involving high molecular weight dissolved organic matter from the soil/manure matrix is (together with pH) the most important driving force for heavy metal solubilization. As a consequence, chemical and microbial processes (e.g. nitrification) that influence dissolved organic matter concentrations in the soil solution, determine the degree of heavy metal solubilization in manured soil.

KEY WORDS: Soil, animal manure, heavy metals, dissolved organic matter, incubation, complexation.

INTRODUCTION

In the Netherlands large amounts of liquid animal manure (faeces mixed with urine) are applied to agricultural soils. Although manure is a rich plant nutrient source and can be useful for soil physical structure improvement, it gradually became an environmental problem in recent years. Part of the problem is caused by its excessive use; extensive manure production and its application on agricultural soils lead to ammonia emission to the atmosphere (250,000 tons per year), which is one of the major sources of acid precipitation in the Netherlands[1]. In certain areas, soils have become saturated with phosphate which eventually can reach surface waters, causing eutrophication[2]. Nitrate can leach down to subsoil drinking water supplies[3], which already has led to the closure of wells.

In studying the effects of manure on the soil system, two aspects have to be distinguished:

—The introduction of nutrients and other elements into the system.

—The environmental changes imposed onto the soil system (pH, redox potential, shifts in ion-exchange equilibria etc.), which affect the mobility of elements present in the soil/manure system.

In this contribution we will focus on the second aspect and discuss in detail the role of dissolved organic matter. Animal manure introduces large amounts of organic matter into the soil system. A considerable part of the organic matter exists in the liquid fraction (around 20% for a typical liquid manure). The high molecular weight dissolved organic matter originating from manure possibly acts as a carrier for contaminants; subsoil and groundwater pollution may result. Indications for such organic colloid facilitated transport of organic and inorganic pollutants exist in sediment, sewage sludge and wastewater studies, e.g.[4–7]. Animal manure, however, is chemically less stable and more reactive than sewage sludge when interacting with soil, so that a different behaviour may be expected. Mobilization of heavy metals in the soil profile due to the addition of animal manures has been observed in feedlots[8]. Indications for enhanced heavy metal solubilization due to manure application were observed too during field studies recently carried out at the DLO Institute for Soil Fertility Research. Three different experimental approaches were used to narrow down the processes which affect the solubility of heavy metals in manured soil:

1 Laboratory incubation studies.

Changes in heavy metal concentrations are studied in soil extracts of aerobically and anaerobically digested soil/manure mixtures. Heavy metal solubilization is related to changes in gross parameters of the soil/manure mixtures with special emphasis on dissolved organic matter content.

2 Desorption studies.

The "stripping" of heavy metals from soils by manure liquid fractions is studied using radio-isotopes. The contribution of dissolved organic matter to heavy metal solubilization (desorption) is estimated.

3 GPC-fractionation of manure derived dissolved organic matter.

The objective is to identify the type of dissolved organic matter (e.g. estimated molecular weight fraction), responsible for heavy metal complexation in the soil/manure system.

MATERIALS AND METHODS

Laboratory incubation studies

Experimental set-up   Slightly acidic sandy soil, relatively rich in organic matter, was sieved through 3 mm sieves. Animal manure was homogenized and sieved through 2 mm sieves. Soil and manure were analysed as well as manure liquid fractions obtained by high speed centrifugation (at 40,000 g) and subsequent filtration through

0.45 μm filters. Gross chemical compositions of soil, manure and manure liquid fractions are given in the Results and Discussion section (Table 1).

Aerobic digestion Sieved soil was thoroughly mixed with homogenized and sieved animal manure in a 10:1 weight ratio and the mixture was tightly sealed into polythene bags, designed to permit permeation of gases. The low water content of the soil/manure mixtures (around 10% w/w) admits aerobic processes. The bags, containing 55–60 grams of soil/manure mixture were located in a well ventilated, temperature controlled room at 20°C. Care was taken to guarantee free access of air to each individual incubation bag. Periodically (initially every few days, later weekly) 3–4 bags were removed from the incubation area; 50 grams of the bag contents were mixed with 50 ml of CO_2-free water and shaken vigorously for 16 hours. After high-speed centrifugation (at 40,000 g) the centrifugates were filtered under pressure through 0.45 μm filters. In the filtrates heavy metal (Cu and Cd) concentrations were determined as well as other relevant parameters like pH, dissolved organic carbon content ([DOC]), ammonium and nitrate concentrations.

Anaerobic digestion Sieved soil was thoroughly mixed with homogenized and sieved animal manure and distilled water in a 10:1:10 weight ratio. The mixtures were placed in closed plastic vessels; ponding of water on top of the soil/manure surface provides anaerobic conditions in the closed vessels. The total contents of the vessels were 100–110 grams. The vessels were located in a well ventilated, temperature controlled room at 20°C. Periodically (initially every few days, later weekly) 3–4 vessels were removed from the incubation area. After high-speed centrifugation (at 40,000 g) of the vessel contents, the centrifugates were filtered through 0.45 μm filters. In the filtrates, heavy metal (Cu and Cd) concentrations were determined as well as other relevant parameters like pH and [DOC].

Analytical procedures

Nitrate concentrations and pH were determined electrochemically using ion-specific electrodes. For the nitrate determination no correction for interfering components was made, resulting in only approximate data.

Concentrations of Cu and Cd were measured with carbon furnace AAS using standard methods. Mineralization was carried out by heating with 1:3 sulphuric acid/nitric acid mixtures. After evaporating the water and nitric acid, nitric acid was added and boiled out until the solution became slightly yellow. Water was added and the solution was boiled out; after filtration and adequate dilution, the AAS determination was made.

Ammonia concentrations were determined on the Traacs 800 Autoanalyzer. The method is based on segmented flow sample introduction, formation of an ammonia salicylate complex and finally colorimetric detection at 660 nm.

Total dissolved carbon and inorganic carbon were measured in the filtrate using a Shimadzu TC Analyzer; DOC-values were calculated by difference.

Desorption studies

Desorption of heavy metals from soil labelled with Zn-65, Cd-109 and Pb-210, as affected by pig manure liquid fraction Labelling of the soil with Zn-65, Cd-109 and Pb-210 was achieved by shaking an aqueous solution of a known amount of these isotopes with sandy soil in a 5000:1 solution to soil ratio for 7 days at pH = 7.5. Temperature was maintained constant at 20°C. Heavy metal concentrations in the added aqueous solutions were $10 \mu g \, l^{-1}$ for cadmium and lead and $100 \mu g \, l^{-1}$ for zinc. pH was controlled, using closed vessels with Metrohm automatic pH regulation equipment, which maintains constant carbon dioxide concentrations in the headspace through direct regulation of pCO_2 and without acid/base additions.

Desorption was studied in the same mixture substituting part of the liquid phase with pig manure liquid fraction (PM-LF) and shaking for 2 days. The concentration of PM-LF in the extracting liquid was varied between 0 and 20 volume %. Radioactivity was measured in the filtered solution by gamma-spectrometry.

Desorption of cadmium from Cd-109 labelled soil, as affected by pig manure liquid fractions with different concentrations of high molecular weight organic matter Air dried sandy loam soil was mixed with an aqueous solution containing a known amount of carrier-free Cd-109 (solid/liquid ratio: 8:1). The moistened soil was then gently dried in the open air. This procedure was repeated several times with portions of the same soil (6 years, 117 days, 13 days and 1 day before analysis). Thus obtained labelled soil samples with different degrees of "aging" were used for desorption studies. Fifteen grams portions of labelled soil were shaken with 50 ml of the extracting liquid for 16 hours. During extractions temperature and pH were maintained constant in the way described in the preceding section. The following extracting liquids were used:

—deionized water

—PM-LF

—PM-LF with reduced high molecular weight organic matter content, prepared as follows: PM-LF was mixed with analytical grade charcoal in a 20:1 weight ratio and gently shaken for 30 minutes at room temperature. The active carbon treated PM-LF was filtered over a 0.45 μm filter and [DOC] was determined using standard techniques, described in a previous section. The resulting filtrate was coloured slightly yellow. After filtration radioactivity in 5 ml of the filtrate was measured against an internal standard in a fixed geometry using a LKB gammaspectrometer with a 3″ NaI well-type crystal. The standard deviation of the countate was <1%.

GPC-fractionation of manure derived dissolved organic matter

Pig manure (PM) was mixed with water in a 1:2 ratio. The diluted PM was then thoroughly mixed with air dried sandy soil. The composition of both PM and sandy soil are given in Table 1. After overnight equilibration the soil/manure/water mixture was centrifuged in special centrifuge tubes mounted with supported paper filters in

Table 1 Gross composition of dry soil, cattle manure (CM), pig manure (PM) and pig manure (PM) liquid fraction.

	Dry soil:	CM:	PM:	PM (liquid fraction)
Dry matter (%)	—	11.0	7.0	—
Organic carbon (%)	1.9	3.7	3.0	0.85
pH (in filtrate)	—	7.2	7.6	7.6
K $(mg\ g^{-1})$	0.70	4.6	6.0	6.0
Na $(mg\ g^{-1})$	0.04	0.3	0.6	0.6
Ca $(mg\ g^{-1})$	0.69	1.6	1.3	0.17
Mg $(mg\ g^{-1})$	0.35	1.0	0.5	0.024
Fe $(mg\ g^{-1})$	2.7	0.26	0.14	0.0016
Mn $(mg\ g^{-1})$	0.09	0.032	0.018	0.0008
Al $(mg\ g^{-1})$	4.6	0.17	0.09	0.004
Cu $(\mu g\ g^{-1})$	6.5	8	32	0.4
Cd $(\mu g\ g^{-1})$	0.24	—	0.16	0.001
Cl $(mg\ g^{-1})$	—	3.9	2.9	2.9
P $(mg\ g^{-1})$	—	0.8	0.5	0.1
Volatile fatty acid $(meq\ g^{-1})$	—	—	—	0.20
ammonium ion $(meq\ g^{-1})$	—	—	—	0.40

the lower part. This permits the recovery of soil solution during the centrifugation[9]. The obtained soil solution was then filtered over a 0.45 μm filter. 0.5 ml of the filtrate was introduced on top of a Sephadex 25 GPC-column, mounted in a Pharmacia automatic elution and sample collection system. The column was eluted with a 0.01 M KCl aqueous solution (pH approximately 6) and 40 elution fractions were collected. Copper concentrations ([Cu]) and [DOC] were determined in the last 30 fractions (the first 10 fractions correspond to the column void volume) using standard procedures indicated in one of the preceding sections.

RESULTS AND DISCUSSION

Laboratory incubation studies

In the laboratory experiments, a decrease of more than three pH units within four weeks was observed in the aqueous extracts (Figure 1a). The main reason for this effect becomes clear when the change of pH values is compared with the change in chemical forms of inorganic nitrogen in the same aqueous extracts (Figure 1b).

During the aerobic incubation experiments, nitrification takes place: the microbial transformation of ammonium into nitrate. During this process hydrogen ions are produced and thus pH is lowered:

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O$$

In a typical laboratory experiment carried out with pig manure and sandy soil, nitrification started after 20 days and was completed after 45 days. As Figure 1b shows, the time dependent disappearance of ammonium ion in the extracts is closely

pH   **a**

N (meq l⁻¹)   **b**

nitrate

ammonium

[DOC] (mg l⁻¹)   **c**

time (days)
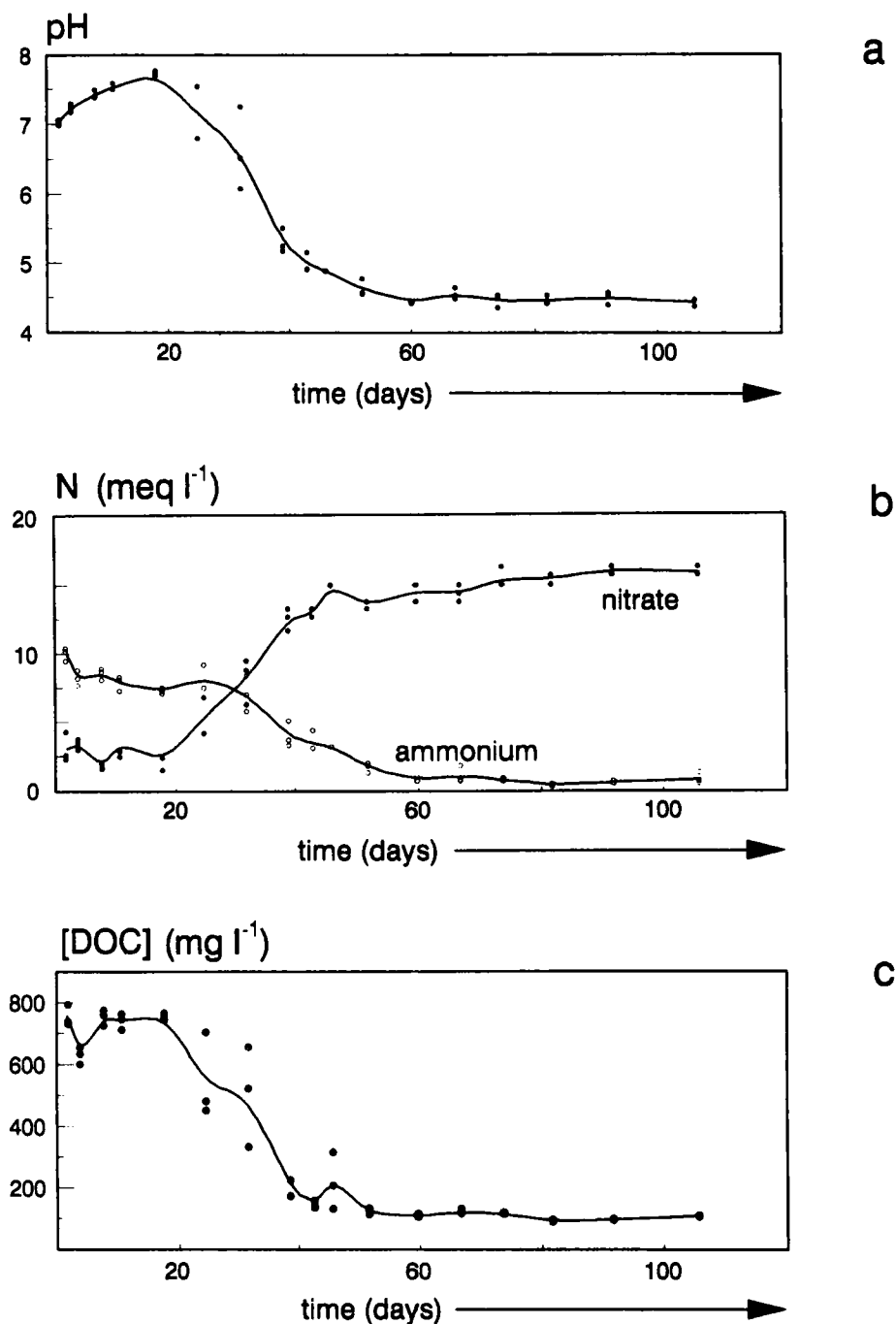
Figure 1 Aerobic incubation of a 10:1 sandy soil/pig manure mixture. Time dependency of pH (a), mineral N concentrations (b) and dissolved organic carbon content (c) in aqueous extracts of the incubated mixtures.

accompanied by an increase in nitrate concentration. The strong correlation between Figures 1a and 1b lead to the conclusion that nitrification is one of the main causes of pH changes in the liquid fraction of soil/manure mixtures throughout the aerobic incubation experiments. The slight pH increase in the first weeks of the incubation experiment (cf. Figure 1b) probably relates to loss of carbon dioxide from the liquid and through the bag walls or slow establishment of equilibrium between the solid and liquid fractions. For example, slow dissolution of struvite, a known component of the manure solid fraction[10], produces hydroxyl ions:

$$MgNH_4PO_4 + H_2O \rightleftharpoons Mg^{2+} + HPO_4^{2-} + NH_4^+ + OH^-$$
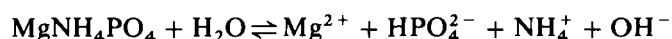
Unpublished results indicate that both processes may occur. Figure 1c shows that [DOC] changes follow the same pattern in time as pH changes. This can be explained at least partially by the precipitation or adsorption of higher molecular weight organic matter at lower pH values, as it contains many weakly acidic functional groups. Another reason may be the influence of pH (and incubation time) on biodegradation of DOC both with respect to kinetics and to degradation pathways. In the first week after the start of the incubation experiment, a pH independent drop in [DOC] was observed; this effect was due to rapid biodegradation of volatile fatty acid anions (unpublished results; cf.[11]). During the anaerobic incubation experiment, pH values showed a general tendency to decrease slightly in time (Figure 2a). The decrease is not related to nitrification; under anaerobic conditions nitrification cannot take place (no nitrate was indeed observed in the filtered extracts). pH values in replicate samples vary more than in the aerobic incubation experiment; this is probably due to a lack of sample homogeneity in the anaerobic incubation experimental set up. Figure 2b shows the time-dependency of [DOC] for the anaerobic incubation experiment.

Aerobic and anaerobic incubation of mixtures of pig manure (PM) and cattle manure (CM) with sandy soil show a good correlation between [DOC] and [Cu], suggesting complexation of copper by DOC (Figure 3). At low [DOC] values in the aerobic experiments, which correspond to low pH values, no signs of acid-related desorption or redissolution of Cu were observed. In general the relation between [DOC] and [Cu] is the same for all four experiments. Some differences do, however, occur:

1) For PM the [Cu]/[DOC] ratio is higher for the aerobic experiment than for the anaerobic experiment. This can be explained by a higher volatile fatty acid anion (mainly acetate) fraction in total DOC throughout the anaerobic incubation experiment; this was confirmed experimentally (unpublished results). Volatile fatty acid anions are expected to have lower complexation capacity[12], this assumption is supported by the GPC-fractionation experiment described in one of the next sections.

2) In general the [Cu]/[DOC] ratio is higher in the case of PM incubation experiments, especially when aerobic incubation is involved. This is in accordance with the total amounts of copper in PM and CM mixtures with sandy soil: PM/soil: 0.435 mg and CM/soil: 0.330 mg (in 50 grams of 10:1 soil/manure mixtures). The percentage of copper in solution at a 1:1 solid/liquid ratio used in the extraction or
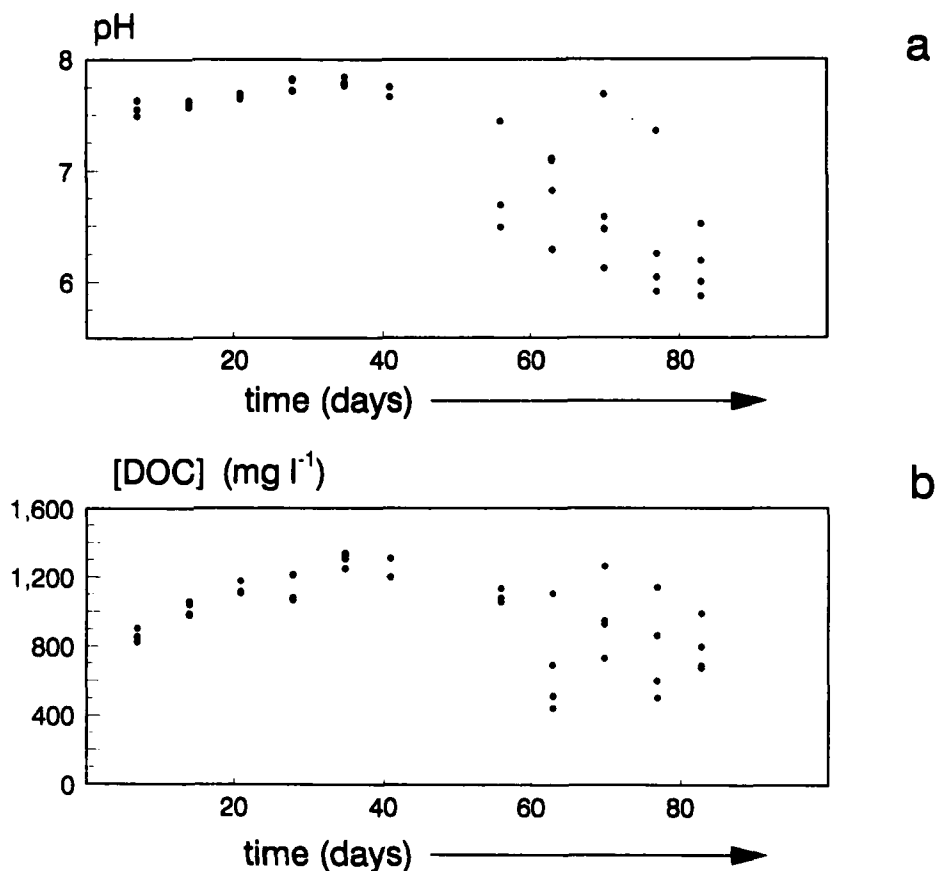
Figure 2 Anaerobic incubation of a 10:1:10 sandy soil/pig manure/water mixture. Time dependency of pH (a) and dissolved organic carbon content (b) in the liquid fraction of the incubated mixtures.

in the anaerobic incubation experiment, can be calculated from Table 1 data. For example at the highest copper levels found (1.3 mg l^{-1}, cf. Figure 3) about 15% of total copper is in solution.

3) The [Cu]/[DOC] ratio is higher at higher [DOC] levels. High [DOC] levels correspond to high pH values (cf. Figure 1). From copper/fulvic acid complexation data it is known that conditional stability constants for this complexation increase with increasing pH[13]. If high molecular weight organic matter originating from manure can be compared with fulvic acid, pH dependency of complexation constants can explain the observed higher [Cu]/[DOC] ratios at high [DOC] levels.

Results for cadmium (Figure 4) are similar to copper results, including the observed difference between the aerobic and anaerobic incubation experiments. Cadmium levels were only determined in PM incubation experiments. One difference was however observed. At low [DOC] (<400 mg l^{-1}) [Cd] increases with decreasing
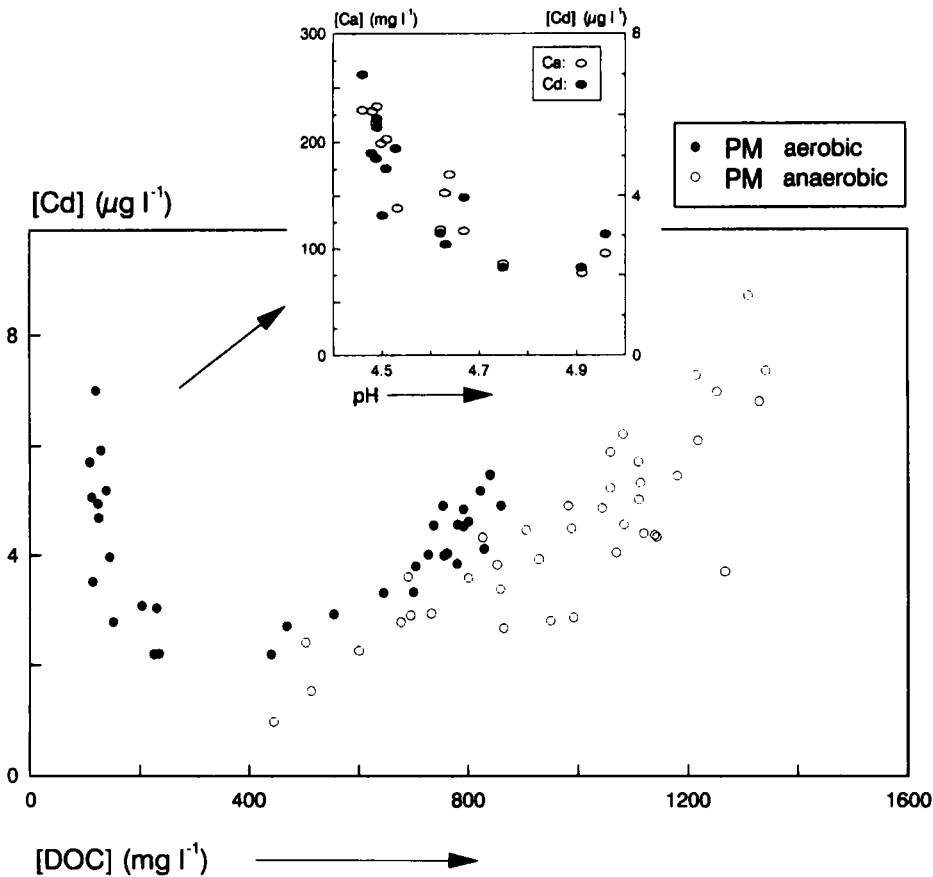
[Cu] (mg l⁻¹)
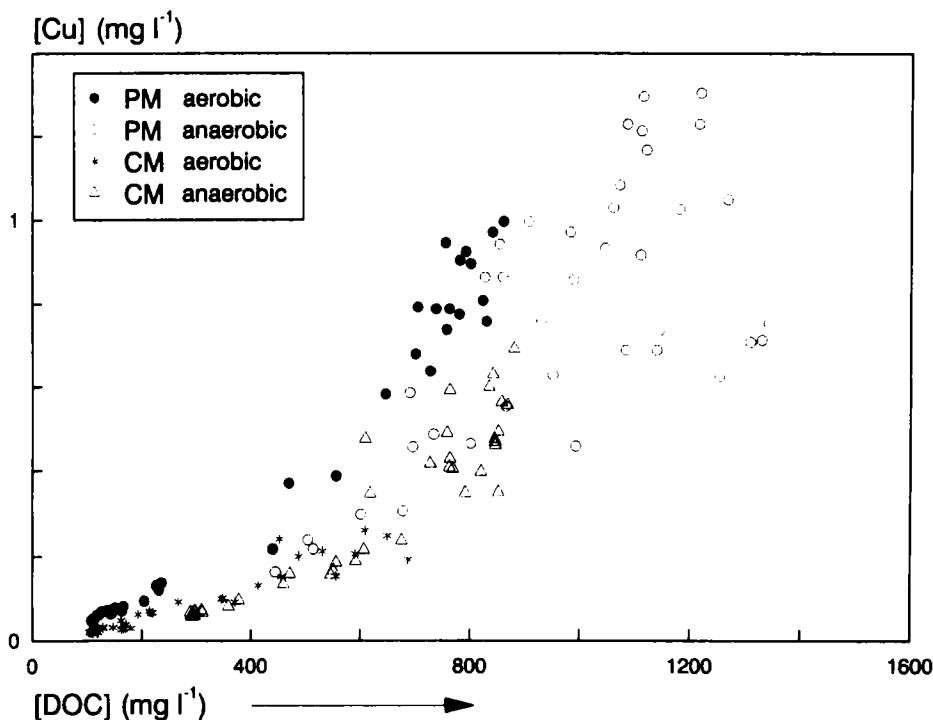
Figure 3 Incubation of soil/manure mixtures. Relation between measured dissolved copper concentrations and dissolved organic carbon concentrations in aqueous extracts.

[DOC]. The inset in Figure 4 shows the relation between pH and [Cd] for samples with [DOC] < 400 mg l⁻¹. All those samples have pH < 5.0 and on the other hand none of the other samples has a pH value that low. The pH-dependency of [Cd] at pH < 5.0 is typical for acid-related desorption. This is further illustrated by data on calcium concentrations in the same samples. Soil aluminium brought in solution at pH < 5 replaces calcium (and other ions like magnesium and manganese) on the soil adsorption complex[14]. The inset in Figure 4 shows that the behaviour of cadmium is very similar to that of calcium at pH < 5.0, where calcium carbonate is completely dissolved and only calcium desorption takes place. These data support the hypothesis that cadmium desorption also occurs at pH < 5.0. Calculations based on Table 1, show that at the highest [Cd] values observed (8 μg l⁻¹ at low pH or high [DOC]), about 3% of total cadmium is in solution (applying 1:1 solid/liquid ratios in extraction or anaerobic incubation procedures).

Desorption studies

Desorption of heavy metals from soil, labelled with Zn-65, Cd-109 and Pb-210, using different amounts of pig manure liquid fraction Figure 5 shows the desorption
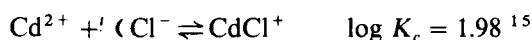
Figure 4 Incubation of soil/manure mixtures. Relation between measured dissolved cadmium concentrations and dissolved organic carbon concentrations in aqueous extracts.

of Zn-65, Cd-109 and Pb-210 at pH-7.5 from sandy soil upon extraction with water containing different amounts of PM-LF. Gross soil and PM-LF compositions are as used in the incubation experiments (cf. Table 1). Results show a clear relationship between the amount desorbed from the soil and the amount of PM-LF present in the extracting liquid. High molecular weight dissolved organic matter (HMW-DOC) from PM-LF is a possible complexant, but also chloride and volatile fatty acid anions (mainly acetate). The latter two are present in high concentrations in manure liquid fractions and are known to form complexes with cadmium. If manure derived HMW-DOC is considered to be comparable to natural fulvic acids, an estimation of the relative amounts of heavy metal complexed with HMW-DOC, chloride and acetate can be made. The relative importance of inorganic and organic complexation will be shown by using cadmium as an example.

% desorbed

% PM liquid fraction in extraction mixture ⟶
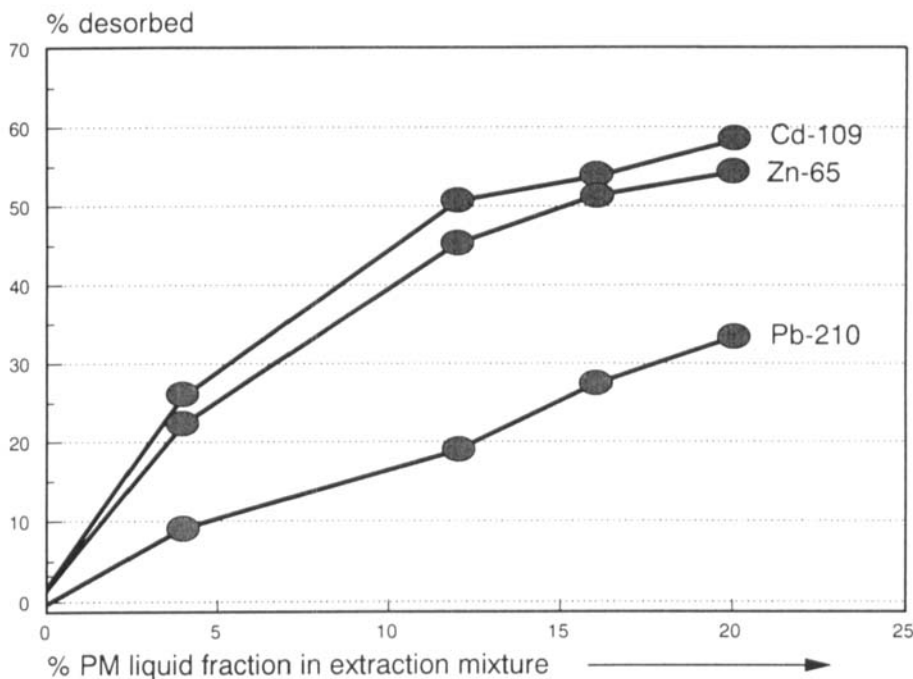
Figure 5 Desorption of heavy metals as a function of pig manure liquid fraction content in the extracting liquid.

Complexation constants for 1:1 cadmium/chloride, cadmium/acetate, and cadmium/fulvic acid complexation are:

$$Cd^{2+} +^{\prime} (Cl^- \rightleftharpoons CdCl^+ \qquad \log K_c = 1.98 \ [15]$$

$$Cd^{2+} + OAc^- \rightleftharpoons CdOAc^+ \qquad \log K_c = 2.6 \ [12]$$

$$Cd^{2+} + \{FA\}^n \rightleftharpoons Cd\{FA\}^{n+2} \log K_{c,cond.} = 5$$

K_c values are complexation constants; $K_{c,cond.}$ is a conditional stability constant normalized to represent a fulvic acid (FA) complexing capacity ("active concentration") of 2 mmole g^{-1} FA carbon[13] and adjusted empirically for pH[13]. The ratio between K_c and $K_{c,cond.}$ values implies that chloride complexation is only comparable to fulvic acid complexation if the chloride activity is at least 1000 times the fulvic acid "active concentration". Similarly, volatile fatty acid anion ("acetate") complexation is only comparable to fulvic acid complexation if the "acetate" activity is 250 times the fulvic acid "active concentration". The extracting liquid with 10 weight % PM-LF contains 850 mg $DOCl^{-1}$ (Table 1); from this amount about 480 mg l^{-1} correspond to volatile fatty acid anion ("acetate") and 370 mg l^{-1} to high molecular weight dissolved organic matter (HMW-DOC) (cf. Table 1). If HMW-DOC in soil/manure aqueous extracts is considered comparable to fulvic acid, this corresponds to a HMW-DOC "active concentration" of about 0.74 mM. The chloride

concentration in the 10% PM-LF extracting liquid is 8 mM (calculated from data in Table 1). This means that in this experiment complexation of cadmium with chloride probably was not important relative to HMW-DOC complexation. The volatile fatty acid anion ("acetate") concentration in the 10% PM-LF extracting liquid is 20 mM (Table 1). So "acetate" complexation is expected to be about 10 times less important if compared to HMW-DOC complexation.

Desorption of cadmium from Cd-109 labelled soil using pig manure liquid fractions with and without high molecular weight organic matter; influence of labelling date and extraction pH   In order to distinguish between possible complexation mechanisms experiments were carried out using PM-LF with a reduced concentration of (higher molecular weight) organic matter. For this purpose a portion of PM-LF was treated with active carbon, which is known to selectively adsorb higher molecular weight organic molecules. Active carbon treatment of PM-LF resulted in a reduction of [DOC] from 8.5 mg g^{-1} to 4.6 mg g^{-1}. The latter concentration is comparable to the volatile fatty acid concentration in PM-LF (cf. Table 1; 0.20 meq g^{-1} volatile fatty acid correspond to [DOC] = 4.8 mg g^{-1} if all volatile fatty acid is considered to be acetate). Desorption experiments were carried out at three different pH values using sandy loam soil with varying labelling dates: soil with Cd-109 added shortly before the experiment (1–117 days) and soil with Cd-109 added six years earlier. Only cadmium desorption was studied, because no "aged" Zn-65 or Pb-210 labelled soils were available. Data for freshly labelled soils (aged 1, 13 and 117 days) were averaged. The sandy loam soil used was slightly alkaline (pH of an 1:5 aqueous extract: 7.8), contained 0.5% organic carbon, 2.1% calcium carbonate, and 0.16 μg g^{-1} Cd.

Results are given in Figure 6. It is shown clearly that more than 75% of the desorbing capacity of PM-LF is related to the higher molecular weight fraction of DOC. This strongly supports the assumption that HMW-DOC is an important complexing agent in animal manure. Anions (volatile fatty acid anions; cf. the preceding section) and ionic strength also contribute to the desorbing capacity of PM-LF as shown by the differences between active carbon treated PM-LF and deionized water. Results are in accordance with predictions made in the previous section for the complexation of cadmium with different possible complexants.

GPC-fractionation of manure derived dissolved organic matter

Figure 7 shows [DOC] and [Cu] in GPC elution fractions of soil solution of a sandy soil/PM/water mixture. Corresponding [Cu]/[DOC] ratios are shown as well. The elution chromatogram of DOC shows two main peaks, one around elution fraction 15, representing high molecular weight compounds, and one another around elution fraction 29, mainly volatile fatty acid anion (acetate, propionate). The latter peak also contains other low molecular weight anions (bicarbonate, chloride, orthophosphate). The elution chromatogram of copper shows high concentrations in the earlier elution fractions and a small but clear elution peak around fraction 30. The latter corresponds to free copper ions or copper complexed with small inorganic anions (chloride, acetate etc.). The first conclusion is that copper in the soil solution is mainly
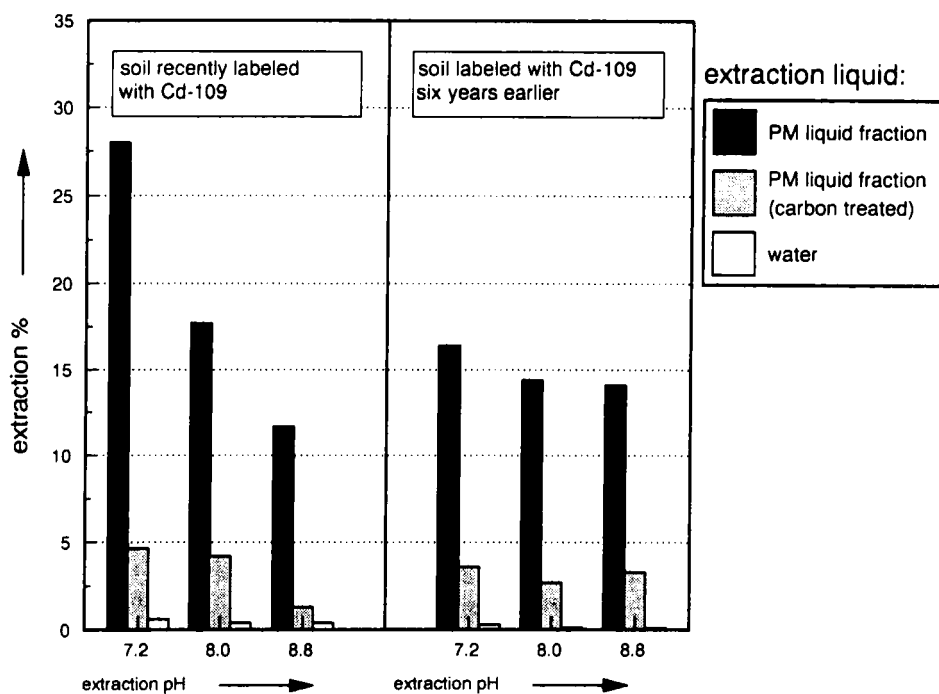
Figure 6 Desorption of cadmium from soil as a function of aging and extraction pH. Comparison of extracting liquids with different dissolved organic matter content.
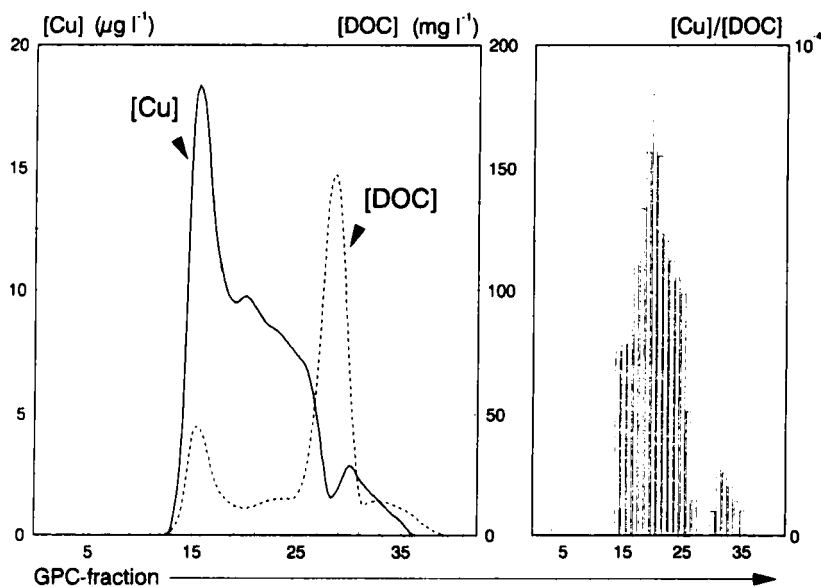
Figure 7 Gel permeation chromatography of the liquid fraction of a pig manure/soil/water mixture. Elution behaviour of copper and dissolved organic carbon.

present (for at least 90%) as higher molecular weight complexes; comparable results were obtained earlier for sewage sludge extracts[16]. Results are further supported by data on complexation or conditional stability constants for copper/acetate and copper/fulvic acid complexation respectively[12,13]. Our conclusion is further substantiated by the [Cu]/[DOC] ratios given in Figure 7. It can be concluded that an intermediate DOC molecular weight fraction (around elution fraction 20) is mainly responsible for copper solubilization.

CONCLUSIONS

Dissolved organic matter plays an important role in the solubilization of heavy metals present in the soil after application of liquid animal manure. The fate of heavy metals in manured soil is related to the fate of organic matter. The organic matter behaviour in soils after liquid manure application is strongly dependent on chemical and microbial processes taking place when a highly reactive material like liquid manure is introduced in the soil. Nitrification proved to be important in this respect as it indirectly influences (through pH changes) the presence of organic matter in the soil solution. Other important processes are rapid biodegradation of the most reactive manure organic matter (e.g. volatile fatty acids) and carbon dioxide production.

In the incubation experiments it was shown that no great difference existed between different types of manure with respect to the interaction between dissolved organic matter and heavy metals in soil. This can facilitate future modelling of the behaviour of heavy metals in the soil/manure system.

The application of liquid animal manure results in the solubilization of solid phase adsorbed and precipitated heavy metals, which can lead to enhanced transport of heavy metals through the soil profile until dissolved organic matter is digested. Repeated manure application can again remobilize the heavy metals by percolation and lixivication, leading either to transport to even greater depths or to uptake by the plants.

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