

This article was downloaded by:

On: 15 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Chemistry and Ecology

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713455114>

Effect of clay minerals on extractability of heavy metals and sewage sludge mineralization in soil

A. R. A. Usman; Y. Kuzyakov; K. Stahr

Online publication date: 12 May 2010

To cite this Article Usman, A. R. A. , Kuzyakov, Y. and Stahr, K.(2004) 'Effect of clay minerals on extractability of heavy metals and sewage sludge mineralization in soil', *Chemistry and Ecology*, 20: 2, 123 – 135

To link to this Article: DOI: 10.1080/02757540410001665971

URL: <http://dx.doi.org/10.1080/02757540410001665971>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

EFFECT OF CLAY MINERALS ON EXTRACTABILITY OF HEAVY METALS AND SEWAGE SLUDGE MINERALIZATION IN SOIL

A. R. A. USMAN*, Y. KUZUYAKOV and K. STAHR

*Institute of Soil Science and Land Evaluation (310), University of Hohenheim,
D-70593 Stuttgart, Germany*

(Received 2 December 2003; In final form 19 January 2004)

An incubation experiment lasting 111 d was carried out to study the effect of the addition of three clay minerals (Na-bentonite, Ca-bentonite, and zeolite) to soil derived from sewage sludge on water-extractable and exchangeable forms of four heavy metals (Zn, Cd, Cu, and Ni), as well as on soil organic matter mineralization, microbial biomass C and the release of inorganic N. The addition of clay minerals led to a significant decrease in water-extractable and exchangeable forms of heavy metals. The extent of decrease ranged from 14 to 75% for the water-extractable heavy metals and from 12 to 42% for the exchangeable form over the incubation time, as compared with untreated soil. The reduction in extractability of heavy metals was greater due to the addition of Na-bentonite and Ca-bentonite than that due to the addition of zeolite. Addition of clay minerals did not affect any of the following microbiological parameters in the soil: microbial biomass C, organic C (C_{org}) mineralization, and metabolic quotient (qCO_2), and release of inorganic N during the first 3 weeks of incubation. However, as the incubation period increased, these parameters were significantly increased by the addition of clay minerals, especially by the addition of Na-bentonite and Ca-bentonite. This result is explained by a strong reduction in extractability of heavy metals after the addition of Na-bentonite and Ca-bentonite.

Keywords: Clay minerals; Heavy metals; Organic matter mineralization; Microbial biomass C; Metabolic quotient; Inorganic N

1 INTRODUCTION

Agricultural use of sewage sludge has been common practice in waste disposal in recent decades. However, this practice is generally associated with the problem of heavy-metal accumulation in soils. It has been demonstrated in many studies that heavy metals adversely affect biological and biochemical functions in soil (Fließbach *et al.*, 1994; Kandeler *et al.*, 1996; Kelly and Tate III, 1998). Heavy metals introduced with compost or sewage sludge caused the accumulation of soil organic matter (SOM) and decreased the turnover rate of organic matter, because of inhibitory effects on microbial biomass (Chander *et al.*, 1995; Leita *et al.*, 1995). Chander and Brookes (1991) also found lower biomass and higher qCO_2 values in heavy-metal-contaminated soils than in uncontaminated soils. The toxicity of heavy metals depends mainly on their bioavailability, and therefore on their chemical

*Corresponding author. E-mail: adel@uni-hohenheim.de

forms in both organic and inorganic matrices (Leita *et al.*, 1999). When Zn and Cu were present together in the soils, the increase in bioavailability of Zn above $123 \mu\text{g g}^{-1}$ soil and Cu above $3.0 \mu\text{g g}^{-1}$ soil caused marked decreases in the amounts of soil microbial biomass (Chander and Brookes, 1993). Reduction of the solubility and bioavailability of heavy metals in contaminated soils without removing them from the soil is commonly carried out to reduce the negative impacts on the environment and improve the quality of contaminated soils. Therefore, the study focused on reducing the availability of heavy metals and thus its effect on some of the parameters related to microbial activity.

Welp (1999) reported that the sorption and immobilization of toxic metals in soil is an effective detoxification process and thus an essential part of the buffer capacity of soil. Immobilization of heavy metals caused an increase in basal respiration, litter decomposition and microbial activity (Kiiikilä *et al.*, 2001). There are several methods for immobilization of heavy metals in soil. Immobilization can be carried out by adding natural and synthetic chemical additives such as alkaline materials, phosphate minerals, iron and manganese oxides, aluminosilicates or coal fly ashes (Mench *et al.*, 1998). Clay minerals are among the major materials that interact with almost all soil contaminants (Prost and Yaron, 2001). The adsorption of Ni, Cd, Zn, and Pb by montmorillonite was reported by Schulthess and Huang (1990). Immobilization of heavy metals by natural zeolite (clinoptilolite) and six synthetic zeolites was studied by Oste *et al.* (2002), who found that the synthetic zeolites had an effect on immobilization of Cd and Zn, but the amount of metals bound to the natural zeolite (clinoptilolite) is almost negligible.

Therefore, our first aim was to compare three clay minerals, Na-bentonite, Ca-bentonite, and zeolite, in their ability to reduce the bioavailability of heavy metals (Zn, Cd, Cu and Ni). In most studies investigating the effect of addition of different substances reducing the availability of heavy metals, only the heavy-metal concentration in different solutions and soil materials was investigated. The effect of addition on biochemical parameters was not investigated. As shown above, the reduction in extractability of heavy metals may help to improve the biochemical parameters. Therefore, the second aim was to monitor the changes in C_{org} mineralization (as CO_2 evolution), inorganic N, microbial biomass C and metabolic quotient ($q\text{CO}_2$) during the incubation of soil derived from sewage sludge with and without the addition of natural clay minerals. Our hypothesis was that the heavy-metal-polluted soil can be ameliorated by adding clay minerals, and this could find future use in plant production.

2 MATERIALS AND METHODS

2.1 Soil and Treatments

Soil samples were collected from a sewage sludge deposit area located 15 km north-east of Stuttgart. According to the FAO–UNESCO (1997) system, the soil type is an Urbic Anthrosol. The German name for this soil type is a ‘Reduktosol’ (Lehmann *et al.*, 2000). X-ray diffraction analysis to determine the soil clay minerals was performed using a Siemens Instrument (D-500) with $\text{Cu-K}\alpha$ radiation (Zarei *et al.*, 2001). In the clay fraction, poorly crystalline clay minerals of kaolinite, illite and vermiculite/smectite were detected. The soil samples were taken from the 15- to 35-cm layer, corresponding to the Ah2 horizon. This soil had a high content of C_{org} and CaCO_3 and a very high content of heavy metals (Tab. I). The soil was air-dried and sieved to pass through a 2-mm sieve before the experiment and chemical analysis.

Three clay minerals of Na-bentonite, Ca-bentonite and zeolite (Fa. IKO Minerals GmbH, 45772 Marl) were used as additives to the soil as treatments. Na-bentonite and Ca-bentonite

TABLE I Physico-chemical properties of soil derived from sewage sludge.

<i>Properties</i>	<i>Value</i>
<i>Particle size distribution (%)</i>	
Sand	42
Silt	40
Clay	18
<i>Chemical properties</i>	
pH	7.0
CaCO ₃ (%)	8.9
Organic C (%)	13.3
Total N (%)	1.7
<i>Total heavy-metal content (mg kg⁻¹)</i>	
Zn	4500
Cd	77
Cu	2000
Ni	442

used in this study are composed of clay minerals of the smectites group, mostly montmorillonite (62–70%). Ca-bentonite with smectites that are predominantly occupied with Ca²⁺ ions originated from Bavarian mines. Na-bentonite was produced by exchange of initial earth-alkaline cations of smectites by Na⁺ ions in a technical process (alkali activation). Clinoptilolite (zeolite) is the most abundant naturally occurring zeolite consisting of hydrated aluminosilicate with alkali and alkaline earth cations in a three-dimensional crystal structure. Zeolite is composed of clay minerals of clinoptilolite (80%), montmorillonite (10%) and feldspar (5%). Each clay mineral (0.5 g) was added to 25 g of soil. The soil–clay mineral mixtures were put into glass vessels (250 ml). Distilled water was added to each soil mixture to bring it to 70% of water-holding capacity (WHC). A soil without addition of clay minerals was incubated as the control. Small vials with 5 ml of 1 M NaOH solution were placed in vessels to trap CO₂. The NaOH solution in the vials was changed after 10, 15, 21, 30, 39, 45, 54, 62, 74, 83, 95 and 111 d. After the addition of NaOH, the vessels were closed airtight and incubated 111 d at 35 °C. This temperature was chosen, because the optimal temperature for microbial activity ranges from 20 to 35 °C (Scheffer and Schachtschabel, 2002).

2.2 Analyses

Soil pH was measured with a glass electrode using a soil-to-0.01 M CaCl₂ ratio of 1 : 2.5. Total soil C and N were measured using a LECO 2000 CN analyser. The inorganic carbon was determined using a Scheibler apparatus (carbonates were dissolved with 10% HCl, and the volume of released CO₂ was measured). The carbonate concentrations were calculated using the universal gas law (Schlichting *et al.*, 1995). Soil organic carbon was calculated as the difference between total carbon and inorganic carbon. The soil texture was determined by a pipette method (Schlichting *et al.*, 1995). The total content of Zn, Cd, Cu and Ni was determined using an aqua regia microwave digestion method. Microwave digestion was performed using 10 ml of aqua regia with a nine-stage program; the microwave power ranged from 0 to 750 W, the temperature ranged from 70 to 105 °C, and the digestion time was 30 min. Heavy-metal concentrations were determined by atomic absorption spectrometry (AAS Perkin Elmer 3100).

After 21, 62 and 111 d of incubation, the soil was destructively sampled, and concentrations of water-soluble Zn, Cd, Cu and Ni were measured after extracting 2 g of air-dried soil with 50 ml of H₂O for 2 h. After the water extraction, the soil sediment was extracted

with 50 ml of 1 M NH_4NO_3 for 2 h to estimate the exchangeable amounts of heavy metals (Schlichting *et al.*, 1995). The heavy-metal content in the filtered solution was analysed by AAS.

Soil microbial biomass C was measured after 21, 62 and 111 d using a fumigation–extraction method (Vance *et al.*, 1987). In this technique, three replicates of each treatment were fumigated with ethanol-free chloroform for 24 h at 25 °C. The soil samples were then extracted with 0.5 M K_2SO_4 for 30 min. Three replicates of non-fumigated soil samples were extracted similarly. The extracted C was determined by dichromate oxidation at 100°C (2 ml of extract + 1.5 ml of 15 M H_2SO_4 + 1.5 ml of saturated aqueous solution of $\text{K}_2\text{Cr}_2\text{O}_7$). The residual $\text{K}_2\text{Cr}_2\text{O}_7$ was determined photometrically at 565 nm (Kuzyakov, 1997). The calibration of the extracted C measurements was carried out using glucose. Microbial biomass C was calculated as Ec/k -factor, where Ec is organic C extracted from fumigated soils minus organic C extracted from non-fumigated soils, and k -factor = 0.45 (Wu *et al.*, 1990; Jørgensen, 1996).

CO_2 evolved during the incubation was trapped in 1 M NaOH, and the excess NaOH was titrated with 0.1 M HCl after addition of BaCl_2 (Black, 1965). Total C_{org} mineralized was calculated as cumulative CO_2 evolution (Leifeld *et al.*, 2002). The specific respiration activity ($q\text{CO}_2$) was expressed as the production of CO_2 -C per unit biomass C and time (Anderson and Domsch, 1978).

Soil inorganic N (NH_4 -N and NO_3 -N) in 0.02 M CaCl_2 extracts (1 : 4 soil-to-solution ratio) from all treatments was determined using an autoanalyser (Fa. Scalar).

2.3 Statistical Analysis

Differences among treatments were tested by separate two-way ANOVAs and subsequent post-hoc comparisons of means (L.S.D. test, at $P = 0.05$).

3 RESULTS AND DISCUSSION

3.1 Dynamics of Water-Extractable and Exchangeable Forms of Heavy Metals in Soil Derived from Sewage Sludge Following Addition of Clay Minerals

The water-extractable and exchangeable forms of heavy metals were redistributed to other forms by incubation and addition of clay minerals. For all the treatments, water-extractable Cd and Ni concentrations decreased significantly during the first 3 weeks of incubation (Fig. 1). In the untreated soil (control), water-extractable Cd decreased by 71, 66 and 33% of initial content, and Ni decreased by 54, 70, and 58%, after 21, 62 and 111 d of incubation, respectively. The reduction in water-extractable Cd and Ni concentrations can be explained by their retention by soil organic matter and calcium carbonate (El-Bassam and Stühmeier, 1978; Tyler and McBride, 1982; McBride *et al.*, 2000). Sewage-sludge constituents can also lower Cd activity in soil solution via complexing by soluble ligands or colloidal surfaces (Bell *et al.*, 1991). Villarroel *et al.* (1993) found that Cd in the saturation extracts of the sludge-treated soil was distributed among free ligand (38.7%), chloride complexes (8.4%), sulfate complexes (10.3%) and organic complexes (38.7%). Gray *et al.* (1998) reported that soil organic matter was important in controlling Cd sorption and desorption. It was observed that the rate of decrease in water-extractable Cd tended to decline as incubation progressed.

In contrast, water-extractable Cu in the untreated soil increased and changed little with time. The results showed that water-extractable Cu increased by about 12, 24 and 3.8% of

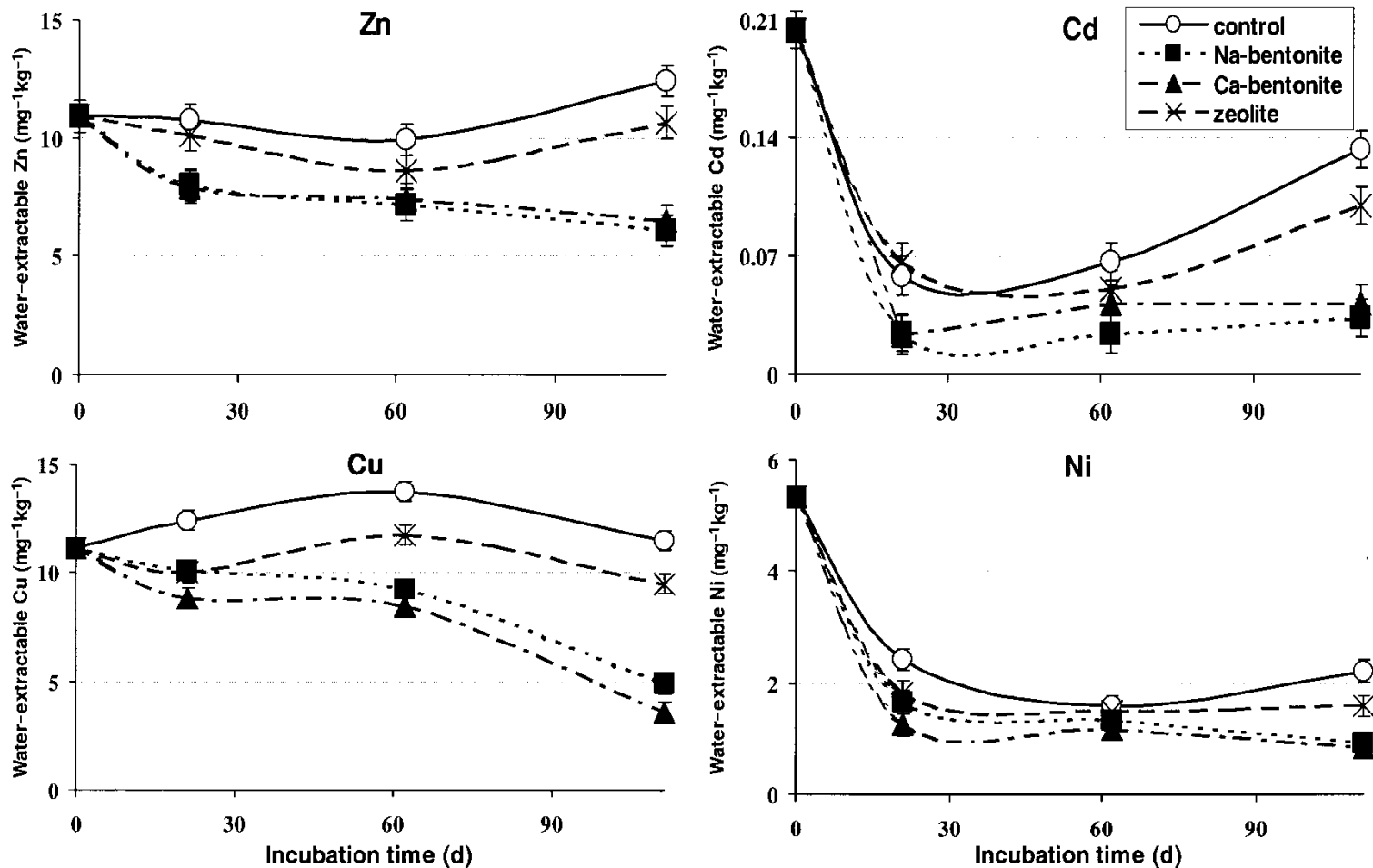


FIGURE 1 Dynamics of water-extractable heavy metals in soil derived from sewage sludge after the addition of clay minerals. Mean \pm L.S.D./2; where absent, bars fall within symbols.

initial content after 21, 62 and 111 d, respectively. Water-extractable Zn decreased by about 1.5% at 21 d and 9% at 62 d but increased by about 14% at 111 d, as compared with initial soil, so it changed little with time. These increases in water-extractable Zn (at 111 d) and Cu (at all sampling dates) may be explained by dissolved organic matter, which promoted the dissolution of Cu and Zn by building organic complexes. Almas *et al.* (2000) found that the addition of organic matter increased the solubility of Zn by the formation of organo-metallic complexes. In this study, it was observed that the increase in water-extractable Cu tended to decrease at the end of the incubation. This result is attributed to the tendency of soluble Cu to bind with organic matter or solid-phase materials. Organic matter in soluble and insoluble forms plays contrasting roles in controlling total soluble Cu and other metals as well. In sequential extractions of sludge-amended soils, Cu was found to predominate in the organic fraction (Sposito *et al.*, 1982). Tyler and McBride (1982) found that Cu and Ni were less extractable from the organic soil than Zn and Cd.

In all the treatments, incubation of soil derived from sewage sludge caused a decline in exchangeable form of all heavy metals tested (Fig. 2). As compared with initial soil, in untreated soil, the exchangeable form of heavy metals decreased by 21, 26 and 27% for Zn, by 38, 36 and 32% for Cd, by 23, 22 and 29% for Cu, and by 46, 50 and 55% for Ni after 21, 62 and 111 d of incubation, respectively. The results showed that the strongest reduction in the exchangeable form of all four heavy metals occurred during the first 3 weeks of incubation. After that, the reduction in exchangeable Zn, Cu and Ni increased very little up to the end of the experiment. However, the rate of decrease in exchangeable Cd tended to decline slowly, as incubation progressed. A decrease in reduction in water-extractable and exchangeable Cd may be attributed to the formation of soluble Cd-organic associations over the time of incubation. Neal and Sposito (1986) found that soil sorption of Cd was reduced by the formation of soluble-organic associations in the aqueous solution. In our soil, the reduction in extractability of heavy metals is attributed, in part, to the neutral pH, the presence of free calcium carbonate and, in part, the high organic matter content. This result concurs with that of McBride *et al.* (2000), who found that heavy metals were strongly retained in sewage sludge soil, which has a high organic matter and lime content. Ong and Bisque (1968) explained the phenomena of metal reduction by the fact that humic substances behave as negatively charged colloids, which may be coagulated by the electrolytes. Another phenomenon is that after the release of heavy metals from the sewage sludge, they react chemically with the soil so that metal toxicity declines with time (Lewin and Beckett, 1980).

The decrease in water-extractable and exchangeable forms of heavy metals in the soil treated with clay minerals was greater than without clay minerals. This effect was especially pronounced for the treatments with Na-bentonite and Ca-bentonite addition. For example, addition of clay minerals decreased water-extractable heavy metals at the end of the incubation as follows: Zn decreased by 51, 48 and 14%, Cd by 75, 68 and 25%, Cu by 57, 69 and 17, and Ni by 59, 63 and 29% at the end of the experiment for Na-bentonite, Ca-bentonite and zeolite, as compared with untreated soil, respectively. Na-bentonite and Ca-bentonite have a strong effect on the decrease in water-extractable heavy metals more than zeolite. This could be explained by high contents of the clay minerals in montmorillonite. Ca-bentonite and Na-bentonite have a higher proportion of montmorillonite (62–70%) than that for zeolite (10%). The binding of Ni, Cd, Zn and Pb by montmorillonite was reported by Schulthess and Huang (1990).

In the soil treated with clay minerals, the exchangeable form of heavy metals decreased during the incubation. This decrease was relevant for Cu, especially with Na-bentonite and Ca-bentonite after 111 d of incubation. After 21 d of incubation, exchangeable Zn was significantly affected by the addition of Na-bentonite and Ca-bentonite. However, the amounts of

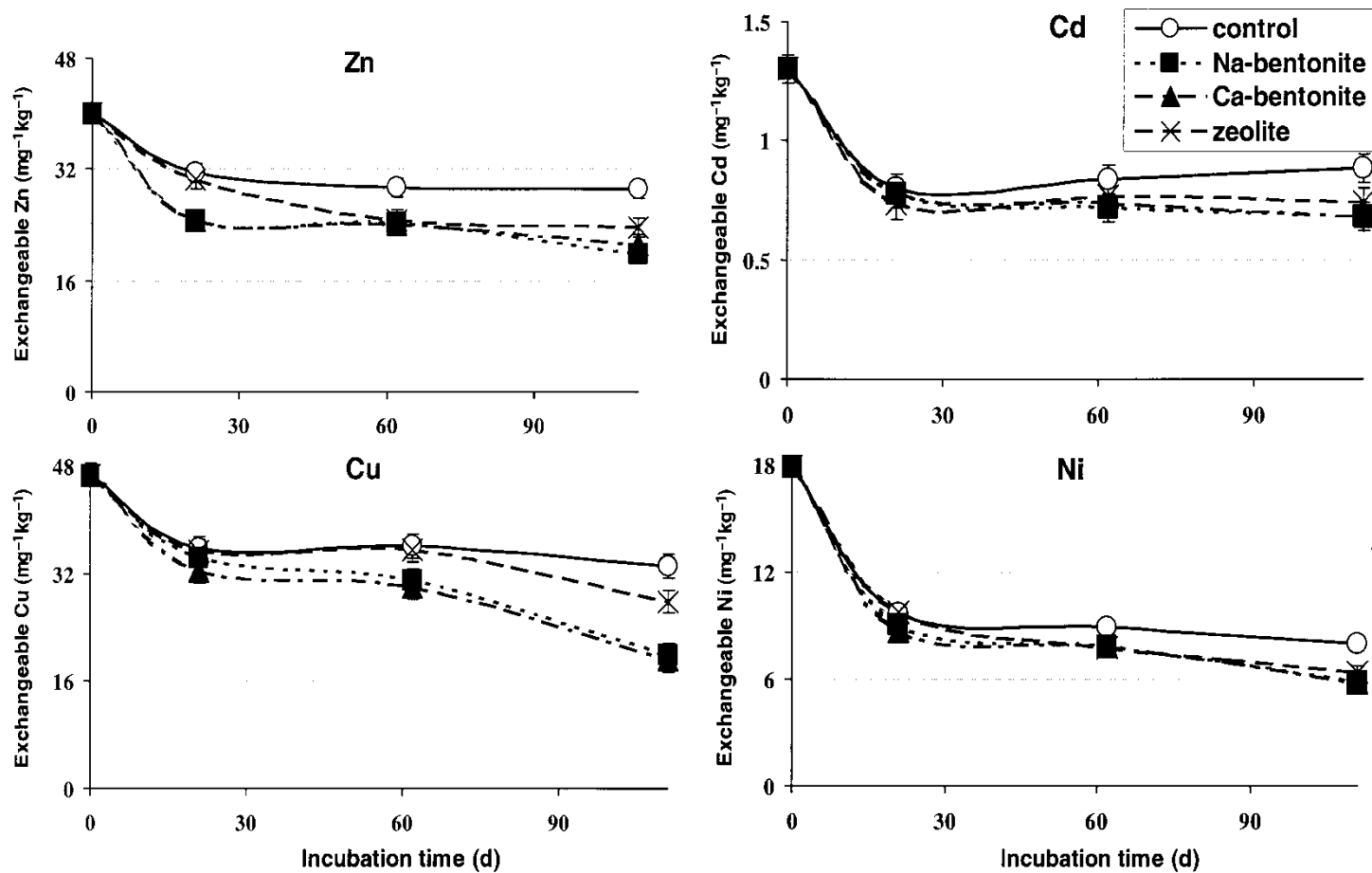


FIGURE 2 Dynamics of exchangeable heavy metals (extracted by NH_4NO_3) in soil derived from sewage sludge after the addition of clay minerals. Mean \pm L.S.D./2; where absent, bars fall within symbols.

exchangeable form of Cu, Cd and Ni were not significantly affected by the addition of clay minerals, as compared with untreated soil (control). At 62 and 111 d of incubation, addition of Ca-bentonite and Na-bentonite significantly decreased the amounts of exchangeable form of all four heavy metals, as compared with untreated soil (control). The addition of zeolite caused a significant reduction in the exchangeable form of Zn and Ni at 62 and 111 d but only resulted in a significant reduction in the exchangeable form of Cu and Cd at the end of the experiment, as compared with untreated soil (control). It was observed that the exchangeable form of heavy metals was significantly affected by the three added clay minerals. Compared with the untreated soil, the addition of clay minerals decreased the exchangeable Zn by 31, 27 and 19%, Cd by 22, 23 and 16%, Cu by 40, 42 and 16%, and Ni by 27, 28 and 20% for Na-bentonite, Ca-bentonite and zeolite, as compared with untreated soil, respectively. There were no significant differences in the exchangeable forms of heavy metals between Na-bentonite and Ca-bentonite, but significant differences were found between the bentonites and zeolite for the exchangeable Zn and Cu during the incubation.

3.2 Effect of Incubation Time and Addition of Clay Minerals on Organic C Mineralization, Microbial Biomass C, Metabolic Quotient and N Mineralization

The C_{org} mineralization during the experiment was recorded as cumulative CO_2 evolution. Numerous investigations have clearly demonstrated that inorganic colloids such as clays affect microbial biomass and turnover of soil organic matter (Martin *et al.*, 1976; Ladd *et al.*, 1985, 1992; Saggar *et al.*, 1996; Nelson *et al.*, 1997). The rate of decay of organic material is reduced by the presence of clay (Sørensen, 1975). In our investigation, cumulative C_{org} mineralization (as a percentage of initial C_{org} content) in soil derived from sewage sludge treated with clay minerals was higher than in untreated soil (control), especially for Ca-bentonite and Na-bentonite (Fig. 3). In the soil treated with clay minerals, C_{org} mineralization increased by about 12, 9 and 2.6% for Ca-bentonite, Na-bentonite and zeolite compared with untreated soil, respectively.

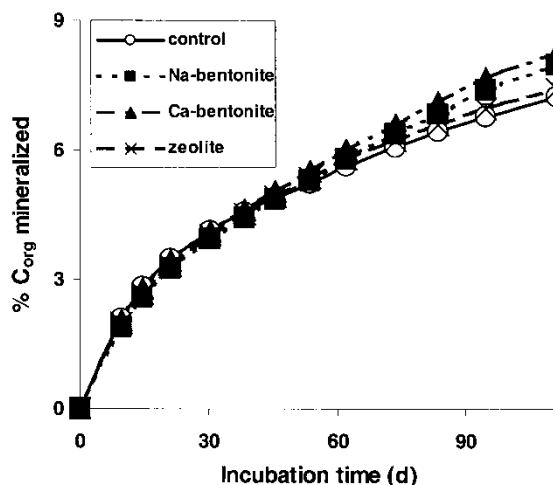


FIGURE 3 Effect of addition of clay minerals on cumulative organic C (C_{org}) mineralization during 111 days' incubation (as a percentage of initial C_{org} content). Mean \pm L.S.D./2; where absent, bars fall within symbols.

The soil microbial biomass was used as a sensitive indicator of changing soil conditions (Leita *et al.*, 1999). The control soil initially contained about $16.2 \text{ mg biomass C g}^{-1} \text{ C}_{\text{org}}$. For all treatments, microbial biomass C increased during the first 3 weeks of incubation, as compared with the initial soil. After day 21, microbial biomass C decreased with incubation time (Fig. 4). During the first 3 weeks of incubation, there were no significant differences in the effects of all treatments on the microbial biomass C levels. However, after 62 and 111 d of incubation, the addition of Ca-bentonite and Na-bentonite increased microbial biomass C significantly compared with untreated soil (control). Addition of zeolite increased microbial biomass C significantly only at the end of the incubation compared with untreated soil (control). It was observed that there were no significant effects on biomass C between Ca-bentonite and Na-bentonite, but significant differences were found between the clay minerals of bentonite and zeolite after 62 and 111 d of incubation. After 21 d of incubation, microbial biomass C values were 18.5 (control), 19.2 (with addition of Na-bentonite), 18.6 (with addition of Ca-bentonite) and 17.9 $\text{mg g}^{-1} \text{ C}_{\text{org}}$ (with addition of zeolite). At the end of the incubation (111 d), they were 6.7, 14, 15 and 9 $\text{mg g}^{-1} \text{ C}_{\text{org}}$, respectively. At the end of the incubation, clay mineral application increased the microbial biomass C content in soil derived from sewage sludge about 53% for Na-bentonite, 55% for Ca-bentonite and 28% for zeolite, as compared with untreated soil. Addition of clay mineral increased the microbial activity and then organic matter mineralization, because clay minerals reduced the availability of heavy metals to soil micro-organisms. This result concurs with Kiihilä *et al.* (2001), who reported that immobilization of heavy metals caused an increase in basal respiration, litter decomposition and microbial activity.

The metabolic quotient ($q\text{CO}_2$) is a relationship between soil respiration and microbial biomass C and is expressed as $\text{mg CO}_2\text{-C h}^{-1} \mu\text{g}^{-1} \text{ biomass C}$ (Anderson and Domsch, 1978). The $q\text{CO}_2$ can be used as a marker of the environmental stress of the microbial population (Anderson and Domsch, 1993; Moreno *et al.*, 1999). Our results showed that $q\text{CO}_2$ was higher in untreated soil (control) than in soil treated with clay minerals as incubation progressed (Fig. 5). The higher values of $q\text{CO}_2$ at the end of the experiment in the control were due to the lower values of microbial biomass C than in soil treated with clay minerals. The lower values of microbial biomass C and thus the higher values of the $q\text{CO}_2$ found in the control at the end of the incubation are also related to the high availability of heavy metals (Leita *et al.*, 1999).

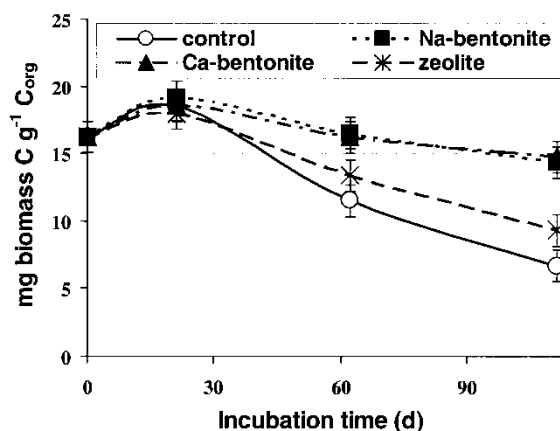


FIGURE 4 Changes in microbial biomass C in soil derived from sewage sludge after the addition of clay minerals. Mean \pm L.S.D./2.

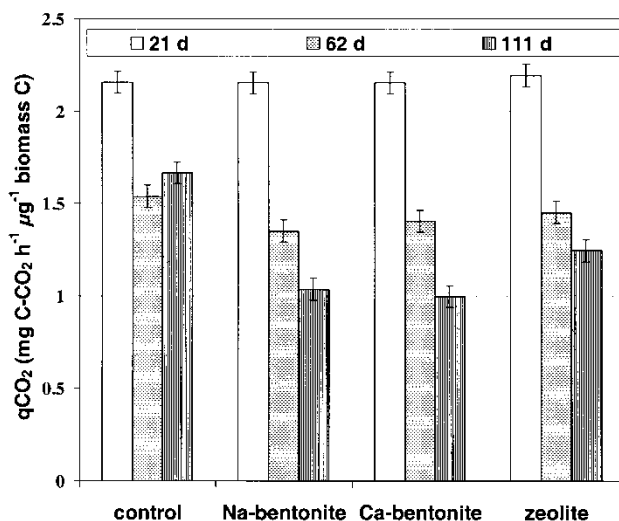


FIGURE 5 Changes in metabolic quotient (qCO_2) in soil derived from sewage sludge after the addition of clay minerals. Mean \pm L.S.D./2.

The control soil initially contained $1.33\ g\ inorganic\ N\ kg^{-1}\ soil$. In all the treatments, inorganic N was immobilized by micro-organisms during the first 3 weeks of incubation (Fig. 6), showing a high C availability. After this initial decline, the inorganic N content of all treatments began to increase steadily until the end of the experiment. During the N immobilization phase, no significant differences were found between any of the treatments in inorganic N. However, after 111 d of incubation, addition of Na-bentonite and Ca-bentonite significantly increased the amounts of inorganic N compared with untreated soil (control) and addition of zeolite. There were no significant differences in terms of the effects between addition of zeolite and untreated soil on inorganic N. At the end of the incubation, the amounts of inorganic N increased by about 1.8, 2.2 and $0.35\ g\ N\ kg^{-1}\ soil$ for Na-bentonite, Ca-bentonite and zeolite, respectively, compared with control. The availability of heavy metals in soil treated with Na-bentonite and Ca-bentonite was less than that in untreated

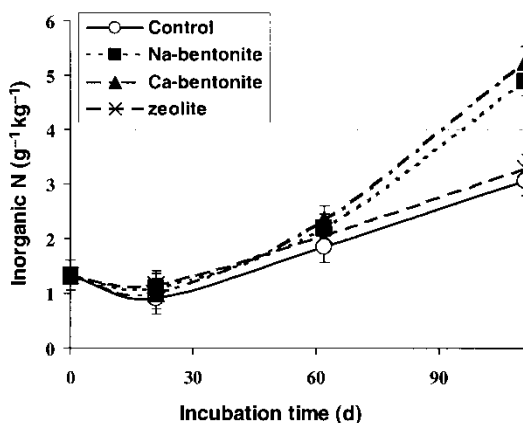


FIGURE 6 Changes in the amounts of inorganic N in soil derived from sewage sludge after the addition of clay minerals. Mean \pm L.S.D./2.

soil and in soil treated with zeolite. This is related to higher amounts of inorganic N in soil treated with Na-bentonite and Ca-bentonite. N mineralization is very sensitive to heavy-metal pollution (Liang and Tabatabai, 1977; 1978).

4 CONCLUSIONS

The addition of clay minerals, especially of Na-bentonite and Ca-bentonite, decreased the extractability of heavy metals during incubation. After addition of Ca-bentonite and Na-bentonite to soil derived from sewage sludge, the decreased toxicity of heavy metals over the time of incubation was reflected as increased C_{org} mineralization, microbial biomass C and inorganic N, and as a decreased metabolic quotient ($q\text{CO}_2$), as compared with untreated soil and addition of zeolite. The sensitivity of these parameters to a reduction in the extractability of heavy metals after addition of Na-bentonite and Ca-bentonite was as follows: microbial biomass C > $q\text{CO}_2$ > inorganic N > C_{org} mineralization. The use of Na-bentonite and Ca-bentonite is a promising method for reducing the extractability and possibly the bioavailability of heavy metals in sewage-sludge-contaminated soil, and therefore for remediation of the soil.

Acknowledgements

The authors would like to thank S. Köhler for determination of inorganic N, K. Ruf for determination of total N, Dr A. Lehmann for soil information, Dr M. Zarei and D. Frobel for analysis of clay mineralogy, and A. Hardie for linguistic help. We are very thankful to Fa. IKO Minerals GmbH for the use of their bentonites and zeolite. This work was partly funded by the Egyptian government in the scope of a fellowship for A. R. A. Usman.

References

- Almas, A. R., McBride, M. B. and Singh, B. R. (2000). Solubility and lability of cadmium and zinc in two soils treated with organic matter. *Soil Science*, **165**, 250–259.
- Anderson, J. P. E. and Domsch, K. H. (1978). A physiological method for the quantitative measurement of microbial biomass in soil. *Soil Biology and Biochemistry*, **10**, 215–221.
- Anderson, T. and Domsch, K. H. (1993). The metabolic quotient for CO_2 ($q\text{CO}_2$) as a specific activity parameter to assess the effects of environmental conditions, such as pH, on the microbial biomass of the soil. *Soil Biology and Biochemistry*, **25**, 393–395.
- Bell, P. F., James, B. R. and Chaney, R. L. (1991). Heavy metal extractability in long-term sewage sludge and metal salt-amended soils. *Journal of Environmental Quality*, **20**, 481–486.
- Black, C. A. (1965). *Methods of soil analysis*, American Society of Agronomy, Madison, WI.
- Chander, K. and Brookes, P. C. (1991). Microbial biomass dynamics during the decomposition of glucose and maize in metal-contaminated and non-contaminated soils. *Soil Biology and Biochemistry*, **23**, 917–925.
- Chander, K. and Brookes, P. C. (1993). Residual effects of zinc, copper and nickel in sewage sludge on microbial biomass in a sandy loam. *Soil Biology and Biochemistry*, **25**, 1231–1239.
- Chander, K., Brookes, P. C. and Harding, S. A. (1995). Microbial biomass dynamic following addition of metal-enriched sewage sludge to a sandy loam. *Soil Biology and Biochemistry*, **27**, 1409–1421.
- El-Bassam, N. and Stühmeier, K. (1978). Immobilisierung einiger spuren- und schadelemente durch zufuhr organischer siedlungsabfälle. *Mitteilungen der Deutschen Bodenkundlichen Gesellschaft*, **27**, 221–230.
- FAO-UNESCO (1997). Soil map of the world, revised legend, with corrections, World Resources Report 60, FAO, Rome, [Reprinted as Technical Paper 20. International Soil Reference and Information Center, Wageningen.].
- Fließbach, A., Martens, R. and Reber, H. H. (1994). Soil microbial biomass and microbial activity in soil treated with heavy metal contaminated sewage sludge. *Soil Biology and Biochemistry*, **26**, 1201–1205.
- Gray, C. W., McLaren, R. G., Roberts, A. H. C. and Condorn, L. M. (1998). Sorption and desorption of cadmium from some new zealand soils: Effect of pH and contact time. *Australian Journal of Soil Research*, **36**, 199–216.
- Jørgensen, R. G. (1996). The fumigation-extraction method to estimate soil microbial biomass: Calibration of the k_{EC} value. *Soil Biology and Biochemistry*, **28**, 25–31.

- Kandeler, E., Kampichler, C. and Horak, O. (1996). Influence of heavy metals on the functional diversity of soil microbial communities. *Biology and Fertility of Soils*, **23**, 299–306.
- Kelly, J. J. and Tate, R. L., III (1998). Effects of heavy metals contamination and remediation on soil microbial communities in the vicinity of a zinc smelter. *Journal of Environmental Quality*, **27**, 609–617.
- Kiikilä, O., Perkiömäki, J., Barnette, M., Derome, J., Pennanen, T., Tulisalo, E. and Fritze, H. (2001). *In situ* bioremediation through mulching of soil polluted by a copper–nickel smelter. *Journal of Environmental Quality*, **30**, 1134–1143.
- Kuz'yakov, Y. V. (1997). The role of amino acids and nucleic bases in turnover of nitrogen and carbon in soil humic fractions. *European Journal of Soil Science*, **48**, 121–130.
- Ladd, J. N., Amato, M. and Oades, J. M. (1985). Decomposition of plant material in Australian soils. III. Residual organic and microbial biomass C and N from isotope-labelled plant material and soil organic matter decomposition under field conditions. *Australian Journal of Soil Research*, **23**, 603–611.
- Ladd, J. N., Jocteur-Monrozier, L. and Amato, M. (1992). Carbon turnover and nitrogen transformation in an alfisol and vertisol amended with [^{14}C] glucose and [^{15}N] ammonium sulphate. *Soil Biology and Biochemistry*, **24**, 359–371.
- Lehmann, A. E. H., Holland, K. and Stahr, K. (2000). Flows and chemical fractions in a soil from sewage sludge. *Zeitschrift für Kulturtechnik und Landentwicklung*, **41**, 206–210.
- Leifeld, J., Siebert, S. and Kögel-Knabner, I. (2002). Biological activity and organic matter mineralization of soil amended with biowaste composts. *Journal of Plant Nutrition and Soil Science*, **165**, 151–159.
- Leita, L., De Nobili, M., Muhlbachova, G., Mondini, C., Marchiol, L. and Zerbi, G. (1995). Bioavailability and effects of heavy metals on soil microbial biomass survival during laboratory incubation. *Biology and Fertility of Soils*, **19**, 103–108.
- Leita, L., Nobili, M. D. and Mondini, C. (1999). Influence of inorganic and organic fertilization on soil microbial biomass, metabolic quotient and heavy metal bioavailability. *Biology and Fertility of Soils*, **28**, 371–376.
- Lewin, V. H. and Beckett, P. H. T. (1980). Monitoring heavy metal accumulation in agricultural soils treated with sewage sludge. *Effluent and Water Treatment Journal*, **20**, 217–221.
- Liang, C. N. and Tabatabai, M. A. (1977). Effects of trace elements on nitrogen mineralization in soils. *Environmental Pollution*, **12**, 141–147.
- Liang, C. N. and Tabatabai, M. A. (1978). Effects of trace elements on nitrification in soils. *Journal of Environmental Quality*, **7**, 291–293.
- McBride, M., Martinez, C. E., Topp, E. and Evans, L. (2000). Trace metal solubility and speciation in a calcareous soil 18 years after no-till sludge application. *Soil Science*, **165**, 646–656.
- Martin, J. P., Filip, Z. and Haider, K. (1976). Effect of montmorillonite and humate on growth and metabolic activity of some actinomycetes. *Soil Biology and Biochemistry*, **8**, 409–413.
- Mench, M., Vangroensveld, J., Lepp, N. M. and Edwards, R. (1998). Physico–chemical aspects and efficiency of trace element immobilization by soil amendments, in Vangroensveld, J. and Cunningham, S. D. (eds.), *Metal-contaminated soils: In situ inactivation and phytoremediation*. Springer and R. G. Landes, Berlin, pp. 151–182.
- Moreno, J. L., Hernandez, T. and Garcia, C. (1999). Effects of a cadmium-contaminated sewage sludge compost on dynamics of organic matter and microbial activity in an arid soil. *Biology and Fertility of Soils*, **28**, 230–237.
- Neal, R. H. and Sposito, G. (1986). Effects of soluble organic matter and sewage sludge amendments on Cd sorption by soils at low cadmium concentrations. *Soil Science*, **142**, 164–172.
- Nelson, P. N., Barzegar, A. R. and Oades, J. M. (1997). Sodicity and clay type: Influence on decomposition of added organic matter. *Soil Science Society of America Journal*, **61**, 1052–1057.
- Ong, H. and Bisque, R. E. (1968). Coagulation of humic colloids by metal ions. *Soil Science*, **106**, 220–224.
- Oste, L. A., Lexmond, T. M. and Van Riemsdijk, W. H. (2002). Metal immobilization in soils using synthetic zeolites. *Journal of Environmental Quality*, **31**, 813–821.
- Prost, R. and Yaron, B. (2001) Use of modified clays for controlling soil environmental quality. *Social Science*, **166**, 880–894.
- Saggar, S., Parshotam, A., Sparling, G. P., Feltham, C. W. and Hart, P. B. S. (1996). ^{14}C -labelled ryegrass turnover and residence time in soils varying in clay content and mineralogy. *Soil Biology and Biochemistry*, **28**, 1677–1686.
- Scheffer, F. and Schachtschabel, P. (2002). *Lehrbuch der Bodenkunde*. 15. Auflage., Spektrum Akademischer, Heidelberg.
- Schlichting, E., Blume, H. P. and Stahr, K. (1995). *Bodenkundliches Praktikum*, 2nd ed., Blackwell, Berlin.
- Schulthess, C. P. and Huang, C. P. (1990). Adsorption of heavy metals by silicon and aluminum oxide surfaces on clay minerals. *Soil Science Society of America Journal*, **54**, 679–688.
- Sørensen, L. H. (1975). The influence of clay on the rate of decay of amino acid metabolites synthesized in soil during decomposition of cellulose. *Soil Biology and Biochemistry*, **7**, 171–177.
- Sposito, G., Lund, L. J. and Chang, A. C. (1982). Trace metal chemistry in arid-zone field soils amended with sewage sludge: I. Fractionation of Ni, Cu, Zn, Cd, and Pb in solid phases. *Soil Science Society of America Journal*, **46**, 260–264.
- Tyler, L. D. and McBride, M. B. (1982). Mobility and extractability of cadmium, copper, nickel, and zinc in organic and mineral soil columns. *Soil Science*, **134**, 198–205.
- Vance, E. D., Brookes, P. C. and Jenkinson, D. S. (1987). An extraction method for measuring microbial biomass C. *Soil Biology and Biochemistry*, **19**, 703–707.

- Villarroel, J. R., Chang, A. C. and Amrhein, C. (1993). Cd and zn phytoavailability of a field-stabilized sludge-treated soil. *Soil Science*, **155**, 197–205.
- Welp, G. (1999). Inhibitory effects of the total and water-soluble concentrations of nine different metals on the dehydrogenase activity of a loess soil. *Biology and Fertility of Soils*, **30**, 132–139.
- Wu, J., Jörgensen, R. G., Pommerening, B., Chaussod, R. and Brookes, P. C. (1990). Measurement of soil microbial biomass C by fumigation-extraction—an automated procedure. *Soil Biology and Biochemistry*, **22**, 1167–1169.
- Zarei, M., Sommer, M. and Stahr, K. (2001). Neoformed halloysite in podzols developed on the Bärhalde granite, southern black forest, germany, *Proceedings of the 12th International Clay Conference*. Bahia Blanca, Argentina, 227–234.