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ORIGINAL PAPER

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Effect of cropping systems on the mobility and uptake of Cd and Zn

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Abstract A field experiment was carried out to determine the effect of different land use systems such as continuous grass and agricultural crops rotation on the bioavailability of heavy metals in soils contaminated by former excessive sewage sludge application. The results show that Cd and Zn concentrations increased to 2 and 3.5 folds within 3 cuts of grass, respectively. Even 10 years after the end of excessive sewage sludge application the concentration of Cd in winter and summer wheat is 3.4 and 2.5 folds higher than the control, respectively. Zn concentration increased by two folds for both crops. In conclusion, the uptake depends on plant species and the degree of soil contamination. The availability of heavy metals was not changed with time.

Keywords Contamination · Heavy metals · Land use · Sewage Sludge

Introduction

The main environmental concern about utilisation of sewage sludge and compost on agricultural land is the accumulation of heavy metals in soils and the contamination of the food chain. While the municipal wastes, sewage sludge in particular, may contain high concentrations of mineral nutrients (N, P, Ca, etc.), they may also contain toxic heavy metals. As heavy metals generally are much higher concentrated in sewage sludges than commonly found in soils, the concentration of extractable heavy metals in soils such as Cd, Zn, Cu and Ni can be increased by sludge application (Barbera 1987).

There are a large number of publications on the subject of excessive use of sewage sludge in agriculture, and the influence of the resulting heavy metals contamination on the binding form and the mobility of heavy metals in the soil as well as their availability to plants (Berrow 1986). Different hypotheses concerning the long term bioavailability of heavy metals were offered. Chaney and Ryan (1993) pointed out that ‘Sludge-borne heavy metals are remained in complexation form with the inorganic components of the sludge, and that the specific metal absorption capacity added in sludge will persist as long as the heavy metals of concern persist in the soil. Accordingly sludge-borne heavy metals should become less bioavailable with time as surface-adsorbed metals become occluded’. In contrast, McBride (1995) assumed that ‘the sludge-derived organic matter contributes significantly to the metal adsorption capacity, and the slow mineralisation of this organic matter could release metals into more soluble forms’. Because the decomposition of sludge organic matter is often associated with an acidification of the soil (if soil is not limed) further increase in the bioavailability of the sludge-borne heavy metals would be expected (McGrath et al. 2000).

Although much has been published considering the possibilities and limitations of fertilising with municipal and industrial wastes (Schulz and Roemheld, 1997), none of these publications reflected the influence of different land use systems on the bioavailability of the heavy metals in soils after long time termination of sewage sludge application.

The results presented in this study are based on long-term sewage sludge application in the field (1972–1989), in which the effect of different levels of sewage sludge application on growth, yield, mineral and heavy metal concentration of various crops were studied. Additionally, the effects of soil properties and heavy metal binding form on the mobility of heavy metals in soil and the availability and uptake of heavy metals by plants are examined. The main objective of this research was to

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determine the effect of different land use systems ten years after the end of excessive sewage sludge application (1972–1989) on the bioavailability of heavy metals. It is assumed that the different land use systems could influence the mobility of heavy metals in the soil due to soluble organic matter. Two approaches were followed: (i) the uptake of heavy metals (Cd, Zn, Cu and Ni) by grass and wheat with relation to the amount of applied sewage sludge and (ii) the effect of time and crop on the availability of heavy metals in the high sewage sludge treatment.

Experimental

Different amounts of sewage sludge dry matter were applied to a loess derived luvisol in South West Germany (mean annual temperature is 8.5°C and 685 mm rainfall) during 1972–1989 annually in 5 treatments: (i) control (without fertilisation), (ii) mineral fertiliser application, (iii) 5 t dry matter ha^{-1} a^{-1}, (iv) 15 t ha^{-1} a^{-1} and (v) 30 t ha^{-1} a^{-1}. The plot area is 50 m^2 and each treatment has 4 replicates. The upper soil layer (0–30 cm) without sewage sludge application is silty loam with pH 7, organic matter content 2% and cation exchange capacity 25 mval/100 g.

After 10 years of sewage sludge termination each plot was divided into two parts: continuous grass since 1997 and crop rotation with summer wheat (1999), potatoes (2000) and maize (2001). The harvested plant material was digested by microwave with HNO_3 (65%) and H_2O_2 (30%). The soil was extracted for heavy metal concentration by “Aqua Regia” (mixture of hydrochloric acid and nitric acid). Metal concentration of the plant digests and soil extracts were determined by inductively coupled plasma-mass sepctrometry (ICP/MS). Data were statically analysed by analysis of variance using “Sigmastat 2.03” package and one way analysis of variance using the TUKEY test. The results of statistical analysis were shown in the figures by alphabetical letters. Variants with the same letters mean no significant differences.

Table 1 (a) Total Cd, Zn, Cu and Ni concentration in the top soil (0–30 cm) in various treatments after ten years of sewage sludge termination
Table 1 (b) Total Cd, Zn, Cu and Ni concentration in grass (1999)

(a) Total Cd, Zn, Cu and Ni concentration in the top soil (0–30 cm) in various treatments after ten years of sewage sludge termination

Treatments	Cd	Zn	Cu	Ni
(iii)–(v) = SS	mg kg^{-1} soil			
(i) Control	0.2±0.0 (a)	82±2 (a)	21±2 (a)	24±1 (a)
(ii) NPK	0.3±0.0 (a)	95±4 (b)	23±1 (a)	23±1 (a)
(iii) 5 t ha^{-1} a^{-1}	0.4±0.0 (b)	123±2 (c)	29±3 (b)	25±2 (a)
(iv) 15 t ha^{-1} a^{-1}	0.7±0.1 (c)	182±7 (d)	41±0 (c)	26±1 (a)
(v) 30 t ha^{-1} a^{-1}	1.4±0.1 (d)	270±4 (e)	59±3 (d)	26±1 (a)

(b) Total Cd, Zn, Cu and Ni concentration in grass (1999)

Treatments	Cd	Zn	Cu*	Ni*
(iii)-(v) = SS	μg kg^{-1} d.m	mg kg^{-1} d.m		
(i) Control	42±1 (a)	28±1 (a)	6±1	1.4±0.1
(ii) NPK	46±5 (a)	30±4 (a)	6±1	1.4±0.3
(iii) 5 t ha^{-1} a^{-1}	47±7 (a)	37±5 (ab)	7±0	1.3±0.1
(iv) 15 t ha^{-1} a^{-1}	83±9 (b)	41±2 (b)	8±1	1.4±0.1
(v) 30 t ha^{-1} a^{-1}	105±8 (c)	51±3 (c)	8±1	1.4±0.1

*No significant Cu and Ni concentrations among different treatments

Results and discussion

Accumulation of heavy metals from sewage sludge

Beside improvement of soil structure and nutritional status (N and P) of the soil, excessive sewage sludge application caused an accumulation of heavy metals and organic matter. As shown in Table 1a, total Cd and Zn concentration in the soil increased with increasing amount of sewage sludge applied. For instance, treatment (v) of 30 t ha^{-1} a^{-1} increased the total concentration of Cd, Zn and Cu in the soil by factor 7, 3 and 3, respectively, in comparison with the control treatment. Ni concentration was not significantly influenced. Leaching of heavy metals into deeper soil layers was not higher than 10–20 g Cd ha^{-1} a^{-1} in treatment (v).

Many authors investigated an accumulation of heavy metals in soils caused by repeated excessive sewage sludge application (Barbera 1987). The accumulation depends on the type of the sewage system (household or industry) and the amount of sewage sludge applied. Most field studies have shown no difference in heavy metal concentration between control and sewage sludge treated soil below 30 cm soil depth, although leaching of mobile heavy metals to 40–60 cm depth can occur when large amounts of liquid sewage are applied (Robertson et al. 1982), especially on acidic sandy soils. In this experiment the addition of sewage sludge was terminated 10 years before the different land use systems were established. In spite of that, high accumulation of Cd, Zn and Cu is still found in various sewage sludge treatments.

Heavy metals availability due to land use systems

The uptake of heavy metals by plants can be considered as indication of its bioavailability in soils. The uptake of Cd and Zn by grass and summer wheat of all sewage sludge treatments was significantly different to the control in the first year (1999) (Table 1). Summer wheat showed higher concentrations of Cd and Zn in treatment (v) than grass. The uptake of Cd from treatment (v) by grass was two folds higher than from the control, while it was three folds higher in case of summer wheat. Moreover, the uptake of Zn from treatment (v) was two folds higher than from the control for both grass and summer wheat. Nearly the same trend of Cd uptake was shown by potatoes and

Table 2 (a) Total Cd and Zn concentration in potato and maize total shoot cultivated in years 2000 and 2001, respectively
Table 2 (b) Cd, Zn, Cu and Ni concentration in grains of summer wheat (1999) and winter wheat cultivated during sewage sludge application (1988) in ()*

(a) Total Cd and Zn concentration in potato and maize total shoot cultivated in years 2000 and 2001, respectively

Treatments (iii)–(v) = SS	Cd $\mu g\ kg^{-1}$ d.m		Zn $mg\ kg^{-1}$ d.m	
	Potato	Maize	Potato	Maize
(i) Control	41±7 (a)	100±5 (a)	26±3 (a)	19±2 (a)
(ii) NPK	51±5 (b)	112±24 (a)	24±6 (a)	22±3 (a)
(iii) 5 t ha^{-1} a^{-1}	51±6 (b)	126±25 (a)	26±5 (a)	24±3 (ab)
(iv) 15 t ha^{-1} a^{-1}	60±4 (b)	176±23 (b)	26±5 (a)	28±3 (b)
(v) 30 t ha^{-1} a^{-1}	63±9 (b)	265±27 (c)	28±7 (a)	40±2 (c)

(b) Cd, Zn, Cu and Ni concentration in grains of summer wheat (1999) and winter wheat cultivated during sewage sludge application (1988) in ()*

Treatments (iii)–(v) = SS	Cd $\mu g\ kg^{-1}$ d.m	Zn $mg\ kg^{-1}$ d.m	Cu	Ni
(i) Control	36±1 (120)*	33±2 (25)	6±0 (4)	0.2±0.0 (0.2)
(ii) NPK	51±9 (130)	39±5 (27)	6±0 (4)	0.2±0.0 (0.1)
(iii) 5 t ha^{-1} a^{-1}	55±8 (140)	44±3 (31)	6±0 (5)	0.4±0.1 (0.2)
(iv) 15 t ha^{-1} a^{-1}	88±8 (180)	49±9 (44)	5±1 (5)	0.3±0.0 (0.2)
(v) 30 t ha^{-1} a^{-1}	124±4 (300)	61±3 (59)	6±0 (6)	0.2±0.0 (0.3)

maize, increasing with increasing concentration of Cd in the soil, but at different levels. Zn uptake by potatoes was not significantly different among the various treatments, while it was significant for the next crop (maize). In general the uptake of Cd and Zn differed between grass and crop rotation (summer wheat, potatoes and maize) but was proportional to the amount of sewage sludge applied (Tables 1b, 2a and b). Obviously, the amount of heavy metals removed by plants mainly depends on the crop species (Petruzzelli 1994). There are no significant differences on the uptake of Cu and Ni among the control and sewage sludge treatments for grass, summer wheat, potatoes and maize. To avoid repetition of data, Cu and Ni concentration in grass and summer wheat are shown in Table 1b and 2b.

Beside the increase of the total concentration in sewage sludge treatments (Table 1a), the mobile fraction (extracted by 1 M NH_4NO_3) increased, too and accounted for a 6, 10 and 3 fold higher concentration of Cd, Zn and Cu, respectively, in treatment (v) compared with the control (data not shown). This indicates that the uptake of Cd and Zn is not only related to the total concentration, but to the mobile fraction and the available forms to the plants which are influenced by soil pH. The soil pH is decreased from 7 to 6.5 due to 30 ton sewage sludge application. The results show that Cd and Zn are highly available in the soil even after ten years of sewage sludge termination. The comparison between control and treatment (v) were selected to be described as a case of extreme treatments. Noteworthy it has to be considered that the amount of sewage sludge applied in treatment (v) was 18 fold higher than allowed by German legislation (5 t ha^{-1} in 3 years interval). Further more, legal steps have been taken to implement stricter controls which have resulted in a marked reduction of heavy metals in sewage sludges in the last two decades, especially in the case of Cd (Schulz and Roemheld 1997).

At present, legislation in different countries limits the use of organic wastes in agriculture referring to total trace element concentrations in soil and sewage sludge. However, this is not a sufficient criterion since mobility and bioavailability of heavy metals in soils will largely depend on their binding forms. Rhizosphere changes due to various crops in addition to the ability of soils to replenish the mobile fractions from less available fractions have to be considered (Al-Najar et al. 2003). Generally, the mobility of heavy metals in soils increases at low soil pH and low organic matter and clay content. Sanders and Adams (1987) reported that Cu is largely immobile at pH above 5.5. This result is in agreement with ours. The three fold increase of the total Cu concentration in treatment (v) did not increase the uptake by both grass and summer wheat due to the limited increase on the mobile fraction.

It was reported by Chaney and Ryan (1993), that heavy metal binding forms in soils range from easily-extractable and exchangeable forms for Cd to more fixed oxide and strongly-bound organic and inorganic forms for Cu and Ni. Therefore, the uptake of Cd and Zn could refer to a high bioavailability of both elements to the plants, while Cu is fixed in non-available binding forms. It was expected that the land use system could affect the chemical behaviour of the elements in the soil, but the results show that grass within 3 consequent cuts and summer wheat potato, and maize have the same trend of Cd and Zn uptake while the uptake of Cu from the various treatments was kept constant. This could be the case for Ni, too, but no accumulation of Ni was shown due to sewage sludge application.

Availability of heavy metals as a time function

It is assumed that the mobility of heavy metals in soils could be affected by time. Therefore, the uptake form treatment (v) was shown for three grass cuts ten years after the last sewage sludge application. In addition, long term comparison between winter wheat uptake of heavy metals during the time of sewage sludge application (1988) and the uptake of the same heavy metals by summer wheat ten years after sewage sludge termination (1999) were investigated (Table 2b).

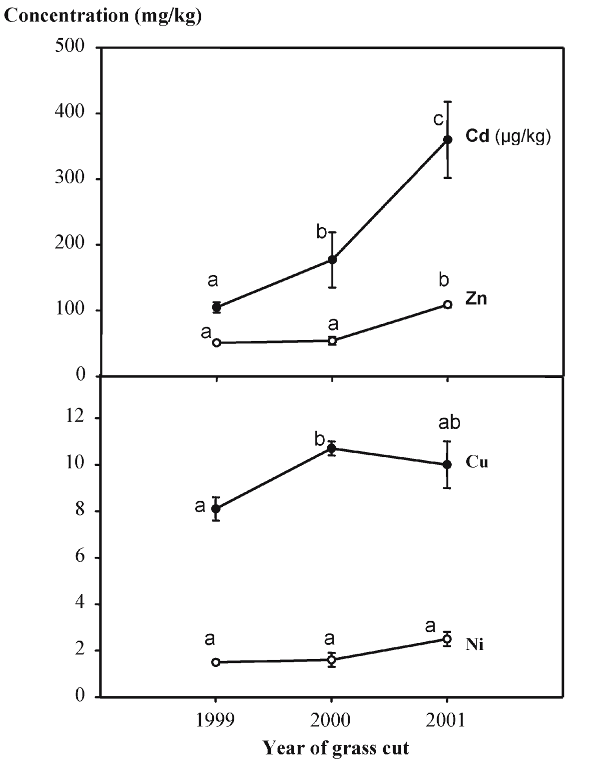

Fig. 1 Cd, Zn, Cu and Ni concentrations of grass dry matter in three cuts (1999, 2000 and 2001) from treatment (v) (30 t ha^{-1} a^{-1})

As shown in Fig. 1 the concentration of Cd and Zn in the above ground biomass increased by factor 3 and 2 from treatment (v), respectively, within three cuts. This could be referred not only to the availability of Cd and Zn, but also to the variation of grass species composition with time. Grass classification in treatment (v) showed that 46% are grasses (gramineae) and 54% legumes in 1999, while the grasses became the dominant species in 2001 probably as a consequence of a high nitrogen availability resulting from the high amounts of organic matter via sewage sludge. The organic matter content increased by 1.5% due to 30 ton sewage sludge application. The concentration of Cu and Ni of grass did not show any significant differences between 1999 and 2001. Even the changed composition of grass and legumes did not affect the uptake of Cu. In addition, it was shown that the differences between the uptake of Cu and Ni from various sewage sludge treatments and the control are not significant within the same year (Table 1b). Therefore, it can be concluded that the Cu formerly added by sewage sludge application is not available for grass in the period of time since the onset of this experiment.

The constant concentration of Ni of the soil in all treatments (Table 1a) is the main reason behind the constant uptake during the three years and from various sewage sludge treatments.

As shown in Table 2b, the concentration of Cd of winter wheat grains is three folds higher than the concentration of summer wheat grains in the control treatment. These differences between winter wheat and summer wheat depend on the individual plant species and genotype, regardless of the amount of Cd in the soil. Therefore, in highly contaminated soils, selection of crops and genotypes towards fewer uptakes of heavy metals is preferred to reduce food chain contamination.

In spite of the fact that summer wheat was cultivated ten years after sewage sludge termination, the same trend of increase of the Cd concentration was seen in both winter and summer wheat grains with increasing application rate of sewage sludge. The same is also true for the Zn concentration of winter and summer wheat. Cu availability to the plant uptake during sewage sludge application and even ten years after sewage sludge termination was not noticed. The uptake of Cu is not significant not only among the various sewage sludge treatments, but even between the different crops. It accounts for 5 mg Cu kg^{-1} dry matter grains of both winter and summer wheat. Most of the studied elements (Cd, Zn, Cu and Ni) have the same trend of concentrations among winter and summer wheat straw (data not shown).

The results show that Cd and Zn are available to plants regardless of crop species and application time. Therefore, the continuous high availability of Cd and Zn may depend on the mineralisation of organic matter with time and the subsequent release of heavy metals (McBride 1995) or the replenishment of the mobile fractions from less available binding forms (e.g. Mn and Fe oxides).

In spite of that no significant increase in Cu uptake either by grass or crops due to higher sewage sludge application was detected. Chaney and Ryan (1993) stated that the specific metal adsorption capacity added with sludge will persist as long as the heavy metals of concern persist in the soil. The four heavy metals examined in this research (Cd, Zn, Cu and Ni) have different chemical properties and consequently each metal reacts differently once applied with municipal wastes to soils.

Conclusion

As a consequence of former application of excessive amounts of sewage sludge Cd and Zn are highly plant-available and are taken up by grass and summer wheat at the same trend. Within the frame of this experiment the different land use systems, "conservative" versus "intensive", did not affect the total uptake of Cd and Zn. The comparison between the uptake of summer wheat 1999 and winter wheat 1988 showed that the availability of Cd and Zn is not reduced even 10 years after the end of sewage sludge application. In contrast to Cd and Zn, the uptake of Cu did not differ between control and sewage sludge treatments, in spite of the 3 fold increase in soil concentration of total Cu in treatment (v). There is no difference in the uptake of Ni between the various treatments because this element is not significantly accumulated in soil as a result of sewage sludge application.

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