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The role of dissolved organic carbon in the mobility of Cd, Ni and Zn in sewage sludge-amended soils

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"Capsule": *Applications of natural dissolved organic carbon significantly increased metal (Cd, Ni, Zn) extractability from soils and their uptake by ryegrass.*

Abstract

A pot experiment was conducted to investigate the effect of application of naturally derived dissolved organic compounds (DOC) on the uptake of Cd, Ni and Zn by *Lolium perenne* L. from mixtures of soil and sewage sludge and on their extractability with $CaCl_2$. DOC was applied at concentrations of 0, 285 and 470 mg l^{-1} to a loamy sand (LS) and a sandy clay loam (SCL) soil mixed with sewage sludge at rates equivalent to 0, 10 and 50 t ha^{-1}. DOC applications significantly increased the extractability of metals and also their uptake by ryegrass, but the increase was greater where sludge was applied at 50 t ha^{-1}. It is suggested that DOC in soils significantly increased the availability of the metals to plants. This was especially the case in the LS soil, where DOC had less competition with surface sorption than in the SCL soil. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: DOC; Heavy metals; Availability

1. Introduction

Dissolved organic carbon (DOC) consists of several types of low molecular weight organic compounds, such as polyphenols, simple aliphatic acids, amino acids and sugar acids (Fox and Comerfield, 1990). DOC stays dissolved in the soil solution under natural conditions and it has been found that it may be responsible for the dissolution equilibria of metals in the soil solution especially at neutral pH values (Harter and Naidu, 1995). DOC also has a unique role in the chemistry of heavy metals in soils; it reduces metal adsorption onto soil surfaces by either competing more effectively for the free metal ion and forming soluble organo-metallic complexes or being preferentially adsorbed onto the surfaces instead of the metals it is competing with (Guisquiani et al., 1998). DOC can also be taken up by plant roots, along with the metals it has bound (Hamon et al., 1995) and this can increase metal availbility to plants. Krishnamurti et al. (1997) maintained that this

could establish a diffusion gradient to transport more chelated metals towards the root surface.

The effects of DOC on the chemistry of heavy metals in sludge-treated soils is of great environmental importance for two main reasons. The first is that the pH conditions in which DOC is more effective in competing with heavy metals are the same as those found in agricultural soils (pH 5–7) and this implies risks for increased heavy metal accumulation in crops and possible movement of heavy metals down the soil profile. (Lamy et al., 1993). The second implication is that DOC can be more effective over time after the application of sewage sludge has ended. This is because the decomposition of the sludge organic matter can increase the DOC concentration in the soil (Lineham, 1985). Neil and Sposito (1986) suggested that sewage sludge can provide amounts of DOC which are sufficient to reduce the adsorption of Cd onto soil surfaces. This was also recognised by Singh and Pandeya (1998), who found that the complexes of Cd with fulvic acids were positively correlated with the soil organic matter content and the CEC value of the soil. Moreover, Baziramakenga and Simard (1998) suggested that it is not only the quantity of DOC that changes over time, but the quality as well.

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They reported that in fresh sludges aliphatic acids with high pK organo-metallic association values are predominant, while in mature sludges aliphatic acids with lower pK values become more predominant. Lower pK values indicate more stable associations between DOC and metals. This means that over time DOC can become more effective in controlling metal solubility highlighting the importance of the role that DOC can have on heavy metal availability in soil–sludge mixtures.

Although many workers have dealt with the adsorption characteristics of DOC on soil constituents and its effect in metal adsorption and solubility in the soil solution (e.g. Kaizer and Zech, 1997; Spark et al., 1997), there is a lack of information concerning the influence of DOC on the availability of heavy metals to plants. Because DOC compounds are relatively short-lived, many researchers have used synthetic compounds in their experiments. The conclusions drawn from such experiments are difficult to extrapolate from and more evidence on the role of natural DOC on the soil–plant interactions is necessary.

The aim of this experiment was to investigate the role of elevated concentrations of naturally extracted DOC on heavy metal availability to plants in pots with soil–sludge mixtures. The hypothesis tested was that the presence of extra DOC in the soil solution will enhance the availability of heavy metals to plants in sewage sludge-treated soils.

2. Materials and methods

2.1. Experimental design

Two different Brown Earth soils were used and were collected from the Reading University Farm at Sonning. The first soil was a loamy sand (LS) of the Rowland series, and the second soil was a sandy clay loam (SCL) of the Sonning series. Liquid anaerobically digested sewage sludge with 6% total solids content was collected from a wastewater treatment plant. The soils were mixed with the sewage sludge at rates equivalent to 0, 10 and 50 t ha^{-1} dry matter. The mixtures were placed in 100 ml plastic pots, sown with ryegrass (*Lolium perenne* L.) seeds and the treatments were replicated three times. One set of pots was to be irrigated with ultra pure water, the second set with a solution containing 285 mg DOC l^{-1} and the remaining set with a solution containing 470 mg DOC l^{-1} (three DOC levels). Each of these 18 treatments (i.e. 2 soils×three rates of sludge ×three DOC levels = 18) was duplicated and this resulted in a total of 36 pots. The experiment was left to run for 6 weeks, which allowed sufficient time for the plants to grow. During this period the pots were in a greenhouse at a temperature of around 22°C and under normal daytime light. The pots were watered from underneath (sub-irrigation) to maintain the field capacity of the soils. The pots were moved around at regular intervals to compensate for light differences. For the sake of simplicity, the treatments where plants were watered with ultra pure water, were called DOC-0, the treatments where plants were watered with a solution containing 285 mg DOC l^{-1} were called DOC-1 and the treatments where plants were watered with a solution containing 470 mg DOC l^{-1} were called DOC-2. In addition, the 0 t ha^{-1} sludge treatment was called the control, while the other 2 sewage sludge application rates were called 10 and 50 t ha^{-1}.

2.2. Extraction of DOC to use as a watering solution

DOC was extracted from a clay loam soil, containing 5% organic carbon using a dilute solution of 10^{-3} M NaOH. Air dry soil (300 g) was weighed into a plastic centrifuge bottle with 300 ml of 10^{-3} M NaOH. The bottle was shaken overnight in a mechanical horizontal shaker. Next day the bottle was centrifuged for 1 h at 3600 rpm and the supernatant was collected into 50-ml plastic centrifuge tubes. These were again centrifuged for 1 h at 3600 rpm, in order to remove most of the suspended solids. The supernatant was then filtered through a medium filter paper followed by a 0.45-μm membrane filter under vacuum. This was done in order to remove any large colloids from the solution and retain only the dissolved solid matter. The organic compounds in this dissolved solid matter were DOC. One third of this clear solution was then diluted twice with ultra pure water. Both of the clear solutions (the diluted and the undiluted) were kept in a refrigerator at 4°C and used for watering the pots. Extractions were performed once a week in order to make sure that the DOC solutions did not undergo major decomposition by microbes. A small aliquot was kept from each extraction batch in the freezer in order to measure the concentrations of DOC in each weekly extraction (Table 1 shows the concentrations of DOC extracted in the weekly extractions). The weekly extraction procedure resulted in 750 ml of 470 mg l^{-1} DOC solution (the undiluted) and 750 ml of 285 mg l^{-1} DOC solution (the diluted). The concentrations of Na in the extracted DOC solution were very low (10^{-3} M) and not expected to have had a significant effect on the chemistry of the mixtures. Watering solutions of DOC were also measured for concentrations of Cd, Ni and Zn, but the levels of these metals were below the detection limits.

Table 1
Concentrations of extracted dissolved organic carbon (DOC) used as a watering solution (mg l^{-1})

	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6	Mean
DOC	470.53	470.83	468.53	475.37	465.86	470.31	470.24

2.3. Analyses

Selected chemical and physical properties of soils and sludge are shown in Table 2. These included: pH, organic matter by loss on ignition, $CaCO_3$, Al and Fe oxides, electrical conductivity and bulk density (Rowell, 1994). Soil texture (Sheldrick and Wang, 1993), water soluble cations (Roades, 1982), and total Cd, Ni and Zn concentrations (McGrath and Cuncliffe, 1985) were also determined.

At the end of the 6-week period, the plants were harvested, washed in de-ionised water and dried in forced draught oven at 70 °C for 48 h. They were then ground to powder in a Tema mill and stored in glass jars ready for analysis. They were subsequently digested with concentrated HNO_3. The soil samples were taken out of the pots, air dried, sieved through a 2-mm sieve and digested for total concentrations of Cd, Ni and Zn in *Aqua regia*. They were also extracted with 0.05 M $CaCl_2$ which provides an indication of 'bioavailable' forms of metals (Morgan and Alloway, 1984). The soil–sludge mixtures were also measured for pH water (1:2.5 ratio) and organic matter by the loss-on-ignition method. The ground plant material and the soil digests and extracts were analysed for the heavy metals Cd, Ni and Zn using a Perkin-Elmer Optima 3000 Inductively Coupled Plasma-Optical Emission Spectrometer. For Cd and Ni, the concentrations in the plant digests were below the instrument's detection limit and so it was necessary for them to be analysed by Graphite Furnace Atomic Absorption Spectrophotometer. Also, an extraction of DOC was performed on all the soil samples. The method adopted was the one used by Baham and Sposito (1983) and the DOC was analysed with a Shimadzu TOC-5000 Total Organic Carbon Analyser. Analytical quality assurance was addressed by the systematic use of blanks, duplicates and analysis of a Certified Reference Soil (CRM 143R) and in-house sludged soil and barley leaf standard materials.

All results were analysed statistically using analysis of variance (ANOVA) and the least significant difference (LSD) test was employed to determine the significance of the differences between treatments. The statistical package used was SAS and the confidence limit was 95% ($P < 0.05$).

3. Results

The total concentrations of Cd, Ni and Zn in the soils are shown in Table 3. As expected, the concentration of these metals in the soil–sludge mixtures were higher ($P < 0.05$) in the higher sewage sludge application rates compared with the controls.

3.1. Organic matter

Organic matter was significantly ($P < 0.05$) greater in the higher rate of sewage sludge (Table 4). Organic matter was also higher in the higher DOC application rates, but not significantly ($P > 0.05$). Watering with DOC solutions meant that low molecular weight and non-colloidal

Table 2
Selected physical and chemical properties of the soils and sewage sludge

	Sand	Silt (%)	Clay	CEC[a] (cmol$_c$ kg^{-1})	LOI[b] (%)	EC[c] (dS m^{-1})	Aqua regia			DOC[d] (mg l^{-1})	pH	
							Cd	Ni	Zn		H$_2$O	CaCl$_2$
LS soil	78.37	14.64	6.99	8.47	2.42	0.17	0.37	12.47	32.08	22.95	7.21	6.68
SCL soil	74.61	5.09	20.30	15.21	4.12	0.48	0.10	9.9	42.67	41.94	7.19	6.46
Sludge	–	–	–	–	60.67	–	0.31	30.56	512.28	2574.53	6.89	6.67

[a] Cation exchange capacity.
[b] Loss on ignition.
[c] Electrical conductivity.
[d] Dissolved organic carbon.

Table 3
Total concentration of Cd, Ni, and Zn in soil samples (µg g^{-1})

	Loamy sand soil			Sandy clay loam soil		
	Cd	Ni	Zn	Cd	Ni	Zn
Control	0.37	12.47	32.08	0.10	9.09	42.68
10 t ha^{-1}	0.44	13.01	39.15	0.12	9.62	48.30
50 t ha^{-1}	0.69	15.05	66.75	0.19	11.62	72.46
LSD	0.05	1.31	10.32	0.05	1.31	10.32

compounds were introduced into the soil–sludge mixtures, but in quantities that were not sufficient to change significantly the bulk composition of the organic matter.

3.2. DOC measurement in the soil–sludge mixtures

DOC increased linearly in both soils as the rate of sewage sludge increased (Fig. 1). The same linear increase was observed for the soils in the treatments DOC-0, DOC-1 and DOC-2.

3.3. Concentration of Cd, Ni and Zn in the ryegrass

The concentrations of Cd, Ni and Zn were greater in the plants in the higher rate of sewage sludge application in both soils and in all DOC treatments (Table 5). This effect was significant for Ni and Zn ($P < 0.05$) but not for Cd ($P > 0.05$). In some cases, however, the concentrations of Cd at 50 t ha^{-1} were slightly lower than at 10 t ha^{-1}, probably due to a 'dilution effect'. This suggests that the plant dry matter production at 50 t ha^{-1} was higher and the quantities of Cd absorbed from

the soil were lower than in the 10 t ha^{-1} treatment in terms of μg Cd per g of plant. The DOC treatments did not have any significant effect on the Ni concentrations. For Cd, the DOC additions from DOC-0 to DOC-2 caused a significant increase ($P < 0.05$) in the 10 and the 50 t ha^{-1} treatments in the LS soil, but there were no significant increases in the SCL soil. As for Zn, the DOC increases caused a significant increase ($P < 0.05$) in the concentrations of this metal in the 10 and 50 t ha^{-1} treatments in both soils.

3.4. Concentrations of CaCl$_2$-extratable Cd, Ni and Zn in the soils

In the higher sludge application, CaCl$_2$ extractability was also significantly higher ($P < 0.05$; Table 6). As for the DOC treatments, the picture was very much the same as with the metal concentrations in ryegrass, with Cd and Zn having a significant increase ($P < 0.05$) especially at 50 t ha^{-1} in both soils. The difference with the metal concentrations in ryegrass was that Ni concentrations in the CaCl$_2$ extracts increasased significantly

Table 4
Organic matter (%)

	Loamy sand soil			Sandy clay loam soil			LSD (DOC)
	DOC-0	DOC-1	DOC-2	DOC-0	DOC-1	DOC-2	
Control	2.42	2.56	2.55	4.12	4.31	4.48	
10 t ha^{-1}	2.96	2.79	3.06	4.65	4.65	4.60	0.45
50 t ha^{-1}	4.80	4.85	5.11	6.15	6.78	6.29	
LSD (sludge)				1.15			

Table 5
Concentrations of Cd, Ni and Zn in ryegrass (μg g^{-1}, Cd in μg kg^{-1})

	Loamy sand soil			Sandy clay loam soil			LSD (DOC)
	DOC-0	DOC-1	DOC-2	DOC-0	DOC-1	DOC-2	
Cd							
Control	30	20	23	15	14	15	
10 t ha^{-1}	75	78	98	21	26	28	13.57
50 t ha^{-1}	73	83	113	26	26	27	
LSD (sludge)				28.21			
Ni							
Control	2.18	1.95	2.14	2.80	3.33	2.25	
10 t ha^{-1}	6.52	6.34	6.01	3.95	3.20	3.73	1.34
50 t ha^{-1}	6.60	6.77	8.18	5.49	4.39	6.64	
LSD (sludge)				1.91			
Zn							
Control	2.64	2.23	2.11	2.88	2.37	2.21	
10 t ha^{-1}	7.72	8.65	9.75	9.41	11.20	12.73	1.48
50 t ha^{-1}	18.05	22.40	26.32	23.28	27.03	25.97	
LSD (sludge)				1.29			

Table 6
0.05 M CaCl$_2$-extractable Cd, Ni Zn (μg kg^{-1})

	Loamy sand soil			Sandy clay loam soil			LSD (DOC)
	DOC-0	DOC-1	DOC-2	DOC-0	DOC-1	DOC-2	
Cd							
Control	2.0	2.4	2.4	2.4	2.7	2.0	
10 t ha^{-1}	3.8	4.3	4.8	3.2	3.4	3.9	0.81
50 t ha^{-1}	7.8	9.6	10.9	9.5	9.5	9.8	
LSD (sludge)			2.24				
Ni							
Control	22.0	20.0	24.8	26.9	29.8	33.1	
10 t ha^{-1}	40.7	40.9	45.3	32.4	45.1	56.3	10.88
50 t ha^{-1}	141.1	132.8	168.5	100.4	116.9	120.1	
LSD (sludge)			46.55				
Zn							
Control	159.3	142.4	184.6	174.1	177.6	171.5	
10 t ha^{-1}	206.3	174.1	294.5	183.9	232.5	266.7	31.02
50 t ha^{-1}	277.6	357.6	416.0	503.0	522.2	572.4	
LSD (sludge)			88.54				

($P < 0.05$) at 10 t ha^{-1} in the SCL soil and at 50 t ha^{-1} in both soils.

4. Discussion

The additions of DOC probably affected the chemical reactions of Cd, Ni and Zn in the soil system and it is likely that organo-metallic complexes became predominant in controlling metal solubility, especially in the higher sludge application rate and in the higher DOC additions. This is likely because the pH values in this experiment were around neutrality and elevated concentrations of DOC were introduced. Reddy et al. (1995) and Naidu and Harter (1998) suggested that these two conditions are likely to make DOC very effective in its competition with solid surfaces for adsorbing heavy metals. Moreover, there are many examples in the literature of evidence that DOC can reduce metal adsorption onto soils (Elliott and Denneny, 1982; Davis, 1984; Xu et al., 1989; Baham and Sposito, 1994). This reduction in turn may have caused this increase in the availability of Cd, Ni and Zn to the ryegrass. Besides, DOC watering solution did not contain any significant amounts of heavy metals and this is evident from Table 6, where in the concentrations of all three metals, in the control treatments, the differences between DOC-0 and DOC-2 were statistically not important.

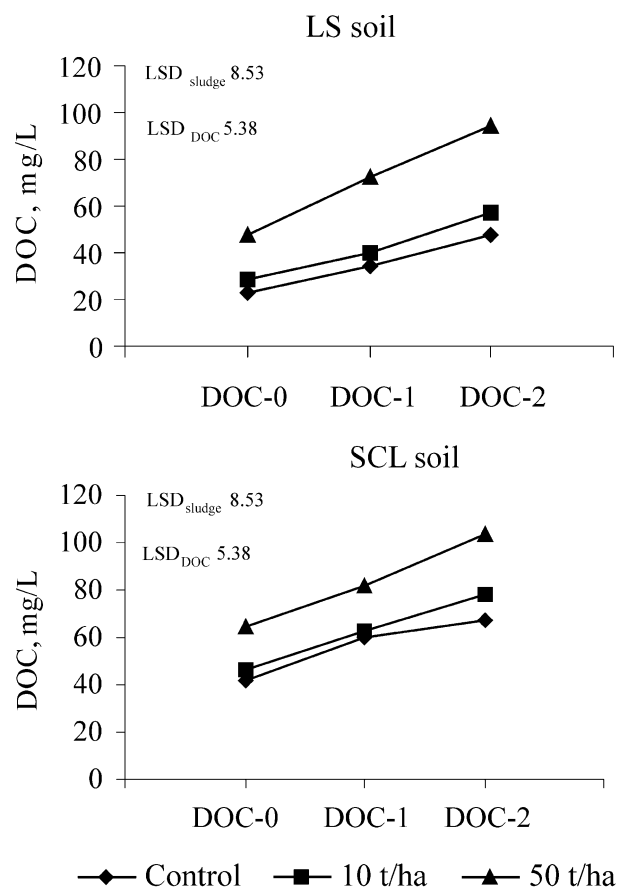This increase in heavy metal availability was evident in the concentrations of Cd and Zn in the ryegrass, as

Fig. 1. Extracted concentrations of dissolved organic carbon (DOC) (mg l^{-1}).

DOC additions increased (Ni increase was not significant). This was most apparent in the LS soil, where the solid phase was less important and did not compete for metal adsorption as much as the SCL soil, and where DOC was more effective in binding metals (LS soil had a CEC of 8.47, while SCL soil 15.21 $cmol_c$ kg^{-1}). This difference between the two soils was more evident in the 50 t ha^{-1} treatments than in the 10 t ha^{-1} and the control, and it may be explained by the fact that the less the solid surfaces the more effective the DOC may be in competing with them for binding metals (Evans, 1989). So, at 10 t ha^{-1} the added DOC is likely to have competed more effectively with the solid phases (clay particles and sludge-borne organic matter) for the metals. As sludge applications increased to 50 t ha^{-1}, more organic matter was added to the soil system and this resulted in the DOC competing less effectively for metals, especially in the soil with the higher CEC value.

The increase in metal availability to ryegass was also reflected in the extractions of Cd, Ni and Zn with $CaCl_2$ in both soils,; as sludge application rate increased, the DOC effect was more pronounced, especially in the LS soil. DOC did not have a great effect on Ni concentrations in ryegrass at 10 t ha^{-1}. This meant that at low total Ni concentrations in the soil system, its solubility was still controlled by surface adsorption and the addition of 285 and 470 mg l^{-1} of DOC did not affect its affinity characteristics. At 50 t ha^{-1} sludge Ni concentrations increased in the $CaCl_2$ extractions, probably because the competition between DOC in the solution and the solid particles became more favourable for DOC. Thus, Ni solubility (reflected by the $CaCl_2$ extractions) increased at 50 t ha^{-1}, due to the greater affinity it showed for dissolved organic compounds. The explanation given was also supported by Senesi et al. (1989), who reported that in sewage sludge-treated soils, organic compounds showed a well defined selectivity in binding metal ions added to soils with sewage sludge. As the metal loadings increased, the metal adsorption–desorption equilibria shifted to preferential binding of metals such as Cu, Fe, Ni and Cr, which formed stable complexes with the organic ligands.

It should be noted that these results, that exhibited increased heavy metal availability to plants with added DOC, are of great importance, since the DOC used here was naturally extracted from a CL soil, and availability was assessed directly in the test crops. Most of the works deal with synthetic DOC and batch tests, which cannot give a clear indication about the role of DOC on the metal availability to plants. Since DOC can be synthesised under natural conditions in the soil (such as root exudates and decomposition of organic matter), it can have an important role in the chemistry of heavy metals added with sewage sludge, as it was shown that DOC can significantly increase metal availability to plants.

The formation and composition of DOC is probably very complex due to the dynamic nature of microbial decomposition of organic substances in soils. Further investigations should include studies on the behaviour of microbial biomass in the soils, since it is recognised that by using solutions containing DOC, an associated population of micro-organisms will have given rise to complex interactions in the treated soils.

5. Conclusions

Increasing concentrations of DOC resulted in increasing metal extractability from the soils and elevated metal concentration and uptake in the plants. As sewage sludge applications increased to 50 t ha^{-1}, this effect was facilitated and accelerated in the LS soil for Cd and Zn. In the SCL soil, where the solid phase has a stronger effect on solubility due to higher CEC, the rate of increase in plant availability was less at 50 than at 10 t ha^{-1}, for Cd and Zn but not for Ni. As DOC may be the product of a variety of microbial degradation processes, acting upon a variety of substances including root exudates and sewage sludge, the environmental implications are important as sludge is applied to agricultural soils with pH 5–7 (which is the optimum range for DOC activity). Although DOC is generally thought to be short-lived, its dynamics may have an important influence in the chemical reactions in a wide range of sludge-amended agricultural soils, especially at high sewage sludge application rates.

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