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Soil residuals and plant uptake of Cu and Zn from biosolids applied to a clay loam soil under field conditions in Victoria, Australia

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Abstract. A field experiment was conducted to investigate the effects of incorporating anaerobically digested dewatered biosolids (DWB) and composted biosolids (CB) on the availability of the heavy metals Cu and Zn to canola (*Brassica napus* cv. Beacon) and oats (*Avena sativa* cv. Echidna) grown in a clay loam soil. DWB at rates of 0, 5, 25, 45 and 65 t dry solids (ds) ha^{-1} and CB at rates of 0, 10 30, 50 and 70 t ds ha^{-1} were incorporated into the soil to a depth of approximately 15 cm. The plots were arranged in triplicate, in a randomised complete block design. Canola and oat seeds were sown at a seeding rate of 5 and 100 kg ha^{-1}, respectively. After the crop harvest, total and diethylenetriamine penta-acetic acid (DTPA)-extractable heavy metals in biosolids-amended soil were determined using X-ray fluorescence (XRF) and inductively coupled plasma mass spectrometry (ICP-MS), respectively. Total metals in plant leaves were analysed using ICP-MS. In these biosolids, only Cu and Zn were high enough to significantly increase their concentration in the soil and plant tissue. The results showed that application of biosolids significantly ($P < 0.001$) increased DTPA-extractable and total concentrations of Cu and Zn in the amended soil. The ratio of DTPA-extractable to total (XRF) Cu and Zn also changed with increasing application rates of DWB and CB. The change in the ratio was more pronounced in soils receiving DWB, probably associated with the significant ($P < 0.001$) decrease in soil pH_w with their loading rate. Positive correlations were also noted between the application rate of biosolids and the Cu and Zn levels in the canola and oat leaves.

Additional keywords: application rates, canola, composted biosolids, diethylenetriamine penta-acetic acid (DTPA) extractable, heavy metals, oats, X-ray fluorescence.

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Introduction

The application of biosolids to agricultural land offers the potential for safe disposal of biosolids while realising the value of plant available nutrients. For this practice to be accepted, it needs to be demonstrated that potential contaminants, such as heavy metals, do not over accumulate in soil receiving biosolids.

The total concentration of heavy metals is an essential indicator of soil quality and, indeed, is used as a global index of contamination (Alva *et al*. 2000; Walter *et al*. 2002; McLaughlin *et al*. 2000; Zhong *et al*. 2010; Saha and Hossain 2011); however, it provides little indication of the specific bioavailability, mobility or reactivity in soils amended with biosolids.

In contrast, diethylenetriamine penta-acetic acid (DTPA)-extractable concentration of metals in biosolids provides an indication of metal solubility and mobility, which correlates with plant uptake (Sommers *et al*. 1991; Hooda and Alloway 1994; Arnesen and Singh 1998; Evanylo *et al*. 2006; Shaheen *et al*. 2012). Nevertheless, the amount of metal uptake depends on the type of metal, soil characteristics, properties of the biosolids and the type of plant.

In the present study, a different approach was taken. In addition to monitoring the total and DTPA-extractable concentrations of heavy metals in the soil following the application of biosolids, changes in the ratio of DTPA-extractable to total metal residuals of heavy metals were measured. Two types of biosolids were applied to a clay loam in Victoria, Australia. The two types of biosolids used were a dewatered anaerobically digested biosolid (DWB) and one that had been composted (CB). These biosolids were chosen because they are typical of the types of biosolids and products produced from biosolids in Victoria. The crops tested were canola (*Brassica napus* cv. Beacon) and oats (*Avena sativa* cv. Echidna).

The work presented herein is part of a larger field trial in which the mobility of both nutrients and metals was studied. This paper concentrates on the results for copper (Cu) and zinc (Zn), because these were the two metals with highest concentrations in the biosolids.

The hypothesis tested in the present study was that adding biosolids would change the characteristics of the soil, which, in turn, would affect the bioavailability of heavy metals. This was

tested by measuring the ratio of DTPA-extractable to total metal concentrations in the biosolids and soils before and after application. The concentrations of Cu and Zn were measured in the leaves from the two crops grown as an indicator of plant uptake.

Materials and methods

Field site

The experimental field site was located at the Melton Recycled Water Plant (MRWP), Surbiton Park, South Melton in Victoria, Australia (37°45′13″S, 144°35′13″E). The Melton shire is situated on the western volcanic basalt plains of Victoria; it has a dry temperate climate, within the rain shadow of the Otway Ranges. Consequently, annual rainfall is low and variable, averaging between 465 and 600 mm, with higher rainfall in the hilly northern part of the shire. The average annual maximum temperatures around Melton and the south-east of the shire range from 18 to 20°C (Melton City Council 2007). The soils in the Melton South district are derived from New Volcanics basalt yielding red sodosols (Melton City Council 2007). The soil profile across the experimental site has a relatively uniform depth of topsoil and thickness of horizons. The slope of the site was gentle with consistent topographical drainage. There was minimal shade and uniform aspect.

Spring rainfall, low spring frosts, winter chilling and moderate summer temperatures typical of the Melton shire make the area suitable for growing canola and oats.

Experimental design

The experimental site was 40 × 37 m in size and was partitioned into 60 experimental plots (20 treatments in triplicate), each 12 m^2 in area. The 20 treatments consisted of two crop types × two types of biosolids × five application rates. The treatments were divided into four blocks, each planted with either canola or oats, and treated with one type of biosolid. Within each block, the treatments were arranged in a randomised complete block design.

The DWB, obtained from the MRWP, needed to be crushed before incorporation into the soil. The CB were obtained from Pinegro Products (Deer Park, Vic., Australia) and were used as supplied.

After the experimental site had been ploughed, the biosolids were incorporated to a depth of approximately 15 cm using a rotary hoe. Gypsum was applied at a rate of 3 t ha^{-1} to inhibit soil dispersion, prevent surface crusting and improve soil structure and water drainage. The plots were irrigated with potable water from Western Water's Melton water supply using an overhead sprinkler system.

DWB was applied at rates of 0, 5, 25, 45 and 65 t dry solids (ds) ha^{-1}, whereas CB was applied at rates of 0, 10, 30, 50 and 70 t ds ha^{-1} to both canola and oats. These values include the typical application rates of 10 t ds ha^{-1} for DWB and 20 t ds ha^{-1} for CB based on the nitrogen limited biosolids application rate (1 NLBAR; New South Wales Environment Protection Authority 1995) for canola. The corresponding NLBAR for oats is slightly higher, at 11 t ds ha^{-1} for DWB and 22 t ds ha^{-1} for CB.

The two crops chosen for the field experiment have different root systems; canola (*B. napus* cv. Beacon) has roots that extend to 1 m in depth, whereas oats (*A. sativa* cv. Echidna) have shallow roots (McConkey and Kutcher 2000). Canola and oat seeds were sown at a seeding rate of 5 and 100 kg ha^{-1}, respectively.

Sampling and analyses of soil and biosolids

The DWB had been anaerobically digested at the MRWP and was harvested from the anaerobic lagoon at the site. They were then stockpiled on a 10-ha site for over 2 years. The CB were obtained from Pinegro, a local composting company that blends biosolids from Western Water with screened green waste from local council collections. The blended material had been passed through a 12-week biosolids composting process that produces sufficient heat to destroy pathogens, producing a composted biosolids product safe for use by the public.

Before establishing the field experiment at MRWP, composite soil samples from the experimental site and DWB were air dried for 2 weeks; after drying, they were sieved through a 2-mm mesh and analysed for pH, electrical conductivity (EC), cation exchange capacity (CEC) and total and extractable plant nutrients and metals (Table 1).

After crop harvest, 30 soil plugs (10 cm) per plot were randomly sampled and made into one composite sample, providing a total of 60 composite biosolids-amended soil samples.

The pH_w and EC 1 : 5 of soil and biosolids were determined as per Methods 4A1 and 3A1 of Rayment and Lyons (2011). The major cations in soils and biosolids were extracted using 1 M NH_4Cl according to Method 15A1 of Rayment and Lyons (2011). Standards, samples and blanks were analysed by inductively coupled plasma mass spectrometry (ICP-MS) using an Agilent Technologies (Palo Alto, CA, USA) Model 4500 series 300 ICP-MS with HP ChemStation software and a detection limits for the quadrupole and magnetic sector of 1–10 and 0.01–0.1 ng L^{-1}, respectively. The CEC of soil and biosolids samples was calculated according to Method 15B1 of Rayment and Lyons (2010, 2011).

An indication of plant available metals in biosolids and biosolids-amended soils samples was determined by extraction with DTPA extracting solution as per Method 12A1 of Rayment and Lyons (2010, 2011). Extracts were analysed using ICP-MS as described above.

To validate the analytical procedures for the DTPA-extractable metals, a multi-element stock certified standard solution containing the relevant heavy metals was analysed in duplicate for every 10 samples and percentage recovery calculated. The measured and certified values of the DTPA-extractable heavy metals indicated that the recovery of the laboratory check sample (multi-element stock ICP-MS solution) was 100% for Cu, 99% for Zn, 100% for Mn, 99% for Ni, 99% for Pb and 101.6% for Fe, in good agreement with the certified values (see Supplementary Materials table S1, as available on journal's website).

Total metals in soil and biosolid samples were analysed using a Bruker (Karlsruhe, Germany) S4 pioneer wavelength dispersion X-ray fluorescence spectrophotometer (WD-XRF) equipped with LiF (200), Ge, PET, ovo-55 crystals with

Table 1. Physicochemical properties of soil and biosolids used for the experiments

Data are the mean ± s.e.m. ($n = 3$). Total P, S, Cu, Zn, and Mn were determined using wavelength dispersion X-ray fluorescence spectrometry, whereas Na, Mg, K, Ca and Al were analysed using inductively coupled plasma mass spectrometry. All analytical results are expressed on an air-dried basis. EC, electrical conductivity; CEC, cation exchange capacity

Analytes	Soil	Dewatered biosolids	Composted biosolids
pH_w	6.5	6.7	6.4
Moisture (%)	2	8	11
pH_{Ca}	5.5	6.2	6.1
EC (1:5; μ S/cm)	67.4	1350	2704
CEC (mEq kg^{-1})	6.9	24	62
Total N (%)	0.17 ± 0.002	4.22 ± 0.01	1.44 ± 0.003
Total C (%)	2.04 ± 0.02	31 ± 0.1	13.85 ± 0.04
C/N ratio	12.2	7.4	9.6
Total P (μg g^{-1})	855 ± 3	15003 ± 4	21290 ± 566
Total S (μg g^{-1})	239 ± 1	11380 ± 1	5265 ± 6
Total Cu (μg g^{-1})	17 ± 1	648 ± 1	210 ± 4
Total Zn (μg g^{-1})	37 ± 2	1062 ± 1	813 ± 8
Total Mn (μg g^{-1})	247 ± 2	213 ± 1	299 ± 6
Total Ni (μg g^{-1})	23.3 ± 0.4	27.17 ± 0.01	21 ± 0.4
Total Pb (μg g^{-1})	11.4 ± 0.2	28 ± 3	47 ± 1
Total K (%)	1.071 ± 0.005	0.389 ± 0.001	1.240 ± 0.002
Total Fe (%)	2.60 ± 0.01	1.36 ± 0.01	2.5 ± 0.1
Olsen-P (μg g^{-1})	14.8	691	762
NO_3-N (μg g^{-1})	2.9	830	1864
NH_4-N (μg g^{-1})	5 ± 3	3740 ± 74	2113 ± 8
Mineral-N (μg g^{-1})	7.9	4570	3977
Organic-N (μg g^{-1})	1692	37630	10423
1 M NH_4Cl-extractable major cations:			
Na	76 ± 2	749 ± 59	1557 ± 50
Mg	264 ± 4	1200 ± 86	3564 ± 17
K	316 ± 11	735 ± 65	4546 ± 79
Ca	697 ± 13	1831 ± 118	2864 ± 51
Al	1.3 ± 0.2	144 ± 31	11 ± 9

detection limits between 10 and 100 μg g^{-1} for soil (Schlotz and Uhlig 2002).

X-Ray fluorescence (XRF) was performed by combining 8 g sample with two 0.5-g wax-based briquetting tablets (PXR-250; Choice Analytical, Thornleigh, NSW, Australia). The samples were ground using a zirconia ring mill (Rocklabs, Auckland, New Zealand). The fine particulate samples were transferred into 40-mm aluminium cups and pressed at 10 tonnes. The pressed pellets were analysed in triplicate.

To certify the accuracy of the results obtained from WD-XRF, eight soil standard reference materials were analysed for total metal concentrations. The results were consistent with the certified values for all heavy metals analysed. These results were used to establish calibration curves for each of the metals (see Supplementary Materials table S2).

As an additional check on the validity of the method, the calibration curve determined from the eight standards above was used to calculate levels of Cu, Zn, Mn, Fe, Ni and Pb in two separate soil standard reference materials (Till1 and Till3). The recovery of each heavy metal was calculated based on the mean values for Till1 and Till3. In general, the recoveries ranged between 91% and 101%. The Pb value in Till3 was below the detection limit. There were no significant differences between the measured and certified values ($P > 0.05$, *t*-test; Supplementary Materials table S3).

Plant sampling and analysis

Thirty mature canola leaves at the four- to five-leaf stage and 20 oat plants at the five- to six-tillering stage were randomly sampled from the centre of each of the plots.

Harvested plant tissue was dried at 60°C for 3 days, after which the samples were ground using a ring mill to obtain a fine particulate mixture for further analysis. Total heavy metal concentrations in plant tissue were determined by digestion with concentrated HNO_3 and 30% H_2O_2 according to the laboratory procedures described by Benton Jones (2001).

The accuracy of the results of plant analysis was validated by digesting plant standard reference materials (SRM1573a tomato leaves) along with the samples. The recovery values for the standard reference material for SRM1573a were slightly lower than the certified values. This was not unexpected because the values obtained for SRM1573a reference material had been obtained using perchloric, nitric, hydrochloric and hydrogen fluoride acid digestion, whereas in the present study the reference material was digested using HNO_3 and H_2O_2. Hence, the amount determined may slightly underestimate plant uptake. Nevertheless, the recoveries of the measured values for all the heavy metals were high (Supplementary Materials table S4).

Statistical analysis

The analytical data were subjected to analysis of variance (ANOVA) for each experiment using GENSTAT Release 9 (GENSTAT 2007). Differences between means were compared by Fisher's least significant difference (l.s.d.) test, with $P < 0.05$ considered significant.

Pearson correlation coefficients were used to determine the significance of correlations between plant uptake of metals and application of biosolids. Correlations were declared significant at $P < 0.05$ and highly significant at $P < 0.01$.

Results and Discussion

Physicochemical properties of soil and biosolids

Results for selected physical and chemical properties of the soil type, DWB and CB used in the field experiment are given in Table 1. Table 2 lists concentrations of DTPA-extractable heavy metals in the biosolids and soil.

The pH_w of soil and biosolids products were similar, as were the concentrations of total Mn and total Ni.

The EC and CEC values of CB were significantly higher than DWB, which indicates that, in the long term, repeated applications of CB would elevate levels of soluble salts in the soil. In addition, CB had higher concentrations of total P, Olsen-P and NO_3-N.

The concentrations of major cations (Na^+, K^+, Ca^{2+} and Mg^{2+}), with the exception of aluminium, were substantially higher in CB than in DWB, presumably because of the addition of green wastes during the composting process. The concentrations of total C, N, S, Cu and Zn were higher in DWB than in CB.

Levels of DTPA-extractable Cu, Zn, Mn and Ni were higher in DWB than in CB, but the concentrations of DTPA-extractable Fe and Pb were higher in CB (Table 2). For all the DTPA-extractable metals, soil background concentrations were much lower than in the biosolids.

Effect of biosolids on soil pH

The change in pH_w as a result of the application of biosolids is of particular significance because it has an effect on the solubility of heavy metals contained in the biosolids. The change in pH is shown in Fig. 1.

DWB had a significant ($P < 0.001$) effect in reducing soil pH_w, with the oat plots being more affected than the canola plots. In contrast, plots treated with CB had a slight increase in pH_w over the course of the experiment. The change in pH cannot be attributed to the pH of the biosolids themselves because they both had a very similar pH to that of the soil. Several researchers (Bolan *et al*. 1991; Kirchmann *et al*. 1996; Bergkvist *et al*. 2003) suggested that adding biosolids leads to an increase in NO_3^- ions resulting from the mineralisation of organic nitrogen contained in the biosolids and its accumulation in soil. The process of nitrification leads to an increase in hydrogen ions, which replace the major cations. The displaced cations may then be leached from the soil along with nitrate ions, leaving behind an acidified soil (Paul and Clark 1996). The difference between the crops may have been because of the greater requirement for N by canola (Ministry of Agriculture, Food and Rural Affairs 2015).

In the case of composted biosolids, the build up of H^+ resulting from the mineralisation of organic nitrogen contained in the composted biosolids could be partly off-set by the simultaneous increase in the concentration of major cations from the CB, which was double that of the DWB (Table 1). The amount of organic nitrogen was also much less (~¼) than that contained in the DWB.

It is expected that any change in pH from the effect of nitrification of the organic nitrogen will be more pronounced in biosolids having a high organic nitrogen load, as with the DWB.

Table 2. Concentrations of diethylenetriamine penta-acetic acid (DTPA)-extractable metals in soil, dewatered biosolids and composted biosolids

Data are the mean ± s.d. ($n = 3$)

Analytes	Soil	Dewatered biosolids	Composted biosolids
Cu ($\mu g\,g^{-1}$)	1.1 ± 0.1	185 ± 32	22 ± 4
Zn ($\mu g\,g^{-1}$)	0.9 ± 0.3	368 ± 3	271 ± 57
Mn ($\mu g\,g^{-1}$)	12 ± 1	98 ± 3	28 ± 5
Fe ($\mu g\,g^{-1}$)	82.0 ± 0.1	208 ± 3	270 ± 62
Ni ($\mu g\,g^{-1}$)	0.94 ± 0.06	4.8 ± 0.3	1.6 ± 0.4
Pb ($\mu g\,g^{-1}$)	0.5 ± 0.3	4.9 ± 0.1	9 ± 2

Effect of biosolids on the ratio of DTPA-extractable to total soil Cu and Zn

To demonstrate the effects of DWB and CB on the change in the residual bioavailable fractions of Cu and Zn after one harvest, the ratios of DTPA-extractable to total concentrations of metals (as determined by XRF) in biosolid-amended soil samples were plotted against the biosolid application rate (Figs 2, 3); the expected ratios were also plotted for comparison. Expected ratios were calculated based on the bulk density of the soil ($1.51\,g\,cm^{-3}$) and an average incorporation depth of 15 cm, assuming no conversion of total to DTPA-extractable metals. The ratios for the soil and biosolids before application are given in Table 3.

From Table 3, it can be seen that the ratio of DTPA-extractable to XRF-determined total metals was higher for Cu in DWB than CB. The ratios for Zn were similar for the two biosolids. The ratios for both metals were a factor of 10 higher in the biosolids than in the background soil.

Given that the pH_w of the soil was reduced by the addition of DWB, it is expected that the metals would be more readily

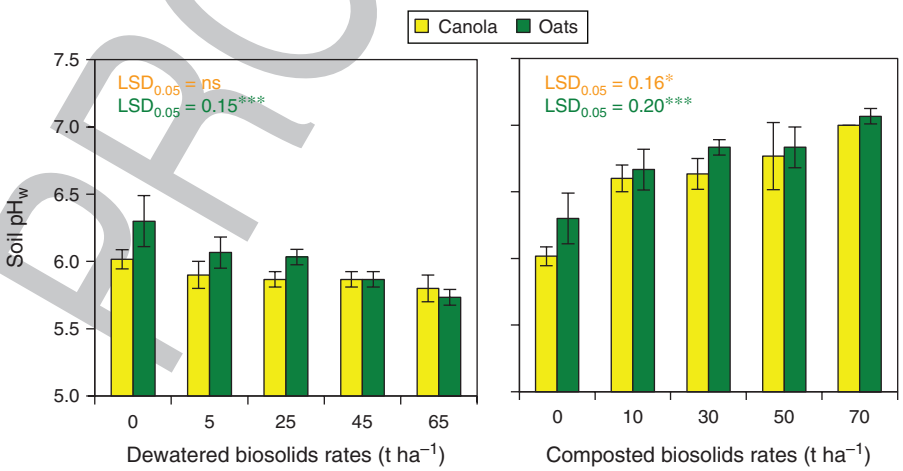

Fig. 1. Effects of different application rates of dewatered biosolids and composted biosolids on soil pH_w. Data are the mean ± s.d. of triplicate measurements (except for the controls, for which data for the six canola plots were pooled, as were data for the six oat plots). $LSD_{0.05}$, least significant difference for the means at 5% probability. $^*P < 0.05$; $^{***}P < 0.001$ (ANOVA (F-test); $n = 3$).

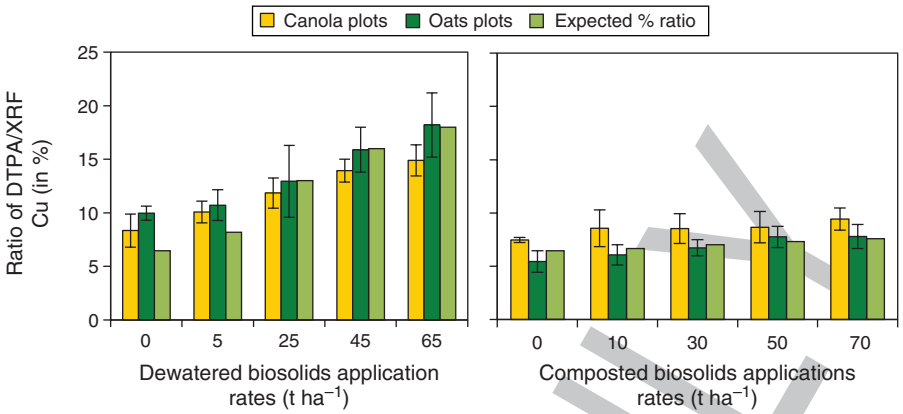

Fig. 2. Effects of different application rates of dewatered biosolids and composted biosolids on the ratio of diethylenetriamine penta-acetic acid (DTPA)-extractable to X-ray fluorescence spectrometry (XRF)-determined Cu levels in canola and oat plots. Expected ratios were calculated based on a soil density of 1.51 g cm^{-3} and a ploughing depth of 15 cm. Data are the mean ± s.d.

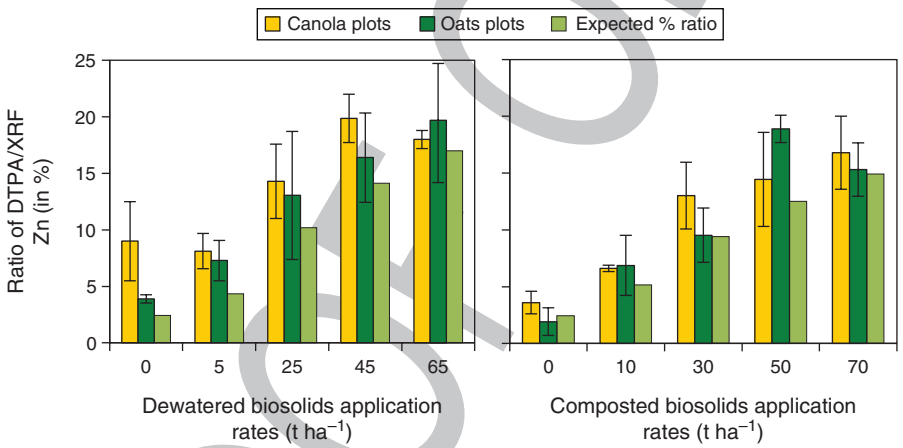

Fig. 3. Effects of different application rates of dewatered biosolids and composted biosolids on the ratio of diethylenetriamine penta-acetic acid (DTPA)-extractable to X-ray fluorescence spectrometry (XRF)-determined Zn levels in canola and oat plots. Expected ratios were calculated based on a soil density of 1.51 g cm^{-3} and a ploughing depth of 15 cm. Data are the mean ± s.d.

mobilised with increasing application rates, thereby increasing the DTPA-extractable fraction. This effect was not expected with CB because the pH_w of the amended soil was increased slightly by their addition. However, there are competing processes, including uptake by plants, sequestering by organic matter and leaching. The effects for Cu and Zn are discussed separately below.

Cu

In plots treated with DWB, the ratio of DTPA-extractable to XRF-determined total Cu levels clearly increased with application rate (Fig. 2). At the higher application rates, this increase was close to the calculated value. At lower application rates, the difference was more pronounced, with the ratio being slightly higher than expected. The difference at the lower concentrations could be because the plants receiving the lower application rates were not as well supplied with nutrients and therefore did not produce as much foliage.

The residuals in the plots on which canola was grown had a lower DTPA-extractable : XRF-determined total Cu ratio than plots growing oats. This suggests that either more Cu was taken up by the plants in the plots on which canola was grown or that Cu was lost through leaching in the canola plots. The potential for leaching through channelling should also be enhanced in the canola plots given the depth of their roots compared with the roots of oats. In either scenario, the concentration of extractable Cu in the residual soil would be depleted.

There was no obvious increase in the ratio of DTPA-extractable : XRF-determined total Cu in the plots treated with CB. This was to be expected because there was very little difference in the ratio between the soil and CB (6% and 11%, respectively), and the pH increased rather than decreased.

Zn

As with Cu, the ratio of DTPA-extractable : XRF-determined total Zn levels increased with the addition of

DWB; however, unlike Cu, this ratio also increased with addition of CB (Fig. 4). In the case of Zn, the initial ratio in CB was very similar to that in DWB (33% and 34%, respectively).

The observed ratios for the two biosolids were similar, although slightly higher in the canola plots, the reverse of the situation for Cu. In all cases, the measured ratio was higher than the calculated ratio. Again, the difference was more pronounced at the lower concentrations, and with DWB.

Plant uptake of Cu and Zn

Heavy metal accumulation in plants differs with plant species, cultivars and plant parts. In most cases, heavy metals are more concentrated in the leaves than in the grain (González *et al.* 2012). Thus, to investigate the concentrations of Cu and Zn in the leaves of canola and oats amended with DWB and CB, plant samples taken at the four- to five-leaf stages for canola and at the five- to six-tillering stages for oats were analysed for total metal concentrations.

Results from the analysis of plant leaves showed that when the unamended control plot was compared to the highest DWB application rate (65 t ha^{-1}), the uptake of Cu by canola increased significantly ($P < 0.05$) from 10 to 20 µg g^{-1} on a dry matter basis. Similarly, Zn uptake by canola increased significantly ($P < 0.05$) from 64 to 86 µg g^{-1} on a dry matter basis (Fig. 4).

Although Cu and Zn uptake by oat leaves was lower than the corresponding values observed in canola leaves, the oat crop also responded positively. Following the application of DWB, Cu and Zn uptake by oats increased from 3.5 to 7.0 mg kg^{-1} and from 16 to 61 mg kg^{-1}, respectively.

As shown in Fig. 4, both Cu and Zn uptake by canola and oats increased following the application of DWB. The uptake of Cu into the leafy tissue by canola was more than double the amount observed in oat leaves. This is consistent with greater removal of DTPA-extractable Cu from the canola plots. The difference in uptake of Zn between the two crops was much less (80 vs 60 mg kg^{-1} for canola and oats, respectively, from DWB).

Similar findings were observed when canola and oats were treated with CB.

Cu and Zn uptake by canola and oats was slightly higher in the DWB-treated plots than in the CB-treated plots, most likely because of the higher concentration of plant available Cu and Zn in the DWB (Table 2).

Initially, both DWB and CB increased Cu and Zn uptake by both crops, in some cases reaching a response plateau (Figs 4, 5). Because the amount of organic matter was higher in the DWB, sequestering of any remobilised Cu may also have occurred.

Table 3. Ratio (expressed as a percentage) of diethylenetriamine penta-acetic acid (DTPA)-extractable to X-ray fluorescence spectrometry (XRF)-determined total heavy metals in soil, dewatered biosolids and composted biosolids

Concentrations of DTPA-extractable and XRF-determined total heavy metals were analysed before planting

Analytes	Soil	Dewatered biosolids	Composted biosolids
Cu	6.5%	28.5%	11.0%
Zn	2.4%	34.7%	33.0%
Mn	4.9%	46.0%	9.4%
Fe	0.3%	1.5%	1.1%
Ni	4.0%	17.7%	7.5%
Pb	4.7%	17.5%	19.0%

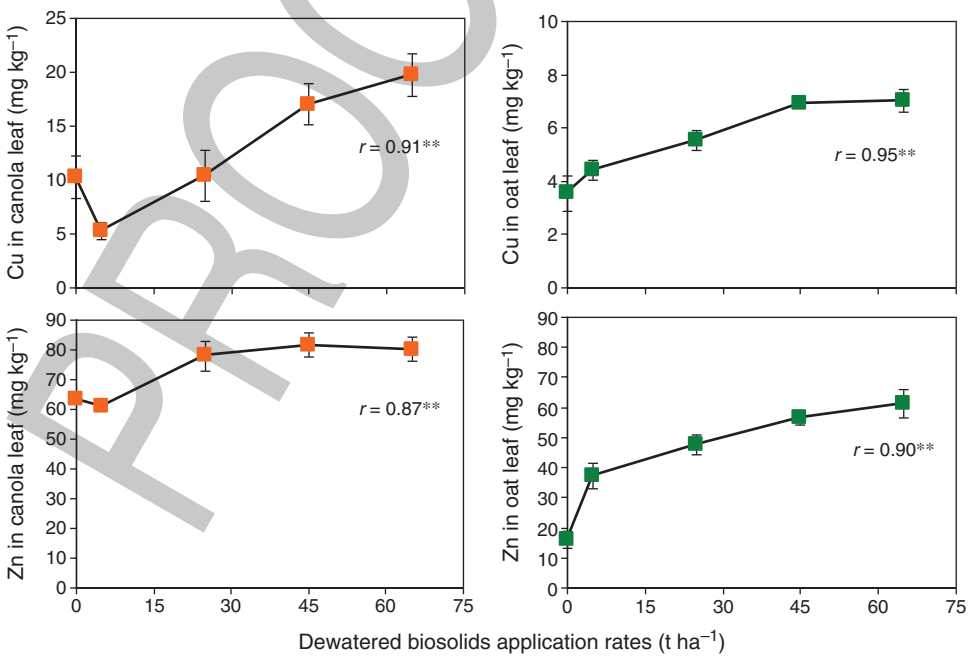

Fig. 4. Effects of different application rates of anaerobically digested dewatered biosolids on the uptake of Cu and Zn by canola and oats (in mg kg^{-1} on a dry weight basis). Data are the mean ± s.d. of triplicate measurements. *r*, Pearson correlation coefficient.

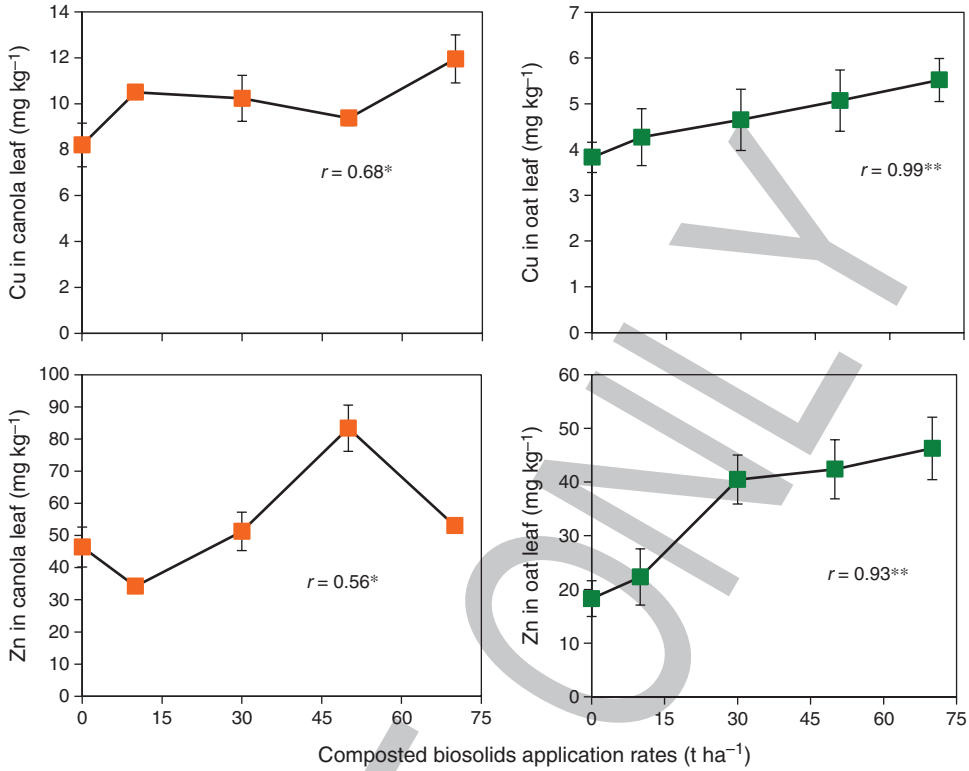

Fig. 5. Effects of different application rates of anaerobically composted biosolids on the uptake of Cu and Zn by canola and oats (in mg kg^{-1} on a dry weight basis). Data are the mean ± s.d. of triplicate measurements. *r*, Pearson correlation coefficient.

Several other researchers (Chaney and Ryan 1993; Hamon *et al*. 1999; Mahdy *et al*. 2007) have reported similar observations in that the uptake of metals by various crops is not linear with the application rate of either heavy metals or sludge or biosolids, but rather approaches a maximum and then levels out or decreases.

Phytotoxicity of Cu to most plants can occur at concentrations of approximately 25–40 µg g^{-1} on a dry matter basis, with normal Cu levels in plants ranging between 5 and 20 µg g^{-1} on a dry matter basis (Page 1974; Chaney and Giordano 1977). In the present study, the maximum leaf Cu concentrations recorded at the maximum application rate of 65 t ha^{-1} (19.7 and 7.0 µg g^{-1} dry matter for canola and oat tissue, respectively) were below the toxicity levels specified above and caused no observable changes in the plants.

Conclusion

The application of DWB decreased the pH_w of the soil, whereas CB increased it slightly. Therefore, the expected outcome of applying DWB was an increase in the mobility of metal ions, and hence an increase in the percentage of DTPA-extractable metals. This was not expected to occur with CB.

The behaviour of Cu was as predicted, with the increase in the ratio of DTPA-extractable to total metal occurring with DWB but not CB. The increase in the ratio for DTPA-extractable to total Zn (as measured by XRF) was greater than for Cu, and observed with both DWB and CB, despite the increased pH of plots receiving CB.

The uptake of Cu into canola and oats was greater than that of Zn, and uptake was more pronounced in canola. It was also noted that the ratio of DTPA to total metal in the residual soils, relative to the calculated values (Figs 2 and 3), were noticeably higher at the lower concentrations for Cu from DWB, indicating a less efficient take up of heavy metals. Certainly, the concentrations of Cu and Zn in plant tissues were lower at lower application rates. This is consistent with the plants being poorly nourished at application rates below the NLBAR.

It is clear from the present field trial that the application of both biosolids did affect soil pHw, and there was a change in the ratio of DTPA-extractable to total metal in the soil residuals with increasing application rate. The change appears to be clearly linked to pH with Cu, but the results are not as clear with Zn. It is evident that the relationship between pH and the uptake of heavy metals is not a simple one; it depends upon the type of metal, the source (and hence speciation of the metal) and the crop being grown.

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