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The application of mixed waste organic output (MWOO) to soils: Effects on metal and metalloid concentrations, distribution, bioavailability and mobility in NSW soils

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Abstract

Mixed waste organic output (MWOO) has been used as a soil amendment for many years. However, concern regarding the introduction of contaminants to soil ecosystems can potentially restrict its use and there is growing need to fully understand the risk associated with utilizing this potentially beneficial resource, in particular with regard associated metal and metalloid contamination.

The aim of this project was to examine the impact of MWOO application on concentration, distribution, bioavailability and mobility of seven targeted priority pollutants including As, Cd, Cr, Cu, Ni, Pb and Zn on different soils of NSW. MWOO is frequently used for different purposes such as agricultural or rehabilitation of the minesite in NSW and it is specifically regulated for this. Hence the soils studied were collected from different, mainly agricultural, areas within NSW, Australia. One of the soils used was collected from a NSW coal mine rehabilitation site. This was achieved through a sequence of experiment that progressed from method development, investigating the impact of MWOO application rate and method on concentration and down soil profile distribution of these contaminants, evaluating their distribution in different soil fractions by a sequential extraction and a leaching batch experiment to estimate the leachability and mobility of targeted metals and metalloids to achieve better estimation of the potential bioavailability and soil water contamination resulted from MWOO application to soils.

As a precursor comprehensive method evaluation was carried out for determination of total concentration of metals and metalloids in MWOO and MWOO amended soil. An ultrawave microwave digestion using aqua regia extractant with Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) analysis showed the optimum extraction efficiency and precision, and was used for further analysis of total metals and metalloids.

A glasshouse column experiment over 18 months was established to evaluate and compare the accumulation and distribution of the targeted metals and metalloids with MWOO amendment in ten different NSW soils. The MWOO was both surface applied and incorporated (to 15 cm) at three different rates (20, 50 t ha^{-1} and 140 t ha^{-1}) to the soils that encompassed a range of pH, texture and organic matter. Soil samples were collected at 6, 12 and 18 months to 70 cm depth. Total concentration of some the elements studied in MWOO contact depths, (which were 0–5 cm depth in surface applied treatments and 0–15 cm depth in incorporated applied treatments, was increased in soils). The significance of this, however varied depending on the element, soil type, initial concentration in MWOO and in background soils, application method and rate. Generally, Cu, Pb and Zn, with the highest concentration in MWOO, (180.8 ± 40.4, 275.1 ± 35.5 and 411.1 ± 16.3 mg kg^{-1}, respectively), showed the greatest increase in MWOO contact application depths. These three elements also showed significant increases at depths below MWOO contact application in some of the sandy soils, silt loams and one of the clays, most significantly at the depth immediately below the MWOO contact zone. The elements As, Cd, Ni and Cr were present at lower concentrations (5.3 ± 0.5, 2.2 ± 2.1, 40.2 ± 10.8 and 85.4 ± 12.2 mg kg^{-1}, respectively) in MWOO and slight but significant increases were only observed in MWOO contact depths in the sandy soil and silt soils, but also for depths below MWOO application As, Cd, Cr were in higher concentrations in some sandy soils and for Ni in the silty loams. In the high organic matter content soil, however, no change in metal or metalloid concentration was observed below MWOO contact depth for any of the elements, nor for As, Cd, Cr in the silty loams and clay soils. This experiment has evaluated the metal and metalloid concentration in different soil types from NSW for the first time and has demonstrated that MWOO additions can result in metal and metalloid accumulation that persists and usually maintained to 18 months and can cause down profile movement especially in sandy soils.

It is well accepted that total metal and metalloid concentration in MWOO provides limited information about actual risk to biological receptors and this may be better assessed by determining the bioavailability of these elements in amended soils.

Hence, the speciation and distribution of the metals and metalloids was determined in the exchangeable fraction (acid soluble), reducible fraction (associated with soil Fe and Mn oxides), oxidisable fraction (associated with soil organic matter) and residual fraction was determined for the controls and MWOO amended soil by the three step BCR (Community Bureau of Reference of the European Commission) sequential extraction method. To compare the impact of soil texture and low pH content on the availability and speciation of the metals and metalloids following MWOO amendment, the acidic sandy loam and clay soils used in the glasshouse experiment with acidic pH were chosen for this experiment. The proportion of metals in MWOO in the exchangeable fraction followed the sequence: Zn > As > Cd > Ni > Cu > Pb > Cr. This was, however < 20 % of total concentration. The highest proportion of metals and metalloids studied was in the residual fraction (> 45.5 %) in all the controls and MWOO amended soil samples. The impact of MWOO application on element distribution was most important for those elements with the highest concentrations in the MWOO i.e. Zn, Cu and Pb, and was relative to soil background concentrations. Following application of MWOO to the soils, the greatest increase in the exchangeable fraction was observed for Zn in the sandy loam, reaching 20 % of total soil Zn concentration. Application of MWOO to the soils also mostly increased the proportion of the elements in the reducible or oxidisable fractions. Both these fractions are considered relatively unavailable under consistent soil conditions, and in our study were largely stable during the 18 month study period. The result demonstrates that generally low risk if compliant MWOO applied at moderate rates. The fraction of the elements of greatest concern in terms of risk to soil systems is the exchangeable fraction, and Zn showed the greatest increase in exchangeable forms with MWOO addition in the sandy loam, approximately 6 mg kg^{-1}. Cations such as Zn in MWOO are high risk for plant uptake or availability for other organisms, however, the concentration in this exchangeable form following amendment with NSW MWOO for 50 t ha^{-1} application seems to present little risk.

A number of studies have reported increases in metals leached from soils that have been amended with MWOO which can be of concern in regards to ground water contamination or their availability to the plants and other soil organisms. Hence, the impact of MWOO application on the metals and metalloids leachability in acidic sandy loam soil was subsequently examined with three agents; deionised water, 0.01 M $CaCl_2$ and 0.05 M EDTA over 48 hours in a batch experiment. The application of MWOO to the acidic sandy loam soil significantly increased the concentration of most of the metals and metalloids in all three extractants. Generally, concentrations of Zn, Pb and Cu were the greatest in all extractants, which can be explained by their high concentrations in MWOO and also formation of soluble organic complexes following MWOO application. Even though only a low % of total soil metal was extracted (< 4 % in both water and 0.01 M $CaCl_2$), extractant concentrations indicate potential risks for water contamination following MWOO application, with the greatest concern being for Zn in leachate. Of the three extractants, EDTA extracted the largest concentration of all elements (up to 7.48 mg kg^{-1} for Zn), indicating potentially higher risk for plant availability, but only if EDTA can in fact be confirmed as a good measure of this.

The results from the EDTA extraction in the batch experiment were applied in a kinetic model using first order kinetic study with both two step and one step first order models to predict the lability of the elements studied. The data showed a good fit for the one step first order model, suggesting that either the desorption of the labile and non–labile element components were similar, or, more likely, that the labile fraction was too small to be easily identified in the model. This is quite probable in this well matured MWOO amended system. Overall, Zn, Cd and Pb showed the fastest desorption whereas As and Cr were slowest. Sequential extraction of the residue showed that effects of MWOO application were evident in the soil 48 hours after leaching. Zinc showed the highest proportion in the exchangeable fraction (in water and 0.01 M $CaCl_2$, 26 and 25 %, respectively) and Pb showed the highest proportion in the reducible fraction (26 % and 21 %, respectively). The proportion of these elements in the exchangeable fraction and the reducible fraction increased in MWOO amended samples compared to controls. This shows the impact of MWOO application in increasing the availability especially of Zn. The largest proportion of all the elements studied was still in the residual fraction (> 44.6 %) which is considered not available to plant and soil organisms.

In conclusion, MWOO application can significantly increase contaminant concentrations when applied to soils, with the increase most significant for those contaminants present at higher concentrations in MWOO, notably Cu, Pb and Zn. Further, these effects persist for at least 18 months and some down profile movement can occur, to the greatest extent in sandy soils. The effects of MWOO are evident also in increased potential bioavailability of contaminants such as Zn and Pb and also increased contaminant in the aqueous phase. However, the risks for soil systems in NSW seem to be low if MWOO meets the current NSW General Exemption Guidelines and is used for soil application at rates suitable for plantation forestry, broad acre agriculture and non-contact agriculture (< 50 t ha^{-1}). Concern is greater if MWOO is applied at higher rates and/or in repeat applications.

I certify that the substance of this thesis has not already been submitted for any degree and is not currently being submitted for any other degree or qualification.

I certify that any help received in preparing this thesis and all sources used have been acknowledged in this thesis

Signature [redacted] Date 30/11/2015

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