

Bioavailability of metals in Australian biosolids.

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Abstract

The presence of metal contaminants in biosolids is one of the key factors restricting their use in agriculture. Moreover, the regulation of such activities is complicated by an incomplete understanding of the likelihood of long-term changes in metal bioavailability occurring following land application. This study seeks to address this knowledge gap by subjecting a wide range of Australian sewage sludge samples to a combination of standard chemical characterisation methods, isotopic dilution lability assessment, and advanced spectroscopic analyses. Key results and differences between these samples will be presented, providing insight into the variation in concentration and bioavailability of major metal contaminants in Australian biosolids. Discussion will focus on the role of key sorbent phases and mechanistic factors as identified through spectroscopic interrogation.

Key Words

Sewage sludge, Biosolids, Metals, Bioavailability, Fixation, Oxides.

Introduction

Sewage sludges are continuously produced as a by-product of municipal wastewater treatment and their subsequent disposal presents a major management issue for the wastewater industry. Among the disposal options for stabilised sewage sludges (biosolids) application to land as a soil conditioner is of major importance, particularly in countries such as Australia where soils are typically nutrient poor and low in organic matter. Nevertheless, the land application pathway has recently been subject to widespread scrutiny due to uncertainties regarding the long term fate and release of contaminants from sludge-derived products. The inevitable presence of metal contaminants in biosolids is of particular concern due to their accumulative and persistent nature in the environment. In fact, exceedance of regulatory metal limits currently presents one of the most common barriers to the beneficial reuse of biosolids in agriculture. Despite this, knowledge of the factors controlling metal bioavailability in biosolids and biosolids-amended soils remains far from complete. For instance, although it is well known that metal contaminants in sewage sludge can potentially be sorbed by both inorganic and organic constituents, the nature of the key metal sorbing phases is still a matter of debate (Basta *et al.* 2005). While some authors have suggested that organic matter is the dominant sorbent (Beckett *et al.* 1979; McBride 1995) others have indicated that inorganic constituents such as iron and manganese oxides play the dominant role (Chaney *et al.* 1999; Li *et al.* 2001; Hettiarachchi *et al.* 2003, 2006). How much this may vary between different biosolids products due to temporal and spatial variations in wastewater treatment plant (WWTP) influent characteristics and wastewater processing is not yet well understood but with the nature of the constituents controlling metal sorption having important repercussions in terms of long-term bioavailability it is important for such knowledge gaps to be addressed.

It has generally been postulated that metal chemistry and bioavailability in biosolids-amended soils will predominantly be controlled by the properties of the biosolids in the short to medium term but that soil properties will play an increasingly important role in the long term (Merrington *et al.* (2003). However the time frame over which this change is likely to occur is quite uncertain, with estimates in the literature ranging from weeks to years (Parkpain *et al.* 1998; Smith 1996). Moreover, the factors that govern this temporal change have not yet been determined (Merrington *et al.* 2003). If the dominant sorptive phase is indeed organic matter, mineralisation processes may lead to contaminants being released from the biosolids over time. This possibility has prompted various authors (Beckett *et al.* 1979; McBride 1995) to advance a 'time bomb' hypothesis by which a long-term increase in contaminant bioavailability is envisaged. On the other hand, if the contaminants are mainly sorbed by stable inorganic constituents it is feasible that substantial changes in their long-term bioavailability may not occur. To date, evidence in favour of either hypothesis is inconclusive (e.g. Hettiarachchi *et al.* 2003, 2006; Oliver *et al.* 2006). In fact, very little research has actually been conducted to systematically assess the partitioning of biosolids contaminants

between the organic and mineral sludge phases. Yet this knowledge would be invaluable for predicting the long-term effects of land application and associated risks, and could also potentially advance efforts to maximise stable associations of contaminants in sewage sludge derived end-products.

The primary objective of the study described here is to bring enhanced understanding of the mechanisms controlling the fixation of metal contaminants in biosolids. This will be achieved through the completion of a targeted laboratory programme combining conventional environmental research techniques such as total metal extractions, salt extractions and standard sample characterisation with the use of isotopic dilution for metal lability assessment and advanced spectroscopic techniques specifically suited to the analysis of key biosolids constituents and the interrogation of mechanistic factors.

Methods

Sewage sludge samples have been collected from over 40 Australian WWTPs. The samples have been sourced from all states and territories of Australia and comprise samples from a wide range of WWTPs with differing influent characteristics and network scales, as well as varying unit treatment processes and plant design. Samples have been obtained from both metropolitan and rural WWTPs. Detailed information regarding the wastewater treatment steps and sludge stabilisation methods at the individual plants have also been collected through the use of a WWTP process survey. Samples are being characterised for a range of parameters that are likely to affect the bioavailability and fixation of metal contaminants in the sludge matrix, for example, pH, EC, organic matter content, oxide content and form (e.g. crystalline, amorphous) etc. The materials will also be fractionated in order to assess whether key contaminants (e.g. Cd, Zn, Cu, Pb) are associated with the organic or mineral phases. Metal lability/chemical reactivity in the samples will be investigated using a CaCl_2 extraction in combination with a multilabelled isotopic dilution technique. These analyses will provide a measure of the extractable and isotopically exchangeable metals which will be correlated with the chemical characterisation of the biosolids described above. On the basis of results from these analyses, biosolids with particularly interesting characteristics will be selected for further investigation using advanced spectroscopic techniques. In particular, the nature of aluminium oxides present in the samples will be studied using ^{27}Al Nuclear Magnetic Resonance (NMR) spectroscopy and the nature of the iron oxides will be probed via Mössbauer spectroscopy.

Results and Discussion

A collection of over 40 sludge samples is currently undergoing detailed characterisation for a range of both standard and non-standard chemical and physical parameters. These samples have been sourced from a wide range of WWTPs with differing influent characteristics and network scales, as well as varying unit treatment processes and plant design. Key results and differences between samples from these systems will be presented and discussed, providing insight into the variation in concentration and bioavailability of key metal contaminants in Australian biosolids from different geographical regions and catchment types. Advanced spectroscopic techniques provide an ideal means of characterising such samples, facilitating the detailed inspection of sludge constituents and their role as sorbents.

There are many potential sludge treatment processes that can be applied prior to land disposal but in order for the suitability of these options to be properly assessed further understanding of the range in existing properties in both raw and stabilised sewage sludges is needed. Currently, there is a paucity of information showing the true variability in metal sorption and fixation among different biosolids and sewage sludge products even though this can be expected to be an important regulator of bioavailability. Furthermore, although it is increasingly well recognised that total metal concentrations are not an accurate determinant of bioavailability based risk, lack of understanding of the key mechanisms controlling metal bioavailability in biosolids amended soils, particularly in the long term, slow the adoption of more suitable bioavailability based guidelines. Even good quality biosolids contain substantial quantities of metal contaminants, and a thorough understanding of their long-term fate when added to soils is clearly a necessity if risk assessments and measures for environmental protection are to be effective.

Conclusions

A clear understanding of the factors controlling metal bioavailability in biosolids and the potential for long term changes is paramount to appropriate risk management. Further research combining detailed chemical analyses and powerful spectroscopic methods are needed to provide this knowledge.

References

- Basta NT, Ryan JA, Chaney RL (2005) Trace Element Chemistry in Residual-Treated Soil: Key Concepts and Metal Bioavailability. *Journal of Environmental Quality* **34**, 49–63.
- Beckett PHT, Davis RD, Brindley P (1979) The disposal of sewage sludge onto farmland: The scope of the problems of toxic elements. *Water Pollution Control* **78**, 419–445.
- Chaney RL, JA Ryan, SL Brown (1999) Environmentally acceptable endpoints for soil metals. In 'Environmental availability in soils: Chlorinated organics, explosives, metals'. (Eds WC Anderson *et al.*) pp. 111–154. (American Academy of Environmental Engineering: Annapolis, MD).
- Hettiarachchi GM, Scheckel KG, Ryan JA, Sutton SR, Newville M (2006) μ -XANES and μ -XRF investigations of metal binding mechanisms in biosolids. *Journal of Environmental Quality* **35**, 342–351.
- Hettiarachchi GM, Ryan JA, Chaney RL, LaFleur CM (2003) Sorption and desorption of cadmium by different fractions of biosolids-amended soils. *Journal of Environmental Quality* **32**, 1684–1693.
- Li Z, Ryan JA, Chen J-L, and Al-Abed SR (2001) Cadmium adsorption on biosolids-amended soils. *Journal of Environmental Quality* **30**, 903–911.
- McBride MB (1995) Toxic metal accumulation from agricultural use of sludge: Are USEPA regulations protective? *Journal of Environmental Quality* **24**, 5-18.
- Merrington G, Oliver I, Smernik RJ, McLaughlin MJ (2003) The influence of sewage sludge properties on sludge-borne metal availability. *Advances in Environmental Research* **8**, 21-36.
- Parkpain P, Sirisukhodom S, Carbonell-Barrachina AA (1998) Heavy metal and nutrient chemistry in sewage sludge amended Thai soils. *Journal of Environmental Science and Health* **33**, 573-597.
- Oliver IW, Merrington G, McLaughlin MJ (2006). Copper partitioning among mineral and organic fractions in biosolids. *Environmental Chemistry* **3**, 48-52.
- Smith SR (1996) Agricultural recycling of sewage sludge and the environment. CAB International, Wallingford.