Environmental behaviour of pharmaceuticals, personal care products and endocrine disrupting compounds following land application of biosolids

Kate Langdon

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School of Agriculture, Food and Wine
The University of Adelaide

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ABSTRACT

The reuse of biosolids through application onto agricultural land has been shown to provide plants with additional nutrients and organic carbon and improve moisture retention in soils. This practice can however be a route of entry into the environment for numerous contaminants that may be contained within the biosolids. The work presented in this thesis aims to gain a better understanding of the environmental behaviour of pharmaceuticals and personal care products (PPCPs) and endocrine disrupting compounds (EDCs) following the addition of biosolids to land. This work involved initially conducting an aquatic hazard assessment for PPCPs and EDCs following biosolids addition to land. Following this, seven compounds were selected, 4-nonylphenol (4NP), 4-t-octylphenol (4tOP), bisphenol A (BPA), triclosan (TCS), 17β-estradiol (E2), estrone (E1), estriol (E3) and 17α-ethinylestradiol (EE2), for an Australian biosolids survey. Four of these compounds were then chosen (i.e. 4NP, 4tOP, BPA and TCS) for a series of experiments assessing their dissipation (i.e. decreases in concentration) following the addition of biosolids to soil in the laboratory and in the field, as well as the suitability of using spiking experiments (i.e. spiking elevated concentrations of compounds into a soil and biosolids sample) to predict the persistence of these compounds following biosolids addition. Finally, the yeast estrogen screen (YES) bioassay was conducted on several soil sample extracts from the field trial to determine if estrogenic activity could be measured in soils following biosolids addition.

The results from the hazard assessment showed that the majority of PPCPs and EDCs that have been detected in biosolids pose low hazard to adjacent aquatic ecosystems. However, there were ten compounds that posed a high hazard and therefore warrant further investigation. These compounds were the fragrance compounds, tonalide and galaxolide, the estrogen compounds, 17β-estradiol and 17α-ethinylestradiol, the antibiotic compounds

ciprofloxacin, doxycycline and norfloxacin and the antimicrobial agents triclosan and triclocarban. The survey of Australian biosolids detected concentrations of 0.35 to 513 mg/kg for 4NP, 0.05 to 3.08 mg/kg for 4tOP, < 0.01 to 11.2 mg/kg for TCS, < 0.01 to 1.47 mg/kg for BPA and < 0.05 to 0.37 mg/kg for E1. The remaining compounds, E2, E3 and EE2, were below the limit of detection (i.e. 45 µg/kg) in all samples. These concentrations were similar to those that have been measured internationally.

The dissipation of the compounds 4NP, 4tOP, BPA and TCS was assessed over 32 weeks in the laboratory, following the addition of biosolids to a soil. The dissipation of 4NP, BPA and TCS followed a biphasic pattern which consisted of a dissipating fraction and a recalcitrant fraction. When the dissipation rates of the same four compounds were assessed under field conditions, 4NP and 4tOP dissipated 10- to 20-times slower in the field and BPA dissipated 2.5-times slower compared to the laboratory-based dissipation rates. The compound TCS, however, showed no dissipation in the field, however, in the laboratory-based study approximately 30% to 50% dissipation was observed. These results showed that there was the potential for PPCPs and EDCs to accumulate in agricultural soils and that laboratory studies overestimated dissipation rates.

The suitability of using spiking experiments to predict the dissipation of compounds following the addition of biosolids to a soil was assessed. This was tested using two methods: (i) spiking isotopically labelled surrogate compounds (i.e. BPA-d_{16} and TCS-$^{13}C_{12}$) into a biosolids amended soil and, (ii) spiking elevated levels of the same compound (i.e. non-labelled 4NP and 4tOP) into a biosolids amended soil and comparing the dissipation rates and patterns with those of the same compounds indigenous to the biosolids. Overall, it was determined that degradation experiments that involved spiking, yielded both faster rates of dissipation (up to 5-times faster) and, particularly in the case of

BPA, variations in the pattern of dissipation, in terms of the presence of a recalcitrant fraction. It was concluded that spiking experiments were not suitable to predict the dissipation of compounds following land application of biosolids.

Finally, estrogenic activity was measured in extracts of agricultural soil that had received biosolids, for at least the initial four months of the field trial. Overall this activity was low, however, it was still present at a level that may pose a high hazard to aquatic ecosystems (based on the results of the hazard assessment conducted earlier as part of this project).

The results presented in this thesis indicate that there is a need for further research with regards to the risks associated with PPCPs and EDCs in biosolids, relating to both their mobility and persistence. The results presented show that the biosolids matrix and the specific field conditions of application should be taken into consideration when determining the environmental behaviour of these compounds. It is also likely that the overall conclusions of the current project will apply to other groups of organic compounds present in biosolids. The data provided in this thesis will assist in future hazard and risk assessments and management of organic contaminants in biosolids applied to agricultural soils.

STATEMENT OF DECALRATION

This work contains no material which has been accepted for the award of any other degree or diploma in any university or other tertiary institution to Kate Langdon and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due references have been made in the text.

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THESIS STRUCTURE

The experimental chapters in this thesis are all written as journal articles. Since journal articles must be self-contained there is some degree of repetition in this thesis

Chapter 1 discusses the potential environmental risks associated with pharmaceuticals and personal care products (PPCPs) and endocrine disrupting compounds (EDCs) following the land application of biosolids. It highlights several important factors that need to be considered in order to assess these risks, including the influence of waste water treatment plant catchment characteristics and waste treatment processes in the final concentrations, the expected dissipation of the compounds in the environment (from both degradation and mobility) and the environmental toxicity.

Chapter 2 outlines the hazard posed to aquatic ecosystems from PPCPs and EDCs following the addition of biosolids to land, by predicting runoff water concentrations and comparing these to aquatic toxicity data.

Chapter 3 presents the data from an Australian biosolids survey, which was conducted to obtain data on the concentration in biosolids of several selected PPCP and EDCs (4-nonylphenol, 4-t-octylphenol, bisphenol A, triclosan, 17β-estradiol, estrone, estriol and 17α-ethinylestradiol) in representative Australian biosolids.

Chapters 4 and 5 examine the dissipation of 4-nonylphenol, 4-t-octylphenol, bisphenol A and triclosan following the addition of biosolids to a soil, under laboratory and field conditions, respectively.

Chapters 6 and 7 examine the standard method of "spiking" contaminants into soil and biosolids for its suitability in predicting the persistence of compounds when they are added to a soil by biosolids addition.

Chapter 8 determines the presence of estrogenic activity in soil extracts from a soil where biosolids have been applied and aged in the field.

Chapter 9 summarises and discusses the findings from this thesis and makes several recommendations for future research arising from the experimental work presented.