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Research article

Evaluating cadmium bioavailability in contaminated rice paddy soils and assessing potential for contaminant immobilisation with biochar

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ABSTRACT

Cadmium (Cd) contaminated soils from the Mae Sot district in northwest Thailand, a region in which rice Cd concentrations often exceed health limits (0.4 mg/kg) set by the World Health Organisation, were examined for isotopically exchangeable Cd (Cd E values using a ^{111}Cd spike) to determine how this rates as a predictor of rice grain Cd in comparison with soil total Cd and solution extractable Cd (using the commonly applied BCR scheme and, in an attempt to distinguish carbonate bound forms, the Tessier soil sequential extraction scheme reagents). Step 1 of the BCR scheme (0.11 M CH_3COOH) and step 1 of the Tessier scheme (1M $MgCl_2$) showed the highest R^2 values in regressions with rice Cd (91% and 90%, respectively), but all predictors were strongly linked to rice Cd ($p < 0.001$) and could be used for prediction purposes. One soil, of the six tested, was an exception to this, where all predictors over-estimated grain Cd by a factor of 2.5–5.7, suggesting that rice grain Cd had been restricted here by the differing flooding regime and subsequent changes to redox conditions. E values and Tessier step 1 extractions were closely related, indicating that these measurements access similar pools of soil Cd. Separately, the isotopic exchangeability (representing bioavailability) of Cd was also assessed in two soils amended with rice husk and miscanthus biochars (0, 1, 5, 10, 15 and 20% w/w) in order to assess the utility of the biochars as a soil amendment for immobilising Cd in situ. One soil showed significant reductions in Cd E value at 5% rice husk biochar addition and at 15% miscanthus biochar addition however, based on the E value-rice grain Cd regression relationship previously established, the E values in the amended soils still predicted for a rice Cd concentration above the health limit. In the second soil, neither of the biochars successfully reduced the Cd E value. This indicates that further work is needed to customise biochar properties to suit specific soil and contaminant situations if they are to be used successfully for remediation of metal contaminated soils.

1. Introduction

Metal contamination of soils is a long recognised and persistent environmental problem in many parts of the world. Indeed, ecological and/or human health concerns linked with elevated soil metal concentrations have been reported in every continent (e.g. Basta and Gradwohl, 2000; de Lima Neto et al., 2017; Farmer et al., 2011; Flynn et al., 2002; Mungai et al., 2016; Pereira et al., 2017; Taylor et al., 2010; Zhao et al., 2015). Contamination can arise from many potential sources, including mining and smelting activities, the use of rock phosphate or sewage sludge in agriculture, gaseous and particulate emissions from coal combustion, other industrial releases, and vehicular emissions (e.g. Atkinson et al., 2011; McGrath et al., 1988; McLaughlin et al., 1999; Santos et al., 2015). Transfer from soil to plants and so entry into food chains is a primary concern in relation to soil metal content and, while any metal can become toxic at elevated concentrations, cadmium (Cd) is a particular problem because it is a non-essential element that can accumulate in plants at levels that are harmful to humans and other animals before becoming phytotoxic (Prince et al., 2002). Rice is known to accumulate Cd when grown on contaminated soils and human health impacts, particularly kidney disease and associated conditions, have been conclusively linked to Cd exposure via rice consumption (Cai et al., 1990; Chaney, 2015; Swaddiwudhipong et al., 2012).

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One avenue of research that is receiving increasing attention is the use of soil amendments to bind Cd (and other contaminants) in situ and so restrict bioavailability and assimilation into plants. Biochar, a charcoal-like material created via thermal decomposition (or pyrolysis) of organic biomass under limited supply of oxygen (Lehmann and Joseph, 2009), has shown promise in this regard with several studies having highlighted the capacity of biochars made from various feedstocks to restrict mobility and availability of metals in soils (Beesley and Marmiroli, 2011; Fellet et al., 2014; Houben et al., 2013). Such studies have shown decreased concentrations of metals (e.g. Cd, Pb and Zn) in the porewaters and vegetation of mining or otherwise metal contaminated soils following treatment with biochar (Puga et al., 2015). However, other studies have reported mixed results, including cases where biochar additions were found to lower the water soluble Cu and Cd concentrations in soil but left unchanged or enhanced the concentrations in earthworms (Gomez-Eyles et al., 2011). The contaminant binding capacity of biochars and their use in environmental management is therefore a growing and evolving area of research. It is understood that the structure of biochar, being porous with high surface area and reactive surfaces, is what leads to this high potential binding capacity (Lehmann and Joseph, 2009; Sohi et al., 2009). Its alkalinity, i.e. typically pH 7–9 (Beesley et al., 2011), also likely contributes to its binding potential. However, the nature of the feedstock and the pyrolysis conditions during biochar production will have an influence on the properties of the end product (Buss et al., 2016) and so research is needed to establish the efficacy of various types of biochars for this application. Furthermore, in order to be of practical use in a soil remediation situation, the feedstock materials need to be available locally or regionally and so this must also be considered when trials or treatments with biochars are conducted.

The Tak province of northwest Thailand has areas of Cd contaminated soils where health and environmental problems have been identified hence numerous studies have investigated the Cd levels in soils and rice of the region as well as the health effects (Akkajit and Tongcumpou, 2010; Kosolsaksakul et al., 2014; Simmons et al., 2005; Swaddiwudhipong et al., 2012). The aims of the current study were to further examine the mobility and bioavailability of Cd in soils from one important area within this region of Thailand by employing isotopic exchange techniques and comparing them with previous assessments based on single and sequential extraction methods. Isotopic exchange techniques have been described as a rigorous and direct way of assessing the lability of metals in soil (e.g. Huang et al., 2011; Nakhone and Young, 1993; Smolders et al., 1999) and, as outlined by Degryse et al. (2011), they function by discriminating between isotopically exchangeable ('labile') and nonexchangeable ('non-labile') metal pools in soils. The technique involves adding a small amount of an isotopic tracer of the analyte of interest to the soil and determining the degree to which the native element within the soil can exchange with it between solid and solution phases. Moreover, the study aimed to examine properties (surface functional groups) of biochars produced from locally available materials (rice husk and miscanthus) and evaluate the feasibility of using them as a soil amendment to restrict the mobility, and thus bioavailability, of Cd.

2. Methods

2.1. Sampling sites

Soils (top 20 cm) and rice grain were collected from sites within a set of 18 rice paddy fields located in a Cd contaminated region in the Mae Tao watershed, Mae Sot District, Tak Provence, Thailand (Fig. 1), the location and contamination history of which has been fully described in our previous paper (Kosolsaksakul et al., 2014). In brief, the area supports regionally important cascade-irrigated rice paddy fields that are linked to the Mae Tao Creek (the main water supply) through a system of canals. The soils within the set of 18 fields examined in this study have pH ranging 6.8–7.7, organic matter between 1.1 and 3.7% and a loamy texture with 16–27% clay (Kosolsaksakul et al., 2014). These soils have been found to have Cd concentrations from 2.5 to 88 mg/kg (Kosolsaksakul et al., 2014), while other soils in the nearby region were found to have even higher Cd levels, e.g. up to 284 mg/kg at Ban Pha Te (Simmons et al., 2005). The elevated Cd observed in many soils of this area is likely linked to the close proximity (<5 km in places) of large scale Zn mining operations (Padaeng deposit – a major Zn mineralisation with substantial levels of Cd as an impurity) (Kosolsaksakul et al., 2014). The general area is recognised as being Cd contaminated and has been the focus of multiple soil remediation and human health investigations (e.g. Akkajit and Tongcumpou, 2010; Khaokaew et al., 2011; Khaokaew and Landrot, 2015; Simmons et al., 2009; Simmons et al., 2005; Swaddiwudhipong et al., 2012).

Details of soil and rice grain collection from each of the 18 fields and the sample processing methods employed (i.e. air-drying and grinding to <2 mm for soils; rice grains were rinsed in de-ionised water, dried at 60 °C and ground to a powder) were described previously, as were details of total Cd determinations following *aqua regia* (3:1 HCl:HNO_3, trace analysis grade) digestion and ICP-OES analysis (Optima 5300 DV instrument, Perkin Elmer, UK) (Kosolsaksakul et al., 2014). Soil samples from selected fields (Table 1), chosen in order to give a spread of the total Cd concentrations observed across the site, were used in the Cd bioavailability and sequential extraction procedures.

2.2. Soil extractions

For our previous study (Kosolsaksakul et al., 2014), soils were subjected to the European Communities Bureau (BCR) sequential extraction method (Ure et al., 1993), the first step of which is an extraction with 0.11 M CH_3COOH at pH 2.85 (targeting the 'exchangeable' fraction, i.e. nominally that bound to carbonates as well as loosely held elements). The soils were also subjected to the first two steps of the Tessier sequential extraction scheme (Tessier et al., 1979) in an attempt to distinguish easily exchangeable forms of Cd (i.e. Cd extractable by 1M $MgCl_2$ at pH 7; Tessier 1) from those nominally bound to carbonates (i.e. extractable by 1M CH_3COONa at pH 4.5; Tessier 2). The extract solutions generated were analysed via ICP-OES (Optima 5300 DV instrument, Perkin Elmer, UK) using reagent-specific calibration standards. Further details of the extraction scheme methods, including all quality control measures employed, are provided in our previous paper (Kosolsaksakul et al., 2014). The extractable element concentrations of soils for the first step of the BCR (BCR-1), and first and second step of the Tessier (Tessier-1 and Tessier-2, respectively) schemes determined in that previous study are presented in Table 1 to facilitate comparison with the isotopically exchangeable Cd concentrations determined in the present study.

2.3. Isotopically exchangeable Cd

Following the stable isotope exchange method described in Sterckeman et al. (2009), an enriched ^{111}Cd solution (IES-Cd111, Innovative Solutions in Chemistry; 10.224 ± 0.029 mg Cd/kg, isotopic abundances ^{106}Cd 0.008%, ^{108}Cd 0.008%, ^{110}Cd 0.351%, ^{111}Cd 96.167%, ^{112}Cd 2.004%, ^{113}Cd 0.487%, ^{114}Cd 0.867% and ^{116}Cd 0.108%; matrix 2% v/v HNO_3) was used to spike samples with ^{111}Cd. For calculations of isotope mixing and exchange ^{114}Cd, the most abundant naturally occurring isotope (28.73% abundance), was