



Can earthworm-secreted calcium carbonate immobilise Zn in contaminated soils?



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ABSTRACT

We investigated the interaction of soil Zn with calcium carbonate granules secreted by the earthworm *Lumbricus terrestris*. Earthworms were kept in agricultural soil amended with ZnSO₄ to give Zn concentrations up to 750 mg kg⁻¹ and in two former mine site soils containing 500 and 120 mg Zn kg⁻¹. After 21–42 days the earthworms accumulated 260–470 mg Zn kg⁻¹. Granule production was 0.027–2.11 mg CaCO₃ earthworm⁻¹ day⁻¹ and was positively correlated with soil and soil solution pH ($r = 0.66$ and 0.85 respectively, $p \leq 0.01$). Granule Zn concentration was 34–163 mg kg⁻¹. Granules collected from Zn-free control soil and left in Zn-bearing soil for 28 days contained 49–60 mg Zn kg⁻¹ suggesting that the majority of Zn associates with granules after their secretion. However, synchrotron X-ray fluorescence indicates some incorporation of Zn into granules during their formation. X-ray diffraction and X-ray absorption spectroscopy indicate that the granules are predominantly calcite and the spectroscopy suggests that the Zn is either adsorbed to, or incorporated into, the calcite lattice. X-ray diffraction of the outer c. 35 μm of the granules supports incorporation of Zn into the calcite lattice. The low granule production rates in the mine site soils and the granule Zn concentrations suggest that earthworm secreted calcium carbonate is unlikely to impact significantly on Zn mobility in soils.

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1. Introduction

Earthworms are ecosystem engineers, contributing to a range of soil processes that result in ecosystem services (Blouin et al., 2013). This has led to the use of earthworms in environmental remediation (e.g. Butt, 1999; Wong and Ma, 2008; Boyer and Wratten, 2010). Additionally, earthworms are routinely found in contaminated soils, apparently adapted to high-metal conditions (e.g. Arnold et al., 2008; Andre et al., 2010; Kille et al., 2013). The net effect of earthworms at contaminated sites appears to be, at least on the time-scale of laboratory experiments, an increase in the mobility of contaminants (e.g. Sizmur and Hodson, 2009; Sizmur et al., 2011). However, over significantly longer time scales they may have other impacts.

Calcium carbonate has been proposed as an *in situ* soil amendment to reduce Zn mobility in contaminated soils (e.g. Lee et al.,

2009; Padmavathiamma and Li, 2010) with reductions in Zn mobility being attributed to both increases in soil pH, formation of Zn-bearing carbonates and adsorption of Zn onto the carbonate surfaces. Many species of earthworm secrete granules of calcium carbonate (Darwin, 1881; Canti and Pearce, 2003) raising the intriguing prospect of earthworms assisting the remediation of metal contaminated soil via their secretions. The granules are predominantly calcite but also contain aragonite, vaterite and amorphous calcium carbonate (Gago-Duport et al., 2008; Lee et al., 2008). In the UK, granule production is dominated by *Lumbricus rubellus* and *Lumbricus terrestris* (Canti and Pearce, 2003). Estimates of granule production rate are highly dependent on estimates of earthworm density. Lambkin et al. (2011) report production rates of 0.18–31 g CaCO₃ ha⁻¹ yr⁻¹ on the basis of laboratory measured production rates and assuming an earthworm density of 10–20 *L. terrestris* m⁻² (Briones et al., 2008) whilst Wiecek and Messenger (1972) estimated that earthworm excreted calcium carbonate could contribute up to 0.11 g CaCO₃ ha⁻¹ yr⁻¹ to forest soils on the basis of soil measurements. The function of the granules remains unclear with possible functions including

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regulation of tissue pH and secretion of Ca (Robertson, 1936; Pearce, 1972).

A link has been suggested between the Ca-rich chloragogenous tissue in which metals such as Pb and Zn accumulate (Laverack, 1963; Prentø, 1979; Morgan, 1981) and the secretion of the calcite granules; though in previous studies using electron microprobe analysis (e.g. Prentø, 1979; Morgan, 1981; Schrader, 1992) no Zn was detected in the calcium carbonate produced by *L. terrestris*. The studies of Morgan (1981) and Prentø (1979) give little or no detail of the soils from which the earthworms were collected but they appear to be uncontaminated. Schrader (1992) exposed earthworms to soil amended with sewage sludge; the concentration of Zn in the amended soil was 129 mg kg⁻¹ which is well within the range of concentrations observed in uncontaminated soils (Mertens and Smolders (2013)). Given the low soil Zn concentrations and the detection limit of electron probe analysis (0.04%, 400 ppm) it is perhaps not surprising that no Zn was detected in the granules. However, in our previous work, analysing granules from uncontaminated soils by acid digestion and analysis with inductively coupled plasma – optical emission spectrometry (Lee et al., 2008) we did detect Zn in the granules so we know that Zn can be present. Additionally we have shown that granules can incorporate both Sr (Brinza et al., 2013) and Pb (Fraser et al., 2011) during the formation process and that in soils with elevated levels of Sr and Pb the concentrations of these elements in granules can be elevated as well. Therefore it seems possible that Zn could also accumulate in the granules, particularly given that for inorganic systems distribution coefficients for the partitioning of Zn into calcite suggest that calcite will contain more Zn than the solution from which it precipitates (Veizer, 1983) and that smithsonite (Zn carbonate) and calcite both have rhombohedral calcite-type crystal structures (Reeder, 1983). Mitigating against this is the fact that the ionic radius of Zn²⁺ at 0.74 Å is further from that of Ca²⁺ (1.00 Å) than is Sr²⁺ (1.18 Å) or Pb²⁺ (1.19 Å) (Shannon and Prewitt, 1969; Shannon, 1976). Thus involvement of Zn²⁺ ions in physiological pathways designed for Ca²⁺ and substitution of Zn into the calcite lattice may be problematic.

Nonetheless the aim of the investigation reported here was to determine whether earthworm secreted calcium carbonate granules would incorporate Zn during their production or post-production and whether sufficient Zn was associated with granules to significantly impact on Zn mobility in Zn-contaminated soils.

2. Methods

2.1. Earthworms and soils

Mature (clitellate) *L. terrestris* earthworms were purchased from The Recycle Works Ltd, Ribchester, PR3 3XJ, UK and kept for at least one week in a moist mixture of peat and Kettering Loam (Boughton Loam and Turf Management, Kettering, Northamptonshire, NN16 8UN, UK) (1:2 by volume) before being used in these experiments in order for non-viable earthworms to be identified and avoided for use in our experiments.

Three soils were used in this study: Hamble (HS), an arable soil collected from near Theale, Berkshire (UK Ordnance survey map coordinates SU-618-702); and two former mine site soils, Cwmystwyth, CWM, (SN-803-748), a former Pb–Zn mine and Devon Great Consols, DGC, (SX-426-733), a former Cu–As mine.

2.2. Soil characterization

The soils were oven-dried at 40 °C and sieved to <250 µm. Subsamples were dried to 105 °C overnight and all results are

expressed on an oven-dry basis. Water holding capacity (ISO11446:1993, ISO, 1993), pH (ISO 10390:2005, BSI, 2005), organic matter content (by loss on ignition, BS EN15935, BSI, 2009) and Ca and Zn concentration (by inductively coupled plasma – optical emission spectrometry (ICP-OES) after microwave digestion; BS ISO 12914, BSI 2010) were determined. An in house soil certified reference material (SS50) traceable to BCR-143R (Commission of the European Communities, Community Bureau of Reference) was also digested in triplicate, and gave a recovery of 103% for Ca and 95% for Zn. Repeated analysis of individual samples indicated a precision of 0.7% for Ca and 0.4% for Zn. Detection limits were 35 and 3.7 mg kg⁻¹ for Ca and Zn respectively.

2.3. Earthworm incubation experiments

L. terrestris earthworms were weighed and kept individually in a Memmert ICP 600 incubator set at 16 °C in sealed, perforated plastic bags, each containing 300 g of air-dried, <250 µm soil moistened to 50–70% of the soil water holding capacity. For the Hamble soil, incubations used either unamended Hamble soil or soil amended with ZnSO₄ solution to give target Zn concentrations of 250, 500 and 750 mg Zn kg⁻¹ oven dry soil (HS Zn 250, HS Zn 500 and HS Zn 750 respectively) in addition to the appropriate soil moisture content. Subsamples of the amended soils were digested using a microwave digester and analysed by ICP-OES as above to check their Zn concentration. 5 replicates were established per treatment.

During the experiment earthworm survival was monitored daily. The initial aim had been to leave earthworms in the experimental soils for 28 days. However, several unforeseen circumstances prevented this from happening and earthworms were left in the soil between 21 and 42 days. Earthworms were removed from the soil, weighed, depurated for 48 h (Arnold and Hodson, 2007), digested by aqua regia and analysed for Zn and Ca by ICP-OES. Mussel tissue (ERM-CE278, sample no. 1570) was used as a certified reference material for the earthworm digests with a recovery of 94% for Zn. Precision was 0.9 and 0.5% for Ca and Zn respectively. Detection limits were 70 and 7.4 mg kg⁻¹ for Ca and Zn respectively. Following removal of earthworms, soil solution was extracted overnight with 100 mm epoxy bodied MOM Rhizon samplers. pH was measured and then the solutions were analysed for Ca and Zn by ICP-OES. Precision was 0.28 and 1.6% for Ca and Zn respectively; detection limits were 1.0 and 1.4 µg L⁻¹ respectively.

Granules were extracted from the soil by sieving to 500 µm following the approach of Lambkin et al. (2011). Granules were weighed (for HS Zn 500 granules were pooled prior to weighing to ensure sufficient granules for analysis). A few granules from each treatment were reserved for either X-ray diffraction analysis or sectioning and analysis by electron microprobe analysis (EMPA; detailed in SI, Supporting information), X-ray fluorescence (XRF) and X-ray absorption spectroscopy (XAS) (see below). The remainder were digested in 5% HNO₃ and analysed for Ca and Zn by ICP-OES. Dolomite BCS No386 from the Bureau of Analysed Standards was digested as a certified reference material for Ca and gave recoveries of 98%. A synthetic limestone prepared by the China National Analysis Centre for Iron and Steel (NCS DC73345, GBW07719) was digested as a Certified reference material for Zn and gave recoveries of 104%. Precision was 1.0 and 1.4% for Ca and Zn respectively; detection limits were 0.8 and 1.1 mg kg⁻¹.

Two sets of thin sections were prepared. For use in the UK, demountable thin sections of the granules were produced by embedding the granules in EpoFIX (Struers) resin and grinding to a thickness of 50–70 µm, that is, 25–35 µm either side of the granule centre. The granule slices were then mounted on Chance Glass Ltd. glass slides and mechanically polished using a 1 µm particle size

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