Release of antimony from contaminated soil induced by redox changes

KERSTIN HOCKMANN[1]*, SUSAN TANDY[1], MARKUS LENZ[2] AND RAINER SCHULIN[1]

[1]Institute of Terrestrial Ecosystems, ETH Zurich, Switzerland, (*correspondence: kerstin.hockmann@env.ethz.ch)
[2]University of Applied Sciences and Arts Northwestern Switzerland (FHNW), Institute for Ecopreneurship, Muttenz, Switzerland

Due to its rapid growth in industial use, soil contamination by antimony (Sb) has become a matter of increasing environmental concern. A key factor of Sb mobility in soils is its redox state, which is closely related to soil aeration and thus to the soil water regime. Under aerobic conditions, thermodynamics predicts Sb to be stable as the pentavalent $Sb(OH)_6^-$, while under reducing conditions, the more toxic trivalent $Sb(OH)_3$ predominates [1]. Both species strongly differ in their affinity to iron (Fe) and manganese (Mn) (hydr)oxides, which, in turn, may be reductively dissolved under reducing conditions.

Here, we investigated how the interplay of reduction, sorption and dissolution processes affects Sb mobility in saturated soil subject to alternating redox conditions induced by autochthonous bacterial communities. Columns with Sb-contaminated shooting range soil (pH 7.8) were eluted with 15 mM sodium lactate solution for ~60 pore volumes (PV), interrupted by a 24 days stop-flow phase after 30 PV. With the transition to reducing conditions, Sb(V) and Mn concentrations showed a concomitant increase, providing evidence that sorbed Sb(V) was released by reductive dissolution of Mn minerals. As reducing conditions continued, Sb was immobilized again by reduction of Sb(V) to Sb(III), since the latter binds stronger to Fe (hydr)oxides at circumneutral pH. However, as these Fe phases started to dissolve with the onset of Fe-reducing conditions, the previously bound Sb(III) was released back into the solution. Characteriztion of the solid phased by laser ablation inductively coupled plasma-mass spectrometry (LA ICP-MS) underpinned the important role of Mn and Fe (hydr)oxides as Sb sorbents.

Our study shows for the first time that Sb can be mobilized under reducing conditions in soil also in form of Sb(V) with the dissolution of Mn and thus provides further reason for concern that release of Sb from insufficiently drained contaminated soil may pose a significant risk to the environment.

[1] Filella, Belzile & Chen (2002), *Earth-Sci. Rev.* 57, 125 - 176.

The role of earthworm-produced $CaCO_3$ in the terrestrial calcium and carbon cycles

MARK E. HODSON[1]*, EMMA A. A. VERSTEEGH[2] AND STUART BLACK[3]

[1]Environment Department, University of York, Heslington, York YO10 5DD, UK, (mark.hodson@york.ac.uk *presenting author)
[2]Department of Geography and Environmental Science, University of Reading, Reading RG6 6DW, UK, (e.a.versteegh@reading.ac.uk)
[3]Department of Archaeology, University of Reading, Reading RG6 6AB, UK, (s.black@reading.ac.uk)

Earthworm-produced calcium carbonate granules form a considerable proportion of soil carbonate and can be preserved for up to ~2 Ma. They may play an important role in the immobilisation of metals [1,2] and can be used to reconstruct temperatures of the past [3]. The physiological function of these carbonates and their role in the terrestrial calcium and carbon cycles remain poorly understood.

Experiments were performed with *Lumbricus terrestris*, one of the two main earthworm producers of $CaCO_3$ granules in many temperate soils. Earthworms were kept at different temperatures (3–20 °C) and, in a separate experiment, at different atmospheric CO_2 levels (440–3800 ppm). Granule production rate was correlated with temperature ($R^2 = 0.55$, $p < 0.0005$) increasing from 0.8 to 2.7 $mgCaCO_3$ $earthworm^{-1}$ day^{-1} between 3 and 20 °C. In contrast, granule production rate only showed a non-significant increasing trend under elevated $[CO_2]$.

In the variable temperature experiment the stable carbon isotopic composition ($\delta^{13}C$ values) was measured for soils, food (manure), air, earthworm tissues, and $CaCO_3$ granules. $\delta^{13}C$ values show that the majority of C in the granules comes from the food offered to the earthworms. As such, $\delta^{13}C$ values of granules originating from archaeological finds could be a useful proxy for vegetation type or agricultural practice (manuring) employed by past societies. In addition it suggests that earthworms are converting carbon from a more labile organic-hosted form to a less labile mineral-hosted form.

[1] Brinza *et al* (2013) *GCA*, 10.1016/j.gca.2013.03.011; [2] Fraser *et al* (2011) *GCA* **75**, 2544–2556, 10.1016/j.gca.2011.02.015; [3] Versteegh *et al* (submitted). [3] Versteegh et al (2013) 10.1016/j.gca.2013.06.020

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