

PORE WATER METALS IN CU, SN AND AS TAILINGS AT DEVON GREAT CONSOLS, SOUTH-WEST ENGLAND

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Three arrays of MacroRhizone pore water samplers were deployed at the abandoned mine complex of Devon Great Consols (DGC) to investigate water/substrate interactions that lead to potential contamination of the surrounding environment. Three contrasting tailings types are available at DGC – from Sn, As and Cu processing conducted at different stages in the history of the mine complex. The site is therefore ideal to study in detail the ongoing biogeochemical evolution of the spoils as they react with surface waters and the atmosphere. Although designed specifically for use in soils, these tension-assisted pore water samplers have proved effective in providing samples for analysis, from the dry summer of 2014. The results obtained from pore waters differ significantly from those of acid extraction methods used on the tailings, but metal concentrations are in the same range as those of distilled water extractions. Average pore water compositions vary significantly between the tailings types, with Cu tailings being richest in Cu, Al and Mn. Samples from the Sn tailings were richest in Sn but lowest in Mg, Co, Ni and Zn and those from the As tailings were highest in As, Na and Sr but lowest in Cu. These observations suggest that on-going chemistry in the weathering tailings piles influences pore water compositions. SEM-EDX X-ray maps of element distributions within the tailings suggest a widespread association of As with secondary iron oxides in all tailings types. The multi-element pattern of the Cu tailings is sub-parallel to that of samples from a drainage pipe, suggesting significant dilution with meteoric water. This work highlights the potential use of MacroRhizone samplers to collect pore water data on a seasonal basis, and to combine them with detailed mineralogical investigation of the degrading tailings materials in order to constrain the on-going geochemistry.

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INTRODUCTION

Environmental contamination by heavy metals is a global concern, occurring from both natural and anthropogenic impacts, with human activities often enhancing natural background levels (e.g. Camm *et al.*, 2004). Anthropogenic impacts include the legacy of mining and its associated activities (Larios *et al.*, 2012; Rieuwerts *et al.*, 2014), which has taken place over millennia. Today, mine wastes consist of large quantities of spoil and tailings, and the unwanted ore following various separation processes to retrieve the heavier metal-rich particles from the lighter waste fraction. While spoil is generally the broken uneconomical and unprocessed host-rock, tailings are the by-product from the final ore processing, which can include heated treatments, for example the use of calciners for the refining of marketable arsenic from the arsenic-rich ore, arsenopyrite (FeAsS). Today, in recognition of the large quantities of potentially contaminated wastes, the Mining Waste Directive 2006/12/EC (Mining) (DEFRA, 2011) aims to prevent or reduce the negative effects from mine waste on the environment and human health.

Due to the toxicity of heavy metals found in mine wastes, the effect on ecology has been well studied for plants (Chenery *et al.*, 2012; Jana *et al.*, 2012), livestock (Rodríguez-Estival *et al.*, 2012) and wild animals (Erry *et al.*, 1999; Erry *et al.*, 2000; Mateo *et al.*, 2003), as has the impact on soils (Drahota *et al.*, 2012), sediments (Larios *et al.*, 2012; Rieuwerts *et al.*, 2014), dust (Bruce *et al.*, 2013; Sánchez de la Campa *et al.*, 2011; Csavina *et al.*, 2012) and surface waters (Casiot *et al.*, 2005) at or around former mining areas. The metalloid As, and metals Cd and Pb,

are recognised as some of the most toxic metals in the environment (Williams *et al.*, 2009; Wragg *et al.*, 2011), and while background levels are found in uncontaminated soils, concentrations at former metalliferous mining areas typically far exceed natural levels. An investigation carried out by Palumbo-Roe and Klinck (2007) identified levels of As which were substantially higher (31,700 mgkg⁻¹) in mine tailings compared to background soils (105 mgkg⁻¹) at Devon Great Consols, a former metalliferous mine in South-West England (Figure 1). Environmental conditions can affect the mobility of non-residual metals (not part of the parent rock silicate matrix) in the environment, releasing metals previously locked up in complexes or adsorbed to particles from a soluble form. Fine particulate matter (<53 µm), can physically move from mining areas in the form of airborne dusts and via surface run off, where it can enter nearby streams and rivers, deposit on plants, contaminate soils, and pose a risk of inhalation/ingestion by animals, including humans. Additionally, metals in solution can move freely between environmental compartments, making them bio-available for plant uptake (Concas *et al.*, 2015), whereby contaminated plant tissue may subsequently move through trophic levels (bio-accumulation).

Characterisation of mined ore mineralogy (solid phase), and analysis of surface soils and waters is important to ascertain concentrations of metals in the environment. While many studies have been undertaken on surface waters, few have been conducted on the pore waters found within mine wastes. Pore water is influenced by particle size, bulk substrate density and