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The availability and mobility of arsenic and antimony in an acid sulfate soil pasture system

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HIGHLIGHTS

- We examine the effect of flooding acid soils on the mobility of As and Sb.
- Mobility and uptake of metalloids were relatively high in the floodplain soils examined.
- Pasture uptake of Sb is associated with non-crystalline Fe hydroxide content and flooding status of the soil.

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ABSTRACT

The Macleay floodplain on the north coast of New South Wales, Australia, has surface soil concentrations of up to 40 mg kg^{-1} arsenic (As) and antimony (Sb), due to historical mining practices in the upper catchment. The floodplain also contains areas of active and potential acid sulfate soils (ASS). Some of these areas are purposely re-flooded to halt oxidation processes, but the effect of this management on the metalloid mobility and phytoavailability of the metalloids present is unknown. This study investigated the changes to soil solution As and Sb, associations of metalloids with soil solid phases, and uptake into two common pasture species following 20 weeks of flooding in a controlled environment. The effect of an ASS subsoil was also investigated. The soil solution concentration and availability of the metalloids was in some instances higher in the floodplain soils than would generally be expected in soils with comparable contamination. There appeared to be few changes to soil solution concentrations or phase associations with flooding in this short term study, due to the high acid buffering and poise of the investigated soils. A strong relationship was found between the relative uptake of Sb into pastures and the oxalate extractable Fe in the soil, which was taken as a proxy for non-crystalline iron (Fe) hydroxides. This relationship was dependent on flooding and was absent for As. Further targeted investigations into metalloid speciation kinetics and the stability of soil solid phases with flooding management are recommended.

1. Introduction

The surface soils of the Macleay River floodplain on the north coast of New South Wales, Australia, are enriched with both arsenic (As) and antimony (Sb) (up to 40 mg kg^{-1} of both metalloids) (Tighe et al., 2005). This metalloid enrichment is due to the production and subsequent redistribution of sediment from the upper catchment related to historical mining practices (Ashley et al., 2007). Lower lying areas of the floodplain also include active and potential acid sulfate soils (AAS). Advocated management of these areas includes controlled re-flooding to limit oxidation processes and initiate the reduction of sulphuric acid (Burton et al., 2008). Previous sampling has indicated that pastures on the floodplain have higher than expected concentrations of Sb compared to local and regional background values (Tighe et al., 2005), but knowledge regarding the influence of different soil components on metalloid binding and mobility is lacking. Some of the aims of the re-flooding management of ASS in the Macleay floodplain are to increase pH and lower redox potential (Smith and Yerbury, 1996). It is well established that metalloid soil solution concentrations can increase with increases in pH in an acidic system, and toxicity can also increase as the soil system is reduced (Wilson et al., 2010). These changes in mobility and toxicity depend on the Sb associations with components of the soil.

Associations between soil solid phases and Sb have most often been assessed via sequential extraction procedures, in which a soil is treated with a series of chemical reagents. Each reagent is designed to remove the element in question from a particular operationally defined pool or component of the soil (Gleyzes et al., 2002; Savonina et al., 2012;

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Tighe and Lockwood, 2007; Wenzel et al., 2001). Using such operational definitions, Sb may be found in soluble or exchangeable forms, bound to crystalline or non-crystalline hydrated soil phases, complexed with organic matter, or in strongly recalcitrant, insoluble forms (Lintschinger et al., 1998; McLaren et al., 1998; Wilson et al., 2010).

Arsenic in soil solution can range from <1 μg L^{-1} in soils with low (<40 mg kg^{-1}) total As (Doyle and Otte, 1997) up to mg L^{-1} concentrations in soils with several hundred mg kg^{-1} As (Hamon et al., 2004). Soluble Sb is typically lower than As, but can reach mg L^{-1} levels in soils with high levels of anthropogenic Sb contamination (Okkenhaug et al., 2012). Several studies examine the relationships between dissolved or soil solution metalloid concentrations and metalloid concentrations associated with soil solid phases (Hamon et al., 2004; Johnson et al., 2005; Okkenhaug et al., 2012), but only a few studies have attempted to examine relationships between dissolved or soil solution metalloid concentrations and phytoavailability, especially for Sb (Wan et al., 2013a, 2013b). Most studies use artificial spiking or soils with very high metalloid concentrations (Huang et al., 2012; Okkenhaug et al., 2012; Otte et al., 1991), as determining relationships in moderately contaminated soils with complex redox and pH fluctuations can be challenging, especially under pseudo-representative field conditions (Wan et al., 2013b). Such investigations, however, will greatly improve our understanding of processes governing mobility and availability of metalloids, particularly Sb.

Antimony in soil has a strong affinity with non-crystalline Al and Fe hydroxides (Huang et al., 2012; Wilson et al., 2010). This affinity increases as soil pH decreases and the positive surface charge of the solid phases increases. The importance of the non-crystalline hydroxide phase for binding has been demonstrated in soils with high (100–500 mg kg^{-1}) and moderate (<30 mg kg^{-1}) total soil Sb concentrations (Lintschinger et al., 1998; Tighe and Lockwood, 2007). Changes in hydrolysis and charge of Sb species that accompany pH and redox fluxes probably influence this affinity, similar to As (Elkhatib et al., 1984; Pierce and Moore, 1982; Smith et al., 1998; Thanabalasingam and Pickering, 1990). Dissolution or precipitation of hydroxide phases in soils that experience large pH or redox fluxes, and particularly the formation of Fe plaques in the rhizosphere, have been related to the mobility and plant uptake of both As and Sb in contaminated rice growing systems (Chen et al., 2005; Huang et al., 2012; Liu et al., 2004b; Okkenhaug et al., 2012). Acid sulfate soils comprise one such system, and while the non-crystalline hydroxide phase has been noted to play a major role in As retention in acid sulfate soils (ASS) (Dudas, 1987), the importance of this phase for Sb retention, and the influence of redox and pH fluctuations in these soils has not been determined.

In this study, a glasshouse trial was undertaken to determine the effects of flooding on the behaviour of Sb in moderately contaminated field soils (up to 30 mg kg^{-1} Sb), with no additional spiking of metalloids. The effects on phytoavailability, solid phase associations and soil solution concentrations of Sb were investigated, with measurements and comparison made with As. Specific objectives of this experiment were to determine the importance of the 'non-crystalline hydroxide' and other operationally defined soil phases for Sb retention in these soils, and to determine if any of the measured variables (such as redox potential or pH) played a role in governing mobility and phytoavailability of Sb.

2. Materials and methods

2.1. Characteristics of the soils

Surface soils (low and moderate Sb concentrations) for the trial were sampled from two floodplain environments (Table 1). Subsoil high in sulfidic material was collected from the floodplain in one locality at a depth of 1 m. This subsoil had an acid generating history, a general oxidised state, and exhibited extensive visual signs of ASS mineralogy.

Bulked soils were air-dried, thoroughly mixed and mechanically broken into aggregates of 4 mm mean diameter. Triplicate sub-samples of each soil were ground to <2 mm and used for aqua regia digestible element determinations (Al, Fe, As, Sb and S) (Tighe et al., 2004), loss on ignition (LOI) (400 °C) organic matter, particle size distribution (pipette method, Day, 1965), pH and electrical conductivity (EC) in 1:5 water: soil suspensions, and powder X-ray diffraction analysis. As LOI is not an appropriate method for determining organic matter in soils with high amounts of non-crystalline hydroxide phases due to hydroxide decomposition at >500 °C (Schulte and Hopkins, 1996), a lower temperature method (400 °C) was used to counteract this. Electrical conductivity (μS cm^{-1}) and pH were measured using a TPS-81 combination meter (TPS Pty. Ltd. Brisbane, Australia). X-ray diffraction analysis was performed using an automated Philips diffractometer. The surface soils were extracted using the oxalate-based extraction detailed by Tighe and Lockwood (2007) to determine oxalate extractable Al and Fe. Analytical recoveries from spikes and standard reference materials (NIST SRM 2711) and precisions from duplicate analyses were

Table 1
Properties of experimental soils (n = 3).

	Soil L	Soil M	Sulfidic subsoil
$pH_{1:5\ water}$	3.49	2.78	2.57
$EC_{1:5\ water}$ (μS cm^{-1})	2890	2677	3297
LOI (400) (%)	33.6	26.2	7.43
% Sand	68.4	63.5	55.3
% Silt	13.2	16.3	24.0
% Clay	18.4	20.2	20.7
Texture (McDonald et al., 1990)	Loam	Loam	Loam
Australian Soil Classification (Isbell, 1996)	Sulfuric, redoxic hydrosol	Sulfuric/sulfidic, redoxic hydrosol	Sulfuric, redoxic hydrosol
Soil mineralogy — Major	Quartz, smectite	Quartz, albite, montmorillonite	Quartz, jarosite, natrojarosite
Soil mineralogy — Minor	Nontronite, aluminium sulfate hydroxide	Vermiculite	Albite, aluminium sulfate hydroxide
Clay minerals	Montmorillonite	Vermiculite, illite, montmorillonite	Montmorillonite
As (mg kg^{-1})	27.9	26.8	15.0
Sb (mg kg^{-1})	10.7	22.5	3.75
Fe (mg kg^{-1})	95,800	93,900	86,900
Fe_{ox} (%)[a]	37.8	62.2	–
Al (mg kg^{-1})	48,700	28,200	28,100
Al_{ox} (%)[a]	27.2	10.5	–
S (mg kg^{-1})	11,300	15,600	32,700

[a] Calculated as percent compared to total Fe and Al in the soil, respectively.