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Exchangeable and secondary mineral reactive pools of aluminium in coastal lowland acid sulfate soils

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HIGHLIGHTS

- Exchangeable Al concentrations are very high in coastal acid sulfate soils.
- Al–organic matter complexes form a significant fraction of exchangeable Al.
- Dissolved organic matter increases aqueous Al concentrations at pH values >5.
- 0.2 M $CuCl_2$ can be considered an alternative to 1 M KCl to measure exchangeable Al.

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ABSTRACT

The use of coastal floodplain sulfidic sediments for agricultural activities has resulted in the environmental degradation of many areas worldwide. The generation of acidity and transport of aluminium (Al) and other metals to adjacent aquatic systems are the main causes of adverse effects. Here, a five-step sequential extraction procedure (SEP) was applied to 30 coastal lowland acid sulfate soils (CLASS) from north-eastern New South Wales, Australia. This enabled quantification of the proportion of aluminium present in 'water-soluble', 'exchangeable', 'organically-complexed', 'reducible iron(III) (oxyhydr)oxide/hydroxysulfate-incorporated' and 'amorphous Al mineral' fractions. The first three extractions represented an average of 5% of '*aqua regia*' extractable Al and their cumulative concentrations were extremely high, reaching up to 4000 $mg \cdot kg^{-1}$. Comparison of Al concentrations in the final two extractions indicated that 'amorphous Al minerals' are quantitatively a much more important sink for the removal of aqueous Al derived from the acidic weathering of these soils than reducible Fe(III) minerals. Correlations were observed between soil pH, dissolved and total organic carbon (DOC and TOC) and Al concentrations in organic carbon-rich CLASS soil horizons. These results suggest that complexation of Al by dissolved organic matter significantly increases soluble Al concentrations at pH values >5.0. As such, present land management practices would benefit with redefinition of an 'optimal' soil from pH ≥5.5 to ~4.8 for the preservation of aquatic environments adjacent to organic-rich CLASS where Al is the sole or principle inorganic contaminant of concern. Furthermore, it was observed that currently-accepted standard procedures (i.e. 1 M KCl extraction) to measure exchangeable Al concentrations in these types of soils severely underestimate exchangeable Al and a more accurate representation may be obtained through the use of 0.2 M $CuCl_2$.

1. Introduction

Extensive areas of low-lying (<2 m of the mean sea level) floodplains around coastlines ranging from warm-climate (e.g. Australia) to cold-climate (e.g. Northern Europe) zones have been drained for agricultural use (Boman et al., 2010; Dent and Pons, 1995; Stone et al., 1998). This artificial drainage has induced the oxidation of pyrite present within these Holocene marine sulfidic sediments resulting in the generation of acid and the formation of so-called coastal lowland acid sulfate soils (CLASS). Consequently, acidified waters, aluminium, iron and trace metals are periodically released from these soils resulting in the severe degradation of surrounding aquatic environments (Dent and Pons, 1995; Fältmarsch et al., 2008; Macdonald et al., 2007).

The discharge of drainage waters containing high concentrations of aluminium occurs regularly in rivers worldwide affected by CLASS and other surrounding waterways (Jones et al., 2011; Kinsela and Melville, 2004; Macdonald et al., 2007; Roos and Åström, 2005; Rosicky et al., 2004a). For example, concentrations of Al in pore and surface waters of up to 50 and 40 $mg \cdot L^{-1}$, respectively, have been reported in the Tweed River catchment, north-eastern NSW, Australia (Jones et al., 2011). Aluminium concentrations up to 124 and 100 $mg \cdot L^{-1}$ have also

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been observed in the Vora stream catchment, western Finland (Åström et al., 2010). Compared to the extensive investigations that have been undertaken of the behaviour of trace metals and iron in these systems (Burton et al., 2006; Claff et al., 2011a; Claff et al., 2011b; Johnston et al., 2010a; Johnston et al., 2010b; Sundström et al., 2002), studies on Al mobility, partitioning and geochemistry have been surprisingly limited (Johnston et al., 2010a; Jones, 2010).

While most organisms are tolerant to high concentrations of iron (Fe) (10's to 100's of $mg \cdot L^{-1}$) before toxic effects are observed (Gerhardt, 1995; Maltby et al., 1987; Martin and Holdich, 1986), concentrations of Al as low as 0.1 $mg \cdot L^{-1}$ are toxic to aquatic life including rock oysters, fish, shrimp and algae (Gensemer and Playle, 1999; Sammut et al., 1995; Wilson and Hyne, 1997). Aluminium interferes with ion regulation and can result in fish gill damage and, at high concentrations, is the primary cause of fish kills and fish injuries in acid sulfate soil areas (Peuranen et al., 2003; White et al., 1996; Willet et al., 1992).

Most of the Al in soils is sequestered in crystalline alumino-silicate minerals relatively resistant to dissolution even in the extreme conditions prevalent in acid sulfate soils. However, a portion of the Al may still be expected to be more reactive and pose a threat to living organisms. While quantification of this more reactive Al is non-trivial, some insight into the relative proportions of Al present in various solid forms can be obtained through the use of multi-element (Claff et al., 2010; Claff et al., 2011b; Gleyzes et al., 2002; Johnston et al., 2010a; Tessier et al., 1979) or element-specific sequential extraction procedures (SEPs) (Garcia-Rodeja et al., 2004; Matús et al., 2006; Soon, 1993; Walna et al., 2005). Using such procedures, aluminium present in operationally-defined 'water-soluble', 'exchangeable', 'iron(III)-incorporated' and 'amorphous Al mineral' pools may be quantified, with Al present in these fractions substantially more mobile than that present in clay minerals (Gleyzes et al., 2002; Matús et al., 2006; Walna et al., 2005). As such, the main objective of this study was to examine the partitioning of Al within various reactive pools in a variety of CLASS materials with different geochemical characteristics, in order to quantitatively assess the potential reactivity and mobility of Al in these materials.

2. Material and methods

2.1. Study area description

Soil sampling was undertaken in north-eastern New South Wales, Australia. Three sampling sites were selected for this study; two sites in the Tweed valley catchment approximately 13 and 30 km upstream from the Tweed river coastal outlet into the Pacific Ocean (Ledday's creek and Black's drain respectively) and one site about 3.5 km inland in the Christie's creek catchment (Fig. 1). The sampling areas have been previously described in detail (Collins et al., 2010; Jones et al., 2011; Kinsela et al., 2011; Kinsela and Melville, 2004; Macdonald et al., 2007).

2.2. Sample collection

Soil samples from fifteen soil profiles were collected with a 10-cm diameter hand auger to a depth of 60 cm. The soil profiles were initially separated into two horizons (Table A1, Appendix A), namely the surficial organic soil A horizon (approximately 0–30 cm depth, sample code 's') and the lower actual acid sulfate soil B horizon (approximately 30–60 cm depth, sample code 'l') (Collins et al., 2010). Approximately 400 g of soil was collected for each soil horizon. Samples were double bagged and stored at 4 °C until processing and analysis in the laboratory.

The soils were obtained from operational sugar cane farms with five soil profiles sampled at each of the three sites: Black's drain (BD, samples 1 to 5), Ledday's creek (LC, samples 6 to 10) and Christie's creek (CC, samples 11 to 15). Average values ($n = 5$) of selected chemical properties of the soils from the three sites are provided in Table 1. Results for the individual soils are also provided in Appendix A as Table A1.

2.3. Sample analyses

All chemical reagents used for the experiments were of analytical grade and freshly prepared using high-purity ($>18.2\ M\Omega\ cm^{-1}$) water. All plastic and glassware were acid washed in 10% nitric acid for 24 h, rinsed with high-purity water and oven-dried at 40 °C.

Soil samples were analysed for pH, soil moisture content, total organic carbon, dissolved organic carbon (DOC) and metal concentrations. Dissolved organic carbon is described here as the fraction of organic carbon that is present in solution after filtration through 0.22 μm PVDF Durapore membrane filters (Millipore, Merck Pty, Ltd.) in order to be able to directly compare these concentrations to soluble metal concentrations.

Soil pH was determined in double deionised water (Milli-Q) in 1:5 soil:solution suspensions with a calibrated Orion 2 star pH probe. Measurements of pH were recorded after 24 h of equilibration (for solution pH measurements). Moisture content was determined on 20–50 g homogenised subsamples after heating at 105 °C for over 48 h. Total organic carbon content was determined using a LECO CHN TruSpec analyser on finely crushed ~1 g subsamples. Dissolved organic carbon concentrations were measured with a Shimadzu TOC-V_{CSH} total organic carbon analyser (fitted with an ASI-V automatic sample injector) in the filtered (0.22 μm) supernatant of 1:5 soil:solution suspensions. Elemental concentrations were determined by ICP-OES (Agilent Varian vista pro) from acidified solutions filtered through the same 0.22 μm PVDF durapore membrane filters used for DOC measurements. The cation exchange capacity of the soils was calculated from the concentration of the major cations (Ca, Mg, Na, Al, and Fe) in a 1 M KCl solution. Aluminium measurements by ICP-OES were performed using 3 different wavelengths (308.215, 309.271 and 396.152 nm) in order to detect potential interferences from other elements present in the complex sample matrices.

2.4. Sequential extraction procedure (SEP)

All extractions were performed on field-moist samples in 1:5 soil: solution suspensions (based on soil dry weight) that were vortex mixed and agitated for 24 h before being centrifuged (15 min at 3000 rpm), filtered (0.22 μm), acidified by dropwise addition of 70% HNO_3 and stored at 4 °C until analysis.

The SEP was designed to isolate environmentally significant fractions of Al. The Al fractions of interest were 'water soluble' (Al_{H_2O}), 'exchangeable' (Al_{KCl}), 'organically-complexed' (Al_{CuCl_2}), 'reducible Fe(III) oxyhydroxide/hydroxysulfate-incorporated' ($Al_{A.A}$), 'amorphous/poorly crystalline minerals' ($Al_{A.O}$), and 'residual' (Al_{Res}). Details of the experimental procedure for each extraction are given in Table 2. It should be noted that hot *aqua-regia* (Al_{Tot}) is not expected to fully dissolve recalcitrant minerals within the soils and is used here as a *pseudo*-total extraction to estimate the quantity of Al in these soils. Hence, residual and, therefore, total concentrations of Al are likely to be underestimated.

2.5. Data and statistical analyses

The results presented here are all expressed as the mean of triplicate samples unless otherwise specified. Aqueous Al concentrations and selected parameters were subjected to Pearson's correlation and multivariate regression analyses. Multiple linear regression analyses ($\alpha = 0.01$ unless otherwise specified) were used to assess the soil characteristics dominating Al partitioning and exchangeability. The data were log transformed ($\log_{10}x$) to meet the normality assumption when appropriate for both correlation and multiple regression tests.