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Isotopically exchangeable Al in coastal lowland acid sulfate soils

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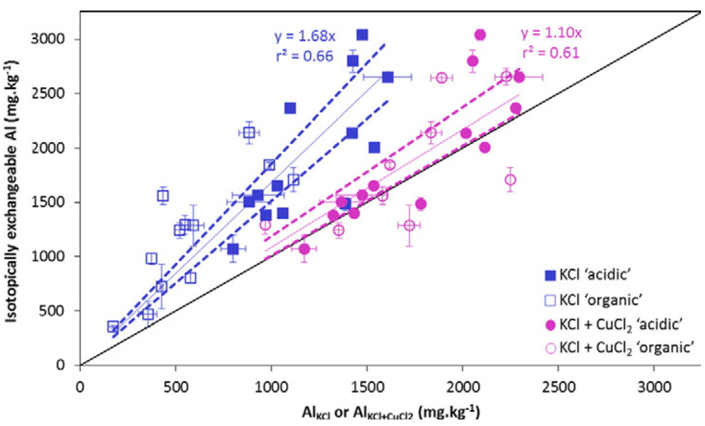
HIGHLIGHTS

- Isotopically exchangeable Al was compared to 1 M KCl or 0.2 M $CuCl_2$ extractable Al.
- 1 M KCl always underestimated isotopically exchangeable Al concentrations.
- 0.2 M $CuCl_2$ mobilised non-isotopically exchangeable Al
- 1 M KCl values require correction of ~ 1.7 to reflect exchangeable Al concentrations.

GRAPHICAL ABSTRACT



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ABSTRACT

Periodic discharges of high concentrations of aluminium (Al) causing fish kills and other adverse effects occur worldwide in waterways affected by coastal lowland acid sulfate soils (CLASS). The exchangeability — a metal's ability to readily transfer between the soil solid- and solution-phases — of Al in these soils is therefore of particular importance as it has implications for metal transport, plant availability and toxicity to living organisms. In the present study, the concentrations of isotopically exchangeable Al (E values) were measured in 27 CLASS and compared with common salt extractions (*i.e.* KCl and $CuCl_2$) used to estimate exchangeable soil pools of Al. E values of Al were high in the soils, ranging from 357 to 3040 $mg \cdot kg^{-1}$. Exchangeable concentrations estimated using 1 M KCl were consistently lower than measured E values, although a reasonable correlation was obtained between the two values ($E = 1.68 \times Al_{KCl}$, $r^2 = 0.66$, $n = 25$). The addition of a 0.2 M $CuCl_2$ extraction step improved the 1:1 agreement between extractable and isotopically exchangeable Al concentrations, but lead to significant mobilisation of non-isotopically exchangeable Al in surficial 'organic-rich' CLASS having E values < 1000 $mg \cdot kg^{-1}$. It was concluded that currently used (*i.e.* 1 M KCl) methodology severely underestimates exchangeable Al and total actual acidity values in CLASS and should be corrected by a factor similar to the one determined here.

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1. Introduction

High concentrations of labile and reactive aluminium (Al) in coastal lowland acid sulfate soils (CLASS) are responsible for the periodic discharge of large quantities of Al (Macdonald et al., 2007; Yvanes-Giuliani et al., 2014) into adjacent aquatic systems resulting in adverse toxic effects to living organisms. Some of the more labile forms of Al in CLASS, such as the water soluble and exchangeable fractions, are of particular interest as they are the most easily mobilised into drains following rainfall events (Yvanes-Giuliani et al., 2014).

Measuring 'water soluble' Al is relatively straightforward, however, quantifying the exchangeable fraction of Al is more challenging. While there is no consensus on how to measure the most available fraction of contaminants in soils, various chemical extractions have been used to try and isolate the 'exchangeable' pool of aluminium. The standard extraction solution for determining exchangeable acid-generating cations, principally Al, in CLASS is the use of 1 M KCl (Ahern et al., 2004). Chemical extractions have also been regularly used to chemically parameterise CLASS (Claff et al., 2011; Johnston et al., 2010; Yvanes-Giuliani et al., 2014); however, data on the lability of Al in CLASS is quasi non-existent (Johnston et al., 2010; Yvanes-Giuliani et al., 2014). Although chemical extractions have some limitations, they are the most convenient and therefore the most widely used tool to estimate the potentially bioavailable and phytoavailable fraction of metals in soils.

Isotope exchange can be used to determine the concentration of (isotopically) exchangeable elements in soils and, because it does not disturb the geochemical equilibrium, can be considered a reference method to quantify exchangeable concentrations of a range of elements in CLASS and other soil types (Hamon et al., 2002). Possibly due to limited supply, financial constraints and the requirement of specialist counting techniques (*e.g.* Accelerator Mass Spectrometry (AMS)), isotopic tracer studies of Al are rare (Kleja et al., 2005; Kotzé et al., 1984) and comparable isotope exchange data on Al in CLASS is currently lacking. Exchangeable concentrations estimated from KCl extraction (the most commonly used method for CLASS) have never been compared to the concentrations of Al that are isotopically exchangeable at prevailing geochemical conditions. A significant lack of understanding regarding the nature of the Al brought into solution from chemical extractions therefore exists. Furthermore, it is unclear if the concentrations of exchangeable Al determined from use of chemical extractants have any resemblance to actual exchangeable concentrations in the soils. As such, the main objective of this study was to compare the use of conventional extraction methods for measurement of exchangeable Al with the use of ^{26}Al isotope exchange.

2. Materials and methods

2.1. Study area and sample collection

Twenty-seven samples were collected on sugar cane farms across three catchments in north eastern New South Wales, Australia (Appendix A, Fig. A1): Black's drain and Ledday's creek on the Tweed valley floodplain (samples in the B and L series) and Christie's creek, a coastal catchment ~20 km south of the Tweed valley (samples in the C series). A CLASS profile in these farms is typically composed of an organic rich surface soil horizon (0 to ~30 cm), an oxidised and acidified (actual) acid sulfate soil horizon (~30 to ~60 cm), a transition zone (60 to ~120 cm) and a potential acid sulfate soil horizon (−120 cm and below) (Collins et al., 2010; Jones et al., 2011; Kinsela et al., 2011; Kinsela and Melville, 2004; Macdonald et al., 2007). Multiple distinct samples were collected from surface (14) and actual acid sulfate soil (13) layers at 15 different sites in order to provide a range of soil variability. In some cases, both soil layers were collected from a site whereas at other times only a surface or actual acid sulfate soil layer was collected.

2.2. Sample analyses

General chemical analysis methods, sample preparation procedures and methods for determination of pH, cation exchange capacity (CEC, 1 M KCl), soil total organic carbon content (TOC, LECO CHN TruSpec analyser) and 'pseudo-total' Al concentrations (Al_{tot}, *aqua* '*regia*') were identical to those described by Yvanes-Giuliani et al. (2014). A summary of selected soil chemical characteristics of the soils are presented in Appendix A, Table A1.

2.3. Theoretical background to isotope exchange

Isotope exchange techniques can be used to determine the labile fraction (*i.e.* the solid phase exchangeable fraction in dynamic equilibrium with the solution phase over a defined period of time) of elements in soils. A tracer isotope is added to a soil suspension and allowed to equilibrate with the soil solution for a defined amount of time during which the isotope redistributes itself between the solid and solution phases in an identical fashion to the corresponding 'native' exchangeable element. The isotopically exchangeable concentration (E) is most often defined as (Hamon et al., 2002):

$$E\left(\mathrm{mg\cdot kg^{-1}}\right) = \mathrm{K_d} \times \mathrm{c_s} + \mathrm{c_s} \times \frac{\mathrm{v}}{\mathrm{m}} \tag{1}$$

where K_d is the partitioning coefficient of the isotope tracer in $L\cdot kg^{-1}$ soil, c_s is the concentration of the stable element of interest in $mg\cdot L^{-1}$, and v/m is the solution-to-solid ratio of the suspension ($L\cdot kg^{-1}$) in which isotope exchange is conducted. K_d is usually calculated as:

$$\mathrm{K_d}\left(\mathrm{L\cdot kg^{-1}}\right) = \frac{\mathrm{R-r}}{\mathrm{r}} \times \frac{\mathrm{v}}{\mathrm{m}} \tag{2}$$

where R is the quantity of the isotope tracer added to the sample and r is the quantity of tracer remaining in solution after equilibration.

In the present study, however, because we measure a ratio — ^{26}Al:^{27}Al — rather than directly measuring the concentration of ^{26}Al remaining in solution, Eq. (2) may be modified as follows:

$$\mathrm{K_d}\left(\mathrm{L\cdot kg^{-1}}\right) = \frac{\left({}^{26}\mathrm{Al}/{}_{27}\mathrm{Al}\right) - \left({}^{26}\mathrm{Al}/{}_{27}\mathrm{Al}^{\mathrm{AMS}}\right)}{\left({}^{26}\mathrm{Al}/{}_{27}\mathrm{Al}^{\mathrm{AMS}}\right)} \times \frac{\mathrm{v}}{\mathrm{m}} \tag{3}$$

where $\frac{^{26}\mathrm{Al}^*}{^{27}\mathrm{Al}}$ is the ratio calculated based on the quantity of tracer added to the sample and $\frac{^{26}\mathrm{Al}^{\mathrm{AMS}}}{^{27}\mathrm{Al}}$ is the ratio measured by AMS after equilibration. In Eq. (3), R (*i.e.* $^{26}\mathrm{Al}^*$) and r (*i.e.* $^{26}\mathrm{Al}^{\mathrm{AMS}}$) are just expressed relative to the concentration of carrier (^{27}Al) added for AMS measurement.

2.4. ^{26}Al spiking, equilibration and extractions

Isotope exchange experiments were conducted on all 27 soil samples with 12 soils analysed in duplicate in order to provide an indication of sample variability.

For the isotope exchange experiments, approximately 5 g (dry weight equivalent) of field moist soil was suspended in >18.2 $M\Omega\cdot cm^{-1}$ water (to obtain a soil:solution of 1:5) and allowed to pre-equilibrate on an orbital shaker for 24 h. The ^{26}Al used for these experiments was purchased from Los Alamos National Laboratory, NM, USA. An appropriate amount of ^{26}Al from a diluted spike solution (5.74×10^{-12}–1.78×10^{-11} mol ^{26}Al and 2.02×10^{-10}–6.26×10^{-10} mol of carrier ^{27}Al, Appendix A, Table A2) was added to each soil suspension and allowed to equilibrate for a further 24 h, the typical duration used when CLASS are extracted with 1 M KCl (Ahern et al., 2004). After centrifugation (15 min at 3000 rpm) and filtration (0.22 μm PVDF durapore membrane