



# A revised method for determining existing acidity in re-flooded acid sulfate soils



Scott G. Johnston<sup>a,\*</sup>, Edward D. Burton<sup>a</sup>, Roslyn Hagan<sup>a</sup>, Thor Aaso<sup>b</sup>, Gerard Tuckerman<sup>c</sup>

<sup>a</sup> Southern Cross GeoScience, Southern Cross University, Lismore, NSW 2480, Australia

<sup>b</sup> Port Macquarie-Hastings Council, Port Macquarie, NSW 2444, Australia

<sup>c</sup> Great Lakes Council, Forster, NSW 2428, Australia

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## ABSTRACT

Titratable actual acidity (TAA) is a technique commonly used to estimate the existing pool of exchangeable  $H^+$  in acid sulfate soils (ASS). A widely adopted version of the TAA method involves titrating a 1M KCl suspension of oven-dry soil (1:40) with NaOH to a known pH endpoint. However, when ASS are subject to long term re-flooding during wetland remediation, former sulfuric horizons can develop substantial quantities of porewater  $Fe^{2+}$ , non-sulfidic solid-phase Fe(II) and a variety of reduced inorganic sulfur (RIS) species (e.g. pyrite, mackinawite, greigite and elemental sulfur). For these sediments, an oven-drying approach may induce oxidation of the abundant Fe(II) and/or reactive RIS species, thereby generating  $H^+$  and leading to overestimation of existing in situ exchangeable  $H^+$ . In this study, we compare TAA via the standard approach (1M KCl; 1:40; oven-dry soil, 4 hr extract; TAA<sub>D</sub>) with an identical  $O_2$ -free extraction approach using wet-sediment (TAA<sub>W</sub>). We apply both methods to former sulfuric horizon sediments from freshwater re-flooded ASS wetlands. There are significant ( $\alpha = 0.01$ ) differences (up to 12 $\times$ ) between TAA measured by the two methods, with the oven-dried standard approach overestimating TAA relative to the wet,  $O_2$ -free approach in 85% of cases. Despite the fact that all AVS-S and some S(0) was oxidised during the oven-drying process, the increases in TAA (TAA<sub>D</sub>–TAA<sub>W</sub>) show very weak correlation(s) with corresponding losses in RIS species or increases in water soluble sulfate and KCl extractable sulfate. However, oven-drying caused substantial loss of 1M KCl exchangeable Fe(II) and 1 M HCl-extractable Fe(II) and led to large increases in 1 M HCl-extractable Fe(III). These changes in Fe fractions displayed strong positive linear correlation ( $\alpha = 0.01$ ) with increases in TAA. Although this is not evidence of causality, it suggests that oxidation of Fe(II) species are playing an important role in the development of additional exchangeable  $H^+$  and may be largely responsible for the contrasting TAA derived by the two methods. The differences in TAA between the two methods are greatest in organic-rich surface sediments and are significantly positively correlated with total organic carbon content. These findings have major implications for accurately assessing TAA in re-flooded ASS wetlands.

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## 1. Introduction

Titratable actual acidity (TAA) is a fundamental and widely used standard technique for estimating the pool of exchangeable  $H^+$  in acid sulfate soils (ASS) (Andriessse, 1993; Lin et al., 2000; McElnea et al., 2002a; Vithana et al., 2013). TAA is part of a suite of standardised assessment procedures required by various State Government agencies in Australia during developments that involve disturbance of ASS (Ahern et al., 1998; McElnea and Ahern, 2004). It is intended to provide an estimate of existing soluble and exchangeable acidity and thus provide an indication of the magnitude of the actual (ie. currently manifest) acidity

hazard posed by the soils and, if appropriate, to provide part of the basis for calculating neutralisation requirements.

The current widely adopted TAA technique is based on a titrating a 1M KCl soil suspension (1:40) with a weak base (0.1 M NaOH) to a known pH end-point (6.5) (McElnea et al., 2002a). The origins of the technique as it is currently applied to ASS can be traced to a field method initially developed by Konsten et al. (1988), that was subsequently refined by Dent and Bowman (1996), Lin et al. (2000) and finally by McElnea et al. (2002a). The current method, that has been widely adopted by various Government agencies and industry (ie. McElnea and Ahern, 2004), is based on the approach outlined by McElnea et al. (2002a). The technique employs rapid drying of soil at 85 °C in a fan-forced oven and relies on the assumption that this will not generate additional exchangeable  $H^+$  via oxidation of reduced inorganic sulfur (RIS) or iron species.

\* Corresponding author.

E-mail address: [scott.johnston@scu.edu.au](mailto:scott.johnston@scu.edu.au) (S.G. Johnston).

Many years of application of rapid oven-drying of ASS materials demonstrate that this assumption appears to be generally valid for most oxic, sulfuric horizons and also for many typical sulfidic materials (e.g. Burton et al., 2008; McElnea et al., 2002b; Sullivan et al., 2000; Ward et al., 2002).

When ASS are subject to long term re-flooding as part of wetland remediation, former sulfuric horizons are subject to redox conditions that promote iron and sulfate reduction (Burton et al., 2011a; Johnston et al., 2014, 2009a; 2009b). This can lead to the development of high concentrations of porewater and solid-phase Fe(II) and a variety of nano-particulate RIS species including pyrite, mackinawite, greigite and elemental sulfur (Burton et al., 2011a, 2011b; Johnston et al., 2014, 2011; Keene et al., 2011). Re-flooding of ASS is often accompanied by large increases in the field pH of soils (Johnston et al., 2014, 2009b). When such re-flooded ASS sediments are subject to rapid oven-drying, there is potential for oxidation of Fe(II) and reactive RIS species. Oxidation may lead to the generation of H<sup>+</sup> and thereby introduce artefacts that contribute to an overestimate of existing exchangeable H<sup>+</sup>. However, the potential for such artefacts in this context has not been systematically investigated. This is important to resolve, especially given the standard TAA approach is used as one of the tools to assess the efficacy of re-flooding as a wetland remediation approach (Johnston et al., 2009b).

In this study, we compare TAA via the standard approach using oven-dried soil (1M KCl; 1:40 soil–water suspension; 4 h extract; McElnea et al., 2002a; McElnea and Ahern, 2004) with an identical approach using wet-sediment (correctly weighed to obtain the same dry mass equivalent) and employing strict O<sub>2</sub>-free extraction procedures. We apply both approaches to a series of soils collected from the former sulfuric horizons of re-flooded freshwater ASS wetlands. We aim to compare the approaches in terms of TAA and also compare differences in key RIS species and Fe fractions that may help explain any differences in TAA results. The underlying intention is to identify the most suitable approach for assessing TAA in re-flooded ASS.

## 2. Methods

### 2.1. Soil sample collection

Soils were collected from two freshwater re-flooded ASS wetlands in which iron and sulfate reduction have led to the contemporary (within the last 10 years) formation of substantial Fe(II) and RIS species in former sulfuric horizons (Johnston et al., 2014). Soil collection procedures are detailed in Johnston et al. (2014). Soil samples were selected to span a range of concentrations in organic carbon, Fe(II) and RIS species. Samples were sealed in air-tight polyethylene bags, completely filled with soil and placed in a portable freezer at –16 °C immediately following collection. Samples were kept frozen until analysis to minimise sample oxidation.

### 2.2. General methods

All laboratory glass-ware was soaked in 5% (*v/v*) HNO<sub>3</sub> for at least 24 h, followed by repeated rinsing with deionized water. All chemicals were analytical reagent grade. All reagent solutions were prepared with deionized water (MilliQ).

### 2.3. Solid-phase methods

Frozen soil samples were defrosted under oxygen-free conditions in an anaerobic chamber (1–5% H<sub>2</sub> in N<sub>2</sub>), containing an O<sub>2</sub>-consuming Pd catalyst. Defrosted samples were homogenised with a plastic spatula prior to sub-sampling. Soil moisture content was determined by mass loss after oven drying a 15–20 g

sub-sample at 105 °C (Rayment and Higginson, 1992). The moisture content was used to calculate the mass of wet-sediment required to obtain the dry-weight mass equivalent during wet-sediment, O<sub>2</sub>-free extractions. All samples were analysed in triplicate. Analyses were performed on both wet and oven-dried sediment samples according to extraction procedures that are summarised in Table 1.

#### 2.3.1. Oven-dried sediments

Soils were dried in a fan-forced convection oven at 85 °C to a constant weight. The oven dried soils were sieved (2 mm) and milled using a ceramic milling bowl and stored at room temperature in sealed polypropylene containers. Total actual acidity (TAA) was determined using the technique outlined by McElnea et al. (2002a,b). In brief, a 1M KCl soil suspension (1:40) was shaken (orbital shaker, 125 rpm) for 4 h and titrated to a known pH (6.5) endpoint with 0.1 M NaOH. An additional 1M KCl extraction (1:40) soil solution was also used to quantify KCl-exchangeable Fe(II), Total Fe and SO<sub>4</sub><sup>2-</sup>. Samples were shaken for 4 h, centrifuged at 4000 rpm for 10 min and the extract filtered (0.45 μm). Aliquots of filtered extract were analysed for Fe(II) and Total Fe [Fe<sub>Tot</sub>] by spectrophotometry using the 1,10-phenanthroline method, with the addition of hydroxylammonium chloride for Fe<sub>Tot</sub> (APHA, 2005). Sulfate was determined via ion chromatography (Metrosep A Supp 4-250 column, an RP2 guard column and eluent containing 2 mM NaHCO<sub>3</sub>, 2.4 mM Na<sub>2</sub>CO<sub>3</sub> and 5% acetone, in conjunction with a Metrohm MSM module for background suppression). Sulfate was also extracted from a 1:5 soil:water extract (1 h) as per Rayment and Higginson (1992), with filtered (0.45 μm) aliquots processed as above. Total organic C (TOC) and Total S were determined via a LECO CNS-2000.

Reactive, poorly crystalline Fe species were quantified using the extraction procedure of Claff et al. (2010), using cold 1 M HCl at a 1:40 soil:solution ratio and an extraction time of 4 h. Aliquots of 0.45 μm filtered extract were analysed by the 1,10-phenanthroline method to determine Fe(II) and Total Fe [Fe<sub>Tot</sub>] with the addition of hydroxylammonium chloride for Fe<sub>Tot</sub> (APHA, 2005). 1 M HCl extractable Fe(III) was determined via difference.

Reduced inorganic sulphur (RIS) species were quantified by a sequential extraction procedure, as outlined by Burton et al. (2009). For acid volatile sulfur (AVS) ~2 g of sediment was extracted for 16 h with 6 M HCl/0.1 M ascorbic acid. The evolved H<sub>2</sub>S was trapped in 5 mL 3% Zn acetate in 2 M NaOH and measured via iodometric titration. Samples were rinsed once with 50 mL Milli-Q water before extracting for elemental-S [S(0)]. S(0) was extracted by shaking the sediment with 20 mL methanol for 16 h, followed by quantification by high performance liquid chromatography (HPLC) with a Dionex UltiMate 3000 system (mobile phase = 95% methanol; column = reverse-phase C18; flow rate = 2 mL/min; column temp = 40 °C; UV detection at 254 nm). Residual S(0) was removed from the sediment by rinsing 3 times with 40 mL methanol. Pyrite-S in the centrifuged residue was quantified as Cr(II) – reducible-S (S<sub>CR</sub>), using the method described by Burton et al. (2008).

**Table 1**  
Summary of extraction procedures.

Extraction procedure	References
Titrateable actual acidity (TAA), 1M KCl, 1:40, extracted for 4 h	McElnea et al. (2002a,b)
1M KCl extractable Fe(II), total Fe, SO <sub>4</sub> <sup>2-</sup> , 1:40, extracted for 4 h	(Extract as per above)
Water Soluble SO <sub>4</sub> <sup>2-</sup> , 1:5, extracted for 1 h	Rayment and Higginson (1992)
1 M HCl extractable Fe(II), total Fe, 1:40, extracted for 4 h	Claff et al. (2010), Poulton and Canfield (2005)
Reduced inorganic sulfur (RIS) suite	Burton et al. (2009), Burton et al. (2008)

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