

Quantifying retained acidity in acid sulfate soil materials: An evaluation of routine methods

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Abstract

Retained Acidity is an important aspect of acid sulfate soil (ASS) but techniques for the quantification of this property have not yet been systematically assessed. In this study, the utility of routine techniques for quantifying the Retained Acidity fraction will be examined. The relatively insoluble minerals such as jarosite and schwertmannite are major contributors to Retained Acidity in ASS. Known quantities of synthetic and natural jarosites and schwertmannite will be added to two non-acid sulfate soil samples plus to one quartz sand sample. By using S_{NAS} in the chromium suite and S_{RAS} in the SPOCAS suite (Ahern *et al.* 2004), the Retained Acidity fraction of the spiked samples will be assessed. The method introduced by Li *et al.* (2007) and the acidified ammonium oxalate method (Regenspurg *et al.* 2004) will be undertaken to recover the added jarosite and schwertmannite, respectively. The mineralogy of the samples will be characterized by X-ray diffraction (XRD). In the second part of this study, the potential interference from other common sulfate minerals, $CaSO_4 \cdot 2H_2O$ (gypsum) and $BaSO_4$ (barite) will be examined.

Key words

Sulfidic soils, Schwertmannite, Jarosite, Soil tests

Introduction

Retained Acidity is one of the main components of the Existing Acidity in the Acid Base Account (ABA) method of Ahern *et al.* (2004) for ASS. The Retained acidity fraction is generally associated with the insoluble sulfate salts such as schwertmannite, jarosite, natrojarosite and other iron, aluminium hydroxysulfates. These secondary minerals naturally exist in highly acidic ($pH < 4$) ASS materials, and continue to release acidity as they weather by hydrolysis (Ahern *et al.* 2004; Burton *et al.* 2007; Wang *et al.* 2006). The hydrolysis of secondary minerals is generally a slow process and the acidity generated is considered to be in a less available form than readily soluble or exchangeable sources of acidity (Ahern *et al.* 2004; Fitzpatrick *et al.* 2009). In practice, both the Retained Acidity and Actual Acidity fractions are operationally defined fractions, dependent on the specific analytical approach used for their quantification.

Often the Actual Acidity fraction in the Existing Acidity represents the dominant and most available pool of acidity in acidified and oxidised ASS and hence has been studied extensively. Nevertheless, in oxidised soils and soils with little or no sulfide, the Retained Acidity fraction can be a significant source of acidity (McElnea *et al.* 2004). The kinetics and processes of acidity generation by the Retained Acidity fraction is not as well known as that of pyrite oxidation, yet the data to hand indicates that this acidity fraction could add substantial amounts of acidity to the soil in the long run. For this reason the risk of acidity production by the Retained Acidity store in soils must be taken into account to manage the acidification risk posed by ASS materials. Consequently, an accurate quantification of the major insoluble minerals such as schwertmannite, jarosite etc. is a particularly important factor which should be considered when developing management strategies. Despite this fact, there has not been any rigorous research published on the reliability of the currently available methods to date. The present study aims to conduct a systematic analysis of each method in the recovery of the two major minerals (jarosite and schwertmannite) in the retained acidity fraction.

Insoluble sulfate minerals such as gypsum and barite (which do not produce the acidity) could affect the estimation of sulfur associated with acidifying minerals when measured after the peroxide digestion (Sullivan *et al.* 1999 and reference therein). Thus, the second part of this study will focus on the potential interferences caused by gypsum and barite on the currently available methods for assessing Retained Acidity.

Assessment Methods

Assessment methods will consist of the following:

- i. S_{NAS} – This is the difference of $S_{HCl(4M)} - S_{KCl}$
- ii. S_{RAS} . The sulfur measured by 4M HCl extraction on the soil residue remaining after peroxide digestion and TPA titration of the SPOCAS method.
- iii. Schwertmannite is generally analysed by using the acidified ammonium oxalate method (Carlson and Schwertmann 1981) which is described in a later section of this paper.
- iv. Jarosite will be recovered by the method described by Li *et al.* (2007).
- v. XRD – to characterize the synthesised solid.

Some of the possible problems and the interferences that could affect the final result of the analyses of above mentioned methods are described below.

S_{NAS} (Net acid soluble sulfur)

S_{NAS} gives an overall estimation of the retained acid soluble sulfur fraction of the sample yet, it does not account for the individual contribution of the different insoluble sulfate minerals present in the sample. The acidity that could be generated from this fraction is estimated based on the following assumption.

1 mole of jarosite gives 3 moles of H^+

Nonetheless, as the S_{NAS} is not only derived from jarosite but could also be derived from other relatively insoluble sulfates such as schwertmannite, iron and aluminium hydroxyl sulfates the validity of the above assumption is questionable. Clearly, prior knowledge of the mineralogy of the ASS materials may be essential to the development of the appropriate stoichiometry for acidity estimations using this method.

S_{RAS} (Residual acid soluble sulfur)

The S_{RAS} , is measured by extracting the washed soil residue after the peroxide digestion with 4M HCl (Ahern *et al.* 2004). Nevertheless, Ward *et al.* (2002) found that the peroxide digestion could provide necessary conditions for the formation of jarosite including low pH (2-4), higher concentrations of sulfate and iron (which originate from pyrite oxidation) and K^+ . Hence, the estimated sulfur concentration at the end of this procedure may be an overestimation or underestimation of the exact amount present in the sample.

Schwertmannite recovery method

Experiments have shown that the oxalate dissolution in the dark dissolves schwertmannite and ferrihydrite completely leaving goethite and jarosite as a solid precipitate. However, some researchers have found that, this method doesn't completely dissolve schwertmannite in sediments (Gagliano 2004).

Jarosite recovery method

One of the limitations of this method is to keep the temperature below 550°C (Li *et al.* 2007). According to Li *et al.* (2007), sulfate in jarosite could release as SO_3 when the temperature is above 550°C. Though the overall temperature in the oven is set to 550°C, there is a possibility of generating greater temperatures in microenvironments of jarosite due to the ignition of organic matter in the sample (Henderson *et al.* 2007). Thus, the final estimated quantity of jarosite may not represent the actual concentration as some of the jarositic sulfur could have been removed as SO_3 during pyrolysis.

Experimental methods and procedure

Two non-acid sulfate soil sample sets were collected from 2 sites in north-eastern NSW (Tukean Swamp on the Richmond River catchment and Shark Creek on the Clarence River catchment). Within 24hr of sampling, two soil samples were put in the oven at 80° C for two weeks until a constant weight was reached. Clean quartz sand samples will be used for comparison.

Synthetic/natural jarosites and schwertmannite ranging in proportions up to 20 %, will be added to two non-

acid sulfate soil samples and the quartz sand sample. The homogenised samples will then be analysed as soon as possible (1hr) using the methods described earlier. A similar procedure will be undertaken to assess the potential interferences of gypsum and barite. Each sample will be analysed in triplicate.

Recovery and synthesis methods

Retained Acidity recovery methods

S_{NAS} – Chromium Suite (Ahern *et al.* 2004)

S_{RAS} – SPOCAS Suite (Ahern *et al.* 2004)

*Jarosite recovery method (Li *et al.* 2007)*

Jarosite in a sample can be extracted by three sequential steps which are outlined below.

- i. Argon purged water extraction- This step takes ~ 3 minutes, and removes the soluble sulfate salts such as gypsum, epsomite and melanterite. The extract is then analysed for Fe, Mg, Ca etc. using ICP.
- ii. Pyrolysis- The residue remaining after the extraction in the first step, is then roasted at 550°C for 1hr. During this step all reactive sulfides are removed.
- iii. 4M HCl extraction- The residue is then treated with 4M HCl for 30 minutes, and the extract is analysed for insoluble sulfate salts such as jarosite using ICP.

Schwertmannite recovery method (Carlson and Schwertmann 1981)

Schwertmannite recovery in the soil samples will be assessed using the method originally introduced by Carlson and Schwertmann (1981). In this method, schwertmannite in the sample (~0.05g) is dissolved completely by extracting with 0.05L acidified ammonium oxalate solution (pH 3) in the dark for 15 minutes. This extraction separates the schwertmannite from goethite and jarosite since schwertmannite is soluble in acid ammonium oxalate with respect to those two minerals. The stoichiometric composition of the dissolved schwertmannite will be then determined by assessing the Fe and S concentrations in the extracts using flame AAS and ICP-AES respectively. The Fe:S ratio in the extract can be further used to verify the complete dissolution of schwertmannite which is typically in the range of 5-8 (Regensberg *et al.* 2004 and reference therein)

*Synthesis of schwertmannite (Regenspurg *et al.* 2004)*

Synthesis of schwertmannite will be carried out according to the method of Pentinghaus (Regenspurg *et al.* 2004).

Synthesis of jarosite (Baron and Palmer 1996).

Jarosite will be synthesized according to the method of Baron and Palmer (1996).

Conclusion

Methods for the assessment of Retained Acidity, despite being a critical component of the acidity risk assessment of acid sulfate soil materials, have not yet been critically assessed in a systematic fashion for acid sulfate soil materials and the common acidity containing minerals that do not readily dissolve (such as jarosite and schwertmannite). This issue is well known to scientists and land managers who work with acid sulfate soils. This paper firstly examines some of the potential limitations of the existing methods for estimating retained acidity and secondly outlines an approach that will be used to systematically assess the efficacy of existing methods for assessing Retained Acidity.

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