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The classification of acid sulfate soil materials: further modifications

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Introduction

Recently, the Acid Sulfate Soil Working Group of the International Union of Soil Sciences agreed in principle in August 2008 to adopt changes to the classification of acid sulfate soil materials and horizons as proposed by Fanning and Rabenhorst (2008) and Sullivan *et al*. (2008a) at the 6th International Acid Sulfate Soil and Acid Rock Drainage Conference in September 2008 in Guangzhou, China. These proposed changes to the classification of acid sulfate soil materials have also been recently (October 2008) tested and adopted by the Scientific Reference Panel of the Murray-Darling Basin Acid Sulfate Soil Risk Assessment Group for use in the rapid and detailed assessment of acid sulfate soil materials in the Murray-Darling Basin.

The technical report of Sullivan *et al.* (2009a) described and defined some of these improvements, the need for such changes, and provided an approximate correlation of the modified classification system (arising as a result of these changes) with other acid sulfate soil classification systems. This report contains further modifications to clarify the definitions of Sullivan *et al.* (2009a).

Background

General comments on classification

Classification has been defined as *the ordering or arrangement of objects into groups or sets on the basis of their relationships* (Sokal, 1974). As science uncovers and describes new relationships, existing scientific classification schemes periodically require change to accommodate these new relationships. Soil classification provides a case in point: the development of the USDA Soil Taxonomy (Soil Survey Staff (1960) was necessitated by deficiencies – including vague and ill-defined soil terminology (Ahrens et al., 2002) - apparent in the previous soil classification system used in the USA (i.e. Baldwin et al., 1938). The USDA Soil Taxonomy (Soil Survey Staff 1960) adopted a rationale that "to be useful, definitions must be precise enough that different readers have approximately the same understanding of the meanings" and accordingly, incorporated new terminologies and precise definitions. Since its inception in 1960 the USDA Soil Taxonomy has been amended many times (Soil Survey Staff, 2003).

Acid sulfate soil materials and their classification

The distinguishing feature of acid sulfate soil materials has been either the presence of sulfide minerals sufficient to cause severe acidification, or severe acidity as a result of the oxidation of those sulfide minerals (e.g. van Breeman, 1973; Pons, 1973). More recently, environmental hazards arising from sulfide-containing materials in soils and sediments additional to acidification have been recognized (e.g. Sullivan *et al*., 2002; Sullivan *et al.* 2004, Bush *et al.* 2004; Burton *et al.* 2008) and include: deoxygenation, metal and metalloid release, enhanced nutrient release, and release of gases. Some of these additional environmental hazards are the result of sulfide-related processes that are redox-driven and not directly associated with acidification (e.g. Burton et al. 2008; Sullivan et al. 2008b). Indeed, the mobilisation of arsenic (Burton *et al*. 2008; Sullivan *et al.* 2008b) and some nutrients such as phosphate and ammonium (Sullivan *et al*. 2008b) from sulfide-affected soil materials appears to be maximised at neutral-alkaline pHs (Burton *et al.* 2008; Sullivan *et al.* 2008b).

Similarly, deoxygenation of waterways by mobilisation of Monosulfidic Black Ooze (MBO) does not require, nor does it necessarily lead to, acidification (Sullivan *et al.* 2002; Burton *et al*. 2006). The recognition of the occurrence and importance of monosulfides in soil materials led, in 2005, to the inclusion of monosulfidic materials as a distinguishing property within mapping units of the Australian Atlas of Acid Sulfate Soils (Fitzpatrick *et al.* 2008a).

The Atlas of Australian ASS is a web-based hazard assessment tool with a nationally consistent legend, which provides information about the distribution and properties of both coastal and inland ASS across Australia (Fitzpatrick *et al.* 2008a). This tool is available on ASRIS (Australian Soil Resource Information System: www.asris.gov.au).

Although severe acidification is a major environmental hazard that can arise from the disturbance or mismanagement of sulfide-affected soil materials, much recent literature on the behaviour of sulfide-containing soil materials indicates: (i) acidification is not the only important environmental hazard arising from these soil materials, and (ii) soil classification systems for acid sulfate soil materials should be modified to accommodate sulfide-containing soil materials that do not have the capacity to acidify, but do have the capacity to pose other sulfide-related environmental hazards.

In the most soil classification systems (e.g. Isbell, 1996; Soil Survey Staff, 2003; IUSS Working Group WRB, 2006) the term ‘sulfidic’ refers to soil materials or horizons that are capable of severe acidification (e.g. pH < 4 or, alternatively in some classification systems, pH < 3.5) upon oxidation of the sulfides contained in those materials or horizons. The concept underlying the term ‘sulfidic’, as used this way in soil classification, has proven very useful. However, sulfide-containing soil materials that are not capable of acidification and yet also pose important environmental hazards as a result of sulfide-related processes, cannot be classified as ‘sulfidic’ in the

published soil classification systems. At present there is no appropriate place in soil classification systems for these non-sulfidic yet sulfide-containing soil materials.

The way that soil classification has used the term 'sulfidic' has also proved to be problematic in terms of communicating effectively with the broader scientific community. When describing soil, sediment, rocks and water, scientists in related disciplines (e.g. ecology, geology, geochemistry, zoology) use the term 'sulfidic' differently from the way that soil classification systems have used it. For example, Sullivan *et al.* (2008a) conducted a literature survey of the twenty scientific papers that appeared first in literature search results arising when the term 'sulfidic' was associated with each of the terms 'soil', 'rock', 'sediment', and 'water'. It is clear from Table 1 that when scientists in disciplines related to soil science use the term 'sulfidic' to describe their media, they use essentially the plain english meaning of sulfidic (i.e. materials that contain sulfides). In contrast, Table 1 confirms that in the large majority of instances when authors of scientific literature explicitly referring to 'soil' use the term 'sulfidic', the soil materials must not only contain sulfides, but they must also be capable of becoming strongly acidic (e.g. pH < 4) upon oxidation.

Table 1. Meaning of the term 'sulfidic' when used to describe soil, rock, sediment and water in the scientific literature (adapted from Sullivan et al., 2008a)

	Google Scholar® search term			
The meaning of 'sulfidic' in the papers identified	**Sulfidic soil**	**Sulfidic rock**	**Sulfidic sediment**	**Sulfidic water**
Contains sulfides <u>and</u> capable of severe acidification	85%	10%	5%	0%
Contains sulfides	15%	90%	95%	100%

As a result, in soil classification, seemingly alone, we cannot describe all sulfide-containing soil materials as being 'sulfidic' soil materials. Therefore, we have, strictly taxonomically-speaking, 'sulfide-containing non-sulfidic soil materials': an oxymoronic term that is understandably confusing. As described previously, sulfide-containing soil materials can pose considerable environmental hazards via sulfide-related processes regardless of whether or not they experience severe acidification.

Although identifying soil materials that can severely acidify as a result of sulfide oxidation is clearly a very useful concept, we believe that the term 'sulfidic' for this concept as currently used in several soil taxonomies (e.g. Isbell, 1996; Soil Survey Staff, 2003; IUSS Working Group WRB, 2006) is misleading. We also believe that the disconnect between the accepted use of this term in the broad science community and

the special meaning accorded this term within soil classification, hinders effective communication within the broad science community and will continue to do so unless we address these issues.

Changes to the classification of acid sulfate soil materials

To address the issues identified in the preceding discussion, the following conceptual changes to the classification system of acid sulfate soil materials were proposed and accepted in principle by the Acid Sulfate Soil Working Group in September 2008. Consequently, we have altered the definition of the term that essentially replaces 'sulfidic' i.e. *hypersulfidic*, and its complementary term *hyposulfidic* to account for these conceptual changes, and also to account for recent improvements in the incubation method that underpins the identification of these soil materials (Sullivan *et al.*, 2009b). The recommended improved incubation procedure is a modification of the duration of incubation from the fixed 8 week period in the formal Australian Soil Classification (Isbell 1996) and Soil Taxonomy (Soil Survey Staff 2003) definitions, to that proposed by Sullivan *et al.* (2009b), i.e. where a stable pH is reached after at least 8 weeks of incubation.

Another recent modification is the field collection and storage of moist soil samples in chip trays, which can produce similar incubation conditions: chip trays are suitable for incubation testing (Fitzpatrick *et al.* 2008 b,c,d,e).

In addition, the ASS Working Group in September 2008 also accepted in principle the proposed changes by Fanning and Rabenhorst (2008) to the definition of the Sulfuric Horizon (and Sulfuric materials).

The following definitions for acid sulfate soil materials are therefore suggested.

1) Sulfidic
(note: an existing term but with a modified meaning in the modified classification system presented here)

Concept:
Soil material containing detectable inorganic sulfides.

Definition:
Soil material containing ≥ 0.01% sulfidic S.

2) Hypersulfidic
(a new term)

Concept:
Sulfidic soil material that is capable of severe acidification as a result of oxidation of contained sulfides.
(note: hypersulfidic soil materials are conceptually the same soil materials defined previously in soil classifications as 'sulfidic')

Definition:
(adapted from Isbell (1996) with modifications to *inter alia* account for recent improvements to the incubation method (Sullivan *et al*., 2009b)):

Hypersulfidic material is a sulfidic material that has a field pH of 4 or more and is identified by experiencing a substantial drop in pH to 4 or less (1:1 by weight in water, or in a minimum of water to permit measurement) when a 2 - 10 mm thick layer is incubated aerobically at field capacity. The duration of the incubation is either: a) until the soil pH changes by at least 0.5 pH unit to below 4, or b) until a stable** pH is reached after at least 8 weeks of incubation.*

**A substantial drop in pH arising from incubation is regarded as an overall decrease of at least 0.5 pH unit.*

***A stable pH is assumed to have been reached after at least 8 weeks of incubation when either the decrease in pH is < 0.1 pH unit over at least a 14 day period, or the pH begins to increase.*

3) Hyposulfidic
(a new term)

Concept:
Sulfidic soil material that is not capable of severe acidification as a result of oxidation of contained sulfides.

Definition:
(adapted from Isbell (1996) with modifications to *inter alia* account for recent improvements to the incubation method (Sullivan *et al*., 2009b)):

Hyposulfidic material is a sulfidic material that (i) has a field pH of 4 or more and (ii) does not experience a substantial drop in pH to 4 or less (1:1 by weight in water, or in a minimum of water to permit measurement) when a 2 - 10 mm thick layer is incubated aerobically at field capacity. The duration of the incubation is until a stable** pH is reached after at least 8 weeks of incubation.*

**A substantial drop in pH arising from incubation is regarded as an overall decrease of at least 0.5 pH unit.*

***A stable pH is assumed to have been reached after at least 8 weeks of incubation when either the decrease in pH is < 0.1 pH unit over at least a 14 day period, or the pH begins to increase.*

4) Monosulfidic
(a new term)

Concept:
Soil material containing detectable monosulfides.

Definition:
Soil material containing ≥ 0.01% acid volatile sulfide.

Notes:
1. monosulfidic soil materials are conceptually similar to Monosulfidic Black Oozes (MBOs) - they differ from MBOs in that monosulfidic soil materials encompass a wider array of soil textures and consistencies. For example, monosulfidic soil materials include monosulfidic sands, which are excluded (on the basis of consistency) from being MBOs.

2. As a result of the Working Group's in principle decision to have a 'side-by-side' classification for *monosulfidic* and *sulfidic*, it follows that *monosulfidic* soil materials, which will also qualify as being *sulfidic* soil materials (i.e. as acid volatile sulfide is a subset of the inorganic sulfides) could be described in several ways. The schema below provides such an example:

- *monosulfidic* (if the capacity for severe acidification of the soil materials has not been determined)

or

- *hypermonosulfidic* (if the soil material is both *hypersulfidic* and *monosulfidic*)

or

- *hypomonosulfidic* (if the soil material is both *hyposulfidic* and *monosulfidic*).

5) Sulfuric material or horizon (retained terms):

The term *sulfuric* material (Isbell 1996) remains conceptually unchanged from present usage. However, we propose the following modifications to the definition based on the proposed changes by Fanning and Rabenhorst (2008) together with supporting evidence from recently published information in Australia:

Soil material that has a pH less than 4 (1:1 by weight in water, or in a minimum of water to permit measurement) when measured in dry season conditions as a result of the oxidation of sulfidic materials. Evidence that low pH is caused by oxidation of sulfides is one of the following:

** mottles and coatings with accumulations of jarosite or other iron and aluminium sulfate or hydroxysulfate minerals such as natrojarosite, schwertmannite, sideronatrite, tamarugite, etc.*
** 0.05 percent or more by weight of water-soluble sulfate*
** underlying sulfidic material.*

In accordance with Fanning and Rabenhorst (2008), we propose to eliminate from the current definition reference to the following presumed colours of jarosite: *hue of 2.5Y or yellower and chroma of 6 or more.* We have also observed that these Munsell colours do not accurately encompass the range of colours of jarosite, especially natrojarosite, which supports the findings of Fanning and Rabenhorst (2008).

In accordance with Fanning and Rabenhorst (2008), we also propose to add the presence of "schwertmannite' because: (i) it is an acceptable indicator of low acidity (pH <4) and (ii) of documented X-ray diffraction evidence of its occurrence at many sites across Australia (e.g. Sullivan and Bush 2004; Fitzpatrick et al. 2008 b,c,d,e; 2009). In addition, we propose to add sideronatrite $[Na_2Fe(SO_4)_2.OH.3H_2O]$ and tamarugite $[Na_2Al(SO_4)_2.6H_2O]$, which have also been well documented by X-ray diffraction evidence to occur in sulfuric materials with extremely low pH values (pH <2.5) at several sites across Australia (e.g. Fitzpatrick et al. 2008 b,c,d,e; 2009).
Finally, we propose to add "0.05 percent or more by weight of water-soluble sulfate" to the definition of "sulfuric material" in the Australian Soil Classification (Isbell 1996), which Fanning and Rabenhorst (2008) proposed to retain in the Soil Taxonomy (Soil Survey Staff 2003) definition of the sulfuric horizon.

One of the reasons for including the "0.05 percent or more by weight of water-soluble sulfate" in these definitions is that this measurement will identify the presence of appreciable quantities of other Al-Fe hydroxysulfates in sulfuric materials that are soluble, such as, halotrichite $[Fe^{2+}Al_2(SO_4)_4{\cdot}22H_2O]$, alunogen $[Al_2(SO_4)_3\ 17H_2O]$, hexahydrite $(MgSO_4.6H_2O)$, epsomite $[MgSO_4{\cdot}7H_2O]$, botryogen $[MgFe^{3+}(SO_4)_2(OH){\cdot}7H_2O]$, pickeringite $[MgAl_2(SO_4)_4{\cdot}22H_2O]$, redingtonite $(Fe^{2+},Mg,Ni)(Cr,Al)_2(SO_4)_4{\cdot}22H_2O]$, tschermigite $[(NH_4)Al(SO_4)_2{\cdot}12H_2O]$, copiapite $[Fe^{2+}Fe^{3+}{}_4(SO_4)_6(OH)_2{\cdot}20H_2O]$, all of which have recently been identified by Fitzpatrick et al. (2008 a,b). These minerals have recently been identified in widespread areas in the Murray-Darling Basin (Fitzpatrick et al. 2008 a,b,c,d,e).

Approximate correlations of acid sulfate soil material/horizon classification

Table 2 below provides correlations of acid sulfate soil material and horizon classifications between the different major soil taxonomic systems and common descriptive terms. It is important to note that these correlations are approximate only and that the precise definitions of these terms varies across the classifications.

Table 2. Approximate correlations of classification of acid sulfate soil materials/horizons between different major soil taxonomic systems and common descriptive terms

Modified Acid Sulfate Soil Working Group Classification	Australian Soil Classification (Isbell, 1996)	USDA Soil Taxonomy (Soil Survey Staff, 2003)	World Reference Base (IUSS Working Group WRB, 2006)	Common description
Sulfuric material	Sulfuric material	Sulfuric horizon	Thionic horizon	Actual acid sulfate soil material
Sulfidic material	*No equivalent class*	*No equivalent class*	*No equivalent class*	*No equivalent class*
Hypersulfidic material	Sulfidic material	Sulfidic material	Sulphidic material	Potential acid sulfate soil material
Hyposulfidic material	*No equivalent class*	*No equivalent class*	*No equivalent class*	*No equivalent class*
Monosulfidic material	*No equivalent class*	*No equivalent class*	*No equivalent class*	Monosulfidic Black Ooze (MBO)

Future implications and proposals for soil classification systems

It is proposed that the modifications to the classification of acid sulfate soil materials presented here and approved in principle by the Acid Sulfate Soil Working Group of the International Union of Soil Sciences, including that the current soil classification term "sulfidic" be replaced by the term "hypersulfidic", be recommended for adoption in international general purpose soil classifications [e.g. Australian Soil Classification (Isbell, 1996), Soil Taxonomy (Soil Survey Staff, 2003), World Reference Base (IUSS Working Group WRB, 2006)].

The term "sulfidic" has now been replaced with "hypersulfidic" in the simplified Soil Identification Key for ASS in the River Murray and Lower Lakes systems to identify and classify the various subtypes of ASS and non-ASS (Fitzpatrick et al. 2008b,c,d,e). The key is essentially a special purpose or technical soil classification system, which uses a collection of plain english language names for ASS types and subtypes in accordance with the legend for the Atlas of Australian ASS (Fitzpatrick et al. 2008c).

Summary

Whilst the acidification from the oxidation of acid sulfate soil materials poses a major environmental hazard, there are a wide range of other environmental hazards posed by sulfide-containing soil materials, only some of which are necessarily related to acidification. In addition, it is clear that the use of the term 'sulfidic' for the classification of sulfide-containing soil materials needs to be made consistent with the broader usage of this term within science.

Consequently, the Acid Sulfate Soil Working Group of the International Union of Soil Sciences has accepted in principle changes to the classification of sulfide-containing soil materials that include:

1. the revision of the concept underlying the existing term *sulfidic* to 'soil material containing detectable inorganic sulfides' and defined as "*Soil material containing ≥ 0.01% sulfidic S",*

2. a new term, *hypersulfidic*, to describe *sulfidic* soil materials that are capable of severe acidification (pH < 4) from oxidation (this is essentially the same concept underlying the 'sulfidic' term as used previously by Isbell 1996),

3. a new term, *hyposulfidic*, to describe *sulfidic* soil materials that are not capable of severe acidification from oxidation, and

4. a new term, *monosulfidic*, to describe soil materials containing detectable monosulfides.

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