

# Chip-tray incubation: A new field and laboratory method to support Acid Sulfate Soil Hazard Assessment, Classification and Communication

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## Abstract

Chip-trays are plastic containers that are 50.5 cm long by 5.5 cm wide by 3.5 cm deep, and contain 20 compartments - or cells - that can be closed with a snap lock lid. Traditionally used by geologists (e.g. to store drill core fragments), for the past 5 years we have routinely used chip trays in a range of soil applications including soil survey, forensic investigations and mineralogical studies. This paper, however, focuses on recent adaptations to acid sulfate soil (ASS) protocols that rely on the use of chip-trays, which offer significant improvements to field sampling and soil storage, and provide the means for a new laboratory incubation method of ASS materials to better characterise and classify ASS types, including hypersulfidic, hyposulfidic and sulfuric materials. The chip tray-based improvements to ASS protocols have found use in a wide range of projects in diverse Australian ASS landscapes (e.g. coastal, and inland upland, wetland and riverine environments). For example, characterising hydro-toposequences, constructing ASS processes models and use in ASS risk assessment protocols.

## Key Words

Acid sulfate Soils, incubation, pH, plastic chip-trays, wetlands.

## Introduction

The Acid Sulfate Soil Working Group of the International Union of Soil Sciences has recently accepted in principle (see Sullivan *et al.* 2009b) the following changes to the classification of sulfide-containing materials: (i) revision of the concept underlying the existing term of “sulfidic” to “soil material containing detectable inorganic sulfides” and defined as “soil material containing  $\geq 0.01\%$  sulfidic S”; (ii) hypersulfidic material, to describe sulfidic materials that are capable of severe acidification ( $\text{pH} < 4$ ) by sulfide oxidation (this is essentially the same concept underlying the ‘sulfidic’ term as used previously by Isbell 1996 and Soil Survey Staff 2003), (iii) hyposulfidic material, to describe sulfidic soil materials that are not capable of severe acidification from oxidation ( $\text{pH} > 4$  after full oxidation), and (iv) monosulfidic material, to describe soil materials containing detectable monosulfides. In addition, Sullivan *et al.* (2009a) recently reviewed and proposed several improvements to the incubation method that underpins identification of ASS materials. The recommended improved incubation procedure is a modification of the duration of incubation from the fixed 8-week period in the Australian Soil Classification (Isbell 1996) and Soil Taxonomy (Soil Survey Staff 2003) definitions, to that proposed by Sullivan *et al.* (2009b), i.e. until a stable pH is reached after at least 8 weeks of incubation. Sulfuric material is defined by Isbell (1996) as having a  $\text{pH} < 4$ , whereas Survey Staff (2003) has defined a sulfuric horizon as having a  $\text{pH} < 3.5$ .

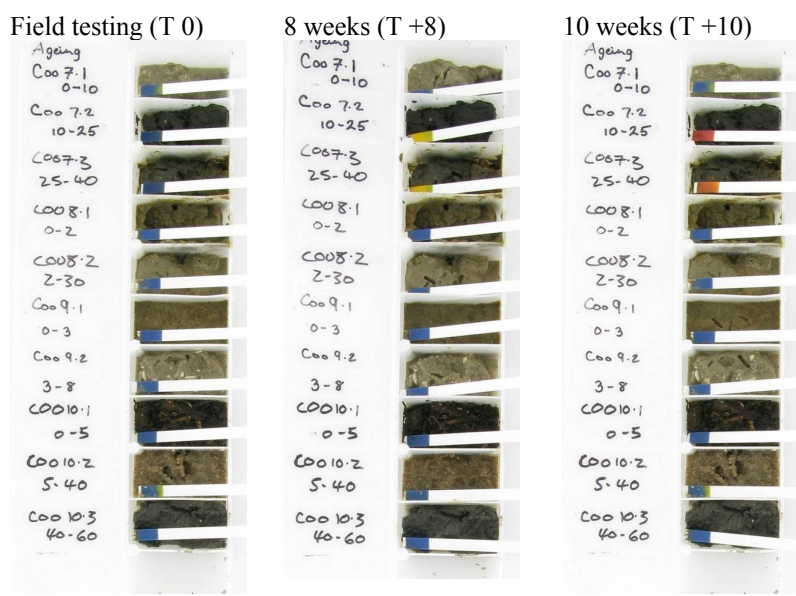
The objective of this paper is to describe improvements in field sampling, storage and incubation methods to help better characterise and classify hypersulfidic, hyposulfidic, sulfuric and monosulfidic materials in a wide range of landscapes in Australia. The improvements described include field collection and storage of moist soil samples in chip-trays, which offer standardised and improved incubation conditions to those previously used. This new approach has been extensively tested and refined since 2007 during several ASS investigations (e.g. Fitzpatrick *et al.* 2008a,b,c; 2009 a,b; Shand *et al.* 2008 a,b; 2009), and has been adopted by the Scientific Reference Panel of the Murray-Darling Basin (MDB) Acid Sulfate Soil Risk Assessment Group for use in the rapid and detailed assessment of acid sulfate soil materials in the MDB (MDBA 2010).

## Methods

### *Use of chip trays for sample collection and preparation*

Chip-trays (Figure 1) are plastic containers that are 50.5 cm long by 5.5 cm wide by 3.5 cm deep, and

contain 20 compartments - or cells - that can be closed with a snap lock lid (i.e. partly air-tight). Our adapted ASS field protocol involves soil layer sub-samples to be placed in two separate plastic chip-trays [i.e. protocol routinely used by MDBA (2010) and CSIRO Land and Water Acid Sulfate Soils team in Adelaide see Fitzpatrick *et al.* (2008a,b,c; 2009a,b); Shand *et al.* (2008 a,b; 2009)]. The first chip-tray is used to display morphologically representative aggregates for each of the sampled layers (compartments filled to  $\frac{3}{4}$  full with representative, intact aggregates or peds) for later-date visual reference (e.g. during report writing), and subsequently placed in the CSIRO Land and Water Acid Sulfate Soil archival system. If present, samples of salt efflorescences and/or coatings observed in the field should also be carefully collected and placed in soil morphology chip-tray for further mineralogical analysis. The second chip-tray (Figure 1) is used for ASS incubation testing ( $pH_{INC}$ ) in the laboratory. Compartments are filled to approximately  $\frac{1}{3}$  full (Figure 1) by representative layer samples that are then moistened (not saturated) when necessary with deionised water. After at least 8-weeks of laboratory ageing (or in some cases more than 8 weeks) at approximately 25 °C, the soil samples are visually checked for formation of minerals (e.g. jarosite) that indicate significant acidification. Since the solution in contact with the soil in the chip-tray compartments is likely to be in equilibrium with the soil, the ageing pH of the whole soil in the tray can be measured using a calibrated pH meter or Merck pH indicator strips (Merck item numbers: pH 2.5–4.5: 1.09541.0001; pH 4.0–7.0: 1.09541.0002; pH 6.5–10.0: 1.09543.0001). A pH value of 4 or less measured in the chip-tray sample after at least 8-weeks confirms that the sample, which had a  $pH > 4$  when measured in the field, is likely to develop sulfuric material on drying (i.e. is hypersulfidic). Soil treated with peroxide and then tested for pH is considered the extreme for oxidising soils and is used as an indicator to characterise ASS when the  $pH_{OX}$  [laboratory equivalent to the field pH after treatment with hydrogen peroxide  $pH_{FOX}$  (Ahern *et al.* 2004)] value is compared with the pre-treatment pH value. Therefore, we routinely compare the incubated pH values with  $pH_{FOX}$  as a test for identification of acid sulfate soils.



**Figure 1. Time sequence (T 0, T +8, T +10) for a chip-tray of soils from the Coorong in South Australia undergoing incubation. Each photograph shows soil pH as indicated by Merck pH strip colours at: (i) T 0, at sampling in the field, (ii) at T +8, after incubation for 8 weeks and (iii) at T +10, at 10 weeks. Here pH indicator strip colours indicate that most samples remain alkaline or neutral (blue colour  $>pH 7$ ) with only two becoming acid after incubation for 10 weeks (red or pink colour -  $pH 3.9$  to 4). (Fitzpatrick *et al.* 2008c).**

## Results and Discussion

The following five case studies describe the versatile use of the chip-trays for storing and incubating soil samples to determine ASS characteristics.

### Case study 1 – Lower Lakes (SA) samples showing close relationship between $pH_{INC}$ and $pH_{FOX}$

Eighty five soils from Lower Lakes and adjacent wetlands in South Australia were assessed by Fitzpatrick *et al.* (2008c) for ASS using  $pH_{INC}$ ,  $pH_{OX}$  and net acid generating potential (NAGP; see Ahern *et al.* 2004) measurements. There is good agreement between  $pH_{OX}$  and NAGP (see Fitzpatrick *et al.* 2008c). The  $pH_{INC}$  (8 weeks) also generally correlates well with  $pH_{OX}$ , although pH values were not usually as low as those measured after peroxide treatment (usually 0.5 to 1.5 units greater). Some incubated samples from the

Lower Lakes do not proceed to full oxidation within 8 weeks, especially when the soil sample is kept either too moist or too dry.

*Case Study 2 – large data set comparison of  $pH_{INC}$  with  $pH_{OX}$ , and identification of acid sulfate soil materials, River Murray and Lower Lakes, SA*

Data from three separate surveys conducted in the lower River Murray and Lower Lakes region were combined and evaluated (Grealish *et al.* 2009; Fitzpatrick *et al.* 2009a). This comprised a total of 1,452 samples and of these, 996 classified as either sulfuric or hypersulfidic. Of the 996 classified samples, 832 classified as hypersulfidic using  $pH_{INC}$  (8 weeks). The following results were obtained when comparing  $pH_{INC}$  (8 weeks - for hypersulfidic materials) and  $pH_{OX}$  (i.e.  $pH_{OX}$  of <2.5):

- 69% of samples classify as hypersulfidic using  $pH_{INC}$  and have  $pH_{OX}$  values of <2.5.
- 2% of samples classify as hypersulfidic using  $pH_{INC}$  and do not have  $pH_{OX}$  values of <2.5.
- 29% of samples were not classified as hypersulfidic using  $pH_{INC}$  but have  $pH_{OX}$  values of <2.5.

Therefore  $pH_{INC}$  (8 weeks) in general compares favourably with  $pH_{OX}$ . However, about one third of samples do not classify as hypersulfidic using  $pH_{INC}$  (8 weeks) but do have  $pH_{OX}$  values <2.5. Hence,  $pH_{INC}$  (19 weeks) will be determined on these samples and compared with  $pH_{OX}$  values <2.5 to establish if this subset of samples will classify as either hypersulfidic or hyposulfidic materials.

*Case Study 3 - to identify acid sulfate soil risk areas requiring further investigation, Murray-Darling Basin*

For the MDB ASS risk assessment project, initiated by the Murray-Darling Basin Authority, a total of 1,329 wetlands from SA, NSW, Vic, and QLD were assessed by wetland officers resulting in over 8,000 soil samples being submitted for incubation analysis (Creeper *et al.* 2010). The large number of samples collected in chip-trays allowed for comprehensive testing of this combined field sampling procedure and incubation method across the MDB. The data obtained using this method triggered the requirement for further detailed ASS investigations to be conducted. The chip-tray approach both streamlines data acquisition and enhances correct hazard identification.

*Case Study 4 – community volunteer ASS monitoring, Lower Lakes (SA)*

An ASS field guide was developed for easy use by community volunteers to monitor ASS at fixed sites over a quarterly interval as the water levels in the Lower Lakes and tributaries fall (drought conditions) or rise (from reflooding). The field guide outlined a systematic protocol for site selection, soil description and sampling methodology using the chip-tray approach. The chip trays provided an ideal system for the community volunteers to closely observe and discuss the samples they had taken for description, and also provided an easy way to transport soil samples to the CSIRO laboratories for pH incubation measurements. The chip-trays served as easy-to-use storage media for soil samples for the moderately experienced soil surveyors. The community survey results for the ASS samples are collated and presented via a Google Earth interface, which shows the pH data and down-profile trends for scientific and community monitoring.

*Case Study 5 – seasonal evaluation of nine wetlands, River Murray (SA)*

Nine wetlands adjoining the River Murray were assessed for ASS by Shand *et al.* (2009) using  $pH_{INC}$ ,  $pH_{OX}$  and net acid generating potential (NAGP; see Ahern *et al.* 2004) measurements on four occasions over a 12 month period. Although NAGP predicted a greater incidence of net acidification,  $pH_{INC}$  (using chip trays) and  $pH_{OX}$  in most cases suggested similar outcomes. Spatial variation, which can be considerable in ASS, becomes a factor with sequential sampling. For those wetlands that dried over time, the clayey wetlands, which developed strong polygonal cracking tended to neutralise by mixing as the soil columns degraded and winter rainfall moved solutes. It is also probable that very slow reactions may become a factor affecting the soil materials over the extended periods of sampling.

## Conclusions

In summary, the chip tray field sampling incubation method is considered to represent a “realistic tool” for ASS testing based on allowing the soil to “speak for itself” (Dent 1986). A number of specific techniques are employed, but incubation tests are based on keeping the sample moist for a specified period (number of weeks). Recent recommendations by Sullivan *et al.* (2009a) have increased the period from 8 weeks “until a stable pH is reached after at least 19 weeks of incubation”, which allows slow oxidation of sulfide minerals to occur. Although chip tray incubation may mimic nature more closely than the extreme hydrogen peroxide oxidation because chip tray incubation conditions do not force acidification reactions to occur in totality, it can be argued that the complex processes occurring in the field are not adequately reproduced during

laboratory ageing in chip-trays, e.g. complex landscape processes, which may include exchange with sub-surface waters (containing Acid Neutralizing Capacity) or biogeochemical reactions. These complex processes should also be taken into consideration wherever possible with interpretation of acid sulfate soil findings, which will often require a thorough understanding of water movement that is often site and scenario specific. The use of chip-trays as a valuable tool for characterising ASS has also proved remarkably useful for community volunteers to collect, discuss, describe and test samples to identify ASS materials.

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