A systematic analysis procedure incorporating the chip-tray incubation method for the hazard assessment of Acid Sulfate Soils in the Murray-Darling Basin

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Abstract
During a Murray-Darling Basin wide assessment of Acid Sulfate Soils (ASS), soil samples from over 3500 soil profiles were collected by staff from state and regional Natural Resource Management (NRM) agencies and submitted for pH incubation analysis. The large number of soil samples triggered the requirement for a new systematic analysis procedure to be developed. A reliable and systematic analysis procedure using chip trays was successfully developed and tested, which allowed: (i) a rapid and convenient means to incubate the soils in order to assess the hazards of soil acidification on all samples based mainly on pH incubation measurements and (ii) streamlined data acquisition for a wide range of ASS subtypes covering over 8,000 soil samples.

Key Words
pH, incubation, Acid Sulfate Soils, wetland, Murray-Darling basin, chip-tray.

Introduction
Acid Sulfate Soils (ASS) is the name given to those soils containing soil materials affected by iron sulfide minerals. These soils either contain sulfuric materials or have the potential to generate sulfuric materials in amounts that have an effect on soil pH. The Murray-Darling Basin (MDB) is currently experiencing the worst drought conditions in recent history. Declining water levels have caused non-acidic soils with previously accumulated sulfide minerals in wetlands, creeks, and lakes to be exposed to the atmosphere and undergo oxidation reactions, which generate sulfuric material and can turn these soil material acidic (pH < 4). Following their oxidation, ASS can cause detrimental impacts on the surrounding ecosystem in a variety of ways. The release of sulfuric acid and toxic elements can lead to the acidification of water bodies and toxic impacts of wetland ecosystems, aquatic biota and human health. Additionally, the disturbance of monosulfidic material can cause the surface waters to become rapidly deoxygenated.

The MDB ASS Risk Assessment Project, initiated by the Murray-Darling Basin Authority (MDBA), aims to assess the spatial extent of, and risks posed by these hazards in wetlands of environmental significance, as well as those that could pose a risk to surrounding waters. These wetlands were subjected to a tiered assessment process, whereby wetlands were screened through a desktop assessment stage, followed by a rapid on-ground appraisal (RAP), and then detailed on-ground assessment if results of previous stages indicate an increased likelihood of occurrence of ASS. More than 19,000 wetlands underwent desktop assessment, and this identified approximately 1,450 wetlands considered to have a higher likelihood of ASS occurrence which required further assessment. The RAPs were performed by state and regional NRM agency staff that had completed one of the six ASS rapid assessment training courses.

During the RAP, wetland soil samples were collected from up to 3 different soil profiles within a wetland representing a toposequence. As part of the RAP these soil samples were then submitted for incubation analysis. pH incubation is a method whereby ASS are kept in a moist state and exposed to the atmosphere allowing them to undergo oxidation reactions in an attempt to simulate the natural acidification behaviour of the soil. If the soil in question is hypersulfidic the pH will reduce substantially during incubation to a pH < 4, as a result of sulphide oxidation and hence pose an acidity hazard (Sullivan *et al.* 2009a,b). The use of pH incubation for classification is often considered preferable to other methods, such as peroxide addition, because the result of the experiment is arguably more representative of what would be expected to occur in the field (Dent 1986).

A total of 1,329 wetlands from South Australia (SA), New South Wales (NSW), Victoria and Queensland (QLD) were assessed resulting in over 8,000 soil samples being submitted for pH incubation analysis. The

large number of samples triggered the requirement for, and allowed the testing of, a new systematic analysis procedure.

Methods

The analysis procedure and associated pH incubation method using plastic chip-trays (Fitzpatrick *et al.* 2010) for the analyses of MDB soil samples is illustrated in the flow chart outlined in Figure 1. It illustrates the systematic order in which observations and analyses were conducted. Sections of the flow chart are examined further under subheadings below.

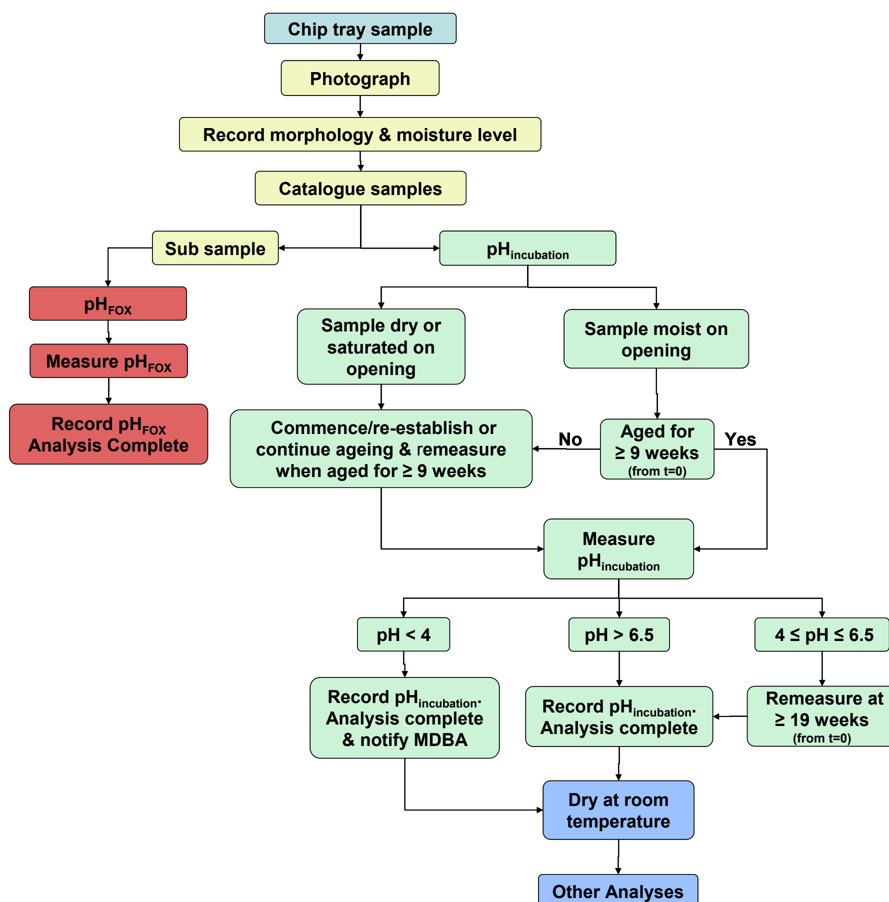

Figure 1. Flow chart of the analysis procedure and pH incubation method of chip-tray samples.

Sample collection and preparation

Approximately 50g of soil was collected at up to 3 depths (0-5cm, 5-30cm, and >30cm), designated as top, middle and bottom and placed into chip-trays (Figure 2). This was repeated for up to three different profiles selected along a toposequence. The samples were then moistened if dry to initiate incubation before wrapping the chip-tray tightly in Gladwrap® to prevent desiccation and spillage during transport and posting to the laboratory. Thus, the incubation period start date is the date of collection in the field. The practical consequence of this is that all samples for a wetland can be analysed simultaneously without the need to consider, for example, which samples were moist in the field and which were dry and not moistened until a later stage.

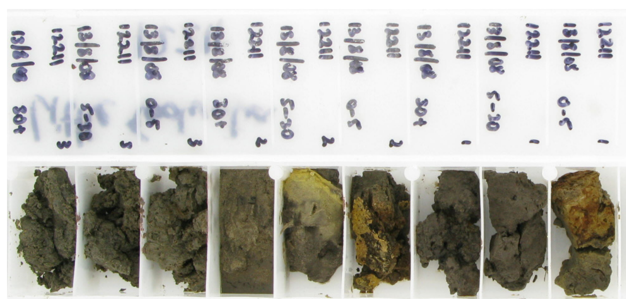

Figure 2. Photograph of plastic chip-tray filled with soil from a wetland in South Australia.

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In previous studies, small squares of non-antibacterial sponge were placed in chip-trays over the soil samples to help reduce desiccation. This was later revised when many sponges were found to be decomposed upon opening in the laboratory. The addition of organic matter from the decomposition of the sponge had the potential to adversely affect results. The sponges were also found to remove the permanent marker labelling. Due to this the use of sponges was discontinued. Also in support of this move, it was later realised that the chip-tray construction was ideally suited to prevent excessive desiccation, whereby a slightly moistened sample has been found to remain at or slightly below field capacity for periods up to 9 weeks without attention.

Photography
Photographs of chip-tray samples from each wetland were obtained for reference purposes. Each photograph was acquired using an Ortary Photosmile™ light box, which provided consistent lighting for natural white-balanced and shadow-free photographs.

Basic morphology and moisture level
A simplified soil morphology description was collected for each sample. Descriptors were chosen on the added usefulness of the information they provide in relation to ASS hazard. Chosen descriptors include moisture status, colour, consistence, texture, and any other comments. Because a high sample throughput was essential for this project each morphology descriptor was refined to a limited number of choices. These are shown in Figure 3. To further assist with sample throughput, a virtual tick sheet was created in Visual Basic for Applications (VBA), which allowed the user to rapidly input morphology data by simply clicking on the appropriate buttons. When completed the virtual tick sheet would then insert the recorded information into an Excel® spreadsheet in the required format. Albeit limited, the simplified soil morphology description allowed the capture of key morphology information that otherwise would not have been collected.

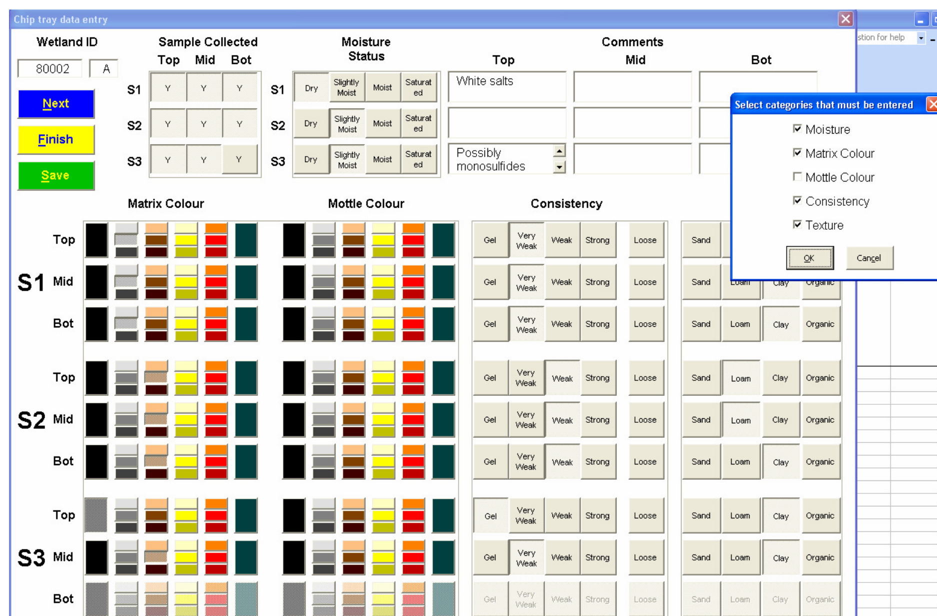

Figure 3. Screen capture of virtual tick sheet with details filled out for wetland ID 80002.

The moisture status of each sample was recorded on a scale of 1 to 4. This was done each time the chip-tray was opened. During the incubation period moisture is required for the oxidation reactions to occur. Hence, this observation was used to determine whether or not a sample had been aging between the time of collection in the field and first opening in the laboratory or any subsequent openings.

pH peroxide (pH_{FOX})
As part of the analysis procedure soils were subjected to the peroxide field oxidation method (pH_{FOX}). The method involves measuring the soil pH after the rapid oxygenation of reduced inorganic sulfur materials caused by the addition of hydrogen peroxide. pH_{FOX} provides another means of assessing the acidity hazard.

pH incubation
All soil samples, except for soil surface efflorescences, were submitted for pH incubation analysis. The soil sample was homogenised by mixing with a glass rod while deionised water was added until an approximate

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soil-to-solution ratio of 1:1 was achieved. These steps and the pH measurement take place in the chip-tray. All pH measurements were obtained using an Ionode^{TM} intermediate junction electrode that was calibrated at pH 4 and 7 at the beginning and end of each sample batch. The electrode was connected to a WP-81 TPS^{TM} pH meter and referenced against temperature with a Pt sensor.

If a sample was found to have a moisture status of 2 or 3 (slightly moist or moist) on receipt it was stored and allowed to undergo incubation for ≥ 9 weeks starting from the date of collection. If a sample was found to be dry or saturated (moisture status 1 or 4) the appropriate amount of water was added or subtracted before incubating the sample for ≥ 9 weeks starting from that days date.

If a soil sample was found to acidify to a pH < 4 after an incubation period of 9 weeks or more, that sample was classified as hypersulfidic material and analysis for that sample was considered complete. Additionally, if a soil sample did not acidify over the same period to a pH below 6.5 analysis was also considered complete. In the case that the pH of a sample lies between a pH of 4 and 6.5 (4 ≤ pH ≤ 6.5) incubation is continued for a further ≥ 10 week period (i.e. total incubation period ≥19 weeks) before pH re-measurement. For these samples, analysis was considered complete after this second incubation period.

Samples were discriminated this way because it was reasoned that if after ≥ 9 weeks of incubation the pH of a sample did not drop below a pH of 6.5 the sample will not age to a pH < 4 given more time. This assumption was based on the fact that if a sample has a pH of > 6.5 it still contains an amount of acid neutralising capacity (ANC) and, hence, has ability to buffer acidity and resist changes in pH.

Ideally sample analysis would continue until a stable pH was obtained as suggested in recent literature (Sullivan *et al.* 2009b). However, when the scope of the project does not allow for this it is suggested that this method of sample discrimination is adopted as a suitable alternative.

Results and Discussion

The systematic analysis procedure has functioned successfully throughout the project allowing the large number of samples to be managed and analysed efficiently and accurately. The analysis procedure has so far been used in the identification of over 400 wetlands containing hypersulfidic soils. Conversely, the analysis procedure has identified approximately 930 wetlands that are unlikely to contain ASS with hypersulfidic materials, a potentially greater achievement when considering the necessity for economical assignment of finite funds and time.

Conclusion

The use of the chip-tray pH incubation method like other incubation methods is considered favourable over other methods for classification of hypersulfidic materials because it is a direct measurement and produces a more realistic result for testing of hypersulfidic soil materials in ASS by allowing the soil to "speak for itself" (Dent 1986). However, incubation methods are also very time exhaustive in that in some instances it can require > 19 weeks to give a conclusive determination and that soil samples must be periodically monitored for moisture status during the incubation. The systematic analysis procedure presented here provides a tested means that streamlines data acquisition, assures correct hazard identification, and is able to handle these and other problems even with very large sample numbers.

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