A Best Protocol for Acid Sulphate Soil Detection, Ashfield

Abstract

An early analysis of data for Acid Sulphate Soil ASS detection uses field based measurements of pH and laboratory based measurements of Cl/SO$_4$ and SPOCAS at Ashfield, Western Australia. Statistically, no test is outstanding and the tests are not necessarily the same. Field pH testing is inexpensive and worth doing but statistically Field pH and Cl/SO$_4$ are insignificantly related ($P = 0.045$) Fisher’s Exact Test. Cl/SO$_4$ testing rarely gives a negative result. When the Field pH gives a negative result, Cl/SO$_4$ is unlikely to confirm it. Field pH and SPOCAS are significantly related ($P = 0.022$, Fisher’s Exact Test); large numbers of positive and negative results lend power to this statement. It is particularly concerning that when the Field pH and Cl/SO$_4$ agree, the SPOCAS only gives a positive result 68% of the time, a figure not statistically different to 50%. The follow-up suggests numerical readjustments of the cutoff for the tests and the protocol for ASS in Western Australia, in the shape of a decision tree.

The Problem

Acid sulphate soils, ASS, are soil-like strata with significant amounts of sulphides which, when oxidised in the presence of water, produce sulphuric acid. ASS may be of recent or ancient geological origin and are usually associated with marine or wetland deposits from the anaerobic metabolism of iron and sulphur bacteria. On exposure to the atmosphere or oxygenated water, acidity in associated water and soils may approach a pH of 2 and is harmful in its own right but such acidity also corrodes and erodes steel and concrete structures as well as mobilising heavy metals, arsenic, and the aluminium in clays. At risk are activities which expose the layers, including canal developments along the coast near present or ancient waterbodies where the water table is close to the surface. There are many types of acid sulphate soils*:

1) Ancient or coastal regions with the groundwater < 5 m above sea level;

2) Wetland areas, particularly those filled in or with groundwater < 2 m below the ground surface;

3) Industrial sites which have imported sulphidic materials, perhaps mined pyrites in piles;

4) Paleowetlands, which may contain sulphides deep in the profile, perhaps deeper than 10 m.

Note that most of the original wetlands in Perth have been filled and contain significant amounts of peat and organic material which must contain sulphur from the constitution of the original proteins. Also, the clay material, mostly spoil from the Darling Scarp and the Yilgarn Craton and lateritic profiles is heavily laden with iron. This means that the normal situation in swales with the dune system would

* From ASS Workshop, 2003 and Fitzpatrick et al. (2002)

‡ Paper not presented at ISBW because of time constraints. Comments by reviewers at end.
create ASS strata but also one expects a significant amount of acidity from oxidation of the peaty organic materials.

Nonetheless, much of the Swan Coastal Plain is underlain by layering of marine sediments from its recent geological past. Such layers may be close to the surface or deep, perhaps more than 10 m below the surface. The development in East Perth exhibits effects from the very recent past, only a metre or two below the surface. Deep excavations as are made for freeways and the Northbridge tunnel may well be affected even though they are removed from the coast.

The situation in regard to ASS in Western Australia is now being defined, in terms of severity and extent. Scientifically it is unclear how the measurements should be made and it is unclear how they should be interpreted. Generally the techniques used in eastern Australia are not necessarily right for the conditions in the West. Here we attempt to assess the tests and the protocol involved in a special series of tests set up by the Department of Environment in 2002 and 2003.

Specifically, there have been continuing investigations of pollution in borewater, surface waters and soils in Ashfield (Kellenberger, 1998) which identified industrial sources with associated, mobilised heavy metals. In 2002, arsenic, heavy metals and acidity were found in borewater near several homes on the south side of the industrial park bordering Ashfield, Bassendean and Bayswater. A sampling regime was set up that involved the drilling of a number of monitoring/sampling bores across and along the regional groundwater flow. In terms of sample coverage, the sampling effort is a small part of the whole region. This, of course depends on the local variability or consistency from its geological past and alterations by man. Nonetheless the sampling, including private bores and drains, would cover an area around 1% of the total and might represent, perhaps 10% of the whole. It is known that ASS tend to be in ‘hot spots’ and the sampling that was done actually tried to pinpoint the hot spots, based on earlier information and history, the perceived risk and the geology.
Soil Samples

Soil samples were collected through the profile to depths of about 10m. A total of 270 samples were screened for pH in the field at 22 sites. The samples were collected in 600mm-long, clear plastic tubes with a hydraulic rig (above). The sampling protocol and chain of custody follows advice from the Queensland Guidelines (Ahern et al., 1998). The soil was logged for its colour, texture and fibre content; a small portion of each sample was immediately removed from the tubes for field investigation and the tubes were capped. The remaining soil samples were stored in a styrofoam box in ice and delivered to the laboratory within 24 hours where the samples were frozen until oven dried at 85°C for 48 hours. If monosulphides were suspected, the samples were submitted without delay and frozen until further analysis. Some water samples were also collected, from groundwater during the drilling operation, from monitoring wells and backyard bores as well as drains but the results are not reported here.

Field pH Testing

The guidelines do not allow that these field analyses substitute for laboratory analysis, but they are considered a useful additional tool. The Field pH uses two separate measurements of pH to make an assessment as to whether the sample is an Actual Acid Sulphate Soil, AASS, or Potential Acid Sulphate Soil, PASS. Measurements were made on the 1:5 soil:water paste or a saturated soil SS paste. One aliquot is mixed with water and the pH is measured as pH_f; another aliquot is mixed with a 30% hydrogen peroxide solution and, after reaction, the pH remeasured: the pH_fox value. The intent is to oxidise reduced forms of sulphur and pyrites. The intensity of the oxidation by peroxide is qualitatively assessed as low, medium or high where low signifies only a notable reaction and high, a near-to-violent reaction. The Queensland regulations suggest that tests be conducted on the time required for the oxidation reaction to be completed by monitoring the change in pH. In the sandy soils encountered, a time period of 10 minutes was found to be sufficient (Loos, 2003).

A combination of three factors is used; (a) the strength of the reaction, (b) pH_fox – pH_f > 1 and (c) pH_fox < 3. The judgement is that, if (b) applies, the material may be PASS. The greater the difference in pH values, the more indicative of PASS and a positive result. If pH_fox is less than 3 following (c) and there is a substantial reaction as in (a) and (b), there is a strong case for PASS. A pH_fox of 3-4 requires further laboratory testing to confirm the presence of sulphides. A low pH_f and pH_fox would indicate that the material is simply acid or AASS, but does not rule out PASS. That is because the sample may simply react slowly or contain carbonate or basic material that would be able to neutralise the acid formed during oxidation. Low values of pH_fox may be due to the production of organic acids without the presence of reduced forms of sulphur. Sands with a low sulphur analysis (<.03 % S -- as on the Swan Coastal Plain) are a particular problem, as are organic layers, peat and coffee rock.

The Field pH technique is robust, quick and inexpensive while giving an on-site, early estimate of
ASS. In the context of this paper, it is good for guiding further analyses. Nonetheless, the regulations require that field measurements alone cannot confirm or deny the presence of ASS. In this study soil samples with a pH less than 5 or a unit difference between pH$_{i}$ and pH$_{ox}$ were submitted to the laboratory for SPOCAS analysis.

### Table 1 Interpretation of Cl/SO$_4$ ratio in relation to pH

<table>
<thead>
<tr>
<th>Class</th>
<th>pH</th>
<th>Cl/SO$_4$ ratio</th>
<th>Other Factors</th>
<th>Sulphide Behaviour</th>
<th>Appropriate Management Response</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6 to 8</td>
<td>5 to 9</td>
<td>All ratios similar to sea</td>
<td>Sulphide absent or never oxidised</td>
<td>Preliminary soil study</td>
</tr>
<tr>
<td>2</td>
<td>7 to 8.5</td>
<td>&gt;9</td>
<td>Rotten egg gas smell</td>
<td>SO$_4$ converted to sulphides</td>
<td>Preliminary soil study</td>
</tr>
<tr>
<td>3</td>
<td>&lt;4</td>
<td>&gt;5</td>
<td>All ratios similar to sea</td>
<td>Acidity due to other causes</td>
<td>Find acidity source</td>
</tr>
<tr>
<td>4</td>
<td>&lt;4</td>
<td>&gt;5</td>
<td>No similarity to seawater ratio</td>
<td>Acidity due to other causes</td>
<td>Find acidity source</td>
</tr>
<tr>
<td>5</td>
<td>5 to 8</td>
<td>&lt;4</td>
<td>Other ratios similar to sea HCO$_3$ elevated</td>
<td>Sulphides oxidised, neutralised by shell grit</td>
<td>Preliminary soil study</td>
</tr>
<tr>
<td>6</td>
<td>4 to 8</td>
<td>&lt;2</td>
<td>Other ratios similar to sea, HCO$_3$ highly elevated</td>
<td>Abundant sulphides</td>
<td>Detailed soil study</td>
</tr>
<tr>
<td>7</td>
<td>2 to 4</td>
<td>&lt;2</td>
<td>Other ratios similar to sea</td>
<td>Some sulphides, little buffering</td>
<td>Detailed soil study</td>
</tr>
</tbody>
</table>

### Chloride to Sulphate Ratios

The Cl/SO$_4$ ratio is an indicator of the presence of seawater (Webb, 1983). The association between marine origins and ASS tends to be close, particularly near the coast. Chloride is chemically a good tracer but sulphate (which is a reasonable tracer) decreases with distance inland. Hence, if the Cl/SO$_4$ ratio is less than 7.2, the sample has an enhanced sulphur content and may be an ASS. A Cl/SO$_4$ ratio less than 2 is considered an indication of pyritic oxidation. If the pH is neutral to basic, the sample has neutralization capacity (shells). Suggested interpretations of measured Cl/SO$_4$ ratios are listed in Table 1 (Mulvey, 2003).

The Cl/SO$_4$ ratio is an indicator simply because of the marine association and should be used with caution. Not all ASS are from marine sources. Also, the degree of oxidation of the soil is critical in an ASS. The testing process is valid if all the sulphur becomes oxidised, provided there is not an alternate (industrial) source of sulphate. The Cl/SO$_4$ ratio can be significantly affected if water lacking in chloride (fresh water) is present.

### Suspended Peroxide Oxidation Combined Acidity and Sulphate SPOCAS

For the most part, SPOCAS is a combination judgement based on pH and oxidised sulphur. As presented by the Queensland Department of Natural Resources and Mines, (Ahern et al., 2003) the technique allows for 2 short digestions by hydrogen peroxide. After the first digestion, if pH > 6.5 and the undigested soil has a positive fizz test, the sample is back titrated with dilute HCl to a pH of 4. A further peroxide oxidation is followed by a back titration to a pH of 6.5. In alkaline situations with excess carbonate, peroxide oxidation of pyrite is inefficient (coatings and low iron in solution); the SPOCAS procedure allows oxidation at a low pH. Following McElnea et al. (2002) an improvement allows that the soil solution ratio is increased to 1:40, the titrations are performed in suspension, and the digestion stage is shortened. With fine grinding of soils an efficient oxidation of sulphur is achieved with no loss, despite milder digestion. It remains that highly sulphidic and organic soils are difficult with either the improved method or the chromium method. They recommend the improved peroxide method combined with the chromium method and a 4 M HCl extraction for a best, informed decision.
The Chemistry Centre (see McCafferty, 2004) has produced a number of analyses that may be variously interpreted. The percent Suspension Peroxide Oxidisable Sulphur SPOS follows the sulphur trail and the Suspension Total Potential Acidity STPA follows the acidity trail. A 1:40 suspension of the sample is extracted with KCl solution for 4 hours and allowed to stand overnight. The suspension is then titrated to pH 5.5 and filtered to a standard volume for determination of sulphur, calcium (optional) and magnesium (optional). The extraction with KCl is used to determine soluble and absorbed, non-sulphidic sulphur and the actual acidity STAA of the sample. SPOS is the sulphur extracted after oxidation with 30% hydrogen peroxide minus the sulphur extractable by the KCl. STPA is defined by titration of total acidity to pH 5.5 after oxidation with 30% hydrogen peroxide, moles of acid per tonne of soil, converted to equivalent oxidisable (pyrite) S% for comparison. Suspension Total Actual Acidity STAA is a measure of the acidity prior to oxidation of sulphidic material and is determined by titration of a 1M KCl solution extract to pH 5.

Following Mulvey (2003) the Net Acid Generation Potential*, NAGP = STPA - STAA is a measure of sulphidic oxidation and is the expected liming requirement in moles of lime per tonne of soil. AASS, however, have been oxidised and their liming requirement is STPA in moles of lime per tonne of soil. On low pH soils STPA may vastly underestimate environmental risk if shell is present. Peat/swamp, coffee rock and podzols with high organic matter may have high STAA from organic acids. Peroxide digestion may also remove acidity from organic matter and make STSA negative; then STSA is reported as zero. Note that the extraction removes water soluble sulphates and oxidised, non-water-soluble sulphates such as jarosite KFe(OH)₆(SO₄)₂ or natrosite NaFe₃(OH)₆(SO₄)₂.

Table 2, from Mulvey(2003) defines the classes of ASS according to the given texture classes, as no sulphides, no risk, moderate risk and high risk, depending on SPOS and the Net Acid Generation Potential NAGP.

As an example, sands are judged to be ASS if SPOS > 0.03%S and NAGP > 3.

* As used with suspensions NAGP would be the Suspension Total Sulphidic Acidity STSA.
Table 3 FIELD * Cl/\text{SO}_4^4\ Cross Tabulation

<table>
<thead>
<tr>
<th>FIELD</th>
<th>Cl/\text{SO}_4^4</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pos</td>
<td>neg</td>
</tr>
<tr>
<td>FIELD pos</td>
<td>27</td>
<td>1</td>
</tr>
<tr>
<td>neg</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>Total</td>
<td>32</td>
<td>3</td>
</tr>
</tbody>
</table>

Table 3 ASS identified with the Field pH and Cl/\text{SO}_4^4\ tests

Field and Cl/\text{SO}_4^4\ comparison

Following the above criteria, the soil samples from Ashfield were identified as ASS. These data are presented in tables by Loos (2003) and are not presented here. In this case two methods were used to determine ASS, Field pH and Cl/\text{SO}_4^4\ ratios. Is one of these two methods better at predicting ASS? The results are presented as a cross tabulation in Table 3. Importantly, these results are not quite significantly related (P=0.095, Fisher’s Exact test). That is, the data are not (significantly) inconsistent with the hypothesis that the Field pH and Cl/\text{SO}_4^4\ test give independent results. A reason for this lack of a statistically significant relationship between these two tests is the fact that the Cl/\text{SO}_4^4\ test rarely gives a negative result (only 3/35 = 8.6% of cases) and this results in statistics with low power. The field test gives a higher proportion of negative results (7/35 = 20%) but the tendency for the two tests to give a different proportion of negative results is not statistically significant (P=0.212, McNemar’s test).

Note that when the field test gives a positive result, the Cl/\text{SO}_4^4\ test agrees 27/28 = 96% of the time but when the Field pH gives a negative result, the Cl/\text{SO}_4^4\ test only agrees 2/7 = 29% of the time. These proportions (96% and 29%) are significantly different (P<0.001, chi-squared test). Thus the Cl/\text{SO}_4^4\ test is more likely to confirm the result of the Field pH when the Field pH is positive and therefore of less value. When the Field pH gives a negative result, the Cl/\text{SO}_4^4\ test is unlikely to confirm the result. We would suggest that the Cl/\text{SO}_4^4\ measurements are calibrated differently, perhaps so they do not give as many negative results.

Table 4 FIELD * SPOCAS Cross Tabulation

<table>
<thead>
<tr>
<th>FIELD</th>
<th>SPOCAS</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pos</td>
<td>neg</td>
</tr>
<tr>
<td>FIELD pos</td>
<td>18</td>
<td>7</td>
</tr>
<tr>
<td>neg</td>
<td>1</td>
<td>5</td>
</tr>
<tr>
<td>Total</td>
<td>19</td>
<td>12</td>
</tr>
</tbody>
</table>

Table 4 ASS identified with the Field pH and SPOCAS tests

Field and SPOCAS comparison

Comparisons between Cl/\text{SO}_4^4\ and SPOCAS measurements show that they are not significantly related (P=0.374, Fisher’s Exact test). Now the probability that the SPOCAS test agrees with the Cl/\text{SO}_4^4\ test is approximately 60% no matter whether the Cl/\text{SO}_4^4\ test is positive or negative (these percentages are not significantly different, P=1.000, chi-squared test).
<table>
<thead>
<tr>
<th>Cl/\text{SO}_4</th>
<th>SPOCAS2</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>\text{pos}</td>
<td>Count</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>10</td>
<td>27</td>
</tr>
<tr>
<td>\text{neg}</td>
<td>Count</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td>\text{Total}</td>
<td>Count</td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>13</td>
<td>32</td>
</tr>
</tbody>
</table>

Table 5  ASS identified with the Cl/\text{SO}_4 and SPOCAS tests

**Cl/\text{SO}_4 relative to SPOCAS comparison**

Once again, this result could be due to a calibration issue caused by the Cl/\text{SO}_4 result being positive too often. We suggest that the 10 results where Cl/\text{SO}_4 is positive but SPOCAS is negative are due to Cl/\text{SO}_4 values being close to a cutoff which should be changed. Put simply, the Cl/\text{SO}_4 test is of little use because it almost always gives a positive result (and even if it does give a negative result this is not correlated with the other two tests)! Alternatively, the Cl/\text{SO}_4 ratios simply measure some other effect.

**Three-fold comparison: Field pH and Cl/\text{SO}_4 relative to SPOCAS**

Although comparisons between all three tests result in small numbers for each combination of test results, a few observations are worthy of noting:

1. When determinations from Field pH and Cl/\text{SO}_4 agree and both give positive results, SPOCAS only gives a positive result $15/22 = 68\%$ of the time.

2. When determinations from Field pH and Cl/\text{SO}_4 agree and both give negative results, SPOCAS gives a negative result $2/2 = 100\%$ of the time. The SPOCAS agrees with both other tests but note the very small numbers!

3. When determinations from Field pH and Cl/\text{SO}_4 disagree (with the Field pH positive), SPOCAS gives a positive result $2/3 = 67\%$ of the time. The SPOCAS tends to agree with the Field pH more often. Note very small numbers again!

4. When determinations from Field pH and Cl/\text{SO}_4 disagree (with the field test negative), the SPOCAS test gives a negative result $3/4 = 75\%$ of the time. Once again, the SPOCAS tends to agree with the Field pH more often. Still--small numbers again!

Observation 1 is concerning. When both Field pH and Cl/\text{SO}_4 tests agree, it is expected the SPOCAS test will give a positive result also. It only does so $15/22 = 68\%$ of the time, which is not significantly different to 50\% (\(P=0.134\), Binomial test). This again could be a calibration issue: perhaps the Field pH and Cl/\text{SO}_4 tests are giving too many positive results or the SPOCAS test too many negative results? Again, an investigation of cut-off values is in order.

Observations 3 and 4 are consistent with the higher correlation between the Field pH and the SPOCAS test as compared with the Field pH and Cl/\text{SO}_4 test (as above). When the Field pH and Cl/\text{SO}_4 tests disagree, the SPOCAS test agrees with the Field pH $5/7 = 71\%$ of the time, but this is not significantly different to 50\% (\(P=0.453\), Binomial test).
Discussion

Two elements seem to have been given little regard in the decision process; the 3-fold nature of the decision process and a logical protocol, in the form of a Decision Tree. It seems that the judgements should include at least three categories of judgements PASS, AASS, and NASS, and specifically include Non Acid Sulphate Soils NASS. Mulvey(2003) identifies NASS—and they are important in the logic. The regulation (Stone et al., 1998) defines ASS but also non acid sulphate soils, NASS.

Note:
Cl/SO₄ ratios are not included in this decision tree; they were not available for all results
If these are further abbreviated as P, A and N; doubtful categories could also be considered such as P/A which could be either PASS or AASS but also AASS with some potential acidity, P/N would have benign soils with borderline or unknown PASS, N/A would have almost no sulphides or borderline amounts—any acidity would have already been exhibited. This will be followed up with the data from Ashfield in another paper.

Included is a first draft of a Decision tree to help with the decisions. First is a look at the site; does it have any of the bulleted conditions? Be aware that some activity may be spawned that would cause ASS conditions in a situation the would, nonetheless, naturally be quite benign. Second, is the Field pH < 4? If so, go straight to SPOCAS analysis. If not, does the pH lower by more that one unit on oxidation? If so, go to SPOCAS. If not, the sample is NASS but, even then, random samples are retested with SPOCAS to allow for mistakes, heterogeneity or specific chemistry. Lastly, the AASS, PASS and NASS are selected in reference to the regulated exceedance criteria.

Overall it is quite clear that the Cl/\text{SO}_4 ratio is not a replacement for the Field pH measurements at Ashfield. This could well be an effect of the cut-off value, a ratio of 4 or 2 dependent on the pH.

It is known that the heterogenous and time dependent nature of soils and the chemical reactions must produce an historical effect that depends on the order and timing of activities. In the chemistry, the acid trail itself can take no account of the carbonate content or the buffering capacity and may give ‘false positives’ in routine laboratories; it may underestimate the potential risk of acid leakage to the environment as not all shell is available for immediate neutralisation. These effects make it improbable that the simple judgements (AASS, PASS or NASS) will produce the expected result, as required in the regulations, but seem to be required by politicians.

Conclusions

There is a continuing need for new and improved field and laboratory techniques to define real and legalistic interpretations of ASS. The tests, Field pH and laboratory SPOCAS, are consistent. The Field pH is reliable even though done under less than ideal conditions; it does have the advantages of on-site sampling with immediate results that can be used to direct the sampling effort and freedom from problems due to sample storage. The SPOCAS test is time consuming and expensive to run. However, in combination, the tests appear to provide some reliability for taking appropriate actions, such as preparing management plans for areas affected with ASS material.

Investigations of ASS should be classified into AASS, PASS and NASS and a protocol is presented as a decision tree to assist in processing the field and laboratory data.

The Cl/\text{SO}_4 ratios have not aided the ASS assessment at Ashfield; the ratio is expected to be more applicable to ASS investigations involving marine or estuarine situations. The classification of ASS is not simple or necessarily even rational but there is a continuing real and legal need to defining ASS hot spots.

In closing, we note the absolute necessity in such measurements of maintaining sample integrity in the field for laboratory analysis. In-situ is best; inappropriate exchange, storage and storage times are critical. The oxidation processes continue and require that lab preparation is carried out as quickly as possible, and that a non-oxidating atmosphere is maintained.
Comments by Peter McCafferty:

The paper is very good and presents a logical decision tree that is useful in the analysis process. The decision tree lays out the logic nicely, and also makes the decisions much easier for developers to follow.

Specific points:
1) The lack of correlation between Field pH and Cl/\text{SO}_4 needs more investigation.

2) The difference in soil and geography in WA does not fit with the statement that the model doesn’t fit, therefore the model is wrong. The techniques are evolving and differences in clay and organics, hydrodynamics and hydrophobicity, as well as salinity very likely contribute to difficult ASS situations.

3) The model presumes that ASS occur in ‘hot spots’ and the experimental data confirm this. Nonetheless, the primary sampling program should not assume that ‘hot spots’ will be encountered. Anecdotal evidence or physical observations are needed to highlight where ‘hot spots’ might occur or have been created.

4) Perhaps the Cl/\text{SO}_4 ratio is not a valid indicator of ASS for WA conditions simply because the background and groundwater are already saline.

Acknowledgements

The work was funded and carried out as a component of an MSc by Christa Loos in Environmental Science at Murdoch University in Perth, Western Australia. Sampling for this project was funded by and completed with advice from the Department of Environment, Water and Catchment Protection and WA Chemistry Centre.

Please note that the analyses were undertaken using the methods thought to be most appropriate at the time. Since the finalisation of the report, a national framework for assessment of acid sulphate soils has been developed (with some input from the authors). Should the work be undertaken now, it might be more beneficial to utilise the nationally accepted methods which would then allow a greater distinction of potential and actual acidity.

References


