



Department of  
Environment and Conservation



# Experimental oxidation of **Bassendean sands in soil columns**

March 2012

Prepared by Contaminated Sites Branch Environmental Regulation Division  
Department of Environment and Conservation



**ACID SULFATE SOILS**

information and awareness



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# Summary

The primary purpose of this study is to determine the adequacy of the current action criterion for managing the sandy soils of the BDS. These sands have low sulfur content while producing extremely low  $\text{pH}_{\text{FOX}}$  values. The experimental study carried out natural soil oxidation to determine the rate of acid generation from Bassendean sands with less than 0.03%S.

The criterion for managing sandy soils generally assumes that there is sufficient neutralising capacity within the soils to buffer minor acidity generated when the sulfur content is less than 0.03%. However, the recent acid sulfate soil survey has shown that its applicability for carbonate free Bassendean sands containing less than 1% clay may be deficient to resist acidification with increased soil oxidation.

The experimental study found that six of the eight targeted sites were in areas where previous investigations revealed low sulfur content soils generally less than 0.03%S. The leachate for these sites recorded a pH ranging from 2.2 to 4.1, with an average of pH 3.0. A relatively smaller decline in leachate pH for one of the sites could be attributed to residual acid buffering provided by amorphous organic-aluminosilicate complexes.

The strong correlations between sulfate, titratable acidity, leachate pH, total dissolved salts and iron concentrations clearly identify sulfide oxidation as the primary source of acidity. The titratable acidity was significantly greater than the baseline of the local groundwater quality in the area. The observation indicates that oxidation of these soils can produce unacceptable levels of acidity that have the potential to impact surface and groundwater resources.

With the exception of one site that had coffee rock formation, the leachate pH values from all sites were about one unit greater than their initial field  $\text{pH}_{\text{FOX}}$  values before the experiment started. In view of the findings it is reasonable to assume that the low  $\text{pH}_{\text{FOX}}$  values generated in poorly buffered Bassendean sands are likely caused by pyrite oxidation. However it should be noted that the  $\text{pH}_{\text{FOX}}$  value takes into account the potential acidity as well the natural soil acid buffering capacity, thus providing an approximation of net acidity.

The conclusion from this study indicates that poorly buffered sandy soils with low  $\text{pH}_{\text{FOX}}$  values coupled with detectable sulfur content of less than 0.03%S have the potential to acidify when exposed to air by activities such as lowering of the watertable and soil excavation.

# 1 Introduction

## 1.1 General information

Most development activities in Perth metropolitan area are on the Swan Coastal Plain, a series of distinct landforms running roughly parallel to the current coastline (McArthur and Bettenay 1960). The predominant landform in the region is the BDS which forms a subdued landscape comprising low hills and extensive intervening low-lying areas. It consists of mainly white to grey quartz sand with only minor fine grained sediments. This landform has a maximum thickness over 20 metres (m) and has been highly leached since its deposition during the early to mid Pleistocene (Playford et al., 1976; Gozzard, 2007). These sandy soil materials are consequently devoid of carbonate minerals and contain a negligible clay mineral content, the two primary natural buffers against soil acidification.

The ASS survey (2008-10) in the Perth metropolitan region has identified sandy soils of the BDS consistently recorded low  $\text{pH}_{\text{FOX}}$  values less than 3 and in some instances as low as 1.8. On the basis of  $\text{pH}_{\text{FOX}}$  value alone, it may seem highly probable that Bassendean sands can severely acidify when exposed to natural oxidation. However, the trigger that requires ASS management is based on soil texture criteria for inorganic sulfur content developed by Ahern et al (1998). For coarse textured soils, a criterion of 0.03%S is used by most regulatory agencies to trigger ASS assessment and management. This criterion assumes that there is sufficient neutralising capacity in sandy soils to buffer acidity generated by less than 0.03%S. While this criterion may work well for the sandy to sandy loam soils on the coastal margins of eastern Australia, the recently completed ASS survey showed that its applicability for the medium to fine textured soils of the BDS which contain less than 1% clay and are devoid of carbonates may be deficient to prevent acidification. With an increase in urban development within the Perth metropolitan area, the risk associated with disturbing Bassendean sands with low sulfur content and low  $\text{pH}_{\text{FOX}}$  values could be under estimated and adversely affect superficial groundwater quality.

This study is focussed on the sandy soils of the mid slope and low lying areas that commonly show low  $\text{pH}_{\text{FOX}}$  values in spite of their relatively low sulfur content.

## 1.2 Aims

The broad objective of this study is to oxidise Bassendean sands with low  $\text{pH}_{\text{FOX}}$  values less than 3 and inorganic sulfur content of less than 0.03%. The specific aim of the study, therefore:

- subject columns of Bassendean sands to natural oxidation in a glasshouse
- leach the column periodically to monitor changes in pH and titratable acidity
- assess the acidification potential of Bassendean sands
- review the adequacy of the current action criterion for Bassendean sands.

## 2 Method and Materials

### 2.1 Sampling and field analysis

Sites for the study were selected from previous ASS surveys in the Perth metropolitan area. The specific criteria for site selection were:

- $\text{pH}_{\text{FOX}}$  less than 3 for at least one metre continuous length
- $\text{pH}_{\text{F}}$  less than 5
- sulfur content lower than in regulatory action criteria (0.03%S)

An example of soil pH profile is shown in Figure 1A, and the  $\text{pH}_{\text{F}}$  and  $\text{pH}_{\text{FOX}}$  along with sulfur content for sites selected for the study are given in Figure 1B. Two sites with sulfur content greater than the action criterion were also included in the selected sites to provide a comparison. Table 1 shows the site locations of the soil cores recovered for the leaching experiment.

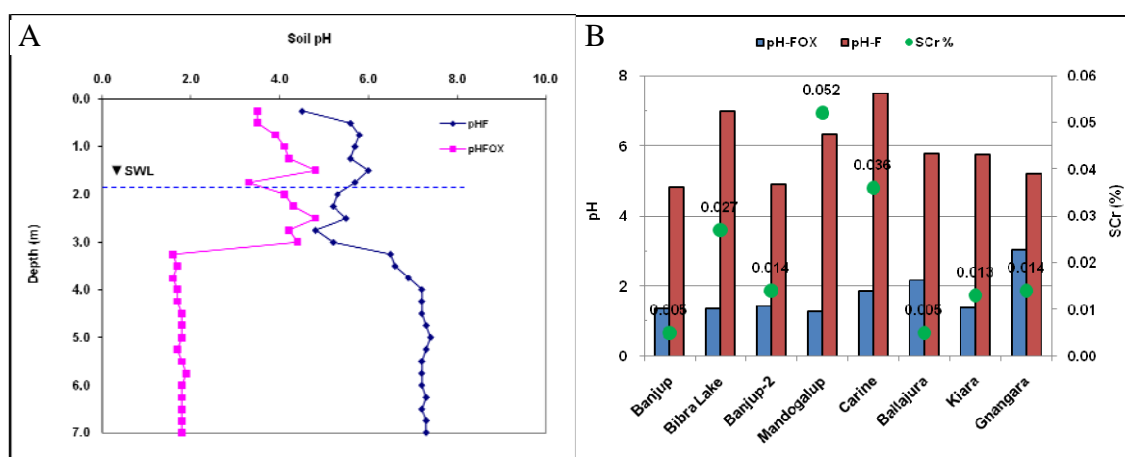


Figure 1 (A) A typical pH profile of a site selected for column studies. (B) Sulfur content,  $\text{pH}_{\text{F}}$  and  $\text{pH}_{\text{FOX}}$  of soil materials selected for column studies.

Soil samples were typically recovered by coring down to 8m below natural surface using a sonic direct push soil coring system to obtain a continuous 85 millimetres (mm) diameter soil core. The soil cores were inserted directly into transparent polyethylene sleeves and logged using recommended ASS investigation methods. These procedures involved description of lithology, textures, colours (including identified mottling using the 2000 edition Munsell Soil colour charts), concretions, consistency, organic materials and the depth of standing water table if encountered.

Soil core materials were analysed in the field for pH in water ( $\text{pH}_{\text{F}}$ ) and peroxide pH ( $\text{pH}_{\text{FOX}}$ ) at depth intervals of 0.25m. A one metre section (at least) of the undisturbed soil core which recorded low  $\text{pH}_{\text{FOX}}$  value was retained for the study. The selected section was sealed and refrigerated in the field to minimise oxidation during transportation.

## 2.2 Chemical and physical characterisation

The results of  $\text{pH}_F$  and  $\text{pH}_{\text{FOX}}$  measurements in soil profiles were used to select soil zones for further laboratory analysis using both the Suspended Peroxide Oxidation Combined Acidity and Sulfur (SPOCAS) and Chromium Reducible Sulfur ( $S_{\text{CR}}$ ) analytical suites for sulfur content and acid-base accounting.

Representative soil samples were taken from profile zones where  $\text{pH}_{\text{FOX}}$  values were below 3.0. The selected samples were placed in air-tight zip lock bags and air was excluded to the maximum possible extent before closing each zip lock. The sample bags were kept in field refrigerators for transport to the laboratory. Soil chemical properties were determined by Australian Laboratory Services (ALS) using procedures as described in the 'Australian Laboratory Handbook of Soils and Water Chemical Methods' (Rayment and Higginson, 1992).

The  $S_{\text{CR}}$  analysis excludes mono-sulfidic materials as the samples are often exposed to oxygen during sample handling and preparation. Actual acidity was determined from measurements of pH ( $\text{pH}_{\text{KCl}}$  determined in 1M KCl extracts). This method takes account of acidity contributed by cation exchange sites, organic matter and soluble acidity. These are obviously not accounted for by simple pH measurement which determines soluble  $\text{H}^+$  (AS 4969.4-2008)).

Detailed characterisation of the chemistry and mineralogy of the soil materials was carried out in the laboratories of the University of Western Australia using procedures outlined by Prakongreep et al (2011).

## 2.3 Oxidation and leaching procedure

Oxidation and leaching of selected soil cores was conducted in plastic columns of 80mm diameter and 1,000mm length. The columns were held upright by a vertical wooden board fitted on to a metal frame (Figure 2), and kept in a glasshouse at a room temperature of between 20°C and 25°C. The bottom end of the columns was fitted with a closable outlet for draining and recharging the soil columns during the experiment.

The weight of the empty column was determined so that the soil weight could be calculated. Each column was filled with the selected section of the soil core by sliding the core material from the top while gently tapping the column.

The outlet at the bottom of the columns was kept open during the oxidation phase to facilitate soil draining under gravity. The leachate was collected in plastic containers for volumetric measurement and chemical analysis. At the end of the desired oxidation period, the columns were re-saturated with deionised water through the bottom outlet using a pressure head equal to top of the soil column. It took about three days to saturate the columns. Once all columns were saturated, a period of 24 hours was allowed to let the deionised water equilibrate with the soil solution before the columns were drained to commence the next oxidation phase. The length of the oxidation phase varied on the basis of leachate analysis as the study progressed.



## 2.4 Leachate analysis

Leachate samples collected from all of the cycles were analysed for pH, EC and titratable acidity. In addition, leachate samples from the 2<sup>rd</sup>, 3<sup>th</sup>, 4<sup>th</sup> and 7<sup>th</sup> cycles were analysed for alkalinity, total dissolved salts, sulfate, chloride, total and dissolved forms of Al, Fe, Ca, Mg, Na, K, Zn, Cu, Mn, Cr, Se, Cd and nutrient elements. Leachate samples were filtered through 0.45µm filter membrane prior to submission to Analytical Reference Laboratory (ARL) for analysis.



*Figure 2. A photograph of the experimental set for oxidation and leaching of soil columns.*

## 3 Results and discussion

The sulfur content of the selected sites varied from 0.005%S to 0.052%S and the numbers assigned to each site were based on the increasing sulfur content. Six sites recorded sulfur content below the current action criterion (0.03%S) while the remaining sites are marginally above the action criterion. It should be noted that the analysis close to the laboratory detection limit at 0.005%S can vary by up to 50%. Site location and basic properties of the selected cores are shown in Table 1.

Table 1. Site description of eight soils used for the column leaching experiment.

| Site   | Suburb     | Depth<br>(cm) | Texture    | Colour        | pH <sub>F</sub> | pH <sub>FOX</sub> | S <sub>CR</sub><br>(%) | CEC<br>meq/100g |
|--------|------------|---------------|------------|---------------|-----------------|-------------------|------------------------|-----------------|
| Site 1 | Ballajura  | 4.3-5.5       | Loamy sand | Brown         | 5.8             | 2.2               | 0.005                  | 2.94            |
| Site 2 | Banjup     | 2.4-4.0       | Sand       | Brown         | 4.8             | 1.4               | 0.005                  | 5.72            |
| Site 3 | Kiara      | 4.8-6.0       | Loamy sand | Greyish brown | 5.8             | 1.4               | 0.013                  | 2.77            |
| Site 4 | Banjup     | 4.5-6.0       | Sand       | Greyish brown | 4.9             | 1.4               | 0.014                  | 0.37            |
| Site 5 | Gnangara   | 6.3-7.9       | Sand       | Grey          | 5.2             | 3.0               | 0.014                  | 0.46            |
| Site 6 | Bibra Lake | 4.5-6.0       | Sand       | Brown         | 7.0             | 1.3               | 0.027                  | 0.37            |
| Site 7 | Carine     | 4.3-6.0       | Sand       | Grey          | 7.5             | 1.9               | 0.036                  | 0.40            |
| Site 8 | Mandogalup | 6.3-7.8       | Sand       | Dark grey     | 6.3             | 1.3               | 0.052                  | 0.21            |

The pH<sub>FOX</sub> profile for all the sites are shown in Figure 3 and the section of each profile marked by a red bar in the figures was used for the oxidation in the column experiments. Soil materials with sulfur content below or just above the action criterion can produce pH<sub>FOX</sub> values close to 2, which suggest that these soils could potentially become very acidic if allowed to oxidise. The pH<sub>FOX</sub> field screening may be a useful screening method for a quick estimation of equilibrium pH after natural oxidation of soil materials. The results discussed below show how well pH<sub>FOX</sub> values approximate the soil pH after natural oxidation in air.

### 3.1 Leachate flow rate and volume

The soil columns were packed with minimal soil disturbance to provide sufficient soil drainage and oxidation following each leaching cycle. Leachate flow rates, measured for the initial cycle, are shown in Figure 4. There are differences in the volume of leachate released from the columns in the first few hours after the addition of deionised water in each leaching cycle. The difference in flow rate could be attributed to the densely packed pockets in the soil columns, particularly at the base of the columns, which controlled the water release rate. The total volume leached from each column was also measured for all cycles. This data showed that 10-17% porosity was generated as a result of free drainage over several days, which is considered sufficient to promote pyrite oxidation. The differences in soil porosity are likely to affect the rate of acidification rather than the final extent of acidity. The soil column experiment was conducted over a year to minimise the effect from the differences in oxidation kinetics on the end point acidity as indicated by the lowest oxidation pH and cumulative titratable acidity of the leachate from each column.

### 3.2 Leachate electrical conductivity

Electrical conductivity (EC) was measured for the first four leaching cycles, as shown in Table 2. During the first leaching cycle, the leachate EC varied from 7mS/cm to 70mS/cm. The Gngara site had a very low EC value compared to other sites. This is due to the highly leached nature of the sandy soils in the higher topographic setting on the Gngara mound where the watertable has declined to more than 5m below ground level. The EC values dropped dramatically after the first cycle and remained consistently low (less than 5mS/cm) in subsequent cycles, indicating that most of the soluble salts had been leached in the first leaching cycle. Some of the sites had very low initial EC and retained similar values throughout the study period.

Table 2. Electrical conductivity expressed as mS/cm of leachate from soil columns.

| Site   | 1 week | 3 weeks | 16 weeks | 28 weeks |
|--------|--------|---------|----------|----------|
| Site 1 | 60     | 0.3     | 0.5      | 0.8      |
| Site 2 | 60     | 0.1     | 1.0      | 0.3      |
| Site 3 | 60     | 2.4     | 2.4      | 1.9      |
| Site 4 | 1.9    | 2.3     | 2.6      | 1.1      |
| Site 5 | na     | 0.2     | 0.2      | 0.2      |
| Site 6 | 70     | 0.5     | 3.2      | 1.7      |
| Site 7 | 1.4    | 3.0     | 5.4      | 4.1      |
| Site 8 | 50     | 0.4     | 3.7      | 2.3      |

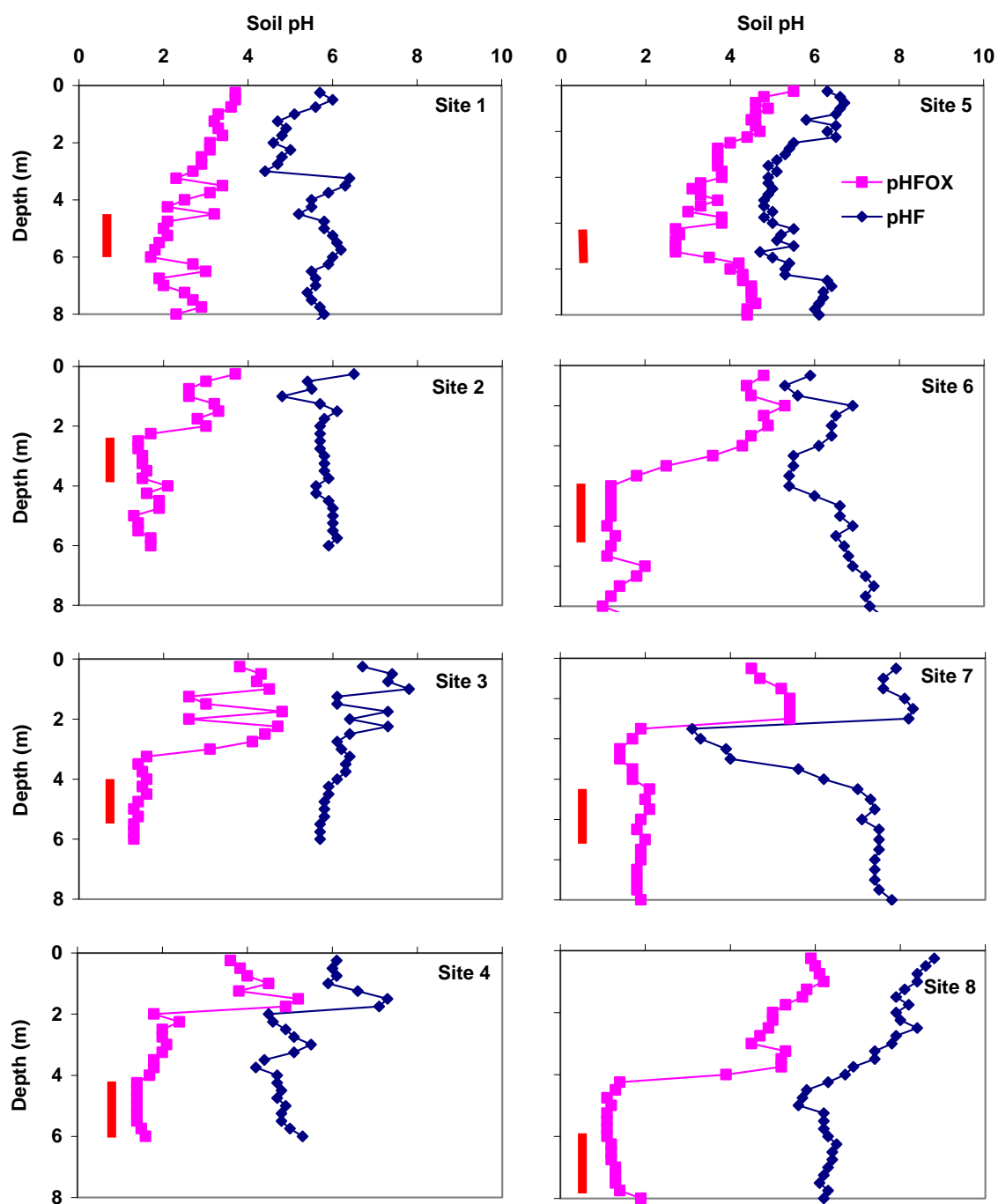


Figure 3. Field  $pH_F$  and  $pH_{FOX}$  determined in water and 30% hydrogen peroxide. Note: red vertical bars indicate section of soil profile used in the column experiment.

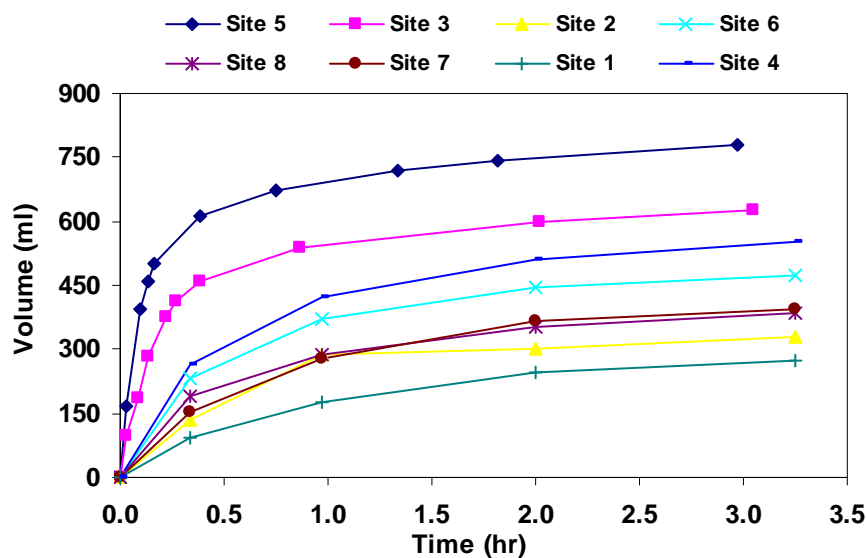


Figure 4. Leachate flow rates for all soil columns measured for 3 hours after the addition of deionised water

### 3.3 Leachate pH

Histograms of  $\text{pH}_{\text{FOX}}$ ,  $\text{pH}_{\text{F}}$ , and leachate pH for each of the seven cycles are shown in Figure 5. The first and second bars represent  $\text{pH}_{\text{FOX}}$  and  $\text{pH}_{\text{F}}$  respectively. The rest of the bars represent leachate pH for the subsequent cycles over time.

With the exception of Site 2 and Site 5, the study found that leachate pH for most sites declined to a range from 1.8 to 3.3 after 48 weeks and no further reduction in pH was observed. A minimum leachate pH equivalent to the initial field  $\text{pH}_{\text{FOX}}$  was attained from the core from Site 7 (Carine).

Leachate pH for Site 2 remained unaffected for the first five cycles but declined to 4 in the last two cycles. Had the experiment continued it may have declined further. This profile contains significant amount coffee sand/rock materials, comprising complex amorphous material primarily of hydrous aluminosilicate (largely allophane) and organic matter. The presence of this material is indicated by field colour, cation exchange capacity and extractable Al and Fe (Table 3). It is considered that dissolution of amorphous aluminosilicate buffered the pH decline for these soils. The gel like amorphous material might have protected the pyrite from oxidation during the experiment. However, as discussed below, the total titratable acidity of these soils remained unaffected by the presence of amorphous aluminosilicate.

The soil column for Site 5 (Gnangara) also displayed minimal leachate pH decline. However, it should be noted that the soils from Gnangara are highly leached, resulting in negligible acid producing materials being retained within the soil profiles in this area.

Leachate pH from all the sites with sulfur content less than the current action criterion declined to well below 4. Site 1 with measured  $\text{pH}_{\text{FOX}}$  2 and Scr 0.005% S, recorded a final leachate pH of 3.2, while leachate pH from Site 6, Site 4 and Site 3 all registered below 3. Site 7 and 8 with sulfur content above the action criterion also produced leachate with pH less than 3.

In summary, natural oxidation of Bassendean sand with sulfur content below the current action criterion generated acidic leachate with pH in the range of 2 and 3. Although slightly higher than

the  $pH_{FOX}$ , the leachate pH is extremely low and could trigger a number of secondary environmental problems.

### 3.4 Titratable acidity

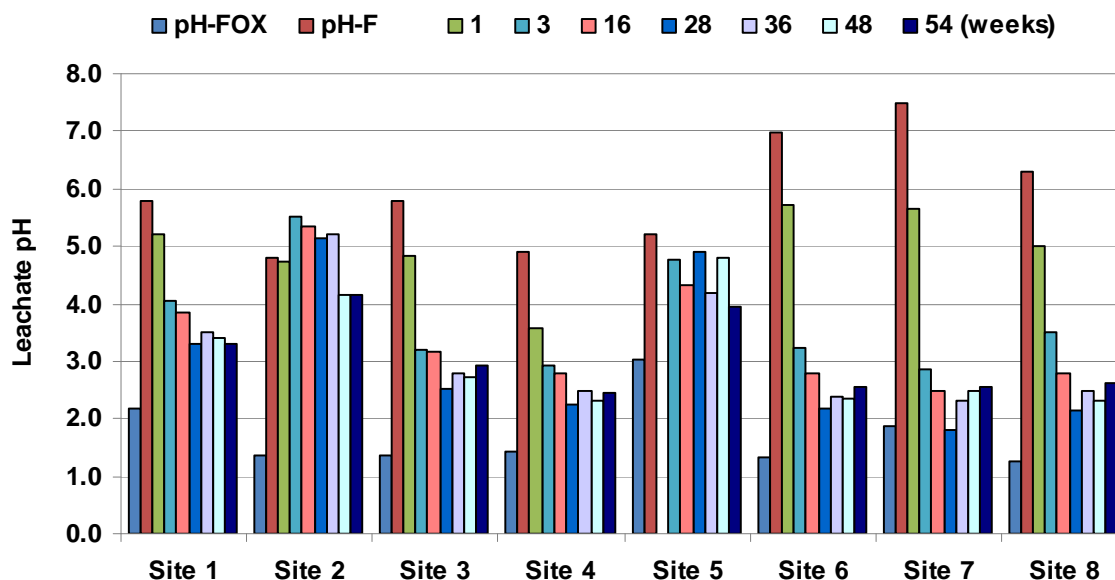


Figure 5. Leachate pH for all sites measured after the indicated oxidation period. The first and second columns represent  $pH_F$  and  $pH_{FOX}$  respectively.

Titrate acidity (TA) provides a measure of total acidity in a solution by titrating it with sodium hydroxide to a point close to neutrality. It is commonly expressed in units of the equivalent mass of calcium carbonate required per unit of solution. The baseline TA at landscape scale on the BDS is about 30mg  $CaCO_3/l$ , and DEC guidelines require neutralisation of dewatering effluent with acidity less than 40mg  $CaCO_3/l$ . Values of titratable leachate acidity for each cycle are presented in Figure 6. The TA for first cycle leachate is generally similar to the baseline for the area as the soils remain largely in un-oxidised state during this period. This is also reflected by only a small reduction in pH.

However, in subsequent leaching cycles, TA increased sharply to reach levels several times greater than the Department of Environment and Conservation action trigger for dewatering effluent management. Increases in TA values corresponded with decreases in leachate pH measured in the columns from all sites, including those with sulfur content less than 0.03%. The measured TA values demonstrate that Bassendean sands with  $pH_{FOX}$  less than 3 are likely to discharge acidity in excess of DEC recommended TA criterion for managing dewatering effluent quality even though their sulfur content was lower than the current action criteria.

Table 3. Amount of aluminium and iron extracted by dithionite citrate bicarbonate (d); oxalic acid (ox) and Na-pyrophosphate (p) for whole wet soil samples\* (in  $mg\ kg^{-1}$  unit).

| Site   | $Al_d$ | $Al_{ox}$ | $Al_p$ | $Fe_d$ | $Fe_{ox}$ | $Fe_p$ |
|--------|--------|-----------|--------|--------|-----------|--------|
| Site 1 | 1223   | 826       | 1098   | 1711   | 1417      | 1133   |
| Site 2 | 1021   | 2208      | 4392   | 237    | 274       | 350    |
| Site 3 | 190    | 173       | 327    | 128    | 113       | 208    |
| Site 4 | 28     | 27        | 31     | 121    | 117       | 171    |
| Site 5 | 92     | 90        | 311    | 230    | 196       | 153    |
| Site 6 | 46     | 43        | 378    | 229    | 242       | 309    |
| Site 7 | 154    | 68        | 101    | 699    | 355       | 522    |
| Site 8 | 51     | 40        | 135    | 304    | 247       | 365    |

Values of cumulative acidity for leachate from each soil column, expressed as equivalent mgCaCO<sub>3</sub>/kg soil in the column, are shown in Figure 7. Values of the total acidity released in 7 leaching cycles, expressed in units of equivalent sulfur content, are compared with sulfur levels measured by chemical analysis in Table 4.

Cumulative titratable acidity values for Sites 1, 2 and 5 showed comparatively lower values ranging from 19 to 34mg/kg. With the exception of Site 5, the S<sub>CR</sub> values for these sites were at or below the detection limit at 0.005%S.

Soils from Sites 3, 4, 6, 7 and 8 showed values of cumulative acidity ranging from 388mg/kg to 1130mg/kg soil CaCO<sub>3</sub>. Site 7 released the greatest amount of acidity followed by Sites 3, 4, 8 and 6. Soil material from Site 8 contained the highest S<sub>CR</sub> at 0.05% S followed by Sites 7, 6, 4 and 3 (Table 1). Samples from Site 1 and 2 contained very low S<sub>CR</sub> values (0.005% S), which is reflected in the relatively high leachate pH and low titratable acidity. Site 6 and 4 had S<sub>CR</sub> values less than regulatory action criteria at 0.03% S, yet produced leachate with a high titratable acidity.

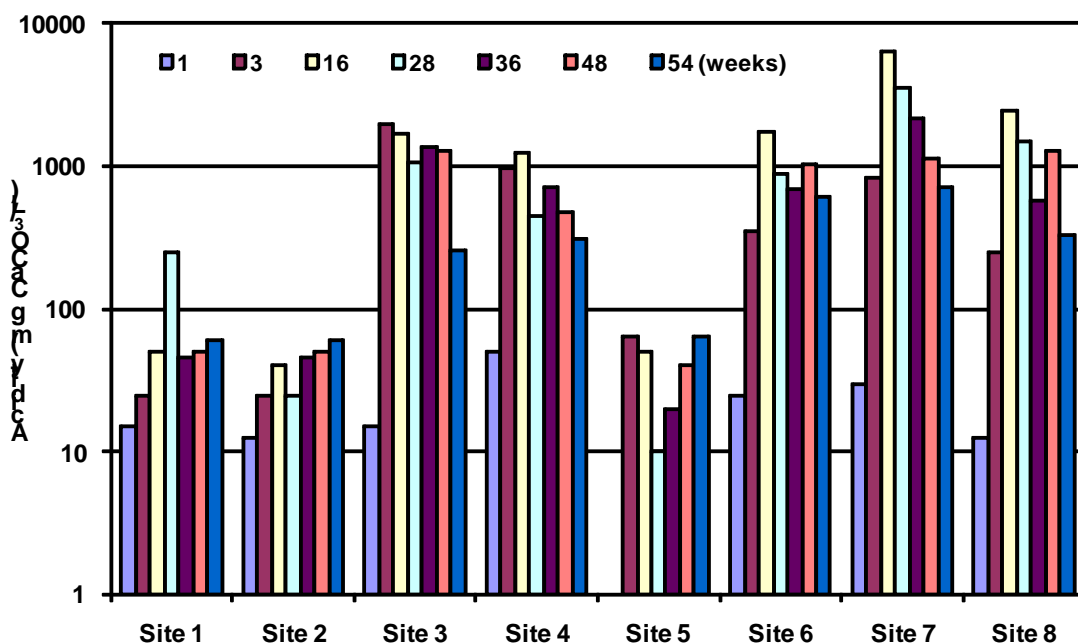


Figure 6. Leachate titratable acidity for all sites measured after the indicated oxidation period.

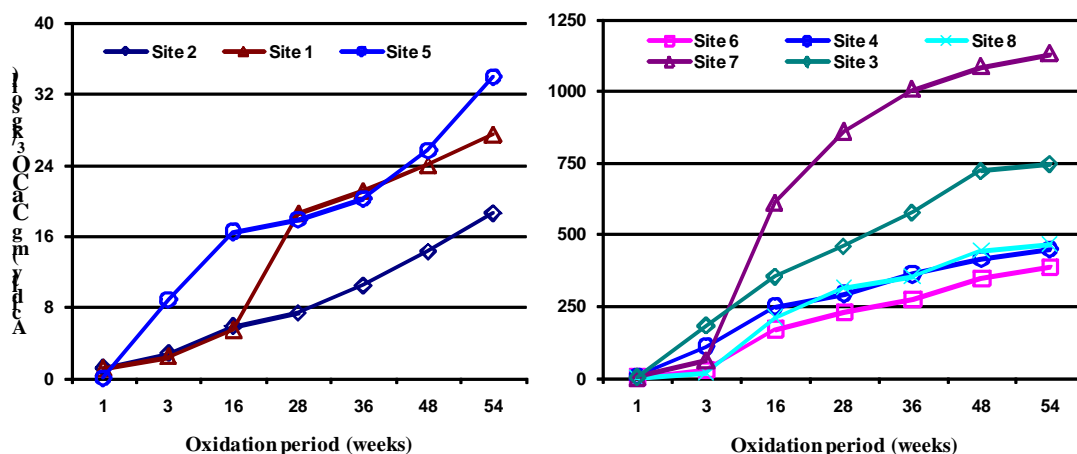


Figure 7. Cumulative amounts of titraable acidity released in seven leaching cycle over a 54 week period.

Sites 3, 4 and 6 had  $S_{CR}$  analyses below the current action criterion but released amounts of cumulative acidity ranging from 348mg to 722mg/kg equivalent  $CaCO_3$ , and produced leachate with a pH less than 2.5. Although Site 3 had a lower  $S_{CR}$  value than Site 6 and Site 4 (Table 1), it recorded higher amounts of TA. These inconsistencies are attributed to errors in sulfur analyses which have a large analytical variation close to the detection limit (0.005%).

The remaining two sites, Site 7 and 8, contained sulfur levels greater than the current action criterion and produced leachates with high TA values and an acidic pH of around 2.0.

Table 4. Amount of sulfur oxidised over a 54 week period calculated from titratable acidity.

| Site   | $S_{CR}$<br>% S | pH <sub>F</sub> | pH <sub>FOX</sub> | Leachate<br>pH | TA<br>mg $CaO_3$ /kg | TA<br>%S | Sulfur<br>oxidised<br>% |
|--------|-----------------|-----------------|-------------------|----------------|----------------------|----------|-------------------------|
| Site 1 | <0.005          | 5.8             | 2.2               | 3.3            | 28                   | 0.0008   | 18                      |
| Site 2 | 0.005           | 4.8             | 1.4               | 4.1            | 19                   | 0.0005   | 12                      |
| Site 3 | 0.013           | 5.8             | 1.4               | 2.5            | 748                  | 0.023    | 184                     |
| Site 4 | 0.014           | 4.9             | 1.4               | 2.3            | 449                  | 0.013    | 100                     |
| Site 5 | 0.014           | 5.2             | 3.0               | 4.0            | 34                   | 0.0008   | 8                       |
| Site 6 | 0.027           | 7.0             | 1.3               | 2.2            | 388                  | 0.011    | 46                      |
| Site 7 | 0.036           | 7.5             | 1.9               | 1.8            | 1130                 | 0.035    | 100                     |
| Site 8 | 0.052           | 6.3             | 1.3               | 2.2            | 466                  | 0.014    | 29                      |

### 3.5 Leachate chemistry

In addition to pH, EC and TA analysis, leachate samples collected after 3, 16, 28 and 54 weeks were analysed for selected metals and anions to characterise the chemical reactions occurring during soil oxidation. The highest concentrations of dissolved metals were observed for the 4th leaching cycle carried out at the 28 week period when leachate pH values were at their lowest. Concentrations of Al, Fe,  $SO_4$  and TDS for the 4th cycle are given in Table 5 along with leachate pH and TA. The remaining data for all analytes are provided in Appendix 1.

Table 5. Dissolved chemical constituents measured in leachate after 28 weeks of oxidation.

|        | pH  | TA<br>mg $CaCO_3$ /l | TDS   | $SO_4$ | Cl<br>mg/l | Al  | Fe  |
|--------|-----|----------------------|-------|--------|------------|-----|-----|
| Site 1 | 3.3 | 250                  | 560   | 190    | 5          | 1.2 | 0.7 |
| Site 2 | 5.1 | 25                   | 550   | 400    | 5          | 0.2 | 0.3 |
| Site 3 | 2.5 | 1050                 | 3200  | 2300   | 5          | 240 | 5.6 |
| Site 4 | 2.2 | 450                  | 2200  | 1500   | 5          | 40  | 46  |
| Site 5 | 4.9 | 10                   | 150   | 58     | 5          | 0.9 | 0.3 |
| Site 6 | 2.2 | 875                  | 3000  | 2100   | 5          | 45  | 110 |
| Site 7 | 1.8 | 3500                 | 11000 | 4900   | 5          | 190 | 710 |
| Site 8 | 2.1 | 1465                 | 3900  | 2800   | 5          | 150 | 130 |

The Al content in leachate samples for the investigated sites ranged from 1.2 to 240mg/L (Table 5) after 3 weeks of oxidation. Leachate samples for Sites 1, 2 and 5 contained generally lower levels of Al (~1.0mg/L) which is consistent with their relatively high leachate pH and low TA values. The high Al content for Site 3 in the early stages (three weeks) may be due to the presence of coffee rock which contains amorphous aluminosilicate minerals as a cementing material. As can be seen in Table 5, some of the sites that contained  $S_{CR}$  values less than 0.03%S (Sites 1, 3, 4 and 6) produced leachate with soluble Al in concentrations well above 1mg/L.

Iron concentrations in the leachate samples largely show a pattern similar to Al. Leachate samples for Sites 1, 2 and 5 contained generally low levels of Fe (~1.0mg/L), while the remaining



sites, including those with Scr values less than 0.03, leached Fe concentrations at much higher levels.

Table 6. Correlation coefficient matrix for a selected group of leachate analytes

|          | Iron  | TA    | Sulfate | TDS   | Aluminum | pH    |
|----------|-------|-------|---------|-------|----------|-------|
| Iron     | 1.00  | 0.92  | 0.86    | 0.95  | 0.57     | -0.53 |
| TA       | 0.92  | 1.00  | 0.99    | 0.98  | 0.83     | -0.73 |
| Sulfate  | 0.86  | 0.99  | 1.00    | 0.96  | 0.87     | -0.76 |
| TDS      | 0.95  | 0.98  | 0.96    | 1.00  | 0.79     | -0.66 |
| Aluminum | 0.57  | 0.83  | 0.87    | 0.79  | 1.00     | -0.70 |
| pH       | -0.53 | -0.73 | -0.76   | -0.66 | -0.70    | 1.00  |

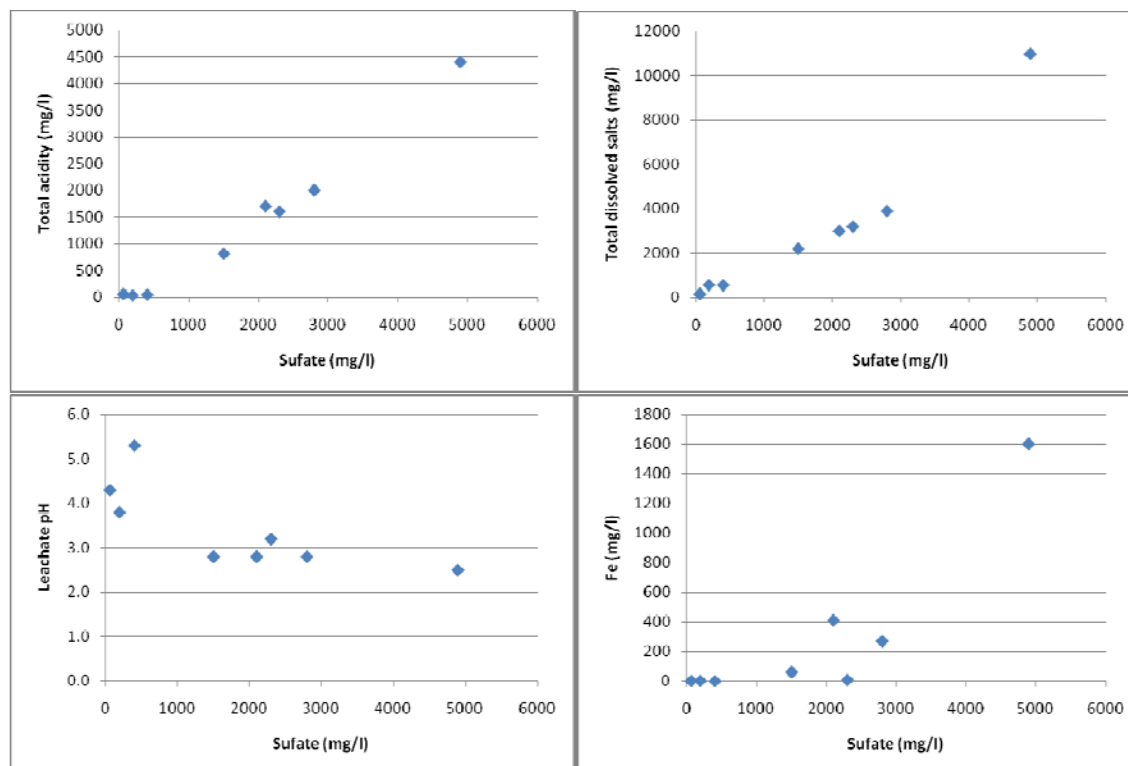


Figure 8. Plots of sulfate concentration against total acidity, total dissolved salts, leachate pH and Fe concentrations.

Total dissolved salts and  $\text{SO}_4$  also showed a pattern similar to that of Al and Fe concentrations (Table 5), while Cl concentrations were below detection limit for all leachates. It appears that chloride ions had been leached out in previous leaching cycles, and relatively high concentrations of sulfate are the result of pyrite oxidation in the preceding oxidation cycle.

Plots of  $\text{SO}_4$  against leachate pH, TA, TDS and Fe are shown in Figures 8, and a correlation coefficient matrix for Al, Fe,  $\text{SO}_4$ , TA, pH and TDS are given in Table 6. A strong correlation of  $\text{SO}_4$  with TDS and TA demonstrates that sulfate, a reaction product of pyrite oxidation, is a significant component of the dissolved salt load in the leachate. The Al and Fe concentrations also strongly correlate with  $\text{SO}_4$ . While Fe is a direct reaction product of pyrite oxidation, Al concentrations are probably linked through the dissolution of aluminosilicate minerals by  $\text{H}^+$  released by pyrite oxidation. The elevated levels of these leachate parameters and their correlations provide strong evidence of pyrite oxidation during the experiment for all sites, including those with a sulfur content less than 0.03%.

## 4 Conclusions

This study focused on the vulnerability of the Bassendean sands to acidification even though their sulfur contents were generally considered low. Soil samples from six out of a total of eight targeted sites had sulfur content below 0.03%S and  $\text{pH}_{\text{FOX}}$  values that were less than 3. The study also assessed the reliability of the  $\text{pH}_{\text{FOX}}$  values to predict extreme soil acidification under natural oxidising conditions.

The leachate from soil columns with sulfur content less than the action criterion declined to well below pH 4. Site 1, with  $\text{pH}_{\text{FOX}}$  2 and Scr 0.005%S, recorded a leachate pH of 3.2, while the leachate pH for Sites 3, 4 and 6 was well below 3. Two other sites with sulfur content above 0.03%S produced the expected acidic leachate pH of less than 3. Only one soil column leachate (Site 2) recorded a relatively smaller decline in leachate pH and this could be attributed to some minor buffering provided by amorphous organic-aluminosilicate complexes. With the exception of one column that had coffee rock materials, the leachate pH values from all the leaching columns were generally about one unit greater than their initial field  $\text{pH}_{\text{FOX}}$  values.

Titrateable acidity values from soil column leachate were significantly greater than the baseline groundwater value generally around 30 mg  $\text{CaCO}_3/\text{l}$ . The strong correlations between concentrations of sulfate, TA, leachate pH, TDS, Fe and Al suggest that sulfide oxidation is the most likely cause of acidic leachate. This observation confirmed that sandy soils with low sulfur content (less than 0.03%S) have the potential to generate acidity through inappropriate soil disturbances.

However, the current texture-based criterion developed by Ahern et al (1998) for sand to sandy loamy soils containing up to 5% clay may not be appropriate for Bassendean sand. Bassendean sands have less than 1% clay and are extremely porous to oxidation when disturbed. On this basis, it is recommended that a separate action trigger may be required for Bassendean sands with low sulfur content and low  $\text{pH}_{\text{FOX}}$  values.

Findings from this study suggest that sandy soils with low  $\text{pH}_{\text{FOX}}$  values (less than 3) in the Perth metropolitan area and a detectable sulfur content of less than 0.03%S have the potential to acidify when exposed to air through inappropriate dewatering or other soil disturbing activities. It should be noted that the  $\text{pH}_{\text{FOX}}$  test takes into account the potential acidity as well the natural soil buffering capacity, providing an approximation of the net acidity in poorly buffered soils.

From the results of the experimental study it can reasonably be assumed that  $\text{pH}_{\text{FOX}}$  values are a good indicator of extreme soil oxidation for Bassendean sands that have negligible acid buffering capacity.

# Appendix 1A: Base line soil solution chemistry

|                    | Detection Limit | Yokine          | Whiteman        | Banjup          | Bedford         | Baldavis        | BibraLake       | Wandi           |
|--------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| S <sub>CR</sub>    | 0.005           | 0.005           | 0.005           | 0.005           | 0.009           | 0.016           | 0.027           | 0.180           |
| Al                 | 0.01            | less than 0.001 | 0.030           | 0.001           | 0.002           | 0.001           | 0.006           | less than 0.001 |
| As                 | 0.001           | 32              | 14              | 3.1             | 59              | 6.9             | 60              | 38              |
| Ca                 | 0.1             | less than 0.002 | less than 0.002 | less than 0.002 | less than 0.002 | less than 0.002 | less than 0.002 | less than 0.002 |
| Cd                 | 0.001           | less than 0.01  | less than 0.01  | 0.02            | less than 0.01  | less than 0.01  | 0.01            | less than 0.01  |
| Cr                 | 0.001           | less than 0.01  | less than 0.01  | less than 0.01  | less than 0.01  | less than 0.01  | 0.01            | less than 0.01  |
| Co                 | 0.01            | less than 0.01  | less than 0.01  | less than 0.01  | 0.01            | less than 0.01  | 0.01            | less than 0.01  |
| Cu                 | 0.001           | 0.01            | 0.18            | 0.16            | 0.09            | 0.04            | 0.01            | 0.10            |
| Fe                 | 0.01            | 6.0             | 4.6             | 3.2             | 12              | 5.0             | 3.8             | 8.4             |
| K                  | 0.1             | 13              | 9.3             | 3.6             | 9.8             | 5.4             | 6.9             | 25              |
| Mg                 | 0.1             | less than 0.01  | 0.10            | less than 0.01  | 0.03            | 0.13            | 0.01            | 0.12            |
| Mn                 | 0.01            | 105             | 54              | 54              | 130             | 63              | 47              | 120             |
| Na                 | 0.1             | less than 0.01  | less than 0.01  | less than 0.01  | less than 0.01  | less than 0.01  | less than 0.01  | less than 0.01  |
| Ni                 | 0.001           | less than 0.01  | less than 0.01  | less than 0.01  | less than 0.01  | less than 0.01  | less than 0.01  | less than 0.01  |
| Pb                 | 0.001           | less than 0.001 | less than 0.001 | less than 0.001 | less than 0.001 | less than 0.001 | less than 0.001 | less than 0.001 |
| U                  |                 | 0.05            | 0.12            | 0.41            | 0.06            | 0.26            | 0.04            | 0.13            |
| Zn                 | 0.005           | 56              | less than 5     | less than 5     | 68              | 110             | 110             | 10              |
| Alkalinity         | 5               | 56              | less than 5     | less than 5     | 68              | 110             | 110             | 10              |
| Bicarbonate        | 5               | less than 5     | less than 5     | less than 5     | less than 5     | less than 5     | less than 5     | less than 5     |
| Carbonate          | 5               | less than 5     | less than 5     | less than 5     | less than 5     | less than 5     | less than 5     | less than 5     |
| Hydroxide          | 5               | 175             | 56              | 52              | 160             | 75              | 86              | 200             |
| Chloride           | 5               | 92              | 78              | 17              | 130             | 16              | 21              | 140             |
| Sulphate           | 3               | 47              | 43              | 854             | 117             | 608             | 22              | 138             |
| DOC                | 0.2             | less than 0.2   | 0.7             | 0.6             | less than 0.2   | 0.3             | less than 0.2   | less than 0.2   |
| Ammonia-N          | 0.2             | 1.4             | less than 0.01  | less than 0.01  | less than 0.01  | 0.25            | less than 0.01  | 0.01            |
| NO <sub>x</sub> -N | 0.01            | less than 0.01  | less than 0.01  | less than 0.01  | less than 0.01  | less than 0.01  | less than 0.01  | 0.02            |
| Reactive P         | 0.01            | 3.1             | 0.27            | 0.16            | 1.2             | 7.2             | 0.24            | 1.5             |

# Appendix 1B: Leachate chemistry

| <b>March-2010</b> | <b>Site 1</b> | <b>Site 2</b> | <b>Site 3</b> | <b>Site 4</b> | <b>Site 5</b> | <b>Site 6</b> | <b>Site 7</b> | <b>Site 8</b> |        |
|-------------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|--------|
| Al                | 0.01          | 0.09          | 0.75          | 210           | 42            | 1.2           | 8.5           | 22            | 1.1    |
| As                | 0.001         | 0.001         | 0.001         | 0.001         | 0.001         | 0.004         | 0.001         | 0.018         | 0.001  |
| Ca                | 0.1           | 31            | 6.8           | 66            | 290           | 3.9           | 100           | 460           | 150    |
| Cd                | 0.001         | 0.0001        | 0.0001        | 0.0002        | 0.0001        | 0.0001        | 0.0002        | 0.0057        | 0.0001 |
| Cr                | 0.001         | 0.002         | 0.005         | 0.007         | 0.027         | 0.003         | 0.001         | 0.12          | 0.006  |
| Fe                | 0.01          | 0.34          | 0.37          | 140           | 240           | 0.34          | 120           | 340           | 33     |
| K                 | 0.1           | 3.8           | 3.7           | 7.5           | 4.6           | 1.1           | 3.1           | 11            | 11     |
| Mg                | 0.1           | 8.2           | 2.9           | 60            | 34            | 5.2           | 8.9           | 61            | 40     |
| Mn                | 0.01          | 0.15          | 0.02          | 0.16          | 1.6           | 0.03          | 0.31          | 5.6           | 0.17   |
| Na                | 0.1           | 27            | 23            | 30            | 82            | 30            | 7.0           | 20            | 8.0    |
| Ni                | 0.001         | 0.005         | 0.008         | 0.99          | 0.41          | 0.001         | 0.063         | 0.43          | 0.19   |
| Se                | 0.001         | 0.001         | 0.001         | 0.001         | 0.001         | 0.001         | 0.002         | 0.001         | 0.001  |
| Zn                | 0.005         | 0.17          | 0.14          | 0.23          | 0.80          | 0.40          | 0.12          | 0.37          | 0.17   |
| pH                |               | 4.7           | 5.2           | 2.2           | 2.2           | 3.5           | 2.3           | 2.0           | 2.3    |
| Total Acidity     |               | 28            | 530           | 1800          | 1000          | 140           | 440           | 1700          | 260    |

| <b>June-2010</b> |       |       |       |       |       |       |       |       |       |
|------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Al               | 0.01  | 0.36  | 0.38  | 330   | 140   | 0.46  | 90    | 330   | 210   |
| As               | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 |
| Ca               | 0.1   | 39    | 38    | 22    | 100   | 9.9   | 110   | 220   | 190   |
| Cd               | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.014 | 0.051 | 0.005 |
| Cr               | 0.001 | 0.002 | 0.004 | 0.006 | 0.11  | 0.003 | 0.076 | 2.3   | 0.075 |
| Fe               | 0.01  | 2.2   | 0.46  | 7.7   | 61    | 1.7   | 410   | 1600  | 270   |
| K                | 0.1   | 2.6   | 4.5   | 4.3   | 2.0   | 0.4   | 2.0   | 5.1   | 10    |
| Mg               | 0.1   | 11    | 64    | 20    | 15    | 7.5   | 12    | 48    | 62    |
| Mn               | 0.01  | 0.08  | 0.19  | 0.03  | 0.46  | 0.02  | 0.25  | 0.99  | 0.16  |
| Na               | 0.1   | 26    | 51    | 17    | 52    | 9     | 13    | 14    | 16    |
| Ni               | 0.001 | 0.002 | 0.001 | 0.19  | 0.32  | 0.002 | 0.16  | 0.57  | 0.36  |
| Se               | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 |
| Zn               | 0.005 | 0.006 | 0.012 | 0.047 | 0.38  | 0.006 | 0.16  | 0.50  | 0.16  |
| pH               | -     | 3.0   | 4.2   | 7.8   | 4.5   | 7.0   | 3.8   | 3.4   | 6.5   |
| Conductivity     | -     | 0.94  | 0.74  | 3.7   | 1.6   | 0.25  | 0.68  | 6.7   | 2.6   |
| Alkalinity       | 5     | 5     | 12    | 5     | 5     | 12    | 5     | 5     | 5     |
| Bicarbonate      | 5     | 5     | 12    | 5     | 5     | 12    | 5     | 5     | 5     |
| Carbonate        | 5     | 5     | 5     | 5     | 5     | 5     | 5     | 5     | 5     |
| Hydroxide        | 5     | 5     | 5     | 5     | 5     | 5     | 5     | 5     | 5     |
| Total Acidity    | 5     | 27    | *     | 1600  | 810   | *     | *     | 4400  | 2000  |
| Chloride         | 5     | 29    | 29    | 18    | 66    | 14    | 9     | 15    | 14    |
| Sulphate         | 3     | 190   | 400   | 2300  | 1500  | 58    | 2100  | 4900  | 2800  |
| TDS              | 5     | 560   | 550   | 3200  | 2200  | 150   | 3000  | 11000 | 3900  |

| <b>September-2010</b> |       |        |        |        |        |        |        |       |        |
|-----------------------|-------|--------|--------|--------|--------|--------|--------|-------|--------|
| Al                    | 0.01  | 1.2    | 0.24   | 240    | 40     | 0.9    | 45     | 190   | 150    |
| As                    | 0.001 | 0.001  | 0.001  | 0.001  | 0.001  | 0.001  | 0.001  | 0.19  | 0.001  |
| Ca                    | 0.1   | 48     | 13     | 10     | 28     | 3.3    | 57     | 100   | 110    |
| Cd                    | 0.001 | 0.0001 | 0.0001 | 0.0002 | 0.0002 | 0.0001 | 0.0010 | 0.032 | 0.0018 |
| Cr                    | 0.001 | 0.003  | 0.002  | 0.013  | 0.15   | 0.004  | 0.084  | 2.4   | 0.19   |
| Fe                    | 0.01  | 0.71   | 0.34   | 5.6    | 46     | 0.34   | 110    | 710   | 130    |
| K                     | 0.1   | 3.0    | 4.0    | 3.1    | 0.8    | 0.3    | 1.2    | 1.0   | 1.7    |
| Mg                    | 0.1   | 13     | 29     | 14     | 4.0    | 4.4    | 5.1    | 25    | 29     |
| Mn                    | 0.01  | 0.27   | 0.15   | 0.02   | 0.20   | 0.02   | 0.16   | 0.71  | 0.12   |
| Na                    | 0.1   | 14     | 13     | 9.7    | 13     | 2.8    | 4.7    | 4.0   | 7.3    |
| Ni                    | 0.001 | 0.010  | 0.001  | 0.34   | 0.29   | 0.001  | 0.12   | 0.47  | 0.42   |
| Se                    | 0.001 | 0.001  | 0.001  | 0.001  | 0.001  | 0.001  | 0.001  | 0.004 | 0.001  |
| Zn                    | 0.005 | 0.028  | 0.028  | 0.071  | 0.19   | 0.012  | 0.13   | 0.37  | 0.14   |

|               |   |     |     |      |     |     |     |      |      |
|---------------|---|-----|-----|------|-----|-----|-----|------|------|
| pH            | - | 4.3 | 5.2 | 3.5  | 3.2 | 6.2 | 3.0 | 2.8  | 2.9  |
| Total Acidity | - | 180 | 37  | 1700 | 460 | 140 | 740 | 2700 | 1500 |
| Alkalinity    | 5 | 5   | 5   | 5    | 5   | 13  | 5   | 5    | 5    |
| Bicarbonate   | 5 | 5   | 5   | 5    | 5   | 13  | 5   | 5    | 5    |
| Carbonate     | 5 | 5   | 5   | 5    | 5   | 5   | 5   | 5    | 5    |
| Hydroxide     | 5 | 5   | 5   | 5    | 5   | 5   | 5   | 5    | 5    |

**March-2011**

|               |       |        |        |        |        |        |        |        |        |
|---------------|-------|--------|--------|--------|--------|--------|--------|--------|--------|
| Al            | 0.01  | 0.81   | 1.5    | 20     | 11     | 2.2    | 43     | 56     | 27     |
| As            | 0.001 | 0.001  | 0.001  | 0.001  | 0.001  | 0.001  | 0.001  | 0.021  | 0.001  |
| Ca            | 0.1   | 34     | 12     | 2.8    | 11     | 9.1    | 10     | 20     | 12     |
| Cd            | 0.001 | 0.0001 | 0.0001 | 0.0001 | 0.0001 | 0.0001 | 0.0004 | 0.0087 | 0.0002 |
| Cr            | 0.001 | 0.001  | 0.002  | 0.005  | 0.09   | 0.001  | 0.080  | 0.24   | 0.030  |
| Fe            | 0.01  | 0.55   | 0.36   | 3.7    | 26     | 0.81   | 24     | 41     | 11     |
| K             | 0.1   | 33     | 2.1    | 0.5    | 0.4    | 0.2    | 0.3    | 0.4    | 0.2    |
| Mg            | 0.1   | 5.0    | 14     | 0.8    | 1.2    | 3.0    | 1.1    | 4.6    | 2.4    |
| Mn            | 0.01  | 0.31   | 0.12   | 0.01   | 0.07   | 0.08   | 0.04   | 0.20   | 0.02   |
| Na            | 0.1   | 4.7    | 7.1    | 0.7    | 5.2    | 0.8    | 1.1    | 0.7    | 1.0    |
| Ni            | 0.001 | 0.007  | 0.002  | 0.033  | 0.079  | 0.005  | 0.029  | 0.092  | 0.047  |
| Se            | 0.001 | 0.001  | 0.001  | 0.001  | 0.001  | 0.001  | 0.001  | 0.001  | 0.001  |
| Zn            | 0.005 | 0.015  | 0.018  | 0.014  | 0.051  | 0.010  | 0.036  | 0.067  | 0.017  |
| pH            | -     | 3.5    | 4.5    | 3.2    | 2.7    | 4.1    | 2.8    | 2.8    | 2.9    |
| Conductivity  | -     | 0.40   | 0.25   | 0.50   | 1.0    | 0.15   | 1.1    | 1.3    | 0.88   |
| Alkalinity    | 5     | 5      | 5      | 5      | 5      | 5      | 5      | 5      | 5      |
| Bicarbonate   | 5     | 5      | 5      | 5      | 5      | 5      | 5      | 5      | 5      |
| Carbonate     | 5     | 5      | 5      | 5      | 5      | 5      | 5      | 5      | 5      |
| Hydroxide     | 5     | 5      | 5      | 5      | 5      | 5      | 5      | 5      | 5      |
| Chloride      | 5     | 5      | 5      | 5      | 5      | 5      | 5      | 5      | 5      |
| Sulphate      | 3     | 140    | 120    | 190    | 260    | 60     | 470    | 770    | 290    |
| TDS           | 5     | 200    | 160    | 300    | 530    | 90     | 630    | 780    | 530    |
| Total Acidity | 5     | 31     | *      | 220    | 320    | 24     | 490    | 670    | 320    |
| Ammonia-N     | 0.2   | 0.2    | 0.2    | 0.2    | 1.3    | 0.2    | 0.2    | 0.2    | 0.2    |
| NOx-N         | 0.01  | 0.01   | 0.01   | 0.01   | 0.01   | 0.01   | 0.01   | 0.01   | 0.01   |
| Nitrate-N     | 0.01  | 0.01   | 0.01   | 0.01   | 0.01   | 0.01   | 0.01   | 0.01   | 0.01   |
| Total N       | 0.2   | 0.2    | 1.0    | 0.2    | 1.8    | 0.2    | 0.2    | 0.3    | 0.2    |
| Reactive P    | 0.01  | 0.01   | 0.01   | 0.01   | 0.02   | 0.01   | 0.01   | 0.01   | 0.01   |
| Total P       | 0.01  | 0.01   | 0.01   | 0.01   | 0.22   | 0.01   | 0.01   | 0.12   | 0.01   |