

Abstract

Surface pH and chloride measurements, microbiological assays and analysis of distilled water washings from the rocks on the Burrup Peninsula of Western Australia have been made. Data were collected during a hot dry winter, warm moist spring and desiccating extreme summer temperatures. Natural buffering of the rock surfaces by wind-borne sea salts minimizes the impact of microbiological processes. There is a direct link between nitrate ion concentration, bacterial populations and the surface pH, which is interdependent on the amount of moisture. The mechanisms for dissolution of minerals containing aluminium, iron, copper and zinc have been established.

Keywords

rock engravings, micronutrients, microbiological activity, acidification, conservation

Effects of moisture, micronutrient supplies and microbiological activity on the surface pH of rocks in the Burrup Peninsula

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Introduction

The removal of hundreds of engraved rocks from the sites destined for industrial development associated with the onshore gas processing facilities in the Pilbara region of Western Australia occurred in the early 1980s. Where possible the rocks were relocated to a fenced open-air compound and they have remained there for more than 20 years. The impending development of several nearby major industries, producing a range of petrochemical products, necessitated a detailed 'pre-disturbance' survey of the microenvironment of the rocks in the compound to establish the background microenvironment and condition of the rocks.

Method

The microenvironment of the rocks was assessed through a combination of surface chloride (Orion combination Cl electrode) and surface pH (BDH Gelplas flat electrode) measurements on the rock surfaces. A weak electrolyte solution of 0.05 M NaNO₃ in distilled water was used for chloride measurements and the pH was recorded after equilibration with two to three drops of distilled water on the rock surface. The soluble nitrate, nitrite, sulphate, chloride, oxalate concentrations on the rock surfaces were determined by ion chromatography from 15 ml samples of distilled water washings collected from the rock surfaces and standardized to a 200 cm² area. Metal ions in the wash solutions were determined by inductively coupled plasma-mass spectrometric (ICP-MS) methods. Microbiological analyses were determined under standard laboratory conditions from the previously sterilized 2 ml pentone solutions that had been inoculated with cotton wool swabs collected from 20 cm² areas on the rock surfaces and stored in sterile ice-cold conditions (King 2003). This study is based on an initial survey in June 2003 (winter) of relocated engraved rocks which was then extended in August 2003 (spring) to include several sites located at a distance from known emission sources was concluded in February 2004 (summer) with repeated measurements on the Burrup. The location of the sites is shown in Figure 1.

Results and discussion

Anions in wash solutions

Analyses from the three field trips showed that only two reference rocks in the collection of the Western Australian Museum had measurable amounts of oxalate ions, C₂O₄²⁻, which were 1.8 mg/l from Enderby Island (B7477) and 0.7 mg/l from Happy Valley (B2494) in the Burrup. So oxalate does not appear to have a significant present role in biodeterioration on the Burrup. The amounts of surface chloride detected on the rock surfaces provide direct evidence of the impact of the marine environment and indicate that salt weathering of rocks, with extensive dehydration and rehydration cycles playing a significant role in the local environment. The wash solutions from the rock surfaces showed up a range of ions commonly associated with sea water, namely Na⁺, K⁺, Mg²⁺, Ca²⁺, SO₄²⁻ and Cl⁻. Analysis of the way in which the concentrations varied across the Burrup

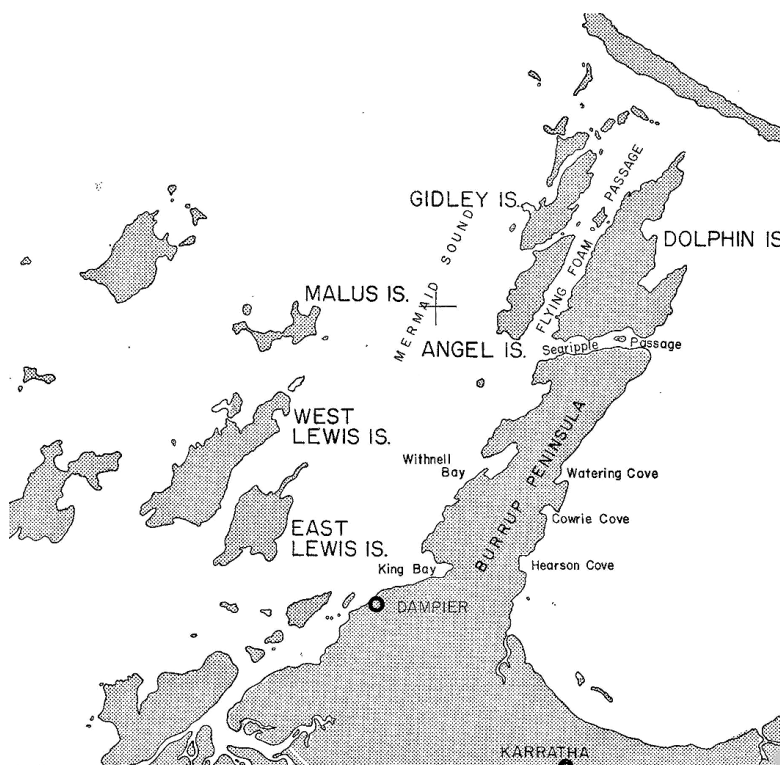


Figure 1. Location map of the Burrup Peninsula, Pilbara Region, Western Australia

was consistent with known weather patterns, prevailing winds and proximity to the sea. When the wash concentrations of sulphate are plotted as a function of the chloride, most of the data follow a linear relation that reflects the common ratios of the anions that are found in seawater. The activity of chloride ions on Burrup rocks is lower than would have been expected on the basis of the analytical concentrations in sea salt; this is likely due to strong adsorption of chloride by the iron minerals such as lepidocrocite ($\gamma\text{FeO.OH}$), which are known to be capable of holding up to 18 per cent (by mass) chloride in their crystal lattice (North 1982). Lowered sulphate activities are associated with the presence of significant amounts of calcareous inclusions on the rock surfaces, which tend to 'trap' free sulphate as gypsum. Analysis of the wash data also confirms that the major source of magnesium ions is from the deposition of sea salts.

Mobilization of metal cations from parent rocks

Analysis of the wash solutions from the three sets of measurements has shown up significant concentrations of aluminium, iron, manganese, nickel, copper and some zinc and lead from the parent rocks. Because the mineralogy of the highly weathered gabbro and granophyre is characterized by a series of mixed amorphous iron–manganese oxides, in the form of desert varnish, iron(III) oxyhydroxides and weathered minerals such as smectite, kaolinite, illite and mica (Clark 2004) it is not unexpected to find mobilization of metallic cations under the acidic conditions. When metal hydroxides are mobilized by acid dissolution according to Equation (1)



the concentration of the metal ions can be expressed by the formula

$$\text{pM}_{\text{OH}} = (\text{pK}_s - n\text{pK}_w) + n\text{pH}, \quad (2)$$

where pM is the negative value of the log of the metal ion concentration, pK_w has the value of 14 and pK_s is the negative of the log of the solubility product. For metal oxides of the general formula M_xO_y , the concentration of the metal

ions is given by the relationship

$$pM_{\text{oxides}} = \frac{1}{x} p(K_s + \gamma pH). \quad (3)$$

Plots of the values of $p[M^{n+}]$ vs. pH can elucidate the nature of the species being dissolved. The more acidic surfaces in the spring and summer measurements were amenable to this form of analysis and plots for iron showed that for both seasons the $p[\text{Fe}]$ vs. pH plots have an average slope of $+1.98 \pm 0.06$ pH which confirms the following mechanism:



The Pourbaix diagram for iron in the range of pH observed on the rock surfaces shows that the $\text{Fe}(\text{OH})^{2+}$ ion is the dominant form of soluble iron(III) under oxidizing conditions. The intercept values at zero pH ranged from -9.0 to -7.3 , which are more negative than the -2.6 for $\text{Fe}(\text{OH})_3$ (Figure 2). Similar plots indicate that copper is mobilized by dissolution reactions involving two protons per metal ion as is the case for nickel. Similar plots for the solubility of aluminium with surface pH had an average slope of $+1.4$ pH, which is consistent with the dissolution of kaolinite to give the $\text{Al}(\text{OH})^{2+}$ ion and $\text{AlSi}_2\text{O}_5^+$, as shown in Equation 5. Kaolinite has been identified as one of the aluminium containing minerals on the Burrup rocks along with feldspar, chlorite, mica, smectite and some gibbsite (Clark 2004).

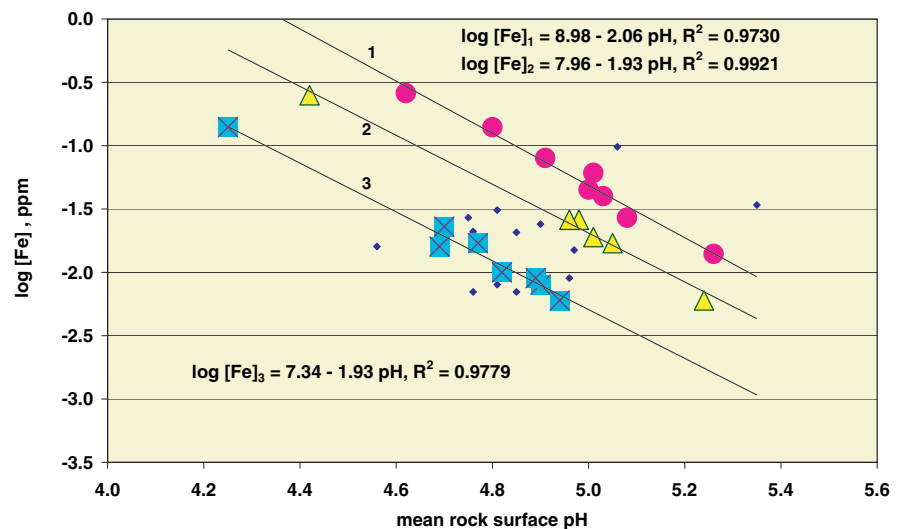
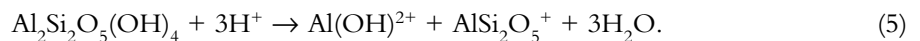


Figure 2. Solubility of iron on Burrup rocks as a function of pH

It is not unexpected for aluminium ions to have been mobilized under the very mild sample collection regime that was used. The dissolution of manganese species from the solid phase is more complex because the only stable ionic species in the pH range of 4.0–5.5 is the Mn^{2+} ion and the average slope is 0.75. This probably reflects other oxide-containing species being involved in the mobilization, because dissolving higher oxides to provide Mn^{2+} ions involves redox processes that are commonly facilitated by fungi that reduce Mn(IV) species to Mn^{2+} ions (Gadd 2004). There is a direct increase in the manganese ions in the wash solution with increasing acidity of the rock surfaces.

Nitrate and nitrite

The mean concentration of nitrate ions for the winter of 2003 was 1.2 ± 0.3 mg/l; the spring data were higher at 6.3 ± 5.1 mg/l, with values ranging from a maximum of 19 mg/l at Withnell Bay (adjacent to the Woodside plant) to 1.4

± 0.1 at Burrup SW 1–2 in the Pistol Ranges and at King Bay 1. The lower mean summer concentration of nitrate was 4.3 ± 2.5 mg/l, if the maximum of 22 mg/l recorded at Dolphin Island 3 is considered to be atypical because of the presence of nearby animal (euro) scats. The summer maximum was 9.2 mg/l on rock 938 in the compound and the minimum value of 1.3 mg/l was recorded at Deep Gorge 3. Nitrite, as an indicator of atmospheric NO_x , was only found in the spring washings. The museum reference rock from Enderby Island B7477 had a very high nitrate level of 44 mg/l, which is possibly related to animal droppings whereas the other pre-industrialization rock B2494 from Happy Valley had a background level of 0.3 mg/l of nitrate, which is typical of normal anthropogenic background materials.

Surface pH

More than 750 surface pH measurements were taken on rocks in the Burrup Peninsula over the three sets of field measurements. In general, the acidity of the rocks from all areas was greater than the pH of 6.8 ± 0.2 found on the reference specimens from the museum collection. That the acidity is associated with chemical and or biological activity on the upward-facing rock surfaces was indicated by the more alkaline values of the ground facing surfaces, which had a mean pH of 5.84 ± 0.85 (37 sets of data) compared with a mean of 5.28 ± 0.64 from 110 sets of upward-facing rocks. The higher standard deviation of the underneath surfaces is due to soil contamination as several of the rocks were over a midden area, which recorded a maximum pH of 7.43. Most of the surface ^{winter}pH values fall between the range 4.25–5.75. The most acidic rock in June 2003 (pH 3.58) was found down in a gully a few hundred metres downwind from the gas production facility; it was also the most acidic site (pH 3.04) in August, but some other rocks were more acidic than the summer value of pH 3.61 in February 2004. It appears that the relocation of the rocks did not change the surface chemistry of the exposed faces because the winter survey established that there was no statistical difference between the mean pH of rocks in the compound ($\text{pH}_{\text{yard}} = 5.46 \pm 0.49$) and those of the surrounding areas, which had a mean $\text{pH}_{\text{outside yard}} = 5.38 \pm 0.68$. Reproducibility of the pH data was checked in the spring (August 2003) by repeating the same sets of measurements on several pairs of adjacent rocks as well as at new sites that represented different rock types (see Figure 3 for data from Gidley Island). The spring pH measurements indicated that the overall acidity of the rocks had increased because the mean pH had fallen from 5.28 ± 0.64 (144 measurements) to 4.79 ± 0.43 (221 measurements).

When measurements were made in the summer of 2004 the mean pH (385 measurements) had increased slightly to 4.88 ± 0.40 but the best way to gauge the changing microenvironment is to look at specific rocks, rather than statistical averages. An example of the changes in pH of a rock in the compound is shown

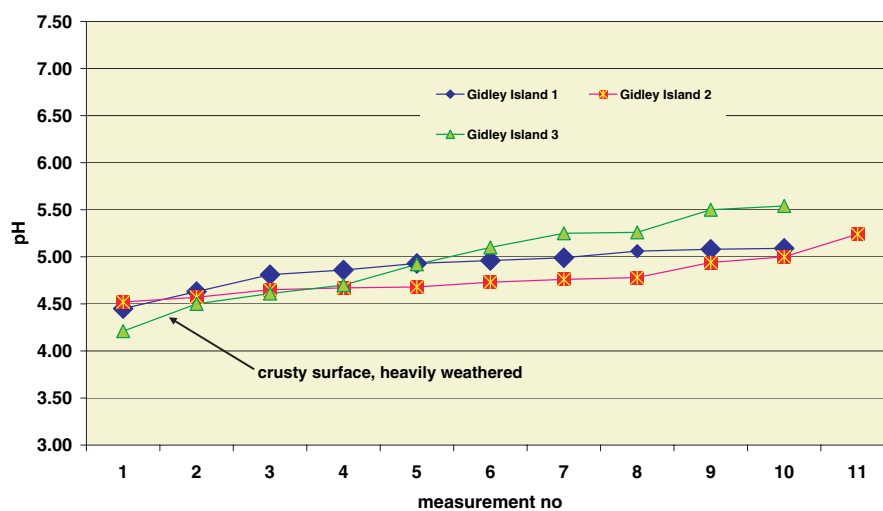


Figure 3. Surface pH measurements of rocks on Gidley Island, August 2003

in Figure 4, where the spring pH data are clearly the most acidic and the summer values are in between the winter and spring data. When 10 pH measurements are made on adjacent rocks of similar mineralogy and aspect, statistical analysis of the pH data shows that the results are highly reproducible. Thus differences in surface acidity are due to a combination of the underlying mineralogy, the microenvironment in terms of aspect and in terms of the amount of microflora present on the surfaces. It should be noted that the ranges of pH observed among the rocks in the compound fall within the general range of values from locations that represent the geological and chemical environments from which they were originally recovered. For example, rock 1681 is quite similar in pH to those rocks measured at King Bay, which is the region whence the rock was initially abstracted and brought to the compound.

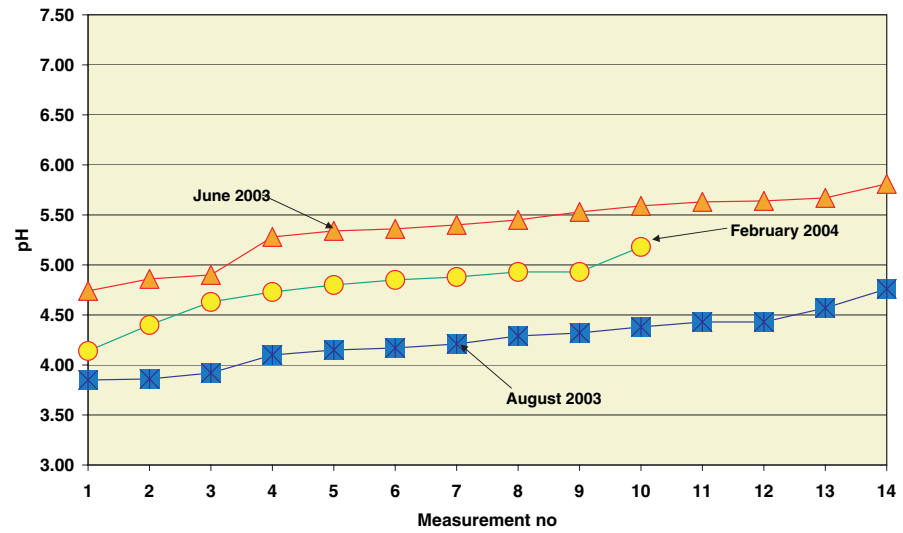


Figure 4. Surface pH of rock 1633 in the 'compound' as a function of time

The deposition of sea salt on the rock surfaces means that the carbonate and bicarbonate ions will tend to act as buffers and minimize any changes in the surface acidity resulting from a combination of microbiological and chemical reactions on the surfaces. This buffering reaction is demonstrated by the relation between the pH and chloride concentration on the rocks as shown in Equation 6

$$\text{pH}_{\text{mean}} = a + b [\text{Cl}^-]. \quad (6)$$

The general nature of Equation 6 was obtained by linear regression and the data from the three field measurement series generally showed up a common slope or dependence on [Cl] but with different intercepts, as shown in Table 1. The common buffering action of the sea salts is seen through the similarity of the slopes for all three seasons whereas the differences in the values of the intercepts are a reflection of the underlying mineralogy of the rocks and differences in the amount of biological activity.

Table 1. Relation between pH and chloride concentration on rock surfaces

Date	Intercept, <i>a</i>	Slope, <i>b</i>	R ²	Data points
June 2003	3.75	0.027	0.9994	3
August 2003	3.69	0.019	0.8862	5
February 2004	3.25	0.024	0.9914	3
	4.07	0.023	0.9938	7
	4.34	0.022	0.9650	7
	4.72	0.021	0.9890	5

Effect of nitrate ions on biological activity and pH

When the plate counts of the bacteria, yeasts, moulds and fungi were plotted as a function of pH there were simple linear relations found between the number

of microorganisms and the acidity of the rocks. It was apparent that a major source of acidity was likely to be associated with metabolites. The overall level of microbiological activity in the summer, with surface temperatures up to 54 °C, was much lower than during the spring temperatures of 37 °C and the winter of temperatures around 32 °C. The summer data indicated a general trend to less acidic values of the surface pH; most of the rocks were 'sterile' for the number of bacteria, but the overall level of activity of yeasts and moulds indicated that they have a greater viability in extreme temperatures. After an overnight summer thunderstorm, four sites were re-measured for pH, chloride and overall microbiological activity. The assays showed that the bacterial populations from previously 'sterile' sites were now active, that the counts of yeasts and moulds had increased and that the pH had decreased, as shown in Figure 5. Linear regression analysis supports the contention that there is a logarithmic increase in the number of bacteria per millilitre associated with linear increased nitrate concentrations, as shown in Equation 7

$$\log N_{\text{bacteria}} = a + b [\text{NO}_3^-]. \quad (7)$$

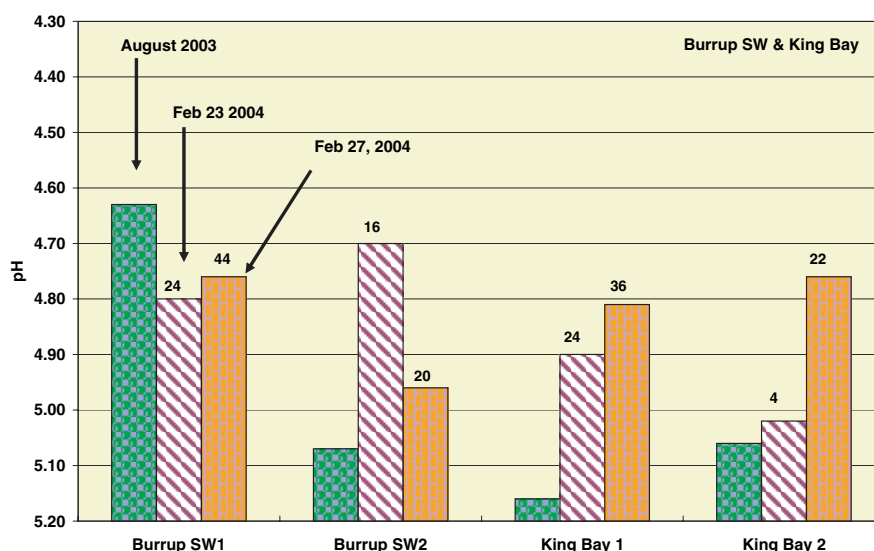


Figure 5. Distribution of pH as a function of a rain event, February 2004

The limited data from the winter measurements had a much higher slope than the common value of the spring and summer. A possible reason for the differences in the apparent sensitivity to nitrate concentration is that the experimental procedures used during the initial measurements were less rigorous in keeping the samples 'ice-cold' to prevent bacteria multiplying in the sterile medium before being counted. For rock 162 the intercept value of Equation 7 in August was 3.60 compared with 3.89 in the winter months; this difference shows that the winter has double the bacterial activity, which is probably due to the greater availability of moisture (Table 2).

Given the direct link between the surface pH and the number of bacteria per millilitre, as previously noted, and that there was a logarithmic relation between the counts of bacteria and the nitrate concentration, the dependence of the pH on nitrate was evaluated. Just as the winter data for the bacteria had a much greater dependence on nitrate, this was also reflected in the dependence of pH on nitrate for the same season, as shown in Table 3. Linear regression analysis of the pH and nitrate data from the three seasons followed a general relationship given by Equation 8

$$\text{mean}_{\text{pH}} = a - b [\text{NO}_3^-]. \quad (8)$$

Table 2. Regression analyses between log of the bacteria per millilitre and nitrate concentration

Date	Intercept, a	Slope, b	R ²	Data points	Rocks
June 2003	3.89	1.34	0.9770	5	3, 86, 162, 975, 1690
August 2003	3.60	0.17	0.9157	7	KB1, NWB, BPSW1, CM1, CM1-2, 162, 1233
	2.89	0.17	0.9859	5	
	2.60	0.16	0.9567	3	DI, DG1, DG2, CM2, OFS KB2, DG2-2, 1681
February 2004	3.12	0.16	0.9735	6	BSW1R, DGA, DGB high, DGC, CM1B, 975

Table 3. Relation between mean pH and nitrate ion concentration

Date	Intercept, a	Slope, b	R ²	Data points	Rocks
June 2003	5.77	-0.46	0.5610	6	DG2, CM1, 86, 162, 975, 1681
August 2003	5.26	-0.084	0.6123	9	DW1, KB2, COS, BPSW1, WB, 86, 162, 938, 1233
	4.83	-0.086	0.6123	4	NWB, DG1, 975, 1681
February 2004	5.58	-0.076	0.9902	7	KB2, CM2B, DI3, 162, 1014, 1586
	5.21	-0.088	0.9042	8	BPSW2, KB1, DG3, 86, 97, 975, 1233, 1681
	5.04	-0.096	0.9763	7	BPSW1R, BPSW2R, KB1R, WB1, NWB2, GI 1, GI 2
	4.85	-0.093	0.9608	8	DW1, BPSW1, NWB1, DG1, DG2, DI 3, 3, 938
	4.61	-0.096	0.9364	6	DW2, CM1, CMF, OFS8, GI 3, DI 2
	4.13	-0.097	0.9396	5	CM1B, CMVB, CM2A, OFS1

When consideration is given to the common geology of the rock surfaces, it was found that the 41 data points from the summer measurements all had the same dependence on nitrate as was found in the spring data, with a mean value 0.0910 ± 0.0083 and the intercept or pH at zero nitrate concentration ranging from 5.58 to 4.13. The relation between the values of the intercept is illustrated in the data for rock 975, where the zero nitrate pH varied from 5.77 (nitrate 1.0 mg/l) in winter, to 5.21 (nitrate 2.6 mg/l) in summer, and the most acidic value was a pH of 4.83 in spring when the nitrate was 4.3 mg/l. This implies that some other environmental factors are affecting the pH. Unpublished studies by the author indicate that both bacterial as well as yeast, mould and fungal counts are also influenced by sulphate concentrations. Acidic metabolites are associated with the mould *Aspergillus niger*, which was identified on several sites in the Burrup (Arthur 2004); and fungi are commonly reported as being major players in the bioweathering of rocks and minerals (Burford et al. 2003).

Conclusion

Comparison of reference rocks from museum collections and the current pH of engraved rock surfaces and associated rocks indicates that the current microenvironment of the Burrup Peninsula is more acidic than before industrialization. Preliminary studies indicate that the level of microbiological activity is strongly associated with the amount of soluble nitrate ions on the rock surfaces but the source of the nitrate has not been established. Wind-borne sea salts are routinely deposited on the rocks, and the alkaline nature of the salts tends to act as a buffer to changes induced as a result of microbiological activity. The overall level of biological activity is seen to be very dependent on the availability of moisture, which is significantly reduced during the desiccating extremes of summer heat.

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