Surface chemistry of Burrup Rock art at the Yara monitoring sites

Report for Yara Pilbara Nitrates by
CBG Solutions

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Figure 1: View of the TAN plant from site

Contents

Executive Summary

- Measurements in September 2018 were conducted on gabbro sites (7, 22 & 23) and granophyre sites (5, 6 & 21) with the sites determined through the CSIRO monitoring program. An additional set of measurements were taken adjacent to the CSIRO site 4.
- In addition to the surface pH and chloride, the redox voltages were measured and the Pourbaix plots of the voltage vs. pH have established new decay mechanisms which are dominated by manganese solution chemistry
- There was no soluble iron detected in any of the washed rock surfaces.
- There is a correlation of increased colour difference between the engravings and the host rock with the differences in minimum pH between 2017 and 2018 values.
- Twenty-four sets of measurements of colour show that nearly 80% show NO colour difference between 2017 and 2018. The differences are only definite for 8% of the assessment points.
- The only site with a measurable amount of boron in the wash solution was for the Water Tanks which shows there is not a problem with mobilisation of chlorite.
- Prolonged dry spells lead to accumulation of wind-borne sea salts which resist acidification.
- A downpour in June 2018 reduced the amount of soluble chloride and nitrate. The lower concentration of nitrate appears to be biologically inhibiting due to buffering by NH_4^+/NH_3.
- The mean nitrate concentration in wash solutions was 6.3 ppm in 2003, 4.5 ppm in 2004 and 0.6 ppm in 2017 with a mean value of 0.7 ± 0.4 ppm for 2018.
- There is a need to continue surface measurements and washing of rocks to ensure that the sites are stable.
- There is a compelling need to conduct microbiome assessment of the microflora through DNA analysis to determine the nature of the colonising organisms.
- Data from the ASD spectrophotometer readings is yet to be quantified by others.

Background

To comply with the regulations concerning retention of its operating licence, EPBC 2008/4546, Yara Pilbara Nitrates engaged CBG Solutions to develop appropriate methodologies to conduct colour monitoring measurements on the six sites surrounding the ammonia and ammonium nitrate plants in the Burrup. The lead consultant (Warren Fish) conducted meetings with the management team from Yara to develop the time table and to engage with key community members of the Murujuga Aboriginal Corporation for permission to come to country September 2018 to repeat the colour measurements done in previous years by the CSIRO team. Owing to the inability of Bill Carr to attend a training session was undertaken by MacLeod who, with the assistance of Nigel Tonkin, conducted all the necessary spectral and colour measurements to provide relevant data for the assessment of the condition of the rock engravings. MacLeod retired from the Western Australian Museum in 2016 and is now the Principal of Heritage Conservation Solutions and has published peer-reviewed papers on the conservation of Aboriginal rock art and has 40-years' experience in materials conservation (Appendix I).

During the first phase (2003-2004) of research into the condition of the rock surfaces in the Burrup, several engraved rocks in the "Museum Compound" were examined regarding their acidity (as measured with a surface pH electrode), the water-soluble minerals on the rock surfaces and the microbiological activity. Samples of the rock surface were swabbed with sterile culture material and placed into prepared phials. The biological material was stored at zero degrees before being taken to laboratories in Perth (Department of Agriculture) for characterisation. Other reference measurements were conducted on Gidley and Dolphin Islands in the Dampier Archipelago to act as reference points away from industrial activities associated with the Woodside gas plant and iron ore shipping out of Dampier ports.

Analysis of the solution chemistry collected between 2003 and 2004 provided strong indications of the causal link between the amount of nitrate on the rocks and the level of microbiological activity. This in turn indicated that the acidic metabolites from the organisms were significantly contributing to the overall acidification of the rock surfaces and mobilisation of key minerals containing both iron and manganese, as well as copper and nickel. In the light of this background information it was decided to conduct solution sampling on the rock surfaces on the six CSIRO approved sites within the 2 km radius of the Pilbara Nitrates plant. The rock irrigation data was done in conjunction with surface measurements of the pH and chloride ion activity. The wash solutions were analysed for sulphate, sulphite, nitrate and nitrite ions, as well as for oxalate, of which there was none. The electrical conductivity of the wash solutions was also measured as a guide to the overall nature of the soluble minerals and salts that were mobilised during the five minutes of sample collection.

Field work was conducted on the six monitoring stations around the Yara plant in September 2018 and at an additional site 4 which is close to the service road near the Woodside old flare tower. This report includes commentary on the interpretation of the colour measurements from the Konica Minolta Chromameter. The sites are part of the CSIRO colour and mineralogy monitoring of the Burrup that has been undergoing continuous evaluation for the past 14 years. In addition to conducting the required ASD spectrophotometer readings, used to determine the mineralogy of the rock surfaces and that of the associated engravings, and the chromameter measurements, a series of pH, chloride and redox potential readings were taken directly on the rocks adjacent to the CSIRO monitoring points. In order to quantify the relationship between the surface chemistry, as measured by the contact with the flat surface pH and chloride electrodes, standard volumes of distilled water were used to temporarily irrigate (wash) the rocks, to collect the water-soluble metal ions and all discernible anions (chloride, nitrate, nitrite, oxalate, and sulphate). The refrigerated samples were stored off site until they were transported by air to the Bentley based laboratories of the ChemCentre for independent NATA accredited chemical analyses.

This report examines in detail the solution chemistry and provides a synthesis on the historical data relating to two sets of solution and surface pH measurements conducted in 13-14 years before the present work was conducted. The referenced sites of interest to Yara included granophyre at the Burrup Road (5), the Water Tanks (6) and Yara West (21) sites, while gabbro rocks were found on sites at Deep Gorge (7), Yara North East (22) and Yara East (23). All these sites lie within a 2 km radius of the present operational sites of the ammonia plant and the Technical Ammonium Nitrate (TAN) site. The additional site that was chemically assessed was number 4, adjacent to the Woodside plant about two hundred metres from the flare tower.

Measurement of the rock surface pH and chloride concentration

The pH and chloride ion measurements taken on rocks adjacent to the CSIRO reference engraved sites so that the colour reference rocks would be kept in a "pristine state" as requested by Bill Carr. The pH data was recorded using a flat surface pH electrode which had been calibrated each morning using standard pH buffers at pH 4 and pH 7 before the field measurements commenced. The pH meter was temperature compensated using a thermocouple connected to the Kensington Scientific pH meter (KS-pH-220-BASIC) and the glass electrode was a VWR model no W7567287. Readings of the surface pH were standardised by recording the values after an elapsed interval of one minute. If the surface was more responsive and the pH reading stabilised in 40 seconds, then that value was recorded and keeping the probe in position did not alter the steady value that had been noted. Owing to the porous nature of the rock substrate prolonged equilibration times can result in pH values that are not reflective of the local microenvironment. A small amount of water is needed to keep the bulb wet and the solution in contact with the internal reference electrode. The electrical circuit of the pH electrode is completed through connecting the internal Ag/AgCl reference electrode through two fine wicks which are situated at 180° to each other on either side of the glass membrane and held in place by the soft plastic ring fitting inside the 12-mm external diameter solid epoxy body. The chloride ion activity was measured using a TPS WP-90 ion-pH-mV-°C meter coupled with an Orion Thermo 1609-186881 chloride ion specific electrode. The rocks were wetted with two drops (0.08 ml) of a 0.05 molar sodium nitrate solution to provide an electrolyte to stabilise the liquid junction between the sensing head and the rock surface. Stable readings of the chloride activity were obtained within a minute. The electrode was calibrated daily with a 1,000 and a 100-ppm chloride reference solution before any field measurements were made.

Analysis of sea borne salts on the rocks

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 apparently 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^+, Mg^{2+}, Ca^{2+}, Cl^- and SO_4^{2-}. Analysis of the way in which the concentrations varied across the Burrup was consistent with known weather patterns of 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. Data from the most recent irrigation data obtained in September 2018 is shown in Table 1. Significant differences from the normal ratios found in seawater are found on the rock surfaces in the Burrup.

The microenvironment of the rocks was assessed through a combination of surface chloride (Orion Thermo combination Cl electrode) and surface pH (WVR flat electrode) measurements on the rock surfaces. The first round of measurements was made using a 0.05 M $NaNO_3$ solution in distilled water electrolyte was used for chloride measurements and the pH was recorded after equilibration with two to three drops (0.04-0.06 ml) 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 cm^2 area. Metal ions in the wash solutions were determined by inductively coupled plasma–mass spectrometric (ICP–MS) methods. 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. Data obtained for the 2017 measurements for cations measurements were made on 200 ml samples and anions in 100 ml sample bottles collected over an area of approximately 500 cm^2.

Table 1: Ratio of salts in sea water and in the rock washings around the Yara plant

Solution ratios	Seawater	Site 4 Gabbro	Site 5 Grano.	Site 6 Grano.	Site 7 Gabbro	Site 21 Grano.	Site 22 Gabbro	Site 23 Gabbro
Cl^-/Na^+	1.8	1.3	1.4	1.4	1.8	1.0	1.6	1.5
Cl^-/SO_4^{2-}	7.1	0.7	2.6	1.0	2.1	3.4	6.0	3.6
Cl^-/Ca^{2+}	47.0	1.4	7.0	1.0	2.8	7.7	9.0	4.5
Ca^{2+}/K^+	1.0	1.3	0.4	7.3	2.3	1.4	0.1	0.7
Ca^{2+}/Ba^{2+}	8,000	474	250	957	429	292	222	364
Mg^{2+}/Ca^{2+}	3.1	0.1	n.a.	0.1	0.2	0.6	n.a.	n.a.
Na^+/K^+	27.0	1.4	1.9	5.3	3.5	10.6	0.5	2.0

It is interesting to note that site 21 had the highest electrical conductivity at 4.0 mS/m which indicates that some sodium containing minerals are being removed with rain water, and this is also reflected in the highest Na^+/K^+ value of 10.6, while across the other sites the mean value was 2.4 ± 1.7. Examining the data from the Cl^-/Na^+ ratios gives a mean ratio of 1.4 ± 0.2 which is close to the 1.8 value for seawater, which is consistent with the bulk of the chloride ions coming from deposited sea salts. The much higher calcium content of the gabbro rock crust, 10.9±1.9% CaO, compared with the granophyre crust of 1.4±0.8 % CaO, is not reflected in the relative amounts of calcium to potassium in the wash solutions (Ramanaidou and Fonteneau, 2017). There does not appear to be any systematic difference in the cation ratios for salts derived from seawater than can be correlated with the different types of crusts that have typically formed on the two different types of rocks. The CSIRO analysis of the weathered crusts on granophyre rocks had 3.7 % Na_2O while the gabbro rocks had 1.9%, so some of the elevated sodium levels may be associated with a specific weathering pattern.

The mean Cl^-/SO_4^{2-} ratio for sites 4 and 6 had a mean value 0.8 ± 0.3 while all the other sites had a mean ratio of 3.5 ± 1.5, which is statistically significant. Lower chloride to sulphate ratios implies elevated sulphate at sites 4, close to the Woodside flare stack, and site 6, which is just over the low hills surrounding the Woodside plant. Both these sites also have significantly lower chloride to calcium ratios in solution (table 1) with a mean value of 1.2 ± 0.3 while the other five sites have ratios of 6.2 ± 2.5, which is statistically significant. This information indicates that some calcium minerals are being mobilised in these two locations. Data from the air monitoring sites at site 6 indicates that there is a direct relationship between the solution pH of the rainwater and the amount of soluble nitrate in solution, as given by the regression equation 1 viz.,

$$pH_{\text{rain water site 6}} = 5.86\ (0.25) - 0.94\ (0.40)\ [NO_3] \quad \text{..............................} \ (1)$$

This data is very valuable in that it shows the direct relationship of acidity of the rain water with the nitrate concentration in an inherently sterile condition i.e. without the complications of microflora and the minerals on the weathered rock surfaces. No systematic trend of rain water pH was found for the sites in Deep Gorge (site 7) or at the Burrup Road site (site 5). When the data was fitted to a quadratic expression the R^2 value improved from 0.73 to 0.99, as seen in Equation 2,

$$pH_{\text{rain water site 6}} = 6.42 - 5.55\ [NO3] + 3.51\ [NO3]^2 \quad \text{............................} \ (2)$$

The turning point for this relationship is around a nitrate concentration of 0.8 ppm, after which the increased nitrate loses the capacity to increase the acidity, due to competing equilibria. Inspection of the time plot of the rain water and the total nitrogen contents i.e. NO_3^-, NH_3 and NH_4^+ shown in Figure 2 for the air monitoring station near site 6 shows that the reason why the acidity began to curve back was due to the buffering capacity of the ammonia/ammonium system.

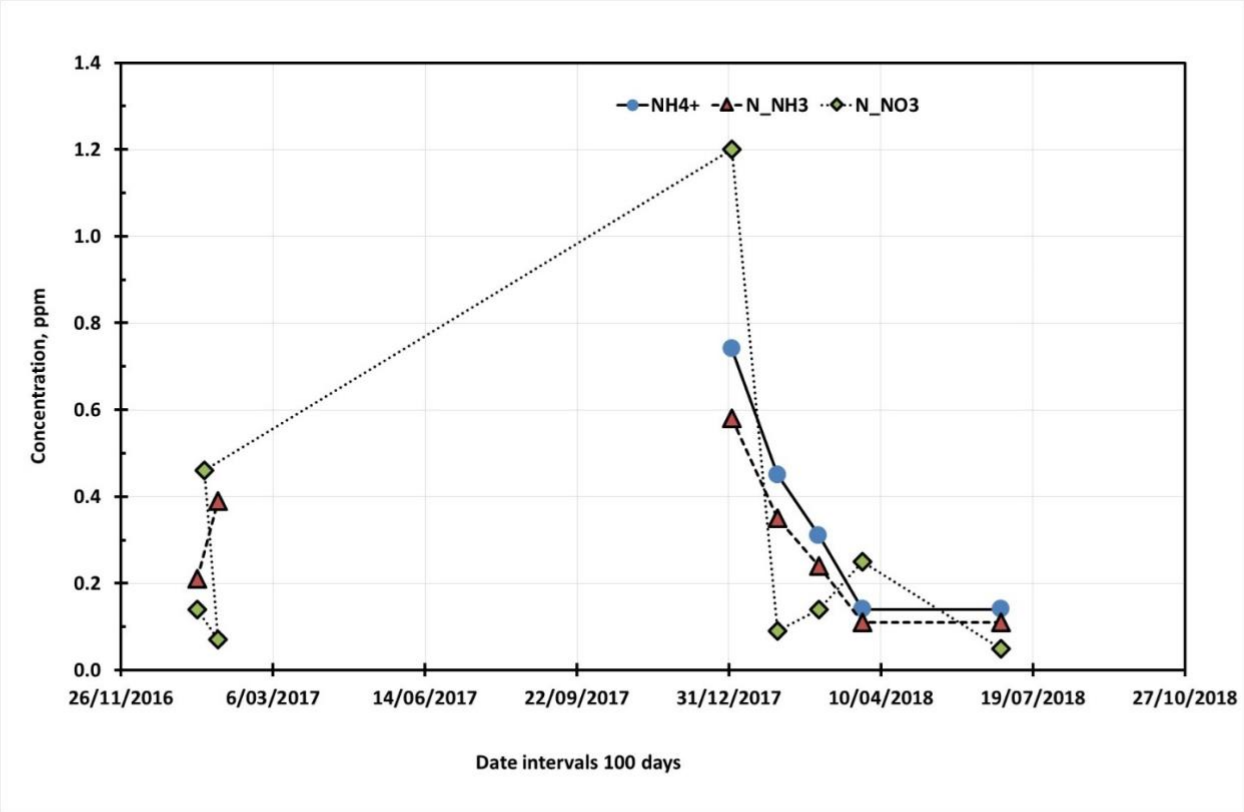

Figure 2: Distribution of nitrogen species in rain water from no 6, water tanks site.

Four of the sites (4, 6, 7 & 21) have varying Ca^{2+}/K^+ ratios which are all significantly greater than that found in seawater at a mean value of 3.1 ± 2.9 which indicates that the potassium is being selectively bound in weathering products such as clays on the rock crusts. The surface chemistry at site 5, 22 and 23 appears to be different with a mean ratio of 0.4 ± 0.3, but this is not statistically significant. The mean Ca/Ba ratio is 427 ± 251 which is very different to the value of 8,000 for sea water and this is simply due to the solubilisation of barium containing minerals in the weathered crusts on both the gabbro and granophyre rocks. The potassium containing minerals in the rocks on site 22 explain the very different sodium to potassium and the calcium to potassium solution washing data ratios.

Interpretation of solution chemistry and cation mobilisation

Because the concentrations of cations in the wash solutions are low, it is more convenient to use a logarithmic value, expressed as pM, in the same format as pH represents the hydrogen ion activity. Higher pM values mean less metal ion activity since pM is equal to the log of the inverse of the metal ion concentration. When mineralisation (rock corrosion) products from the weathering of the rock crusts are dissolved this involves neutralisation of either oxides or hydroxides of metal ions. When metal hydroxides are mobilized by acid dissolution the generic dissolution reaction can be written in the form show in Equation (3),

$$M(OH)_n + n\,H^+ \longrightarrow Mn^{n+} + n\,H_2O \quad \text{...} \quad (3)$$

In equation 3 the *n* value is the oxidation state of the metal, typically 2 and 3 for iron and mixtures of 2, 3, 4 etc. for manganese. The concentration of the metal ions is derived from the general equilibrium constant for the dissolution of a metal hydroxide into the component elements. Thus $K_{sp} = [OH^-]^n \times [M^{n+}]$, is mathematically the same if we rewrite the expression using the reciprocal values i.e.

$$^{1}/K_{sp} = \{^{1}/_{[OH^-]^n}\} \times \{^{1}/_{[M^{n+}].}\} \dots\dots (4)$$

Since the logarithm of $\{^{1}/_{x}\}$ is pX, then equation 4 can be expressed by the formula

$$pK_{sp} = n\ p[OH] + pM_{OH} \dots\dots (5)$$

By definition, $p[OH] = pK_w - pH$ which can be substituted into equation 5 then rearranged to give equation no 6, remembering that the self-ionisation constant of water, pK_w has a value of 14.

$$pM_{\ hydroxides} = pK_{sp} + n(pH\text{-}14) \dots\dots (6)$$

Thus, for plots of the pM values for metal ions the intercept at zero pH is equal to (pK_{sp} -14 *n*). For metal oxides of the general formula M_xO_y dissolving to give metal ions and water, the concentration of the metal is given by Equation 7,

$$pM_{oxides} = {}^{1}/x\ \{pK_{sp}\} + 2\{y/x\}\ pH \dots\dots (7)$$

When the pM values are plotted as a function of pH it is theoretically possible to determine if the dissolution process involves a hydroxide, which has a slope of *n* for the pM vs. pH plot. If the product dissolving is a mixed valency oxide, the slope of the pM vs. pH plot is $2^{y}/_{x}$, if the soluble ion is an un-complexed free metal ion.

Mobilisation of barium and calcium

The chemical analysis done by CSIRO on the mineralogy of the rock crusts' weathered zones did not show up any significant amounts of barium, so it is considered likely that the presence of varying amounts of this heavy alkaline earth metal came from the sea. The chemistry of the barium minerals was considered a likely candidate to see if there was any systematic change in the rock chemistry from the time of the original measurements made in 2003 and the present round of data collected in 2018. Plots of the $p[Ba^{2+}]$ versus pH conformed to the equation 8, viz.,

$$p[Ba^{2+}] = 7.25 + 0.15\ pH \dots\dots (8)$$

For this relationship the R^2 value was 0.79 so there is a reasonable degree of fit for the linear regression. This means that as the pH falls there is a regular increase in the solubility of barium ions into the wash solution, but it is still essentially a mineral associated with low solubility. Because the slope is not an integer this simply means that the minerals containing the barium ions are complex and not simple oxides or hydroxides.

The most significant difference in the behaviour is that for the February 2004 data there is a change of mechanism of solubilisation of calcium as the slope of the p [Ca] vs pH plots changed from one to two. The most likely mechanism is that for a 1:1 reaction it is the dissolution of calcium carbonate to form a soluble bicarbonate complex,

$$CaCO_3 + H^+ \rightarrow Ca(HCO_3)^+ \dots\dots (9)$$

This is the reaction that dominates the solution processes for the 2003 and the 2017 conditions. For some reason the mechanism changed to a 1:2 reaction for February 2004 in which the calcium carbonate would have dissolved fully as the disassociated bicarbonate, as shown in Equation 2.,

$$CaCO_3 + 2\ H^+ \rightarrow Ca^{2+} + H_2CO_3 \dots\dots (10)$$

Table 2: Solution properties of calcium and barium washings on the Burrup rocks

Date	mean pH	mean p[Ca]	mean p[Ba]	slope p[Ca]/pH	slope p[Ba]/pH
August '03	5.0 ± 0.5	3.6 ±0.4	6.6 ± 0.2	1.0 ± 0.1	0.4±0.2
February '04	4.3 ± 0.5	4.1 ± 0.6	7.2 ± 0.4	2.0 ± 0.2	2.0
November '17	5.7 ± 0.5	2.0 ± 0.6	5.2 ± 0.3	1.3 ± 0.3	0.5±0.1
Sept. '18	5.5 ± 0.8	3.3 ± 0.2	7.9 ± 3.2	1.3 ± 0.5	0.2 ± 0.1

Considering the mobilisation of calcium minerals, the slope in both November 2017 and September 2018 is the same as originally observed in August 2003 but it is also noted that the solubility of the calcium minerals in 2018 is lower than in previous year, even though the pH is essentially unchanged. During the same period the mobilisation of barium, which is likely to exist as barium carbonate as part of the sea water evaporite, also changed mechanism. For the solubilization of barium carbonate the reactions are the same as shown in equations 9 and 10, but with barium replacing calcium in the equations. The February 2004 data also showed the lowest free calcium and free barium ion concentrations, compared with the other three sets of measurements and so the likely difference in mechanism is likely to be due to the smaller amounts being mobilised and so the full dissolution reactions shown in equation 10 are more readily facilitated. The mean pH associated with the dissolution reactions in February 2004 was quite low at pH 4.3±0.5 which was nearly five times more acidic than the August 2003 data and more than 20 times more acidic than the measurements made at the six Yara sites. The mechanism of the mobilisation of barium in 2018 has the same slope as in other seasons of data collection, other than in February 2004 when it appears that a barium carbonate was being mobilised. It is likely that this data set, which is limited, does not relate to simple evaporites but it reflects minerology associated with co-precipitation of barium with calcium.

Interpretation of the pH effects on iron and manganese mobilisation

Previously published work by MacLeod (2005) and MacLeod et. al. (2017) has shown that at the pH values recorded in 2003 and 2004 (Appendix IV) there was measurable mobilisation of iron and manganese containing minerals. Analysis of the wash solutions from the early data sets has shown up significant concentrations of aluminium, iron, manganese, nickel, copper and some zinc and lead from the parent rock crusts. 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) oxy-hydroxides 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. It is helpful when undertaking a review of metal ion solubility to understand that the dissolution of the key elements in the rock patina is controlled by the pH or the acidity of the microenvironment.

The more acidic surfaces in the 2003 spring and the February 2004 summer measurements were amenable to this form of analysis and plots for iron showed that for both seasons the p[Fe] vs. pH plots have an average slope of +1.98 ± 0.06 pH which confirms the following mechanism:

$$FeOOH + 2H^+ \rightarrow Fe(OH)_2^+ + H_2O \quad \text{...} (11)$$

The Pourbaix diagram for iron in the range of pH observed on the rock surfaces shows that the $Fe(OH)_2^+$ ion is the dominant form of soluble iron(III) under oxidizing conditions (Pourbaix 1974). The pH data is shown in Appendix IV. Similar plots indicate that copper is mobilized by dissolution reactions involving two protons per metal ion as is the case for nickel.

Using washing solution data for the mobilisation of aluminium allows similar plots for the solubility of aluminium with surface pH to be determined. For the Burrup rocks the aluminium mobilisation graphs had an average slope of 1.4±0.2 pH, which is consistent with the dissolution of kaolinite ($Al_2Si_2O_5(OH)_4$) to give the $Al(OH)_2^+$ ion and $AlSi_2O_5^{+,}$ as shown in Equation 12.

$$Al_2Si_2O_5(OH)_4 + 3H^+ \rightarrow Al(OH)^{2+} + AlSi_2O_5^+ + 3\ H_2O \quad \text{.........................} (12)$$

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) and it was a major mineral identified in the CSIRO Accelerated Weathering experiments (CSIRO 2016). It is not unexpected for aluminium ions to have been mobilized under the very mild sample collection regime that was used. In September 2018 there was only one site, the water tanks site no 6, that showed any presence of aluminium in the solution washings and it was only 2.6×10^{-7} M which is close to the detection limit of 1.9×10^{-7} M.

The concentration of manganese in the rock irrigation measurements done in September 2018 had a maximum of 5.8×10^{-7} M or a pMn of 6.24 at the Deep Gorge (site 7) and when the data was plotted as a function of surface pH the regression analysis confirms that the likely dissolution reaction is shown in equation 12 for sites 6, 21 and 22 viz.,

$MnO + H^+ \rightarrow Mn(OH)^+$ .... (12)

There was significant scatter of the data, with a low R^2 of 0.64, and so the pM vs. pH slope was 1.24 ± 0.93 which could easily represent the mobilisation of manganese oxide to manganous ions, as shown in equation 13 viz.

$MnO + 2\,H^+ \rightarrow Mn^{2+} + H_2O$ .... (13)

Previously it had been noted that there was considerable value in being able to plot the redox potential of the soluble metal ions on a rock art site as a function of the surface pH. The most responsive site for mobilisation of manganese is shown in Figure 3, which is the Pourbaix diagram for site 7 at Deep Gorge.

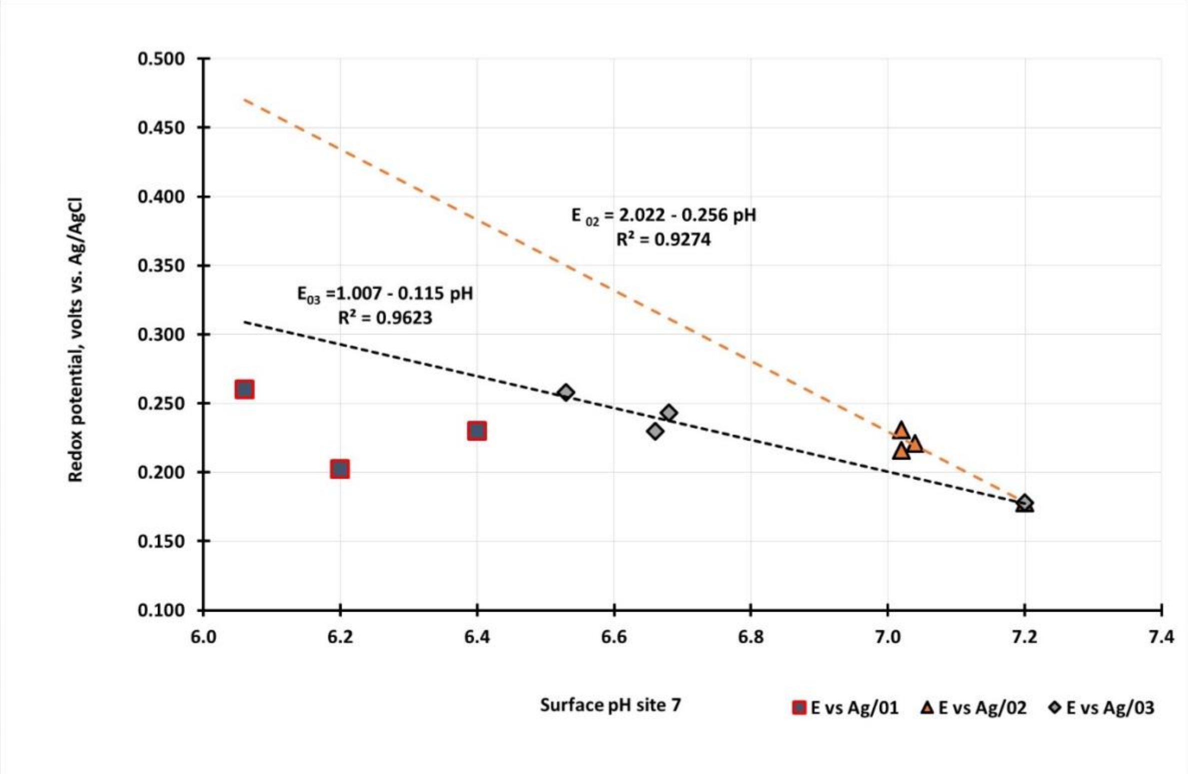

Figure 3: Pourbaix plot for site 7 at Deep Gorge, September 2018

Inspection of the slopes in the Pourbaix diagram in Figure 3 shows that there are two mechanisms controlling the precipitation of solid phases and dissolution of the same. The reaction scheme shown in equation 14 is for the formation of insoluble blue-black Mn_3O_4 from oxidation of soluble Mn^{2+} ions viz.,

$3\,Mn^{2+} + 4\,H_2O \rightarrow Mn_3O_4 + 8\,H^+ + 2\,e^-$ .... (14)

The slope of line E_{02} is -0.256 ± 0.050 pH per volt which matches very well the theoretical slope for equation 14 is -0.236 pH per volt. The manganese equivalent of magnetite is called manganomanganic oxide, which reflects the composition of one Mn^{2+} ion and two Mn^{3+} ion in the lattice of oxides. The second regression line for E_{03} had a slope of -0.113 ± 0.016 pH per volt which is entirely consistent with equation 15 viz.,

$Mn^{2+} + 4\,H_2O \rightarrow MnO_4^{2-} + 8\,H^+ + 4e^-$ .... (15)

The theoretical slope for equation 15 is -0.118 pH per volt. The Pourbaix data has provided unequivocal information about the competing reactions that are taking place on the surface of the rock on the reverse side of site 7. The range of pH readings taken across the surface of the rock is shown in Figure 4, along with Nigel Tonkin who recorded the pH, chloride and voltage data on all the sites.

Figure 4: Deep Gorge site 7 with pH data recorded onto the image, September 2018

As previously noted, there was no measurable iron in solution observed for the September 2018 data. A summary of the data from the redox potentials and the pH recorded on the seven sites in Table 3 which gives the mean redox potential, standard deviation of the same and the Pourbaix slope in mV per pH and the redox potential at a pH of zero. The value of conducting the Pourbaix analyses and fitting regression equations to the data is that it provides a unique insight into the competing equilibria on the rock surfaces and gives an understanding of the vast array of redox reactions that may occur which have the potential for bacteria, yeasts, moulds and fungi to utilise the suite of oxidation and reduction reactions to provide them with the energy they need for effective colonisation and metabolism. It is not surprising that most of the identified redox reactions on the rocks are reflections of the multi-valent stat of manganese, with only one example on site 5, Burrup Road, of a redox couple involving iron.

Table 3: Redox potentials$^{\#}$ & theoretical E^{o} at pH zero with Pourbaix slopes

Site location	^{Mean} E redox	standard deviation	Pourbaix slope, mV/pH	$^{zero\ pH}$ E_{NHE}	Standard E^{0} & reaction
Site 23 Yara East	0.484	± 0.016	-24 ± 4^{d} -233^{a}	0.600 1.480	0.564 MnO_4^-/MnO_4^{-2} 1.510 Mn^{3+}/Mn^{2+}
Site 22 Yara NE	0.492	± 0.012	-37 ± 7^{d}	0.731	0.771 Fe^{3+}/Fe^{2+}
Site 21 Yara West	0.487	± 0.007	-27 ± 4^{d} -25 ± 5^{d}	0.659 0.615	0.662 Mn_2O_3/Mn_3O_4 0.564 MnO_4^-/MnO_4^{-2}

Site 7 Deep Gorge	0.429	±0. 025	-256 ± 50[a] -115 ± 16[b]	2.020 1.073	1.742 MnO_4^-/Mn^{2+} 1.104 MnO_2/Mn_2O_3
Site 6 Water tanks	0.396	± 0.020	-35 ± 5[d]	0.591	0.564 MnO_4^-/ MnO_4^{-2}
Site 5 Burrup road	0.467	±0.021	-57 ± 5[c] -23 ± 4	0.782 0.591	0.771 Fe^{3+}/Fe^{2+} 0.564 MnO_4^-/ MnO_4^{-2}
Site 4 Woodside	0.485	± 0.011	-28 [d]	0.664	

[#]Voltages corrected to NHE by adding calibrated voltage of 0.202 volts for the Ag/AgCl electrode

[a] Theoretical slope for 4 protons per electron is -236 mV/pH as in equation 14,
[b] Theoretical slope for 2 protons per electron is -118 mV/pH as in equation 15
[c] Theoretical slope for 1 proton per electron is -59 mV/pH as in equation 16

$$Fe^{2+} \rightarrow Fe^{3+} + e^- \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (16)$$

[d] Theoretical slope for 1 proton per 2 electrons is -29.5 mV/pH as in equation 17

$$Mn^{2+} + 2\,H_2O \rightarrow MnO_2 + 4\,H^+ + 2\,e^- \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (17)$$

Inspection of the data in Table 3 illustrates the complexity of 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. 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. The solution chemistry of manganese is very complex, with solid phases of Mn^{2+} being MnO and $Mn(OH)_2$, for Mn^{3+} there is Mn_2O_3 and for the mixed valence of Mn_3O_4, which is a mixture. like its iron analogue magnetite, of one Mn^{2+} and two Mn^{3+} ions. In addition, there are equilibria involving the precipitation of MnO_2 as in equation 17.

For the 2003-2004 data the slope of the pM vs. pH plots for iron had a slope of 2.0, which is consistent with the dissolution of iron (III) oxyhydroxide, FeOOH viz.,

$$FeO(OH) + 2\,H^+ \rightarrow Fe(OH)^{2+} + H_2O \qquad (18)$$

The 2017 November data showed that there was a slope of 0.3 pH per pM i.e. there is a completely different dissolution mechanism in the present (2007) rock data around the Yara compound compared with the 2003-2004 measurements. The lack of acidity on the rocks has kept iron minerals in an insoluble condition during the 2018 season of measurements. The detailed examination by CSIRO of the parent and weathered rock surfaces of the gabbro and granophyre rocks in the Burrup has provided an exhaustive list of the minerals that are present in the mineral crusts on the gabbro and granophyre rocks (Ramanaidou et.al. 2017). Iron containing minerals that do not follow simple stoichiometry include actinolite, $Ca_2(Mg, Fe)_5Si_8O_{22}(OH)_2$, augite, $(Ca, Mg, Fe)_2(Si, Al)_2O_6$ and chlorite $(Mg, Al, Fe, Li, Mn, Ni)_{4\text{-}6}(Si, Al, B, Fe)_4O_{10}(OH, O)_8$ which are all found on the Burrup rocks (idem 2017). The accelerated acid ageing study showed that chlorite appeared to be one of the first minerals to dissolve. It is important to conduct additional studies on the Yara sites in 2019 to ensure that the September 2018 data are not an anomaly, which should be able to be discerned through detailed analyses as discussed above.

One of the main factors affecting the rocks appears to be associated with the six massive rainfall events, due to cyclonic activity, in the intervening 13-years. The rainfall events are summarised in Table 3. The main difference between the six Yara sites and their pH values is that since the 2003-2004 measurements is that it appears that there has been a significant alkaline shift from a mean pH of 4.78 ± 0.27 in February 2003 to 5.69 ± 0.51 in November 2017. The shift of just over one pH unit means that the six sites are on average ten times less acidic that the other rocks in the region which were sampled by solution washing. Although the rain event in June 2018 was less intense than in previous years the mean surface pH for the September data was 5.52 ± 0.84, which is statistically the same as the mean data in the previous year. **In other words, there has been no increase in acidification of the rocks in the vicinity of the Yara plant.**

Table 4: Major cyclonic rainfall (mm) events in the Burrup 2003-2017

02 March 2004	10 Jan. 2006	25 June 2013	31 Dec. 2013	06 May 2014	09 Feb. 2017	06 June 2018
190.8	212.4	209.4	112.8	107.4	210.6	62.4

Despite apparent simple changes to the solubility of iron and manganese compounds with pH, the absence of a common dissolution mechanism across the three seasons of measurements makes it difficult to interpret the data. The large standard deviation in the p Fe values (±2.6) for August 2003 measurements makes it impossible to tell if there is any real difference between this data and the material sampled in February 2004.

Table 5: Mean pH and solubility of iron and manganese minerals from rock irrigation

Period	Mean pH	Mean p Fe	mean p Mn	Slope p Fe/pH	slope p Mn/pH
August 2003	4.97 ± 0.48	6.01 ± 2.60	7.17 ± 0.45	2.0 ± 0.1	0.9 ± 0.4
February 2004*	4.78 ± 0.27	6.34 ± 0.44	7.31 ± 0.35	2.0 ± 0.1	2.1 ± 0.1
November ‘17	5.69 ± 0.51	6.80 ± 0.15	5.03 ± 0.35	0.3	1.1 ± 0.1
September ‘18	5.52 ± 0.84	Nil soluble	6.79 ± 0.35	Not applicable	1.2 ± 0.9

* the mean pH is determined for the points that were used in the regression analyses.

The lower standard deviation of the Feb 2004 and the Nov 2017 data on iron solubility provides evidence that the solubility of the iron minerals decreases with increasing pH, despite the apparent change of mechanism. Manganese compounds are more soluble at neutral pH than their iron analogues are reflected in the 2018 data from the Burrup rock art washings, where no soluble iron was detected. The reasons for this lie in the ability of acidic metabolites to complex the cations found in the weathered crusts. The mean p Mn values show an average of 50 times lower solubility in 2018 than in 2017, pMn 6.8 for 2018 compared with 5.0 in November 2017, as seen in Table 5. This observation is supported by data from Krauskopf (1957) who found that Fe compounds are less soluble than corresponding Mn compounds under naturally occurring Eh-pH conditions.

Solubilisation of Mn and Fe compounds in rock varnish can lead to removal of important compounds required to bind clay minerals to form the hard, outer layer of the varnish and to bind it to rock inner surfaces. A predominant Mn compound in rock varnish is birnessite, which has hexagonal structured sheets with binding clay minerals $\{(Na_{0.3}Ca_{0.1}K_{0.1})(Mn^{4+},Mn^{3+})_2O_4\cdot 1.5H_2O\}$. Lefkowitz et al. (2013) demonstrated that birnessite sheets were disrupted when pH was < 7.0. Under mildly acidic conditions observed in the Burrup the varnish would become thinner and softer with removal of these manganese compounds.

Mobilisation of boron from parent rocks and crusts

The presence of measurable amounts of boron in the wash solutions seemed to vary with the surface pH values recorded in both the 2003 and 2004 measurements. To discriminate between the boron coming from seawater, where it is a minor component at 4.6 ppm compared with chloride at 18,980 it was decided to plot the chloride to boron ratio as a function of the mean surface pH values. The data recorded in the first set of washing solutions from August 2003 showed some interesting patterns. What became clear was that normal Cl/B ratio in seawater of 4,130 was massively lower in the washings from all the Burrup rock art sites, where the maximum value was 143 on rock 938 in the “museum compound”. This supported the view that boron containing minerals were being dissolved leading to much lower chloride to boron ratio from that expected from wind borne sea salts. As the mean rock surface pH fell the ratio also fell, which supports the data from accelerated weathering conducted by CSIRO (Ramanaidou et.al. 2017). This effect is illustrated in Figure 5 and is most dramatic for the mainly granophyre rocks where the Cl/B ratio fell from a maximum of 143 at pH of 4.8 to 16 at a pH of 4.5, which shows that with a pH change of 0.3 (doubling of the acidity) there was a nine-fold increase in the amount of boron in the wash solution. For the gabbro rocks the maximum ratio of 50 at a pH of 5.4 fell to the same minimum of 16 at the same minimum pH values of 4.5 i.e. a three-fold drop in the ratio for an 8-fold increase in acidity. Although there are only one of the seven wash solutions in 2018, site 6 by the water tanks, that had a measurable amount of boron in it, the data from this single measurement was added to that from 2003 and 2004, as seen in Figure 5. This red data point fits on the gabbro line although rock 6 is listed as granophyre. However, it was noted in the field that the adjacent rock that was chosen for pH and washing measurements was indeed a gabbro rock. The ratio of $(^{Cl}/_{B})$ for the 2018 sample was 314, which was much higher that any previously observed and yet it fitted in very well on the regression line.

The mineralogy of the weathered gabbro crusts is different to that of the granophyre as it has an apparently higher buffer capacity. The changes in acidity appears to be mobilising more of the boron containing minerals such as chlorite, $(Mg, Al, Fe, Li, Mn, Ni)_{4\text{-}6}(Si, Al, B, Fe)_4O_{10}(OH, O)_8$. An indication of the relative sensitivity of the two different rock types to increased mobilisation of chlorite is seen in the slopes of the data in Figure 5, which plots the mean pH of the rock surfaces against the chloride to boron ratio. Inspection of equations 19 and 20 show that the granophyre rocks are about eight times more sensitive to the chlorine to boron ratio than the gabbro rocks, which seem to have a greater buffer capacity, owing to the complex mineralogy of the weathered crusts.

$$pH_{\text{granophyre}} = 4.17 + 0.0264\,\{Cl/B\} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (19)$$

$$pH_{\text{gabbro}} = 4.40 + 0.0034\,\{Cl/B\} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (20)$$

The mean pH of the 20 washed rocks in August 2003 was 4.97 ± 0.45 which was slightly more alkaline that the February 2004 value of 4.82±0.32 that covered a total of 40 sites. It is to be expected that there will be significant differences in the results for the two sets of measurements, since the February 2004 data includes three reference sites each from Gidley and Dolphin Islands.

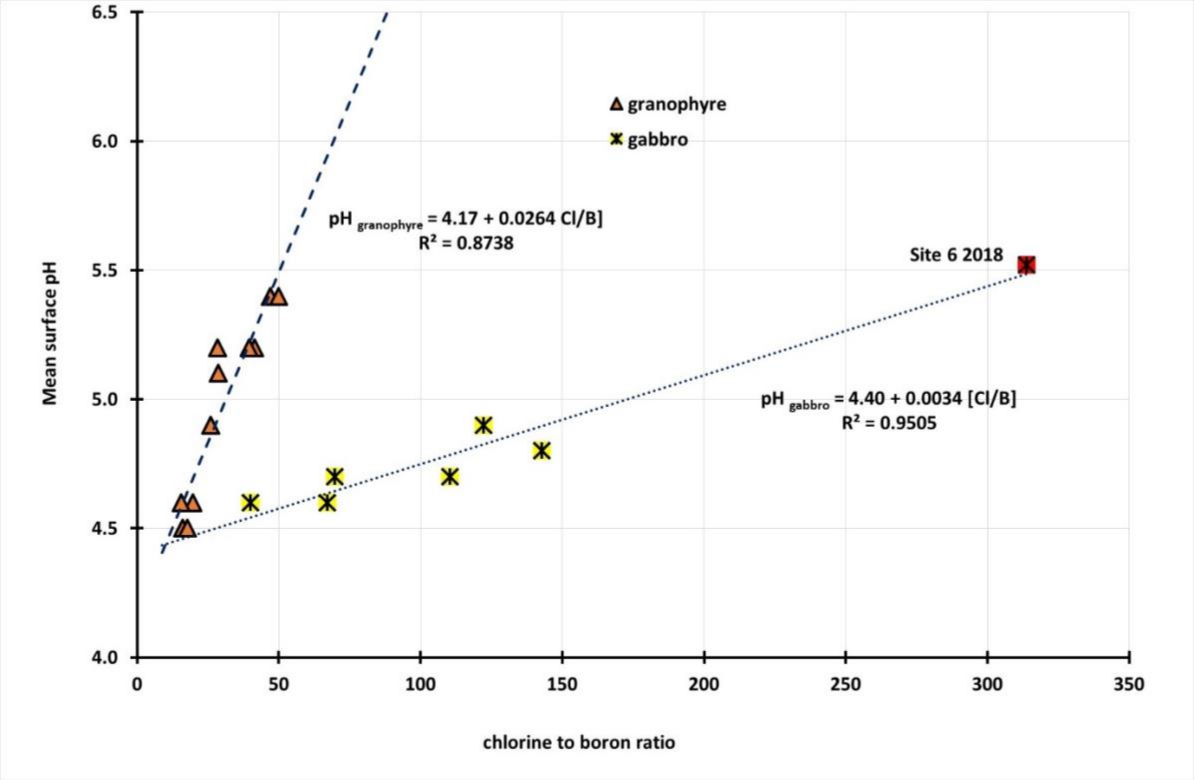

Figure 5: Ratio of chloride to boron vs mean surface pH 2003

Given that the 2003 data indicated that the mobilisation of boron was very pH sensitive, particularly for gabbro rocks it is not unexpected that there would be an increased mobilisation of chlorite i.e. increased boron or lowered chloride to boron ratios in the February 2014 data which had a pH range was from a maximum of 5.4 to a minimum of 4.2 which is one pH unit less (maximum value) than that found in the August 2003 washing. When the logarithm of the slopes of the plots of the pH against the (Cl/B) ratio was plotted against the mean pH of the rock surfaces a linear relationship (shown in Equation 21) was found,

$$\log \{Cl/B\} \text{ slope} = 6.85 - 1.035 \text{ pH} \quad \ldots\ldots (21)$$

For this equation there was a very high R^2 value of 0.9939 which gives confidence that there is a sound physical chemical process controlling the dissolution of chlorite. Rather than having a series of apparently non-related slopes there is a common thread controlling the rates at which the chloride to boron ratio falls as the acidity increases. The most dramatic difference between the data collected in 2003 and 2004 and with both the November 2017 and September 2018 that only site 6 had a measurable amount of boron. It can be concluded that the analysis of the wash solutions provides a unique insight into the chemistry of the reactions taking place on the rock surface. It is also clear that the more acidic the rock surface the more chlorite will dissolve from the crust and the parent rock, which will lead to increased chances of disbondment of the engraving from the substrate. It is likely that a combination of surface pH measurements on reference rocks being analysed for their mineral composition will provide a quantitative method for assessing the dissolution of weathered crusts on Burrup rocks.

Anions in wash solutions

Oxalates:

Analyses from the five field trips showed that only two reference rocks in the collection of the Western Australian Museum had measurable amounts of oxalate ions, $C_2O_4^{2-}$, which were 1.8 mg/l from Enderby Island (B7477) and 0.7 mg/l from Happy Valley (B2494) in the Burrup. These rocks were collected at a time before there was any industrial activity on the Burrup. The washing samples analysed for oxalate were from June and August 2003, February 2004, November 2017 and September 2018 and there were no oxalates found in the wash solutions. Oxalates are major biodeterioration of pigments in the Kimberley region where the monsoonal climate has characteristic wet and dry periods. By comparison the arid climate of the Burrup is less amenable to a wide range of bacteria and plants which produce oxalates as their metabolites. Based on this information, oxalate does not appear to have a significant present role in biodeterioration of the rock art in the Burrup.

Chlorides:

The amounts of surface chloride detected on the rock surfaces provide direct evidence of the impact of the marine environment and indicates that salt weathering of rocks, with extensive dehydration and rehydration cycles, play 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^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, B^{3+}, SO_4^{2-} and Cl^-. Analysis of the way in which the concentrations varied across the Burrup was possible as the February 2004 data included several remote sites such as Gidley and Dolphin Islands in the Dampier Archipelago (MacLeod 2005). 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.

The initial monitoring conducted in 2003 and 2004 involved direct measurement of the surface pH and the surface chloride ion concentrations. In addition, the washing of the rock surfaces in August 2003 and February 2004 provided data on the solution concentrations of chloride ions. All the data was then assessed through linear regression analyses and the results are summarised in Table 6, which showed that the pH increased with increasing chloride ion activity. This buffering reaction is demonstrated by the relation between the pH and chloride concentration on the rocks as shown in Equation 22,

$$\mathrm{pH}_{\text{mean}} = a + b\,[\mathrm{Cl}^-] \quad \ldots\ldots\ldots \quad (22)$$

The 2003-2004 linear regression analyses showed that there was a common slope of the pH vs [Cl] plots but they had different intercepts, as shown in Table 6. The intercept values relate to their primary geology of the underlying rocks and the impact of factors such as the amount of nitrate on the rock surfaces, which is discussed in the following section of this report. When the median surface pH from 2018 is plotted against the mean surface chloride values it was found that for the gabbro rocks measured adjacent to the CSIRO rocks

$$\mathrm{pH}_{\text{median}} = 4.90 + 0.093\,[\mathrm{Cl}]_{\text{surface}} \quad \ldots\ldots\ldots \quad (23)$$

This regression had an R^2 of 0.93 which provides a high degree of confidence that it is a meaningful result. By way of contrast, it can be seen in Figure 6 that the granophyre sites, including sites 6, 21 and 23, seem to follow the reverse trend, with a quadratic relationship that shows diminishing pH with increasing chloride ion activity. This parabolic curve intercept gives a median pH of 6.0 and it may be a reflection that on these sites there are chloride obligate bacteria present. If such microorganisms are present, then their metabolites will be acidic and overcome the buffering effect of the increased amount of sea salt deposition.

It is important that metagenomic analysis of the rock surfaces in the field conditions be conducted to establish the nature of the different groups of organisms that are controlling the pH and to see if there are measurable biological differences in the colonisation of the two rock types.

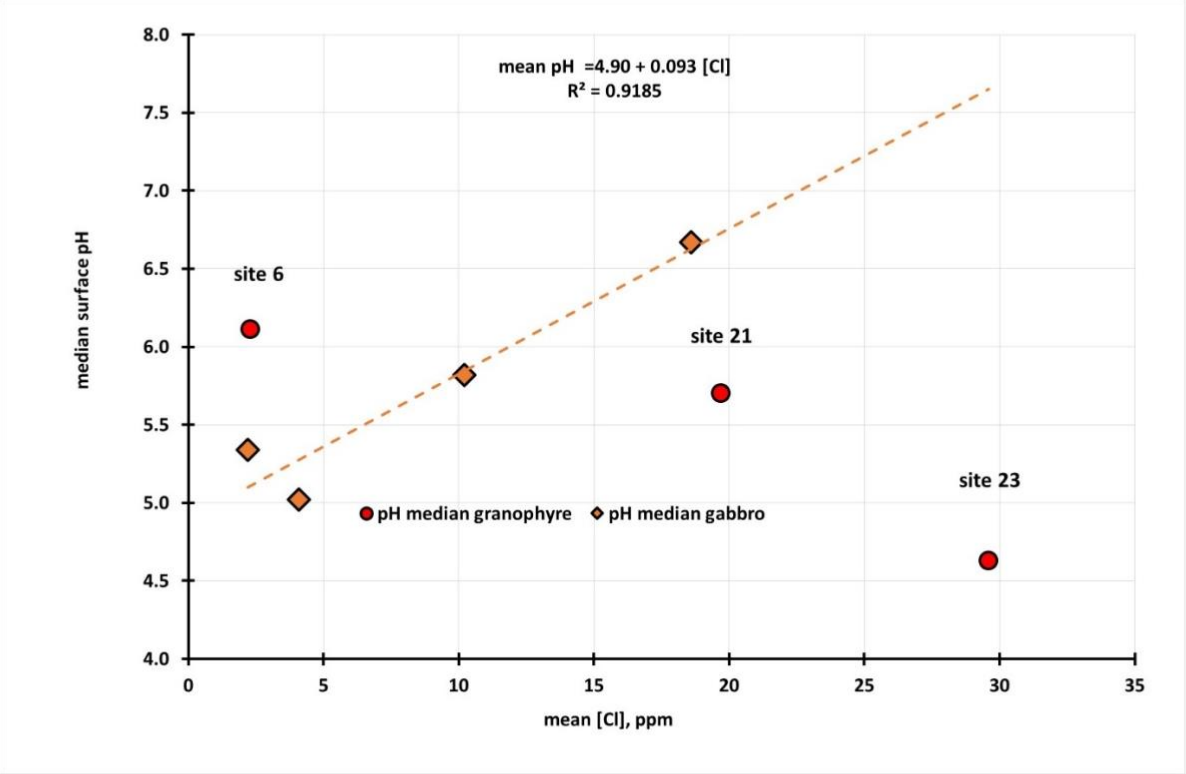

Figure 6: Plot of $[\mathrm{Cl}]_{\text{solution}}$ on the rocks vs. the mean surface pH, 2018 readings

The data in Table 6 covers all the sets of measurements of rocks in the Burrup and in the Dampier, Archipelago shows that the build-up of sea salt deposits on the rocks does have a measurable impact on the way in which the rocks respond to changes in the chemical environment, as seen in Figure 6.

From the data presented in Table 6 there appears to have been a systematic decrease in the slopes of the pH vs. [Cl] graphs between 2002 and 2017, as shown in Figure 7 and equation 24 viz.,

$$\text{slope } \{{}^{pH}/_{Cl}\} = 0.0725 - 0.0121 \text{ pH} \quad \ldots\ldots (24)$$

This relationship confirms that all the pH and chloride data are closely linked and that, in the absence of other factors, the ability of the rocks to minimise the response to the development of an acidic microenvironment is largely controlled by the amount of salt deposition. Inspection of the data in Table 6 shows that the solution washing concentration of chloride is very similar to the surface readings at sites 4, 5 and 6 and that the mean values recorded in 2018 are much lower than those in 2017 so it is not surprising that the trend shown in Figure 5 was not continued and that the median surface pH was the same, within one standard deviation, as the value in 2017 but the sensitivity of the surface pH to chloride activity is significantly different.

Further studies to determine the precise nature of the interactions are needed and it should be noted that the solution washings were taken on rocks adjacent to the chloride and pH testing sites, other than in site 7 which had sufficient flat areas on which to place the collection device and to irrigate the areas that had been measured for pH and for chloride. Future work is naturally constrained by the geology and the aspects of the rocks on each site location. When choosing the surfaces for pH and chloride measurements a significant factor is the choice of rocks with a similar aspect and orientation to the CSIRO reference sites. Many of these rocks have near vertical surfaces and this makes it impractical to recover samples of enough volume to allow for efficient chemical analysis of the surface wash solutions.

Table 6: Analysis of the relationship between chloride and mean pH

Date	mean Cl ppm	Intercept, *a*	Slope, *b*	R^2
June 2003 (winter)	38 ± 40	3.4 ± 0.6	0.030 ±0.004	0.98
August 2003 (spring)	34±31	3.4 ± 0.8	0.033 ± 0.003	0.98
February 2004 (summer)	21±15	4.1 ± 0.6	0.023 ± 0.001	0.98
November 2017				
Wash solution analysis	601±377	4.3	0.0028	0.94
Site 5: Burrup road	32±28	5.0 ± 0.9	0.0079 ± 0.0005	0.95
Site 6: Water tanks	191±97	5.4	0.0014	0.96
Site 7: Deep Gorge	22±12	5.0	0.026	0.77
Site 21 Yara west	125±44	5.8	0.0064	0.64
Site 22: Yara north east	373±24	5.3	0.0085	0.70
Site 23: Yara east	13±17	5.5	0.021	0.77
September 2018				
Wash solution analyses	2.4 ± 1.4	2.0	1.8	0.65
Site 4 Woodside road	2.2 ± 2.1	3.0	2.7	0.93
Site 5: Burrup road	4.1 ± 3.4	4.5	0.22	0.45
Site 6: Water tanks	2.3 ± 3.2	6.1	0.13	0.01
Site 7: Deep Gorge	18.6 ± 7.8	6.0	0.03	0.99
Site 21 Yara west	19.7 ± 12.8	5.0	0.12	0.94
Site 22: Yara north east	10.2 ± 11.2	5.5	0.03	0.34
Site 23: Yara east	29.6 ± 17.2	3.9	0.02	0.96

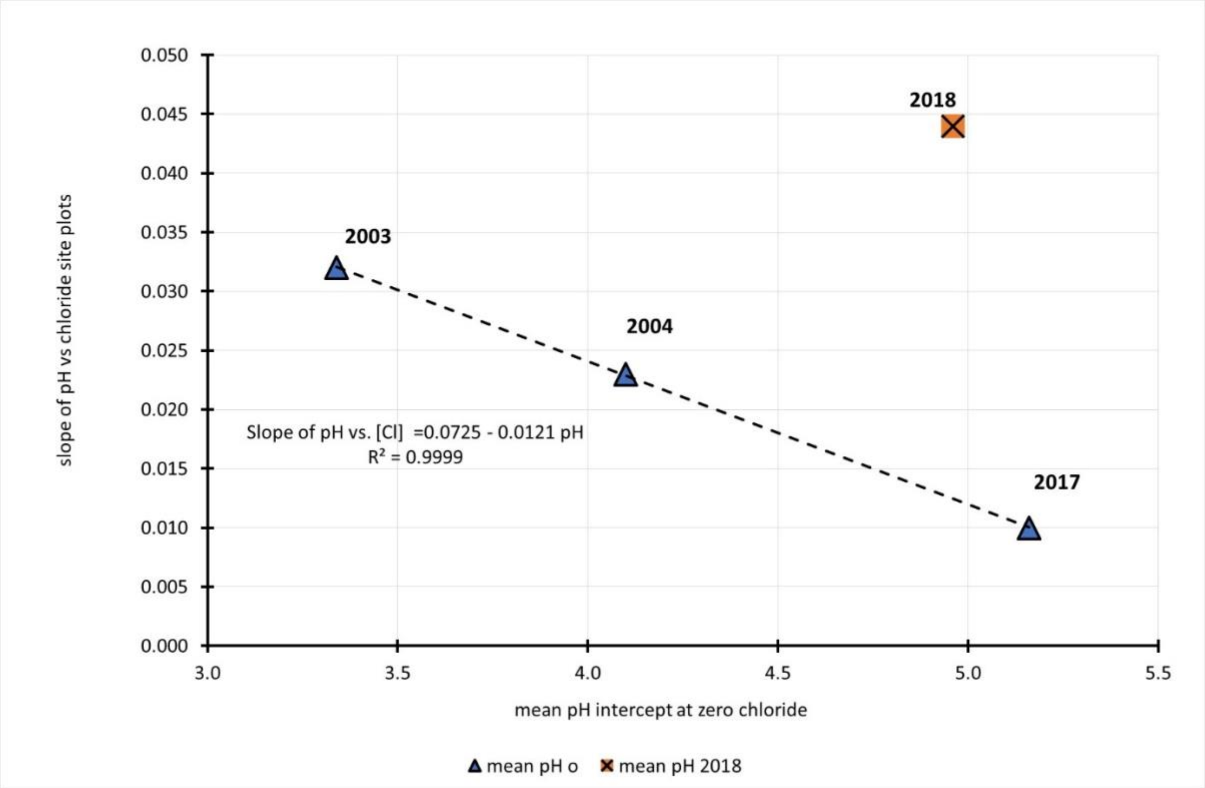

Figure 7: Sensitivity of pH vs [Cl] plots versus the mean pH $_{\text{intercept}}$ at zero chloride

Nitrates:

Previous studies in 2003 and 2004 had focused on the acidity and the concentration of nitrate ions, since there was very strong data supporting the inference that nitrate ions were stimulating the overall microbiological activity on the rocks. Since bacterial and fungal metabolites are often acidic it was decided to check to see if there was a correlation with the number of bacteria and the nitrate levels. Data published in 2005 by MacLeod demonstrated that the logarithm of the number of bacteria was directly related to the decreasing pH, thus the amount of nitrate ions, from both natural and human sources, was likely to be a key determinant in the overall rates of weathering of the rock surfaces in the Burrup. Owing to the contrasting nature of the engraved and background areas there was concern about the long-term impact of such accelerated ageing on the rock surfaces. Surface pH values as low as 3.5 were recorded on rocks near the Climbing Man panels adjacent to the Woodside operational flare tower servicing trains 1-4, as Pluto had not yet been constructed let alone become operational. As part of the February 2004 data collection, samples of rock pH, chloride and nitrate ions were collected on rock engraving sites at Gidley and Dolphin Islands in the Dampier Archipelago, in the belief that these remote sites would be low in nitrates, owing to their distance from apparent point sources on the coastal lands associated with industrial developments. A summary of the relevant data is shown below in Table 6, which lists the mean nitrate for 2003, 2004, 2017 and 2018 as well as the range of the maximum to the minimum values that were recorded.

Table 7: Nitrate concentration ranges across Burrup, ppm

Date	Maximum	Minimum	Mean ppm
August 2003	19, Withnell Bay	1.5, at Burrup SW 1–2	6.3 ± 5.1
February 2004	9.2, rock 938	1.3, Deep Gorge	4.5 ± 3.7

November 2017	1.8, site 21	0.10, site 5	0.6 ± 0.7
September 2018	1.4, site 7	0.19, site 22	0.7 ± 0.4

Although the nitrate concentration was essentially the same in August 2003 and February 2004, the slope of the pH vs $[NO3]_{ppm}$, as seen in Table 8, was diminished by over 40%. This is roughly in line with the 30% reduction in the mean nitrate concentration between the two sets of measurements. The data in Table 8 shows that common intercept pH values, at zero nitrate, at 5.69 for the 2003 and 2004 analyses. The common intercept value shows that the same chemical mechanism is controlling the response of the rocks in those two seasons of measurements. It should be noted that with the R^2 value of 0.97 the 2003 intercept value of 5.33 value is within experimental line fitting error the same as the 5.44 from rocks in the museum compound that was noted in February 2004. Of concern were the lower $pH_{intercept}$ values of 4.95 and 4.66 for sites that included rocks in the museum compound as well as those at the Climbing Man, Deep Gorges and Withnell Bay sites.

In the 15-years since the February 2003 data was collected, there were six cyclonic rain events, as listed in Table 3, which deposited between 63-212 mm of rain in the region in a 24-hour period. These periods of inundation of the rock surfaces is likely to be the underlying reason for the big drop in the nitrate ion concentration found in the rock washings in November 2017. There was a 62.4 mm rainfall event on 6th June 2018 which would have caused significant washing of the rocks in the test areas. The five-fold fall in nitrate concentration would have been expected to reduce the impact of the biological activity due to the nitrate concentration but other factors appear to have weighed heavily in bringing about a change in acidification. It has been noted that the mean chloride ion concentration on the Yara sites is approximately 30 times saltier in November 2017 than the rocks that were sampled in February 2003.

Table 8: Dependence of pH on the nitrate concentration found in wash solutions

Date	$pH_{zero\ NO3}$	Slope pH/[NO3]	R^2
August 2003	5.69, Climbing man, Deep Gorge & Compound 5.33, Burrup SW, King Bay & Compound	-0.14 -0.14	0.92 0.97
February 2004	5.69, Withnell & Compound 5.44, Compound 4.95, Withnell & Compound 4.66, Deep Gorge & Climbing Man	-0.08 -0.08 -0.07 -0.08	0.91 0.99 0.66 0.78
November 2017	6.18, Sites 5,6,7, 21, 22 & 23	+0.94 log [NO3]	0.99
September 2018	3.14 all sites other than 22	non-linear	0.86

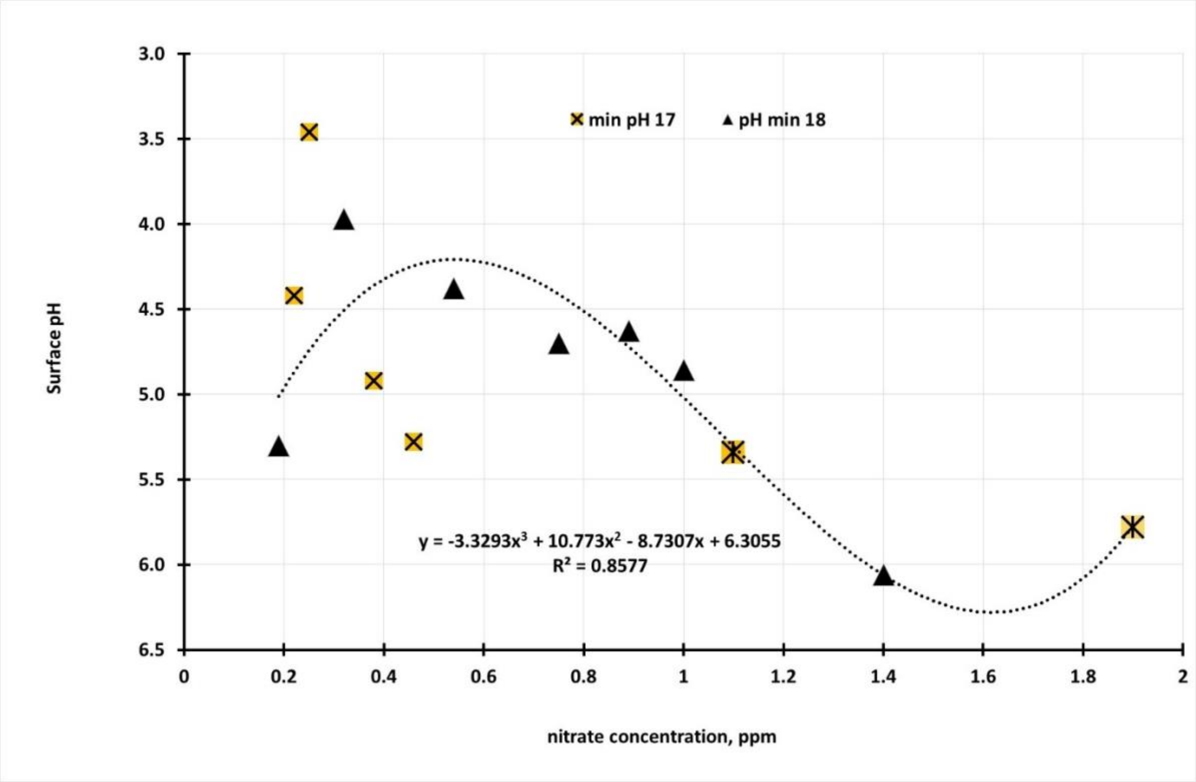

Figure 8: Surface pH in 2017 and in 2018, indicating acidification inhibition at low nitrate.

The increase in buffer capacity due to salt accumulation will naturally result in the changes in the surface pH of the rocks being reduced. However, the complete change of direction of the response of the rock pH to the nitrate concentration needs additional clarification. The dependence of pH on the nitrate concentration for the Yara monitoring stations was not as expected, since the mean surface pH at the Yara monitoring sites **increases** with nitrate concentration. The graphed results are shown in Figure 8 where the linear regression analysis shows,

$$^{\text{Yara 2017}}\text{pH}_{\text{mean}} = 6.18 + 0.94 \log [NO_3^-] \quad \text{..} \quad (25)$$

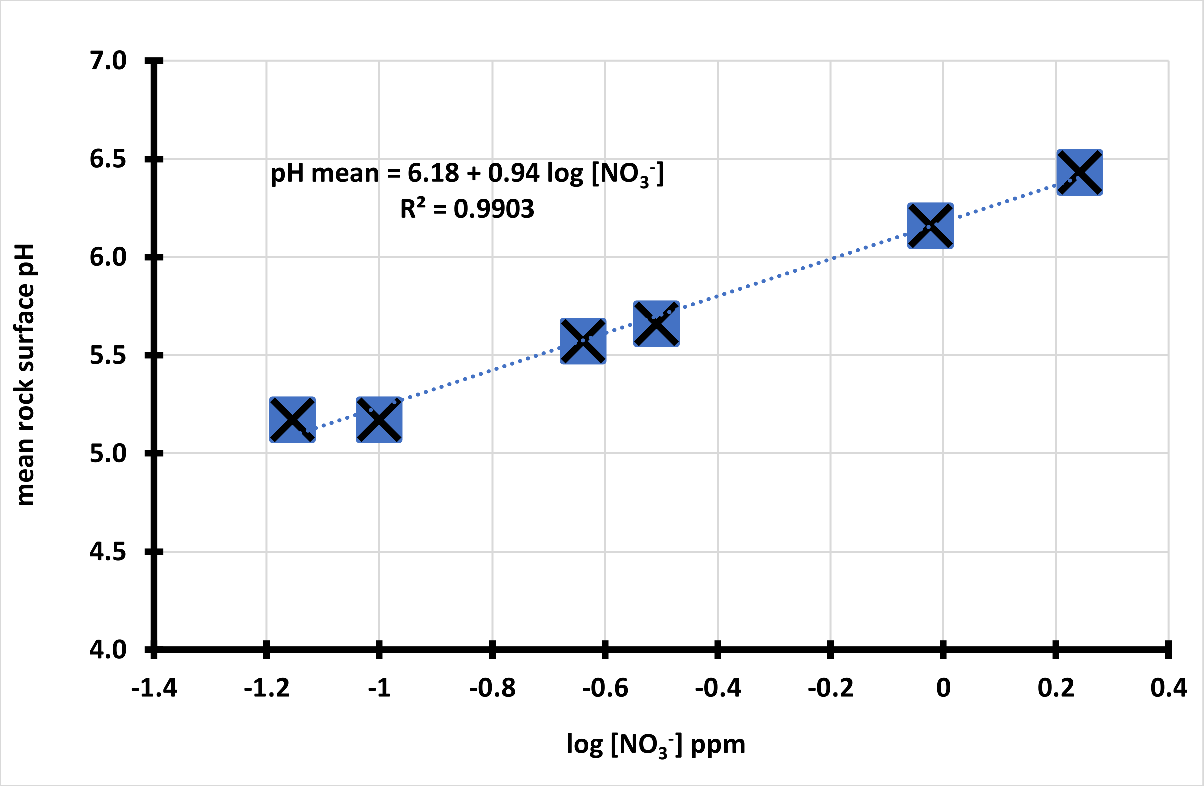

Figure 9: Mean rock surface pH on Yara sites vs. log of nitrate wash concentration

A possible explanation for this behaviour is that to bring about an overall increase in the acidity of the rock surfaces a significantly higher than 1 ppm nitrate needs to be present to provide the bacteria, yeasts moulds and fungi with enough nutrient to overcome the inhibition that the high salt content of the rock surface appears to be providing. Additional monitoring needs to be done on the Yara sites and sites that were previously addressed in the 2003-2004 field work need to be sampled at the same time to see if the Yara sites represent a niche microenvironment or if the overall conditions in the Burrup have changed. It is most unlikely that the latter is the case since independent measurements of many of the previous sites in June 2017 (MacLeod 2017b) has shown increasing acidification of sites near the Climbing Man in the same gully. Rocks from the relocated museum compound were found to have more alkaline pH than in 2003 when they had been thoroughly scrubbed to remove all the paint residues when their “registration numbers” were chemically removed. In an instance when the number had failed to be removed the pH of the rock had fallen i.e. it showed increasing signs of acidification.

In the discussion regarding the pH of the rainfall collected at site 6, the only site to provide measurable amounts of boron in 2018, it was noted that the change in apparent sensitivity of the pH to the nitrate concentration is due to increased amounts of ammonia and ammonium salts (Figure 2). This buffering affect shows up the complicated nature of the interactions between inherently sterile rain water samples and the pH readings collected form the bio-active rock surfaces. In reviewing all the pH and nitrate data from the rock washings it **can be concluded that the operations of the TAN plant by Pilbara Fertilisers has had little measurable impact on the acidification of the Burrup rocks.**

Sulphate:

The amount of sulphate in the washings also varied from one year to the next, as shown in Table 9, which reports the data from the August 2003 and February 2004 rinses, along with the most recent data on the Yara sites from November 2017 and from September 2018.

Table 9: Range of sulphate ions in the wash solutions on Burrup and Yara sites

Date	Maximum	Minimum	Mean ± SD
August 2003	66.7 Rock 938	1.2 Burrup SW2	9.8 ± 14.2
February 2004	26.1 Rock 938	0.8, Deep Gorge, site 7	4.9 ± 5.5
November 2017	9.8, Site 23	1.5, Yara NE, site 22	5.2 ± 3.0
September 2018	2.2, Site 6	0.3, Yara NE, site 22	1.2 ± 0.7

It is apparent that there is a two-fold drop in the mean sulphate concentration in the wash solutions between August 2003 and February 2004. The data shows that there has been essentially no change in the amount of sulphate present in the 2017 compared with the 2004 readings, other than the maximum value for 2004 was nearly three times that observed in 2017 at the Yara sites. The highest values reported were found on rock 938 in the "museum compound" which lay inland from the Climbing Man gully and was located behind the hills from the Woodside gas production facility. Unfortunately, there is no corresponding wash solution data from the relocated rock 938 in the June 2017 report. In August 2003 the pH was 4.8 ± 0.4 and in February 2004 it was 4.9 ± 0.6 which makes them statistically the same i.e. there was no correlation between the wash solution sulphate concentration and the underlying acidity. It has been previously noted that the pH of the rock surfaces is significantly affected by the chloride levels, coming from the sea salts, so it is instructive to see how the $^{Cl}/_{SO4}$ ratios vary across the Burrup in the different periods of measurement.

Table 10: Ratios of chloride to sulphate ions in the wash solutions from Burrup rocks.

Date	**$Cl^-:SO_4^{2-}$ mean**	**$Cl^-:SO_4^{2-}$ high**	**$Cl^-:SO_4^{2-}$ low**	**$Cl^-:SO_4^{2-}$ sea**
August 2003	5.7 ± 5.4	6 sites @ 11.8 ± 6.6 Climbing Man, off museum site rock 162,	14 sites @ 3.1 ± 1.2 Dampier, King Bay, Deep Gorge	7.1
February 2004	21 ± 15	14 sites @ 9.9 ± 5.1 Climbing Man, off museum site, Rock 3	27 sites @ 4.3 ± 1.2 Gidley & Dolphin Islands, Dampier, Rocks 86, 162, 938,	7.1
November 2017	1.1 ± 0.3	site 22, 2.2	site 7, 0.7	7.1
September 2018	2.8 ± 1.8	Site 22 Yara NE 6.0	Site 4 Woodside 0.7	7.1

Despite the large standard deviations of the mean values for 2003 and 2004 data the high ratios of $Cl^-:SO_4^{2-}$ do reflect the expected amount of sulphate present in the individual rock washings when compared with the chloride ratios found in seawater. From the numbers of sites sampled, roughly one-third of the rocks had the expected chloride to sulphate ratio. For the ratios that are significantly lower than those found in normal seawater, this implies that there is additional sulphate present in the rock surface washings i.e. sulphate is not coming from the sea. For the Yara sites there is a further significant reduction in the $Cl^-:SO_4^{2-}$ ratio which means that additional sulphate is coming from sources other than the sea. These sources appear to be altering the surface chemistry of the sites. It is likely that deposition of SO_x is affecting 60% of the Burrup rock art sites and that this impact is felt even on remote sites such as Gidley and Dolphin Islands. However, it is noted that in the 2018 data site 4, near the Woodside flare tower, had the lowest ratio of chloride to sulphate, which is consistent with the deposition of SO_x from the combustion products of the flared gases. The exposed position of site 22 at Yara NE gave a near normal ratio of 6.0, compared with 7.1 for seawater.

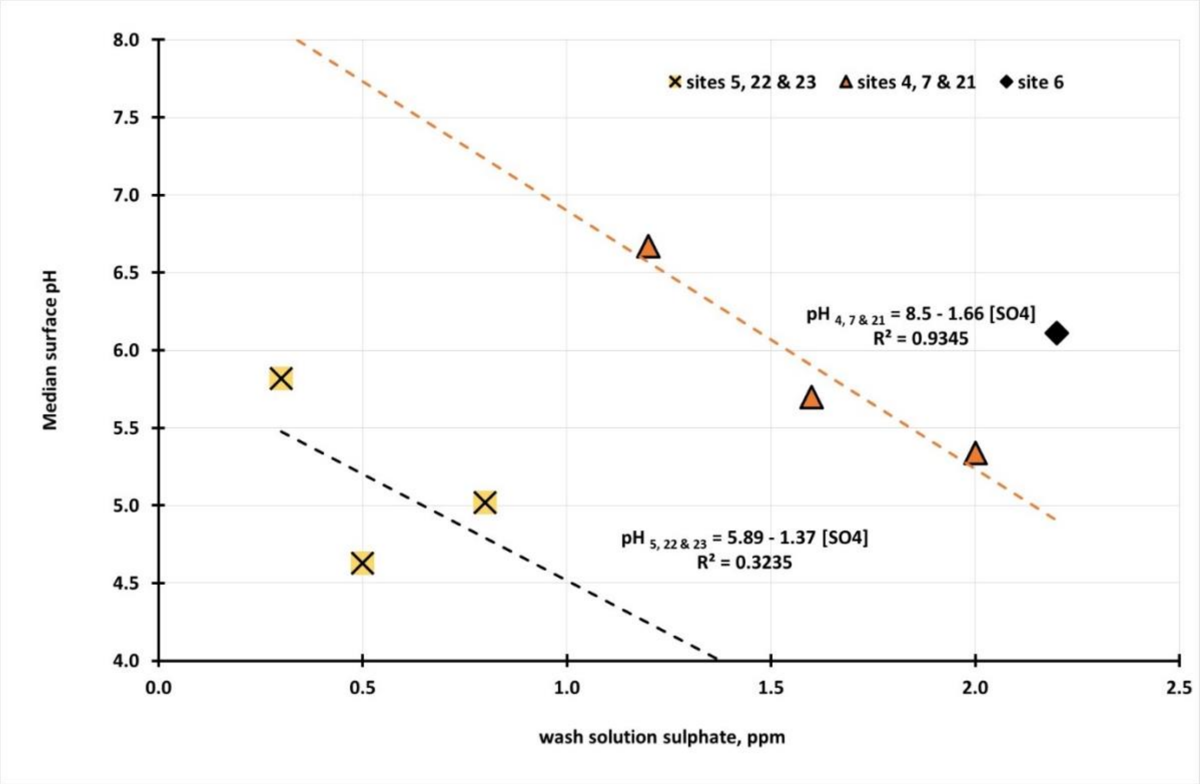

Figure 10: Plot of the median rock surface pH for all sites vs. 2018 SO_4^{2-}wash.

It is noted that the two regression lines in Figure 10 have the same slope, for the upper line with the intercept (pH at zero sulphate) has a value of 8.5 ± 0.7 which is the pH of normal sea water. This indicates that the surface pH is largely controlled by the amount of sea salt that is deposited on the rocks. The second set of data covers sites 5, 22 and 23 and it has an intercept value of pH 5.9 ± 1.1 (large error due to low R^2 value) which is typical of the natural surface pH of hydrated iron and manganese minerals. For the sites 4, 7 and 21 the slope is 1.7 ± 0.4 which is statistically the same as the other slope of 1.4 ± 2.0! In November 2017 the intercept value at zero sulphate was 6.25 for sites 6, 7, 22 and 23 but the slope was such that the pH fell only by 0.12 per ppm of sulphate.

When the pH scale was changed to the pH intercept values, calculated from the linear regression analyses of how pH responded to chloride ion concentration at the particular sites, the intercept pH value increased from 6.25 to 6.39 and the slope of the equation increased from 0.12 to 0.20, which indicates that the sensitivity of pH to the sulphate levels, with the effect of the chloride "eliminated" through use of the $pH_{\text{intercept}}$ values, is higher due to the effective removal of the buffering capacity of the chloride bearing sea salts. The site with a more alkaline mean pH than the rest of the sites in and around the Yara plants was site 21. This site is in a very open location on the flat ground in between the two ranges of hills in which the industrial estate has been established. It is subject strong airflow patterns from Hearson's Cove, and this may be a contributing factor to the more alkaline surface. This site has the highest chloride ion content reported in the wash solutions and so the increased alkalinity is understandable, without having to invoke unusual chemistry. This site also had the lowest chloride to sulphate ratio and the highest amount of nitrate, which is directly downstream from the production plants.

Comparison of pH between 2017 and 2018

A summary of the differences between the two seasons of measurements is found in Table 10 and in Figure 11 below. For site 22 (gabbro), 6 and 5 (granophyre) the differences between the two sets of measurements is within experimental error i.e. there is no statistically significant difference in the acidity of the three sites. For site 23 (gabbro) and site 21 (granophyre) there was a similar increase of 0.64 ± 0.03 which is statistically the same as the mean and standard deviation when the value of site 4 is included.

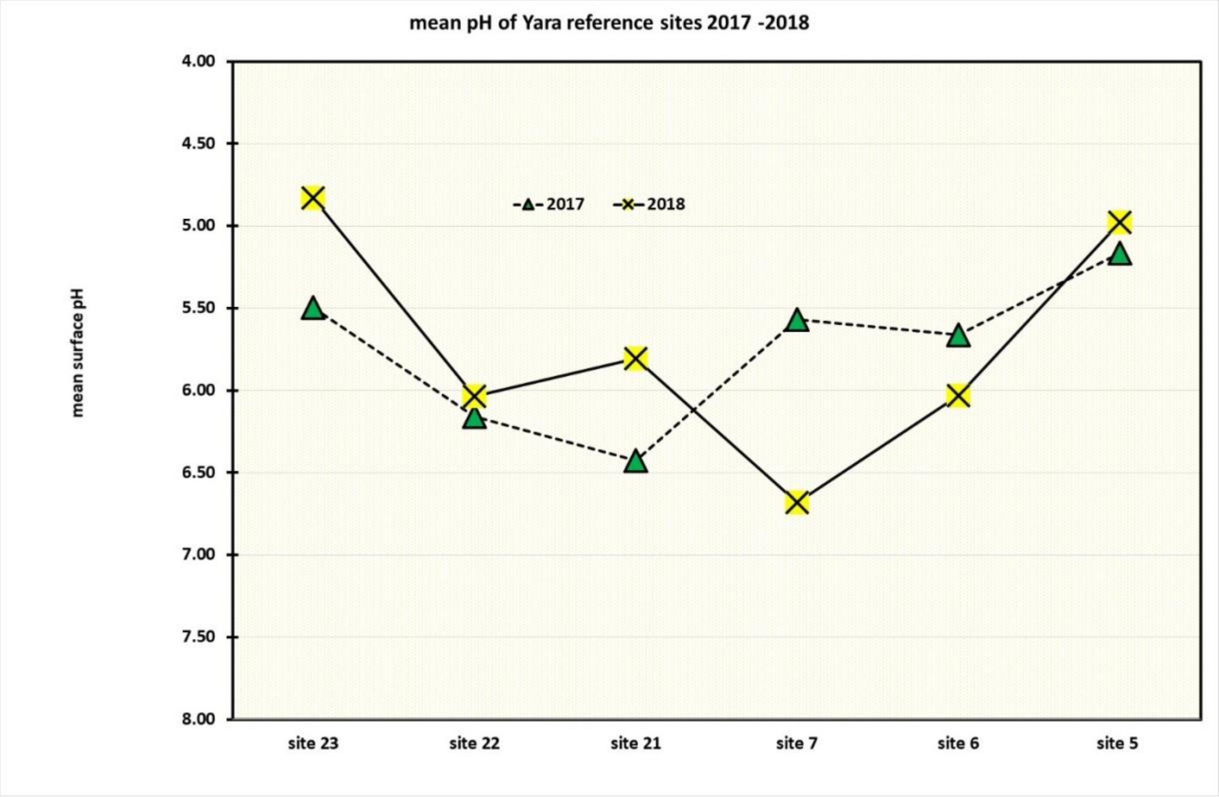

Figure 11: Comparative plots of mean surface pH across the Yara sites

Table 10: Changes in mean surface pH between Nov 2017 and September 2018

Location	2017	Std dev 2017	2018	Std dev 2018	Fall in pH 2071- 2018
site 23	5.50	0.62	4.83	0.64	0.67
site 22	6.16	0.48	6.04	0.57	0.12
site 21	6.43	0.45	5.81	0.65	0.62
site 7	**5.57**	**0.42**	**6.68**	**0.39**	**-1.11**
site 6	5.66	0.70	6.03	0.54	-0.37
site 5	5.17	0.60	4.98	0.43	0.19
site 4	3.81	0.52	4.28	0.59	-0.48
Climbing Man	6.04	0.61	5.81	0.39	0.23

When the standard deviations of the site pH measurements are considered there is only one site, site 7 at Deep Gorge, which is statistically significantly different, and this site had become more alkaline. The significance of the differences is assessed by dividing the difference in pH by the sum of the standard deviations of the two sets of data. If the quotient is less than 1 it is not significant and if above 1 then it is and at 1.4 the differences are significant.

Summary of the surface pH, chloride & redox at Yara sites

It should be noted that in the 2017 measurements on the Yara test sites that only the surface pH and chloride ion activities were recorded. The utilisation of redox data on the Burrup rocks was not developed until July 2017 and was not adopted until after peer review had confirmed it was a viable indicator of chemical activity on the rock surfaces.

site 23 Yara N West

	2018 pH	2017 pH	2018 Cl	2017 Cl	2018 E vs AgCl
Mean	4.83	5.50	29.6	18.5	0.282
Standard Error	0.18	0.20	4.6	5.5	0.004
Median	4.63	5.65	25.0	11.5	0.286
Mode	4.63	#N/A	#N/A	6	0.287
Standard Deviation	0.64	0.62	17.2	17.4	0.016
Range	2.15	1.97	53.7	50.5	0.068
Minimum	4.16	4.42	11.5	4.5	0.238
Maximum	6.31	6.39	65.2	55	0.306
Count	13	10	14	10	14

Generally, there was no statistically significant shift in the pH and the ranges of acidity were similar but the minimum pH for 2018 of 4.16 was more acidic than the 2017 value of 4.42, despite the apparent buffering capacity of the site which had a higher mean chloride activity in 2018 owing to its exposed location catching the winds coming up from Hearson’s Cove.

site 22 Yara North East

	2018 pH	2017 pH	2018 Cl	2017 Cl	2018 E vs AgCl
Mean	6.04	6.16	10.2	33.3	0.290
Standard Error	0.17	0.15	3.4	7.7	0.004
Median	5.82	6.42	8.5	26.3	0.293
Standard Deviation	0.57	0.48	11.2	24.3	0.012
Range	2.01	1.25	39.6	82.5	0.044
Minimum	5.3	5.34	1.4	14.5	0.256
Maximum	7.31	6.59	41	97	0.3
Count	11	10	11	10	11

Site 22 which is to the North East of the Pilbara nitrates plant and although the mean pH is the same for both 2018 and 2017 the median value is more acidic in 2018 although the minimum pH of the site is the same in both seasons. This site is characterised by a lower chloride concentration on the rock surface which may account for the lower median value of the pH since there is less sea salt residues to buffer the rock surface. The mean redox potential of sites 23 and 22 is very similar which is not surprising since they are both gabbro rocks. However, the mean redox potential is much the same as for the granophyre rocks at site 21.

For Site 21, at Yara West, an inspection of the pH data indicates that this site has increased the acidity in 2018 compared with 2017, with falls averaging 0.6 for both the mean and the median values. Similarly, the minimum pH recorded in 2018 was 4.9 compared with 5.8 in 2018 and this may reflect the much lower chloride surface reading of 20 ppm compared with 143 ppm the year before. Lower chlorides are associated with a reduced buffering capacity to resist the acidification due to metabolic activity of the microflora.

site 21 Yara West

	2018 pH	2017 pH	2018 Cl	2017 Cl	2018 E vs Ag/AgCl
Mean	5.81	6.43	19.7	142.8	0.285
Standard Error	0.18	0.14	3.6	13.9	0.002
Median	5.70	6.44	21.0	136.0	0.287
Standard Deviation	0.65	0.45	12.8	44.0	0.007
Range	2.07	1.51	45.6	126	0.027
Minimum	4.86	5.78	0.9	88	0.270
Maximum	6.93	7.29	46.5	214	0.297
Count	13	10	13	10	13

site 7 Deep Gorge

	2018 pH	2017 pH	2018 Cl ppm	2017 Cl	2018 E vs AgCl
Mean	6.68	5.57	18.6	21.5	0.227
Standard Error	0.12	0.11	2.5	3.7	0.008
Median	6.67	5.53	17.3	24.0	0.230
Mode	7.02	5.90	#N/A	30.0	0.230
Standard Deviation	0.39	0.42	7.8	11.7	0.025
Range	1.14	1.49	28.8	27.8	0.082
Minimum	6.06	4.92	8.2	7.2	0.178
Maximum	7.20	6.41	37.0	35.0	0.260
Sum	66.81	83.54	185.9	215.4	2.269
Count	10	15	10	10	10

The acidity on this site has significantly decreased with the 2018 mean pH being 6.7 ± 0.4 which is much more alkaline than the mean value in 2017 of 5.6 ± 0.4 but the reduction in acidity is not due to any increase in chloride content on the surface, as the 2018 values are the same as those recorded in 2017. It is interesting to note that on this gabbro rock the mean redox potential is significantly lower than those observed on the sites 21, 22 and 23. It was noted that the grey-black mineralogy on the surface of this rock is due to the formation of significant amounts of the manganese equivalent of magnetite, namely Mn_3O_4 and this lower voltage is consistent with the general trend in iron (III)/(II) couples having a more oxidizing power than the corresponding Mn (III)/(II) couples. The reader is referred to the detailed discussion noted in preceding sections covering the issue of mobilisation of iron and manganese minerals.

Site 6 Water tanks

	2018 pH	2017 pH	2018 Cl	2017 Cl	2018 E vs AgCl
Mean	5.85	5.66	2.3	190.8	0.194
Standard Error	0.19	0.07	0.9	48.6	0.006
Median	6.11	5.76	1.2	164.5	0.201
Mode	4.70	5.85	#N/A	#N/A	0.201
Standard Deviation	0.70	0.22	3.2	97.3	0.020
Range	1.7	0.57	11.3	218	0.068
Minimum	4.7	5.28	0.3	108	0.156
Maximum	6.4	5.85	11.6	326	0.224
Count	13	10	13	4	11

The rocks adjacent to site 6 were systematically assessed for surface pH, chloride and redox potential. The mean pH of 5.9 ± 0.7 was not statistically different to the 2017 value of 5.7 ± 0.2 and although there was the full suite of chloride readings taken (13 compared with 4 in 2017) the much lower chloride content is perhaps only reflected in the more acidic minimum pH reading of 4.7 in 2018 compared with 5.3 in 2017. With less sea salt to buffer the acidic metabolites it is not unexpected to have a more acidic minimum pH value. The mean redox voltage was 0.194 ± 0.020 which is the lowest voltage of all the seven sites examined.

Site 5 Burrup Road

	2018 pH	2017pH	2018 Cl	2017 Cl	2018 E vs AgCl
Mean	4.98	5.17	4.1	31.7	0.265
Standard Error	0.12	0.18	1.0	8.6	0.003
Median	5.02	5.17	3.1	24.0	0.264
Standard Deviation	0.43	0.60	3.5	28.5	0.011
Range	1.61	1.68	12.8	101.8	0.032
Minimum	3.97	4.36	1.2	4.2	0.251
Maximum	5.58	6.04	14	106.0	0.283
Count	12	11	12	11	12

Although there is not any statistically significant difference in the mean pH of the 2018 and 2017 readings, the 2018 data shows a tighter spread of surface acidity values than that from 2017. Both seasons have essentially the same range of pH (1.6-1.7) but the minimum pH for 2018 is slightly lower at 4.0 than the value of 4.4 in 2017. Along with other sites it is noted that there is a significantly lower mean and median chloride reading which supports the view that with less sea salt around there is less buffering of the acidic metabolites of the resident microflora.

Non Yara sites: CSIRO Site 4: Climbing Man gully near flare tower

The data for the CSIRO reference rock no 4 was collected in the same manner as the other sites – the site is about 75^{o} to the vertical.

2018	**pH**	**Cl**	**E vs AgCl**
Mean	5.52	2.2	0.283
Standard Error	0.24	0.5	0.003
Median	5.34	1.4	0.283
Mode	5.34	1.5	0.278
Standard Deviation	0.92	2.1	0.011
Sample Variance	0.85	4.4	0.000
Kurtosis	-0.88	1.8	1.741
Skewness	0.46	1.7	0.601
Range	2.90	6.6	0.046
Minimum	4.38	0.5	0.265
Maximum	7.28	7	0.311
Count	15	15	15

The distribution of the measurements appeared to be quite sensitive to the location on the large rock, with similar groupings of pH and chloride in similar locations on the surface. Data was more similar in the vertical profiles than the horizontal values, which indicates that the microclimate is a major factor in controlling deposition of sea salts and other materials. The equation for the surface pH at the rock adjacent to the engraved goannas at site 4 is given by the following expression,

$$\text{pH site 4} = 2.99 + 2.67\,[\text{Cl}] \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (26)$$

The mean value of the pH at the site in 2018 was 4.3 ± 0.6 with a minimum pH of 4.4 and a maximum of 7.3 which is less acidic than it was in 2017 when the mean pH was 3.8 ± 0.5 with a minimum of 3.5 and a maximum of 5.5. The intercept of the pH vs. chloride plot for site 4 in 2018 is the same pH as the minimum recorded in 2017.

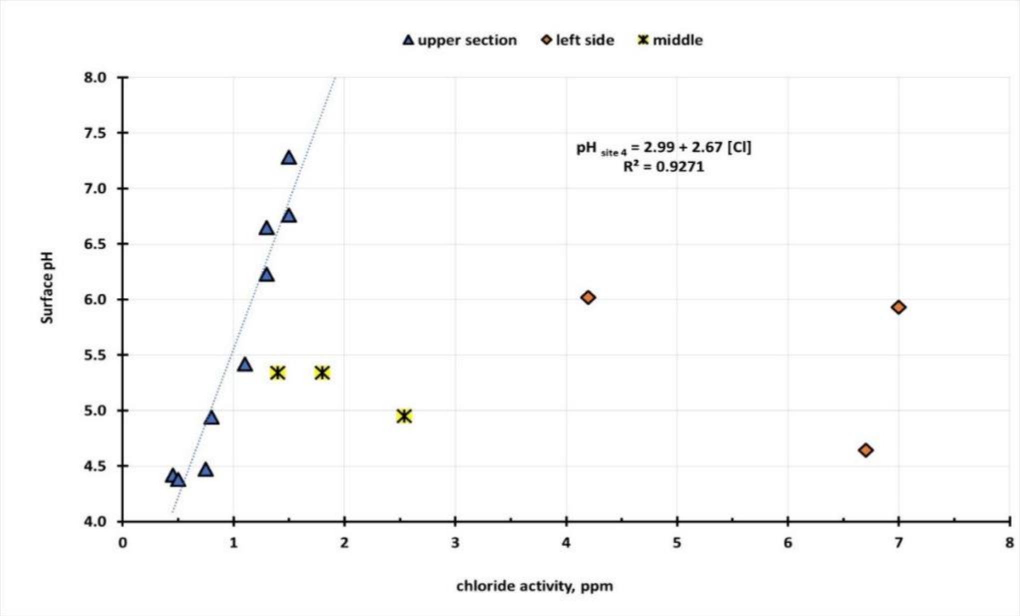

Figure 12: Site 4 pH vs. surface chloride in Climbing Man gully near the road.

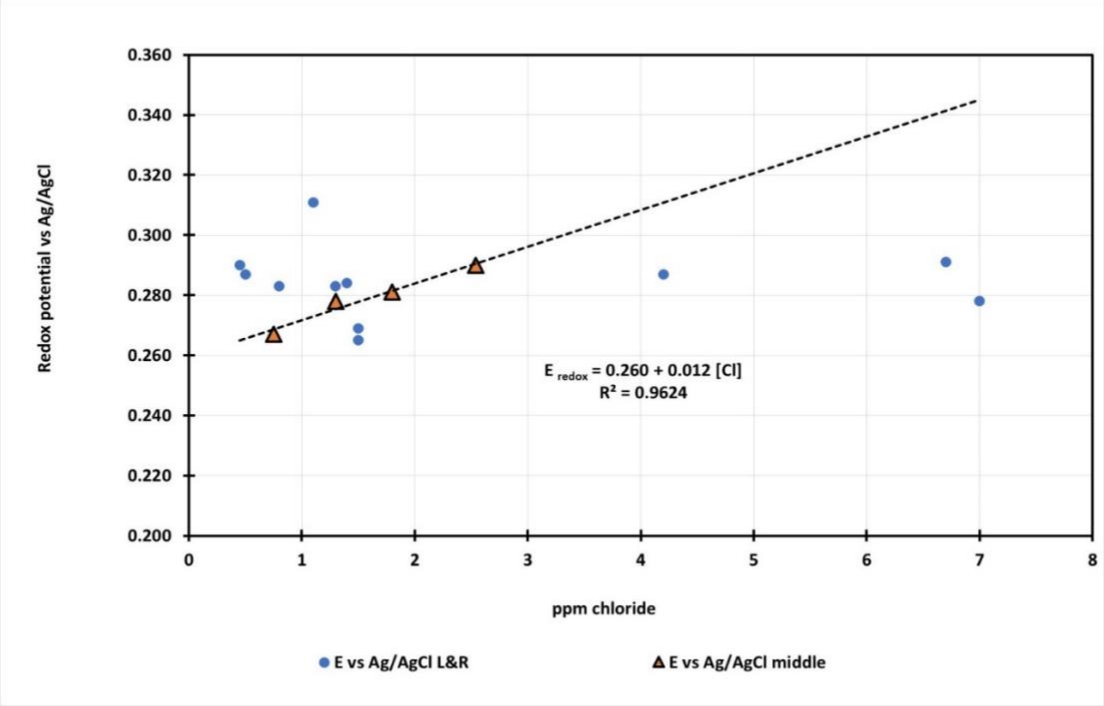

Figure 13: Dependence of the redox potential at site 4 on chloride concentration

This change in the mean pH at site 4 is consistent with the data from site 7 at Deep Gorge and may be associated with the cyclonic rainfall earlier in the year. It was also noted that the redox chemistry was location dependent, as seen in Figure 13 above. The apparent sensitivity of the location of the measurement points on the rock surface was again reflected in the redox voltage measurements.

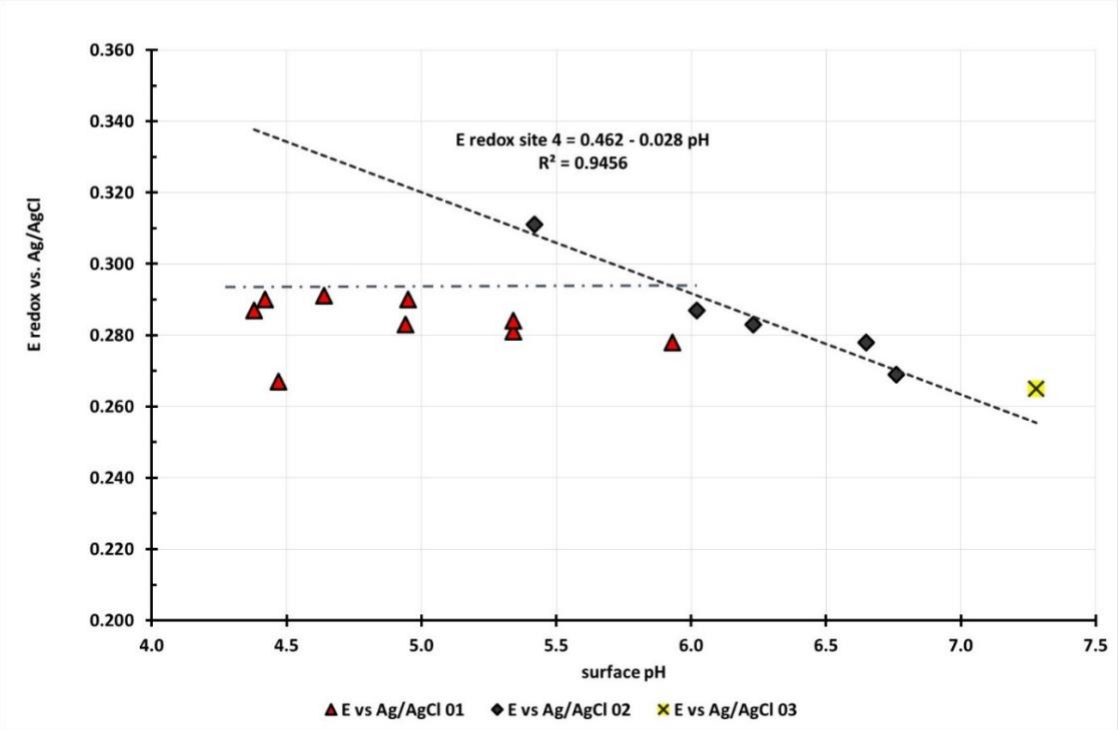

Figure 14: Pourbaix plot for site 4 area showing standard slope of 28 ± 2 mV for hydrolysis of metal ions

The Pourbaix diagram for this site is provided for interest and as a comparison for the data collected on the six Yara monitoring sites. Inspection of the plot in Figure 14 shows that the voltage is invariant from around 4.3 up to a pH of about 5.3 and then it responds with a standard 29 mV/pH slope associated with hydrolysis of metal ions, as shown by equation 27.

$E_{\text{redox site 4}} = 0.462 + 0.028\ \text{pH}$ .... (27)

The simple explanation for the period of apparent "inactivity" is due to the surface pH is too acidic to allow for the formation of $M(OH)^{n+}$ ions.

Comparison of Yara and Climbing Man gully sites in September 2018

In reviewing the mean pH of the rock surfaces in 2017 and 2018 the only significant change is that the Deep Gorge site has become more alkaline. All the sites at Burrup Road (5), Water Tanks (6), Yara West (21), Yara North East (22) and Yara East (23) were within one standard deviation of each other, as seen in Figure 15. It should be noted that the ordinate scale is with values of pH reversed, so that the most acidic sites lie with the highest profile in the graphical plot. It is disappointing that the rainfall data for site 5, on the Burrup Road and so it is close to the monitoring station, showed no systematic trends of pH and nitrate or other nitrogenous anions, cations and neutral molecules. There is a need for closer cooperation between the Yara and the Woodside air quality monitoring teams and the rock art conservation team to work through the mechanisms of connecting aerial data and deposition data with the net outcomes of all these events, engaging as they do on the biodynamic surfaces of the engraved Burrup boulders. The graph in Figure 15 gives strong indications that the proximity of the monitoring rocks to flare towers may well be a contributing factor to the more acidic surfaces on site 4 and site 5.

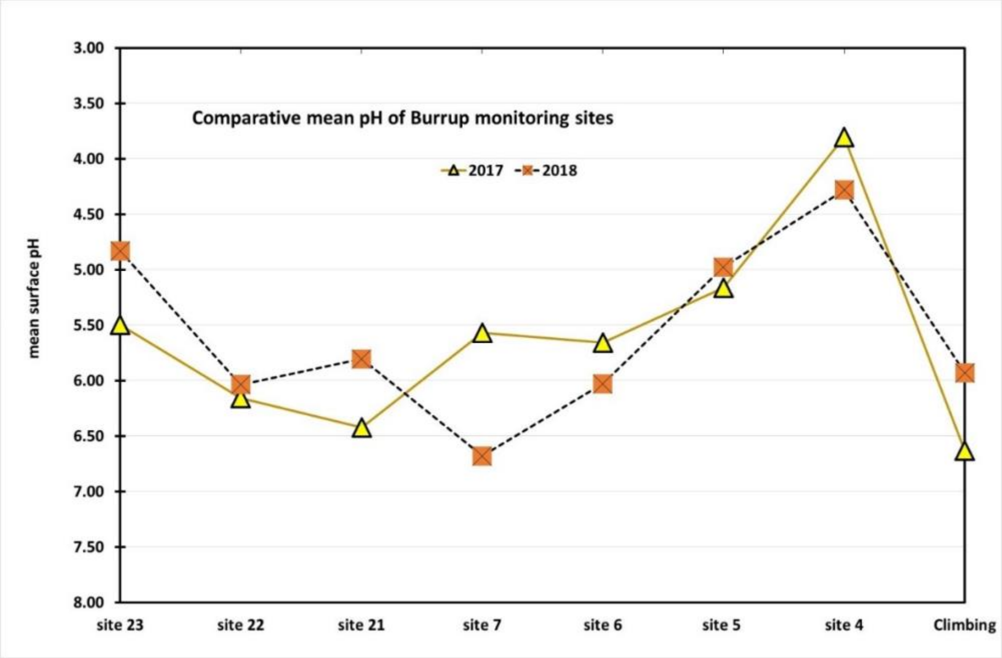

Figure 15: Distribution of mean surface pH across the Burrup sites in Sept. 2018

Colour measurements

Colour measurements using the ASD spectrophotometer to record the complex mineralogy of background and engraved areas were digitally recorded. At the same time the colour measurements using the Konica-Minolta Chromameter (KMC) were made on the designated CSIRO reference rocks. A total of 20 separate readings, with the relocation of the sampling head, were made on every background spot and on the engraved areas.

The initial analysis of the colour differences was conducted using the methodology outlined in the CSIRO September 2008 Report (Burrup Peninsula Aboriginal Petroglyphs: Colour Change and Spectral Mineralogy 2004–2007 D. Lau, E. Ramanaidou , S. Furman , A. Hacket , M. Caccetta , M. Wells & B. McDonald). This involved using the CIE standard formula for colour difference by taking the square root of the differences between the L, a and b values recorded by the Konica Minolta Chromameter. The formula used for determining the colour difference was as noted below,

$$\text{delta } E_{97} = \{(L_b\text{-}L_e)^2 + (a_b\text{-}a_e)^2 + (b_b\text{-}b_e)^2\}^{½} \quad \text{...} \quad (28)$$

Unlike the 2017 measurements there was much less dust on the rock surfaces, and this is likely due to the heavy rainfall that took place in June 2018. Owing to uncertainties associated with the assessment of the colour difference readings on each of the six sites, both the original data and the calculated delta E values were reviewed by Bruce Ford of www.microfading.com since there have been major revisions by colour conservators regarding the evaluation of what are statistically reliable measurement of colour differences. Using the criterion that the MCDMt (total mean colour distance from the mean)/Delta E > 0.5 the sites were assessed for colour change and the results are noted below in Table 11.

It is noted that when the contrast between the $L^*a^*b^*$ is made between the background and the engraved areas on each measurement point and in each location, the authors erred on the side of caution and accepted that a just significant difference could, in the first instance, be regarded as being significant. For site 5 at Burrup Road the 2017 data points were all significantly different in contrast and all were still clearly showing differences in 2018. The only statistically significant difference between the two years was spot Site 5-3 which recorded a decrease in contrast of 4.05.

Table 11: Colour differences for 2018 on four spots on each site compared with 2017

site	**MCDM (t)00**	**ΔE00**	**MCDM/ ΔE00**	**significant?**	**ΔE change**	MCDM(t)	MCDM(t) /ΔE	
S5 spot1	0.75	5.39	0.14	Yes	0.81	0.95	1.17	No
S5 spot2	1.07	5.96	0.18	Yes	0.71	1.31	1.84	No
S5 spot3	2.08	3.57	0.43	Yes	4.05	2.26	0.56	Yes
S5 spot4	0.80	6.48	0.12	Yes	-2.12	0.88	0.42	No
S6 spot1	0.87	1.94	0.45	Just	-0.31	1.03	3.33	No
S6 spot2	1.20	1.86	0.65	No	-0.83	1.31	1.58	No
S6 spot3	1.00	2.74	0.37	Yes	-0.89	1.18	1.33	No
S6 spot4	1.05	2.48	0.42	Just	-0.06	1.25	21.02	No
S7 spot1	2.03	3.31	0.61	No	3.83	2.51	0.65	barely
S7 spot2	2.34	1.97	1.19	No	1.04	2.41	2.31	No
S7 spot3	1.54	5.45	0.28	Yes	-1.42	1.56	1.09	No
S7 spot4	2.11	5.32	0.40	barely	-0.45	2.16	4.81	No
S21 spot1	1.64	8.90	0.18	Yes	-3.65	1.65	0.45	Yes
S21 spot2	0.96	4.46	0.22	Yes	-2.72	2.17	0.80	No
S21 spot3	0.82	4.08	0.20	Yes	1.43	1.06	0.74	No
S21 spot4	0.90	6.87	0.13	y	-2.36	1.38	0.58	barely
S22 spot1	3.08	3.09	1.00	n	3.58	3.09	0.86	No
S22 spot2	0.88	1.29	0.68	n	0.87	0.94	1.08	No
S22 spot3	0.75	3.26	0.23	Yes	1.23	1.20	0.98	No
S22 spot4	0.83	4.11	0.20	Yes	-0.36	1.01	2.81	No
S23 spot1	1.69	3.60	0.49	just	-1.34	1.85	1.38	No
S23 spot2	1.07	4.33	0.25	Yes	-1.52	1.24	0.81	No
S23 spot3	1.04	3.90	0.30	Yes	3.14	1.38	0.44	barely
S23 spot4	1.13	3.40	0.34	Yes	-0.78	1.44	1.85	No

The site 7 spot 1 had a barely significant decrease in contrast of 3.83, Site 21 spot 1 was significant at -3.65 i.e. the contrast had increased and spot 4 on the same site was barely significant increase in contrast at a delta E of -2.36. There was no statistically significant colour change on the four spots on site 22 and only spot 3 on site 23 was barely significant at 3.14.

When this data was plotted as a function of the difference between the minimum pH in 2018 and 2017 there was a quadratic function that connected the variables. This equation (no 29) shows that the contrast differences between the 2018 and the 2017 values are related through the differences in the minimum pH. When the 2018 pH minimum values were more acidic the delta E values were negative, i.e. there was an increased contrast between the engraved and the background materials. In the cast of when there was essentially much the same value, like on site 5 spot 3and it was only 0.15 pH units more acidic, there was a barely significant difference in the contrast. When the pH in 2018 was more alkaline, such as on site 7 spot 1, there was significantly less contrast, which equates to reduced differential rates of dissolution of the mineralised surfaces as they become more alkaline – as seen in Figure 16. All the colour measurements (median values of the 20 measurements on each point on each spot on each site) are summarised in Appendix VII.

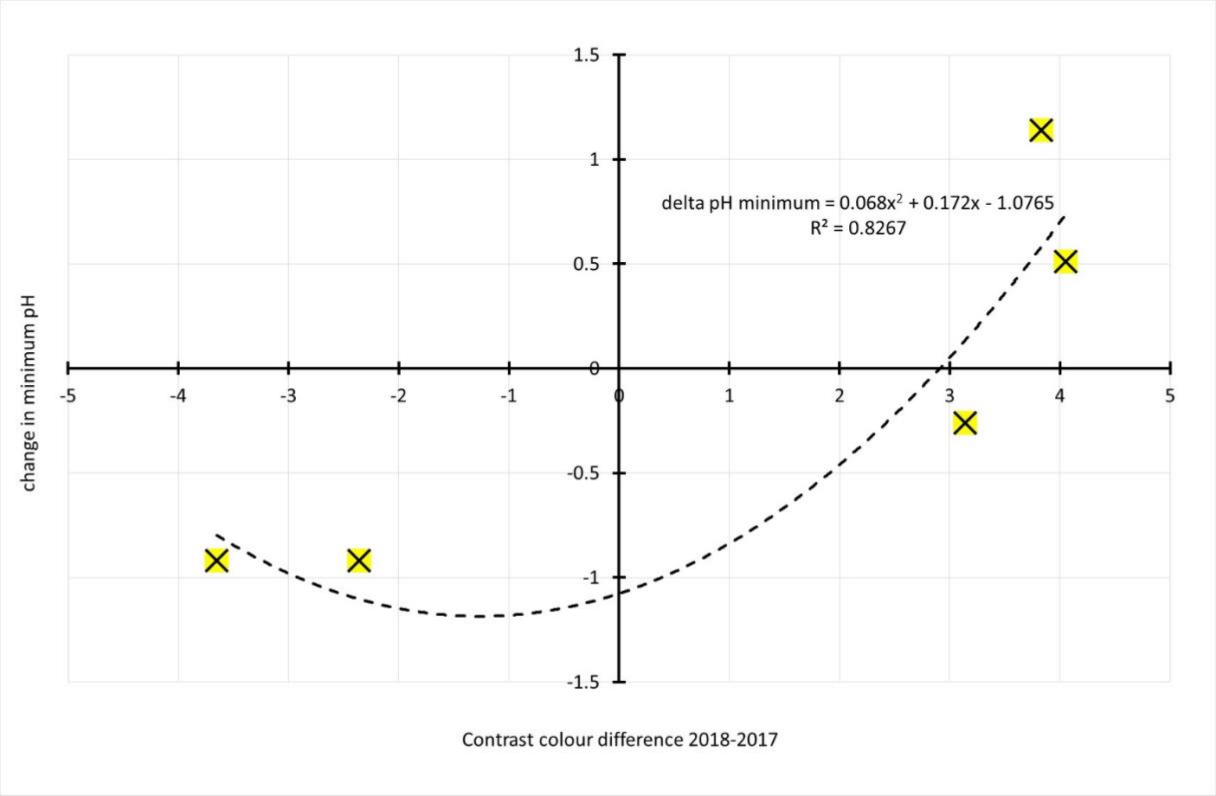

Figure 16: Plot of the contrast difference versus the changes in minimum pH

Conclusion

The analysis of the relationship between the pH and the amount of metal ions reporting to the wash solutions enabled the mechanism controlling the release of manganese containing minerals to the wash solutions to be determined. From a combination of the Pourbaix diagrams and the regression analyses of the voltages at zero pH, the formal redox voltages of the electroactive species could be obtained. In all but one site, the dominant minerals were manganese related materials. The only site where the redox potential involved iron was on the Burrup Road location. The redox data has confirmed that manganese exists in a range of oxidation states on the rock surface and this will be a controlling factor in the rock patination. The re-examination of the data obtained from the previous studies indicates that this change of mechanism for the release of manganese ions into the wash appears to be subtly controlled by the alkalinity associated with increased salt deposits.

Analysis of the relationships between the surface pH and the ions associated with wind borne sea salts has shown that it is most likely that calcium is reporting to solution through the formation of a mixture of calcium carbonate dissolving to produce either free Ca^{2+} ions or the soluble calcium bicarbonate. Increasing chloride ion concentration is an indicator of increasing deposition of sea salts on the rock surfaces. One major effect of the increased salts is that it produces a buffering effect and appears to be inhibiting the activity of micro-organisms associated with the metabolism of nitrogen (nitrate) containing species found on the rock surfaces. The impact of seven major cyclonic downpours between February 2003 and March 2017 has significantly reduced the amount of soluble nitrate being bio-available and this has brought about a change in deterioration mechanism for the more alkaline Yara sites. Measurements at other locations in June 2017, November 2017 and in September 2018 provide evidence of continuing acidification of rocks near the Climbing Man gully.

For the six sites examined in and around the Yara facility there is a decreased amount of sulphate ions than cannot be explained by the increased presence of sea salts. The mean sulphate in 2017 was 5.2 ± 3.0 which decreased to a value of 1.2 ± 0.7 ppm and the decreases were across all the six sites. Sites 5, 6, 7, 21 and 22 had a mean decrease by a factor of 3.9 ± 1.3 but for Yara East the drop was by a factor of nearly 20 times.

The complex behaviour of the concentration of nitrate on the rain water pH at the monitoring stations reflects some of the altered sensitivity of the pH on the rock surfaces. It appears to be related to the adsorption of ammonia and conversion to ammonium ions by the acidic metabolites of the rock microflora. The present analysis strongly supports the view that the operations of the TAN plant by Pilbara Fertilisers has had no measurable impact on the acidification of the Burrup rocks, through a changed distribution of available nitrate ions.

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APPENDIX I: MacLeod publications on rock art conservation

Refereed journal articles

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APPENDIX II: Chemical analysis of the wash solutions from the CSIRO monitoring sites September 2018.

Concentrations are in mg/L other than electrical conductivity which is in mS/m
Report 18S0974

Chem Centre Id	Method Code	*Limits of Reporting*	18S0974 /001	18S0974 /002	18S0974 /007	18S0974 /003	18S0974 /004	18S0974 /005	18S0974 /006
			Site 4	Site 5	Site 6	Site 7	Site 21	Site 22	Site 23
			7/09/18	4/09/18	3/09/18	4/09/18	5/09/18	5/09/18	6/09/18
Al	ICP	*0.005*	<0.005	<0.005	0.009	<0.005	<0.005	<0.005	<0.005
As	WCMS	*0.001*	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
B	WCMS	*0.005*	<0.005	<0.005	0.007	<0.005	<0.005	<0.005	<0.005
Ba	WCMS	*0.0001*	0.0019	0.0012	0.0023	0.0021	0.0024	0.0009	0.0011
Ca	ICP	*0.1*	0.9	0.3	2.2	0.9	0.7	0.2	0.4
Cd	WCMS	*0.0001*	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Cl	IC	*0.5*	1.3	2.1	2.2	2.5	5.4	1.8	1.8
Co	WCMS	*0.0001*	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Cr	WCMS	*0.0005*	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005
Cu	WCMS	*0.0001*	0.0008	0.0012	0.0017	0.0009	0.0014	0.0011	0.0013
ECond	WZSE	*0.2*	1.6	1.6	2.5	1.9	4	1.7	1.2
Fe	ICP	*0.005*	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
K	ICP	*0.1*	0.7	0.8	0.3	0.4	0.5	2.1	0.6
Mg	ICP	*0.1*	0.1	<0.1	0.2	0.2	0.4	<0.1	<0.1
Mn	WCMS	*0.0001*	0.0024	0.0013	0.0006	0.0041	0.0014	0.001	0.0014
NO2	WFIA	*0.1*	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
NO3	WFIA	*0.05*	0.54	0.32	0.89	0.75	1.4	1	0.19
Na	ICP	*0.1*	1	1.5	1.6	1.4	5.3	1.1	1.2
Ni	WCMS	*0.001*	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Oxalate	IC	*0.1*	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Pb	WCMS	*0.0001*	0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	0.0002
S	WCICP	*0.1*	0.7	0.3	0.7	0.4	0.6	0.1	0.2
SO4	IC	*0.1*	2	0.8	2.2	1.2	1.6	0.3	0.5
V	WCMS	*0.0001*	0.0002	<0.0001	0.0002	0.0001	<0.0001	<0.0001	<0.0001
Zn	WCMS	*0.001*	0.003	0.006	<0.001	<0.001	0.006	0.005	0.002

Sample volumes for the metal ion analyses were 200 ml and for the anions the volume was 100 ml
Samples were collected on the same rocks and stored in different containers which were kept cool with ice-bricks

APPENDIX III: Chemical analysis of the wash solutions from the CSIRO monitoring sites.

Concentrations are in mg/L other than electrical conductivity which is in mS/m
Report dated 7 December 2017

ChemCentre Id	Method Code	Limits of Reporting	17S2175-002	17S2175-001	17S2175-004	17S2175-005	17S2175-006	17S2175-003	17S2175-007
Client Id			Site 5	Site 6	Site 7	Site 21	Site 22	Site 23	Blank
Sampled			21/11/2017	20/11/2017	22/11/2017	22/11/2017	23/11/2017	21/11/2017	24/11/2017
Al	iMET1WCICP	0.005	<0.005	0.016	0.007	0.009	0.006	0.019	<0.005
As	iMET1WCMS	0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
B	iMET1WCMS	0.005	<0.005	0.008	<0.005	<0.005	<0.005	<0.005	<0.005
Ba	iMET1WCMS	0.0001	0.0061	0.011	0.0043	0.0097	0.0024	0.0064	0.0004
Ca	iMET1WCICP	0.1	1.1	11.5	3.2	2.5	0.5	5	0.1
Cd	iMET1WCMS	0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Cl	iANIO1WAIC	0.5	3.2	5.3	3.9	7.4	3.3	13	<0.5
Co	iMET1WCMS	0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Cr	iMET1WCMS	0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005
Cu	iMET1WCMS	0.0001	0.0066	0.0016	0.0007	0.017	0.001	0.0021	0.0023
E Cond	iEC1WZSE	0.2	1.6	12.2	3.1	5.2	0.8	7.6	<0.2
Fe	iMET1WCICP	0.005	<0.005	0.012	0.008	0.011	0.005	0.01	<0.005
K	iMET1WCICP	0.1	0.5	0.6	0.4	1	0.2	0.7	0.2
Mg	iMET1WCICP	0.1	0.1	0.7	0.5	0.7	<0.1	0.6	<0.1
Mn	iMET1WCMS	0.0001	0.0026	0.0038	0.0051	0.006	0.0011	0.0009	0.0003
NO2	iNTR1WFIA	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
NO3	iNTA1WFIA	0.05	0.25	0.46	0.38	1.9	1.1	0.22	0.15
Na	iMET1WCICP	0.1	1.2	7.2	1.6	5.2	1.4	9.3	0.3
Ni	iMET1WCMS	0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Oxalate	iANIO1WAIC	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	
Pb	iMET1WCMS	0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
S	iMET1WCICP	0.1	1	2.6	2	2.5	0.3	3.2	<0.1
SO4	iANIO1WAIC	0.1	2.8	4.2	5.8	7.1	1.5	9.8	<0.1
V	iMET1WCMS	0.0001	0.0003	0.0006	0.0004	0.0004	0.0002	0.0006	<0.0001
Zn	iMET1WCMS	0.001	0.008	0.009	0.003	0.01	0.004	0.004	0.004

Sample volumes for the metal ion analyses were 200 ml and for the anions the volume was 100 ml
Samples were collected on the same rocks and stored in different containers which were kept cool with ice-bricks

APPENDIX IV: Acidity and chlorinity measurements adjacent to the CSIRO monitoring sites November 2017

Site 6: Water Tanks **20-Nov-17**

Location	**pH**	**Cl ppm**
1	5.61	134
2	5.72	195
3	5.83	
4	5.33	
5	5.85	
6	5.54	108
7	5.85	326
8	5.81	
9	5.28	
10	5.80	
mean	**5.66**	**191**
stdev	**0.22**	**97**

RH	49.9%
T air	31.4
T surface	45.9
T dew point	19.6

Date **21/11/2017**

Site 5: Location off Burrup road

location	**pH**	**Cl ppm**
1	6.04	55
2	5.79	28
3	5.7	12
4	5.75	30
5	5.17	24
6	5.19	22
7	5.06	106
8	4.37	10
9	4.36	18
10	4.82	4.2
11	4.57	40
mean	**5.17**	**32**
stdev	**0.60**	**28**

Latitude	-20.62109
Longitude	116.76925

Time	07:15	08:45
RH	77%	42%
T air	23.7	34
T surface	25.7	32
T dew	19.2	
Ts-Td	8.4	

Location	**pH**	**Cl ppm**
1	5.68	4.5
2	5.75	6.2
3	5.62	15
4	4.45	55
5	5.49	8
6	6.39	42
7	4.42	26
8	5.47	6
9	5.76	6
10	5.93	16
mean pH	**5.50**	**18**
stdev pH	**0.62**	**17**

Site 23
Yara East
21/11/2017

Latitude	-20.6229
Longitude	116.797
Time	09:30
RH	37.3
T air	34.9
T surface	34.2
T dew	17.3
Ts-Td	17.6

Site 7 Deep Gorge

location	**pH**	**Cl ppm**
1	6.21	35
2	5.16	
3	5.53	32
4	5.93	30
5	4.92	
6	5.29	7.2
7	5.43	30
8	5.57	
9	5.3	12
10	5.9	34
11	5.32	
12	5.58	9
13	5.9	18
14	6.41	
15	5.09	8.2
mean pH	**5.57**	**22**
stdev pH	**0.42**	**12**

Date	**22-Nov-17**
Latitude	-20.63722
Longitude	116.78831
Time started	06:30
Time finished	08:30
Relative humidity	40.40%
Temperature air	31.4
Temperature surface	37.8
Temperature dew pt.	17
Ts-Td	21.3

Location no Site 21 Yara West **Date of measurements 22-Nov-17**

Location	**pH**	**Cl ppm**
1	7.29	214
2	6.91	132
3	6.35	140
4	6.52	90
5	6.39	88
6	6.56	140
7	6.49	214
8	5.78	165
9	5.98	125
10	5.98	120
mean	**6.43**	**143**
stdev	**0.45**	**44**

Time of initiation	09:45
T air	38.6
T rock	38.8
T dew	11.3
Ts -Td	26

Site 22 **Date 23/11/2017**

Location	**pH**	**Cl ppm**
1	**6.58**	**26.5**
2	**6.42**	**14.5**
3	**6.42**	**27.6**
4	**6.16**	**97**
5	**6.49**	**21**
6	**5.43**	**46**
7	**6.59**	**36**
8	**5.34**	**14.6**
9	**6.42**	**24**
10	**5.74**	**26**
mean	**6.16**	**33**
stdev	**0.48**	**24**

Latitude	-20.6176
Longitude	116.7996

	Begin	End
Relative humidity	86.80%	15.20%
Temperature air	26.5	43.7
Temperature rock	30.8	33
T dew point	24.4	
Ts-Td	5.2	

APPENDIX V: Acidity and chlorinity measurements adjacent to the CSIRO monitoring sites September 2018

Site 4: Woodside 35% RH, air 24.3° & rock 26.8° 7 Sept. 18

location no	pH	Cl	E vs Ag/AgCl
1	7.28	1.5	0.265
2	6.65	1.3	0.278
3	6.76	1.5	0.269
4	5.42	1.1	0.311
5	5.34	1.8	0.281
6	6.23	1.3	0.283
7	6.02	4.2	0.287
8	5.34	1.4	0.284
9	4.94	0.8	0.283
10	4.64	6.7	0.291
11	4.47	0.75	0.267
12	4.42	0.45	0.29
13	4.95	2.54	0.29
14	5.93	7	0.278
15	4.38	0.5	0.287
average	5.52	2.2	0.283
stdev	0.92	2.1	0.011

Site 5: Burrup Road 27% RH, air 33.2°, rock 39.5° 4 September 2018

location	pH	Cl ppm	E vs AgCl
1	3.97	14	0.254
2	4.65	1.4	0.256
3	4.66	1.88	0.256
4	4.88	4.59	0.259
5	5.58	2.7	0.259
6	5.15	3.8	0.269
7	5.41	4.1	0.271
8	5.33	3.1	0.273
9	5.18	2.65	0.251
10	4.87	3	0.274
11	5.17	6.9	0.283
12	4.87	1.2	0.277
mean	**4.98**	**4.1**	**0.265**
stdev	**0.43**	**3.5**	**0.011**

Site 6 on 3 September 2018

Reference no	pH	Cl	E V vs AgCl
1	6.11	0.76	0.156
2	6.08	1.7	0.173
3	6.38	1.15	0.193
4	6.09	1.8	0.175
5	5.52	0.34	0.186
6	6.40	0.9	0.208
7	6.37	0.41	0.201
8	6.37	1.22	0.201
9	6.27	6.9	0.201
10 a	4.70	1.51	0.215
10 b	4.70	11.6	0.224
10 c	4.70	0.82	
11	6.36	1.33	
Average	5.85	2.34	0.194
Stdev	0.70	3.24	0.020

Site 7: Deep Gorge, air 08:45 25.7^o, rock 33.2^o 4 September

Location ref	pH	Cl	E vs Ag/AgCl
1	7.02	17	0.231
2	7.02	37	0.216
3	7.20	18	0.178
4	6.40	14	0.23
5	6.20	15.6	0.202
6	6.66	14.6	0.23
7	6.68	25.3	0.243
8	6.06	18.6	0.260
9	6.53	17.6	0.258
10	7.04	8.2	0.221
average	6.68	18.6	0.227
stdev	0.39	7.8	0.025

Site 21: 5 Sept. 18 RH 25%, air 25.7° rock 29°

Location no	pH	Cl	E vs. Ag/Ag Cl
1	6.93	26	0.28
2	6.29	27.2	0.275
3	6.37	21	0.279
4	6.15	15.5	0.282
5	6.63	9.7	0.282
6	5.7	30	0.27
7	5.63	22	0.289
8	6.01	10.4	0.287
9	4.96	1.4	0.287
10	5.36	46.5	0.288
11	5.38	0.9	0.291
12	4.86	30.9	0.292
13	5.21	15	0.297
Average	5.81	19.7	0.285
stdev	0.65	12.8	0.007

site 22 Yara North East
5 September 18 RH
30%, rock 40° air 35° C

Location no	pH	Cl	E vs. Ag/Ag Cl
1	7.31	10.1	0.256
2	6.51	2.07	0.286
3	6.5	41	0.293
4	6.33	13.5	0.289
5	5.82	8.5	0.298
6	5.85	2.7	0.296
7	5.75	12.4	0.3
8	5.6	5.43	0.299
9	5.68	12.1	0.297
10	5.3	1.4	0.284
11	5.76	2.9	0.289
Mean	6.04	10.2	0.290
Stdev	0.57	11.2	0.012

Site 23: 6 Sept 2018 RH 22%, Temperature rock 35.9^o, air 31.3^o

Location no	pH	Cl	E vs. Ag/Ag Cl
1	5.59	53	0.264
2	5.25	27.5	0.272
3	4.75	55	0.281
4	4.5	23.6	0.289
5	4.36	26.4	0.293
6	4.4	65.2	0.294
7	4.63	40	0.278
8	4.16	17.2	0.287
9	4.37	28.5	0.238
10	4.37	17.5	0.285
11	6.31	11.5	0.282
12	4.63	11.7	0.287
13	5.48	14.5	0.295
14		22.9	0.306
mean	4.83	29.6	0.282
stdev	0.64	17.2	0.016

APPENDIX VI: Surface pH measurements 2003-2004 in the Burrup

	17-Jun-03	28-Aug-03	23-Feb-04
Location		pH	pH
Dampier W1		5.03	4.90
Dampier W1		4.85	4.82
Dampier W1		5.14	4.77
Dampier W1		5.13	5.18
Dampier W1		4.61	4.47
Dampier W1		4.95	4.59
Dampier W1		4.37	4.80
Dampier W1		4.10	4.88
Dampier W1		4.49	4.76
Dampier W1			4.71
Dampier W1			4.64
Dampier W1 mean		**4.74**	**4.77**
Dampier W1 st. dev.		**0.37**	**0.19**

Dampier W2		4.30	4.41	
Dampier W2		4.34	4.32	
Dampier W2		4.96	4.61	
Dampier W2		4.80	4.63	
Dampier W2		4.86	4.40	
Dampier W2		4.72	4.27	
Dampier W2		4.78	4.16	
Dampier W2		4.94	4.78	
Dampier W2		4.82	4.50	
Dampier W2		4.33	4.68	
Dampier W2 mean		**4.7**	**4.5**	
Dampier W2 st. dev.		**0.3**	**0.2**	
				27-Feb-04
Burrup SW1		4.70	4.43	4.63
Burrup SW1		4.69	5.33	4.76
Burrup SW1		4.94	4.52	4.97
Burrup SW1		4.49	4.89	4.79
Burrup SW1		4.96	4.68	4.78
Burrup SW1		4.16	4.60	4.92
Burrup SW1		4.42	4.92	3.89
Burrup SW1		4.66	4.98	4.94
Burrup SW1			5.01	4.94
Burrup SW1			4.65	5.02
Burrup SW1 mean		**4.63**	**4.80**	**4.76**
Burrup SW1 st. dev.		**0.27**	**0.27**	**0.33**

				27-Feb-04
Burrup SW2		5.39	4.88	4.87
Burrup SW2		5.32	4.49	4.68
Burrup SW2		4.64	4.82	4.83
Burrup SW2		4.44	4.83	5.16
Burrup SW2		4.60	4.72	4.83
Burrup SW2		5.43	4.69	4.80
Burrup SW2		5.00	4.65	4.98
Burrup SW2		5.40	4.72	5.00
Burrup SW2		5.38	4.63	5.19
Burrup SW2			4.59	5.24
Burrup SW2 mean		**5.07**	**4.70**	**4.96**
Burrup SW2 st. dev.		**0.40**	**0.12**	**0.19**

				27-Feb-04
King Bay 1		4.89	4.61	4.91
King Bay 1		4.37	5.34	4.73
King Bay 1		5.27	5.15	4.46
King Bay 1		4.98	4.69	4.79
King Bay 1		5.41	4.39	4.64
King Bay 1		5.30	4.70	4.98
King Bay 1		4.85	5.02	4.80
King Bay 1		4.94	5.00	4.87
King Bay 1		6.04	5.12	4.93
King Bay 1		5.33	4.93	4.88
King Bay 1		5.36		4.91
King Bay 1		5.17		
King Bay 1 mean		**5.16**	**4.90**	**4.81**
King Bay 1 st. dev.		**0.41**	**0.29**	**0.15**

				27-Feb-04
King Bay 2		5.27	4.85	4.61
King Bay 2		5.24	4.89	4.75
King Bay 2		5.27	4.89	4.80
King Bay 2		5.41	4.74	4.95
King Bay 2		5.31	5.29	4.86
King Bay 2		4.59	4.77	5.30
King Bay 2		4.88	5.22	4.78
King Bay 2		3.82	5.41	4.76
King Bay 2		5.05	4.93	5.02
King Bay 2		4.91	5.17	3.54
King Bay 2		5.48		5.02
King Bay 2		5.44		4.78
King Bay 2 mean		**5.06**	**5.02**	**4.76**
King Bay 2 st. dev.		**0.5**	**0.2**	**0.42**

Withnell Bay		5.15	5.02

Withnell Bay		4.95	5.01
Withnell Bay		5.18	5.27
Withnell Bay		4.95	4.97
Withnell Bay		4.98	4.73
Withnell Bay		4.79	5.19
Withnell Bay		4.47	4.82
Withnell Bay		4.70	5.50
Withnell Bay		4.85	5.04
Withnell Bay		4.46	4.55
Withnell Bay		4.91	5.01
Withnell Bay mean		**4.85**	**5.01**
Withnell Bay st. dev.		**0.24**	**0.26**

Withnell Bay 2		4.92	5.76
Withnell Bay 2		4.73	5.28
Withnell Bay 2		4.26	5.52
Withnell Bay 2		4.45	5.52
Withnell Bay 2		4.89	5.24
Withnell Bay 2		4.97	5.26
Withnell Bay 2		4.78	5.44
Withnell Bay 2		4.83	5.26
Withnell Bay 2		4.93	5.50
Withnell Bay 2		4.66	5.68
Withnell Bay 2 mean		**4.74**	**5.45**
Withnell Bay 2 st. dev.		**0.23**	**0.18**

North Withnell Bay 1		4.48	4.66
North Withnell Bay 1		4.59	4.80
North Withnell Bay 1		4.17	4.85
North Withnell Bay 1		4.86	4.62
North Withnell Bay 1		4.37	4.66
North Withnell Bay 1		4.54	4.75
North Withnell Bay 1		4.29	4.76
North Withnell Bay 1		4.51	5.03
North Withnell Bay 1			5.16
North Withnell Bay 1			4.89
North Withnell Bay 1			
North Withnell Bay 1			
North Withnell Bay 1			
North Withnell Bay 1 mean		**4.48**	**4.82**
North Withnell Bay 1 st. dev.		**0.21**	**0.17**

North Withnell Bay 2		4.77	4.65

North Withnell Bay 2		4.74	3.45 soil area
North Withnell Bay 2		4.66	4.87
North Withnell Bay 2		4.31	4.79
North Withnell Bay 2		4.83	5.09
North Withnell Bay 2		4.65	4.76
North Withnell Bay 2		4.58	4.88
North Withnell Bay 2		4.50	5.13
North Withnell Bay 2		4.63	5.05
North Withnell Bay 2			4.73
North Withnell Bay 2			5.03
North Withnell Bay 2 mean, no soil		4.63	4.90
North Withnell Bay 2 st. dev. no soil		0.15	0.17
North Withnell Bay 2 mean			**4.9**
North Withnell Bay 2 st. dev.			**0.2**

Deep Gorge 1		4.91	4.71
Deep Gorge 1		4.54	5.06
Deep Gorge 1		4.87	4.74
Deep Gorge 1		4.72	4.87
Deep Gorge 1		4.89	4.90
Deep Gorge 1		4.10	5.14
Deep Gorge 1		4.32	4.98
Deep Gorge 1		4.06	4.80
Deep Gorge 1		5.19	4.80
Deep Gorge 1		4.17	5.07
Deep Gorge 1		4.14	
Deep Gorge 1 mean		**4.54**	**4.91**
Deep Gorge 1 st. dev.		**0.40**	**0.15**

Deep Gorge 2		4.59	4.69
Deep Gorge 2		4.93	4.97
Deep Gorge 2		4.46	5.45
Deep Gorge 2		4.63	5.31
Deep Gorge 2		4.57	5.20
Deep Gorge 2		4.79	5.04
Deep Gorge 2		4.71	5.16
Deep Gorge 2		4.36	5.12
Deep Gorge 2		4.70	5.31
Deep Gorge 2			3.85
Deep Gorge 2			
Deep Gorge 2 mean		**4.64**	**5.01**
Deep Gorge 2 st. dev.		**0.17**	**0.46**

Deep Gorge 3			5.19
Deep Gorge 3			4.91
Deep Gorge 3			5.06
Deep Gorge 3			4.73
Deep Gorge 3			4.78
Deep Gorge 3			4.91
Deep Gorge 3			5.39
Deep Gorge 3			5.27
Deep Gorge 3			5.23
Deep Gorge 3			5.10
Deep Gorge 3 mean			**5.06**
Deep Gorge 3 st. dev.			**0.22**

Climbing Man Gully 1		5.37	4.96
Climbing Man Gully 1		5.53	4.80
Climbing Man Gully 1		5.39	5.03
Climbing Man Gully 1		4.84	4.78
Climbing Man Gully 1		5.41	4.97
Climbing Man Gully 1		4.83	4.63
Climbing Man Gully 1		4.81	4.93
Climbing Man Gully 1		5.70	5.03
Climbing Man Gully 1		3.04	5.37
Climbing Man Gully 1		5.55	4.22
Climbing Man Gully 1		5.42	5.53
Climbing Man Gully 1		4.62	4.26
Climbing Man Gully 1			4.58
Climbing Man Gully 1 mean		**5.0**	**4.9**
Climbing Man Gully 1 st. dev.		**0.7**	**0.4**
Climbing Man Gully 1 mean (-acid spot)		5.22	
Climbing Man Gully 1 st. dev. (-acid spot)		0.37	

Climbing Man Gully 1-1		5.05	4.92
Climbing Man Gully 1-1		4.85	5.00
Climbing Man Gully 1-1		5.03	3.95
Climbing Man Gully 1-1		5.97	4.45
Climbing Man Gully 1-1		5.78	3.94
Climbing Man Gully 1-1		5.46	3.83
Climbing Man Gully 1-1		5.79	3.97
Climbing Man Gully 1-1		5.45	3.68
Climbing Man Gully 1-1		5.23	4.94
Climbing Man Gully 1-1		5.31	3.85
Climbing Man Gully 1-1 mean		**5.39**	**4.25**
Climbing Man Gully 1-1 st. dev.		**0.37**	**0.52**

June 03 Adjacent to Climbing Man	3.74		4.86

Feb 04 Climbing Man itself	4.31		4.85
Feb 04 Climbing Man itself	4.54		3.91
Feb 04 Climbing Man itself	4.19		3.61
Feb 04 Climbing Man itself	4.1		4.87
Feb 04 Climbing Man itself	4.27		3.75
Feb 04 Climbing Man itself	4.78		4.86
Feb 04 Climbing Man itself	4.55		4.82
Feb 04 Climbing Man itself	3.58		4.68
Feb 04 Climbing Man itself			5.13
Feb 04 Climbing Man itself			4.68
Feb 04 Climbing Man itself mean	**4.23**		**4.55**
Feb 04 Climbing Man itself st. dev.	**0.39**		**0.53**

Climbing Man gully 2B			5.19
Climbing Man gully 2B			5.04
Climbing Man gully 2B			5.23
Climbing Man gully 2B			5.28
Climbing Man gully 2B			5.21
Climbing Man gully 2B			5.06
Climbing Man gully 2B			5.35
Climbing Man gully 2B			5.43
Climbing Man gully 2B			5.29
Climbing Man gully 2B			5.53
Climbing Man gully 2B mean			**5.26**
Climbing Man gully 2B st. dev.			**0.15**

Compound, off site up hill		4.88	3.81
Compound, off site up hill		4.49	5.06
Compound, off site up hill		4.76	4.94
Compound, off site up hill		4.33	4.76
Compound, off site up hill		5.17	5.67
Compound, off site up hill		4.17	4.65
Compound, off site up hill		4.16	3.88
Compound, off site up hill		4.73	3.86
Compound, off site up hill		4.61	4.59
Compound, off site up hill		4.67	4.40
Compound, off site up hill		4.64	
Compound, off site, uphill, mean		**4.60**	**4.56**
Compound, off site, uphill st. dev.		**0.30**	**0.60**

Compound off site, 2			3.85
Compound off site, 2			4.62
Compound off site, 2			3.82
Compound off site, 2			4.66
Compound off site, 2			4.58
Compound off site, 2			4.91
Compound off site, 2			4.51
Compound off site, 2			4.52
Compound off site, 2			4.83
Compound off site, 2			3.94
Compound off site, 2 mean			**4.42**
Compound off site, 2 st. dev.			**0.40**

Rock 3	4.67		4.46
Rock 3	4.76		4.79
Rock 3			4.63
Rock 3			5.03
Rock 3			4.40
Rock 3			4.16
Rock 3			4.71
Rock 3			4.69
Rock 3			4.82
Rock 3			4.54
Rock 3 mean	**4.72**		**4.62**
Rock 3 st. dev.	**0.06**		**0.25**

Rock 86	4.56	4.71	4.98
Rock 86	4.67	4.72	4.95
Rock 86	4.46	4.62	5.09
Rock 86	4.63	5.04	5.08
Rock 86	5.57	4.89	4.86
Rock 86	5.3	4.96	5.10
Rock 86	5.12	5.22	4.90
Rock 86		4.99	4.92
Rock 86		4.96	4.64
Rock 86		5.05	5.21
Rock 86			5.05
Rock 86 mean	**4.90**	**4.92**	**4.98**
Rock 86 st. dev.	**0.43**	**0.18**	**0.15**

Rock 97	5.21		4.87
Rock 97	5.26		5.30
Rock 97	5.74		5.11
Rock 97			5.03
Rock 97			6.06
Rock 97			5.68
Rock 97			5.34
Rock 97			5.41
Rock 97			5.67
Rock 97			5.00
Rock 97 mean	**5.40**		**5.35**
Rock 97 st. dev.	**0.29**		**0.37**

Rock 162	4.92	4.72	4.88
Rock 162	5.87	4.63	4.82
Rock 162	5.29	4.86	4.81
Rock 162		4.73	4.88
Rock 162		4.68	5.21
Rock 162		4.50	5.41
Rock 162		4.54	5.12
Rock 162		4.68	5.14
Rock 162		4.71	5.21
Rock 162			5.06
Rock 162 mean	**5.36**	**4.67**	**5.05**
Rock 162 st. dev.	**0.48**	**0.11**	**0.20**

Rock 938		3.97	5.83
Rock 938		4.38	5.12
Rock 938		4.75	5.06
Rock 938		5.15	4.83
Rock 938		4.87	5.45
Rock 938		4.57	4.56
Rock 938		4.64	5.75
Rock 938		5.20	4.35
Rock 938		4.50	4.47
Rock 938		4.80	3.98
Rock 938		5.00	
Rock 938		4.85	
Rock 938		5.63	
Rock 938		**4.7**	
Rock 938		**5.4**	
Rock 938 mean		**4.82**	**4.94**
Rock 938 st. dev.		**0.41**	**0.61**

Rock 1681	5.63	4.57	4.14
Rock 1681	5.36	4.43	5.18
Rock 1681	5.53	4.38	4.93
Rock 1681	5.59	4.17	4.40
Rock 1681	5.28	4.29	4.88
Rock 1681	5.45	4.43	4.8
Rock 1681	5.40	4.21	4.93
Rock 1681	4.86	4.76	4.73
Rock 1681	5.34	4.32	4.85
Rock 1681	4.90	4.10	4.63
Rock 1681	5.64	4.15	
Rock 1681	5.67	3.92	
Rock 1681	4.74	3.86	
Rock 1681	5.81	3.85	
Rock 1681 mean	**5.37**	**4.25**	**4.75**
Rock 1681 st. dev.	**0.33**	**0.26**	**0.30**

Gidley Island 1			25-Feb-04
Gidley Island 1			10:00
Gidley Island 1			4.45
Gidley Island 1			4.81
Gidley Island 1			5.09
Gidley Island 1			4.96
Gidley Island 1			5.06
Gidley Island 1			4.93
Gidley Island 1			4.86
Gidley Island 1			5.08
Gidley Island 1			4.63
Gidley Island 1 mean			**4.17**
Gidley Island 1 st. dev.			**1.67**

Gidley Island 2			25-Feb-04
Gidley Island 2			10:30
Gidley Island 2			4.73
Gidley Island 2			4.52
Gidley Island 2			4.68
Gidley Island 2			4.67
Gidley Island 2			5.24
Gidley Island 2			4.94
Gidley Island 2			4.65
Gidley Island 2			4.78
Gidley Island 2			4.76
Gidley Island 2			5.00
Gidley Island 2			4.57
Gidley Island 2 mean			**4.78**
Gidley Island 2 st. dev.			**0.21**

Gidley Island 3			25-Feb-04
Gidley Island 3			11:00
Gidley Island 3			4.61
Gidley Island 3			5.54
Gidley Island 3			4.70
Gidley Island 3			5.10
Gidley Island 3			4.50
Gidley Island 3			4.92
Gidley Island 3			5.25
Gidley Island 3			5.26
Gidley Island 3			5.50
Gidley Island 3			4.21
Gidley Island 3 mean			**4.96**
Gidley Island 3 st. dev.			**0.45**

Dolphin Island 1			25-Feb-04
Dolphin Island 1			12:10
Dolphin Island 1			4.93
Dolphin Island 1			4.85
Dolphin Island 1			4.72
Dolphin Island 1			4.63
Dolphin Island 1			4.61
Dolphin Island 1			5.05
Dolphin Island 1			4.86
Dolphin Island 1			4.71
Dolphin Island 1			5.08
Dolphin Island 1			4.95
Dolphin Island 1			4.52
Dolphin Island 1 mean			**4.81**
Dolphin Island 1 st. dev.			**0.19**

Dolphin Island 2			25-Feb-04
Dolphin Island 2			12:35
Dolphin Island 2			5.14
Dolphin Island 2			4.91
Dolphin Island 2			4.89
Dolphin Island 2			3.68
Dolphin Island 2			3.74
Dolphin Island 2			5.04
Dolphin Island 2			4.85
Dolphin Island 2			5.07
Dolphin Island 2			4.79
Dolphin Island 2			5.04
Dolphin Island 2			4.72
Dolphin Island 2			0.54
Dolphin Island 2			
Dolphin Island 2 mean			**4.97**
Dolphin Island 2 st. dev.			**0.12**

Dolphin Island 3			25-Feb-04 12:55
Dolphin Island 3			
Dolphin Island 3			5.22
Dolphin Island 3			5.32
Dolphin Island 3			5.15
Dolphin Island 3			5.66
Dolphin Island 3			5.07
Dolphin Island 3			4.65
Dolphin Island 3			3.87
Dolphin Island 3			4.81
Dolphin Island 3			5.25
Dolphin Island 3			5.07
Dolphin Island 3			5.22
Dolphin Island 3 mean			**5.03**
Dolphin Island 3 st. dev.			**0.46**

Appendix VII: Colour measurements in 2018

	Engraved	Engraved	Engraved	Parent	Parent	Parent		E-P	
Location	**L***	**a***	**b***	**L***	**a***	**b***	**ΔL***	**Δa***	**Δb***
S4Spot1	33.97	15.73	18.49	30.20	13.79	14.48	3.77	1.94	4.01
S4Spot2	33.95	15.38	19.03	32.46	14.82	15.73	1.49	0.56	3.30
S4Spot3	35.41	16.58	19.49	32.86	14.44	16.61	2.55	2.14	2.88
S4Spot4	33.61	15.81	18.32	32.76	14.37	15.33	0.85	1.44	2.99
S5spot1	37.64	19.06	22.58	34.47	13.72	14.57	3.17	5.34	8.01
S5spot2	37.28	19.72	23.12	32.14	14.81	15.72	5.14	4.91	7.40
S5spot3	33.16	15.23	17.55	29.22	13.69	14.62	3.94	1.54	2.93
S5spot4	36.87	19.26	22.09	30.40	14.55	15.64	6.47	4.71	6.45
S6spot1	40.23	12.00	17.82	38.50	13.40	17.62	1.73	-1.40	0.20
S6spot2	39.15	11.43	16.89	37.50	12.45	16.16	1.65	-1.02	0.73
S6spot3	39.56	10.64	15.62	37.51	13.30	16.93	2.05	-2.66	-1.31
S6spot4	40.31	10.70	16.25	39.17	13.64	17.83	1.14	-2.94	-1.58
S7spot1	33.03	13.64	17.13	29.26	14.41	15.50	3.77	-0.77	1.63
S7spot2	31.56	14.49	16.47	29.76	13.75	14.21	1.80	0.74	2.26
S7spot3	31.78	13.49	16.34	25.52	11.09	12.35	6.26	2.40	3.99
S7spot4	33.89	14.11	18.33	27.67	13.46	14.79	6.22	0.65	3.54
S21spot1	39.67	16.71	22.50	31.27	12.72	12.83	8.40	3.99	9.67
S21spot2	38.56	15.73	21.47	34.75	14.37	16.03	3.81	1.36	5.44
S21spot3	37.76	16.98	22.38	33.89	14.54	17.80	3.87	2.44	4.58
S21spot4	39.04	15.98	21.85	32.71	12.27	14.16	6.33	3.71	7.69
S22spot1	35.49	12.49	16.32	33.18	12.06	12.60	2.31	0.43	3.72
S22spot2	33.99	13.60	15.90	33.11	12.75	14.16	0.88	0.85	1.74
S22spot3	37.31	14.47	19.11	34.48	13.22	15.24	2.83	1.25	3.87
S22spot4	37.28	14.03	19.13	33.94	12.55	14.01	3.34	1.48	5.12
S23spot1	37.77	10.78	16.58	33.88	12.32	16.05	3.89	-1.54	0.53
S23spot2	33.29	12.07	17.90	38.15	14.21	19.41	-4.86	-2.14	-1.51
S23spot3	34.93	10.97	17.32	32.04	13.91	15.80	2.89	-2.94	1.52
S23spot4	34.76	10.42	16.45	32.39	8.62	12.03	2.37	1.80	4.42