Evidence of destruction of rock patina by emissions on Burrup Peninsula

John L Black - May 2017

Airborne industrial emissions are deposited in dry form and in wet form in rain, fog or dew. The majority of acid forming pollutants are deposited on Burrup Peninsula in dry form because of the few days of rain per year (average of 20). These pollutants accumulate, particularly on the foliage of plants, where they remain inactive until mixed with water. Tree canopies can retain large amounts of deposited acid-forming NO_x and SO_x compounds because of their many layers of foliage. Rain water falling through the foliage concentrates these acid forming chemicals. Bednarik (2007) collected the 'through-fall' rain under trees at sites on Burrup Peninsula and found it to be highly acidic with pH as low as 3.2. Evidence by Black et al. (2017) shows, from experiments on Burrup Peninsula and from electrochemical theory, that rock patina required for maintenance of the integrity of the rock art is dissolved by acid.

Figures 1 and 2 are photographs taken from Bednarik (2007) and show complete removal of the rock patina below a tree on Burrup Peninsula. These photographs suggest organic acids and other compounds from the tree have dissolved the patina on the tops of rocks where organic material has fallen from the tree. The tree will be very recent in the landscape compared with the time taken for the patina to develop.

Figure 1. 'Bleaching' of patina under a tree on Burrup Peninsula. The close up shows removal of patina from the top of rocks, but not on side or underneath surfaces (From Bednarik, 2007).

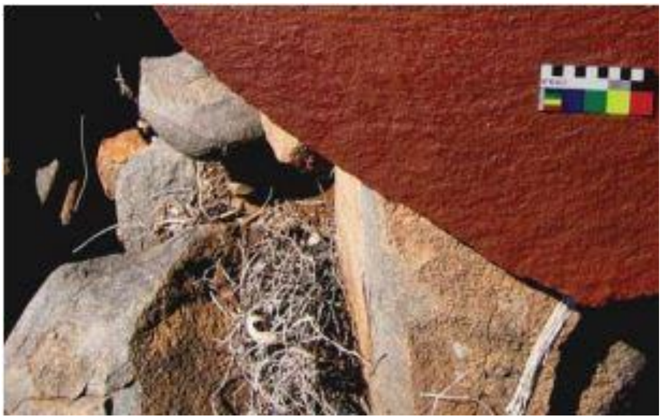

Figure 2. Comparison of 'bleached' and 'unbleached' rocks at the location shown in Figure 1, showing complete removal of the rock patina by extracts from the tree. (From Bednarik, 2007).

Other evidence showing the dissolution of rock patina in desert environments by surface acid comes from Bednarik (1979), where the patina disappeared under bird droppings where the average pH was 5.9 across 30 sites in an area adjacent to Burrup Peninsula. Similarly, Engel and Sharp (1958) and Dragovich (1986) showed that desert varnish was not present beneath growing lichen, because of accumulated organic acids secreted by the lichen.

Bednarik (2002) has been photographing rock sites on Burrup Peninsula since the mid 1960's. He used the International Federation of Rock Art Organisations standard colour assessment system to show marked changes in colour from pre-industrial times to 2002. Based on these observed changes, Bednarik (2002) predicted the petroglyphs would disappear during the second half of the 21st century at the then current levels of acid emissions and by around 2030 if emissions trebled (Figure 3). In 2014, Woodside released 22,400 tonnes of acid load into the environment (Woodside 2016) and, in the same year, the Yara Pilbara fertiliser plant released 13,600 tonnes of acid into the environment (Yara Pilbara 2016). These are extremely large amounts of acid forming emissions.

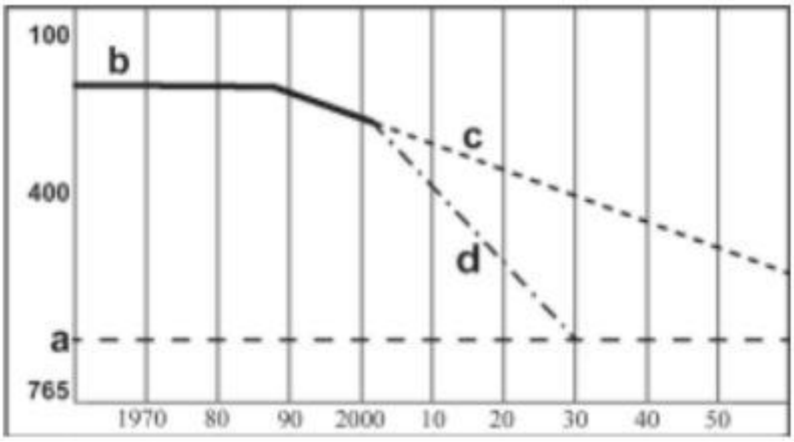

Figure 3. Deterioration of ferruginous crust on Murujuga rock surfaces as determined by measurement (b); as predicted at the present level of atmospheric pollution (c); and as predicted in the event of a trebling of the ambient air-shed pollution (d). The average value of the buff-coloured substrate, the threshold at which the rock art becomes imperceptible, is indicated by (a). From Bednarik (2002, Fig 5).

There is irrefutable empirical and theoretical evidence that any increasing acid accumulation on the surface of rocks on Burrup Peninsula is now destroying and will completely dissolve the desert varnish patina. These processes is likely to result in the destruction of the petroglyphs within the next 20-30 years at the current rate of acid emissions. However, detailed experiments are needed to prove the precise rate of destruction of the patina.

Limit to emissions from Yara International new Technical Ammonium Nitrate Plant

The current proposed acid emissions from the Technical Ammonium Nitrate are 200 meq/m^2/year, based on the report by Gillett (2008). This Gillett report used evidence from Cinderby *et al*. (1998) who examined world soil maps developed by the United Nations Food and Agriculture Organisation to suggest areas of the world that would be more and less sensitive to acid-producing pollutants. Australia is included in their map, but the resolution of critical load areas is extremely low, with a scale of 1:5,000,000. The buffering capacity of soils and therefore acid critical load of an ecosystem depends mainly on the rate of erosion of the parent rock. The rock types on Burrup Peninsula are different in geological formation that rocks of the larger Pilbara area and relatively extremely slow eroding.

The Cinderby et al. (1998) critical loads are for ecosystems and not for rocks.

Evidence provided by the then PhD student, now Professor Johan Kuylenstierna, who undertook the work reported by Cinderby et al. (1998) gave evidence to the recent Senate Inquiry into protection of Aboriginal rock art of Burrup Peninsula. He stated that suggesting the rock art would withstand the highest critical acid load of any environment in the world was a complete misuse of the Cinderby et al. (1998) report. The Senate Inquiry asked for the recommendation that rock art had a critical acid load of 200 meq/m^2/year to be removed from the Gillett (2008) report.

Total acid load emitted from the ammonium nitrate plant should be as low as possible and definitely less than 25 meq/m^2/year.

Justification for this limit comes from i) scientific principles and empirical evidence showing acidity below neutral dissolves manganese and iron compounds from the rock patina, and ii) critical acid loads set for other environments around the world.

Scientific principles showing dissolution of rock patina commences once pH falls into the acidic range (Black et al. 2017). The acidity of rock surfaces on Burrup Peninsula was pre-industrialisation around neutral (pH 7) and is already down in the strongly acid pH range of 4-5. This acidity is already causing the patina to become thinner or disappear and be lighter in colour (Bednarik 2007).

Critical load is an estimate of an exposure to one or more pollutants below which significant harmful effects on specified elements of the environment do not occur. Critical load relates to a specific pollutant for a specific risk on a nominated target such as trees, fish or people. Consequently, critical acid load for rock art on Burrup Peninsula is one specific application of this principle: the effect of acid on rock patina.

No measurements of critical acid load for rock patina on Burrup Peninsula have been made, because the buffering capacity of the rock surfaces has never been measured. Thus, there is no empirical evidence for critical acid load for rock surfaces on Burrup Peninsula.

The value of < 25 meq/m^2/year is derived from comparisons of critical loads for other parent rock types and ecosystems. The rocks on the Burrup Peninsula are igneous and formed under great pressure to make them extremely hard. Pillans and Fifield (2013) showed these rocks to be among the slowest eroding rocks anywhere in the world. Consequently, little soil is formed where petroglyphs occur. Erosion rate of parent rocks is strongly related to buffering capacity.

Important evidence can be obtained from studies in other parts of the world (Nilsson and Grennfelt 1988). Figure 4 shows the impact of parent rock on the critical loads of nitrogen and sulphur for forests in Europe. The slower degrading granite rock has lower buffering capacity and therefore lower critical loads than the faster degrading limestone. The lower extremes of the bars in Figure 4 represent unmanaged forests. The critical nitrogen load for undisturbed European forests growing on granitic soil was from 3-5 kg/ha/year (15 to 25 meq/m^2/year) depending on the sulphur load. Since the rocks on Burrup Peninsula are extremely slow degrading and do not produce soils sufficient to maintain substantial plant growth, the critical loads would be below the bar for granite in the graph.

Hence, the recommendation of a limit for critical acid load on Burrup Peninsula of less than 25 meq/m^2/year.

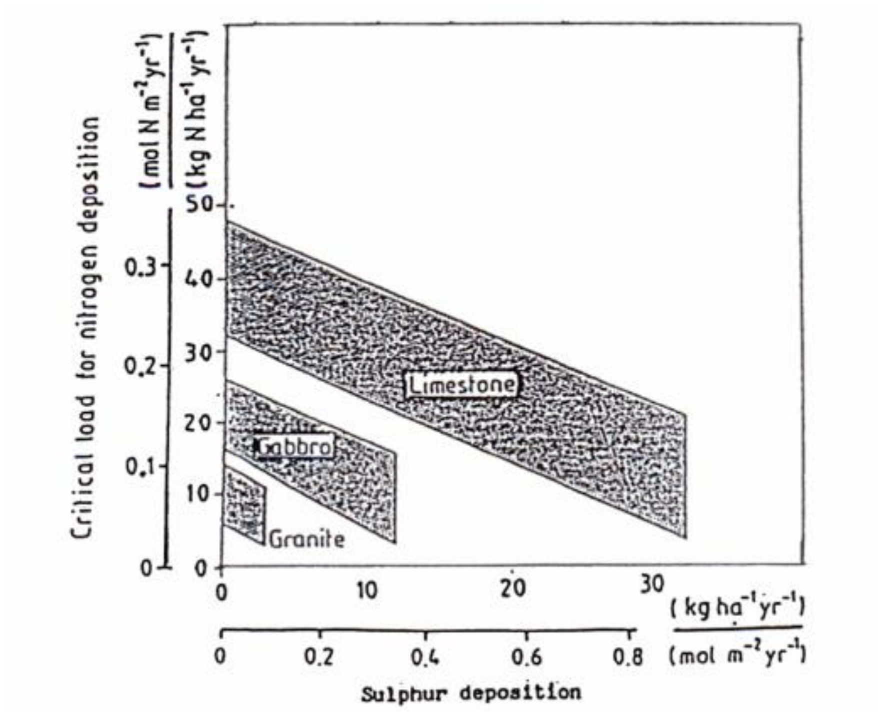

Figure 4. Nitrogen and Sulphur critical loads for European forests growing on soils formed from different base rock types. (From Nilsson and Grennfelt 1988, Fig 1).

References

Bednarik, R.G. 1979. The potential of rock patination analysis in Australian archaeology - part 1. *The Artefact* 4:14-38.

Bednarik, R.G. 2002. The survival of the Murujuga (Burrup) petroglyphs. *Rock Art Research* 19:29-40.

Bednarik, R.G. 2007. The science of Dampier rock art - Part 1. *Rock Art Research* 24:209–246.

Black, J.L., MacLeod, I.D. and Smith, B.W. (2017). Theoretical effects of industrial emissions on colour change at rock art sites on Burrup Peninsula, Western Australia. *Journal of Archaeological Science: Reports* 12, 457-462.

Dragovich, D. 1986. Weathering of desert varnish by lichens. In: *Readings in Australian geography : proceedings of the 21st Institute of Australian Geographers' Conference, Perth, 10-18 May 1986* , Edited by Arthur Conacher. Published by Institute of Australian Geographers (WA Branch) and Dept. of Geography, University of W.A Perth [W.A.]

Engel, C.G. & Sharp, R.S. 1958. Chemical data on desert varnish. *Geological Society of America Bulletin* 69:487-518.

Gillett, R. (2008). Burrup Peninsula Air Pollution Study: Report for 2004/2005 and 2007/2008. 168 pages.

Nilsson J. and P. Grennfelt 1988 Critical loads for sulphur and nitrogen: Report from a workshop held at Skokloster, Sweden *Critical loads for sulphur and nitrogen*, vol. Miljørapport 1988 : 15, eds J. Nilsson & P. Grennfelt, UN-ECE, Nordic Council of Ministers, Skokloster, Sweden.

Pillans, B., and L. K. Fifield 2013. Erosion rates and weathering history of rock surfaces associated with Aboriginal rock art engravings (petroglyphs) on Burrup Peninsula, Western Australia, from cosmogenic nuclide measurements. *Quaternary Science Reviews* 69:98–106. DOI: 10.1016/j.quascirev.2013.03.001.

Woodside 2016. http://www.woodside.com.au/Working-Sustainably/Documents/2014%20Sustainable%20Development%20Report%20-%20Interactive.pdf.

Yara Pilbara Nitrates (2016). Annual Compliance Report EPBC 2008/4546 February 2015 – February 2016 Technical Ammonium Nitrate Plant. http://www.yara.com.au/images/2-250-329-REPTRE-8055%20TAN%20Plant%20EPBC%20CAR%202014_tcm583-240486.pdf

http://www.apis.ac.uk/overview/issues/overview_Cloadslevels.htm#_Toc279788050

Table1 - Critical levels of air pollutants.

Pollutant	Receptor	Time Period	Critical Level	Reference
NOX	All	Annual mean	30 µg/m^3	WHO, CLRTAP, AQ Directive
NOX	All	24 hour mean	75 µg/m^3	WHO, CLRTAP, AQ Directive
SO_2	Crops	Annual mean	30 µg/m^3	WHO, CLRTAP
SO_2	Forests and natural Vegetation	Winter mean (1 Oct to 31 Mar)	20 µg/m^3	WHO, CLRTAP
SO_2	Forests and natural Vegetation	Annual mean	20 µg/m^3	WHO, CLRTAP, AQ Directive
SO_2	Sensitive lichens	Annual mean	10 µg/m^3	WHO
Ozone*	All	AOT40, calculated from 1h values May-July. Mean of 5 years.	18,000 µg/m^3.hr (9000 ppb hours)	AQ Directive
Ozone*	Crops	AOT40, May to July	3,000 ppb hours	CLRTAP
Ozone*	Forests	AOT40, April to September	10,000 ppb hours	CLRTAP
Ozone*	Forests, semi-natural vegetation dominated by perennials	AOT40, April to September (semi-nat) growing season (trees)	5,000 ppb h	CLRTAP
Ozone*	Semi-natural vegetation dominated by annuals	AOT40, May to July	3,000 ppb h	CLRTAP
Ammonia	Lichens and bryophytes (where they form a key part of the ecosystem integrity)	Annual mean	1 µg/m^3	CLRTAP
Ammonia	Other vegetation	Annual mean	3 µg/m^3 (with an uncertainty range of 2-4 µg/m^3)	CLRTAP

**For Ozone another method exists called the Stomatal flux-based critical levels for ozone. These take into account the varying influences of temperature, water vapour pressure deficit (VPD), light (irradiance), soil water potential (SWP), ozone concentration and plant development (phenology) on the stomatal flux of ozone. They therefore provide an estimate of the critical amount of ozone entering through the stomata and reaching the sites of action inside the plant. See http://www.pbl.nl/en/themasites/icpmm/manual-and-downloads/manual-englis...*

http://www.apis.ac.uk/unit-conversion