Murujuga Rock Art Monitoring Program

Monitoring Studies Data Collection and Analysis Plan Amendments 2024

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Revision history

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Rev 0	28-03-2024	Issued for use
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Rev 2	11-04-2025	Issued for publication
Rev 3	01-05-2025	Reissued for publication with additional rock sample site location map included.

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1 Introduction

This document sets out amendments to the *Monitoring Studies Data Collection and Analysis Plan* (Curtin University, 2022; hereafter referred to as MSDCA Plan) that are being made because of new information which has become available since development of the Plan.

The MSDCA Plan should be referred to if necessary for background context and is available online via the Department of Water and Environmental Regulation (DWER).

The changes being made to the Plan fall under the following categories:

1. Scope reductions
    a) Activities that will be discontinued or deleted from the program as they have proven infeasible based on concentrations of target analytes. These activities were considered highly experimental approaches in the original MSDCA Plan and were always intended to undergo further feasibility assessment before implementation.
    b) Activities which may be discontinued prior to the end of the study period if the scientists and chief statistician deem them of insufficient value following analysis of a sufficient body of collected data.
2. Scope increases
    a) Additions or expansions of some aspects of MSDCA Plan in response to new findings. These will be included in years 3 and 4 of the research study phase.

2 Scope reductions

2.1 Activities to be discontinued from the MSDCA Plan

2.1.1 Plutonium isotope analysis

(Ref: MSDCA Plan Section 3.3.2.x; Appendix 1, Section 7.5)

Measurement of plutonium (Pu) and related isotopes were proposed as an exploratory approach to potentially measure weathering, as such substances have only existed in the environment since the recent Anthropocene. This work was highly experimental and was only detailed as an initial pilot experiment in the MSDCA Plan.

Preliminary investigations were conducted, including discussions with world leading inorganic isotope experts at the Australian Nuclear Science and Technology Organisation (ANSTO), Australian National University (ANU), and several international facilities. Researchers at ANSTO reported collecting previous samples for Pu isotope analysis from the Murujuga region. It was determined that although Murujuga has a relatively strong Pu background with an isotope signature consistent with previous nuclear testing at the nearby Montebello Islands, the sample mass required for reliable measurements would require harvesting too large an area of additional rock patina/surface from Murujuga and would therefore be undesirable due to visual impact and excessive removal of material.

Furthermore, even if this sample mass was collected, conclusive findings are still not guaranteed. Investigations to date indicate that the need for the Pu isotope technique as a measure of weathering has likely been replaced by porosity (see Section 3.1 below).

2.1.2 Open Path-Fourier Transform Infra-Red (OP-FTIR) scanning campaign

(Ref: MSDCA Plan Section 3.5.1.vi)

A comprehensive campaign of OP-FTIR measurements was proposed, based around the four powered air quality monitoring (AQM) sites (labelled AQ-01, EX-02, EX-07, and EX-09) included in the MRAMP AQM network. OP-FTIR is capable of measuring organics and species such as ammonia (NH_3) transiting a line between the infra-red emission source (laser) and reflector. The MRAMP research team identified that Prof. David Griffith from the University of Wollongong (UoW) and colleagues had significant expertise in OP-FTIR scanning, including building their own instruments on a commercial and research basis (Bai et al. 2022). Although it was proposed to hire an OP-FTIR from the USA and utilise a local (WA) expert operator, due diligence required consultation with the leading experts in OP-FTIR in Australia at UoW.

In light of the levels of volatile organic carbons (VOCs) and NH_3 detected by passive samplers in the MRAMP AQM network to date, our considered view following consultation with experts at UoW is that OP-FTIR based at the powered MRAMP air quality monitoring sites would likely be of limited utility as most measurements would be below applicable detection limits within the measurement region.

The best application of OP-FTIR is instead considered to be operation closer to current and future NH_3 sources, primarily to detect NH_3. However, no powered monitoring sites exist in the MRAMP AQM network at these locations.

DWER's Midac M4401-S FTIR is more portable than the previously proposed instruments and was investigated as an option to undertake this work. However the unit was found to require components which are no longer available as the manufacturer has ceased trading.

Therefore, this component has been removed from the program.

2.2 Activities to possibly be discontinued if determined by the chief statistician to have insufficient value

2.2.1 Passive sampling of atmospheric volatile organic carbon concentrations

(Ref: MSDCA Plan Section 3.5.1.vi)

The 21 air quality monitoring stations operated by MRAMP include Carbopack VOC passive sampling tubes which are analysed by IVL (Sweden) for BTEX compounds (benzene, toluene, ethylbenzene, xylene) and related compounds. Due to the complexity of organic chemical analysis, the cost of these samplers and associated analyses are significantly higher than the other inorganic passive samplers.

The three reference-grade (powered) AQMs each include a real-time methane/non-methane hydrocarbon analyser and AQM EX-09 includes a methane/ethane (isotopic) spectrometer. While the real-time instruments are returning data that appears to be useful for the development of EQC, many of the data from the passive BTEX suite of chemicals are below detection limits.

Passive VOC monitoring was discontinued in December 2024 following review of 12 months of data by the chief statistician.

3 Proposed additions and expansions to the MSDCA Plan

3.1 Inorganic geochemistry rock surface porosity and permeability investigations

(Ref: MSDCA Plan Section 3.3.2)

Laboratory-based inorganic geochemistry investigations conducted on sample rocks collected from the Murujuga area have yielded important information about the rock surface morphology and composition. When considered in the context of the spatial distribution of air pollutants observed from the MRAMP air quality monitoring network, this warrants further sample collection and analysis to confirm trends observed to date.

The original MSDCA Plan included the collection of 64 sample rocks from across the Burrup Peninsula and 12 of the 42 islands of the Dampier Archipelago. The majority of these samples are granophyre, due to this being the most spatially abundant rock type and also as it is the surface which contains the bulk of the known petroglyphs (due to both its spatial abundance and surface morphology providing a good surface for rock art production).

These sample rocks were prepared in billets and thin sections and have undergone detailed laboratory characterisation. Duplicate billets from pseudo-random locations in the sample rocks have been imaged and characterised. This work has included measuring porosity in the weathered rind and patina (generally the outer 0.5 - 1 mm layer of rock. Figure 3-1 shows an example of the rock surface porosity observed (note that billets were encased in epoxy to prevent the patina detaching). Mineral maps demonstrate that the voids were most likely originally occupied by feldspar minerals.

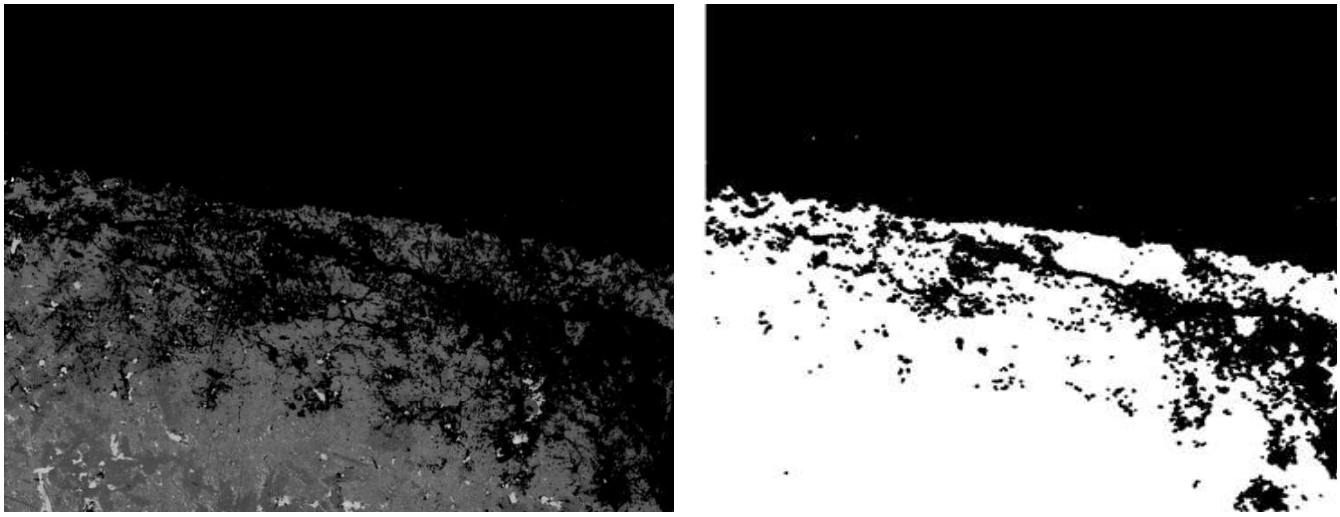

Figure 3-1: Granophyre thin section showing pores/voids (black) in the original image (left), and binary image (right).

A rigorous method has been developed to extract porosity data from these thin sections, and this process has been fully validated. Mapping with a validated spatial interpolation method has been undertaken using these porosity

values and the sample rock collection locations to create spatial maps of the rock surface porosity. Figure 3-2 shows these data.

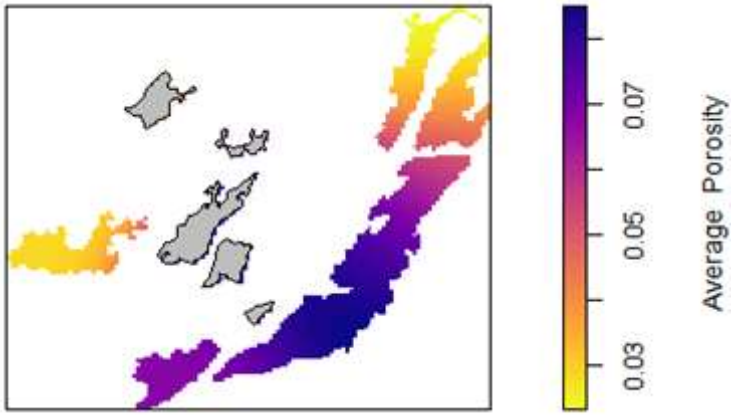

Figure 3-2: Granophyre surface porosity interpolated across island from which samples were taken. Islands without granophyre samples are shaded in grey.

Figure 3-3 shows some typical NO_2 profiles across Murujuga developed using measurements from IVL brand passive samplers installed at the air quality monitoring stations. These maps have been plotted using the same spatial interpolation approach as per Figure 3-2. By comparing these figures, a similar spatial pattern can be seen to exist between the NO_2 concentration maps and the porosity map.

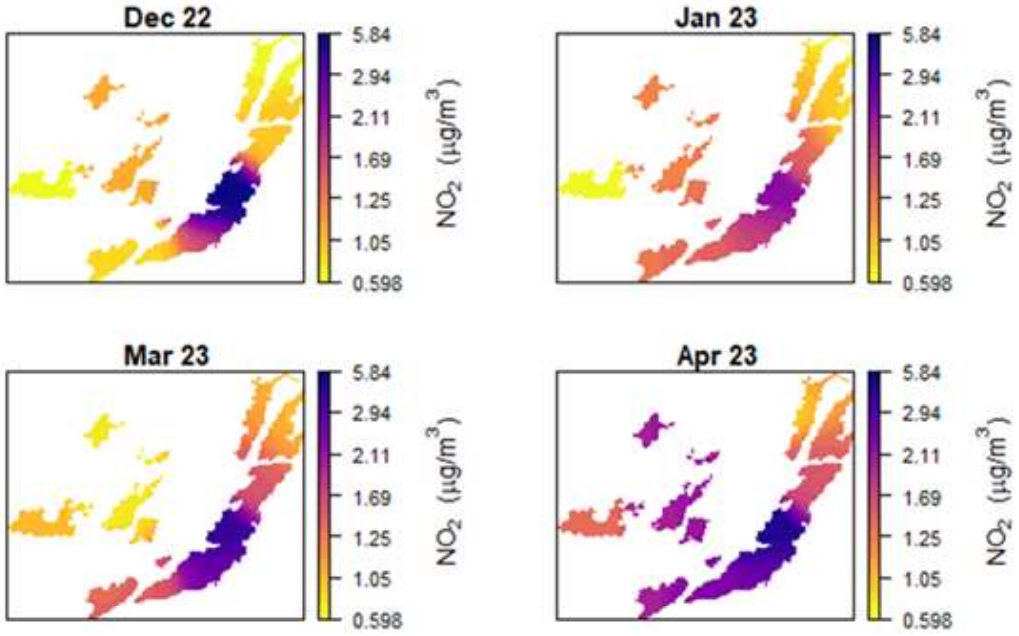

Figure 3-3: Typical spatial pattern of monthly NO_2 measurements from passive samplers.

The chamber exposure studies have been exploring the hypothesis that combustion products (such as NO_2 and SO_2) and other gases which can form acids, bases or other reactive secondary chemicals, can chemically erode the more susceptible elements in exposed rock. This appears to have been proven in the chamber studies.

3.1.1 Sample rock collection and laboratory porosity measurements

Based on the research findings outlined above and the gaps in the spatial map in Figure 3-2 (shown as grey areas), additional granophyre and gabbro samples will be collected from any islands or regions which were not sampled previously. This nominally includes another 15 to 20 samples, collected from opportunistically selected in-situ rock surfaces at culturally appropriate locations. These samples will then undergo the same processing and porosity imaging specified in the MSDCA Plan for previous rock samples.

The intended outcome of this additional work is to confirm that the spatial trends in porosity found to date hold true once these spatial data gaps are filled (Figure 3-2). This will give added statistical confidence in any correlations between air pollutants and porosity.

The target additional sample rock collection sites are shown in Figure 3-4. This includes approximately 15 sites for which cultural approval was obtained from the Murujuga Aboriginal Corporation Board and Circle of Elders in December 2023, and some additional sites at the study area extremities that were subsequently requested for statistical assessment purposes and approved in April 2024. Rock collection has subsequently been completed in the field with an Elder to provide final approval for removal of individual sample rocks in the field at the time of collection.

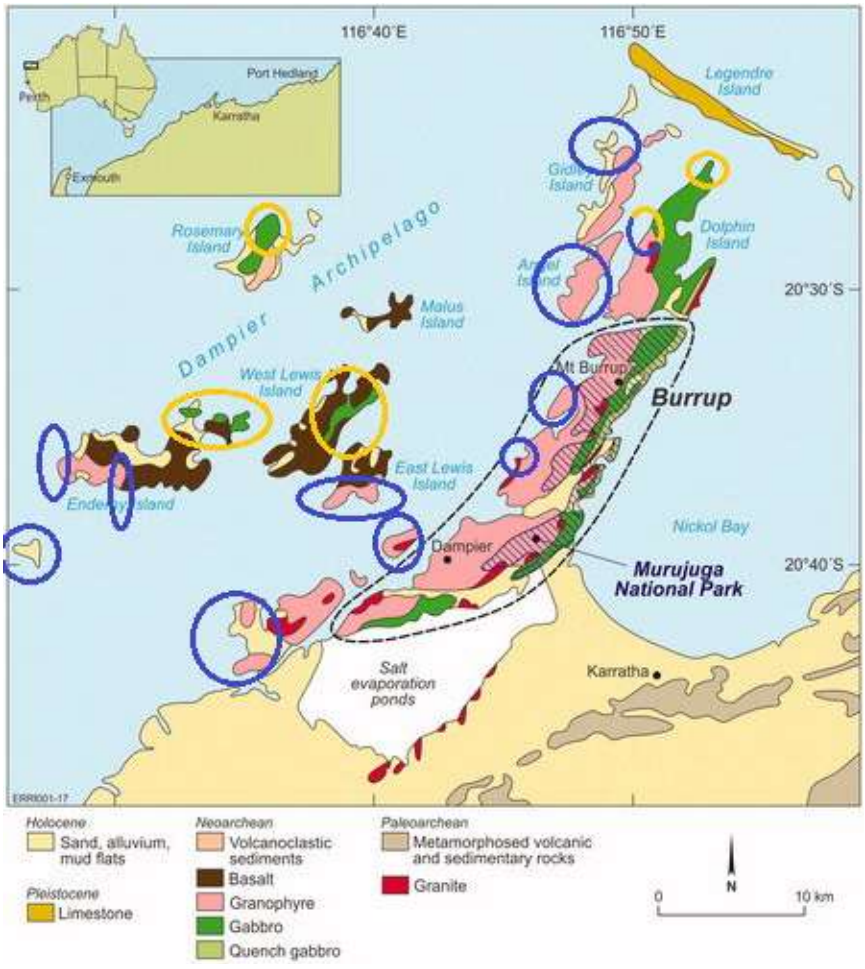

Figure 3-4: Site locations for additional rock sample collection.

Further rock samples have been collected from railway cuttings with known provenance.

3.1.2 Historical emissions inventory calculation

If the hypothesis that porosity in the patina and weathered rind layer has been increased by exposure to anthropogenic emissions holds true, this becomes a measure of cumulative impact during the recent Anthropocene, and conceptually replaces the Pu measurements as proposed in Section 2.1.

With respect to developing Environmental Quality Criteria (EQC) exposure limits for the airshed, utilising porosity observations requires accounting for major historic emissions sources. This requires more work to develop historic emissions inventories and calculate approximate cumulative emissions across the airshed. This work will be undertaken in conjunction with the additional porosity measurements, with a focus on the decommissioned Dampier (Parker Point) power station, which is likely the largest single historic source.

The emissions inventory will be developed based on the best available data for the former Dampier power station including:

- the operational period
- capacity
- combustion and aftertreatment technology
- utilisation factor
- fuels
- literature-based emissions data.

3.1.3 Field permeability measurements

Porosity is a measure of void versus solid ratios in a material. Permeability is a measure of how readily a fluid can flow through a porous structure. These may be related in a porous media with sufficient pore connectivity. For example, a closed-cell foam has no permeability, whereas open cell foams are highly permeable. Porosity measurements cannot be undertaken in a non-invasive manner in the field, however permeability can be measured.

To compare with laboratory investigations on porosity , a TinyPerm3 (Figure 3-5) will be trialled in the field This instrument is a non-invasive air permeability measurement device and could be used for measurement of rock surface permeability in the field on the rock art panels included in the MRAMP program for regular monitoring. If the instrument proves to be successful during the remaining study phase, use of the field permeameter will likely be included in the ongoing monitoring to detect any long-term changes in permeability and/or porosity.

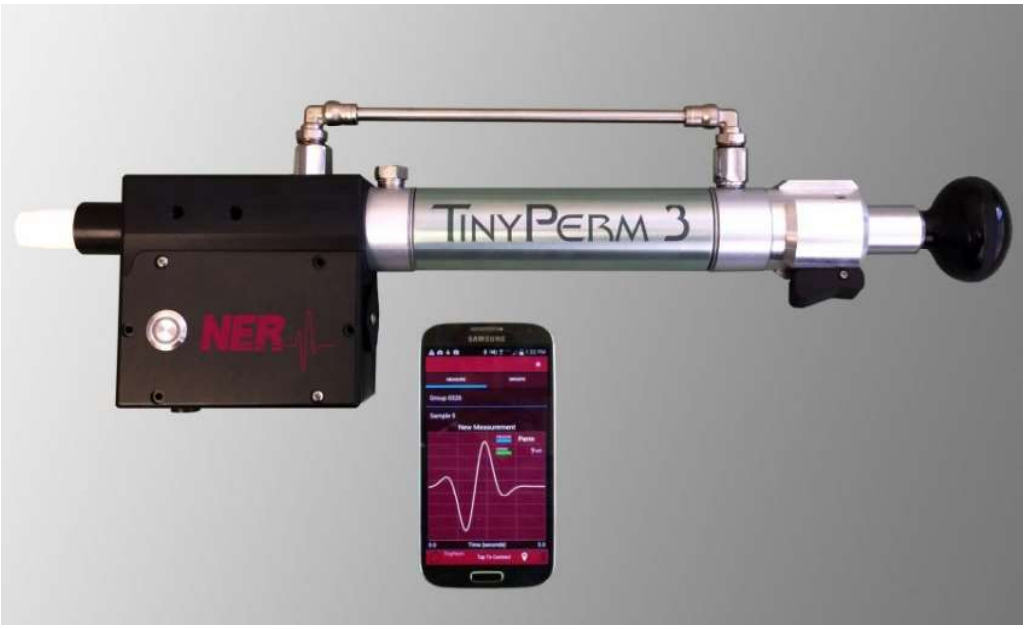

Figure 3-5: Field permeameter (for porosity/permeability measurement).

Initial field testing (post laboratory validation) will determine if the spatial pattern of porosity from field measurements corresponds to spatial patterns from laboratory measurements on field-sampled rocks. It is expected that connectedness of pores will be a determining factor in this. Further work will be required to determine if the permeameter resolution and repeatability is sufficient to detect changes in porosity over time, however the approach appears promising.

3.2 Microbiome chamber studies workflow development

(Ref: MSDCA Plan Section 3.4)

Further development of the chamber studies experimental design and trials of microbiome experiments have determined that the microbiome work needs to utilise green fluorescent protein (GFP) “labelled” bacteria and fungi. This is needed to permit pre and post exposure measures on live organisms. This modification creates a genetically modified organism (GMO) and since the Murujuga species are relatively novel to science, these are not on the “exempt dealing” list for use in Australia. Therefore, all microbiome chamber studies experiments need to be conducted entirely in a PC2 laboratory, thereby duplicating many workflows for the inorganic/abiotic arm of the chamber studies.

The microbiome chamber exposure analysis does not require any additional sample collection beyond the bulk dust samples noted in Section 3.4.3 following, however due to the necessity of separating the geochemical and microbiome workflows, additional laboratory resources and labour will be required to finalise the methodology and conduct the studies. Short-term engagement of a specialist senior researcher with expertise in this area is necessary to finalise the microbiome chamber study methodology.

3.3 Organic geochemistry investigation of hydrocarbon residues

(Ref: MSDCA Plan Section 3.3.4)

The 64 initially collected rock samples have undergone a process of patina harvesting and solvent extraction for organic compositional analysis. Organic geochemical analysis to date has revealed some complex organic mixtures extracted from some of the rock patina samples. These extractions appear to be partially biodegraded hydrocarbon mixtures, which may originate from various petrochemicals.

Gas chromatography – gas chromatography time of flight mass spectrometry (CG-GC TOFMS) analysis will be undertaken on the extracted samples in an attempt to differentiate and identify the component chemicals in these complex mixtures. This additional analysis does not require any further sample collection, however due to the complexity of identifying complex hydrocarbon mixtures it is expected to take up to 12 months labour.

If confirmed, the presence of anthropogenic petrochemicals incorporated in the patina of rock samples may meet the contractual definition of measurable anthropogenic impact. Furthermore, these chemicals are likely to alter microbiome response.

3.4 Air quality monitoring

(Ref: MSDCA Plan Section 3.5)

3.4.1 Use of a second MAx-DOAS Skyscan instrument

The Skyscan Compact 1D MAx-DOAS installed in AQM EX-09 has proven extremely useful at measuring ground level and full air column concentrations of NO_2 SO_2, HONO and other species at distances up to 25 km from its location. An example of the data obtained is shown in Figure 3-6.

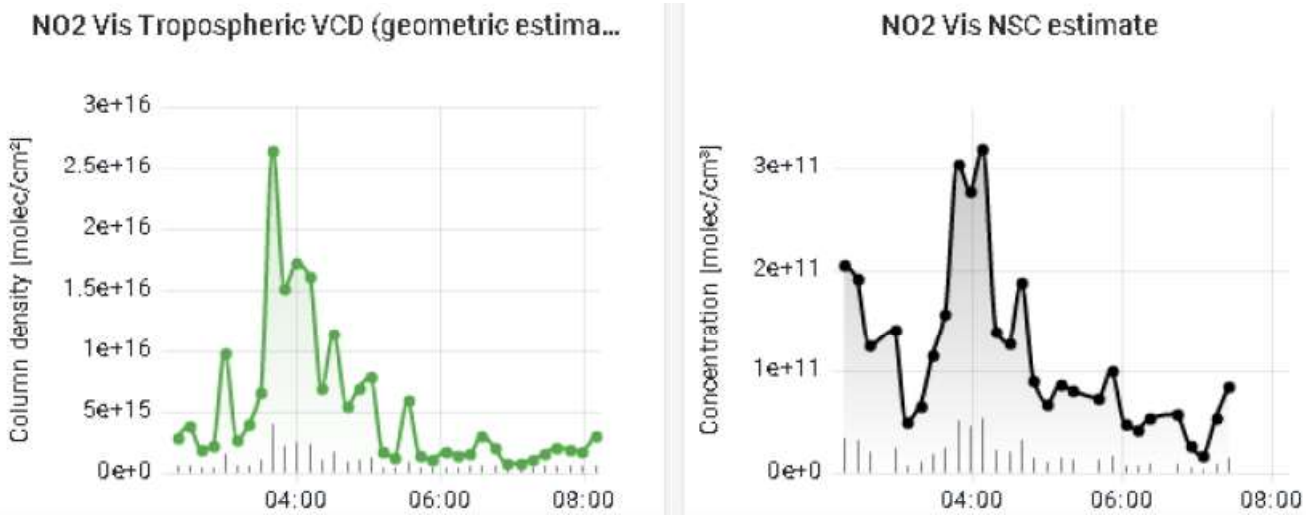

Figure 3-6: Sample MAx DOAS data showing time-resolved full air column (left) and near surface concentration (NSC, right) of NO_2.

Rather than measuring gas concentrations at a single location, as the passive and other real-time instruments included in the AQM network do, the MAx-DOAS operates on a principle similar to satellite remote sensing that

permits retrieval of both vertical and horizontal air pollutant profiles for distances of up to 25 km, depending on atmospheric conditions. The single axis (1D) instrument initially employed by MRAMP can undertake a scan (for a 90° horizontal-vertical sweep of measurement angles) approximately every 15 minutes.

NO_2 and SO_2 are the most significant non-particulate emissions in the Murujuga airshed, so monitoring peaks and trends of these species across the entire archipelago is highly desirable. A second (2D) MAx-DOAS has been deployed to improve upon current measurement capacity. The new unit is a 2D scanner which permits multiple angles to be measured automatically.

It was decided that it would be most beneficial to install the new 2D unit at the elevated EX-09 AQM at Mt Wongama, and relocate the Program's current 1D unit to AQM EX-02 on the Dampier foreshore. This arrangement is outlined in Figure 3-7. It may also be advantageous to alter measurement angles seasonally in response to dominant wind patterns.

It is worth noting that the configuration of the proposed 2D MAx-DOAS Skyscan unit is an improvement on the 1D model already installed. The spectrometer/computer module in the 2D model is housed separately to the telescope and can be situated inside the air conditioned AQM station. This makes it more robust with the extreme heat experienced over the summer in Murujuga.

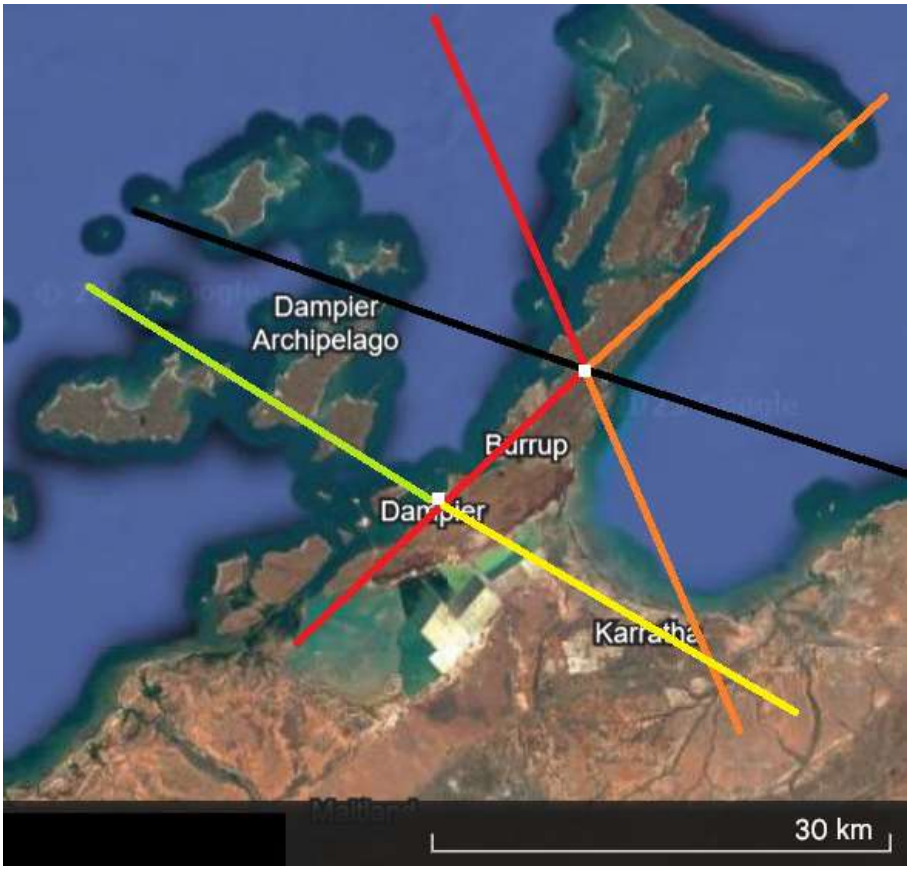

Figure 3-7: Potential measurement paths and maximum measurement distances from a MAxDOAS at EX-02 (Dampier) and EX-09 (Northern Burrup).

3.4.2 Inclusion of additional passive samplers at industry AQM EX-04 or nearby

(Ref: MSDCA Plan Section 3.5.1)

The MRAMP AQM network includes a suite of passive gas samplers in 21 locations in the Murujuga airshed. The Program utilises samplers supplied by IVL which are deployed and collected on a four-weekly cycle. The Program also has agreements with industry stakeholders to access passive and real time industry data from a number of additional industry AQMs. However, delays in receiving industry data and the complexities involved in combining datasets from different sampler types and sampling intervals limit the statistical confidence in utilising these data.

The only AQM located to the east of industrial facilities in the study area that are likely to emit NH_3 is a passive industry AQM situated in the vicinity of Hearson's Cove (referenced by the MRAMP identifier EX-04). In certain meteorological conditions, this is the only AQM suitably positioned to monitor NH_3 concentrations downstream of potential emission sources. For the reasons outlined above, this is impeding the Program's ability to develop robust NH_3 spatial gradient maps.

We have expanded the MRAMP managed AQM network by adding duplicate IVL passive NH_3 samplers in the vicinity of Hearson's Cove as determined by the Chief Statistician. This will fill any gaps in the monitoring network under prevailing westerly wind conditions.

Additional samplers for NO_2 and SO_2 were deployed in the north-west, as this represents another gap in the monitoring network. A site near the existing Rosemary Island fishing shack is suitable for this purpose.

The final site selection for the additional samplers was also dependent on cultural and heritage approval from MAC and any other land owner and regulatory approvals needed for the selected locations. Additional samplers will be deployed for a minimum period of 12 months, with possible continuation subject to a recommendation by the chief statistician following analysis of data collected.

3.4.3 High-volume dust collection and laboratory analysis

(refer MSDCA Plan Sections 3.4 and 3.5.1)

Geogenic dust (clay minerals, and elements such as Fe, Mn, etc) are the principle building blocks for the patina on the rocks at Murujuga. Anthropogenic activity (such as stockpiling and transport of mined ore or other local ground-breaking construction work) has increased airborne particulate matter in the airshed above pre-anthropogenic levels.

Geogenic particulate matter has not previously been proposed to represent a detrimental impact to the rock art in and of itself, however correlations between PM_{10} and measurements of pH on the rock surface were found by the MRAMP researchers in the first year of scientific studies (Curtin University, 2023). This may be due to dust acting as a carrier for adsorbed or absorbed substances. Some gas-phase reactions capable of generating new particulate matter (such as salts and sulphur compounds) may also be occurring. Such reactions could occur as a nucleation event or a catalysed reaction on the surface of geogenic matter.

Two high-volume (High-Vol) samplers were installed as dust collectors at suitable locations in the study area to collect a sufficient mass of particulate matter samples for further laboratory assessment. This will enable the Program to:

1. Undertake detailed elemental and (geo)chemical characterisation to investigate the hypotheses outlined above with respect to dust composition.

2. Conduct laboratory chamber exposure studies using bulk dust samples to investigate both abiotic (geochemical) effects and impact of dust on the microbiome.

The King Bay locality is one of the most readily accessible dusty locations in the study area, and one of the commercial workshop yards in King Bay has been identified as a suitable location for installation of a dust collector. The second dust collector will be installed at AQM EX-02 on the Dampier foreshore to collect concurrent samples for comparative purposes. The EX-02 AQM site is closer to dust emission sources (iron ore stockpiles) but further from many other industrial emission sources, which may permit a useful comparison.

Curtin have two suitable Hi-Vol samplers that were deployed for an initial 3 months, with weekly sample collection from each site This duration is not fixed – it is expected that three months of sampling will yield a sufficient quantity of dust for the proposed analysis, however the duration may need to be adjusted to suit. Similarly, there may be some benefit in sampling under different seasonal conditions and this will be further assessed following analysis of the initial samples.

3.4.4 Additional calibration unit for real time gas analysers

(Ref: MSDCA Plan Section 3.5.1)

In addition to initial commissioning calibration, the reference-grade gas monitors in the three MRAMP powered AQMs (AQ-01, EX-02 and EX-09) require periodic calibration while in use. The Program purchased a portable calibration unit for this purpose, and regular calibration is conducted during the four-weekly passive sampler changeover schedule.

A second calibration unit was procured to provide redundancy in the event that the first unit needs service or repair, so that calibration intervals are not missed. Additional calibration capacity was a formal recommendation from the DWER Air Quality Branch following an audit in December 2023. The calibration unit purchased by the Program has already required repair during the initial AQM commissioning calibrations, so the expectation of future down-time is not unreasonable.

3.4.5 Additional LiDAR units for particulate remote sensing

(Ref: MSDCA Plan Section 3.5.1)

The original draft of the MSDCA Plan proposed utilising an “Airbox” portable containerised air quality monitoring station from the University of Melbourne (see: https://airbox.earthsci.unimelb.edu.au/) which includes a Mini-Micro Pulse LiDAR (MPL). During the independent peer review of the draft Plan, reviewers requested inclusion of permanent real-time air quality monitoring stations with reference-grade gas analysers in the Program, and these ultimately replaced the Airbox proposal in the approved Plan.

Concurrent with the draft MSDCA Plan review, DWER’s Air Quality Branch offered the use of their Windcube 200s LiDAR unit, which potentially replaced the need for the MPL instrument. A scanning campaign using the DWER LiDAR was subsequently incorporated into the approved MSDCA Plan.

Since commencement of the Program, a more detailed investigation of potential LiDAR systems and their advantages and disadvantages has been undertaken. From this, a three-month multi-LiDAR scanning campaign using complimentary systems was undertaken.

Table 3-1: LiDAR systems deployed for particle sensing.

LiDAR unit type and source	Laser wavelength (nm)	Principal (particle measurement) Application
Windcube 200s (DWER Air Quality Branch)	1,540	Coarse dust / PM10 Lower resolution due to measurement method and wavelength Nominal measurement distance: ~3.5 km
MPL (University of Melbourne)	532	Broad spectrum high resolution aerosols (closest to satellite remote sensing), aerosol optical depth, etc. Nominal measurement distance: ~10-20 km
Experimental battery powered/portable LiDAR (University of Newcastle)	330	High resolution research instrument Nominal measurements distance ~2 km

Table 3-1 lists the three LiDAR systems included in a multi-device monitoring campaign. Each device performs better for different applications and different measurement ranges. The MPL and University of Newcastle experimental instruments are superior in observing nucleation and fine aerosol clouds (refer to Section 3.4.3). The University of Newcastle instrument has specifically been used to measure diesel soot plumes from mining plant previously, which would be similar in chemistry, size and morphology to some of the soot plumes observed from industries at Murujuga.

The deployment site is the powered AQM EX-09 at Mt Wongama due to its elevation and proximity to industry source within the LiDAR measurement distance limitations.

The transport and fate of particulate matter in the airshed at Murujuga is still poorly characterised, particularly for fine and ultrafine particles (which may be chemically more important to the rock art longevity). Ramboll modelling massively underpredicted $PM_{2.5}$ levels in the airshed, due to gaps in environmental source (inventory) data, however this may equally be related to underprediction of the $PM_{2.5}$ composition of geogenic dusts and ores and also secondary organic and inorganic aerosol generation which were not accounted for. Deployment of the three LiDAR system will enable much more detailed characterisation of some of these processes of components of particulate matter and their sources, over and above the particle spectrometers installed at the powered AQMs.

4 Summary

It is believed that the changes included in this Plan will significantly improve the outcomes of the Murujuga Rock Art Monitoring Program.

Table 4-1 summarises the additional activities included in the MRAMP studies through this MSDCA Plan Amendment.

Table 4-1: Recommended prioritisation of additional scope inclusions

No.	Component Study	Activity	Notes
1	Inorganic geochemistry	Section 3.1.1 Additional sample rock collection and laboratory porosity investigations	These two activities need to be completed together to provide all relevant information required for statistical analysis
	Air quality monitoring	Section 3.1.2 Historical emissions inventory	
2	Inorganic geochemistry	Section 3.1.3 Field permeability measurements	
3	Microbiome	Section 3.2 Microbiome chamber studies workflow stream	
4	Organic geochemistry	Section 3.3 Investigation of hydrocarbon residues found in patina samples	
5	Air quality monitoring	Section 3.4.1 Use of a second MAx-DOAS Skyscan instrument	
6	Air quality monitoring	Section 3.4.2 Inclusion of NH3 passive samplers at industry AQM EX-04	
7	Air quality monitoring	Section 3.4.3 High volume dust collection and laboratory analysis	
8	Air quality monitoring	Section 3.4.4 Additional calibration unit for real time gas analysers	
9	Air quality monitoring	Section 3.4.5 Additional LiDAR units for remote aerosol and PM sensing	

Cessation of plutonium isotope analysis (Section 2.1.1), and removal of OP-FTIR scanning (Section 2.1.2) are recommended as we do not believe they provide sufficient value to the project (in terms of outcomes) to continue them in the originally proposed format. Other activities are proposed which will replace their potential benefit.

Similarly, cessation of passive VOC sampling (Section 2.2) is recommended by the Chief Statistician following analysis of the first 12 months of VOC data measured by the program.

5 References

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Curtin University (2022). *Murujuga Rock Art Monitoring Program: Monitoring Studies Data Collection and Analysis Plan*. Report prepared by Curtin University for the Murujuga Aboriginal Corporation and Department of Water and Environmental Regulation, Government of Western Australia (COPP21065-PLN-G-102_0 / RES-HS-SPH-BM-62312_3). Government of Western Australia. https://www.wa.gov.au/government/publications/murujuga-rock-art-monitoring-program-monitoring-studies-data-collection-and-analysis-plan.

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