

Soil properties at archaeological site, Darling Quarter Site (Formerly Darling Walk), Sydney

Report by Roy Lawrie, Soil Scientist, with photographs by Lisa Lawrie

Introduction

The soil was examined on 26/3/09 in shallow pits at two locations near the original shoreline of Darling Harbour to determine the possible extent of disturbance to soil profile features by human activity, prior to or during the early colonial period. One location was at a former aboriginal shell midden where two layers were sampled (Site 1); the other appeared to be on the original shoreline where four layers of a soil profile were sampled (Site 2).

Midden Site (Site 1)

Site 1: in Area 5, an aboriginal shell midden site located on a small sandstone knob on the foreshore apparently preserved beneath a thin layer of stony fill.

Depth cm	Profile features	Comment
0	Height datum 1.38m RL; broken sandstone in mixed fill; abrupt boundary to	Not sampled
10	Black sand with brown streaks and many shells, some in fragments; clear boundary to	Original pre-European topsoil, upper portion probably missing; sampled
22	Black loamy sand with no coarse fragments; abrupt boundary to	Possible pre-midden A horizon or topsoil; sampled
35	Yellow and grey mottled clayey sand; abrupt boundary to	Top of C horizon, derived from deeply weathered sandstone, undisturbed, not sampled
40	Hard sandstone	



Photo 1. The midden exposed in a shallow trench about 35 cm deep. The shells are protruding from the centre of the dark profile. The floor of the trench is the mottled clayey sand resting on sandstone.

Comment on Chemical Properties

Effect of shell content

A wide range of laboratory analyses (see Report WN10/1698/E) have revealed many similarities between the two sampled layers from the midden. The main differences between their chemical properties are in their pH, calcium and carbon contents. These differences are related to the presence of shells and the higher organic matter level in the upper layer of the midden.

Most shells were removed from the upper sample (Laboratory No 5799, sample ID 213) prior to lab testing, but crushing and grinding of the remaining small fragments during sample preparation has probably affected its pH, raising it to 6.9. This has also elevated its total calcium content to 2.8%, well above the content of 1% in the lower shell-free sample (Laboratory No 5800, sample ID 215). A crushed shell content of only 2% in the upper sample would be enough to boost its total calcium content to this level, considering there is also calcium present in the soil organic matter (SOM). The upper sample does have a significantly higher content of organic carbon (5.7%, equivalent to 9.8% SOM) than the lower sample (3.0%, or 5.2% SOM). Much of the calcium associated with SOM is in the exchangeable form. The upper sample contains much more exchangeable calcium (32 cmol(+)/kg) than the lower sample (13cmol(+)/kg).

The shell fragments, together with some additional resistant organic matter (such as finely-divided charcoal), have also contributed to the higher total carbon content of the upper sample (7.5%, compared to 4.4% in the lower sample). The difference between the two carbon tests (total carbon and organic carbon) is most likely related to the presence of charcoal¹, probably from cooking fires at the site.

The upper sample has more calcium (both exchangeable and total) than the lower sample. Together with a higher organic matter level this is the main difference between the two layers. If the upper layer had been tested with the original shell content retained, the difference in calcium content would have been much more pronounced. The differences in the concentrations of the other elements, both major and minor, are much less.

The carbon, nitrogen and total calcium contents are comparable to the levels found recently in the dark inland soils associated with aboriginal oven mounds along the Murray river².

Major nutrients – phosphorus and nitrogen

The higher organic matter concentration in the upper sample also means a boost to its content of phosphorus and nitrogen (they are present in only negligible amounts in the shell fragments). The ratio of organic carbon to total nitrogen is very similar in both samples (upper 11.2:1, lower 11.5:1); the organic carbon to total phosphorus ratios are also very close (upper 219:1, lower 214:1). This close similarity suggests that both layers contain the same type of organic matter, and that the concentration of phosphorus and nitrogen in their various inorganic forms is very similar in each layer, or more likely, very small.

Unlike many soils from other archaeological sites from the colonial period, the midden's concentration of plant-available phosphorus (as estimated by the Colwell test) is relatively low. This suggests that the midden has not received deposits of animal or poultry manure, and that any additions of domestic waste during the colonial period were unlikely.

Sulphur and sulphate

The ratio of organic carbon to total sulphur however is not the same in both samples, because there is a significant amount of inorganic sulphur, particularly in the lower sample. The proportion of

sulphur present as sulphate can be estimated by comparing the KCl40 level to the total sulphur level in each layer - the ratio in the upper layer is 0.31 (i.e. less than a third), but is 0.59 in the lower layer. In coastal areas the soils can receive sulphate (the main form of inorganic sulphur) from sea spray in rainfall, from shallow watertables in low-lying areas or directly from sea water during high tides along the shoreline. These processes have resulted in very high sulphate levels (KCl40 test) in both samples, especially in the lower one. Sea water however contains about seven times as much chloride as sulphate, and these two midden samples have extremely low chloride contents, given their foreshore location (and their high salinity, as measured by the EC test). It appears that both samples have lost chloride but have retained sulphate. Chloride is readily leached out of the soil when it rains, and so is sulphate unless it can react with (shell-derived) calcium to form weakly-soluble gypsum (calcium sulphate). Over time, the gypsum is slowly leached downwards, and this process has probably contributed to the raised sulphate level in the lower sample. Alternatively in waterlogged conditions sulphate may form insoluble sulphide minerals (as in acid sulphate soils), but this seems very unlikely because the midden is sufficiently elevated (RL 1.28m at the top), perched on sandstone above any local watertable.

Metal content

Metal concentrations in the midden are very low. There is no evidence of heavy metal contamination resulting from industrial activity. Had this occurred, the elevated pH would have favoured accumulation of heavy metals in the upper layer. The content of metals like cadmium, copper, lead and zinc in both layers is generally below the background median of these metals in surface soils of the Sydney region³, and well below the median level of these metals in the soil around the inner city suburb of Glebe. The nearby suburb was the site of a range of industries that could have generated the contamination in the 19th century⁴. The absence of contamination in the midden suggests that the broken sandstone layer may have been placed over it prior to any 19th industrial activity.

Other trace elements

The upper part of the midden has a higher content of boron and manganese (as well as copper, lead and zinc) than the lower part. This could be associated with the higher pH of the shell-rich upper layer, or with the extra organic matter content. The boron concentration (12 mg/kg) is high, above the top level found in 70 Sydney region³ topsoils (5.9 mg/kg), but is below the global⁵ soils median (20 mg/kg).

Two other trace elements are also present in elevated concentrations, but in the lower layer of the midden. The molybdenum content here (7.2 mg/kg) is well above the top level found around Sydney³ (0.6 mg/kg), and is at the high end of the range for most Australian soils⁶, but below the global⁵ median (12 mg/kg). More significantly the arsenic content in the lower layer (8.9 mg/kg) is above the global median (6mg/kg) and in the upper range of Sydney region topsoils. The reason for this combination of elevated concentrations is unknown, but is unlikely to be associated with industrial activity because it appears in the lower part of the midden, well below the surface which is the zone where contaminants normally are found.

Summary

The impact of prehistoric occupation and settlement on the underlying soil profile has received international attention in recent years, particularly regarding the extent of soil carbon elevation. The Brazilian terra preta and terra mulata soils are well known examples. The equally dark fine earth fraction within and beneath Australian shell middens however has received little attention.

The carbon, nitrogen and total calcium contents of the midden are comparable to the levels found recently in dark soils associated with aboriginal oven mounds. These mounds also contain carbon

compounds that have been compared to those in Brazilian terra preta², a soil whose fertility has been increased by human activity rather than degraded. More study of the midden's carbon chemistry is needed to make a direct comparison.

Analysis of nutrient levels suggests that the midden has not received deposits of animal or poultry manure, and that any additions of domestic waste during the colonial period were unlikely. Ash from cooking fires is probably the main reason for the elevated exchangeable potassium content. Metal concentrations in both layers of the midden are very low. There is no evidence of heavy metal contamination resulting from industrial activity.

Original Foreshore Profile (Site 2)

Site 2: in Area 9, below a large piped drain in the mill yard, slightly downslope from Site 1, close to the original shoreline of Darling Harbour.

Depth cm	Profile features	Comment
	Height datum RL 1.02 m at top of drain, 40 cm above a layer of mixed fill 25 cm thick; abrupt boundary to	High tide level approx. RL 0.3 m, equivalent to 72 cm below top of drain
0	Dark grey light clay with many fibrous roots; rests on a layer of brown beach sand 5 cm thick; high tide level at approx depth of 7 cm	Lower part of former topsoil, with remnant of beach sand underneath
10	Grey brown light clay containing preserved plant debris	Lagoon or wetland floor; sampled 0-15 cm (including topsoil from above but omitting beach sand layer)
15	Dark grey sandy clay to clayey sand with plant debris	Sampled 15-30 cm
30	Bluish grey waterlogged light medium clay, dense and impermeable; abrupt boundary to	Sampled 30-45 cm Potential acid sulphate layer
65	Dark grey clayey sand with bands of light grey sandy clay; waterlogged throughout	Sampled 65-90 cm potential acid sulphate layer
90	Maximum depth of inspection	



Photo 2. The dark grey old foreshore profile sits under the large piped drain.

Profile features

The various layers in the profile give some indication of how the soil was formed. The many plant roots in the light clay topsoil signify the absence of tidal action, despite the low elevation. This suggests formation/deposition behind some natural or man-made barrier along the shoreline that protected the soil from erosion by wave action; an early 19th century age for the layer is possible.

The brown sand below occurs very close to the high water mark, but is fairly thin, suggesting that wave action occurred here for only a short period. A quiet backswamp environment is suggested for the underlying dark grey sandy clay containing plant debris. This layer was once reasonably aerated, enough to allow some plant growth.

The bluish grey clay underneath however was not aerated; it was permanently waterlogged, allowing sulphide minerals to form. Like many other coastal/estuarine soils in NSW it formed during the late Holocene, after the sea level rose at the end of the last Ice Age and then oscillated with some minor fluctuations during the last few thousand years. The clay formed in a quiet, protected location behind the beach, most likely in a shallow fresh water lagoon capable of trapping fine muddy sediments. It is fairly thick (35 cm), and would probably have needed a long period of time to accumulate, during the period of aboriginal occupation. The thin sandy and clayey bands of the layer below were deposited during individual rainfall or flood events, probably in shallow non-tidal water.

Interpretation of soil test results

The profile has many features commonly found in acid sulphate soils, especially the bluish grey clay below 30 cm. The elevation of this layer is below the high tide level, and it is very salty, but not because of the sea water. Prolonged drying after sampling however has oxidised most of its sulphide minerals to sulphuric acid, lowering the pH and raising the total actual acidity, exchangeable aluminium and sulphate content. The very low chloride concentration indicates that it was originally waterlogged with fresh rather than salt water.

The surface soil has a very high carbon content, consistent with the presence of abundant plant remains, but the levels of nutrients like phosphorus and potassium are relatively modest. This suggests that there has been little or no change to these nutrient concentrations as a result of human activity during the colonial period. There may have been only a short period of activities such as manure deposition from livestock grazing, gardening, or disposal of household wastes. The upper clay layer above the brown beach sand is rather thin, suggesting some could have been removed prior to the dumping of the overlying fill layer. This infilling above the shoreline appears to have occurred early in the colonial period, before nutrient levels in the topsoil underneath had a chance to rise.

Nutrient levels in the layers underneath are very low, typical of bushland soils that have never been cleared or cultivated. There is no indication of any downward movement of nutrients into the subsoil, a feature that is often seen in soil profiles at other archaeological sites in Sydney⁷.

References

1. Conyers, MK, Poile, GJ, Oates, AA, Waters, D & Chan, KY. Comparison of three carbon determination methods on naturally occurring substrates and the implication for the quantification of 'soil carbon'. *Aust J Soil Res.* 49 (2011) 27-33.
2. Downie, AE, van Zwieten, L, Smernik, RJ, Morris, S & Munroe, PR. Terra Preta Australis: reassessing the carbon storage capacity of temperate soils. *Agriculture, Ecosystems and Environment* 140 (2011) 137-147.

3. Lawrie, RA, Keneally, JP & ML Stevens. Background trace elements in soils around Sydney. Proc. Fourth National Soils Conference, Adelaide, April 1992.
4. Markus, JA & McBratney, AB. An urban soil study: heavy metals in Glebe, Australia. Aust. J. Soil Res. 34 (1996) 453-65.
5. Bowen, HJM. Trace elements in biochemistry. Academic Press, New York 1979.
6. CSIRO Division of Soils. Soils: An Australian Viewpoint. CSIRO, Melbourne 1983.
7. Lawrie, RA. Soil chemical properties at Historical Archaeological Sites of Inner Sydney, NSW, *Australasian Historical Archaeology* Volume 17, 1999, 70-80.

Appendix

Soil laboratory test reports: in separate attachments

WN10/1698: Midden

Sample ID: 213 – depth 0-20 cm
215 – depth 20-30 cm

WN10/1699: foreshore profile

Sample ID: 231 – depth 0-15 cm
232 – depth 15-30 cm
233 – depth 30-45 cm
234 – depth 65-90 cm

Owner **CASEY & LOWE PTY LTD**
51 REUSS STREET
LEICHHARDT 2040

Submitted: 1.9.10
 Received: 3.9.10

Samples received: 2 x soil
 The samples have been assigned the following laboratory numbers. Lab No 5799 & 5800 / Darling Walk - Aboriginal

Soil Analysis Report

Analytical Method	Method number	Date Analysed
Soil pH (CaCl ₂)	R&H 4B2	6/9/10
Available orthophosphate phosphorus in soil using bicarbonate extraction, Colwell	R&H 9B1	8/9/10
Extraction of Sulfur (KCl ₄₀) and determination by ICP	Blair et al (1991) USEPA 6010	15/9/10
Soil Conductivity	R&H 3A1	6/9/10
Determination of Gillman and Sumpter Exchangeable Cations by ICP	R&H 15E1 USEPA 6010	15/9/10
Organic Carbon % (Walkley & Black)	In-house 236	9/9/10
Total Nitrogen and Total Carbon by Dumas combustion method	In house 630	21/9/10
Acid Extraction	USEPA 3050B	9/9/10
Chloride	R&H 5A1	6/9/10
Acid Extractable Elements and Metals by ICP	USEPA 6010	10/9/10

R&H ~ Rayment and Higginson
 USEPA ~ United States Environmental Protection Agency
 In-house methods 235 & 236 are based on R&H methods 6B1 & 6A1, respectively
 Blair et al (1991). A soil sulfur test for pastures and crops *Aust J Soil Res* 29:619-26

Laboratory No		Limit of reporting	5799	5800
Sample ID	Unit		213	215
EC	dS/m	0.01	1.2	1.5
pH (CaCl₂)	pH units	0.04	6.9	5.0
Chloride	mg/kg	1.5	23	17
Total Nitrogen	%	0.02	0.51	0.26
Total Carbon	%		7.5	4.4
Organic Carbon	%	0.05	5.7	3.0
Sulfur (KCl₄₀)	mg/kg	2	680	1000
Colwell Phosphorus	mg/kg	2	25	19
<u>Exchangeable Cations</u>				
Aluminium	cmol(+)/kg	0.01	<0.01	0.045
Calcium	cmol(+)/kg	0.01	32	13
Potassium	cmol(+)/kg	0.02	0.44	0.37
Magnesium	cmol(+)/kg	0.008	1.6	1.2
Sodium	cmol(+)/kg	0.02	0.66	0.40
CEC	cmol(+)/kg		35	15
Calcium/Magnesium Ratio			20	11
Aluminium Saturation	%		<0.04	0.30
Exchangeable Calcium	%		92	87
Exchangeable Potassium	%		1.3	2.5
Exchangeable Magnesium	%		4.6	7.9
Exchangeable Sodium	%		1.9	2.7

This document is issued in accordance with NATA's accreditation requirements.



NATA Accredited Laboratory Number: 14173

Printed on 21 September, 2010

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2 x 110005 17180 117106 117099 17030 18480 18465 117003 110008 18320 → 136-1

Laboratory No		Limit of reporting	5799	5800
Sample ID	Unit		213	215
Total Elements				
Aluminium	%	0.0005	0.20	0.23
Arsenic	mg/kg	5	<5	8.9
Boron	mg/kg	4	12	5.8
Calcium	%	0.0003	2.8	1.0
Cadmium	mg/kg	0.2	<0.2	<0.2
Cobalt	mg/kg	0.4	3.4	2.7
Chromium	mg/kg	0.2	6.1	9.9
Copper	mg/kg	0.2	3.9	2.5
Iron	%	0.00003	1.0	1.4
Potassium	%	0.0004	0.039	0.040
Magnesium	%	0.00006	0.030	0.028
Manganese	mg/kg	0.1	11	6.4
Molybdenum	mg/kg	0.3	5.2	7.2
Sodium	%	0.0005	0.032	0.014
Nickel	mg/kg	0.7	0.54	0.54
Phosphorus	%	0.0003	0.026	0.014
Lead	mg/kg	2	8.5	3.2
Sulfur	%	0.0006	0.22	0.17
Selenium	mg/kg	4	<4	<4
Zinc	mg/kg	0.8	3.6	1.6

GLEN RANGOTT
CHEMIST
21 SEPTEMBER, 2010 SGJ

FINAL REPORT M CASEY

- Samples air dried at 40 °C in dehydrators according to Method 1B1 (Rayment and Higginson, 1992).
- These results apply to the sample(s) as provided and are expressed on a dry weight basis unless otherwise stated.
- This report should not be reproduced except in full.
- Samples will be retained for one month from the date of the final report. Samples will then be discarded. Clients wishing to recover their samples must contact the laboratory within this period. The laboratory will return residual samples at client expense when requested.
- Test results and findings may be provided to authorised staff and used for statistical, surveillance, extension, certification and regulatory purposes in accordance with Departmental policies. The information assists disease and residue control programs and underpins market access for agricultural products. The source of the information will remain confidential unless otherwise required by Law or regulatory policies.



Owner **CASEY & LOWE PTY LTD**
51 REUSS STREET
LEICHHARDT 2040

Submitted: 1.9.10
 Received: 3.9.10

Samples received: 4 x soil

The samples have been assigned the following laboratory numbers. Lab No 5801 - 5804 / Darling Walk - Historic

Soil Analysis Report

Analytical Method	Method number	Date Analysed
Soil pH (CaCl ₂)	R&H 4B2	6/9/10
Available orthophosphate phosphorus in soil using bicarbonate extraction, Colwell	R&H 9B1	8/9/10
Extraction of Sulfur (KCl ₄₀) and determination by ICP	Blair et al (1991) USEPA 6010	17/9/10
Soil Conductivity	R&H 3A1	6/9/10
Determination of Gillman and Sumpter Exchangeable Cations by ICP	R&H 15E1 USEPA 6010	15/9/10
Organic Carbon % (Walkley & Black)	In-house 236	16/9/10
Total Nitrogen and Total Carbon by Dumas combustion method	In house 630	16/9/10
Chloride	R&H 5A1	6/9/10
Total Actual Acidity (TAA)	ASSMAC 23F	29/9/10

R&H ~ Rayment and Higginson
 USEPA ~ United States Environmental Protection Agency
 In-house methods 235 & 236 are based on R&H methods 6B1 & 6A1, respectively
 Blair et al (1991). A soil sulfur test for pastures and crops *Aust J Soil Res* 29:619-26

Laboratory No		Limit of reporting	5801	5802	5803	5804
Sample ID	Unit		231	232	233	234
EC	dS/m	0.01	4.5	6.1	2.2	1.6
pH (CaCl ₂)	pH units	0.04	3.1	2.1	3.1	3.3
Chloride	mg/kg	1.5	73	13	13	12
Total Nitrogen	%	0.02	0.56	0.086	0.030	0.036
Total Carbon	%	0.2	11	3.4	0.35	0.37
Organic Carbon	%	0.05	8.8	3.0	0.34	0.39
Sulfur (KCl ₄₀)	mg/kg	2	6800	8000	2600	1800
Colwell Phosphorus	mg/kg	2	39	2.9	<2	2.5
Total Actual Acidity	moles H+/t	5	390	610	240	140
Exchangeable Cations						
Aluminium	cmol(+)/kg	0.01	27	14	15	9.2
Calcium	cmol(+)/kg	0.01	17	2.5	0.70	0.62
Potassium	cmol(+)/kg	0.02	0.040	<0.02	0.022	0.13
Magnesium	cmol(+)/kg	0.008	6.7	1.6	3.6	3.3
Sodium	cmol(+)/kg	0.02	1.2	0.35	0.19	0.31
CEC	cmol(+)/kg		52	18	20	14
Calcium/Magnesium Ratio			2.5	1.6	0.20	0.19
Aluminium Saturation	%		53	76	78	68
Exchangeable Calcium	%		32	14	3.5	4.6
Exchangeable Potassium	%		0.08	<0.08	0.11	0.96
Exchangeable Magnesium	%		13	8.6	18	24
Exchangeable Sodium	%		2.3	1.9	0.95	2.3

Chromium reducible sulfur testing was undertaken at Environmental Analysis Laboratory, Southern Cross University, Lismore, EA 0010753256. Results attached.



GLEN RANGOTT
CHEMIST
30 SEPTEMBER, 2010 SGJ

FINAL REPORT M CASEY

- *Samples air dried at 40 °C in dehydrators according to Method 1B1 (Rayment and Higginson, 1992).*
- *These results apply to the sample(s) as provided and are expressed on a dry weight basis unless otherwise stated.*
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- *Test results and findings may be provided to authorised staff and used for statistical, surveillance, extension, certification and regulatory purposes in accordance with Departmental policies. The information assists disease and residue control programs and underpins market access for agricultural products. The source of the information will remain confidential unless otherwise required by Law or regulatory policies.*



RESULTS OF ACID SULFATE SOIL ANALYSIS

4 samples supplied by Department of Primary Industries on the 7th September, 2010 - Lab. Job No. B0521

Analysis requested by Craig Hunt. - **Your Project: WN 10/1699 EA 0010753256**

Sample Site	EAL lab code	REDUCED INORGANIC SULFUR		POTENTIAL ACIDITY CRS ONLY	LIME CALCULATION CRS ONLY
		(% chromium reducible S)		mole H ⁺ /tonne	kg CaCO ₃ /tonne DW
		(%Scr)	(mole H ⁺ /tonne)	(based on %Scrs)	(includes 1.5 safety Factor when liming rate is +ve)
Method No.				note 5	note 4 and 6
5801	B0521/1	0.06	37	37	2.8
5802	B0521/2	0.08	50	50	3.7
5803	B0521/3	0.18	112	112	8.4
5804	B0521/4	0.12	75	75	5.6

NOTE:

- 1 - All analysis is Dry Weight (DW) - samples dried and ground immediately upon arrival (unless supplied dried and ground)
- 2 - Samples analysed by SPOCAS method 23 (ie Suspension Peroxide Oxidation Combined Acidity & sulfate) and 'Chromium Reducible Sulfur' technique (Scr - Method 22B)
- 3 - Methods from Ahern, CR, McElnea AE, Sullivan LA (2004). **Acid Sulfate Soils Laboratory Methods Guidelines**. QLD DNRME.
- 4 - Bulk Density is required for liming rate calculations per soil volume. Lab. Bulk Density is no longer applicable - field bulk density rings can be used and dried/ weighed in the laboratory.
- 5 - **ABA Equation: Net Acidity = Potential Sulfidic Acidity (ie. Scrs or Sox) + Actual Acidity + Retained Acidity - measured ANC/FF (with FF currently defaulted to 1.5)**
- 6 - The neutralising requirement, lime calculation, includes a 1.5 safety margin for acid neutralisation (an increased safety factor may be required in some cases)
- 7 - For Texture: coarse = sands to loamy sands; medium = sandy loams to light clays; fine = medium to heavy clays and silty clays
- 8 - .. denotes not requested or required. '0' is used for ANC and Snag calcs if TAA pH <6.5 or >4.5
- 9 - SCREENING, CRS, TAA and ANC are NATA accredited but other SPOCAS segments are currently not NATA accredited
- 10- Results at or below detection limits are replaced with '0' for calculation purposes.
- 11 - **Projects that disturb >1000 tonnes of soil, the ≥0.03% S classification guideline would apply (refer to acid sulfate management guidelines).**
- 12 - Results refer to samples as received at the laboratory. This report is not to be reproduced except in full.

(Classification of potential acid sulfate material if: coarse Scr≥0.03%S or 19mole H⁺/t; medium Scr≥0.06%S or 37mole H⁺/t; fine Scr≥0.1%S or 62mole H⁺/t) - as per QUASSIT Guidelines



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