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Metal concentrations in Rapid Creek sediment cores

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CONTENTS

Executive Summary

- Rapid Creek is a small tropical tidal creek in a suburban setting. The mouth of the creek opens between the Nightcliff and Casuarina beachfront area with the estuarine reach of the creek flanked by mangroves. The upper freshwater reaches are fringed by monsoon forest with the most upper section dominated by paperbark swamp. The waterway flows through largely urban land uses where the upper seasonally flowing reach receives diffuse runoff from the Darwin International Airport and other commercial and urban land uses, and Department of Defense land.

- An estimation of mangrove core metal concentration changes and the identification of contaminant origin within a local context was undertaken to provide a basis for an environmental archive.

- Elemental analysis, including metals and metalloids, revealed a sharp transition in one in-channel core from pre-development strata with low concentrations of Cu, Zn, Cd and Pb and low Pb isotope ratios to overlying strata with significantly elevated levels of the same metals and isotope ratios. This core was dated by the ^{210}Pb method and an age of the transition of 77 +/- 9 years was obtained corresponding to the WW2 development of Darwin Airport and surrounding areas within the catchment.

- The lower sections of two cores provided pre-development metal and metalloid baseline concentrations. The elevated metal levels in the upper sections of cores most likely have a range of diffuse urban / industrial sources but were all below the ANZECC (2000) interim sediment quality guideline 'low' (ISQG-Low) values and are unlikely to constitute a toxicity risk.

- Despite the increasing development in the catchment, the sediment profiles since WW2 do not show increasing pollutant concentrations. The results provide some insight into pre-impact concentration of metals in this small estuarine creek.

1. Introduction and study objectives

Rapid Creek is a small seasonally flowing coastal stream in a largely urban setting (Fig. 1). The waterway flows through mixed commercial and urban land uses to the estuarine mouth between the beachside suburbs of Nightcliff and Casuarina.

Significant nutrient and metal diffuse sources discharge to the creek from mainly urban stormwater. The creek typically ceases to flow by mid to late dry season each year. The lower reaches are subject to tidal inundation.

Figure 1. Rapid Creek in the Darwin region of the Northern Territory.

The monthly mean discharge in Rapid Creek upstream of the sampling sites clearly indicate that a large proportion of the stream flow occurs from December to March in association with the wet season (Fig. 2).

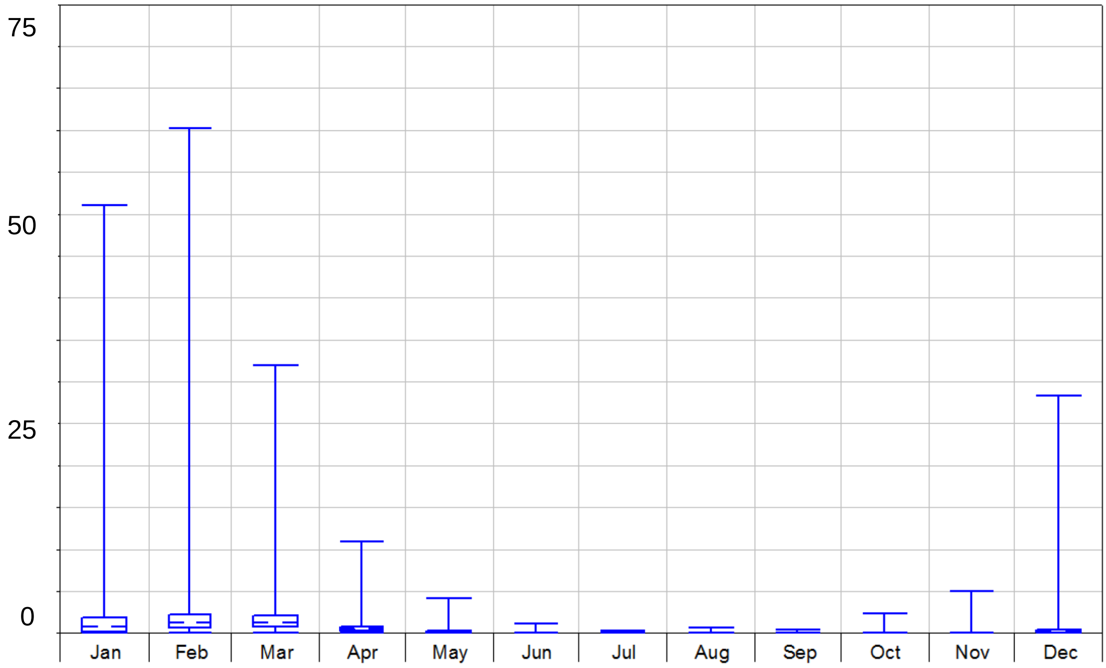

Figure 2. Monthly median discharge (cumecs) with inter-quartiles (25th and 75th), minimum and maximum values for G8150127 (Rapid Creek at Weir-upstream) 1963-2014. Source Hydstra database, Department of Land Resource Management.

Pollutant loads assessed at the upstream Moil gauge station are consistent with typical urban loads (Table 1) where impervious surfaces can convey significant loads in comparison to undisturbed catchments. These loads are 2-9 times higher than those for undisturbed areas of the Darwin region catchment (Skinner et al. 2008).

Table 1. Typical annual stormwater pollutant loads to Rapid Creek

Parameter	Load*
Total Nitrogen (tonnes/yr)	21.7
Total Phosphorus (tonnes/yr)	2.23
Al (tonnes/yr)	114
As (kg/yr)	22.3
Cd (kg/yr)	4.56
Cr (kg/yr)	90.3
Cu (kg/yr)	501
Ni (kg/yr)	28.7
Pb (kg/yr)	553
Zn (kg/yr)	1660
TSS (kg/yr)	1680
VSS (kg/yr)	375

*Based on measured loads from Moil Gauge Station (G8150231). *Source: Skinner et al. 2008*.

To date no sediment monitoring has been undertaken in the estuary of the Rapid Creek catchment by DLRM. Metal concentrations in the tributary have been examined by the Department of Land Resource Management (DLRM) in conjunction with pollutant load assessment (Skinner et al. 2008). Darwin International Airport (DIA) has routinely sampled Rapid Creek in the freshwater reaches downstream of airport activities for a number of years for metals.

Prior to the development of a more comprehensive sediment monitoring program some insight into historical pollutant trends is proposed via strategic core sampling to capture contaminant history. The estimation of sediment temporal concentration and the identification of contaminant origin within the local context could provide a basis for an environmental archive.

The study objectives are:

1. Undertake core sampling of Rapid Creek estuary to construct a pollutant history. Metal pollutant trends identified will enable reconstruction of pollution histories associated with land use change (development, urbanisation, and erosion); and

2. Provide valuable baseline data to progress the development of a sediment monitoring program in the Darwin Harbour region.

This work will provide a precursor to future sediment monitoring across other parts of Darwin harbour with a focus on areas subject to increasing anthropogenic pressures.

2. Methodology

Sampling

Fieldwork was carried out by boat on August 21, 2014. Within the creek, sampling site selection was focused on sites of sediment deposition. A number of test cores were used to locate muddy sediment and with absence of coarse-grained layers which indicate the best chance of preserving long term records of sediment accumulation.

Three sites (RC1, RC2 and RC6, Figs. 3 and 4) along a 1 km stretch of Rapid Creek yielded suitable cores, all located within the channel in close proximity to the bank and at water depths of approx. 0.3-0.5 m. A fourth core (RC7) was obtained from the Rapid Creek floodplain on August 22, 2014, in a vegetation-free area within the mangrove forest approximately 150 m from the creek itself (Fig. 4). This site is likely to be covered by creek water only at high spring tides. Table 2 summarises the pertinent core sampling information.

Two types of coring devices were used: (1) An Eijkelkamp C-section, 25 mm diameter, 1 m long steel corer was used at all sites to obtain samples for elemental and lead isotope analysis. The cores were sub sampled in the field using a plastic spatula and samples stored in sealed plastic bags; (2) An AMS barrel corer with a plastic core catcher/sleeve was used to obtain cores at sites RC1 and RC7 for potential dating analysis. Due to the corer design and sediment 'stickyness' compaction of the retrieved cores relative to the penetration depth of the corer could not be avoided (measured at 23-25% for RC1 and RC7 respectively). The AMS cores were left intact in the sleeve and transported to the Australian Nuclear Science and Technology Organisation (ANSTO) in a frozen state for further processing.

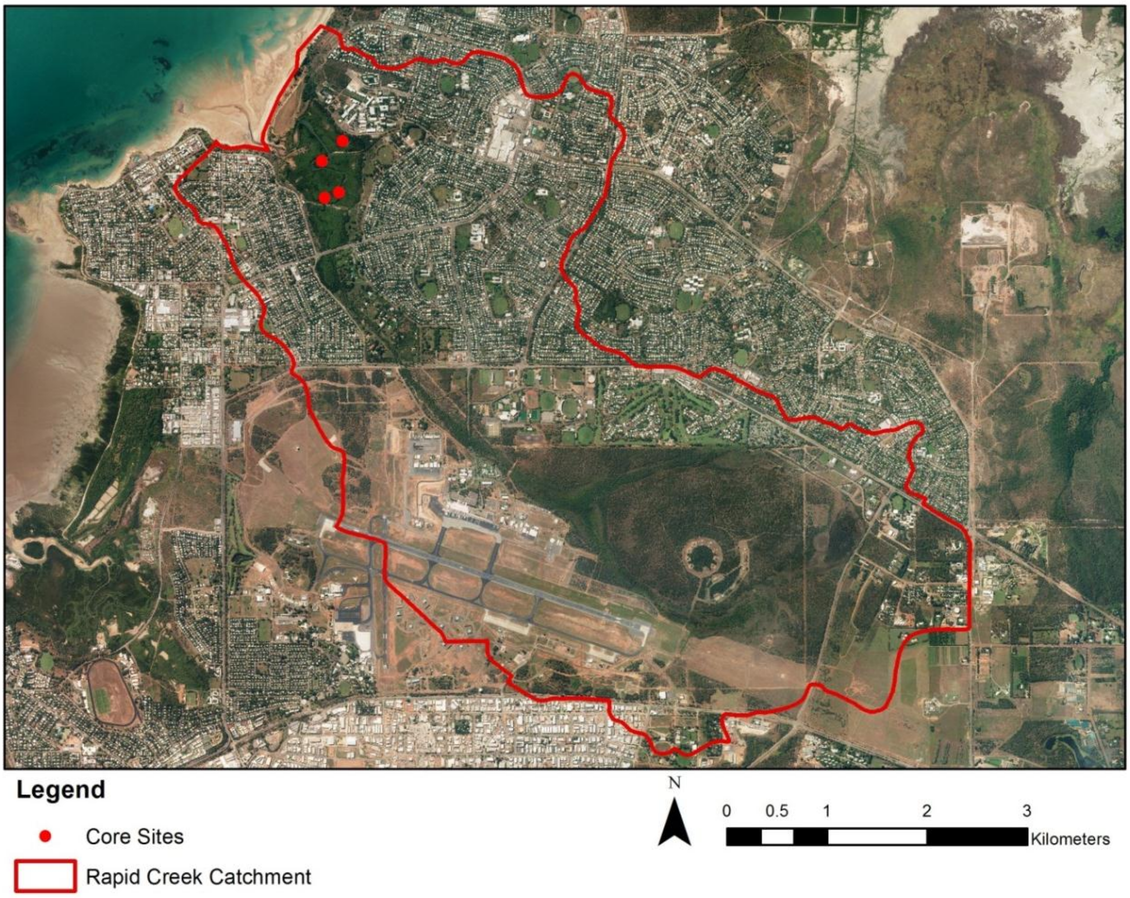

Figure 3. Rapid Creek catchment with Darwin International Airport and surrounding suburbs.

Figure 4. Mouth of Rapid Creek with coring sites.

Table 2. Rapid Creek cores and sample intervals

Site	Date	ICPMS core Depth	Intervals sampled	Dating core depth	Intervals sampled
RC1 12°22.82'S 130° 51.92'E	21/8/2014	50 cm	2cm at 0-20cm; 5cm at 20cm-bottom	23 cm (compacted from 30 cm)	0-1, 2-3, 4-5, 6-7, 8-9, 10-11, 12-13, 14-15 cm
RC2 12° 22.79'S 130° 51.99'E	21/8/2014	60 cm	2cm at 0-20cm; 5cm at 20cm-bottom	Not cored	Not processed
RC6 12° 22.62'S 130° 51.89'E	21/8/2014	80 cm	2cm at 0-20cm; 5cm at 20cm-bottom	Not cored	Not processed
RC7 12° 22.52'S 130° 52.01'E	22/8/2014	70 cm	2cm at 0-20cm; 5cm at 20cm-bottom	21 cm (compacted from 28 cm)	Not processed

Analytical methods

Samples for elemental analysis were oven dried at 60 ^{o}C, dry sieved to <2 mm grain size and homogenised.

Samples for Inductively Coupled Plasma Mass Spectrometry (ICPMS) analysis were digested in open digestion tubes using concentrated nitric + perchloric acid at 200^{o}C for 4 hours. An Agilent 7700 ICPMS was used to analyse solutions for Mg, Al, P, S, Ca, V, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Mo, Cd, Pb, Rare Earth Elements (La-Lu) and Pb isotope ratios (^{208}Pb/^{206}Pb and ^{207}Pb/^{206}Pb). Analysis of certified reference materials, blank samples and duplicate samples were carried out for quality control.

Total Kjeldahl Nitrogen (TKN) analysis was carried out by flow injection analysis (FIA) following acid digestion. Total Organic Carbon (TOC) analysis was carried out with a LECO carbon analyser at the Environmental Analytical Laboratory (SCU, Lismore, NSW).

The RC1 and RC7 cores were submitted intact (in core sleeve) to the Environmental Radioactivity Measurement Centre at ANSTO for ^{210}Pb dating. The cores were extracted, split and scanned optically and radiographically (ITREX Scan). Following advice from ANSTO, core RC7 were deemed unsuitable for dating due to its heterogeneous texture. Eight 1 cm thick core slices from the deepest core (23 cm) from RC1 were digested and ^{210}Po (^{210}Pb progeny) and ^{226}Ra sources prepared and their activities then individually counted by alpha spectrometry and used to calculate excess ^{210}Pb. The Constant Initial Concentration (CIC) and Constant Rate of Supply (CRS) models were used to determine the sediment chronology.

Grain size analysis of core RC1 was carried out using a Malvern Mastersizer 2000 Laser Diffraction Spectrophotometer. Samples were heated with hydrogen peroxide prior to analysis.

3. Results and Discussion

Core descriptions

Cores RC1, RC2 and RC6 from the channel bed are composed mainly of dark organic-rich silt and clay reflecting predominantly anoxic conditions (Figures 5-7). In contrast, the floodplain core RC7 is composed of yellow-red oxidized clay-rich sediment.

Core RC1

Core RC2

Core RC6

Core RC7

Figure 5. Rapid Creek cores (Eijkelkamp cores for ICPMS analysis)

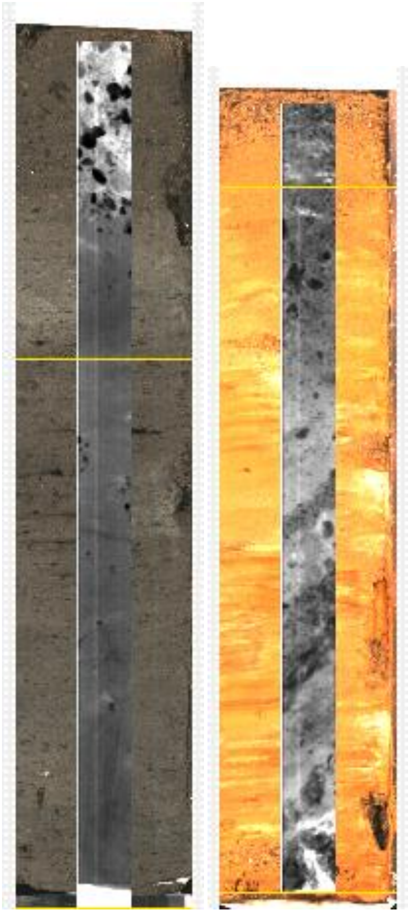

Figure 6. ITRAX images of Rapid Creek cores Rc1 and RC7 (AMS cores for ^{210}Pb dating). Optical (back) and radiographic images (front) of cores RC1 (left, 23 cm long) and RC7 (right, 21 cm long).

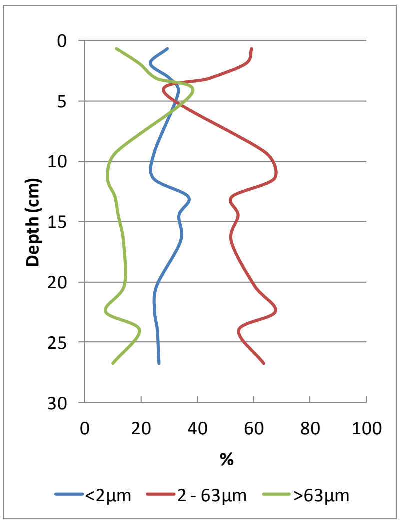

Figure 7. Grain size distribution in core RC1

Elemental and lead isotope profiles

Rapid Creek core RC1 had relatively high and uniform total organic carbon (TOC) and total sulfur (S) concentrations throughout (Figure 8) reflecting its anoxic state. In comparison to RC1, cores RC2, RC6 and RC7 had substantially lower TOC and S concentrations with RC7 having very low TOC and S (below detection limit) in the upper oxidized section. This pattern is consistent with a downstream gradient of diminishing accumulation of organic matter as the importance of marine tidal inflows increases. Total Kjeldahl nitrogen (TKN) levels were also high in the top section of core RC1 but decreased with depth, possibly as a result of denitrification upon burial. Aluminium concentrations were higher, and more variable, in RC1 and RC7 than in RC2 and RC6 which reflects higher clay mineral abundance in RC1 and RC7.

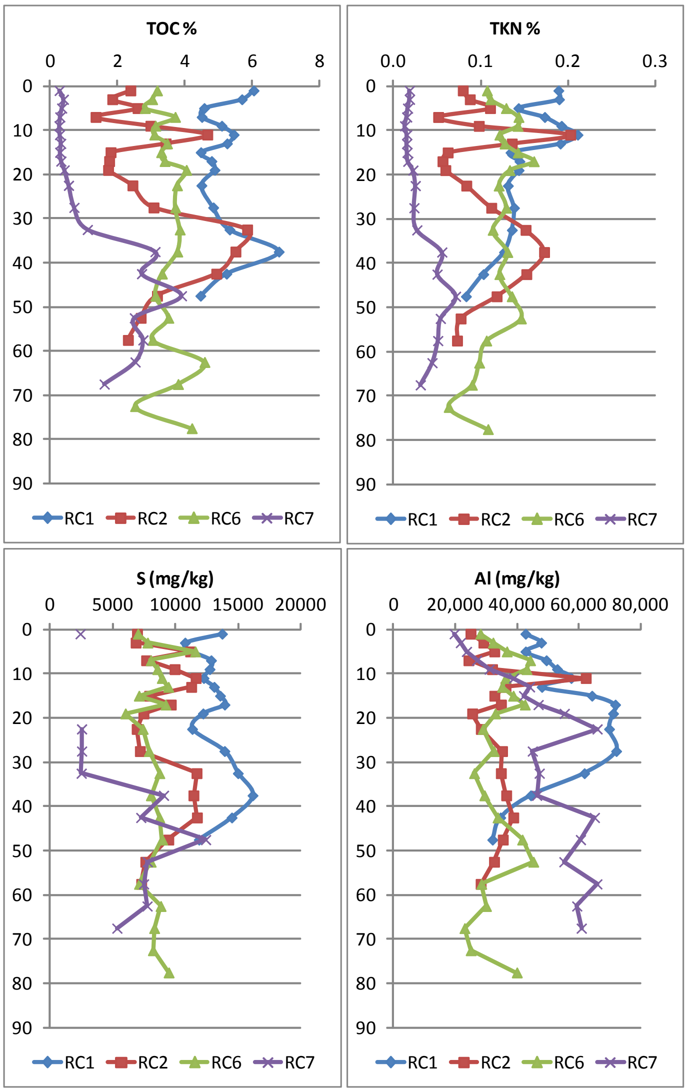

Figure 8. Total organic carbon (TOC), total Kjeldahl nitrrogen (TKN), total sulfur and aluminium concentrations in Rapid Creek cores (depth in cm).

Metal and metalloid concentration data are commonly used to directly assess sediment quality. However, the confounding factor of variable grain size on the distribution of metals has long been recognised (Loring and Rantala 1995, Birch 2003). The grainsize effect has been reduced by either separating or analysing a uniform sediment grain size (usually the <63 μm fraction), or the total sample data are normalized to a conservative element. Since grainsize separation of small core slices is impractical, normalization to the Al concentration was used as a proxy for fine material similar to a previous study of Darwin Harbour sediment (Munksgaard et al. 2012). The Al-normalised metal concentrations were calculated as the equivalent metal concentration at an Al concentration of 10,000 mg/kg (1% by weight) e.g.:

Zn/Al = [Zn] measured / [Al] measured x 10,000 mg/kg

Core RC1, which is dominated by clay and silt, has high concentrations of Al and S concentrations are also relatively high and indicative of anoxic conditions (Fig. 8, Appendix 1). It is notable that copper, zinc, cadmium and lead concentrations (Al-normalized concentrations) increase sharply and substantially above a depth of approximately 15 cm (mid-slice depth) compared to concentrations in the lower core (15 to 50 cm depth).

Throughout its length core RC2 have concentrations similar to the top 15 cm of core RC1 with respect to Al, S, Cu, Zn, Cd and Pb (Fig. 9, Appendix 1). In contrast to core RC1, the deeper levels of RC2 do not show relatively low metal concentrations. Core RC6 is characterized by high Ca, Mg and Mn concentrations compared to cores RC1 and RC2 (Appendix 1). This reflects the presence of shell derived material and increased marine influence in the downstream section of Rapid Creek. Aluminium-normalized Cu, Zn, Cd and Pb concentrations are elevated similar to the top of core RC1 and all of core RC2. However, below approximately 60 cm depth metal levels are lower and similar to those recorded at the base of core RC1. This suggests that 60 cm of sediment, or more in the case of RC2, accumulated at RC2 and RC6 within the same time interval that 15 cm of sediment accumulated at RC1. High spatial and temporal variability in the rate of sediment accumulation (including erosion events) is to be expected in an estuarine creek system subject to occasional high discharge events as well the influence of tidal flows.

The elevated levels of Cu, Zn, Cd and Pb found in cores RC1, RC2 and RC6 are all below the ANZECC (2000) interim sediment quality guidelines 'low' level (Table 3) and as such are unlikely to constitute a toxicity risk. The source of the elevated metals is most likely diffuse with contributions from airport runoff, urban construction, and traffic and legacy fuel lead additives.

Core RC7 from the Rapid Creek flood plain is compositionally distinct from the in-channel cores RC1, RC2 and RC6. From the surface to approximately 40 cm depth Fe, V, P, As, Se and Mo levels are substantially higher than those recorded in the other three cores (Fig. 8, Appendix 1). However, Fe concentrations decrease and Al and S concentrations are higher towards the bottom of the core (40 – 70 cm depth). Some metal and metalloid concentrations are higher (e.g. Ni, Cu, Pb) whilst others are lower (e.g. Mn, As, Mo) in the bottom section compared to the top section (Fig. 9). The compositional profile is suggestive of post-depositional mobility of elements due to the cycle of tidal inundation and drying on the floodplain. This cycle leads to a net upwards migration of pore waters and precipitation of metals and metalloids in the upper part of the profile due to evaporation. Iron, Mn, P, As and Mo, which are relatively soluble in their reduced forms or when present as oxy-anions, are especially susceptible to mobilisation.

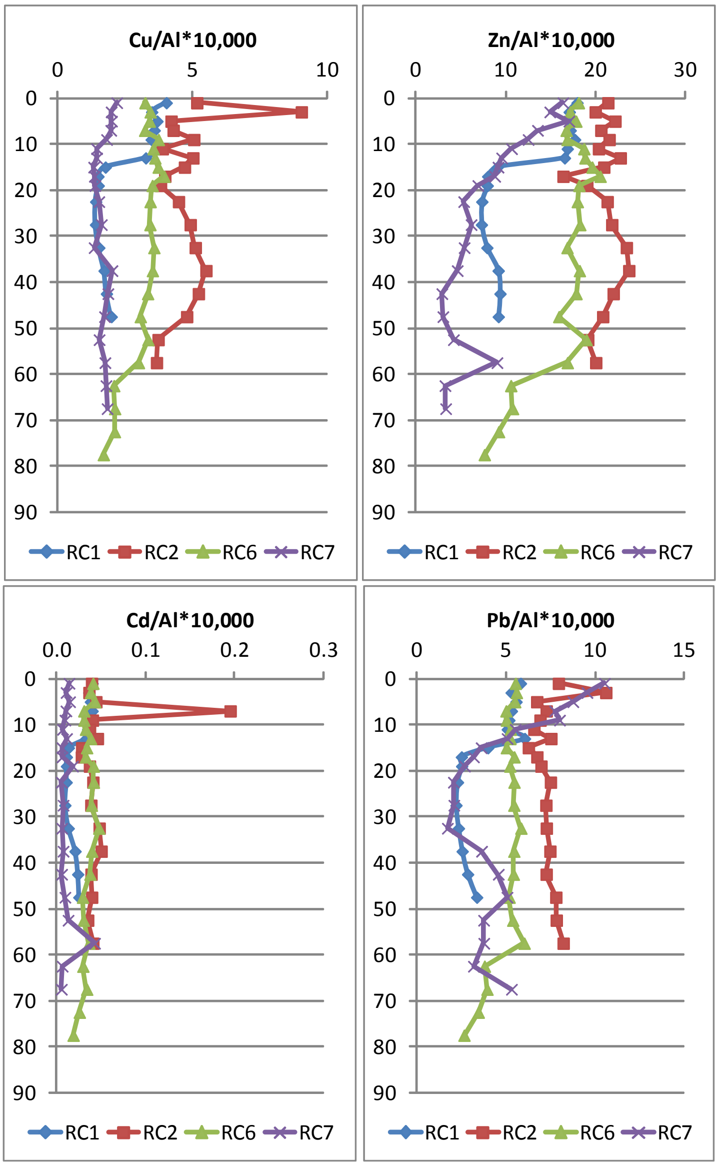

Figure 9. Aluminium-normalised copper, zinc, cadmium and lead concentrations (dry weight) in Rapid Creek cores (depth in cm).

The isotopic composition of Pb can be used to characterise the origin and movement of both natural and anthropogenic Pb in the north Australian environment and can often resolve ambiguities where pollution events and natural effects may not be easily distinguishable (Munksgaard et al. 2003a). Most major lead deposits and hence anthropogenic lead sources such as industrial use of lead and (previously) automotive fuel sources are relatively non-radiogenic leading to high $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ ratios relative to natural lead found in uncontaminated sediment and soil (present-day crustal Pb). As a result, anthropogenic Pb is often readily identified by its isotopic composition.

In Rapid Creek core RC1 (Figure 10) there is a marked increase in Pb isotope ratios ($^{208}Pb/^{206}Pb \approx$ 2.10-2.11 and $^{207}Pb/^{206}Pb \approx$ 0.86-0.87) above the 15 cm level coincident with the increase in Cu, Zn, Cd and Pb concentrations. Below the 15 cm level Pb isotope ratios are at background values similar to the average crustal Pb composition ($^{208}Pb/^{206}Pb \approx$ 2.04-2.05 and $^{207}Pb/^{206}Pb \approx$ 0.81-0.82). These background ratios are similar to previously published data for estuarine sediment from several North Australian catchments (Munksgaard et al. 2002) and contrasts strongly with Pb isotope ratios in sediment containing significant amounts of anthropogenic (mining-derived) lead (Munksgaard et al., 2003a). Cores RC2 and RC6 have elevated Pb isotope ratios throughout most of their length, again similar to their elevated metal concentrations. The elevated Pb isotope ratios are an unambiguous anthropogenic signal indicating that the sediments were deposited after the commencement of urban/industrial development commenced in the catchment. In contrast, the lead isotope ratios throughout core RC7 from the floodplain are at background levels and are indicative of little, or no, anthropogenic input to the floodplain sediment. It is noticeable that Pb concentrations, but not Pb isotope ratios, are substantially elevated in the top section of core RC7 compared to the bottom section. This confirms that the increased Pb concentration in the top of the core is mainly due to redistribution of natural Pb as discussed above.

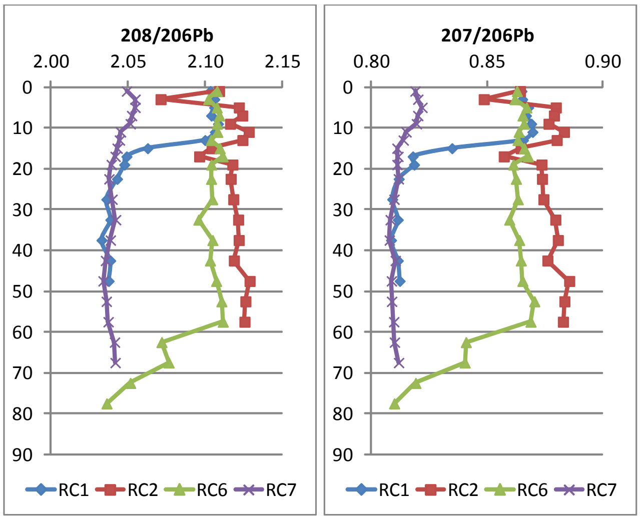

Figure 10. Lead isotope ratios in Rapid Creek cores (depth in cm).

Rare earth element (REE) characteristics of catchment source rocks can be preserved in downstream clay-rich sediments and used as provenance indicators (Munksgaard et al. 2003b). The REE profiles (i.e. light/medium and light/heavy REE relationships) are commonly used to characterize sediments rather than absolute REE concentrations. Furthermore, REE concentrations are usually normalized to accepted values for Post Achaean Australian Shale (PAAS). The full PASS normalised REE data set is provided in Appendix 1. In Figure 11 the ratios La/Gd and La/Yb represent the light/medium and light/heavy REE ratios, respectively. Throughout most of the sections of cores RC1, RC2 and RC7 (except extreme bottom sections of RC1 and RC7 and top sections of RC2 and RC7), La/Gd and La/Yb ratios are uniform suggesting a constant sediment source during deposition. In contrast, La/Gd and La/Yb ratios are significantly different ($p<0.001$) in core RC6 which is likely to reflect an increased marine sediment source at RC6 relative to RC1, RC2 and RC7.

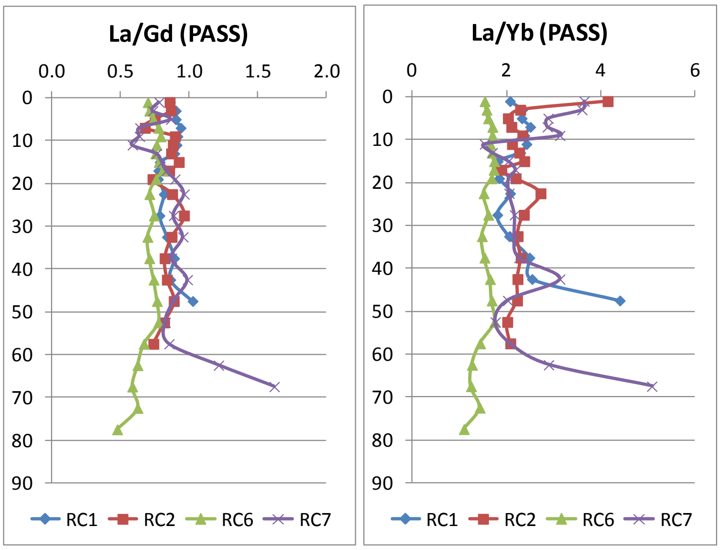

Figure 11. Rare earth element ratios (Lathanum/Gadolinium at left; Lanthanum/Yterbium at right) in Rapid Creek cores (depth in cm). Concentrations were normalized to Post Achaean Australian Shale (PAAS) values.

Baseline metal concentrations

Estimates of baseline (natural background) concentrations of metals and metalloids in sediment prior to the urban/industrial development of the Rapid Creek catchment are provided in Table 3 and is based on the compositions of the bottom sections (below 15 cm depth) of cores RC1 (in-channel sediment) and RC7 (floodplain sediment). It is notable that baseline concentrations of both Ni and As exceed the ANZECC (2000) interim sediment quality guideline 'low' (ISQG-Low) values. The Rapid Creek baseline data, in conjunction with other evidence of pre-development metal and metalloid levels in sediment, will assist in the development of local sediment quality guideline values for the Darwin Harbour region.

The highest Ni and As concentrations were recorded in the floodplain sediment affected by secondary alteration. Table 3 also provides ranges of metal and metalloid concentrations in sediment from two mangrove lined creeks in Darwin Harbour, Reichardt Creek and Mitchell Creek (Munksgaard et al. 2012). The lower range of concentrations in Reichardt and Mitchell Creek sediment are similar to the baseline concentrations obtained for Rapid Creek although some sites in Reichardt and Mitchell Creek had substantially higher concentrations of Zn, As and Pb.

The Rapid Creek sediment data is consistent with previous reports (e.g. Padovan 2003, Munksgaard et al. 2012) that metal concentrations in most areas of Darwin Harbour are at relatively low levels and, in general, are free of impacts from urban and industrial development. However, localized accumulation of anthropogenic metals, although at low levels, is measurable in a number of small creek systems such as Rapid Creek.

Table 3. Estimated baseline concentrations of metals and metalloids in Rapid Creek pre-development sediment from RC1 and RC7 core slices below 15 cm depth.

	RC1 (in stream)* mg/kg dry wt.	RC7 (floodplain)* mg/kg dry wt.	Darwin Harbour mangrove creeks** mg/kg dry wt.	ANZECC (2000) 'ISQG-Low' guideline
V	34-51	95-350	23-150	No guideline
Co	8-13	5-32	1-9	No guideline
Ni	18-29	14-49	3-18	21
Cu	6-11	6-12	4-23	65
Zn	29-57	18-59	12-190	200
As	12-17	20-73	4-117	20
Se	1.9-3.4	2.1-3.5	No data	No guideline
Cd	0.07-0.08	0.03-0.28	0.01-0.12	1.5
Pb	10-17	8-32	6-50	50
$^{207/206}Pb$	0.81-0.82	0.81	No data	No guideline
$^{208/206}Pb$	2.03-2.05	2.03-2.04	No data	No guideline

*: HNO3+HClO4 digest of whole sediment <2mm grain size (see method section). **: Reichardt Creek and Mitchell Creek intertidal flat (n=51, HNO3+HClO4 digest of <2mm grain size (Munksgaard et al. 2012).

^{210}Pb dating

The ^{210}Pb dating method is based on the U/Th radioactive decay series and can be used to date sediments up to 100-150 years old. The noble gas ^{222}Rn escapes from sediments to the atmosphere and here decays to ^{210}Pb. The particle-reactive ^{210}Pb attaches to aerosols and is subsequently deposited. However, most sediment contains U and ^{210}Pb is also produced in situ (this portion is termed 'supported' ^{210}Pb). The difference between total ^{210}Pb and 'supported' ^{210}Pb is the 'unsupported' ^{210}Pb content used for dating. Two different assumptions, (a) that the initial concentration of 'unsupported' ^{210}Pb in sediment is constant with time (CIC model), or (b) that the rate of 'unsupported' ^{210}Pb supply is constant but sedimentation rate varies with time (CRS model) are behind the two models used to compute sedimentation dates.

The calculated CIC and CRS chronologies are shown in Table 4 and the full data set is provided in Appendix 2. The CIC and CRS chronologies are not quite in agreement. An independent method, such as ^{137}Cs, pollen, diatom and/or trace metal records, could be used to determine which ^{210}Pb dating model provides a more reliable chronology. The chronology shown in Table 4 includes a depth correction for the compaction of the soft sediment at the top of the core that occurred during the coring process. The unusually high dry bulk densities measured at the top of the core (Appendix 2) and comparison to the adjacent (non-compacted) Eijkelkamp core supports the validity of the applied correction. However, the correction introduces some uncertainty in correlating the dating and the elemental/Pb isotope profiles.

The sharp increases in metal concentrations and Pb-isotope ratios at approximately 15 cm depth in core RC1 corresponds to ages of about 98 +/- 8 and 77 +/- 9 years, for the CIC and CRS models respectively. Applying the CRS model age means that the increase in metal concentrations and Pb-isotope ratios corresponds to the time of the Second World War and the development of the current Darwin Airport and surrounding areas which took place around 1938-1940. Correlation with the metal and Pb isotope ratios profiles therefore support the CRS model ages as well as the compaction correction applied to the dating core. Without this correction the 15 cm depth level of the RC1 dating core would be substantially older and predate the known time of development of the Rapid Creek catchment.

For the CRS model, all unsupported ^{210}Pb data between 0 and 9 cm depth were used to calculate mass accumulation rates varying between 0.069 and 0.149 g/cm^2/year (equivalent to a range of 1.6 to 2.9 mm/year corrected for core compaction).

Table 4. ^{210}Pb dating of Rapid Creek Core RC1 (based on ANSTO report, Appendix 2 and compaction correction of depth intervals).

Depth interval (cm) of analysed core slice	Mid depth (cm) of core slice corrected for compaction	Calculated CIC ages (Years prior to 2014)*	Calculated CRS ages (Years prior to 2014)*
0-1	0.9	6 +/- 6	3 +/- 2
2-3	4.4	29 +/- 6	18 +/- 4
4-5	8.0	51 +/- 6	38 +/- 6
6-7	11.6	75 +/- 7	57 +/- 8
8-9	15.1	98 +/- 8	77 +/- 9
10-11	17.5	No ages could be calculated	
12-13	19.5		
14-15	21.5		

*: CIC = Constant Initial Concentration model; CRS = Constant Rate of Supply model

4. Conclusions

Sediment cores were obtained from the estuarine section of Rapid Creek, three cores sampled in-channel sediment and one core was obtained from the adjacent floodplain. Elemental analysis, including metals and metalloids, revealed a sharp transition in one in-channel core from pre-development strata with low concentrations of Cu, Zn, Cd and Pb and low Pb isotope ratios to overlying strata with significantly elevated levels of the same metals and isotope ratios. This core was dated by the ^{210}Pb method and an age of the transition of 77 +/- 9 years was obtained corresponding to the WW2 development of Darwin Airport and surrounding areas within the catchment.

The lower sections of two cores provided pre-development metal and metalloid baseline concentrations. The elevated metal levels in the upper sections of cores most likely have a range of diffuse urban / industrial sources but were all below the ANZECC (2000) interim sediment quality guideline ‘low’ (ISQG-Low) values and are unlikely to constitute a toxicity risk. Despite the increasing development in the catchment, e.g. new suburbs, greater vehicle and plane traffic, and airport expansion, the sediment profiles since WW2 do not show increasing pollutant concentrations.

Acknowledgements

Aquatic Health Unit (Matt Majid; DLRM) provided fieldwork assistance and Dion Lambrinidis, Dylan Campbell and Francoise Foti (CDU) carried out the analytical laboratory work at ECMU. Atun Zawadzki and Jack Goralewski carried out the ^{210}Pb dating analyses at ANSTO. Simon Townsend (DLRM) provided helpful comments that improved the report.

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Appendix 1.

Chemical data

ICPMS analysis of elemental composition of Rapid Creek sediment cores August 2014

Whole sediment analysed HNO3+HClO4 acid extraction Concentrations in mg/kg dry weight

Sample Name	mid depth cm	Mg mg/kg	Al mg/kg	P mg/kg	S mg/kg	Ca mg/kg	V mg/kg	Mn mg/kg	Fe mg/kg	Co mg/kg	Ni mg/kg	Cu mg/kg	Zn mg/kg	Ga mg/kg	As mg/kg	Se mg/kg	Mo mg/kg	Cd mg/kg	Pb mg/kg	PbIR 207/206	PbIR 208/206
RC1																					
RC1 0-2	1.0	6,382	42,680	170	13,706	12,091	36.8	107	19,789	8.87	18.60	17.13	76.47	11.47	11.93	2.27	2.54	0.17	24.73	0.8648	2.1031
RC1 2-4	3.0	7,179	47,784	174	10,747	12,012	57.3	119	23,369	8.69	18.67	16.61	81.49	13.92	11.44	2.69	2.78	0.17	25.21	0.8651	2.1058
RC1 4-6	5.0	6,235	42,710	141	11,343	14,094	32.3	109	18,222	8.10	17.26	15.68	73.44	11.50	9.70	2.19	2.25	0.16	23.69	0.8677	2.1057
RC1 6-8	7.0	7,421	49,410	142	12,828	11,866	32.9	116	16,088	10.77	21.01	17.64	84.76	12.88	11.17	1.78	2.29	0.20	26.13	0.8668	2.1038
RC1 8-10	9.0	8,320	52,929	165	12,713	12,100	33.5	118	18,727	9.65	20.97	18.29	93.42	13.74	10.45	1.96	1.98	0.20	27.23	0.8690	2.1082
RC1 10-12	11.0	9,009	57,445	186	12,232	13,791	34.3	117	18,040	9.82	22.15	21.61	96.70	14.96	10.68	2.31	2.06	0.20	29.07	0.8696	2.1062
RC1 12-14	13.0	7,405	47,954	137	13,068	10,312	33.1	106	18,778	9.13	19.57	15.58	79.21	12.58	9.88	2.36	2.09	0.16	28.90	0.8655	2.0997
RC1 14-16	15.0	9,513	64,165	157	13,549	6,401	46.4	130	22,620	11.37	25.99	11.24	57.97	17.11	14.87	2.96	2.40	0.08	25.41	0.8347	2.0625
RC1 16-18	17.0	10,663	71,722	178	13,905	6,527	51.4	137	22,934	12.55	28.87	10.64	57.21	18.79	17.53	3.40	2.37	0.08	17.80	0.8178	2.0489
RC1 18-20	19.0	10,490	71,049	168	12,185	8,263	48.1	130	20,330	12.60	28.51	10.60	56.34	18.76	16.52	3.41	2.06	0.08	17.74	0.8184	2.0475
RC1 20-25	22.5	10,158	69,750	124	11,320	10,604	34.8	193	19,272	11.98	27.93	9.76	51.11	18.17	11.66	2.99	2.42	0.07	15.77	0.8118	2.0428
RC1 25-30	27.5	10,442	72,051	155	13,897	11,949	42.6	216	20,853	12.32	28.63	10.02	52.48	18.96	15.66	3.53	2.34	0.07	15.70	0.8090	2.0358
RC1 30-35	32.5	8,834	61,724	135	14,969	11,242	37.4	246	19,527	11.12	25.88	9.34	48.69	16.55	12.60	2.92	3.32	0.08	14.30	0.8114	2.0384
RC1 35-40	37.5	6,736	44,384	107	16,145	14,119	34.1	141	16,550	10.33	21.77	7.59	40.58	12.05	15.18	2.04	3.72	0.09	11.21	0.8085	2.0327
RC1 40-45	42.5	5,206	34,572	96	14,475	11,792	34.2	154	15,010	8.49	18.80	6.21	32.31	9.46	12.19	1.93	5.14	0.08	9.79	0.8114	2.0383
RC1 45-50	47.5	4,510	31,983	87	11,856	11,949	37.8	119	11,859	8.59	18.04	6.32	29.29	9.78	13.42	2.00	3.81	0.08	10.67	0.8122	2.0373
RC2																					
RC2 0-2	1.0	2,831	24,930	190	6,927	7,701	28.7	69	16,835	5.01	10.21	12.83	53.23	8.89	8.32	2.53	1.43	0.10	19.76	0.8642	2.1089
RC2 2-4	3.0	3,047	29,106	159	6,822	5,712	45.3	78	22,495	5.38	12.49	26.27	58.04	8.50	8.74	1.61	1.68	0.11	30.82	0.8485	2.0710
RC2 4-6	5.0	3,565	32,638	195	11,166	6,947	43.9	82	20,812	5.63	12.47	13.69	72.25	9.63	9.63	1.82	1.88	0.14	21.90	0.8796	2.1217
RC2 6-8	7.0	2,760	24,275	141	7,659	9,937	29.9	64	16,122	4.66	12.77	10.37	49.94	7.07	6.91	1.65	1.07	0.47	17.58	0.8788	2.1239
RC2 8-10	9.0	3,699	31,914	187	9,925	7,550	45.4	75	21,934	6.14	13.11	16.07	68.55	9.50	9.94	2.02	1.99	0.13	22.00	0.8765	2.1160
RC2 10-12	11.0	8,153	62,210	276	11,609	13,078	49.9	113	22,984	9.18	22.48	24.07	126.31	16.64	12.92	2.97	2.32	0.23	40.76	0.8831	2.1282
RC2 12-14	13.0	4,873	36,259	202	11,248	10,693	41.3	96	20,190	6.56	14.16	18.14	82.41	10.25	9.64	1.87	2.04	0.17	27.21	0.8800	2.1241
RC2 14-16	15.0	3,401	32,658	197	7,899	10,369	70.0	86	31,050	5.97	21.53	15.32	68.24	10.17	10.60	2.07	2.41	0.09	20.39	0.8645	2.1041
RC2 16-18	17.0	3,187	34,771	216	9,621	6,630	182	89	79,986	6.71	17.72	13.77	56.87	10.14	16.65	1.80	2.80	0.10	23.36	0.8572	2.0960
RC2 18-20	19.0	2,891	25,485	138	7,437	9,387	41.0	68	22,281	4.64	10.22	9.69	48.45	7.72	7.51	1.65	1.37	0.09	17.70	0.8735	2.1175
RC2 20-25	22.5	3,387	28,265	146	6,903	7,385	32.4	87	15,633	5.79	11.61	12.63	60.11	8.47	7.65	1.85	1.69	0.11	21.14	0.8737	2.1164
RC2 25-30	27.5	4,222	35,145	166	7,155	9,196	45.7	96	23,729	6.12	14.06	17.23	76.54	10.45	7.41	1.94	1.91	0.13	25.40	0.8743	2.1181
RC2 30-35	32.5	4,687	34,749	182	11,677	11,156	46.2	98	20,301	6.54	14.26	17.69	81.33	9.95	10.88	2.04	2.65	0.17	25.20	0.8794	2.1212
RC2 35-40	37.5	5,317	36,493	221	11,428	11,664	41.1	97	18,002	6.90	15.30	20.03	86.40	10.54	9.66	1.97	2.56	0.18	27.19	0.8805	2.1216
RC2 40-45	42.5	5,490	38,764	257	11,706	10,999	67.5	104	26,058	7.31	16.35	20.19	85.04	11.66	11.83	2.42	3.00	0.15	28.06	0.8760	2.1185
RC2 45-50	47.5	4,698	35,383	146	9,424	11,928	40.5	88	19,437	6.62	14.63	16.88	73.48	10.54	8.43	1.80	1.96	0.14	27.54	0.8854	2.1287
RC2 50-55	52.5	3,790	32,538	185	7,592	9,469	82.6	93	29,862	5.98	13.25	12.08	62.18	10.23	11.36	1.57	2.71	0.11	25.40	0.8833	2.1260
RC2 55-60	57.5	3,405	28,225	121	7,263	9,875	40.9	90	21,552	5.66	11.57	10.31	56.44	8.67	7.92	1.99	1.84	0.11	23.12	0.8827	2.1254

Sample Name	mid depth cm	Mg mg/kg	Al mg/kg	P mg/kg	S mg/kg	Ca mg/kg	V mg/kg	Mn mg/kg	Fe mg/kg	Co mg/kg	Ni mg/kg	Cu mg/kg	Zn mg/kg	Ga mg/kg	As mg/kg	Se mg/kg	Mo mg/kg	Cd mg/kg	Pb mg/kg	PbIR 207/206	PbIR 208/206
RC6																					
RC6 0-2	1.0	11,909	28,106	458	6,995	161,810	35.4	284	21,044	5.17	11.39	9.07	50.79	8.41	13.66	2.48	1.22	0.11	15.49	0.8628	2.1075
RC6 2-4	3.0	13,169	32,191	565	7,761	172,076	44.8	310	25,509	5.74	12.88	11.01	55.16	9.43	16.17	2.53	1.38	0.12	17.93	0.8618	2.1019
RC6 4-6	5.0	13,138	36,652	539	11,567	155,259	48.4	293	26,933	6.23	14.23	12.41	65.20	10.30	16.31	2.61	1.57	0.16	20.06	0.8669	2.1074
RC6 6-8	7.0	12,447	44,201	383	8,026	123,679	39.8	254	23,520	7.04	16.62	14.21	73.84	12.36	11.67	2.92	1.37	0.13	22.02	0.8653	2.1091
RC6 8-10	9.0	12,479	43,059	359	8,548	125,359	40.3	266	21,146	6.98	16.19	16.03	72.37	11.76	13.39	3.07	1.56	0.13	21.56	0.8658	2.1075
RC6 10-12	11.0	12,760	36,275	421	8,909	149,489	40.5	288	20,891	6.09	13.82	12.81	67.75	10.19	13.30	3.01	1.32	0.12	18.98	0.8636	2.1078
RC6 12-14	13.0	12,729	35,141	419	9,421	153,118	38.8	287	20,369	6.17	13.71	12.63	66.06	9.86	13.47	2.63	1.37	0.13	18.31	0.8631	2.1036
RC6 14-16	15.0	12,406	38,725	347	7,076	136,443	34.6	276	17,025	6.42	14.91	14.40	75.83	10.79	11.75	2.58	1.08	0.13	19.39	0.8659	2.1093
RC6 16-18	17.0	12,208	42,502	392	9,199	121,043	40.4	258	20,093	6.88	16.39	16.73	87.08	11.66	13.44	2.72	1.63	0.14	23.10	0.8677	2.1112
RC6 18-20	19.0	11,958	32,924	285	5,995	143,701	27.9	263	15,072	5.84	13.04	11.50	59.68	9.36	9.70	2.43	1.04	0.14	17.11	0.8612	2.1038
RC6 20-25	22.5	11,948	28,920	351	7,381	161,799	28.8	288	15,144	5.38	11.73	9.88	51.91	8.39	11.80	2.56	1.17	0.12	15.72	0.8624	2.1037
RC6 25-30	27.5	12,510	32,458	328	7,873	154,982	30.8	275	15,686	5.95	12.93	11.07	59.15	9.21	11.88	3.02	1.34	0.13	17.61	0.8632	2.1044
RC6 30-35	32.5	11,875	26,090	348	8,711	166,556	28.7	290	14,827	5.20	10.85	9.28	43.84	7.71	12.59	2.73	1.31	0.12	15.19	0.8595	2.0955
RC6 35-40	37.5	11,844	29,421	354	8,036	156,551	30.6	279	14,888	5.61	12.14	10.30	53.49	8.41	11.90	2.54	1.33	0.12	15.96	0.8638	2.1046
RC6 40-45	42.5	12,781	33,704	391	8,703	157,924	34.8	275	18,406	6.11	13.59	11.21	60.01	9.56	12.65	2.47	1.24	0.13	18.19	0.8645	2.1030
RC6 45-50	47.5	13,531	41,641	436	8,939	140,170	43.8	275	23,437	7.07	16.32	12.71	66.15	11.72	13.15	3.19	1.09	0.12	21.49	0.8652	2.1070
RC6 50-55	52.5	13,415	45,240	411	8,021	137,222	36.3	268	21,504	7.09	16.67	15.09	85.66	11.95	12.05	2.73	1.11	0.14	24.26	0.8703	2.1104
RC6 55-60	57.5	12,147	28,417	434	7,089	180,219	34.1	305	17,321	5.18	11.14	8.48	47.84	8.04	12.43	2.37	1.17	0.10	17.06	0.8687	2.1113
RC6 60-65	62.5	11,602	29,940	308	8,810	147,920	35.8	325	15,377	5.98	12.41	6.19	31.57	8.49	14.12	2.69	1.87	0.09	11.29	0.8408	2.0716
RC6 65-70	67.5	10,995	22,982	289	8,295	148,228	27.7	361	10,847	4.87	9.76	4.83	24.69	6.61	11.74	2.16	2.48	0.08	9.00	0.8403	2.0762
RC6 70-75	72.5	9,512	25,002	230	8,198	124,466	52.7	320	15,019	13.99	13.47	5.24	22.98	7.53	14.14	2.82	2.18	0.06	8.57	0.8190	2.0513
RC6 75-80	77.5	10,656	39,913	240	9,451	96,137	52.8	288	16,859	7.84	17.69	6.71	30.35	11.41	12.73	3.71	2.19	0.07	10.48	0.8098	2.0360
RC7																					
RC7 0-2	1.0	6,504	19,686	724	2,395	1,924	409	81	122,131	7.00	17.19	4.29	32.16	10.33	64.70	4.39	29.17	0.03	20.70	0.8188	2.0489
RC7 2-4	3.0	5,653	21,674	716	<	1,464	345	92	117,612	7.23	16.94	4.27	32.27	11.03	59.17	3.44	27.41	0.02	20.65	0.8200	2.0544
RC7 4-6	5.0	5,315	23,630	668	<	978	451	112	133,692	8.81	19.49	4.69	40.18	11.13	74.92	3.12	37.90	0.03	20.65	0.8218	2.0544
RC7 6-8	7.0	5,043	26,915	729	<	933	376	128	119,188	8.77	19.74	5.27	36.39	12.24	61.06	4.70	28.16	0.03	20.76	0.8200	2.0522
RC7 8-10	9.0	4,792	30,956	812	<	1,075	363	138	120,134	9.64	21.83	5.58	38.61	13.85	64.94	6.25	28.96	0.03	24.72	0.8194	2.0513
RC7 10-12	11.0	5,403	38,876	568	<	872	287	260	100,416	18.41	24.28	5.56	41.33	14.14	53.00	4.90	25.32	0.03	21.40	0.8149	2.0451
RC7 12-14	13.0	5,463	44,030	505	<	860	252	149	101,772	11.66	22.57	6.30	41.96	14.52	49.61	4.41	23.30	0.05	22.22	0.8137	2.0444
RC7 14-16	15.0	4,947	42,117	493	<	794	241	107	100,469	7.97	20.74	5.57	38.44	13.58	49.46	3.40	24.56	0.02	15.13	0.8110	2.0428
RC7 16-18	17.0	5,009	46,828	491	<	824	236	109	107,522	9.48	20.57	6.31	41.01	14.58	56.19	3.86	27.55	0.03	14.79	0.8114	2.0415
RC7 18-20	19.0	5,679	55,259	420	<	822	204	88	94,268	9.16	20.46	7.57	38.03	15.51	54.41	2.64	26.98	0.10	14.69	0.8110	2.0390
RC7 20-25	22.5	6,734	65,888	338	2,508	922	222	60	106,863	7.39	19.13	9.98	34.98	18.02	73.19	2.84	33.15	0.03	13.39	0.8116	2.0375
RC7 25-30	27.5	4,558	44,955	354	2,510	691	228	48	139,712	5.21	14.69	7.23	27.56	14.16	58.33	2.67	24.78	0.03	9.25	0.8097	2.0395
RC7 30-35	32.5	5,013	47,177	325	2,481	760	231	45	129,580	4.56	13.93	6.32	25.28	14.17	54.53	2.27	23.13	0.03	7.99	0.8081	2.0418
RC7 35-40	37.5	5,481	46,335	247	9,043	970	351	38	81,150	13.23	22.22	9.28	21.27	14.91	41.75	3.17	16.19	0.03	16.74	0.8077	2.0384
RC7 40-45	42.5	4,754	65,013	142	7,230	1,098	109	34	37,050	20.11	37.36	12.03	18.70	21.02	22.31	2.85	7.80	0.04	29.59	0.8103	2.0353
RC7 45-50	47.5	5,348	60,512	77	12,398	1,109	94.5	34	28,710	31.64	48.55	10.45	18.10	17.29	20.94	2.83	7.57	0.06	30.50	0.8086	2.0337
RC7 50-55	52.5	5,615	55,158	115	7,746	1,219	126	41	41,167	17.61	37.97	8.41	22.97	15.31	22.47	2.41	7.55	0.07	20.56	0.8087	2.0358
RC7 55-60	57.5	3,905	65,810	161	7,454	967	232	38	52,898	11.83	32.23	11.45	59.30	21.89	33.96	3.53	10.61	0.28	24.58	0.8096	2.0370
RC7 60-65	62.5	3,418	59,311	125	7,732	845	221	36	50,371	8.01	26.46	10.56	19.14	20.93	30.80	2.18	8.51	0.04	18.72	0.8099	2.0411
RC7 65-70	67.5	2,970	60,770	291	5,321	868	324	47	75,935	8.18	27.76	11.07	20.06	22.89	26.22	3.00	6.71	0.03	32.14	0.8117	2.0415
Reporting Limit		**4**	**4**	**30**	**2,000**	**20**	**0.04**	**0.02**	**3**	**0.005**	**0.1**	**0.04**	**0.2**	**0.003**	**0.04**	**0.3**	**0.05**	**0.02**	**0.02**		

Quality Control	Mg mg/kg	Al mg/kg	P mg/kg	S mg/kg	Ca mg/kg	V mg/kg	Mn mg/kg	Fe mg/kg	Co mg/kg	Ni mg/kg	Cu mg/kg	Zn mg/kg	Ga mg/kg	As mg/kg	Se mg/kg	Mo mg/kg	Cd mg/kg	Pb mg/kg
Digest blank average	<	<	<	<	<	<	<	<	<	<	0.043	0.78	<	<	<	<	<	0.042
MESS-3 average	16,958	77,879	1,149	<	14,485	184	308	41,593	12.1	44.7	31.5	149	22.8	22.1	4.04	2.10	0.218	20.0
MESS-3 certified	16,000	85,900	1200*	1900*	14,700	243	324	43,400	14.4	46.9	33.9	159	nc	21.1	0.72	2.78	0.240	21.1

<: less than detection limit; nc: not certified; na: not analysed, *: information value only

Note: Concentration data is precise to 2-3 digits depending on element

LECO analysis of total organic carbon concentrations in Rapid Creek sediment cores August 2014
FIA analysis of total Kjeldahl nitrogen concentrations in Rapid Creek sediment cores August 2014
Whole sediment analysed   Concentrations in % dry weight

Sample Name	mid depth cm	TOC %	TKN %
RC1			
RC1 0-2	1.0	6.04	0.189
RC1 2-4	3.0	5.69	0.190
RC1 4-6	5.0	4.57	0.143
RC1 6-8	7.0	4.50	0.173
RC1 8-10	9.0	5.09	0.192
RC1 10-12	11.0	5.45	0.211
RC1 12-14	13.0	5.25	0.191
RC1 14-16	15.0	4.47	0.134
RC1 16-18	17.0	4.79	0.144
RC1 18-20	19.0	4.88	0.143
RC1 20-25	22.5	4.49	0.131
RC1 25-30	27.5	4.84	0.138
RC1 30-35	32.5	5.33	0.136
RC1 35-40	37.5	6.79	0.127
RC1 40-45	42.5	5.23	0.103
RC1 45-50	47.5	4.46	0.083
RC2			
RC2 0-2	1.0	2.38	0.079
RC2 2-4	3.0	1.85	0.087
RC2 4-6	5.0	2.60	0.111
RC2 6-8	7.0	1.35	0.051
RC2 8-10	9.0	2.98	0.098
RC2 10-12	11.0	4.67	0.202
RC2 12-14	13.0	3.43	0.136
RC2 14-16	15.0	1.79	0.062
RC2 16-18	17.0	1.75	0.056
RC2 18-20	19.0	1.72	0.059
RC2 20-25	22.5	2.44	0.083
RC2 25-30	27.5	3.07	0.112
RC2 30-35	32.5	5.85	0.151
RC2 35-40	37.5	5.50	0.173
RC2 40-45	42.5	4.94	0.152
RC2 45-50	47.5	3.17	0.118
RC2 50-55	52.5	2.69	0.077
RC2 55-60	57.5	2.31	0.073
RC6			
RC6 0-2	1.0	3.17	0.107
RC6 2-4	3.0	3.03	0.111
RC6 4-6	5.0	2.81	0.129
RC6 6-8	7.0	3.71	0.143
RC6 8-10	9.0	3.12	0.142
RC6 10-12	11.0	3.10	0.121
RC6 12-14	13.0	3.47	0.127
RC6 14-16	15.0	3.30	0.142
RC6 16-18	17.0	3.40	0.161
RC6 18-20	19.0	4.04	0.133
RC6 20-25	22.5	3.77	0.121
RC6 25-30	27.5	3.72	0.129
RC6 30-35	32.5	3.85	0.114
RC6 35-40	37.5	3.78	0.130
RC6 40-45	42.5	3.32	0.121
RC6 45-50	47.5	3.12	0.136
RC6 50-55	52.5	3.51	0.146
RC6 55-60	57.5	3.04	0.106
RC6 60-65	62.5	4.58	0.098
RC6 65-70	67.5	3.80	0.090
RC6 70-75	72.5	2.52	0.063
RC6 75-80	77.5	4.21	0.108
RC7			
RC7 0-2	1.0	0.27	0.018
RC7 2-4	3.0	0.39	0.018
RC7 4-6	5.0	0.34	0.016
RC7 6-8	7.0	0.29	0.015
RC7 8-10	9.0	0.26	0.013
RC7 10-12	11.0	0.28	0.015
RC7 12-14	13.0	0.31	0.015
RC7 14-16	15.0	0.29	0.016
RC7 16-18	17.0	0.32	0.017
RC7 18-20	19.0	0.42	0.022
RC7 20-25	22.5	0.54	0.025
RC7 25-30	27.5	0.71	0.024
RC7 30-35	32.5	1.10	0.027
RC7 35-40	37.5	3.11	0.055
RC7 40-45	42.5	2.72	0.050
RC7 45-50	47.5	3.90	0.071
RC7 50-55	52.5	2.50	0.054
RC7 55-60	57.5	2.76	0.051
RC7 60-65	62.5	2.52	0.044
RC7 65-70	67.5	1.61	0.031
Reporting Limit			0.001
Quality Control			
Digest blank average			
Loam A average			0.099
Loam A certified			0.100

<: less than detection limit; nc: not certified; na: not analysed, *: information value only

ICPMS analysis of rare earth element composition of Rapid Creek sediment cores August 2014

Whole sediment analysed HNO3+HClO4 acid extraction PAAS normalised ratios

Sample Name	mid depth cm	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	La/Gd	La/Yb	Eu/Eu*
RC1																		
RC1 0-2	1.0	0.620	0.480	0.606	0.562	0.689	0.721	0.721	0.568	0.500	0.418	0.391	0.362	0.299	0.265	0.860	2.07	1.02
RC1 2-4	3.0	0.822	0.697	0.817	0.761	0.866	0.951	0.911	0.684	0.583	0.483	0.456	0.422	0.353	0.307	0.903	2.33	1.07
RC1 4-6	5.0	0.628	0.464	0.607	0.565	0.642	0.701	0.695	0.537	0.465	0.387	0.356	0.325	0.271	0.243	0.903	2.32	1.05
RC1 6-8	7.0	0.707	0.447	0.674	0.616	0.698	0.756	0.753	0.584	0.507	0.422	0.384	0.353	0.282	0.245	0.938	2.50	1.04
RC1 8-10	9.0	0.725	0.493	0.703	0.647	0.734	0.790	0.793	0.610	0.530	0.441	0.410	0.373	0.305	0.266	0.915	2.38	1.04
RC1 10-12	11.0	0.799	0.555	0.753	0.692	0.792	0.866	0.880	0.683	0.580	0.475	0.444	0.398	0.330	0.295	0.908	2.42	1.04
RC1 12-14	13.0	0.669	0.465	0.642	0.593	0.762	0.750	0.750	0.585	0.509	0.419	0.387	0.358	0.292	0.255	0.892	2.29	0.99
RC1 14-16	15.0	0.878	0.733	0.889	0.837	0.995	1.102	1.118	0.881	0.780	0.659	0.615	0.574	0.485	0.432	0.785	1.81	1.04
RC1 16-18	17.0	0.962	0.819	0.980	0.923	1.108	1.223	1.242	0.976	0.858	0.726	0.684	0.634	0.538	0.482	0.775	1.79	1.04
RC1 18-20	19.0	0.983	0.828	1.017	0.960	1.144	1.273	1.272	0.992	0.878	0.717	0.682	0.636	0.534	0.487	0.773	1.84	1.06
RC1 20-25	22.5	0.921	0.694	0.937	0.881	1.031	1.137	1.130	0.892	0.776	0.637	0.597	0.547	0.444	0.396	0.815	2.07	1.05
RC1 25-30	27.5	0.958	0.765	0.972	0.917	1.096	1.211	1.222	0.964	0.867	0.713	0.696	0.632	0.531	0.472	0.784	1.80	1.05
RC1 30-35	32.5	0.844	0.586	0.842	0.791	0.922	1.015	1.007	0.795	0.705	0.574	0.544	0.509	0.411	0.367	0.838	2.05	1.05
RC1 35-40	37.5	0.687	0.358	0.671	0.629	0.714	0.790	0.772	0.596	0.522	0.422	0.389	0.355	0.277	0.244	0.890	2.48	1.06
RC1 40-45	42.5	0.571	0.317	0.558	0.523	0.602	0.667	0.662	0.506	0.431	0.349	0.321	0.292	0.225	0.195	0.863	2.54	1.06
RC1 45-50	47.5	0.758	0.340	0.737	0.671	0.723	0.793	0.740	0.512	0.409	0.306	0.272	0.236	0.172	0.145	1.025	4.40	1.08
RC2																		
RC2 0-2	1.0	0.910	0.785	1.113	1.181	1.303	1.356	1.061	0.668	0.483	0.336	0.302	0.273	0.219	0.193	0.858	4.15	1.15
RC2 2-4	3.0	0.495	0.433	0.464	0.428	0.511	0.578	0.571	0.421	0.352	0.281	0.269	0.257	0.216	0.188	0.867	2.29	1.07
RC2 4-6	5.0	0.477	0.452	0.494	0.472	0.583	0.674	0.636	0.466	0.389	0.307	0.295	0.288	0.235	0.206	0.749	2.03	1.11
RC2 6-8	7.0	0.385	0.351	0.380	0.354	0.434	0.535	0.569	0.427	0.346	0.259	0.238	0.230	0.183	0.162	0.676	2.10	1.08
RC2 8-10	9.0	0.607	0.545	0.579	0.535	0.609	0.685	0.677	0.502	0.417	0.334	0.321	0.313	0.260	0.229	0.896	2.34	1.07
RC2 10-12	11.0	0.910	0.791	0.847	0.783	0.922	1.042	1.033	0.794	0.693	0.563	0.541	0.508	0.430	0.391	0.881	2.12	1.07
RC2 12-14	13.0	0.620	0.522	0.577	0.528	0.614	0.691	0.714	0.542	0.456	0.367	0.347	0.338	0.273	0.250	0.868	2.27	1.04
RC2 14-16	15.0	0.644	0.524	0.573	0.515	0.612	0.711	0.697	0.504	0.426	0.335	0.320	0.338	0.271	0.239	0.924	2.37	1.09
RC2 16-18	17.0	0.549	0.497	0.486	0.444	0.523	0.614	0.643	0.501	0.447	0.362	0.351	0.366	0.291	0.256	0.854	1.89	1.06
RC2 18-20	19.0	0.460	0.422	0.452	0.422	0.526	0.625	0.627	0.447	0.367	0.278	0.262	0.277	0.210	0.189	0.733	2.19	1.09
RC2 20-25	22.5	0.578	0.472	0.531	0.493	0.591	0.687	0.661	0.457	0.374	0.289	0.272	0.278	0.213	0.187	0.876	2.72	1.10
RC2 25-30	27.5	0.642	0.532	0.560	0.504	0.578	0.659	0.667	0.499	0.438	0.349	0.333	0.346	0.271	0.243	0.962	2.37	1.06
RC2 30-35	32.5	0.602	0.520	0.552	0.512	0.602	0.685	0.691	0.519	0.446	0.361	0.343	0.344	0.269	0.236	0.872	2.23	1.06
RC2 35-40	37.5	0.623	0.499	0.584	0.543	0.653	0.762	0.759	0.571	0.497	0.393	0.367	0.361	0.271	0.242	0.822	2.30	1.08
RC2 40-45	42.5	0.717	0.620	0.673	0.632	0.748	0.865	0.856	0.627	0.537	0.420	0.403	0.406	0.321	0.286	0.838	2.23	1.08
RC2 45-50	47.5	0.585	0.488	0.545	0.502	0.577	0.666	0.659	0.495	0.433	0.350	0.337	0.349	0.263	0.231	0.888	2.22	1.08
RC2 50-55	52.5	0.578	0.526	0.548	0.515	0.614	0.718	0.708	0.525	0.466	0.374	0.360	0.368	0.287	0.250	0.817	2.01	1.09
RC2 55-60	57.5	0.467	0.439	0.478	0.450	0.538	0.626	0.632	0.471	0.389	0.301	0.285	0.295	0.225	0.199	0.739	2.08	1.07

Sample Name	mid depth cm	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	La/Gd	La/Yb	Eu/Eu*
RC6																		
RC6 0-2	1.0	0.651	0.647	0.664	0.638	0.794	0.901	0.932	0.722	0.658	0.544	0.520	0.517	0.424	0.383	0.698	1.53	1.05
RC6 2-4	3.0	0.717	0.709	0.727	0.695	0.857	0.969	1.011	0.793	0.713	0.584	0.563	0.550	0.455	0.414	0.709	1.57	1.04
RC6 4-6	5.0	0.725	0.707	0.720	0.689	0.843	0.959	0.983	0.763	0.702	0.581	0.554	0.554	0.451	0.422	0.737	1.61	1.05
RC6 6-8	7.0	0.788	0.755	0.775	0.732	0.874	0.991	1.015	0.779	0.714	0.590	0.568	0.567	0.464	0.422	0.776	1.70	1.05
RC6 8-10	9.0	0.751	0.722	0.733	0.695	0.828	0.925	0.948	0.740	0.676	0.557	0.540	0.551	0.443	0.399	0.792	1.70	1.04
RC6 10-12	11.0	0.688	0.678	0.675	0.642	0.774	0.885	0.904	0.694	0.639	0.533	0.511	0.523	0.417	0.373	0.761	1.65	1.06
RC6 12-14	13.0	0.686	0.667	0.679	0.649	0.786	0.894	0.909	0.697	0.633	0.527	0.500	0.511	0.407	0.368	0.754	1.69	1.06
RC6 14-16	15.0	0.717	0.689	0.705	0.667	0.799	0.903	0.921	0.706	0.642	0.535	0.515	0.530	0.414	0.369	0.779	1.73	1.05
RC6 16-18	17.0	0.757	0.714	0.730	0.686	0.816	0.926	0.941	0.722	0.671	0.561	0.541	0.555	0.438	0.398	0.804	1.73	1.06
RC6 18-20	19.0	0.678	0.647	0.669	0.639	0.778	0.883	0.895	0.693	0.631	0.527	0.502	0.515	0.403	0.366	0.758	1.68	1.06
RC6 20-25	22.5	0.629	0.607	0.636	0.614	0.753	0.865	0.886	0.696	0.646	0.559	0.519	0.526	0.416	0.368	0.710	1.51	1.06
RC6 25-30	27.5	0.688	0.661	0.685	0.659	0.800	0.896	0.926	0.728	0.674	0.553	0.536	0.541	0.428	0.384	0.743	1.61	1.04
RC6 30-35	32.5	0.619	0.609	0.637	0.616	0.763	0.876	0.890	0.706	0.657	0.546	0.530	0.542	0.420	0.373	0.696	1.47	1.06
RC6 35-40	37.5	0.639	0.619	0.649	0.623	0.769	0.879	0.901	0.705	0.649	0.536	0.526	0.525	0.417	0.373	0.709	1.53	1.06
RC6 40-45	42.5	0.698	0.670	0.688	0.660	0.806	0.930	0.943	0.726	0.661	0.549	0.523	0.536	0.424	0.378	0.741	1.65	1.07
RC6 45-50	47.5	0.761	0.734	0.739	0.700	0.854	0.980	0.995	0.775	0.704	0.583	0.551	0.570	0.452	0.404	0.765	1.68	1.06
RC6 50-55	52.5	0.758	0.723	0.742	0.705	0.856	0.979	0.979	0.741	0.676	0.559	0.540	0.549	0.435	0.389	0.775	1.74	1.07
RC6 55-60	57.5	0.561	0.600	0.600	0.581	0.708	0.819	0.838	0.667	0.600	0.511	0.481	0.511	0.390	0.346	0.669	1.44	1.06
RC6 60-65	62.5	0.542	0.560	0.604	0.588	0.728	0.851	0.869	0.719	0.651	0.566	0.526	0.561	0.429	0.371	0.623	1.26	1.07
RC6 65-70	67.5	0.478	0.495	0.544	0.534	0.680	0.812	0.817	0.665	0.590	0.517	0.477	0.510	0.384	0.337	0.585	1.24	1.09
RC6 70-75	72.5	0.505	0.513	0.565	0.548	0.710	0.828	0.810	0.634	0.562	0.481	0.447	0.476	0.354	0.304	0.623	1.43	1.09
RC6 75-80	77.5	0.685	0.602	0.701	0.697	1.022	1.355	1.443	1.211	1.091	0.933	0.844	0.823	0.627	0.551	0.474	1.09	1.12
RC7																		
RC7 0-2	1.0	1.055	0.831	0.947	0.898	1.150	1.396	1.352	0.951	0.640	0.431	0.359	0.397	0.289	0.245	0.780	3.65	1.12
RC7 2-4	3.0	1.076	0.973	1.140	1.152	1.483	1.698	1.464	0.971	0.655	0.447	0.381	0.406	0.299	0.260	0.735	3.60	1.15
RC7 4-6	5.0	0.983	0.854	0.915	0.842	1.008	1.174	1.136	0.848	0.639	0.470	0.416	0.451	0.341	0.300	0.865	2.88	1.10
RC7 6-8	7.0	1.119	1.049	1.163	1.175	1.560	1.879	1.749	1.233	0.852	0.585	0.505	0.520	0.391	0.351	0.640	2.86	1.14
RC7 8-10	9.0	1.424	1.358	1.506	1.527	2.056	2.455	2.235	1.519	1.027	0.707	0.606	0.598	0.455	0.415	0.637	3.13	1.15
RC7 10-12	11.0	0.975	1.213	1.097	1.067	1.394	1.659	1.665	1.316	1.073	0.853	0.785	0.809	0.637	0.586	0.586	1.53	1.09
RC7 12-14	13.0	0.995	0.887	0.986	0.921	1.166	1.341	1.306	1.056	0.909	0.739	0.692	0.722	0.587	0.538	0.762	1.70	1.09
RC7 14-16	15.0	0.883	0.739	0.827	0.773	0.981	1.137	1.100	0.845	0.695	0.540	0.505	0.554	0.434	0.390	0.803	2.03	1.09
RC7 16-18	17.0	0.878	0.801	0.849	0.794	0.976	1.103	1.053	0.813	0.657	0.508	0.468	0.522	0.402	0.366	0.834	2.19	1.09
RC7 18-20	19.0	0.773	0.701	0.720	0.660	0.810	0.914	0.863	0.679	0.579	0.469	0.440	0.485	0.378	0.336	0.896	2.04	1.09
RC7 20-25	22.5	0.684	0.585	0.602	0.550	0.675	0.759	0.710	0.573	0.472	0.393	0.358	0.429	0.333	0.297	0.963	2.05	1.10
RC7 25-30	27.5	0.519	0.487	0.490	0.442	0.530	0.596	0.586	0.463	0.366	0.293	0.259	0.331	0.240	0.210	0.886	2.17	1.07
RC7 30-35	32.5	0.553	0.524	0.525	0.469	0.556	0.605	0.580	0.464	0.376	0.302	0.273	0.344	0.255	0.223	0.955	2.17	1.07
RC7 35-40	37.5	0.668	0.611	0.653	0.633	0.796	0.880	0.765	0.571	0.434	0.351	0.320	0.394	0.295	0.260	0.872	2.26	1.13
RC7 40-45	42.5	0.970	0.735	0.835	0.770	0.928	1.070	0.983	0.742	0.534	0.401	0.352	0.412	0.310	0.274	0.987	3.13	1.12
RC7 45-50	47.5	0.718	0.571	0.675	0.645	0.847	0.940	0.809	0.645	0.530	0.437	0.400	0.469	0.355	0.302	0.889	2.02	1.14
RC7 50-55	52.5	0.717	0.630	0.674	0.632	0.802	0.927	0.869	0.714	0.592	0.498	0.460	0.529	0.408	0.354	0.825	1.76	1.11
RC7 55-60	57.5	0.945	0.959	0.942	0.849	0.961	1.074	1.108	0.888	0.761	0.677	0.610	0.634	0.457	0.421	0.853	2.07	1.04
RC7 60-65	62.5	0.834	0.753	0.654	0.556	0.559	0.635	0.687	0.531	0.442	0.389	0.353	0.403	0.289	0.256	1.214	2.89	1.03
RC7 65-70	67.5	1.444	1.131	1.099	0.911	0.934	0.994	0.891	0.618	0.470	0.383	0.344	0.394	0.284	0.242	1.620	5.08	1.09
PAAS concentrations (mg/kg)		38.2	79.6	8.83	33.9	5.55	1.08	4.66	0.774	4.68	0.991	2.85	0.405	2.82	0.433			

Note: Acid digestion is not a total REE digest

Appendix 2.

^{210}Pb dating report by ANSTO

Client Name:	Niels Munksgaard
Client Institution:	Charles Darwin University
Project Title:	2014rc0118a
Core Description:	RC1A

CIC model
Mass Accumulation Rate 0.076 ± 0.004 g/cm2/y
r2 = 0.9966

ANSTO ID	Depth (cm)	Dry Bulk Density (g/cm^3)	Cumulative Dry Mass (g/cm^2)	Count Date	Total ^{210}Pb (Bq/kg)	Supported ^{210}Pb (Bq/kg)	Unsupported ^{210}Pb Decay corrected to 16-Oct-14 (Bq/kg)	Calculated CIC Ages (years)	Calculated CRS Ages (years)	CRS model Mass Accumulation Rates (g/cm^2/year)
Q543	0 - 1	0.93	0.5 ± 0.5	19-Nov-14	96 ± 4	48 ± 5	48 ± 6	6 ± 6	3 ± 2	0.148 ± 0.017
Q544	2 - 3	0.79	2.2 ± 0.4	19-Nov-14	91 ± 4	39 ± 5	52 ± 6	29 ± 6	18 ± 4	0.086 ± 0.009
Q545	4 - 5	0.90	3.9 ± 0.4	19-Nov-14	54 ± 2	26 ± 2	28 ± 3	51 ± 6	38 ± 6	0.087 ± 0.011
Q546	6 - 7	0.97	5.7 ± 0.4	19-Nov-14	58 ± 2	46 ± 4	12 ± 4	75 ± 7	57 ± 8	0.110 ± 0.027
Q547	8 - 9	0.77	7.5 ± 0.4	19-Nov-14	44 ± 2	34 ± 3	11 ± 4	98 ± 8	77 ± 9	0.069 ± 0.014
Q548	10 - 11	0.72	9.0 ± 0.4	19-Nov-14	40 ± 2	26 ± 2	14 ± 3			
Q549	12 - 13	0.67	10.4 ± 0.4	19-Nov-14	61 ± 2	31 ± 2	30 ± 4			
Q550	14 - 15	0.71	11.8 ± 0.4	19-Nov-14	47 ± 2	33 ± 3	13 ± 4			

Unsupported 210Pb activities for this core exhibit a decreasing profile between 2 and 9 cm.
Below 9 cm the profile is almost vertical (except for the sample at 12-13 cm depth).
For the CIC model, unsupported 210Pb activities between 2 and 7 cm were used to calculate a single mass accumulation rate of 0.076 g/cm2/g (equivalent to 0.087 cm/year)
Assuming a constant mass accumulation rate between 0 and 9 cm, CIC model sediment ages were calculated and shown in the Table above.
For the CRS model, all unsupported 210Pb data between 0 and 9 cm were used to calculate the mass accumulation rate at each interval as well as sediment ages, see Table above.
The calculated CIC and CRS chronologies are not quite in a greement.
An independent method, such as 137Cs, pollen, diatom and/or trace metal records, should be used to determine which 210Pb dating model provides a more reliable chronology.

The sediment core was sub-sampled by Atun Zawadzki, followed by dry bulk density determination.
Samples were processed for alpha spectrometry analysis by Jack Goralewski
210Pb dating calculations by Atun Zawadzki - 2 Dec 2014

Figure 1

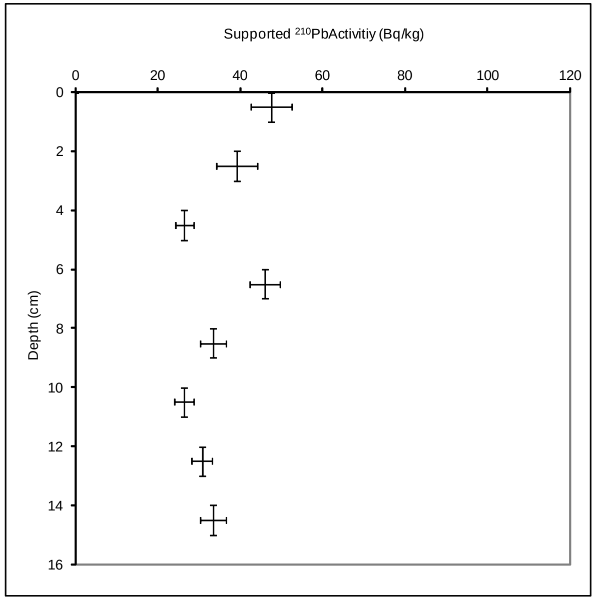

Figure 2

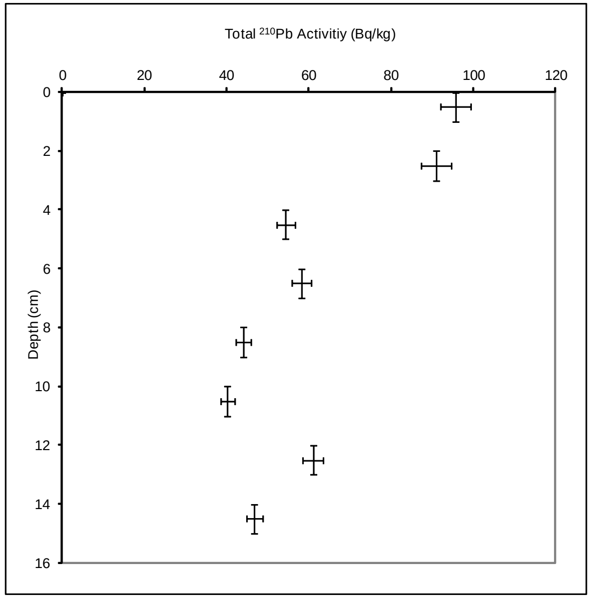

Figure 3