

# Acid Sulfate Soils Research Program

The Potential for Contaminant Mobilisation  
Following Acid Sulfate Soil Rewetting : Lab Experiment

Report 4 | August 2009



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**Cover image**

Western Lake Albert, March 2010 (DENR 2010)

# The Potential for Contaminant Mobilisation Following Acid Sulfate Soil Rewetting: Lab Experiment

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# 1 Executive Summary

Laboratory-based experiments have been undertaken to quantify the potential for mobilisation of acid and metals from acid sulfate soils (ASS) in the Lower Lakes following inundation with seawater or freshwater. The experiments were designed to assist in the interpretation of results from field-based inundation experiments being undertaken concurrently (Hicks et al., 2009), and also to allow better comparison with results from rapid-release tests previously undertaken by Simpson et al. (2008) on a wider range of ASS.

The experiments were undertaken using sediment cores collected from the same sites as the concurrent field experiments, and inundation was using freshwater from the River Murray or seawater collected near the barrages. Undisturbed sediment cores from Boggy Creek and Point Sturt were inundated with the test water in purpose-built corer-reactors, in which the cores were collected. The water quality parameters, pH, specific electrical conductance and dissolved concentrations of alkalinity, chloride, sulfate and metal/metalloids were monitored. For the first 17 days, the water was replaced with new water on days 2, 4, 7, 10, and 17; with gentle stirring of overlying water in between. Beyond day 17, no further water exchanges were made, but the experiments were modified to investigate the effects of sediment resuspension on water quality. On days 17, 21 and 28, a short period of intense stirring of the overlying water was used to resuspend the top 3 cm layer of the sediments in each corer-reactor. From days 28 to 53, the corer-reactors were stirred, and measurements made weekly. The experiments were terminated on day 54, and 10 cm sediment cores were taken from the centre of each of the reactors and porewater extracted for the measurement of pH and porewater metal concentrations.

The pH of the overlying water remained above pH 7 during the water-renewal phase of the corer reactor experiments. Upon contact of the freshwater and seawater with the Point Sturt soils, the water alkalinity generally decreased, however for the Boggy Creek soils there was a release of alkalinity. For both soil types, seawater inundation of the cores caused significantly greater release Al, Mn, Co and Pb (and Zn for Boggy Creek cores), than the freshwater inundation. This was attributed to the higher ionic strength of seawater increasing the exchange of metals from sediment particles.

Following resuspension of the surface sediments, the overlying water pH dropped by 0.3 to 0.8 pH units. For the Point Sturt cores, the resuspension of surface sediments resulted in removal of alkalinity in both freshwater and seawater inundation experiments. For the Boggy Creek cores, the resuspension of surface sediments resulted in large increases of alkalinity for the freshwater inundation experiment, but small decrease or unchanged alkalinity for the seawater inundation experiments. For both freshwater and seawater inundation experiments, the resuspension of the surface sediments resulted in minor to moderate changes (increases or decreases) in the metals released from the Point Sturt cores, but generally caused large increases in metals released for the Boggy Creek cores. For Boggy Creek, the resuspension-induced release of iron was 20 to >100-fold (both waters) and manganese was ~ 2-fold for seawater and >100-fold for freshwater inundation tests. Most of the iron and manganese release was likely to have been directly from the pore waters. The resuspension of the surface sediments caused increases of the order of 2-10 fold for As, Co, Ni, Pb, and Zn, but had little effect on the concentrations of Cd and Cr, and induced moderate removal of Al, Cu, and V.

Porewater metal concentrations were generally much greater in the seawater inundation tests than the freshwater inundation tests. Pore water concentrations increased with increasing sediment depth, consistent with the higher acidity (lower pH) of the deeper sediments, which were generally pH  $\leq 3$  from 15 cm below the sediment water interface to the base of the cores at -20 cm. The dissolved metal concentrations within the sediment pore waters were much greater than the concentrations being released to the overlying water and the increased rate of release of metals from the sediments during resuspension was likely to be in part due to porewater-derived metals.

In order to provide supplementary information, rapid release tests were undertaken for each soil using the same procedures as used previously (Simpson et al., 2008). These additional tests also investigated the influence of water type, solid:water ratio, leaching duration rates and sequential leaches on water quality. In the rapid-release tests, greater concentrations of metals were generally released from the soils by mixing with seawater than with fresh water. In general, the magnitude of the metal release from the soils was similar to that observed previously by Simpson et al. (2008). Aluminium, Fe and Mn release generally increased with increasing period of resuspension, but the concentrations of other metals/metalloids released within 30 min was not generally significantly different to that measured after 24 h (i.e. concentrations varied within a 2-4 fold range). Increases in total suspended solids (TSS) concentration had only minor effects on the release of most of the metals/metalloids, indicating that after 24 h of resuspension the majority of the metals appear to be in pseudo-equilibrium with the solid phase. The repeated leaches of the same soil indicated that while acidity may be washed out of the soils, significant acidity carried through to the next cycle. With each successive leach of the soils, the concentrations of most metals (not V) released from the soils generally decreased 2-10 fold compared to the previous leach cycle. This is consistent with there being a finite pool of metals available for release, rather than there being an ongoing source of weakly bound metals being released from the soil particles.

The potential ecological effects were considered with respect to water pH and concentrations of dissolved metals and metalloids released from the soils to the overlying water relative to the Australian water quality guidelines (WQGs) ANZECC/ARMCANZ (2000). The 80% and 95% protection concentrations were used. For metals whose toxicity is known to be influenced by hardness, and for which hardness algorithms are available (i.e. Cd, Cr(III), Cu, Ni, Zn, and Pb), the freshwater trigger values were adjusted based on a water hardness of 400 mg/L.



Simpson et al. (2008) previously observed that when sulfidic/sulfuric soils from the Lower Lakes region were resuspended in River Murray water, the water quality guidelines (WQGs) were exceeded only in cases where the waters became pH 5 or less. In the corer-reactor experiments the mean pH of the overlying water was greater than pH 7 throughout the first 17 days (weekly water renewal phase). During the resuspension phase, the pH dropped significantly, but generally remained above pH 5. Despite the pH remaining above pH 5, there were exceedances of WQGs, and the exceedances were much greater for the inundation with seawater than for freshwater. For seawater, the exceedances were (in order of magnitude) Al > Mn > Co > Pb > Cu > Cd ~ Zn, and for the freshwater inundation experiments there were minor exceedances for Cu, Cd and V.

Overall, the study indicated that only short-term exceedances to the WQGs for metals would be expected to occur if the pH of the overlying water remained above pH 6. Moderate dilution of the waters overlying the inundated sediments with surrounding waters is expected to result in both increased water pH and attenuation of dissolved metals released from the sediments. Exceedances of WQGs would be expected to be more frequent in shallow regions of the lake where water exchange is restricted.

To provide a better understanding of how the spatial variability in soil properties may affect metal-release when inundated with seawater and fresh water, it is recommended that rapid-release tests using seawater and freshwater are undertaken using soils collected from a greater range of sites in the lakes. While these tests may not provide accurate information on actual rates of metal release, they provide a useful means of determining which metals are available and contrasting the likely worst-case metal release from soils when inundated with different water types, and would thereby aid the risk assessment process.

## 2 Introduction

The South Australian Environmental Protection Authority (SA EPA) has requested that both laboratory- and field-based mobilisation experiments be undertaken to quantify the potential for mobilisation of contaminants from acid sulfate soils (ASS) in the Lower Lakes following rewetting with seawater or fresh water. It is intended that the results of the experiments be used to inform the Environmental Impact Statement (EIS) being prepared for the introduction of Seawater in the Lakes system. In order to meet the tight deadline of the EIS, results from experiments were requested in a final draft report by July 31, 2009.

In a recent ecological risk assessment (ERA) of the impact of acidification, acid and a number of metals (Al, Co, Cu, Fe-floc, and V) were identified as contaminants of concern in relation to their possible elevated concentrations, bioavailability, and potential effects, when compared to water quality guidelines (Stauber et al., 2008). While rapid (24-h) acid and metal mobilisation experiments provided some information on the risks posed by these contaminants mobilised by freshwaters (Simpson et al. 2008), limited information was available for seawater-induced mobilisation. The preliminary risk assessment highlighted that to provide information on likely chronic effects to aquatic and benthic organisms, greater information was required on the mid-term (e.g. 96-h) mobilisation of acid and metals/metalloids and formation of potentially toxic metal flocs caused by the inundation of sulfidic/sulfuric ASS with either fresh water or seawater (Simpson et al. 2008; Stauber et al., 2008).

To provide information for an environmental impact statement (EIS), long-term field-trials were undertaken in parallel with this study at two sites in the lower Lakes system to contrast the difference in response of two soil types to inundation with freshwater and seawater. The two sites were selected on the basis of being representative of air-exposed soils that have developed considerable acidity: Point Sturt, a sandy soil; and Boggy Creek, an organic-rich clayey soil.

To assist the interpretation of results from the field-trial seawater/freshwater inundation experiments being undertaken concurrently (Hicks et al., 2009), laboratory-based experiments were used to assess the release of acidity and metals/metalloids from soils. Sediment cores were collected from each of the field-trail sites and re-wetting was undertaken using both freshwater and seawater. In these corer-reactors tests, the overlying water was gently stirred and renewed weekly during the first 17 days. From day 17, resuspension of the surface sediments was induced at the start of each week to simulate the action of strong water currents. Gentle stirring was then applied and no further water changes were made.

To assist in the comparison of the results of the rapid remobilisation experiments undertaken by Simpson et al (2008) with the long term field trials and the mid-term corer-reactor experiments, additional rapid remobilisation tests were undertaken on a range of soil samples collected from the two sites. These experiments investigated rapid remobilisation of metals/metalloids following rewetting with freshwater and seawater. Then influence of solid:water ratio, leaching duration rates and sequential leaches with new water was also investigated.

The results of the short- to medium-term laboratory-based experiments are discussed in terms of potential environmental impacts associated with the release of metals/metalloids from the soils under scenarios of rewetting with both freshwater and seawater.

## 3 Methods

### 3.1 *Sampling Sites and Samples*

#### 3.1.1 Soil samples

The site selection and sample collection was made at the same sites as used for the field-trials. The two sites were Boggy Creek and Point Sturt and photographs of the site at the time of collection, and the collection of the samples are shown in Appendix A. The sampling of both sites was undertaken on July 7, 2009.

The soils in the area to the south of the Point Sturt mesocosms (Appendix B) was disturbed by the deployment machinery used to construct the experimental site. The reactor cores were thus collected from the northern, undisturbed side of the mesocosms, generally within 5 m of a tank. Descriptions of the coring sites are given in Appendix A, Table A1. Three cores were collected from Point Sturt.

The sediment sampled at Point Sturt was a fairly uniform moist sand with no pronounced morphological stratification. Coring was achieved by pushing the corer with its attached handle firmly into the sediment, in a clockwise spiral direction, so that the lid did not unscrew from the core tube. Gradually (within a minute or two) the tube penetrated to the required depth (~16 cm) as marked by a measuring rod. To minimise disturbance of the soil within the corer, one side of the sand was dug out with a stainless steel spade to remove the core, and from this side a flexible polyethylene cutter was pushed in immediately underneath it. A 20 mm thick disk of closed cell foam was then worked in under the core, immediately above the inserted PE cutter. This was done in a manner so as to not lose wet sand from the core. The sand was firm enough for this task to be completed fairly easy. A closed cell foam disk was pushed up into the base of the core tube to retain the core contents while the outer rim was cleaned (washed and wiped with tissue). The core was secured with the PVC base and then its breather hole taped. After this, two pieces of the same closed cell foam were placed immediately above the top of the cores to better secure them for road transport. Immediately after the core was secured, additional samples (~300 g) were taken from the site (0-5 cm depth) using a plastic trowel. All 0-5 cm samples were taken within 0.5 m of the coring in non-disturbed ground.

The cores from Boggy Creek were collected here using the same technique as at Point Sturt. In this case, the disturbed site was the northern side and so coring took place south of the microcosms. Descriptions of the coring sites are given in Appendix A, Table A1. Three cores were collected from Boggy Creek. The soils at this site were very non-uniform and layered. There was a black hard clayey cracked soil layer on top that after 5-10 cm depth, changed to a lighter coloured sand. There was underlain by a light-coloured clay underneath that. As well as 0-5 cm samples, 0-1 cm soil samples were taken. All 0-5 cm and 0-1 cm samples were collected within 1 m of the cores.

#### 3.1.2 Water samples

The freshwater for the rewetting experiments was collected from the River Murray at Wellington on 30 July, 2009. The seawater for the field and laboratory rewetting experiments was collected from the Coorong at Mundoo Island Barrage on 29 July, 2009. This water was stored in 5000 L plastic tanks at each site and sub-sampled for the laboratory experiment on the 13 July 2009. Three 20-L containers of freshwater and three 20-L containers of seawater were collected into acid-washed containers and transported to CSIRO at Lucas Heights.

### 3.2 *Corer-reactor Acid/Metal Release Tests*

#### 3.2.1 General analytical

All glass and plasticware for trace metals analyses were usually new and were cleaned by soaking in 10% (v/v) HNO<sub>3</sub> (BDH, Analytical Reagent grade) for a minimum of 24 h, followed by repeated rinsing with deionised water (Milli-Q, 18 MΩ). New bottles, washed and rinsed with Milli-Q, were used for sampling and analyses of major elements, alkalinity and nutrients. All chemicals were analytical reagent grade or equivalent analytical purity. Measurements of pH and redox potential were made using pH and Eh probes and meters (Simpson and Batley, 2003). The specific electrical conductance (SEC: WTW LF 320 meter and TetraCon 325 probe) and dissolved oxygen (DO: WTW Oxi 196 meter and EO96 oxygen electrode) were measured according to manufacturers' instructions. Measurements of sediment pH was made using a combination spear-tip electrode (Hanna). Water samples were filtered through 0.45 μm membrane filters immediately following collection. For major and trace element analyses, samples were preserved with 0.2% concentrated HNO<sub>3</sub> (Tracepur, Merck). For other analytes, samples were refrigerated at 4 °C and analysed within 7 days. Dissolved concentrations of Na, K, Ca, Mg, Al, and Fe in water samples were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES, CIROS, Spectro) and all other trace elements were analysed by inductively coupled plasma mass spectrometry (ICPMS, Agilent 7500 CE). Water alkalinity was measured by automated titration with a pH 4.5 end-point for total alkalinity (APHA 2005; Method 2320 B). Dissolved concentrations of major anions and dissolved organic carbon

(DOC) were analysed using standard methods (USEPA, 1996; APHA, 2005); namely chloride by titration, sulfate by ICP-AES, and DOC using an automated carbon analyser. Analysis blanks and duplicate analyses comprised at least 10% of the samples, spiked recoveries analyses of certified reference materials were used to check the accuracy of the methods.

Particulate metals were analysed following digestion of dried and ground samples in hot concentrated 2:1 HCl:HNO<sub>3</sub> (aqua-regia microwave digestion) followed by dilution and filtration (<0.45 µm). Acids were high purity (Merck Suprapur). QA/QC included sample blanks and duplicates and a certified reference material (PACS-2, National Research Council, Canada). Total organic carbon (TOC) was analysed using an automated carbon analyser (APHA, 2005).

The significance of data relationships was determined using t-tests and correlations (Pearson's product moment) using NCSS statistical software (NCSS, Utah, USA).

### 3.2.2 Corer-reactor operation

Corer-reactors were used for assessing acid and metal fluxes from sediments (Jung et al., 2003; Simpson et al., 2002) (Appendix B). The corer-reactor chambers had a 146 mm diameter (167.4 cm<sup>2</sup> area × 5.97 cm depth = 1 L) and allowed for control of stirring rate and dissolved oxygen concentration, the measurement of water quality parameters (e.g. pH, EC, DO), ready sampling and renewal of waters. These corer-reactors were used in paired experiments inundated with freshwater and seawater, respectively. The inundation with freshwater or seawater was undertaken by trickling in the desired amount of water using a clean plastic volumetric cylinder which had a series of holes at the bottle to allow the water to trickle out at a rate of approximately 100 mL/min.

For the seawater rewetting experiments, two cores were used from Boggy Creek and one core from Point Sturt (Table 2). For the freshwater rewetting experiments, one core was from Boggy Creek and two cores were from Point Sturt (Table 1). For each freshwater/seawater pair, the two cores were chosen as those that appeared to be most similar. The Point Sturt cores all appeared quite similar (Cores 3, 4 = fresh water, Core 5 = seawater). Of the Boggy Creek cores, two were similar with surface efflorescences (Core 1 = fresh water; Core 2 = seawater), while the third did not and appeared darker in colour (Core 9 = seawater).

#### Water renewal mode

The rewetting schedule for the corer-reactors is given in Appendix B (Table B1). The rewetting water undertaken in stages, in which the water was initially added to a depth of 10 cm above the soil surface (~1.67 L of overlying water), the water was stirred gently (~30 rpm), and after 1 h 100 mL of water was taken for analyses. The water inundation was then continued to achieve a 15-cm water depth and stirring was commenced. After 6 h from commencement, a second 100 mL of water was taken for analyses, then replaced with new water. On days 2, 4, 7 and 10, 100 mL of water was removed for analyses in the morning, then the entire water-column was removed and replaced with new water. On each of these days, after 5-6 h, a second 100 mL of water was taken for analyses, then replaced with new water.

#### Resuspension mode

Wind-induced water currents (seiches) are expected to occur in the lake, and the impacts of these currents is expected to increase the movement of porewater near the soil surface and resuspend surface sediments. From day 17, the experimental program was modified to induce resuspension of the top 2-3 cm of the sediment cores (Appendix B, Table B2). This was achieved using a more powerful stirrer (~300 rpm), through three 5-second stirring periods within 30 seconds, with the stirring blade placed just above the sediment surface. These resuspension events were applied on days 17, 21 and 28, and water quality was monitored for a regular period following the resuspension events. No further water exchanges were made.

Column surface water pH, conductivity and dissolved oxygen were measured on every sampling occasion. When complete renewal of the water column occurred (at the start of each sampling day), and before addition of the new water, the pH of the surface sediment was measured using a spear-tipped (penetrating) pH electrode. This electrode was pushed up to 5 cm into the sediment and the pH recorded.

#### Monitoring mode and deconstruction of cores

For the final four weeks (to day 53) the corer-reactors continued to be stirred, water quality monitored and the samples collected at the end of each week. On day 54, 10-cm sediment cores were taken from the centre of each of the reactors and porewater extracted for the measurement of pH and porewater metal concentrations. Sediment pore water was extracted by centrifugation (5 min, 1700 g, 18-22 °C) under a nitrogen atmosphere. Pore water and overlying water samples were rapidly filtered through acid-washed 0.45 µm membrane filters (Minisart, Sartorius) immediately following collection and acidified with concentrated HNO<sub>3</sub> (2% HNO<sub>3</sub> (v/v), Tracepur, Merck). Dissolved metals in the pore waters were measured by ICP-AES calibrated with matrix-matched standards.

**Table 1. Corer reactors Samples and Tests**

Point Sturt	Water	Release Tests	
		Static	Resuspension
Core 3	Murray River	Weeks 1-3	Weeks 3-5
Core 4	Murray River	Weeks 1-3	Weeks 3-5
Core 5	Seawater	Weeks 1-3	Weeks 3-5
<b>Boggy Creek</b>			
Core 1	Seawater	Weeks 1-3	Weeks 3-5
Core 2	Seawater	Weeks 1-3	Weeks 3-5
Core 9	Murray River	Weeks 1-3	Weeks 3-5

### 3.3 Rapid Release Tests

These tests were undertaken to allow the rapid release data that had been gathered in previous research studies (e.g. Simpson et al., 2008; Fitzpatrick et al., 2009) to be better interpreted in relation to the mid-term reactor tests and long-term field tests.

Rapid release tests were performed as described previously (Simpson et al., 2008a), but with additional experiments undertaken to provide information on (i) sequential leaching, the effects of solid:water ratio, and (iii) release rates.

#### 3.3.1 Acid and metal mobilisation tests

The soils were used as collected, i.e. they were not dried further. The rapid remobilisation of acidity and metals was evaluated by resuspending the test soil in the test water (fresh water or seawater) for the required period of time. The containers were 250 mL low density polyethylene bottles (Nalgene), which were rolled at 50 rpm on a bottle roller.

At the completion of the resuspension period, a 0.45 µm-filtered water sample was taken for analyses of alkalinity and major ions (Cl, SO<sub>4</sub>, Na, K, Ca, Mg), and dissolved trace metals and metalloids (Ag, Al, As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, V, Zn). The pH and SEC of the water were measured at the start and finish of all tests. The waters stayed well-oxygenated (e.g. dissolved oxygen was >6 mg/L) throughout the experiments.

The standard leach tests involved resuspending 15 g of soil in 150 mL of test water for 24 h. The samples selected for the standard rapid release tests were Point Sturt samples Core 4/0-5 cm and Core 5/0-5 cm, and Boggy Creek samples Core 9/0-1 cm, and Core 9/1-5 cm (Table 1). For each of these tests, the leaching was repeated several times to determine whether there is likely to be on-going acid and metal release, or whether the subsequent leaching of greatly diminished.

The relationship between metal release and TSS was investigated for three soils using both freshwater and seawater at soil:water ratios of 0.1, 1, 10 and 100 g soil/L and a resuspension period of 24 h. The kinetics of metal mobilisation was investigated for three soils using both freshwater and seawater at a soil:water ratio of 100 g soil/L and a resuspension period of 0.5, 3, 7 and 24 h.

## 4 Results

### 4.1 Corer-reactor Experiments

#### 4.1.1 Soil pH

The paste-pH values measured for surface soil samples collected close to the sediment cores are shown in Table 2. There was no distinctly different surface layer at Point Sturt and the pH measured represents an average of the top 5 cm. For all the Point Sturt soils, the pH was  $\leq 3$ . At Boggy Creek, the windy conditions that had prevailed in the days before sample collection had dried out the soil surface, and two layers were sampled for paste-pH measurements: 0-1 cm and 1-5 cm depth. The Boggy Creek soils had near neutral pH in the top 1 cm, but were acidic in the 1-5 cm depth fraction.

**Table 2. Soil Samples for Rapid Remobilisation Tests**

Location <sup>a</sup>	Depth, cm	Paste pH
<b>Point Sturt <sup>b</sup></b>		
Core 3	0-5	2.9
Core 4	0-5	3.0
Core 5	0-5	2.9
<b>Boggy Creek <sup>b</sup></b>		
Core 1	0-1	7.4
Core 1	1-5	5.6
Core 2	0-1	7.1
Core 2	1-5	3.9
Core 9	0-1	6.8
Core 9	1-5	3.3

<sup>a</sup> Soil samples were collected immediately adjacent to where the cores were collected for the corer-reactor tests

<sup>b</sup> At Point Sturt, there was no major horizon in the top 0-5 cm and this depth section was collected as one. At Boggy Creek, the top 0-1 cm appear more oxidised than the deeper soil, and two sections were collected

#### 4.1.2 Overlying water pH and SEC

The freshwater and seawater used for the experiments had pH of 7.6 and 7.8, respectively, and SEC of  $1.80 \pm 0.05$  and  $52 \pm 1$  mS/cm, respectively. The pH and specific electrical conductivity (SEC) measured following re-wetting of cores with freshwater and seawater from Boggy Creek and Point Sturt is shown in Tables 3-5.

The fresh water from the River Murray was pH 7.5 and the seawater was pH 8.0. The pH of the water overlying the sediment cores remained  $> \text{pH } 6.5$  throughout the re-wetting cycles (weeks 1-3) (Table R1). During this period, the water overlying the Boggy Creek cores had pH  $7.6 \pm 0.2$ ,  $7.3 \pm 0.3$ ,  $7.6 \pm 0.1$  (mean  $\pm$  standard deviation) for cores 1 (freshwater), 2 and 9 (both seawater), respectively. For the Point Sturt cores, the overlying water had pH  $7.5 \pm 0.3$ ,  $7.3 \pm 0.4$ ,  $7.6 \pm 0.2$  (mean  $\pm$  standard deviation) for cores 3, 4 (both freshwater) and 5 (seawater), respectively.

The pH of the porewater in the surface sediments was measured on two occasions, on days 2 and 10. For all cores the pH in the surface sediments appeared to be less acidic than the deeper sediments (Table 1).

For the Port Sturt cores, the conductivity of the overlying water was 1.8-2.0 mS/cm for freshwater tests and 51-54 mS/cm for seawater tests. For the Boggy Creek cores, the conductivity of the overlying water was 2.0-4.1 mS/cm for freshwater tests and 52-55 mS/cm for seawater tests.

The sediment resuspension experiments were undertaken to simulate a scenario of significant wind-induced high turbulence within the water column, which could be expected to resuspend the surface sediments. Following resuspension of the surface sediments the water pH dropped by 0.3 to 0.8 pH units. For the freshwater inundation of Point Sturt core 3, the weekly sediment resuspension events caused further decreases in the pH of the overlying water, but did not greatly affect the pH in the other experiments. The sediment resuspension resulted in increases in SEC for the Boggy Creek – Freshwater experiment (from  $\sim 7$  to  $\sim 8$  mS/cm), but did not cause large changes to the SEC for the other tests.

From day 28 to day 54 the overlying water was stirred and weekly monitoring indicated that the water pH and SEC did not change significantly.

### 4.1.3 Trace metal and metalloid concentrations

The concentrations of alkalinity, chloride, sulfate and trace metals/metalloids measured following re-wetting of cores with freshwater and seawater from Boggy Creek and Point Sturt is shown in Tables 6-11. The QA/QC procedures for the analyses are provided in Appendix C. The variation between duplicate analyses was low, spiked recoveries were excellent and results for the certified reference materials within the certified range.

The alkalinity of the River Murray freshwater (FW) was approximately 80 mg CaCO<sub>3</sub>/L, which is relatively high. The alkalinity of the seawater (SW) was approximately 135 mg CaCO<sub>3</sub>/L. Upon contact of the FW and SW with the Point Sturt soils, the water alkalinity generally decreased, however the Boggy Creek soils appeared to release alkalinity during the freshwater inundation experiments (Tables 6-11).

For both soil types, seawater inundation caused significantly greater release Al, Mn, Co and Pb (and Zn for Boggy Creek cores), than the freshwater inundation (Figures 1 and 2). This was expected due to the higher ionic strength of seawater increasing the displacement of metals from soils particles by exchange reactions. For Cu, Fe and V, the release may have been initially greater for seawater than freshwater, but Cu and V were expected to be rapidly scavenged by iron hydroxide phases that form due to the oxidation of released Fe(II), followed by precipitation of Fe(OH)<sub>3</sub> at the sediment-water interface (Simpson and Batley, 2003; Simpson et al., 2009).

### 4.1.4 Effect of surface sediment resuspension

For the Point Sturt cores, the resuspension of surface sediments resulted in a decrease in the water alkalinity in both freshwater and seawater inundation experiments. For the Boggy Creek cores, the resuspension of surface sediments resulted in large increases of alkalinity for the freshwater inundation experiment, but small decreases or unchanged alkalinity for the seawater inundation experiments.

The resuspension of the surface layers of the submerged soils/sediments generally caused significant changes in the release rates of many substances compared to that occurring without disturbance (Tables 6 to 11). For the Boggy Creek freshwater laboratory inundation experiment, the resuspension of surface sediments also released significant amounts of chloride and sulfate. For both freshwater and seawater inundation experiments, the resuspension of the surface sediments resulted in minor to moderate changes (increases or decreases) in the metal released from the Point Sturt cores, but generally caused large increases in metals released from the Boggy Creek cores (Figures 1 and 2). For the Boggy Creek cores, the sediment resuspension caused large increases in release of Fe, Mn, Co, Pb, and Zn and small increases in the release of arsenic and nickel.

**Table 3. pH of Water and Surface Sediments during Corer-reactor Experiments**

Core Water	Boggy Creek Reactors			Point Sturt Reactors		
	Core 1 Freshwater	Core 2 Seawater	Core 9 Seawater	Core 3 Freshwater	Core 4 Freshwater	Core 5 Seawater
<b>Day 1 (week 1)</b>						
9:00 AM	7.2	6.6	7.8	7.0	6.8	7.6
12:00 PM	7.5	7.2	7.6	7.3	7.4	7.8
3:00 PM	7.6	7.2	7.6	7.4	7.6	7.8
<b>Day 2</b>						
9:00 AM	7.8	7.1	7.5	7.5	7.7	7.5
3:00 PM	7.5	7.5	7.9	7.4	7.4	7.8
<b>Day 4</b>						
9:00 AM	7.8	7.3	7.5	7.7	7.8	7.3
3:00 PM	7.6	7.7	7.8	7.4	7.7	7.8
<b>Day 7 (week 2)</b>						
9:00 AM	7.9	7.5	7.6	7.8	7.9	7.3
<b>Day 10</b>						
9:00 AM	7.9	7.5	7.6	7.9	7.9	7.5
<b>Day 17 (week 3)</b>						
9:00 AM	7.4	7.3	7.5	7.4	7.3	7.6
<b>Day / depth in sediment</b>						
<b>Sediment pH</b>						
2 / 2 cm depth	7.3	6.8	5.8	3.5	3.7	6.2
2 / 3 cm depth	7.3	6.6	5.0	2.8	2.8	2.7
2 / 4 cm depth	7.2	6.1	3.1	2.6	2.6	2.4
10 / 2 cm depth	7.0	6.3	6.5	3.8	5.4	6.3
10 / 3 cm depth	7.2	6.3	6.2	3.1	3.7	4.8
10 / 4 cm depth	6.8	5.7	4.3	2.8	3.3	3.4
10 / 5 cm depth	6.3	4.5	4.0	2.6	3.1	3.0

**Table 4. Water Specific Electrical Conductivity (SEC) during Corer-reactor Experiments**

Core Water	Boggy Creek Reactors			Point Sturt Reactors		
	Core 1 Freshwater	Core 2 Seawater	Core 9 Seawater	Core 3 Freshwater	Core 4 Freshwater	Core 5 Seawater
<b>Specific Electrical Conductivity (SEC, mS/cm)</b>						
<b>Day 1 (week 1)</b>						
9:00 AM	4.1	52.6	52.3	1.8	1.9	52.6
12:00 PM	3.3	52.6	52.3	1.8	1.8	53.0
3:00 PM	3.0	52.5	52.4	1.8	1.8	52.8
<b>Day 2</b>						
9:00 AM	3.2	52.4	51.7	1.8	1.8	53.0
3:00 PM	2.1	52.4	52.4	1.8	1.8	52.6
<b>Day 4</b>						
9:00 AM	2.7	51.1	52.6	1.8	1.8	52.9
3:00 PM	2.0	52.5	52.7	1.8	1.8	52.7
<b>Day 7 (week 2)</b>						
9:00 AM	2.7	51.8	52.7	1.8	2.0	53.3
<b>Day 17 (week 3)</b>						
9:00 AM	3.2	53.2	53	1.8	1.8	53.4



Table 5. Water pH and SEC during Sediment Resuspension Phase of Experiments

Core Water	Boggy Creek Reactors			Point Sturt Reactors		
	Core 1 Freshwater	Core 2 Seawater	Core 9 Seawater	Core 3 Freshwater	Core 4 Freshwater	Core 5 Seawater
<b>Resuspension event 1</b>						
<b>pH</b>						
<b>Day 17 (week 3)</b>						
3:00 PM	7.1	6.5	6.4	6.5	6.9	6.4
<b>Day 18</b>						
9:00 AM	7.3	6.9	6.8	7.0	7.2	6.8
<b>Resuspension event 2</b>						
<b>Day 21 (week 4)</b>						
9:00 AM	7.5	7.3	7.4	7.2	7.5	7.3
11:30 PM	6.9	6.4	6.5	5.6	6.7	6.3
3:00 PM	7.0	6.6	6.6	5.6	6.8	6.3
<b>Day 23</b>						
9:00 AM	7.3	6.8	6.8	6.2	7.1	7.0
<b>Day 25</b>						
9:00 AM	7.3	6.9	7.0	6.7	7.3	7.2
<b>Resuspension event 3</b>						
<b>Day 28 (week 5)</b>						
9:00 AM	7.3	6.9	7.1	6.3	7.5	7.3
3:00 PM	6.8	6.5	6.6	4.7	6.9	6.5
<b>Day 30, 9 am</b>	7.3	6.7	6.7	4.7	7.4	7.1
<b>Day 32, 9 am</b>	7.5	6.9	6.9	4.8	7.5	7.3
<b>Day 39, 9 am</b>	7.4	7.2	7.3	4.3	7.3	7.3
<b>Day 46, 9 am</b>	7.6	7.3	7.4	4.4	7.3	7.5
<b>Day 53, 9 am</b>	7.6	7.4	7.5	4.3	7.4	7.7
<b>Resuspension event 1</b>						
<b>Specific Electrical Conductivity (SEC, mS/cm)</b>						
<b>Day 17 (week 3)</b>						
3:00 PM	5.1	53.9	54.5	1.9	1.8	55.2
<b>Day 18</b>						
9:00 AM	5.3	54.6	55.1	1.9	1.9	55.3
<b>Resuspension event 2</b>						
<b>Day 21 (week 4)</b>						
9:00 AM	5.5	56.7	57.4	2.0	2.0	57.6
11:30 PM	6.8	26.1	57.1	2.0	1.9	57.5
3:00 PM	6.8	55.9	55.6	2.0	1.9	56.9
<b>Day 23</b>						
9:00 AM	6.7	57.1	56.4	2	1.9	57.7
<b>Day 25</b>						
9:00 AM	6.9	59	58.2	2.1	1.9	59.4
<b>Resuspension event 3</b>						
<b>Day 28 (week 5)</b>						
9:00 AM	6.9	59.7	59.3	2.1	2.0	60.1
3:00 PM	8.2	59.3	58.5	2.2	1.9	59.7
<b>Day 30, 9 am</b>	8.2	59.1	58.1	2.1	1.9	59.8
<b>Day 32, 9 am</b>	8.1	59.0	58.1	2.1	1.9	59.6
<b>Day 39, 9 am</b>	8.1	58.9	58.1	2.2	2.0	59.7
<b>Day 46, 9 am</b>	8.3	59.4	58.8	2.3	2.2	60.4
<b>Day 53, 9 am</b>	8.1	59.3	58.8	2.3	2.0	60.1

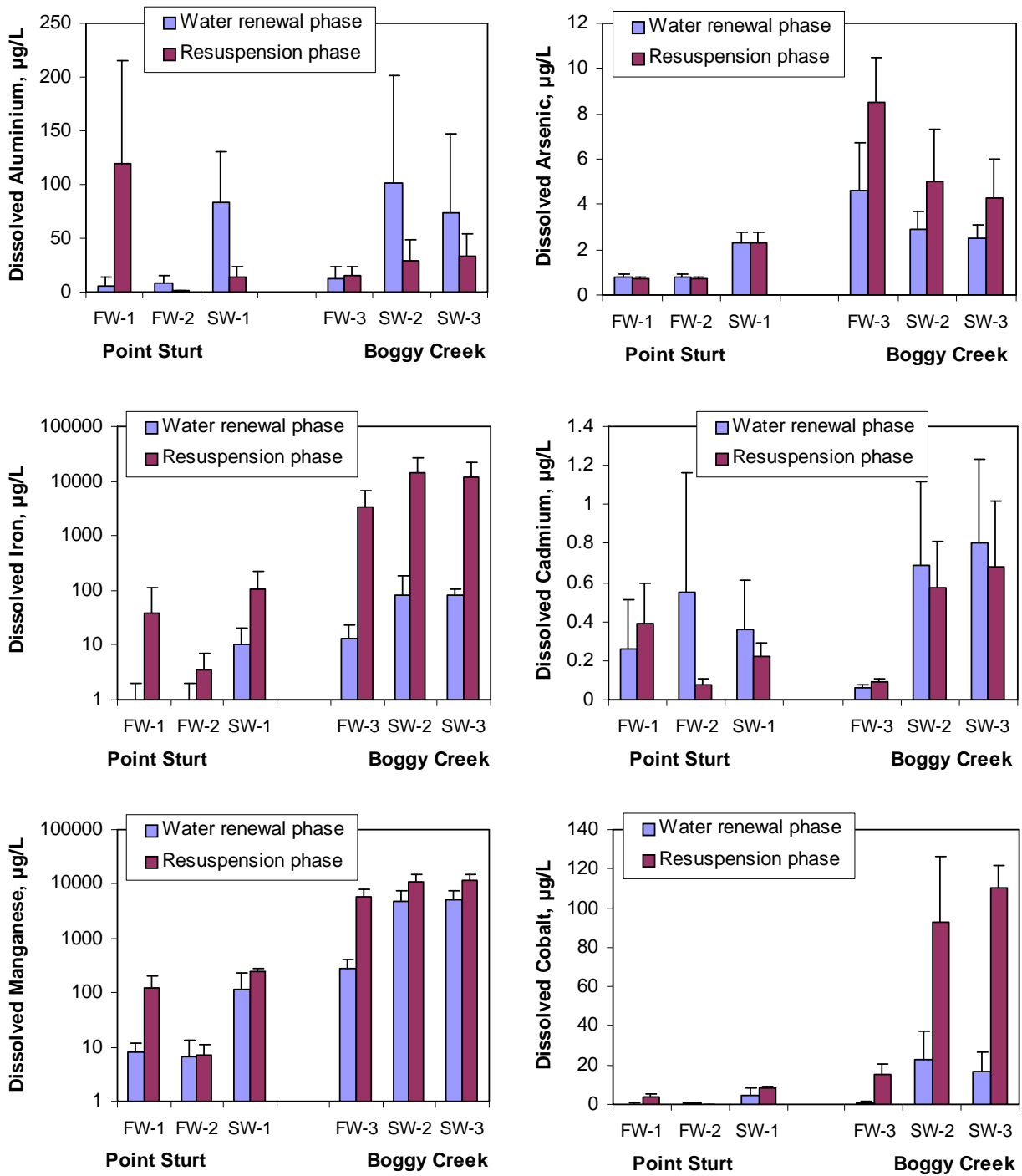


Figure 1. Comparison of the dissolved Al, Fe, Mn, As, Cd and Co concentrations measured in the six corer-reactors (mean ± standard deviation) for the weekly water renewal and resuspension periods: Point Sturt (2x fresh water, 1x seawater) and Bogy Creek (1x fresh water, 2x seawater)

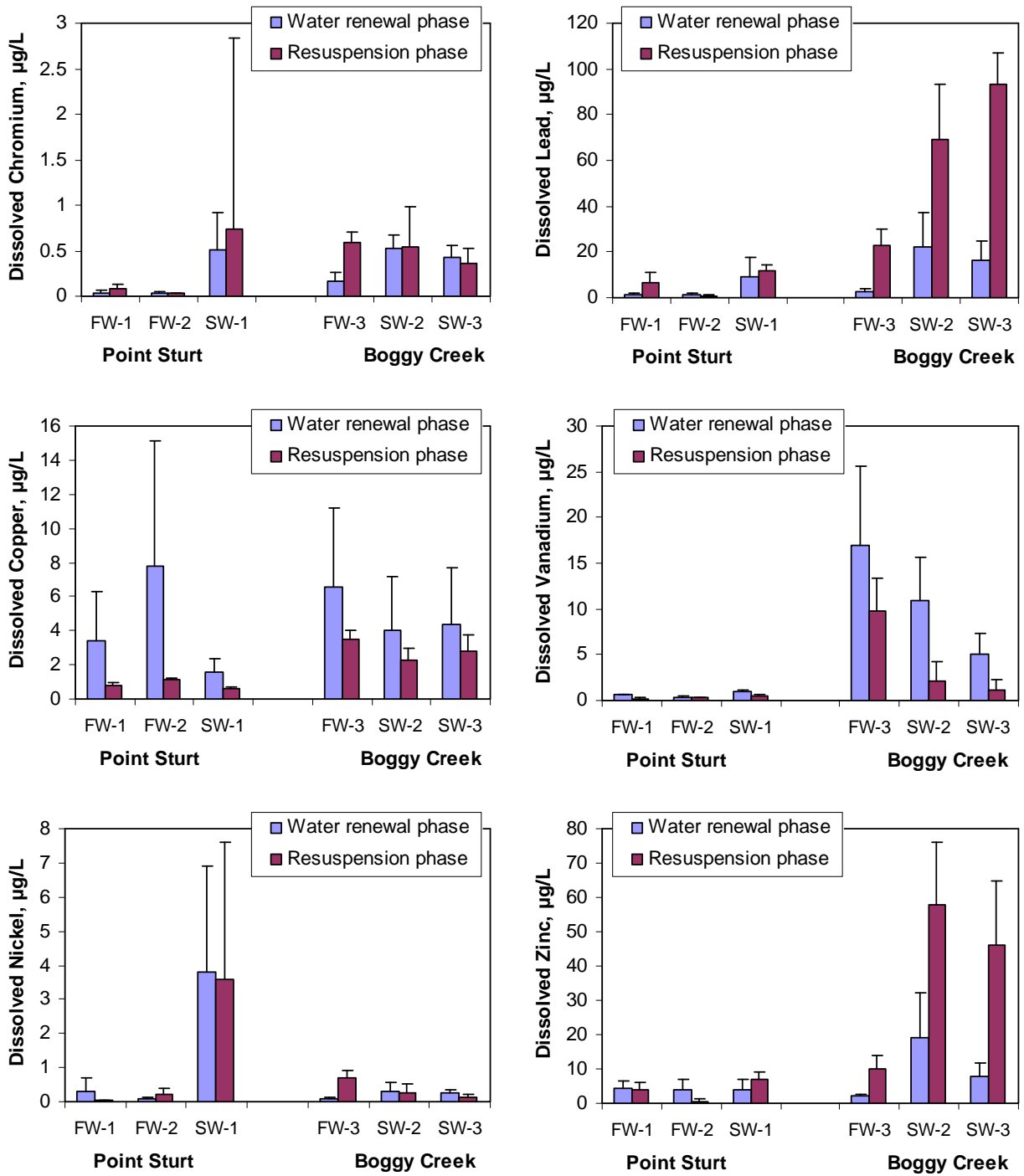


Figure 2. Comparison of the dissolved Cr, Cu, Ni, Pb, V and Zn concentrations measured in the six corer-reactors (mean  $\pm$  standard deviation) for the weekly water renewal and resuspension periods: Point Sturt (2 $\times$  freshwater, 1 $\times$  seawater) and Boggy Creek (1 $\times$  fresh water, 2 $\times$  seawater).

Table 6. Alkalinity and Concentrations of Trace Metals and Metalloids Released: Point Sturt, Freshwater Core 3

Sampling	Alkalinity mg CaCO <sub>3</sub> /L	Acidity	Cl mg/L	SO <sub>4</sub> mg/L	Al µg/L	Fe µg/L	Mn µg/L	As µg/L	Cd µg/L	Co µg/L	Cr µg/L	Cu µg/L	Ni µg/L	Pb µg/L	V µg/L	Zn µg/L
Day 1, 9 am					21	1	15	0.68	0.81	0.56	<0.02	1.75	<0.03	1.65	0.66	4.42
Day 1, 12 pm					2	<1	9	0.84	0.35	0.32	<0.02	6.49	0.07	1.22	0.60	4.06
Day 1, 3 pm		4	501		2	<1	7	0.81	0.66	0.25	<0.02	8.77	0.90	1.33	0.62	7.15
Day 2, 9 am		6	513		<1	<1	11	0.72	0.29	0.35	<0.02	8.11	0.16	1.21	0.56	3.29
<b>Water change</b>																
Day 2, 3 pm		8	492		2	<1	2	0.72	0.144	0.099	0.03	1.904	0.016	0.956	0.731	9.14
Day 4, 9 am	68		516		<2	<1	11	0.81	0.11	0.27	<0.02	2.29	<0.03	1.08	0.61	4.07
<b>Water change</b>																
Day 4, 10 am					5	<1	2	0.84	0.09	<0.15	<0.02	1.59	<0.03	0.84	0.66	5.77
Day 4, 3 pm	95		495	92	<2	<1	3	0.86	0.08	<0.15	<0.02	1.34	<0.03	0.81	0.64	2.59
Day 7, 9 am	77	2	505	95	4	<1	11	0.91	0.11	0.20	<0.02	1.66	<0.03	1.34	0.68	3.73
<b>Water change</b>																
Day 10, 9 am	77	6	506	94	<2	<1	8	0.85	0.11	<0.15	<0.02	1.48	<0.03	1.41	0.65	1.75
<b>Water change</b>																
Day 17, 9 am	59	2	519	91	<2	<1	2	0.84	0.09	<0.15	<0.02	1.53	<0.03	2.06	0.69	1.58
<b>Resuspension event 1</b>																
Day 17, 11 pm					<2	4	100	0.65	0.26	2.93	<0.02	0.94	<0.03	5.58	0.17	3.38
Day 17, 3 pm	33	2	513	104	<2	1	100	0.72	0.30	2.81	<0.02	0.92	0.03	5.05	0.20	2.61
Day 18, 9 am	18	2	518	105	<2	<1	99	0.63	0.16	2.04	<0.02	0.91	<0.03	3.20	0.21	1.08
Day 21, 9 am	18	2	528	107	<2	<1	52	0.82	0.09	0.57	<0.02	1.02	<0.03	2.02	0.31	0.66
<b>Resuspension event 2</b>																
Day 21, 11 am					70	26	140	0.58	0.41	4.26	<0.02	0.71	0.05	7.44	0.10	4.67
Day 21, 3 pm	18	4	537	117	39	12	150	0.68	0.41	4.05	<0.02	0.60	<0.03	8.03	0.10	4.45
Day 23, 9 am	7	19	538	114	<4	22	143	0.83	<0.05	<0.15	<0.02	1.06	<0.03	5.28	0.28	0.10
Day 25, 9 am					<1	2	130	0.69	0.26	2.35	<0.02	0.62	<0.03	4.36	0.17	2.08
Day 28, 9 am					1	2	120	0.62	0.32	2.32	<0.02	0.62	<0.03	0.40	0.18	3.07
<b>Resuspension event 3</b>																
Day 28, 3 pm					200	12	200	0.69	0.62	5.11	0.05	0.77	<0.03	12.7	0.10	6.81
Day 30, 9 am					230	9	210	0.65	0.70	6.18	0.12	0.86	<0.03	13.6	0.10	7.52
Day 32, 9 am					180	8	210	0.70	0.71	5.71	0.10	0.86	0.04	11.7	0.10	7.94
Day 39, 9 am					284	8	224	0.70	0.82	6.35	0.12	0.96	0.03	14.5	<2	7.75
Day 46, 9 am	<1	15	560	139	386	12	242	1.01	0.90	7.41	0.16	1.33	0.13	17.1	0.73	8.79
Day 53, 9 am					308	5	234	6	<1	7	<1	<1	20	45	1	12

Table 7. Alkalinity and Concentrations of Trace Metals and Metalloids Released: Point Sturt, Freshwater Core 4

Sampling	Alkalinity mg CaCO <sub>3</sub> /L	Acidity	Cl mg/L	SO <sub>4</sub> mg/L	Al µg/L	Fe µg/L	Mn µg/L	As µg/L	Cd µg/L	Co µg/L	Cr µg/L	Cu µg/L	Ni µg/L	Pb µg/L	V µg/L	Zn µg/L
Day 1, 9 am					23	1	24	0.86	1.20	0.87	<0.02	10.3	0.17	2.30	0.51	11.7
Day 1, 12 pm					6	<1	9	0.91	1.67	0.30	<0.02	18.4	0.06	1.23	0.56	6.38
Day 1, 3 pm		6			<1	<1	7	0.79	1.30	0.21	<0.02	19.0	0.03	1.06	0.38	4.14
Day 2, 9 am		3			<1	<1	9	0.70	0.98	0.28	<0.02	18.5	0.06	1.13	0.31	3.75
<b>Water change</b>																
Day 2, 3 pm		6	503		<1	<1	2	0.83	0.15	<0.15	0.30	3.34	0.14	2.12	0.50	2.52
Day 4, 9 am	72		502		5	4	1	0.74	0.16	<0.15	<0.02	4.59	<0.03	0.74	0.31	1.24
<b>Water change</b>																
Day 4, 10 am					9	<1	1	0.89	0.10	<0.15	<0.02	1.83	<0.03	0.67	0.60	2.16
Day 4, 3 pm	81		501	83	<2	<1	2	0.87	0.10	<0.15	<0.02	1.95	<0.03	0.71	0.50	2.35
Day 7, 9 am	83	2	497	84	3	<1	1	0.80	0.09	<0.15	<0.02	3.47	0.06	0.78	0.40	4.22
<b>Water change</b>																
Day 10, 9 am	85	12	496	84	4	<1	<1	0.74	0.07	<0.15	<0.02	2.10	0.06	0.67	0.42	0.72
<b>Water change</b>																
Day 17, 9 am	82	2	502	78	<2	<1	<1	0.94	0.26	<0.15	<0.02	2.32	<0.03	0.66	0.38	1.44
<b>Resuspension event 1</b>																
Day 17, 11 pm					<2	<1	11	0.70	0.09	0.34	<0.02	1.28	<0.03	1.28	0.18	0.82
Day 17, 3 pm	55	2	498	81	<2	<1	11	0.74	0.08	0.34	<0.02	1.25	<0.03	1.22	0.21	0.75
Day 18, 9 am	48	2	502	80	<2	<1	9	0.74	0.06	0.25	<0.02	1.20	<0.03	1.01	0.24	0.67
Day 21, 9 am	48	4	504	83	<2	<1	<1	0.91	<0.05	<0.15	<0.02	1.27	<0.03	0.59	0.32	0.30
<b>Resuspension event 2</b>																
Day 21, 11 am					<2	1	8	0.58	0.13	0.22	<0.02	1.01	0.05	0.89	0.19	0.87
Day 21, 3 pm	33	2	491	85	<2	<1	8	0.56	0.06	0.20	<0.02	1.19	0.14	0.87	0.20	2.20
Day 23, 9 am	35	8	505	82	<1	<1	2	0.83	<0.05	<0.15	<0.02	1.06	<0.03	0.54	0.28	0.10
Day 25, 9 am					<1	<1	<1	0.73	<0.05	<0.15	<0.02	1.07	<0.03	0.45	0.32	0.13
Day 28, 9 am					<1	<1	<1	0.96	<0.05	<0.15	<0.02	1.16	0.40	<0.14	0.34	0.18
<b>Resuspension event 3</b>																
Day 28, 3 pm					<1	<1	<1	0.61	<0.05	<0.15	<0.02	0.97	<0.03	0.43	0.24	0.12
Day 30, 9 am					1	<1	<1	0.81	<0.05	0.04	0.03	1.11	<0.03	0.51	0.35	0.06
Day 32, 9 am					<1	6	<1	0.79	<0.05	0.04	0.02	1.11	<0.03	0.43	0.39	0.08
Day 39, 9 am					<2	<1	<1	1.09	0.02	<0.15	0.04	1.19	<0.03	0.51	<2	<0.59
Day 46, 9 am	33	1	515	81	19	1	<1	1.06	<0.05	0.08	0.03	1.18	<0.03	0.61	<1	<0.59
Day 53, 9 am					17	6	<0.3	6	<1	0	<1	<1	2	33	1	2

Table 8. Alkalinity and Concentrations of Trace Metals and Metalloids Released: Point Sturt, Seawater Core 5

Sampling	Alkalinity mg CaCO <sub>3</sub> /L	Acidity	Cl mg/L	SO <sub>4</sub> mg/L	Al µg/L	Fe µg/L	Mn µg/L	As µg/L	Cd µg/L	Co µg/L	Cr µg/L	Cu µg/L	Ni µg/L	Pb µg/L	V µg/L	Zn µg/L
Day 1, 9 am					86	52	300	3.04	0.85	1.93	1.67	0.67	<0.03	4.30	0.83	4.33
Day 1, 12 pm					11	<7	10	2.42	0.52	0.554	0.17	1.89	<0.03	1.24	0.95	1.94
Day 1, 3 pm		15	19900		13	<7	14	2.16	0.42	0.57	0.34	2.35	<0.03	1.20	1.02	1.31
Day 2, 9 am		17	19700		97	<7	84	2.68	0.53	3.28	0.69	2.65	1.47	7.10	1.21	5.08
<b>Water change</b>																
Day 2, 3 pm		19	19500		140	<7	39	1.37	0.13	1.45	0.45	0.76	0.45	3.16	1.17	1.42
Day 4, 9 am	81		19500		120	<7	300	2.68	0.60	11.7	0.28	2.32	5.94	25.4	0.87	10.5
<b>Water change</b>																
Day 4, 10 am					110	<7	37	2.35	0.05	1.51	0.36	0.53	0.81	3.18	1.33	0.84
Day 4, 3 pm	113		19800	3190	150	<7	50	2.64	0.11	2.09	0.48	0.71	1.03	4.16	1.33	1.12
Day 7, 9 am	81	18	19300	3190	72	<7	320	2.29	0.41	12.0	0.41	2.42	8.00	24.6	0.86	8.27
<b>Water change</b>																
Day 10, 9 am	99		19500	3080	74	<7	180	1.85	0.18	6.67	0.32	1.85	6.10	13.5	0.94	4.91
<b>Water change</b>																
Day 17, 9 am	82	8			49	<7	200	2.33	0.17	6.4	0.42	1.56	6.59	11.8	0.98	4.36
<b>Resuspension event 1</b>																
Day 17, 11 pm					<4	<7	250	2.05	0.21	8.26	0.33	0.87	2.72	14.6	0.33	9.34
Day 17, 3 pm	55	12			<4	<7	250	1.44	0.13	8.30	0.20	0.65	2.74	14.4	0.29	7.13
Day 18, 9 am	49	2			<4	<7	250	1.84	0.22	8.19	0.20	0.51	1.60	13.6	0.47	7.83
Day 21, 9 am	55	12			<4	<7	230	2.79	0.04	7.13	0.08	0.90	0.49	9.84	0.88	5.71
<b>Resuspension event 2</b>																
Day 21, 11 am					25	<7	290	2.79	0.29	9.88	0.15	0.68	12.3	14.1	0.35	9.57
Day 21, 3 pm	29	12			12	<7	280	3.01	0.19	10.4	0.11	0.58	11.2	14.9	0.47	11.0
Day 23, 9 am	29	12			<4	<7	260	2.73	0.31	8.69	0.09	0.59	4.08	12.2	0.56	7.75
Day 25, 9 am					<4	<7	240	1.91	0.25	7.69	0.10	0.62	1.87	9.97	0.59	6.79
Day 28, 9 am					<4	<7	240	2.36	0.26	7.03	0.09	0.68	1.10	8.11	0.67	4.98
<b>Resuspension event 3</b>																
Day 28, 3 pm					5	22	260	1.74	0.24	7.99	0.08	0.45	3.20	10.7	0.49	6.73
Day 30, 9 am					<4	4	250	2.35	0.28	<0.15	7.41	0.55	1.08	8.86	0.45	4.28
Day 32, 9 am					<4	<7	230	2.70	0.25	6.54	0.06	0.47	0.42	7.68	0.53	3.44
Day 39, 9 am					<10	<10	184	1.90	0.28	4.59	0.04	0.71	0.15	6.58	<2	2.33
Day 46, 9 am	40	12	17800	2600	<10	<10	100	2.39	0.21	2.47	0.24	0.94	0.19	4.99	12	2.13
Day 53, 9 am					49	78	44	83	<11	<11	<3	<1	35	767	14	65

Table 9. Alkalinity and Concentrations of Trace Metals and Metalloids Released: Boggy Creek, Freshwater Core 1

Sampling	Alkalinity mg CaCO <sub>3</sub> /L	Acidity	Cl mg/L	SO <sub>4</sub> mg/L	Al µg/L	Fe µg/L	Mn µg/L	As µg/L	Cd µg/L	Co µg/L	Cr µg/L	Cu µg/L	Ni µg/L	Pb µg/L	V µg/L	Zn µg/L
Day 1, 9 am					5	3	180	2.39	0.07	0.66	<0.02	5.09	<0.03	1.59	5.78	2.44
Day 1, 12 pm					29	9	350	4.37	0.08	1.38	0.07	11.6	0.05	2.65	12.8	3.11
Day 1, 3 pm		3			22	9	290	4.45	0.08	1.21	0.03	15.1	0.06	2.49	13.1	2.58
Day 2, 9 am		6	734		16	17	380	6.26	0.08	1.71	0.15	13.6	0.07	3.56	22.1	1.65
<b>Water change</b>																
Day 2, 3 pm		4	547		<1	3	97	2.02	0.06	0.44	<0.02	3.24	<0.03	1.40	7.42	2.25
Day 4, 9 am	104		634		3	18	280	6.42	0.03	1.37	0.18	6.36	0.18	3.35	25.8	1.80
<b>Water change</b>																
Day 4, 10 am					<2	3	79	2.04	0.05	0.31	<0.02	1.98	<0.03	1.14	7.97	1.93
Day 4, 3 pm	95		542		<2	3	110	2.37	<0.05	0.38	0.05	2.20	<0.03	1.33	10.9	1.72
Day 7, 9 am	126		648	355	2	19	290	6.49	<0.05	1.29	0.23	5.29	0.05	3.61	28.0	1.75
<b>Water change</b>																
Day 10, 9 am	135		630	325	<2	18	280	6.76	<0.05	1.03	0.24	4.25	0.06	3.35	26.7	1.65
<b>Water change</b>																
Day 17, 9 am	124	4	710	413	<2	36	520	7.47	<0.05	1.23	0.32	4.31	0.08	4.42	23.7	1.89
<b>Resuspension event 1</b>																
Day 17, 11 pm					21	2700	3700	9.93	0.11	13.9	0.54	3.98	0.59	19.9	15.3	9.80
Day 17, 3 pm	163	8	919	1180	15	1300	3700	9.12	0.10	11.9	0.52	3.79	0.58	17.4	13.5	8.60
Day 18, 9 am	150	8	922	1260	8	490	3600	9.56	0.12	6.44	0.47	3.92	0.63	13.1	15.3	5.10
Day 21, 9 am	156	12	932	1300	3	310	3400	9.54	0.05	5.09	0.50	3.61	0.45	11.0	13.6	4.90
<b>Resuspension event 2</b>																
Day 21, 11 am					34	7600	5900	12.0	0.09	21.1	0.74	3.08	0.71	29.7	9.75	17.1
Day 21, 3 pm	146	12	1050	1910	17	5500	5800	8.43	0.08	21.4	0.69	2.91	0.52	30.5	8.71	16.9
Day 23, 9 am	126	8	1040	1790	12	5800	1300	6.15	0.11	16.7	0.48	3.92	0.57	24.0	5.70	10.3
Day 25, 9 am					9	5900	1100	6.07	0.10	13.8	0.49	4.04	0.56	20.8	6.91	9.09
Day 28, 9 am					8	6000	1100	6.17	0.10	12.2	0.48	3.53	0.63	18.7	6.68	8.25
<b>Resuspension event 3</b>																
Day 28, 3 pm					18	10000	9500	10.6	0.08	20.8	0.72	2.46	1.04	31.5	8.06	14.9
Day 30, 9 am					16	9200	3400	6.98	0.06	22.3	0.79	3.22	1.04	30.1	6.54	10.0
Day 32, 9 am					12	8900	3400	6.99	0.09	17.8	0.61	3.22	1.01	23.2	7.05	7.87
Day 39, 9 am					14	8140	3100	7.76	0.11	12.0	0.52	4.71	0.84	22.5	<10	9.42
Day 46, 9 am	128	8	1130	2430	10	7620	2540	6.62	0.11	9.80	0.51	5.23	0.97	17.6	14	8.48
Day 53, 9 am					39	2480	7840	12	<1	6	<1	<1	14	68	10	12

Table 10. Alkalinity and Concentrations of Trace Metals and Metalloids Released: Boggy Creek, Seawater Core 2

Sampling	Alkalinity mg CaCO <sub>3</sub> /L	Acidity	Cl mg/L	SO <sub>4</sub> mg/L	Al µg/L	Fe µg/L	Mn µg/L	As µg/L	Cd µg/L	Co µg/L	Cr µg/L	Cu µg/L	Ni µg/L	Pb µg/L	V µg/L	Zn µg/L
Day 1, 9 am					300	7	4600	4.16	0.63	23.0	0.45	4.22	0.64	30.9	9.00	28.1
Day 1, 12 pm					180	<7	5900	2.97	1.13	32.2	0.41	8.40	0.32	35.4	9.86	32.6
Day 1, 3 pm		23	19600		160	<7	5800	3.64	0.92	31.0	0.55	9.31	0.29	32.1	10.5	30.1
Day 2, 9 am		25	19000		145	31	9550	3.72	1.61	51.8	0.92	8.28	0.30	51.4	16.8	43.9
<b>Water change</b>																
Day 2, 3 pm		17	19700		56	<7	1700	1.80	0.33	8.35	0.57	1.76	<0.03	8.51	5.19	7.16
Day 4, 9 am	118		19600		39	55	5400	3.70	0.87	26.7	0.66	3.82	0.05	22.3	17.8	18.7
<b>Water change</b>																
Day 4, 10 am					5	<7	840	2.41	0.14	4.71	0.40	0.80	<0.03	4.07	5.15	2.89
Day 4, 3 pm	118		19800	3250	19	<7	1100	1.98	0.21	6.62	0.41	1.01	<0.03	5.61	7.17	4.45
Day 7, 9 am	143	23	19500	3560	8	110	4100	3.27	0.60	21.9	0.56	2.70	0.60	17.1	16.3	16.4
<b>Water change</b>																
Day 10, 9 am	151	18	19700	3490	<4	140	3200	2.25	0.60	19.3	0.35	1.89	0.06	13.7	13.0	12.7
<b>Water change</b>																
Day 17, 9 am	141	19			<4	350	4200	2.25	0.50	25.2	0.40	2.20	<0.03	17.1	7.89	14.5
<b>Resuspension event 1</b>																
Day 17, 11 pm					31	19000	8400	3.74	0.72	78.3	0.59	1.99	0.40	66.3	6.45	69.4
Day 17, 3 pm	106	31			23	17000	8500	3.75	0.77	79.2	0.56	2.51	0.40	67.6	2.84	79.0
Day 18, 9 am	128	35			<4	8600	8800	3.00	0.91	82.7	0.45	1.88	<0.03	66.4	1.12	63.6
Day 21, 9 am	134	12			<4	410	8800	2.58	0.72	72.3	0.21	3.77	0.03	47.6	0.65	36.9
<b>Resuspension event 2</b>																
Day 21, 11 am					38	26000	12000	7.61	0.66	129	1.76	2.87	0.75	88.6	5.63	84.0
Day 21, 3 pm	126	42			27	24000	13000	5.69	0.67	119	0.58	2.70	0.20	80.1	2.30	82.8
Day 23, 9 am	130	23			<4	6000	12000	4.14	0.73	108	0.358	2.61	0.04	71.4	0.63	56.3
Day 25, 9 am					<4	2900	11000	3.00	0.51	101	0.16	2.38	0.03	66.1	0.40	50.3
Day 28, 9 am					4	8200	12000	3.58	0.51	97.8	0.31	2.25	<0.03	5.90	0.57	42.5
<b>Resuspension event 3</b>																
Day 28, 3 pm					63	49000	15000	10.4	0.17	117	0.62	1.69	0.22	89.3	2.81	51.3
Day 30, 9 am					15	19000	14000	6.34	0.20	7.41	<0.053	1.27	<0.03	82.6	0.64	41.5
Day 32, 9 am					<4	5100	14000	5.89	0.25	126	0.31	1.62	<0.03	91.8	0.64	37.0
Day 39, 9 am					<10	514	13900	5.72	0.28	76.1	0.45	3.55	<0.03	74.8	<2	18.6
Day 46, 9 am	118	31	1650	459	<10	1290	14300	4.36	0.25	64.7	0.32	3.80	0.04	64.1	<10	17.1
Day 53, 9 am					4	214	13400	68	<11	38	<3	<1	67	686	31	46



Table 11 Alkalinity and Concentrations of Trace Metals and Metalloids Released: Boggy Creek, Seawater Core 9

Sampling	Alkalinity mg CaCO <sub>3</sub> /L	Acidity	Cl mg/L	SO <sub>4</sub> mg/L	Al µg/L	Fe µg/L	Mn µg/L	As µg/L	Cd µg/L	Co µg/L	Cr µg/L	Cu µg/L	Ni µg/L	Pb µg/L	V µg/L	Zn µg/L
Day 1, 9 am					190	<7	6000	2.50	0.96	17.4	0.43	4.80	<0.03	27.9	3.24	14.1
Day 1, 12 pm					170	<7	4800	3.77	1.14	14.2	0.57	7.41	0.33	18.1	5.02	10.4
Day 1, 3 pm		19	19800		140	<7	4800	2.29	1.02	15.0	0.51	9.31	<0.03	16.4	5.42	8.35
Day 2, 9 am		19	20200		71	<7	7700	2.47	1.39	20.8	0.63	10.0	0.20	20.0	8.59	9.75
<b>Water change</b>																
Day 2, 3 pm		17	19800		23	<7	1400	2.76	0.25	4.16	0.38	1.75	<0.03	3.83	3.06	1.23
Day 4, 9 am	118				14	<7	7200	2.44	1.18	19.8	0.35	4.17	<0.03	16.7	9.08	6.40
<b>Water change</b>																
Day 4, 10 am					<4	<7	1200	2.03	0.18	3.87	0.45	1.03	<0.03	3.23	3.14	1.64
Day 4, 3 pm	118		19700	3320	42	<7	1600	1.88	0.28	5.64	0.44	1.14	<0.03	4.41	3.95	2.38
Day 7, 9 am	143	17	19800	3750	9	57	7700	3.48	1.14	28.5	0.44	5.37	<0.03	21.5	7.73	9.86
<b>Water change</b>																
Day 10, 9 am	144	18	19400	3550	7	110	5600	2.01	0.67	28.1	0.38	1.83	<0.03	21.2	4.58	9.71
<b>Water change</b>																
Day 17, 9 am	128	15			<4	79	6000	2.09	0.55	34.1	0.18	2.01	<0.03	24.1	2.47	10.6
<b>Resuspension event 1</b>																
Day 17, 11 pm					56	19000	11000	3.86	1.02	101.0	0.65	1.89	0.15	108	3.16	71.6
Day 17, 3 pm	18	27			31	18000	11000	3.53	1.16	107.2	0.58	2.89	<0.03	113	0.85	74.0
Day 18, 9 am	77	19			<4	8400	11000	2.27	1.02	103	0.35	2.14	<0.03	105	0.30	63.2
Day 21, 9 am	108	23			<4	100	10000	3.02	0.85	89.7	0.25	5.35	<0.03	73.1	0.23	32.9
<b>Resuspension event 2</b>																
Day 21, 11 am					34	18000	13000	5.60	0.75	128	0.48	3.07	0.22	100	3.78	59.5
Day 21, 3 pm	95	39			15	16000	13000	5.25	0.75	127	0.42	3.14	0.09	100	1.45	62.9
Day 23, 9 am	95	23			<4	3200	12000	3.96	0.80	114	0.17	2.97	<0.03	86.1	0.27	42.8
Day 25, 9 am					<4	750	12000	2.64	0.72	103	0.19	3.07	<0.03	76.0	0.20	33.4
Day 28, 9 am					<4	6100	12000	3.70	0.60	103	0.23	2.86	<0.03	77.7	0.30	28.4
<b>Resuspension event 3</b>																
Day 28, 3 pm					58	41000	14000	8.56	0.17	129	0.40	1.49	0.04	104	1.96	35.5
Day 30, 9 am					12	13000	14000	4.88	0.22	111	0.42	2.12	<0.03	91.5	0.35	26.9
Day 32, 9 am					<4	2300	13000	3.79	0.15	110	0.16	2.12	<0.03	82.3	0.44	22.1
Day 39, 9 am					<10	867	13400	4.55	0.25	86.7	0.21	5.80	0.10	85.7	<2	15.8
Day 46, 9 am	93	26	17880	4230	<10	527	12800	3.90	<0.05	80.7	0.19	5.66	0.03	75.0	7	12.8
Day 53, 9 am					8	90	12600	85	<11	69	0	<1	95	703	26	47

#### 4.1.5 Porewater pH and dissolved metals

The greater density of seawater than freshwater may potentially induce greater downward transport of acidity and metals during the initial infiltration period. Although pH measurements were made on days 2 and 10, to depths of up to 5 cm below the sediment water interface (Table 3), it was unclear whether differences in water density influenced the differences in pH between treatments (insufficient data to test significance).

At the completion of the 8-week reactor experiments, the sediment cores were deconstructed and the porewater pH and dissolved metals measured (Table 12). Due to the short periods of resuspension of the top 2-3 cm of the cores in the middle stages of the tests, differences in porewater pH were difficult to interpret in relation to water type. For both Boggy Creek soil cores inundated with seawater the pH was lower than the one Boggy Creek soil core inundated with freshwater, at all depths. However, due to the low number of replicates, it was not possible to determine whether these differences were significant.

There was relatively high variability in the final porewater pH between the replicate cores (i.e. same site, same inundation water type). However, the trend was the same for all treatments. Although the pH of the surface sediment was similar to that measured in soils collected from nearby sites (Table 2), the pH of the pore water became increasing more acidic at greater depths. These final pH values were also similar to those measured on days 2 and 10 of the inundation experiments. Comparison of the porewater pH values measured at a depth of 4 cm on the various days (2, 10, and 54) indicated that there may have been some neutralisation of the porewater in the seawater inundation tests with both soils (Tables 3 and 12).

In general, these porewater pH measurements indicated that little neutralisation of the acidity had occurred during the 8-week tests, and was consistent with the only minor changes to the overlying water pH that were observed (Tables 3 and 5). Generally the pH was  $\leq 3$  from 15 cm below the sediment water interface to the base of the cores at -20 cm.

**Table 12. Porewater pH at the Completion of the 8-week Inundation Experiments**

Depth cm	Boggy Creek Reactors			Point Sturt Reactors		
	Core 1 Freshwater	Core 2 Seawater	Core 9 Seawater	Core 3 Freshwater	Core 4 Freshwater	Core 5 Seawater
Paste-pH, 0-1	7.4	7.1	6.8			
Paste-pH, 1-5	5.6	3.9	3.3	2.9	3.0	2.9
0-3	6.8	6.1	6.0	3.9	6.5	6.5
3-6	6.5	6.0	5.2	3.2	4.2	5.4
6-9	6.0	5.8	4.3	3.0	3.4	3.5
9-12	4.7	4.1	3.4	2.8	3.2	3.1
12-15	3.9	3.3	3.2	2.7	3.0	3.0
15-18	3.1	2.8	2.7	2.6	2.9	2.8

The metal concentrations in the pore waters of the cores at the completion of the 56-day tests are shown in Table 13. For all elements, porewater concentrations were generally much greater in the seawater inundation tests than the freshwater inundation tests (Figure 3). For the majority of the metals and metalloids, the pore water concentrations increased with increasing sediment depth. This was consistent with the higher acidity (lower pH) of the deeper sediments (Figure 3). Iron(II), the major dissolved form of iron in the pore waters, is particularly redox sensitive (i.e. readily oxidised) and appeared to have a maxima at approximate 10 cm depth for most sediment cores. The concentrations of arsenic, a metalloid and oxy-anion that readily adsorbs to iron hydroxide phases and is also redox sensitive, is likely to have been significantly influenced by the porewater iron chemistry.

Table 13. Trace Metals and Metalloids in Sediment Pore Waters

Core	Al	Fe	Mn	As	Cd	Co	Cr	Cu	Ni	Pb	V	Zn
Depth, cm	mg/L			µg/L								
BC-1, 0-3	0.013	0.97	14.9	30	1	12	4	<10	35	206	<6	10
BC-1, 3-6	0.011	20.1	19.0	<20	<1	12	2	<10	49	204	<6	5
BC-1, 6-9	0.007	65.8	21.3	<20	<1	44	<2	<10	55	216	<6	15
BC-1, 9-11	0.22	378	30.5	50	3	236	4	<10	235	272	9	326
BC-1, 11-13	4.48	600	35.8	90	15	441	10	<10	472	247	52	915
BC-1, 13-15	22.1	234	45.0	50	15	534	16	40	636	354	73	1490
BC-2, 0-3	0.012	58.5	16.4	60	<1	26	4	<10	60	663	<6	10
BC-2, 3-6	0.012	146	20.7	50	<1	43	4	<10	85	664	<6	17
BC-2, 6-9	0.043	483	24.4	60	5	122	2	<10	91	683	9	55
BC-2, 9-12	0.49	1190	30.1	90	15	319	10	<10	177	606	42	386
BC-2, 12-15	18.9	881	33.2	120	23	400	16	<10	431	513	112	1110
BC-2, 15-17	62.5	22.2	35.2	60	11	390	31	97	638	636	6	1510
BC-9, 0-3	0.015	179	20.8	50	<1	122	<2	<10	166	746	8	1330
BC-9, 3-6	0.039	469	29.4	90	5	247	5	<10	244	654	15	1470
BC-9, 6-9	3.62	809	37.6	120	16	453	7	<10	482	578	45	1800
BC-9, 9-11	23.2	765	45.3	90	21	533	16	<10	629	630	147	1330
BC-9, 11-13	38.8	604	45.4	60	17	510	19	22	677	592	229	1480
BC-9, 13-15	100	220	52.4	90	17	523	42	99	805	527	215	1800
BC-9, 15-17	119	110	52.9	70	17	514	50	95	838	654	111	1710
PS-3, 0-3	1.35	0.11	0.54	<20	5	22	2	<10	40	42	<6	55
PS-3, 3-6	4.20	1.16	1.4	<20	5	52	16	<10	92	43	<6	52
PS-3, 6-9	88.6	4.90	2.4	90	9	89	42	18	149	50	10	103
PS-3, 9-11	1.88	11.7	4.2	<20	5	156	82	34	266	71	53	175
PS-3, 11-13	28.7	14.2	5.1	20	10	181	103	38	287	51	49	264
PS-3, 13-16	45.0	9.77	6.7	30	5	239	56	36	365	54	10	161
PS-4, 0-3	0.31	0.006	0.004	40	<1	<10	<2	<10	3	30	<6	<5
PS-4, 3-6	0.38	0.072	0.049	<20	29	<10	4	<10	7	81	<6	27
PS-4, 6-9	0.83	0.30	0.25	<20	1	11	6	<10	16	36	<6	21
PS-4, 9-12	1.06	0.44	0.48	<20	1	19	7	<10	40	39	<6	<5
PS-4, 12-15	1.16	0.57	0.69	<20	1	23	11	<10	51	79	<6	6
PS-4, 15-17	1.57	0.49	0.86	<20	1	27	3	<10	66	45	<6	59
PS-5, 0-3	0.003	0.008	0.022	30	<1	<10	4	<10	26	662	<6	72
PS-5, 3-6	0.14	0.050	0.045	50	<1	<10	2	<10	29	689	11	108
PS-5, 6-9	1.75	0.37	0.13	70	1	<10	5	14	39	1350	8	222
PS-5, 9-12	2.36	0.73	0.19	50	3	<10	10	15	27	1000	7	219
PS-5, 12-14	4.53	2.57	0.37	60	2	17	11	25	39	841	9	34
PS-5, 14-16	26.3	1.70	1.20	40	<1	51	32	42	99	723	15	140
PS-5, 16-18	33.1	1.93	1.43	40	<1	61	37	41	126	709	9	759

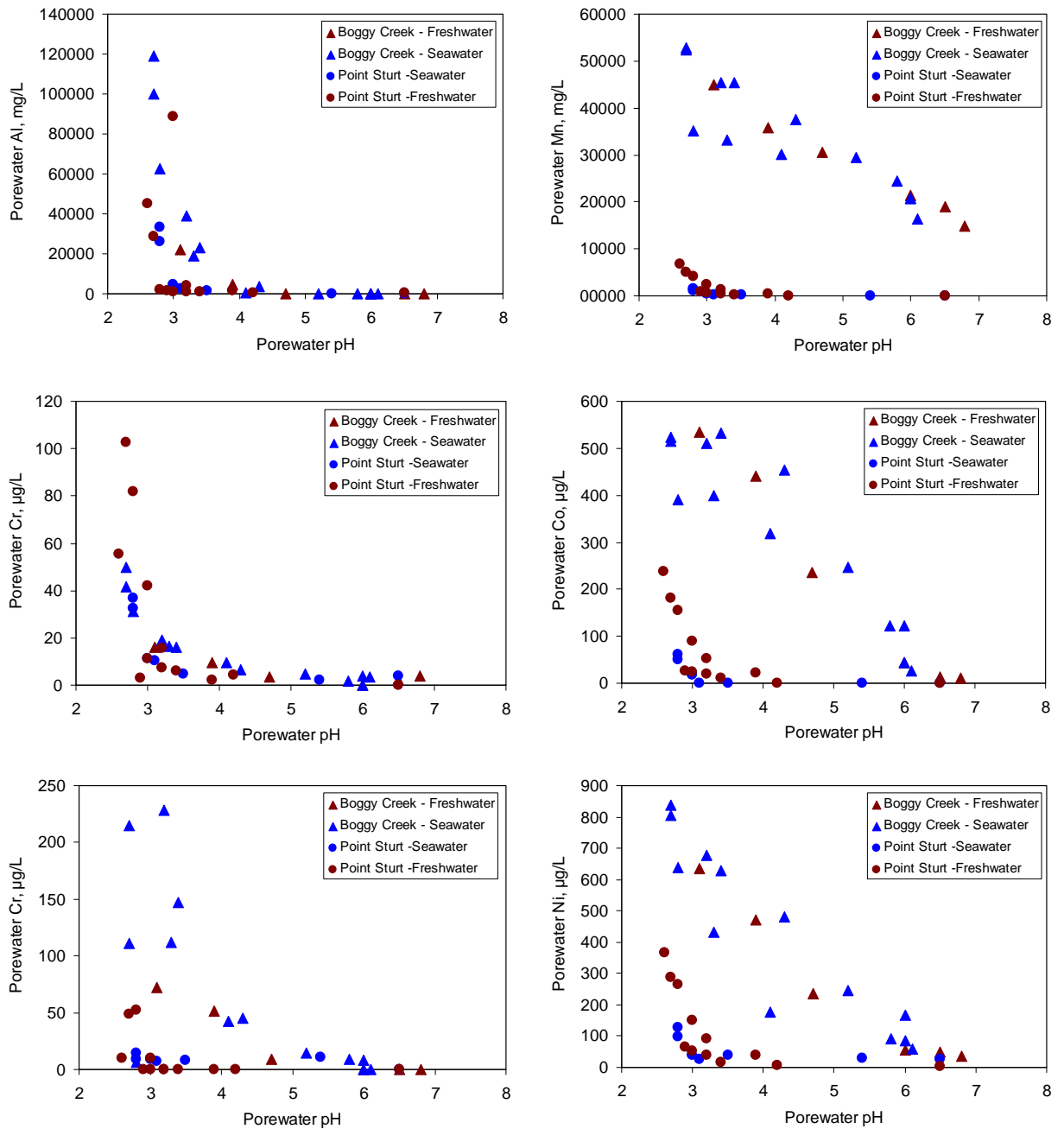


Figure 3. Relationship between porewater pH and porewater Al, Mn, Cr, Co, Cr and Ni concentrations: Point Sturt (2× freshwater, 1× seawater) and Boggy Creek (1× freshwater, 2× seawater) cores.

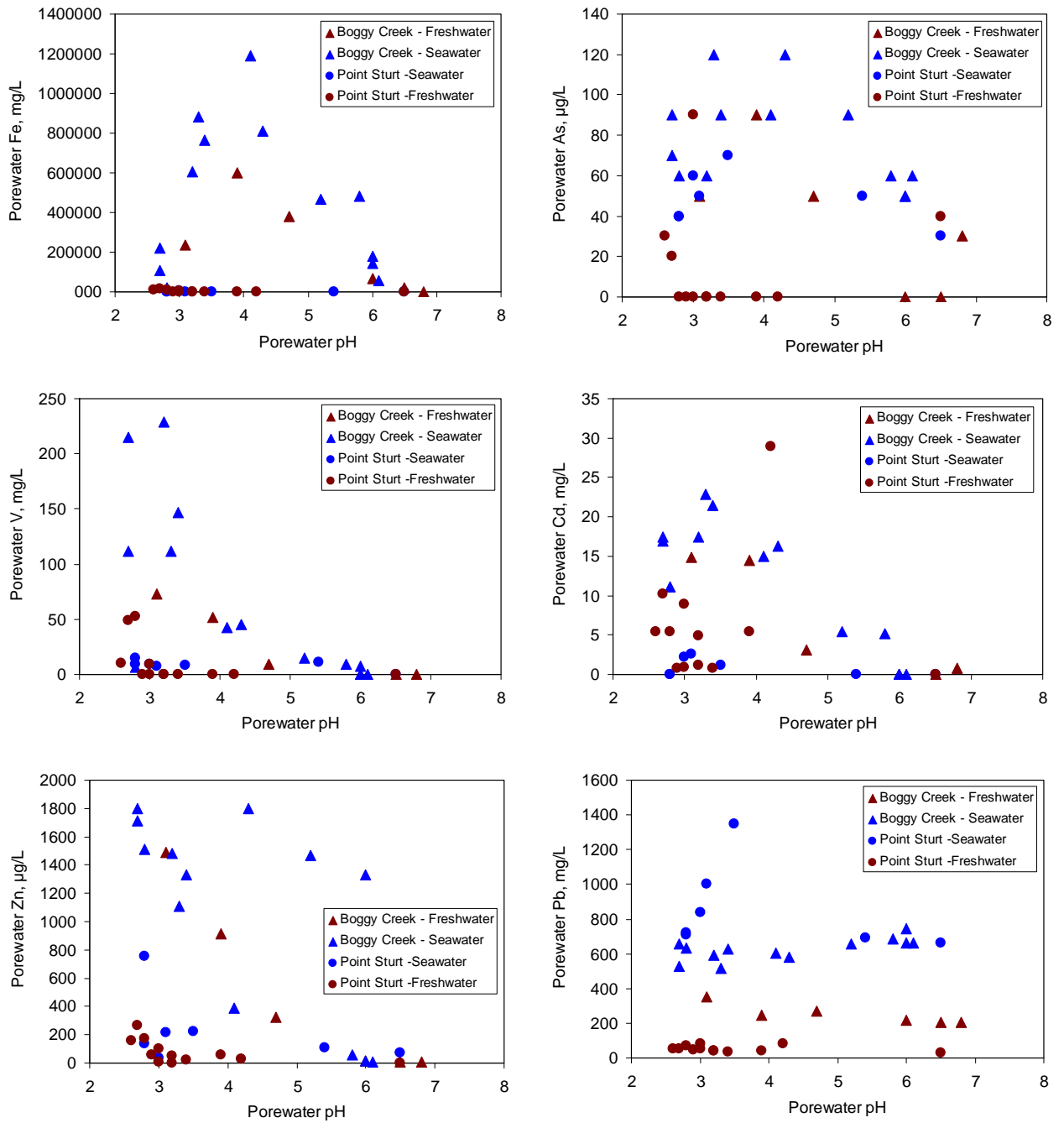


Figure 4. Relationship between porewater pH and porewater Fe, As, V, Cd, Zn and Pb concentrations: Point Sturt (2× freshwater, 1× seawater) and Boggy Creek (1× freshwater, 2× seawater) cores.

## 4.2 Short-term, Rapid Release of Acidity and Metals from Soils

To enable better comparisons between the results of the field trials, the mid-term acidity and metal release in the corer-reactors, and the rapid remobilisation experiments undertaken previously, the short-term, rapid release of acidity and metals from a number of the soils was also investigated. To provide information of mechanisms of acid and metal release, experiments were undertaken to determine: (i) the kinetics of metal release over 24 h; (ii) the influence of soil:water ratio on the amount of substance released; and (iii) acid and metal release in 2<sup>nd</sup> and 3<sup>rd</sup> cycles.

### 4.2.1 Effect of time on acidity and metal release

The kinetics of metal mobilisation, along with changes in pH, was investigated for three soils using both freshwater and seawater at a soil:water ratio of 100 g soil/L and a mixing (remobilisation) period of 0.5, 3, 7 and 24 h (Tables 14-16). The dissolved oxygen concentrations were 8-9 mg/L during these tests.

For both freshwater and seawater experiments, the mixing of the soil and waters caused the pH to decrease (Table 14). The decrease in water pH was greater for freshwater than for seawater. The pH change caused by mixing of the soil and water tended to stabilise within a few hours of mixing, after which the pH remained relatively constant. The soils collected from greater depth was more acidic and caused a larger decrease in water pH.

The metal release measured after 0.5 h was within an order of magnitude of the metal release measured after 24 h. All metal concentrations measured during the resuspension period were within a factor of two of the mean concentration measured.

For Al, Fe and Mn, the metal release generally increased with increasing period of resuspension. For the other metals/metalloids, the concentration of metals released with 30 minutes was not generally significantly different to that measured after 24 h (i.e. concentrations varied within a 2-4 fold range) (Table 15). For the majority of cases (for all time periods), greater concentrations of metals were released from the soils by mixing with seawater than for the soils mixed with freshwater. Greater concentrations of iron were measured in the freshwater rapid release tests than in the seawater tests and was attributed not to greater release of iron, but greater removal of iron which rapidly flocculates in the higher ionic strength seawater.

**Table 14. Effect of Time on Acidity and Metal Release during Rapid Remobilisation Tests**

Sample site	Time, h			
	0.5	3	7	24
<i>Remobilisation pH in freshwater</i>				
Murray River Water Control (Blank)	7.6	7.6	7.6	7.6
<b>Boggy Creek</b>				
Core 9, 0-1 cm	7.2	6.9	7.0	7.2
Core 9, 0-5 cm	4.6	4.4	4.1	4.2
Core 9, 0-5 cm (dup.)	5.1	4.2	4.1	4.3
<b>Pt. Sturt</b>				
Core 4, 0-5cm	6.7	6.5	6.4	6.5
<i>Remobilisation pH in seawater</i>				
Seawater Control (Blank)	7.7	7.7	7.7	7.7
<b>Boggy Creek</b>				
Core 9, 0-1 cm	7.0	6.7	6.7	6.9
Core 9, 0-5 cm	5.4	4.3	4.2	4.3
Core 9, 0-5 cm (dup.)	5.4	4.3	4.7	4.1
<b>Pt. Sturt</b>				
Core 4, 0-5cm	6.8	6.6	6.5	6.6

Table 15. Effect of Time on the Rapid Remobilisation of Trace Metals and Metalloids

Sampling	Time h	Al µg/L	Fe µg/L	Mn µg/L	As µg/L	Cd µg/L	Co µg/L	Cr µg/L	Cu µg/L	Ni µg/L	Pb µg/L	V µg/L	Zn µg/L
<b>Boggy Creek in freshwater</b>													
Core 9, 0-1 cm	0.5	2	10	3700	2.24	0.09	3.20	0.17	4.10	0.06	5.7	12.1	9.83
Core 9, 0-1 cm	3	<1	11	5700	2.68	0.12	10.3	0.12	5.87	<0.03	11.5	6.86	5.94
Core 9, 0-1 cm	7	<1	14	6000	2.87	0.14	6.11	0.15	6.86	0.02	8.1	6.87	3.95
Core 9, 0-1 cm	24	3400	130	4000	3.31	0.10	4.32	0.17	8.54	<0.03	6.23	16.7	3.31
<b>Boggy Creek in seawater</b>													
Core 9, 0-1 cm	0.5	7	8	9600	2.07	1.13	26.2	0.68	3.45	0.13	22.7	5.62	14.1
Core 9, 0-1 cm	3	<4	12	14000	3.23	1.79	16.6	0.74	5.84	<0.03	15.5	8.72	12.4
Core 9, 0-1 cm	7	<4	<7	12000	5.68	1.55	17.2	0.45	5.87	0.07	14.5	7.35	10.3
Core 9, 0-1 cm	24	<4	<7	18000	4.82	1.54	9.79	0.34	8.14	<0.03	8.9	11.1	10.4
<b>Boggy Creek in freshwater</b>													
Core 9, 0-5 cm	0.5	2400	50	2400	4.63	0.93	41.8	0.60	2.54	0.09	96	0.31	55.7
Core 9, 0-5 cm	3	3000	110	3100	6.68	1.25	51.5	0.87	3.82	0.29	116	0.55	73.5
Core 9, 0-5 cm	7	3200	110	4200	6.63	2.03	90.5	0.92	1.96	2.81	173	0.48	106
Core 9, 0-5 cm	24	3500	120	5100	5.75	1.67	95.0	0.83	4.00	0.46	177	0.53	114
<b>Boggy Creek in seawater</b>													
Core 9, 0-5 cm	0.5	650	7	2500	6.24	1.16	47.3	0.71	1.71	0.74	111	0.56	54.4
Core 9, 0-5 cm	3	6200	94	4500	12.6	2.49	98.7	1.48	5.01	7.10	225	0.49	129
Core 9, 0-5 cm	7	6200	150	4000	4.01	1.21	57.1	0.82	3.87	0.42	123	0.48	76.1
Core 9, 0-5 cm	24	6200	200	3900	12.0	1.68	74.6	1.55	6.19	12.3	171	1.15	114

Table 15. Effect of Time on the Rapid Remobilisation of Trace Metals and Metalloids (Continued)

Sampling	Time h	Al µg/L	Fe µg/L	Mn µg/L	As µg/L	Cd µg/L	Co µg/L	Cr µg/L	Cu µg/L	Ni µg/L	Pb µg/L	V µg/L	Zn µg/L
<b>Point Sturt in freshwater</b>													
Core 4, 0-5 cm	0.5	1	<1	79	0.56	0.12	1.96	<0.02	0.75	<0.03	3.69	0.17	12.1
Core 4, 0-5 cm	3	<1	<1	82	0.41	0.23	1.77	<0.02	0.69	<0.03	2.35	0.22	3.29
Core 4, 0-5 cm	7	2	2	80	0.53	0.11	1.63	<0.02	0.77	0.08	2.06	0.23	7.18
Core 4, 0-5 cm	24	<1	17	73	0.58	0.08	1.44	<0.02	0.54	<0.03	1.80	0.23	1.42
<b>Point Sturt in seawater</b>													
Core 4, 0-5 cm	0.5	7	<7	100	2.07	0.47	3.48	0.36	0.60	<0.03	6.98	0.21	3.44
Core 4, 0-5 cm	3	<4	<7	92	2.38	0.50	2.97	0.60	0.55	<0.03	4.48	0.32	1.40
Core 4, 0-5 cm	7	<4	<7	94	2.40	0.22	3.03	0.43	0.61	<0.03	5.09	0.28	1.33
Core 4, 0-5 cm	24	<4	<7	100	2.73	0.37	3.49	0.40	0.43	<0.03	5.10	0.27	1.74
<b>Boggy Creek in freshwater</b>													
Core 9, 0-5 cm (dup.)	0.5	780	27	2500	3.43	0.76	35.2	0.35	1.73	0.07	81.1	0.33	48.6
Core 9, 0-5 cm (dup.)	3	1700	71	3300	4.00	1.07	49.8	0.62	2.33	0.24	105	0.38	62.7
Core 9, 0-5 cm (dup.)	7	5100	170	3700	7.78	1.54	57.3	1.00	4.77	0.42	136	0.55	78.5
Core 9, 0-5 cm (dup.)	24	3400	130	4000	4.28	1.70	89.6	0.91	3.35	0.44	157	0.47	112
<b>Boggy Creek in seawater</b>													
Core 9, 0-5 cm (dup.)	0.5	980	25	3300	9.97	1.53	56.4	0.54	1.84	0.93	139	0.64	66.8
Core 9, 0-5 cm (dup.)	3	5800	92	3800	15.8	16.3	69.8	1.18	5.19	4.92	183	0.65	98.6
Core 9, 0-5 cm (dup.)	7	6200	97	3800	14.9	2.51	74.8	1.20	5.14	7.05	190	0.30	103
Core 9, 0-5 cm (dup.)	24	4500	79	3700	9.16	1.56	67.1	1.05	3.70	3.31	148	0.32	101



## 4.2.2 Effect of soil:water ratio on acidity and metal release

The amount of solute released from soils shaken in water may increase with increasing total suspended solids (TSS) concentration, and for metals present as soluble salts (e.g.  $\text{MgSO}_4$ ), this release may continue with increasing TSS concentration, until saturation (relative to maximum solubility) is reached. The relationship between TSS and metal release, pH and conductivity was investigated for three soils using both fresh water and seawater at soil:water ratios of 0.1, 1, 10 and 100 g soil/L and a resuspension period of 24 h (Tables 16-18). The dissolved oxygen concentrations were 8-9 mg/L during these tests.

At higher TSS concentration, the soil-water suspension pH decreased by a greater extent. The changes in pH were slightly greater for freshwater than seawater experiments, consistent with the greater pH-buffering capacity of seawater. Increasing the ratio of soil:water resulted in increased SEC of the waters for the Boggy Creek soils, but not for the Point Sturt soil (particularly evident from the freshwater tests). This indicates that the Boggy Creek soils have higher somewhat higher labile 'salt' concentrations (major anions and cations) than the Point Sturt soils.

The differences in TSS resulted in a wide variety of changes in the concentrations of dissolved metals/metalloids being released. For the Boggy Creek soils, the amount of iron released increased in freshwater tests with increasing TSS concentration and the amount of manganese released in seawater tests increased with increasing TSS concentration. However, increases in TSS concentration had only minor effects on the release of most of the metals/metalloids (i.e. the concentrations varied without clear trend by a factor of 2-4) (Table 18). These results indicate that, beyond the initial release of relatively large amounts of Fe and Mn, the majority of the metals appear to be in pseudo-equilibrium with the solid phase, i.e. the dissolved concentrations become relatively independent of concentration of soil phase material (as predicted for thermodynamic equilibrium). The kinetics of mineral solubilisation and the formation of new mineral phases are likely to control concentrations of dissolved metals over longer time periods.

**Table 16. Effect of Soil:water Ratio on pH During Rapid Remobilisation Tests**

Sample site	Soil:water ratio			
	0.1	1	10	100
<i>Remobilisation pH in freshwater</i>				
Murray River Water Control (Blank)	7.3			
<b>Boggy Creek in freshwater</b>				
Core 9, 0-1 cm	7.3	7.7	7.7	7.3
Core 9, 0-5 cm	7.6	7.5	6.8	4.4
<b>Point Sturt in freshwater</b>				
Core 4, 0-5cm	7.3	7.6	7.6	6.9
Core 4, 0-5 cm (dup.)	7.7	7.6	7.5	7.1
<i>Remobilisation pH in seawater</i>				
Seawater Control (Blank)	7.7			
<b>Boggy Creek in seawater</b>				
Core 9, 0-1 cm	7.8	7.8	7.6	7.3
Core 9, 0-5 cm	7.9	7.7	6.9	4.6
<b>Point Sturt in seawater</b>				
Core 4, 0-5cm	7.7	7.9	7.8	7.0
Core 4, 0-5 cm (dup.)	7.8	7.9	7.7	7.0

**Table 17. Effect of Soil:water Ratio on SEC (mS/cm) During Rapid Remobilisation Tests**

Sample site	Soil:water ratio			
	0.1	1	10	100
<i>Remobilisation SEC (mS/cm) in freshwater</i>				
Murray River Water Control (Blank)	1.8			
<b>Boggy Creek in freshwater</b>				
Core 9, 0-1 cm	1.8	1.9	2.5	6.7
Core 9, 0-5 cm	1.8	1.9	2.2	4.6
<b>Point Sturt in freshwater</b>				
Core 4, 0-5cm	1.8	1.8	1.8	1.8
Core 4, 0-5 cm (dup.)	1.8	1.8	1.8	1.8
<i>Remobilisation SEC (mS/cm) in seawater</i>				
Seawater Control (Blank)	54.2			
<b>Boggy Creek in seawater</b>				
Core 9, 0-1 cm	54.4	54.6	54.7	55.6
Core 9, 0-5 cm	54.1	54.3	54.5	54.2
<b>Point Sturt in seawater</b>				
Core 4, 0-5cm	54.6	54.2	54.7	53.8
Core 4, 0-5 cm (dup.)	54.9	54.1	54.4	53.7

Table 18. Effect of Soil:water Ratio on Rapid Remobilisation of Trace Metals and Metalloids

Sampling	TSS g/L	Al µg/L	Fe µg/L	Mn µg/L	As µg/L	Cd µg/L	Co µg/L	Cr µg/L	Cu µg/L	Ni µg/L	Pb µg/L	V µg/L	Zn µg/L
<b>Boggy Creek in fresh water</b>													
Core 9, 0-1 cm	0.01	<1	<1	<7	0.79	0.06	<0.15	<0.02	1.01	<0.03	0.73	0.72	1.69
Core 9, 0-1 cm	0.1	3	3	160	0.87	0.60	0.20	<0.02	1.03	0.04	0.76	2.19	2.25
Core 9, 0-1 cm	1	4	5	830	1.46	<0.05	0.91	<0.02	2.22	<0.03	1.84	6.75	0.77
Core 9, 0-1 cm	10	2	17	4900	2.80	0.093	5.57	0.280	7.90	<0.03	8.4	16.7	3.37
Core 9, 0-5 cm	0.01	4	16	17	0.85	0.05	<0.15	<0.02	2.78	0.04	0.68	1.30	8.63
Core 9, 0-5 cm	0.1	<1	3	54	0.79	<0.05	0.41	<0.02	1.10	<0.03	1.19	1.20	1.83
Core 9, 0-5 cm	1	3	7	360	0.71	<0.05	3.36	0.02	9.14	<0.03	3.85	0.59	3.38
Core 9, 0-5 cm	10	2100	100	4400	2.93	1.29	79	0.75	2.38	0.37	144	0.43	110
<b>Boggy Creek in seawater</b>													
Core 9, 0-1 cm	0.01	<4	<7	31	2.84	0.12	0.369	0.17	0.88	<0.03	0.64	1.95	1.77
Core 9, 0-1 cm	0.1	5	<7	220	3.05	0.11	1.01	0.21	3.09	<0.03	1.20	4.08	5.51
Core 9, 0-1 cm	1	<4	<7	1900	2.67	0.23	2.39	0.40	2.00	<0.03	2.62	5.71	2.61
Core 9, 0-1 cm	10	<4	13	13000	4.21	1.17	11.3	0.49	7.27	<0.03	10.5	11.2	6.96
Core 9, 0-5 cm	0.01	7	<7	8	2.76	<0.05	0.181	0.35	1.13	<0.03	0.51	1.15	14.1
Core 9, 0-5 cm	0.1	180	<7	47	2.84	<0.05	0.78	0.36	0.99	<0.03	1.41	1.13	5.20
Core 9, 0-5 cm	1	7	<7	410	2.63	0.19	7.38	0.30	1.15	0.15	13.0	0.66	5.83
Core 9, 0-5 cm	10	5800	100	4100	10.8	2.15	89	1.14	4.22	5.19	202	0.29	129
<b>Point Sturt in fresh water</b>													
Core 4, 0-5cm	0.01	<1	<1	<1	0.85	0.07	0.02	0.04	0.93	<0.03	0.72	0.69	2.06
Core 4, 0-5cm	0.1	2	<1	<1	0.91	0.09	<0.15	<0.02	1.02	<0.03	0.72	0.70	2.57
Core 4, 0-5cm	1	5	7	<7	0.89	<0.05	0.16	<0.02	0.87	<0.03	0.91	0.40	3.60
Core 4, 0-5cm	10	7	3	70	0.54	0.07	1.39	<0.02	0.50	<0.03	1.89	0.20	0.85
<b>Point Sturt in seawater</b>													
Core 4, 0-5cm	0.01	<4	<7	31	3.07	<0.05	0.08	0.22	1.24	<0.03	0.31	1.07	0.92
Core 4, 0-5cm	0.1	<4	<7	220	2.70	<0.05	0.09	0.30	1.11	<0.03	0.27	1.00	1.17
Core 4, 0-5cm	1	5	<7	1900	2.59	0.08	0.40	0.33	0.65	<0.03	0.60	0.56	<0.59
Core 4, 0-5cm	10	<4	<7	13000	1.85	0.27	3.44	0.34	0.48	<0.03	5.31	0.38	2.74

### 4.2.3 Effect of standard and repeated leaching on acidity and metal release

Several of the soil samples were repeatedly leached (three times), with the original water removed by centrifugation and replaced with new water, using 24-h leaching periods. The metal mobilisation and changes in pH and SEC were investigated for three soils using both freshwater and seawater at a soil:water ratio of 100 g soil/L and a resuspension period of 24 h. The dissolved oxygen concentrations were 8-9 mg/L during these tests. Standard rapid remobilisation tests (100 g soil/L, 24-h leach) were undertaken using both freshwater and seawater on five soils samples. The pH and SEC data from these tests are shown in Tables 19.

The repeated leaches were undertaken using both freshwater and seawater on the two more acidic soil samples: Core 9, 0-5 cm and Core 4, 0-5 cm. For successive leaches the pH increased but remained much lower than the pH of the leach water (Table 17). This indicates that while acidity may be being washed out of the soils, significant acidity remained and was carried through to the next cycle. For successive freshwater leaches, for soil 'Core 9, 0-5 cm' the SEC decreased from 4.9 to 1.9 mS/cm, which was the same SEC as the leach water (Table 19). For the other soils, the SEC was more similar to that of the original leach water, but varied a little erratically. For successive seawater leaches, the SEC became more similar to the SEC of the first leach water (Tables 19).

With each successive leach of the soils, the concentrations of most metals (not vanadium) released from the soils generally decreased 2-10 fold compared to the previous leach cycle (Table 20). This is consistent with there being a finite pool of metals available for rapid release, rather than there being an ongoing source of easily available metals being released from the soil particles.

**Table 19. Effect of Standard and Additional Leaches on pH During Remobilisation Tests**

	<b>Freshwater: 24-h leach cycles</b>					
	<b>pH</b>			<b>SEC (mS/cm)</b>		
	<b>1<sup>st</sup></b>	<b>2<sup>nd</sup></b>	<b>3<sup>rd</sup></b>	<b>1<sup>st</sup></b>	<b>2<sup>nd</sup></b>	<b>3<sup>rd</sup></b>
Murray River Water (Blank)	7.5	7.5	7.5	1.9	1.9	1.9
<b>Boggy Creek</b>						
Core 9, 0-1 cm	7.2	NAL	NAL	6.8	NAL	NAL
Core 9, 0-5 cm	4.2	4.6	4.9	4.9	2.5	1.9
<b>Pt. Sturt</b>						
Core 4, 0-5 cm	6.8	7.3	7.5	1.9	2.7	2.0
Core 4, 0-5 cm (dup.)	6.9	NAL	NAL	1.9	NAL	NAL
Core 5, 0-5 cm (dup.)	7.0	NAL	NAL	1.9	NAL	NAL
	<b>Seawater: 24-h leach cycles</b>					
	<b>1<sup>st</sup></b>	<b>2<sup>nd</sup></b>	<b>3<sup>rd</sup></b>	<b>1<sup>st</sup></b>	<b>2<sup>nd</sup></b>	<b>3<sup>rd</sup></b>
Seawater Control (Blank)	7.9	7.9	7.9	56.7	56.7	56.7
<b>Boggy Creek</b>						
Core 9, 0-1 cm	7.1	NAL	NAL	58.4	NAL	NAL
Core 9, 0-5 cm	4.8	5.4	6.1	57.3	57.2	55.6
<b>Pt. Sturt</b>						
Core 4, 0-5 cm	7.1	7.5	7.7	56.2	57.0	56.9
Core 4, 0-5 cm (dup.)	7.0	NAL	NAL	55.7	NAL	NAL
Core 5, 0-5 cm (dup.)	7.1	NAL	NAL	55.9	NAL	NAL

NAL = no additional leach

Table 20. Effect of Standard and Additional Leaches on Remobilisation of Trace Metals and Metalloids

Sampling	24-h leach cycle	Al µg/L	Fe µg/L	Mn µg/L	As µg/L	Cd µg/L	Co µg/L	Cr µg/L	Cu µg/L	Ni µg/L	Pb µg/L	V µg/L	Zn µg/L
<b>Boggy Creek in Freshwater</b>													
Core 9, 0-1 cm	1 <sup>st</sup>	7000	320	7100	4.24	2.80	149	1.00	5.20	1.11	283	0.68	174
Core 9, 0-1 cm	2 <sup>nd</sup>	820	67	1000	1.24	0.28	19.7	0.29	1.72	<0.03	48.9	0.45	26.5
Core 9, 0-1 cm	3 <sup>rd</sup>	100	16	356	0.61	0.08	6.65	0.14	1.04	0.05	15.6	0.39	9.47
<b>Boggy Creek in seawater</b>													
Core 9, 0-5 cm	1 <sup>st</sup>	4100	52	5800	7.09	2.34	92.2	1.04	3.17	4.18	208	0.49	119
Core 9, 0-5 cm	2 <sup>nd</sup>	330	13	1200	2.70	0.70	34.5	0.42	1.45	1.48	60.3	0.65	43.9
Core 9, 0-5 cm	3 <sup>rd</sup>	46	<7	330	3.38	0.32	14.8	0.16	1.18	0.26	22.9	0.72	17.0
<b>Point Sturt in Freshwater</b>													
Core 4, 0-5 cm	1 <sup>st</sup>	16	1	75	0.59	<0.05	1.55	<0.02	0.78	<0.03	2.06	0.35	1.33
Core 4, 0-5 cm	2 <sup>nd</sup>	4	1	9	0.96	<0.05	0.21	<0.02	0.95	<0.03	0.81	0.45	0.06
Core 4, 0-5 cm	3 <sup>rd</sup>	<4	<1	12	0.82	<0.05	<0.15	<0.02	0.98	<0.03	0.62	0.59	0.02
<b>Point Sturt in seawater</b>													
Core 4, 0-5 cm	1 <sup>st</sup>	<4	<7	99	2.06	0.28	3.60	0.16	0.55	<0.03	4.81	0.51	1.05
Core 4, 0-5 cm	2 <sup>nd</sup>	<4	<7	1	2.79	0.10	0.516	0.13	0.85	<0.03	0.55	1.19	<0.59
Core 4, 0-5 cm	3 <sup>rd</sup>	<4	<7	<1	1.79	0.11	0.352	0.08	0.50	<0.03	0.48	1.48	0.79

#### 4.2.4 Comparison of freshwater and seawater rapid metal release for additional soils

For eight additional soils collected from the lower lakes during the 2008 study by Simpson et al. (2008), rapid release tests using both freshwater and seawater were undertaken (Table 21). For a given soil, the release of Al and Fe was often greater in freshwater than in seawater. However, the magnitude of the release of the other metals appeared less dependent on water type.

This additional data allowed the differences between freshwater and seawater rewetting to the pH-metal release relationships previously observed (Figure 5). The data for both the freshwater and seawater rapid release tests of soils from field-trail sites are compared with the previous rapid-release tests undertaken using freshwater on Lakes Albert and Alexandrina soils (Simpson et al., 2008) in Figure 5. In general, the magnitude of the metal release from the soils was similar to that observed in the previous work. As shown for Al, Zn, Cu and Cr, for which strong pH-metal release relationships were observed by Simpson et al. (2008), at a similar pH the metal release was generally greater in seawater than in freshwater, the water pH had the strongest influence on the magnitude of the metal release.

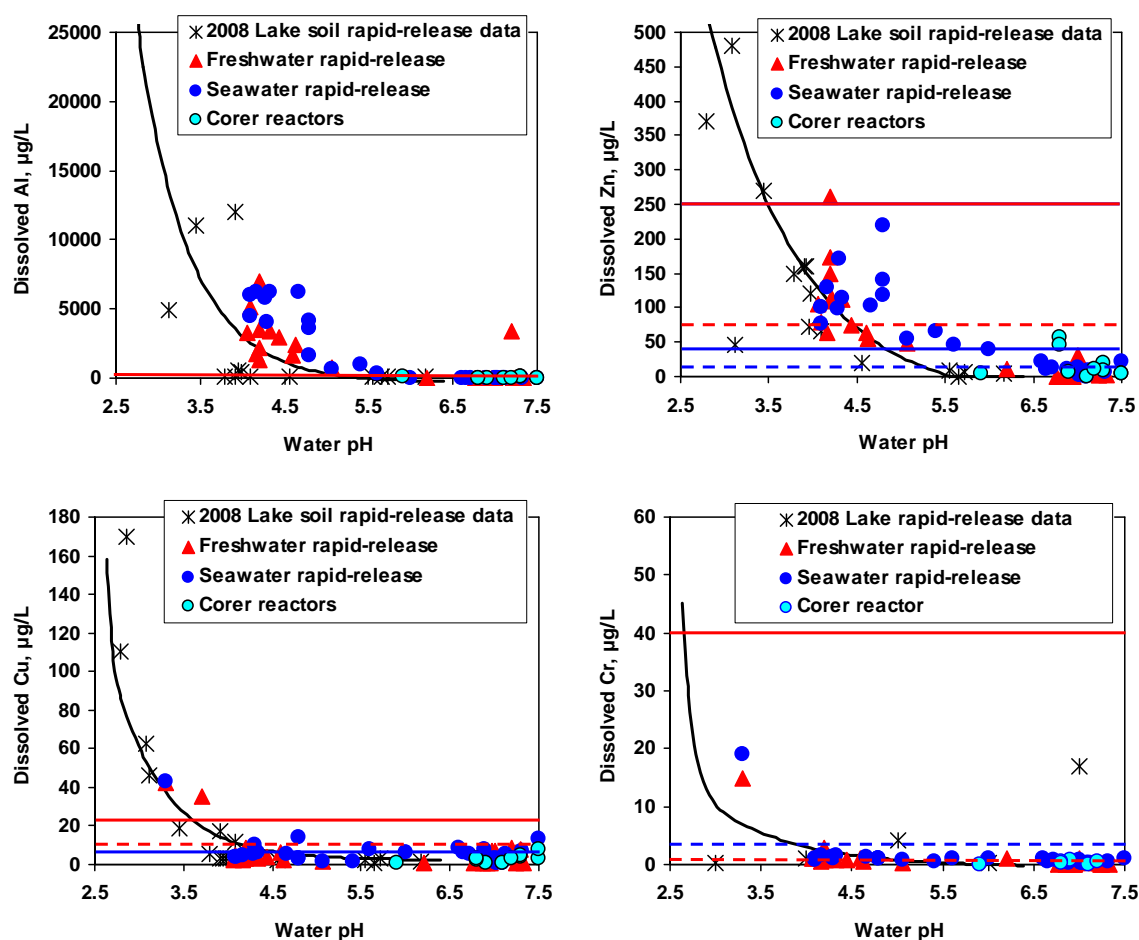


Figure 5. Comparison between the dissolved Al, Cu and Zn concentrations measured in the rapid-release tests undertaken for (i) Lakes Albert and Alexandrina soils (\*) previous rapid-release data (Freshwater, Simpson et al., 2008), (ii) freshwater tests for soils from field-trail sites ( $\blacktriangle$ ), (iii) seawater tests for soils from field-trail sites ( $\bullet$ ), and (iv) for mean metal release during the resuspension phase of the mid-term corer reactor experiments (weeks 3-6) ( $\odot$ ). Where shown, the lines represent the freshwater (red) and seawater (blue) water quality guidelines for 80% (solid) and 95% (dashed) species protection (Table 22).

Table 21. Standard Leaches using Freshwater and Seawater on additional Soil Samples

Sampling	SEC	Al	Fe	Mn	Cd	Co	Cr	Cu	Ni	V	Zn	
	pH	mS/cm	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	
<b>Freshwater inundation</b>												
River Murray water	7.6	2.1	<60	<60	< 2	<5	<10	<2	5	<10	<2	33
AT 19.3 (18-28 cm) (4.1)	4.2	2.4	2235	2900	1200	<5	140	3	8	160	2	150
AT 21.1 (0-1 cm) (6.2)	7.0	6.9	<60	<60	760	<5	<10	<2	7	10	3	6
AA 29.5 (0-3 cm) (3.9)	4.2	3.8	6900	5400	7500	<5	110	<2	9	330	20	260
AA 29.6 (3-10 cm) (4.4)	4.6	2.1	1600	5700	780	<5	20	<2	6	45	4	63
AA 33.2 (0-10 cm) (2.9)	3.7	2.4	26000	29000	2700	<5	180	54	35	250	940	650
AA 33.3 (10-25 cm) (2.8)	3.3	4.4	32000	18000	2600	<5	200	15	42	320	160	680
AA 13.2 (5-15 cm) (3.8)	4.2	2.5	1300	2500	2200	<5	320	2	3	260	< 2	110
AA 10.2* (10-30 cm) (5.7)	6.2	2.0	<60	<60	4600	<5	50	<2	<2	20	10	10
<b>Seawater inundation</b>												
Seawater	7.5	57.9	<60	<60	< 2	<5	<10	<2	13	10	5	23
AT 19.3 (18-28 cm) (4.1)	4.8	58.1	1600	1500	1000	<5	110	<2	14	140	10	140
AT 21.1 (0-1 cm) (6.2)	6.6	61.4	<60	<60	2800	<5	<10	<2	9	10	6	23
AA 29.5 (0-3 cm) (3.9)	4.8	59.3	3600	4300	6200	<5	90	<2	3	280	10	220
AA 29.6 (3-10 cm) (4.4)	5.6	58.0	300	2700	580	<5	10	<2	8	52	8	47
AA 33.2 (0-10 cm) (2.9)	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
AA 33.3 (10-25 cm) (2.8)	3.3	58.8	69000	19000	2500	<5	190	19	43	350	110	700
AA 13.2 (5-15 cm) (3.8)	4.3	58.2	4000	3300	2600	<5	370	<2	10	320	4	170
AA 10.2* (10-30 cm) (5.7)	6.0	58.1	<60	<60	9100	<5	120	<2	6	78	4	40

## 5 Discussion

### 5.1 Ecological Risk Assessment

Ecotoxicological effects due to released metals may occur when the dissolved metal concentrations in the water column, or sediment pore water in the case of some plants or benthic organisms, exceed the water quality guideline values (WQGs) (Table 22). For the purpose of this discussion, the mean dissolved metal concentrations measured during the tests are compared with the ANZECC/ARMCANZ (2000) water quality guidelines 80% and 95% protection concentrations.

Table 22. Water Quality Guidelines ( $\mu\text{g/L}$ ) for Fresh water of varying Hardness and Seawater

Metal	Hardness correction <sup>†</sup>	Fresh water			Seawater		
		Acute <sup>§</sup>	Chronic		Acute <sup>§</sup>	Chronic	
Level of protection		95%	95%	80%	95%	95%	80%
Al <sup>a</sup>	NA	6.6	55	150	5	0.5	NV
As (V) <sup>b</sup>	NA	13	13	140	45	4.5	NV
Cd <sup>*</sup>	10 $\times$	20	2	8	55	5.5	36
Co <sup>*</sup>	9 $\times$	126 <sup>e</sup>	12.6 <sup>e</sup>	NV	10	1	150
Cr(VI) <sup>c</sup>	NA	10	1	40	44	4.4	85
Cu <sup>*</sup>	9 $\times$	126	12.6	22.5	13	1.3	8
Mn <sup>d</sup>	NA	17000	1900	3600	230	230	NA
Ni <sup>*</sup>	9 $\times$	990	99	153	70	70	560
Pb <sup>*</sup>	26.7 $\times$	908	91	251	44	4.4	12
V	NA	60 <sup>e</sup>	6 <sup>e</sup>	NV	1000	100	280
Zn <sup>*</sup>	9 $\times$	720	72	248	150	15	43

NV = no value due to inadequate data for undertaking species sensitivity distribution

\* = Hardness correction applied at 400 mg CaCO<sub>3</sub>/L level for this element

NA = Hardness correction not applicable for this element

<sup>§</sup> The acute values were calculated from by multiplying the chronic guideline values by 10 (Stauber et al., 2008)

<sup>†</sup> The freshwater guidelines for Cd, Cr(III), Cu, Ni, Zn, and Pb have been adjusted using the ANZECC/ARMCANZ (2000) algorithms based on a water hardness of 400 mg CaCO<sub>3</sub>/L

<sup>a</sup> The WQG for Al in freshwaters is the pH>6.5 value as during most tests that waters were pH >6.5. For WQG for Al in seawater is an 'environmental concern level (very low reliability)

<sup>b</sup> The freshwater WQG for As assumes all is as As(V), which is more toxic than As(III) (WQG = 24  $\mu\text{g/L}$ ).

<sup>c</sup> The WQGs for Cr assumes all is as Cr(VI), which is more toxic that Cr(III), however it is expected that there would be a mixture of both Cr(III) and Cr(VI)

<sup>d</sup> A WQG value of 230  $\mu\text{g/L}$  is used for Mn, which may be considered as a moderate reliability value (Stauber et al., unpublished results).

<sup>e</sup>Low reliability WQG values. For Co, the 99% PL level WQG is used due to low reliability of 95% PL value.

For the freshwater WQGs, hardness corrections were applied. The water hardness was quite variable, being approximately 100 mg CaCO<sub>3</sub>/L for River Murray water and greater than 400 mg/L for the Lake Alexandrina water and reactor waters. For metals whose toxicity is known to be influenced by hardness, and for which hardness algorithms are available (i.e. Cd, Cr(III), Cu, Ni, Zn, and Pb), the freshwater trigger values were adjusted based on a water hardness of 400 mg/L. The hardness algorithms (ANZECC/ARMCANZ, 2000) were derived using effects data for fish using toxicity data spanning water hardness from 25-400 mg CaCO<sub>3</sub>/L. Their applicability at higher hardness is unknown. The toxicity of other metals such as manganese, is known to be reduced as water hardness increases, however, no algorithms were available for hardness corrections. It is also important to note that recent studies with algae and cladocerans have found that copper toxicity to these sensitive species is not ameliorated in high hardness waters, suggesting that hardness-corrected trigger values for copper at least, may be under-protective for some species (Markich et al. 2005). For seawater, the WQG for manganese (PC95% = 70  $\mu\text{g/L}$ ) is a low reliability value. It is recommended that a value of 230  $\mu\text{g Mn/L}$  be used, which may be considered as a moderate reliability value (Stauber et al., unpublished results).



## Overlying water pH and dissolved Al, Fe and Mn

In the corer-reactor experiments the mean pH of the overlying water was greater than pH 7 throughout the first 17 days (weekly water renewal phase). Following inundation of the soils with fresh water, the mean dissolved aluminium concentration remained below the WQG value for freshwaters of 55 µg/L (Table 20). Following inundation of the soils with seawater, the mean dissolved aluminium concentration greatly exceeded the WQG value for seawaters of 0.5 µg/L, however it should be noted that this is a low reliability, WQG value. Dissolved iron concentrations were lower in the Point Sturt tests than the Boggy Creek tests. Greater release of iron occurred during inundation using seawater. The mean dissolved manganese concentration remained well below the WQG value of 1900 µg/L for fresh waters. For seawater, the WQG is 70 µg/L and is a low reliability value. It is recommended that a value of 230 µg Mn/L be used, which may be considered as a moderate reliability value (Stauber et al., unpublished results). For the Boggy Creek soils following seawater inundation, the mean dissolved manganese concentration exceeded 230 µg/L (Table 20).

## Trace metals and metalloids

The mean concentrations of dissolved cadmium were greatest in the seawater inundation tests, but did not exceed the WQG values for any of the tests. The mean concentrations of dissolved cobalt were higher in inundation tests with seawater than those with freshwater and exceeded the WQG value for seawater inundation but not for freshwater inundation (hardness corrected WQG). For Boggy Creek, the dissolved cobalt concentrations were greater than 10× WQG during the seawater renewal phase. While dissolved copper concentrations were greater in the freshwater inundation experiments than in the seawater inundation experiments, the hardness corrected WQG for freshwater was not exceeded. The mean dissolved copper concentrations exceeded the WQGs for seawater in all tests, but were less than 10× WQG seawater. Dissolved lead concentrations were greater in the seawater inundation experiments than in the freshwater inundation experiments. The mean dissolved lead concentrations exceeded the WQGs for seawater, but not for freshwater inundation tests (hardness corrected WQG). The mean dissolved zinc concentrations did not exceed the WQG for freshwater (hardness corrected WQG) and only exceeded the WQG for seawater in one of the Boggy Creek soil tests. The mean concentrations of dissolved As, Cr, Ni, and V did not exceed their respective WQGs during either the water-renewal phases of the corer-reactor tests.

### 5.1.1 Sediment resuspension

For the overlying water (discussed above), significant dilution of released acidity and metals is expected to occur through mixing with the surrounding waters. Removal of released metal through precipitation or increased adsorption to suspended solids is also likely to occur (Simpson et al., 2008). A comparison between the mean water pH, SEC and dissolved metals concentrations during the water-renewal and resuspension periods is made in Table 23. During the resuspension phase, the pH dropped significantly, but remained above pH 5.

For Boggy Creek, resuspension of the surface sediments caused large increases in the release of iron (20 to >100-fold increase) and manganese (~ 2-fold for seawater and >100-fold for freshwater inundation tests). These metals would have been expected to be present in the pore waters as Fe(II) and Mn(II). The resuspension of the surface sediments caused increases of the order of 2-10 fold for As, Co, Ni, Pb, and Zn, but had little effect on the concentrations of Cd and Cr, and induced moderate removal of Al, Cu, and V. These results indicate that disturbances to the deeper pore waters are likely to have the greatest influence of dissolved metal release to the overlying water.

The dissolved concentrations of metals released to the overlying water during the water-renewal and resuspension phases of the corer-reactor tests are compared with the WQGs for freshwater and seawater in Tables 23 and 24. Following sediment resuspension the dissolved aluminium concentrations generally decreased, but remained above the WQG for seawater. Dissolved manganese concentrations increased significantly and greatly exceeded 230 µg/L in both freshwater and seawater tests for all Boggy Creek samples, and exceeded the WQG for Point Sturt in the seawater test. For Boggy Creek, the dissolved cobalt concentrations were near 100× WQG during the seawater resuspension phases of the experiments. The dissolved copper concentrations decreased during the resuspension phase. The dissolved lead concentrations were significantly greater during the resuspension phase, exceeding >10× WQG for Boggy Creek in seawater. For the Boggy Creek soils, the dissolved zinc concentrations were 2-4 times greater during the resuspension phase of the experiments and exceeded the WQGs during all Boggy Creek resuspension tests. Arsenic, but not Cr or Ni exceeded the WQGs for seawater during the resuspension phase, but only in one test.

### 5.1.2 Sediment pore waters

The dissolved metal concentrations in the sediment pore waters were much greater than the concentrations being released to the overlying water and the increased rate of release of metals from the sediments during resuspension was likely to be in part due to porewater derived metals. Metals in the sediment pore waters, along with direct effects due to the decreased sediment pH may have significant detrimental effects to both

plants that have roots extending into the deeper sediments and also to benthic invertebrates that inhabit the sediments (Simpson and Batley, 2007).

Analyses of the sediment pore waters indicated that only minor neutralisation of the pore waters occurred during the 8-week tests, and this only occurred for the seawater inundation experiments. In all tests, regardless of whether seawater or freshwater was used for the inundation experiments, at a depth of greater than 20 cm below the sediment water interface the pore waters pH values were low: pH ~3. Porewater metal concentrations were generally much greater in the seawater inundation tests than the freshwater inundation tests. Pore water concentrations increased with increasing sediment depth, which was consistent with the higher acidity (lower pH) of the deeper sediments.

Table 23. Mean Concentrations of pH, SEC, and Dissolved Metals and Metalloids during Water Exchange and Resuspension (non-renewal) Periods and WQG Values for Fresh Water and Seawater.

Sampling		pH	SFC mS/cm	Al µg/L	Fe µg/L	Mn µg/L	As µg/L	Cd µg/L	Cu µg/L	Cr µg/L	Cu µg/L	Ni µg/L	Ph µg/L	V µg/L	Zn µg/L
<b>Point Sturt, Freshwater Core 3</b>															
Water renewal period	Mean	7.5	1.8	6.0	1	8	0.8	0.26	0.3	<0.02	3.8	0.3	1.3	1	4.2
	SD	0.3	0.0	7.5	NV	4	0.1	0.24	0.1	NV	3.1	0.4	0.3	0.1	2.2
Resuspension period	Mean	5.9	2.0	120	39	126	0.7	0.45	4.0	0.6	0.8	0.1	7.9	0	4.5
	SD	0.9	0.1	95	71	73	0.1	0.26	2.0	1.2	0.2	0.0	5.1	0.1	2.8
<b>Point Sturt, Freshwater Core 4</b>															
Water renewal period	Mean	7.5	1.8	8.3	1.0	6.8	0.8	0.59	0.4	0.3	8.7	0.1	1.1	0	3.7
	SD	0.3	0.1	7.5	0.0	6.9	0.1	0.59	0.3	NV	7.7	0.0	0.6	0.1	3.0
Resuspension period	Mean	7.1	1.9	1.0	3.5	7.1	0.8	0.07	0.2	0.03	1.1	0.2	0.7	0	0.6
	SD	0.3	0.1	NV	3.5	4.1	0.2	0.04	0.1	0.01	0.1	0.2	0.3	0.1	0.7
<b>Boggy Creek, Freshwater Core 1</b>															
Water renewal period	Mean	7.6	2.9	13	13	269	4.8	0.07	1.1	0.2	7.2	0.1	2.7	17	2.0
	SD	0.2	0.6	11	10	132	2.1	0.01	0.5	0.1	4.8	0.0	1.1	8.3	0.5
Resuspension period	Mean	7.2	6.8	15	3450	5900	8.3	0.09	14.7	0.6	3.7	0.7	22.1	10	10.1
	SD	0.2	1.1	8.3	3040	2310	1.9	0.02	5.6	0.1	0.7	0.2	6.5	3.6	3.8
<b>Freshwater WQG (95% PC) <sup>a, b</sup></b>		<b>NV</b>	<b>NV</b>	<b>55</b>	<b>NV</b>	<b>1900</b>	<b>13</b>	<b>2</b>	<b>12.6</b>	<b>1</b>	<b>12.6</b>	<b>99</b>	<b>91</b>	<b>6.0</b>	<b>72</b>
<b>Point Sturt, Seawater Core 5</b>															
Water renewal period	Mean	7.6	53	84	~10	114	2.4	0.38	4.3	0.5	1.7	3.5	8.9	1	4.1
	SD	0.2	0.7	46	NV	110	0.4	0.25	4.1	0.4	0.8	3.0	8.4	0.2	3.0
Resuspension period	Mean	6.9	57	14	103	241	2.3	0.23	7.5	0.7	0.7	3.1	10.8	1	6.4
	SD	0.4	1.7	10	115	46	0.5	0.07	2.1	1.9	0.2	3.9	3.3	0.2	2.7
<b>Boggy Creek, Seawater Core 2</b>															
Water renewal period	Mean	7.3	53	101	80	4660	3.0	0.76	25	0.6	4.4	0.3	24	11	21.3
	SD	0.3	0.7	101	111	2860	0.8	0.49	15	0.2	3.2	0.2	16	4.7	14.3
Resuspension period	Mean	6.8	58	29	14300	10900	5.0	0.52	90	0.5	2.5	0.2	69	2	52.2
	SD	0.3	1.8	19	13000	3790	2.1	0.25	32	0.4	0.8	0.2	22	2.1	21.7
<b>Boggy Creek, Seawater Core 9</b>															
Water renewal period	Mean	7.3	53	74	81	5150	2.5	0.85	18	0.4	4.9	0.2	16	5.4	7.8
	SD	0.3	0.7	73	26	2480	0.6	0.44	9.8	0.1	3.5	0.1	8.2	2.5	4.1
Resuspension period	Mean	6.8	58	34	11440	11400	4.3	0.65	107	0.3	3.2	0.1	91	1.1	42
	SD	0.3	1.8	20	11000	3240	1.6	0.35	15	0.2	1.4	0.1	14	1.2	21
<b>Seawater WQG (95% PC) <sup>a</sup></b>		<b>NV</b>	<b>NV</b>	<b>0.5</b>	<b>NV</b>	<b>230</b>	<b>4.5</b>	<b>5.5</b>	<b>1</b>	<b>4.4</b>	<b>1.3</b>	<b>70</b>	<b>4.4</b>	<b>100</b>	<b>15</b>

<sup>a</sup> Water quality guideline, 95% level of ecosystem protection in ANZECC/ARMCANZ (2000).

<sup>b</sup> The WQGs for freshwaters are the 95% PL for chronic effects and have been adjusted for the effects of hardness at 400 mg/L level. The freshwater WQG for As assumes all is as As(V), which is less toxic than As(III) (WQG = 24 µg/L). The WQGs for Cr assumes all is as Cr(VI).

Table 24. Exceedances of WQG Values for Fresh Water and Seawater (renewal phase) (ratio of dissolved concentration to WQG value).

	Quotient = Dissolved concentration / WQG value											
	Al	Mn	Fe	As	Cd	Co	Cr	Cu	Ni	Pb	V	Zn
Point Sturt, Freshwater Core 3	0.11	NV	0.00	0.06	0.13	0.02	0.03	0.27	0.00	0.01	0.10	0.06
Point Sturt, Freshwater Core 4	0.15	NV	0.00	0.06	0.28	0.03	0.03	0.62	0.00	0.01	0.07	0.05
Boggy Creek, Freshwater Core 1	0.24	NV	0.01	0.35	0.03	0.08	0.16	0.52	0.00	0.03	2.8	0.03
<b>WQG (95% PC) for freshwater <sup>a, b</sup></b>	<b>55</b>	<b>1900</b>	<b>NV</b>	<b>13</b>	<b>2</b>	<b>12.6</b>	<b>1</b>	<b>12.6</b>	<b>99</b>	<b>91</b>	<b>6</b>	<b>72</b>
Point Sturt, Seawater Core 5	168	NV	0.51	0.51	0.51	4.4	0.12	1.2	0.05	2.1	0.01	0.27
Boggy Creek, Seawater Core 2	202	NV	18	0.64	0.99	23	0.12	3.1	0.00	5.0	0.11	1.3
Boggy Creek, Seawater Core 9	148	NV	21	0.56	1.1	17	0.10	3.4	0.00	3.6	0.05	0.51
<b>WQG (95% PC) for seawater a, b</b>	<b>0.5</b>	<b>230</b>	<b>NV</b>	<b>4.5</b>	<b>5.5</b>	<b>1</b>	<b>4.4</b>	<b>1.3</b>	<b>70</b>	<b>4.4</b>	<b>100</b>	<b>15</b>

<sup>a</sup> Water quality guideline, 95% level of ecosystem protection in ANZECC/ARMCANZ (2000).

<sup>b</sup> The WQGs for freshwaters are the 95% PL for chronic effects and have been adjusted for the effects of hardness at 400 mg/L level. The freshwater WQG for As assumes all is as As(V), which is less toxic than As(III) (WQG = 24 µg/L). The WQGs for Cr assumes all is as Cr(VI). For Mn in seawater, the value of 230 µg/L has been used based on the research by Stauber et al (unpublished results, 2008), in place of the low reliability value of 80 µg/L.

### 5.1.3 Comparison of short-term and mid-term metal release

The rapid 24-h release tests, involving shaking of soils with test water as described in detail in Simpson et al. (2008), were designed as potential worst-case scenarios for short-term acidity and metal release from soils. For the 47 sulfidic/sulfuric acid sulfate soils studied by Simpson et al. (2008), the metal release was rapid and dissolved concentrations of Al, Cd, Co, Cu, Cr, Mn, Ni, V and Zn greatly exceeded the Australian WQGs for protection of ecosystem health. In that study, the concentrations of Al, Cd, Co, Cu, Cr, Ni and Zn were often greater than 100×WQGs values for freshwaters. For most of these metals there were significant relationships between the pH of the sulfidic/sulfuric soils and the concentrations of dissolved metals released.

The corer-reactor experiments were designed to provide information on the potential metal release due to inundation of soils with fresh water or seawater over periods of 1-4 weeks. Despite the moderate to high acidity of the soil cores collected from Point Sturt and Boggy Creek, during the corer-reactor tests the overlying water pH did not decrease below pH 5.5. Based on the rapid remobilisation study undertaken by Simpson et al (2008), only for waters with pH 5 or less, would dissolved metal concentrations likely to exceed the WQGs to the extent that significant impacts on organisms within the water column be likely.

Direct comparison with the results from the rapid release tests with the results of the mid-term corer-reactor tests is not simple (see Figure 5). However, as expected, the rapid release tests undertaken on soils from Point Sturt and Boggy Creek generally resulted in a greater decrease in water pH and greater metal concentrations than that measured in waters overlying the corer-reactors, indicating that hydrological controls may be critical in determining the transport of acidity and metals from and within these soils. Comparison of the rapid-release test results for the Point Sturt and Boggy Creek soils with the past results indicates, however, that these two soils may not represent the worse case scenario for metal release for soils in Lake Alexandrina or Lake Albert. Because of the time required to undertake the mid-term tests, and the need to match these soils with those being used for the field-trials (Hicks et al., 2009), only two soil types were studied. With respect to undertaking a risk assessment, a significant limitation of this detailed approach is the small sample size (i.e. two soil types, two inundation water types). It is apparent from the pH values shown in Figure 5 that soils exist in lakes Albert and Alexandrina that have significantly greater acidity than the Boggy Creek and Point Sturt soils. It is likely therefore, that there may be a number of areas of the lake where the alkalinity of the inundation water (freshwater or seawater) and may be exhausted more rapidly. This would be expected to result in lower pH of the overlying water, higher metal release rates, and a greater likelihood of the water quality guidelines being exceeded; to a greater degree and for a longer duration.

## 6 Conclusions

To provide a better understanding of how the spatial variability in soil properties may affect metal-release when inundated with seawater and fresh water, it is recommended that rapid-release tests using seawater and fresh water are undertaken using soils collected from a greater range of sites in the lakes. While these tests may not provide accurate information on actual rates of metal release, they provide a useful means of contrasting the likely worst-case metal release from soils when inundated with different water types and would thereby aid the risk assessment process.

Greater release of metals and metalloids from the lake soils occurred during inundation with seawater than with fresh water. This was expected and can be attributed to the greater ionic strength of seawater causing greater exchange of metals from sediment particles. Pore water concentrations increased with increasing sediment depth, which was consistent with the higher acidity of the deeper sediments, which were generally pH  $\leq 3$  from 15 cm below the sediment water interface to the base of the cores at -20 cm. The dissolved metal concentrations within the sediment pore waters were much greater than the concentrations being released to the overlying water, and the increased rate of release of metals from the sediments during resuspension was likely to be in part due to release of porewater metals.

The tests indicated that only short-term exceedances to the WQGs for metals would be expected to occur if the pH of the overlying water remained above pH 6. Moderate dilution of the waters overlying the inundated sediments with surrounding waters is expected to result in both increased water pH and attenuation of the concentrations of dissolved metals released from the sediments. Exceedances of WQGs would be expected to be more frequent in shallow regions of the lake where water exchange is restricted. The impact of elevated porewater metal concentrations was not addressed in this study, but may have ecological impacts of both plants and benthic organisms.

To provide a better understanding of how the spatial variability in soil properties may affect metal-release when inundated with seawater and freshwater, it is recommended that rapid-release tests with seawater and freshwater are undertaken using soils collected from a greater range of sites in Lower Lakes region. While these tests may not provide accurate information on actual rates of metal release, they provide a rapid and relatively cheap means of contrasting the worst-case metal release from soils when inundated with different water types and would thereby aid the risk assessment process.

## 7 References

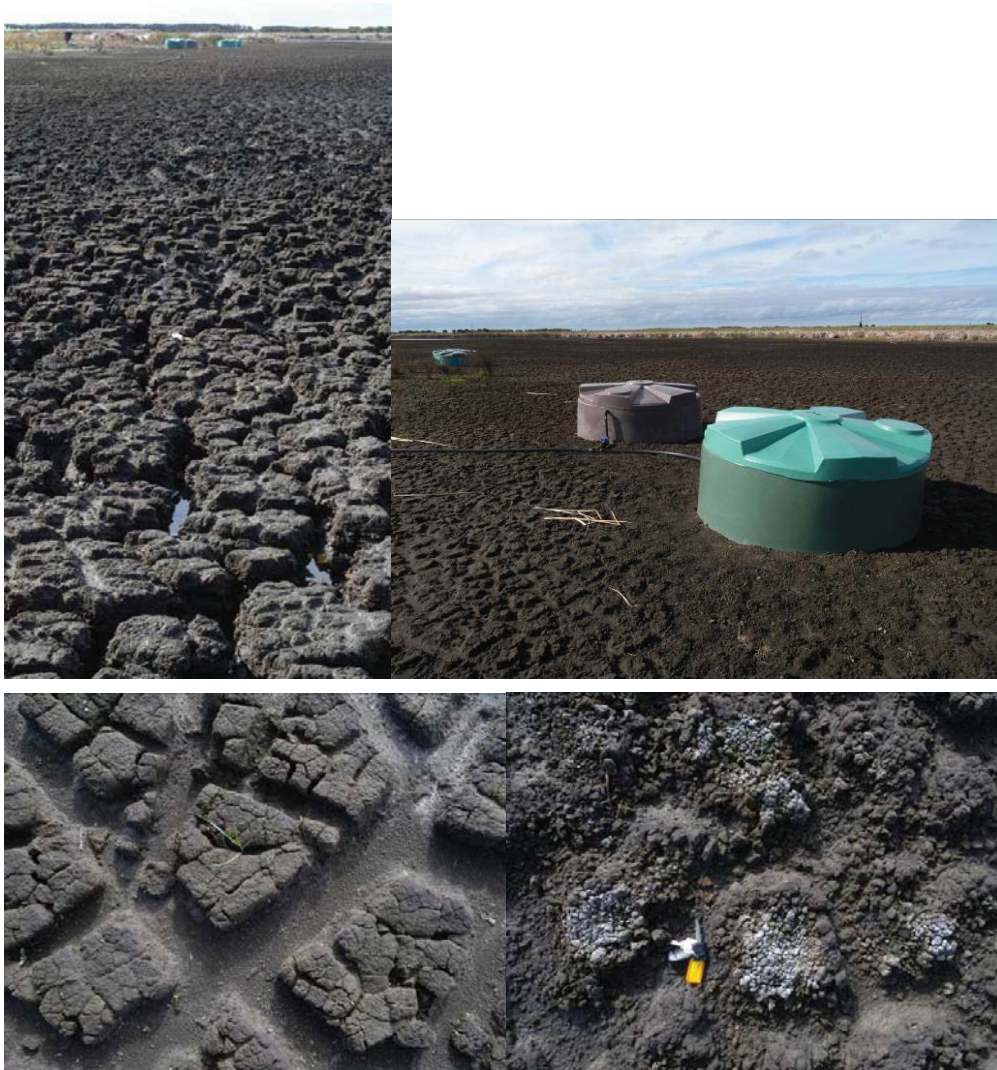
- Hicks, W.S., Creeper, N., Hutson, J., Fitzpatrick, R.W., Grocke, S. and Shand, P. (2009) The potential for contaminant mobilisation following acid sulfate soil rewetting: field experiment. Prepared by the Commonwealth Scientific and Industrial Research Organisation (CSIRO) Land and Water for the SA Department of Environment and Natural Resources, Adelaide.
- Jung, R.F., Jones, D.R. and Batley, G.E. (2003). Corer-reactors for contaminant flux measurement in sediments. *Journal of Environmental Quality*, 32, 1905-1910.
- Markich, S.J., Batley, G.E., Stauber, J.L., Rogers, N.J., Apte, S.C., Hyne, R.V., Bowles, K.C. (2005) Hardness corrections for copper are inappropriate for protecting sensitive freshwater biota. *Chemosphere* 60:1-8.
- Simpson, S.L., Pryor, I.D., Mewburn, B., Batley, G.E., and Jolley, D.F. (2002). Considerations for capping metal-contaminated sediments in dynamic estuarine environments. *Environmental Science and Technology*, 36, 3772-3778.
- Stauber, J.L., Chariton, A.A., Binet, M.T., Adams, M.S, Simpson, S.L., Batley, G.E., Durr, M., Bentley, K., Fitzpatrick, R.W., Shand, P. (2008) Water Quality Screening Risk Assessment of Acid Sulfate Soil Impacts in the Lower Murray, SA. CSIRO Land and Water Science Report 35/08, 133 pages.
- Simpson, S.L., Angel, B.A. Spadaro, D.A., Fitzpatrick, R.W., Shand, P., Merry R.H., and Thomas, M. (2008). Acid, Metal and Nutrient Mobilisation Following Rewetting of Acid Sulfate Soils in the Lower Murray. CSIRO Land and Water Science Report CLW27/08, 189 pages.
- Simpson, S.L. and Batley, G.E. (2003). Disturbances to metal partitioning during toxicity testing of iron(II)-rich porewaters and whole sediments. *Environmental Toxicology and Chemistry*, 22, 424-432.
- Simpson, S.L., Fitzpatrick, R.W., Shand, P., Angel, B.M., Spadaro, D.A. and Mosley, L. (2009). Climate-driven mobilisation of acid and metals from acid sulfate soils. *Marine and Freshwater Research*, (accepted).
- Simpson, S.L. and Batley, G.E. (2007). Predicting metal toxicity in sediments: A critique of current approaches. *Integrated Environmental Assessment and Management*, 3, 18-31.

## 8 Appendices



# APPENDIX A. SAMPLING USING CORER-REACTORS

## A1.1 Boggy Creek Sampling





**Table A1. Cores and Additional Samples Taken at Point Sturt**

<b>Time</b>	<b>Corer No.</b>	<b>Microcosm</b>	<b>0-5 cm sample</b>	<b>Description</b>
0925	4	Western most tank	2 samples	Moist sand. Some rusty streaks in beige sand.
0940	3	Second from western end	1 sample	Beige sand - rusty streaks not so visible. Wetter sand than core 4, with water accumulating slowly at base of core.
1000	5	Eastern-most tank	1 sample	Beige sand - rusty streaks, but not as visible as core 4. Wetter sand than core 4, with water accumulating slowly at base of core. Perhaps wettest of these 3 cores?



## A1.2 Point Sturt Sampling





**Table A2. Cores and Additional Samples Taken at Boggy Creek**

Time	Corer No.	Microcosm	0-5 cm sample	0-1 cm sample	Description
1230	9	SW end tank	1 sample	1 sample	3.5 m S of tank
1250	1	Second tank from SW end	2 sample	1 sample -sampled white effloresce on hardened "soil-rocks"	4 m S of tank. Sandy layer did not start until about 5 cm deep. This layer was approx. 5 cm deep.
1320	2	Second tank from NE end	1 sample	1 sample - sampled white effloresce as above	3 m S of tank. Sandy layer did not start until about 10 cm deep.

# APPENDIX B. CORER-REACTOR LABORATORY EXPERIMENTS

## B1.1. Corer-reactor rewetting scheme

Table B1. Initial Rewetting, Sampling and Water Renewal Scheme used for the Corer-reactors

Task #	Day	Time, h	Task
0	0	0	Corer-reactors sealed, dry and at 20°C
<b>Cycle 1 (Week 1) ~12 L (12 L)</b>			
1	1	0.1 – 1 (Tues, 9 am)	Test water added slowly until 10 cm depth of overlying water achieved (~1.67 L) Determine total amount of water added
2	1	2	Sample 100 mL of overlying water for analyses
3	1	2.1 – 3	Continue adding test water until 15 cm depth of overlying water achieved
4	1	3 – 6	Stirring
5	1	6 (3 pm)	Sample 100 mL of overlying water for analyses
6 (4 L)	1	6.1	Add 100 mL to test water to return to 15 cm depth
<b>Cycle 2 (Week 1) ~10 L (22 L)</b>			
7	1	Wed, 9 am	Sample 100 mL of overlying water for analyses
8	1-2	9 am	Remove 3 L, then slowly replace with new 3.1 L
9	2	1 pm	Sample 100 mL of overlying water for analyses
10 (4 L)	2	4 pm	Add 100 mL to test water to return to 15 cm depth
<b>Cycle 3 (Week 1) ~10 L (32 L)</b>			
11	4	Fri, 9 am	Sample 100 mL of overlying water for analyses
12	4	9 am	Remove 3 L, then slowly replace with new 3.1 L
13	4	1 pm	Sample 100 mL of overlying water for analyses
14 (4 L)	4	4 pm	Add 100 mL to test water to return to 15 cm depth
<b>Cycle 3 (Week 2) ~10 L (42 L)</b>			
15	7	Monday ~9 am	Sample 100 mL of overlying water for analyses
16	7	~10 am	Remove 3 L, then slowly replace with new 3.1 L
<b>Cycle 4 (Week 2) ~10 L (52 L)</b>			
17	10	Thursday ~9 am	Sample 100 mL of overlying water for analyses
18	10	~10 am	Remove 3 L, then slowly replace with new 3.1 L

Phase 1 = gradual water inundation (Core diameter = 146 mm, 167.4 cm<sup>2</sup> area × 5.97 cm depth = 1 L)

Analyses: 1. Centrifuge. 2. Filter 20 mL for analyses of trace metals. 3. Subsample 60 mL to Green ALS bottle for analyses of alkalinity/acidity, SO<sub>4</sub>, Cl. 4. Subsample 10 mL to measure pH

B1.2 Temperature-controlled laboratory (15°C)





### B1.3 Slow addition of water





### B1.4 Seawater-rewetting reactors



## B1.5 Freshwater-rewetting reactors



## B1.6 Corer-reactor resuspension scheme

Table B2. Surface-resuspension and Sampling Scheme used for the Corer-reactors

Task #	Day	Time, h	Task
<b>Reactors continuing on from re-wetting scheme (Table B1.1)</b>			
<b>Cycle 4R1.1 (Week 3)</b>			
19	17	Thursday ~9 am	Sample 100 mL of overlying water for analyses, replace with 100 mL new water
20	17	~10 am	The stirring rate of the water within the reactors was increase to a rate that caused resuspension of the top 2-3 cm of the sediment in each reactor.
20	17	~11 am	Sample 10 mL of overlying water for dissolved metals analyses
21	17	~3 pm	Sample 100 mL of overlying water for analyses, replace with 100 mL new water
<b>Cycle 4R1.2 (Week 3)</b>			
22	18	Friday	Sample 100 mL of overlying water for analyses, replace with 100 mL new water
<b>Cycle 4R2.1 (Week 4)</b>			
23	21	Monday ~9 am	Sample 100 mL of overlying water for analyses, replace with 100 mL new water
24	21	~10 am	The stirring rate of the water within the reactors was increase to a rate that caused resuspension of the top 2-3 cm of the sediment in each reactor.
25	21	~3 pm	Sample 100 mL of overlying water for analyses, replace with 100 mL new water
<b>Cycle 4R1.2 (Week 4)</b>			
26	23	Wednesday	Sample 100 mL of overlying water for analyses, replace with 100 mL new water
<b>Cycle 4R1.3 (Week 4)</b>			
27	25	Friday	Sample 100 mL of overlying water for analyses, replace with 100 mL new water
<b>Cycle 4R3.1 (Week 5)</b>			
28	28	Monday ~9 am	Sample 100 mL of overlying water for analyses, replace with 100 mL new water
29	28	~10 am	The stirring rate of the water within the reactors was increase to a rate that caused resuspension of the top 2-3 cm of the sediment in each reactor.
30	28	~3 pm	Sample 100 mL of overlying water for analyses, replace with 100 mL new water
<b>Cycle 4R3.2 (Week 5)</b>			
31	30	Wednesday	Sample 100 mL of overlying water for analyses, replace with 100 mL new water
<b>Cycle 4R3.3 (Week 5)</b>			
32	32	Friday	Sample 100 mL of overlying water for analyses, replace with 100 mL new water
<b>Cycle 4R3.4 (Week 6)</b>			
33	39	Friday	Sample 100 mL of overlying water for analyses, replace with 100 mL new water
<b>Cycle 4R3.5 (Week 7)</b>			
34	46	Friday	Sample 100 mL of overlying water for analyses, replace with 100 mL new water
<b>Cycle 4R3.6 (Week 8)</b>			
35	53	Friday	Sample 100 mL of overlying water for analyses, replace with 100 mL new water

### B1.7 Resuspension (Day 18, day-after 1st resuspension)

Freshwater



Seawater      Seawater



Freshwater



Freshwater



Seawater



## **APPENDIX C. QUALITY ASSURANCE FOR DATA ANALYSES**



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**Quality Control**

**Replicates (Method C-229)**

LABORATORY I.D.	CLIENT I.D.	Dissolved Metals		
		Aluminium (µg/L)	Manganese (µg/L)	Iron (µg/L)
CE90-4	FW Core 9 (0-5) - 0.5hr	800	2500	27
CE90-4 Duplicate	FW Core 9 (0-5) - 0.5hr Duplicate	770	2500	26
CE90-4 Average	FW Core 9 (0-5) - 0.5hr Average	780	2500	27
CE90-14	FW Blank - 24hr	<1	<1	0.7
CE90-14 Duplicate	FW Blank - 24hr Duplicate	<1	<1	1.1
CE90-14 Average	FW Blank - 24hr Average	<1	<1	0.9
CE90-59	FW Core 4 (1g)	0.1	6	6
CE90-59 Duplicate	FW Core 4 (1g) Duplicate	0.3	6	7
CE90-59 Average	FW Core 4 (1g) Average	0.2	6	6
CE90-69	FW Core 9 (0-5) 1g	3	360	7
CE90-69 Duplicate	FW Core 9 (0-5) 1g Duplicate	3	360	7
CE90-69 Average	FW Core 9 (0-5) 1g Average	3	360	7
CE90-89	FW 4-1-1	6	9	<1
CE90-89 Duplicate	FW 4-1-1 Duplicate	6	9	<1
CE90-89 Average	FW 4-1-1 Average	6	9	<1
CE90-95	FW 3-2-1 A	0.2	11	<1
CE90-95 Duplicate	FW 3-2-1 A Duplicate	0.4	11	<1
CE90-95 Average	FW 3-2-1 A Average	0.3	11	<1
CE90-113	FW 4-7-1	3	1	<1
CE90-113 Duplicate	FW 4-7-1 Duplicate	3	1	<1
CE90-113 Average	FW 4-7-1 Average	3	1	<1
CE90-178	FW 1-17-3	15	3700	1300
CE90-178 Duplicate	FW 1-17-3 Duplicate	14	3700	1300
CE90-178 Average	FW 1-17-3 Average	15	3700	1300
CE90-191	FW 3-21-3	38	150	4
CE90-191 Duplicate	FW 3-21-3 Duplicate	40	150	4
CE90-191 Average	FW 3-21-3 Average	39	150	4
CE90-238	FW 3.39.1	281	224	8
CE90-238 Duplicate	FW 3.39.1 Duplicate	287	225	8
CE90-238 Average	FW 3.39.1 Average	284	224	8

**Spike Recoveries (Method C-229)**

LABORATORY I.D.	CLIENT I.D.	Aluminium (µg/L)	Iron (µg/L)	Manganese (µg/L)
CE90-3 % Recovery	FW Core 9 (0-1) - 0.5hr	95	87	---
CE90-31 % Recovery	SW Core 9A (0-5) - 7hr	102	77	---
CE90-58 % Recovery	FW Core 90.1g Duplicate	106	93	91
CE90-68 % Recovery	FW Core 9 (0-5) 0.1g	100	94	89
CE90-88 % Recovery	FW 3-1-1	99	88	87
CE90-94 % Recovery	FW 1-2-1 B	92	89	---
CE90-102 % Recovery	FW 1-4-1	96	98	72
CE90-112 % Recovery	FW 3-7-1	101	105	89
CE90-177 % Recovery	FW 4-17-2	101	102	87
CE90-192 % Recovery	FW 4-21-3	95	101	87

**Reference Material (Method C-229)**

Reference Material	Aluminium (µg/L)	Iron (µg/L)	Manganese (µg/L)
TM-28.3 Measured Value-1	57.1	6.93	18.3
TM-28.3 Measured Value-2	53.9	7.08	15.7
TM-28.3 Measured Value-3	55.9	7.45	17.8
TM-28.3 Measured Value-4	54.3	7.57	18.4
TM28.3 Average (n=4)	55.3	7.26	17.6
% Recovery	110	110	110
TM-28.3 (Certified Value)	51.3 ± 5.57	6.90 ± 0.521	16.5 ± 3.71

Replicates (Method C-209)

LABORATORY I.D.	CLIENT I.D.	Dissolved Metals								
		Arsenic (µg/L)	Cadmium (µg/L)	Cobalt (µg/L)	Chromium (µg/L)	Copper (µg/L)	Lead (µg/L)	Nickel (µg/L)	Vanadium (µg/L)	Zinc (µg/L)
CE90-2	FW Core 4 (0-5) - 0.5hr	0.66	0.13	1.97	<0.02	0.70	<0.03	3.60	0.18	11.6
CE90-2 Duplicate	FW Core 4 (0-5) - 0.5hr Duplicate	0.46	0.11	1.96	<0.02	0.80	<0.03	3.79	0.17	12.6
CE90-2 Average	FW Core 4 (0-5) - 0.5hr Average	0.56	0.12	1.96	<0.02	0.75	<0.03	3.69	0.17	12.1
CE90-12	FW Core 9 (0-5) - 7hr	7.77	1.59	56.8	0.99	4.83	0.42	137	0.53	78.8
CE90-12 Duplicate	FW Core 9 (0-5) - 7hr Duplicate	7.79	1.50	57.8	1.01	4.72	0.41	136	0.56	78.1
CE90-12 Average	FW Core 9 (0-5) - 7hr Average	7.78	1.54	57.3	1.00	4.77	0.42	136	0.55	78.5
CE90-20	SW Core 4 (0-5) -0.5hr	1.64	0.49	0.33	3.45	0.61	<0.03	6.88	0.24	3.41
CE90-20 dup	SW Core 4 (0-5) -0.5hr	2.49	0.45	0.38	3.50	0.59	<0.03	7.07	0.18	3.47
CE90-20 Average	SW Core 4 (0-5) -0.5hr	2.07	0.47	0.36	3.48	0.60	<0.03	6.98	0.21	3.44
CE90-30	SW Core 9 (0-5) - 7hr	14.6	2.78	1.19	76.1	5.09	7.63	193	0.44	105
CE90-30 dup	SW Core 9 (0-5) - 7hr	15.1	2.23	1.22	73.4	5.19	6.48	187	0.16	100
CE90-30 Average	SW Core 9 (0-5) - 7hr	14.9	2.51	1.20	74.8	5.14	7.05	190	0.30	103
CE90-40	SW Core 9 (0-1) - 1g	3.11	0.26	0.38	2.37	2.03	<0.03	2.80	5.63	2.97
CE90-40 dup	SW Core 9 (0-1) - 1g	2.23	0.20	0.42	2.40	1.98	<0.03	2.44	5.79	2.26
CE90-40 Average	SW Core 9 (0-1) - 1g	2.67	0.23	0.40	2.39	2.00	<0.03	2.62	5.71	2.61
CE90-49	SW Core 4 (0.1g) Duplicate	2.41	0.09	0.28	0.13	1.36	<0.03	0.30	1.11	1.37
CE90-49 dup	SW Core 4 (0.1g) Duplicate	3.34	0.01	0.31	0.13	1.32	<0.03	0.29	0.84	0.99
CE90-49 Average	SW Core 4 (0.1g) Duplicate	2.88	0.05	0.29	0.13	1.34	<0.03	0.30	0.98	1.18
CE90-57	FW Core 4 (0.1g)	0.81	0.09	0.04	<0.02	1.04	<0.03	0.72	0.73	2.70
CE90-57 Duplicate	FW Core 4 (0.1g) Duplicate	1.01	0.09	0.05	<0.02	1.00	<0.03	0.72	0.68	2.44
CE90-57 Average	FW Core 4 (0.1g) Average	0.91	0.09	0.04	<0.02	1.02	<0.03	0.72	0.70	2.57
CE90-67	FW Core 9 (0-5) 0.01g	0.86	0.05	0.09	<0.02	2.75	0.04	0.68	1.31	8.73
CE90-67 Duplicate	FW Core 9 (0-5) 0.01g Duplicate	0.83	0.05	0.09	<0.02	2.80	0.04	0.68	1.29	8.54
CE90-67 Average	FW Core 9 (0-5) 0.01g Average	0.85	0.05	0.09	<0.02	2.78	0.04	0.68	1.30	8.63
CE90-82	SW Core 9 (0-5)	7.54	2.35	1.10	92.6	3.16	4.20	207	0.44	121
CE90-82 dup	SW Core 9 (0-5)	6.64	2.33	0.98	91.7	3.17	4.16	208	0.54	117
CE90-82 Average	SW Core 9 (0-5)	7.09	2.34	1.04	92.2	3.17	4.18	208	0.49	119
CE90-87	FW 1-1-1	4.43	0.09	1.34	0.06	11.5	0.06	2.64	12.4	3.20
CE90-87 Duplicate	FW 1-1-1 Duplicate	4.31	0.07	1.41	0.07	11.6	0.05	2.67	13.2	3.03
CE90-87 Average	FW 1-1-1 Average	4.37	0.08	1.38	0.07	11.6	0.05	2.65	12.8	3.11
CE90-93	FW 1-2-1 A	6.65	0.03	1.66	0.14	13.5	0.07	3.62	21.8	1.59
CE90-93 Duplicate	FW 1-2-1 A Duplicate	6.34	0.03	1.72	0.15	13.7	0.08	3.54	22.0	1.48
CE90-93 Average	FW 1-2-1 A Average	6.50	0.03	1.69	0.14	13.6	0.07	3.58	21.9	1.53

LABORATORY I.D.	CLIENT I.D.	Dissolved Metals								
		Arsenic (µg/L)	Cadmium (µg/L)	Cobalt (µg/L)	Chromium (µg/L)	Copper (µg/L)	Lead (µg/L)	Nickel (µg/L)	Vanadium (µg/L)	Zinc (µg/L)
CE90-101	FW 4-2-2	0.82	0.16	0.12	0.27	3.38	0.14	2.14	0.48	2.57
CE90-101 Duplicate	FW 4-2-2 Duplicate	0.84	0.15	0.10	0.34	3.31	0.13	2.09	0.51	2.47
CE90-101 Average	FW 4-2-2 Average	0.83	0.15	0.11	0.30	3.34	0.14	2.12	0.50	2.52
CE90-111	FW 1-7-1	6.46	0.02	1.29	0.23	5.32	0.05	3.62	27.9	1.83
CE90-111 Duplicate	FW 1-7-1 Duplicate	6.52	0.02	1.29	0.23	5.25	0.05	3.59	28.2	1.66
CE90-111 Average	FW 1-7-1 Average	6.49	0.02	1.29	0.23	5.29	0.05	3.61	28.0	1.75
CE90-176	FW 3-17-2	0.64	0.27	2.91	<0.04	0.95	<0.03	5.66	0.16	3.29
CE90-176 Duplicate	FW 3-17-2 Duplicate	0.66	0.26	2.96	<0.04	0.93	<0.03	5.49	0.17	3.48
CE90-176 Average	FW 3-17-2 Average	0.65	0.26	2.93	<0.04	0.94	<0.03	5.58	0.17	3.38
CE90-186	FW 4-21-1	0.88	0.04	0.05	<0.04	1.28	<0.03	0.58	0.34	0.43
CE90-186 Duplicate	FW 4-21-1 Duplicate	0.93	0.02	0.04	<0.04	1.27	<0.03	0.59	0.31	0.17
CE90-186 Average	FW 4-21-1 Average	0.91	0.03	0.04	<0.04	1.27	<0.03	0.59	0.32	0.30
CE90-200	FE Core 4 - 72 hr leach	0.87	<0.01	0.08	<0.04	1.02	<0.03	0.63	0.59	0.02
CE90-200 Duplicate	FE Core 4 - 72 hr leach Duplicate	0.77	<0.01	0.08	<0.04	0.95	<0.03	0.61	0.59	0.03
CE90-200 Average	FE Core 4 - 72 hr leach Average	0.82	<0.01	0.08	<0.04	0.98	<0.03	0.62	0.59	0.02
CE90-219	FW 1.28.2	10.5	0.08	20.9	0.72	2.47	1.02	31.6	8.12	14.8
CE90-219 Duplicate	FW 1.28.2 Duplicate	10.7	0.08	20.7	0.72	2.44	1.05	31.4	8.01	14.9
CE90-219 Average	FW 1.28.2 Average	10.6	0.08	20.8	0.72	2.46	1.04	31.5	8.06	14.9



**Spike Recoveries (Method C-209)**

LABORATORY I.D.	CLIENT I.D.	Arsenic (µg/L)	Cadmium (µg/L)	Cobalt (µg/L)	Chromium (µg/L)	Copper (µg/L)	Lead (µg/L)	Nickel (µg/L)	Vanadium (µg/L)	Zinc (µg/L)
CE90-1 % Recovery	FW Blank - 0.5hr % Recovery	105	91	97	102	101	87	101	101	101
CE90-11 % Recovery	FW Core 9 (0-1) - 7hr % Recovery	122	91	103	109	99	89	102	109	98
CE90-19 % Recovery	SW Blank - 0.5hr	114	87	107	99	103	88	105	112	100
CE90-29 % Recovery	SW Core 9 (0-1) - 7hr	114	91	110	103	101	89	104	112	98
CE90-39 % Recovery	SW Core 9 (0-1) - 0.1g	113	92	111	105	103	90	106	118	99
CE90-48 % Recovery	SW Core 4 (0.1g)	109	88	106	100	97	85	100	112	94
CE90-81 % Recovery	SW Core 9 (0-1)	118	95	109	104	100	90	103	114	97
CE90-56 % Recovery	FW Core 4 (0.01g) Duplicate % Recovery	116	99	112	115	107	99	110	119	108
CE90-66 % Recovery	FW Core 9 (0-1) 10g % Recovery	120	92	105	110	100	89	104	114	101
CE90-76 % Recovery	FW Core 9 (0-5) % Recovery	122	89	123	110	99	74	---	119	72
CE90-92 % Recovery	FW 4-1-2 % Recovery	108	96	103	108	98	98	103	111	97
CE90-100 % Recovery	FW 3-2-2 % Recovery	100	97	101	107	100	96	102	107	76
CE90-110 % Recovery	FW 4-4-3 % Recovery	103	99	101	106	98	98	101	108	96
CE90-175 % Recovery	FW 1-17-2 % Recovery	111	94	106	112	100	96	106	114	96
CE90-185 % Recovery	FW 3-21-1 % Recovery	103	97	107	109	99	98	102	112	97
CE90-199 % Recovery	FW Core 9 (0-5) - 72 hr leach % Recovery	105	96	101	104	94	96	94	109	92
CE90-216 % Recovery	FW 4.28.1 % Recovery	105	96	109	111	100	97	105	112	99

**Certified Reference Material (Method C-209)**

Sample:	Arsenic (µg/L)	Cadmium (µg/L)	Cobalt (µg/L)	Chromium (µg/L)	Copper (µg/L)	Lead (µg/L)	Nickel (µg/L)	Vanadium (µg/L)	Zinc (µg/L)
TM-28.3 Measured Value-1	6.05	1.74	3.11	4.89	5.92	3.66	8.91	3.12	24.8
TM-28.3 Measured Value-2	5.86	1.81	3.22	4.99	6.44	3.73	9.35	3.20	25.4
TM-28.3 Measured Value-3	5.93	1.69	4.71	3.02	6.08	3.53	9.15	2.96	28.9
TM-28.3 (Certified)	6.22±0.848	1.91±0.23	3.53±0.519	4.83±0.768	6.15±0.863	3.97±0.567	9.8±1.16	3.07±0.394	27.5±3.37
TM-28.3 (Average n=3)	5.95	1.75	3.68	4.30	6.15	3.64	9.14	3.09	26.37
% Recovery	96	91	100	89	100	92	100	100	96

**Miscellaneous Information**

**Method Codes:**

C-209 Inductively Coupled Plasma-Mass Spectrometry  
 C-229 Inductively Coupled Plasma-Atomic Emission Spectrometry



Environmental Division

**QUALITY CONTROL REPORT**

<b>Work Order</b>	<b>: EB0912220</b>	<b>Page</b>	: 1 of 6
<b>Client</b>	<b>: CSIRO AUSTRALIA</b>	<b>Laboratory</b>	: Environmental Division Brisbane
<b>Contact</b>	<b>: DR STUART SIMPSON</b>	<b>Contact</b>	: Tim Kilmister
<b>Address</b>	<b>: CENTRE FOR ENVIRONMENTAL CONTAMINANTS RESEARCH CSIRO ENERGY TECHNOLOGY NEW ILLAWARRA ROAD LUCAS HEIGHTS NSW, AUSTRALIA 2234</b>	<b>Address</b>	: 32 Shand Street Stafford QLD Australia 4053
<b>E-mail</b>	<b>: stuart.simpson@csiro.au</b>	<b>E-mail</b>	: Services.Brisbane@alsenviro.com
<b>Telephone</b>	<b>: +61 02 97106807</b>	<b>Telephone</b>	: +61-7-3243 7222
<b>Facsimile</b>	<b>: +61 02 97106837</b>	<b>Facsimile</b>	: +61-7-3243 7218
<b>Project</b>	<b>: CSIRO Land and Water CECR (Sydney)</b>	<b>QC Level</b>	: NEPM 1999 Schedule B(3) and ALS QCS3 requirement
<b>Site</b>	<b>: ----</b>	<b>Date Samples Received</b>	: 04-AUG-2009
<b>C-O-C number</b>	<b>: ----</b>	<b>Issue Date</b>	: 10-AUG-2009
<b>Sampler</b>	<b>: ----</b>	<b>No. of samples received</b>	: 42
<b>Order number</b>	<b>: ----</b>	<b>No. of samples analysed</b>	: 42
<b>Quote number</b>	<b>: BN/032/09</b>		

This report supersedes any previous report(s) with this reference. Results apply to the sample(s) as submitted. All pages of this report have been checked and approved for release.

This Quality Control Report contains the following information:

- Laboratory Duplicate (DUP) Report; Relative Percentage Difference (RPD) and Acceptance Limits
- Method Blank (MB) and Laboratory Control Spike (LCS) Report; Recovery and Acceptance Limits
- Matrix Spike (MS) Report; Recovery and Acceptance Limits



NATA Accredited Laboratory 825

This document is issued in accordance with NATA accreditation requirements.

Accredited for compliance with ISO/IEC 17025.

**Signatories**

This document has been electronically signed by the authorized signatories indicated below. Electronic signing has been carried out in compliance with procedures specified in 21 CFR Part 11.

<i>Signatories</i>	<i>Position</i>	<i>Accreditation Category</i>
Kim McCabe	Senior Inorganic Chemist	Inorganics



## General Comments

The analytical procedures used by the Environmental Division have been developed from established internationally recognized procedures such as those published by the USEPA, APHA, AS and NEPM. In house developed procedures are employed in the absence of documented standards or by client request.

Where moisture determination has been performed, results are reported on a dry weight basis.

Where a reported less than (<) result is higher than the LOR, this may be due to primary sample extract/digestate dilution and/or insufficient sample for analysis.

Where the LOR of a reported result differs from standard LOR, this may be due to high moisture content, insufficient sample (reduced weight employed) or matrix interference.

Key :  
Anonymous = Refers to samples which are not specifically part of this work order but formed part of the QC process lot  
CAS Number = CAS registry number from database maintained by Chemical Abstracts Services. The Chemical Abstracts Service is a division of the American Chemical Society.  
LOR = Limit of reporting  
RPD = Relative Percentage Difference  
# = Indicates failed QC



## Laboratory Duplicate (DUP) Report

The quality control term Laboratory Duplicate refers to a randomly selected intralaboratory split. Laboratory duplicates provide information regarding method precision and sample heterogeneity. The permitted ranges for the Relative Percent Deviation (RPD) of Laboratory Duplicates are specified in ALS Method QWI-EN/38 and are dependent on the magnitude of results in comparison to the level of reporting: Result < 10 times LOR:- No Limit; Result between 10 and 20 times LOR:- 0% - 50%; Result > 20 times LOR:- 0% - 20%.

Sub-Matrix: **WATER**

				Laboratory Duplicate (DUP) Report					
Laboratory sample ID	Client sample ID	Method: Compound	CAS Number	LOR	Unit	Original Result	Duplicate Result	RPD (%)	Recovery Limits (%)
<b>ED037P: Alkalinity by PC Titrator (QC Lot: 1059446)</b>									
EB0912201-001	Anonymous	ED037-P: Hydroxide Alkalinity as CaCO3	DMO-210-001	1	mg/L	<1	<1	0.0	No Limit
		ED037-P: Carbonate Alkalinity as CaCO3	3812-32-6	1	mg/L	<1	<1	0.0	No Limit
		ED037-P: Bicarbonate Alkalinity as CaCO3	71-52-3	1	mg/L	92	92	0.0	0% - 20%
		ED037-P: Total Alkalinity as CaCO3	----	1	mg/L	92	92	0.0	0% - 20%
EB0912220-024	Core 9 4.1	ED037-P: Hydroxide Alkalinity as CaCO3	DMO-210-001	1	mg/L	<1	<1	0.0	No Limit
		ED037-P: Carbonate Alkalinity as CaCO3	3812-32-6	1	mg/L	<1	<1	0.0	No Limit
		ED037-P: Bicarbonate Alkalinity as CaCO3	71-52-3	1	mg/L	118	118	0.0	0% - 20%
		ED037-P: Total Alkalinity as CaCO3	----	1	mg/L	118	118	0.0	0% - 20%
<b>ED037P: Alkalinity by PC Titrator (QC Lot: 1060557)</b>									
EB0912220-031	Core 1 7.1	ED037-P: Hydroxide Alkalinity as CaCO3	DMO-210-001	1	mg/L	<1	<1	0.0	No Limit
		ED037-P: Carbonate Alkalinity as CaCO3	3812-32-6	1	mg/L	<1	<1	0.0	No Limit
		ED037-P: Bicarbonate Alkalinity as CaCO3	71-52-3	1	mg/L	126	122	2.7	0% - 20%
		ED037-P: Total Alkalinity as CaCO3	----	1	mg/L	126	122	2.7	0% - 20%
EB0912220-040	Core 4 10.1	ED037-P: Hydroxide Alkalinity as CaCO3	DMO-210-001	1	mg/L	<1	<1	0.0	No Limit
		ED037-P: Carbonate Alkalinity as CaCO3	3812-32-6	1	mg/L	<1	<1	0.0	No Limit
		ED037-P: Bicarbonate Alkalinity as CaCO3	71-52-3	1	mg/L	85	82	2.8	0% - 20%
		ED037-P: Total Alkalinity as CaCO3	----	1	mg/L	85	82	2.8	0% - 20%
<b>ED038A: Acidity (QC Lot: 1059449)</b>									
EB0912220-001	Core 1 1.2	ED038: Acidity as CaCO3	----	1	mg/L	3	3	0.0	No Limit
EB0912220-010	Core 4 2.1	ED038: Acidity as CaCO3	----	1	mg/L	3	3	0.0	No Limit
<b>ED038A: Acidity (QC Lot: 1060997)</b>									
EB0912305-001	Anonymous	ED038: Acidity as CaCO3	----	1	mg/L	129	129	0.0	0% - 20%
<b>ED040F: Dissolved Major Anions (QC Lot: 1061192)</b>									
EB0912220-030	Core 9 4.3	ED040F: Sulfate as SO4 2-	14808-79-8	1	mg/L	3320	3280	1.2	0% - 20%
<b>ED040F: Dissolved Major Anions (QC Lot: 1061207)</b>									
EB0912198-001	Anonymous	ED040F: Sulfate as SO4 2-	14808-79-8	1	mg/L	<1	<1	0.0	No Limit
EB0912290-001	Anonymous	ED040F: Sulfate as SO4 2-	14808-79-8	1	mg/L	208	210	0.9	0% - 20%
<b>ED045G: Chloride Discrete analyser (QC Lot: 1061191)</b>									
EB0912220-002	Core 2 1.2	ED045G: Chloride	16887-00-6	1	mg/L	19600	19200	2.1	0% - 20%
EB0912220-011	Core 5 2.1	ED045G: Chloride	16887-00-6	1	mg/L	19700	19600	0.5	0% - 20%
<b>ED045G: Chloride Discrete analyser (QC Lot: 1061193)</b>									
EB0912220-021	Core 3 4.1	ED045G: Chloride	16887-00-6	1	mg/L	516	509	1.4	0% - 20%
EB0912220-030	Core 9 4.3	ED045G: Chloride	16887-00-6	1	mg/L	19700	19100	3.1	0% - 20%
<b>ED045G: Chloride Discrete analyser (QC Lot: 1061209)</b>									

Page : 4 of 6  
 Work Order : EB0912220  
 Client : C S I R O AUSTRALIA  
 Project : CSIRO Land and Water CECR (Sydney)



Sub-Matrix: **WATER**

				Laboratory Duplicate (DUP) Report					
Laboratory sample ID	Client sample ID	Method: Compound	CAS Number	LOR	Unit	Original Result	Duplicate Result	RPD (%)	Recovery Limits (%)
<b>ED045G: Chloride Discrete analyser (QC Lot: 1061209) - continued</b>									
EB0912198-001	Anonymous	ED045G: Chloride	16887-00-6	1	mg/L	<1	<1	0.0	No Limit



### Method Blank (MB) and Laboratory Control Spike (LCS) Report

The quality control term Method / Laboratory Blank refers to an analyte free matrix to which all reagents are added in the same volumes or proportions as used in standard sample preparation. The purpose of this QC parameter is to monitor potential laboratory contamination. The quality control term Laboratory Control Sample (LCS) refers to a certified reference material, or a known interference free matrix spiked with target analytes. The purpose of this QC parameter is to monitor method precision and accuracy independent of sample matrix. Dynamic Recovery Limits are based on statistical evaluation of processed LCS.

Sub-Matrix: **WATER**

				Method Blank (MB) Report Result	Laboratory Control Spike (LCS) Report			
					Spike Concentration	Spike Recovery (%)	Recovery Limits (%)	
Method: Compound	CAS Number	LOR	Unit			LCS	Low	High
<b>ED037P: Alkalinity by PC Titrator (QCLot: 1059446)</b>								
ED037-P: Total Alkalinity as CaCO3	----	1	mg/L	----	500 mg/L	101	83	111
<b>ED037P: Alkalinity by PC Titrator (QCLot: 1060557)</b>								
ED037-P: Total Alkalinity as CaCO3	----	1	mg/L	----	200 mg/L	86.0	83	111
<b>ED038A: Acidity (QCLot: 1059449)</b>								
ED038: Acidity as CaCO3	----	1	mg/L	----	100 mg/L	98.0	93	107
<b>ED038A: Acidity (QCLot: 1060996)</b>								
ED038: Acidity as CaCO3	----	1	mg/L	----	100 mg/L	97.0	93	107
<b>ED038A: Acidity (QCLot: 1060997)</b>								
ED038: Acidity as CaCO3	----	1	mg/L	----	100 mg/L	97.0	93	107
<b>ED040F: Dissolved Major Anions (QCLot: 1061207)</b>								
ED040F: Sulfate as SO4 2-	14808-79-8	1	mg/L	<1	----	----	----	----
<b>ED045G: Chloride Discrete analyser (QCLot: 1061191)</b>								
ED045G: Chloride	16887-00-6	1	mg/L	<1	1000 mg/L	99.7	90	130
<b>ED045G: Chloride Discrete analyser (QCLot: 1061193)</b>								
ED045G: Chloride	16887-00-6	1	mg/L	<1	1000 mg/L	98.9	90	130
<b>ED045G: Chloride Discrete analyser (QCLot: 1061209)</b>								
ED045G: Chloride	16887-00-6	1	mg/L	<1	1000 mg/L	98.8	90	130



### Matrix Spike (MS) Report

The quality control term Matrix Spike (MS) refers to an intralaboratory split sample spiked with a representative set of target analytes. The purpose of this QC parameter is to monitor potential matrix effects on analyte recoveries. Static Recovery Limits as per laboratory Data Quality Objectives (DQOs). Ideal recovery ranges stated may be waived in the event of sample matrix interference.

Sub-Matrix: **WATER**

				<i>Matrix Spike (MS) Report</i>			
				<i>Spike</i>	<i>Spike Recovery (%)</i>	<i>Recovery Limits (%)</i>	
<i>Laboratory sample ID</i>	<i>Client sample ID</i>	<i>Method: Compound</i>	<i>CAS Number</i>	<i>Concentration</i>	<i>MS</i>	<i>Low</i>	<i>High</i>
<b>ED045G: Chloride Discrete analyser (QCLot: 1061191)</b>							
EB0912220-002	Core 2 1.2	ED045G: Chloride	16887-00-6	400 mg/L	# Not Determined	70	130
<b>ED045G: Chloride Discrete analyser (QCLot: 1061193)</b>							
EB0912220-022	Core 4 4.1	ED045G: Chloride	16887-00-6	400 mg/L	83.2	70	130
<b>ED045G: Chloride Discrete analyser (QCLot: 1061209)</b>							
EB0912198-007	Anonymous	ED045G: Chloride	16887-00-6	400 mg/L	101	70	130



## Environmental Division

### QUALITY CONTROL REPORT

Work Order	: <b>EB0914086</b>	Page	: 1 of 5
Client	: <b>CSIRO AUSTRALIA</b>	Laboratory	: Environmental Division Brisbane
Contact	: DR STUART SIMPSON	Contact	: Tim Kilmister
Address	: CENTRE FOR ENVIRONMENTAL CONTAMINANTS RESEARCH CSIRO ENERGY TECHNOLOGY NEW ILLAWARRA ROAD LUCAS HEIGHTS NSW, AUSTRALIA 2234	Address	: 32 Shand Street Stafford QLD Australia 4053
E-mail	: stuart.simpson@csiro.au	E-mail	: Services.Brisbane@alsenviro.com
Telephone	: +61 02 97106807	Telephone	: +61-7-3243 7222
Facsimile	: +61 02 97106837	Facsimile	: +61-7-3243 7218
Project	: ----	QC Level	: NEPM 1999 Schedule B(3) and ALS QCS3 requirement
Site	: ----	Date Samples Received	: 07-SEP-2009
C-O-C number	: ----	Issue Date	: 14-SEP-2009
Sampler	: ----	No. of samples received	: 6
Order number	: ----	No. of samples analysed	: 6
Quote number	: BN/032/09		

This report supersedes any previous report(s) with this reference. Results apply to the sample(s) as submitted. All pages of this report have been checked and approved for release.

This Quality Control Report contains the following information:

- Laboratory Duplicate (DUP) Report; Relative Percentage Difference (RPD) and Acceptance Limits
- Method Blank (MB) and Laboratory Control Spike (LCS) Report; Recovery and Acceptance Limits
- Matrix Spike (MS) Report; Recovery and Acceptance Limits



NATA Accredited Laboratory 825

This document is issued in accordance with NATA accreditation requirements.

Accredited for compliance with ISO/IEC 17025.

### Signatories

This document has been electronically signed by the authorized signatories indicated below. Electronic signing has been carried out in compliance with procedures specified in 21 CFR Part 11.

Signatories	Position	Accreditation Category
Stephen Hislop	Senior Inorganic Chemist	Inorganics





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### **General Comments**

The analytical procedures used by the Environmental Division have been developed from established internationally recognized procedures such as those published by the USEPA, APHA, AS and NEPM. In house developed procedures are employed in the absence of documented standards or by client request.

Where moisture determination has been performed, results are reported on a dry weight basis.

Where a reported less than (<) result is higher than the LOR, this may be due to primary sample extract/digestate dilution and/or insufficient sample for analysis.

Where the LOR of a reported result differs from standard LOR, this may be due to high moisture content, insufficient sample (reduced weight employed) or matrix interference.

Key :            Anonymous = Refers to samples which are not specifically part of this work order but formed part of the QC process lot  
                  CAS Number = CAS registry number from database maintained by Chemical Abstracts Services. The Chemical Abstracts Service is a division of the American Chemical Society.  
                  LOR = Limit of reporting  
                  RPD = Relative Percentage Difference  
                  # = Indicates failed QC



### Laboratory Duplicate (DUP) Report

The quality control term Laboratory Duplicate refers to a randomly selected intralaboratory split. Laboratory duplicates provide information regarding method precision and sample heterogeneity. The permitted ranges for the Relative Percent Deviation (RPD) of Laboratory Duplicates are specified in ALS Method QWI-EN/38 and are dependent on the magnitude of results in comparison to the level of reporting: Result < 10 times LOR:- No Limit; Result between 10 and 20 times LOR:- 0% - 50%; Result > 20 times LOR:- 0% - 20%.

Sub-Matrix: **WATER**

				Laboratory Duplicate (DUP) Report					
Laboratory sample ID	Client sample ID	Method: Compound	CAS Number	LOR	Unit	Original Result	Duplicate Result	RPD (%)	Recovery Limits (%)
<b>ED037P: Alkalinity by PC Titrator (QC Lot: 1092859)</b>									
EB0914021-004	Anonymous	ED037-P: Hydroxide Alkalinity as CaCO3	DMO-210-001	1	mg/L	<1	<1	0.0	No Limit
		ED037-P: Carbonate Alkalinity as CaCO3	3812-32-6	1	mg/L	<1	<1	0.0	No Limit
		ED037-P: Bicarbonate Alkalinity as CaCO3	71-52-3	1	mg/L	106	106	0.0	0% - 20%
		ED037-P: Total Alkalinity as CaCO3	----	1	mg/L	106	106	0.0	0% - 20%
<b>ED038A: Acidity (QC Lot: 1092873)</b>									
EB0914086-002	Core 2.46.1	ED038: Acidity as CaCO3	----	1	mg/L	31	31	0.0	0% - 20%
<b>ED040F: Dissolved Major Anions (QC Lot: 1094305)</b>									
EB0914058-001	Anonymous	ED040F: Sulfate as SO4 2-	14808-79-8	1	mg/L	920	930	1.0	0% - 20%
EB0914078-001	Anonymous	ED040F: Sulfate as SO4 2-	14808-79-8	1	mg/L	146	149	2.2	0% - 20%
<b>ED045G: Chloride Discrete analyser (QC Lot: 1094304)</b>									
EB0914058-001	Anonymous	ED045G: Chloride	16887-00-6	1	mg/L	4820	4800	0.4	0% - 20%
EB0914078-001	Anonymous	ED045G: Chloride	16887-00-6	1	mg/L	44	43	2.3	0% - 20%



### Method Blank (MB) and Laboratory Control Spike (LCS) Report

The quality control term Method / Laboratory Blank refers to an analyte free matrix to which all reagents are added in the same volumes or proportions as used in standard sample preparation. The purpose of this QC parameter is to monitor potential laboratory contamination. The quality control term Laboratory Control Sample (LCS) refers to a certified reference material, or a known interference free matrix spiked with target analytes. The purpose of this QC parameter is to monitor method precision and accuracy independent of sample matrix. Dynamic Recovery Limits are based on statistical evaluation of processed LCS.

Sub-Matrix: **WATER**

				Method Blank (MB) Report Result	Laboratory Control Spike (LCS) Report			
					Spike Concentration	Spike Recovery (%)		Recovery Limits (%)
Method: Compound	CAS Number	LOR	Unit			LCS	Low	High
<b>ED037P: Alkalinity by PC Titrator (QCLot: 1092859)</b>								
ED037-P: Total Alkalinity as CaCO3	----	1	mg/L	----	200 mg/L	98.5	83	111
<b>ED038A: Acidity (QCLot: 1092873)</b>								
ED038: Acidity as CaCO3	----	1	mg/L	----	100 mg/L	100	93	107
<b>ED040F: Dissolved Major Anions (QCLot: 1094305)</b>								
ED040F: Sulfate as SO4 2-	14808-79-8	1	mg/L	<1	----	----	----	----
<b>ED045G: Chloride Discrete analyser (QCLot: 1094304)</b>								
ED045G: Chloride	16887-00-6	1	mg/L	<1	1000 mg/L	94.4	90	130



### Matrix Spike (MS) Report

The quality control term Matrix Spike (MS) refers to an intralaboratory split sample spiked with a representative set of target analytes. The purpose of this QC parameter is to monitor potential matrix effects on analyte recoveries. Static Recovery Limits as per laboratory Data Quality Objectives (DQOs). Ideal recovery ranges stated may be waived in the event of sample matrix interference.

Sub-Matrix: **WATER**

				<i>Matrix Spike (MS) Report</i>			
		<i>Spike</i>	<i>Spike Recovery (%)</i>		<i>Recovery Limits (%)</i>		
<i>Laboratory sample ID</i>	<i>Client sample ID</i>	<i>Method: Compound</i>	<i>CAS Number</i>	<i>Concentration</i>	<i>MS</i>	<i>Low</i>	<i>High</i>
<b>ED045G: Chloride Discrete analyser (QCLot: 1094304)</b>							
EB0913886-002	Anonymous	ED045G: Chloride	16887-00-6	400 mg/L	85.6	70	130

