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# RESEARCH PAPER

## BOORAGOON LAKE: ENVIRONMENTAL IMPLICATION OF TRACE ELEMENTS DERIVED FROM ROAD RUNOFF STORMWATER IN WETLAND SEDIMENTS DURING WETTING AND DRYING CYCLES

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### ABSTRACT

Booragoon Lake is one of the shallow groundwater lakes that comprise the Beelihar Wetlands chain, a string of wetlands that sit in a north-south trending interdunal depression on the Swan Coastal Plain, in Perth, Western Australia. Situated on the southern boundary of the lake is Leach Highway, a major arterial road with traffic volumes of up to 60 000 vehicles per day. Stormwater runoff from Leach Highway is a major source of contamination in the lake environment. In this study we investigated changes in the concentrations of metals (Cr, Co, Ni, Cu, Zn, As and Pb) in lake water and sediments throughout a three-month period from February to April 2012, during which the lake dried out. Eleven sets of water samples were taken between February and April from Booragoon Lake and stormwater inputs, to assess the geochemical conditions of the lake, and the concentrations of metals derived from road stormwater runoff. Fourteen sediment samples were also collected from the dry lake bed to analyse for major and trace element concentrations. The results of the analyses showed that the concentration of metals in dry sediments was higher than that in wet sediment, most likely as a result of evaporative concentration and drying of metal enriched pore fluids during the drying cycle. Furthermore, these metals were shown to be readily soluble upon rewetting, presenting a danger of a first flush of metal-rich waters during heavy rainfall events.

**Keywords:** Geochemistry; Anthropogenic contamination; Metal; Organic matter; Environmental monitoring

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## INTRODUCTION

Booragoon Lake (Reserve 25318), with an area of 13.2 hectares (Smith 1986), plays an important role as a breeding ground for the Australian white ibis (*Threskiornis moluccus*), and the long-necked turtle (*Chelodina colliei*) (Giles 2001). It serves as a recreational amenity and is an important groundwater recharge basin, receiving stormwater runoff from Leach Highway and residential streets surrounding the lake. The wetland is situated 10 km due south of the Perth central business district and 12 km east of Fremantle Harbour in Western Australia. It lies in an interdunal depression that runs parallel to the coastline of the Swan Coastal Plain, and together with Piney, North, Blue Gum, Bibra, Thompson and Yangebup lakes, comprise the East Beeliar chain of wetlands (Fox and MacShane 2004). The geomorphology of the area is the Spearwood dunes systems (in the western margin of the lake) and the Bassendean Dune system (in the eastern margin). Booragoon Lake and Blue Gum Lake, 500 m to the north, are formed in the Karrakatta Soil complex of the Spearwood Dunes (Davidson 1995).

Historically, the wetland has been impacted by human activities. The lake originally experienced seasonal fluctuations of the water levels in response to seasonal recharge of the underlying shallow aquifer (Hollick et al. 1987). However, in the 1970s, as a consequence of artificial recharge by deep groundwater to maintain open water, Booragoon Lake changed from an ephemeral wetland ecosystem to a permanent water body (Fox and MacShane 2004). The encroaching urban environment has contributed anthropogenic contamination into the Lake, such as metals, fuels and oils, nutrients, and particulates in stormwater input from surrounding roads and also the spread of exotic plant and animal species (Smith 1986). Previous studies (Oldmeadow 2000) have shown that the organic-rich lake bed sediments have accumulated significant concentrations of metals, especially lead (Pb) as a legacy of the use of leaded petrol.

The previous practice of water level maintenance was discontinued in the late 1990s. The lake now functions as a through-flow lake, with seasonal fluctuations in water levels once again reflecting the shallow underlying aquifer which responds to the highly seasonal climatic variations in rainfall and recharge (Appleyard et al. 2004; Fox and MacShane 2004). Perth has experienced a significant and steady reduction in rainfall since the 1970s, which, coupled with increasing extraction of groundwater to supply Perth's water needs, has seen significant reductions in water levels in the shallow aquifer across the Swan Coastal Plain (Fox and MacShane 2004).

As a result of the decline in water levels, the upper layers of the organic-rich sediments of the lake bed currently undergo cycles of complete drying during the hot dry summer and seasonal inundation during the wet winter months (Qiu and McComb 2000). This results in significant changes in the geochemical conditions of the sediments, which historically had maintained sufficient residual sediment pore water to prevent total desiccation of the organic-rich lake bed. These changes may have important consequences in terms of the development of Acid Sulfate Soils (ASS). With decrease in water level, pyritic material contained in the organic-rich lake bed may be exposed and oxidised and the geochemical cycling of stormwater derived metals bound to those sediments enhanced due to the development of ASS (Smith 1986; Appleyard et al. 2004).

The purpose of this paper was to investigate changes in the concentrations of metals (Cr, Co, Ni, Cu, Zn, Pb) and arsenic (As) in lake water and surface sediments throughout a three-month period from February to April 2012, during which the lake dried out. Concentrations of metals were determined in the uppermost sediments of the lake bed during wet and dry conditions, and in the readily mobilised fractions of metals in the dry sediments which may become solubilised at the time of the next seasonal inundation.



## MATERIALS AND METHODS

Water and sediment samples were collected from three stormwater drains on the north-west, west and south of Booragoon Lake, and from the centre of the lake between February and April 2012 for monitoring water and sediments (Figure 1).

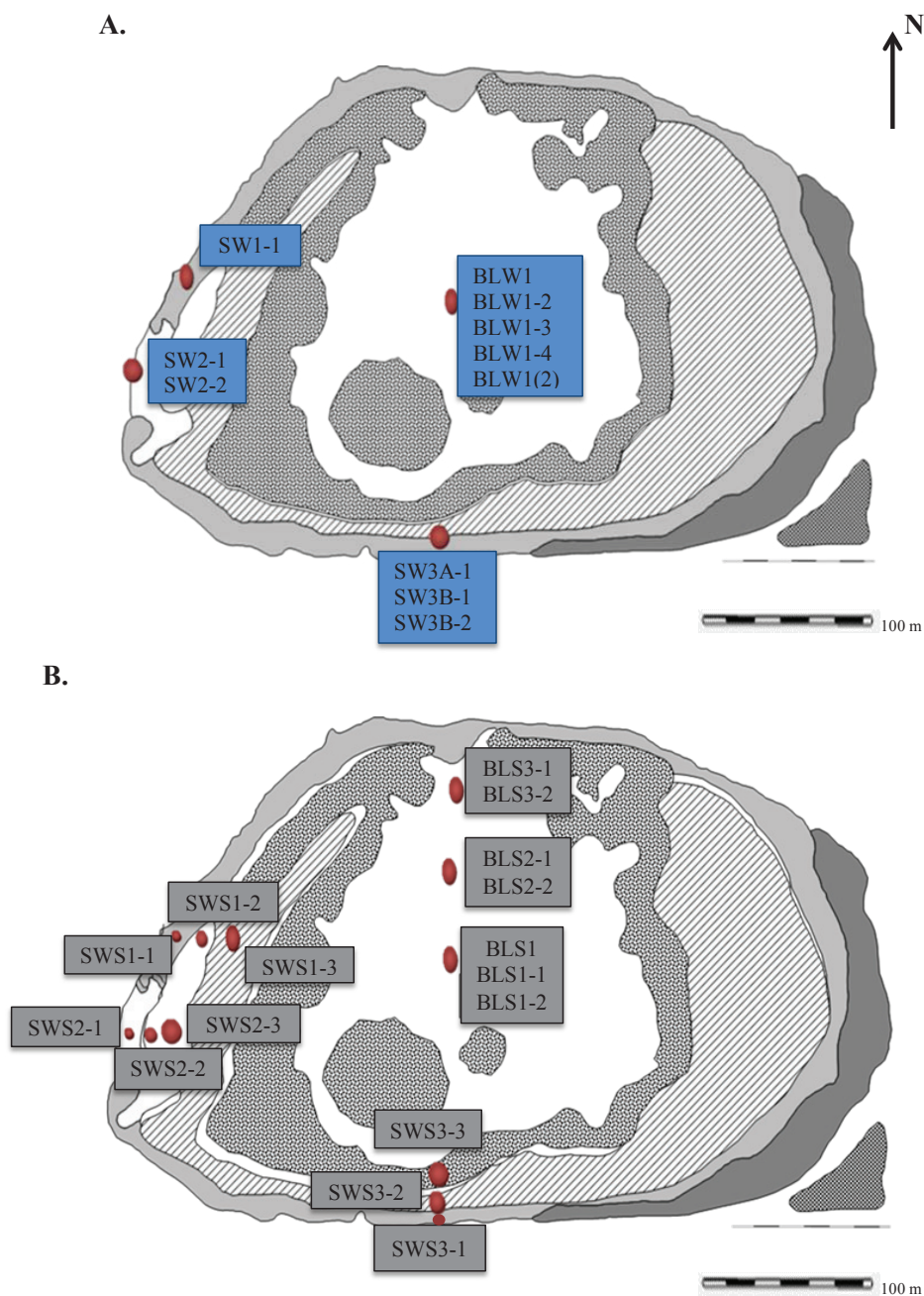
Eleven water samples were collected from the centre of the lake and from stormwater drains around the periphery of the lake using 125-mL clean plastic bottles during February (2012) to determine the concentrations of metals in the lake (Figure 1). The Booragoon Lake water (BLW) samples were taken weekly from the centre of the lake. The BLW samples were ordered with regards to their sampling dates, such as BLW1, BLW1(2), BLW1-2, BLW1-3 and BLW1-4 samples. The lake water was sampled on 3<sup>rd</sup>, 9<sup>th</sup>, 16<sup>th</sup> and 24<sup>th</sup> February 2012. All BLW samples were collected from surface of the lake, except BLW1(2), which was sampled only once by removing the lid of plastic bottles in the lake bottom (a depth of 20 cm from the lake surface). The stormwater (SW) sampling sites were ordered according to locations and dates of water samples, including SW1-1, SW2-1, SW2-2, SW3A-1, SW3B-1, and SW3B-2. Although all SW samples were collected on 3<sup>rd</sup> February 2012, SW3B-2 was taken from the drainage on 9<sup>th</sup> February 2012; because the sampling sites had dried up (Table 1). For example, SW1-1 was taken on the 3<sup>rd</sup> of February. At the same time, conductivity and pH of water samples were measured in the field using an Orion® pH and electrical conductivity (EC) meter, and the total alkalinity of the lake water was determined by titration.

In the laboratory, water samples were filtered through 0.45 µm nitrocellulose membranes prior to analysis of major and trace elements by ICP-AES and ICP-MS, and major anions and cations using a Dionex ICS 1000 High Performance Ion Chromatography system (HPIC). Water samples for ICP analysis were acidified (4% HNO<sub>3</sub>) and samples for HPIC were refrigerated (<4 °C) prior to analysis. The detection limit of the HPIC techniques that was used to detect major anions and cations was 0.2 ppm. The instruments used in this research were calibrated with commercial standards.

Sediments were also sampled from the lake and drainages in February and April 2012. Further surface sediment samples were taken at 4 m, 10 m and 20 m from the mouth of stormwater drains entering the lake (Figure 1). The stormwater sediment (SWS) sampling points were ordered with regards to dates and locations of sediments samples around of the lake; such as SWS1-1, SWS1-2,

**Table 1. Key to sampling dates for stormwater (SW) sampled in the mouths of drainages and Booragoon lake water (BLW) samples.**

Sample number	Date	Location of samples
SW1-1	3/02/2012	North-west of the Booragoon Lake (Aldridge Road)
SW2-1	3/02/2012	West of the Booragoon Lake (Aldridge Road)
SW2-2	3/02/2012	
SW3A-1	3/02/2012	South of the Booragoon Lake (Main drainage in Leach Highway)
SW3B-1	3/02/2012	South of the Booragoon Lake (Small white pipe in close proximity to main drainage from Leach Highway)
SW3B-2	3/02/2012	
BLW1	3/02/2012	Centre of the lake (taken from the lake surface)
BLW1-2	9/02/2012	
BLW1-3	16/02/2012	
BLW1-4	24/02/2012	
BLW1(2)	3/02/2012	Centre of the lake (taken from the lake bottom)



**Fig 1. A.** Location of water samples collected from around and within Booragoon Lake. Solid grey areas represent fringing vegetation. Hatched areas represent extent of past seasonal flooding. Mottled area represents a zone of permanently flooded *Melaleuca* sp., and unshaded area represents open water. **B.** Location of sediment samples collected from around the lake and within the lake.

SWS1-3, SWS2-1, SWS2-2, SWS2-3, SWS3-1, SWS3-2, and SWS3-3. Booragoon Lake sediments were taken from the centre, edge and between the centre and edge of the lake. The Booragoon Lake sediments are notated by BLS and are ordered with regards to the sampling dates and locations; including BLS1-1, BLS2-1, BLS3-1, BLS1, BLS1-2, BLS2-2, and BLS3-2 (Table 2). All sediment samples were collected by trowel at a depth of 5 cm from the surface, except for BLS1, which were sampled using a core sampler to a depth of 20 cm from the surface. Stormwater sediments were only collected on 9<sup>th</sup> February, as drainages were dried out on the 17<sup>th</sup> April, whereas Booragoon Lake sediments were taken on 9<sup>th</sup> February and 17<sup>th</sup> April. Therefore, the samples that were sampled on 9<sup>th</sup> February were generally wet, while the sediments collected on 17<sup>th</sup> April were almost dry.

In the laboratory, sediment samples were dried in an oven at 45 °C. This low temperature was selected to prevent oxidation of sulfide minerals during drying. The dried sediment samples were sieved through 2-mm nylon mesh to remove large organic fragments. They were then ground to a fine powder using an acid-washed ceramic mortar and pestle. A representative sub-sample of each sample was digested using a hot concentrated nitric/perchloric acid mix and solutions derived were analysed for major elements using a Thermo Scientific iCAP 6500 Duo Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES), and for trace elements using an Agilent Technologies 7500cs Inductively Coupled Plasma-Mass Spectrometer (ICP-MS). These lake sediments were also subjected to a CaCl<sub>2</sub> extraction to determine readily exchangeable major and trace elements (McBride et al. 2004). In this method, 20 mL of 0.01 M CaCl<sub>2</sub> solution was added to 1 g of sediment in a 50 mL centrifuge tube to extract labile metals from the sediments. Tubes were agitated on a Ratek reciprocating platform shaker for 2 hours. The tubes were then centrifuged at 4300 RCF for 30 minutes. The supernatants were analysed by ICP-MS.

**Table 2. Key to sampling dates for stormwater sediment samples (SWS) and Booragoon Lake sediment samples (BLS).**

Sample number	Date	Location of samples
SWS1-1	9/02/2012	4 m from main drainage (North-west)
SWS1-2	9/02/2012	10 m from main drainage (North-west)
SWS1-3	9/02/2012	20 m from main drainage (North-west)
SWS2-1	9/02/2012	4 m from main drainage (West)
SWS2-2	9/02/2012	10 m from main drainage (West)
SWS2-3	9/02/2012	20 m from main drainage (West)
SWS3-1	9/02/2012	4 m from main drainage (South)
SWS3-2	9/02/2012	10 m from main drainage (South)
SWS3-3	9/02/2012	20 m from main drainage (South)
BLS1-1	9/02/2012	The centre of the lake
BLS2-1	9/02/2012	Between the centre and edge of the lake
BLS3-1	9/02/2012	The edge of the lake
BLS1	9/02/2012	The centre of the lake (taken from the lake bottom)
BLS1-2	17/04/2012	The centre of the lake
BLS2-2	17/04/2012	Between the centre and edge of the lake
BLS3-2	17/04/2012	The edge of the lake

## RESULTS

### Lake Water and Stormwater

#### Lake water and stormwater physico-chemistry

Values for EC of water samples are shown in Table 3. EC values for stormwater were considered as 'freshwater' and ranged from 967  $\mu\text{S}/\text{cm}$  to 73.9  $\mu\text{S}/\text{cm}$ . By contrast lake water was considered 'brackish' with EC values ranging from 6150  $\mu\text{S}/\text{cm}$  to 13870  $\mu\text{S}/\text{cm}$ . Lower EC values reflect dilution of lake water from inputs of large volumes of fresh stormwater, whereas higher values sampled in late summer reflect evaporative concentration.

Values for pH of stormwater and Booragoon Lake water are also shown in Table 3. Lake water pH ranged from 8.00 to 6.80. The lowest pH values for lake water were recorded on the 3<sup>rd</sup> February 2012. The lowest pH recorded in lake water was on rainy days, whereas the highest was recorded on days with no rain. Higher pH values may reflect the presence of dissolved carbonate in groundwater, taken up as it flows through the lake sediments. The variance in results obtained for pH of stormwater was small from 3<sup>rd</sup> February to 9<sup>th</sup> February. Values for pH varied between 6.90 and 7.20.

Table 3 also shows the levels of total alkalinity in stormwater samples. Alkalinity was generally low in stormwater with the exception of SW2-2 on 9<sup>th</sup> February 2012. This outlet drains a residential area and may reflect alkalinity inputs from detergents or garden additives. Alkalinity was higher in lake water indicating dissolved carbonate. The total alkalinity value of water sample of BLW1-4 from the centre of the lake was highest on 24<sup>th</sup> February 2012.

#### Common anions

The results of analysis of lake and stormwater samples by HPIC for common anions are shown in Table 4. Values for  $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$ , obtained using HPIC, were generally low, reflecting uptake of these nutrients species by aquatic flora. As the lake dried out, due to evaporation, results obtained for  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  from samples of lake water between 3<sup>rd</sup> February and 24<sup>th</sup> February, increased.

#### Major elements

Concentrations of major elements present in lake and stormwater samples are shown in Table 4. The highest concentrations of S, Na and Ca were in water samples taken from the centre of the lake.

**Table 3. Electrical conductivity (EC), pH and total alkalinity values for Booragoon Lake water and stormwater samples.**

Water sample	Date	EC ( $\mu\text{S}/\text{cm}$ )	pH	Alkalinity (mg $\text{CaCO}_3/\text{L}$ )
SW1-1	3/02/2012	161	7.20	38.0
SW2-1	3/02/2012	97.30	7.20	24.0
SW3A-1	3/02/2012	98.80	6.90	24.0
SW3B-1	3/02/2012	73.90	7.00	16.0
BLW1	3/02/2012	6150	6.80	142
BLW1(2)	3/02/2012	6180	6.90	138
SW2-2	9/02/2012	967	7.20	110
SW3B-2	9/02/2012	93.30	7.20	30.0
BLW1-2	9/02/2012	7030	7.40	134
BLW1-3	16/02/2012	9510	7.00	70.0
BLW1-4	24/02/2012	13870	8.00	150



**Table 4. Common anions analysed using HPIC, major elements analysed using ICP-AES and concentrations of elements of environmental significance analysed by ICP-MS present in Booragoon Lake water and stormwater samples. Red shading indicates where concentrations exceed ANZECC & ARM CANZ (2000) trigger values for the protection of slightly to moderately disturbed aquatic ecosystems.**

Samples Guideline*	Common anions (mg/L)						Major elements (mg/L)								Elements of environmental significance (µg/L)											
	F <sup>-</sup>	Cl <sup>-</sup>	Br <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	PO <sub>4</sub> <sup>3-</sup>	SO <sub>4</sub> <sup>2-</sup>	Na	Mg	Al	Si	P	S	K	Ca	Fe	Cr	Co	Ni	Cu	Zn	As	Se	Hg	Pb		
SW1-1	0.06	17.2	0.02	0.25	0.24	2.96	19.3	169	0.681	1.78	<0.10	11.00	211	12.50	<0.10	3.00	<0.10	1.10	6.73	9.46	0.91	<0.10	0.16	4.57		
SW2-1	0.06	9.86	0.02	0.60	0.24	4.16	10.8	143	0.996	1.10	0.171	1.54	239	6.13	0.244	2.21	<0.10	1.04	8.75	38.86	0.54	0.87	0.16	2.47		
SW2-2	0.14	187	0.5	0.10	<0.2	14.3	131	12.5	<0.10	5.96	0.206	7.41	10.5	41.5	0.632	1.08	0.22	1.85	1.28	<0.10	1.01	2.94	0.14	0.83		
SW3A-1	0.10	6.77	0.02	3.34	<0.2	4.09	6.59	134	<0.10	0.881	<0.10	2.06	174	8.99	<0.10	2.75	0.25	3.25	28.97	156	0.42	0.50	<0.10	6.14		
SW3B-1	0.05	4.91	<0.2	0.12	<0.2	3.08	5.35	0.602	<0.10	0.761	<0.10	1.08	119	7.03	<0.10	1.75	<0.10	0.32	0.91	<0.10	1.45	0.91	<0.10	1.20		
SW3B-2	0.06	16.7	0.02	0.25	0.21	2.94	5.72	113	<0.10	1.49	<0.10	18.00	197	11.1	0.162	1.03	<0.10	0.72	2.39	<0.10	1.03	1.45	<0.10	0.81		
BLW1	0.43	920	4.11	<0.2	<0.2	1882	680	265	2.87	0.616	0.149	592	59.1	344	0.436	3.90	1.04	10.51	4.62	788	6.41	9.84	0.24	7.20		
BLW1-2	0.80	1165	2.51	<0.2	<0.2	2278	759	310	<0.10	0.597	0.169	717	76.7	401	0.374	1.10	1.06	11.63	1.34	4.09	6.15	13.2	0.19	0.83		
BLW1-3	0.34	1670	7.83	<0.2	<0.2	3251	1197	410	0.428	<0.10	0.233	1018	98.2	576	0.148	1.32	1.30	15.20	4.32	<0.10	8.39	16.5	0.38	0.95		
BLW1-4	0.38	2413	5.56	<0.2	<0.2	4777	1782	538	0.195	6.91	0.249	1469	143	876	<0.10	1.28	1.79	21.73	7.93	<0.10	11.5	29.3	0.22	0.58		

\* Guideline for the protection of slightly to moderately disturbed aquatic ecosystems (ANZECC & ARM CANZ 2000).

## Elements of environmental significance

The levels of contamination in the water samples by nine elements of particular environmental interest are shown in Table 4, in which values that exceed National guidelines for fresh and marine waters (ANZECC & ARM CANZ 2000) are highlighted.

## Sediments

### Major elements and elements of environmental significance

The concentrations of major elements and elements of environmental significance present in sediment samples are shown in Table 5. The concentrations were compared with the low and high interim sediment quality guidelines (ISQG-Low and ISQG-High) (DEC 2010). Some exceedances of guideline values were recorded for Ni, Cu, Zn, As and Pb.

### Bioavailable major elements and metals

The concentrations of labile major elements released by CaCl<sub>2</sub> extraction are presented in Table 6. The results obtained were compared with the ISQG-Low and ISQG-High (DEC 2010). None exceeded the guideline values.

## DISCUSSION

### Lake Water and Stormwater

Booragoon Lake is a surface expression of the underlying groundwater; however, there is a rapid hydrological response during heavy rainfall events, which, due to the large impervious surface areas of the catchment, deliver large volumes of relatively fresh water to the lake. This results in both dilution of the lake water and changes in physiochemical parameters such as pH and presumably dissolved oxygen, although this parameter was not recorded in this study. Although concentrations of dissolved salts in stormwater were generally low, stormwater is also the major source for contaminant metals to the lake, which can also contribute to high EC values (Herngren et al. 2005). Lake water EC increased during the study period as rainfall ceased and evaporative processes became the

**Table 5. The concentration of major elements and elements of environmental significance in the Booragoon Lake sediment samples. Orange shading indicates where the concentrations exceed the recommended sediment quality trigger values, and red shading indicates where the concentrations exceed the recommended interim sediment quality guideline (ISQG)-High (DEC 2010).**

Sample	Date	Major elements (mg/kg)								Elements of environmental significance (mg/kg)							
		Na	Mg	Al	Si	P	S	K	Ca	Fe	Cr	Co	Ni	Cu	Zn	As	Pb
Guideline*											80/370	21/52	21/52	65/270	200/410	20/70	50/220
SWSI-1	9/02/2012	5.28	496	1550	3.57	46.30	179.46	48.10	2089	1816	3.84	0.85	2.69	12.80	43.2	0.54	18.10
SWSI-2	9/02/2012	27.1	987	4771	8.95	221	601	218	3990	5026	9.91	1.92	7.08	28.80	117	1.94	57.2
SWSI-3	9/02/2012	899	2670	5123	<0.10	1470	7451	247	14921	14972	12.90	1.78	9.28	51.40	142	4.36	332
SWSI-1	9/02/2012	38.1	759	4674	43.50	882	603	160	2825	11463	11.10	1.19	5.43	23.90	119	1.69	100
SWSI-2	9/02/2012	85.7	1696	7283	23.40	1848	1317	294	5374	21771	23.70	3.74	12.80	70.80	331	3.05	152
SWSI-3	9/02/2012	2578	3426	11538	49.00	24848	2885	1463	5398	92511	30.20	2.79	12.40	62.50	183	23.4	952
SWSI-1	9/02/2012	44.6	905	6613	9.10	266	586	391	2411	10388	26.50	2.55	15.10	63.70	403	2.13	184
SWSI-2	9/02/2012	44.7	508	4474	39.10	127	244	142	3524	6819	16.40	1.20	6.52	27.50	174	1.26	166
SWSI-3	9/02/2012	178	1955	12857	153	652	6752	781	8088	18574	60.80	4.54	26.30	220.00	944	4.89	566
BLS1	9/02/2012	2433	4409	6967	120	6636	16385	441	13517	28789	26.20	2.16	8.93	26.40	209	11.5	136
BLS1-1	9/02/2012	3015	4061	8171	259	3498	12335	331	10699	11993	34.00	1.06	6.21	8.17	93.90	6.04	27.00
BLS2-1	9/02/2012	2516	4454	7441	34.60	2442	11798	373	12528	7954	31.50	1.18	6.79	16.20	70.60	6.92	69.50
BLS3-1	9/02/2012	3006	3811	6689	78.30	1797	10742	408	10976	7078	29.40	0.91	6.09	13.00	56.30	5.64	61.80
BLS1-2	17/04/2012	8771	7873	6123	192	1977	21788	749	15920	8875	25.10	1.13	6.33	17.80	61.10	5.69	89.20
BLS2-2	17/04/2012	6197	6722	6864	18.30	2284	17879	679	13542	11721	30.70	1.54	7.75	25.70	77.50	7.26	133
BLS3-2	17/04/2012	7335	6809	6373	84.30	4137	17598	661	11564	15569	25.60	1.10	5.77	13.60	96.10	6.74	63.8

\* ISQG-Low (Trigger Value) / ISQG-High (DEC 2010).

**Table 6. Concentrations of labile major elements and trace metals released from Booragoon Lake sediment samples using CaCl<sub>2</sub> extraction.**

Sample	Date	Major trace metals released by CaCl <sub>2</sub> extraction (mg/kg)								Metals released by CaCl <sub>2</sub> extraction (µg/kg)							
		Na	Mg	Al	Si	P	S	K	Ca	Fe	Cr	Co	Ni	Cu	Zn	As	Pb
Guideline*											80/370	21/52	21/52	65/270	200/410	20/70	50/220
BLS1-1	9/02/2012	2771	3252	17.10	8.47	<0.10	3678	282	<0.10	21.1	<0.10	90.00	180	<0.10	21600	<0.10	90.00
BLS2-1	9/02/2012	2531	3717	8.88	1.02	<0.10	3190	288	<0.10	<0.10	<0.10	10.00	60.00	<0.10	5610	<0.10	90.00
BLS3-1	9/02/2012	3012	3179	10.80	<0.10	<0.10	3141	323	<0.10	<0.10	<0.10	30.00	50.00	<0.10	5710	<0.10	110
BLS1-2	17/04/2012	7053	5656	12.80	9.09	<0.10	5716	542	<0.10	6.06	<0.10	50.00	130	<0.10	18900	10.00	130
BLS2-2	17/04/2012	5985	5425	38.30	14.70	<0.10	5535	513	<0.10	2.28	<0.10	70.00	90.00	<0.10	11800	50.00	430
BLS3-2	17/04/2012	8496	6495	11.30	5.87	<0.10	5949	637	<0.10	1.58	10.00	50.00	110	<0.10	12100	<0.10	420

dominant influence on water quality.  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{HCO}_3^-$  were the dominant ions present. These species, excepting  $\text{Cl}^-$ , are typically elevated in Acid Sulfate Soil (ASS) situations where carbonate neutralising capacity is present as a result of iron sulfide oxidation, producing sulfuric acid, which then consumes carbonate, resulting in high concentrations of  $\text{SO}_4^{2-}$  and free Ca/Mg and bicarbonate ions in solution. The chloride:sulfate ratios calculated for lake water are between 0.48 and 0.51. A chloride:sulfate ratio of less than four has been used to indicate ASS development (Kilminster et al. 2011) and a ratio less than two is considered a strong indication of sulfide oxidation (Mulvey 1993).

The concentrations of all major elements present in the lake water increased as evaporation of lake water occurred. Of the elements of environmental significance that were assessed in stormwater samples, those commonly found in road runoff (Characklis and Weisner 1997) were also present in lake water, notably Zn, Cu, Pb, Co and Ni with smaller amounts of Cr, As, Se and Hg.

Dissolved metals in the lake water generally show a trend of increasing in concentration as the water evaporates, with the notable exception of Zn, Pb and Cr, which show initial high concentrations that are absent in subsequent sampling events, indicating adsorption mechanisms for these metals in the underlying sediments or aquatic biota.

## Lake Sediments

### Major elements in the lake sediment

Sulfur and iron were the dominant major elements present, again indicating either iron sulfide minerals present or secondary iron sulfate minerals present as a result of oxidation of sulfides. The concentrations of the major elements present in the lake sediment increased as evaporation of the lake water occurred, except for aluminium. Sediment at the centre of the lake, which retained standing water for the longest time, contained the highest concentrations of major elements, indicating an evaporative concentration effect as the lake dried.

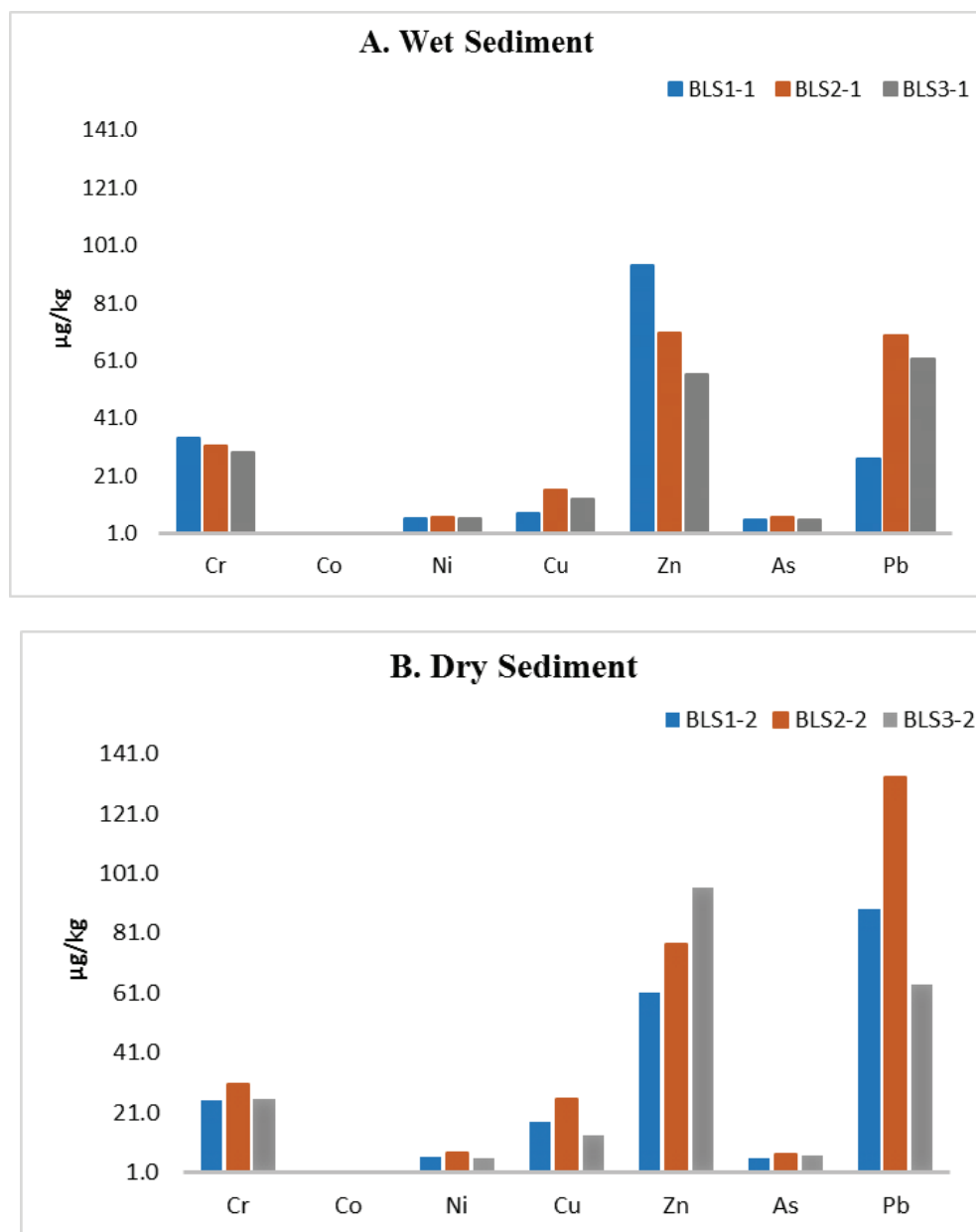
### Trace elements in the lake sediment

The trace elements assessed in the lake sediments were Cr, Co, Ni, Cu, Zn, As and Pb, of which, some concentrations of Ni, Cu and As exceeded recommended sediment quality trigger values (ISQG-Low), and some concentrations of Zn, and Pb exceeded either sediment quality trigger values (ISQG-Low) or ISQG- High guideline values (DEC 2010).

The majority of these elements are being concentrated in the lake water as the lake dries, indicating they are present as soluble species that are then either adsorbed onto sediments or precipitated in pore spaces of dry sediments as the lake dries out. However, Cr and Cu showed a different concentration trend in that there were relatively high levels of these elements present in wet sediment samples taken on 9<sup>th</sup> February. These metals may be adsorbed from the lake water onto the organic sediment (Figure 2).

Concentrations of Co, Ni, Cu, As and Se all display a trend of increasing concentration over time as the lake water evaporated. This indicates that these elements are not being adsorbed by underlying sediments. This may be due to oversaturation of sediment binding capacity. In contrast, the concentrations of Cr, Zn and Pb showed a different concentration trend, in that there were relatively high levels of these elements present in lake water samples taken on the first sampling occasion on 3<sup>rd</sup> February 2012, with very low concentrations found in subsequent sampling. This may indicate preferential adsorption mechanisms for these elements in the lake sediments.

Concentrations of Cu, Ni, Co, Zn, As and Pb indicate a trend of increasing concentration from wet sediment to dry sediment. This shows that these elements are being concentrated in the lake water,



**Fig 2. A.** Concentration of metals in wet sediments on 9<sup>th</sup> February 2012. **B.** Concentration of metals in dry sediments in Booragoon Lake on 17<sup>th</sup> April 2012.

then either adsorbed onto sediments or precipitated in pore spaces of dry sediments as the lake dries out. However, Cr and Cu showed a different concentration trend in that there were relatively high levels of these elements present in wet sediment samples, and lower concentrations in dry sediments (Figure 2). Concentrations of Zn and Pb were higher than other elements in the lake sediment.

### **The bioavailability of major elements and trace elements in the lake sediments**

Analysis of  $\text{CaCl}_2$  extractions showed that major elements were readily solubilised during rewetting of the lake sediment. Evaporative processes cause precipitation of these elements as mineral salts on the lake bed surface and interstitial sediment pore spaces as the sediment dries. These elements are readily solubilised during rewetting events and become available for uptake by biological processes.

The concentrations of the labile trace elements liberated from the sediments by the  $\text{CaCl}_2$  extraction of the lake sediments were generally low (less than 1 mg/kg), except for Zn, which ranged between 5.61 mg/kg and 21.59 mg/kg.

Generally, the adsorption of Zn on dry sediment was higher than on wet sediment; however, in the centre of the lake the concentrations of sorbed metals were higher in the wet sediments.

The lake evaporates during the dry season and the edge of the lake dries completely as a consequence of a recession in the level of groundwater. As the water recedes, there is an increase in salinity. When this occurs, salt crusts form on the dry surfaces of the lake at the edge. Pollutant metals such as Zn that were dissolved in the lake water precipitate in the lake sediments. A capillary action effect can lead to transport of soluble metals and water vertically through the pores sediment. Capillary forces lift water vertically and metals precipitate in pore space of the upper sediment horizon. During the rainy season, these metals may be remobilised to the lake water. High levels of readily solubilised Zn in the surface sediments present the possibility of migration of Zn to groundwater or uptake by plants (Mann et al. 2011) during rewetting events.

### **Impacts of Metals in Booragoon Lake**

Leach Highway, which carries high volumes of traffic, is the predominant source for metal pollution via stormwater into Booragoon Lake (Fox and MacShane 2004). In the past, when water levels were maintained, metals were strongly bound to the wet reduced organic rich sediments of Booragoon Lake, which provided a highly effective geochemical sink. However, with changing conditions geochemical pollution must be viewed in terms of a dynamic system. These metals can present a potential risk for human health and wildlife.

The adsorption of the contaminants in the sediment of Booragoon Lake has provided a useful geochemical sink for metals, but with oxidising conditions now seasonally present in wetland sediment, this may no longer be the case. If the capacity of these organic sediments to sequester metals pollution is exceeded, or prevailing physico-chemical conditions change in the event of acidification events through the development of ASS conditions, the high levels of metals present in these sediments may be mobilised with potentially detrimental effects on the environment and underlying groundwater quality. Water chemistry and high concentrations of sulfur and iron in sediments give an indication that sulfide oxidation has commenced, although acidic conditions were not noted during this study. Presumably this is due to sufficient neutralising capacity present in the sediments or through flowing groundwater to neutralise acidity produced; however, if water tables continue to fall, as is likely in a drying climate, and ASS oxidation proceeds, the neutralising capacity may well prove insufficient to buffer acidity in the long term. In that scenario, release of metals poses a serious threat to both wetland ecosystem functions and the underlying aquifer.



## CONCLUSION

At the time of this study in early 2012, Booragoon Lake contained neutral to alkaline water throughout a seasonal drying episode. Lake water was brackish for most of the study period due to evaporative concentration of lake water during summer drying, and resolubilisation of mineral salts during the annual rewetting in early winter.

Stormwater from roadways, especially the Leach Highway, is the main source of pollution inputs that enter the lake. Metal pollutants within stormwater are typically derived from vehicle emissions such as exhaust particulates, exhaust gases and fuel leaks or physical deterioration of vehicles. As a result of stormwater influx to the lake, there is a progressive increase in the overall metal content in the wetland environment. Generally, the concentration of metal pollutants in the dry sediments was higher than wet sediments as metal rich lake waters precipitated soluble metal species in the pore spaces of drying sediments.

This situation is geochemically unusual as the wet organic rich sediments of the lake should sequester soluble metals from the water. This indicates that either the organic sediments may have reached their adsorptive capacity, or that acidification events (ASS) have occurred, resulting in metals bound to organic sediments being released. This scenario is supported by water chemistry and the high levels of S and Fe present, indicating oxidation of sulfide minerals. If so, some buffering capacity (carbonate minerals or biogenic shell material) must have been available to neutralise acidity as the lake water remained neutral to alkaline for the duration of this study.

Booragoon Lake has been identified as an area of high risk, because the lake bed has been identified as sink for heavy metals (Oldmeadow 2000). If ASS conditions develop as a result of further decreases in water levels and greater areas of organic-rich (sulfide-bearing) sediment are exposed, the current neutralising capacity of the sediments may be exceeded. If acidic conditions develop, then released metals may not be cycled as they currently are in surface/near surface as soluble mineral precipitations, but rather, become mobilised in acid plumes within the shallow groundwater. Further work on assessing the ASS potential of the lake and changes in its acidification status is identified as a research priority.

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