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Speciation of Arsenic in a Large Endoheric Lake

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The bioavailibility of a trace metal, and consequently its toxicity, is dependent on the physical and chemical form of the metal. Metal speciation is dependent on oxidation state, precipitation and sorption, complexation, and the formation of organometallic compounds. Generally, it is the free form of a metal that results in waterbody toxicity (Florence et al. 1992). Several organisations such as Australian & New Zealand Environmental Conservation Council (ANZECC), WHO, and various EPA have suggested maximum acceptable levels of environmental heavy metals. However, until the 1999 draft water quality guidelines from ANZECC (1998, 2000), these guidelines only state maximum levels for total metals. Given that different chemical states of metals results in different risk of environmental toxicity, one questions whether water quality guidelines should consider levels of free species present, where applicable, rather than the total amount of metal present.

Arsenic is a ubiquitous element exhibiting metalloid properties (Sproal et al. 2002). Its complex chemistry results in numerous compounds of both inorganic and organic forms. In nature, it is widely distributed and found in a number of minerals, mainly as the arsenides of copper, nickel, and iron, or as arsenic sulphide or oxide. The major arsenic-containing minerals are arsenopyrite (FeAsS), realgar (As_4S_4), and orpiment (As_2S_3) (Alam et al. 2002a). Arsenic compounds are mainly used in agriculture and forestry (NAS, 1977). Compounds such as lead arsenate, copper acetoarsenite, sodium arsenite, calcium arsenate, and organic arsenic compounds are used as pesticides. Substantial amount of methylarsonic acid and dimethylarsinic acid are used as selective herbicides. For example, dimethylarsinic acid was the Agent Blue used in Vietnam as a defoliant for military purposes. Some phenylarsenic compounds such as arsanilic acid are used as feed additives for poultry and swine and to combat certain diseases in chickens. Chromated copper arsenate, sodium arsenate, and zinc arsenate are used as wood preservatives.

In water, arsenic is usually found in the inorganic forms of arsenate (As(III)) or arsenite (As(V)). The main organic arsenic species, methylarsonic acid and dimethylarsinic acid, are generally present in smaller amounts. The chemistry of arsenic in aqueous environments was extensively reviewed by Phillips (1990). Thermodynamically, the most stable state of arsenic is As(V), or arsenate, in oxygenated water, however the conversion from As(III) to As(V) can be kinetically slow. Therefore it is possible for significant levels of As(III), or arsenite, to be present in water bodies. The oxidation state of arsenic in surface waters in various parts of the world remains largely unknown (Phillips, 1990).

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The biological toxicity of arsenic to aquatic organisms has been extensively reviewed in Phillips (1990) and to humans and animals in Alam et al. (2002a,b,c).

In the Western District of Victoria Australia, natural sources of arsenic (eg. resulting from leaching, over-exploitation of groundwater or as a result of gold mining operations) is a significant polluter of water bodies (Sproal et al. 2002). In addition, significant arsenic pollution in the region also results from anthropocentric activities such as wash-offs from sheep dips. In this study, the speciation, distribution and complexation of arsenic determined from water samples taken from Lake Colongulac, a large endoheric drainage basin situated in south-west Victoria, Australia is systematically examined using Polarographic and Electrothermal AAS techniques.

The central aim of the investigation was to develop an understanding of the environmental fate of arsenic in the Lake and how it might be managed.

MATERIALS AND METHODS

Lake Colongulac is a naturally formed, shallow, large plains lake located approximately 3 kilometers north of Camperdown, in the western district of Victoria, Australia (Figure 1). The endoheric nature of this lake, unusual in temperate coastal locations, has produced an aquatic environment thought to be unique, and hence of significant scientific value. A physical description of the Lake is summarized in Table 1. The Lake has been used as an effluent basin by the Camperdown municipal water treatement plant and wastewater discharge from the local meat and dairy processing operations are common. The urban and rural stormwater runoff, and in some instances domestic sewage and trade wastes discharged into the lake result in high heavy metals (Cu, Cd, Pb, Hg, Zn) and arsenic concentrations in comparison to other lakes in the region.

Deionised water was produced by passing singly-distilled water through a Milli-Q water purification system (Millipore). The resistivity of the deionised water produced was always greater than 18 MΩcm. All glassware, sampling bottles, equipment and other utensils (eg. plastic spatula, autopipette tips, etc.) were cleaned in the following manner: An initial soaking for approximately 24 to 48 h in a 2% Extran 300 detergent/deionised water solution; followed by triple rinsing with deionised water; soaking for approximately 24 h in a 10% [HNO_3]/deionised water solution. Prior to use and in between analyses, equipment were triple rinsed with deionised water, and left soaking in 10% [HNO_3]/deionised water solution. High density polyethylene (HDPE) containers were selected as storage vessels, as Subramanian et al. (1978) showed that this type of container significantly decreased loses of trace metals in storage. The commercially prepared chemicals used in this study are listed, together with their source, in Table 2.

Sixteen randomly selected sites within Lake Colongulac were selected for sampling (Figure 2). All sites were sampled at the surface. Samples from other depths occurred at four sites (LC4, LC7, LC12 and LC15). Total metal samples were collected as grab samples and transferred to pre-washed 500ml HDPE storage vessels and preserved with the addition of HNO_3. Total metal samples in the water column were collected using a pre-cleaned Nisken bottle and then transferred to pre-washed 500ml HDPE storage vessels and preserved. Dissolved metal samples were collected from the pre-cleaned Nisken bottle and filtered into 30ml HDPE bottles using 0.45μ cellulose acetate disposable syringe filters.

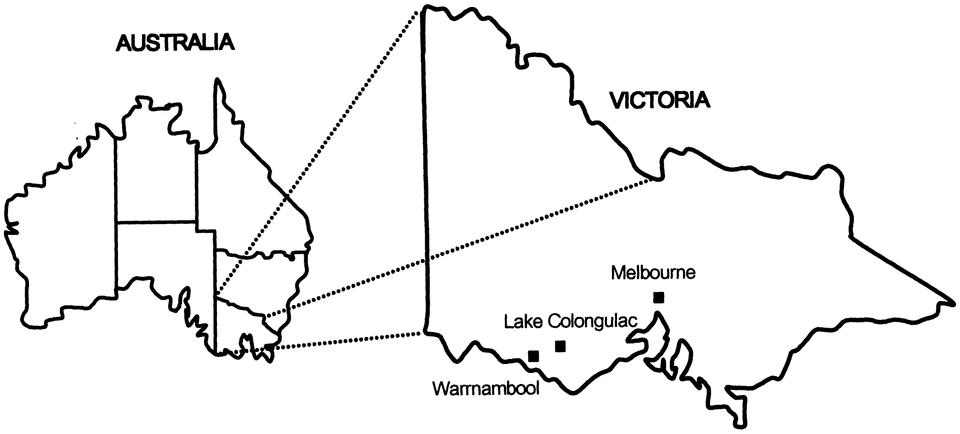

Figure 1. Location of Lake Colongulac, southwest Victoria, Australia.

Bottles were filled to capacity as to reduce the amount of oxygen. Acidification was not suitable for preserving these samples as an alteration in pH may affect arsenic speciation. Instead samples were stored in the dark and refrigerated at 4°C, and analyzed as soon as possible.

Table 1. Physical description of Lake Colongulac.

Physical Variable	*Attributes*
Geographical Coordinates (approx.)	38o10'S 143o31'E
Lake Elevation (m a.s.l)	130
Lake Area (ha)	1460
Watershed Area (ha)	8340
Shoreline Length (km)	23.0
Lake Volume (ML)	32 000
Mean Depth (m)	2.20
Lake Area/Watershed Area Ratio	0.18
Mean Annual Rainfall (mm)	730
Mean Annual Evaporation (mm)	1180
Mean Salinity (EC mS cm^{-1})	24
Lake Type	Plains Lake
Geology	Shallow water filled depression between lava flows in the plains; endoheric
Water Quality	Usually turbid with fine suspended particulates, well mixed by wind and wave, well oxygenated, low BOD in winter wet
Ecology	Mildly stressed

Table 2. Commercially prepared chemicals and source.

Chemical	*Grade*	*Source*
Arsenic Nitrate	Spectrosol	Ajax Chemicals
Amberlite 401 Resin (Cl)	Standard Grade	BDH Chemicals
APG -Sample 2-	Reference Std	Analytical Products
Cadmium Nitrate	Spectrosol	Ajax Chemicals
Copper Nitrate	Spectrosol	Ajax Chemicals
Extran 300 Detergent	Industrial	BDH Chemicals
Hydrochloric Acid	AnalaR	BDH Chemicals
Hydrogen Peroxide	AnalaR	Ajax Chemicals
Iron(III) Nitrate	Spectrosol	Ajax Chemicals
Lead(II) Nitrate	Spectrosol	Ajax Chemicals
Magnesium Nitrate	AnalaR	BDH Chemicals
Manganese Nitrate	Spectrosol	Ajax Chemicals
Nickel Nitrate	AnalaR	BDH Chemicals
Nitric Acid	AnalaR	Ajax Chemicals
Sodium Sulphite	AnalaR	BDH Chemicals
Tin Nitrate	Spectrosol	Ajax Chemicals
Zinc Nitate	Spectrosol	Ajax Chemicals

During the sampling process, in situ temperature, dissolved oxygen concentration, conductivity, pH, oxidation/reduction potential and turbidity were measured using a calibrated YEO-CAL Model 611 - Intelligent Water Quality Analyser. A Hitachi 7000 Polarised Zeeman Atomic Absorption Spectrophotometer, fitted with a Hitachi auto-sampler, was used to make all graphite furnace AAS measurements. Standard operating conditions for this instrument were utilized, except that an atomization time of 5s was employed instead of 10s in order to prolong tube life. This modification was found not to affect atomic absorption measurement. A PAR Model 364 Polarographic Analyser in combination with a PAR Model 303A Static Mercury Dropping Electrode (SMDE) Model 303A were used to make all polarographic measurements. An Ag/AgCl 3M KCl electrode was used as the reference electrode and a platinum wire was used as the auxiliary electrode.

Samples were purged with N_2 for 8 min in order to remove O_2 and to mix the solutions prior to analysis. Samples were then analyzed using a differential pulse scan, with a pulse height of 50mV and a scan rate of 5mV/s, over the potential range -40mV to -95mV. This procedure detects As(III) in the sample. Peak heights were quantified using standard addition of 0.1g/L Na_3AsO_3 solution.

Total metal samples were digested using the nitric acid digestion described by Standard Methods for the Evaluation of Water and Wastewater (Anon, 1995). Essentially this involved 100ml of sample and 10ml of HNO_3 being heated and reduced to a final volume of 25ml. Digests were then analyzed for Cr, Fe, Mn and Zn using flame atomic absorbance spectroscopy (FAAS) and for As, Cu, Cd, Pb, Sn and Ni by graphite furnace atomic absorption spectroscopy (GFAAS). For arsenic, nickel nitrate matrix modifier was added to each sample as recommended in Anon, (1995). Dissolved metal samples were analyzed using a methodology described in PAR (1976) based on Myers and Osteryoung (1973). The technique for differentiating arsenic species was previously described in Sproal et al. (2002).

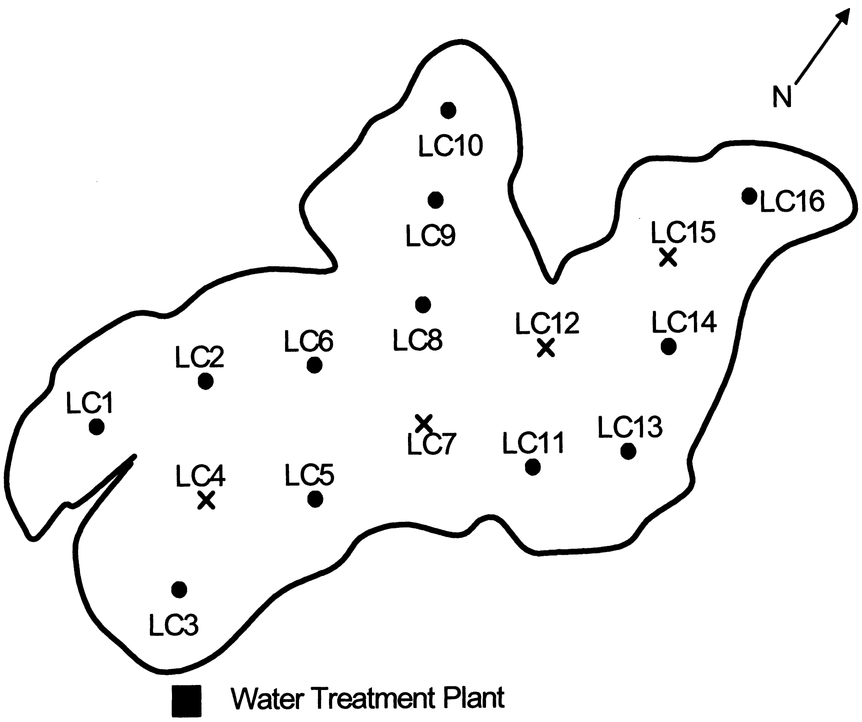

Figure 2. Location of sampling sites in Lake Colongulac (dots and crosses). The crosses also represent water column sample sites.

RESULTS AND DISCUSSION

A preliminary survey of total metal concentrations in surface samples of Lake Colongulac is presented in Table 3, along with the maximum recommended concentrations based on the 1992 and 1999 ANZECC Guidelines. Iron appears to exceed the recommended guidelines for freshwater. Arsenic, although elevated does not appear to exceed the 1992 guidelines. Arsenic speciation is required in order to determine if the 1999 guidelines are exceeded. Copper and nickel did not exceed the 1992 guidelines, although the measured levels did exceed the 1999 guidelines. These results suggest that more detailed sampling of the Lake is required and the aquatic ecotoxicity of Cu and Ni should also be further investigated.

Table 4 presents concentrations of species of arsenic and iron, pH, water temperature, turbidity and conductivity for each site at several depths. The total arsenic concentration in the surface water was highly variable (Mean = 61.4 μg L^{-1}; SD = 21.2 μg L^{-1}). In the water column, (ie. below the water surface sample sites LC4, LC 7, LC 12 and LC 15 middle and bottom), the total As concentrations (Mean = 70.9 μg L^{-1}; SD = 45.7 μg L^{-1}) were slightly higher but not statistically different from the surface samples. The mean total Fe concentration in the surface water samples was 0.8 mg L^{-1} (SD = 0.3 mg L^{-1}) and in the water column 0.83 mg L^{-1} (SD = 15.2 mg L^{-1}). The Fe concentrations were very highly variable. The mean surface water temperature was 22.5°C (SD = 1.1°C) and water column 21.0°C (SD = 0.9°C). There was little variation in pH between surface water samples (Mean = 8.91, SD = 0.04) and in the water column (Mean = 9.01, SD = 0.03). On the other hand, turbidity varied considerably between surface samples (Mean = 17.9 ntu, SD = 5.1) and in the water column samples (Mean = 88, SD = 139), however this was largely attributably to one sample (LC15 bottom) being highly turbid.

Given the water quality parameter values for Eh and pH presented in Table 4, the main form of arsenic expected under the conditions predominating at the time of sampling is As(V) (Carbonell-Barrachina et al. 2000). However no detectable 'free' arsenic (V) was observed, and given the relatively high total concentration of arsenic within sample solutions, some form of adsorption or complexation of arsenic was occurring. Complexation or adsorption phenomena was not observed for measurements of total dissolved As by polarography, therefore much of the arsenic is associated with particulate matter in the aquatic samples. Even after filtering, sufficient material remained to complex any additional free arsenic. The ability of Lake Colongulac to complex, adsorb or otherwise remove added arsenic was then investigated by means complexation capacity (CC) titrations. The CC titrations were performed on water samples from four sites (LC4-top-, mid, bot, and LC15-mid). In all cases, the analyses indicated the presence of a single strong ligand binding site and from the analysis, we estimate that the Lake had a complexation capacity of 250 μg L^{-1}.

Since no samples had a total concentration of greater than 170 μg L^{-1}, these results offer an explanation as to why no bioavailable forms of arsenic were found in the water samples. Sorption and coprecipitation of arsenic by iron and manganese oxides and oxyhydroxides on particulate matrices eg. soils, sediments, etc have been previously shown in lacustrine or estuarine systems (eg. see Seyler and Martin 1989). Ferguson and Anderson (1974) also observed that arsenate was much more strongly adsorbed than arsenite onto iron and aluminium hydroxides. The results from their study indicated that highly correlated increases of pentavalent arsenic and dissolved iron concentrations between 60 and 70m reflect the gradual solubilisation of iron oxyhyroxides and the concomitant desorption of As(V). A significant correlation (R^2=0.73, $p<0.05$) was found between [As] and [Fe] in Lake Colongulac, concurring previous findings.

In conclusion, a heavy metal inventory (Cd, Cr, Cu, Fe, Mn, Ni, Sn, Pb, Zn) of Lake Colongulac indicated elevated levels of Cu, Fe and Ni. Only particulate/ adsorbed arsenic levels were found. The lack of dissolved arsenic species is attributed to metal complexation with elevated levels of total iron. Very little information is currently available in the literature regarding the complexation capacity of metalloid arsenic and hence this paper may be an important reference for further investigations.

Table 3. Total metal concentrations (μg L^{-1}) from 16 sites in Lake Colongulac.

Metal	Observed		ANZECC (1992) Guidelines				ANZECC (1999) Guidelines			
	Method	[ ]	Fresh Water	Stock Water	Irrigation	Fish Prod.	Fresh Water	Stock Water	Irrigation	Fish Prod.
Cu	GFAA	1.6	2.0-5.0	50	200	ns	0.33^	500-5000*	200	< 0.5
Cd	GFAA	< 0.30	0.2-2.0	10	10	0.3	0.013^	10	10	< 0.2-1.8
Cr	FAA	< 100	100	1000	1000	ns	Cr(III) 9^	1000	(VI) 100	< 20
Cr	FAA	< 100	100	1000	1000	ns	Cr(VI) 1.1	1000	(VI) 100	< 20
Fe	FAA	1600	1000	ns	1000	ns	ns	ns	200	< 10
Pb	GFAA	< 6	1.0-5.0	100	5000	0.03	1.2^	100	5000	< 1
Zn	FAA	< 8	5.0-50.0	20000	2000	ns	2.4^	20000	2000	< 10
Mn	FAA	< 30	ns	ns	2000	ns	47	ns	200	< 100
Sn	GFAA	< 50	0.008	ns	ns	ns	ns	ns	ns	ns
Ni	GFAA	6.4	15-150	1000	200	ns	0.7^	1000	200	< 100
As	GFAA	23	50	500	100	ns	As(III) 1.6	500-5000#	100	< 50
As	GFAA	23	50	500	100	ns	As(V) 2.4	500-5000#	100	< 50

ns = not specified, *dependant on livestock,
^dependant on water hardness, #dependant on [As] in diet

Table 4. Water quality, arsenic species (μg L^{-1}) and iron (mg L^{-1}) concentrations.

Site	Depth (m)	Temp (K)	pH	O/R Pot. (mV)	Cond. (mS /cm)	Turb. (ntu)	[Fe] (mg/L)	$[As]_{Total}$ (μg/L)	[As(III)] (μg/L)	[As(V)] (μg/L)	$[As]_{Dissol}$ (μg/L)
LC 1	0.5	295.6	8.96	68	24	15.9	0.9	76	C		< 20
LC 2	0.5	294.5	9	71	24	19.2	0.8	58	C		< 20
LC 3	0.5	293.9	9.02	77	24	21.1	1.1	88	C		< 20
LC 4 top	0.5	294.9	9.03	66	24	21.3	1	30	C	C	< 20
LC 4 mid	1	293.7	9.06	72	24	23.1	1	36	C	C	< 20
LC 4 bot	1.5	293.4	9.06	77	24	49.1	1.1	36	C	C	< 20
LC 5	0.5	295.1	8.97	75	24.1	19.8	0.7	53	C		< 20
LC 6	0.5	294.1	9.02	82	24	21.7	0.9	49	C		< 20
LC 7 top	0.5	295.8	8.97	75	24	17.9	0.6	47	C	C	< 20
LC 7 mid	1	293.5	9.01	82	24.1	31.6	0.7	44	C	C	< 20
LC 7 bot	1.5	293.2	9.02	85	24.1	61.4	42	164	C	C	< 20
LC 8	0.5	296.7	8.93	64	24.1	16	0.5	38	C		< 20
LC 9	0.5	297.7	8.91	63	24.1	12.7	0.4	55	C		< 20
LC 10	0.5	296.5	8.93	71	24.1	15.6	0.6	48	C		< 20
LC 11	0.5	294.8	8.99	108	24.1	16.6	0.8	91	C		< 20
LC 12 top	0.5	297.4	8.91	70	24.1	11.3	0.4	30	C	C	< 20
LC 12 mid	1	294	8.99	77	24.1	26.7	0.7	40	C	C	< 20
LC 12 bot	1.5	293.7	8.99	82	24.1	41.5	10	65	C	C	< 20
LC 13	0.5	295.4	9	105	24	26.6	1	88	C		< 20
LC 14	0.5	295.7	8.99	101	24.1	28.1	1.6	83	C		< 20
LC 15 top	0.5	296.3	8.95	89	24.2	10.7	0.5	62	C	C	< 20
LC 15 mid	1	295.8	8.97	92	24	14.2	0.5	64	C	C	< 20
LC 15 bot	1.5	295	8.99	96	24	403	2.9	91	C	C	< 20
LC 16	0.5	296.4	8.96	66	24.2	12	1	86	C		< 20

C = Complexation

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