

Arsenic and major cation hydrogeochemistry of the Central Victorian (Australia) surface waters

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Abstract: This paper reports on the major cations (Ca, Mg, Na and K) and arsenic (As) compositions of surface waters collected from major creeks, rivers and lakes in Central Victoria (Australia). The surface waters were found to be neutral to alkaline (pH 6.7–9.4), oxidised (average redox potential (Eh) about 130 mV) and showed variable concentrations of dissolved ions (EC, about 51–4386 $\mu\text{S}/\text{cm}$). The concentrations of dissolved major cations in surface waters were found to be in the order of $\text{Na} \gg \text{Mg} > \text{Ca} > \text{K}$ and in soils the contents of metals followed an order of abundance as: $\text{Ca} > \text{Mg} \gg \text{K} > \text{Na}$. While Na was the least abundant in soils, it registered the highest dissolved cation in surface waters. Of the four major cations, the average concentration of Na (98.7 mg/L) was attributed to the weathering of feldspars and atmospheric input. Relatively highly dissolved concentrations of Na and Mg compared with the world average values of rivers reflected the weathering of rock and soil minerals within the catchments.

The As soil level is naturally high (linked to lithology) as reflected by high background soil values and mining operations are also considered to be a contributory factor. Under relatively alkaline-oxidative conditions low mobility of dissolved As (average about 7.9 $\mu\text{g}/\text{L}$) was observed in most of the surface waters with a few higher values ($> 15 \mu\text{g}/\text{L}$) around a sewage disposal site and mine tailings. Arsenic in soils is slowly released into water under alkaline and/or lower Eh conditions. The efficient sink of Fe, Al and Mn oxides acts as a barrier against the As release under near neutral-oxidising conditions. High As content (average about 28.3 mg/kg) in soils was found to be associated with Fe-hydroxides as revealed by XRD and SEM analysis. The dissolved As concentration was found to be below the recommended maximum levels for recreational water in all surface waters (lakes and rivers) in the study area. Catchment lithology exerted the fundamental control on surface water chemistry. Sites impacted by mining waste dumps showed a decline in water quality.

Keywords: surface water; major cations; arsenic; soil; Australia

Introduction

The major cation composition of fresh water reflects the various sources (e.g. precipitation, rock and soils weathering) of dissolved material, which strongly influence its suitability for domestic, industrial and agricultural use (Meybeck, 1981; Kim *et al.*, 1999). Catchment lithology and mineral abundances have been recognized as the most important controls on river water composition (Berner and Berner, 1987; Stallard and Edmond, 1987). Apart from natural sources affecting water quality, pollution sources are responsible for high concentration of metal/metalloids in freshwaters (Garcia and Alvarez, 2003; Sultan and Dowling, 2005).

Arsenic is naturally widespread throughout the Earth's crust and its additional input from anthropogenic activities (e.g. mining) has posed major health risks in various parts of the world (Smith *et al.*, 1998; Smedley and Kinniburgh, 2002). Arsenic liberation from solid material phases to a liquid phase depends primarily upon the following factors: pH, redox conditions, organic matter and sorption/desorption by oxides of Fe, Al and Mn (Jain *et al.*, 1999; Frau and Arda, 2003; Le Guern *et al.*, 2003). Understanding

processes critical to surface water quality helps assess natural and/or anthropogenic impacts on the aquatic environment and drinking water quality. The occurrence and mobility of As in natural waters have been studied around the world (e.g. USA, India, Bangladesh and Chile) due to the adverse effects of As on human health.

The catchment hydrology in Victoria has been significantly altered by anthropogenic activities such as land clearing, water harvesting and water storage, and this has adversely affected the water quality and aquatic ecosystems (OCE, 1988). High concentrations of arsenic have been reported in surface soils, 36000 mg/kg, and in groundwater, 300 mg/L, in Victoria (Hinwood *et al.*, 1998). The ANZECC/NHMRC (1992) health investigation guideline for arsenic in soils is 100 mg/kg and for drinking water it is 7 $\mu\text{g}/\text{L}$. Large mine dumps present a visible environmental impact in the study area due to mining operations in the past. Waste mining material contains arsenic primarily as arsenopyrite and as sorbed species on the oxides and hydroxides of Fe (Lamb *et al.*, 1996).

The study investigated the hydrogeochemical processes controlling major cations and As concentration in surface waters (creeks, rivers and lakes) of

the Central Victorian region of Australia. The study also maps the basic water quality aspects in Central Victoria.

1 Methods

1.1 Study area

The study area (latitude $37^{\circ}16'–37^{\circ}38'S$; longitude $143^{\circ}35'–144^{\circ}00'E$) situated 120 km west of Melbourne, Australia and includes the city of Ballarat and the smaller historical gold mining town of Creswick. It covers an area of approximately 1100 km² with an altitude ranging from 300 to 744 m above sea level. The landscape consists of undulating low hills of Ordovician bedrock separated by plains of Tertiary basaltic lavas. Average seasonal maximum temperatures range between 6°C in winter to 18°C in summer. The total average annual precipitation ranges between 600 to 700 mm, most of which is received in winter (Taylor *et al.*, 2000).

The study area comprises the headwaters of numerous creeks. The north-flowing upland creeks are Creswick, Birch and Middle (Fig.1), which drain into the larger drainage of Tullaroop Creek. Creswick Creek traverses highly modified farmland with a small forested downstream area and has been mined for gold in the past. The Yarowee is a south-flowing river and also carries treated sewage effluent from Ballarat City. Eastward flowing Burrumbeet Creek is one of the major waterways of the sub-catchment within the Hopkins Basin. Streams within the area are numerous, and hence small, and record negligible flow during the summer and autumn. Most streams are subject to rapid runoff and flood discharges subsequent to storms. The area also contains several fresh water lakes, namely Burrumbeet, Learmonth, Wendouree and Saint George, all of which have been sampled (Fig.1). The present levels of water in these lakes have decreased due to drought, increased use of catchment pastures, growth of grasses and high retention of rain at the expense of run off.

1.2 Sampling

Surface water samples were collected from 40 different locations in Central Victoria from creeks, rivers and lakes. Samples ($n = 40$) of approximately 100 ml were collected using a syringe attached to a filter (0.45 μm) and placed into pre-cleaned polyethylene bottles. These were acidified ($\text{pH} < 2$) with analytical grade HNO_3 for stabilisation. Surface water pH, Eh, electrical conductivity (EC) and temperature were measured *in situ* by precalibrated portable standard meters. This sampling regime represented the surface water samples from the low-flow period

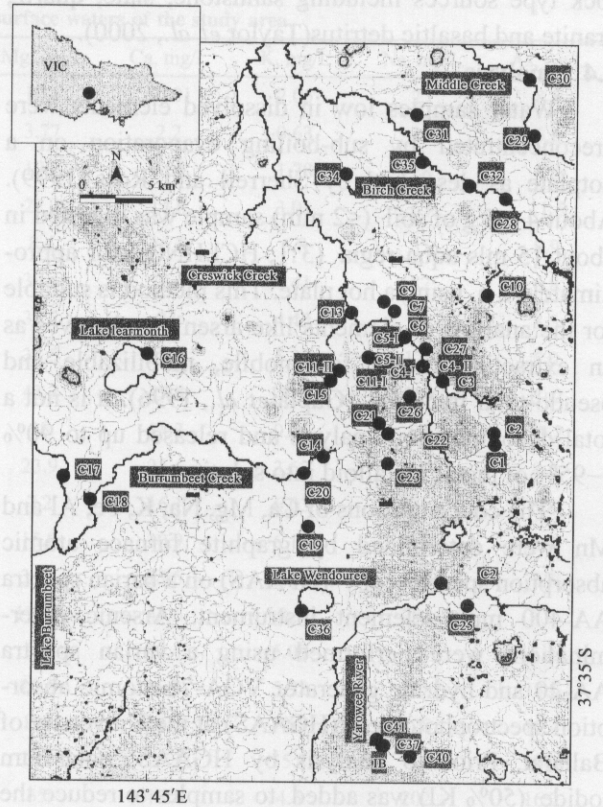


Fig.1 Sampling locations in the study area(Central Victoria, Australia)

(January to March).

Surface soil (0–10 cm, $n = 22$) samples were obtained using a hand auger around the rivers, creeks and lakes and an effort was made to obtain soils on the various rock units in the area. The location map of water and soil samples is shown in Fig.1. A GPS was used to record the Australian Map Grid (AMG) coordinates for all sampling locations.

1.3 Geology

The bedrock geology of the study area consists of the broad groupings of lower Ordovician bedrock, Devonian granitic intrusions, Tertiary Newer Volcanics and Quaternary alluvium (Douglas and Ferguson, 1988; Taylor *et al.*, 2000). The main geological unit is the Castlemaine Group of Ordovician age, consisting of marine deposits of metasandstone and slate. The Ordovician bedrock is host to a variety of gold deposit styles. Pyrite (FeS_2) and arsenopyrite (FeAsS) are widely distributed through the gold-bearing areas and disseminated in the sedimentary strata (Houston, 1956). Devonian biotite Granodiorite occurs only in limited areas. Tertiary Newer Volcanics cover much of the study area. The flows are mostly porphyritic olivine basalts to hawaiites and contain phenocrysts of clinopyroxene (augite) and plagioclase (andesine to labradorite)(McKenzie *et al.*, 1984). The lithology of alluvium is variable and reflects various

rock type sources including sandstone, slate, quartz, granite and basaltic detritus (Taylor *et al.*, 2000).

1.4 Analysis

Water samples low in dissolved elements were preconcentrated by sub-boiling evaporation on a hotplate as described by Sherrell and Ross (1999). About 4–5 g of soil (<2 mm) sample was digested in about 15 mls aqua-regia (3:1, HCl:HNO₃) for approximately 2 h, using a hot plate. This method is suitable for the analysis of elements like arsenic and serves as an extracting media for mobile, mobilizable and pseudo-total fractions (Gupta *et al.*, 1996). It is not a total decomposition analysis and released up to 90%–95% of metal/metalloid into solution.

The concentrations of Ca, Mg, Na, K, Fe, Al and Mn were determined by graphite furnace atomic absorption spectroscopy (GFAAS) on a barian spectra AA-400 multi element instrument. Arsenic determinations were performed using a varian spectra AA-20 and hydride generator VGA-76 atomic absorption spectrophotometer (HGAAS) at the University of Ballarat. Prior to analysis by HGAAS, potassium iodide (50% KI) was added to samples to reduce the arsenic to As (III) form. From certified aqueous standards (BDH Spectrosol®), intermediate standards of various concentrations were prepared. Standard reference material (GBW-07401) was analysed for QA/QC program. The results were verified by standard addition measurements of selected samples. Accuracy and precision were $\pm 10\%$ or better. Appropriate batch blanks were included with each set of samples. All reagents used were of analytical grade and ultrapure deionized water (resistivity about 18 M Ω cm) was used during the analysis.

Soil pH (pH_{1:5}) was determined in 1:5 of soil: distilled water (w/v) suspensions after shaking for 1 h on an end-over-end shaker followed by 0.5 h equilibration (Rayment and Higginson, 1992). This measured the water-soluble concentrations of cations and anions (Beckett, 1989).

Bulk soil samples were analysed in a scanning electron microscope (SEM) to determine the mineral composition. These were prepared in an epoxy resin diluted with acetone, allowed to set and dry, and then polished and carbon coated. X-ray diffraction (XRD) traces were obtained using a siemens diffractometer D501 with Co-K α radiation, generated at 40 kV and 20 mA in the School of Science and Engineering, University of Ballarat. The concentration distribution maps were developed by using MapInfo GIS software.

2 Results

2.1 Water

Table 1 summarises the physico-chemical parameters of surface waters. As the sampling was carried out during summer, the surface water temperature was relatively high and varied between 14.4 to 26.7°C with an average of 20.0°C. The redox potential (Eh) varied from -135 to 253 mV. Generally the surface waters were oxidising (average about 130 mV) with the exception of two locations, C5-I and C5-II, on the Creswick Creek where waters were observed as being reduced, -135 and -70 mV, respectively. Surface water pH varied from 6.7 to 9.4 with an average value of 7.8. All lake waters recorded high pH values (pH 9.0) except for the Saint George Lake (C3, pH=7.0). While Middle Creek registered pH increase of 0.25, Birch Creek of 0.92, Burrumbeet Creek of 0.4 and Creswick Creek of 0.9, the Yarowee-river did not register a systematic pH change downstream.

The EC values ranged from 51 to 4386 μ S/cm (Fig.2). The highest EC was measured in the water of Lake Burrumbeet and the lowest value was recorded in the upstream water from Burrumbeet Creek.

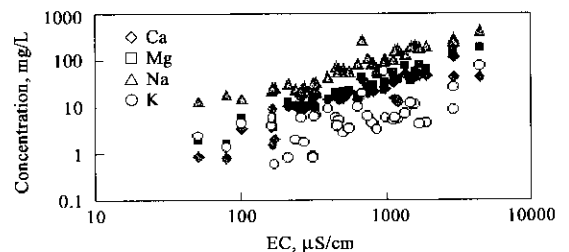


Fig.2 Plot of major cations vs. EC values in surface water ($n = 40$)

Dissolved Ca concentrations ranged from 0.84 to 112.0 mg/L with an average value of 22.6 mg/L. The highest Ca value was measured in sample (C31) from a water body along Birch Creek near mine tailings and the lowest value in Creswick Creek (C26) flowing through the state forest area. Overall, lower Ca concentrations were recorded in surface waters draining Ordovician bedrock due to low contents of Ca-containing minerals.

Magnesium varied from 1.7 to 189.0 mg/L with an average of 34.8 mg/L. The downstream surface waters draining Ordovician bedrock recorded more than two fold higher Mg concentrations (average about 42 mg/L) than the upstream locations draining Basalt bedrock (average about 16 mg/L), with few exceptions along Birch and Middle Creek. The soils developed on Basalt bedrock had two fold higher Mg content (average about 1750 mg/kg) than the soils derived from Ordovician bedrock (average about 870 mg/kg). Olivine (up to 20 wt.%) weathering in basalts might be

Table 1 Chemical composition of surface waters of the study area

Location	T, °C	Eh, mV	pH	EC, $\mu\text{S}/\text{cm}$	Mg, mg/L	Ca, mg/L	K, mg/L	Na, mg/L	As, $\mu\text{g}/\text{L}$
C1	15.0	139	7.0	241	10.6	10.01	2.05	25	8.5
C2	15.7	122	6.8	174	3.77	2.2	0.63	26	6.8
C3	20.2	136	7.0	273	10.2	9.03	1.78	28	4.8
C4- I	19.5	88	7.5	510	22.2	14.6	3.01	63	11.5
C4- II	18.4	102	9.4	324	8.4	16.7	6.8	35	8.9
C5- I	23.0	-135	6.7	816	30.4	22.4	4.41	82	6.8
C5- II	24.1	-70	6.8	795	30.7	23	4.43	81	8.5
C6	24.2	50	7.8	1214	38.5	12.4	5.39	174	5.0
C7	25.9	48	8.1	683	43.7	37.8	18.77	279	10.2
C9	19.3	74	7.3	640	18	14.3	9.55	82	10.2
C10	21.5	69	7.8	560	23.9	21.6	3.62	55	8.5
C11	15.3	96	7.9	264	7.2	16.1	6.03	24	6.8
C12	26.2	71	8.0	319	15.8	20.9	6.17	25	5.4
C13	20.0	108	7.7	984	34.7	25.5	5.94	106	7.5
C14	15.0	234	7.4	2934	116.5	43.6	8.5	291	6.9
C15	14.5	156	7.7	1126	54	33.4	5.09	98	5.1
C16	17.9	145	9.4	456	20.5	16.8	5.92	70	13.6
C17	14.8	170	9.0	4386	189	44.6	72.8	428	10.4
C18	14.4	169	7.8	974	23.1	26.3	55.7	91	10.2
C19	14.5	162	7.5	1885	65	46.1	4.5	202	16.2
C20	15.4	165	8.0	1558	56	43.4	10.92	214	6.8
C21	16.0	20	7.8	102	5.7	3.59	4.52	15	6.5
C22	19.5	107	8.1	166	4.22	1.59	5.61	24	17.0
C23	17.0	133	7.9	51	1.96	0.91	2.5	13	15.3
C24	14.8	82	7.2	478	19.4	14.3	5.1	62	8.5
C25	14.7	145	6.7	470	17.2	17.1	4.13	56	8.4
C26	23.0	162	8.0	79	1.7	0.84	1.38	18	5.4
C27	26.3	83	7.0	1471	37	10.7	11.43	192	6.8
C28	17	104	7.6	312	13.2	11	0.89	32	5.2
C29	19	168	7.4	1673	75	45.8	4.2	190	6.8
C30	16	202	7.6	1356	70	48.1	7.25	128	4.8
C31	23	253	7.5	2921	166.5	112	26.74	255	5.1
C32	25	195	8.2	311	12.4	11.4	0.86	32	4.1
C34	24	225	7.6	401	14.9	14.4	8.83	44	6.9
C35	26.7	185	8.5	217	12.3	10.6	0.83	31	7.3
C36	24	128	9.24	733	27	19.7	6.44	104	8.5
C37	19	139	8	1151	36.1	14.9	5.7	164	5.1
C40	21	41	8.1	160	4.94	3.7	3.92	23	7.2
C41	19.5	155	7.9	870	46.5	53.1	3.43	59	7.1
IB	18	152	7.5	165	5.7	9.21	5.71	26	6.8

the possible source of high Mg in surface waters. Mg was the second most dominant cation(Fig.2) after Na, which was mainly a function of catchment geology.

Dissolved Na concentrations varied between 13 and 428 mg/L and had the largest average concentration of 98.7 mg/L of the major cations. Sodium showed the greatest spatial variability of all the major cations and did not show systematic change

along the path downstream. The dissolved Na was poorly correlated with K ($r^2 = 0.39$, $n = 40$). The Na concentration is also affected by the contribution of precipitation as the predominant cation in the local rain is Na(Sultan and Dowling, 2003).

Potassium concentration ranged between 0.63 and 72.8 mg/L with an average of 8.8 mg/L. Burrumbeet Creek and Lake Burrumbeet surface

waters measured the highest *K* values (>55.0 mg/L), but generally dissolved *K* concentration was relatively constant. High average *K* values as compared to the world average *K* concentrations in rivers (<5 mg/L) reflected a higher weathering of *K*-containing minerals(e.g. muscovite) in the catchment area.

The dissolved concentrations of arsenic ranged from 4.1 to 17.0 µg/L with an average value of 7.9 µg/L. Higher values (>15 µg/L) were found in water samples around the sewage disposal site and mine tailing sites. The dissolved As concentration did not show significant spatial variation and about 80% of sampled waters were below 8.5 µg/L (Fig.3a). This behaviour of As indicated the presence of initial sources in soils, with additional sources being mining waste dumps. There were significant gold mining activities in the area and a high concentration of As resulting from dissolution of As-minerals is expected. Stability of As under prevailing soil conditions

explained the lower total concentrations in surface waters.

2.2 Soils

Table 2 presents soil data on Na, Ca, Mg, K, Fe, Al, Mn and As contents, and soil pH (1 : 5). Soil values of Na, Ca, Mg and K ranged from 31—1940, 85—9895, 154—4582, and 75—1205 mg/kg, respectively. Ca was the most dominant element in soils developed on Basalt and Mg in soils developed on Ordovician bedrock. Na was the least abundant among the four base metals(Ca, Mg, Na and K) in all soils. Ca and Na contents were highly correlated ($r^2 = 0.93$) and each also correlated to Fe contents, $r^2 = 0.74$ and $r^2 = 0.73$, respectively.

Arsenic content in soils varied from 7.4 to 64.0 mg/kg. The highest value was in soil sampled from mining waste material (C30). This is five fold higher than average As content (28.2 mg/kg) as compared to the world soil average, 5—6 mg/kg (Cullen and

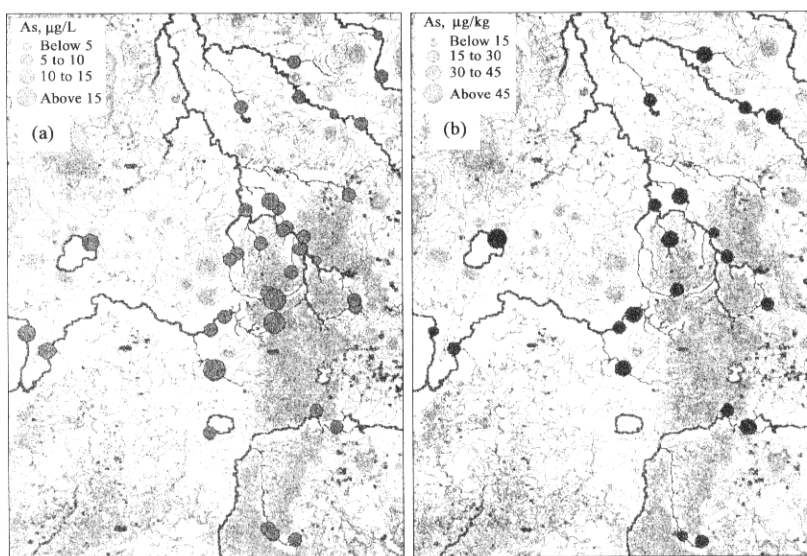


Fig.3 Map showing the distribution of arsenic in soils

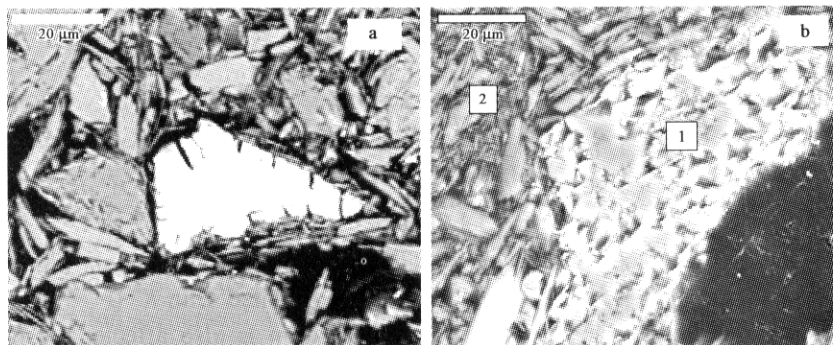


Fig.4 (a) Backscattered-electron (BSE) scanning-electron microscope (SEM) image, bright grain at centre of field is arsenopyrite showing partial oxidation of surface only (Sample C30; AMG 762109-5869877); (b) backscattered-electron (BSE) image of fragment of magnesium siderite [1] found in surface soils near mine tailings. In the field also chlorite and illite [2] occur as flakes, black region at lower right is mounting resin(Sample C9; AMG 753946-5857251)

Table 2 Soil pH (1:5) and element concentration data of surface soils(0–10 cm) of Central Victoria

Location	pH _{1:5}	mg/kg							
		Mg	Ca	K	Na	Fe	Al	Mn	As
C1	6.4	367	751	106	68	44288	4536	123.1	25.5
C3	6.3	163	85	452	106	29927	5696	8.7	22.3
C9	6.3	1017	1594	560	100	54134	6166	118.9	56.9
C11	6.0	168	319	635	69	27276	7162	140.0	41.5
C13	6.6	491	748	505	145	24831	3686	86.7	22.4
C14	6.3	403	835	798	46	40868	6770	589.6	32.5
C16	8.1	1190	1389	1003	392	41202	9743	736.8	46.0
C17	6.2	173	361	214	31	4160	3629	88.7	7.4
C18	6.2	2335	3139	1097	429	23035	14322	550.0	27.7
C19	6.6	3255	2516	1205	417	29111	21259	360.0	38.8
C20	7.1	670	926	291	282	26122	8177	382.3	19.8
C21	5.6	1248	730	631	158	18346	9582	57.3	24.9
C24	5.4	469	686	206	51	14448	4810	142.8	18.8
C25	6.0	2808	1643	1123	165	28278	9209	474.3	31.0
C27	5.9	3041	1391	416	108	25517	4708	255.3	10.5
C29	6.5	883	375	516	256	39587	8821	443.7	30.9
C30	6.4	4582	9895	1061	1940	165422	13930	680.0	64.0
C31	6.6	1351	1565	711	131	74900	12233	633.0	56.6
C32	6.5	1531	1971	123	162	51000	12053	326.0	28.4
C34	6.3	644	905	75	90	20681	7495	540.0	24.3
C40	7.5	641	1626	515	104	26161	12147	633.3	27.2
IB	6.1	154	555	193	54	8499	6479	32.2	9.9

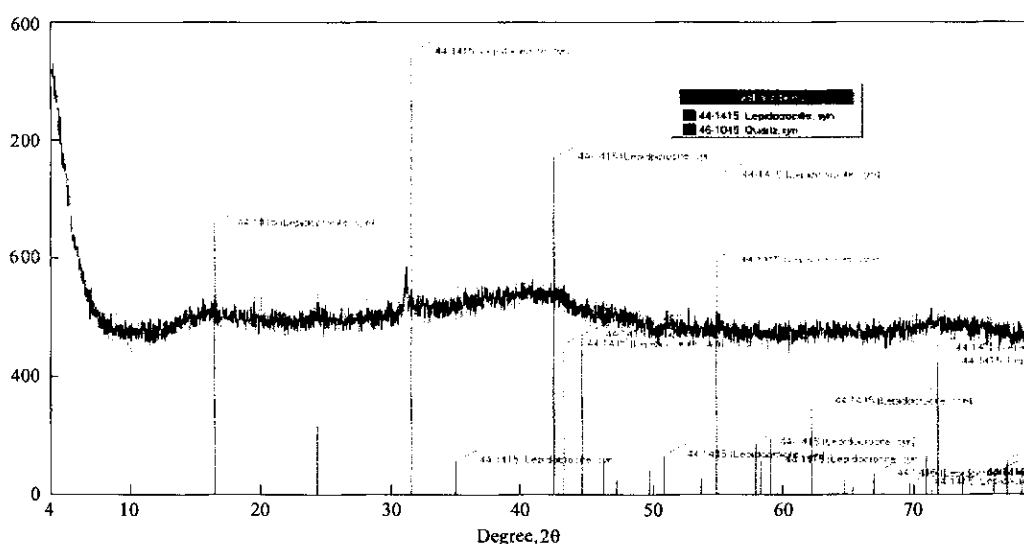


Fig.5 XRD trace of red precipitate occurring on soil (0–5 cm depth) sample around the old ore crushing battery (Sample C4; AMG 756273-5853647). Note the near amorphous nature (i.e. no well defined peaks) and broad swells corresponding to the expected positions of the iron oxide mineral lepidocrocite($\text{FeO}(\text{OH})$) which are indexed and labelled

Reimer, 1989), it reflected elevated natural background levels in soils. A map showing the distribution of As in soils is shown in Fig.3b. High levels of As retained in surface soil (0–10 cm) could also be due to the atmospheric input by smelting activities during the gold-rush period and/or retention by the secondary oxides (e.g. Fe, Mn). Arsenic showed a good positive correlation ($r^2 = 0.60$, $n = 22$) with Fe, this could be the result of weathering of arsenopyrite and adsorption of As onto the Fe hydroxides. SEM analysis revealed the presence of arsenopyrite grain and XRD analysis showed the presence of Fe hydroxides (Figs.4a and 5, respectively).

Soil Fe content ranged between 4160 to 165422 mg/kg with an average of 36132 mg/kg. Soils of basaltic bedrock origin had about two fold higher Fe contents than soils derived from Ordovician bedrock. Al contents varied from 3629 to 21259 mg/kg, Mn contents from 8.7 to 736.8 mg/kg, with average values of 8755 and 336.5 mg/kg, respectively. Fe, Al and Mn contents in soils were poorly correlated with each other. Soil pH (1:5) varied between 5.4 to 8.1 with an average value of 6.4. Average soil pH_{1:5} (about 6.4) was observed to be 1.4 pH units lower than the surface water pH (about 7.8).

3 Discussion

High pH values could be due to the abundance of carbonates and high concentration of dissolved solids due to carbonate and silicate weathering. SEM analysis showed the presence of Mg containing minerals (Fig.4b). The near neutral pH water could be due to the agricultural and urban development at few locations (Creswick Creek). A pH value >9.0 is above the guidelines for recreational water quality (ANZECC, 2000).

High EC values, for example along Birch Creek (location C31), were found to be due to the interaction of infiltrating water with the waste-rock dumps as a point source. The dissolution and precipitation of carbonates could be the reason for increasing or decreasing EC values downstream. The higher EC values were also due to low flow conditions and evaporation in the area. Overall waters draining Ordovician bedrock had lower EC values than waters draining Quaternary deposits.

The overall order of abundance of dissolved major cations in surface water was $\text{Na} \gg \text{Mg} > \text{Ca} > \text{K}$. In soils the contents of metals followed an order of $\text{Ca} > \text{Mg} \gg \text{K} > \text{Na}$. While Na was the least abundant element in soils, registering the highest dissolved cation concentration in surface waters. This is most

likely due to extensive leaching of Na from soils. The dissolution of Mg-containing minerals in the rock, soil and clays appeared to be a major weathering process in the area. Overall neutral to alkaline-oxidative conditions were recorded in surface waters. Among the four sampled lakes, Lake Burrumbeet had about 3 times higher EC values than the creek flowing into it, which was probably due to evaporative concentration and recharge through groundwater. Dissolved As concentration in lakes was 5.7–11.6 $\mu\text{g/L}$, well below the water quality guideline (about 50 $\mu\text{g/L}$) by ANZECC(1992) for recreational fresh waters. The plot of major cation concentration versus EC (Fig.2) showed a strong correlation in surface waters. Dissolved Na and Mg are the highest contributors to EC of surface waters. In the absence of limestone-bearing rocks, calcite (CaCO_3) and Ca-bearing silicate minerals are the possible sources of Ca in the study area. Near neutral to alkaline surface water pH is due to the presence of acid neutralizing minerals as indicated by high Ca and Mg soil contents (Fig.4b).

The triangular diagram of major cations (Mg vs. Ca vs. Na+K; Fig.6), indicates that the surface waters are dominated by Na+K, with little influence from Mg and Ca. The percentage composition of Na+K is much higher than the average value for global rivers and reflects the link of catchment geology with surface water composition. These results can be explained by the strong weathering of Na-containing minerals and atmospheric input. Unfortunately, since Cl was not measured in water samples, the atmospheric input of sea-salt cannot be confirmed. For the individual creeks, Creswick Creek showed the most variability in Na+K ionic concentration. The data tend to fall above the composition line ($\text{Ca} = \text{Mg}$) of Ca and Mg in the triangular plot and demonstrate the enrichment of Mg over Ca. Weathering of olivine and pyroxene, the dominant minerals of basalt, is the most likely reason for higher dissolved Mg over Ca in surface waters.

Mineral hydrolysis is probably the primary controlling process of hydrogeochemistry of most surface waters. Plagioclase, a common rock forming mineral, the Na end-member (albite) is dominant over the Ca end-member (anorthite) and weathers to produce soils of kaolinitic nature. While Na content is the lowest in soils, dissolved Na^+ concentration dominates in all surface waters as a major cation. This can be explained by the leaching of Na as a result of chemical weathering. Dissolution of plagioclase (albite) which produces kaolinite plus Na cations can be written as:

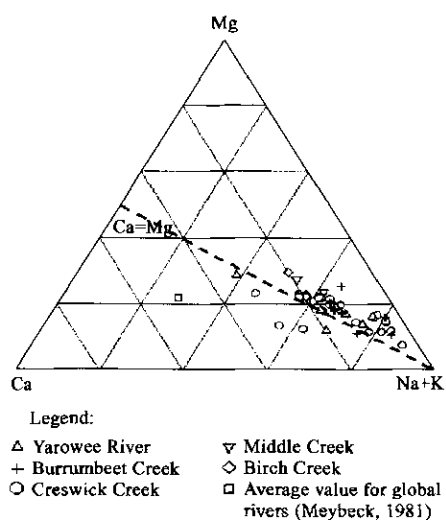
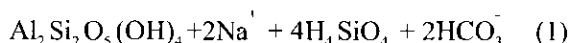
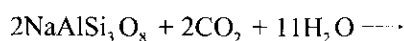


Fig.6 Triangular diagram of major cations compositions, Mg vs. Ca vs. Na+K



Kaolinite($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) is one of the most common clay minerals in the study area (Sultan, 2005) and generally secondary clay minerals follow an order of abundance as: Kaolinite >> illite > smectite > vermiculite \approx mixed-layer. Ca and Mg can exchange for the sorbed Na on soil mineral particles. The high concentration of Na in surface water, average 98.7 mg/L, which is more than thirty times the average concentration of 3.1 mg/L in rainfall indicated evaporation/evapotranspiration can not alone be responsible for high Na, rather it pointed towards the significant input by weathering of rock/soil minerals. Surface water in creeks draining Ordovician bedrock is lower in Na content than other bedrock sources and indicates the catchment lithology control over water chemistry. Agricultural activities could be an additional source contributing to the increase of dissolved Na.

Relatively high arsenic in soils developed on Ordovician bedrock are due to the presence of arsenopyrite (FeAsS) (Taylor *et al.*, 2000) as also revealed by SEM analysis in one of the soil sample (Fig.4a). The weathering of sulphides produces Fe oxide/hydroxides(e.g. $\text{FeO}(\text{OH})$, Fig.5) which serve as sink or source for As, depending upon prevailing pH-Eh conditions. Under near neutral soil pH conditions, the oxides and hydroxides of Fe, Al and Mn tend to (co-) precipitate (Brookins, 1988) and hence act as scavenger for As. Sorption of As on the (hydr)oxides of Fe(Equation (3)), Al and Mn possibly prevents As mobilization in As-contaminated soils. Fig.7 shows the correlation between As against

combined contents of Fe, Al and Mn in soils. Fordham and Norrish (1979) reported that Fe oxides were more important in adsorption of arsenic in soils in comparison to clay minerals and did not highlight the role

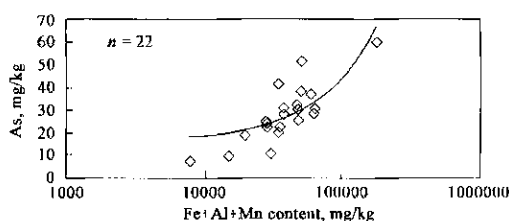
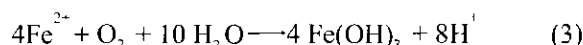
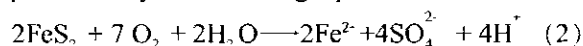


Fig.7 Plot of As contents against Fe+Al+Mn contents in soils

of Al and Mn.

Under lower Eh and alkaline conditions the mobility of As may increase (Stumm and Modrgan, 1996; Smedley and Kinniburgh, 2002) by desorption processes. The oxidation of the iron sulphides (FeS_2) from tailing and bedrock by the infiltrating rainwater will produce acidification and forms Fe-oxyhydroxides. The acid generated is neutralised by carbonates (Equation (4), $\text{M}=\text{Ca}^{2+}$, Mg^{2+}). The reaction processes are presented by the following equations:



Some waste rock dumps of loose materials, subject to strong erosion, may cause significant flux of As into streams as a result of storm events. The recharging water may follow unique paths and supply unprocessed, metal/metalloid rich water to streams. Low concentrations of As in surface waters might be due to oxidation of arsenopyrite and/or release into waters by desorption mechanism under slightly reducing conditions. Moderate annual rain (about 700 mm/a) in the area could be an important factor by allowing slow mobilization and transport of As from solid phases into water.

4 Conclusions

In the goldfields region of Central Victoria, catchment lithology exerts the fundamental control on the surface water chemistry, which was found to be locally impacted by mining waste dumps. The weathering of the primary silicate mineral, Na-plagioclase and potentially atmospheric input contribute high amounts of Na to surface waters. Although Na content was found to be low in soils, it dominated in surface waters among the major cations which indicated extensive leaching of Na. Major cations composition was not within the average valuc

for global rivers as Na+K registered higher with little influence of Ca and Mg.

The As adsorption affinity for Fe and Al(hydr) oxides under neutral to slightly alkaline-oxidative conditions prevents significant mobilization into surface waters. A gradual and slow release possibly occurs when low redox-alkaline conditions prevail. Arsenic trapped in soils is slowly released under relatively lower redox and alkaline conditions.

Human activities (e.g. mining) have altered the environments of creek/river catchments in the area, however, all of the four lakes sampled registered As levels well below the ANZECC (1992) guidelines. Generally, the slow release of arsenic from soils with high background arsenic levels was observed, but arsenic concentrations in surface waters were found to be below the guideline values for the water quality for recreational fresh waters (ANZECC, 2000) in the Central Goldfields region of Victoria.

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