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Arsenic speciation and trace element analysis of the volcanic río Agrio and the geothermal waters of Copahue, Argentina

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ABSTRACT

Surface water originating from the Copahue volcano crater-lake was analysed for total arsenic and four arsenic species: arsenite (iAs^{III}), arsenate (iAs^{V}), monomethylarsonic acid (MA^{V}) and dimethylarsinic acid (DMA^{V}) and other trace elements (Fe, Mn, V, Cr, Ni, Zn). A novel in-field technique for the preconcentration and separation of four arsenic species was, for the first time, used for the analysis of geothermal and volcanic waters. Total arsenic levels along the río Agrio ranged from <0.2–3783 μg/l As_T. The highest arsenic levels were recorded in the el Vertedero spring (3783 μg/l As_T) on the flank of the Copahue volcano, which feeds the acidic río Agrio. Arsenite (H_3AsO_3) predominated along the upper río Agrio (78.9–81.2% iAs^{III}) but the species distribution changed at lago Caviahue and arsenate ($H_2AsO_4^-$) became the main species (51.4–61.4% iAs^{V}) up until Salto del Agrio. The change in arsenic species is potentially a result of an increase in redox potential and the formation of iron-based precipitates. Arsenic speciation showed a statistically significant correlation with redox potential ($r=0.9697$, $P=0.01$). Both total arsenic and arsenic speciation displayed a statistically significant correlation with vanadium levels along the river ($r=0.9961$, $P=0.01$ and $r=0.8488$, $P=0.05$, respectively). This study highlights that chemical speciation analysis of volcanic waters is important in providing ideas on potential chemical toxicity. Furthermore there is a need for further work evaluating how arsenic (and other trace elements), released in volcanic and geothermal streams/vents, impacts on both biota and humans (via exposure in thermal pools or consuming commercial drinking water).

1. Introduction

Arsenic contamination of ground and surface water sources is a global health concern. Arsenic concentrations above the World Health Organisation (WHO) guideline limit for arsenic in drinking water (10 μg/l As_T) (WHO, 2008) have been reported globally, including in South American countries such as Chile (Caceres et al., 2005; Queirolo et al., 2000), and Argentina (Farías et al., 2003; Nicolli et al., 1989; Smedley et al., 2002).

In many regions volcanic and geothermal activity is believed to be one of the causes of high arsenic concentrations in ground and surface waters. Geothermal reservoirs have been found to contain arsenic levels up to 50,000 μg/l As_T (Ballantyne and Moore, 1988). Natural surface manifestations, such as hot springs and fumaroles, typically have lower arsenic levels (Table 1). Limited research is available on arsenic speciation in volcanic water systems. However, arsenite (iAs^{III}) has been found to dominate in geothermal reservoir fluids (Ballantyne and Moore, 1988) as well as in groundwater samples surrounding volcanoes in Italy (Aiuppa et al., 2003).

The focus of the present study is the río Agrio, an acidic river whose waters originate from the crater-lake of the Copahue volcano. The Copahue volcano is an active stratovolcano (2997 m) along the Argentina–Chile border, in the province of Neuquén, Argentina. The most recent recorded eruption of the volcano occurred during July–October 2000 (Varekamp, 2008). The eastern summit crater contains a briny, acidic (pH<1) 300 m wide crater-lake (El Agrio or Del Agrio). Acidic hot springs below the eastern outlet of the crater-lake feed the highly acidic (pH<2) upper río Agrio (sour river), which flows into lago Caviahue (pH 2.5), a horse-shoe shaped lake with an area of approximately 10 km^2. The pH of the lower río Agrio, which flows out from the north-eastern point of the lake, gradually neutralises due to the influx of tributary streams (snow-melt and mountain surface water) before reaching the town of Loncopue approximately 60 km downstream (Gammons et al., 2005).

Annual variation in the chemical composition of the river and lake occurs due to variances in volcanic activity and the volume of glacial melt-water. Varekamp (2008) monitored the trace element levels of the upper and lower río Agrio and the lago Caviahue over a 5 year period (1999–2004). During this period the total arsenic (As_T) concentrations ranged from <detection (no value stated) to 640 μg/l As_T (upper río Agrio). Another study reported 4780–5694 μg/l As_T in the el Vertedero spring at the source of the río Agrio (Gammons et al.,

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Table 1
Literature values for arsenic (total and species) and iron levels in volcanic and geothermal surface/groundwater sources around the world.

Country: Volcano/Volcanic Region	State of Sample	Water Type	pH	As (μg/l)	As Species	Fe (mg/l)	Reference
Volcanic surface water:							
Azores: Lagoa das Furnas, Furnas Volcano, São Miguel Island	F/A[a]	–	7.5	0.9	–	0.011	Cruz et al., 1999
Indonesia: Kawah Putih Crater Lake, Patuha Volcano	F/A[a]	SO_4^{2-}–Cl^-	<0.5–1.3	147–858	–	24–48	Sriwana et al., 2000
Mexico: El Chichón Volcano Crater Lake	F/A[a]	Cl^-	2.1–2.2	50–125	–	5.2–16.5	Taran et al., 2008
Volcanic groundwater:							
Italy: Vulcano Island, Phlegrean Fields, Stromboli	–	SO_4^{2-}–Cl^-	1.5–7.9	0.6–6940	iAs^{III}	0.006–506	Aiuppa et al., 2003
Italy: Vesuvius, Etna	–	HCO_3^-	5.8–8.0	0.1–92	iAs^{III}	0.01–30.8	Aiuppa et al., 2003
Italy: Phlegrean Fields, Ischia Island	F/A[a]	HCO_3^-	5.9–8.7	2–804	–	–	Aiuppa et al., 2006
		SO_4^{2-}	1.6–2.6	10–22	–	–	
		NaCl brines	5.5–9.1	6–8345	–	–	
Mexico: Los Humeros and Los Azufres	F/A[a]	HCO_3^-	6.8–7.9	9400–27,500	–	–	Birkle et al., 2010
Geothermal Reservoirs (TMV[c])		NaCl brines	6.6–8.7	500–73,600	–	–	
Geothermal springs:							
Azores: Furnas Volcano, São Miguel Island	F/A[a]	–	3.4–8.7	<dl[b]–850	–	0.002–20	Cruz et al., 1999
Indonesia: Patuha Volcano	F/A[a]	SO_4^{2-}–Cl^-	2.5–7.6	5.1–45	–	<dl[b]–65	Sriwana et al., 2000
Mexico: El Chichón Volcano	F/A[a]	Na–Ca–Cl	2.2–5.6	16–146	–	0.93–22.5	Taran et al., 2008
		Na–Cl	5.6–6.4	10–37	–	0.78–4.2	

[a] F/A = filtered and acidified.
[b] <dl = below detection limit; [c]TMV = Transmexican Volcanic Belt.

2005; Parker et al., 2008). This is diluted by glacial melt-water along the upper río Agrio. After the river flows over a series of cascades it reaches lago Caviahue at which point the water is further diluted, with levels in the lake ranging from <detection (no LOD value stated) to 40 μg/l As_T (Gammons et al., 2005; Parker et al., 2008; Varekamp, 2008). No data has yet been published on arsenic speciation or the effect of physicochemical parameters on the levels of total arsenic and its species. The toxicity of arsenic is highly dependent on the type of species present (Hughes, 2002). Naturally occurring inorganic arsenic species are, in general, more toxic than organic arsenic species. The acute toxicity of inorganic arsenite (iAs^{III}) is greater than arsenate (iAs^V) and the lethal dose of inorganic arsenic (iAs) for a human adult is estimated as 1–3 mg As/kg (Hughes, 2002).

Geothermal activity in the local area is used for human recreational and health purposes. A thermal spa located 7 km from the volcano draws tourists to this region because of the healing properties of the pools, steam vents and mud pools. The thermal (ferruginous and sulphurous) waters are recommended for the treatment of skin diseases, sciatica, rheumatism, lumbago, general tiredness and for disorders associated with the nervous system. The impact of arsenic and associated elements on human health has been a growing concern for several decades. Many studies have highlighted an increased risk in skin, lung and bladder cancers, as well as a range of non-cancer diseases among populations drinking elevated levels of arsenic (Duker et al., 2005; Hopenhayn-Rich et al., 1996, 1998; Smith et al., 1998; Tseng et al., 2003).

The aim of the present study was to determine the levels of total arsenic and the distribution of its species within the volcanic río Agrio water system over a two year period (2010–2011). A novel in-field technique for the preconcentration and separation of arsenic species (Watts et al., 2010) was applied for the first time in geothermal and volcanic waters. Physicochemical parameters were measured and trace element levels were determined using inductively coupled plasma mass spectrometry (ICP-MS) with collision cell technology. The influence of physicochemical parameters and trace element levels on arsenic speciation was evaluated providing information on the toxicity of the arsenic present in the water system.

2. Site description

The río Agrio is an acidic glacial river fed by the crater-lake of the Copahue volcano. The crater-lake waters (URA 1) are Cl–SO_4 brines formed by the dissolution of magmatic SO_2 and HCl gases (Varekamp et al., 2009). The addition of SO_2 gas to water can cause a disproportionation reaction to occur ($3SO_2 + 2H_2O \rightarrow 2HSO_4^- + 2H^+ + S$) generating acidity and solid sulphur. Subsequently the acid fluids will react with the surrounding rocks and can acquire trace elements (Varekamp et al., 2009). The crater-lake water feeds a series of hot springs of which the largest is 'el Vertedero', the source of the río Agrio (URA 2). From the spring the upper río Agrio (URA) descends down the flank of the volcano and merges with a series of glacial melt-water tributaries. After entering the Caviahue caldera the river goes over a series of cascades (URA 3–9), with further input from a small fresh-water tributary (C 1) between sites URA 6 and 7, before discharging into lago Caviahue (LC 1–4). The main water inputs into the lake are the río Agrio and the río Dulce (C 2). The lake drains from the north-eastern part of the lake into the lower río Agrio (LRA 1), which merges with río Trolope before going over a large cascade (Salta del Agrio: LRA 3). Further downstream the river merges with the río Norquin before passing through the town of Loncopue (LRA 4). Further samples were collected from lagunas las Mellizas (C 3), the fresh water lakes at the base of the volcano which provide drinking water to the town of Caviahue and from two geothermal springs located near the spa town of Copahue: agua Limón (G 1) and las Maquinitas (G 2). Surface water samples were collected from each site in January 2010 and/or 2011. Alongside the water samples an arsenic speciation sample was collected in 2011 (Section 3.2). Descriptions and physicochemical properties of the sampling sites are provided in Table 2 and Fig. 1.

3. Materials and methods

3.1. Sample collection

All volcanic crater and geothermal surface and spring water samples for total elemental analysis were collected in Sterilin® bottles (Fisher Scientific Ltd, UK). Water was taken up in clean 20 ml BD™ plastic syringes (Becton Dickinson Ltd, UK) and injected into a bottle through a 0.45 μm membrane filter (Millipore, UK). All filtered samples were acidified using 0.1 ml concentrated nitric acid (15.8 M) (Fisher Scientific Ltd, UK). A further 30 ml water sample was passed through the solid phase extraction (SPE) cartridges for arsenic species separation (Section 3.2). All filtered samples were transported to the University of Surrey (UK) and stored at <4 °C until analysis. Physicochemical parameter measurements: