

Greenpeace Research Laboratories Analytical Results 2016-04

Analysis of samples of water and solid materials related to a copper mine in Chile. April 2016

Introduction

Two samples of water and two solid samples were received from Greenpeace Chile for analysis at the Greenpeace Research Laboratories on the 6th April 2016. All samples were collected on 24th March 2016. Information on the samples received is provided in Table 1.

All samples were analysed quantitatively for the presence of a range of metals and metalloids.

Sample code	NRO Code	Sample type	Date	Description
CH16001	Chile 1A	river water	24.03.16	Rio Blanco River, Los Andes City
CH16002	Chile 2A	water	24.03.16	Rio Blanco River, Los Andes City
CH16003	Chile 3B	sediment	24.03.16	Rio Blanco River, Los Andes City
CH16004	Chile 4B	sediment	24.03.16	Irrigation canal near Rio Blanco River, Los Andes City

Table 1: details of samples received and analysed at the Greenpeace Research Laboratories

Materials and methods

Metal and metalloid concentrations were determined for all samples at the Greenpeace Research laboratory by ICP mass spectrometry (MS), following acid digestion and using appropriate intra-laboratory standards (water samples) or an appropriate certified reference material (solid samples). The two water samples were clear and colourless and so the total metal concentrations in the whole (unfiltered) samples were determined in each case.

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Results and Discussion

The results for the samples are reported in Table 2. Where the concentration of a metal or metalloid was below the limit of quantification for the analytical method employed the result is presented as '<xx' where xx is the method limit of quantification for the individual metal or metalloid.

Sample type	river water	river water	sediment	sediment
Sample code	CH16001	CH16002	CH16003	CH16004
Description	clear colourless	clear colourless	sediment from Rio Blanco	sediment from Irrigation canal
	concentrations (µg/L)		concentrations (mg/kg dry weight)	
Antimony	3.1	3.5	104	0.7
Arsenic	13	14	1460	108
Barium	38	42	56.7	224
Beryllium	<0.1	<0.1	0.32	1.32
Cadmium	<0.1	<0.1	14.0	2.3
Chromium	0.5	0.4	8.65	21.8
Cobalt	0.2	0.2	29.7	36.8
Copper	134	136	199000	7800
Lead	0.9	1.0	452	37.4
Manganese	91	103	720	892
Mercury	<0.2	<0.2	9.1	0.24
Nickel	<2	<2	12	18
Strontium	473	519	21.0	93.2
Vanadium	2.0	2.0	29.9	80.4
Zinc	8	8	3650	672

Table 2: Concentrations of metals and metalloids in water (µg/L) and solid (mg/kg dry weight) samples

The two river water samples (CH16001 & CH16002) both contained concentrations of copper above those typically found in uncontaminated surface waters, which are typically below 10 µg/l, and often far lower (ATSDR 2004, Comber *et al.* 2008). Concentrations of the other quantified metals/metalloids were not unusual for uncontaminated surface waters.

The sediment from the Rio Blanco (CH16003) had a very high concentration of copper (199000 mg/kg, 19.9% by mass), as well as high concentrations of antimony, arsenic, cadmium, lead, mercury and zinc compared to concentrations typically found in uncontaminated freshwater sediments.

The sediment from an irrigation canal near to the Rio Blanco (CH16004) also had a high concentration of copper (7800 mg/kg, 0.78% by mass), though this was less than in the river sediment (CH16003), as well as somewhat high concentrations of arsenic, cadmium and zinc, though again this was less than detected in river sediment sample (CH16003).

For more information please contact:

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References

- ATSDR (2004) Toxicological profile for copper. Agency for Toxic Substances and Disease Registry, US Public Health Service, September 2004
- Comber, S.D.W., Merrington, G., Sturdy, L., Delbeke, K., van Assche, F. (2008) Copper and zinc water quality standards under the EU Water Framework Directive: The use of a tiered approach to estimate the levels of failure. *Science of the Total Environment* 403(1-3): 12-22

Appendix 1: Details of methodologies: Analysis using acid digestion and ICP mass spectrometry (MS) analysis

Preparation

Water samples

A representative portion of each whole (unfiltered) water sample was acidified by the addition of concentrated nitric acid to give a final concentration of 5% v/v. 25 ml of each acidified sample was digested firstly overnight at room temperature, then using microwave-assisted digestion with a CEM MARS Xpress system, with a temperature ramp to 180°C over 20 minutes followed by holding at 180°C for a further 20 minutes. Cooled digests were filtered and made up to 25 ml with deionised water.

Solid samples

A representative portion of each sample was air dried to constant weight, homogenised and ground to a powder using a pestle and mortar. Approximately 0.15 g of each dried and ground sample was digested with 2.5 ml concentrated nitric acid and 0.25 ml concentrated hydrochloric acid, firstly overnight at room temperature, then using microwave-assisted digestion with a CEM MARS Xpress system, with a temperature ramp to 180°C over 20 minutes followed by holding at 180°C for a further 20 minutes. Following cooling, digests were filtered and made up to 25 ml with deionised water.

Analysis

Prepared sample digests were analysed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) using an Agilent 7900 Spectrometer utilizing a collision cell with helium as the collision gas to minimize polyatomic interferences. Multi-element standards, matrix matched to the samples, at concentrations of 1, 10, 100 and 1000 µg/l respectively, other than for mercury (0.5, 2, 5, 20 µg/l respectively) were used for instrument calibration. Analysis employed in-line addition of an internal standard mix at 1000 µg/l (Scandium, Germanium, Yttrium, Indium and Terbium).

Quality control

Water samples

One sample was prepared for ICP analysis in duplicate and analysed to verify method reproducibility, along with a blank sample (5% v/v nitric acid in deionised water). Two mixed metal quality control

solution of 80 and 800 µg/l for each metal, other than mercury at 4 and 16 µg/l, were digested and analysed. All control samples were prepared in an identical manor to the samples.

Solid samples

One of the samples were prepared for ICP analysis in duplicate and analysed to verify method reproducibility, along with a blank sample. To check the method efficiency, a certified reference material (CRM) was prepared in an identical manner; GBW07311, stream sediment certified by the China National Analysis Centre for Iron and Steel, Beijing, China.

Calibration of the ICP-MS was validated by the use of quality control standards 80 µg/l and 800 µg/l (4 µg/l and 16 µg/l for mercury) prepared in an identical manner but from different reagent stocks to the instrument calibration standards.

Further details of the methods employed can be provided on request.