

Greenpeace Research Laboratories Analytical Results 2018-01

**Metals and metalloids in wastewater samples from the Elektráreň Nováky coal
fired power plant in Slovakia**

January 2018

Introduction

8 samples of wastewater were received from Greenpeace CEE (Slovakia) for analysis at the Greenpeace Research Laboratories on 29th November 2017. According to documentation supplied, all samples were collected on 28th November 2017, from the wastewater discharge channel of the Elektráreň Nováky coal fired power plant in Zemianske Kostol'any, Slovakia (48.69076°N, 18.52509°E).

Details of the samples received are provided in Table 1. All samples were collected from a treated wastewater discharge channel at the site, and at approximately 1-hour intervals, from 05:23 to 12:30 on 28th November 2017.

Sample code	Date	Time
SK17009F	28-11-2017	05:23
SK17010F	28-11-2017	06:12
SK17011F	28-11-2017	07:20
SK17012F	28-11-2017	08:15
SK17013F	28-11-2017	09:44
SK17014F	28-11-2017	10:35
SK17015F	28-11-2017	11:28
SK17016F	28-11-2017	12:30

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

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Materials and methods

All samples were collected in pre-cleaned glass bottles and kept cold and dark before shipment to our laboratory in the UK for analysis.

For each sample, both the total concentrations in the whole (unfiltered) sample and the concentrations of dissolved forms in a filtered sample were determined separately by ICP mass spectrometry (MS) following acid digestion and using appropriate laboratory reference samples. Hexavalent chromium concentrations in filtered water samples were determined colourimetrically using a diphenylcarbazide method. More detailed descriptions of the sample preparation and analytical procedures are presented in the Appendix 1.

Results and Discussion

The results for the samples are outlined below. The dissolved concentrations of metals and metalloids in filtered sub-samples, and total concentrations in whole sub-samples, are reported in Table 2. In some cases, concentrations of metals or metalloids were below limits of detection for the analytical methods employed in this study. These are shown in the results tables as '<xx' where xx is the method detection limit for the individual metal or metalloid.

Sample code	SK17009		SK17010		SK17011		SK17012		SK17013		SK17014		SK17015		SK17016	
	filt.	wh	filt.	wh	filt.	wh	filt.	wh	filt.	wh	filt.	wh	filt.	wh	filt.	wh
Arsenic	8.84	9.73	8.52	9.81	7.90	10.0	7.55	9.58	6.83	8.82	7.51	8.93	7.20	8.59	7.01	8.81
Barium	26.7	27.9	25.4	28.2	24.6	29.5	24.4	28.6	23.4	28.7	24.6	28.8	24.2	28.1	23.9	29.6
Cadmium	<0.04	0.08	<0.04	0.35	<0.04	0.08	<0.04	0.06	0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
Chromium	0.7	0.7	0.5	0.6	0.5	0.7	0.4	0.6	0.3	0.7	0.3	0.4	0.3	0.5	0.3	0.9
Chromium (VI)	<50	-	<50	-	<50	-	<50	-	<50	-	<50	-	<50	-	<50	-
Cobalt	0.24	0.33	0.23	0.37	0.22	0.40	0.23	0.33	0.22	0.34	0.26	0.37	0.24	0.35	0.24	0.39
Copper	4.0	8.9	4.3	11.9	7.4	19.1	10.2	23.9	13.6	29.8	10.7	20.9	12.2	22.7	9.5	19.6
Iron	97	241	107	295	112	387	115	292	112	366	106	294	108	273	111	415
Lead	<0.1	1.1	<0.1	1.2	<0.1	0.7	<0.1	0.5	<0.1	0.6	<0.1	0.6	<0.1	0.8	<0.1	0.9
Manganese	36.2	39.3	41.0	45.2	40.5	47.7	40.4	48.1	39.0	45.7	37.4	42.2	37.7	42.3	36.9	42.7
Mercury	0.1	<0.1	<0.1	0.4	0.2	0.4	0.3	0.4	0.1	0.3	<0.1	<0.1	<0.1	0.5	<0.1	0.3
Molybdenum	0.47	0.59	0.44	0.59	0.51	0.70	0.55	0.73	0.50	0.66	0.51	0.65	0.51	0.63	0.56	0.67
Nickel	<1	2	<1	<1	<1	2	<1	2	<1	2	<1	<1	<1	<1	<1	<1
Selenium	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Titanium	0.4	2.7	0.5	3.6	0.6	4.8	0.6	2.9	0.7	5.3	0.5	4.4	0.8	3.5	1.3	7.4
Vanadium	0.79	1.27	0.68	1.26	0.66	1.42	0.63	1.17	0.63	1.35	0.67	1.28	0.67	1.20	0.70	1.59
Zinc	12	28	10	36	13	56	13	48	16	56	14	32	18	46	18	52

Table 2: Concentrations of metals and metalloids ($\mu\text{g/l}$) in filtered (filt.) and whole (wh.) wastewater samples

The concentrations quantified in the samples indicate that wastewaters were not notably contaminated with these metals/metalloids, with little sign of elevation in concentrations above typical background concentrations for uncontaminated surface freshwaters.

The concentrations of individual metals/metalloids did not vary notably over time, with the exception of copper, for which the concentrations of dissolved copper ranging from 4.0 to 13.6 µg/l, and those of total copper from 8.9 to 29.8 µg/l, over the sampling period.

For more information please contact:

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Appendix 1: Details of methodologies

Analysis for metals

Preparation

To obtain total metal concentrations, a representative portion of each whole water sample was acidified by the addition of concentrated nitric acid to give a final concentration of 5% v/v. Separately, a portion of each whole sample was filtered through a 0.45 micron filter and then acidified in the same way to enable determination of dissolved metal concentrations. 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 15 minutes followed by holding at 180°C for a further 15 minutes. Cooled 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).

Concentrations of chromium (VI) were determined colorimetric for each water sample following filtration. 0.5 ml of a 1,5-diphenylcarbazide testing solution (freshly prepared from 0.4 g of 1,5-diphenylcarbazide, 20 ml acetone, 20 ml ethanol, 20 ml orthophosphoric acid solution and 20 ml of demineralised water) was added to 9.5 ml of each filtered sample. The solution was mixed and let to stand for 10 minutes to allow full colour development. Concentrations were determined using a spectrophotometer at 540 nm, correcting with a blank prepared from deionised water, using standards freshly prepared from potassium dichromate at concentrations of 0, 50, 100, 200 and 500 µg/l respectively. Any sample exceeding the calibration range was diluted accordingly, in duplicate, and re-analysed.

Quality control

One sample, both filtered and whole sub-samples, was prepared for ICP analysis in duplicate and analysed to verify method reproducibility, along with a blank sample. 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.

Calibration of the ICP-MS was validated by the use of quality control standards at 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.