

# Metals, metalloids and organic contaminants in wastewater, river water, sediment and ash samples associated with the Bobov Dol coal fired power plant, Golemo Selo, Bulgaria

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## Summary

The burning of coal by coal fired power stations generates large quantities of ash wastes, which contain residues of metals and metalloids originating from within the coal. These ashes are often transferred to large storage sites, which can generate their own waste streams in the form of run-off and/or leachate. This study investigated the composition of waste streams generated by ash storage sites of the Bobov Dol coal-fired power plant (CFPP), a 1716 MWth (630 MWe) plant located on the banks of the Razmetanitza River near the village of Golemo Selo in Western Bulgaria. The investigation included wastewaters released to the Razmetanitza River from a short term ash storage site known as 'Black Lake' located adjacent to the CFPP, and those released from the larger, long-term, Kamenik ash disposal site to the Kamenishka River, a tributary to the Razmetanitza River.

A total of 29 samples were collected during three visits between November 2018 and May 2019. Details of the locations from where individual samples were collected are given in the main report, including maps showing sampling locations relative to the CFPP and ash storage sites.

This study found that waste waters containing elevated concentrations of a range of metals and metalloids associated with coal fly ashes are routinely released to the local environment from sites where ashes generated by the Bobov Dol CFPP are stored.

Key results included:

- Samples of wastewater released from the lower equalizer facility (LEF), situated immediately below the dike of the Kamenik ash disposal site, contained far higher concentrations of many metals and metalloids compared to local surface waters, including;
  - Concentrations of certain dissolved metals over 100 times higher than local background concentrations;
  - Other toxic metals and metalloids at concentrations elevated above local background concentrations, including arsenic and mercury;
  - Leachates from coal ashes are known sources of the range of the metals and metalloids found at elevated concentrations.
- The accumulation of some of these metals and metalloids in sediments from the Kamenishka River, through which the LEF wastewater flows;
- Higher concentrations of the same range of metals and metalloids in the Razmetanitza River, downstream of the two official discharge points of the Black Lake ash storage site;
- Evidence indicating the release of substantial quantities of ash itself into the Razmetanitza River from the vicinity of the CFPP and Black Lake ash storage site during May 2019

The creation of large quantities of contaminated ash will continue while the Bobov Dol coal-fired power plant continues to operate, as will ongoing impacts on the quality of local surface water environments until measures are put in place to prevent releases of contaminated wastewaters and solid wastes from the Bobov Dol CFPP and its ash storage sites.

## Introduction

The Bobov Dol coal-fired power plant (CFPP) is a 1716 MWth (630 MWe) plant located on the banks of the Razmetanitza River near the village of Golemo Selo in Western Bulgaria and is comprised of three units each of 210 MW capacity. The power plant uses lignite and sub-bituminous coals from multiple coal basins in Bulgaria, including the Bobov Dol deposit (Kostova *et al.* 2011, TPP Bobov Dol GmbH 2018).

Coal contains traces of a wide range of metals and metalloids, including naturally occurring radioactive constituents such as uranium and thorium (EPRI 2009), with the composition varying widely between different sources of coal. Following combustion, a fraction of these metals/metalloids will be retained within the fly ash, in many cases at higher concentrations than in the unburned coal (Lecomte *et al.* 2017). As composition of the coal is a major factor in the composition of the resulting fly ash, the composition of coal fly ash also varies widely between different sources. Metals and metalloids within the fly ash can leach over time to varying degrees due to weathering, which can reduce their concentrations within the ash, but in the same process produce leachates contaminated with these metals/metalloids (Donahoe 2004, Izquierdo & Querol 2012, Kosson *et al.* 2009, Vassilev *et al.* 2010).

Coal from the Bobov Dol deposit is sub-bituminous with a high ash content (Vassilev *et al.* 2010). A number of studies have been published on the composition of coal from the Bobov Dol deposit, and of wastes from the Bobov Dol CFPP, including fly ash, bottom ash and lagooned ashes from the disposal site, though the data apply to samples collected prior to 1996 (Vassilev *et al.* 2010 and references therein).

Bobov Dol CFPP is fired coals from multiple coal basins in Bulgaria as well as other combustible materials. A total of 2537 thousand tonnes of hard fuel was used in 2018, made up of 1925 thousand tonnes of coal, 565 thousand tonnes of biomass, and 47 thousand tonnes of refuse derived fuel (RDF). The coal mix included coal from the Oranovo-Simitli basin, the Sofia basin, briquettes from the Maritsa basin and brown coal (region unspecified) according to the Bobov Dol CFPP 2018 annual report (TPP Bobov Dol 2019), though the mix of coals from different sources used at the Bobov Dol CFPP is known to vary over time (Kostova *et al.* 2011, TPP Bobov Dol GmbH 2018), and the composition of wastes generated may therefore be expected to vary also. On 9th April 2019 TPP Bobov dol received a new Integrated Permit introducing the use of alternative fuels (Ministry of Environment and Water 2019) and prior to this the co-incineration of non-hazardous waste was permitted from 12 November 2018 for a period of 6 months (Regional Inspection of Environment and Water 2019).

This study was carried out to determine the current composition, and the variation in composition over time, of waste streams generated by the Bobov Dol CFPP and sites where generated ashes are stored, including those released to the local environment. These included wastewaters released to the Razmetanitza River from an ash storage site located adjacent to the CFPP and those released from the larger, long-term, Kamenik ash disposal site to Kamenishka River, a tributary to the Razmetanitza River.

## Materials and methods

### Sample description

Three visits were made to the Bobov Dol coal fired power plant (CFPP) and its surrounding infrastructure between November 2018 and May 2019, and a range of samples collected during each visit.

- The first set of samples was collected on the 8<sup>th</sup> and 9<sup>th</sup> November 2018 and consisted of six samples, collected mainly from the Razmetanitza River in the immediate vicinity of the CFPP itself and its associated short-term ash storage site (known as 'Black Lake'). One river water sample (BG18001) broke during transport to our laboratory and could not be analysed.
- The second set of samples was collected between the 11<sup>th</sup> and 13<sup>th</sup> March 2019 and consisted of 18 samples, again including samples around the CFPP but also with a more detailed focus on waste going to and exiting from the Kamenik ash disposal site located at the head of the Kamenishka River, a smaller tributary that joins the Razmetanitza River approximately 10 km downstream from the CFPP. Three samples collected in March 2019 did not pass quality control checks and therefore results are not included for these three samples.
- A third set of five samples was collected on 21<sup>st</sup> May 2019, focusing in particular on waters and sediments both immediately upstream and downstream of the confluence of the Kamenishka with the Razmetanitza rivers.

Details of the samples are provided in Table 1 and the following text.

The Black Lake ash storage site is situated adjacent to the Bobov Dol CFPP. Fly ash is transferred from the CFPP to this site for temporary storage and treatment, and subsequently transported to the Kamenik ash disposal site. Wastewater is discharged from the Black Lake site via two official discharge points into the Razmetanitza River, a tributary to the Dzherman River, which in turn flows into the Struma River. In November 2018, samples of river water and sediment were collected from the Razmetanitza River both upstream (BG18003-04) and downstream (BG18001-02) of the two discharge points, though unfortunately, the river water sample collected downstream of the discharge points during this visit broke in transit and could not be analysed. Samples of sediment were collected from the sides of the riverbed of the Razmetanitza River, below the water surface, as the bottom of the river is concrete lined in this area and no sediment was present in the middle of the river.

In addition, a sample of wastewater was collected directly from the higher of the two discharge points (BG18005). It was not possible to access the 2<sup>nd</sup> wastewater discharge point, which is situated approximately 150m further downstream. An oily liquid was observed to be leaching from ground nearby into a channel which flows to the Razmetanitza River close to the discharge points of the Black Lake ash storage pond, though it was not possible to sample this at the time. It is not known whether there are other significant inputs to this stretch of the Razmetanitza River due to diffuse leaching from the Black Lake ash storage site.

The site was revisited in March 2019 and the locations listed above were resampled, including the same (upper) wastewater discharge point (BG19016) and river water from the Razmetanitza River both upstream (BG19014) and downstream (BG19015) of the two discharge points. During this visit, a sample of river water (BG19017) and river sediment (BG19018) were also collected from the Razmetanitza River adjacent to the channel into which the black leachate was flowing in November 2018, though no leaching was observed on this second visit.

Sample code	Type	Site	Sampling location	N degree (°)	E degree (°)
<b>November 2018</b>					
BG18001*	RW	Razmetanitza River	200 m downstream of sampled discharge point of Black Lake ash storage pond	42.275210	23.041309
BG18002	Sed				
BG18003	RW	Razmetanitza River	200 m upstream of sampled discharge point of Black Lake ash storage pond	42.289540	23.040256
BG18004	Sed				
BG18005	WW	Discharge pipe	1 of 2 official discharge points of the Black Lake ash storage pond to the Razmetanitza river	42.280232	23.040712
BG18006	WW	Lower equalizer facility (LEF)	Facility immediately below the dike of the Kamenik ash disposal site. Water flows into a storage area, which over- flows into a concrete channel which becomes the Kamenishka River. Collected at entry point of water into channel	42.223011	23.012717
<b>March 2019</b>					
BG19001	WW	LEF overflow	Point where wastewater enters channel, after overflowing from LEF area. Same as BG18006	42.22300	23.01262
BG19002	Sed				
BG19003	WW	Downstream of LEF	Concrete channel downstream from where BG19001/02 were collected, immediately after the channel flows underground for a short distance, below a road	42.22294	23.01361
BG19004	Sed				
BG19005	Sed	Further downstream of LEF	Small channel into which the concrete channel flows, and later becomes the Kamenishka River. Wastewater not collected at this location: no visible water inputs to channel between BG19003/04 and this location	42.22176	23.01516
BG19006	WW	Kamenik ash disposal site	Concrete channel that usually transports ash slurry from a conveyor belt to a pipe which deposits ash at the Kamenik ash disposal site. At time of sampling (11 <sup>th</sup> March) only water flowed through the channel, and the flow rate was lower than previously observed	42.236907	23.005676
BG19007	Solid, ash?	Kamenik ash disposal site	Solid material built up on sides of the concrete channel. Collected on 11 <sup>th</sup> March at same location as BG19006		
BG19008	Ash slurry	Kamenik ash disposal site	From same channel as BG19006, on a different day (13.03.2019), approx. 150m downstream of BG19006. Steady flow of slurry along the channel at this time.		
BG19009	RW	Razmetanitza River up -stream of Kamenishka	Approx. 10 Km downstream from the Bobov Dol CFPP, about 10 m upstream of confluence with the Kamenishka River (the continuation of the LEF concrete channel flow)	42.22327	23.05083
BG19010	Sed				

Table 1a: details of samples of river water (RW), wastewater (WW), river sediment (Sed) and ash collected in the vicinity of the Bobov Dol coal fired power plant (CFPP) in Golemo Selo, Bulgaria, including GPS coordinates of sample collection locations. \* - broken bottle, unable to analyse

Sample code	Type	Site	Sampling location	N degree (°)	E degree (°)
<b>March 2019</b>					
BG19014	RW	Razmetanitza River	200 m upstream of sampled discharge point of Black Lake ash storage pond, as BG18003	42.28962	23.04024
BG19015	RW	Razmetanitza River	200 m downstream of the sampled discharge point of Black Lake ash storage pond, as BG18001	42.275212	23.041309
BG19016	WW	Discharge pipe	1 of 2 official discharge points of the Black Lake ash storage pond to Razmetanitza River, as BG18005	42.280232	23.040712
BG19017	RW	Razmetanitza River	Location where an oily liquid was observed in November 2018 to leach from adjacent ground and enter the river via a channel, close to the discharge point of the Black Lake ash storage pond. Leaching was not observed in 2019. Sample collected from river adjacent to the channel	42.28429	23.03980
BG19018	Sed				
<b>May 2019</b>					
BG19019	RW	Razmetanitza River up	Approx 10 m upstream of confluence with the Kamenishka River (same as BG19009; BG19010)	42.22328	23.05086
BG19020	Sed	-stream of Kamenishka			
BG19021	RW	Razmetanitza River down	Approx. 20 m downstream of confluence with the Kamenishka River	42.22251	23.05244
BG19022	Sed	-stream of Kamenishka			
BG19023	RW	Kamenishka River	Approx. 40 m upstream of confluence with Razmetanitza River	42.22252	23.05005

Table 1a continued: details of samples of river water (RW), wastewater (WW), sediment (Sed) and ash collected in the vicinity of the Bobov Dol coal fired power plant (CFPP) in Giolemo Selo, Bulgaria, including GPS coordinates of sample collection locations. \* - broken bottle, unable to analyse

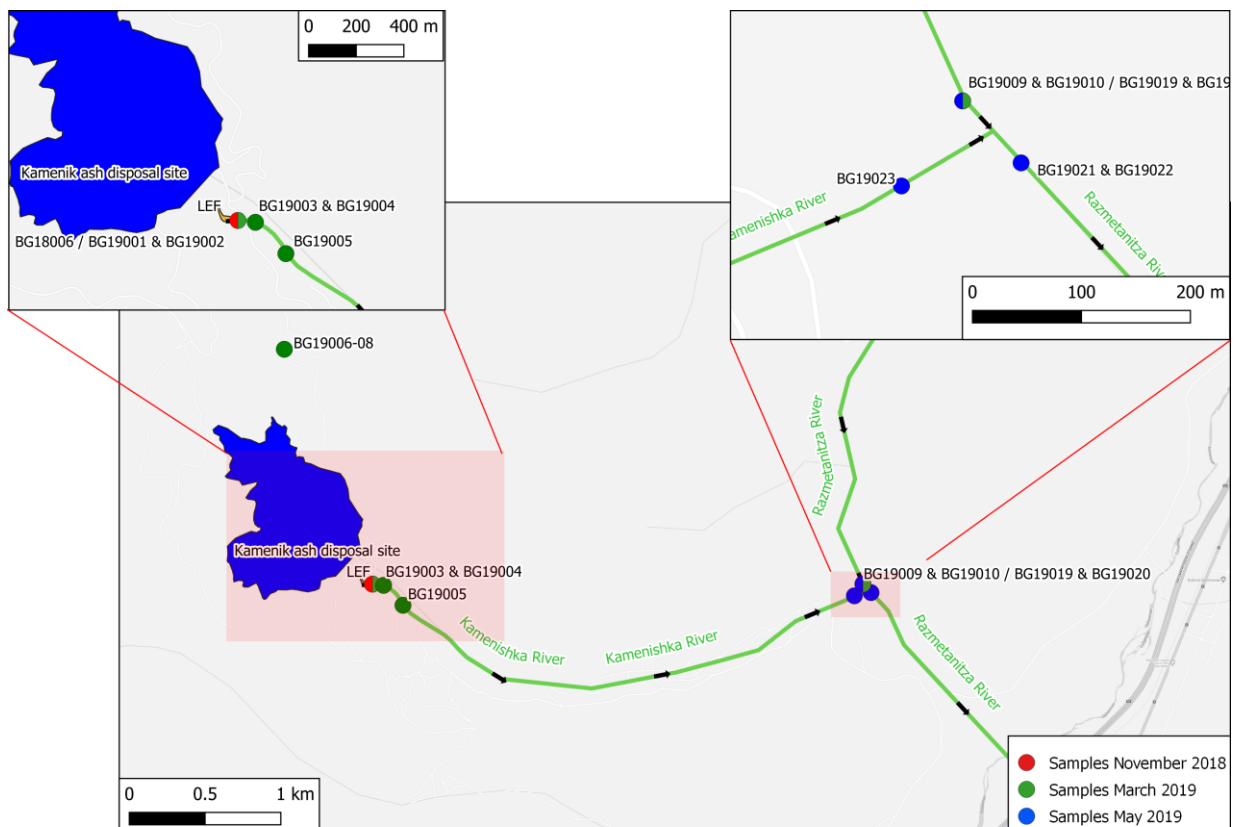
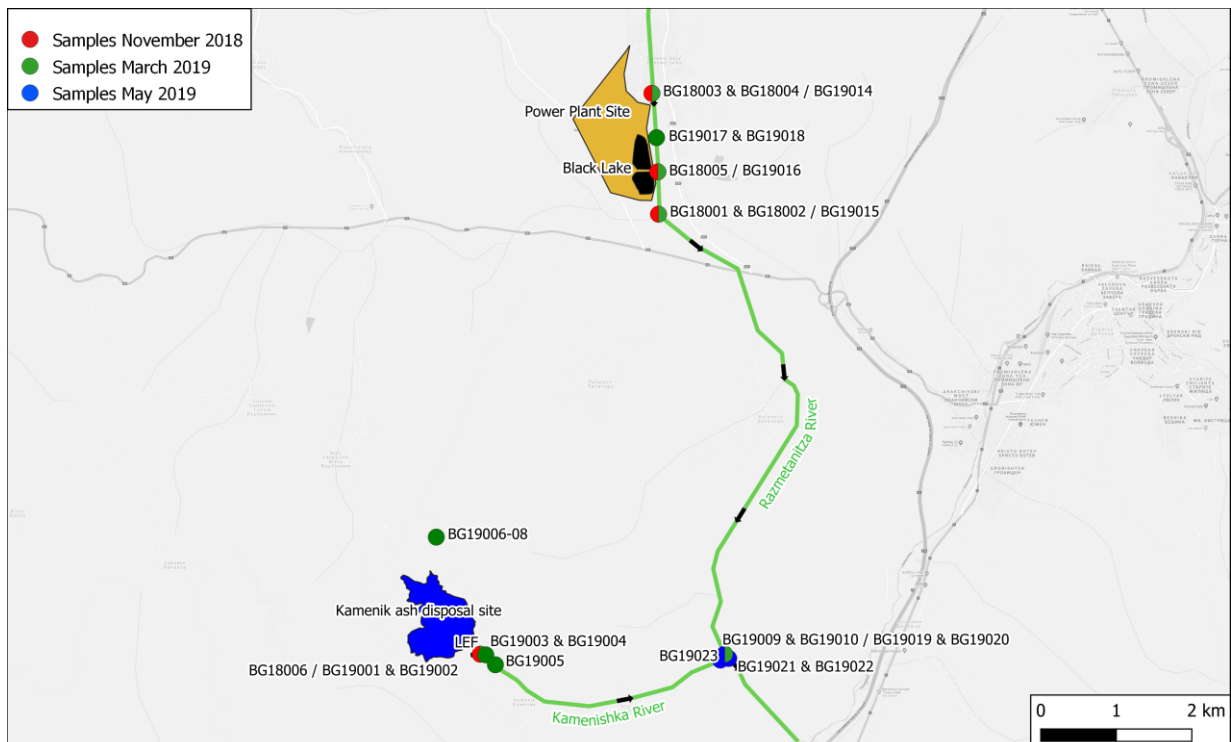


Figure 1. (a) Map of the Bobov Dol CFPP, the Black Lake and Kamenik ash storage sites, and the locations from which samples were collected, with (b) expanded sections in the vicinity of the LEF facility and river confluence

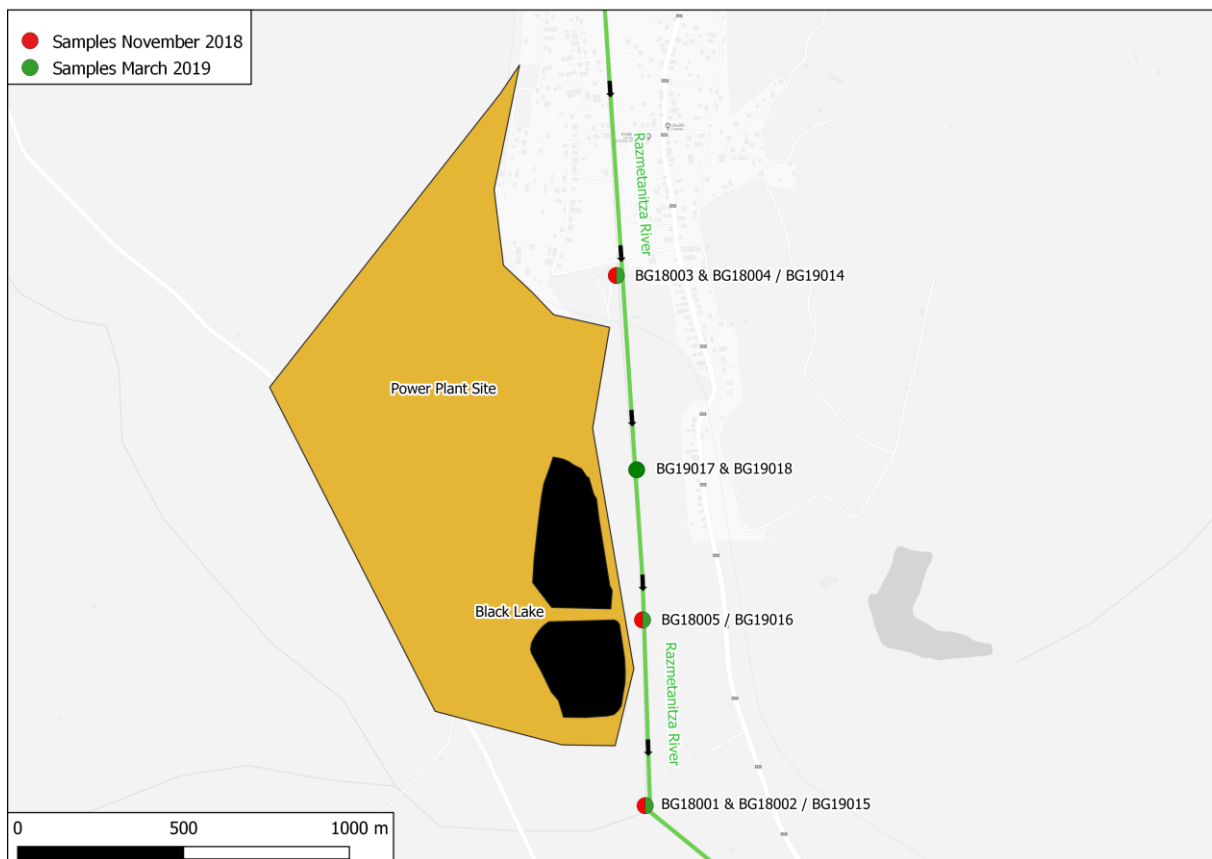


Figure 1. (c) Map of the Bobov Dol CFPP and the Black Lake ash storage site, including the locations from which samples were collected

At the Kamenik ash disposal site, a facility is located immediately below the dike of the ash storage area. A recent application document for a new operational permit for the Kamenik ash disposal site refers to a facility at this location as the "lower equalizer" (TPP Bobov Dol GmbH 2018). This document describes a process of collecting water from the Kamenik ash disposal site and transferring it to the lower equalizer facility. From there clarified water is transferred through a 12 km long gravity-fed pipeline (Regional Inspection of Environment and Water 2018) to a pumping station situated at the Black Lake site adjacent to the CFPP, from where it is reused in the industrial water cycle of the CFPP.

At the time of the sampling visits to the lower equalizer facility (LEF), what appeared to be wastewater was flowing into a water storage area which is not fully contained (Figure 2), and some of this wastewater was observed to be overflowing from the storage area into a concrete channel which is the origin of the Kamenishka River and which flows to the Razmetanitzka River.

In November 2018 a water sample (BG18006) was collected from the water overflowing from the LEF, at the point where it enters the concrete channel. In March 2019 another water sample was collected from the same location (BG19001), together with a sediment sample from below the water flow at this location (BG19002). A short distance downstream from the overflow sampling location, the concrete channel section of the River Kamenishka flows underground, below a road, before flowing through another small channel (Figure 3) and joining the Razmetanitzka River approximately 3.5 Km from the underground section, and approximately 10 Km downstream from the CFPP. In March 2019, a water sample (BG19003) and an associated sediment (BG19004) were collected from the channel



immediately after it re-emerges from under the road, together with a sediment (BG19005) from the channel further downstream.



*Figure 2. Uncontained water at the lower equalizer facility, and overflow of water from the storage area into a concrete channel*



*Figure 3. Concrete channel downstream of the lower equalizer facility as it re-emerges after flowing underneath the road, and small channel further downstream*

In March 2019, a sample of river water (BG19009) and another of sediment (BG19010) were collected from the Razmetanitza River immediately upstream of its confluence with the Kamenishka River. During the sampling visits the Kamenishka River flowed through a swampy area for a short distance prior to joining the Razmetanitza River, and at the confluence there was no visible water flow above

ground. This area was revisited in May 2019 and another set of river water (BG19019) and associated sediment (BG19020) samples were collected from the same location. On that occasion, a sample of river water (BG19023) was also collected from the Kamenishka River, approximately 40 m upstream of the same confluence, and before the Kamenishka flows through the swampy area. In addition, a further set of river water (BG19021) and associated sediment (BG19022) samples were collected from the two combined river water flows (still known as the Razmetanitza River), immediately downstream of their confluence.

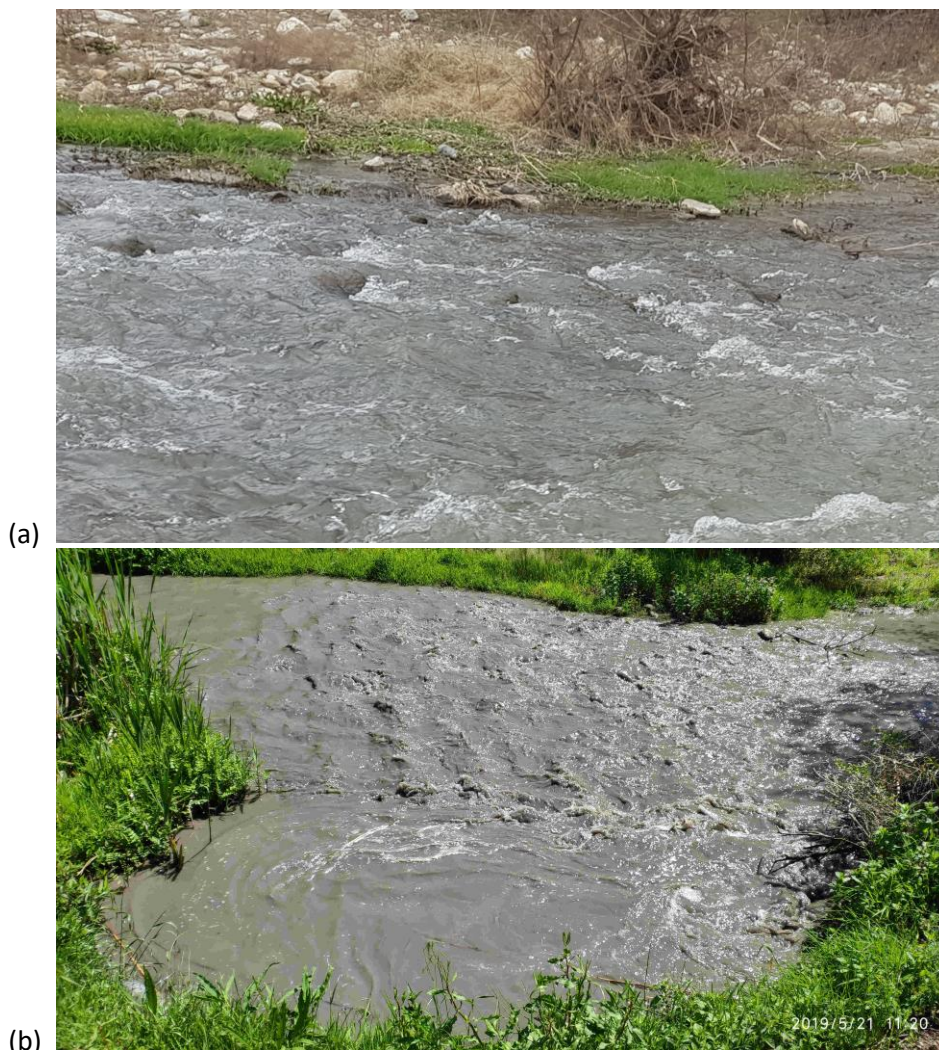
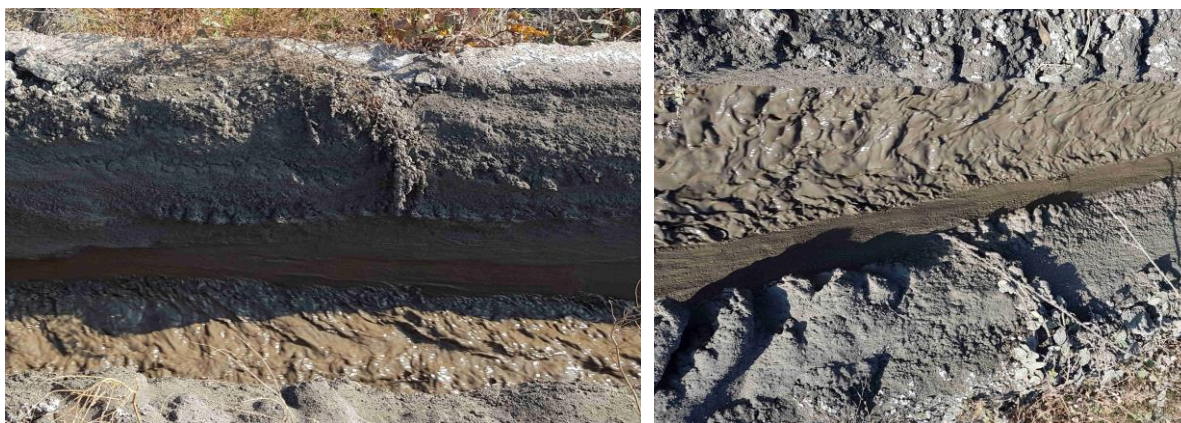


Figure 4. Razmetanitza River upstream of the confluence with the Kamenishka River; (a) March 2019, (b) May 2019

During the visit to the site in May 2019, the water flowing in the Razmetanitza River upstream of the confluence with the Kamenishka River was opaque and dark grey in colour, markedly different to the appearance in March when the river water was far more transparent and appeared to contain far less suspended solids (Figure 4). This was also observed to be the case at a location further upstream towards the CFPP, approximately 1.5 km below the discharges from the Black Lake ash storage site. The appearance in May would be consistent with the water carrying considerable quantities of coal ash, though this could not be verified at the time.

In light of the visibly different nature of the Razmetanitzka River water in May 2019, compared to March 2019, in addition to analysis of the whole, unfiltered, sample and of a filtered portion of each sample (BG19019 and BG19021), the suspended solids filtered out in the process were also separately analysed as a solid sample, to enable comparison with samples of ash collected in March.

In addition to samples collected from discharges and rivers, samples were collected in March 2019 from a concrete channel close to the Kamenik ash disposal site which is used to transport ash slurry from a conveyor belt to a pipe to the Kamenik ash disposal site. These samples were collected to enable comparison with other samples suspected to be impacted by ash arising from the CFPP, either directly or due to metals and metalloids leached from the ash. On 13th March a sample of ash slurry (BG19008) was collected directly from the channel. Two days earlier, only water was observed to flow through the channel, and the flow rate was noticeably lower than had been observed on other occasions. A sample of this water (BG19006) was collected at that time, together with a sample of solid material built up on the sides of the concrete channel (BG19007) (Figure 5).



*Figure 5. Solid material built up on the sides of the concrete channel used to transport ash slurry, close to the Kamenik ash disposal site*

## **Analytical methods**

Concentrations of metals and metalloids were determined for all samples by inductively coupled plasma mass spectrometry (ICP-MS) following acid digestion and using appropriate certified reference samples and laboratory reference samples.

For the first set of samples (BG18001-06), semi-volatile organic compounds (sVOCs) were also isolated from the water samples using solid phase extraction (SPE). Extracted compounds were subsequently identified as far as possible using gas chromatography/mass spectrometry (GC/MS) operated in simultaneous SCAN/SIM mode.

More detailed descriptions of the sample preparation and analytical procedures are presented in Appendix 1.

## **Results and Discussion**

The results for the samples are outlined below. For the water samples, the concentrations of metals and metalloids are reported in Tables 2 and 3, and the organic chemicals identified in samples from the

first set of samples are given in Table 6. Concentrations of metals and metalloids in the river sediment and solid waste samples are given in Tables 4 and 5.

Sample year	2018				March 2019									
	BG18003		BG18005		BG19014		BG19015		BG19016		BG19017		BG19006	
	Razmetanitza, upstream of discharge		Discharge from Black Lake		Razmetanitza, upstream of discharge		Razmetanitza, down of discharges		Discharge pipe		Razmetanitza, leachate point		ash slurry channel	
	F	W	F	W	F	W	F	W	F	W	F	W	F	W
Aluminium	<5	778	32	210	<5	598	141	3750	24	4175	<5	1650	66	37300
Antimony	<0.1	<0.1	<0.1	<0.1	0.1	0.3	0.8	0.9	0.1	0.3	0.1	0.2	0.3	1.1
Arsenic	1.9	2.3	0.7	0.7	1.6	2.0	8.7	12.1	1.9	4.0	1.5	2.9	10.7	24.9
Barium	39.1	46.4	24.3	28.3	33.3	44.6	45.7	87.4	23.0	63.1	33.0	53.3	45.7	703
Boron	76.8	81.0	13.8	13.8	52.6	59.0	173	197	13.2	20.0	54.9	62.4	42.7	99
Cadmium	<0.05	<0.05	<0.05	<0.05	<0.05	0.17	<0.05	0.06	<0.05	0.12	<0.05	0.12	<0.05	0.14
Calcium	8920	9140	4735	4850	7280	8260	38500	41300	4375	4930	7200	8220	5390	14800
Chromium total	<0.05	1.66	0.14	1.05	<0.1	1.5	1.1	5.2	0.3	5.3	0.1	3.2	0.7	32.3
Chromium (VI)	<20	-	<20	-	<50	-	<20	-	<20	-	<20	-	<20	-
Cobalt	0.06	0.26	0.05	0.12	<0.1	0.5	<0.1	0.9	<0.1	1.3	<0.1	0.8	<0.1	11.3
Copper	1.4	3.5	4.8	8.7	1.2	3.5	1.5	6.6	4.3	17.8	1.5	6.5	3.0	49.2
Gallium	<0.2	0.2	<0.2	<0.2	<0.2	0.3	0.9	2.1	<0.2	1.4	<0.2	0.6	0.3	11.6
Iron	9	531	37	258	10	514	7	2380	21	3550	9	1470	5	35300
Lead	<0.1	1.3	<0.1	1.1	0.6	1.2	0.1	2.9	0.4	4.3	0.2	4.0	0.2	11.7
Manganese	<0.2	71.6	<0.2	7.2	0.3	269	4.9	172	0.4	60.8	0.2	357	<0.2	357
Mercury	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Molybdenum	2.5	2.9	3.0	3.1	1.9	2.3	21.4	21.1	1.3	1.5	1.8	2.0	3.3	6.8
Nickel	1.6	2.6	0.5	1.2	1.7	2.9	1.2	6.1	0.9	6.5	1.8	4.4	1.2	49.7
Potassium	7150	7490	1890	1950	5250	6360	4650	6830	1915	2680	5770	6490	2300	7180
Rubidium	2.7	4.1	1.1	1.3	2.6	3.8	5.3	9.7	1.2	5.9	2.5	5.5	1.9	25.8
Strontium	818	825	169	172	574	585	614	650	130	148	570	583	186	412
Thallium	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.3
Uranium	4.41	4.37	1.13	1.12	3.75	3.76	1.81	2.18	1.21	1.62	3.49	3.74	1.34	6.81
Vanadium	0.81	1.98	1.42	1.78	0.7	2.1	42.9	55.5	2.7	13.1	0.8	4.3	14.0	116
Zinc	1.1	6.9	1.2	6.1	<2	13	<2	18	5	38	<2	24	<2	52
pH	-	7.7	-	8.2	-	6.7	-	7.5	-	7.5	-	6.8	-	7.6

Table 2. Concentrations of dissolved metals and metalloids in (F)iltered, and of total metal and metalloid concentrations in (W)hole, unfiltered, water samples (µg/l)

### Lower equalizer facility (LEF)

The sample of wastewater (BG18006) collected in November 2018 below the LEF, from the point at which it was seen to be flowing from a water storage area into the Kameniska River channel, had a very different composition to local surface water, as represented by river water from the Razmetanitza River collected upstream of the CFPP and Black Lake ash storage site (BG18003). The LEF wastewater contained far higher concentrations of many metals and metalloids in dissolved forms, especially molybdenum at almost 500 times higher, and gallium and rubidium at approximately 100 times higher. In addition, aluminium, arsenic, manganese, potassium and vanadium dissolved concentrations were at over 10 times the respective upstream river water concentrations, and those of boron, calcium, mercury and strontium were approximately 5 times their respective river water concentrations.

Though lower than most other metal/metalloids, the concentration of dissolved mercury in the wastewater (1.0 µg/l) was higher than environmental quality standards (EQS) for inland waters in the

EU (EU 2008), which includes a maximum allowable EQS of 0.07 µg/l (and an annual average EQS of 0.05 µg/l). Fly ash from the Bobov Dol CFPP is reported to contain traces of mercury, at around half the average concentration reported for coal fly ashes but in a relatively mobile form (Kostova *et al.* 2011).

Sample year	2018		March 2019						May 2019					
	BG18006		BG19001		BG19003		BG19009		BG19019		BG19021		BG19023	
Sample code	Overflow from LEF		Overflow from LEF		Downstream of LEF		Razmetanitza upstream of Kamenishka		Razmetanitza upstream of Kamenishka		Razmetanitza downstream of Kamenishka		Kamenishka	
	F	W	F	F	F	W	F	W	F	W	F	W	F	W
Aluminium	222	283	136	208	160	219	63	1210	124	216000	126	168000	32	2200
Antimony	0.4	0.4	0.6	0.5	0.5	0.5	0.9	0.9	2.6	8.3	2.7	6.7	0.4	0.6
Arsenic	27.8	28.4	29.5	29.5	29.5	29.4	10.6	13.1	42.0	321	43.1	282	23.6	24.5
Barium	49.0	51.0	44.4	48.2	46.3	50.6	62.1	80.3	74.6	1980	67.9	1670	67.3	84.8
Boron	345	337	298	326	304	334	239	252	312	587	277	614	321	327
Cadmium	0.12	0.15	0.13	0.15	0.13	0.17	<0.05	<0.05	0.10	3.02	<0.05	1.73	0.18	0.16
Calcium	41000	41400	41300	41400	43400	44600	29000	30000	64900	148000	56700	127000	46300	46950
Chromium total	<0.05	0.23	0.7	0.9	0.6	0.8	0.8	2.5	1.6	286	1.5	215	0.3	3.2
Chromium (VI)	<20	-	<20	-	<20	-	<20	-	<20	-	<20	-	<20	-
Cobalt	0.05	0.06	<0.1	<0.1	<0.1	<0.1	<0.1	0.5	<0.1	53.4	<0.1	44.0	<0.1	0.8
Copper	0.5	1.3	0.6	1.9	0.5	1.9	1.2	4.1	1.6	274	1.4	220	2.9	7.1
Gallium	17.5	17.6	15.5	15.9	13.5	13.9	0.6	1.1	1.1	67.4	1.1	55.5	7.6	9.8
Iron	<5	43	<5	<5	<5	7	12	890	6	141000	7	117000	<5	1695
Lead	0.2	0.6	0.3	0.5	0.2	0.7	0.4	2.0	0.2	139	0.1	119	0.4	1.8
Manganese	39.1	44.8	51.0	51.7	56.5	57.5	12.0	293	35.3	1680	30.8	1400	11.6	65.4
Mercury	1.0	1.1	1.1	1.1	1.0	1.0	<0.2	<0.2	0.2	2.0	0.3	1.7	0.5	0.5
Molybdenum	1170	1155	1070	1120	1020	1040	23.9	23.6	26.5	47.1	26.1	41.6	972	936
Nickel	0.4	1.1	<0.5	1.0	<0.5	1.7	1.0	3.4	1.2	322	1.1	261	0.8	3.7
Potassium	111000	114000	101000	104000	99300	101000	6250	7070	5970	37100	5970	30500	96150	96550
Rubidium	279	280	252	249	227	225	4.7	5.8	7.6	254	7.7	197	198	200
Strontium	3660	3685	2810	2850	2950	2990	823	813	955	2270	904	2010	3230	3250
Thallium	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	3.5	<0.1	2.9	<0.1	<0.1
Uranium	0.49	0.48	0.74	0.73	0.95	0.93	5.19	5.16	5.89	43.3	5.66	37.1	4.60	4.80
Vanadium	15.5	15.5	13.6	14.3	12.1	12.6	38.6	47.6	45.6	877	45.9	723	9.3	13.5
Zinc	0.6	3.1	<2	9	<2	8	4	12	<2	432	<2	350	<2	12
pH	-	-	-	6.9	-	6.9	-	6.8	-	7.5	-	7.8	-	-

Table 3. Concentrations of dissolved metals and metalloids in (F)iltered and of total metal and metalloid concentrations in (W)hole, unfiltered, water samples (µg/l)

The wastewater sample collected from the same location in March 2019 (BG19001) contained similar concentrations of metals and metalloids to those found in the 2018 sample (BG18006)

Wastewater (BG19003) collected from the concrete channel further downstream, immediately after the channel flows underground for a short distance below a road, also contained very similar concentrations of all metals/metalloids to those in BG19001. This indicates that the channel which re-emerges from underground is the same channel into which the LEF overflows, and that there are no significant additional inputs of water to the portion of this channel within the underground section.

For all three wastewater samples, the concentrations for most metals and metalloids in the whole (unfiltered) samples were only moderately higher than the respective dissolved concentrations, indicating that the majority of the metals and metalloids were predominantly present in dissolved forms.

The metals and metalloids found in higher concentrations in the LEF wastewater are elements known to leach from coal fly ash, though numerous other sources also exist (Kosson *et al.* 2009, Izquierdo & Querol 2012). Molybdenum and boron readily leach from coal fly ash, which is also a known source of gallium (Lu *et al.* 2017, Ruhl *et al.* 2014), though the amount and rate of leaching from the ash is dependent on the individual metal/metalloid, and can also vary considerable between fly ash from different types of coal (Kosson *et al.* 2009, Vassilev *et al.* 2010).

Sample year	2018		March 2019			
Sample code	BG18004	BG18002	BG19018	BG19002	BG19004	BG19005
Location	Razmetan- itza, upstream of discharges	Razmetan- itza, downstream of discharges	Razmetan- itza, leachate point	Overflow from LEF	Downstream of LEF	Further downstream of LEF
Aluminium	27150	29200	23400	11300	2350	6240
Antimony	<0.05	<0.05	0.08	0.08	<0.04	0.04
Arsenic	18.0	38.6	16.2	149	99.7	77.0
Barium	225	327	204	192	152	148
Boron	21.4	35.9	16.4	29.3	25.4	16.6
Cadmium	0.21	0.22	0.21	0.07	<0.02	0.04
Calcium	2035	23100	1420	41800	49600	32900
Chromium	31.1	35.4	31.3	9.02	1.52	14.3
Cobalt	9.5	7.9	9.41	2.30	0.37	2.05
Copper	28.6	39.7	35.1	5.3	1.5	5.3
Gallium	11.5	13.0	8.7	14.1	18.8	17.2
Iron	26400	28300	26700	6000	889	8510
Lead	22.0	16.1	23.4	4.48	0.93	3.03
Manganese	2015	1270	975	1260	651	620
Mercury	<0.1	0.2	<0.1	<0.1	<0.1	0.12
Molybdenum	0.7	1.1	1.89	4.00	4.43	3.61
Nickel	24.8	35.7	27.9	7.7	1.3	6.4
Potassium	4705	3780	2960	2220	544	1140
Rubidium	24.9	20.8	35.2	17.0	2.3	8.3
Strontium	65	207	90.9	1050	1170	666
Thallium	0.4	0.4	0.38	0.11	<0.04	0.05
Uranium	1.97	3.80	2.13	2.17	2.81	2.15
Vanadium	42.2	83.5	41.0	18.7	16.4	23.2
Zinc	90	64	108	16	4	12

Table 4: Concentrations of metals and metalloids (mg/kg dry weight) in sediment samples

Though over 20 years old, previously reported data for waste streams from the Bobov Dol CFPP also showed relatively high concentrations of many of these metals and metalloids in pond wastewater, including arsenic, boron, manganese, vanadium and calcium at even higher concentrations than those in the LEF wastewater samples from this study (Vassileu & Vassileua 1997). Molybdenum, strontium and potassium concentrations were also reported to be high in pond water relative to surface waters at that time, though concentrations found in LEF wastewater in our study (BG18006 and BG19001) were even higher. It is not known whether the pond water from that study was collected from any of the locations from which samples were collected for the current study.

Sample year	March 2019			May 2019				Literature		
Sample code	BG19007	BG19008	BG19010	BG19020	BG19022	BG19019 SS	BG19021 SS	-		
Type	ash	ash	sed	sed	sed	SS	SS	ash		
Location	side of slurry channel	Ash slurry	Razmetan - itza, upstream of confluence	Razmetan - itza, upstream of confluence	Razmetan - itza, downstream of confluence	Razmetan - tza, upstream of confluence	Razmetan - tza, downstream of confluence	fly ash, typical <sup>(a)</sup>	Lagoon ash, Bobov Dol <sup>(b)</sup>	fly ash, Bobov Dol <sup>(b)</sup>
Aluminium	47150	44500	20000	29600	41400	42600	41500	70000-140000	-	-
Antimony	0.09	0.18	0.05	<0.1	<0.1	<0.1	<0.1	BDL-16	3.3	3.4
Arsenic	50.2	67.8	18.4	17.2	20.8	38.2	36.0	22-260	45	56
Barium	460	441	198	220	343	337	334	380-5100	650	875
Boron	97.3	117	11.7	24.0	48.0	56.4	55.8	120-1000	-	-
Cadmium	0.27	0.36	0.15	0.14	0.15	0.39	0.23	BDL-3.7	-	-
Calcium	12150	10600	1880	4320	10400	10300	10300	7,400 – 150000	-	-
Chromium	70.2	72.8	29.1	46.0	59.4	65.8	63.6	27-300	110	118
Cobalt	18.1	17.6	9.13	10.3	12.8	12.4	12.2	-	24	25
Copper	39.5	40.5	21.8	28.1	49.6	54.7	52.8	62-220	45	55
Gallium	16.5	16.9	8.7	10.4	12.8	14.2	13.7	-	20	25
Iron	43000	38900	24700	26100	35800	32200	31800	34000-130000	-	-
Lead	20.6	25.0	19.4	14.4	13.1	16.4	16.4	21-230	35	40
Manganese	225	187	570	420	362	291	282	91-700	-	-
Mercury	<0.1	<0.1	<0.1	0.1	0.1	0.4	0.2	0.01-0.51	-	0.035-0.055 <sup>(c)</sup>
Molybdenum	6.56	8.09	0.76	0.92	2.52	3.73	3.52	9.0 – 60	6	7
Nickel	43.7	47.9	27.1	37.8	64.9	71.9	75.4	47-230	90	110
Potassium	4805	4430	2480	4455	5460	5400	5330	6200 – 21000	-	-
Rubidium	51.5	47.8	33.0	35.7	38.6	40.0	38.7	-	175	146
Strontium	368	335	73.1	116	242	234	230	270-3100	400	430
Thallium	0.59	0.70	0.35	0.43	0.44	0.56	0.53	BDL-45	<1	<1
Uranium	5.61	5.69	1.79	3.20	6.14	6.81	6.81	BDL-19	14	10
Vanadium	160	165	45.9	80.1	122	146	143	BDL-360	196	244
Zinc	81	94	69	54.3	59.5	73.7	67.8	63-680	130	155

Table 5: Concentrations of metals and metalloids (mg/kg dry weight) in ash, sediment (sed), and river water suspended solids (SS) samples. (a) Typical range of concentrations in fly ash (EPRI 2009); (b) reported concentrations in lagooned ash at the Bobov Dol facility (Vassileva et al. 1997); data from Kostova et al. 2011

Results for analysis of fly ash and lagooned ash from the Bobov Dol CFPP were also reported in the 1997 study, confirming relatively high concentrations of arsenic, vanadium and rubidium for these type of materials. In contrast, however, concentrations of molybdenum and gallium, which were particularly elevated in LEF wastewater samples in our study, were not notably high in Bobov Dol CFPP ashes as reported in 1997. As noted above, however, the mix of coals from different sources used at the Bobov Dol CFPP can vary over time (Kostova et al. 2011, TPP Bobov Dol GmbH 2018).

In addition to the metals and metalloids in the LEF wastewater, one organic chemical was identified in the wastewater sample from November 2018 (BG18006), namely diethylene glycol diethyl ether (Table

6). This chemical is used in organic synthesis, as a solvent, and as a non-ionic surfactant in multicomponent cleaning compositions (Lin *et al.* 2003). It is not known whether this chemical is used as part of treatment operations at the site. Its origin requires further investigation.

Sample Code	BG18003	BG18005	BG18006
Number of sVOCs isolated	7	8	3
Number of sVOCs identified to > 90%	1	5	1
<b>POLYCYCLIC AROMATIC HYDROCARBONS (PAHs)</b>			
Pyrene		1*	
<b>PHTHALATE ESTERS</b>			
Diethyl phthalate (DEP)	1*	1*	
Dibutyl phthalate (DBP)		1*	
Diisobutyl phthalate (DiBP)		1*	
Bis(2-ethylhexyl) phthalate (DEHP)		1*	
<b>OTHERS</b>			
Diethylene glycol diethyl ether			1

Table 6: Summary of results of organic compounds analysis in water samples BG18003, BG18005 & BG18006 determined by GC/MS. \* - signifies compounds that were detected at trace levels, using Selective Ion Monitoring (SIM) mode.

Sediment collected from the location at which wastewater overflows from the LEF water storage area into the concrete channel at the head of the Kamenishka River (BG19002) contained a number of metals/metalloids at elevated concentrations, higher than those in both the sediment from the Razmetanitza River upstream of the Black Lake ash storage discharges (BG18004) and that from the same river immediately upstream of its confluence with the Kamenishka river (BG19010). The concentrations of calcium and strontium were particularly elevated over those in the Razmetanitza River sediments, as were those of arsenic, molybdenum and to a lesser extent boron and manganese. Although the wastewater samples from this location (BG18006 & BG19001) contained relatively high concentrations of additional metals and metalloids, these were not found at elevated levels in the associated sediment (BG19002).

Two samples of solid material collected from locations further downstream in the same channel contained high proportions of stones mixed with finer sediments, stones that were removed from the sediments prior to analysis. The sediment portion of one of those samples (BG19004), collected after the channel emerges from its underground section, contained similar or lower concentrations of all metals and metalloids compared to that collected directly below the LEF outflow (BG19002), with many being markedly lower, by a factor of between 4 to 7 times. Similarly, the sediment portion of the second downstream sample (BG19005), collected even further downstream, also contained all metals and metalloids at concentrations similar to or lower than the sediment from the LEF overflow (BG19002), though the differences were smaller than for BG19004.

Although differences exist in the composition of sediment along the Kamenishka River, all sediment samples showed elevated concentrations of metals and metalloids present in wastewaters discharged from the LEF compared to sediment from the Razmetanitza River upstream of the CFPP and ash disposal sites

A sample of what appeared to be ash slurry flowing along a concrete channel on 13<sup>th</sup> March 2019 (BG19008) contained concentrations of most metals/metalloids within the typical ranges reported for



coal fly ash, though generally towards the lower end of reported concentration ranges, and in some cases below the typically range, including for boron, molybdenum and potassium (EPRI 2009).

The content of metals and metalloids in coal fly ash can vary widely between different sources, as shown in the ranges given in Table 5 (EPRI 2009, Lecomte *et al.* 2017). In comparison with values reported for fly ash and lagooned ash from the Bobov Dol facility in the early 1990s (Vassileva *et al.* 1997), the ash from the slurry sample contained similar, or slightly lower, concentrations of most metals and metalloids, with values 60 - 111% of the respective previously reported value for lagooned ash from Bobov Dol CFPP. Concentrations of some were somewhat lower, however, with values for nickel, rubidium, and uranium between 29-49% of the literature values, and that of antimony below 5%. The mix of coals used in the early 1990s at the Bobov Dol CFPP may have been somewhat different to that used currently (Kostova *et al.* 2011, TPP Bobov Dol GmbH 2018). Although mercury was below the detection limit for this study (0.1 mg/kg), fly ash from this facility has been reported to contain mercury at between 0.035-0.054 mg/kg, around half the average concentration in coal fly ashes (Kostova *et al.* 2011). In addition to its content of metals and metalloids, the ash slurry was notably alkaline, with a pH of 12.7.

A sample of solid material (BG19007) collected from a build-up on the sides of the ash slurry channel two days earlier (11<sup>th</sup> March 2019) visually appeared to be ash, though on that day, the water itself flowing through the channel appeared to contain almost no suspended solids (BG19006). The chemical composition of this solid material was very similar to that of the suspended solids part of the ash slurry (BG19008) collected from the channel two days later, indicating that the solid material on the sides of the channel was dried ash accumulated from previous periodic slurry flows.

The water sample (BG19006) collected from the channel on 11<sup>th</sup> March was somewhat similar in composition to local surface water, as represented by water from the Razmetanitza River upstream of the CFPP (BG19014). Though it nonetheless did contain somewhat higher concentrations of dissolved aluminium, arsenic and vanadium, and lower concentrations of dissolved strontium & uranium, than local surface water. In addition, the channel water on that day was close to neutral (pH 7.6), far less alkaline than the ash slurry encountered 2 days later (BG19008, pH=12.7). These results suggest that water flowing in the channel on the 11<sup>th</sup> March was not, or only minimally, impacted by dissolved metals and metalloids arising from ashes.

### **Wastewater discharge from Black Lake ash storage pond**

The water samples collected from the Razmetanitza River upstream of the official discharge points of Black Lake ash storage pond in November 2018 (BG18003) and March 2019 (BG19014), contained concentrations of metals and metalloids within the ranges typical for uncontaminated surface waters (Flem *et al.* 2018).

The wastewater samples collected from the uppermost official discharge point of the Black Lake ash storage pond (BG18005 in 2018 and BG19016 in March 2019) also had a similar composition to the upstream river water samples, though with slightly higher dissolved concentrations of a few metals. The total concentrations in the whole (unfiltered) discharge collected in 2019 (BG19016) were notably higher than the respective values in the 2018 sample (BG18005), especially for aluminium and iron, though this probably indicates only that the 2019 discharge sample contained a higher amount of

suspended material than that collected in 2018, with a composition more indicative of soil or sediment than of solid waste derived from coal combustion. These results indicate that the upstream discharge was not having a notable impact on water quality in the Razmetanitza River at these times.

Unfortunately, it was not possible to sample the 2<sup>nd</sup> discharge point located approximately 150 m further downstream, and investigation of the impact of the 2<sup>nd</sup> discharge on the river water in November 2018, in terms of the analysed metals, was not possible due to breakage of the river water sample (BG18001) collected downstream of both discharges.

In addition to metals and metalloids, one organic chemical was identified in the water sample collected in November 2018 from the Razmetanitza River upstream of the Black lake discharges (BG18003), diethyl phthalate (DEP), though this was present at only a trace level (Table 6). This chemical was also present in the discharged wastewater from the Black Lake from the same set of samples (BG18005), together with three other phthalates, again all present at only trace levels. Due to their widespread use, phthalates are ubiquitous in the environment and the presence of these phthalates at trace levels in the discharged wastewater sample does not necessarily indicate that their presence is due to their use at this site.

The wastewater (BG18005) also contained a polycyclic aromatic hydrocarbon (PAH), namely pyrene, though again this was present at only a trace level. PAHs can arise from a variety of sources including natural sources such as forest fires, and anthropogenic activities including from the combustion of fossil fuels. It is feasible that the trace of pyrene arose from wastes generated by the coal power plant. The detection of only one PAH representative, however, does not strongly indicate that its presence in the wastewater sample was due to the coal fired power plant operations because usually a group of several PAHs is formed during combustion of coal (ATSDR 1995). As for phthalates, PAHs are widespread in the environment, and as such the trace level of pyrene in the wastewater could have originated from sources unconnected to the coal power plant.

In 2019, an additional set of river water (BG19017) and associated sediment (BG19018) samples were collected from the Razmetanitza River where leachate had been observed entering the river during the previous 2018 visit. This location is situated between the upstream river sampling point (BG19014) and the discharge from the Black Lake ash storage pond (BG19016). The river water (BG19017) had a very similar composition and pH to the river water collected upstream of all known discharges on the same day (BG19014), indicating no noticeable input of dissolved metals/metalloids to the river at this time via the channel through which the flow of a leachate had previously been observed. River sediment collected from the same location (BG19018) contained metal/metalloid concentrations which were similar to, or lower than, those measured in sediment collected further upstream in the Razmetanitza River in 2018 (BG18004).

In contrast, the river water sample (BG19015) collected from the Razmetanitza River downstream of both Black Lake discharge points in March 2019 contained many dissolved metals/metalloids at higher concentrations compared to river water collected at both the leachate point (BG19017) and that collected further upstream (BG19014) on the same day. Concentrations of molybdenum, manganese and vanadium, as well as aluminium, arsenic, boron and calcium, were particularly elevated. This pattern of elevation was similar to that found in the LEF wastewater samples (BG18006 & BG19001). These results suggest that wastes from the Bobov Dol CFPP and/or its associated Black Lake ash storage site are impacting on the water quality of the Razmetanitza River, even if it has not been possible to investigate and sample all possible discharge points from the facility to the river. Given

that the concentrations of metals were far higher in river water collected below the 2<sup>nd</sup> of the two identified discharge points from the Black Lake, and that waters collected both from the 1<sup>st</sup> discharge point and further upstream on the same day did not show such contamination, it seems likely that the 2<sup>nd</sup> discharge point is the source of such contamination, though unfortunately it was not possible to sample that discharge and confirm this inference directly.

In addition, concentrations of some metals/metalloids in the sediment sample collected at the same location in 2018 (BG18002) were higher than those in the upstream river sediments (BG18004 and BG19018), most notably for calcium and strontium, as well arsenic, boron, uranium and vanadium. These results suggest accumulation of metals/metalloids in the river sediment due to ongoing releases over times *via* the 2<sup>nd</sup>, downstream, discharge point and also possibly *via* the upstream discharge point at other times.

### **Confluence of Razmetanitza and Kamenishka Rivers**

The water sample (BG19009) collected from the Razmetanitza River in March 2019 immediately upstream of the confluence with the Kamenishka River generally contained dissolved metal/metalloid concentrations which were similar to, or slightly lower than, those found in water sample BG19015 (described above), collected just below the two Black Lake discharge points. A second sample collected from the same location in May 2019 (BG19019) contained similar or slightly higher concentrations. Leaching of metals and metalloids from what appeared to be substantial amounts of ash suspended in the river water at the time could account for the somewhat higher concentrations of some dissolved metals in the river water in May 2019.

Similarly, and as may be expected, a sample of water (BG19023) collected from the Kamenishka River just before it joins the Razmetanitza River contained a similar composition of key metals and metalloids to the water samples collected upstream within this channel, closer to the LEF (BG18006, BG19001, BG19003).

The water sample from the two combined river water flows (still known as the Razmetanitza River), collected immediately downstream of their confluence (BG19021), had a very similar composition to that of the Razmetanitza River water collected upstream of the confluence on the same day (BG19019), despite the mixing of the two rivers, probably as a result of the much higher flow-rates in the Razmetanitza compared to the Kamenishka. Nonetheless, the presence of high metal concentrations in the Kamenishka River confirms that wastewaters flowing from the ash disposal site and overflowing from the LEF are a significant additional source of environmental contamination to the river system.

Incidentally, both whole (unfiltered) river water samples collected from the Razmetanitza River in May (BG19019 & BG19021) contained far higher concentrations of all metals and metalloids compared to the water sample collected in March 2019 (BG19009), as expected from the far higher loading of suspended solids in the river water in May.

Samples of the suspended solids filtered out from both the May 2019 water samples (BG19019SS and BG19021SS) contained a very similar composition to each other in terms of metal and metalloid concentrations.

Comparison of these suspended solids samples with sediment collected from the Razmetanitzka River in March 2019, when the river water was far less turbid, indicates that the suspended solids in May 2019 were very different in composition to that of the river sediment, most notably for boron, calcium, molybdenum, strontium, uranium and vanadium. This pattern of higher metal content matches that found in other samples associated with the ash storage site and releases from it, and to that of ash collected from the channel used to transport ash as a slurry to the Kamenik disposal site (BG19008).

A comparison of the concentrations of key metals and metalloids between the suspended solids from one river water sample (BG19019-SS), sediment from the same part of the Razmetanitzka River in March 2019 when the river water was not loaded with suspended solids (BG19010), and ash from the slurry channel (BG19008) is given in Figure 6

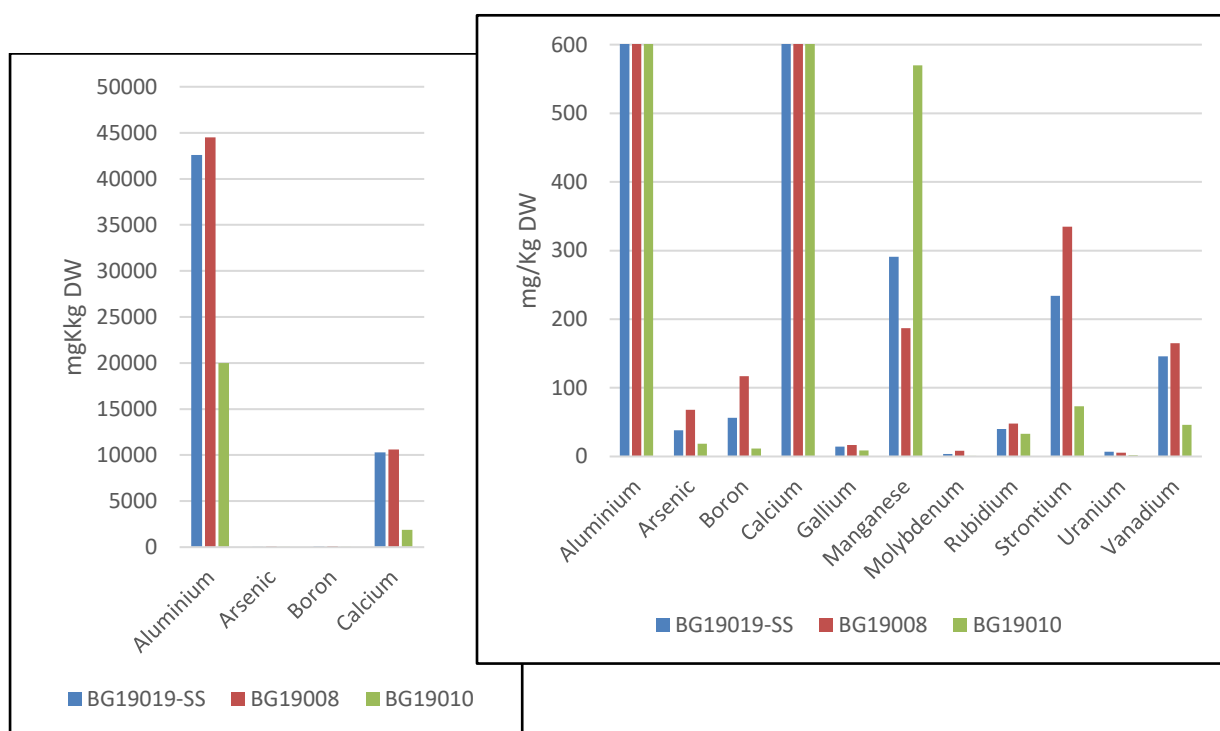


Figure 6. Concentrations (mg/Kg dry weight) of key metals and metalloids in suspended solids from one river water sample (BG19019-SS), sediment from the same part of the Razmetanitzka River when the river was not loaded with suspended solids (BG19010), and ash from the slurry channel (BG19008), including an inset graph with expanded y-axis to show those metals and metalloids present at lower concentrations

Sediment collected in March 2019 (BG19010) and May 2019 (BG19020) from the Razmetanitzka River immediately upstream of the confluence had similar compositions to those of sediment samples collected upstream of the Black Lake discharges during the previous visit (BG18004) and in the most upstream sample collected in March 2019 (BG19018).

The slight to moderate elevations in sediment concentrations in the samples from May 2019 may be due to some deposition of suspended solids being carried in the river at that time (BG19019SS & BG19021SS).

Sediment collected in May 2019 from the Razmetanitzka River downstream of the confluence (BG19022) did show higher levels of some metals compared to sediment collected from the same river upstream of the confluence (BG19020), though whether this is a measurable influence from the Kamenishka River

discharge or arises from higher deposition of the suspended solids carried by the Razmetanitza River itself at this location cannot be determined without further investigations.

## Conclusions

This study has demonstrated that waste waters containing a range of metals and metalloids associated with coal fly ashes at elevated concentrations are routinely released to the local environment from sites where ashes generated by the Bobov Dol CFPP are stored. These include wastewaters released to a tributary to the Razmetanitza River from the lower equalizer facility (LEF) which is situated immediately below the dike of the Kamenik ash disposal site. The composition of these wastewaters was consistent during the sampling periods from November 2018 to May 2019. Accumulation of some metals and metalloids present in the wastewaters was evident in sediments from the Kamenishka River, through which the LEF wastewater flows.

In addition, the study findings suggest that waste streams from the Bobov Dol CFPP and/or its associated Black Lake ash storage site are impacting the quality of river water and sediments of the Razmetanitza River further upstream, most likely due to releases from the more downstream of the two official discharge points of the Black Lake ash storage site.

Furthermore, this study found evidence which indicated the release of substantial quantities of ash into the Razmetanitza River from the vicinity of the CFPP and Black Lake ash storage site during May 2019, the composition of which was consistent with ash collected from a channel through which it is transported to the Kamenik ash disposal site.

Until measures are put in place to prevent releases of contaminated wastewaters and solid wastes from the Bobov Dol CFPP and its ash storage sites, there will remain ongoing impacts on the quality of local surface water environments. Such measures should include an investigation into the apparent release of substantial quantities of ash into the Razmetanitza River during May 2019, and whether similar releases have occurred at other times, with the aim of preventing any such release in the future.

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## **Appendix 1: Details of methodologies**

### **Analysis for metals**

#### **Preparation**

For water samples, 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, to obtain total metal concentrations. 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.

For sediment samples, a representative portion of each sample was air dried to constant weight, homogenised and then ground to a powder using a pestle and mortar. Approximately 0.25 g of the ground sample was accurately weighed and digested with 0.5 ml concentrated hydrochloric acid and 5.0 ml concentrated nitric acid, firstly overnight at room temperature, then using microwave-assisted digestion with a CEM MARS Xpress system with temperature ramping: heating to 180°C over 20 minutes, held at 180°C for 20 minutes, heating to 220°C over 20 minutes, held at 220°C for 20 minutes. Following cooling, each digest solution was filtered and made up to 25 ml with deionised water. Prior to analysis, each digest solution was diluted 1:4 using 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 (1, 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). Any sample exceeding the calibration range was diluted accordingly, in duplicate, and re-analysed.

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 and 200 µg/l respectively. Any sample exceeding the calibration range was diluted accordingly, in duplicate, and re-analysed.

#### **Quality control**

For water samples, one filtered sample and one whole sample were prepared in duplicate from each batch for ICP analysis 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.

For solid samples, one sample from each batch was prepared for ICP analysis in duplicate and analysed to verify method reproducibility, along with a blank sample. To check the method efficiency, three certified reference material (CRM) samples were prepared in an identical manner, namely LGC6187, leachable metals in river sediment certified by the Laboratory of the Government Chemist, UK and GBW07311 stream sediment and GBW07406 soil, 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 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.

For chromium (VI) analysis, one sample from each batch was prepared in duplicate, together with a blank sample and a quality control solution of 140 µg/l. Analysis of all samples spiked with the addition of 20 µg/l was also carried out to ensure no interference in the method due to other components of the sample.

### **pH determination for water and slurry samples**

The pH of each sample was determined using a Hanna Instruments HI98129 pH meter calibrated using pH 4.01, pH 7.01 and pH 10.01 Hanna buffer solutions. The pH meter and electrode was rinsed with deionised water between samples.

### **Analysis for extractable organic compounds**

#### **Preparation**

20 µg of deuterated naphthalene was added as an Internal Standard (IS) to each portion of sample that was subject to extraction. 500ml of each sample was extracted using solid phase extraction technique with Dionex AutoTrace workstation, eluting with ethyl acetate followed by a mixture of pentane and toluene (95:5). Obtained extracts were concentrated to a volume of 3ml with a stream of clean nitrogen and cleaned up prior to analysis.

For the clean-up stage, each extract was shaken with 3ml isopropyl alcohol and 3ml TBA-reagent (mixture of 3% tetrabutylammonium hydrogen sulphate and 20% sodium sulphite in deionised water) and left to stand until the aqueous and organic phases had separated. The pentane phase was collected and eluted through a Florisil column, using a 95:5 pentane:toluene mixed eluent, and the cleaned extract was concentrated to a final volume of 1ml. 20 µg of bromonaphthalene was added to each extract as a second IS prior to GC-MS analysis.

#### **Analysis**

##### GC/MS analysis

For the total organic compounds screening, samples were analysed using an Agilent 6890 Series II GC with Restek Rxi-17Sil column (30m, 0.25mm ID, 0.25 µm film thickness) linked to an Agilent 5975B MSD operated in EI mode and interfaced with an Agilent Enhanced Chem Station data system. The GC oven temperature program employed was as follows: an initial temperature of 70°C, held for 2 minutes, raised to 160°C at 20°C/min, then to 220°C at 5°C/min, held for 2 minutes, then to 300°C at 15°C/min, held for 8min, and finally raised to 330°C at 50°C/min, held for 26min. The carrier gas was helium,



supplied initially at 1ml/min for 10 min and then raised to 5ml/min for the rest of the run. Extracts (1 ul) were injected automatically by means of an Agilent 6890 Autosampler in pulsed splitless mode (pulse pressure 33 psig, pulse time 1 min). MSD was operating in both total ion monitoring mode (TIC) and selective ion monitoring mode (SIM). Identification of compounds detected in TIC mode was carried out by matching spectra against both the Wiley W10N11 and Pesticides Libraries, using expert judgment as necessary in order to avoid misidentifications. Identification of compounds detected in SIM mode was performed by matching compound's mass-spectra and its retention time (RT) against those obtained for a range of known organic pollutants (see Table A1) at the same analytical conditions as was used for samples. The analysis in SIM mode enabled detection of compounds present in samples at trace levels.

#	RT, min	Compound Name	Ions monitored	Group #
1	4.778	Benzene, 1,3-dichloro-	146, 148, 111	1
2	4.952	Benzene, 1,4-dichloro-	146, 148, 111	
3	5.246	Benzene, chloromethyl-	91, 125.9, 127.9	
4	5.288	Benzene, 1,2-dichloro-	146, 148, 111	
5	5.374	Ethane, hexachloro-	117, 119, 201	2
6	6.054	Benzene, 1,3,5-trichloro-	180, 182, 184	3
7	6.540	Butadiene, hexachloro-	225, 227, 223	
8	6.679	Benzene, 1,2,4-trichloro-	180, 182, 184	4
9	7.068	Naphthalene	128, 129, 127	
10	7.136	Benzene, 1,2,3-trichloro-	180, 182, 184	
11	7.189	Benzene, trichloromethyl-	159, 161, 89	5
12	7.718	Hexachlorocyclopentadiene	237, 239, 235	
13	8.124	Benzene, 1,2,3,5-tetrachloro-	216, 214, 218	6
14	8.168	Benzene, 1,2,4,5-tetrachloro-	216, 214, 218	
15	8.460	Acenaphthene	153, 154, 152	
16	8.921	Benzene, 1,2,3,4-tetrachloro-	216, 214, 218	
17	9.200	Naphthalene, 1-chloro-	162, 127, 164	7
18	10.456	Acenaphthylene	152, 151, 153	
19	10.502	Dimethyl phthalate	163, 164, 77	8
20	10.534	Benzene, pentachloro-	250, 252, 215	
21	10.720	4-tert-octyl phenol	135.1, 136.1, 134	9
22	11.280	Diethyl phthalate	149, 150, 177	10
23	11.296	Fluorene	166, 165, 163	
24	11.32 - 11.93	Nonylphenol, isomeric	135, 121, 149, 107, 163.1	11
25	12.025	Benzene, hexachloro-	284, 286, 282	12
26	13.542	Di-iso-butyl phthalate	149, 150, 223	
27	13.713	Phenanthrene	178, 176, 179	13
28	13.81	Anthracene	178, 176, 179	
29	13.899	gamma-HCH	181, 183, 219	
30	13.921	Heptachlor	272, 274, 270	14
31	14.983	Di-n-butyl phthalate	149, 150, 223	
32	15.681	Bis(4-methyl-2-pentyl) phthalate isom. 1	149, 167, 150	

33	15.743	Bis(4-methyl-2-pentyl) phthalate isom. 2	149, 167, 150	15
34	16.549	Heptachlor epoxide	353, 355, 351	
35	16.907	Bis(2-methoxyethyl) phthalate	59, 58, 149	16
36	17.182	cis-Chlordane	373, 375, 377	
37	17.537	Di-n-pentyl phthalate	149, 150, 237	17
38	17.58	trans-Chlordane	373, 375, 377	
39	17.693	Endosulfan I	241, 195, 239	18
40	18.041	Fluoranthene	202, 200, 101	
41	18.202	Bis(2-ethoxyethyl) phthalate	72, 45, 149	19
42	18.615	p,p'-DDE	246, 248, 318	
43	18.715	Dieldrin	79, 81, 263	20
44	19.213	Pyrene	202, 200, 101	
45	19.997	Endrin	81, 263, 265	21
46	20.466	Di-n-hexyl phthalate	149, 150, 251	
47	21.036	p,p'-DDD	235, 237, 165	22
48	21.059	BDE-28	246, 248, 405.8	
49	21.175	Endosulfan II	195, 237, 241	23
50	21.929	p,p'-DDT	235, 237, 165	
51	22.126	Endrin aldehyde	250, 345, 347	24
52	22.389	Butyl benzyl phthalate	149, 91, 150	
53	22.580	Endosulfan sulfate	272, 274, 387	25
54	22.649	Bis(2-ethylhexyl)phthalate	149, 167, 150	
55	22.998	Bis(2-butoxyethyl) phthalate	149, 85, 193	26
56	23.747	Bis(2-ethylhexyl) terephthalate	70, 149, 167	
57	23.863	Dicyclohexyl phthalate	149, 167, 150	27
58	23.976	Benz[a]Anthracene	228, 226, 114	
59	24.047	Endrin ketone	317, 315, 319	28
60	24.178	BDE-47	325.9, 485.7, 483.7	
61	24.181	Chrysene	228, 226, 113	29
62	24.335	Di-n-octyl phthalate	149, 150, 279	
63	25.454	Di-n-nonyl phthalate	149, 150, 167	30
64	25.662	BDE-99	403.8, 405.8, 563.7	
65	26.039	BDE-100	405.8, 403.8, 563.7	31
66	26.375	Benzo[b]Fluoranthene	252, 250, 253	
67	26.432	Benzo[k]Fluoranthene	252, 250, 253	32
68	27.300	BDE-154	483.7, 481.6, 643.6	
69	27.312	Benzo[a]Pyrene	252, 250, 126	33
70	28.000	BDE-153	483.7, 481.6, 643.6	
71	30.719	Indeno[123-cd]pyrene	276, 277	34
72	30.761	Dibenzo[a,h]anthracene	278, 279	
73	31.706	BDE-183	563.6, 561.6, 721.6	33
74	32.128	Benzo[ghi]Perylene	276, 277	
75	36.763	BDE-197	320.7, 321.7, 641.5	34

76	43.781	BDE-207	359.6, 360.6, 721.5	
77	57.984	BDE-209	399.6, 398.5, 799.3	35

Table A1. The list of standard compounds and their GC/MS parameters employed during SIM analysis.

### **Quality control**

A number of extraction and solvent blanks were also analysed to ensure the detection of any possible contamination resulting from sample handling in the laboratory. Any background contaminants detected in blanks are subtracted from the chromatograms obtained for the samples before mass spectra are interpreted.

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

## Appendix 2: Detailed semi-volatile organic (sVOCs) analytical screening data

Note: Compounds detected in SIM mode were present at trace levels only

### **BG18003**

**Number of compounds isolated: 7**

**Compounds identified to better than 90%:**

<b>CAS#</b>	<b>Name</b>	
000084-66-2	diethyl phthalate	(SIM)

### **BG18005**

**Number of compounds isolated: 8**

**Compounds identified to better than 90%:**

<b>CAS#</b>	<b>Name</b>	
000084-66-2	diethyl phthalate	(SIM)
000117-81-7	bis(2-ethylhexyl) phthalate	(SIM)
000084-74-2	dibutyl phthalate	(SIM)
000084-69-5	diisobutyl phthalate	(SIM)
000129-00-0	Pyrene	(SIM)

### **BG18006**

**Number of compounds isolated: 3**

**Compounds identified to better than 90%:**

<b>CAS#</b>	<b>Name</b>
000112-36-7	Ethane, 1,1'-oxybis[2-ethoxy- (synonym: diethylene glycol diethyl ether)