Greenpeace Research Laboratories Analytical Results 2018-07

Organic contaminants and metals in wastewater and sediment samples associated with brown coal mine in Slovakia

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Introduction

Currently, there is an intensive ongoing debate in Slovakia about future of the Horná Nitra region and of the coal mining industry in this region. The region is considered to be the most important for coal mining in Slovakia. Several scientific/official sources claim that coal mining in this region is one of the significant polluters of surface waters in the area of the River Nitra drainage basin (Stanovič et al. 2017, SHU 2002, SVP 2010). To investigate this further, Greenpeace Slovakia collected waters discharged from the brown coal mine Hornonitrianske bane Prievidza, a.s. (HBP), located in Horná Nitra/Upper Nitra, Lehota pod Vtáčnikom district, Slovakia.

At each of 5 investigated locations, one sample of the water being discharged from the mine territory via pipe or concrete channel, as well as two sediment samples from the receiving watercourses (Krivý potok (Buchlová), Hlinky, Kristovček, Ťakov, and Handlovka), making up 15 samples in total (10 sediment samples and 5 wastewater samples), were collected by Greenpeace Slovakia and received for analysis at the Greenpeace Research Laboratories on 12.10.2018. According to documentation supplied, all samples were collected on 09.10.2018. Details of the samples received are provided in Table 1a, together with GPS coordinates for the sample collection location in Table 1b.

For purpose of the current study, all waters discharging from the territory of the HBP mine are referred to as wastewaters. However, it is important to note that it was not possible to find out whether these waters contain only wastewater or a mixture of wastewater and natural surface water.

Materials and methods

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

Semi-volatile organic compounds (sVOCs) were isolated from sediment samples using Accelerated Solvent Extraction (ASE) system with a mixture of pentane and acetone. For wastewater samples, sVOCs were isolated using solid phase extraction (SPE), eluting with ethyl acetate, pentane and toluene. 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.

Location / Receiving stream	Sample code	Type	Sampling location description
Krivý Potok	SK18001	ww	Point of ww discharge from the fenced mine territory into Krivý Potok stream
	SK18002	sed	Below the point of ww discharge from the fenced mine territory
	SK18003	sed	Krivý Potok stream, downstream of sample SK18002
Hlinky	SK18004	ww	Point of ww discharge via concrete pipe
	SK18005	sed	Point of ww discharge via concrete pipe, directly from the pipe
	SK18006	sed	Hlinky stream, downstream of sample SK18005
Kristovček	SK18007	ww	Point of ww discharge via concrete pipe, directly from the pipe
	SK18008	sed	Kristovček stream downstream of ww discharge via underground pipe into the stream
	SK18009	sed	Kristovček stream, downstream of sample SK18008
Ťakov	SK18010	ww	Point of ww discharge via concrete pipe, directly from the pipe
	SK18011	sed	Ťakov, downstream of ww discharge via concrete pipe
	SK18012	sed	Ťakov downstream of sample SK180011
Handlovka	SK18013	ww	Point of ww discharge via channel (not direct discharge point) that joins Handlovka stream
	SK18014	sed	Handlovka stream, downstream of ww discharge
	SK18015	sed	Handlovka stream, downstream of sample SK180014

Table 1a: details of samples collected in association with the brown coal mine HBP, a.s., that were received and analysed at the Greenpeace Research Laboratories. ww – wastewater, sed – sediment

Sample code	N degree (º)	E degree (º)
SK18001	48.697	18.623
SK18002	48.697	18.623
SK18003	48.697	18.621
SK18004	48.735	18.640
SK18005	48.735	18.640
SK18006	48.736	18.639
SK18007	48.717	18.646
SK18008	48.718	18.647
SK18009	48.718	18.646
SK18010	48.730	18.573
SK18011	48.730	18.573
SK18012	48.731	18.572
SK18013	48.722	18.756
SK18014	48.723	18.756
SK18015	48.724	18.756

Table 1b: GPS coordinates of sample collection locations.

GRL-AR-2018-07

Results and Discussion

The results for the samples are outlined in the following sections. The concentrations of metals and metalloids in wastewater samples are reported in Table 2. The organic chemicals identified in individual wastewater and sediment samples are summarised in Tables 3a and 3b.

Detailed lists of organic chemicals that were identified in each sample using GC-MS analysis are provided in Appendix 2.

3.1 Metals

Sample code	Concentration, µg/l									
	SK18001		SK18004		SK18007		SK18010		SK18013	
Sample status	Filtered	Whole	Filtered	Whole	Filtered	Whole	Filtered	Whole	Filtered	Whole
Aluminium	10	12	23	33	23	32	49	880	3	81
Antimony	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	0.4	0.9	<0.2	<0.2
Arsenic	8.4	15.6	5.8	8.7	2.3	4.3	72.2	134	10.4	12.5
Barium	98.0	104	60.7	68.4	52.4	58.2	102	127	60.1	66.7
Beryllium	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Boron	121	124	66.6	68.0	51.2	51.6	358	360	267	288
Cadmium	<0.02	<0.02	<0.02	0.04	<0.02	<0.02	0.05	0.16	<0.02	<0.02
Chromium	<0.1	0.4	<0.1	0.3	<0.1	0.2	<0.1	1.7	<0.1	0.3
Chromium (VI)	<20	n/a	<20	n/a	<20	n/a	<20	n/a	<20	n/a
Cobalt	0.24	0.29	0.30	0.51	0.28	0.43	0.36	0.75	0.07	0.13
Copper	<0.2	0.6	<0.2	0.9	<0.2	0.5	<0.2	4.4	<0.2	2.4
Lead	<0.2	<0.2	<0.2	0.3	<0.2	0.5	<0.2	4.9	<0.2	0.8
Iron	100	831	51	703	26	383	43	1815	11	377
Manganese	210	240	124	208	133	182	256	356	9.83	34.6
Mercury	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Nickel	0.2	0.9	0.4	1.1	0.4	1.3	0.7	1.6	0.6	0.8
Selenium	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Strontium	281	290	236	243	185	195	1050	1090	1710	1780
Vanadium	0.22	0.35	1.21	1.53	0.01	0.04	1.68	3.53	0.23	0.39
Zinc	2	3	7	8	6	8	8	18	13	15

Table 2: Concentrations of metals and metalloids (µg/l) in filtered and whole wastewater samples. n/a – not analysed

Concentrations of dissolved arsenic and manganese were generally higher in the water samples compared to concentrations of these metals typical for uncontaminated surface water. Four of the samples had concentrations of dissolved arsenic in the range 2.3-10.4 µg/l, with sample SK18010 discharged to the Ťakov stream containing a notably higher concentration of 72.2 µg/l. Concentrations of arsenic in surface water can vary with location but are typically below 5 µg/l, and often below 1 µg/l (ATSDR 2007, Salomen & Forstner 1984). Other than one sample (SK18013, Handlovka stream), the concentrations of dissolved manganese were in the range 124-256 µg/l, notably higher than levels typically reported for uncontaminated surface waters, which are generally below 10 µg/l (ATSDR 2012, Salomen & Forstner 1984).

The arsenic content of coal can vary considerably between different coal sources, though some lignite and brown coals can contain relatively high arsenic content (Yudovich & Ketris 2005). In addition, the forms of arsenic present in coal, which can affect how readily arsenic leaches from the coal into the surrounding environment, can also vary depending on the source of coal (Yudovich & Ketris 2005, Kanduč et al. 2018)

For two samples, SK18010 (water discharged to the Ťakov stream) and SK18013 (water discharged to the Handlovka stream), the concentrations of dissolved boron and dissolved strontium were somewhat higher than the other samples, at 267-358 µg/l (boron) and 1045-1710 (strontium), and also somewhat higher than those typically found in uncontaminated surface waters. Concentrations of boron in uncontaminated surface waters are generally below 100 µg/l, though can vary greatly with local geology, while those of strontium are generally below 300-500 µg/l (ATSDR 2004, 2010, Marchina et al. 2018). Leaching from coal fly ash is a known source of boron and strontium to the environment (Ruhl et al. 2014), though in the case of these mines sites, the origins of these elements are unclear.

For other metals and metalloids analysed, the dissolved concentrations in the samples indicate that the waters were not notably contaminated with these metals/metalloids, with little sign of elevation in concentrations above typical background concentrations for uncontaminated surface freshwaters

In most case, the metal and metalloid concentrations for the whole (unfiltered) sample were 1-2 times the respective dissolved concentrations, indicating that the quantities of these elements associated with suspended matter in the water were similar to those present in dissolved forms. In all water samples, far higher concentrations of iron were found in the whole samples compared to the filtered samples. This was also the case for aluminium in two of the water samples (SK18010 and SK18013).

3.2 Organic contaminants

3.2.1 Semi-volatile organic compounds (sVOCs, determined by GC-MS)

Tables 3a & 3b present summary of the organic compounds reliably identified in samples; more detailed information for individual samples is presented in Appendix 2.

In general, lower numbers of organic compounds could be isolated from wastewater samples (range: 1 – 5 compounds) in comparison to sediments (range: 2 – 97 compounds), with the exception of sediment sample SK18005 from which only 2 organic compounds were isolated. The highest number of organic compounds was isolated from sediment sample SK18006 (97 compounds). The percentage of the organic compounds present that could be reliably identified varied from sample to sample, in the range from only 30% (sample SK18006) to 100%, as was the case for 7 samples, including 5 wastewaters and 2 sediments. In some cases, therefore, the identity of the majority of the organic compounds isolated could not be reliably determined, even through application of advanced environmental forensic screening techniques.

Those organic compounds that could be identified were represented by several classes of toxic chemicals, with polycyclic aromatic hydrocarbons (PAHs) being the most dominant; for example, sample SK18006 contained 18 representatives of PAHs and their derivatives, which accounted for 62% of all reliably identified compounds in this sample. The other samples containing high percentages of reliably identified PAHs were sediment samples SK18003 (78%) and SK18009 (56%). In is important to note,

though, that PAHs in some samples were detected at only trace levels; for example, in sediment samples SK18002 and SK18008, and, for a majority of PAHs, in SK18012 and SK18014. Concerning wastewater samples, only two samples (SK18004 & SK18010) contained PAHs (including fluoranthene and pyrene), and again detected only at trace levels.

Sample Code	SK18001	SK18002	SK18003	SK18004	SK18005	SK18006	SK18007	SK18008
Sample type	ww	sed	sed	ww	sed	sed	ww	sed
Number of sVOCs isolated	2	36	26	3	2	97	3	9
Number of sVOCs identified to > 90%	2	13	14	3	2	29	3	9
Percentage of sVOCs identified to > 90%, (%)	100	36	54	100	100	30	100	100
PAHs & DERIVATIVES								
Benz[a]anthracene						1		
Benzo[a]pyrene			1			1		1*
Benzo[k]fluoranthene			1			1		1*
Benzo[b]fluoranthene			1			1		1*
Benzo[ghi]perylene			1*			1		1*
Chrysene & derivatives			2			3		1*
Dibenzo[a,h]anthracene			1*					1*
Fluoranthene		1*	1	1*	1*	1		1*
9H-Fluorene & derivatives						2		
Indeno[1,2,3-cd]pyrene						1		
Naphthalene & derivatives		1*	1			1		1*
Phenanthrene & derivatives			1			3		
Pyrene & derivatives		1*	1	1*	1*	2		1*
PHTHALATE ESTERS								
1,2-Benzenedicarboxylic acid, diethyl ester (DEP)	1		1*	1			1	
1,2-Benzenedicarboxylic acid, dimethyl ester (DMP)			1				1	
1,2-Benzenedicarboxylic acid, dibutyl ester (DBP)			1*					
1,2-Benzenedicarboxylic acid, diisobutyl ester (DiBP)							1	
1,2-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester (DEHP)						1		
OTHER GROUPS								
Alkylated benzenes		6				1		
Aliphatic hydrocarbons		4				4		
Terpenoids						1		
Miscellaneous compounds	1		1			4		

Table 3a: Summary of results of organic compounds analysis in samples SK18001-SK18008 determined by GC/MS. * - signifies compounds that were detected at trace levels only using Selective Ion Monitoring (SIM) mode.

Therefore, the wider range of PAHs detected in sediment samples in comparison to wastewater samples may suggest historical contamination of sediments at these locations that is not related to the wastewater discharged at the time of the sampling. However, PAHs might be expected to accumulate to higher levels in the sediments from relatively low concentrations in the water particularly near the sediment interface (Bedlles et al. 2017). In the same time, PAHs can arise in sediments from a variety of sources including both natural sources such as forest fires and volcanic eruptions and due to anthropogenic activities (e.g., incomplete combustion of fossil fuels), among others. While confirmation of their presence in the sediments does not provide in itself firm evidence of the sources of

contamination, it does indicate the need for more detailed quantitative analysis to characterise that contamination and to determine possible sources. Such investigations are important as some PAHs exhibit carcinogenic, genotoxic and mutagenic properties.

Phthalate esters, chemicals that broadly used in a range of industrial applications including as plasticisers or softeners in plastics, were frequently detected in samples in the current study. Some phthalate esters are known or suspected endocrine disruptors. Phthalates where identified in all 5 wastewater samples and in two sediment samples, SK18006 and SK18003, though in the latter at trace levels only. DEP was identified in 6 samples (SK18001, SK18003, SK18004, SK18007, SK18010, and SK18013), DMP - in 3 samples (SK18003, SK18007, and SK18010), while DBP, DiBP, and DEHP were identified in one sample (SK18003, SK18007, and SK18006, respectively).

Sample Code	SK18009	SK18010	SK18011	SK18012	SK18013	SK18014	SK18015
Sample type	sed	ww	sed	sed	ww	sed	sed
Number of sVOCs isolated	34	5	18	21	1	31	17
Number of sVOCs identified to > 90%	25	5	10	14	1	18	9
Percentage of sVOCs identified to > 90%, (%)	74	100	56	67	100	58	53
PAHs & DERIVATIVES							
Anthracene	1						
Benz[a]anthracene	1		1	1*			
Benzo[a]pyrene	1		1	1*			
Benzo[k]fluoranthene	1		1	1*			
Benzo[b]fluoranthene	1		1	1*			
Benzo[ghi]perylene				1*		1*	
Chrysene & derivatives	2		1	1*			
Dibenzo[a,h]anthracene						1*	
Fluoranthene	1	1*	1	1		1	1
9H-Fluorene & derivatives						1*	1*
Indeno[1,2,3-cd]pyrene				1*		1*	
Naphthalene & derivatives	1					1	1,1*
Phenanthrene & derivatives	4		1	1		3	1
Pyrene & derivatives	1	1*	1	1		1	1*
PHTHALATE ESTERS							
1,2-Benzenedicarboxylic acid, diethyl ester		1			1		
1,2-Benzenedicarboxylic acid, dimethyl ester		1					
1,2-Benzenedicarboxylic acid, diisobutyl ester		1					
OTHER GROUPS							
Alkylated benzenes	1			1		1	
Aliphatic hydrocarbons	2					1	1
Terpenoids	5		2			3	
Steroids				2			
Miscellaneous compounds	3			1		3	2

Table 3b: Summary of results of organic compounds analysis in samples SK18009-SK18015 determined by GC/MS. * - signifies compounds that were detected at trace levels only using Selective Ion Monitoring (SIM) mode.

As phthalates are only physically bound to plastics, they can be easily released into environment during their manufacture, use, and disposal. Hence, they have become ubiquitous environmental

contaminants arising in the environment from multiple sources. Therefore, it is unclear what the sources of these contaminants in sediments were because those phthalates that were detected in the wastewater samples are, in most cases, different from those found in the corresponding sediments.

Conclusion

Concentrations of several metals/metalloids including dissolved arsenic, manganese, boron and strontium were higher in one or more wastewater samples compared to concentrations of these metals typical for uncontaminated surface waters. The reasons for elevated concentrations of boron and strontium in wastewaters is unknown and should be further investigated. A limited number of organic compounds were isolated from wastewater samples, with phthalate esters the most frequently detected compounds. Sediment samples contained higher number of organic compounds than corresponding wastewaters, with PAHs being the predominant contaminants. However, while the results of qualitative organic analysis confirm the presence of PAHs, they do not indicate high levels of contamination by PAHs. The origins of the phthalates and PAHs found in samples in the current study are not known but deserve investigation.

References

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Appendix 1: Details of methodologies

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.

Sediment sample extraction: approximately 10 g of each sample (wet weight) was extracted employing an Accelerated Solvent Extraction (ASE) technique, using a Dionex ASE-350, with a mixture of pentane and acetone in a ratio of 3:1, and at a temperature of $100^{o}C$. Obtained extracts were concentrated to a volume of 3ml with a stream of clean nitrogen and cleaned up prior to analysis.

Wastewater sample 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 $70^{0}C$, held for 2 minutes, raised to $160^{0}C$ at $20^{0}C/min$, then to $220^{0}C$ at $5^{0}C/min$, held for 2 minutes, then to $300^{0}C$ at $15^{0}C/min$, held for 8min, and finally raised to $330^{0}C$ at $50^{0}C/min$, 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 it's 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	
2	4.952	Benzene, 1,4-dichloro-	146, 148, 111	1
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	Hexachlorcyclopentadiene	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	
62	24.335	Di-n-octyl phthalate	149, 150, 279	29
63	25.454	Di-n-nonyl phthalate	149, 150, 167	
64	25.662	BDE-99	403.8, 405.8, 563.7	
65	26.039	BDE-100	405.8, 403.8, 563.7	
66	26.375	Benzo[b]Fluoranthene	252, 250, 253	30
67	26.432	Benzo[k]Fluoranthene	252, 250, 253	
68	27.300	BDE-154	483.7, 481.6, 643.6	31
69	27.312	Benzo[a]Pyrene	252, 250, 126	
70	28.000	BDE-153	483.7, 481.6, 643.6	
71	30.719	Indeno[123-cd]pyrene	276, 277	32
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.

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 (1, 2, 5, 20 µg/l respectively) were used for instrument calibration. Analysis employed in-line addition of an internal standard mix at 100 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 filtered 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 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 whole and one filtered sample were 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.

For chromium (VI) analysis, one sample 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 50 µg/l was also carried out to ensure no interference in the method due to other components of the sample.

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

SK18001, wastewater

Number of compounds isolated: **2**
Compounds identified to better than 90%:

CAS#	Name	
000084-66-2	1,2-Benzenedicarboxylic acid, diethyl ester	
004813-57-4	2-Propenoic acid, octadecyl ester	

SK18002, sediment

Number of compounds isolated: **36**
Compounds identified to better than 90%:

CAS#	Name	
007206-21-5	(5E)-5-Octadecene	
000629-73-2	1-Hexadecene	
035507-09-6	7-Hexadecene, (Z)-	
004537-15-9	Benzene, (1-butylheptyl)-	
002400-00-2	Benzene, (1-ethyldecyl)-	
004536-88-3	Benzene, (1-methyldecyl)-	
002719-61-1	Benzene, (1-methylundecyl)-	
002719-64-4	Benzene, (1-propylnonyl)-	
004536-86-1	Benzene, (1-propyloctyl)-	
000206-44-0	Fluoranthene	(SIM)
000091-20-3	Naphthalene	(SIM)
000129-00-0	Pyrene	(SIM)
000629-50-5	Tridecane	

SK18003, sediment

Number of compounds isolated: **26**
Compounds identified to better than 90%:

CAS#	Name	
000084-74-2	1,2-Benzenedicarboxylic acid, dibutyl ester	(SIM)
000131-11-3	1,2-Benzenedicarboxylic acid, dimethyl ester	
000084-66-2	1,2-Benzenedicarboxylic acid, diethyl ester	(SIM)
000050-32-8	Benzo[a]pyrene	
000207-08-9	Benzo[k]fluoranthene	
000205-99-2	Benzo[b]fluoranthene	
000191-24-2	Benzo[ghi]perylene	(SIM)
000218-01-9	Chrysene	
000000-00-0	Chrysene 3,3,7-trimethyl-1,2,3,4-	
000053-70-3	Dibenzo[a,h]anthracene	(SIM)
000206-44-0	Fluoranthene	
000091-20-3	Naphthalene	
007390-81-0	Oxirane, hexadecyl-	
000085-01-8	Phenanthrene	(SIM)
000129-00-0	Pyrene	

GRL-AR-2018-07

SK18004, wastewater
Number of compounds isolated: **3**
Compounds identified to better than 90%:
CAS#	Name	
000084-66-2	1,2-Benzenedicarboxylic acid, diethyl ester	
000206-44-0	Fluoranthene	(SIM)
000129-00-0	Pyrene	(SIM)

SK18005, sediment
Number of compounds isolated: **2**
Compounds identified to better than 90%:
CAS#	Name	
000206-44-0	Fluoranthene	(SIM)
000129-00-0	Pyrene	(SIM)

SK18006, sediment
Number of compounds isolated: **97**
Compounds identified to better than 90%:
CAS#	Name
000117-81-7	1,2-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester
000112-55-0	1-Dodecanethiol
013567-54-9	1H-3a,7-Methanoazulene, octahydro-
053584-60-4	1H-Cyclopenta[a]chrysene, 3-ethyl-5a,5b,8,8,11a,13b-hexamethylicosahydro-
074685-33-9	3-Eicosene, (E)-
006051-98-5	7H-benzo[c]fluoren-7-one
000514-62-5	Abieta-9(11),8(14),12-trien-12-ol
016982-00-6	Benzene, 1-methyl-4-(1,2,2-trimethylcyclopentyl)-
000056-55-3	Benz[a]anthracene
000050-32-8	Benzo[a]pyrene
000205-99-2	Benzo[b]fluoranthene
000243-42-5	Benzo[b]naphtho[2,3-d]furan
000191-24-2	Benzo[ghi]perylene
000207-08-9	Benzo[k]fluoranthene
000218-01-9	Chrysene
000000-00-0	Chrysene, 3,3,7-trimethyl-1,2,3,4-tetrahydro-
000297-03-0	Cyclotetracosane
054482-31-4	d-Homoandrostane
000206-44-0	Fluoranthene
000086-73-7	9H-Fluorene
000629-94-7	Heneicosane
000544-76-3	Hexadecane
000193-39-5	Indeno[1,2,3-cd]pyrene
000483-78-3	Naphthalene, 1,6-dimethyl-4-(1-methylethyl)-
088399-25-1	Phenanthrene, 8-ethyl-1,2,3,4,4a,9,10,10a-octahydro-1,1,4a,7-tetramethyl-
000129-00-0	Pyrene
002381-21-7	Pyrene, 1-methyl-
000483-65-8	Retene
027530-79-6	Simonellite

GRL-AR-2018-07

SK18007, wastewater
Number of compounds isolated: **3**
Compounds identified to better than 90%:

CAS#	Name
000131-11-3	1,2-Benzenedicarboxylic acid, dimethyl ester
000084-66-2	1,2-Benzenedicarboxylic acid, diethyl ester
000084-69-5	1,2-Benzenedicarboxylic acid, diisobutyl ester

SK18008, sediment
Number of compounds isolated: **9**
Compounds identified to better than 90%:

CAS#	Name	
000050-32-8	Benzo[a]pyrene	(SIM)
000207-08-9	Benzo[k]fluoranthene	(SIM)
000205-99-2	Benzo[b]fluoranthene	(SIM)
000191-24-2	Benzo[ghi]perylene	(SIM)
000218-01-9	Chrysene	(SIM)
000053-70-3	Dibenzo[a,h]anthracene	(SIM)
000206-44-0	Fluoranthene	(SIM)
000091-20-3	Naphthalene	(SIM)
000129-00-0	Pyrene	(SIM)

SK18009, sediment
Number of compounds isolated: **34**
Compounds identified to better than 90%:

CAS#	Name
014811-95-1	1,19-Eicosadiene
000000-00-0	Ethanone, 1-(1,8-dimethyltetracyclo[6.6.2.0(2,7).0(9,14)]hexadeca-2,4,6,9,11,13,15-heptaen-15-yl)-
000469-61-4	1H-3a,7-Methanoazulene, 2,3,4,7,8,8a-hexahydro-3,6,8,8-tetramethyl-
013567-54-9	1H-3a,7-Methanoazulene, octahydro-3,6,8,8-tetramethyl-
001135-66-6	2H-2,4a-Methanonaphthalene, 1,3,4,5,6,7-hexahydro-1,1,5,5-tetramethyl-
000514-62-5	Abieta-9(11),8(14),12-trien-12-ol
000120-12-7	Anthracene
016982-00-6	Benzene, 1-methyl-4-(1,2,2-trimethylcyclopentyl)-
000050-32-8	Benzo[a]pyrene
000056-55-3	Benz[a]anthracene
000205-99-2	Benzo[b]fluoranthene
000207-08-9	Benzo[k]fluoranthene
000218-01-9	Chrysene
000000-00-0	Chrysene, 3,3,7-Trimethyl-1,2,3,4-tetrahydro-
000206-44-0	Fluoranthene
000630-01-3	Hexacosane
000483-78-3	Naphthalene, 1,6-dimethyl-4-(1-methylethyl)-
000630-02-4	Octacosane
067860-04-2	Oxirane, heptadecyl-
007390-81-0	Oxirane, hexadecyl-

GRL-AR-2018-07

000085-01-8	Phenanthrene
019407-28-4	Phenanthrene, 1,2,3,4,4a,9,10,10a-
000000-00-0	Phenanthrene, 1,1,4a- trimethyl-7-(1-methylethyl)-perhydro-
000129-00-0	Pyrene
027530-79-6	Simonellite

SK18010, wastewater

Number of compounds isolated: 5
Compounds identified to better than 90%:

CAS#	Name	
000131-11-3	1,2-Benzenedicarboxylic acid, dimethyl ester	
000084-66-2	1,2-Benzenedicarboxylic acid, diethyl ester	
000084-69-5	1,2-Benzenedicarboxylic acid, diisobutyl ester	
000206-44-0	Fluoranthene	SIM
000129-00-0	Pyrene	SIM

SK18011, sediment

Number of compounds isolated: 18
Compounds identified to better than 90%:

CAS#	Name
074685-29-3	(9E)-9-Icosene
082053-48-3	1-Naphthaleneethanol, decahydro-2-hydroxy-5,8a-dimethyl-
036728-72-0	28-nor-17.beta.(h)-Hopane
040071-70-3	Cholestane, (5.alpha.,14.beta.)-
000050-32-8	Benzo[a]pyrene
000205-99-2	Benzo[b]fluoranthene
000207-08-9	Benzo[k]fluoranthene
000056-55-3	Benz[a]anthracene
000218-01-9	Chrysene
000206-44-0	Fluoranthene
000129-00-0	Pyrene
027530-79-6	Simonellite

SK18012, sediment

Number of compounds isolated: 21
Compounds identified to better than 90%:

CAS#	Name	
016982-00-6	Benzene, 1-methyl-4-(1,2,2-trimethylcyclopentyl)-	
000056-55-3	Benz[a]anthracene	(SIM)
000191-24-2	Benzo[ghi]perylene	(SIM)
000050-32-8	Benzo[a]pyrene	(SIM)
000207-08-9	Benzo[k]fluoranthene	(SIM)
000205-99-2	Benzo[b]fluoranthene	(SIM)
022599-96-8	Cholestan-3-ol, 2-methylene-	
000218-01-9	Chrysene	(SIM)
054482-31-4	D-Homoandrostane	
000206-44-0	Fluoranthene	
000193-39-5	Indeno[1,2,3-cd]pyrene	(SIM)

GRL-AR-2018-07

000120-72-9	Indole
000085-01-8	Phenanthrene
000129-00-0	Pyrene
027530-79-6	Simonellite

SK18013, wastewater
Number of compounds isolated: 1
Compounds identified to better than 90%:

CAS#	Name
000084-66-2	1,2-Benzenedicarboxylic acid, diethyl ester

SK18014, sediment
Number of compounds isolated: 31
Compounds identified to better than 90%:

CAS#	Name	
000000-00-0	1H-Indene 1,1,4,5,6-pentamethyl-2,3-dihydro-	
013567-54-9	1H-3a,7-Methanoazulene, octahydro-3,6,8,8-tetramethyl-	
000086-73-7	9H-Fluorene	(SIM)
000489-84-9	Azulene, 1,4-dimethyl-7-(1-methyle	
016982-00-6	Benzene, 1-Methyl-4-(1,2,2-trimethylcyclopentyl)-	
000191-24-2	Benzo[ghi]perylene	(SIM)-
000053-70-3	Dibenzo[a,h]anthracene	(SIM)
000206-44-0	Fluoranthene	
000193-39-5	Indeno[1,2,3-cd]pyrene	(SIM)
000091-20-3	Naphthalene	
000630-02-4	Octacosane	
000085-01-8	Phenanthrene	
000000-00-0	Phenanthrene, 1,2,3,4,4a,9,10,10a-octahydro-1,14a-trimethyl-7-(1-methylethyl)-	
000483-65-8	Phenanthrene, 1-methyl-7-(1-methylethyl)-	
000129-00-0	Pyrene	
000111-02-4	Squalene	
066394-74-9	Urs-20-en-16-ol	

SK18015, sediment
Number of compounds isolated: 17
Compounds identified to better than 90%:

CAS#	Name	
002922-51-2	2-Heptadecanone	
000086-73-7	9H-Fluorene	(SIM)
000206-44-0	Fluoranthene	(SIM)
000630-01-3	Hexacosane	
000091-20-3	Naphthalene	(SIM)
000483-78-3	Naphthalene, 1,6-dimethyl-4-(1-methylethyl)-	
000483-65-8	Phenanthrene, 1-methyl-7-(1-methylethyl)-	
000129-00-0	Pyrene	(SIM)
000059-02-9	Vitamin E	

GRL-AR-2018-07