

Appendix 1. Analytical methodology

All samples were collected and stored in pre-cleaned glass bottles that had been rinsed thoroughly with nitric acid and analytical grade pentane in order to remove all heavy metal and organic residues. At wastewater sampling locations, a 1 litre sample was collected in a screw-cap bottle. Sediment, sludge and soil samples were collected in 100ml bottles.

On arrival at the lab, two sub-samples were taken from each original. One of the sub-samples was subjected to qualitative organic analysis and the other one was analysed for a range of metals and metalloids. Details of the methods for sample preparation and for GC-MS screening analysis and heavy metals analysis are given in Sections A1.1 and A2.1 respectively.

For those samples analysed for volatile organic chemicals, a sample was collected in a separate 125 ml amber bottle with a ground-glass stopper. The details of the analysis for VOCs are presented in the Section A1.1.3.

A1.1 Organic analysis

A1.1.1 Preparation of samples for standard organic screen analysis

All solvents were of High Purity Grade (PRAG or low haloform). Glassware used in the extraction and clean up procedures was cleaned in detergent, rinsed with tap water and deionised water, dried in the oven overnight at 105⁰C, and rinsed three times with low haloform pentane.

A1.1.1.1 Solid Samples

In preparation for analysis of extractable organic compounds, approximately 30g of each sample was weighed and transferred to a clean 100 ml glass bottle. Samples were spiked with deuterated naphthalene (an internal standard) at a concentration of 4.7 mg/kg. 15ml of pentane was added, followed by 5ml of acetone in the case of wet samples. Samples that were originally dry or air dried were extracted only with 20ml of pentane. The samples were then sonicated for 2 hours.

The extracts were decanted, filtered through a pre-cleaned hydrophobic phase separator filter and collected in reagent tubes. The samples were then acidified to pH 2 with 10% nitric acid. Following this, a second portion of 15ml of pentane was added, followed by 5ml of acetone and the extraction procedure repeated. Finally, both extracts obtained for each sample were combined and evaporated to a volume of approximately 3ml. 3ml of iso-propanol and 3ml of fresh prepared TBA-reagent (mixture of 3% tetrabutylammonium hydrogen sulfate and 20% sodium sulfite anhydrous in deionised water) were added to the concentrated extract, and the mixture shaken for 1 min. After shaking, 20ml of deionised water was added to reagent tube and the phases were allowed to separate. Finally, the organic layer was transferred into a pentane pre-washed Florisil column. The compounds were eluted with a 95:5 mixture of pentane: toluene, and the eluent evaporated down to a volume of 2 ml under a stream of analytical grade nitrogen. 1-Bromonaphthalene was then added at a concentration of 10mg/l to provide an indication of GC/MS performance.

A1.1.1.2 Aqueous Samples

Prior to the extraction, the samples were spiked with deuterated naphthalene (an internal standard) at a concentration of 10mg/l. 20ml of pentane was added, and the sample agitated for 2 hours on a bottle roller to maximise contact between solvent and sample.

After separation of the phases, the solvent extract was filtered through a pre-cleaned hydrophobic phase separator filter and collected in a pre-cleaned reagent tube. The aqueous sample was acidified to pH 2 with 10% nitric acid, a second portion of 20ml pentane was added and the extraction procedure repeated. Both extracts were combined and cleaned up as described above for solid samples.

A1.1.2 Chromatographic Analysis

Organic compounds were identified qualitatively using Gas Chromatography Mass Spectrometry (GC-MS). Instrumentation was an Agilent 6890 Series gas chromatograph, interfaced with a Agilent Enhanced Chem-Station data system and linked to a Agilent 5973N inert Mass Selective Detector operated in SCAN mode. The identification of compounds was carried out by computer matching against Agilent Wiley7N and Pesticides Libraries of over 390,000 mass spectra combined with expert interpretation. Also all extracts were analysed using selective ion monitoring (SIM) method against three standard solutions. The lists of compounds containing in Standard I, Standard II and Standard III are presented below. Individual standards of chlorinated benzenes, chlorinated phenols and chlorinated pesticides were obtained from Chem Service Inc., USA; individual standards of brominated diphenyl ethers were obtained from Wellington Laboratories Inc., Canada. All standards were supplied by Greyhound Chromatography & Allied Chemicals, UK.

Compound	Ions to monitor
Benzene, 1,3-dichloro-	146, 148, 111, 75
Benzene, 1,4-dichloro-	146, 148, 111, 75
Benzene, 1,2-dichloro-	146, 148, 111, 75
Benzene, 1,3,5-trichloro-	180, 182, 145, 74
Phenol, 2,4-dichloro-	162, 164, 63, 98
Benzene, 1,2,4-trichloro-	180, 182, 145, 109
Benzene, 1,2,3-trichloro-	180, 182, 145, 109
Dichlorvos	109, 185, 79, 47
Benzene, 1,2,3,5-tetrachloro-	216, 214, 218, 179
Benzene, 1,2,4,5-tetrachloro-	216, 214, 218, 179
Benzene, 1,2,3,4-tetrachloro-	216, 214, 218, 179
Benzene, pentachloro-	250, 252, 248, 215
alpha-HCH	181, 183, 219, 217
Benzene, hexachloro-	284, 286, 282, 249
Atrazine	200, 215, 202, 217
beta-HCH	181, 183, 219, 217
gamma-HCH	181, 183, 219, 217
delta-HCH	181, 183, 219, 217
o,p'-DDE	246, 248, 318, 176
p,p'-DDE	246, 318, 246, 316
o,p'-DDD	235, 237, 165, 199

p,p'-DDD	235, 237, 165, 199
o,p'-DDT	235, 237, 165, 199
p,p'-DDT	235, 237, 165, 199
Heptachlor	272, 274, 100, 270
Aldrin	66, 263, 265, 261
Dieldrin	79, 77, 81, 263
Endrin aldehyde	345, 67, 347, 343
Methoxychlor	227, 228, 274, 344
Endosulfan I	170, 237, 172, 239
Octachlorostyrene	308, 310, 380, 343

Table A1.1. List of compounds in the Standard I used for SIM analysis

Results are reported as either reliably or tentatively identified. Match qualities of 90% or greater against Agilent Wiley7N and Pesticides Libraries or identification confirmed against standard compounds (using retention times and mass-spectra obtained during calibration) are assumed to give reliable identifications. Identification of hepta- and octabrominated diphenyl ethers was done by matching the spectra fragmentation pattern against published data (see note below). *Tentative identification refers to qualities between 51% and 90% against Agilent Wiley7N and Pesticides Libraries only. Analytes yielding match qualities of 50% or less are taken to be unidentified.

Compound	Ions to monitor
Phenol	94, 66, 65, 95
Phenol, 2-chloro-	128, 64, 92, 39
Phenol, 2-methyl-	108, 79, 90, 51
Phenol, 3-methyl- and 4-methyl-	108, 107, 79, 77
Phenol, 2-nitro-	139, 65, 81, 109
Phenol, 2,5-dichloro-	162, 164, 63, 99
Phenol, 2,3-dichloro-	162, 126, 63, 99
Phenol, 4-chloro-	128, 65, 130, 100
Phenol, 2,6-dichloro-	162, 164, 63, 98
Butadiene, hexachloro-	225, 190, 260, 118
Phenol, 4-chloro-3-methyl-	107, 142, 77, 144
Phenol, 2,3,5-trichloro-	196, 198, 160, 97
Phenol, 2,4,6-trichloro-	196, 198, 97, 132
Phenol, 2,4,5-trichloro-	196, 198, 97, 132
Phenol, 2,3,4-trichloro-	196, 198, 97, 160
Phenol, 2,3,6-trichloro-	196, 198, 97, 132
Phenol, 3,5-dichloro-	162, 164, 99, 63
Phenol, 3,4-dichloro-	162, 164, 99, 63
Phenol, 2,3,5,6-tetrachloro-	232, 234, 230, 131
Phenol, 2,3,4,6-tetrachloro-	232, 234, 230, 131
Phenol, pentachloro-	266, 268, 264, 165
Dinoseb	211, 163, 147, 117
PCB-28	256, 258, 186, 150

PCB-52	292, 220, 290, 222
Chlordane I	373, 375, 272, 237
PCB-101	326, 324, 254, 328
Chlordane II	373, 375, 272, 237
PCB-81	292, 290, 294, 220
PCB-77	292, 290, 294, 220
PCB-123	326, 324, 254, 328
PCB-118	326, 324, 256, 328
PCB-114	326, 324, 256, 328
PCB-153	360, 362, 290, 358
PCB-105	326, 324, 254, 328
PCB-138	360, 362, 290, 358
PCB-126	326, 324, 254, 328
PCB-167	360, 362, 290, 358
PCB-156	360, 362, 290, 358
PCB-157	360, 362, 290, 358
PCB-180	396, 394, 324, 162
PCB-169	360, 362, 358, 145
PCB-170	396, 394, 324, 326
PCB-189	396, 394, 398, 324

Table A1.2. List of compounds in the Standard II used for SIM analysis

Compound	Ions to monitor
Tetrabrominated diphenyl ethers including BDE-47	485, 487, 483, 326, 328, 324
Pentabrominated diphenyl ethers including BDE-99	563, 565, 561, 404, 406, 402
Hexabrominated diphenyl ethers including BDE-153	643, 641, 645, 483, 481, 485

Table A1.3. List of compounds in the Standard III used for SIM analysis

* Tu, C. & Prest, H.F. (2005) Determination of polybrominated diphenyl ethers in polymeric materials using the 6890 GC/ 5973N inert MSD with electron impact ionization. Application Note 5989-2850EN. Environmental, Component Testing. Agilent Technologies Inc. 2005. Printed in the USA. April 5, 2005.

A1.1.3 Volatile Organic Compounds (VOCs) analysis

For volatile organic compound analysis, no sample preparation was required. The original sample was sub-sampled immediately after opening. Four portions of 10ml each were transferred into 20ml headspace vials and sealed with Teflon-lined vial caps. Three blanks of the laboratory air, which were taken at the time of sub-sampling, have been analysed in every run together with the samples. One sub-sample was used for the organic screen analysis to evaluate the whole range of volatile compounds in the sample using total ion monitoring mode. The second sub-sample was analysed using Selective Ion Monitoring (SIM) method to detect the VOCs listed in the Table A1.4.

Compound	Ions to monitor
Methane, dibromo-	93, 95, 174, 176
Methane, bromodichloro-	83, 85, 127, 129
Methane, dibromochloro-	129, 127, 131, 79
Methane, chloro-	50, 52, 15, 49
Methane, dichloro-	84, 49, 86, 51
Methane, trichloro-	83, 47, 35, 118
Methane, tribromo-	173, 175, 171, 254
Methane, tetrachloro-	117, 35, 47, 82
Ethane, 1,1-dichloro-	63, 27, 83, 98
Ethane, 1,2-dichloro-	62, 27, 64, 49
Ethane, 1-bromo-2-chloro-	63, 65, 27, 26
Ethane, 1,1,1-trichloro-	97, 61, 26, 117
Ethane, 1,1,1,2-tetrachloro-	131, 133, 117, 119
Ethane, 1,1,2,2-tetrachloro-	83, 85, 95, 131
Ethane, pentachloro-	167, 165, 169, 117
Ethane, hexachloro-	117, 201, 203, 199
Ethene, chloro-	27, 62, 37, 47
Ethene, 1,1-dichloro-	61, 96, 26, 35
Ethene, 1,2-dichloro-, cis-	61, 96, 26, 35
Ethene, 1,2-dichloro-, trans-	61, 96, 26, 37
Ethene, trichloro-	95, 130, 132, 97
Ethene, tetrachloro-	166, 129, 94, 47
Butane, 1,3-dichloro-	55, 54, 90, 63
Butane, 1,4-dichloro-	55, 54, 90, 64
2-Butene, 1,4-dichloro-	53, 75, 88, 27
1,3-Butadiene, 2-chloro-	53, 50, 51, 52
1,3-Butadiene, hexachloro-	225, 260, 190, 118
Propane, 2-bromo-1-chloro-	41, 39, 77, 79

Table A1.4. List of VOCs in the Standard used for SIM analysis

The third and fourth sub-samples were used as duplicates for quantitative analysis of those VOCs which have been detected in the samples. The names of the VOCs which were subject to quantification, and their retention times (RT), are presented in the Table A1.5. Standard deviation (SD), relative standard deviation (RSD) and limits of detection (LOD) were calculated using data of the analysis of seven replicas of the VOCs standard mixture containing 1ppb of each analyte. Limit of quantification (LOQ) is the lowest concentration in the linear regression used for quantification (r^2 – corresponding correlation coefficient). All standard compounds were obtained from Chem Service Inc., USA, and supplied by Greyhound Chromatography & Allied Chemicals, UK.

COMPOUND	RT, MIN	SD, μ /L	RSD, %	LIMIT OF DETECTION (LOD), μ /L	LIMIT OF QUANTIFICATION (LOQ), μ /L	CORRELATION COEFFICIENT, R^2
Bromoform	18.06	0.06	6	0.2	0.5	0.999
Chloroform	8.03	0.08	10	0.3	0.5	0.999
Ethane, 1,1,1-trichloro-	8.26	0.06	5	0.2	0.5	0.997
Ethane, 1,1-dichloro-	6.21	0.07	10	0.2	0.5	1.000
Ethane, chloro-	2.83	0.04	9	0.1	0.5	0.999
Ethene, 1,1-dichloro-	3.98	0.02	3	0.1	0.1	0.997
Ethene, 1,2-dichloro-, cis-	7.37	0.06	9	0.2	0.5	1.000
Ethene, 1,2-dichloro-, trans-	5.34	0.04	6	0.1	0.1	1.000
Ethene, tetrachloro-	12.34	0.04	4	0.1	0.1	0.997
Ethene, trichloro-	9.99	0.15	18	0.5	1.0	0.999
Hexachlorobutadiene	18.06	0.06	6	0.2	0.5	0.997
Methane, bromodichloro-	10.76	0.09	11	0.3	0.5	1.000
Methane, chloro-	2.10	0.04	4	0.1	0.1	0.999
Methane, dibromochloro-	12.71	0.06	6	0.2	0.5	0.999
Methane, dichloro-	4.93	0.06	8	0.2	0.5	1.000
Methane, tetrachloro-	8.50	0.05	4	0.1	0.1	0.996

Table A1.5. List of VOCs that were quantified in the samples using SIM analysis.

VOCs were analysed using Gas Chromatography Mass Spectrometry (GC-MS) technique. Instrumentation was a Hewlett Packard 5890 Series II gas chromatograph with Agilent 7694 Headspace Sampler. Gas chromatograph was interfaced with a Hewlett Packard Enhanced Chem-Station data system and linked to a Hewlett Packard 5972 Mass Selective Detector operated in SCAN or SIM mode. The identification of unknown compounds was carried out by computer matching against Hewlett Packard Wiley275 Library combined with expert interpretation.

A1.2 Inorganic Analysis for metals and metalloids

A1.2.1 Preparation of samples for analysis

All chemicals were of High Purity Aristar Grade. All glassware was cleaned in detergent, rinsed with deionised water, soaked in 10% nitric acid overnight, rinsed with deionised water and dried in an oven.

A1.2.1.1 Solid Samples; sediment, soil and sludge

All solid samples were air dried until weighing readings became constant. They were then crushed using a pestle and mortar until homogenous and sieved through a 2-mm mesh. Approximately 0.5 g of sample was accurately weighed into a glass 100 ml boiling tube and to this 10 ml of deionised water was added, followed by 7.5 ml of concentrated hydrochloric acid and 2.5 ml of concentrated nitric acid. The samples were digested at room temperature overnight prior to being placed onto a Gerhardt Kjeldatherm digestion block (40 space) connected to a Gerhardt Turbosog scrubber unit (filled with 10% w/v sodium hydroxide). The samples were then refluxed at 130°C for four hours. To prepare samples for mercury analysis, this procedure was repeated in an identical manner other than using a digest temperature of 90°C. After cooling to ambient temperature, the digests were filtered into volumetric flasks, diluted with deionised water, made up to a volume of 50 ml and mixed.

With every batch of samples digested, approximately one in ten samples were analysed in duplicate to verify method reproducibility. Furthermore, a blank sample, and appropriate certified reference material (CRM) samples were prepared in an identical manner. The CRMs analysed were; GBW07406, yellow-red soil, certified by the China National Analysis Centre for Iron and Steel, Beijing, China; LGC6187, leachable metals in river sediment certified by the Laboratory of the Government Chemist, UK; GBW07311, stream sediment, certified by the China National Analysis Centre for Iron and Steel, Beijing, China; and PACS-2, marine sediment, certified by the National Research Council of Canada.

A1.2.1.3 Water samples

For all groundwater samples, 45ml of the mixed sample was transferred to a 50ml volumetric flask and then each sample was acidified (10% v/v) with by the addition of concentrated nitric acid to make up the volume to 50 ml, ready for analysis.

For all other water samples, 100ml of the sample was transferred to a clean glass bottle and acidified with nitric acid (10% v/v). For samples containing very high amounts of suspended solids a separate 100ml representative portion was filtered into a clean glass bottle prior to acidification with concentrated nitric acid (10% v/v). For each acidified sub-sample, 50 ml was subsequently transferred to a 100ml boiling tube, placed onto the Gerhardt Kjeldatherm digestion block, and refluxed at 130°C for four hours. After cooling to ambient temperature, each digest was filtered into a volumetric flask, diluted with deionised water, made up to a volume of 50 ml and mixed.

With each batch of sample analyses, approximately one in ten samples were analysed in duplicate to verify method reproducibility, and a mixed metal quality control solution of 0.8 mg/l (for groundwaters) and 8 mg/l (for wastewaters) and a blank sample were separately prepared in an identical manner. To prepare wastewater samples for mercury analysis, the procedure was repeated in an identical manner other than using 25 ml of each acidified sample solution and a digest temperature of 90°C.

A1.2.2 Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)

Following preparation, samples were analysed by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES), using a Varian MPX Simultaneous Spectrometer. The following metals were quantified directly: antimony (Sb), arsenic (As), barium (Ba), beryllium (Be), bismuth (Bi), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), gallium (Ga), germanium (Ge), indium (In), lead (Pb), manganese (Mn), mercury (Hg), molybdenum (Mo), nickel (Ni), selenium (Se), thallium (Tl), tin (Sn), vanadium (V), and zinc (Zn). A multi-element instrument calibration standard was prepared at a concentration of 10 mg/l, matrix matched to the samples (i.e. in 10% v/v nitric acid for water samples and in 15% v/v hydrochloric acid and 5% v/v nitric acid for solid samples). The calibration was validated using a quality control standard (8 mg/l), prepared internally from different reagent stocks. Any sample exceeding the calibration range was diluted accordingly, in duplicate, and re-analysed.

Metal	Sediment, soil & sludge (mg/kg dry weight)	Wastewater & Groundwater (µg/l)
Arsenic*	<20	<20
Antimony	<20	<20
Barium	<0.5	<5
Beryllium	<0.2	<2
Bismuth	<20	<20
Cadmium	<0.5	<5
Chromium	<2	<20
Cobalt	<2	<20
Copper	<2	<20
Gallium*	<20	<20
Germanium*	<30	<30
Indium*	<20	<20
Lead	<10	<10
Manganese	<1	<10
Mercury*	<10	<50
Molybdenum	<2	<20
Nickel	<2	<20
Selenium*	<30	<50
Thallium*	<20	<50
Tin	<10	<20
Vanadium	<2	<20
Zinc	<1	<10

Table A1.6. Metals quantified in all samples, including those not present in any of the samples above method detection limits*, and the method detection limits for different sample types