Greenpeace Research Laboratories Analytical Results 2016-06

Organic contaminants and metals arising in wastewater samples from two industrial sites in Slovakia

September 2016

Introduction

8 samples of wastewater were received from Greenpeace CEE (Slovakia) for analysis at the Greenpeace Research Laboratories on 14 June 2016. According to documentation supplied, all samples were collected between 9th and 10th of June, 2016, from two industrial sites: Fortischem, a. s. (District of Nováky town) and Duslo, a. s. (District of Šaľa town). Unfortunately, the bottle containing one of the samples from Duslo, a. s. that was intended for analysis of semi-volatile organic compounds (SVOCs) and metals was broken during transportation; therefore we were able to conduct analyses only for 7 samples.

Details of the samples received are provided in Table 1a, together with GPS coordinates for the sample collection locations in Table 1b. All samples were collected directly from treated wastewater discharge pipes at each of the two sites as described below.

Each of the samples SK16001a and SK16002a were prepared as composites from 4 equal parts of the wastewater discharged from Fortischem, a. s. industrial site during 24 hours period: SK16001a represents the first 12 hours of sampling, and SK16002a, the second 12 hours. These samples were subject to a qualitative analysis for the presence of SVOCs (solvent-extractable compounds) and subject to a quantitative analysis for metals. Concentrations of metals in both whole and filtered water were determined in order to distinguish between metals associated with suspended matter and those present in dissolved form in the water. Samples SK16001b and SK16002b were collected in the middle of the first and of the second 12-hourly sampling periods, respectively, and were subject to qualitative analysis for the presence of volatile organic compounds (VOCs) in addition to a quantitative analysis for a more specific range of VOCs classified as common environmental contaminants.

The samples from the Duslo, a. s. industrial site were collected in a similar manner to that from Fortischem, a. s. industrial site, i.e. samples SK16003a (not analysed) and SK16004a were composites of the first and of the second 12-hourly sampling periods, respectively, while SK16003b and SK16004b were individual samples for VOC analysis collected in the middle of the each sampling period.

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Description of Fortischem, a. s. and Duslo, a. s. industrial sites

There are 3 plants operating at the Fortischem, a. s. industrial site, which manufacture a range of chemicals, including the following:

Manufacture of inorganic chemicals, organic chemicals, polymers and PVC processing products, such as:

1. chloroparaffines
2. dichlorethane and vinyl chloride from dichlorethane
3. NaOH, H, Cl, NaClO, drying and liquefaction of Cl, manufacture of HCl
4. calcium carbide and C2H2
5. propylene oxide, polyether polyols and amines
6. PVC and initiators
7. PVAL/PVAC
8. acetylenic alcohols
9. Ethylene Chlorhydrin and its processing into a Novamal Novamal
10. vinyl chloride from acetylhene

Duslo, a. s. industrial site is situated in the immediate vicinity of the town of Šaľa that is located in the Nitra region in the south of the western Slovakia, 65 kilometres from the capital city of the Slovak Republic - Bratislava. Duslo, a. s. is one of the most significant companies of the chemical industry in Slovakia, manufacturing fertilisers for the European market, as well as supplying rubber chemicals, polyvinyl acetate and polyacrylic glues and dispersions globally. The company´s products portfolio includes:

1. Industrial fertilisers;
2. Rubber chemicals;
3. Dispersions and glues;
4. Products of magnesium chemistry;
5. Special products

Sample code	Location	Sample type	Date	Description
Fortischem, a. s. Industrial site				
SK16001a	Nováky town, District of Prievidza city	wastewater	9 – 10.06.2016	Treated wastewater, composite of the 4 sub-samples collected during the first 12 hours of sampling
SK16001b				Treated wastewater, individual sample collected in the middle of the first 12 hours of sampling
SK16002a				Treated wastewater, composite of the 4 sub-samples collected during the second 12 hours of sampling
SK16002b				Treated wastewater, individual sample collected in the middle of the second 12 hours of sampling
Duslo, a. s. Industrial site				
SK16003a	Trnovec nad Váhom village, District of Šaľa town	wastewater	9 – 10.06.2016	Broken sampling bottle, no analysis has been conducted
SK16003b				Treated wastewater, individual sample collected in the middle of the first 12 hours of sampling
SK16004a				Treated wastewater, composite of the 4 sub-samples collected during the second 12 hours of sampling
SK16004b				Treated wastewater, individual sample collected in the middle of the second 12 hours of sampling

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

Sample code	N			E		
	degree (º)	minutes (')	seconds (")	degree (º)	minutes (')	seconds (")
SK16001&2	48	41	51.48	018	31	18.30
SK16003&4	48	08	01.58	017	55	20.56

Table 1b: GPS coordinates of sample collection locations

Materials and methods

Heavy metal concentrations were determined for all samples by ICP atomic emission spectrometry (AES) following acid digestion and using appropriate certified reference materials in addition to intra-laboratory standards. Both the total concentrations in the whole (unfiltered) sample and the concentrations of dissolved forms in a filtered sample were determined separately for each sample. Hexavalent chromium concentrations in filtered samples were determined colourimetrically using a diphenylcarbazide method.

Semi-volatile organic compounds were isolated from each sample 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). Volatile organic chemicals (VOCs) were identified and quantified in samples as received (with no pre-treatment) using GC/MS with HeadSpace sample introduction technique. Quantification of the detected VOCs was carried out using internal standards calibration. More detailed descriptions of the sample preparation and analytical procedures are presented in Appendix 1, including a list of VOCs quantified in the samples, with their limits of quantification (Table 6).

Results and Discussion

The results for the samples are outlined in the following sections, divided into areas in which the samples were collected. For each section, the concentrations of metals and metalloids in filtered (dissolved metals) and in whole waters (dissolved and suspended metals) are reported, in Table 2. In addition, the organic chemicals identified in composite and individual samples are summarised in Tables 3 and 4, respectively. The results for quantitative VOCs analysis are presented in Table 5. A full list of organic chemicals identified in each sample is provided in Appendix 2.

In some cases, concentrations of metals and metalloids were below limits of detection for the analytical methods employed in this study. These are shown in the results tables as '<xx' where xx is the method detection limit for the individual metal or metalloid.

3.1 Fortischem, District of Nováky town.

3.1.1 Metals

Among the metals quantified in our study, the presence of mercury in the treated wastewater from Fortischem a. s. was of the highest concern due to high concentrations detected in samples SK16001a and SK16002a (30 µg/l and 1.3 µg/l (filtered samples), respectively). Both samples exceed the level of 0.005 µg/l of total mercury reported for freshwaters without known sources of mercury contamination (Gilmour and Henry 1991). In the case of the sample SK16001a, the concentration of mercury was 6000 times over the levels for uncontaminated freshwaters. Mercury concentrations in the whole wastewater samples SK16001a and SK16002a were higher still, due to the presence of the suspended particulates, which tend to absorb contaminants from the water. Similarly, the concentrations of the other metals in the whole samples were higher than that in the filtered samples, for the same reason.

Concentrations of barium in filtered samples SK16001a and SK16002a (837 µg/L and 1010 µg/L, respectively) fell in the wide range reported for raw surface waters and public drinking water supplies (≤5 to 15,000 µg/l), but were higher than reported average (mean) concentrations for such waters, which are generally in the order of 10–60 µg/l (ATSDR 2007).

	Concentration, µg/l					
	Fortischem				Duslo	
Sample code	SK16001a		SK16002a		SK16004a	
Sample	filtered	whole	filtered	whole	filtered	whole
Antimony (Sb)	1.4	3.0	<0.2	1.3	2.2	2.1
Arsenic (As)	17	35	6	19	4	4
Barium (Ba)	837	1,060	1010	940	50	48
Beryllium (Be)	<1	<1	<1	<1	<1	<1
Cadmium (Cd)	<0.1	0.5	<0.1	0.3	<0.1	0.2
Chromium (Cr)	35.6	56.4	6.9	10.4	0.7	1.0
Cobalt (Co)	2.8	3.9	<0.5	<0.5	<0.5	<0.5
Copper (Cu)	1	24	<1	6	5	22
Iron (Fe)	861	6,390	452	561	<20	223
Lead (Pb)	0.6	20	1.5	5.35	<0.5	14
Manganese (Mn)	483	608	97	91	4	19
Mercury (Hg)	30	305	1.3	256	<0.5	<0.5
Nickel (Ni)	<10	<10	<10	<10	<10	<10
Selenium (Se)	<1	<1	<1	<1	<1	<1
Vanadium (V)	4.7	17.8	1.8	1.8	19.2	18.1
Zinc (Zn)	16	270	23	33	11	77

Table 2: Concentrations of metals and metalloids (µg/l) in filtered and whole wastewater samples.

The concentrations of the rest of the metals quantified in both samples of wastewater SK16001a & SK16002a collected in this area indicated that wastewaters were not notably contaminated with these metals, with little sign of elevation in concentrations above typical background concentrations for uncontaminated surface freshwaters (see e.g. Salomons & Forstner 1984, ATSDR 2005a, Comber *et al.* 2008).

3.1.2 Organic contaminants

3.1.2.1 Semi-volatile organic compounds

As both samples SK16001a and SK16002a represent compounds in the treated wastewater collected from the same pipe during the first and the second 12-hourly discharge, respectively, the patterns of organic compounds detected in them were quite similar (see Table 3). Both samples contained a range of chlorinated and non-chlorinated organic contaminants, clearly indicating insufficiency of the treatment techniques used for these wastewaters before they have been discharged. From the relatively high number of compounds isolated in both samples (115 and 116 in samples SK16001a and SK16002a, respectively), it was possible to identify to a high degree of reliability only 17% and 13% of them respectively, due to the complexity of the samples. The key organic contaminants detected in both samples were:

Sample code	SK16001a	SK16002a	SK16004a
Location	Fortischem	Fortischem	Duslo
Sample type	**Wastewater**	**Wastewater**	**Wastewater**
Number of compounds isolated	115	116	15
Number of compounds identified to >90%	20	15	4
Percentage identified to >90%	17%	13%	27%
ALKYL PHENOLIC COMPOUNDS			
Phenol, 4,4'-(1-methylethylidene)bis-	✓	✓	
Phenol, 4-methyl-	✓	✓	
Phenol, p-tert-butyl-	✓		
CHLORINATED COMPOUNDS			
Propane, 2,2'-oxybis[1-chloro-	✓	✓	
Propane, 2,2'-oxybis[2-chloro	✓	✓	
Ethane, 1,1'-[methylenebis(oxy)]bis[2-chloro-	✓	✓	
PHTHALATE ESTERS			
Diethyl phthalate	✓	✓	✓
GLYCOLS & DERIVATIVES			
2-Propanol, 1-(2-butoxy-1-methylethoxy)-	✓		
2-Propanol, 1-[1-methyl-2-(2-propenyloxy)ethoxy]-	✓		
1-Propanol, 2-(2-hydroxypropoxy)-		✓	
Hexaethylene glycol dimethyl ether		✓	
PAHs & ALKYLATED DERIVATIVES			
Naphthalene	✓		
Naphthalene, 1,2,3,4-tetrahydro-	✓		
CARBOXYLIC ACIDS & DERIVATIVES			
Propanoic acid, 2-methyl-3-[4-t-butyl]phenyl-	✓		
Hexanoic acid, 3,5,5-trimethyl-	✓		
Benzoic acid, p-tert-butyl-	✓		
Benzoic acid		✓	
Propionic acid, 3,5-di-tert-butyl-4-hydroxyphenyl-		✓	
ORGANOPHOSPHORUS COMPOUNDS			
Phosphoric acid, triethyl ester	✓		
ORGANOSULPHUR COMPOUNDS			
Benzothiazole, 2-methyl			✓
Benzothiazole, 2-(methylthio)-			✓
OTHERS			
Ibuprofen	✓	✓	
2,4,7,9-Tetramethyl-5-decyn-4,7-diol	✓	✓	✓
4-Piperidinone, 2,2,6,6-tetramethyl-	✓		
Camphor	✓		
Diethyltoluamide	✓		
1,3-Propanediol, 2-(hydroxymethyl)-2-methyl-		✓	

Table 3: Summary of key organic contaminants present in samples in which semi-volatile (solvent extractable) organic compounds were identified to >90% reliability.

- Alkylated phenolic compounds including Phenol, 4,4'-(1-methylethylidene)bis-, also known as Bisphenol A or BPA, is the starting material in the manufacture of polycarbonate polymers. BPA, being an endocrine disruptor, has well documented history of adverse health effects in mammalian and non-mammalian laboratory animals, wildlife, and in-vitro models (Rochester 2013). Recently, it was hypothesised that BPA interferes with epigenetic programming and, consequently, may accelerate cancer initiation; however, the exact mechanisms of action are not completely understood (Ferreira et al. 2015). Also, genetic damages, endocrine disruption, oxidative stress and metabolic changes have also been linked with the deleterious impact of BPA.
- Two isomers of bis(chloroisopropyl) ether (Propane, 2,2'-oxybis[2-chloro- and Propane, 2,2'-oxybis[1-chloro-), which has a variety of applications including as a pesticide to control nematodes in agriculture and as an intermediate in pharmaceuticals and fine chemicals manufacture.
- Ethane, 1,1'-[methylenebis(oxy)]bis[2-chloro-, also known as bis(2-chloroethoxy)methane, is used as a solvent. This chemical may be toxic by ingestion or inhalation and can severely irritates skin, eyes, and mucous membranes.
- Diethyl phthalate (DEP), well known as a plasticizer in a variety of products including for cellulose ester plastic films and sheets. It is also used as an ingredient in a range of cosmetic formulations and, in particular, in nail polish as a solvent for nitrocellulose and cellulose acetate, in perfumes as a fixative and solvent, and in toilet preparations as an alcohol denaturant (ATSDR 1995).
- Ibuprofen, a chemical that is commonly used as a painkiller and anti-inflammatory medication.
- 2,4,7,9-Tetramethyl-5-decyn-4,7-diol **(**TMDD), also known by its trade name as Surfynol 104, is classified as a High Production Volume (HPV) chemical. Most of the TMDD manufactured is used as an industrial defoaming, nonionic surfactant. The other uses of TMDD include as an intermediate in the production of polyethylene glycol ether surfactants, in dyes and water-based printing inks applications, and as wetting agent in the formulations of herbicides, fungicides, and insecticides. TMDD has been found to be toxic to aquatic organisms in laboratory experiments on fish (fathead minnows and carp), aquatic invertebrates (*Daphnia magna*), and green algae (*Selenastrum capricornutum)* (US EPA 2001).
- Dipropylene glycol ethers (SK16001) and both dipropylene & hexaethylene glycol ether (SK16002) have a variety of uses, mainly as a solvent in dyes, paints, ink, detergents and cleaners; as a chemical intermediate for production of epoxides, acid ester derivatives, solvents, and plasticizers (OECD, 2003).
- Representatives of carboxylic acids and their derivatives, which have been identified in both samples, have a number of uses such as solvents, food additives, cosmetic products constituents as well as starting material in polymers and pharmaceuticals production.

In addition, sample SK16001a contained the following compounds identified at the high degree of reliability:

- Two representatives of polycyclic aromatic hydrocarbons (PAHs), naphthalene and its derivative tetrahydronaphthalene, which may originate from coal or petroleum. One of the main uses of naphthalene is as an intermediate in the production of phthalic anhydride, which is used then in the production of various materials including phthalate plasticizers, resins, phthaleins, dyes, pharmaceuticals, insect repellents, and others. Tetrahydronaphthalene, also called as tetralin, is used as a solvent.

- Phosphoric acid, triethyl ester, or triethyl phosphate (TEP), is used as a flame retardant in unsaturated polyesters resins and also as a plasticizer. TEP in high doses may be harmful, with a narcotic effect, and shows certain neurotoxic properties (inhibition of cholinesterase) without indicating delayed neurotoxicity (OECD 1998).
- 4-Piperidinone, 2,2,6,6-tetramethyl-, also known as triacetoneamine , is used primarily as a light stabilizer in plastics manufacture and as a starting material in organic synthesis, for example, to produce radical oxydizer 2,2,6,6-tetramethylpiperidine-1-oxyl – (TEMPO) (Ciriminna & Pagliaro 2010).
- Camphor, the chemical belonging to a class of terpenoids, which is a naturally originating compound and can be found in trees and other vegetation, but can also be synthetically produced. The uses of camphor include as a plasticizer for manufacture of nitrocellulose, as a constituent of explosive material, in addition to its uses as scent and medicinal purposes.
- Diethyltoluamide is a well-known insect repellent also called as DEET; the other use of this chemical is as a solvent for synthetic fabrics.

One more chemical that was also identified in sample SK16002a, but not present in the sample SK16001a (1,3-Propanediol, 2-(hydroxymethyl)-2-methyl-), is used as an intermediate in the manufacture of polyester resins, stabilizers and plasticizers, among others.

3.1.2.2 Volatile organic compounds (VOCs)

Both samples SK16001b & SK16002b contained a diverse range, and relatively high number, of VOCs (71 and 64, respectively) and over half of these (53%) were reliably identified (see Table 4). Among those identified, halogenated VOCs accounted for 40% and 53% in samples SK16001b & SK16002b, respectively. The results for quantitative VOCs analysis are presented in Table 5. In general, all halogenated VOCs express toxic properties and some of them are carcinogenic. The most of the concern in this study was detection of chloroethene-, also called as vinyl chloride monomer (VCM), at very high concentrations of 16,000 µg/l and 9,000 µg/l, respectively.

Sample code	SK16001b	SK16002b	SK16004b	SK16004b
Location	Fortischem	Fortischem	Duslo	Duslo
Sample type	Wastewater	Wastewater	Wastewater	Wastewater
Number of compounds isolated	71	64	10	8
Number of compounds identified to >90%	40	34	8	8
Percentage identified to >90%	53%	53%	80%	100%
Chlorinated ethanes & ethenes	9	9	4	4
Halogenated methanes	2	4	1	1
Chlorinated benzenes	5	5	1	1
Benzene & aklylbenzenes	8	6	2	2
Aliphatic hydrocarbons & alkyl derivatives	12	5		
PAHs & derivatives	2	1		
Others	2	4		

Table 4: Summary of key organic contaminant groups present in samples in which volatile organic compounds were identified (to >90% reliability), including an indication of presence for the compounds most commonly identified in these samples, and providing the number of individual compounds where more than one compound was identified for a group.

VCM is among the highest production volume chemicals in the world, with annual worldwide demand of about 7.3 million tonnes (ATSDR 2016). The majority of the VCM produced is used in the production of polyvinyl chloride (PVC) plastic, which is used extensively in construction materials, packaging, electrical and electronic equipment, textiles, coatings, furniture and many other products. Recently some interest was expressed for the use of PVC in the production of nano-composites (Mamunya *et al.* 2008, Rodríguez-Fernández *et al.* 2008) by adding inorganic nano-scale fillers (Feldman 2014).

VCM itself is highly toxic chemical, with a wide spectrum of toxic effects, including carcinogenicity in both humans and animals, which was recognised many years ago (IARC 1979). VCM is classified as known to be a human carcinogen (DHHS 2014, ATSDR 2016), with the liver being the primary target. A rare type of liver tumor, angiosarcoma, has been strongly associated with occupational exposure to VCM (WHO 2004, DHHS 2014).

Compound	SK16001b	SK16002b	SK16003b	SK16004b
1,1,2-trichloroethane	4.6	<2.0	ND	ND
1,2,4-trichlorobenzene	<2.0	<2.0	ND	ND
1,2-dichlorobenzene	<2.0	<2.0	ND	ND
1,3-dichlorobenzene	<2.0	<2.0	ND	ND
1,4-dichlorobenzene	<2.0	<2.0	<2.0	<2.0
Benzene	149	31.0	<2.0	<2.0
Benzene, chloro-	6.8	<2.0	ND	ND
Benzene, ethyl-	8.5	5.3	ND	ND
Benzene, isopropyl-	<2.0	<2.0	ND	ND
Bromoform	<2.0	<2.0	<2.0	<2.0
Carbon disulfide	<2.0	13.1	ND	ND
Chloroform	9.5	46.8	ND	ND
Cyclohexane	9.8	4.2	ND	ND
Cyclohexane, methyl-	5.3	3.2	ND	ND
Ethane, 1,1-dichloro-	69.8	19.0	ND	ND
Ethane, 1,2-dichloro-	6.0	6.3	<2.0	<2.0
Ethene, 1,1-dichloro-	<2.0	<2.0	ND	ND
Ethene, 1,2-dichloro-, *cis-*	7.0	5.8	<2.0	<2.0
Ethene, 1,2-dichloro-, *trans-*	<2.0	<2.0	ND	ND
Ethene, Chloro-	16000	9000	ND	ND
Ethene, tetrachloro-	<2.0	<2.0	<2.0	<2.0
Ethene, trichloro-	5.7	12.1	<2.0	<2.0
m- and/or *p*-Xylene	5.3	10.7	<2.0	<2.0
Methane, dibromochloro-	ND	<2.0	ND	ND
Methane, dichloro-	ND	<2.0	ND	ND
o-Xylene	<2.0	<2.0	ND	ND
Toluene	15.3	21.3	ND	ND

Table 5: Concentrations of volatile organic compounds, in μg/l. ND – not detected

Abdominal pain, weakness, fatigue, and weight loss are the most prominent clinical symptoms of VCM poisoning, and hepatosplenomegaly, ascites and jaundice are the most common clinical signs (WHO 2004). Because of its toxicity, VCM has been a subject to many regulations (DHHS 2014), including the

US EPA’s Clean Air Act, Clean Water Act (Water Quality Criteria: based on fish/shellfish and water consumption - 2 µg/l; based on fish/shellfish only - 530 µg/l) and Safe Water Drinking Act (Maximum Contaminant Level - 2 µg/l). However, the WHO drinking water Quality Guideline Value for VCM is 0.3 µg/l (WHO 2011). OSHA’s Permissible Exposure Limit (OSHA 2012) in the air is set to 1ppm (over any 8-hour period) and ceiling concentration to 5ppm (over any period not exceeding 15 min). Concentrations of VCM in both samples SK16001b & SK16002b exceeded by far all limits mentioned above that is of the great concern in relation to both environmental and human health.

Two further chemicals, *cis*-1,2-dichloroethene and *trans*-1,2-dichloroethene, are well known by-product contaminants of the wastewaters arising from the production of vinyl chloride, as well as arising from the degradation of other chlorinated solvents such as trichloroethene and tetrachloroethene.

The majority of other chlorinated ethenes, ethanes and methanes detected in the samples, such as 1,1-dichloroethane, 1,2-dichloroethane, trichloroethene, 1,1,2-trichloroethane, & tetrachloroethene are primarily used as solvents and/or as intermediates in the organic synthesis.

Water disinfection by-products, trihalomethanes, were detected in both samples, and while some of them were present at trace levels only (Methane, dibromochloro- & bromoform), chloroform was found at 9.5 and 46.8 µg/l in samples SK16001b & SK16002b, respectively.

Some of the chemicals mentioned above (1,2-dichloroethane, tetrachloroethene & chlorofom) are listed as “reasonably anticipated to be Human Carcinogens” (ATSDR 2011a,b &c), in addition to other identified toxic effects to human health.

Overall, the presence of highly toxic VOCs in the treated wastewater samples, especially of extremely high concentrations of VCM, is of great concern and needs urgent further investigations in order to prevent ongoing discharges of contaminants to wider environment.

3.2 Duslo, District of Šaľa town.

3.2.1 Metals

The concentrations of the metals quantified in sample SK16004a indicated that wastewaters were not notably contaminated with these metals, with little sign of elevation in concentrations above typical background concentrations for uncontaminated surface freshwaters (see e.g. Salomons & Forstner 1984, ATSDR 2005a, and Comber *et al.* 2008).

3.2.2 Organic contaminants

3.2.2.1. Semi-volatile organic compounds

In contrast to samples of wastewaters from the Fortischem a. s. industrial site, a relatively small number (15) of organic compounds was isolated from sample SK16004a, and only four of these could be reliably identified (see Table 3).

Two of these compounds have been also detected in samples SK16001a and SK16002a: Diethyl phthalate and 2,4,7,9-Tetramethyl-5-decyn-4,7-diol (see information about them in section 3.1.2.1). In addition, two derivatives of benzothiazole, namely 2-methylbenzothiazole and 2-

(methylthio)benzothiazole, were identified in sample SK16004a. Benzothiazoles are high production volume chemicals, used as vulcanization accelerators in rubber production, and as corrosion inhibitors, among other applications (Jover et al. 2009).

3.2.2.2. Volatile organic compounds (VOCs)

Totals of 10 and 8 VOC compounds were isolated from samples SK16003b & SK16004b, respectively, and 8 of them were reliably identified in each sample (see Table 4). Six of the identified compounds were halogenated (1,4-dichlorobenzene, bromoform, and 4 derivatives of chlorinated ethanes/ethenes), and two belongs to the class of aromatic hydrocarbons (benzene and a derivative). Though these chemicals were present only at trace levels in both samples, their presence still indicated insufficient treatment practices employed at the Duslo industrial site.

For more information please contact:

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Appendix 1: Details of methodologies

Analysis for Volatile Organic Compounds (VOCs)

Methods

VOCs were analysed using an Agilent 6890 gas chromatograph with an Rtx-624 column (30m, 0.25mm ID, 1.4µm film thickness) connected to an Agilent 7694 Headspace Sampler and linked to an Agilent 5973N MSD operated in EI mode. The GC oven temperature program included an initial temperature of 35^{0}C (held for 4min), rising to 55^{0}C at 5^{0}C/min, and then to 210^{0}C at 15^{0}C/min. The carrier gas was helium, supplied at 1ml/min. From each sample, three 10ml portions were sub-sampled into 20ml headspace vials. One sub-sample was analysed with the GC-MS in total ion monitoring (SCAN) mode to identify as many of the volatile organic compounds present as possible. Identification of compounds was carried out by matching spectra against the Wiley7N Library, employing expert judgment in order to avoid misidentifications. The two remaining sub-samples were then used for duplicate quantitative analysis for those halogenated (chlorinated, brominated and mixed) VOCs which had been detected in the samples through screening. Quantification was performed in Selective Ion Monitoring (SIM) mode using a 5 point internal calibration method. Chlorinated VOCs quantified in the water samples with limits of quantification are presented in Table 6 below.

Quality control

Method detection limits (MDL) and limits of quantification (LOQ) were obtained using data of 9 replicas of standard solution analysis. A number of blanks of laboratory air capped at the time that sub-sampling had taken place were also analysed, alongside samples of the ultra pure reagent water which was used for the preparation of standard calibration solutions. The initial calibration curve for each compound of interest was verified immediately prior to sample analysis by analyzing a calibration standard at a concentration near the midpoint concentration for the calibration range of the GC-MS.

Compound	MDL, µg/L
Ethene, 1,1-dichloro-	1.3
Carbon disulfide	1.3
Methane, dichloro-	0.3
Ethene, 1,2-dichloro-, trans-	0.9
Ethane, 1,1-dichloro-	0.5
Ethene, 1,2-dichloro-, cis-	0.5
Chloroform	0.5
Cyclohexane	1.0
Benzene	0.6
Ethane, 1,2-dichloro-	0.3
Ethene, trichloro-	1.1
Cyclohexane, methyl-	1.1
Toluene	0.3
1,1,2-trichloroethane	0.5

Ethene, tetrachloro-	1.8
Methane, dibromochloro-	0.3
Benzene, chloro-	0.3
Benzene, ethyl-	1.0
m- and/or p-xylene	2.1
o--xylene	0.9
Bromoform	0.4
Benzene, isopropyl-	1.3
1,3-dichlorobenzene	0.9
1,4-dichlorobenzene	0.9
1,2-dichlorobenzene	0.5
1,2,4-trichlorobenzene	0.9

Table 6. Method detection limit (MDL) for VOCs being identified. 4.0 µg/L is the lowest quantification limit (LOQ) for m- and/or p-xylene; while 2.0 µg/L is the lowest quantification limit for all the other compounds

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. Water samples (500ml) were prepared 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 concentrated to a final volume of 1ml as before. 20 µg of bromonaphthalene was added to each extract as a second IS prior to GC-MS analysis.

Analysis

For the total organic compounds screening, samples were analysed using an Agilent 6890 Series II GC with Restek Rtx-XLB column (30m, 0.25mm ID, 0.25 µm film thickness) linked to an Agilent 5973 Inert 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 35^{0}C, held for 2 minutes, raised to 260^{0}C at 10^{0}C/min, then to 320^{0}C at 6^{0}C/min (held for 8min). The carrier gas was helium, supplied at 1ml/min. Identification of compounds was carried out by matching spectra against both the Wiley 7N and Pesticides Libraries, using expert judgment as necessary in order to avoid misidentifications. Additionally, both the spectra and retention times of compounds isolated from the samples were matched against those obtained during GC-MS analysis of standard mixtures containing a range of chlorinated benzenes, phenols and pesticides, polychlorinated biphenyls (PCBs), phthalates, polycyclic aromatic hydrocarbons (PAHs) and aliphatic hydrocarbons.

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 (0.5, 2, 5, 20 μg/l respectively) were used for instrument calibration. Analysis employed in-line addition of an internal standard mix at 1000 μg/l (Scandium, Germanium, Yttrium, Indium and Terbium).

Quality control

One sample was prepared for ICP analysis in duplicate and analysed to verify method reproducibility, along with a blank sample. Two mixed metal quality control solution of 80 and 800 μg/l for each metal, other than mercury at 4 and 16 μg/l, were digested and analysed. All control samples were prepared in an identical manor to the samples.

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

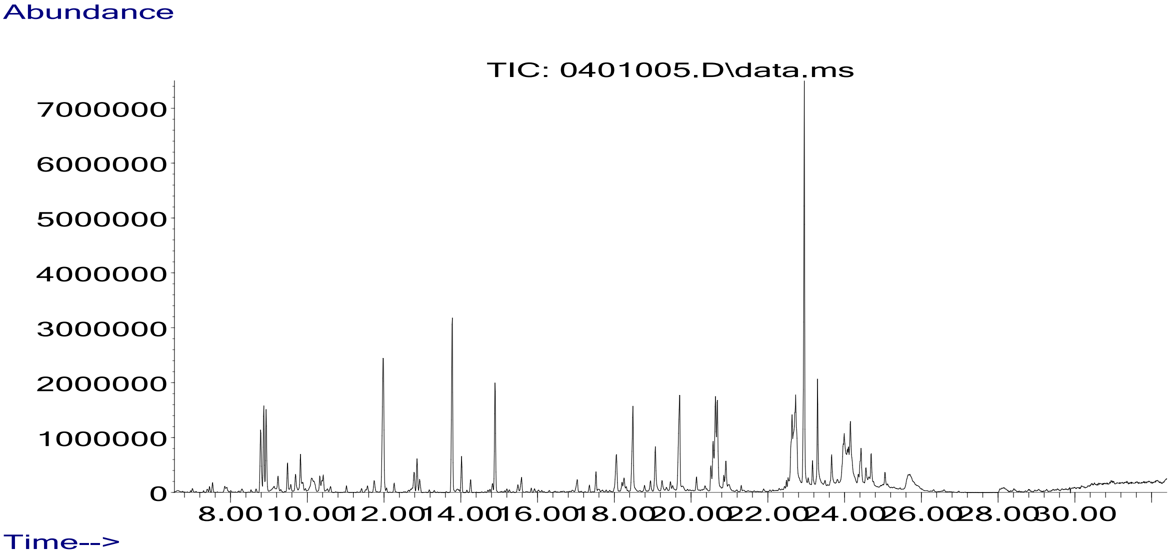
Further details of the methods employed can be provided on request.

Appendix 2: Detailed semi-volatile organic and volatile organic analytical screening data

Detailed screening data arising from GC-MS analysis of each of the samples are presented below. These data list separately semi-volatile organic compounds identified following solvent extraction and volatile organic compounds (VOCs) identified through separate headspace GC-MS analysis. Only those substances identified to greater than 90% quality match (following verification by expert interpretation) are listed here.

Semi-volatile organic analysis results

Sample code	SK16001a
Location	Fortischem, a. s. Industrial site, Nováky town, District of Prievidza city, Slovakia
Sample type	Treated wastewater
Date & time	9 – 10.06.2016
Description	Composite of the 4 sub-samples collected during the first 12 hours of sampling

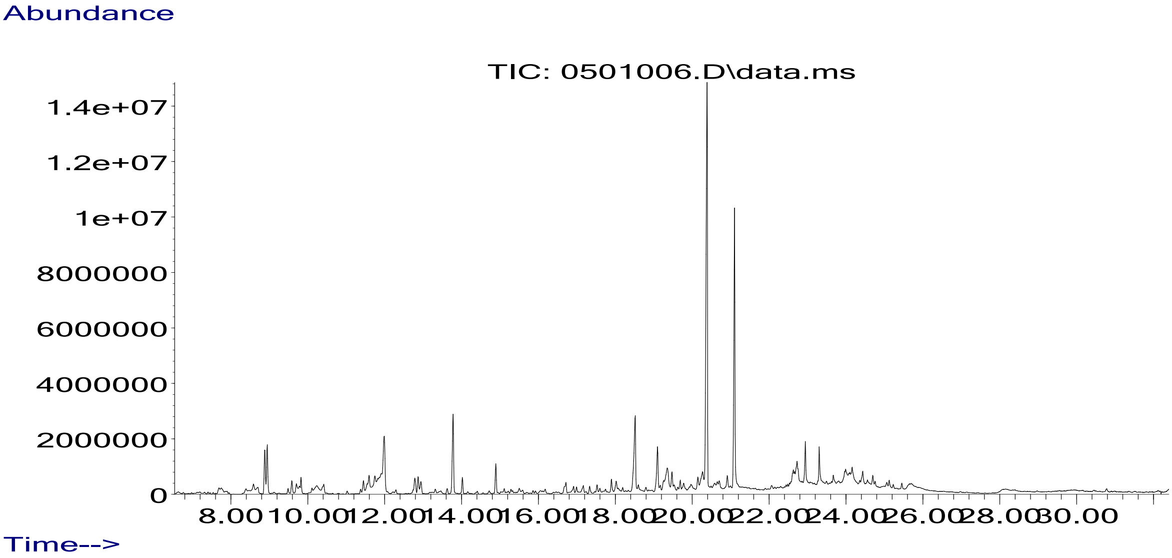


Number of compounds isolated: 115

Compounds identified to better than 90%:

CAS#	Name
000084-66-2	1,2-Benzenedicarboxylic acid, diethyl ester
000126-86-3	2,4,7,9-Tetramethyl-5-decyn-4,7-diol
029911-28-2	2-Propanol, 1-(2-butoxy-1-methylethoxy)-
055956-25-7	2-Propanol, 1-[1-methyl-2-(2-propenyloxy)ethoxy]-
000826-36-8	4-Piperidinone, 2,2,6,6-tetramethyl-
000098-73-7	Benzoic acid, p-tert-butyl-
000076-22-2	Camphor
000134-62-3	Diethyltoluamide
000111-91-1	Ethane, 1,1'-[methylenebis(oxy)]bis[2-chloro-
003302-10-1	Hexanoic acid, 3,5,5-trimethyl-
015687-27-1	Ibuprofen
000091-20-3	Naphthalene
000078-40-0	Naphthalene, 1,2,3,4-tetrahydro-
000080-05-7	Phenol, 4,4'-(1-methylethylidene)bis-
000106-44-5	Phenol, 4-methyl-
000098-54-4	Phenol, p-tert-butyl-
000076-22-2	Phosphoric acid, triethyl ester
000108-60-1	Propane, 2,2'-oxybis[1-chloro-
000108-60-1	Propane, 2,2'-oxybis[2-chloro-
066735-04-4	Propanoic acid, 2-methyl-3-[4-t-butyl]phenyl-

Sample code	SK16002a
Location	Fortischem, a. s. Industrial site, Nováky town, District of Prievidza city, Slovakia
Sample type	Treated wastewater
Date & time	9 – 10.06.2016
Description	Composite of the 4 sub-samples collected during the second 12 hours of sampling

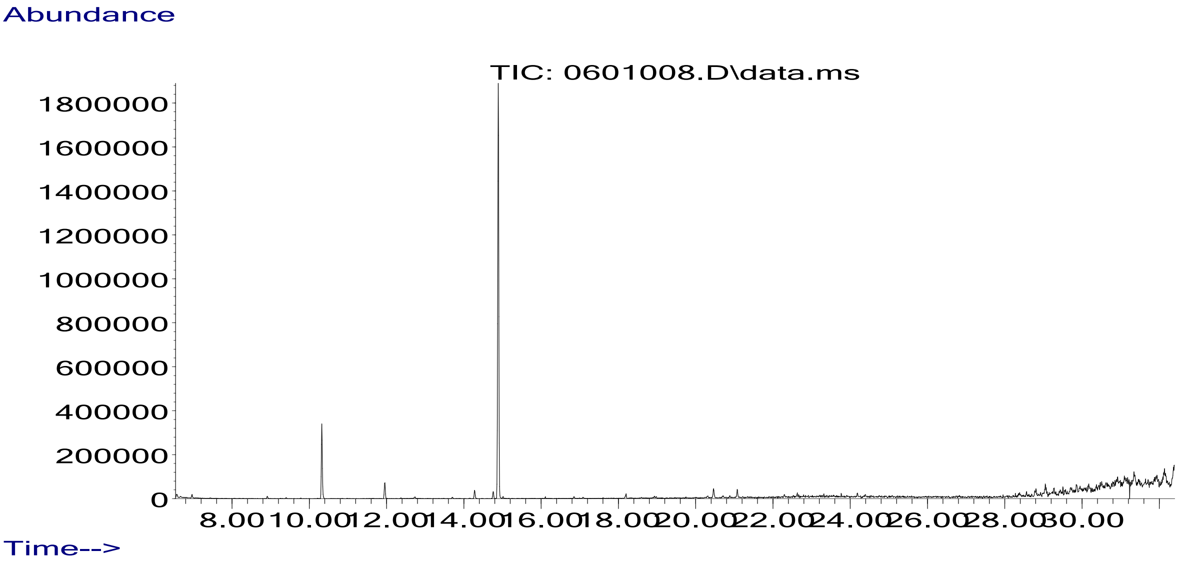


Number of compounds isolated: 116

Compounds identified to better than 90%:

CAS#	Name
000084-66-2	1,2-Benzenedicarboxylic acid, diethyl ester
000077-85-0	1,3-Propanediol, 2-(hydroxymethyl)-2-methyl-
000106-62-7	1-Propanol, 2-(2-hydroxypropoxy)-
000126-86-3	2,4,7,9-Tetramethyl-5-decyn-4,7-diol
000065-85-0	Benzoic acid
000111-91-1	Ethane, 1,1'-[methylenebis(oxy)]bis[2-chloro-
001072-40-8	Hexaethylene glycol dimethyl ether
015687-27-1	Ibuprofen
000091-20-3	Naphthalene
000119-64-2	Naphthalene, 1,2,3,4-tetrahydro-
000080-05-7	Phenol, 4,4'-(1-methylethylidene)bis-
000106-44-5	Phenol, 4-methyl-
000108-60-1	Propane, 2,2'-oxybis[1-chloro-
000108-60-1	Propane, 2,2'-oxybis[2-chloro-
020170-32-5	Propionic acid, 3,5-di-tert-butyl-4-hydroxyphenyl-

Sample code	SK16004a
Location	Duslo, a. s. Industrial site, Trnovec nad Váhom village, District of Šaľa town, Slovakia
Sample type	Treated wastewater
Date & time	9 – 10.06.2016
Description	Composite of the 4 sub-samples collected during the second 12 hours of sampling



Number of compounds isolated: 15

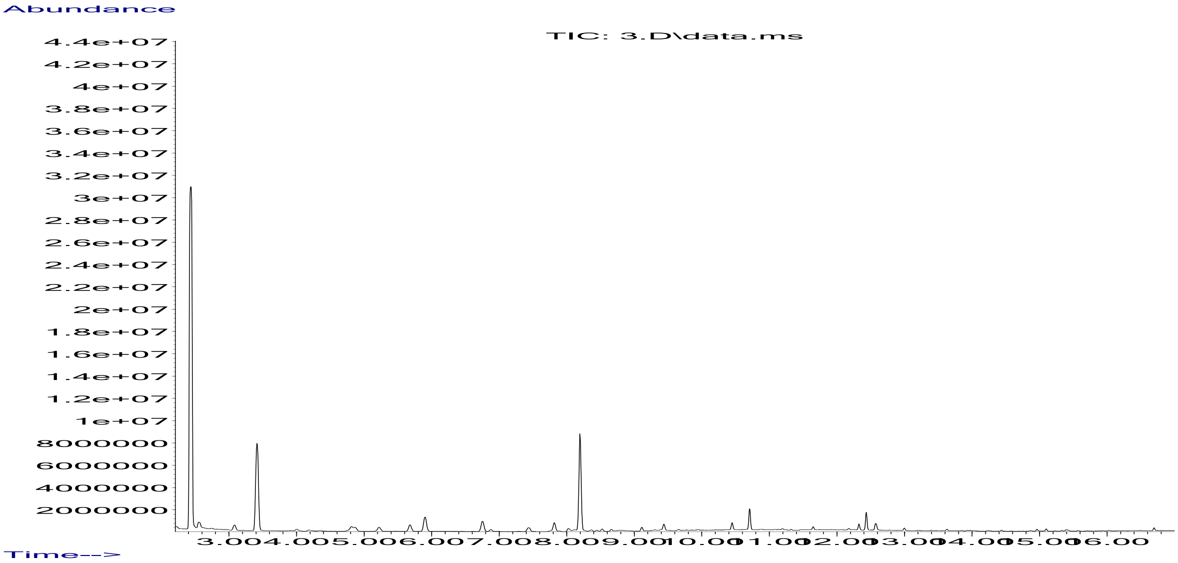
Compounds identified to better than 90%:

CAS#	**Name**
000084-66-2	1,2-Benzenedicarboxylic acid, diethyl ester
000126-86-3	2,4,7,9-Tetramethyl-5-decyn-4,7-diol
000615-22-5	Benzothiazole, 2-(methylthio)-
000120-75-2	Benzothiazole, 2-methyl-

Volatile organic analysis results

Note: Some compounds have been identified only at trace levels using Selective Ion Monitoring (SIM) method, which is indicated below next to the name of the such compound.

Sample code	SK16001b
Location	Fortischem, a. s. Industrial site, Nováky town, District of Prievidza city, Slovakia
Sample type	Treated wastewater
Date & time	9 – 10.06.2016
Description	Individual sample collected in the middle of the second 12 hours of sampling



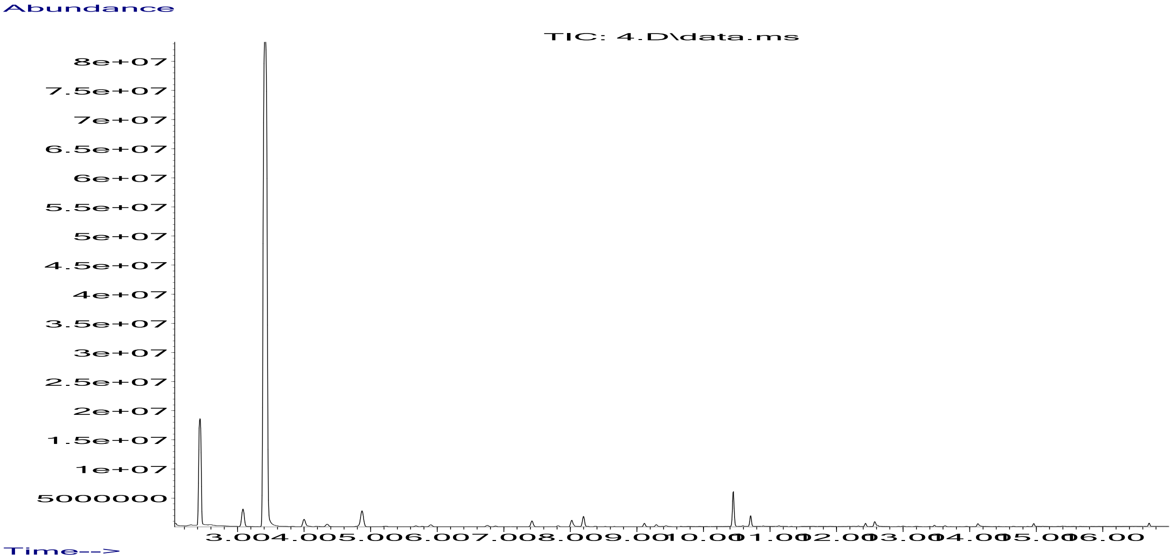
Number of compounds isolated: **71**

Compounds identified to better than 90%:

CAS#	**Name**
000000-00-0	2-Pentanone, methyl-
000071-43-2	Benzene
000000-00-0	Benzene, ethylmethyl- or Benzene, trimethyl-
000106-46-7	Benzene, 1,4-dichloro-
000108-90-7	Benzene, chloro-
000100-41-4	Benzene, ethyl-
000098-82-8	Benzene, isopropyl-
000078-78-4	Butane, 2-methyl-
000075-15-0	Carbon disulfide

000067-66-3	Chloroform
000110-82-7	Cyclohexane
000108-87-2	Cyclohexane, methyl-
002532-58-3	Cyclopentane, 1,3-dimethyl-, cis-
001759-58-6	Cyclopentane, 1,3-dimethyl-,trans-
001640-89-7	Cyclopentane, ethyl-
000096-37-7	Cyclopentane, methyl-
000000-00-0	Cyclopentane, 1,2-dimethyl- or Cyclobutane, isopropyl-
000079-00-5	Ethane, 1,1,2-trichloro-
000075-34-3	Ethane, 1,1-dichloro-
000156-59-2	Ethene, 1,2-dichloro-, cis-
000075-01-4	Ethene, chloro-
000127-18-4	Ethene, tetrachloro-
000079-01-6	Ethene, trichloro-
000142-82-5	Heptane
000110-54-3	Hexane
000000-00-0	Indene or toluene, p-ethynyl-
000091-20-3	Naphthalene
000119-64-2	Naphthalene, 1,2,3,4-tetrahydro-
000107-83-5	Pentane, 2-methyl-
000096-14-0	Pentane, 3-methyl-
000108-88-3	Toluene
000000-00-0	m- and/or p- Xylene
000095-47-6	o-xylene
000095-50-1	Benzene-1,2-dichloro- (SIM)
000075-25-2	Bromoform (SIM)
000075-35-4	Ethene, 1,1-dichloro- (SIM)
000156-60-5	Ethene, 1,2-dichloro-, trans- (SIM)
000107-06-2	Ethane, 1,2-dichloro- (SIM)
000541-73-1	Benzene-1,3-dichloro- (SIM)
000120-82-1	Benzene-1,2,4-tichloro- (SIM)

Sample type	Treated wastewater
Date & time	9 – 10.06.2016
Description	Individual sample collected in the middle of the second 12 hours of sampling



Number of compounds isolated: **64**

Compounds identified to better than 90%:

CAS#	Name
000000-00-0	1-Propanol, 2-methyl- or 1-Propanol, 2-butanol-
000108-10-1	2-Pentanone, 4-methyl-
000071-43-2	Benzene
000108-90-7	Benzene, chloro-
000100-41-4	Benzene, ethyl-
000098-82-8	Benzene, isopropyl-
000078-78-4	Butane, 2-methyl-
000075-15-0	Carbon disulfide
000067-66-3	Chloroform
000000-00-0	Cyclohexanamine, n-ethyl- or Cyclohexanamine, n,n-dimethyl-
000110-82-7	Cyclohexane
000108-87-2	Cyclohexane, methyl-
000108-94-1	Cyclohexanone
000096-37-7	Cyclopentane, methyl-
000075-34-3	Ethane, 1,1-dichloro-
000107-06-2	Ethane, 1,2-dichloro-
000079-00-5	Ethane, 1,1,2-trichloro-
000075-01-4	Ethene, chloro-
000156-60-5	Ethene, 1,2-dichloro-, trans-
000156-59-2	Ethene, 1,2-dichloro-,cis-
000079-01-6	Ethene, trichloro-
000127-18-4	Ethene, tetrachloro-
000119-64-2	Naphthalene, 1,2,3,4-tetrahydro-
000108-88-3	Toluene

000000-00-0	m- and/or p-Xylene
000095-47-6	o-Xylene
000095-50-1	Benzene-1,2-dichloro- (SIM)
000541-73-1	Benzene-1,3-dichloro- (SIM)
000106-46-7	Benzene-1,4-dichloro- (SIM)
000120-82-1	Benzene-1,2,4-tichloro- (SIM)
000075-25-2	Bromoform (SIM)
000075-35-4	Ethene, 1,1-dichloro- (SIM)
000075-09-2	Methane, dichloro- (SIM)
000124-48-1	Methane, dibromochloro- (SIM)

Note: All compounds in samples SK16003b and SK16004b have been detected only at trace levels, hence no total ion chromatogram is provided below.

Sample code	SK16003b
Location	Duslo, a. s. Industrial site, Trnovec nad Váhom village, District of Šaľa town, Slovakia
Sample type	Treated wastewater
Date & time	9 – 10.06.2016
Description	Individual sample collected in the middle of the second 12 hours of sampling

Number of compounds isolated: 10

Compounds identified to better than 90%:

CAS#	**Name**
000071-43-2	Benzene (SIM)
000106-46-7	Benzene, 1,4-dichloro- (SIM)
000075-25-2	Bromoform (SIM)
000107-06-2	Ethane, 1,2-dichloro- (SIM)
000156-59-2	Ethene, 1,2-dichloro-, cis- (SIM)
000079-01-6	Ethene, trichloro- (SIM)
000127-18-4	Ethene, tetrachloro- (SIM)
000000-00-0	m- and/or p- Xylene (SIM)

Sample code	SK16004b
Location	Duslo, a. s. Industrial site, Trnovec nad Váhom village, District of Šaľa town, Slovakia
Sample type	Treated wastewater
Date & time	9 – 10.06.2016
Description	Individual sample collected in the middle of the second 12 hours of sampling

Number of compounds isolated: 8

Compounds identified to better than 90%:

CAS#	**Name**
000071-43-2	Benzene (SIM)
000106-46-7	Benzene, 1,4-dichloro- (SIM)
000075-25-2	Bromoform (SIM)
000107-06-2	Ethane, 1,2-dichloro- (SIM)
000156-59-2	Ethene, 1,2-dichloro-, cis- (SIM)
000079-01-6	Ethene, trichloro- (SIM)
000127-18-4	Ethene, tetrachloro- (SIM)
000000-00-0	m- and/or p- Xylene (SIM)