Analysis of discharged water, water from the River Cotzacoalcos, and of soil and surface dust collected in the vicinity of the Complejo Petroquimico Pajaritos PVC and related chemicals facility, Veracruz (Mexico) for the presence of metals and organic chemical contaminants following the explosion and fire in April 2016

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Introduction

A total of 10 samples were received from Greenpeace Mexico for analysis at the Greenpeace Research Laboratories on 28th April 2016, including one sample of discharged water, four river water samples, four samples of soil and one of surface dust, all collected between the 23rd and 24th April 2016 in the vicinity of the Complejo Petroquimico Pajaritos chemicals manufacturing facility in Veracruz within days of a major explosion and fire at the site.

A summary of the samples received is provided in Table 1a, together with the GPS coordinates for the sampling locations in Table 1b.

All water samples were analysed qualitatively for the presence of semi-volatile (solvent-extractable) organic compounds, and separately for the presence of volatile organic compounds (VOCs). The concentrations of a number of VOC compounds were also quantified in the water samples. The discharged water sample (MX16012) were also analysed quantitatively for the presence of a range of metals and metalloids. In addition, for the four soil samples and the surface dust sample, the concentrations of polychlorinated dioxins and furans were determined at an accredited independent laboratory.

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Sample code	type	Location	Description
MX16008	river water	River Cotzacoalcos	from location between the confluence with the Arroyo Nuevo Teepa and River Cotzacoalcos estuary
MX16009	river water	River Cotzacoalcos	from location at River Cotzacoalcos estuary
MX16010	river water	River Cotzacoalcos	from location between confluence with the Arroyo Nuevo Teepa and the River Cotzacoalcos estuary
MX16011	river water	River Cotzacoalcos	from location upstream of the confluence of the Arroyo Nuevo Teepa and the River Cotzacoalcos
MX16012	discharged water	discharge pipe	water discharge via a pipe from the facility to the Arroyo Nuevo Teepa
MX16014	soil	Paso elevado	surface soil from a garden, approximately 400m south-west of the facility perimeter
MX16015	soil	Mundo nuevo	surface soil from a garden, approximately 2 km south of the facility
MX16016	soil	Nanchital	surface soil from farm land, approximately 3.5 km south-west of the facility
MX16017	soil	Ixhuatlan	surface soil from a garden, approximately 10 km south south-west of the facility
MX16018	dust	Paso elevado	house roof, approximately 400m south-west of the facility perimeter

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

Sample code	N (º)	W (º)
MX16008	18.13911	94.40583
MX16009	18.14653	94.4135
MX16010	18.11658	94.4155
MX16011	18.11136	94.42519
MX16012	18.10641	94.39832
MX16014	18.10094	94.39606
MX16015	18.08778	94.38831
MX16016	18.07989	94.40783
MX16017	18.02522	94.39436
MX16018	18.10081	94.39628

Table 1b: GPS coordinates of sample collection locations

Materials and methods

All water samples were collected in amber glass bottles. Soil and dust samples were collected in aluminium foil and stored in zip lock plastic bags. All samples were kept cold and dark during shipment to the laboratory in the UK.

Each water sample consisted of two subsamples collected in different types of bottles depending on the subsequent analyses to be carried out. The first subsample was collected in a 0.5 litre screw-cap

glass bottle, for use in the quantitative analysis of metals and metalloids, as well as the qualitative analysis of solvent extractable (semi-volatile) organic compounds. With the exception of the discharged water sample, a second sub-sample was collected in a separate 125 ml amber glass bottle with a ground-glass stopper (filled to leave no headspace) to be analysed for volatile organic chemicals (VOCs) and for metals/metalloids. For the discharged water sample, a second duplicate sample was collected in a 0.5 litre screw-cap glass bottle due to limited availability of bottles with a ground-glass stopper. VOC analysis for discharged water was carried out for both 0.5 litre bottles to check reproducibility, with qualitative analysis of solvent extractable (semi-volatile) organic compounds carried out for 1 of these bottles.

All water samples were analysed qualitatively for semi-volatile organic compounds (sVOCs) and both qualitatively and quantitatively for volatile organic chemicals (VOCs). The discharged water sample was also analysed quantitatively for metals/metalloids. Semi-volatile organic compounds were isolated from each sample using solid phase extraction (SPE) with ethyl acetate, pentane and toluene. Analysis for volatile organic chemicals (VOCs) was conducted on all samples as received (with no pre-treatment) using GC/MS with HeadSpace sample introduction technique. Metal concentrations were determined by ICP mass spectroscopy (ICP-MS) following acid digestion and using appropriate intra-laboratory standards. More detailed descriptions of the sample preparation and analytical procedures are presented in the Appendix 1.

Polychlorinated dioxins and furans in soil and dust samples were quantified at an accredited independent laboratory according to USEPA 1613, using solvent extraction followed by chromatographic clean-up and High Resolution GCMS using the latest Micromass Ultima Autospec instrumentation. Samples were analysed for 17 target dioxin/furan congeners to enable calculation of the I-TEQ value for comparative purposes.

Results and Discussion

The volatile (VOC) and semi-volatile (sVOC, solvent extractable) organic chemicals identified in individual water samples are summarised in Tables 2 and 4 respectively. A full list of semi-volatile organic chemicals identified in each water sample is provided in Appendix 2. Volatile organic compounds (VOCs) quantified in these samples are listed in Table 3. In addition, the concentrations of metals and metalloids in the discharged water sample are reported Table 5. Polychlorinated dioxins and furans identified in the soil and dust samples are presented in Table 6 and Table 7.

Type	Cotzacoalcos River water				discharged water
Location	confluence with Arroyo Nuevo Teepa	river estuary	between confluence & estuary	upstream of confluence	discharge pipe
Sample code	MX16008	MX16009	MX16010	MX16011	MX16012
Number of compounds isolated	12	13	63	0	35
Number of compounds identified to >90%	10	13	30	0	26
Percentage identified to >90%	83%	100%	48%	N.A.	75%
Ethane derivatives:					
Ethane, 1,1-dichloro-		SIM	SIM		✓
Ethane, 1,2-dichloro-	✓	✓	✓		✓
Ethane, 1,1,2-trichloro-	SIM	SIM	✓		✓
Ethane, 1,1,2,2-tetrachloro-			SIM		✓
Ethane, 1-bromo-2-chloro-					
Ethene derivatives:					
Ethene, chloro- (VCM)					✓
Ethene, 1,1-dichloro-		SIM	SIM		✓
Ethene, 1,2-dichloro-, trans-		SIM	✓		✓
Ethene, 1,2-dichloro-, cis-	SIM	SIM	SIM		✓
Ethene, trichloro-		SIM	✓		✓
Ethene, tetrachloro-	SIM		✓		✓
Methane derivatives:					
Methane, dichloro-			SIM		✓
Chloroform			✓		✓
Methane, tetrachloro-		SIM	✓		✓
Bromoform			SIM		SIM
Methane, bromodichloro-			SIM		SIM
Methane, dibromochloro-			SIM		SIM
Benzene & derivatives:					
Benzene	✓	✓			✓
Benzene, chloro-					✓
Benzene, 1,3-dichloro-					SIM
Benzene, 1,4-dichloro-					✓
Benzene, 1,2-dichloro-					✓
Benzene, 1,2,4-trichloro-					✓
m- or p-xylene	✓	SIM	✓		✓
o-xylene	✓	SIM	✓		✓
Styrene	✓	SIM	SIM		SIM
Benzene, ethyl-	✓	SIM			✓
Benzene, diethyl-			1 isomer		
Benzene, ethyl-dimethyl-			1 isomer		
Benzene, 1-ethyl-methyl-, or trimethyl-			4 isomers		
Xylene-ethyl-			1 isomer		
Other VOCs:					
Cyclohexane, methyl-			SIM		
Butane, 2-methyl-	✓				
Propane, 1,2-dichloro-			SIM		
Naphthalene, 1,2,3,4-tetrahydro-methyl-/dimethyl-			3 isomers		

Table 2: summary of volatile organic compounds (VOCs) identified for each water sample (to >90% reliability). SIM indicates detection of trace amounts in the more sensitive Selective Ion Monitoring mode

Sample	MX 16008	MX 16009	MX 16010	MX 16011	MX 16012
VOCs quantified	µg/L				
Ethane derivatives:					
Ethane, 1,1-dichloro-	N.D.	<2	<2	N.D.	15
Ethane, 1,2-dichloro-	12	17	590	N.D.	5900
Ethane, 1,1,2-trichloro-	<2	<2	16	N.D.	260
Ethane, 1,1,2,2-tetrachloro-	N.D.	N.D.	<2	N.D.	12
Ethene derivatives					
Ethene, 1,1-dichloro-	N.D.	<2	<2	N.D.	<2
Ethene, 1,2-dichloro-, trans-	N.D.	<2	<2	N.D.	4.2
Ethene, 1,2-dichloro-, cis-	<2	<2	<2	N.D.	21
Ethene, trichloro-	N.D.	<2	<2	N.D.	4.5
Ethene, tetrachloro-	<2	N.D.	<2	N.D.	18
Methane derivatives					
Methane, dichloro-	N.D.	N.D.	<2	N.D.	<2
Chloroform	N.D.	N.D.	5.9	N.D.	67
Methane, tetrachloro-	N.D.	<2	<2	N.D.	29
Bromoform	N.D.	N.D.	<2	N.D.	<2
Methane, bromodichloro-	N.D.	N.D.	<2	N.D.	<2
Methane, dibromochloro-	N.D.	N.D.	<2	N.D.	<2
Benzene & derivatives					
Benzene	<2	<2	N.D.	N.D.	3.2
Benzene, chloro-	N.D.	N.D.	N.D.	N.D.	<2
Benzene, 1,3-dichloro-	N.D.	N.D.	N.D.	N.D.	<2
Benzene, 1,4-dichloro-	N.D.	N.D.	N.D.	N.D.	<2
Benzene, 1,2-dichloro-	N.D.	N.D.	N.D.	N.D.	<2
Benzene, 1,2,4-trichloro-	N.D.	N.D.	N.D.	N.D.	<2
m- or p-xylene	<4	<4	<4	N.D.	<4
o-xylene	<2	<2	3.1	N.D.	<2
Styrene	<2	<2	<2	N.D.	<2
Benzene, ethyl-	<2	<2	N.D.	N.D.	<2
Other VOCs					
Cyclohexane, methyl-	N.D.	N.D.	<2	N.D.	N.D.

Table 3: VOCs quantification results (unit: µg/L). < xx means the compound is detected in the sample, but the concentration is lower than the corresponding LOQ (limit of quantification). N.D.: not detected in the sample.

3.1 discharged water (MX16012)

3.1.1 Organic contaminants

The sample of discharged water (MX16012) contained a wide range of volatile chlorinated chemicals, many which are either known to be used in the manufacture of PVC or closely related to those chemicals (Stringer et al. 2001, Stringer & Johnston 2002). These were predominantly chlorinated ethanes, chlorinated ethenes, and chlorinated methanes as well as chlorinated benzenes (see Table 2). In addition, a range of semi-volatile organic chemicals were also identified in the discharged water, including polycyclic aromatic hydrocarbons (PAHs), alkyl benzenes and phthalates (see Table 4).

Of the volatile chemicals, by far the predominant chemical was 1,2-dichloroethane, also known as ethylene dichloride (EDC), at 5900 µg/L (see Table 3 for details). This chemical, which is known to be

manufactured at this complex, is used in the manufacturing of vinyl chloride (VCM), the monomer from which PVC is produced.

EDC is a toxic volatile liquid. Inhalation or ingestion can impact the central nervous system, liver, kidneys, lungs and cardiovascular system in humans (ATSDR 2001). EDC is classified by the International Agency for IARC in Group 2B (possibly carcinogenic to humans) and the US Department of Health and Human Services classifies it as reasonably anticipated to be a human carcinogen (USDHHS 2015). In addition, the production of EDC commonly results in the generation of chlorinated toxic distillation residues called heavy ends which are contaminated with polychlorinated dioxins/furans (Stringer & Johnston 2002). EDC is also listed as a Substance of Very High Concern (SVHC) under the EU REACH regulations (ECHA 2013).

Information disclosed under the Mexican Pollutant Release and Transfer Register (PRTR) regulation indicates that this facility also releases substantial quantities of 1,2-dichloroethane (EDC) to air; 567.6 kg of in 2010, 17.52 kg in 2011, 0.003Kg in 2012 and 17.52 Kg in 2013. However, no data is provided in the register for any other releases of EDC, including releases to water (RETC 2016).

Other predominant chlorinated volatiles in the discharged water included examples of chlorinated ethanes (1,1,2-trichloroethane (260 µg/L), 1,1-dichloroethane (15 µg/L) and 1,1,2,2-tetrachloroethane (12 µg/L)), chlorinated ethenes (including *cis*-1,2-dichloroethene (21 µg/L) and tetrachloroethene (18 µg/L)) and chlorinated methanes (trichlorethane also known as chloroform (67 µg/L), and tetrachloromethane (29 µg/L)). In addition, traces of a range of chlorinated benzenes were also identified (see Table 2 & Table 4).

In addition, chloroethene, also known as vinyl chloride monomer (VCM), was identified in the discharged water (MX16012), though quantification data is not currently available.

Some of these chlorinated chemicals have well characterised hazardous properties. Information on some key examples are presented below, though many of the other chemicals which were identified but are not discussed below also posses hazardous properties.

Tetrachloroethene, also known as perchloroethylene (PERC) and tetrachloroethylene, is a well-known environmental contaminant, having been detected in a wide range of matrices, including drinking water (ATSDR 2014). Tetrachloroethene is primarily toxic to the central nervous system, with other effects including toxicity to the kidney, liver and reproductive system (ATSDT 2014). Tetrachloroethene is also classified as Group 2A carcinogen (probably carcinogenic to humans) by the International Agency for Research on Cancer, and reasonably anticipated to be a human carcinogen by the US Department of Health and Human Services (USDHHS 2015).

Chloroform and tetrachloromethane have both been specified by the International Agency for Research on Cancer as Group 2B chemicals (possibly carcinogenic to humans) and reasonably anticipated to be a human carcinogen by the US Department of Health and Human Services (USDHHS 2015), and both also have other addition toxic properties.

Though not directly applicable to this facility, limits in the United States for wastewaters discharged by the plastics sector provide a useful comparison. The concentration of EDC in the water was far

higher than would be permissible under US limits, which sets a daily maximum of 211 µg/L (for sources that use end-of-pipe biological treatment) and 574 µg/L (for sources that do not use end of-pipe biological treatment) (US GPO 2000). The EDC concentrations in the discharged water sample were 28 times, and 10 times these two limits, respectively. Similarly, the concentration of 1,1,2-trichloroethane (260 µg/L) was higher than the daily maximum limits of 54 and 127 µg/L allowable in the US for sources that use, and do not use, end-of-pipe biological treatment, respectively.

Continuing with those comparisons for illustrative purposes, the concentrations of chloroform (67 µg/L) were higher than the daily maximum limits for sources that use end-of-pipe biological treatment (46 µg/L), though below that for facilities which do not (325 µg/L), while those of tetrachloromethane, also known as carbon tetrachloride (29 µg/L) were just below the US daily maximum limits of 38 and 56 µg/L for these 2 types of facilities, respectively.

Type	Cotzacoalcos River water				discharged water
Location	confluence with Arroyo Nuevo Teepa	river estuary	between confluence & estuary	upstream of confluence	discharge pipe
Sample code	MX16008	MX16009	MX16010	MX16011	MX16012
Number of compounds isolated	3	19	150	5	81
Number of compounds identified to >90%	3	15	61	3	32
Percentage identified to >90%	100%	79%	41%	60%	40%
Phthalates:					
Dimethyl phthalate		1	1	1	1
Diethyl phthalate	1	1	1	1	1
Diisobutyl phthalate	1	1	1	1	1
Dibutyl phthalate		1			1
PAHs:					
Anthracene & derivatives			3		
9H-Fluorene & derivatives			5		1
Fluoranthene			1		1
Naphthalene & derivatives			14		1
Pyrene			1		1
Phenanthrene & derivatives			1		1
Chlorinated compounds:					
Dichlorobenzenes					2
Trichlorobenzenes					2
Tetrachlorobenzenes					2
Chlorinated butanes/butenes					3
Chlorinated propanes/propenes					3
Chlorinated ethanes & derivatives					1
Other compounds:					
Phenol & derivatives	1		1		
Nonylphenol isomers		9			
1H-Indene/Indane & derivatives		2	10		3
1H-Benzotriazole & derivatives			1		3
1,1'-Biphenyl & derivatives			2		
Acetophenone			1		
Alkylated benzenes			14		1
5-Phenylbicyclo[2.2.1]hept-2-ene			1		
Quinolone & derivatives			2		1

Phenylpropylene oxide			1		
Phosphoric acid, triethyl ester					1

Table 4: summary of organic contaminants for each sample in which semi-volatile (solvent extractable) organic compounds (SVOCs) were identified (to >90% reliability).

In addition to the volatile organic chemicals (VOCs), a range of semi-volatile organic chemicals were also identified in the discharged water, including polycyclic aromatic hydrocarbons (PAHs), alkyl benzenes and phthalates (see Table 4). PAHs and alkyl benzenes are commonly found as products of incomplete combustion, or due to their presence in crude oil and petroleum products (ATSDR 1995, Dagaut & Cathonnet 2006). PAHs are widespread environmental contaminants and some PAHs have been classified by the International Agency for IARC in Group 2B (possibly carcinogenic to humans). The US Department of Health and Human Services classifies some PAHs as reasonably anticipated to be a human carcinogen (USDHHS 2015).

In a previous study, samples were collected in the vicinity of this facility in 2000 and 2001, during normal operations (Stringer et al. 2001). Two samples from this previous study (AM0150 & AM0151) were collected from 2 adjacent pipes in the same location as a single pipe found to be discharging water to the Arroyo Nuevo Teepa that was sampled for the current investigation (MX16012).

One of these samples (AM0150) contained a similar contaminant composition to that found in the current study (MX16012), including EDC at 7500 µg/L, a similar concentration to that in MX16012. Other chlorinated chemicals were also present in similar concentrations to the current study, including chloroform (130 µg/L; 67 µg/L in the current study), carbon tetrachloride (40 µg/L; 29 µg/L in the current study) and tetrachloroethene (60 µg/L; 18 µg/L in the current study). In addition, chlorinated benzenes and PAHs were also identified in the discharged water collected in 2000 (AM0150).

3.1.2 Metals

sample type	discharged water, whole (µg/l)
location	discharge pipe
Sample code	MX16012
Arsenic	1.0
Barium	124
Cadmium	1.04
Chromium	2.2
Cobalt	5.0
Copper	22.0
Iron	552
Lead	<5
Manganese	269
Mercury	<0.5
Nickel	11
Strontium	265

Vanadium	0.92
Zinc	480

Table 5: Concentrations of metals and metalloids in whole discharged water sample (µg/l)

The concentrations of metals/metalloids in the discharged water (MX16012) were not unusual for uncontaminated surface waters, with the exception of zinc (480 µg/l) and to a lesser extent copper (22.0 µg/l). Concentrations of zinc in uncontaminated surface waters are typically below 50 µg/l (ATSDR 2005, Salomons & Forstner 1984), while those of copper are typically below 10 µg/l, and often far lower (ATSDR 2004, Comber *et al.* 2008). Copper and zinc were also found in high concentration in water discharged from a pipe in the same location in 2000 (AM0150), being notably higher than for the current study; 110 µg/l copper and 5048 µg/l zinc.

3.2 River

3.2.1 Organic contaminants

No VOCs were detected in the river water upstream of the Arroyo Nuevo Teepa (MX16011), in which only 3 phthalates were detected (of unknown origin)

River water collected at the point where the Arroyo Nuevo Teepa joins the River Cotzacoalcos (MX16010) contained many of the VOCs detected in the discharge water (MX16012), including chlorinated ethanes, chlorinated ethenes and chlorinated methanes (see Tables 2 & 3). The predominant volatile chlorinated chemicals in the discharged water (MX16012) were also the predominant volatile chlorinated chemicals in this river water sample, though at concentrations 10-20 times lower than in the discharged water. The concentration of EDC in this sample was 590 µg/L (see Table 3 for details).

Two other samples of river water were collected from the River Cotzacoalcos; one (MX16008) from a location between the confluence of the Arroyo Nuevo Teepa and the River Cotzacoalcos estuary, and the other (MX16009) at the estuary of the River Cotzacoalcos. Both samples contained examples of volatile organic chemicals including chlorinated ethanes, chlorinated ethenes and alkyl benzenes, though the concentrations of VOCs were far lower than in the discharged water (MX16012) or river water collected at the confluence with the Arroyo Nuevo Teepa (MX16010). EDC was nonetheless still detectable, at 12 and 17 µg/L for MX16008 and MX16009 respectively.

Some sVOCs were detected in these two river water samples (see Table 4), though the only compounds that were present in these river water samples and in the discharged water (MX16012) were 2 phthalates, which were also detected in river water collected upstream of the confluence with the Arroyo Nuevo Teepa (MX16011).

In the 2001 study of this site, river water was not collected from the location sampled for the current study (Stringer et al. 2001).

3.3 Soils and surface dusts

Sample	MX16014	MX16015	MX16016	MX16017	MX16018
Type	soil	soil	soil	soil	dust
Direction from facility	SW	S	SW	SSW	SW
Distance (Km)	0.4	2	3.5	10	0.4
Congeners	Concentration, ng/kg				
2378-TCDF	0.385	0.243	**n/d**	**n/d**	0.681
12378-PCDF	0.428	0.456	0.229	**n/d**	1.18
23478-PCDF	0.382	0.398	0.219	0.205	1.46
123478-HxCDF	0.828	0.605	0.282	0.312	3.44
123678-HxCDF	0.485	0.425	0.248	0.234	3.64
234678-HxCDF	0.629	0.522	0.242	0.285	4.09
123789-HxCDF	0.179	**n/d**	**n/d**	**n/d**	0.344
1234678-HpCDF	5.54	3.26	1.35	0.938	45
1234789-HpCDF	0.794	0.449	0.258	0.125	2.98
OCDF	20.7	7.24	3.39	0.567	63.3
2378-TCDD	**n/d**	**n/d**	**n/d**	**n/d**	0.238
12378-PCDD	**n/d**	0.354	**n/d**	**n/d**	1.04
123478-HxCDD	0.505	0.492	0.267	**n/d**	1.19
123678-HxCDD	1.14	1.24	0.54	0.287	1.98
123789-HxCDD	0.978	1.01	0.634	0.243	1.75
1234678-HpCDD	35	23.9	13.9	3.71	43.7
OCDD	393	175	620	65.6	387

Table 6: Concentrations of polychlorinated dioxins & furans identified in the soil and dust samples MX16014-MX16018

Sample Code	Type	Direction from facility	Distance (Km)	Concentration ∑PCDFs, ng/kg	Concentration ∑PCDDs, ng/kg	ng TEQ[1] /kg	ng TEQ[2] /kg
MX16014	Soil	SW	0.4	30.35	430.623	1.69	1.18
MX16015	Soil	S	2	13.598	201.996	1.41	1.27
MX16016	Soil	SW	3.5	6.218	635.341	1.08	0.64
MX16017	Soil	SSW	10	2.666	69.84	0.67	0.27
MX16018	Surface dust	SW	0.4	126.115	436.898	4.52	4.52

Table 7: Summed concentrations of polychlorinated dioxins & furans identified in the soil and dust samples MX16014-MX16018, and their WHO-2005 Toxic Equivalent Values (TEQ):
TEQ[1] calculated with concentrations of non-detected congeners set at detection limits

TEQ[2] calculated with concentrations of non-detected congeners set at zero

3.3.1 polychlorinated dioxins and furans

The concentrations of polychlorinated dioxins and furans in the soils samples ranged from 0.67-1.69 ng TEQ/kg, taking the concentration of non-detected congeners at detection limit, or 0.27-1.27 ng TEQ/kg, taking the concentration of non-detected congeners at zero (See Table 7).

Concentrations did decrease with distance from the facility; from 1.69 ng TEQ/kg at 0.4 km from the facility (MX16014) to 0.67 ng TEQ/kg at 10 km from the facility (MX16017). The concentrations in all samples, however, are within the ranges typically found in uncontaminated soils, which are typically below 10 ng TEQ/kg (Zhu et al. 2008, Paustenbach et al. 2006).

The concentration in the surface dust (MX16018) collected 0.4 km from the facility (MX16018) was 4.52 ng TEQ/kg. Though somewhat higher than that for the soil samples from the same location (MX16014, 1.69 ng TEQ/kg), the dust concentration is still within the ranges typically found in uncontaminated soils. The higher concentration in the dust may be due in part to less mixing of deposited material with other materials onto which it is deposited, such as soil.

Though the soil and surface dust samples were collected in the direction in which the plume from the recent fire travelled, it is not possible to know whether the decrease in concentrations with distance from the facility is a result of deposition of materials generated during the recent fire, due to long term releases from the facility during normal operations, or a combinations of both. Due to the limited number of samples, including samples from locations in other directions from the facility, it is not possible to determine whether the concentrations determined are typical for the area.

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Appendix 1: Details of methodologies

Analysis for Volatile Organic Compounds (VOCs)

Methods

VOCs were analysed using an Agilent 7890B gas chromatograph with a Restek Rxi-624Sil column (30m, 0.25mm ID, 1.4µm film thickness) connected to an Agilent 7697A Headspace Sampler and linked to an Agilent 5977A MSD operated in EI mode. The GC oven temperature program included an initial temperature of 43^0C (held for 4min), rising to 55^0C at 5^0C/min, and then to 210^0C at 15^0C/min (held for 2.5min). The carrier gas was helium, supplied at 1.5 ml/min. From each sample, three 10ml portions were sub-sampled into 20ml headspace vials with 3g of anhydrous sodium sulfate (analytical reagent grade). 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. At the same time, the sample was also analysed with the GC-MS in selective ion monitoring (SIM) to match against those obtained during GC-MS analysis of standard mixtures containing a range of aromatic volatile organic compounds and haloalkanes volatile organic compounds. The two remaining sub-samples were then used for duplicate quantitative analysis for some of those VOCs which had been detected in the samples through screening. Quantification was performed in Selective Ion Monitoring (SIM) mode using a 4 point internal standard method. VOCs quantified in the samples with limits of quantification are presented in Table A1 below.

Quality control

Method detection limits (MDL) were obtained using data of 7 replicas of standard solution (at 4 ppb for m- & p- xylene, at 2 ppb for all the other compounds) 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 (with 3g of anhydrous sodium sulfate (analytical reagent grade))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	LOQ	r^2
Ethene, 1,1-dichloro-	0.6	2.0	0.998
Methane, dichloro-	0.2	2.0	0.999
Ethene, 1,2-dichloro-, trans-	0.4	2.0	0.999
Ethane, 1,1-dichloro-	0.3	2.0	0.999
Ethene, 1,2-dichloro-, cis-	0.2	2.0	0.999
Chloroform	0.3	2.0	0.999
Methane, tetrachloro-	0.7	2.0	0.999
Benzene	0.3	2.0	0.999
Ethane, 1,2-dichloro-	0.5	2.0	0.999
		200.0	0.995
Ethene, trichloro-	0.4	2.0	0.999
Cyclohexane, methyl-	0.6	2.0	0.999
Methane, bromodichloro-	0.3	2.0	0.999
Ethane, 1,1,2-trichloro-	0.3	2.0	0.999
		200.0	0.994
Ethene, tetrachloro-	0.6	2.0	0.998
Methane, dibromochloro-	0.9	2.0	1.000
Benzene, chloro-	0.3	2.0	0.999
Benzene, ethyl-	0.3	2.0	0.999
m- or p-xylene	0.5	4.0	0.999
o-xylene	0.2	2.0	0.999
Styrene	0.3	2.0	0.999
Bromoform	1.4	2.0	0.999
Ethane, 1,1,2,2-tetrachloro-	0.4	2.0	0.999
Benzene, 1,3-dichloro-	0.3	2.0	0.999
Benzene, 1,4-dichloro-	0.5	2.0	0.999
Benzene, 1,2-dichloro-	0.4	2.0	0.999
Benzene, 1,2,4-trichloro-	1.2	2.0	0.999

Table A1. Method detection limits (MDL) and limits of quantification (LOQ) (which is the lowest concentration in the linear regression (r^2 – corresponding correlation coefficient) used for quantification) of compounds being identified & quantified in the samples. (note: For the compounds Ethane, 1,2-dichloro- and Ethane, 1,1,2-trichloro-, calibration were carried out in 2 ranges, i.e. 2 ppb-100ppb, as well as 200ppb-8ppm, to accommodate the wide differences in levels of concentration in the samples)

Analysis for extractable organic compounds

Preparation

20 µg of deuterated naphthalene was added as an Internal Standard (IS) to each portion of sample that was subject to extraction. 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) 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 7890B GC with Restek Rxi-17Sil MS column (30m, 0.25mm ID, 0.25 µm film thickness) linked to an Agilent 5977A MSD operated in EI mode and interfaced with an Agilent Mass Hunter system. The GC oven temperature program employed was as follows: an initial temperature of 40^0C, raised to 260^0C at 10^0C/min, then to 295^0C at 50^0C/min (held for 15min), and finally to 320^0C at 50^0C/min (held for 12min). The carrier gas was helium, supplied at 1ml/min. Identification of compounds was carried out by matching spectra against the Wiley 7N Library, 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 the sample was acidified by the addition of concentrated nitric acid to give a final concentration of 5% v/v. 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 500 μg/l (Scandium, Germanium, Yttrium, Indium and Terbium).

Quality control

To check for reproducibility, two subsamples of the discharged water were analysed separately. In addition, a blank sample was digested and analysed, as well as two mixed metal quality control solution of 80 and 800 μg/l for each metal, other than mercury at 4 and 16 μg/l. 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 analytical screening data

Detailed screening data arising from GC-MS analysis of solvent extracts of each of the samples are presented below. These data list only those semi-volatile organic compounds identified following solvent extraction and do not include any volatile organic compounds (VOCs) identified through separate headspace GC-MS analysis of sub-samples; the VOCs identified in each sample are listed in Table 2 in the main body of the report. Only those semi-volatile substances identified to greater than 90% quality match (following verification by expert interpretation) are listed here.

MX16008
River water

Number of compounds isolated: 3

Compounds identified to better than 90%:

CAS#	Name
000084-66-2	1,2-Benzenedicarboxylic acid, diethyl ester
000084-69-5	1,2-Benzenedicarboxylic acid, diisobutyl ester
000108-95-2	Phenol

MX16009
River water

Number of compounds isolated: 19

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
000084-74-2	1,2-Benzenedicarboxylic acid, dibutyl ester
000084-69-5	1,2-Benzenedicarboxylic acid, diisobutyl ester
000083-33-0	1H-Inden-1-one, 2,3-dihydro-
000095-13-6	1H-Indene
084852-15-3	Phenol, nonyl-, mixture of 9 isomers

MX16010
River water

Number of compounds isolated: 150

Compounds identified to better than 90%:

CAS#	Name
000092-52-4	1,1'-Biphenyl
000643-93-6	1,1'-Biphenyl, 3-methyl-
000082-86-0	1,2-Acenaphthylenedione
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
000081-84-5	1,8-Naphtalic anhydride
004780-79-4	1-Naphthalenemethanol
000518-86-5	1H,3H-Naphtho[1,8-cd]pyran-1-one
000000-00-0	1H-Benzotriazole, 4-methyl-
006351-10-6	1H-Inden-1-ol, 2,3-dihydro-
000083-33-0	1H-Inden-1-one, 2,3-dihydro-
000824-22-6	1H-Indene, 2,3-dihydro-4-methyl-
001075-22-5	1H-Indene, 2,3-dihydro-5,6-dimethy
004505-48-0	1H-Indene, 2-phenyl-
035465-71-5	2-Phenylnaphthalene
000615-13-4	2H-Inden-2-one, 1,3-dihydro-
000000-00-0	4-Methyl-1-indanone
006143-30-2	5-Phenylbicyclo[2.2.1]hept-2-ene
000084-65-1	9,10-Anthracenedione
001689-64-1	9H-Fluoren-9-ol
000486-25-9	9H-Fluoren-9-one
000086-73-7	9H-Fluorene
001430-97-3	9H-Fluorene, 2-methyl-
001556-99-6	9H-Fluorene, 4-methyl-
000098-86-2	Acetophenone
000120-12-7	Anthracene
000613-12-7	Anthracene, 2-methyl-
065051-83-4	Benzene, (1-methyl-2-cyclopropen-1-yl)-
000612-00-0	Benzene, 1,1'-ethylidenebis-
000526-73-8	Benzene, 1,2,3-trimethyl-
000095-93-2	Benzene, 1,2,4,5-tetramethyl-
000095-63-6	Benzene, 1,2,4-trimethyl-
000108-67-8	Benzene, 1,3,5-trimethyl-
000100-80-1	Benzene, 1-ethenyl-3-methyl-
000622-97-9	Benzene, 1-ethenyl-4-methyl-
000611-14-3	Benzene, 1-ethyl-2-methyl-
000620-14-4	Benzene, 1-ethyl-3-methyl-
000535-77-3	Benzene, 1-methyl-3-(1-methylethyl
001758-88-9	Benzene, 2-ethyl-1,4-dimethyl-
000934-80-5	Benzene, 4-ethyl-1,2-dimethyl-
000230-27-3	Benzo[h]quinoline
000206-44-0	Fluoranthene
000767-58-8	Indan, 1-methyl-
000496-11-7	Indane
000000-00-0	Indenol
000119-65-3	Isoquinoline
003877-19-8	Naphthalene, 1,2,3,4-tetrahydro-2-methyl-

002809-64-5	Naphthalene, 1,2,3,4-tetrahydro-5-methyl-
001076-61-5	Naphthalene, 1,2,3,4-tetrahydro-6,7-dimethtyl-
002717-44-4	Naphthalene, 1,2-dihydro-3-methyl-
000575-41-7	Naphthalene, 1,3-dimethyl-
000090-12-0	Naphthalene, 1-methyl-
000581-40-8	Naphthalene, 2,3-dimethyl-
000581-42-0	Naphthalene, 2,6-dimethyl-
000091-57-6	Naphthalene, 2-methyl-
000085-01-8	Phenanthrene
000095-48-7	Phenol, 2-methyl-
014212-54-5	Phenylpropylene oxide
000129-00-0	Pyrene
000100-42-5	Styrene

MX16011
River water

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

MX16012
Discharged water

Number of compounds isolated: 81

Compounds identified to better than 90%:

CAS#	Name
000000-00-0	1,1-Dichloro-2-chloromethyl-cyclopropane
000084-74-2	1,2-Benzenedicarboxylic acid, dibutyl ester
000084-69-5	1,2-Benzenedicarboxylic acid, diisobutyl ester
000084-66-2	1,2-Benzenedicarboxylic acid, diethyl ester
000131-11-3	1,2-Benzenedicarboxylic acid, dimethyl ester
004749-27-3	1-Propene, 3,3,3-trichloro-2-methyl-
000095-14-7	1H-Benzotriazole
000000-00-0	1H-Benzotriazole, 4-methyl-
000136-85-6	1H-Benzotriazole, 5-methyl-
000083-33-0	1H-Inden-1-one, 2,3-dihydro-
000874-35-1	1H-Indene, 2,3-dihydro-5-methyl-

000203-64-5	4H-Cyclopenta[def]phenanthrene
001430-97-3	9H-Fluorene, 2-methyl-
000634-66-2	Benzene, 1,2,3,4-tetrachloro-
000634-90-2	Benzene, 1,2,3,5-tetrachloro-
000087-61-6	Benzene, 1,2,3-trichloro-
000120-82-1	Benzene, 1,2,4-trichloro-
000095-50-1	Benzene, 1,2-dichloro-
000106-46-7	Benzene, 1,4-dichloro-
000620-14-4	Benzene, 1-ethyl-3-methyl-
042525-60-0	Butane, 1,2,2,4-tetrachloro-
030028-27-4	Butane, trichloro-
000111-44-4	Ethane, 1,1'-oxybis[2-chloro-
000206-44-0	Fluoranthene
000630-01-3	Hexacosane
000496-11-7	Indane
000090-12-0	Naphthalene, 1-methyl-
000000-00-0	Pentachlorobutene
000078-40-0	Phosphoric acid, triethyl ester
018495-30-2	Propane, 1,1,2,3-tetrachloro-
000129-00-0	Pyrene
000091-22-5	Quinoline