

Case study: PCDDs/PCDFs, PCBs and other organic contaminants in soil and ash samples from the scene of a fire at a hazardous waste dumpsite in Poland

Labunska I¹, Johnston PA¹, Casado J¹, Brigden K¹, Wang M¹, Santillo D¹

¹Greenpeace Research Laboratories, Innovation Centre Phase 2, Rennes Drive, University of Exeter, Exeter, EX4 4RN, United Kingdom, Iryna.Labunska@greenpeace.org

Introduction

6 soil samples and 3 ash samples were collected on 06.09.2018, from the grounds of a hazardous waste dumpsite located in Jakubów, Radwanice (Lower Silesia), Poland, after several fires including at least one of a significant scale which took two days to bring under control and extinguish. At the time, the site was thought to be storing an estimated 1700 pallets of containers, including DPPL containers (intermediate bulk containers – 1000 litres), metal barrels (200 litres) and other containers with capacities up to several tens of litres. In 2016, the Polish Environmental Protection services¹ confirmed that the dumpsite was being used to store a wide variety of wastes, including paints and varnishes containing solvents or other dangerous substances, aqueous suspensions of paints/varnishes, printing toner, adhesives and sealants, sludges of printing inks, emulsions and solutions from metalworking, engine/gear/lubricating oils, packaging formerly used to contain hazardous substances, sorbents, and plastics.



The objective of the work reported here was to investigate the types of contaminants present in a number of samples of soils, ashes and other solid materials within the areas of the site affected by fire (see Table 1), including analysis of a subset of the samples for contamination with PCDDs/PCDFs and PCBs.

Sample code	Sample type	Sampling location	N (degree)	E (degree)
PL18001	Soil & ash	soil wetted with wastewater from fire suppression actions	51.59652	16.00472
PL18002	Soil & ash	bottom of the mound of earth (a hill that existed before the fire), just next to the firemen's wastewater flow	51.59669	16.0051
PL18003	Soil & ash	burnt area formerly covered in vegetation in central part of the dumpsite	51.59637	16.00534
PL18004	Soil & ash	soil from flat ground opposite to a large mound of burnt down trash; area that was probably cleaned after fire	51.59622	16.00475
PL18005	Soil & ash	ground in the forest that remained in central part of the dumpsite, just next to the warehouse that was burnt to the ground	51.59589	16.00566
PL18006	Soil & slime	soil wetted with wastewater from fire suppression actions, in the forest outside the dumpsite	51.59716	16.00371
PL18007	Ash	pile of ash taken from under burnt metal barrels	51.59665	16.00371
PL18008	Ash	pile of ash taken from under burnt/melted plastic canisters and dislocated burnt metal barrels	51.59661	16.00575
PL18009	Ash	pile of burnt/melted trash, possibly roofing felts or other kind of construction material	51.59601	16.00663

Table 1: Details of samples and GPS co-ordinates, chemical dumpsite at Jakubów, Radwanice (Lower Silesia).

Materials and methods

Samples were collected into 100 mL screw-cap glass bottles (to a depth of about 5 cm for soils and from the ground surface for ashes) using a pre-cleaned stainless steel spatula or trowel. Prior to collection, bottles were cleaned with detergent, rinsed with tap and deionised water followed by soaking in 10% nitric acid, rinsing in deionised water and drying in an oven at approximately 100°C, before rinsing three times with analytical grade pentane. Samples were kept cool and dark during transportation to the laboratory. Upon arrival to the laboratory, samples were subjected to qualitative forensic screening of semi-volatile organic compounds (sVOCs) using GC-MS, following solvent extraction of the samples using an Accelerated Solvent Extraction (ASE) system with a mixture of pentane and acetone (3:1). Extracts were treated with water solution of tetrabutylammonium sulphite to remove elemental sulfur. After the separation of the extracted compounds between organic (e.g., pentane) and aqueous phases, the latter was further extracted into methanol using a Solid Phase Extraction (SPE) technique. Extracted compounds were subsequently identified as far as possible using gas chromatography/mass spectrometry (GC/MS) operated in SCAN mode and using liquid chromatography-Orbitrap-mass spectrometry (LC-Orbitrap-MS) to screen for a range of target and non-target chemicals. Further details of the methods employed can be found in an online analytical report.² On the basis of the results obtained from the GC/MS screening, two samples were selected for analysis for chlorinated dioxins/furans and PCBs, which was subsequently carried out by Marchwood Scientific Services, Southampton, UK.

Results and Discussion

The organic chemicals isolated and, as far as possible, identified in the qualitative forensic analyses are tabulated by group in Table 2. The online report referred to above includes specimen chromatograms and detailed lists of the organic chemicals that were identified in each sample using GC-MS analysis, together with a selection of images from the dumpsite.

Sample Code	PL18001	PL18002	PL18003	PL18004	PL18005	PL18006	PL18007	PL18008	PL18009
Sample type	soil	soil	soil	soil	soil	soil	ash	ash	ash
Number of sVOCs isolated	97	194	114	455	159	399	341	251	357
Number of sVOCs identified to >90%	39	67	39	125	62	120	104	89	108
Percentage of sVOCs identified to > 90%	40%	35%	34%	27%	39%	30%	30%	35%	30%
Chlorinated compounds	11	20	6	89	22	16	2	10	11
Nitrogen-containing chlorinated	nd	2	nd	3	nd	1	1	nd	nd
Nitrogen-containing compounds	nd	4	1	1	nd	5	2	5	7
Phosphorus-containing chlorinated	nd	3	nd	2	nd	3	3	2	nd
Phosphorus-containing compounds	nd	2	1	nd	2	2	nd	nd	nd
Phthalates, adipates & relative	3	7	1	1	2	1	30	7	nd
Carboxylic/fatty acids and derivatives	1	6	2	9	8	15	17	15	8
Phenol and its derivatives	nd	6	nd	2	1	7	4	8	2
PAHs and their derivatives	nd	2	1	nd	4	1	1	nd	15
Alcohols & their derivatives	nd	1	1	2	1	9	5	3	nd
Aldehydes & ketones	nd	2	nd	2	3	7	6	3	2
Alkylated benzenes	7	2	4	nd	3	21	2	2	19
Linear & branched aliphatic	15	7	19	8	13	18	24	27	31
Indane/Indene and derivatives	2	nd	2	nd	1	3	1	2	2
1,1'-Biphenyl and its derivatives	nd	1	nd	1	nd	4	1	1	9
Cholestane and derivatives	nd	1	nd	2	1	1	1	1	nd
Other compounds	nd	3	1	3	1	9	5	2	1

Table 2: Summary of results of organic compounds analysis (numbers of individual compounds isolated) in samples determined by GC/MS. nd – not detected

The percentage of the organic compounds present that could be reliably identified varied from sample to sample, in the range from only 27% (sample PL18004) to 40% (sample PL18001). In all cases, therefore, the identity of the majority of organic compounds isolated could not be reliably determined, even through application of the advanced environmental forensic screening techniques outlined here.

Those organic compounds that could be identified were represented by a diverse range of toxic chemicals, with chlorinated compounds being the most common; for example, sample PL18004 contained 89 identifiable organochlorine compounds, 3 nitrogen-containing organochlorine compounds, and 2 phosphorous-containing organochlorine compounds, which together represented 74% of all reliably identified compounds in this sample. It is important to note that organic chemicals detected in samples in this study could have arisen not only from the waste stocks localised at this dump site, but also as a result of thermal degradation and incomplete combustion of toxic wastes during the fires.

Sample Nr	PL18004	PL18006		PL18004	PL18006
Congener	Conc, ng/kg	Conc, ng/kg	WHO 2005 TEF ³	Conc, ppt TEQ	Conc, ppt TEQ
2378-TCDF	71.1	45.3	0.1	7.11	4.53
12378-PCDF	112	57.9	0.03	3.36	1.74
23478-PCDF	235	139	0.3	70.50	41.70
123478-HxCDF	1260	712	0.1	126.00	71.20
123678-HxCDF	253	158	0.1	25.30	15.80
234678-HxCDF	242	185	0.1	24.20	18.50
123789-HxCDF	85.1	47.5	0.1	8.51	4.75
1234678-HpCDF	1620	1290	0.01	16.20	12.90
1234789-HpCDF	1930	1020	0.01	19.30	10.20
OCDF	27600	21700	0.0003	8.28	6.51
Total 2,3,7,8-Furans	33400	25300		308.76	187.83
Congener	Conc, ng/kg	Conc, ng/kg	WHO 2005 TEF ³	Conc, ppt TEQ	Conc, ppt TEQ
2378-TCDD	0	0	1	0.00	0.00
12378-PCDD	0	0	1	0.00	0.00
123478-HxCDD	0	13.7	0.1	0.00	1.37
123678-HxCDD	0	0	0.1	0.00	0.00
123789-HxCDD	0	0	0.1	0.00	0.00
1234678-HpCDD	70.4	70.2	0.01	0.70	0.70
OCDD	460	625	0.0003	0.14	0.19
Total 2,3,7,8-Dioxins	530	709		0.84	2.26
Congener	Conc, ng/kg	Conc, ng/kg	WHO 2005 TEF ³	Conc, ppt TEQ	Conc, ppt TEQ
PCB-81	1870	1080	0.0003	0.56	0.32
PCB-77	9980	7320	0.0001	1.00	0.73
PCB-123	2350	1420	0.00003	0.07	0.04
PCB-118	80900	44800	0.00003	2.43	1.34
PCB-114	3930	2340	0.00003	0.12	0.07
PCB-105	25600	13300	0.00003	0.77	0.40
PCB-126	2140	1800	0.1	214.00	180.00
PCB-167	20500	11700	0.00003	0.62	0.35
PCB-156	34300	18800	0.00003	1.03	0.56
PCB-157	6020	3270	0.00003	0.18	0.10
PCB-169	673	623	0.03	20.19	18.69
PCB-189	10800	6740	0.00003	0.32	0.20
Total PCBs				241.28	202.82
Total TEQ				550.88	392.90

Table 3. Results of analysis for chlorinated dioxins and dioxin-like PCBs expressed in absolute quantities and as WHO TEQs (all as ng/kg, or ppt).

Additional targeted screening using LC-MS to complement the GC-MS analyses described above identified eleven different substances across the nine analysed samples. Two polyfluorinated surfactants were found, including PFBS in sample PL18006 and PFOS in samples PL18002, PL18006, PL18007 and PL18008. Five different phthalate plasticizers were also identified through the LC-MS analysis, including BBP, DMEP, DPP, DIHP and TCEP, the latter one being present in all the samples. Benzotriazole and tolyltriazole, both used as corrosion inhibitors, were also found in all the samples. In addition, two derivatives of benzotriazole, XTri (another corrosion inhibitor), and UV P (a photodegradation inhibitor), were present in samples PL18006 and

PL18007, and in samples PL18002, PL18006 and PL18007, respectively. In parallel, in addition to the non-targeted screening approach, another set of sixteen substances was found using more targeted LC-MS analysis, to complement further the analyses described above. Four pesticides were identified in this way as contaminants in the group of samples, including imidacloprid (found in eight of the samples), thiamethoxam, DMST and DEET, the latter being present in all the samples. Nine components of industrial products, including triphenylphosphine oxide, abietic acid, DEHA, a plasticiser, the plasticizer Ciproflex A4 and five chemicals used for the production of polymers, including caprolactam, PPG n7, PPG, n8, PPG, n9 and PPG n10. The four latter compounds were present in 8 of the samples. One personal care product ingredient used as a sunscreen (7-Hydroxycoumarine), and a metabolite of palmitic acid, which is used to produce soaps and cosmetics, were present in 7 and 4 of the samples, respectively.

Finally, the endogenous lipid oleoyl ethanolamide was present in some of the samples. One compound, benzotriazole, was detected by both complementary LC-MS methods, i.e. both the targeted and the non-targeted screening. In total, the samples containing highest number of substances in the aqueous phase of the samples' extracts were PL18007, with 25, followed by sample PL18006, with 24, and samples PL18002 and PL18008, with 22 substances.

Results from the analysis of chlorinated dioxin and dioxin like PCBs carried out at Marchwood Scientific Services are reproduced in Table 3 above. The two samples contained 550.88 and 392.90 ng kg⁻¹TEQ respectively of chlorinated dioxins, dibenzofurans and dioxin-like PCBs combined, with the TEQs dominated in both samples by the contribution from furans and PCBs. This implies that there may be serious hotspots of contamination on the site. It is possible that this contamination may have arisen as a result of the incomplete combustion of the organochlorine chemicals present in the waste stockpile. Given the preponderance of dioxin-like PCBs and chlorinated dibenzofuran congeners, it is also possible that this dumpsite has at some stage been used to store or dispose of PCB technical mixtures. As has been known for many years, such mixtures can be contaminated with chlorinated dibenzofurans, as a result of their formation during manufacture or usage of PCBs.⁴

Irrespective of the sources of these contaminants, the TEQ-based levels of PCDDs/PCDFs and PCBs found in our study are comparable with those found in the vicinity of sites where e-wastes are known to have been burned under uncontrolled conditions (Suzuki *et al.* 2016).⁵ Background levels in soils are generally one to two orders of magnitude lower⁶⁻⁷ than those detected in our study.

Overall, the current study has shown that soils and ashes collected during July and August 2018 from areas of a chemical dumpsite located in Jakubów, Radwanice (Lower Silesia), Poland, that have been affected by several large-scale fires, are highly contaminated by a diverse range of toxic organic contaminants, including persistent organic pollutants, either as a result of the storage of such chemicals on site or their subsequent formation as products of incomplete combustion during the fires. This site must be subject with some urgency to more detailed investigations and analytical characterisation in order to determine the precise nature, extent and severity of chemical contamination in the soils and residues on site, as well as looking for the potential spread of contamination to the surrounding area. Steps must also be taken to contain hazardous residues until they can be properly dealt with, to compile thorough documentation on wastes stored at the site prior to the fire, and to review the suitability of such sites for storage or disposal of hazardous wastes.

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