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Environmental Contamination Following the Grenfell Tower Fire

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Abstract

The Grenfell Tower fire in central London, started within a flat, engulfed the whole 24 storey building in flames, killed 72 people and spread toxic effluent via the plume and particulate deposits.

Soil samples from 6 locations up to 1,2 km from the Tower, together with semi-burnt fire debris and char samples, were collected 1 and 6 months after the fire. Additionally, dust samples and condensates were collected from a flat 160 m away from the Tower after 17 months. Samples were analysed for common potentially toxic components of fire effluents and synthetic vitreous fibres.

Samples collected within 140 m of the Tower showed, amongst other toxicants, polychlorinated dibenzo-p-dioxin concentrations 60 times greater than UK urban reference soil levels; benzene levels were 40 times greater; levels of 6 key polycyclic aromatic hydrocarbons (PAHs) were approximately 160 times greater. PAHs levels are approximately 20 times greater than those reported from nearby Hyde Park before the fire. To explain the presence of these pyrogenic contaminants char and partially burnt debris were also collected and analysed. Benzene, PAHs, isocyanates and phosphorus flame retardants were found. Hydrogen cyanide and synthetic vitreous fibres were present in both soil and debris.

Particulate and pyrogenic contamination in the immediate vicinity is clearly evident, and may have leached out of fire debris, char and dust. Further analysis of the area around the Tower is necessary to understand potential health risks.

1. Introduction

1.1 Harmful Effects of Fire Effluents

UK National Fire Statistics (2018) show that the acute toxicity of fire effluents is the biggest short-term cause of death and injury from unwanted fires. Large fires produce smoke containing high concentrations of particulates and toxic gases such as, the asphyxiant gases, carbon monoxide (CO), hydrogen cyanide (HCN) and respiratory tract deep lung irritants. As the fire develops, the yields of all products of incomplete combustion including CO, HCN, organic compounds and soot increase - typically by factors of 10 to 50. Molecular toxicants bind to smoke particles (airborne soot and tarry droplets) allowing them to penetrate deep into the lung causing respiratory distress and pulmonary oedema (flooding of the lungs). This is closely followed by incapacitation and death, from few hours to several days or even years after exposure (Stec and Hull 2010; Stec 2017).

There have been surprisingly few reports of the long term consequences of unwanted fires. Persson and Simonson (1998) showed that in Sweden they contributed around 10% as much as transport-derived particulate emissions. Fires also release a rich cocktail of pollutants, many of them acutely or chronically toxic, including carcinogens such as semi and volatile organic compounds (SVOC/VOCs), PAHs, respiratory sensitizers such as isocyanates from some nitrogen-containing fuels, and persistent, bioaccumulative and toxic compounds such as polychloro- and polybromo dibenzo-p-dioxins and dibenzofurans (PCDD/Fs and PBDD/Fs) and polychlorinated biphenyls (PCBs), formed by burning halogen containing fuels (McGee *et al.* 2003; Landrigan *et al.* 2004).

Benzene is a carcinogen in its own right (ATSDR 2018a). Other aromatic SVOC/VOCs are of particular toxicological significance as precursors of PAHs and carcinogens Some PAHs, PCDD/Fs and PBDD/Fs (the most toxic is 2,3,7,8-tetrachlorodibenzodioxin (TCDD)) are also genotoxic and mutagenic (ATSDR 2018b). Benzo(a)pyrene (BaP) was initially identified as the most toxic PAH species, however more recent studies have identified 7,12-dimethylbenzo(a)anthracene as having a 20-fold higher toxic equivalence factor (TEF) than its parent compound and twice that of BaP (Andersson and Achten 2015). A study by Wang *et al.* (2009) showed that PAHs are transformed in the atmosphere or metabolically into hydroxy-PAHs, which are more genotoxic than the parental PAHs. These compounds have been linked to firefighter cancers through the analysis of their exposure (Stec 2018).

The study by Bengtström *et al.* (2016) showed that isocyanates have been positively identified in fire smoke and are widely used in the manufacture of flexible polyurethane (PU) foams for upholstered furniture and rigid PU or polyisocyanurate (PIR) foams for insulation in buildings. Isocyanates are respiratory sensitizers that can cause asthma attacks. They also trigger irritant and allergic forms of contact dermatitis (rashes, itching, swelling of extremities etc.) and less frequently hypersensitivity pneumonitis - an inflammation of the alveoli caused by inhaled isocyanate particles. A common decomposition product of isocyanates is methyl isocyanate (MIC) which also causes swelling of the lungs and breathing difficulties.

Studies by Lippmann (2014 and 2015) on the aftermath of the World Trade Centre showed that synthetic vitreous fibres (SVF) were one of the most significant health damaging contaminants after the fire. Inhalation exposure to airborne SVFs is a public health concern because like other particulate matter, fibres that are released in fires can be suspended in air (as dust or ash), inhaled and deposited in the lung (ATSDR 2018c). Lippmann (2014) identified the minimum critical fibre lengths for asbestosis (interstitial fibrosis), mesothelioma and lung cancer to be ~2 μm, ~5 μm and ~15 μm, respectively. With regard to fibre diameter for asbestosis and lung cancer, fibres with diameters >0.15 μm appear to be of predominant significance (as thinner fibres can be more readily cleared via the lymphatic system) whilst for mesothelioma (and other lesions of the mesothelium), fibre diameters <0.1 μm seem to be the most pathogenic.

1.2 Environmental Pathways

The interaction between a fire and its surroundings or environment proceeds via direct gaseous and particulate emissions to the atmosphere and localised deposition to soil and water. Subsequent dispersion and deposition of atmospheric emissions results in widespread, low level contamination of soil, ground and surface water, as shown Figure 1. Van Loon and Duffy (2000) reported that particles with diameters less than 10 μm will have a deposition rate of around 3 mm s^{-1} and will tend to remain airborne, travelling with the smoke plume. Particles with diameters greater than 100 μm will have a settling velocity of 0.3 m s^{-1} and are likely to be deposited close to the fire.

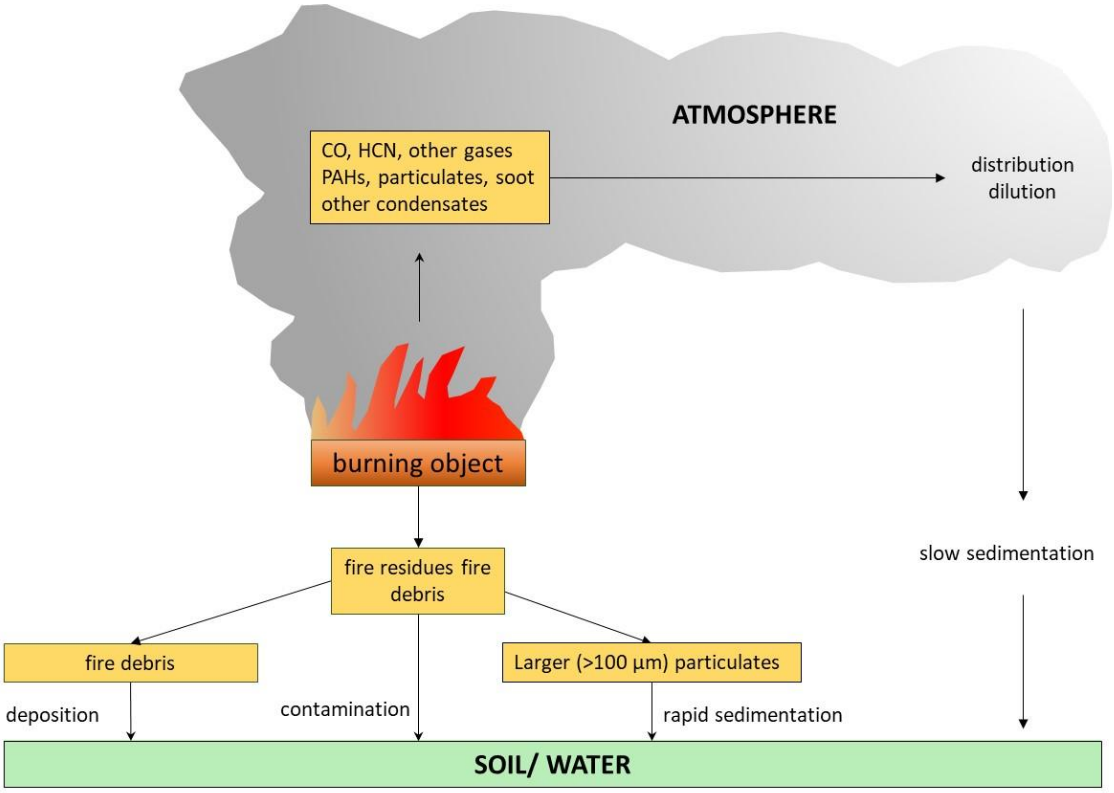


Figure 1. Emission pathways from fires (adapted from ISO 26367-1 (2011).

The degree to which fire species are partitioned between different phases (gaseous, aqueous, solid etc.) also depends on their physical characteristics and weather conditions (temperature, rain, wind speed etc.). For example, PAHs will agglomerate eventually leading to soot formation. The agglomerating species will initially travel as airborne particulates, but may grow large enough to sediment into water or soil, while CO will remain in the gas phase. Cyanide is released into air as a gas and to a lesser extent as particulate bound cyanides (ATSDR 2006). Cyanide can be transported over long distances before decomposition by reaction with hydroxyl radicals. In soil, HCN co-exists with alkali metal salts where it volatilises or degrades rapidly. Alternatively, HCN may be immobilised into metallo-cyanide complexes such as ferricyanides or ferrocyanides (ATSDR 2006). MIC will only persist in the atmosphere from a few hours to a few days, while in soil it will be broken down into other compounds upon contact with moisture (ATSDR 2014). PAHs and VOCs are comprised of species that partition differently according to their mass, with lighter species remaining primarily in the gaseous phase and heavier species tending to deposit on surface water or soil when absorbed on particulates (>2.5 µm) such as fly ash and soot (Van Loon and Duffy 2000). Humans can also be exposed to PAHs through inhalation or dermal contact with re-suspended soil and dust (Stec *et al.* 2018). While human-soil contact generally occurs outdoors, inhalation is also identified as a source of PAHs indoors, where people spent 80–93% of their time (WHO 2010). SVFs with smaller diameters become airborne more readily than fibres with larger diameters. SVFs remain unchanged in air, soil or sediment over long periods (Bernstein *et al.* 2005).

The UK's Public Health England (PHE) provides specialist advice on health including health advice on air quality, smoke exposure, asbestos, and the clean-up process (PHE 2018a). The data from the air quality monitoring in the area surrounding Grenfell Tower, since the start of the fire on 14 June, has shown that the risk to people's health from air pollution around the Grenfell Tower site was consistently low. Levels of gas particulate matter (PM_{10}) remained low and monitoring results for dioxins, furans, PCBs and PAHs were broadly equivalent to background levels for London. No asbestos was reported as found, despite being present in the Grenfell tower. There are no reports of contamination measurements being taken from the soil or water run-off. No measurements appear to have been carried out by UK's Environmental Agency or the local authority (the Royal Borough of Kensington and Chelsea (RBKC). RBKC are legally responsible for assessing and quantifying contaminated land within their community (PHE 2018b). The rationale for the current study was to address concerns from the Grenfell community related to the potential soil contamination and establish whether more detailed investigation is required.

2. Materials and Methods

Two char samples were collected from balconies 50 and 100 m from the Tower 1 month after the fire and analysed (Char1 and Char2). Based on the findings soil samples, together with fallen fire debris and more charred soot samples (Res and Char3) were collected 6 months after the fire at different distances from the Tower. Sampling was limited by locations where there was permission to collect soil and aimed to follow the direction of the prevailing wind at the time of the fire (South Easterly), with location shown in Figure 2a and wind on the day of fire Figure 2b (TimeandDate 2018). 17 months after the fire char from a balcony (Char4), indoor dust and a yellow oily deposit on a vertical fabric window blind (described by the occupier as “contaminated by the fire”) were collected from a flat 160 m from the Tower. Table 1 shows the details of the char and soil samples. A standard soil sample, Kettering loam soil, was obtained from Boughton Loam Ltd (containing clay 24%, silt 18%, sand 58%, organic content 6.72%). It is a preferred natural soil used as a standard in contamination analyses.

Quantitative analyses for PCDD/Fs, PAHs, benzene and metals were carried out on the char and soil samples. Gas chromatography-mass spectrometry (GC-MS) was used for SVOC/VOCs. Qualitative screening (thermogravimetric analysis coupled with gas phase Fourier Transform Infrared Spectroscopy, (TGA-FTIR)) was used to check for the presence of common fire effluents on all samples. Finally, the contaminated window blind was extracted and analysed for the presence of isocyanates, in order to characterise the yellow oily deposits.

2.1 Sample Collection

Soil samples (approximately 2 kg) were collected from the ground at depths of up to 200 mm. A fresh pair of gloves was used for each sample collection and the trowel was cleaned before and after each collection. The samples were stored in airtight 1 L dark glass jars covered in aluminium foil and kept at 4°C.

Approximately 60 pieces of what appeared to be char from insulation foam (the largest being 300 mm in width and 460 mm in length, with an approximate density of 18 kg/m^3) were collected from the ground within 90 m of the Tower. A semi-burnt piece of fire debris, recognisable as a sheet of insulation material (Res), was also found and collected. Samples were stored in dark polyethylene bags.

Char samples were also collected from three balconies (Char 1, 2 and 4) between 50 and 160 m from the Tower. Dust samples were collected from five different locations within one apartment, 160 m from the Tower, and combined. Two pieces of the window blind, one with visible soot and yellow oily deposits and the other without, were also collected from the same apartment.

2.2 Sample preparation

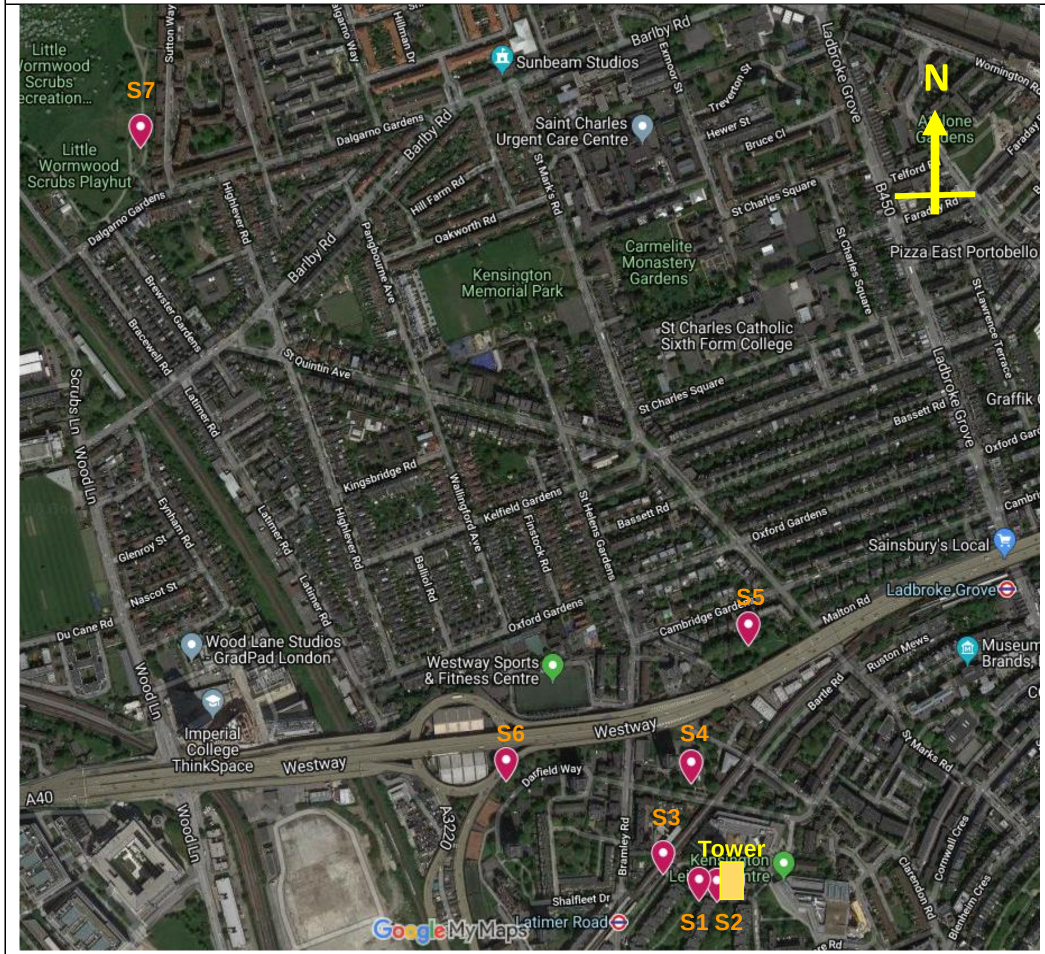
Up to 5 g of each soil sample was then dried to a constant weight on a watch glass in an oven (VWR Dry-Line 115) at 60 °C to determine the moisture content, then sieved (5 mm) and ground to ensure a homogenous sample (the smell of fire smoke was observed for the soil samples 1 to 3). The moisture content, based on triplicate analyses, is reported in Table 1. Non-dried samples were used for TGA-FTIR analysis in order to avoid volatile losses.

Table 1. Sample descriptions, locations, moisture, pH and nitrogen content.

Sample Type	Abbreviation	Sample location* /(m)	Collection data**/ (months)	Average Moisture/ %	pH	Nitrogen content %
Kettering loam soil (control)	Ref			0.2	7.2	0.7
Soil	S1	27	6	34.9	5.4	1.9
	S2	50	6	35.7	6.1	1.7
	S3	90	6	26.2	8.5	1.2
	S4	142	6	24.2	4.2	1.2
	S5	316	6	23.6	6.7	1.2
	S6	332	6	14.9	6.9	1.2
	S7	1260	6	18.3	8.3	1.0
Fire debris	Res	90	6		6.4	UB: 2.1 B: 1.1
Char from balconies	Char1	50	1		-	6.1
	Char2	90	1		-	6.3
Charred samples from the ground	Char3	90	6		5.3	6.2
Char from balconies	Char4	160	17		5.5	4.9
Dust samples from the flat	Dust	160	17		-	-
Oily residue from window blind from the flat	WB	160	17		-	-

Notes: UB, Unburnt; B, Burnt; -, None detected; *Sample location in respect to distance from Grenfell Tower; **Data collection carried out months after the fire; “Fire debris refers to semi-burnt insulation material.

a)



b)

Time /am Wednesday 14th June	Wind Direction (↑ North)	Wind speed /mph
00:50 (fire started)	↖	5
1:50	↖	6
2:50	←	1
3:50	↗	1
4:50	↗	1
5:50	↓	no wind
6:50	←	3
7:50	←	5
8:50	↖	5
9:50	←	8
10:50	↖	7
11:50	←	7
12:50	↖	9
13:50	↖	9
14:50	↖	10
15:50	↖	9
16:50	↑	9
17:50	↑	9
18:50	↖	10
19:50	↑	10
20:50	←	12
21:50 (internal fires still visible)	←	7
22:50	←	9
23:50	←	1

Figure 2. Samples locations and meteorological reports of wind speed and direction during the fire (TimeandDate.com 2018).

2.2.1 Chemical analysis

All glassware was baked at 300 °C and rinsed with the appropriate solvent before use. Laboratory blanks were run alongside samples (intervals specified in individual sections below). All water was distilled. All samples were kept at 4 °C in a locked enclosure prior to analysis. All analyses were conducted in the analytical laboratories of the University of Central Lancashire except for the dioxins and furans which were quantified in a private UKAS accredited laboratory. The limits of detection (LOD) and limits of quantification (LOQ) for analysed fire effluents together with the dioxins and furans recoveries can be found in the supplementary material (Tables S1-S8).

2.2.1.1 pH

Approximately 20 g of each soil was mixed with 20 mL of deionised water and the water pH measured using a glass electrode in triplicate (Jenway 3540).

2.2.1.2 CHNS analysis

Approximately 2 mg of dried sample was placed into a tin capsule and run on a ThermoScientific Flash 2000 CHNS/O analyser (detection sensitivity within ±1%), in order to determine the presence of nitrogen. Each sample was analysed in triplicate with a blank run as part of the initial CHNS calibration daily. The instrument was calibrated with BBOT (2,5-Bis (5-tertbutylbenzoxazol-2-yl) thiopene) (Elemental Microanalysis, B2135) (6.51 N%, 72.53 C%, 6.09 H%, 7.44 S%) using the K-factor calibration method. In place of laboratory blanks between samples, BBOT standard was run every 15 samples in order to check the response of the CHNS analyser.

2.2.1.3 ICP-OES screening

The method used was based on EPA 6010D (U.S. EPA 2014). 0.1 g of the sample was digested in 10 mL of concentrated nitric acid (Fisherbrand) in a microwave digester (Milestone Ethos EZ SR12) at 200 °C for 45 min. 0.1 mL of the digested sample was added to 9.9 mL of water, which was then analysed by Inductively Coupled Plasma-Optical Emission Spectrometry (Thermo Scientific iCAP 7000 ICP-OES) for elemental composition. Samples were run in quadruplicate with each individual sample tested three times for consistency. The RSD for all final results was less than 5%. Blanks prepared from digested acid were run after every fifteen samples, and were all below the limits of detection (LOD) for all elements analysed. The LOD and LOQ were calculated as three and ten times the standard deviation from the analysis of the standards and the blanks (Table S1). The standards used for comparison were the TraceCERT® 1000 mg/L P in water and the multi-element standard 5 TraceCERT® in 10% nitric acid (Sigma Aldrich).

2.2.2 Fire effluent analysis

2.2.2.1 Benzene quantification

3.5 g of soil sample, or 1 g of residue or char material, was added to 3 mL of a 3:1 hexane:acetone mixture (Sigma Aldrich) and the sample was sonicated (Sonicor SC52-H) for 40 min. 1.5 mL of the solution was extracted, centrifuged at 15 000 rpm for 30 min (Sanyo MSE Micro Centaur MSB010.CX2.5) and 2 µL of the extracted solution was injected into the GC-MS (Agilent HP 6890 coupled to Agilent MS 5973) with the software: Agilent MSD Chemstation version F.01.00.1903). All analyses were run in quadruplicate. Laboratory blanks run every ten samples. The chromatograms used for analysis were blank subtracted. The LOD was calculated using three times the signal to noise ratio of the analyte, while the LOQ was calculated using ten times the signal to noise ratio. The LOD and LOQ were 0.11 and 0.54 ppm respectively.

2.2.2.2 PAHs and phosphorus flame retardants

5 g of soil was passed through a 5 mm sieve and added to 40 mL of a 1:1 ratio of dichloromethane:acetone mixture (Sigma Aldrich) and sonicated (Sonicor SC52-H) for 2 h. For the next 6 h the samples were sonicated for 10 min each hour. Once sonication was complete, 2 mL of the liquid was centrifuged at 15 000 rpm for 30 min (Sanyo MSE Micro

Centaur MSB010.CX2.5) and 2 µL of the centrifuged extracted solution was injected into the GC-MS (Agilent HP6890 coupled to Agilent MS 5973). Approximately 1 g of residue or char sample was added to 3 mL of a 3:1 hexane:acetone mixture (Sigma Aldrich) and the samples sonicated for 40 min. 1.5 mL of the solution was extracted, centrifuged at 15 000 rpm for 30 min and 2 µL of the extracted solvent was injected into the GC-MS. Each analysis was repeated five times.

Quantification of PAHs was based on the method described by Guerin (1999). Analysis was performed for PAHs using a HP 6890 Series GC System equipped with a 5973 Mass Selective Detector (Hewlett Packard) and a TraceGOLD TG-5MS column with the dimensions 30 m x 0.25 mm x 0.1 µm (Thermo Scientific). An injection volume of 2 µL was used with a splitless injection with a flow rate of 35 mL/min. Samples were analysed in SIM mode. The GC was set to a start temperature of 100 °C with a 2 min hold, then with 8 °C/min to 210 °C, with 2 °C/min to 280 °C and was held at 280 °C for 3 min. The results were then processed using Agilent MSD Chemstation version F.01.00.1903. Calibration standards were obtained from Sigma Aldrich. Laboratory blanks were analysed with every ten samples. The PAHs were quantified using external standard calibrations. The LOD was based on three times the signal-to-noise ratio of each analyte (related to the 5g samples) while the LOQ was based on ten times the signal-to-noise ratio, as shown in Table S2. Responses below the LOQ were not included in this analysis. The average blank levels were below the LOD for all PAHs.

2.2.2.3 Polychlorinated dibenzo-p-dioxin and polychlorinated dibenzofuran analysis

Quantification of PCDD/Fs was based on EPA1613 (US EPA 1994). The analysis was undertaken in a UKAS accredited laboratory, approved to quantify dioxins. This includes a spiked sample and a reference material analysed alongside the samples on a weekly basis. The LOD and recoveries for each sample are shown in the supplementary document (Table S3-S8). Approximately 1 g of sample was fortified with ^{13}C dioxin/furan standards (Wellington) at 1 ng for each congener. Samples were then extracted in a Soxhlet apparatus in toluene (Rathburn), for 16 h. Samples were solvent extracted with hexane (Rathburn) followed by rotary evaporation (Buchi 310). Sample clean-up was achieved using a Miura system (GO-HT) with silica, alumina and carbon columns - eluting with hexane and then toluene. The final volume of samples was reduced to 20 µL and fortified with recovery standards ((Wellington). Analysis was carried out by using 60 m DB5 capillary column (Agilent) and Waters NT Ultima high resolution mass spectrometer operating at 10000 resolving power, which was quantified against isotope dilution calibration curve. Analysis was done using Masslynx Software.

2.2.2.4 Isocyanate analysis

0.5 g of each sample was added to 1 mL of a 0.01 M di-n-butylamine in toluene solution (Sigma Aldrich) and sonicated (Sonicor SC52-H) for 30 min. Post-sonication 500 µL of a 500 ng/mL standard solution was added to 500 µL of extract and the samples were evaporated to dryness under a stream of nitrogen (Energas). 0.5 mL of UPLCMS grade acetonitrile (Fisherbrand) was then added to the vial which was gently swirled for 30 s before the solution was transferred to the UPLCMS system (Bengtström *et al.* 2018). The results were compared to a standard solution containing a number of isocyanates (Sigma Aldrich, DBA Isocyanate Standard Mixture). The UPLCMS was purged before testing with the UPLCMS grade solvents, and three blanks were run immediately prior to the samples. Due to the low quantity of the samples, they were treated as qualitative samples and the MS spectra compared to spectra obtained from a purchased calibration standard mixture used as a reference. The detailed analytical settings are presented in Table 2.

Table 2. UPLCMS settings for the isocyanate analysis.

UPLCMS settings	
Equipment specifications	Waters Acquity UPLC coupled to a Waters TQD MS Software: Mass lynx version V4.1 SCN714
Column	Waters BEH C18 column (130Å, 1.7 µm, 2.1 mm X 50 mm)
Mobile Phases	A) 95:5 *v/v* water (VWR, 83645.320) and acetonitrile (VWR, 84865.260) and 0.05% formic acid (VWR, 20318.297) B) Acetonitrile and 0.05% formic acid
Flow rate	0.25 ml/min
Gradient program (time/min - %A)	Start – 40, 5 – 2, 6 – 40, 9 – 40
Total program length (min)	10
Column temperature (°C)	40

2.2.2.5 TGA-FTIR analysis

Thermogravimetric analysis coupled to gas phase Fourier Transform Infrared Spectroscopy (TGA-FTIR) was used to qualitatively assess the presence of other fire effluents as a function of sample's temperature. Additional to analyses of the soil samples, cyanide may be present in soil as ferricyanide ($Fe(CN)_6{}^{3-}$) or ferrocyanide ($Fe(CN)_6{}^{4-}$), both analysed by TGA-FTIR in order to determine the HCN release temperatures from the iron complexes. Samples were analysed in a Mettler Toledo TGA/DSC2 connected directly to a Thermo Nicolet iS50 FTIR via a heated line held at 250 °C. 100 mg of soil and 5 mg of residue were heated at 10 °C/min from ambient to 700 °C in nitrogen. The FTIR was set to a resolution of 1 cm^{-1} with a DGTS detector and a scan rate of 10 averaged spectra in a 10 cm pathlength gas cell. The FTIR spectra were compared with the HR Nicolet Vapour Phase and TGA Vapour Phase libraries using OMNIC 9.3.32 software. The wavelength range used for HCN profiles was 3278-3292 cm^{-1}. Each sample was analysed in triplicate in both air and nitrogen. The sample crucibles were cleaned after each run. TGA-FTIR instrument was cleaned by and an isotherm run after five tests. In addition, the gas phase FTIR was run using automatic atmospheric suppression.

2.2.2.6 Synthetic vitreous fibre analysis

SVFs were found in samples of soil, char and residue by manual searching and optical microscopy (Nikon Eclipse E200). Composition of SVF was estimated using a Jeol JCM-6000 with Scanning Electron Microscope (SEM) using BED-C COMPO with an integrated JED-2300 Energy Dispersive X-Ray Spectroscopy module (EDX). The software programs used for analyses were JCM-6000 Plus version 1.4.0 and Analysis Station version 3.8.0.59. The fibres were prepared on carbon stickers which were placed on SEM stubs for the analyses.

3. Results

3.1 ICP-OES analysis

Aluminium, zinc, copper, lead and other metals were present in soil within UK Environment Agency baseline pollutant levels in soil (EA 2007a). Phosphorus, occurring naturally in the soil, was present at higher levels for soils S1-S3 collected near the Tower (within the range of 140-170 mg/kg) than for S4 to S7 with values between 85 and 35 mg/kg, respectively.

3.2 Benzene analysis

Data in Figure 3 shows elevated benzene concentrations for the first 4 soil samples when compared to the residential soils (EA 2007b). Benzene concentrations decrease with increasing distance from the Tower.

3.3 PAHs quantification

The sum of the six main PAH concentrations (BaP, fluoranthene, benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, and benzo(ghi)perylene) in London’s urban soils, sampled in nearby Hyde Park (3.9 km away from the Tower), is estimated at 4512 µg/kg (as an average from three locations) (EA 2007b). Similarly to benzene, PAH concentrations - Figure 3 (c and d), show decrease with increasing distance from the Tower.

a)	b)

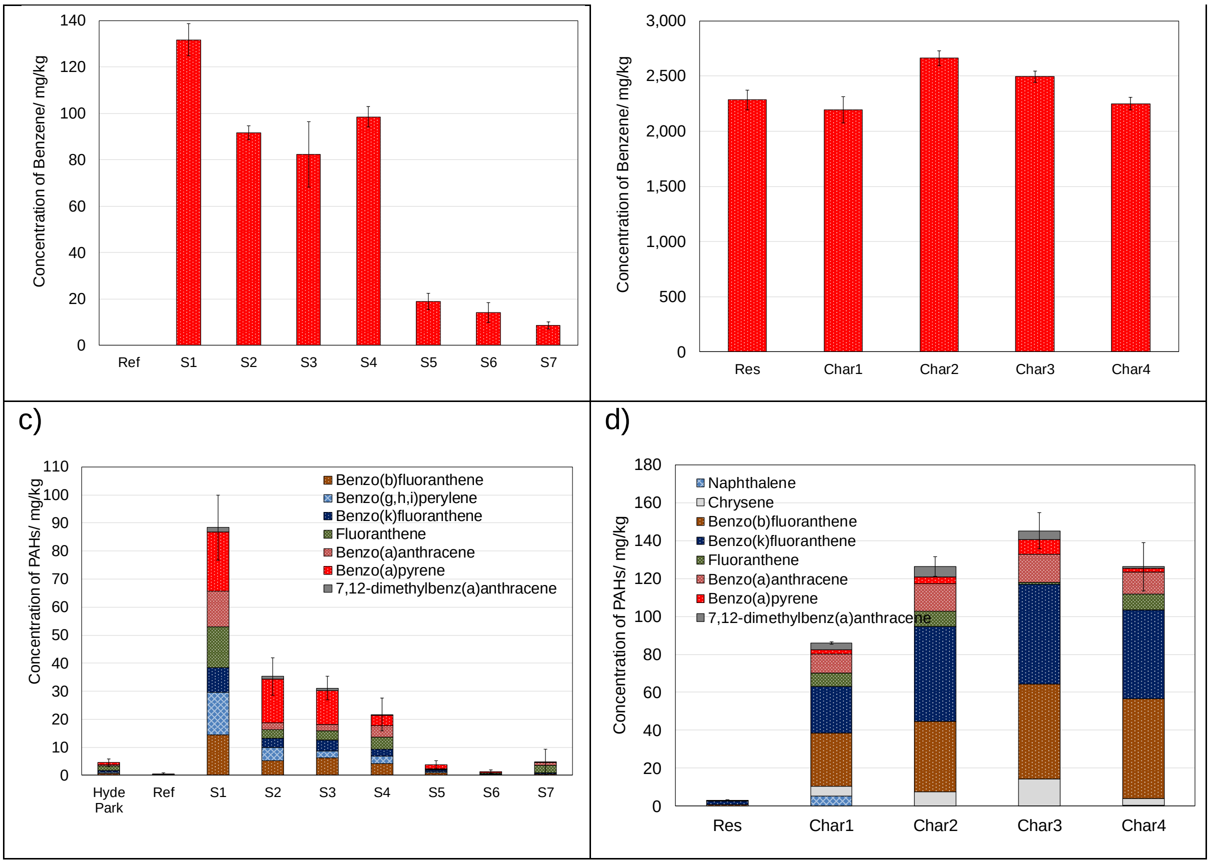


Figure 3. Benzene (a and b) and PAHs (c and d) concentrations showing errors bar for total concentrations in soil samples and fire debris in mg/kg.

3.4 PCDDs and PCDFs analysis

Table 3 shows median soil concentrations of different PCDDs and PCDFs found in soil samples around Grenfell Tower compared to values in urban UK locations and nearby Hyde Park (EA 2009a). PCDD/Fs concentrations are higher for the soil samples collected closer to the Tower, appearing to peak around 100 m from it.

Table 3. PCDD/Fs levels in soil samples and Char3.

	UK urban/ ng/kg	**Hyde Park/ ng/kg**	**Ref/ ng/kg**	**S1/ ng/kg**	**S2/ ng/kg**	**S3/ ng/kg**	**S4/ ng/kg**	**Char3/ ng/kg**
Dioxins								
2,3,7,8-TCDD	0.4	0.5	-	1.05	1.3	1.6	-	-
1,2,3,7,8-PeCDD	1.4	1.6	-	8.7	6.7	9.2	1.3	1.8
1,2,3,4,7,8-HxCDD	1.6	1.5	0.3	14.9	14	16.8	1.3	1.5
1,2,3,6,7,8-HxCDD	2.9	3.5	0.7	39.8	36.8	45.7	2.9	2.9
1,2,3,7,8,9-HxCDD	2.6	3.0	0.5	30.2	31.4	34.9	2. 5	2.5
1,2,3,4,6,7,8-HpCDD	25.2	27.5	7.3	889	965	1120	54.8	15.7
OCDD	104	88.8	25.3	6450	7370	8730	356	27.8
Furans								
2,3,7,8-TCDF	2.5	4.4	-	8.3	5.5	11	3.8	22.5
1,2,3,7,8-PeCDF	2.8	3.8	-	5.7	3.0	3.6	2.4	8.8
2,3,4,7,8-PeCDF	4.1	6.9	-	8.4	6.6	5.2	3.2	17.3
1,2,3,4,7,8-HxCDF	3.6	3.3	0.7	8.7	6.7	7.4	3.5	11.9
1,2,3,6,7,8-HxCDF	2.6	2.5	0.4	6.4	6.2	4.5	2.4	14.5
2,3,4,6,7,8-HxCDF	3.8	4.5	0.6	9.8	11.2	9.0	3.1	19.3
1,2,3,7,8,9-HxCDF	1.1	0.9	-	3.1	2.7	0.7	-	5.2
1,2,3,4,6,7,8-HpCDF	24.2	23.6	3.7	83.6	103	116	21.5	52.0
1,2,3,4,7,8,9-HpCDF	1.4	1.0	-	8.9	9.5	12.5	1.8	7.6
OCDF	26.0	19.4	3.7	202	222	239	23.6	19.6
∑PCDDs	138	126.5	34.1	7434	8425	9958	416	52.2
∑PCDFs	72.1	70.3	9.1	345	376	409	65.3	179
Total PCDDs and PCDFs	**210**	**197**	**43**	**7779**	**8802**	**10367**	**482**	**231**
TEQ-WHO (mammals)	**6.48**	**8.65**	**1.39***	**36.4***	**34.6***	**40.6***	**5.63***	**16.4***

Notes: ∑, sum of; -, None detected; * concentration of non-detected congeners at detection limit

3.5 Phosphorus flame retardants analysis

Tris(chloroisopropyl) phosphate (TCPP), tris(2-ethylhexyl) phosphate (TEHP) and tricresyl phosphate (TCP) were identified in samples S1 and S2, fire debris and Char3. These are commonly used in insulation foam and upholstered furniture foam and do not occur naturally in the soil (Hewitt *et al.* 2017).

3.6 Isocyanates analysis

MIC, isocyanic acid, ethyl isocyanate and propyl isocyanate were identified in the yellow deposit on the window blind.

3.7 TGA-FTIR analysis

TGA shows the mass loss as a function of temperature when the sample is heated in an inert atmosphere (nitrogen) while FTIR allows identification of volatiles as a function of temperature. Thus, the species observed at elevated temperatures may have been trapped or otherwise adsorbed particularly if they were released below 150 °C. At higher temperatures they are more likely to be decomposition products.

There are broad similarities in terms of released volatiles, shown in Figure 4a. Initial TGA mass losses, up to around 120 ºC, are largely assigned to water release followed by other volatiles. HCN and alkyl cyanides were evolved from over a temperature range of 210 °C. HCN release from soil samples (S1, S2, S4 and S5), fire debris and char collected from individuals balconies is observed from 280 to 310 °C, reaching a peak of around 350 °C. Ferrocyanide releases HCN between 250 and 450 °C, while ferricyanide have two distinguish HCN release maxima at 330 °C and 540 °C. Figure 4b shows the HCN profile of the iron cyanide complexes alongside S1 to S7.

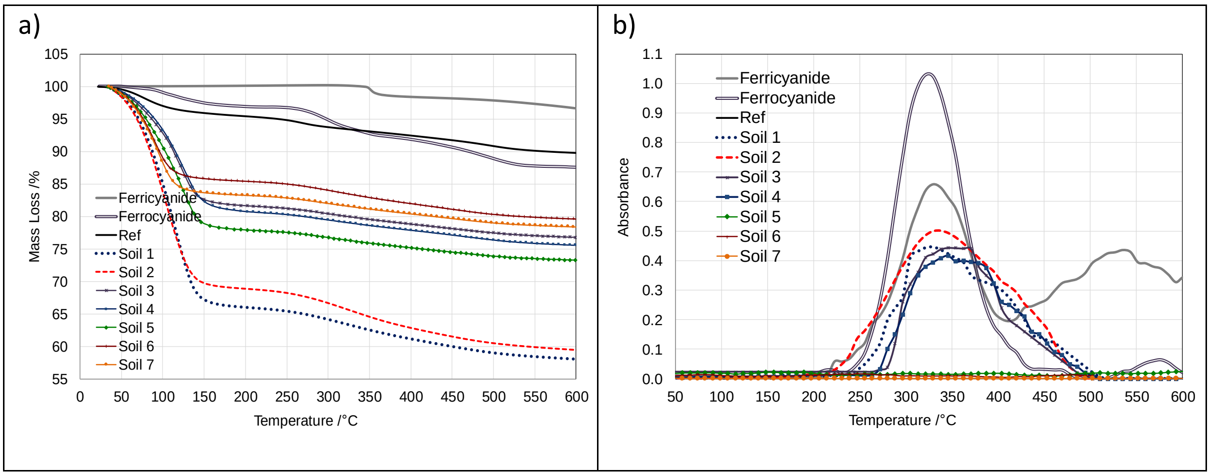


Figure 4. TGA mass loss curves of soil, Res and Char3 samples (a) and HCN release profiles for the soil samples (b).

3.8 Synthetic Vitreous Fibres analysis

SVFs were identified and isolated from soil samples S1 and S2 and were found attached to fallen debris and char samples. In order to identify the possible origins of the SVFs, samples of commercially available polyisocyanurate (PIR), phenolic foam (PhF) and stone wool (SW) were used as reference samples. The PIR sample had two layers of glass wool embedded at depths of approximately 25 and 55 mm within the foam. The phenolic foam sample had layers of glass wool embedded into the outer surface layers inside the foil covering. The foil covering was also reinforced with glass fibres. Reference samples were of the same manufacturer and product names as those reported to have been used on the Tower refurbishment (Grenfell Tower Inquiry 2018). An example of the SVF attached to the foam residue can be seen in Figure 5 and elemental composition in Table 4. Samples were run in quadruplicate.

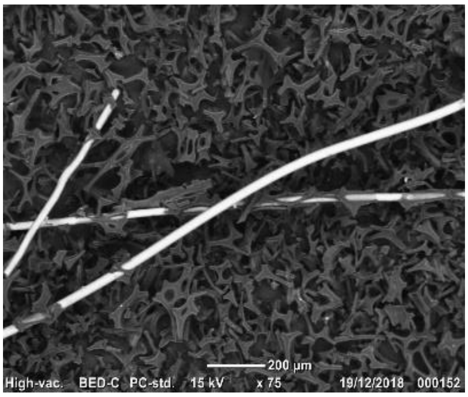


Figure 5. Picture of SVF in Char3.

Table 4. Elemental analysis of the fibres.

	Abbr.	**Na_2O**	**MgO**	**Al_2O_3**	**SiO_2**	**P_2O_5**	**SO_3**	**K_2O**	**CaO**	**TiO_2**	**FeO**	**Diameter range /µm**
Reference Materials	SW	3.7	9.7	19.4	39.5	0.7	1.6	0.9	17.8	1.8	6.0	8.4 – 11.1
	PIR	19.8	3.8	2.5	70.0		0.3	0.4	3.6			24.5-29.9
	PhF	1.7	3.4	17.0	59.7	2.5	8.2	0.8	15.3			9.7-14.6
Samples	Res	3.7	2.3	15.5	53.5		7.0	0.9	17.9	3.7	2.3	12.1 - 14.4
	Char2	15.2	4.3	2.2	72.3	1.0	0.4	0.5	4.8	15.2	4.3	28.8-31.7
	Char3	12.8	3.9	2.3	74.8	1.0	0.2	0.5	4.7	12.8	3.9	25.1-28.8
	S1	17.8	3.4	2.5	71.3		0.2	0.5	4.3	17.8	3.4	24.5 - 26.1
	S2	1.2	2.3	15.3	57.4	0.8	0.9	0.3	22.1	1.2	2.3	12.0 - 12.5

Note: Abbr, Abbreviation

4. Discussion and Conclusions

Soil guideline values provide a reliable baseline against which intensive local surveys and future national surveys can be assessed (EA 2009b). If representative soil concentrations are above the baseline values then further investigation is required to determine whether the substances pose a risk and to determine the scale and urgency of further action. The greater the exceedance of the assessment level, the greater the likelihood that the substance will pose a risk to human health and/or the environment (EA 2009b).

Soil guideline values for benzene for residential land are between 0.87 – 3.3 mg/kg and 95 mg/kg for commercial land use where contamination is expected (i.e. petrochemical and petroleum refining industries) (PHE 2014; EA 2009c). Values are based on a consideration of the oral, dermal and inhalation routes of exposure. Benzene is typically found in petrol and in vehicle emissions, therefore elevated levels may be expected at roadside locations. Data in Figure 3 shows benzene concentrations exceeded these values by factors between 25 and 40 for the four soil samples taken closest to the Tower when compared to the residential soils.

The British Geological Survey defined the normal background concentrations for BaP in England to be 3.6 mg/kg in urban areas and 0.5 mg/kg in all other areas. Guidance levels for BaP are set at 5.0 to 5.3 mg/kg for residential land and up to 77 mg/kg for commercial land (EA 2007b; PHE 2018c). BaP concentrations obtained from the first three soil samples exceed residential values (33, 24 and 17 mg/kg respectively). For soil S5 the value is 2.0 mg/kg, with S6 and S7 values at 0.3 mg/kg - showing the localised distribution of the contamination. The total sum of 6 PAH concentrations (S1), 45 m away from the Tower, is approximately 20 times higher than that reported in Hyde Park (or approximately 160 times greater than the reference soil). S2 to S4 exceeded these reference values by factors between 40 and 60. S5 to S7 are comparable to the reference soils. PCDD levels are around a factor of 70 greater than those collected in Hyde Park or a factor of 60 greater than the UK urban reference soil values. S4 contains lower concentrations than S1 to S3, but these are still three times higher than the UK urban or Hyde Park concentrations.

Seventeen 2,3,7,8-substituted PCDD and PCDF congeners (Table 3) and 15 PAHs (BaP, benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, indeno(1,2,3-cd)pyrene, chrysene, acenaphthene, acenaphthylene, anthracene, benzo(g,h,i)perylene, fluoranthene, fluorene, phenanthrene, pyrene and naphthalene) with their respective TEFs were used to conduct non-cancer and cancer risks assessment using 2,3,7,8 – TeCDD and BaP toxicity equivalence (PCDD/F WHO-TEQ and PAHs WHO-TEQ) (Van den Berg *et al.* 2013; U.S. EPA 2001; 2009; 2018). Results, as Non-Cancer Hazard Quotient (HQ of 1 for non-carcinogens) and Cancer Risk (CR corresponding to a 10^{-6} risk level for carcinogens) are presented in Table 5. Reference doses, slope factors and other parameters for estimating human non-cancer and cancer risks were taken from Regional Screening Levels Tables and EPA equations (U.S. EPA 1989; 1991; 2001; 2009; 2018). In this study, the body weight was chosen 70 kg for adults and 15 kg for children. Exposure duration of 25 years for adults and 6 years for children was chosen with ingestion rates of soil 30 and 15 mg/day, respectively. Exposure frequency was assumed to be 50 days/year and exposure time of 1 hr/day for inhalation, ingestion and dermal pathway. Surface area of skin that contacts the soil was taken as 1500 and 500 cm^2 for adults and children, respectively (EA 2008). A life time average of 60 years was taken to calculate the average time exposure for carcinogenic chemical exposure.

The Hazard Quotient (HQ) together with the lifetime cancer risk was calculated and is presented in Table 5. $HQ \leq 1$ indicates no adverse health effects, whereas $HQ > 1$ indicates likely adverse health effects (NYS DOH 2007). An estimated increased excess lifetime cancer risk is not a specific estimate of expected cancers (when values exceed the unity). Rather, it is a plausible upper bound estimate of the probability that a person may develop cancer sometime in his or her lifetime following exposure to that contaminant (Van den Berg *et al.* 1998).

Table 5 Hazard quotient and cancer risk from exposure to residue, soil and char samples.

	Hazard quotient (HQ) of adult			**Hazard quotient (HQ) of children**			**Cancer risk of human (*10^{-6}*)**		
	Ingestion	**Dermal contact**	**Inhalation**	**Ingestion**	**Dermal contact**	**Inhalation**	**Ingestion**	**Dermal contact**	**Inhalation**
Dioxins/Furans									
UK urban	6.43E-05	3.86E-05	3.86E-09	6.01E-04	6.01E-05	3.86E-09	5.86E-03	5.02E+06	5.87E-12
Hyde Park	6.02E-05	3.61E-05	1.45E-16	5.62E-04	5.62E-05	3.62E-09	5.48E-03	4.70E+06	1.45E-10
Ref	1.32E-05	7.93E-06	3.18E-17	1.23E-04	1.23E-05	7.94E-10	1.20E-03	1.03E+06	3.18E-11
S1	2.38E-03	1.43E-03	5.72E-15	2.22E-02	2.22E-03	1.43E-07	2.17E-01	**1.86E+08**	5.72E-09
S2	2.69E-03	1.62E-03	6.47E-15	2.51E-02	2.51E-03	1.62E-07	2.45E-01	**2.10E+08**	6.47E-09
S3	3.17E-03	1.90E-03	7.62E-15	2.96E-02	2.96E-03	1.91E-07	2.89E-01	**2.48E+08**	7.62E-09
S4	1.48E-04	8.89E-05	3.56E-16	1.38E-03	1.38E-04	8.90E-09	1.35E-02	**1.16E+07**	3.56E-10
Char3	7.07E-05	4.24E-05	1.70E-16	6.60E-04	6.60E-05	4.24E-09	6.43E-03	5.51E+06	1.70E-10
Polycyclic Aromatic Hydrocarbons									
Ref	9.55E-05	3.72E-02	2.46E-03	8.91E-04	5.79E-02	2.46E-03	2.86E-02	9.68E+03	2.47E-11
S1	1.95E-02	**7.61E+00**	5.02E-01	1.82E-01	**1.18E+01**	5.02E-01	5.85E+00	**1.98E+06**	5.05E-09
S2	1.23E-02	**4.80E+00**	3.17E-01	1.15E-01	**7.47E+00**	3.17E-01	3.69E+00	**1.25E+06**	3.19E-09
S3	9.76E-03	**3.81E+00**	2.51E-01	9.11E-02	**5.92E+00**	2.51E-01	2.93E+00	**9.89E+05**	2.53E-09
S4	3.47E-03	**1.35E+00**	8.92E-02	3.24E-02	**2.10E+00**	8.92E-02	1.04E+00	3.51E+05	8.98E-10
S5	1.03E-03	4.00E-01	2.64E-02	9.57E-03	6.22E-01	2.64E-02	3.08E-01	1.04E+05	2.66E-10
S6	2.42E-04	9.45E-02	6.23E-03	2.26E-03	1.47E-01	6.23E-03	7.27E-02	2.46E+04	6.28E-11
S7	2.92E-04	1.14E-01	7.51E-03	2.72E-03	1.77E-01	7.51E-03	8.75E-02	2.96E+04	7.56E-11
Res	1.09E-03	4.26E-01	2.81E-02	1.02E-02	6.63E-01	2.81E-02	3.28E-01	1.11E+05	2.83E-10
Char1	6.20E-03	**2.42E+00**	1.59E-01	5.78E-02	**3.76E+00**	1.59E-01	1.86E+00	6.28E+05	1.61E-09
Char2	9.89E-03	**3.86E+00**	2.55E-01	9.24E-02	**6.00E+00**	2.55E-01	2.97E+00	**1.00E+06**	2.56E-09
Char3	1.41E-02	**5.51E+00**	3.63E-01	1.32E-01	**8.57E+00**	3.63E-01	4.24E+00	**1.43E+06**	3.66E-09
Char4	9.29E-03	**3.62E+00**	2.39E-01	8.67E-02	**5.63E+00**	2.39E-01	2.79E+00	9.42E+05	2.41E-09

Note: Values correspond to a 10^{-6} risk level for carcinogens and an HQ of 1 for non-carcinogens.

The table shows the HQ for PAHs for dermal contact for both adults and children. The values exceed one are shown in bold. They are for the char and the four soil samples collected nearest to the Tower. This corresponds to an increased risk of any adverse health effects from PAHs, but not from dioxins and furans. The table also shows the cancer risk to humans multiplied by a factor of 10^6. Values exceeding 1 x 10^6 indicate an increased cancer risk. These are also shown in bold in Table 5. The four soil samples (S1-S4) closest to the Tower indicate significantly increased cancer risk from dioxin and furans, as well as for PAHs, via dermal intake.

Soil samples, collected 6 months after the fire, show significant quantities of fire effluents. As soil samples were dried at 60 ºC prior to analysis, reported levels of benzene, PAHs, and dioxins may be lower than actually presented. The distributions of benzene, PAHs and PCDD/Fs show very clearly that particulates/soot/char and fragments of fire debris were distributed within the vicinity of the Tower. Concentrations of PAHs, PCDD/Fs and benzene in the soils suggests that these particulates released toxic substances. Soil concentrations exceed guideline values within 150 m of the Tower. HCN was also observed in TGA-FTIR. Figure 6, shows the localisation of toxicant distribution following the fire. Results suggest that the major sources of contamination for the toxicants analysed in this study are particulates of diameter greater than 100 µm deposited up to 200 m away from the Tower and greater than 10 µm within 2000 m distance from the Tower.

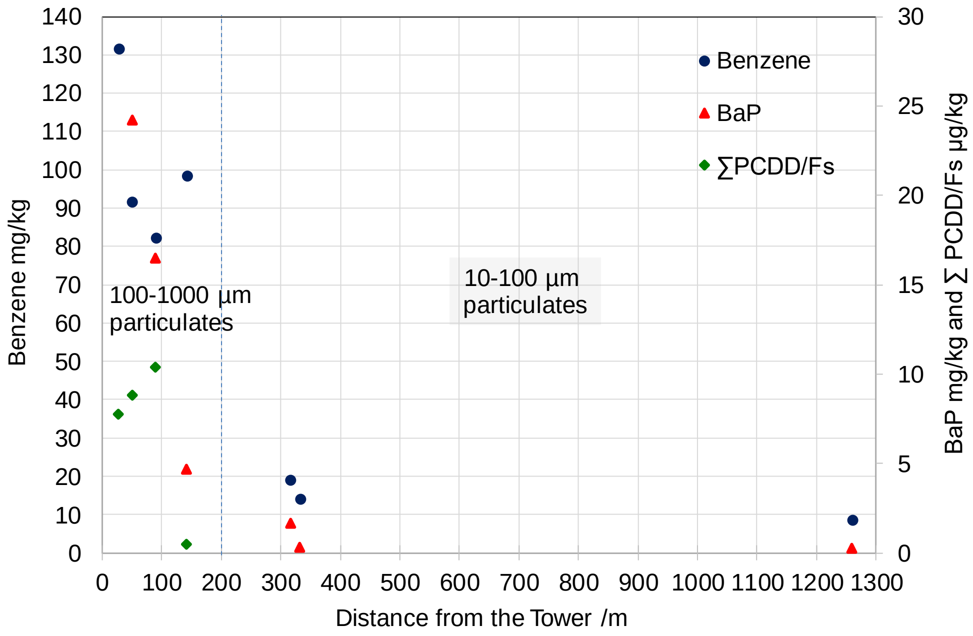


Figure 6. Concentrations of fire effluents in soil samples (Benzene and BaP in mg/kg, PCDD/Fs in µg/kg).

The elevated levels of dioxins and furans and PAHs found in soil samples is in stark contrast to the undetectable levels found during air monitoring by PHE (PHE 2018a). This is unsurprising since any gas phase PAHs or PCDD/Fs will have been dispersed prior to commenced of the PHE analysis (month after the fire) (PHE. 2018b).

The HCN evolution from the soil, mirrors the temperature range of release from ferri- and ferro-cyanides. This suggests that S1 to S4 were exposed to significant quantities of HCN, particularly as S5 –S7 show no such release. TGA-FTIR analysis showed release of MIC as a decomposition product of the fire debris and char samples. The yellow oil on the window blind has been previously characterised as a part polymerised product of isocyanates. Discovery of MIC deposition a volatile liquid (boiling point at 38 °C), on part of the window blind that was exposed to the outside air, is an obvious health concern particularly as it was found 17 months after the fire within a living space.

Analysis of the SVFs from the three insulation panels (PIR, PhF, SW) used on the Tower was compared to that of the SVFs found in soil, char and residue (see section 3.8). It was found that SVFs isolated from the soils are more likely to originate from PIR for S1 and PhF for S2.

The composition of the SVF from the fire debris corresponded to that of phenolic foam, whereas the SVF on the chars (Char2 and Char3) displayed close similarities to the SVF from the PIR foam.

Soon after the fire, there was little evidence of environmental, indoor or health surveillance to identify the types of fire effluents or populations at risk. The Grenfell Tower fire released both acute and chronic toxicants in the fire effluent which may have potential long-term adverse health effects on emergency responders, clean-up workers and local residents.

The data needs to be interpreted with caution as soil is a complex matrix which can vary significantly, even within a small area such as the Grenfell environments. A much more valuable study could have been undertaken in the immediate aftermath after the fire. The absorption and release of toxicants will depend both on their chemical nature and the characteristics of the soil. Sampling from better controlled environments such as plant pots, where a known potting compost has been used and the medium has been undisturbed since the fire, have potential to identify fire contaminants more reliably. In addition, indoor contaminants resulting from deposits within residents homes (dust) have greater potential for positive identification and establishing their relationship to any long-term health effects.

From earlier study on the fire behaviour of façade materials, it has been found that brominated flame retardants were not present in significant quantities on the exterior face of the building (McKenna *et al.* 2019). It is acknowledged that furniture and other products in the Tower may and will contain them, but less clear how much effluent would be released to the surrounding environment.

The presence of chlorinated PCDD/Fs and the presence of brominated flame retardants in furniture etc. suggests the likely presence of brominated and mixed brominated-chlorinated dioxins and furans. Significant quantities of chlorinated, brominated and mixed dioxins and furans were identified around the World Trade Centre (Landrigan *et al.* 2004). The presence of both PAHs and halogenated PCDD/Fs also strongly indicates the likely presence of halogenated PAHs, polychlorinated and polybrominated biphenyls (Xu *et al.* 2018). None of these substances were analysed in this study. They have health risks associated with their presence and should be quantified in any follow-up study.

Any health effects, together with long-term fire exposure monitoring, should also be carried out and supervised by a multidisciplinary team with medical, environmental, fire and combustion toxicology expertise. Public agencies need to be adequately prepared to provide reliable guidance to the public on more appropriate means of exposure assessment, risk assessment, and preventive measures - in the event of a recurrence such as this tragic fire.

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