

Aerostat Sampling of PCDD/PCDF Emissions from the Gulf Oil Spill In Situ Burns

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Emissions from the in situ burning of oil in the Gulf of Mexico after the catastrophic failure of the Deepwater Horizon drilling platform were sampled for polychlorinated dibenzodioxins and polychlorinated dibenzofurans (PCDD/PCDF). A battery-operated instrument package was lofted into the plumes of 27 surface oil fires over a period of four days via a tethered aerostat to determine and characterize emissions of PCDD/PCDF. A single composite sample resulted in an emission factor of 2.0 ng toxic equivalency (TEQ) per kg of carbon burned, or 1.7 ng TEQ per kg of oil burned, determined by a carbon balance method. Carbon was measured as CO₂ plus particulate matter, the latter of which has an emission factor of 0.088 kg/kg carbon burned. The average plume concentration approximately 200–300 m from the fire and about 75–200 m above sea level was <0.0002 ng TEQ/m³.

Introduction

The Deepwater Horizon oil drilling platform located in the Gulf of Mexico, owned and managed by Transocean for British Petroleum (BP), caught fire on April 20, 2010 and sank. Eleven lives were lost and the ensuing oil leak resulted in an environmental disaster for the Gulf region. The U.S. Coast Guard (USCG) and BP undertook operations to collect and burn the surface oil as one means of limiting its environmental impact. Pairs of vessels, typically fishing trawlers, towed a collection boom through surface oil slicks, accumulating oil. Smaller “igniter” boats placed an incendiary starter charge (gelled diesel in a plastic container with foam flotation and a road flare) within the boom’s oil pool to promote ignition. Under appropriate conditions of the oil and the sea/wind state, the collected oil would ignite, burning for times varying from minutes to hours. The USCG estimated that between 220,000 and 310,000 barrels of oil were consumed during 411 in situ burns between April 28, 2010 and July 19, 2010 (1).

In situ burning of oil spills has the benefit of minimizing contamination of coastal marine environments. Probably the largest detriment is the emissions from the incomplete combustion of the oil, as indicated by the copious volumes of black, particle-laden smoke. Various efforts have been

undertaken to quantify the emissions from in situ burns, the most comprehensive at-sea effort being the Newfoundland offshore burn experiments (2). Particle and gas concentrations sampled by aircraft-borne instruments were developed into emission factors (3) using a carbon balance approach (mass of pollutant per mass of fuel carbon). Other measurements were made using samplers aboard remotely controlled marine vessels and tethered aerostats (4).

Emissions of polychlorinated dibenzodioxins and polychlorinated dibenzofurans (PCDD/PCDF) from the oil burns are of interest due to their health effects (5) including immunotoxicity, carcinogenicity, and teratogenicity. The potential for PCDD/PCDF emissions from the Gulf in situ burns exists due to the apparent presence of the prerequisite conditions for formation: incomplete combustion, the presence of trace metals as catalysts, and availability of chloride in the seawater. Few measurements of PCDD/PCDF have been made from oil fires and only one (2) to our knowledge from an at-sea burn similar to those of the Gulf in situ burns. Results from two samples at sea level were reported as indistinguishable from background levels, leading to the conclusion that PCDD/PCDF were not formed from oil spill burns (6, 7). Similar conclusions were reached during experimental, mesoscale burns (4) when ground-based emission samples were compared against upwind sampling. In both of these cases the PCDD/PCDF sampling was done at sea/ground level, apparently outside of the visible plume, so questions remain regarding their ability to resolve whether or not PCDD/PCDF are formed.

To measure the potential emissions of PCDD/PCDF from the Gulf in situ oil burns, an aerostat-lofted instrument package was used to sample the plume emissions to determine PCDD/PCDF concentrations and an emission factor.

Materials and Methods

Aerostat Operations at Sea. A 4.0-m diameter, helium-filled aerostat (Kingfisher model, Aerial Products Inc., FL) was used to loft an instrument package (termed the “Flyer”) into oil fire plumes for sample collection. The aerostat/Flyer were launched from the deck of the MV Allison (Aries Corporation), a 67-m long oil platform work boat. The aerostat was secured to an electric winch by a 609-m long, 2.5-mm diameter Spectra tether. Tethered aerostat flight operations were conducted in accordance with regulations for moored aerostats (8). Because of increased air traffic in support of oil spill operations, several additional operational requirements were coordinated with the Federal Aviation Administration (FAA) and Incident Command Post (ICP). These requirements included daily altitude restrictions, a dedicated air traffic observer, two-way radio contact on Common Traffic Advisory Frequency, and availability of a signal flare if necessary to visually alert aircraft to our presence. The FAA published a daily Notice to Airmen (NOTAM) advising pilots that tethered aerostat operations were being conducted in the area. The FAA also required notification prior to each flight operations period including precise location in relation to the Deepwater Horizon source, any position changes of more than 1.85 km, and termination of the daily flight operations. As a further precaution, the Aerostat Flyer was equipped with a radio-controlled deflation valve in the unlikely event it became loose from its tether. Filling the aerostat with helium and lofting the Flyer to the sampling altitude took approximately 30 min. The MV Allison maneuvered directly underneath the burn plumes, maintaining a distance of at least three to five burn diameters from the

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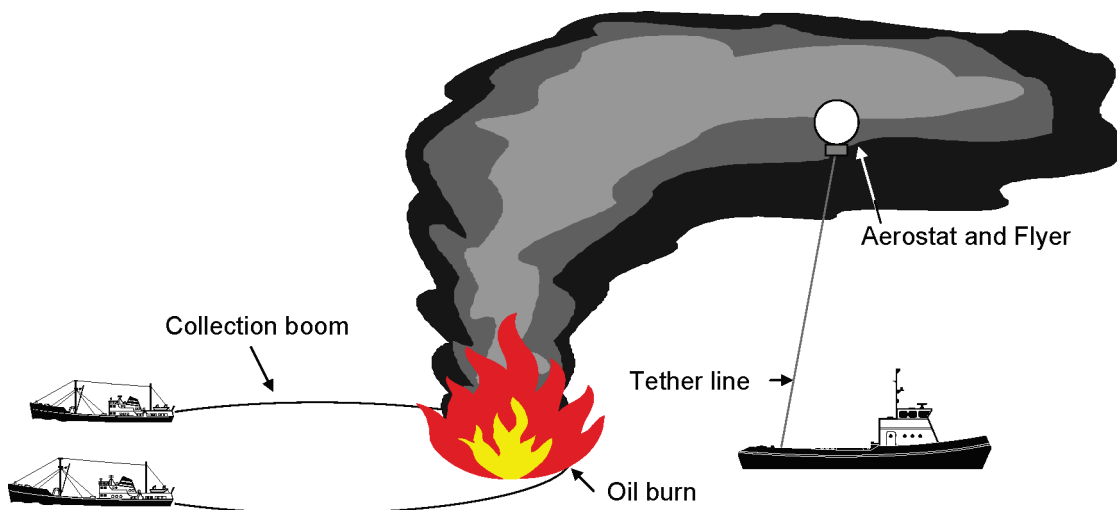


FIGURE 1. Schematic illustration of the in situ burn operations and plume sampling.

fire as required by the U.S. Coast Guard (USCG) for safety. Sampling was opportunistic and was conducted on a noninterference basis to the burns. As such, the MV Allison avoided crossing the path of the boom vessels and creating a wake, each which would disrupt the oil collection and potentially extinguish the flame (see Figure 1). An industrial hygienist on board the MV Allison monitored the air conditions for the aerostat team. The aerostat height, maintained below the FAA-mandated ceiling of 228 m, was adjusted to the center of the plume by the length of the tether; this was aided by spotters aboard a second, nearby vessel, the MV Jamie G. Minor lateral corrections for the plume center were done by walking the tether line fore and aft of the winch. When the oil fire diminished, the MV Allison withdrew and proceeded to the next likely oil fire, with the aerostat staying aloft and the sampler off.

Sampling. The intention of the sampling effort was to take at least three samples to target statistical robustness of the determined plume concentration and emission factor. The minimum amount of emission mass targeted for sampling was based on the authors' prior experience with burning multiple fuel types (9–11). Relatively clean-burning fuels, in terms of PCDD/PCDF production per mass of fuel combusted, require collection of a minimum of 4 g of carbon from the combusted fuel emissions in order to avoid nondetects among the 17 PCDD and PCDF congeners which comprise the toxic equivalency (TEQ). This carbon is measured, in part, during the course of the run by online measurement of CO₂. Other sources of carbon in the emissions include particulate matter (PM), CO, and total hydrocarbons. Of these, only PM was considered a relatively significant contributor to the total carbon emitted (up to 10% by mass (3)) and targeted for sampling. Over 80% of the PM mass was considered to be elemental carbon based on previously published measurements of oil fires (3). As such, plume sampling consisted of online measurement of CO₂ and simultaneous filter sampling of PM.

It was anticipated that each of the three targeted samples would take at least 4 hours of in-plume sampling to get the minimum of 4 g of carbon to comprise a single, complete sample. This anticipated sampling duration was based on the sampling rate as well as the CO₂ concentration data of others (6) during at-sea oil burns, although dissimilarities in experimental approaches made this comparison approximate. Since fires typically were less than 1 hour, multiple plumes would be sampled with the same sorbent, resulting in a single, composite sample.

A background sample was taken to compare the plume concentration with ambient levels. The same design of

sampler was used for the background and the lofted plume sampling to ensure consistency of methods. Background sampling was conducted overnight when burns were suspended and during the departure and return to port in order to compare PCDD/PCDF levels against those found while sampling the burning oil plume. The Flyer was positioned on the bridge of the MV Allison to avoid capture of any fumes from the diesel engines. A trip blank and a field blank were also included for quality assurance.

Instruments. The Flyer (Figure 2) comprised multiple instruments powered by 12 V Li-ion and AA batteries. CO₂ was continuously measured in accordance with EPA Method 3A (12) using a nondispersive infrared (NDIR) instrument (LI-820 model, LI-COR Biosciences, USA). This unit was configured with an optional 14-cm optical bench, giving it an analytical range of 0–20,000 ppm with an accuracy specification of less than 2.5% of reading. The LI-820 calibration range was set to 0–4500 ppm. A particulate filter preceded the optical lens. The LI-820 was equipped with a programmable trigger circuit which activated collection of all samples at a user-set CO₂ concentration above background levels, indicating that the Flyer was within the emission plume. This trigger conserved batteries and avoided dilution of the sample with ambient air. The initial trigger setting was 500 ppm CO₂ but was changed to 400 ppm CO₂ after the first two plumes showed minimal CO₂ elevation above the background CO₂ concentration. Daily measurements of background CO₂ were used to calculate the CO₂ elevation in the plumes. These measurements were taken from the lofted Flyer and ranged from 371 to 374 ppm over the 4 days of sampling. The CO₂ level also triggered a total PM sampler comprising a 47-mm tared Teflon filter (pore size of 2.0 μm) and a Leland Legacy sample pump (SKC Inc., USA) with a constant airflow of 13 L/min. An internal flow sensor on the Leland pump measured flow directly and acted as a secondary standard to constantly maintain the set flow. Total PM was measured gravimetrically using pretared filters transported in sealed Petri dishes. The weigh scale was accurate to ±1 μg and all filters were conditioned to 20–23 °C and 30–40% relative humidity for a minimum of 24 h before weighing. Measurements are reported at actual sample temperature and humidity without normalization.

Emissions were sampled for PCDD/PCDF by drawing the plume sample through a polyurethane foam/XAD-2/polyurethane foam (PUF) sorbent cartridge. In a modification of EPA Method TO9A (13), the cartridge was followed, rather than preceded, by a glass fiber filter (70-mm diameter) to ensure that the filter catch did not fall off during flight. This filter was changed out daily. The 12-V sampling pump

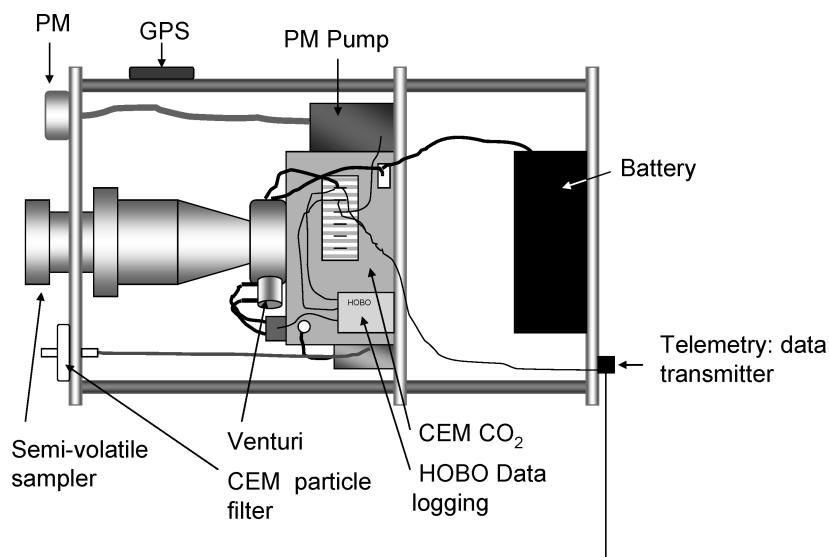


FIGURE 2. Schematic illustration of the "Flyer" used for plume sampling.

(MINIjammer, AMETEK, USA) had a nominal sampling rate of 160 L/min. Flow rate through the pump was measured by pressure drop through a precalibrated venturi and the voltage equivalent was recorded on a data logger. An on-board data recorder (HOBO U12-013, Onset Computer Corporation, USA) saved the CO₂ concentrations and flow rate as voltage equivalents data every 2–3 s. The HOBO also measured temperature and relative humidity. The HOBO maintained an internal time with an accuracy of ±1 min per month.

The Flyer also had a Geko 301 (Garmin, USA) global position system (GPS) for location and height above sea level, saving data every 10 s. A wireless telemetry and data recorder system (Seagull Sea Pro 900, Eagle Tree Systems, LLC) on the Flyer was used to transmit signals to the vessel. This 9-V system transmitted CO₂ concentrations (as a voltage), flow rate (as a voltage), ambient temperature, and battery output to the aerostat crew on the MV Allison. This information was used as an aid in positioning the aerostat within the plume, monitoring volumetric sampling rate to determine whether a filter change was necessary, and conveying residual battery capacity. These data together with the telemetry's GPS data were saved every millisecond and used as a secondary data logger.

Quality Assurance. Prior to field sampling and analysis, a quality assurance (QA) project plan was written and approved by the EPA QA Manager to ensure that the operation of the instruments, sampling procedures, analytical data, and calculations were consistent with QA Category 1, EPA's highest category of quality assurance (14). A technical systems audit of the sampling was conducted by the EPA QA Manager, who was present for the entire duration of the sampling. A technical systems audit of the dioxin laboratory analysis was also performed with auditors witnessing the extraction, cleanup, and HRGC/MS injection of the sample and blanks. Auditors also witnessed the weighing of the PM samples. The results from the audits suggested that appropriate controls and methods were applied to ensure the quality and usefulness of the data.

The LI-820 was calibrated for CO₂ on a daily basis in the field using a zero (nitrogen) and one span gas (4500 ppm CO₂ in nitrogen) and checks with two intermediate CO₂ gas concentrations (1500 and 400 ppm CO₂) in accordance with U.S. EPA Method 3A (12). The Leland Legacy sample pump was calibrated daily in the field with a Gilibrator Air Flow Calibration System (Sensidyne LP, USA), which is a primary standard airflow calibrator; the accuracy goal for the Leland Legacy pump system was ±5%. The flow rate through the

venturi was measured with a pressure transducer and verified by a Roots meter both prior to and after the field campaign.

A field and trip blank were taken during the sampling for determination of PCDD/PCDF concentration. The trip blank was sealed at the laboratory, taken to the test site, and returned to the laboratory unopened. During a period when no oil burns were present, the field blank was assembled into the Flyer's sampler, left on the deck for 1 h, and removed for return to the laboratory. Both field and trip blanks underwent analysis as per the plume and background sample.

Analysis Methods. Analysis of PCDD/PCDF followed procedures in EPA Method 8290A (15). Presampling, pre-extraction, and recovery standards were used, allowing sample collection, extraction, and instrument efficiency to be determined as well as sample quantification via the method's isotope dilution procedure. The combined PUF/XAD-2/PUF and glass filters were extracted in a Soxhlet apparatus overnight with toluene. The raw extracts were concentrated using three-ball Snyder columns to about 100 mL, filtered with a 0.2- μ m Teflon syringe filter, and concentrated further with flowing N₂ using an automated evaporator (Biotage, Sweden) to 0.5 mL. The extracts were diluted in hexane then cleaned and fractionated using an automated, multicolumn liquid chromatography system (Power Prep Dioxin System, FMS Fluid Management Systems, Inc., USA). The columns consisted of acidic/basic/neutral (ABN) silica gel, basic alumina, and carbon/Celite. The plume sample was precleaned through an additional ABN silica gel column due to the amount of residual color in the extract.

Concentrations of PCDDs/PCDFs in the sample were determined by high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS) consisting of a Hewlett-Packard gas chromatograph 6890 Series equipped with a CTC Analytics Combi PAL autosampler (CTC Analytics, Switzerland) and coupled to a Micromass Premiere (Waters Inc., UK) double-focusing high-resolution mass spectrometer. A 60-m DB-Dioxin (Agilent/J&W Scientific, USA) column was used (0.15- μ m film thickness \times 0.25-mm i.d.). The temperature program for PCDDs/PCDFs was from an initial temperature of 150 to 260 at 10 °C/min with a final hold time of 55 min. Two microliters (2 μ L) of the extract was injected under splitless mode (the injection port temperature was 270 °C). The HRMS was operated in an electron impact (35 eV and 650 μ A current) selective ion recording (SIR) mode at resolution $R > 10\,000$ (5% valley). The temperature of the ion source was kept at 250 °C. The presampling HRGC/HRMS calibration curve was developed with standards appropriate

TABLE 1. Plume and Sampling Parameters and Results

plume ID	date	burn start	burn stop	cumulative sample time (min)	average temperature (°C)	PCDD/PCDF plume sample volume (m ³)	average ΔCO ₂ (ppm)	carbon from CO ₂ (g)	PM density (g/m ³)	PM emission factor (g/g carbon)	carbon from PM (g)	total carbon (g)
1	2010-07-13	13:24	13:36	5.9	31	0.472	109	0.036				
2	2010-07-13	14:21	14:41	2.1	29	0.112	84	0.007				
3	2010-07-13	15:05	15:20	2.9	30	0.270	27	0.005				
4	2010-07-13	16:24	16:56	12.4	31	1.427	58	0.053				
5	2010-07-13	17:04	17:21	13.2	31	1.629	99	0.099				
6	2010-07-13	18:23	19:58	22.0	31	2.314	57	0.084				
sum				58.4	31	6.224	72	0.284	0.0041	0.10	0.021	0.305
7	2010-07-14	11:03	11:10	1.1	30	0.110	38	0.003				
8	2010-07-14	12:36	12:53	1.9	30	0.156	22	0.002				
9	2010-07-14	14:31	14:45	10.6	31	1.414	73	0.064				
10	2010-07-14	15:08	15:12	1.8	31	0.192	57	0.008				
11	2010-07-14	15:49	15:55	1.4	31	0.137	26	0.002				
12	2010-07-14	17:15	17:35	4.1	34	0.458	37	0.012				
13	2010-07-14	17:56	18:09	7.0	32	0.805	31	0.016				
14	2010-07-14	18:16	18:30	6.7	31	0.728	37	0.019				
15	2010-07-14	18:49	19:04	9.5	31	1.219	62	0.097				
16	2010-07-14	19:41	19:50	4.7	30	0.625	66	0.023				
17	2010-07-14	19:52	20:25	17.7	30	2.500	76	0.106				
sum				66.6	31	8.344	47	0.352	0.0044	0.11	0.031	0.383
18	2010-07-15	15:08	15:19	7.6	31	0.994	55	0.035				
19	2010-07-15	16:42	17:25	6.9	31	0.811	33	0.002				
20	2010-07-15	17:39	17:45	3.8	35	0.452	29	0.008				
21	2010-07-15	18:20	18:22	1.0	36	0.100	28	0.002				
22	2010-07-15	19:26	20:03	28.3	30	3.700	52	0.121				
sum				47.6	33	6.057	39	0.184	0.0028	0.10	0.014	0.198
23	2010-07-16	09:51	10:10	14.1	31	2.061	142	0.174				
24	2010-07-16	10:45	10:53	0.2	30	0.026	59	0.001				
sum				14.3	31	2.087	101	0.175	0.0073	0.087	0.013	0.188
25	2010-07-16	14:48	15:09	14.6	31	2.103	153	0.194				
26	2010-07-16	16:53	17:23	6.0	31	0.905	195	0.101				
27	2010-07-16	17:43	17:57	7.9	30	0.940	46	0.028				
sum				28.6	31	3.948	131	0.323	0.0032	0.044	0.011	0.334
total average				215	31	26.660	70	1.318	0.0044	0.088	0.090	1.408

for a final extract volume of 20 μL. The criterion for identification of a congener peak was a 2.5/1 signal-to-noise ratio. TEQ values were calculated from the World Health Organization 2005 factors (16) using nondetect congeners as zeros and as their detection limit values.

Calculations. CO₂ concentrations determined by the NDIR and PM mass from gravimetric filter analyses were linked with their corresponding flow rate measurements to determine the total carbon mass sampled, volume sampled, and time of sampling. This permitted normalization of the PCDD/PCDF mass by the amount of gas volume sampled and the amount of carbon collected, the latter using the carbon mass balance method (17). Gravimetric determinations of particulate mass were related to carbon mass captured based on the carbon percentage (~84%) determined by particle sampling (3) during in situ oil burn trials (2). The amount of carbon collected can be related to the amount of fuel combusted by the oil stoichiometry, resulting in an emission factor in terms of the amount of oil burned. The fuel's carbon mass percentage was 85% based on an average of cited literature (86% (3), 84% (18)).

Results and Discussion

Four days of sampling, from July 13 to 16, 2010, resulted in capture of emissions from 27 plumes (Table 1) from which only a single, composite PCDD/PCDF sample was obtained. This single sample contained less carbon than was projected to be necessary for PCDD/PCDF analysis. Five composite PM samples were obtained (Table 1) over four sampling days.

The plumes from the oil fire were typically lofted and did not impinge on the water surface. Characteristic vortices of black smoke were the norm. Substantial variation of in-plume CO₂ concentration indicated significant dilution and mixing even at a nominal 250-m distance from the fire source. Minimal elevation of plume temperature (about 1–2 C°) above ambient levels was observed (Table 1). Pressure drop and filter plugging were minor; the largest decline in flow rate for the PCDD/PCDF sampler during a sampling day was 11% of its maximum.

The average, cumulative residence time of the Flyer in each plume when the CO₂ concentration exceeded the 400 ppm trigger was 7.98 min (standard deviation, σ, 6.88 min), recording an average CO₂ rise over ambient of 70 ppm (σ = 43 ppm). Only a single, composite PCDD/PCDF sample was collected; by July 15 the well leak had been capped, the surface oil had diminished, and the sea state prevented further sustainable in situ burns. The total carbon collected as CO₂ from the 26.6 m³ sample volume was 1.318 g. PM filters were collected daily during the 27 plumes, amassing 0.01094 g from 2.731 m³ sample volume on the five filters. Of this PM mass, 84% was assumed to be carbon based on data cited earlier (3). The PM emission factor was 0.088 g/g_{carbon} with a relative standard deviation (rsd) of 26% over the five measurements (Table 1). This low rsd value affirms the assumption that plume mixing was sufficient to meet the carbon balance requirement that PCDD/PCDF, CO₂, and PM are in constant proportion. The total carbon collected was 1.41 g, 95% of it from CO₂. This was less than that desired

TABLE 2. PCDD/PCDF Concentration and Emission Factor Values for the Plume Sample^a

	PCDD/PCDF plume concentration (fg TEQ/m ³) ^b	emission factor (ng TEQ/kg carbon burned) ^b	emission factor (ng TEQ/kg fuel burned) ^b
2,3,7,8-TCDD	ND [19.]	ND [0.36]	ND [0.30]
1,2,3,7,8-PeCDD	ND [58.]	ND [1.1]	ND [0.94]
1,2,3,4,7,8-HxCDD	6.8	0.13	0.11
1,2,3,6,7,8-HxCDD	4.5	0.085	0.072
1,2,3,7,8,9-HxCDD	9.0	0.17	0.14
1,2,3,4,6,7,8-HpCDD	1.5	0.028	0.024
1,2,3,4,6,7,8,9-OCDD	0.14	0.0027	0.0023
sum PCDD	22.	0.41	0.35
2,3,7,8-TCDF	18.	0.34	0.29
1,2,3,7,8-PeCDF	3.4	0.064	0.054
2,3,4,7,8-PeCDF	40.	0.77	0.65
1,2,3,4,7,8-HxCDF ^c	13.	0.24	0.21
1,2,3,6,7,8-HxCDF	4.5	0.085	0.072
1,2,3,7,8,9-HxCDF	ND [1.6]	ND [0.031]	ND [0.027]
2,3,4,6,7,8-HxCDF	3.8	0.071	0.060
1,2,3,4,6,7,8-HpCDF	1.3	0.024	0.020
1,2,3,4,7,8,9-HpCDF	0.75	0.014	0.012
1,2,3,4,6,7,8,9-OCDF	ND [0.026]	ND [0.0050]	ND [0.00043]
sum PCDF	85.	1.6	1.4
sum PCDD/PCDF (ND = 0)	110.	2.0	1.7
sum PCDD/PCDF (ND = DL)	190.	3.5	3.0

^a Sums may not add directly after accounting for significant digits. ^b Limit of detection values within brackets. ^c Uncorrected for contaminant observed in the trip and field blanks. Correction would decrease the sum values <6%.

for a single sample (4 g) and the sole sample from the field was short of the targeted number of three samples for the campaign.

The trip blank and field blank resulted in nondetects (Supporting Information, Table S-2) for all but one congener, implying confidence in the overall cleanliness of the sampling media and handling procedures. The one detected congener (1,2,3,4,7,8-HxCDF) is a contaminant in the surrogate standards (presampling spike) and is a consequence of the relatively high level of the surrogate to target concentrations. This contamination was confirmed by analysis of the commercial standard solutions. The single, composite background PCDD/PCDF sample was collected intermittently over six days, primarily during nighttime, for a total of 24 h 8 min (1448 min) resulting in a total sample volume of 170.9 m³. As with the trip and field blanks, the only detected congener in the background sample was that of the standard contaminant (1,2,3,4,7,8-HxCDF).

Concurrent background measurements were taken of CO₂ and PM. The average CO₂ concentration was 373 ppm. The background PM concentration was 0.0127 μg/m³ during collection of 18.46 m³.

The emission sample from the in situ burn plume (26.6 m³) had 13 detectable 2,3,7,8-Cl-substituted congeners of the 17 that comprise the TEQ value. This is in distinct contrast with the background sample which had all nondetects (excluding the standard contaminant) despite almost seven times the sample volume. This confirms the net formation of PCDD/PCDF from the in situ oil fires.

Measurement of PCDD/PCDF above background levels is in contrast with conclusions from limited, previous data from in situ ocean (6, 7) and mesoscale laboratory oil spill burns (4). Their conclusions may have been reached based on insufficient sampling due to positioning their sampler outside of the plume at sea/ground level, low sample volume, high trip blank concentrations, and high detection limits (6).

Concentration and emission factor data by congeners and TEQ values are listed in Table 2. Table 3 lists the homologue data. Values are listed with the nondetect (ND) congeners treated as both zeros (0) and at their detection limit (DL).

TABLE 3. PCDD/PCDF Homologue Concentrations for the Plume Sample^a

homologue	PCDD/PCDF concentration	
	(fg/m ³)	(fg TEQ/m ³) ^b
TCDD	ND	ND [18]
PeCDD	ND	ND [58]
HxCDD	270	20
HpCDD	240	1.5
OCDD	470	0.14
sum PCDD	980	22
TCDF	2500	18
PeCDF	580	44
HxCDF ^c	350	21
HpCDF	200	2.0
OCDF	ND	ND [0.026]
sum PCDF	3600	85
total PCDD/PCDF (ND = 0)	4600	110

^a Sums may not add directly after accounting for significant digits. ^b Limit of detection values within brackets. ^c Uncorrected for contaminant observed in the trip and field blanks.

The use of ND = DL provides for an upper bound of the concentration and emission factor based upon these sampling data. The 27-sample PCDD/PCDF concentration is 110 fg TEQ/m³ (190 fg TEQ/m³ at ND = DL). The calculated emission factor is 2.0 ng TEQ/kg carbon burned (3.5 ng TEQ/kg carbon burned at ND = DL) or 1.7 ng TEQ/kg fuel burned (3.0 ng TEQ/kg fuel burned at ND = DL). These values are roughly 25–65 times higher than those observed for controlled combustion of waste engine oil (19), within the range of PCDD/PCDF emission factors determined for open biomass burning (20–22), and over 2 orders of magnitude lower than open burning of residential waste (10). Although only a single, composite sample from 27 plumes could be obtained, the precision of its emission factor would likely be better than those from burning of more heterogeneous

biomass samples, where the relative standard deviations were significantly less than 100% (20, 23). This fact, combined with the low rsd value for the PM emission factor (26% over five measurements) suggests that the PCDD/PCDF emission factor is accurate within a factor of 2. When the emission factor range, 1.7 ng TEQ/kg fuel burned (ND = 0) to 3.0 ng TEQ/kg fuel burned (ND = DL), is applied to the estimated amount of oil burned in the Gulf clean up operation, 220,000 and 310,000 barrels of oil (1), the total amount of PCDD/PCDF released is about 0.05 to 0.13 g TEQ. This can be compared with the U.S. EPA inventory of sources (24) which amounts to over 1300 g TEQ/year from all quantifiable sources.

Sea, weather, and oil conditions during this sampling resulted in plumes of varying appearance, duration, and intensity. A composite sample from 27 of these plumes resulted in emission factors and concentrations that were representative of the Gulf in situ oil fires. The extent to which these values may be applied to emissions from other in situ oil fires remains to be determined. Incorporation of the emission factor into transport and deposition models can provide information on potential receptor exposure on land and water, allowing the impact of PCDD/PCDF emissions from in situ oil burns on environmental and other routes of human health exposures to be assessed. These studies would be useful in balancing the overall ecosystem and health impact of in situ burning versus alternative cleanup strategies and their environmental impacts.

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Supporting Information Available

Analytical notes and detailed sample results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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