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

- Supporting information -

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The targeted sample size (carbon) in the initial quality assurance plan was twice as much as was collected. Accordingly, the PUF/XAD-2/PUF had been spiked with pre-sampling standards at higher concentrations than would be warranted by the actual sample obtained. The HRGC/HRMS calibration solutions for the 5-point calibration curve were tailored to the actual concentrations of the standards in the final extract volume of 20 μL. The concentrations of the calibration solutions are given in Table S-1. The concentration of the surrogate (pre-sampling), internal (pre-extraction), and recovery (pre-

injection) standards in the samples are given in Table S-2. This adjustment of the concentrations in the initial calibration resulted in the pre-sampling surrogates being up to ten times more concentrated than the pre-extraction spikes (Table S-2). The high ratio of pre-sampling to pre-extraction surrogate caused overlapping peaks for HxCDD/F on the DB-Dioxin column (the hexa-chlorinated pre-extractions spikes were a small peak on the trailing edge of the pre-sampling hexa-chlorinated spikes). The same phenomenon was observed on the DB-5 column that was tested to obtain better chromatographic separation of $^{13}C_{12}$-1,2,3,4,7,8-HxCDD/F from $^{13}C_{12}$-1,2,3,6,7,8 HxCDD/F . The hexa-chlorinated pre-extraction spikes were integrated tangentially instead of to baseline (both for the calibration solutions and samples). Due to the overlapping HxCDD/F peaks, elevated recoveries of hexachlorinated internal standards and consequent lower recoveries of hexachlorinated pre-sampling spikes were observed.

Table S-1. Composition and Concentrations of the Calibration Solutions.

Calibration solution	Native PCDDs/Fs	Pre-sampling surrogates		Pre-extraction surrogates			Pre-injection surrogates
	TCDD/F to OCDD/F	$^{37}Cl_{14}$-TCDD	$^{13}C_{12}$PeCDD/F to HpCDD/F	$^{13}C_{12}$ TCDD/F	$^{13}C_{12}$PeCDD/F to HpCDD/F	$^{13}C_{12}$ OCDD	$^{13}C_{12}$ TCDD to HxCDD
ICAL1	1	25	50	25	50	100	50
ICAL2	2.5	100	200	25	50	100	50
ICAL3	5	150	300	25	50	100	50
ICAL4	25	200	400	25	50	100	50
ICAL5	50	250	500	25	50	100	50

Table S-2. Concentrations and Recovery Criteria for the Surrogate (Pre-Sampling) and Internal (Pre-Extraction) Standards for the Plume Sample, Background Sample, Trip Blank, and Field Blank.

Spiking Solution	Analytes	Std. Concen. in sample (pg/μL)	Recovery (%)			
			Plume Sample	Background Sample	Trip Blank	Field Blank
Surrogate standards (Pre-sampling)	$^{37}Cl_{14}$-2,3,7,8-TCDD	250	90	85	86	82
	$^{13}C_{12}$-2,3,4,7,8-PeCDF	500	87	80.	84	81
	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	500	**64**	**51**	**53**	**39**
	$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	500	84	77	78	75
	$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	500	89	81	82	74
Internal standards (Pre-extraction)	$^{13}C_{12}$-2,3,7,8 TCDF	25	95	99.	90	92
	$^{13}C_{12}$-2,3,7,8 TCDD	25	89	92.	92	93
	$^{13}C_{12}$-1,2,3,7,8 PeCDF	50	91	94	88	84
	$^{13}C_{12}$-1,2,3,7,8 PeCDD	50	44	101	96	98
	$^{13}C_{12}$-1,2,3,6,7,8 HxCDF	50	120	**141**	**133**	**171**
	$^{13}C_{12}$-1,2,3,6,7,8 HxCDD	50	88	94	94	96
	$^{13}C_{12}$-1,2,3,4,6,7,8 HpCDF	50	75	76	75	72
	$^{13}C_{12}$-1,2,3,4,6,7,8 HpCDD	50	83	88	82	86
	$^{13}C_{12}$-1,2,3,4,6,7,8,9 OCDD	100	73	76	76	76
Recovery Standards	$^{13}C_{12}$-1,2,3,4-TCDD	50	NA	NA	NA	NA
	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	50	NA	NA	NA	NA

Bold values fall outside the recovery criteria of U.S. EPA Method 23.

All four samples met the recovery acceptance criterion recommended by U.S. EPA Method 23 *(1)* for surrogate standards (between 70% and 130%) except for the HxCDF standard. The internal standards all meet the recovery criteria for U.S. EPA Method 23 (between 40% and 130%) except for the HxCDF standard on the non-plume samples.

Table S-3 presents all of the analytical results for the four samples. The congener mass relationships, or patterns, have typically been used as source identifiers. The pattern in the last column of the table for the plume sample is similar to those found in this laboratory for a variety of biomass sources.

The plume sample data suffer limitations of four non-detects for the 17 toxic congeners that comprise the PCDD/PCDF toxic equivalency (TEQ) measure. The range of the signal to noise ratios observed for the 13 detected congeners was 6/1 to 29/1, meeting the S/N detection criteria of 2.5/1 but was below the lowest point of the calibration curve (S/N of 31/1 to 115/1). This is an understandable outcome, as it is not possible a priori to know how much sample mass is sufficient to provide a quantifiable value for each congener and to avoid non-detect congeners.

Table S-3. PCDD/PCDF Analytical Results for All Four Samples.

	Trip blank pg/train	Field blank pg/train	Background Sample pg/train	Plume Sample pg/train
2,3,7,8-TCDD	ND (0.46)	ND (0.46)	ND (0.56)	ND (0.50)
1,2,3,7,8-PeCDD	ND (0.74)	ND (0.62)	ND (0.80)	ND (1.6)
1,2,3,4,7,8-HxCDD	ND (0.70)	ND (0.64)	ND (0.76)	1.8 (0.64)
1,2,3,6,7,8-HxCDD	ND (0.70)	ND (0.64)	ND (0.76)	1.2 (0.66)
1,2,3,7,8,9-HxCDD	ND (0.74)	ND (0.68)	ND (0.80)	2.4 (0.68)
1,2,3,4,6,7,8-HpCDD	ND (0.94)	ND (0.86)	ND (1.0)	4.0 (0.90)
1,2,3,4,6,7,8,9-OCDD	ND (2.0)	ND (1.9)	ND (2.2)	13 (1.6)
2,3,7,8-TCDF	ND (0.76)	ND (0.78)	ND (0.80)	4.8 (0.68)
1,2,3,7,8-PeCDF	ND (0.70)	ND (0.78)	ND (0.72)	3.0 (0.92)
2,3,4,7,8-PeCDF	ND (0.62)	ND (0.70)	ND (0.64)	3.6 (0.82)
1,2,3,4,7,8-HxCDF	1.6 (0.32)	1.4 (0.24)	1.8 (0.32)	3.4 (0.36)
1,2,3,6,7,8-HxCDF	ND (0.30)	ND (0.22)	ND (0.30)	1.2 (0.34)

1,2,3,7,8,9-HxCDF	ND (0.40)	ND (0.30)	ND (0.40)	ND (0.44)
2,3,4,6,7,8-HxCDF	ND (0.36)	ND (0.28)	ND (0.36)	1.0 (0.40)
1,2,3,4,6,7,8-HpCDF	ND 0.74)	ND (0.72)	ND (0.78)	3.4 (0.66)
1,2,3,4,7,8,9-HpCDF	ND (0.96)	ND (0.94)	ND (1.0)	2.0 (0.86)
1,2,3,4,6,7,8,9-OCDF	ND (3.8)	ND (3.4)	ND (3.5)	ND (2.4)

Limit of detection in parentheses.

REFERENCES

(1) U.S. EPA. Method 23. *Determination of Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans from Municipal Waste Combustors*. United States Environmental Protection Agency; http://www.epa.gov/ttn/emc/promgate/m-23.pdf (accessed, July 29, 2010).