

# LEVELS IN THE ENVIRONMENT

## Dioxin / Furan Air Analyses From Times Beach Incinerator

Jeffrey C. Archer and Terry A. Crone, U.S. EPA Region VII, Kansas City, KS 66115-1303 USA

### Abstract:

Times Beach was formerly an incorporated city in southwest St. Louis County, approximately 20 miles southwest of the City of St Louis. On the north and east, the site is bordered by the Meramec River. The Times Beach site and 26 other sites in eastern Missouri were contaminated in the early 1970's with dioxin mixed with waste oil and sprayed on streets and parking lots for dust control. A temporary incinerator was constructed at Times Beach to burn the dioxin contaminated soil from all 27 sites. Six ambient air monitoring stations, one with a co-located sampler, were positioned in the breathing zone surrounding the site of the incinerator to allow the collection of 1100 m<sup>3</sup> (72 hours) of air through each polyurethane (PUF) plug. These plugs were extracted and analyzed for the seventeen 2,3,7,8-chlorine containing dioxins and furans using procedures similar to EPA Method 1613.

### Introduction:

Times Beach, Missouri - an EPA Superfund Site - became a temporary site for the thermal destruction of dioxin contaminated soil. The incinerator was erected with the intent to burn over 250,000 tons of soil at a rate of up to 41.7 tons per hour. Several eastern Missouri areas were discovered to contain high levels of 2,3,7,8-TCDD in the soil after they were sprayed for dust control with dioxin contaminated waste oil<sup>1)</sup> in the early 1970's. Severe illnesses and deaths of animals prompted an investigation that led to the discovery of 2,3,7,8-TCDD in the soil.

The incinerator, previously used in Crosby, Texas, was re-assembled at Times Beach. Upon completion of construction, six air monitoring stations were placed on- and off- site for PCDD/PCDF analyses. A background sample set was analyzed just prior to the burning of blank soil spiked with surrogates, which was used to test incinerator performance. After the surrogate - Principal Organic Hazardous Compounds (POHC) - burn was complete (11/11/95-11/14/95), soil from the highest contaminated site was then excavated and burned while stack samples were collected for PCDD/PCDF analyses. At the completion of the Dioxin Stack Test (11/19/95-11/20/95) the incinerator was shut down to evaluate the data. The incinerator was required to destroy surrogate POHC's at 99.9999%. The production burn for the remaining materials from the 27 sites began March 17, 1996. Air sampling, which began in November of 1995, is planned to continue through June of 1997. The results shown are for EPA Region VII Environmental Services Laboratory samples analyzed through December of 1996.

### Experimental:

Samples were collected every 72 hours from six air monitoring stations, one of which had a co-located sampler to allow for the collection of precision data. The PCDDs/PCDFs were

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collected on polyurethane foam (PUF) plugs and a paper pre-filter via a Hi-Vol (General Metals PS-1) sampler. Roughly 1100 m<sup>3</sup> of air were pulled through the PUF during each 72 hour collection period. The glass cartridges containing the PUFs were wrapped in foil and shipped to the Region VII Laboratory for analysis.

Method blanks were extracted with each set of seven samples and a performance evaluation (PE) sample was extracted with every other set of seven, to insure quality control. The analytes were extracted from the PUFs by Soxhlet extraction during a 16 hour cycle using 500 mL of methylene chloride. After the extraction period had been completed, the solvent was accumulated in the Soxhlet extractor until it was almost full, at which time it was removed. The solvent remaining in the flask was evaporated in a TurboVap apparatus (Zymark Corp.) to 1 mL and solvent exchanged to iso-octane. The extract was then passed through a clean-up column containing silica gel (acidic, basic and neutral) capped with sodium sulfate. Hexane was used to elute the PCDD/PCDF analytes from the silica gel. If additional clean-up was needed, acidic alumina columns were used, following EPA Method 1613<sup>2)</sup> protocol. The hexane was evaporated to 1 mL in the TurboVap apparatus and transferred to a 2 mL conical vial for final blow down to dryness via an N-Evap (Organomation, Inc.). The vials were placed in a refrigerator until just prior to analysis, at which time nonane and the recovery standard were added. The analysis portion closely followed EPA Method 1613, an Isotope Dilution technique using GC/HRMS.

Initial studies, which included an Initial Precision and Recovery, a blank study, and a Method Detection Limit (MDL) study based upon 40 CFR Part 136 Appendix B<sup>3)</sup> were completed. The MDL study was completed in lieu of the determination of sample dependent detection limits, which are based on instrument noise levels.

## Results & Discussion:

The Initial Precision and Recovery (IPR) study was completed per Method 1613 with four replicates. Each analyte was within the average concentration range and the standard deviation of the concentration suggested for the IPR study via the Method except for the average concentration of OCDD and 1,2,3,4,6,7,8-HpCDF. Both of these analyte concentrations were high. Although both were initially believed to be contamination from the PUF that was extracted, only the HpCDF was actually from the PUF.

A MDL was statistically determined for each of the 17 dioxins and furans of interest. This precision based method of calculation was used with seven replicate samples spiked at 2-5 times the suspected detection limit. The MDL was then calculated at the 99% confidence level. The MDLs (rounded up) were generally comparable to the low calibration standard (or minimum levels) of EPA Method 1613, shown in Table I. HpCDD was about a factor of two greater than the minimum calibration standard, while OCDD was roughly 7 times greater than the minimum calibration standard. The elevated detection limit for OCDD was due to contamination in two of the solvent evaporation tubes. The contaminated glassware was promptly discarded. Using only five of the seven replicates for OCDD lowered the MDL by an order of magnitude, to roughly 0.06 pg/m<sup>3</sup>. This value was slightly less than the minimum level listed in Method 1613. The elevated detection limits were used, since the MDLs were more than sufficient to meet the requested action level.

Table I shows a comparison of the MDL results, previously discussed, to the blank data. The latter represents an average of 2.5 times the noise from all blanks collected during background and production burns. For most analytes, the DLs are lower due to averaging over a

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large sample set and improving the analytical technique.

**TABLE I: Detection Limits (pg/m<sup>3</sup>)**

Analyte	Original MDL- 7 Replicates	Blank, Real Sample DL- 2.5 times noise	Method 1613 Minimum Levels - Equated
TCDD	0.0100	0.0017	0.0091
PeCDD	0.0500	0.0083	0.0455
123478-HxCDD	0.0500	0.0025	0.0455
HpCDD	0.100	0.0060	0.0455
OCDD	0.600	0.0102	0.0909

Performance evaluation samples were prepared in lieu of the Method 1613 recommendation of Ongoing Precision and Recovery (OPR) studies. These samples have been used to determine upper and lower control limits, based upon recoveries. All of the PE results, based upon a 95% confidence level, fit a tighter range than that of the OPR limits. These data were collected with every other set of seven samples. True value concentrations that were greater than the calculated MDLs were included for the determination of control limits. A summary of these results are shown in Table II, along with OPR limits from Method 1613, Revision B.

**TABLE II - Performance Evaluation Percent Recovery Bias**

Analyte	# of samples	Lower Control Limit	Upper Control Limit	OPR Limits Method 1613
TCDD	34	80.26	159.40	67-158
PeCDD	33	99.15	148.03	70-142
123478-HxCDD	31	85.18	123.90	70-164
HpCDD	32	75.13	105.85	70-140
OCDD	30	68.95	123.75	78-144

Precision data, summarized in Table III, was a combination of field and laboratory precision, since the data were collected from duplicate samplers. HpCDD and OCDD were the only analytes that had calculated values greater than the MDL values, thus were the only positively reported results. The relative percent difference of the duplicates in both cases were less than the 26% limit<sup>4)</sup> specified in the project plan. Using the lower DL values obtained from real sample blanks, precision remained acceptable.

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TABLE III - Field and Laboratory Precision

Analyte	No. of Pairs >MDL	% Difference of Duplicate	No. of Pairs >Blank DL - 2.5 times noise	% Difference of Duplicate
TCDD	0		0	
PeCDD	0		2	2.17
123478-HxCDD	0		15	12.4
HpCDD	32	10.3	48	20.0
OCDD	20	6.01	50	22.7

HpCDD and OCDD were routinely found, which is similar to other work,<sup>5,6)</sup> even in the pre-burn and background studies. Column two in Table IV shows the average concentrations of HpCDD and OCDD analytes for all samples with the exception of blank and PE samples. These were the only averages greater than the MDL results. An average of values greater than the MDLs for the 352 samples were included in column three. This was roughly 80% of HpCDD analytes and 53% of OCDD analytes. The background study shown in column four was based upon 118 extracts after the Dioxin Stack Test but prior to the production burn. According to the study, 58% of the HpCDD analytes were greater than the MDL values, while 33% of the OCDD analytes were above MDL values.

TABLE IV - Sample Concentration (pg/m<sup>3</sup>)

Analyte	X - 352 samples	>MDL	background >MDL
HpCDD	0.2755	0.329	0.431
OCDD	0.9937	1.532	1.56

The incinerator is scheduled to continue production burn through the end of May 1997. Background monitoring will then take place for an additional month, at which time a thorough evaluation of the data will take place by EPA officials and others.

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## Literature Cited:

- (1) Record of Decision, Region VII **1988**, No. 15 (1 of 2) Times Beach, MO.
- (2) USEPA , Office of Water Engineering and Analysis Division, EPA821-B-94-005 *Method 1613: Tetra-Through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS. Revision B; October, 1994.*
- (3) Title 40 of the Code of Federal Regulations, Part 136, Appendix B *Definition and Procedures for the Determination of the Method Detection Limit.*
- (4) Thomas, M.J.; Davis, M.F.; Grooms, L.P. *Quality Assurance Project Plan For Ambient Dioxin and Particulate Monitoring at the Times Beach Superfund Site Times Beach, Missouri, Revision 2 November 07, 1995.*
- (5) Lugar, R.M.; Harless, R.L.; Dupuy Jr.,A.E.; McDaniel, D.D. *Environ. Sci. Technol.* **1996**, 30, 555-561.
- (6) Eltzer, B.D.; Hites, R.A. *Environ. Sci. Technol.* **1989**, 23, 1396-1401.