

SAMPLING AND ANALYSIS FOR POLYCHLORINATED  
DIBENZO-P-DIOXINS AND DIBENZOFURANS IN AMBIENT AIR

R. L. Harless\* and R. G. Lewis

U. S. Environmental Protection Agency  
Atmospheric Research and Exposure  
Assessment Laboratory (MD-44)  
Research Triangle Park, North Carolina 27711

D. D. McDaniel and A. E. Dupuy, Jr.

U. S. Environmental Protection Agency  
Environmental Chemistry Laboratory  
Building 1105 John C. Stennis Space Center  
Stennis Space Center, Mississippi 39529

ABSTRACT

A short-term study for determination of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in ambient air in Green Bay, Wisconsin, has been completed. General Metals Works PS-1 air samplers equipped with particle filters and polyurethane foam (PUF) sorbent were used to sample ambient air for 24-hour periods. Analytical procedures based on high resolution gas chromatography-high resolution mass spectrometry (HRGC-HRMS) were used for the analysis. Total concentrations detected in ambient air for PCDDs ranged from 0.78 to 1.7  $\text{pg}/\text{m}^3$  and those for PCDFs ranged from 0.67 to 2.6  $\text{pg}/\text{m}^3$ . Minimum limits of detection were in the range of 0.01 to 0.08  $\text{pg}/\text{m}^3$ .

INTRODUCTION

The Atmospheric Research and Exposure Assessment Laboratory (AREAL) provided assistance to the Great Lakes National Program Office (GLNPO) in evaluation of sampling, analytical techniques, quality assurance/quality control (QA/QC), and a pilot-scale site for ambient air monitoring purposes in Green Bay, Wisconsin in September 1989. The sampling and analytical procedures described here had been used in a previous two-year ambient air monitoring study and found to be reliable, accurate and adequate for the study objectives(1). The findings of low levels of PCDDs and PCDFs in this study are in agreement with those reported by many laboratories(2,3,4).

## EXPERIMENTAL

### Sampling

General Metals Works PS-1 air samplers equipped with precleaned quartz fiber filters and polyurethane foam (PUF) sorbant were used for sampling 320-350 m<sup>3</sup> ambient air during 24-hour sampling periods. Samples were collected each week for five weeks. However, samples from the first sampling period were not meaningful, due to electrical malfunctions. The particle filters for all PS-1 samplers were spiked with 0.8 ng <sup>13</sup>C<sub>12</sub>-1234-TCDD prior to shipping the assembled sampling cartridge to the field in order to determine retention efficiencies. Two collocated samplers were used each sampling period; one sampled ambient air and one was not operated to serve as the field blank. After sampling, respective filters and PUF in glass cylinders were shipped to the laboratory for sample preparation.

### Sample Preparation

Sample preparation was performed on a "set" of 12 samples consisting of nine test samples, method blank, field blank(s) and a laboratory method spike. The filters and PUF plugs from each sampler were combined prior to extraction. An aliquot of a spike solution containing 1.0 ng each of <sup>13</sup>C<sub>12</sub>-labeled PCDD/PCDF internal standards was spiked into each sample immediately before Soxhlet extraction for 16 hours with benzene. Cleanup of extracts was accomplished using an acid/base procedure and a micro-alumina column followed by a micro-carbon column. An aliquot of a solution containing 0.5 ng <sup>37</sup>Cl<sub>4</sub>-2378-TCDD was spiked into each extract prior to final concentration to 60 μl for analysis. The extracts were fire sealed in glass tubes and shipped to the EPA laboratory for analysis in a blind manner, i.e., test samples and QA samples were not identified as such.

### Instrumentation and Quantification

All samples were analyzed using a Finnigan MAT 90 HRMS system operating in the electron ionization and multiple ion detection mode at 8000-10000 mass resolution and equipped with a 30m x 0.25 mm i.d. SE-54 fused silica capillary column and a 60m x 0.24 i.d. SP-2331 fused silica capillary column. The areas of exact masses of the molecular ion clusters of <sup>37</sup>Cl<sub>4</sub> and <sup>13</sup>C<sub>12</sub> labeled and unlabeled PCDDs and PCDFs and respective response factors were used for quantification purposes. The <sup>37</sup>Cl<sub>4</sub>-2378-TCDD was used to determine the method efficiency for <sup>13</sup>C<sub>12</sub>-labeled PCDD/PCDF internal standards. Respective <sup>13</sup>C<sub>12</sub>-labeled PCDD/PCDF internal standards were used for quantification of respective unlabeled PCDDs and PCDFs and for determination of the minimum limits of detection (MLDs) with two exceptions, <sup>13</sup>C<sub>12</sub>-labeled HpCDD was used for HpCDF and <sup>13</sup>C<sub>12</sub>-OCDD was used for OCDF. The <sup>13</sup>C<sub>12</sub> labeled 1234-TCDD was used to determine PS-1 air sampler collection and retention efficiency. Total concentrations and isomer specific concentrations were reported in pg/m<sup>3</sup>.

TABLE 1 ANALYTICAL RESULTS FOR PCDDs AND PCDFs IN GREEN BAY AMBIENT AIR

IDENTIFICATION CUBIC METERS	WEEK-2 327.9	WEEK-3 330.6	WEEK-4 329.4	WEEK-5 330.1	WEEK-2** 327.9***
PS-1 SAMPLER COLLECTION & RETENTION EFFICIENCY (%)					
<sup>13</sup> C <sub>12</sub> -1234-TCDD	85	89	93	99	95
METHOD EFFICIENCY (% RECOVERY)					
<sup>13</sup> C <sub>12</sub> -2378-TCDF	81	81	84	82	97
<sup>13</sup> C <sub>12</sub> -2378-TCDD	83	81	82	78	83
<sup>13</sup> C <sub>12</sub> -12378-PeCDF	87	82	87	84	76
<sup>13</sup> C <sub>12</sub> -12378-PeCDD	72	64	71	69	73
<sup>13</sup> C <sub>12</sub> -123478-HxCDF	80	78	84	81	71
<sup>13</sup> C <sub>12</sub> -123678-HxCDD	77	73	81	78	89
<sup>13</sup> C <sub>12</sub> -1234678-HpCDD	79	76	84	76	69
<sup>13</sup> C <sub>12</sub> -OCDD	64	69	70	69	60
CONCENTRATION DETECTED OR MLD (pg/m <sup>3</sup> )					
TCDDs (TOTAL)	0.3	0.09	0.2	0.08	ND(0.02)
2378-TCDD	ND(0.04)	ND(0.02)	ND(0.02)	ND(0.01)	ND(0.02)
PeCDDs (TOTAL)	0.4	0.1	0.2	ND(0.09)	ND(0.03)
12378-PeCDD	ND(0.08)	ND(0.03)	ND(0.02)	ND(0.02)	ND(0.03)
HxCDDs (TOTAL)	0.4	0.2	0.3	0.2	ND(0.04)
123478-HxCDD	0.01	ND(0.01)	ND(0.01)	ND(0.01)	ND(0.02)
123678-HxCDD	0.03	0.02	0.02	0.01	ND(0.02)
123789-HxCDD	ND(0.02)	ND(0.01)	0.02	0.01	ND(0.02)
HpCDDs (TOTAL)	0.3	0.2	0.3	0.2	0.1
1234678-HpCDD	0.1	0.1	0.2	0.1	0.05
OCDD	0.3	0.3	0.4	0.3	0.2
TOTAL PCDDs	1.7	0.89	1.4	0.78	0.3
TCDFs (TOTAL)	0.8	0.4	0.7	0.3	ND(0.05)
2378-TCDF	0.04	0.02	0.03	ND(0.01)	ND(0.01)
PeCDFs (TOTAL)	1.2	0.4	0.7	0.2	ND(0.02)
23478-PeCDF*	0.09	0.03	0.07	0.02	ND(0.02)
23478-PeCDF	0.07	0.02	0.03	ND(0.02)	ND(0.02)
HxCDFs (TOTAL)	0.5	0.2	0.4	0.1	ND(0.02)
123478-HxCDF*	0.05	0.02	0.05	0.01	ND(0.02)
123678-HxCDF	0.05	0.02	0.04	0.01	ND(0.02)
123789-HxCDF	ND(0.02)	ND(0.01)	0.01	ND(0.01)	ND(0.02)
234678-HxCDF	ND(0.02)	ND(0.01)	ND(0.01)	ND(0.01)	ND(0.02)
HpCDFs (TOTAL)	0.1	0.06	0.23	0.05	0.02
1234678-HpCDF	0.08	0.04	0.15	0.03	ND(0.01)
1234789-HpCDF	ND(0.05)	ND(0.02)	0.01	ND(0.03)	ND(0.01)
OCDF	0.05	0.02	0.2	0.02	ND(0.02)
TOTAL PCDFs	2.65	1.08	2.23	0.67	0.02

ND = NOT DETECTED AT SPECIFIED MLD.  
 \* = 12378-/12348-PCDF and 123478-/123479-HxCDF NOT RESOLVED  
 ON THIS COLUMN.  
 \*\* = FIELD BLANK FOR WEEK-2.  
 \*\*\* = USED FOR CALCULATION PURPOSES ONLY.

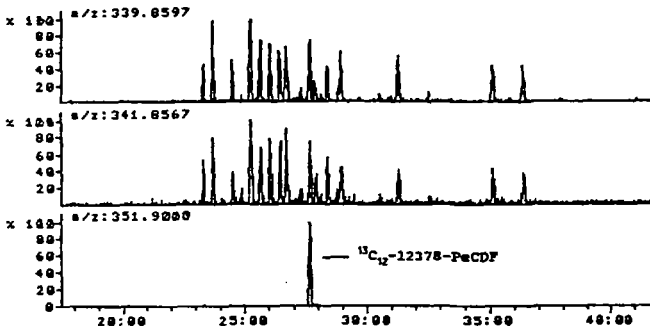


Figure 1. Analysis of the PeCDFs in sample from week-2.

#### Quality Assurance/Quality Control

The HRGC-HRMS analytical criteria used for confirmation of PCDDs and PCDFs were: chlorine isotope ratios of molecular ions ( $\pm 1\%$  of theoretical values, tetra - 0.77, penta - 1.55, hexa - 1.24, hepta - 1.04, and octa - 0.89); simultaneous responses ( $\pm 3$  sec) for exact masses of  $^{13}\text{C}_{12}$ -labeled and nonlabeled 2378 chlorine substituted congeners on a known isomer specific column(5); resolution of PCDDs and PCDFs on the SP-2331 isomer specific column demonstrated and confirmed using a standard containing all tetra- through hexa- PCDD/PCDF isomers; analysis that confirm the absence of respective chlorinated diphenylethers; HRGC-HRMS peak matching analysis of exact masses if necessary and responses of non-labeled PCDD/PCDF masses must be greater than  $2.5 \times$  area of the noise level.

The data from a "set" of 12 samples was evaluated using the analytical criteria and following QA/QC requirements: method recovery efficiency for  $^{13}\text{C}_{12}$  labeled tetra- penta- and hexa- CDDs and CDFs, 50 to 120%, hepta- and octa- CDDs, 40 to 120%; satisfy the analytical criteria described for PCDDs/PCDFs; accuracy and precision achieved for laboratory method spike(s) at  $0.5 \text{ pg/m}^3$  to  $2.0 \text{ pg/m}^3$ ,  $\pm 50\%$ ; method blank and field blank free of significant PCDD/PCDF contamination at the MLDs required for generation of useful and meaningful data, 0.01 to 0.08  $\text{pg/m}^3$  for tetra- penta- and hexa-CDDs and CDFs. Trace levels, 0.1 to 0.3  $\text{pg/m}^3$ , of HpCDDs and OCDD are always detectable in our method blanks and field blanks (background levels).

#### RESULTS AND DISCUSSION

The results shown in Table 1 satisfied the QA/QC requirements for analytical data. Comparison of the test sample data with field blanks and method blank data, example of field blank shown in Table 1, indicated this was a very consistent set of data in which very low levels of PCDDs and PCDFs were detected. There were only small differences detectable in the total concentrations of PCDDs and PCDFs, mostly in the tetra-, penta- and hexa- concentrations. The "pattern" of PCDDs/PCDFs is similar to that detected in ambient air background from other areas and is characteristic of patterns detected in combustion processes. However, the HpCDDs and OCDD concentrations are usually higher than those of the lower chlorinated congeners. Analysis of the PCDFs is shown in Figure 1.

#### REFERENCES

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