

U.S. EPA's NATIONAL DIOXIN AIR MONITORING NETWORK: ANALYTICAL ISSUES

Joseph Ferrario¹, Christian Byrne¹, David H. Cleverly², Dwain Winters³,
Aubry E. Dupuy, Jr.¹, and John Schaum²

1. Environmental Chemistry Laboratory, United States Environmental Protection Agency, Stennis Space Center, MS 39529; 2. National Center for Environmental Assessment (8623D), Office of Research and Development, United States Environmental Protection Agency, 1200 Pennsylvania Ave., NW, Washington, DC 20460; 3. Office of Prevention, Pesticides and Toxic Substances, United States Environmental Protection Agency, 401 M St., SW, Washington, DC 20460

Introduction

The U.S. EPA has established a National Dioxin Air Monitoring Network (NDAMN) to determine the temporal and geographical variability of atmospheric chlorinated dibenzo-p-dioxins (CDDs), -furans (CDFs), and coplanar polychlorinated biphenyls (PCBs) at rural and non-impacted locations throughout the United States. Currently operating at 32 sampling stations, NDAMN has three primary purposes: (1) to determine the atmospheric levels and occurrences of dioxin-like compounds in rural and agricultural areas where livestock, poultry and animal feed crops are grown; (2) to provide measurements of atmospheric levels of dioxin-like compounds in different geographic regions of the U.S.; and (3) to provide information regarding the long-range transport of dioxin-like compounds in air over the U.S. Designed in 1997, NDAMN has been implemented in phases, with the first phase consisting of 9 monitoring stations and is achieving congener-specific detection limits of 0.1 fg/m^3 for 2,3,7,8-TCDD and 10 fg/m^3 for OCDD. With respect to the coplanar PCBs, the detection limits are generally higher due to the presence of background levels in the air during the preparation and processing of the samples. Achieving these extremely low levels of detection present a host of analytical issues. Among these issues are the methods used to establish ultra-trace detection limits, measures to ensure against and monitor for breakthrough of native analytes when sampling large volumes of air, and procedures for handling and evaluating field blanks. Despite such procedural difficulties, these methods make it possible to measure dioxin-like compounds at extraordinarily low concentrations.

Methods

The analytes of interest in this program are the chlorinated dioxins and furans (tetra through octa congeners), the homologue totals, and the several selected coplanar PCBs (IUPAC PCB-77, 105, 118, 126, 156, 157 and 169). NDAMN began operations in June 1998. Thirty-two stations are now operational. Each station consists of a PS-I polyurethane (PUF) sampler, and is operated according to a modification of EPA Method TO-9A¹. The method and sampling frequency of NDAMN has been previously described by Cleverly et al². Briefly, the samplers are operated for four-six day periods, collecting approximately

8000 cubic meters of air. The quartz fiber filters (QFFs) are changed once each period to prevent the collected particulates from drastically reducing the flow rate. The harvested samples (PUF/QFFs) and their associated field blanks are shipped to EPA's Environmental Chemistry Laboratory for extraction, clean-up, and analysis with high resolution gas chromatography coupled with high resolution mass spectrometry (HRGC/HRMS) in accordance with a modification of EPA Method 1613³. The combined PUF and QFFs of the samples and field blanks are extracted with benzene using a Soxhlet apparatus. Prior to the initiation of the extraction period, the PUF is spiked with 100 pg of ¹³C labeled analogs of all native target analytes. The extract is collected and stirred with acidified silica gel and followed by acid/base silica gel clean-up and alumina and carbon chromatography. The final extract is concentrated to approximately 10 μ l and fortified with ¹³C internal standards prior to HRGC/HRMS analysis. The chromatographic separation is achieved on a DB-5MS capillary column and the mass spectrometer is operated in the lock mass drift correction mode at a resolution of 10,000. A set of samples consists of 10 field samples and/or field blanks, one method blank, and one laboratory control spiked sample fortified with natives at twice the limit of quantitation (LOQ).

Results

Detection Limits: In order to achieve the ultra-trace detection limits (0.1 fg/m^3 for 2,3,7,8-TCDD) required to reliably measure CDD/CDFs in rural and non-impacted areas, large volumes of air must be sampled. In addition to the volume of air sampled, the method detection limit is also based on the instrumental sensitivity and the method used to calculate the LOD. The method used for actually calculating and demonstrating these detection limits are based on results from a demonstration of capability phase. Initially, these results were used to estimate target LOD/LOQs that were subsequently verified by fortified replicate sub-samples at the specified levels and assessing the precision and accuracy⁴.

The target LOD/LOQs for the CDDs, CDFs, and co-planar PCBs are based on the minimum amount that can be detected based on the acceptance criteria and the volume of sampled air. For the tetra-CDD/CDFs and PCBs 126 and 169, the instrumental detection limit is 50 femtograms. For the penta-, hexa-, and hepta-CDDs/CDFs, the detection limit is 150 femtograms and for the octa-CDD/CDF, the detection limit is 1 picogram. These estimates are based on the S/N ratios of the quantitation ions from the native congeners from a 1 μ l injection of the lowest calibration standard and from the results of the demonstration phase. For the remaining PCBs and the hepta-CDD/CDFs, OCDD and OCDF for which detectable amounts are present in the method blanks, the detection limits are based on the minimum amount that can be reliably detected above background as described in Ferrario et. al., 1997⁵. The target LODs are one half of the concentrations of the LOQs.

The target instrumental detection limits for the analyses based on a 2/20 μ l injection of a sample extract and considering the background amounts for several of the congeners normally present in method blanks. The detection limits for the analytical procedure expressed as total picograms for each congener are:

ANALYSIS I

TCDD/CDF	0.5 pg	PCB 77	20 pg
PeCDD/CDF & HxCDD/CDF	1.5	PCB 118	500
HpCDF	1.5	PCB 105	300
HpCDD	2.5	PCB 126	2.0
OCDF	4.0	PCB 156	80.0
OCDD	20.0	PCB 157	20.0
		PCB 169	1.0

The method detection and quantitation limits are calculated by dividing the calculated amounts of each congener by the volume of air sampled. A chromatogram displaying the quantitation ions for the 2,3,7,8-TCDD and TCDF in PUFs fortified at the detection limit is presented on Figure 1.

Breakthrough: Sampling the large volumes of air required to calculate detectable and measurable quantities of CDD/CDFs in rural sites introduces several method and procedural problems that must be addressed. One of the most important issues to consider is the breakthrough and loss of the native analytes collected on the PUFs. This problem is addressed by the fortification of a 2" PUF with the relatively volatile ^{13}C 1,2,3,4-TCDF and ^{13}C PCB 81 and the placement of a 1" PUF behind it in the sample cartridge. The 2" and 1" PUFs were then analyzed separately and the quantities of the ^{13}C labels present were compared to the quantities found on the field blanks. The results from several sites are presented on Table 1. As is evident from the table, three of the PUFs showed migration of the field spike onto the 1" PUF. The total amount found on both PUFs was comparable to that found on the control field blanks which suggests that breakthrough should not be a problem when using a 3" PUF. Some of the problems encountered when addressing this issue are: 1) How representative are the volatile tetra-CDD/CDFs congeners to the higher chlorinated congeners (e.g., penta-, hexa-, and hepta-CDD/CDFs)? and 2) Since 70-80% of the CDD/CDFs are absorbed on the particulates which are collected on the surface of the QFFs and not on the PUF, how representative is any field spike that is applied to the PUF of analytes absorbed to particulates that are collected on QFFs?

Field Blanks: Another important issue to consider in trace analytical work is the evaluation of controls, specifically field blanks, to ensure that compounds detected on the sampling media in fact originated from the sampled air. In TO-9A the blank filters and PUFs are passively exposed during the sampling period. However, since the purpose of the field blanks was to determine the contamination affecting the active samples (which are only passively exposed during set-up and collection), it is more representative to expose the field blanks only during set-up and collection. PUF field blanks, after initially being installed and removed from the sampling head, remained inside the sampler housing in a closed jar, which was only opened while the on-site operators were performing sampler activities. QFF field blanks consisted of four QFFs; one initially installed in the sampling head and removed and three others that were exposed during the time the sample QFFs were being changed. Originally all the field blanks from each site were analyzed and only minimal background detected. From this result it was decided to analyze a randomly selected sub-set of field blanks after sites that had been in operation for two or three sampling periods and the analyses of these field blanks revealed that no contamination was present.

ANALYSIS I

These procedures have been employed to successfully measure CDD/CDFs and co-planar PCBs in rural air at a detection limit of 15.0 parts-per-quadrillion for the tetra-chlorinated congeners. The issues discussed here provide examples of the types of problems encountered and the measures taken to ensure the collection of representative samples. The results and approaches to the various problems are based on data collected during the pilot program and the first year of operation of the NDAM and are currently being investigated and reviewed.

Acknowledgements

We thank the following people for their assistance in various stages of this project: Stanley Mecomber and Ray Shaw, OPP/ECB for the preparation of the samples, Battelle Memorial Institute, Columbus, Ohio and Versar, Inc., Springfield, Virginia for their technical assistance. This paper has not been subject to the USEPA publication review process and, therefore, does not necessarily reflect the views of the Agency and no official endorsement should be inferred. The mention of trade names, or commercial products constitute neither endorsement nor recommendation of use.

References

1. Cleverly, D.H., D. Winter, J. Ferrario, J. Schaum (2000) *Organohalogen Compounds* 45: 248-251.
2. USEPA (1997) Compendium Method TO-9A. EPA/625/R-96/010b.
3. USEPA (1998) Quality Assurance Plan and Work Plan, DEI: National Dioxin Air Monitoring Network. Versar, Inc. under EPA Contract 68-D5-0051.
4. J. B. Ferrario, C. Byrne, D. McDaniel, A. E. Dupuy, Jr., R. Harless (1996) *Analytical Chemistry* 68 (4): 647-652.
5. J. Ferrario, C. Byrne, A. E. Dupuy, Jr. (1997) *Chemosphere* 34 (11): 2451-2466.

Field Spike PUF	¹³ C-1,2,3,4-TCDF			¹³ C-PCB 81		
	1"	2"	Total	1"	2"	Total
Field Blank Average			103			86
Site 1	69	24	93	71	24	95
Site 2	40	49	89	42	32	74
Site 3	41	48	89	32	53	85
Site 4	23	38	61	10	33	43

Table 1- Recovery of Field Spikes (%)

ANALYSIS I

Figure 1 – Quantitation Ions for 2,3,7,8 - TCDD/TCDF from PUF fortified at Method LOD. (50 fg)

