

QUALITY ASSURANCE CONSIDERATIONS FOR AN AMBIENT DIOXIN MONITORING NETWORK

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Introduction

The U.S. Environmental Protection Agency (EPA) initiated the National Dioxin Air Monitoring Network (NDAMN) in 1998. NDAMN has three primary purposes:

1. To provide measurements of background atmospheric levels of dioxin-like compounds in different geographic regions of the United States
2. To determine the atmospheric levels of dioxin-like compounds in agricultural areas where livestock, poultry, and animal feed crops are grown; and
3. To provide data to evaluate results from long-range transport and deposition air models.

At the end of 2001, 32 NDAMN sites were operational. Ambient air measurement results from NDAMN have been presented elsewhere ⁽¹⁾. This paper focuses on procedures implemented in NDAMN to assure quality and the results associated with such procedures.

Methods and Materials

A PS-1 sampler is used to collect ambient air at each NDAMN site. The PS-1 sampler employs a quartz fiber filter (QFF) to collect particulate matter and polyurethane foam (PUF) sorbent to collect gaseous compounds. An NDAMN sampling moment lasts 28 days, with 5 to 6 days of active sampling followed by an inactive day for filter change. Approximately 7000 cubic meters of ambient air is sampled during a moment. A single PUF cartridge and four QFFs are collected from each site for each sampling moment. Sampling is conducted concurrently at the 32 NDAMN sampling sites at four different periods each year. Samples are analyzed for 2,3,7,8-substituted polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (CDDs and CDFs) and co-planar polychlorinated biphenyls (PCBs) using high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) techniques.

Quality assurance/quality control procedures implemented in NDAMN include the following:

Equipment Calibration

New motor brushes or a new motor in the PS-1 sampler are required each sampling moment. A multi-point calibration of each PS-1 sampler is conducted at the beginning and end of each 28-day sampling moment. In addition to initial and final multi-point calibrations, a single-point flow check is conducted each week of sampling to ensure the accuracy of flow rates.

Sample Custody

Given that CDDs, CDFs, and PCBs are semi-volatile compounds, care is taken in NDAMN to ensure that samples are stored under refrigeration at all times. NDAMN on-site operators return

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collected QFFs to refrigerated storage after collection each week. All samples are shipped from the on-site operators to Battelle and from Battelle to the EPA analytical laboratory on frozen "blue ice". Conditions of sample receipt and sample storage are recorded at all locations.

PUF/Filter Certification

The PUF and QFF sampling media are pre-cleaned prior to use in the field. At least 10 percent of sampling media are tested and certified as clean prior to shipment to the NDAMN sites. Certification consists of extracting the PUF/filter media with solvent and analyzing the resulting extract for CDDs, CDFs, and PCBs using the same procedures as for actual samples.

Field Blanks

Field blanks are collected at each NDAMN site during each sampling moment. Field blanks consist of one PUF and four QFFs that are exposed to ambient air during the time that the on-site operator is present at the site for sample collection. Approximately half of the field blanks collected during a sampling moment are analyzed.

Duplicate Samples

At one NDAMN site (Penn Nursery, Pennsylvania), two PS-1 samplers are co-located and operated in each sampling moment. The purpose of these duplicate samplers is to provide data necessary to evaluate variability resulting from sampling procedures and from the nonhomogeneity of the sample matrix. The duplicate PS-1 samplers are located approximately 10 feet apart.

Backup PUF

In 1998-1999 NDAMN sampling moments, the PUF sorbent consisted of two components – a 2" PUF plug and a 1" PUF plug. In most cases, these two PUF were extracted together with the four QFF for a single analysis. In one 1998 sampling moment, 2" and 1" PUFs from some samples were analyzed separately. These separate analyses were intended to determine if any significant breakthrough of gaseous CDDs, CDFs, and PCBs occurred with the PUF media given the long sampling periods and the large sample volumes collected for NDAMN.

Laboratory Quality Control

A laboratory control spike is generated and analyzed with each batch of NDAMN samples. The laboratory control spike consists of PUF and QFF spiked with native CDDs, CDFs, and PCBs processed through the same analytical procedures as actual samples. The purpose of this laboratory control spike is to demonstrate that efficient recovery of native analytes is obtained. Sampling media and samples are spiked with labeled CDD, CDF, and PCB internal standards prior to sampling and extraction, respectively, as another measure to evaluate analyte recovery. Laboratory method blanks are processed with each NDAMN sample set to ensure that laboratory procedures do not contribute background contamination to samples.

Results and Discussion

Results from NDAMN sampling moments in 1998, 1999, and 2000 are provided for the more critical and quantitative quality assurance procedures described above.

Field Blanks

In most cases, CDDs and CDFs detected in field blanks were at levels considerably below levels detected in associated samples. Only two CDD/CDF compounds - 1,2,3,4,6,7,8-HpCDD and OCDD -

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were consistently detected in almost all field blanks. In most instances, amounts of CDDs/CDFs (on a pg basis) were considerably less (2 % or less) than sample amounts and did not interfere with sample results.

Co-planar PCBs are ubiquitous in the field and laboratory environment and NDAMN field blanks analyzed for co-planar PCBs typically show contamination. In all field blanks collected in 1998 – 2000, PCBs 77, 105, 118, 156, and 157 were detected. Table 1 provides a summary of PCB field blank results. In some instances, the amount of PCB 156 and 157 in the field blank was over 100 % of the amount of PCB 156 or 157, respectively, in the associated sample. The PCB 156 and 157 results for these samples are considered suspect.

Table 1. Comparison of PCB field blank results to PCB sample results by compound

	Minimum	CompoundPCB field blank to PCB sample (%)			SE Mean
		Maximum	Mean	Median	
PCB 77	0.0	92	10	6.0	1.6
PCB 105	0.0	90	13	8.2	1.7
PCB 118	0.0	61	11	6.8	1.4
PCB 126	0.0	35	4.2	1.1	0.7
PCB 156	0.0	296	23	8.3	5.6
PCB 157	0.0	326	21	7.4	5.5
PCB 169	0.0	31	0.5	0.0	0.4

Duplicate Samples

Results from duplicate samples for 1998, 1999, and 2000 are provided in Table 2. This table provides the relative percent difference (RPD) for duplicate results by sampling moment. The minimum, maximum, mean, median, and standard error of the mean for the RPD are included. In most instances, the RPD was calculated from 24 data points.

As shown in Table 2, RPD means and medians were both below 20% for all sampling moments, except Nov/Dec 1998; Aug/Sep 1999; Jan/Feb 2000; and Aug/Sep 2000. Field sampling and laboratory analysis records were examined for these sampling moments and no single cause could be identified. Additional duplicate results are being obtained in NDAMN in order to establish acceptable duplicate precision objectives for long-term monitoring of CDDs, CDFs, and PCBs.

Backup PUF

Very little breakthrough of CDDs/CDFs was detected in the separate PUFs analyzed for selected samples from the Jun/Jul 1998 sampling moment. In only nine cases (out of 85 measurements) were CDD/CDF compounds detected in the 1" PUF. In five of these nine cases, the compounds detected were OCDD. This detection may not indicate actual breakthrough,

but may be due instead to background OCDD contamination that was found in most field and laboratory blanks. Most PCBs were found on both the 2" and 1" PUFs in all separate analyses. The amount of PCB on the 2" PUF was higher than the amount on the 1" PUF in all cases and the amount on the 1" PUF could not be distinguished from background PCB contamination. Based on these separate PUF analyses, breakthrough from the PUF sampling media was eliminated as a concern in NDAMN. A single 2" PUF was deemed sufficient for all future sampling moments.

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Table 2. Relative percent difference for duplicate results by sampling moment

Sampling Moment	Relative percent difference (%)				SE Mean
	Minimum	Maximum	Mean	Median	
Jun/Jul 1998 (1)	0.3	29	9.4	7.3	1.5
Aug/Sep 1998 (2)	0.1	55	14	11	2.6
Nov/Dec 1998 (3)	0.1	73	27	22	4.6
Jan/Feb 1999 (4)	0.1	39	9.4	5.4	2.0
Mar/Apr 1999 (5)	0.04	100	11	6.6	4.0
May/Jun 1999 (6)	0.7	37	10	7.5	1.9
Jul/Aug 1999 (7)	1.1	100	22	13	6.3
Aug/Sep 1999 (8)	3.7	76	31	30	3.4
Nov/Dec 1999 (9)	0.7	25	7.0	6.2	1.0
Jan/Feb 2000 (10)	3.1	105	61	66	5.7
Apr/May 2000 (11)	4.1	56	21	17	2.5
Aug/Sep 2000 (12)	46	65	56	57	1.2
Nov/Dec 2000 (13)	0.4	123	34	12	8.4

Notice

The views expressed in this paper are those of the author and do not necessarily reflect the views and policies of the U.S. Environmental Protection Agency.

References

1. Cleverly, D. H., Winters, D., Ferrario, J., Riggs, K., Hartford, P., Joseph, D., Wisbith, T., Dupuy, A. The National Dioxin Air Monitoring Network (NDAMN): Measurements of CDDs, CDFs, and Coplanar PCBs at 15 Rural and 6 National Park Areas of the United States; Abstract submitted for presentation at Dioxin 2002.