

ANOMALOUS RESULTS FROM NATIONAL DIOXIN AIR MONITORING NETWORK

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Introduction

The U.S. EPA established the National Dioxin Monitoring Network (NDAMN) to meet an identified need for a national network to monitor ambient air concentrations of dioxin-like compounds. The overall goal of NDAMN is to provide information that may link sources with human exposures to dioxin-like compounds. To achieve this goal, NDAMN is focused on 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 atmospheric levels of dioxin-like compounds in agricultural areas where livestock, poultry, and animal feed crops are grown,
3. To provide data to evaluate results from long-range transport and deposition air models.

NDAMN consists of numerous sites situated in rural, non-impacted locations across the United States. Locations were selected to meet specific criteria including:

- Not impacted by nearby sources of dioxin-like compounds
- Surrounded by land where animal feed predominantly grown
- Representative of variable climate conditions in terms of temperature, humidity, and precipitation,
- Located in different U.S. geographic regions.

This paper discusses results from 2000 for specific NDAMN sites which indicate that some sites may be impacted by local sources and not represent true background locations, and/or may have been impacted by a one-time source. The discussion is restricted to PCDD/PCDF compounds measured in NDAMN.

Methods and Materials

The location of NDAMN sites are illustrated in Figure 1. Ambient air samples are collected concurrently at each NDAMN site and analyzed for polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and dioxin-like polychlorinated biphenyls (PCBs). A ambient air samples at each site. Each sampling moment consists of 20 to 24 days of sampling over a 28-day period. Collected samples are analyzed for PCDD, PCDF, and PCB by high resolution gas chromatography/high resolution mass spectrometry. Ambient air concentrations are

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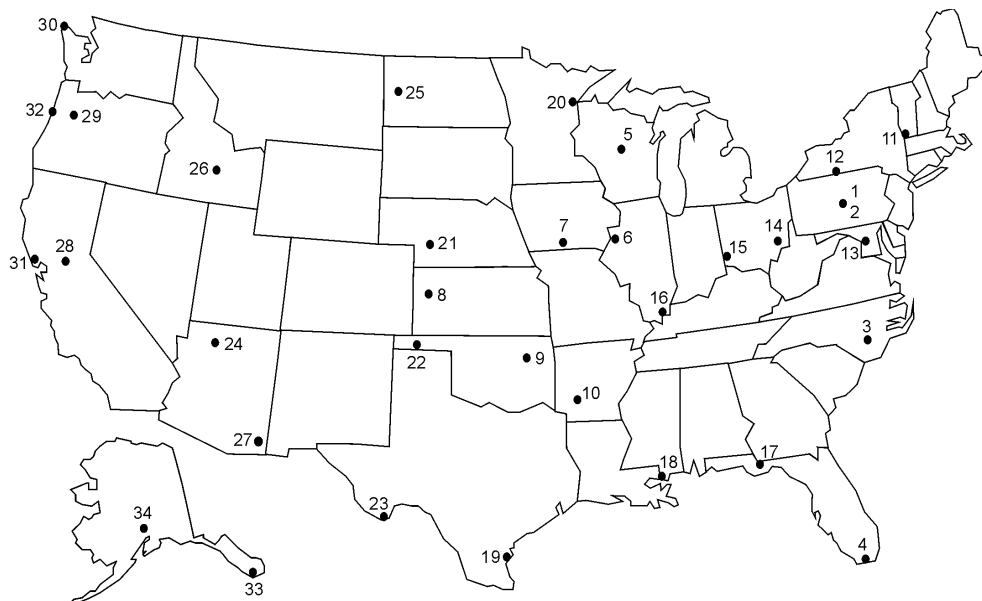


Figure 1. Location of NDAMN Sites

calculated in femtogram/cubic meter (fg/m^3) and in total toxic equivalence (TEQ) fg/m^3 based on toxic equivalent factors (TEF) accepted by the World Health Organization (WHO). Individual PCDD/PCDF/PCB concentrations are determined for each sampling moment at each site, and annual averages are determined for each site.

Results and Discussion

Given that NDAMN sites were selected for measurement of background concentrations of PCDD/PCDF, it was expected that, in general, NDAMN results would be similar across all sites, and across all moments at a single site. Ambient PCDD/PCDF concentrations in 2000 ranged from non-detected for several PCDD/PCDF compounds to $2630 \text{ fg}/\text{m}^3$ for octachlorinated dibenzo-p-dioxins (OCDD). Congener profiles across most NDAMN sites were similar. The higher-chlorinated PCDD/PCDF compounds – 1,2,3,4,6,7,8-HpCDD, OCDD, 1,2,3,4,6,7,8-HpCDF, and OCDF – were generally found in highest concentrations relative to other PCDD/PCDF compounds at most sites. Congener class profiles across NDAMN sites were also similar with total HpCDD, total HxCDD, and total TCDF being most predominant. As well, congener and congener class profiles across the sampling moments conducted at a single site were similar.

Two types of anomalous results were observed:

Type 1: A site had significantly different concentrations and/or congener profiles relative to other NDAMN sites

Type 2: One moment conducted at a site in 2000 had significantly different concentrations and/or congener profiles than the other moments conducted in 2000 at that same site.

Such anomalous results are discussed for three NDAMN sites below.

- Hyslop Farm, OR (Site 29) - Type 1
- Moment 10 at Fond Du Lac, MN (Site 20) Moment 10 - Type 2
- Moment 11 at Everglades, FL (Site 4) - Type 2

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Hyslop Farm, OR (Site 29)

Hyslop Farm, OR has generally higher and more variable PCDD/PCDF concentrations than most other NDAMN sites. For example, the average OCDD concentration over all 2000 sampling moments was 1,850 fg/m³. For other NDAMN sites, average OCDD concentrations were 1,050 fg/m³ or below. For total HpCDD, the average 2000 concentration was 1,750 fg/m³ at Hyslop Farm, OR and 630 fg/m³ or less at all other sites. This NDAMN site is located on the Crop and Soil Science Department research farm associated with the Oregon Agricultural Experiment Station and the College of Agricultural Sciences of Oregon State University. The research farm is located about midway between Corvallis, OR and Albany, OR, just off of U.S. Highway 20. The research farm provides support related to the development, production, and management of agronomic crops.

There are at least three possible causes for the generally high and variable PCDD/PCDF concentrations reported at Hyslop Farm, OR:

- Pesticide application at the research farm and on adjacent commercial farms;
- Proximity of a U.S. highway and railroad tracks to the NDAMN monitoring station;
- Pulp and paper mill located near the research farm.

The research farm uses the pesticide 2,4-D (2,4-dichlorophenoxy acetic acid) on the fields surrounding the NDAMN site. It has been reported in EPA's Dioxin Reassessment¹ that a dioxin-like compound is formed in the production of this pesticide. The adjacent commercial farm may also use this pesticide. U.S. Highway 20, which is situated between Corvallis, OR and Albany, OR, is located within 100 yards of the NDAMN site. A diesel locomotive also runs within 75 yards of the NDAMN site, twice a day. Emissions from diesel trucks and locomotives are known to contain dioxin-like compounds and may contribute to the higher and more variable NDAMN results at this NDAMN site. A pulp and paper mill is located in Millersburg, OR, 7 miles to the East/Northeast of the research farm. Pulp and paper mills are suspected sources of dioxin-like compounds.¹ Visual observation of congener group profiles shows that Hyslop Farm, OR generally has a higher percentage of PCDD than PCDF compared to other sites. Comparison of individual congener and congener group profiles from Hyslop Farm, OR to known source profiles² did not identify a single source that could account for the observed difference in relative amounts of PCDD versus PCDF at Hyslop Farm, OR versus other sites. Multiple sources may be contributing to the higher PCDD/PCDF concentrations at Hyslop Farm, OR.

Moment 10 at Fond du Lac, MN (Site 20)

Unique to Moment 10 at Fond Du Lac, MN was an element of wind direction out of the Northwest. Larger urban areas, Grand Rapids and Hibbing, MN, are located about 50 miles to the North. The PCDD/PCDF and PCB congener and congener group profiles were different for Moment 10 than for other sampling moments at Fond du Lac, MN. The PCDD/PCDF congener profile shows a higher predominance of PCDF compounds than the other moments at this site which have generally higher concentrations of PCDD congeners. More specifically, 1,2,3,4,6,7,8-HpCDF and OCDF have the highest concentration of 2,3,7,8-substituted PCDD/PCDF compounds in Moment 10. In all other moments, OCDD had the highest concentration. In considering congener group profiles, TCDF, PeCDF, and HxCDF are at highest concentrations in Moment 10; in Moments 11, 12, and 13 at this same site, total TCDF and total HpCDD are highest in concentration. When compared to typical source profiles², the congener and congener group profiles at Moment 10 appear to resemble profiles for emissions from industrial/utility coal-fired combustors as shown in Figure 2.

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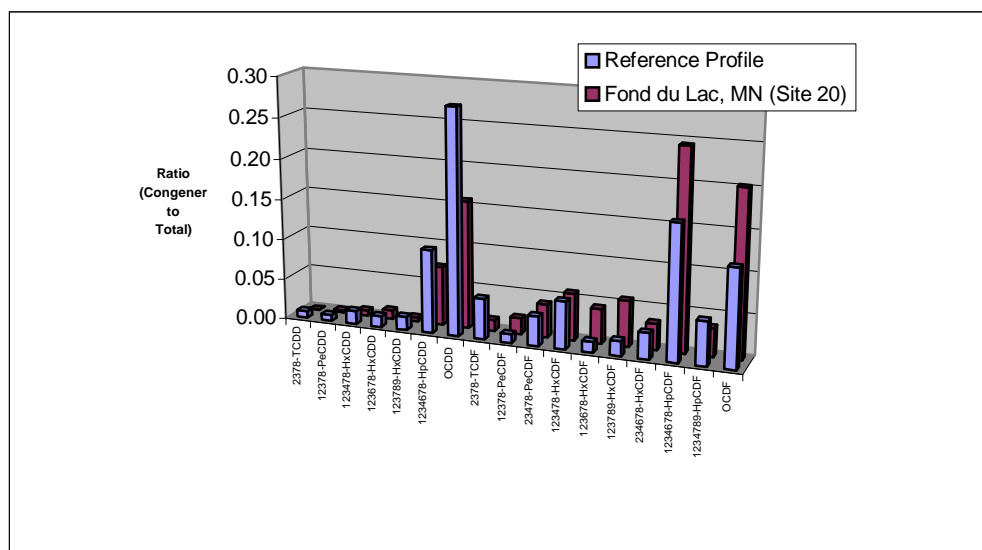


Figure 2. Comparison of Congener Profiles for Fond du Lac, MN (Site 20) and Emissions from Coal-Fired Combustors

Moment 11 at Everglades, FL (Site 4)

Comparison of the congener and congener group profiles for Everglades, FL (Site 4) sampling moments revealed differences between Moment 11 and the other moments. Moment 11 had higher (almost double) concentrations of OCDD and total HpCDD relative to other PCDD/PCDF congener groups. Wind roses and other meteorological data for Moments 10 - 13 at Everglades, FL did not indicate any unusual local conditions during Moment 11 that might have perturbed the PCDD/PCDF concentrations. Backward trajectory plots show observable differences for Moment 12 (stronger wind coming more from the southeast) rather than Moment 11. Examination of field data records and local weather (i.e., NOAA hurricane reports) also did not identify unusual circumstances during Moment 11. Examination of typical source profiles² did not identify a single source type that might have contributed to this difference.

Conclusions

Anomalous results from NDAMN during 2000 for ambient PCDD/PCDF concentrations suggested that some sites may not be established at true background locations and that some sites may have been impacted by a one-time source. After evaluation of these results, the NDAMN site at Hyslop Farm, OR (Site 29) was re-established at a new location which is expected to represent true background levels. NDAMN data from 2001 did not show similar anomalies at Fond du Lac, MN (Site 10) or Everglades, FL (Site 4) so these sites remained in their current locations. Results for the Site 10 and Site 4 moments in 2000 with anomalous results remained statistical outliers and were removed from the NDAMN database.

References

1. Exposure and Human Health Reassessment of 2,3,7,8-Tetrachlorodibenzo-p-Dioxin (TCDD) and Related Compounds. U.S. EPA, Office of Research and Development, National Center for Environmental Assessment. EPA/600/P-00/001, Bb. September 2000.
2. The Inventory of Sources of Dioxin in the United States. U.S. EPA, Office of Research and Development, National Center for Environmental Assessment. EPA/600/P-98/002Aa.

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