THE NATIONAL DIOXIN AIR MONITORING NETWORK (NDAMN): MEASUREMENTS OF CDDs, CDFs AND COPLANAR PCBs AT 18 RURAL , 8 NATIONAL PARKS, AND 2 SUBURBAN AREAS OF THE UNITED STATES: RESULTS FOR THE YEAR 2000*

David H. Cleverly[1], Dwain Winters[2], Joseph Ferrario[3], Karen Riggs[4], Pamela Hartford[4], Darrell Joseph[4], Tony Wisbith[4], Aubry Dupuy[3], and Christian Byrne[3]

[1]National Center for Environmental Assessment (8623D), Office of Research and Development, United States Environmental Protection Agency, 1200 Pennsylvania Ave., NW, Washington, DC 20460
[2]Office of Prevention, Pesticides and Toxic Substances, United States Environmental Protection Agency, 401 M St., SW, Washington, DC 20460
[3]Environmental Chemistry Laboratory, United States Environmental Protection Agency, Stennis Space Center, MS 39520
[4]Battelle Memorial Institute, 505 King St. Columbus, OH 43201.

Introduction

In June, 1998, the U.S. EPA established the National Dioxin Air Monitoring Network (NDAMN). The primary goal of NDAMN is determine the temporal and geographical variability of atmospheric CDDs, CDFs and coplanar PCBs at rural and nonimpacted locations throughout the United States. Currently operating at 32 sampling stations (Figure 1), 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. At DIOXIN2000, we reported on the preliminary results of monitoring at 9 rural locations from June1998 through June 1999[1]. By the end of 1999, NDAMN had expanded to 21 sampling stations. Then, at Dioxin2001, we reported the results of the first 18 months of operation of NDAMN at 15 rural and 6 National Park stations in the United States.[2] The following is intended to be an update to this national monitoring effort. We are reporting the air monitoring results of 17 rural and 8 National Park NDAMN stations operational over 4 sampling moments during calendar year 2000. Two stations located in suburban Washington DC and San Fransico, CA are more urban in character and serve as an indicator of CDD/F and coplanar PCB levels in more populated areas.

Methods

The analytes of interest in this monitoring program are the CDDs; CDFs substituted in the 2,3,7,8 positions on the molecule, and the coplanar PCBs (IUPAC PCB-77; PCB-105; PCB-118; PCB-126; PCB-156; PCB-157 and PCB-169). NDAMN began operations in June 1998. Sampling stations were selected based on the following criteria: (1) NDAMN must provide reasonable geographical coverage of the continental U.S.; and (2) whenever possible, NDAMN sites are to be located in rural, wilderness

* 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

and other non-impacted areas. To enhance cost savings, many of the sites are co-located at pre-existing air monitoring network stations located in rural areas. Thirty-two stations have been established using these criteria (Figure 1). Due to the complexity in operation, and resource constraints, NDAMN has been implemented in phases. Each station consists of a PS-1 PUF sampler[3]. The sampling medium has two components to collect and retain both the particle-bound and gaseous-phase dioxins and PCBs, i.e., a quartz fiber filter (QFF) to collect and retain atmospheric particles (particles ³0.1 microns diameter); and a polyurethane foam (PUF) vapor trap. In order to achieve a target 0.1 fg m^{-3} level of detection (LOD) necessary to avoid non-detects in air, the sampling moment was generally 24/day of sampling over a 28-day period. In this manner, approximately 7000 m^3 of air was sampled. Each week the QFF was harvested yielding a composite of 4 QFF samples per sampling moment. The PUF was harvested once at the end of the sampling moment. Strict QA/QC procedures are described in the Quality Assurance Project Plan[4]. Sampling proceeded with a regime of sampling 24 days, every other month. This produced 4 sampling moments over the 12 months: (1) Jan/Feb; (2) April/May; (3) August/September; (4) Nov/DEC.. Although not perfectly aligned with seasons, such a scheme has encompassed different climatic conditions. Samples were 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 1613[5].

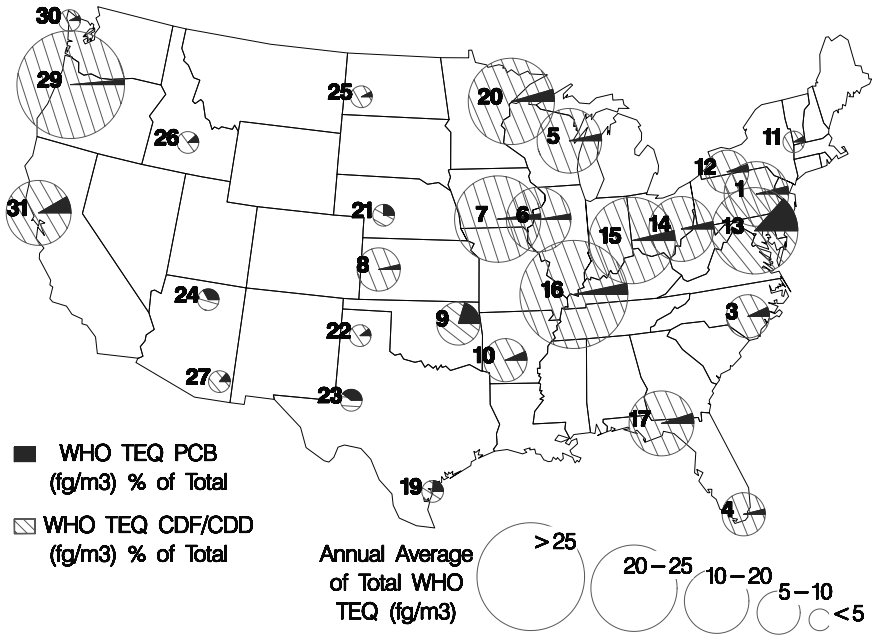
Results

The following are the results of the operation of NDAMN during calendar year 2000 at 21 rural and 8 National Park NDAMN stations in the United States. For comparisons, we have included the data from the one urban/suburban site in Beltsville, MD. These are considered interim results; data interpretation may change in the future as data are collected and analyzed from the year 2000 and 2001 monitoring efforts. The following are a summary of results:

1. All 2,3,7,8-substituted CDD/CDF congeners were detected in ambient air at the 15 rural stations. CDD/CDF compounds were detected in over 70% of the samples. Excluding PCB 169, PCB compounds were detected in all samples. In general, these results indicate that NDAMN sampling and analytical procedures are appropriate for generating sufficient data to assess background levels of CDD/CDFs and PCBs in rural areas of the United States.

2. For the most part, 2,3,7,88-TCDD was not detected (DL= 0.07 fg m^{-3}) at the following National Park locations: Grand Canyon, AZ (Figure 1, site 24); Roosevelt NP, NM (site 25); Craters-of-the-Moon, ID (site 26); Chiricahua, AZ (site 27), and Ozette Lake, WA (site 30). However, 2,3,7,8-TCDD was detected at the Everglades National Park, FL (site 4). However 2,3,7,8-TCDD was not detected at the Everglades during the Jan/Feb sampling moment when the wind direction was predominately easterly (from the Atlantic Ocean).

3. Figure 2 summarizes the annual mean CDD/F and PCB TEQ for each of the NDAMN Stations. There was a 28-fold range in TEQ_{DF}–WHO_{98} annual average air concentrations at the rural sites: 2.5 fg m^{-3} (station 21, Figure 1), and 58.3 fg m^{-3} (station 29). PCB-TEQ air concentrations ranged from 0.2 fg m^{-3} (station 22) to 9.9 fg m^{-3} (station 3), a range of approximately50. The mean TEQ_{DF}–WHO_{98} and PCB-TEQ air concentration measured at 17 rural areas is 14.6 fg m^{-3}, and 1.1 fg m^{-3}, receptively. These means compare favorably with the results of NDAMN for the year 1999 (11.3 fg m^{-3} DF-TEQ, and 0.6 fg m^{-3} PCB-TEQ). The mean TEQ_{DF}–WHO_{98} and PCB-TEQ air concentration measured at 8 National Parks is 2.0 fg m^{-3} and 0.2 fg $m^{-3,}$ respectively. This is almost identical to measurements taken in 1999 at 6 National Parks (2.1 fg m^{-3} DF-TEQ and 0.3 fg m^{-3} PCB-TEQ). The two suburban site (stations 13 and 31) had a mean TEQ_{DF}–WHO_{98} and PCB-TEQ of 15.5 fg m^{-3} and 2.0 fg m^{-}, respectively. Thus the suburban sites had similar air concentrations of DF-TEQ as rural areas, but 10-fold higher mean PCB levels as compared to rural areas.



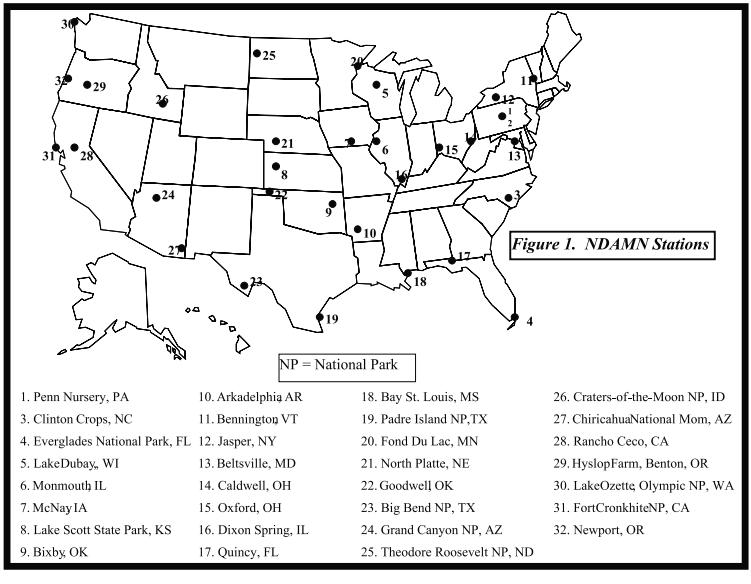


Figure 2. Average atmospheric concentrations of dioxin TEQ (from PCDDs, PCDFs, coplanar PCBs) in femtograms (10^{-15} grams) per cubic meter for the year 2000, collected by the National Dioxin Air Monitoring Network (NDAMN). Site locations listed in Figure 1.

4. The articulation of "background" concentrations of CDDs, CDFs and PCBs requires prolonged measurements taken annually over the course of several years. Furthermore, "background" should be associated with at least 3 distinct classifications of human habitation: rural, wilderness, and urban/suburban. The lowest mean annual air concentration of dioxin-like compounds has consistently been observed at the Grand Canyon National Park (site 24), with a mean of 0.3 fg m^{-3} DF-TEQ and 0.1 fg m^{-3} PCB-TEQ. This is barely above the minimum detection limit of analytical capabilities. This may be the lowest mean air concentrations measured in any developed country. The highest mean annual average air concentration for any rural area in the U.S. in 2000 was measured at Fond du Lac, MN (site 20), with an annual mean of 248 fg m^{-3} DF-TEQ and 20 fg m^{-3} PCB-TEQ. Currently we have no explanation for this relatively high level observed at this one rural site, but EPA currently considers this as a statistical outlier and excluded it from the averaging for rural areas.

5. Figure 2 shows some interesting trends. It appears that, for the most part, dioxin air measurements are highest in rural areas located near heavily populated regions of the U.S. For example, the area bounded by Chicago – Washington DC-Boston appears to be relatively uniform in rural air concentrations. The National Parks in the west, northwest and southwest have uniformly the lowest air concentrations in the U.S. This pattern may have implications for any conclusions that may be reached with regard to the distance dioxins may travel from a source. After 2 years of air monitoring across the U.S., NDAMN has not yet produced any firm evidence supporting a postulate that CDDs/CDFs are subject to long-range transport. Thus far, it appears that dioxin may be regional phenomena. We expected sites 19,23 and 27 to capture transboundary fluxes from Mexico, but levels at these stations were similar to other National Parks. Only continued monitoring and statistical analysis of wind direction and migrating parcels of air at select sites will provide much needed information upon which to derive further observations of this issue.

References

1. Cleverly, D.H.; D. Winter; J. Ferrario; J. Schaum et al. (2000). Organohalogen Compounds 45: 248-251. Presented at Dioxin '00, 20th International Symposium on Halogenated Environmental Organic Pollutants & POPs, Monterey, CA, August 13-17, 2000.
2. Cleverly, D.H.; D. Winter; J. Ferrario; J. Schaum et al. (2000). Organohalogen Compounds 45: 248-251. Presented at Dioxin '01, 21th International Symposium on Halogenated Environmental Organic Pollutants & POPs, Gyeongju, Korea, Sept 0-14, 2001.
3. USEPA (1997). Compendium Method TO9a. EPA/625/R-96/010b.
4. USEPA (1998). Quality Assurance Plan and Work Plan, DEI: National Dioxin Air Monitoring Network. Versar, Inc. under EPA Contract 68-D5-0051.
5. USEPA (1995). EPA 821-B-94-005.