*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: JUNE 1998 – DECEMBER 1999

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Introduction

The U.S. EPA has established a National Dioxin Air Monitoring Network (NDAMN) to 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. Designed in 1997, NDAMN has been implemented in phases, with the first phase consisting of 9 monitoring stations. Previously EPA has reported on the preliminary results of monitoring at 9 rural locations from June1998 through June 1999[1]. The one-year measurement at the 9 stations indicated an annual mean TEQ_{DF}–WHO_{98} air concentration of 12 fg m^{-3}. Since this reporting, NDAMN has been extended to include additional stations. The following is intended to be an update to this national monitoring effort. We are reporting the air monitoring results of 22 NDAMN stations operational over 9 sampling moments from June 1998 to December 1999. Fifteen stations are in rural areas, and 6 are located in National Parks. One station is located in suburban Washington DC and is more urban in character and serves 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

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

geographical coverage of the continental U.S.; and (2) whenever possible, NDAMN sites are to be located in rural, wilderness 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. Phase 1 consisted of an array of 10 monitors at 9 sites, which are identified as stations 1-10 on Figure 1. A duplicate sampler (station 2) is co-located at site 1. By August 1999, 14 stations were operational. By November 1999, 21 stations were on line. Each station consists of a PS-1 PUF sampler[2]. 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 ≥0.1 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[3]. Sampling proceeded with a regime of sampling 24 days, every other month. This produced 9 sampling moments over the 18 months: (1) June – July 1998; (2) August – September 1998; (3) November – December 1998; (4) January – Feburary 1999; (5) March – April 1999; (6) May – June 1999. (7) July – August 1999; (8) August – September 1999, and (9) November – December 1999. 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[4].

Results

The following are the results of the first 18 months of operation of NDAMN during 1998 and 1999 at 15 rural and 6 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.
2. 2,3,7,8-TCDD was not detected (DL= 0.07 fg m^{-3}) at the following National Park locations: Grand Canyon, AZ (Figure 1, site 24); Craters-of-the-Moon, ID (site 26); and Chiricahua, AZ (site 27). However, 2,3,7,8-TCDD was detected at the Everglades National Park, FL.
3. Figure 2 summarized the mean CDD/F and PCB TEQ for each of the 22 NDAMN Stations. There was a 10-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 24.5 fg m^{-3} (station 6). PCB-TEQ air concentrations ranged from 0.2 fg m^{-3} (station 8) to 1.1 fg m^{-3} (station 1), a range of 5.5. The mean TEQ_{DF}–WHO_{98} and PCB-TEQ air concentration measured at 15 rural areas.is 11.3 fg m^{-3}, and 0.6 fg m^{-3}, receptively. The mean TEQ_{DF}–WHO_{98} and PCB-TEQ air concentration measured at 6 National Parks is 2.1 fg m^{-3} and 0.3 fg m^{-3}, respectively. In contrast the one urban site (station 13) had a mean TEQ_{DF}–WHO_{98} and PCB-TEQ of 19.4 fg m^{-3} and 3.0 fg m^{-3}, respectively.

4. Figure 3 displays the variability of TEQ_{DF}–WHO_{98} over 9 monitoring moments at 8 rural stations from 1998 - 1999. These data indicate a general tendency towards an increase in TEQ_{DF}–WHO_{98} at the rural stations during the November/December monitoring moments. The increase in TEQ is characterized by an increase in actual measured concentrations of 1,2,3,7,8-PeCDD, 2,3,4,7,8-PeCDF, 1,2,3,7,8-PeCDF, 2,3,7,8-TCDF, and 2,3,7,8-TCDD congeners. The observation of an increase during the winter months is consistent with a recent long-term and seasonal air monitoring study of rural areas of New Zealand[5]. In that study, Buckland *et al.* noted a positive correlation in this increase with atmospheric retene (a marker compound for residential wood combustion[5]). Lohmann *et al.*[6] found a similar seasonal pattern in air monitoring study in the U.K., but attributed the change to seasonal changes in the predominant air mass movement carrying concentrated CDD/CDF from urban into rural areas. For the other sampling moments, TEQ_{DF}–WHO_{98} varies from 2 to 17 fg m^{-3}, with the exception of station 6 (Monmouth, IL) and station 7 (McNay, IA), which remained elevated through March/April, 1999. The largest relative change (measured as the ratio of the winter concentrations to those of the prior sampling moment) occurs at station 8 (Lake Scott, KS.)

References

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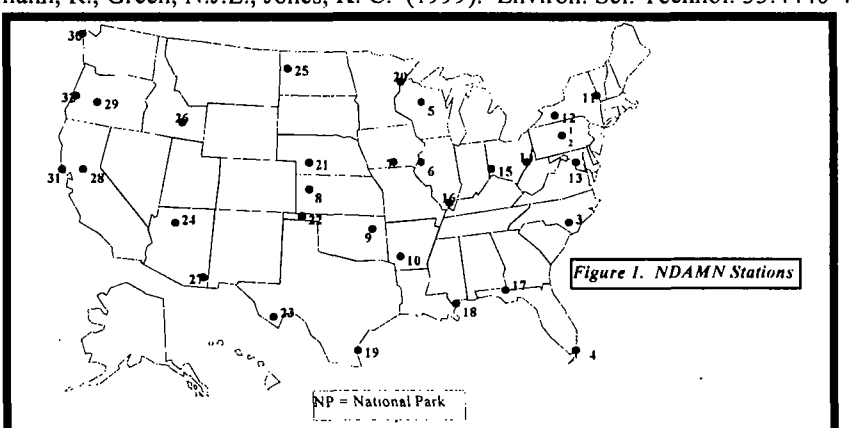

Figure 1. NDAMN Stations

Figure 2. Mean CDD/F and PCB TEQ (WHO 1998)
15 Rural (*); 6 National Parks (**) and 1 Urban (***) NDAMN Stations
June 1998 - Dec 1999

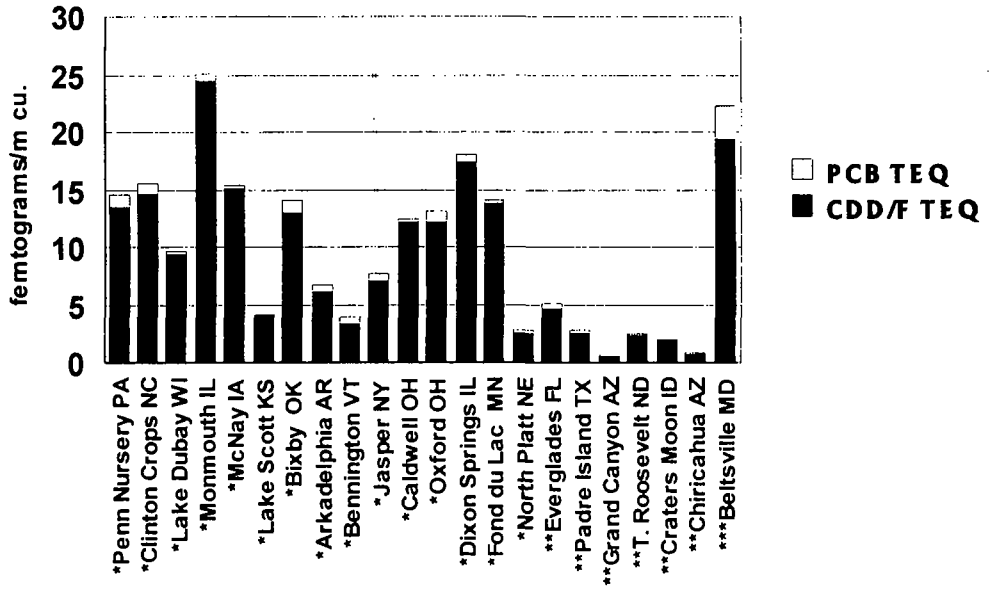

Figure 3. Seasonal Variation in WHO-TEQ of CDDs/CDFs