ATMOSPHERIC MEASUREMENTS OF CDDs, CDFs AND COPLANAR PCBs IN RURAL AND REMOTE LOCATIONS OF THE UNITED STATES IN THE YEAR 2001 FROM THE NATIONAL DIOXIN AIR MONITORING NETWORK (NDAMN)

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Introduction

The U.S. EPA has established a National Dioxin Air Monitoring Network (NDAMN) to address three primary objectives: (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 remote areas of the U.S.; and (3) to provide information regarding the long-range and transboundary transport of dioxin-like compounds in air over the United States. Figure 1 shows the locations of NDAMN sites. Previously EPA has reported on the preliminary results of monitoring at 9 rural locations from June1998 through December 1999[1], and calendar year 2000[2]. The year 1999 measurement at the 9 rural stations indicated an annual mean TEQ_{DF}–WHO_{98} air concentration of about 11.3 fg m^{-3}. In the year 2000, the mean of 18 rural stations and 8 remote areas were 14.6 fg m^{-3} and 2.0 fg m^{-3}, respectively. Since this reporting, NDAMN has been extended to include additional stations. We are reporting the air monitoring results of NDAMN for calendar year 2001 at both rural and remote sites in the U.S. The rural sites are indicated as circles and remote sites are indicted as squares on Figure 1.

Methods

The analytes of interest in this monitoring program are the polychlorinated dibenzo-*p*-dioxins (CDDs) and polychlorinated dibenzofurans (CDFs) substituted with chlorines in the 2,3,7,8 positions on the molecule. Additionally the coplanar PCBs (IUPAC PCB-77; PCB-105; PCB-118; PCB-126; PCB-156; PCB-157 and PCB-169) were included because of their dioxin-like activity. Each station consists of a PS-1 PUF dioxin air 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 ≥0.1 microns diameter); and a polyurethane foam (PUF) vapor trap. Sampling occurred continuously over a 28-day period. In this manner, approximately 5,000 –7,000 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]. There were 4 sampling moments in 2001: (1) Jan/Feb (2) April/May; (3) July/August; (4) October/November. Although not perfectly aligned with seasons, such a sampling regime has encompassed different climatic conditions. Samples were analyzed 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 atmospheric measurements taken in the year 2001at 22 rural and 8 remote NDAMN sites in the United States.

1. Rural Sites (refer to Fig. 2): The annual mean dioxin TEQ (WHO method) air concentrations measured at each of 22 rural sites in 2001 ranged from 2 fg m^{-3} to 28 fg m^{-3}; the overall mean of 22 stations combined was 12 fg m^{-3}. Mean annual PCB TEQ air concentrations ranged from 0.15 – 9 fg m^{-3}, with an overall mean of 1 fg m^{-3}. The PCB concentrations were relatively high at site 18. Site 18 is a government complex consisting of buildings built in the early 1960's when the use of PCBs in building materials was prevalent. We speculate that the high PCB measurement observed reflects PCB off gassing from the buildings.
2. Remote Sites (refer to Fig.3): The mean dioxin TEQ (WHO_{98} method) air concentrations at 8 NDAMN remote sites in 2001 ranged from 0.5 to 3 fg m^{-3} (see Figure 3), with an overall mean of 1.05 fg m^{-3}. The mean PCB TEQ ranged from 0.05 – 1.0 fg m^{-3}, with an overall mean of 0.23 fg m^{-3}. Dioxin concentrations at remote sites were on average one order of magnitude lower than what was measured at rural sites. Although not statistically significant, PCBs were approximately 5-times lower in remote sites as compared to rural sites.
3. Figure 4 displays the average CDD/CDF congener profile of ambient air at the NDAMN rural and remote sites. The dominant congeners were the OCDD>1,2,3,4,6,7,8-HpCDD> 1,2,3,4,6,7,8-HpCDF> OCDF. This profile was constant over all NDAMN sites.
4. Figure 5 displays the percent each CDD and CDF congener contributes, on average, to the dioxin TEQ at all NDAMN sites. The 1,2,3,7,8-PCDD contributes over 40% of the dioxin TEQ.
5. Figure 6 displays the coplanar PCB congener profile in ambient air at the NDAMN rural and remote sites. PCB-118 dominates followed by PCB-105, PCB-77 and PCB-156.
6. Figure 7 is a comparison of winter to summer mean air concentrations of coplanar PCBs at remote NDAMN sites. PCB mass air concentrations at the NDAMN sites generally were higher in the summer months as compared to the winter months. This difference is statistically significant (Pearson Correlation = 0.76 at P=.05). This observation is consistent with the

expected exchange of the PCB from the soil reservoir to the air as average ambient temperatures increase, which, in turn, increases volatilization from soils.

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; K.Riggs et al. (2002). *Organohalogen Compounds* 56: 437-440. Presented at Dioxin2002, 22nd International Symposium on Halogenated Environmental Organic Pollutants and POPs, August 11-16, 2002, Barcelona, Spain.
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.

Figure 1. Locations of NDAMN Stations

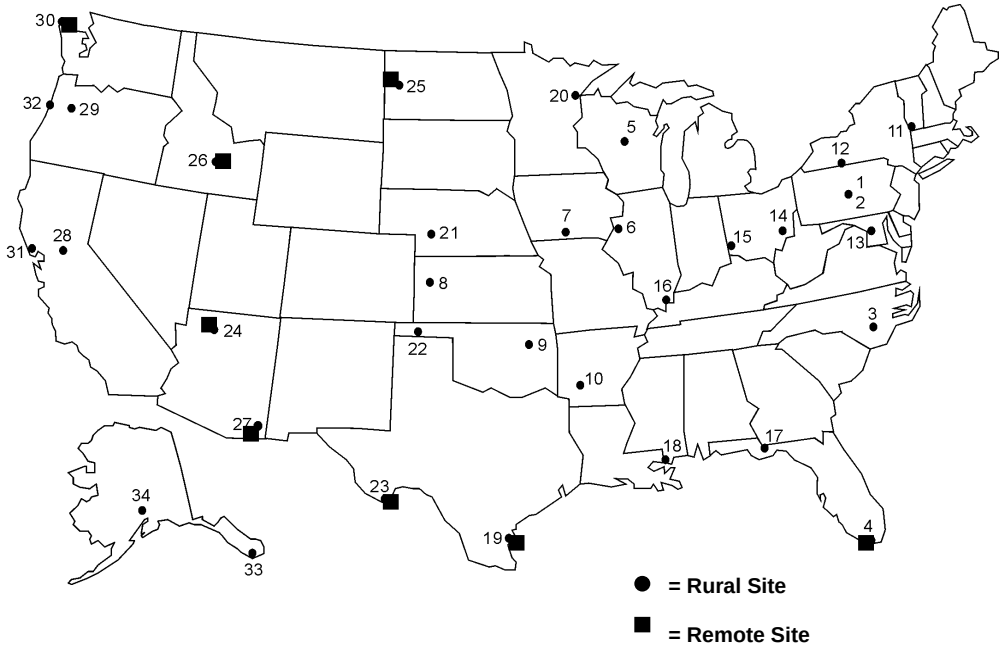

Figure 2. Annual Average Air Concentration (fg/m3) of Dioxin and PCB TEQ (WHO Method) at Rural Sites in the United States in 2001

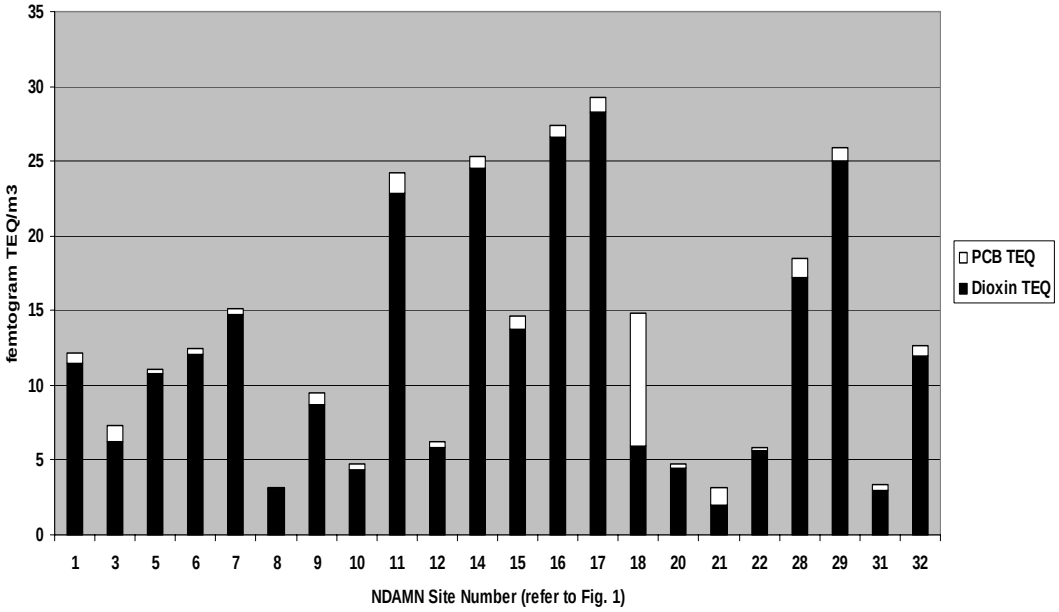

Figure 3. Annual Average Air Concentration (fg/m3) of Dioxin and PCB TEQ (WHO Method) at Remote Sites in the United States in 2001

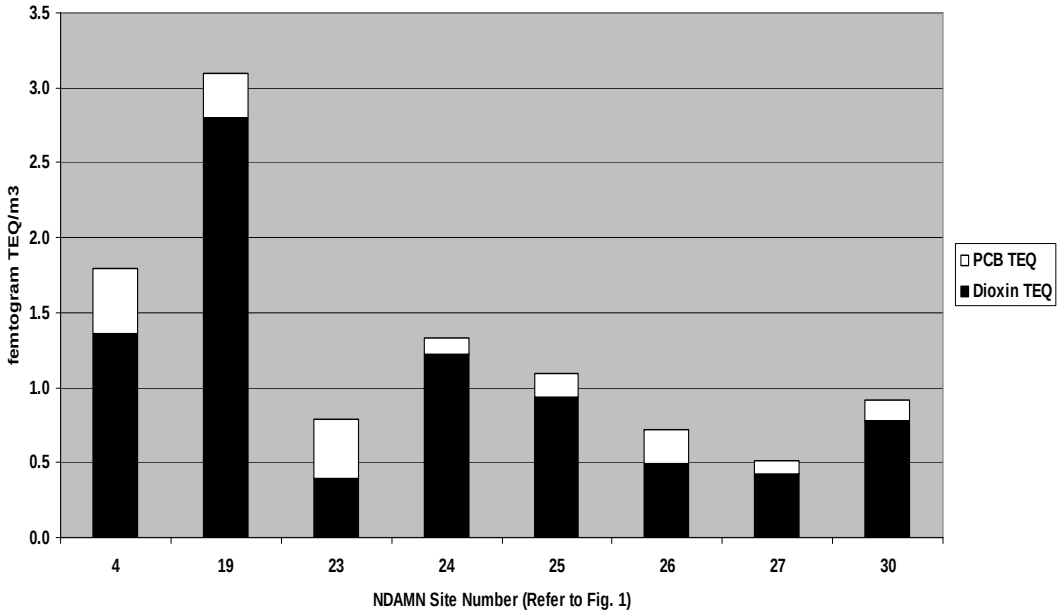

Figure 4. Average CDD/CDF Congener Profile at all NDAMN Sites ((congener concentration/sum of congener concentration) X 100)

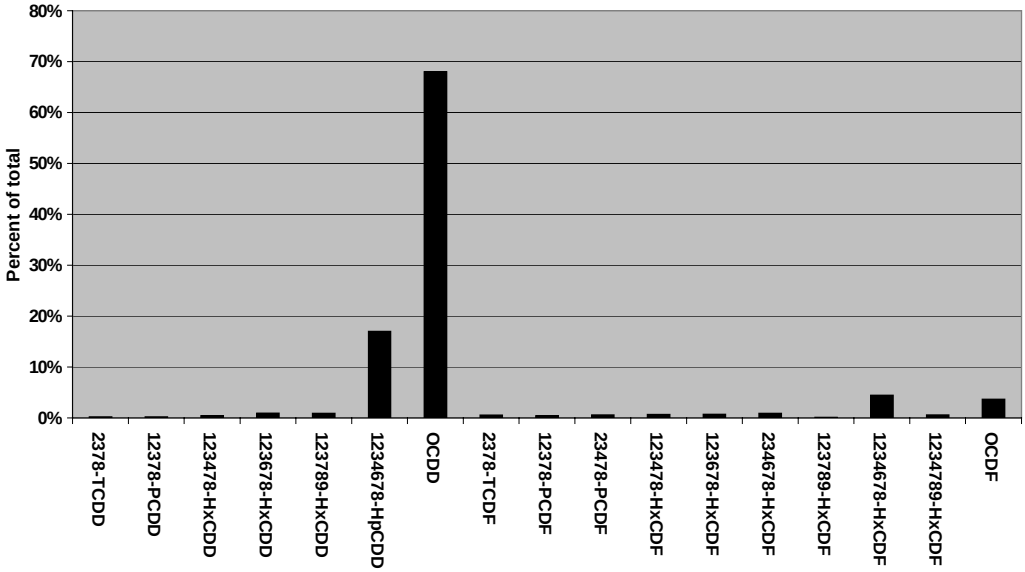

Figure 5. Congener Contribution to TEQ in Rural Air (percent of total TEQ)

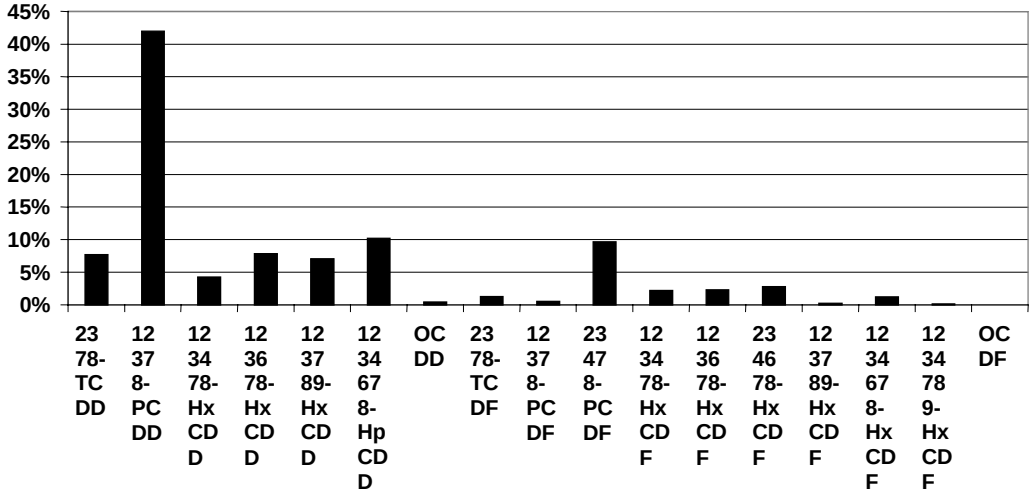

Figure 7. Comparison of PCB TEQ Air Concentrations Between the Winter and Summer Seasons in Remote Locations

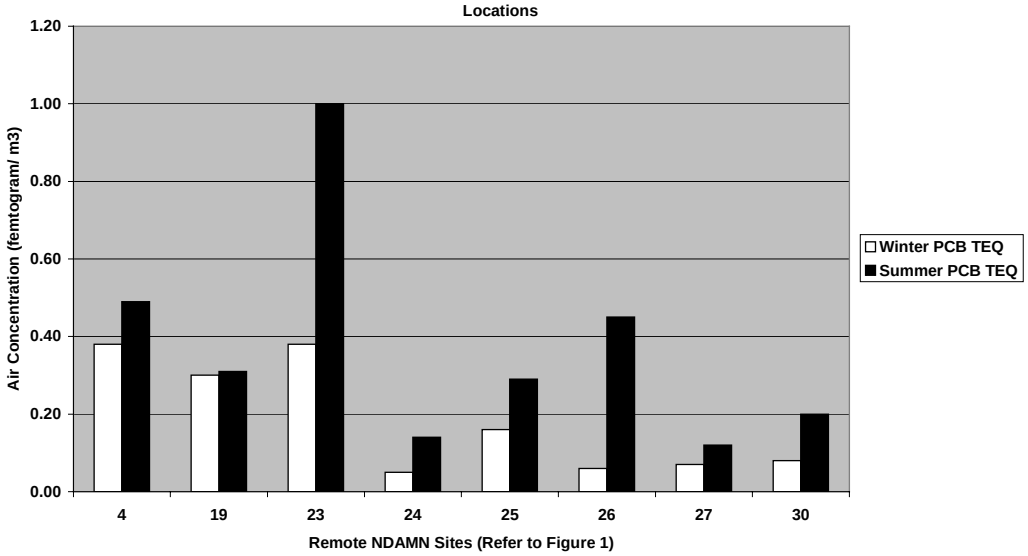

Figure 6. Coplanar PCB Congener Profile in Air at NDAMN Sites (PCB congener / sum of coplanar PCB congeners)