

THE NATIONAL DIOXIN AIR MONITORING NETWORK OF THE UNITED STATES

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Introduction

The United States Environmental Protection Agency (US EPA) has completed analysis of all samples of the National Dioxin Air Monitoring Network, or NDAMN. This network operated between 1998 and 2004, and samples were collected from 35 stations in the continental United States (US). The aim of NDAMN was to determine background air concentrations of polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and dioxin-like polychlorinated biphenyls (DL PCBs) in rural and remote areas of the US. Four urban sites were also sampled. Preliminary results from this network were published in the open literature¹, where further information on design and methods can be found, and updates were also provided at previous International Dioxin Conferences. This abstract reports on a selection of the final results from the network.

Methods

NDAMN included 35 sites. Twenty-four rural sites were chosen to obtain air concentrations in areas where crops and livestock are grown, and that encompassed a range of geographic locations. Seven remote sites were located in National park sites far from human habitation, perhaps more than 100 km away from possible dioxin sources. Four sites characterized as urban include two locations in CA, one in MD near the Washington DC metropolitan area, and one near Newport, OR. The collection of NDAMN sites does not represent a statistically random sampling of rural, remote, and urban areas of the U.S. However, the locations of sampling sites covered a wide range of climate conditions from tropical sub-humid to sub-Arctic climates. There were four sampling “moments” per year, covering the four seasons. A winter sample was taken during the month of Feb, a spring sample during Apr-May, a summer sample during June-Aug, and a fall sample during Nov. The first set of 9 sites was established for the summer 1998 sample. Others came on line during 1999 and 2000. There were a total of 29 “moments” from the start in the fall of 1998 until the conclusion of sampling with the summer 2004 sample (1998 had 3 moments, 1999 had 6 moments, all other years had 4 moments). If all 35 sites obtained successful samples from their start date until the summer of 2004, there would be a total of 763 samples. There were 37 samples that had problems with either the sample site (inactive or monitor failure) or the laboratory (QA failure), and additionally, there were 6 samples for which there was a QA failure for the dioxin/furan measurements, but DL PCB measurements were available. TEQ results focus only on the 720 samples with a full suite of dioxin and furan measurements.

Ambient air sampling was conducted with a Tisch Environmental TE 1000 PUF (polyurethane foam) sampler using a modification of EPA Method TO-9A. Each sampling moment consisted of 20-24 days of active sampling over a 28-day period, on a weekly schedule of 5 or 6 days of continuous operation followed by 1 or 2 days of inactivity. This resulted in a passage of 6000 to 8000 m³ of air through the sampler per event. Four sample sets were generated for each sampling moment at each NDAMN site: one PUF filter from active sampling; one PUF field blank; one set of four quartz fiber filters (QFFs) from active sampling; and one set of four QFF field blanks. Daily meteorological measurements were recorded at each site. Harvested samples were packed in dry ice and sent to the EPA Environmental Chemistry Laboratory at NASA Stennis Space Center, Mississippi, for sample extraction and chemical analysis. Analysis was accomplished using isotope dilution and high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS). Seventeen dioxin-like dioxin and furan congeners and homologue group concentrations were included in every measurement. Dioxin-like PCBs measured in all samples included PCBs 77, 105, 118, 126, 156, 157, and 169. Starting in the summer 2002 sample, additional PCBs

included 81, 114, 123, 167, and 189. Detection limits are presented in terms of picograms per sample; concentration based limits can be determined for each sample as this amount divided by the recorded air volume. These detection limits are: 0.5 to 0.8 for the tetra through hepta congeners (except 3.5 for 123478-HpCDD), 1.0 for OCDF and 20 for OCDD. All TEQ results were determined using WHO-2005 TEFs. All mean and TEQ concentrations were determined assuming non-detects were equal to zero.

Results

Table 1 provides the overall concentrations for all congeners, homologue groups, and TEQ over the entire dataset. Table 2 provides station averages, and Figure 1 shows the temporal variability of all rural, remote, and urban stations. A few key observations from these results include: 1) percent detection was always above 90% except for 2378-TCDD, which was detected 85% of the time; 2) DL PCBs only contributed 6-8% of TEQ, 3) the maximum concentration found was 857 fg TEQ/m³ in MN in the Jan, 2001 sample. Only 4 of 720 samples exceeded 100 fg TEQ/m³; 4) rural and urban concentrations were generally similar with average concentrations of 13.7 fg TEQ/m³ and 15.9 fg TEQ/m³, respectively, while remote area concentrations were about an order of magnitude lower averaging 1.2 fg TEQ/m³; and 5) the seasonal trends of urban and rural tended to track together, with the highest concentrations between Nov and Feb, while remote area concentrations did not appear to follow such a trend with also a narrow range of average TEQ concentrations over time.

Disclaimer

The views expressed in this article are those of the authors and do not necessarily reflect the views or policies of the U.S. Environmental Protection Agency. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

References

1. Cleverly D, Ferrario J, Byrne C, Riggs K, Joseph D, Hartford P (2006); *Env. Sci. Tech.* 41: 1537-1544.

Figure 1. Temporal variability of TEQ concentrations averaged by station characterization (note: calendar year 1999 had 6 sample moments; 1998 had 3 moments, and all other years had 4 moments).

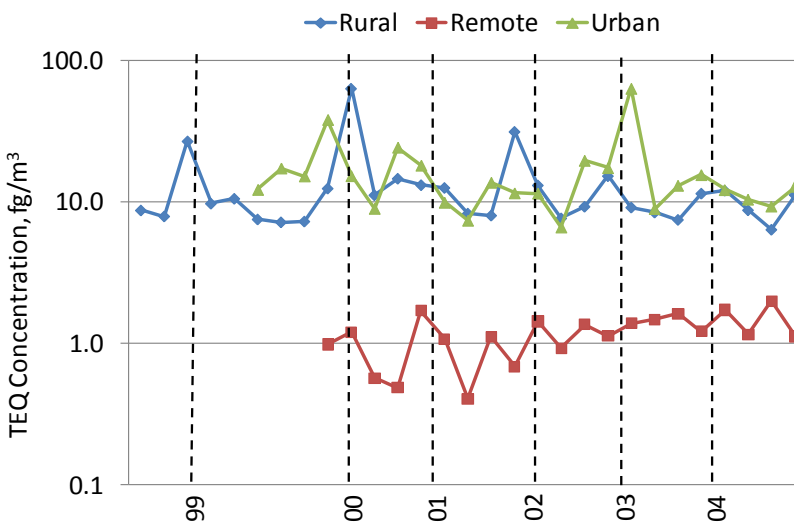


Table 1. Simple statistics for each congener, homologue group, and TEQ over all stations in NDAMN.¹

Congener	Percent Detect	Concentrations, fg/m ³			
		Mean	median	95 th perc	Max
2378-TCDD	85	0.6	0.3	1.8	22.6
12378-PCDD	90	3.2	1.8	10.8	86.5
123478-HxCDD	94	4.2	2.1	13.5	209.0
123678-HxCDD	97	7.2	3.9	24.3	257.0
123789-HxCDD	96	7.2	3.6	24.1	304.9
1234678-HpCDD	>99	103.0	52.9	343.5	5487.4
OCDD	>99	358.1	193.8	1093.8	23953.0
2378-TCDF	96	2.2	1.2	5.1	249.0
12378-PCDF	94	2.4	1.1	5.4	361.3
23478-PCDF	97	4.3	1.9	10.3	738.0
123478-HxCDF	98	5.7	2.4	11.6	1055.9
123678-HxCDF	98	4.9	2.3	10.7	786.7
234678-HxCDF	99	6.4	2.7	15.0	1030.5
123789-HxCDF	75	1.5	0.3	2.5	596.9
1234678-HpCDF	>99	27.5	12.2	57.2	4498.2
1234789-HpCDF	91	3.5	1.3	7.5	644.4
OCDF	99	22.2	10.3	48.3	3721.4
PCB 77	99	154.3	37.6	189.5	31167.2
PCB 81	100	11.9	2.9	9.5	1539.3
PCB 105	100	625.7	194.3	1395.8	80653.1
PCB 114	100	46.1	13.5	84.5	6894.9
PCB 118	100	1429.2	506.2	3778.5	134845.9
PCB 123	100	31.6	8.9	53.1	4923.1
PCB 126	100	7.1	3.2	15.2	758.2
PCB 156	100	68.9	31.3	214.9	2633.3
PCB 157	100	15.1	7.0	45.8	590.3
PCB 167	100	23.0	9.9	78.0	1082.6
PCB 169	100	1.0	0.4	2.1	260.4
PCB 189	100	2.7	1.7	7.1	50.1
TOTAL TCDD	98	18.7	9.4	54.6	1732.2
TOTAL PCDD	94	40.1	18.7	117.4	2962.4
TOTAL HxCDD	99	102.5	53.3	325.0	3293.2
TOTAL HpCDD	98	245.3	135.5	851.6	10974.8
TOTAL TCDF	98	76.9	45.9	175.5	6299.9
TOTAL PCDF	98	57.8	28.1	144.7	7619.2
TOTAL HxCDF	99	59.1	29.3	149.9	6467.3
TOTAL HpCDD	99	44.5	20.7	100.9	5735.3
TEQ – PCDD/F		10.4	5.8	29.1	773.3
TEQ – PCB		0.8	0.4	1.7	83.8
TEQ - TOTAL		11.2	6.5	30.3	857.1

¹ The number of samples, n, for each grouping was: 1) 720 for all dioxin and furan congeners, homologue groups, and TEQ; 2) 726 for PCBs 77, 105, 118, 126, 156, 157, and 169; and 3) 330 for PCBs 81, 114, 123, 167, and 189.

Table 2. Identification of stations and summary statistics.

Complete site name	Nearest town	Start Date ¹	n	Mean Conc, fg/m ³ TEQ	Max Conc, fg/m ³ TEQ
I. RURAL					
Penn Dept. of Cons Tree Nursery	Potters Mill, PA	6/98	29	12.7	45.2
Clinton Crops Research Station	Clinton, NC	8/98	26	22.3	292.3
Duplicates, Clinton & Penn Nursery ²	NC and PA	6/98	28	13.7	44.5
Everglades National Park	Florida City, FL	8/98	23	4.1	27.4
Lake Dubay State Park	Dancy, WI	6/98	28	10.2	28.6
NW Illinois Agricultural Center	Monmouth, IL	6/98	25	15.9	40.9
McNay Agr Res Farm	Chariton, IA	6/98	29	15.3	38.0
Lake Scott State Park	Scott City, KS	6/98	28	3.8	12.3
Bixby & Lake Keystone State Park ³	Bixby/Sand Sp, OK	6/98	23	11.8	33.4
Caddo Valley, Arkadelphia	Arkadelphia, AR	6/98	28	5.4	10.9
Bennington County Farm	Bennington, VT	8/99	21	7.5	71.6
Jasper Farm	Jasper, NY	7/99	18	6.1	8.6
Yaquina Head State Park	Newport, Oregon	2/03	7	4.8	9.2
Caldwell Farm	Caldwell, OH	7/99	20	17.7	43.1
Oxford Farm	Oxford, OH	7/99	22	14.7	28.5
Dixon Springs Agricultural Center	Dixon Springs, IL	11/99	20	23.9	43.1
North Florida Res & Ed Center	Quincy, FL	4/00	18	22.3	67.9
NASA Stennis Space Center	Bay St. Louis, MS	11/00	14	14.7	44.4
Padre Island National Seashore	Corpus Christi, TX	11/99	19	3.5	6.9
Fond du Lac Indian Reservation	Cloque, MN	11/99	21	47.4	857.1
North Platte Agr Res Center	North Platte, NE	11/99	21	2.8	3.8
Goodwell Agr Res Station	Goodwell, OK	1/00	20	1.7	2.5
Craig	Craig, AK	2/02	12	7.6	17.3
Hyslop Farm Ag Exp St & Marval ³	Albany/Corv, OR	1/00	20	24.4	132.6
TOTALS FOR RURAL			492	13.7	857.1
II. REMOTE					
Big Bend National Park	Alpine, TX	1/00	20	0.8	2.2
Grand Canyon National Park	Tuba City, AZ	11/99	21	0.9	7.7
Theodore Roosevelt National Park	Medora, ND	11/99	21	1.3	3.1
Craters of the Moon National Park	Hailey, ID	11/99	21	0.9	2.1
Chiricahua National Monument	Willcox, AZ	11/99	20	0.7	2.0
Denali National Park	Trapper Creek, AK	2/02	12	3.0	8.0
Lake Ozette , Olympia Nat Park	Ozette, WA	8/00	16	1.6	3.5
TOTALS FOR REMOTE			131	1.2	8.0
III. URBAN					
Rancho Seco (closed power plant)	Herald, CA	1/00	20	35.7	241.2
USDA Agr Res Center	Beltsville, MD	5/99	22	15.6	47.3
Fort Cronkhite National Monument	San Francisco, CA	11/00	17	4.7	13.8
EPA Eco Res Lab	Newport, OR	5/01	15	9.4	15.2
TOTALS FOR URBAN			69	15.9	241.2

¹All stations were shut down in November of 2004 except Beltsville, which discontinued operation in June, 2004

² Co-located samples for quality assurance were taken at Penn Nursery site, and then the Clinton Site for a total of 28 moments. These were not included in the totals for rural. ³ Two stations switched physical location to a nearby site during sampling.