Supporting information for "A general indication of the contemporary background levels of PCDDs, PCDFs, and coplanar PCBs in the ambient air over rural and remote areas of the United States."

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Number of pages: 15

Number of tables: 2

Number of figures: 5

Note: All references are consistent with the main text.

Analysis of NDAMN Samples. The harvested NDAMN samples were packaged with freezer packs and shipped overnight to an EPA laboratory for analysis. All samples were verified to have arrived cold, inspected, logged in, and stored in a freezer until analyzed. Samples were processed in analytical sets consisting of a group of 12: nine samples, one fortified laboratory control sample, and two method blanks. The QFFs from each individual field sample or field blank were combined with its corresponding PUF in a Soxhlet apparatus, fortified with the 17- ^{13}C labeled 2,3,7,8-Cl substituted dioxins/furans and 7 -^{13}C labeled coplanar PCBs (all twelve WHO coplanar PCB are analyzed after 2002) and extracted for 24 hours with toluene. The volume was reduced to 50 ml and the solvent exchanged to hexane. The extracts were then stirred for 3 hours with 50 grams of acidified silica and passed through acidified and basic silica gel. The volume was then reduced to less then 1 ml in a Zymark Turbovap II™ and fractionated on PX-21

graphitized carbon. The dioxin fraction was then further "cleaned-up" on neutral alumina prior to analyses. All reagents were prepared according to procedures detailed in EPA Method 1613 and the analyses and QA/QC procedures and thresholds are consistent with those described in the method with several notable exceptions:

(1) Standard calibration solutions were prepared at lower concentrations. For the NDAMN, the lowest calibration standard contained 50 fg of TCDD and 5 pg/µl of ^{13}C-labeled surrogates; Method 1613's lowest calibration standard contains 500 fg and 100 pg/µl of surrogates. The samples in this study are fortified to deliver 5 pg/µ l where 1613 delivers 100 pg/µl from the same 20 µl final volume. The lower ^{13}C surrogate fortification level allows for a more realistic approximation of the actual recovery of native analytes at the sub parts-per-trillion level and better approximates the behavior of trace levels of natives during sample processing and analyses;

(2) A DB-5MS column was used in place of the DB-5 specified by Method 1613. The DB-5MS has superior separation of the 2,3,7,8-TCDD from the other tetra isomers and better resolves the 2,3,7,8-Cl –substituted dioxins and furans;

(3) Method 1613 uses an AX21/Celite mixture of graphitized carbon where we use a mixture consisting of 0.5 g of BioSil A silica gel and 0.5 g of Amoco PX-21 carbon. The eluting solvents and fractionization are also different. The column was conditioned with 10 ml of 50/50 benzene/methylene chloride, 10 ml toluene, and 5 ml hexane. The sample was added to the column in 0.5 ml hexane and following 2 - 0.5 ml rinses of the sample. Fraction 1, containing most of the ortho-PCBs, was eluted with 4.5 ml of 25/75 MeCl /hexane. Fraction 2, collected in one vessel, consisted of 5.5 ml of MeCl and contained the mono-ortho PCBs and 11.5 ml of benzene/MeCl which contained the non-ortho

PCBs. The column was then reversed and the dioxins and furans collected with 13 ml of toluene. Fractions were reduced to less than 10 µl and solvent exchanged with hexane and stored in the freezer until analyzed.

Instrumental Analyses. All analyses were performed on either a Kratos Concept or a Micromass Ultraspec high resolution mass spectrometer using isotope dilution. The HRMS was operated in the electron impact ionization mode using selected ion monitoring. Chromatographic separations were achieved using a Hewlett Packard 6890 Series II high-resolution gas chromatograph, utilizing a 60 m x 0.32 mm (0.25 µm film thickness) DB-5MS capillary column. The GC conditions were optimized to completely separate the various 2,3,7,8-Cl-substituted dioxins/furans: initial oven temperature, 130º C; injector temperature, 270º C; interface temperature, 275º C; temperature programming, time 1, 1.0 min, rate 1, 5º C/min, time 2, 15.0 min, rate 2, 6º C/min; temperature 3, 295º C; injector, splitless, 1.0 min; split flow, 30-40 ml/min; purge flow, 1-2 ml/ min; and temperature equilibration time, 2 min. The mass spectrometer was tuned and calibrated prior to all analyses. It was tuned to a minimum resolution of 10,000 ppm (10% valley) using *m/z* = 330.9792 (or any suitable reference peak) at full accelerating voltage of 8,000 V. Pertinent MS parameters were as follows: cycle time for each congener group, ~1.0 s; ESA sweep (analytes), 10 ppm; native ion dwell, ~100 ms; ^{13}C-labeled ion dwell, ~35 ms; lock mass sweep, 200 ppm; lock mass dwell, 50 ms; ionization voltage, ~35 eV; source temperature, 250º C; accelerating voltage, 8,000 V; and trap current, 500 µA.

***Quality Control and Calibration*.** Between four and six calibration standards with native analyte concentrations bracketing the expected analyte concentrations were analyzed prior to analyzing samples. The analyses of calibration standards permitted the response

factors to be determined as a function of concentration using linear regression. The response factor (RF) for each native analyte at each concentration was calculated relative to its ^{13}C-labeled analog. The relative standard deviation (RSD) for average response factor for each of the native analytes had to be <20%. Similarly, the RF for each ^{13}C recovery surrogate relative to the appropriate internal standard was also calculated. The RSD for the average RF for each labeled surrogate had to be <35%. The calibration curves were considered linear under these conditions, and the analytical system was considered calibrated when these conditions had been satisfied. If these conditions could be not satisfied, corrective actions were taken. The average RFs were used for subsequent quantitations. Prior to sample analysis, the linearity of the calibration curve was verified by analyzing calibration solution 2 (200 fg of TCDD) and calculating the RF as described previously. The percent difference between the new RF and the average had to be <20% for the native analytes and <35% for the ^{13}C recovery surrogates. The mass chromatogram was also examined to ensure that all the 2,3,7,8-Cl-substituted congeners were clearly separated. If the S/N values were $\geq$10, the ion abundance ratios were $\pm$15% of the theoretical, and the RF and isomer separations were within specified limits, then sample analyses proceeded. Corrective actions were initiated if specified control limits were exceeded. On the days that samples were analyzed, 10 µl of the internal standard solution (20 pg/µl) was added to each sample, and the final volume was adjusted to 20 µl. Once all QA/QC parameters had been verified to be within specified limits, sample analyses proceeded. The mass spectrometer was operated in a mass drift correction mode using PFK to provide lock masses. The selected ion current profile (SICP) areas for the characteristic ions for each native and labeled analyte were measured. Native analyte concentrations were determined by isotope dilution. Peak areas from the characteristic

ions for each native analyte and its ^{13}C-labeled analog were used in conjunction with RFs from the internal calibration data to determine concentrations directly. Labeled surrogate concentrations (expressed as % recovery) were similarly calculated using an internal standard method. Samples were organized and analyzed in sets: method blank, matrix blank, laboratory control spike (LCS), and the nine samples. Peak identification criteria were as follows: S/N $\geq$ 3.5; the isotope ratio of the two characteristic ions for each congener class within 15% of the theoretical value; the peak maxima for the molecular cluster ions coincide within 2 s; and native analytes elute within $\pm$3 s of their corresponding ^{13}C-labeled analogs. Method blanks were examined for the presence of interfering background. For furans, an ion for the appropriate chlorinated diphenyl ether was monitored and the ion chromatogram examined to ensure the absence of chlorinated diphenyl ether contamination. The amount of any native analyte detected was listed on the quantitation report, along with the recovery of its labeled analog. Recoveries of ^{13}C-labeled analogs for the samples were between 30 and 150%. Sample sets were reviewed by the QA/QC officer to ensure compliance with QA/QC guidelines/criteria. The analytical detection limits ranged from 0.5 pg for TCDD/F to 20 pg for OCDD/F, and from 1 pg (PCB-169) to 500 pg (PCB-118) for the individual PCBs.

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Table S1. National Dioxin Air Monitoring Network Sites

Site No.	Name	Latitude D/M/S	Longitude D/M/S	Elevation meters	Classification
1	Penn Nursery, PA	40 46 30	77 37 17	466	Rural
2	Penn Nursery, PA (duplicate)	40 46 30	77 37 17	466	Rural
3	Clinton Crops, NC	35 01 33	78 16 39	40	Rural
4	Everglades, FL	25 23 24	80 40 48	2	Rural
5	Lake Dubay, WI	44 39 52	89 39 08	350	Rural
6	Monmouth, IL	40 56 02	90 43 23	230	Rural
7	McNay, IA	40 57 47	93 23 30	320	Rural
8	Lake Scott, KS	38 40 19	100 55 05	863	Rural
9	Bixby/Lake Keystone, OK	36 08 19	96 15 48	260	Rural
10	Arkadelphia, AR	34 10 46	93 05 55	71	Rural
11	Bennington, VT	42 52 34	73 09 48	305	Rural
12	Jasper, NY	42 06 23	77 32 09	634	Rural
13	Beltsville, MD	39 01 00	76 56 45	46	Urban
14	Caldwell, OH	39 47 34	81 31 52	276	Rural
15	Oxford, OH	39 31 53	84 43 27	284	Rural

16	Dixon Springs, IL	37 26 08	88 40 19	161	Rural
17	Quincy, FL	30 32 53	84 36 03	60	Rural
18	Bay St. Louis, MS	30 22 06	89 37 01	8	Rural
19	Padre Island, TX	27 25 37	97 17 55	8	Rural
20	Fond du Lac, MN	46 42 47	92 30 39	390	Rural
21	North Platte, NE	41 03 33	100 44 47	919	Rural
22	Goodwell, OK	36 35 27	101 37 03	999	Rural
23	Big Bend, TX	29 18 08	103 10 38	1056	Remote
24	Grand Canyon, AZ	36 03 35	112 11 01	2152	Remote
25	T. Roosevelt N.P., ND	46 53 41	103 22 40	841	Remote
26	Craters Moon, ID	43 27 41	113 33 17	1807	Remote
27	Chiricahua, AZ	32 00 35	109 23 20	1570	Remote
28	Rancho Seco, CA	38 20 36	121 06 27	64	Rural
29	Hyslop Farm, OR	44 38 05	123 11 24	69	Rural
30	Ozette Lake, WA	48 09 13	124 40 04	25	Remote
31	Fort Cronkhite, CA	37 50 03	122 31 54	30	Urban
32	Newport, OR	44 37 18	124 02 35	5	Urban
33	Craig, AK	55 28 19	133 07 49	5	Rural
34	Trapper Creek, AK	62 18 57	150 18 42	150	Remote

Table S2. Summary of mean annual average air concentration (fg m^{-3}) of PCDD, PCDF and coplanar PCB congeners (along with their TEQs) in rural and remote NDAMN sites in 1999, 2000, 2001, and 2002

	1999		2000		2001		2002	
	RURAL	REMOTE	RURAL	REMOTE	RURAL	REMOTE	RURAL	REMOTE
2,3,7,8-TCDD	0.53	0.03	0.54	0.03	0.52	0.02	0.55	0.07
1,2,3,7,8-PeCDD	3.01	0.37	3.15	0.24	3.10	0.14	3.47	0.36
1,2,3,4,7,8-HxCDD	4.07	0.71	4.25	0.37	4.04	0.26	4.59	0.40
1,2,3,6,7,8-HxCDD	7.72	1.28	8.50	0.88	7.53	0.51	8.20	0.74
1,2,3,7,8,9-HxCDD	7.22	1.08	8.48	0.79	7.21	0.48	8.19	0.66
1,2,3,4,6,7,8-HpCDD	105.50	16.05	117.23	11.96	106.14	8.97	122.11	10.07
OCDD	345.16	43.95	433.93	46.28	361.86	31.12	408.94	34.51
2,3,7,8-TCDF	1.95	0.16	2.25	0.21	1.88	0.25	1.69	0.23
1,2,3,7,8-PeCDF	2.06	0.30	2.33	0.11	1.99	0.16	1.65	0.24
2,3,4,7,8-PeCDF	3.73	0.50	4.08	0.35	3.42	0.27	2.92	0.33
1,2,3,4,7,8-HxCDF	4.30	0.58	4.98	0.47	4.70	0.39	3.65	0.50
1,2,3,6,7,8-HxCDF	3.90	0.51	4.56	0.45	4.22	0.37	3.44	0.42
2,3,4,6,7,8-HxCDF	5.23	0.78	6.30	0.67	5.64	0.61	4.76	0.64
1,2,3,7,8,9-HxCDF	1.61	0.29	0.91	0.07	0.51	0.03	0.41	0.06
1,2,3,4,6,7,8-HpCDF	21.57	3.26	27.42	3.04	27.05	2.99	20.27	3.78
1,2,3,4,7,8,9-HpCDF	2.81	0.53	3.45	0.31	3.15	0.21	2.27	0.49
OCDF	18.90	7.57	29.67	4.84	18.39	2.75	14.72	6.00
Total TCDD	12.50	0.70	16.49	1.47	14.14	0.73	18.35	1.33

	1999		2000		2001		2002	
	RURAL	REMOTE	RURAL	REMOTE	RURAL	REMOTE	RURAL	REMOTE
Total PeCDD	25.88	1.72	32.16	2.23	34.76	1.60	45.30	3.45
Total HxCDD	102.34	13.33	106.54	11.85	104.37	8.11	123.62	9.88
Total HpCDD	242.58	34.94	263.47	27.06	250.76	16.69	294.55	22.04
Total TCDF	76.37	7.64	76.37	11.18	71.09	7.68	62.99	8.16
Total PeCDF	47.38	2.63	48.75	4.82	43.01	2.43	41.38	5.28
Total HxCDF	50.32	4.88	52.56	5.97	53.10	5.69	46.24	6.34
Total HpCDF	36.92	5.26	45.49	4.89	41.98	3.81	34.47	6.07
PCDD + PCDF	958.35	122.62	1,105.43	120.59	993.45	80.61	1,090.56	103.05
TEQ_{DF}	10.43	1.41	11.39	0.99	10.40	0.70	10.47	1.07
PCB-77	45.37	14.58	140.84	58.05	54.47	7.85	48.13	31.87
PCB-105	289.04	167.36	684.62	334.28	333.80	24.97	280.64	129.87
PCB-118	810.16	520.30	1,671.08	871.65	832.10	462.05	1,104.79	360.62
PCB-126	4.68	1.17	6.73	1.43	4.43	1.25	4.58	1.42
PCB-156	52.83	37.21	102.99	61.45	54.91	41.64	45.42	16.49
PCB-157	11.60	10.43	20.86	12.71	12.16	9.39	9.72	3.27
PCB-169	0.60	0.06	0.84	0.06	0.64	0.01	0.68	0.03
TEQ_{PCB}	0.62	0.16	0.69	0.22	0.59	0.18	0.70	0.32

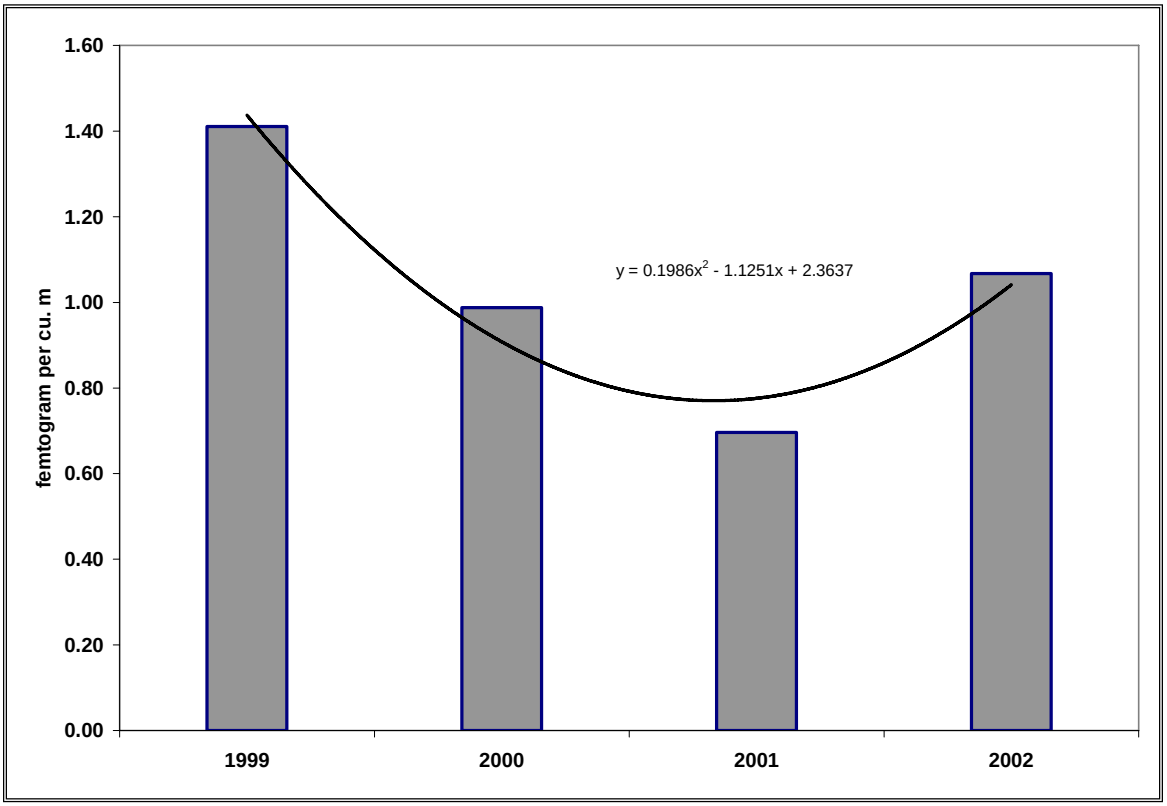


Figure S1. Mean annual ambient air concentration (fg m^{-3}) of WHO-TEQ_{DF} at remote NDAMN sites.

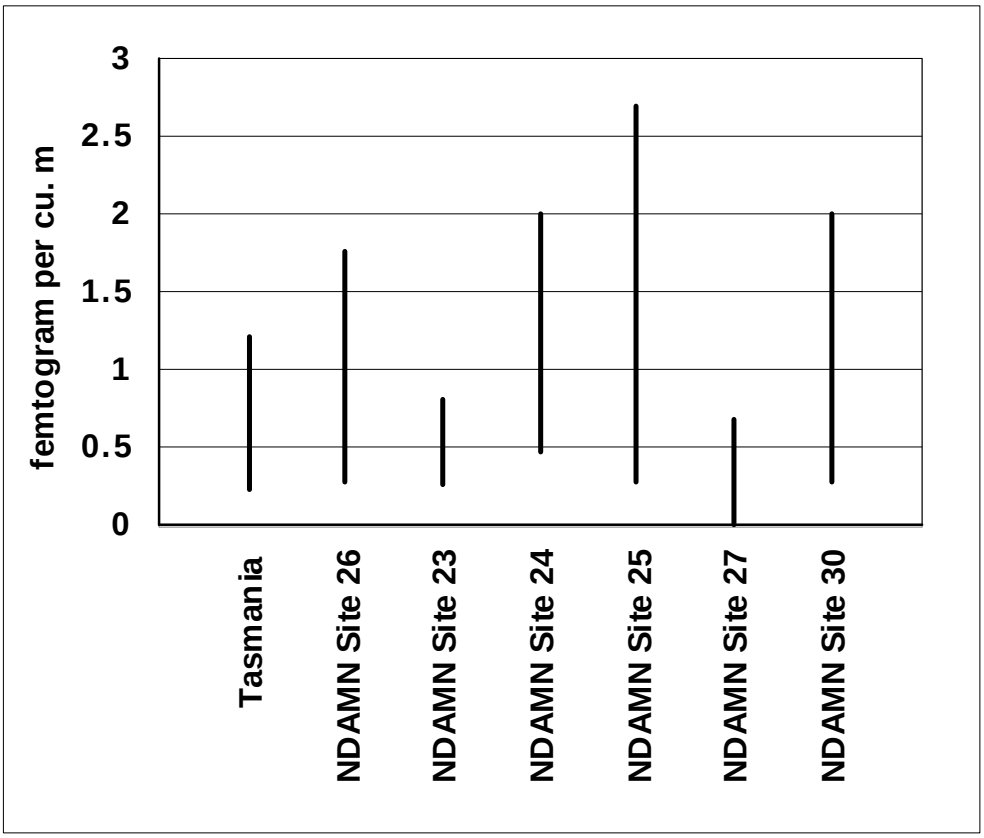


Figure S2. Comparison of ranges in TEQ_{DF} ambient air concentrations (fg m^{-3}) in NDAMN remote areas to Tasmania in the year 2002.

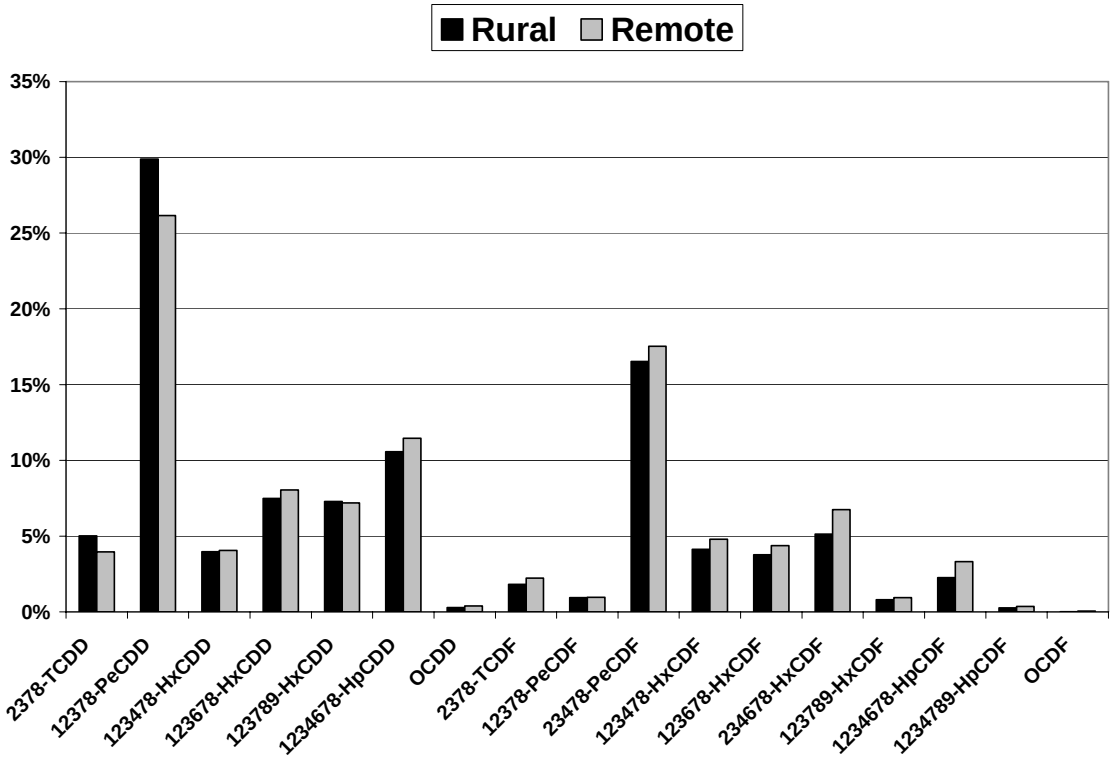
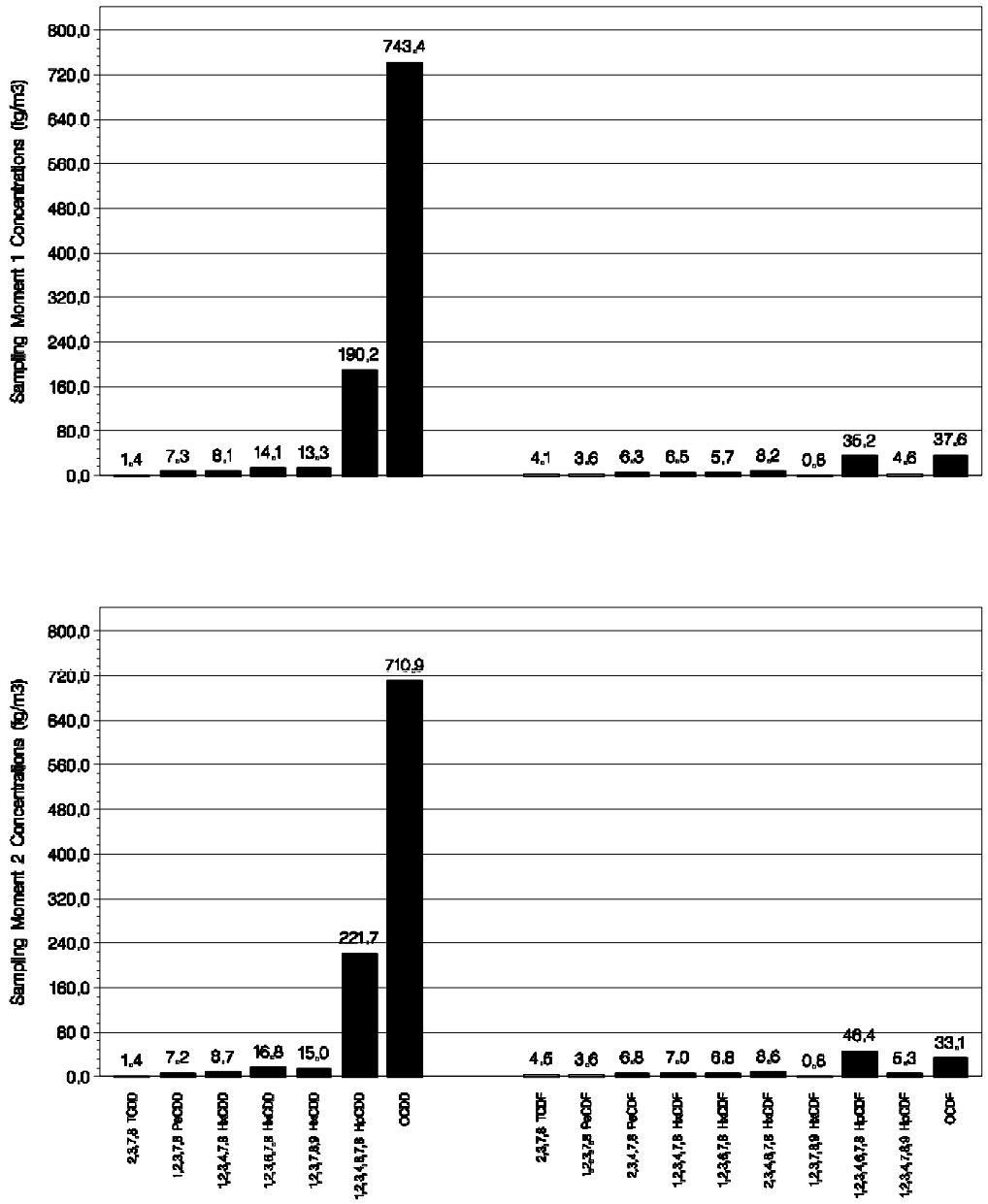


Figure S3. Mean PCDD and PCDF congener profile in rural and remote NDAMN sites (percent of TEQ)

Figure S4. PCDD/PCDF congener pattern in air of an urban center from two sampling periods one year apart (2000 and 2001).



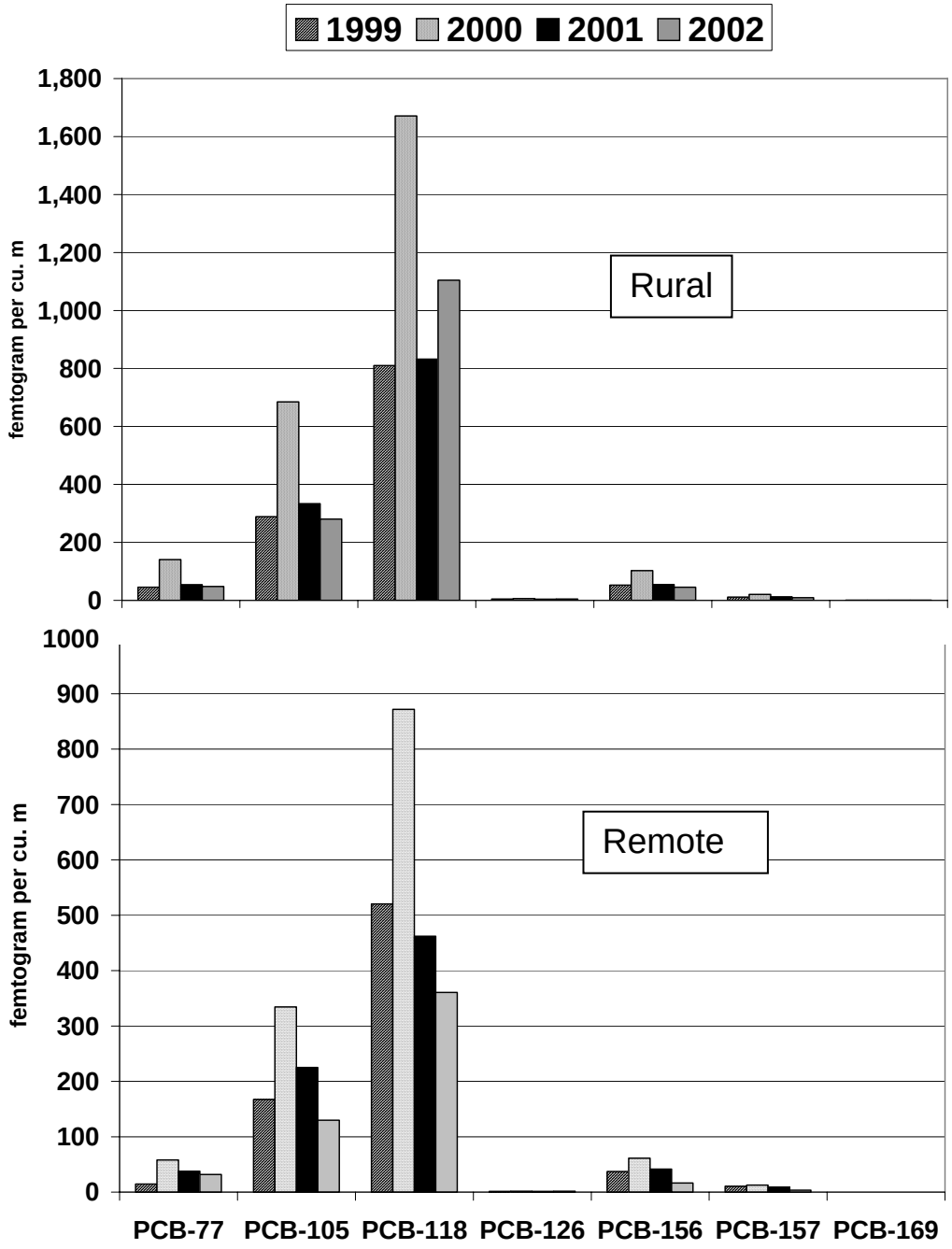


Figure S5. The mean coplanar PCB congener profile at rural and remote NDAMN sites from1999-2002