

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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Long-term measurements of the atmospheric concentrations of PCDDs, PCDFs, and coplanar PCBs were taken in rural and remote areas of the United States by the National Dioxin Air Monitoring Network (NDAMN). A total of 21 quarterly sampling moments occurred from June, 1998 to December, 2002 at 34 locations geographically distributed throughout the United States. Sampling sites were located in rural and remote areas to obtain background air concentrations of dioxin-like compounds. Results were reported as the toxic equivalent (TEQ) of the mix of PCDDs/PCDFs (TEQ_{DF}) and the mix of coplanar PCBs (TEQ_{PCB}). At the studied rural sites the mean annual TEQ_{DF} for each of the NDAMN sampling years was 10.43, 11.39, 10.40, and 10.47 fg m⁻³ for 1999, 2000, 2001, and 2002, respectively. There was no statistically significant difference in the rural mean TEQ_{DF} air concentrations across the sampling years (at 0.05 level of significance), although the mean concentration in sampling year 2000 increased 10% relative to the other sampling years. The 95th percent confidence interval of TEQ_{DF} air concentrations in rural areas of the United States is from 6.4 to 15.4 fg m⁻³, indicating there is a 95% probability that the true mean falls within this range. Mean annual atmospheric concentrations (TEQ_{DF}) at the remote sites were 1.41, 0.99, 0.7, and 1.07 fg m⁻³ in 1999, 2000, 2001, and 2002, respectively. The 95th percent confidence interval of TEQ_{DF} air concentrations suggest that the true mean annual atmospheric TEQ_{DF} concentration in remote areas of the United States is between 0.1 and 3 fg m⁻³. The remote sites have average air TEQ_{DF} concentrations that are approximately 10 times lower than those of the rural sites. For the rural sites, there was close agreement in the mean annual air concentrations of coplanar PCBs (TEQ_{PCB}) among the years 1999, 2000, 2001, and 2002 (i.e., 0.62, 0.69, 0.59, and 0.7 fg m⁻³, respectively).

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However, as is the case with PCDDs/PCDFs, there was a marked increase (i.e., $\approx 13\%$) in the annual rural mean air concentration in 2000 as compared to the other sampling years. The confidence intervals across the NDAMN sampling years suggests a 95% probability that mean TEQ_{PCB} atmospheric concentrations in rural and remote areas of the United States are within the range of 0.5–0.9 fg m⁻³ and 0.1–0.5 fg m⁻³, respectively. The congener distributional patterns of PCDDs/PCDFs in air were relatively constant at all locations, and match the profile of urban air. We propose the hypothesis that urban areas are regional sources of PCDDs/PCDFs and are affecting atmospheric levels in rural and remote areas of the United States.

Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and coplanar polychlorinated biphenyls (cp-PCBs) represent a class of toxic semivolatile aromatic compounds commonly referred to as being “dioxin-like”. This term defines the chemical class as mirroring 2,3,7,8-tetrachlorinated dibenzo-*p*-dioxin (TCDD) with respect to having very similar chemical and physical properties and chlorine substitution patterns, a planar molecular orientation, and a common mode of action of toxicity in mammals. The environmental effects and toxicology of PCDDs/PCDFs are largely controlled by the presence of chlorine atoms in the 2,3,7,8 positions. The coplanar PCBs are non-ortho substituted compounds with chlorine atoms on the para and, minimally, two meta positions. Dioxin-like compounds [henceforth referred to as dioxin] appear as mixtures in environmental samples. The toxic equivalence (or TEQ) procedure is an accepted convention for translating the proportion of congeners within the mixture to an equivalent concentration of 2,3,7,8-TCDD (the most toxic member of the class) (1).

Dioxin binds to organic carbon in soils, sediments, and atmospheric particles, and readily bioaccumulates into the fatty tissues of animals. Although there is evidence that dioxin can be formed in nature, the dominant sources to the environment are anthropogenic. Combustion-related activities such as incineration of human-generated waste materials, secondary and primary metal smelting, production of electrical energy using coal and oil, and combustion of gasoline and diesel fuel are viewed as the leading sources to the atmosphere (2). The physical mechanisms of atmospheric transport and deposition are understood to be responsible for the ubiquitous distribution of dioxin in the terrestrial and aquatic environment. Contamination of the ecological and terrestrial food chains arise by atmospheric deposition into photosynthesizing plants and grasses that are eventually consumed by animals (3, 4). The PCDDs and PCDFs then sequester to the fat reservoir whereby the chemicals increasingly concentrate from one organism to another up the food web. Humans are at the top of the food chain through their consumption of beef, pork, chicken, fish, and dairy products, and this dietary pathway accounts for most daily exposures.

This paradigm points to the importance of the atmosphere as an essential transport media ultimately causing environmental exposures to dioxin, albeit through indirect pathways. Given the importance of the atmosphere in distributing dioxin, it is surprising that very few atmospheric measurements have been undertaken in rural and remote locations

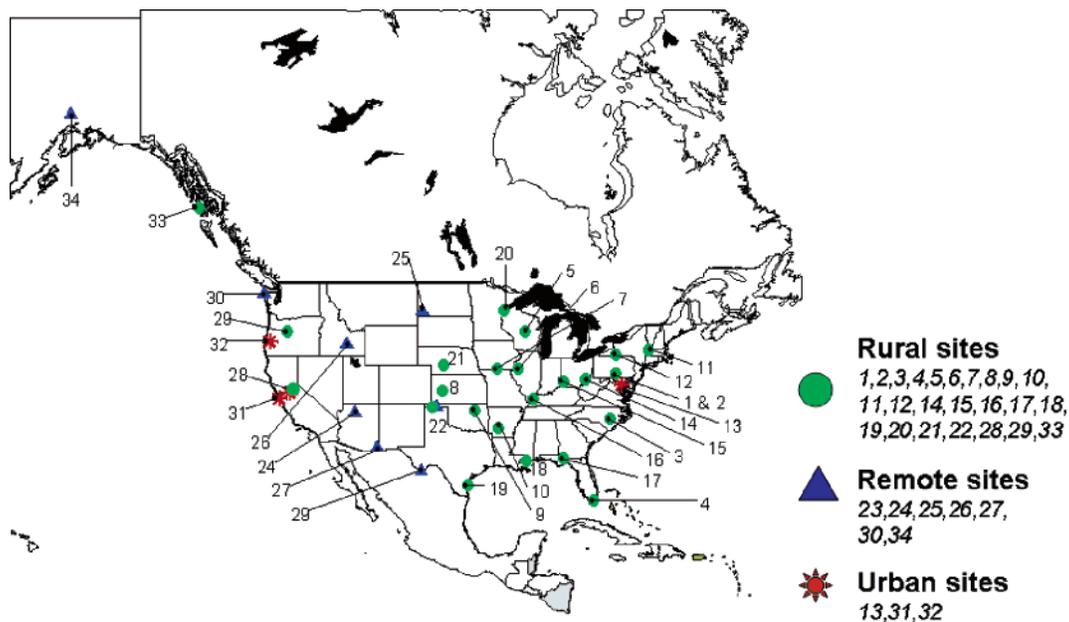


FIGURE 1. Locations of NDAMN sampling stations.

sufficient to establish general background levels in air. The USEPA has been operating a National Dioxin Air Monitoring Network (NDAMN) specifically designed to determine the long-term and background air concentrations of these contaminants over air in agricultural and remote regions of the United States. This paper reports on the interpretation of NDAMN results from air monitoring activities conducted from June, 1998 through December, 2002.

Materials and Methods

The aim of NDAMN was to determine background air concentrations of PCDDs, PCDFs, and cp-PCBs in rural and remote areas of the United States. Background is defined as average ambient air concentrations inferred from long-term and multi-year atmospheric measurements at the same locations using identical monitoring and analytical procedures. The rural sites were chosen in order to obtain air concentrations in areas where crops and livestock are grown, and that encompassed a range of geographic locations in terms of latitudinal and longitudinal positions. Remote sites were selected on the basis that they were relatively free of human habitation and >100 km away from human dioxin sources. The locations of sampling sites covered a wide range of climate conditions from tropical sub-humid to sub-Arctic climates. The idea behind the sampling configuration was to provide reasonable geographic coverage of the United States limited only by budgetary constraints. Funding was sufficient for the establishment and maintenance of 34 NDAMN stations over a period of 6 years. Figure 1 displays a map of the United States showing the approximate locations of all 34 NDAMN sites. Sites 1 and 2 were collocated monitors for purposes of duplicate sampling. Cost savings was achieved by “piggybacking” on pre-existing nationally based air monitoring networks. Details on the sampling sites and locations are summarized in Table S1 of the Supporting Information (SI). From 1998 to 2002 there were a total of 21 separate sampling periods (moments) conducted nationwide. The totality of the sampling moments generally encompassed all four climate seasons (winter, spring, summer, and fall).

Air Sampling Procedures. Ambient air sampling was conducted with a Tisch Environmental TE 1000PUF (polyurethane foam) sampler in accordance with EPA Method TO-9A (5) as modified in the Quality Assurance Project Plan (6). The TE 1000PUF sampler consisted of a sampling head,

a meter equipped with a magnehelic gauge to measure air flow, and a blower type vacuum pump. The sampling head assembly consisted of a 10.16 cm i.d. quartz-fiber filter (QFF) and a 5.85 cm (i.d.) by 12.7 cm (length) glass sample cartridge containing a 5.08 cm (length) PUF absorbent plug. A regulated air flow was drawn into the top of the sampling head assembly, and the particle-bound phase of the contaminants in the air stream was collected on the filter surface (porosity down to 0.1 μm), while the vapor phase was absorbed into the PUF. A second PUF in a glass cartridge and a QFF were placed into an inactive sampling head assembly at the site to act as a field blank for quality assurance. Detection of the analytes in the field blank was an indication of contamination of the sample media prior to active sampling. 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. In this manner approximately 6000 to 8000 m^3 of air passed through the sampling head assembly. Each week the QFF was harvested and a new QFF was placed in the sampler, yielding four QFFs per sampling moment. This was done to prevent saturation and clogging of the filter media with collected particles. Another benefit of changing the QFFs was the potential to reduce volatile loss of particle-bound dioxin. The PUF was collected once at the end of the sampling moment. Prior to sampling, the PUFs were commercially pre-cleaned by heating at 100 °C for 16 hrs, and then analytically determined to be free of dioxin contamination. The QFFs were also pre-cleaned of dioxins. ^{13}C labeled 1,2,3,4-TCDF and PCB-81 were added to the PUF as a quality assurance procedure. Both compounds were selected to represent the most volatile members of the class of analytes, and were intended to gauge any loss of sample during the duration of the sampling period. 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 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 an EPA laboratory for sample extraction and chemical analysis. The analytical method used in the determination of dioxin present in each sample is described in the Supporting Information and will not be reviewed here. Analysis was accomplished with isotope dilution on high-

TABLE 1. Annual Mean Atmospheric TEQ_{DF} and TEQ_{PCB} Concentrations at Rural and Remote Sites in the United States (from the National Dioxin Ambient Air Monitoring Network)^a

location	units	1999 ^b	2000	2001	2002
rural mean TEQ _{DF}	fg m ⁻³	10.43 ± 6.18 (7.25–13.60)	11.39 ± 8.6 (7.37–15.42)	10.40 ± 8.85 (6.37–14.43)	10.47 ± 6.85 (7.43–13.5)
remote mean TEQ _{DF}	fg m ⁻³	1.41 ± 0.94 (0.1–2.91)	0.99 ± 0.59 (0.36–1.61)	0.7 ± 0.25 (0.44–0.96)	1.07 ± 0.61 (0.50–1.63)
rural mean TEQ _{PCB}	fg m ⁻³	0.62 ± 0.28 (0.45–0.80)	0.69 ± 0.47 (0.46–0.91)	0.59 ± 0.31 (0.44–0.74)	0.70 ± 0.46 (0.49–0.92)
remote mean TEQ _{PCB}	fg m ⁻³	0.16 ± 0.01 (0.12–0.21)	0.22 ± 0.15 (0.06–0.38)	0.18 ± 0.11 (0.06–0.30)	0.32 ± 0.21 (0.13–0.52)
no. of sampling stations		8–23	26–30	30–31	34
no. of valid samples		98	99	119	136
no. of sampling moments		9	4	4	4

^a ± One standard deviation about the mean. Numbers in parentheses (..) are 95% confidence interval. ^b Includes 1998 sampling moments.

resolution gas chromatography and high-resolution mass spectrometry.

Results and Discussion

Although three urban sites were included in NDAMN, the focus of this paper is on background concentrations of dioxin in non-urban areas. Results of annual air measurements in rural and remote sampling sites are displayed in Table 1. PCDD, PCDF, and cp-PCB congener-specific atmospheric concentrations for all sampling years are summarized in Table S2 in the SI. In this paper, the shorthand for the dioxin TEQ is “TEQ_{DF}” and for PCB TEQ is “TEQ_{PCB}”. Results are displayed by years 1999, 2000, 2001, and 2002. In 1998 there were only three sampling periods toward the end of the year; therefore, these results were merged with the 1999 data. Of the 34 NDAMN sites, 24 are classified as rural, 7 sites are remote, and 3 sites are urban (as identified in Table S1 of the SI).

PCDD and PCDF Measured in Air at Rural and Remote NDAMN Sites. At rural sites the mean annual TEQ_{DF} for each of the NDAMN sampling years was 10.43, 11.39, 10.40, and 10.47 fg m⁻³ for 1999, 2000, 2001, and 2002, respectively. There was no statistically significant difference in the rural mean TEQ_{DF} air concentrations across the sampling years (at 0.05 level of significance), although the mean concentration in sampling year 2000 increased 10% relative to the other years. One standard deviation around the mean provides a close concordance of dispersion of these data indicating similar variability in TEQ_{DF} from year to year. The 95th percent confidence interval of the annual TEQ_{DF} concentration for rural areas of the United States suggests that the true annual mean falls within a range of 6.4–15.4 TEQ_{DF} fg m⁻³.

Mean annual atmospheric TEQ_{DF} concentrations at remote sites were 1.41, 0.99, 0.7, and 1.07 fg m⁻³ in 1999, 2000, 2001, and 2002, respectively. From 1999 through 2001, there was an average annual reduction of about 0.36 fg m⁻³ per year in mean TEQ_{DF} air concentration at the remote sites. From 2001 to 2002, there was an increase of 0.37 fg m⁻³, suggesting an overall curvilinear trend line from 1999 to 2002 (see Figure S1 in the SI). When compared with rural NDAMN sites, the remote sites have average air TEQ_{DF} concentrations that are approximately a factor of 10 lower. The confidence intervals suggest that there is a 95% probability that the true mean annual atmospheric TEQ_{DF} concentration in remote areas of the United States is between 0.1 and 3 fg m⁻³. These mean air concentrations are in general agreement with air measurements taken at a pristine and remote site in Tasmania, Australia (7). The Australian remote measurements were obtained under wind-vector controlled conditions whereby only clean marine air emanating from the open ocean was sampled. The long-term ambient air measurements taken in 2002 in a remote region of in northwestern Tasmania produced a range of TEQ_{DF} air concentration from

0.23 to 1.22 fg m⁻³, with a mean of 0.57 fg m⁻³ (7). The individual NDAMN remote site annual average air concentration in the year 2002 was compared to the Tasmanian results. The plot of these ranges (see Figure S2 in the SI) gives an indication that global remote areas may have contemporary TEQ_{DF} air concentrations that are <3.0 fg m⁻³. The concentrations of the PCDD congeners 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD were relatively constant from year to year at the rural sites. However, the 1,2,3,7,8-PeCDD congener was 6 times higher in concentration than 2,3,7,8-TCDD. The relative decrease in annual air concentration of 1,2,3,7,8-PeCDD at remote sites from years 1999–2001 and increase from 2001 to 2002 mimic the time-trend of TEQ_{DF} air concentration, suggesting that this is the main cause of the observed variable TEQ_{DF}.

Figure 2 shows the PCDD/PCDF congener profile in ambient air at rural and remote sites. The rural and remote NDAMN sites displayed very similar and consistent distributional patterns of PCDD and PCDF congeners from year to year. The 1,2,3,4,6,7,8-HpCDD and OCDD congeners dominated the congener profile. 1,2,3,4,6,7,8-HpCDD and OCDD ranged from 10.6 to 11.2% and 36 to 39% of the sum of PCDD + PCDF concentrations in rural air, respectively, with a central estimate of about 10% and 37%. In remote air these congeners ranged from 10 to 13% and 33.5 to 38.6%, respectively, with a central estimate of about 11% and 36%. The 1,2,3,4,6,7,8-HpCDF was the third most elevated congener in rural air, representing 1.9–2.7% of total PCDD/PCDF concentration. The fourth most abundant congener in rural and remote air was the OCDF, which represented approximately 2–6% of total PCDD/PCDF concentration. Together, these four congeners accounted for 50–55% of all PCDD and PCDF present in rural and remote air. All other congeners were less than 5% of total PCDD and PCDF concentration. The highly toxic congeners 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD were detected in 96% and 97% of the NDAMN rural samples, and only 49% and 60% in remote samples. When detected in both rural and remote NDAMN sites, the 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD constituted 0.1%, 0.04% and 0.3%, 0.3% of total PCDD and PCDF concentration, respectively. With regard to the mean TEQ_{DF}, there appear to be seven congeners that contribute approximately 80% of the TEQ_{DF} in the ambient air of rural and remote areas of the United States (see Figure S3 in the SI). Ranked in order, these congeners are 1,2,3,7,8-PeCDD (~28% of the TEQ_{DF}); 2,3,4,7,8-PeCDF (~17%); 1,2,3,4,6,7,8-HpCDD (~11%); 1,2,3,6,7,8-HxCDD (~8%); 1,2,3,7,8,9-HxCDD (~7%); 2,3,4,6,7,8-HxCDF (~6%), and 2,3,7,8-TCDD (~5%). Figure 3 gives the annual mean TEQ_{DF} air concentration (fg m⁻³) for each NDAMN site over all sampling years.

Are Urban Areas the Main Source of Dioxin in Rural and Remote Areas? The pattern of the PCDD and PCDF

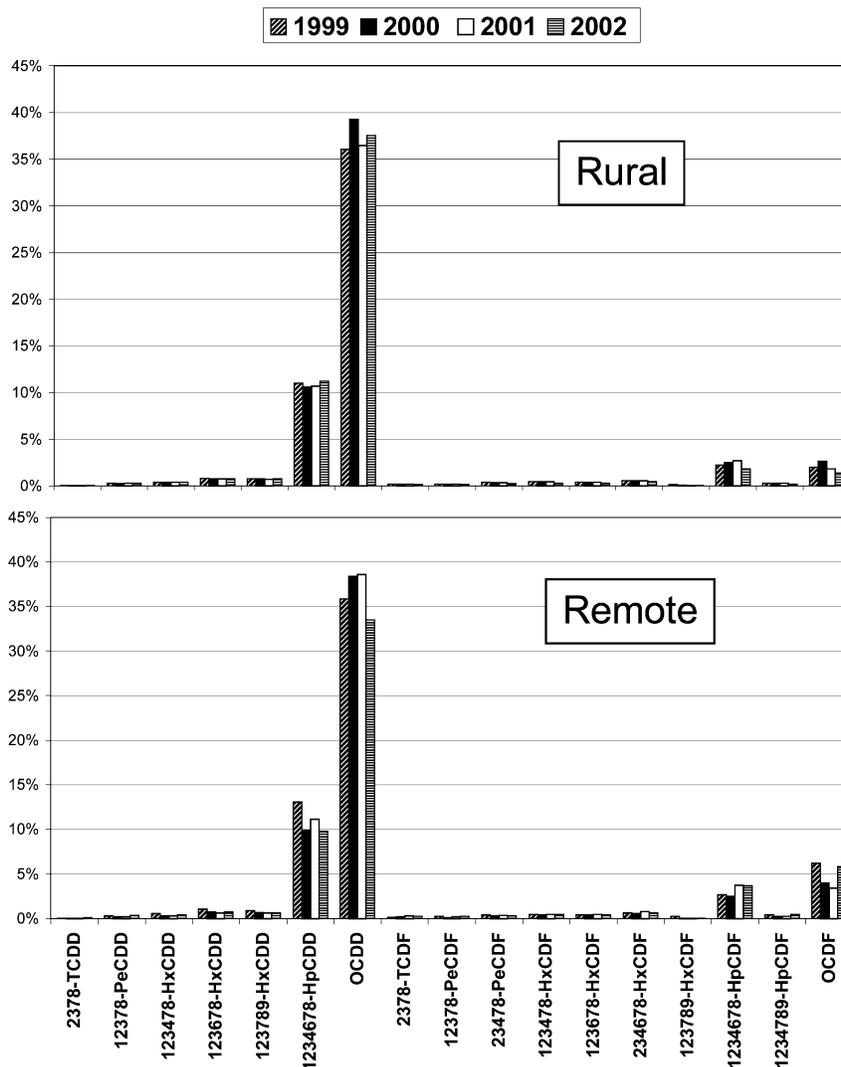


FIGURE 2. Mean PCDD and PCDF congener distribution in air, percent of total PCDD + PCDF, at rural and remote NDAMN sites from 1999 to 2002.

congener distributions in ambient air is remarkably similar between the rural and the remote sites and over the time-span of 4 years. The magnitude of concentration may vary, but the pattern and proportionality of congeners is relatively constant. These largely unaltered distributions suggest that the PCDD and PCDF patterns in rural and remote air sheds are a consequence of the atmospheric “weathering” effect. The wet and dry deposition of atmospheric particles, combined with atmospheric photochemical reactions, alter both the concentration and distribution of PCDD/PCDF congeners in air. PCDDs/PCDFs that are adsorbed to atmospheric particles are removed by gravitational settling, Brownian diffusion of aerosol particles to surfaces, and scavenging of particles by cloud and precipitation. It is generally accepted that, in air, the low-molecular-weight PCDDs and PCDFs partition to the gas phase and the high-molecular-weight compounds partition to atmospheric particles (8). The physics of this behavior is controlled by ambient atmospheric temperature, relative humidity, and the vapor pressure of the compounds. Thus Cl₄–Cl₆ congeners primarily exist in the gas phase. The half-lives of PCDDs/PCDFs in the gas phase have been estimated to range from hours to days (9). The higher chlorinated congeners are predominantly particle-bound, and this increases with decreasing vapor pressure. With respect to the particle-bound phase, it has been determined that PCDDs and PCDFs are largely found on the sub-micrometer fraction of the aerosol

(10). Based on fugacity modeling and in consideration of fate processes, Bennett et al. have calculated that the theoretical geographical travel distance for particle-bound PCDDs and PCDFs to be in a range of 100–1000 km with a best estimate of 600 km (11). This was observed to be the average distance between urban centers in the United States, implying that the geographically scattered urban areas may be acting as large geographical and regional scale sources of PCDDs and PCDFs in air (11). In a field study of the atmospheric measurement of PCDDs and PCDFs along a northerly to southerly urban transect, Cleverly et al. provided strong evidence that urban areas are area-wide sources of dioxin, and, as such, are contributing to the general atmospheric background levels of dioxin observed in rural areas (12). Increasing air concentrations of PCDDs/PCDFs were observed along the NW–SE wind flow from rural areas through the urban environ and then back out to rural areas. A maximum air concentration corresponded to the center of the city (downtown). In downwind rural monitoring sites, PCDD/PCDF levels were elevated above the upwind background sites out at a distance of 160 km from the city center. The PCDD/PCDF congener pattern in air over the city center (see Figure S4 in the SI) is identical to the congener pattern of rural and remote sites from the NDAMN study (Figure 2), albeit, there is a difference in mean air concentrations. This indicates that fate processes likely occur quite rapidly near the sources of releases to transform PCDDs/PCDFs and

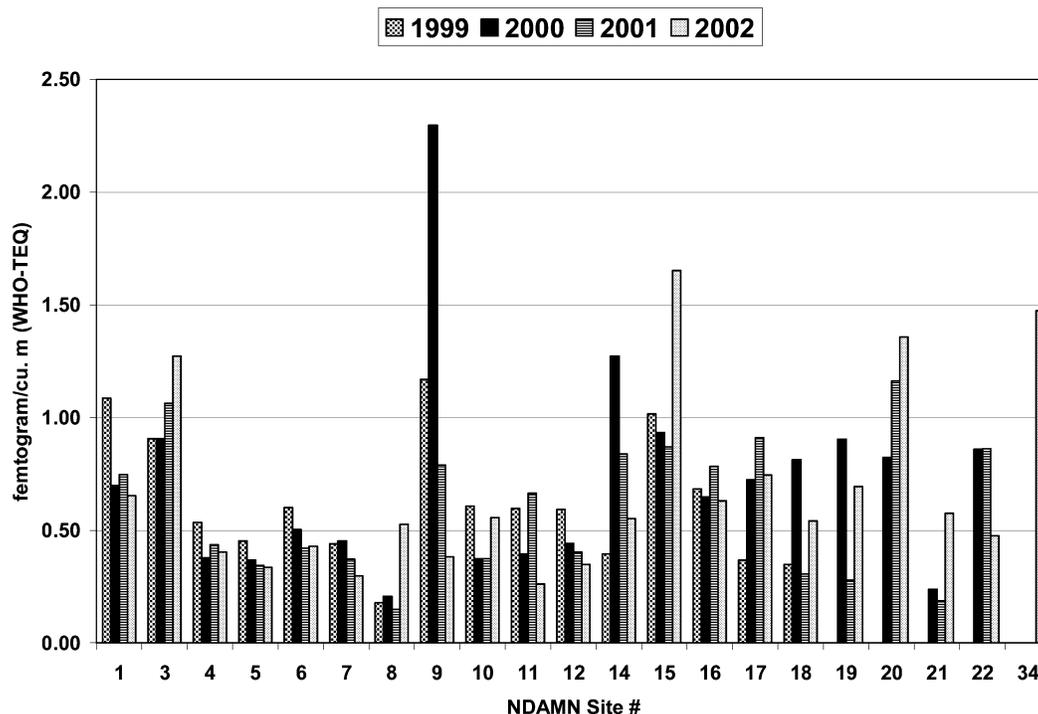


FIGURE 3. Annual mean atmospheric concentration of TEQ_{DF} (fg m⁻³) for each NDAMN site from 1999 to 2002.

produce a stable congener distributional pattern in air. It is postulated that advection and turbulent diffusion spread and move the PCDD/PCDF out from the urban source to rural and remote areas, induced by a negative concentration gradient from the urban to the rural and then out to the remote areas. Broman et al. observed this phenomena in a field study in which air was sampled for PCDDs/PCDFs along a transect to the prevailing winds from the urban center of Stockholm out to a remote area on the Swedish coast (13). Broman et al. found that the highest concentrations of PCDDs/PCDFs in air corresponded to the center of the city and systematically decreased in concentration as air moved out from the city to the rural and then to remote areas (13). Long-term measurements by Broman et al. indicated a mean I-TEQ concentration of 2.6 fg m⁻³ at the remote coastal location compared to a mean of 24 fg m⁻³ at the central city location, which agrees with observations of this study that remote areas tend to have mean air concentrations of <3 fg m⁻³ TEQ_{DF}. From these studies it is observed that the rural and remote areas are being affected by the central city at a radial distance of greater than 160 km. In a study by Baker and Hites, the regional urban and highly populated areas of the east coast of the United States were seen as elevating the background levels of PCDDs/PCDFs in the air over Bermuda, a distance > 1000 km from the United States (14). Antarctica is an ideal setting to further investigate this phenomenon, because it is a remote continent having scattered, year round, urban-like scientific communities. Under the auspices of the National Science Foundation, Lugar et al. took atmospheric measurements of PCDDs and PCDFs at the McMurdo scientific research station in Antarctica, as well as remote locations and sites upwind of the station (15). The aim of this study was to determine any air impacts resulting from the operation of an on-site refuse incinerator. They observed that detectable levels of PCDDs and PCDFs in air in Antarctica were only associated with the semi-urban operations of the McMurdo scientific research station and no PCDDs/PCDFs could be detected in the air in remote areas completely absent of human habitation. These results clearly showed that the collective human activities of the semi-urban environment were the only source of atmospheric PCDDs/PCDFs in

Antarctica. When NDAMN results for 2001 and 2002 are plotted on a map of U.S. population density for the same years (Figure 4), the relationship of proximity to the urban source and mean dioxin levels in air becomes more apparent. Areas of higher mean annual atmospheric levels of PCDDs/PCDFs appear to correspond to areas of higher population density, and, conversely, areas of low mean PCDDs/PCDFs are observed to be in areas of low population density. In consideration of all the evidence, we propose the hypothesis that urban areas are the primary sources of atmospheric PCDDs and PCDFs in rural and remote areas of the United States.

Dioxin-Like PCBs Measured in Air at Rural and Remote NDAMN Sites. Seven cp-PCB congeners were routinely measured in ambient air at the NDAMN sites. These compounds were PCB-77, PCB-105, PCB-118, PCB-126, PCB-156, PCB-157, and PCB-169. With the exception of PCB-169, all cp-PCB congeners were detected in 100% of the samples. PCB-169 was detected at a frequency of 92% in rural sites, but only 42% in remote sites. For the rural sites, there was close agreement in the mean annual air concentrations (TEQ_{PCB}) among the years 1999, 2001, and 2002 (i.e., 0.62, 0.59, and 0.7 fg m⁻³, respectively). However, as is the case with PCDDs/PCDFs there was a marked increase (i.e., ~13%) in the annual rural mean air concentration in 2000 as compared to the other sampling years. With the exception of 2000, the mean measurement of TEQ_{PCB} concentration in rural areas remained approximately constant over the sampling years. Buehler et al. (2001) also observed close agreement in annual atmospheric measurements of PCBs at two rural sites adjacent to the Great Lakes (18). This was attributed to the volatilization of PCBs to the air from the soils and surface waters in rural areas in close proximity to urban centers. Indeed, the city of Chicago and the urban megalopolis of the northeast United States have been observed to be major area sources of PCBs measured in the atmosphere to the Great Lakes region (18, 19). Thus, by this evidence, PCBs emanate out from urban areas to rural areas whereby they cycle among the atmosphere and the terrestrial and aquatic compartments.

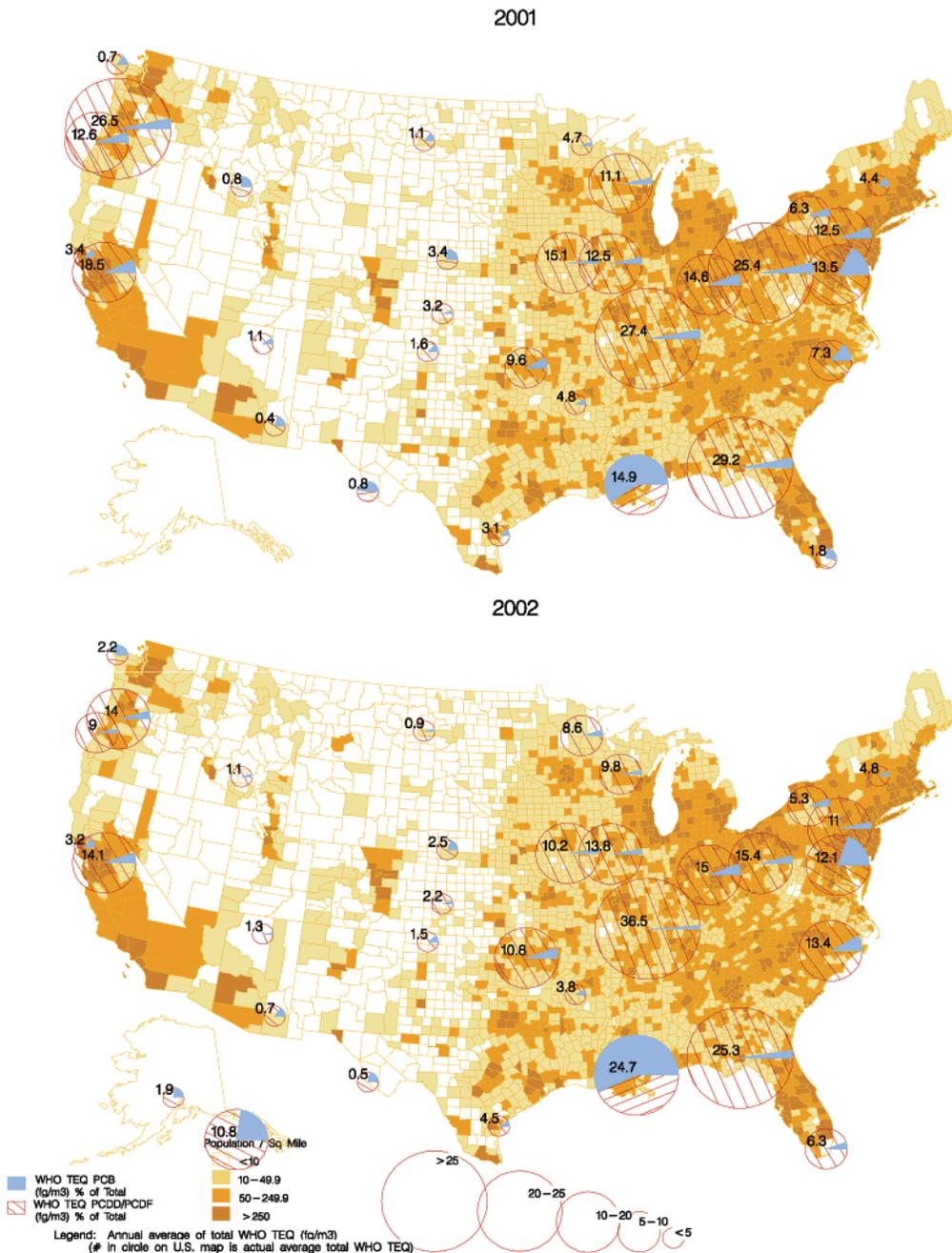


FIGURE 4. Mean annual TEQ_{DF} air concentration (fg m⁻³) at each NDAMN site compared with population density for 2001 (top) and 2002 (bottom).

The confidence intervals across the NDAMN sampling years suggest a 95% probability that mean atmospheric concentrations in rural and remote areas of the United States are within the range of 0.5–1.0 fg m⁻³ TEQ_{PCB} and 0.1–0.5 fg m⁻³ TEQ_{PCB}, respectively. The cp-PCB congener distributional pattern was relatively similar across the NDAMN sampling years at both rural and remote sites (see Figure S5 in the SI). Among the congeners measured, PCB-118 consistently had the highest concentration in air for all sampling years, followed in order by PCB-105, PCB-77, and PCB-156. Note that in the year 2000, PCBs-118, 77, and 105 significantly increased in comparison to 1999, 2001, and 2002. In terms of the contribution to the TEQ, PCB-126 represents approximately 60%, and PCB-118 accounts for approximately 12–28% of the TEQ_{PCB}. When the TEQ_{PCB} is added to the TEQ_{DF}, they represent on average only 10–15% of the total TEQ air concentration.

Seasonal Variability. Seasonal variability was able to be determined with quarterly air measurements of PCDDs, PCDFs, and cp-PCBs. The atmospheric concentrations of PCDDs and PCDFs are higher in the fall and winter as compared to spring and summer. For the PCBs, the inverse is true, namely that concentrations are higher in the spring and summer as compared to the fall and winter. Regressing the mean quarterly TEQ_{DF} air concentration at all the NDAMN rural sites against the inverse of the mean atmospheric temperature, PCDDs and PCDFs are negatively correlated with temperature (K), meaning that as atmospheric mean temperatures decrease, the concentrations of PCDD/PCDF in air increase. This correlation is statistically significant ($r^2 = 0.81$, at 0.0001 level of confidence). PCB measurements at NDAMN rural sites show a statistically significant positive and linear correlation with temperature ($r^2 = 0.56$, at 0.013 level of confidence). The behavior of PCBs is consistent with

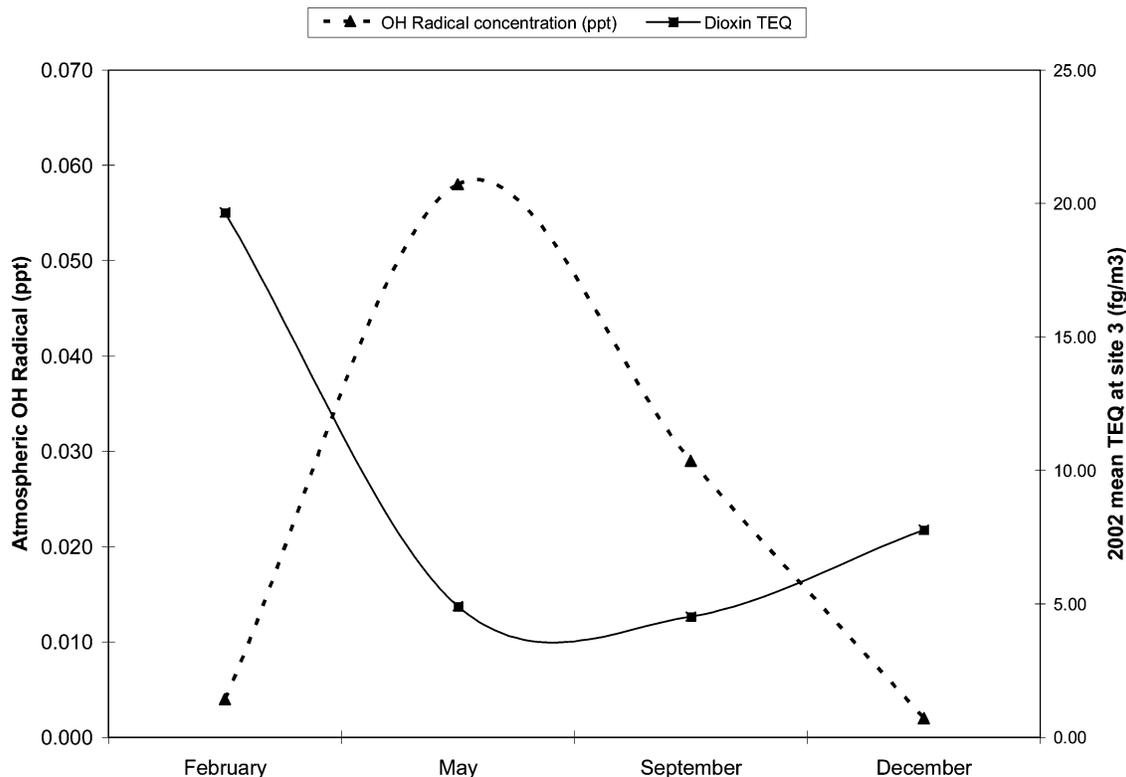


FIGURE 5. Seasonal atmospheric OH radical concentration (ppt) plotted against seasonal mean TEQ_{DF} concentration (fg m⁻³) at rural site 3.

the theory that PCBs more readily volatilize from the soil and surface water sinks into the atmosphere during the warm seasons, but the process is muted during the cooler months of fall and winter when soil and water temperatures are cold. However, the behavior of the PCDDs and PCDFs is not so easily explained. It has been proposed that the increase in PCDDs/PCDFs during the fall and winter is associated with a general increase in combustion activity related to the increased demand in home and commercial heating (7). These are widely distributed and diffusive sources. By this hypothesis, more dioxin is emitted to the atmosphere during fall and winter from diffusive heating sources combusting fossil fuels, which, in turn, causes an increase in the atmospheric concentration of PCDDs/PCDFs. Another plausible hypothesis is that the consistently observed seasonal variation may be caused by the seasonal variation of the atmospheric concentration of hydroxyl radicals that photochemically react with PCDD/PCDF. The gas-phase photochemical reaction of PCDD and PCDF having Cl₁-Cl₆ atoms with the tropospheric OH radicals has been experimentally determined to be an important atmospheric removal pathway (16, 17). At 20 °C and an average 12-h daytime global atmospheric OH radical concentration of 1 × 10⁶ molecules cm⁻³, the gas-phase rate of reaction of 2,3,7,8-TCDD with the OH radical has been estimated to range from 4.7 × 10⁻¹³ to 9 × 10⁻¹² cm³ s⁻¹, corresponding to atmospheric half-lives of hours to several days (16, 17). Modeling these reactions, Brubaker and Hites concluded that the photochemical reaction with the OH radical influences the characteristic atmospheric PCDD/PCDF congener profile by the reduction of congeners having ≤ Cl₆ atoms on the molecule, thus leaving the higher chlorinated species subject only to atmospheric particle deposition as the primary removal process (17). The ubiquitous and low-level concentration of ozone in the troposphere is sufficient to efficiently form OH radicals at wavelengths of solar radiation of ≥290 nm (20). In the northern hemisphere, the inclination of the Earth on its axis is tilting away from the Sun in fall and winter seasons. This

further dilutes the intensity of solar flux of the troposphere by increasing the angle of the travel path of solar radiation that passes through the atmospheric boundary layer. Additionally this angle increases the scattering of light by the reflective properties of dust particles and water vapor in the atmosphere. The sun appears to be lower on the horizon, and hours of daylight are decreased and the length of nighttime is increased. During this time, the photolysis of ozone to yield OH radicals in the atmosphere is significantly retarded and there is less tropospheric concentration of OH radicals available in fall and winter to photochemically react with the atmospheric PCDD/PCDF. The net effect is the appearance of a general increase in PCDD/PCDF atmospheric concentration during the fall and winter in northern latitudes when actually the photochemical atmospheric removal processes have diminished during these seasons. We have preliminarily investigated this hypothesis by plotting annual monthly mean atmospheric OH radical concentrations measured by Hakola et al. (21) against seasonal measurements of dioxin at rural NDAMN Site 3 (Figure 5). This plot implies an inverse relationship, i.e., lowest dioxin air concentrations during the summer months when the OH radical is at its peak, and highest dioxin air concentrations during the winter when the OH radical is minimal. The seasonal fluctuation in dioxin appears to correspond to the fluctuation in atmospheric OH. This hypothesis is in need of further testing before the role of the OH radical can be definitively stated as the primary cause of the seasonal variation of dioxin.

NDAMN has been the most comprehensive and extensive air monitoring program for dioxin ever conducted in North America. NDAMN has provided valuable information on the nature and extent of PCDDs, PCDFs, and coplanar PCBs in ambient air of rural and remote areas of the United States that has aided scientific understanding of the sources, fate, time-trends, and distribution of these compounds. Dioxin is present in extremely low concentrations (i.e., parts per quadrillion for PCDDs and PCDFs, and parts per trillion for

PCBs on a volume basis). The assessment and analysis of data from 1999 to 2002 suggests that there has been little or no change in the amount of these compounds present in ambient air in areas of the country that are distant from known anthropogenic source activities. Furthermore, data collected at over 34 geographically dispersed sites supports the hypothesis that urban areas are the primary sources of PCDDs, PCDFs, and PCBs present in ambient air over agricultural and remote regions of the United States. The uniform pattern of PCDD and PCDF congeners present in ambient air in cities, rural areas, and remote areas is forensic evidence that further associates the collective human activities of the urban environment with measurable contamination of dioxin in rural and remote areas hundreds of km away. In this context, cities can be viewed as regional sources. NDAMN data strongly suggest that mean contemporary background concentrations of TEQ_{DF} in rural areas of the United States are within a range of 6–15 fg m⁻³, and the mean background concentrations in ambient air in remote areas ranges from 0.1 to 3 fg m⁻³. Measurements of coplanar PCBs suggest that the mean background levels of TEQ_{PCB} in ambient air ranges from 0.5 to 0.9 fg m³, and 0.06 to 0.5 fg m³ in rural and remote areas of the United States, respectively. The most dominant congener is PCB-118, but PCB-126 accounts for most of the TEQ. In rural areas there was no statistically significant year to year variation in mean TEQ_{PCB} air concentrations. Remote areas did show variation in mean TEQ_{PCB} air concentrations, but there was no discernible time-trend.

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Supporting Information Available

Additional analytical details, data tables, and figures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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