URBAN AIR TRANSECT STUDY TO INVESTIGATE URBAN AREAS AS SOURCES OF PCDDs AND PCDFs TO THE ENVIRONMENT*

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Introduction

An urban air transect study was undertaken in Oklahoma City, Oklahoma to investigate whether urban areas represent sources of dioxin-like compounds to the rural environment. This study proposed the hypothesis that the collective human activities characteristic of cities cause urban areas to behave as sources of dioxin-like compounds, and, as such, contribute to the general atmospheric background levels of dioxin-like compounds observed in rural areas. To test this hypothesis, a study was designed and field sampling campaigns were conducted in December 2000 and December 2001. Eight samplers were placed in urban, rural, and background locations and the collected data were used to develop profiles of the ambient air concentrations of dioxin-like compounds as air masses traveled from upwind of Oklahoma City through the center of the urban area, then downwind of the area. Oklahoma City was selected as the site of the study because it has a well-defined city center; well-defined uniform, consistent and predictable wind directions by season; relatively flat terrain; -and a population of over 100,000. In addition, Oklahoma City's economy is service oriented and generally lacks an industrial base. Well-defined transportation corridors connect the outlying areas to the central city, and automobiles are the primary mode of transportation.

Methods and Materials

Ambient air sampling was carried out from December 1 through December 18, 2000, and from December 3 through December 20, 2001. Eight samplers were used during each sampling moment and were placed at downtown urban, rural, and background locations (including one duplicate in the downtown area). The air sampling stations were located along a transect having a northwest/southeast angle along a 340° to 160° line bisecting the center of the city. This placement was to account for the prevailing wind flow patterns in December. Sites were chosen on the basis that they were likely to maintain well-defined upwind/downwind characteristics to best characterize the concentration profile of dioxin-like compounds as parcels of air move from upwind, through the city, and downwind to the rural area. Four ambient air samplers were located within the urban area. Two of these samplers were collocated at the urban center, one sampler was placed to the north of the urban center, and one sampler was placed to the south of the urban center. The exact locations are presented in Figure 1 and are as follows: Downtown (Stations 1 and 2); Urban South (Station 3); and Urban North (Station 4). Four monitoring locations were designated as rural and background: one site to the north (Station 5) of the urban location, one site to the south (Station 8), and two sites (Stations 6 and 7) located outside the prevailing winds to and from the city. The north and south sites were roughly equidistant from the center of Oklahoma City and were located so that they were not impacted by the major roads and railroads, but would catch nearly one 100 percent of the wind to and from the city. Two rural background sites were

[**]incorporated into the study to be the controls against which the other stations would be compared. These sites met the design requirement of being 24 to 36 km outside the urban area. Because of the changing wind patterns in Oklahoma City, a site located outside the prevailing wind pattern and away from any large potential sources such as a city was thought to better represent the background levels that would be observed at an upwind rural site. Two monitoring sites were placed in this background area to obtain a measure of variability in concentration levels. The samplers were located in areas west/northwest of the urban area that should not be influenced by urban air. These control sites are indicated as Stations 6 and 7 on Figure 1.

USEPA Method TO-9A[1] was employed as a general guide for field sampling procedures in this study. The analytes of interest in this study were the polychlorinated dibenzo-p-dioxins (PCDDs); polychlorinated dibenzofurans (PCDFs) substituted in the 2,3,7, and 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). Each station consisted of a PS-1 polyurethane foam (PUF) sampler. The sampling medium has two components to collect and retain both the particle-bound and gaseous-phase PCDDs, PCDFs and PCBs, i.e., a quartz fiber filter (QFF) to collect and retain atmospheric particles (particles ≥0.1 microns diameter), and a PUF vapor trap to collect and retain the gaseous phase of the contaminant. Each sampler was set to collect approximately 350 m^3 of air during every 24-hours of operation. Over an 18-day period 5,000 to 7000 m^3 of air were sampled at each location. Actual sample volumes were determined by multiplying the length of time each sampler was operational by the average recorded flow rate. The field operators logged all routine field operating and maintenance checks on the PS-1 samplers onto field test data forms. Critical log-in items included the date/time of operator's visit, temperature, barometric pressure, Magnehelic flow reading, and elapsed time. These forms are contained in the study file. Approximately every three days (for urban sites) and every week (for rural/background sites), sample filters were changed. This procedure was implemented to minimize restriction of air flow through the filter as a result of particle build-up. The sampler was only off line for several minutes when the filter was changed. All QFFs obtained from a specific site were grouped and stored in a single container. PUFs and QFFs were recovered and stored in a freezer (< 4^0 C). Sampling information was verified and chain-of-custody forms were prepared. All samples and blanks were packed with bubble wrap and placed in a cooler containing frozen blue ice. A single shipment with next-day delivery was made after the sampling period. The samples, blanks, and chain-of-custody forms were shipped to USEPA's Environmental Chemistry Laboratory for extraction, clean-up and analysis with high resolution gas chromatography coupled with high resolution mass spectrometry in accordance with a modification of EPA Method 1613[2]. The results of the PCDD/PCDF air measurements are presented in this paper. PCBs will be reported on a future date.

Results and Discussion

For the PCDDs and PCDFs, the pattern observed was that the background sites had the lowest average concentrations. The average concentrations of the rural upwind/downwind area sites were higher than the background sites, and generally lower than the urban north/south sites. The highest average concentrations were observed at the downtown sites. Toxic equivalent (TEQ) concentrations for the PCDDs and PCDFs also followed the same trend, i.e. increasing concentrations from the background to the downtown sites. Figure 2 represents the topology of

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

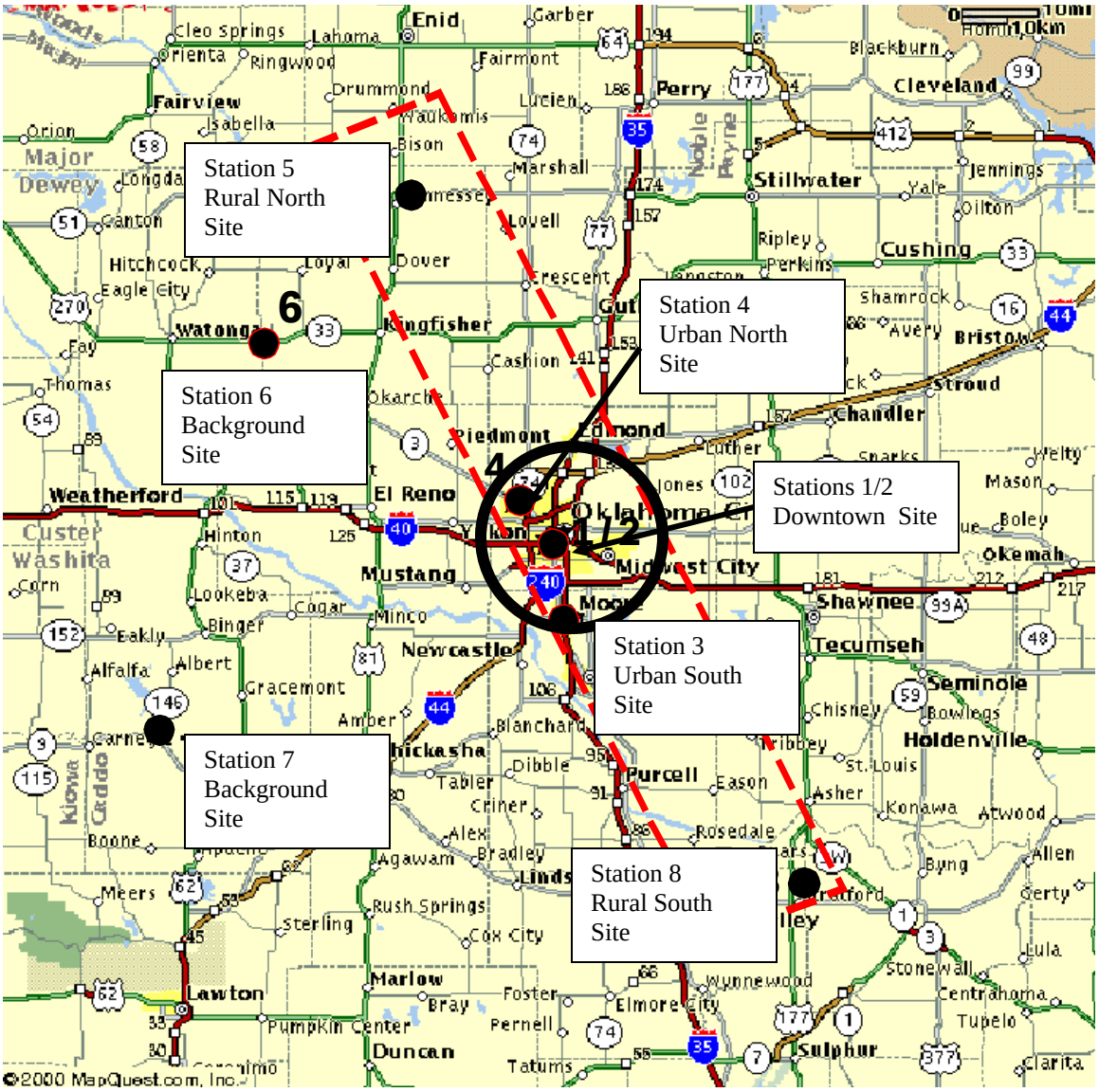
the progression of PCDD/PCDF air concentration (in units of femtogram (fg) WHO-TEQ/m^3). The following results were observed:

1. There was good agreement between the overall mean air concentrations of sampling moments 1 and 2 (14.9 and 14.7 fg WHO -TEQ /m^3, respectively), indicating good reproducibility of study results.
2. The mean air concentrations of the downtown Oklahoma City sampling site for sampling moments 1 and 2 was approximately 21 fg WHO -TEQ /m^3. This was about two-fold higher than the background (control) sampling stations (Stations 6 and 7) located outside the influence of Oklahoma City. Mean background for this study was approximately 10 fg WHO-TEQ /m^3.
3. The observed PCDD/PCDF air concentrations were strongly influenced by the central core of Oklahoma City. Aligned along the direction of prevailing winds the sampling stations indicated an increase in air concentrations of PCDD/PCDF as parcels of air moved south from the rural areas to the urban environment with a maximum air concentration corresponding to the center of the city (downtown). Then there was an observed decrease in PCDD/PCDF air concentrations as air parcels moved south of the city center and back out into the rural areas.
4. This study suggests that the collective human activities characteristic of typical urban areas are sources of PCDDs and PCDFs in the ambient air. The lack of any identifiable stationary sources of these contaminants within the study area suggests that vehicular traffic or some other area-wide source (e.g. home and commercial heating) may be the main source, although this would have to be verified with further research. The human activities of Oklahoma City proper appear to add to ambient air concentrations of PCDDs/PCDFs within a radius of 50 km north and south of the downtown area, and along the prevailing wind directions.
5. The result of this study supports the hypothesis that urban areas behave as area-wide sources of PCDDs and PCDFs, and are contributing to measurable levels observed in rural areas.

References

1. USEPA (1997). Compendium Method TO9a. EPA/625/R-96/010b.
2. USEPA (1995). EPA 821-B-94-005.

Figure 1. Location of Sampling Stations - Oklahoma City



Oklahoma City

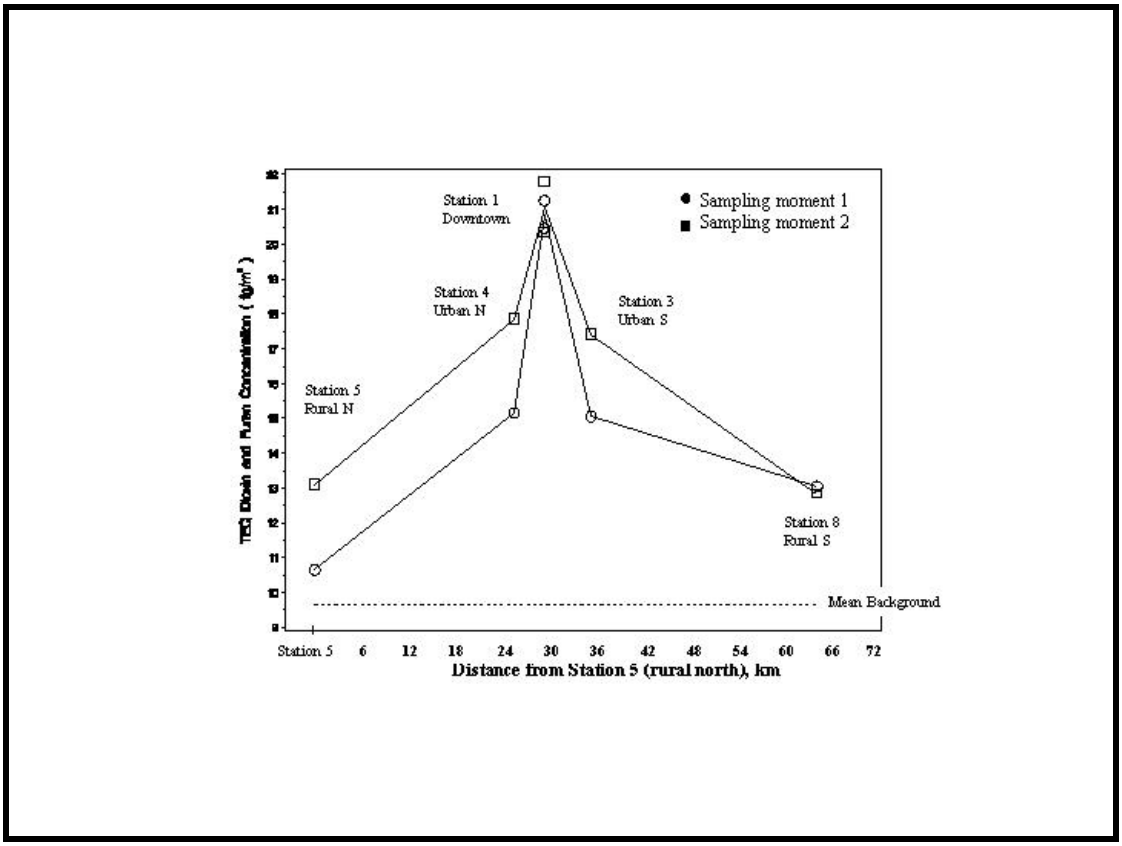


Figure 2. Progression of PCDD/PCDF Air Concentration from Rural North (Station 5) through Downtown Oklahoma City (Station 1), to Rural South (Station 8)