

2,3,7,8-CHLORINE SUBSTITUTED DIBENZO-*para*-DIOXINS AND DIBENZOFURANS IN TREE BARK FROM A HEAVILY INDUSTRIALIZED AREA IN SAUGET, ILLINOIS, USA.

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Introduction

Tree bark is known to be a sensitive passive accumulator and indicator of atmospheric organic contaminant conditions near the site where the tree is growing and during the lifetime of the tree¹. It has been used as an indicator of historic atmospheric polychlorinated biphenyl (PCBs) patterns and exposures at known contaminated sites and in remote areas distant from modern industrial activity². It can be an indicator of organic contaminant spread through the atmosphere or of soil contaminant conditions where the tree is growing, which could result either from atmospheric deposition or disposal of contaminated material on the soil near the site of the tree. Our objective is to identify the qualitative and quantitative spatial profile of 2,3,7,8-Cl substituted dibenzo-*para*-dioxins (CDD) and dibenzofurans (CDF) in a heavily industrialized area in and around Sauget, IL which includes nearby areas in E. St. Louis and Cahokia, IL USA. A complex of 2 chemical plants, one of which, the W. G. Krummrich (WGK) facility, historically manufactured PCBs, and 2 metal factories located there form the largest single source of air pollution in the St. Louis Metropolitan Statistical Area (MSA), accounting for 24.2% of exposure risk from regulated air pollutants in the region from 1988 – 2000³. The WGK site has a long history of chlorine release even after PCB production ended: Beginning in 1988, this chemical plant reported air emissions of chlorine that over 13 years totaled 521 mt (not including HCl release, which was another 3000 mt at the time), comprising 82.1% of the WGK facility air pollution exposure risk. During the final 5 years of PCB production (1972-1977), the PCB plant at WGK also operated an incinerator to burn PCBs returned by customers and PCB production waste (Montars), all of which was heavily chlorinated and was certainly a source of chlorine emission to the atmosphere. We assume that since CDD and CDF form from heating or incinerating organic materials in the presence of chlorine⁴, that this facility has been the primary contributor to PCDDs and PCDFs found in the area, probably for many years.

Materials and methods

In February 2009, we collected 27 tree bark samples at places around the Sauget chemicals/metals complex up to a distance of 4.2 km from the central area within the WGK site. Samples were collected by chiseling bark into pre-cleaned jars from breast height on the tree. The jars were sealed with teflon-lined lids, and stored refrigerated to prevent deterioration. Two thirds of the samples were collected in residential areas downwind to the east and north from the chemical/metals complex. Six other samples were collected along an intermittent stream that drains this complex, 2 were collected at Site P (one of the PCB plant waste sites used from 1973 – 1984) and one sample was collected near the Mississippi River in St. Louis.

Tree bark samples (~25g) were analyzed for seven 2,3,7,8-Cl substituted tetra through octaCDD, and 10 CDF congeners based on USEPA method 1613B using Soxhlet extraction in 80:20 toluene : acetone, cleanup by elution through silica, carbon and alumina, and analysis by high-resolution GC-MS. Lipids were analyzed on a small aliquot of sample using methods noted elsewhere.¹ Results are expressed as pg g⁻¹ lipid.

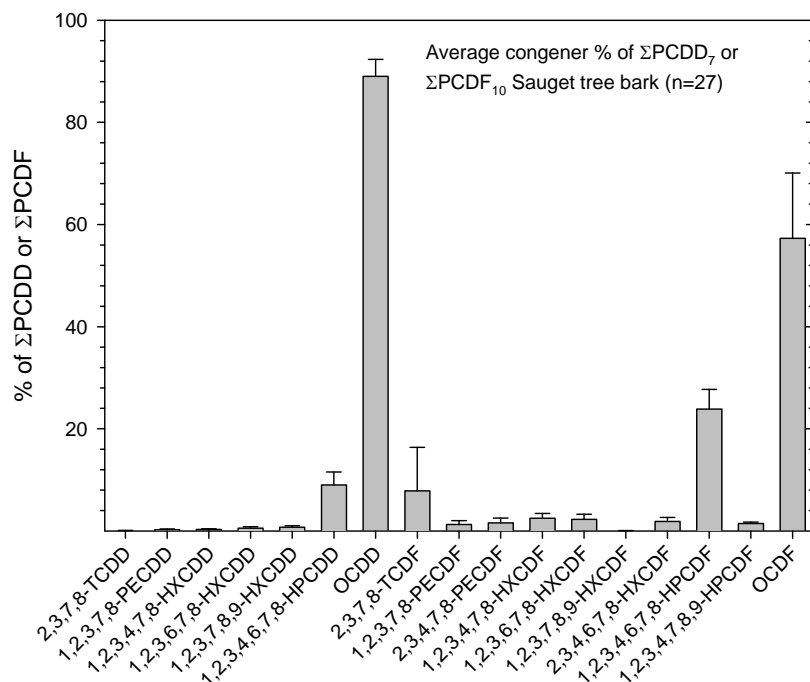


Figure 1. The average % of total contributed by each congener to the class of compounds for all 27 samples. All congener profiles were similar, showing that all sites were affected by the same types of PCDD and PCDF sources, but at varying concentrations. The pattern dominated by OCDD is considered a “sink” pattern of the most persistent CDDs and CDFs. It is also characteristic of a CDD pattern resulting from incineration of PCBs or waste with a high % of chlorine.

Results and discussion:

Average congener profiles, as % of total PCDD or PCDF, are shown in Figure 1. The profiles for all samples were similar: all PCDD were dominated by octaCDD (OCDD) (average 89% of all CDD) and all PCDF by OCDF (average 57% of all CDF). This congener profile, particularly for CDDs, is considered to be a “sink” pattern⁵ which shows an enrichment in hexa through OCDD congeners in contrast to a “source” pattern which is dominated by furans, particularly tetraCDF congeners. A sink pattern represents the remnant of historic sources in the area with the most persistent particle-associated congeners dominating the profile. Additionally, this profile may result, at least in part, from incineration of PCBs which is known to produce a PCDD profile dominated by OCDD in crude exhaust containing mostly particles⁶. Combustion of some PCBs is also known to produce CDFs.⁷ Therefore, this profile is likely to be at least a partial remnant of historic PCB incineration. The fact that the profiles for all 27 samples are similar for trees ranging in age from 8 to 92 years suggests that the profile in atmospheric particles has changed little over time, and that the PCDD and PCDF appearing in these bark samples are from the atmospheric particle phase.⁴ A high-OCDD pattern like this one also results from heating chlorophenols⁸ but there is no evidence of this process occurring in the Sauguet area.

The PCDD concentrations (Table 1) range from 2214 to 71821 pg g⁻¹ lipid and PCDF from 355 to 13707 pg g⁻¹ lipid in samples 19 and 24, respectively. The geographic distribution of OCDD and OCDF results are shown as standard deviations relative to the respective means in Figures 2 & 3. Three of the least concentrated samples for OCDD and OCDF (15, 18, 19) were located to the south. Two other samples there (7 & 17) have concentrations slightly above the mean value (16). Among samples collected elsewhere, the highest samples for PCDD and PCDF are all downwind from the chemical/metals complex, with the exception of Site P.

Considering the diversity of values relative to the mean in areas downwind from the plant, it is likely that the highest concentrated trees are affected by contaminated soil at the site where they are growing, again suggesting that trees are sensitive indicators of conditions nearby. This is particularly relevant to samples 10, 11 and 12 which were collected very near to each other. Samples 10 and 11 were taken from trees growing in wooded

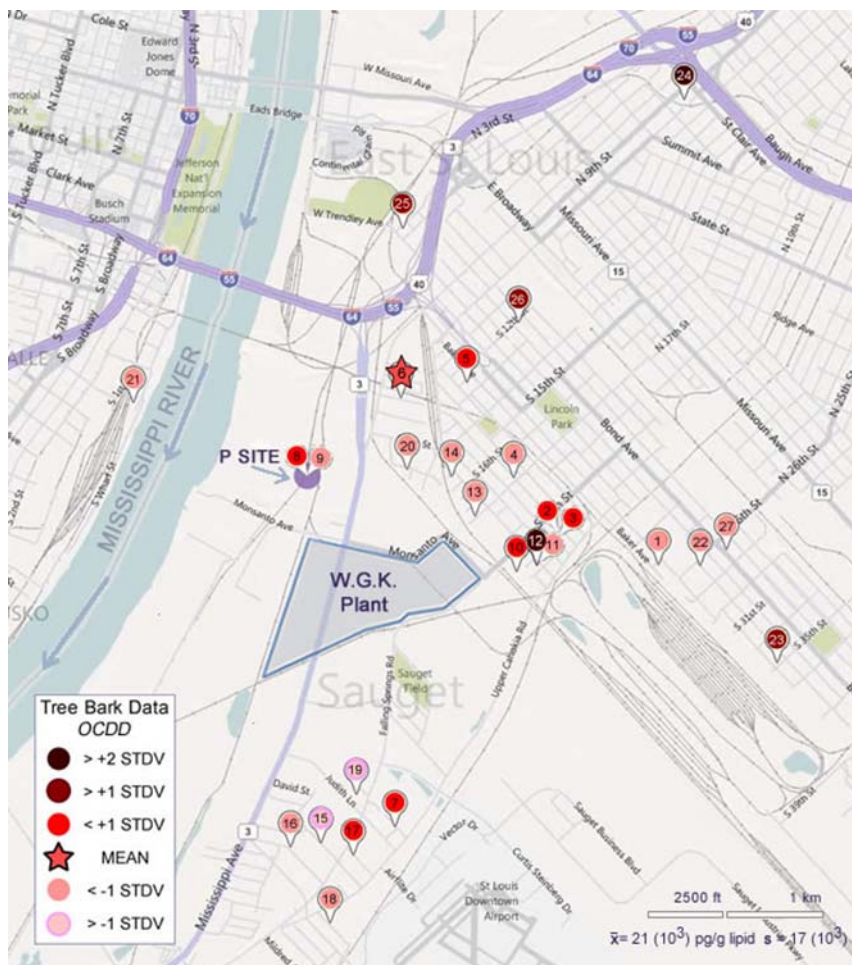


Figure 2. Map of OCDD range by standard deviation (SD) relative to the mean value (close to the value of sample #6, shown as a star, = 23245 pg g⁻¹ lipid). The SD = 17056. OCDD was an average of 89% of all 7 2,3,7,8 chlorine substituted CDDs in all samples. The maximum concentration was in sample #12 an 8 year old tree located a short distance to the east from the WGK site. Second highest was sample 24 (located in the NE corner of the map), 19 years old, was 99% as concentrated as #12. The third most concentrated sample, #26 (38 years old), was 70% as concentrated as #12, was collected from the Lincoln High School site. The WGK site is the largest part of the 4-industry complex accounting for the largest single contribution to regulated air pollutants in the St. Louis area.

Table 1. PCDD and PCDF concentrations in tree bark near Sauget, IL, USA, pg g⁻¹ lipid

Sample	ΣPCDD	ΣPCDF	Sample	ΣPCDD	ΣPCDF	Sample	ΣPCDD	ΣPCDF
1	5067	1024	10	27003	1690	19	2214	355
2	27182	2115	11	15731	1510	20	13156	1364
3	24895	4656	12	69486	8113	21	13262	697
4	11191	936	13	5582	563	22	9353	1124
5	29287	3247	14	5517	551	23	43064	3796
6	23245	1967	15	3547	404	24	71821	13707
7	24775	1617	16	9769	2176	25	46032	4181
8	41615	4610	17	24469	1912	26	49655	4518
9	22361	3161	18	4721	439	27	7805	923

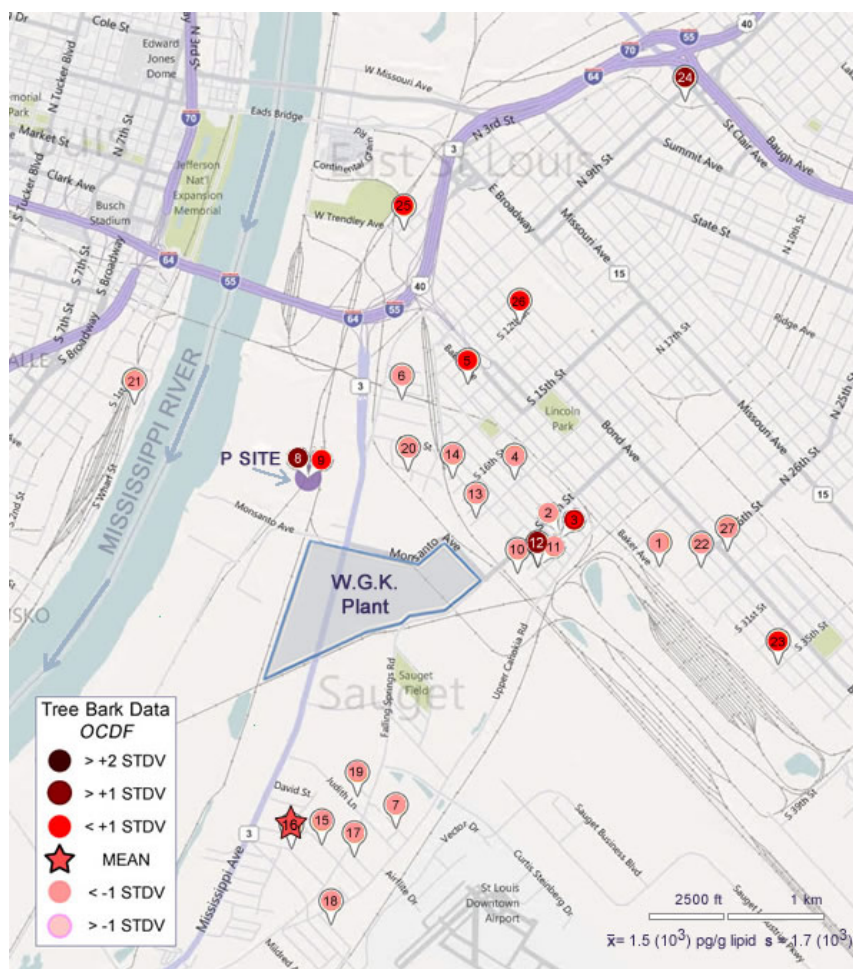


Figure 3. Map of OCDF range by standard deviation (SD) relative to the mean value (close to the value of sample #16, shown as a star, = 1631 pg g⁻¹ lipid). The SD = 1701. OCDF was an average of 57% of all 17 2,3,7,8 chlorine-substituted CDFs in all samples. The OCDF maximum concentration was in sample #24 a 19-year old tree (in the NE corner of the map). Second highest was sample #12, 8 years old, was 65% as concentrated as #24, located a short distance to the east from the WGK site. The third most concentrated sample, #8 (8 years old), was 43% as concentrated as #24, was collected from Site P, a landfill used by the WGK plant from 1973 - 1984. OCDF values are much lower and less variable than OCDD.

areas, while sample 12, which happens to have the highest OCDD concentration and is also the youngest tree sampled (age 8), was collected from a yard where soil had been disturbed by grading or perhaps by being transported from elsewhere. The same applied to sample 24 (age 19) growing in what appeared to be a park.

In comparison to other studies, the Sauget area concentrations are generally higher. The minimum OCDD seen here (1899 pg g⁻¹ lipid, sample 19) is 27% higher than the average at an industrial site in China.⁹ Another site in Illinois near Chicago, 437 km to the NE from Sauget, showed a sample with twice as much OCDD as sample 24 in a congener pattern also dominated by OCDD.⁵ However, Sauget samples are more concentrated than most other tree bark sampling sites in North America.⁵

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