A Study on the Photochemical Transformation of Particle-Borne Tetrachloro-Dibenzo-p-Dioxins

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Abstract

The phototransformation of particle-borne tetrachloro-dibenzo-p-dioxins (TCDDs) was studied with an experimental setup consisting of photoreactor, particle generator, differential mobility analyzer (DMA), condensation nuclei counter (CNC), and an online carbon trap. The residual analytes and photoproducts were desorbed from the trap and analyzed with a gas chromatography - mass spectrometer (GC/MS). The approach permitted deposition and irradiation of selected TCDDs at known concentrations on aerosols with a narrow size distribution. The particle borne TCDDs were irradiated at 313nm for varied time periods. The residual contaminant and phototransformation products were collected on the carbon impregnated filter traps and analyzed with a GC/MS. The correlation between the phototransformation rate and the number and position of chlorine substitution were monitored. The results showed that the aerosol bound TCDDs undergo a preferential chlorine loss at the peri positions. The phototransformation of laterally substituted congeners occurs at a significantly slower rate than the peri substituted ones. The reductive dechlorination was evidenced through the formation of products with less chlorine substitution. The phototransformation rates of aerosol bound contaminants were also dependent on the size of aerosols.

Introduction

Persistent chlorinated aromatics once released into the atmosphere are dispersed through atmospheric transport and subsequent deposition. This mode of transportation has been shown to be an important pathway for presence of these chemicals even in the remote oceanic and arctic regions.^{1,2} It has been estimated that between 60-90% of PCB burden in the Great Lakes region is a result of atmospheric transport and subsequent deposition³. It has also been reported that approximately 20-60% of TCDDs present in the urban environment is of atmospheric origin⁴. From their assessment of the atmospheric transport and deposition of PCDDs and PCDFs, Hites and Harless have suggested that transformations occurring during the atmospheric transport are responsible for observed congener profiles of PCDDs and PCDFs in soils⁵.

Air borne particles, ranging from 1nm molecular clusters to 0.1mm dust particles, play a key role in the atmospheric transport of dioxin-like compounds. The studies on particle-bound PCDDs and PCDFs by Towara et al. have shown that particles with aerodynamic diameters of less than 1.35 um accounted for 85-90 percent of the total mass of PCDDs/PCDFs found in all particles.⁶ These particles exhibit long residence time in the atmosphere and are effective in transportation of particle bound organics. In a similar distribution study of bound semivolatile organics in the atmosphere, Poster et al. has also shown that PAHs are most often associated with particles less than 1.4 um in both the rural and urban environments.⁷

To minimize the perceived ill health effects of small size air-borne particles, the US EPA has

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recently proposed new particulate standards for ambient air quality, which lowered size of particulate matters to 2.5 um. It is likely that the ill effects of the particles on the human health may not be related to particles themselves but most likely to the toxicity of the materials that are absorbed on the particles. Since contaminants such as polychlorinated aromatics undergo light induced transformation and can affect the toxicity of the contaminants, photodegradation of particle bound PCDDs/ PCDFs can have important consequences.^{8,9} However, only limited data is available on phototransformation of particle bound PCDDs/PCDFs.¹⁰ The present study was initiated to examine phototransformation of particle borne TCDDs under controlled laboratory conditions. The study was aimed at determining the effect of particle size on the phototransformation pathways and rates.

Experimental

An apparatus consisting of serial arrangement of a hydrocarbon burner, a differential mobility analyzer, a fused silica photoreactor and a carbon impregnated glass fiber trap was used for the phototransformation experiments. A simplified schematic of the apparatus is shown in Figure 1. The burner was of a low NO_x -lean premixed design and mounted in stainless steel enclosure. The burner was operated with aviation fuel to produce polydispersed carbonaceous aerosols. The enclosure permitted operation of burner under standard atmospheric conditions or simulated atmospheric conditions to produce aerosols with varied size distributions. The combustion aerosols were swept out of the chamber with make-up airflow and passed through a cold trap to remove moisture. The density of polydispersed aerosol was varied by changing the volume flow rate of the make-up gas.



Figure 1. Schematic of the photoreactor system

The particles were then passed through a bipolar diffusion charger and ionized prior to their introduction into DMA. The DMA used in the present study was fabricated at the Cloud and Aerosol Sciences Laboratory (CASL) - University of Missouri. The device was based on a pin-cup configuration, in which the outer cylinder (cup) was kept at ground potential while the concentric inner rod (pin) was held at negative potentials ranging 2-10K volt. The particle laden air stream was introduced into the annulus region at the top of the analyzer along with a particle free air stream. Particles with a much narrower size distribution were withdrawn through an outlet at the bottom of the

ORGANOHALOGEN COMPOUNDS 422 Vol. 41 (1999) analyzer. The size-fractionated aerosols were either introduced into the photo-irradiation chamber or a CNC to determine the particle number density.

The photo-irradiation system consisted of a one-liter quartz reactor, which was covered with a polished aluminum foil and placed in a thermostated oven. A xenon arc lamp was used as the source of UV radiation. The reactor was filled with particle free air or particle laden air and brought to 270 °C. The TCDDs of interest were introduced into the reactor and the temperature of the reactor was brought to ambient. The particles in the reactor was then irradiated for selected time intervals. The residual solute and photoproducts were swept out of the reactor and trapped on the carbon impregnated filter, which was fortified with a known amount of ¹³C labeled TCDD analog. The trapped analyte and photoproducts were eluted with benzene.

Analysis of TCDDs and photodechlorination products were carried out with a capillary gas chromatograph interfaced to a quadrupole mass spectrometer. Chromatographic separations were achieved with a 15 m x 0.25 mm (i.d) fused silica capillary column coated with polymethyl siloxane stationary phase. Helium was used as a carrier gas. The gas chromatographic oven temperature was initially kept at 120 °C for 1 min. and ramped to 280 °C at 10 °C/min. The mass spectrometer was operated in the selected ion mode (SIM), and two ions were monitored for each of TCDD congener. The abundance of two ions for corresponding ¹³C labeled TCDD analog was also monitored.

Results and Discussion

Adsorption of TCDD on Sub-Micron Particles: The average particle density yielded by the burner with the aviation kerosene as fuel under lean conditions was found to be 1.5- 3.0×10^6 particles per cm⁻³. The size of majority of these carbonaceous particle were in the 40-90 nm range. The results of TCDD adsorption in the presence and absence of particles showed that a significant portion of the TCDD was intercepted by the particles at near ambient temperatures. Approximately, 45% of the TCDD introduced into the reactor was recovered from the chamber in the presence of the particles at the ambient temperature. By contrast only 5% of the analyte was recovered from the reactor in the absence of particles. These results, though somewhat surprising, can be attributed to the high thermodynamic motion of sub-micron particles and the high collision frequency of the particles and vapor molecules, consequently, resulting in a very large dynamic surface area when the chamber was cooled down.

<u>Phototransformation of Particle-Bound TCDD</u>: The phototransformation 1,2,3,4-TCDD and 2,3,7,8-TCDD under broad band UV radiation was examined in the presence of particles. The first order transformation was observed and shown in Figure 2. It was evident that 1,2,3,4-TCDD transformation occurs at a faster rate than the transformation of 2,3,7,8-TCDD. The question needed to be clarified for the above results is that if the loss of TCDDs in particulate phase was really resulted from the photodegradation. The transformation can result from the fact that in our photoreactor setup only a small portion of the vessel surface could be irradiated and in the absence of particles only TCDD adsorbed on this portion of the vessel surface was degraded.

A comparison of degradation rates of particle-bound TCDDs and the TCDDs in the gas phase which were carried out with the same photoirradiation setup, revealed that degradation of particle

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Figure 2. Phototransformation of particle-bound TCDD congeners

bound TCDD takes place at a slower rate than in the gas phase. However, photodegradation does take place and leads to neutral photoproducts which appeared at m/z 286 and 288 and indicated the formation of trichloro-dioxin (TriCDD). The retention time of the product matched that of 1,2,3-TriCDD and the peak was also confirmed with the co-chromatography. The appearance of this product indicates a preferential loss of chlorine from the peri position.

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