

**Atmospheric Deposition of Organic contaminants  
to Galveston Bay, Texas**

## **Junesoo Park**

Geochemical and Environmental Research Group  
College of Geosciences  
Texas A&M University  
833 Graham Road  
College Station, Texas 77845  
409-862-2323, EXT 135  
jsp0724@unix.tamu.edu

### Education

- Ph.D. Candidate, Texas A&M University, College Station, Texas, USA, 1995-Present (Oceanography)
- M.S. Texas A&M University, College Station, Texas, USA, 1995 (Oceanography)
- B.S. Chonnam National University, Korea, 1991 (Oceanography)

### Experience

- 1996-Present Research Assistant and Graduate Student, Geochemical and Environmental Research Group, Texas A&M University, College Station, Texas
- 1992-1995 Research Assistant and Graduate Student, Trace Element Research Laboratory, Oceanography, Texas A&M University, College Station, Texas
- 1987-1988 Military Service, Korean Army, Korea

## **Atmospheric Deposition of Polycyclic Aromatic Hydrocarbons (PAHs), Polychlorinated Biphenyls (PCBs), and Pesticides to Galveston Bay**

Junesoo Park  
Terry L. Wade  
Steve Sweet

Geochemical and Environmental Research Group  
College of Geoscience, Texas A&M University  
College Station, Texas 77845

The atmosphere plays an important role in the transport, deposition, and cycling of anthropogenic semi-volatile organic compounds, such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and pesticides. Thus atmospheric deposition may be a significant source of these pollutants to surface waters, especially coastal waters downwind of urban and industrialized areas (Leister & Baker, 1994; Golomb et al., 1997). The atmosphere is also a source of those anthropogenic organic contaminants to large lakes (Eisenreich et al., 1981), the remote ocean (Duce et al., 1991), and the Arctic (Norstrom et al., 1988). Due to chemical/microbiological stability, low water solubility, and lipophilic, PAHs, PCBs, and pesticides are important in terms of their global cycling in the atmosphere (Duce et al., 1991) and their accumulation in both the aquatic and terrestrial food webs (Harding et al., 1997). Since many commercial fisheries are in estuaries, the atmospheric loadings of persistent contaminants to these areas are also of concern.

In order to fulfill the mandates of the Great Waters Program and the Clean Air Act Amendments of 1990 (112m), the US EPA initiated monitoring research in important and representative water bodies, including coastal waters. As part of this program the Texas Regional Integrated Atmospheric Deposition Study (TRIADS) was established with a sampling site located in Seabrook, Texas, in order to monitor atmospheric deposition of contaminants to Galveston Bay (Figure 1). Monitoring at the TRIADS site located at Seabrook (at an existing State of Texas, TNRCC site) started on February 2, 1995 and was in continuous operation until August 6, 1996. Rain samples were collected with a "Baker" wet deposition sampler that collects the rain falling into a 1m<sup>2</sup> surface area. The rain was then gravity-filtered through a glass wool plug and a glass fiber filter that remove particles and then a column containing XAD-2 resin that collects the dissolved organic contaminants. The contaminants on the XAD-2 resin are operationally defined as dissolved, while the contaminants on the glass wool/filter are operationally defined as particulate. The organic air samples were collected by pulling air through a sampling train consisting of two filters and a large and a small polyurethane foam plug. PAHs were analyzed by GC-MS, and PCBs and pesticides by GC-ECD (Figure 2). When concentrations of some PAH compounds, especially on air filters, were very low, the levels of PAH compounds in the matrix blanks such as laboratory and field blanks became significant. Thus the data was carefully analyzed relative to the matrix blanks.

The total PAH concentration in the vapor phase (the sum of large and small PUFs) ranged from

3.29 to 160 ng/m<sup>3</sup> with the average of 52 ng/m<sup>3</sup>, while in the particulate phase (the sum of initial filter and backup filter) from 0.3 to 4.96 ng/m<sup>3</sup> with mean concentrations of 0.93 ng/m<sup>3</sup>. Particulate PAHs did not contribute greatly to the total PAH concentrations in the air. Thus, total PAH concentration (the sum of particulate and vapor PAHs) in air during sampling period ranged from 4.37 to 161 ng/m<sup>3</sup> with average concentration of 53 ng/m<sup>3</sup>. The total concentrations of PAHs detected on the glass wool/filter and XAD-2 resin ranged from 5.5 to 161 ng/L and 44 to 247 ng/L, respectively. The sum of the particulate and dissolved PAHs in rain ranged from 50 to 312 ng/L with the volume weighted mean concentration of 108 ng/L (Table 1). In this study, most PAHs in the rain were found on the XAD-2 resin (dissolved phase).

In this study area, PAH concentrations in the air and rain were unpredictable. No strong relationship between particulate and vapor PAHs ( $R^2 = 0.06$ ) and very weak relationships between particulate and dissolved PAHs ( $R^2 = 0.27$ ) and between rain volume and PAH concentrations ( $R^2 = 0.34$ ) were found in this study. And there were no clear seasonal trends in PAH concentrations in air and rain even if there were large variations in total PAH levels in air ( $53 \pm 42$  ng/m<sup>3</sup>) and precipitation ( $144 \pm 84$  ng/L) among the sampling periods. For example, samples collected in May and the beginning of June, 1995 had much lower levels of PAHs in the air ( $3.29 \sim 7.59$  ng/m<sup>3</sup>) relative to other sampling periods. And there were also large variation in the concentrations of some individual compounds among the sampling periods, probably depending on meteorological factors like air mass trajectory, wind direction and speed, and temperature. For example, vapor phenanthrene and chrysene concentrations were highly variable but showed very similar distribution during the sampling period. No relationship between NO<sub>2</sub>/NO<sub>3</sub> and PAH concentrations was found, making it hard to predict the interactions between NO<sub>x</sub> and high molecular weight PAH compounds.

The most dominant PAH compounds (vapor and particulate) in the air during 1995-1996 were 2~4 ring compounds, such as phenanthrene (44%), fluoranthene (21%), pyrene (12%), and fluorene (6%). Naphthalene (31%), phenanthrene (14%), fluoranthene (12%), pyrene (8%), benzo(b)fluoranthene (5%), chrysene (5%), and benzo(g,h,i)perylene (4%) were the dominant PAHs found in rain. Particulate PAHs in air and rain were predominantly 4~6 ring compounds, such as fluoranthene, benzo(b)fluoranthene, and pyrene. Higher molecular weight PAHs showed greater proportion in particle phase in rain. This indicates that high molecular weight PAHs are predominantly particle scavenged via precipitation rather than being scavenged as dissolved phase. Phenanthrene and fluoranthene were predominant in the vapor and dissolved phase throughout the year in this study.

PAHs in the air were predominantly dry deposited, based on calculated wet and dry deposition rates of 130 and 2548 μg/m<sup>2</sup>/year, respectively. Phenanthrene was dominantly dry-deposited while wet deposition contained higher relative concentration of naphthalene, due to its higher solubility (Mackay et al., 1992). Therefore, it is not surprising that naphthalene and substituted naphthalenes contributed about 33% to the total wet deposition. Fluoranthene and pyrene contributed significantly to both dry and wet-deposition.

Several observations support the hypothesis that PAHs in the air near Galveston Bay are predominantly from local urban and industrialized areas such as Sea Brook, Galveston, and

sometimes Houston. The distributions of PAH compounds in the air in this study area were not significantly different ( $p < 0.05$ ) from other areas like Chesapeake Bay ( $R^2 = 0.92$ , Leister and Baker (1994)), Portland, Oregon ( $R^2 = 0.95$ , Ligocki et al., 1985), and Denver, Colorado ( $R^2 = 0.88$ , Foreman and Bidleman, 1990). And PAH compounds in the air and rain from different sampling periods were also correlated, indicating little variation of PAH sources from month to month. Ratio of benzo(e)pyrene to benzo(a)pyrene in air was very low (1.34).

In this study, the distributions of PAHs in the air and rain were indicative of intermediate sources between combustion and petroleum. The air and rain contained predominantly PAH compounds with 2~4 rings and the average ratio of phenanthrene/anthracene was 25~30. This observation is also supported by the distributions of substituted PAHs which showed the mixture of bell-shaped and decreasing trend, indicating the characteristics of both petroleum and combustion source (Yunker and Macdonald, 1995).

The relationship between compounds in the air and rain samples may be interesting. PAHs with similar physical properties and sources were likely to distribute similarly. For example, naphthalene in dry deposition was likely to be correlated with biphenyl, acenaphthylene, acenaphthene, and fluorene while phenanthrene was correlated with anthracene, dibenzothiophene, flouranthene, and pyrene. Phenanthrene and anthracene have similar combustion source and vapor pressure of about 0.07 and 0.066 Pa, respectively, at 25°C. Benzo(g,h,i)perylene was also correlated with other 5 and 6 ring PAH compounds.

The total concentration of 18 selected PCBs (NS&T recommended) in the air tends to decrease during the 2 year sampling period ( $R^2 = 0.6$ ). And also some seasonal trends were shown in the distribution of the individual homologues. Individual vapor PCB concentrations in 1995 were much higher than those in 1996. For example, samples collected in February 2 and June 8, 1995 were much higher than those collected during the same time period in 1996. Di- and tri-PCBs showed the sharp increase in the earlier 1995, while tetra-, penta-, and hexa-PCB distribution increased during the mid-summer season. Tri-(42%), tetra-(31%), di-(14%), and penta-PCBs (6%) were dominant in the air. The total PCBs in the air ranged from 0.24 ~ 4.91 ng/m<sup>3</sup>.

The concentrations of dissolved total HCHs and PCBs revealed no seasonal trend and these two contaminants do not co-vary. Total PCBs in rain ranged from 0.13 to 3.68 ng/L. The cumulative PCB wet deposition was 1.53  $\mu\text{g}/\text{m}^2/\text{year}$ . The yearly input of PCB from wet deposition, directly to Galveston Bay, was estimated to be 2.19 kg/year. However, such trends found in dry deposition were not shown in wet deposition. Tri- (27%), tetra- (22%), di- (19%), penta- (11%), and hexa-PCBs (11%) were dominant in the precipitation.

Interestingly, the high total HCHs (Hexachlorocyclohexane) corresponded to the high nutrient nitrogen concentration for the same rain event (June 23, 1995). However, HCHs and nutrient nitrogen were not correlated in the entire sampling periods. The total HCHs in air and rain ranged from 68 to 666  $\text{pg}/\text{m}^3$  and from ND to 7,184  $\text{pg}/\text{L}$ , respectively. The concentrations of 4,4'-DDE were low in rain (2 to 246  $\text{pg}/\text{L}$ ) and air (ND to 40  $\text{pg}/\text{m}^3$ ). Chlordane concentrations in rain ranged from 5 to 1935  $\text{pg}/\text{L}$  and from 33 to 293  $\text{pg}/\text{m}^3$  in air. The ratios of  $\alpha$  to  $\gamma$  HCHs were very low (about 1~2) in wet and dry deposition. The concentration of 4,4' DDE in the vapor phase

ranged from 2.9 to 140 ng/m<sup>3</sup>. There was no apparent seasonal trend in these contaminant concentrations and the relative abundance of these contaminants at various collection times was different.

This study provides information on the atmospheric deposition of PAHs, pesticides and PCBs to Galveston Bay. It is difficult to compare these inputs to other input sources due to the lack of information on these other inputs. The atmospheric deposition for Galveston Bay of these contaminants is similar to other studies in Chesapeake Bay, Narragansett Bay, and the Great Lakes.

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