

Evidence for Reactions of PCBs with OH Radical During Tropospheric Transport

Lisa A. Totten and Steven J. Eisenreich*

Department of Environmental Sciences, 14 College Farm Road, Rutgers University, New Brunswick, NJ 08901 USA

Introduction

Polychlorinated biphenyls (PCBs) are ubiquitous contaminants in air, soil, water, and sediments. PCBs are recalcitrant, prone to decomposition via only a limited number of pathways, most notably via anaerobic and aerobic (*1-4*) biodegradation. Recently, several researchers (*5-7*) have demonstrated in laboratory studies that PCBs react with hydroxyl (OH) radical in the gas phase at environmentally-significant rates. Anderson and Hites (*6*) observed that PCBs containing 2 to 4 chlorines react with OH radical at faster rates than the more highly chlorinated congeners. They calculated that such reactions may represent the single most important permanent PCB sink on a global scale. Indeed, field data collected in the Great Lakes region of North America as part of the Integrated Atmospheric Deposition Network (IADN) show that ambient PCB concentrations have generally decreased with ecosystem half-lives of 0.1 yr^{-1} (*8*).

In order to detect losses of PCBs that might be attributed to reactions with hydroxyl radical during daytime tropospheric transport, information about diurnal variations in PCB concentrations is needed. Such data were previously collected during three different intensive sampling campaigns in which air was sampled on either continuous 4- or 12-hour cycles. The data was collected as part of the AEOLOS Project (Atmospheric Exchange Over Lakes and Oceans) Project in Chicago during July of 1994 and in Baltimore during July of 1997 (*9*). The Rutgers Atmospheric Deposition Network (RADN) project collected data at a site near Newark, NJ during July of 1998.

Experimental Methods

Procedures for the collection and analysis of air samples from the AEOLOS project are described in detail elsewhere (*10*) and (*11*). In summary, atmospheric PCBs (gas and particle) were collected in consecutive 4 or 12-hour periods at all sites with Graseby GMW modified Hi-Vols equipped with a glass fibre filter and a backup polyurethane foam (PUF) adsorbent at calibrated flow rates of 0.5 to $0.8 \text{ m}^3/\text{min}$ (*12*). All samples were analyzed for ~ 85 PCB congeners by high resolution gas chromatography (GC) with electron capture detection (ECD) on 60 m DB5 capillary columns. Air samples were taken during July of 1994 at the Illinois Institute of Technology in Chicago, IL (*12*) and during July of 1997 on the roof of the Maryland Science Center in Baltimore, MD. The PCB congeners quantified from the Chicago samples included some dichlorobiphenyls, whereas the dichloro congeners were not quantified in the Baltimore samples. Only gas phase PCBs were used in the data analysis for evidence of OH attack.

Procedures for collection and analysis of air samples from the NJADN network were similar to those employed in the AEOLOS study. These samples were collected on the roof of the Liberty Science Center in Jersey City, NJ during July 1998. Analysis of the NJADN samples involved detection and quantitation of 85 PCB congeners, but no dichlorobiphenyls.

Results and Discussion

For each of the sampling dates listed in Table 1, diurnal variations in PCB concentrations revealed that the PCB congeners containing 2-4 chlorine substituents were relatively more depleted during the day than the higher MW congeners.

The Chicago AEOLUS study involved 9 periods in which day and night 12-hour PUF samples were collected. From these 9 periods, three can be identified (Table 1) during which the winds blew directly from the west (over the Chicago urban/industrial area) for the major portion of the 24-hour sampling period. PCB concentrations varied diurnally for all three of these days, with gas-phase PCB concentrations being consistently lower during the day. Figure 1 is a plot of the calculated PCB loss vs. congener number for one of these days. Depletion is plotted as natural log of $(C_{\text{day}}/C_{\text{night}})$, where C_{day} = PCB concentration in the air during the day (pg/m^3), and C_{night} = PCB concentration in the air during the night (pg/m^3). Figure 1 clearly demonstrates that the PCBs containing fewer chlorines are more heavily depleted during the day, a pattern observed for each of the three days.

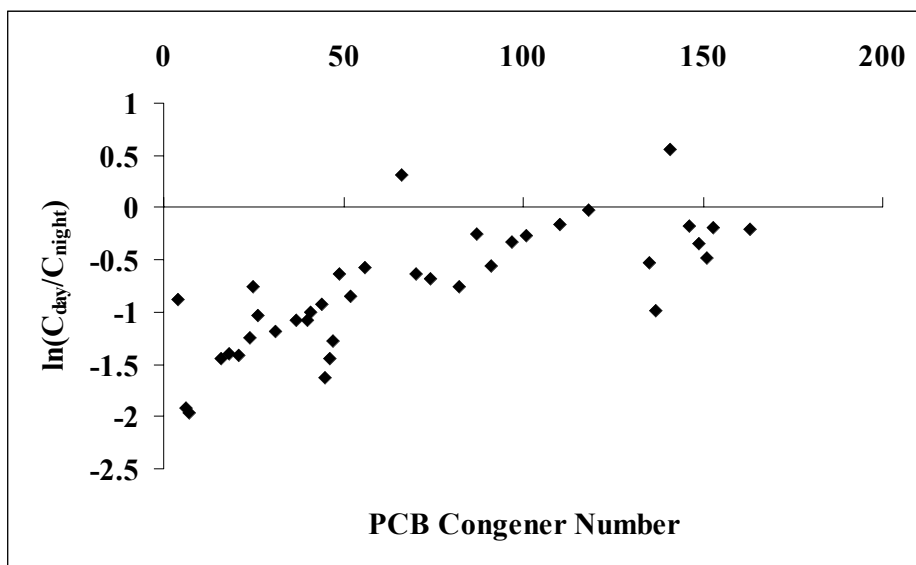


Figure 1: PCB congener loss plotted as natural log of initial (nighttime) concentration over daytime concentration vs. PCB congener number for data collected in Chicago on 7/26/94. The data indicate that the congeners possessing fewer chlorine substituents are more heavily depleted during daytime tropospheric transport.

The Baltimore data from July of 1997 reveal similar trends. Of the six days for which 4 or 12 hour samples were collected, three display significant diurnal variations in gas-phase PCB concentrations. Winds on these days were light. Data collected during July 1998 from the Jersey City, NJ area also display diurnal variations in gas-phase PCB concentrations on two of the six sampling days. No clear trend in wind speed or direction was apparent in the meteorological data for these two days.

Environmental Fate and Transport II

Calculating an intrinsic rate constant (k) for the reaction of each PCB congener with OH radical from these data is problematic, because the reaction time (t) is unknown although it is less than the sampling period of 4 or 12 hours. The OH radical concentration, $[\text{OH}]$, assumedly varies from day to day and over the course of each day. However, if $[\text{OH}]$ is assumed to equal 3×10^6 molecules/cm³ (12, 13), and the reaction time is assumed to be 12 hours, a second-order environmental rate constant, k_e , can be calculated (Table 2). Considering the uncertainties in $[\text{OH}]$ and t , the absolute values of the environmental rate constants are in reasonable agreement with rate constants measured by Anderson and Hites (6) in laboratory studies for reactions of these PCB congeners with OH radical.

The environmental rate constants also agree with laboratory measurements in a relative sense. This conclusion is reached by plotting the relative rate data from each of the sampling dates listed in Table 1 as $\log k_e$ vs. the number of chlorine substituents (#Cl) for each PCB congener, in the form a quantitative structure activity relationship. Although both t and $[\text{OH}]$ are unknown, they can be assumed to be the same for all PCB congeners on any given day. For simplicity, they are once again assumed to be equal to 12 hours and 3×10^6 molecules/cm³, respectively. The absolute values of these parameters are unimportant, however, since differences in t and $[\text{OH}]$ for different days will affect the intercepts of the regression lines, but not the slopes. Table 1 lists the slopes derived from linear regression of the $\log k_e$ vs. #Cl data for the different sampling days. In most cases, the slopes (-0.14 to -0.39) are not statistically different from those observed by Kwok et al. (5) (-0.21) and Anderson and Hites (-0.22) (6). The p-values indicate that the slopes are statistically significant (*i.e.*, the rate constant is indeed a function of the number of chlorine substituents).

In summary, we have presented the first examples of environmental measurements supporting the hypothesis that PCBs are destroyed during daytime tropospheric transport, assumedly due to reactions with OH radicals. We know of no other partitioning or transport process which would preferentially remove the lower molecular weight PCB congeners only during daylight hours in urban-industrial settings. The environmental rate constants observed for the disappearance of various PCB congeners agree well in both absolute and relative terms with laboratory measurements of rate constants for reactions of PCBs with OH radical.

Acknowledgements

The AEOLOS project was funded by the National Exposure Research Laboratory (RTP, NC) of the US Environmental Protection Agency under Cooperative Agreement CR 822046-01 (S.J. Eisenreich, PI; A. Hoffman, Project Officer; Ret.). We gratefully acknowledge the encouragement of D. Pahl, G. Foley and G. Evans of the US EPA during this project. We received considerable ship-time and logistical support as well as encouragement from the Great Lakes National Program of the US EPA in Chicago, IL, especially from A. Bandemehr. The NJADN is funded by the Hudson River Foundation, NOAA's New Jersey Sea Grant Program and the New Jersey Department of Environmental Protection (Project Officer – Stuart Nagourney).

Table 1: Sampling dates at various urban/industrial locations that display significant diurnal variations in atmospheric gas-phase PCB concentrations. Slopes are derived from plots of $\log k_e$ vs. number of chlorine or homologue group.

Environmental Fate and Transport II

Sampling Location	Date	Slope \pm (95% CI)	p-value
Chicago/ Illinois Institute of Technology	07/18/94	0.39 \pm (0.14)	5 \times 10 ⁻⁶
	07/25/94	0.24 \pm (0.10)	5 \times 10 ⁻⁵
	07/26/94	0.22 \pm (0.08)	6 \times 10 ⁻⁶
Baltimore/ Maryland Science Center	07/24/97	0.22 \pm (0.07)	4 \times 10 ⁻⁷
	07/26/97	0.18 \pm (0.13)	9 \times 10 ⁻³
	07/27/97	0.26 \pm (0.07)	3 \times 10 ⁻⁸
Jersey City/ Liberty Science Center	07/07/98	0.14 \pm (0.07)	1 \times 10 ⁻⁴
	07/10/98	0.23 \pm (0.10)	1 \times 10 ⁻⁴

Table 2: Average rate constants (k_e in 10⁻¹² cm³s⁻¹) for loss of specific PCB congeners derived from environmental data for the 12 sampling days listed in Table 1 versus k measured by Anderson and Hites (6) for reactions of PCBs with OH radical.

Congener		
Number	$k_e \pm$ (sd)	k ref (6)
4	6.0 \pm (1.1)	2.2
7	12.1 \pm (4.0)	2.6
31	6.8 \pm (2.9)	1.2
44	5.7 \pm (2.3)	0.8
47	6.4 \pm (2.4)	1.0
110	2.7 \pm (2.2)	0.6

References

- (1) Takase, I.; Omori, T.; Minoda, Y. *Agric. Biol. Chem.* **1986**, *50*, 681-686.
- (2) Sugiura, K. *Chemosphere* **1992**, *24*, 881-890.
- (3) Adriaens, P.; Grbic-Galic, D. *Environ. Sci. Technol.* **1994**, *28*, 1325-1330.
- (4) Flanagan, W. P.; May, R. J. *Environ. Sci. Technol.* **1993**, *27*, 2207-2212.
- (5) Kwok, E. S.; Atkinson, R.; Arey, J. *Environ. Sci. Technol.* **1995**, *29*, 1591-1598.
- (6) Anderson, P. N.; Hites, R. A. *Environ. Sci. Technol.* **1996**, *30*, 1756-1763.
- (7) Brubaker, W. W., Jr.; Hites, R. A. *Environ. Sci. Technol.* **1998**, *32*, 3913-3918.
- (8) Hillery, B. R.; Basu, I.; Sweet, C. W.; Hites, R. A. *Environ. Sci. Technol.* **1997**, *31*, 1811-1816.
- (9) Zhang, H.; Eisenreich, S. J.; Franz, T. R.; Baker, J. E.; Offenber, J. H. *Environ. Sci. Technol.* **1999**, *33*,
- (10) Simcik, M. F. PhD Dissertation, Rutgers University, 1998.
- (11) Zhang, H. PhD Thesis, University of Minnesota, 1996.
- (12) Simcik, M. F.; Zhang, H.; Eisenreich, S. J.; Franz, T. P. *Environ. Sci. Technol.* **1997**, *31*, 2141-2147.
- (13) Mackay, D.; Shiu, W. Y.; Ma, K. C. *Illustrated Handbook of Physical-Chemical Properties of and Environmental Fate for Organic Chemicals*; Lewis: Ann Arbor, MI, 1993; Vol. 3.