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Gas-Particle Partitioning of PCBs and PAHs During AEOLOS: Sorption Mechanisms and Equilibrium

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Abstract

Simultaneous air samples were taken in Chicago and over southern Lake Michigan as part of the AEOLOS Project (Atmospheric Exchange Over Lakes and Oceans). Gas and particulate phase concentrations of polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs), and total suspended particles (TSP) were measured over 12 hour periods during July, 1994 and January, 1995. Data are presented which suggest that the PCBs and PAHs are at equilibrium, despite having slopes for $\log K_p$ vs. $\log p^0_L$ regressions that are different from -1, and that both surface adsorption and absorption into organic matter are important partitioning mechanisms.

Introduction

The partitioning of semivolatile organic compounds (SOCs) in the atmosphere is an important factor in their fate and transport in urban and adjacent coastal atmospheres. Theory to predict the partitioning of SOC between the gas and particulate phases has been developed for both surface adsorption¹ and absorption into organic matter². According to both paradigms the equilibrium partitioning of SOC will result in slopes near -1 for regressions of $\log K_p$ vs. $\log p^0_L$ given the following assumptions: for adsorption, the difference between the enthalpies of desorption and volatilization, and the number of sites available for adsorption remain constant over a compound class; for absorption, the activity coefficient of the SOC in organic matter remains constant over a compound class. It is not clear that the difference in enthalpies are constant for PAHs and PCBs. For the case of absorption into organic matter results of experiments for partitioning between air and octanol indicate that the activity coefficients for PAHs and PCBs remain constant.

Experimental

Simultaneous air samples were taken at an urban location in south Chicago, IL, and over Lake Michigan aboard the *RV Lake Guardian* during May, and July 1994 and January 1995. The high volume air samplers were equipped with glass fiber filters (GFFs) to collect particulate phase compounds and polyurethane foam plugs (PUF) to collect the gas phase compounds. They were run for two 12 hour periods per day, one at night and one during the day, to minimize effects of changing temperature, and atmospheric concentrations of the SOC and TSP. Total suspended particulate mass was only sampled during July and January using an Anderson Dichotomous sampler dividing the TSP into two size ranges ($>2.5 \mu\text{m}$, and $<2.5 \mu\text{m}$), collected on Teflon filters, and analyzed gravimetrically. TSP samples were also run for the same 12 hour periods. Multiple orifice impactors (MOI's) were used to obtain size distributions of atmospheric particles as well as SOC's. The ten stages of the MOI corresponded to size cuts of 9.6, 3.1, 1.73, 0.96, 0.54, 0.31, 0.17, 0.096, 0.054, and 0.03 μm . The MOI's were equipped with aluminum foil substrates for the first nine stages and a quartz fiber filter for the tenth stage, and run at 31

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m^3/min for 12 to 72 hours. The foils were weighed before and after sampling to obtain the mass of particles on each stage. Temperature, wind direction and speed, and relative humidity were collected with meteorological towers at both sites and the data stored by computer.

Results and Discussion

ΣPCBs and ΣPAHs concentrations ranged from 0.1 to 14 ng/m^3 and 1 to 430 ng/m^3 , respectively. Lower molecular weight species were predominantly in the gas phase, higher molecular weight species predominantly in the particulate phase, and mid molecular weight species were distributed more evenly between the two phases. TSP concentrations ranged from 11 to 71 $\mu\text{g}/\text{m}^3$ in Chicago and 1.5 to 29 $\mu\text{g}/\text{m}^3$ over Lake Michigan. Twelve hour average temperature and relative humidity ranged from 277 to 302 K and 56 to 96%, respectively. The temperature dependent vapor pressures were calculated for all congeners based on GC retention data³, and for eleven PAHs from a compilation of literature data by Liu⁴ at the average ambient temperature of the sampling period.

Regressions of log-log plots of K_p vs p_L^0 for both Chicago and Lake Michigan gave high correlations for individual samples for both PAHs and PCBs, but the slopes and intercepts amongst samples varied greatly. For all PCBs at the Chicago and Lake Michigan sites and all but 7 of the PAH plots for Chicago and 2 for Lake Michigan the 95% confidence intervals about the regressed slopes of $\log K_p$ vs. $\log p_L^0$ exclude the value of -1. When all of the data for PAH partitioning in Chicago is regressed, the slope of -0.64 and intercept of -3.47 ($r^2 = 0.78$) compare well with results by Cotham and Bidleman⁵ in Chicago during February, 1988 (-0.69, and -4.61, $r^2 = 0.73$).

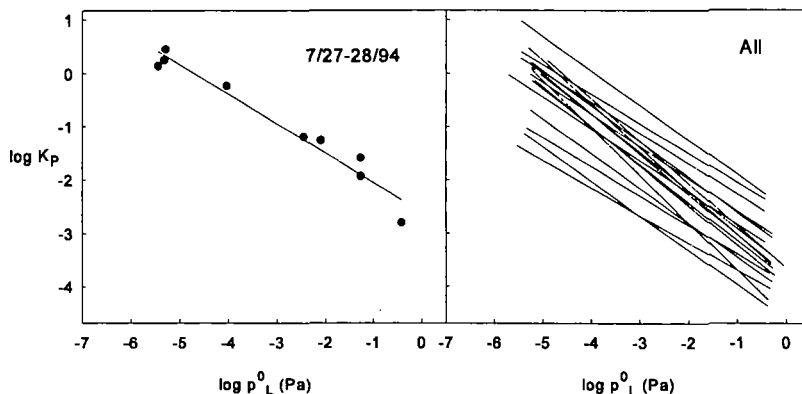


Figure 1. $\log K_p$ vs. $\log p_L^0$ for a single sample and all samples in Chicago

The issue of non-equilibrium represents a kinetic problem in which the lower molecular weight SOCs have higher diffusivities and therefore approach equilibrium much faster than the higher

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molecular weight species, causing shallower slopes. One way of investigating this is to look at air masses that have traveled further from their sources and therefore both the gas and particle phases had much longer atmospheric residence times, and are allowed to reach equilibrium. Several samples over Lake Michigan were taken when the wind was from the north bringing aged aerosol representative of the continental background signal⁶. One would expect that these SOCs have traveled great distances and therefore are at equilibrium. For PAHs the slopes of these samples are among the highest observed (-0.65 to -0.55). PCBs also have very shallow slopes (-0.16 to -0.56) during this time, suggesting that the a slope of -1 isn't required to describe SOC's at equilibrium. Chicago also received wind from the north during this same time period, but in this situation the samples represent relatively clean particles entering a contaminated area, and the assumption of long residence time for both gas and particle phases is not valid.

Another approach to addressing the question of non-equilibrium is to look and see if the slope approaches -1 as the air mass moves from the urban to adjacent coastal atmosphere. For the over-night sample of July 22 in particular, the wind over the ship was consistently from the direction of the urban sampling site. The wind speed during this sample was 2.4 m/s and the distance of 30 km gives a transport time of approximately 3.4 hrs between sites. Studies of relative times to equilibrium suggest that the kinetics of gas-particle sorption are fast and a few hours is sufficient for the SOCs to show progression towards equilibrium^{7,8}. However, the log-log plot of K_p vs. p_L^0 shows virtually no change in partitioning between the Chicago and Lake Michigan samples for either PCBs or PAHs despite the fact that the concentrations over Lake Michigan are on the order of 1/3 that found in Chicago⁶. This suggests that perhaps the samples are at equilibrium and that there are other factors affecting the slopes of these plots. The only factor which the authors feel can be responsible for the differing slopes is that the differences in enthalpies are not constant over a compound class, and that this difference varies for different types of atmospheric particles.

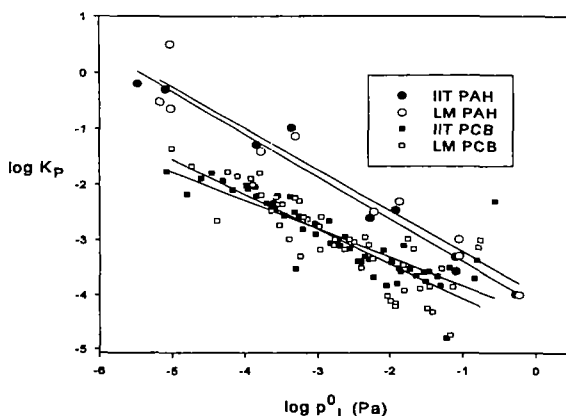


Figure 2. $\log K_p$ vs. $\log p_L^0$ for the same air mass in Chicago and over Lake Michigan

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Results from the MOI's indicate that for both May 17-19, and July 17-18 the size distribution of particle mass had two modes, one in the accumulation range, 0.02 to 1.0 μm , and one in the super-micron range, 1.0 to 20 μm (Figure 3). The accumulation range particles are generally associated with primary anthropogenic sources such as combustion, and secondary aerosol formation while the coarse range particles are primarily erosional including wind blown dust and plant particles⁹. The size distributions of PAHs with moderate vapor pressures (0.5 to 10^{-4} Pa) that partition readily between the gas and particle phases such as phenanthrene, chrysene, and beno[a]pyrene, are also bimodal with the super-micron mode being dominant. However, the distribution of coronene which has a lower vapor pressure ($<10^{-9}$ Pa) and is almost exclusively found on particles, has very little concentration on the larger particles, indicating that the SOC's found on super-micron particles are a result of sorption from the gas phase. The surface area distribution of particles is unimodal in the sub-micron range indicating that sorption to the larger particles is not a surface adsorption mechanism. If the coarse mode particles are rich in organic carbon from soil dust, or plant particles the mechanism may be absorption into an organic matrix. Unfortunately, the organic carbon size distribution of the aerosol is not available to test this theory.

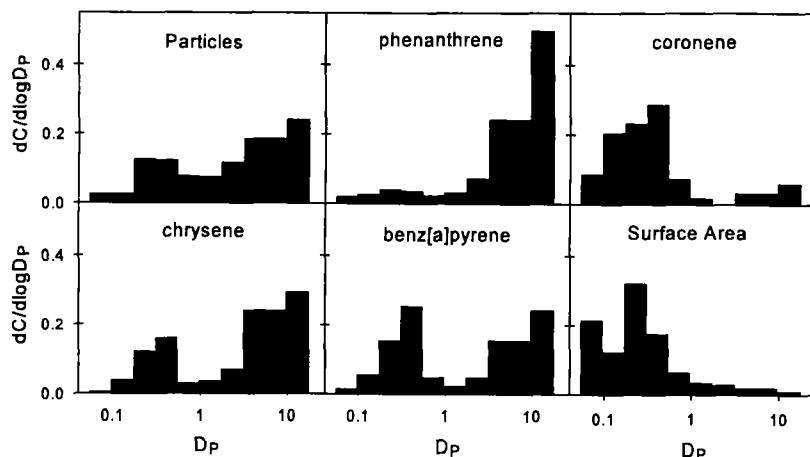


Figure 3. Size distribution for particle mass, PAHs, and surface area for May 17-19

If absorption of SOCs to atmospheric particulate matter is the sole mechanism, then a log-log plot of organic carbon normalized partition coefficient, K_{OC} , vs. K_{OA} should yield a one-to-one line given the following assumptions: 1) the SOCs are at equilibrium and 2) octanol is a good surrogate for organic matter associated with atmospheric particles. The units for K_{OA} are mass per unit volume of octanol over mass per unit volume of air. In order to convert K_p to the same units

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it must normalized by the following relationship:

$$K_{OC} = \frac{K_p \times 10^{12} \times \rho_{OC}}{f_{OC}}$$

where ρ_{OC} is the density of organic matter (g/cm^3), f_{OC} is the fraction of TSP that is organic carbon, and 10^{12} is a units conversion factor. Because organic carbon content is not available for the individual samples from this study a value typical of the central United States of 30% was assumed [10] and the density of organic matter is assumed to be $1.0 \text{ g}/\text{cm}^3$ [11]. Plots of $\log K_{OC}$ vs. $\log K_{OA}$ for PCBs and PAHs for Chicago and Lake Michigan are shown below. Some of the scatter in the plots may be a result of varying organic carbon content between samples.

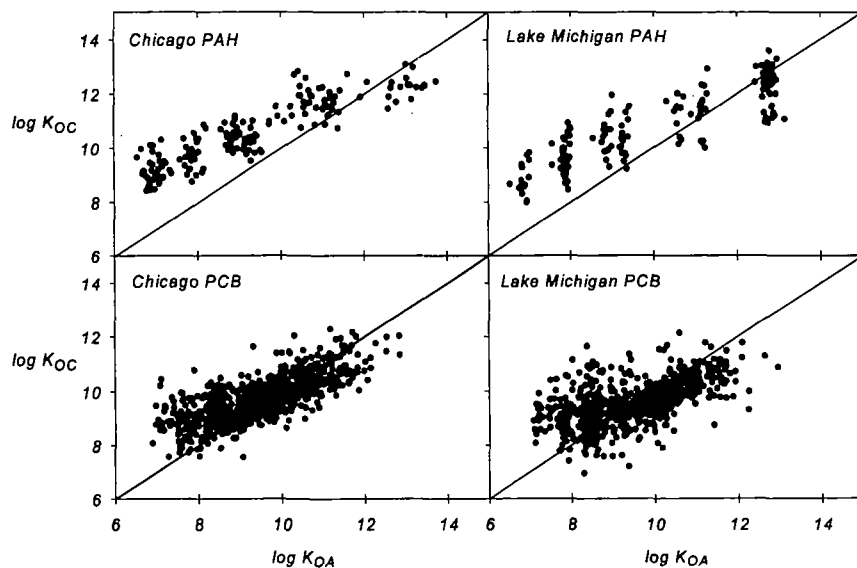


Figure 4. $\log K_{OC}$ vs. $\log K_{OA}$ for PAHs and PCBs in Chicago and over Lake Michigan

Partitioning of all but the highest molecular weight PAHs to atmospheric particles is underestimated by the octanol-air partition coefficients, more so for the lower molecular weight species. Partitioning of PCBs is much better predicted by K_{OA} values, but in general is underestimated especially for the lower molecular weight congeners. Some uncertainty is introduced by assuming 30% organic carbon in the particles, a better approach would certainly be

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to measure the organic carbon whenever a study like this is carried out. Data from Cotham and Bidleman [5] also indicates that the partitioning of SOCs in Chicago is underestimated by octanol-air partition coefficients.

Partitioning of SOCs to different particle sizes shows some difference in slope of $\log K_p$ vs $\log p^0_L$, but not all slopes are significantly different from one another. Different particle sizes are made up of different types of particulate matter, and partitioning would therefore be expected to differ.

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