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Gas—Particle Partitioning of Organic Compounds and Its Interpretation Using Relative Solubilities

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A review is presented of the current understanding of the partitioning phenomena of relatively low vapor pressure organic chemicals between the gas phase and atmospheric particulates. The phenomena have been interpreted as adsorption, absorption, or a combination of both and corresponding theoretical equations suggested to quantify partitioning. Empirical correlations involving the chemical's vapor pressure and octanol–air partition coefficient are discussed. It is suggested that insights into selecting preferred correlations and into the nature of the partitioning phenomena can be enhanced by treating the partition coefficient as a ratio of a solubility or pseudo-solubility of the chemical in the aerosol particle to that in air. Such particle solubilities when calculated for PCBs, alkanes, and PAHs show remarkable constancy and are generally consistent with near-ideal absorption into organic matter. An exception occurs when the PAH is generated simultaneously with the aerosol and unusually high solubilities are observed, indicative of adsorption to active carbon surfaces. Recommendations are made for interpreting experimental partitioning data and for the use of correlations for predictive purposes.

Introduction

The partitioning of semivolatile organic substances between the gaseous and aerosol phases in the atmosphere is a key factor that controls their deposition to aquatic and terrestrial surfaces (1, 2) and influences their reactivity with oxidants and hence their atmospheric persistence (3, 4). It is thus important that gas–particle partitioning phenomena are well understood and quantified so that rates of atmospheric deposition and removal processes can be estimated with acceptable accuracy.

Gas–particle partitioning of organics in the atmosphere was first described quantitatively in 1977 by Junge (5), who used Langmuir isotherm adsorption theory, implying that the adsorption is controlled by the vapor pressure of the organic compound and the available surface area on the particles. In the last 23 years, considerable progress has been made by field and laboratory measurements as well as by correlations, interpretations, and theoretical treatments, notably by Pankow, Bidleman, Kamens and co-workers (6–16).

There is still some debate whether the mechanism of partitioning is absorption into a liquid-like organic film on the particles or adsorption to active sites on the particle's

surface, or a combination of both, as discussed by Pankow (11, 12). It is, however, clear that aerosols of different origin have different sorptive properties (16–19), that humidity affects sorption (20–22), and that chemical-to-chemical differences and the effect of temperature are best described by the chemicals' subcooled liquid vapor pressure (6–13) or the octanol–air partition coefficient (14, 15). Although several correlation approaches exist and are widely used, the relationships between them and their relative merits in terms of accuracy, applicability, and convenience of use are not obvious, especially to the nonexpert. Here we review the various approaches and suggest that valuable insights into the relationships between correlations and the nature of the phenomena can be gained by expressing the interactions between the chemical and the particulate matter as a readily appreciated "solubility" or "pseudo-solubility", an idea that was inspired by the work of Jang, Kamens, and colleagues (16, 22). We thus review existing correlations; present the pseudo-solubility approach; apply it to 10 published studies involving PCBs, PAHs, and alkanes in a variety of different aerosol types; and discuss the implications.

Review of Theory

The extent of sorption to particles is now commonly expressed using the group $(F/TSP)/A$, where F (filtered) and A (air) are respectively the particle-associated and gaseous concentrations per unit volume of air (ng/m^3) and TSP is the total suspended particle per concentration ($\mu\text{g}/\text{m}^3$). This approach was first suggested by Yamasaki (6), and its validity has been confirmed by experimental observations and theoretical considerations by Pankow (8) and by Pankow and Bidleman (10). The group $(F/TSP)/A$ is essentially a particle–gas partition coefficient K_p , which has units of $\text{m}^3/\mu\text{g}$.

When the partitioning is dominated by adsorption, K_p has been shown to be given by (7)

$$K_p = \frac{RTN_s A_{TSP} e^{(Q_d - Q_v)/RT}}{P_L} \quad (1)$$

where N_s is the moles of adsorption sites (mol cm^{-2}), A_{TSP} is the surface area of the TSP ($\text{cm}^2/\mu\text{g}$), T is the temperature (K), R is gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), P_L is liquid vapor pressure (Pa) of the pure organic compound (supercooled liquid in the case of solids), and Q_d and Q_v are the enthalpies of desorption and volatilization (kJ/mol), respectively, which differ between compound classes. When partitioning is dominated by absorption into organic matter present in the particle, the following expression for K_p applies (11, 12):

$$K_p = \frac{RTf_{OM}}{10^6 M_{OM} \gamma_{OM} P_L} \quad (2)$$

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where M_{OM} (g/mol) is the mean molar mass of the organic matter phase, f_{OM} is the fraction of organic matter in the aerosol, and γ_{OM} is the activity coefficient of the chemical in the organic matter phase on a mole fraction basis. The activity coefficient γ_{OM} is a function of the chemical's properties and the composition of the aerosol and characterizes the non-ideality of the interaction between the chemical and the organic matter of the particle.

Pankow (11, 12) has shown that both absorptive and adsorptive partitioning mechanisms predict a fundamental inverse proportionality between K_P and P_L . Therefore, it is difficult to determine the mechanism of sorption based solely on the dependence of K_P on P_L . It is also difficult to validate the models suggested by eqs 1 and 2 because many of the parameters in these equations (e.g., N_S , A_{TSP} , M_{OM} , γ_{OM}) are unknown or uncertain for atmospheric aerosols.

It has been shown recently that the vapor pressure can be replaced with the octanol-air partition coefficient (K_{OA}) to describe absorption onto aerosols (14, 15):

$$K_P = f_{OM} \frac{\gamma_O}{\gamma_{OM}} \frac{M_{OCT}}{M_{OM} \rho_{OCT} 10^{12}} K_{OA} \quad (3)$$

where γ_O is the activity coefficient of the sorbate in octanol, M_{OCT} is molar mass of octanol, and ρ_{OCT} is the density of octanol (kg/L). Justification for the use of K_{OA} rather than P_L lies in the definition of K_{OA} as $RT/(\gamma_O v_O P_L)$ where γ_O is the activity coefficient in octanol and v_O is the molar volume of octanol. Both K_P and K_{OA} are thus inversely proportional to P_L . If the ratio γ_{OM}/γ_O is fairly constant for a series of chemicals, there should be an almost linear relationship between K_P and K_{OA} , and the slope of a plot of $\log K_P$ versus $\log K_{OA}$ should also be 1.0 unless some property of the chemical systematically causes changes in the ratio of activity coefficients. K_{OA} also has the advantage that, unlike P_L , it can be measured experimentally at ambient temperatures for solid solutes. K_{OA} values have been reported for several classes of organic compounds (23–27). Equation 3 has been simplified by using an octanol density of 0.82 g/cm³ and assuming that the products of activity coefficients and molar masses of octanol and organic matter are equal (i.e., $M_{OCT}/M_{OM} \sim 1$ and $\gamma_O/\gamma_{OM} \sim 1$) yielding

$$\log K_P = \log K_{OA} + \log f_{OM} - 11.91 \quad (4)$$

This equation can also be written

$$K_P = 1.23 \times 10^{-12} f_{OM} K_{OA} \quad (5)$$

Essentially the solvent properties of octanol and the organic matter in the ambient aerosol are treated as being equivalent. Equation 5 is appealing because it mimics the Karickhoff method of calculating soil–water partitioning (28), except that partitioning is now from air instead of water: thus K_{OA} replaces K_{OW} . If an organic carbon fraction for urban aerosols of 0.2 (20%) is assumed, we obtain a one-parameter approach for estimating gas–particle partitioning, which might be useful for screening purposes:

$$K_P = B K_{OA} \quad (6)$$

where B is 2.5×10^{-13} (i.e., $0.2 \times 1.23 \times 10^{-12}$). This is essentially an assumption that the group $10^{-12} f_{OM} M_{OCT} \gamma_O / M_{OM} \gamma_{OM} \rho_{OCT}$ in eq 3 has the value of B . Finizio et al. (14) have previously suggested this one-parameter model and obtained empirical values for B an order of magnitude higher than suggested by the simplified theory of 1.88×10^{-12} and 1.50×10^{-12} for PAHs and organochlorine compounds, respectively.

Another simple one-parameter equation was devised by Mackay et al. (29). It can be expressed as

$$K_{QA} = 6.0 \times 10^6 / P_L; \quad K_P = 10^{-12} K_{QA} / \sigma \quad (7)$$

where K_{QA} is a dimensionless aerosol–air partition coefficient, and σ is the density of the aerosol (g/cm³). The factor of 10^{12} converts cm³/g to m³/μg. If we assume absorption is the mechanism of partitioning, this is essentially an assumption that the group $(\sigma RT f_{OM}) / (M_{OM} \gamma_{OM})$ from eq 2 and eq 7 has a value of 6.0 Pa. Given the presence of activity coefficients and densities in the single parameter, it is likely that one-parameter equations will be of limited accuracy when applied to multiple classes of chemicals or to multiple classes of aerosols.

Jang et al. (16) have probed the validity of eq 2 by calculating the activity coefficients γ_{OM} using group contribution methods (i.e., Hansen's method or UNIFAC) for a variety of organic substances in different aerosol types and correlating the product of K_P and γ_{OM} with P_L . They obtained significantly improved fits and slopes closer to -1.0 than were obtained when K_P was plotted against P_L . This supports the fundamental validity of eq 2 as a basis for correlation. They also showed that the same chemical has different activity coefficients in polar (e.g., secondary organic aerosol) and nonpolar aerosols (e.g., wood soot). It remains uncertain if octanol can adequately represent both polar and nonpolar classes of organic matter (i.e., the validity of the assumption that γ_O and γ_{OM} are equal), which is a possible limitation of the K_{OA} -based model.

From this assessment of the theory, it can be concluded that aerosol–air partitioning is characterized by (i) a fundamental inverse relationship with subcooled liquid vapor pressure, either expressed directly or through its relationship with octanol–air partition coefficient, (ii) differences in aerosol composition that are manifested in differences in organic matter content and type and possibly surface areas, and (iii) differences in interactions between the chemical and the sorbing medium expressed as activity coefficients or enthalpies of adsorption. Any accurate correlation must treat all three factors, although useful but less accurate empirical correlations can be developed that include broad assumptions about average properties of aerosols and interactions.

Empirical Correlations

The conventional empirical approach is to obtain and fit K_P data for a class of chemicals to an equation of the form

$$\log K_P = m \log P_L + b \quad (8)$$

where m and b are constants. The logarithmic form of this relationship is dictated by the wide variation in K_P and P_L . Excellent summary tables of the various values of m and b obtained from field measurements are contained in refs 15 and 30 and are not repeated here. The coefficient m is generally close to the theoretically expected -1.0 but is typically in the range -0.7 to -1.0 . Possible reasons for this deviation are sampling artifacts, nonequilibrium partitioning (a kinetic effect), a lack of constancy in the heat of desorption within a class of compounds (a thermodynamic effect), and the lack of constancy in activities within a class of compounds (15, 30, 31). For example, if increasing molar mass leads to both a decrease in P_L and an increase in γ_{OM} in eq 2, then the fitted coefficient m will not be -1.0 and could be, for example, -0.8 .

Finizio et al. (14) obtained a two-parameter correlation analogous to eq 8 using K_{OA} for describing the gas–particle partitioning of PAHs at 298 K:

$$\log K_P = m \log K_{OA} - b \quad (n = 10) \quad (R^2 = 0.97) \quad (9)$$

where m is 0.79 and b is 10.01. Theory suggests a slope of 1, but it is clearly not obtained, possibly because γ_0/γ_{OM} is not constant.

Two issues arise from the theory and correlations described above. First, the theory is compelling in suggesting that the slope m should be -1.0 when correlating K_p against P_L and 1 when correlating against K_{OA} , if equilibrium partitioning applies. Second, there is effective autocorrelation implicit in the correlation equations because the highly variable (from chemical-to-chemical) quantity P_L appears in both dependent and independent variables, either directly or as a contributor to K_{OA} . These quantities vary by 5 orders of magnitude for the range of chemicals for which aerosol partitioning is significant, thus it becomes difficult to detect and quantify the smaller and more subtle differences in variables such as activity coefficients in organic matter, which may vary over a much narrower range of 1 order of magnitude or less. The nature of the interactions between the chemical and the aerosol may be better evaluated by canceling out the variation in P_L and examining the chemical-to-chemical variation of the product $K_p P_L$ [as was done by Jang et al. (16)] or the ratio K_p/K_{OA} with K_{OA} (as was tested by Finizio et al. in their simple one-parameter correlation).

An alternative method of addressing this issue is to regard K_p as a ratio of "solubilities" following the example that K_{OW} can be regarded as a ratio of solubilities in octanol and water. This approach has been generalized by Cole and Mackay (32) as the "three solubility" approach, which we outline and then apply below.

Three Solubility Approach

In the three solubility approach (32), it is suggested that physical-chemical partitioning in environmental systems can be usefully described by determining the actual or pseudo-solubility (S) of the liquid phase substance in three key phases as a function of temperature, namely, in air (S_A), water (S_W), and octanol (S_O). These three solubilities (with identical units such as g/m³) are essentially convenient measures of activity coefficients, indeed they are $1/\gamma$ where v is the molar volume of the solution and γ is the activity coefficient of the chemical. They apply at very dilute or infinite dilution conditions and are not necessarily the actual solubilities when solubility is very high, i.e., at a mole fraction exceeding 0.01. The three partition coefficients K_{AW} (air-water), K_{OW} (octanol-water), and K_{OA} (octanol-air) are then simply the ratios S_A/S_W , S_O/S_W , and S_O/S_A , respectively. By defining solubilities, consistency among the partition coefficients is ensured, and problems with autocorrelation are avoided that occur when correlations are sought between partition coefficients [e.g., K_{OW} versus K_{OC} or K_{OA} versus K_p (33)]. Furthermore, if the temperature coefficients of the three solubilities are known, the corresponding temperature coefficients (enthalpies of phase transfer) are also known for the partition coefficients and again are consistent because their sum around the air-water-octanol thermodynamic cycle must be zero.

In this case, we calculate a "pseudo-solubility" in the aerosol phase S_Q such that by definition:

$$K_p = S_Q/S_A \quad (10)$$

where S_Q is the solubility in aerosol (ng/ μ g) or the equivalent (mg/g), and S_A is the solubility in air (ng/m³) or $10^9 WP_L/RT$, where W is the molar mass of the substance (g/mol). The difference in the units of solubility is necessitated by the units of K_p (m³/ μ g). Substituting S_A into eq 10 gives

$$K_p = RTS_Q/(10^9 WP_L) \quad (11)$$

TABLE 1. Calculated Pseudo-Solubilities (S_Q) of PCBs (g/g) from Various Studies

compd	urban aerosol ^a	Great Lakes aerosol ^b	urban aerosol ^c	semirural aerosol ^d
PCB-8	0.36			
PCB-33	0.25			
PCB-40	0.22			
PCB-44	0.23	0.26		
PCB-49	0.25			
PCB-52	0.25	0.28		0.43
PCB-66	0.19		0.13	
PCB-70	0.19			
PCB-87	0.16			
PCB-99	0.18			
PCB-101	0.18	0.20	0.14	0.26
PCB-110	0.15		0.13	
PCB-153	0.13			0.15
PCB-138	0.12			
PCB-170	0.08			
PCB-180	0.09			
mean for PCBs	0.20	0.25	0.13	0.28
SD	0.07	0.05	0.01	0.14

^a Cotham and Bidleman (35), outdoor measurements from Chicago.

^b Hoff et al. (40), measurements taken above Lakes Erie and Ontario.

^c Foreman and Bidleman (38), outdoor measurements from Denver.

^d Kaupp and Umlauf (39), outdoor measurements in the vicinity of Bayreuth, Germany.

From eqs 2 and 11, the relationship between S_Q , γ_{OM} , and f_{OM} can be deduced:

$$S_Q = 10^3 f_{OM} W / M_{OM} \gamma_{OM} \quad (12)$$

When viewed in terms of solubilities, the potential for autocorrelation becomes obvious because the vapor pressure expresses the solubility in air S_A , and K_p can be viewed as the ratio of the activity or solubility of the chemical in the aerosol and air phases, i.e., S_Q/S_A . A logarithmic plot of K_p versus P_L is essentially a plot of S_Q/S_A versus S_A and is thus expected to have a slope m of -1.0 . The wide variation in vapor pressure of the chemicals is likely to obscure subtle differences in activity coefficients or solubilities. There is thus a compelling theoretical incentive to correlate S_Q directly, or the product $K_p P_L$, with properties of the chemicals, which is essentially what was done by Jang et al. (16).

To test this suggestion, we use literature reported values of K_p and P_L to deduce values of S_Q and explore their constancy and dependencies.

Data Analysis

Using literature data (16–19, 34–40) for K_p and P_L (i.e., S_A), S_Q was calculated in units of g/g using eq 10 for PCBs, PAHs, and alkanes in a wide range of aerosol types (Tables 1 and 2). In most cases, K_p and P_L data (at the same temperature) for calculation of S_Q were taken directly from the source references. For PCBs, we obtained K_p and P_L data at 298 K from a summary table in ref 14. For the study by Dachs and Eisenreich (19), K_p data measured in Chesapeake Bay at 297.9 K and P_L data from ref 18 at 298 K were used. Full details of the calculations can be obtained from the corresponding author on request. Arithmetic means and standard deviations of S_Q were also calculated for each chemical class.

A first observation is that the S_Q data for PCBs in Table 1 calculated using K_p data from various studies are remarkably constant, especially when it is considered that K_p varies by 2 orders of magnitude between congeners. Second, the absolute values of S_Q average about 0.2 g/g and range less than an order or magnitude from 0.08 to 0.43 g/g. The wide variation in K_p is thus almost entirely due to the variation in air solubility or vapor pressure, which varies by 3 orders of

TABLE 2. Calculated Pseudo-Solubilities (S_0) of Alkanes (g/g) in a Variety of Aerosol Types

compd	wood smoke ^a	secondary aerosol ^a	gasoline ^b	DOP ^{b,c}	ETS ^d	ETS ^e
hexadecane			0.08	0.65	0.92	0.18
heptadecane			0.16	0.70	0.28	0.21
<i>d</i> ₃₆ -heptadecane	0.016	0.006				
octadecane			0.14		0.16	0.18
nonadecane			0.21		0.11	0.17
<i>d</i> ₃₈ -nonadecane	0.007	0.002				
eicosane			0.07		0.14	0.16
<i>d</i> ₄₂ -eicosane	0.013	0.001				
heneicosane			0.32	0.97	0.12	0.16
docosane		0.004	0.08	1.9	0.17	0.10
tetracosane			0.39	0.49		
pentacosane			0.54			
mean for alkanes	0.012	0.003	0.22	0.95	0.27	0.16
SD	0.005	0.002	0.15	0.58	0.29	0.03

^a Jang et al. (16), smog chamber measurements. ^b Liang et al. (17), smog chamber measurements. ^c DOP, dioctyl phthalate particles, smog chamber measurements. ^d Liang and Pankow (18), indoor air from a smoky room. ETS, environmental tobacco smoke. ^e K_p measured by filter desorption. ^f Pankow et al. (37), indoor air from a smoky room. ETS, environmental tobacco smoke. K_p measured by gas-particle sampling and analysis.

magnitude for the PCBs considered. The constancy in the solubility of PCBs is equivalent to constancy in the activity coefficients for compounds in a homologous series in the given aerosol (16). For example, for PCBs in the Chicago urban aerosols the range in S_0 is 0.08–0.36 g/g with a mean of 0.20 and standard deviation of 0.07. For PCBs, the arithmetic mean values of S_0 for different aerosols are fairly consistent (0.13–0.28 g/g).

If it is accepted that the partitioning is absorption and primarily into the organic matter in the aerosol, then a solubility of 0.2 g/g is consistent with near ideal dissolution in an aerosol of 20% organic matter. There is, however, a distinct trend for a decrease in solubility by a factor of 4 with increasing molar mass, which is consistent with an increase in activity coefficient for the congeners of higher molar volume. This trend has been demonstrated for solubility in octanol (32). This strongly suggests that partitioning is by absorption and is close to ideal in behavior.

The S_0 values for alkanes (Table 2) are much lower, especially in wood smoke and secondary aerosols, averaging about 0.007 g/g, again consistent with a higher activity

coefficient of these long chain molecules. There is also a higher solubility in environmental tobacco smoke, DOP, and gasoline-derived aerosols. This may reflect the presence of alkanes at relatively high concentrations during the combustion process that generates the aerosol.

The PAH data are particularly interesting and illuminating (Table 3). Values of S_0 for PAHs in ambient coastal, urban, and roadway aerosols and secondary aerosols are comparable to those obtained for PCBs (0.09–0.38 g/g) but are consistently lower than the values of S_0 for PAHs obtained in gasoline, dioctyl phthalate, environmental tobacco smoke, and aerosols containing high amounts of soot (0.17–4.45 g/g).

PAHs and alkanes sorbed to aerosols, which contain these compounds on formation (e.g., gasoline and tobacco smoke), are known to form a special case (25, 41, 42). It has been hypothesized that the high K_p values observed for PAHs close to combustion sources is due to the fact that the PAHs in the aerosols may not have achieved a lower equilibrium partition coefficient on dilution following formation. There may be a “nonexchangeable” strongly sorbed fraction of compound in the aerosol that will only slowly re-equilibrate as the aerosols are diluted in ambient air (25, 41, 42). It is thus possible that the equilibrium value of S_0 in the organic matter of these aerosols is not higher than in ambient aerosols, but it appears to be higher because of these formation and kinetic effects. The recent study by Dachs and Eisenreich (19) is particularly valuable because estimates were made of partitioning both to soot by adsorption and to organic matter by absorption. It was shown clearly that adsorption to soot was a major process. This is consistent with solubilities exceeding 1.0 g/g. It is difficult to conceive that a PAH could have a solubility in organic matter that exceeds its solubility in itself, i.e., the activity coefficient in solution is less than 1.0. We suggest that when S_0 is observed to exceed the fraction of organic matter in the aerosol, this is an indication of adsorption to soot of high specific area. This applies to combustion-generated aerosols and especially when there is simultaneous formation of PAH and soot particles. An unresolved issue remains as to whether the surface adsorption sites remain active as the aerosol ages and associates with semivolatile material in the gas phase.

When undertaking such interpretations, it is essential to note that a value of S_0 is subject to considerable error in sampling and deducing K_p [Jang and Kamens (16) having estimated an error of $\pm 25\%$] and errors in vapor pressures

TABLE 3. Calculated Pseudo-Solubilities (S_0) of PAHs (g/g) in a Variety of Aerosol Types

compd	coastal aerosols ^a	urban aerosols ^b	roadway aerosols ^c	wood smoke ^d	secondary aerosol ^d	gasoline ^e	DOP ^{e,f}	ETS ^g	ETS ^h	sooty aerosols ⁱ
naphthalene						2.2				
acenaphthene						0.17				
fluorene	0.34			0.67		0.26	1.5	0.79	0.43	
<i>d</i> ₁₀ -fluorene					0.13					
phenanthrene	0.11	0.29	0.22	0.15	0.83	0.42	1.3	3.8	2.0	4.5
<i>d</i> ₁₀ -phenanthrene					0.039					
anthracene	0.09	0.25	0.27	0.58	0.49	1.5	1.0		3.8	
<i>d</i> ₁₀ -anthracene				0.22						
fluoranthene	0.15	0.14	0.16	0.14	0.055	0.64	2.9	2.4	1.2	1.5
<i>d</i> ₁₀ -fluoranthene					0.035					
pyrene	0.38	0.12	0.10		0.078	0.60	2.0	1.9	1.2	1.8
<i>d</i> ₁₀ -pyrene				0.16						
chrysene	0.15	0.08				4.7		3.4	0.79	1.2
mean for PAHs	0.20	0.18	0.19	0.32	0.24	1.3	1.8	2.5	1.6	2.3
SD	0.12	0.15	0.11	0.24	0.31	1.4	0.73	1.2	1.2	1.5

^a Ligocki and Pankow (34), outdoor measurements on the coast of Oregon. ^b Cotham and Bidleman (35), outdoor measurements in Chicago. ^c Benner et al. (36), measurements in a roadway tunnel in Baltimore. ^d Jang et al. (16), smog chamber measurements. ^e Liang et al. (17), smog chamber measurements. ^f DOP, dioctyl phthalate particles. ^g Liang and Pankow (18), indoor air from a smoky room. ETS, environmental tobacco smoke. ^h K_p measured by filter desorption. ⁱ Pankow et al. (37), indoor air from a smoky room. ETS, environmental tobacco smoke. K_p measured by gas-particle sampling and analysis. ^j Dachs and Eisenreich (19), outdoor measurements from Chesapeake Bay, high adsorption to soot suspected.

associated with experimental determination, estimation of fugacity ratios (i.e., ratio of solid and liquid vapor pressures), and uncertainties about the temperature history of the aerosol. It may be that accuracy better than a factor of 2 cannot be easily achieved.

In summary, examination of K_p data transformed into S_Q is revealing in that it suggests that there are systematic differences between chemical classes such as PCB, alkanes, and PAHs in which there is apparently near-ideal absorption of PCBs into the organic matter, less ideal absorption by alkanes, but also adsorption of PAHs to soot when substances are present during aerosol formation. There is also an apparent decrease in solubility with increasing molar mass.

The implication is that K_p depends primarily on liquid vapor pressure, but it is also a function of chemical class and molar mass in each class, and different extents of sorption are expected to aerosols of different origin, age, organic matter, and soot contents. These insights into the partitioning phenomena are facilitated by calculating and interpreting the solubility.

Whereas empirical correlations between K_p , P_L , and K_{OA} are invaluable, they must be used with care and an appreciation that they can be expected to vary between chemical and aerosol classes. The most accurate correlations are likely to be those that seek a more mechanistic expression of absorption and adsorption equilibria as a function of the nature of both the sorbate and the sorbing medium.

It is thus suggested that when reporting measured values of K_p it is useful to calculate and report the corresponding solubility S_Q as a method of assessing consistency with previous data and as an indication of the presence of adsorption as distinct from absorption. When estimating K_p from correlations, for screening purposes, a one-parameter equation in P_L or K_{OA} can be used or a solubility of approximately 0.2 g/g assumed. For more accurate purposes, a two-parameter correlation with P_L or K_{OA} specific to the aerosol type and chemical class can be employed. The most accurate correlations are likely to be those that involve estimation of activity coefficients as a function of the nature of the interactions between the chemical and the organic matter or adsorbing surfaces present in the aerosol. Ultimately the latter correlations have the potential to include the effect of relative humidity, provided that it can be related to the water content of the aerosol (22).

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Literature Cited

- (1) Bidleman, T. F. *Environ. Sci. Technol.* **1988**, *22*, 361–367.
- (2) Hoff, R. M.; Strachan, W. M. J.; Sweet, C. W.; Chan, C. H.; Shackleton, M.; Bidleman, T. F.; Brice, K. A.; Burniston, D. A.; Cussion, S.; Gatz, D. F.; Karlin, K.; Schroeder, W. H. *Atmos. Environ.* **1996**, *30*, 3505–3527.
- (3) Anderson, P. N.; Hites, R. A. *Environ. Sci. Technol.* **1996**, *30*, 301–306.
- (4) Kamens, R. M.; Fan, Z.-F.; Yao, Y.; Chen, D.; Chen, S.; Vartiainen, M. *Chemosphere* **1994**, *28*, 1623–1632.
- (5) Junge, C. In *Fate of Pollutants in the Air and Water Environments*; Suffet, I. H., Ed.; John Wiley: New York, 1977; pp 7–26.
- (6) Yamasaki, H.; Kuwata, K.; Miyamoto, H. *Environ. Sci. Technol.* **1982**, *16*, 189–194.
- (7) Pankow, J. F. *Atmos. Environ.* **1987**, *21*, 2275–2283.
- (8) Pankow, J. F. *Atmos. Environ.* **1991**, *25A*, 2229–2239.
- (9) Pankow, J. F.; Bidleman, T. F. *Atmos. Environ.* **1991**, *25A*, 2241–2249.
- (10) Pankow, J. F.; Bidleman, T. F. *Atmos. Environ.* **1992**, *26A*, 1071–1080.
- (11) Pankow, J. F. *Atmos. Environ.* **1994**, *28*, 185–188.
- (12) Pankow, J. F. *Atmos. Environ.* **1994**, *28*, 189–193.
- (13) Mackay, D.; Paterson, S.; Schroeder, W. H. *Environ. Sci. Technol.* **1986**, *20*, 810–816.
- (14) Finizio, A.; Mackay, D.; Bidleman, T.; Harner, T. *Atmos. Environ.* **1997**, *31*, 15, 2289–2296.
- (15) Harner, T.; Bidleman, T. *Environ. Sci. Technol.* **1998**, *32*, 1494–1502.
- (16) Jang, M. J.; Kamens, R. M.; Leach, K. B.; Strommen, M. R. *Environ. Sci. Technol.* **1997**, *31*, 10, 2805–2811.
- (17) Liang, C.; Pankow, J. F.; Odum, J. R.; Seinfeld, J. H. *Environ. Sci. Technol.* **1997**, *31*, 3086–3092.
- (18) Liang, C.; Pankow, J. F. *Environ. Sci. Technol.* **1996**, *30*, 2800–2805.
- (19) Dachs, J.; Eisenreich, S. J. *Environ. Sci. Technol.* **2000**, *34*, 3690–3697.
- (20) Pankow, J. F.; Storey, J. M. E.; Yamasaki, H. *Environ. Sci. Technol.* **1993**, *27*, 2220–2226.
- (21) Thibodeaux, L. J.; Nadler, K. C.; Valsaraj, K. T.; Reible, D. D. *Atmos. Environ.* **1991**, *25A*, 8, 1649–1656.
- (22) Jang, M. J.; Kamens, R. M. *Environ. Sci. Technol.* **1998**, *32*, 1237–1243.
- (23) Harner, T.; Mackay, D. *Environ. Sci. Technol.* **1995**, *29*, 1599–1606.
- (24) Harner, T.; Bidleman, T. F. *J. Chem. Data* **1996**, *41*, 895–899.
- (25) Harner, T.; Bidleman, T. F. *Environ. Sci. Technol.* **1998**, *32*, 1494–1502.
- (26) Kömp, P.; McLachlan, M. S. *Environ. Toxicol. Chem.* **1997**, *16*, 2433–2437.
- (27) Harner, T.; Green, N. J. L.; Jones, K. C. *Environ. Sci. Technol.* **2000**, *34*, 3109–3114.
- (28) Karickhoff, S. W. *Chemosphere* **1981**, *10*, 844–849.
- (29) Mackay, D.; Paterson, S.; Schroeder, W. H. *Environ. Sci. Technol.* **1986**, *20*, 810–816.
- (30) Bidleman, T.; Harner, T. Sorption to Aerosols. In *Handbook of Property Estimation Methods for Chemicals: Environmental and Health Sciences*; Boethling, R. S., Mackay, D., Eds.; Lewis Publishers: Boca Raton, FL, 2000; Chapter 10.
- (31) Goss, K.-U.; Schwarzenbach, R. P. *Environ. Sci. Technol.* **1998**, *32*, 2025–2032.
- (32) Cole, J. G.; Mackay, D. *Environ. Toxicol. Chem.* **2000**, *19*, 265–270.
- (33) Seth, R.; Mackay, D.; Muncke, J. *Environ. Sci. Technol.* **1999**, *33*, 2390–2394.
- (34) Ligocki, M. P.; Pankow, J. P. *Environ. Sci. Technol.* **1989**, *23*, 77–83.
- (35) Cotham, W. E.; Bidleman, W. E. *Environ. Sci. Technol.* **1995**, *29*, 2782–2789.
- (36) Benner, B. A.; Gordon, G. F.; Wise, S. A. *Environ. Sci. Technol.* **1989**, *23*, 1269–1278.
- (37) Pankow, J. F.; Isabelle, L. M.; Buchholz, D. A.; Luo, W.; Reeves, B. D. *Environ. Sci. Technol.* **1994**, *28*, 363–365.
- (38) Foreman, W. T.; Bidleman, T. F. *Atmos. Environ.* **1990**, *24A*, 2405–2416.
- (39) Kaupp, H.; Umlauf, G. *Atmos. Environ.* **1992**, *26A*, 2259–2267.
- (40) Hoff, R. M.; Strachan, W. M. J.; Sweet, C. W.; Chan, C. H.; Shackleton, M.; Bidleman, T. F.; Brice, K. A.; Burniston, D. A.; Cussion, S.; Gatz, D. F.; Harlin, K.; Schroeder, W. H. *Atmos. Environ.* **1996**, *30*, 3505–3527.
- (41) Pankow, J. F. *Atmos. Environ.* **1988**, *22*, 1405–1409.
- (42) Odum, J. R.; Yu, J.; Kamens, R. M. *Environ. Sci. Technol.* **1994**, *28*, 2278–2285.

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