



# AN ABSORPTION MODEL OF GAS/PARTICLE PARTITIONING OF ORGANIC COMPOUNDS IN THE ATMOSPHERE

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**Abstract**—An equation that can successfully parameterize gas-particle partitioning is  $K_p(\text{m}^3 \mu\text{g}^{-1}) = (F/TSP)/A$ , where  $K_p$  is a partitioning constant,  $TSP$  ( $\mu\text{g m}^{-3}$ ) is the concentration of total suspended particulate material, and  $F$  ( $\text{ng m}^{-3}$ ) and  $A$  ( $\text{ng m}^{-3}$ ), respectively, are the particulate-associated and gaseous concentrations of the compound of interest. By itself, this equation does not indicate whether the partitioning is primarily adsorptive to surfaces, primarily absorptive into some phase(s), or some combination thereof. Much past research has indicated that plots of  $\log K_p$  vs  $\log p_L^0$  (compound vapor pressure) tend to be highly correlated, with slopes near  $-1$ . Such correlation is consistent with (though not proof of) adsorption. The governing equations are now developed for absorptive partitioning into an organic material (om) phase making up part of the  $TSP$ . The equations indicate that absorptive partitioning could well be an important sorption mechanism in the urban environment. Plots of  $\log K_p$  vs  $\log p_L^0$  are predicted to be linearly correlated when the sorption is absorptive, just as earlier theoretical work predicted such correlatability when the sorption is adsorptive. In the general case, observed  $K_p$  values may contain contributions from both mechanisms. Regardless of the relative importance of adsorptive vs absorptive partitioning in any given situation, a plot of  $\log K_p$  values vs  $\log p_L^0$  values will be correlated with a slope of near  $-1$ .

**Key word index:** Gas-particle partitioning, gas-particle distribution, absorption, adsorption, sorption, organic compounds, polycyclic aromatic hydrocarbons, PAHs, particulate matter, urban particulate material, UPM,  $TSP$ .

## NOMENCLATURE

$a_{i,g}$	activity of compound $i$ in the gas phase	$p_{L,i}^0$	vapor pressure of pure compound $i$ at the temperature of interest, sub-cooled if necessary (torr)
$a_{i,om}$	activity of compound $i$ in the om phase	$Q_d$	enthalpy of desorption from adsorbing surface ( $\text{kJ mol}^{-1}$ )
$A$	gas phase concentration ( $\text{ng m}^{-3}$ )	$Q_v$	enthalpy of vaporization of the liquid, sub-cooled if necessary ( $\text{kJ mol}^{-1}$ )
$A_i$	gas phase concentration of compound $i$ ( $\text{ng m}^{-3}$ )	$R$	gas constant ( $=8.314 \text{ J mol}^{-1} \text{ K}^{-1} = 8.2 \times 10^{-5} \text{ m}^3 \text{ atm mol}^{-1} \text{ K}^{-1}$ )
$a_{isp}$	specific surface area of suspended particles ( $\text{m}^2 \text{ g}^{-1}$ )	$T$	temperature (K)
APM	atmospheric particulate material	$TSP$	concentration of total suspended particulate material ( $\mu\text{g m}^{-3}$ )
$b_r$	intercept in a plot of $\log K_p$ vs $\log p_L^0$	UPM	urban particulate material
$f_{om}$	weight fraction that is the absorbing om phase	$X_{i,om}$	mole fraction of compound $i$ in the om phase
$F$	concentration as associated with suspended particles ( $\text{ng m}^{-3}$ )	$\zeta$	activity coefficient of a compound in the om phase on the mole fraction scale
$F_{i,om}$	concentration of compound $i$ as associated with the om phase of the suspended particles ( $\text{ng m}^{-3}$ )	$\zeta_i$	activity coefficient of compound $i$ in the om phase on the mole fraction scale.
$K_p$	gas-particle partitioning constant ( $\text{m}^3 \mu\text{g}^{-1}$ )		
$m_i$	slope in a plot of $\log K_p$ vs $\log p_L^0$		
$MW_i$	molecular weight of compound $i$ ( $\text{g mol}^{-1}$ )		
$MW_{om}$	mean molecular weight of the absorbing organic material ( $\text{g mol}^{-1}$ )		
$n_{i,om}$	number of moles of compound $i$ adsorbed in the om phase of the $TSP$ in $1 \text{ m}^3$ of air		
$n_{tot,om}$	total number of moles of all organic compounds making up the absorbing om phase in $1 \text{ m}^3$ of air		
$n_{i,g}/V$	concentration of compound $i$ in the gas phase ( $\text{mol m}^{-3}$ )		
$N_s$	surface concentration of sorption sites for adsorbing surface (sites $\text{cm}^{-2}$ )		
om	organic material		
$p_i$	gas phase pressure of compound $i$ (torr)		

## INTRODUCTION

To date, most of the modeling of gas-particle partitioning of semivolatile organic compounds (SOCs) in the atmosphere has been carried out under the assumption that the partitioning process involves mainly simple physical adsorption (Junge, 1977; Yamasaki *et al.*, 1982; Pankow, 1987). When atmospheric particulate material (APM) is mainly mineral material of continental origin, it does seem likely that simple physical adsorption will dominate the sorption

process. However, it also seems clear that phase partitioning of an absorptive nature must be playing at least some role in many circumstances; in some subset of circumstances, it might even play a dominant role. Indeed, even suspended particulate material found in remote areas will contain some organic phase material (e.g. particles of plant wax). Also, we know that urban particulate matter always contains some amorphous organic carbon from primary emissions (Turpin and Huntzicker, 1991), and from the formation of secondary organic aerosol (Pandis *et al.*, 1992). Some absorption of SOCs of interest into these types of particulate organic matter seems certain to occur. It is of interest, therefore, to determine the functionality of the corresponding equilibrium partitioning constant, as well as to determine just how important absorptive partitioning can be.

An equation that has been used with success to parameterize gas/particle partitioning is (Yamasaki *et al.*, 1982; Pankow, 1991; Pankow and Bidleman, 1992)

$$K_p = \frac{F/TSP}{A} \quad (1)$$

where  $K_p$  ( $\text{m}^3 \mu\text{g}^{-1}$ ) is a temperature-dependent partitioning constant,  $TSP$  ( $\mu\text{g m}^{-3}$ ) is the concentration of total suspended particulate material, and  $F$  ( $\text{ng m}^{-3}$ ) and  $A$  ( $\text{ng m}^{-3}$ ) are the particulate-associated and gaseous concentrations of the compound of interest, respectively. With UPM, it has become quite clear that a given SOC at a given temperature will exhibit  $K_p$  values that are reasonably similar from city to city. However, equation (1) does not, by itself, say anything about the nature of the partitioning process, i.e. whether the partitioning is primarily adsorptive, primarily absorptive, or some combination thereof.

If the partitioning is assumed to be simple physical adsorption, then theory would predict that (Pankow, 1987)

$$K_p = \frac{N_s a_{isp} T e^{(Q_1 - Q_v)/RT}}{1600 p_L^0} \quad (2)$$

where  $N_s$  (sites  $\text{cm}^{-2}$ ) is the surface concentration of sorption sites,  $a_{isp}$  ( $\text{m}^2 \text{g}^{-1}$ ) is the specific surface area for the APM,  $Q_1$  ( $\text{kJ mol}^{-1}$ ) is the enthalpy of desorption from the surface,  $Q_v$  ( $\text{kJ mol}^{-1}$ ) is the enthalpy of vaporization of the sub-cooled liquid (sub-cooled, if necessary),  $R$  is the gas constant,  $T$  is the temperature (K), and  $p_L^0$  is the vapor pressure (torr) of the compound of interest as a liquid (sub-cooled, if necessary).

Observed  $\log K_p$  vs  $\log p_L^0$  data for sorption to UPM and other types of APM tend to be well correlated according to

$$\log K_p = m_r \log p_L^0 + b_r \quad (3)$$

Equation (2) predicts that for a given temperature and for a given sample of APM, when the group  $N_s e^{(Q_1 - Q_v)/RT}$  remains nearly constant within a com-

pound class of interest (e.g. PAHs, or PCBs, etc.), then a plot of  $\log K_p$  vs  $\log p_L^0$  will be linear with a slope  $m_r = -1$  and a  $y$ -intercept of  $b_r = \log(N_s a_{isp} T e^{(Q_1 - Q_v)/RT} / 1600)$ . Pankow (1991) has discussed the reasons why the group  $N_s e^{(Q_1 - Q_v)/RT}$  can be expected to exhibit this type of constancy, and Pankow and Bidleman (1992) have discussed the fact that many field and laboratory studies of specific compound classes have obtained  $m_r$  values that are, in fact, quite similar to  $-1$ .

In a given situation, good linearity with a slope near  $-1$  in a plot of  $\log K_p$  vs  $\log p_L^0$  is a necessary, but not sufficient, condition in a proof that gas/particle sorption to APM is governed by simple physical adsorption. That is, if simple physical adsorption is the dominant mechanism in a given situation, this type of linearity needs to be present, but such an observation does not exclude other sorption mechanisms. Indeed, another mechanism that would follow this type of functionality is absorption into a liquid organic phase, or at least an amorphous organic phase. Thus, in order to determine the relative importance of adsorption and absorption in a given situation, we need to understand the equations governing both types of sorption. Thus, if slopes of near  $-1$  can be expected from both absorption and adsorption, then an important test in any given situation will be a comparison of the relative abilities of the  $y$ -intercepts predicted for the two mechanisms to cause the theoretical lines to fall near the observed lines. The purpose of this paper will be to develop the equations governing phase adsorption, and then to use those equations to test whether absorption might be playing an important role in determining gas-particle partitioning in the atmosphere.

## THEORY

When compound  $i$  is at equilibrium between the gas phase and an absorbing, organic phase, the activity of  $i$  must be equal in both phases. Thus, we have

$$a_{i,g} = a_{i,om} \quad (4)$$

where  $a_{i,g}$  is the activity of  $i$  in the gas phase, and  $a_{i,om}$  is its activity in the organic material (om) phase. When the activity of  $i$  is the same in both phases, both phases must specify the same gas phase pressure. Including activity corrections in the absorbing om phase, for gas-liquid equilibrium with compound  $i$ , we therefore have

$$p_i = X_{i,om} \zeta_i p_{L,i}^0 \quad (5)$$

where  $p_i$  is the gas phase pressure of compound  $i$ ,  $X_{i,om}$  is its mole fraction in the om phase, and  $\zeta_i$  is its activity coefficient in the om phase on the mole fraction scale. Another possible symbol for the activity coefficient would be  $\gamma$ , but this author has reserved  $\gamma$  for the activity coefficient on the molal scale. The parameter  $p_{L,i}^0$  is the vapor pressure of the compound

as a liquid (sub-cooled, if necessary). Rubel (1991) used an equation similar to equation (5) to examine equilibrium between the gas phase and liquid aerosol droplets.

If  $p_i$  has units of torr, then by the Ideal Gas Law

$$\frac{n_{i,g}}{V} (\text{mols m}^{-3}) = \frac{p_i}{760 RT} \quad (6)$$

where  $n_{i,g}/V$  represents the concentration in the gas phase in units of  $\text{mol m}^{-3}$ , and  $R = 8.2 \times 10^{-5} \text{ m}^3 \text{ atm mol}^{-1} \text{ K}^{-1}$ . The relationship between  $A_i$  and  $n_{i,g}/V$  is simply

$$A_i (\text{ng m}^{-3}) = \frac{n_{i,g}}{V} MW_i 10^9 \quad (7)$$

where  $MW_i$  ( $\text{g mol}^{-1}$ ) is the molecular weight of compound  $i$ . Combining equations (5)–(7), we obtain that

$$A_i (\text{ng m}^{-3}) = \frac{X_{i,om} \zeta_i p_{L,i}^0}{760 RT} MW_i 10^9 \quad (8)$$

Let us now focus on a unit volume of air, namely  $1 \text{ m}^3$ . For compound  $i$ , in that unit volume, we have in the om phase that

$$X_{i,om} = \frac{n_{i,om}}{n_{\text{tot},om}} \quad (9)$$

where  $n_{i,om}$  is the number of moles of  $i$  adsorbed in the om phase of the TSP in that  $1 \text{ m}^3$ , and  $n_{\text{tot},om}$  is the total number of moles of all organic compounds (including compound  $i$ ) making up that absorbing phase. (Note that if a portion of compound  $i$  is physically adsorbed onto surfaces, then that portion is *not* counted in  $n_{i,om}$ .) Combining equations (8) and (9), we then have that

$$A_i (\text{ng m}^{-3}) = \frac{n_{i,om}}{n_{\text{tot},om}} \frac{\zeta_i p_{L,i}^0}{760 RT} MW_i 10^9 \quad (10)$$

For  $n_{i,om}$ , we have in our  $1 \text{ m}^3$  volume of air that

$$n_{i,om} = \frac{F_{i,om}}{MW_i 10^9} \quad (11)$$

Of the total TSP, we now let  $f_{om}$  represent the weight fraction that is the absorbing om phase. We then have in our  $1 \text{ m}^3$  volume of air that

$$n_{\text{tot},om} = \frac{f_{om} \text{ TSP}}{MW_{om} 10^6} \quad (12)$$

where  $MW_{om}$  is the mean molecular weight of the absorbing organic material phase in units of  $\text{g mol}^{-1}$ , so that  $MW_{om} 10^6$  is the mean molecular weight in units of  $\mu\text{g mol}^{-1}$ . (The presence of compound  $i$  in the om phase will affect  $MW_{om}$ .) Therefore, by equations (11)–(12), we obtain

$$\frac{n_{i,om}}{n_{\text{tot},om}} = \frac{F_{i,om}/(MW_i 10^9)}{f_{om} \text{ TSP} \cdot MW_{om} 10^6} = \frac{F_{i,om} MW_{om}}{f_{om} \text{ TSP} MW_i 10^3} \quad (13)$$

Substituting equation (13) into equation (10), we have

$$A_i = \frac{F_{i,om} MW_{om} \zeta_i p_{L,i}^0}{f_{om} \text{ TSP} 760 RT} \quad (14)$$

When gas/particle partitioning is dominated by absorptive partitioning so that  $F = F_{i,om}$ , the partition constant  $K_p$  for compound  $i$  is thus given by

$$K_p = \frac{F_{i,om}/\text{TSP}}{A_i} = \frac{f_{om} 760 RT}{MW_{om} \zeta_i p_{L,i}^0} \quad (15)$$

Taking the logarithm of equation (15), we have

$$\log K_p = -\log p_{L,i}^0 + \log \frac{f_{om} 760 RT}{MW_{om} \zeta_i 10^6} \quad (16)$$

which may be compared with equation (3). Thus, just as when adsorptive partitioning dominates, equation (16) indicates that when absorptive partitioning dominates, then a plot of  $\log K_p$  vs  $\log p_{L,i}^0$  will tend to have a slope of near  $-1$ .

In the case of adsorptive partitioning, the Introduction discussed that when the group  $N_s e^{(Q_1 - Q_s)/RT}$  remains nearly constant within a given compound class, then a slope of near  $-1$  would be obtained in a plot of  $\log K_p$  vs  $\log p_{L,i}^0$ . For absorptive partitioning, a plot of  $\log K_p$  vs  $\log p_{L,i}^0$  will have a slope of near  $-1$  when  $1/\zeta_i$  remains constant within the compound class of interest. In equation (16), we note that  $1/\zeta_i$  appears with  $MW_{om}$  as the group  $1/(MW_{om} \zeta_i)$ .

The groups  $N_s e^{(Q_1 - Q_s)/RT}$  and  $1/(MW_{om} \zeta_i)$  are highly analogous quantities. Indeed, for adsorption,  $N_s$  (sites  $\text{cm}^{-2}$ ) is a measure of the physical accommodation of sorbing molecules on the aerosol surface area, and  $e^{(Q_1 - Q_s)/RT}$  is a measure of the energy difference for a mole  $i$  in two different states: adsorbed on a surface of interest, and in pure liquid  $i$ . For absorption,  $1/MW_{om}$  ( $\text{mol g}^{-1}$ ) is a measure of the colligative driving force for condensation into the sorbing organic matter: for a given organic matter density ( $\text{g cm}^{-3}$ ), when  $X_{i,om}$  is small one can view  $1/MW_{om}$  as being related to the moles of sites  $\text{cm}^{-3}$  into which the dissolving compound can be accommodated. Finally, we note that for a given sorbing compound,  $1/\zeta_i$  is a measure of the energy difference for a mol of  $i$  adsorbed in the om phase of interest, vs in pure liquid  $i$ .

By substituting values for the various parameters in equation (16), we can obtain an estimate of the type of  $y$ -intercept which absorptive partitioning would specify. For  $f_{om}$ , a range of 0.1–0.3 is probably reasonable. For UPM, since secondary aerosol is derived from the oxidation of fairly low molecular weight species (Pandis *et al.*, 1992), a reasonable range for  $MW_{om}$  might be around 100–300. For  $\zeta_i$ , a range of 1–5 seems reasonable for dissolution of a non-polar SOC into the at least somewhat polar organic matter in UPM. Using these values, as a range for the  $y$ -intercept, we obtain

$$\log \frac{f_{om} 760 RT}{MW_{om} \zeta_i 10^6} = -8.9 \text{ to } -7.3 \quad (17)$$

For the specific PAH chrysene,  $\log p_{L,i}^0 \approx 10^{-5.7}$  torr at  $20^\circ\text{C}$ , so that as a range for absorptive partitioning at this temperature, equations (16) and (17) give  $\log K_p \approx -3.2$  to  $-1.6$ . At  $20^\circ\text{C}$ , the “common- $y$  inter-

cept" regression parameters reported by Pankow (1991) for the co-determined group chrysene + benz[a]anthracene + triphylene give  $\log K_p = -2.0$ , which is well inside the range just given.

#### COMPARISON WITH OBSERVED $\log K_p$ vs $\log p_L^0$ CORRELATION EQUATIONS FOR UPM

As noted above, observed  $\log K_p$  vs  $\log p_L^0$  data for sorption to UPM tend to be well correlated according to equation (3). As has already been discussed, the values of the slope  $m_r$  are often similar to  $-1$ , though there is some variability. Equation (17) gives a range of possible values for  $b_r$  when  $m_r = -1$ . Pankow and Bidleman (1992) report that  $m_r$  and  $b_r$  values themselves tend to be well correlated. For PAHs, they find

$$b_r = 5.83m_r - 1.98 \quad (18)$$

and for organochlorines

$$b_r = 6.63m_r - 1.91. \quad (19)$$

Thus, when  $m_r = -1$ , for PAHs, the field data tend to give  $b_r$  values of about  $-7.8$ , and for organochlorines, the field data tend to give  $b_r$  values of about  $-8.5$ . Both of these values are well inside the range of values given by equation (17). We take this to mean that absorptive partitioning could be important in determining the gas/particle partitioning observed in the atmospheric environment.

#### CONCLUSIONS

In any given situation, both adsorptive and absorptive partitioning may be operative. The observed value of  $K_p$  will then contain contributions from both mechanisms so that for a given compound

$$K_p = \frac{1}{p_L^0} \left[ \frac{N_s a_{isp} T e^{(Q_1 - Q_v)/RT}}{1600} + \frac{f_{om} 760 RT}{MW_{om} \zeta 10^6} \right] \quad (20)$$

Thus, regardless of the relative importance of adsorptive vs absorptive partitioning, a plot of  $\log K_p$  values vs  $\log p_L^0$  may be expected to be correlated with a slope of near  $-1$ . The actual relative importance of adsorptive and absorptive partitioning in a given situation will depend on the values of the various parameters in equation (20); increasing  $a_{isp}$  and  $e^{(Q_1 - Q_v)/RT}$  will favor adsorption; increasing  $f_{om}$ , decreasing  $MW_{om}$ , and decreasing  $\zeta$  will favor absorption.

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