

## Hydrophobic Partitioning from Bulk Water to the Water/Air Interface: potential implications for fate and transport of low-solubility compounds

Örjan Gustafsson<sup>1,2</sup> and Philip M. Gschwend<sup>2</sup>

<sup>1</sup>present address: Laboratory for Isotope Geology, Swedish Museum of Natural History, Box 50007, 10405 Stockholm, Sweden. orjan.gustafsson@nrm.se

<sup>2</sup>R. M. Parsons Laboratory, MIT 48-415, Department of Civil and Environmental Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA.

### Introduction

The distribution of hydrophobic organic compounds (HOCs) between bulk air and bulk water phases is described by the chemicals' Henry's Law constants ( $K_H$ ). However, several studies have found significantly higher concentrations of HOCs associated with ambient fog droplets than what could be explained by the surrounding gas-phase concentrations and knowledge of  $K_H$  (e.g., 1,2). While initial explanations centered around fog-associated colloids, investigators are now focusing on sorption to the air/water interface as the key process accounting for the enhanced association (e.g., 3,4).

There is convincing evidence from laboratory studies that compounds such as short-chain alkanes ( $\leq C_{10}$ ) and substituted benzenes partition to the air/water-interface (e.g., 5,6). However, while several studies have predicted that this process may be of even higher significance for compounds more hydrophobic than these relatively water-soluble chemicals, the experimental data to support this expectation is largely missing. Recently, Pankow (ref. 4) estimated the air - air/water interface partition coefficients ( $K_{a-awi}$ ) for five PAHs up to and including benz[a]anthracene (aqueous activity coefficient  $\log \gamma_w = 7.7$ ; mole fraction basis). We here report on measurements of the water - air/water interface partition coefficient ( $K_{w-awi}$ ) for methylperylene ( $\log \gamma_w = 8.7$ ); this extends the range of hydrophobicities examined to include those of compounds such as benzo[a]pyrene, p,p'-DDT, most PCBs and many PCDD/Fs.

## Experimental Section

1-Methylperylene has an estimated aqueous solubility ( $4 \mu\text{g/L}$ ) which is an order of magnitude higher than perylene, yet the methyl substitution causes it to be more hydrophobic than perylene (perylene  $\log \gamma_w = 8.1$ ). These properties, in addition to expectations from its structural similarity to perylene of a high extinction coefficient and fluorescence quantum yield, makes methylperylene a good fluorescent probe for investigation of hydrophobic sorption.

All fluorescence intensity measurements were obtained with an ISS K2-Digital Fluorometer (ISS Inc., Champaign, IL) equipped with a 300-W Xe lamp, operated at 18A. The cuvette compartment was always temperature-controlled to  $25 \pm 1^\circ\text{C}$  and was constantly purged with either nitrogen or argon gas to create an atmosphere devoid of oxygen. Single-wavelength intensity data were acquired in photon-counting mode, using a PMT cooled to  $-8^\circ\text{C}$  by means of an auxiliary Peltier system in order to decrease the dark counts. Methylperylene was excited at 406 nm (8 or 16 nm bandwidth) and emissions were acquired at 442 nm (8 nm bandwidth) with a KV 418 high-pass filter inserted in the emission path. The resulting single wavelength intensities were corrected for variations in excitation intensity using a Rhodamine B quantum counter in a reference light path and for background fluorescence using an identical reference cuvette containing the clean water matrix, but without methylperylene probe.

Variations in fluorescence intensity of aqueous methylperylene solutions were used to elucidate interface sorption of this highly hydrophobic probe. The experimental system was manipulated (a) by adding incremental amounts of silica beads to the quartz cuvettes, and (b) by varying the ratio of quartz-wall surface area (SA) - in contact with the aqueous solution - to the solution volume ( $V_w$ ). The air-water interface surface area ( $SA_{a-wi}$ ) stayed constant throughout these manipulation.

## Results and Discussion

In initial experiments, we observed no additional loss of methylperylene fluorescence at equilibrium due to substantial addition of silica surface area in the form of beads. We interpret this to mean that sorption to silica was insignificant in our system. Subsequently, partitioning experiments with varying  $SA_{a-wi}/V_w$  ratios were allowed to reach equilibrium. The data showed fluorescence differences which were not simply due to dilution. Since neither photodecomposition (7) nor sorption to silica were significant, we interpret this result as partitioning to the water/air interface.

Best-fit values for the air/water-interface - water partition coefficient,  $K_{w-a-wi}$ , of methylperylene in three independent experiments were deduced to be  $1.6 \pm 0.7$ ,  $0.9 \pm 0.5$  and  $1.2 \pm 0.1$  ( $\text{mol cm}^{-2}_{a-wi}$ )/( $\text{mol mL}^{-1}_w$ ).

To the best of our knowledge, the phenomenon of hydrophobic partitioning to the air/water-interface has previously only been approached from the air side. Pankow (4) reported a good correlation for  $K_{a-a-wi}$  of PAHs with their subcooled liquid vapor pressures,  $P^*(L)$ . The ratio between our  $K_{w-a-wi}$  and Pankow's  $K_{a-a-wi}$  should simply

be given by  $K_H$ . To facilitate comparison, we converted Pankow's airside regression (of Fig. 1 in Pankow, 1997) to instead express waterside partitioning by multiplying with  $K_H$  and changing the units of pressure (from Torr to atm.):

$$K_{w-awi} = \frac{K_H}{RT} (P^{\circ}L)^{-1.20} 10^{-6.70} \quad (1)$$

where  $R$  is the gas constant ( $= 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}$ ) and  $T$  is the absolute temperature (i.e., 293 K). Substituting these values for  $R$  and  $T$  and recognizing that  $K_H$  is equal to the product of  $P^{\circ}(L) \gamma_w V_w$  (where  $V_w$  is the molar volume of water) a predictive expression for waterside partitioning of PAHs may be formulated:

$$K_{w-awi} = 10^{-9.83} (P^{\circ}L)^{-0.20} \gamma_w \quad (2)$$

Substituting the parameters for methylperylene into Equation 2 suggests a methylperylene  $K_{w-awi}$  of  $8 \text{ (cm}^{-2}_{awi}/\text{mL}^{-1}_w)$ . Considering the uncertainties involved in estimating this compound's thermodynamic properties, a factor of four difference in partition coefficient between our measurement of waterside interface partitioning and this estimate using Pankow's result must be considered as encouraging.

While this regression was developed strictly for PAHs, we have evaluated the potential role of this same process for a compound such as 2,3,7,8-TCDD. Using readily available thermodynamic data for this chlorinated dioxin, Eqn. 2 predicts a  $K_{w-awi}$  of  $15 \text{ (cm}^{-2}_{awi}/\text{mL}^{-1}_w)$  for this compound.

Partitioning to the interface between water and air may have wide implications to the environmental chemistry of hydrophobic compounds in general. In addition to enhanced bubble-mediated transport in water and droplet-mediated scavenging in air, enhanced chemical retardation observed during gaseous advection in the soil vadose zone may be explained by this process in analogy to gas-chromatographic retention. The exchange from surface water to the overlying atmosphere may be much faster than expected if diffusion across the water-side boundary layer may be "by-passed" (we calculate this pathway to become quantitatively important for compounds with  $\log Kow \geq 6$  for a mixed surface water column 10 m. The existing results suggest that the surface of a fog- or rain-drop will contain a larger fraction of a chemical than the bulk interior of the drop for compounds with hydrophobicities similar to, for instance, many PCBs. It may be anticipated that such interfacial species would be differentially available for reactions with, for example, hydroxy radicals than corresponding compounds "dissolved" inside the droplet. This work demonstrates that HOCs may partition to a significant extent from bulk water to the water/air interface. These initial results are quantitatively consistent with recent reports of airside partitioning for PAHs, and they extend the empirical evidences of partitioning to the interface between air and water to a range of hydrophobicity that is relevant to many xenobiotic compounds. Further studies investigating reactions taking place at this interface are particularly urgent.

### Acknowledgments

This work was supported by ONR grant# N00014-93-1-0883 and NOAA grant# NA36RM044-UM-S242. The first author was supported by a post-doctoral fellowship from the Swedish Natural Sciences Research Council (NFR # G-GU6331-316) while writing this abstract. The views expressed herein are those of the authors and do not necessarily reflect the views of NOAA or any of its subagencies.

### References

1. Glotfelty, D.E., Seiber, J.N. and Liljedahl, L.A. (1987) Pesticides in fog. *Nature* **321**, 603-605.
2. Capel, P.D., Leuenberger, C. and Giger, W. (1992) Hydrophobic organic chemicals in urban fog. *Atmos. Environ.* **25**, 1335-1346.
3. Goss, K.U. (1994) Predicting the enrichment of organic compounds in fog caused by adsorption on the water surface. *Atmos. Environ.* **28**, 3513-3517.
4. Pankow, J.F. (1997) Partitioning of semi-volatile organic compounds to the air/water interface. *Atmos. Environ.* **31**, 927-929.
5. Hartkopf, A. and Karger, B.L. (1973) Study of interfacial properties of water by gas chromatography. *Acc. Chem. Res.* **6**, 209-216.
6. Goss, K.U. (1994) Adsorption of organic vapors on polar mineral surfaces and on a bulk water surface: Development of an empirical predictive model. *Environ. Sci. Technol.* **28**, 640-645.
7. Gustafsson, Ö. (1997) Ph.D. Dissertation Massachusetts Institute of Technology - Woods Hole Oceanographic Institution, Cambridge, MA and Woods Hole, MA, 306 pg.