

Evaluation of Surface Adsorption on Water Droplets in the Atmosphere of Semivolatile Pesticides

Yuso Kobara¹, Motoki Nishimori¹, Wei Yongfen¹, Satoru Ishihara¹, Atsushi Yokoyama¹, Kazuhisa Ohtsu¹

¹National Institute For Agro-environmental Sciences

Introduction

Persistent organic compounds (POPs) have been detected in remote areas such as polar region, due to long-range atmospheric transport (LRAT) from source regions to more remote locations. Furthermore, semivolatile organic compounds (SOCs) of many kinds such as pesticides are present in both particle and gas phases in the atmosphere. Global transport of these SOCs has resulted in atmospheric measurements far from original sources and subsequent deposition from the atmosphere has resulted in measurable quantities of SOCs in water, sediments and biota in remote regions where they were neither used nor produced¹. Many of these compounds are known or suspected toxicants to humans and wildlife. Therefore, there is great interest in understanding, modeling and predicting their atmospheric fate and transport. One component of that fate and transport is wet deposition, which can take the form of rain, fog, clouds, and snow.

Holding capacity and washout of atmospheric SOCs by water droplets has been shown to be important as both an atmospheric removal mechanism and a source to terrestrial and aquatic systems. Washout of atmospheric SOCs has often been found to be much higher than expected based on Henry's law partitioning for fog water and cloud water². Early investigation concluded that this supersaturation was due to colloidal association, adsorption to the surface of water droplets and sub-micron particles that were not filtered out of the rainwater.

This paper refines the holding capacity and gas-phase washout equation to include adsorption to the surface of water droplets in the atmosphere. The relative importance of surface adsorption of water droplets to bulk dissolution controlled by Henry's law are also investigated.

Materials and Methods

Standard washout equation

The Washout of SOCs can be described by the total washout ratio, which is a function of both particle-phase washout and gas-phase washout³ given in the following Fig.1.

Air-water interface adsorption constant values (K_{ia})

Air-water interface adsorption constants can be inferred by extrapolation of gas-particle partitioning coefficients to 100 % humidity on a variety of surfaces, but unfortunately, direct experimental values of K_{ia} values are not available for pesticides, so estimations

$$W_r = \frac{C_s}{C_a} = W_p \phi + W_c (1 - \phi) = W_p \phi + \frac{(1 - \phi)}{H'} + K_{oa} \frac{6000}{d_s} (1 - \phi)$$

W_r : unitless total washout
 C_s : concentration of SOC in rain (ng/m^3 rain)
 C_a : concentration of SOC in air (ng/m^3 air)
 ϕ : fraction of SOC associated with particles
 W_p : unitless particle-phase washout
 W_c : unitless gas-phase washout
 H' : dimensionless Henry's law
 K_{oa} : air-water interface adsorption constant
 d_s : diameter of waterdrops (mm)

Fig. 1. The Washout of SOCs described by the total washout ratio, which is a function of both particle-phase washout and gas-phase washout

must be made by a poly-parameter linear free energy relationship^{4,5} (Fig. 2).

$$\ln K_{oa} = 8.39 + 0.14 R_2 - 0.33 \pi_2^N + 1.18 \sum \alpha_n^N + 4.64 \sum \beta_n^N + 0.68 \log K_{oa}$$

$\sum \alpha_n^N$, $\sum \beta_n^N$: Abraham's hydrogen bond parameters relating to electron acceptor and donor parameters, respectively
 R_2 : excess molar refraction
 π_2^N : dipolarity/polarisability
 $K_{oa} = K_{oa} / K_{oa} = K_{oa} (RT/H)$

Fig. 2 Air-water interface adsorption constants by a poly-parameter linear free energy relationship (pp-LFER).

Results and Discussion

Both PAHs and nitrogen-containing herbicides exhibit strong relationships between Henry's law constants and sub-cooled liquid saturated vapor pressures (Fig. 3). The fitted relationships for PAHs and nitrogen-containing herbicides indicate in Fig. 3. Henry's law constants for organochlorine and organophosphorous pesticides range from 1.5×10^{-1} to $1.72 \times 10^2 \text{ Pa m}^3 \text{ mol}^{-1}$ and from 1.1×10^{-5} to $3.2 \text{ Pa m}^3 \text{ mol}^{-1}$, respectively, but there are no relationship with sub-cooled liquid saturated vapor pressures.

The air-water adsorption constants for both PAHs and nitrogen-containing herbicides correlate with sub-cooled liquid saturated vapor pressure (Fig. 4), giving rise to the indicated relationships in Fig. 4. The air-water adsorption constants for organochlorine and organophosphorous pesticides are independent of sub-cooled liquid saturated vapor pressure due to a counteraction between increasing octanol/air partitioning (K_{OA}) and decreasing Abraham's hydrogen bond basicity values with decreasing vapor pressure.

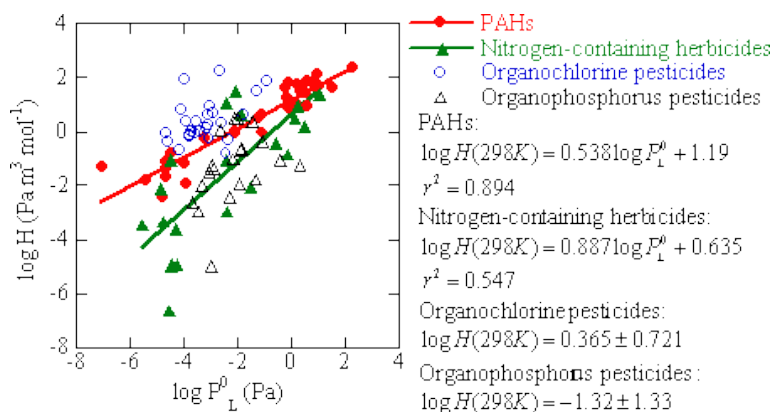


Fig. 3 Relationship between Henry's law constants and sub-cooled liquid saturated vapor pressures at 288 K.

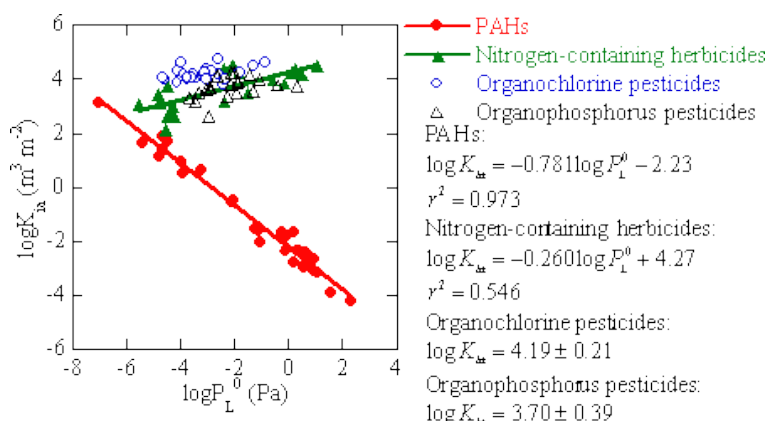


Fig. 4 Relationship between estimated air-water interface adsorption constants with sub-cooled liquid saturated vapor pressures at 288 K.

Rain, fog, clouds, and snow do not contain a single size droplet, but a spectrum of water droplets diameters described by the drop size distribution (DSD). In this study, the relative importance of bulk dissolution controlled by Henry's law can be compared to adsorption to the surface of water droplets assuming 10 mm/h rainfall, spherical water droplets (1 mm) and equilibrium conditions between the air and water droplets in the atmosphere. Both dissolution into the bulk water of the water droplet and adsorption to the surface of the water droplet are strong function of f , the fraction of compound associated with particles in the atmosphere. As f decreases, the gas-phase washout ratio for both adsorption and dissolution increases. This is to be expected since $1-f$, is available to partition to either the surface of the raindrop or the bulk water. As a sub-cooled liquid saturated vapor pressure of approximately 10^{-3} Pa, there is a switch from dissolution dominated partitioning to adsorption dominated partitioning (Fig. 5). PAHs with sub-cooled liquid saturated vapor pressures 10^{-3} Pa at 298 K include those with four more aromatic rings. The corresponding plots for nitrogen-containing herbicides indicate that adsorption to the surface of water droplets greatly exceeds dissolution to the bulk of water droplets (Fig. 5).

For instance, more polar compounds such as currently used pesticides have relatively high, calculated K_{ia} values, and gas adsorption may be even more important than nonpolarSOCs may be even more important than the nonpolarSOCs. These results indicate traditional evaluation methods may underestimate holding capacity and washout of atmospheric SOC by water droplets and even loadings to terrestrial and aquatic surfaces.

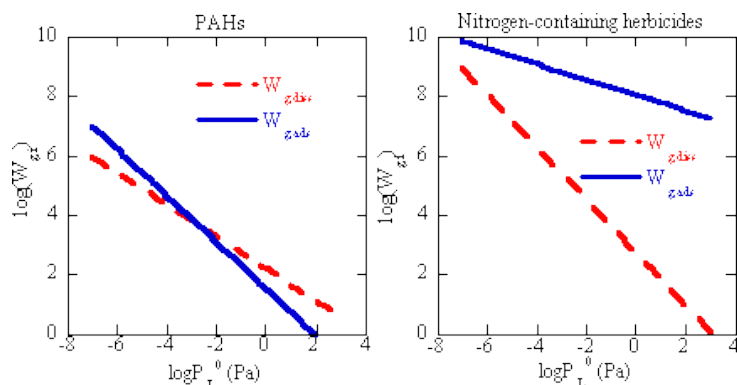


Fig. 5 Calculated equilibrium gas-phase washout due to adsorption and dissolution with respect to the sub-cooled liquid saturated vapor pressure (rainfall 10 mm/hr, raindrop diameter 1 mm, $\phi=0.5$)

References

1. AMAP Assessment 2002: *Persistent Organic Pollutants in the Arctic*, Arctic Monitoring and Assessment Programme (AMAP).

2. Goss, K.-U., *Atmospheric Environment* 28: 3513-3517.
3. Simcik M.F. (2004) *Atmospheric Environment* 38: 491-501.
4. Abraham, M.H., Chadha, H.S., Whiting, G.S. and Mitchell, R.C. (1994) *J. Pharm. Sci.* 83: 1085-1100.
5. Abraham, M.H., Le, J., Acree, Jr., W.E., Carr, P.W. and Dallas, A.J. (2001) *Chemosphere* 44: 855-863.