

Scavenging Effect of Precipitation on Volatile Organic Compounds in Ambient Atmosphere

Emi Sato,² Kiyoshi Matsumoto,¹
Hiroshi Okochi,² and Manabu Igawa*¹

¹Department of Applied Chemistry, Faculty of Engineering,
Kanagawa University, 3-27-1 Rokkakubashi, Kanagawa-ku,
Yokohama 221-8686

²Faculty of Urban Environmental Sciences,
Tokyo Metropolitan University, Asahigaoka,
Hino, Tokyo 191-0065

Received August 30, 2005; E-mail: igawam01@kanagawa-u.ac.jp

Hydrophobic volatile organic compounds (VOCs) are usually found in rainwater with higher concentrations than the values determined from Henry's law partitioning. Laboratory experiments demonstrated that dissolved organic compounds, such as humic acids, act as cosolvents to solubilize the VOCs. Wet removal by rainfall is a significant sink of trace VOCs.

Hydrophobic volatile organic compounds (VOCs) emitted to the atmosphere are decomposed by photochemical reactions in the troposphere and transferred in parts to the stratosphere. A small amount of the hydrophobic VOCs is thought to be scavenged by rainwater from the atmosphere and deposited on the Earth's surface. Wet scavenging processes of VOCs are not yet clearly understood, although several studies have focused on VOCs in rainwater.^{1,2}

It has been found that rainwater contains a few hydrophobic organic compounds with concentrations much higher than estimated from Henry's law constants and ambient atmospheric concentrations.^{2,3} In order to understand the behavior of VOCs in the atmospheric–terrestrial system, it is necessary to clarify the mechanism concerning the supersaturation of organic compounds in atmospheric liquid droplets. Previous studies have reported that this supersaturation can be attributable to adsorption onto droplet and/or ice surfaces,^{2,3} and submicron particles in the droplets.⁴ Okochi et al.² also suggested that the presence of surfactants in rain droplets could contribute to this supersaturation.

Both from field observation and laboratory experiments, we found cosolvent effects due to dissolved organic compounds, which keep VOCs with supersaturated concentrations in the rain droplets. Our results also suggest that wet removal processes by rainfall is a significant sink for trace hydrophobic VOCs, such as carbon tetrachloride and 1,1,1-trichloroethane.

VOCs in air and rainwater samples were collected simultaneously on the roof of a six-story building on the campus

of Kanagawa University in Yokohama, a large industrial and commercial city with a population of 3.5 million, from September to November (from late summer to early winter), 2003. During 10 rain events, 70 rainwater samples were collected simultaneously with air samples.

Gaseous VOCs were collected on an adsorbent consisting of Carboxen 1000 (140 mg, 60–80 mesh size, from Supelco, Inc.) and Carbopack B (190 mg, 60–80 mesh size, from Supelco Inc.), which were filled in series vertically (Carbopack B on top, Carboxen 1000 at the bottom) in a glass or stainless steel air-sampling tube, at a flow rate of 20 mL min^{−1} using an automatic sampling system (Perkin-Elmer, Inc., STS 25) with an interval of 3 h. Rainwater samples were collected by an automatic rain sampler (Konan Kaihatsu, Ltd.). After sampling, the VOCs in the rainwater were collected by a purge-and-trap (PT) method on the same adsorbent as in the case of air sampling.² The purge was performed using high-purity nitrogen at 40 mL min^{−1} during 15 min. The tubes were conditioned by purging them with high-purity helium at 350 °C for 6 h beforehand and then sealed with diffusion limiting caps at their inlets until just before use.

VOCs collected on the adsorbent by air sampling, or PT method, were desorbed by heating in an automatic thermal desorption system (ATD) (Perkin-Elmer, Inc., ATD400) and then injected into a gas chromatograph/mass spectrometer (GC/MS) (Perkin-Elmer, Inc., Autosystem GC/Q-Mass) equipped with a capillary column (Supelco Inc., VOCOL). Water blank values were generally below detection limits, so that the measurements were expected to be free of contaminants. Detailed explanations of the VOCs analyses by the ATD-GC/MS system have been reported elsewhere.²

Table 1 summarizes the measured concentrations of the VOCs in the atmosphere and rainwater, the predicted values in the rainwater from Henry's law partitioning, and the Henry's law constants.⁵ Toluene was determined as the dominant VOC compound in the atmosphere, which is similar to previous studies.⁶ Each VOC in the atmosphere had concentrations within the range reported by the other recent investigations at an urban site in Japan.⁶ On the other hand, dichloromethane, benzene, and toluene were found as major compounds of the VOCs in rainwater. Hydrophobic VOCs were detected in rainwater with higher concentrations than the values predicted from Henry's law partitioning, which mean that larger amounts of VOCs are removed efficiently from atmosphere by rain processes and deposited on the surface aquatic system as reported previously.^{2,3} This effect is more significant for the species with lower atmospheric concentrations, such as carbon tetrachloride and 1,1,1-trichloroethane.

It is important to understand the mechanisms that allocate VOCs in rain droplets with higher concentrations than the predicted values. The decreased polarity of the solution probably influences the supersaturation of VOCs in liquid phase, although other mechanisms have been also suggested in previous studies. It is possible that the co-existence of dissolved organic compounds that come from ambient air in the rainwater contributes to the decreased polarity which makes the VOCs more soluble in the droplets. In order to estimate the influence of co-existing dissolved organic compounds on the supersaturation of VOCs in liquid phase, a laboratory experiment involving

Table 1. Measured Concentrations of VOCs in the Atmosphere and Rainwater, Their Predicted Values, the Ratio of Measured/Predicted in Rainwater, and Henry's Law Constant (H) at 298.15 K^{a)}

	Atmosphere/ppbv				Rainwater/nM				H/L atm mol ⁻¹		
	Measured concentrations				Predicted values					Ratio of measurement to prediction	
	Mean	Std.	Min.	Max.	Mean	Std.	Min.	Max.			
Dichloromethane	0.878	0.764	0.076	2.57	2.67	2.19	n.d.	9.59	0.319	8.4	2.0
Carbon tetrachloride	0.084	0.034	n.d.	0.129	0.914	0.463	0.142	2.79	0.007	136	23.0
1,2-Dichloroethane	0.043	0.026	n.d.	0.078	0.518	0.431	n.d.	1.81	0.022	23.6	0.9
1,1,1-Trichloroethane	0.029	0.020	n.d.	0.079	0.663	1.12	n.d.	9.11	0.003	241	13.0
Trichloroethylene	0.686	0.546	0.640	1.71	0.906	1.10	n.d.	5.19	0.113	8.0	9.1
Tetrachloroethylene	0.123	0.137	n.d.	0.562	0.332	0.347	n.d.	2.55	0.015	22.3	15.3
Benzene	0.364	0.273	0.059	0.884	3.20	1.45	1.27	8.27	0.094	34.0	5.5
Toluene	4.41	4.42	0.539	14.9	2.88	2.36	n.d.	7.96	1.18	2.4	6.7
<i>m,p</i> -Xylene	0.485	0.503	n.d.	1.43	1.06	0.759	0.468	6.25	0.141	7.5	7.0
<i>o</i> -Xylene	0.281	0.219	0.036	0.631	0.855	0.508	0.144	2.56	0.083	10.4	5.0

a) The predicted values were calculated by using atmospheric concentrations and Henry's law constant.⁵

the partitioning of VOCs was conducted by means of the EP-ICS (equilibrium partitioning in closed systems) technique in combination with SPME (solid-phase microextraction)⁷ using methanol and humic acid as the substitute for the dissolved organic compounds in rainwater.

For the determination of the partition coefficients of VOCs, six vials with a total volume of 20 mL each and methanol at concentrations of 0.4, 1.0, 2.0, 5.0, and 10% (v/v) were prepared. Into three vials, 0.5 mL each methanol solution was injected, and 16 mL each methanol solution was pipetted into the other set of three vials. Subsequently, 2 μ L of a 50 ppm VOCs stock solution, which was prepared from a 1000 ppm in methanol of standard mixture solution including 23 VOCs (Kanto Kagaku Corp.) in use, was injected under the solution surface, and the vials were immediately capped. After a 24 h incubation period, in which each vial was kept at 25 °C in an aluminum block thermostatic bath (Taitec Corp., DTU-1C), the VOCs in the headspace (HS) were determined by the HS SPME-GC/MS. The partition coefficient is defined as $H = C_w/C_g$ where C_w and C_g are the aqueous and headspace concentration of the compounds (mol m^{-3}). H can be then calculated from the following equation:

$$H = \frac{V_{g2} - rV_{g1}}{rV_{w1} - V_{w2}}, \quad (1)$$

where r is the ratio of the headspace concentrations ($r = C_{g1}/C_{g2}$ with C_{g1} and C_{g2} the concentration in closed two-phase systems with a low and a high liquid content, respectively) and V_{g1} and V_{g2} are the gas volumes and V_{w1} and V_{w2} are the liquid volumes of the closed two-phase systems. The subscripts 1 and 2 indicate that the systems with a low and high liquid volume, i.e., 0.5 and 16 mL, respectively. The ratio r in the EPICS-SPME method was directly calculated from the ratio of the peak areas in the chromatograms. Comparison between the determined partition coefficient of each of the VOCs and the concentration of methanol suggests that co-existence of methanol contributes to the solubilization of VOCs in aqueous solution. The results for benzene and toluene are shown in Fig. 1. El-Zoobi et al.⁸ have reported that the water solubility of most hydrocarbons can be increased considerably when a cosolvent such as methanol and ethanol, is present in water phase. In our experiments, it is also thought that methanol acts as a cosolvent to increase the solubility of hydrophobic VOCs. However, methanol concentrations below 5% (v/v) have little affect on the air–water equilibrium partitioning.

In ambient rainwater, methanol is not dissolved in such a high concentration as the above experiment, but many different organic compounds are dissolved, which can be analyzed as dissolved organic carbon (DOC). Although chemical compositions of DOC in rainwater have not yet been sufficiently characterized, considerable amounts of macromolecular compounds, such as humic-like substances, have been found in fogwater and water-soluble fraction of aerosols.⁹ In this study, humic acid was used as a substitute for dissolved organic compounds to estimate the influence of DOC on the supersaturations of VOCs in liquid phase.

Humic acid solutions, filtered through a membrane filter (pore size, 0.45 μ m), were prepared in the vials with concentrations of 0, 0.5, 0.9, 3.7, and 7.5 ppmC, and then 2 μ L of a 50 ppm VOCs stock solution was added. Here, humic acid

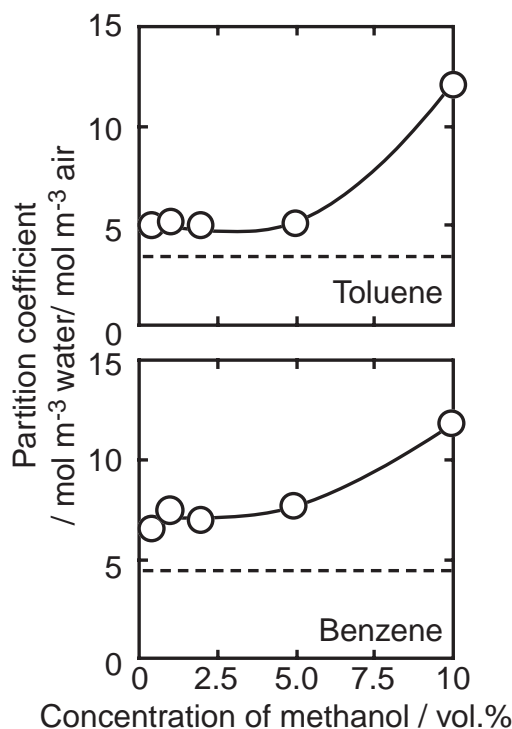


Fig. 1. Comparison of the partition coefficients of benzene and toluene with the concentration of methanol. The coefficient at each concentration is the average of nine experimental data points, and the mean R.S.D. is 18% for benzene and 15% for toluene, respectively. The dotted lines indicate the values calculated from the Henry's law constant at 25°C, which is shown in Table 1.

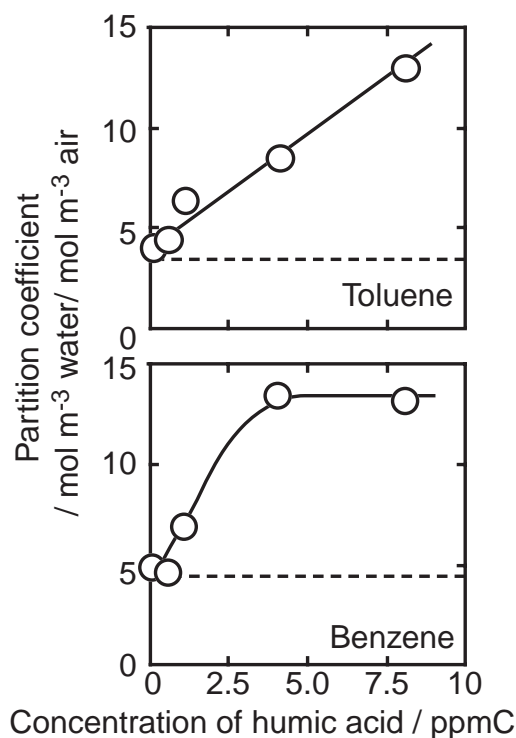


Fig. 2. Comparison of the partition coefficients of benzene and toluene with the concentration of humic acid. The coefficient at each concentration is the average of nine experimental data, and the mean R.S.D. is 13% for benzene and 11% for toluene, respectively. The dotted lines indicate the values calculated from the Henry's law constant at 25°C, which is shown in Table 1.

powder derived from low-carbonized peat (C: 60–65, H: 4–5, and O: 30–35%; Wako Pure Chemical Industries, Ltd.) was used. After a 24 h incubation period, in which was kept at 25 °C, the VOCs in the headspace were determined, and the partition coefficient of each VOCs were calculated in the same manner as the case of the experiments using methanol. On comparison of the partition coefficients of the VOCs with those of humic acid, the co-existence of humic acid increases the solubility of the VOCs. Figure 2 shows the results for benzene and toluene. DOC concentrations in continental rainwater have been estimated to be about 0.1–5 ppmC.¹⁰ Our results indicated the presence of humic acid with concentrations from 0.5 to 7.5 ppmC, which correspond to expected range of DOC concentration in the ambient precipitation, contributes to the solubility of the VOCs in ambient rainwater. The solubilities of the VOCs may be increased by the presence of some surfactants,² while the humic acid slightly affected the surface tension; the surface tension decreased to about 99% at 8 ppmC of humic acid concentration.

The present study demonstrated that VOCs are usually contained in rainwater with higher concentrations than the values theoretically expected from Henry's law partitioning. Both field and laboratory experiments suggest that a cosolvent effect of dissolved organic compounds that come from ambient air causes the supersaturation and increases deposition flux of the VOCs from the atmosphere to land surface. Wet removal pathways by rainfall are a significant sink of VOCs, especially

for trace VOCs, such as carbon tetrachloride and 1,1,1-trichloroethane.

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References

- 1 K. Kawamura, I. R. Kaplan, *Environ. Sci. Technol.* **1983**, 17, 497.
- 2 H. Okochi, D. Sugimoto, M. Igawa, *Atmos. Environ.* **2004**, 38, 4403.
- 3 K. U. Gross, *Atmos. Environ.* **1994**, 28, 3513.
- 4 D. L. Poster, J. E. Baker, *Environ. Sci. Technol.* **1996**, 30, 341.
- 5 K. Urano, *Haikibutsu Gakkaishi* **1995**, 6, 13.
- 6 N. Yamamoto, H. Okayasu, S. Murayama, S. Mori, K. Hunahashi, K. Suzuki, *Atmos. Environ.* **2000**, 34, 4441.
- 7 J. Dewulf, H. V. Langenhove, P. Everaert, *J. Chromatogr., A* **1999**, 830, 353.
- 8 M. A. El-Zoobi, G. E. Ruch, F. R. Groves, *Environ. Sci. Technol.* **1990**, 24, 1332.
- 9 M. C. Facchini, S. Fuzzi, S. Zappoli, A. Andracchio, A. Gelencsér, G. Kiss, Z. Krivácsy, E. Mészáros, H.-C. Hansson, T. Alsberg, Y. Zebühr, *J. Geophys. Res.* **1999**, 104, 26821.
- 10 R. J. Kieber, B. Peake, J. D. Willey, G. B. Avery, *Atmos. Environ.* **2002**, 36, 3557.