ELSEVIER

AE International – Asia

Atmospheric Environment 38 (2004) 4403–4414

ATMOSPHERIC
ENVIRONMENT

www.elsevier.com/locate/atmosenv

The enhanced dissolution of some chlorinated hydrocarbons and monocyclic aromatic hydrocarbons in rainwater collected in Yokohama, Japan

Hiroshi Okochi*, Daisuke Sugimoto, Manabu Igawa

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

Received 8 September 2003; received in revised form 20 February 2004; accepted 3 March 2004

Abstract

By simultaneous sequential sampling of gas and rainwater from 1999 to 2000 in the campus of Kanagawa University in Yokohama, Japan, we investigated the wet-scavenging process of volatile organic compounds, some chlorinated hydrocarbons (CHs) and monocyclic aromatic hydrocarbons (MAHs), via rain droplets. Their volume-weighted mean concentrations in 125 rainwater were 4.98 nM for dichloromethane, 3.71 nM for toluene, 2.00 nM for benzene, 0.93 nM for 1,2-dichloroethane, 0.62 nM for o-xylene, 0.57 nM for *m,p*-xylene, 0.51 nM for *p*-dichlorobenzene, and 0.35 nM for trichloromethylene. Their rainwater concentrations did not depend on the rainfall intensity, and the temporal variation of their concentrations was similar to that of gas-phase concentrations. The dissolution of CHs and MAHs into rainwater, however, was larger than expected from their gas-phase concentrations at the ground and their temperature-corrected Henry's law constants. A simple below-cloud scavenging model, which was developed by Levine and Schwartz (Atmos. Environ. 16 (1982) 1725) could explain the independence of the rainfall intensity but not explain their enhanced dissolution in rainwater. The results of this study indicate the estimated concentrations, which were based on the Henry's law equilibrium, considerably underestimate the wet-deposition fluxes of CHs and MAHs onto the ground.

Keywords: Chlorinated hydrocarbons; Monocyclic aromatic hydrocarbons; Henry's law; Rainwater; The falling droplet approach

1. Introduction

The fate of volatile organic compounds (VOCs), which are emitted into the troposphere from various anthropogenic and biogenic sources, remains to be elucidated. In general, air pollutants in the lower troposphere are dispersed by horizontal advection and upward diffusion, and removed by deposition process (wet and dry deposition) and chemical transformation, depending on their physico-chemical properties. A mathematical model of the fate of 1,4-dichlorobenzene, which is one of the representative VOCs used often as an insecticide and antiseptic, in the lower troposphere, for example, indicates that both the horizontal advection and the upward diffusion are the main factors for controlling their concentration in the air and that the contribution of the wet-deposition is minor (Yoshida and Shigeoka, 1992). The wet-deposition process of VOCs, which are less hydrophobic compounds below octanol–water coefficient 10^5, is generally described simply based on Henry's law equilibrium in such mathematical models although the hypothesis that the equilibriums are established at the interface of air/precipitation is not verified.

---

*Corresponding author. Division of Environmental and Amenity Ergonomics, Department of Intelligent Systems, Tokyo Metropolitan Institute of Technology, 6-6 Asahigaoka, Hino City, Tokyo 191-0065, Japan. Tel./fax: +81-42-585-8626.
E-mail address: hokouchi@cc.tmit.ac.jp (H. Okochi).

1352-2310/$ - see front matter
doi:10.1016/j.atmosenv.2004.03.053

The presence of hydrophobic organic compounds (HOCs) such as PAHs, PCBs, and pesticides has been reported in fogwater and rainwater (e.g. Kawamura and Kaplan, 1983; Ligocki et al., 1985; Czuczwa et al., 1988; Capel et al., 1991; Hart et al., 1993, Poster and Baker, 1996a,b; Igawa et al., 1993). Some investigators have reported that the dissolution of HOCs into fogwater is considerably larger than expected from the surrounding gas-phase concentration and Henry's law constants (Glotfelty et al., 1987; Gross, 1994). This is in striking contrast to the dissolution of inorganic water-soluble gases such as nitric acid into the droplets, whose concentration is considerably lower than Henry's law prediction. There are several hypotheses to explain the discrepancy. Valsaraj et al. (1993) have divided these hypotheses into the following three aspects and demonstrated that the third is the most important factor in explaining the enhanced uptake of HOCs into fogwater:

(i) the temperature correction for Henry's law constant at 25°C,
(ii) the effect of dissolved and colloidal organic materials in fogwater, and
(iii) the effect of the large specific air–water interfacial area available for adsorption of hydrophobic organics.

The concentration of a variety of VOCs in rainwater has been also reported, but there is limited data on coupling of air and rainwater (Czuczwa et al., 1988; Capel et al., 1991; Hart et al., 1993). Some researches have reported that VOCs in rainwater can be predicted by equilibrium partitioning between air and water according to Henry's law (Ligocki et al., 1985; Hart et al., 1993). These results are in contrast to their dissolution into fogwater. This might be because of lower concentration of dissolved and colloidal organic materials in rainwater, which leads to the reduction of the effect of the second factor as stated above, and larger rain droplets radius, which leads to the reduction of the effect of the third factor. To our knowledge, however, the details of wet-scavenging process of atmospheric VOCs via rainwater has never been discussed.

We here report that the concentrations of six chlorinated hydrocarbons (CHs) and five monocyclic aromatic hydrocarbons (MAHs) in rainwater collected in Yokohama, which is one of representative urban areas in Japan, and they are higher than expected from their gas-phase concentration at the ground and their temperature-corrected Henry's law constants. In addition, we discuss the mechanism of the enrichment of VOCs in rainwater.

2. Experimental section

Sampling of gas and rainwater was performed on the rooftop of a four (until July, 1999) or six-storied building (from July, 1999) in the campus of Kanagawa University in Yokohama (N 35.26°, E139.38°), Japan. Kanagawa University is less than 3 km from the Yokohama Bay area and is in a residential area near the city center. Eleven 3-day sampling campaigns for gas-phase VOCs were performed from May, 1999 to November, 2000 and 73 samples were collected during rain periods. Thirteeen rain events (125 samples) were collected during the same period. We performed the analysis based on data sets of coupling of air and rainwater.

VOCs in the gas phase were collected at a rate of 5 ml min^{-1} every 3 h using Perkin-Elmer Model STS-25 (Woolfenden, 1997) equipped with 24 silanized glass tubes (3.5 inch long, 4 mm i.d., and 6 mm o.d.), in which a quantity of 190 mg Carbopack B ($S = 100\,\mathrm{g\,m^{-2}}$, 60/80 mesh) and a quantity of 140 mg Carboxene 1000 ($S = 1200\,\mathrm{g\,m^{-2}}$, 60/80 mesh) were fixed in series vertically (Carbopack B on top, Carboxene 1000 at the bottom) (Nagai et al., 1991; Ichihashi et al., 1995). All adsorbents were obtained from Supelco, Co. One microliter of 5 mg L^{-1} fluorobenzene was added to the sampling tube from the side of Carbopack B under the flow of high purity nitrogen (over 99.9999%) at 50 ml min^{-1} and then purged for 30 min. Condensation was prevented using a trap tube (1/4″ × 3/8″, Tygon SE-2000, Norton Inc.) filled with 1 g $\mathrm{Mg(ClO_4)_2}$ (8–24 mesh, Wako Chemical), which was connected to the inlet of the sampling tube (on the Carbopack B filled side). Diffusion limiting caps were installed at the inlet of the trap tubes. Before sampling, the glass tubes were conditioned by purging them with high-purity helium (over 99.9999%) at 100 ml min^{-1} and 350°C for 6 h. After cooling down to room temperature, the tubes were sealed with 1/4″ caps (Swagelock). The tubes were held in a desiccator for storage.

Rainwater was collected at 1 mm intervals from the beginning by an originally developed automatic rain sampler (Conan Hard & Soft Co.), which consists of a 246 mm diameter funnel with a cover, rain sensor, volume sensor, and turntable equipped with 36 Teflon® bottles in a refrigerator. The opening and shutting time of the cover and the rotating time of the turntable were recorded using a personal computer (NEC PC-98 note). After weighing, the rainwater samples were immediately transferred into the 8 ml brown vials sealed with Teflon® liner and stored in a refrigerator at 4°C. Before the use, the clean brown vials were heated at 105°C for 2 h and cooled to room temperature in a desiccator filled with high-purity nitrogen (over 99.9999%) until they went down to the room temperature. After sampling, VOCs in 5 ml rainwater were collected using purge and trap method (Nagai et al., 1991; Ichihashi et al., 1995) with the same glass tubes, which was used for sampling VOCs in the ambient air. The purge was performed using high-purity nitrogen (over 99.9999%) at 40 ml min^{-1} during

15 min. Likely impurities in the nitrogen were removed by a glass tube plugged with Carboxene 563 (Supelco Co.). Water vapor was also removed by a trap tube, which was filled with 1 g $Mg(ClO_4)_2$, in front of a sampling glass tube.

For the analysis of VOCs in atmospheric and rainwater samples, a GC-MS (AutoSystem GC and Q-MASS 910, Perkin-Elmer Co.) system connected to a thermal desorption unit ATD 400 (Perkin-Elmer Co.) was used. The GC column used was VOCOL (60 m × 0.25 mm i.d., 1.5 μm film thickness, Supelco Co.). Details of analytical conditions are given in Igawa et al. (1999). The standard deviations of the relative peak height of the reference compounds (corresponding to 50 ng) to the internal standard (Fluorobenzene, Kanto Chemical Co.) were found to range from 2.7% to 9.0% of the mean values ($n=5$). Recoveries of analytical surrogate into ultrapure water (Milli-Q VOC SP) ranged from 90 to 109% ($n=3$). Water blanks were generally free of contaminants, i.e. below instrumental detection limits.

3. Results and discussion

3.1. Physico-chemical properties of VOCs determined in this study

Some physico-chemical properties of six chlorinated hydrocarbons and five aromatic hydrocarbons, which were determined in this study, are summarized in Table 1. We here define Henry's law constant as the ratio of concentration in water to partial pressure in air, i.e. $M\,atm^{-1}$. Some properties, except the right three columns, are well known but data for enthalpy changes of air–water transfer, vaporization, and solubility are sparse. Values of enthalpy change are needed to discuss their temperature dependence so the estimates are used. The enthalpy change of air–water transfer, ΔH_{Henry}, was estimated for dichloromethane and carbon tetrachloride from the data of Gossett (1987) and for the other compounds from the data of Dewulf et al., 1995. Both the enthalpy change of vapor pressure, ΔH_{VAP} and the enthalpy change of water solubility, ΔH_{ws}, were estimated according to Schwarzenbach et al. (1995) using the data from Lide (2001) and Weast (1986).

3.2. Atmospheric and rainwater concentration of CHs and MAHs

The arithmetic mean and the range of concentration of VOCs in the atmosphere during rain periods are presented in Table 2, together with both the arithmetic and volume-weighted mean and their ranges of rainwater concentration. Their means were calculated assuming concentrations below the detection limits to be zero. The order of atmospheric concentration was as follows: for chlorinated hydrocarbons, dichloromethane (DCM) > trichloromethylene (TRL) > tetrachloroethylene (TEL) > 1,2-dichloroethane (1,2-DCE) > carbon tetrachloride (CTC) > 1,1,1-trichloroethane (1,1,1-TCE), and for monocyclic aromatic hydrocarbons, toluene (TOL) ≫ benzene (BEN) > *m,p*-xylene (*m,p*-XY) > *p*-dichlorobenzene (*p*-DCB) > *o*-xylene (*o*-XY). These range are the same as our previous ones (Igawa et al., 1999). The order of rainwater concentrations was as follows: for CHs, DCM ≫ 1,2-DCE > TRL > CTC, TEL, 1,1,1-TCE, and for MACs; TOL > BEN > *o*-XY, *m,p*-XY, *p*-DCB. The average concentrations of CTC, TEC, and 1,1,1-TCE were below detection limits. It was the same order as our previous reported values for both CHs and MAHs in rainwater, (Igawa et al. (1999)), too. However, the concentrations of CHs in this study were lower than our previous reported values, while the concentrations of MAHs were higher than those reported. The order of CHs this ordering concided with the previous ones in concentration in rainwater was somewhat different from that in the atmosphere, probably due to their dissolution process into rain droplets.

The enrichment factors, E_{avg} are also shown in the last column in Table 2. Here we define the enrichment factor as D_{obs}/K_H, where K_H is the Henry's law constant ($M\,atm^{-1}$) corrected at the average temperature during rainy periods and D_{obs} is an observed distribution constant between rainwater and gas-phase, i.e. C_{rain}/p_{gas} ($M\,atm^{-1}$). The average concentrations shown in Table 2 were used as C_{rain} and p_{gas}, respectively. The E values are higher than 1, indicating that the observed concentration of each VOCs in rainwater is larger than the values expected from their gas-phase concentration at the ground and their Henry's law constants corrected by the ground-level temperature. These results differ from the dissolution behavior of PAHs into rainwater according to Henry's law, which was observed by Ligocki et al. (1985).

The temporal variation of selected CHs and MAHs in the gas phase and rainwater collected in June 17–20, 1999 together with wind direction and speed is shown in Fig. 1. DCM and TOL were the most abundant in rainwater among CHs and MAHs, respectively, while 1,2-DCE and BEN were the second abundant. The atmospheric concentrations of DCM and TOL tended to increase with the change of wind direction from southern to northern, while the concentrations of 1,2-DCE and BEN fluctuated. It started to rain when the southern strong wind changed to the northern middle wind, which continued to prevail during the rain periods. Their concentrations in rainwater changed like their corresponding atmospheric concentrations, which were simultaneously observed at the ground. This result indicates that below-cloud scavenging process may control their rainwater concentrations.

Table 1
Some physical properties of VOCs measured in this study

	MW ($g\,mol^{-1}$)	MP (°C)	BP (°C)	VP (mmHg)	WS (mM)	K_H ($M\,atm^{-1}$)	$\log K_{ow}$	ΔH_{Henry} ($kJ\,mol^{-1}$)	ΔH_{vap} ($kJ\,mol^{-1}$)	ΔH_{ws} ($kJ\,mol^{-1}$)
Chlorinated hydrocarbons										
Dichloromethane	84.9	−96.7	39.8	435	153	0.308	1.25	31.7	31.7	0
Carbon tetrachloride	154	−22.9	76.8	115	5.16	0.036	2.83	36.7	33.1	−3.6
1,2-Dichloroethane	99.0	−35.3	83.5	78.9	86.1	0.987	1.48	36.0	34.5	−1.5
1,1,1-Trichloroethane	133	−32.6	74.0	124	11.2	0.067	2.49	31.9	32.7	0.8
Trichloroethylene	131	−84.7	87.2	69	8.37	0.116	2.42	30.3	34.8	4.5
Tetrachloroethylene	166	−22.3	121	18.5	1.21	0.068	3.40	37.7	37.9	0.3
Aromatic hydrocarbons										
Benzene	78.1	5.5	80.0	94.8	22.9	0.210	2.13	30.3	39.0	8.8
Toluene	92.1	−94.9	111	28.4	5.71	0.181	2.73	33.8	38.0	4.2
o-Xylene	106	−25.2	145	6.61	1.68	0.235	3.12	35.2	41.8	6.7
m-Xylene	106	−47.9	139	8.29	1.52	0.164	3.20	33.5	41.4	8.0
p-Xylene	106	13.3	138	8.84	1.53	0.175	3.15	37.2	41.1	3.8
p-Dichlorobenzene	147	53.1	173	1.74	0.55	0.415	3.44	–	44.4	—

MW, molecular weight; MP, melting point; BP, boiling point; VP, vapor pressure at 25°C; WS, water solubility at 25°C, K_H, Henry's law constant at 25°C K_{ow}, octanol–water partition constant; ΔH_{Henry}, the enthalpy change of air–water transfer, which was estimated for dichloromethane and carbon tetrachloride from Gosset (1987) and for other VOCs except them from Dewulf et al. (1995).

$K_H(T) = K_H\ (298.15)\ \exp\ \{-\Delta H_{Henry}/R\ (1/298.15-1/T)\}$.

K_H (298.15), Henry's law constant at 298.15 K; R, gas constant ($8.315\,J\,mol^{-1}\,K^{-1}$); T, Kelvin temperature (K);

ΔH_{VAP}, the enthalpy change of vapor pressure, which was calculated using CRC *Handbook of Chemistry and Physics, 66th edition* (1986)

ΔH_{ws}; the enthalpy change of water solubility, which was estimated using the following relationship (Schwarzenbach et al., 1995)

$\Delta H_{HENRY} = \Delta H_{VAP} - \Delta H_{ws}$.

Table 2
The concentration of VOCs in the air during rain periods and in the rainwater in Yokohama in 1999–2000

	Atmosphere (ppb)		Rainwater (nM)			E_{avg}[d]
	$n = 73$		$n = 125$			
	AM[a]	Range	AM[a]	VWM[b] ± $\mathrm{SEM}_{\mathrm{w}}$[c]	Range	
Chlorinated hydrocarbons						
Dichloromethane (DCM)	0.85	<0.01–4.05	4.98	4.47 ± 0.48	<0.67–22.1	12.8
Carbon tetrachloride (CTC)	0.15	<0.01–0.60	<0.20	<0.20	<0.20–2.25	—
1,2-Dichloroethane (1,2-DCE)	0.16	<0.01–0.86	1.06	0.93 ± 0.14	<0.47–9.92	4.23
1,1,1-Trichloroethane (1,1,1-TCE)	0.06	<0.01–0.13	<0.16	<0.16	<0.16–1.13	—
Trichloroethylene (TRL)	0.38	<0.03–1.49	0.40	0.35 ± 0.07	<0.17–5.83	6.07
Tetrachloroethylene (TEL)	0.39	<0.01–2.61	<0.13	<0.13	<0.13–2.79	—
Aromatic hydrocarbons						
Benzene (BEN)	0.67	<0.01–2.27	1.97	2.00 ± 0.27	<0.42–15.3	10.8
Toluene (TOL)	4.12	<0.01–14.4	3.77	3.71 ± 0.38	<0.08–25.9	3.66
o-Xylene (o-XY)	0.27	<0.01–0.98	0.72	0.62 ± 0.09	<0.10–3.84	7.15
m, *p*-Xylene (m,p-XY)	0.41	0.02–3.38	0.69	0.57 ± 0.10	<0.12–13.2	6.21
p-Dichlorobenzene (p-DCB)	0.45	0.02–1.63	0.58	0.51 ± 0.07	<0.09–5.72	—

[a] Arithmetic mean.

[b] Volume-weighted mean.

[c] The standard error of the weighted mean (Offenberg and Baker, 1997).

$$(\mathrm{SEM}_w)^2 = \frac{n}{(n-1)(\sum P_i)^2}\left[\sum (P_iX_i - \overline{PX_w})^2 - 2\overline{X_w}\sum (P_i - \bar{P})(P_iX_i - \overline{PX_w}) + \overline{X_w}^2 \sum (P_i - \bar{P})^2\right]$$

where P_i is the precipitation amount of sample i, X_i is the concentration in sample i, $\bar{P}$ is the mean precipitation amount for samples 1 to n, and $\bar{X}_w$ is the precipitation weighted mean concentration.

[d] The enrichment factors, E_{avg} were defined as $C_{\mathrm{VMW}}/(p_{\mathrm{AVG}} \cdot K_{\mathrm{H}})$. Their Henry's law constants, K_{H}, were corrected by the average temperature during rain periods (18.5°C).

3.3. *Influence of the rainfall intensity on their concentrations of CHs and MAHs in rainwater*

The rainwater concentrations of chemical compounds are generally influenced by the rainfall intensity as well as their atmospheric concentrations. Fig. 2 shows the relationship between the rainfall intensity and their rainwater concentrations of DCM ($n = 95$), 1,2-DCE ($n = 75$), TOL ($n = 109$), and BEN ($n = 71$), provided that their correlation coefficients are calculated for data above detection limits. We can see there were no significant correlations between the rainfall intensity and their rainwater concentrations. The correlation coefficients of other CHs and MAHs measured in this study ranged from −0.318 for CTC ($n = 20$) to 0.436 for TEL ($n = 16$). This is in striking contrast to the relatively high negative correlation between the rainfall intensity and total inorganic ion concentrations (TIC) ($r = -0.547$). The poor correlations between the rainfall intensity and their rainwater concentrations of CHs and MAHs indicate that their concentrations are not influenced by both dilution and concentration effects probably because of their reversible dissolution from the air-to-rain droplets. In the following section, we will discuss the dissolution of CHs and MAHs into a rain droplet and their vaporization from a rain droplet using a simple below-cloud scavenging model, which was developed by Levine and Schwartz (1982) at first.

3.4. *The dissolution of VOCs into a falling droplet and their vaporization—the falling droplet approach*

Here we use the falling drop approach presented by Levine and Schwartz (1982) and Seinfeld and Pandis (1992). Let us consider that a droplet, whose diameter is D_{p} (m), reaches the ground at the terminal velocity v_{t} (m s^{-1}) after a fall through a homogeneous stationary atmospheric layer of thickness, z (m). The rate of transfer of a gas to the surface of a falling droplet can be calculated as follows:

$$F = k_{\mathrm{g}}(C_{\mathrm{g}} - C_{\mathrm{eq}}), \tag{1}$$

where k_{g} is the mass transfer coefficient (m s^{-1}), C_{g} the concentration of a gas in the gas phase far away from the droplet surface (mol m^{-3}), C_{eq} the concentration of a gas at the droplet surface (mol m^{-3}), which is in equilibrium with the aqueous-phase concentration of the dissolved gas, C_{aq} (M). The rate of increase of C_{aq} of an irreversibly scavenged gas in a droplet should be

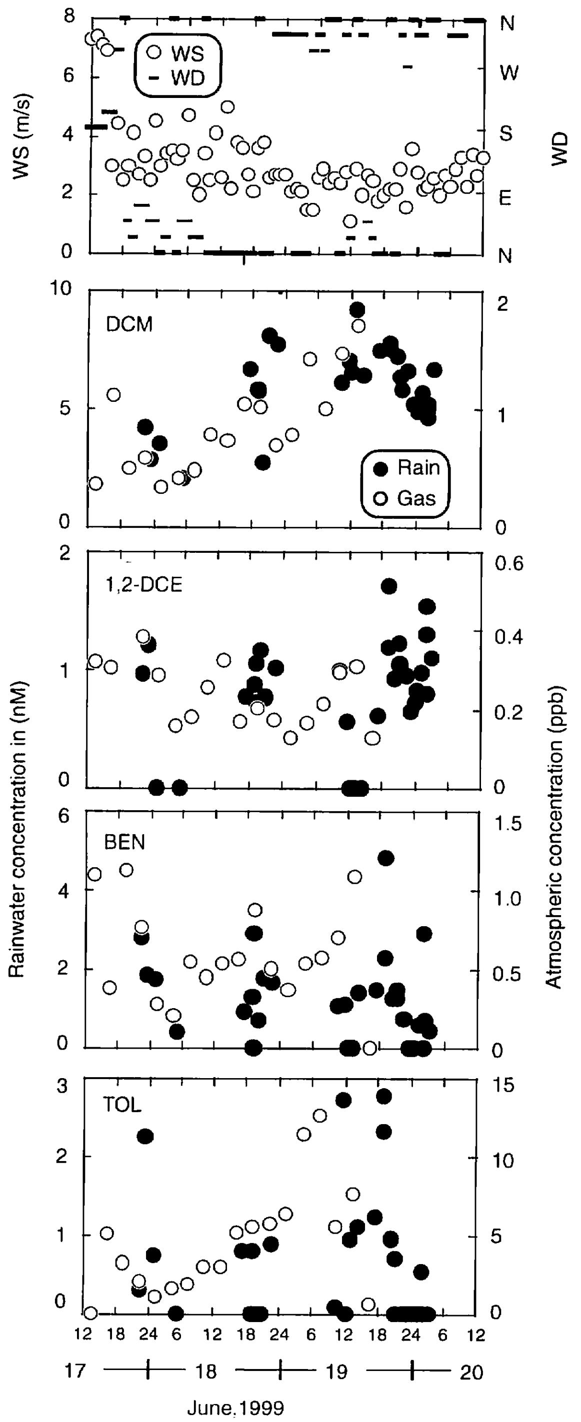

Fig. 1. The temporal variation of DCM, 1,2-DCE, BEN, and TOL in the gas phase and rainwater together with wind direction (WD) and wind speed (WS) during 17–20 June, 1999.

equal to the rate of transport of a gas to the drop:

$$\frac{4}{3}\pi\left(\frac{D_p}{2}\right)^3\frac{dC_{aq}}{dt} = 4\pi\left(\frac{D_p}{2}\right)^2 F. \tag{2}$$

i.e.,

$$\frac{1}{6}\pi D_p^3\frac{dC_{aq}}{dt} = \pi D_p^2 F. \tag{3}$$

Substituting Eq. (1) for Eq. (3), we obtain Eq. (4).

$$\frac{1}{6}\pi D_p^3\frac{dC_{aq}}{dt} = \pi D_p^2 k_g(C_g - C_{eq}). \tag{4}$$

Applying $dC_{aq}/dt = v_t dC_{aq}/dz$ to the left-hand side of the Eq. (4) and applying the ideal gas law, $C_g = p_g/RT \times 10^3$ (mol m^{-3}) and $C_{eq} = p_{eq}/RT \times 10^3$ (mol m^{-3}) and Henry's law constant, $C_{aq} = K_H p_{eq}$ to the right-hand side, we obtain Eq. (5).

$$\frac{dC_{aq}}{dz} = -\frac{6\times 10^3 k_g}{v_t D_p RTK_H}(C_{aq} - p_g K_H), \tag{5}$$

where R is the gas constant (0.08205 atm l mol^{-1} K^{-1}), T the Kelvin temperature (K), K_H the Henry's law constant (M atm^{-1}), and p_g is the partial pressure of a gas (atm). Assuming that the droplet diameter, the temperature, and the partial pressure of a gas are constant while a droplet falls from cloud base to the ground, we get Eq. (6) by separating variables , i.e. C_{aq} and z in Eq. (5) and then integrating the resulting equation between the boundary conditions $C_{aq} = C^0_{aq}$ to C_{aq}, and $z = 0$ to z:

$$C_{aq} = K_H p_g - (K_H p_g - C^0_{aq})\exp\left(-\frac{6\times 10^3 k_g}{v_t D_p RTK_H}z\right), \tag{6}$$

$$k_g = \frac{K_g}{D_p}\left[2 + 0.6\left(\frac{D_p v_t}{\mu_{air}}\right)^{\frac{1}{2}}\left(\frac{\mu_{air}}{K_g}\right)^{\frac{1}{3}}\right],$$

$$v_t = 9.58\left[1 - \exp\left(-\left(\frac{D_p}{0.1710}\right)^{1.147}\right)\right],$$

$$\mu_{air} = 1.328\times 10^{-5}\left(\frac{1}{p}\right)\left(\frac{273.15 + T}{273.15}\right)^{1.754},$$

where C^0_{aq} is the initial concentration in a droplet, in other words in-cloud scavenging, K_g is the diffusivity of the gas in the air (m^2 s^{-1}), μ_{air} is the kinematic viscosity (m^2 s^{-1}), and p is the atmospheric pressure (atm).

As an example, we discuss the wet-scavenging process of dichloromethane (DCM), whose concentration in rainwater was the highest among CHs and MAHs measured in this study (See Table 2). Fig. 3 (a) shows the DCM concentration in a droplet with diameter D_p 20 mm, falling through an atmosphere containing 1 ppb of DCM. Case A represents that C^0_{aq} is zero, i.e. no in-cloud scavenging, and that the temperature below cloud is constant at 25°C. We can see C_{aq} increase with falling

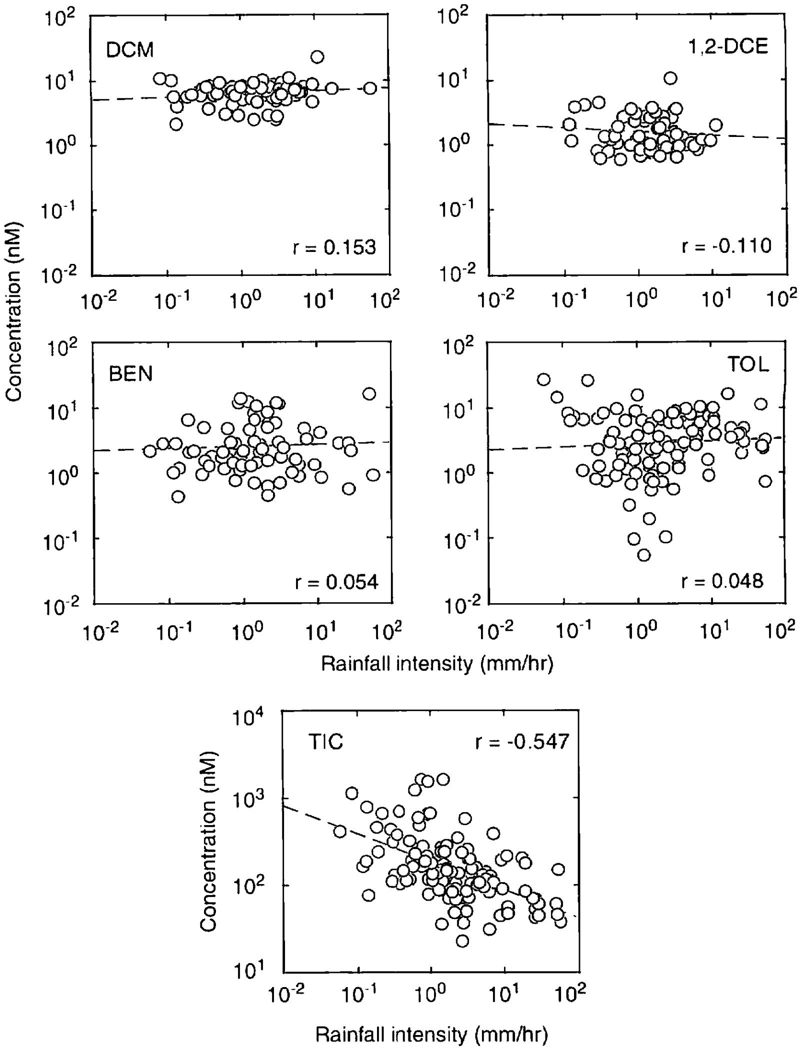

Fig. 2. The relationship between the rainfall intensity and the concentrations of DCM, 1,2-DCE, TOL, and BEN in rainwater together with total inorganic ion concentration (TIC). The presented correlation coefficients were calculated only for data above detection limits.

distance of a droplet until the equilibrium is reached at the below-cloud temperature. The equilibrium has been reached as quick as a droplet falls (on the order of micrometer) because of low Henry's law constant of DCM. The falling distance of other VOCs listed in Table1 to reach the equilibrium between gas and droplet is smaller than that of DCM because their Henry's law constant is smaller except for 1,2-DCE. In case C, the equilibrium between the droplet and the air at 25°C is already reached in cloud. Although the assumption of the same temperature at in-cloud and below-cloud is not realistic, comparing by cases A and C we can see no dissolution of DCM into a falling droplet below cloud. In case E, the temperature below cloud is also at 25°C, while the temperature in cloud is 0°C. Comparing A, C, and E, we can see DCM is released from a falling droplet into the ambient air below cloud until the equilibrium is reached at the below-cloud temperature. In this case, DCM is released as quickly as a droplet falls. Case E is the most realistic simulation among the three cases because the temperature is well-known to decrease with height in a linear fashion up to the tropopause (Pruppacher and Klett, 1997). Cases B, D, and F replace the temperature at 25°C with the temperature at 12.5°C in cases A, C, and E, respectively. Comparing a set of A/C/E and a set of B/D/F, we can see the decrease in temperature makes both the equilibrium concentration and a falling distance to reach the equilibrium increase because of the increase of K_H values.

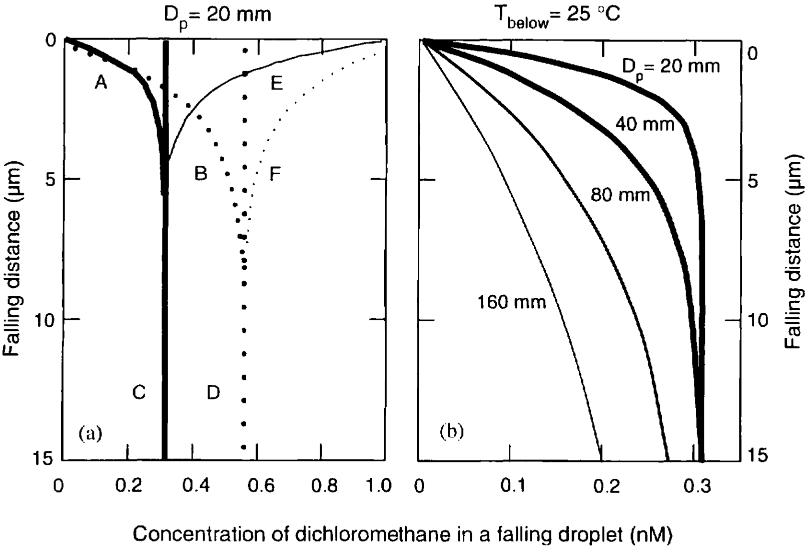

Fig. 3. Calculated concentration of dissolved dichloromethane in a falling droplet as a function of falling distance from a cloud base for atmospheric partial pressure of dichloromethane of 10^{-9} atm (1 ppb). (a) A: no in-cloud scavenging and the below-cloud atmosphere is constant at 25°C, B: the same condition as case A except for 12.5°C, C: the equilibrium is reached in cloud at 25°C and the below-cloud atmosphere is constant at 25°C, D: the same condition as case C except for 12.5°C, E: the equilibrium is reached in cloud at 0°C and the below-cloud atmosphere is constant at 25°C, F: the same condition as case E except for the below-cloud atmosphere at 12.5°C, (b) the dependence of the concentration on droplet size at the condition of no in-cloud scavenging and the temperature of below-cloud atmosphere at 25°C.

Fig. 3(b) shows the dependence of DCM concentration on droplet size in the case of $C^0_{aq} = 0$, i.e. no in-cloud scavenging. The falling distance to reach the equilibrium in smaller droplet is smaller than that in larger droplet because the mass transfer coefficient is larger to a smaller droplet and the terminal velocity of smaller droplet is smaller. However, Fig. 3 (b) also indicates that there is no difference of DCM concentration in rain droplets when they passed through a given layer (for example, 0.5–2 km) at the ground because the equilibrium of DCM between air and droplets has been reached just below the cloud (on the order of micrometer). Therefore the rainwater concentrations of CHs and MAHs do not depend on the rainfall intensity and rainfall amount.

To sum up, the rainwater concentration of gases, which are reversibly dissolved and do not participate in aqueous phase reactions, such as CHs and MAHs, targeted in this study may be predicted by their gas concentration at the ground and Henry's law constants corrected by the ground level temperature only when the temperature profile below cloud is nearly constant.

3.5. Application of the falling droplet approach to authentic rainwater

Assuming that the concentration of VOCs in "bulk" rainwater is equal to the volume weighted mean concentration of VOCs in each droplet, the concentration of VOCs in rainwater, C_{rain} (M) can be estimated by the following equation. We here used Marshall–Palmer equation (Seinfeld and Pandis, 1992) as a size distribution of rain droplets.

$$C_{rain} = \frac{\int_{0.02}^{\infty} \frac{\pi}{6} C_{aq} D_p^3 N(D_p) dD_p}{\int_{0.02}^{\infty} \frac{\pi}{6} D_p^3 N(D_p) dD_p}, \tag{7}$$

$$N(D_p) = \frac{dN}{dD_p} = 0.08 \exp(-41 D_p I^{-0.21}),$$

where I is the rainfall intensity (mm h^{-1}).

Fig. 4 shows the relationship between the measured and calculated values of VOCs in rainwater. The dotted line shows the 1:1 line. The calculations were made only for the initial rainfall of three events, i.e. 11 May, 19 May, and 24 September, 1999. We used only the atmospheric concentration of each VOC just before each rain event and their rainwater concentration at the initial rainfall, which were observed at the ground, to discuss the below-cloud scavenging of atmospheric VOCs via rain droplets rigorously. The molecular diffusivity of carbon tetrachloride (0.08 cm^2 s^{-1} at the ground level, Ghosh, 1983) was used for the diffusivity of all other VOCs because of lack of their diffusivity data for each VOCs. The molecular diffusivities make little difference among gases (Ghosh, 1983), so the use of

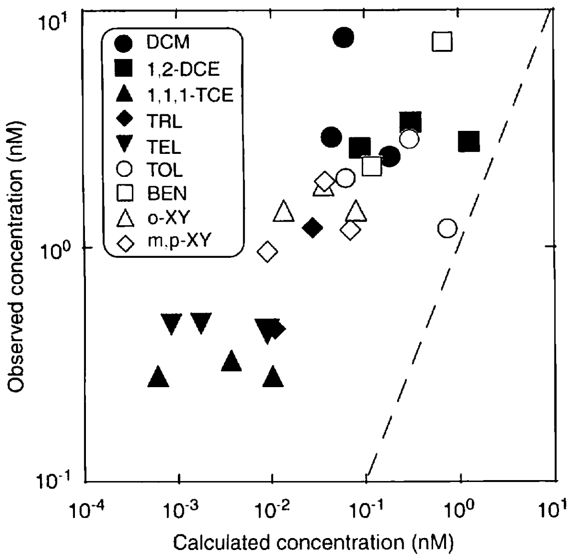

Fig. 4. The relationship between the observed and calculated VOCs concentration in three initial rainwater collected on 11 May, 19 May and 24 September, 1999. The dotted line shows the 1:1 line.

the diffusivity of carbon tetrachloride does not influence these calculations. The altitude of cloud base (thickness of atmospheric layer) is regarded as 1 km because cloud base altitude generally ranged from 500 m to 2 km in our sampling area. As shown in Fig. 4, their observed values of most VOCs were considerably higher than the calculated values, in particular, VOCs with lower Henry's law constants such as 1,1,1-TCE and TEL. We must say here that the estimated values by a simple below-cloud scavenging model were completely equal to the estimated values only by Henry's law. It indicates that the gas-phase diffusion onto the droplet surface is not important process for VOCs and that the transfer process through the water/air is the dominant factor.

A great gap between the observed and calculated values is caused by various factors. There is a possibility of analytical error. However, it is estimated to be 10% at most, so the analytical error cannot explain the gap. It is possible that the use of mixing ratios of VOCs at the ground probably overestimates the calculated values, while the use of temperature at the ground underestimates the values. Vertical profile of chlorinated hydrocarbons such as carbon tetrachloride and 1,1,1-trichloroethane, which are targeted in this study, is reported to be nearly constant in the lower troposphere although they were reduced in the stratosphere (Tominaga and Makide, 1991). Therefore, the assumption of constant profile of VOCs mixing ratio is possibly appropriate. On the other hand, it might be not appropriate to assume the constant temperature profile even if in the lower troposphere. The temperature correction increases the solubility of VOCs and might explain the gap. The below-zero temperature below cloud is required to explain their rainwater concentration using Henry's law constant, but it is not realistic this season in our sampling area. Therefore, it is indicated that the dissolution of VOCs into rain droplets according to the temperature-corrected physical Henry's law constant below cloud is not responsible for their rainwater concentration.

We propose two likely mechanisms as their scavenging process, i.e. (i) the adsorption of VOCs at the interface of air–cloud droplet/ice crystal within cloud (in-cloud scavenging), and (ii) the dissolution of VOCs into droplet according to the effective Henry's law constant induced by surface-active agents (in-cloud and/or below-cloud scavenging).

3.5.1. The adsorption of VOCs at the air–droplet/ice interface

Valsaraj et al. (1993) discussed the enrichment of hydrophobic organic compounds into fogwater via the adsorption at the air–water interfacial area using the octanol–water coefficient. Fig. 5 presents the enrichment factor E as a function of the octanol–water partition constant K_{ow}. The symbols are the averages of each VOC and the bars are their ranges. The enrichment factors for both CHs and MAHs tend to increase as the octanol–water partition constant increases although the data shown in Fig. 4 are only of three rain events. The

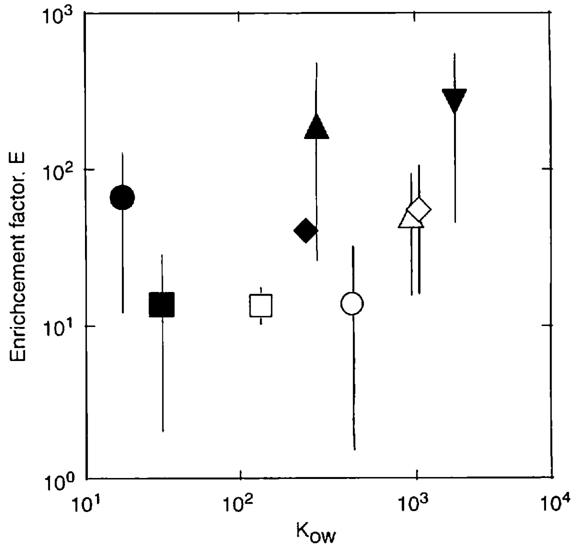

Fig. 5. The relationship between the octanol–water partition constant K_{ow} and the enhancement factor E in three initial rainwater samples collected on 11 May, 19 May and 24 September, 1999. The symbols are the same as shown in Fig. 4 and the vertical bars represent their ranges of E values.

correlation coefficient between the average of E_{CHs} and K_{ow} was 0.737, while the coefficient between the average of E_{MAHs} and K_{ow} was 0.852. The contribution of the surface adsorption decreases as the droplet radius increases, so the surface adsorption is not an important process for rain droplets as mentioned in the Introduction. Therefore these correlations indicate that the adsorption at the air/droplets interfacial occurs not below but within cloud if the surface adsorption is the process responsible for their rainwater concentration. However, their enrichment factors are quite higher (roughly ten fold) than the values expected from the octanol–water partition constants using the equation by Valsaraj et al. (1993), indicating the rainwater concentration cannot be explained by the surface adsorption onto cloud droplets.

In more recent years Wania et al. (1999) have reported that the adsorption at the air-ice interface is the process responsible for vapor scavenging of PCBs and PAHs via snow. They estimated snow scavenging of their vapor phase on the basis of the negative correlation between snow scavenging ratio for their vapor phase, W_{G} and their vapor pressure of the supercooled liquid, p_{L} following the equation.

$$\log W_{\mathrm{G}} = \log K_{\mathrm{ia}} + \log S = -a \log p_{\mathrm{L}} + b + \log S, \qquad (8)$$

where K_{ia} is the interfacial partition coefficient, S the specific surface area, and a and b are the constants given by the regression analysis. W_{G} is defined as the ratio of $C_{\mathrm{rain}}/C_{\mathrm{gas}}$, so the enrichment factor, E is proportional to W_{G} when the temperature is constant as follows:

$$E = \frac{D_{\mathrm{obs}}}{K_{\mathrm{H}}} = \frac{C_{\mathrm{rain}}}{p_{\mathrm{gas}} K_{\mathrm{H}}} = \frac{C_{\mathrm{rain}}}{C_{\mathrm{gas}} RT K_{\mathrm{H}}} = \frac{W_{\mathrm{G}}}{K_{\mathrm{H}} RT}. \qquad (9)$$

If the adsorption of VOCs onto the ice surface is the process responsible for them in rainwater, E should be positively correlated with K_{ia} and negatively correlated with p_{L}. The interfacial partition coefficients of the CHs, except 1,2-DCE, are available, while the coefficients of the MAHs, except BEN, are not available (Hoff et al., 1995). So the regression analysis of the logarithm of the vapor pressure at 0°C, p_0 vs. $\log E$ was made for the MAHs, while both regression analyses of $\log K_{\mathrm{ia}}$ vs. $\log E$ and $\log p_0$ vs. $\log E$ were made for the CHs in this study. The p_0 can be estimated by the vapor pressure at 25°C and the enthalpy change of vapor pressure in Table 1. The correlation coefficient between the $\log K_{\mathrm{ia}}$ and $\log E$ for the CHs is 0.640 ($n = 4$), while the coefficient between the $\log p_0$ and $\log E$ is –0.952 for MAHs ($n = 4$) and –0.420 for CHs ($n = 5$), respectively. This indicates that the adsorption at the air–ice crystal interface within clouds could be a process responsible for the VOCs, in particular MAHs in rainwater.

3.5.2. The enhanced dissolution into droplets according to the effective Henry's law constant

There is another explanation of the linearity between $\log E$ and $\log K_{\mathrm{ow}}$. The logarithm of the partition coefficient between the colloidal dissolved organic compounds and water, $\log K_{\mathrm{oc}}$ also shows a linear relationship with $\log K_{\mathrm{ow}}$ (Valsaraj, 1993), so $\log E$ should also shows a linear relationship with $\log K_{\mathrm{oc}}$. Some investigators have reported the change of the physical property of cloudwater and fogwater compared to that of water, i.e. the decrease of the surface tension with the increase of dissolved organic carbon (Seidl and Hänel, 1983; Capel et al., 1990; Facchini et al., 2000). The reduction of the surface tension, in other words the presence of surfactants, probably increases the dissolution of atmospheric VOCs into the droplets (Law and Diamond, 1998; Vane and Giroux, 2000). One of the most likely atmospheric surfactants is humic-like substances (Facchini et al., 2000). It has been reported that 10% and more of the organic carbon in atmospheric aerosol can be attributed to humic-like substances, which are rich in aliphatic and carbohydrate substances compared to humic and fulvic acids from soils and aquatic system (Havers et al., 1998). In more recent years Sukhapan and Brimblecombe (2002) have reported that surfactants, which are expressed as methylene blue active substances (MBAS), are present in the ranges from 6 to 170 pmol m^{-3} in the atmospheric aerosols collected in rural area. They pointed out that atmospheric surfactants are derived from the continental source based on their positive correlation with aerosol nitrate and NO_x. We have no observation of any surfactants and the surface tension in rainwater and cloudwater in this study, so we cannot discuss the effect of the surfactants on the dissolution of VOCs into the droplets. However, we would like to suggest that VOCs could be scavenged both within and below the cloud via this mechanism if the surfactants could enhance their Henry's law constants. Krivácsy et al. (2000) have reported that humic-like substances may play a role in cloud condensation. The concentration of humic-like substances may be higher near the ground, so their contribution to for the dissolution of VOCs is likely larger near the ground.

We need to consider not only the dissolution of VOCs but also their release from the falling rain droplets. VOCs should be released from the droplets in the melting process during falling and reach the physical Henry's law equilibrium in the absence of any surfactants when they are scavenged by the surface adsorption onto ice crystal within cloud (See Fig. 3 (a)). Therefore, the enhanced dissolution of VOCs into rainwater possibly indicates the presence of surfactants in rain droplets because the surfactants possibly prevent their release from the droplets. However, this is still no better than a conjecture. Unfortunately, we cannot conclude which is the more important process between in-cloud and below-cloud scavenging for the dissolution of VOCs into rainwater, because there is a lack of information of atmospheric surfactants up to now. Further investigations are needed to make the role of atmospheric surfactants on the dissolution and the release of VOCs clear.

Acknowledgements

We would like to thank many students and graduates in our laboratory for sampling and analysis and Dr. Mario Massucci in British Antarctic Survey and Prof. Peter Brimblecombe in UEA, UK for valuable comments. This work was supported in part by Core Research for Evolutional Science and Technology (1996-2001), Japanese Science and Technology Corporation.

References

Capel, P.D., Gunde, R., Zürcher, F., Giger, W., 1990. Carbon speciation and surface tension of fog. Environmental Science and Technology 24, 722–727.

Capel, P.D., Leuenberger, C., Giger, W., 1991. Hydrophobic organic chemicals in urban fog. Atmospheric Environment 25A, 1335–1346.

Czuczwa, J., Leuenberger, C., Giger, W., 1988. Seasonal and temporal change of organic compounds in rain and snow. Atmospheric Environment 22, 907–916.

Dewulf, Jo., Drijvers, D., Langenhove, H.V., 1995. Measurement of Henry's law constant as function of temperature and salinity for the low temperature range. Atmospheric Environment 29, 323–331.

Facchini, M.C., Decesari, S., Mircea, M., Fuzzi, S., Loglio, G., 2000. Surface tension of atmospheric wet aerosol and cloud/fog droplets in relation to their organic carbon content and chemical composition. Atmospheric Environment 34, 4853–4857.

Ghosh, S., 1983. On the diffusivity of trace gases under stratospheric conditions. Journal of Atmospheric Chemistry 17, 391–397.

Glotfelty, D.E., Seiber, J.N., Liljedahl, L.A., 1987. Pesticides in fog. Nature 325, 602–605.

Gossett, J.M., 1987. Measurement of Henry's law constants for C1 and C2 chlorinated hydrocarbons. Environmental Science and Technology 21, 202–208.

Gross, K.U., 1994. Prediciting the enrichment of organic compounds in fog caused by adsorption on the water surface. Atmospheric Environment 28, 3513–3517.

Hart, K.M., Tremp, J., Molnar, E., Giger, W., 1993. The occurrence and the fate of organic pollutants in the atmosphere. Water Air Soil Pollution 68, 91–112.

Havers, N., Burba, P., Lambert, J., Klockow, D.J., 1998. Spectroscopic characterization of humic-like substances in airborne particulate matter. Journal of Atmospheric Chemistry, 45–54.

Hoff, J.T., Wania, F., Mackay, D., Gillham, R., 1995. Sorption of nonpolar organic vapors by ice and snow. Environmental Science and Technology 29, 1982–1989.

Ichihashi, K., Kanazawa, Y., Isomura, K., Teranishi, K., 1995. Full automatic and continuous measurement of the volatile organics in drinking water with the purge and trap/gas chromatography/mass spectrometry. Yosui to Haisui 37, 455–460.

Igawa, M., Nakata, N., Okochi, H., 1999. Determination of volatile organic compounds in rainwater and the dominant factors controlling their concentrations. Taiki Kankyo Gakkaishi 34, 211–218.

Kawamura, K., Kaplan, I.R., 1983. Organic compounds in the rainwater of Los Angeles. Environmental Science and Technology 17, 497–501.

Krivácsy, Z., Kiss, Gy., Varga, B., Galambos, I., Sárvári, Zs., Gelencsér, A., Molnár, A., Fuzzi, S., Facchini, M.C., Zappoli, S., Andracchio, A., Alsberg, T., Hansson, H.C., Persson, L., 2000. Study of humic-like substances in fog and interstitial aerosol by size-exclusion chromatography and capillary electrophoresis. Atmospheric Environment 34, 4273–4281.

Law, N.L., Diamond, M.L., 1998. The role of organic films and the effect on hydrophobic organic compounds in urban areas: an hypothesis. Chemosphere 36, 2607–2620.

Levine, S.Z., Schwartz, S.E., 1982. In-cloud and below-cloud scavenging of nitric acid vapor. Atmospheric Environment 16, 1725–1734.

Lide, D.R. (Ed.), 2001. CRC Handbook of Chemistry and Physics. 82 Edition. CRC press, Florida.

Ligocki, M.P., Leuenberger, C., Pankow, J.F., 1985. Trace organic compounds in rain—II. Gas scavenging of neutral organic compounds. Atmospheric Environment, 1609–1617.

Nagai, K., Hattori, Y., Takahashi, K., Nakamoto, M., 1991. Determination of volatile halogenated hydrocarbons in water samples using capillary GC/MS connected with an automatic purge and trap concentrator. Bunseki Kagaku 40, T137–T143.

Offenberg, J.H., Baker, J.E, 1997. Polychlorinated biphenyls in Chicago precipitation: Enhanced wet deposition to near-shore lake Michigan. Environmental Science and Technology 31, 1534–1538.

Poster, D.L., Baker, J.E., 1996a. Influence of submicron particles on hydrophobic organic contaminants in precipitation. 1. Concentrations and distributions of polycyclic aromatic hydrocarbons and polychlorinated biphenyls in rainwater. Environmental Science and Technology 30, 341–348.

Poster, D.L., Baker, J.E., 1996b. Influence of submicron particles on hydrophobic organic contaminants in precipitation. 1. Scavenging of polycyclc aromatic hydrocarbons by rain. Environmental Science and Technology 30, 349–354.

Pruppacher, H.R., Klett, J.D., 1997. Microphysics of clouds and precipitation. Kulwer Academic Publisher, Dordrecth.

Schwarzenbach, R.P., Gshwend, P.M., Imboden, D.M., 1995. Environmental Organic Chemistry. Wiley, New York.

Seidl, W., Hänel, G., 1983. Surface-active substances on rainwater and atmospheric particles. Pure and Applied Geophysics 121, 1077–1093.

Seinfeld, J.H., Pandis, S.N., 1992. Atmospheric Chemistry and Physics. Wiley-Interscience, New York.

Sukhapan, J., Brimblecombe, P., 2002. Inonic Surface Active Compounds in Atmospheric Aerosols. The Scientific World Journal, 1138–1146.

Tominaga, T., Makide, Y., 1991. Halocarbons in the atmosphere: trend and vertical profiles. Nippon Kagakukaishi, 351–357.

Valsaraj, K.T., Thoma, G.J., Reible, D.D., Thibodeaux, L.J., 1993. On the enrichment of hydrophobic orhanic compounds in fog droplets. Atmospheric Environment 27A, 203–210.

Vane, L.M., Giroux, E.L., 2000. Henry's law constants and micellar partitioning of volatile organic compounds in surfactant solutions. Journal of Environmental Engineering Data 45, 38–47.

Wania, F., Mackay, D., Hoff, J.T., 1999. The importance of snow scavenging of polychloribated biphenyl and polycyclic aromatic hydrocarbon vapors. Environmemta Science and Technology 33, 195–197.

Weast, R.J. (Ed.), 1986. CRC Handbook of Chemistry and Physics, 66 Edition. CRC press, Florida.

Woolfenden, E., 1997. Monitoring VOCs in air using sorbent tubes followed by thermal desorption-capillary GC analysis: summary of data and practical guidelines. Journal of Air and Waste Management Association 47, 20–36.

Yoshida, K., Shigeoka, T., 1992. Estimation of environmental concentrations of 1,4-dichlorobenzene in the east. Kanagawa prefecture. Environmental Science 5, 33–44.