

Enhanced dissolution of volatile organic compounds into urban dew water collected in Yokohama, Japan

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Abstract

Simultaneous sampling of six chlorinated hydrocarbons (CHs) and five monocyclic aromatic hydrocarbons (MAHs) in dew water and in the ambient air was performed from 1998 to 2000 in Yokohama, Japan. Dichloromethane (volume-weighted mean concentration (VWM): 2.43 nM) and trichloroethylene (VWM: 2.91 nM) were abundant among CHs in dew water, while toluene (VWM: 9.69 nM) and *p*-dichlorobenzene (VWM: 6.06 nM) were abundant among MAHs. The contribution of total measured volatile organic compounds (VOCs) concentration to dissolved organic carbon (DOC) concentration in dew water was only 0.02 wt% on average. The concentrations of VOCs except for dichloromethane and benzene in dew water were several hundred times higher than those in rainwater collected at the same site. In particular more hydrophobic VOCs with higher octanol–water partition coefficient K_{OW} tended to be concentrated in dew water, indicating that urban dew water has stronger hydrophobicity than rainwater. Dew water contained higher amounts of VOCs than would have been expected from the ambient gas-phase concentrations and Henry's law constants. The enrichment factors, which were defined as the ratio of the observed concentration to the estimated, ranged from 6.98 (for dichloromethane) to 62.7 (for trichloroethylene) on average. Relatively high correlations ($r > 0.55$) between the enrichment factors of highly hydrophobic VOCs ($K_{OW} > 10^3$) and the ratios of DOC to total inorganic ion concentration (TIC), which could be a potential surrogate of surface tension for urban dew water, indicated that the existence of any dissolved organic compounds, which could reduce the surface tension, in dew water also caused the enrichment of highly hydrophobic VOCs.

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1. Introduction

Volatile organic compounds (VOCs), which are emitted into the troposphere, play important roles in

the formation of ozone, particles, and other species of interest. Some of the individual species, e.g., benzene is one of the carcinogens, cause harmful effects on human health. To predict the fate of atmospheric VOCs, it is necessary to understand removal process by both wet and dry deposition as well as advection, diffusion, and chemical transformation such as depletion by the reaction with OH radical. Wet deposition process of atmospheric VOCs, i.e. the mechanisms of incorporation into atmospheric liquid water and removal from the

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troposphere, has been paid little attention although there are plenty of research about the mechanisms and rate constants of the reaction of gas-phase VOCs with oxidants such as O_3 and OH radical (e.g. Atkinson, 1994). This is probably because of poor water solubility of VOCs. The wet deposition fluxes, which are less than hydrophobic compounds below octanol–water coefficient K_{OW} 10^5 , have been simply estimated based on Henry's law equilibrium (e.g. Yoshida and Shigeoka, 1992).

During the last decade, some researchers have revealed that atmospheric droplets such as fog water and rainwater contain higher amounts of hydrophobic organic compounds (HOCs) and VOCs than would have been expected from Henry's law constants and the corresponding gas-phase concentrations (Capel et al., 1991; Valsaraj et al., 1993; Gross, 1994; Poster and Baker, 1996a; Poster and Baker, 1996b; Offenberg and Baker, 1997). The air–water interfacial adsorption is the most likely explanation for the dissolution of the hydrophobic organic compounds into fog water (Valsaraj et al., 1993). Another possible reason is the adsorption of hydrophobic organics onto dissolved and/or colloidal organic materials in fog water (Capel et al., 1990). The concentration of VOCs in rainwater has been also reported (Kawamura and Kaplan, 1983; Ligocki et al., 1985; Igawa et al., 1993) and the observed concentration of some VOCs in rainwater is reported to be much higher than would be expected from Henry's law prediction (Okochi et al., 2004).

Dry deposition is another important process for removing atmospheric pollutants onto the ground as well as wet deposition. Takeuchi et al. (2000) has reported that the annual frequency of dew, which was defined as the percentage of the dew occurrence days in a year, was 22% and the annual dewfall amount was about 8 mm in Yokohama, Japan. The presence of dew on materials at nighttime and early in the morning has been reported to enhance the dry deposition velocities of water-soluble air pollutants such as HNO_3 and SO_2 (Okochi et al., 1996; Takeuchi et al., 2002). Little attention, however, has been paid to dew water organic chemistry, in particular the dry deposition of hydrophobic/volatile organic compounds into dew water probably because the dissolution has been believed to be limited depending on Henry's law equilibrium. If the dissolution of VOCs into dew droplets is enhanced as well, the presence of dew might also increase both dry deposition fluxes and velocities of them.

In this paper, we report the concentrations of six chlorinated hydrocarbons (CHs) and five monocyclic aromatic hydrocarbons (MAHs) in urban dew water as well as gas-phase concentrations in the ambient. To our knowledge, this is the first report of VOCs concentrations in urban dew water. We also discuss the enhanced dissolution mechanism of CHs and MAHs into dew

droplets, which are higher than would be expected by the temperature-corrected Henry's law constant for plain water and their gas-phase concentrations.

2. Experimental section

Simultaneous sampling of dew water and ambient air was performed on the rooftop of four (until July, 1999) or six story buildings (from July, 1999) in the campus of Kanagawa University in Yokohama (N 35.26°, E 139.38°), which is a representative urban area in Japan, with a population of over 300 million, situated near Tokyo. Kanagawa University is located less than 3 km from the Yokohama Bay area and lies in a residential area nearby the city center. Twelve three-day sampling campaigns for atmospheric VOCs (196 samples) were performed during the period from May 1998 to November 2000, whereas 14 dew events (46 samples) were collected during the same period.

Dew water, which was formed on the dew collector, was collected by scraping it off with a Teflon[®] scraper. Details of the collector have been previously described (Okochi et al., 1996). After weighing, the dew-water samples were immediately transferred into 8 mL brown vials. The vials were filled with the samples and sealed with a Teflon[®] liner and stored in a refrigerator at 4 °C. Prior to use, the clean brown vials were heated at 105 °C for 2 h and used after they were cooled to room temperature in a high-purity nitrogen (over 99.9999%) filled dessicator. After sampling, VOCs in 5 mL aliquots of dew water were collected using the purge and trap method with the same glass tubes that were used for sampling VOCs in the ambient air. The purge was performed using high-purity nitrogen (over 99.9999%) at 40 mL min⁻¹ for 15 min. Impurities in the nitrogen were removed by a glass tube plugged with Carboxene 563 (Supelco, Inc.). Water vapor was removed with a 1 g Mg(ClO₄)₂ filled trap, in front of the sampling glass tube.

VOCs in the gas phase were collected at a rate of 20 mL min⁻¹ every 3 h using Perkin–Elmer Model STS-25 (Woelfenden, 1997) equipped with 24 silanized glass tubes (3.5 in long, 4 mm i.d., and 6 mm o.d.), in which a quantity of 190 mg Carboxene B ($S = 100 \text{ g m}^{-2}$, 60/80 mesh) and a quantity of 140 mg Carboxene 1000 ($S = 1200 \text{ g m}^{-2}$, 60/80 mesh) were fixed in series vertically (Carboxene 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 Carboxene 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 Mg(ClO₄)₂ (8–24 mesh,

Wako Chemical), which was connected to the inlet of the sampling tube (on the Carboxpack 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.

For the analysis of VOCs in atmospheric and dew-water 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. (1993). The standard deviations of the relative peak height of the reference compounds (corresponding to 50 ng) from 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% ($n = 3$). In addition, VOCs in 5 mL aliquots of ultrapure water, which

included both water blank and vial head space blank, were collected using the purge and trap method and the blank was generally free of contaminants, i.e. below instrumental detection limits. Major inorganic ions and dissolved organic carbon (DOC) in dew water and in rainwater have been made according to standard methods and the details have been recently described (Okochi et al., 2004).

3. Results and discussion

3.1. Comparison of VOCs in dew water with those in rainwater

VOCs concentrations in dew water, which was collected in Yokohama during three years from 1998 to 2000, are shown in Table 1 together with the concentrations of DOC, pH, and total inorganic ions concentration (TIC). The volume-weighted means were calculated assuming that the concentrations below the detection limits were regarded as zero. Dichloromethane (DCM, C₁Cl₂) and trichloroethylene (TRL, C₂DCl₃) were abundant among CHs in dew water, while toluene

Table 1

The concentrations of VOCs in dew water in Yokohama during three years from 1998 to 2000

Compounds (abbreviation ^a)	Dew water (nM)		<i>E</i> ^d
	<i>n</i> = 46 ^b		
	VWM ^c	Range	
Chlorinated hydrocarbons			
Dichloromethane (DCM, C ₁ Cl ₂)	2.43	<0.67–8.52	6.98
Carbon Tetrachloride (CTC, C ₁ Cl ₄)	0.21	<0.20–2.73	38.1
1,2-Dichloroethane (1,2-DCE, C ₂ Cl ₂)	1.71	<0.47–13.3	9.46
1,1,1-Trichloroethane (1,1,1-TCE, C ₂ Cl ₃)	0.22	<0.16–2.49	49.4
Trichloroethylene (TRL, C _{2D} Cl ₃)	2.91	<0.17–22.6	62.7
Tetrachloroethylene (TEL, C _{2D} Cl ₄)	0.18	<0.13–1.22	10.1
Monocyclic Aromatic hydrocarbons			
Benzene (BEN, C _{6A} C ₀)	1.79	<0.42–8.59	8.07
Toluene (TOL, C _{6A} C ₁)	9.69	<0.08–47.1	7.87
o-Xylene (o-XY, C _{6A} C _{2o})	2.31	<0.10–10.6	20.2
<i>m,p</i> -Xylene (<i>m,p</i> -XY, C _{6A} C _{2mp})	1.47	<0.12–6.32	12.3
p-Dichlorobenzene (p-DCB, C _{6A} Cl ₂)	6.04	<0.09–33.9	—
∑VOCs	21.5		
DOC (mg L ^{−1})	9.26	2.65–42.4	
∑VOCs-C/DOC (wt%)	0.02	0.001–0.09	
pH	5.02	3.79–7.34	
TIC ^e (meq L ^{−1})	0.96	0.31–4.62	

^a2D in C_{2D} means a C–C double bond while 6A in C_{6A} means aromatic hydrocarbon.

^bsample number.

^cVWM = volume-weighted mean concentration.

^dThe enrichment factor (E) is defined as the ratio of the observed to the estimated concentrations of VOCs in dew water. See the text in detail.

^eTotal inorganic ion concentration.

(TOL, $C_6A C_1$) and *p*-dichlorobenzene (*p*-DCB, $C_6A Cl_2$) were abundant among MAHs. The contribution of total measured VOCs concentration to DOC in dew water ranged from 0.001 to 0.09 wt% and the average was 0.02 wt%.

Fig. 1(a) shows the mean concentrations of VOCs in dew water along with those in the ambient air and Henry's law constants K_H of the VOCs for plain water. The concentrations of CHs in dew water decreased with the increase of chlorine number for a given carbon chain length. This is because both the concentrations of VOCs in the ambient air and the Henry's law constants decrease with the increase of chlorine numbers for the same carbon number. Compared with the VOCs, which have two chlorine atoms per molecule, the concentration of *p*-DCB ($C_6A Cl_2$), which has six carbon atoms, in dew water was higher than those of DCM ($C_1 Cl_2$) and 1,2-dichloromethane (1,2-DCE, $C_2 Cl_2$), but there was no difference in the concentrations between DCM and 1,2-DCE. The trend of the concentrations of MAHs except *p*-DCB in dew water was close to the trend of those in the ambient probably because the Henry's law constants were nearly equal to one another.

Fig. 1(b) shows the ratios of the concentrations of the VOCs in dew water to those in rainwater, which was abbreviated to Dew/Rain VOCs Ratio in the vertical axis, together with the octanol–water coefficients, K_{ow} ,

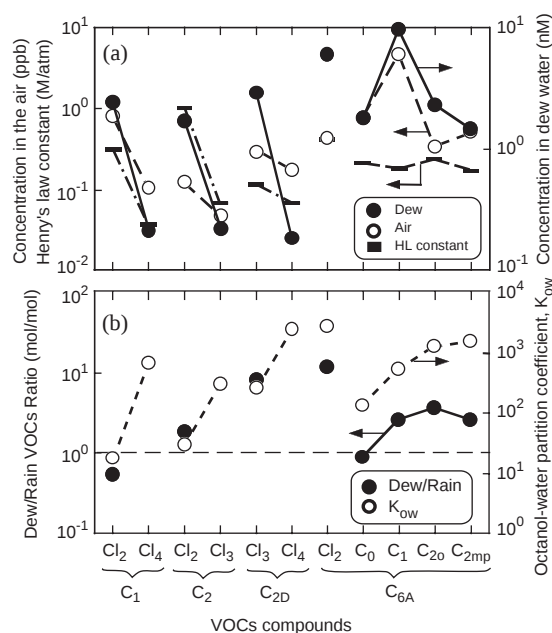


Fig. 1. (a) Volume-weighted mean concentrations of VOCs in dew water together with those in the ambient air and their Henry's law constants for plain water. (b) The ratios of the concentrations of VOCs in dew water to those in rainwater together with their octanol–water coefficients.

which is an indicator of hydrophobicity of organic compounds. The ratios for carbon tetrachloride (CTC, $C_1 Cl_4$), 1,1,1-trichloroethane (1,1,1-TCE, $C_2 Cl_3$), and tetrachloroethylene (TEL, $C_{2D} Cl_4$) are not shown in the figure because their concentrations in rainwater, which was collected in the same place, were below their detection limits. The concentrations of the VOCs except for DCM ($C_1 Cl_2$) and benzene (BEN, $C_6A C_0$) in dew water were several times higher than those in rainwater. The higher hydrophobic CHs and MAHs tended to be concentrated in dew water rather than in rainwater. The property of *p*-DCB, which is a chlorinated monocyclic aromatic hydrocarbon, was similar to that of CHs although we distinguished *p*-DCB as one of MAHs for convenience.

The differences between the concentrations of VOCs in dew water and in rainwater could be explained by the following if no formation and degradation of VOCs, which are out of our investigation in this study, in atmospheric water droplets occurred. One reason may be a difference in gas-phase concentrations of the VOCs in the presence of dew and during rainfall. The other is the difference in the chemical and/or physical properties of dew droplets and rain droplets, i.e. dew droplets may be more hydrophobic than rain droplets. There is obvious difference in the time of occurrence between dew and rain, i.e. dew forms only at night and early in the morning, while rain falls both at night and day. The ratio of the atmospheric concentrations of the VOCs at night ($n = 103$) to those in the daytime ($n = 93$) ranged from 0.61 (TEL, $C_{2D} Cl_4$) to 1.21 (DCM, $C_1 Cl_2$) for CHs and from 1.16 (BEN, $C_6A C_0$) to 1.57 (*m,p*-xylene (*m,p*-XY, $C_6A C_{2m,p}$)) for MAHs during the study period at our sampling site. There was no significant difference in the concentrations of all the CHs and MAHs between night and daytime at 1% significant level although concentrations of the MAHs at night tended to be higher than those in the daytime. Therefore the difference cannot be explained only by the gas-phase concentrations of the VOCs. This indicates that the difference of the physical/chemical properties between dew and rain droplets might be important in explaining the concentration of the VOCs in dew water. We will discuss it in detail later.

3.2. Temporal variation of concentrations of VOCs in dew water and in the ambient air

Figs. 2 and 3 shows the temporal variation of the concentrations of the CHs and the MAHs in dew water together with those in the ambient air during the study periods from 10 to 12 October 2000, respectively. The VOCs concentration in dew water was plotted at each sampling time in the figures, i.e. 4:00, 5:00, 6:00, 7:00, 8:00, and 9:00 a.m. Japan Standard Time. The variation of wind direction (WD) and wind speed (WS) is also

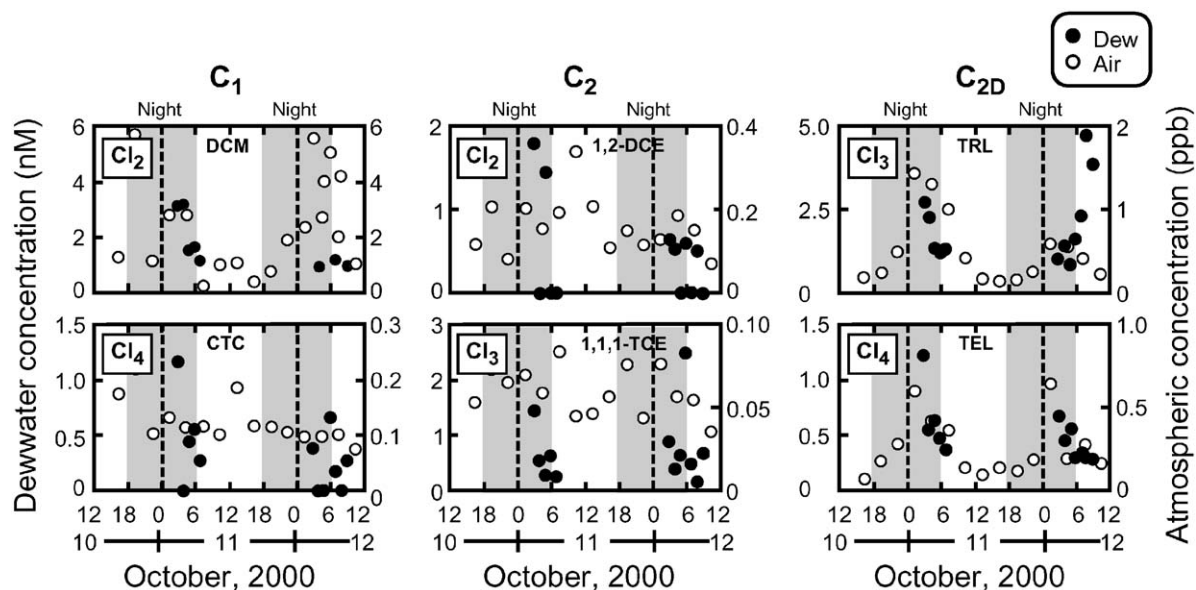


Fig. 2. The temporal variation of the concentration of chlorinated hydrocarbons (CHs) in dew water (●) together with those in the ambient air (○) during 10–12 October 2000. The shaded areas show nighttime.

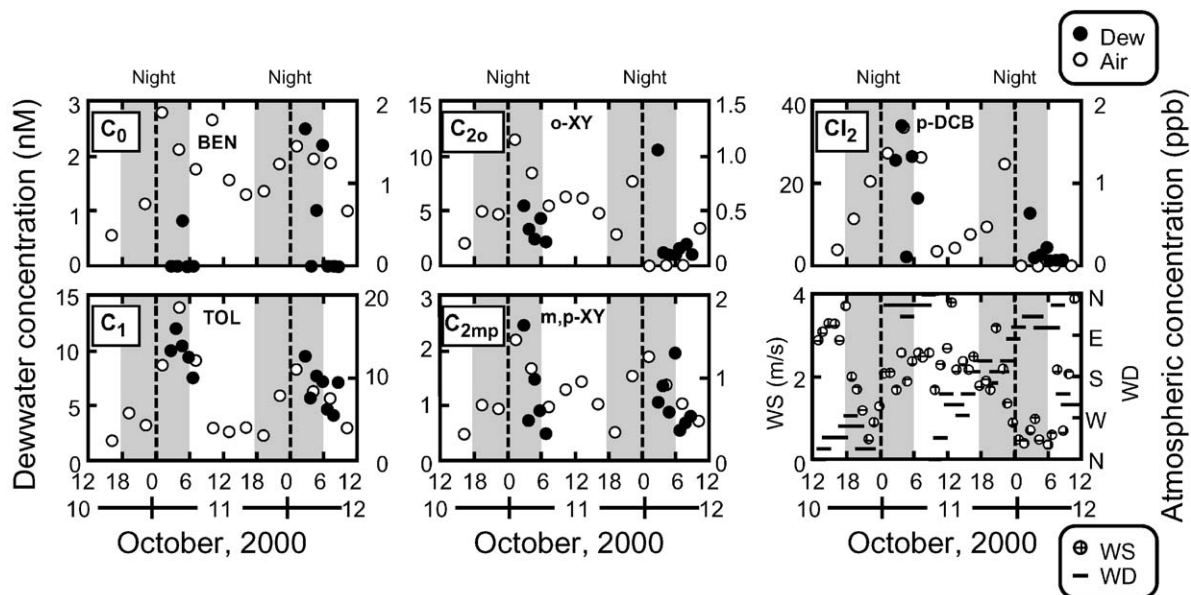


Fig. 3. The temporal variation of the concentration of monocyclic aromatic hydrocarbons (MAHs) in dew water (●) together with those in the ambient air (○) during 10–12 October 2000. The shaded areas show nighttime. The acronyms WS and WD indicate wind speed and wind direction, respectively.

shown in Fig. 3. Dew formed in the evening on 10 October when the northwesterly wind decreased and the maximum dewfall amount was observed to be 183 g m^{-2} at 7:00 a.m. in the following morning. Dew also formed in the evening on 11 October when the southeasterly

wind decreased and the maximum dewfall amount was observed to be 176 g m^{-2} in the following morning. The pHs ranged from 5.99 to 6.75 for dew water collected on 10–11 October and from 5.42 to 5.99 for dew water collected on 11–12 October. The pHs of both dew events

decreased during the observation from the evening to the following morning.

The VOCs, except for CTC (C_1Cl_4) and 1,2-DCE (C_2Cl_2), in the ambient air were higher at night than in the daytime during this period. The trend of some VOCs concentrations, such as DCM (C_1Cl_2), TEL (C_2DCl_4), and TOL (C_6AC_1), in the dew water was relatively similar to that of the corresponding VOCs concentrations in the ambient air and their concentrations in the dew water tended to decrease, i.e. evaporation in the morning due to the rise in temperature and wind speed. An exception was observed for TRL (C_2DCl_3) in the dew water collected on 12 October due to reasons unknown.

3.3. The enhanced dissolution of VOCs into urban dew water

We here define the enrichment factor E as D_{obs}/K_H , where K_H is the temperature-corrected Henry's law constant ($Matm^{-1}$) for plain water and D_{obs} is an observed distribution constant between in dew water and in the gas-phase, i.e. C_{rain}/p_{gas} ($Matm^{-1}$). The E values, which are shown in the right column in Table 1, were estimated using the Henry's law constants corrected at 17.2 °C, which was the average temperature of the sampling periods. The temperature correction of the Henry's law constants was performed using the following Eq. (1). The mean E values ranged from 6.98 (DCM) to 62.7 (TRL), respectively. This indicates that the dissolution of the atmospheric VOCs into the dew water was enhanced.

Fig. 4 shows the relationship between the calculated and the observed VOCs in dew water collected on 10–11 and 11–12 October, and 24–25 November, 2000. The calculated concentrations of VOCs in the dew water, C_{calc} were estimated using the observed concentrations in the ambient air, P_{VOCs} as follows:

$$C_{calc} = K_H(T)P_{VOCs}$$

$$K_H(T) = K_H(298.15) \exp \left\{ \frac{-\Delta H}{R} \left(\frac{1}{298.15} - \frac{1}{T} \right) \right\}, \quad (1)$$

where $K_H(T)$ is the Henry's law constant ($Matm^{-1}$) corrected at T (K), $K_H(298.15)$ is the Henry's law constant ($Matm^{-1}$) at 298.15 K for plain water, ΔH is the enthalpy change of air–water transfer, R is the gas constant ($8.314 J mol^{-1} K^{-1}$), T is the temperature (K). The enthalpy change of air–water transfer, ΔH_{Henry} , was estimated from Gossett (1987), Dewulf et al. (1995), Schwarzenbach et al. (1995) and CRC Handbook of Chemistry and Physics (Weast, 1986; Lide, 2001) and described in detail by Okochi et al. (2004). We see that the observed concentrations of the VOCs in the three dew events where there was simultaneous sampling of dew water and ambient air were higher than the calculated concentrations. Therefore the trend of the

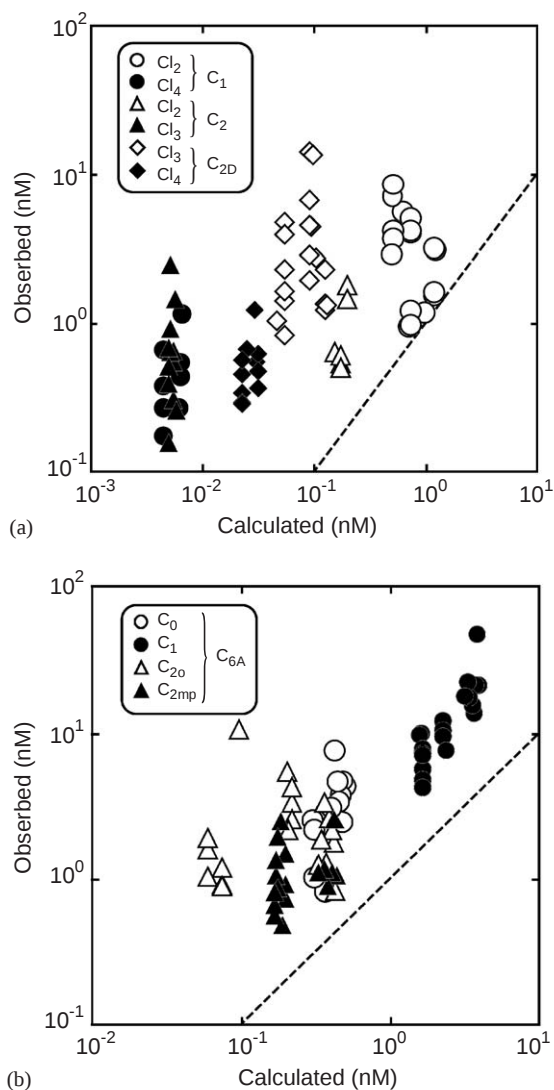


Fig. 4. The relationship between the observed and calculated VOCs concentration in dew water collected on 10–11 and 11–12 October and 24 November 2000. The dotted line shows the 1:1 line: (a) CHs and (b) MAHs.

mean E values shown in Table 1, which indicates that the dissolution of the atmospheric VOCs into the dew water is enhanced, is sensible.

The enrichment of the VOCs in dew water may be caused by the same mechanism as the enrichment of hydrophobic organic compounds in fog droplets (Valsaraj et al., 1993; Law and Diamond, 1998), namely; (1) the air–water interfacial adsorption and (2) the adsorption onto dissolved and/or colloidal organic materials in the droplets. Both mechanisms are related to the octanol–water coefficient K_{ow} (Valsaraj et al., 1993). The relationship between the K_{ow} and the

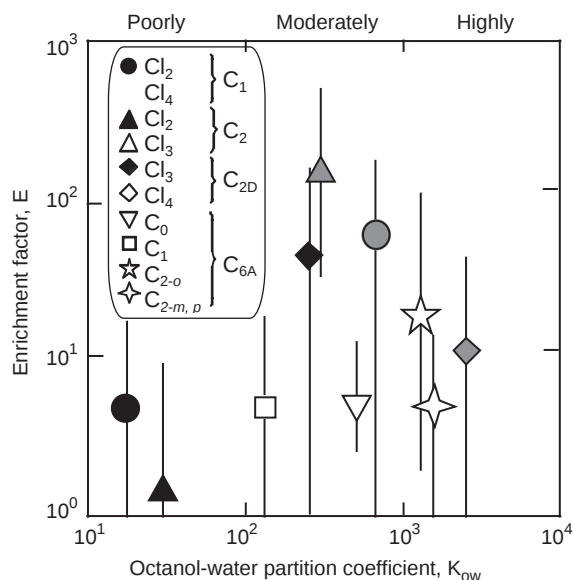


Fig. 5. The relationship between the octanol–water coefficient, K_{ow} and the enrichment factor, E of VOCs in dew water collected on 10–11 and 11–12 October and 24 November 2000. The vertical bars show the ranges in the enrichment factors. The poorly, moderately, and highly hydrophobic VOCs are defined as VOCs with $K_{ow} < 10^2$, $10^2 \leq K_{ow} < 10^3$, and $K_{ow} \geq 10^3$, respectively.

E values of the VOCs during the three dew events is shown in Fig. 5. The E values can be calculated as the ratio of the vertical axis to the horizontal axis in Fig. 4. The moderately hydrophobic CHs, with K_{ow} in the range 10^2 – 10^3 , tended to be more enhanced in the dew water.

As mentioned in Table 1, the highly hydrophobic VOCs tended to be more concentrated in dew water than in rainwater. This indicates that dew water has more hydrophobic property than does rainwater. Differences in the chemical properties of dew water and rainwater may cause differences in physical properties such as surface tension. It has been already shown that there are significant differences in the chemical composition and in the concentrations of major inorganic ions and DOC between those in dew water and in rainwater at our sampling site (Takeuchi et al., 2002). The decrease in the surface tension of fog water compared to that of pure water with the increase of dissolved organic carbon has been also reported (Capel et al., 1990; Facchini et al., 2000). The decrease of the surface tension indicates the presence of surfactants, which could increase 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; Krivácsy et al., 2000) because humic substances are well known to

reduce surface tension in an aqueous solution (e.g. Tombácz and Regdon, 1994; Terashima et al., 2004). Havers et al. (1998) have reported that over 10% 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. If the humic-like substances originated from soils and/or plants, the atmospheric concentration may be higher near the ground. Therefore the concentration of humic-like substances in dew water should be higher than that in rainwater because dew forms near the ground.

We had no observations of surfactants and the surface tension of dew water collected until 2000, so we need to look for the surrogates of surfactants or surface tension using our available data to investigate the influence of atmospheric surfactants on the enhanced dissolution of atmospheric VOCs into dew water. In general, surface tension is well known to decrease with the increase in concentration of organic compounds and increase with the increase in concentration of inorganic compounds (Moore, 1972). Therefore surface tension of each dew droplet might decrease with DOC and might increase with TIC, whose measurements were made in this study. It is likely that the ratio of DOC/TIC might be a surrogate for surface tension, and so this possibility was

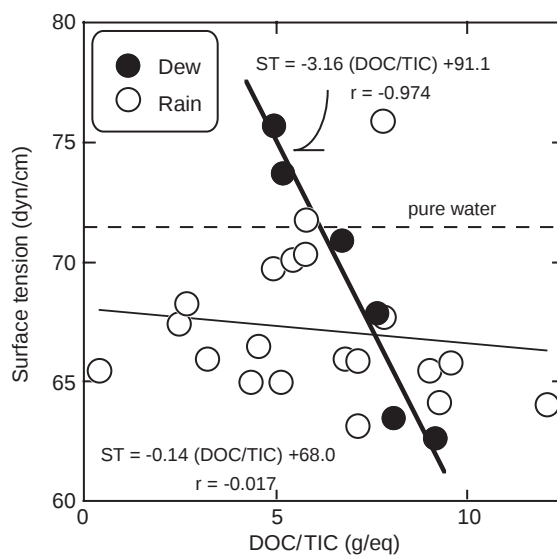


Fig. 6. The relationship between the ratio of dissolved organic carbon concentration (DOC) to total inorganic ions concentration (TIC) and the surface tension of six dew water samples collected in 2002. For comparison, the relationship for rainwater is also shown. The dotted line indicates the surface tension of pure water at 25 °C, while the thick and thin lines indicate the regression line between the DOC/TIC ratio and the surface tension for dew water and rainwater, respectively.

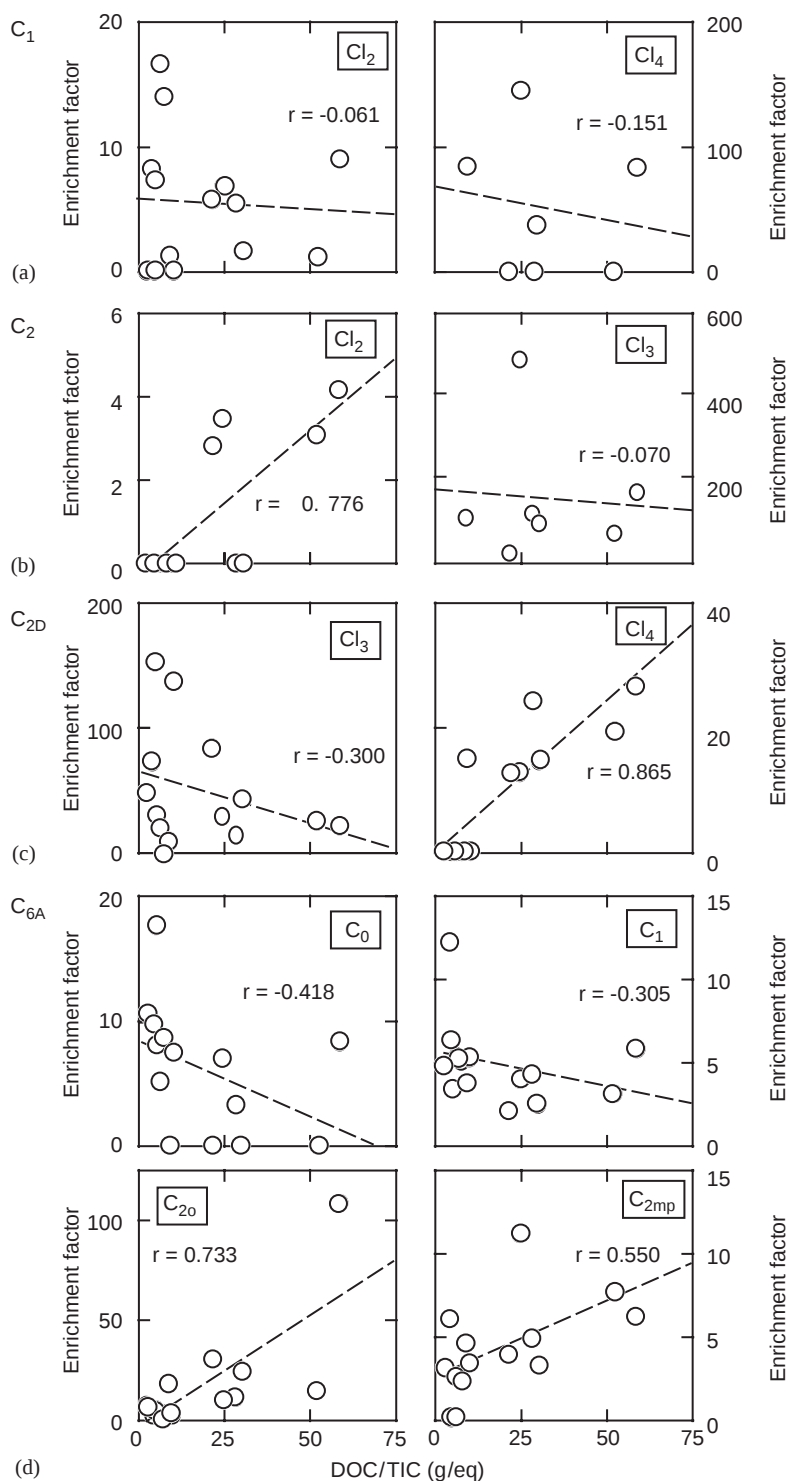


Fig. 7. The relationship between the DOC/TIC ratios and the enrichment factors, E of VOCs in dew water collected on 10–11 and 11–12 October and 24 November 2000: (a) C_1 , chlorinated hydrocarbons with one carbon number, (b) C_2 , chlorinated hydrocarbons with two carbon numbers, (c) C_{2D} , chlorinated hydrocarbons including one double bond, (d) C_{6A} , monocyclic aromatic hydrocarbons.

tested. We measured the surface tension, DOC, and TIC in six dew water samples collected in 2002 and the relationship between the ratio of DOC/TIC in dew water and the surface tension is shown in Fig. 6. The relationship for rainwater is also shown. We can see that there is significant negative correlation between them for dew water, indicating that the DOC/TIC ratio could be a surrogate for the surface tension of dew water. On the other hand, there is poor correlation between them for rainwater although the reason is not clear. One likely reason is the difference of the concentration and/or sorts of DOC, which might be a factor to decrease surface tension, between that in dew water and that in rainwater because the increment of surface tension by salts is much smaller than the decrement of organic compounds (Moore, 1972). Unfortunately, we have no more information about the differences of concentrations and sorts of DOC between dew water and rainwater. However, there is a possibility that humic-like substances are contained in dew water more than in rainwater, as mentioned already, because dew chemistry is strongly influenced by the ambient air near ground (Okochi et al., 1996).

Fig. 7 shows the relationship between the DOC/TIC ratios, which could be a surrogate for the surface tension of dew water as mentioned before, and the E values of the VOCs measured in dew water samples collected in October and November, 2000. There are relatively high correlations between them for the highly hydrophobic VOCs with $K_{ow} > 10^3$, namely TEL ($C_{2D}Cl_4$), *o*-xylene (*o*-XY, $C_{6A}C_{2o}$), and *m,p*-XY ($C_{6A}C_{2mp}$), at 5% significant level. Although there are few data, these correlations indicate that the existence of any dissolved organic compounds, which could reduce the surface tension, in dew water also cause the enrichment of the highly hydrophobic VOCs. On the other hand, there are insignificant correlations between the DOC/TIC ratios and the E values of the poorly ($K_{ow} < 10^3$) and moderately ($10^2 < K_{ow} < 10^3$) hydrophobic VOCs except for 1,2-DCE (C_2Cl_2). This indicates that there are some controlling factors of the enhanced dissolution of atmospheric VOCs into dew water, for example the adsorption on colloidal organic materials and the air–water interfacial adsorption as already pointed out for fog water chemistry by Valsaraj et al. (1993). The effect of the air–water interfacial adsorption on the enrichment of gas-phase VOCs into atmospheric droplets can be discussed using octanol–water partition coefficient (Valsaraj et al., 1993; Okochi et al., 2004). As shown in Fig. 5, poor correlations between the enrichment factors and the octanol–water partition coefficients indicate that the adsorption at the air–dew droplet interfacial is not important. Unfortunately we have no information to discuss the effect of colloidal organic materials in dew water on the enrichment of VOCs, but the contribution of colloidal organic matters including

humic-like substances could be of significance in explaining the enhanced dissolution of VOCs into dew droplets. Further investigations are needed to make clear the enrichment of gas-phase VOCs into dew water because we have poor information about the source, specification, and physicochemical properties of atmospheric humic-like substances.

Aknowledgements

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