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

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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 10^7, 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.
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. Thirteen 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 g m⁻², 60/80 mesh) and a quantity of 140 mg Carboxene 1000 (S = 1200 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 Mg(ClO₄)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(ClO₄)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 coincided 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

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

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; \(\Delta H_{Henry}\), 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);

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

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

\(\Delta H_{HENRY} = \Delta H_{VAP} - \Delta H_{ws}\).
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 ions 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 Dp (m), reaches the ground at the terminal velocity v1 (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:

$$ F = k_g(C_g - C_{eq}) $$

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, $C_{eq}$ (M). The rate of increase of $C_{eq}$ of an irreversibly scavenged gas in a droplet should be

---

Table 2

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

<table>
<thead>
<tr>
<th></th>
<th>Atmosphere (ppb)</th>
<th>Rainwater (nM)</th>
<th>$E_{avg}^{d}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$n = 73$</td>
<td>$n = 125$</td>
<td></td>
</tr>
<tr>
<td>Chlorinated hydrocarbons</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dichloromethane (DCM)</td>
<td>0.85</td>
<td>4.98</td>
<td>&lt;0.67–22.1</td>
</tr>
<tr>
<td>Carbon tetrachloride (CTC)</td>
<td>0.15</td>
<td>&lt;0.20</td>
<td>&lt;0.20–2.25</td>
</tr>
<tr>
<td>1,2-Dichloroethane (1,2-DCE)</td>
<td>0.16</td>
<td>1.06</td>
<td>&lt;0.47–9.92</td>
</tr>
<tr>
<td>1,1,1-Trichloroethane (1,1,1-TCE)</td>
<td>0.06</td>
<td>&lt;0.16</td>
<td>&lt;0.16–1.13</td>
</tr>
<tr>
<td>Trichloroethylene (TRL)</td>
<td>0.38</td>
<td>0.40</td>
<td>&lt;0.17–5.83</td>
</tr>
<tr>
<td>Tetrachloroethylene (TEL)</td>
<td>0.39</td>
<td>&lt;0.13</td>
<td>&lt;0.13–2.79</td>
</tr>
<tr>
<td>Aromatic hydrocarbons</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene (BEN)</td>
<td>0.67</td>
<td>1.97</td>
<td>&lt;0.42–15.3</td>
</tr>
<tr>
<td>Toluene (TOL)</td>
<td>4.12</td>
<td>3.77</td>
<td>&lt;0.08–25.9</td>
</tr>
<tr>
<td>o-Xylene (o-XY)</td>
<td>0.27</td>
<td>0.72</td>
<td>&lt;0.10–3.84</td>
</tr>
<tr>
<td>m, p-Xylene (m,p-XY)</td>
<td>0.41</td>
<td>0.69</td>
<td>&lt;0.12–13.2</td>
</tr>
<tr>
<td>p-Dichlorobenzene (p-DCB)</td>
<td>0.45</td>
<td>0.58</td>
<td>&lt;0.09–5.72</td>
</tr>
</tbody>
</table>

$^a$Arithmetic mean.

$^b$Volume-weighted mean.

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

$^d$The enrichment factors, $E_{avg}$ were defined as $C_{VMW}/(\rho_{AVG} \cdot K_H)$. Their Henry’s law constants, $K_H$, were corrected by the average temperature during rain periods (18.5°C).
equal to the rate of transport of a gas to the drop:

$$\frac{4}{3} \pi \left(\frac{D_p}{2}\right)^3 \frac{dC_{aq}}{dt} = 4\pi \left(\frac{D_p}{2}\right)^2 F.$$  \hspace{1cm} (2)

i.e.,

$$\frac{1}{6} \pi D_p^3 \frac{dC_{aq}}{dt} = \pi D_p^2 F.$$  \hspace{1cm} (3)

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

$$\frac{1}{6} \pi D_p^3 \frac{dC_{aq}}{dt} = \pi D_p^2 \kappa g (C_{aq} - C_{aq}) \quad \text{for} \quad z = 0.$$  \hspace{1cm} (4)

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

$$\frac{dC_{aq}}{dz} = -6 \times 10^3 \kappa g \frac{p_g}{v_d D_p RT K_{H}} (C_{aq} - p_g K_{H}).$$  \hspace{1cm} (5)

where $R$ is the gas constant (0.08205 atm 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 $C_{aq} = C_{aq}^0$ to $C_{aq}$, and $z = 0$ to $z$:

$$C_{aq} = K_{H} p_{aq} - (K_{H} p_{aq} - C_{aq}^0) \exp \left( -6 \times 10^3 \kappa g \frac{p_g}{v_d D_p RT K_{H}} z \right).$$  \hspace{1cm} (6)

$$k_g = \frac{K_{g}}{D_p} \left[ 2 + 0.6 \left( \frac{D_p}{\nu_{air}} \right)^{1/2} \left( \frac{\mu_{air}}{K_{g}} \right)^{1.147} \right],$$

$$\nu_{air} = 9.58 \left[ 1 - \exp \left( - \left( \frac{D_p}{0.17110} \right)^{1.147} \right) \right],$$

$$\mu_{air} = 1.328 \times 10^{-5} \left( \frac{1}{p} \right)^{1.754} \left( \frac{273.15 + T}{273.15} \right)^{1.147},$$

where $C_{aq}^0$ 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$^{-1}$), $\mu_{air}$ 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 $C_{aq}^0$ 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
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 Table 1 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. 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.
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, $C_{\text{rain}}$ (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.

$$C_{\text{rain}} = \frac{\int_{0.02}^{\infty} \pi C_{0,aq} D_{p}^{3} N(D_{p}) dD_{p}}{\int_{0.02}^{\infty} \pi D_{p}^{3} N(D_{p}) dD_{p}}.$$  

(7)

$N(D_{p}) = \frac{dN}{dD_{p}} = 0.08 \exp(-41D_{p}I^{-0.21}),$

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
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 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
correlation coefficient between the average of $E_{\text{CH}}$ and $K_{\text{ow}}$ was 0.737, while the coefficient between the average of $E_{\text{MAHs}}$ and $K_{\text{ow}}$ 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 Valasaraj 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.

$$
\log W_G = \log K_{ia} + \log S = -a \log p_L + b + \log S,
$$

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 $C_{\text{rain}}/C_{\text{gas}}$, so the enrichment factor, $E$ is proportional to $W_G$ when the temperature is constant as follows:

$$
E = \frac{D_{\text{obs}}}{K_H} = \frac{C_{\text{rain}}}{p_{\text{gas}}K_H} = \frac{C_{\text{rain}}{\text{RTK}}_H}{W_G K_H{\text{RT}}},
$$

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 $K_{ia}$ 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 $K_{ia}$ 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 $K_{\text{ow}}$. The logarithm of the partition coefficient between the colloidal dissolved organic compounds and water, log $K_{oc}$ also shows a linear relationship with log $K_{\text{ow}}$ (Valasaraj, 1993), so log $E$ should also shows a linear relationship with log $K_{oc}$. 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. Krivačevy 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.

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