Distributions and sea-to-air fluxes of volatile halocarbons in the southern Yellow Sea and the East China Sea

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Abstract

Distributions and sea-to-air fluxes of five kinds of volatile halocarbons (VHCs) were studied in the southern Yellow Sea (SYS) and the East China Sea (ECS) in November 2007. The results showed that the concentrations of 1,1,1-trichloroethane (C2H3Cl3), 1,1,2-trichloroethene (C2H2Cl2), C2HCl3, CHCl3 and CCl4 in the surface water were 0.31–4.81, 2.75–21.3, 1.21–17.1, 5.02–233 and 0.045–4.47 pmol/L, respectively, with the average values of 1.89, 12.20, 6.93, 60.90 and 0.33 pmol/L. On the whole, the horizontal distributions of C2H3Cl3, C2H2Cl2 and CCl4 were affected mainly by anthropogenic activities, while C2HCl3 and CHCl3 were influenced by biological factors as well as anthropogenic activities. In the study area, the concentrations of VHCs (except C2HCl3) exhibited a decreasing trend from inshore to offshore sites, with the higher values occurring in the coastal waters. The sea-to-air fluxes of C2H3Cl3, C2H2Cl2, C2HCl3 and CHCl3 were calculated to be −56.00–(−5.68), −7.31–123.42, 148.00–1 309.31 and −83.32–(−1.53) nmol/(m²·d), respectively, with the average values of −6.77, 17.14, 183.38 and −21.27 nmol/(m²·d). Our data showed that the SYS and ECS in autumn was a sink for C2H3Cl3 and CHCl3, while it was a source for C2H2Cl2 and CCl4 in the atmosphere.

Key words: volatile halocarbons, distribution, southern Yellow Sea, East China Sea, sea-to-air flux


1 Introduction

Volatile halocarbons (VHCs) are ozone depleting substances (Shon and Kim, 2002; McCulloch, 2003; Abrahamsson and Edkahl, 1993; Abrahamsson et al., 1995, 2003; Abrahamsson, Lorén et al., 2004; Abrahamsson, Bertilssonb et al., 2004). Chlorinated halocarbons are believed to be important carriers of chlorine to the stratosphere. Among them, 1,1,1-trichloroethane (C2H3Cl3), 1,1,2-trichloroethene (C2H2Cl2), C2HCl3, CHCl3 and CCl4 account for an estimated 15% of the total organic chlorine in the troposphere. Among them, 1,1,1-trichloroethane (C2H3Cl3), trichloromethane (CHCl3) and tetrachloromethane (CCl4) account for an estimated 15% of the total organic chlorine in the troposphere. In addition, the VHCs are the greenhouse gases (Rhew et al., 2008; Lee et al., 2000). Up to date, little information has been available on the distribution of VHCs in the area. In this study, we present the first shipboard measurements of C2H3Cl3, 1,1-dichloroethene (C2H4Cl2), C2HCl3, CHCl3 and CCl4 in the SYS and ECS. The purposes of this survey are to describe the spatial distribution of these compounds and to estimate their sea-to-air fluxes in this area.

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Seawater samples were collected from the Niskin bottles of the rosette sampler using 100 mL gas-tight syringes, immediately after the rosette was returned onto the board. The syringes were stored in the dark at in situ seawater temperature until analysis, usually within 6 h. The concentrations of the VHCs in the seawater samples did not vary significantly within 6 h (Lu et al., 2010; He et al., 2013c). The environmental and hydrographic conditions of the sampling stations, such as location, surface seawater temperature and salinity, are described in Table 1. The wind speeds were measured at about 10 m elevation from the sea surface using the Model 27600-4X Ship-borne Weather Instrument (Young, US). The wind speeds were extracted with 90% acetone according to Parsons et al. (1984). The precision for determining Chl a was 0.001 μg/L.

2.2 Sea-to-air flux calculations

The sea-to-air fluxes of these five VHCs were calculated by the following equation (Liss and Slater, 1974):

\[ F = K_a (C_a - C_f) H^{-1}, \]

where \( C_a \) and \( C_f \) are the concentrations of VHCs in seawater and the atmosphere, respectively. \( H \) is the Henry’s law constant. \( K_a \) is the gas exchange velocity, which is computed as a function of wind speed and the Schmidt number. \( K_a \) was calculated using the relationship established by Wanninkhof (1992) (Lu et al., 2010; Hu et al., 2010; He et al., 2013a):

\[ K_a = 0.31 u^2 (S / 660)^{-1/2}, \]

where \( u \) is wind speed (m/s) about 10 m elevation from the sea-surface. \( S \) is the Schmidt number, which is rate of water dynamic conglutination and the diffusion factor. In this work, \( S \) number was calculated using the empirical formula of Khalil and Rasmussen (1998).

\[ S = 335.6 M^{0.5} (1 - 0.065 t + 0.002 043 t^2 - 2.6 \times 10^{-3} t^3), \]

where \( M \) is the molecule weight of VHCs, \( t \) is surface seawater temperature.

In this work, Henry’s law constants of \( C_2HCl_3 \) and \( CCl_4 \) were derived from the empirical relationship given by Warneck (2007), with the unit of \( H \) being atm∙dm\(^3\)/mol, while Henry’s law constants of \( CH_3Cl \) and \( CHCl_3 \) were obtained from the relationship given by Moore et al. (1995) and Moore (2000), with the unit of \( H \) being non-dimensional. \( T \) is the Kelvin temperature (K).

\[ C_2HCl_3: \ln H = -(15.193 \pm 0.323) - (3.6973 \pm 95.7) / T, \]

\[ CCl_4: \ln H = -(17.600 \pm 0.403) - (4.2842 \pm 119.4) / T, \]

\[ CH_3Cl: \ln H = -(11.17 \pm 0.01) - (3.840 \pm 31.3) / T, \]

\[ CHCl_3: \ln H = -(14.88 \pm 0.02) - (4.624 \pm 69.5) / T. \]

The concentrations of VHCs in the air were needed to calculate their sea-to-air fluxes. Nevertheless, no atmospheric concentrations of these VHCs were determined in the present study. In this case, we used the values of the literature instead (49×10\(^{-15}\) for \( C_2HCl_3 \), 114×10\(^{-16}\) for \( CCl_4 \), 2.00 pmol/L for \( CH_3Cl \), and 0.87 pmol/L for \( CHCl_3 \) in the atmosphere of 45 China’s cities) (Barletta et al., 2006). The fluxes of \( C_2HCl_3 \) were not calculated, due to the absence of its atmospheric concentration in the literature.
3 Results and discussion

3.1 Horizontal distributions of the five kinds of VHCs in the surface water

3.1.1 C₂H₃Cl₃, C₂H₂Cl₂ and C₂HCl₃

In the study area, concentrations of C₂H₃Cl₃ in the surface water ranged from 0.31 to 4.81 pmol/L, with an average of 1.89 pmol/L. Overall, C₂H₃Cl₃ concentrations declined gradually from inshore to offshore stations. In contrast, concentrations of C₄H₈Clᵢ in the surface water fluctuated between 2.75 and 21.30 pmol/L, with an average of 12.20 pmol/L. The distribution of C₂H₂Cl₂ was similar to that of C₂H₃Cl₃. The higher concentrations of C₂H₃Cl₃ and C₂H₂Cl₂ observed near the Changjiang River Estuary and in the coastal waters might be attributed to evident terrestrial input and the Changjiang River water dispersal, while the lower concentrations of C₂H₂Cl₂ in the open sea might be influenced by the Kurishio water.

Table 1. Description of sampling stations and their surface seawater temperature, salinity, Chl a and wind speed data

<table>
<thead>
<tr>
<th>Station No.</th>
<th>Location</th>
<th>Depth/m</th>
<th>Temperature/ °C</th>
<th>Salinity</th>
<th>Wind speed/ m·s⁻¹</th>
<th>Chl a/ μg·L⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>F0301</td>
<td>35.00°N</td>
<td>119.98°E</td>
<td>27</td>
<td>15.533</td>
<td>30.641</td>
<td>4.9</td>
</tr>
<tr>
<td>...</td>
<td>...</td>
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<td>...</td>
<td>...</td>
<td>...</td>
</tr>
</tbody>
</table>
Compared to the results of Karlsson et al. (2008) (6.4 pmol/L in the Baltic Sea) and Ekdahl et al. (1998) (29–37 pmol/L in a rock pool), the concentrations of CHCl₃ were lower in this study. Our data of CH₂Cl₂ concentrations fell within the range (0–182 pmol/L) reported in Liverpool Bay by Bravo-Linares et al. (2007). The CH₂Cl₂ concentrations were similar to those of Huybrechts et al. (2005) in southern North Sea (12.37 pmol/L). and were obviously lower than those of Yamamoto et al. (1997) (4.12–11.34 nmol/L in river waters and their estuaries) and Yamamoto et al. (2001) (13.30 nmol/L in shallow urban rivers) in Osaka City of Japan.

The CH₃Cl concentrations in the surface water varied from 1.21 to 17.10 pmol/L (mean: 6.93 pmol/L). Higher values were observed at stations F0403, F0704 and F1101. Traditionally, the presence of CH₃Cl in the marine environment was usually attributed to human activities. Karlsson et al. (2008) found that cyanobacterial algae did not produce CH₂Cl₂. However, Abrahamsson et al. (1995) and Ekdahl et al. (1998) reported that some algae could produce CH₂Cl₂. This suggested that the biological source of CH₃Cl was related with the algal species. In this study, not all regions with elevated CH₃Cl concentrations displayed high Chl a levels, suggesting that the phytoplankton release was not the main source of CH₂Cl₂. The high concentrations of CH₂Cl₂ might result mainly from anthropogenic activities. In the Changjiang River Estuary, however, the concentration of CH₃Cl was lower than that in the outer estuary, which might be attributed to the particulate adsorption. He et al. (2013c) also found that the concentration of CH₃Cl was lower in this area.

CHCl₃ concentrations in this study were lower than those of Yang et al. (2010) (15.4 pmol/L in the northern Yellow Sea), Yang et al. (2009) (11.90 pmol/L in the subsurface water of the YS), He et al. (2013a, b) (29.7 pmol/L in spring in the Yellow Sea and the East China Sea, 16.27 pmol/L in winter in the East China Sea) and Abrahamsson and Ekdahl (1996) (7.15–29.66 pmol/L in the Skagerrak strait), but higher than those of Karlsson et al. (2008) (5.3 pmol/L in surface water) and Abrahamsson, Bertilssonb et al. (2004b) (2.5–7.5 pmol/L in the Southern Atlantic). The difference in the VHCs concentrations was caused mainly by different regions and diverse hydrographic features.

3.1.2 CHCl₃ and CCl₄

The concentrations of CHCl₃ in the surface water varied from 5.02 to 233.00 pmol/L (mean: 60.90 pmol/L). Higher concentrations of CHCl₃ were observed in the Changjiang River Estuary, the south of Cheju and the northeast of Taiwan (Fig. 2). In these areas, the Changjiang River runoff, the coastal current and Kuroshio existed (Zhu et al., 2003; Zhou et al., 2007). The higher concentrations of Chl a were generally observed in these areas, for instance, 0.97, 2.06 and 0.92 pg/L at Stas F0501, F1006 and F1105, respectively. Previous studies showed that micro-algae (H. spinella, F. hillebrandii and G. cornea) and some species of macro-algae could produce CHCl₃ (Ekdahl et al., 1998; Nignantale, 1995), while cyanobacterial algae could not produce CHCl₃ (Karlsson et al., 2008). Overall, the concentrations of CHCl₃ were affected by the phytoplankton biomass as well as anthropogenic activities.

CHCl₃ concentrations in this study were similar to those of Ekdahl et al. (1998) (10–250 pmol/L), Fogelqvist et al. (1996) (16.73–100.42 pmol/L in the surface water of Bosphorus Strait), and He et al. (2013a) (10.3–250.5 pmol/L in spring in the Yellow Sea and the East China Sea). The concentrations of CHCl₃ in this study were higher than those of Karlsson et al. (2008) (3.3 pmol/L in the Baltic Sea) and Abrahamsson, Lörén et al. (2004a) (0.21–0.25 pmol/L in the South Atlantic). Data obtained in this study were higher than those of Yang et al. (2010) (9.9–63.4 pmol/L in autumn in the northern Yellow Sea), Yang et al. (2009) (2.02–38.55 pmol/L in the subsurface water of the Yellow Sea), and He et al. (2013b) (0.4–62.92 pmol/L in winter in the East China Sea).

The concentrations of CCl₄ in the surface water varied from 0.045 to 4.47 pmol/L, with an average value of 0.33 pmol/L. The higher levels of CCl₄ were observed at the coastal stations, possibly due to the influence of anthropogenic activities. Our data were lower than those of Yang et al. (2009) (0.80 pmol/L in the subsurface water of Yellow Sea), Liss and Salter (1974) (2.68 pmol/L in Atlantic), He et al. (2013b) (0.39–8.13 pmol/L in winter in the East China Sea), Karlsson et al. (2008) (7.8 pmol/L in the Baltic Sea), and Abrahamsson and Ekdahl (1996) (4.81–6.49 pmol/L in Skagerrak strait). Compared to the study of Huybrechts et al. (2004), the average CCl₄ concentration was significantly lower than that in the Scheldt estuary (213.64 pmol/L). This difference might be due to different survey area and time.

We investigated the relationships among the concentrations of VHCs in order to understand their sources. Krysell and Nightingale (1994) reported that common sources of different compounds could be identified by the significant correlation. However, we did not observe the significant relationships among the concentrations of VHCs. The combination of anthropogenic and natural sources would reduce the correlation between the compounds (Krysell and Nightingale, 1994). In addition, high anthropogenic inputs might conceal the natural production which also decreased the correlation (Christof et al., 2002). The correlation might also be reduced by phytoplankton species (major producers of VHCs) and water masses (Abrahamsson, Bertilssonb et al., 2004b).

We also investigated the relationships between VHCs and surface seawater temperature, salinity and Chl a in this study. Linear regression analyses indicated that no correlation was found between VHCs and these factors, which agreed with the results reported by Roy (2010), Christof et al. (2002), Abrahamsson, Lörén et al. (2004) and Abrahamsson, Bertilssonb et al. (2004). Our study suggested that the phytoplankton release was not the main source of VHCs in the study area.

3.2 Vertical profiles of VHCs

The vertical profiles of five VHCs, seawater temperature and salinity along F03 and F05 transects are depicted in Figs 3 and 4, respectively. Transect F05 spreads from the Changjiang River Estuary to the open sea in the ECS, while transect F03 crosses the shelf of the SYS.

3.2.1 Vertical profiles of VHCs along transect F03

At transect F03, overall, the seawater temperatures were slightly higher in the surface than those at the bottom, and the temperatures in the open water were lower than those in the coastal water. In contrast, the salinity in the bottom and offshore areas were higher than those in the surface and inshore areas. However, the seawater temperatures at stations F0303 and F0305 were higher than those at stations F0301 and F0307, indicating that Yellow Sea Warm Current existed at Transect F03, which agreed with the finding of Li et al. (2006). The vertical concentrations of the five VHCs at Transect F03 are shown in Fig. 3. Higher concentrations of CH₂Cl₂ appeared at station F0305, especially at the bottom of this station. Zoccolillo et al. (1996) reported that CH₂Cl₂ was difficult to decompose and easy to be carried by water mass. At the same time, we also observed that the concentrations of CH₃Cl were higher in the ECS than in the SYS (Fig. 2). This suggested the higher concentrations of CH₃Cl observed here might be caused by the Yellow Sea warm current which contained high level of CH₃Cl.

The CH₂Cl₂ concentrations at inshore stations were higher...
than those at offshore stations, and the values in the surface were
differently lower than those at the bottom. CHCl_3 and CCl_4 had sim-
ilar vertical profiles to that of C_2H_2Cl_2. For C_2HCl_3, no manifest
variation pattern was observed at transect F03. Higher concentra-
tions of VHCs at inshore sites might be attributed to the Yellow
Sea coastal current and terrestrial input. Weissflog et al. (2001,
2004, 2005) found that C_2H_3Cl_3, CCl_4, C_2HCl_3 and CHCl_3 were emi-
ted from salt marsh sediment. Therefore, the higher concent-
rations of VHCs at the bottom possibly derived from the sediment
emission.

3.2.2 Transect F05

At Transect F05, the distributions of temperature and salinity
in vertical profiles were uniform at the most stations. At Stas
F0510 and F0512, the temperature decreased with the depth,
while the salinity increased with the depth. The variations of tem-
perature and salinity indicated the dispersal of the Changjiang
River diluted water at inshore sites and the intrusion of Kuroshio
water at Stas F0510 and F0512 (Fig. 4). The vertical concentra-
tions of the five VHCs at transect F05 are shown in Fig. 4.

Fig. 2.
Fig. 2. Horizontal distributions of temperature(°C), salinity, Chl α (µg/L) and five VHCs (pmol/L) in the surface seawater of the SYS and the ECS in November 2007.

At Transect F05, the concentrations of VHCs (except C₂HCl₃) increased with the depth at the most stations, while the concentrations of C₂HCl₃ decreased at offshore Stas F0510 and F0512. Variation in the concentrations of VHCs at the different depths might be attributed to water masses mixing and their own physicochemical properties. For example, at Sta. F0508, the highest concentrations of C₂H₃Cl₃, CHCl₃ and CCl₄ appeared in the bottom water, while the highest concentrations of C₂H₂Cl₂ and C₂HCl₃ occurred in the surface water and in the middle of water column, respectively (Fig. 4). Min et al. (2010) indicated that the high concentrations of CCl₄ in the deep water resulted from active vertical water exchange in the Sea of Japan. Zoccolillo et al. (2009) reported that the mixing of the different water masses influenced the vertical profile distribution of C₂H₃Cl₃, C₂HCl₃ and CCl₄.

3.3 Sea-to-air fluxes of four kinds of halocarbons

The sea-to-air fluxes of C₂H₃Cl₃, CHCl₃, CCl₄ and C₂HCl₃ were estimated to be -56.6-(-5.68), 148-1309.31, -83.32-(-1.53) and -7.31-123.42 nmol/(m²·d), respectively, and exhibited considerable spatial variability (Fig. 5). The mean fluxes of C₂H₃Cl₃, CHCl₃, CCl₄ and C₂HCl₃ in the investigated area were -6.77, 183.38, -21.27 and 17.14 nmol/(m²·d), respectively. The fluxes of VHCs were affected primarily by the concentrations of VHCs, wind speeds and surface water temperature from the calculating process.
of the flux. In the present study, the distribution of VHCs fluxes, to some extent, showed a similar pattern to that of VHCs concentrations in the surface seawater, suggesting that the VHCs fluxes were largely controlled by the surface concentrations rather than by wind speeds. Our results showed that, on the whole, the study area was the source of C₂HCl₃ and CHCl₃ in the atmosphere and the sink of C₃H₇Cl and CCl₄ in the atmosphere.

Fig. 3.
Fig. 3. Vertical profiles of the temperature, salinity, and five VHCs (pmol/L) at Transect F03.

Fig. 4.
Fig. 4. Vertical profiles of the temperature(°C), salinity and five VHCs (pmol/L) at Transect F05.

The fluxes of C$_2$H$_3$Cl$_3$, C$_2$HCl$_3$, CHCl$_3$, and CCl$_4$ in the Pacific were 2.0, 1.4, 2.1, and 1.2 Gg/year in 2002, respectively (Yokouchi et al., 2005). C$_2$HCl$_3$ and CCl$_4$ fluxes were 0.2 and −2 Gg/year in the Skagerrak (Abrahamsson and Ekdahl, 1996). In order to compare our fluxes with literature values, we extrapolated the VHCs fluxes to one year in this area. The average fluxes of C$_2$H$_3$Cl$_3$, C$_2$HCl$_3$, CHCl$_3$, and CCl$_4$ in our study were −0.37, 0.93, 9.07 and −1.37 Gg/year, respectively. In the process of calculating fluxes of VHCs, we used the literature values (the average values in the 45 China’s cities) (Barletta et al., 2006) instead of the actual concentrations in the atmosphere, which might make the fluxes underestimated because the concentrations in cities were higher than the real atmospheric concentrations in this study area. Moreover, Montzka et al. (1996) reported the C$_2$H$_3$Cl$_3$ and CCl$_4$ in the atmosphere were decreasing, consequently, the fluxes of the C$_2$H$_3$Cl$_3$ and CCl$_4$ might be underestimated. On the other hand, no investigations of VHCs were conducted in other seasons in the study area, which increased the uncertainty in calculating fluxes. In order to obtain an accurate estimation of the VHCs fluxes, the concentrations of VHCs in the atmosphere should be measured. Moreover, the study of VHCs should be carried out in different seasons in future.

4 Conclusions

The concentrations and sea-to-air fluxes of C$_2$H$_3$Cl$_3$, C$_2$H$_2$Cl$_2$, C$_2$HCl$_3$, CHCl$_3$, and CCl$_4$ were quantified in the SYS and ECS. In the study area, the distributions of the five VHCs in the surface C$_2$H$_2$Cl$_2$, CHCl$_3$, and CCl$_4$ (except C$_2$HCl$_3$) all revealed higher waters were affected by the Changjiang River discharge, coastal current, the Yellow Warm Current and Kuroshio water. C$_2$H$_3$Cl$_3$, concentrations off the Changjiang River Estuary. In general, the concentrations of C$_2$H$_3$Cl$_3$, C$_2$H$_2$Cl$_2$, CHCl$_3$, and CCl$_4$ decreased from inshore to offshore sites. C$_2$H$_3$Cl$_3$, C$_2$H$_2$Cl$_2$, and CCl$_4$ were affected mainly by anthropogenic activities, while CHCl$_3$ and C$_2$HCl$_3$ were influenced by in situ biological production as well as anthropogenic activities. For vertical distribution, the concentrations of VHCs in the coastal waters exhibited a uniform pattern, due to strong mixing of water masses. However, the maxima of VHCs varied among different stations in vertical profile of the open sea. Our study indicated that the SYS and ECS in autumn was the sink of C$_2$H$_3$Cl$_3$ and CCl$_4$, while it was the source of CHCl$_3$ and C$_2$HCl$_3$ in the atmosphere.
Fig. 5. Distribution of the sea-to-air fluxes of C2H3Cl3, C2HCl3, CHCl3 and CCl4 in November 2007 [unit: nmol/(m²·d)].

References


