EXPRESS LETTER

Determination of Henry's law constant of halocarbons in seawater and analysis of sea-to-air flux of iodoethane (C₂H₅I) in the Indian and Southern oceans based on partial pressure measurements

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The sea-to-air flux of C_2H_5I (iodoethane) in the Indian Ocean and the Southern Ocean was estimated from the Henry's law constant (K_H) and the measured partial pressures of C_2H_5I in surface seawater and air. The values of K_H, defined as the ratio of molar concentration (mol l^{-1}) to partial pressure (atm), for ten volatile organic compounds (VOCs) ($CFCl_3$ (CFC-11), C_5H_8 (isoprene), $C_2H_2F_4$ (HFC-134a), CHF_2Cl (HCFC-22), CH_3I, CH_2Br_2, C_2H_5I, CH_2Cl_2, CH_2ClI, and $CHBr_3$) were measured with an equilibrator and a purge-and-trap system in combination with gas chromatography-mass spectrometry. Ours is the first report of the K_H values for C_2H_5I and C_5H_8 as functions of temperature. The K_H values for the other VOCs were in good agreement with previously reported values. We calculated the sea-to-air flux of C_2H_5I using the newly determined K_H. Large sea-to-air fluxes (average, 0.04 nmol m^{-2}h^{-1}) were widespread in the Southern Ocean. We suggest that high biological productivity led to a high rate of C_2H_5I production in the subpolar water, and that the strong winds that frequently blow over the Southern Ocean resulted in the large sea-to-air flux.

Keywords: solubility, equilibrator, volatile organic compounds, isoprene, ethyl iodide

INTRODUCTION

The ocean is an important source of volatile organic compounds (VOCs) such as halogenated organic compounds (halocarbons) and nonmethane hydrocarbons (e.g., Broadgate *et al.*, 1997; Scarratt and Moore, 1998). Oceanic VOCs are believed to play important roles in atmospheric chemistry. For example, long-lived halocarbons such as CH_3Cl and CH_3Br contribute to ozone destruction in the stratosphere and upper troposphere (World Meteorological Organization, 2007; Chameides and Davis, 1980). Iodine monoxide derived from short-lived iodinated halocarbons such as CH_3I, C_2H_5I, CH_2ClI, and CH_2I_2 is likely to contribute to the formation of new particles in coastal air (O'Dowd *et al.*, 2002), and many kinds of short-lived VOCs including nonmethane hydrocarbons and halocarbons contribute to the removal of OH radicals in remote marine air (Donahue and Prinn, 1993). Oceanic fluxes of these VOCs have been measured with equilibrators at high time resolution (1-min to 1-h intervals; e.g., Chuck *et al.*, 2005; Kameyama *et al.*, 2010; Ooki *et al.*, 2010).

The sea-to-air flux of a VOC can be calculated from the following equation:

$$\text{Flux} = V(p\text{VOC}_{\text{water}} - p\text{VOC}_{\text{air}})K_H, \qquad (1)$$

where V is the gas transfer velocity (cm s^{-1}), which depends on wind speed; $p\text{VOC}_{\text{water}}$ and $p\text{VOC}_{\text{air}}$ are the partial pressures of the VOC in water and air, respectively; and K_H is the Henry's law constant for the VOC. The gas transfer velocity can be calculated from the Wanninkhof (1992) formulation as follows

$$V = 0.31 \times u^2(\text{Sc}/660)^{-0.5}, \qquad (2)$$

where u is the wind speed and Sc is the Schmidt number. The K_H values for chlorofluorocarbons CFC-11 and CFC-12 (which are used as tracers to track the history of deep seawater previously exposed to the atmosphere) as functions of seawater temperature and salinity have been reported by several investigators (Hunter-Smith *et al.*, 1983; Warner and Weiss, 1985; Wisegarver and Cline, 1985), and values for some halocarbons (e.g., CH_3I, CH_2Br_2, and CH_2ClI) in seawater have also been reported (Hunter-Smith *et al.*, 1983; Elliott and Rowland, 1993; Gossett, 1987; Moore *et al.*, 1995; Moore, 2000). However, the K_H values of C_2H_5I and C_5H_8 in seawater as functions of

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temperature have not yet been reported by experimental study, and the lack of K_H values has prevented calculations of their sea-to-air fluxes from Eq. (1).

In this study, we determined the K_H values for ten VOC species, including C_2H_5I and C_5H_8, in natural seawater by measuring the partial pressures and the molar concentrations of the VOCs with a liquid-gas equilibrator and a purge-and-trap system, respectively, in combination with gas chromatography-mass spectrometry (GC-MS) during shipboard observations. The sea-to-air flux of C_2H_5I was calculated from the newly determined K_H and pVOC data observed in the Indian Ocean and the Southern Ocean.

METHODS

Henry's law constant measurement

The Henry's law constant for a VOC (K_H, mol l^{-1} atm^{-1}) is defined as the ratio of the molar concentration of the VOC (M_{VOC}, mol l^{-1}) to the partial pressure of the VOC (pVOC$_{water}$, atm) in seawater:

$$K_H = M_{VOC}/p\text{VOC}_{water}. \qquad (3)$$

We measured M_{VOC} and pVOC$_{water}$ for VOCs in seawater samples onboard during a cruise as we will describe later. Surface seawater was pumped from a seawater intake on the bottom of the ship (5-m depth) and continuously supplied to the ship's laboratory. The gas samples for pVOC$_{water}$ measurements were collected from the seawater sample with a silicone membrane tube equilibrator (Ooki and Yokouchi, 2008), and the samples for M_{VOC} measurements were collected with a purge-and-trap system. The VOC partial pressures and molar concentrations in the collected samples were determined by GC-MS as described below.

Partial pressure measurement with the gas-liquid equilibrator

The equilibrator consisted of six silicone tubes housed in a poly vinyl chloride pipe (Ooki and Yokouchi, 2008). The seawater sample was continuously supplied from the seawater outlet to the equilibrator at a flow rate of 20 l min^{-1}. Pure air was continuously supplied to the silicone tubes at a flow rate of 20 ml min^{-1} regulating the inner pressure to be 1.4 atm. The gas sample at equilibrium with the seawater continuously flowed from the silicone tube outlet and was then transferred to an automated pre-concentration system (Yokouchi *et al*., 2006). The pre-concentration time of the gas sample was 30 min. After pre-concentration, the trapped VOCs were transferred to the GC-MS system. The partial pressure of each VOC in air (pVOC$_{air}$) was measured as described by Ooki *et al*. (2010).

Table 1. Precisions of χ_{VOC}, pVOC$_{water}$, M_{VOC}, and K_H

	χ_{VOC} Standard gas[a] ($n = 7$)	pVOC$_{water}$ Seawater sample[b] ($n = 8$)	M_{VOC} Standard solution[c] ($n = 6$)	K_H
CFC-11	<1.4%	±0.9%	±0.7%	±2%
C_5H_8	<1.4%	±3%	±4%	±7%
HFC-134a	<1.4%	±0.7%	±5%	±6%
HCFC-22	<1.4%	±0.8%	±2%	±3%
CH_3I	<1.4%	±4%	±2%	±6%
CH_2Br_2	<1.4%	±4%	±2%	±6%
C_2H_5I	—	±6%	±2%	±8%
CH_2Cl_2	<1.4%	±4%	±3%	±7%
CH_2ClI	—	±4%	±4%	±8%
$CHBr_3$	—	±23%	±2%	±26%

[a]Gravimetrically prepared standard gas at concentrations of 100–260 ppt.
[b]Surface seawater measurement at a fixed sampling location over the course of 2 days during the cruise.
[c]Deionized water-based standard solution containing C_5H_8, CH_3I, CH_2Br_2, C_2H_5I, CH_2Cl_2, CH_2ClI, and $CHBr_3$. Dissolved CFC-11, HFC-134a, and HCFC-22 in the standard solution would be nearly equilibrium with respect to the ambient air levels.

Molar concentration measurement with the purge-and-trap system

Seawater was collected from another seawater outlet into a 125-ml glass bottle during the middle of the collection of the equilibrated VOCs sample so that the molar concentration measurements would be synchronized with the partial pressure measurements. The bottles were crimp-sealed with no headspace by means of a Teflon-lined septum and an aluminum cap. The sample bottles were kept in the dark at 4°C until analysis, typically within 2 h or 4 days, depending on the observation schedule. The total volume of seawater in each bottle was transferred to a bubbling vessel by means of helium carrier gas (flow rate, 40 ml min^{-1}). The dissolved VOCs in the seawater sample were purged with helium (flow rate, 80 ml min^{-1}) for 40 min to maximize the purge efficiency within 1-hour measurement interval, and were simultaneously transferred to the pre-concentration-GC-MS system. The purge efficiencies (determined by repetitive analysis of a single seawater sample with the purge-and-trap system) for CFC-11, C_5H_8, HFC-134a, HCFC-22, CH_3I, CH_2Cl_2, and C_2H_5I, were nearly 100%, and those for CH_2ClI, CH_2Br_2, and $CHBr_3$ were 87 ± 4% ($n = 8$), 84 ± 4% ($n = 8$), and 84 ± 5% ($n = 8$), respectively. The molar concentrations were corrected by the purge efficiencies.

Synthetic halocarbons such as HFC-134a and HCFC-22, which are used as refrigerants in the ship's laboratory, might have contaminated the sample bottles during storage. To check for this possibility, we used the proce-
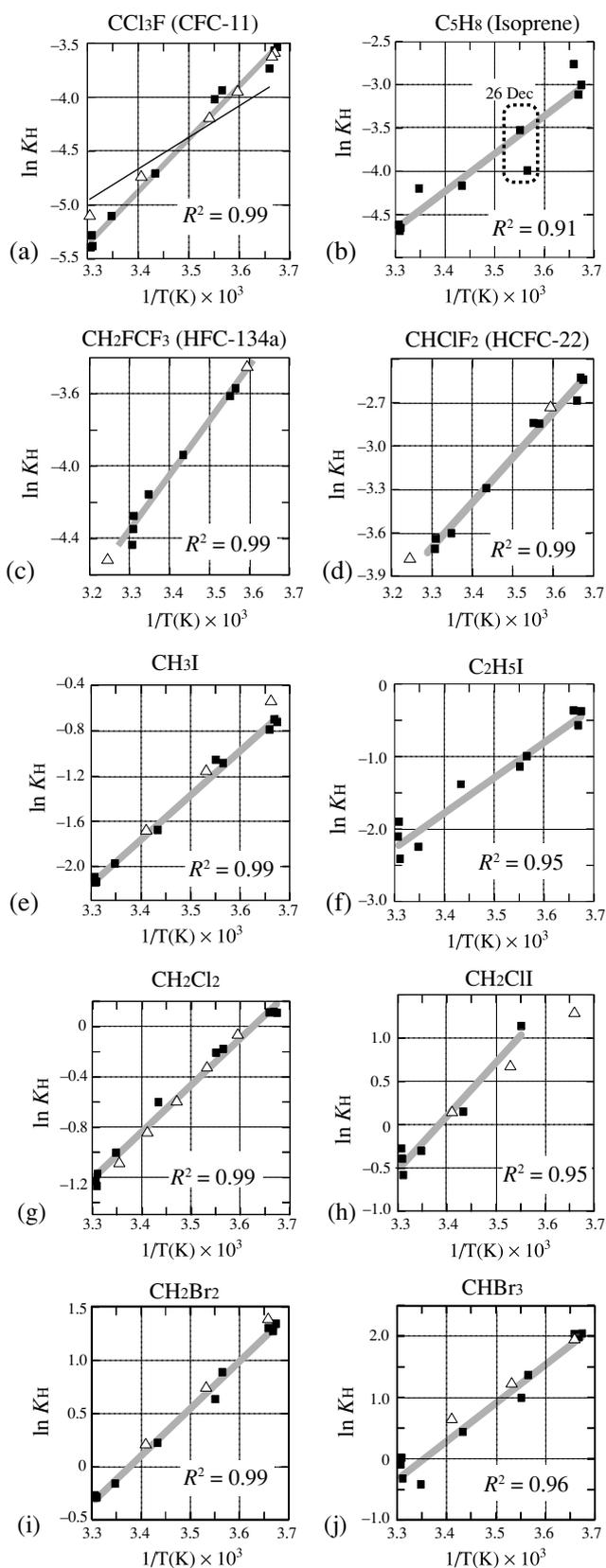
Fig. 1. Measured K_H (solid squares) for CFC-11 (a), C_5H_8 (b), HFC-134a (c), HCFC-22 (d), CH_3I (e), C_2H_5I (f), CH_2Cl_2 (g), CH_2ClI (h), CH_2Br_2 (i), and $CHBr_3$ (j). Gray lines denote the linear regression lines; open triangles in panels a, c–e, g–j and the solid line in panel (a) correspond to reference data obtained from the previous studies listed in Table 2.

dure described above to measure the concentrations of VOCs in the South Indian Ocean (20°S) at depths below 3000 m, where the concentrations of the synthetic halocarbons (CFC-11, HFC-134a and HCFC-22) are expected to be considerably lower than the corresponding surface concentrations. The concentrations of CFC-11, HFC-134a and HCFC-22 at 3000–4400 m were below the detection limit, and the concentrations of C_2H_5I, CH_2ClI, CH_2Cl_2, and CH_3I were within 10% of the surface concentrations. These results indicate that contamination of the bottle samples was not significant if the samples were analyzed within several days of collection. As for CH_2Br_2 and $CHBr_3$, the concentrations at 3000–4400 m (0.2–0.5 pmol l⁻¹) were similar to the surface concentrations; however, we regarded the significant concentrations of CH_2Br_2 and $CHBr_3$ in deep water to be natural level, because high levels of these compounds (0.4–4 pmol l⁻¹) have been also observed in the North Atlantic deep water (Moore and Tokarczyk, 1993).

Calibration and precision

A gravimetrically prepared standard gas (Taiyo Nissan, Inc., Tokyo) containing CFC-11, C_5H_8, HFC-134a, HCFC-22, CH_3I, CH_2Cl_2, and CH_2Br_2 at concentrations of 100–260 ppt (dry air mole fraction) was analyzed with the pre-concentration-GC-MS system. The dry air mole fraction of VOC (χ_{VOC}, ppt) and M_{VOC} (pmol l⁻¹) values of these compounds in seawater samples were determined on the basis of the standard measurements.

To calibrate for the concentrations of C_2H_5I, CH_2ClI, and $CHBr_3$, which were not contained in the standard gas, we prepared a methanol-based liquid standard containing these compounds as well as CH_3I. The methanol-based standard solution was crimp-sealed in a glass bottle at the laboratory before the cruise, and the standard bottle was stored in the refrigerator until measurement during the cruise. The sensitivities of the analyses for these compounds relative to the sensitivity of CH_3I were determined by analysis of the vaporized liquid standard. The χ_{VOC} and M_{VOC} values of C_2H_5I, CH_2ClI, and $CHBr_3$ in seawater samples were calibrated on the basis of their relative sensitivities. The partial pressure of VOC (patm) can be converted from χ_{VOC} (ppt) as following equation (Richter, 2003), assuming the ideal gas.

Table 2. Henry's law constants at $T = 273.17 + 25$ K ($K_H^{\ominus}$; mol l^{-1}atm^{-1}) for various VOCs in seawater, and their temperature dependence $d(lnK_H)/d(1/T)$

VOC	This study		Previous studies		Salinity (‰)	Reference
	$K_H^{\ominus}$	$d(\ln K_H)/d(1/T)$	$K_H^{\ominus}$	$d(\ln K_H)/d(1/T)$		
CFC-11	0.0061	4900	0.0075		34	Warner and Weiss (1985)[a]
			0.0082	2700	35	Hunter-Smith *et al.* (1983)[b]
C_5H_8	0.012	4400	0.013	−0.028	0	Sander (1999)[c]
			0.01–0.021[d]		35	
HFC-134a	0.015	3100	0.015	3100	39.6	Zheng *et al.* (1997)[e]
HCFC-22	0.029	3100	0.032	3000	39.6	Zheng *et al.* (1997)[e]
CH_3I	0.14	3900	0.14	4300	30.4	Moore *et al.* (1995)
C_2H_5I	0.14	4800	0.14–0.18		0	Sander (1999)[c]
			0.11–0.14[d]		35	
CH_2Cl_2	0.36	3700	0.34	3900	34.3	Moore (2000)
CH_2ClI	0.84	6200	0.88	4300	30.4	Moore *et al.* (1995)
CH_2Br_2	0.90	4400	0.92	4400	30.4	Moore *et al.* (1995)
$CHBr_3$	1.0	6200	1.4	5000	30.4	Moore *et al.* (1995)

The temperature and salinity values in this study ranged from −1°C to 29.3°C and from 33.1‰ to 36.1‰, respectively.
[a]K_H values given as a function of temperature and salinity by Warner and Weiss (1985); experimental data are plotted as open triangles in Fig. 1(a).
[b]A regression line is indicated by a solid line in Fig. 1(a).
[c]From the $K_H^{\ominus}$ data set reported by Sander (1999).
[d]$K_H^{\ominus}$ value at salinity 35‰ was calculated from that at 0‰ using formulas by Johnson (2010).
[e]We calculated $K_H^{\ominus}$ and $d(\ln K_H)/d(1/T)$ values from the Henry's law constants at $T = 278$ and 308 K in NaCl solution reported by Zheng et al. (1997).

$$pVOC = (p - pH_2O)/p \times \chi_{VOC}, \qquad (4)$$

where p is the total pressure (in equilibrator or air), and pH_2O is the saturated partial pressure of water.

The detection limits (S/N = 3) for CFC-11 and HCFC-22 were 1 ppt, and those for other VOCs were 0.05 ppt. Precisions for χ_{VOC}, $pVOC_{water}$, M_{VOC}, and K_H values were summarized in Table 1. Analytical precisions of χ_{VOC} and M_{VOC} were evaluated from the standard gas measurements and the standard solution measurements, respectively. Overall precisions for the $pVOC_{water}$ measurements were also evaluated on the basis of measurements at a fixed sampling location over the course of 2 days during the cruise. Note that the overall precisions reflect natural variability in addition to measurement errors. The precisions for the K_H values were calculated from the overall precisions of $pVOC_{water}$ and the analytical precision of M_{VOC}.

Shipboard observation

Observations were conducted during a cruise of the R/V *Hakuho-maru* (cruise KH-09-5; GEOTRACES project) from November 2009 to January 2010 in the Indian Ocean and the Southern Ocean. The data used in this study were obtained during Leg 2 of the cruise from Cochin, India (27 November 2009) to Port Louis, Mauritius (16 December 2009) and during Leg 3 from Port Louis (16 December 2009) to Cape Town, South Africa (9 Janu-

ary 2010). The cruise track was shown in a distribution map for concentrations of C_2H_5I (Fig. 3) as mentioned in a later chapter.

RESULTS AND DISCUSSION

Determination of Henry's law constants

Samples for the determination of Henry's law constants were collected at 10 locations during the cruise at seawater temperatures and salinities ranging from −1°C to 29.3°C and from 33.1‰ to 36.1‰, respectively. The partial pressures of CH_2ClI in cold water (<7°C) were below the detection limit (<0.05 patm, 0.05 ppt in dry air mole fraction). The K_H values were calculated from Eq. (3) using observed $pVOC_{water}$ and M_{VOC} values, and $\ln K_H$ is expressed by a linear regression line (Eq. (5)) as a function of (1/T), where T is absolute temperature (Sander, 1999).

$$\ln K_H = [-d(\ln K_H)/d(1/T)] \times (1/T) + I, \qquad (5)$$

where $-d(\ln K_H)/d(1/T)$ and I are the slope and y-intercept of the linear regression line, respectively. We plotted $\ln K_H$ against $(1/T) \times 1000$ (Fig. 1). High correlations ($R^2 > 0.99$) between $\ln K_H$ and $1/T$ were observed for CFC-11, HFC-134a, HCFC-22, CH_3I, CH_2Cl_2, and CH_2Br_2. The correlation coefficients for C_2H_5I, CH_2ClI, and $CHBr_3$ were in the 0.95–0.96 range, and C_5H_8 had a lower correlation
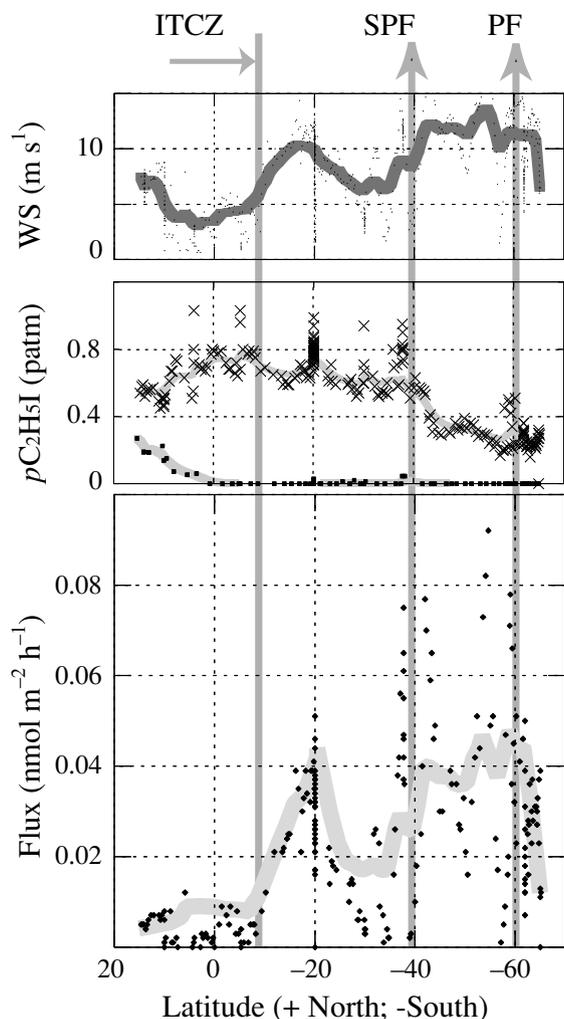
Fig. 2. Latitudinal distribution of wind speed (WS; m s⁻¹), pC₂H₅I (patm) in air (■) and water (×), and sea-to-air flux of C₂H₅I (nmol m⁻²h⁻¹) over the Indian Ocean. The data were applied for the Stineman function to obtain smoothed curves. The bold gray lines denote the smoothed curves for the wind speed, pVOC, and the flux. The locations of the ITCZ, the subpolar front (SPF), and the polar front (PF) are indicated with gray arrows.
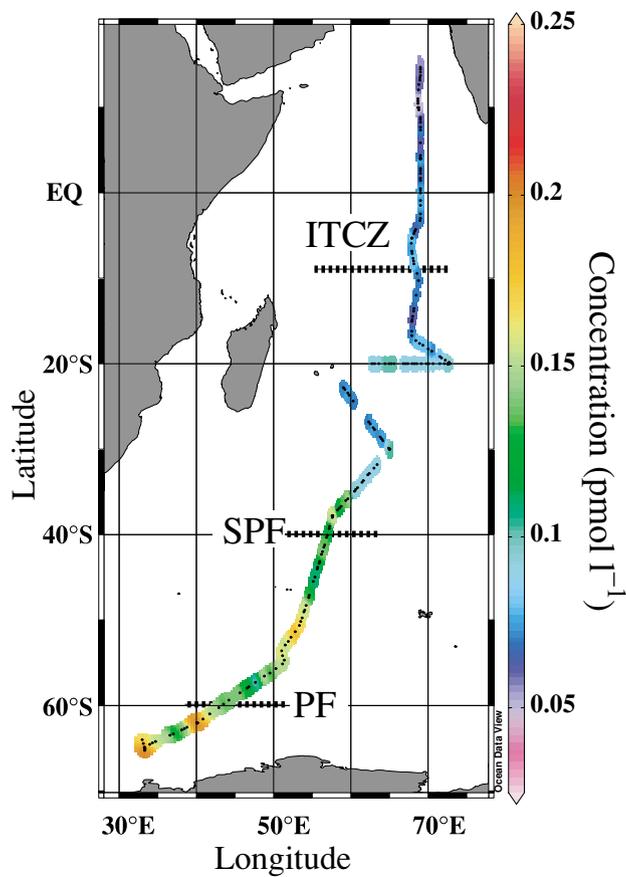

Fig. 3. Molar concentrations (M_{VOC}) of C_2H_5I in surface seawater of the Indian Ocean (Dec. 2009–Jan. 2010). The $pVOC_{water}$ values (patm; n = 230) were converted to M_{VOC} values (pmol l⁻¹) by means of Eq. (3) using the K_H value. The southern boundary of the ITCZ, the subpolar front (SPF), and the polar front (PF) are indicated by dashed lines.

coefficient ($R^2 = 0.91$). The lower correlation coefficients may have been partly due to the natural variability of $pVOC_{water}$. For example, $pVOC_{water}$ of C_5H_8 varied from 2100 to 200 patm on 26 December at $T = 7$–9°C ($1/T \times 10^3 = 3.54$–3.57). The seawater samples used for M_{VOC} measurements were collected in the middle of the 30-minute collection period for equilibrated VOC samples, and the discrepancy between the collection times of the samples for M_{VOC} and $pVOC_{water}$ measurements might have caused the large variability of K_H (C_5H_8) on 26 December (Fig. 1(b)).

In Fig. 1, we also plotted reference data from the pre-

vious studies listed in Table 2. Our K_H values for CFC-11, HFC-134a, HCFC-22, CH_3I, CH_2Cl_2, CH_2ClI, CH_2Br_2, and $CHBr_3$ were in good agreement with the previously reported values. The K_H value at standard temperature ($T = 273.15 + 25$ K) is expressed as K_H^Θ. The $d(\ln K_H)/d(1/T)$ and K_H^Θ values are listed in Table 2, along with reference data obtained from saline water or seawater samples. These are the first reported values of K_H for C_2H_5I and C_5H_8 as functions of seawater temperature. In addition to the temperature effect, which should be a primary factor to change K_H value for each VOC, the change of seawater salinity would also affect K_H value (salting-out effect) to some extent. Warner and Weiss (1985) reported that K_H value for CFC-11 at salinity 33‰ with temperature 25°C (0.0076 mol l⁻¹atm⁻¹) is 3% higher than that at salinity 36‰ with the same temperature (0.0074 mol l⁻¹atm⁻¹). The variation range of K_H for other VOCs in seawater with salinity range between 33‰ and 36‰ at the same temperature might be approximately 3%.

Distributions of C_2H_5I concentration and sea-to-air flux

Latitudinal distributions of $pC_2H_5I_{water}$ and $pC_2H_5I_{air}$ were plotted in Fig. 2. Higher $pC_2H_5I_{air}$ values (up to 0.27 patm) were found in higher latitude of the North Indian Ocean. Coastal emissions of C_2H_5I might have influenced on the $pC_2H_5I_{air}$ over the Arabian Sea where there is under the influence of the northeast Monsoon (Koppmann *et al.*, 1993; Ooki and Yokouchi, in press). In the southern hemisphere, most of $pC_2H_5I_{air}$ values were below the detection limit (<0.05 patm, 0.05 ppt in dry air mole fraction). The molar concentrations and sea-to-air flux of C_2H_5I were calculated from the observed pVOC data by means of Eqs. (3) and (1) and the newly determined K_H value. We plotted the spatial distribution of C_2H_5I concentrations and the latitudinal distributions of sea-to-air flux and wind speed (Figs. 3 and 2, respectively). The C_2H_5I concentrations generally increased toward the south with decreasing sea surface temperature (Fig. 3). The trend of the latitudinal distribution of C_2H_5I flux corresponded to the trend of the wind speed distribution with exception of the trend in the North Indian Ocean where the high levels of $pC_2H_5I_{air}$ were found (Fig. 2).

The lowest C_2H_5I concentrations (<0.1 pmol l^{-1}) were observed in the tropical and subtropical waters between 17°N and 10°S, where the sea surface temperature was above 28°C. Biological productivity was low in tropical and subtropical waters having chlorophyll-*a* concentrations of 0.09–0.17 μg l^{-1} in the surface layer, which were obtained from CTD-bottle sampling observations during the cruise. Note that the surface layer depth was defined as the depth where the potential density has increased by 0.125 kg m^{-3} compared to that at the reference depth of 10 m. The southern boundary of the Intertropical Convergence Zone (ITCZ) was located around 10°S in the Indian Ocean. In the ITCZ, wind speed was relatively low (<5 m s^{-1}) compared to that in the other regions. Small sea-to-air flux values (average, 0.004 nmol m^{-2}h^{-1}) were observed in this calm, warm region.

High C_2H_5I concentrations (up to 0.18 pmol l^{-1}) were frequently observed in the Southern Ocean between the subpolar front (around 40°S) and the polar front (around 60°S), where biological productivity is high and chlorophyll-*a* concentrations have been reported to be in the range of 0.2–1.2 μg l^{-1} (Hirawake *et al.*, 2005). The average C_2H_5I concentration (0.14 pmol l^{-1}) was within the range of previously reported values (0.10–0.27 pmol l^{-1}) in the Atlantic section of the Southern Ocean (50–60°S) during the austral summer (Abrahamsson *et al.*, 2004). Hughes *et al.* (2008) have reported that biogenic marine aggregates collected in the subarctic Atlantic water, including plankton concentrate, diatom mucilage, and phytodetritus, produce C_2H_5I at a high rate (0.31 pmol l^{-1}h^{-1}). The high biological productivity in subpolar water containing high levels of biogenic aggregates would lead to a high rate of C_2H_5I production in seawater. In contrast, the C_2H_5I concentrations observed in the pelagic Southern Ocean water were much lower than the concentrations (annual average, 1.5 pmol l^{-1}) observed in coastal subarctic water of the western English Channel (50°N; Archer *et al.*, 2007). In the Southern Ocean, where strong winds frequently blow over the sea, large sea-to-air fluxes of C_2H_5I were widespread (Fig. 2). The average flux (0.04 nmol m^{-2}h^{-1}) in the Southern Ocean was approximately half the flux observed in the subarctic coastal water (0.1 nmol m^{-2}h^{-1}) by Archer *et al.*, even though the concentration in the Southern Ocean was only 1/10 that in the subarctic coastal water. The vast Southern Ocean is thus expected to be a significant source of oceanic halocarbons such as C_2H_5I associated with marine biological productivity in subpolar water.

CONCLUSION

We determined the Henry's law constants (K_H) for CFC-11, C_5H_8, HFC-134a, HCFC-22, CH_3I, C_2H_5I, CH_2Cl_2, CH_2ClI, CH_2Br_2, and $CHBr_3$ in natural seawater by measuring their partial pressures and molar concentrations during shipboard observations in the Indian Ocean and the Southern Ocean. We report the first K_H values for C_2H_5I and C_5H_8 in seawater as functions of temperature, and the K_H values for the other VOCs were in good agreement with previously reported values. The latitudinal distribution of the sea-to-air flux of C_2H_5I was estimated from the newly determined K_H and the observed partial pressures during the cruise. The sea-to-air flux of C_2H_5I was large (average, 0.04 nmol m^{-2}h^{-1}) in the Southern Ocean, where biological productivity was high. The vast Southern Ocean is thus expected to be a significant source of oceanic halocarbons such as C_2H_5I associated with marine biological productivity in subpolar water.

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