The air-sea exchange of volatile organic compounds (VOCs) plays an important role in the Earth’s biogeochemical cycles, and in the chemistry of the atmosphere. For example, nonmethane hydrocarbons (NMHCs), including alkanes, alkenes, and aromatics, and oxygenated VOCs, including aldehydes, ketones, and alcohols, contribute to the formation of photochemical oxidants and secondary organic aerosols (Donahue and Prinn 1990; Singh et al. 1995; Murphy et al. 1998). The ocean surface is a substantial natural source of atmospheric VOCs (5 Tg C yr⁻¹, Guenther et al. 1995) through a variety of biogeochemical and photo-induced processes. Light alkenes (e.g., ethene and propene) are produced mainly by photochemi-
cal reactions of dissolved organic matter (Ratte et al. 1993), and light alkanes (e.g., ethane and propane) are produced during the autolysis of some phytoplanktons (McKay et al. 1996). Isoprene production is closely related to phytoplankton activity, as indicated by the correlation between isoprene concentrations and chlorophyll content in surface seawater (Broadgate et al. 1997). Laboratory studies have shown that isoprene is produced by marine phytoplankton cultures (Moore et al. 1994; Milne et al. 1995; Shaw et al. 2003) and by bacteria (Kuzma et al. 1995). Although the production processes of NMHCs are relatively well known from previous studies, information about the distribution of NMHCs in seawater, and their emission rates to the atmosphere, is limited. Although photochemical production has been suggested as a major source for low-molecular-weight carbonyl compounds in surface seawater (Zhou and Mopper 1997), the mechanisms of the formation and destruction of oxygenated VOCs in seawater are still largely unknown (Singh et al. 2003). As a major natural source of atmospheric sulfur, dimethyl sulfide (DMS) plays an important role in climate regulation (Charlson et al. 1987). Atmospheric DMS is photo-oxidized to form sulfate aerosols, which may affect the radiative budget of the atmosphere by serving as precursors of cloud condensation nuclei.Investigators have proposed that phytoplankton releases dimethylsulfiniopropionate (DMSP), which is enzymatically cleaved by microorganisms to produce DMS (Stefels and Vanboekel 1993; Ledyard and Dacey 1994; Liss et al. 1997).

Some of the uncertainty most likely results from the limited number of measurements of dissolved VOC concentrations in seawater. A purge-and-trap (P&T) method combined with gas chromatographic (GC) detection has been widely used to measure trace gases dissolved in seawater. The P&T-GC method permits measurements of dissolved VOC concentrations with high sensitivity (pmol L^{-1}) in seawater samples collected with Niskin bottles, or by means of shipboard pumping systems (e.g., Bonsang et al. 1988; Baker et al. 2000; Kettle et al. 2001). However, this method is not continuous, and each measurement typically takes minutes to hours, owing to the need for pre-concentration and pre-separation procedures. Especially for measurements of reactive VOCs, adsorption during pre-treatment of samples sometimes makes obtaining accurate and precise measurements by means of the P&T-GC method difficult. Consequently, the development of a highly time-resolved measurement method that does not require pre-treatment is strongly needed. Such a method would improve our understanding of the global and regional distributions of VOCs at the ocean surface, and their production and consumption processes.

Tortell (2005a, b) and Nemcek et al. (2008) developed a membrane inlet-mass spectrometry technique for continuous, underway measurement of dissolved DMS, and used the technique to measure DMS concentrations in marine continental shelf waters and coastal waters. Marandino et al. (2005, 2007, 2008, 2009) and Saltzman et al. (2009) made high-frequency underway measurements of acetone and DMS in surface seawater using an atmospheric pressure chemical ionization mass spectrometry system coupled with a continuous-flow membrane equilibrator. The sensitivity of the system was high enough to enable the detection of dissolved acetone and DMS even in the open ocean.

Proton transfer reaction-mass spectrometry (PTR-MS) enables the online measurement of multiple atmospheric VOCs with relatively high sensitivity (pptv levels) and a rapid response time (0.1–10 s) (Lindinger et al. 1998; de Gouw and Warneke 2007). One of the main weak-
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nesses of PTR-MS is that compound identification relies solely on mass spectrometry, which means that isobaric species cannot be distinguished, particularly with a quadrupole mass filter. Therefore, the rigorous comparison of PTR-MS measurements to measurements obtained by a well-established GC technique is still useful for the accurate identification and quantification of individual VOCs. PTR-MS has a potential advantage for measurements of reactive VOCs, because the method does not require sample pre-treatment (such as dehydration or pre-concentration), which sometimes limits the range of detectable species. In principle, dissolved VOCs can be analyzed by PTR-MS by the extraction of VOCs from the liquid phase to the gas phase. Williams et al. (2004) used a P&T PTR-MS method to measure several VOCs (e.g., methanol, acetonitrile, acetone, and DMS) in surface water.

To measure dissolved VOCs with high sensitivity and time resolution, we developed an equilibrator inlet (EI)-PTR-MS system by combining a PTR-MS instrument with a bubbling-type equilibrator for equilibration between seawater and air (e.g., Takahashi 1961; Frankignoulle et al. 2001). Although a bubbling-type equilibrator generally requires a lot of space on research vessels, it is less subject to interruption of the water stream than a shower-type equilibrator (e.g., Keeling et al. 1965; Kelley 1970; Weiss 1981; Butler et al. 1991; Johnson 1999) and less subject to adsorptive loss than is a membrane-type equilibrator (e.g., Saito et al. 1995; Groszko and Moore 1998; Ooki and Yokouchi 2008; Loose et al. 2009), depending on the membrane material. Here we report a comprehensive laboratory characterization of the EI-PTR-MS system for the measurement of six VOCs (DMS, isoprene, propene, acetone, acetaldehyde, and methanol) dissolved in seawater. We determined the dependence of the equilibrator correction factor on instrumental parameters, and then investigated the instrumental response time and the detection limits for each VOC. On the basis of field deployment of the EI-PTR-MS system on a research cruise, we evaluated seawater sampling methods, compared our results with results obtained by a GC method for DMS and isoprene, and obtained the first VOC concentration data for the western North Pacific Ocean.

Experimental

EI-PTR-MS instrument

Figure 1 shows a schematic diagram of the EI-PTR-MS system, including the equipment that supplied artificial and natural seawater samples to the equilibrator. The equilibrator, modeled on the equilibrator for $f_{\text{CO}_2}$ measurements developed by the National Institute for Environmental Studies (Murphy et al. 2001), consisted of brown (to prevent photolysis) vertical glass tubes (I.D. 15.3 cm) and was equipped at the bottom with a bubbler head (mesh size 20–30 $\mu$m) for the carrier gas and a seawater outlet and at the top with a carrier gas outlet and a seawater inlet. The height of the water column in the equilibrator was adjusted to be 40, 60, or 100 cm by means of tubes of different lengths (20, 40, and 80 cm) in the middle part of the equilibrator. Dissolved VOCs were extracted into a VOC-free carrier gas (ultrapure $N_2$, >99.99995%, Japan Fine Products Co., Kawasaki, Japan). The carrier gas and sample seawater stream in the equilibrator flowed in opposite directions, and part of the extracted gas was continuously directed to the PTR-MS instrument at ambient pressure, without pre-treatment such as dehydration and pre-concentration. Perfluoroalkoxy (PFA) tubing (3/8” and 1/8” O.D.) and fittings were used to deliver the extracted gas samples to the PTR-MS. Tygon tubing (Saint-Gobain, Courbevoie, France) was used for seawater samples.
The flow of seawater was controlled with a peristaltic tubing pump (flow rate <2 L min⁻¹, MasterFlex 7554-95, Cole-Parmer Instrument Company, Illinois, USA) or a magnetic drive pump (flow rate >2 L min⁻¹, MD-2DRZ, Iwaki, Tokyo, Japan). The seawater flow rate was continuously monitored with a flow meter (LD10-TATAAA-RC and DU-5TGS1, Horiba Stec, Kyoto, Japan). Water temperature was monitored with a temperature probe and a logger (TidbiT V2 Temp, Onset Computer Corporation, Massachusetts, USA) at the bottom of the equilibrator.

We used a commercially-available PTR-MS instrument (PTRMS-FDT-hs, Ionicon Analytik GmbH, Innsbruck, Austria). Briefly, the PTR-MS instrument consisted of a discharge ion source to produce the H₃O⁺ ions; a drift tube, in which the proton transfer reactions between H₃O⁺ and VOCs took place; and a quadrupole mass spectrometer for the detection of reagent and product ions. In a hollow cathode discharge ion source, H₃O⁺ ions were produced from pure water vapor (flow rate 7.8 sccm). Sample air was introduced into the drift tube at approximately 22 sccm; the drift tube pressure was held at 2.1 mbar. The sampling inlet and the drift tube were held at 105°C. In the drift tube, VOCs in the sample air were ionized by proton transfer reactions as follows:

\[ \text{H}_3\text{O}^+ + \text{VOC} \rightarrow \text{VOC}^+ + \text{H}_2\text{O}. \]  

A fraction of the reagent ion, H₃O⁺, and the product ions was extracted through a
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small orifice into the quadrupole mass spectrometer, where they were detected by a secondary electron multiplier operated in the ion pulse counting mode.

The field strength, $E/N$, of the drift tube, where $E$ is the electric field strength ($\text{V cm}^{-1}$) and $N$ is the buffer gas number density (molecule cm$^{-3}$), was set to 108 Td (Td = $10^{-17}$ cm$^2$ V molecule$^{-1}$) to reduce the fragmentation of detected VOCs. The source current was 6.0 mA, and the accelerating voltages of the PTR-MS instrument from the upper stream defined as $U_{4}$, $U_{5}$, $U_{\text{drift}}$, $U_{1}$, and $U_{\text{NC}}$ were 50, 120, 400, 48, and 5.8 V, respectively. The count rate of H$_3$O$^+$, calculated from the count rate at $m/z$ 21 (H$_3^{18}$O$^+$) multiplied by 500, was typically $1–2 \times 10^7$ cps. To determine water vapor concentrations in the sample air, $[\text{H}_2\text{O}]_{\text{sample}}$, we used a calibration curve for the plot of $[\text{H}_2\text{O}]_{\text{sample}}$ versus the relative intensity of H$_3$O$^+$·H$_2$O to H$_3$O$^+$ (the ratio of $m/z$ 37 to $m/z$ 19) using air samples with known water vapor concentrations, as described in Inomata et al. (2008). The intensity of H$_3$O$^+$·H$_2$O was calculated from the intensity of the peak at $m/z$ 39 (H$_4^{18}$O$^+$) multiplied by 250, because the signals at $m/z$ 37 (H$_4$O$^+$·H$_2$O) were intense ($\sim10^6$ cps) enough in humidified air samples to possibly damage the ion detector. The signals at $m/z$ 33, 43, 45, 59, 63, and 69 were assigned to methanol, propene, acetaldehyde, acetone, DMS, and isoprene, respectively. These assignments are in accordance with previous measurements, although minor contributions from other species, such as propanal to $m/z$ 59, could not be ruled out (Lindinger et al. 1998; Williams et al. 2001). The detection sensitivities for VOCs under dry conditions were determined by the dynamic dilution of gravimetrically prepared standard gases with ultrapure N$_2$ gas.

Laboratory experiments with artificial seawater

The EI-PTR-MS system, particularly the equilibrator, was evaluated in the laboratory with artificially-prepared seawater containing VOCs. Concentrations of the highly-water-soluble species (DMS, acetone, acetaldehyde, and methanol) in the artificial seawater sample were expected to be stable, even if portions of these species were extracted by the carrier gas under the equilibrator conditions. We added NaCl to pure water and controlled its salinity at 35‰, and then the salt water was supplemented with aliquots of authentic reagents for the highly-soluble species to dissolve these species. In contrast, concentrations of species with a low water solubility (isoprene and propene) in the artificial seawater were expected to decrease during the extraction procedure. In this study, therefore, we used the apparatus described by Ooki and Yokouchi (2008) to dissolve these species in salt water (Fig. 1). Artificial seawater for the low-solubility VOCs was continuously produced with a silicone hollow fiber membrane module (NAGASEP, Nagayanagi Co., Tokyo, Japan; 6000 silicone tubes; length 20 cm; O.D. 0.25 mm; I.D. 0.17 mm). Sample gases, prepared by dynamic dilution of the gravimetric gas standards, were supplied to the module at 5 L min$^{-1}$. The sample gases passing through the module were bubbled through water in a bucket (water volume 15 L). Thus, VOCs in the sample gases permeated the silicone of the module and dissolved in the circulation water.

The degree of equilibration between the gas phase and the liquid phase depends on the contact time between the carrier gas and the water in the equilibrator and on the solubility of the target gases (Johnson 1999). We defined the degree of equilibration ($D$) as $p/p'$, where $p$ was the observed partial pressure in the carrier gas stream and $p'$ was the expected Henry’s Law partial pressure ($D < 100\%$ for disequilibrium conditions). Furthermore, as for low-solubility species, the concentrations in artificial seawater decrease in the equilibrator
because the carrier gas removes a substantial fraction of the dissolved gases from the liquid phase. This “stripping effect (S)” would be 1 for high-solubility species, but <1 for low-solubility species such as isoprene and propene. Consequently, we obtained an equilibrator correction factor \( F_{eq} \), which was the product of both \( D \) and \( S \): \( F_{eq} = D \times S \), through a series of laboratory experiments. We conducted three types of experiments in the laboratory to investigate \( F_{eq} \) in various setups of the equilibrator: (1) We varied the carrier gas flow rate in the range of 75–1000 sccm to determine how the variation affected the equilibrium of the target species between the carrier gas and the artificial seawater. (2) For species in disequilibrium at any of the carrier gas flow rates tested, we examined the dependence of \( F_{eq} \) on the water flow rate and the height of the water column. The flow rate of artificial seawater was varied from 0.8 to 6.5 L min\(^{-1} \), and the tested heights of the water column were 40, 60, and 100 cm. (3) The dependence of \( F_{eq} \) on the water temperature, an important determinant of gas solubility, was also examined in the range from 17 to 34°C.

**Field observation during a research cruise**

Field observations were made during the SPEEDS/SOLAS (Subarctic Pacific Experiment for Ecosystem Dynamics Study/Surface Ocean Lower Atmosphere Study) 2008 cruise of the R/V Hakuho-Maru in the western subarctic North Pacific Ocean in July–August 2008. We collected seawater samples from the sea surface by means of three different continuous pumping methods (Fig. 1) to evaluate the possible contamination of VOCs from the sampling apparatus.

The first method involved the collection of surface seawater with the built-in pumping system of the R/V Hakuho-Maru (hereafter referred to as BI sampling). Surface seawater was pumped from an inlet at the bottom of the ship (5 m below sea level) with a residence time of approximately 1 min. The use of BI sampling allowed us to collect a large volume of seawater continuously, both underway and during heave-to periods. However, the sampling line, some of which consisted of metals (stainless steel), remained connected and in use for long periods and was a potential source of interference (e.g., artifacts, contamination, adsorption/desorption) for some VOCs and their precursors, such as organic matter in the seawater samples.

The second pumping method involved an external pumping system (hereafter referred to as EX sampling); this method was employed only in heave-to periods. The screw pump (WS-20, Nishigaki Pump, Gifu, Japan) in the EX sampling line was made partly of metals, but the water flow rate was high (>15 L min\(^{-1} \)). The line for the sample stream was made from new fluororesin tubing and Tygon tubing.

The third method was an underway sampling method involving a towed torpedo-shaped fish to keep the sampling inlet below the sea surface (hereafter referred to as TF sampling). Seawater samples were collected at 0.5–1.5 m below sea level. The sampling system, which included tubing and a pump (AstiPure PFD2 bellows pump and AstiPure AMC pulsation damper, Saint-Gobain), was made of Teflon. TF sampling was available only during underway periods. Although the pumping rate of surface water was 7 L min\(^{-1} \), the seawater flow rate introduced to the equilibrator was limited to approximately 1 L min\(^{-1} \) when the TF sample was shared by several groups. None of the seawater samples collected by any of the three methods were filtered, because filtering might have interrupted the seawater stream and disrupted planktonic cells.

We used an equilibrator with a 60-cm column height (water volume 10 L) with carrier gas and water flow rates of 75 sccm and 1 L min\(^{-1} \), respectively, during the
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Cruise. PTR-MS measurements were conducted in a multiple ion detection (MID) mode at 5-s integration for each mass per cycle, to obtain mass signals at 1-min intervals. We also carried out the analysis in a scan mode (m/z 21–100 with 0.5- or 1-s data integration per cycle) several times during the observation period to determine whether species other than those monitored in the MID mode could be detected.

In the field measurements, we compared the EI-PTR-MS results for DMS and isoprene to those obtained by membrane equilibrator-gas chromatography/mass spectrometry (ME-GC/MS). The ME-GC/MS system was originally developed for the automatic measurement of trace marine halocarbons, typical concentrations of which range from 0.1 to hundreds of picomoles per liter. The GC/MS system was coupled with a silicone membrane equilibrator, as described in detail in Ooki and Yokouchi (2008). Surface seawater samples for ME-GC/MS were obtained by means of BI and EX sampling. Seawater samples were continuously passed through a silicone membrane equilibrator at 15 L min⁻¹; the equilibrator consisted of six silicone tubes (length 10 m; O.D. 2.0 mm; I.D. 1.5 mm, material Q7-4780, 80SH, Fuji System Co., Tokyo, Japan) housed in a polyvinyl chloride pipe (I.D. 16 mm). Dissolved VOCs (including isoprene) permeated the silicone membrane into the gas phase within the silicone tubing. Ultrapure air was continuously supplied to the equilibrator inlet at 25 sccm. The collected VOC samples in the gas phase were dehydrated with a Nafion dryer (Perma Pure LLC, New Jersey, USA) and transferred to a pre-concentration/capillary GC/MS system. The VOC sample was collected in a trap containing Carboxene 1000 and Carbopak B cooled to −50°C in a small freezer for 30 min. Concentrated VOCs in the first trap were thermally (200°C) desorbed and transferred to a second trap, which contained Tenax TA and Carboxene 1000 cooled to −50°C. Then the second trap was heated to 200°C, and the desorbed components were transferred to a capillary column (Porabond Q, 0.32 mm × 50 m) for GC/MS analysis. A gravimetrically-prepared standard gas (isoprene 970 pptv; Taiyo Nippon Sanso Co., Tokyo, Japan) was analyzed for quantification through the pre-concentration/capillary GC/MS system in the same manner used for the extracted gas sample measurements.

We confirmed that DMS and isoprene reached equilibrium between the liquid phase and the gas phase in the membrane equilibrator. Other polar organics, such as acetone and methanol, were not detectable with this ME-GC/MS system because the Nafion dryer was used. The procedure for checking the DMS and isoprene equilibrium was essentially same as the procedure used for the laboratory EI-PTR-MS experiments. Ambient air was introduced into the membrane module at a flow rate of 10 L min⁻¹ to dissolve DMS and isoprene in the sample water. The concentrations of DMS and isoprene in the ambient air and in the air extracted through the membrane equilibrator were compared by alternate measurements at 1-h intervals. Agreement of the ratio of the concentrations in the ambient air and the extracted air at the closest measurement times was calculated to be 0.99, indicating that complete equilibrium between the liquid and gas phases for DMS and isoprene was achieved with the membrane equilibrator, and that the efficiency of the pre-concentration system did not depend on the humidity in the sample gas. Analytical precision (2σ), based on repeated analyses of the standard gas, was 2%. Isoprene, DMS, and several halocarbons were measured with this system every 70 min during the cruise.

**Quantification of dissolved VOC concentrations**

To calculate the VOC concentrations in sample water, we applied correction fac-
tors to the concentrations in the sample gas extracted from the equilibrator on the basis of thermodynamic principles. Given that VOCs were in equilibrium between the gas and liquid phases, the concentrations of the VOCs in the liquid phase \((c_a)\) should have been equal to the product of the Henry’s law constant \((k_H)\) and the partial pressure of VOCs in the gas phase \((p_g)\):

\[
c_a = k_H \times p_g. \tag{2}
\]

Henry’s law constants depend on temperature \((T)\):

\[
k_H = k_{H0} \times \exp[-\Delta_{soln}H/R \times (1/T - 1/T_0)], \tag{3}
\]

where \(k_{H0}\) is the Henry’s law constant under standard conditions \((T_0 = 298.15 \text{ K})\), \(\Delta_{soln}H\) is the enthalpy of the solution, and \(R\) is the gas constant. The temperature dependence is given by:

\[
-d\ln k_H/(d(1/T)) = -\Delta_{soln}H/R. \tag{4}
\]

In this study, we used data for Henry’s law constants reported in previous studies in seawater (salinity = 35‰) for DMS, acetone and acetaldehyde and in freshwater for isoprene, propene, and methanol. We estimated the Henry’s law constants and their temperature dependence by averaging all the data (Table 1). The constant \(k_{H0}\) and its temperature dependence, were calculated from the fitting curve based on Eq. (3). We used the calculated Henry’s law constants to calculate the concentration of each VOC dissolved in seawater.

### Results and Discussion

#### Humidity dependence of detection sensitivity

In the EI-PTR-MS system, the sample gases extracted through the equilibrator contained a lot of water vapor. Therefore, we measured the humidity dependence of the detection sensitivity for VOCs by varying the humidity of gas mixtures as described in detail by Inomata et al. (2008). The humidity was varied by mixing 100% humidified pure \(N_2\) and dry pure \(N_2\) as a diluent gas by means of a humidity generator/controller (SRG-1R-10, SHINYEI, Kobe, Japan). The water vapor concentra-

### Table 1. Henry’s law constant and its temperature dependence for six VOCs.

<table>
<thead>
<tr>
<th>m/z (amu)</th>
<th>(k_{soln}) (M/atm)</th>
<th>(-d\ln k_H/(d (1/T))) (K)</th>
<th>Water type</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propene   43</td>
<td>0.00074</td>
<td>3400</td>
<td>Freshwater</td>
<td>Wilhelm et al. (1977)</td>
</tr>
<tr>
<td>Acetone   59</td>
<td>27.0 ± 1.8</td>
<td>5090 ± 285</td>
<td>Seawater</td>
<td>Zhou and Mopper (1990) Benkelberg et al. (1995)</td>
</tr>
<tr>
<td>Methanol  33</td>
<td>220</td>
<td>5200</td>
<td>Freshwater</td>
<td>Snider and Dawson (1985)</td>
</tr>
</tbody>
</table>
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The detection sensitivity for the six VOCs depended markedly on the humidity, which indicates that the VOCs reacted not only with $H_3O^+$ ions but also with water clusters in the drift tube. For example, the detection sensitivity for isoprene showed a significant dependence on humidity (Fig. 2). Because the number of cluster ions increased with increasing humidity in the air samples, a simple function was used to correlate the humidity and the detection sensitivity. For all VOCs, the humidity dependence of the detection sensitivities was better fitted by a quadratic function than a linear one, so we used the following quadratic functions to correct the detected signals:

\[
RS = 0.000253 \times [H_2O]_{\text{sample}}^2 + 1,
\]
\[R^2 = 0.98\] for DMS, (5.a)

\[
RS = 0.000235 \times [H_2O]_{\text{sample}}^2 + 1,
\]
\[R^2 = 0.98\] for isoprene, (5.b)

\[
RS = 0.000287 \times [H_2O]_{\text{sample}}^2 + 1,
\]
\[R^2 = 0.98\] for acetone, (5.c)

\[
RS = 0.000274 \times [H_2O]_{\text{sample}}^2 + 1,
\]
\[R^2 = 0.98\] for acetaldehyde, (5.d)

\[
RS = 0.000218 \times [H_2O]_{\text{sample}}^2 + 1,
\]
\[R^2 = 0.86\] for methanol, (5.e)

where $RS$ is the detection sensitivity relative to that under dry conditions. The measured detection sensitivity under dry conditions for DMS, isoprene, propene, acetone, acetaldehyde, and methanol were 6.0, 5.1, 4.8, 9.5, 13.8, and 10.6 normalized counts per second (ncps) ppbv$^{-1}$, respectively; the count rates of the product ions are expressed as ion count rates normalized to an $H_3O^+$ intensity of $10^6$ cps.

Equilibrator correction factor

Figure 3 shows the dependence of the equilibrator correction factor ($F_{eq}$) on the...
carrier gas flow rate for target VOCs. The artificial seawater flow rate and the water column height were set to 1 L min⁻¹ and 60 cm, respectively. Artificial seawater was circulated without carrier gas flowing for long enough (at least a half day) so that equilibrium between the VOCs in the equilibrator’s headspace and those dissolved in the seawater was achieved. Then we determined $F_{eq}$ from the ratio of the signals in the equilibrium experiments to the signals in the headspace gas measurement. $F_{eq}$ for acetone, acetaldehyde, methanol, and DMS reached 100% at flow rates ranging from 75 to 1000 sccm (Fig. 3(a)). The carrier gas did not remove a substantial fraction of these three gases dissolved in the artificial seawater with this equilibrator setup. The solubility of these VOCs, which reached equilibrium at all the carrier gas flow rates, was higher than that of DMS (Henry’s law constant, 0.42 M atm⁻¹ at 25°C). These results suggest that species with a water solubility higher than that of
DMS were extractable to the gas phase in the complete equilibrium with the liquid phase from seawater using the equilibrator at the seawater flow rate and column height used for the experiments.

In contrast, \( F_{eq} \) for isoprene and propene decreased markedly with increasing carrier gas flow rate (Figs. 3(b) and (c)). Concentrations of isoprene and propene dissolved in artificial seawater decreased in the equilibrator, because the carrier gas removed a substantial fraction of the dissolved gases from the liquid phase. Assuming that isoprene in the carrier gas reached equilibrium with isoprene in the liquid phase, the concentrations of isoprene dissolved in seawater theoretically decreased by approximately 20% relative to the concentrations in the incoming seawater at a carrier gas flow rate of 75 sccm, a seawater flow rate of 1 L min\(^{-1}\), and a water volume of 10 L (60 cm column height). Therefore, both the disequilibration between the gas and liquid phases and the decrease of the concentrations in the equilibrator should have contributed to \( F_{eq} \) for isoprene and propene. The lines shown in Figs. 3(b) and (c) indicate the theoretically-derived dependence of the degree of equilibration (\( D \)) on the carrier gas flow rate, if the dissolved gases were extracted at a constant ratio of equilibration regardless of the carrier gas flow rate. Assuming complete equilibrium between carrier and dissolved gases, \( F_{eq} \) should have coincided with the 100% lines, but the highest data for isoprene and propene did not reach the 100% lines. This result suggests that extracted gases were not in complete equilibrium with the dissolved gases for either isoprene or propene. If the bubble size was constant regardless of the carrier gas flow rate, then the ratio of equilibration between the gas and liquid phases ought to have been stable, and therefore the variations in \( F_{eq} \) should have depended only on the decrease of the concentrations of isoprene and propene in the liquid phase. However, we found that decrease of \( F_{eq} \) was greater than that expected from the “stripping effect (S)” alone, which implies that the high carrier gas flow rate induced the production of bigger bubbles. Hence, the reduction of the gross contact area between the carrier gas and the seawater contributed to the decrease in the exchange rate. We found that \( F_{eq} \) including S for isoprene and propene were approximately 67% and 28%, respectively, at the lowest carrier gas flow rate (75 sccm). We confirmed good consistency for \( F_{eq} \) between the start and the end of measurements during a series of laboratory experiment with the same carrier gas flow rate (75 sccm), which suggests that the concentrations of VOCs in circulated artificial seawater, which decreased in the equilibrator, recovered to the initial concentrations before the seawater re-entered the equilibrator after being mixed in the large buffer (15 L) in the bucket and after re-addition of isoprene and propene by the generator of VOC-containing artificial seawater.

Figures 4(a) and (b) show the dependence of \( F_{eq} \) of isoprene on the artificial seawater flow rate and the height of the water column. \( F_{eq} \) significantly increased with increasing artificial seawater flow rate and water column height at all the carrier gas flow rates. However, \( F_{eq} \) did not reach 100%; that is, the equilibrium condition, taking S in the equilibrator into consideration. Therefore, we had to correct the measurement data using \( F_{eq} \) to determine the concentrations of the dissolved VOCs with a low water solubility (e.g., isoprene and propene), which were not in equilibrium with the dissolved gases in the equilibrator.

Figure 4(c) shows the dependence of \( F_{eq} \) of isoprene on the water temperature. In this experiment, the carrier gas flow rate, seawater flow rate, and water column height were set at 75 sccm, 1 L min\(^{-1}\), and 60 cm, respectively. \( F_{eq} \) showed no significant dependence on water temperature in
Fig. 4. Dependence of equilibrator correction factor for isoprene on (a) artificial seawater flow rate at 60-cm water column height, (b) water column height at a seawater flow rate of 1 L min⁻¹, and (c) water temperature. The dependence on carrier gas flow rate is also shown by the colored lines in views (a) and (b). Vertical bars represent 2σ.
Fig. 5. Response of the EI-PTR-MS system to abrupt changes in the concentrations of target VOCs in the artificial seawater stream under various experimental conditions: with a PFA-Teflon tube at low water temperature (~15°C, blue) and high water temperature (~25°C, red) with water droplets on the inner wall of the headspace, with a stainless steel tube (green) at ~15°C with water droplets, and with a PFA-Teflon tube at ~15°C without water droplets (black). The artificial seawater was switched between two batches of different concentrations at the time of 0 min. The final concentrations were calculated by extrapolating changes in VOC concentrations. Data are normalized to ratios of concentration changes from initial concentration (0%) to final concentration (100%). Data collected at 1-s integration are plotted at 7-s intervals. For more details, see Kameyama et al. (2010)
the range of 17–34°C. The changes in solubility of isoprene due to differences in the water temperature (calculated as 0.005–0.033 M atm⁻¹ with the Henry’s law constant for isoprene) did not contribute to $F_{eq}$ in the range of 17–34°C. We suspect that the higher (lower) $D$ led to the lower (higher) concentration of VOCs in the equilibrator, and that these two effects cancelled each other out. $F_{eq}$ depended only on the equilibrator conditions (carrier gas flow rate, seawater flow rate, and height of water column); therefore, $F_{eq}$ is also applicable to field observations through a careful characterization of its dependence on the equilibrator conditions in the laboratory.

### Response time

To estimate the response time of the EI-PTR-MS system for the target VOCs, we evaluated the change in concentrations when two batches of artificial seawater with greatly different VOC concentrations were switched at the inlet of the equilibrator. We prepared a VOC-containing batch, as described earlier, and a VOC-free batch, consisting of salted Milli-Q water with no added VOCs. By switching the intake tube between the two batches, we induced an instantaneous change in VOC concentration. The carrier gas flow rate, seawater flow rate, and water column height were set at 75 sccm, 1 L min⁻¹, and 60 cm, respectively (i.e., the same settings used for oceanic observation).

Figure 5 shows the changes in the concentrations measured by EI-PTR-MS corresponding to the abrupt changes of the artificial seawater streams. We found no significant difference in response time due to water temperature (15 and 25°C), or tubing materials (PFA and stainless steel tubing), with our equilibrator setup. The response time (defined as the e-folding time of change of detected concentration) of the entire measurement system clearly depended on the VOC species (Table 2).
with a response time of \(~1\) min. Acetaldehyde also had a short response time (3–4 min). The residence times of the carrier gas in the headspace, and of seawater in the equilibrator, were calculated to be 8 and 10 min, respectively; that is, the instrumental response time for DMS and acetaldehyde, and acetone (6–7 min) was also much shorter than the residence times in the equilibrator. The shorter-than-expected response time most likely resulted from an immediate achievement of equilibrium between seawater directed from the inlet and gases residing in the headspace. Although methanol was one of the species that reached equilibrium, the response time was relatively slow (18–19 min). A longer response time tended to be associated with species with a high solubility among the equilibration species, which suggests the influence of the uptake of these soluble species into water droplets present on the inner wall of the headspace. The spray from bubbles breaking at the surface of the water column in the equilibrator is responsible for the production of water droplets in the headspace. We minimized the influence of water droplets on the response time by floating a polyethylene sheet on the surface of the water column to minimize spray. Notches were added to the polyethylene sheet to prevent water and carrier gas from stagnating at the surface. We confirmed that the polyethylene sheet did not adsorb the target VOCs. Under these conditions, the response time of methanol was improved greatly to 2 min, and was shorter than that of any other equilibration species in the absence of water droplets. These results suggest that the response times for acetone, acetaldehyde, and methanol were delayed by the presence of water droplets and that the influence of the droplets was larger for the more-soluble species.

In contrast, the response times of isoprene and propene were relatively long (12–13 and 15 min, respectively). Isoprene and propene did not reach equilibrium in our equilibrator. The response time of isoprene was not influenced by the presence of water droplets. Although we did not carry out the experiments for propene, we hypothesized that propene would not be affected by water droplets, because its solubility is lower than that of isoprene. Thus the achievement of equilibrium, and solubility, were likely the dominant factors in controlling the response time of the VOCs.

We expected the response time during the oceanic observations to be similar to that determined in the laboratory with regard to the influence of water droplets, because the spray shield was not used during the oceanic observations. Minimizing the presence of “aged” water droplets on the headspace wall is important for achieving a shorter response time. For the next-generation instrument, we will cover the spray as we did in the laboratory, or redesign and rebuild the headspace to maintain the flow of fresh seawater. Heating the tube between the equilibrator and PTR-MS is also needed to minimize condensation.

**Background signals and detection limits**

To determine the background signals for VOCs in the system, we analyzed N₂-purged pure water samples. Background signals were measured in the MID mode at 1-s integration for each mass per cycle. The pure water (Milli-Q water) stored in the equilibrator was purged with pure N₂ gas at 1.0 L min\(^{-1}\) for 6 h, and then the VOCs signals were analyzed at a carrier gas flow of 75 sccm. Theoretically, the dissolved isoprene and propene were almost completely extracted into the gas phase by means of this degassing treatment. In contrast, the highly-soluble species (DMS, acetaldehyde, acetone, and methanol) remained in the stored water after the purging treatment for a long time, prohibiting us from accurately estimating the background signals for those VOCs. For DMS,
Fig. 6. PTR mass spectra of extracted gas from seawater samples with BI sampling (red bars) and with EX sampling (blue bars), along with difference spectra (BI minus EX, green bars). PTR mass spectra of extracted gas from N₂-purged pure water (solid bars) and of pure N₂ gas (open bars) are also shown. The ion signals at \( m/z \) 21, 29, 30, 31, 32, 34, 36, 37, 38, 39, 55, and 57 affected by primary ions are masked.
acetaldehyde, acetone, and methanol, therefore, the signals obtained when monitoring the pure N2 gas that did not pass through the equilibrator were assumed to be the lower-limit background signals. Background signals were measured with N2-purged pure water and pure N2 gas 3 and 4 times, respectively, during the cruise. These measurements provided the opportunity to account for the temporal variability of background signals during the cruise on the order of weeks. All the oceanic data were corrected by subtracting the background signals.

Detection limits were defined as the lowest signals that were statistically different from the background signals at the 95% confidence level. Concentrations of detection limits for each species were calculated assuming the water temperature to be 25°C and the water vapor concentration to be the saturated vapor concentration at 25°C (Table 2). Only acetaldehyde was undetectable in the open ocean by comparing the detection limit (3 nmol L−1) to the value reported in a previous study (1.38 ± 0.08 nmol L−1, Zhou and Mopper 1997). The detection limits of other VOCs were low enough to permit detection of the dissolved VOCs in the open ocean. Detection limits depend on the intensity of the background signals and the integration time of mass detection. By reducing the influence of the background signals and extending the integration time, we expect to be able to reduce the detection limits sufficiently, in the future, to enable measurements of dissolved acetaldehyde in the open ocean.

**PTR mass spectra and evaluation of sampling methods**

Figure 6 shows examples of PTR mass spectra of extracted gas from samples obtained by BI sampling (with the vessel’s built-in pumping system) and EX sampling (with the external pumping system employed in the heave-to period) at an observational station (42°N, 160°E) during the cruise. Both samples exhibited significant signals for VOCs at m/z 33, 43, 45, 47, 49, 59, 63, 69, 71, and 85, which were assigned to methanol, propene, acetaldehyde, ethanol, methanethiol, acetone, DMS, isoprene, total C5 alkenes (C5H10·H+), and total C6 alkenes (C6H12·H+), respectively. The signals for methanethiol (m/z 49) were higher in the BI samples than in the EX samples, which suggests that some of the methanethiol detected in the BI samples resulted from contamination in the BI sampling line. Selection of the sampling method and sampling line will enable us to measure dissolved methanethiol continuously. The difference between the DMS signal intensities of the BI and EX mass spectra was only 5 ncps, which was smaller than the statistical fluctuations (approximately 30 ncps) resulting from the intensity of the DMS signals. Therefore, this difference was not due to contamination during BI sampling.

Significant signals at m/z 47 and 71 in N2-purged pure water were found. These signals were comparable to those detected in the BI and EX samples. In contrast, signals at m/z 47 and 71 in pure N2 gas were smaller than those in the BI and EX samples, and in N2-purged pure water. These results suggest that the m/z 47 and 71 were due to contaminants in the equilibrator. Again, because of the total C6 alkenes, we could not explicitly identify the species at m/z 85. The signals at m/z 47, 49, 71, and 85 are not discussed further in this paper. A significant signal at m/z 43 (propene) was found in N2-purged pure water, although this signal was smaller than the signal for the BI and EX samples. This signal probably resulted from fragmentation of other species (e.g., propanol and acetic acid) because propene was expected to be almost completely extracted during the degassing treatment. The signal at m/z 45 (acetaldehyde) in the N2-purged pure water and the pure N2 gas was significant, making up a large fraction of the signals detected in the BI and EX samples. This
result indicates that there was a large blank associated with contamination in a part of the measurement line used for both seawater and N\textsubscript{2} gas measurements (e.g., the inlet of the PTR-MS). Evaluating the background signals of both the equilibrator and the line is important for accurate measurements.

Figures 7(a) and (b) show the temporal variations of dissolved VOC concentrations during measurements of samples obtained by EX and TF sampling (underway sampling with a towed fish), compared with samples obtained by BI sampling. The measurements were made alternately to minimize the influence of natural variations. The use of the EX and TF sampling methods likely minimized contamination during the sampling procedure because the sampling lines were newly prepared for the cruise, and most of the lines contained no metals. Although signals during alternate measurements were associated with natural variations, we found no significant dif-
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Field observation and comparison of EI-PTR-MS to ME-GC/MS

Figure 8 shows examples of the temporal variations of the concentrations of six VOCs dissolved in surface seawater measured by EI-PTR-MS during the cruise. The temporal variations of the VOC concentrations were captured well by means of EI-PTR-MS. The temporal variations for DMS and isoprene during the cruise were large, likely reflecting great spatial variations in DMS and isoprene distributions associated with highly-variable biological activities in the western North Pacific Ocean. The phases in the concentration variations were well correlated to those of chlorophyll-a concentration variations (e.g., 12–13 August), which suggest that phytoplankton biomass is a major controlling factor for DMS and isoprene concentrations in the ocean surface.
Fig. 8. Track of the SPEEDS/SOLAS 2008 cruise and examples of temporal variations of sea surface water temperature (dotted gray line), chlorophyll-a concentrations (black line), and VOCs dissolved in surface seawater (black dots). VOC data from part of the cruise (bold line) are plotted. ME-GC/MS data are also shown for DMS and isoprene (open circles). Data collected at 5-s integration are plotted at 1-min intervals for EI-PTR-MS. Note that the data for acetaldehyde below the detection limit are plotted as the concentration of a half of the detection limit.
Fig. 9. Scatter plots of EI-PTR-MS data versus ME-GC/MS data for DMS and isoprene. The solid line is a regression line, the dashed line indicates 1:1 correspondence. The error ranges for the slope and intercept of the regression line are defined at the 95% confidence level.
The variation patterns of propene and acetone were well correlated. Although many of the data for acetaldehyde were below the detection limit, episodes of high acetaldehyde concentrations (e.g., 10–11 August) were detected in synchrony with episodes of high propene and acetone concentrations. The similar production sources of these species (photolysis of organic matter has been proposed; Ratte et al. 1993; Zhou and Mopper 1997) probably contributed to the simultaneous occurrence. EI-PTR-MS detected small-scale variations for DMS, isoprene, propene, and acetone (e.g., 12–13 August), likely resulting from rapid production or consumption processes due to diverse biophysicochemical parameters. In contrast, variations in the methanol concentrations were generally broad; therefore, we expect that its production and consumption processes were not induced by regional variability of biological activity. In general, although there were some offsets in EI-PTR-MS data, agreement in the variability for DMS and isoprene between EI-PTR-MS and MI-GC/MS was reasonably good. ME-GC/MS sometimes did not capture the high variability (e.g., early morning on 13 August) because of the method’s limited measurement frequency (i.e., 70-min intervals at maximum). This result indicates that EI-PTR-MS is a powerful tool for monitoring highly-variable features of VOCs in a wide dynamic region of the open ocean.

DMS and isoprene concentrations determined by EI-PTR-MS were compared to those obtained by ME-GC/MS (Fig. 9). The slopes and intercepts of the regression lines are based on the reduced-major-axis (RMA) regression method because both data sets are measured variables and, thus, both are subject to error (Ayers 2001). The EI-PTR-MS concentrations compared here were averaged over 30 min to match the time resolution of ME-GC/MS.

For DMS, both data sets were tightly correlated. The slope of the overall regression line for DMS was $0.90 \pm 0.02$, and the intercept was negligible ($-0.03 \pm 0.30$ nmol L$^{-1}$, $R^2 = 0.99$). EI-PTR-MS tended to underestimate DMS concentrations compared to ME-GC/MS at high concentrations (>10 nmol L$^{-1}$) were detected in a relatively warm water region (>16°C), where the humidity of extracted gases reached 35 mmol mol$^{-1}$. In the high-humidity range, the uncertainty associated with the fitting curve for humidity correction was large ($\pm4\%$ at 35 mmol mol$^{-1}$ humidity). This uncertainty likely contributed to the difference between the EI-PTR-MS and the ME-GC/MS data. Other possible explanations include uncertainties in the correction factors for background signals ($\pm1\%$ at 10 nmol L$^{-1}$) for EI-PTR-MS. In contrast, EI-PTR-MS is powerful tool for monitoring high variability of VOCs in a wide dynamic region of the open ocean.

For isoprene, the two data sets were consistent with each other at the 95% confidence interval for the slope of $0.98 \pm 0.09$. We found a small but significant intercept of $7.0 \pm 6.1$ pmol L$^{-1}$ at the 95% confidence interval. Although isoprene is often the dominant species at m/z 69 among various VOCs (de Gouw and Warneke 2007), the detection of several other VOC species such as methyl butanal, ethyl vinyl alcohol, and furan at m/z 69 in atmospheric observations has also been reported (Karl et al. 2001; de Gouw et al. 2003; Christian et al. 2004). We calculated the ratio between m/z 69 and 70 to narrow down the potential contributors to the m/z 69 signals. If C$_2$H$_3$O$^+$ contributed to m/z 69, the ratio of m/z 70 to m/z 69 (M70/M69) can be calculated to be approximately 5%, owing to the contribution of $^{13}$C; otherwise, M70/M69 would tend to be lower, indicating the contribution from other species including oxygen or sulfur (e.g., furan or C$_3$S). The M70/M69 ratio observed during the oceanic observations was approximately 6%, which indicates that the offset of m/z 69 detected during the oceanic ob-
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Table 3. Statistics for concentrations of VOCs dissolved in surface seawater measured during the SPEEDS/SOLAS 2008 cruise.

<table>
<thead>
<tr>
<th></th>
<th>Average</th>
<th>S.D.*,</th>
<th>Minimum</th>
<th>Median</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMS (pmol L⁻¹)</td>
<td>4.6</td>
<td>3.9</td>
<td>1.1</td>
<td>3.4</td>
<td>30.4</td>
</tr>
<tr>
<td>Isoprene (pmol L⁻¹)</td>
<td>70.6</td>
<td>17.3</td>
<td>36.9</td>
<td>71.6</td>
<td>118.7</td>
</tr>
<tr>
<td>Propene (pmol L⁻¹)</td>
<td>174.3</td>
<td>34.9</td>
<td>84.9</td>
<td>169.3</td>
<td>286.4</td>
</tr>
<tr>
<td>Acetone (nmol L⁻¹)</td>
<td>19.0</td>
<td>4.4</td>
<td>4.4</td>
<td>18.9</td>
<td>41.3</td>
</tr>
<tr>
<td>Acetaldehyde (nmol L⁻¹)</td>
<td>BDL**</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>5.9</td>
</tr>
<tr>
<td>Methanol (nmol L⁻¹)</td>
<td>158.9</td>
<td>33.1</td>
<td>77.9</td>
<td>162.9</td>
<td>325.0</td>
</tr>
</tbody>
</table>

*S.D., standard deviation.
**BDL, below detection limit.

Our data for acetone and methanol were slightly higher than but consistent with the values reported in previous studies within the range of variation. The high biological productivity in the subarctic North Pacific Ocean may also have contributed to the higher concentrations for acetone and methanol that we observed.

Conclusions

We developed an EI-PTR-MS system for continuous measurements of the con-
centrations of multiple VOCs (DMS, isoprene, propene, acetone, acetaldehyde, and methanol) dissolved in seawater (Kameyama et al. 2009, 2010). Important correction factors including the humidity dependence of the detection sensitivity, \( F_{eq} \), and the subtraction of background signals were investigated so that the dissolved VOCs could be accurately quantified by means of the EI-PTR-MS system with a high time-resolution. However, for low-solubility species such as isoprene and propene, \( F_{eq} \) may vary according to changes in the bubble size and/or stripping effect related to the existence of surfactants in surface seawater. In order to evaluate the uncertainties, inter-comparison with the GC/MS method for each species should be addressed under a variety of conditions (such as coastal and open ocean waters) in future field studies. The inter-comparison of EI-PTR-MS to GC-PTR-MS measurements is a most important subject for future work because it can evaluate not only \( F_{eq} \) but also in-situ background signals including interferences, having the same mass number of the target species. This investigation should assess all target VOCs other than DMS and isoprene and under various conditions to test whether the EI-PTR-MS system is universally applicable. In particular, for the low-solubility species, \( S \) should be minimized by using a greater rate of water flow for seawater samples.

Although the measurement of acetaldehyde concentrations will require a longer integration time than that used in this study, the detection limits of the EI-PTR-MS system for DMS and isoprene, propene, acetone, and methanol were low enough for detection in the open ocean. Reduction of contamination in the sampling line and the EI-PTR-MS system will enable the detection of other VOCs (e.g., ethanol and methanethiol) by means of the EI-PTR-MS. Thus, the EI-PTR-MS system has the potential to enhance the spatial and temporal coverage of dissolved VOC concentrations in the open ocean surface, and will be useful for an investigation into the production and consumption of VOCs to changes in biological activities; for example, as seen in iron enrichment experiments and natural phytoplanktonic bloom. Therefore, we conclude that it will be a useful tool for improving our understanding of the global budget and production processes of VOCs.

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