

High-Resolution Measurement of Volatile Organic Compounds Dissolved in Seawater Using Equilibrator Inlet-Proton Transfer Reaction-Mass Spectrometry (EI-PTR-MS)

Hiroshi Tanimoto^{1*}, Sohiko Kameyama², Yuko Omori¹, Satoshi Inomata¹
and Urumu Tsunogai³

¹Center for Global Environmental Research, National Institute for Environmental Studies,
16-2 Onogawa, Tsukuba, Ibaraki 305-8506, Japan

²Faculty of Environmental Earth Science, Hokkaido University,
North 10 West 5, Sapporo, Hokkaido 060-0810, Japan

³Graduate School of Environmental Studies, Nagoya University,
Furo-cho, Chikusa-ku, Nagoya, Aichi 464-8601, Japan

*E-mail: tanimoto@nies.go.jp

Abstract. We have developed an equilibrator inlet-proton transfer reaction-mass spectrometry (EI-PTR-MS) system for the high-resolution measurement of the concentrations of multiple volatile organic compounds (VOCs) dissolved in seawater. The equilibration of six VOCs (dimethyl sulfide (DMS), isoprene, propene, acetone, acetaldehyde, and methanol) between seawater samples and the carrier gas, and the response time of the system, were evaluated by means of a series of laboratory experiments. Although equilibrium between the seawater sample and the carrier gas in the equilibrator was not achieved for isoprene and propene (likely because of their low water solubility), the other species did reach equilibrium. The EI-PTR-MS system was deployed during a research cruise in the western North Pacific Ocean. An evaluation of several seawater sampling methods indicated that there was no significant contamination from the sampling apparatus for the target VOCs. For DMS and isoprene, a comparison of EI-PTR-MS measurements with measurements obtained with a membrane equilibrator-gas chromatography/mass spectrometry system showed generally good agreement. EI-PTR-MS captured the temporal variations of dissolved VOCs, including small-scale variability, which demonstrates that the performance of the EI-PTR-MS system was sufficient for simultaneous and continuous measurements of multiple VOCs of environmental importance in seawater.

Keywords: Volatile Organic Compounds; PTR-MS; Equilibrator; Western North Pacific Ocean

Introduction

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, con-

tribute 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 dimethylsulfoniopropionate (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-

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 is 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 equi-

brator 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 μm) 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.

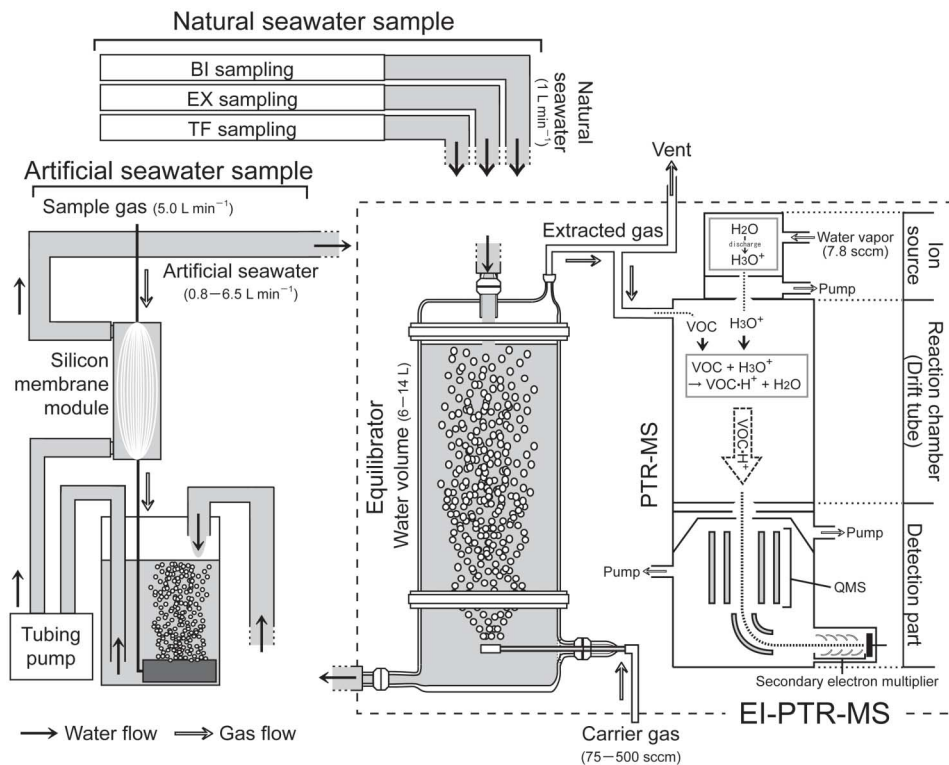


Fig. 1. Schematic diagram of the EI-TR-MS system, including equipment that supplies artificial and natural seawater to the equilibrator, used to measure concentrations of VOCs dissolved in seawater.

The flow of seawater was controlled with a peristaltic tubing pump (flow rate $<2 \text{ L min}^{-1}$, MasterFlex 7554-95, Cole-Parmer Instrument Company, Illinois, USA) or a magnetic drive pump (flow rate $>2 \text{ L min}^{-1}$, 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 H_3O^+ ions; a drift tube, in which the proton transfer reactions between H_3O^+ and VOCs took place; and a quadrupole mass spectrometer for the detection of reagent and product ions. In a hollow cathode discharge ion source, H_3O^+ 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:



A fraction of the reagent ion, H_3O^+ , and the product ions was extracted through a

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 (V cm^{-1}) and N is the buffer gas number density (molecule cm^{-3}), was set to 108 Td ($\text{Td} = 10^{-17} \text{ cm}^2 \text{ V molecule}^{-1}$) 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_{drift} , U_1 , and U_{NC} were 50, 120, 400, 48, and 5.8 V, respectively. The count rate of H_3O^+ , calculated from the count rate at m/z 21 ($\text{H}_3^{18}\text{O}^+$) multiplied by 500, was typically $1\text{--}2 \times 10^7$ 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 $\text{H}_3\text{O}^+\cdot\text{H}_2\text{O}$ to H_3O^+ (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 $\text{H}_3\text{O}^+\cdot\text{H}_2\text{O}$ was calculated from the intensity of the peak at m/z 39 ($\text{H}_5\text{O}^{18}\text{O}^+$) multiplied by 250, because the signals at m/z 37 ($\text{H}_3\text{O}^+\cdot\text{H}_2\text{O}$) were intense ($\sim 10^6$ 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 Oooki 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

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 \times 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-

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

	m/z (amu)	k_{H0} (M/atm)	$-\text{dln}k_H/\text{d}(1/T)$ (K)	Water type	References
DMS	63	0.42	3593	Seawater	Cline and Bates (1983) Przyjazny <i>et al.</i> (1983) Dacey <i>et al.</i> (1984) De Bruyn <i>et al.</i> (1995) Wong and Wang (1997)
Isoprene	69	0.013	9950	Freshwater	Mackay and Shiu (1981) Karl <i>et al.</i> (2003)
Propene	43	0.00074	3400	Freshwater	Wilhelm <i>et al.</i> (1977)
Acetone	59	27.0 ± 1.8	5090 ± 285	Seawater	Zhou and Mopper (1990) Benkelberg <i>et al.</i> (1995)
Acetaldehyde	45	12.3 ± 1.2	2476 ± 743	Seawater	Zhou and Mopper (1990) Benkelberg <i>et al.</i> (1995)
Methanol	33	220	5200	Freshwater	Snider and Dawson (1985)

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):

$$c_a = k_H \times p_g. \quad (2)$$

Henry's law constants depend on temperature (T):

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

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

$$-\text{dln}k_H/\text{d}(1/T) = -\Delta_{\text{soln}}H/R. \quad (4)$$

In this study, we used data for Henry's law constants reported in previous studies in

seawater (salinity $\approx 35\text{‰}$) 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-

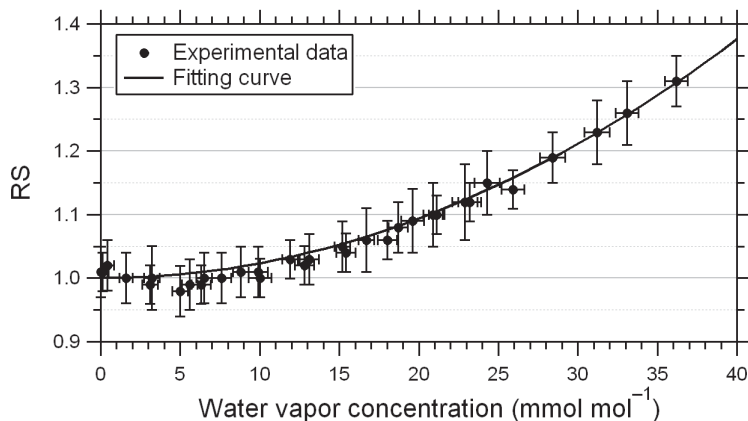


Fig. 2. Dependence of RS for isoprene on water vapor concentrations in the samples, where RS is the detection sensitivity relative to that under dry conditions. Vertical and horizontal bars represent 2σ .

tions, $[\text{H}_2\text{O}]_{\text{sample}}$, in VOC standard gases mixed with the moist air generated with the humidity controller were in the range of 0–19 mmol mol^{-1} for methanol and 0–36 mmol mol^{-1} for other VOCs.

The detection sensitivity for the six VOCs depended markedly on the humidity, which indicates that the VOCs reacted with not only H_3O^+ ions but also cluster ions 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:

$$\text{RS} = 0.000253 \times \{[\text{H}_2\text{O}]_{\text{sample}}\}^2 + 1, \quad R^2 = 0.98 \text{ for DMS}, \quad (5.a)$$

$$\text{RS} = 0.000235 \times \{[\text{H}_2\text{O}]_{\text{sample}}\}^2 + 1, \quad R^2 = 0.98 \text{ for isoprene}, \quad (5.b)$$

$$\text{RS} = 0.000157 \times \{[\text{H}_2\text{O}]_{\text{sample}}\}^2 + 1, \quad R^2 = 0.97 \text{ for propene}, \quad (5.c)$$

$$\text{RS} = 0.000287 \times \{[\text{H}_2\text{O}]_{\text{sample}}\}^2 + 1, \quad R^2 = 0.98 \text{ for acetone}, \quad (5.d)$$

$$\text{RS} = 0.000274 \times \{[\text{H}_2\text{O}]_{\text{sample}}\}^2 + 1, \quad R^2 = 0.98 \text{ for acetaldehyde}, \quad (5.e)$$

$$\text{RS} = 0.000218 \times \{[\text{H}_2\text{O}]_{\text{sample}}\}^2 + 1, \quad R^2 = 0.86 \text{ for methanol}, \quad (5.f)$$

$[\text{H}_2\text{O}]_{\text{sample}} = 0\text{--}36 \text{ mmol mol}^{-1}$;
 $0\text{--}19 \text{ mmol mol}^{-1}$ for methanol,

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

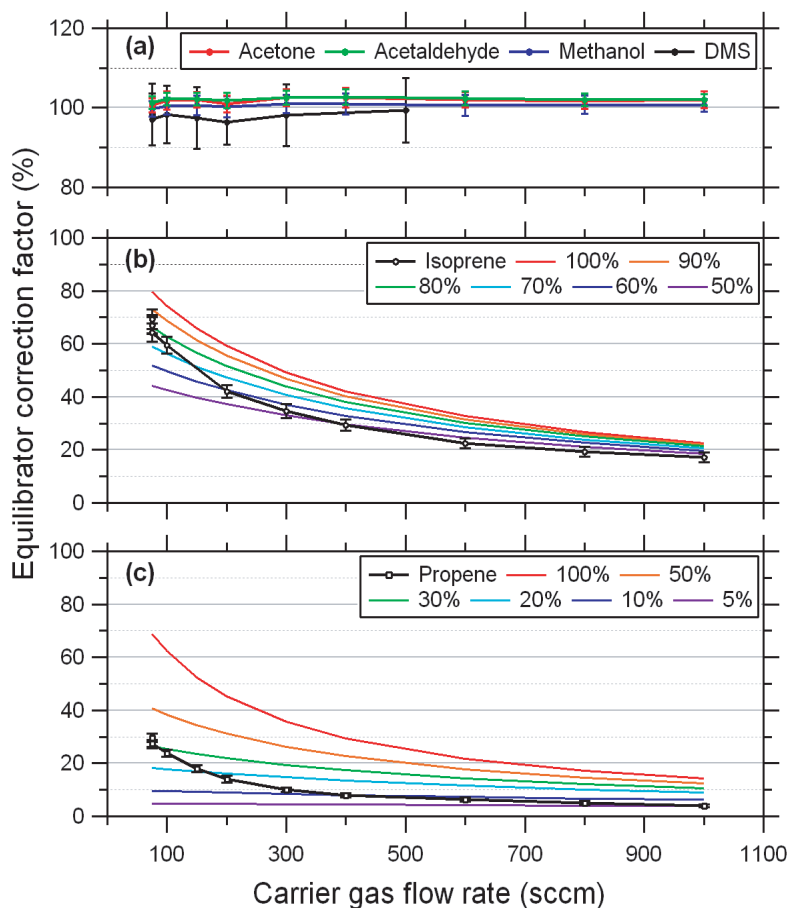


Fig. 3. Dependence of equilibrator correction factor of (a) acetone, acetaldehyde, methanol, DMS, (b) isoprene, and (c) propene on carrier gas flow rate. Vertical bars represent 2σ . The colored lines indicate the theoretically determined degree of equilibration with different carrier gas flow rates if dissolved gases were extracted at a constant ratio of equilibration regardless of the carrier gas flow rate.

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 disequilibrium 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 de-

crease 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

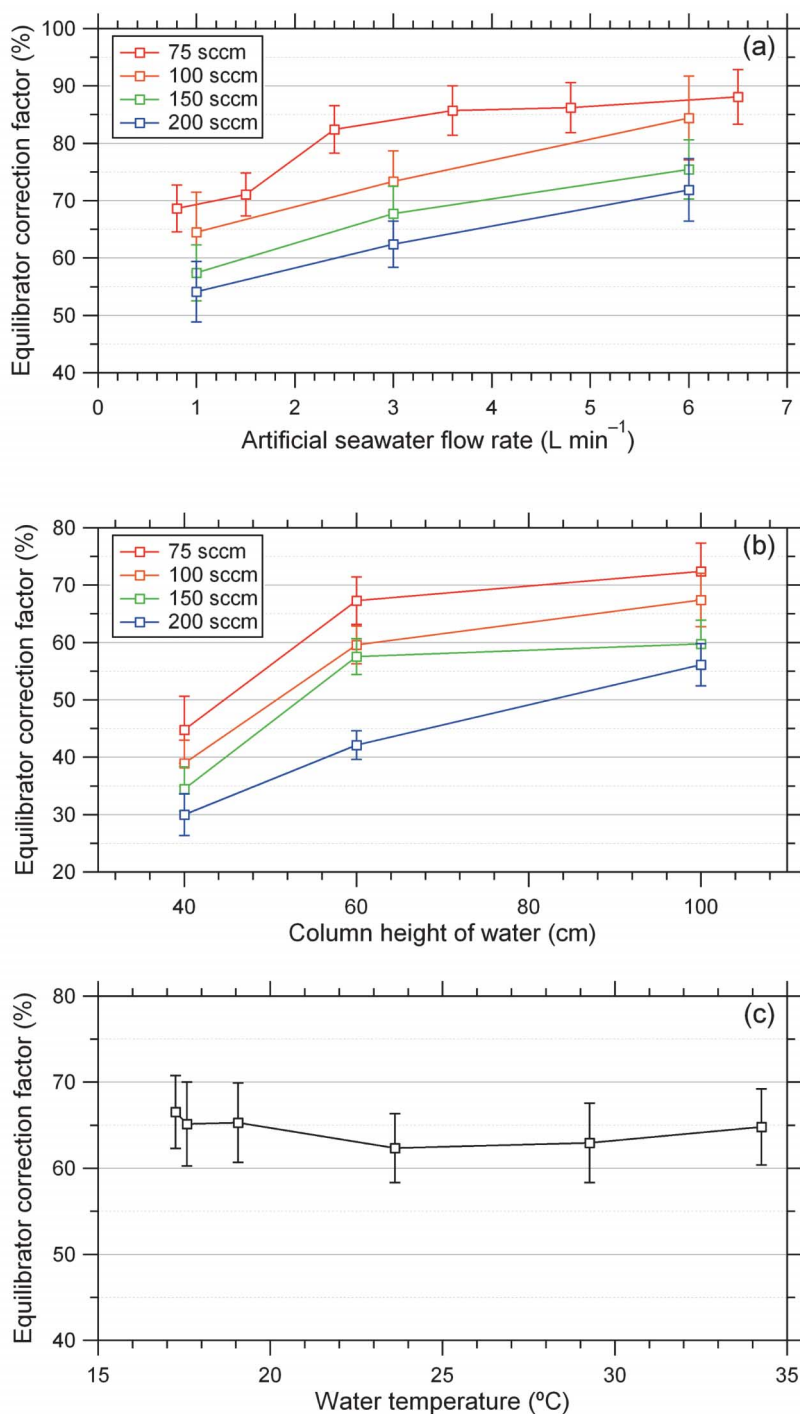


Fig. 4. Dependence of equilibrator correction factor for isoprene on (a) artificial seawater flow rate at 60-cm water column height, (b) water column height at a seawater flow rate of 1 L min⁻¹, and (c) water temperature. The dependence on carrier gas flow rate is also shown by the colored lines in views (a) and (b). Vertical bars represent 2σ .

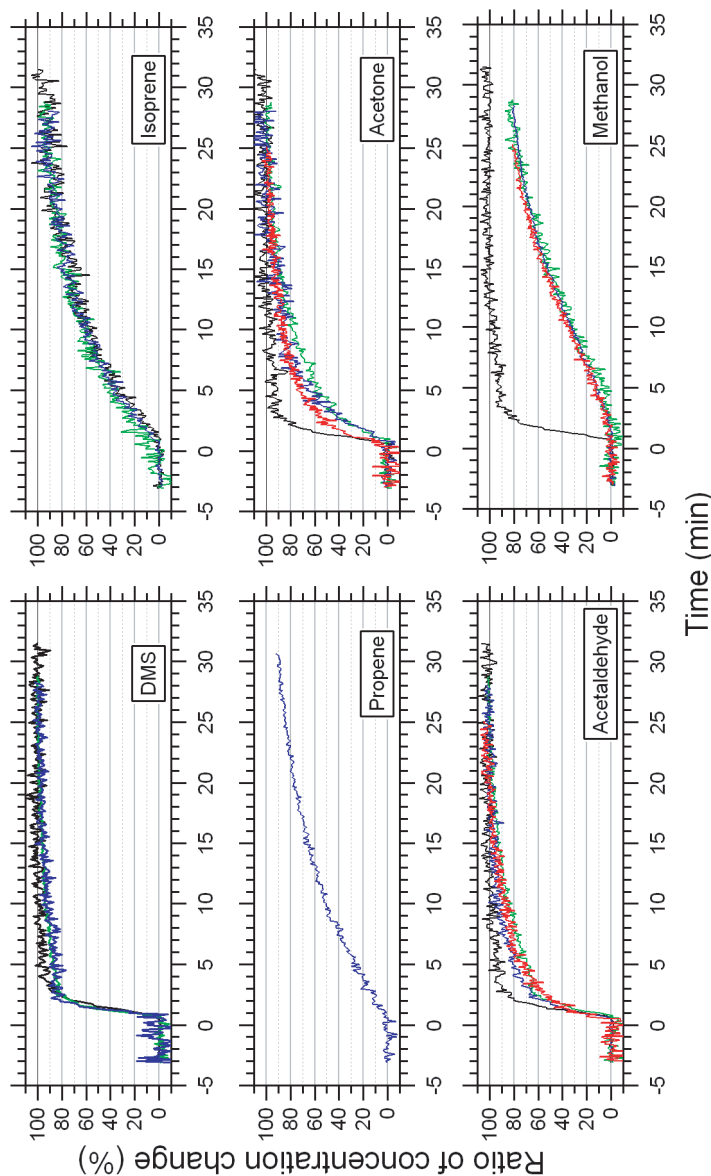


Fig. 5. Response of the EI-PTR-MS system to abrupt changes in the concentrations of target VOCs in the artificial seawater stream under various experimental conditions: with a PFA-Teflon tube at low water temperature ($\sim 15^{\circ}\text{C}$, blue) and high water temperature ($\sim 25^{\circ}\text{C}$, red) with water droplets on the inner wall of the headspace, with a stainless steel tube (green) at $\sim 15^{\circ}\text{C}$ with water droplets, and with a PFA-Teflon tube at $\sim 15^{\circ}\text{C}$ 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)

Table 2. Detection limit and response time of the EI-PTR-MS.

	DMS	Isoprene	Propene	Acetone	Acetaldehyde	Methanol
Detection limit ^a	50 pmol L ⁻¹	3 pmol L ⁻¹	7 pmol L ⁻¹	4 nmol L ⁻¹	3 nmol L ⁻¹	36 nmol L ⁻¹
Response time (min) ^b						
With water droplets in headspace	1	12–13	15	6–7	3–4	18–19
Without water droplets in headspace	1	12	NA ^c	2	2	2

^aDetection limit is estimated as the lowest signal which is statistically different from the background signal at 95% confidence level. Concentration is calculated assuming the water temperature to be 25°C, and the water vapor concentration to be saturated vapor concentration at 25°C (28.7 mmol mol⁻¹).

^bResponse time is defined as *e*-folding time of change of detected concentration.

^cNA, not analyzed.

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 the entire measurement system clearly depended on the VOC species (Table 2). The response for DMS was quite rapid,

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 N_2 -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 N_2 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,

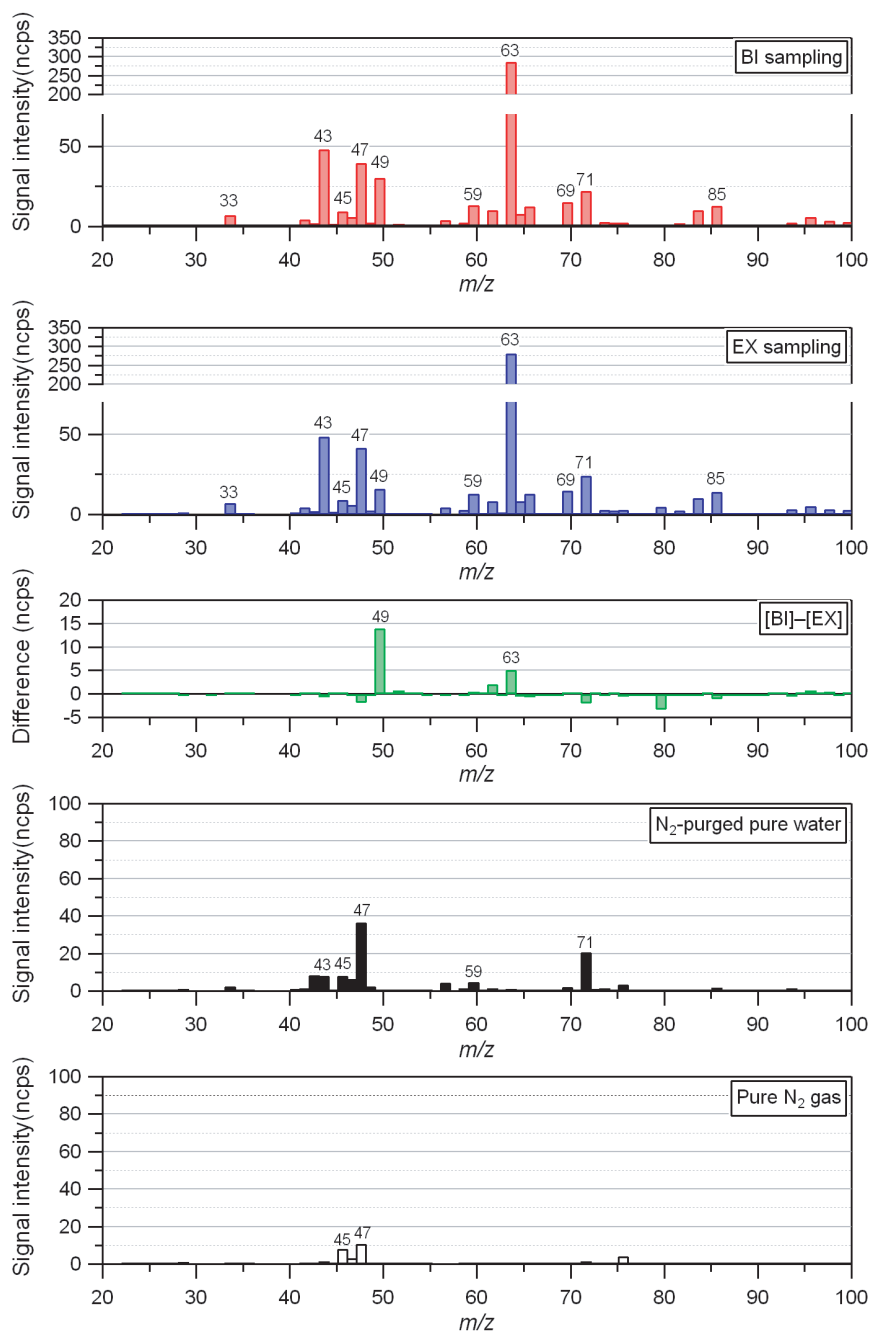


Fig. 6. PTR mass spectra of extracted gas from seawater samples with BI sampling (red bars) and with EX sampling (blue bars), along with difference spectra (BI minus EX, green bars). PTR mass spectra of extracted gas from N_2 -purged pure water (solid bars) and of pure N_2 gas (open bars) are also shown. 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 N_2 gas that did not pass through the equilibrator were assumed to be the lower-limit background signals. Background signals were measured with N_2 -purged pure water and pure N_2 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 ($1.38 \pm 0.08 \text{ nmol L}^{-1}$, 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 C_5 alkenes ($C_5H_{10} \cdot H^+$), and total C_6 alkenes ($C_6H_{12} \cdot H^+$), 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 N_2 -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 N_2 gas were smaller than those in the BI and EX samples, and in N_2 -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 C_6 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 N_2 -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 N_2 -purged pure water and the pure N_2 gas was significant, making up a large fraction of the signals detected in the BI and EX samples. This

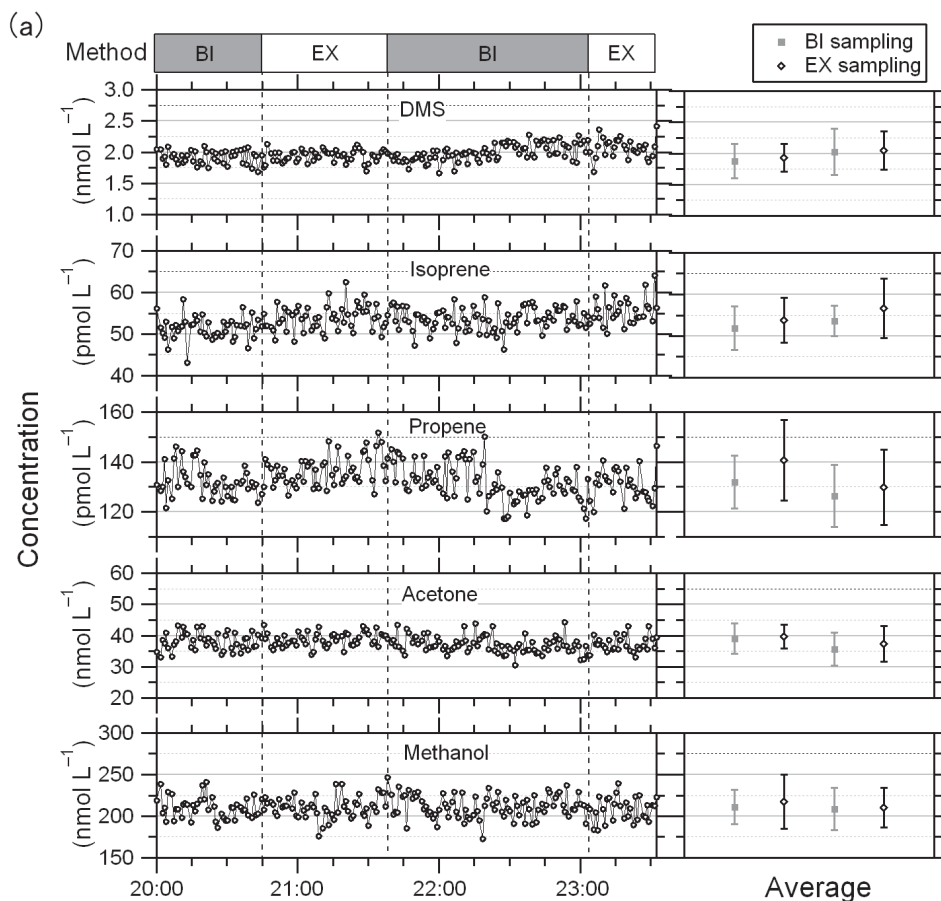


Fig. 7. Temporal variation of dissolved VOC concentrations during alternate measurements made by means of (a) BI sampling and EX sampling and (b) BI sampling and TF sampling. Data collected at 5-s integration are plotted at 1-min intervals. Averages were calculated from the data collected during the last 10 min of each sampling period. Data for acetaldehyde are not shown, because large portions of the data were below the detection limit.

result indicates that there was a large blank associated with contamination in a part of the measurement line used for both seawater and N_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-

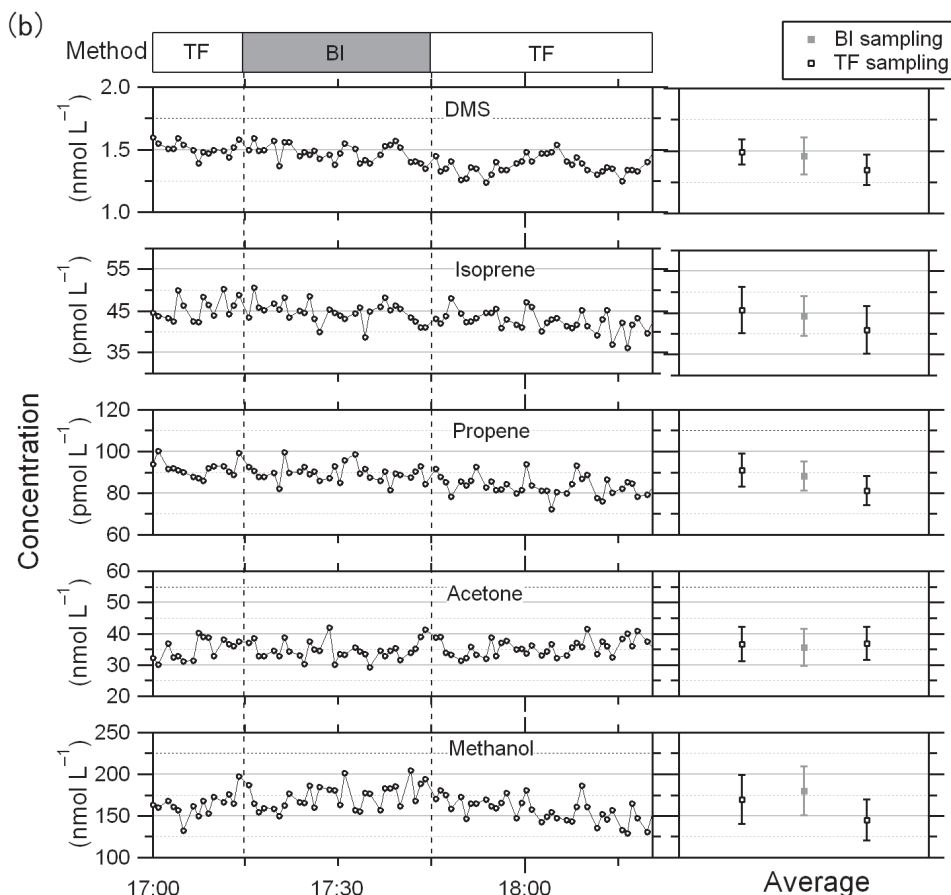


Fig. 7. (continued).

ferences before or after the change in sampling methods in the alternate measurements. This result indicates that the target VOCs were not influenced by contamination from the BI sampling line of the R/V *Hakuho-Maru*, and hereafter, field observation data are given without mention of the sampling methods.

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.

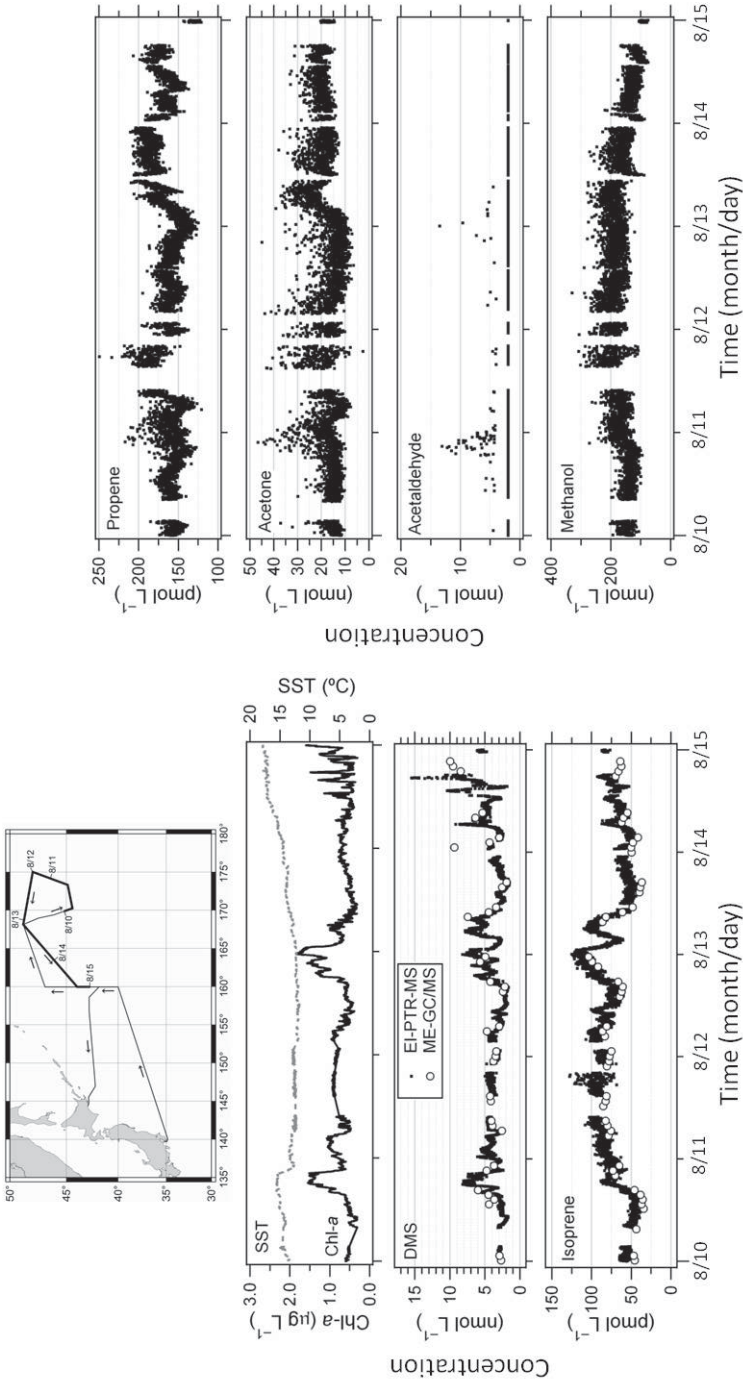


Fig. 8. Track of the SPEEDS/SOLAS 2008 cruise and examples of temporal variations of sea surface water temperature (dotted gray line), chlorophyll-a concentrations (black line), and VOCs dissolved in surface seawater (black dots). VOC data from part of the cruise (bold line) are plotted. ME-GC/MS data 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.

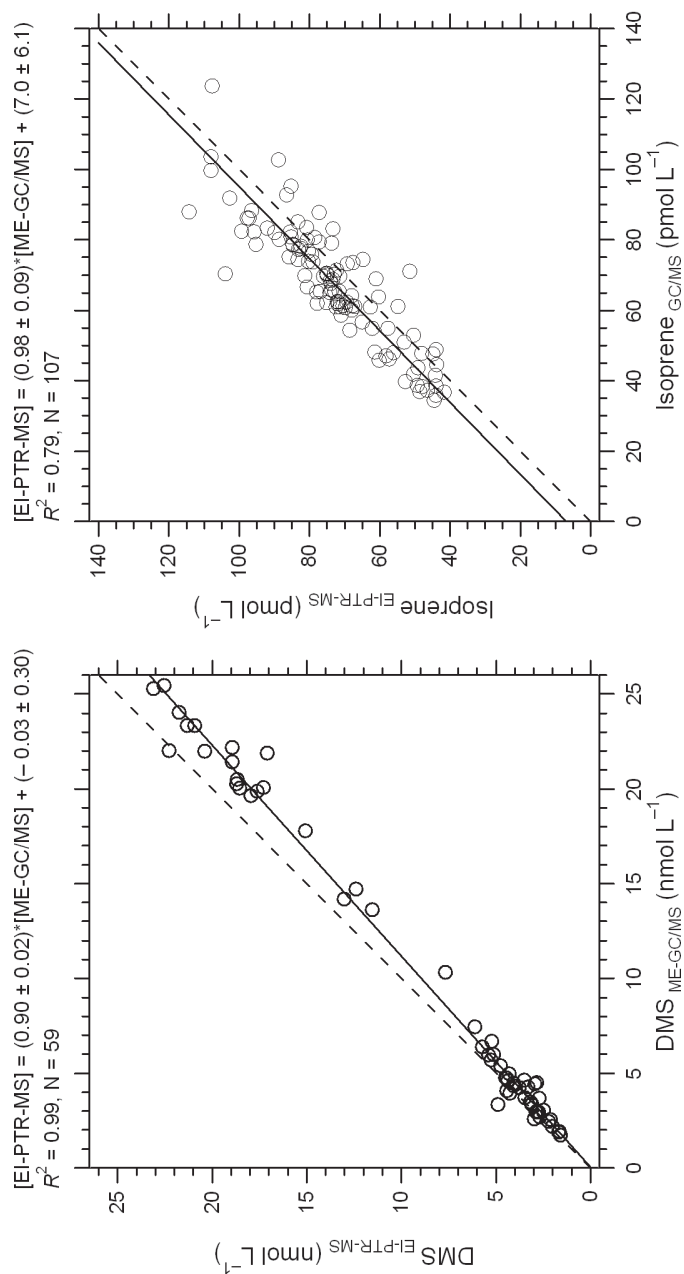


Fig. 9. Scatter plots of EI-PTR-MS data versus ME-GC/MS data for DMS and isoprene. The solid line is a regression line; the dashed line indicates 1:1 correspondence. The error ranges for the slope and intercept of the regression line are defined at the 95% confidence level.

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 ME-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 regres-

sion line for DMS was 0.90 ± 0.02 , and the intercept was negligible (-0.03 ± 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 ($>16^\circ\text{C}$), 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 ($\pm 4\%$ 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 ($\pm 1\%$ at 10 nmol L⁻¹) for EI-PTR-MS. As for ME-GC/MS, the background signals due to artifacts may have been underestimated at higher concentrations.

For isoprene, the two data sets were consistent with each other at the 95% confidence interval for the slope of 0.98 ± 0.09 . We found a small but significant intercept of 7.0 ± 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_5H_9^+ 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_3S). 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-

Table 3. Statistics for concentrations of VOCs dissolved in surface seawater measured during the SPEEDS/SOLAS 2008 cruise.

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

*S.D., standard deviation.

**BDL, below detection limit.

servation probably resulted from the C₅H₉⁺ ion. Efforts to identify the species interfering with the *m/z* 69 signals in seawater will be made in future work; for example, by using a GC interfaced with the PTR-MS system.

Comparison with previous measurements

Table 3 shows statistics for the concentrations of VOCs dissolved in surface seawater during the cruise. The mean DMS concentration for all samples was 4.6 ± 3.9 nmol L⁻¹, which agrees well with summertime levels of 4.3 ± 3.2 nmol L⁻¹ in the same region obtained by means of a general GC method (Aranami and Tsunogai 2004). We transformed all the observed data into grid data once, taking an average at 0.1° intervals, and then we obtained statistics for the grid data. As for acetaldehyde, many of the data were below the detection limit (3 nmol L⁻¹) during the cruise. The isoprene statistics were comparable to the concentration range of <12–94 pmol L⁻¹ (Matsunaga *et al.* 2002) previously reported for the western North Pacific Ocean. The concentrations of acetone measured in this study were similar to a previously-reported concentration (12.1 ± 3.0 nmol L⁻¹) for the eastern North Pacific Ocean (Marandino *et al.* 2005). Data for propene and methanol in surface seawater are sparse; we found no previous

measurements of these species in the western North Pacific Ocean. In the other regions, concentrations in the surface seawater of 20–148 pmol L⁻¹ for propene (Plass-Dülmer *et al.* 1995) and 118.4 ± 48.2 nmol L⁻¹ for methanol have been reported (Williams *et al.* 2004). The propene concentrations we measured in this study tended to be higher than the values reported in a previous study (Plass-Dülmer *et al.* 1995). Gist and Lewis (2006) reported a drastic increase in the propene concentration in the summer, an increase corresponding to increases in the intensity of insolation and phytoplankton biomass. This result suggests that the fact that the cruise occurred during the summer season (July–August), and that the biological productivity in the research area was high, contributed to the high propene concentration. 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 methanediol) 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.

Acknowledgements

We express our sincere thanks to Dr. Y. Nojiri for fruitful comments on the development of the equilibrator. Our thanks go to Drs. Y. Yokouchi, A. Ooki, S. Takeda, H. Obata, A. Tsuda, M. Uematsu, and the captain and crew of the R/V *Hakuho-Maru* for their support during the cruise. This research is a contribution to the Surface Ocean Lower Atmosphere Study (SOLAS) Core Project of the International Geosphere-Biosphere Programme (IGBP).

References

- Aranami K, Tsunogai S (2004) Seasonal and regional comparison of oceanic and atmospheric dimethylsulfide in the northern North Pacific: Dilution effects on its concentration during winter. *J. Geophys. Res.* **109**: D12303, doi:10.2929/2003JD004288.
- Ayers GP (2001) Comment on regression analysis of air quality data. *Atmos. Environ.* **35**: 2423–2425.
- Baker AR, Turner SM, Broadgate WJ, Thompson A, McFiggans GB, Vesperi O, Nightengale PD, Liss PS, Jickells TD (2000) Distribution and sea-air fluxes of biogenic trace gases in the eastern Atlantic Ocean. *Global Biogeochem. Cycles* **14**: 871–886.
- Benkelberg HJ, Hamm S, Warneck P (1995) Henry's law coefficients for aqueous solutions of acetone, acetaldehyde and acetonitrile, equilibrium constants for the addition-compounds of acetone and acetaldehyde with bisulfite. *J. Atmos. Chem.* **20**: 17–34.
- Bonsang B, Kanakidou M, Lambert G, Monfray P (1988) The marine source of C_2 – C_6 aliphatic hydro-

- carbons. *J. Atmos. Chem.* **6**: 3–20.
- Broadgate WJ, Liss PS, Penkett SA (1997) Seasonal emissions of isoprene and other reactive hydrocarbon gases from the ocean. *Geophys. Res. Lett.* **24**: 2675–2678.
- Butler JH, Elkins JW, Thompson TM, Hall BD, Swanson TH, Koropalov V (1991) Oceanic consumption of CH_3CCl_3 : implications for tropospheric OH. *J. Geophys. Res.* **96**: 22347–22355.
- Charlson RJ, Lovelock JE, Andreae MO, Warren SG (1987) Oceanic phytoplankton, atmospheric sulfur, cloud albedo and climate. *Nature* **326**: 655–661.
- Christian TJ, Kleiss B, Yokelson RJ, Holzinger R, Crutzen PJ, Hao WM, Shirai T, Blake DR (2004) Comprehensive laboratory measurements of biomass-burning emissions: 2. First intercomparison of open-path FTIR, PTR-MS, and GC-MS/FID/ECD. *J. Geophys. Res.* **109**: doi:10.1029/2003JD003874.
- Cline JD, Bates TS (1983) Dimethylsulfide in the equatorial Pacific Ocean—A natural source of sulfur to the atmosphere. *Geophys. Res. Lett.* **10**: 949–952.
- Dacey JWH, Wakeham SG, Howes BL (1984) Henry law constants for dimethylsulfide in fresh-water and seawater. *Geophys. Res. Lett.* **11**: 991–994.
- De Bruyn WJ, Swartz E, Hu JH, Shorter JA, Davidovits P, Worsnop DR, Zahniser MS, Kolb CE (1995) Henry's law solubilities and Setchenow coefficients for biogenic reduced sulfur species obtained from gas-liquid uptake measurements. *J. Geophys. Res.* **100**: 7245–7251.
- de Gouw J, Warneke C (2007) Measurements of volatile organic compounds in the Earth's atmosphere using proton-transfer-reaction mass spectrometry. *Mass Spectrom. Rev.* **26**: 223–257, doi:10.1002/mas.20119.
- de Gouw J, Warneke C, Karl T, Eerdekens G, van der Veen C, Fall R (2003) Sensitivity and specificity of atmospheric trace gas detection by proton-transfer-reaction mass spectrometry. *Int. J. Mass Spectrom.* **223**: 365–382.
- Donahue NM, Prinn RG (1990) Nonmethane hydrocarbon chemistry in the remote marine boundary-layer. *J. Geophys. Res.* **95**: 18387–18411.
- Frankignoulle M, Borges A, Biondo R (2001) A new design of equilibrator to monitor carbon dioxide in highly dynamic and turbid environments. *Water Res.* **35**: 1344–1347.
- Gist N, Lewis AC (2006) Seasonal variations of dissolved alkenes in coastal waters. *Mar. Chem.* **100**: 1–10.
- Groszko W, Moore RM (1998) A semipermeable membrane equilibrator for halomethanes in seawater. *Chemosphere* **36**: 3083–3092.
- Guenther A, Hewitt CN, Erickson D, Fall R, Geron C, Graedel T, Harley P, Klinger L, Lerdau M, McKay WA, Pierce T, Scholes B, Steinbrecher R, Tallamraju R, Taylor J, Zimmerman P (1995) A global model of natural volatile organic compound emissions. *J. Geophys. Res.* **100**: 8873–8892.
- Inomata S, Tanimoto H, Kameyama S, Tsunogai U, Irie H, Kanaya Y, Wang Z (2008) Technical note: Determination of formaldehyde mixing ratios in air with PTR-MS: Laboratory experiments and field measurements. *Atmos. Chem. Phys.* **8**: 273–284.
- Johnson JE (1999) Evaluation of a seawater equilibrator for shipboard analysis of dissolved oceanic trace gases. *Anal. Chim. Acta* **395**: 119–132.
- Kameyama S, Tanimoto H, Inomata S, Tsunogai U, Ooki A, Yokouchi Y, Takeda S, Obata H, Uematsu M (2009) Equilibrator inlet-proton transfer reaction-mass spectrometry (EI-PTR-MS) for sensitive, high-resolution measurement of dimethyl sulfide dissolved in seawater. *Anal. Chem.* **81**: 9021–9026, doi:10.1021/ac901630h.
- Kameyama S, Tanimoto H, Inomata S, Tsunogai U, Ooki A, Takeda S, Obata H, Tsuda A, Uematsu M (2010) High-resolution measurement of multiple volatile organic compounds dissolved in seawater using equilibrator inlet-proton transfer reaction-mass spectrometry (EI-PTR-MS). *Mar. Chem.* **122**: 59–73.
- Karl T, Fall R, Crutzen PJ, Jordan A, Lindinger W (2001) High concentrations of reactive biogenic VOCs at a high altitude site in late autumn. *Geophys. Res. Lett.* **28**: 507–510.
- Karl T, Yeretzyan C, Jordan A, Lindinger W (2003) Dynamic measurements of partition coefficients using proton-transfer-reaction mass spectrometry (PTR-MS). *Int. J. Mass Spectrom.* **223**: 383–395.
- Keeling CD, Rakestraw NW, Waterman LS (1965) Carbon dioxide in surface waters of the Pacific Ocean. 1. Measurement of the distribution. *J. Geophys. Res.* **70**: 6087–6097.
- Kelley JJ (1970) Carbon dioxide in the surface waters of the North Atlantic Ocean and the Barents and Kara Seas. *Limnol. Oceanogr.* **15**: 80–97.
- Kettle AJ, Rhee TS, von Hobe M, Poulton A, Aiken J, Andreae MO (2001) Assessing the flux of different volatile sulfur gases from the ocean to the atmosphere. *J. Geophys. Res.* **106**: 12193–12209.
- Kuzma J, Nemecek-Marshall M, Pollock WH, Fall R (1995) Bacteria produce the volatile hydrocarbon

- isoprene. *Curr. Microbiol.* **30**: 97–103.
- Ledyard KM, Dacey JWH (1994) Dimethylsulfide production from dimethylsulfoniopropionate by a marine bacterium. *Mar. Ecol. Prog. Ser.* **110**: 95–103.
- Lindinger W, Hansel A, Jordan A (1998) On-line monitoring of volatile organic compounds at pptv levels by means of proton-transfer-reaction mass spectrometry (PTR-MS) medical applications, food control and environmental research. *Int. J. Mass Spectrom.* **173**: 191–241.
- Liss PS, Hatton AD, Malin G, Nightingale PD, Turner SM (1997) Marine sulphur emissions. *Philos. Trans. R. Soc. B.* **352**: 159–168.
- Loose B, Stute M, Alexander P, Smethie WM (2009) Design and deployment of a portable membrane equilibrator for sampling aqueous dissolved gases. *Water Resour. Res.* **45**: doi:10.1029/2008WR006969.
- Mackay D, Shiu WY (1981) A critical review of Henry's law constants for chemicals of environmental interest. *J. Phys. Chem. Ref. Data* **10**: 1175–1199.
- Marandino CA, De Bruyn WJ, Miller SD, Prather MJ, Saltzman ES (2005) Oceanic uptake and the global atmospheric acetone budget. *Geophys. Res. Lett.* **32**: L15806, doi:10.1029/2005GL023285.
- Marandino CA, De Bruyn WJ, Miller SD, Saltzman ES (2007) Eddy correlation measurements of the air/sea flux of dimethylsulfide over the North Pacific Ocean. *J. Geophys. Res.* **112**: D03301, doi:10.1029/2006JD007293.
- Marandino CA, De Bruyn WJ, Miller SD, Saltzman ES (2008) DMS air/sea flux and gas transfer coefficients from the North Atlantic summertime coccolithophore bloom. *Geophys. Res. Lett.* **35**: L23812, doi:10.1029/2008GL036370.
- Marandino CA, De Bruyn WJ, Miller SD, Saltzman ES (2009) Open ocean DMS air/sea fluxes over the eastern South Pacific Ocean. *Atmos. Chem. Phys.* **9**: 345–356.
- Matsunaga S, Mochida M, Saito T, Kawamura K (2002) In situ measurement of isoprene in the marine air and surface seawater from the western North Pacific. *Atmos. Environ.* **36**: 6051–6057.
- McKay WA, Turner MF, Jones BMR, Halliwell CM (1996) Emissions of hydrocarbons from marine phytoplankton—Some results from controlled laboratory experiments. *Atmos. Environ.* **30**: 2583–2593.
- Milne PJ, Riemer DD, Zika RG, Brand LE (1995) Measurement of vertical distribution of isoprene in surface seawater, its chemical fate, and its emission from several phytoplankton monocultures. *Mar. Chem.* **48**: 237–244.
- Moore RM, Oram DE, Penkett SA (1994) Production of isoprene by marine phytoplankton cultures. *Geophys. Res. Lett.* **21**: 2507–2510.
- Murphy DM, Thomson DS, Mahoney TMJ (1998) In situ measurements of organics, meteoritic material, mercury, and other elements in aerosols at 5 to 19 kilometers. *Science* **282**: 1664–1669.
- Murphy PP, Nojiri Y, Fujinuma Y, Wong CS, Zeng J, Kimoto T, Kimoto H (2001) Measurements of surface seawater $f\text{CO}_2$ from volunteer commercial ships: Techniques and experiences from *Skaugran*. *J. Atmos. Ocean. Technol.* **18**: 1719–1734.
- Nemcek N, Ianson D, Tortell PD (2008) A high-resolution survey of DMS, CO_2 , and O_2/Ar distributions in productive coastal waters. *Global Biogeochem. Cycles* **22**: GB2009, doi:10.1029/2006GB002879.
- Ooki A, Yokouchi Y (2008) Development of a silicone membrane tube equilibrator for measuring partial pressures of volatile organic compounds in natural water. *Environ. Sci. Technol.* **42**: 5706–5711, doi:10.1021/es800912j.
- Plass-Dülmer C, Koppmann R, Ratte M, Rudolph J (1995) Light nonmethane hydrocarbons in seawater. *Global Biogeochem. Cycles* **9**: 79–100.
- Przyjazny A, Janicki W, Chrzanowski W, Staszewski R (1983) Headspace gas-chromatographic determination of distribution coefficients of selected organosulfur compounds and their dependence on some parameters. *J. Chromatogr.* **280**: 249–260.
- Ratte M, Plass-Dülmer C, Koppmann R, Rudolph J, Denga J (1993) Production mechanism of C_2 – C_4 hydrocarbons in seawater: Field measurements and experiments. *Global Biogeochem. Cycles* **7**: 369–378.
- Saito H, Tamura N, Kitano H, Mito A, Takahashi C, Suzuki A, Kayanne H (1995) A compact seawater pCO_2 measurement system with membrane equilibrator and nondispersive infrared gas analyzer. *Deep-Sea Res. I* **42**: 2025–2033.
- Saltzman ES, De Bruyn WJ, Lawler MJ, Marandino CA, McCormick CA (2009) A chemical ionization mass spectrometer for continuous underway shipboard analysis of dimethylsulfide in near-surface seawater. *Ocean Sci.* **5**(4): 537–546.
- Shaw SL, Chisholm SW, Prinn RG (2003) Isoprene production by *Prochlorococcus*, a marine

- cyanobacterium, and other phytoplankton. *Mar. Chem.* **80**: 227–245.
- Singh HB, Kanakidou M, Crutzen PJ, Jacob DJ (1995) High concentrations and photochemical fate of oxygenated hydrocarbons in the global troposphere. *Nature* **378**: 50–54.
- Singh HB, Tabazadeh A, Evans MJ, Field BD, Jacob DJ, Sachse G, Crawford JH, Shetter R, Brune WH (2003) Oxygenated volatile organic chemicals in the oceans: Inferences and implications based on atmospheric observations and air-sea exchange models. *Geophys. Res. Lett.* **30**: doi:10.1029/2003GL017933.
- Snider JR, Dawson GA (1985) Tropospheric light alcohols, carbonyls, and acetonitrile: Concentrations in the southwestern United States and Henry's law data. *J. Geophys. Res.* **90**: 3797–3805.
- Stefels J, Vanboekel WHM (1993) Production of DMS from dissolved DMSP in axenic cultures of the marine-phytoplankton species *Phaeocystis* sp. *Mar. Ecol. Prog. Ser.* **97**: 11–18.
- Takahashi T (1961) Carbon dioxide in the atmosphere and in Atlantic Ocean water. *J. Geophys. Res.* **66**: 477–494.
- Tortell PD (2005a) Small-scale heterogeneity of dissolved gas concentrations in marine continental shelf waters. *Geochem. Geophys. Geosyst.* **6**: Q11M04, doi:10.1029/2005GC000953.
- Tortell PD (2005b) Dissolved gas measurements in oceanic waters made by membrane inlet mass spectrometry. *Limnol. Oceanogr. Meth.* **3**: 24–37.
- Weiss RF (1981) Determinations of carbon dioxide and methane by dual catalyst flame ionization chromatography and nitrous oxide by electron capture chromatography. *J. Chromatogr. Sci.* **19**: 611–616.
- Wilhelm E, Battino R, Wilcock RJ (1977) Low-pressure solubility of gases in liquid water. *Chem. Rev.* **77**: 219–262.
- Williams J, Poschl U, Crutzen PJ, Hansel A, Holzinger R, Warneke C, Lindinger W, Lelieveld J (2001) An atmospheric chemistry interpretation of mass scans obtained from a proton transfer mass spectrometer flown over the tropical rainforest of Surinam. *J. Atmos. Chem.* **38**: 133–166.
- Williams J, Holzinger R, Gros V, Xu X, Atlas E, Wallace DWR (2004) Measurements of organic species in air and seawater from the tropical Atlantic. *Geophys. Res. Lett.* **31**: doi:10.1029/2004GL020012.
- Wong PK, Wang YH (1997) Determination of the Henry's law constant for dimethyl sulfide in seawater. *Chemosphere* **35**, 535–544.
- Zhou XL, Mopper K (1990) Apparent partition coefficients of 15 carbonyl compounds between air and seawater and between air and freshwater; Implications for air-sea exchange. *Environ. Sci. Technol.* **24**: 1864–1869.
- Zhou XL, Mopper K (1997) Photochemical production of low-molecular-weight carbonyl compounds in seawater and surface microlayer and their air-sea exchange. *Mar. Chem.* **56**: 201–213.