to be submitted to Atmospheric Environment

In situ measurement of isoprene in the marine air and surface seawater from the western North Pacific

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Abstract

Isoprene (2-methyl-1,3-butadiene) was measured on board of R/V Mirai for eight air samples and fourteen seawater samples collected in the western North Pacific during ACE-Asia campaign (from May 18 to May 26, 2001). The measurements were conducted *in situ* using a cryo focus/gas chromatography/mass spectrometry (Cryo/GC/MS). Concentrations of isoprene ranged from 7.2 to 111 parts-per-trillion (pptv) in the marine air, and ranged from below 1.2 pmol L^{-1} to 9.4 pmol L^{-1} in the seawater. Based on these results, sea-to-air emissions of isoprene were calculated to be from 16.4 to 24.6 nmol m^{-2} day^{-1}. The upper limits of the emission rates were also calculated to be from 3.2 to 30.4 nmol m^{-2} day^{-1}. Atmospheric isoprene concentrations cannot be explained only by the emission from the seawater. Thus the concentrations of isoprene in the marine air in western North Pacific should be significantly affected by terrestrial vegetational emission and subsequent long-range atmospheric transport of isoprene.

Keywords: sea-to-air emission, VOCs, long-range transport, cryo-focus, liquid CO_2

1. Introduction

Non-methane hydrocarbons (NMHCs) of both biogenic and anthropogenic origin are important species in controlling the atmospheric chemistry. First, they react with atmospheric oxidants, and act as a sink of the oxidants such as OH, which is the most important oxidant in the atmosphere. Second, some oxidation products of NMHCs are known to condense to form atmospheric particles. Such aerosol particles play important roles in scattering the solar radiation and acting as cloud condensation nuclei. Therefore, the emissions of NMHCs to the atmosphere may have important effects on a global scale climate system. Isoprene (2-methyl-1,3-butadiene) is highly reactive in the atmosphere and its emission rate in a global scale is the largest among all the NMHCs, being estimated to be 500 Tg yr^{-1} (Guenther, 1999).

Isoprene is known to be emitted from terrestrial vegetation, however, recent studies revealed that isoprene is also released from the ocean (Bonsang *et al.*, 1992, Yokouchi *et al.*, 1999). The emission rate of isoprene from the ocean to the atmosphere has been estimated to be 1 Tg yr^{-1} (Bonsang *et al.*, 1992, Guenther, 1999). As a sparingly soluble gas, sea-to-air flux of isoprene can be calculated from its transfer velocity in the seawater, solubility and difference in the concentrations between the ambient air and surface seawater. Milne *et al*. (1995) reported isoprene emission rate in Florida coast, ranging from 9.51 to 101.2 nmol m^{-2} day^{-1}. Broadgate *et al*. (1997) reported the seasonal variation of isoprene emission rates (1.4 to 68 nmol m^{-2} day^{-1}) in the North Sea and Southern Ocean.

Isoprene is known as the most important NMHC that affects the atmospheric chemistry in the terrestrial region. Although its emission and degradation in the continents are relatively well known by previous studies, there are only few reports about the emission rate and distribution of isoprene in the open ocean. Especially, the production and degradation balance of isoprene in the North Pacific have rarely been

studied. In addition, the oceanic isoprene should mostly react with the oxidants such as OH, ozone and chlorine atoms in the marine atmosphere (Tuazon and Atkinson, 1990; Atkinson, 1990; Keene *et al*., 1993; Ragains and Finlayson-Pitts, 1997), serving as a sink for the oxidants in the marine boundary layer. In this study, we report the distributions of isoprene concentrations in the marine atmosphere and surface seawater in the western North Pacific, and determined its sea-to-air fluxes.

2. Experimental section

2.1. Sampling site and GC/MS System

The sampling of marine air and seawater was conducted in the western North Pacific along the 146°25'E transect (from 30°45'N, 146°25'E to 35°45'N, 146°23'E) during the cruise of R/V Mirai (MR01-K02, Japan Marine Science & Technology Center) as part of ACE-Asia (Asian Pacific Aerosol Characterization Experiment) campaign (from May 18 to 26 , 2001). Figure 1 shows the map with the sampling sites. Eight air and fourteen seawater samples were analyzed in this study.

In order to avoid the potential degradation and production of NMHCs during a sample storage, *in situ* measurement is sometimes required for biogenic and reactive compounds such as isoprene in seawater. Hydrocarbon analysis using the cryo focus preconcentration system generally needs liquid N_2 for cooling traps, however, there is a difficulty in using and loading the liquid N_2 on a ship in the open ocean. We developed the cryo focus preconcentration system that does not require liquid N_2, but needs only liquid CO_2 as cooling media (see Figure 2). The cryo focus system coupled with GC/MS on R/V Mirai allowed us to measure *in situ* isoprene in the air and surface seawater in the open ocean.

2.2. Determination of isoprene in the air samples

The marine air samples were collected into the pre-evacuated 6 L stainless steel canister (Silco-Can, RESTEC Corp., Bellefonte, PA), and pressurized to approximately 2 atm using Teflon bellows pump at compass deck of the ship (approximately 25 m above the sea level). The air samples were stored approximately 1.5 hour at room temperature, during which the atmospheric oxidants are considered to be destroyed on the surface of the canister. Thus oxidation of isoprene on the trap during the adsorption should be avoided.

The air samples were analyzed using a preconcentration/cryo focus/capillary gas chromatograph/mass spectrometer (Cryo/GC/MS) system on board, as illustrated in Figure 2. The preconcentration unit (GAS 30, DKK corporation, Tokyo, Japan) is consisted of adsorption trap (60 mg of Carbotrap, SUPELCO, Bellefonte, PA), capillary trap (top 5 cm of capillary GC column) and two switching valves. The two traps were designed to be cooled down by liquid CO_2. A 750 mL of sample air was drawn from the canister through a water trap (approximately 5 g $Mg(ClO_4)_2$) and then adsorption trap, the later had been cooled to approximately -50 °C by liquid CO_2. Adsorption of isoprene onto the former trap was checked to be negligible. The latter trap was then heated to 150 °C in order to desorb the isoprene that was trapped in the adsorption trap, and then transferred to the capillary cryo focus trap that had been cooled down to approximately -70 °C by liquid CO_2. Finally, the capillary trap was heated to 175 °C, and the isoprene was transferred into GC/MS (Finnigan MAT GCQ). Helium was used as a carrier gas. Compounds in the sample air were separated on a capillary column (Al_2O_3 PLOT, Chrompack, 0.32 mm i.d.×50 m long). Analysis of one air sample was completed within 30 minutes.

2.3. Determination of isoprene in the seawater samples

Surface seawater samples were collected from 10 m in water depth using Niskin bottles installed in a CTD system. The seawaters were transferred into 730 mL glass bottles immediately after the CTD was recovered on the ship. The samples were analyzed within 30 minutes after the collection. The seawater sample was fully removed from the bottle into a 1 L glass cell in the gas extraction system (Figure 3). Then, the isoprene in the sample water was stripped with a pure helium bubble flow (50 mL min^{-1}) for 30 minutes. The helium gas containing isoprene was drawn through the first water trap (approximately 1 g $Mg(ClO_4)_2$) and then transferred to the preconcentration unit of a capillary GC as mentioned above. Analysis of one seawater sample needed 45 minutes.

3. Results and discussion

3.1. Concentrations of isoprene in the marine air and surface seawater

Table 1 presents the analytical results of isoprene in the western North Pacific. Concentrations of atmospheric isoprene ranged from 7.2 to 111 pptv (average, 45.6 pptv). The seawater concentrations ranged from the below detection limit (the detection limit was 1.2 pmol L^{-1}) to 9.4 pmol L^{-1}, with the average concentration of 3.1 pmol L^{-1}. Figure 4 presents the isoprene concentrations in the surface seawater samples collected at the water depth of 10 m. The averaged daytime concentration of isoprene (5.6 pmol L^{-1}) exceeded that of nighttime (2.7 pmol L^{-1}; see Table 1). This suggests that isoprene production by marine biological processes was greater in daytime (see Table 1). In contrast, the results of air samples showed that the nighttime averaged concentration of isoprene exceeded that of daytime.

If isoprene could be assumed to be in equilibrium between the air and surface seawater, its concentration in the seawater should be equivalent to the product of Henry's law constant (K_H) and the partial pressure of isoprene ($P_{isoprene}$) in the air. Table 1 shows the average and median of the products ($P_{isoprene} \times K_H$) for the different sampling sites. The average concentration in the seawater (3.1 pmol L^{-1}) exceeded the product ($P_{isoprene} \times K_H$; 1.3 pmol L^{-1}). This indicates that the isoprene flux was directed from the sea surface to the atmosphere.

3.2. Emission rate of isoprene

The sea-to-air flux of isoprene (F in mol m^{-2} s^{-1}) can be calculated by the following equation:

$$F = k_L(C_w - K_H P_{isoprene}) \qquad (1)$$

, where k_L is the liquid phase transfer velocity. C_w, K_H and $P_{isoprene}$ are defined as concentration in surface seawater, Henry's law constant and partial pressure of isoprene, respectively. Wanninkhof (1992) has proposed a relationship of k_L in m s^{-1} with wind speed U (m s^{-1}) and Schmidt number Sc as follows.

$$k_L = 2.778 \times 10^{-6}(0.31U^2(Sc/660)^{-1/2}) \qquad (2)$$

Schmidt number of isoprene was adapted from Milne *et al.* (1995) for the calculation of isoprene emission rate. Table 2 presents wind speed at the sampling site and the emission rates of isoprene from the ocean. The emission rates (16.4-24.6 nmol m^{-2} day^{-1}) were lower than the previous results (see Table 2) reported in Florida coast, North Sea and Southern Ocean (Milne *et al.*, 1995; Broadgate *et al.*, 1997). This suggests that the biological production of isoprene in the western North Pacific may be lower than the oceans studied previously. The upper limits of the emission rate of isoprene can be calculated on the assumption that concentrations of isoprene in the

marine air were zero. The upper limits of the emission rates were also lower than those of the previous reports (see Table 2).

3.3. Source of isoprene in the marine air

The height of the marine boundary layer (MBL) at the sampling site was approximately 1000 ~ 1200 m (a personal communication with K. Miura, Tokyo University of Science). Assuming that the marine air in the MBL was convected within half day, the lifetime of isoprene was 2 hours, we estimated the emission rate of isoprene from sea surface to be 20 nmol m^{-2} day^{-1}. This means that the daytime concentration of isoprene derived only from the ocean is very low (0.016 pptv). Therefore we concluded that the sea-to-air emission of isoprene did not contribute to the measured concentrations (ca. 50 pptv) in the western North Pacific.

The result of back trajectory analysis (see Figure 5) and radon concentration (a personal communication with K. Miura) suggested that most of the air parcels at the sampling site had passed through the terrestrial regions in Asia 1 to 5 days before the sampling. The concentration of terrestrial isoprene would decrease to 50 pptv (nearly equal to the observed concentration in the marine air) within 5 days on the assumption that initial concentration was 1 ppbv and averaged daytime concentration of OH was 5×10^4 to 1×10^5 molecules cm^{-3}. These assumptions are realistic and do not contradict to the observed concentrations of isoprene in the marine air in this study. Thus, the isoprene in the marine air (7.2 to 111 pptv) were probably significantly influenced by the terrestrial emission and long-range atmospheric transport in the western North Pacific.

4. Conclusion

Concentrations of isoprene in both marine air and surface seawater have been *in situ* measured in the western North Pacific during an early summer, and the isoprene sea-to-air fluxes were calculated. The isoprene flux in the western North Pacific was estimated to be 20 nmol m^{-2} day^{-1}. Although this is 5 times lower than the isoprene flux estimated on a global scale in the previous modeling study (110 nmol m^{-2} day^{-1}, Guenther, 1999), the results are consistent with the general knowledge that the biological productivity in the studied area (open ocean) was lower than that of the global average. Considering low emission rates of isoprene from the ocean, we suggest that atmospheric isoprene in the western North Pacific is mostly derived from terrestrial regions in Asia. *In situ* measurement of biogenic reactive compounds such as isoprene in the seawater sample allowed us to estimate the accurate the sea-to-air emission rate of such gases.

Acknowledgements

We thank the captain and clues of R/V Mirai (MR01-K02), Japan Marine Science & Technology Center. We also thank Dr. Shungo Kato (Research Center for Advanced Science and Technology, The University of Tokyo) for valuable discussion and Mr. Katsunori Sagishima (Marine Works Japan) for maintenance of the GC/MS. This study was in part supported by the Grant-in-Aid for Scientific Research of Japan Society for the Promotion of Science (No. 07109) and Japanese Ministry of Education, Science, Sports and Culture (No. 10354009).

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Figure 1 Sampling sites of the seawater samples (opened squares) and air samples (solid circles) collected in the western North Pacific (May 18 to 26, 2001).

Figure 2 An outline of the preconcentration system interfaced to capillary GC/MS.

Figure 3 An outline of the purge and trap system for isoprene in the seawater samples. This system is interfaced to cryo focus capillary GC/MS (see Figure 2).

Figure 4 The concentrations of isoprene in the seawater and air samples at daytime (06:00-19:00, local time) and nighttime (19:00-06:00) in the 146°25'E transect of the western North Pacific. Black (nighttime) and white (daytime) bar mean the calculated concentrations of isoprene based on the Henry's law constant (K_H) and the partial pressure of isoprene ($P_{isoprene}$, see the text for details).

Figure 5 The result of back trajectory analysis. Opened circles are sampling sites of the atmospheric isoprene, solid lines are calculated trajectory of the air parcel before 5 days of the sampling. The trajectory data was obtained from HYSPLIT model provided by NOAA Air Resources Laboratory.

Fig. 1 (Matsunaga *et al.*)

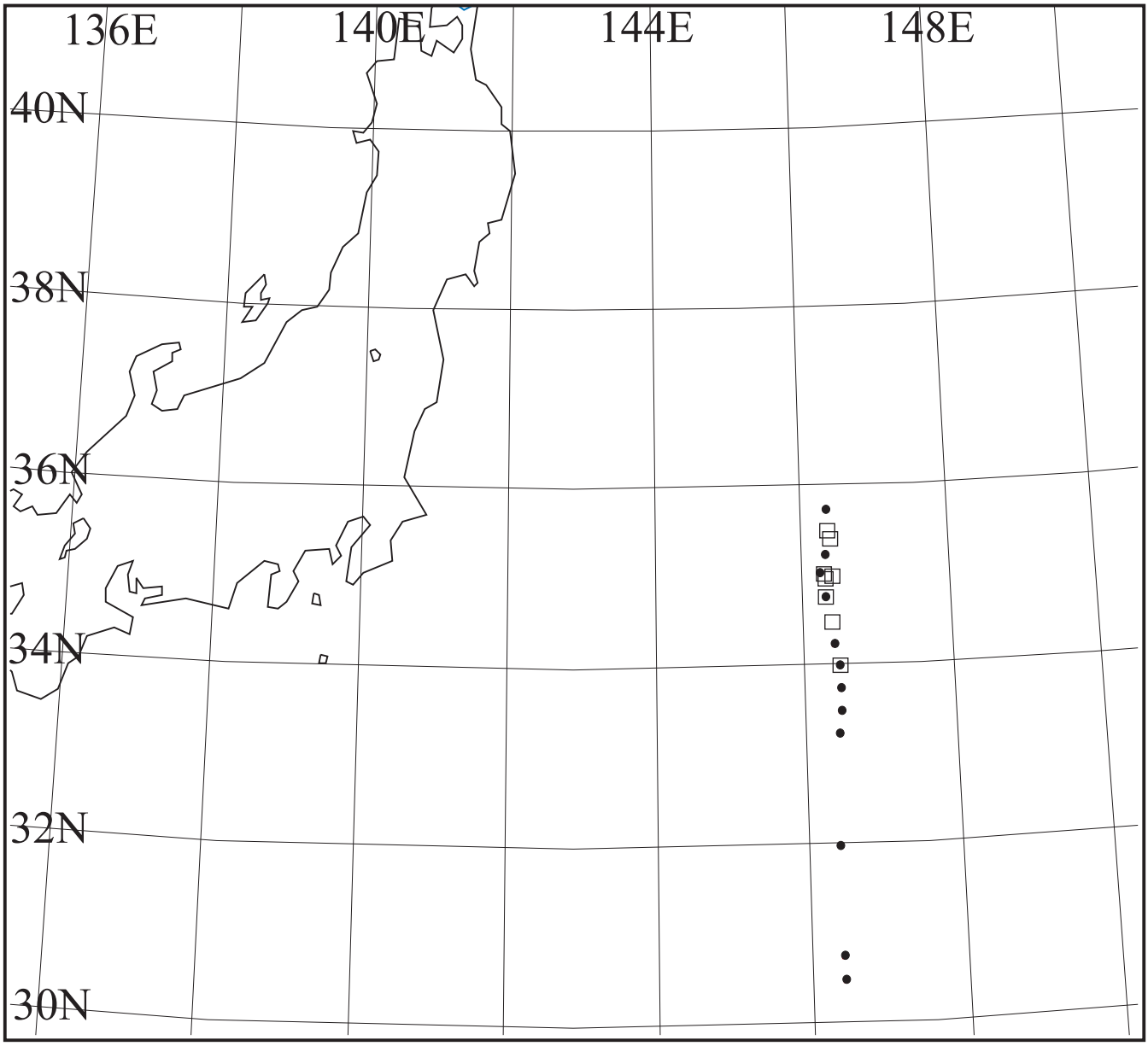

Figure 2 (Matsunaga *et al.*)

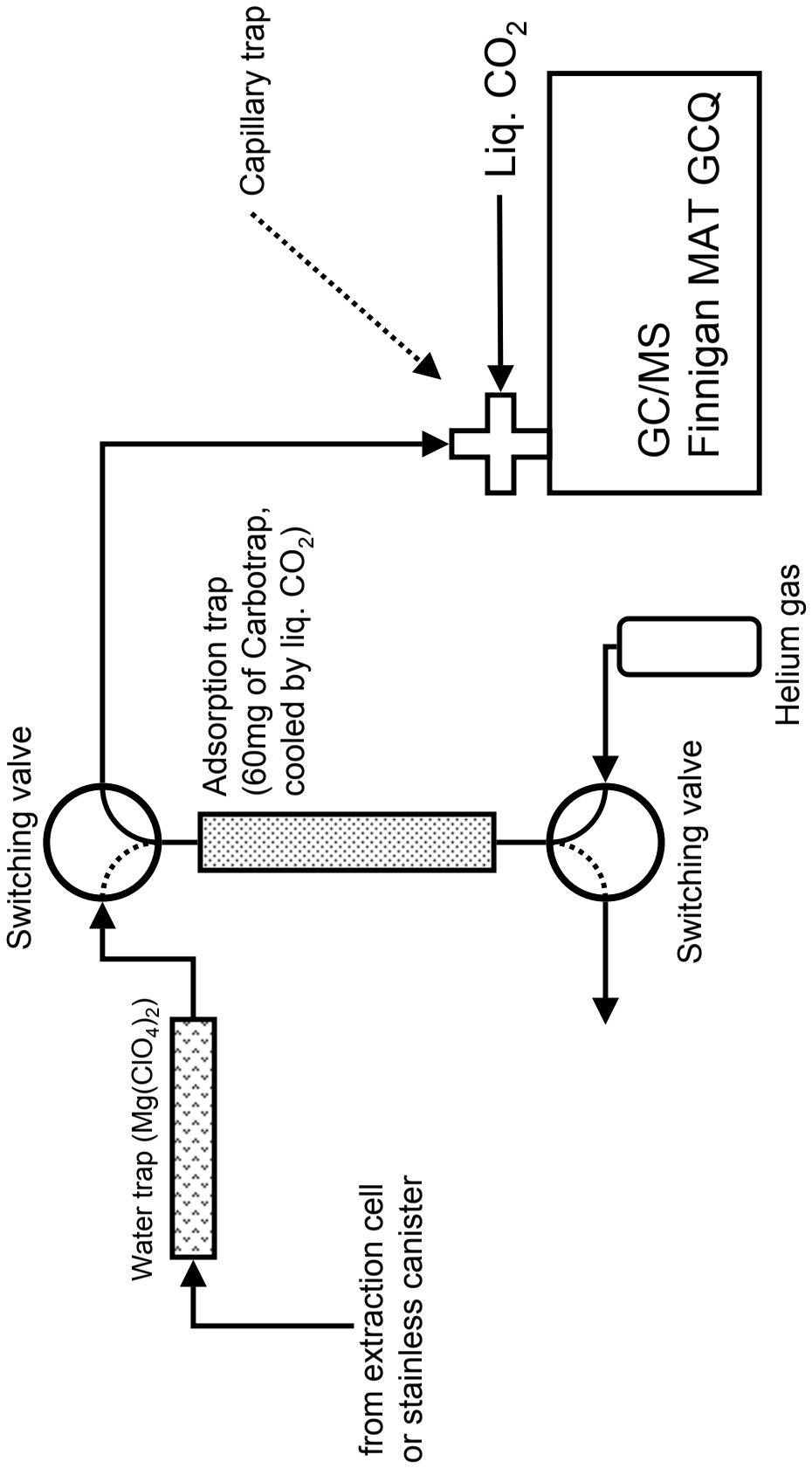

Figure 3 (Matsunaga *et al.*)

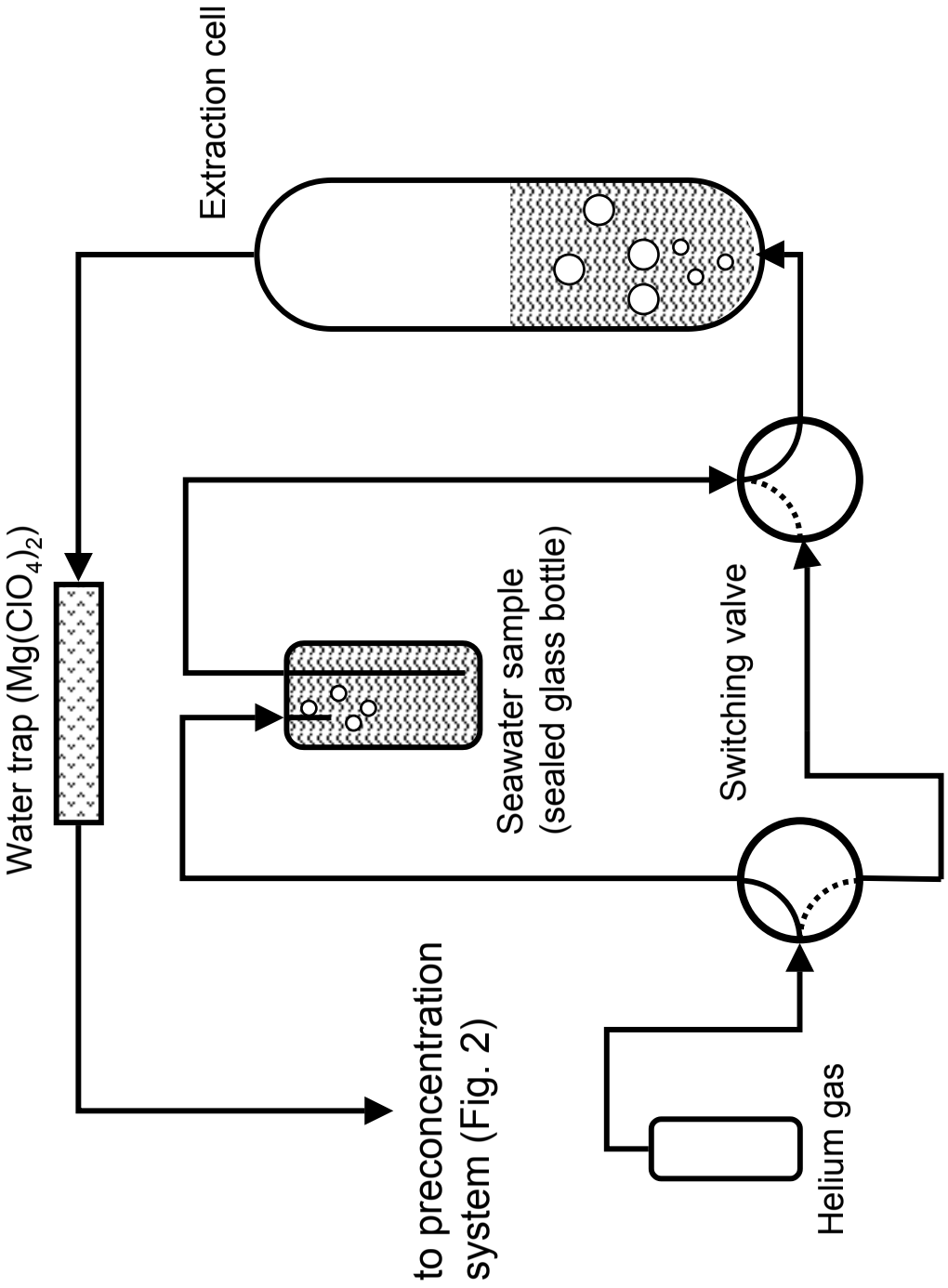

Figure 4 (Matsunaga et al.)

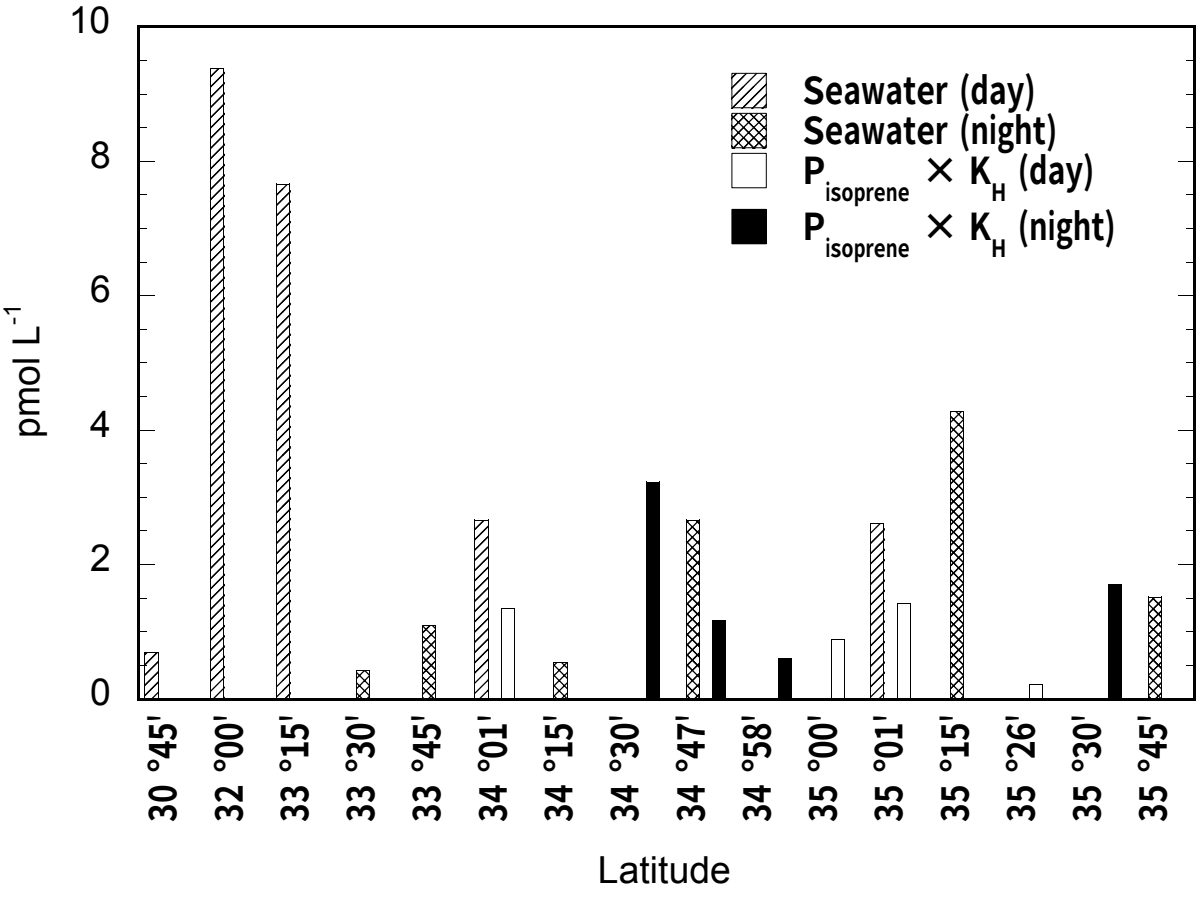

Figure 5 (Matsunaga et al.)

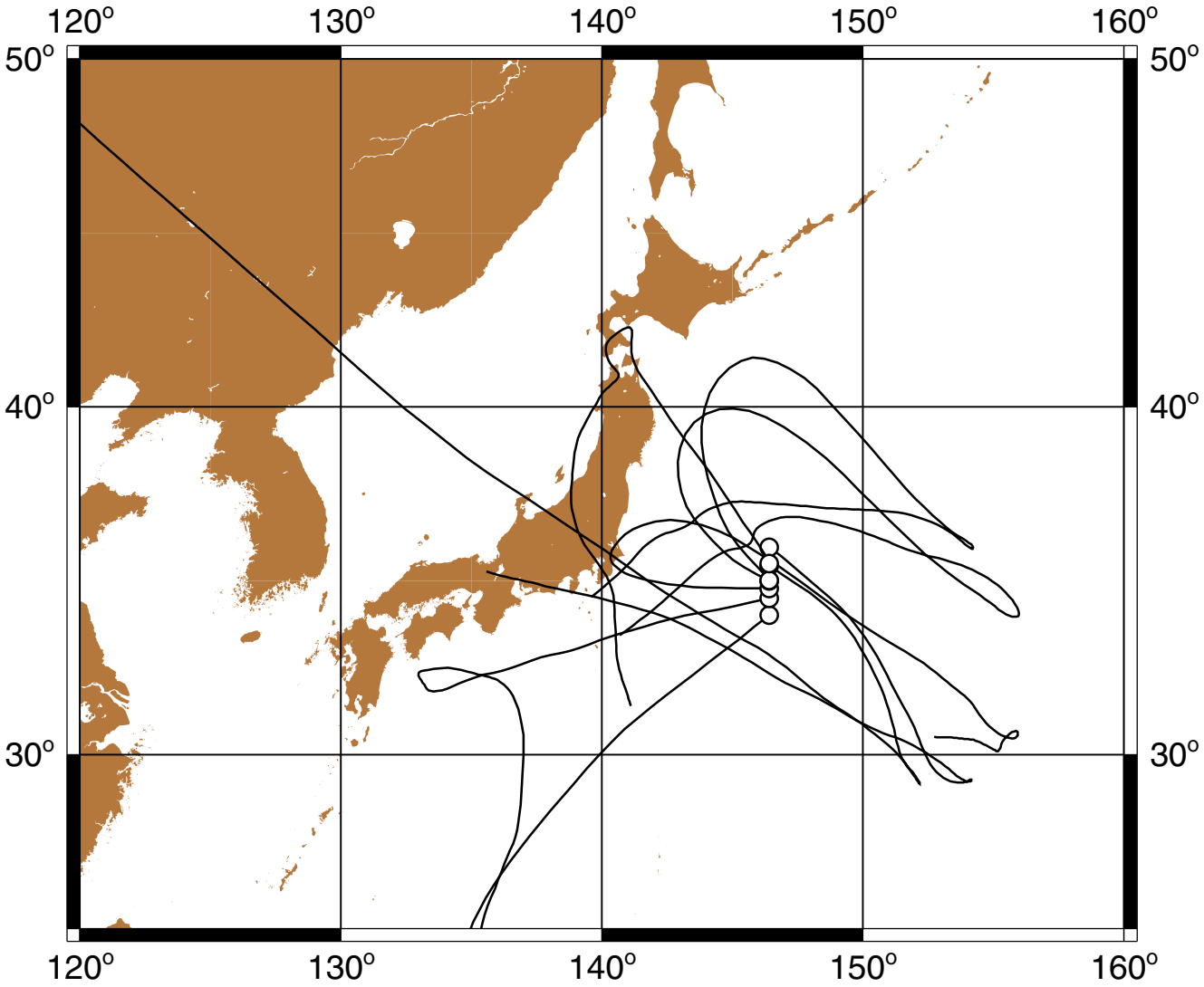

Table 1 Concentrations of isoprene in the marine air and surface seawater in the western North Pacific along the 146°25'E transect.

Date	Time	Latitude	Air (pptv)	$P_{isoprene} \times K_H$ (pmol L^{-1})	Seawater (pmol L^{-1})
18-May	12:45	30°45'N			BDL
19-May	12:18	32°00'N			9.4
20-May	13:00	33°15'N			7.7
20-May	20:00	33°30'N			BDL
21-May	22:30	33°45'N			BDL
23-May	13:30	35°26'N	7.2	0.2	
23-May	18:30	34°58'N	20.8	0.6	
24-May	15:40	34°01'N	46.4	1.3	2.7*
24-May	20:30	34°15'N			BDL
25-May	00:48	34°30'N	111	3.2	
25-May	06:05	34°47'N	40.3	1.2	2.7*
25-May	10:47	35°00'N	30.5	0.9	
25-May	13:52	35°01'N	49.1	1.4	
25-May	14:50	35°01'N			2.6
25-May	20:30	35°15'N			4.3
26-May	01:05	35°30'N	58.8	1.7	
26-May	06:00	35°45'N			1.5
Maximum			**111**	**3.2**	**9.4**
Minimum			**7.2**	**0.2**	**BDL**
Average			**45.6**	**1.3**	**3.1**
Median			**43.4**	**1.3**	**2.7**
Average (daytime)			**30.8**	**0.9**	**5.6**
Median (daytime)			**30.5**	**0.9**	**5.2**
Average (night time)			**70.1**	**2.0**	**2.7**
Median (nighttime)			**58.8**	**1.7**	**2.7**

BDL: below detection limit. Detection limit for air sample and seawater sample were 5 pptv and 1.2 pmol L^{-1}, respectively. Henry's law constant K_H for isoprene was adapted from Karl *et al.*.

*: The data were used for the calculation of sea-to-air flux of isoprene (see Table 2).

Table 2 Estimated emission rate of isoprene from the ocean.

Date	Time	Location	Wind speed (m s^{-1})	**Flux (nmol m^{-2} day^{-1})**	Reference
19-May	12:18	western North Pacific	3.6	**7.7**[*]	this study
20-May	13:00	western North Pacific	7.1	**24.6**[*]	this study
24-May	15:40	western North Pacific	10.4	**16.4 (18.6**[*]**)**	this study
25-May	6:05	western North Pacific	13.3	**24.6 (30.4**[*]**)**	this study
25-May	14:50	western North Pacific	7.2	**8.6**[*]	this study
25-May	20:30	western North Pacific	3.4	**3.2**[*]	this study
26-May	06:00	western North Pacific	7.6	**5.6**[*]	this study
10-Sep	15:45	Florida Straits	3.33	**38.6**	Milne *et al.*
10-Sep	18:30	Florida Straits	1.28	**12.6**	Milne *et al.*
10-Sep	22:00	Florida Straits	2.01	**9.5**	Milne *et al.*
11-Sep	8:30	Florida Straits	5.00	**39.1**	Milne *et al.*
12-Sep	16:00	Florida Straits	4.49	**101.2**	Milne *et al.*
13-Sep	5:00	Florida Straits	7.99	**65.5**	Milne *et al.*
13-Sep	8:00	Florida Straits	7.11	**71.8**	Milne *et al.*
		North Sea		**24.4**[**]	Broadgate *et al.*

[*]: Calculated upper limit of the isoprene flux. [**]: Annual mean value.