Identification of coastal emissions of methyl chloride and methyl bromide based on high-frequency measurements on Hateruma Island

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Hourly measurements of atmospheric methyl chloride (CH_3Cl) and methyl bromide (CH_3Br), as well as some other halocarbons, were performed by using automated preconcentration gas chromatography/mass spectrometry at Hateruma Island, the southernmost inhabited island in the Japanese archipelago. Our data indicate that CH_3Cl and CH_3Br concentrations were occasionally increased without corresponding increases of anthropogenic halocarbons, such as HCFC-22. Those nonpollution high-CH_3Cl and high-CH_3Br events were observed mostly when the wind was blowing at rather low speed along the shore (a partially vegetated raised coral beach). Presuming that these methyl halides were accumulated while the air mass traveled over the beach, the emission strengths of CH_3Cl and CH_3Br from the beach were roughly estimated to be 900 ± 350 μg m^{-2}h^{-1} and 21 ± 10 μg m^{-2}h^{-1}, respectively. Coastal beach is likely a new important source for CH_3Cl and CH_3Br on a global scale.

INTRODUCTION

Methyl chloride (CH_3Cl) is the most abundant halocarbon in the atmosphere, with a global average mixing ratio of about 550 ppt. Most atmospheric CH_3Cl is believed to be of natural origin. Because this compound contributes to stratospheric ozone depletion, its atmospheric burden, sources, and sinks have been of a great concern (World Meteorological Organization (WMO), 1999, 2003, 2007). Because CH_3Cl has an atmospheric lifetime of 1.3 years—which is long enough for hemispheric mixing, yet short enough to reflect year-to-year emission changes—the variability of CH_3Cl concentration might serve as an indicator of changes in the source ecosystems, possibly caused by climate change. Thus, it is important to gain a full understanding of the natural sources and the emission mechanisms of CH_3Cl.

The major known sources of CH_3Cl are tropical and subtropical plants (Yokouchi *et al.*, 2000, 2002a; Saito and Yokouchi, 2006), oceans (Khalil *et al.*, 1999; Moore, 2000), salt marshes (Rhew *et al.*, 2000, 2002), wood-rot fungi (Watling and Harper, 1998), rice fields (Redeker *et al.*, 2000; Redeker and Cicerone, 2004), and biomass burning (Lobert *et al.*, 1999; Andreae and Merlet, 2001). Recent observations and model studies have provided more evidence about biogenic sources of CH_3Cl in the

tropics and subtropics (WMO, 2007). Three-dimensional models have suggested that two-thirds of the atmospheric CH_3Cl is emitted from terrestrial sources at low latitudes (Lee-Taylor *et al.*, 2001; Yoshida *et al.*, 2004), and to date dozens of plant species have been identified as CH_3Cl emitters (Yokouchi *et al.*, 2002a, 2007).

Methyl bromide (CH_3Br) also appears to play an important role in stratospheric ozone depletion (WMO, 1999, 2003, 2007) and has both natural and anthropogenic sources, with the main anthropogenic source being pesticides. The use of such pesticides has been greatly reduced in the last decade because of the Montreal Protocol and subsequent amendments (Yokouchi *et al.*, 2002b; Montzka *et al.*, 2003), making natural CH_3Br sources relatively more important. The natural sources of CH_3Br are less well understood than those of CH_3Cl, although plants, salt marshes, and the ocean have been suggested as sources (WMO, 1999, 2003, 2007).

On the basis of high-frequency monitoring data from a remote subtropical island, we present evidence that CH_3Cl as well as CH_3Br are emitted from coastal beaches.

OBSERVATIONS

Since March 2004, measurements of atmospheric CH_3Cl, CH_3Br, and other halocarbons have been conducted at a ground station on Hateruma Island (lat. 24.1°N, long. 123.8°E) as a part of a halocarbon monitoring project. Hateruma Island, which was formed by a raised coral reef, is the southernmost inhabited island in

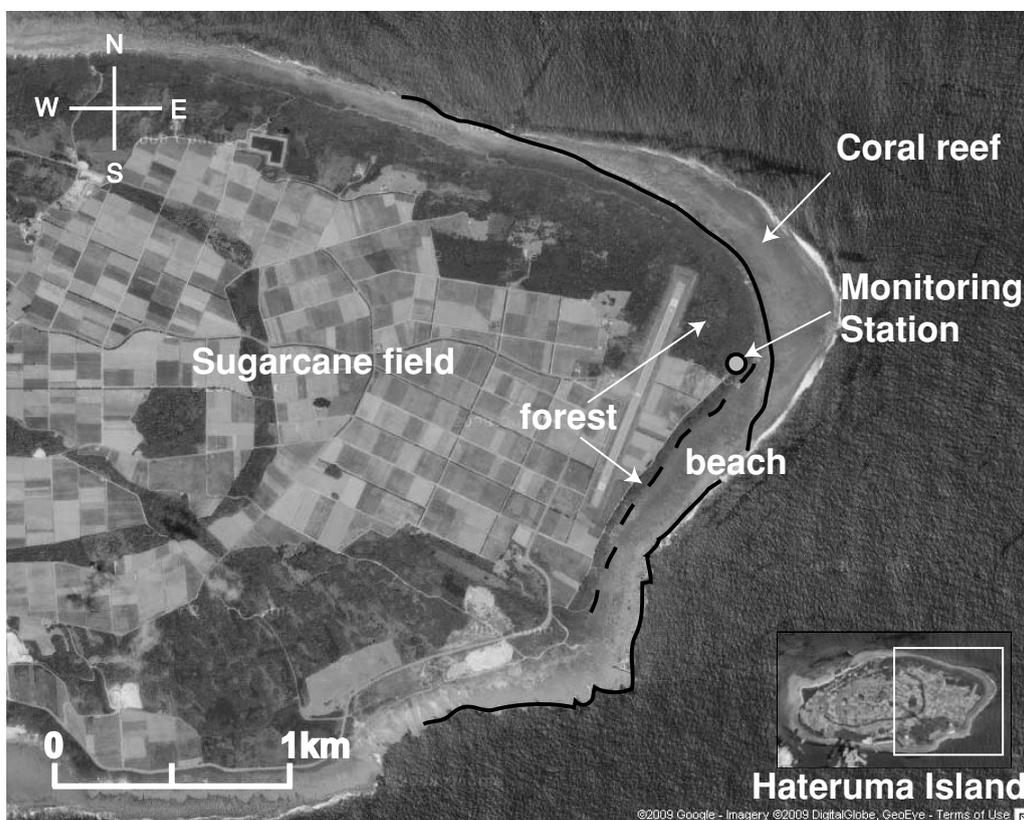*Corresponding author (e-mail: yokouchi@nies.go.jp)

Fig. 1. Overview of Hateruma Island (lat. 24.1°N, long. 123.8°E) and the surrounding area of the monitoring station (resource: Google Map). Coastline and boundary line between forest and beach are defined with solid line and broken line, respectively.

the Japanese archipelago. The island measures about 6 km east-west and 4 km north-south, with a total area of about 12.5 km^2. The island is mostly covered with sugarcane fields with scattered forests, and is surrounded by fringing coral reefs facing the open ocean. Our previous work indicated that sugarcane plants do not emit CH$_3$Cl (unpublished). The station is located at the eastern end of the island, about 100 m from the shore and 10 m above sea level (Fig. 1). The station has a forest (1000 × 500 m) to the northwest and sugarcane fields to the west and southwest. A raised coral beach with a width of 150–250 m extends south~southwest from the station. Between the beach and sugarcane field, there is a thin (~50 m) windbreak forest. The raised coral beach is covered by seashore grasses.

At the monitoring station, outside air drawn from the 40-m tower (sampling inlet: 36.5-m-high) was analyzed every hour with an automated halocarbon measurement system based on cryogenic preconcentration and capillary gas chromatography/mass spectrometry (Enomoto *et al.*, 2005; Yokouchi *et al.*, 2006). After every five air analyses, a gravimetrically prepared standard gas (Taiyo Nissan Co. Ltd.) was analyzed for quantification using the same procedure as was used for the samples. In place

of this regular monitoring, alternate measurements of air drawn from the 40-m tower and drawn from another 10-m tower were conducted during May~June of 2008.

RESULTS AND DISCUSSION

The dataset of CH$_3$Cl mixing ratios from May 2004 to April 2005 is plotted in Fig. 2. The baseline mixing ratio of CH$_3$Cl (dotted line) shows a clear seasonal variation, being lowest in autumn and highest in spring. This seasonal pattern of atmospheric CH$_3$Cl was reported previously for the Northern Hemisphere (Khalil and Rasmussen, 1999; Yokouchi *et al.*, 2000). The seasonal change can be explained by reaction of CH$_3$Cl with OH radicals, which are more abundant during summer.

In addition to the baseline seasonal change, occasional short-term enhancements of CH$_3$Cl mixing ratios lasting hours to days were observed. Such high-concentration events were also observed for other anthropogenic halocarbons that were measured simultaneously at the station. Our previous study indicated that short-term enhancements of hydrofluorochlorocarbons (HFCs) and hydrochlorofluorocarbons (HCFCs) at Hateruma Island were closely related to air transport from China or other
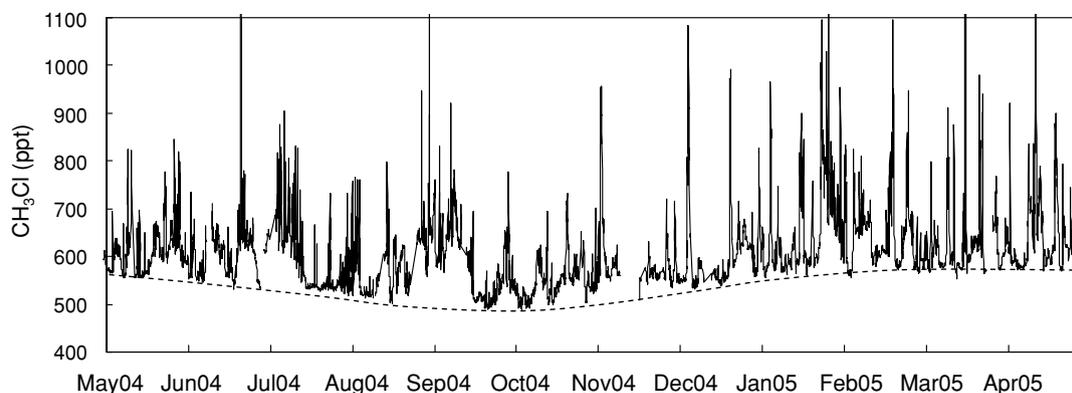
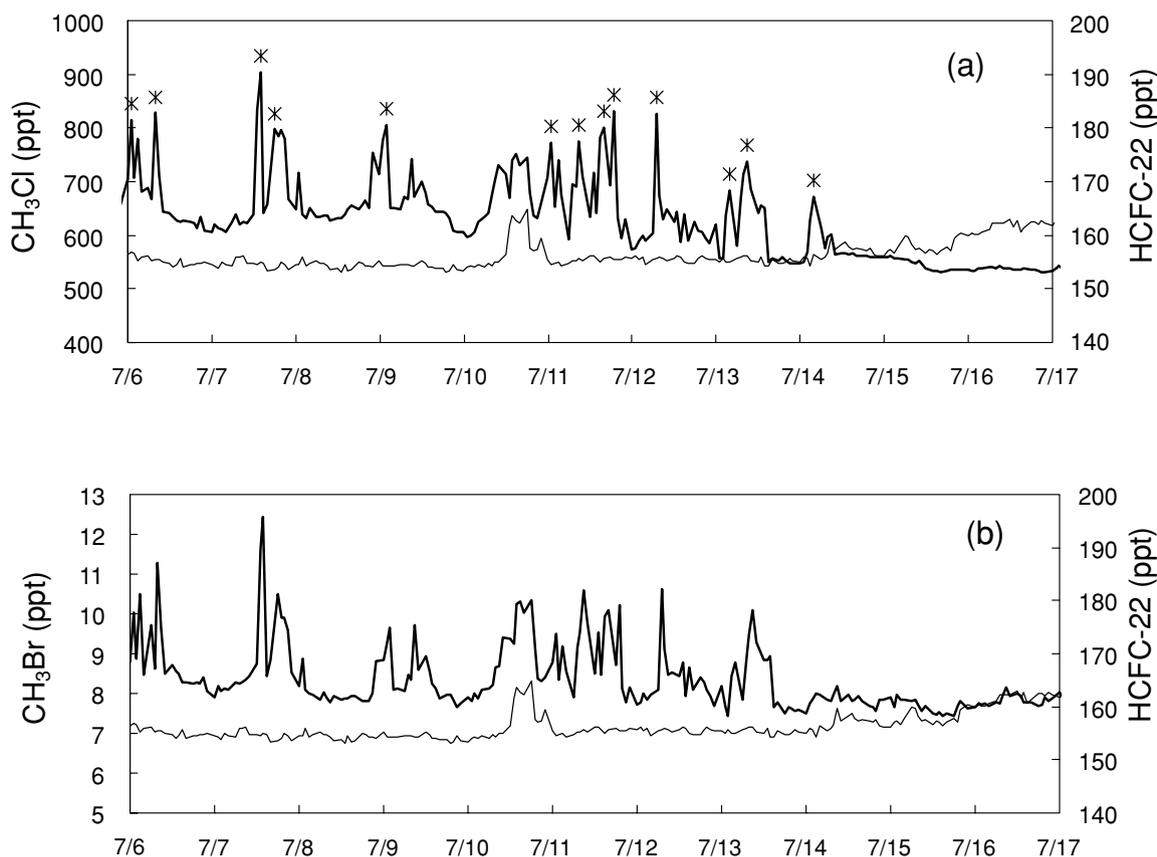Fig. 2. Atmospheric CH₃Cl mixing ratios observed at Hateruma Island from May 2004 to April 2005.

Fig. 3. (a) CH₃Cl (thick line) and HCFC-22 (thin line) mixing ratios during the nonpollution period in the summer (6–17 July 2004). The occasional enhancement of CH₃Cl without a simultaneous increase in HCFC-22 was specified as a nonpollution high-CH₃Cl event, each of which is marked with an asterisk. (b) CH₃Br (thick line) and HCFC-22 (thin line) mixing ratios during the same period as (a).

surrounding countries (Yokouchi *et al*., 2006). Considering that CH₃Cl has anthropogenic sources such as fuel combustion, these short-term enhancements might also be attributed to the transport of pollution to the island.

Therefore, we compared the precise variation of CH₃Cl with that of HCFC-22, the mixing ratio of which is closely correlated with many other anthropogenic compounds such as C₂Cl₄, C₂HCl₃, and HFC-134a. During the win-

ter, short-term enhancements of CH_3Cl and HCFC-22 were generally observed at the same time, but during the other seasons, particularly summer, CH_3Cl had some peaks that did not correspond to peaks of HCFC-22 (e.g., 6–17 July 2004, Fig. 3a). We considered those CH_3Cl peaks to reflect natural emission sources and defined them as nonpollution high-CH_3Cl events. Likewise, we com-

pared CH_3Br and HCFC-22 during the same period (Fig. 3b) and found that short-term enhancements of CH_3Br were closely related with the nonpollution high-CH_3Cl events, suggesting common sources for these CH_3Cl and CH_3Br emissions.

To identify the source of these nonpollution CH_3Cl peaks, we investigated the wind conditions at the times those peaks were recorded. Wind speed and direction data (May 2004 to April 2005) were obtained from meteorological observation instruments at the tower top, and the heads of all the wind vectors were plotted in a direction coordinate (Fig. 4). The data corresponding to the nonpollution high-CH_3Cl events (with a peak > 50 ppt) are designated with open circles in Fig. 4. Despite the fact that northeast or southeast winds from the ocean prevail at the station site, most of the nonpollution high-CH_3Cl events were observed when the wind was blowing from the south or south-southwest at rather low speed (mean: 4.6 m sec^{-1}). Histograms of wind speed frequency in Fig. 5 indicate that the nonpollution high-CH_3Cl events are shifted toward low wind speed when compared to all the cases with south~southwest wind direction or with every wind direction, suggesting local sources of CH_3Cl. The geographical features of Hateruma Island indicate that during these events the air masses came from along the beach. Contribution of CH_3Cl emission from the thin windbreak forest adjacent to the west border of the beach was considered to be not much, since the forest is extending more west of the source distribution suggested from Fig. 4. Biomass burning, another possible source of CH_3Cl and CH_3Br (WMO, 2003 2007), is also not likely to be the cause of the "non-pollution high-CH_3Cl events", since biomass burning is not common in this area. Thus, our data indicate that a beach as short as 1500 m can be a strong source of CH_3Cl and CH_3Br emissions.

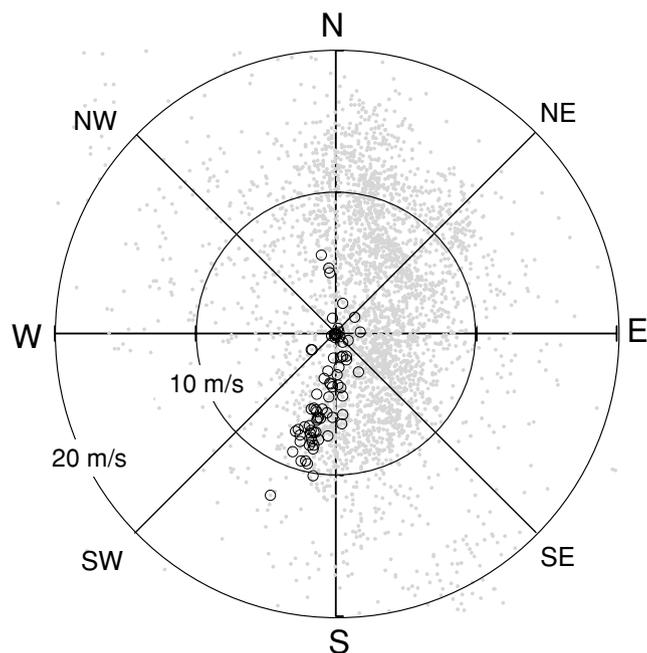Fig. 4. Wind speed and direction observed throughout the year (gray dots) and during the nonpollution high-CH_3Cl events (open circles). An arrow drawn from each point to the origin would indicate the wind vector.
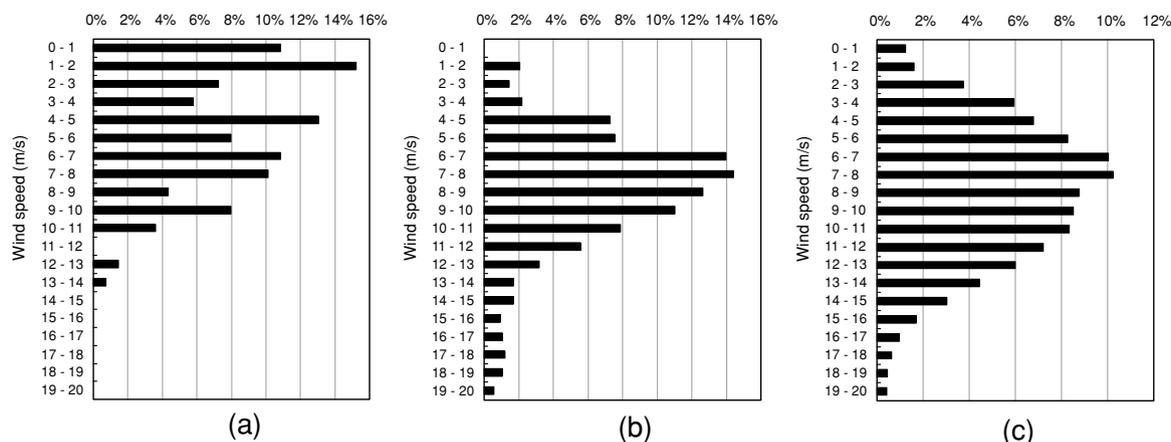

Fig. 5. Histograms of wind speed frequency for the nonpollution high-CH_3Cl events (a), for all the cases with south ~ southwest wind direction throughout the one year (b), and for all the cases with every wind direction throughout the one year (c).

In the following discussion, we try to estimate the emission strengths of CH_3Cl and CH_3Br from the beach, based on their atmospheric mixing ratios measured at two different heights (36.5 m and 10 m) during May–June, 2008. The observed temporal variations of the mixing ratios of the CH_3Cl and CH_3Br at each height are plotted in Figs. 6a and 6b, respectively, together with those of HCFC-22 as anthropogenic tracer. Figure 6c presents the ten-minute average data for the wind speed and direction in the same period. Both of CH_3Cl and CH_3Br show higher mixing ratio at 10 m than at 36.5 m in most parts of the observation, while the difference for HCFC-22 is negligible. This would be another indication of the local/natural sources of CH_3Cl and CH_3Br. Short-term enhancements of CH_3Cl (and CH_3Br) mixing ratios were more often observed for the 10 m-samples. Among them, events A~E accompanied CH_3Cl (and CH_3Br) enhancement at

36.5 m high, and also had no corresponding peaks of HCFC-22. The increases of CH_3Cl and CH_3Br from their baseline mixing ratios in these events should be reflecting their accumulation while the airmass was traveling over the beach and carrying the fresh emissions from there. If we could assume linear vertical profile of their mixing ratios as shown in Fig. 7, the increases of CH_3Cl and CH_3Br from their baseline mixing ratio (ΔC (ppt)) at both of the heights (h1 (m) and h2 (m)) could be related to their accumulated amounts (ΔA ($\mu g\ m^{-2}$)) with the following equation.

$$\Delta A = (h1 \times \Delta C_{h2} - h2 \times \Delta C_{h1})^2/(h1 - h2)$$
$$/(\Delta C_{h2} - \Delta C_{h1})/2 \times M/22.4/1000,$$

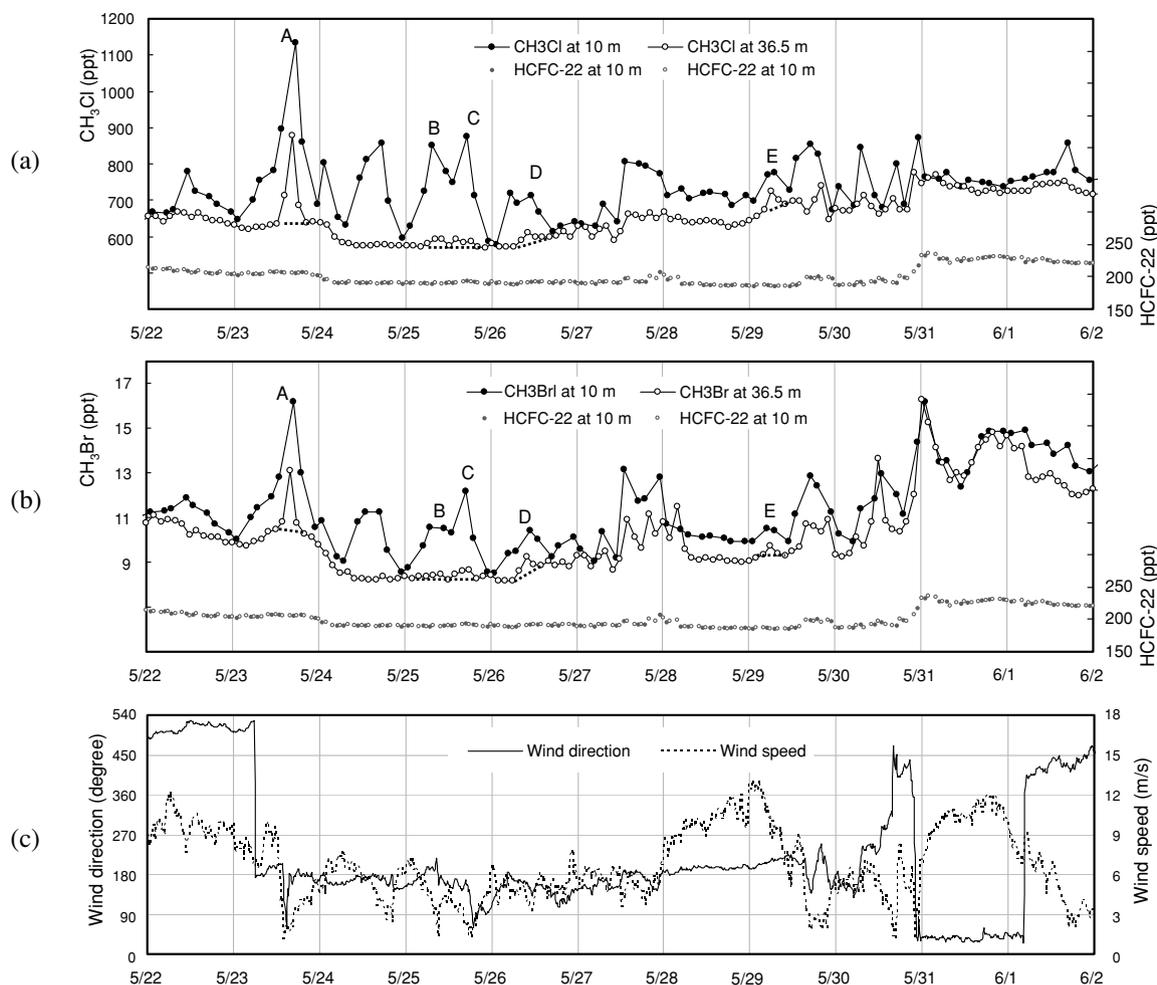where M = molecular weight (50.5 for CH_3Cl, 94.9 for CH_3Br), h1 = 36.5 (m), h2 = 10 (m).

Fig. 6. (a) Mixing ratios of CH_3Cl and HCFC-22 measured at 36.5 m and 10 m high. (b) Mixing ratios of CH_3Br and HCFC-22 measured at 36.5 m and 10 m high. (c) Ten-minute average wind direction and wind speed (at 40 m high). Dashed lines are drawn to approximate background levels during non-pollution high events.
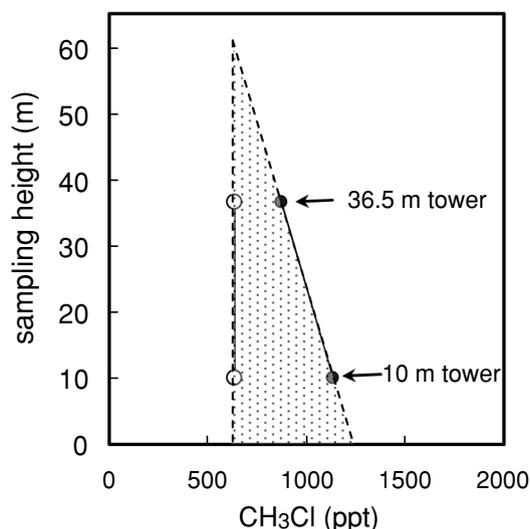
Fig. 7. A simplified model for the calculation of the increased amount at high-CH_3Cl events. Solid circles: CH_3Cl mixing ratios measured at 10 m and 36.5 m at the event, open circles: CH_3Cl baseline mixing ratio for the event (from the broken line in Fig. 6(a)), The shaded area corresponds to the accumulated amount of CH_3Cl in the airmass.

The accumulated amount (ΔA (μg m^{-2})), divided by the travel time (s) over the beach, would give the emission rates (μg m^{-2}s^{-1}) from the beach. The travel time could be approximated from the distance (m) between the station and the coastline in the windward direction and the wind speed (m s^{-1}). This simplified model was applied for each of the five events A~E in Fig. 6. Since the measurements at the two heights have time-lag of one hour, and there was a slight difference in the wind data, the calculations were done for either case, and then averaged. The estimated emission rates from the beach (converted to hourly rates)—were 900 ± 350 μg m^{-2}h^{-1} (570~1390 μg m^{-2}s^{-1}) for CH_3Cl, and 21 ± 10 μg m^{-2}h^{-1} (9~29 μg m^{-2}h^{-1}) for CH_3Br. They could be converted to daily emissions, 22 ± 8 mg m^{-2}d^{-1} for CH_3Cl and 0.6 ± 0.2 mg m^{-2}d^{-1} for CH_3Br. The emission estimates, however, should have greater uncertainties mostly due to the assumed simplification of the vertical profiles. Another error cause would be slightly different wind speed by altitude (10~40 m). Despite these uncertainties, CH_3Cl emission rates per unit area from the beach does seem to be higher or similar to those from some other known terrestrial ecosystem sources: (sub)tropical forests; 12~33 μg m^{-2}h^{-1} for CH_3Cl (Yokouchi *et al.*, 2007; Saito *et al.*, 2008), rice field; 3.3 mg m^{-2} y^{-1} for CH_3Cl, 2.3 mg m^{-2} y^{-1} for CH_3Br (Redeker and Cicerone, 2004), salt marsh; 150–550 μmol m^{-2} d^{-1} or 7.6~28 mg m^{-2} d^{-1} for CH_3Cl, 5~40 μmol m^{-2} d^{-1} or 0.48–3.8 mg m^{-2} d^{-1} for CH_3Br (Bill *et al.*, 2002).

As for the specific sources of CH_3Cl and CH_3Br on the beach, we have little information at this stage. We tested CH_3Cl emission from three major species of the grasses growing on the beach using a vial method (Yokouchi *et al.*, 2007) and found that one of them, *Vitex rotundifolia* L., was a high emitter of CH_3Cl (emission rate: ~2 μg g (dry weight)$^{-1}$h^{-1}). However, the rather small amount of plant biomass suggests that some biome other than seashore plants or non-biogenic sources might be more important for the emission of CH_3Cl and CH_3Br from the beach. A known abiotic formation of CH_3Cl and CH_3Br is the reaction of Fe(III) and organic matter in the presence of halide ions (Keppler *et al.*, 2000). There also might be some contribution from rock pools, since parts of the coral beach are inundated by daily high-tides.

Our high-frequency observations indicated that CH_3Cl and CH_3Br are likely to be strongly emitted from subtropical coastal beaches. The fact that the island is covered by sugarcane, which does not emit CH_3Cl and CH_3Br, allowed the beach emissions to be discerned. Because some remote monitoring sites are located on islands or capes, measurements of methyl halides at these sites may be affected by local coastal emissions. Considering that beaches are widely distributed in the world, "coastal beach" is likely a new important source for CH_3Cl and CH_3Br on a global scale. Further work is required to identify the mechanism of methyl halide production on coastal beaches and to assess the contribution of the beach sources to the global budget of CH_3Cl and CH_3Br.

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