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Distributions and fluxes of methyl chloride and methyl bromide in the East China Sea and the Southern Yellow Sea in autumn

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ABSTRACT

We determined the distributions and fluxes of methyl chloride and methyl bromide in the East China Sea (ECS) and the Southern Yellow Sea (SYS) in November 2007. Methyl chloride and methyl bromide concentrations in the surface waters ranged from 47.1 to 163 pmol L^{-1} and from 0.70 to 9.82 pmol L^{-1}, with average values of 87.6 and 2.97 pmol L^{-1}, respectively. The distributions of the two methyl halides were clearly influenced by the Yangtze (Changjiang) River effluent and Kuroshio water, with high concentrations appearing in the coastal zone and low values occurring in the open waters. A positive linear correlation was observed between methyl chloride and methyl bromide concentration anomalies in the surface waters, suggesting that they may share some origins in this coastal area. However, no correlation was found between the two methyl halide concentration anomalies and chlorophyll *a* in the surface waters. The vertical profiles of the two methyl halides were characterized by the maxima in the upper mixed layer. Both gases were generally supersaturated in the surface seawater, with mean sea-to-air fluxes of methyl chloride and methyl bromide of 391 and 20.0 nmol m^{-2} d^{-1}, respectively.

1. Introduction

Methyl chloride (CH_3Cl) and methyl bromide (CH_3Br) are major contributors of ozone-depleting chlorine and bromine, respectively, to the atmosphere (Schauffler et al., 1998; Penkett et al., 1980). Both gases originate largely from natural sources, while CH_3Br, as a commonly used fumigant, is also of anthropogenic origin. Due to its environmental effects, CH_3Br has been restricted by international agreement (UNEP, 1992). Over the last decade, a number of attempts have been made to identify and quantify the sources of CH_3Cl and CH_3Br, but the atmospheric budgets for the two gases remain largely unbalanced, with known sinks outweighing the sources. The reason for this discrepancy could be overestimated sinks and/or missing or underestimated sources (King et al., 2000; Tokarczyk and Moore, 2006).

The ocean plays important and complex roles in the global biogeochemical cycles of these methyl halides. Previous studies have shown that the ocean is both the largest known source and the second largest known sink of atmospheric CH_3Br (Butler and Rodriguez, 1996; Yvon-Lewis and Butler, 1997), as well as a source of about 15% of the natural flux of CH_3Cl (Moore and Wang, 2006). In early studies, some researchers have shown widespread undersaturations of CH_3Br in the open ocean (Lobert et al., 1995, 1996, 1997; Groszko and Moore, 1998; King et al., 2000, 2002; Yvon-Lewis et al., 2004; Tokarczyk and Moore, 2006), while others have identified supersaturated regions of CH_3Br, especially in temperate waters (Lobert et al., 1996; Groszko and Moore, 1998; Baker et al., 1999). CH_3Cl, on the other hand, is supersaturated over middle and low latitudes, but undersaturated at high latitudes (Moore et al., 1996; Yvon-lewis et al., 2004). These observations suggest the existence of a major spatial variation in the concentrations of methyl halides. There is, therefore, a particular need to better understand the source areas such as coastal waters, where supersaturations and presumably productivity are particularly high.

The East China Sea (ECS) and the Yellow Sea (YS) together form an important marginal area of the northwest Pacific Ocean, i.e. one of the largest continental shelves in the world, with a total surface area of 1×10^6 km^2, of which approximately 75% has a water depth of less than 50–100 m. Their boundary is defined by a line connecting the Yangtze River (Changjiang) mouth and Cheju Island. The hydrographic character of this region is heavily influenced by a circulation system that includes the Kuroshio, the Tsushima Warm Current, the Yellow Sea Warm Current on the eastern boundary of the shelf, the Yellow Sea and the East China Sea Coastal Currents on the western side and the Taiwan Warm Current into the middle shelf (Yuan et al., 2008; Su, 1998; Lee et al., 2000). The Kuroshio, with low concentrations of nutrients and chlorophyll and high temperature and salinity, enters the East China Sea east of Taiwan, flows northeastward along the edge of the continental shelf approximately along the 200 m isobath, and leaves the East China Sea through the Tokara Strait southwest of Kyushu, which transports open ocean materials across the shelf into the East China Sea (Hsueh et al., 1992). The Yangtze

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River, one of the largest rivers in the world, has huge amounts of freshwater discharge ($9.24\times10^{11}\,\mathrm{m}^3\,\mathrm{yr}^{-1}$), sediment load ($4.86\times10^{8}\,\mathrm{t\,yr}^{-1}$), and abundant nutrients, and merges into the ECS and the YS from the west (Tian et al., 1993; Zhang, 1996).

Until now, no data have been available on CH_3Cl and CH_3Br in this area. This study represents the first attempt to carry out in situ measurements of CH_3Cl and CH_3Br in the ECS and YS. The primary purpose of this investigation is to study the spatial distribution of CH_3Cl and CH_3Br in the ECS and SYS and to estimate the sea-to-air fluxes of the two compounds in this area.

2. Materials and methods

2.1. Sample collection and analysis

The cruise was conducted aboard the R/V "Dong Fang Hong No. 2" in the ECS and SYS during 1–25 November, 2007. The locations of sampling stations are shown in Fig. 1. The cruise included 56 grid stations and two 25-h anchor stations. The horizontal distributions of CH_3Cl and CH_3Br were measured in the surface waters of all grid stations. The environmental and hydrographic conditions of the sampling stations, such as the location, surface seawater temperature and salinity, are described in Table 1. The vertical distributions of CH_3Cl and CH_3Br were studied at 17 stations covering different hydrographic regions, such as transect F05 off the Yangtze River Estuary and crossing the ESC Shelf and transect F03 crossing the SYS Shelf.

Water samples were collected using 8-L Niskin bottles mounted on a Seabird CTD Rosette (General Oceanics Co.). Samples were drawn into 100 mL glass syringes without any contact with air and stored in a bucket of seawater in the dark until analysis, usually within 6 h. Analysis for methyl halides was conducted by a purge and trap system coupled to a gas chromatograph with an electron capture detector (ECD), similar to the method of Moore et al. (1996). Volatiles were stripped from 100 mL seawater sample by bubbling with ultra-pure N_2 passing through a glass frit in the purge vessel at a flow rate of 50 mL min^{-11} for 12 min. The sample was maintained at 40 °C during the purge. The extracted gases were allowed to pass through two 4 cm-long glass drying tubes containing $MgClO_4$ and Ascarite to remove water vapor and carbon dioxide, respectively. The drying stream then passed through a 30 cm-long trap of stainless steel tubing (ID 0.8 mm) immersed in liquid nitrogen. The trapped gases were desorbed by a boiling water bath for 2 min and then analyzed with a GC-ECD (Agilent 6890N) after separation using a Rtx624 capillary column (60 m long; ID, 0.32 mm; film thickness, 1.8 µm) by the carrier gas (N_2) at a flow rate of 2.1 mL min^{-1}.

Calibration was conducted by injecting a certain volume of standard gases of 40 ppbv CH_3Cl/N_2 and 1 ppbv CH_3Br/N_2 (DaLian Special Gases Co. LTD, China), into the stripper filled with blank seawater without CH_3Cl and CH_3Br, and subjecting them to the same manipulations as the sample. The resulting calibration curves were linear over the concentration range of interest. A blank was established each day by running the system without a water sample or by repeatedly purging a water sample so that it was free of dissolved CH_3Cl and CH_3Br. The detection limits for CH_3Cl and CH_3Br analyses in this study were 1.8 and 0.2 pmol L^{-1}, respectively. The precisions of the analytical method are better than 2% and 8% in routine sample analyses for CH_3Cl and CH_3Br, respectively.

Chlorophyll *a* was measured fluorometrically with a Turner Design Fluorometer after filtration of 200 mL of seawater through a Whatman

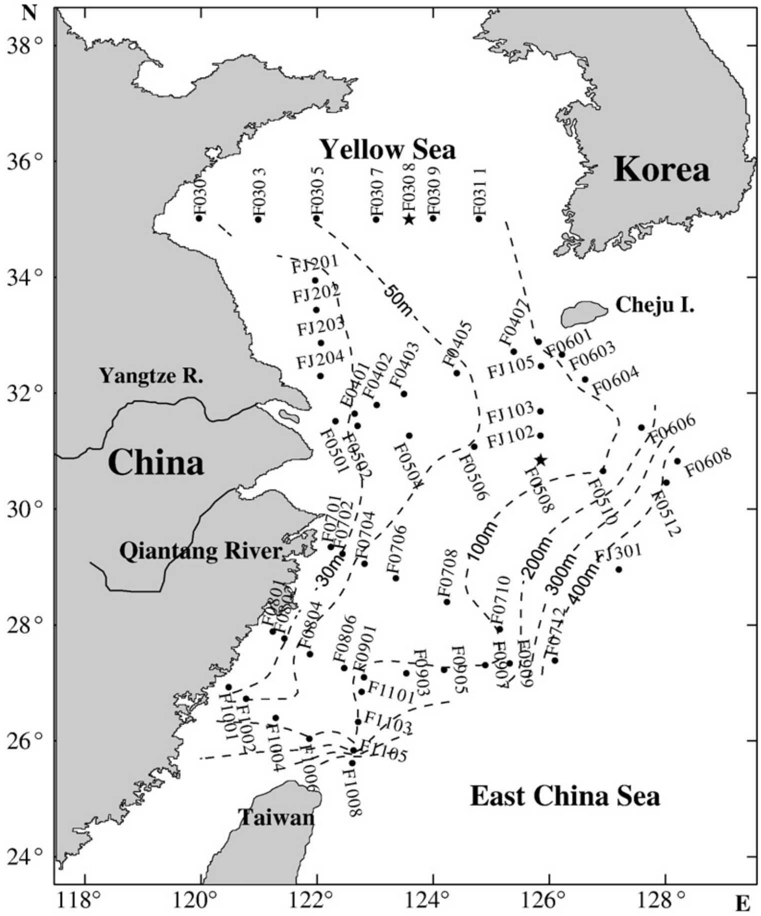

Fig. 1. Locations of the sampling stations in the East China Sea and the Southern Yellow Sea in November 2007. Two 25-h anchor stations (F0508 and F0308) for diurnal variation are indicated by (★).