



Halocarbons in the marine atmosphere and surface seawater of the south Yellow Sea during spring



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HIGHLIGHTS

- Spatial distributions and sources of halocarbons over and in the SYS were studied.
- Long-range transportation contributed to the high atmospheric halocarbon levels.
- Elevated levels of halocarbons in coastal water were related to terrestrial input.
- The SYS significantly contributed to global coastal CH₃Cl and CH₃Br emissions.

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ABSTRACT

The concentrations of eight halocarbons, including methyl chloride (CH₃Cl), methyl bromide (CH₃Br), trichloroethene (C₂HCl₃), tetrachloroethene (C₂Cl₄), methyl chloroform (CH₃CCl₃), and three chloro-fluorocarbons (CFCs) (CFC-11, CFC-113, and CFC-114), were measured using a canister sampling technique and an automated preconcentration gas chromatograph–mass spectrometer system in the marine atmosphere of the south Yellow Sea (SYS) in May 2012. The atmospheric concentrations of these halocarbons ranged from single digits to hundreds of pptv. Our results revealed elevated regional mixing ratios for most halocarbons (particularly C₂HCl₃ and C₂Cl₄) compared with the levels found in literature, thus suggesting substantial releases of C₂HCl₃ and C₂Cl₄ from anthropogenic sources in China. By contrast, the mean concentration of CFC-11 in the present study was lower than the global average value. The diffusion and transportation of terrestrial pollutants from coastal areas are important sources of halocarbons in the SYS, whilst terrestrial sources contribute to elevated concentrations of the selected halocarbons in coastal water. The sea-to-air fluxes of CH₃Cl and CH₃Br were estimated based on the simultaneous measurement of the atmospheric and seawater concentrations of these two gases. By simple extrapolation, the emissions of CH₃Cl and CH₃Br from the study area could account for 0.04% and 3% of the global oceanic emissions, respectively, thus indicating that the coastal area constituted important sources of atmospheric CH₃Cl and CH₃Br.

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1. Introduction

Halogen-containing volatile organic compounds (halocarbons) are important carriers of chlorine, bromine, and iodine in the atmosphere. Halocarbons, such as chlorofluorocarbons (CFCs) [CFC-11 (CCl₃F), CFC-113 (CCl₂FCClF₂), and CFC-114 (CCl₂FCF₃)], methyl chloroform (CH₃CCl₃), methyl halides [methane chloride (CH₃Cl) and methane bromide (CH₃Br)], trichloroethylene (C₂HCl₃), and tetrachloroethene (C₂Cl₄) with atmospheric lifetimes ranging from days to years (Table 1), have received attention from researchers

because they have important roles in stratospheric ozone depletion (World Meteorological Organization (WMO), 2011). Numerous halocarbons (e.g., CFCs) can act as greenhouse gases in the troposphere, and thus, have implications on climate (Ramanathan, 1975; WMO, 2011). Meanwhile, a number of chlorinated compounds such as C₂HCl₃ and C₂Cl₄ are environmentally significant because of their toxicity, thus posing hazards to human health (Zhang et al., 2010). CH₃CCl₃, C₂HCl₃, and C₂Cl₄ are anthropogenically produced halocarbons widely used as refrigerants, solvents, dry cleaning fluids, or in several cases, for CFC production; whereas CH₃Cl and CH₃Br have powerful anthropogenic and natural sources (Yokouchi et al., 2005; Zhang et al., 2010). Production and consumption controls have decreased the atmospheric loading of CFCs and related chlorinated compounds under the Montreal Protocol and its amendments. For

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Table 1
Method detection limits (MDL), precision, accuracy and lifetime of the selected halocarbons.

Compound	MDL (pptv)	Precision	Accuracy	Lifetime ^a (years)
CFC-11	1.0	2%	4%	45
CFC-113	1.0	2%	4%	85
CFC-114	1.0	2%	4%	190
CH ₃ CCl ₃	4.2	6%	5%	5
CH ₃ Cl	1.0	3%	2%	1
CH ₃ Br	1.0	2%	10%	0.8
C ₂ HCl ₃	0.5	2%	2%	0.01
C ₂ Cl ₄	0.6	2%	2%	0.27

^a WMO, (2011).

example, CFC-11 and CFC-113 are the two most abundant CFCs in the atmosphere. However, their global surface mean mixing ratios had declined significantly from 2007 to 2008 at the rate of -2.0 pptv/yr and -0.7 pptv/yr, respectively (WMO, 2011).

The ocean and the atmosphere have a complex role in the biogeochemical cycling of halocarbons. The spatial distribution of halocarbons in different air masses is influenced by their sources and atmospheric lifetimes, as well as by meteorological conditions including wind speed and mixing height (Quack and Suess, 1999; Blake et al., 2003). The marine atmosphere is the main vector that transports volatile terrestrial pollutants into the ocean and it constitutes an important link between land and ocean. Extensive studies on oceanic and atmospheric halocarbon concentrations have been carried out aboard ships or on remote islands over the past three decades (Blake et al., 2003; WMO, 2011). For example, global annual mean concentrations of CFC-11, CFC-113, and CFC-114 in 2008 were 243.4, 76.5, and 16.4 pptv, respectively, based on the results of the Advanced Global Atmospheric Gases Experiment (AGAGE). Moreover, the AGAGE observations showed that the mean global annual mixing ratios for CH₃Cl, CH₃Br, CH₃CCl₃, C₂Cl₄, and C₂HCl₃ were 545.0, 7.5, 10.7, 1.7, and 0.28 pptv, respectively.

Halocarbon emissions in China have attracted tremendous interest and are expected to be a significant contributor to East Asian and global total emissions (Xue et al., 2011). To date, halocarbon emissions have been measured in China, such as in the Pearl River Delta (PRD) region (Zhang et al., 2010; Shao et al., 2011). Halocarbon emissions from China were also estimated by Fang et al. (2012). Zhang et al. (2010) analyzed the annual trends of halocarbons in the PRD region and found that the atmospheric level of CFC-11 have gradually declined since 2001. Fang et al. (2012) also found that the emissions of CFC-11 in China exhibited an obvious decreasing trend from 2001 to 2009. By contrast, Shao et al. (2011) showed that the levels of halocarbons (e.g., C₂HCl₃, C₂Cl₄, CH₃Br, and CH₃CCl₃) in the PRD region were elevated. In spite of the increasing number of studies on atmospheric halocarbons in the Chinese mainland, less study has been conducted on the marginal seas in the country. Blake et al. (2003) investigated the spatial distributions of halocarbons over the western and central Pacific Ocean to reveal halocarbon emissions from Shanghai City. The present study is the first to measure eight kinds of halocarbons, including CH₃Cl, CH₃Br, C₂HCl₃, C₂Cl₄, CH₃CCl₃, CFC-11, CFC-113, and CFC-114, in the marine atmosphere over the south Yellow Sea (SYS) in spring. The objective of the current study is to determine the spatial distributions of these halocarbons in the SYS and to discuss possible sources of these trace gases. In addition, surface seawater concentrations of CH₃Cl, CH₃Br, C₂HCl₃, CH₃CCl₃, and CFC-113 were studied, and the fluxes of CH₃Cl and CH₃Br during the study period were estimated to evaluate the contribution of this region to global coastal oceanic CH₃Cl and CH₃Br emissions.

2. Experiment

2.1. Site description

The Yellow Sea, with a surface area of 0.38×10^6 km² and an average depth of 44 m, is a semi-enclosed water body in the northwestern Pacific surrounded by areas with high population and economic development in China (e.g., Shandong and Jiangsu Provinces) and the Korean Peninsula. As shown in Fig. 1, several rivers merge into the SYS from the west, including the Yangtze, Xinyi, Huaihe, and Sheyang Rivers. The SYS receives a huge amount of terrestrial inputs from these rivers (Wu et al., 2006; Lu et al., 2010). The Yellow Sea is heavily affected by several water masses, including the Subei Coastal Current in the western region, a low-temperature water mass called the Yellow Sea Cold Water in the central region, and the Yellow Sea Warm Current in the eastern region (Su, 1998; Lin et al., 2005). Previous studies indicate that these regional circulations can influence the spatial distributions of halocarbons in seawater (Lu et al., 2010; He et al., 2013). The study of atmospheric halocarbons in and over the SYS is of particular interest because this region, where an extremely powerful outflow was encountered during the Transport and Chemical Evolution over the Pacific Field Campaign (Blake et al., 2003), is along the pathway of the polluted continental air masses transported from Asia to the central north Pacific. In addition, numerous large cities are located on the SYS coast (Fig. 1). Therefore, a huge amount of terrestrial pollutants can enter the SYS via river runoff, and long-range transportation of air masses from the highly industrialized Chinese mainland and the Korean Peninsula can affect the distributions of atmospheric halocarbons over the SYS.

2.2. Sample collection

Halocarbon samples from the marine atmosphere were collected using a fused-silica lined canister with a ball valve. Samples were collected at 10 m elevation from the sea surface while facing the wind on the top deck of the R/V *Dong Fang Hong 2* in the SYS from May 2 to 9, 2012. The cruise track and sampling stations are shown in Fig. 1. All air samples were analyzed within a month after returning to the shore laboratory. Halocarbons can be stored stably for six months after sampling (Li et al., 1999).

2.3. Analysis of halocarbons in the air

The samples were analyzed using a preconcentrator (Entech 7100) coupled with a gas chromatograph–mass spectrometer (GC–MS, Agilent 6890N/5973N). The preconcentrator had multi-stage traps for removing H₂O and CO₂. A 500 mL air sample from the canister was drawn into the first trap (with glass beads as adsorbents), which was cooled to -150 °C by liquid nitrogen. All the halocarbons and other volatile compounds in the air were caught in the trap, whereas O₂ and N₂ passed through it. Then, the primary trap was heated to 10 °C (which was low enough to keep the H₂O in liquid state yet high enough to desorb target compounds). Pure He carried the desorbed compounds and CO₂ to the second trap (with Tenax TA as adsorbent) at -30 °C, which was high enough to prevent trapping CO₂ but low enough to trap all target compounds. The second trap was heated to 190 °C, and the target compounds caught in the second trap were desorbed and transferred by He to the third trap. The third trap was cooled to -170 °C for cryofocusing, which was necessary to achieve better separation and peak shapes. The ensnared compounds were desorbed by heating the third trap to 100 °C and then analyzed using GC–MS. A DB-624 capillary column (30 m × 0.25 mm inner

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