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Spatio-temporal distributions of chlorofluorocarbons and methyl iodide in the Changjiang (Yangtze River) estuary and its adjacent marine area

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ABSTRACT

Temporal and spatial distribution patterns of volatile halogenated organic compounds (VHOCs), such as dichlorodifluoromethane (CFC-12), trichlorofluoromethane (CFC-11), trichlorotrifluoroethane (CFC-113), and methyl iodide (CH₃I), in the Changjiang (Yangtze River) estuary and its adjacent marine area were measured during two cruises from 21 February to 10 March 2014 and from 10 to 21 July 2014. VHOC concentrations showed seasonal variation with higher values during winter. VHOC distributions evidently decreased along the freshwater plume from the river mouth to the open sea and from inshore to offshore regions. VHOC distributions were obviously influenced by the Changjiang runoff, anthropogenic inputs, and biological release of phytoplankton. The study area was a net sink for CFC-12 and CFC-11, but a net source for atmospheric CH₃I during the study periods.

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1. Introduction

Volatile halogenated organic compounds (VHOCs) are important radiatively active trace gases and ubiquitous organic pollutants in the atmosphere. These compounds are natural sources of reactive halogens, which play important roles in biogeochemical element cycles, atmospheric chemistry, and global environment (Montzka et al., 2011; Liu et al., 2013). VHOCs emitted from the ocean to the atmosphere are immediately broken down by photolysis or interaction with OH radicals to release inorganic chlorine, bromine, and iodine, which play important roles in the stratospheric and tropospheric ozone depletion (Lovelock et al., 1973; Yang et al., 2014). VHOC emissions from the ocean could be affected by global warming, with feedback effects on the climate (Yokouchi et al., 2012). Spatio-temporal distributions of VHOCs are influenced by various factors, such as riverine inputs, anthropogenic activities, biogenic production, and complex water masses (Yang et al., 2015). Zhou et al. (2005) reported that relatively short-lived VHOCs are emitted from local estuarine and coastal oceanic regions.

Chlorofluorocarbons (CFCs) are the first generation of refrigerants and foam blowing substances widely used in many aspects of modern society. These compounds have been suggested to be major contributors

to the seasonal ozone depletion over the Antarctic continent. CFCs are regulated under the Montreal Protocol because of their high ozone depletion potentials. Therefore, CFC emissions have been decreasing steadily since the late 1990s as a result of the phase-out program (Manzer, 1990). The usage of CFCs as transient tracers to resolve dynamic ocean processes (circulation and mixing) and determine water mass exchange rates has been widely practiced for decades (Bullister and Weiss, 1983, 1988; Wallace and Moore, 1985; Warner, 1988; Warner and Weiss, 1992). CFC-11, which is one of the most commonly measured CFCs, was commonly used as refrigerant until it was phased out in 1997 (Montreal Protocol on Substances that Deplete the Ozone Layer, 1987). This compound is used to estimate the ozone depletion potentials (World Meteorological Organization (WMO), 1999). Trichlorotrifluoroethane (CFC-113), which replaced CFC-11 and CFC-12, is used primarily as a solvent in electronics, resulting in the rapid increase of this compound in the atmosphere during the 1980s.

Atmospheric methyl iodide (CH₃I) is relatively short-lived (~5 days). However, CH₃I is globally ubiquitous as the dominant carrier of gas-phase iodine from the oceans into the atmosphere (Lovelock et al., 1973). This compound is also an aerosol precursor (O'Dowd et al., 2002). Numerous studies have considered possible reactions of iodine in the atmosphere, which lead to stratospheric and tropospheric ozone depletion through rapid production of IO radicals and regeneration of iodine atoms on photolysis (Zafriou, 1974; Chameides and Davis, 1980; McFiggans et al., 2000; Li et al., 2001). Biological activity is a major source of CH₃I (Singh et al., 1983; Manley and Dastoor,

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1987, 1988; Amachi et al., 2001). However, possible production by phytoplankton has not been proven, and the major producers of CH_3I in the ocean remain unknown. Nightingale et al. (1995) indicated that macroalgae were not an important source of CH_3I to the atmosphere. Laboratory studies suggest that photochemical reaction in surface seawater is a dominant production pathway for CH_3I (Moore and Zafriou, 1994). Previous studies showed that CH_3I production has strong and positive relation to sea surface temperature, suggesting that CH_3I emission may increase under global warming (Yokouchi et al., 2001, 2012).

Estuaries are quite complex systems in the physical environment. Various processes occur in estuaries, such as tidal effects, mixing, particle interaction, and various inputs of natural and anthropogenic sources, which influence VHOc distributions and emissions to the atmosphere (Christof et al., 2002). The Changjiang (Yangtze River) is the largest river in Asia. A large portion of the Changjiang discharge enters its estuary and is emptied into the East China Sea (ECS) (Wang et al., 2008; Zhang et al., 2008). The adjacent coastal water is influenced by the nutrient load and other pollutants of the Changjiang River. This phenomenon leads to the deposition of high amounts of organic matter which could enhance phytoplankton biomass and VHOc emission.

Although VHOcs have been investigated in a wide range of marine regions, no data are available for the distributions, fluxes, and producing processes of VHOcs in the Changjiang estuary and its adjacent area. In this study, we present VHOc data, which were collected from two cruises, such as the concentration range and composition, anthropogenic and natural sources, and transformation processes of VHOcs in the Changjiang estuary and its adjacent marine area. The study was performed to determine the distribution of VHOcs along the Changjiang estuary. Moreover, the VHOc emission into the atmosphere was estimated. The contribution of Changjiang to the VHOcs in the ECS was also evaluated.

2. Method

2.1. Seawater sampling

Two cruises were conducted aboard the R/V “Run Jiang” in the Changjiang estuary and its adjacent marine area from 21 February to 10 March 2014 and from 10 to 21 July 2014, respectively. Sampling stations are shown in Fig. 1. Horizontal distributions of the four VHOcs were investigated in the surface seawater of all stations. The surface (0–5 m) and deep water samples were obtained with 8 L Niskin samplers mounted on a Seabird CTD (conductivity, temperature, and depth)-equipped rosette (General Oceanics Co.) and transferred into 135 mL brown glass bottles using a silicone connecting tube with a glass pipette end. After overflow of approximately 1.5- to 2-fold of bottle volume, 0.5 mL of saturated solution of NaN_3 was added to inhibit microbial activity. Afterward, sample bottle was immediately sealed with a butyl rubber stopper and an aluminum cap to avoid any headspace. The sample was stored in the dark at 4 °C until analyzed, usually within 20 days of collection. Time courses of the trace gas concentrations were analyzed to evaluate the stability of the four VHOcs in the stored seawater samples. Results showed that the concentrations of the target compounds were not significantly altered 20 days after sampling. Environmental and hydrographic conditions of sampling stations, such as temperature, salinity, and dissolved oxygen, were obtained from the shipboard CTD apparatus.

2.2. Analysis of VHOcs

The concentrations of VHOcs were analyzed with a purge and trap system coupled to a gas chromatograph (Agilent 6890) with an electron capture detector, according to the method described by Yang et al. (2010). In brief, each sample (100 mL) was purged at 40 °C with ultra-pure nitrogen at a flow rate of 40 mL min⁻¹ for 12 min. The

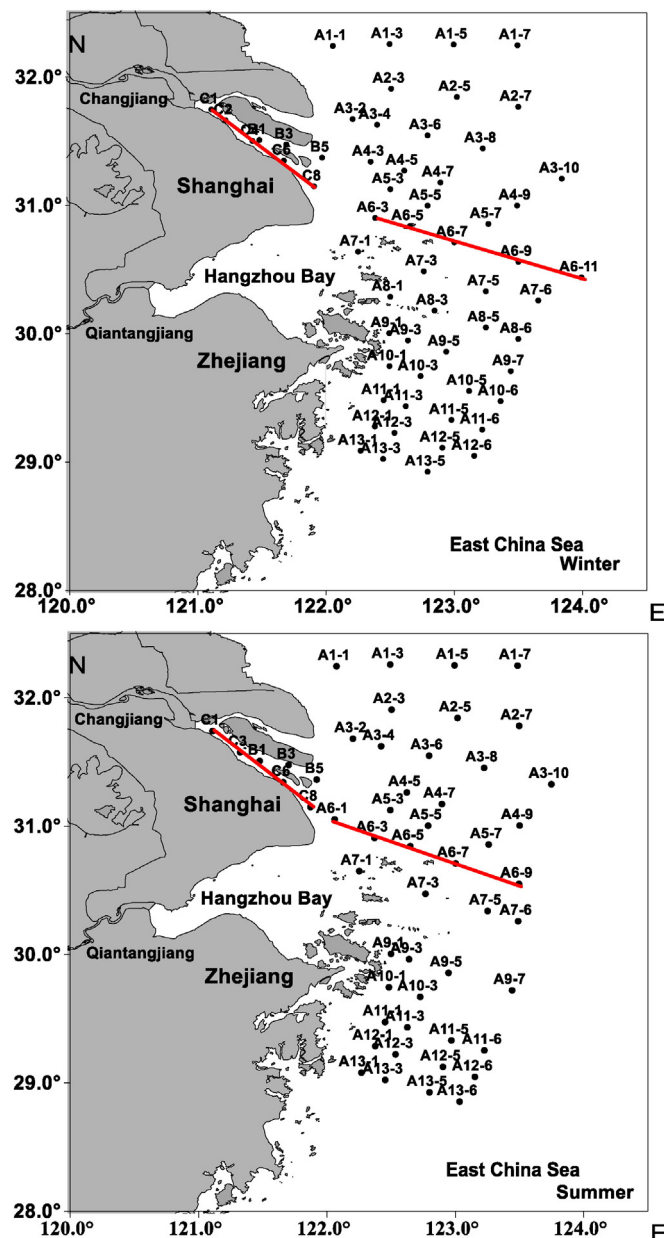


Fig. 1. Sampling locations in the Changjiang estuary and its adjacent area in winter and summer.

extracted compounds were dried in two glass tubes filled with magnesium perchlorate [$\text{Mg}(\text{ClO}_4)_2$] and ascarite, respectively, to remove water vapor and carbon dioxide. The compounds were then trapped in a stainless steel tube (a coiled 30 cm long piece of stainless steel tubing, i.d. 0.8 mm) that had been held at -195 °C using liquid nitrogen. The compounds were released from the trap by heating the trap with boiling water for 2 min and then introduced into the gas chromatographic system for analysis, after separating the compounds on a DB-624 capillary column (length, 60 m; i.d., 0.53 mm; film thickness, 3 μm) by the carrier gas (N_2) at a flow rate of 3.0 mL min⁻¹. The GC oven temperature was initially held for 8 min at 45 °C, then raised to 150 °C at a rate of 15 °C min⁻¹, and maintained isothermally with final temperature for 12 min. The total run time was 32 min. The retention times of CFC-12, CFC-11, CFC-113, and CH_3I were 5.49, 8.09, 9.51, and 9.94 min, respectively. The trace gases were quantified according to the retention times and peak areas of the calibration standards. A measured amount of calibration standards (Sigma) were diluted with methanol to prepare working standards. A concentration gradient at

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