



Distribution and sea-to-air flux of isoprene in the East China Sea and the South Yellow Sea during summer



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HIGHLIGHTS

- Isoprene was determined for the first time in the China marginal seas.
- Significant correlation was observed between isoprene and Chl-*a* concentrations.
- High concentrations of isoprene occurred in waters dominated by diatoms.
- The ECS and SYS was an important source for atmospheric isoprene during summer.

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ABSTRACT

Spatial distribution and sea-to-air flux of isoprene in the East China Sea and the South Yellow Sea in July 2013 were investigated. This study is the first to report the concentrations of isoprene in the China marginal seas. Isoprene concentrations in the surface seawater during summer ranged from 32.46 to 173.5 pM, with an average of 83.62 ± 29.22 pM. Distribution of isoprene in the study area was influenced by the diluted water from the Yangtze River, which stimulated higher in-situ phytoplankton production of isoprene rather than direct freshwater input. Variations in isoprene concentrations were found to be diurnal, with high values observed during daytime. A significant correlation was observed between isoprene and chlorophyll *a* in the study area. Relatively higher isoprene concentrations were recorded at stations where the phytoplankton biomass was dominated by *Chaetoceros*, *Skeletonema*, *Pennate-nitzschia*, and *Thalassiosira*. Positive correlation was observed between isoprene and methyl iodide. In addition, sea-to-air fluxes of isoprene approximately ranged from $22.17 \text{ nmol m}^{-2} \text{ d}^{-1}$ to $537.2 \text{ nmol m}^{-2} \text{ d}^{-1}$, with an average of $161.5 \pm 133.3 \text{ nmol m}^{-2} \text{ d}^{-1}$. These results indicate that the coastal and shelf areas may be important sources of atmospheric isoprene.

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1. Introduction

Non-methane hydrocarbons (NMHCs), which are primarily produced by terrestrial vegetation, are the most important components of volatile organic compounds (VOCs) (Liakakou et al., 2007; Baker et al., 2008; Saito et al., 2009). Anthropogenic and

natural NMHCs may not only contribute to the global carbon cycle (Sahu et al., 2011), but these hydrocarbons are also important contributors in atmospheric chemistry. NMHCs affect the balance of atmospheric oxidants and serve chemically as precursors of ozone in the troposphere (Pszenny et al., 1999; Liakakou et al., 2009; Zindler et al., 2014). Additionally, NMHCs are known to condense to generate atmospheric secondary organic aerosol (SOA) particles (Hudson and Ariya, 2007), which play significant roles in reflecting of solar radiation as cloud-condensation nuclei (Matsunaga et al., 2002). Isoprene (2-Methyl-1,3-butadiene, C₅H₈) is the most abundant trace gas among all NMHCs (Pacífico et al., 2009). Isoprene is ubiquitous in seawater and can be released from the ocean to the atmosphere, with an estimated oceanic

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emission of 0.1–1.9 Tg a⁻¹ (Bonsang et al., 1992; Palmer and Shaw, 2005; Arnold et al., 2009). Furthermore, remote sensing data combining with in-situ observations were adopted to estimate isoprene emission on a global scale, such as satellite observations of ocean biological productivity (Palmer and Shaw, 2005), phytoplankton functional types (PFTs) (Arnold et al., 2009) and new physical parameters (Gantt et al., 2009), which all reveal the global ocean is a net source of atmospheric isoprene.

Isoprene is produced by marine phytoplankton (Colomb et al., 2008), heterotrophic bacteria (Kuzma et al., 1995; Alvarez et al., 2009), and seaweeds (Broadgate et al., 2004; Carpenter et al., 2012), with phytoplankton as the major contributor. In addition, the photochemical degradation of dissolved organic matter in the sea-surface microlayer is also an abiotic source of isoprene (Ciuraru et al., 2015). Marine isoprene and chlorophyll *a* (Chl-*a*) concentrations have been positively correlated in the North Sea, Southern Ocean (Broadgate et al., 1997), and in the western North Pacific Ocean (Kurihara et al., 2010). This characteristic suggests a close connection between isoprene production and phytoplankton metabolism. Arnold et al. (2009) and Gantt et al. (2009) integrated laboratory measurements of isoprene production and satellite-derived PFTs developed by Alvain et al. (2005, 2008) to estimate global marine isoprene emissions. Moreover, previous studies also showed that isoprene concentrations in the surface waters are closely related to phytoplankton species (Broadgate et al., 1997; Yassaa et al., 2008; Shaw et al., 2010), irradiation and seawater temperature (Shaw et al., 2003; Gantt et al., 2009), apart from phytoplankton biomass (Broadgate et al., 2004). Once produced, isoprene can be easily removed from the surface water through various processes, such as microbial consumption (Sinha et al., 2007; Alvarez et al., 2009), photochemical oxidation (Palmer and Shaw, 2005; Rudziński et al., 2016), and emission to the atmosphere (Palmer and Shaw, 2005; Arnold et al., 2009). However, limited information on the chemical and microbial losses of marine isoprene is available. Emission to the atmosphere through sea-air gas exchange has been inferred as the primary sink of oceanic isoprene (Matsunaga et al., 2002).

The distribution and emission of isoprene in remote oceans exhibit significant considerable spatial and temporal variation (Peter et al., 1995; Riemer et al., 2000; Matsunaga et al., 2002; Zindler et al., 2014). Very few studies have reported on the marine isoprene in eutrophic coastal areas and upwelling regions (Kurihara et al., 2012). High eutrophication and other related factors may contribute to greater production of marine phytoplankton, thereby increasing isoprene emission. In the present study, the distributions and sea-to-air fluxes of isoprene in the marginal seas of China were determined for the first time, although China has a coastline of over 18×10^3 km and seas covering more than 3.8×10^6 km². The distribution of isoprene and its controlling factors in the surface seawater of the East China Sea (ECS) and the South Yellow Sea (SYS) were investigated. The potential relationships between the variability and physical processes of isoprene, as well as phytoplankton biomass, were discussed. Atmospheric isoprene emission in the study area was also estimated.

2. Materials and methods

2.1. Study area

The ECS and the SYS are located at the margin of the Northwest Pacific Ocean, which is one of the largest continental shelves in the world. As shown in Fig. 1 (a), the hydrographic characteristics of this region are heavily affected by the following water masses: Yellow Sea (YS) Coastal Current and YS Cold Water Mass in the western region; Kuroshio Current, Tsushima Current and YS Warm

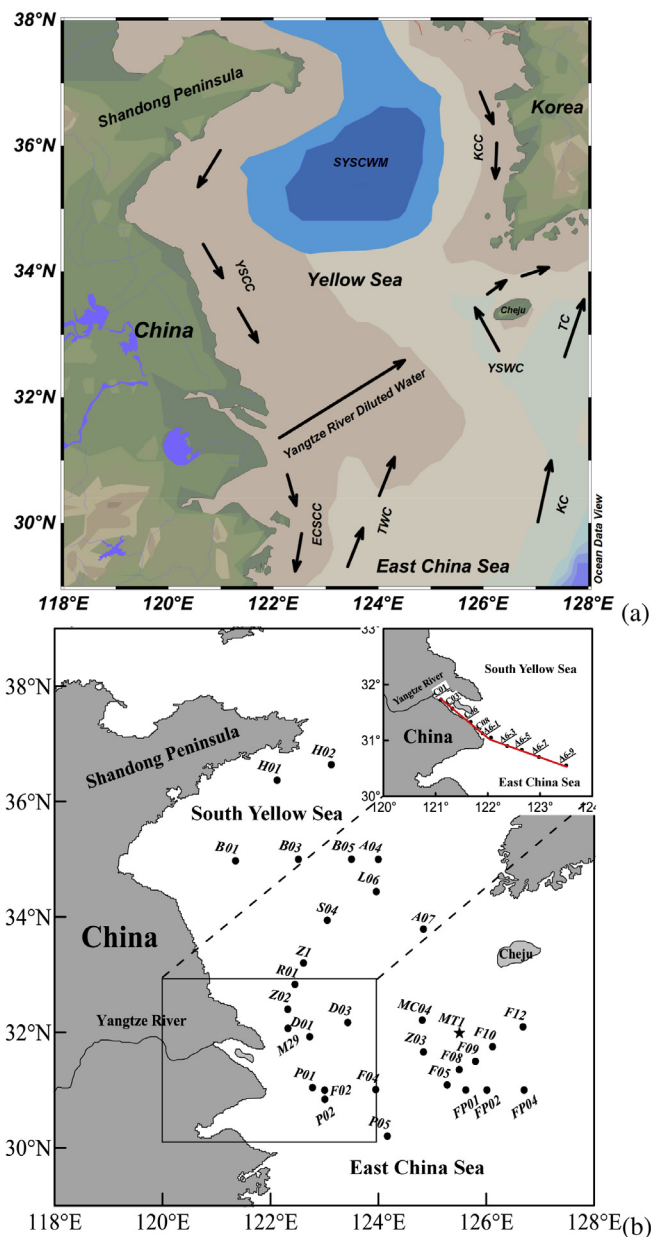


Fig. 1. (a) Schematic diagrams of the cold water masses and current system in the South Yellow Sea and the East China Sea in summer. The dominant water masses are classified as previously described (Lee et al., 2000; Zhang et al., 2008; Li et al., 2012; Qi et al., 2014). YSCC: Yellow Sea Coastal Current; YSWC: Yellow Sea Warm Current; TC: Tsushima Current; KCC: Korea Coastal Current; KC: Kuroshio Current; ECSCC: East China Sea Coastal Current; TWC: Taiwan Warm Current; SYSCWM: South Yellow Sea Cold Water Mass. (b) Locations of the sampling stations in the East China Sea and the South Yellow Sea (★ represents the continuous stations of 24 h).

Current in the eastern region of the SYS (Lin et al., 2005; Li et al., 2012); ECS Coastal Current; and the Taiwan Warm Current of the ECS (Su, 1988; Lee et al., 2000; Qi et al., 2014). The Kuroshio Current with oligotrophic nutrients, high temperature, and high salinity flows along the northeast Asia continental margin. The SYS Cold Water Mass (SYSCWM) has a characteristic of low temperature. The SYSCWM forms in May, reaches its peak in July and August, and gradually disappears after September because of the vertical mixing of seawater. These currents and water masses may influence the distribution and biomass of the phytoplankton with seasonal changes, consequently affecting the production and variation of

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