Marine Pollution Bulletin 136 (2018) 276–281

Contents lists available at ScienceDirect

Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul

Accumulation of quaternary ammonium compounds as emerging contaminants in sediments collected from the Pearl River Estuary, China and Tokyo Bay, Japan

Xi Dai[a], Cuicui Wang[a], James C.W. Lam[b], Nobuyoshi Yamashita[c], Eriko Yamazaki[c], Yuichi Horii[d], Weifang Chen[a], Xiaolin Li[a,*]

[a] State Key Laboratory of Marine Environmental Science, College of Oceanography & Earth Science, Xiamen University, Xiamen 361100, China
[b] Department of Science and Environmental Studies, The Education University of Hong Kong, Hong Kong, China
[c] National Institute of Advanced Industrial Science and Technology, 16-1 Onogawa, Tsukuba, Ibaraki 305-8569, Japan
[d] Center for Environmental Science in Saitama, 914 Kamitanadare, Kazo, Saitama 347-0115, Japan

ARTICLE INFO

Keywords:
Quaternary ammonium compounds
Sediment
Organic pollutants
Pearl River Estuary
Tokyo Bay

ABSTRACT

In this work, the distribution of quaternary ammonium compounds (QACs) in two dated sediment cores, collected from the Pearl River Estuary (PRE) and Tokyo Bay (TB), were investigated to understand the historical input of QACs and their diagenetic behavior in urban estuarine environments. The vertical variation profiles of QAC concentrations showed that benzylalkyldimethyl ammonium compounds (BACs) and dialkyldimethyl ammonium compounds (DADMACs) were widely used during 1970s and 1980s both in China and Japan. The declining environmental concentrations of QACs suggested a compositional change of commodities and the effectiveness of emission control strategies. For the individual QAC homologues, BAC homologues decreased significantly over time, while DADMAC compositions remained relatively stable. The differences in concentration and composition profiles of BACs and DADMACs in the sediment cores provided useful information on the patterns of use of QACs in China and Japan, as well as their diagenetic behaviors in the sediments.

1. Introduction

Quaternary ammonium compounds (QACs) are a major fraction of cationic surfactants (Tezel, 2009; Ren et al., 2011) and are widely used in phase transfer catalysts, detergents, fabric softeners, disinfectants and preservatives (Levinson, 1999; Ruan et al., 2014). QACs have a positively charged quaternary nitrogen atom containing four functional groups, which readily adsorb negatively charged sludge and suspended particles (Ying, 2006). Due to high particle reactivity, very high levels of QACs were observed in the estuarine sediments. Pintado-Herrera et al. (2017) found that QACs contributed to about 70% of the mass inventory of the legacy and emerging organic contaminants (> 100 chemicals) in the surface sediments of Pearl River Estuary (PRE), China. The high concentration of QACs in the environment would inhibit the nutrient uptake by algae, increase the antibiotic-resistant bacteria and limit the anaerobic digestion process (Clara et al., 2007).

The QACs are released into the environment due to the discharge of effluent and sludge from domestic sewage and industrial wastewater treatment plants (Clara et al., 2007) together with other local point sources, including hospitals, laundry wastewater and roof runoff (Van de Voorde et al., 2012; C. Zhang et al., 2015; Z. Zhang et al., 2015). As hydrophobic cation exchangers, QACs have a strong affinity for suspended particulates, which leads to their subsequent settlement in sediments (Brownawell et al., 1990; Martinez-Carballo et al., 2007; Ismail et al., 2010). Generally, QACs are found to be persistent in the reduced sedimentation environments and their compositional pattern is identical to what is observed in the sewage sludge (Li and Brownawell, 2010; Li et al., 2014). Marine sediments are recognized as one of the sinks for a wide range of persistent organic pollutants (POPs) (Yang et al., 2005; Chen et al., 2014; Zeng, 2015). Dated sediment core is a feasible tool for reconstructing historical records of contaminant inputs to environment (Van Meter et al., 1997; Lima et al., 2003). Although QACs detected in the sediments are ubiquitous and in high concentration in several urban estuaries in China and the United States (Li and Brownawell, 2010; Li et al., 2014), the knowledge about their discharge histories and environmental fates is still limited, while no chronology of their existence has been reported in Asian countries.

In this work, two typical urban estuaries, the PRE in southern China

* Corresponding author.
E-mail address: xlli@xmu.edu.cn (X. Li).

https://doi.org/10.1016/j.marpolbul.2018.09.027
Received 29 June 2018; Received in revised form 12 September 2018; Accepted 15 September 2018

and the Tokyo Bay (TB) in Japan, were chosen as the study areas. These two estuaries have experienced fast economic development and population growth. Several POPs, including PAHs, dioxins and brominated flame retardants have been widely detected in these two regions over the past few decades with different distributional patterns due to the different production history and applications (Hosomi et al., 2003; Minh et al., 2007; Chen et al., 2014; C. Zhang et al., 2015; Z. Zhang et al., 2015). The comparison of chronological records in the two regions would help to better understand different applications and discharge histories of these pollutants in the two countries.

On the basis of the application profiles and toxicological properties of QACs (Gaze et al., 2005; Yu et al., 2012), benzylalkyldimethyl ammonium compounds (BACs; C12–C18) and dialkyldimethyl ammonium compounds (DADMACs; with alkyl chain lengths ranging from C8 to C18) were selected as the key compounds for this study (Li and Brownawell, 2009; Lara-Martín et al., 2010). Globally, the first generation of disinfectants containing BACs and DADMACs has been used for > 60 years, and the diagenetic fate of QACs in the sediment cores suggested the persistence of some QAC homologues, which could be used as indicators for the historical production records of these compounds (Li et al., 2018). However, limited data are reported for the urbanized estuaries of Asia. QACs have been found in the surface sediments of PRE, however their time history in Asia is still not well-understood (Li et al., 2014; Pintado-Herrera et al., 2017). Therefore, the aim of this work was to investigate the vertical distribution of QACs in the dated sediment cores, which were collected from PRE and TB to assess the chronological records of QACs. The information on the current and historical contamination statuses of QACs in PRE and TB is beneficial to reconstruct the pollution history and environmental fates of these compounds. Finally, it is expected that the research would offer first chronological data on QACs in Asia and provide practical guidance to control the environment pollution caused by them.

2. Materials and methods

2.1. Study area and sample collection

Both the PRE and TB are typical, large urban estuaries in Asia. PRE is located in the extensively developed and urbanized Pearl River Delta (PRD) region of south China, and is a bell-shaped estuary with the area of approximately 2440 km^2 (Fig. 1a). PRE is one of the largest economically developed and densely populated regions of China, which receives 14,000 kilotons of wastewater per day from the upriver cities, such as Guangzhou, Shenzhen and Dongguan to the South China Sea (Peng et al., 2008). Furthermore, sediments from PRE are considered as the main reservoir for particle reactive pollutants discharged from the PRD (Chen et al., 2006; Peng et al., 2007). Similarly, TB is a semi-enclosed bay surrounded by three prefectures, and has water volume of 14.4×10^9 m^3 with an average depth of 15 m and the average water residence time of 1.6 months (Pan et al., 2014). Numerous municipal and industrial facilities are located in this bay, including 27 sewage treatment plants, 21 municipal incinerators, 5 landfills, 3 ironworks, 8 oil refineries, and 14 thermal power plants (Pan et al., 2014; TBEIC, 2013).

A sediment core was collected from PRE using a standard box corer ($20 \times 20 \times 60$ cm^3) in November 2013, while a gravity corer equipped with an inner polycarbonate tube was used to sample a sediment core from TB in 2012 (Fig. 1). The cores were visually inspected to ensure that the interface was intact. The cores were sectioned immediately at 2 cm intervals on a board using a clean stainless-steel slicer. Each section was wrapped in aluminum foil, baked at 450 °C and sealed in polyethylene bags. Then, all the samples were immediately transported to laboratory and stored at −20 °C until further treatment. All sediment samples were homogenized, freeze-dried and transferred into the pre-cleaned glass containers before analyzing for QACs.

2.2. Sample analysis and quantification

The QACs were analyzed using the method reported by Li and Brownawell (2009) and Li et al. (2014) with some minor modifications. Briefly speaking, approximately 0.1 g of freeze-dried sediment was spiked with 50 ng deuterated DADMAC12:12-d25 as the recovery surrogate, and was extracted ultrasonically for 1 h with 5 mL acidic methanol (1 M hydrochloric acid) at 60 °C for three times. The extracts were combined after centrifugation and concentrated by drying at 40 °C using a vacuum tube evaporator (EYELA TVE-1100). Then, the residue was dissolved in 5 mL ultrapure water and transferred to a 50 mL separatory funnel. The aqueous phase was extracted three times with 5 mL chloroform, and the combined chloroform extracts were dried using a slow stream of nitrogen. Finally, the samples were dissolved in acetonitrile-water (95:5 v/v, respectively) and 20 ng tridodecyl was added as the internal standard prior to further analysis.

The determination of QACs was performed using an Agilent 1290 ultra-high performance chromatography (UPLC) coupled with 6490 triple quadrupole mass spectrometer (UPLC-MS-MS). The separation of compounds was conducted using C18 column (50 × 2.1 mm, 1.9 mm, Thermo Scientific, USA). The mobile phases and elution gradients are described in Table S1, given in the Supporting information (SI). The

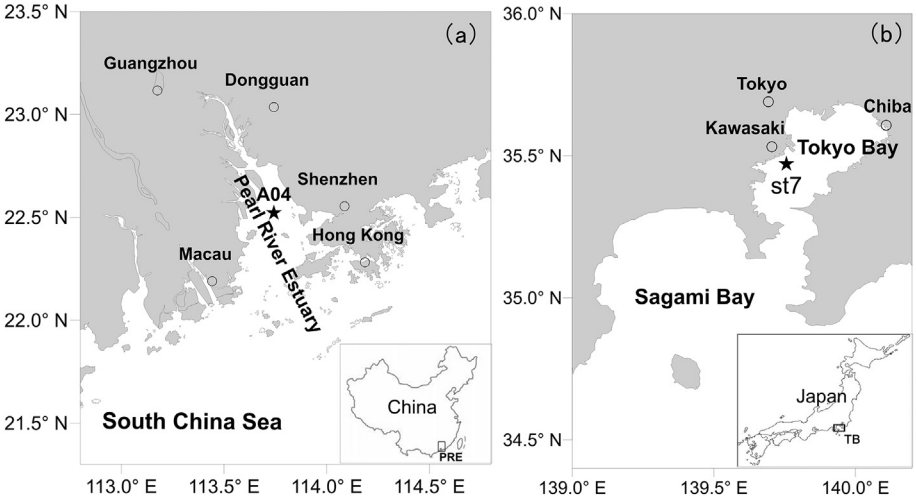

Fig. 1. Study areas showing the sediment sampling sites in (a) PRE and (b) TB.