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Linear alkylbenzenes in riverine runoff of the Pearl River Delta (China) and their application as anthropogenic molecular markers in coastal environments

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Occurrence of LABs in riverine runoff of the Pearl River Delta (China) was examined.

Abstract

The average concentrations of ∑LABs (sum of C_{10}–C_{13}-LABs) in runoff samples collected from the eight major riverine outlets of the Pearl River Delta (PRD) of China ranged from 1.4 to 6124 ng/L in the dissolved phase and from 0.01 to 11.4 μg/g dry weight in the particulate phase during March 2005–February 2006. The annual riverine flux of ∑LABs from the PRD to the coastal ocean was estimated at approximately 14 tons/yr. The inventories of ∑LABs in agricultural lands of Guangdong Province ranged from 313 to 1825 kg/yr. The early and late rice fields were the major sink of LABs, accounting for approximately 68% of total LABs inventory in agricultural lands. The social-economically estimated annual discharge of LABs from household detergents in the PRD was ~696 tons/yr, more than an order of magnitude higher than that estimated from field measurements (about 14 tons/yr), which was attributed to several factors.

Keywords: Linear alkylbenzenes; Molecular marker; Riverine flux; Inventory; Pearl River Delta

1. Introduction

Linear alkylbenzenes (LABs) with C_{10}–C_{14} normal alkyl chains have been used to produce linear alkylbenzene sulfonates (LAS), one of the most widely used anionic surfactants for manufacturing detergents since the 1960s. As a result small amounts of LABs are likely contained in LAS-type detergents (Takada and Eganhouse, 1998), and use of detergents and subsequent disposal bring LABs into aquatic environments. Another surfactant-related source of LABs is industrial wastewater discharge from LAS synthesis plants (Takada and Eganhouse, 1998). Frequently, the behavior and fate of organic contaminants can be examined using a widely used chemical with similar physiochemical properties. In this regard LABs have been used as molecular markers of domestic wastewater (Eganhouse et al., 1983; Ishiwatari et al., 1983; Chalaux et al., 1995; Takada and Eganhouse, 1998). Because of their high hydrophobicity, LABs are mainly associated with particulate matter. Therefore, LABs can be used as tracers of sewage-derived particles and to indicate sources and transport pathways of hydrophobic organic pollutants.

Since the first reports on the occurrence of LABs in the environment and their utility as molecular markers in 1983 (Eganhouse et al., 1983; Ishiwatari et al., 1983), LABs have been widely employed as markers of anthropogenic inputs in

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many regions of the world (Eganhouse et al., 1983; Takada and Ishiwatari, 1987; Chalaux et al., 1992, 1995; Takada et al., 1994; Hong et al., 1995; Bayona et al., 1996; Phillips et al., 1997; Zeng et al., 1997). The Pearl River Delta (PRD; Fig. 1), one of the most economically developed regions in China, contains rich watercourses and numerous entrances to the coastal ocean. The rapid economic development and urbanization have resulted in severe air and water pollution (Fu et al., 2003). Inevitably, contaminants from the PRD are likely carried into adjacent watercourses and ultimately discharged to the South China Sea (SCS) via the eight major riverine outlets (Fig. 1), creating long-term adverse effects on the coastal resources. Despite the increasing attention recently paid to the pollution of the PRD aquatic systems, most research efforts have focused in sediments (Zheng et al., 2001, 2002a, 2004; Mai et al., 2003, 2005a,b; Chen et al., 2006a,b), and applications of LABs as anthropogenic indicators in the PRD are scarce.

In addition, large amounts of river water are used to irrigate agriculture lands in Guangdong Province. As a result, organic contaminants in river water inevitably enter the sown soil and are sorbed by crops (Mieure et al., 1990), but this impact has not been addressed. This study aimed to determine the total annual flux of LABs from the PRD to the coastal ocean and estimate the mass inventory of LABs in the agriculture lands of Guangdong Province stemming from irrigation. In this study, individual LAB isomers are often expressed as i-C_n, where n indicates the number of carbon atoms in the alkyl chain and i the position of the benzene insertion.

2. Materials and methods

Individual LAB compounds, 1-C_n ($n = 10-14$), were purchased from Sigma–Aldrich (St. Louis, MO, USA) and used as primary standards. A pure LAB mixture was obtained from Procter & Gamble Company (Guangzhou, China) and used as a secondary standard. This mixture contains isomers of C_{10}-LABs, C_{11}-LABs, C_{12}-LABs, and C_{13}-LABs except for 1-C_n ($n = 10-13$). The internal standards, 1-phenylpentadecane-d_{30}, and the surrogate standard, 1-phenyldodecane-d_{30}, were acquired from C/D/N Isotopes (Pointe-Claire, Quebec, Canada). All working solutions were prepared in hexane.

2.1. Field sampling

The sampling locations and adjacent areas are displayed in Fig. 1. The PRD aquatic systems contain three main tributaries, i.e. the Beijiang, Xijiang, and Dongjiang Rivers. The Beijiang and Dongjiang Rivers flow into the SCS mainly via the eastern outlets including Humen (HM), Jiaomen (JM), Hongqilimen (HQ), and Hengmen (HE), whereas the Xijiang River mostly drains through the western outlets including Modaomen (MD), Jitimen (JT), Hutiaomen (HT), and Yamen (YM). Water samples were collected monthly from

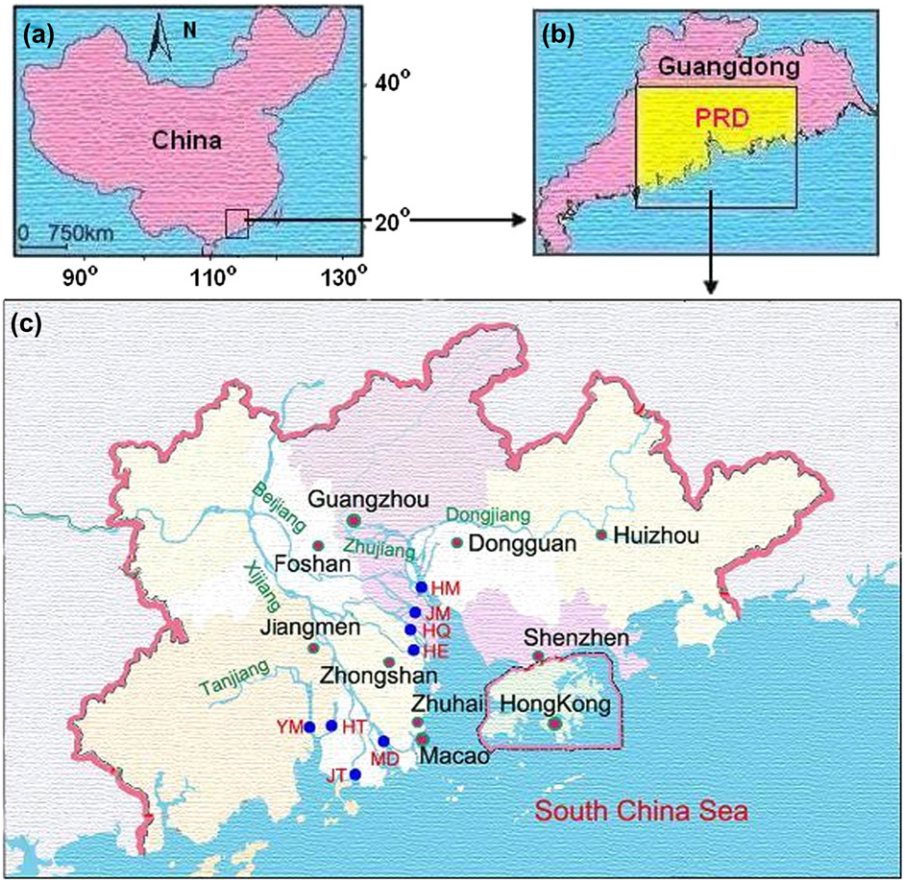

Fig. 1. (a) Schematic showing the geographical locality of the Guangdong Province. (b) Geographical locality of Pearl River Delta in Guangdong Province. (c) Map of the general study area and sampling sites symbolized by dots (•). The eight major runoff outlets are labeled with HM (Humen), JM (Jiaomen), HQ (Hongqilimen), HE (Hengmen), MD (Modaomen), JT (Jitimen), HT (Hutiaomen), and YM (Yamen).