

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 \sum LABs (sum of C₁₀–C₁₃-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 μ g/g dry weight in the particulate phase during March 2005–February 2006. The annual riverine flux of \sum LABs from the PRD to the coastal ocean was estimated at approximately 14 tons/yr. The inventories of \sum 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 \sim 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.

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1. Introduction

Linear alkylbenzenes (LABs) with C₁₀–C₁₄ 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; Chaloux 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_{36} , and the surrogate standard, 1-phenyldecane- 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

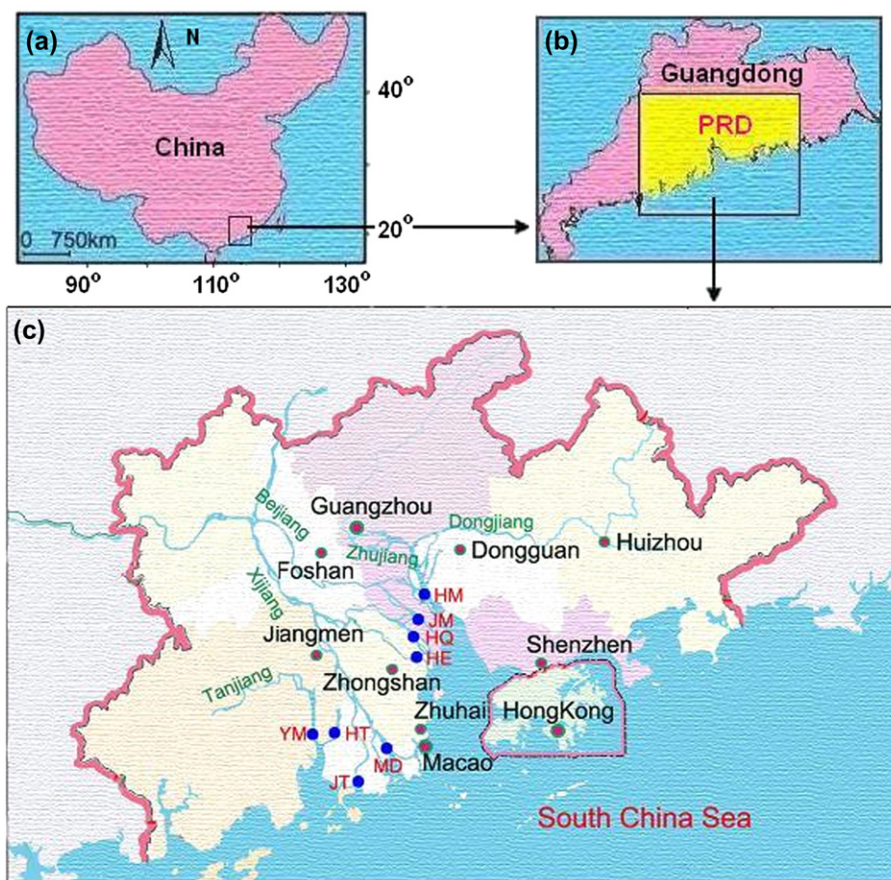


Fig. 1. (a) Schematic showing the geographical locality of the Guangdong Province. (b) Geographical locality of Pearl River Delta in Guangdong Province. (c) Map of the general study area and sampling sites symbolized by dots (●). The eight major runoff outlets are labeled with HM (Humen), JM (Jiaomen),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

March 2005 to February 2006 during monthly neap tides to avoid tidal influences, and detailed sampling procedures are provided in the [Supplementary material](#) (“S” designates tables and figures in the [Supplementary material](#) thereafter). In addition, six brands of powder detergents, six brands of liquid detergents, and five brands of shampoos, which are most commonly used in the PRD, were collected and analyzed with the field samples.

2.2. Sample extraction

All water samples were filtered immediately upon delivery to the laboratory, and suspended particulate matter (SPM) was collected with GF/F glass fiber filters (0.7 μm nominal pore size, 142-mm diameter; Whatman International, Maidstone, England) pre-combusted at 450 °C for at least 5 h. The filter papers loaded with SPM were freeze-dried and crumbed, and Soxhlet extracted with a mixture of dichloromethane and acetone with 1:1 volume ratio for 48 h. Each extract was concentrated to about 1 mL with a Zymark Turbo-Vap 500 (Zymark Corporation, Hopkinton, MA, USA), solvent-exchanged to hexane, and reduced to a final volume of approximately 1 mL. About 20 L of each filtrate sample were passed immediately upon collection through a glass column (25 mm I.D., 400 mm length) packed with a mixture of XAD-2 and XAD-4 resins at a 1:1 weight ratio. The resin column was eluted with dichloromethane and the eluate was further processed with the same procedure as used for the SPM samples. Detergent samples were weighed carefully, dissolved in hyper pure water, and extracted with dichloromethane. Extracts were also treated with the same procedure as described above.

All concentrated extracts were cleaned and fractionated with a 1:2 alumina:silica gel glass column (alumina: 100- to 200-mesh; neutral silica gel: 80- to 100-mesh). Each extract was eluted into two fractions. The first fraction containing mostly aliphatic hydrocarbons was eluted with 15 mL hexane and discarded. The second fraction containing LABs was eluted with 15 mL hexane. This fraction was concentrated with the TurboVap 500–0.5 mL. Internal standards were added to the extract prior to instrumental analysis.

2.3. Instrumental analysis

Concentrations of LABs were determined using a Varian CP-3800 gas chromatograph (GC) interfaced with a Saturn 2000 mass selective detector. Chromatographic separation was obtained with a 60 m \times 0.25 mm I.D. (0.25 μm film thickness) DB-5 capillary column. Mass spectra were acquired in the range of m/z 45–400. Injection was done in the splitless mode and the split mode was turned on after 1 min. Ultra high purity helium was used as a carrier gas with a constant flow rate of 1.3 mL/min. The oven temperature was initially set at 80 °C, immediately ramped to 180 °C at 10 °C/min (held for 10 min), and then to 270 °C at 3 °C/min.

2.4. Quantitation of the LAB mixture by GC/MS

Detailed procedures used to quantify a mixture of LABs that was later employed as a calibration standard is given in [Supplementary material](#).

2.5. Quality assurance/quality control

The correlation coefficients for five-point calibration curves were all higher than 0.993. Recoveries of $\sum\text{LABs}$ (sum of C_{10} – C_{13} -LABs) were $64 \pm 9.8\%$ for filtrate samples, $74 \pm 14\%$ for SPM samples, and $91 \pm 15\%$ for detergents. One procedural blank, one spiked blank and one matrix spiked were analyzed for each set of 20 samples. The average recoveries of the target analytes in the spiked blank and matrix spiked samples were $74 \pm 17\%$ and $69 \pm 13\%$, respectively. The average blank value of $\sum\text{LABs}$ was 0.3 ng/L and no blank corrections were applied to the final results. The lowest concentration level in each calibration curve was defined as the reporting limit (RL) for that specific analyte. The RL was 0.03–0.34 ng/L for individual LAB congeners in filtrate samples based on a sample volume of 20 L and 0.33–3.4 ng/g for 2 g of SPM sample in the selective ion monitoring mode (detailed RL values for individual LAB congeners are presented in [Table S3](#)). Because one of the aims for this study was to estimate the flux of LABs to the SCS, any concentration below

the RL was set as half of the RL. In addition, two bottles (~ 40 L) of deionized and contaminant-free water were carried to the field and exposed to the ambient environment during the course of each field sampling (designated as field blanks). The field blanks were processed in the same manner as the field samples. The concentrations of LABs in all field blanks were below the RLs. Reported concentrations were not surrogate recovery corrected.

3. Results and discussion

3.1. Occurrence of LABs in riverine runoff

C_{10} – C_{13} -LABs were detectable in all 96 filtrate and 96 SPM samples, whereas C_{14} -LABs were not detected in any sample. The concentrations of $\sum\text{LABs}$ in filtrate samples from HM, JM, HQ, HE, MD, JT, HT, and YM ranged from 1.8 to 156, 4.5 to 53, 3.0 to 15, 1.5 to 29, 2.3 to 6124, 1.4 to 394, 4.4 to 31, and 3.2 to 21 ng/L, respectively, as graphically displayed in [Fig. 2a](#) and [Table S2](#). These values were similar to those obtained in South and Southeast Asia, such as Tokyo, Malaysia, and the Mekong Delta ([Isobe et al., 2004](#)). In addition, $\sum\text{LABs}$ concentrations in SPM samples from the same riverine outlets ranged from 0.13 to 11.4, 0.04 to 11.2, 0.04 to 0.76, 0.13 to 2.59, 0.08 to 3.36, 0.01 to 4.39, 0.06 to 10.9, and 0.10 to 7.61 $\mu\text{g/g}$ dry, respectively ([Fig. 2b](#) and [Table S2](#)). These values were generally higher than the concentrations of $\sum\text{LABs}$ from Malaysia and Vietnam but lower than the extremely high concentrations of $\sum\text{LABs}$ (5.29–42.6 $\mu\text{g/g}$ dry) obtained in Jakarta, Indonesia ([Isobe et al., 2004](#)). This indicates that $\sum\text{LABs}$ concentrations in the PRD aquatic environment were slightly higher than the average level of $\sum\text{LABs}$ in South and Southeast Asia.

Concentration ranges of $\sum\text{LABs}$ in both the dissolved and SPM phases (designated as “ $\sum\text{LABs(D + S)}$ ” hereafter) from the eight major runoff outlets are presented in [Table 1](#). The monthly $\sum\text{LABs(D + S)}$ concentrations varied widely with the sampling sites ([Fig. 3](#)). The mean concentrations of $\sum\text{LABs(D + S)}$ in HM, JM, HQ, HE, MD, JT, HT, and YM were 44.3, 91.0, 18.5, 41.4, 46.0, 70.8, 81.2, and 95.7 ng/L, respectively. Overall, the average concentrations of $\sum\text{LABs(D + S)}$ in samples collected from the western four outlets were higher than those from the eastern outlets with the sequence of $\text{YM} > \text{JM} > \text{HT} > \text{JT} > \text{MD} > \text{HM} > \text{HE} > \text{HQ}$ ([Table 1](#)). This may be explained by the fact that watercourses draining into the western outlets run through mostly rural areas where wastewater is largely discharged directly into rivers and streams without treatment, while the populations in the western and eastern regions are quite similar (14.85 versus 15.86 millions) ([National Bureau Statistics of China, 2006](#)). On the other hand, watercourses flowing into the eastern outlets largely pass through several metropolitan centers such as Guangzhou, Huizhou, and Dongguan ([Fig. 1](#)) where a number of municipal sewage treatment plants have been built to treat domestic wastewater ([Yang et al., 2006](#)).

3.2. Biodegradation of LABs

The values of *I/E* (a ratio of the sum of 6- C_{12} , and 5- C_{12} relative to that of 4- C_{12} , 3- C_{12} , and 2- C_{12}), C_{13} -LABs/ C_{12} -LABs,

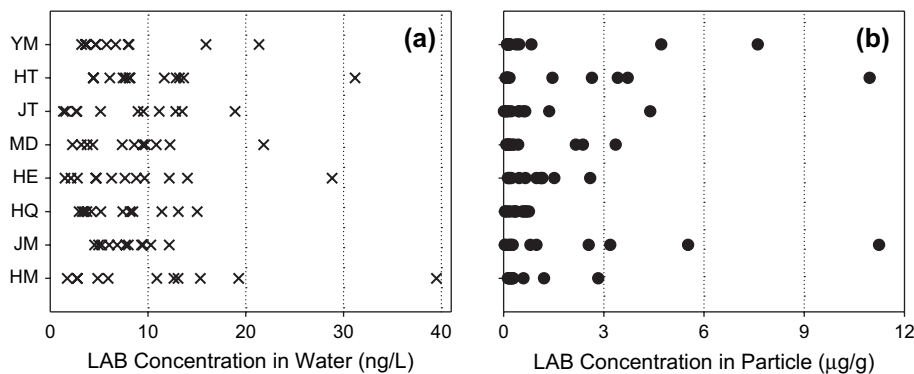


Fig. 2. Concentrations of linear alkylbenzenes (LABs) in water samples collected from the eight major riverine runoff outlets within the Pearl River Delta, China. (a) LABs concentration in water and (b) LABs concentration in particles.

and $(5-C_{13} + 5-C_{12}) / (5-C_{11} + 5-C_{10})$ in riverine samples and detergents are compared in Table 1 and Fig. 4. These ratios have been proposed as indicators of LAB degradation in aquatic environments (Takada and Ishiwatari, 1990; Gustafsson et al., 2001; Luo et al., in press). The *I/E* ratio has been used widely to indicate the degradation of LABs in the environment because previous experiments reported selective biodegradation of the external isomers relative to the internal isomers (Takada and Ishiwatari, 1987, 1990). The ratio, $(5-C_{13} + 5-C_{12}) / (5-C_{11} + 5-C_{10})$, was proposed as another index to indicate LABs degradation in 2001 (Gustafsson et al., 2001). However, the ratio is highly variable among different commercial detergents (Table 1), suggesting that it is difficult to quantitatively evaluate the degree of LAB degradation with this ratio. More recently, a new indicator, $C_{13}\text{-LABs} / C_{12}\text{-LABs}$, was put forward to scale the biodegradation of LABs in aquatic environments (Luo et al., in press).

The ratios of $C_{13}\text{-LABs} / C_{12}\text{-LABs}$ and $(5-C_{13} + 5-C_{12}) / (5-C_{11} + 5-C_{10})$ in riverine samples were consistently lower than those in detergents (Fig. 4b, c), suggesting that LABs present near the runoff outlets of the PRD were degraded to some extent. However, the rate of LABs degradation could not be computed precisely. On the other hand, all the *I/E* ratios in riverine samples were lower than those in detergents (Fig. 4a), contradicting the conclusions based on the ratios of $C_{13}\text{-LABs} / C_{12}\text{-LABs}$ and $(5-C_{13} + 5-C_{12}) / (5-C_{11} + 5-C_{10})$. These results were also inconsistent with previous findings that the *I/E* ratio increased with increasing degree of LAB degradation (Takada and Ishiwatari, 1990). Previous studies also questioned the utility of *I/E* ratio as a suitable indicator of LAB degradation (Gustafsson et al., 2001; Luo et al., in press). A survey of LABs in the coastal environment near Boston Harbor conducted by Gustafsson et al. (2001) found that *I/E* decreased with increasing seaward distance in both water and sediment samples, contrary to the expectation from biodegradation experiments. They put forward three explanations: (1) additional LAB sources around the sampling sites (e.g. ship discharges); (2) some unexamined removal processes enriching the external isomers; and (3) certain mechanisms leading to specific LAB congener interconversion. Apparently, a simple use of *I/E* to indicate the extent of LAB biodegradation at offshore locations has become questionable.

Table 1
LABs in surface water and common detergents

Site	$\sum \text{LABs(D+S)} P^a$	Flux ^b	<i>I/E</i> ratio ^c	C_{13}/C_{12}^d	<i>L/S</i> ratio ^e
HM	10.7–189	1883	0.5–1.0	1.3–3.7	1.9–27
JM	9.8–299	3217	0.5–1.0	1.3–5.8	1.9–17
HQ	5.8–35.8	631.6	0.4–0.7	0.8–3.2	1.3–5.4
HE	9.6–142	1737	0.5–1.2	0.9–2.8	1.2–13
MD	6.3–184	3261	0.5–0.9	1.2–4.5	2.0–14
JT	10.2–397	1837	0.5–1.1	1.2–5.4	2.2–28
HT	8.7–305	496.1	0.5–1.1	1.2–4.2	2.4–18
YM	8.8–634	1197	0.5–1.3	1.0–4.3	1.4–17
PR	5.8–634 ^f	14,259 ^g	0.4–1.7 ^f	0.8–5.8 ^f	1.8–17 ^f
LD			1.0–1.2	0.5–0.9	1.3–2.1
PD			0.9–1.1	0.7–1.2	1.8–3.1
SP			0.5–1.6	0.4–1.0	0.2–2.2

PR: the Pearl River system; LD: liquid detergents; PD: powder detergents; SP: shampoos.

^a All LABs data are for summation of dissolved and particulate phase (in ng/L).

^b Total flux of LABs (in kg/yr).

^c Ratio of $(6-C_{12} + 5-C_{12})$ relative to $(4-C_{12} + 3-C_{12} + 2-C_{12})$.

^d $C_{13}\text{-LABs} / C_{12}\text{-LABs}$ ratio.

^e $(5-C_{13} + 5-C_{12}) / (5-C_{11} + 5-C_{10})$ ratio.

^f Annual mean values.

^g Total flux of LABs from the PRD to the SCS.

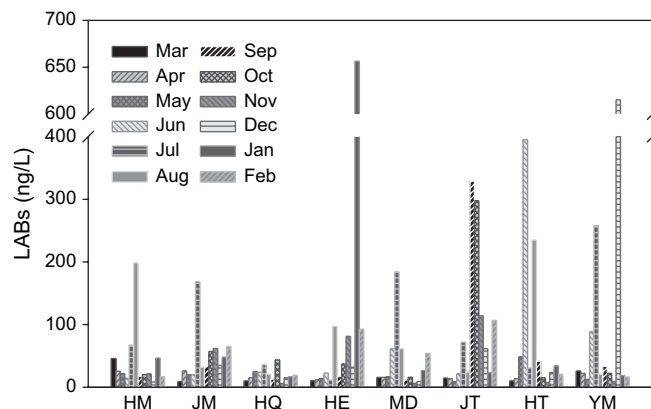


Fig. 3. Temporal and spatial distribution of linear alkylbenzenes (LABs) in the eight major riverine runoff outlets within the Pearl River Delta, China.

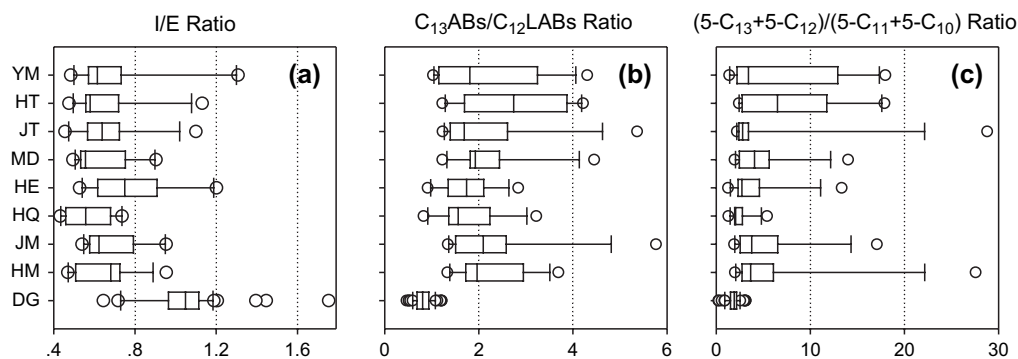


Fig. 4. *I/E* ratio (a), C_{13} -LABs/ C_{12} -LABs ratio (b) and $(5-C_{13}+5-C_{12})/(5-C_{11}+5-C_{10})$ ratio (c) in water samples and detergents around the Pearl River Delta. *I/E* ratio: a ratio of $(6-C_{12}+5-C_{12})$ relative to $(4-C_{12}+3-C_{12}+2-C_{12})$.

To identify any compositional alteration of LABs upon releasing to the aquatic environment, the abundances of LABs with different carbon numbers in filtrate and SPM samples as well as in detergents were calculated (Fig. 5). C_{12} -LAB is the major component in detergents while C_{10} -LAB and C_{13} -LAB are predominant in SPM and filtrate samples, respectively. Obviously, unknown physiochemical changes may have occurred with LAB congeners after they entered the environment. Additionally, all the discussions above were based on an assumption that LABs distributed only between water and SPM and equilibrium was reached. In reality, colloids may be an important phase that LABs would affiliate with, and would affect the phase distribution of LABs. In river water samples, over 90% of LABs were sorbed onto particles larger than $0.1 \mu\text{m}$, and most of the remaining 10% was thought to associate with colloids in the filtrates (Takada and Eganhouse, 1998). Nevertheless, the combined abundance of C_{11} -LABs and C_{12} -LABs decreased notably in environmental samples compared to that in detergents (Fig. 5). This appears to indicate that the combined abundance of C_{11} -LAB and C_{12} -LAB decreases with increasing LABs degradation in aquatic environments. Undoubtedly, more comprehensive data are needed to confirm such a possibility.

3.3. Relationship between riverine fluxes of LABs and hydrophobic organic compounds

The riverine fluxes of LABs from the eight major runoff outlets are summarized in Table 1 (detailed procedures to estimate the fluxes are presented in the Supplementary material). The annual riverine flux of LABs from the PRD to the SCS during 2005–2006 was about 14 tons. This means that approximately 8500 (14 tons/0.00165) tons (the ratio of detergent to LABs is 1:0.00165 determined from the present study) of detergents were discharged to the SCS directly through riverine runoff during our sampling period.

Positive correlations between the concentrations of certain hydrophobic organic compounds (HOCs) and total organic carbon (TOC) have been reported previously (Arzayus et al., 2001; Accardi-Dey and Gschwend, 2002; Hinga, 2003; Chen et al., 2005, 2006b). However, these relationships were mainly

derived from a microcosmic standpoint, and might not account for macroscopic factors (such as local hydrologic conditions) that greatly impact the occurrence of organic contaminants. In the present study we observed a positive relationship between the fluxes of LABs and TOC measured simultaneously

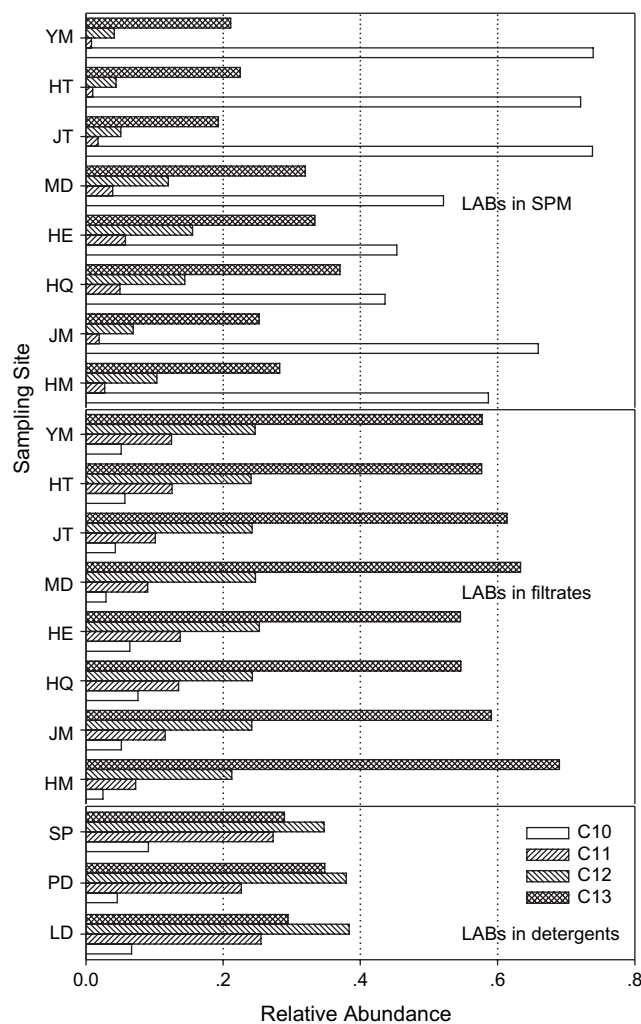


Fig. 5. Distribution of chain length of LABs in suspended particulate matters, water column from the eight major runoff outlets to the SCS, and detergents. LD: liquid detergents; PD: powder detergents; SP: shampoos.

(Fig. 6). In addition, we also investigated the possible relationships between the fluxes of LABs and HOCs that have similar physicochemical properties. Figure S1 shows a positive correlation between the fluxes of LABs and polycyclic aromatic hydrocarbons (PAHs). It is well known that LABs are mainly derived from household detergents (Takada and Eganhouse, 1998) while PAHs mainly from combustion of fossil fuel and biomass in the PRD (Deng et al., 2006). The positive correlation between the fluxes of LABs and PAHs may indicate that the main sources of these two HOCs are associated with human activities or the transport pathways are similar for these two groups of compounds. It also points to the likelihood that LABs can be used as indicators to identify the transport pathways of hydrophobic contaminants, such as PAHs and polychlorinated biphenyls (PCBs). Because the physicochemical properties of LABs are similar to those of PAHs and PCBs (Takada and Eganhouse, 1998), the environmental behavior of LABs can be considered similar to those of PAHs and PCBs as well. On the contrary, LABs and PBDEs were slightly negatively correlated (Figure S2), which means that LABs and PBDEs may have different sources or transport pathways.

3.4. Inventory of LABs in agriculture lands of Guangdong Province

River water is often utilized to irrigate agriculture lands in the PRD. Previous studies (Zhang et al., 1998, 2002b,c; Peng et al., 2002) have found that river water contains high concentrations of LABs and other organic pollutants. The terrestrial environmental compartments, especially agriculture lands, have become a significant sink for LABs and other organic pollutant that have similar physicochemical properties compared to LABs. To use river water safely, it is necessary to assess the loadings of organic pollutants on the soil-dwelling organisms, especially plants such as leafy green vegetables which are the favorite vegetables for the residents living in the PRD, using LABs as the chemical indicators. Because

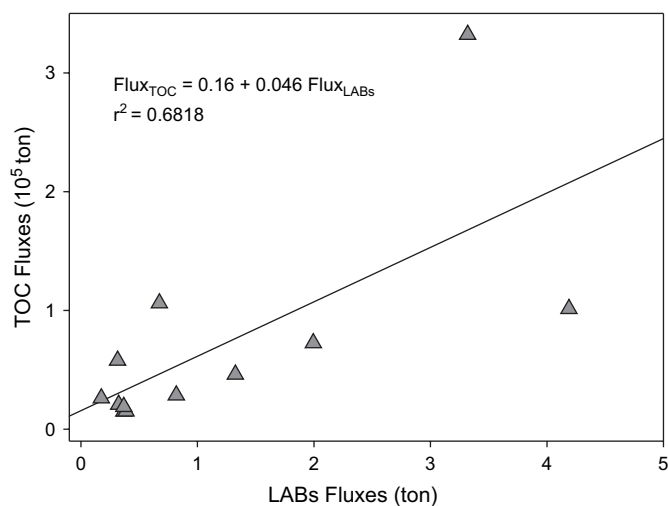


Fig. 6. Relationship between the fluxes of linear alkylbenzenes (LABs) and total organic carbon (TOC).

toxicity is highly dependent upon body loading, a good estimate of the soil inventory of a pollutant should be useful for referring the associated toxicity. Furthermore, the inventory of LABs in the agriculture lands within the PRD should be an indicator of the organic pollutant contributions to leafy green vegetables and crops.

The inventory (I ; in kg/yr) of LABs in agriculture lands was estimated with the following equation:

$$I = k \sum \text{LABs}(D + S)Q_i \quad (1)$$

where Q_i (in $10^8 \text{ m}^3/\text{yr}$) is the consumption of irrigation water in a year (Chen et al., 2000) and k is a conversion factor. The irrigated area, annual mean consumption of irrigation water, and inventories of LABs in different types of farm lands in Guangdong Province are summarized in Table 2. It is obvious that the inventory of LABs in agriculture soil was primarily governed by the annual consumption of irrigation water. Therefore early and late rice fields received more LABs than other crop fields and accounted for approximately 68% of total inventory of LABs in the agriculture lands. Vegetable soil also received a large amount of LABs ($\sim 17\%$ of total inventory), followed by tubers and peanuts fields. Because organic contaminants with similar physicochemical properties to LABs are possibly transported with LABs into agricultural fields and accumulated into crops such as rice and vegetables, food may have become an important “carrier” of organic pollutants.

3.5. Comparison of LABs inputs from social-economic estimates and field measurements

The household detergents are the major source of LABs in the environment; therefore, population may be a major factor controlling the amount of LABs occurring in aquatic environments. To examine this possibility, we estimated the discharge of LABs from domestic wastewater to the coastal ocean by the following equation:

$$D_{\text{LABs}} = kPC_m W_m - I \quad (2)$$

where D_{LABs} is the annual discharge of LABs to the coastal ocean; k is a conversion factor; P is the population in the PRD; C_m is the annual mean consumption of detergents per

Table 2
Inventory of LABs in the effective irrigated agriculture lands of Guangdong Province

Major Products	I.A. ^a	I.W. ^b	I. LABs ^c
Early Rice	10	55	98.8–576
Late Rice	11	64	115–672
Vegetables	9.7	30	53.1–310
Tubers	2.9	5.2	9.4–55
Peanuts	2.7	5.1	9.1–53
Other	4.9	15	27.3–159
Total	41	174	313–1825

^a Irrigated area in 10^5 hectare.

^b Irrigation water in 10^8 m^3 .

^c Inventory of $\sum \text{LABs}(D + S)$ in agriculture lands (kg/yr).

person in the PRD (kg/person/yr); W_m is the mean \sum LABs content in common household detergents (including laundry powders, laundry liquids, and shampoo) determined from the present study; and I is defined in Eq. (1). The figures for world's and China's mean consumption of detergent were estimated at 8–9 and 2–3 kg/person/yr, respectively (Guo, 2001; Wang, 2006). On the other hand, the mean consumption in developed countries is ~ 20 kg/person/yr (Guo, 2001). We suspect that the consumption figure for China could be underestimated. In addition, the PRD has been regarded as a developed region in China. Based on these assessments, we assume that the mean consumption of detergent in the PRD is at least 10 kg/person/yr. With the population of 42,280,000 within the PRD (including Guangzhou, Foshan, Zhongshan, Zhuhai, Jiangmen, Dongguan, Huizhou, and Shenzhen; Fig. 1) (National Bureau Statistics of China, 2006), W_m at 0.00165, and the inventory data (Table 2), the amount of LABs discharged from the PRD to the coastal ocean was estimated at 696 tons/yr. This figure is more than an order of magnitude higher than that estimated from field measurements (Table 1). Three reasons can be given for this. First, the actual consumption of detergents may be lower than the number used in the calculation. Second, degradation of LABs is inevitable after LABs are released into the environment, which would lower the actual LABs concentrations measured in the riverine runoff samples. Third, besides farm soil other kinds of soil (terrestrial particulate matter) may also adsorb LABs.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.envpol.2007.09.010](https://doi.org/10.1016/j.envpol.2007.09.010).

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