Science of the Total Environment 487 (2014) 528–536

Contents lists available at ScienceDirect

Science of the Total Environment

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

# Utility of soil linear alkylbenzenes to assess regional anthropogenic influences with special reference to atmospheric transport

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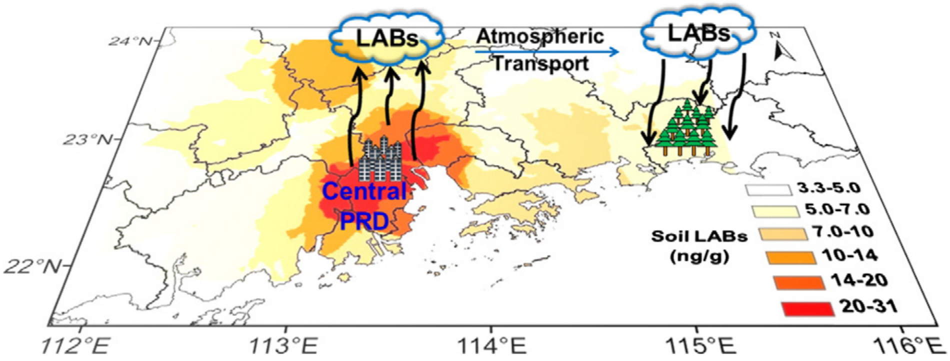
## HIGHLIGHTS

- Soil sewage contamination is light in the Pearl River Delta and its adjacent areas.
- Impact of sewage inputs is mainly confined within the points of discharge.
- Anthropogenic impacts play a major role in the spatial pattern of soil LABs.
- Atmospheric transport is the main route for LABs to diffuse to remote areas.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

*Article history:*
Received 18 February 2014
Received in revised form 28 March 2014
Accepted 16 April 2014
Available online 8 May 2014

Editor: Adrian Covaci

*Keywords:*
Soil linear alkylbenzenes
Sewage pollution
Spatial pattern
Atmospheric transport
Pearl River Delta

## ABSTRACT

Tracing regional anthropogenic influences is important for assessing the magnitude of human interferences with the environment. In the present study, the utility of soil linear alkylbenzenes (LABs) as indicators of anthropogenic influences was examined, with the emphasis on the role of atmospheric transport in dissipating LABs from input sources to remote areas. The Pearl River Delta, South China, which has experienced rapid economic growth and urbanization, was selected as the study region. The concentrations of LABs (mean: 8.6 ng/g and median: 5.7 ng/g, with an outlier of 2020 ng/g excluded) suggested that sewage contamination throughout the entire study region was generally light. The spatial variation of sewage pollution was significantly positively correlated with population density and per capita gross domestic product, with hot spots concentrated in the central PRD. Atmospheric deposition was hypothesized as an important input route for soil LABs in forestry and drinking water source areas with little impact of irrigation or direct wastewater discharge. This proposition could explain the opposite spatial patterns of LAB concentrations and values of a biodegradation index $(5\text{-C}_{12} + 5\text{-C}_{13}) / (5\text{-C}_{11} + 5\text{-C}_{10})$, where $i\text{-C}_n$ defines a specific LAB congener with $i$ and $n$ indicating the position of the phenyl group and the number of carbon atoms on the alkyl chain, respectively. These findings somewhat validated LABs as tracers of regional anthropogenically derived contamination, with atmospheric transport of LABs as a viable dissipating mechanism.

## 1. Introduction

Rapid urbanization and population growth have posed increasing anthropogenic influences on the environment at multiple scales

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http://dx.doi.org/10.1016/j.scitotenv.2014.04.067
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(Hardoy et al., 2001; Grimm et al., 2008; Marcotullio et al., 2008). Soil, an important compartment of the environment, is regarded as a major reservoir of pollutants (Wild et al., 1990; Wild and Jones, 1995), and thus can be used to reflect anthropogenic footprints. Anthropogenic pollutants generated from diverse sources (Doney, 2010) can be redistributed via a number of routes, such as hydrodynamic and atmospheric transport, and exerted impacts even on areas distant from points of discharge (Heywood et al., 2006; Nam et al., 2009). Due to the complexity of input sources and transport mechanisms, geochemical markers have often been utilized in tracking anthropogenic influences.

Our previous study (Wei et al., 2014b) utilized soil polycyclic aromatic hydrocarbons (PAHs) to elucidate anthropogenic impacts on the terrestrial environment of a large watershed in South China, the Pearl River Delta (PRD; Fig. S1 of the Supplementary data; “S” indicates tables and figures in the Supplementary data thereafter), and the central PRD was found to have become a secondary source of PAHs to the adjacent areas through atmospheric transport. Because PAHs are not exclusively derived from anthropogenic sources but also generated from natural origins (Gagosian et al., 1981; Mai et al., 2003a), our previous conclusion required further solidification. To this end, additional evidence can be obtained from linear alkylbenzenes (LABs), which are uniquely associated with the production of linear alkylbenzene sulfonates (LASs) (Eganhouse et al., 1983), one of the most widely used anionic detergents and surfactants. Linear alkylbenzenes can be discharged into the environment as residues (1–3%) of commercial detergents (Hartmann et al., 2000; Eganhouse and Sherblom, 2001; Heim et al., 2004; Isobe et al., 2004), and in fact have been detected in various environmental matrices from different regions worldwide (Eganhouse et al., 1983; Takada and Ishiwatari, 1987; Takada et al., 1992; Isobe et al., 2004; Medeiros and Bícego, 2004; Martins et al., 2010, 2012; Venkatesan et al., 2010; Rinawati et al., 2012). For example, previous studies presented evidence for direct discharge of untreated wastewater, which may have exerted strong impacts on aquatic systems of the PRD and the adjacent South China Sea (Luo et al., 2008; Ni et al., 2008; Zhang et al., 2012). Fluvial runoff was regarded as the dominant route for transporting LABs from sources to the riverine and coastal systems (Luo et al., 2008; Ni et al., 2008, 2009). In addition, irrigation with polluted river water was assessed as an important input mode for LABs in agricultural lands (Ni et al., 2009). Despite these previous efforts, whether soil LABs can be used for assessing anthropogenic influences on a regional scale, particularly if LABs can be volatilized into the atmosphere and transported to remote areas, a largely unverified proposition, remained to be examined.

We set out to address the above-mentioned issues by collecting a large number of surface soil samples from the PRD and adjacent regions (Fig. S1), one of the economically fastest growing but also most contaminated regions in China, and analyzed them for LABs. The magnitude of sewage contamination was assessed by exploring the spatial distribution and compositional profiles of soil LABs. To examine the importance of atmospheric transport in dispersing LABs, we also analyzed rainfall, dry particle deposition and aerosol samples collected in Guangzhou, a megalopolis within the PRD.

## 2. Materials and methods

### 2.1. Materials

Linear alkylbenzene components are abbreviated as $i$-$C_n$, where $n$ represents the number of carbon atoms in the alkyl chain and $i$ indicates the position of the phenyl group. Because there were only a few individual LAB standards available commercially (all were 1-$C_n$), these LAB standards consisting of 1-$C_n$ ($n = 10$–$14$) obtained from Sigma Aldrich (St. Louis, MO, USA) were used as primary calibration standards. A mixture of LABs containing homologues of $C_{10}$, $C_{11}$, $C_{12}$ and $C_{13}$ except for 1-$C_n$ ($n = 10$–$13$), the sum of which is designated as ΣLAB (sum of the LAB congeners in each homologue is labeled as Σ$C_n$-LAB), was purchased from Procter & Gamble (Guangzhou, China) and used as a secondary standard. 1-Phenyldodecane-$d_{30}$ and 1-phenylpentadecane-$d_{36}$ were utilized as the surrogate and internal standards, respectively, both obtained from C/D/N Isotopes (Pointe-Claire, Quebec, Canada). Assuming that the relative response factors of all LABs in an isomeric group were identical, the secondary standards, including $C_{10}$-LABs, $C_{11}$-LABs, $C_{12}$-LABs, and $C_{13}$-LABs, were quantified with the calibration curves of 1-$C_{10}$, 1-$C_{11}$, 1-$C_{12}$, and 1-$C_{13}$, respectively. The calibration procedures were detailed in a previous study (Ni et al., 2008).

### 2.2. Field sampling

The procedures for soil sampling design and collection were detailed previously (Wei et al., 2014b). Briefly, a total of 224 surface soil samples were collected between December 2009 and March 2010 in the PRD and adjacent areas from six land-use types, i.e., industry, agriculture, drinking water source, landfill, residency, and forestry (Fig. S1). For further comparison of spatial patterns, the study sites were also divided into four geographic regions (Fig. S1) containing various numbers of administrative districts (listed in parentheses): (a) the West region (Yangjiang and Yunfu); (b) the PRD's periphery (Zhaoqing, Qingyuan, Jiangmen and Huizhou); (c) the central PRD (Guangzhou, Foshan, Dongguan, Zhongshan, Zhuhai and Shenzhen); and (d) the East region (Heyuan, Shanwei and Shaoguan). In addition, a total of 157 rainfall samples were collected from three districts (Tianhe, Haizhu and Luogang) of Guangzhou, whereas dry particle deposition and aerosol samples were collected monthly at Tianhe District. The detailed procedures for sample collection and pretreatment were described in a previous study (Guo et al., 2014).

### 2.3. Sample extraction

The procedures of sample extraction and purification/fractionation used in the present study were detailed previously (Zeng et al., 1997; Ni et al., 2008). Briefly, freeze-dried soil samples (~25 g), loaded GF/F filters, and PUF plugs were spiked with the surrogate standard, and Soxhlet-extracted with 200 mL of a mixture of dichloromethane and acetone (1:1 in volume) for 48 h, separately. For filtered rain samples, glass columns packed with a mixture of XAD-2 and XAD-4 resins (1:1 in mass) were used to retain the target analytes, which were eluted three times with dichloromethane. The extract was concentrated, solvent-exchanged to hexane, and purified/fractionated on a glass column filled with alumina/silica gel (1:2 in volume). The fraction containing LABs was eluted with 30 mL of hexane, evaporated to 0.5 mL, and spiked with the internal standard prior to instrumental analysis.

### 2.4. Instrumental analysis

Concentrations of LABs were quantified with a Shimadzu GC/MS-QP2010. Chromatographic separation was achieved with a 30 m × 0.25 mm × 0.25 μm DB-5MS column (J&W Scientific, Folsom, CA, USA). Column temperature was programmed from 80 °C to 290 °C at a rate of 5 °C/min and held for 30 min. Temperatures of injection, ion source and interface were maintained at 280, 250 and 250 °C, respectively. Mass spectra were acquired in the electron impact and selective ion monitoring modes, with characteristic ions at $m/z$ 91 and 105 for $C_{10}$–$C_{13}$-LABs except for 1-$C_n$, $m/z$ 100 for the surrogate and internal standards, and $m/z$ 92 for 1-$C_n$-LABs (Luo et al., 2008; Ni et al., 2008). Typical capillary gas chromatograms of LABs are displayed in Fig. S2.

### 2.5. Measurements of total organic carbon

Measurement of total organic carbon (TOC) followed a previously described procedure (Mai et al., 2003b). Briefly, approximately 1 g of each dried soil sample was treated with 10% hydrochloric acid to remove inorganic carbon, washed with deionized water for 5 times, and dried at 60 °C to constant weight. The content of TOC was determined with a C230 carbon determinator (LECO, MI, USA) (Table S1). Acetanilide was used as an external calibration standard.

### 2.6. Quality assurance and quality control

For every 15 field samples, a procedural blank, a spiked blank and a matrix spiked sample were also processed, where the primary calibration standards were used in the blank and matrix spiked samples. Recoveries (mean ± standard deviation) of the surrogate standard were 90 ± 12% for QA/QC samples, 97 ± 19% for soil samples, 91 ± 20% for wet deposition samples, and 75 ± 15% for dry deposition samples. In addition, the recoveries of the target analytes from spiked blank and matrix spiked samples were 84 ± 10% and 87 ± 9.6%, respectively. If the concentrations of LABs in the procedural blanks were greater than the lowest calibration levels (1.32–5.85 ng/mL; Fig. S2a), the average blank values of LABs in a final extract volume of 0.5 mL divided by the average sample weight (482 m$^3$ and 30 L for aerosol and rainfall samples, respectively) were defined as the reporting limits (RL; Table S2). Otherwise, the lowest calibration levels were divided by the average sample weight (25.2 g and 0.36 g for soil and dry particle deposition samples, respectively) and a final extract volume of 0.5 mL to obtain RL (Table S2). Consequently, the reported LAB concentrations in soil and dry particle deposition samples were not blank corrected, while the LAB levels in aerosol and wet deposition samples were corrected with blank values. A zero value was reported for any concentration below the RL in concentration calculation, whereas half a RL was used in compositional analysis.

### 2.7. Data analysis

In the present study, three molecular indices, i.e., $(6\text{-}C_{12} + 5\text{-}C_{12}) / (4\text{-}C_{12} + 3\text{-}C_{12} + 2\text{-}C_{12})$, $(5\text{-}C_{12} + 5\text{-}C_{13}) / (5\text{-}C_{11} + 5\text{-}C_{10})$ and $\Sigma C_{13}$-LAB / $\Sigma C_{12}$-LAB (abbreviated as I/E, L/S, and $C_{13}/C_{12}$, respectively), were employed to evaluate the likelihood for the degradation of LABs, which is based on the preferential biodegradation of external isomers over inner isomers (Eganhouse et al., 1983; Takada and Ishiwatari, 1990), as well as more susceptibility to degradation of short-chain homologues than long-chain homologues (Gustafsson et al., 2001; Eganhouse and Pontolillo, 2008). Compared with detergents, the indices with higher values indicate the occurrence of degradation and they all increase with increasing extent of degradation.

Significant differences in concentrations, degradation indicators and compositional profiles of LABs were examined using one-way analysis of variance and nonparametric Kruskal–Wallis H tests with statistical significance defined at $p < 0.05$, performed with SPSS 13.0 (Chicago, IL, USA). The Ordinary Kriging interpolation method was used to characterize the spatial distribution of LABs in soils for assessing sewage contamination, which was carried out with ArcGIS 9.3 (ESRI, Redlands, California, USA) (Juang and Lee, 1998; Carlon et al., 2001; Hu et al., 2006, 2009).

## 3. Results and discussion

### 3.1. Occurrence of linear alkylbenzenes in soil and precipitation

The concentrations of $\Sigma$LAB (ng/g; in dry sample weight thereafter) varied in a range of 1.2–2020 ng/g with an arithmetic mean of 18 ng/g and a median of 5.8 ng/g, and the range, mean and median values became 1.2–122, 8.6 and 5.7 ng/g, respectively, after an extremely high concentration of 2020 ng/g in an industrial soil collected near a paper mill in Dongguan was excluded (Tables 1 and S1). Descriptive analysis indicated that the value of 2020 ng/g was substantially greater than the sum of median (5.8 ng/g) and three times of standard deviation (135 ng/g), thereby it was treated as an outlier. Conversely, all other concentrations (1.2–122 ng/g, $n = 223$) were considered as normal values for spatial distribution. Interestingly, this high concentration was comparable to those (with a mean of 2300 ng/g) in sediments near paper mill outfalls in Dongguan since LASs were extensively used for dyeing in papermaking industries (Zhang et al., 2012). In addition, the relative abundances of individual LAB components in this soil sample were similar to those in industrial effluents (dissolved and particulate phases combined) and sediments near the paper mill outfalls (Fig. 1) (Zhang et al., 2012). Furthermore, this industrial soil was also enriched with TOC (25.7%) and PAHs (21,000 and 12,000 ng/g for $\Sigma_{28}$PAH and $\Sigma_{15}$PAH, respectively) (Wei et al., 2014b). Hence, the soil sample was probably contaminated by point sources (e.g., wastewater from paper mills (Zhang et al., 2012) and petroleum industry (Wei et al., 2014b)), and can be treated as a point-source soil. As a result, it is reasonable to exclude this sample from significant difference tests and Kriging interpolation for spatial distribution. Besides, we detected notable levels of $\Sigma$LAB (range; mean; median) in wet deposition (3.28–3300; 393; 189 ng/L), dry particle deposition (0.54–4.66; 1.57; 0.94 μg/g) and aerosol samples (10.5–146; 58.6; 38.6 ng/m$^3$) collected in Guangzhou.

Compared with available LAB data in various environments around the world (Table S3), the concentrations of LABs in most soil samples in the present study were substantially lower than those in sewage sludge (Takada et al., 1994; Luo et al., 2008) and the particulate phase of riverine runoff (Takada and Ishiwatari, 1987; Ni et al., 2008). They were also substantially lower than those in river sediments from Zhujiang River, Xijiang River and Dongjiang River of the PRD (Luo et al., 2008; Zhang et al., 2012), Sumidagawa River and Tamagawa River in Japan (Takada and Ishiwatari, 1987), and Arakawa River (Takada et al., 1992), lake sediments from Chaohu Lake (Wang et al., 2012), and coastal sediments from the coastal zones of Guangdong

**Table 1**
Concentrations (ng/g, dry weight) of linear alkylbenzenes in soils collected in the Pearl River Delta (PRD) and adjacent areas.

| District | No. of samples | Range | Mean | Median |
|---|---|---|---|---|
| Guangzhou | 26 | 1.8–21 | 9.0 | 9.1 |
| Foshan | 11 | 1.2–48 | 8.5 | 3.2 |
| Dongguan[a] | 18 | 2.3–48 | 17 | 12 |
| Zhongshan | 9 | 3.7–122 | 22 | 8.6 |
| Zhuhai | 7 | 3.6–14 | 6.9 | 5.8 |
| Shenzhen | 9 | 3.8–14 | 9.3 | 11 |
| Huizhou | 37 | 1.8–18 | 6.0 | 4.8 |
| Shanwei | 4 | 1.8–2.8 | 2.3 | 2.3 |
| Heyuan | 19 | 1.9–11 | 4.2 | 3.1 |
| Shaoguan | 3 | 1.5–8.8 | 4.3 | 2.7 |
| Qingyuan | 17 | 1.5–52 | 11 | 7.6 |
| Zhaoqing | 29 | 1.4–38 | 8.0 | 6.1 |
| Yunfu | 8 | 1.9–10 | 5.7 | 5.7 |
| Jiangmen | 24 | 1.3–35 | 7.0 | 5.7 |
| Yangjiang | 3 | 1.6–6.4 | 4.4 | 5.1 |
| West region[b] | 11 | 1.6–10 | 5.3 | 5.6 |
| PRD's periphery[b] | 107 | 1.4–52 | 7.5 | 5.7 |
| Central PRD[a, b] | 80 | 1.2–122 | 12 | 8.6 |
| East region[b] | 25 | 1.5–9.0 | 3.8 | 2.8 |
| Total [a] | 224 | 1.2–122 | 8.6 | 5.7 |

[a] An extremely high concentration (2020 ng/g dry weight) was found in an industrial soil close to a paper mill, which was excluded in the calculation of mean and median values.

[b] The study region is divided into four geographic regions (Fig. S1): the West region (Yangjiang and Yunfu); PRD's periphery (Zhaoqing, Qingyuan, Jiangmen and Huizhou); central PRD (Guangzhou, Foshan, Dongguan, Zhongshan, Zhuhai and Shenzhen); and East region (Heyuan, Shanwei and Shaoguan).

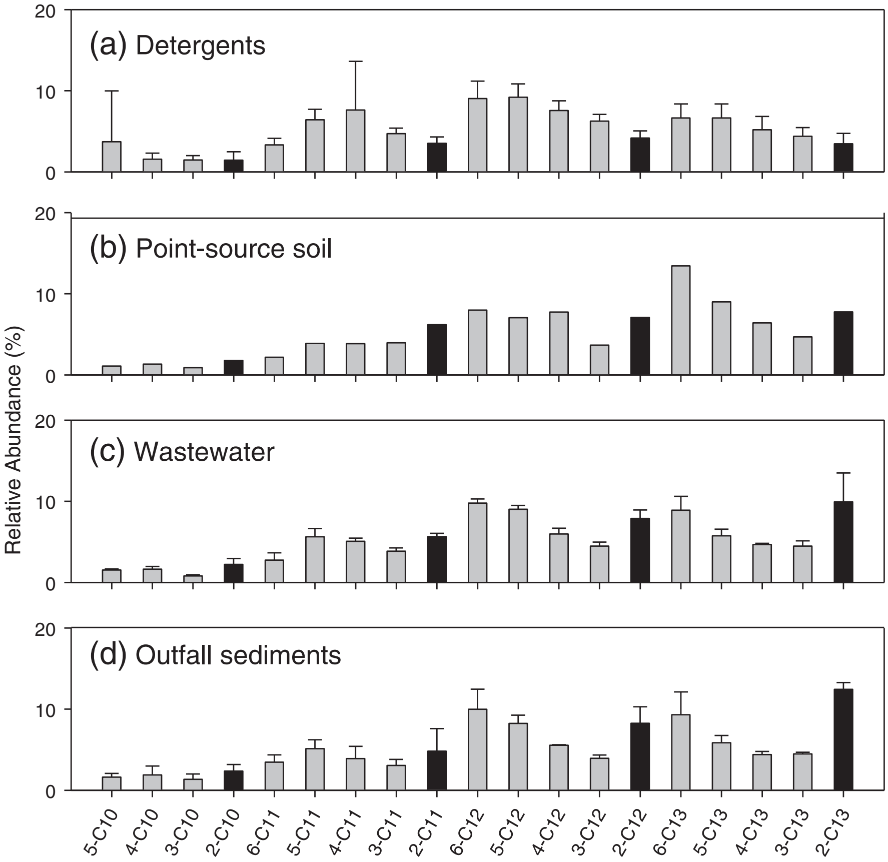

**Fig. 1.** The relative abundances (%) of individual linear alkylbenzene congeners in (a) detergents (Ni et al., 2008); (b) an industrial soil close to a paper mill in Dongguan (with an extremely high concentration of 2020 ng/g; present study); (c) wastewater; and (d) sediments from paper mill outfalls in Dongguan (Zhang et al., 2012).

Province (Liu et al., 2013), Jakarta Bay (Rinawati et al., 2012), Santa Monica Bay (Venkatesan et al., 2010), Victoria Harbor (Hong et al., 1995), Barcelona Harbor (Díez et al., 2006), Tokyo Bay (Takada et al., 1992), South and Southeast Asia (Isobe et al., 2004), and Southern California Bight (Macías-Zamora and Ramírez-Alvarez, 2004). They were slightly lower than those in nearshore sediments from the Pearl River Estuary and the northern South China Sea (Luo et al., 2008) and Admiralty Bay (Martins et al., 2012). These findings suggested that contamination of soil by sewage was generally light in the PRD; the impacts of wastewater discharge appeared to be mostly confined around the points of discharge.

### 3.2. Spatial distribution

Spatially, the levels of ΣLAB (Table 1) in the West region were not significantly ($p > 0.05$) different from those in the other three geographical regions, but ΣLAB levels considerably varied ($p < 0.05$) among the PRD's periphery, central PRD and East region (Table S4). Hot spots were concentrated around the large metropolises within the central PRD (Fig. 2a), which are more economically prosperous and densely populated and subsequently are supposed to bear more intensive anthropogenic influences than other three regions. As expected, samples from the West and East regions less economically developed and populated contained substantially lower concentrations of ΣLAB than those from the central PRD. Apparently, the spatial distribution pattern of ΣLAB levels indicated greater anthropogenic impacts on the terrestrial environment of the central PRD than the other three regions, and the central PRD may have served as an important source of LABs found in remote areas. This spatial pattern of soil LABs was similar to that of soil PAHs with higher concentrations of both $\Sigma_{28}$PAH and $\Sigma_{15}$PAH in the central PRD than in other three geographic regions (Wei et al., 2014b), indicating that the concentrations of both LABs and PAHs were well reflective of anthropogenic influences on the regional terrestrial environment.

Among six land-use types, there was no significant difference for ΣLAB concentrations among industry, agriculture and residency ($p > 0.05$), while other land-use types had significant differences ($p < 0.05$) between each other (Tables 2 and S5). The magnitude of sewage pollution (and therefore anthropogenic impact) was also strongly associated with land-use types, with heavier sewage contamination in anthropogenic landscapes than in natural landscapes (Su et al., 2011; Wang et al., 2013).

### 3.3. Implications of anthropogenic influences

The central PRD is more populated (1870 persons/km$^2$) and discharges larger amounts of domestic wastewater (5.68 million m$^3$/d) than the other three regions (in the ranges of 228–307 persons/km$^2$ and 0.1–0.53 million m$^3$/d, respectively) (Statistical Bureau of Guangdong Province, 2011). Although daily wastewater treatment capacity in the central PRD (8.43 million m$^3$/d) was much larger than those in the PRD's periphery, East and West regions (1.31, 0.66 and 0.19 million m$^3$/d, respectively) (JianQiang Environmental, 2011), higher ΣLAB levels within the central PRD suggested that some portions of the large volume of wastewater generated in the central PRD may have been discharged without treatment. This was consistent with a previously reached conclusion that population was a major factor in controlling ΣLAB levels in riverine runoffs (Ni et al., 2008), as LABs were predominantly derived from domestic wastewater discharge. Besides, Ni et al. (2008) obtained the highest degradation rate of LABs in wastewater collected from the oxidation ponds of wastewater treatment plants and ascribed biodegradation under aerobic conditions

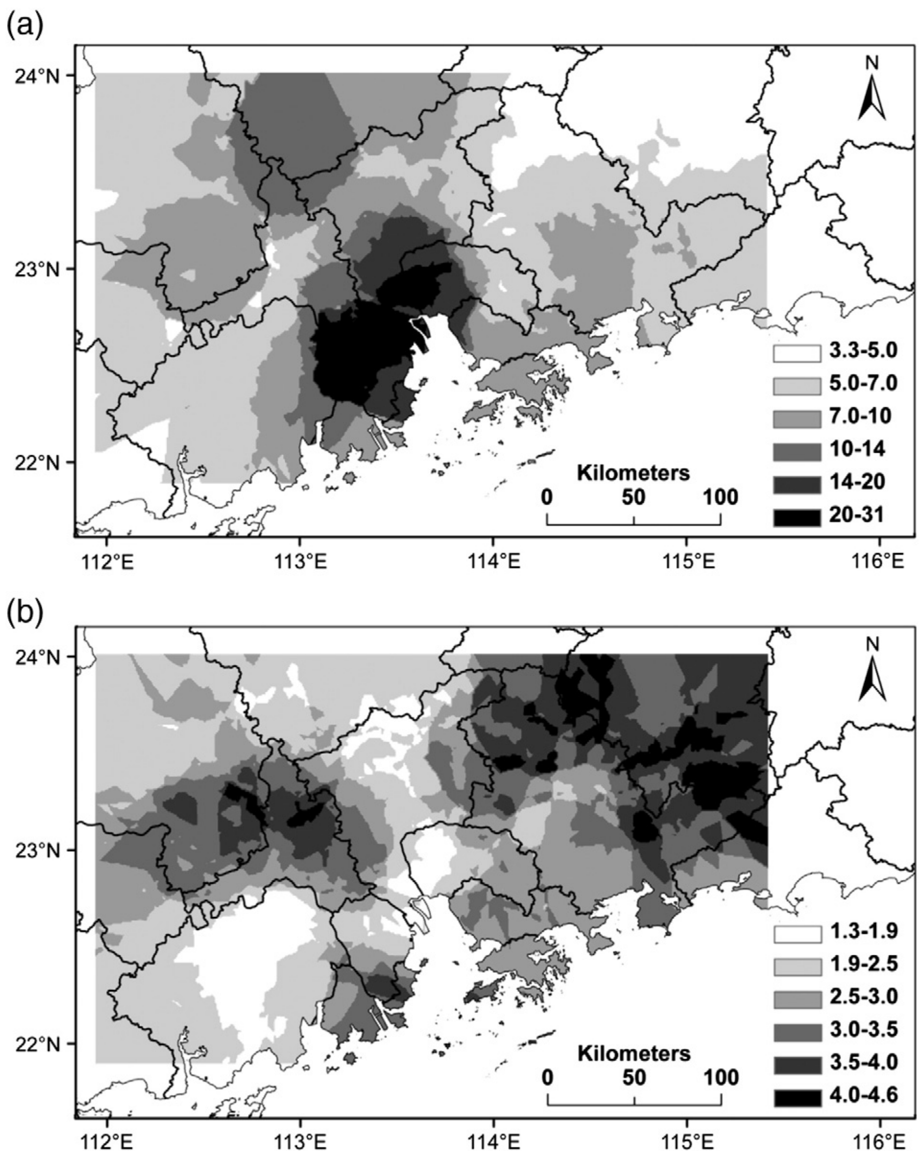

**Fig. 2.** Spatial distribution patterns of (a) the concentrations (ng/g dry weight) of linear alkylbenzenes (LABs) and (b) $(5\text{-C}_{13} + 5\text{-C}_{12}) / (5\text{-C}_{11} + 5\text{-C}_{10})$ values in soils from the Pearl River Delta and adjacent areas with Kriging interpolation. An extremely high concentration (2020 ng/g dry weight) of LABs detected in an industrial soil close to a paper mill in Dongguan was excluded in Kriging interpolation.

as the principal removal mechanism for LABs, which was in accordance with a previous study (Takada et al., 1992). As a result, enhanced oxidation during wastewater treatment may be an effective way for aggressive removal or mitigation of LABs.

Arithmetic mean concentrations of soil ΣLAB were moderately correlated with the population densities ($r^2 = 0.44$, $p < 0.05$; Fig. 3a) of the administrative districts (Statistical Bureau of Guangdong Province, 2011). This implied that domestic wastewater discharge was mainly responsible for soil pollution by sewage in the PRD. However, limited industrial usage of LASs in papermaking, textile printing and dyeing industries (Zhang et al., 2012) may account for an insignificant relationship between the mean ΣLAB levels and per capita gross domestic product (GDP) ($r^2 = 0.19$, $p > 0.05$; Fig. 3c). Moreover, high concentrations of ΣLAB in landfill soils from Zhongshan (121 ng/g) and Qingyuan (52 ng/g) and in industrial soils from Dongguan (with a mean of 22 ng/g), probably suggested the existence of point sources that increased the mean ΣLAB levels in these administrative districts. If these data points are excluded, significant correlations can be obtained between the arithmetic average ΣLAB concentrations and population densities ($r^2 = 0.75$, $p < 0.05$; Fig. 3b), as well as between ΣLAB concentrations and per capita GDP ($r^2 = 0.75$, $p < 0.05$; Fig. 3d). These significant positive correlations suggested that both population density and economic prosperity may have dictated the regional consumption pattern of LAS-type detergents and domestic wastewater discharge, and consequently implicated the influences of human activities. However, no significant correlation between the ΣLAB levels and TOC

**Table 2**
Concentrations (ng/g dry weight) of linear alkylbenzenes in soils of various land-use types.

| Land-use type | No. of samples | Range | Mean | Median |
|---|---|---|---|---|
| Industry[a] | 28 | 1.9–44 | 13 | 8.7 |
| Agriculture | 64 | 1.4–48 | 8.4 | 5.7 |
| Drinking water source | 21 | 1.5–6.9 | 3.6 | 3.5 |
| Landfill | 7 | 7.0–122 | 32 | 10 |
| Residency | 30 | 1.8–38 | 9.8 | 9.5 |
| Forestry | 74 | 1.2–16 | 6.1 | 5.2 |
| Total[a] | 224 | 1.2–122 | 8.6 | 5.7 |

[a] An extremely high concentration (2020 ng/g dry weight) was found in an industrial soil close to a paper mill, which was excluded in the calculation of mean and median values.

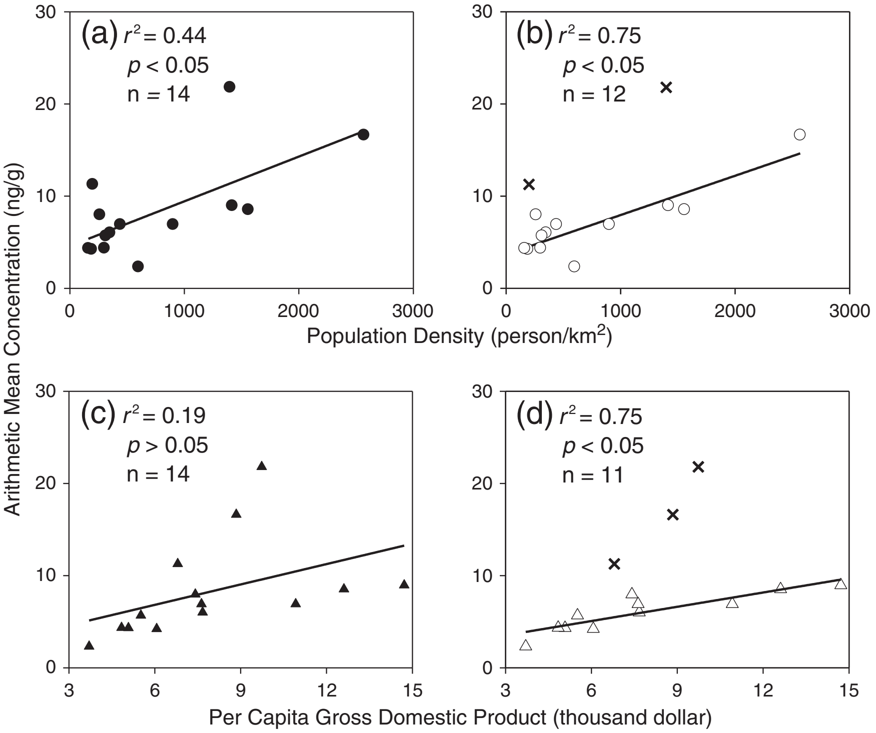

**Fig. 3.** Correlation between arithmetic mean concentrations of linear alkylbenzenes (LABs) and (a) population densities for individual administrative districts; (b) population densities except for Zhongshan and Qingyuan (in crosses); (c) per capita gross domestic product (GDP); and (d) per capita GDP except for Dongguan, Zhongshan and Qingyuan (in crosses). The data of population density and per capita GDP for the administrative districts were documented from Guangdong Statistical Yearbook (Statistical Bureau of Guangdong Province, 2011).

($r^2 = 0.06$, $p < 0.05$; Fig. S3a) possibly implied that soil organic matter was not the key factor controlling the distribution of hydrophobic compounds in soils, which was also corroborated by the poor correlation between TOC and PAHs (Wei et al., 2014b). Besides, a weak relationship between the concentrations of ΣLAB and anthropogenic PAHs ($\Sigma_{15}$PAH) (Wei et al., 2014b) ($r^2 = 0.18$, $p < 0.05$; Fig. S3b) in soils was ascribed to different input sources for LABs and PAHs.

Higher L/S values (range; mean; 95% confidence interval) in soils (0.20–16; 2.9; 2.6–3.2) than those in domestic detergents (0.22–3.1; 1.8; 1.7–2.0) (Ni et al., 2008) indicated possible degradation of LABs in soils, whereas comparable values of I/E (0.42–5.9; 1.0; 0.93–1.1) and $C_{13}/C_{12}$ (0.07–7.4; 0.77; 0.70–0.85) to those for detergents (0.52–1.6; 1.0; 0.96–1.1 for I/E, and 0.46–1.2; 0.83; 0.78–0.88 for $C_{13}/C_{12}$) (Ni et al., 2008) suggested no progressive degradation of LABs.

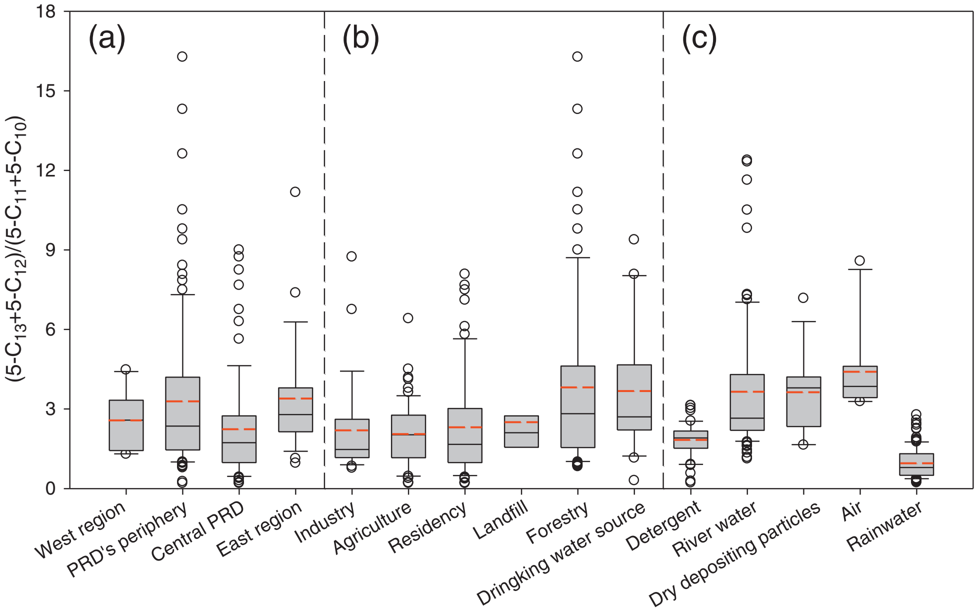

**Fig. 4.** Box plots (10th, 25th, 50th, 75th, and 90th percentiles and mean values) of ($5\text{-}C_{13} + 5\text{-}C_{12}$) / ($5\text{-}C_{11} + 5\text{-}C_{10}$) for (a) soils from four geographic regions (defined in Fig. S1); (b) soils of six land-use types, i.e., industry, agriculture, residency, landfill, forestry and drinking water source; and (c) various environmental matrices, including detergent (Ni et al., 2008), river water (Ni et al., 2008), and dry depositing particles, air, and rainwater samples (present study).

Similar contradiction was also reported previously and L/S was suggested as a more reliable indicator of LAB degradation in offshore sediments (Gustafsson et al., 2001; Luo et al., 2008). For soils, statistically higher L/S values ($p < 0.05$) were observed in the PRD's periphery, East and West regions than in the central PRD (Fig. 4a). Visually, the spatial distribution pattern of L/S values (Fig. 2b) was basically opposite to that of ΣLAB concentrations (Fig. 2a). In fact, with the exception of Zhongshan, Qingyuan, Zhuhai and Shanwei, the L/S values were negatively correlated with ΣLAB concentrations ($r^2 = 0.45$, $p < 0.05$; Fig. S4b) based on the administrative districts. Apparently, the spatial variability of the L/S values was well reflective of the patterns of regional sewage contamination and LAB degradation.

### 3.4. Transport mechanisms

The compositional profiles of soil LABs were predominated by $C_{12}$-LABs (44 ± 11%), followed by $C_{13}$-LABs (31 ± 9%), $C_{11}$-LABs (13 ± 11%) and $C_{10}$-LABs (11 ± 7%) (Fig. 5). Among all correlations (Table S4), there were significant differences ($p < 0.05$) for values of $C_{11}$-LABs and $C_{12}$-LABs among the PRD's periphery, central PRD, and East region, for $C_{10}$-LABs between the PRD's periphery and central PRD, and for $C_{12}$-LABs between the East and West regions. A previous study found similar compositional profiles of LABs for commercial detergents commonly used in Guangdong Province, which implicated a quite unanimous source of LABs in the study region (Ni et al., 2008). In addition, the compositional profiles of LABs were similar in river water from both the central PRD and the West region (Ni et al., 2008). However, LAB compositions varied among different environmental compartments of the PRD, i.e., detergent (Ni et al., 2009), soil (present study), wastewater (Zhang et al., 2012), river water (Ni et al., 2008), and air and rainwater (Fig. 5 and Table S6), possibly suggesting congener specificity of transport mechanisms, as well as subsequent phase partitioning and degradation potentials, for LAB components from sources to receptors.

Hydrodynamic flow and atmospheric transport are considered as the dominant input routes for hydrophobic contaminants in soils (Wania et al., 1998; Jones and de Voogt, 1999). Ni et al. (2009) observed the widespread occurrence of LABs in riverine runoff of the PRD and estimated that irrigation with polluted river water was a key pathway for LABs to enter agricultural lands. Moreover, direct wastewater discharge from paper mills around Dongguan (Zhang et al., 2012) was suggested as a point source for soil LABs, but it might be confined in a small area. Although 45% of the sewage sludge produced was utilized in agricultural soils of China (Chen et al., 2012), the extremely poor correlation of ΣLAB levels and TOC (Fig. S3a; $p < 0.05$) dismissed the application of composted sewage sludge in soils as the main input route for soil LABs.

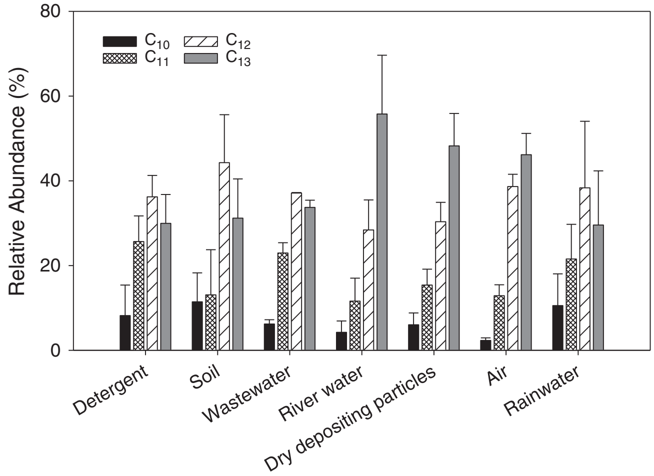

**Fig. 5.** Compositional profiles of linear alkyl benzenes in detergents (Ni et al., 2008), soils (present study), wastewater of paper mills in Dongguan (Zhang et al., 2012), river water (Ni et al., 2008), and dry depositing particles, air, and rainwater collected from Guangzhou (present study).

Because of the low vapor pressures for LABs (from 0.015 Pa for 2-$C_{13}$-LAB to 0.418 Pa for 5-$C_{10}$-LAB) (Sherblom et al., 1992) and no report of LABs in the atmosphere, atmospheric transport of LABs has not been considered a viable transport mechanism (Gustafsson et al., 2001; Ni et al., 2009). In the present study, we detected considerable levels of LABs in precipitation, dry particle deposition, and aerosol samples, which pointed to the possibility for volatilization of LABs into the atmosphere, atmospheric transport, and aerial deposition into soils. A previous study (Takada et al., 1992) on hydrodynamic transport of LABs in coastal zones demonstrated that hydrophobic LABs were associated with lower-density particles and could be transported greater distances than PAHs. On one hand, high average concentrations of fine particulate matter ($PM_{2.5}$) in Guangdong Province (ranging from 37 to 139 μg/m$^3$ for 2001–2008) (Cao et al., 2003; Hagler et al., 2006; Deng et al., 2013) are possibly the basis for atmospheric transport of particle-bound hydrophobic pollutants. On the other hand, a previous study suggested a significant contribution of atmospheric inputs to sedimentary LABs in open sea distant from the coastline of China (Wei et al., 2014a). All these findings favor atmospheric transport and aerial deposition as the predominant mechanisms for the widespread occurrence of LABs on a regional scale.

In fact, atmospheric deposition can reasonably explain the occurrence of soil LABs in the forestry and drinking water source areas, which are without irrigation inputs and/or away from any points of direct wastewater discharge (Fig. S5). The L/S values in soil samples from the forestry and drinking water source areas were higher than those from other land-use types (Fig. 4b), i.e., LABs may have degraded considerably during atmospheric transport from input sources to distant areas. This notion is further supported by the roughly opposite spatial patterns of ΣLAB levels and L/S values (Fig. 2). The central PRD with higher LAB levels appeared to serve as an important emission source and dissipated LABs to other areas via atmospheric transport, which was also observed for PAHs (Wei et al., 2014b). Conversely, higher L/S values and lower sewage contamination in the remote areas than in the central PRD (Fig. 2b) suggested additional degradation of LABs during atmospheric transport of LABs and after deposition into soil. Although much work is needed to quantify the relative importance of transport pathways and the soil–air exchange of LABs, the results from the present study clearly implicated atmospheric transport as a viable mechanism for redistributing LABs from input sources to distant areas. As such, LABs can be used as an indicator of anthropogenic impacts on a regional scale.

## 4. Conclusions

Soil pollution by sewage within the PRD and adjacent areas was generally light, while the impacts of direct wastewater discharge were mostly confined around point sources. The spatial distribution of sewage contamination was significantly related to population density and per capita GDP, validating the utilization of soil LABs as tracers of anthropogenic influences at a regional scale. Finally, atmospheric deposition was proposed as an important input mechanism for LABs to enter soil in remote areas.

## Acknowledgments

The present study was financially supported by the National Natural Science Foundation of China (Nos. 41121063 and 41390240) and Guangzhou Institute of Geochemistry, Chinese Academy of Sciences

(No. GIGCAS 135 project Y234081001). Sampling and laboratory assistance by Yan-Li Wei, Liang-Ying Liu, Hai-Yan Hu, Bo Liang, Wei-Hao Feng, Xiao-Min Lin and Ru-Lang Shen is greatly acknowledged. This is contribution No. IS-1885 from GIGCAS.

## Appendix A. Supplementary data

Additional tables and figures containing information about the sampling sites, reporting limits and the chromatograms of LABs, comparisons of LABs concentrations worldwide, as well as data analysis about the concentrations, compositional profiles and L/S values of LABs are presented in Supplementary data. Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2014.04.067.

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