



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



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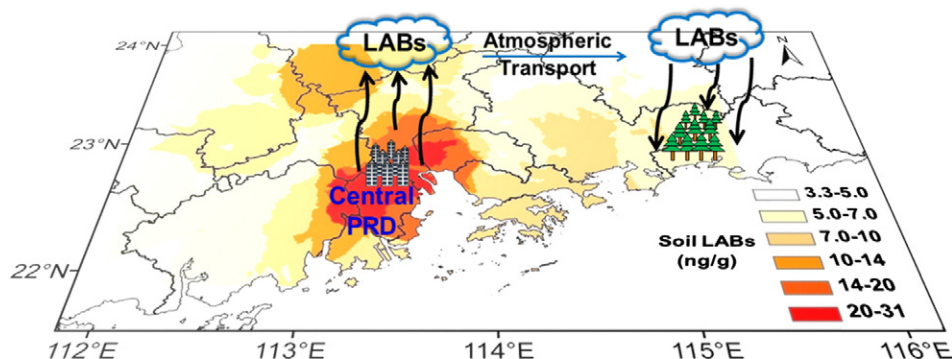
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HIGHLIGHTS

- 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



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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 $(5-C_{12} + 5-C_{13}) / (5-C_{11} + 5-C_{10})$, where $i-C_n$ 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.

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1. Introduction

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

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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 Bicego, 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 C₁₀, C₁₁, C₁₂ and C₁₃ 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 ΣC_{*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 C₁₀-LABs, C₁₁-LABs, C₁₂-LABs, and C₁₃-LABs, were quantified with the calibration curves of 1-C₁₀, 1-C₁₁, 1-C₁₂, and 1-C₁₃, 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 C₁₀–C₁₃-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.

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