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Characterization and health risk assessment of $PM_{2.5}$-bound organics in indoor public places: a study in smoking longue after restrict indoor air pollution control policy executed

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ABSTRACT

Smoking longue (SL), an enclosed room indoor for smokers, is developed in most indoor public places (IPPs) after execution of restrict smoking control in Hong Kong and Macau. Exposure to airborne fine particles ($PM_{2.5}$) emitted from environmental tobacco smoke (ETS) resulted adverse health impacts. $PM_{2.5}$ samples were collected at six IPPs. Organic carbon (OC), elemental carbon (EC), and non-polar organic compounds including polycyclic aromatic hydrocarbons (PAHs), *n*-alkanes (n-C_{16}-n-C_{40}), iso/anteiso-alkanes (C_{29}-C_{33}), hopanes and phthalate esters (PAEs) were quantified. Average $PM_{2.5}$ levels of 170.2±85.9 $\mu g/m^3$ in SL exceeded the international standards of 25 $\mu g/m^3$ set by World Health Organization (WHO) and was 5.4 and 3.9 times higher than other indoor areas and outdoor air, respectively. The high ratios of OC to $PM_{2.5}$, OC to EC, the PAHs diagnostic ratios in SL appointed to the impact of tobacco combustions. The maximum carbon number (C_{max}) and carbon preference indices (CPI) for *n*-alkanes were applied to further differentiate the sources, suggesting air penetrations from SL to other indoor area rather than air circulation from outdoor environments. Organic markers of iso/anteiso-alkanes in SL was 876.5 ng /m^3 in SL, ~80 times higher than that of outdoor. Abundance of two hopanes, 17α(H)-21β(H),30-norhopane and 17α(H)-21β(H),(22R)-homohopane found in SL, may serve as organic markers for ETS. The estimated carcinogenic risks of PAHs in SL much exceeded the acceptable level of 10^{-6}. The cardiovascular risk of ETS in an enclosed room posed an acute threat to smokers.

Keywords: Environmental tobacco smoke; Indoor public places; Smoking-free policy; $PM_{2.5}$; PAHs; Iso/anteiso-alkanes

1. Introduction

ETS, associated with adverse health effect, can be referred to a combination of volatile organic compounds (VOCs), nicotine, PM (Bansal and Kim, 2016; Kavouras et al., 1998) from burning tobacco products such as cigarette, cigar, pipe smoke, or e-cigarettes, taken as synonymous to passive smoking or second hand smoke (SHS) (WHO, 2007). PM, a major component of ETS, is composed of organic matter with diverse compounds such as PAHs, alkanes, and some nitrogen-containing compounds, which are known to be genotoxic and carcinogenic (And and Pankow, 1996; Rogge et al., 1994). Previous studies demonstrated that ETS could also elevate the risks of respiratory diseases and lung cancer for both of children and adults (Kim et al., 2014; Lee et al., 2016).

Exposure to ETS in IPPs imposes health risks on employees and visitors. Increase of nicotine metabolite in urine have been found for casino and hospitality workers (Achutan et al., 2009; Larsson and Montgomery, 2008). The ETS pollutant levels in gaming venues were reported to be 2.4–18.5 times higher than that in office buildings (Siegel and Skeer, 2003). Repace (2004) shows that smoking in IPPs generated 50 times more cancer-causing particles than that found in city streets and highways during rush-hour traffic. Clinical investigation of short-term ETS exposure and acute cardiac morbidity have been conducted (Pope et al., 2001). Acute exposure to ETS could disorder micro vascular function (Adamopoulos et al., 2008).

The smoking-free policies in workplace and public area are effective in reducing the number of smokers and SHS exposure levels (Bauer et al., 2005; MacNaughton et al., 2016; Seo et al., 2011). After the execution of the smoke-free workplace law (D-2002SFL) in Delaware, USA in 2002, $PM_{2.5}$ mass and $PM_{2.5}$-bound PAHs concentrations decreased 20 to 40 fold, from 205 $\mu g/m^3$and 163 ng/m^3 to 9 $\mu g/m^3$ and 4 ng/m^3, respectively, in entertainment venues (EVs) (Repace, 2004). Laws for indoor smoking control have been introduced in eighteen Chinese megacities in 2014. However, SL, an enclosed room indoor (e.g., IPPs and airports) is often allowed. Although the pollutants of ETS in SL could be ventilated through powerful air circulation and/or filtration system, it alleviated but not removed the risk of ETS exposure. General (2010) concluded that exposures to low levels of ETS can lead to a sharp increase of endothelial dysfunction and inflammation risks.

This study characterizes indoor $PM_{2.5}$ pollutions from ETS inside and outside of the SL at six IPPs during spring 2016, in Hong Kong and Macau, Special Administrative Region of China. Chemical profiles of OC, EC, PAHs, n-Alkanes, iso/ anteiso-Alkanes, PAES and hopanes are measured. The diagnostic ratios of PAHs, indices of n-alkanes, and influences of SL-to-non-smoking indoor areas ($NSIA_{2m}$) were calculated to discuss their representatives on source characterization. The potential discharges of pollutants from SL to non-smoking indoor areas are investigated. Health risks in term of carcinogenic potency on toxic organics such as PAHs and PAEs are assessed.

2. Methodology

2.1 Site description and sample collection

The six IPPs, average 192 visitors per day, are operated per day, seven days a week. Smoking was forbidden outside of the SL and monitored by security guards. Besides ETS, there was no other obvious pollution sources. Four sampling locations were selected for each IPP, including a) inside SL, b) 2 m away from the entry of SL($NSIA_{2m}$), and c) 5 m away from the entry/exit of SL ($NSIA_{5m}$), and d) fresh air intake (ca. 25 m outdoor) for comparison. Table 1 summary the properties of six IPPs.

Simultaneous $PM_{2.5}$ samples were collected onto quartz-fiber filters (47mm, QMA, Whatman, Clifton, NJ, USA) using mini-volume air samplers (Airmetrics, Eugene, OR, USA) at a flow rate of 5 L min^{-1} for 24 hours (from 08:00 to 07:59 local standard time next day). Before sampling, filters were pre-fired (780 °C, 3 h) to remove any contaminants. $PM_{2.5}$ mass were obtained by gravimetry using a Sartorius ME 5-Felectronic microbalance (±1μg sensitivity; Sartorius, Göttingen, Germany). Each filter was weighed at least two times before and after sampling which were equilibrated at temperature (22±2 °C) and relative humidity (RH, 35-45 %) controlled room. The maximum differences between the repeated measurements were <15 and <20 μg, for blank filters and loaded filters, respectively. To prevent any loss of volatiles, samples were packed in pre-baked aluminum foil and stored in a freezer at −20 °C until chemical analysis.

2.2 Carbonaceous aerosol analyses

OC and EC were quantified from a 0.53 cm^2 punch of each sample. A DRI model 2001 carbon analyzer (Atmoslytic, Inc., Calabasas, CA, USA) following the IMPROVE thermal/optical reflectance protocol was used for the carbon analyses (Cao et al., 2007; Chow et al., 1993; Ho et al., 2004). This produced data for four OC fractions (OC1, OC2, OC3, and OC4 at 120, 250, 450, and 550 °C in a helium [He] atmosphere, respectively); the pyrolyzed carbon fraction (OP, determined when reflected laser light attained its original intensity after oxygen [O_2] was added to the analysis atmosphere) and three EC fractions (EC1, EC2, and EC3 at 550, 700, and 800 °C, in a 2%O_2/ 98% He atmosphere, respectively). OC is defined as the sum of the four OC fractions (OC1-OC4) plus OP, and EC is defined as the sum of the three EC fractions (EC1-EC3) minus OP.

2.3 Non-polar organic speciation analysis

Non-polar organic compounds including PAHs, *n*-alkanes (*n*-C_{14}-*n*-C_{40}), iso/anteiso-alkanes, hopanes and PAEs in $PM_{2.5}$ were quantified using in-injection port-thermal desorption/mass spectrometry (TD-GC/MS) method(Ho et al., 2008; Ho and Yu, 2004). Briefly, aliquots of the filters (0.53–2.63 cm^2) were cut into small pieces and inserted into the TD tube for analyses. The temperature of the injector port was at 50°C before sample loading, then raised to 275 °C for desorption in a splitless mode while the GC oven temperature was kept at 30 °C. After the injector temperature reached the set point, the oven program started. The MSD was scanned from 50 to 550 amu under electron impact ionization (EI) at a voltage 70 eV and source temperature of 230 °C. A full-scan mode in a mass range of 50 to 650 amu was applied. Identification was achieved by characteristic ion and comparing the retention times of the chromatographic peaks with those of standards. Field blank filters were analyzed using the same procedures.

2.4 Health risk assessment

Acute exposures to second hand tobacco smoke lead to a remarkable change in aortic waveform and weaken microvascular function, even after exposure ends(Argacha et al., 2008). We assessed the acute health risks of ETS using a second clinical investigation of short-term ETS exposure and acute cardiac morbidity of non-smokers by Pope et al. (2001). They exposed adult non-smokers for 1.75h to an average increase of 53μg/m^3. PM_3 (range 23–123μg/m^3.) due to ETS in airport SL. Their study concluded that ETS exposure at this level produced a 12% increase in cardiac mortality risk, which means 2.3% per10 mg/m^3 increase in PM_3 (Repace et al., 2011).

Health risk estimation can be calculated using PAHs and PAEs exposure expressed in terms of a lifetime average daily dose (LADD) through inhalation of air particles (Kong et al., 2015; Li et al., 2013; Ma et al., 2014). The incremental lifetime cancer risk (ILCR) can be determined (Kong et al., 2015; Ma et al., 2014),

$$\mathrm{LADD} = C \times \mathrm{IR} \times \mathrm{ED} \times \mathrm{EF}/(\mathrm{BW} \times \mathrm{AT}) \qquad (1)$$

$$\mathrm{ILCR} = \mathrm{LADD} \times \mathrm{CSF} \qquad (2)$$

where C is the mass concentration of PAHs and PAEs in $PM_{2.5}$ (mg/m^3); IR is the inhalation rate (32.73 m^3/day for adult); ED is the lifetime exposure duration (5 years for workers); EF is the exposure frequency (240 working days/year); BW is the body weight (70 kg for adult); AT is the averaging lifetime for carcinogens (70 years × 365 day/year = 25550 days); The cancer slope factor (CSF) for bis(2-ethylhexyl)phthalate（DEHP）and benzo[a]pyrene (BaP) inhalation exposure was 0.014 and 3.14 $(mg/kg/day)^{-1}$, respectively. In this study, we used the BaP equivalent concentration (BaP_{eq}) to calculate LADD instead of *C*. BaP_{eq} was calculated as following:

$$\sum BaP_{eq} = \sum PAH_i \times TEF_i \quad (3)$$

where BaP_{eq} is the carcinogenic potency of a congener evaluated based on BaP-equivalent concentration, TEF is the toxic equivalent factor (Nisbet and Lagoy, 1992). Table S1 showed the abbreviations and the TEF values of eighteen PAHs

2.6 Quality assurance and quality control (QA/QC)

Airmetrics mini-volume samplers were checked and calibrated before each sampling event. Field blanks were collected to correct for backgrounds. Detailed QA/QC procedures for measurements of OC/EC and non-polar organic compounds have been described in previously publications (Cao et al., 2013; Ho et al., 2008; Ho et al., 2011; Xu et al., 2013).

For the OC/EC analysis, the instrument was calibrated with known quantities of methane gas daily. Replicate analyses were done for each group of ten samples with relative standard deviation (RSD) of <5% for TC (total carbon), and <10% for OC and EC. Average field blanks were 1.72 and 0.09 μg/m^3 for OC and EC, respectively, close and below method detection limits (MDL) for EC and OC were 1.0 μg/m^3.

For TD-GC/MS analysis, chrysene-d_{12} ($C_{18}D_{12}$) (98%, Sigma-Aldrich, Bellefonte, PA, USA) was added as internal standard (IS) for the PAH and PAEs, and *n*-tetracosane-d_{50} (*n*-$C_{24}D_{50}$) (98%, Aldrich, Milwaukee, WI, USA) was used for the *n*-alkanes, iso/anteiso-alkanes and hopanes. A six-point calibration over a concentration range of 0.5–10.0 ng for each of the target compounds from a standard mixture (Sigma-Aldrich, Bellefonte, PA, USA) was established, and the correlation coefficients (R^2) for linear regressions of the calibration curves were >0.99. For each ten samples, one replicate analysis was performed; the RSDs of these replicates were <15%. All data were corrected for the average blank values.

3. Results and Discussion

3.1 $PM_{2.5}$ mass concentrations

Levels of $PM_{2.5}$ concentrations at IPPs have been associated with numbers of smokers accessed, types of cigarettes, size and volume of the room, and efficiency of air-exchange ventilation system. As shown in Table 2, the highest $PM_{2.5}$ were seen in SL, ranged from 65.7 - 297 μg/m^3 with an average of 170.2±85.9 μg/m^3. These levels are 5.4 and 3.9 times, higher than that in NSIA and outdoor environment respectively. It also exceeded the guidelines of 25-75 μg/m^3 recommended by the international environmental departments and health agencies for indoor air quality (ANSI, 2007; JGJ/T309-2013; WHO, 2006). It should be noted that even though the outdoor $PM_{2.5}$ concentrations ranged from 31.1–65.1 μg/m^3 with an average of 44.2±14 μg/m^3 exceeding U.S. 24-h national ambient air quality standards of 35 μg/m^3.

The results are consistent with previous studies shown in Table S2 (Nafees et al., 2012; Repace et al., 2011; Jiang et al., 2011). $PM_{2.5}$ concentrations in NSIA ranged from 28.8-32.4 μg /m^3 were higher than those of measured in U.S. non-smoking IPPs of 3.1-22.3 μg/m^3 (Jiang et al., 2011), may partically due to filteration from outdoor. $PM_{2.5}$ levels in SLs are three times higher than of those measured at IPPs in western countries.

3.2 OC and EC

Table 3 showed that total carbon (TC) account for over 83% of $PM_{2.5}$ in SL. Average $PM_{2.5}$

OC concentrations in SL was 133.1.1±69.0 μg/m^3, accounted for 94.1% of TC which was 7.8-9.7 times higher than those in NSIA and outdoor. OC/EC ratio was 15.8±3.9 in SL, with a descending trend from distances apart from the SL at two NSIA points (NSIA$_{2m}$: 5.19±1.7 > NSIA$_{5m}$: 4.3±0.7).

Abundance of thermal carbon fractions varied by source types (Chow et al., 2004). Figure1 shows that pyrolyzed OC (i.e., OP) at SL accounted for 17.9% of TC. It has been reported water-soluble OC (WSOC) accounts for a significant fraction of overall OP, contributing to 13–66% of OP (Andreae1 and Gelencse´r, 2006; Yang and Yu, 2002).Thus, high contents of water-soluble OC are expected in atmosphere of SL. Elevated low temperature OC1 at SL may reflected the VOCs emitted from cigarette combustion. High percentages of EC1 and EC2 were found outdoors, ascribed to the heavy vehicular emissions from traffic (Watson et al., 1994). Supporting Information Table S3 shows the Spearman correlation between PM$_{2.5}$ mass and levels of OC1, OC2, OC3, OC4, OP, EC1, EC2, EC3. There were strong correlations ($r_s > 0.9$, $p_s < 0.05$) between PM$_{2.5}$ mass and OC1, OC2, OC3, OP. However, the Spearman correlation coefficients suggested the correlation between the PM2.5 concentrations and OC4 is $r = -0.77$, $p = 0.10$.

3.3 PAHs

Total quantified PAH concentrations (∑TPAHs) of SL (217.42±63.05 ng/m^3) was one order of magnitude higher than those of NSIA (28.07±9.67, 36.53±19.22 ng/m^3 for NSIA$_{2m}$ and NSIA$_{5m}$, respectively) and outdoor (46.53±33.41 ng/m^3) (Figure 2). Total PAHs concentration of SL was 1.4 times higher than that of the Delaware Park casino, before the execution of indoor smoking ban in U.S.A(Repace et al., 2011). However, total PAHs in NSIA (14.52-62.58 ng/m^3) were still ten times higher than the concentrations with smoking ban.

The three most abundant PAHs in SL are PHE, CHR, and BaA, with an average concentration of 39.3±35.6, 40.0±27.6, 23.5±11.6 ng/m^3, respectively, account for 18.1, 18.4, 10.8 % of ∑TPAHs. The high contribution of PHE could reflect a certain degree of ETS combustion. Exposure to PHE could result in cardiac hypertrophy (Huang et al., 2016). On average, the sum of middle molecular weight PAHs (∑PAHs$_{MMW}$, with 4 aromatic rings) was much higher than that of low molecular weight PAHs (∑PAHs$_{LMW}$, with 2-3 aromatic rings) and high molecular weight PAHs (∑PAHs$_{HMW}$, with 5-6 aromatic rings) in the SL. These abundance demonstrate the differences in PAHs distribution between smoking and nonsmoking environment (Figure 3).

Average BaP was 10.1 ng/m^3 on average in SL, accounting for 4.9% of the ∑PAHs, was 5.4~10.2 times higher than those in NSIA. BaP is often used as a marker for carcinogenic risk assessment. The level in SL was 10 times higher than the indoor air quality guideline of 1.0 ng/m^3 set by World Health Organization (WHO), suggesting high potential risk of SL.

PAHs diagnostic ratios have been used to identify potential pollution sources (Table 4) (Yunker et al., 2002). The ratios of (ANT)/(ANT + PHE) >0.10 and BaA/(BaA + CHR) > 0.35 also suggested significant contributions from combustion sources in both indoor and outdoor (Tobiszewski and Namieśnik, 2012). These ratios may change significantly during short distance transport and should be used with care for source identification especially within indoors (Ding et al., 2012). Ratios of FLU/(FLU + PYR) in the indoor samples were greater than 0.5, the value of this diagnostic ratio is higher indoor than outdoor, thus it could be supposed that the contribution of the grass/coal/wood combustion is more important inside than outside (Katsoyiannis et al., 2011). The BaP/BghiP value was higher in SL than outdoor, revealing a higher contribution of tobacco combustion (Zhang et al., 2009) and traffic emissions in SL and outdoor (Katsoyiannis et al., 2007), respectively.

3.4 *n*-Alkanes and Iso/ Anteiso-Alkanes

The homologue of *n*-alkanes ranged between C_{16} and C_{40} is illustrated in Figure 2. The highest total *n*-alkanes ($\sum n$-alkanes) measured in SL (2554.3 ng/m^3), was ten times higher than other sampling points. Different profiles were observed between indoor and outdoor samples. The maximum carbon number (C_{max}) of C_{31} was found for both indoor samples (i.e., SL and NSIA), compared with outdoor C_{max} of C_{24}. The heavier *n*-alkanes (i.e., from *n*-C24 to *n*-C33) accounted for 89.3% and 69.8% of $\sum n$-alkanes in SL and outdoor, respectively.

Carbon Preference Indices (CPI) for *n*-alkanes is an index for characterization of pollution sources which was calculated as,

$$\mathrm{CPI} = \sum C_{17} - C_{39} / \sum C_{16-} C_{40} \tag{4}$$

n-alkanes originate from vehicular emissions and other anthropogenic activities with a value close to unity (CPI≈1). On the other hand, CPI for epicuticular waxes of terrestrial plants are higher than unity (Bray and Evans, 1961; Choi et al., 2015; Wang et al., 2016). Stronger odd/even predominance was observed in SL (2.97) than in NSIA (1.28~1.31) and outdoor (1.02) (Table 4). Both C_{max} and CPI values support the contributions from tobacco combustion indoor and vehicular emission outdoor (Rogge et al., 1993; Rogge et al., 1994).

Due to their low reactivity, iso/anteiso-alkanes have a long atmospheric residence time which represent the most stable particulate tracers for ETS emissions. Kavouras et al. (1998) used the ratios of the most abundant n-, iso/anteiso-alkanes to indicate that the iso/anteiso-alkanes found in the urban atmosphere originate from cigarette smoke. ETS is a source of aliphatic hydrocarbons to indoor and outdoor atmosphere. Indoor iso/anteiso-alkanes with carbon number of C_{29} to C_{34} had characteristic profile (Figure 2), similar to tobacco leaf surface wax (Schauer et al., 2007). Average total iso/anteiso-alkanes (∑iso/anteiso-alkanes) in SL was 1392.8±505.2 ng /m^3, two orders of magnitudes higher than that of outdoor (11.8±10.4ng /m^3) (Figure 2). In addition, the ∑iso/anteiso-alkanes in NSIA were also 29.4-32.4 times higher than the outdoor values, implying the transport of airflow from SL to NSIA. Iso-C_{31} and anteiso-C_{32} were the two most abundant species from ETS in iso/anteiso-alkanes. As shown in Table 5 large differences in diagnostic ratios of iso/anteiso to straight chain alkanes were found between indoor and outdoor samples (Table 5). High ratios indoor than outdoor further support the effect of ETS, in line with those found by Bi et al. (2005).

3.5 PAES

Six PAEs (i.e., dimethylphthalate, [DMP]; diethyl phthalate, [DEP]; di-n-butyl phthalate, [DBP]; bis(2-ethylhexyl)phthalate, [DEHP]; di-n-octyl phthalate, [DNOP]and one plasticizer of di-2-ethylhexyladipate [DEHA]) were quantified (Figure 2). Total PAEs (∑PAEs) ranged from 926.5 - 1391.2 ng/m^3 indoor to 610.4 ng/m^3 outdoor. The Spearman correlation coefficients for ∑PAEs and ∑iso/anteiso-alkanes, OC in SL (Table S4) were negatively correlated and non-significant, suggesting that ETS may not be the major source of PAEs.

PAEs are widely used in numerous consumer products and poly vinyl chloride (PVC), such as personal care products, plastics, household, flooring, wall coverings and industry products (Afshari et al., 2004; Ejaredar et al., 2015; Myridakis et al., 2015). DEHP was the most dominant species indoor and outdoor, accounting for 33-67% of the ∑PAEs, followed by DBP (21-45%). DEHP is the most common PAE mainly stored in PVC devices, while DBP is widely used as a component of latex adhesives (Mariana et al., 2016). In this study, recreational facilities and other PVC devices used in IPPs may contribute to the indoor PAEs.

3.6 Hopanes

Figure 2 showed that average total hopanes (ΣHopanes) of 11.25 ng /m^3 in SL was 7.9 times higher than that of outdoor (1.43 ng/m^3) and 12.8 times higher than those found indoor(0.17 to 1.09 ng /m^3). Hopanes have been often used as markers for motor vehicle exhaust in urban area. High abundances in SL suggest the presence of hopanes in tobacco combustion. Two hopanes, 17α (H)-21β(H),30-norhopane and 17α(H)-21β(H),(22R)-homohopane, were ten times of those in outdoors, may serve as markers for ETS.

3.7 Influences of smoking lounge (SL)-to-non-smoking indoor areas

The SL/NSIA$_{2m}$ and SL/NSIA$_{5m}$ ratios of the PM$_{2.5}$ and non-polar organic compounds are presented in Figure 4. Most ratios were much greater than 1, except for PAEs, demonstrating the impact from ETS. Among the PAE ratios of SL/NSIA for DMP, DEHP, DNOP and DEHA was near unity, suggesting similar impact indoor. The two PAEs, DEP and DBP are commonly used in cosmetics and skin care products, yield SL/NSIA ratio less than one, signifying influence of other sources.

Due to high volatility of PAHs$_{LMW}$, their SL/NSIA ratios are slightly lower than those for PAHs$_{MMW}$ and PAHs$_{HMW}$. Higher than unity ratios were also found for iso/anteiso-alkanes and hopanes (i.e., 17α(H)-21β(H),30-norhopane and 17α(H)-21β(H),(22R)–homohopane).

3.8 Health risk assessment

Repace et al. (2011) estimated the PM$_{2.5}$ acute health risks in the U.S. EVs by using a parameter of 2.3% per 10 μg/m^3. In this study, the difference between SL and outdoor of the PM$_{2.5}$ concentrations was 170.2-44.2 μg/m^3 =126.0 μg/m^3. The estimated acute health risks for patrons and workers is (126.0 μg/m^3 x 2.3%/10 μg/m^3) = 29% for 1–2 h of exposure in SL. About half the sites in SL were at or above this level. The high percentage proves that ETS poses an acute threat to the health of smokers and workers in SL, even with short exposure durations (<1 h).

3.8.1 Cancer risk of PAHs

The total carcinogenic potency of PAH, referred as BaP$_{eq}$, for inhalation exposure in SL was 20.5±8.0 ng/m^3, while lower values were found in NSIA, ranging from 2.2±1.7 to 3.4±2.6 ng/m^3, close to the outdoors levels of 3.6±3.9 ng/m^3. The incremental lifetime cancer risk (ILCR) in SL was 1.4×10^{-6}, which was 6-10 times of those in NSIA (on a range of 1.5×10^{-7} to 2.3×10^{-7}) and 5.6 times of that in outdoor (2.5×10^{-7}). The estimated carcinogenic risks of PAHs in SL exceeded the acceptable level of 10^{-6}, suggesting concerns on the health impacts.

The carcinogenicity estimated in the SL samples was mostly attributed to DahA, followed by BaP and a group of tobacco combustion products (e.g., BaA, BbF, BkF, and PER). Considering the high TEF values, DahA and BaP contributed to 57%~65% of the total carcinogenicity in PM$_{2.5}$. Such contributions implied that the potential carcinogenicity of PAHs$_{HMW}$ was higher than that of PAHs$_{LMW}$ from biomass combustion, in agreement with the findings of previous studies (Hanahati et al., 2015; Jarvis et al., 2014; Mohammed et al., 2016; Shen et al., 2013). Even though the visitors in NSIA had exposure to relatively lower concentrations of PAHs and the ILCR values were below than threshold value, the impacts from SL should not be underestimated.

3.8.2 Risk assessment of PAEs

The LADD estimates of DEHP in the IPPs in a descending order of SL (1.4×10^{-6} mg/kg/d) > NSIA (1.2×10^{-6} to 1.3×10^{-6} mg/kg/d) > outdoor (4.7×10^{-7} mg/kg/d). The carcinogenic risks of inhalation of DEHP in SL was 1.9×10^{-8}, close to 1.6×10^{-8} to 1.9×10^{-8} in NSIA, and higher than the outdoor value of 6×10^{-9}. The estimated carcinogenic risks of inhalation of DEHP were below the acceptable level of 10^{-6}, representing low health concern of PAE from ETS exposure.

4. Conclusion

This study supports the fact that ETS leads to elevated of $PM_{2.5}$ and organic toxics indoor. The results implied that the enclosed of SL might solve the needs for smokers, but impacts to non-smoking areas in IPPs are still of concerns. The application of organic tracers to identify the pollution sources is efficient. Beside traditional iso-/anteiso alkanes, hopanes such as 17α(H)-21β(H),30-norhopane and 17α(H)-21β(H),(22R)-homohopane can act as markers for ETS.

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Table 1. The properties of smoking lounge at each IPP*

	IPPs					
	I	II	III	IV	V	VI
Area (m^2)	6	50	23	20	12	50
No. of people accessed /hr	5	1	10	12	6	16
Frequency of opening the doors /hr	10	5	20	20	10	30

*The names of the IPPs are not shown due to the privacy agreement

Table 2. $PM_{2.5}$ concentrations ($\mu g/m^3$) in different IPPs

	IPPs						
Sampling point	I	II	III	IV	V	VI	Mean±SD
SL	120.9	65.7	118.3	238.7	180.9	297.0	170.2±85.9
$NSIA_{2m}$	23.7	31.3	32.2	42.7	33.4	34.2	32.9±6.1
$NSIA_{5m}$	15.8	28.7	36.2	30.3	26.9	34.6	28.8±7.2
Outdoor	44.8	65.1	48.2	31.8	31.1	43.6	44.2±14.0

Table 3. The average concentrations of TC, OC, EC, and OC/EC ratios in $PM_{2.5}$

	SL	$NSIA_{2m}$	$NSIA_{5m}$	Outdoor
TC(μg /m^3)	141.5±71.8	20.2±3.9	17.8±2.2	18.7±5.5
OC(μg /m^3)	133.1±69.0	17.0±3.3	14.4±2.0	13.7±5.9
EC(μg /m^3)	8.4±3.1	3.3±1.2	3.4±0.5	5.0±1.7
OC/EC	15.8±3.9	5.19±1.7	4.3±0.7	2.7±2.3

Table 4. PAHs diagnostic ratios, indices of *n*-alkanes and cancer risks for the IPP samples

Diagnostic ratios or Indices *	SL	$NSIA_{2m}$	$NSIA_{5m}$	Outdoor
ANT/(ANT + PHE)	0.14	0.18	0.12	0.13
BaA/(BaA + CHR)	0.37	0.42	0.44	0.54
Flu/(Flu + PYR)	0.51	0.55	0.55	0.51
BaP/BghiP	1.18	0.47	0.39	0.64
CPAH/TPAHS	0.42	0.37	0.48	0.51
C_{max}	C31	C31	C31	C24
CPI	2.97	1.31	1.28	1.02

* Abbreviations for PAHs and indices for n-alkanes were shown in the texts.

Table 5. Diagnostic ratios of iso/anteiso-alkanes

	This study				(Bi et al., 2005)
Alkanes ^	SL	NSIA$_{2m}$	NSIA$_{5m}$	Outdoor	Office
a-C30/n-C30	2.1	0.9	1.2	0.3	2.51± 0.53
i-C31/n-C31	0.5	0.4	0.5	0.2	0.53 ± 0.04
a-C32/n-C32	2.0	1.6	2.0	0.6	3.11 ± 0.44
i-C33/n-C33	0.5	0.4	0.5	0.3	0.44 ± 0.05
a-C30/i-C31	0.7	0.8	0.8	0.8	0.68 ± 0.08
i-C33/i-C31	0.5	0.5	0.4	0.5	0.25± 0.07
a-C32/i-C33	1.8	2.6	2.8	2.2	3.44± 0.58
∑ (i+a)-Cn/∑n-Cn	0.9	0.7	0.9	0.4	0.94 ± 0.10

^ i represents iso-, a- represents for anteiso-, and n- represents for straight chain of alkane.

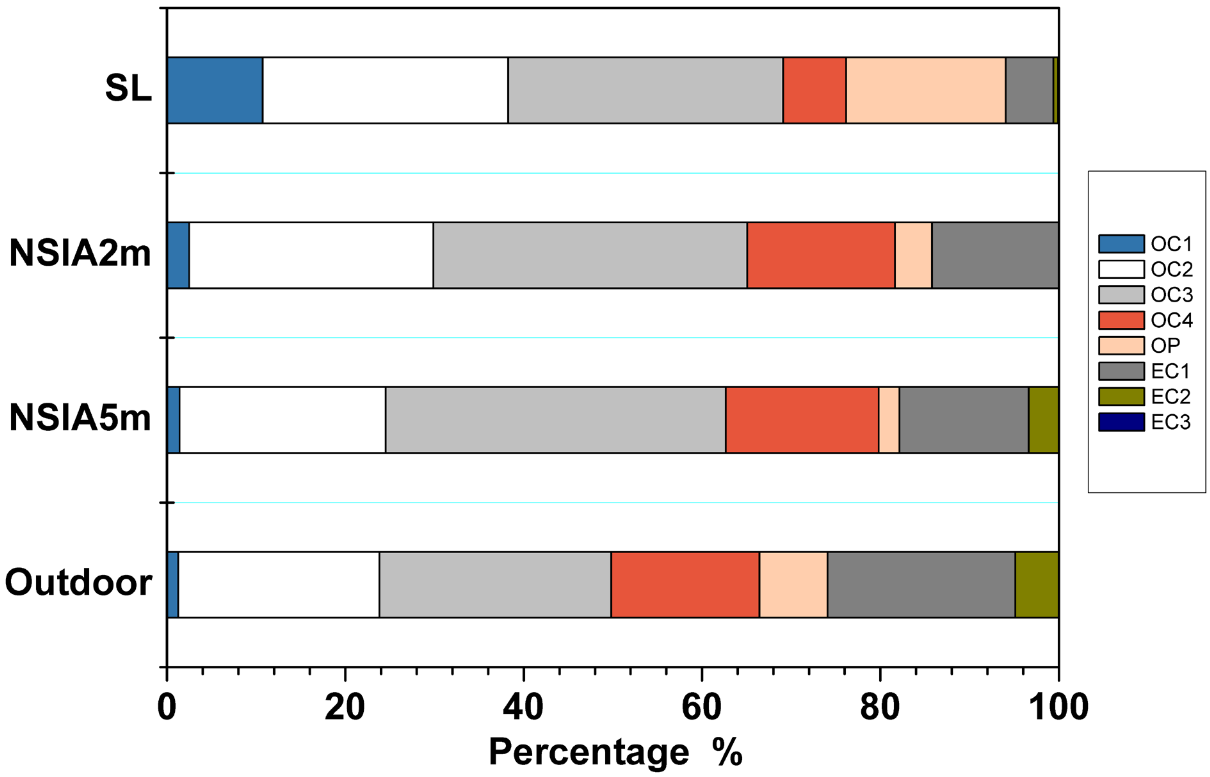

Figure 1. Average compositions of eight carbon fractions in $PM_{2.5}$ TC

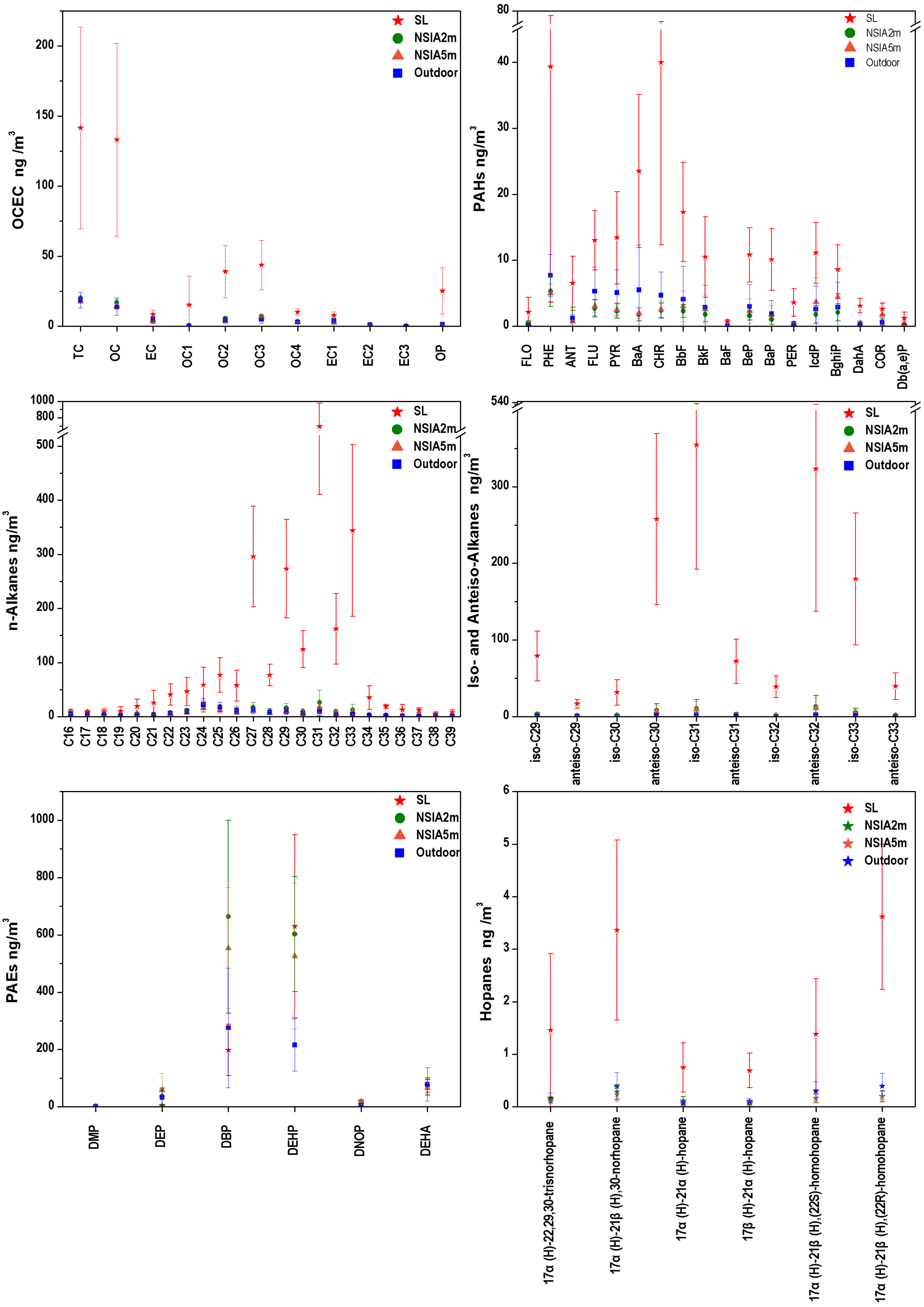

Figure 2. Chemical profiles of OC EC, PAHs, alkanes, PAEs and hopanes in $PM_{2.5}$ (Abbreviations for PAHs and PAEs are shown in the texts).

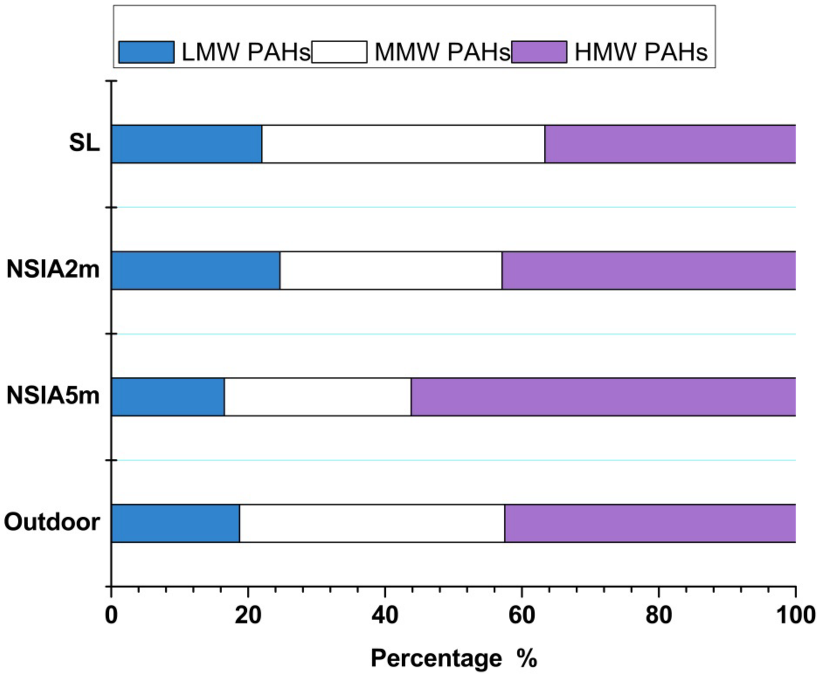

Figure 3. Compositions of PAHs$_{LMW}$, PAHs$_{MMW}$ and PAHs$_{HMW}$ to total quantified PAHs. (LMW-PAHs is sum of FLO, PHE, and ANT; MMW-PAHs is sum of FLU, PYR, BaA, and CHR; HMW-PAHs is sum of BbF, BkF, BaF, BeP, BaP, PER, IcdP, BghiP, DahA, COR, and DaeP.)

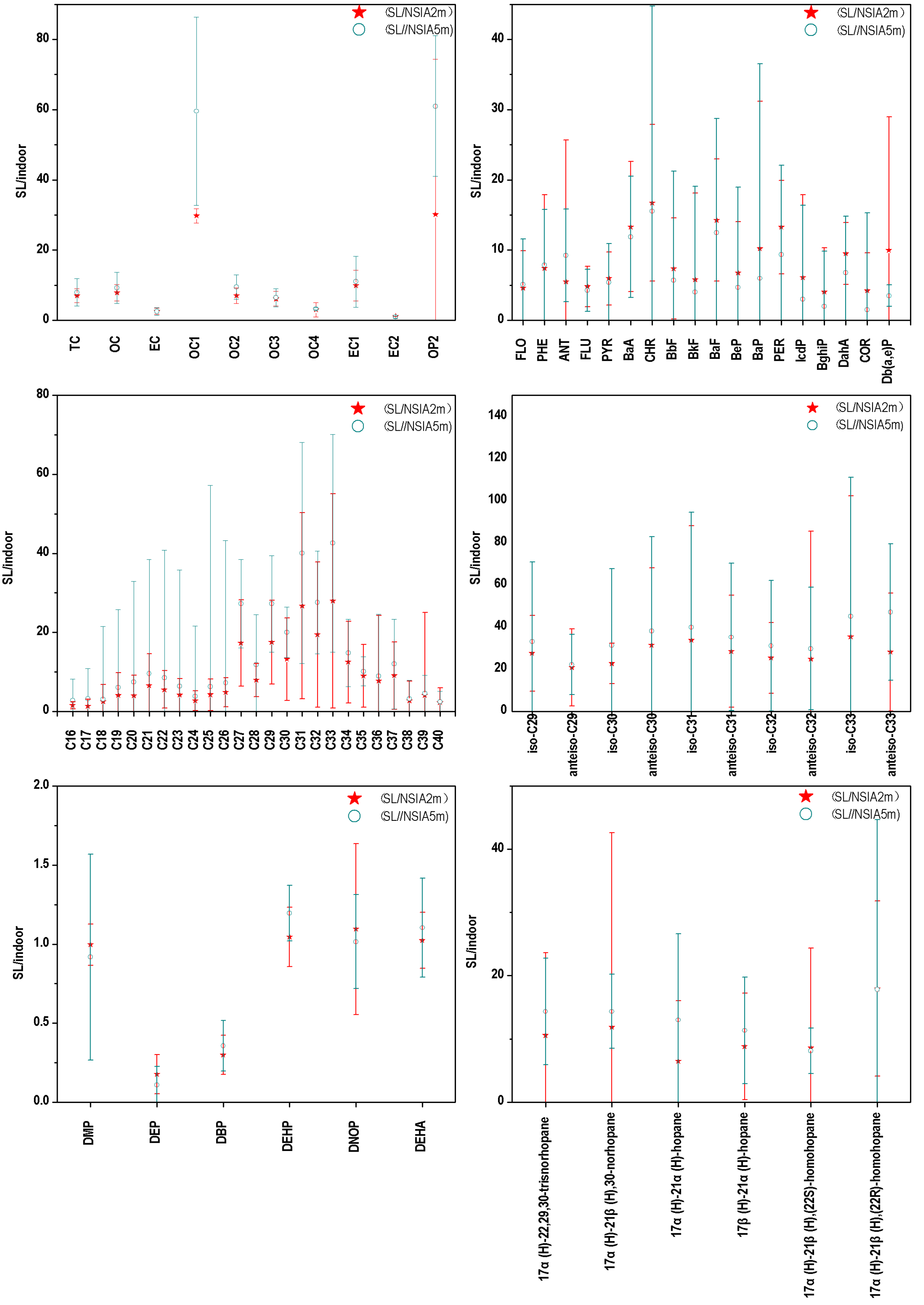

Figure 4. The SL/NISA$_{2m}$ and SL/NISA$_{5m}$ ratios of non-polar organic compounds (Abbreviations for PAHs and PAEs are shown in the texts).

Table S1. Abbreviation and the TEF values of eighteen PAHs

Compounds	Abbreviation	TEF
fluorene	FLO	0.001
phenanthrene	PHE	0.001
anthracene	ANT	0.01
fluoranthene	FLU	0.001
pyrene	PYR	0.001
benzo[a]anthracene	BaA	0.1
chrysene	CHR	0.01
benzo[b]fluoranthene	BbF	0.1
benzo[k]fluoranthene	BkF	0.1
benzo[a]fluoranthene	BaF	-
benzo[e]pyrene	BeP	-
benzo[a]pyrene	BaP	1
perylene	PER	0.1
indeno[1,2,3-cd]pyrene	IcdP	0.1
benzo[ghi]perylene	BghiP	0.01
dibenzo[a,h]anthracene	DahA	1
coronene	COR	-
dibenzo(a,e)pyrene	DaeP	-

Table S2. Concentrations of $PM_{2.5}$ in IPPs ($\mu g/m^3$)

Venue	Smoking Area	Non-smoking Area	Outdoor Environment
Gaming zones (Nafees et al., 2012)	93±45.3	-	30±8.5
Smoking EVs (Repace et al., 2011)	53.8	-	4.3
Nonsmoking EVs (Repace et al., 2011)	-	3.1	-
Smoking EVs (Jiang et al., 2011)	63.2	22.3	6.7
This study	170.2±85.9	32.9±6.1/28.8±7.2	44.1±14.0

Table S3. The spearman correlation coefficients for $PM_{2.5}$ mass and OC, EC fractions in SL.

	OC1	OC2	OC3	OC4	OP	EC1	EC2	EC3
r	1.00	1.00	0.94	-0.77	0.94	0.83	0.77	0.88
p	0.003	0.003	0.02	0.10	0.02	0.06	0.10	0.67

Table S4. The spearman correlation coefficients for ∑PAEs and ∑iso/anteiso-alkanes, OC in SL.

	Σ iso/anteiso-alkanes	OC
r	-0.54	-0.60
p	0.27	0.21