Distribution and source of alkyl polycyclic aromatic hydrocarbons in dustfall in Shanghai, China: the effect on the coastal area

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Alkyl polycyclic aromatic hydrocarbons (APAHs) are a group of persistent organic pollutants which are widely distributed in the atmospheric environment. To estimate the seasonal and spatial distribution of APAHs in dustfall in Shanghai, supercritical fluid extraction (SFE) followed by gas chromatography/mass spectrometry (GC/MS) were the analytical methods applied to the dustfall samples collected in this area from Dec. 2004 to Oct. 2005. Forty-one APAHs were found and divided into six groups which were alkyl naphthalenes (ANAs), alkyl phenanthrenes (APHs), alkyl anthracenes (AANs), alkyl fluoranthenes (AFLs), alkyl pyrenes (APYs) and alkyl chrysenes (ACHs). ANAs and APHs were two dominant APAHs in the proportion of more than 50%. The concentrations of total APAHs ranged from 1.6 to 9.0 $\mu g\ g^{-1}$. The ratios of APAHs to TPAHs (PAHs plus APAHs) fell into the range of 28~50%. The APAH levels were found to be higher in winter and spring than in summer and autumn. In terms of spatial distribution, concentration of APAHs was found to be higher in western Shanghai than eastern Shanghai. The source analysis showed that dustfall APAHs mainly derived from vehicle emissions and used crankcase oil. The annual fluxes of APAHs and PAHs in dustfall in urban Shanghai were 0.53~2.97 T and 0.96~5.34 T, respectively.

Introduction

As deposited atmospheric particulate matter, dustfall is an important carrier of various semi-volatile organic pollutants due to their low vapor pressure and strong affinity for particulates, and it is dominant in the removal of anthropogenically derived compounds such as PAHs.[1] In urban and industrial areas, these toxic organic compounds associated with dustfall are brought to buildings and streets, doing harm to the health of human beings. Direct skin contact and uptake *via* diet and respiration are the three main ways for dustfall pollutants of chronic toxicity to attack the human body. In recent years, dustfall has posed a more serious environmental problem in developing countries than in other countries. And attention has been paid to this pollutant in China, the largest developing country.[2] Priority PAHs have been found in dustfall at Macao[3] and Tianjin.[4] Dustfall PAHs in Shanghai were also reported in our previous work.[5–7] Mai *et al.*[8] further explored the impact of dustfall on the transport of PAHs and concluded that both atmospheric deposition and street runoff could be significant input pathways for alkylated and S/O PAHs found on the coast of Macao.

APAHs are a group of persistent organic pollutants (POPs) which are widely distributed in the atmospheric environment[3,8–11] and accumulated in sediment by deposition.[12–14] And more than 100 alkylated derivatives were found in surface sediments from Bransfield Strait, Antarctica.[15] They largely resulted from the

release of oil or the combustion of fuels at low to moderate temperatures[16–21] Thus, APAHs should be more ubiquitous in urban or industrial area due to the large amount of fossil fuels consumed. Due to their mutagenic and carcinogenic properties,[22] they pose a high risk to the health of humans and wildlife, especially aquatic life like fish.[23] And in the atmosphere these compounds could be transformed into other more toxic compounds such as nitro-PAHs.[24]

Shanghai (31°14′N, 121°29′E) is the most important and influential industrial and commercial city in China, housing a population of over 16 million at present. Shanghai is washed by the East China Sea on the east and Hangzhou Bay on the south. North of the city, the Yangtze River pours into the East China Sea. With a pleasant northern subtropical maritime monsoon climate, Shanghai enjoys four distinct seasons, generous sunshine and abundant rainfall. In the present decade, dustfall has been one of the main environmental problems along with NO_2 and SO_2 in the Shanghai area. The risk of human exposure to dustfall APAHs and PAHs is enhanced in the urban area because a large amount of fossil fuels is consumed each year both industrially and domestically and a lot of pollutants are emitted into the atmosphere. It is believed that urban and industrial areas are major sources of organic contamination of the adjacent coastal environment.[8,25–29] Dustfall may be conveyed into the East China Sea by rain, and APAHs eventually accumulate in coastal sediment, thus potentially affecting the fishery nearby.

This study investigated the profiles and levels of APAHs in dustfall samples from the urban region of Shanghai, and gave their seasonal and spatial distribution. In addition, the possible source of the pollutants was discussed in order to understand the risk of exposure to dustfall and to gain the knowledge of the distribution and effects of APAHs in dustfall on the coastal area.

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Experimental

Sampling

Sets of stainless steel trays (area 60×40 cm^2, depth 5 cm) for collecting bulk deposition were placed at thirteen sites in the urban area of Shanghai during 2004~2005 (Dec. 2004, Apr. 2005, Jul. 2005 and Oct. 2005 representing winter, spring, summer and autumn, respectively). The sampling sites were selected to be representative of the local environment situation, as shown in Fig. 1 and described in Table 1. The height of all sampling sites from the ground was about 1 m. Dustfall particles were collected from plates with a brush, dried in desiccators for 24 h, and then sieved by 200-mesh sieve. The samples were stored in a refrigerator at $-18\ ^\circ$C. Fifty samples were collected altogether, but the autumn sample of site 2 and the winter one of site 7 proved unsatisfactory and were not adopted.

Chemicals and reagents

1-Methyl-naphthalene (98.2%), 2-methyl-naphthalene (99.5%), 2,6-dimethyl-naph- thalene (99.9%), 1,3-dimethyl-naphthalene (96.2%), 2,3,5-trimethyl-naphthalene (99.0%), 1-methyl-phenanthrene (99.1%), 2-methyl-phenanthrene (100%), 1-methyl- anthracene (100%), 2-methyl-anthracene (99.7%), 2-methyl-fluoranthene (98.2%), 1-methyl-pyrene (97.9%), 6-methyl-chrysene (99.0%) were mixed equivalently as APAHs standard solution. Naphthalene-d$_8$ (100%) and phenanthrene-d$_{10}$ (99.3%) were internal standards. Pyrene-d$_{10}$ (98.8%) was added to all samples prior to extraction to monitor the whole process. All compounds were purchased from AccuStandard (USA). Residual grade dichloromethane was purchased from Sigma-Aldrich Lab (Milwaukee, WI, USA).

Instrument and analysis conditions

SFE was performed with a SFX™ 220 Supercritical Fluid Extraction System (Isco, Inc. USA) using SFE-grade CO$_2$. Each dustfall sample was extracted in a 10 ml extraction cell. Collection of the extracted analytes was carried out in a test tube filled with 10 ml dichloromethane. SFE parameters were set as follows: 5000 psi and 120 $^\circ$C. After 30 min extraction, all solutions were evaporated by N$_2$ (99.999%) and concentrated to 500 μl in dichloromethane.

The analysis was performed on GC/MS (Agilent 6890/5973, USA). A VF-5MS (Varian USA), 30 m $\times$ 0.25 mm I.D., FactorFour™ capillary column of 0.25 μm film thickness was used. The carrier gas was high purity helium (99.999%, 1.0 ml min^{-1}). The temperature program was: initial 60 $^\circ$C, hold 4 min, to 300 $^\circ$C at 10 $^\circ$C min^{-1}, hold 5 min. The injector temperature was set at 250 $^\circ$C and 1 μl analyte was injected in splitless mode. The mass spectrometer was operated in the electron ionization (EI) mode at the electron energy of 70 eV. The transfer line and ion source temperatures were set at 280 $^\circ$C and 230 $^\circ$C, respectively. The qualitative analysis was performed in full scan mode in the range of 40~350 and the quantitative analysis in SIM mode, in which selected ions are their molecular ions.

Quantitative analysis

Quantitative analysis was done using the internal calibration method (five-point standard curves). The calibration curves showed good linear behavior (r^2>0.99). The detection limits obtained for the relationship signal-to-noise of 3 ranged from 0.33~3.05 pg. Recovery and relative standard deviation of the method fell in the range of 74~105% and 4~18%, respectively. Only 12 APAH standards were available due to the scarcity of
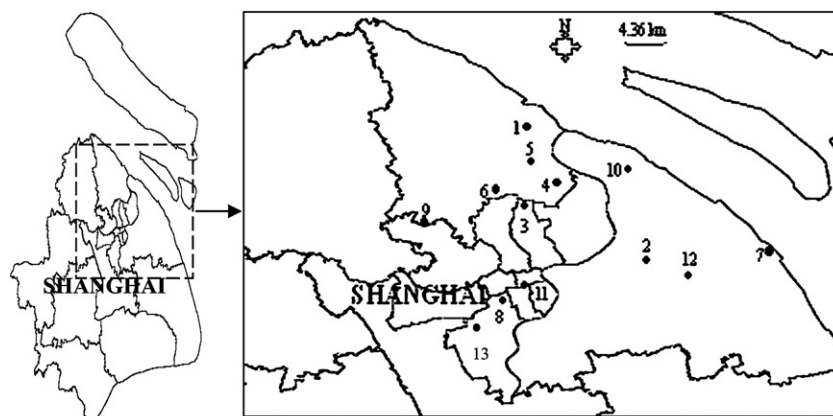
Table 1 Environmental situation of sampling sites in Shanghai

Site No.	Environmental situation
1	Steel industry area
2	Large park
3	Intersection of main roads
4	Educational area
5	Area of light traffic
6	Residential area
7	Outskirts
8	Educational area
9	Logistic center
10	Industrial region of chemical plants
11	Shopping center
12	Industrial region of Electronic Industries
13	One main roadside

Fig. 1 Sampling sites of dustfall in Shanghai (Numbers correspond with those in Table 1).

pure standard solution, so quantitative analysis of the rest had to be calculated by the calibration curves of their homologues. During analysis, method blanks were routinely performed once a day. The recoveries of Pyrene-d$_{10}$ were controlled in the range of 82~120% and the results indicated the validity of each analysis.

Results and discussion

Composition of APAHs in dustfall

Fig. 2 is the representative chromatogram of APAHs in the dustfall sample and shows that all APAHs were satisfactorily separated. Forty-one organic compounds in dustfall samples were identified as APAHs by mass spectrum, most of which were methyl-/dimethyl-/trimethyl- compounds. Naphthalene and alkyl naphthalene are abundant semi-volatile PAHs present in ambient air as a result of emissions from combustion sources.[24] Also, seventeen ANAs were found in dustfall samples, such as 1-methyl-naphthalene, 2-methyl-naphthalene, 2,6-dimethyl-naphthalene, 1,3-dimethyl-naphthalene, 2,3,5-trimethyl-naphthalene and so on. Methyl-/dimethyl-phenanthrenes were the main alkylated PAHs in aerosols,[29,30] and also present in collected dustfall samples. Methyl-pyrenes and methyl-chrysenes were two groups of APAHs available in both aerosol[29,30] and dustfall, such as 1-methyl-pyrene, 4-methyl-pyrene, 6-methyl-chrysene and so on. The other APAHs detected in dustfall samples were AANs and AFLs. It was noticed that parent-rings of all APAHs were low-molecular-weight PAHs and 5~7-ring APAHs were not detected. This was consistent with the APAHs profile in sediment pore water[31] and crude oil.[20]

Due to the lack of pure standard solutions, it was difficult to distinguish one compound exactly from its homologues. In addition, the individual APAHs were at a low level. In this case, APAHs were just classified by their parent rings and the total concentrations were calculated. Composition proportion is shown in Fig. 3. It exhibited that APHs and ANAs were two dominant APAHs in dustfall samples, and accounted for 30% and 23% of total APAHs, respectively. AFLs and APYs were present in the equal proportion of 15%. At the same time, AANs and ACHs occupied less than 10% of total APAHs. This characteristic was consistent with parent PAHs in dustfall[6,7] in which phenanthrene (PH), fluoranthene (FL) and pyrene (PY) were abundant while naphthalene, which is more easily volatilized, was not. And APHs were the dominant alkylated PAHs in aerosols.[10,11]

The concentrations of total APAHs ranged from 1.6 µg g^{-1} (or 16.6 µg m^{-2} month^{-1}) in site 7 to 9.0 µg g^{-1} (or 93.6 µg m^{-2} month^{-1}) in site 13 during the sampling period of one month. Compared with PAH levels in the same dustfall samples,[6,7] APAHs in this study were at lower levels. And they were higher than PAHs levels in dry deposition for a week in the Miami area[1] and in street dust in urban Malaysia area,[32] which were 5.67 ± 4.34 µg m^{-2} and 1.1~4.6 µg g^{-1}, respectively.

Impact of seasons on the distribution of APAHs

Because of the diversity of APAH levels in these 13 sites, the seasonal proportions of APAHs in one site were employed to estimate the impact of the seasons on the distribution of dustfall

APAHs, shown as Fig. 4. Dustfall APAHs were higher in winter and spring than in autumn and summer at most sites (except sites 1 and 6). It is believed that temperature was an important factor
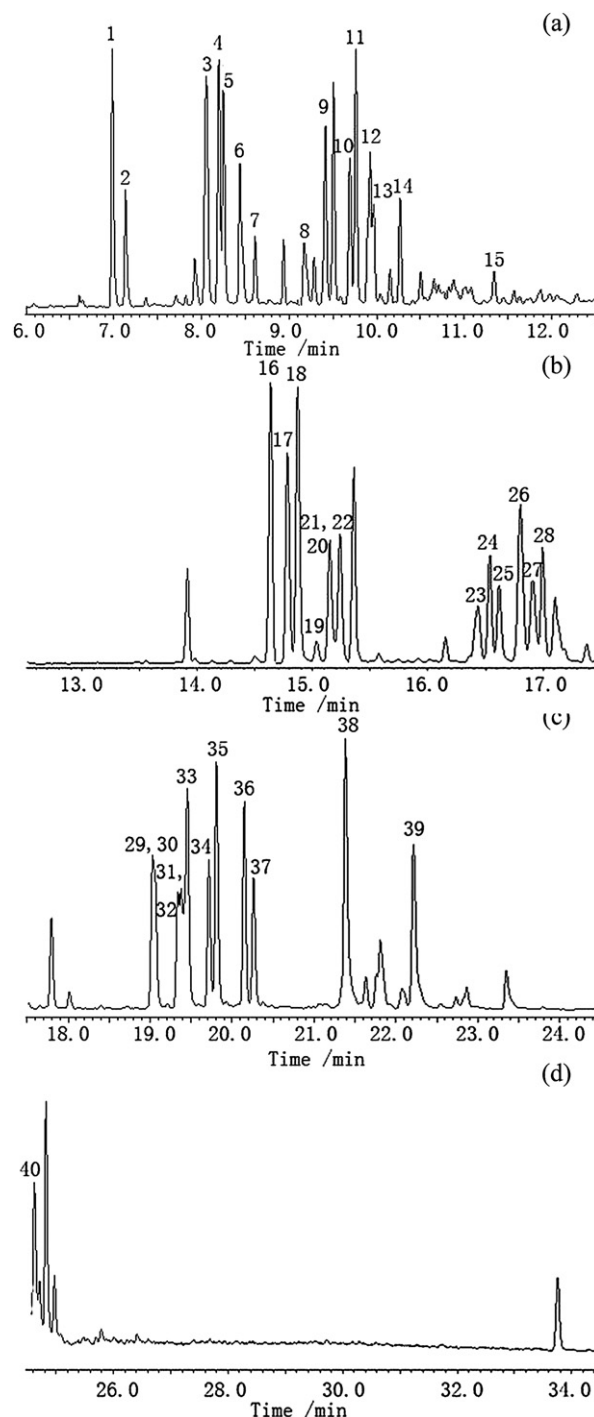

Fig. 2 The representative chromatograph of APAHs in dustfall (Parts a, b, c and d formed a whole chromatograph with the absence of an ANA homologue. 1 and 2 represent methyl-naphthalene. 3~7 represent dimethyl-naphthalene. 8~15 represent trimethyl-naphthalene. 16~22 represent methyl-phenanthrene/anthracene. 23~28 represent dimethyl-phenanthrene/anthracene. 29~37 represent methyl-pyrene/fluorathene. 38 and 39 represent dimethyl-pyrene/fluorathene. 40 represents methyl-chrysene).
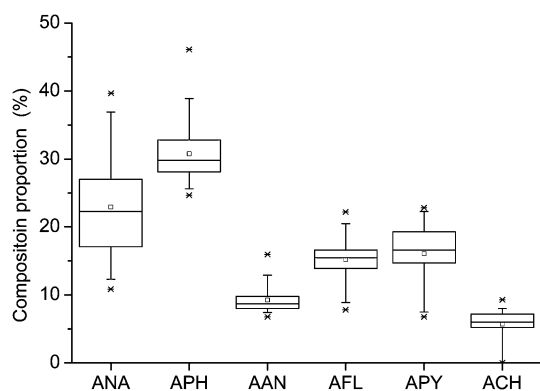
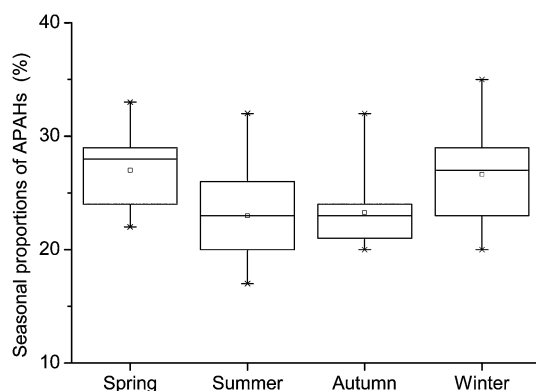**Fig. 3** Average composition proportion of dustfall APAHs (n = 50).

Fig. 4 Seasonal proportions of total APAHs.

and had an effect on the gas-particle equilibrium.[33] Particulate APAHs increased with decreased temperature. The average temperatures in the sampling periods were 7.0 °C (winter), 8.5 °C (spring), 18.5 °C (autumn) and 27.5 °C (summer). The seasonal distribution of dustfall APAHs coincided with the trend in the temperatures of the sampling periods. Photo degradation of polycyclic aromatic compounds was reported as another possible factor.[34] The long duration and strong intensity of sunshine in summer and autumn enhanced this degradation,[35,36] so dustfall APAHs were lower in summer and autumn.

APAHs in different districts of Shanghai

As coarse particles, dustfall could not pass over a long distance and tended to be deposited within a short time. And the average concentrations of APAHs in the four seasons should represent the state of local pollution, shown as Fig. 5. The highest APAH concentrations occurred in site 13, which was close to a heavy traffic intersection, implying that vehicle emissions might be an important source. And APAH levels were a little higher in the steel industry area (site 1), the residential region (site 6) and the traffic area (sites 3 and 5) than in other sites. A considerable amount of fossil fuels was consumed in the steel industry area and there was heavy traffic in the residential region. Site 4 was located in a college campus with few vehicles and site 7 was situated on the outskirts without any traffic or industry plant, so APAH levels in these two sites were lower. If the reader compares

the sampling sites in Fig. 1 with Fig. 5, it will be easily seen that the abundance of APAHs was higher on the west side of Shanghai, which incorporates a large proportion of the population, industrial business and heavy traffic. And APAH levels were lower on the east side, which was designed as a centre for financial activities and trading.

Comparison between APAHs and PAHs

Data concerning on dustfall PAHs over two months were also available form our previous studies,[6,7] shown as Fig. 5. Average PAHs concentrations were in the range of 2.9~16.2 μg g^{-1}, 1.2~2.8 times higher than APAH levels. The curve in Fig. 5 shows that the ratios of APAHs to TPAHs varied from 28% to 53% during sampling periods of PAHs. The ratios of 10~28% in aerosol were much lower than the values in this study.[10,11] The diversity indicates that APAHs trend to be adsorbed to coarse particles more than fine particles. It was surprising that APAH levels were almost equal to PAHs levels in site 7. Given the lack of direct emission sources, the pollutants in this site might originate from other areas *via* air transportation.

Total PAHs, low-molecular-weight (LMW) PAHs and high-molecular-weight (HMW) PAHs showed positive correlation with APAHs with r^2 value of 0.51, 0.40 and 0.51, respectively, indicating APAHs and PAHs had similar sources.

Sources of APAHs in dustfall

Emissions from oil and the combustion of fossil fuels were the dominant sources of APAHs in the urban region. The ratio of methyl-phenanthrenes to phenanthrene (MP/P) was often employed in discriminating between the sources. The ratio <1 was found in combustion mixture, and the values fell over the range of 2~6 in fossil oils.[16,37] MP/P ranged from 0.5 to 3.1 in this study. The ratios <1 in four sites and the ratios >2 in three sites indicated that dustfall APAHs in the urban area of Shanghai were affected both by pyrogenic and petrogenic input.

It is believed that the industry, energy plant and vehicles were the main pyrogenic sources. Moreover, domestic cooking and heating could produce some PAHs compounds. But the contribution of various combustion sources to APAHs was not confirmed due to poor data concerned with source emission. In this work, good correlation (r^2 = 0.51) between APAHs and PAHs in dustfall indicated that these two groups of pollutants had similar source. According to our previous work,[6,7] PAHs derived mainly from traffic sources. Thus, it was inferred that the
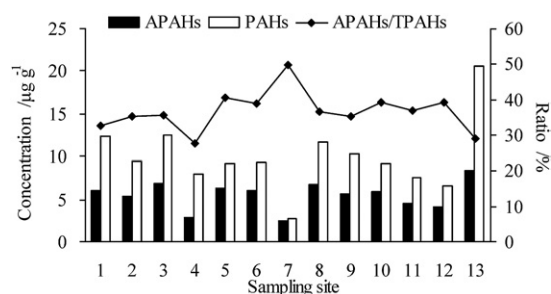

Fig. 5 Annual average concentrations of APAHs and PAHs and ratios of APAH to TPAHs (APAHs plus PAHs) in 13 sites.

main pyrogenic source of APAHs in dustfall was vehicle emission, which was consistent with the high value of APAHs that appeared in sites of heavy traffic.

It was reported that fossil oil, fresh crankcase oil and used crankcase oil were three petrogenic sources of both PAHs and APAHs in the industrial or urban areas.[32] The relative amount of the alkyl PAHs compared to the parent PAHs could be used to distinguish the source on the basis of abundance in fossil oil and a deficiency in combusted mass. For example, the ratios in fossil oil were 3.7~7.3.[16,38] In this study, the values were in the range of 0.4~1.1. And this fact implied that fossil oil wasn't the main source of APAHs in dustfall samples. The ratios of HMW PAHs to LMW PAHs in crude oil and fresh crankcase oil were in the range of 0.02~0.13 and 0.06~0.23, respectively. And both APAHs and HMW PAHs were abundant in used crankcase oil. In this study, the ratio ranged from 1.16 to 3.54, indicating that used crankcase oil was the main petrogenic input.

Annual flux of dustfall APAHs

The dustfall amount was 10.4 ton km^{-2} $month^{-1}$ according to the Shanghai Environmental Bulletin 2004 (www.envir.gov.cn/law/bulletin/b2004/, accessed July 2007), and the concentrations of APAHs and PAHs were estimated to be 16.6~93.6 g km^{-2} $month^{-1}$ and 30.2~168.5 g km^{-2} $month^{-1}$, respectively. The area of the Shanghai urban district is 2643.06 km^2. So, the annual flux of APAHs and PAHs in dustfall in urban Shanghai were 0.53~2.97 T and 0.96~5.34 T, respectively.

It is believed that both street dust flushed by street runoff and atmospheric deposition over the sea were the two main inputs of coastal sediment PAHs and their alkylated derivatives.[8] Due to abundant rainfall and a large amount of dustfall in this area, PAHs and APAHs associated with dustfall were transported to coastal sediment by street runoff. The analysis of PAHs in 14 surface sediments of tidal flats on the Yangtze Estuary showed that petrogenic contamination may be the dominant source in the study area.[39] They were, moreover, characterized by the greatest content near sewage discharge points with a trend to decrease as the distance from the city increased. The large amount of dustfall APAHs and PAHs would make a strong impact on the coastal environment if they were flushed and transported to coastal areas by street runoff.

Conclusion

Fifty dustfall samples were collected from 13 sites in the urban area of Shanghai during 2004~2005 and analyzed by SFE and sequent GC/MS. Forty-one organic compounds were identified as APAHs, which APHs and ANAs dominated. The total APAHs concentrations were in the range of 1.6~9.0 μg g^{-1} or 16.6~93.6 μg m^{-2} (per month). The ratio of APAHs to TPAHs (28~53%) showed clearly that APAHs constituted an important part of polycyclic aromatic hydrocarbons in dustfall and should not be ignored. The seasonal distribution of dustfall APAHs could be affected mainly by temperature and sunshine intensity. A large part of the population in western Shanghai is exposed to the higher levels of dustfall APAHs. According to source discrimination, the principal sources of dustfall APAHs were vehicle emissions and used crankcase oil, and more attention

should be paid to the inadequate source data for APAHs. Every year, a large amount of APAHs and PAHs (0.53~2.97 T and 0.96~5.34 T, respectively) associated with dustfall are transported to coastal sediment by street runoff and have made a great impact on the coastal environment.

Shanghai is the industrial and commercial center of China, and could represent the typical environmental status of most Chinese cities. At the same time, a similar situation may well exist in other developing countries with similar climatic, geographical and socioeconomic conditions. More studies need to be undertaken to understand the impact of APAHs and PAHs on coastal environment in developing countries and regions.

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