

Polycyclic Aromatic Hydrocarbons in Riverine Runoff of the Pearl River Delta (China): Concentrations, Fluxes, and Fate

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On the basis of a monthly sampling effort from March 2005 to February 2006, the total concentrations of the sums of 27 and 15 polycyclic aromatic hydrocarbons (defined as Σ_{27} PAHs and Σ_{15} PAHs, respectively) in riverine runoff of the Pearl River Delta (PRD), China, and associated fluxes were determined. No clear temporal and spatial trends of PAH concentrations were found at all eight riverine runoff outlets where the samples were collected. The annual fluxes of Σ_{27} PAHs and Σ_{15} PAHs from the PRD to the coastal ocean were 60.2 and 33.9 metric tons, respectively. Assuming that riverine flux was positively related to the regional emission of PAHs, the annual riverine fluxes from five major rivers in China to the global oceans were estimated, which are quite significant relative to other major rivers of the world. On the basis of mass balance considerations, approximately 87% of Σ_{15} PAHs inputting to the Pearl River Estuary and northern South China Sea was derived from riverine runoff from the PRD. In addition, ~ 22.3 metric tons of Σ_{15} PAHs annually outflow to open seas, which is equivalent to a concentration of 0.34 $\mu\text{g/L}$ in the global oceans if the PAHs are evenly distributed in the upper 200 m of the water column. A comparison with the global background level of PAHs indicated that $\sim 0.4\%$ of PAHs in the open oceans may have been contributed by 1-year discharge from the PRD.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a class of ubiquitous contaminants in the environment. They are formed mainly from incomplete combustion of organic matter, such as coal, fossil fuel, and wood, and from forest fires, volcano activities, and petroleum seeps (1). PAHs have been found in remote areas, such as the polar regions (2). In addition, the global oceans are a gigantic sink for organic contaminants derived from various sources. It has been shown that the riverine runoff and atmosphere are the two most important vectors of transportation into the oceans.

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FIGURE 1. Maps of sampling sites in the Pearl River Delta, China: 1-Humen; 2-Jiaomen; 3-Hongqilimen; 4-Hengmen; 5-Modaomen; 6-Jitimen; 7-Hutiaomen; 8-Yamen.

For example, previous studies demonstrated that runoff was largely responsible for transport of PAHs to the oceanic environments (3, 4). In addition, Moore and Manoli estimated that about 10–80% of the PAHs input to the oceans was transported through the atmosphere (5).

Typically, coastal zones are economically well developed and densely populated due to the availability of rich resources and favorable climate conditions, which likely results in the release of large amounts of contaminants to the coastal oceans. Therefore quantifying the contaminant fluxes from coastal regions to the oceans should be valuable for understanding the sources, transport, and fate of contaminants on a global scale.

The Pearl River Delta (PRD) is one of the most developed and populated regions in China, connecting the Pearl River Estuary (PRE) and South China Sea (SCS) via eight major riverine runoff outlets (Figure 1). By 2005, the PRD region had approximately 25 million permanent residents and nine million registered motored vehicles (6) which was considered the most important anthropogenic source of PAHs in urban areas (7). It was estimated that about 1.73×10^{10} metric tons/yr of wastewater are discharged from the PRD into the PRE and SCS (8). On the other hand, the SCS is the largest semiencllosed sea in the western tropical Pacific Ocean (9) and receives freshwater from the PRD partly via the PRE. However, despite the numerous efforts to characterize the occurrence of PAHs in sediments and water in the coastal region adjacent to the SCS (10–14), the riverine fluxes of PAHs have not been quantified.

The present study was conducted to determine the riverine fluxes of PAHs from the PRD to the coastal ocean based on a 1-year sampling effort. In addition, the annual fluxes of PAHs from five major rivers in China were estimated from

the regional population densities and PAH emission rates. Finally, the outflow of PAHs from the PRD to the global oceans was estimated based on mass balance considerations.

Materials and Methods

Field Sampling. The sampling sites and sample collection methods are described in detail in the Supporting Information, and therefore only a brief description is presented here. The eight runoff outlets, i.e., Humen, Jiaomen, Hongqilimen, and Hengmen on the eastern side and Modaomen, Jitimen, Hutiaomen, and Yamen on the western side (Figure 1), were sampled monthly from March 2005 to February 2006. Water samples were collected into 10 L brown glass containers using stainless-steel submersible pumps. Fifteen (for Humen and Modaomen) or nine (for the other outlets) subsamples were combined into one composite sample of 40 L during each sampling cruise. The water samples were cooled with ice during transport to the laboratory where they were processed immediately.

Sample Extraction. The procedures of extraction, cleanup, and chromatographic separation were largely based on a previously reported protocol (11). Water samples were filtered with a vermicular system with filter flask, and suspended particulate matter (SPM) was retained by GF/F glass fiber filters (Whatman International Ltd., Maidstone, England) that were baked at 450 °C for 4 h prior to use. Filtrates were passed through a mixture of XAD-2:XAD-4 resin (1:1 in mass) in a glass column (25 mm i.d. and 400 mm length) to collect dissolved-phase organics. The glass column was washed three times with 50 mL of methanol each, followed by three consecutive extractions with 50 mL of a methylene chloride:methanol mixture (1:1 in volume) in an ultrasonic bath. The extracts were combined and spiked with a known amount of surrogate standards, and 500 mL of distilled water and an appropriate amount of NaCl were added, and the mixture was back-extracted five times with 50 mL of methylene chloride each. The organic fraction was further extracted with 10 mL of distilled water three times for removal of residual methanol. The filters loaded with SPM were freeze-dried, weighed, and Soxhlet-extracted for 72 h with 400 mL of a mixture of methylene chloride:acetone (1:1) upon addition of surrogate standards.

All extracts were condensed, solvent-exchanged to hexane, and further reduced to 1 mL with a Zymark TurboVap 500 (Zymark Corporation, Hopkinton, MA). They were subject to chromatographic separation on a glass column packed with alumina:silica gel (1:2, v:v). The fraction containing PAHs was eluted with 70 mL of a mixture of hexane and methylene chloride (7:3, v:v) and was concentrated by the Zymark TurboVap 500 to 0.5 mL. Internal standards were added to each extract (Supporting Information) prior to instrumental analysis. Target analytes, surrogate standards, and internal standards are summarized in Table S1 of the Supporting Information ("S" indicates tables and figures presented in the Supporting Information thereafter).

Instrumental Analysis. A Varian 3800 gas chromatograph/Saturn 2000 ion trap mass spectrometer was used for sample analysis. A 60 m × 0.25 mm-i.d. (0.25 μm film thickness) DB-5MS column (J&W Scientific, Folsom, CA) was used for separating the target analytes. Column temperature was programmed for 60 °C to 160 °C at a rate of 25 °C/min, followed by a ramp to 230 °C at a rate of 5 °C/min (held for 4 min), to 260 °C at a rate of 20 °C/min (held for 5 min), to 270 °C at a rate of 1 °C/min (held for 8 min), and to 290 °C at a rate of 25 °C/min (held for 20 min). Injector temperature was programmed for 100 °C to 280 °C at a rate 180 °C/min and held for 36 min. Extract injection was conducted in the splitless mode with a split time of 5 min. The injection port, ion trap, manifold, and transfer line temperatures were maintained at 280, 190, 40, and 280 °C, respectively. Mass

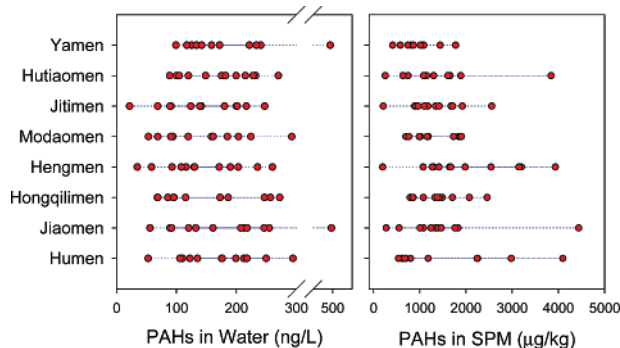


FIGURE 2. Concentrations of Σ_{27} PAHs in water and SPM sampled from March 2005 to February 2006 at the eight riverine outlets of the Pearl River Delta, China.

fragments were generated in the positive electron impact mode at an electron voltage of 70 eV and scanned in the selective ion storage mode with an electron multiplier voltage of 1850 V.

Quality Assurance/Quality Control Program. Thirty-four field blanks, laboratory blanks, spiked blanks, and replicate samples were analyzed with the field samples. The recoveries of the surrogate standards, naphthalene-*d*₈, acenaphthene-*d*₁₀, phenanthrene-*d*₁₀, chrysene-*d*₁₂, and benzo[*g,h,i*]perylene-*d*₁₂, from all filtrate samples and blanks were 57 ± 19%, 72 ± 21%, 73 ± 24%, 125 ± 29%, and 94 ± 23%, respectively. Perylene-*d*₁₂ was also used as a surrogate standard initially; however, a broad peak from the filtrate and blank samples interfered with the quantification of perylene-*d*₁₂, resulting in peculiarly high recoveries of perylene-*d*₁₂. As a result, perylene-*d*₁₂ was deemed an inappropriate surrogate standard for the analysis of filtrate samples, and it was excluded entirely from the list of surrogate standards. The average recoveries of the same surrogate standards from the SPM samples were 33.6 ± 20.8%, 44.3 ± 18.8%, 56.3 ± 20.7%, 80.4 ± 21.4%, 73.8 ± 41.7%, and 74.0 ± 32.9%. Low levels of low molecular PAHs (from 2-methylnaphthalene to phenanthrene; Table S1) were detected in field and laboratory blanks. Therefore, a mean concentration plus one standard deviation in the blanks was calculated for each of these compounds and used as the reporting limit (RL) if the concentrations of individual PAHs in blanks were higher than the lowest concentrations of the calibration standards. The concentrations of the other PAHs in blanks were lower than the lowest concentrations of the calibration standards, and as a result we chose the lowest concentrations as RLs (Table S1).

Data Analysis. Detailed procedures for calculating PAH flux is given in the Supporting Information. In the present study, the target analytes contain 28 PAH compounds, including the 16 PAHs identified as the priority pollutants by the United States Environmental Protection Agency (Table S1). However, naphthalene had to be excluded from the target list because the solvent blank contained high abundant naphthalene. The sums of the 27 and 15 PAH compounds are defined as Σ_{27} PAHs and Σ_{15} PAHs, respectively. For a measured concentration below the reporting limit, zero was used for concentration calculation and half of the reporting limit was employed for flux estimation. The concentrations were not corrected by the surrogate recovery data.

Results and Discussion

Concentrations and Fluxes of PAHs. Detailed concentration data are presented in Tables S2–S5, and the distribution of Σ_{27} PAHs concentrations is depicted in Figure 2. The arithmetic mean concentrations of Σ_{27} PAHs in the aqueous and SPM phases were 161 ng/L with a range of 21.8 to 497 ng/L

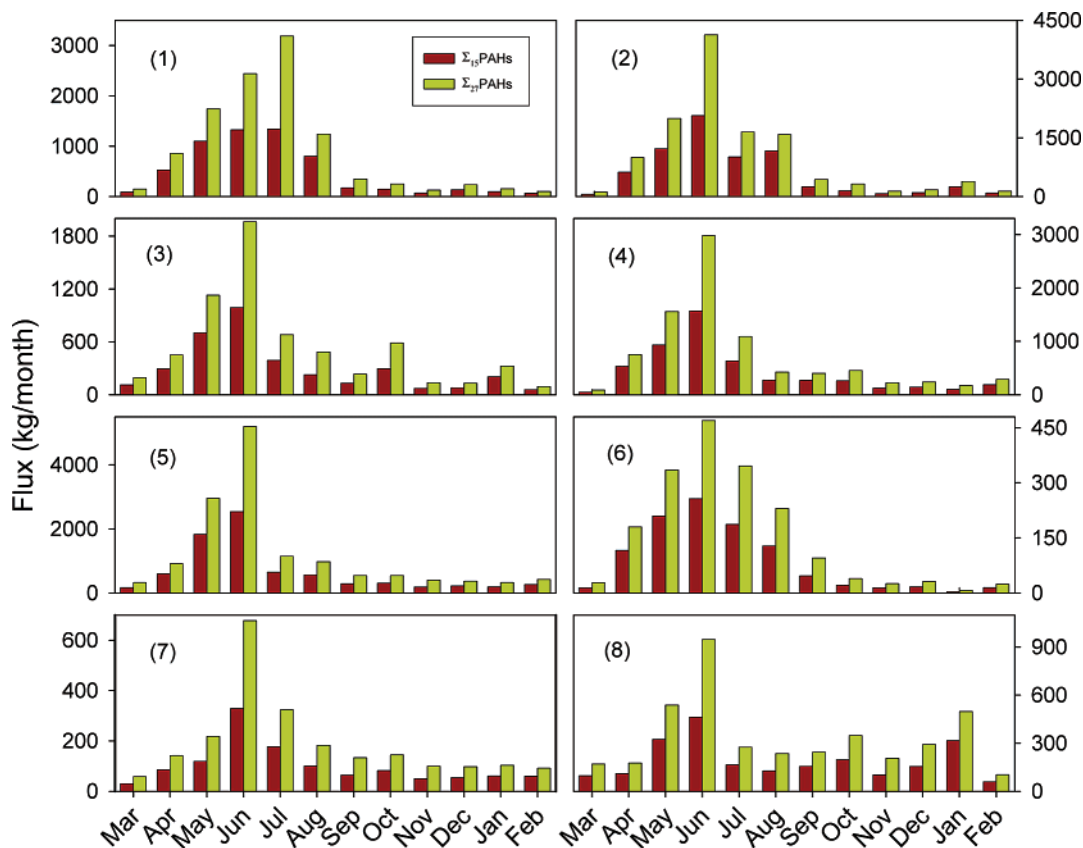


FIGURE 3. Fluxes of Σ_{27} PAHs and Σ_{15} PAHs from the eight riverine outlets of the Pearl River Delta, China, from March 2005 to February 2006: (1) Humen; (2) Jiaomen; (3) Hongqilimen; (4) Hengmen; (5) Modaomen; (6) Jitimen; (7) Hutiaomen; (8) Yamen.

and 1400 $\mu\text{g}/\text{kg}$ with a range of 196 to 4440 $\mu\text{g}/\text{kg}$, respectively. Furthermore, Σ_{15} PAHs concentrations in the aqueous and SPM phases ranged from 10.8 to 323 ng/L and 100 to 3840 $\mu\text{g}/\text{kg}$, respectively. The temporal variations (12 months) of Σ_{27} PAHs and Σ_{15} PAHs concentrations in both the aqueous and SPM phases (Figures S2–S4) were not significantly different among the eight outlets as determined by a two-way analysis of variance. However, Luo et al. (11) found that the Σ_{16} PAHs (Σ_{15} PAHs plus naphthalene) concentration in both the aqueous and SPM phases in the coastal area off Macao (adjacent to the western region of the PRD; Figure S1) was higher than that in the water column of Baiertang in the Guangzhou channel of the PRD (Figure S1). A main reason for the spatial variance is that naphthalene, constituting $\sim 90\%$ of the total PAHs, was included in the analysis. The variance would have been insignificant if naphthalene was excluded (11).

The fluxes of Σ_{27} PAHs and Σ_{15} PAHs were 60.2 and 33.9 metric tons/yr (Tables S6–S7), respectively, with the seasonal variability for each outlet shown in Figure 3. Approximately 81% of the total mass flux occurred during the wet weather season (from April to October) (Table S8), clearly because the flow rate was much higher during this period than that in the dry weather season. Spatially, Modaomen, Humen, and Jiaomen Outlets contributed about 61% of the total mass emission (Table S7). Apparently, water discharge amount is the most important factor controlling the contaminant flux to the coastal ocean in the PRD.

The sources of PAHs inputs in a river include upstream runoff (15), atmospheric deposition (16), urban and municipal waste discharge (7, 17), industrial effluent, and oil leakage (18). Historically, industrialization and urbanization in the western PRD region has been slower than those in the eastern and northern regions. Hence, upstream runoff instead of local sources may be a major source of pollutants to the four

western outlets. This is corroborated by a previous study (19) that reported an annual flux of Σ_{15} PAHs at 19.4 metric tons from Xijiang River which drains directly into the western outlets (Figure 1). In addition, the rich tributaries in the PRD and rainy subtropical monsoon climate are favorable for atmospheric fallout of contaminants. We estimated that approximately 10.8 metric tons of atmospheric Σ_{15} PAHs were introduced into rivers in Guangdong Province annually if 463 $\text{ng}/\text{m}^2 \text{d}$ was used as the mean value of dry and wet deposition (20). These assessments suggest that upstream runoff and atmospheric deposition are two main sources of PAHs to the riverine outlets.

Comparison of Fluxes of Σ_{15} PAHs from Five Main Rivers in China. The five main rivers in China are Yangtze River, Yellow River, Pearl River (a general name for all rivers in the PRD), Heilongjiang River, and Brahmaputra (21). All except for Brahmaputra eventually flow into the Pacific Ocean, and Brahmaputra passes through India and finally reaches the Indian Ocean. Total water discharge for these five rivers is $1.87 \times 10^{12} \text{ m}^3$, with the Yangtze River having the largest effluent discharge at $9.7 \times 10^{10} \text{ m}^3$, followed by the Pearl River with an annual discharge of $3.49 \times 10^{10} \text{ m}^3$. Brahmaputra has the least annual discharge at $1.4 \times 10^{10} \text{ m}^3$ (Figure 4). So far, no quantitative measurements of PAHs fluxes have been conducted for these rivers other than the Pearl River in the present study, and only a qualitative assessment can be made.

If the riverine flux is assumed to positively correlate with the regional total emission of PAHs, the annual flux from a specific river can be estimated based on the total annual flux of PAHs from Pearl River by

$$\frac{F_i}{TE_i} = \frac{F_{\text{PRD}}}{TE_{\text{PRD}}} \quad (1)$$

where F_i and F_{PRD} are the annual fluxes of Σ_{15} PAHs from the

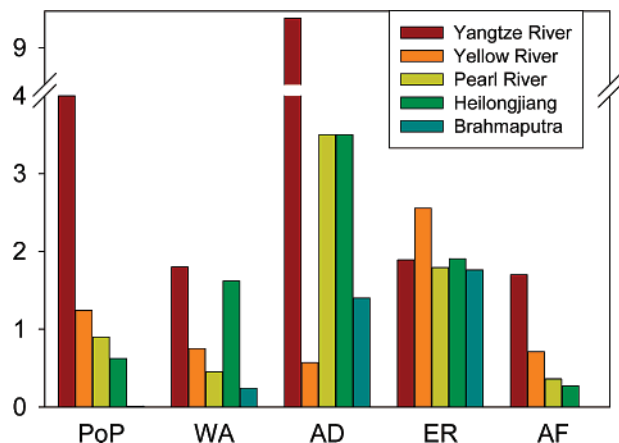


FIGURE 4. Basic information and annual fluxes of Σ_{15} PAHs from the five major rivers in China: PoP, population ($\times 10^8$) (21); WA, watershed area ($\times 10^6$ km²) (21); AD, annual water discharge ($\times 10^{10}$ m³) (21); ER, emission rate of PAHs ($\times 10$ g/ca) (22); AF, annual flux ($\times 10^2$ metric tons/yr).

ith river and Pearl River, respectively, and TE_i and TE_{PRD} are the total annual emissions of Σ_{15} PAHs from the *i*th river and Pearl River basins, respectively. TE_i was computed by the population for the portion of a specific province the *i*th river runs through and the emission rate of the province (per capita). The emission rate for each province was calculated by its emission amounts of PAHs (22) and the total population. It is noted that the emission rates were estimated for Σ_{16} PAHs (Σ_{15} PAHs plus naphthalene); however, because both TE_i and TE_{PRD} are estimated for Σ_{16} PAHs any error arising from the difference between Σ_{15} PAHs and Σ_{16} PAHs should be off-set. To obtain total annual emission of Σ_{16} PAHs from the Yangtze River basin which covers a total of 18 provinces and cities, the population figures for these regions are obtained: 8.17×10^7 , 6.55×10^7 , 5.89×10^7 , 1.26×10^6 , 4.17×10^7 , 2.63×10^7 , 1.21×10^7 , 3.14×10^7 , 1.31×10^7 , 3.03×10^7 , 2.88×10^7 , 2.22×10^6 , 6.45×10^4 , 1.58×10^7 , 1.71×10^7 , 5.62×10^6 , 1.74×10^6 , and 2.23×10^5 respectively (Table S9). In addition, the associated emission rates were calculated as 29.2, 13.8, 21.1, 23.0, 14.3, 44.3, 22.6, 21.8, 16.6, 19.3, 10.9, 20.3, 17.2, 11.7, 20.4, 6.90, 13.7, and 32.5 g/ca respectively (Table S9). Therefore, approximately 9050 metric tons of Σ_{16} PAHs were released from the Yangtze River basin annually. Similarly, the total annual emission of Σ_{16} PAHs from the

Pearl River basin was 1320 metric tons (Table S9). According to eq 1, the annual flux of Σ_{15} PAHs from the Yangtze River = $33.9 \times 9050/1320 = 232$ metric tons. By this procedure, the total annual flux of Σ_{15} PAHs from these five rivers was estimated at 367 metric tons, and the discharge amounts of Σ_{15} PAHs follow the order of Yangtze River (232 metric tons) > Yellow River (70.5 metric tons) > Pearl River (33.9 metric tons) ~ Heilongjiang River (30.2 metric tons) > Brahmaputra (0.4 metric tons) (Table 1). Yellow River transports considerably larger amounts of PAHs despite its low water flow, apparently due to the high population density and energy consumption in the Yellow River basin (22). On the other hand, only 0.4 metric tons of Σ_{15} PAHs were discharged annually from Brahmaputra, probably because both the emission rate and population density in the river basin are low. A previous study pegged the total PAH emission from all sources in China at 25 300 metric tons (22). If that is a reasonable estimate, it shows that the riverine flux represents only a tiny fraction of the total PAHs emission to the environment of China. The issue of where the majority of PAHs generated has gone merits further research efforts, with an objective to better follow the fate of PAHs or organic contaminants in general.

The validity of these flux estimates can be qualitatively examined using data from a previous study that obtained the concentrations of Σ_{15} PAHs (89 ng/L in water and 72.7 μ g/kg in SPM) at Dongming which lies in the lower reach of the Yellow River (23). The following equation can be used to estimate the riverine flux (*F*) from the Yellow River:

$$F = (C_{\text{water}} + C_{\text{SPM}} \times f_{\text{silt}}) \times Q \quad (2)$$

where C_{water} and C_{SPM} are the concentrations of Σ_{15} PAHs in water and SPM, respectively, f_{silt} is the silt content, and *Q* is the water discharge. The multiannual content of silt was reported at 36.9 kg/m³ (24), and *Q* was 57.5 billion m³ (21). Therefore, *F* is 158 metric tons/yr, which qualitatively agrees with the value (70.5 metric tons) estimated using eq 1. The difference can be attributed to the unusually high amounts of silt discharged via the Yellow River, resulting in an overestimate of the PAH flux through SPM. Another explanation for the difference is that the concentration was obtained from a specific site in the Yellow River, whereas the fluxes were estimated for the entire river.

Global Riverine Fluxes of PAHs. It is quite a challenge to compare global riverine PAHs inputs because of the

TABLE 1. PAHs Concentrations (Water + SPM), Water Discharge, and Fluxes of PAHs from Global Rivers

	PAHs, (ng/L) ^b	discharge, (10 ⁸ m ³ /yr)	PAH flux, (tons/yr) ^b	coast	references
Pearl River	126	3500	33.9	South China Sea	this study
Yangtze River		9800	232	East China Sea	a
Yellow River		570	70.5	Bohai Sea	a
Heilongjiang River		3500	30.2	Bohai Sea	a
Brahmaputra		1400	0.4	India Ocean	a
Qiangtangjiang River ^{b,c}	283	404	11.4	East China Sea	33, 34
Mississippi River ^{b,c}	207.1	580	12.0	Gulf of Mexico	25, 35
Susquehanna River ^b			3.16	Chesapeake Bay	28
Anacostia River ^b		1	0.36	Chesapeake Bay	7
Niagara River ^{b,c}	16.8	189	3.18	Ontario Lake	36, 37
San Francisco River ^b			0.03	San Francisco Bay	30
St. Lawrence River ^b			6.49	Gulf of St. Lawrence	15
Seine River, France ^b	583	137	7.99	English Channel	26
Le Havre River ^b			0.01	English Channel	4
Rhone River ^b			5.3–33	Western	3
Ebro River ^b			1.30	Mediterranean Sea	3
Danube River ^{b,c}	1.30	2100	0.27	Black Sea	29, 32

^a The annual fluxes of Σ_{15} PAHs were estimated in the present study. ^b The number of PAH components used in different studies may vary, and a detailed list of PAHs in each study is summarized in the Supporting Information. ^c Fluxes were estimated from concentration and discharge data from two different references cited.

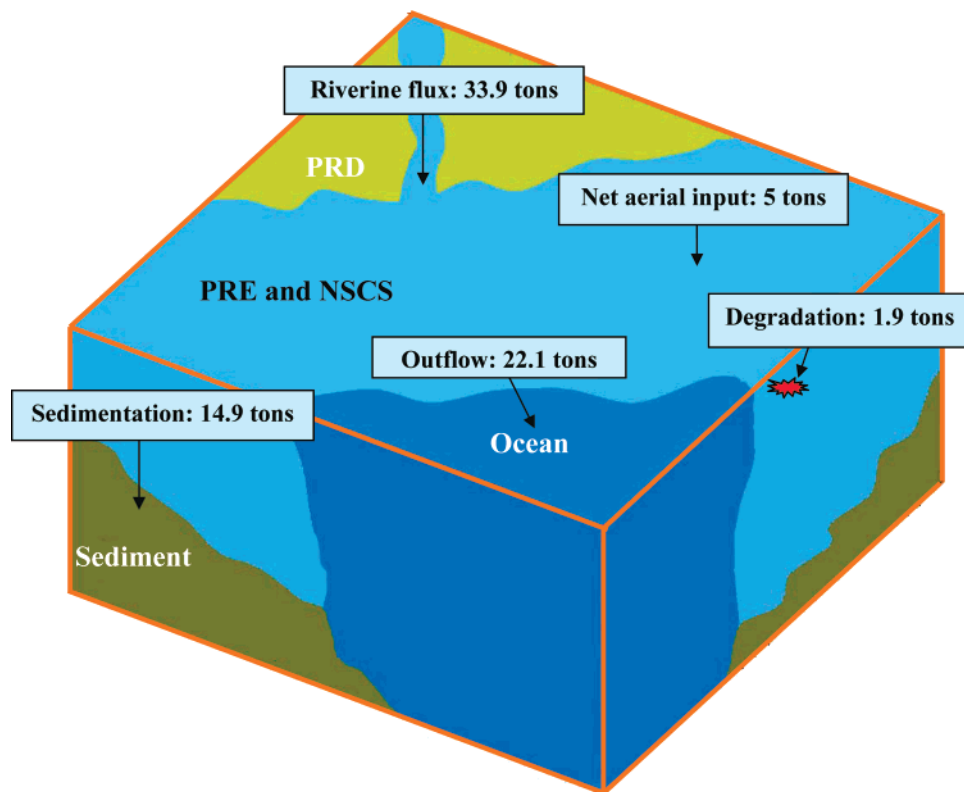


FIGURE 5. A mass balance scheme for input and output pathways of $\Sigma_{15}\text{PAHs}$ in the Pearl River Estuary (PRE) and northern South China Sea (NSCS).

different numbers of target analytes employed in individual studies. Hence the comparison made herein is qualitative at best. The annual PAHs fluxes from the rivers in China are evidently higher than those from other rivers around the globe (Table 1). For example, Mississippi River, the largest river in North America, had an annual flux of 18 PAHs including 12 priority pollutants (25) that was three times lower than that of the PRD. The annual flux of $\Sigma_{10}\text{PAHs}$ from Seine River of France was 7.99 metric tons/yr (26). Mackay and Hickie (15) derived the annual output amount of $\Sigma_7\text{PAHs}$ from St. Lawrence River of Canada at 6.49 metric tons/yr using a mass balance model. Furthermore, the fluxes of PAHs from Susquehanna River (United States), Niagara River (North America), and Ebro River (Spain) (3, 27, 28) were about an order of magnitude lower than the annual output amount from the PRD. The annual fluxes of PAHs from some small rivers were 2–3 orders of magnitude lower than that from the PRD (4, 7, 29–32). All these results suggest that the runoff inputs of PAHs from rivers of China constitute a significant portion of the total riverine contribution to the global oceans.

Contribution of PAHs from the PRD to Global Oceans Based on Mass Balance Considerations. Organic pollutants enter into the water body of estuaries or coastal regions mainly via runoff and aerial deposition, and the loss mechanisms include sedimentation, degradation, and outflow to oceans. The net outflow of $\Sigma_{15}\text{PAHs}$ from the PRD to the coastal ocean can be estimated based a mass balance consideration. The above scenario leads to

$$F_r + F_a = F_o + F_s + F_d \quad (3)$$

where F_r , F_a , F_o , F_s , and F_d are the annual fluxes by riverine runoff from the eight mouths, aerial deposition, outflow to ocean, sedimentation, and degradation, respectively.

The riverine flux (F_r) of $\Sigma_{15}\text{PAHs}$ was 33.9 metric tons/yr (Table 1). Other flux values had to be estimated based on certain assumptions. The depositional flux was set at 103

ng/m² d measured in a previous study in the coast of Hong Kong (20). Therefore F_a was approximately 5 metric tons/yr assuming the area of the PRE and northern SCS (NSCS) was $2.33 \times 10^4 \text{ km}^2$. The annual sedimentary flux (F_s) of $\Sigma_{15}\text{PAHs}$ was calculated as 14.9 metric tons in the PRE and NSCS based on a previous study (14). The average loss efficiency of total $\Sigma_{15}\text{PAHs}$ due to microbial and photochemical degradation is assumed to be 5% of the total input in the aqueous environment (30). Hence F_d was 1.9 metric tons/yr. According to eq 3, F_o was estimated at 22.1 metric tons/yr (Figure 5).

The above assessments indicate that riverine input was approximately seven times higher than aerial flux, or 87% of the total annual loading of PAHs to the PRE and NSCS was transported by riverine discharge, which suggests that riverine input is the most important contributor of PAHs to the coastal ocean off South China, and aerial deposition represents only a small portion of the PAHs loading. The same conclusion was also drawn in San Francisco Bay (30). In addition, sedimentation appears to be an important loss pathway in the study area, i.e., ~38% of the total annual input deposits to bottom sediments.

The majority of PAHs entering to the PRE and NSCS eventually outflows to the open seas (Figure 5), with the possibility of involving in the global cycling process. This amount of PAHs is equivalent to a concentration of 0.34 pg/L in the global oceans if the PAHs, without further losses, are evenly distributed in the upper 200 m of the water column. The concentration of $\Sigma_6\text{PAHs}$ (including PHE, ANT, FLU, PYR, BaA, and CHR; see Table S1 for acronyms) in the water column of the Faeroe Bank Channel was 90 pg/L, which was the lowest among PAH concentrations reported in the literature and therefore can be regarded as the background concentration of PAHs in the global oceans. This means that 0.4% of PAHs in the open oceans may have been contributed by 1-year discharge from the PRD. Apparently, the PRD is a significant source of PAHs to the global oceans.

Acknowledgments

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Supporting Information Available

Detailed description of sampling methods and data analysis, tables of data, and additional figures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Literature Cited

- Seruto, C.; Sapozhnikova, Y.; Schlenk, D. Evaluation of the relationships between biochemical endpoints of PAH exposure and physiological endpoints of reproduction in male California Halibut (*Paralichthys californicus*) exposed to sediments from a natural oil seep. *Mar. Environ. Res.* **2005**, *60*, 454–465.
- Macdonald, R. W.; Barrie, L. A.; Bidleman, T. F.; Diamond, M. L.; Gregor, D. J.; Semkin, R. G.; Strachan, W. M. J.; Li, Y. F.; Wania, F.; Alae, M.; Alexeeva, L. B.; Backus, S. M.; Bailey, R.; Bewers, J. M.; Gobeil, C.; Halsall, C. J.; Harner, T.; Hoff, J. T.; Jantunen, L. M. M.; Lockhart, W. L.; Mackay, D.; Muir, D. C. G.; Pudykiewicz, J.; Reimer, K. J.; Smith, J. N.; Stern, G. A.; Schroeder, W. H.; Wagemann, R.; Yunker, M. B. Contaminants in the Canadian Arctic: 5 years of progress in understanding sources, occurrence and pathways. *Sci. Total Environ.* **2000**, *254*, 93–234.
- Lipiatou, E.; Tolosa, I.; Simo, R.; Bouloubassi, I.; Dachs, J.; Marti, S.; Sicre, M.-A.; Bayona, J. M.; Grimalt, J. O.; Saliott, A.; Albaiges, J. Mass budget and dynamics of polycyclic aromatic hydrocarbons in the Mediterranean Sea. *Deep-Sea Res. II* **1997**, *44*, 881–905.
- Motelay-Massei, A.; Garbon, B.; Tiphagne-larcher, K.; Chevereuil, M.; Ollivon, D. Mass balance for polycyclic aromatic hydrocarbons in the urban watershed of Le Havre (France): Transport and fate of PAHs from the atmosphere to the outlet. *Water Res.* **2006**, *40*, 1995–2006.
- Moore, S. W.; Ramamoorthy, S. *Organic Chemicals in Natural Water*; Springer-Verlag: New York, 1984.
- Guangdong Statistical Yearbook *Principal aggregate indicators on national economic and social development and their related indices and growth rates/Main indicators on industry*, 2005.
- Hwang, H.-M.; Foster, G. D. Characterization of polycyclic aromatic hydrocarbons in urban stormwater runoff flowing into the tidal Anacostia River, Washington, DC, U.S.A. *Environ. Pollut.* **2006**, *140*, 416–426.
- He, X. Y.; Shi, J. H.; Xin, H. H.; Wang, B.; He, S. D. Dynamic changes of land-originated oils from 8 mouths of Pearl River. *China Sci. Technol. Info.* **2005**, *21*, 84–85.
- Su, J. L. Overview of the South China Sea circulation and its influence on the coastal physical oceanography outside the Pearl River Estuary. *Cont. Shelf Res.* **2004**, *24*, 1745–1760.
- Mai, B. X.; Fu, J. M.; Sheng, G. Y.; Kang, Y. H.; Lin, Z.; Zhang, G.; Min, Y. S.; Zeng, E. Y. Chlorinated and polycyclic aromatic hydrocarbons in riverine and estuarine sediments from Pearl River Delta, China. *Environ. Pollut.* **2002**, *117*, 457–474.
- Luo, X. J.; Mai, B. X.; Yang, Q. S.; Fu, J. M.; Sheng, G. Y.; Wang, Z. S. Polycyclic aromatic hydrocarbons (PAHs) and organochlorine pesticides in water columns from the Pearl River and the Macao harbor in the Pearl River Delta in South China. *Mar. Pollut. Bull.* **2004**, *48*, 1102–1115.
- Mai, B. X.; Qi, S. H.; Zeng, E. Y.; Yang, Q. S.; Zhang, G.; Fu, J. M.; Sheng, G. Y.; Peng, P. A.; Wang, Z. S. Distribution of polycyclic aromatic hydrocarbons in the coastal region off Macao, China: Assessment of input sources and transport pathways using compositional analysis. *Environ. Sci. Technol.* **2003**, *37*, 4855–4863.
- Luo, X. J.; Chen, S. J.; Mai, B. X.; Yang, Q. S.; Sheng, G. Y.; Fu, J. M. Polycyclic aromatic hydrocarbons in suspended particulate matter and sediments from the Pearl River Estuary and adjacent coastal areas, China. *Environ. Pollut.* **2006**, *139*, 9–20.
- Chen, S.-J.; Luo, X.-J.; Mai, B.-X.; Fu, J.-M.; Sheng, G.-Y.; Zeng, E. Y. Distribution and mass inventories of polycyclic aromatic hydrocarbons and organochlorine pesticides in sediments of the Pearl River Estuary and the northern South China Sea. *Environ. Sci. Technol.* **2006**, *40*, 709–714.
- Mackay, D.; Hickie, B. Mass balance model of source apportionment, transport and fate of PAHs in Lac Saint Louis, Quebec. *Chemosphere* **2000**, *41*, 681–692.
- Gocht, T.; Klemm, O.; Grathwohl, P. Long-term atmospheric bulk deposition of polycyclic aromatic hydrocarbons (PAHs) in rural areas of Southern Germany. *Atmos. Environ.* **2007**, *41*, 1315–1327.
- Thanh-Thao, P.; Proulx, S. PCBs and PAHs in the Montreal Urban Community (Quebec, Canada) wastewater treatment plant and in the effluent plume in the St Lawrence River. *Water Res.* **1997**, *31*, 1887–1896.
- González, J. J.; Viñas, L.; Franco, M. A.; Fumega, J.; Soriano, J. A.; Grueiro, G.; Muniategui, S.; López-Mahía, P.; Prada, D.; Bayona, J. M.; Alzaga, R.; Albaiges, J. Spatial and temporal distribution of dissolved/dispersed aromatic hydrocarbons in seawater in the area affected by the Prestige oil spill. *Mar. Pollut. Bull.* **2006**, *53*, 250–259.
- Deng, H. M.; Peng, P. A.; Huang, W. L.; Song, J. Z. Distribution and loadings of polycyclic aromatic hydrocarbons in the Xijiang River in Guangdong, South China. *Chemosphere* **2006**, *64*, 1401–1411.
- Ye, Z.; Zhang, G.; Zou, S.; Li, J.; Qi, S.; Liu, G. Dry and wet depositions of atmospheric PAHs in the Pearl River Delta region. *Acta Sci. Nat. Univ. Sunyatseni* **2005**, *44*, 49–52 (in Chinese).
- China Folklore Photographic Association. *Rivers and Lakes*. <http://www.china-fpa.org/course/dl/dili2-hl.htm#head> (accessed April 2007).
- Xu, S. S.; Liu, W. X.; Tao, S. Emission of polycyclic aromatic hydrocarbons in China. *Environ. Sci. Technol.* **2006**, *40*, 702–708.
- Li, G. C.; Xia, X. H.; Yang, Z. F.; Wang, R.; Voulvoulis, N. Distribution and sources of polycyclic aromatic hydrocarbons in the middle and lower reaches of the Yellow River, China. *Environ. Pollut.* **2006**, *144*, 985–993.
- Loess Plateau Geodata Analysis Center. *Data of Loess Plateau's rainfall process* <http://loess.geodata.cn/Portal/metadata/view-Metadata.jsp?id=712100-8900&isCookieChecked=true> (accessed April 2007).
- Mitra, S.; Bianchi, T. S. A preliminary assessment of polycyclic aromatic hydrocarbon distributions on the lower Mississippi River and Gulf of Mexico. *Mar. Chem.* **2003**, *82*, 273–288.
- Fernandes, M. B.; Sicre, M. A.; Boireau, A.; Tronczynski, J. Polyaromatic hydrocarbon (PAH) distributions in the Seine River and its estuary. *Mar. Pollut. Bull.* **1997**, *34*, 857–867.
- Vilanova, R. M.; Fernández, P.; Martínez, C.; Grimalt, J. Polycyclic aromatic hydrocarbons in remote mountain lake waters. *Water Res.* **2001**, *35*, 3916–3926.
- Ko, F.-C.; Baker, J. E. Seasonal and annual loads of hydrophobic organic contaminants from the Susquehanna River basin to the Chesapeake Bay. *Mar. Pollut. Bull.* **2004**, *48*, 840–851.
- Humborg, C. Primary productivity regime and nutrient removal in the Danube Estuary. *Estuarine Coastal Shelf Sci.* **1997**, *45*, 579–589.
- Greenfield, B. K.; Davis, J. A. A PAH fate model for San Francisco Bay. *Chemosphere* **2005**, *60*, 515–530.
- Olivella, M. A. Polycyclic aromatic hydrocarbons in rainwater and surface waters of Lake Maggiore, a subalpine lake in northern Italy. *Chemosphere* **2006**, *63*, 116–131.
- Maldonado, C.; Bayona, J.; Bodineau, L. Sources, distribution, and water column processes of aliphatic and polycyclic aromatic hydrocarbons in the northwestern Black Sea Water. *Environ. Sci. Technol.* **1999**, *33*, 2693–2702.
- Chen, Y. Y.; Zhu, L. Z.; Zhou, R. B. Characterization and distribution of polycyclic aromatic hydrocarbon in surface water and sediment from Qiantang River, China. *J. Hazard. Mater.* **2006**, *1143*, 207–214.
- China Water Power Press. *Qiantangjiang River*. <http://www.waterpub.com.cn/JHDB/DetailRiver.asp?ID=10> (accessed April 2007).
- Wang, X. C.; Chen, R. F.; Gardner, G. B. Sources and transport of dissolved and particulate organic carbon in the Mississippi River estuary and adjacent coastal waters of the northern Gulf of Mexico. *Mar. Chem.* **2004**, *89*, 241–256.
- Michor, G.; Carron, J.; Bruce, S.; Cancilla, D. A. Analysis of 23 polynuclear aromatic hydrocarbons from natural water at the sub-ng/l level using solid-phase disk extraction and mass-selective detection. *J. Chromatogr. A* **1996**, *732*, 85–99.
- Halfon, E.; Allan, R. J. Modelling the fate of PCBs and mirex in aquatic ecosystems using the TOXFATE model. *Environ. Int.* **1995**, *21*, 557–569.

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