

OCCURRENCE AND MASS LOADINGS OF *n*-ALKANES IN RIVERINE RUNOFF OF THE PEARL RIVER DELTA, SOUTH CHINA: GLOBAL IMPLICATIONS FOR LEVELS AND INPUTSJI-ZHONG WANG,^{†‡} HONG-GANG NI,^{†‡} YU-FENG GUAN,^{†‡} and EDDY Y. ZENG^{*†}[†]State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Science, 511 Kehua Street, Tianhe District Guangzhou 510640, China[‡]Graduate School, Chinese Academy of Sciences, 19A Yuquan Road, Shijingshan District Beijing 100049, China

(Received 23 January 2008; Accepted 8 April 2008)

Abstract—Riverine runoff samples were collected monthly from March 2005 to February 2006 from the eight major outlets of the Pearl River Delta (PRD), South China, and analyzed to obtain the concentrations of *n*-alkanes in both the filtrate and particulate phases. The average concentrations of $\Sigma(C_{15}\text{--}C_{34})$ (i.e., sum of C_{15} to C_{34} normal alkanes) ranged from 0.06 to 2.97 $\mu\text{g/L}$ (mean, 0.64 $\mu\text{g/L}$) in filtrate samples and from 1.00 to 98.8 $\mu\text{g/g}$ (average, 19.8 $\mu\text{g/g}$ dry weight) in particulate samples. Compared to results from around the world, the levels of hydrocarbon compounds in the PRD were at the high end of the global range. Evaluation of compositional indices of *n*-alkanes indicated that petroleum-related sources are the main contributor of *n*-alkanes found in the PRD, with minor contributions from high plant wax. Regression analyses appeared to suggest that *n*-alkanes are transported into the aquatic environment of the PRD via various pathways, and the transport mechanisms also are considerably influenced by the complex hydrologic conditions in the PRD. The annual riverine input of $\Sigma(C_{15}\text{--}C_{34})$ from the PRD to the coastal ocean was 360 tons/year, or the equivalent of approximately 8,800 tons/year of petroleum hydrocarbons. The emission of $\Sigma(C_{15}\text{--}C_{34})$ from all sources in the PRD was estimated at 39,000 tons/year, or 2.4 g/day per capita. Overall, the PRD contributes approximately 0.2% of the annual global input of *n*-alkanes to the coastal oceans, similar to the contributions of polycyclic aromatic hydrocarbons, further indicating that the PRD has been a significant source of hydrocarbon contamination to the global coastal marine environment.

Keywords—*n*-Alkanes Pearl River Delta Riverine runoff Source assessment Global input

INTRODUCTION

Presently, more than half the world's population lives within coastal regions, and the number continues to rise [1]. As the development of modern civilization has accelerated, the quality of the coastal marine environments has gradually become a global concern [2]. As a consequence, assessing the exchange of organic carbon, a useful indicator of anthropogenic activities, between the continents and oceans is critically important to contain the anthropogenic impact on the coastal marine environment. For example, more than 4×10^8 tons of organic carbon are discharged annually into the oceans via riverine runoff [3], compared with 2×10^7 tons/year by atmospheric transport [4].

Although *n*-alkanes constitute only a small portion of terrestrial organic matter, riverine flux of these compounds is an inalienable part of carbon cycling from a global perspective, and these compounds also are important markers/tracers of the influence of regional anthropogenic activities on the marine system. Furthermore, assessments of the sources and environmental behavior of *n*-alkanes can shed lights into the biogeochemical processes controlling the transport and fate of organic contaminants.

The Pearl River Delta (PRD) economic zone, adjacent to the South China Sea, is one of the most developed regions in China, with a permanent population of 45 million and 8.7 million motor vehicles by the end of 2005 [5]. The annual consumptions of coal, crude oil, and natural gas were $6.9 \times$

10^7 , 3.4×10^7 , and 3.9×10^5 tons of standard coal (1 ton of standard coal is equivalent to 29.3 billion J), respectively, in Guangdong Province in 2005 [5]. The Pearl River, a collection of numerous tributaries within the PRD, discharges approximately 3.3×10^{11} m³ of freshwater annually into the South China Sea through eight riverine outlets [6]. Rapid economic growth and lack of rigorous law enforcement have generated enormous amounts of pollutants that are discharged directly into the Pearl River Estuary and the northern South China Sea [7,8].

The present study was intended to examine the occurrence and estimate the mass loadings of *n*-alkanes in riverine runoff of the PRD based on a comprehensive sampling campaign. Compositional indices of *n*-alkanes were employed to assess the distribution, environmental behavior, and origins of *n*-alkanes. In addition, the monthly and annual riverine inputs of *n*-alkanes were estimated, and their implications for marine hydrocarbon pollution are discussed.

MATERIALS AND METHODS

Sample collection

The sampling sites and procedures have been described in detail previously [9] and are detailed in the *Supporting Information* (<http://dx.doi.org/10.1897/08-034.S1>). Therefore, only a brief description is presented here. Ninety-six water samples (containing suspended particulate matter) from the eight runoff outlets, including Humen, Jiaomen, Hongqilimen, Hengmen, Modaomen, Jitimen, Hutiaomen, and Yamen (Fig. 1), were collected from March 2005 to February 2006. Fifteen subsamples (for Humen and Modaomen) or nine subsamples

* To whom correspondence may be addressed (eddyzeng@gig.ac.cn).

Published on the Web 5/13/2008.



Fig. 1. Locations of sampling sites at the eight riverine runoff outlets of the Pearl River Delta, China. HE = Hengmen; HM = Humen; HQ = Hongqilimen; HT = Hutiaomen; JM = Jiaomen; JT = Jitimen; MD = Modaomen; YM = Yamen.

(for the other outlets) were combined into one composite sample of 40 L at each outlet. The samples were cooled with ice during transport to the laboratory, where they were processed immediately.

Sample processing

The procedures for sample extraction and purification were identical to those described by Wang et al. [7] and are detailed in the *Supporting Information* (<http://dx.doi.org/10.1897/08-034.S1>), except for the chromatographic separation. For chromatographic separation, all extracts were concentrated, solvent-exchanged to hexane, and further reduced to 1 ml with a TurboVap 500 (Zymark, Hopkinton, MA, USA). Each extract was fractionated by column chromatography using a glass column packed with alumina:silica gel (AiBi, Shanghai, China). The fraction containing *n*-alkanes was eluted with 15 ml of hexane and concentrated to 0.5 ml using the TurboVap 500. An internal standard (*n*-C₃₀-d₇₂) was added to the extract before instrumental analysis.

Instrumental analysis

A Varian 3800 gas chromatograph/Saturn 2000 ion-trap mass spectrometer (Varian, Walnut Creek, CA, USA) was employed for peak identification and quantification. A DB-5MS column (length, 60 m; inner diameter, 0.25 mm; film thickness, 0.25 μ m; J&W Scientific, Folsom, CA, USA) was used for separation. Column temperature was programmed to hold at 70°C for 4 min, ramped to 290°C at a rate of 10°C/min, and then held for 40 min. The injector temperature was set at 280°C. Extract injection was conducted in the splitless mode, with a split time of 3 min. The injection port, ion trap, manifold, and transfer line temperatures were maintained at 280, 190, 40, and 280°C, respectively. Mass fragments were generated in the positive electron-impact mode at an electron voltage of 70 eV and scanned in the total ion scan mode within the range of *m/z* 45 to 450. Ion with *m/z* 85 served as the quantitation ion.

Quality assurance and quality control

A standard mixture, containing C₁₅, C₁₆, C₁₇, C₁₈, C₁₉, C₂₀, C₂₁, C₂₃, C₂₅, C₂₇, C₂₉, C₃₁, and C₃₃, was obtained from AccuStandard (New Haven, CT, USA) and used for qualitative and quantitative analyses and spiking experiments. Quantification was performed using the internal calibration method based on seven-point calibration (0.05, 0.1, 0.2, 0.5, 1, 2, and 5 μ g/ml). Target analytes without corresponding standard compounds were quantified using the response factors of the standard compounds with retention times closest to those of the target analytes. The reporting limit for a specific analyte was defined as the lowest concentration on the standard calibration curve divided by the sample weight.

Field, laboratory, and spiked blanks, as well as replicate samples, were processed along with field samples (procedures for preparing these samples are detailed in the *Supporting Information* [<http://dx.doi.org/10.1897/08-034.S1>]). Recovery (average \pm standard deviation) of the target analytes from spiked blanks ranged from 76% \pm 7.7% to 96% \pm 4.2% for the filtrate phase and from 73% \pm 16% to 102% \pm 13% for the particulate phase. A surrogate standard, *n*-C₂₄-d₅₀, was added to all samples to monitor the efficacy of sample processing. Recovery of the surrogate standard from all filtrate and particulate samples was 100% \pm 25% and 89% \pm 15%, respectively. Some low-molecular-weight (LMW) compounds (C₁₅–C₂₄) were found in the field blanks, and the amount of each target detected in the field blanks was less than 20% of the concentration determined in all samples. Therefore, the reporting concentration of each sample was corrected by subtracting the mean concentrations of blanks. The measured concentrations were not corrected by the surrogate recovery data.

Data presentation and analysis

Concentrations of *n*-alkanes in filtrate and combined (filtrate plus particulate) samples were expressed in terms of unit (liter) of water, and those in particulate samples were presented on the basis of dry sample weight. Concentrations of individual

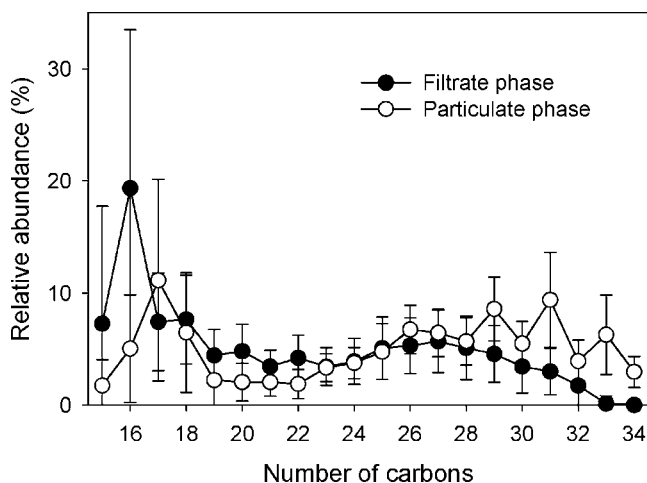


Fig. 2. Average relative abundances of individual *n*-alkanes in both the filtrate (●) and particulate (○) phases.

n-alkane compounds were normalized to the total concentrations of *n*-alkanes when concentration profiles were computed. Several compositional indices were computed to diagnose the input sources of *n*-alkanes, and these are defined specifically in the *Supporting Information* (<http://dx.doi.org/10.1897/08-034.S1>).

All the compositional indices were computed using the summed concentrations of individual *n*-alkane compounds in the combined filtrate and particulate phase. In addition, carbon preference indices (CPIs) were calculated separately for the filtrate and particulate samples to examine any discrepancy in sources for dissolved and particulate *n*-alkanes.

RESULTS AND DISCUSSION

Concentration levels and compositional profiles

Detailed concentration data are summarized in Table S1 (<http://dx.doi.org/10.1897/08-034.S1>). The concentrations of all target compounds, defined as $\Sigma(C_{15}-C_{34})$, ranged from 0.06 to 2.97 $\mu\text{g/L}$ (mean, 0.64 $\mu\text{g/L}$) in the filtrate samples and from 1.00 to 98.8 $\mu\text{g/g}$ (average, 19.8 $\mu\text{g/g}$ dry weight) in the particulate samples. In addition, the total concentrations in both dissolved and particulate phases ranged from 0.18 to 16.2 $\mu\text{g/L}$ (mean, 1.47 $\mu\text{g/L}$) if the concentration unit in the particulate phase was converted to $\mu\text{g/L}$. The total concentrations in more than 83% of the samples, however, were lower than 2 $\mu\text{g/L}$, and two substantially high concentrations (6.08 and 16.2 $\mu\text{g/L}$) occurred in the samples from Humen Outlet in July 2005 and August 2005, respectively. The temporal (in a 12-month period) and spatial (over eight outlets) variations of $\Sigma(C_{15}-C_{34})$ were not significantly different among the eight outlets as determined by a two-way analysis of variance ($p < 0.01$). Compared with other aquatic systems, the particulate concentrations of $\Sigma(C_{15}-C_{34})$ from the present study were significantly higher than those of $\Sigma(C_{16}-C_{36})$ found on Kara Sea shelves [10]. The $\Sigma(C_{15}-C_{34})$ values from the present study were similar to the $\Sigma(C_{15}-C_{35})$ values in the Rhone River (France; 0.17–2.8 $\mu\text{g/L}$) and the Yangtze River (China; 0.18–2.02 $\mu\text{g/L}$) but were relatively lower than the levels in the Yellow River (China) [11].

The average relative abundances and related standard deviations of *n*-alkanes in both the dissolved and particulate phases are presented in Figure 2. Obviously, the LMW components ($C_{15}-C_{18}$) corresponded to the maximum abundant

n-alkane (defined as C_{max}) in most samples. Specifically, approximately 84% of the dissolved samples showed C_{max} at C_{15} to C_{18} , whereas approximately 49% of the particulate samples contained C_{max} at C_{29}/C_{31} . Furthermore, the profiles of *n*-alkane homologues were characterized by a hump around C_{15} to C_{17} in both the dissolved and particulate samples, a second hump around C_{26} to C_{28} in the dissolved phase samples, and a sawtooth pattern at C_{29} to C_{33} , with a strong odd-carbon number preference in the particulate samples.

Although the ratio of $\Sigma(C_{15}-C_{34})$ in the dissolved and particulate phases (designated as D/P) was less than unity for most samples, the average D/P for all the samples was 1.4. In general, D/P values were more than unity in samples collected during the dry-weather season (September to March) and less than unity in samples collected during the wet-weather season. This difference can be attributed to the fact that samples collected in the wet-weather season contained higher suspended matter than samples collected in the dry-weather season. The difference also reflected the different transport modes carrying *n*-alkanes into the aquatic system of the PRD. In the dry-weather season, a large portion of *n*-alkanes may be transported via air–water exchange, whereas in the wet-weather season, *n*-alkanes are mostly moved by wet deposition and soil erosion. In addition, the D/P for LMW *n*-alkanes ($C_{15}-C_{24}$) of 2.9 ± 5.7 was higher than the D/P for high-molecular-weight (HMW) components ($C_{25}-C_{34}$) of 0.94 ± 1.2 , apparently resulting from the difference in hydrophobicity for different-molecular-weight *n*-alkanes that favors the partitioning of LMW components in the dissolved phase.

Source assessment

The occurrence of C_{max} ($C_{15}-C_{17}$) and the sawtooth pattern ($C_{27}-C_{33}$) discussed above points to petroleum residues [12] or marine phytoplanktonic algae [13] as the dominant input sources of *n*-alkanes, with a minor contribution from epicuticular waxes [14]. Microbial activities also could transform HMW *n*-alkanes with pronounced odd-to-even carbon number preference to LMW *n*-alkanes without such preference [15]. Similar profiles of *n*-alkanes also were found in suspended particulate matter collected from the western Mediterranean [16] and the eastern Mediterranean [17], where *n*-alkanes were believed to derive from mixed sources.

Compositional indices are detailed in Table S1 (<http://dx.doi.org/10.1897/08-034.S1>) and are displayed graphically in Figure 3. The CPI calculated for the total *n*-alkanes concentration was 1.10 ± 0.34 , which is comparable to those for urban aerosol particulates [18,19], and the CPI calculated for biogenic *n*-alkanes ($C_{27}-C_{34}$; CPI_2) was 1.6 ± 0.50 . Previous studies found that *n*-alkanes generated from epicuticular waxes of terrestrial plants exhibited high CPIs ($\text{CPI} \gg 1$) [14], whereas the CPI of *n*-alkanes from vehicular emissions and other anthropogenic sources was close to one [20]. Therefore, anthropogenic activities are the main cause for the occurrence of *n*-alkanes in the PRD, with minor contributions from high plant waxes. Furthermore, the particulate samples had a higher CPI_2 (1.9 ± 0.82) than the dissolved samples phase (1.5 ± 1.3 ; $p < 0.05$), suggesting that compared to LMW components, HMW *n*-alkanes from terrestrial high plant waxes are transported more readily with particulate matter, also as described previously [11,21,22]. On the other hand, the odd–even carbon number preference value ranged from 0.3 to 3.3 (mean, 1.1) in the present study. The low odd–even carbon number preference values suggest that *n*-alkanes found in the riverine run-

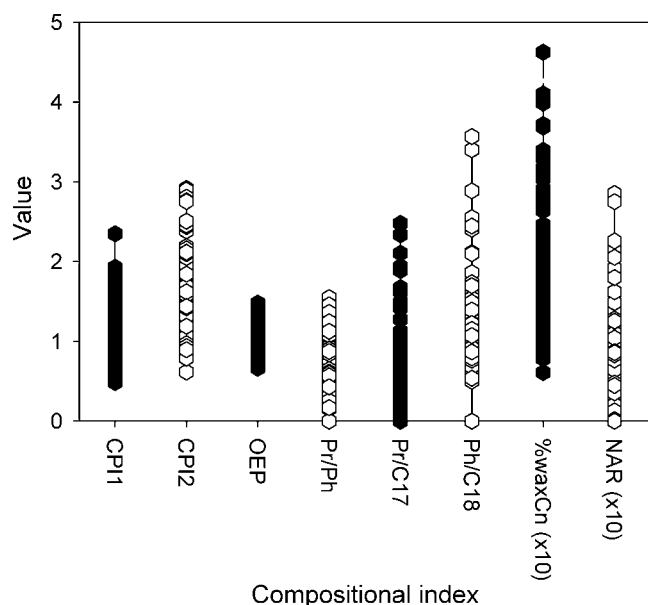


Fig. 3. Compositional indices of *n*-alkanes in the combined filtrate and particulate phase. CPI_1 = carbon preference index calculated for the total *n*-alkanes concentration; CPI_2 = carbon preference index calculated for biogenic *n*-alkanes (C_{27} – C_{34}) concentration; NAR = natural *n*-alkane ratio; OEP = odd–even carbon number preference; Ph/C_{18} = phytane/octadecane; Pr/C_{17} = pristane/heptadecane; Pr/Ph = pristane/phytane; %waxCn = plant wax alkane.

off of the PRD are dominated by petroleum inputs or are indicative of strong bacterial activities, consistent with the conclusion drawn in the preceding paragraph. The low pristane/phytane (Pr/Ph) value (0.66 ± 0.30) also suggested that *n*-alkanes were mainly derived from petroleum. In addition, the values of Pr/C_{17} and Ph/C_{18} were 0.7 ± 0.4 and 1.2 ± 0.5 , respectively, pointing to minor biodegradation of *n*-alkanes with a few exceptions—namely, high Ph/C_{18} values at Humen in August and December (2.55 and 2.89, respectively), at Modaomen in September and February (3.40 and 2.41, respectively), and at Jitimen in July and August (2.44 and 2.57, respectively).

The contribution of biogenic wax *n*-alkanes relative to the total *n*-alkanes (%waxCn) was 6 to 46% (mean, 22%). These values are substantially higher than those found in urban aerosols [18,19] and clearly result from heavy inputs of fossil fuel combustion residues in urban areas. Also, no clear seasonal variability in the contribution of high plant wax was observed in the present study, contrary to the results of a previous study that found high plant wax inputs were more pronounced in winter than in summer in South China [19]. Obviously, a variety of input pathways, such as aerial deposition, soil erosion, upstream runoff, and discharge from plant remnants, confounded the seasonal pattern of *n*-alkanes in the riverine runoff samples under investigation. In the present study, the natural *n*-alkane ratio ranged from 0 to 44% (mean, 9%) in all the samples, which indicates the importance of petroleum-related residues as the source of *n*-alkanes. Therefore, *n*-alkanes in the aquatic environment of the PRD originate mainly from anthropogenic activities.

Factors affecting *n*-alkane concentrations

No linear correlation was found between the dissolved $\Sigma(C_{15}$ – $C_{34})$ and dissolved organic carbon or the runoff discharge (Fig. S1 [http://dx.doi.org/10.1897/08-034.S1]), and

the particulate $\Sigma(C_{15}$ – $C_{34})$ also was not linearly correlated with particulate organic carbon or suspended particulate matter concentrations (Fig. S2 [http://dx.doi.org/10.1897/08-034.S1]). A main reason could be that *n*-alkanes are derived from multiple local sources and are transported into the aquatic system through various paths in the PRD.

By 2006, more than 28,000 enterprises (e.g., mining and washing of coal, extraction of petroleum and natural gas, recycling and disposal of waste, and production and supply of gas) had been founded in the PRD, which at the time possessed 8.7 million motor vehicles and discharged 1.1×10^9 tons of industrial wastewater and 2.9×10^9 tons of domestic wastewater into the aquatic environment [5]. On the other hand, *n*-alkanes also could be derived from soil erosion and atmospheric fallout as a result of ample rainfalls typical in this region. In addition, complex hydrologic conditions may have been responsible for the observed relationship between the concentrations of *n*-alkanes and organic matter. The sampling sites, located in freshwater–seawater mixing zones, are heavily subject to tidal influences. Salinity is known to play an important role in transporting terrestrial organic matter in similar mixing zones [23,24]. The salinity gradient can cause various distribution patterns of organic matter (and, therefore, *n*-alkanes) at different water depths and seasons [16]. Furthermore, sediment resuspension is another factor that compromises the sources of organic matter in these mixing zones [16,25].

Riverine inputs and implications for global contribution

The total annual input of *n*-alkanes from the PRD (via all the riverine runoff outlets) to the coastal ocean was 360 tons/year. Humen Outlet constituted the largest proportion (40.5%), followed by Jiaomen and Modaomen outlets (14.4 and 14.1%, respectively). Coincidentally, the amounts of water discharged through these three outlets are the largest among the eight outlets. The input from Humen Outlet was affected by two extraordinarily high concentrations obtained in July 2005 and August 2005. The impact of water discharge also was obvious, because 80.4% of the $\Sigma(C_{15}$ – $C_{34})$ was discharged during the wet-weather season (April to September). A significantly linear relationship between the monthly fluxes of total *n*-alkanes and water discharge was found ($p < 0.01$) if two samples (collected from Humen in July 2005 and August 2005) were removed from the dataset (Fig. 4). Apparently, hydrological factors dictated the riverine inputs of *n*-alkanes in the PRD, as also observed for polycyclic aromatic hydrocarbons (PAHs) [7], polybrominated diphenyl ethers [8], and linear alkylbenzenes [26], reflecting the climatic characteristics in the region.

Based on the %waxCn estimated above, 22% of the riverine *n*-alkanes were derived from high plants, and the rest originated from petroleum. This results in the annual riverine input for petroleum-derived *n*-alkanes of 280 tons/year, which is equivalent to 8,800 tons/year of total petroleum-derived hydrocarbons, if total petroleum hydrocarbons are assumed to contain, on average, 3.2% of *n*-alkanes (a range of 1.1–9.1% in unfiltered samples was obtained by Eganhouse and Kaplan [12]). Previous studies estimated that approximately 150 tons/year of 16 PAHs identified as priority pollutants by the U.S. Environmental Protection Agency were emitted from all sources in the PRD [27] and that 33.9 tons/year of 15 PAHs (16 PAHs minus naphthalene) were discharged via riverine runoff [7]. Therefore, the riverine runoff carried approximately 23% of the PAHs generated in the region into the coastal marine environment. If the same ratio was employed to estimate the

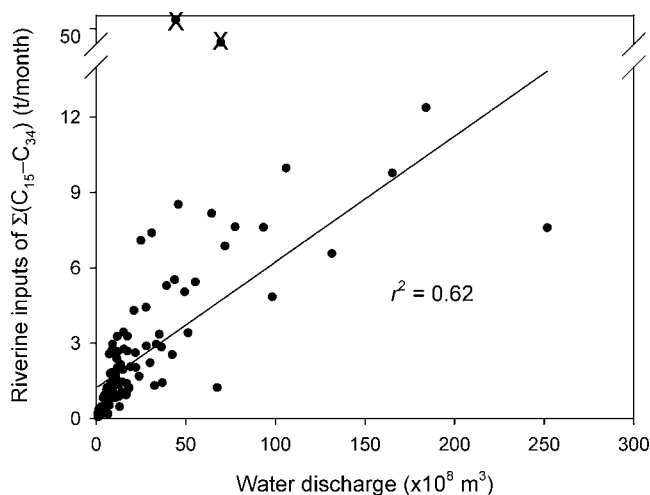


Fig. 4. Relationship between the monthly riverine inputs of $\Sigma(C_{15}-C_{34})$ (i.e., sum of C_{15} to C_{34} normal alkanes; tons/month) and water discharge (m^3).

total amount of petroleum hydrocarbons from all sources, approximately 39,000 tons of petroleum hydrocarbons were emitted annually from the PRD. The emission rate per capita was estimated at 2.4 g/d based on the population of 45 million in the PRD [5]. This emission rate was similar to those (range, 3.3–6.0 g/d; mean, 4.9 g/d) estimated for Southern California (USA) during the 1980s [28]. Interestingly, the gross domestic product in the PRD in 2005 was $US\$2.2 \times 10^{11}$ [5], similar to that in California ($US\$3.3 \times 10^{11}$) in 1980 [29] (<http://countingcalifornia.cdlib.org/matrix/c79.html>). This indicates that the emission rate of anthropogenic *n*-alkane or petroleum hydrocarbons may be a good indicator for the level of economic development.

If 6 million tons of petroleum hydrocarbons from all sources are assumed to discharge into the marine environments around the world per annum [28], and if these hydrocarbons contain 3.2% of *n*-alkanes [12], approximately 190,000 tons/year of *n*-alkanes are expected to discharge into the global coastal oceans. Based on this estimate and the present results, the PRD attributed approximately 0.2% of the annual global input of *n*-alkanes to the coastal oceans. Interestingly, the riverine contribution of PAHs (0.4%) [7] from the PRD was similar to that of *n*-alkanes, further indicating that the PRD has been a significant source of hydrocarbon contamination to the global coastal marine environment.

CONCLUSION

The present study estimated, to our knowledge for the first time, the riverine fluxes of *n*-alkanes from the PRD to the coastal ocean via a comprehensive field sampling campaign. A detailed analysis of the data acquired suggested that *n*-alkanes in the study region were generated mostly from anthropogenic sources. The PRD was estimated to contribute 0.2% of the total global production of *n*-alkanes to the coastal oceans, comparable to the contribution of PAHs (0.4%). The aquatic environment of the PRD has been considerably contaminated by hydrocarbons from mainly anthropogenic sources, and the PRD has been an important source of hydrocarbons to the global oceans.

SUPPORTING INFORMATION

Table S1. Concentrations of *n*-alkanes in filtrate, particulate, and combined filtrate and particulate samples, compositional indices, and monthly inputs.

Figure S1. Concentrations of $\Sigma(C_{15}-C_{34})$ (i.e., sum of C_{15} to C_{34} normal alkanes) in filtrate samples ($\mu\text{g/L}$) versus the levels of dissolved organic carbon (mg/L) and water discharge (m^3).

Figure S2. Concentrations of $\Sigma(C_{15}-C_{34})$ (i.e., sum of C_{15} to C_{34} normal alkanes) in particulate samples ($\mu\text{g/L}$) versus the levels of particulate organic carbon (mg/L) and suspended particulate matter (mg/L).

All found at DOI: 10.1897/08-034.S1 (134 KB PDF).

Acknowledgement—Financial support for the present study was provided by the National Natural Science Foundation of China (40588001 and 40532013), the K.C. Wong Education Foundation (Hong Kong, China), and the One Hundred Talents Program of the Chinese Academy of Sciences. We also thank the participants from the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, and Sun Yat-sen University.

REFERENCES

- De Souza R-M, Williams JS, Meyerson FAB. 2003. Critical links: Population, health, and the environment. *Pop Bull* 58:3–42.
- Global Investigation of Pollution in the Marine Environment. 1976. A comprehensive plan for the global investigation of pollution in the marine environment and baseline study guidelines. United Nations Educational, Scientific and Cultural Organization, Paris, France.
- Schlesinger WH, Melack JM. 1981. Transport of organic carbon in the world's rivers. *Tellus* 33:172–187.
- Buat-Ménard P, Cachier H, Chesslet R. 1989. *Sources of Particulate Carbon in the Marine Atmosphere*. Academic, Chemical Oceanography, New York, NY, USA.
- Statistical Bureau of Guangdong Province 2006. *Guangdong Statistical Yearbook 2005*. China Statistics Press, Beijing.
- Luo XL, Zeng EY, Ji RY, Wang CP. 2007. Effects of in-channel sand excavation on the hydrology of the Pearl River Delta, China. *J Hydrol* 343:230–239.
- Wang JZ, Guan YF, Ni HG, Luo XL, Zeng EY. 2007. Polycyclic aromatic hydrocarbons in riverine runoff of the Pearl River Delta (China): Concentrations, fluxes, and fate. *Environ Sci Technol* 41:5614–5619.
- Guan YF, Wang JZ, Ni HG, Luo XL, Mai BX, Zeng EY. 2007. Riverine inputs of polybrominated diphenyl ethers from the Pearl River Delta (China) to the coastal ocean. *Environ Sci Technol* 41:6007–6013.
- Ni HG, Lu FH, Luo XL, Tian HY, Wang JZ, Guan YF, Chen SJ, Luo XJ, Zeng EY. 2008. Assessment of sampling designs to measure riverine fluxes from the Pearl River Delta, China, to the South China Sea. *Environ Monit Assess* 143:291–301.
- Fernandes MB, Sicre M-A. 2000. The importance of terrestrial organic carbon inputs on Kara Sea shelves as revealed by *n*-alkanes, OC, and $\delta^{13}\text{C}$ values. *Organic Geochemistry* 31:363–374.
- Saliot A, Bigot M, Bouloubassi I, Lipiatou E, Qiu YJ, Scribe P. 1990. Transport and fate of hydrocarbons in rivers and their estuaries. Partitioning between dissolved and particulate phases: Case studies of the Rhône, France, and the Huanghe and the Changjiang, China. *Sci Total Environ* 97/98:55–68.
- Eganhouse RP, Kaplan IR. 1982. Extractable organic matter in municipal wastewaters. 2. Hydrocarbons molecular characterization. *Environ Sci Technol* 16:541–551.
- Blumer M, Guillard RRL, Chase T. 1971. Hydrocarbons of marine phytoplankton. *Mar Biol* 8:183–189.
- Rieley G, Collier RJ, Jones DM, Eglinton G. 1991. The biogeochemistry of Ellesmere Lake, U.K. I: source correlation of leaf wax inputs to the sedimentary lipid record. *Organic Geochemistry* 17:901–912.
- Giorgio B, Lauretta D. 1988. Bacterial reworking of sedimentary lipids during sample storage. *Organic Geochemistry* 13:735–740.
- Dachs J, Bayona JM, Fillaux J, Saliot A, Albaigés J. 1999. Eval-

- uation of anthropogenic and biogenic inputs into the western Mediterranean using molecular markers. *Mar Chem* 65:195–210.
17. Ehrhardt M, Petrick G. 1993. On the composition of dissolved and particle-associated fossil fuel residues in Mediterranean surface water. *Mar Chem* 42:57–70.
 18. Bi XH, Sheng GY, Peng PA, Chen YJ, Zhang ZQ, Fu JM. 2003. Distribution of particulate- and vapor-phase *n*-alkanes and polycyclic aromatic hydrocarbons in urban atmosphere of Guangzhou, China. *Atmos Environ* 37:289–298.
 19. Zheng M, Fang M, Wang F, To KL. 2000. Characterization of the solvent extractable organic compounds in PM_{2.5} aerosols in Hong Kong. *Atmos Environ* 34:2691–2702.
 20. Bi XH, Simoneit BRT, Sheng GY, Fu JM. 2008. Characterization of molecular markers in smoke from residential coal combustion in China. *Fuel* 87:112–119.
 21. Albaigés J, Grimalt J, Bayona JM, Risebrough R, de Lappe B, Walker W. 1984. Dissolved, particulate and sedimentary hydrocarbons in a deltaic environment. *Organic Geochemistry* 6:237–248.
 22. Qiu YJ, Saliot A. 1991. Nonaromatic hydrocarbons in “dissolved phase” (<0.7 μm) and their fractionation between “dissolved” and particulate phases in the Changjiang (Yangtse River) estuary. *Mar Environ Res* 31:287–308.
 23. Saliot A, Parrish CC, Sadouni N, Bouloubassi I, Fillaux J, Cauwet G. 2002. Transport and fate of Danube Delta terrestrial organic matter in the Northwest Black Sea mixing zone. *Mar Chem* 79:243–259.
 24. Saliot A, Derieux S, Sadouni N, Bouloubassi I, Fillaux J, Dagaut J, Momzikoff A, Gondry G, Guillou C, Breas O, Cauwet G, Deliat G. 2002. Winter and spring characterization of particulate and dissolved organic matter in the Danube–Black Sea mixing zone. *Estuar Coast Shelf Sci* 54:355–367.
 25. Sekia O, Yoshikawa C, Nakatsuka T, Kawamura K, Wakatsuchi M. 2006. Fluxes, source, and transport of organic matter in the western Sea of Okhotsk: Stable carbon isotopic ratios of *n*-alkanes and total organic carbon. *Deep Sea Res* 53:253–270.
 26. Ni HG, Lu FH, Wang JZ, Guan YF, Luo XL, Zeng EY. 2008. Linear alkylbenzenes in riverine runoff of the Pearl River Delta (China) and their application as anthropogenic molecular markers in coastal environments. *Environ Pollut* 154:348–355.
 27. Lang C, Tao S, Wang XJ, Zhang G, Fu JM. 2008. Modeling polycyclic aromatic hydrocarbon composition profiles of sources and receptors in the Pearl River Delta, China. *Environ Toxicol Chem* 27:4–9.
 28. Eganhouse RP, Kaplan IR. 1982. Extractable organic matter in municipal wastewaters. 1. Petroleum hydrocarbons: Temporal variations and mass emission rates to the ocean. *Environ Sci Technol* 16:180–186.
 29. Counting California. *California Gross State Product, 1963 to 1997*. University of California, Oakland, CA, USA.