

DISTRIBUTIONS AND SOURCES OF POLYCYCLIC AROMATIC HYDROCARBONS IN THE SURFACE SEAWATER FROM THE NORTHERN SOUTH CHINA SEA

Cai MG*, Wang Y, Li WQ, Wang XH, Liu XY, Guo JQ, Qi AX, Sun JH, Qiu CR, Huang SY, Hong LY
College of Oceanography and Environmental Science, Xiamen University, Xiamen 361005, China

Abstract

41 surface seawater samples were collected during the two cruises in the surface water from the northern South China Sea (SCS) in September 2004 and September 2005, respectively, to examine spatial variability in particulate and dissolved 16 Polycyclic aromatic hydrocarbon (PAH) concentrations and their potential sources. Total concentrations of 16 dissolved PAHs ranged from 1.13 to 11.03 ng/l with a mean value of 4.24 ng/l in 2005, while that of total particulate PAHs were 0.62-9.39 ng/l (2.69 ng/l in average) in 2004 and 0.40-3.62 ng/l (1.33 ng/l in average) in 2005, respectively. As to individual PAHs, 3-4 rings PAHs (except Chrysene) were the dominant contaminants in dissolved phases, while 2-3 rings PAHs predominated in SPM samples. In both phases, PAHs contents in coastal regions were higher than those from open sea in study area and declined as the distance from coast increased, indicating that influences of anthropogenic activities were the major reasons for this distribution pattern. However, water-mass transportation might be another factor which affects the distribution of PAHs in surface water of some regions in SCS. Two isomer ratios of PAHs (Phenanthrene/Anthracene and Fluoranthene/ Pyrene) were used to investigate the sources of PAHs in northern SCS, implying that the most important source of PAHs in northern South China Sea is combustion processes and petroleum input might be another source in some places of study area.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of persistent organic pollutants (POPs) composed of two or more fused benzene rings, which have been found to be widespread ubiquitous contaminants in the natural environment. As many PAH and their metabolic products (epoxides) may induce a number of adverse effects, such as immunotoxicity, genotoxicity, reproductive toxicity and/or carcinogenicity, 16 of them are listed as priority pollutants by national and international environmental agencies (e.g., EPA-US, EEA-EU). PAHs in marine environment are mainly from anthropogenic activities, such as the incomplete combustion of fossil fuels, municipal and industrial effluents, creosote, oil spills, urban and agricultural runoff, asphalt production, and waste incineration¹. Thus, they could be introduced into marine environment via various routes, including river runoff, atmospheric precipitation and maritime transport etc.

In aquatic systems, PAHs exist mainly in freely dissolved, dissolved organic matter (DOM) associated, suspended particulate matter (SPM) associated, and sediment-associated phases. Because of their low solubility and evaporation express, part of PAHs can easily be absorbed onto the surface of the suspended particles once they come into the seawater, and then transfer into sediment following the vertical transportation. As a result, marine ecosystem becomes one of the major sinks of PAH contamination, and it has received more attention because of their lipophilic characteristic and bioconcentration effect. Thus, the determination of concentration and fate of dissolved and particulate PAHs of seawater could provide crucial information on anthropogenic impact on marine environment. Most investigations of PAHs were performed in these regions, where anthropic impact and thus pollutant release are greater, such as coastal areas, estuaries, urban areas, and so on². As the studies of the fates of PAHs in marginal seas are still very limited³, it is therefore necessary to provide

* Corresponding author. Tel.: +86 592 218 6491; fax: +86 592 218 6397. E-mail address: mgcai@xmu.edu.cn (M. G. Cai)

information on the levels of PAHs in such areas.

The South China Sea (SCS) is the largest marginal Sea next to the western boundary of the tropical Pacific Ocean, with an area of 3.5×10^6 km² (23 °N ~ 3 °S, 102 ~ 121.0 °E). Along the boundaries of SCS, there are extensive shelf systems where industrialization and urbanization have been speeded up, such as the southern coasts of China and the southern coast of Vietnam. The present study aims to investigate the concentrations of these contaminants in dissolved and particulate phases, which might help to understand the geochemistry of PAHs in the northern SCS, where so far, only limited studies have been performed.

Materials and Methods

Sample Collection. 41 surface seawater samples were collected during the two cruises in the northern SCS aboard the R/V *Experiment III* in September 2004 and September 2005, respectively (Fig.1). Sampling volume was about 30-40 L. The suspended particulate matters (SPM) were collected by filtering water sample through the glass fiber filters (Whatmen GF/F, 0.7µm). After filtering, the filtered seawater (4L) was passed through solid-phase extraction (SPE, Supelco, USA), envi-C18 columns at the rate about 6ml/min under vacuum to retain the dissolved phase. The envi-C18 columns were conditioned by 5ml of methanol followed 5ml deionised water (Millipore, Watford, UK) before using. The filters and columns were stored at -20°C until further treatment.

Analyses of PAHs. For dissolved phase PAHs, 100 µL, 1ppm surrogate standards (naphthalene-d₈, acenaphthene-d₁₀, phenanthrene-d₁₀, chrysene-d₁₂, and perylene-d₁₂) from Accustandards Inc. (New Heaven, CT, USA) were spiked for each sample, and then 10ml ethyl acetate was used to wash the column. The eluant was concentrated to 2ml by a rotary evaporator, and then residual water was removed by precombusted anhydrous roasted Na₂SO₄. The fraction was finally concentrated to 200µL under a gentle N₂ internal standard (2-Fluorobiphenyl) from Accustandards Inc. (New Heaven, CT, USA) and then added to the sample prior to instrument analysis. For SPM samples, filters were freeze-dried, weight and spiked with surrogate standards. Ultrasonic method was then used for extraction. The following steps are similar to that of dissolved phase. An Agilent 6890 gas chromatography equipped with an Agilent 5975 mass selective detector was used for analyses of 16 PAHs, installed with a auto sampler and a HP-5capillary column (60 m×0.25 mm-i.d; 0.25 µm film thickness Agilent). Selected ion monitoring (SIM) mode was adopted during the analysis process, and quantification of individual PAH compounds. Sixteen individual PAHs given in the US-EPA norm were quantified.

Results and Discussion

Concentrations of PAHs in dissolved and particulate phase. Total concentrations of 16 dissolved PAHs ranged from 1.13 to 11.03 ng/l with a mean of 4.24 ng/l in surface waters from the northern SCS, while that of total particulate PAHs, were 0.62-9.39 ng/l (2.69 ng/l in average) in 2004 and 0.40-3.62 ng/l (1.33 ng/l in average) in 2005, respectively. Both of concentrations of dissolved and particulate PAHs in the northern SCS were higher than other marginal seas, such as Western Mediterranean Sea⁴, Black sea⁵ etc., and much higher than that of open sea, like Northern Atlantic where the concentrations varied from <0.5 to 6.5 pg/l for dissolved phase and 2.1-18 pg/l for particulate phase⁶.

As to each individual PAH, the 5-6-ring PAHs (including Benzo(b)Fluoranthene, Benzo(k)Fluoranthene, Benzo(a)pyrene, Benzo(g,h,i)pyrene, ibenzo(a,h)anthracene, Indeno(1,2,3-c,d)pyrene) were not detected at all of stations, while the 3-4 ring PAHs (except Chrysene) were the dominant pollutants in study areas, ranging from 75% to 100% of 16 EPA priority parent PAHs. Among the 3-4 rings PAHs, Phenanthrene and Anthracene are the most abundant isomers, occupying 8-29% and 2-38%, respectively.

Contrary to composition of individual PAHs in surface water samples, the 2-3 rings PAHs predominated in SPM samples in study area in 2004 and 2005, while high molecular weight PAHs (4-6 rings PAHs, except Fluoranthene and Pyrene) were not found at most of the stations in northern SCS. More than 70% of the total concentrations was represented by PAHs with 2-3 rings. In 2004, Naphthalene was the most dominant

component in SPM, accounting for 22%-93% of total PAHs concentrations, while Phenanthrene was the next dominant PAH comprising 0-28% of \sum PAH content. In 2005, Anthracene are the most abundant isomers instead (occupying 6%-47% of total PAHs concentrations), meanwhile Phenanthrene and Naphthalene also contributed to large amounts of total PAHs in particles, ranged from 2% to 44% and from 4%-21%, respectively.

Distribution of PAHs in surface waters. In both phases, PAHs contents in coastal regions were higher than those from open sea in study area and declined as the distance from coast increased. The higher concentrations were detected at coastal regions, such as Guangdong offshore regions and stations off Hainan Island (Fig. 3). Especially at these stations near Guangdong coastal areas, PAHs concentrations were highest not only in dissolved phases but also in particulate phases, where possible routes of PAHs into study area were concentrated, such as industrial and residential waste water discharge, urban and surface runoff, and petroleum pollution. Because of slight influence by anthropogenic activities, concentrations of PAHs were relatively low at these stations located in open sea (Fig. 3).

Furthermore, water-mass transportation might be another factor which affects the distribution of PAHs in surface water of SCS. For example, surface water from western Pacific, containing minor PAHs compared with surface water from study area, flows into SCS through the Bashi Strait by Kuroshio intrusion, which might be one of the major factors leading to low PAHs values in such regions near the Bashi Strait in both cruises.

Sources of PAHs. Two isomer ratios of PAHs components, Phenanthrene/Anthracene and Fluoranthene/Pyrene were chose to be chemical tracers to examine possible sources of PAHs. Based on the isomer measurements^{7,8}, the fuel oil/combustion transition point for Phenanthrene/Anthracene is 10, while Fluoranthene/Pyrene < 1 implies petroleum and Fluoranthene/Pyrene > 1 indicates combustion processes.

For SPM samples, ratios of Phenanthrene/Anthracene ranged from 2 to 7 and 0.28 to 1 in 2004 and 2005, respectively, indicating that PAHs were mainly originated from combustion processes. The ratios of Fluoranthene/Pyrene ranged from 0.67 to 1.5 in 2004 and from 0.83 to 1.5 in 2005, respectively. For water samples, Phenanthrene/Anthracene and Fluoranthene/Pyrene ratios are 0.76-2.40 and 0.82-1.15. Phenanthrene/Anthracene ratios in surface water also implied the pyrolytic source. The stations where Fluoranthene/Pyrene ratios were lower than 1 in both phases mainly located at southwestern of study area, indicating that fuel oil was a major source of PAHs in this region. As a whole, the most important source of PAHs in northern South China Sea is combustion processes, while petroleum input might be another source in some places of study area.

Partition of PAHs between particulate and dissolved phase. In 2005, Total concentrations of \sum PAH ranged from 1.84 to 11.62 ng/l with a mean value of 5.39 ng/l, and dissolved PAHs occupied 45%-95% of total PAHs (75% in average) which means volatilization and solution are major controlling factors on the partition between two phases. As to individual PAHs, the partition of PAHs between particulate and dissolved phase varies with physical/chemical properties. The solid-water distribution coefficient, K_p ($\text{g}_{\text{total dry solid}}/\text{ml}_{\text{water}}$) was calculated with different rings in this study. The values of K_p were in the following order: 4 rings > 3 rings > 2rings, with the mean values of 30.75, 12.55, 10.05 g/ml, respectively. The decreasing order mentioned above can be explained by lots of factors, such as volatility, solubility, desorption/absorption of organic matters etc.

Acknowledgements

Financially support for this work mainly came from the Natural Science Foundation of China (NSFC) through a grant #40306012. This research was also funded partly by Fujian Provincial department of Science & technology through a grant #2005Y021. We also thank board the R/V *Experiment III* support from South China Sea Institute of Oceanology (SCSIO), Chinese Academy of Sciences (CAS).

References

1. Yim U. H, Hong S.H., Shim W.J. *Chemosphere*. 2007; 68: 85.
2. Bouloubassi I., Mejanelle L., Pete R., et al. *Mar. Pollut. Bull.* 2006; 52: 560.
3. Cai M.G., Wang X.H., Qiu C.R., Guo J.Q., Qi A.X., Huang S.Y., Hong L.Y. *Organohalogen Comp.* 2007; 69.
4. Dachs J., Bayona J.M., Raoux C., Albaiges J. *Environ. Sci. Technol.* 1997; 31: 682.
5. Maldonado C., Bayona J.M., Bodineau L. *Environ. Sci. Technol.* 1999; 33: 2693.
6. Schulz-Bull D.E., Petrick G., Bruhn R., Duinker J.C. *Mar. Chem.* 1998; 61: 101.
7. Colombo J.C., Pelletier E., Brochu C., Khalil M., Catoggio J. *Environ. Sci. Technol.* 1989; 23: 888.
8. Benlahcen K.T., Chaoui A., Budzinski H., Bellocq J., Garrigues P.H. *Mar. Pollut. Bull.* 1997; 34: 298.

Fig. 1: Sampling stations of SCS(S: 2004.09; K: 2005.09)

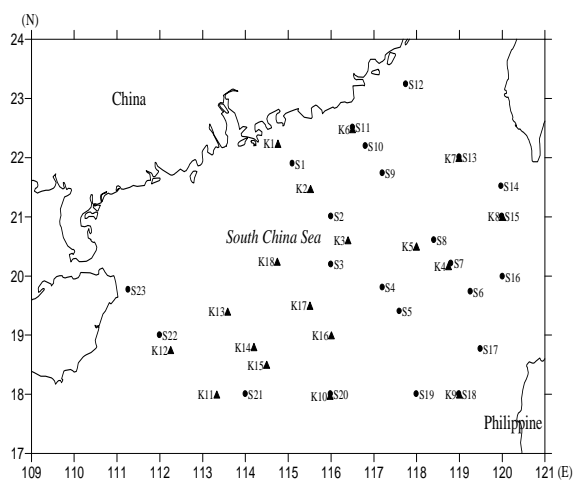


Fig. 2: Distribution of Σ PAH in northern SCS

(a: particulate phase, 2004; b: particulate phase, 2005; c: dissolved phase, 2005)

