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Levels of polycyclic aromatic hydrocarbons in some agricultural, industrial and urban areas along Xiamen coastal waters, China

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Abstract: An intensive investigation was conducted to study the distribution of polycyclic aromatic hydrocarbons (PAHs), to show firstly the level of pollution in the agricultural areas and analyses specifically the status of soil polluted by these persistent pollutants in some locations of Xiamen region. Soil samples collected from Jiulong agricultural catchment have been analysed for 16 PAH compounds, using gas chromatography flame ionization detection in order to determine the level of selected PAH components and to identify the factors that may control their distribution and persistence in the area. The main PAHs found in soil samples were the low molecular weight. The total PAHs detected in soil samples ranged from 0.50 to 0.95 μg/g soil. The highest values of PAHs were significantly detected in the orange tree leaves, which range from 236.1 to 249.3 μg/g soil showing recent atmospheric inputs of these volatile pollutants. The distribution of PAHs in vegetable were monitored and indicating that the concentration were high and ranged from 8.24 to 58.87 μg/g. Other sediment samples were also collected and analysed from urban sewage (5.26 μg/g dw), aquacultural (0.52 μg/g dw) and industrial areas (from 0.62 to 2.09 μg/g dw), during this investigation. The contamination of Jiulong river estuary and Xiamen Western Sea by PAHs has been then widely justified by wastewater discharges and soil runoffs from these areas. The results, therefore, provide important information on the current contamination status caused by the atmospheric transport and point to the need for urgent actions to stop the release of these hydrocarbons to the environment. The necessity of implementing systematic monitoring of PAHs is also emphasized.
Keywords: PAHs; soil; Jiulong River Estuary; Xiamen Western Sea

Introduction

As a result of current use in the rapidly industrializing countries of low-latitude tropical and subtropical Asia regions, persistent organic pollutants (POPs) (e.g. polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), alkylphenols, and some pesticides) have entered and are still being eased into the global environment. Atmospheric transport and ocean circulation are the primary mechanisms for circum-global dispersion of these trace organic pollutants. Polycyclic aromatic hydrocarbons (PAHs) form a group of compounds composed of two or more fused aromatic rings. They are formed by the incomplete combustion of organic matter. Although natural sources of PAHs exist, the combustion of fossil fuels is the primary anthropomorphic source of PAHs released into the environment. PAHs are hydrophobic compounds; their persistence in ecosystems is largely due to their low water solubility, which also results in their association with particulate and sedimentary material.

The Environmental Protection Agencies of U.S. in the most developed and developing countries have identified 16 un-substituted PAHs as priority pollutants, 8 of which are probable or possible human carcinogens. A variety of PAHs are found in the marine environment. Sources range from oil spills and petroleum seepage to atmospheric deposition following forest and grass fires. Effects of PAH in the marine environment include toxicity and carcino-genesis in marine organisms and possible transfer to humans via seafood(Malins *et al.*, 1985; Stegeman, 1981).

The recent studies have shown that elevated concentrations of PAHs have been recorded in some locations in Xiamen coastal sediments. The sewage outfalls, waste dumping and petroleum related origin PAH, are a major source of PAHs (Maskaoui *et al.*, 2001; 2002; Zhou *et al.*, 2000). In Daya bay the major source of pollutants is related to urban/industrialized discharges, oil petroleum spill and atmospheric fallout (Zhou *et al.*, 2001). Recently, a collection of as yet uncharacterized PAH-degrading strains were obtained from the sediment and water samples in Xiamen harbor, especially in the most polluted sites of natural petroleum hydrocarbon (Guo *et al.*, 2001). These studies have shown that elevated concentrations of PAHs have been recorded in some locations in Xiamen coastal sediments. The detailed data of the level of these organic pollutants from different proposed sources of contamination is still needed to be investigated. Also some results concerning assessment of the levels of PCBs in Xiamen region, which were published recently, showed the contamination of the soil, plants, leaves and vegetables posing a risk to human health (Maskaoui *et al.*, 2005). The purpose of this work is to continue making a comparison of vertical profiles but this time for PAHs in the area

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with different source background. With the lack of data about this kind of pollutants, a similar investigation program already done for PCBs by Maskaoui *et al.* (2005) will be conducted in sediments from aquaculture area, wastewater discharges, agriculture locations, industrial effluents at the same sites around Xiamen Western Bay. To estimate the sources and transport pathways of the PAHs and to facilitate the determination of sediment accumulation rate, sediment cores, soil and plant samples, will be taken from contrasting marine and land locations.

1 Materials and methods

1.1 Geographic features, climates and rainfall distribution

The total land area of the Xiamen Municipality's administrative jurisdiction, including islands, is 1516 km^2; it is located in the southern coast of the Fujian Province(Fig.1). The bay has a complex structure with several islands and different seas, i.e. the West Harbour, Maluan Bay, Tong'an Bay, Jiulong River Estuary, the Southern Sea and the Eastern Sea. The average annual temperature is 20.9℃.

The warmest month is July and August with 28.4℃ and the coldest period is January and February with an average 12.6℃ . Rainfall has an annual average of 1143 mm. The cultivated soil in the Municipality of the Xiamen area was 427 km^2. The major crops are rice (29.8 km^2), peanuts (12.6 km^2), vegetable(22.2 km^2) and fruits(32 km^2).

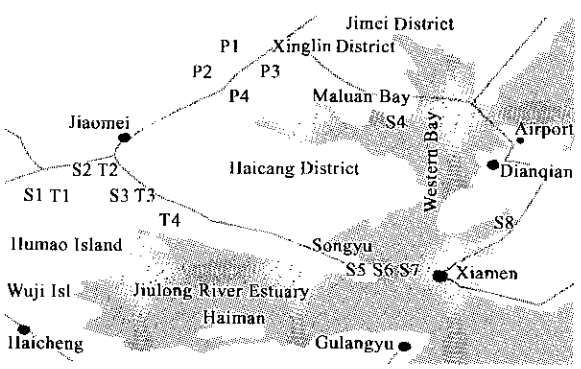

Fig.1 Map of Xiamen region showing the sampling sites

1.2 Chemical standards

Reference PAHs (16 compounds, each at 2000 μg/ml) were obtained from Supelco. Working standard was prepared by diluting the stock solution in cyclohexane. These were further diluted with cyclohexane to prepare calibration solutions for capillary GC analyses in the range 0.01—2.00 ng/ μl. All solvents used for sample processing and analyses (dichloromethane, ethyl acetate, acetone, hexane, cyclohexane, and methanol) were analytical grade and further distilled twice to remove impurities. Deionised water was taken from a Milli-Q system (Millipore, Watford).

1.3 Sampling and sample treatment

Samples of top soil in the cultivated areas along the Juilong River and subsurface sediment from other different areas of Western Xiamen Sea (Maluan and Yuandang Lake) were collected during surveys on June 26, 2002 (Fig.1). The grid reference of each sampling site is given in Table 1.

Table 1 The grid reference of each sampling site

Sample	Time	Source
S1	14: 00	Orange tree field
S2	14: 20	Orange tree field
S3	14: 35	Orange tree field
S4	9: 30	Aquacultural area(Maluan)
S5	12: 30	Electrical Industrial Factory(Songyu)
S6/S7	13: 00	Electrical Industrial Factory(Songyu)
S8	8: 30	Urban sewage(Wastewater Treatment Station of the Yuandang Lake)
T1	14: 10	Leaves from orange tree field
T2	14: 15	Leaves from orange tree field
T3	14: 20	Leaves from orange tree field
T4	14: 30	Leaves from orange tree field
P1	15: 00	Vegetables(Xinglin district)
P2/P3	15: 15	Vegetables(Xinglin district)
P4	15: 30	Vegetables(Xinglin district)

Samples were taken using pre-cleaned glass bottles. After the surface sediment samples were collected, the top 1 cm surface layer was carefully removed with a stainless steel spoon and stored in pre-washed glass bottles. After returning to the laboratory, the sediments were then stored at -20℃ till extraction.

1.4 Sample extraction

Soil, sediment, leaves and vegetable samples were extracted in an ultrasonication bath, where SPM or sediment samples (approximately 10 g dw) were extracted twice in 100 ml of hexane:ethyl acetate, 2:1 (v:v) for 30 min (Zhou *et al.*, 2000; Maskaoui *et al.*, 2002). The extracts were blown down to 0.5 ml, and purified in a silica gel column (4 mm i.d. × 90 mm). The column was then eluted first with 3.5 ml of hexane and the solution discarded. Further elution was by benzene(5 ml) to obtain PAHs(Hong *et al.*, 1995; Zhou *et al.*, 2000). All the extracts were concentrated by gentle N_2 blow-down to about 100 μl. Good recovery was obtained using this procedure as shown by Zhou *et al.*(2000).

1.5 Analyses

A Hewlett-Packard 5890 GC with a flame ionisation detector (FID), an autosampler, and Chemstation software were used for determining the

level of PAHs in soil and sediment samples. The capillary column used for the analyses was BPX-5 (Hewlett Packard HP-5 equivalent, 45 m×0.22 mm i.d. × 0.25 μm film thickness). The oven temperature of analyses was programmed from 60℃(initial time, 1 min) to 140℃ at a rate of 20℃/min. 140 to 236℃ at a rate of 3℃/min, 236 to 290℃ at a rate of 4℃/min, and held at 290℃ for 1 min.

Before analysis, relevant standards were run to check column performance, peak height and resolution, and the limits of detection(LD). With each set of samples to be analysed, a solvent blank, a standard mixture and a procedural blank were run in sequence to check for contamination, peak of identification and quantification. Compounds were identified mainly by their retention times. Selected samples were analysed by full scan GC/MS for confirmation. All results for the samples were reported on a day-weight basis.

1.6 Quality assurance

All analytical data were subject to strict quality control. Spiked soil and sediment samples were determined with good precision, and recoveries ranged from 60 ±8% to 94 ±10% for the samples (Zhou *et al.*, 2000; Maskaoui, 2000; Maskaoui *et al.*, 2002, Zhou and Maskaoui, 2003). In addition, the errors involved in sampling were assessed by carrying out triplicate sampling of water at the same site and the analysis of sample extracts. Results showed good reproducibility of the sampling process.

2 Results and discussion

This part reports the results obtained from a comprehensive survey of some locations in Xiamen region for the levels of PAHs and represents an attempt to understand current contamination status in the area. A summary of data for the levels of PAHs in five locations is shown in Table 2 and the following interpretation and discussion will be focused on sources of PAHs in Xiamen region.

Table 2 Concentration of PAH compounds from some sampling sites in Xiamen region, ng/g dw

Compound	S4	S5	S6	S7	S8
Naphthalene	2.835	0.142	3.068	3.101	2.531
Acenaphthylene	14.87	13.68	20.83	23.7	107.5
Acenaphthene	6.314	57.63	9.127	17.96	9.027
Fluorene	12.14	11.37	54.47	104.8	167.2
Phenanthrene	9.539	5.759	77.23	51.73	684.8
Anthracene	16.62	2.027	19.17	13.29	276.8
Fluoranthene	9.301	0.196	7.76	2.741	82.64
Pyrene	16.34	15.96	56.43	26.96	487.1
Benzo[a]anthracene	13.03	26.39	97.81	69.35	647.3
Chrysene	17.65	21.11	0	3.417	58.53
Benzo[b]fluoranthene	54.37	194.7	166.3	89.36	544.8
Benzo[k]fluoranthene	29.14	97.22	65.32	51.72	504.4
Benzo[a]pyrene	109.7	966.3	155.6	80.08	623.3
Indeno[1,2,3-cd]pyrene	94.51	176.3	147.8	19.13	525.7
Dibenzo[a,h]anthracene	71.76	216.8	78.18	33.48	373.9
Benzo[ghi]perylene	37.41	283.6	69.61	31.3	161.8
Total PAHs	516	2089	1029	622	5257

The total PAH concentrations ranged from 0.52 μg/g dw at Station S4 and 5.26 μg/g dw at Station S8 with a mean concentration of 1.90 μg/g dw. The highest concentration was observed at station S8. The amount of PAHs detected is obviously related to urban runoffs, sewage outfalls and wastewater discharges which is observed during our sampling inside the wastewater treatment station at the end of Yuandang Lake(Fig.1). The high concentration was also obtained from one of the three locations where the Electrical factory is sited at Songyu. The three levels of PAHs detected in the samples (S5, S6 and S7) showed that this installation presents one of the source of PAH contamination of Xiamen coastal waters and consequently could explain the PAH amounts found at station S4(0.52 μg/g dw). After these short description of the PAH levels, it is clear to conclude that the major sources of PAHs are related to the sewage and to the discharges from the Electrical factory located just at the mouth of the harbor in front of the beautiful Gulang Island. These major sources of PAHs will be added to many non-point sources in the area, contributing to the very high concentration of PAHs.

It is clear that in terms of individual PAH composition, all target compounds were detected at all the stations expect Chrysene at station S6, only few of the PAH compounds were present at concentration lower than 10 ng/g dw (Table 2). In terms of the composition of PAHs in the samples, 5-ring PAHs (benzo[b] fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, and dibenzo[a,h] anthracene) and 6-ring PAHs(indeno[1,2,3-cd]pyrene, and benzo[ghi]perylene) are the most abundant PAHs as shown in Fig.2. In addition, 3-ring PAHs (acenaphthylene, fluorene, phenanthrene, and anthracene) and 4-ring PAHs (fluoranthene, pyrene, and benzo[a] anthracene) also showed dominance at few sites(S6, S7 and S8).

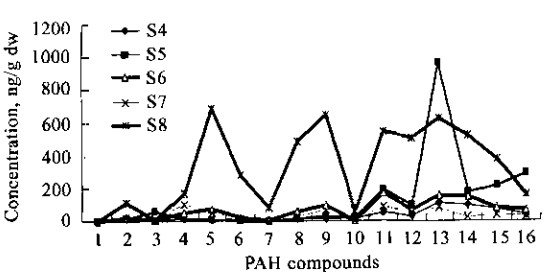

Fig.2 Concentration of PAHs compounds in different stations
1. Naphtalene; 2. acernaphthylene; 3. acenaphtene; 4. fluorine; 5. phenanthrene; 6. anthracene; 7.fluoranthene; 8. pyrene; 9. benzo[a] anthracene; 10. chrysene; 11. benzo[b]fluoranthene; 12. benzo[k] fluoranthene; 13. benzo[a]pyrene; 14. indeno[1,2,3-cd]pyrene; 15. dibenzo[a,h] anthracene; 16. benzo[ghi]perylene

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Polycyclic aromatic hydrocarbons PAHs are widely distributed in the environment where they have the potential to form carcinogenic and mutagenic diols and epoxides that react with DNA. They can be used as tracers in the vegetable, leaves and soil of river and atmospheric transport of anthropogenic contaminants because of their relative environmental stability and variable composition (Mc Veety and Hites, 1988; Yunker *et al.*, 1995, 1996; Halsall *et al.*, 1997). In contrast to the OCs, PAHs are produced in large quantities by natural processes with the result that environmental samples may contain both natural and contaminant PAHs. Natural sources include: natural fires; natural losses or seeps of petroleum or coal deposits; and diagenetic production in soils and sediments.

PAHs are an important component of both crude and refined oil and are produced during the incomplete combustion of coal, wood, and oil. PAHs, found in crude and refined oil (Yunker *et al.*, 1995), often have greater adverse effects than parent PAH without alkyl substitutions on biota(Hellou *et al.*, 1995). PAHs are semi-volatile and those of high molecular weight tend to become attached to particles. The concentration of total PAHs as shown in Table 3 are extremely high with range of 74.61—249.3 μg/g in leaves, 8.24—58.87 μg/g in vegetables, and with a mean concentration of 0.724 μg/g in soil samples.

Table 3 Concentration of PAH compounds from soil, leaves, vegetable samples in Xiamen region, ng/g dw

Compound	P1	P2/P3	P4	S1	S2	T1	T2	T3	T4
Naphtalene	17.61	11.34	19.25	0	4.444	13.07	10.37	6.456	1.863
Acenaphthylene	59.29	24.61	37.02	29.51	27.26	69.32	87.81	68.39	53.85
Acenaphtene	82.89	16.49	41.43	50.43	5.388	246.6	238.4	206.2	71.2
Fluorene	26.6	25.94	37.38	35.15	25.59	130.3	120	82.34	6.328
Phenanthrene	36.83	10.28	24.14	8.505	8.08	92.09	36.55	58.99	11.4
Anthracene	163.9	14.7	81.14	15.63	15.51	158.2	175.6	135.7	10.55
Fluoranthene	204.1	20.37	40.05	23.89	8.927	80.56	80.31	65.8	13.16
Pyrene	159.9	16.49	58	31.45	8.044	402	312.8	331.9	285.4
Benzo[a]anthracene	387.8	51.47	35.40	0	15.53	1070	844.7	628.6	368.7
Chrysene	0	0	0	0	0	66.9	58.08	55.35	32.52
Benzo[b]fluoranthene	113.4	997	869.9	0	52.76	1865	1837	1971	1718
Benzo[k]fluoranthene	125.5	8.944	5.952	0	18.11	274.7	257.8	246.8	73.17
Benzo[a]pyrene	27.2	17.04	6.904	0	19.97	2441	2760	2438	3470
Indeno[1,2,3-cd]pyrene	9884	6541	54245	493.9	218.2	2E+05	2E+05	2E+05	57123
Dibenzo[a,h]anthracene	24.11	22.37	14.12	123.5	38.19	201.1	162	276.3	100.4
Benzo[ghi]perylene	719.8	458.3	3357	133.2	36.68	42164	41621	29526	11270
Total PAHs	12033	8236	58873	945.2	502.7	249275	248602	236098	74610

Release of PAHs by human activities has increased dramatically during the past century as a result of increased combustion of fossil fuels. Most of the samples have been shown to contain combustion PAHs transported atmospherically to the Xiamen environment.

Contamination was dominated by high molecular weight compounds, particularly 5-ring PAHs. The PAH distribution profile in the study area indicated inputs from both point and diffuse, as the levels were high throughout the sampling sites. The ratios of certain related PAH compounds indicated that the PAHs were mainly derived from urban air deposition. Also the pollutants can be transported through water column from the contaminated areas by sewage and discharge inputs to these locations. Other evidence of these high concentrations are based on potential inputs from the large river (Jiulong) which drains intensive accidental spills during handling in the port and from the industrial and domestic wastes.

3 Conclusions

Global transport pathways have existed as long as the Earth has had oceans and an atmosphere. Although, there is an evidence of pre-industrial long-range contamination, it is only during the last 20 years, and particularly after the Chinese open policy, that human activities have significantly affected remote environments of the globe. These global impacts have been due largely to the increase in emissions to the atmosphere as a result of the industrial revolution.

This contamination has been scientifically recognized as a manifestation of long-range transport of pollutants to the Xiamen areas. Problems caused by contaminants depend on their distinctive characteristics and how these interact with biogeochemical pathways. In general, polycyclic aromatic

hydrocarbons PAHs have been produced and released to the environment in large quantities. Once released, they are often long-lived and become widely dispersed.

Because of the lack of previous studies from the same sampling areas, it is not possible to make any conclusion about the temporal variation of the sediment quality in the area during the recent years. In order to develop and maintain an adequate level of environment protection, there is an urgent need to develop a robust monitoring program for the continued surveillance of PAHs in the area, and consequently to adopt an efficient risk assessment strategy to determine the likely impacts of these compounds may have on the local ecosystems.

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