

澳门环境与城市发展科学研究

INVESTIGAÇÃO CIENTÍFICA SOBRE O AMBIENTE E DESENVOLVIMENTO
URBANO EM MACAU

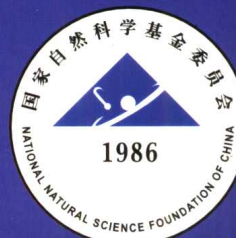
王志石 陈吉宁 杜鹏飞



澳门大学



清华大学



国家自然科学基金委员会

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2002

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王志石 陳吉寧 杜鵬飛

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PREFACE

The joint research program on Macau environment and city development has been carrying out since 1994, jointly sponsored by National Natural Science Foundation and University of Macau as well as Macau Foundation. Under such a cooperation framework, the professors in Department of Environmental Science and Engineering, Tsinghua University, Beijing have actively participated in the collaborative researches for years and contributed to the research program productively and constructively. Together with the professors in Faculty of Science and Technology, University of Macau, Macau, they have studied the Macau urban air and noise pollutions and the coastal water environment surrounding Macau by field monitoring, computer modeling, as well as remote sensing technique. Part of the updated research achievements was published in this book, together with research contributions by the other joint research program partners in Department of Hydraulic and Hydropower Engineering, Tsinghua University, and in Guangzhou Research Institute of Geochemistry, Chinese Science Academy, and in Environmental Science Research Center, Beijing University. The local research teams of Macau have also contributed their research achievements to publication of this book. We are sincerely grateful for all these contributors.

Zhishi Wang, Jining Chen, Pengfei Du

前 言

自 1994 年以来,在国家自然科学基金委员会,澳门大学及澳门基金会的联合资助下,清华大学环境科学与工程系与澳门大学科技学院在澳门环境与城市发展领域进行了卓有成效的合作研究,共同研究了澳门市区空气和噪音污染,遥感在澳门水域环境研究的应用,南湾湖生态环境评价等。清华大学水利水电工程系教育部泥沙重点实验室,中科院广州地球化学研究所以及北京大学环境科学研究中心等也参与了这项合作研究计划,并在澳门河口污染物迁移数学模型,澳门大气和水环境中的有害有机物污染监测与评价,澳门街区风洞试验等方面做出了很有价值的贡献。他们研究的最新成果都收入此论文集之中。澳门大学科技学院教授们的有关研究成果也一并收入论文集中,包括澳门空气质量预测预报模型,室内空气质量控制技术。在此,我们向所有作者表示衷心的感谢。

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Fate and Pathways of Organic and Inorganic Toxicant Pollution in Macau Coastal Waters

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ABSTRACT: Toxicant pollution usually involves persistent organic pollution (PAHs, PCBs, organochlorine pesticides) and heavy metals (Pb, Cd, Cr, etc) in water and sediment as well as biota phases. A long term field monitoring research has been made since 1994 regarding to the toxicant pollution in Macau coastal waters, aiming at finding out the pollution sources of the specific pollutants such as PAHs and tracing back to the pollution histories such as DDTs residue variation along the sediment column samples (1 m depth) as well as identifying high risky pollution zones of the coastal waters (such as Porto Interior or inner port). However, it has been found that solely based on the field monitoring data, the above-listed tasks can only be partially completed, particularly for identification of fate and pathways of the toxicant pollution in the coastal waters. Therefore, it is vitally needed to establish the conceptual models to insight the complex pollution processes occurring in the coastal waters, especially these processes such as volatile organic species exchange between atmosphere and water phases, adsorption and absorption of inorganic and organic compounds on suspended particulate matter, particle settling and pollutants vertical transport, and mass transfer at water/sediment interfaces, as well as tide flow patterns and long distance pollution transport in the coastal waters.

Macau coastal waters are characterized by high turbidity with high suspended solid contents in water column and active mass transfer at water/sediment interfaces. For fate and pathways of organic and inorganic toxic pollution in the coastal waters, it is believed that the pollutant adsorption and absorption on suspended solid surfaces and exchange between water/sediment phases are important while the atmosphere/water exchange is not, because of nonvolatile nature of the persistent organic pollutants. The study of conceptual modeling for the pollution fate and pathways was focused on the water-particulates interaction and exchange processes, particularly for water-solid phase partitioning of persistent organic pollution (e.g., PAHs) in water column and in surface sediments as well as for adsorption and remobilization of heavy metals in the coastal water sediments.

KEYWORDS: water-sediment phase partitioning, adsorption and absorption, neutral no polar organic compounds, heavy metals

Fate and Pathways of Organic and Inorganic Toxicant Pollution in Macau Coastal Waters

Usually an estuary converges a large quantity of runoff from a wide basin such as the Pearl River delta, leading to transport of continent pollutants including anthropogenic inorganic and organic toxicants to the estuary. Urban runoff outfalls from a metropolitan coastal city like Macau also exert adverse impacts on the estuary such as nutrient overloads and persistent toxicant accumulation. The acid rain widely occur in the Pearl River delta including Macao and its neighboring areas, which contributes to nutrient and toxicant pollution of the estuary, too. It is of a common recognition in the scientific society that suspended particles are scavengers for various dissolved toxicants (heavy metals and petro-hydrocarbons) in the coastal waters, particularly the fine particles with diameters less than micrometers being the major media for adsorption of heavy metals and absorption of organic toxicants due to their large specific surface areas. In the estuary region, there usually exist high saline gradients and high energy dissipation which lead to coagulation and sedimentation of fluvial fine particles there so that the heavy metals and organic toxicants attached to the fine particles go to the sediment together with the coagulated particles. So the sediment in an estuary is usually a sink for these toxicants where the toxicant compounds are accumulated and immobilized.

With rapid economic development, the coastal waters of South China Sea faces increasingly environmental stresses, one of which is organic and inorganic toxicant pollution in water and sediment phases, specifically involving persistent organic pollution and heavy metals. The persistent organic pollution can be subdivided into polycyclic aromatic hydrocarbons PAHs, polychlorinated biphenyls PCBs, and organochlorine pesticides such as DDTs and HCHs. The field monitoring and assessment of these toxicant pollutants have been widely made since 90s, particularly in Macau coastal waters^{[1][2]}, Victoria Bay of Hong Kong^[3], Xiamen Bay^{[3][4]}, as well as the whole Pearl River estuary^{[5][6][7]}. These studies were focused on field sites sampling of water and sediment and biota samples, and laboratory atomic absorption and chromatographic analysis of the samples for quantifying contents of the toxicant species in water and sediments. One of the research objectives of these studies was to trace back to the pollutant origins by collecting and analyzing the field monitoring data, which may includes atmospheric input, long distance fluvial transport, as well as local waste dumping (municipal wastewater, urban runoff).

The Pearl River delta is situated in the lower reaches of the Pearl River network which includes West River, Pearl River and East River as well as lots of tributaries connecting these main rivers as a net. Macau is just located at the west tip of the delta. The Macau coastal waters looks like a giant sink of suspended solids converging most of the solids transport fluxes through the west delta water network and in the same time collecting large quantities of organic and inorganic toxicants attached to the suspended particulates and accumulated in the coastal water sediments annually. It has been already recognized that most of the persistent organic pollutants in water environment are hydrophobic and preferring to staying in particulate phase instead of water phase. High affinity of the heavy metals pollutants to particulate phase has also been widely recognized. Therefore the sediments of the coastal waters become a sink of the organic and inorganic toxic pollutants from the upstream regions as well as the local sources. The Macau coastal waters are characterized by high turbidity with high suspended solids levels and active pollution interactions at water/sediment boundary. Therefore, the physicochemical interactions and exchange processes between water and particulate phases are the key for understanding fate and pathways of the toxic pollution of the coastal waters, which involve heavy metals accumulation and possible remobilization of the sediments^{[8][9][10]} and persistent organic pollutants transport and transformation in the sediments^{[11][12]}.

1. Field Monitoring Assessment of Toxic Pollution in Sediments^{[1][2][13]}

In March 1997, the first field monitoring program was made over the Pearl River estuary and its upstream waterways. Totally 17 sampling sites were selected to collect surface sediment samples with depths of 10-20 cm, including Guangzhou harbor and Macau coasts. The persistent organic compounds PAHs, PCBs and organochlorine pesticide residues in the samples were measured in

laboratory by GC-MSD and GC-ECD chromatographic analytic procedures. It was found that one of the highest persistent organic concentrations occurred in the surface sediments sampled at Porto Interio of Macau (ZB13) which is a sink of suspended fine particles transporting from the upstream waterways. Because of affinity of the hydrophobic organic compounds PAHs and PCBs to solid phase, the fine particles deposition led to accumulation of the toxic compounds in the sediments of Macau. The atmospheric dry deposition might be of another source of the organic pollutants accumulation in the sediments. Table 1 presents the details of the field monitoring results.

Table 1 Concentrations of organic contaminants in sediment samples ^[1]

Sample number	ZB07	ZB08	ZB09	ZB10	ZB11	ZB12	ZB13
Sampling sites	Lingdingyang Bay						Macau Porto Interio
	Wanqingsha	Shenzhen bay	Lingding island	Qiao	Jiuzhou Bay	Macau Nam Van Lake	
Organochlorinated pesticides							
HCHs	1.6	0.14	1.45	2.64	1.65	2.36	2.85
DDTs	10.17	2.6	12.31	10	10.63	115.61	1628.81
Other pesticides	5.98	2.89	3.87	9.68	8.09	11.46	26.52
Total pesticides	17.75	5.63	17.63	22.32	20.37	129.43	1658.18
Polycyclic Aromated Hydrocarbons PAHs							
Naphthalene (Na)	55.77	10.77	32.81	40.22	43.72	43.29	50.15
acenaphthene	10.84	nd	nd	nd	43.72	43.29	3.58
acenaphthylene	nd	nd	nd	nd	nd	nd	7.16
Fluorine (Fl)	54.22	nd	15.44	65.36	87.43	86.58	32.24
Phenanthrene (Ph)	109.3	11.24	60.15	65.36	65.57	64.94	136.69
Anthracene (An)	10.41	nd	5.47	5.45	5.46	5.41	20.63
Fluoranthracene (Flu)	33.83	5.5	20.41	21.28	25.66	25.41	247.58
Pyrene (Py)	26.02	5.5	23.33	18.24	14.26	14.12	221.79
Benzo(a)anthracene	23.42	5.5	14.58	9.12	8.55	8.47	162.48
Chrysene (Chr)	62.46	11	35	39.52	37.06	36.7	232.11
Benzo(b)fluoranthracen	54.65	22.48	28.87	130.72	206.09	204.08	1786.87
Benzo(k)fluoranthracen	31.23	22.48	18.37	65.36	131.15	129.87	1326.33
Benzo(a)pyrene (BaP)	31.23	11.24	18.37	43.57	74.94	74.21	1492.12
Indene(1,2,3-cd)pyrene	33.83	22.48	21	87.15	112.41	111.32	1326.33
Dibenzo(a,h)anthracene	26.02	5.62	10.5	43.57	56.21	55.66	957.91
Benzo(ghi)pyrene	36.43	22.48	26.25	98.04	93.68	92.76	1215.81
16 TCL PAHs	599.68	156.32	330.55	732.96	1005.91	996.11	9219.78
2-3 ring PAHs (%)	40.11	14.08	34.45	24.07	24.45	24.45	2.72
Total PAHs*	2284.1	323.07	995.76	1959.96	2372.16	2349.06	14811.5

*: Total PAHs include parent PAHs, Alkyl-PAHs, N/S – PAHs (μ g/kg, dry weight)

Therefore, the Macau coastal waters has become the highly ecologically risky water zone of the persistent organic pollution because of high accumulation of these compounds in the sediments of the coastal waters. In order to further clarify the highly risky persistent organic pollution in the coastal waters, particularly to find out specific sources and pathways of specific persistent organic compounds, the follow-up field monitoring program was made in October 1998 with 45 sampling sites located around the coastal waters (e.g., at Porto Interio, Porto Externio, Nam Van Lake, Coloane water area, etc.) and the surrounding waterways such as Qianshan river, Shizimen waterway, Maliuzhou waterway, Jiuzhou port. The persistent organic compounds in the surface sediment samples were analyzed and measured by the same procedures in laboratory as it did in March 1997. It was found that the distribution profiles of unsubstituted PAHs or parent PAHs (P-PAHs) among these sampling sites were following the similar patterns. The P-PAHs analyzed included benzo[e]pyrene(BeP), benzo[a]pyrene(BaP), benzo[b]fluoranthene(BbFlu), inde[1,2,3-cd] pyrene (In[1,2,3-cd]P). The

monitoring data clearly indicated that these PAHs pollutants came from the identical source through the similar pathways to the coastal waters, i.e., fluvial transport of suspended solids with highly accumulated PAHs. It is some sort of non-point pollution source initiated over large areas of the upstream delta.

The PAHs contents in the surface sediment samples at Porto Interior sites (MC25-34) were found to be in the range of 4000-7000 ng/g dry weight dramatically higher than these of the other sites (1000-2000 ng/g dw), which indicates that there exists another local pollution source leading to the extremely high PAHs pollution level in the Porto Interior samples. It is believed the source was of Macau urban runoff and municipal wastewater discharge into the water zone surrounding Porto Interior. Table 2 presents the details of the field monitoring output.

Among these samples taken at sampling sites except Porto Interior, the values reflecting the dependencies of the ratio of Alkyl-PAHs/P-PAHs vs. the ratio of low molecular weight (LMW)/high molecular weight (HMW) were found to be close each other (1.3-2 vs. 0.6-1.2) while the dependencies of these two ratios at Porto Interior showed a different picture with quite scattering of the ratio dependency values, which further confirmed existence of the local pollution source near Porto Interior. Another dependency between the ratios of BaP/BeP and BaA/Chr were studied among these sample sites, too. The BaP/BeP and BaA/Chr ratio dependency reflects bio-degradation of the PAHs compounds in water environment, which can also be used to indirectly identify the pollution sources and pathways. The ratios of BaP/BeP for the Porto Interior sediment samples were found to be close to these of the other sites, which means that the high rings PAHs (>5 rings) pollution sources are identical among these sites including Porto Interior. On the other hand, the ratios of BaP/Chr at Porto Interior were much higher than the other sites, which means that for the low ring PAHs (< 4 rings) pollution, Porto Interior is near the local point pollution source and the other sites are far away from the source.

By further analyzing the chemical compositions of the low and high ring PAHs in the samples from the different sites and on comparison with the PAHs compositions of aerosol and dust in ambient air samples of Macau, the third pollution source of the PAHs in the coastal waters was identified by this field monitoring study, i.e., atmospheric dry deposition. Figure 1 a, b, c, d present the 3-4 rings P-PAHs and 5-6 rings P-PAHs compositions, respectively among the samples of Porto Interior and the other sites in the coastal water sediments as well as the aerosol and dust samples of ambient air of Macau. It was found that the low ring (3-4 rings) PAHs compositions were quite different among these samples while the high ring (5-6 rings) PAHs compositions are similar between the air particulate and water sediment samples including these of Porto Interior, which means that part of the high ring PAHs came

Table 2 Field Monitoring Results for PAHs in Sediments (ng/g, dw)^[2]

	Na	Fl	An	Ph	Py	Flu	BaA	BaP	P-PAH	A-PAH	O/S-PAH
qMC43	12.6	10.2	3.1	48.1	27.8	29.2	7.3	14.1	224.1	342.6	43.4
qMC42	22.7	34.1	15.5	164	81.8	86.2	39.4	40.9	800.9	1265.8	161.4
qMC41	0	8.5	4.7	43.4	35.1	33.6	14.6	11.3	232.4	373.6	63.7
qMC40	0	8.5	7.8	72.9	64.3	59.9	39.4	29.6	534.1	794.7	134.2
qMC39	2.5	25.6	7.8	96.1	57	55.5	29.2	28.2	532	983	163.7
qMC38	37.9	23.9	10.9	89.9	67.2	59.9	27.8	22.6	541.9	928.7	169
qMC37	42.9	30.7	14	110	74.5	78.9	40.9	31	707.2	1159.5	194.4
qMC36	15.2	35.8	23.3	178	115	129	73	49.3	1025.6	1462.8	260.9
qMC35	40.4	25.6	12.4	89.9	70.1	61.4	46.8	33.8	692.7	1364.9	249.6
qMC34	27.8	23.9	14	79.1	57	46.8	27.8	28.2	551.2	1104.2	175.8
iMC25	32.8	29	31	135	208	226	127	94.5	1676	1794.8	371.9
iMC26	53	46	27.9	167	189	118	71.6	40.9	1043.3	3558.8	792.3
iMC27	20.2	17	27.9	126	260	301	234	161	2658.9	1022.1	216.2
iMC28	42.9	54.5	34.1	178	304	254	158	97.3	1940.2	3569.6	697.2
iMC29	48	40.9	23.3	126	142	126	107	66.3	1247.6	2303.6	433.1
iMC31	50.5	46	15.5	133	127	110	62.8	40.9	1012.7	2700.9	575.2

iMC30	50.5	44.3	12.4	150	136	110	61.4	45.1	962.4	2691.8	650.1
iMC33	53	186	94.6	1002	763	722	218	111	4178.4	2692.3	498.1
iMC32	17.7	30.7	15.5	99.2	87.7	80.4	55.5	47.9	836.2	1346.6	247.2
sMC11	27.8	27.3	18.6	158	118	108	39.4	33.8	874.7	1251.3	220.2
sMC12	40.4	18.7	9.3	101	52.6	48.2	24.8	22.6	513.2	860.1	140
sMC13	58.1	18.7	9.3	82.2	36.5	35.1	17.5	18.3	432.9	820.1	106.2
mMC45	30.3	18.7	17.1	126	104	95	32.1	24	654.2	842.7	176.8
mMC47	50.3	25.6	9.3	123	71.6	70.1	24.8	22.6	600.6	963	165.8
mMC24	12.6	3.4	1.6	15.5	7.3	5.8	4.4	2.8	91.8	153.6	15.1
mMC23	15.2	5.1	3.1	20.2	14.6	16.1	10.2	8.5	175.6	170.2	22.5
nMC14	30.3	22.1	10.1	87.6	40.2	37.3	22.6	28.2	470.8	1012.3	122.6
nMC15	48	11.9	4.7	57.4	20.5	20.5	10.2	9.9	283.3	492.9	65.3
nMC16	42.9	32.4	17.1	152	95	87.7	29.2	24	738.2	1247.7	219
nMC17	17.7	23.9	12.4	119	101	81.8	33.6	29.6	680.9	1307.3	254.4
nMC18	15.2	8.5	4.7	40.3	24.8	23.4	11.7	9.9	232.9	347.8	60.8
nMC19	17.7	23.9	9.3	119	57	49.7	14.6	12.7	461.6	1050	147
nMC22	0	13.6	10.9	107	68.7	61.4	20.5	18.3	499.4	871.1	178.8
nMC21	25.3	23.9	14	119	70.1	64.3	24.8	19.7	569	1147	202.1
nMC20	15.2	25.6	14	144	99.3	90.6	27.8	25.4	682.8	1108.9	214.5
cMC08	15.2	10.2	4.7	45	24.8	24.8	7.3	5.6	220.8	353.5	48.3
cMC09	22.7	22.1	17.1	127	87.7	80.4	27.8	26.8	680.7	975.9	171.5
cMC10	73.2	22.1	12.4	115	67.2	65.7	35.1	33.8	682.1	922.8	150.4
jMC01	40.4	17	9.3	79.1	40.9	36.5	24.8	29.6	475.9	784	113.9
jMC02	7.6	17	7.8	82.2	40.9	35.1	26.3	22.6	457.5	801.9	122.8
jMC03	45.5	15.3	7.8	69.8	36.5	30.7	23.4	18.3	450	859.8	116.8
eMC06	53	25.6	9.3	99.2	48.2	43.8	32.1	24	567.6	1050.4	136.4
eMC04	30.3	15.3	7.8	72.9	35.1	32.1	23.4	14.1	413.5	649	87.4
eMC05	104	30.7	18.6	163	92	87.7	45.3	35.2	886.8	1237.8	191.7
eMC07	50.5	20.4	9.3	85.3	43.8	39.4	23.4	18.3	460.8	846.3	118.4

Note: qMCxx – Qianshan River; iMCxx – Porto Interior; sMCxx – Shizimen Waterway; mMCxx – Maliuzhou Waterway; nMCxx – NamVan Waterway; cMCxx – Coloane Waters; jMCxx – Jiuzhou Port; eMCxx – Porto Exterior. Na – naphthalene, Fl – fluorine, Ph – phenanthrene, An – anthracene, Flu – fluoranthrene, Py – pyrene, BaA – benzo(a)anthracene, BaP – benzo(a)pyrene, P-PAHs – parent PAHs, A-PAHs – alkyl-PAHs, O/S-PAHs – oxygen/sulfur PAHs, T-PAHs – total PAHs

from the atmospheric dry deposition and the PAHs transfer at water/air boundary is one of the important pathways of the PAHs pollution in the coastal water sediments, particularly for the high ring PAHs.

By further analyzing the PAHs compositions in the sediment samples, it was found that the PAHs pollution was constituted by three main PAHs groups caused by three different pollution sources, i.e., group I Alkyl-PAHs and O/S PAHs counting for about 30% of the total, which reflects petroleum pollution related to the urban runoff from the Macau city; and group II high molecular weight PAHs (228-302) counting for 27% and resulting from high temperature combustion of fuels. The composition was close to that of the aerosols in ambient air. It may come from vehicular exhaustion emission of the Macau city through the atmospheric dry deposition. The group III was of low molecular weight PAHs counting for 18% of the total which are products of low temperature combustion of oil and may be input by fluvial transport from the upstream delta. The remaining PAHs included 6.5% volatile polycyclic naphthalene and dimethylnaphthlene and 2% PAHs species from

geological mineralization in nature.

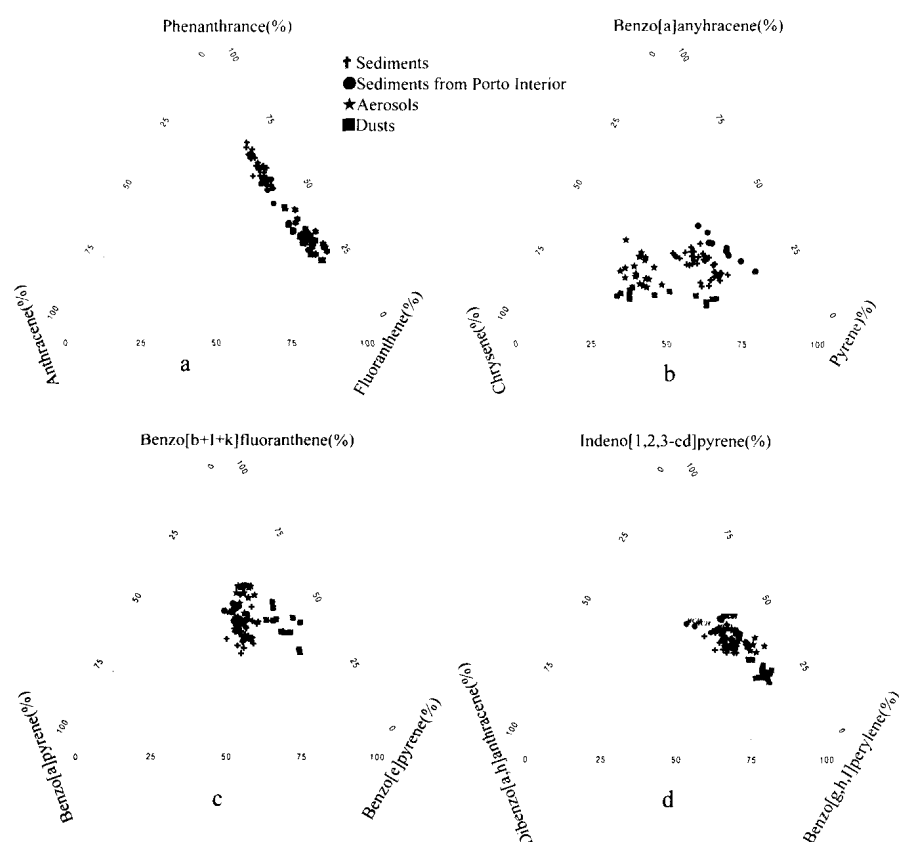


Figure 1 P-PAHs chemical compositions in sediments and aerosols in Macau ^[13]

The laboratory affiliated to Macau Medication Bureau has made a long term field monitoring program since 1992 for monitoring the annual variation of heavy metals in the surface sediments of the Macau coastal waters. Table 3 gives the 1997 monitoring results [9] of the heavy metals Pb, Cd, Cr and non-metal As in the sediments. It was found that the partitioning coefficients (K_d) were 7,600 - 20,000 l/kg among these species at interfaces between pore water and sediment, which means that the pollution species have been already accumulated in the sediment as the persistent organic pollutants (e.g., PAHs) were.

Table 3. Monitoring results of heavy metals and other toxic species in the water phase (W) and the sediment phase (S) ^[9]

	water	solid	water	solid	water	solid	water	Solid
Porto Interio 1		8.4		44		4		26
Porto Interio 2	0.04	1.8	2	35	1.1	36	2.3	22
Areia Preta	0.2	1.8	3.5	28	3.5	37	2.15	20
Praia Grande		4	2.5	45	1.3	29	3.6	22.5
Coloane	0.1	0.6	6.5	15	2.8	24	3.25	17.5
Pac On		6.2		37		35		31.6
K_d (l/g)	20		11.3		18.8		7.6	

In March 1997, a sediment column with 70 cm depth was taken at Nam Van Lake for measuring variations of heavy metals contents along the column depth. The heavy metal contents then were measured in laboratory by atomic absorption procedure. The heavy metals involved were Pb, Cu, Zn, Ni, Cr and Cd as well as As. By the ^{210}Pb measurement, the sediment column was aged to estimate annual variation of the heavy metal species in the period of 60s to 90s. It was found that there were

peak contents of these heavy metal pollutants occurring in 90s, which is just a period of rapid economic development of the Pearl River delta. It has been recognized that the estuary sediment is not only a sink for heavy metal pollution but also a second source for heavy metals 'fixed' in the sediment releasing back to the water body. The sediment 'fixed' heavy metals may be remobilized from the sediment if the environmental chemical condition at water/sediment interfaces changes due to coincidence of other pollution events. For example, overloading of degradable organic and nutrient wastes from sewage at the interface may lead to anoxic environment there and anaerobic acidification of organic wastes will produce various volatile fatty acids accumulated in the surface sediment [14]. Some physical processes occurring at the interface can also cause metal remobilization. For example, resuspension of the surface sediment resulting from high shear stress near shores may dramatically change the pH and redox conditions, leading to metal release from the sediment. It has been shown that the pH change and periodic redox cycles can shift the metal binding fractions on the sediment particulate surfaces to more mobilizing and soluble ^[15].

2. Physicochemical Modeling for Toxic Pollution in Water and Sediment Phases

Undoubtedly the field monitoring data can directly reflect the real world but a complex world. The toxic pollution in the coastal water sediments is a quite complicated problem involving various different pollution sources and pathways such as air/water exchange, surface adsorption and absorption, suspended particulates settling and transfer together with toxicants attached, resuspension of surface sediments, as well as long distance suspended solids transport in the tide flow field of the coastal waters. Only depending upon the field monitoring study, one cannot clearly understand the pollution fate and pathways. One of the reasons is that contaminated waters and sediments contain a mixture of aliphatic and aromatic organic compounds, each differing in its reactivity, solubility, toxicity, volatility, mineral surface affinity, and biodegradability. Another reason is that the suspended particulate matter and the sediment in natural systems are of a mixture containing phytoplankton, detritus, and clays and silts with different organic carbon contents and wide ranges of particle sizes. These different adsorbents do not behave independently. The accessibility of certain sorption reservoirs is probably influenced by the presence of others, and depends on the structure of the particles. The third reason may be that the hydrophobic organic compounds partitioning between suspended and solution phases is not always at equilibrium in water column. The field monitoring data are just reflecting the apparent consequence of interactions among these complicated processes. To clarify the fate and pathways of so many toxicant pollutions (various persistent organic species and heavy metals), physicochemical modeling for these processes and pollutants is essentially needed so as to imitate the reality by stressing those aspects that are assumed to be important and omitting all properties considered to be nonessential.

Bioavailability and ecotoxicology of the persistent toxicants (inorganic and organic) are closely related to their physicochemical transformation and partitioning between the overlying water phase and the suspended solid phase as well as the surface sediment phase. At present the laboratory assessment studies in the process mechanisms are still the most important tools to assess the impacts of these trace species on aquatic ecosystems of the coastal waters. The fundamental understanding of the process mechanisms is based on the chemical equilibrium concept, i.e., the equilibrium models for partitioning between the water and the sediment phases. In order to verify the validation of the laboratory-established models, the field monitoring for typical pollutants and sediments is necessary. Sometimes, considerations of the process kinetics are indispensable to extrapolate the laboratory study output to the actual cases.

2.1. Modeling for Water-Solid Phase Partition of Organic Compounds

Examining field monitoring data in Table 2 for various P-PAHs contents in surface sediment samples at different sites, one can see that the contents are only related to specific compounds in spite of different sites with different sediment particulates. The concentrations of different PAHs compounds in the sediment particulates vary in certain manner from the PAHs with low rings and low molecular weights to the high rings and high molecular weights. In order to insight the phase partitioning and distribution between pore water and sediment particulates, the partitioning coefficient

K_d is defined for a single compound (e.g., pyrene) to measure the compound phase distribution between pore water and sediment particles:

$$K_d = C_s/C_w \quad 1)$$

Where C_s - concentration of the compound partitioning to the particulate phase, ng/g; C_w - concentration of the compound in pore water, ng/l.

Chemically, the persistent organic pollutants in natural water environment are mostly of neutral and nonpolar organic compounds constructed primarily from carbon, hydrogen and halogen (e.g., Cl) atoms such as PAHs compounds. Most natural minerals such as sediment particulates are polar and expose a combination of hydroxyl- and oxy-moieties to their exterior^[16]. Naturally, then these polar surfaces strongly favor interactions which allow them to form hydrogen bonds with polar water molecules, and unfavourably directly adsorbing the nonpolar organic compound molecules such as pyrene and other PAHs on the natural mineral surfaces. In other words, replacing the water molecules at such a surface by nonpolar organic molecules is unfavorable from an energetic point of view. On the other hand, penetration of neutral organic chemicals into any natural organic matter such as humic substances in sediments does not require displacement of tightly bound water molecules. In light of this discussion, we may not be too surprised to find that nonreactive, neutral organic chemicals like PAHs show greater solid-water distribution ratios (K_d) for soils and sediments that contain high amounts of natural organic matter. The neutral and nonpolar organic compounds are absorbed in the natural organic matter attached with sediment particulates instead of directly adsorbing to the mineral surfaces of the sediment particles. Therefore, another partitioning coefficient K_{om} is defined to measure allocation of the neutral organic chemicals between pore water and the natural organic matter in the sediment:

$$K_{om} = C_{om}/C_w \quad 2)$$

Where C_{om} - concentrations of the compound absorbing in the natural organic matter e.g., humic substances in the sediment particulates, ng/g. The relationship between K_d and K_{om} is given by

$$K_d = f_{om}K_{om} \quad 3)$$

Where f_{om} - fraction of the natural organic matter content in the sediment particulates, %. The organic matter-water partition coefficient K_{om} is solely of an organic matter's property with no difference to different sediment particles. It has been found that the K_{om} values for a single neutral nonpolar chemical sorbing to a variety of soils and sediments are almost the same [16]. The K_d values are solely related to the natural organic matter contents f_{om} ; the higher the f_{om} value, the larger the K_d value will be. The C_s values should follow the same pattern if the C_w values do not change too much.

Table 4 presents the analytic results for mineral compositions of the sediment particulates at different sampling sites of the coastal waters. We can see that the organic carbon fractions f_{oc} are almost the same for different sites ranging from 1 - 1.27 %, and the organic matter fractions f_{om} can be calculated by doubling the f_{oc} values. As a result, the K_d values for a single neutral PAH chemical e.g. naphthalene (Na) or phenanthrene (Ph) should be almost the same among these different sites. Referring to Table 2, one can see that the C_s values for a single PAH chemical are in the same level, indeed, no matter where it was sampled. For example, the monitored Na contents (C_s) among the different sampling sites are mostly in the limited range of 30-50 ng/g dw and for the Ph contents, the C_s values vary in limited range from 110 to 160 ng/g dw.

In a fashion analogous to sediment-water partitioning, we can envision the molecules of a given compound partitioning between the organic phase and the aqueous phase. This partitioning process is determined by the relative fugacity of the compound in each phase and at equilibrium may be described by a dimensionless equilibrium constant.

The equilibrium constant can be also named as n-octanol-water partition coefficient:

$$K_{ow} = C_o/C_w \quad 4)$$

Table 4 Analytical Result for Mineral Composition of Sediments

	$f_{oc}(\%)$	$f_{om}(\%)$	Silica(%)	Clay(%)	$\rho_s(\text{kg/l})$	ϕ	r_{sw}	$r_{swl}(\text{kg/l})$
qMC	1.27	2.54	40.4	48.2	2.2	0.7	0.94	
iMC	1.35	2.7	36.3	51.6	2.2	0.7	0.94	7.34×10^{-5}
sMC	1.09	2.2	44	49.5	2.2	0.7	0.94	
mMC	1	2	32	54	2.2	0.7	0.94	
nMC	1.01	2	42.9	46.9	2.2	0.7	0.94	
cMC	1.29	2.58	35.5	58.1	2.2	0.7	0.94	
jMC	1.15	2.3	26.7	67.3	2.2	0.7	0.94	
eMC	1.25	2.5	32	61.5	2.2	0.7	0.94	

Where C_o - the concentration of the compound in the organic phase, ng/l. Partially because of the choices of early workers [16] and the special amorphous nature of C4 to C10 alcohols, but mostly because n-octonal is a reasonable surrogate for many kinds of natural and environmental organic solvents, the n-octonal-water partition constant for a single nonpolar organic chemical such as pyrene is used to generalize the compound partitioning between any organic phase and the aqueous phase. The n-octonal-water partitioning coefficient has been investigated extensively. Because the attachment of a neutral nonpolar organic chemical on sediment particles is essentially of absorption process of the compound to the natural organic matter in the sediments, there is certain relation between the K_{om} and the K_{ow} for the single compound. An empirical equation has been established to quantify the relationship:

$$\log K_{om} = c \log K_{ow} + d \quad 5)$$

Where c and d are empirical parameters whose values depend upon different compound classes. Karichhoff [17] examined the relationship between K_{om} and K_{ow} for a series of the neutral nonpolar compounds (aromatic hydrocarbons, chlorinated hydrocarbons, chliro-S-triazines, phenyl ureas) by compiling the relevant data from different sources, and found that generally the values of parameters c and d were almost invariable and $c = 0.82$ and $d = 0.14$ if the unit of K_{om} is l/kg, instead of l/g. Table 5 gives the values of the K_{ow} for a series of P-PAHs compound including the 2-ring PAH Na, and the 3-ring PAHs Fl, An, Ph, and the 4-ring PAHs Py, Flu, BaA as well as the 5-ring compound BaP. The calculated K_{om} values based on Equation 5) are also given by that table. One can see that the higher the molecular weight and ring numbers of the compound, the larger the K_{om} value it has, which means that the neutral nonpolar PAH compounds with high ring numbers and high molecular weights are more favorable to absorb into the natural organic matter attached to the sediment particulates than low ring and low molecular weight compounds. Combining Equations 3) and 5), one can get the following equation:

$$\log K_d = c \log K_{om} + d + \log f_{om} \quad 6)$$

Table 5 Calculated Partition Coefficients of P-PAHs

	M.W.	$-\log C_{sat}$	$\log K_{ow}$	$\log K_{om}$	$\log K_d$
Na	128.2	3.61	3.36	2.9	1.27
Fl	166.2	4.96	4.18	3.58	1.95
An	178.2	6.46	4.54	3.86	2.23
Ph	178.2	5.2	4.57	3.89	2.26
Py	202.3	6.17	5.13	4.35	2.72
Flu	202.3	5.93	5.22	4.42	2.79
BaA	228.3	7.31	5.91	4.99	3.36
BaP	252.3	8.22	6.5	5.47	3.84

MW – molecular weight of PAH compound; C_{sat} – solubility of the compound

With it, one can calculate K_d values for these P-PAHs compounds which are also given in Table 5. Armed with such a K_d parameter for a case of interest, we may evaluate what fraction of a compound is in water phase f_w in a volume containing both solids and water by

$$f_w = C_w V_w / (C_w V_w + C_s M_s) \quad (7)$$

Where V_w - volume of water in total volume V_t , l; M_s - solid mass in the same total volume, kg. So considering Equation 1), one have:

$$f_w = 1 / \{ 1 + (M_s / V_w) K_d \} = 1 / (1 + r K_d) \quad (8)$$

Where r - solid mass concentration in the total volume, kg/l. For the surface sediment bed, the solid concentration can be expressed by the sediment bed porosity Φ , which is defined by pore water volume/total volume. That is

$$r = \rho_s (1 - \Phi) / \Phi \quad (9)$$

Where ρ_s - density of the solid, kg/l. The mineral compositions of the sediment particulates in the sampling sites are similar referring to Table 4. There are two major minerals silica and clay in the sediment particulates. Generally the silica counts for about 40% while the clay for 55%. The density of the sediment can be calculated by the weighting summary of silica density and clay density, which is 2.2 kg/l.

The compacted sediment bed porosity is usually 0.2 to 0.4, depending upon the particle size distribution. The larger the particle sizes, the larger the bed porosity values are. However, the surface sediment bed is not completely compacted. And there is a strong tendency of resuspension of the surface sediment due to strong shear stresses at the water/sediment interface. These both lead to a high porosity of the surface sediment bed, i.e., 0.7 - 0.8. With Equation 9), one can calculate the r value of the surface sediments in the coastal waters, which equals 0.94 kg/l. Substituting the K_d values in Table 5 into Equation 8), the f_w values for the P-PAHs species in Table 5 can be calculated. The calculation results show an interesting fact that most of the PAHs are partitioning into the sediment phase while in pore water the PAHs are almost undetectable ($f_w = 0$) except the 2-ring PAH Na ($f_w = 0.05$). The higher the ring number and molecular weight, the favorable the compound is to partition into the sediment phase.

In April 2001, the water samples were taken at the water depths of 0.5, 1.2, 3.5, 4.8, 5.5 and 6 meter (bottom), respectively along a water column at Porto Interior, aiming at analyzing partitioning of the persistent organic compounds (organochlorine pesticides DDTs and HCHs, and 16 US EPA TCL PAHs) between the bulk water phase and the suspended solid phase in the column with different water depths. The suspended solid concentrations at different depths of the column were measured to be 1.7, 17.9, 42.5, 54, 58.5 and 73.4 mg/l at the depths of 0.5, 1.2, 3.5, 4.8, 5.5 and 6 meters, respectively. Based on the K_d and r values of different compounds and different depths, the f_w values were calculated by Equation 8). The calculation shows a fact just opposite to the case of water-sediment partition that most of the PAHs are partitioning to the water phase instead of the suspended solids, particularly for 2-ring P-PAH Na. The calculated f_w values for Na are all equal to 1 at different column depths, which means that the Na pollutants are in dissolved phase instead of particulate phase. On the other hand, the calculated f_w value at the bottom for the 5-ring P-PAH BaP is 0.66, that is, the aqueous BaP pollution only counts for 66% of the total pollution and there still remain 34% absorbing onto the suspended particulates. However, at the top of the column (0.5m depth) where the suspended solids was only 1.7 mg/l, the calculated BaP f_w value is 0.99, that is most of the BaP species are in dissolved phase at that depth.

The field monitoring data also show the same trend, i.e., all the 2-ring PAHs were in dissolved phase at these depths while most of the 5-6 ring P-PAHs in suspended particulate phase, particularly at the bottom of the column. The 3-4 ring P-PAHs were detected in both phases and the dissolved phase partition fractions decreased with the depth. The 4-ring PAHs more favored the solid phase than the 3-ring P-PAHs (please refer to Figure 2).

In light of the above discussion, we can conclude that for a certain neutral nonpolar compound like Na or BaP, the dissolved and adsorbed (particulate) concentrations per total volume of a water

column, C_a and C_p can be expressed as

$$C_d = f_w C_t \quad (10)$$

$$C_p = (1 - f_w) C_t \quad (11)$$

Where $C_t = C_d + C_p$, representing the total compound concentration in the water column. For low ring and low molecular weight compound at top layer of the column, the K_d value is small and the r value is also small, $f_w \rightarrow 1$ and $C_d \rightarrow C_t$ and $C_p \rightarrow 0$, i.e., the dissolved phase partition is dominant. On the other hand, for high ring and high molecular weight at the bottom of the column (large K_d and r), $f_w \rightarrow 0$ and $C_p \rightarrow 1$ and $C_d \rightarrow 0$, this means that the absorbing or particulate phase is dominant.

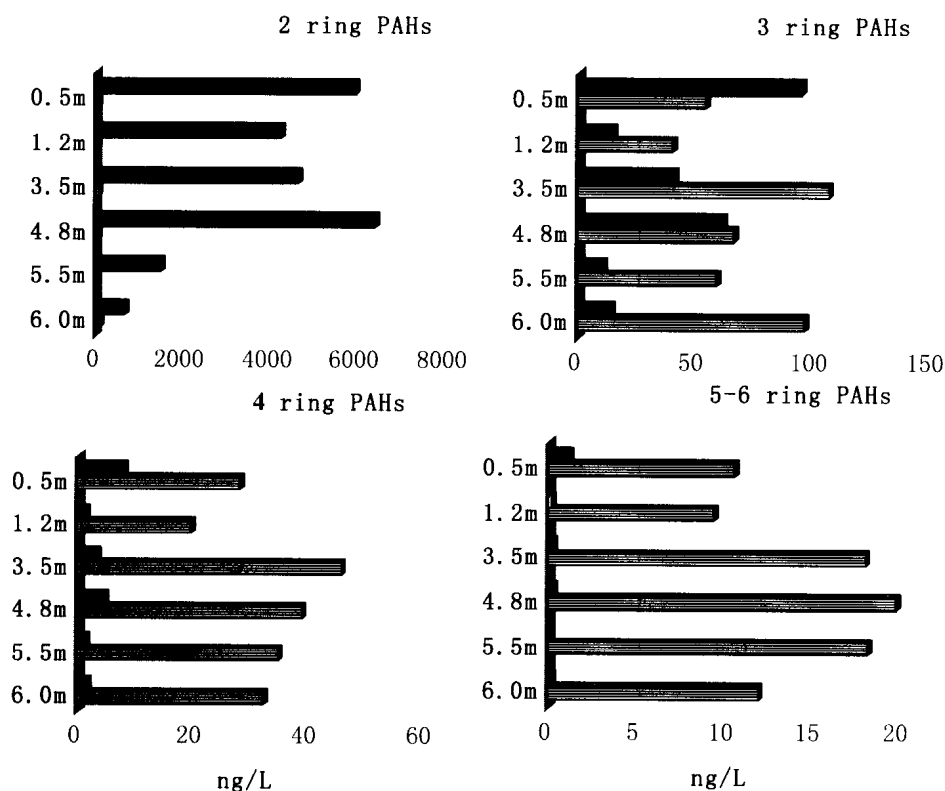


Figure 2. Field Monitoring Results for PAHs of Water-Suspended Solid Phases Partition in Water Column

(blue bar with vertical lines – dissolved phase; red bar with horizontal lines – suspended solid phase)

The conceptual model for the concentration of a persistent organic compound for which dissolved and particulate phases are both important can be established based on mass balance principle, i.e., the accumulation rate of the compound equals input rate subtracting output rate and interphase transfer loss rate as well as reaction decay rate. For the dissolved phase, we have

$$dC_d/dt = I_d - k_w C_d - k_g(C_w - C_a/K_h) - k_r C_d - J_{tr} \quad (12)$$

Where I_d - input rate of the compound in dissolved phase; k_w - output rate constant and $k_w = 1/t$ and t - water column detention time; $k_r C_d$ - reaction decay rate by hydrolysis, photolysis, biodegradation of the compound. Because most of the toxic organic pollutants are chemically persistent, this term can be omitted. J_{tr} - the compound transfer rate from the dissolved to the absorbing phases per unit volume. The term $k_g(C_w - C_a/K_h)$ represents the compound transfer from the water phase to the air, where K_h is the water-air partitioning coefficient of the compound and C_a is the compound mass concentration in the air. The air/water phase exchange rate constant k_g is determined by the compound molecular diffusion (D_w) and turbulent condition of the water/air boundary layers (e.g., wind speed at the water surface). For the sorbing or particulate phase, we have

$$dC_p/dt = I_p - k_w C_p - k_s C_p - k_r C_p + J_{tr} \quad 13)$$

where I_p - input rate of the compound in sorbing phase; $k_w C_p$ - output rate; $k_r C_p$ - reaction decay rate which can be omitted for most of the persistent organic pollutants. The term $k_s C_p$ represents the sorbing compound transfer rate with the particle settling to the bottom where k_s is the particle settling rate constant which is determined by particle Stoke's terminal velocity. Combining Equations 12) and 13), we have

$$dC_t/dt = I_t + k_g C_a/K_h - k_w C_t - f_w k_g C_t - (1 - f_w) k_s C_t \quad 14)$$

At steady state, i.e., $dC_t/dt = 0$, we have

$$C_t = (I_t + k_g C_a/K_h)/(k_w + k_g + (1 - f_w) k_s) \quad 15)$$

Where the air-water partitioning constant K_h is related to the Henry's constant by K_h/RT and the Henry's constant K_h' representing air/water phase equilibrium. For most of the persistent organic pollutants such as PAHs, it is generally quite small (less than 10^{-3}). The air-water phase transfer rate constant k_g is equal to v_w/h , where v_w is the compound transfer velocity in the viscous layer at the water surface and related to the compound molecular diffusion constant D_w . For most of the persistent organic pollutants D_w is also small (less than $10^{-6} \text{ cm}^2/\text{s}$). The water-solid transfer rate constant k_s is equal to v_s/h where v_s is the particle Stokes' terminal velocity. h is the water column depth.

2.2. Modeling for Heavy Metal Accumulation and Remobilization in Sediments

Table 3 gives the monitoring data for concentrations of Cd, Pb, Cr, and As species in the water phase and the sediment phase. A partitioning constant is defined to assess the accumulation of these heavy metals and the As species in the sediment as below:

$$K_d = [S \equiv M]/[M] \quad 16)$$

where $[S \equiv M]$ represents the concentration of the metal M in the sediment ($\mu \text{ g/g}$) while $[M]$ represents its concentration in water ($\mu \text{g/l}$). The measured partitioning constants for these species were in 7.6 – 20 l/g. With Equation 8), one can calculate the f_w values for these species. For the water-sediment partitioning, the calculated values are all equal to 1, that is, all these pollutants accumulated in the sediment phase and undetectable in the pore water, just as the cases of the PAHs absorbing in sediments. For the water-suspended solid partitioning, the calculated values are in the narrow range near 0.5, i.e., the partitioning between the suspended and dissolved phases is just half to half.

The processes that govern the scavenging of trace metal elements by the particulate matter are complex, but generally can be considered to include adsorption, absorption, surface precipitation, and co-precipitation. In the oxic environment such as the oxygen-rich water column or the overlying suspended mud layers, the surface adsorption is dominant, and the allocation of the trace metals at water/solid interface can be estimated by the solid/water partitioning coefficients (K_d). The surface properties of the particles are an important key to understand interactions of trace metals and organic toxicants between dissolved and mineral phases in the coastal waters. The studies in particle surface characterization have suggested that an almost uniform coating of amorphous oxides or organic matter exists on the surfaces of the estuarine particles [18]. It is generally thought that iron and manganese oxides and organic matter coating are important phases for binding of trace metals in the sediment while clays can be only as a support for oxide and organic matter deposition or coating. The interactions of trace metals with the particle surfaces can be considered to be metal-ligand surface complex formations. The conceptual model can be established for interpreting the adsorption isotherms of trace metals at goethite oxide surface, based on the thermodynamic concept of surface coordination. The pH is a master parameter controlling the metal adsorption on oxide surfaces, and for a certain metal there is a special pH range where the adsorption dramatically increases.

Figures 3 gives experimental results of adsorption of Cu, Pb, Cd metal ions on goethite^[10], which show that there was a narrow special pH range for each of the metal ions that an adsorption jump occurred, and the adsorption increased gradually with the solution pHs while the desorption occurred when the solution pHs decreased.