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Estimation of PAHs Fluxes via Atmospheric Deposition and Riverine Discharge into the Masan Bay, Korea

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Atmospheric deposition and riverine waters were sampled throughout a year, to estimate the loading fluxes of polycyclic aromatic hydrocarbons (PAHs) into the Masan Bay and its vicinity, Korea. Atmospheric deposition fluxes of total PAHs in the surveyed area varied from 62.2 to 464 μg/m^2/year. Concentration of total PAHs in water samples from six rivers ranged from 34.6 to 239 ng/L. Contribution of the carcinogenic PAHs to the total PAHs occupied 38% and 50% for atmospheric deposition and river waters, respectively. Atmospheric deposition fluxes and water concentrations of PAHs were slightly low or moderate to those in locations from some countries. Correspondence analysis was used to investigate the loading characteristics of PAHs according to transport routes. Atmospheric deposition samples were corresponded to higher molecular aromatics of PAHs, while riverine water samples were associated with lower molecular weight of PAHs. The results indicate that the higher-molecular-weight PAHs can be primarily transported by atmosphere deposition and the lower-molecular-weight PAHs can be mainly contaminated by riverine discharge into the Masan Bay and its vicinity. Loadings fluxes of PAHs into the Masan Bay and its vicinity were 39.2 g/day via atmosphere and 10.3 g/day via rivers, showing that atmospheric input was about 4 times higher than riverine one. Therefore, in order to minimize the contamination burden of PAHs from terrestrial sources to the Masan Bay and its vicinity, the control and management of PAHs deriving from atmosphere will be necessary.

Key words: Atmospheric deposition, Riverine discharge, Masan Bay, PAHs, Loading fluxes

Introduction

Masan Bay is a typical semi-closed embayment in Korea. The bay is characterized by strong semi-diurnal tidal currents at the bay mouth, while the inner part of the bay has very weak tidal currents. The average water depth is about 5 m in the inner bay and about 20 m in the central bay (Cho and Chae, 1997). Because the bay is surrounded by numerous industrial complexes in Masan, Changwon and Jinhae cities, this area has been recognized by the one of the most contaminated areas with various environmental problems in Korea (MOMAF, 2002). Many studies have been performed for this area, to understand the distribution, fate and effect of heavy metals and toxic organic contaminants in the marine environment (Kwon and Lee, 1998; Khim et al., 1999; Hong et al., 2003; Yim et al., 2005).

A large variety of toxic organic contaminants are transported into coastal environments via atmospheric deposition and/or riverine discharge. Although atmospheric deposition on a large scale is very important route of transporting organic contaminants to the marine ecosystems, in the case of coastal zones the local influence by the riverine discharge is of greater importance (Tolosa et al., 1996; Lipiatou et al., 1997). Actually, riverine discharge has been perceived to be the main route of organic contamination in coastal zones (Gschwend and Hites, 1981; Hoffman et al., 1984; Readman et al., 1987; Dachs et al., 1997; Choi et al., 2005). Therefore, to evaluate health impact of anthropogenic compounds from terrestrial sources to coastal marine environments, both atmospheric deposition and/or riverine discharge should be simultaneously considered for one bay system.

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous hydrophobic organic pollutants in the marine ecosystems and toxic, carcinogenic and mutagenic to all organisms including humans (Yan, 1985;

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Mix, 1986). They occur mainly as a result of anthropogenic activities (Adamo et al., 1997; Hendriks et al., 1998). The main sources of these compounds are byproducts of incomplete fuel combustion (Hites et al., 1977), domestic and industrial wastewaters (Wakeham et al., 1980), and spillage of crude oil and its refined products (Lee and Page, 1997; Pettersen et al., 1997).

Until now, national studies have been focused on the distributions, fate and effects of PAHs in seawater, sediments and biota from Masan Bay and its vicinity (Moon et al., 2001a; Yim et al., 2005). However, there were a few data on loading fluxes of PAHs from land-based sources. The estimation of loading fluxes on toxic organic contaminants in coastal environments is a fundamental work, in order to establish management strategies and to minimize the adverse impacts to the marine ecosystem. Therefore, the objectives of this study were to estimate the PAHs loading fluxes through atmospheric deposition and riverine discharge into the Masan Bay and its vicinity and to assess the contribution of contamination route in the surveyed bay.

Materials and Methods

Sample collection

The sampling locations of atmospheric deposition fluxes and riverine discharges of PAHs into the Masan and Haengam Bays of Korea were presented in Fig. 1. The most common approach currently used for estimating atmospheric deposition fluxes of toxic organic contaminants is to sample and analyse bulk deposition (Sievers et al., 1993; Duarte-Davidson et al., 1994; Moon et al., 2005). The atmospheric deposition bulk samples were monthly collected at Masan and Haengam areas in 2004, using stainless steel pots with an inner diameter of 50 cm and a height 50 cm. The bulk samples were set at 120 cm above the rooftops of a four storey building in Masan area and a three storey building in Haengam area. Two sampling sites of Masan and Haengam areas were located at the southern coastal area within 500 m from the coastal line. The sampling site of Masan was located in an urban area with the influence of vehicle emission and industrial complex. The Haengam was located in a suburban area with slight vehicle emission.

Before sample collection, approximately 5 L of purified water with *n*-hexane was added to the sampler to prevent the resuspension of dry deposition. Deposition bulk samples were transferred to polyethylene bottles with the aid of water and the insides of the bulk sampler were wiped with glass wool precleaned with toluene. These sampling procedures were similar to those reported by Moon et al. (2005).

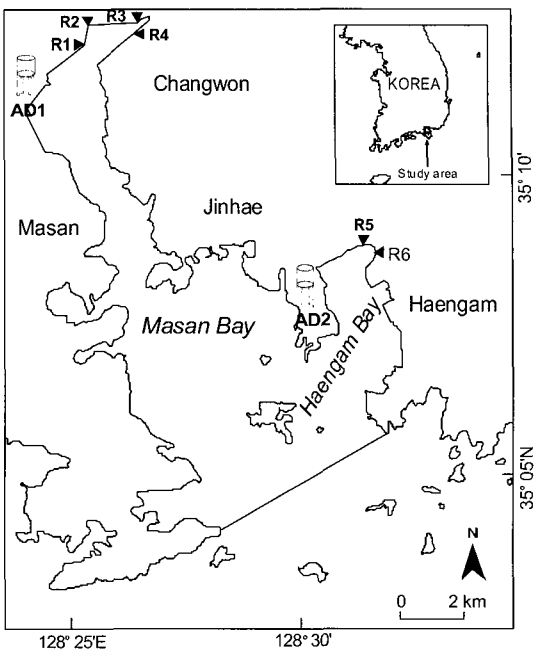

Fig. 1. Sampling stations of atmospheric deposition (AD1-AD2) and the six river waters (R1-R6) into the Masan and Haengam Bays of Korea. R1, Hoewon-Kyobang River; R2, Sanho-Samho River; R3, Changwon River; R4, Nam River; R5, Guidong River; R6, Sini River.

To estimate the riverine discharges of PAHs into the Masan Bay and its vicinity, water samples were collected from six rivers; Hoewon-Kyobang River (R1), Sanho-Samho River (R2), Changwon River (R3), Nam River (R4), Guidong River (R5) and Sini River (R6). The water sample collection was conducted at the duration of low tide in the surveyed bay using flow-meter (BFM001, Valeport, England) and water sampler.

Experimental procedures

Atmospheric deposition and river water samples were separated by particle and liquid phase. Particle samples were isolated by filtering through glass fiber filters (GFFs 47 mm, 0.7 μm, Whatman, England). Particle samples were dried in a desiccator. Liquid phase parts were filtered with disk-type solid phase extraction (SPE) material (ENVI-18 DISK, 47 mm, Supelco, USA). The flow was set up at 15 mL/min to prevent a breakthrough of PAHs in air deposition and river water samples. The GFFs, SPE disks and glass

wools were extracted with 200 mL of toluene (Ultra residue analysis, J. T. Baker, USA) for 5 hours under reflux after the spike of 7 species internal standard (D_8-naphthalene, D_8-acenaphthylene, D_{10}-fluoranthene, D_{10}-phenanthrene, D_{10}-pyrene, D_{12}-benzo(a)pyrene and D_{12}-benzo(g,h,i)perylene, ES-2044, Cambridge Isotope Laboratories, USA). The extracts were filtered through glass wool and concentrated to 1-2 mL in a rotary evaporator. The residues were transferred to *n*-hexane (Dioxin analysis, Kanto, Japan) and adjusted to a volume of 10 mL.

The extracts were cleaned up on an activated silica gel (Art No. 7734, 70-230 mesh, Merck, USA) column chromatography with successive eluants of *n*-hexane and 15% methylene chloride (Dioxin analysis, Wako, Japan) in *n*-hexane. The eluants were concentrated to less than 1 mL, and left at room temperature for one day to evaporate to 50-100 μL. The residues were dissolved with 50 μL of *n*-nonane (Pesticide residue analysis, Fluka, Switzerland) and analyzed for PAHs with GC/MSD (Agilent 5973N, USA). The detailed instrumental analysis of PAHs was presented in Moon et al. (2001b; 2003).

The 16 non-alkylated PAH compounds recommended as the toxic priority pollutants by the United States Environmental Protection Agency (US EPA) were analyzed for each sample. These were as follows: naphthalene (NaP), acenaphthylene (AcPy), acenaphthene (AcP), fluorene (Flu), phenanthrene (PhA), anthracene (AnT), fluoranthene (FluA), pyrene (Pyr), benzo(a)anthracene (BaA), chrysene (Chr), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), indeno(1,2,3-c,d) pyrene (InP), dibenzo(a,h)anthracene (DbA) and benzo (g,h,i)perylene (BghiP).

All the spike isotope compounds were detected with no interfering peak. The average recoveries for all bulk samples were in the range of 67-109%. Procedural blanks were processed in the same way as real samples, and they were below 10% of analytes abundance. Blanks were run before and after the injection of standards to check for any carryover.

Calculation of loading fluxes of PAHs

Total surface area of the surveyed bayments, 74.1×10^6 m^2 reported by Cho and Chae (1997), was used in this study. The sampling area covers both Masan Bay and Haengam Bay. The loading fluxes of PAHs (g/day) for the bay through atmosphere were calculated by multiplying the atmospheric deposition fluxes of PAHs (μg/m^2/year) with average values of two sampling sites by the surface area of the bay (m^2).

The loading fluxes of PAHs (g/day) for Masan Bay and its vicinity via riverine discharge were calculated by multiplying the concentrations of PAHs in river water (ng/L) by the average flow rate (m^3/sec) of six rivers. The estimated flow rates of six rivers into the Masan Bay using flow-meter were presented in Table 1. Riverine flow rate from Masan and Changwon cities occupied approximately over 90% of total flow rates into the study area.

Results and Discussion

Atmospheric deposition fluxes

Once PAHs enter the atmosphere, they redistribute between gas and particle phases and are subject to transformational and degradational mechanism such as oxidative and photolytic reactions and wet/dry deposition (Gigliotti et al., 2000; Garban et al., 2002). Atmospheric transport is the primary distribution pathway moving PAHs from various anthropogenic sources via deposition to marine ecosystems (Mackay and Hickie, 2000).

Atmospheric deposition fluxes of individual PAH compound in Masan and Haengam areas of Korea were summarized in Table 2. Deposition fluxes of total PAHs in atmospheric bulk samples from Masan area varied from 135 to 464 μg/m^2/year. Total PAHs deposition fluxes in Haengam area ranged from 62.2 to 194 μg/m^2/year. The deposition fluxes of total PAHs in Masan area were higher than those in Haengam area with a significant difference (Student's *t* test, $p<0.05$). The deposition fluxes of the potentially carcinogenic PAHs (the sum of BaA, BbF, BkF, BaP, InP and DbA) (IARC, 1987) were in the range of 51-178 μg/m^2/year in Masan area and 24.4-72.6 μg/m^2/year in Haengam area. The deposition fluxes of the carcinogenic PAHs to the total PAHs fluxes

Table 1. Estimated flow rates (ton/day) of riverine discharge from six rivers into the Masan Bay, Korea

Sampling month	Hoewon-Kyobang River (R1)	Sanho-Samho River. (R2)	Changwon River (R3)	Nam River (R4)	Guidong River (R5)	Sini River (R6)
February	13,910	59,868	22,971	43,719	2,827	4,110
May	5,314	51,111	10,818	47,400	3,910	6,249
August	10,170	22,353	29,918	43,615	7,458	5,098
December	12,509	28,047	18,721	24,445	6,905	2,532

Table 2. Atmospheric deposition fluxes (μg/m^2/year) of PAHs in bulk samples from Masan and Haengam areas in 2004

	Jan.	Feb.	Mar.	Apr.	May	Jun.	Jul.	Aug.	Sep.	Oct.	Nov.	Dec.
Masan area												
NaP	10.8	14.4	24.3	24.9	32.1	10.4	12.1	9.36	16.9	13.4	19.8	9.30
AcPy	0.96	1.47	1.21	1.01	1.15	0.49	0.92	0.83	1.25	1.27	2.17	1.29
AcP	0.53	0.63	0.96	0.81	0.62	0.42	0.47	0.41	0.42	0.63	0.90	0.52
Flu	1.50	2.62	2.85	3.60	2.28	2.16	2.24	1.91	1.70	1.34	2.86	2.20
PhA	20.1	34.7	33.6	38.9	16.3	15.3	11.2	12.1	12.5	17.8	27.9	44.5
AnT	1.68	2.91	1.44	3.02	1.58	0.99	0.67	0.78	1.31	1.16	1.88	2.23
FluA	25.5	58.1	38.0	36.6	16.5	14.7	9.88	12.6	12.4	20.6	27.8	45.7
Pyr	27.3	51.9	32.2	39.6	15.7	13.9	10.6	13.7	14.7	24.5	32.8	44.0
BaA	5.46	14.3	8.36	9.77	4.41	3.10	2.92	2.93	3.56	5.72	7.56	5.95
Chr	17.5	66.4	36.9	33.0	17.6	15.8	13.7	12.1	15.4	21.4	32.7	32.8
BbF	14.1	55.2	37.0	33.9	17.4	17.8	15.1	13.1	17.0	19.4	33.5	37.0
BkF	3.76	17.9	12.0	13.7	5.59	7.92	5.11	3.77	5.60	6.61	8.53	13.0
BaP	9.85	18.8	15.8	16.2	6.07	5.13	6.26	6.36	10.3	10.7	17.4	20.4
InP	25.4	63.4	44.5	42.2	29.0	30.1	24.4	21.5	29.6	31.9	41.1	45.2
DbA	5.56	8.72	5.33	6.89	3.75	4.44	3.68	3.34	4.38	3.05	1.61	7.16
BghiP	26.2	52.7	32.2	30.9	21.1	21.5	18.9	20.2	29.7	39.1	50.7	42.2
∑CPAH	64.1	178	123	123	66.6	68.5	57.5	51.0	70.4	77.4	110	129
∑PAH	196	464	327	335	192	164	138	135	177	218	309	353
Haengam area												
NaP	8.10	13.5	28.9	36.5	28.8	13.5	5.32	14.9	7.88	6.02	9.50	11.9
AcPy	0.64	1.21	0.97	1.16	0.91	1.16	0.96	0.78	0.35	0.50	0.81	0.88
AcP	0.41	0.61	0.81	0.57	0.58	0.81	0.20	0.78	0.26	0.53	0.95	0.62
Flu	0.89	2.53	2.20	2.35	1.61	2.70	3.24	2.60	0.93	1.04	1.90	2.45
PhA	10.9	24.6	21.1	21.7	12.1	15.6	16.1	11.4	5.47	12.3	20.9	15.1
AnT	0.82	1.48	0.85	1.87	0.65	1.29	1.19	0.55	0.48	1.10	1.69	2.25
FluA	9.35	25.2	22.1	18.0	10.5	15.2	9.21	11.0	5.40	15.6	22.1	14.7
Pyr	8.69	19.5	16.9	16.6	8.95	13.4	8.70	9.62	4.56	12.9	17.5	12.1
BaA	3.22	3.33	2.93	2.37	1.37	3.58	1.60	2.10	0.94	2.19	3.04	1.89
Chr	4.08	15.0	16.09	12.9	6.43	11.4	6.87	8.29	4.36	9.36	14.8	7.80
BbF	5.93	15.3	14.8	12.7	7.15	20.3	9.19	9.72	5.13	9.13	18.2	8.91
BkF	3.58	5.48	4.97	5.80	1.92	10.2	4.83	4.90	3.00	3.41	7.29	3.60
BaP	3.75	6.87	5.72	6.15	3.83	7.11	2.83	4.65	2.97	4.73	3.86	3.55
InP	25.8	31.9	26.8	31.2	18.4	27.9	17.0	15.8	10.8	14.5	21.3	17.1
DbA	3.84	3.02	2.71	4.38	1.65	3.60	2.15	2.00	1.57	1.23	3.14	2.45
BghiP	21.8	21.3	17.3	19.8	11.4	16.4	11.3	11.8	8.11	12.4	15.9	14.3
∑CPAH	46.1	65.9	57.9	62.5	34.3	72.6	37.6	39.2	24.4	35.1	56.9	37.5
∑PAH	112	191	185	194	116	164	101	111	62.2	107	163	120

CPAH, the sum of carcinogenic PAHs; PAH, total fluxes of PAHs.

occupied approximately 37% and 40% in Masan and Haengam areas, respectively.

Previous reports showed that atmospheric deposition fluxes of PAHs in Busan area varied from 135 to 1,455 μg/m^2/year (Moon et al., 2003) and dry deposition fluxes of PAHs in Seoul, Incheon, Yangpyoung and Yangsu-ri ranged from 1,476 to 8,640 μg/m^2/year (Bae et al., 2002). Some foreign authors also reported that PAHs deposition flux were in the ranges of 376-8,833 μg/m^2/year for Manchester, 295-7,154 μg/m^2/year for Cardiff of UK (Halsall et al., 1997), 350 μg/m^2/year in Tihany of Hungary (Bodnár and Hlavay, 2005), 139-336 μg/m^2/year in Paris of France (Ollivon et al., 2002). From these results, atmospheric deposition fluxes of PAHs in this study were comparable to or slightly higher than those of several sites from Korea and foreign countries.

Atmospheric deposition fluxes of PAHs in two sampling areas had a tendency with higher values in winter than in summer. In Masan area, the average flux of PAHs in winter season (November to February) showed 331 μg/m^2/year and 153 μg/m^2/year in summer season (June to September). In the case of Haengam area, the average flux (146 μg/m^2/year) in the winter season was higher than in summer season (109 μg/m^2/year). Panther et al. (1999) and Ollivon et al. (2002) also reported similar results. Two possible reasons for higher PAHs deposition fluxes in winter

than in summer were temperature dependence of gas/particle partitioning of PAHs and higher emissions by heating using fossil fuels during winter season (Lipiatou et al., 1997; Bae et al., 2002).

Concentrations of riverine water into the Masan Bay

Individual and total PAHs in water samples from six rivers into the Masan Bay were given in Table 3. The 16 PAHs were detected in all of the water samples. Total concentrations of PAHs in water samples from six rivers varied from 34.6 to 239 ng/L. The highest concentration was found at water sample from Hoewon-Kyobang River (R1), while the lowest level was at Sini River (R6). The carcinogenic PAHs in riverine waters occupied approximately 50% to the total PAHs concentrations, showing that a proportion of the carcinogenic PAHs in riverine waters was higher than that of atmospheric deposition.

Some surveys have been reported that the concentrations of PAHs in waters from Gao-ping River of Taiwan (430±750 ng/L) (Doong and Lin, 2004), Tianjin River of China (45.8-1,272 ng/L) (Shi et al., 2005), and Lac Saint Luis River of Canada (5.0-86.0 ng/L) (Mackay and Hickie, 2000). The results showed that the higher levels of PAHs in this study were comparable to those from other countries.

Individual PAHs were quantified in the phases of liquid and particle of water samples. The partitioning for liquid and particle phases of individual PAH from riverine water samples was presented in Fig. 2. The contribution of particle phase for individual aromatic

Table 3. Concentrations (ng/L) of PAHs in water samples from six rivers into the Masan Bay, Korea

	Hoewon-Kyobang River (R1)				Sanho-Samho River (R2)				Changwon River (R3)			
	Feb.	May	Aug.	Dec.	Feb.	May	Aug.	Dec.	Feb.	May	Aug.	Dec.
NaP	22.0	13.5	12.1	31.1	14.3	20.1	14.3	32.7	24.8	8.35	15.8	30.6
AcPy	0.57	0.39	0.29	0.55	0.61	0.27	0.27	0.55	0.61	0.22	0.30	0.57
AcP	1.47	0.78	0.21	5.19	3.57	0.37	0.57	1.55	2.07	1.04	0.54	0.53
Flu	2.73	1.78	3.93	11.5	4.82	1.52	5.35	6.52	11.09	1.12	4.99	1.94
PhA	8.22	7.02	7.84	39.4	5.84	2.59	7.16	8.88	32.91	1.15	8.68	7.40
AnT	0.31	0.71	0.38	5.04	0.33	0.25	0.28	0.73	0.15	0.24	0.44	0.46
FluA	4.11	7.57	2.57	2.38	3.68	1.56	1.83	2.68	11.05	0.81	3.44	5.52
Pyr	4.95	7.00	2.95	2.39	4.82	1.80	2.38	3.26	5.41	0.94	3.95	5.37
BaA	0.39	2.11	0.46	0.54	0.34	1.16	0.56	0.50	0.42	1.43	1.01	1.49
Chr	1.29	5.27	0.63	2.61	1.52	1.42	0.71	1.42	1.79	2.39	1.04	3.83
BbF	9.63	111	17.8	51.4	7.84	20.6	16.6	46.8	12.7	22.8	35.2	95.7
BkF	2.31	32.2	4.02	9.55	1.50	3.59	4.51	7.79	2.80	13.8	6.98	17.4
BaP	1.41	7.71	1.26	1.73	1.93	4.30	1.47	1.18	2.18	3.92	2.00	2.42
InP	0.33	13.0	1.52	1.60	0.51	9.30	1.94	1.36	0.48	10.8	2.01	3.89
DbA	0.14	13.5	1.20	1.94	0.27	10.2	1.70	1.69	0.18	20.5	1.96	3.02
BghiP	1.62	8.77	0.76	1.44	1.34	5.11	1.18	1.37	0.89	8.96	1.84	4.06
∑CPAH	14.2	179	26.2	66.8	12.4	49.2	26.8	59.3	18.8	73.3	49.2	124
∑PAH	61.5	232	57.9	168	53.2	84.2	60.9	119	110	98.5	90.2	184
	Nam River (R4)				Guidong River (R5)				Sini River (R6)			
	Feb.	May	Aug.	Dec.	Feb.	May	Aug.	Dec.	Feb.	May	Aug.	Dec.
NaP	18.9	15.9	9.41	17.1	37.6	14.8	10.5	66.9	14.5	12.0	8.42	17.7
AcPy	0.73	1.01	0.47	0.50	1.09	0.41	0.20	0.53	0.75	0.24	0.28	0.66
AcP	1.05	0.34	0.25	0.35	1.34	0.21	0.25	0.62	0.71	0.25	0.19	0.47
Flu	3.18	1.25	2.80	0.78	2.46	0.52	1.50	1.57	1.70	0.65	1.95	0.83
PhA	6.40	2.97	5.05	2.28	5.78	0.99	2.74	6.56	3.99	1.28	3.03	3.22
AnT	0.28	0.49	0.35	0.22	0.52	0.44	0.24	0.39	0.22	0.11	0.52	0.27
FluA	5.01	2.17	2.83	1.73	4.81	0.83	1.92	4.41	2.05	0.86	1.63	2.33
Pyr	7.15	2.64	5.56	1.59	5.87	0.97	2.90	3.97	2.15	1.04	2.45	1.80
BaA	0.55	1.85	0.69	0.60	0.47	2.28	0.44	0.71	0.22	0.62	0.35	0.39
Chr	2.78	1.83	1.31	1.05	1.99	2.40	0.69	2.37	0.98	0.99	0.52	2.08
BbF	6.09	16.8	8.33	18.7	12.1	30.5	14.2	115	7.54	46.3	9.36	35.2
BkF	1.32	3.65	1.47	3.59	2.65	5.18	3.07	25.5	1.56	9.57	1.70	7.39
BaP	0.74	6.32	1.47	1.80	0.88	7.51	1.28	2.60	1.24	2.92	0.96	1.14
InP	1.04	10.7	5.11	1.52	1.11	26.7	2.15	1.80	0.31	5.13	1.41	1.75
DbA	0.26	18.8	3.53	1.05	0.21	26.9	2.07	3.95	0.15	5.93	1.10	1.41
BghiP	2.91	9.69	2.00	1.28	1.71	11.5	1.12	1.93	0.60	3.23	0.70	1.12
∑CPAH	10.0	58.1	20.6	27.3	17.4	99.1	23.2	150	11.0	70.4	14.9	47.3
∑PAH	58.4	96.4	50.6	54.1	80.6	132	45.3	239	38.7	91.1	34.6	77.8

∑CPAH, the sum of carcinogenic PAHs; ∑PAH, total concentrations of PAHs.

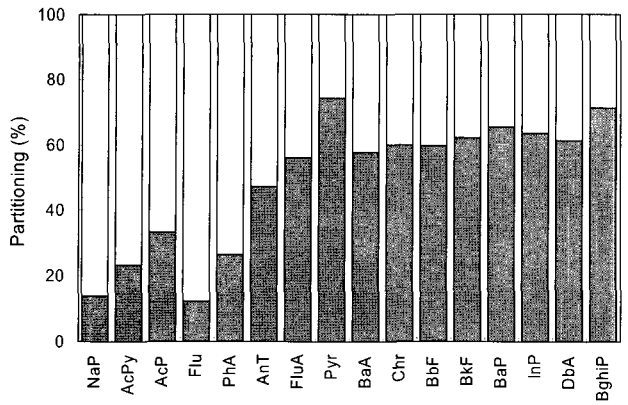

Fig. 2. Partitioning of liquid and particle phases for the individual PAH compound in river waters into the Masan Bay, Korea. White (□) and black (■) boxes indicate the liquid and particle phases of river water samples, respectively.

compound in river water increased significantly with increasing molecular weight from low molecular weight. This is due to persistence based on liphophilic and hydrophobic properties of PAHs in water column (Shi et al., 2005). The solubility of PAHs in water is low and decreases with increasing molecular weight. Similar findings have been reported by other researchers (Bouloubassi and Saliot, 1991; Lipiatou et al., 1997; Moon et al., 2001b).

Loading characteristics of PAHs

The PAHs profiles among the atmospheric deposition and river water samples were compared using the correspondence analysis on the percentage corresponding to the sixteen PAH compositions. The relationship plot on the factorial plane is shown in Fig. 3. Statistical analysis was performed using MVSP (Multi-variate statistical package) Windows 3.0 software (Kovach Computing Services, UK).

Axis I and II represents 46% and 23% of total variance of the original data, respectively. Two groups were distinguished according to the types of lading route for PAHs. The samples from atmospheric deposition belonged to group with higher molecular aromatics of PAHs, while the samples from riverine water were associated with the lower molecular weight of PAHs. Namely, one group was characterized by a high contribution of the higher molecular weight aromatics, while other group included the lower molecular weight aromatics. The results indicated that the PAHs compositions were different according to their transport routes such as atmosphere and river. Actually, the average composition of atmospheric deposition was dominated by the higher molecular aromatics such as indeno(1,2,3-c,d)pyrene, benzo(g,h,i)perylene, chrysene and benzo (b)fluoranthene (Fig. 4). The predominant compounds in river waters were mostly two- and three-ring aromatics such as naphthalene and phenanthrene except benzo(b)fluoranthene. Therefore, the higher-molecular-weight PAHs seemed primarily to be transported by atmosphere deposition and the lower-molecular-weight PAHs mainly seemed to be contaminated by riveine discharge into the Masan Bay.

Estimation of PAHs loading fluxes

The loading fluxes of PAHs by atmospheric deposition into the Masan Bay showed the highest value in February (66.5 g/day) and the lowest value in July (24.2 g/day). From riverine discharges, the input fluxes of PAHs were estimated to be 9.49 g/day in February, 12.3 g/day in May, 7.37 g/day in August, and 12.1 g/day in December. The loading fluxes of toxic chemicals via riverine discharge can be dependant on the concentrations of chemicals in river water, inflow rate and meteorological parameters (Stow and Borsuk, 2003). In general, the loading fluxes of PAHs from four rivers (R1 to R4) into the Masan Bay were higher than those from two rivers (R5 to R6) into the Haengam Bay. In particular, the Sanho-Samho River (R2) was the highest burden of PAHs with a value of 12.2 g/day, while Sini River (R6) showed the lowest burden with a value of 1.10 g/day. The results suggest that the toxic organic contaminants including PAHs can be concentrated at the inner part of Masan Bay near some rivers. Actually, the authors have been reported that the inner part in all of Masan Bay was the most contaminated zone with various toxic chemicals (Khim et al., 1999; Hong et al., 2003; Yim et al., 2005).

The loading fluxes of PAHs via atmosphere and rivers and the respective contribution were presented in Table 4. For total PAHs loading fluxes, naphthalene, phenanthrene, fluoranthene, benzo(b)fluoranthene, indeno(1,2,3-c,d)pyrene and benzo(g,h,i) perylene showed the higher burdens with approximately 70% of total fluxes of PAHs. The loading fluxes of naphthalene, acenaphthene, fluorene, benzo (b)fluoranthene, and dibenzo(a,h)anthracene into the Masan Bay and its vicinity had a similar contribution for atmosphere and river. However, other compounds of 16 PAHs revealed the higher loading fluxes through atmosphere than river. The loading fluxes of PAHs into the Masan Bay and its vicinity were 39.2 and 10.3 g/day via atmosphere and rivers, respectively. The loading flux of total and carcinogenic PAHs via atmosphere was higher 4 times than that via riverine discharge. Lipiatou et al. (1997) reported

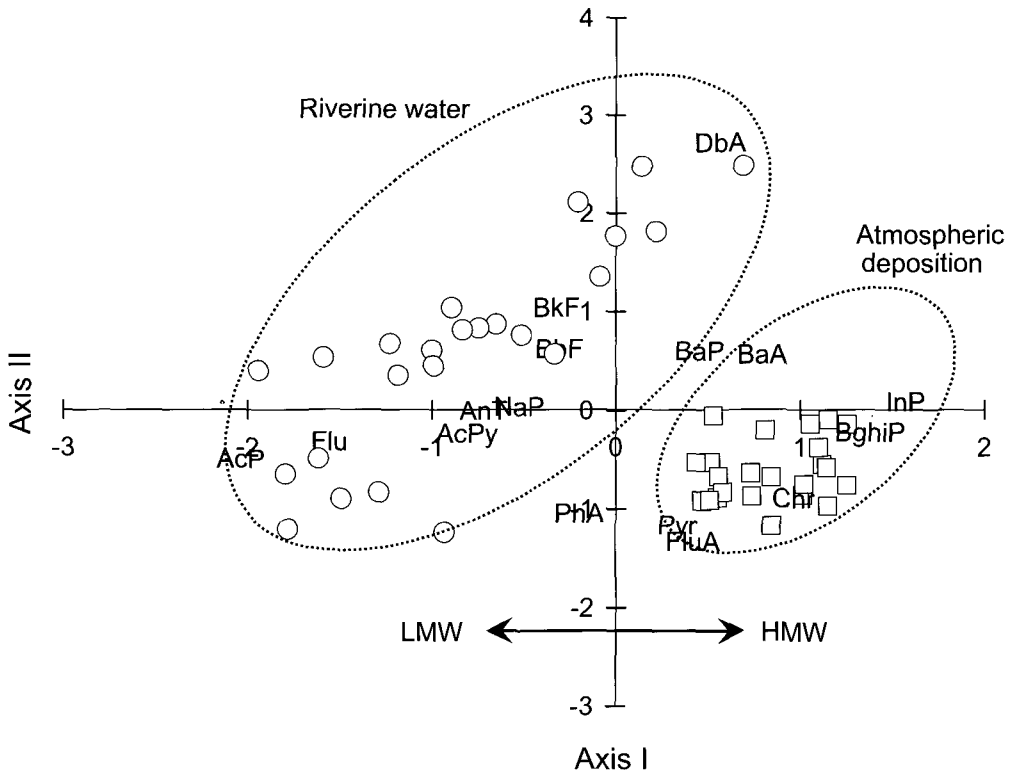

Fig. 3. Correspondence analysis of the sixteen PAH distribution for the atmospheric deposition and river water samples into the Masan Bay. Dotted circles in the plot were grouped by their molecular weight of PAHs. White circles (○) indicate river water samples and white boxes (□) indicate atmospheric deposition samples. LMW: lower-molecular-weight PAHs, HMW: higher-molecular-weight PAHs.

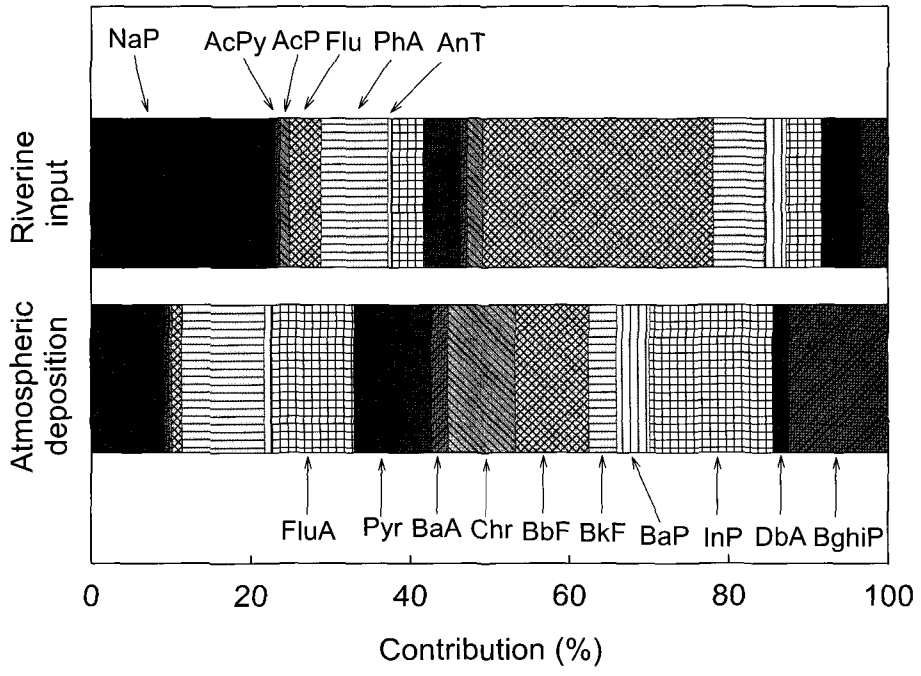

Fig. 4. Normalized PAHs profiles to total concentration in atmospheric deposition bulk and river water samples.

Table 4. Estimated loading fluxes (g/day) of PAHs and a respective contribution (%) according to each transport route into the Masan Bay, Korea

	Loading fluxes (g/day)			Contribution (%)	
	Atmosphere	River	Sum	Atmosphere	River
NaP	3.24	2.26	5.50	58.9	41.1
AcPy	0.21	0.06	0.27	76.2	23.8
AcP	0.12	0.14	0.26	46.4	53.6
Flu	0.44	0.44	0.87	50.1	49.9
PhA	3.99	0.90	4.90	81.6	18.4
AnT	0.29	0.06	0.34	83.2	16.8
FluA	4.21	0.40	4.61	91.2	8.76
Pyr	3.98	0.47	4.44	89.5	10.5
BaA	0.87	0.10	0.97	89.7	10.3
Chr	3.66	0.20	3.86	94.7	5.30
BbF	3.78	2.88	6.66	56.7	43.3
BkF	1.37	0.60	1.98	69.5	30.5
BaP	1.68	0.31	1.99	84.6	15.4
InP	5.81	0.49	6.30	92.3	7.74
DbA	0.76	0.59	1.35	56.3	43.7
BghiP	4.80	0.39	5.19	92.5	7.50
∑CPAH	14.3	4.97	19.2	74.2	25.8
∑PAH	39.2	10.3	49.5	79.2	20.8

∑CPAH, the sum of carcinogenic PAHs; ∑PAH, total loading fluxes of PAHs.

that the loading fluxes of PAHs into the Mediterranean Sea were 35-70 ton/year by atmospheric deposition and 1.3-38 ton/year by Rhone and Ebro Rivers, France, showing that the loading fluxes of PAHs via atmospheric deposition were higher than those by rivers. Mackay and Hickie (2000) have also calculated the loading fluxes of PAHs for the Lac Saint Louis of Canada through mass balance modeling. These results are well consistent with this study. The results were estimated to be 58.4% from atmosphere and 41.6% from rivers with a similar burden. Therefore, in order to minimize the contamination burden of PAHs from terrestrial sources to the Masan Bay and its vicinity, the management and control of PAHs derived from atmosphere will be necessary.

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