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PAH Contamination Levels in Air Particles and Sediments of Ho Chi Minh City, Vietnam

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Ho Chi Minh City (HCMC), the biggest city of Vietnam with a population of over 5 millions people, is an important centre for culture, science and economy. Rapid urbanisation and industrial expansion accompanying the population growth are major factors responsible for atmospheric pollution in HCMC. Bicycles were a common mode of transportation a few years ago, they are now replaced by motorcycles and personal cars. Public transportation means are old and the network is not developed. Nowadays, the air pollution by traffic is a tense problem and an air monitoring program has been set up by The Environmental Committee of HCMC (ENCO). It focuses only on some parameters like CO, NO,, dust, noise and Pb. The Polycyclic Aromatic Hydrocarbons (PAHs) content in the air is not yet considered in this program although they represent a class of important environmental pollutants due to their carcinogenic and mutagenic capacities for human, aquatic and terrestrial organisms (Environmental Design Ltd. 1992; Slooff et al. 1989). In addition, untreated domestic and industrial wastewater is a considerable source providing contamination matter (including PAHs) for inner city canals and adjacent areas (Saigon-Dongnai river system). In recent years, this river system has also been affected by oil spill pollution; from May 1994 to January 1996, 4 big incidents have been recorded with over 1’900 tons of Diesel Oil spilling into Saigon-Dongnai river system.

As PAHs emitted from vehicle exhausts or industrial gas effluents are strongly associated with particulate matter (Environmental Design Ltd. 1992; Slooff et al. 1989; Peltonen and Kuljukka 1995; Miguel and De Andrade 1989), it is expected that dry/wet deposition may be an important source of PAHs contamination either in water or sediments of HCMC canals. This research has been undertaken to assess the PAHs contamination level of sediments and air particles in HCMC and evaluate the origin of PAHs in these two matrices.

MATERIALS AND METHODS

A total of 11 sampling sites have been chosen for sediments, including 6 urban sites, 3 non-urban sites and 1 reference site; 5 sites have been chosen for air particles, including 4 urban sites and 1 reference site (see Fig. 1). The reference site for sediments is the same as for air particles. The sediment samples have been taken during and at the end of rain season (September and November 1998), always at low tide. The air particle samples were taken only at the end of the rain season (November 1998).

Surface sediment was sampled with an Eckman Grab. For each site, sediments were taken from three points: near the two banks and in the centre of the waterway. Samples were put into a clean aluminium box and stored at 4°C during

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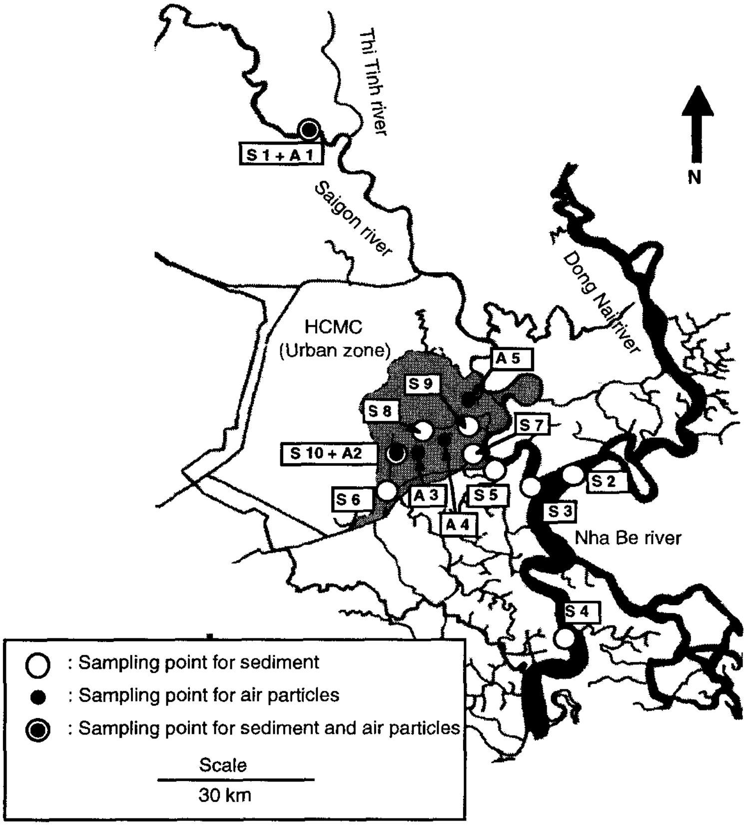

Figure 1. Sampling map for sediment and air particles of HCMC.

transport to the laboratory. In the laboratory, a composite sample was prepared by mixing in same proportions the sediments of the same site. The composite sample was dried at room temperature for about 5-10 days. Dried samples were crushed into powder by means of a ceramic mortar than sifted through a 1x1 mm inox sieve. Samples were stored in brown glass flasks at 4 °C until their analysis. Air particles were sampled by a high volume pump (Sibata HCV-1000 model - Japan), volume ranging between 800-1'600 L/min and equipped with a glass fibre filter (Whatmann GF/A 1.6 mm, 20.3 x 25.3 mm). Before sampling, the glass fibre filter was rinsed with 10 ml Dichloromethane (DCM) pestigrade, dried in an oven for 2 hours and stored in a dessicator until use. Just before sampling, the glass fibre filter weight was determined. After sampling, the filter was wrapped in aluminium paper and stored in a dessicator for one day. After determining their final weight, the samples were stored at 4 °C until analysis.

The water content is determined by heating about 2 g of dried sediment (already crushed and sifted) in an oven at 105 °C for 2 h. After cooling in a dessicator and determining the weight, the organic content was estimated by calcinating the dried sediment at 550 °C for 3 h. The weight loss is assumed due to the organic content (ASTM 1981).

All the glassware has been washed with hexane and acetone. For each series of analyses, a reagent blank has been done, to assess the presence of possible interfering compounds. Prior to use, all the adsorbents have been activated for 8 hours, cooled in a dessicator, then deactivated with 5% (weight/weight) of bidistillated water and washed with hexane.

The analytical procedure is similar to the one proposed by Vu-Due et al. (1995): 5-15 g of sediment (exactly weighted) or glass fibre filter (containing air particles) are extracted with 180 ml dichloromethane (DCM) for 24 h. To avoid PAHs degradation due to light exposure, the soxhlet apparatus are wrapped in aluminium paper. After cooling, the extract is concentrated to l-2 ml, diluted to 30 ml with hexane and transferred into a 500 ml separator funnel. The liquid-liquid partition is achieved b y extracting the hexane solution with 30 ml and then with 15 ml Dimethylsulfoxide (DMSO). The collected DMSO extract (45 ml) is diluted with 150 ml of water and back extracted 2 times with 100 ml and 50 ml of hexane. The hexane phase is dried on anhydrous sodium sulphate and concentrated to about l-2 ml, then a second purification is achieved on a combined alumina/silica gel column, composed of 8 g of silicagel 60, 8 g of alumina and 3 g of anhydrous Na_2SO_4. The elution is done by 20 ml hexane (fraction a), 20 ml hexane:DCM 955 (fraction b) and 40 ml hexane:DCM 80:20 (fraction c). 0.5 ml DMSO are added to the fraction c which contains the PAHs under investigation and is concentrated to 1 ml with a rotavapor. The extract is than transferred in a tared flask and concentrated under nitrogen or diluted to the convenient concentration.

All the samples have been analysed with a HPLC-fluorescence system (HPLC-FD) equipped with a Hewlett Packard series 1050 with a HP 1046A programmable fluorescence detector, automatic liquid sampler, precolumn Supelco LC-18, 2 cm x 4.6 mm; column Vydac RP18 201 TP54, 25 cm x 4.6 mm x 5 µm. In addition, certified sediments and some sediment samples have been also analysed with an HPLC-diode array system (HPLC-DAD) Hewlett Packard 1100, manual injector, precolumn Superguard LC 18,2 cm x 4.6 mm; column Supelcosil LC-PAH, 25 cm x 4.6 mm x 5 µm.

RESULTS AND DISCUSSION

The method recovery for the nine PAHs under study Pyrene (PYR), Benzo(a)anthracene (BAA), Chrysene (CRY), Benzo(b)fluoranthene (BBF), Benzo(k)fluoranthene (BKF), Benzo(a)pyrene (BAP), Dibenzo(a,h)anthracene (DBA), Benzo(g,h,i)perylene (BGP), Indeno(l,2,3-cd)pyrene (IND) has been determined by using a spiked quartz sand (at a level of about 66 ng/g for each PAH congener). The mean recovery (n=5) is between 85 and 100%.

Quality control has been achieved by analysing the certified sediment SRM 1941a (Organics in marine sediment from National Institute of Standard and Technology (NIST)) and also channel sludge N° 744 from an International Exchange for Tests on Organic Contaminants (SETOC 98.4).

The SRM-1941a has been analysed two times in Vietnam with HPLC-DAD and one extract has been re-injected and analysed by HPLC-FD in Switzerland. The results are presented in Table 1.

Results presented in Table 1 indicate that the selected analytical procedure gives acceptable results for sediment samples. However, it has to be mentioned that with some samples with low PAHs levels such as channel sludge, results obtained with HPLC-DAD detection were very different from the certified values, especially for BBF and BKF. Due to incomplete purification of such a complex matrix and the low final volume needed to reach the detection limit (DL) of HPLC-DAD, interfering products may affect the quantification by diode array. For such a situation, the HPLC-FD has been shown to be more specific and is recommended for this kind of analysis. All the following results presented for HCMC sediments and air particles have been determined by HPLC-FD.

Table 1. Experimental PAHs concentration (ng/g dry weight) for SRM-1941a, obtained with a diode array detector (DAD; n=2) and a fluorescence detector (FD; n=l).

PAHs	Experimental value (DAD)	Experimental value (FD)	Certified value	Δ (DAD)[b] (%)	Δ (FD)[c] (%)
PYR	716±(61)[a]	722.3	811±24	-11.8	-10.9
BAA	356±(48)	350.1	427±25	-16.5	-18.0
CRY	390±(46)	421.8	380±24	2.6	11.0
BBF	625±(39)	755.5	740±110	-15.6	2.1
BKF	318±(20)	321.5	361±18	-12.0	-10.9
BAP	475±(29)	467.7	628±52	-24.4	-25.5
DBA	70±(7)	73.0	73.9±9.7	-5.2	-1.2
BGP	523±(102)	527.5	525±67	-0.5	0.5
IND	461±(34)	-	501±72	-8.2	-

[a]: *Value in bracket corresponds to the standard deviation.*

[b]: *Difference between the certified value and the value obtained with DAD.*

[c]: *Difference between the certified value and the value obtained with FD.*

PAHs concentrations in HCMC sediments are presented in Table 2: they have been corrected for recovery and for water content.

Table 2. PAHs concentrations (ng/g dry weight) in HCMC sediments.

Site	Org. Matter (%)	PYR	BAA	CRY	BBF	BKF	BAP	DBA	BGP
Non-urban sites									
S1 (ref.)	12.9	20.7	6.9	18.7	22.3	4.5	5.8	3.6	8.3
S2	15.1	20.2	6.7	10.6	13.2	4.0	7.7	1.2	9.5
S3	13.3	28.0	12.3	30.9	19.9	5.9	8.0	0.7	14.5
S4	9.0	20.8	5.2	10.8	10.8	3.3	6.5	1.1	9.0
Min	9.0	20.2	5.2	10.6	10.8	3.3	5.8	0.7	8.3
Max	15.1	28.0	12.3	30.9	22.3	5.9	8.0	3.6	14.5
Mean	12.6	22.4	7. 8	17.8	16.5	4.4	7.0	1.7	10.3
Median	13.1	20.8	6.8	14.8	16.5	4.3	7.1	1.2	9.3
Urban sites									
S5	10.9	149.3	54.8	105.9	82.0	33.8	69.8	10.2	81.9
S6	11.0	311.6	85.0	177.3	113.3	44.8	87.9	9.7	97.3
S7	12.0	367.0	109.2	233.6	140.3	55.6	115.9	7.6	139.0
S8	6.9	355.3	133.6	206.8	212.9	95.8	227.9	18.9	338.5
S9	16.0	494.9	222.4	313.8	329.1	152.4	329.0	41.3	400.2
S10	47.0	3824.1	1443.3	2382.2	2033.0	891.9	2141.4	213.6	1973.3
Min	6.9	149.3	54.8	105.9	82.0	33.8	69.8	7.6	81.9
Max	47.0	3824.1	1443.3	2382.2	2033.0	891.9	2141.4	213.6	1973.3
Mean	17.3	917.0	341.4	569.9	485.1	212.4	440.5	50.2	505.0
Median	11.5	361.2	121.4	220.2	176.6	75.7	171.9	14.6	238.8
DL	-	13.2	3.3	53.2	6.12	0.9	0.9	0.5	3.3

The PAHs contamination levels of non-urban sites are very low, even for sites where oil spill has been recorded such as S2, S3, S4. This could be explained by the following factors: the PAHs content of the spilled oil (Diesel Oil) is mainly composed of low molecular weight PAHs (Yu et al. 1995), very fast dilution could take place and degradation processes such as photooxidation could be efficient in tropical countries for such products (Muel and Saguem 1985; Lee et al. 1981).

PAHs contamination levels of urban sites are 6 to 20 times higher than those of non-urban sites. The greatest part of urban sites presents PAHs concentration in sediments which are below the Dutch general environmental quality guidelines (Slooff et al. 1981). In general, the PAHs contamination levels in HCMC sediments are acceptable. Only one site (S10) presents high PAHs concentrations. This site is located in the middle of the Tan Hoa canal, which is receiving wastewater from many industrial factories and handicrafts located along it's banks. In this site located next to a big food processing factory (Cau Tre Company), the sediment organic matter content is the highest (47.0 %) of our study.

Normalized PAHs distribution (the ratio between individual PAH and Σ 8 PAHs) in sediments from rural and urban sites have been calculated and are presented for some sites (see Fig. 2). Compared with the non-urban sites, contributions from BAP and BGP are higher and BBF are lower in urbanised zones. This difference could be due to the fact that contamination by PAHs coming from traffic sources may be relevant in the urban sites.

The PAHs concentrations in air at the different sites, corrected for recoveries, are shown in Table 3 below.

Table 3. PAH's concentrations (ng/m^3) in HCMC air.

Site	PYR	BAA	CRY	BBF	BKF	BAP	DBA	BGP	Particles conc. (mg/m^3)
Rural site									
A1 (ref.)	0.26	0.10	0.16	0.37	0.16	0.26	0.05	0.79	4.57 x 10^{-5}
Urban sites									
A2	5.19	5.26	6.86	9.07	4.46	8.98	0.77	21.61	1.12 x 10^{-4}
A3	15.21	5.45	7.25	12.52	5.36	13.86	0.84	56.65	6.65 x 10^{-4}
A4	9.36	4.31	5.72	11.03	4.74	13.81	0.75	44.27	4.62 x 10^{-4}
A5	7.71	3.37	5.08	7.25	3.02	8.91	0.34	30.33	6.70 x 10^{-4}
Min	5.19	3.37	5.08	7.25	3.02	8.91	0.34	21.61	1.12 x 10^{-4}
Max	15.21	5.45	7.25	12.52	5.36	13.86	0.84	56.65	6.70 x 10^{-4}
Mean	9.37	4.60	6.22	9.97	4.40	11.39	0.68	38.22	4.77 x 10^{-4}
Median	8.54	4.79	6.29	10.05	4.60	11.40	0.76	37.30	5.64 x 10^{-4}

In HCMC urban areas, the PAHs contamination levels in air particles are very high (20-40 times higher than in rural area). Especially, the carcinogenic PAHs such as BGP and BAP are the most represented one. Compared with other data for cities like Lahore (Smith et al. 1996); Rio (Miguel and De Andrade 1989) or Paris (Muel and Saguem 1985), the observed levels found at HCMC show concentrations of PYR, CRY, BAP with the same order of magnitude. The mean observed concentration of BAP in urban HCMC air particles is two times higher than the tolerable level of 5 ng/m^3 proposed in the Dutch guidelines (Slooff et al. 1989). This is an alarming signal of environmental degradation and could become a big risk for HCMC inhabitants health.

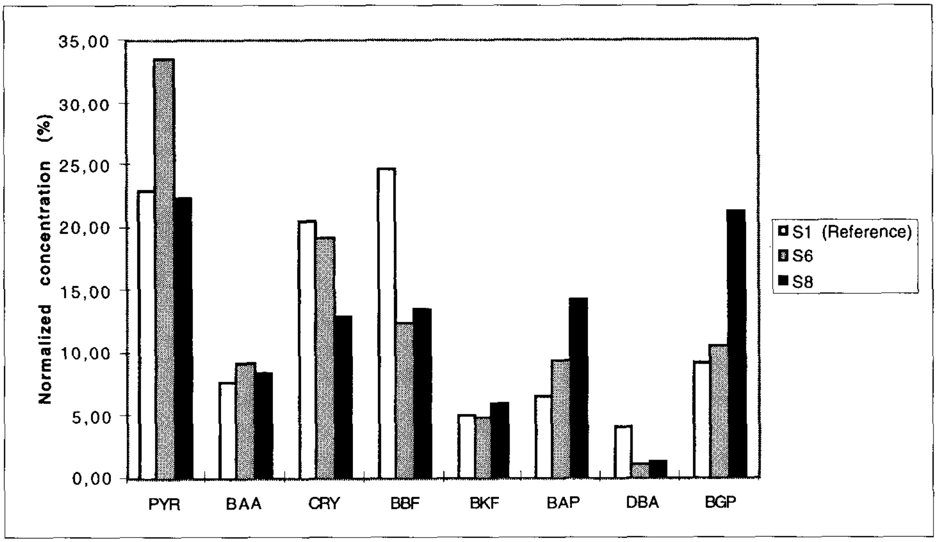

Figure 2. Normalized PAHs concentrations in sediments from the reference site (S1) and two urban sites (S6 and S8).

The normalized PAHs distributions in air particles for all sites are very similar. Figure 3 illustrate such a distribution for the reference and two urban sites. BGP is always predominant; BAP and BBF have also a relatively high contribution compared with the rest of PAHs. PYR, BAP, BAA, BGP are considered as car exhausts indicators (Kayali et al. 1995; Environmental Design Ltd. 1992) and their high level found in this study indicates that motorised traffic plays an important role in HCMC air contamination by PAH.

The comparison of PAHs distributions between air particles and sediments has been evaluated with the help of the index of similarity, developed by De Alencastro et al. (1985). The index of similarity S allows to give a numerical value to the difference between two PAHs distributions in two extracts. The maximum possible S value of 1 occurs when a complete similarity between the two extracts is observed. Smaller values indicate a lower similarity. This calculation is based on the sum of the individual PAHs components in each extract. A sample is taken as reference and the concentrations of the other samples are normalized based on the reference extract. The index gives a numerical representation of the notion of multi-component fingerprint.

The mean concentration of PAHs in air particles, expressed as ng/g of air particles, has been taken as the reference for calculation. The PAHs distribution in air particles of reference site (Al) is compared with PAHs distribution in sediment of the same site (S1). Based on this calculation, it appears that the mean similarity index for non-urban sites between air particles and sediments is lower (0.49 ± 0.04) than the one for urban sites (0.59 ± 0.08). This indicates that the contribution to the PAHs contamination in sediments from the PAHs adsorbed on air particles is more important inside the urban waterways than for rural areas. The fact that BAP and BGP are relatively predominant compounds in the urban sediments shows that a considerable part of PAHs presented in sediment originate from car exhausts (Kayali et al. 1995; Environmental Design Ltd. 1992).

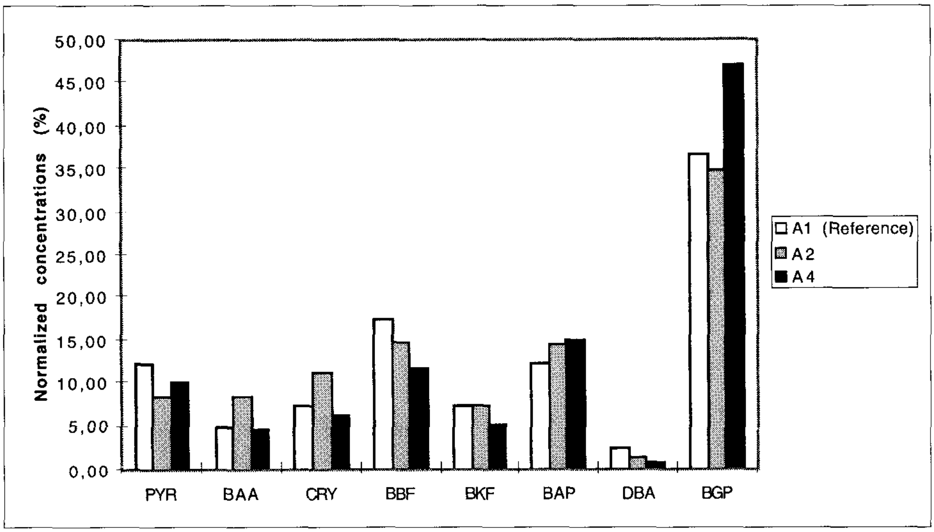

Figure 3. Normalized PAHs concentrations in air particles from the reference site (Al) and from two urban sites (A2 and A4).

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