

Polycyclic Aromatic Hydrocarbons in the Mangrove Species: *Avicennia Marina* from Mumbai, India.

Dr. Akshayya Shete¹, Dr. G.G.Pandit², Dr. V.R.Gunale

¹108, Nav Shakti Sadan, Sector-13, Rohini, Delhi - 110085

²Scientific Officer & Section Head, (EMAS), Bhabha Atomic Research Centre, Trombay, Mumbai -85

³Professor, Department of Botany, University of Pune, Ganesh Khind, Pune- 411007

Received: September 13, 2015

Accepted: December 9, 2015

ABSTRACT

Accumulation and distribution of Polycyclic Aromatic Hydrocarbons (PAH) namely Naphthalene, Acnaphthalene, Fluorene, Anthracene, Fluranthrene, Phenanthrene and Pyrene was studied in leaf, roots and surface sediment samples of *Avicennia marina*, a dominant mangrove in Mumbai. PAH concentration was observed higher in root and leaf samples in comparison to sediment samples. Naphthalene was the most common occurring PAH in all the samples. LMW/HMW (two and three ring PAH)/ (Four to Six PAH) ratio were noted greater than one while FluA/Pyr (Fluranthene/Pyrene) ratio was found lesser than one for majority of the mangrove samples, suggesting PAH input from petrogenic sources. Phe/Anth (Phenanthrene/Anthracene) ratio was lesser than one, again suggesting petrogenic source of input.

KEYWORDS: Persistent, Contamination, Accumulation, Petrogenic, Mangroves

1. INTRODUCTION

Mangrove ecosystems, important intertidal estuarine wetlands along the coastlines of tropical and subtropical regions are frequently exposed to various anthropogenic contaminations including PAH [1,2]. PAH contamination is of an increasing environmental concern in the recent years. Anthropogenic practices such as industrial processing, petroleum spills, and incomplete combustion of fossil fuel have lead to accumulation of PAH in the environment [3]. Elevated concentration of PAH is commonly recorded in marine and coastal sediments near urban and industrial cities [4, 2]. The unique features of mangroves such as high primary productivity and root biomass, abundant detritus, rich organic carbon and reduced conditions favour the retention and accumulation of PAH[2,5].

PAH are naturally occurring contaminants formed by the incomplete combustion of organic materials [6]. They comprise a large group of compounds (several hundreds) that contain two or more fused benzene rings. PAH generally become more lipophilic, less soluble and less volatile with increasing molecular weight. Some of these compounds such as benzo (a) pyrene are known to be carcinogenic while others are suspected of being so [7,8]. Sixteen individual PAH compounds have been identified as priority pollutants by United States Environmental Protection Agency (USEPA) due to their toxic mutagenic and carcinogenic characteristics [9]. Two classes of PAH can be distinguished based on their properties and molecular weight. PAH with 2-3 benzene rings [(e.g., Naphthalene, Acnaphthalene, Fluorene, Anthracene)] and secondly, the high molecular weight PAH with four to six aromatic rings [(e.g., Fluoranthene, Pyrene, Benzo-(a)-Anthracene, Perylene, Benzo-(b)-Fluranthrene, Benzo-K-Fluranthrene, Benzo-(a)-Pyrene, indeno (1, 2, 3-cd pyrene)] [2]. The former class has an acute toxicity while some of the high molecular weight PAH shows high carcinogenic potential.

The quantitative composition of PAH in airborne particles has been widely reported and the major emission sources are fossil fuel combustion and biomass burning (waste incineration, firewood and straw) [10,11]. Atmospheric PAH concentrations in urban localities are often higher than those in rural area because of the emission from motor vehicle and domestic fuel combustion [12, 13]. Preliminary work on PAH contamination in mangrove sediments reported that the PAH concentration in some mangrove swamps were higher than that in marine bottom sediments indicating more PAH were accumulated in coastal sediments. The degree of PAH contamination may vary significantly among mangrove swamps and hot spots of contamination could even be found within a relatively clean swamp.[2] Distribution and accumulation of polycyclic aromatic hydrocarbons has been discussed by many authors in different type of samples but there are few records of PAH in mangrove plant species. This paper helps understand PAH concentration and distribution in *A.marina*.

In present study, accumulation and distribution of 7 PAH namely naphthalene, acnaphthalene, fluorene, anthracene, phenanthrene, fluranthrene and pyrene in mangrove species- *A. marina* from the urban localities of Mumbai were compared and evaluated for possible sources of contamination. PAH in leaf, root and surface sediment samples in *A. marina* from three localities of Mumbai were studied. The study also compares the PAH

*Corresponding Author: Dr. Akshayya Shete, 108, Nav Shakti Sadan, Sector-13, Rohini, Delhi – 110085 Phone No.:+91 (011) 47503033@, (+91)9911575041 Email ID: akshayya@hotmail.com, akshayya@gmail.com

compounds in different (leaf, root, sediment) samples from different sites to evaluate the possible sources of contamination. The profile and characteristic ratios of different individual PAH in sediments such as Phenanthrene/Anthracene and Fluoranthene/Pyrene ratios have been used to determine the dominant origins of PAH [14, 15, 16, 17, 18].

2. MATERIALS AND METHOD

2.1 Study Site

Mumbai, major metropolitan city of India went through many changes over the decades. Reclamation, urbanization and industrialization are the major reasons for depletion of mangroves in Mumbai. Some species are found to grow in these localities despite the urban runoff and effluent discharge from different sources such as anthropogenic and industrial wastes throughout Mumbai. It was observed during field study that amongst all the mangrove species *Avicennia marina* had luxuriant growth even in polluted localities. Remote sensing study and ground truth referencing revealed that maximum mangrove coverage is in Thane creek region which is also known as the industrial belt of Mumbai. The sampling sites namely Koparkhairane (Site1), Ghatkopar (Site2) and Kharghar (Site3) are the localities in the Thane creek region. Kharghar is located on Mumbai- Pune Highway (NH-4). It had many ready and under construction projects both in commercial and residential segments. Koparkhairane is built mostly on reclaimed land. Ghatkopar and Koparkhairane are the residential areas with chemical and electrical factories. The patch of mangrove plant *Avicennia marina* is commonly occurring at these three sites.

2.2 Sampling and Analysis

The samples of leaves, roots and surface sediment of *Avicennia marina* were collected from three points of each sampling site namely Koparkhairane, Ghatkopar and Kharghar, twice in a year. These samples were freeze-dried, powdered and labeled respectively. Each sample was processed separately in different flasks to avoid any kind of mixing. Approximately, 3g of each leaf, root samples along with sediment samples (5g each) were extracted using hexane (50 mL) for 90 minutes using ultrasonic extractor. The extract was filtered to eliminate any particulate impurities. The extract was then dried by a flow of dry nitrogen. The residue obtained was re-dissolved in 200 μ L of acetonitrile for analysis by HPLC. The characterization and quantification of PAH were done by High Performance Liquid Chromatograph (HPLC) system (Schimadzu, LC-10 AD) with UV- visible detector. The analytical column was of 250mm length and 4.6mm i.d., packed with totally porous spherical RP-18 material (particle size 5 μ m). A guard column packed with totally porous spherical RP-18 material (10mm long and 4.6mm i.d.) preceded the analytical column. Acetonitrile – water mixture (75:25) was used as mobile phase at a flow rate of 1.0mL per minute. Samples of 50 μ L were injected into the column through the sample loop. A UV detector set at 254nm for absorption was used for detection of these compounds. The data was processed with a CR7A chromatopac data processor. Several dilutions corresponding to 0.2 to 20ng absolute of synthetic standard mixture of individual component of PAH, supplied by Polyscience, USA, dissolved in HPLC grade acetonitrile was used for determining the retention data and for studying linearity of the detector. The response was linear for a wide range of concentrations mentioned above. All the results are expressed in ng/g of dry weight.

3. RESULTS AND DISCUSSION

Mangrove wetlands support several aerobic and anaerobic biogeochemical processes that are capable of attenuating pollutants. The amount of organic carbon and hydrophobicity of organic matter in sediments substantially decrease the mobility, water solubility and bioavailability of PAH [19]. In present study accumulation of PAH was found to be higher in leaf and root when compared to surface sediment samples (Table 1). The mean concentration of PAH ranged from BDL-8987.83ng/g in leaf samples, BDL-168356.7ng/g in root samples and BDL-3143.42ng/g in surface sediment samples (Table 1). Total PAH (Σ PAH of 7 PAH) for sediment sample ranged from 74.754 -3799.541 ng/g whereas Σ PAH of leaf and root samples ranged from (9709.006 -18745.96) ng/g and (53099.81- 178510.3) ng/g of dry weight basis respectively (Table 1). Kharghar (Site1) had industrial and domestic waste along with wastes from many ongoing building projects and showed higher accumulation of total PAHs (Table 2). Phenanthrene and pyrene remained below detection levels in leaf samples from Kharghar (Site1). Distribution of most PAH was found more in leaf and root samples of Koparkhairane and Ghatkopar as these were localities with more domestic as well as industrial waste (Table 1).

The general trend of accumulation of PAH can be presented as root>leaf>sediment. The concentration of PAH in leaf and root varies with location, source of input of pollutants or uptake of lipophilic pollutants by plants lipid storing cells. PAH are generally lipophilic with low water solubility [7, 8]. Chiou *et al.*, 2001^[20] reported that plant lipids is the major factor causing observed differences in plant uptake of lipophilic contaminants. The fact that lenticels present on the pneumatophores and leaves of *A. marina* which help in gaseous exchange cannot be neglected. Also, Persistent Organic Pollutants (POPs) have propensity to enter gas

phase under environmental temperature, they may volatilize from soils or plants and may get redeposited. Since POPs are lipophilic in nature and have low water solubility they may get easily accumulated in the lipid storing cells. The presence of lipid in leaves and roots could be one of the reasons for more bioaccumulation. The roots always carry the finest particles of sediment and this could be the reason for elevated levels of POP concentration in the roots than in the leaf or sediment [21].

Some of the previous studies with reference to the concentrations of PAH in sediment suggested that concentrations were affected by chemical composition of the sediments such as organic matter and clay content [22]. Sediments with high organic carbon content were characterized with high values of PAH [23, 18]. However, Tam N.F.Y et.al, 2001[2], found no correlation between ΣPAH and organic matter concentrations in the mangrove sediments and demonstrated that nature of the sediment influences distribution and concentration of PAH. The amounts of PAH accumulated in the surface sediment were much higher than marine bottom sediments. Botello and Calva (1998)[24] also demonstrated that PAH concentrations in sediments from three lagoons in southern Gulf of Mexico were independent of the percentages of organic carbon present in lagoons and some of their results even contradicted with sorption theory. This non affinity between PAH and organic matter has been reported in suspended estuarine particles too [25, 26]. The distribution and concentrations of PAH in sediment would be determined more by direct input, rather than by the type of sediments found locally. [2, 27] Different temperature of combustion processes or different fossil materials are responsible factors [27].

Tam et al., 2001, reported low molecular weight (2-3 ring) PAH, like naphthalene, flourene and phenanthrene were dominant in PAH profile study of sediments [2]. In present study naphthalene, acnaphthalene and flourene were more dominant PAH in comparison to other PAH (Table 1). Wu et.al, (1999) [28] who examined the PAH profile of 15 PAH compounds in different sediments to evaluate the possible sources of anthropogenic contamination. Naphthalene was derived mainly from anthropogenic activities, especially from petrogenic inputs. Naphthalene constitutes a significant fraction of crude oils and petroleum products with lighter fractions, and can be used as an indicator of petroleum source of PAH contamination [29].

The abundance ratio of two and three ring hydrocarbons (LMW) to four to six ring hydrocarbons (HMW); (LMW/HMW) can be used to help distinguishing the petrogenic and pyrolytic sources. [30, 31, 2] LMW/HMW ratios were greater than one for all three sites in majority of samples, suggesting significant PAH input from petrogenic sources. Sediment sample of Ghatkopar where ratio was 0.163 implied pyrolytic input (Table 2). LMW PAH such as Naphthalene, Acnaphthalene and Fluorene were dominant when compared to HMW PAH (Anthracene, Fluranthrene, Phenanthrene and Pyrene) (Table 1).

Sicre et.al.,1987 [32] suggested that a Flu/Pyr ratio of less than one was attributed to petrogenic sources and values greater than one were obviously related to a pyrolytic origin. Table 3 suggests the PAH sources based on the ratio of some PAH compounds. FluA/Pyr ratio was found greater than one in root sample of Koparkhairane (10.731 ng/g) and in sediment samples from Kharghar (2.658ng/g) and Ghatkopar (1.416 ng/g) suggesting the pyrolytic input. Phe/Anth ratio was lesser than one or could not be calculated as one of the samples was below detection limit (Table2) suggesting petrogenic source of input. Budzinski et.al; 1997[16] suggested that sediments with Phe/Anth>10 was typical of Pyrolytic sources. As discussed earlier LMW/HMW ratio was greater than one indicating petrogenic input (Table2).The study of different ratios (LMW:HMW; Phen/Anth; FluA/Pyr) suggested that majority of samples of *Avicennia marina* from different localities of Mumbai showed petrogenic source of input.

Table1: Mean concentration of PAHs in *Avicennia marina* from Mumbai

PAH	Kharghar (Site1)			Koparkhairane (Site2)			Ghatkopar (Site 3)		
	Leaf (ng/g)	Root (ng/g)	Sediment (ng/g)	Leaf (ng/g)	Root (ng/g)	Sediment (ng/g)	Leaf (ng/g)	Root (ng/g)	Sediment (ng/g)
Napt	5784.77	9701.798	363.372	6958.853	45760.31	1526.112	4298.836	53182.47	BDL
Acn	6629.051	168356.7	3143.42	2189.73	5484.459	BDL	8987.836	11453.11	2.986
Flu	5554.167	104.924	11.865	175.377	403.573	4.692	2496.133	3694.402	7.494
Anth	44.75	275.857	74.2955	6.296	846.954	BDL	594.419	69.653	BDL
FluA	733.222	BDL	144.011	52.721	533.868	6.822	180.887	96.706	32.45
Phe	BDL	BDL	8.407	5.764	20.894	7.489	66.137	21.886	8.914
Pyr	BDL	71.063	54.1695	320.263	49.748	BDL	207.001	BDL	22.909
ΣPAH	18745.96	178510.3	3799.541	9709.006	53099.81	1545.116	16831.25	68518.23	74.754

Naph=Napthalene, Acn=Acenapthene, Flu=Fluorene, Anth=Anthracene, FluA=Fluoranthene, Phe=Phenanthrene, Pyr=Pyrene
BDL: Below Detection limit (values below 0.01ng/g)

Table2: Ratio of some PAH compounds

Ratio	ΣPAH (ng/g)			FluA/Pyr			Phe/Anth			LMW/HMW		
	Leaf	Root	Sediment	Leaf	Root	Sediment	Leaf	Root	Sediment	Leaf	Root	Sediment
Site1	18745.96	178510.3	3799.541	NC	NC	2.658	NC	NC	0.113	23.095	513.557	12.527
Site2	9709.006	53099.81	1545.116	0.164	10.731	NC	0.915	0.024	NC	24.215	35.583	106.966
Site3	16831.25	68518.23	74.754	0.873	NC	1.416	0.111	0.314	NC	15.053	362.984	0.163

NC: Not calculated,

(One of the values is Below Detection Limit (BDL), therefore cannot be calculated)

Site 1=Kharghar

Site 2= Koparkhairane

Site 3= Ghatkopar

LMW= Low Molecular Weight Hydrocarbons

(Naphthalene+Acenaphthene+Fluorene)

HMW=High Molecular Weight Hydrocarbons

(Anthracene+Fluranhrene+Phenanthrene+Pyrene)

Table3: Suggested PAHs sources based on the ratio of some PAH compounds

Ratio	PAHs source	LMW/HMW	Phe/Ant	Flu/Pyr	BgP/InP	BaA/BaP	Pyr/BaP
	Pyrolytic	<1 ^a		>1 ^b			
	Petrogenic	>1 ^a		<1 ^b			
	Vehicular Exhaust		<4 ^c				1.5 ^d ,2-6 ^c
	Fuel Oil			0.6-0.9 ^f			
	Gasoline exhaust				3.5 ^g	0.5 ^g	
	Diesel exhaust				1.1 ^g	1.1 ^g	

LMW/HMW: (two and three ring PAHs)/ (Four to six ring PAHs); ND: Not detected.

^aYuan *et al.*, 2001^[31] and Tam *et al.*, 2001^[2]

^bSicre *et al.*, 1987^[32]

^cYang *et al.*, 1991^[15]

^dMasclat *et al.*,1986^[33]

^eBarale *et al.*, 1991^[34] and Siegl *et al.*, 1992^[35]

^fGschwend and Hites, 1981^[36]

^gLi and Kamens, 1993^[37]

4. Conclusion and Summary

PAH accumulation was more in mangrove plant samples (leaf and root) in comparison to the surface sediment. It is evident from the study that source of input was petrogenic in majority of samples. Mangrove species like *Avicennia marina* show good adaptability and ability to survive even in presence of various persistent pollutants like PAH. This study can serve as an important addition to baseline studies in monitoring the concentration of persistent pollutants particularly polycyclic aromatic hydrocarbons in mangrove species.

Acknowledgement

This research is funded by BRNS- DAE Funding Scheme and author Akshayya Shete, research scholar from BARC- UoP Collaborative Research Program during the tenure of which above work was carried out.

REFERENCES

1. Klekowski Jr., E.J., Corredor, J.E., Morell, J.M., Delcastello, C.A., 1994. Petroleum pollution and mutation in mangroves. *Marine Pollution Bulletin*, 28, 166-169.
2. Tam, N.F.Y., Ke, L., Wang, X.H., Wong Y.S., 2001. Contamination of polycyclic aromatic hydrocarbons in surface sediments of mangrove swamps. *Environmental Pollution* 114, 255-263.
3. Edwards, N.T., 1983. Polycyclic aromatic hydrocarbons (PAHs) in the terrestrial environment: a review. *Journal of Environmental Quality* 12, 427-441.
4. Connell, D.W., Wu, R.S.S., Richardson, B. J., Leung, K., Lam, P.S.K., Connell, P.A., 1998. Occurrence of persistent organic contaminants and related substances in Hong Kong marine areas: an overview. *Marine Pollution Bulletin* 36, 374-384.

5. Ke, L., Wong T.W.Y., Wong Y.S., Tam N.F.Y., 2002. Fate of polycyclic aromatic hydrocarbon (PAH) contamination in a mangrove swamp in Hong Kong following an oil spill. *Marine Pollution Bulletin* 45 (1-12), 339-347.
6. Smith, I.M., 1984. PAH from Coal Utilization. Emissions and Effects. Report ICTIS/TR29 IEA Coal Research, London, UK.
7. World Health Organization (WHO), 1997. Guidelines for predicting dietary intake of pesticide residues. Programme of safety and Food Aid. WHO, Geneva.
8. Schneider, K., Schuhmacher, U.S., Oltmanns, J., Kalberlah F., Roller, M., 2000. PAK (polyzyklische aromatische kohlenwasserstoffe.)*In: Eikmann, T., Heinrich, U., Heinzow, B., Konietzka, R. (Eds.), Gefahrdungsabschätzung von, Umweltschadstoffen, Ergänzbares Handbuch toxicologischer Basisdaten and irhe Bewertung, kennziffer D 815, 2. Erg. Lfg. 4/00. Erich Schmidt Verlage, Berlin.*
9. Varanasi, U. (Ed.), 1989. Metabolism of Polycyclic Aromatic Hydrocarbons in the Aquatic Environment. CRC Press Inc, Boca Raton, FL, USA.
10. Venkataraman, C., Friedlander, S., 1994. Source resolution of fine particulate polycyclic aromatic hydrocarbons using receptor model modified for reactivity. *Journal of Air Waste Management Association*, 44, 1103-1108.
11. Harrison, R.M., Smith D.J.T., Luhana L., 1996. Source of atmospheric polycyclic aromatic hydrocarbons collected from urban location in Bringaham, U.K., *Environmental Science and Technology* 30, 825-832.
12. Caricchia, A.M., Chiavarini, S., Pezza M., 1999. Polycyclic aromatic hydrocarbons in the urban atmospheric particulate matter in the city of Naples (Italy). *Atmospheric Environment*. 33, 3731-3738.
13. Schnelle-Kreis, J., Gebefugi, I., Welzl, G., Jaensch, T., Kettrup, A., 2001. Occurrence of particle associated polycyclic aromatic compounds in ambient air of the city of Munich. *Atmospheric Environment*, 35, S71-S81.
14. Colombo, J.C., Pelletier, E., Brochu, C., Khalil, M., 1989. Determination of hydrocarbon sources using n-alkane and polyaromatic hydrocarbon distribution indexes. Case study: Rio de La Plata estuary, *Argentina Environmental Science and Technology*, 23, 888-894.
15. Yang, S.Y.N., Connell, D.W., Hawker D.W., Kayal, S.I., 1991. Polycyclic aromatic hydrocarbons in air, soil and vegetation in the vicinity of an urban roadway. *The Science of Total Environment*, 102, 229-240.
16. Budzinski, H., Jones, I., Bellocq, J., Pierard, C., Garrigues, P., 1997. Evaluation of sediment contamination by polycyclic aromatic hydrocarbons in the Gironde estuary. *Marine Chemistry* 58, 85-97.
17. Trapido, M., 1999. Polycyclic aromatic hydrocarbons in Estonian soil: contamination and profiles. *Environmental Pollution* 105, 67-74.
18. Yang, G.P., 2000. Polycyclic aromatic hydrocarbons in the sediments of the South China Sea. *Environmental Pollution*, 108,163-171.
19. Weissenfels, W.D., Klewer, H.J., Langhoff, J., 1992. Adsorption of polycyclic aromatic hydrocarbons (PAHs) by soil particles: influence on biodegradability and biotoxicity. *Applied Microbiology and Biotechnology* 36, 689-696.
20. Chiou, C.T., Sheng G.Y., Manes, M., 2001. A partition-limited model for the plant uptake of organic contaminants from soil and water. *Environmental Science and Technology* 35, 1437-1444.
21. Shete,A., Gunale,V., Pandit,G., 2009. Organochlorine pesticides in *Avicennia marina* from the Mumbai mangroves, India. *Chemosphere*, 76 (1483-1485).
22. Kim, G. B., Maurya, K. A., Lee, R. F., Lee J. H., Koh C. H., Tanabe, S.S., 1999. Distribution and sources of polycyclic aromatic hydrocarbons in sediments from Kyeonggi Bay, Korea. *Marine Pollution Bulletin* 28, 7-15.
23. Witt, G., 1995. Polycyclic aromatic hydrocarbons in water and sediment of the Baltic Sea. *Marine Pollution Bulletin* 31, 237-248.
24. Botello, A.V., and Calva, L.G.B., 1998, Polycyclic aromatic hydrocarbons in sediments from Pueblo Viejo, Tamiagua, and Tampamachoco Lagoons in Southern Gulf of Mexico. *Bulletin of Environmental Contamination and Toxicology* 60, 96-103.

25. Raoux, C.Y., Garrigues, P., 1991. Mechanisms model of polycyclic aromatic hydrocarbons contamination of marine coastal sediments from Mediterranean Sea. *Polycyclic Aromatic Compounds Supplement* 3, 443-450.
26. Coakley, J., Nagy, E., Serodes, J., 1993. Spatial and vertical trends in sediment phase contaminants in the Upper Estuary of the St. Lawrence Rivers. *Estuaries* 16, 653-669.
27. Zhang, J., Cai, L., Yuan, D., Chen, M., 2004. Distribution and sources of polynuclear aromatic hydrocarbons in mangrove surficial sediments of Deep Bay, China. *Marine Pollution Bulletin* 49, 479-486.
28. Wu, Y., Zhang, J., Tang, Y., 1999. Geochemistry of n-alkanes and polycyclic aromatic hydrocarbons in the sediments from the South China Sea. *Journal of Ocean University of Qingdao* 29, 112-120.
29. Sporstol, S., Gjos, N., Lichtenthaler, R.G., Gustavsen, K.O., Urdal, K., Orelid, F., Skei, J., 1983. Source identification of aromatic hydrocarbons in sediment using GC/MS. *Environmental Science and Technology* 17, 282-286.
30. Robertson A., 1998. Petroleum hydrocarbons *In: AMAP Assessment Report: Arctic Pollution Issues*. Arctic Monitoring and Assessment programme (AMAP). Oslo, Norway, pp.661-716.
31. Yuan, D. X., Yang, D. N., Terry, L. W., Qian, Y. R., 2001. Status of persistent organic pollutants in the sediment from several estuaries in China. *Environmental Pollution* 114, 101-111.
32. Sicre, M.A., Marty, J.C., Saliot, A., Aparicio, X., Grimalt, J., Albaiges, J., 1987. Aliphatic and aromatic hydrocarbons in different sized aerosols over the Mediterranean Sea: occurrence and origin. *Atmospheric Environment* 21, 2247-2259.
33. Masclet, P., Mouvier, G., Nikolaou, K., 1986. Relative decay index and sources of polycyclic aromatic hydrocarbons. *Atmospheric Environment* 20, 439-446.
34. Barale, R., Giromini, L., Ghelardini, G., Scapoli, C., Loprieno, N., Pala, M., Valerio, F., Barrai, I., 1991. Correlations between 15 polycyclic aromatic hydrocarbons (PAH) and the mutagenicity of the total PAH fraction in ambient air particles in La Spezia (Italy). *Mutation Research* 249, 227-241.
35. Siegl, W.O., Chladek, E., 1992. Measurement of gas-phase polycyclic aromatic hydrocarbons (PAH) in gasoline vehicle exhaust. *American Chemical Society Division of Petroleum Chemistry* 4, 1499-1504.
36. Gschwend, P. M., Hites, R. A., 1981. Fluxes of polycyclic aromatic hydrocarbons to marine and lacustrine sediments in the northeastern United States. *Geochimica et Cosmochimica Acta* 45, 2359-2367.
37. Li, C. K., Kamens, R. M., 1993. The use of polycyclic aromatic hydrocarbons as sources signatures in receptor modeling. *Atmospheric Environment* 27A, 523-532.