

Polycyclic Aromatic Hydrocarbons in the atmospheric depositions of Venice lagoon

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Introduction

Polycyclic Aromatic Hydrocarbons (PAHs) are harmful semivolatile organic compounds formed during the incomplete combustion and pyrolysis of organic material. Their widespread occurrence is largely due to anthropogenic emissions (coal-, oil- and gas-burning facilities, motor vehicles, waste incineration and industrial activities, such as oil refining, coke and asphalt production, aluminum production, steel and iron industries, etc.),¹ and some of them (benzofluoranthenes, benzo[a]pyrene, benzo[a]anthracene, dibenzo[a,h]anthracene and indeno[1,2,3-cd]pyrene) are among the strongest known human carcinogens.²

This paper shows data of polycyclic aromatic hydrocarbons (PAHs) in atmospheric fall-out, coming from a three-year sampling of monthly bulk depositions in three stations located in the Lagoon of Venice. This study was aimed at estimating the spatial variability of atmospheric fall-out of PAHs into the lagoon and attempting the identification of sources using PAH diagnostic ratios.

Materials and Methods

A total of seventy-seven atmospheric bulk deposition samples were collected monthly from April 2002 to December 2004, at three sites located respectively in the cities of Mestre and Venice and inside the industrial area of Porto Marghera. Atmospheric depositions were collected by 3 bulk samplers already described by Guerzoni et al., 2004³. The samplers were polymer structures, formed by a cylindrical container and a protection ring from damages by birds and animals, clamped to a 60-mm pole. Depositions were collected in a Pyrex bottle with a Pyrex funnel (surface area = 0.043 m²) treated with dimethyl dichlorosilane 5% in toluene⁴.

Total atmospheric samples were first spiked with a series of 5 deuterated PAHs (Acenaphthene-D10, Chrysene-D12, Naphthalene-D8, Perylene-D12, Phenanthrene-D10) as internal standards, and then extracted in a separatory funnel with dichloromethane. Extraction and clean-up procedures are extensively described in Raccanelli et al., 2002⁴. HRGC/HRMS analyses were conducted using a HP 6890 plus gas chromatograph coupled to a Micromass Autospec Ultima mass spectrometer, operating in EI mode at 35 eV and with a resolution of 10.000 (5% valley). Quantitative determination of PAHs was performed by isotope dilution methods, using relative response factors previously obtained from standard solution injections⁵. All solvents were Picograde® reagent grade (Pomochem GmbH, Wesel, Germany). Native and deuterated PAH standards were purchased from Supelco (Belfonte, PA, USA), Acenaphthylene-D8 standard was purchased from Cambridge Isotope Laboratories (Woburn, MA, USA). Recoveries always were 50% to 110%. Reproducibility was 15% for low values, or better. Laboratory blanks, repeated twice a week, were lower than 9% with respect to the minimum concentration found.

Results and Discussion

Atmospheric deposition samples were analysed for Naphthalene (Naph), Acenaphthylene (Acenaph), Acenaphthene (AN), Fluorene (F), Phenanthrene (P), Anthracene (A), Fluoranthene (Fl), Pyrene (Py), Benzo[a]anthracene (BaA), Chrysene (Chry), Benzo[b+k+j]fluoranthene (BbKjFl), Benzo[a]pyrene (BaPy), Indeno[1,2,3-cd]pyrene (IPy), Dibenz[a,h]anthracene (DbahA) and Benzo[g,h,i]perylene (BghiPe). Values below the detection limit (DL) were considered equal to 0.5DL.

Fig. 1 shows the mean PAH profiles (percent contribution of each PAH compound to SPAH) for the three sites. The total PAH mass was dominated by high molecular weight PAHs, with a relative importance of 64%, 61% and 79% at ADM, IBM and EZI, respectively. Naphthalene was the most abundant compound at ADM and IBM (respectively 22% and 25%) whereas at EZI the profile was mainly characterized by Benzo[b+k+j]fluoranthene (16%). Moreover, at this site the highest relative importance of BaA, BaPy, IPy, DbahA and BghiPe has also been observed.

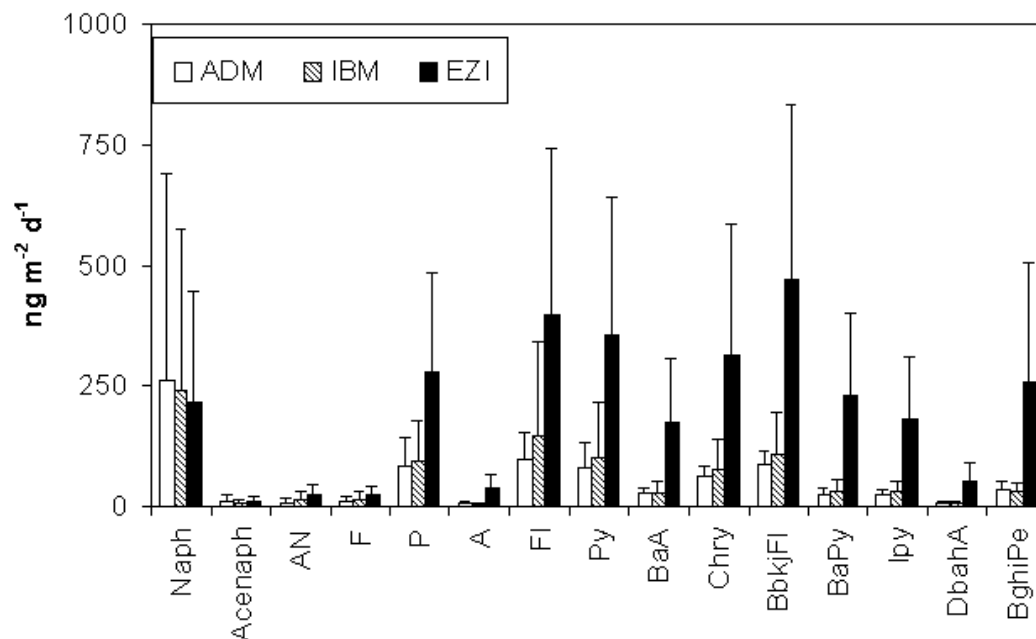


Figure 1. Mean PAHs deposition fluxes observed during the study period.

Several PAHs have been accepted as probable or possible human carcinogens, and most of them are known to be associated with airborne particles.⁶ The sum of the six carcinogenic PAHs (BaA, BbFl, BkFl, BaPy, DbahA, and IPy) accounted for 26%, 24% and 36% of the total PAH deposition at ADM, IBM and EZI, respectively. The WHO considered BaP in their air quality guidelines when deriving a unit risk factor and a number of EU states have, independently, adopted health guidelines or regulations for BaP. The average and ranges of daily atmospheric deposition in the three sites, expressed as BaP equivalents,⁷ are, respectively, 38 (17-72), 44 (4-122) and 328 (76-968) ng m⁻² d⁻¹ at ADM, IBM and EZI. As it can be seen, during the study period the deposition flux at EZI resulted to be on average one order of magnitude higher than other sites. The mean deposition fluxes of SPAHs observed at EZI is 90 ± 59 µg m⁻² month⁻¹, that is threefold higher than the value of 33.5 µg m⁻² month⁻¹ measured by Gevaert et al.⁸ in northwest England. On the contrary, at ADM and IBM sites the SPAHs resulted to be 24 ± 16 and 28 ± 25 µg m⁻² month⁻¹, respectively, comparable with the data of Gevaert et al.⁸

Spatial and temporal variations of atmospheric fall-out were investigated, and source identification was attempted using diagnostic ratios.¹ The ratio values of individual PAH species listed in a previous work by Mantset et al.¹ are reported in table 1, and descriptive statistics of concentration ratios calculated from deposition sampling in the three sites investigated are shown in figure 2 for comparison. The BaA/(BaA + Chry) ratio is characteristic of a faster decay of BaA in comparison to the more stable isomer Chry, thus indicating possible local origin (high values) or transport of PAHs from a distant source (low values). The BF_s/BghiPe ratio discriminates automobiles (low values) from domestic emissions (high values). High values of the BghiPe/BaPy ratio are characteristic of local traffic emissions, suggested by high levels of BghiPe and low levels of BaPy, due to its faster decay in comparison to the more stable isomer Benzo[e]pyrene. The FI/(FI + Py) and IPy/(IPy + BghiPe) ratios indicate traffic emissions (low values) or possible contributions from oil burning (high values).

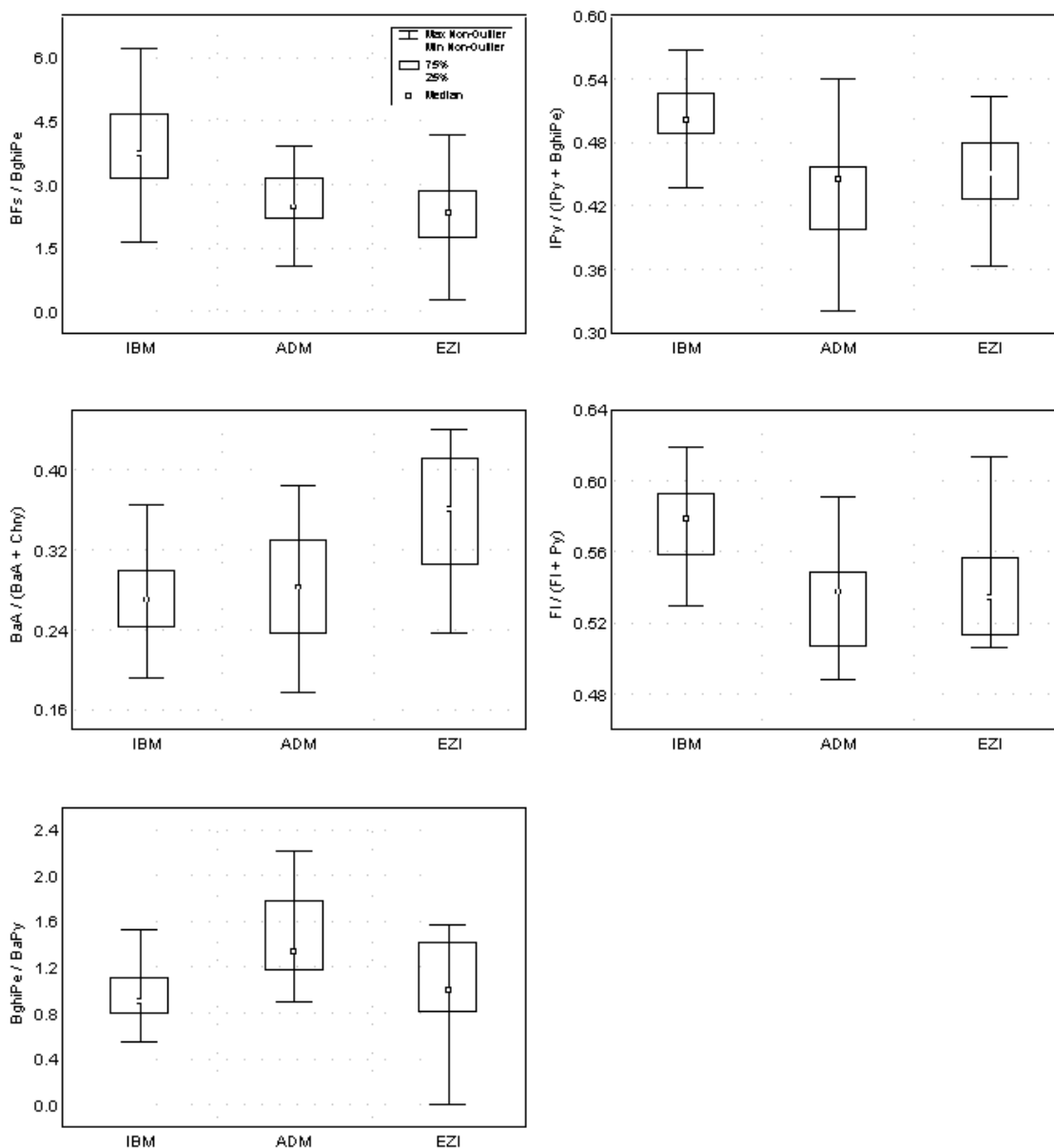


Figure 2. Descriptive statistics of diagnostic PAH ratios during the study period.

In summary, all the three sites resulted affected by combustion sources with variable seasonal contribution, and several differences in deposition fluxes and pollutant patterns between industrial, urban and lagoonal stations can be observed. The comparison of data reported in fig. 2 and in tab. 1 indicate that the signature of the station located inside the industrial area is mainly affected by local industrial sources and diesel engines emissions. The station located in the city of Mestre appears mostly affected by the high traffic density, with a major contribution of gasoline care emissions. The signature of Venice station is characterized by domestic fires and oil burning, with a possible transport of industrial emissions from distant sources.

Given the current level of contamination, a complete analysis of ecological risk requires further investigation aimed at evaluating adverse effects, in particular when considering the possible synergic effects with metals, PCBs and dioxins.

Table 1. Diagnostic PAH ratios (modified from Mantaset al., 2005¹)

	BghiPe/ BaPy	BFs/ BghiPe	IPy/ (IPy + BghiPe)	BaA/ (BaA + Chry)	FI/ (FI + Py)
Diesel vehicles	1.2–2.2 1.16	1.60 2.18	0.35–0.70 0.94	0.38–0.64 0.92	0.60–0.70 0.43
Catalystequippedcars	2.5–3.3 3.05	0.33 0.45	0.21–0.22 0.26	0.22–0.55 0.76	0.40 0.14
Non-catalystcars	1.72	1.17	0.51	0.58	0.17
Oil burning	<0.5, 0.40	2.68	0.82	0.32	0.62
Road dust	0.91, 0.86 1.1–3.5	4.7, 1.8 1.0–2.45	0.36, 0.42 0.51–0.57	0.38	0.42, 0.54 0.42–0.52
Industrialfurnaces	0.02–0.06	7.1–11.2	0.36–0.57	0.23–0.89	0.21–0.26

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References

1. Mantis J., Chaloulakou A. and Samara C. (2005) *Chemosphere* 59: 593-604.
2. IARC, International Agency for Research on Cancer (1987–1991). IARC Monographs on the Evaluation of Carcinogenic Risks to Humans, Lyon, vols. 43–53.
3. Guerzoni S., Rossini P., Molinaroli E., Rampazzo G. and Raccanelli S. (2004) *Chemosphere* 54: 1309-1317.
4. Raccanelli S., Guerzoni S., Rossini P. and Favotto M. (2002) *OrganohalComp* 58: 49-52.
5. Consorzio I.N.C.A., Raccanelli S., Favotto M., (2003) "Determination and quantification of PAH by HRGC/HRMS in environmental matrix by isotope dilution", I.M. POP/002 rev.1.
6. European Commission (2001), Ambient air pollution by Polycyclic Aromatic Hydrocarbons (PAH). Position paper.
7. Larsen J. C. and Larsen P. B. (1998) in: Air Pollution and Health (Hester R.E., Harrison R.M., Eds.), The Royal Society of Chemistry, 33.
8. Geva B., Hamilton-Taylor J. and Jones K.C. (1998) *EnvPoll* 102: 63-75