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POLYCYCLIC AROMATIC HYDROCARBONS IN ATMOSPHERIC DEPOSITIONS AROUND THE VENICE LAGOON

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Studies have revealed the potential risks to which human health and ecosystems are exposed in the Venice Lagoon, due to the atmospheric deposition of persistent pollutants such as trace metals and organic compounds. A total of seventy-seven atmospheric bulk deposition samples were collected monthly from April 2002 to December 2004, from three sites located in the cities of Mestre and Venice, and inside the industrial area of Porto Marghera. Samples were analysed by HRGC/HRMS for polycyclic aromatic hydrocarbon (PAH) content. Spatial variations of atmospheric fallout were investigated, and source identification was attempted using diagnostic ratios and multivariate statistical analysis. Different conditions were recorded, with three anthropic signatures: i) industrial, mainly affected by local industrial sources and diesel engine emissions, ii) urban, mostly influenced by high traffic density, especially petrol car emissions and iii) lagoonal, characterised by diesel emissions from boat engines and oil burning, with random transport of industrial emissions.

Keywords precipitation, atmospheric fallout, persistent organic pollutants, diagnostic ratios, Porto Marghera, Murano

The protection of Venice and its lagoon is at the centre of an international debate[1, 2, 3] which has only recently recognised the existing environmental problems.

In the last 20–30 years, several studies have focused on the potential risks to which both human health and ecosystem are exposed due to the presence of persistent pollutants such as trace metals and persistent organic pollutants (POPs) in the lagoon[4, 5, 6]. Other studies had already revealed the evident influence of atmospheric deposition in the area. Preliminary available data on atmospheric fallout of POPs were provided by bulk deposition samplings[7, 8, 9], and Marcomini et al.[10] showed that atmospheric deposition accounted for a quarter of the total dioxin and furan (PCDD-Fs) load in the Lagoon of Venice. Data on soils collected around the industrial zone revealed an airborne PCDD-Fs fallout effect up to several kilometres downwind[11].

The main anthropogenic activities with important influence on air quality in the area of Venice may be summarised as follows[12]: (i) oil refining; (ii) metallurgy, now mainly confined to the production of Al; (iii) chloro-soda cycles, discharging dichloroethane, vinyl chloride monomer and polyvinylchloride; (iv) power generation (oil and coal-fired); (v) urban waste incineration and (vi) traffic emissions. Most of these activities are carried out inside the industrial area of Porto Marghera. Moreover, a glass-making district is present on the Island of Murano (Fig. 1).

Polycyclic aromatic hydrocarbons (PAHs) are harmful semi-volatile 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 and production of coke, asphalt, aluminium, steel, iron, etc.)[13]. Some of them (benzofluoranthenes, benzo[a]pyrene, benz[a]anthracene dibenz[a,h]anthracene and indeno[1,2,3-cd]pyrene) are among the strongest human carcinogens known[14].

This paper shows data on PAHs in atmospheric fallout, collected during three years of monthly bulk sampling in three stations located in and around the Lagoon of Venice, with a view to estimating the spatial variability of atmospheric fallout in the lagoon and identifying its sources using PAH diagnostic ratios[13] and multivariate statistical analysis[15].

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 in the cities of Mestre and Venice and inside the industrial area of Porto Marghera (Fig. 1). Site ADM was located in the city of Mestre, near an air monitoring station of the local environmental pollution agency (via A. Da Mestre, WGS84 coordinates 12°14’13.5”, 45°29’36.4”). Site EZI was inside the industrial zone of Porto Marghera, close to a meteorological station of the industrial district environmental service (Ente Zona Industriale – CED, WGS84 coordinates 12°14’35.7”, 45°26’44.1”). Site IBM was located in the city of Venice, at the Institute of Marine Sciences (ISMAR-CNR, WGS84 coordinates 12°21’26.4”, 45°25’39.1”).

Atmospheric depositions were collected by 3 bulk samplers already described by Guerzoni et al., 2004[8]. The samplers were polymer structures, composed of a cylindrical container with a ring and a net protecting them from damage caused 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 m^2) treated with 5% dimethyldichlorosilane in toluene[16].

Total atmospheric samples were first spiked with a series of 5 deuterated PAHs (Acenaphthene-D10, Chrysene-D12, Naphtalene-D8, Perylene-D12, Phenanthrene-D10) as internal standards, and then extracted in a separation funnel with dichloromethane. Extraction and clean-up procedures are extensively described in Raccanelli et al., 2002[16]. HRGC/HRMS analyses were conducted using an HP 6890 plus gas chromatograph coupled to a Micromass Autospec Ultima mass spectrometer, operating in EI mode at 35 eV with 10,000 resolution (5% valley). Quantitative determination of PAHs was performed by isotope dilution methods, using relative response factors previously obtained from standard solution injections[17]. All solvents were Picograde® reagent grade (Pomochem GmbH, Wesel, Germany). Native and deuterated PAH standards were purchased from Supelco (Belfonte, PA, USA), Acenaphtylene-D8 standard was purchased from Cambridge Isotope Laboratories (Woburn, MA, USA). Recoveries were always 50% to 110%. Reproducibility was ±15% for lower 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 (PHE), Anthracene (A), Fluoranthene (FA), Pyrene (PY), Benz[a]anthracene (BaA), Chrysene (CHR), Benzo[b+k+j]fluoranthene (BbkjFA), Benzo[a]pyrene (BaP), Indeno[1,2,3-cd]pyrene (IPY), Dibenz[a,h]anthracene (dBahA) and Benzo[ghi]perylene (BghiPE). Values below the detection limit (DL) were considered equal to 0.5DL.

Fig. 2 shows the mean PAH profiles (mean deposition fluxes and the amount of each PAH compound as a percentage of ΣPAHs) for the three sites. The atmospheric bulk deposition fluxes are reported in Table 1.

The PAH mass as a whole was dominated by high-molecular weight PAHs, which accounted for 64%, 61% and 79% at the ADM, IBM and EZI stations respectively. Low-molecular weight PAHs were also important, Naph being the most abundant compound at ADM and IBM (accounting for 22% and 25% of ΣPAHs respectively). At EZI the profile was mainly characterized by BbkjFA (16%), and this site also had the highest relative importance of BaA, BaP, IPY, dBahA and BghiPE (Fig. 2b).

Several PAHs are considered to be probable or possible human carcinogens, and most of them are known to be associated with airborne particles[18]. The sum of the six carcinogenic PAHs (BaA, BbFA, BkFA, BaP, dBahA, and IPY) accounted for 26%, 24% and 36% of the total PAH deposition at ADM, IBM and EZI respectively. The WHO considers BaP in their air quality guidelines when calculating unit risk factors, and a number of EU states have independently adopted health guidelines or regulations for BaP concentrations in the air. However, regarding PAHs in atmospheric depositions, there are currently no recognised quality standards. The average daily atmospheric depositions in the three sites (and the range of values), expressed as BaP equivalents,[19] were 38 (17-72), 44 (4-122) and 328 (76-968) ng m^{-2} d^{-1} at ADM, IBM and EZI respectively. As can be seen, during the study period the deposition flux at EZI was on average one order of magnitude higher than the other sites.

The mean deposition flux of ΣPAHs observed at EZI is 90±59 µg m^{-2} $month^{-1}$, which is three times higher than the value of 33.5 µg m^{-2} $month^{-1}$ measured by Gevao et al.[20] in northwest England. In contrast, at the ADM and IBM sites the ΣPAHs were 24±16 and 28±25 µg m^{-2} $month^{-1}$ respectively, comparable with the data of Gevao et al.[20].

The spatial and temporal variations of atmospheric fallout were also investigated, and source identification was performed using diagnostic ratios[13]. Before attempting to do this, it is important to stress that the relative composition of the different PAH compounds in dry deposition samples does not resemble that of the gas phase. Specifically, low-molecular weight (LMW) PAHs, being mostly in the gas phase, are under-represented, and the main contributors to dry deposition are the high-molecular weight (HMW) PAHs, mainly associated with particulates[21]. However, LMW PAHs are efficiently scavenged during rain events, and given long sampling periods their contribution to bulk deposition can therefore be important. In general, it can be assumed that diagnostic PAH ratios utilising mainly HMW PAHs can give important information when applied to bulk deposition samples.

The ratios of certain PAH species listed in a previous study by Mantis et al.[13] are reported in Table 2, and descriptive statistics of compound ratios calculated from deposition sampling in the three sites investigated are shown in Fig. 3 for comparison. BaA decays faster than the more stable isomer CHR, and the BaA/(BaA + CHR) ratio can thus indicate the distance of the source, higher values indicating a possible local origin and lower values indicating transport of PAHs from further away. Higher values of the BghiPE/BaP ratio are linked to traffic emissions. Lower values of the FA/(FA + PY) and IPY/(IPY + BghiPE) ratios also indicate traffic emissions, whereas higher values indicate contributions from oil burning[13]. The monthly sampling frequency may produce artefacts, due to PAH instability, if compared to traffic and industrial PAH ratios, which are generally calculated on a 24-hour sampling basis. Ambe and Mukai, 1997[21] calculated a 10-20% loss of BaP after a few months of atmospheric particulate matter sample storage. Additional loss is due to reactions with oxidants and therefore some of the results need to be treated with caution. Nevertheless, the bulk deposition samples in this study captured the different signals at industrial, urban and lagoon sites, thus demonstrating that the HMW PAH diagnostic ratios are useful to trace possible sources.

To summarise, all sites were affected by combustion sources with variable contributions, and several differences in deposition fluxes and pollutant patterns among industrial, urban and lagoonal stations can be observed. The comparison of the data reported in Fig. 3 and Table 2 suggests, as expected, that the signature of the station located inside the industrial area (EZI) is mainly affected by local industrial sources and diesel engine emissions (Fig. 3A). The influence of these sources is lower at the ADM and IBM stations. The station located in the city of Mestre (ADM) appears to be mostly affected by the high traffic density, with a major contribution from petrol car emissions (Fig. 3B). The signature of the Venice station (IBM) is characterized by diesel emissions of boat engines and oil burning, with possible transport of industrial emissions from distant sources (Figs. 3C and 3D).

Principal components analysis (PCA) can be used as a classification technique for reducing data to fewer dimensions. In PCA, the number of variables in the data set is reduced while retaining much of their information content, enabling a better visualization of the information in two or three dimensions, which can be interpreted as factors influencing data distribution. The principal components are constructed in such a way that the first principal component (PC) explains the maximum variance or information in the data set. The subsequent components are orthogonal to the previous PCs and they explain the maximum amount of the remaining variance. Hence by definition PC1, PC2 and PC3 contain more variance than any other PCs.

In this study, PCA was applied to the congener profiles of the PAHs, together with diagnostic ratios (Table 3). Three factors were extracted from the analysis (Table 3), accounting for 85% of total variance (extraction method: Principal Component Analysis; rotation method: Varimax with Kaiser Normalization, results achieved in 5 iterations), and each monthly deposition sample can now be ordered by the three factors and plotted in the space of the new variables (Fig. 4).

Factor 1 (F1) is characterised by almost all considered PAH congeners and by BaA/(BaA+CHR). It accounts for 56% of variance and represents the industrial component of the atmospheric deposition. All samples with higher levels of PAHs and with a high BaA/(BaA+CHR) ratio are plotted in the right part of the graph. As Fig.

4 shows, all EZI samples plotted in this area, together with a few ADM and IBM deposition samples. Regarding ADM, which is mostly affected by traffic emissions, positive F1 values are observed for samples collected in July and August (dotted line in Fig. 4A), when the industrial component prevails over the urban one.

Factor 2 (F2) is influenced by low molecular weight PAHs in the positive sense and by BaA/(BaA+CHR) in the negative, and it represents 18% of variance (Table 3). The samples collected in the cold period (Nov - Feb) are mainly located in the upper part of Fig. 4A.

Factor 3 (F3) is influenced by BghiPE and BghiPE/BaP in the positive sense and by IPY/(IPY+BghiPE) in the negative, and accounts for 11% of variance. High levels of BghiPE and higher values of the BghiPE/BaP ratio are characteristic of local traffic emissions, and all ADM samples are plotted in the upper part of Fig. 4B, with samples collected in July and August (dotted line in Fig. 4B) more affected by the industrial component and therefore having positive F1 values. IBM deposition samples fall in the lower part of the plot, corresponding to higher levels of the IPY/(IPY+BghiPE) ratio, which indicate contributions from diesel emissions of boat engines and oil burning. Positive F1 values are observed for a few IBM samples, indicating a greater contribution from industrial emissions. However, since the observed frequency of W and NW winds was always <10%, these samples are probably not strictly related to transport from the Porto Marghera industrial zone. It is more likely that emissions from local industrial activities (glass-making on the nearby Murano Island) are having an impact here and this hypothesis seems to be confirmed by the heavy metal content of bulk samples[23].

CONCLUSIONS

The PAH profiles of three anthropic signatures of atmospheric bulk depositions in and around the Lagoon of Venice were studied, illustrating the different influence of industrial and urban atmospheric emission sources. PAH diagnostic ratios and multivariate statistical analysis were useful in estimating the spatial variability of atmospheric fallout and identifying pollutant sources.

It was confirmed that atmospheric emissions from the industrial district affect depositions fluxes in the city of Mestre. PAH deposition in the city of Venice at times appeared to be influenced by local glass-making activity, carried out on the nearby Island of Murano. Traffic-related PAHs appeared to originate mainly from petrol vehicles in the urban site of Mestre, whereas diesel emissions appeared to be significant in the industrial zone and in the city of Venice.

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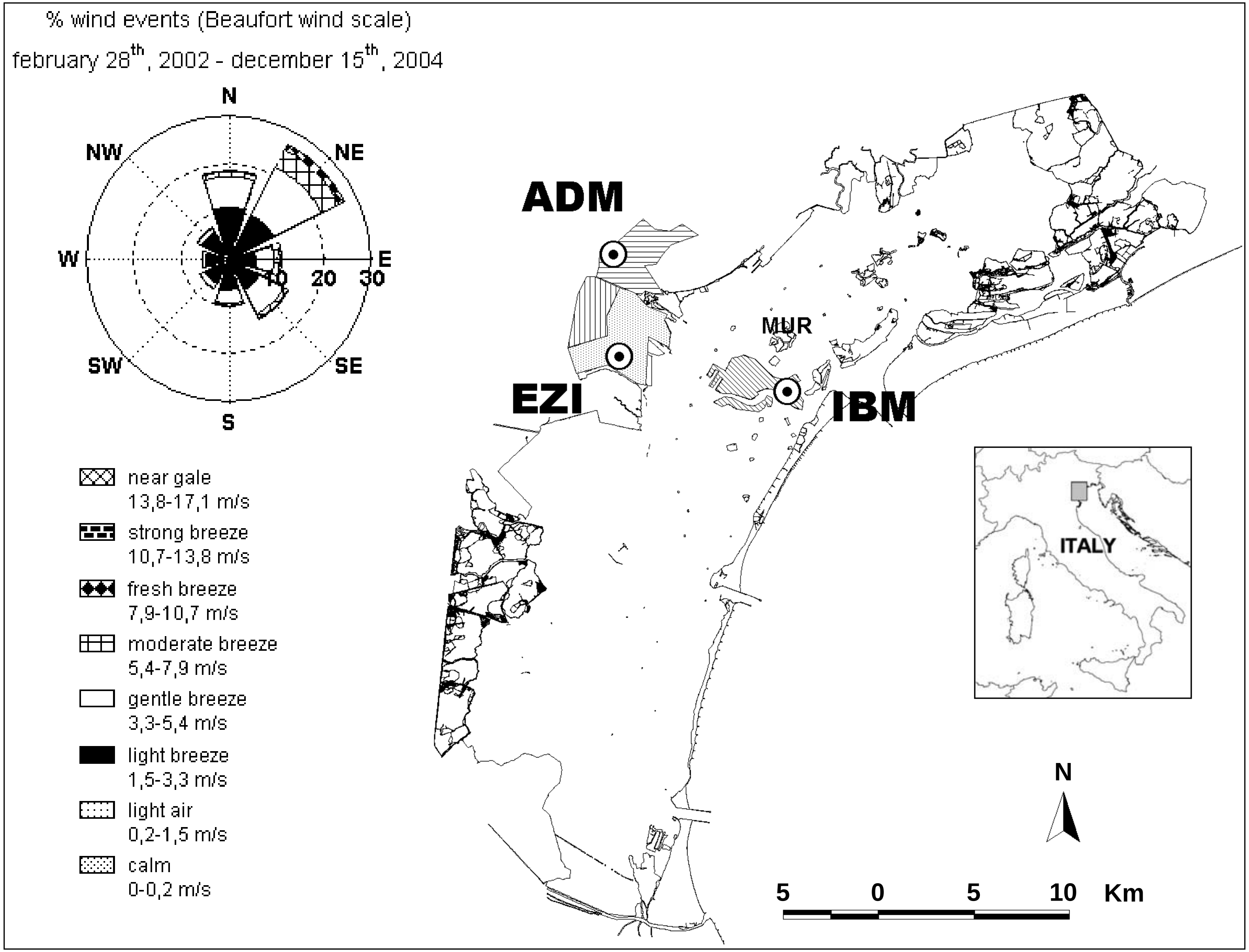
FIGURE CAPTIONS

Figure 1. Location of sampling sites. Highlighted in grey = industrial area; horizontal dotted line = city of Mestre; vertical dotted line = city of Porto Marghera; oblique dotted line = city of Venice; MUR = Murano Island.

Figure 2. Mean PAH deposition profiles observed during the study period. Error bars represent standard deviation.

Figure 3. Descriptive statistics (min, 25%, median, 75%, max) of diagnostic PAH ratios during the study period.

Figure 4. Plots of samples in the dimensional space of factors obtained from PCA applied to the congener profiles of PAHs.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NW
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near gale 13,8-17,1 m/s
strong breeze 10,7-13,8 m/s
fresh breeze 7,9-10,7 m/s
moderate breeze 5,4-7,9 m/s
gentle breeze 3,3-5,4 m/s
light breeze 1,5-3,3 m/s
light air 0,2-1,5 m/s
calm 0-0,2 m/s
ADM
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Figure 1.

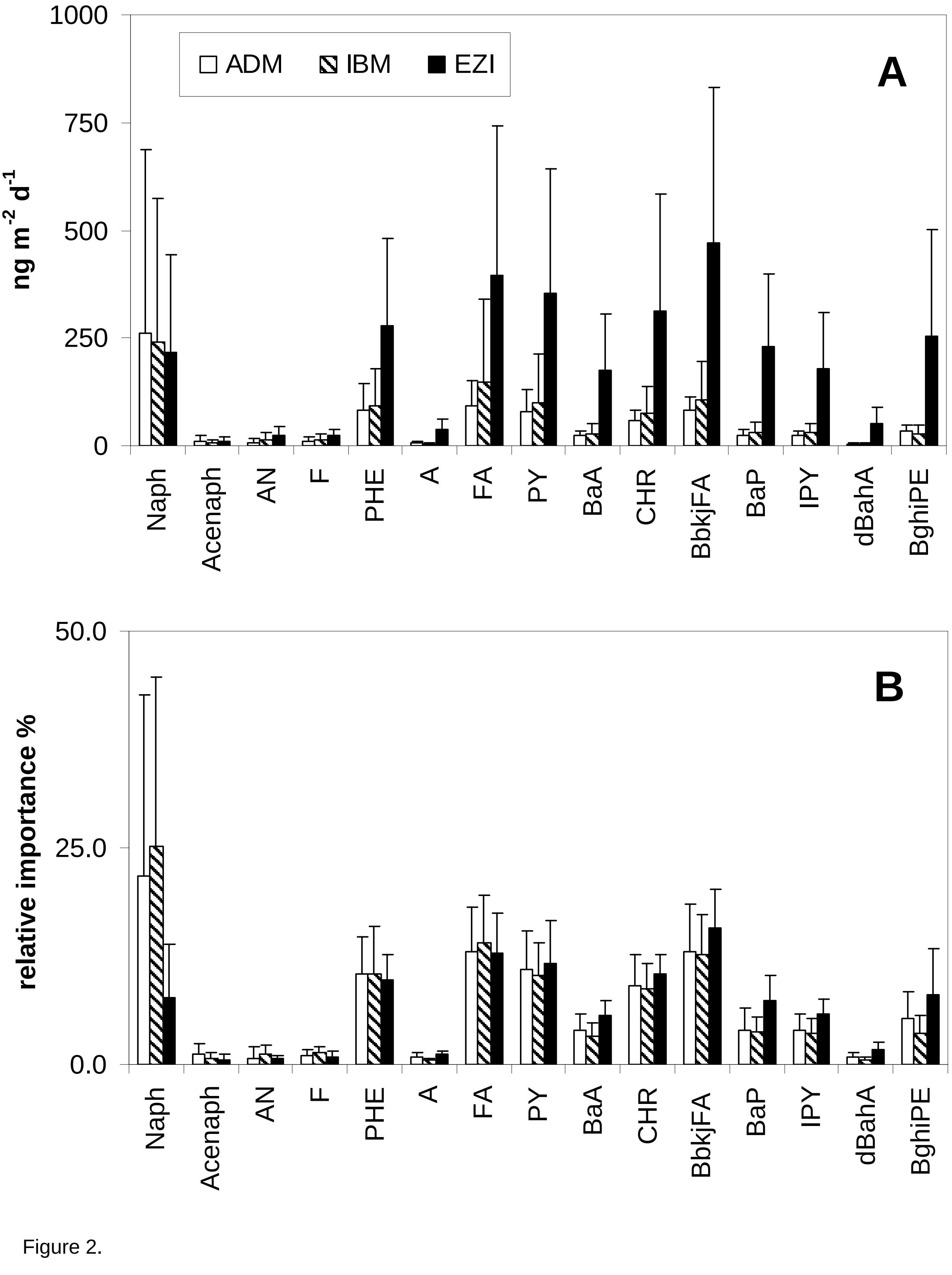
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Figure 2.

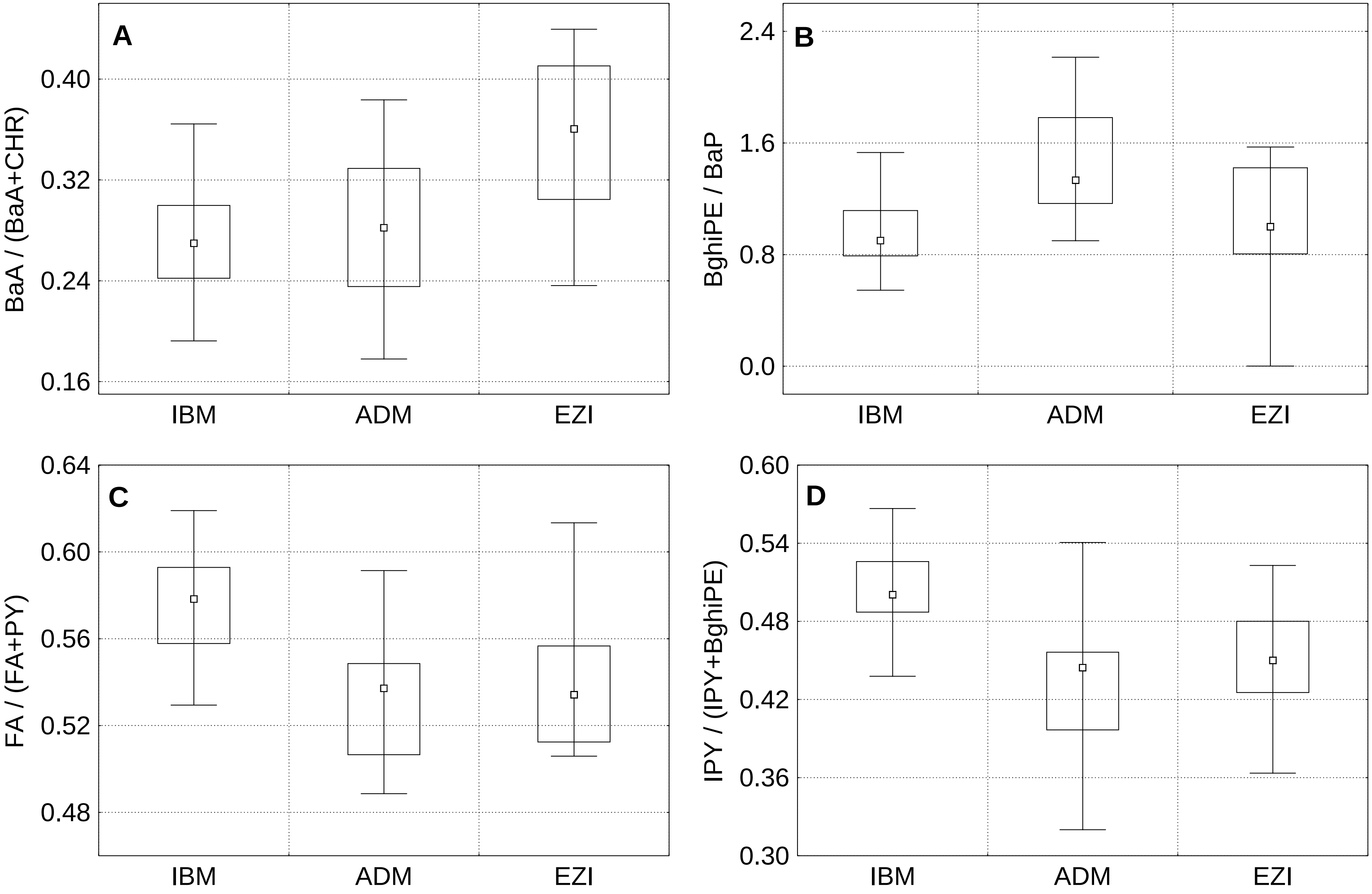
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Figure 3.

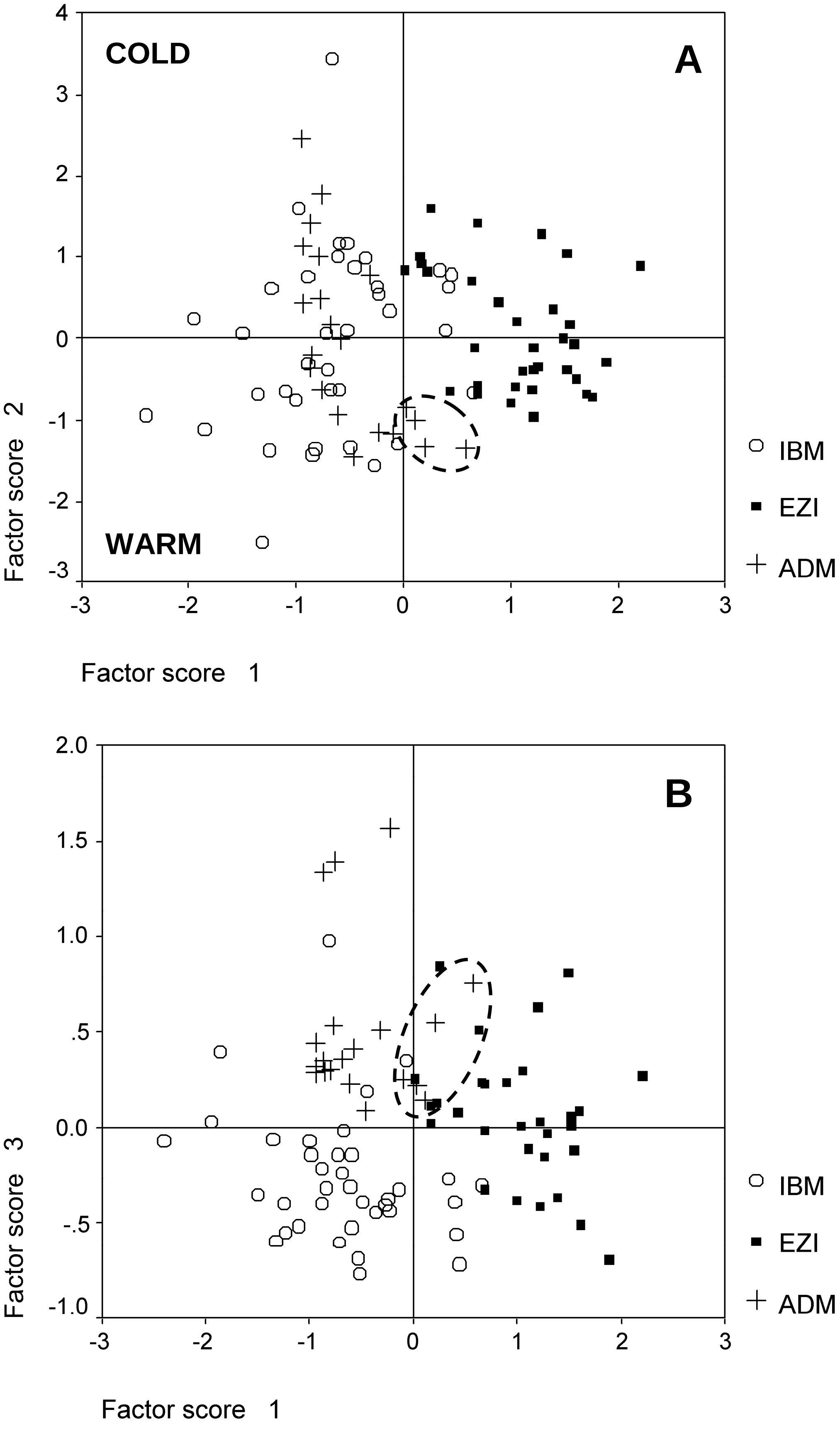
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Figure 4.

Table 1. Atmospheric bulk deposition fluxes of PAHs observed during the study period.

		ADM				**EZI**				**IBM**			
		deposition range	mean value	median value	samples	deposition range	mean value	median value	samples	deposition range	mean value	median value	samples
Naph	**ng m^{-2} d^{-1}**	17-1581	262	91	21	57-1063	215	151	26	3.6-1527	241	141	30
Acenaph	**ng m^{-2} d^{-1}**	0.7-56	10	4.0	21	0.8-44	11	7.7	26	0.3-24	5.8	2.3	30
AN	**ng m^{-2} d^{-1}**	0.8-49	5.4	2.7	21	5-120	23	19	26	0.8-77	13	6.2	30
F	**ng m^{-2} d^{-1}**	1.7-49	8.8	4.8	21	5.8-70	23	18	26	0.8-78	13	8.0	30
PHE	**ng m^{-2} d^{-1}**	25-279	82	53	21	88-1146	278	216	26	4.2-409	93	68	30
A	**ng m^{-2} d^{-1}**	2.2-11	6.2	6.8	21	14-140	37	33	26	0.1-7	3.4	3.2	30
FA	**ng m^{-2} d^{-1}**	32-291	94	76	21	108-1511	396	262	26	7-1010	146	91	30
PY	**ng m^{-2} d^{-1}**	10-263	80	68	21	99-1183	353	241	26	7-548	100	67	30
BaA	**ng m^{-2} d^{-1}**	14-46	25	23	21	50-671	175	153	26	1.7-107	27	19	30
CHR	**ng m^{-2} d^{-1}**	9-117	59	61	21	121-1533	313	253	26	6-269	75	55	30
BbkjFA	**ng m^{-2} d^{-1}**	42-147	84	78	21	147-1951	470	395	26	12-369	107	75	30
BaP	**ng m^{-2} d^{-1}**	8-52	24	20	21	47-686	229	205	26	2.5-90	30	24	30
IPY	**ng m^{-2} d^{-1}**	13-45	25	24	21	44-527	179	133	26	2.5-75	29	21	30
dBahA	**ng m^{-2} d^{-1}**	1.7-12	5.1	3.6	21	9.7-160	53	46	26	0.4-15	4.5	2.9	30
BghiPE	**ng m^{-2} d^{-1}**	2.9-66	34	28	21	0.4-932	256	173	26	2.5-70	28	21	30
ΣPAHs	**ng m^{-2} d^{-1}**	321-2301	806	635	21	1032-10575	3010	2370	26	221-3969	917	547	30
Carcinogenic[14]	**%**	6-42	26	26	21	16-48	36	37	26	7-40	24	25	30
BaP-Eq[19]	**ng m^{-2} d^{-1}**	17-72	38	30	21	76-968	328	300	26	4-122	44	34	30

Table 2. Diagnostic PAH ratios (modified from Mantis et al., 2005[13])

	BghiPE / BaP	IPY / (IPY + BghiPE)	BaA / (BaA + CHR)	FA / (FA + PY)
Diesel vehicles	1.2–2.2	0.35–0.94	0.38–0.92	0.43–0.70
Catalyst equipped cars	2.5–3.3	0.21–0.26	0.22–0.76	0.14–0.40
Non-catalyst cars	1.72	0.51	0.58	0.17
Oil burning	<0.5, 0.40	0.82	0.32	0.62
Road dust	0.86–3.5	0.36–0.57	0.38	0.42–0.54
Industrial furnaces	0.02–0.06	0.36–0.57	0.23–0.89	0.21–0.26

Table 3. Factor loadings from PCA.

	Factor 1	Factor 2	Factor 3
Naph	0.194	**0.642**	0.172
Acenaph	0.213	**0.830**	-0.014
AN	**0.795**	**0.322**	-0.103
F	**0.592**	**0.696**	-0.137
PHE	**0.758**	**0.580**	-0.086
A	**0.871**	0.190	0.106
FA	**0.776**	**0.543**	-0.094
PY	**0.813**	**0.485**	-0.007
BaA	**0.968**	0.170	0.029
CHR	**0.852**	**0.400**	-0.001
BbkjFA	**0.938**	0.252	-0.063
BaP	**0.984**	0.039	0.002
IPY	**0.952**	0.211	-0.039
dBahA	**0.969**	0.052	0.072
BghiPE	**0.790**	0.156	**0.540**
BaA/(BaA+CHR)	**0.606**	**-0.559**	0.077
BghiPE/BaP	-0.214	0.196	**0.880**
IPY/(IPY+BghiPE)	-0.134	0.166	**-0.877**
% of variance	55.96	18.31	10.78

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