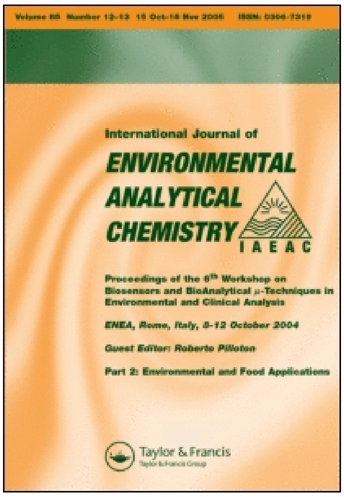

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Source apportionment of polycyclic aromatic hydrocarbons in surface sediments of Izmit Bay (Turkey)

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Source apportionment of polycyclic aromatic hydrocarbons in surface sediments of Izmit Bay (Turkey)

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Thirty-five surface sediment samples were collected from the northeastern coast of the Izmit Bay to apportion the sources of polycyclic aromatic hydrocarbons (PAH) entering the Bay. Samples were collected in February and June, 2002 and they were analyzed for 16 PAH compounds using HPLC-UV. Total PAHs ranged from 1.1 to 68.4 $\mu g\, g^{-1}$-dry wt. Both the factor analysis and the factor analysis-absolute factor score multiple linear regression analysis were applied to the results of 11 PAH compounds which were observed in more than 80% of the samples. From the factor analysis, two factors explaining 91.3% of the total variance were identified. The first factor was petrogenic and explained 76% of the variance. Except for the Anthracene, 57 to 85% of the lower molecular mass PAH compounds (from Fluorene to Chrysene) were contributed by this factor.

Keywords: Polycyclic aromatic hydrocarbons; Source apportionment; Multivariate methods; Factor analysis; Factor analysis-absolute factor score multiple linear regression

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of compounds of great environmental concern due to their carcinogenic properties and their widespread occurrence [1–3]. Once PAHs are formed, they are known to enter the marine environment through industrial discharges, urban run-off, oil spills, combustion processes, discharges of fossil fuels, automobile emissions and atmospheric depositions [1, 4–6]. Because of their mutagenic and carcinogenic properties, the US EPA has incorporated 16 PAH compounds in the list of pollutants to be monitored in the environment [7].

The study area, the Izmit Bay, is a part of the Marmara Sea and it is the most polluted site in the region due to heavy industrialization around the bay. In addition to the industrial and domestic pollution that has been affecting the region for more than

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25 years, a strong earthquake hit the region on 17 August 1999 caused both a fire in refinery and petroleum leakages from the storage tanks to the Bay. The refinery fire and other industrial leakages caused an increase in the total PAH levels in the water column, sediments and mussels [8]. Polycyclic aromatic hydrocarbons deposited into the sediments were disturbed due to the earthquake and increased the concentrations of PAHs both in water column and surface sediments. However, as it was mentioned in a previous study [8], the pollution level in the Bay has almost reached to the pre-earthquake levels.

In this study, the sixteen US EPA priority PAH compounds were studied extensively throughout the most widely polluted northeastern coast of the Izmit Bay. The study area is the region, where both the petrochemical and refinery facilities occur and discharge their pretreated wastewaters to the shore (8). Atmospheric wet, dry and bulk deposition samples, riverine and wastewater samples, surface seawater and surface sediment samples, mussel and fish samples were collected between September 2001 and August 2003. In this article, the PAH source types and the contributions of these sources to the surface sediments of the Bay will be discussed.

2. Experimental

2.1 *Sampling*

Surface sediment samples were collected in February and June 2002 at 35 stations (figure 1) throughout the coastal region, where petrochemical and fertilizer industries

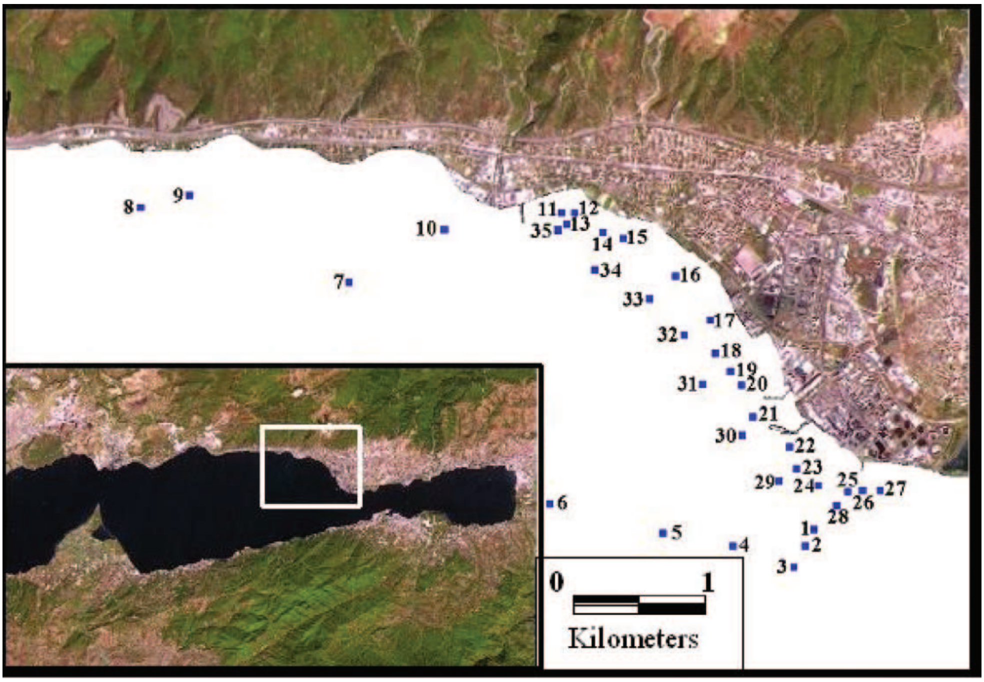

Figure 1. Sampling site (the numbered points are the sampling stations).

and refinery are situated. Samples were collected by means of a van Veen grab sampler and the samples were placed onto an aluminum folio. Depending on the sample amount, 3 to 5 cm of sample from the surface to the bottom were removed from the bulk material with a PTFE spatula, packaged in aluminum folio and immediately placed in labeled polyethylene bags, refrigerated, and returned to the laboratory where they were stored at −20°C until time of analysis.

2.2 *Extraction and analysis*

Ten grams of homogenized wet sediment samples were weighed into 100 mL centrifuge tubes and 2 mL of a 0.8 mg L^{-1} surrogate standard, 2-Fluorobiphenyl (Cerilliant), and 20 mL of tetrahydrofuran (Merck) were added to each centrifuge tube. The tubes were firmly closed and shaken vigorously for a short time and placed in an ultrasonic bath for 2 h. Then the samples were centrifuged at 2000 rpm for 30 min. Five milliliters of supernatant from each tube was taken and evaporated to dryness under a gentle nitrogen stream. The residue was dissolved in 1 mL of *n*-hexane (Merck). A fresh chromatographic column consisting of 2 g of silica (SiO_2, PromoChem) and 1 g of anhydrous sodium sulfate (Na_2SO_4, PromoChem) was washed first with 15 mL of dichloromethane (BDH) and then with 15 mL of *n*-hexane. Samples were added to this column and aliphatics were removed by elution in 4 mL of *n*-hexane. PAHs were subsequently collected by elution in 6 mL of *n*-hexane:dichloromethane (1:1). The eluate was concentrated to 0.5 mL via controlled nitrogen bubbling. 50 µL of dimethyl formamide (Merck) was added and nitrogen bubbling was continued until all the *n*-hexane was removed. Then 950 µL of acetonitrile (BDH) was added to bring the final volume to 1.0 mL [9]. The resulting sample solution was analyzed for 16 PAH compounds by using an Agilent 1100 Series HPLC with Variable Wavelength UV Detector. The HPLC column was VYDAC Reverse Phase C-18, 300 Å, 4.6 mm ID × 250 mm (5 µm). The wavelength and oven temperature was 270 nm and 40°C, respectively. Mobile phase flow rate was kept at 1.5 mL/min and 20 µL of samples were injected. Mobile phase was 40:60 (deionized water:acetonitrile) (in volume percent) from 0.0 to 2.0 min and changed to 10:90 volume percentages of water:acetonitrile until the end of 20th minute. For the post time interval of 3 min the mobile phase was 100% acetonitrile.

Naphthalene was not observed in any of the sediment samples may be due to its short life time in sediments or due to its high volatility, it may be lost during sample handling and preparation for the analysis, especially during concentration operation through nitrogen bubbling.

To determine the water content of the sediment samples, another 10 g of wet sample was weighed and dried at 103°C until constant weight was reached. From the weight percent of water, the dry weights of analyzed samples were calculated.

For the calibration of the HPLC-VWD system, Cerilliant ERS-011 Stock PAH mixture standard was used. To overcome the problems that may be caused due to matrix differences between the samples and the calibration standards, a composite sample was prepared by combining about 200 µL of aliquots from each sample. The calibration standards were prepared in this composite sample. After analyzing each standard and the composite sample, the peak areas corresponding to the composite sample were subtracted from the peak areas of calibration standards and finally the calibration curves for each compound were prepared. For the determination of surrogate recovery and the accuracy of the method, 2-fluorobiphenyl and NIST SRM 1647d were used, respectively. The surrogate recovery for the whole data set was 67.3% (±8.10% for one standard deviation). In order to calculate the recoveries of PAH compounds, NIST SRM 1647d was exposed to sample preparation procedure and handled as samples. Percent recoveries of the PAH compounds determined by this method are given in table 1, the method precision and detection limits for the PAH compounds are given in table 2. For the calculation of method detection limits US EPA, Code of Federal Regulations, Chapter 40, part 136, Appendix B, rev. 1.11, (1986) was used.

Table 1. Percent recoveries of the PAH compounds (NIST-SRM-1647d).

PAH Compound	Certified ± STD* ($mg\,L^{-1}$)	Measured ± STD ($mg\,L^{-1}$)	Recovery ± STD (%)
Acenaphthylene, AcNP	15.49 ± 0.29	17.33 ± 1.10	112.0 ± 16.8
Acenaphthene, AcN	20.77 ± 0.48	22.31 ± 1.60	107.4 ± 6.8
Fluorene, Fl	4.75 ± 0.06	5.13 ± 0.37	108.1 ± 16.2
Phenanthrane, PhA	3.42 ± 0.06	3.10 ± 0.19	90.6 ± 8.8
Anthracene, AN	0.79 ± 0.02	0.73 ± 0.03	92.4 ± 14.5
Fluoranthene, FlA	7.64 ± 0.10	7.47 ± 0.40	97.8 ± 12.2
Pyrene, Py	8.47 ± 0.11	7.53 ± 0.44	88.9 ± 3.5
Benz(a)anthracene, BaA	4.09 ± 0.04	3.60 ± 0.20	88.0 ± 4.8
Chrysene, Chy	3.67 ± 0.04	3.21 ± 0.19	87.5 ± 5.0
Benzo(b)fluoranthene, BbFlA	4.17 ± 0.05	4.21 ± 0.23	101.0 ± 4.5
Benzo(k)fluoranthene, BkFlA	4.72 ± 0.07	4.59 ± 0.24	97.2 ± 4.3
Benzo(a)pyrene, BaP	4.91 ± 0.08	4.60 ± 0.26	93.7 ± 2.5
Dibenz(a,h)anthracene, dBahA	3.54 ± 0.22	3.31 ± 0.18	93.5 ± 2.9
Benzo(g,h,i)perylene, BghiP	3.68 ± 0.13	3.18 ± 0.18	86.4 ± 6.2
Indeno(1,2,3-*c,d*)pyrene, IP	4.28 ± 0.09	3.90 ± 0.22	91.1 ± 4.5

*STD: Standard deviation.

Table 2. Precision (RSD) and method detection limits (MDL).

PAH Compound	RSD (%)	MDL ($ng\,g^{-1}$ wet wt)
Acenaphthylene, AcNP	3.02	17.4
Acenaphthene, AcN	6.39	21.4
Fluorene, Fl	0.81	10.0
Phenanthrane, PhA	1.37	3.13
Anthracene, AN	2.20	8.42
Fluoranthene, FlA	1.45	8.47
Pyrene, Py	1.74	8.10
Benz(a)anthracene, BaA	3.70	4.95
Chrysene, Chy	2.58	2.30
Benzo(b)fluoranthene, BbFlA	0.36	1.00
Benzo(k)fluoranthene, BkFlA	7.72	0.91
Benzo(a)pyrene, BaP	3.23	2.41
Dibenz(a,h)anthracene, dBahA	1.38	0.54
Benzo(g,h,i)perylene, BghiP	2.90	1.36
Indeno(1,2,3-*c,d*)pyrene, IP	0.50	0.23
2-Fluorobiphenyl, surrogate standard	0.67	3.15

3. Results and discussions

3.1 *Statistical characteristics of data*

The number of observations (*N*), the arithmetic and geometric means, medians, standard deviations, minimum, maximum and ranges of the measured concentrations of PAH compounds are presented in table 3. Anthracene, FlA, Py, BaA, BbFlA and BaP were observed in almost all of the samples while PhA and Chy were observed in 34 of 35 samples.

Except for BbFlA, for almost all of the compounds, the arithmetic mean is greater than the corresponding median and geometric mean, which shows deviation from normality. When a goodness of fit test was applied to the data set, it was observed that, other than BbFlA, all of the compounds showed a log-normal distribution at a 90% or higher confidence level. Benzo(b)fluoranthene was observed in all of the samples at very high concentrations that showed little variance from sample to sample. Goodness of fit test showed that BbFlA concentration*s* were normally distributed in the sediment samples.

The samples represented as 16, 17, 18, 19, 20, 27 and 32 (figure 1) contained the highest PAH concentrations due to their closeness to the ports of petrochemical and fertilizer facilities and refinery. This may be because of leakages during loading and unloading petroleum products and from ships themselves. Except the samples given above, the concentrations of PAH compounds were almost at the same order of magnitude. As explained in the experimental section, sediment samples were collected in two different cruises, one in February and another in June 2002. The samples collected at the same region in February and June did not show a significant difference when compared with the repeatability of the analysis method used (table 2). The differences between the measured PAH compounds in the February and June samples changed from ±0.5% to ±8.8% on the average for the samples, namely, sample numbers 1, 2 (February) and 28 (June); samples 11, 12 (February) and 35 (June).

Table 3. Statistical parameters for the measured PAH compounds ($\mu g\,g^{-1}$ dry weight).

PAH compounds	*N**	Arithmetic mean	Median	Geometric mean	Standard deviation	Minimum	Maximum	Range
AcNP	8	0.34	0.11	0.068	0.53	0.0022	1.5	1.5
AcN	17	0.17	0.012	0.023	0.36	0.00090	1.3	1.3
Fl	28	0.26	0.012	0.024	0.67	0.0023	3.2	3.2
PhA	34	1.8	0.26	0.38	4.8	0.062	26.6	26.5
AN	35	1.9	0.33	0.48	3.8	0.014	15.6	15.6
FlA	35	1.4	0.31	0.39	3.3	0.0081	18.2	18.3
Py	35	0.71	0.20	0.26	1.4	0.0039	6.3	6.3
BaA	35	0.40	0.12	0.15	0.73	0.0028	3.2	3.2
Chy	34	0.19	0.054	0.072	0.37	0.0083	1.9	1.9
BbFlA	35	2.6	2.4	2.24	1.28	0.37	5.6	5.3
BkFlA	32	0.10	0.072	0.056	0.13	0.0070	0.71	0.71
BaP	35	0.35	0.19	0.21	0.45	0.027	2.1	2.2
dBahA	27	0.054	0.027	0.028	0.077	0.0029	0.38	0.37
BghiP	19	0.061	0.031	0.035	0.061	0.0025	0.24	0.24
IP	30	0.079	0.040	0.045	0.086	0.0020	0.36	0.36
$\sum$PAH^{+}	35	9.83	4.10	5.23	15.0	1.10	68.4	67.3

**N*: Number of observation.

$^{+}$ $\sum$PAH: Sum of 15 PAH compounds given in table in $\mu g\,g^{-1}$ dry wt.

In order to show patterns of PAH compounds in the sampling area distribution maps of detected PAH compounds were plotted. As an example distribution maps of AcN and BaP were presented as figure 2. Concentrations of PAH compounds were defined as z-axis and "the Inverse Distance Weighing" (IDW) algorithm was used as the interpolation method. The IDW is a type of moving average interpolator usually applied to highly variable data. For certain data types it is possible to return to the collection site and to record a new value that is statistically different from the original reading, but within the general trend of the area. Examples of this type of data include soil chemistry results, bedrock assays, and environmental monitoring data. For this type of data it is not desirable to honour local high/low values but rather to look at a "moving average" of nearby data points and estimate the local trends. The IDW technique calculates a value for each grid node by examining surrounding data points that lie within a user

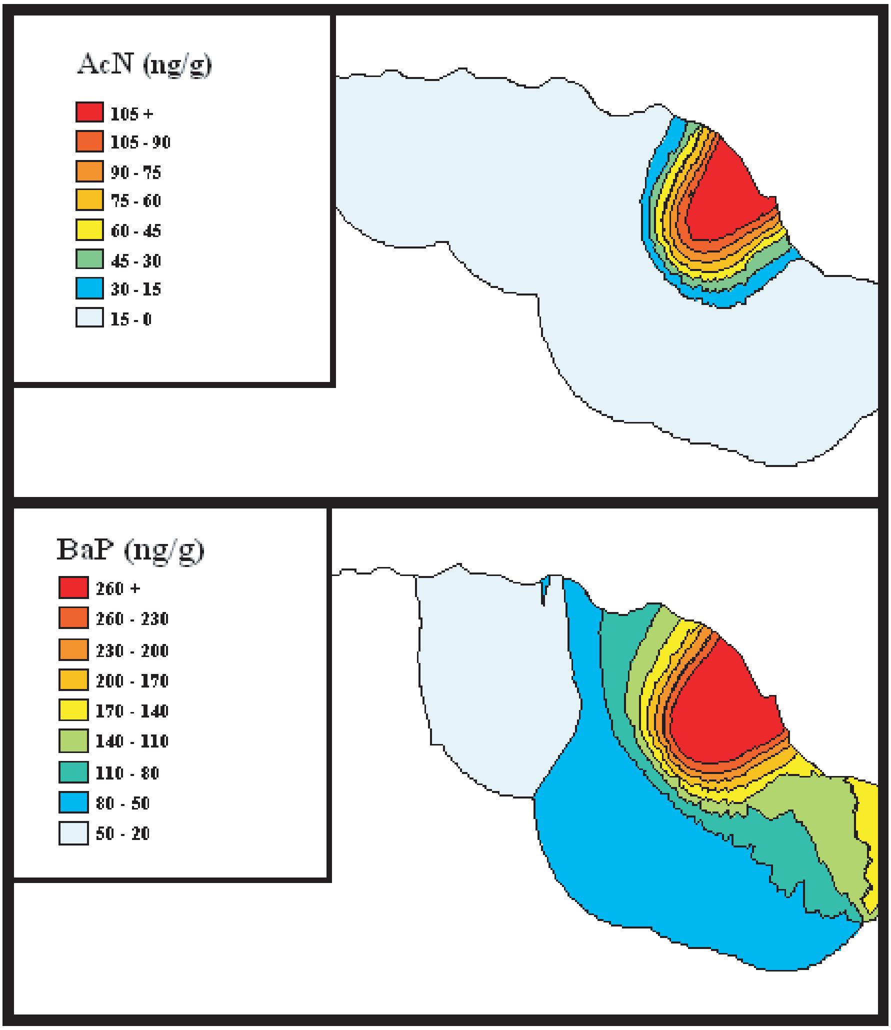

Figure 2. Distribution maps of AcN and BaP as an example of other PAH compounds.

defined search radius. Some or all of the data points can be used in the interpolation process. The node value is calculated by averaging the weighted sum of all the points. Data points lying progressively further from the node influence the computed value far less than those lying closer to the node (Mapinfo Professional, version 5.5, User Manual, 1999). The compounds showing the similar pattern with AcN are BaA, Chy, FlA, PhA, Py and Fl. Compounds, namely, IP, BghiP, BkFlA, AN and dBahA show similar pattern like that of BaP given in figure 2. The distribution patterns are physically similar, however, the concentration ranges are different and compounds have their highest concentration ranges at the wastewater discharging points where the ports of petrochemical and fertilizer facility and refinery also take place.

3.2 *Sources of PAHs*

In order to get knowledge about the sources of PAH compounds, Pearson's correlation matrix was applied to the data set and the correlations lower than 0.30 were considered to be insignificant. Correlation coefficients greater than 0.6 and *p*-values smaller than 0.05 were considered as significantly correlated. From the test it was observed that AcN shows high correlations with AcNP and AN; Fluorene is highly correlated with PhA, FlA, Py, BaA and Chy (table 4). Other highly correlated compounds are; PhA with FlA, Py, BaA and Chy; Py with BaA, Chy, BaP and IP; FlA with Py, BaA and Chy; BaA with Chy, BaP and IP and finally BaP with IP. The Pearson's Correlation Matrix is given in table 4. Pearson's correlation coefficient is a statistic that gives the degree of linear relationship between two variables measured. The degree of correlation between the PAH compounds is often used to indicate the origin of the species. Statistically significant relationships between the compounds were observed when the Pearson's correlation matrix was applied to the variables at a 95% confidence interval.

When the sources of PAH compounds are investigated, environmental studies can distinguish only between combustion and petrogenic origins. Due to the overlap of the source signatures it is difficult to differentiate between the finer sources such as combustion of coal, wood and oil [10]. Factor analysis was used in order to enhance

Table 4. Pearson's correlation matrix for the PAH compounds.

	AcNP	AcN	Fl	PhA	AN	FlA	Py	BaA	Chy	BbFlA	BkFlA	BaP	DBahA	BghiP	IP
AcNP	1.00														
AcN	0.97	1.00													
Fl		0.44	1.00												
PhA		0.33	0.99	1.00											
AN	0.72	0.85	0.58	0.51	1.00										
FlA		0.37	0.98	0.99	0.53	1.00									
Py	0.27	0.55	0.96	0.93	0.75	0.92	1.00								
BaA	0.37	0.62	0.95	0.92	0.79	0.91	0.99	1.00							
Chy		0.42	0.98	0.98	0.59	0.98	0.95	0.95	1.00						
BbFlA		0.45			0.59	0.25	0.40	0.44	0.33	1.00					
BkFlA	0.34	0.60	0.34	0.29	0.71	0.27	0.58	0.60	0.35	0.55	1.00				
BaP	0.44	0.70	0.76	0.72	0.89	0.70	0.91	0.93	0.79	0.61	0.78	1.00			
dBahA			0.31	0.32		0.31	0.31	0.31	0.43	0.41		0.33	100		
BghiP		0.48	0.40	0.42	0.38	0.44	0.52	0.54	0.56	0.55	0.32	0.60	0.83	1.00	
IP	0.42	0.64	0.78	0.73	0.79	0.71	0.89	0.90	0.79	0.57	0.75	0.92	0.32	0.59	1.00

Table 5. Results of factor analysis and probable source types.

Compound	Factor-1	Factor-2	Communality
Fl	**0.97***	0.24	0.99
PhA	**0.98**	0.17	0.99
AN	**0.41**	**0.81**	0.83
FlA	**0.98**	0.17	0.98
Py	**0.87**	**0.49**	0.99
BaA	**0.85**	**0.53**	0.99
Chy	**0.95**	0.28	0.98
BbFlA	0.10	**0.78**	0.61
BkFlA	0.16	**0.88**	0.79
BaP	**0.60**	**0.78**	0.97
IP	**0.64**	**0.70**	0.90
% Variance explained	**76.0**	**15.3**	
Source type	**Petrogenic**	**Pyrolytic/Combustion**	

*Significant loadings in bold.

the degree of source discrimination. PAH compounds observed in 80% or more of the samples were included in the analysis. Therefore, 11 PAH compounds were included in the factor analysis and the missing values were treated with lower quartiles. Samples having factor scores greater than 7.0 were removed from the data set and the factor analysis was re-run and 2 factors having eigen values greater than one and explaining 91.3% of the total variance were obtained (table 5). Except for BbFlA, communalities of all the compounds were around or greater than 0.80.

In this study, the sampling location for the sediments was between the petrochemical facility and the refinery; therefore, there were two industrial discharges, one from refinery and the second from the petrochemical and fertilizer facilities discharging their wastewaters to the bay at the same point. As mentioned above, we also collected land-based sources like riverine and domestic discharges; however, we could not observe any domestic sign in the factor analysis because of the higher contributions of petrogenic and combustion sources like the refinery, petrochemical facility and the atmospheric inputs, which overlapped the domestic signature.

The first factor explained 76% of the total variance and when those compounds with high loadings in this factor were compared with the marker compounds given in literature [11–14] it was observed that PAH compounds, mainly originating from the unburned petroleum were highly loaded in this factor which was subsequently termed *petrogenic*. The compounds having high loadings in the first factor were Fl, PhA, FlA, Chy, Py and BaA while compounds having moderate loadings were BaP, IP and AN, all of which generally originate from oil spills and the vaporization of crude oils.

The second factor, explaining only 15.3% of the variance, mainly contained those PAH compounds produced by combustion and/or pyrolytic processes [11, 13–17]. Almost all of the listed marker compounds were observed in this second factor, which was therefore termed as the *pyrolytic/combustion* factor.

The factor analysis result supported our hypothesis in which we were expecting that the petrogenic PAHs were dominant at the sampling site mostly due to the leakages and fire at the refinery during the quake and loading/unloading activities at the ports. Though factor analysis can supply qualitative information about the source types; it provides little quantitative information. Therefore, to quantify information about

Table 6. Mean contributions (%) of source types on the concentrations of the PAHs in surface sediments (% ± Standard deviation).

Compound	Measured/Estimated	% Explained	Factor-1 (Petrogenic)	Factor-2 (Pyrolysis/Combustion)
Fl	1.04 ± 0.39	99.5	80.0 ± 35.0	20.0 ± 12.0
PhA	1.04 ± 0.68	99.1	85.0 ± 42.5	15.0 ± 7.50
AN	1.10 ± 0.51	82.9	27.5 ± 17.8	72.6 ± 17.7
FlA	1.09 ± 0.49	98.0	85.0 ± 42.5	15.0 ± 7.50
Py	1.02 ± 0.40	99.0	61.3 ± 27.8	39.3 ± 27.6
BaA	1.03 ± 0.37	99.5	56.4 ± 21.4	44.6 ± 17.4
Chy	1.14 ± 0.33	98.2	57.4 ± 50.2	42.7 ± 50.3
BbFlA	1.02 ± 0.26	61.2	10.8 ± 9.20	89.5 ± 9.20
BkFlA	1.04 ± 0.43	79.5	22.2 ± 15.6	77.8 ± 15.3
BaP	0.95 ± 0.27	97.2	27.0 ± 23.3	73.5 ± 23.3
IP	1.02 ± 0.26	90.0	36.4 ± 19.3	64.4 ± 20.0

the contributions of source types determined by factor analysis, factor analysis-absolute factor score multiple linear regressions were used [18, 19]. In the latter approach, the calculated absolute factor scores are taken as variables and plotted against the measured concentrations. The coefficients determined from this multiple linear regression are then used to compute the contribution of each source [19].

A zero sample was generated and added to the data set and the factor analysis was re-run. After computing the regression coefficients corresponding to source types the percent contributions of the sources were calculated. The factor analysis-absolute factor score multiple linear regression results are presented in table 6.

When the contributions of source types are examined, it can be observed that about 60% to 80% of 3- and 4-ringed PAH compounds, except for AN, come from petrogenic sources. Among 5-ringed PAH compounds, 27% of BaP, 22% of BkFlA and 11% of BbFlA are contributed by the petrogenic factor. Being the only 6-ringed PAH, 36% of the IP comes from the petrogenic source.

The *pyrolytic/combustion* factor contributed 73% of the AN in the surface sediment samples. High molecular weight PAHs (5- and 6-ringed PAH compounds) were provided mainly by the second factor. The pyrolysis/combustion source contributed 89.5% of BbFlA, 78% of BkFlA, 74% of BaP and 64% of IP in sediment samples. Again 45% of BaA, 43% of Chy, 39% of BaP and 20% of Fl were also contributed by this second factor.

4. Conclusions

The present work formed part of a detailed investigation of the distribution of 16 PAH compounds in the Izmit Bay in 2002. Factor analysis and factor analysis-absolute factor score multiple linear regressions showed that the investigated part of the bay was contaminated mainly by unburned fossil fuels due to the leakages during the loading and unloading of crude oil and other related products. Another important source of the petrogenic PAHs was thought to be the 1999 earthquake, which caused significant leakages from the refinery. This surmise was also supported by the factor analysis, in which the petrogenic factor explained more than 75% of the total variance while the second factor, pyrolytic/combustion factor, explained only about 15% of the total variance.

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