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# Polycyclic aromatic hydrocarbons sources fingerprints in the environmental samples of Anzali- South of Caspian Sea

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## Abstract

The major emission sources of polycyclic aromatic hydrocarbons (PAHs) in Anzali city, apportionment of these sources and transfer of PAHs through street dust and runoff to rivers and finally the Caspian Sea were studied. PAHs in environmental samples including street dust, runoff and river sediment samples as well as in major sources of hydrocarbons in urban area including vehicles exhaust, gasoline and diesel fuels, engine oils of automobiles and boats, asphalt and tire debris were extracted by Soxhlet and liquid–liquid extraction in solid and liquid phase and were analyzed by GC–MS. Significance of each source in PAHs emission in the area was identified by chemical fingerprinting. According to the spatial distribution of PAHs in receptor samples stations of street dust and runoff located in the center of the city with high traffic of vehicles had higher concentrations of PAHs than stations in the out bonds of the city. In the river sediment samples, the stations located in the port area had the highest concentrations of PAHs. Results of chemical fingerprinting showed that especially in street dust and runoff samples, the isometric patterns of PAHs were rather similar to those in the proposed major sources, showing that they may have been originated from them, especially from asphalt and tire. On the contrary, river sediment samples were confirmed to receive inputs from other unknown independent sources.

Keywords: PAHs, source apportionment, isometric ratios, fingerprinting, petrogenic, pyrogenic

## Introduction

The strong development of urbanization and industrialization of the large cities has produced an increased entrance of the pollutants to the aquatic ecosystems such as the Caspian Sea (Tolosa et al., 2004). About 122,000 tons of petroleum materials are annually entered into the Caspian Sea in various ways, with 75,000 tons of which entering via the rivers (Shirneshan et al., 2016a). Large amounts of different pollutants that generally contain persistent organic compounds enter the rivers through runoffs, channels, and streams and eventually accumulate in the bottom sediments of the sea (Azimi et al., 2018). These materials greatly threaten marine ecosystems (Barakat et al., 2011; Keshavarzifard and Zakaria, 2015).

Considering the fact that currently oil and gas are not being extracted in the southern basin of Caspian Sea (in the Iranian coasts of the Caspian Sea), the entry of petroleum compounds from the coastal cities should be the main source of PAHs in the southern Caspian Sea (Shirneshan et al., 2016a). Release of petroleum compounds from erosion of asphalt in the streets, roads and highways, petroleum and oil leakage from vehicles, consumption of gasoline and diesel fuel, traffic of commercial, fishing, and passenger ships and boats, car tire erosion, coal mines and the use of other petroleum products in the cities are among the most important sources of PAHs emission in the coastal cities of the southern Caspian Sea (Eganhouse et al., 1981; Yunker et al., 2002). These compounds accumulate in the street and road dust and enter the rivers through washing by the runoffs from rainfalls and ultimately are burying in the sea. PAHs belong to the group of persistent organic pollutants (POPs) that are resistant to degradation, can remain in environment for a long period and have the potential to cause adverse environmental effects (Tolosa et al., 2005). Their release to the environment is a major concern because some compounds have been identified as carcinogenic, mutagenic and teratogenic (ECSC, 2002). The list of 16 PAHs that are recognized as carcinogenic PAHs by environmental protection agency (EPA) are shown in Table S1 in supplementary section.

PAHs in water bodies tend to be associated to the suspended particles in the water column due to their low solubility and accumulate in the sediments. Sediments frequently contain higher concentrations of PAHs than those found in the water column. So, lipophilic PAH levels in sediments are generally in several orders of higher magnitude compared to their water phase concentrations (Harris et al., 2011; Li et al., 2012). PAHs are moderately persistent in the environment and can be bio-accumulated in fish and shellfish, especially in mussels, and may lead to serious human health hazards (Zeng and Vista., 1997; Mehdinia et al., 2015; Keshavarzifard et al., 2017).

According to the various studies conducted in different parts of the world regarding source apportionment of petroleum hydrocarbons, the major sources for release of these compounds in the urban areas are mainly related to vehicles and traffic, with different percentages and contributions (Khalili et al., 1995; Yunker et al., 2002; Brown and Peake, 2006; Perrone et al., 2014; Aydin et al., 2014; Teixeira et al., 2015).

Many studies have been conducted in recent years for source identification of PAHs in the southern coasts of Caspian Sea (Tolosa et al., 2004; Nemirovskaya et al., 2006; Nemirovskaya and Brekhovskikh ., 2008; Nemati Varnosfaderany et al., 2014; Nemati Varnosfaderany et al., 2015; Shirneshan et al, 2016a,b; Azimi et al., 2017). Results of most of these studies denote the petrogenic origin of PAHs in the southern coasts of the Caspian Sea. However, no study has been carried out yet for the identification of the major sources as well as for the estimation of their contribution to the release of PAH compounds from the urban areas and through the runoffs and rivers to the southern coasts of the Caspian Sea. This research is still necessary. Therefore, the current work was conducted for completing the studies conducted in the region in order to obtain information about major sources of hydrocarbon emissions in urban environments and to investigate the transfer of these PAH compounds through runoffs and rivers to the southern coasts of Caspian Sea.

In this study, the PAH profiles in the major sources of them in the Anzali region, including the exhaust soot of vehicles, diesel, gasoline, engine oil, asphalt and tire were examined, and by

comparison with receptor samples including street dust, runoff suspended sediment, runoff 80
soluble water and river sediment samples using isometric characteristic ratios, the significance of 81
each of these sources in the emission of PAHs in the region, and the process of transferring these 82
compounds from street dust to the sea has been investigated. 83

## Material and Methods 84

### Sample collection procedures 85

This study was performed in Anzali city, one of the densest coastal cities of Iran in the southwest 86
of the Caspian Sea. Figure 1 shows the location of sampling points. Four types of environmental 87
receptor samples were sampled and analyzed: street dust, runoff suspended sediment, runoff 88
soluble water, and river sediment samples. 89

Figure 1 90

Street dust receptor samples were collected from the surface of all bridges on the urban rivers in 91
Anzali city (8 bridges), and from the surface of the four streets with more traffic using a hairy 92
sweep within a 5 m * 5 m frame. The sampling sites are shown in Figure 1 (red symbols). 93
Sampling was performed a day of sunny weather in September 2016, which was preceded by 94
more than one week of sunny weather. Collected street dust was sieved using a 2.0 mm stainless 95
sieve to remove large materials and to homogenize the sample. Runoff receptor samples were 96
collected from the surface of 7 bridges on the urban rivers of Anzali city and from the surface of 97
the three streets with more traffic (Figure 1, green and yellow symbols) using a water sampler. 98
Sampling was performed in October 2016 during the rain of more than 10 mm after some days of 99
sunny weather. Sampling procedures of street dust and runoff receptor samples were repeated 100
three times per station and mixed together. Runoff samples were filtered by a vacuum pump 101
which separates suspended solids from the water–soluble fraction. River sediment receptor 102
samples were collected from all urban rivers of Anzali city and from the harbor (24 stations) 103
utilizing Van Veen grab (50 cm×50 cm) in 3 replicates for every station (Fig. 1, blue symbols). 104
Only the top 3 cm surface sediments were sub–sampled, placed in aluminum boxes, and then 105
stored in a freezer at –20 °C until analyzed. 106

Six types of specific known pollution source samples were also sampled: tires, street pavement 107
asphalt, gasoline, diesel, engine lubricant oil, and exhaust soot. Six types of the most commonly 108
used tires were selected for analyses (Table S2 in supplementary section). Tire rubber was sliced 109
from the tread surface and cut fine to 2 mm or smaller pieces. Three types of new and old asphalt 110
pavement were crushed finely to 2 mm or smaller pieces for extraction. Three types of 111
automobile fuel in Anzali city including gasoline, super gasoline and diesel were sampled. 112
Different types of the most commonly used engine lubricant oils were selected for analyses. In 113
addition, the engine oil of the boats was sampled (Table S2 in supplementary section). All types 114
of exhaust soot from gasoline, dieseline and gaseous cars including riding cars, minivans, buses 115
and trucks also motorcycles were sampled. In addition, the exhaust soot of the boats was sampled 116
(Table S2 in supplementary section). 117

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River sediment, runoff filtered sediment, and street dust samples were dried in the freeze dryer 120
for 72 h under high vacuum (1.030 mbar and –50 °C). Tire and asphalt samples washed with 121
distilled water for removing dust particles. All solid phase samples including sediment, street 122
dust, runoff filtered sediment, exhaust soot, tire and asphalt samples were extracted by the 123
Soxhlet method. The Extraction and fractionation procedure is based on the method described in 124
Zakaria et al. (2000). The Soxhlet system use 85 ml of Dichloromethane, over 10 h. In order to 125
remove sulfur, some active copper was added to the extracted samples for 12 hours. The volume 126
of the sample was reduced by rotatory evaporation and then transferred to the top of 5 % $H_2O$ 127
deactivated silica gel column (1 cm i.d., × 9 cm). All hydrocarbons were eluted with 20 ml of 128
DCM[1]/hexane (1:3, v/v) and transferred onto the fully activated silica gel column (0.47 cm i.d. × 129
18 cm) to obtain aliphatic and PAH fractions. After eluting with 4 ml hexane to extract the 130
fraction of the aliphatic hydrocarbon, the PAHs were eluted with 14 ml of dichloromethane/ 131
hexane (1:3, v/v). The obtained fraction was evaporated and transferred to a 1.5 ml glass ampoule 132
and blow–down with $N_2$ to dryness. Samples were analyzed in batches of usually 10 samples 133
along with one sample blank. Procedural blanks demonstrated no hydrocarbon interferences. 134

PAHs extraction from runoff soluble water was performed using liquid–liquid extraction, LLE, 135
(Titato and Lancas, 2005; Okoli et al., 2011). LLE separated hydrocarbons based on their relative 136
solubility in immiscible liquids. The water sample poured into a separatory funnel and the 137
mixture of 100 ml n–hexane and dichloromethane (1:1 v/v) was added and shaken for 2min. The 138
water phase was drained and then the organic phase was poured into a glass funnel containing 139
20g of anhydrous sodium sulfate and re–extracted with 50 ml of the same solvent mixture. The 140
extract was concentrated prior to hydrocarbons analysis (Titato and Lancas, 2005; Okoli et al., 141
2011). 142

Twenty milligrams of gasoline, diesel and engine oil samples were accurately weighed and 143
dissolved in 2 ml DCM/n–hexane (1:3, v/v). These sample extracts were purified and fractionated 144
using the same procedure as for the solid phase samples. 145

All standards for PAHs analysis were purchased from Chiron, Norway. All solvents used for 146
sample processing and analyses (dichloromethane, hexane, and methanol) were chromatographic 147
grade from Merck (Table 1). 148

Limits of detection (LOD) and limits of quantification (LOQ) of the analytical methods were 149
between 0.01–0.09 and between 0.05– 0.41 ng.g$^{-1}$, respectively. In water samples LOD was 150
within 0.005 µg.L$^{-1}$ to 0.01 µg.L$^{-1}$ and LOQ was within 0.01 µg.L$^{-1}$ to 0.05 µg.L$^{-1}$. Analytical 151
parameters of linearity, limit of detection, limit of quantification and recovery of PAHs in solid 152
phase and water samples are presented in Table S3 of supplementary section. 153

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Table 1 near hear 155

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[1] Dichloromethane

## GC–MS analysis procedure

GC/MS analyses were carried out by a gas chromatograph (GC, model 7890A, Agilent Technologies, PaloAlto, CA, USA) instrument coupled to a quadrupole mass spectrometer (MS, 5975C, Agilent Technologies, PaloAlto, CA, USA). A fused silica capillary HP–5MS column (30 m× 0.25 mm i.d., 0.25 μm film thickness) was used with split–less injection and the following instrument parameters: initial temperature, 81 °C (maintained for initial 2 min) with ramps of 31 °C/min to 150 °C and then with ramps of 4 °C/min to 311 °C and held for 11 min. The injector's temperature was 310 °C. MS operating conditions were EI ionization, ion source 230 °C, electron energy 70 eV, and interface temperature 300 °C. Injection volumes were 1 μl. Helium was used as the carrier gas at a flow of 1 ml/min.

Identification of sample peaks was based on the comparison of the retention times of the standard samples run on the same day and confirmed by Gas chromatography–mass spectrometry (GC–MS). Characteristic ions were analyzed in single ion monitoring (SIM) mode: based upon reported m/z and retention times of PAHs (Silliman et al., 1998) and retention time of PAHs in chromatogram from external standard in scan mode, PAHs specific SIM were provided.

Recoveries were computed by spiking 200 μl of PAH SIS (the surrogate internal standard). The surrogate internal standard for PAHs consists of 5 ppm of a mixture of naphthalene–d8, acenaphthene–d10, phenanthrene–d10, chrysene–d12, and perylene–d4. Recoveries of individual constituents of the spiked SIS were between 83% -109%.

## Results and discussion

## Descriptive results

Concentration levels and diagnostic ratios of PAHs in the street dust, runoff suspended sediment, runoff soluble water, river sediment samples and in proposed source samples are given in Table S4, S5, S6, S7 and S8 of Supplementary material.

## Street dust receptor samples

The highest concentration of $\sum$PAHs in the street dust samples was observed in stations D11 $(12.7 \pm 2.7) \times 10^3$ ng.g$^{-1}$ and D12 $(12.5 \pm 3.6) \times 10^3$ ng.g$^{-1}$ and the lowest concentration of $\sum$PAHs was obtained in D3 $(2.9 \pm 0.8) \times 10^3$ ng.g$^{-1}$ and D2 $(3.5 \pm 0.7) \times 10^3$ ng.g$^{-1}$ (see Table S4 in supplementary section). Distribution of PAHs in the street dust particles of Anzali showed that stations in the central area of the city where the traffic volume is higher, such as in stations D12, D11, D10, and D5, have higher concentrations than the stations far from the center in low congestion areas such as D2 and D3. Influx of PAHs through motor vehicles, such as emissions from exhaust soot, fuel and engine oil exudation, and erosion of street pavement asphalts and vehicle tires, are the causes for contamination of these compounds in the street dust of urban areas (Hunter et al., 1979; Kumata Et al., 2000; Peng et al., 2009; Loganathan et al., 2013). Kose et al. (2008) in the study of Okayama, Japan and Hongtao et al. (2009) in the study of Xincheng,

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China observed that concentrations of PAHs were higher in urban and central areas with more traffic of vehicles than in residential areas.

The pattern of PAH compounds based upon the number of aromatic rings in the street dust samples was slightly different at various stations (see Figure S1 in the supplementary section). In general terms, about 56% of the PAH compounds in the street dust samples were had 2 and 3 rings, and the rest (44%) heavier constituents.

Low molecular PAHs (LMW PAHs) include 2 and 3 ring compounds (Naph, Acen, Ace, Fl, Phe, and Ant) with alkylated homologs derived from petroleum derivatives (Zakaria et al., 2002; Leite et al., 2011). These compounds stick to street dust by leakage of petroleum products such as gasoline, diesel and engine oil. The heavier PAHs (HMW PAHs) including those with 4 to 6 rings (Flu, Pyr, Ch, BaA, BbF, BkF, BaP, IP, and BiP) are arising from fossil fuels combustion (Wang et al., 1998; Saha et al., 2009). These compounds are introduced into the street dust mainly through vehicles exhaust soot. Also, a part of these compounds is introduced into the street dust through erosion of asphalt and tire. Therefore, dust particles have a complex mixture of petrogenetic and pyrogenic PAHs. More specifically, 4–ring PAHs with 23% and 5, 6–ring PAHs with a 21% had a lower contribution of the 2 and 3 ring PAHs, with 56% of total PAHs. Therefore, it can be stated that the general distribution of PAHs from petroleum derivatives in street dust samples of Anzali (except in stations D1, D3, D7, and D8), is higher than its emission from vehicles exhaust soot. Takada et al. (1991), observed that 3 and 4–ring PAHs and their alkyl–homologs were dominant in street dust particles from the Tokyo metropolitan area and they were originated from vehicles exhaust soot.

<u>Runoff receptor samples</u>

The highest concentration of ∑PAHs in runoff suspended sediments were obtained in stations Ru10 $(15.9 \pm 4.7) \times 10^3$ ng.g$^{-1}$ and Ru1 $(13.2 \pm 5.0) \times 10^3$ ng.g$^{-1}$ and the lowest concentrations of them were obtained at the stations Ru3 $(3.4 \pm 1.0) \times 10^3$ ng.g$^{-1}$ and Ru2 $(5.4 \pm 1.6) \times 10^3$ ng.g$^{-1}$ (see Table S5 in supplementary section). In the same way as in runoff soluble water samples, the highest concentrations of ∑PAHs were obtained in Ruw9 $(1.4 \pm 0.4) \times 10^3$ ng.ml$^{-1}$ and Ruw10 $(1.2 \pm 0.5) \times 10^3$ ng.ml$^{-1}$ and the lowest concentrations of them were obtained at the stations Ruw3 $(0.3 \pm 0.1) \times 10^3$ ng.ml$^{-1}$ and Ruw2 $(0.4 \pm 0.2) \times 10^3$ ng.ml$^{-1}$ (see Table S6 in supplementary section). In runoff samples, like in street dust samples, it was observed that stations located in the center with high traffic area had higher concentrations of PAHs than in the more distant areas, which are located on the outskirts of Anzali. Therefore, PAHs from petroleum products and vehicles combustion deposit in the street dust particles and subsequently enter into the urban runoff by rainfall. Hongtao et al. (2009), in their study on stream and road dust of Xincheng, observed that road dust particles are an important source of hydrocarbons in the city's stream.

The profile of PAHs based upon the number of aromatic rings in runoff suspended sediment samples was similar to the PAHs profile in street dust samples (see Figure S2 in the supplementary section). In runoff sediment samples about 53% of the PAHs had 2 and 3 rings, and the rest (47%) had heavier constituents. Due to the fact that the origin of suspended sediments in urban runoff is the same as for dust particles that are transported by runoff from rainfall, the similarity of the PAHs pattern in runoff suspended sediments with street dust

samples is expected. The distribution of PAHs in Dunedin New Zealand's urban runoff was also similar to street dust in the study of Jeffrey et al. (2006). The chemical fingerprinting results of PAHs in road dust and urban runoff samples in the study of Jeffrey et al. (2006) revealed a mixture of pyrogenic and petrogenic sources with a pyrogenic dominance (due to the combustion of fossil fuels). Motelay-Massei et al. (2006) also investigated PAHs in urban runoffs and street dust particles as well as atmospheric particles in the catchment area of the Seine River Basin and they found that the sources of PAHs in urban runoffs were street dust and atmospheric particles. They observed that the proportion of carcinogenic PAHs in urban runoffs (35%) was higher than in atmospheric deposits (22%) and air (6%).

However, the profile of PAHs in runoff soluble water was different from that of suspended sediments. In these samples, lower molecular weight (LMW) PAHs, which are derived from petroleum derivatives, were dominant. 2 and 3 rings PAHs in runoff soluble water accounted for 82% of the total PAHs, while the heavier compounds contained only 18% (see Figure S3 in the supplementary section). Leite et al., 2011 also found that lower molecular weight PAHs including phenanthrene, fluorene, pyrene, naphthalene, and some their methylated derivatives were dominant PAHs in the urban runoff in the study on urban river basin at the metropolitan region of Curitiba Brazil.

It seems that the washing of petroleum product leaks, including gasoline, diesel and engine oil from street pavements due to runoff from rainfall, is the reason for the dominance of low molecular weight PAHs in runoff soluble water of Anzali. Zakaria et al. (2002) with their study on PAHs in surface waters of western Malaysia stated that the washing of a large volume of engine oil leaks from streets by runoffs is one of the main sources of PAHs in western Malaysia's runoff and surface water.

## River surface sediment receptor samples

The highest amount of $\sum$PAHs in surface sediments of rivers and port of Anzali obtained in stations R24 $(22.2 \pm 8.0) \times 10^3$ ng.g$^{-1}$ and R23 $(21.4 \pm 6.3) \times 10^3$ ng.g$^{-1}$ and the lowest concentration found at station R4 $(5.5 \pm 1.9) \times 10^3$ ng.g$^{-1}$ and R3 $(7.9 \pm 3.3) \times 10^3$ ng.g$^{-1}$) (see Table S7 in supplementary section). The distribution of $\sum$PAHs in surface sediments of Anzali rivers showed that stations in the port area, including R24, R23, R22, R21, R20, and R13, had more pollution than other stations. Since the breakwater in front of the port causes heavy sedimentation and trapping of pollutants and on the other hand, due to fuel and oil leaks from the ships in the port, higher concentrations of PAHs in the sediments of these stations are expected. Also, stations at central areas of the city that receive urban runoff contaminated with high concentrations of PAHs, such as stations R11, R12, R15, R16, R17, R18 and R19 showed higher concentrations of PAHs than stations located at the margins like R4, R3 and R2. Wang et al. (2015) identified the origin of PAHs in the surface sediments of the Zhoushan Archipelago and the Xiangshan Port in the East Sea of China, which is an important commercial, tourist and fishing port and they reported that this is due to the diffusion of vehicles and petroleum sources. Masood et al. (2015) observed a high level of sedimentation of PAHs and LABs in the Malaysian Selangor River during the rainy season. It happened firstly due to the large amounts of domestic

and urban wastewater entering the river and then because of the entry into the river of urban runoff washing contaminations from the surrounding areas.

In contrast to the PAH compound profile with respect to the number of aromatic rings, in street dust and urban runoff suspended sediment samples, the profiles of PAHs in river sediments at different stations were approximately the same (see Figure S4 in supplementary section). In these samples, for all of the studied stations, lower molecular weight PAHs were dominant. The 2 and 3 rings PAHs in the surface sediments of the studied stations were 83% and the heavier PAHs were only 15% of all PAHs. Composites of simple structure or lower molecular weight PAHs include Phe, Flu, Pyr, Nap and some of their methyl derivatives. They are the main compounds of urban and industrial wastewaters (Leite et al., 2011). Therefore, the discharge of different sewage to the Anzali rivers along their pathways is one of the reasons for the dominance of these compounds in river sediments. The fuel and oil leakages from the floats and large ships in the Anzali port, as well as boats in the rivers, are another important source of petrogenic compounds in the area. Azimi–Yancheshmeh et al. 2014 have reported methyl phenanthrene, phenanthrene, pyrene and naphthalene as the dominant PAHs among the 23 studied PAHs in the coastal sediments in Anzali wetland. Also in this study the predominance of naphthalene and the abundance of other naphthalene compounds containing methyl group have particular importance in river and port sediments. Because these compounds are mostly from petroleum origin, they are readily desorbed from the sediment particles and consequently have high bioavailability to the organisms and cause severe toxic effects (Paine et al., 1996; Long and Morgan., 1990). 4 rings PAHs with 7% and 5 and 6 rings with 8% had the lowest contribution of PAHs in river sediment samples. Bin et al. (2007) also observed that in surface sediments of the Haihe River in Tianjin, China, PAHs with 2 to 4 rings were dominant. The contribution of two, three, four, five and six rings PAH compounds in the Tuhai–Majia River sediments of China were 30.30%, 28.48%, 20.22%, 73.3% 14% and 38.8% respectively from total PAHs (Liu et al., 2012).

PAHs source samples

The concentrations of $\sum$PAHs in six proposed sources (asphalt, diesel, gasoline, engine oil, exhaust soot, and tire) are presented in Table S8 in the supplementary section. The pattern of PAHs with respect to the number of aromatic rings in these sources showed that the profile of PAHs in them is quite different (see Figure S5 in the supplementary section). In the sources gasoline, diesel and engine oil, the lower molecular weight (LMW) PAHs were predominant. So that PAHs with 2 and 3–ring account for 90, 95 and 94% of the PAHs, respectively. These sources are therefore pure petrogenic sources. Whereas, the 2 and 3–ring PAHs in the exhaust soot of cars, motorcycles and boats account for an average of 9% of all PAHs and 91% of the PAHs in exhaust emissions are high molecular weight (HMW). Thus, exhaust soot are a pyrogenic source of fossil fuel combustion. The contribution of 2 and 3–ring PAHs in the sources asphalt and tire were 49% and 35% respectively, so asphalt and tire can be a mixture of petrogenic and pyrogenic sources. De Mora et al., 2006 have reported on the coasts of Guilan province (southwest of the Caspian Sea) the predominance of 2–and 3–ring PAHs over 4–6–ring PAHs, which is very close to the results of the present study.

Spatial distribution of PAHs                                                                    317

Figure 2 indicates the spatial distribution of PAHs in the studied environmental samples (street    318
dust, runoff suspended sediment, runoff soluble water, and river sediment). Size of the circles     319
indicates the total amount of PAHs. As observed in Figure 2, the distribution patterns of PAHs in   320
the street dust and runoff samples are almost similar.  Therefore, in the stations located in the   321
center of the city with higher traffic, the concentration of PAHs is higher in the street dust      322
samples and runoff samples than in the stations far from the city center with lower traffic.        323
Therefore, it is completely clear that the main sources of PAHs in the runoff samples are           324
transferred through the street dust.                                                                325

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Figure 2                                                                                            327

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In the surface sediment samples of the rivers in Figure 2, it is observed that the concentrations of 329
PAHs in the stations closer to the Caspian Sea coast are high. Increasing PAH concentrations in     330
these stations are expected due to the presence of the various ships and boats in the port region   331
and because of the construction of the breakwater front of the port, leading to trapping of         332
pollutants in the area and their precipitation on the bottom sediments.                             333

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Identifying Origin of PAHs by Diagnostic Isomer Ratios                                              335

PAHs enter the environment from various sources. So, it is important to identify the sources of     336
these compounds for making the necessary decisions to prevent their release in the environment      337
due to the adverse effects of these compounds on the health of the community. With chemical         338
fingerprinting of PAHs, using the stable and unstable PAHs isomers and the use of these isomers     339
in diagnostic ratios, the origin of PAHs can be identified (Yunker et al., 2002a,b; De Luka et al., 340
2005). In order to determine the predominant origin of PAHs in various studied samples,             341
including street dust, runoff, and river sediments, the relations over some compounds and their     342
isomers were used (Table 2).                                                                        343

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Table 2                                                                                             345

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A ratio of the total concentration of low (2 and 3–ring) to high (4 to 6–ring) molecular weight     347
PAHs used to identify pyrogenic (<1) and petrogenic (>1) sources of the target compounds in         348
current study (Magi et al., 2002; Giuliani et al., 2008). LMW/HMW ratios below 1 were obtained      349
mostly in street dust and runoff suspended sediments samples and LMW/HMW ratio higher than          350
1 was obtained in all stations of runoff soluble water and river surface sediments. Since the street 351
dust particles receive PAHs from the petroleum sources from vehicles such as gasoline, diesel,      352
and engine oil, and from other combustion sources such as exhaust soot, these street dust samples   353

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contain a mixture of petrogenic and pyrogenic PAH compounds. The source of suspended sediments in runoffs is the street dust particles.

Ratios of phe/Ant > 10, Flt/Pyr < 1, and BaA/Chr < 0.4 generally suggest petrogenic source of PAHs, and ratios of phe/Ant < 10, Flt/Pyr > 1, and BaA/Chr > 0.4 indicate pyrogenic source (Budzinski et al., 1997; Baumard et al., 1998; Culotta et al., 2006; Giuliani et al., 2008). Figure 3 indicates the results of the simultaneous plot using Flt/Pyr versus Phe/Ant, in the street dust samples. As seen in Figure 3 (plot a), some street dust stations are in the petrogenic area, and other stations are in the pyrogenic area. The use of the simultaneous plot with BaA/Chr versus Flt/Pyr differentiates the stations with a mixed origin. As seen in Figure 3 (plot b), most of the street dust stations have a mixture of petrogenic and pyrogenic origins.

Figure 3

In Figures 4 and 5, simultaneous plots of ratios Phe/Ant versus Flt/Pyr and BaA/Chr versus Flt/Pyr drawn for runoff suspended sediment and runoff soluble water samples are given. These plots show that most Anzali urban runoff stations have a mixture of pyrogenic and petrogenic origins (plot b in figures 4 &5).

The simultaneous plots of phe/Ant versus Flt/Pyr and BaA/Chr versus Flt/Pyr in Figure 6 indicates that except for a few numbers of stations, the majority of stations of river and port surface sediments have a predominant petrogenic origin.

MP/P ratio, which indicates the ratio of total concentration of four methyl phenanthrene compounds to the concentration of phenanthrene, is another ratio that is extensively used for determining the origin of PAHs (Yunker et al., 2002b; Zakaria et al., 2002). The alkylic PAHs are more sustainable rather than their mother PAH compounds and they are abundantly found in petroleum derived products. MP/P ratio for the pyrogenic origin is below 1, while it is between 2 and 6 for the petrogenic origin (Garrigues et al., 1995). This ratio in street dust and runoff samples of Anzali indicates a mixture of petrogenic and pyrogenic origins. In surface sediments of rivers and port of Anzali, MP/P ratio was obtained between 2 – 6 in all stations except for stations R4, R7, R12, and R21, where it was between 1 and 2. Thus, PAHs predominant origin in the river and port surface sediments was mainly petrogenic. In some rivers, the pyrogenic sources were also effective in the emission of these compounds.

According to the ratios measured by Yunker et al. (2002b), the ratio Flu/(Flu+Pyr) < 0.4 refers to the petrogenic origin, the range of 0.4 – 0.5 refers to the pyrogenic origin, and the ratio above 0.5, suggests coal and biomass combustion. In addition, the ratio Ant/(Ant+Phe) below 0.1 suggests entrance of petroleum (Petrogenic) sources to the region, and above 0.1 show pyrogenic source. The simultaneous plot for Flu/Flu+Pyr versus Ant/(Ant+Phe) ratios in the street dust samples (Figure 3– plot c) indicates that origin of PAHs in some stations is pyrogenic and in some others it is petrogenic. This plot in runoff suspended sediments (Figure 4– plot c) shows that in most of the stations, the origin of the PAHs is a mixture of petrogenic and pyrogenic. This plot in runoff soluble water (Figure 5–plot c) shows petrogenic origin in half of the stations and a

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mixture of petrogenic and pyrogenic origins in the rest of stations. Finally, in the surface sediment of rivers and port, based upon the plot of Flu/Flu+Pyr versus Ant/Ant+Phe in Figure 6 – plot c, the predominant origin of most stations is petrogenic. In the plots c and d of Figures 3 – 5 the proposed sources were also shown. As seen in these plots the sources diesel, engine oil, and gasoline are located in the petrogenic area, while tire and at lower extent asphalt are identified as a mixture of petrogenic and pyrogenic sources. However, the exhaust soot is completely located in the pyrogenic area.

Figure 4 & 5 near hear

 BaA/BaA+Chr is another ratio that is used for detecting the origin of PAHs. If this ratio is below 0.2, it indicates the petrogenic origin, the values between 0.2 and 0.35 indicate a mixture of pyrogenic and petrogenic sources, and the ratio above 0.35 represents the pyrogenic source. In the current study, in street dust samples, in all stations, except for two stations D11 and D12, BaA/BaA+Chr ratio was between 0.2 and 0.35, which represents a mixture of pyrogenic and petrogenic origin. This ratio was above 0.35 in most stations of urban runoff (suspended sediment and soluble water). In the river surface sediment samples, BaA/BaA+Chr ratio in stations R20, R21, R22, R23 and R24, R13 and R12 were below 0.2, and in other stations, it was obtained between 0.2 and 0.35. According to the map of the study area (Figure 1), the stations R20, R21, R22, R23 and R24, R13 and R12 are located in the port area, which is affected by the leakages of oil and fuel from the vessels in the area. So BaA/BaA+Chr ratio below 0.2 in these stations can be due to these petroleum sources. Other stations are located in the rivers of Anzali urban area, which are affected by the influx of urban runoffs containing pyrogenic and petrogenic sources. Therefore, BaA/BaA+Chr ratio is expected to be between 0.2 and 0.35 at these stations.

The simultaneous plot of BaA/BaA+Chr versus Flu/Flu+Pyr well indicates a mixture of petrogenic and pyrogenic sources in all studied samples. This plot shows that almost all stations of street dust samples (Figure3– plot d), runoff suspended sediment samples (Figure 4– plot d), and runoff soluble water (Figure 5– plot d) have a mixture origin of petrogenic and pyrogenic. Just a few stations such as D2 and D3 that were located far from the city center and are located in the forested region had a different situation and located in the pyrogenic area. This could be due to the lack of cars and, consequently, less leakage of petroleum products at these stations. The plot resulting from BaA/BaA+Chr versus Flu/Flu+Pyr ratios in the river and port sediment samples (Figure 6– plot d) indicates that the predominant source of PAHs in about half of the stations is petrogenic, and it is a mixture of petrogenic and pyrogenic in about another half of stations. The simultaneous plot of BaA/BaA+Chr versus Flu/Flu+Pyr indicates that known sources asphalt and tire has more contribution to PAHs emission especially in street dust and runoff samples. The scrutiny of stations showed that stations located in the port area such as stations R12, R13, R20, R21, R22, R23, and R24 have a completely petrogenetic source, While stations which are located in the urban rivers that cross the city and receive polluted runoff from petrogenetic and pyrogenic sources showed mixed sources.

Figure 6                                                                                                      433

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## Conclusions                                                                                            435

Generally, PAHs were found to be at higher concentrations in street dust, urban runoff and     436
surface sediments of rivers and port of Anzali. Therefore, it can be argued that this region in     437
terms of petroleum hydrocarbon compounds is highly polluted. It seems that the high population     438
density and high cars traffic in Anzali small city besides abundant rainfall has led to the entry of     439
large amounts of these hydrocarbons into street dust particles, urban runoffs, and rivers and     440
finally get buried in Caspian Sea coast for a long time. The distribution of PAHs in the street dust     441
and urban runoff samples showed a similar flow. Therefore, it was found that the major sources     442
of PAHs emissions were similar in the street dust and runoff samples. Source identification of     443
PAHs by chemical fingerprinting using PAHs isometric ratios including PHE/ANT, FLU/PYR,     444
ANT/(ANT+PHE), FLU/(FLU+PYR), BaA/CHR, BaA/(BaA+CHR) and MP/P in the receptor     445
samples (street dust, urban runoff and river sediments) and proposed sources (asphalt, gasoline,     446
diesel oil, engine oil, exhaust soot and tire) showed that in most of the street dust and urban     447
runoff samples, distribution patterns of PAHs were relatively similar to the main sources,     448
especially to asphalt and tire. This confirmed that street dust and urban runoff samples could     449
originate from similar common sources. Therefore, it can be demonstrated that street dust     450
particles are a major transport medium for PAHs contamination in urban runoffs. The spatial     451
distribution of PAH compounds in surface sediments showed that the stations in the port area had     452
the highest concentrations of these compounds of the study area. The construction of the     453
breakwater in front of the port, which caused the port's water stagnation and severe     454
sedimentation, resulted in the deposition of pollutants and their accumulation in the bottom     455
sediments. On the other hand, the presence of ships, lagoons, and boats in the Anzali port area     456
causes the entry of petroleum compounds through fuel and oil of these vessels to this area.     457
Moreover, the river sediments stations located in the urban area showed higher concentrations of     458
PAHs relative to stations outside the city. It seems that washing of street dust particles containing     459
petroleum hydrocarbons from various petroleum derivatives via urban runoff due to rainfall is the     460
main reason for polluted river sediments in the urban area relative to forested areas. Finally, we     461
conclude that the results of chemical fingerprinting showed that the PAHs in the majority of     462
street dust and urban runoff samples are related to the six samples of the source material studied.     463
Only some of the river sediment samples were not well described by them, therefore, these     464
samples are likely to receive hydrocarbons from other source inputs not included in the six     465
considered in this work.     466

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Tables;

Table 1. Compounds of standard mixtures of PAHs

| Compounds of PAH standard mixtures | Abbreviation |
|---|---|
| Naphthalene | Na |
| 1M-Naphthalene | 1MNa |
| 2M-Naphthalene | 2MNa |
| 2,6DM-Naphthalene | DMNa |
| Acenaphthylene | Acy |
| Acenaphthene | Ace |
| 2,3,5TM-Naphthalene | TMNa |
| Fluorene | Fl |
| Dibenzothiophen | DBT |
| Phenanthrene | P |
| Anthracene | Ant |
| 3-Methylphenanthrene | 3MP |
| 2-Methylphenanthrene | 2MP |
| 9-Methylohenanthracene | 9MP |
| 1-Methylphenanthrene | 1MP |
| 3,6DM-Phenanthrene | DMP |
| Fluoranthene | Flu |
| Pyrene | Py |
| Benzo(a)fluorine | BaF |
| Benzo(a)anthracene | BaA |
| Chrysene | Chy |
| Benzo(b)fluoranthene | BbF |
| Benzo[k]fluoranthene | BkF |
| Benzo(a)pyrene | BaP |
| Benzo(e)pyrene | BeP |
| Perylene | Per |
| Indeno[1,2,3-cd]pyrene | IP |
| Dibenzo[a,h]anthracene | DBA |
| Benzo[ghi]perylene | BP |

Table 2. Diagnostic ratios for determining the major sources of PAHs

| Reference | Diagnostic ratio | Petrogenic | Pyrogenic | Mixed Sources |
|---|---|---|---|---|
| Soclo et al., 2000; Boitsov et al., 2009 | PHE/ANT | > 10 | < 10 | - |
| De Luca et al., 2005 | FLU/PYR | < 1 | > 1 | - |
| Budzinski et al., 1997; Leite et al., 2011 | ANT/(ANT + PHE) | < 0/1 | > 0/1 | - |
| Soclo et al., 2000; Hu et al., 2010 | FLU/(FLU + PYR) | < 0/4 | 0/4 – 0/5 | > 0/5 |
| Readman et al., 2002 | BaA/CHR | < 0/4 | > 0/4 | - |
| Wu et al., 2001; Leite et al., 2011 | BaA/(BaA + CHR) | <0/2 | > 0/35 | 0/2 – 0/35 |
| Yunker et al., 2002b; Zakaria et al., 2002 | MP/P | 2-6 | < 1 | 1-2 |

PHE– phenanthrene; ANT – anthracene; BaA – benzo[a]anthracene; CHR – chrysene; FLU – fluoranthene; PYR – pyrene; MP– methyl phenanthrene

Figures;
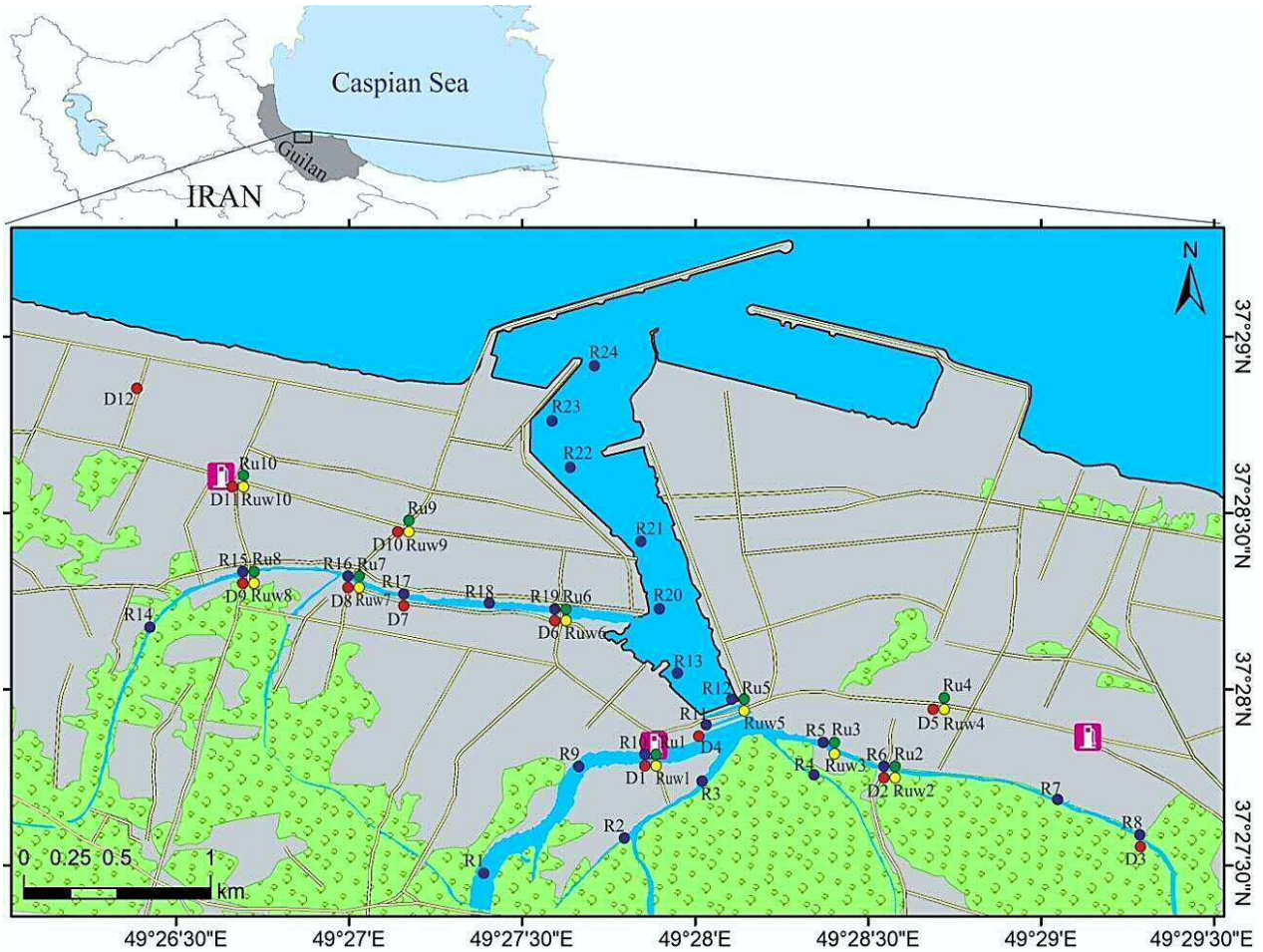


Figure 1. Locations of the studied samples, street dust samples (D), runoff suspended sediment samples (Ru), runoff soluble water samples (Ruw) and river surface sediment samples (R) in the Anzali Port, south of the Caspian Sea, Iran.
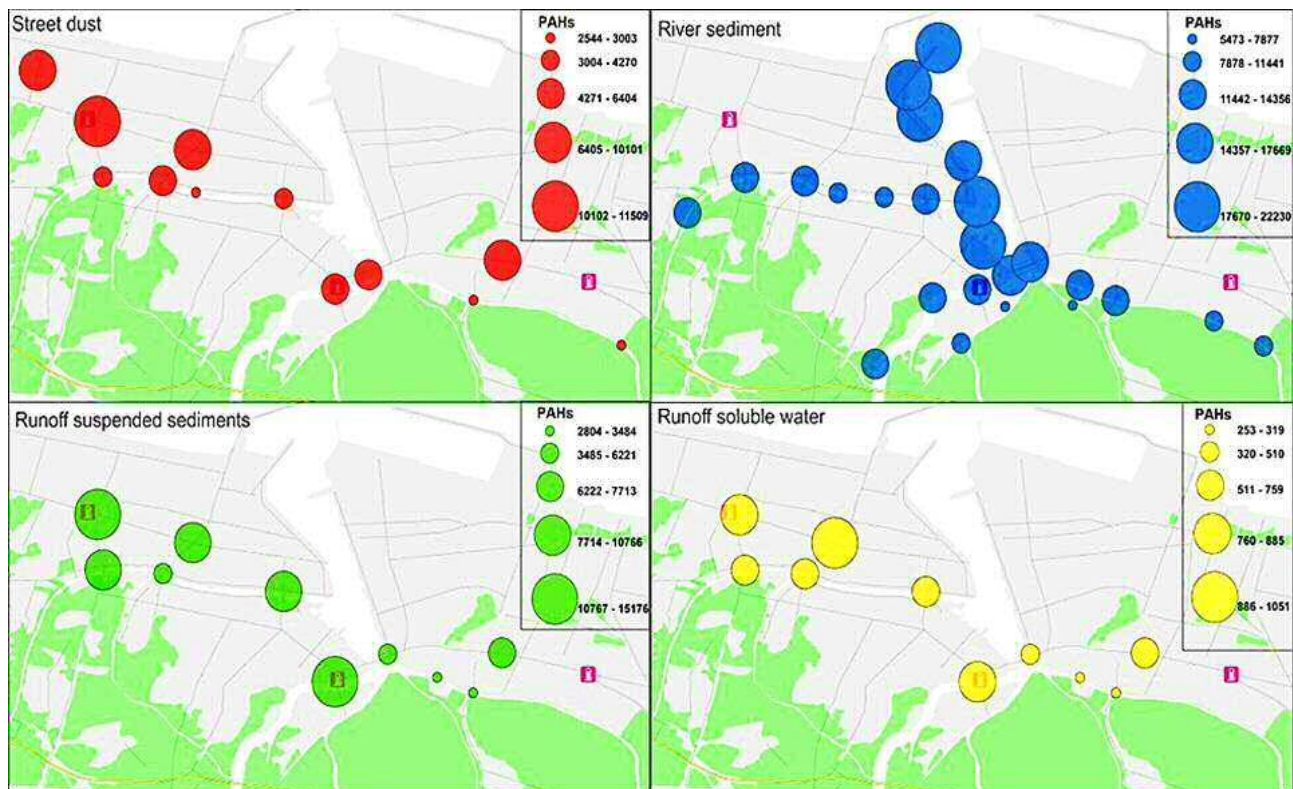
Figure 2. Distribution of PAHs in street dust (ng g$^{-1}$), runoff filtered sediment (ng g$^{-1}$), runoff soluble water (ng.ml$^{-1}$) and river sediment (ng g$^{-1}$) samples from Anzali port. (Bigger circles represent higher concentrations of PAHs than smaller circles).
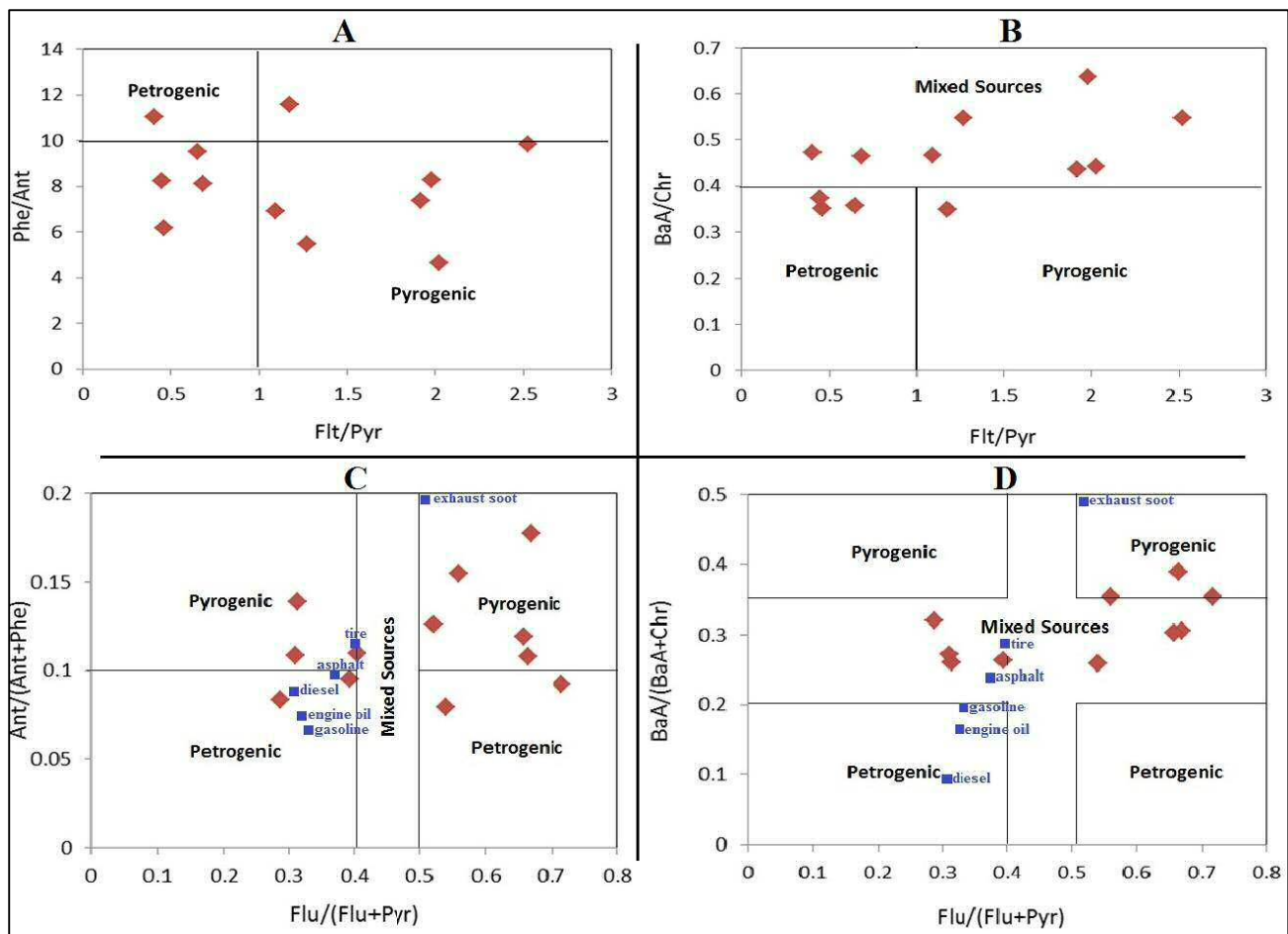
Figure 3. The plots from characteristic isometric ratios of PAHs in street dust samples as well as proposed sources
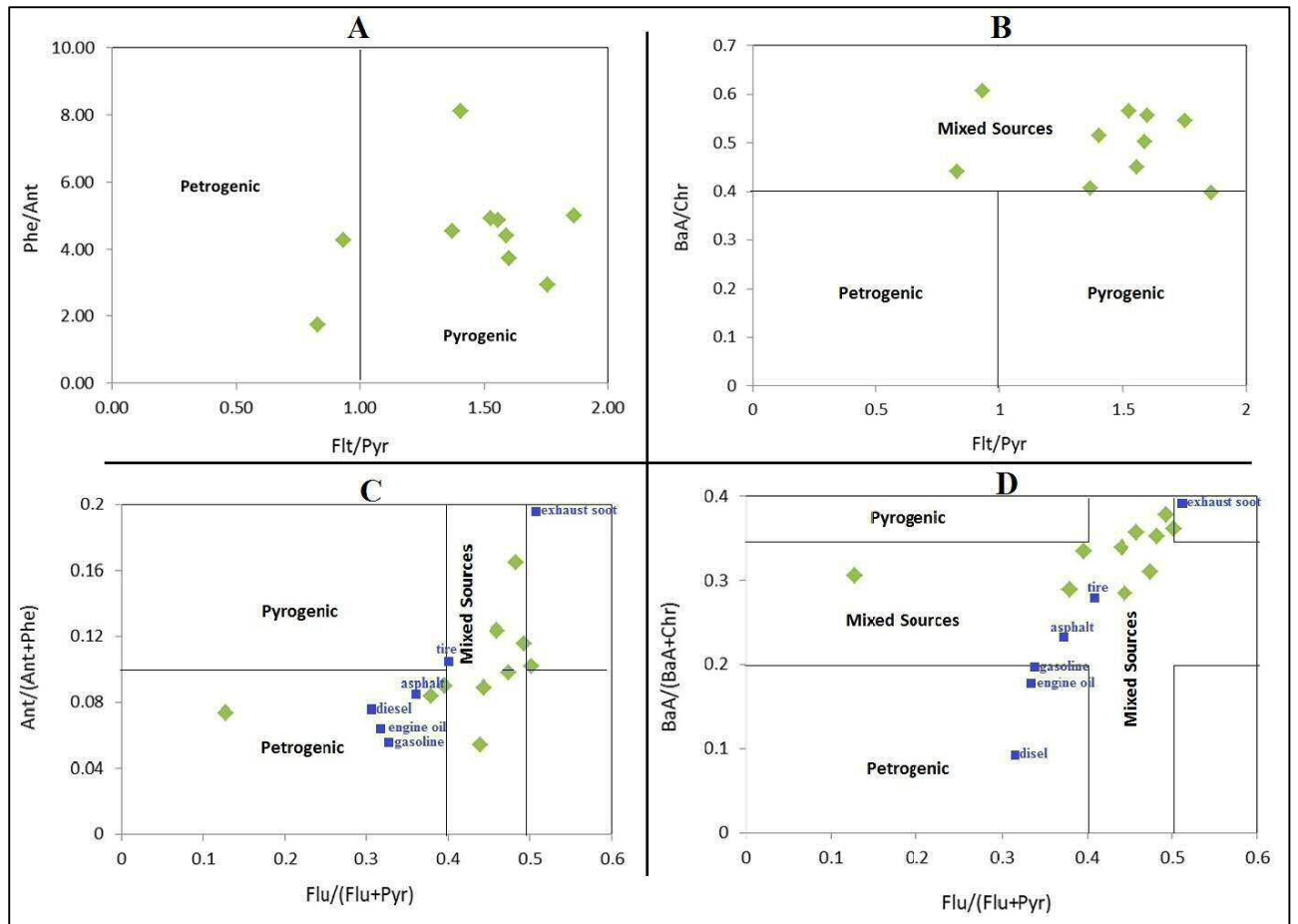
Figure 4. The plots from characteristic isometric ratios of PAHs in suspended sediments of urban runoff samples as well as proposed sources
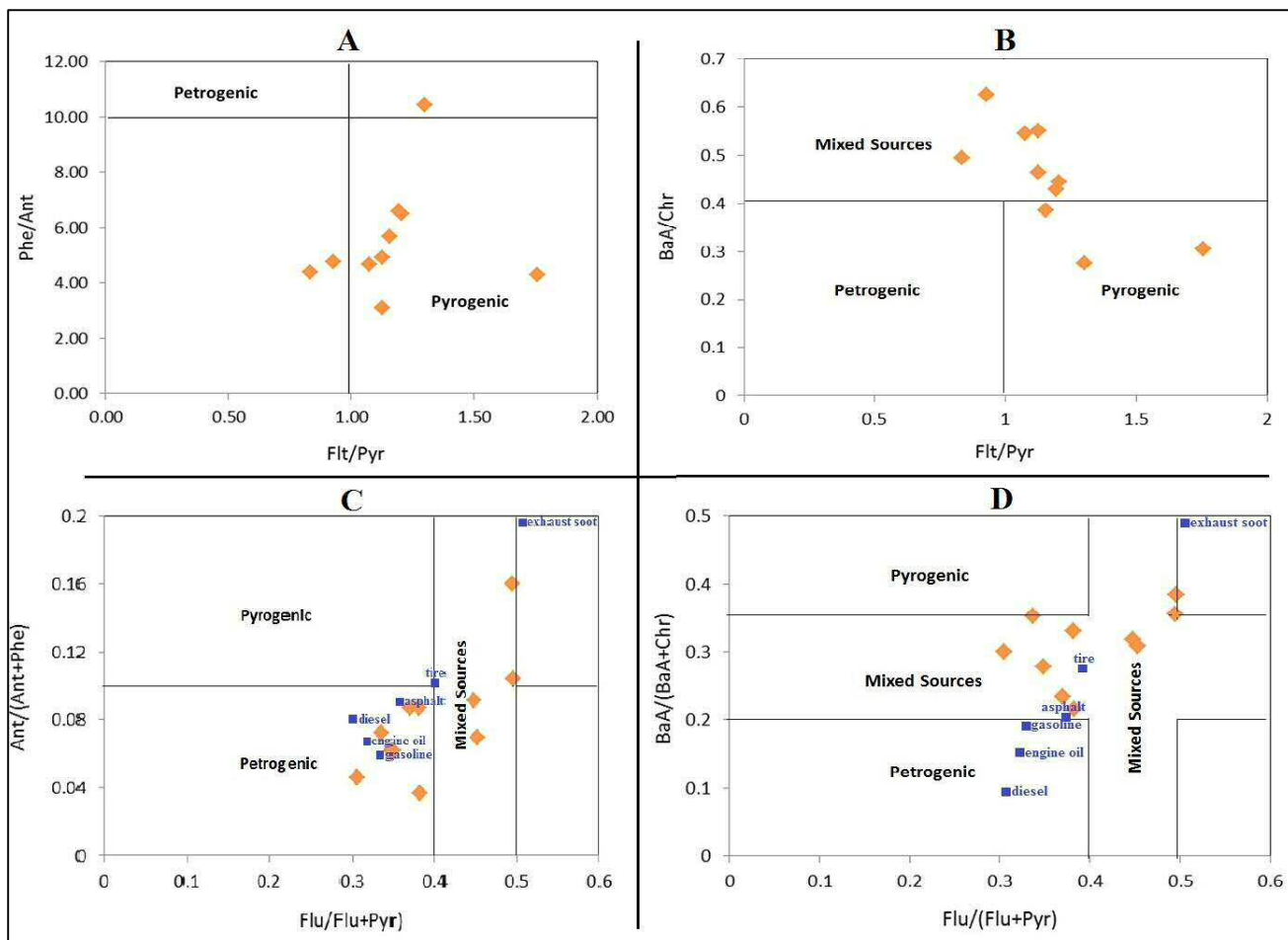
Figure 5. The plots from characteristic isomeric ratios of PAHs in soluble water of urban runoff samples as well as proposed sources
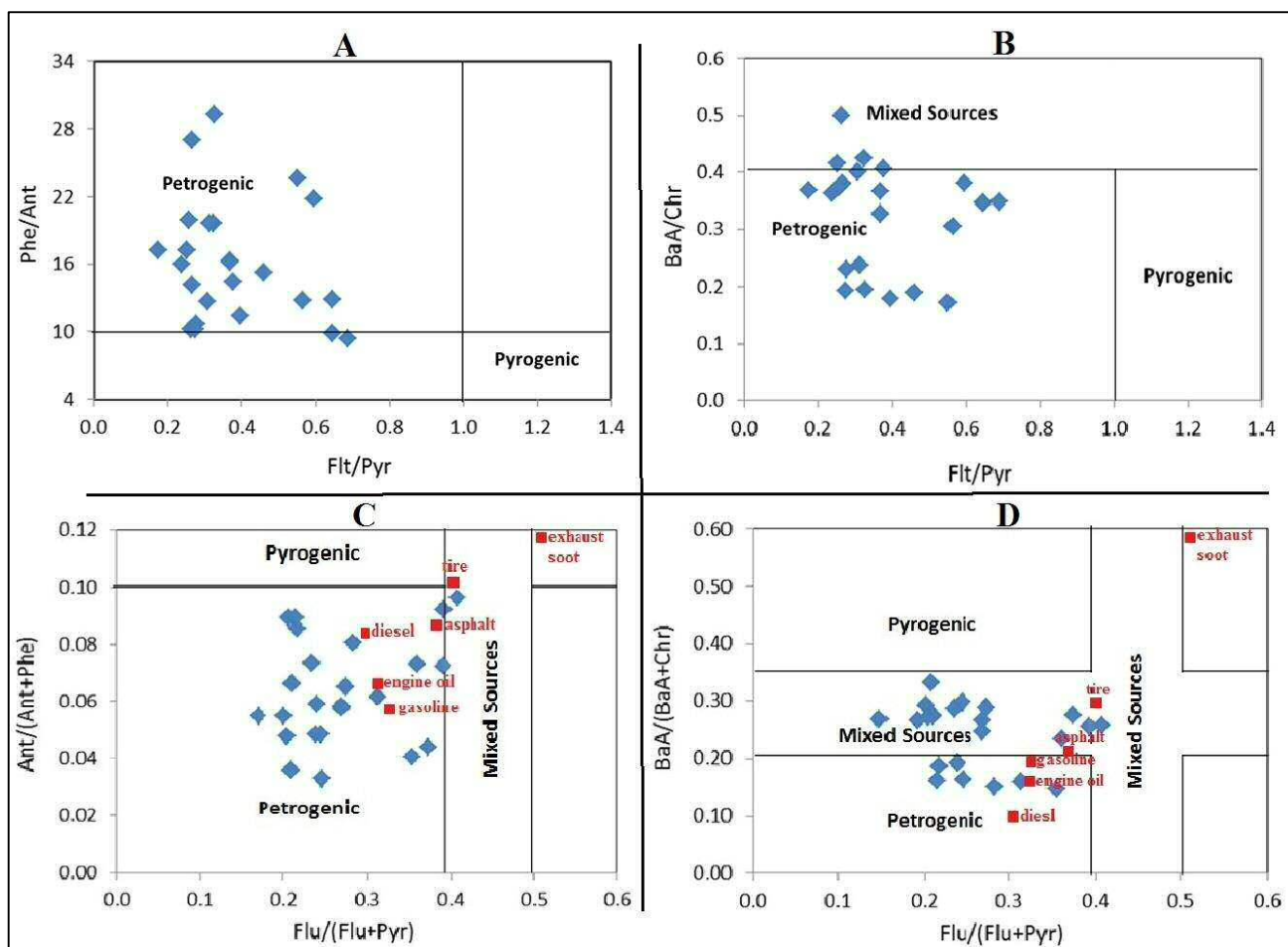
Figure 6. The plots from characteristic isometric ratios of PAHs in surface sediments of Anzali Rivers and port as well as proposed sources