Distribution and characteristic of PAHs in sediments from the southwest Caspian Sea, Guilan Province, Iran

Mohammad Nemati Varnosfaderany, Alireza Riyahi Bakhtiari, Zhaoyan Gu and Guoqiang Chu

ABSTRACT

Contamination by polycyclic aromatic hydrocarbons (PAHs) in the southwest Caspian Sea was assessed by examination of 45 sediment samples, collected from the coasts of the Guilan Province in 2012 and analyzed for 29 PAHs. The concentrations of PAHs were in the range of 232.1–1,014 ng g^{-1} dry weight (mean 520 ± 246.4 ng g^{-1}). The predominance of alkyl-substituted naphthalenes and phenanthrenes and the higher contributions of petrogenic compounds (NPD = 35.4–74.4%) compared to pyrogenic PAH compounds (COM = 18.1–47.4%) reveal a petrogenic source for PAHs with ubiquitous distribution in the study area. Offshore increase of total PAH concentrations was found to be correlated with increase of organic matter content of sediments, but no correlations with particle size fractions were found. The evaluation of ecotoxicological risk by sediment quality guidelines indicated that total PAH concentrations at all sites were below the effects range-low (ERL), but some individual petrogenic PAHs at some stations were significantly above their ERL and likely to adversely affect benthic biota. According to the diagnostic ratios used, most stations revealed the major source of the PAHs to be petrogenic, but some stations suggested a mixed petrogenic-pyrogenic source.

Key words | Caspian Sea, diagnostic ratio, PAHs, petrogenic, sediments

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INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) belong to the group of persistent organic pollutants (POPs) and are prevalent in the atmosphere and soil, marine and freshwater environments. Owing to their low solubility and hydrophobic nature, PAHs tend to be associated with sediments; therefore, sea or lake sediments act as a trap for PAHs (Douben 2003). PAHs may be derived from anthropogenic (fossil fuel and combustion) or natural (oil seeps, bitumens, coal, plant debris, volcanic activity, forest and prairie fires) sources (Zakaria et al. 2002; Yunker et al. 2002). Source discrimination of pollutants is one of the first steps in conservation programs for ecosystems. Land-locked ecosystems such as lakes are especially sensitive to POPs. The Caspian Sea, the largest lake in the world, has huge oil and natural gas reserves that attracted the attention of the international oil and gas industry (Effimoff 2000). Despite the perceived environmental problems arising from oil exploration and production in the Caspian Sea (Efendiyeva 2000), few investigations of petroleum

hydrocarbons especially PAHs, have been published. The only comprehensive research in this regard (Tolosa et al. 2004) revealed high variability of total PAHs (6–2,988 ng g^{-1} dry weight) in collected surface sediment samples from the coastal zones of countries bordering the Caspian Sea, and limited petrogenic contaminations in the shallow north basin but moderate to high petrogenic contaminations in the south basin, especially in the offshore oil fields near Baku. Korotenko et al. (2000), by transport modeling oil spillages along the Azerbaijan coast, predicted worse scenarios for the coasts of Iran, where with southward and south-westward winds an oil spill might reach the Iranian coasts by the fourth day after release. Moreover, due to favorable tectonic conditions and depositional settings, more than 200 active mud volcanoes have been identified in onshore and especially offshore Azerbaijan (Guliyev & Feizullayev 1997; Yusifov & Rabinowitz 2004) as potential sources of petroleum hydrocarbons in the southwest Caspian Sea.

In the present study, surface sediment samples from different depths of the western Iranian coasts were used to investigate the spatial distribution and the current status of PAH contamination in the southwest Caspian Sea and, to some extent, identify the possible sources of PAHs by diagnostic ratios.

MATERIALS AND METHODS

Study area and sampling

The Caspian Sea has virtually no tides and the salinity of its water is low at around $13 \, \text{g} \, \text{l}^{-1}$. Because of its meridional extension, several climatic zones border it including a temperate continental climate at the northern part, a moderately warm climate at the western coasts, a desert climate at the eastern coasts and a subtropical humid climate in the southern and southwestern region. General water circulation along the coasts of the southwest Caspian Sea is affected by anticyclones that are mainly located at the northwest of the south basin (Tuzhilkin & Kosarev 2005). According to Zenkevitch (1963), anaerobic conditions are never reached even in the deepest waters of the Caspian Sea. High terrigenous sediment flux (33 million tons per year) enters the south Caspian Sea through the Iranian rivers, mainly (80% of the total flux) from the Sefidrud River (Krasnozhon *et al.* 1999). The western Iranian coast along the Guilan Province was selected for the current study, due to the high sediment flux of rivers in this region

and proximity to the Azerbaijan mud volcanoes and oil fields that are the main potential sources of PAHs in the southwest Caspian Sea. The catchment area is mostly restricted to Guilan Province with an area of 1,067,736 hectares and has main land uses of forest (52.89%, Hyrcanian forests), range land (22.94%), agriculture (23.73%) and residential (0.44%), respectively (Iran Statistical Year Book 2010).

The coastal surface sediment survey was based on 45 samples collected at 15 stations (each station three replicates) during the period 28 May to 2 June 2012 in accordance with the second Caspian Sea oceanographic excursion (Figure 1; Table 1). Stations along the west–east transects (from Astara to Sefidrud Delta) and onshore–offshore (10, 20 and 50 m) were selected to represent the various depositional settings. All of the surface sediments were collected using a Van Veen Grab sampler. Sediments from the surface (~3 cm) were sub-sampled. All samples were stored in clean aluminum foils, transported to the laboratory in a cool box and stored at $-21 \, °C$ until further analysis (Zakaria *et al.* 2002).

Sedimentology

All samples were first weighed and freeze-dried to calculate water content. Percentages of total organic matter (%TOM) were determined by a loss-on-ignition method used by Dean (1974). Homogenized and representative subsamples of each sample were taken for grain size analysis. The distribution for the fraction coarser than 63 µm was determined using

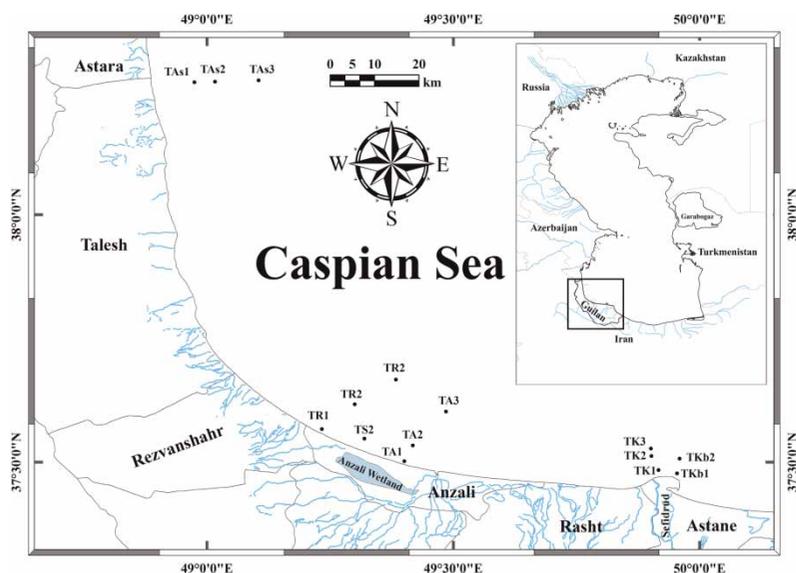**Figure 1** | Study area and sampling stations.

Table 1 | Characteristics of the sampling stations, concentration of $TPAH_{29}$, $TPAH_{16}$, NPD, COM and mean ERL values at the study sites. For abbreviations, see text

Stations	Latitude	Longitude	Depth, m	TOM, %	Sand, %	Silt, %	Clay, %	$TPAH_{29}$, ng g^{-1}	$TPAH_{16}$, ng g^{-1}	NPD, ng g^{-1}	COM, ng g^{-1}	Mean ERL quotient[a]
TAs1	38° 16.2′	48° 58.2′	10	3.1	48.1	36.2	15.7	693.5	346.3	468.1	157.3	0.26
TAs2	38° 16.0′	49° 00.6′	20	6.7	46.9	37.9	15.2	316.9	192.6	190.9	84.8	0.12
TAs3	38° 16.1′	49° 06.1′	50	8.1	49.7	33.2	17.1	374.9	173.3	240.6	98.5	0.13
TR1	37° 34.0′	49° 14.0′	10	2.6	37.7	44.7	17.6	263.8	142.3	173.2	61.1	0.10
TR2	37° 37.0′	49° 18.0′	20	5.3	52.4	29.9	17.7	434.6	262.8	206.5	171.9	0.14
TR3	37° 40.0′	49° 23.0′	50	9.8	57.9	27.3	14.8	1,014.0	519.9	695.9	234.3	0.39
TS2	37° 32.5′	49° 18.9′	20	5.3	31.1	39.0	29.9	832.5	410.3	516.3	237.2	0.27
TA1	37° 30.6′	49° 24.2′	10	2.5	40.9	37.9	21.3	232.1	191.4	157.0	47.1	0.12
TA2	37° 32.1′	49° 25.5′	20	5.7	17.4	60.1	22.5	406.6	232.5	235.1	118.9	0.15
TA3	37° 36.9′	49° 26.8′	50	11.4	59.1	26.8	14.2	612.7	426.8	217.0	290.2	0.18
TK1	37° 29.1′	49° 55.0′	10	2.2	54.0	29.4	16.6	236.0	121.9	156.1	57.1	0.09
TK2	37° 30.4′	49° 54.7′	20	6.6	60.8	22.6	16.6	318.8	212.0	199.5	93.1	0.10
TK3	37° 31.3′	49° 54.9′	50	8.9	45.6	31.2	23.2	792.1	365.5	554.7	153.1	0.32
TKb1	37° 28.7′	49° 57.2′	10	2.4	52.1	30.1	17.8	543.5	262.6	404.3	98.6	0.21
TKb2	37° 30.2′	49° 57.3′	20	6.8	55.7	24.9	19.4	727.2	571.5	471.6	169.0	0.26

[a]Each PAH concentration at the site was divided by the ERL for that contaminant and then averaged to obtain mean ERL (Long et al. 1998).

the standard wet sieving procedure. Grain size for the fraction less than 63 μm was analyzed by a laser particle size analyzer (Malvern Mastersizer 300) after removal of organic matter, carbonates and biogenic silica by 30% H_2O_2, 10% HCl and 0.5 M NaOH, respectively (Gee & Or 2006). Triplicate analyses of the same sample indicated that the relative error was small and that the percent difference error of related size fractions was less than 2%.

Extraction and analysis of PAHs

Authentic PAH standards were purchased from Chiron (Trondheim, Norway). Glassware was rinsed successively with methanol, acetone and hexane to remove any organic contaminants and kept in an oven at 60 °C. Sediments were homogenized by mortar and pestle prior to extraction. About 5 g of each freeze-dried sample was purified and fractionated by a method described elsewhere (Zakaria et al. 2002). Briefly, a Soxhlet apparatus was used for extraction using 100 ml of dichloromethane for 10 h. One hundred microlitres of PAH surrogate internal standard mixture (200 ppb of each component, naphthalene-d_8, anthracene-d_{10}, chrysene-d_{12} and perylene-d_{12}) was added for quality control of PAH analyses. After reducing the solvent to approximately 4–5 ml by rotary evaporation, the extracts were transferred to the top of a 5% H_2O deactivated silica gel column. Hydrocarbons were eluted with 20 ml of

dichloromethane/hexane (1:3, v/v). The eluent after solvent reduction was further fractionated using fully activated silica gel column chromatography to obtain PAH fractions by elution of the column by 14 ml of dichloromethane/hexane (1:3, v/v). Alkanes were eluted with 4 ml of hexane prior to PAHs for other research. Each PAH fraction was evaporated to approximately 1 ml, transferred to a 1.5 ml amber ampoule and evaporated to dryness under a gentle stream of N_2 and re-dissolved in 100 μL of isooctane containing p-terphenyl-d_{14} as an internal injection standard for PAH analysis. PAH analyses were made using an Agilent Technologies 5975C quadrupole mass spectrometer coupled with an Agilent 7890A gas chromatograph equipped with a fused silica capillary DB-5MS column (30 m × 0.25 mm i.d., 0.25 μm film thickness) using He as carrier gas. Twenty-nine PAHs were analyzed including naphthalene (Na), 2-methyl-naphthalene (2MNa), 1-methyl-naphthalene (1MNa), 2,6-dimethyl-naphthalene (DMNa), acenaphthylene (Acy), acenaphthene (Ace), 2,3,5-trimethyl-naphthalene (TMNa), fluorene (Fl), dibenzothiophene (DBT), phenanthrene (Phe), anthracene (Ant), 3-methyl-phenanthrene (3MP), 2-methyl-phenanthrene (2MP), 9-methyl-phenanthrene (9MP), 1-methyl-phenanthrene (1MP), 3,6-dimethyl-phenanthrene (DMP), fluoranthene (Flu), pyrene (Py), benzo[a]fluorene (BaF), 1-methyl-pyrene (MPy), benzo[a]anthracene (BaA), chrysene + triphenylene (Chy), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[e]pyrene (BeP),

benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IP), dibenzo[a, h]anthracene (DBA) and benzo[ghi]perylene (BP). Procedural blanks were performed periodically to prevent contamination. The average recovery efficiencies of four surrogate compounds were $82 \pm 25\%$ in all samples.

Diagnostic ratios of PAHs

The method of PAH diagnostic ratios has been successfully applied in source characterization of PAHs in sediments (e.g., Yunker et al. 2002; Zakaria et al. 2002). Here, we apply a number of diagnostic PAH ratios and their respective source characteristics, with some cautions recommended by Tobiszewski & Namiesnik (2012). Some ratios were used to distinguish between petrogenic and pyrogenic sources including methyl-phenanthrenes/phenanthrene (MP/P), Pyrogenic Index ($\sum$3–6 ring PAHs/C_0–C_4 Na, Phe, DBT, Fl, Chy), Ant/Ant + Phe (Ant/178), BaA/BaA + Chy (BaA/228) and 4,5,6 rings PAHs/total PAHs (4,5,6 rings/TPAH$_{29}$) (Prahl & Carpenter 1983; Wang et al. 1999; Yunker et al. 2002; Zakaria et al. 2002; Yan et al. 2004). To distinguish PAHs from incomplete combustion of organic materials and liquid fossil fuel, we used Flu/Flu + Py (Flu/202) and IP/IP + BP (IP/276) (Yunker et al. 2002).

Statistical analysis

Analysis of variance and Duncan test were performed to determine any significant differences in PAH concentrations in the surface sediments. Differences were considered significant only when p values were lower than 0.05. Prior to the analysis, the data were inspected for homogeneity of variance (Levene's test). Pearson's correlation coefficients with two-tailed test of significance (at 0.05 significance level) were used to evaluate the relationships among the PAH compositions and TOM, as well as particle size fractions (Zar 1999). All statistical calculations were carried out using SPSS 15 for windows.

RESULTS AND DISCUSSION

The results of %TOM and particle size fractions in surface sediment samples from the southwest Caspian Sea are presented in Table 1. TOM contents ranged from 2.2 to 11.4%, with an average value of 5.8%. Sediment grain size fractions were classified as clay ($<4\,\mu m$), silt (4–$63\,\mu m$) and sand (63–$2,000\,\mu m$). Sand generally predominates in most of the samples, although silt is a dominant fraction in some samples (TR1, TS2 and TA2). No statistically

significant correlation between %TOM and grain size fractions was detected.

PAH composition

In total, 29 PAH compounds were identified and quantified. An average PAH molecular profile with upper and lower limit bars is shown in Figure 2. Overall, a large proportion of the sediment PAH load arises from 2–4 ring compounds (both parent and alkylated derivatives), with lesser contribution from 5–6 ring PAHs. The most dominant PAH compounds in the study area are Phe, DMNa, Py and Na. A typical profile of petrogenic PAHs, with a predominance of alkyl-substituted naphthalenes and phenanthrenes, is evident at most of the sites, as previously reported at Iranian coasts of the Caspian Sea (Tolosa et al. 2004). This finding means that petrogenic PAHs remained the same over the 12 years.

PAH concentrations and contamination levels

Only one station in the study area (TR3) exceeds the 1,000 ng g^{-1} sediment quality threshold, which can point to a low risk of liver disease, reproductive impairment and potential effects on growth for bottom-dwelling fishes (Johnson et al. 2002) at the Guilan Province coasts. To assess the potential effects of PAHs determined in samples, each PAH compound and total PAH levels in sediments were compared with the effects-based sediment quality guideline values (SQG) (Long et al. 1995), shown in Table 2. Results showed that total PAH concentrations at all sites were below the effects range low (ERL), but some individual PAHs such as 2MNa, Fl and Phe at some stations (Table 2) were significantly above their ERL. Further, mean ERL quotients were calculated for each station, and also for each PAH compound in the study area, to evaluate the potential ecological risk (Long et al. 1998). All sites had mean PAH ERL quotients <1 (0.08–0.39) (Table 1); therefore, adverse effects to the ecology of the study area are not predicted to occur extensively. However, higher mean ERL values at most of the offshore stations (Table 1) suggest higher risk of toxicity (Long et al. 2006). Mean ERL quotient for each compound (20 PAH compounds, Table 2) ranged from 0.01 to 0.86. The majority of individual PAHs had mean ERL quotients less than 0.2 in the study area. Higher mean ERL quotients for Fl (0.86), C1-phenanthrene (0.46), Phe (0.36), 2MNa (0.34), DMNa (0.34), Acy (0.31), 1MNa (0.24) and Na (0.23) represent higher risks of toxicity
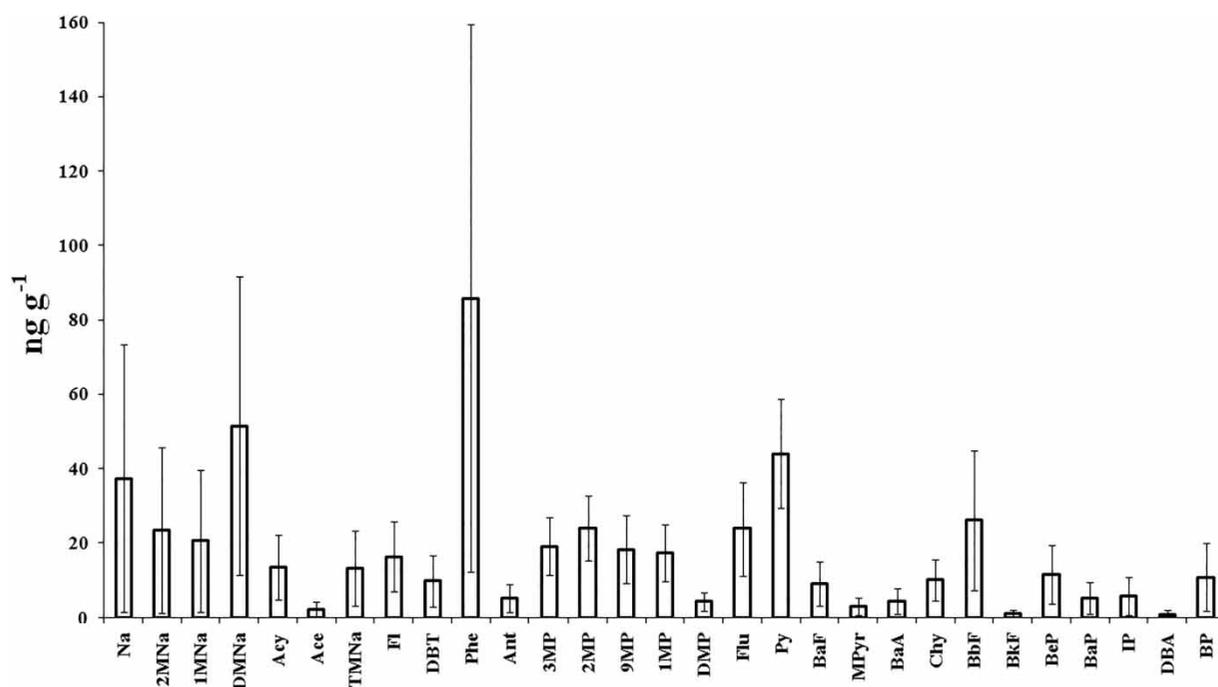
Figure 2 | Molecular profile of sedimentary PAHs with mean concentrations and standard deviations. For abbreviations, see text.

and these individual PAHs could be focused upon in pollution prevention programs in the southwest Caspian Sea.

PAH distribution pattern

In general, total PAH concentrations increased offshore (Table 1). Only at Astara transect (TAs), the nearshore station (TAs1) showed higher concentration of PAHs compared to offshore stations, but was not significant ($p > 0.05$). Only offshore stations TR3 and TK3 showed a significant difference ($p < 0.05$) in total PAH concentrations from their onshore stations (depth 10 and 20 m). Offshore increases of total PAH concentrations appear to contradict the fact that sedimentary PAH concentrations must be decreased further offshore, as a result of a smaller contribution of lateral transport of PAHs resulting from sedimentation (Boonyatumanond et al. 2006). Organic matter content and sediment grain size have been reported as main factors that control the hydrophobic organic contaminant (such as PAHs) distribution in aquatic ecosystems (Bouloubassi et al. 2012, and references therein). In this regard, correlation between total PAH concentrations and both %TOM and particle size fractions were assessed. There were no significant correlations between total PAH concentrations and particle size fractions, but %TOM showed positive significant correlation with total PAH concentrations ($r = 0.56$, $p < 0.05$). Conversely, the

increased PAH concentrations in offshore sediments are correlated with increased TOM content of sediments. However, in previous investigations of Caspian Sea sediments, no significant correlations were reported between total PAH concentrations and both %TOM and particle size fractions (Tolosa et al. 2004).

There was no significant difference between total PAH concentrations at onshore stations (depth 10 m) along the west–east transect. TS2 (in the Kapurchal delta) with the highest total PAH concentrations along the west–east transect (depth 20 m), showed significant differences only with TAs2 and TK2 ($p < 0.05$). Significant differences of total PAH concentrations were found along the offshore transect (depth 50 m), including three groups (TR3; TA3, TK3; TAs3).

To better represent the distribution patterns of PAHs from petrogenic and pyrogenic sources, NPD (sum of Na, DBT, Phe, and their alkylated homologs) as a petrogenic indicator (Boitsov et al. 2009) and COM (sum of Flu, Py, BaA, Chy, BbF, BkF, BeP, IP and BP) as a pyrogenic indicator (Bouloubassi & Saliot 1993) were calculated (Table 1). The dominance of NPD (35.4–74.4%) compared to COM compounds (18.1–47.4%) in the samples revealed the dominance of petrogenic sources in the study area. Overall, the distribution pattern of NPD and COM concentrations was similar to that of total PAH concentrations. There were no significant correlations between NPD, COM concentrations and particle size fractions. TOM content only

Table 2 | Concentration ranges of PAHs in sediment (ng g^{-1}) from the southwest Caspian Sea and SQGs (Long *et al.* 1995)

Compound (abbreviation)	SGQ (ng g^{-1} dry weight)		PAH concentration			
	ERL	ERM[a]	Min.	Max.	Average	Stations > ERL
Naphthalene (Na)	160	2,100	2.2	144.8	37.5	–
2-Methyl-naphthalene (2MNa)	70	670	nd	95.4	23.6	TR3; TK3
1-Methyl-naphthalene (1MNa)	85	800	nd	79.9	20.8	–
C2-Naphthalenes (DMNa)	150	1,450	nd	140.2	51.6	–
Acenaphthylene (Acy)	44	640	nd	30.4	13.5	–
Acenaphthene (Ace)	16	500	0.8	8.3	2.4	–
Fluorene (Fl)	19	540	5.9	43.5	16.3	TR3; TS2; TK3; TKb1,2
Dibenzothiophene (DBT)	190	1,200	nd	21.8	9.9	–
Phenanthrene (Phe)	240	1,500	37.9	332.1	85.8	TKb2
Anthracene (Ant)	85	1,100	1.7	16.1	5.4	–
C1-Phenanthrenes (MP)	170	2,000	38.6	163.7	78.9	–
C2-Phenanthrenes (DMP)	200	2,500	nd	7.4	4.4	–
Fluoranthene (Flu)	600	5,100	11.1	48.7	23.9	–
Pyrene (Py)	665	2,600	20.8	63.2	44.0	–
Benzo[a]anthracene (BaA)	260	1,600	0.2	16.1	4.6	–
Chrysene (Chy)	380	2,800	1.5	19.1	10.1	–
Benzo[a]pyrene (BaP)	430	2,800	0.2	23.7	5.3	–
Indeno[123-cd]pyrene (IP)	240	950	nd	34.8	5.9	–
Dibenzo[ah]anthracene (DBA)	63	260	nd	4.8	1.0	–
Benzo[ghi]perylene (BP)	85	330	nd	36.2	10.9	–
Total PAHs	4,022	44,792	232.1	1,014	520	–

[a]The effects range median.

revealed positive significant correlation with COM concentrations ($r = 0.675$, $p < 0.05$). The distribution pattern of normalized NPD and COM concentrations (divided by % TOM) are shown in Figure 3. A decreasing trend of normalized NPD concentrations was observed with increasing depth from 10 to 20 m. At greater depths, normalized NPD concentrations increased with increasing depth from 20 to 50 m, except at Anzali transect (TA3, Figure 3). Normalized COM concentrations decreased with increasing depth from 10 to 20 m at TAs, TK and TKb, whereas its values increased
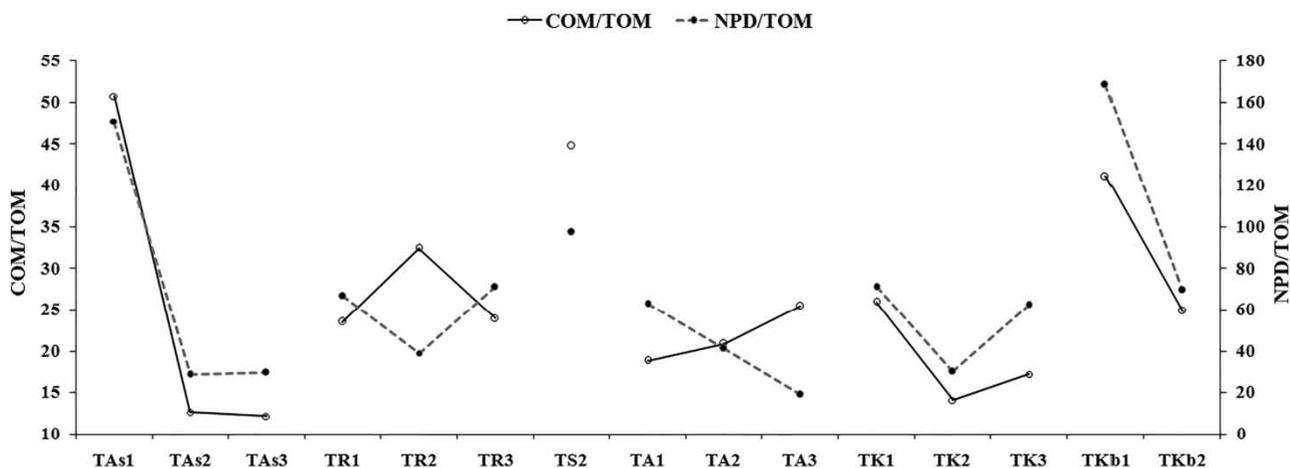

Figure 3 | Distribution of organic matter (TOM) normalized concentrations of NPD and COM. For abbreviations, see text.

at TR and TA. A decreasing trend of normalized COM concentrations was observed with increasing depth from 20 to 50 m at two transects (TAs and TR), whereas its values increased at TA and TK (Figure 3). Normalized NPD and COM concentrations did not reveal distinct trends along the west–east direction of the studied coasts. The increase of normalized NPD and COM concentrations at eastern stations in the Sefidrud delta (TKb1 and TKb2) would be a result of eastward currents on the shelf of the southwest Caspian Sea (Tuzhilkin & Kosarev 2005; Zaker *et al.* 2011), which transported PAHs to eastern parts of the Sefidrud delta.

Sources of PAHs

To survey the sources of PAHs in the surface sediments of the Southwest Caspian Sea, PAH cross-plots for some ratios were plotted (Figure 4). Values of Ant/178 (<0.1) and Flu/202 (mostly <0.4) ratios in surface sediments (Figure 4) suggest that a petrogenic source (Yunker *et al.* 2002) is the main source of PAH compounds in the study area. However, Flu/202 ratios at two deltaic stations (TS2 and TKb2) suggest a petroleum combustion source. Different depositional regimes of the Kapurchal and Sefidrud
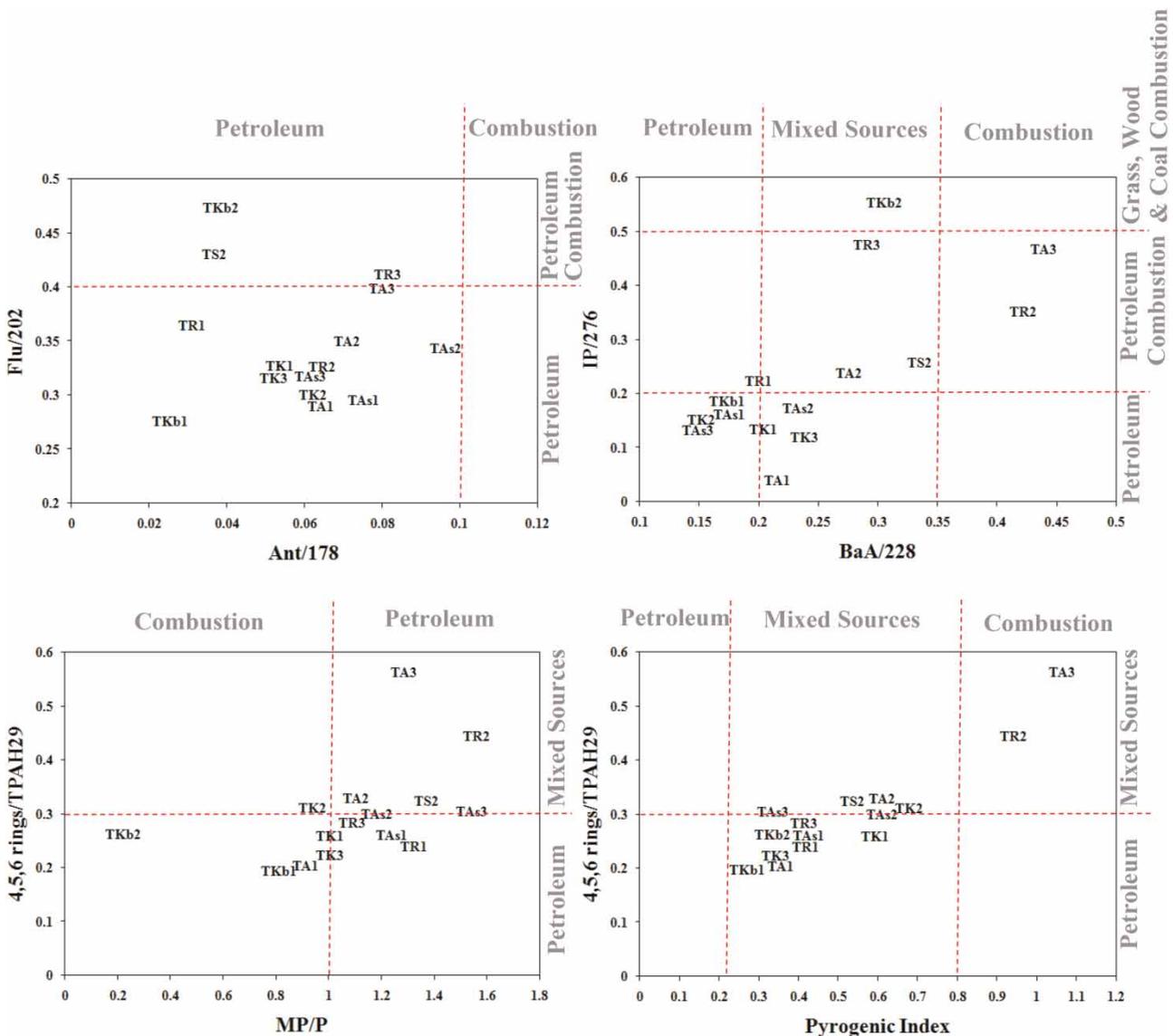
Figure 4 | Cross-plots of diagnostic ratios: Ant/178 versus Flu/202, BaA/228 versus IP/276, MP/P versus 4,5,6 rings/TPAH$_{29}$, Pyrogenic Index versus 4,5,6 rings/TPAH$_{29}$. Dashed lines reveal the proposed intercept values between different sources.

deltas may be responsible for sinking more pyrogenic PAHs at these stations compared to other stations. The cross-plots for other ratios (Figure 4), however, suggest an admixture of pyrolytic and fossil contributions. Values of BaA/228 ratios (Yunker et al. 2002) suggest a mixed petrogenic–pyrogenic (0.2 < BaA/228 < 0.35) source in most of the samples, and pyrogenic sources (BaA/228 > 0.35) at TA3 and TR2. IP/276 ratio confirmed the petroleum combustion source of PAHs at TS2, as indicated by Flu/202, whereas wood combustion is suggested as a main source of PAHs at TKb2. The main PAH sources indicated by IP/276 and BaA/228 ratios are contrary to the dominance of petrogenic PAHs (NPD) in the study area. Parent PAH isomeric ratios may be much less sensitive to petroleum-derived inputs than to combustion sources and may fail to identify fossil PAH contributions since they do not take into account compounds (e.g. alkyl-PAHs) that are at higher levels in petroleum sources (Bouloubassi et al. 2012), whereas alkylated naphthalene and phenanthrene derivatives are dominant in our samples (Figure 2). MP/P ratios measured in combustion mixtures are generally less than 1, while unburned fossil PAH mixtures typically display a range of values from 2 to 6 (Prahl & Carpenter 1983). Values of MP/P ratio are mostly greater than unity in our samples (Figure 4), similar to surface sediments of Malaysian coasts (Zakaria et al. 2002) and core sediments from Todos os Santos Bay in Brazil (Wagener et al. 2010) that are heavily impacted by petrogenic PAHs. The 4,5,6 rings/TPAH$_{29}$ ratios (Yan et al. 2004) reveal that the source of PAHs at most stations is petrogenic (4,5,6 rings/TPAH$_{29}$ < 0.3), but at some stations where 0.3 < 4,5,6 rings/TPAH$_{29}$ < 0.7 the source of PAHs is mixed petrogenic–pyrogenic. Petrogenic sources for PAHs, suggested for the majority of stations by 4,5,6 rings/TPAH$_{29}$ ratios, confirm the weakness of some parent PAH isomeric ratios to identify petrogenic sources in areas that receive PAHs from different sources, especially in the southwest Caspian Sea which receives both oil pollution, mostly from Azerbaijan oil fields, and pyrogenic PAHs from the catchment area.

The Pyrogenic Index (Wang et al. 1999) at most stations gave values between petrogenic (0.004–0.019) and pyrogenic (0.8–2) sources (Figure 4). At two stations (TA3 and TR2), however, the Pyrogenic Index suggested a pyrogenic source for PAHs. These results contradict the sources identified for TA3 and TR2 by Ant/178, MP/P and 4,5,6 rings/TPAH$_{29}$ ratios that suggest mixed sources. However, in this study, the Pyrogenic Index was calculated without alkylated derivatives of DBT, Fl and Chy; their inclusion would probably have decreased the Pyrogenic Index to levels in

accordance with a petrogenic source. Wagener et al. (2010) have reported a weakness of the Pyrogenic Index for samples containing weathered oil residues, similar to those that occur in the southwest Caspian Sea.

According to Bonini et al. (2013), oil seepage occurs at the base of the main mud volcanoes of Azerbaijan. Natural seep oils are normally characterized by a high percentage of unresolved complex mixture (UCM) and low absolute concentrations of alkanes and naphthalene-derived compounds, whereas the opposite is found in oil production areas (Tolosa et al. 2004). In our results, a typical profile of petrogenic PAHs, with a predominance of alkyl-substituted naphthalenes and phenanthrenes is evident at most of the sites. Therefore, the role of natural oil seeps may be low and mainly derived from anthropogenic sources (oil production platforms or recent oil spillages).

CONCLUSIONS

The concentrations of PAHs found in surface sediments of the Iranian coasts in the southwest Caspian Sea (TPAH$_{29}$ = 232.1–1,014 ng g^{-1}) indicate moderate contamination in relation to global levels of PAH contamination, and are comparable to a previous report of PAH concentrations in this area 12 years ago (Tolosa et al. 2004). The predominance of alkyl-substituted naphthalenes and phenanthrenes and also higher contribution of petrogenic compared to pyrogenic compounds in the PAH composition of samples reveal the ubiquitous nature and dominance of anthropogenic (mostly petrogenic) sources in the study area. The offshore increase of total PAH concentrations was found to be mostly simultaneous with increases of the organic matter content of sediments. The evaluation of ecotoxicological risk indicated that total PAH concentrations at all sites were below the ERL, but at some stations individual PAHs such as 2MNa, Fl and Phe were significantly above their ERL, and should be considered in relation to pollution prevention programs in the Caspian Sea. According to values of the diagnostic ratios used in this study, most stations revealed a petrogenic source as a major source of the PAHs, but values for some stations suggested mixed petrogenic–pyrogenic sources. However, some parent PAH isomeric ratios (e.g. IP/276) failed to identify the fossil PAH contributions.

There remains the important work of cross-checking with other indicators such as UCM in the aliphatic fraction for chronic oil contamination, and for other alkylated derivatives of PAHs (especially C$_0$–C$_3$ Fl, DBT and Chy). In addition, analysis of geochemical biomarkers, such as

hopanes and steranes, is necessary to fingerprint (Tolosa *et al.* 2004; Wagener *et al.* 2010) spilled oils and natural seep oils of mud volcanoes in the southwest Caspian Sea; these will feature in future studies.

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