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Baseline

Occurrence and bioaccumulation of persistent toxic substances in sediments and biota from intertidal zone of Abu Ali Island, Arabian Gulf

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ABSTRACT

North Abu Ali Island is contaminated by crude oil from exogenous sources with a variety of persistent toxic substances (PTSs) being input into intertidal sediments. We detected an array of PTSs in sediments and benthic biota off north Abu Ali Island (Arabian Gulf), including 35 polycyclic aromatic hydrocarbons (PAHs), 6 alkylphenols (APEOs), 10 styrene oligomers (SOs), and tributyltin. The PTS concentrations were generally greater than those reported in other areas of Arabian Gulf. PAHs mainly originated from petrogenic sources, and APEOs and SOs seem to be of recent origin. Field-based biota-sediment accumulation factors (BSAF) varied by taxa and compounds, but clearly depended on the log K_{ow} values of individual compounds. Some PTSs exceeded the established guidelines for sediments and biota; we found particularly great BSAFs for alkyl-naphthalenes (C1- and C2-), nonylphenol monoethoxylates, and *2,4,6*-triphenyl-*1*-hexene. Remediation will require on-site clean-up of toxic chemicals together with immediate efforts on preventing input of current pollution sources in the given area.

Coastal pollution by persistent toxic substances (PTSs) in sediments is primirily due to human activities associated with population growth and expansions of industrial and commercial developments. It is well known that PTSs accumulated in sediments adversely impact benthic ecosystems in a variety of ways (Hong et al., 2012; Bae et al., 2017; Lee et al., 2017; Khim et al., 2018). Many PTSs have been studied to understand their fate and bioaccumulation patterns, including investigations of pollutants associated with the polycyclic aromatic hydrocarbons (PAHs), alkylphenol ethoxylates (APEOs), styrene oligomers (SOs), and tributyltin (TBT) (Hong et al., 2016; Kim et al., 2017; Lee et al., 2017; Yoon et al., 2017). Although PTSs have long been studied in coastal environments worldwide, little is known about the distributions and/or bioaccumulation of PTSs in the Arabian Gulf, an area that produces immense quantities of fossil fuels, a known source of PTSs.

PAHs intentionally or unintentionally originate from a variety of sources, including spills of crude and refined oils, incomplete combustion of fossil fuels and wood, coal soot, and from processes involved with smelting metals (Lin and Zhu, 2004; Moon et al., 2006; Ghosh et al., 2015). PAHs are ubiquitous contaminants and are a major component of toxic substances polluting coastal areas adversely impacting the marine ecosystem health because they often accumulate in great concentrations in benthic biota and biomagnify along food chain (Neff, 1979, 2002; Gewurtz et al., 2000).

APEOs are extensively used as nonionic surfactants by industries and households (White et al., 1994). APEOs include nonylphenol polyethoxylates (NPEOs) and octylphenol polyethoxylates (OPEOs), which degrade (via microbial and photochemical processes) to nonylphenols (NPs) and octylphenol (OP), respectively (Li et al., 2013). NPs and OP are endocrine disruptors that adversely affect biota, causing reduced fertility and other adverse developmental, reproductive, neurological, and immunological problems (Giesy and Snyder, 1998; Chen and Yen, 2013).

SOs are emerging contaminants, mostly reported from sediments and beach sands in developed coastal areas worldwide (Kwon et al., 2015; Hong et al., 2016; Lee et al., 2018). SOs originate from the degradation of polystyrene plastics at temperatures of 240–300 °C (Kwon et al., 2014). SOs may cause adverse effects in aquatic biota due to their genotoxic and reproduction toxicities (Ohyama et al., 2001; Tatarazako et al., 2002). However, because SOs are recently recognized as a class of PTS, only a few studies have been conducted on them, limiting to the

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reports of sedimentary distributions in coastal areas.

TBT, a form of butyltins, is mainly used as an antifouling agent in marine paints and industrial applications (Hoch, 2001). TBT is well known endocrine disruptor and leads to deformed growth, impaired reproduction, and sexual disorders (e.g., imposex in sea snails) (Bryan and Gibbs, 1991; Matthiessen and Gibbs, 1998). Due to these adverse effects on marine organisms, the International Maritime Organization (IMO) adopted a ban on the use of TBT in 2003, but some countries still use TBT or have not implemented the ban entirely (Kim et al., 2017).

The ratio of a chemical concentration in an organism to its concentration in sediment (i.e., biota-sediment accumulation factor, BSAF) is an indicator of pollutant bioavailability. BSAF values are often used to predict the accumulation of toxic chemicals in biota of ecosystems. Predicted residue chemicals in biota can be estimated by examining the relationship between the amount of the compound in lipids of biota and the concentration of the compound in the organic carbon of sediments. Field-based BSAFs can be used to assess the risk of bioaccumulation and biomagnification of pollutants and for identifying remedial options for sites with contaminated sediments (Kang et al., 2002; Burkhard, 2009; Zhao et al., 2016).

The Arabian Gulf is a large embayment, characterized by shallow depths, weak clockwise counter-currents, high air and water temperatures, and high salinity. Because water residence time is long (i.e., turnover takes several years) in Arabian Gulf waters, natural purification is difficult and complex (Reynolds, 1993). However, the Arabian Gulf has been contaminated by a variety of human activities, such as the Gulf War Oil Spill (GWOS) in 1991, numerous smaller oil spills, terrestrial runoff, and contaminated groundwater inputs from coastal refineries (de Mora et al., 2003; Bejarano and Michel, 2010; Saeed et al., 2017). Many contaminant studies have been conducted in the Arabian Gulf since the 1991 GWOS, mainly oil-derived chemicals, such as aliphatic hydrocarbons, PAHs, and metals (Freije, 2015; Youssef et al., 2015; Albano et al., 2016; Jafarabadi et al., 2018; Keshavarzifard et al., 2018). However, insufficient research has been conducted on endocrine disruptors and other emerging contaminants, such as chemical pollutants derived from plastics.

Abu Ali Island is located in the Arabian Gulf about in the middle of the eastern coast of Saudi Arabia, northeast of the industrial city of Jubail. Although a sanctuary project (Jubail Marine Wildlife Sanctuary) and a few studies (e.g., aquatic pollution studies) have been conducted near Abu Ali Island, the island was only included as one site of a more extensive Arabian Gulf pollution study, even though it was seriously impacted by the GWOS (Michel et al., 1993; Bejarano and Michel, 2010; de Mora et al., 2010). In addition, studies looking for the ecological response to spilled oil have been limited to specific taxa, such as cyanobacteria community and some macroalgae or seagrasses until now (De Clerck and Coppejans, 1994; Barth, 2003; Al-Thukair et al., 2007). The purpose of the present study was to assess the recent condition of Abu Ali Island and the nearby coastal waters of the Arabian Gulf. Specifically, we: (1) investigated the occurrence of PTSs in sediments and biota in the intertidal zone of north Abu Ali Island; (2) identified potential sources and recent inputs of pollutants by analyzing the composition of chemicals in sediments and benthic biota; (3) investigated field-based BSAF values for characterizing the sediment/biota connection; and (4) identified the chemicals of concern presently impacting the coastal area of Abu Ali Island.

Abu Ali Island is impacted by pollution from industrial and municipal areas located on the island and from nearby coastal cities. The northern shoreline of Abu Ali Island is covered by an asphalt mat, comprised of an immense quantity of crude oil and sand hardened by heat and time. The northern shore of the island intercepted most of the 1991 GWOS, thus inhibiting the spread of the spilled oil to the south. In December 2016, we collected surface sediment (upper 2 cm) and biota samples (e.g., polychaetes, chitons, snapping shrimps, and crabs) at three sites (4 km interval) in the intertidal zone on the north part of Abu Ali Island (Fig. 1). Samples were collected using a stainless steel spatula and hand catch. All field samples were transferred to ice coolers, transported to the lab, and stored at −20 °C until analyzed. The water content of wet sediments was calculated three times by measuring weight loss after drying at 70 °C for 48 h. We measured the grain size distribution of sediments using the dry sieve and pipette method. We determined lipid content of biota gravimetrically. To analyze sediment organic carbon content, we acidified 2 g of dried sediment with 1 M HCl, rinsed the sample with distilled water, and then freeze-dried it.

We prepared all samples for analyses of (alkyl-) PAHs, APEOs, and SOs in sediments and biota following the methods of Khim et al. (1999) and Hong et al. (2016), but with minor modifications. To prepare samples, we weighted to about 10 g of sediment and extracted (alkyl-) PAHs, APEOs, and SOs for 16 h with 300 mL dichloromethane (DCM) (Burdick & Jackson, Muskegon, MI) using a Soxhlet extractor. We extracted 1 g of pre-cleaned and homogenized samples of biota three times with 6 mL of DCM with 5 g pre-combusted sodium sulfate in a Teflon tube. Five surrogate standards (SS) were added before extraction: acenaphthene-d10, phenanthrene-d10, chrysene-d12, perylene-d12, and bisphenol A-d16. We then added activated copper (Sigma Aldrich, Saint Louis, MO) to remove elemental sulfur. Extracts were concentrated and fractionated by passing them through an 8 g silica gel column (70–230 mesh) (Sigma Aldrich). We eluted the first fraction (F1) [for (alkyl-) PAHs and SOs] with 50 mL of 20% DCM in hexane (Burdick & Jackson). We then eluted the remaining APEOs in the second fraction (F2) with 50 mL of 40% acetone in DCM. After concentrating the extracts, we added 2-fluorobiphenyl as an internal standard.

We modified our analytical procedure for TBT after Shim et al. (1998) and Choi et al. (2009). Sediments and biota samples were weighted to about ~0.5–1.0 g in a Teflon tube and extracted twice by shaking samples for 3 h with 0.1% tropolone-methylene chloride (Sigma Aldrich) and 6 N hydrochloric acids (HCl) (Sigma Aldrich), then adding diphenyltin dichloride as a SS. After centrifuging and concentrating extracts under N_2, extracts replaced with hexane and hexylated them with 500 μL of Grignard reagent (Sigma Aldrich). Then, the remained Grignard reagent in the extract was removed by 10 mL of 1 N sulfuric acid (Sigma Aldrich). The aqueous layer, formed by sulfuric acid input, extracted with hexane was purified with Florisil (activated magnesium silicate) prior to subjecting it to column chromatography. Then the cleaned extracts were concentrated and spiked with terphenyl-d14 (Supelco, Bellefonte, PA) as an internal standard.

We quantified 35 (alkyl-) PAHs, 6 APEOs, 10 SOs, and TBT with an Agilent 7890A gas chromatograph equipped with a mass selective detector (GC-MSD, Agilent Technologies, Santa Clara, CA). We equipped a DB-5MS Ultra Inert fused silica capillary column (30 m long, 0.25 mm i.d., 0.25 μm film thick, Agilent) for chromatographic separation. Details on the instrumental condition for PAHs, APEOs, SOs, and TBT analyses are provided in Table S1 of Supplementary Materials (S). Sediment organic carbon was analyzed using an elemental analyzer (Elementar, Hanau, Hesse, Germany).

Concentration ranges for method detection limits (MDLs) were 0.27 to 0.90 ng g^{-1} for PAHs, 0.10 to 0.91 ng g^{-1} for APEOs, 0.24 to 0.91 ng g^{-1} for SOs, and 1.3 ng g^{-1} for TBT. The mean recovery percentages for the five SS were generally within acceptable ranges (e.g., 80–112% for PAHs and SOs, 79% for APEOs, and 86% for TBT) (Table S2). The concentration of sediment samples was expressed at the dry weight (dw) in ng g^{-1}. Because other PAH criteria for biota are not available, we compared the concentration of PAHs in our invertebrate samples with the Environmental Assessment Criteria for bivalves established by the OSPAR Commission (OSPAR, 2009). We defined field-based BSAF, based on Eq. (1), as:

$$\text{Field} - \text{based BSAF} = (C_b/f_{lipid})/(C_s/f_{soc}) \quad (1)$$

where C_b is the concentration of PTSs in the biota (ng g^{-1} wet weight; ww), f_{lipid} is the lipid content of biota (%), C_s is the concentration of

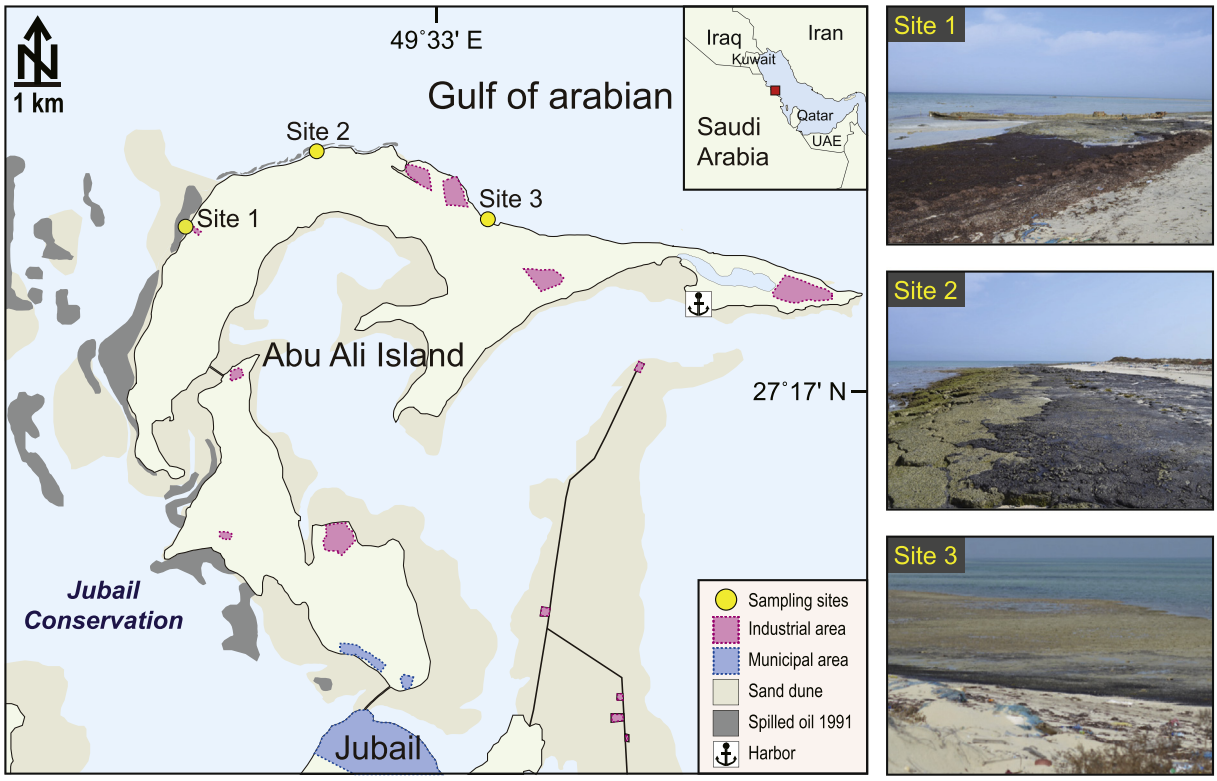

Fig. 1. Sampling sites of the intertidal zone of Abu Ali Island. Images on the right side depict the appearance of each site.

PTSs in sediment (ng g^{-1} dw), and f_{soc} is the fraction of sediment organic carbon (%). Log octanol-water partition coefficient (log K_{ow}) values of PTSs were used from Ahel and Giger (1993), Kang et al. (2014), Hong et al. (2016), and Pub-Chem data base (Available online at https://pubchem.ncbi.nlm.nih.gov/). SigmaPlot 13.0 software (Systat Software Inc., San Jose, CA) was used to analyze data statistically. Linear regression statistics were used to evaluate the strength between BSAF and log K_{ow}.

The PTSs [(alkyl-) PAHs, APEOs, SOs, and TBT] were detected in all sediment samples collected from Abu Ali Island (Fig. 2). The distributions of PTSs among sites varied by the chemical. For example, the concentration of (alkyl-) PAHs at Site 1 was 12,340 ng g^{-1} dw, but concentrations at Sites 2 and 3 were < 200 ng g^{-1} dw, despite the sites being outwardly similar (Table S3). At Site 1, we found small asphalt pellets in sediments, but these were absent from the other two sites, indicating that asphalt pellets caused different concentration among sites. The concentrations of APEOs and SOs in sediments were generally lesser than 100 ng g^{-1} dw. The concentrations of TBT ranged from 8 to

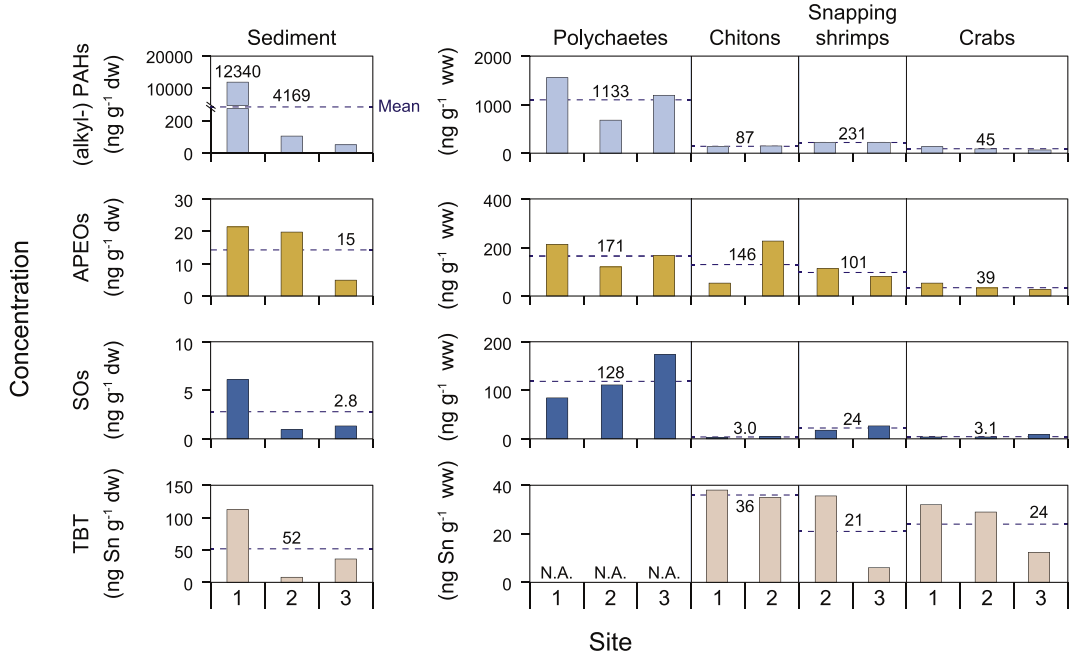

Fig. 2. Concentrations of persistent toxic substances in sediments and biota from samples collected from the intertidal zone of three locations on Abu Ali Island.

Table 1
Comparison of persistent toxic substances in sediments collected from the Arabian Gulf and previous studies [Min.–Max. (Mean)]. Two significant digits were used in the table.

Country	Sampling year	Sampling area	n	16 PAHs	Alkyl-PAHs	APEOs	SOs	TBT	References
				(ng g^{-1} dw)	(ng g^{-1} dw)	(ng g^{-1} dw)	(ng g^{-1} dw)	(ng Sn g^{-1} dw)	
UAE	2000	Bay and coastal	6	0.1–4.0 (1.3)	0.4–9.4 (3.2)[a]	–	–	–	Tolosa et al. (2005)
Qatar			5	0.1-66 (21)	0.6–92 (30)	–	–	–	
Bahrain			4	11.4–6100 (1800)	13–6600 (1920)	–	–	–	
Qatar	2000	Bay and coastal	5	–	–	–	–	0.03–1.7 (0.5)	de Mora et al. (2003)
UAE			6	–	–	–	–	0.04–0.07 (0.05)	
Bahrain			4	–	–	–	–	0.2–80 (11)	
Saudi Arabia	2005	Bay and coastal	8	0.1–3.0 (1.5)	13–130 (38)	–	–	–	de Mora et al. (2010)
Bahrain			5	2.3-1700 (380)	13.6–3500 (390)	–	–	–	
Qatar			5	0.3–68 (17)	6.0–140 (48)	–	–	–	
Kuwait			10	0.8–430 (70)	12–1700 (17)	–	–	–	
UAE			10	0.3–76 (9.1)	8.9–140 (31)	–	–	–	
Iran			4	0.1–34 (12)	9.4–470 (180)	–	–	–	
Iran	2012	Coastal	11	9.7–47	–	–	–	–	Mirvakili et al. (2013)
Iran	2012	Intertidal and coastal	9	15–760 (210)	–	–	–	–	Aagh et al. (2016)
Iran	2012	Bay and coastal	30	93–4100 (1100)	–	–	–	–	Mirza et al. (2014)
Iran	2013	Coastal	6	9.3–200 (100)	–	–	–	–	Khazaali et al. (2016)
Kuwait	2013–2014	Bay and coastal	29	3.8–560 (43)	13–1300 (120)	–	–	–	Lyons et al. (2015)
Iran	2015	Coral reef	13		2.7–42 (14)	–	–	–	Jafarabadi et al. (2018) [a]
Iran	2015	Coastal	8	3.0–250 (72)	–	–	–	–	Akhbarizadeh et al. (2016)
Kuwait	2015–2016	Bay and coastal	5	–	–	0.2–2.8 (1.2)	–	–	Saeed et al. (2017)[b]
Qatar	2016	Coastal	11	3.2-14 (9.0)	–	–	–	–	Hassan et al. (2018)
Iran	2016	Intertidal	16	1.8–81 (18)	–	–	–	–	Keshavarzifard et al. (2018)
Saudi Arabia	2017	Coastal	3	3.8–150 (57)	54–12,000 (4200)	5.0–21 (15)	0.9–6.0 (2.8)	8–112 (52)	This study

- Not analyzed.
[a] 30 individual parent- and alkyl-PAHs.
[b] Octylphenol + nonylphenol.

110 ng g^{-1} dw and were relatively great in Site 1.

Relative to other parts of the Arabian Gulf, the concentrations of 16 PAHs in sediments were similar to or lesser than PAHs in sediments in Bahrain, Kuwait, and Iran, but greater than those in the United Arab Emirates (UAE) and Qatar (Table 1). Although there are regional specific differences, the concentration trend (since 2000) of 16 PAHs was similar. In 2005, a concentration of 3.0 ng g^{-1} dw of 16 PAHs was reported for coastal Abu Ali Island (de Mora et al., 2010), which is much lower than the concentrations of PAHs we recorded at Site 1 in 2016 (Fig. 2). Thus, either other researchers sampled at different locations than we did or more PAHs have accumulated since 2005. We detected the greatest concentrations of alkyl-PAHs, APEOs, and TBT in the sediments of Abu Ali Island. In fact, we found the concentration of alkyl-PAHs in Abu Ali Island to be twice as high as the greatest concentration detected in other regions of Bahrain, Kuwait, Iran, and UAE. It was much higher than what had been reported for Abu Ali Island in 2005 (de Mora et al., 2010). We also found the greatest concentrations of APEOs and TBT than had been previously reported for the Arabian Gulf, however, only one study each was comparable, respectively (de Mora et al., 2003; Saeed et al., 2017). Our study was the first to analyze SOs in sediments from the Arabian Gulf and the concentrations were lower than has been detected in other coastal areas of Korea (Yoon et al., 2017; Lee et al., 2018).

The PTSs were detected in all biota samples collected from the intertidal zone of Abu Ali Island (except for TBT in polychaetes; not analyzed) (Fig. 2). Concentrations of PTSs in biota varied widely, by site and taxon, probably due to differences in feeding behaviors among taxa (Hickey et al., 1995; Hong et al., 2015). For example, the greatest mean concentrations of PTSs were found in polychaetes, particularly PAH and SO concentrations, which were 4.9 to 43 times greater in polychaetes than in other taxa. These great concentrations were caused because deposit feeders tend to exhibit higher rates of bioaccumulation (Meador et al., 1995). Concentrations of APEOs were similar in polychaetes, chitons, and snapping shrimps. Great concentration of APEOs was detected in chitons collected from Site 2 (234 ng g^{-1} ww), but much smaller concentration was found in chitons at Site 1 (59 ng g^{-1} ww). Similarly, we detected relatively great concentrations of TBT in snapping shrimps and crabs collected from Sites 1 and 2, but smaller concentrations were found in snapping shrimps (6 ng g^{-1} ww) and crabs (12 ng g^{-1} ww). As the number of samples was smaller and the size of the biota was larger (Table S3), the concentration was greater, thus special caution should be given for the interpretation when sampling conditions vary (Wenzel et al., 2004; Kim et al., 2017).

All prior studies of PTSs in biota in the Arabian Gulf focused on bivalves and fish (de Mora et al., 2003; Tolosa et al., 2005; de Mora et al., 2010). Although the target taxa differed from those of other studies inhabiting the Arabian Gulf, the PTSs concentrations in benthic biota were greater than what other studies had detected except for TBT in bivalve (Table 2). Differences in biotic uptake of contaminants may be partially due to the tendency of benthic organisms to bioaccumulate toxins from sediments more than doing nekton (Wenzel et al., 2004; Moermond et al., 2005). Concentrations of APEOs have not been obtained for biota inhabiting the Arabian Gulf, but the concentrations in biota were similar to or less than concentrations detected in Gulf of Gdansk of Baltic Sea and East China Sea (Staniszewska et al., 2014; Gu et al., 2016). Our study is the first to analyze for SOs in biota in the world and so we could not compare our values with other studies. Based on the concentrations, we have found that SOs can have a negative impact on deposit feeders. The data of the present study will be compared to other studies in the future.

The composition of PTSs varied between sediments and biota and varied by site (Fig. 3). Variations among sites occurred due to

Table 2
Comparison of persistent toxic substances in biota collected from the Arabian Gulf and previous studies [Min.–Max. (Mean)]. Two significant digits were used in the table.

Country	Biota	Sampling year	n	16 PAHs	Alkyl-PAHs	APEOs	SOs	TBT	References
				(ng g^{-1} ww)	(ng g^{-1} ww)	(ng g^{-1} ww)	(ng g^{-1} ww)	(ng Sn g^{-1} ww)	
Qatar	Fish	2000	6	–	–	–	–	0.3–1.2 (0.6)	de Mora et al. (2003)[a]
UAE	Bivalve		28	–	–	–	–	23–196 (75)	
	Fish		13	–	–	–	–	0.08–0.3 (0.2)	
Bahrain	Bivalve		6	–	–	–	–	20–150 (85)	
	Fish		4	–	–	–	–	0.2–4.0 (1.7)	
UAE	Bivalve	2000	6	3.8–42 (16)	7.3–170 (45)	–	–	–	Tolosa et al. (2005)[a]
	Fish		4	1.1-2.9 (1.9)	3.1–5.9 (4.4)	–	–	–	
Qatar	Bivalve		1	5.2	21	–	–	–	
	Fish		4	2.1–3.3 (2.7)	5.9–23 (12)	–	–	–	
Bahrain	Bivalve		2	3.1–6.1 (4.6)	11–21 (16)	–	–	–	
	Fish		2	0.5–1.5 (1.0)	2.6–7.5 (4.8)	–	–	–	
Saudi Arabia	Bivalve	2005	2	2.8	22–30 (27)	–	–	–	de Mora et al. (2010)[a]
	Fish		3	0.4-0.9 (0.6)	11–16 (13)	–	–	–	
Bahrain	Bivalve		3	1.6–4.8 (2.9)	16–67 (35)	–	–	–	
	Fish		4	0.2–0.7 (0.4)	7.5–17 (11)	–	–	–	
Qatar	Fish		2	0.2–0.4 (0.3)	4.6–15 (10)	–	–	–	
Kuwait	Bivalve		3	3.0–18 (9.3)	29–270 (120)	–	–	–	
	Fish		2	0.6–0.7 (0.6)	16–17 (17)	–	–	–	
UAE	Bivalve		5	0.4–6.2 (2.4)	3.8–32 (19)	–	–	–	
	Fish		6	0.2–0.4 (0.2)	3.8–17 (9.0)	–	–	–	
Iran	Bivalve		1	6.4	70	–	–	–	
	Fish		4	0.1–2.6 (1.0)	4.0–110 (30)	–	–	–	
Saudi Arabia	Fish	–	54	–	–	–	–	8.7–20 (14)	Ashraf et al. (2017)[a]
Saudi Arabia	Polychaete	2017	13	260–450 (350)	630–1600 (1100)	130–210 (170)	89–180 (130)	–	This study
	Chiton		12	3.3–59 (31)	66–110 (87)	59–230 (150)	1.2–4.9 (3.0)	35–38 (36)	
	Shrimp		18	82–130 (110)	220–240 (230)	24–120 (100)	21–26 (24)	6–35 (21)	
	Crab		35	3.6–23 (9.9)	18–72 (45)	26–56 (39)	2.0–5.0 (3.1)	12–32 (24)	

- Not analyzed.
[a] The dry weight basis concentration was converted into wet weight assuming a water content of 80% (Stephen et al., 1985).

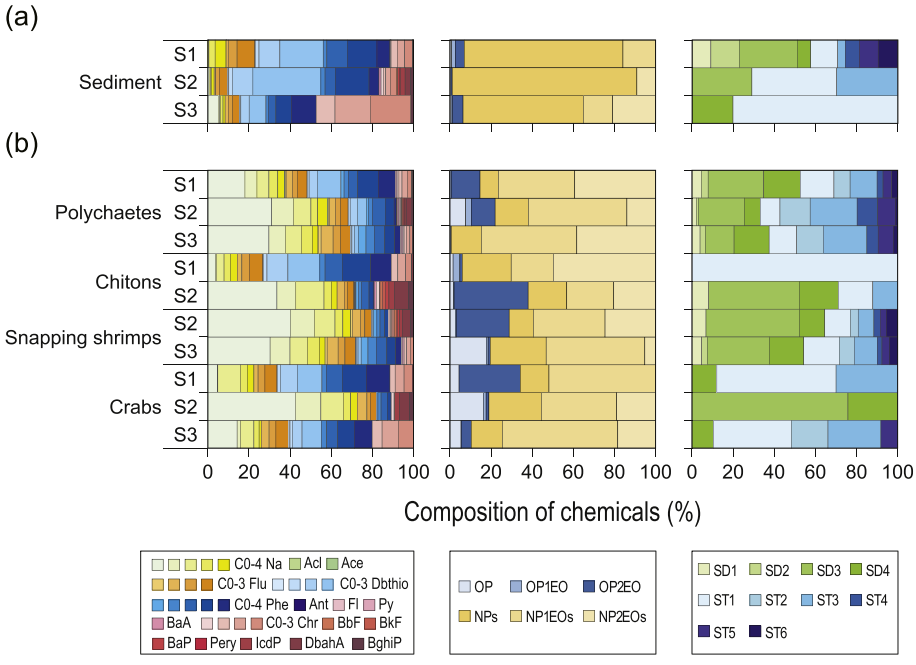

Fig. 3. Relative compositions of persistent toxic substances in (a) sediments and (b) biota obtained from intertidal samples from north Abu Ali Island. The acronyms of each compound were listed in Table S1.

differences in the weathering stage of PAHs in sediments among sites (Fig. S1) (Hong et al., 2012). PAHs in sediments and biota were predominaned by low molecular weight (LMW) and alkylated PAHs, suggesting a petroleum origin (Law and Biscaya, 1994). Alkyl-dibenzothiophene (Dbthio), -phenanthrene (Phe), and -chrysene (Chr) dominated sediments, whereas alkyl-naphthalene (Na) and -fluorene (Flu) dominated tissue in biota. This is because 2–3 PAH ring compounds (LMW) are metabolized less effectively than 4–6 PAH ring compounds (high molecular weight; HMW) (Neff, 2002). However, biota collected at Site 1 possessed relatively great concentrations of alkyl-Flu and alkyl-Phe, which one would expect in response to great concentrations of PAHs in the sediments of Site 1. The extent of

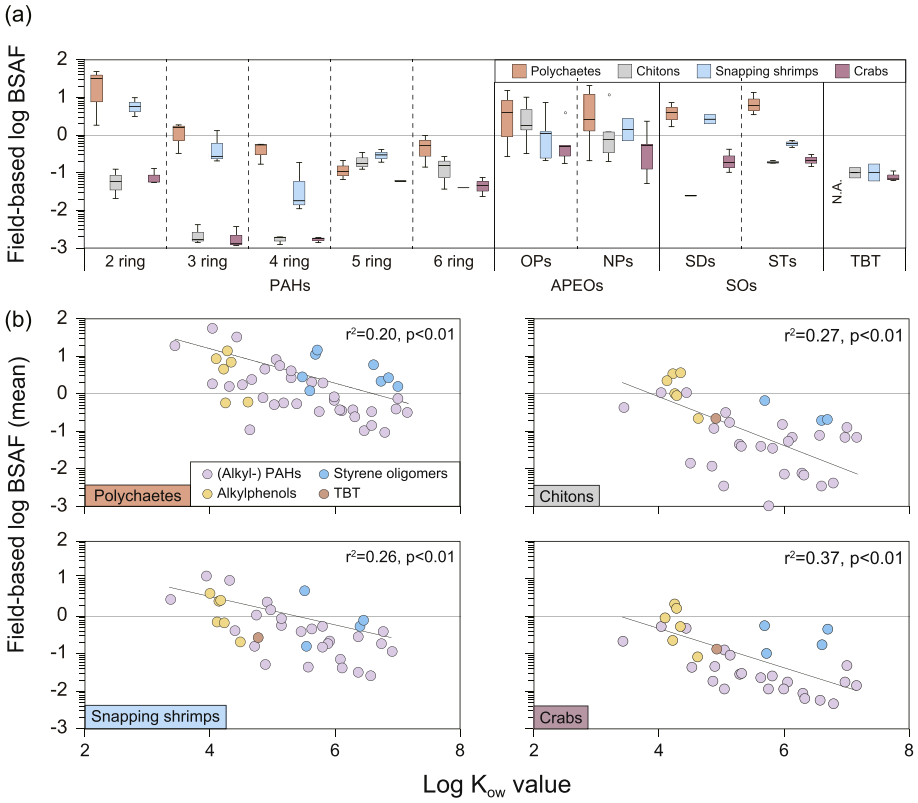

Fig. 4. Field-based biota-sediment accumulation factors (BSAFs) of persistent toxic substances relative to biota. Panels: (a) compound type by log BSAF values and (b) log K_{ow} values by log BSAF values.

alkylation of parent PAHs was generally great in sediments, mainly dominated by C3 and C4 alkyl-PAHs, whereas the C0–C2 alkyl-PAHs dominated tissues of biota (Fig. S2). This difference in PAH carbon chains between sediments and biota suggested that biota do not accumulate alkylated compounds much. The PAHs in the sediments of our study were found to be mostly petrogenic orgin (Fig. S3), but diagnostic ratios of individual chemicals suggest other sources, such as the combustion of biomass and coal. We speculated that PAHs in the sediments of Abu Ali Island originate primarily from petrogenic source, but some other sources of PAHs exist from nearby industrial areas.

There was a large difference in APEOs composition between intertidal sediments and biota. NPs mainly dominated sediments, whereas nonylphenol-monoethoxylates (NP1EOs), nonylphenol-diethoxylates (NP2EOs), and 4-tert-octylphenol-diethoxylate (OP2EO) dominated biota tissue. The ratio OP/(OP1EO + OP2EO) in sediments was < 1.0 at all sites, whereas the ratio of NPs/(NP1EOs + NP2EOs) was > 1.0. This difference suggested that OPEOs are being inputted to sediments much less than are NPs (Yoon et al., 2017). Furthermore, biota appeared to have accumulated more ethoxylated compounds than degraded ones. The predominance of ethoxylate compound could be caused by the effect of APEOs in dissolved phase or slower decomposition rates of APEOs in biota than in sediments (Bennett and Metcalfe, 2000; Rice et al., 2003; Klosterhaus et al., 2013).

SO compositions in sediment and biota showed site-specific or taxon-dependent signature. We detected more than nine SO compounds in the sediments of Site 1 and in polychaetes and snapping shrimps, with concentrations > 10 ng g^{-1} (sediment dw and biota ww). Among SOs, *2,4*-diphenyl-*1*-butene (SD3) and *1a*-phenyl-*4e*-(*1*-phenylethyl)-tetralin (ST3) dominated, followed by *2,4,6*-triphenyl-*1*-hexene (ST1) and *2,4,6*-triphenyl-*1*-hexene (SD4). In other tested sediments and biota, ST1 and SD3 dominated, but concentrations were < 10 ng g^{-1} (sediment dw and biota ww). The ratios of styrene dimers (SDs)/styrene trimers (STs) in sediment and biota varied, but ratios were all generally < 2.0. Hong et al. (2016) suggested that ratio values < 2.0 in sediments indicate that a site is impacted by nearby sources, such as industrial area, municipal area, local input, and wastewater treatment plant outfall. Therefore, we suggest that SO pollution is still being imported to intertidal sediments in north Abu Ali Island and that the biota is accumulating those pollutants.

We determined BSAFs of PTSs in the tissues of various taxa, based on the relative concentrations of PTSs in sediments and biota (Fig. 4a). We found that the log BSAFs of PAHs were compound-specific and species-specific, inversely proportional to ring number or molecular weight. In general, log BSAFs of LMW PAHs (i.e., 2- and 3-ring compounds) were in greater than HMW PAHs (i.e., 4–6 ring compounds). This difference was probably due to the higher bioavailability of petrogenic (LMW) PAHs than pyrogenic (HMW) PAHs. The log BSAFs of PAHs differed widely among taxa (Thorsen et al., 2004). We detected the great log BSAFs for PAH concentrations in polychaetes and snapping shrimps. The variations in log BSAFs among taxa is presumably due to variations in feeding behaviors, a species physiological capacity to bioaccumulate toxins, and/or metabolic differences among taxa (Wenzel et al., 2004; Hong et al., 2015). The log BSAF values for APEOs were similar in distribution to LMW PAHs and not much different from log BSAFs for OPEOs and NPs, similar to the values previously reported in the lagoon and river basin (Salgueiro-González et al., 2015; Ademollo et al., 2017). There were slight variations in BASF values among taxa, indicating that bioavailability of APEOs is similar among benthic macrofauna (Hecht et al., 2004; Zhang et al., 2011; Salgueiro-González et al., 2015). The log BSAF values of SDs and STs differed among taxa. We detected the great log BSAFs for SOs concentrations in polychaetes and snapping shrimps, whereas log BSAFs in chitons and crabs were low. This discrepancy suggests that there may be a difference uptake capacity in SOs among taxa or be due to the similarity of the compound characteristics between PAHs and SOs. The physicochemical properties of SOs are similar to those of PAHs (Hong et al.,

Table 3
Screening of persistent toxic substances concentrations in the sediments and biota, Abu Ali Island, with sediment quality guidelines (SQGs) and criteria of biota (CBs).

Chemicals	SQGs	CBs	Concentrations	Site and biota exceeding guidelines
	(ng g^{-1} dw)	(ng g^{-1} ww)	Min.–Max. (Mean)	
Sediments				
PAHs[a]				
Naphthalene	160/2100		2.2–5.0 (3.4)	
C1-Naphthalene	155/1470		0.2–1.2 (0.5)	
C2-Naphthalene	150/1450		0.2–42 (14)	
Acenaphthene	16/500		1.4	
Fluorene	19/540		5.3	
C1-Dibenzothiophene	85/600		0.5–210 (72)	Site 1
Phenanthrene	240/1500		8.0	
C1-Phenanthrene	170/2000		0.7–200 (69)	Site 1
Anthracene	85.3/1100		7.5	
Fluoranthene	600/5100		7.1	
Pyrene	665/2600		18	
Benzo(a)anthracene	261/1600		1.3–6.9 (4.1)	
Chrysene	384/2800		1.3–34 (18)	
Benzo(b)fluoranthene	320/1880		0.7–8.1 (4.4)	
Benzo(k)fluoranthene	280/1620		12	
Benzo(a)pyrene	430/2800		0.9–7.3 (4.1)	
Indeno(1,2,3-cd)pyrene	240/950		2.7–2.9 (2.8)	
Dibenzo(a,h)anthracene	63.4/260		2.9–4.1 (3.5)	
Benzo(g,h,i)perylene	85/330		0.8–13 (5.2)	
Alkylphenols[b]	1000		37–63 (53)	
Tributyltin[c,f]	5/70		7.7–110 (2.0)	Sites 1, 2, and 3
Biota				
PAHs[d]				
Naphthalene		68	2.6–360 (110)	Polychaetes and snapping shrimps
Phenanthrene		340	1.5–43 (15)	
Anthracene		58	0.6–1.0 (0.8)	
Fluoranthene		22	0.9–5.0 (2.7)	
Pyrene		20	1.4–13 (5.7)	
Benzo(a)anthracene		16	1.0–2.7 (1.5)	
Benzo(k)fluoranthene		52	1.1–3.0 (2.0)	
Benzo(a)pyrene		120	1.0–3.2 (2.0)	
Indeno(1,2,3-cd)pyrene		22	0.3–5.2 (2.4)	
Tributyltin[e,f]		130/500	5.9–38 (27)	

[a] Effect range-low (ERL) and effect range-median (ERM), from Long et al. (1995).
[b] Interim sediment quality guideline (ISQG), Canadian Council of Ministers of the Environment (CCME, 2002). The concentration was normalized to 1% SOC.
[c] Interim sediment quality guideline (ISQG)-Low and ISQG-High, Australian and New Zealand Guidelines for Fresh and Marine Water Quality (ANZECC, 2000).
[d] Environmental assessment criteria (EAC), OSPAR Commission (2009).
[e] Lower threshold and upper threshold, PWGSC (2012).
[f] Unit: ng Sn g^{-1} dw or ww.

2016), which seems to have caused similar great log BSAFs. The log BSAFs of TBT was < 1.0 for all taxa and values were similar to log BSAFs obtained for HMW PAH compounds. There were slight differences among taxa, whereas previous studies, conducted in the North Sea and Estuary of Saint Lawrence, reported great BSAF values and large differences among taxa (Ten Hallers-Tjabbes et al., 2003; Viglino et al., 2006). Wide variation in BSAF values suggests that degree of contamination varies among regions and the capacity of taxa to bioaccumulate toxins (or metabolically neutralize toxins) would vary in a species-specific manner, even for organisms of the same family level (Viglino et al., 2006).

Log K_{ow} and log BSAF values for PTSs were significantly ($p < 0.01$) and negatively correlated for all taxa and log BSAF values (for which log K_{ow} values were < 1) (Fig. 4b). We found the greatest log BSAFs for compounds with log K_{ow} values between 4 and 5 in all taxa, which is identical to the BSAF values reported in previous studies by conducted in the estuary of Tianjin, China and intertidal zone of straits of Malaysia (Qin et al., 2010; Keshavarzifard et al., 2017). Chemicals with log K_{ow} values in the 4–5 range have high trophic magnification impacts (Wan et al., 2007), suggesting that compounds with log K_{ow} values of 4–5 will tend to bioaccumulate extensively in organisms. Although maximum BSAF values at specific log K_{ow} values in our study differed slightly from previous studies, in general, our results indicate that higher lipophilicities of chemicals cause stronger sorption to sediment and lower bioaccumulation (Thorsen et al., 2004; Yates et al., 2011). SOs with log K_{ow} values of 5–7 had relatively great BSAF values in compounds with low log K_{ow} values (< 6), indicating that the lower the log K_{ow} value, the higher the amount of bioaccumulation. However, some studies have shown that BSAF increases with log K_{ow} values of PTSs and with the alkylation of PAHs, which appears to vary regionally, taxonomically, or in response to environmental conditions that affect the rate of biodegradation or microbial activities that inhibit or stimulate biodegradation (Moermond et al., 2005; Harris et al., 2011; Yunker et al., 2011; Xiang et al., 2018). Such results suggest that compounds with the same log K_{ow}, BSAF values might differ in response to various environmental conditions or in response to species-specific physiologies.

When we compared analyzed target compounds with environmental guidelines to identify major contaminants, we found that detected concentrations of C1-Dbthio and C1-Phe in sediment exceeded ERL (effect range low) guidelines (Long et al., 1995). In contrast, TBT exceeded the interim sediment quality guidelines (ISQG)-High recommended by Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand, indicating an adverse effect on the benthic biota (Table 3) (ANZECC, 2000). In addition, the concentration of APEOs was lesser than ISQG of Canadian Council of Ministers of the Environment (CCME, 2002), suggesting that sediments on north Abu Ali Island are mainly contaminated by crude oil and antifouling agents,

whereas the contamination of sediments by APEOs is much less. We could not evaluate sediment quality relative to SOs because guidelines for SOs are not yet available. The concentrations of Na in polychaetes and snapping shrimps only exceeded environmental assessment criteria (EAC) recommended by OSPAR Commission (Table 3) (OSPAR, 2009), whereas the concentration of TBT did not exceed the lower threshold recommended by Public Works and Government Services Canada (PWGSC) for any taxa (PWGSC, 2012). Overall, our toxicological results showed that Abu Ali Islands is chronically contaminated with oil-derived chemicals and other PTSs.

Although we found the three PAHs and TBT as being major contaminants, contaminant designation was only applicable to chemicals for which there are established environmental guidelines. To complement the lack of comprehensive guidelines, we suggest contaminants that potentially persist and/or bioaccumulate (based on field-based BSAF $>$ 10) (Zhao et al., 2016). Of the 52 compounds we analyzed, we determined 13 compounds to be potentially capable of persisting and bioaccumulating (6 PAHs, 4 APEOs, and 3 SOs) (Table 3 and S4). We found that the petrogenic and natural gas emission-derived PAHs were the primary bioaccumulative compounds, particularly Na and C1-Phe, which not only exceeded sediment guidelines but also extensively bioaccumulated in benthic biota. Of the APEOs, only ethoxylated compounds (OP1EO, OP2EO, NP1EOs, and NP2EOs) bioaccumulated to any extent, indicating that they will persist in biota because they degrade to NPs and OP. The SOs also exhibited high bioaccumulation, indicating that plastics-derived compounds are accumulating in biota (Besseling et al., 2012). These plastic compounds will likely biomagnify (become concentrated in higher trophic levels of the food web) due to their high bioavailability (Nilsen et al., 2014). Overall, we found that four compounds exceeded guidelines and 13 compounds show a high risk for bioaccumulation. We suggest that the benthic ecosystem in north Abu Ali Island will become more concentrated with pollutants over time, due to their high potential to bioaccumulate PTSs in sediments. Restoring a healthy benthic ecosystem to north Abu Ali Island will require more effort to control or eliminate the input of toxic chemicals, particularly those that exceed environmental quality guidelines and/or have a high potential for bioaccumulation.

North Abu Ali Island became one of the most polluted parts of the Arabian Gulf following the 1991 GWOS. There have been efforts undertaken to respond to oil spills, but ongoing sedimentary contamination by various PTSs, including crude oil and toxins of other origins has not been evaluated or remediated. Our study confirms the high level of PTSs contamination, potential sources, and recent inputs, and the bioaccumulation potential of a variety of PTSs in sediments and biota of Abu Ali Island. In fact, the level of contamination in sediments and benthic biota of Abu Ali Island was higher than in other areas in the Arabian Gulf. The PTSs on north Abu Ali Island originate from natural and anthropogenic sources. The accumulation of individual compound differed between sediments and biota. We found high levels of bioaccumulation in sediments for some PTSs, but accumulation varied by the compound. Benthic biota in the intertidal zone of Abu Ali Island are still continuously accumulating PTS and so toxic contamination of Abu Ali Island is likely to persist for a long time unless substantial remedial measures are undertaken. The continuous bioaccumulation of PTSs is likely to work its way up the food chain and become even more concentrated in higher trophic levels. On-site remediation will be needed for the site to recover ecologically, but the ongoing input of PTSs from outside sources will also have to be halted. Our study provides useful baseline information on the level of sediment contamination and bioaccumulation in benthic biota on north Abu Ali Island, Arabian Gulf.

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Appendix A. Supplementary data

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<Supplementary Materials>

Occurrence and bioaccumulation of persistent toxic substances in sediment and biota from the intertidal zone of Abu Ali Island, Arabian Gulf

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Supplementary Tables

Supplementary Figures

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Supplementary Tables

Table S1. Instrumental conditions for analyses (GC/MSD) of persistent toxic substances, such as PAHs, SOs, APEOs, and TBT.

GC/MSD system	**Agilent 7890A GC and 5975C MSD**
Column	DB-5MS UI (30 m long, 0.25 mm i.d., 0.25 μm film thickness)
Gas flow	1 mL/min He
Injection mode	Splitless
Injection volume	2 μL
Injector temperature	300 °C
Ionization	EI mode (70 eV)
MS temperature	180 °C
Detector temperature	230 °C
Oven temperature	60 °C hold 2 min
(PAHs and SOs)	Increase 6 °C/min to 300 °C
	300 °C hold 13 min
Oven temperature	60 °C hold 5 min
(APEOs)	Increase 10 °C/min to 100 °C
	Increase 20 °C/min to 300 °C
Oven temperature	60 °C hold 2 min
(BTs)	Increase 6 °C/min to 300 °C
	300 °C hold 4 min
Target PAHs (35)	Naphthalene (Na), C1-Naphthalene (C1-Na), C2-Naphthalene (C2-Na), C3-Naphthalene (C3-Na), C4-Naphthalene (C4-Na), Acenaphthylene (Acl), Acenaphthene (Ace), Fluorene (Flu), C1-Fluorene (C1-Flu), C2-Fluorene (C2-Flu), C3-Fluorene (C3-Flu), Dibenzothiophene (Dbthio), C1- Dibenzothiophene (C1-Dbthio), C3-Dibenzothiophene (C3-Dbthio), Phenanthrene (Phe), C1-Phenanthrene (C1-Phe), C2-Phenanthrene (C2-Phe), C3-Phenanthrene (C3-Phe), C4-Phenanthrene (C4-Phe), Anthracene (Ant), Fluoranthene (Fl), Pyrene (Py), Benzo[*a*]anthracene (BaA), Chrysene (Chr), C1-crysene (C1-Chr), C2-crysene (C2-Chr), C3-crysene (C3-Chr), Benzo[*b*]fluoranthene (BbF), Benzo[*k*]fluoranthene (BkF), Benzo[*a*]pyrene (BaP), Perylene (Pery), Indeno[*1,2,3-cd*]pyrene (IcdP), Dibenz[*a,h*]anthracene (DbahA), and Benzo[*g,h,i*]perylene (BghiP),
Target SOs (10)	1,3-Diphenylproane (SD1), *cis*-1,2Diphenylcyclobutane (SD2), 2,4-Diphenyl-1-butene (SD3), 2,4,6-Triphenyl-1-hexene (SD4), 2,4,6-Triphenyl-1-hexene (ST1), 1e-Phenyl-4e-(1-phenylethyl)-tetralin (ST2), 1a-Phenyl-4e-(1-phenylethyl)-tetralin (ST3), 1a-Phenyl-4a-(1-phenylethyl)-tetralin (ST4), 1e-Phenyl-4a-(1-phenylethyl)-tetralin (ST5), and 1,3,5-Triphenylcyclohexane (isomer mix) (ST6)
Target APEOs (6)	4-tert-Octylphenol (OP), 4-tert-Octylphenol monoethoxylate (OP1EO), 4-tert-Octylphenol diethoxylate (OP2EO), Nonylphenols (NPs, isomer mix), Nonylphenol-monoethoxylates (NP1EOs, isomer mix), and Nonylphenol diethoxylates (NP2EOs, isomer mix)
Target TBT (1)	Tributyltin (TBT)

Table S2. QA/QC data for analytes of persistent toxic substances, such as PAHs, SOs, APEOs, and TBT in the present study.

Target compounds	Surrogate standard	Abbreviations	Method detection limit (ng g dw^{-1}, n = 7)	Surrogate recovery (%, n = 13)
PAHs and SOs				
Naphthalene		Na	0.43	
Acenaphthylene		Acl	0.85	
Acenaphthene		Ace	0.84	
Fluorene		Flu	0.80	
Phenanthrene		Phe	0.79	
Anthracene		Ant	0.41	
Fluoranthene		Fl	0.78	
Pyrene		Py	0.90	
Benzo[a]anthracene		BaA	0.60	
Chrysene		Chr	0.72	
Benzo[b]fluoranthene		BbF	0.69	
Benzo[k]fluoranthene		BkF	0.71	
Benzo[a]pyrene		BaP	0.59	
Perylene		Pery	0.66	
Indeno[1,2,3-cd]pyrene		IcdP	0.43	
Dibenz[a,h]anthracene		DbahA	0.27	
Benzo[g,h,i]perylene		BghiP	0.33	
1,3-Diphenylproane		SD1	0.33	
cis-1,2-Diphenylcyclobutane		SD2	0.67	
2,4-Diphenyl-1-butene		SD3	0.91	
trans-1,2-Diphenylcyclobutane		SD4	0.24	
2,4,6-Triphenyl-1-hexene		ST1	0.56	
1e-Phenyl-4e-(1-phenylethyl)-tetralin		ST2	0.53	
1a-Phenyl-4e-(1-phenylethyl)-tetralin		ST3	0.30	
1a-Phenyl-4a-(1-phenylethyl)-tetralin		ST4	0.49	
1e-Phenyl-4a-(1-phenylethyl)-tetralin		ST5	0.32	
1,3,5-Triphenylcyclohexane (isomer mix)		ST6	0.34	
	Acenaphthene-d10	Ace-d12		80 ± 18[a]
	Phenanthrene-d10	Phe-d10		112 ± 22
	Crysene-d12	Chr-d12		93 ± 19
	Perylene-d12	Pery-d12		88 ± 19
APEOs				
4-tert-Octylphenol		t-OP	0.12	
Iso-Nonylphenol		NPs	0.91	
4-tert-Octylphenol-mono-ethoxylate		t-OP1EO	0.10	
Iso-Nonylphenol-mono-ethoxylate		NP1EOs	0.46	
4-tert-Octylphenol-di-ethoxylate		t-OP2EO	0.10	
Iso-Nonylphenol-di-ethoxylate		NP2EOs	0.85	
	Bisphenol A-d16	BPA-d16		78 ± 16
TBT				
Tributyltin		TBT	1.3	
	Diphenyltin dichloride	DPTC		86 ± 1.6

[a] Mean ± SD

Table S3. Characteristic of sediments and biota (polychaetes, chiton, snapping shrimps, and crabs) samples collected Abu Ali Island, Arabian Gulf.

Analysis	Polychaetes	Chitons	Snapping shrimps	Crabs	Sediments
n	13	12	18	35	3
Length (cm)	3.1 ± 0.8	3.2 ± 0.3	4.4 ± 1.0	4.2 ± 1.6	
Weight (dw)	0.4 ± 0.1	3.6 ± 0.4	1.7 ± 0.7	4.5 ± 0.9	
Lipid (%)	1.2 ± 0.3	2.0 ± 0.1	1.8 ± 0.2	2.4 ± 0.2	
Feeding type	Deposit feeder	Grazer	Omnivore	Omnivore	
Gravel (%)					8.3 ± 2.9
Sand (%)					91 ± 2.8
TOC (%)					0.3 ± 0.1
Water content (%)					17 ± 5.9

Table S4. Persistent toxic substances showing the great BSAF values (> 10) in biota of Abu Ali Island, Arabian Gulf.

Target compounds	Polychaetes	Chitons	Snapping shrimps	Crabs
(Alkyl-) PAHs	Na, C1-Na, C2-Na,C3-Na, C1-Flu, C1-Phe	-	C1-Na, C2-Na	-
Alkylphenol ethoxylates	OP2EO, NP1EOs, NP2EOs	OP1EO, NP2EOs	-	-
Styrene oligomers	SD3, SD4, ST3	-	-	-
TBT	-	-	-	-

Supplementary Figures

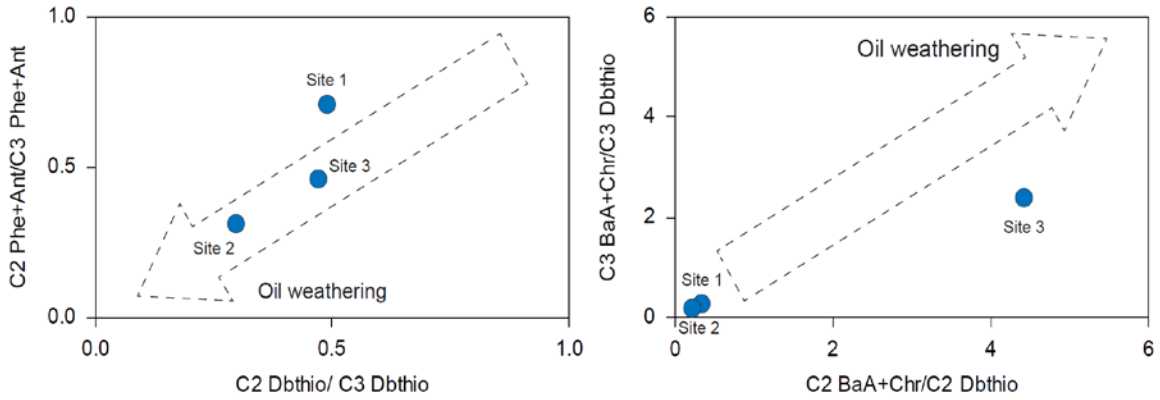

Fig. S1. Diagnostic ratios for weathering characteristics between C2-Dbthio/C3-Dbthio and (C2-Phe+Ant)/(C3-Phe+Ant) double ratios, and (C2-BaA+Chr)/C2-Dbthio and (C3-BaA+Chr)/C3-Dbthio double ratios of all sediment samples.

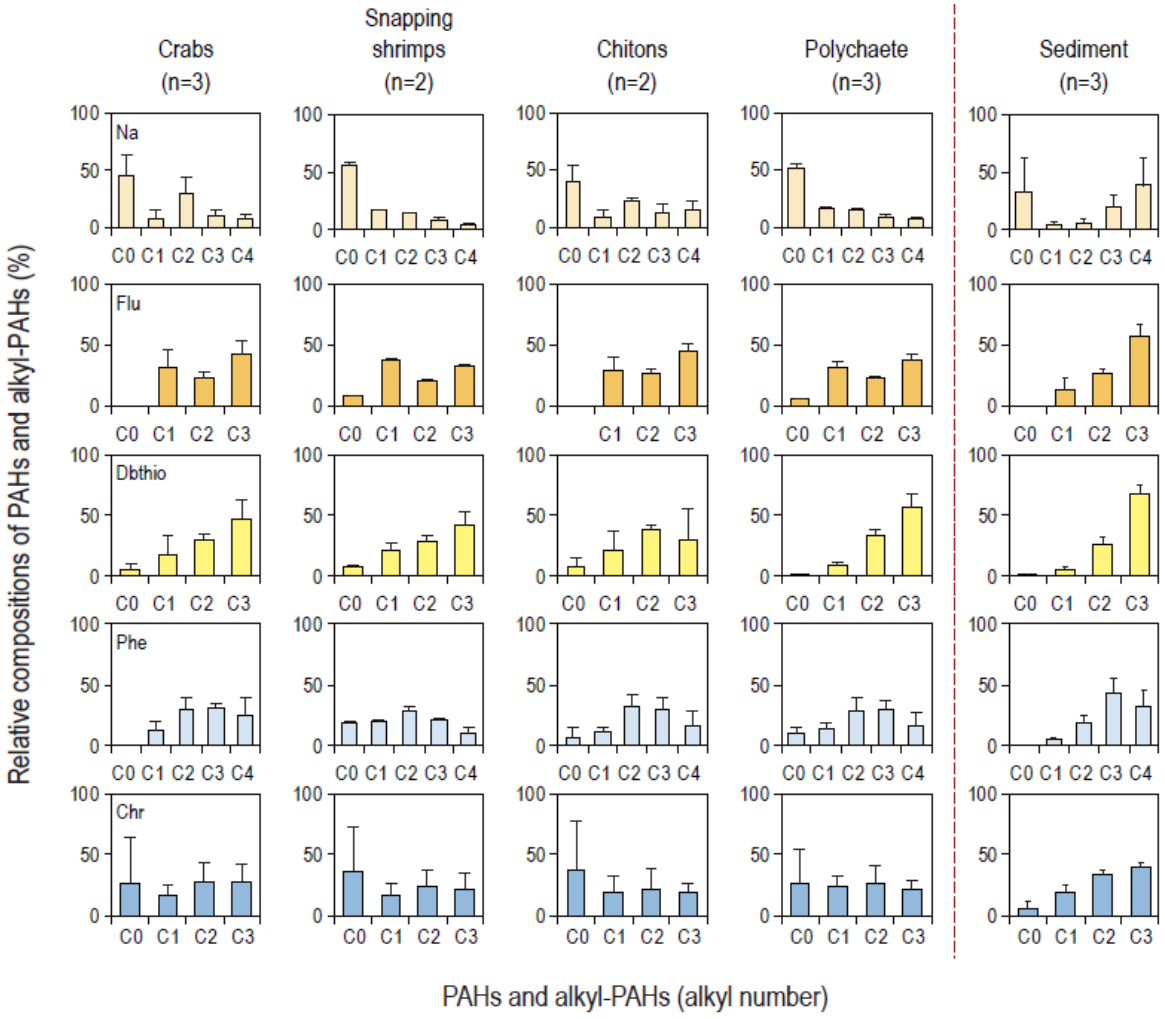

Fig. S2. Relative compositions of PAHs and alkyl-PAHs in biota and sediment samples of Abu Ali Island.

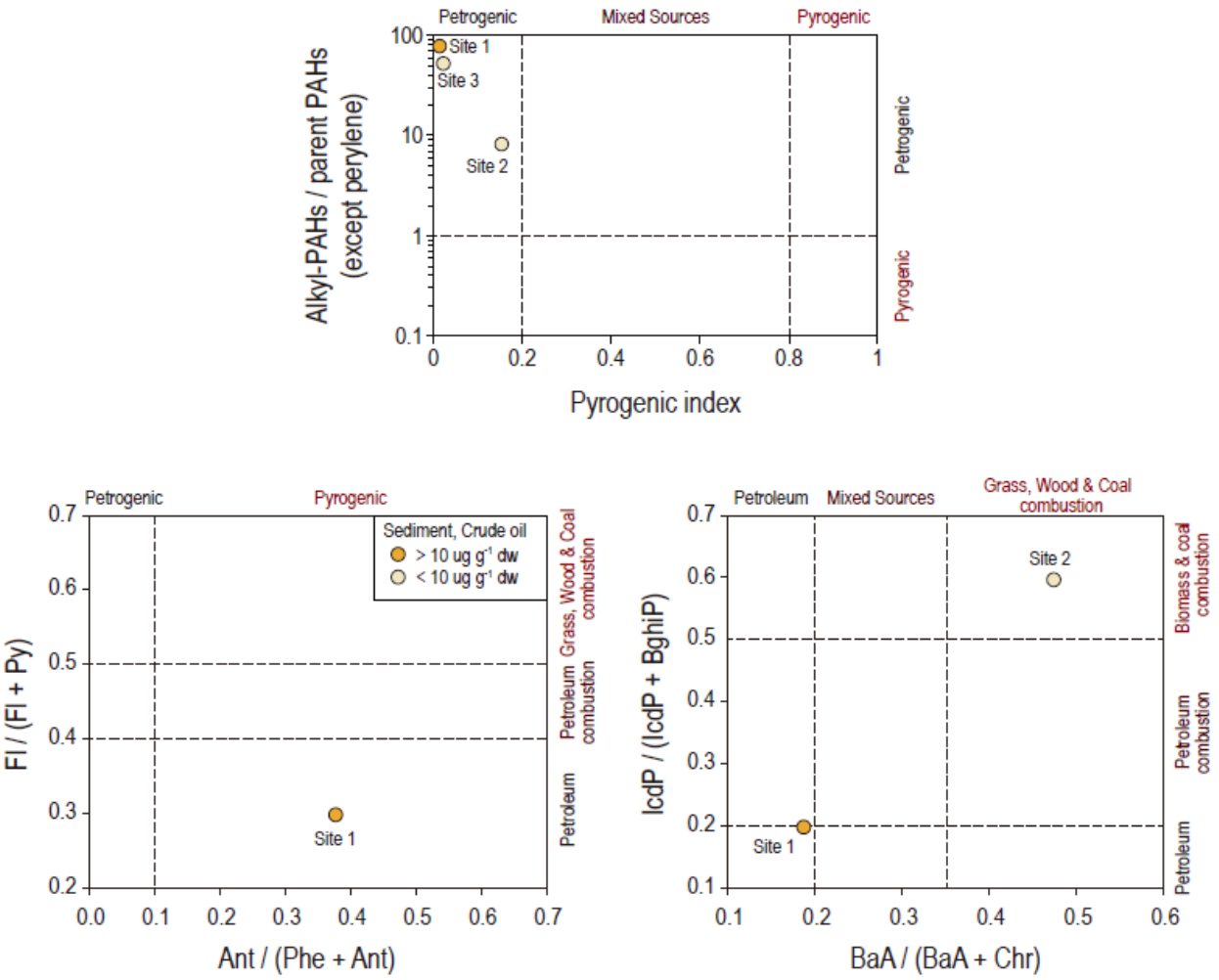

Fig. S3. Diagnostic ratios for prediction of sources of PAHs between alkyl-PAHs/parent PAHs and pyrogenic index, Ant/(Ant+Phe) and Fl/(Fl+Py), and BaA/(BaA+Chr) and IcdP/(IcdP+BghiP).