Marine Pollution Bulletin xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul

Baseline

Sediment PAH: Contrasting levels in the Caspian Sea and Anzali Wetland

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ARTICLE INFO

Article history:
Available online xxxx

Keywords:
PAH
Gas chromatography and mass spectrometry
Sediment quality guidelines
Toxic equivalent concentrations
Anzali Wetland
Caspian Sea

ABSTRACT

A comparative study of 23 PAH congeners in sediment of the Caspian Sea coast and Anzali Wetland was conducted in 2010. Surface sediment was analyzed using chromatography and mass spectrometry. Total PAH concentrations ranged between 212 and 9009 ng g^{-1} dw. Spatial distribution maps revealed that PAH levels were higher in the coastal areas of the Caspian Sea where oil related activities have been common since 1800's. Diagnostic ratios analysis indicated that PAHs largely originated from petrogenic processes. PAH toxicity level was assessed using sediment quality guidelines and toxic equivalent concentrations to determine toxic effects on marine organism. Based on these investigations, in our study areas, the probability of toxicity for benthic organisms is "low to medium". The toxic equivalent concentrations of carcinogenic PAHs varied between 11 and 231 ng TEQ/g; higher total toxic equivalent concentrations values were found in the coastal areas of the Caspian Sea.

Persistent organic pollutants (POPs) constitute a major concern for pubic and environmental health and proper identification of their source is critical for water quality management (Yunker and Macdonald, 2003; Hu et al., 2010). Polycyclic aromatic hydrocarbons (PAHs) are a group of ubiquitous POPs. They are among some of the most persistent pollutants in the aquatic environments (Tam et al., 2001; Harris et al., 2011). PAHs are water insoluble and they readily adhere to particulate matter, in water. Molecular weight of PAHs vary, depending on the number of aromatic rings in their structure (i.e. low or high molecular weight (LMW, HMW) PAHs) (Tam et al., 2001; Readman et al., 2002).

PAHs can directly be released from oil and oil products into the water column (petrogenic source), or they can be the product of incomplete combustion of fossil fuels (pyrolytic source) (Readman et al., 2002; Tolosa et al., 2004; Zaghden et al., 2007; Gao and Chen, 2008; Qin et al., 2011).

PAHs can enter the body via many exposure routes including breathing, eating, or drinking. Exposure to PAHs can also occur by skin contact. Once PAHs enter the body of a living organism, they are metabolized to form carcinogens and highly reactive molecules such as diol epoxides that are PAH intermediate metabolites. Current literature confirms that PAHs are highly carcinogenic and extremely toxic to benthic organisms (Trabelsi and Driss, 2005; Arias et al., 2009; Zhang et al., 2011).

As current industrial societies recklessly generate large amounts of PAHs, ever-increasing amounts of PAHs find their way into global aquatic environments. Long-term PAH "reservoirs" are said to form in the underlying sediments of aquatic environments (Colombo et al., 1989; Tam et al., 2001; Culotta et al., 2006; Wang et al., 2006). Subsequently, when assessing health and ecological risk in aquatic environments, sediment analysis is often chosen to determine source, concentration, and types of contaminants (Ibbotson and Ibhadon, 2010; De Souza et al., 2011).

Our study area, Anzali Wetland, on the southern coast of the Caspian Sea, is a major breeding and wintering ground for numerous species of water birds. Anzali includes lagoons and extensive reed beds making it vital for spawning and nursery of the Caspian fish. Anzali was registered under the Ramsar Convention in 1975, making it one of the oldest Ramsar sites in Iran. Anzali was later listed in the Montreux Record as urgently needing conservation plans. Deteriorating water quality in Anzali is the result of urbanization, agricultural drainage, and sediment influx. Reconstruction and rehabilitation of Anzali has been recommended. We conducted this study to gain a comprehensive understanding of the source, distribution and ecological risk of PAHs in this precious and unique world environment.

Anzali (37° 28′N 49° 25′E) is approximately 200 km^2. The watershed area of this wetland is about 374,000 ha. The basin

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http://dx.doi.org/10.1016/j.marpolbul.2014.05.001
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has a maximum and a minimum height of 3014 and −26 m from the sea level. Mean annual rainfall is 1280 mm and evaporation is 980 mm. Many tributaries (11 rivers and 30 streams) flow into Anzali. In the spring the wetland's water depth can reach 2.5 m in the western areas. Eastern Anzali is shallow compared to the western protected areas. Anzali is connected to the Caspian Sea through a central shipping channel of 5.3 km.

Surface sediment samples were collected from 30 sampling stations in the wetland and coastal areas of Anzali in May and June 2010 (Fig. 1). The coordinates of sampling sites are given in Table 1. A Van Veen Grab Sampler was used to randomly collect surface sediment (0–5 cm) which were stored in clean aluminum foil bags. Samples were transported to the lab on dry ice. In the laboratory samples were stored at −20 °C until analysis (see Table 2).

Sediment preparation, extraction, and analysis has been described earlier Zakaria et al. (2001), Riyahi Bakhtiari et al. (2009, 2011). Briefly, a two-step silica gel chromatography and gas chromatography-mass spectrometry (GC–MS) method is utilized. Organic solvents were distilled in glass before use and glassware was rinsed successively with methanol, acetone and distilled hexane to remove any organic contaminants and kept in an oven at 60 °C. Standard solutions of PAHs were purchased from Sigma chemical Company. Sodium sulphate anhydrous, disposable Pasteur Pipettes, and screw top vials were baked at 500 °C for 2–3 h before use to remove organic impurity. Samples of sediment were freeze-dried, homogenized and precisely weighed for extraction (10 g). Deuterated PAHs surrogate, and internal standard mixture (naphthalene-d_8, anthracene-d_{10}, chrysene-d_{12} and perylene-d_{12}), were added to the each aliquot, and samples were soxhlet-extracted for 10 h with 270 ml of distilled dichloromethane.

The extract was concentrated to ~2 ml by rotary evaporator then transferred onto the top of a 5% H_2O deactivated silica gel column (1 cm i.d.×9 cm, ~6 g, 100–200 mesh; F.C.923, Davison Chemical). Hydrocarbons ranged from *n*-alkanes to PAHs with seven rings were eluted with 20 ml of dichloromethane/hexane

Table 1
Geographical positions of the sampling sites in the Anzali Wetland and Caspian Sea.

	Station	Latitude	Longitude
Anzali Wetland	A1	37° 28′ 271″N	49° 26′ 506″E
	A2	37° 28′ 057″N	49° 26′ 362″E
	A3	37° 27′ 104″N	49° 25′ 631″E
	A4	37° 26′ 647″N	49° 24′ 828″E
	A5	37° 28′ 117″N	49° 24′ 607″E
	A6	37° 27′ 754″N	49° 23′ 479″E
	A7	37° 26′ 803″N	49° 22′ 481″E
	A8	37° 25′ 957″N	49° 26′ 640″E
	A9	37° 26′ 279″N	49° 27′ 222″E
	A10	37° 27′ 581″N	49° 27′ 537″E
	A11	37° 27′ 779″N	49° 27′ 633″E
	A12	37° 27′ 720″N	49° 27′ 977″E
	A13	37° 27′ 591″N	49° 27′ 813″E
	A14	37° 27′ 889″N	49° 28′ 193″E
	A15	37° 27′ 785″N	49° 28′ 532″E
	A16	37° 27′ 767″N	49° 28′ 675″E
	A17	37° 28′ 012″N	49° 28′ 077″E
	A18	37° 28′ 396″N	49° 27′ 825″E
	A19	37° 28′ 310″N	49° 27′ 844″E
	A20	37° 28′ 207″N	49° 27′ 819″E
	A21	37° 28′ 226″N	49° 27′ 657″E
	A22	37° 28′ 256″N	49° 27′ 358″E
Caspian Sea	C1	37° 29′ 293″N	49° 25′ 107″E
	C2	37° 29′ 323″N	49° 24′ 945″E
	C3	37° 29′ 383″N	49° 24′ 712″E
	C4	37° 29′ 377″N	49° 29′ 609″E
	C5	37° 29′ 468″N	49° 24′ 337″E
	C6	37° 28′ 945″N	49° 26′ 479″E
	C7	37° 29′ 034″N	49° 26′ 193″E
	C8	37° 29′ 194″N	49° 25′ 272″E

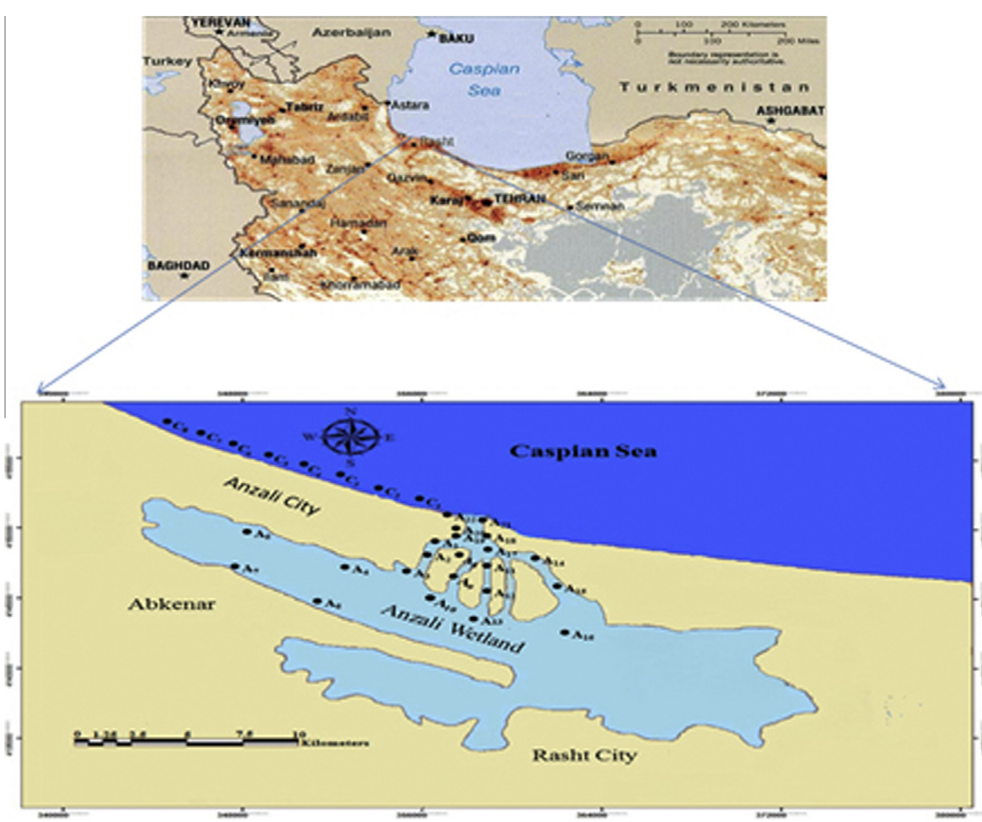

Fig. 1. Location of sampling sites: sample numbers A_1 to A_{22} were collected from Anzali and C_1 to C_8 were collected from the Caspian Sea coast.

Please cite this article in press as: Yancheshmeh, R.A., et al. Sediment PAH: Contrasting levels in the Caspian Sea and Anzali Wetland. Mar. Pollut. Bull. (2014), http://dx.doi.org/10.1016/j.marpolbul.2014.05.001