



# Presence of polycyclic aromatic hydrocarbons in sediments and surface water from Shadegan wetland – Iran: A focus on source apportionment, human and ecological risk assessment and Sediment-Water Exchange

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## ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) contamination in aquatic system is of concern since it may constitute a sink of these contaminants for wetland ecosystem. We investigated pollution characteristics and ecological risks of PAHs by sampling contaminated sediments and water from the Shadegan wetland in Khuzestan province, south-west Iran. Concentrations of total PAHs in water and sediment samples varied from  $42 \pm 2.3$ – $136 \pm 7.5$  ng/L and  $10 \pm 0.5$ – $317 \pm 14.3$  µg/kg, respectively. Source apportionment of PAHs by both approaches (Principal component analysis-multiple linear regression (PCA-MLR) and molecular isomeric ratios of specific PAHs), indicated impact of potential anthropogenic PAH sources including oil spill and incomplete combustion, bulrush combustion, vehicular exhaust and fishing boat emissions. Comparing the PAHs concentration with sediments quality guidelines based on the effect range low values/effects range-median values (ERL/ERM) and the threshold effect levels/probable effect levels (TEL/PEL). Also, a risk quotient (RQ) was elaborated for evaluation of potential toxic effects on aquatic ecosystem. Our data showed relatively insignificant adverse impact for most individual compounds. The toxic equivalent quantity (TEQ) was also calculated to estimation the PAHs toxicity. TEQ value of PAHs (1.9 µg/kg) was lower than the safe level (600 µg/kg). The fugacity fraction approach was applied to explain the trend of the selected PAHs for water–sediment exchange, which showed that the fluxes for most priority PAHs were from water to sediment suggesting no secondary source impact.

## 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) represent a typical category of lipophilic contaminants containing two or more benzene rings (Domínguez et al., 2010; Sun et al., 2017). Various natural processes can release PAHs in to the aquatic environment for example bush fire (pyrolytic origin), slow maturation of organic matter under the geothermal gradient (petroleum hydrocarbons) and short-term degradation of biogenic precursors (early diagenesis) (Arias et al., 2010; Balcıoğlu, 2016; Wu et al., 2001). The largest amount of these organic compounds can be found in locations affected by intense anthropogenic activities even though these organic contaminants may be occurred in all environments (Ololade et al., 2017). Human activities have produced a variety of PAHs sources, and each contamination source can produce a

specific PAH pattern, which leads to a distinct distribution pattern in the environment (Baumard et al., 1998). Anthropogenic PAHs can be released into the water ambient from wastewater effluents, industrial discharges, coke and petroleum refining industries, spillage of petroleum, motor vehicle emissions, atmospheric deposition, rainwater runoff, and domestic heating (Neff, 1979; Yuan et al., 2014).

Polycyclic aromatic hydrocarbons are exist in both dissolved and particulate phases (Culotta et al., 2006). However, due to low water solubility and hydrophobicity, low volatility, high persistence, and particle reactivity, PAHs in aquatic system high affinity to bind preferentially to solid phases (Liu et al., 2016; Sun et al., 2017). Among all controlling processes the presence of PAH compounds in the aquatic ecosystem on can mention sediment–water (Guo et al., 2009). PAHs cause global environmental serious concerns because of their potential

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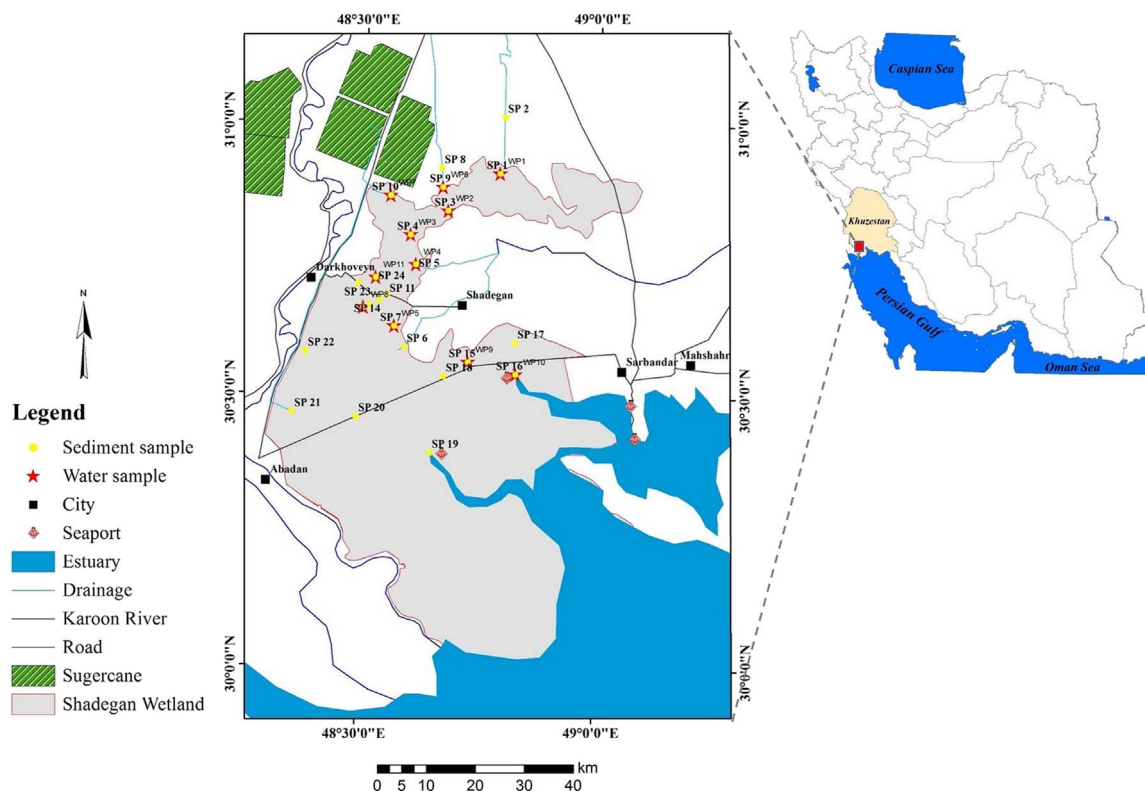


Fig. 1. Study area and location of sampling stations in Shadegan wetland, Iran.

toxicity and carcinogenicity on both the ecosystem and human health (Liang et al., 2017; Scott et al., 2012). PAH accumulation in sediments is regulated by the sediment composition, in particular black carbon and organic matter value (Goswami et al., 2016). Sediments contaminated by PAHs may act as temporary or long-term secondary source (Liu et al., 2013; Qiu et al., 2009; Wu et al., 2001). Move of PAHs from contaminated sediments into overlying waters or uptake by demersal organisms feeding on organic material serves as route of entry to trophic transfer (Eek et al., 2008). PAHs may therefore increase the risk of cancer and other adverse health effects through bioaccumulation in the food chain (Liu et al., 2016). Due to mutagenic and carcinogenic characteristics of PAHs, the United States Environmental Protection Agency (US EPA) has reported some of them as priority contaminants (Duodu et al., 2017). Among them, the potential carcinogenic PAHs include benzo[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, chrysene and dibenz[a,h]anthracene and indeno [1,2,3-cd] pyrene (Jiang et al., 2014). To reduce environmental risks caused by PAHs, adequate measures should be formulated. So determination of quantitatively the contributions of the various sources with their specific PAH patterns is necessary (Chung et al., 2014).

The wetlands are known as one of most biologically diverse important and productive ecosystems in the world. However, unlike coastal areas, studies on PAHs in environmental media of estuarine wetlands are yet scarce, albeit known from all continents (e.g., Domínguez et al., 2010; Kumar et al., 2008; Li et al., 2014; Ma et al., 2014; Wang et al., 2012; Xu et al., 2017; Yancheshmeh et al., 2014; Zhang et al., 2014). Shadegan wetland in Iran, connecting the Jarahi river and Persian Gulf waters is characterized by its unique biodiversity (Nasirian et al., 2013). On the other hand, this wetland is located adjacent to an important oil field. During the last few decades, it was affected by various contamination sources including petrochemical complexes, oil pressure boosting station, oil pipelines and petroleum refineries, which has led to severe damages to its natural resources and potential human health hazard consequences (Chaharlang et al., 2016). Therefore, the determination of impact from local sources is essential

for assessing the significant risk of contamination by PAHs. The main goals of this study were (i) to measure the concentration of 16 priority PAHs in surface water and sediments of the Shadegan wetland, with a view to (ii) identify possible contamination sources using diagnostic ratios and principal components analysis (PCA) in conjunction with multiple linear regression (MLR) analysis for mitigation purposes, (iii) to assess the potential ecological and human health risk caused by the selected PAH assemblages in sediments and water, and (iv) to analyze water-sediment partitioning and hence predict the trend of each of PAH compounds for Sediment-Water Exchange in this unique wetland ecosystem.

## 2. Materials and methods

### 2.1. Study area

Shadegan wetland is located in southwestern Iran of Khuzestan Province, between 48°20'–49°20' E longitude and 30°50'–31°00' N latitude. The Shadegan wetland is about 537,730 ha, of which almost 60% is protected as a wildlife refuge (Malekmohammadi and Rahimi Blouchi, 2014). It is an estuarine system of salinities in between fresh and marine waters, which is surrounded by cities such as Abadan, Bandar-Mahshahr and Shadegan. Abadan and Bandar-Mahshahr are densely populated industrial cities including large refinery/petrochemical industries and harbors for example one of the largest industrial zones in Iran -Bandar Imam Petrochemical Special Economic Zone- is located in distance of 18 km from Bandar-Mahshahr. Port of Mahshahr export 400,000 barrels of crude oil per day. The largest marine port of Iran is located in the city of Imam Khomeini and is directly connected to the Shadegan wetlands (Karimi et al., 2012; Lübeck et al., 2016).

### 2.2. Sample collection

Samples were collected at 24 locations from the top 5 cm bed

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