Marine Pollution Bulletin xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Marine Pollution Bulletin

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

Characterization and ecological risk of polycyclic aromatic hydrocarbons (PAHs) and *n*-alkanes in sediments of Shadegan international wetland, the Persian Gulf

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ARTICLE INFO

Keywords:
PAHs
n-alkanes
Pollution
Sediment
Risk assessment
Shadegan wetland

ABSTRACT

The distribution and sources of PAHs and *n*-alkanes were determined in the surface sediments from 202 locations in Shadegan international wetland with 537,700 ha. The concentrations of total *n*-alkanes and PAHs ranged from 395.3 to 14933.46 μg g^{-1} dw and 593.74 to 53393.86 ng g^{-1} dw, respectively. Compared with other worldwide surveys, the concentration and contamination of sedimentary hydrocarbons were classified very high. A common petrogenic hydrocarbon source was strongly suggested in all sites by *n*-alkanes' profile with a Cmax at n-C_{20}, Pr/Ph and CPI ratios < 1 in all sites, and high percentage of UCM. Typical profile of petrogenic PAHs with alkyl-substituted naphthalenes and phenanthrenes predominance, various PAH ratios and multivariate analysis indicated that PAHs were mainly derived from petrogenic source. Naphthalene-derived compounds in all sites were significantly above their ERL, and adversely affected benthic biota. 92% of the sites had mean ERM values < 0.1, indicating high ecological risk on the wildlife of the wetland.

1. Introduction

Oil pollution has been recognized as one of the most serious threats to aquatic ecosystems, particularly in wetlands. Shadegan wetland is the largest Ramsar site in Iran, and enjoys important and distinctive attributes including immense size, naturalness and habitat diversity. It has a main role in the livelihood of native population; however, it is subjected to petroleum contamination from different sources. In recent decades, the wetland has faced with different impacts on its ecology due to augmented industrial developments. Oil transportation is the most important economic activity in this area. It is important to specify spilled oils and apportion them to the sources for the environmental impact assessment, prediction of the potential long-term effects of spilled oils on the environment, appropriate spill response selection, and taking effective clean-up procedure. In addition, in many cases, source identification of oil spill is critical for determining the environmental liability.

A number of indices such as hydrocarbon concentrations, *n*-alkanes' profiles, composition of polycyclic aromatic hydrocarbons (PAHs), and petroleum biomarkers have been proposed to investigate the pollution level and realize the pollution sources (Kim et al., 2013; Volkman et al., 1992; Witt, 1995). In aquatic environment, hydrocarbons are usually transported to the sediments for their hydrophobic characteristics and low water solubility. Hydrocarbons in sediments might be related to various sources: biogenic, diagenetic, petrogenic and pyrogenic (Bragato et al., 2012; Callén et al., 2013; Hostettler et al., 1999; Lea-Langton et al., 2013; Yunker et al., 1993). Aliphatic alkanes and PAHs play a key role in specification, differentiation and source apportionment in the environmental forensic investigations of oil spills (Colombo et al., 2005; Wang et al., 1999b) because each source (anthropogenic or biogenic) provides specific characteristic forms of these compositions pursuant to their sources (Baumard et al., 1998; Kaivosoja et al., 2012; Zhang et al., 2012). These hydrocarbons might have several origins such as spills from accidental or chronic leakages of marine and land pipelines, fuel tanks, industrial and domestic wastes, combustion of fuels, wood burning and diagenetic transformations of non-hydrocarbon natural products (Commendatore et al., 2012; Readman et al., 2002). However, other sources such as higher plant wax, algae and planktons can introduction them into the environment (Colombo et al., 1989; Commendatore and Esteves, 2004; Deng et al., 2013; Kennicutt

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http://dx.doi.org/10.1016/j.marpolbul.2017.07.015
Received 24 April 2017; Received in revised form 23 June 2017; Accepted 4 July 2017

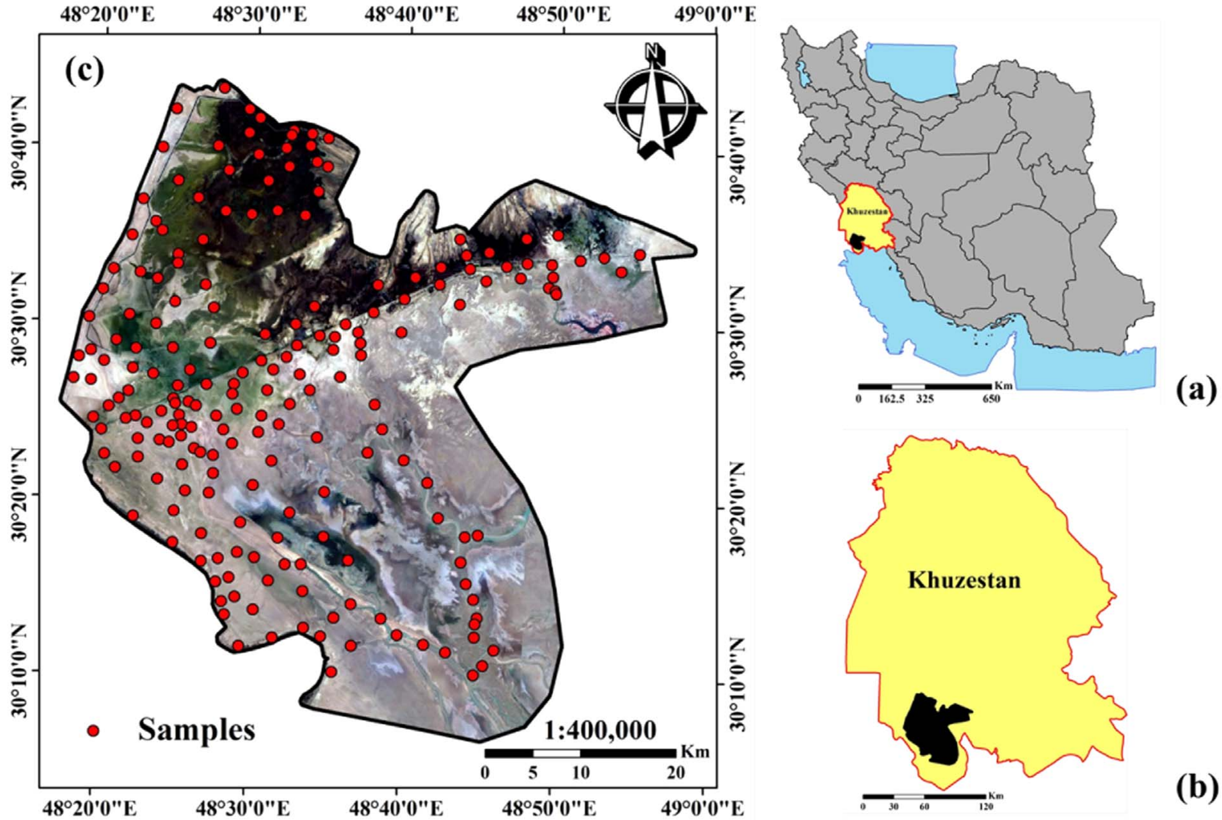

Fig. 1. location of study area in Iran (a), location of study area in Khuzestan province (b) and locations of the sediment sampling sites in Shadegan wetland.

et al., 1994). Study of *n*-alkanes and PAHs distribution provides to distinguish between anthropogenic and biogenic sources, moreover, the diagnostic ratios can be used to determine their sources (Asia et al., 2009). Principally, *n*-alkanes are, generally, used to make a broad overview of hydrocarbon sources ranging from terrestrial vascular plant materials to marine algae to petroleum (Harris-Roxas and Harris, 2011). PAHs molecular indices allow to discriminate between pyrogenic and petrogenic sources because pyrogenic PAHs are generated by partial organic matter combustion at high temperature, and petrogenic PAHs are closely related to crude oil and its refined products (Commendatore and Esteves, 2004; Guo et al., 2012; Maliszewska-Kordybach et al., 2009; Page et al., 2002; Wang et al., 1999b).

Therefore, the aim of the this study is source identification of hydrocarbons in Shadegan wetland by applying different source apportionment methods so that appropriate measures can be considered for pollution prevention and risk management. Furthermore, the paper underlines the necessity of carrying out an accurate study of source apportionment to provide an appropriate forensic investigation in the sites where the impacts caused by multiple sources may result in cumulative effects on human health and environment. Consequently, a multi-criteria approach is needed to differentiate biogenic compositions from petroleum hydrocarbons. Above all, an appropriate policy of pollution prevention must be adopted. To the best of our knowledge, a quantitative source apportionment of hydrocarbons in Shadegan wetland has not been performed in Iran so far.

2. Materials and methods

2.1. Study area and sampling

Shadegan international wetland, which extends over 537,700 ha, is an enormous environmental system including fresh and brackish wetlands, as well as the inter-tidal Khure-Musa bay and offshore islands (Taravati et al., 2012). In the south side, it is linked to the Persian Gulf. A large part of the wetland in the south (tidal flat) is exposed to the tidal effects from the Persian Gulf. As Iran's largest wetland and the second largest wetland recognized in Ramsar's Convention, it is located at the downstream of the Jarrahi river catchment, between Abadan, Shadeganand and Mahshahr Cities in Khuzestan Province, south-west of Iran (Karimi et al., 2012). It has been registered in the UNESCO's Natural Heritage List as one of the 18 international wetlands. The nominated area of the wetland documented in the Ramsar site is 400,000 ha, excluding the littoral and marine parts in the Persian Gulf. 327,000 ha of the wetland (south to Darkhuin-Shadegan road) have been identified as Wildlife Refuge since 1974 and as a no-hunting area. About 117 villages and three cities are located in the vicinity of the wetland (Karimi et al., 2012). It has been recognized as an internationally important wetland that provides valuable rich biodiversity in fish, and hosts a large number of migratory birds that arrive at the wetland from Northern Europe, Canada and Siberia during the winter season every year. High tourism potential and development of infrastructures have converted the wetland into a tourist destination (Kaffashi et al., 2012); however, it is facing a series of environmental crises largely caused by oil pipelines, fuel smuggling, development of sugar cane units, and construction of power plants, transmission lines, steel factories, and different substructures (Zare-Maivan, 2012). The results of degradation of the wetland are so significant that have adversely influenced the totally important biodiversity and many goods that it provides to the local populations. Unfortunately, the wetland has been registered at risk of ecological change since 1993 in the Ramsar Convention's Montreux Record of Wetlands (Kaffashi et al., 2012). Furthermore, there is some evidence on the leakage of pipelines and accidental oil spills, especially from fuel smuggling.

2.1.1. Sampling

In June and October 2014, surface sediment samples from top 5 cm of the sediments (n = 202) were collected according to a systematic-random sampling design in order to cover the whole wetland and