Marine Pollution Bulletin xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Marine Pollution Bulletin

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

Baseline

Levels and sources of heavy metals and PAHs in sediment of Djibouti-city (Republic of Djibouti)

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ARTICLE INFO

Keywords:
Red sea
Marine sediments
PAH's
Heavy metals
Enrichment factor
Diagnostic ratio

ABSTRACT

Selected heavy metals and polycyclic aromatic hydrocarbons (PAHs) were determined in marine sediment from 28 sites Djibouti city. The concentrations of trace elements varied from 0 to 288.1 mg/kg with relative abundance of trace metals in sediments was in the order of Zn > Cu > Ni > Cr > Co > Pb > Cd. Zn, Cu and Ni exceeded consensus based sediment quality guideline values 7, 14, 15 sites respectively. Enrichment factor and pollution load index showed relatively low to moderate contamination. The concentrations of total 16 PAHs varied widely depending on the sample location and ranged from 2.65 to 3760.11 ng·g^{-1}, with the mean concentration value of 387.87 ng·g^{-1}. Compositions and relative abundance of individual PAH using molecular diagnostic ratio using congener's *m/z* 178 and 202 indicated pyrolytic origin and reflecting a petroleum combustion, grass/wood and coal combustion and a petrogenic source. This study represents the first pollution baseline and a reference for future studies in Djibouti.

The contamination of the marine environment with organic and inorganic contaminants is a major concern (Islam and Tanaka, 2004). Red sea appears to suffer from high anthropogenic pressure due to inputs from industrial, sewage effluents, shipping activities, spillage coastal activities and natural seeps (Dou Abul et al., 1998; Khalaf and Kochzius, 2002; Kress et al., 1999; Nemr et al., 2005; Walker and Ormond, 1982). It leads to contamination of the surrounding area not only by organic compounds (e.g. polycyclic aromatic hydrocarbons, PAHs) but also to heavy metals such as Cr, Ni, Cu, Zn, As and Pb (Fiedler et al., 2009; Ugochukwu and Leton, 2004). Furthermore coastal sediments act as temporary or long-term sink and is one of the most important reservoirs of environmental pollutants.

Heavy metals occur naturally in the ecosystem at various levels of concentrations. Some heavy metals are essential for biological function in trace concentrations such as Cu, Cr, Mn, Zn and Co while high concentrations of essential element have adverse effects on living organism (Hogan, 2010). Metals bioaccumulating in the food chain pose a risk to human exposure and damage to predators (Amundsen et al., 1997; El-Moselhy et al., 2014; Muchuweti et al., 2006).

On the other hand polycyclic aromatic hydrocarbons (PAHs) are an important class of persistent organic pollutants in the marine environments, particularly in estuaries, harbors and shallow coastal areas exposed to anthropogenic inputs e.g. a refinery site (Barakat et al., 2011; Baumard et al., 1998; Neff, 1985; Nemr et al., 2005; Syakti et al., 2013). Anthropogenic sources of PAHs in the marine environment are generated through incomplete combustion (e.g. coal, petroleum and wood) or derived from crude and refined petroleum products (oil spills, routine tankers operations, oil exploitation, etc.). PAHs hazardous property, lipophilicity, low water solubility and adsorption to marine particles and sediments make them a group of chemicals that may affect wildlife and humans via the food chain which prompted US EPA to include 16 PAHs within the priority pollutants list (Manoli et al., 2000). PAHs are known to have adverse effects on humans and the environment through mechanism of carcinogenesis (IARC, 2010) as well as acute and developmental toxicity has been observed in the aquatic environment (Neff, 1985).

Several data is available from Yemen, Egypt, Sudan and Saudi Arabia (Al-Shwafi, 2003; Aly Salem et al., 2014; Ashraf and Salam, 2012; Barakat et al., 2011; Bejarano and Michel, 2010; Dou Abul et al., 1998; El Nemr et al., 2007; Jahin et al., 2009; Jiries et al., 2003; Khairy

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http://dx.doi.org/10.1016/j.marpolbul.2017.05.055
Received 11 April 2017; Received in revised form 19 May 2017; Accepted 22 May 2017

Please cite this article as: Ahmed, M.M., Marine Pollution Bulletin (2017), http://dx.doi.org/10.1016/j.marpolbul.2017.05.055

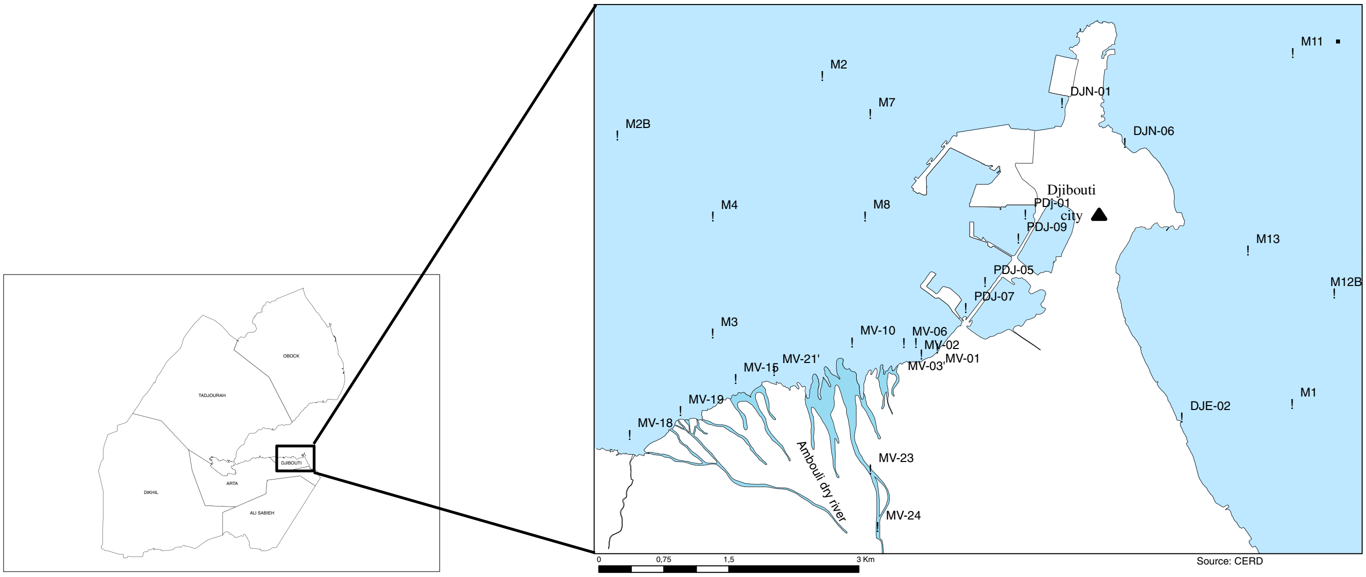

Fig. 1. Map of sampling stations (n = 28) in the East and West coast of Djibouti-city.

et al., 2009). Despite the significance of this coast, to the best of our knowledge this area has never been investigated in detail for organic contaminants and heavy metals both occurring naturally and anthropogenically, which may enter into the marine ecosystem from various point sources.

The present study is the first investigation of the current status of PAHs and heavy metal concentration in surface sediments of Djibouti-city coastal area. The results provide a valuable reference data set for environmental managers.

Djibouti city is located at 11°30′N, 43°00′E in the Horn of Africa, Fig. 1. shows the general outline of the Republic of Djibouti. It has a very hot and humid yet rainless summers (42 °C and less 215 mm annual precipitation) and warm winter season (21 °C). The semi-enclosed nature of the Red Sea limits the opportunity for renewal of the water mass. The coastline is composed of a mixture of eluvial and colluvial deposits, taluses, sheet floods, dunes and beach deposits with tidal range is 0–3 m relative to Chart Datum (Schlüter, 2008). The monsoon wind vary from North-East during winter and South-West during summer season. Increasing activity in the capital has caused oil spills due to accident, chronic release of industrial contaminants mostly untreated. Furthermore untreated or insufficiently treated wastewater is discharged into the sea.

Surficial sediment samples (0–10 cm, n = 28) based on their different potential levels and sources of contamination used in this study were collected in Djibouti-city from January to April 2016. The sampling time coincides with an intense activity of *Ambouli Wadi* (dry river) which renewed surface sediment in Djibouti bay. The landmarks in the adjacent land areas to the sampling sites were recorded and all sampling sites were defined using global positioning system (Table S1). Twelve samples were collected in Djibouti-city bay, eleven stations were collected in Djibouti-city mangrove and five samples in the recreational and tourism area. Sediments along the shore were collected by foot while sediments from the bottom sea (2–50 m) were collected using a diver with an adequate container and stored at 4 °C during transportation to the laboratory. Sediment samples were dried at 30 °C in a ventilated air drying oven and subsequently sieved to < 2 mm and < 0.15 mm for polycyclic aromatic hydrocarbons (ISO 15527:2008) and heavy metal (ISO 11466:1995) determination respectively.

High purity ICP selected heavy metals standard solution (1000 ppm) was obtained from Horiba (Jobin Yvon, France). Hydrochloric and nitric acid (70%) were of analytical grade (Sigma-Aldrich). All the organic solvents used for the analysis n-hexane, dichloromethane and acetone were of HPLC grade (Sigma Aldrich). Mixture standards (PAH Mix, EPA), individual surrogate and internal standards (phenanthrene-d10, pyrene-d10, chrysene-d12) were obtained from Sigma Aldrich for identification and quantification of PAHs. Dichloromethane, *n*-pentane, *n*-hexane, (VWR, France) for PAH extraction and clean-up were of HPLC grade. Silica gel-60 (200–300 mesh), alumina (200–300 mesh) and copper powder (> 230 mesh) were purchased from VWR International (France). Certified Reference Material NIST 1941b “PAHs, PCBs and pesticides on Fresh Water Sediment” and IAEA-158 were purchased from Sigma-Aldrich and International Atomic Energy Agency respectively. All glassware for metal analysis was acid washed while for PAH analysis was rinsed in dichloromethane followed by acetone to remove organic residues (Fig. 2).

Metals extraction from sediment was performed according to procedure described by ISO 11466. Briefly, 3 g the dried sediment at 105 °C was transferred to Kjeldahl tubes and was left overnight after the addition of 21 mL of hydrochloric acid and drop by drop addition of 7 mL nitric acid solution followed by 15 mL of nitric acid. In a Kjeldahl block, the suspension was refluxed for 2 h. After reflux, the tube were let to reaching room temperature, the suspension was filtered using 0.45 μm membrane while thoroughly rinsing the digestion tubes with 30 mL milliQ water (< 18 mΩ/cm). The filtrate was quantitatively transferred to a 50 mL volumetric flask and analyzed.

PAH's extraction was performed accelerated solvent extraction with a Dionex ASE 200. A 33 mL extraction cell was packed with two cellulose filter, glass fibers (pre-cleaned by heating at 450 °C over night) and the spiked sediment Briefly 5 g of finely sediment previously sieved at 2 mm were spiked with deuterated surrogate standards, Ph-d10 and Chr-d12. The extraction cell was left for 20 min to make sure of full percolation through the sample. Extraction conditions were as follow: 100% DCM was used as solvent and a temperature of 100 °C. The heat up time was 5 min and the program had five static cycles with 2 min extraction time at a pressure of 1500 psi and a flush volume of 35% (Tronczyński, 2005). The sediments samples were extracted in two vials which were combined and pre-concentrated to < 5 mL under a gentle stream of nitrogen. Sulfur interference was removed by shaking the extract with copper powder previously activated with 10% HCl and washed five times with dichloromethane and *n*-hexane. The extracts were evaporated to dryness and solvent exchanged to *n*-heptane in order to purify and fractionated on alumina:silica (1:1, w:w) column to eliminate organic interferences. The extracts were then concentrated to