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Occurrence and sources of polar lipid tracers in sediments from the Shatt al-Arab River of Iraq and the northwestern Arabian Gulf

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HIGHLIGHTS

- Few studies have investigated the polar compounds in the Shatt al-Arab and the Arabian Gulf.
- Multi-biomarker approach was used to distinguish the different sources of lipid compounds.
- The results showed that marine sources were major sources followed by terrestrial and sewage waste inputs.
- Anthropogenic sources were major sources in both coastal zone and the Shatt al-Arab River.

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ABSTRACT

Shallow surface sediment samples from the southern part of the Shatt al-Arab River estuary of Iraq and the northwestern Arabian Gulf were analyzed for polar lipid compounds including *n*-alkanoic acids, *n*-alkanols, steroids and triterpenoids. The results showed that the *n*-alkanoic acids, methyl *n*-alkanoates and *n*-alkanols typically ranged from C_{12} to C_{32} with total concentrations of 3.2 to 108.2 μg g^{-1} dwt sample, from C_{12} to C_{30} with totals of 1.1 to 18.9 μg g^{-1} dwt sample, and from C_{14} to C_{32} at 1.8 to 112.6 μg g^{-1} dwt sample, respectively. Steroids and triterpenoids were detected and included stenols, stanols, stenones, stanones, tetrahymanol, tetrahymanone and extended ββ-hopanes. The total steroid concentrations ranged from 2.8 to 78.4 μg g^{-1} dwt sample, whereas the triterpenoids varied from 0.05 to 7.6 μg g^{-1} dwt sample. The simple regression analysis of the results and the spatial distribution patterns of the identified organic tracers indicated that the inter-compound relationships were related mainly to their major sources. Cluster analysis and principal component analysis (PCA) of data set showed that the sampling sites are similar. These sources were allochthonous (terrestrial vegetation), autochthonous (plankton residues and bacteria in the sediments) and anthropogenic (sewage and petroleum).

1. Introduction

The major sources of organic components to the Arabian Gulf are runoff from rivers and air particulate matter transported by wind (Rushdi et al., 2010). The Tigris and Euphrates Rivers have created about 20,000 km^2 of wetlands known as the Mesopotamian Marshes (Partow, 2001; Brasington, 2002). They ultimately drain southeast-wards into the Arabian Gulf via the Shatt al-Arab waterway (Talling, 1980; Al-Saaidi et al., 1981; DouAbul et al., 1988; Partow, 2001), which is the main river discharge into the Arabian Gulf. It is about 200 km in length and deposits abundant amounts of silt into the river (Talling, 1980; DouAbul et al., 1988). Iraq's coastal zone is very limited and consists mainly of intertidal mudflats flanked by bare silt flats, often with an intervening narrow strip of date palm plantations (Maltby, 1994; Partow, 2001). Deposition of silt and other detrital matter via the Shatt al-Arab introduces different types and amounts of organic matter and inorganic materials to the Arabian Gulf. Therefore, determining the distribution, levels and sources of organic matter in the Shatt al-Arab River and coastal zone is important to understand the biogeochemical processes that control their occurrence.

Other major sources of organic matter in the Arabian Gulf are from petroleum contaminants due to onshore and offshore oilfields, discharges from refineries and petrochemical plants, regional recurrent wars and possibly natural oil seeps (PME/UNEP, 1989; Sadiq and McCain, 1993; Vogt, 1995; Massoud et al., 1998; PME, 2003). The major point-source pollutant inputs include sewage outfalls from Kuwait City

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and outfalls associated with industrial, desalination and power plant complexes to the north of Kuwait City (ROPME, 1999; Heil et al., 2001).

Therefore, the main objectives of this study are to determine the characteristics, distributions, and concentrations of the extractable polar organic compounds in shallow sediments from the Shatt al-Arab River and estuary, and the coastal zone of Iraq; and to identify the sources of these lipid compounds based on key parameters and molecular marker analysis.

2. Study area

The Shatt al-Arab River is about 120 km in length and is largely surrounded by alluvial lands and swamps. The width of the river ranges from 232 m at Basra to about 800 m at the mouth. The area also comprises the largest date palm forest in the world. Reeds, flowering shrubs and papyrus are the major aquatic vegetation. The water of the Shatt al-Arab flows to the head of the Arabian Gulf near Kuwait and caries large amounts of silt. Most of the sediments from the river deposit in the mouth as an extended delta and causing the recession of the gulf. The Iraqi city of Basra and the Iranian city of Abdan are the major metropolitan areas along the river. They are the main ports for oil production, storage and shipping. The study area is located in the Shatt al-Arab River to its mouth and the Arabian Gulf (Fig. 1). The sedimentation rate was estimated to be 1 mm yr^{-1} in the Tigris–Euphrates delta (Aqrawi, 1993, 2001). The grain size ranged from 6.2 to 8.0MdΦ (<30 μm) (Abaychi and DouAbul, 1985) and the total organic carbon contents varied from 0.51% to 1.4% (Abaychi and DouAbul, 1985; Abaychi et al., 1988).

3. Experimental procedure

3.1. Sampling

Seventy-two sites were selected from the southern part of the Shatt al-Arab River and estuary in Iraq as well as the northwestern coast of the Arabian Gulf, for shallow surface sediment sampling (Fig. 1). The samples were collected with a Van Veen grab sampler during December 2006 to January 2007. Only sediments representing the end of the Shatt-al-Arab River and the northwestern coast of the Arabian Gulf (sites 57–72) were selected for this study. The sampling sites were divided into three zones: the southern part of the Shatt al-Arab (Stations 57–62, Zone I), the Shatt al-Arab outer bar (Stations 63–66, Zone II) and the offshore zone (Stations 67–72, Zone III).

3.2. Sample preparation

About 10 g of each wet sediment sample was taken, dried at room temperature, then ground and sieved to obtain <125 μm fine particles. Each dried sediment sample (5 g) was extracted three times ultrasonically with 40 mL of dichloromethane and methanol (3:1, v:v) mixture for a 15 min period each in a 150 mL precleaned beaker. The combined extract was filtered through an annealed glass fiber filter for the removal of sediment particles. The filtrate was first concentrated on a rotary evaporator and then reduced using a stream of dry nitrogen gas to a volume of approximately 200 μL. The volume was finally adjusted to 500 μL exactly by addition of dichloromethane:methanol (3:1, v:v). An aliquot (50–100 μL) of each total extract was dried under a flow of nitrogen and derivatized with silylating reagent [30 μL N,O-bis(trimethylsilyl) trifluoroacetamide, BSTFA, Pierce Chemical Co.] for 3 h at 70 °C. Then, the BSTFA was evaporated under a flow of nitrogen and the sample was dissolved in n-hexane before analysis by GC–MS. This derivatizing agent replaces the H on hydroxyl groups with a trimethylsilyl [$(CH_3)_3Si$, i.e. TMS] group for better GC resolution of polar compounds.

3.3. Instrumental analysis

The chemical analysis was carried out by gas chromatography–mass spectrometry (GC–MS) with a Hewlett-Packard 6890 gas chromatograph coupled to a 5973 Mass Selective Detector, using a DB-5MS (Agilent) fused silica capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness) and helium as carrier gas. The GC was temperature programmed from 65 °C (2 min initial time) to 310 °C at 6 °C min^{-1} (isothermal for 20 min final time) and the MS was operated in the electron impact mode at 70 eV ion source energy. Full scan mass spectrometric data were acquired and processed using the GC–MS ChemStation data system.

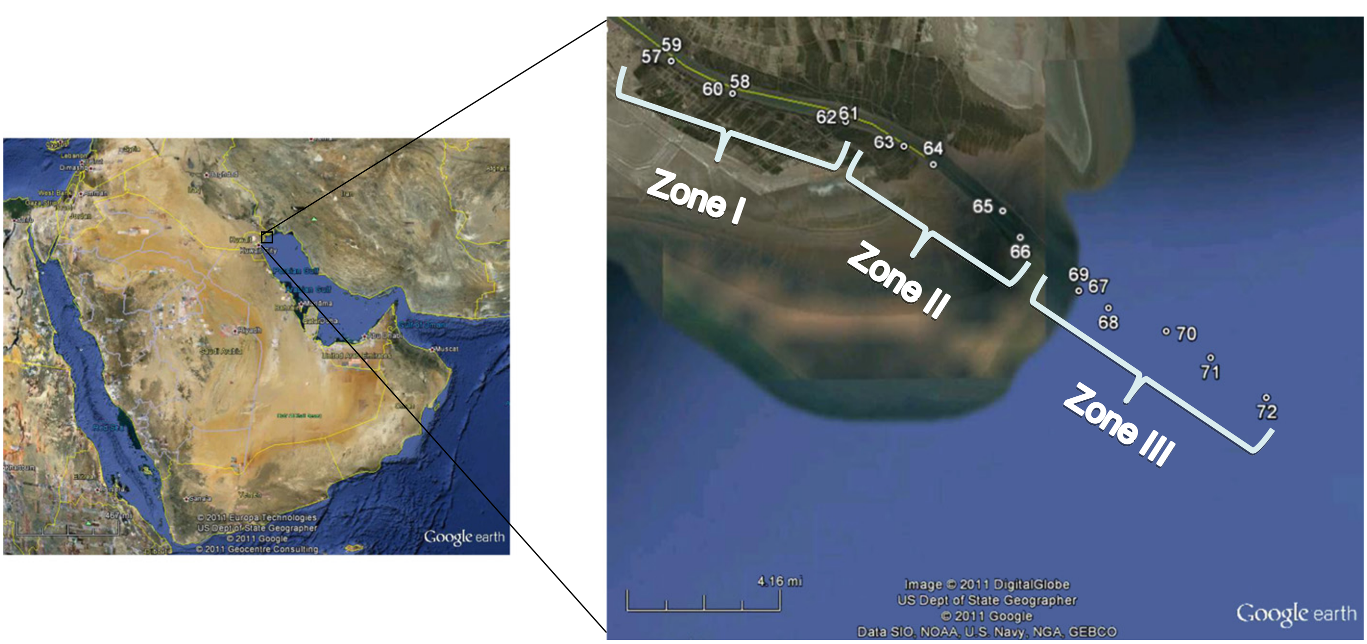

Fig. 1. Location map of the sampling sites in the Shatt al-Arab River estuary.