

Aliphatic and aromatic hydrocarbons in marine biota and coastal sediments from the Gulf and the Gulf of Oman

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Abstract

The composition and spatial distribution of aliphatic and polycyclic aromatic hydrocarbons (PAHs) were investigated in biota and coastal sediments from four countries surrounding the Gulf (Bahrain, Qatar, United Arab Emirates and Oman). The levels of total petroleum hydrocarbons (TPH), aliphatic unresolved mixture and PAHs in sediments and biota were relatively low compared to world-wide locations reported to be chronically contaminated by oil. Only in the case of the sediments collected near the BAPCO oil refinery in Bahrain, having concentrations of $779 \mu\text{g g}^{-1}$ total petroleum hydrocarbon equivalents and $6.6 \mu\text{g g}^{-1} \sum \text{PAHs}$, can they be categorized as chronically contaminated. Some evidence of oil contamination was also apparent in sediments and bivalves around Akkah Head and Abu Dhabi in the UAE, and near Mirbat in Oman. Contaminant patterns in sediments and biota indicated that the PAHs were mainly from fossil sources, with the exception of the high PAH concentrations in sediments near the BAPCO refinery that contained substantial concentrations of carcinogenic PAH combustion products.

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1. Introduction

The Gulf, also known as the Arabian Gulf or Persian Gulf, represents a highly stressful environment due to a combination of both prevailing natural conditions and development pressures along its coastline. The Gulf region has approximately two-thirds of the world's proven oil reserves and the eight riparian states (Iran, Iraq, Kuwait, Bahrain, Qatar, Saudi Arabia, UAE and Oman) currently account for approximately one-fourth of the world's oil production (Khan, 2002). Problems associated with oil pollution and non-living resources appear to be of greater significance in the Gulf compared with

other regions (Munawar et al., 2002). This region has undergone considerable development, and consequently urbanization, industrialization, port areas and refineries have become major sources of pollution to the marine environment. Also, a combination of tanker traffic and either accidental or intentional spills have prevailed. The spill that took place during the 1991 Gulf War is only one of three major events (Fayad et al., 1996). A significant number of studies in the Gulf has looked at petroleum hydrocarbons, mainly with respect to determining concentration, composition and degradation just after the 1991 oil spill (Al-Lihaibi and Al-Omran, 1996; Al-Lihaibi and Ghazi, 1997; Banat et al., 1998; Fowler et al., 1993; Massoud et al., 1998; Massoud et al., 1996; Readman et al., 1996; Readman et al., 1992; Saeed et al., 1996). These investigations provided evidence that firstly, the oil spill was restricted to the Saudi Arabian coastline within 400 km from the point of spillage and

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secondly, the contamination had degraded within some few months due to weathering processes.

In 1994, two tankers collided spilling 16,000 tonnes of Iranian crude oil into the Gulf of Oman. Despite damage caused to the marine environment, studies demonstrated a significant decrease in contamination levels, almost returning to normal conditions within eight months of the accident (Shriadah, 1998; Shriadah, 2000). The recovery was likely accelerated as a result of the physical characteristics of the region and self-purification processes. Enhanced degradation of the petroleum products was inferred due to the existence of microorganisms acclimated to oil pollution, and to the high ambient temperatures in the Gulf causing an increase in evaporation and photo-oxidation rates.

The regional monitoring and surveillance programme organized by ROPME has generated reliable, long-term data for the Gulf. The aim of this survey undertaken in 2000–2001 was to screen for trace inorganic (de Mora et al., 2003, 2004) and organic contaminants (de Mora et al., 2005) in key coastal areas from the Gulf and the Gulf of Oman, and to compare the results with earlier surveys in the same areas. The present work evaluates marine contamination of petroleum hydrocarbons in the coastal zones of UAE, Qatar, Bahrain and Oman based on the quality of sediment and some local seafood species. Sediments are one of the many environmental compartments in which oil pollution accumulates. Therefore, sediments can hold and release pollutants causing detrimental effects to biota long after the initial input of pollution has ceased. These contaminants might be released slowly and be bioaccumulated in organisms that dwell in and around the sediment. Seafood resources are of vital importance to the Gulf States and to date only limited efforts have been made to evaluate seafood quality. Therefore, information on seafood contamination is sparse. For the most part, studies have focussed on potential petroleum hydrocarbon contamination of the fisheries following the massive oil spill during the 1991 Gulf War (Al-Majed et al., 1998; Al-Yakoob et al., 1993; Fayad et al., 1996; Fowler et al., 1993; Krahn et al., 1993; Saeed et al., 1995; Sen Gupta et al., 1993). More recent data on concentrations levels of petroleum hydrocarbons in biota is needed to assess their contamination risk for human consumption. Overall, the results presented here for sediments and biota contribute to the regional database for the Gulf and the Gulf of Oman.

2. Methods

2.1. Sample collection

Marine samples were collected in the ROPME Sea Area (RSA), which covers the entire Gulf and the Gulf

of Oman. In general, all sampling procedures were carried out according to internationally recognized guidelines (UNEP, 1991). The locations in Bahrain, Oman, Qatar and the United Arab Emirates for the collection of sediments and biota are shown in Fig. 1. Sampling dates and locations for the collection of sediments are given in Table 1. The sediments were stored frozen at -18°C in aluminium cartons prior to analyses. Table 2 provides information regarding the type of biological specimens and from where they were obtained.

For bivalves, the soft parts from 1 to 18 individuals were dissected and drained of excess liquid. For fish, 100–300 g of dorsal muscle from a single individual was dissected for the sample. Fish liver tissue was also removed and prepared for analysis in some cases. Analyses of fish reported here, including the two samples from Quriyat, relate to individual fish rather than replicate determinations. All biota samples were stored in glass bottles before freezing at -18°C until subsequently analysed.

2.2. Pre-treatment of sediments

Following freeze-drying, samples were sieved through vibrating stacked stainless steel sieves with mesh sizes from 250 μm to 1000 μm . Sediments were then homogenized prior to extraction. In some cases, an aliquot for each sample was taken in order to perform TOC and grain size analyses. Various internal standards were added to the sediments for quantifying the overall recovery of the analytical procedures: $n\text{-C}_{19}\text{-}d_{40}$ and $n\text{-C}_{24}\text{-}d_{50}$ for the aliphatic hydrocarbon fraction; naphthalene- d_8 , anthracene- d_{10} , pyrene- d_{10} and perylene- d_{12} for the aromatic hydrocarbon fraction.

Samples were Soxhlet extracted for 8 h into 250 ml of hexane:methylene chloride (1:1, v/v). A sulphur removal procedure was performed using activated elemental copper in order to avoid sulphur interferences when using gas chromatography. The Extractable Organic Matter (EOM) was determined by evaporating a measured small volume of this extract on the pan of an electrobalance. The final extracts were then separated into two aliquots: 1/3 for hydrocarbons, and 2/3 for chlorinated hydrocarbon analyses.

For the hydrocarbon measurements, the extract was passed through a silica/alumina column in which the silica and alumina were activated first at 200°C for 4 h and partially deactivated with 5% water. The chromatography column was prepared by slurry packing 10 ml of silica, then 10 ml of alumina and finally 1 g sodium sulphate was added to the surface to avoid disturbance of the top layer when pouring the solvent. Elution was performed using 20 ml of hexane to yield the first fraction (containing the aliphatic hydrocarbons), then 30 ml of hexane:methylene chloride (90:10) and followed by 20 ml of hexane:methylene chloride (50:50). These

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