Marine Pollution Bulletin xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Marine Pollution Bulletin

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

Assessment of heavy metal and petroleum hydrocarbon contamination in the Sultanate of Oman with emphasis on harbours, marinas, terminals and ports

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ARTICLE INFO

Keywords:
Heavy metals
TBT
Hydrocarbons
Sediments
Biota
Oman

ABSTRACT

The assessment here includes data on levels of contaminants (petroleum hydrocarbons and heavy metals) in sediments and biomonitor organisms, including the eulittoral rock oyster *Saccostrea cucullata* and subtidal biomonitors, the barnacle *Balanus trigonus* and the antipatharian coral *Antipathes* sp., at harbours, marinas, terminals and large ports along the coastline of Oman. TBT levels in harbour and port sediments up to a maximum of 100 ppb TBT dry weight are highlighted. Oysters contained concentrations up to 367 ppm mg TPH/kg dry weight. The maximum levels of Cd, Cu, Pb and Zn were found in the subtidal sediments and barnacles at the oil tanker loading Single Buoy Mooring stations in Mina Al Fahal. In general, the levels of most of the contaminants analysed are at low to moderate concentrations compared to those in highly contaminated sites such as shipyards and dry docks, but continued monitoring is recommended especially during any dredging campaigns.

1. Introduction

The coastline of Oman is exposed to high risk from shipping accidents and oil pollution from oil tankers, Very Large Crude Carriers (VLCCs), and increasing numbers of Liquid Natural Gas (LNG) tankers. The adjacent Strait of Hormuz is one of the world's most important oil transit chokepoints due to its daily oil flow of roughly 38% of all seaborne traded oil (http://www.eoearth.org/profile/Eia). The earlier high incidence of tar on Oman's beaches was the impetus for the monitoring programmes initiated between Oman, the United Nations Environment Programme (UNEP) and the International Atomic Energy Agency-Marine Environment Laboratories (IAEA-MEL) in the early 1980s (Burns et al., 1982; UNEP, 1982). Since then, marine pollution monitoring surveys have assessed levels and distribution of heavy metals, petroleum hydrocarbons and organochlorinated compounds in sediments, fish and bivalves under the Regional Organisation for the Protection of the Marine Environment (ROPME)-IAEA contaminant screening projects (Fowler, 1988; de Mora et al., 2003, 2004, 2005, 2010; Tolosa et al., 2005). Following the massive oil spill during the 1991 Gulf War, the same stations in these surveys were sampled to carry out temporal and spatial comparisons (Fowler et al., 1993). All these surveys provide useful data on general coastal conditions, whereas the present paper focuses on marine contaminants in harbours, terminals and ports where either sheltered conditions with restricted tidal exchange or high densities of vessels may lead to increased risks of oil spills, discharges and impacts from antifouling paints.

The surveys included here provide monitoring data on subtidal sediments where toxic contaminants, such as tributyltin (TBT), can accumulate. TBT is a highly toxic organotin compound used previously in antifouling paints (AFPs) and now banned by the International Maritime Organisation (IMO) under its International Convention on the Control of Harmful Anti-fouling Systems on Ships (IMO, 2005), which includes a ban on the use and presence of such compounds on ship hulls since 2008. A number of organotin compounds were used in AFPs, including alkyl tins (trimethyltin, tripropyltin and tributyltin) normally as copolymers to leach into seawater, and were very effective compared to Hg- or Cu-based AFPs (Yebra et al., 2004). Tributyltin is highly toxic to a wide range of marine organisms at very low concentrations and a few

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http://dx.doi.org/10.1016/j.marpolbul.2017.05.015
Received 2 December 2016; Received in revised form 14 April 2017; Accepted 7 May 2017

nanograms of Sn per liter can cause sterility in several species of gastropods. de Mora et al. (2003) quote the classification of > 1.3 ng Sn/g (ppb) in sediments as a 'contaminated' threshold. Nowadays, modern AFPs are composed of Cu and Zn oxide as the main biocides (Almeida et al., 2007), thus increasing concentrations of these heavy metals are now observed in harbours (Schiff et al., 2004). In addition to sediment analyses, the use of a biomonitor organism in these studies, e.g. the rock oyster *Saccostrea cucullata*, provides a useful extra component to water and sediment analysis and has been strongly recommended for any long-term monitoring programme (Phillips and Rainbow, 1994).

In terms of potentially erroneous interpretation of analytical results, earlier surveys have shown that the sediments along the Al Batinah and Muscat coastlines including Quriyat contain high levels of Cr and Ni (de Mora et al., 2004). The northern Oman mountains consist of several massifs of ophiolite cropping out along a 500 km long band trending NW-SE along the northern coast of Oman. This is one of the best exposed sections of oceanic crust and mantle in the world. The large blocks of ophiolite rocks are composed of serpentinised peridotites (dunites, harzburgites) which are rich in metals with up to 2000 ppm of Cr (Hanghøj et al., 2010). The natural leaching and mineralisation of these inland ophiolites leads to deposited sand and gravel material flowing along the wadis and draining into the nearshore sediments. This natural phenomenon explains the high levels of Cr, Ni and V found in sediments from Khabourah to Quriyat (de Mora et al., 2004). These geochemical inputs of heavy metals should be distinguished from contaminant sources discussed here or, for example, from thermal desalination plant discharges as studied at Barka Power/Desalination Plant and Al-Ghubrah Power/Desalination Plant by Abdul-Wahab and Jupp (2009).

With the exception of an ophiolite block present in Masirah Island (de Mora et al., 2004), other sites in Musandam or along the Arabian Sea coastline not bordering such ophiolites but with enhanced metal levels are more likely to have these derived from anthropogenic sources. There is also the interesting case of upwelling-induced bioaccumulation of Cd along Arabian Sea coasts highlighted in a previous temporal study at Sadh in Dhofar (Fowler et al., 2007).

In this paper we review previous information and present new data in order to obtain adequate results for assessing the presence and existing concentrations of selected heavy metals and petroleum hydrocarbons in sediments and biomonitor organisms, e.g. rock oysters and barnacles, in harbours, marinas, terminals and ports of the Sultanate of Oman. To the best of our knowledge, there are no available published data on contaminant levels in harbours, marinas and ports in Oman, thus this paper provides a large baseline dataset to compare with future coastal monitoring. This is particularly important in connection with potential risks of contamination such as oil spillage from vessels, boat waste discharges, and the monitoring of TBT levels in accordance with IMO regulations.

2. Materials and methods

In the case of the majority of reports referenced in compiling these data, the collection and assessment of sediment samples was conducted in accordance with the AS/NZS, Australian/New Zealand Standard (1998) where appropriate. Samples were obtained by divers using jars to skim surface sediment. Once the sample containers were filled, each container was capped and placed in cooler boxes containing ice and transported to the Analytical Reference Laboratory (ARL) in Australia under appropriate Chain of Custody (CoC) protocols (www.arlwa.com.au). Samples were received at the laboratory within 36 h of collection. The in-house method for analyzing metals in soil and sediment, ARL No. 401 corresponding to EPA Method 3120, involved acid digestion and analysis by inductively coupled plasma-optical emission spectroscopy (ICP-OES). Total petroleum hydrocarbons (TPHs) in sediments were analysed by ARL No. 010 (EPA 3550C), involving solvent extraction followed by gas chromatography-flame ionisation detection (GC-FID) analysis. ARL maintains an internal Quality Control (QC) programme and procedures include use of duplicate analyses, matrix spike, certified reference material and laboratory control samples. ARL is a National Association of Testing Authorities, Australia (NATA) accredited laboratory and, as such, is certified to ISO/IEC 17025:2005 parameters.

Table 1
Summary of sediment quality criteria. Adopted trigger levels are shown in bold.

Analyte	Unit	[b]ANZECC, 2000		[c]DCL
		[a]ISQG-low (trigger value)	ISQG High	
Arsenic	mg/kg	**20**	70	29
Cadmium	mg/kg	1.5	10	**0.8**
Chromium	mg/kg	**80**	370	100
Copper	mg/kg	65	270	**36**
Lead	mg/kg	**50**	220	85
Mercury	mg/kg	**0.15**	1	0.3
Nickel	mg/kg	**21**	52	35
Zinc	mg/kg	200	410	**140**
Total polycyclic aromatic hydrocarbons	µg/kg	4000	45,000	**1000**
Tributyl Tin[d]	µg/kg	**9**	70	NR
Total petroleum hydrocarbons[d]	mg/kg	**280**		

NR: No recommendation at this time.
[a] Interim Sediment Quality Guideline
[b] Taken from ANZECC (2000) Australian and New Zealand Guidelines for Fresh and Marine Water Quality.
[c] Taken from Dutch Contaminated Land (DCL, 2000) Target Values
[d] Taken from Simpson et al. (2013)

The important role of sediments both as a source and sink of dissolved contaminants has been recognized for some time (Fowler, 1982). The sediment quality assessment levels and associated trigger values listed below in Table 1 have been extracted from the Australian and New Zealand Guidelines for Fresh and Marine Water (ANZECC, 2000) and the Dutch Contaminated Land Standards (DCL, 2000), whichever are the most stringent. Australian assessment levels reflect data from arid landscapes with low river flows into the nearshore marine environments, a scenario which is analogous to that in the Middle East.

Samples of rock oyster were collected during low tide periods from rocky shores or breakwaters at the harbour sites and at the control stations. Their soft tissues were obtained by prising off the upper shell with acid-cleaned tools, cutting the adductor muscle and transferring the whole animal into acid-rinsed jars. The combined oyster tissues were frozen and then, like the sediments, shipped to the ARL Laboratory. Heavy metals (As, Cd, Cr, Cu, Pb, Hg, Ni, Zn, V and TBT) were analysed and results reported on a dry weight basis. TBT analyses by a sub-contracted laboratory met the QC specifications. TPHs in samples were analysed on a wet weight basis and were converted to dry weight using a dry weight content of 25% of the fresh weight (Bryan, 1984). All sediment and biomonitor analyses are reported on a dry weight basis.

Although there are no national standards or guidelines in Oman for heavy metals in fish and shellfish, there are arbitrary, descriptive guidelines adopted by the Joint Monitoring Programme (JMP) of the Oslo and Paris Commission (OSPARCOM), with other standards or guidelines compiled by the Food and Agriculture Organisation (FAO, 1983), Cole et al. (1999) and the European Commission (EC). Table 2 summarises some relevant guidelines with the adopted criteria used here (lower limits of ranges) shown in bold.

In a 1997 survey of Mina Al Fahal (Jupp, 1998), the collections of sediments and barnacles at the Single Buoy Moorings (SBMs) were carried out by divers from the Petroleum Development Oman (PDO) barge *Fahal 1* when it was installed during 'tanker-free windows' at the SBMs. Bottom sediments were collected in 4 L plastic containers,