ABSTRACT

This is the first study for the analysis of heavy metal in marine sediments, seawater and fish at Single Buoy Mooring (SBM3) in the Mina Al Fahal of Sultanate of Oman. For the purpose of establishing baseline, as well as the assessment of marine contamination due to heavy metals, in sediments, seawater were collected from six different stations at SBM3 of the Mina Al Fahal. This took place between June 2009 and during the mid of April 2010. The heavy metals analyzed were cadmium (Cd), copper (Cu), lead (Pb) and vanadium (V), using Inductively Coupled Plasma Emission Spectroscopy (ICP-OES) and Graphite Furnace Atomic Absorption Spectrophotometry (GF-AAS) techniques. Based on the experimental results, the mean concentrations for heavy metal content Cd, Pb, Cu and V recorded at six different Stations at SBM3 for the sediments and seawater samples, over the entire span of the sampling sites in subtidal sediments exist in the order (V > Cu> Pb > Cd). The mean concentrations for heavy metals Cd, Pb, Cu and V, over the entire span of the sampling sites in whole tissue of one of the popular, namely the grouper fish *Epinephelus coioides* exist in the order: (Cu > Pb > Cd > V). Generally, the results of mean concentrations for heavy metal content (Pb, Cd, V and Cu) suggest that the SBM3 marine sediment, seawaters and fish are of good quality as the mean concentrations of the metal reported in the studied areas were basically below or within acceptable limits set by European Commission (EC) and Omani legislation, as well as other studies carried out in the coast of Oman and the results published for internationally reported values in the Arabian Gulf and Arabian Sea and they posed no threat to public health, with the exception of vanadium (V) in the subtidal sediments at SBM3. There are speculations that the presence of vanadium is perhaps as a result of the accumulation of chronic levels wastes discharged by passing tanker traffic.

ABSTRAK

Untuk tujuan penubuhan garis dasar serta taksiran pencemaran laut disebabkan logam berat dalam endapan, air laut dan ikan di SBM3, siasatan ini ialah yang pertama bagi menganalisis logam berat di SBM 3, Mina Al Fahal. Dengan menggunakan GF-AAS dan ICP-OES teknik, Cd, Cu, Pb dan V telah dianalisis. Sampel diambil antara Jun 2009 dan semasa pertengahan April 2010.Keputusan kepekatan kandungan logam berat (Pb, Cd, V dan Cu) direkodkan di enam stesen lain, di (SBM3) untuk subtidal mendapan pada >125 μm telah dianalisis menggunakan ICP-OES. Tahap logam berat dalam subtidal mendapan wujud dalam susunan V > Cu> Pb > Cd bagi kesemua tempat persampelan. Terdapat spekulasi mengenai kehadiran Vanadium iaitu akibat pengumpulan bahan-bahan buangan dilepaskan oleh kapal minyak perdagangan yang melaui kawasan itu pada peringkat yang kronik. Keputusan untuk kandungan logam berat (Pb, Cd, V dan Cu) direkodkan di enam stesyen berbeza di SBM3 untuk sampel air laut dan ikan yang telah dianalisis menggunakan GF-AAS. Umumnya, keputusan bagi kepekatan logam dari air laut ini telah ditemui tertinggi mengikut susunan: (V > Cu> Pb> Cd). Berdasarkan keputusan eksperimen, boleh disimpulkan bahawa air laut di SBM3 adalah berkualiti baik. Dengan mempertimbangkan fakta itu bahawa contoh air laut yang diambil dari SBM2 di Mina Al Fahal dan kepekaten logam berat yang dilaporkan oleh kajian sebelum ini adalah sama, ia tidak dianggap menjadi kepentingan toksikologi. Tahap logam berat di semua tempat persampelan dalam keseluruhan tisu salah satu ikan yang popular, iaitu kerapu (Epinephelus coioides) wujud dalam susunan: (Cu > Pb > Cd > V). dapat diperhatikan tahap (Pb, Cd, V dan Cu) di SBM3 dalam kebanyakan sample pada asasnya masih dalam had yang ditetapkan oleh Suruhanjaya Eropah (SPR) dan perundangan Oman, dan mereka meyakini tiada ancaman terhadap kesihatan awam.

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CHAPTER 1

INTRODUCTION

1.1 General Introduction

The marine environment contamination by trace metals has become a major issue during the last few years. The marine ecosystems are subject to contamination by trace metals caused by different factors (Cabana, 2001). Heavy metals such as copper, zinc, lead, nickel, cobalt, iron, aluminum, and cadmium, released from different activities and sources reach the sediments and other ecosystem components. The careful research about spatial distribution of heavy metals in beach environments have concentrated chiefly on their location in relation to point sources of pollution as well as their distribution in along–shore and across–shore directions (Cabana, 2001). Sediments can accumulate the received metals depending on the nature and the geological formations of these sediments. The grain size of sediment particulates acts as a main factor controlling the spatial distribution of heavy metals.

The Gulf in general and the Gulf of Oman in particular represent a perfect example for the study of the relationship between heavy metals concentrations and beach states (See Appendix A). The ecosystem is relatively fragile because it is exposed to high temperature, salinity and UV exposure. These distinct zones have

experienced several impacts in recent years that have led pollution problems in the region. The waterways, which are the main sources of anthropogenic pollutants, are heavily utilized, especially with respect to oil tankers' traffic (Stephen de Mora *et al.,* 2004).

The quality of our marine environment is very important for several socio-economic reasons. The economic reason is that seafood, notably fish and shrimp, is of value for both local consumption and export revenue (Stephen de Mora *et al.,* 2004). The sociological reason is that the sea water is exploited as a source of fresh water through desalination (Price *et al.,* 1993).

Mina Al Fahal is of primary importance to the economy of Oman being the export point of crude oil Via Terminal and Offshore Operations at Single Buoy Mooring (SBMs) (See Appendix C and D). Mina Al Fahal is an open sandy bay within the capital area, Muscat (see Figure 1.1 and Appendix B).

SBM3 is the site of Petroleum Development Oman's oil storage facility (tank farm), tanker loading operations and the Oman Refinery Company. Crude oil from the interior is stored at the tank farm (capacity of 4.3 million barrels of oil) and loaded onto tankers (See Appendix F) via the two Single Buoy Moorings, SBM1 (38 m depth and 3.1 km offshore) and SBM2 (47 m depth and 4.3 km offshore). SBM3 (21 m depth) imports and exports refined petroleum products, as illustrated in the Figure 1.1. Regular export of Oman crude started in 1967 (Jupp, 1998).

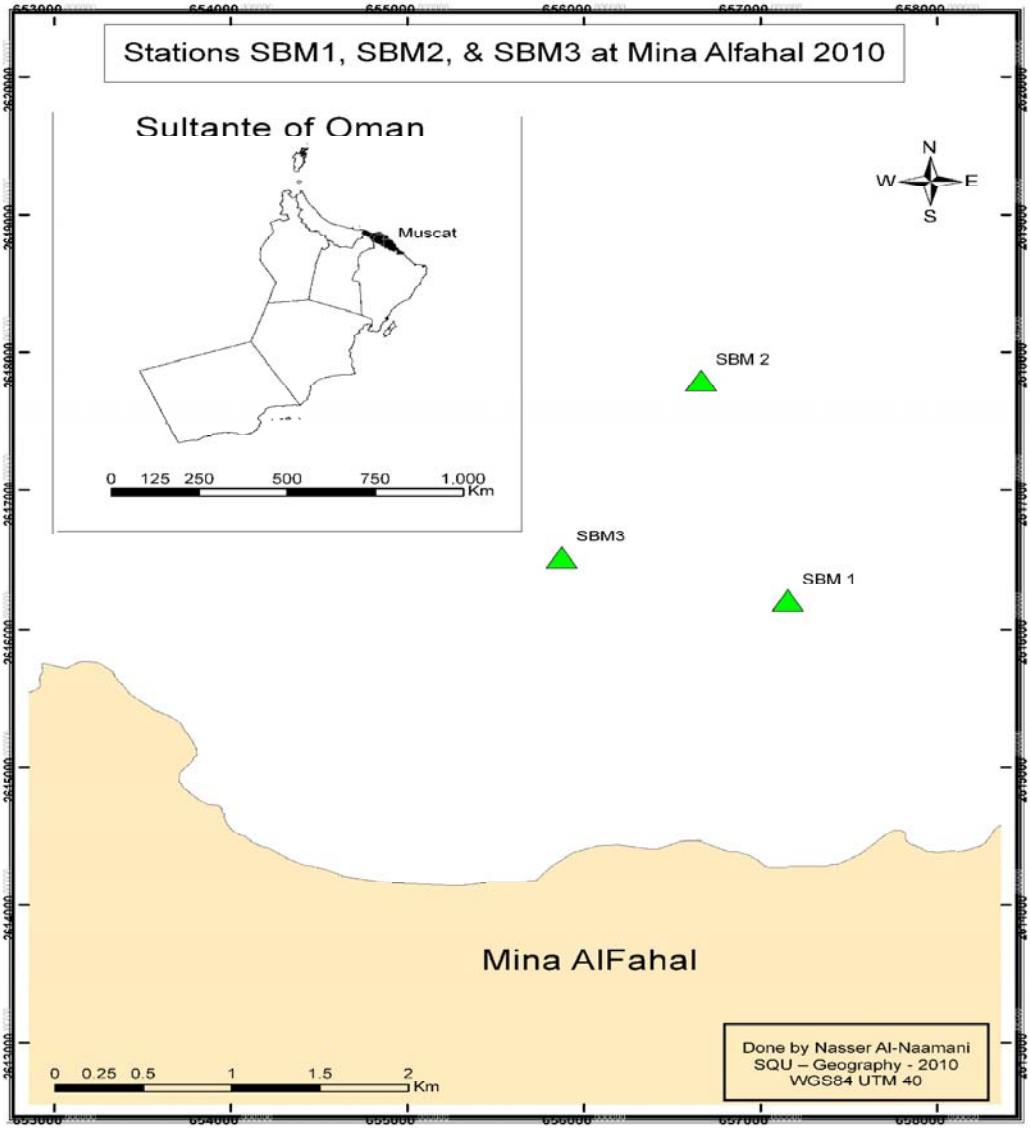

Figure 1.1 Stations SBM1 , SBM2 and SBM3 in Mina Al Fahal, *Coordinates*: UTM and Latitude and Longitude coordinates at stations as measured by Global Positioning System (GPS) using the geodetic Datum WGS 84 are as follows: SBM1 (UTM N 2616206.9 E 657154.9, Latitude and Longitude N 23° 39.150' E 58° 32.620'), SBM2 (N 2617797.7 E 656664.3, Latitude and Longitude N 23° 39.932' E 58° 32.315') and SBM3(UTM N 2616517 E 6655874 , Latitude and Longitude N 23^{o}39' 06.7" E 58^{o}31' 41.9").

1.2 Background of Study

The Marine Pollution Monitoring Programmme (MPMP) of Ministry of Environment and Climate Affairs (MECA), in conjunction with the Food & Environemnt Monitoring Centre (FEMC) uses standard sampling protocols and equipment (MOOPAM, 2006) to carry out sampling of marine sediments (primarily intertidal sediments) and biomonitors such as the rock oyster and fish muscle tissue. This sampling was used in a rapid check of intertidal (beach) sediments and one subtidal sampling of a Single Buoy Mooring (SBM) site in Mina Al Fahal, the tanker-loading bay of Petroleum Development Oman (PDO).

Previous studies have shown some contamination in subtidal sediments at the SBMs. The baseline study of Mina Al Fahal for the Oman Refinery Company (ORC) carried out in 1982 (Taylor/SMBA, 1983) showed evidence of high levels of metals in sediments around SBMs, which were attributed to particulate material discharged in ballast water from tankers (See Appendix G). Taylor/SMBA (1983) attributed the impoverished faunal populations found at both SBM1 and SBM2 to high levels of metals, with up to 505 ppm Cu and 114 ppm Pb and hydrocarbon pollution.

A primary objective of the study by Jupp (1998), commissioned by PDO, was to assess the status of the marine environment of Mina Al Fahal (including Fahal Island) compared to conditions found in the Baseline Study for ORC by Taylor/SMBA (1983) and the study by Cowiconsult (1985). As far as possible, standard methods and similar analytical protocols were employed in order to carry out this comparison.

The routine sediment and biomonitoring analyses of Ministry of Regional Municipalities & Water Resources (MRMWR) were employed. In addition, some new areas of study were incorporated into the 1997 survey. As well as the employment of the standard MRMWR intertidal biomonitor the rock oyster *Saccostrea cucullata* (also used in the Cowiconsult survey in 1985), a subtidal biomonitor, the barnacle

Balanus trigonus, was successfully employed for the first time in Oman. This organism was collected from subsea bunker hoses at the SBMs and analysed for heavy metal content in a collaborative project with the Natural History Museum (NHM), London. The sediment samples collected at various sites in Mina Al Fahal for analysis of contaminants were also assessed for the mollusc fauna retained on sieves. These studies were useful in comparing benthic fauna analysed in the Baseline and Cowiconsult studies.

A monitoring survey of several physicochemical and biological marine environmental components was conducted between May to September 2003 (HMR Consultants, 200) which also showed evidence of high levels of copper in the SBM sediments, compared to those found in the baseline study (1982) these levels are presumed to be derived from antifouling paint from tanker hulls (see Figure 1.2).

The finding of trace amounts of tributyltin (TBT) in the SBM sediments also points to contamination from antifouling paints (Carr, 2003). Cd appears to have decreased from 3 ppm in 1982 to 0.5 in 2003. Levels of Pb have also decreased from over 50 ppm in 1980/82 to 11 ppm in 2003. Levels of vanadium have increased from ~ 3 ppm in 1980/82 to over 20 ppm in 2001/2003 and is presumed to come from the ETP Effluent See Appendix E). SBM sediments usually contain high levels of copper (~ 300 ppm in 2001, mean 170 ppm in 2003) presumed to come from antifouling paints.

The overall conclusion is that industrial activities both onshore and offshore have negligible impact on the marine environments studies in Mina Al Fahal.

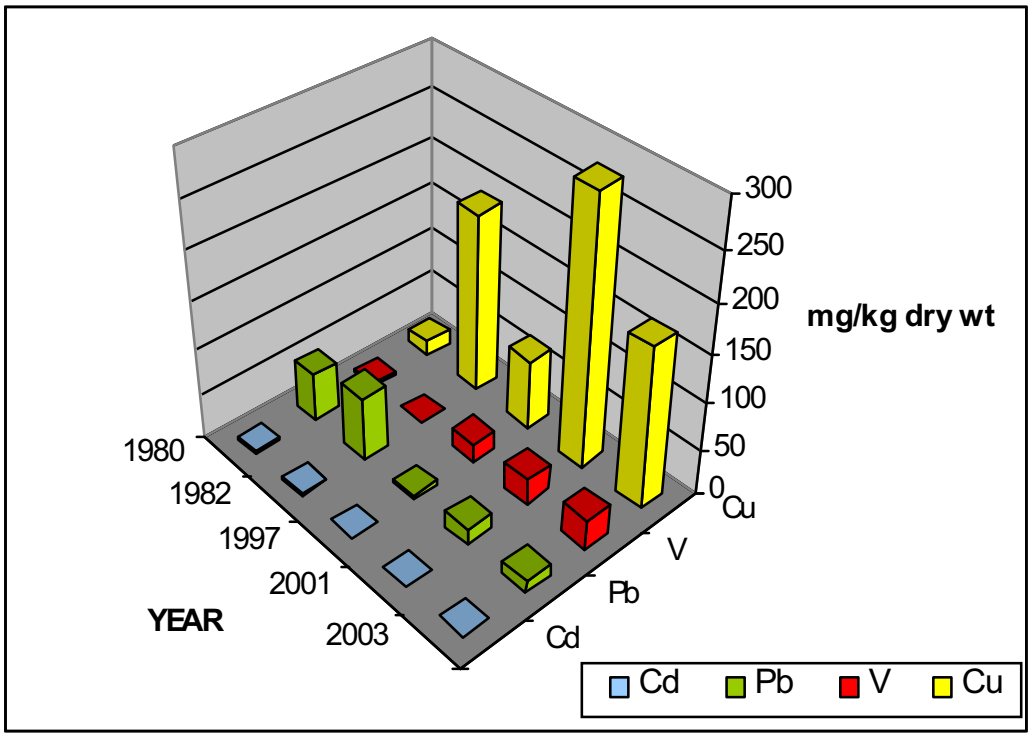

Figure 1.2 Three-dimensional view of long-term changes in mean concentrations (mg/kg dry wt.) of the heavy metals Cd, Cu, Pb and V in subtidal sediments at <250 µm grain size, from SBM sediments (HMR Consultants, 2002).

1.3 Problem Statement

Mina Al Fahal is an important harbor in Muscat, the Sultanate of Oman. Single Buoy Moorings (SBM3) with a 21 m depth, is one of the three locations of the harbor where the main activities involve importing and exports refined petroleum products as illustrated in the Figure 1.1. Due to such activities, there is a possibility of heavy metals contamination in marine sediments around this area. The heavy metals content of the sediments, seawater and selected fish species in other parts of the port have been previously analyzed. However, the sediments, seawater and fish species at SBM3 have not been analyzed before; therefore there is a necessity to analyze the sediments, seawater and fish species from this site in order to assess the heavy metals contamination conditions at this site.

1.4 Objectives of the Research Project

The objectives of this study are as follows:

1. To study the levels of heavy metals (Pb, Cd, V and Cu) in sediments, seawater and selected fish species at Single Buoy Mooring (SBM3), Mina Al Fahal.

2. To assess the trend of variations of (Pb, Cd, V and Cu) measured in selected sampling area from Single Buoy Mooring (SBM3), Mina Al Fahal.

3. To compare the present study (SBM3) with previous studies at different areas from the coast of Oman, as well as other studies in the Arabin Gulf and Arabian Sea in order to assess any long-term trends the data from previous studies of heavy metals in marine sediments, water and fish to the present survey.

1.5 Scope of the Study

The scope of the present study is limited to the determination of Pb, Cd, V, and Cu in sediments, seawater and selected fish species by using Inductively Coupled Plasma- Optical Emission spectrometry (ICP-OES) or Graphite Furnace Atomic Absorption Spectrophotometry (GF-AAS).

1.6 Significance of the Present Study

The study area of Mina Al Fahal extends from the West Headland (Ras Al Abyad) to the East Headland (Ras Al Masita), which form boundaries of the 2 km sandy beach, with the northern limit including Fahal Island in the northwest of this restricted area (see Figure 1.1 and Appendix B). This study is important to obtain evidence of heavy metal pollution in sediments, seawater and selected fish species around this area. Since the bay lies close to the most heavily trafficked tanker routes in the world, it is possible that heavy metals contamination contributed from passing tankers as well as from sources of pollution both within and in the immediate environs of Mina Al Fahal.