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Heavy Metals Contents on Beach Sediments North and South of Sohar Industrial Area, Oman

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Abstract: A total of 63 surface sediment samples from three sites: Harmul north of Sohar industrial area, Majees south of Sohar industrial area and Zafaran nine kilometers south of Majees were collected in November 2005. They were analyzed for 11 heavy metals including: Vanadium (V), chromium (Cr), manganese (Mn), nickel (Ni), copper (Cu), selenium (Se), mercury (Hg), cadmium (Cd), lead (Pb), zinc (Zn) and arsenic (As) using microwave digestion followed by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). The concentrations of chromium, manganese and vanadium were higher in Harmul than Majees and Zafaran. Arsenic concentration was generally low except in some stations. The results revealed that heavy metals concentrations in these sites are not alarming.

Key words: Sohar, ICP-MS, heavy metals, sediments, microwave digestion

INTRODUCTION

Industrial development in the Sultanate of Oman has gathered momentum over the last few years with the introduction of targeted development. The Sohar Industrial Area, SIA (about 123 km²) is such an example where large scale development is having commercial and environmental impacts. The effect of such heavy industrialization has the possibility of affecting the environment in an adverse way. Though a comprehensive master plan which included a Strategic Environmental Impact Assessment (SEIA) has been developed for the SIA, the master plan lacked baseline data on the chemical characteristics of the coastlines north and south of SIA, specifically in Harmul and Majees coastlines which are the closest coastlines to SIA. In order to manage the pollution problems likely to occur due to SIA, baseline data on the chemical, characteristic of the aquatic ecosystem is needed for future monitoring.

Sediments are considered to be the sink for heavy metals (Ramirez *et al.*, 2005) as it can trap more amounts of in-coming heavy metals than sea water. Metal concentrations in sediments may exceed by several orders of magnitude the concentration in seawater (Jupp and Jameison, 2001; Izquierdo, 1997; Luoma and Bryan, 1981). In this study, a total of 63 beach sediments samples were sampled in November 2005. The aim is to investigate the environmental status of beach sediments, with respect to heavy metals, north and south of SIA.

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MATERIALS AND METHODS

Study Site

Three sites were selected for the purpose of this study: Harmul (H) north west of SIA, Majees (M) south east of SIA and Zafaran (Z) about nine kilometers south of Majees (Fig. 1). The beach sediments in this region are mobile with generally northwest drift of sediment along the coastline (Atkins, 1999). The sites consist of sandy substrate with no rocky outcrops in the vicinity (MNE, 2000). The sand is generally made up of medium to fine sand (30-90%). The seabed gently slopes from depth of 30 m offshore up to the highwater mark. The gradient between 0 and 10 m is 1:140 and 1:220 between 10 and 30 m (Atkins, 1999).

Harmul ($24^{\circ} 31' 30''$ N $56^{\circ} 35' 50''$ E) is the closest village to the north west. It has shoreline of about 3 km. The beach slope ranges between 5-8%. The houses are less than 100 m from sea. Majees village ($24^{\circ} 28' 05''$ N $56^{\circ} 38' 00''$ E) is the closest village to the south east. It has a long shoreline of about 10 km with a very gentle beach slope intersected with ephemeral small water streams (Atkins, 1999). The Zafaran site has a shoreline of about four kilometers with a beach slope ranging between 5-7%. The backshore is covered with shrubs and dunes. It has an open beach used by the public, mainly in the afternoon, for sport activities, mainly walking and jogging.

Sampling Sites

Sediments samples were collected in November 2005 from the three sites. Each site was divided into seven transects perpendicular to the coast. Three samples were collected from each transect; one from high water mark (HW), one from the inter-tidal zone (MW) and one from the Surf Zone (SZ). The exact coordinates of all sampling sites were obtained using Global Position System (GPS) and are presented in Table 1.

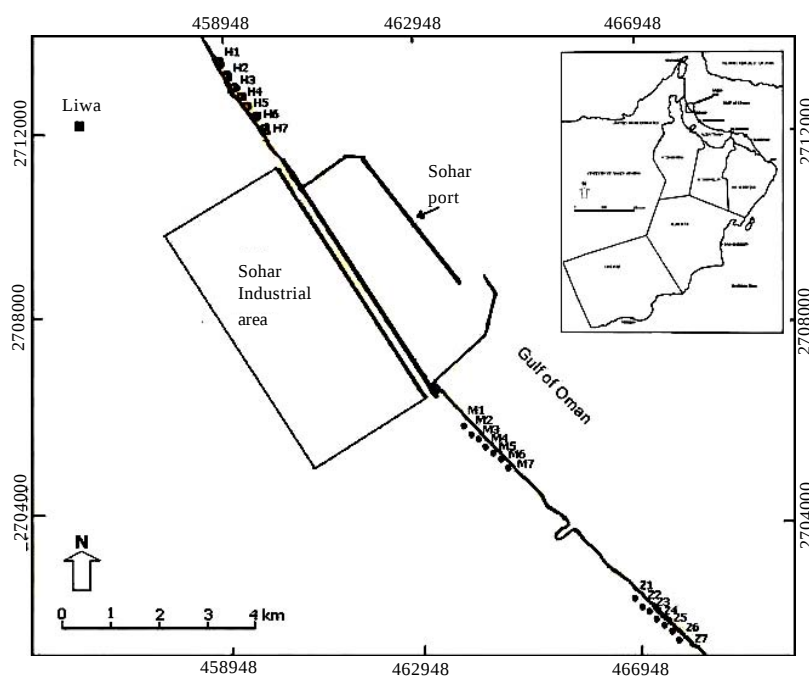


Fig. 1: Sohar industrial area in Oman and sampling locations

Table 1: Coordinates showing the different sampling sites

Site	Highwater		Midwater		Surf zone	
	Northing	Easting	Northing	Easting	Northing	Easting
H1	2713747	458689.3	2713759.5	458711.72	2713770.2	458731.15
H2	2713427	458862.8	2713436.3	45880.095	2713448.4	458902.36
H3	2713175	459024.9	2713178.2	459031.82	2713189.1	459051.99
H4	2713011	459149.4	2713022.0	459170.81	2713029.5	459184.72
H5	2712805	459287.9	2712810.2	459297.29	2712820.5	459314.08
H6	2713011	459529.4	2713017.7	459541.18	2713027.6	459554.90
H7	2712298	459631.2	2712302.8	459637.92	2712306.0	459641.82
M1	2705790	464085.6	2705805.1	464092.57	2705834.2	464112.78
M2	2705757	464181.9	2705770.8	464190.80	2705783.3	464198.06
M3	2705709	464275.4	2705721.6	464282.95	2705736.2	464290.64
M4	2705641	464373.8	2705653.5	464380.81	2705678.0	464398.11
M5	2705525	464532.5	2705533.8	464544.22	2705538.9	464552.43
M6	2705418	464639.7	2705426.6	464652.02	2705440.9	464670.34
M7	2705355	464702.5	2705366.6	464716.16	2705380.8	464729.46
Z1	2702037	468065.2	2702051.5	448079.74	2702069.3	468098.86
Z2	2701952	468142.8	2701980.0	468171.23	2701997.9	468191.22
Z3	2701883	468284.0	2701898.5	468300.27	2701908.4	468311.80
Z4	2701814	468335.4	2701823.5	468346.22	2701843.1	468368.40
Z5	2701726	468415.0	2701740.4	468428.48	2701755.2	468444.62
Z6	2701616	468498.4	2701639.5	468522.47	2701654.5	468538.57
Z7	2701507	468585.4	2701533.0	468609.88	2701558.4	468636.18

Samples and Reagents

Distilled MilliQ water (DDW, Millipore, Bedford USA) was used to dilute the standards and samples and digestion was carried using HPLC grade HCl 37% (Aldrich, Milwaukee, USA) and HNO₃ 70% (Sigma-Aldrich, Germany). Multi Element standard 1 and 2 (Claritass PPT, USA) were used to generate a calibration curve and to quantify the samples.

Pre Treatment and Extraction Method

Since microwave oven was proven to be a suitable method to digest complex matrices such as sediments (Lo and Sakamoto, 2005), it was used to digest sediment samples for this project. Sediment samples were digested in Teflon vessels using USEPA 3050B method in a microwave oven (ETHOSEL, Milestone Microwave Labor System, USA) with the following program: 7 min in phase one and 5 min in phase two. The digested samples were filtered and then transferred to 50 mL polyethylene containers. Samples were then analyzed using an Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Three reagent blanks were analyzed with the samples but they did not show any significant contamination.

RESULTS AND DISCUSSION

The trace elements that were considered for this study were: Vanadium (V), chromium (Cr), manganese (Mn), nickels (Ni), copper (Cu), selenium (Se), mercury (Hg), cadmium (Cd), lead (Pb), zinc (Zn) and arsenic (As). Zn, Pb and Hg were below the instrument detecting limit so they were removed from the analysis.

Table 2 shows the heavy metals concentrations in Harmul, Majees and Zafaran (the control site). Cr, Mn and Ni showed the highest concentration. They were much higher in Harmul than in Majees and Zafaran. The mean concentration of Cr is 0.06377, 0.02115 and 0.03305 mg kg⁻¹ for Harmul, Majees and Zafaran respectively. Mn in Harmul has the highest concentration of all trace metals 0.12711 mg kg⁻¹, in Majees 0.05633 mg kg⁻¹ and Zafaran 0.07115 mg kg⁻¹. Among the three sites, Harmul has the highest Ni concentration 0.08367 mg kg⁻¹ compared with Majees 0.03722 mg kg⁻¹ and

Table 2: Mean±SE, standard deviation and range of heavy metals concentrations in the three sites (mg kg⁻¹)

Variables	Harmul			Majees			Zafaran		
	Mean	SD	Range	Mean	SD	Range	Mean	SD	Range
Vanadium	0.003107±0.0001	0.000848	0.004023	0.001845±0.00005	0.000272	0.001153	0.002018±0.0002	0.000918	0.003094
Chromium	0.063770±0.0050	0.023320	0.098090	0.021150±0.002	0.010360	0.038250	0.033060±0.0030	0.015170	0.052250
Manganese	0.127110±0.0090	0.043410	0.188370	0.056330±0.004	0.021000	0.075050	0.071180±0.0060	0.031570	0.109140
Nickel	0.083670±0.0050	0.027230	0.124620	0.037220±0.002	0.012980	0.047360	0.046840±0.0040	0.021810	0.074490
Copper	0.002685±0.0002	0.001033	0.005693	0.001214±0.0001	0.000281	0.001008	0.003699±0.0008	0.004109	0.011310
Zinc	ND	0	0	ND	0	0	ND	0	0
Selenium	0.000549±0.00001	0.0000468	0.000166	0.000393±0.000004	0.0000215	0.0000768	0.002044±0.0005	0.002519	0.006190
Mercury	ND	0	0	ND	0	0	ND	0	0
Lead	ND	0	0	ND	0	0	ND	0	0
Arsenic	0.008911±0.0007	0.003241	0.014573	0.009563±0.001	0.003053	0.013756	0.011350±0.001	0.00867	0.025360

ND: Not Detected with ICP-MS

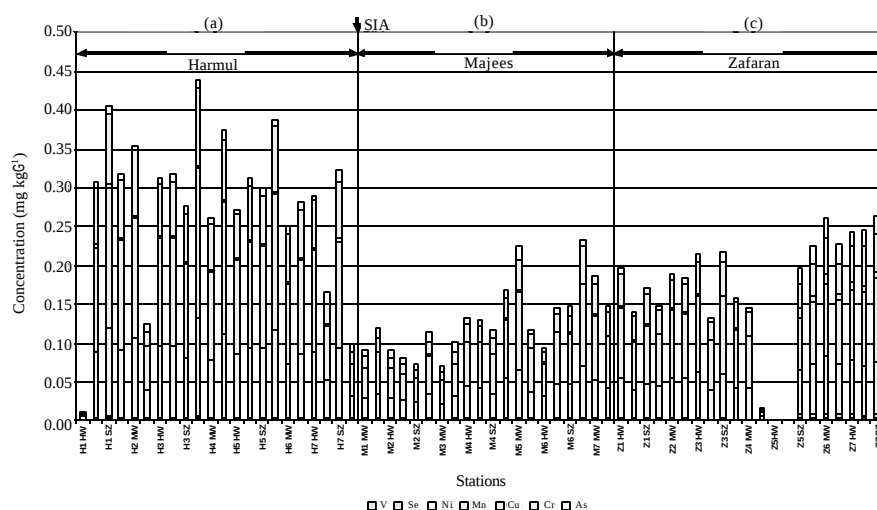


Fig. 2: The heavy metal concentrations (mg kg⁻¹) in all three sites: (a) Harmul site, (b) Majees site and (c) Zafaran site

Zafaran 0.04684 mg kg⁻¹. Surprisingly, Zafaran had the highest As mean concentration 0.01133 mg kg⁻¹, whereas Harmul had the lowest mean concentration 0.008911 mg kg⁻¹ though one would assume Harmul would have a higher concentration of trace elements including As since it is the closest site to SIA whereas Zafaran is the most further site to SIA.

Figure 2a shows heavy metals concentrations in Harmul site. Mn, Ni and Cr recorded the highest concentrations in all zones except in H1HW which recorded the lowest concentration of these elements 0.004, 0.004 and 0.0023 mg kg⁻¹, respectively. Actually, H1HW recorded the lowest trace elements concentration in all Harmul stations. It is worth to mention that H1HW, H1MW and H1SZ are the closest transects to the mangrove forest, whereas H4HW, H4MW and H4SZ which are among the highest concentrations in Mn, Ni and Cr are in the heart of Harmul village. H7HW, H7MW and H7SZ are the closest transects to Sohar Industrial Area (SIA).

Figure 2b shows the heavy metals concentrations in Majees. It is noted the concentration of heavy metals, as a whole, in Majees is lower than Harmul. It is also noted that, in general, transects closer to SIA had lower heavy metals concentration than transects located in the heart of Majees village. For example, M1, M2 and M3 stations had lower heavy metals concentrations than M4, M5, M6 and M7 in most transects. Cr, Ni and Mn concentrations were the highest, especially in transects closer to Majees village. For example, Ni concentration in M1HW, M1MW, M1SZ is (0.0291, 0.0263

and $0.0327 \text{ mg kg}^{-1}$), respectively, whereas Ni concentration in M5HW, M5MW and M5SZ is (0.053 , 0.0632 and $0.0345 \text{ mg kg}^{-1}$), respectively. Also Cr in M1HW, M1MW and M1SZ, which are the closest transects to SIA, are (0.0154 , 0.0137 and 0.0179) respectively, whereas the mean concentration of Cr in M7HW, M7MW and M7SZ, which are also in center of Majees village, are (0.486 , 0.405 and 0.03), respectively. Apparently the cause of Mn, Ni and Cr enrichment in the Majees village stations is not clear. There is no available data which can give us a clue about the source of these concentrations, since this is the first research of its kind in this area. (Se) had the lowest metals concentration in all stations. The concentration of V varies between 0.0017 and $0.0026 \text{ mg kg}^{-1}$.

Figure 2c shows the heavy metals concentrations in Zafaran village. Z7SZ had the highest Mn concentration followed by Z3SZ. Z3SZ and Z6MW had almost equal concentration of Mn, whereas there is a sharp drop in the Mn concentration in Z5HW and Z5MW which were below the detection limit. The highest concentration of Ni was in Z6MW ($0.0745 \text{ mg kg}^{-1}$) and the lowest were in Z5HW and Z5MW. The highest concentration of Cr was in Z7MW ($0.0522 \text{ mg kg}^{-1}$) followed by Z7SZ ($0.0489 \text{ mg kg}^{-1}$), Z6MW ($0.0466 \text{ mg kg}^{-1}$) and Z3SZ ($0.0439 \text{ mg kg}^{-1}$). The lowest concentration in Cr was in Z5HW and Z5MW. The highest As concentration was in Z6MW ($0.0254 \text{ mg kg}^{-1}$) whereas the lowest was in Z5HW and Z5MW. Actually, these two transects did not have any trace elements or their concentration were below the instrument detection limit. Se had the lowest metal concentration in all stations, not only in Zafaran but in all three sites.

Figure 2 gives the concentrations of heavy metals in all three sites combined. With exception to H1HW, Harmul site (H), which is north of SIA, had the highest heavy metals concentration of all three sites. This may be attributed to the northwest drift of sediment in this region (Atkins, 1999). M1, M2 and M3, which are the closest stations to SIA from the south, have lower concentrations than other stations close to Majees village; M5, M6 and M7. The concentration of heavy metals in Zafaran site, which is supposedly to be the control site due to its pristine conditions, is also high except in three transects Z4SZ, Z5HW and Z5MW. This raises a question on the source of these high concentrations of heavy metals whether it is anthropogenic or natural.

High concentrations of Cr, Mn and Ni are found in the sediment samples in almost all three sites. Mn is the most abundant metal in all three sites followed by Ni. With exceptions to the high level of As at some stations, the concentrations of Cr, Mn and Ni don't mean that sediments in these areas are polluted by the heavy construction activities in SIA; it may be a sign of pyretic pollution (Izquierdo *et al.*, 1997). Or it may be this is the natural background concentration of these elements in this area. The concentrations of other metals mentioned in Izquierdo *et al.* (1997) are considered low.

Among the three sites, Harmul site has the highest concentrations in Cr, Mn and Ni. The high concentrations of these metals in Harmul may be attributed to the ophiolites sediment which comes from the northern ophiolites rocks. The highest recorded level of Ni in Oman was in Quraiyat, south east coast of Oman, 1164 mg kg^{-1} and the highest average was 1035 mg kg^{-1} was also in Quraiyat (Al-Jufaili, 2001). In Sohar area the highest Ni is $0.1286 \text{ mg kg}^{-1}$ in H4HW and the highest average is the Harmul site $0.06377 \text{ mg kg}^{-1}$. So compared with Quraiyat area, the concentration of Ni in SIA is far less than Quraiyat. V is an oil related metal present mainly in the organometallic form in crude oil (Fowler *et al.*, 1993; Literathy, 1993 cited at Jupp and Jameison, 2001). The existence of V in sediment samples may be attributed to the illegal discharges of oily wastes from ballast tanks by tankers passing offshore en route to the Gulf (Jupp and Jameison, 2001). According to Fowler *et al.* (1993) most sediments around the coasts of Oman contain over 20 ppm of Vanadium (Jupp and Jameison, 2001). The concentration of V in Harmul, Majees and Zafaran are (0.003107 , 0.001845 and $0.002018 \text{ mg kg}^{-1}$), respectively which far less than 20 ppm.

The concentration of As is high in almost all stations, though it is not as high as Cr, Mn and Ni. The concentration of As in these stations may either be anthropogenic or natural (Chapagain *et al.*, 2008). The accumulation of As as well as other metals like Cr, Hg, Cd and Pb in the mussel tissue of some species (i.e., zebra) can pose life hazard to some species which feed on them like fish and birds (Roper *et al.*, 2001). All other heavy metals are low in all three sites.

Table 3: Heavy metals concentration (mg kg^{-1}) in the study area compared with other studies

	Harmul	Majees	Zafaran	Khasab ^(E)	Al Khaboura ^(E)	Al Suwadi ^(E)	Al Bustan ^(E)
Cu	0.002685	0.001214	0.003698	21.80	43.60	17.50	41.90
Cr	0.0006377	0.0002115	0.0003305	0.00608	0.0957	0.08	0.1203
Ni	0.008370	0.003720	0.004680	0.827	1.24	0.04	0.819
Mn	0.000012711	0.056330	0.071150	0.013	0.0724	0.042	0.1913
V	0.003107	0.001845	0.002018	5.28	34.50	18.40	21.10
Se	0.000549	0.000393	0.002044	-	-	-	-
As	0.008911	0.009563	0.011330	-	-	-	-
	Sur ^(E)	Ras Alduqum ^(E)	Marbat ^(E)	A	B	C	D
Cu	9.74	9.24	2.22	40	136	371.0	15.92
Cr	0.0137	0.00806	0.00059	100	25	44.0	-
Ni	0.151	6.67	5.06	100	20	34.6	233.02
Mn	0.0743	0.0284	0.0057	No threshold or unknown	No threshold or unknown	476.0	171.54
V	-	5.65	0.99	-	-	-	26.39
Se	-	-	-	No threshold or unknown	No threshold or unknown	-	-
As	-	-	-	No threshold or unknown	No threshold or unknown	-	-

A: Ministry of Agriculture, Fisheries and Food of UK (cited in MRMEWR, 2002), B: Environmental Protection Agency of US (cited in MRMEWR, 2002), C: Dalman *et al.* (2006), D: Jupp and Jamieson (2001), E: MRMEWR (2002)



Fig. 3: Location of Khasab, Khaboura, Suwadi, Bustan, Sur, Ras Alduqum and Marbat

Table 3 shows the metals concentrations in Harmul, Majees and Zafaran compared with the Ministry of Agriculture, Fisheries and Food (MAAF) standards of the United Kingdom, Environmental Protection Agency (EPA) standards of the United States and six different locations in five different regions in Oman: Khasab in the northern region, Khaboura and Suwadi in Batinah region, Bustan in the capital region (Muscat), Sur in the eastern region, Ras Alduqum in the central region and Marbat in the southern region (Fig. 3). Comparison with USEPA standards, MAAF standards and

other locations in Oman showed that the metal concentrations in the study area are far less than EPA and MAAF standards as well as the other locations in Oman.

It is important to mention that the results of this study is based on one single site visit, where three samples were collected from each transect; one sample from high-water mark (HW), one sample from inter-tidal zone (MW) and one sample from the surf zone (SZ).

It can be said that the concentration of selenium, manganese, copper, nickel and chromium in sediment are in low level. Zinc, mercury and lead were below the detecting limit

Based on these results, it can be concluded that certain areas of each site are suffering from slight increase in certain metals, though it is not yet confirmed that these heavy metals concentrations are due to SIA heavy construction activities.

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