

Distribution of Heavy Metals Associated with Petroleum in the Northern Persian Gulf: Bushehr and Nayband Bay Area

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Abstract

Parts of oil spills reach Iranian coastline along the Persian Gulf in the form of tar balls and scattered oil patches. There are many published reports regarding oil spills reaching northern coasts of the Persian Gulf, but none report on the content of heavy metals associated with petroleum in sediments and plants of contaminated areas. This research was conducted to determine and map petroleum- related heavy metals (Ni, V and S) distribution in sediments and weathered tar balls and bitumen using XRF analysis. It is determined there was contamination of heavy metals associated with petroleum, for example, Ni, V, and S in sediments of northern coasts of the Persian Gulf in Bushehr and Nayband Bay Area.

Keywords: *Persian Gulf Coastal Contamination, Heavy Metals, Petroleum Contamination, Mangrove Ecosystems*

1. Introduction

It is not unusual to see parts of oil spills reach Iranian coastline along the Persian Gulf in the form of tar balls and scattered oil patches. These spills are usually resulted from exchange of ballast water of oil tankers and or spillage due to man- made accidents, such as oil explorations or the regional wars in the 1980s and 1991. There are reports by expert research teams of Aminipouri, et. al. (1998), Kuroiwa, et. al. (1991), IOC-UNESCO (1993), Gundlach, et. al (1993), DOE of Iran (1996 and 1999), Esmaili Sari and Zare-maivan(1998), Lefloch, Co. (1999), ROPME Report (1999). Zare-maivan, et. al. (1999a and b) and Zare-Maivan (2004) indicating coastal pollution in Northern Persian Gulf. Only the latter

three reports presented quantitative data on the scope of the pollution. This research was conducted to determine and map petroleum- related heavy metals (Ni, V and S) distribution in sediments, plant specimen and weathered tar balls and bitumen. Both Ni and V can be toxic to mangrove trees in higher concentrations (Harbinson, 1986, IPIECA 1992).

Ni is found in sedimentary rocks in the range of 5 to 90 mg/g. Sandstones contain the lowest concentrations of Ni while terrestrial rocks containing sulfides and arsenides harbor Ni mostly in ferromagnesian rocks replacing Fe. Ni is also associated with carbonates, phosphates and silicates and particularly with petroleum.

Vanadium is a component of many magmatic rocks and is present in shale's within the concentration of 100–250 ppm. Vanadium is also associated with petroleum and coal. The

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geochemical characteristics of V are strangely dependent on its oxidation state (+2, +3, +4 and +5), and on the acidity of the media. Vanadium displays various behaviors and can form chemical complexes of cationic, anionic and hydroxyl oxides.

2. Material and Methods

2.1. Description of the study area

Assalouyeh, Nayband Bay Area and Bushehr province coasts, located in the northern coasts of the Persian Gulf, were investigated (Table 1). Mangrove and halophyte communities were growing in Nayband Bay area.

Table 1: Geographic Coordinates of sampling areas in Northern Coasts of the Persian Gulf: Asalouyeh and Nayband Bay Area

Location	Geographic Coordinates				Extent, Length X Width	Sample Type	Dominant Vegetation Type
	Start		End				
	E	N	E	N			
Asalouyeh & Nayband Bay	53	27	52	27	9Km	Sediment	Halophytes
Bushehr	38	29	40	25	X7Km	Tar, Plant	mangrove

Sampling - Forty five sampling stations were selected randomly. At each station, three plots were selected at least 50 m apart. Size of each plot was about 25–100 m², depending on the homogeneity of the vegetation cover and density of sediment (soil). Samples were collected to depth of 10 Cm using a 10 cm diameter steel auger. Samples were stored and transported in clean plastic containers that had been rinsed off with warm deionized water in advance. Containers were labeled appropriately, transported in coolers and were kept in cold place until analyzed in laboratory at the Tarbial Modares University (Table 2).

Table 2- Type and Number of Samples from Northern Coasts of the Persian Gulf

Sample Type	Bushehr coasts	Assalouyeh & Nayband	Total
Sediment	--	140	140
Bitumen	32	23	55
Total	32	163	195

2.2. Sample preparation for XRF Analysis

Each group of substrate, for example, sediment and tar substances, was treated as follows:

Sediment preparation—20 grams of fresh sediment from each sample were weighed in pre-weighed crucibles and were heated in an oven at 120°C for 24 hours. Then, remaining solid part was ground to pass 200 mesh (50 Micron) screen. Three grams of powder were mixed with one gram of preservative wax until homogenous state. Next, the prepared sub-sample was placed under press along with sub-base of Boric Acid until a disc of 40 mm diameter was formed. The disc was, then, placed in the XRF reading chamber to be analyzed in vacuum for designated heavy metals.

Oily substances and tar balls preparation—Samples were placed in Aluminum capped crucibles. Pressing of substance was carried out using a special thin layer under Helium matrix. Calibration of XRF unit was adjusted for measuring heavy metal contents in the presence of Helium and no-vacuum.

3. Results

3.1 Distribution of heavy metals associated with petroleum, mainly Ni, V, and S in Nayband Bay area

Samples of sediment and bitumen were collected at the northern, northeastern, eastern and southeastern parts of the Nayband Bay. Sediment samples were analyzed for their content of Ni, V and S. Inverse distant weighted interpolation at an area of 9 x 7 km, with a pixel size of 30m and 10 layers (surfaces) was performed to draw contamination maps for each metal contaminant.

Ni-Ni content of sediments in Nayband area is variable. Samples containing 0 – 2.5 ppm and those above 42.5 ppm Ni content constituted the most and the least frequency, respectively. Mean Ni content of sediments in Nayband Bay area was 10.9 ppm. Sediments of following areas showed higher

concentrations of Ni, terminal section of Northern Khor, eastern and southeastern part of the Bay. On the contrary, northern and southern parts of the Bay displayed the least content of Ni; Texture of sediments in terminal section of Northern Khor, eastern and southeastern parts was muddy-clay and could adsorb heavy metals and in northern and southern parts was sandy.

V-Vanadium concentrations of 52.5 – 57.5 ppm and 32.5 – 37.5 and less in sediments comprised the highest and the least categories, respectively. Mean concentration of V in sediments was 59.2 ± 13.8 . Vanadium distribution followed a pattern similar to that of Ni except for station No. 8 which was located at northeastern part of the Bay. Northern and southern parts of Nayband Bay sediments contained the least concentration of V. This was primarily attributed to sandy sediment texture of these parts. In other parts, gradual accumulation of V occurred in clay silt particles.

S-Distribution frequency of sulfur in Nayband Bay was not typical. Mean S concentration was 1.2 ppm and most of stations displayed concentrations between 0–0.05 ppm. Greater concentration of S occurred at the northern Khor of the Bay.

3.2. Tar balls and bitumen

Distribution frequency of Ni, V, and S of samples were determined in 23 tar ball samples from northern, north eastern and south eastern coasts of Nayband Bay.

Ni-Distribution of Ni in tar balls did not follow pattern of a normal curve. Mean concentration of Ni was 102.7 ppm. Frequently occurring concentrations were those less than 32.5 ppm and 87.5 – 112.5 ppm and the least frequently occurring concentrations were within the range of 112.5 – 137.5 ppm. Tar balls collected from southeastern part of the Bay contained the highest concentrations of Ni contrary to samples collected from the northern parts. This variation in distribution was attributed either to long

weathering period or exposure to wave action and or different sources of tar ball pollution.

V-Mean V concentration in tar balls was 126.3 ppm, with majority of samples having a V content of 87.5–112.5 ppm (Fig.8). Distribution frequency map of V was similar to that of Ni in tar balls. However, there was a distinct difference in the concentration of V between tar balls collected from northeastern and southeastern parts. This might be because of different sources of pollution and or varying exposure period of tar ball samples to weathering.

S-Sulfur content of tar balls was very high (mean=23313 ppm) with maximum frequency occurring in the 15000–25000 ppm range. Apparently, northeastern tar balls contained the least S content and in this regard, they differed from those of northern and southeastern samples. The latter were similar in their S content and distribution.

3.3. Bitumen and tar balls in Bushehr

Frequency distribution of Ni showed concentrations of Ni in sediments ranging between 12.5 – 137.5 ppm with a mean concentration of 99.4 ppm occurred more frequently (Table 3). Tar balls around city of Bushehr displayed a higher Ni content than either side of Bushehr; for example, Bandar Genaveh at the north and Bandar Gahi at the south of Bushehr. Vanadium content of sampled tar balls in coasts of Bushehr were frequently less than 75 ppm, though a mean V content of 114.5 ppm was recorded. Vanadium distribution pattern was similar to that for Ni.

Table 3-Heavy Metal Content of Tar Balls Collected from Nayband Bay and Bushehr

Element (ppm) Location	Ni	V	S	Ni/V
Nayband Bay	102.7	126.3	23313	0.8
Bushehr	99.4	114.5	36994	0.89

Sulfur content in tar balls was much greater than that in sediments. Majority of samples contained 35000–55000 ppm of sulfur. The distribution map showed there were 43 areas of high sulfur contents in

areas of near Bushehr, Bandar Delvar and Bandar Gahi. Bandar Emam Hassan, Bandar Genaveh and Bandar Rostami samples contained the least sulfur. The latter areas were at considerable distance towards northern coasts of Bushehr where patches of weathered spilled oil were still visible. Results showed some degree of similarity in their Ni and V content, but not necessarily from the same source. Heavy metal content of tar balls collected from Nayband Bay and Bushehr and mean concentration of Ni, V, S and Ni/V of along northern coasts of the Persian Gulf are summarized in Tables 3 and 4, respectively

Table 4 - Mean concentration of Ni, V, S and Ni/V in sediments of the northern coasts of the Persian Gulf: Bushehr and Nayband Bay Area

Element Area	Ni(ppm)	V(ppm)	S(ppm)	Ni/V(ppm)
Bushehr (Bitumen sample)	99.4	114.5	45000	0.87
Nayband Bay	10.9	59.2	1.2	0.16

4. Discussion

4.1. Comparison of distribution of heavy metals associated with oil spill in Nayband

Sediments – Distribution maps of heavy metals of Nayband Bay area showed sediments contained Ni and V. Ratio of Ni to V has been used as a tool for identifying sources of petroleum. Ratio of Ni/V in tar balls around Bushehr reflected a normal pattern. Majority of ratios fell within the range of 0.69–0.118 with a mean of 0.89. Distribution map of these ratios showed ratio of tar balls collected from Bandar Genaveh and Bandar Rostami were high (1.1–1.18) but those of Bandar Gahi (towards Nayband Bay area) were lower and in the range of 0.5–0.6. This suggested different sources for oil pollution despite various degrees of exposure to weathering of samples collected from different locations.

V contents of sediments in Nayband Bay mangrove complex ranged between 40–80 ppm. Presence of Ni

and V have been reported in sediments of other parts of the Persian Gulf, e.g., Qeshm and Khamir mangrove ecosystems (Zaremaivan, 2004). It seems heavy metal retention capacity is affected by sediment texture. Sediments of Nayband Bay, particularly in southern and eastern coasts were sandy unlike sediments of Qeshm–Khamir complex which were clay–silt. Nayband Bay sediments in contrast to sediments of Khamir–Qeshm contained a greater concentration of S (Zaremaivan, 2004). In conclusion, it is determined there was contamination of metals associated with petroleum, for example, Ni, V, and S in sediments of Bushehr and Nayband area as had been reported from Qeshm and Khamir Mangrove Complexes in northern coasts of the Persian Gulf, though in lower concentrations (Zaremaivan, 2004). Further biochemical tests are required. Mangroves of Qeshm–Khamir region despite higher concentrations of Ni and V in their rhizosphere, because of greater affinity of cations to clay–silt particles did not show higher concentrations of these elements in plant parts.

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