



Accumulation of nickel by marine macroalgae from the Saudi coast of the Arabian Gulf

Ali A. Al-Homaidan

Department of Botany and Microbiology, College of Science, King Saud University, P.O. Box 2455, Riyadh, 11451, Saudi Arabia.
e-mail: aahomaidan@gmail.com

Received 17 August 2007, accepted 26 November 2007.

Abstract

Nickel contamination may have an adverse impact on the fragile coastal and marine ecosystems of the Arabian Gulf. Oil pollution is a major source of this heavy metal. The nickel concentrations were measured in seawater and in 12 species of green, brown and red algae which were collected from Dammam area on the Saudi coast of the Arabian Gulf. The algal samples were cleaned, air dried and digested with concentrated nitric acid. The Ni concentrations were measured in seawater and in the aliquot samples of algae using atomic absorption spectrophotometer. High levels of Ni were found in seawater ($1.26-6.73 \mu\text{g L}^{-1}$) and in algal samples ($7.3-57.4 \mu\text{g g}^{-1}$ dry weight). The highest levels of Ni were found in the red algae *Acanthophora spicifera*, *Hypnea cornuta* and *Digenia simplex*, the green alga *Chaetomorpha aerea* and the brown alga *Sargassum latifolium* and these species may be used as biomonitors of Ni contamination in the Arabian Gulf region. The alerting high levels of Ni in the Gulf region must be taken seriously and integrated efforts and serious actions should be taken at once to prevent further deterioration to this invaluable area.

Key words: Nickel, concentrations, seaweeds, Arabian Gulf, Saudi Arabia.

Introduction

The Arabian Gulf is a semi-enclosed, shallow sea with an average depth of 50 m. It covers an area of approximately 230,000 km² and it is characterized by high temperatures and high evaporation rates. The oil-rich countries of the Gulf Cooperation Council, namely Bahrain, Kuwait, Oman, Qatar, Saudi Arabia and the United Arab Emirates, are located on the northern, western and southern parts of the Gulf (Fig. 1). More than 33% of the world's oil is produced by these countries, and of this amount about 94% is exported¹⁵. Oil production and related industries may lead to a significant increase in Ni levels through oil spillages^{4, 15}. Unfortunately, the gulf region has witnessed several major oil spillages during the last two decades. According to ROPME²¹, about 2-4 million barrels of crude oil were spilled to the Gulf during the Iran-Iraq war (1980-1988) and more than nine million barrels of oil flooded the region during the 1991 war on Iraq. In addition to that, about 1.2 million barrels of oil are spilled in the Gulf every year from routine discharge of ballast water¹⁵. Nickel can also be introduced to the coastal areas of the Arabian Gulf through industrial and domestic wastes. The concentration of Ni in these areas should be monitored very carefully by using different organisms that are known to accumulate heavy metals. Several marine organisms have been used to monitor Ni levels in the coastal areas of the Arabian Gulf. These include clams²², sea urchins²³, snails and pearl oysters⁹ and fish and bivalves¹².

A very limited number of studies has been published about the accumulation of heavy metals by the macroalgae of the Arabian Gulf. The levels of numerous metals were measured in several

algal species collected from the coastal waters of Qatar and Kuwait^{8, 17}. The levels of six metals were determined in three species of brown algae recovered from the coastal areas of Saudi Arabia and Qatar¹⁸. More recently, Al-Homaidan² reported on the levels of five elements in four species of macroalgae obtained from two sites on the Saudi coast of the Gulf. In another study, he measured the concentrations of six metals in three species of green algae collected from three sites on the Saudi coast³. The main objective of this study was to determine Ni concentrations in 12 species of macroalgae collected from one site on the Saudi coast of the Arabian Gulf and belonging to different phylogenetic groups (Chlorophyta, Phaeophyta and Rhodophyta). The levels of dissolved Ni were also measured in seawater.

Materials and Methods

Study area: The algal samples were collected from the coastal areas of the city of Dammam (26°26'N, 50°02'E), which is the largest city in the Eastern province of Saudi Arabia with a population of more than 850,000 inhabitants (Fig. 1). It forms a large metropolitan and industrial area, with more than 2 million inhabitants, together with the cities of Khobar, Qateef and Dhahran. The Dammam Port is one of the largest on the Arabian Gulf. There are several major industrial activities in the area including major complexes of primary and secondary industry, desalination plants, sewage treatment plants and a fertilizer factory¹⁹. Parts of domestic sewage and industrial wastes are discharged to the coastal areas of the region without proper treatment¹⁵. Ras Tanura (26°39'N, 50°10'E) is a

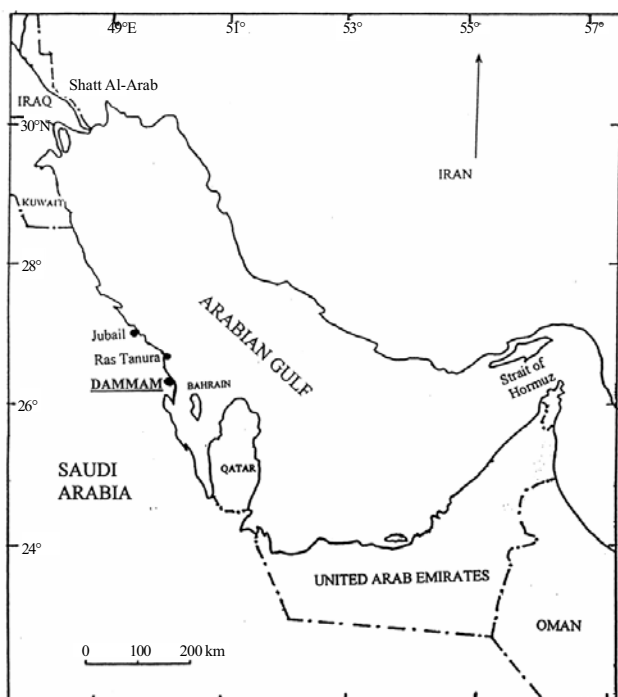


Figure 1. Map of the Arabian Gulf showing algal collection site (Damman).

small industrial city, about 40 km north of Damman and it serves as a major oil port and oil operation center and it contains one of the world largest oil refineries. The city of Jubail (27°00'N, 49°40'E) is located about 80 km north of Damman and it has one of the largest petrochemical plants and iron works in the region. The city of Damman is affected by the industrial discharges of these two cities.

Sampling procedures and analytical methods: Twelve species of macroalgae belonging to green, brown and red algae, four of each group, were collected from the intertidal zones of Damman coastal areas between January and May of 2006. Representatives of the Chlorophyta were *Enteromorpha clathrata* (Roth) Greville, *Ulva lactuca* Linnaeus, *Chaetomorpha aerea* (Dillwyn) Kützing and *Cladophora nitellopsis* Borgesen. The Phaeophyta species were *Padina gymnospora* (Kützing) Vickers, *Cystoseira myrica* (S.G. Gmelin) C. Agardh, *Hormophysa triquetra* (C. Agardh) Kützing and *Sargassum latifolium* (Turner) C. Agardh. The Rhodophyta included *Hypnea cornuta* (Kützing) C. Agardh, *Acanthophora spicifera* (Vahl) Borgesen, *Digenia simplex* (Wulfen) C. Agardh and *Laurencia glandulifera* (Kützing) Kützing.

Entire thalli of macroalgae, a minimum of three samples of each species, were collected and thoroughly washed in seawater at sampling sites. All samples were stored in a refrigerated box until they were returned to the laboratory. In the laboratory the seaweed samples were washed in distilled water to remove any visible epiphytes and organic and mineral particles. They were then air dried at 90°C, ground in a mill and used in the analysis.

Accurately weighed portions of each alga (500 mg dry weight) were placed into acid washed digestion tubes and digested with 25 ml of concentrated AnalarR grade nitric acid (BDH, England). After cooling, 20 ml of double distilled deionized water was added

to each digestion tube and the content was filtered through 0.45 µm Millipore filters. The solutions were transferred to 25 ml volumetric flasks and the volumes were completed to 25 ml with double distilled deionized water^{1, 2, 7, 24}.

Surface seawater samples were collected in 5 litre acid-washed polyethylene bottles during the algal sampling. Water samples were kept in a refrigerated box and transported to the laboratory where they were filtered through 0.45 µm Millipore filters. Nickel was extracted by chelation with ammonium pyrrolidine dithiocarbamate and extraction into methyl isobutyl ketone followed by aspiration into an air-acetylene flame⁵. Concentrations of Ni in the aliquots of algae and in seawater were determined using Shimadzu AA-6650F and AA-6650G atomic absorption spectrophotometers.

Results and Discussion

Nickel in seawater: The total mean concentrations of dissolved Ni in the coastal areas of Damman varied between 1.26 and 6.73 µg L⁻¹ with an average of 4.27 µg L⁻¹. This value is higher than the concentration of dissolved nickel in uncontaminated coastal waters which is usually < 1.8 µg L⁻¹²⁶. Human activities may increase these levels to 2.5-15 µg L⁻¹²⁰. Such high values have previously been reported from the Arabian Gulf region (Table 1). For instance, a concentration of more than 4 µg L⁻¹ has been reported from the surface water of eight reef areas from the Saudi coast²³. Similarly, Ni concentrations of greater than 5 µg L⁻¹ have been recorded in seawater samples collected from thirteen different sites along the Kuwaiti coast of the Gulf¹⁰. In both studies, the high levels of Ni were attributed to oil spillages and domestic discharges to the coastal areas of these two countries. The high concentrations of Ni found in this study could be ascribed to the same reasons. The concentrations of Ni in the Saudi and Kuwaiti crude oils varied between 1 and 29 µg kg⁻¹ oil and oil spills would elevate Ni levels in the area²².

Accumulation of Ni by macroalgae: Nickel concentrations in the 12 species collected from Damman region are shown in Table 2. They are presented in µg g⁻¹ dry weight and they represent the mean value of a minimum of three readings. The mean values varied significantly between 7.3 and 57.4 µg g⁻¹ (one-way ANOVA, P < 0.01). The highest Ni concentration was found in the red alga *A. spicifera*, whereas the lowest was recorded in the brown alga *C. myrica*. The mean concentrations of Ni in all species was higher than 7 µg g⁻¹. According to Moore and Ramamoorthy²⁰ the Ni residues in marine algae are generally low and they reported on concentrations ranging from 0.5 to 39.1 µg g⁻¹ from different areas of the world. The concentrations of Ni found in this study are similar to those found in many contaminated coastal areas of the world (Table 3). For instance, Ni concentrations of greater than 50 µg g⁻¹ have been recorded in many species of green, brown and red algae collected from the coastal area of Beirut,

Table 1. Reported concentrations of Ni (µg L⁻¹) in surface seawater from the coastal areas of the Arabian Gulf.

Location	Range
Saudi Arabia ²²	0.33 - 1.02
Saudi Arabia ²³	0.09 - 4.19
United Arab Emirates ⁶	0.49 - 0.67
Kuwait ¹⁰	1.16 - 6.63
Saudi Arabia (present study)	1.26 - 6.73

Table 2. Mean, standard deviations and ranges (in brackets) of Ni in $\mu\text{g g}^{-1}$ dry weight in 12 species of macroalgae collected from the Saudi coast of the Arabian Gulf.

Algal division and species	Mean, standard deviation and range
Chlorophyta	
<i>E. clathrata</i>	9.2 ± 2.5 (7.1 - 12.3)
<i>U. lactuca</i>	19.8 ± 10.1 (8.5 - 28.2)
<i>C. aerea</i>	39.3 ± 5.1 (34.3 - 44.1)
<i>C. nitellopsis</i>	12.4 ± 4.2 (7.5 - 15.3)
Phaeophyta	
<i>P. gymnospora</i>	24.0 ± 5.6 (18.1 - 28.9)
<i>C. myrica</i>	7.3 ± 5.1 (4.2 - 13.1)
<i>H. triquetra</i>	24.3 ± 3.6 (20.4 - 27.3)
<i>S. latifolium</i>	31.6 ± 6.4 (24.7 - 36.2)
Rhodophyta	
<i>H. cornuta</i>	40.7 ± 5.2 (35.2 - 45.7)
<i>A. spicifera</i>	57.4 ± 5.6 (51.3 - 61.9)
<i>D. simplex</i>	31.2 ± 5.8 (24.5 - 37.7)
<i>L. glandulifera</i>	19.3 ± 5.5 (13.7 - 23.8)

Lebanon, and they were attributed to several reasons including domestic and industrial discharges²⁵. Similarly, Ho¹⁶ measured the levels of several heavy metals, including Ni, in 19 intertidal green, brown and red algae from the polluted coastal areas of Hong Kong Island, and the Ni concentrations in these algae varied between 3.3 and 36.7 $\mu\text{g g}^{-1}$. The Ni concentrations were determined in the brown alga *Fucus vesiculosus* collected from many contaminated and uncontaminated coastal locations of northeast England¹⁴. The levels of Ni in the alga from the uncontaminated sites were very low and varied between 0.3 and 0.7 $\mu\text{g g}^{-1}$. Very high concentrations of this metal were found in the samples from the contaminated areas and they fluctuated between 20 and 71 $\mu\text{g g}^{-1}$. High levels of Ni (> 70 $\mu\text{g g}^{-1}$) were found in the red alga *Phyllophora nervosa* which was collected from the Turkish coast of the Black Sea²⁸. The high levels of Ni and other metals in macroalgae were attributed to oil pollution, airborne contaminants and industrial wastes that are discharged to the Black Sea. In the Arabian Gulf region, the elevated levels of Ni are probably caused by oil pollution.

Several studies have been published about the accumulation of Ni by other organisms from the Arabian Gulf. For example, the high levels of Ni in the clams *Meretrix meretrix* which were collected from the Saudi coastal waters were attributed to oil spills²². Similarly, the high levels of Cu, Ni and Zn in the snail *Lunella coronatus* and in the pearl oyster *Pinctata radiata* that were collected from the Kuwaiti coast were ascribed to the 1991 Gulf War oil spill⁹.

The attribution of elevated levels of Ni to anthropogenic activities is not conclusive. Bioindicator organisms give an idea about heavy metal concentrations in marine environments but they do not provide information on the source of elevated levels, natural or anthropogenic²⁴. The high levels of Ni (> 50 $\mu\text{g g}^{-1}$) in many species of macroalgae collected from the Aegean Sea were ascribed to the metalliferous nature of the rock in the area²⁴. A similar conclusion was reached by de Mora *et al.*¹² who assessed the marine contamination due to heavy metals in the Arabian Gulf and the Gulf of Oman using coastal sediments and various species of fish and bivalves. They attributed the extremely high levels of Ni in the coastal areas of Oman and eastern United Arab Emirates, especially in the sediments, to the local mineralogy of

Table 3. Nickel concentrations ($\mu\text{g g}^{-1}$ dry weight) in macroalgae from different coastal areas of the world.

Location	Range
Mediterranean Sea, Lebanon ²⁵	nd - 60.6
Hong Kong, China ¹⁶	3.3 - 36.7
Red Sea, Saudi Arabia ¹³	0.5 - 3.9
Northeast England, UK ¹⁴	0.3 - 70.5
Aegian Sea, Greece ²⁴	nd - 52.6
Venice Lagoon, Italy ¹¹	0.4 - 5.0
Northwest coast, Spain ²⁹	0.6 - 6.2
Black Sea, Turkey ²⁸	0.1 - 70.6
Southern Baltic, Poland ³⁰	0.1 - 10.2
Arabian Gulf, Saudi Arabia (present study)	7.3 - 57.4

nd = not detected

the area, and they consider it as natural rather than pollution.

The significant differences in Ni concentrations in the different species collected during this study are probably caused by temporal variations or due to morphological features. The studied algae were collected over a period of five months. Several authors have reported on the dependent of metal accumulation by algae on the season. For instance, highly significant seasonal differences in the content of various metals were observed for the green algae *Ulva* sp. and *Enteromorpha* sp. from the northwest coast of Spain²⁹. Similarly, significant temporal variations for Ni content was noted in the green alga *Enteromorpha* sp. from the Gulf of Gdansk, southern Baltic³⁰.

Thallus morphology (filamentous, membranous, parenchymatous... etc.) may also affect the heavy metal content of algae. For examples, Sawidis *et al.*²⁴ have indicated that metal concentrations in the various seaweed species may reflect their morphology and they pointed out that the algae with larger surface area usually have higher internal content of heavy metals. It has also been shown that Zn levels in filamentous algae are higher than in thick-leathery or coarsely branched algae and the highest levels of Zn were found in the representatives of red algae²⁵. A similar result was found in this study; the highest concentrations of Ni were found in the red algae *A. spicifera* and *H. cornuta*. The green, brown and red algae collected during this study belonged to a wide range of morphological groups and those variations are probably responsible for the significant variations in the algal content of Ni.

Conclusions

High levels of Ni were detected in the different species of algae. Irresponsible oil spillages into the Arabian Gulf are probably the main cause of this problem. Integrated governmental and international efforts must be taken to stop the destruction of this fragile and valuable area.

References

- Al-Homaidan, A.A. 2006 a. Heavy metal levels in Saudi Arabian *Spirulina*. Pakistan Journal of Biological Sciences 9(14):2693-2695.
- Al-Homaidan, A.A. 2006 b. Brown algae as biomonitors of heavy metal pollution along the Saudi coast of the Arabian Gulf. Saudi Journal of Biological Sciences 13(2):99-103.
- Al-Homaidan, A.A. 2007. Heavy metal concentrations in three species of green algae from the Saudi coast of the Arabian Gulf. Journal of Food, Agriculture & Environment 5(3&4):354-358.
- Ali, L.N., Mostafa, A.M. and Al-Hasan, R.H. 2001. Oil pollution in the marine environment of Kuwait. Kuwait, Center for Research and Studies on Kuwait. (In Arabic).

- ⁵American Public Health Association, American Water Works Association and Water Environment Federation 1995. Standard Methods for the Examination of Water and Wastewater. 19th edn. APHA, USA.
- ⁶Banat, I.M., Hassan, E.S., El-Shahawi, M.S. and Abu-Hilal, A.H. 1997. Post-gulf-war assessment of nutrients, heavy metals, hydrocarbons and bacterial pollution levels in the United Arab Emirates coastal waters. *Environment International* **24**:109-116.
- ⁷Brown, M.T., Hodgkinson, W.M. and Hurd, C.L. 1999. Spatial and temporal variations in the copper and zinc concentrations of two green seaweeds from Otago Harbour, New Zealand. *Marine Environmental Research* **47**:175-184.
- ⁸Bu-Olayan, A.H. and Subrahmanyam, M.N.V. 1996. Heavy metals in marine algae of the Kuwait coast. *Bulletin of Environmental Contamination and Toxicology* **57**:816-823.
- ⁹Bu-Olayan, A.H. and Subrahmanyam, M.N.V. 1997. Accumulation of copper, nickel, lead and zinc by snail, *Lunella coronatus*, and pearl oyster, *Pinctada radiata*, from the Kuwaiti coast before and after the Gulf war oil spill. *Science of The Total Environment* **197**:161-165.
- ¹⁰Bu-Olayan, A.H., Subrahmanyam, M.N.V., Al-Sarawi, M. and Thomas, B.V. 1998. Effects of the gulf war oil spill in relation to trace metals in water, particulate matter and PAHs from the Kuwait coast. *Environment International* **24**:789-797.
- ¹¹Caliceti, M., Argese, E., Sfriso, A. and Pavoni, B. 2002. Heavy metal contamination in the seaweeds of the Venice lagoon. *Chemosphere* **47**:443-434.
- ¹²de Mora, S., Fowler, S.W., Wyse, E. and Azemard, S. 2004. Distribution of heavy metals in marine bivalves, fish and coastal sediments in the Gulf and Gulf of Oman. *Marine Pollution Bulletin* **49**:410-424.
- ¹³El-Naggar, M.E.E. and Al-Amoudi, O.A. 1989. Heavy metal levels in several species of marine algae from the Red Sea of Saudi Arabia. *Journal of King Abdulaziz University (Science)* **1**:5-13.
- ¹⁴Giusti, L. 2001. Heavy metal contamination of brown seaweed and sediments from the UK coastline between the Wear River and the Tees River. *Environment International* **26**:275-286.
- ¹⁵GRC (Gulf Research Center) 2006. Green Gulf Report. GRC, Dubai.
- ¹⁶Ho, Y.B. 1987. Metals in 19 intertidal macroalgae in Hong Kong waters. *Marine Pollution Bulletin* **18**:546-566.
- ¹⁷Kureishy, T.W. 1991. Heavy metals in algae around the coast of Qatar. *Marine Pollution Bulletin* **22**:414-416.
- ¹⁸Kureishy, T.W., Abdelmoati, M.A.R. and Al-Muftah, A.R. 1995. Marine algae as bioindicators of pollution levels in the Arabian Gulf. *Qatar University Scientific Journal* **15**:215-221.
- ¹⁹MEPA (Meteorology and Environmental Protection Administration) 1992. Saudi Arabia: An assessment of biotopes and coastal zone management requirements for the Arabian Gulf. MEPA, Saudi Arabia.
- ²⁰Moore, J.W. and Ramamoorthy, S. 1984. Heavy metals in natural waters. Springer-Verlag, New York.
- ²¹ROPME (Regional Organization for the Protection of the Marine Environment) 2004. State of the Marine Environment Report. ROPME, Kuwait.
- ²²Sadiq, M., Alam, I.A. and Al-Mohanna, H. 1992. Bioaccumulation of nickel and vanadium by clams (*Meretrix meretrix*) living in different salinities along the Saudi coast of the Arabian Gulf. *Environmental Pollution* **76**:225-231.
- ²³Sadiq, M., Mian, A.A. and Saji, A.F. 1995. Metal bioaccumulation by sea urchin (*Echinometra mathaei*) from the Saudi coast of the Arabian Gulf: I. As, Ni, V, Sb, Al and Fe. *Chemical Speciation and Bioavailability* **7**:101-107.
- ²⁴Sawidis, T., Brown, M.T., Zachariadis, G. and Sratis, I. 2001. Trace metal concentrations in marine macroalgae from different biotopes in the Aegean Sea. *Environment International* **27**:43-47.
- ²⁵Shiber, J.G. 1980. Trace metals with seasonal considerations in coastal algae and molluscs from Beirut, Lebanon. *Hydrobiologia* **69**:147-162.
- ²⁶Snodgrass, W.J. 1980. Distribution and behavior of nickel in the aquatic environment. In Nriagu, J.O. (ed.). *Nickel in the Environment*. Wiley, New York, pp. 203-274.
- ²⁷Stengel, D.B., Macken, A., Morrison, L. and Morley, N. 2004. Zinc concentrations in marine macroalgae and a lichen from western Ireland in relation to phylogenetic grouping, habitat and morphology. *Marine Pollution Bulletin* **48**:902-909.
- ²⁸Topcuoglu, S., Güven, K.C., Balkis, N. and Kirbasoglu, C. 2003. Heavy metal monitoring of marine algae from Turkish coast of the Black Sea, 1998-2000. *Chemosphere* **52**:1683-1688.
- ²⁹Villares, R., Puente, X. and Carballeira, A. 2002. Seasonal variation and background levels of heavy metals in two green seaweeds. *Environmental Pollution* **119**:79-90.
- ³⁰Zbikowski, R., Szefer, P. and Latala, A. 2006. Distribution and relationships between selected chemical elements in green alga *Enteromorpha* sp. from the southern Baltic. *Environmental Pollution* **143**:435-448.