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Metal Bioaccumulation by Sea Urchin (*Echinometra mathaei*) from the Saudi Coastal Areas of the Arabian Gulf: 2. Cadmium, Copper, Chromium, Barium, Calcium, and Strontium

M. Sadiq, A. A. Mian, A. P. Saji

Water Resources and Environment Division, Research Institute, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia

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The sea urchin is a spiny skin animal belonging to the class *Echinoidea.* The species *Echinometra mathaei* is widely distributed in the Saudi northern Arabian Gulf. It often occurs in dense aggregations on subtidal rocks, artificial structures, coral reefs, grass beds, and rocky tidal flats and on dead coral reefs (Downing 1988; Downing and Roberts 1993; Sadiq et al. in press). Kaplan (1982) described urchins as slow-moving grazers of disintegrating organic detritus materials on the surfaces of sand particulates. However they can also scrape the thin film of algae from the surfaces of rocks.

The Saudi coast of the Arabian Gulf was severely impacted by the 1991 oil spill and other Gulf War activities (Sadiq and McCain 1993). Being resident on dead coral reefs, the sea urchin *Echinometra mathaei* was chosen as one of the organisms for monitoring the Gulf War's aftermath on the marine communities of the Arabian Gulf, especially coral reefs (KFUPM/RI 1991). In this paper we report the results of metal concentrations in the sea urchin collected in the above monitoring program.

MATERIALS AND METHODS

Sea urchin, sediment and seawater samples were collected from eight reef areas in the northwestern Arabian Gulf (Saudi coastal waters) shown in Fig. 1 during October 1992, April 1993, October 1993, and January 1994. A brief description of the locations and samplings is given below.

Abu Ali Reef: This reef was exposed to the 1991 oil spill resulting from the Gulf War activities. The coral cover was largely of the species Porites compressa. Sea urchin, sediment, and seawater samples were collected only in October 1992

Abu Ali Reef 3: It is located about 100 m offshore from the beach at Abu Ali Island. *Porites spp* dominate the coral cover. The reef area was slightly impacted by the 1991 oil spill. Sea urchin, sediment, and seawater samples were collected during April 1993 only.

Abu Ali Reef 4: This reef is located down current from an oil impacted area, therefore, it might have been exposed to dissolved hydrocarbons. Sea urchin, sediment, and seawater samples were collected during all sampling periods (October 1992, April 1993, October 1993, and January 1994).

Manifa Bay Reef: This reef is located within 1 km south of Manifa Pier, in the Manifa

Correspondence to: M. Sadiq

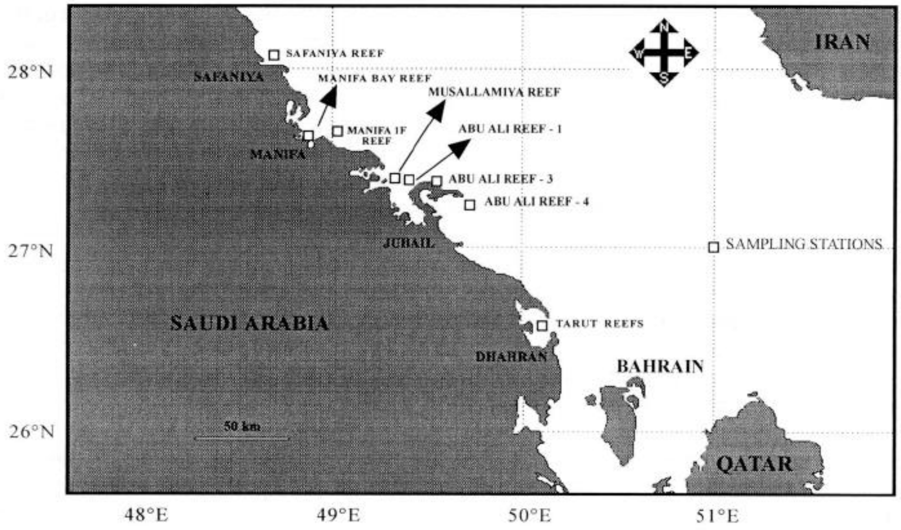

Figure 1. Sea urchin, sediment and seawater sampling stations in the Saudi Arabia coastal areas of the Arabian Gulf.

Bay. This area was heavily oiled during the 1991 oil spill. Samples were collected during October 1992, April 1993, and January 1994.

Manifa Reef 1F: It is about 10 km offshore (from Manifa GOSP) and relatively close to an oil field and, thus, was probably exposed to higher pollution levels during drilling and development of this oil field. The hard coral *Porites* compressa is dominant here. Samples were collected in October 1992, April 1993, and January 1994.

Musallamiyah Reef: This is a shallow reef (0.5 to 3 meters deep during low tide). The area was badly oiled during the 1991 oil spill. Samples were collected during all sampling periods.

Safaniya Reef: A small patch reef located within 1 km from the beach. In addition to moderate exposure to the 1991 oil spill, this reef might have been exposed to drilling muds and other contaminants related to oil field-development activities. Samples were collected during all sampling periods.

Tarut Bay Reefs: Tarut Bay was not exposed to the oil spill. However, untreated agricultural drainage water from the Qateef oasis is discharged to the Bay. Samples were during all sampling periods

Surface seawater samples were collected in 5-liter plastic bottles. A minimum of 10 sea urchins were collected during each sampling period. All samples were stored on ice during transportation to KFUPM/RI laboratories. The hard shell of each sea urchin was cut open and gonadal tissue was removed carefully using a plastic spatula (the remaining material was discarded except for October 1993 samples). Individual gonadal tissue samples were digested in a mixture of 12 ml nitric acid and 3 ml perchloric acid for three hours at 120°C. After cooling, acid digests were filtered and the volume was increased to 50 ml using distilled water (Sadiq et al. 1991, 1996). Gonadal tissues from two or more than two small animals were combined to obtain about one gram sample weight. Concentrations of cadmium (Cd), copper (Cu), barium (Ba), chromium (Cr), calcium (Ca), and strontium (Sr) in the acid digests were determined using an Inductively Coupled Argon Plasma Analyzer (ICAP).

Bioaccumulation of the above metals in sea urchin gonad, mouth opening, gut content, spine, and spineless shell were investigated by dissecting samples collected during October 1993 only. Spines were removed and washed with distilled water. The spineless hard shell was cut and washed with distilled water. Gonad tissue was removed as described above. Mouth opening and abdominal contents (gut) were also separated. All the above parts were weighed individually and digested separately by following the digestion procedure given above. If the weight of a body part was less than one gram, samples from two or more urchins from the same sampling area were combined.

Triplicate samples of about 100 grams of the upper 2-cm layer of sediment from each reef during each sampling period was scooped into plastic containers. The sediment samples were air dried, pulverized by hand, and sieved through a plastic sieve with 0.5mm mesh. Duplicate aliquots of two grams of each sieved sediment sample were wet digested (Sadiq et al. 1993; in press; Sadiq and Zaidi 1985). Concentrations of Cd, Cu, Cr, Ba, and Sr were determined in the acid digests using an ICAP.

Triplicate seawater samples were collected about 6 cm below the surface by divers in plastic containers. These samples were filtered through 0.45-µ Millipore membrane filter paper in the laboratory. Dissolved concentrations of Cd and Cu were determined by chelating these elements with Pyrrolidine CarboDithioic Acid and extracting them with chloroform (Sadiq et al. 1991). Calcium and strontium were determined after appropriate dilution of seawater samples. Because of analytical problems, Ba and Cr in seawater samples could not be determined.

To ensure high quality of the analytical results, reagent blanks and reference standard materials were included in the analytical scheme. Nitric acid and water were doubly distilled. All glassware was cleaned with 20% nitric acid. The chemicals used in the study were of the highest purity. Instrumental readings with relative standard deviation >10% were discarded. The standard reference materials of oyster tissue, estuarine sediment and seawater from US National Institute for Science and Technology (NIST) were analyzed following analytical procedures described above. Except for Cu in oyster tissue (15% lower), Cr in sediment (25% lower), and copper in seawater (20% higher), elemental concentrations in the reference materials samples were found to be within 10% of the recommended concentrations. Analysis of variance, correlation, Chi square, and regression techniques will be used to statistically analyze metal data.

RESULTS AND DISCUSSION

Concentration ranges of Cd, Cu, Ba, Cr, Ca, and Sr in the sea urchin, sediment, and seawater samples are summarized in Table 1. Mean concentrations of the above metals in gonad samples collected during different sampling periods are also included in the table.

The mean Cd concentrations in the gonad samples, along with standard deviations, are plotted in Fig. 2. Analysis of variance of the data indicated that the reef areas had significantly ($p < 0.01$) influenced Cd concentrations in the urchin gonadal tissue (Fig. 2), but the effect of the sampling date (Table 1) was not significant ($p < 0.01$). Gonad samples from the Manifa 1F reef area contained the highest and those from the Manifa Bay reef area had the lowest Cd concentrations.

Calcium was one of the major metallic elements in sea urchin gonads (Table 1). Calcium concentrations were significantly ($p < 0.01$) influenced by the sampling area; however, the effect of sampling period was not significant. The gonad samples from Manifa 1F reef area contained the highest Ca concentrations ($p < 0.01$). The sampling area and period did not significantly ($p < 0.01$) influence Sr concentrations in gonads. The gonad samples from Musallamiyah contained the highest Sr concentrations (Fig. 2).

Table 1. Metal concentrations in sea urchin, sediment, and seawater samples from the coastal areas of Saudi Arabia.

Area	No. of Samples	Cadmium	Copper	Barium	Chromium	Calcium	Strontium
Area-wise gonad tissue concentration ranges (mg/kg wet weight, data for all sampling dates are combined)							
Abu Ali Reef 1	18	nd-1.58c	nd-0.07b	nd-0.08b	nd-0.01b	533-4834b	3.27-27.64c
Abu Ali Reef 3	7	0.33-1.63bc	0.06-0.55b	nd-0.644b	nd-0.06b	2368-11091b	18.30-99.56abc
Abu Ali Reef 4	32	0.48-2.91b	nd-2.52ab	0.22-3.14b	nd-0.52ab	400-61669b	17.43-179.39ab
Manifa Bay Reef	27	nd-1.44c	nd-1.29b	nd-1.13a	nd-0.41b	425-8261b	3.76-115.43bc
Manifa Reef 1F	24	0.04-5.49a	nd-4.93a	0.31-3.12b	nd-4.73a	1190-930148a	6.91-427.66abc
Musallamiyah Reef	34	0.48-2.69ab	0.02-4.93a	0.13-2.10b	nd-0.67b	837-111624b	5.79-567.93a
Safaniya Reef	34	0.22-1.92c	nd-1.35ab	0.09-1.41b	nd-0.41b	981-19108b	12.32-316.54abc
Tarut Bay Reefs	28	0.11-1.65c	nd-1.63a	0.012-5.36b	nd-0.81b	296-25911b	9.67-206.34abc
Date-wise gonad tissue concentration means (mg/kg wet weight, all sampling areas are combined)							
October 1992	73	0.98±0.86a	1.03±0.83a	0.72±0.78a		6901±3943a	47.18±26.03a
April 1993	53	1.04±0.78a	0.58±0.73b	0.89±0.69a	0.32±0.72a	4808±3094a	54.22±46.03a
October 1993	43	0.91±0.63a	0.59±0.50b	0.53±0.46a	0.31±0.19a	5812±3943a	56.49±56.03a
January 1994	35	1.03±0.40a	0.54±0.37b	0.49±0.41a	0.16±0.14a	3151±1943b	24.96±16.03b
Concentration ranges in body parts (mg/kg wet weight, samples collected during October 1993 only)							
Gonad	40	0.11-4.08a	nd-4.93b	0.03-3.92d	nd-4.73b	1284-27771e	12.48-427.31
Intestine	40	0.07-2.22b	0.23-1.86a	1.37-17.38a	0.26-2.36a	18033-171539d	199-17651
Mouth	38	0.91-2.05b	0.02-0.67c	3.73-15.66b	nd-0.19c	70045-294927c	640-896
Spine	39	0.93-3.14b	nd-1.49c	2.38-4.71c	nd-0.94c	114619-382064a	796-1141
Shell	37	0.80-2.08b	nd-1.15c	2.66-14.90b	nd-0.44c	94091-384981b	714-1028
Concentration ranges in sediment samples (mg/kg dry sediment)							
All areas	53	1.18-30.27	0.37-10.24	7.11-67.23	1.63-16.85		302-39668
Concentration ranges in seawater samples(µg/L)							
All areas	47	nd-14.33	0.271-2.98				

nd Concentrations below the detection limits of ICAP.

Blank No information was collected.

Letter a,b,c,d,e, indicate significant differences.

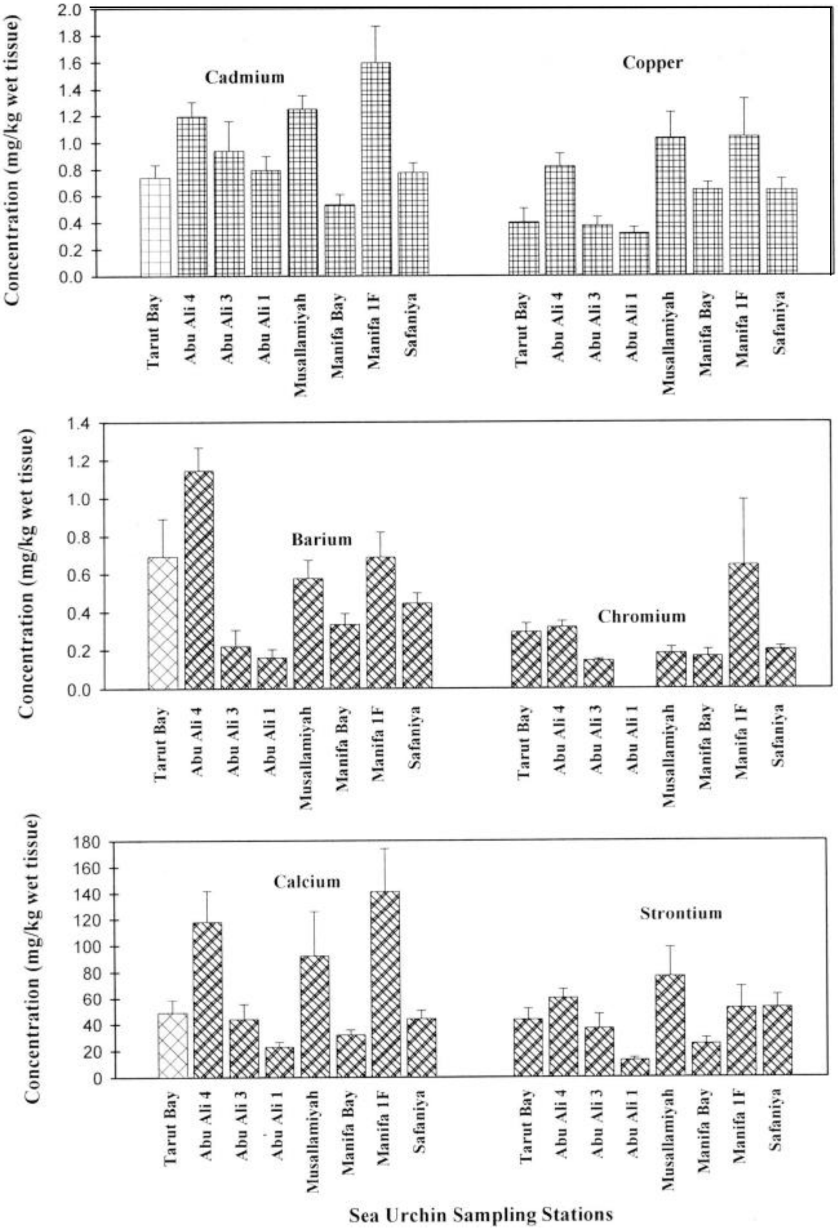

Figure 2. Mean metal concentrations in sea urchin gonad samples from different reefs of Saudi Arabia coastal areas. *Calcium concentrations are in the hundred.*

Both the sampling period (Fig. 2) and area (Table 1) significantly ($p < 0.001$) affected Cu bioaccumulation in sea urchin gonad tissue. The gonad samples collected in October 1992 contained significantly higher Cu concentrations, whereas Cu concentrations in the samples collected during other periods were statistically similar. The urchin samples from Manifa 1F and Musallamiyah reefs contained the highest Cu concentrations. The mean Cu concentrations in the gonad tissue from different reef areas are plotted in Fig. 2. In general

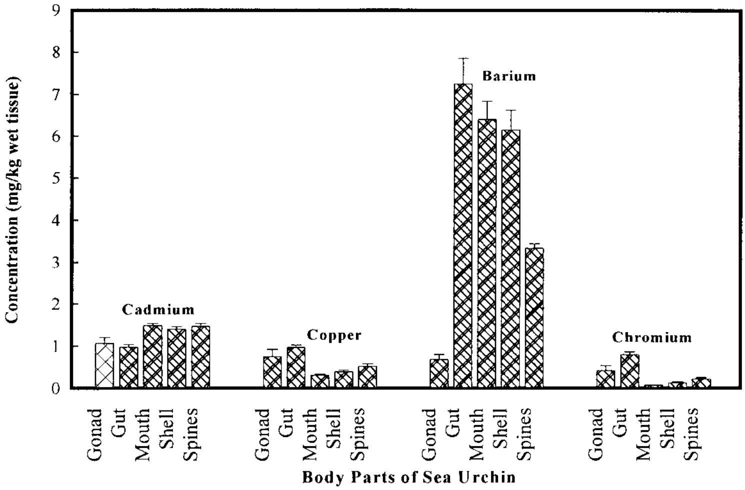

Figure 3. Metal Concentrations in different body parts of sea urchins collected from coastal areas of Saudi Arabia.

it seems that Cu bioaccumulation increased towards the north (from Tarut Bay to Safaniya) as shown in Fig. 1.

Barium concentrations in sea urchin gonads were not significantly ($p < 0.01$) influenced either by the sampling date or area. The highest mean Ba concentration was found in the samples from Abu Ali reef 4 area (Fig. 2). This reef is situated in close proximity to the Berri Oil Field, which may have been a contributing factor to the Ba bioaccumulation (the sediment contained the second highest Ba concentrations, see Fig. 5). Except for Manifa 1F reef area, all gonad samples contained statistically similar Cr concentrations (Fig. 2). The influence of sampling date on Cr concentration was not significant ($p < 0.01$).

Metal concentrations in different body parts of sea urchin were determined and are summarized in Table 1. Cadmium concentrations in different body parts were statistically different ($p < 0.001$). Mouth, spine, and shell (spineless) samples contained statistically similar but significantly ($p < 0.01$) higher Cd concentrations than the gut and gonad samples, Spine and shell are composed largely of carbonates of Ca and these minerals are known to adsorb Cd (Sadiq 1992). The elevated Cd concentrations in the spine, shell, and mouth samples might have resulted from Cd adsorption on the carbonate surfaces. The influence of the sampling area on Cd concentrations in different body organs were significant ($p < 0.0001$, not included in this paper). The mean Cd concentrations in different body parts are plotted in Fig. 3.

Sampling areas did not significantly ($p < 0.01$) affect Cu concentrations in different body organs. However, different organs bioaccumulated Cu in significantly ($p < 0.001$) different concentrations. The distribution pattern of Cu in sea urchin organs is given in Fig. 3 which shows that gut contained the highest Cu concentrations followed by gonads >spine >shell >mouth.

Both tissue type and sampling area significantly ($p < 0.001$) affected bioaccumulation of Ba by sea urchins. The highest and the lowest mean concentrations of Ba were found in the gut and gonad samples, respectively (Fig. 3). The elevated Ba concentrations in the gut content might have been due to ingestion of sediment which was high in Ba. Except for the Manifa 1F and Musallamiyah areas, statistically similar effects of sampling areas were observed on Ba concentrations.

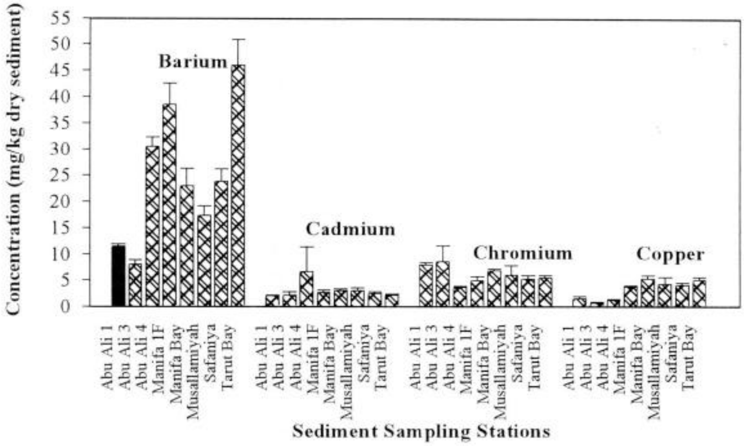

Figure 5. Metal concentrations in the sediment samples from the coastal areas of Saudi Araba.

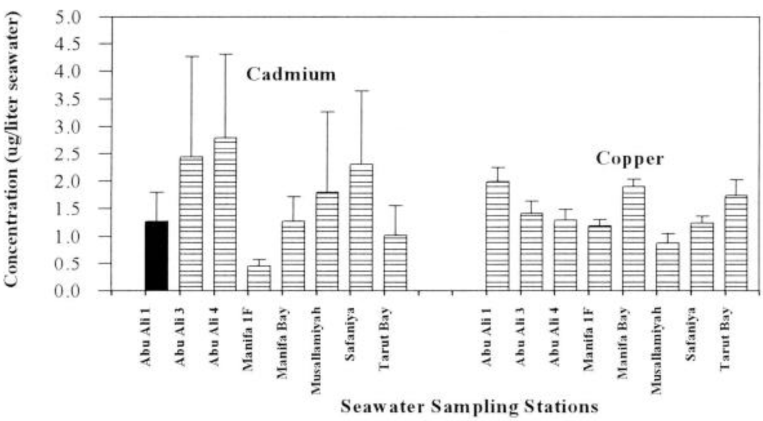

Figure 6. Concentrations of Cd and Cu in seawater samples from the coastal areas of Saudi Arabia.

Concentrations of Cd and Cu in the seawater samples are also given in Table 1. Like sediment, concentrations of Cd and Cu varied widely in the seawater samples. The mean Cd and Cu concentrations are plotted in Fig. 5. It is evident that Cd concentrations varied more widely than those of Cu. The minimum mean Cd concentrations were found in the seawater samples form Manifa 1F reef.

Correlation technique was used to investigate inter-metal interactions in sediment and seawater. In the sediment samples, strong ($p < 0.001$) associations between Ba and Cd, and Cu and Cr were observed. The interactions between Cu and Cr are shown in Fig. 6.

The influence of sediment and seawater composition on bioaccumulation of the above metals by sea urchin was investigated using a correlation technique. It was found that sediment and seawater composition did not significantly ($p < 0.01$) influence bioaccumulation of metals by sea urchin. This appears in line with the feeding habit of sea urchin which is largely herbivorous (organic detritus material and algae consumer).

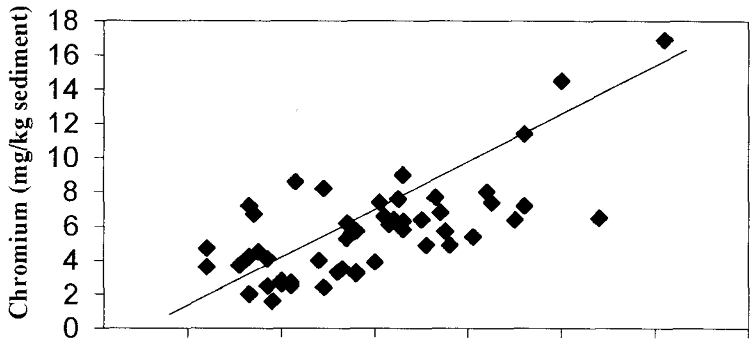

Figure 7. Interaction between Cu and Cr in sediment samples.

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