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TRACE METAL SCREENING

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MESL/IAEA

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1. INTRODUCTION

Under the ROPME-IAEA Contaminant Screening Project and the ROPME Mussel Watch Programme, surveys of heavy metal and organic contaminants have taken place in coastal areas of the Inner RSA and the Sea of Oman, collectively known as ROPME Sea Area (RSA). The results of these surveys have been published by ROPME-IAEA (1996, 1998, 1999, 2001, 2005 and 2013). The aim of the survey undertaken in February-July 2014 was to screen for inorganic and organic contaminants in key coastal areas of Bahrain, I.R. Iran, Iraq, Oman, Saudi Arabia and the United Arab Emirates (UAE) and to compare the results with those from earlier surveys from the same areas. This report summarizes the results of trace elements content in the sediments and bivalves in the RSA. This report should therefore be considered as a follow up report to the 1996, 1998, 1999, 2001, 2005 and 2013 ROPME-IAEA monitoring reports.

2. SAMPLING METHODOLOGY

Sediment and biota samples from selected locations along the coast of Kingdom of Bahrain (K.Bh), Islamic Republic of Iran (I.R. Iran), Republic of Iraq, Sultanate of Oman (Oman), Kingdom of Saudi Arabia (KSA) and the United Arab Emirates (UAE) were collected as part of the ROPME Mussel Watch Programme. The sampling stations, locations and types of samples collected are given on the Figure 1 and in Table 1.

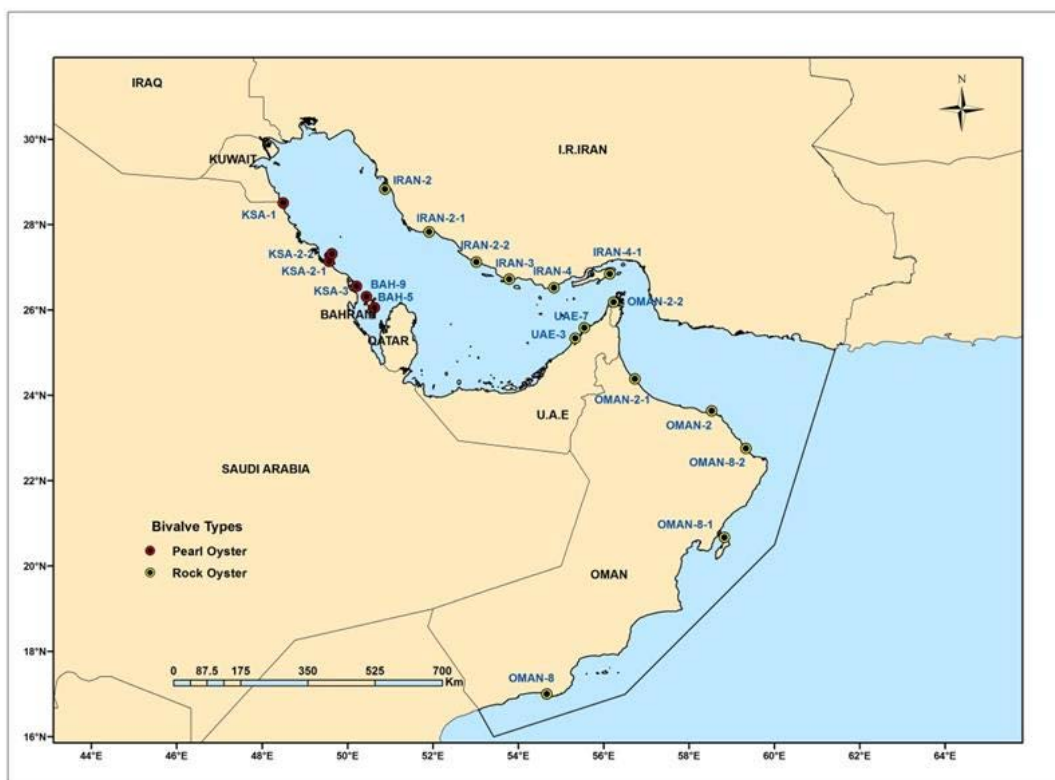


Figure1. Map of sampling station

Table 1. Sediment and bivalves sampling sites

Country	Date	Site Name	Code	Station	Latitude	Longitude	Sample type		Remarks
K.Bh	2014-02-18	Askar *	Bah-5	1	26°3' N	50°37' E	Pearl Oyster	Sediment	
	2014-02-17	Marwada	Bah-9	1	26°18' N	51°26' E	Pearl Oyster	Sediment	
I.R.Iran	2014-02-17	Bushehr *	IRAN-2	1	28°49' N	50°52' E	Rock Oyster	Sediment	
	2014-02-19	Dayer	IRAN-2-1	1	27°49' N	51°54' E	Rock Oyster	Sediment	
	2014-02-20	Gavbandi	IRAN-2-2	1	27°7' N	53°1' E	Rock Oyster		
	2014-02-21	Chiru (new site)		1	26°43' N	53°47' E	Rock Oyster		
	2014-02-22	Lengeh *	IRAN-4	1	26°31' N	54°50' E	Rock Oyster		
	2014-02-24	Qeshm Island	IRAN-4-1	1	26°50' N	56°8' E	Rock Oyster		
Iraq	?/07/2014	Shat Al Arab		1			Pearl Oyster		10 Km offshore
OMAN	2014-04-01	Mirbat *	OMAN-8	1	17°0' N	54°40' E	Rock Oyster	Sediment	
	2014-03-14	Masirah	OMAN-8-1	1	20°40' N	58°50' E	Rock Oyster	Sediment	
	2014-02-08	Qalhat	OMAN-8-2	1	22°45' N	59°20' E	Rock Oyster	Sediment	
	2014-02-06	Mina Al Fahal *	OMAN-2	1	23°37' N	58°31' E	Rock Oyster	Sediment	
	2014-02-10	Sohar	OMAN-2-1	1	24°23' N	56°44' E	Rock Oyster	Sediment	
	2014-04-08	Khasab	OMAN-2-2	1	26°11' N	56°14' E	Rock Oyster	Sediment	
KSA	2014-03-06	Ras Tanura *	KSA-3	1	26°33' N	50°12' E	Pearl Oyster	Sediment	
	2014-03-08	Jubail	KSA-2-1	1	27°8' N	49°34' E	Pearl Oyster	Sediment	Pleasance harbour (Fanateer)
	2014-03-09	KSA-2	KSA-2-2	2	27°18' N	49°38' E	Pearl Oyster	Sediment	30 km N. Jubail (Ras abu Ali)
	2014-03-09	Al Khafji	KSA-1	1	28°30' N	48°29' E	Pearl Oyster	Sediment	little No. of oysters
UAE	2014-02-13	Umm Al-Quwain *	UAE-7-1	1	25°35' N	55°33' E	Rock Oyster	Sediment	
			UAE-7-1	2			Rock Oyster	Sediment	
			UAE-7-1	3			Rock Oyster	Sediment	
			UAE-7-2	1			Pearl Oyster	Sediment	50 m offshore of R. Oyster stations
			UAE-7-2	2			Pearl Oyster	Sediment	
			UAE-7-2	3			Pearl Oyster	Sediment	
	2014-02-18	Dubai (Jebal Ali)	UAE-3	1	25°20' N	55°20' E	Rock Oyster	Sediment	

*Location sampled during the ROPME Contaminant Screening Programme (1994-2005) and Mussel Watch Programme 2011

3. ANALYTICAL PROCEDURES

The analytical protocols for determination of trace elements in sediment and biota samples are presented in this section.

3.1 CHEMICALS AND MATERIALS

High quality demonized water from Milli-Q system (Millipore, Bedford, MA, USA) was used throughout this work. Ultra-pure 70% HNO₃ (Ultrex®, T. T. Baker, Phillipsburg, NJ, USA), 30.5% H₂O₂ (p.a. from Merck, Darmstadt, Germany), 40% HF (Suprapur®, Merck, Darmstadt, Germany) and 36% HCl (Ultrex®, T. T. Baker, Phillipsburg, NJ, USA) were used for sample digestion.

Only new lab ware material (bottles, vessels, tips, syringes etc.) was employed and it was pre-cleaned thoroughly following validated procedure. In order to avoid risk of memory effects from previous experiments, digestion vessels were submitted to an appropriate cleaning procedure. To reduce the risks of airborne contamination all sample processing steps were performed in the Clean chemical laboratory (class <100).

Stock standard solutions with concentration 1000 mg kg⁻¹ (from Merck, Darmstadt, Germany) were used for the preparation of working calibration solutions. Working calibration solutions were prepared gravimetrically by appropriate diluting the stock standard solutions.

Methanol for gas chromatography was purchased from Fluka (Sigma-Aldrich, Steinheim, Germany). Stock calibration standard of methylmercury chloride (CH₃HgCl, 1 mg/L in 0.5% acetic acid, 0.2% hydrochloric acid) was obtained from Brooks Rand Labs. Working standard solutions were prepared gravimetrically weekly by diluting, in pre-cleaned Teflon vials, the stock calibration solution with a solution containing 0.5% (w/w) acetic acid, 0.2% (w/w) hydrochloric acid and Milli-Q water to a range of 0.1–100 µg/L, calculated as Hg. Working solutions were protected from light. The ethylating reagent was prepared by mixing 2 mL of 1.33 M sodium tetraethylborate (NaBEt₄) in tetrahydrofuran (THF) and 38 mL of 2% potassium hydroxide (KOH), both packed with an argon atmosphere and provided by Brooks Rand Labs, in order to obtain 1% NaBEt₄ solution in 2% potassium hydroxide. The ethylating reagent was divided into several 4 mL vials and frozen immediately. Vials were kept at -18°C for short-term storage (up to 1 month) and thawed immediately prior to usage.

Two CRMs produced by IAEA NAEL in Monaco, IAEA-458, marine sediment and IAEA 470 biota oyster, were used for quality control purposes during ICP-MS analysis.. Sediment CRM MESS-3 from the National Research Council of Canada (NRCC, Ottawa, Ontario, Canada) was used for calibration purposes during mercury analysis. Certified reference

material (CRM) DORM-3 (fish protein, certified value: 0.355 ± 0.056 mg/kg) supplied by the NRCC, Canada, was also used in the method validation process for Methyl Mercury determination in biota samples.

3.2 SAMPLE PRE-TREATMENT

The sediment samples were received already freeze-dried and were sieved at 1 mm. Samples OMAN 8 and OMAN 2-2 were 100% above 1mm. As analytical protocols are validated only for sediment sample below 1mm, those samples could not be measured.

Most of biota samples were also received already freeze-dried and grinded, so no pre-treatment was applied. Samples from Oman were in pieces and looks “cooked”, not freeze dried and the homogenization for them was not possible.

3.2.1 Sample digestion

- *Sediment samples*

All samples were digested using a CEM MARS Xpress pressure microwave digestion system. A quantity of 0.25 ± 0.05 g of freeze-dried sediment sample was weighed directly in the acid-cleaned Teflon microwave vessels. Sediment samples were digested with 5 ml of ultrapure nitric acid, 2 ml ultrapure concentrated hydrofluoric acid and 2 ml of hydrogen peroxide.

Each digestion batch included at least 2 reagent blanks and an appropriate 1 matrix certified reference material (CRM): IAEA-458, marine sediment in this case.

The digestion procedure involved gradually increasing of the temperature to 190°C for 15 minutes. This temperature was maintained for around 15 minutes. After cooling, the reactors were opened and 10 ml of 4% boric acid solution added. In order to dissolve completely fluoride precipitates second microwave run (increase of temperature to 170°C for 10 minutes and holding it at 170°C for 15 minutes) was applied. The digested samples were quantitatively transferred with ultrapure water to 50 ml plastic tubes, already containing an extra 10 ml of 4% boric acid solution.

Analysis of the sediment samples can cause particular problems because of difficulties in achieving complete digestion. Incomplete digestion, however, can cause strong matrix effects visible as the molecular interferences, signal suppression or sometimes as signal enhancement. Strong digestion conditions as achievable with the high pressure systems or with a two-stage microwave-assisted digestion procedure. Incomplete digestion of a sediment material could results in silicate residues when evaporating to dryness, demonstrating remaining

matrix substances. The residual matrix can disturb a chromatographic separation and create the matrix effects during isotope ratio determinations. Therefore, carefully developed sample preparation procedure was a key issue for those measurements. In the present study the closed microwave system was used and the sediment samples were dissolved in the mixture of HNO₃, H₂O₂ and HF. The important advantages of a microwave digestion include minimizing contamination, lower reagent and sample consumption, reduction of losses of volatile species and additionally decreasing in analysis time.

- *Biota samples*

Biota samples were digested also in acid-cleaned Teflon microwave vessels with 5 ml of ultrapure nitric acid and 2 ml of hydrogen peroxide. Each digestion batch included at least 2 reagent blanks, and an appropriate natural matrix IAEA 470, oyster tissue (IAEA) in this instance.

Each digestion batch included at least 2 reagent blanks and an appropriate 1 matrix certified reference material (CRM): IAEA-470, oyster biota sample in this case.

The digestion procedure for biota samples involved gradually increasing the temperature to 190° for 15 minute period and maintaining this temperature for additional 15 minutes. After cooling, the reactors are opened, and the digested samples are transferred onto 50 ml plastic tubes and made up to volume with ultrapure water.

The samples digested were diluted 20 times before the analysis with 2% nitric acid.

3.2.2 Moisture determination

Moisture content in samples is to some extent "operationally defined" measurement. Correction for moisture content was obtained from 3 biota subsamples with minimum sample mass 1.0 g. The drying procedure at $85 \pm 2^{\circ}\text{C}$ was established after experimental evaluation of stability and reproducibility of results. The material was dried for 24 hours in a ventilated oven at a temperature of $85 \pm 2^{\circ}\text{C}$. Then weighting and repeated drying was performed until constant mass was attained (0.0002 g difference between two successive weights). Each weighting had to be carried out after the sample reached thermal equilibrium at room temperature in a desiccators. The loss of mass corresponds to the "dry mass correction factor", which was applied for correction of the respective mass fraction for the trace elements determined in this study.

3.2.3 Extraction of Methyl Mercury from biota samples

A 0.15 g portion of IAEA-470 and 10 mL of 25% (w/w) KOH in methanol were put in a pre-cleaned Teflon vessel and placed in an oven at 75°C ($\pm 2^\circ\text{C}$) for 3 hours, and further diluted to 50 mL with Milli-Q water. A 20 μL aliquot was taken from the upper layer of the solution for measurement by (gas chromatography coupled with atomic fluorescence detector) after ethylation at room temperature

3.3 INSTRUMENTATION AND MEASUREMENTS

3.3.1 Flame atomic absorption

Al, Fe, Mn and Zn mass fractions in the digested samples were determined by flame atomic absorption spectrophotometry (AAS) (Analytik Jena) method and external calibration approach. Calibration curves were prepared daily by using 5 calibration standard solutions at concentration levels, covering the working range for the respective element. In order to verify calibration for the measured element one of the standard solutions was analysed randomly through the measurement sequence.

Procedural blanks and CRMs prepared with every batch of samples were measured at the beginning and at the end of the measurement sequence.

Quantification limits were calculated using procedural blanks and IUPAC recommendations. In the cases where absorption signals of the respective elements in the procedural blanks were negligible quantification limits were determined with the lowest calibration standard.

The matrix effects were checked using post digestion matrix spikes. In the cases when the recovery was outside of accepted limits, standard addition was used as calibration mode.

3.3.2 Inductively Coupled Plasma–Mass Spectrometry

Inductively Coupled Plasma–Mass Spectrometry (ICP-MS) was the method used for the determination of Ag, As, Ba, Cd, Co, Cr, Cu, Li, Ni, Pb, Se, Sn, U and V in sediment samples.

All measurements were carried out at the International Atomic Energy Agency in Monaco, using the quadrupole mass spectrometer 2 Q-ICP-MS (XSERIES, Thermo Fisher Scientific). The instrument was equipped with a Micromist nebulizer (0.2 ml/min, Glass Expansion) and a cyclonic spray chamber cooled by Peltier cooling system ESI. 2 Q-ICP-MS (XSERIES, Thermo Fisher Scientific). The instrument is equipped also with collision/reaction cell for interference removal. The collision gas used was He with high degree of purity at flow rate of 3.75 ml/min.

The selection of the isotopes to be measured was done with respect to the abundance of the isotopes and possible spectral interferences in the ICP-MS measurement step.

The signal intensities per replicate were corrected for dead time, instrumental background and possible interferences prior to calculating an average and its relative standard deviation. Ag, Ba, Cd, Co, Cu, Li, Ni, Pb, Sn and U in the present study were measured in normal ICP- MS mode, whereas As, Cr, Se and V were measured in collision reaction ICP-MS mode.

Before the measurements, the method parameters in each of the modes used were optimized for maximum intensity and precision of each single isotope. The instrumentation and summary of the applied measurement modes in the samples is presented in Table 2.

Table 2. Optimized ICP-QMS instrumental parameters for the isotopic measurements (XSERIES 2, THERMO SCIENTIFIC) in standard and collision cell mode

Parameter		
	Standard Mode	Collision Reaction Mode
Plasma gas flow, L·min ⁻¹	13.5	13.5
Nebuliser gas flow, L·min ⁻¹	0.91	0.89
Auxiliary gas flow, L·min ⁻¹	1.05	0.95
RF power, W	1200	1200
Sensitivity for 1 ppb In, cps	>100000	>20000
Background on mass 220, cps	<2	<2
Dead time, ns	39	39
Number of sweeps/ replicate	150	150
Number of replicates	3	3
Dwell time per amu, ms	75	75
Sample uptake, mL/min	0.2	0.2
Oxide formation CeO ⁺ /Ce ⁺ , %	<3	<0.2

Each measurement sequence started by the monitoring of the instrumental background and followed by procedural blank analysis. Every sample was introduced into the plasma at least 2 minutes prior to measurement, to ensure that the isotopic signals were stable.

The concentration of elements in the sediment and biota samples was determined via external calibration using appropriate working standards derived from mono elemental standards (1000 µg/ml). The standards were prepared in 2% HNO₃. The analytical quality control was provided by the analysis of the certified reference material (IAEA-458, IAEA-470) prepared with each digestion batch.

Before ICP-MS analysis sediment and biota digested samples were diluted with 2% nitric acid 50 times and 20 times respectively.

The procedural blanks, which were prepared in the same way as the samples were measured on separate days and were determined by external calibration with 3 different concentrations of element standards prepared by dilution of adequate Merck standards.

3.3.3 Advanced Mercury Analyzer

Advanced Mercury Analyzer (AMA 254, Altech) was applied for determination of mercury in sediment and biota samples. The determination was done in solid state of the samples; therefore no preliminary digestion was required.

A portion of about 100 mg of sediment or biota sub-sample was measured. The internal calibration of the AMA 254 instrument was checked every day using an external standard solution and a CRM (MESS-3 or IAEA 470) sampled at different intake masses, in order to verify the linearity of the calibration from 5 to 30 ng of mercury.

The replicate blanks and CRM were analyzed for quality control purposes throughout the run, as well as the replicate samples.

The quantification limits were calculated using procedural blanks.

3.3.4 Methyl Mercury

Methyl mercury was determined by GC-AFS (gas chromatography coupled with atomic fluorescence detector) purchased for Brooks Rand Laboratories, Seattle, USA, after ethylation at room temperature.

Species separation is accomplished with a packed column OV-3 (Brooks Rand Labs) kept in an isothermal heating oven at 36°C. Thermal decomposition takes place in a quartz packed pyrolytic column heated at approximately 750°C. Argon 5.0 grade gas was used as the carrier gas (17.3 mL min⁻¹). After thermal decomposition, mercury species are introduced to the detector as elemental mercury (Hg⁰) and quantified. The AFS system is an extremely sensitive detector where the Hg⁰ atoms, in an inert carrier gas stream, are excited by a source of UV radiation. Excitation and fluorescence occurs at a wavelength of 253.5 nm. Finally, data were acquired and processed by Mercury Guru Software version 4.0 supplied with the instrument.

Samples were dissolved in KOH/Methanol at 75°C for 3 hours. Each digestion batch included at least 2 reagent blanks, and an appropriate natural matrix IAEA 470, oyster tissue (IAEA) in this instance.

Quantification was performed by external calibration. The matrix effects were checked using post digestion matrix spike, but no matrix effect were detected during the measurements of the samples.

The procedural blanks and CRMs prepared with each batch of samples were measured at the beginning and at the end of each measurement sequence.

3.3.5 Grain size

- *Preparation of samples*

The samples were sieved at 300 µm. Most of the samples have very small fraction below 300 µm. The portion of material above 300 µm was then recorded (by weighing).

Approximately an aliquot of 1 g (or less when not enough material was available) of sediment sample was introduced in a 10 ml tube. 5 ml of Milli Q water was added and the tube was shaken in order to separate the silt particles properly. An equilibration period of about 12 hours was used to insure that the sample was uniformly wet before analysis.

- *Particle Size Analysis*

The particle size distribution was determined using a Malvern Instrument Mastersizer device. The principle of this device is that small particles cause incident light to be diffracted through a large angle whereas large particles will diffract incident light through a small angle. Particle size information is derived by deconvolution of the diffraction data obtained by the instrument.

- *Apparatus used*

The MALVERN Mastersizer Micro v2.12 is designed to analyze particle size of silty sediments (<300 µm), the particles need to stay in suspension during the measurement process (this device is not suited for the analysis of coarse sandy material).

- *Protocol used*

The analysis of the particles is achieved by slurring a sediment sample into a beaker containing 500 ml of water. The mixture is pumped through a cell which is interrogated by the instrument's laser beam. The particle size distribution is determined from the resulting diffraction pattern.

4. RESULTS AND DISCUSSION

4.1 SEDIMENT

The results for trace elements' concentrations in sediments are shown in the Table 3 and Figure 2.

Figure 2 show all measured element concentration. Figures 3, 4, 5, 6, 7, 8, 9 and 10 represent selected measured element concentration of the samples collected in 2015, Ecological Risk Assessment Marine Sediment Screening Benchmarks (black line) from EPA, Detection Limit (DL) for Cd only and Effect Medium Range (ERM) when adequate. The station order follows the coast from east to west (i.e. I.R. Iran to Oman).

The results for grain size analysis are shown in the Table 4.

The size distribution in percentage for each sample is reported as:

% Sand = \sum percentage of particulates between 300 μm and 63 μm ;

% Silts = \sum percentage of particulates between 63 μm and 3.9 μm ;

% Clay = \sum percentage of particulates below 3.9 μm ;

% Mud = \sum % Clay and % Silt.

Table 3. Trace metal results in sediment samples

Sample name	Ag mg kg ⁻¹	Al g kg ⁻¹	As mg kg ⁻¹	Ba mg kg ⁻¹	Cd mg kg ⁻¹	Co mg kg ⁻¹	Cr mg kg ⁻¹	Cu mg kg ⁻¹	Fe g kg ⁻¹	Hg mg kg ⁻¹
Bah-5	0.094	5.58	2.21	39.5	<0.05	<1	23.3	9.71	2.30	0.0234
Bah-9	<0.05	0.148	1.20	17.6	<0.05	<1	2.76	1.69	0.020	0.0004
IRAN-2	0.075	8.55	8.16	109	0.156	4.73	92.6	7.85	7.38	0.0048
IRAN-2-1	0.130	21.2	5.00	104	0.156	8.44	93.5	13.6	13.5	0.0025
OMAN-8-1	0.112	10.2	1.67	43.1	0.144	5.65	131	8.90	9.31	0.0010
OMAN-8-2	<0.05	21.7	1.65	352	0.224	3.57	24.2	5.39	6.61	0.0004
OMAN-2	<0.05	4.88	7.36	13.3	0.153	8.21	336	4.61	11.9	0.0019
OMAN-2-1	<0.05	22.4	12.6	31.8	0.122	52.6	728	15.9	39.6	0.0045
KSA-3	0.059	0.077	2.50	16.3	<0.05	1.87	4.56	1.72	0.315	0.0015
KSA-2-1	0.105	19.3	3.71	185	0.119	3.18	32.6	18.5	6.63	0.0088
KSA-2-2	0.062	5.67	1.28	85.5	<0.05	1.43	11.2	2.48	1.25	0.0017
KSA-1	<0.05	6.17	1.37	77.5	<0.05	1.84	19.5	2.49	1.48	0.0009
UAE-7-1	<0.05	21.6	2.82	132	0.108	3.59	31.5	14.7	7.76	0.0010
UAE-7-1	0.075	13.6	4.42	176	0.166	4.58	79.7	18.7	9.53	0.0050
UAE-7-1	0.062	9.26	2.33	65.3	0.096	3.26	78.0	2.98	3.53	0.0017
UAE-7-2	<0.05	23.3	2.67	129	0.115	3.87	60.0	14.9	10.5	0.0013
UAE-7-2	0.073	12.7	4.71	147	0.126	4.02	60.6	14.5	8.56	0.0044
UAE-7-2	0.061	7.20	2.18	57.4	0.071	2.65	43.1	2.42	2.61	0.0014
UAE-3	0.055	5.17	2.04	37.5	0.049	4.31	64.8	3.29	3.58	0.0006

Table 3. Trace metal results in sediment samples (Contd...)

Sample name	Li mg kg ⁻¹	Mn mg kg ⁻¹	Ni mg kg ⁻¹	Pb mg kg ⁻¹	Se mg kg ⁻¹	Sn mg kg ⁻¹	Sr mg kg ⁻¹	U mg kg ⁻¹	V mg kg ⁻¹	Zn mg kg ⁻¹
Bah-5	9.12	39.9	85.9	8.24	<1.25	<1	4880	3.08	12.4	17.2
Bah-9	3.74	13.9	91.5	0.607	<1.25	<1	6977	3.15	4.13	2.2
IRAN-2	9.44	255	92.1	6.77	<1.25	<1	1797	1.60	26.7	19.1
IRAN-2-1	17.1	368	91.1	5.67	<1.25	<1	947	1.97	45.9	31.5
OMAN-8-1	2.54	193	108	4.21	<1.25	<1	5494	2.21	39.0	13.8
OMAN-8-2	4.16	140	70.0	3.75	<1.25	<1	1655	1.61	25.1	12.4
OMAN-2	2.71	258	124	2.45	<1.25	<1	2360	1.35	47.6	14.2
OMAN-2-1	6.83	734	773	3.34	<1.25	<1	221	0.94	74.0	46.6
KSA-3	1.37	14.4	83.0	1.36	<1.25	<1	6859	2.26	3.62	7.8
KSA-2-1	6.71	112	37.7	6.47	<1.25	<1	1590	1.96	22.1	62.4
KSA-2-2	2.95	37.3	51.6	2.38	<1.25	<1	6156	2.73	7.73	7.8
KSA-1	3.41	38.2	52.1	2.62	<1.25	<1	5983	2.87	9.03	7.1
UAE-7-1	9.95	229	45.7	33.2	<1.25	1.93	2819	2.43	20.0	44.8
UAE-7-1	7.11	257	71.2	8.21	<1.25	2.48	1848	1.96	22.4	186
UAE-7-1	4.02	164	73.7	2.99	<1.25	<1	4362	2.76	15.5	9.3
UAE-7-2	9.03	379	47.4	19.2	<1.25	1.93	2346	4.68	25.8	46.9
UAE-7-2	5.62	215	69.7	10.7	<1.25	1.68	2255	1.95	21.5	62.7
UAE-7-2	2.92	122	76.3	2.45	<1.25	<1	5102	2.77	12.2	7.2
UAE-3	1.94	88.0	109	1.54	<1.25	<1	5883	2.93	12.2	10.2

Table 4. Grain size results

Sample name	Clay (%)	Silt (%)	Sand (%)
Bah-5	0.00	5.83	94.2
Bah-9	0.00	0.00	100.0
Bah-9	0.00	0.00	100.0
IRAN-2	0.00	0.35	99.7
IRAN-2-1	2.06	60.95	37.0
OMAN-8-1	0.00	0.95	99.0
OMAN-8-2	0.00	0.00	100.0
OMAN-2	0.00	0.00	100.0
OMAN-2-1	0.00	0.64	99.4
KSA-3	0.00	0.00	100.0
KSA-2-1	0.32	9.81	89.9
KSA-2-2	0.00	0.00	100.0
KSA-1	0.00	0.00	100.0
UAE-7-1	0.00	1.88	98.1
UAE-7-1	0.00	0.00	100.0
UAE-7-1	0.00	0.07	99.9
UAE-7-2	0.00	0.12	99.9
UAE-7-2	0.00	0.00	100.0
UAE-7-2	0.00	0.85	99.1
UAE-3	0.11	3.52	96.4

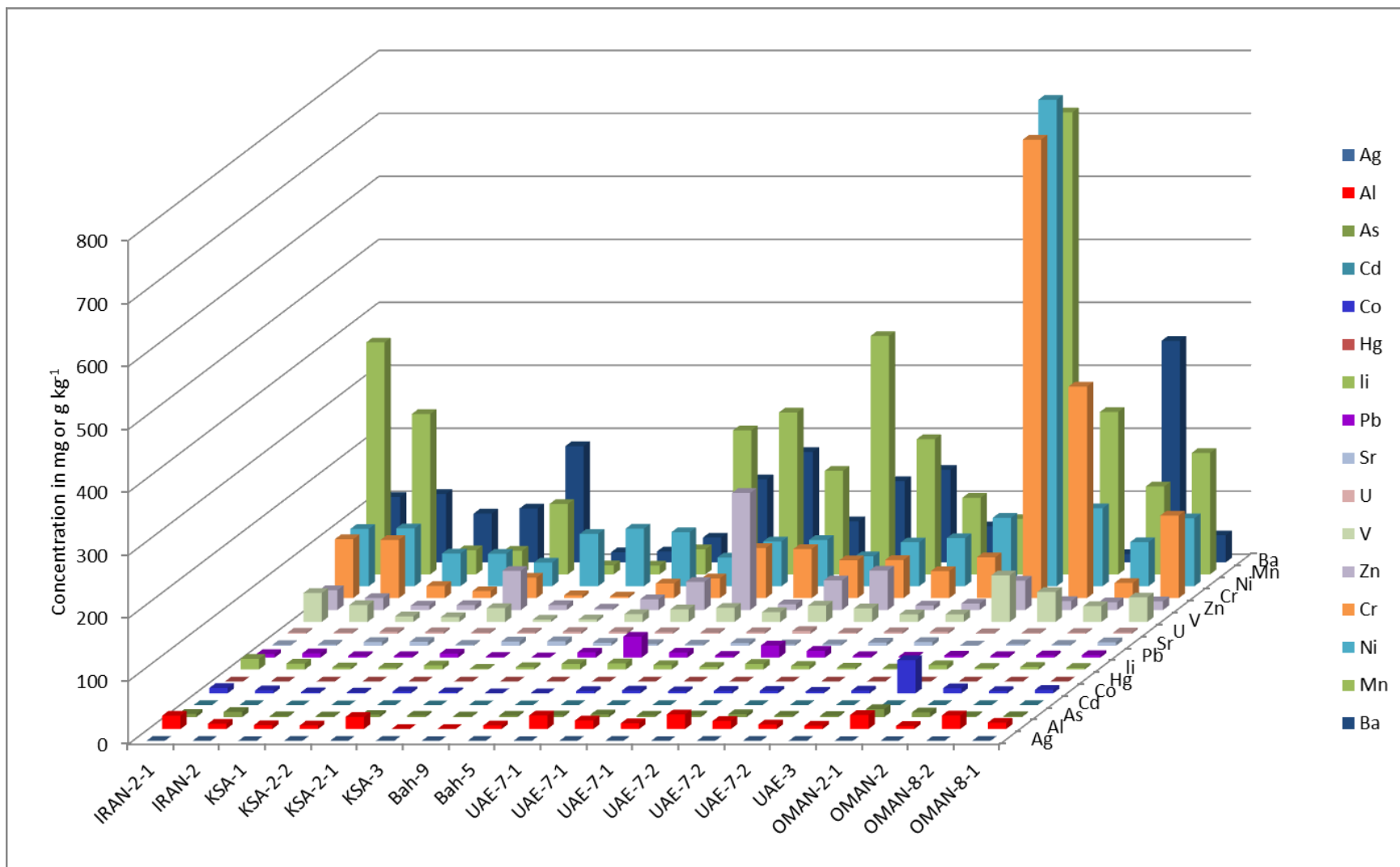


Figure 2. Concentration of measured trace and major elements

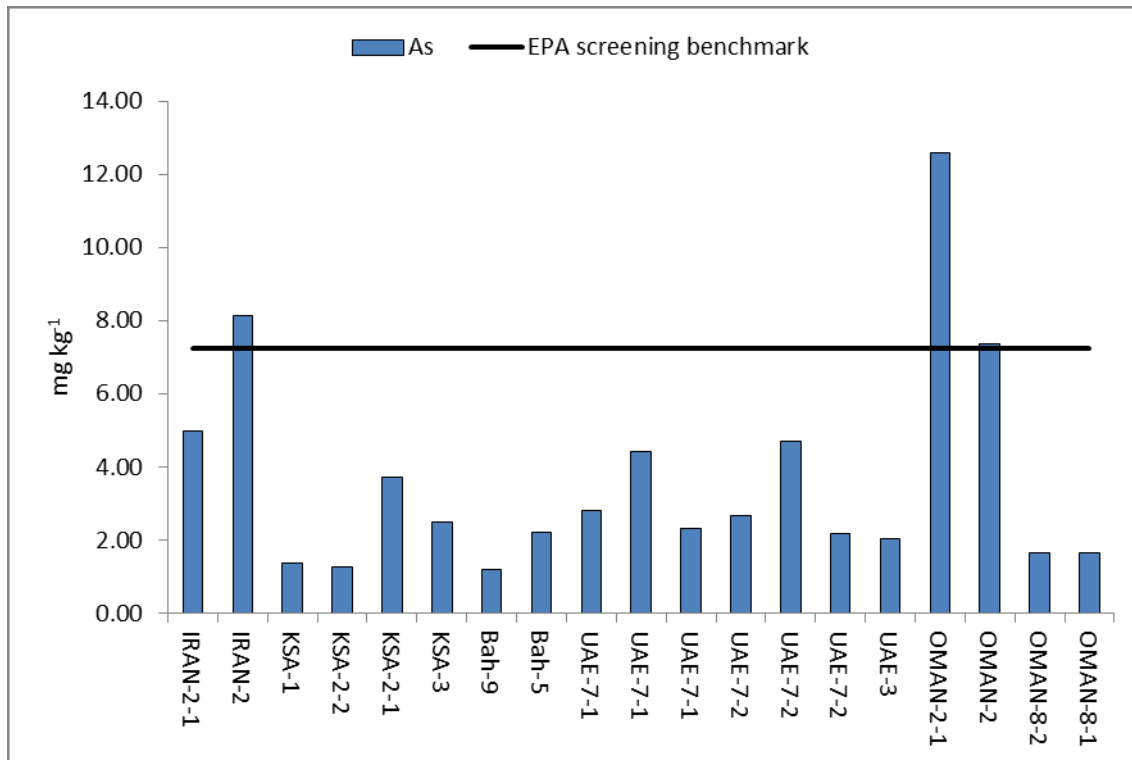


Figure 3. Arsenic concentrations in sediment samples

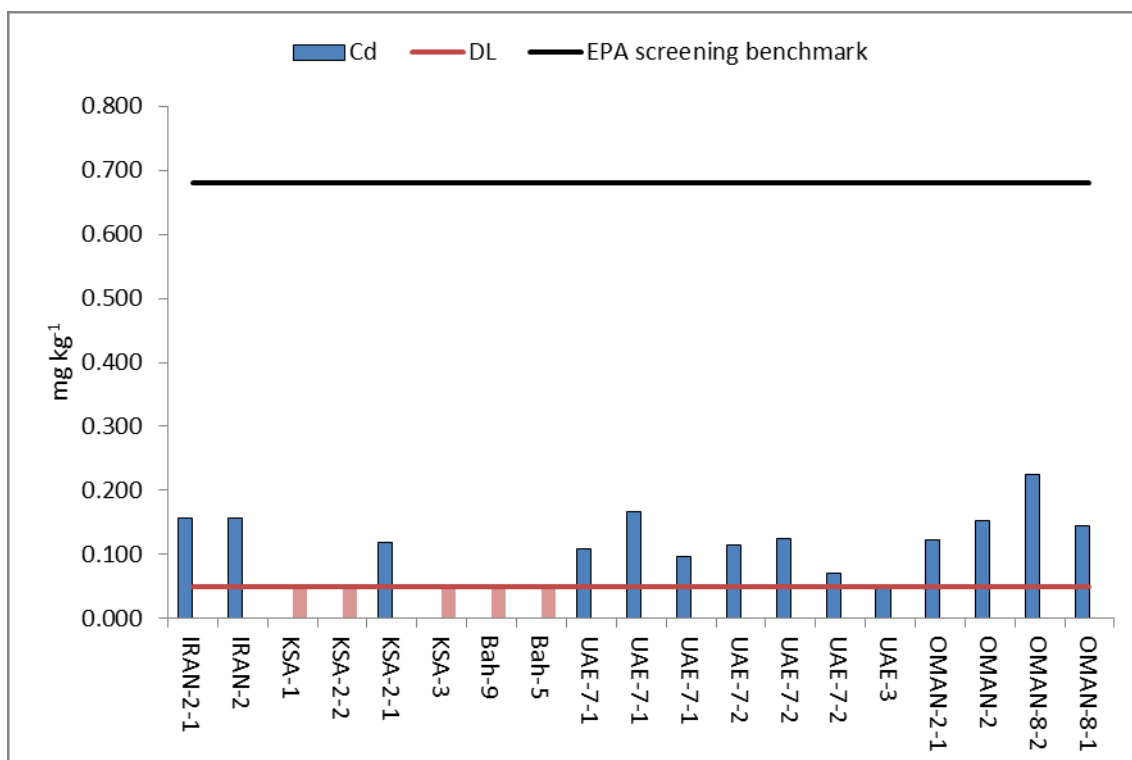


Figure 4. Cadmium concentrations in sediment samples

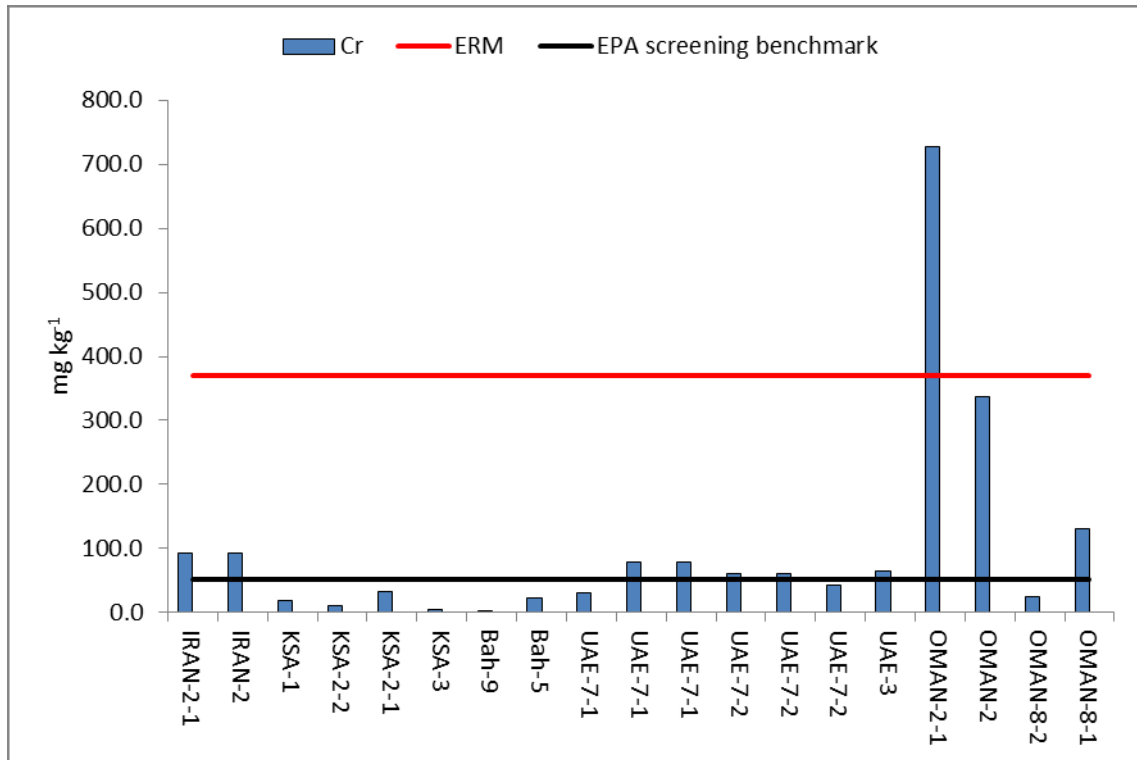


Figure 5. Chromium concentrations in sediment samples

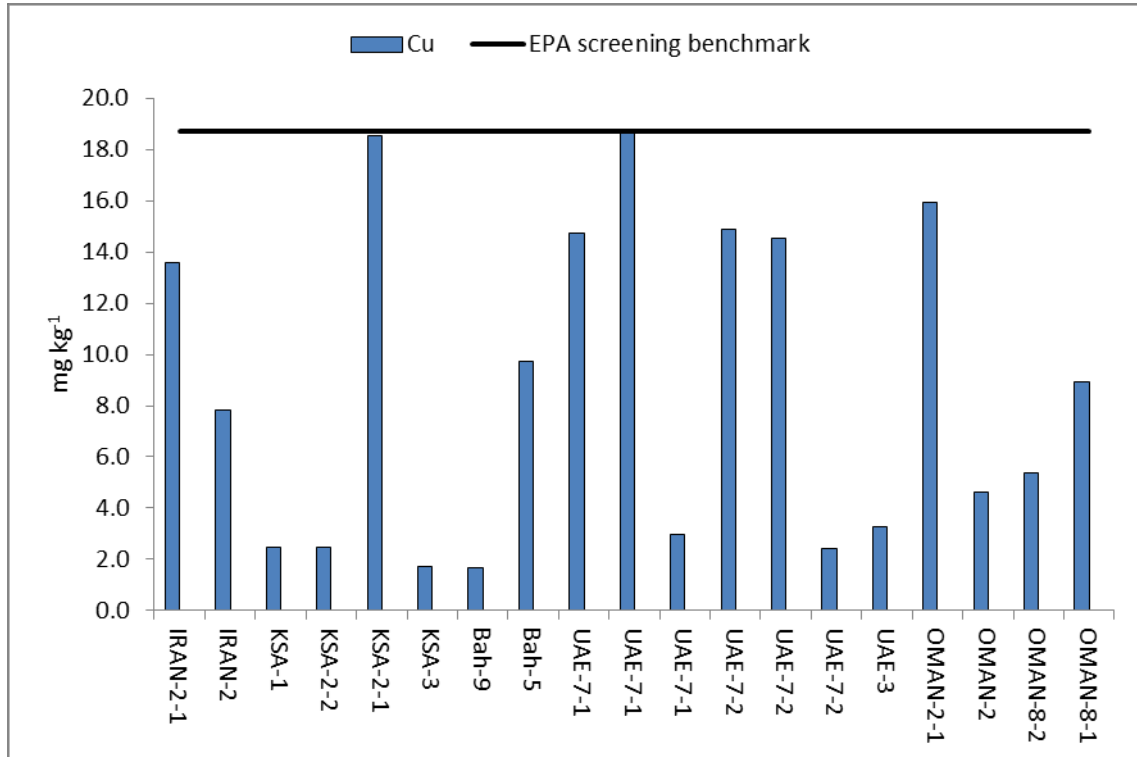


Figure 6. Copper concentrations in sediment samples

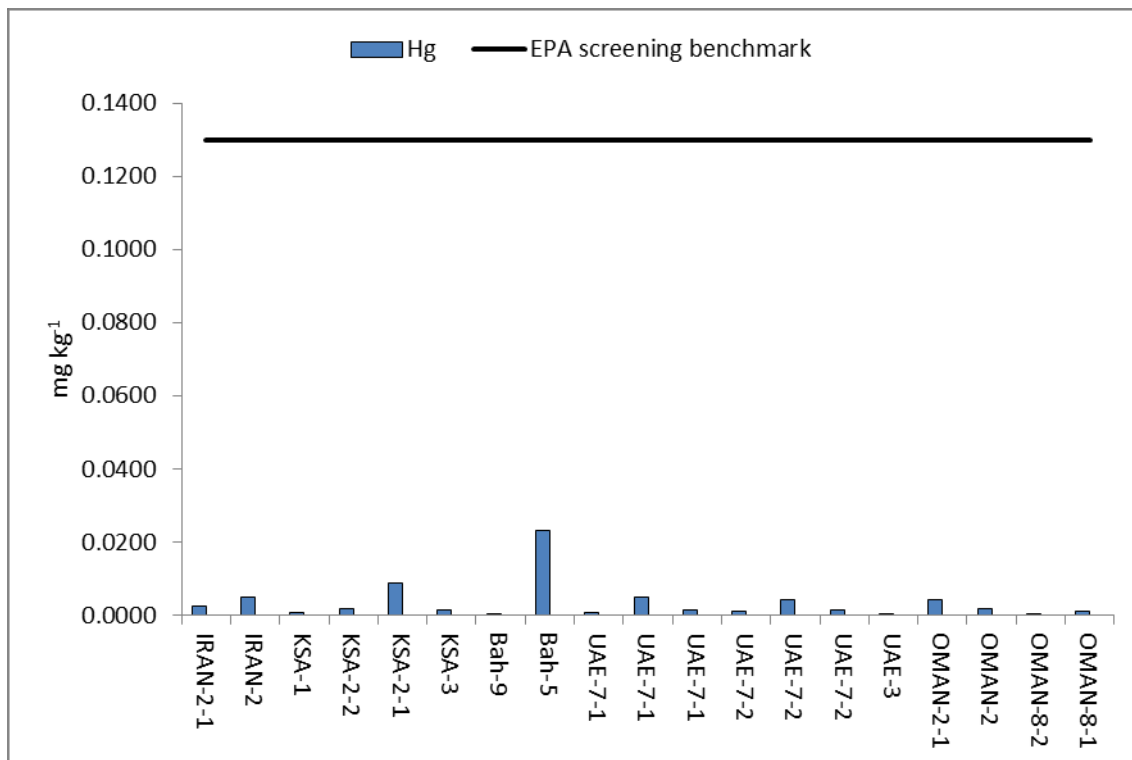


Figure 7. Mercury concentrations in sediment samples

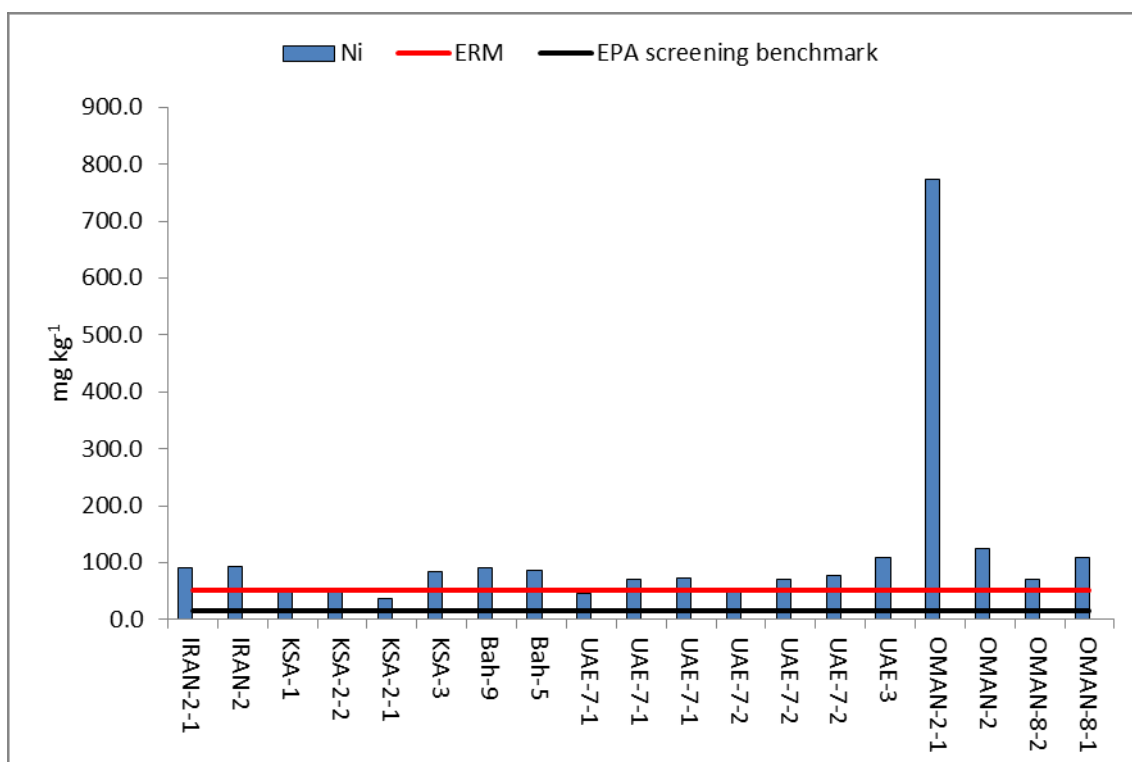


Figure 8. Nickel concentrations in sediment sample

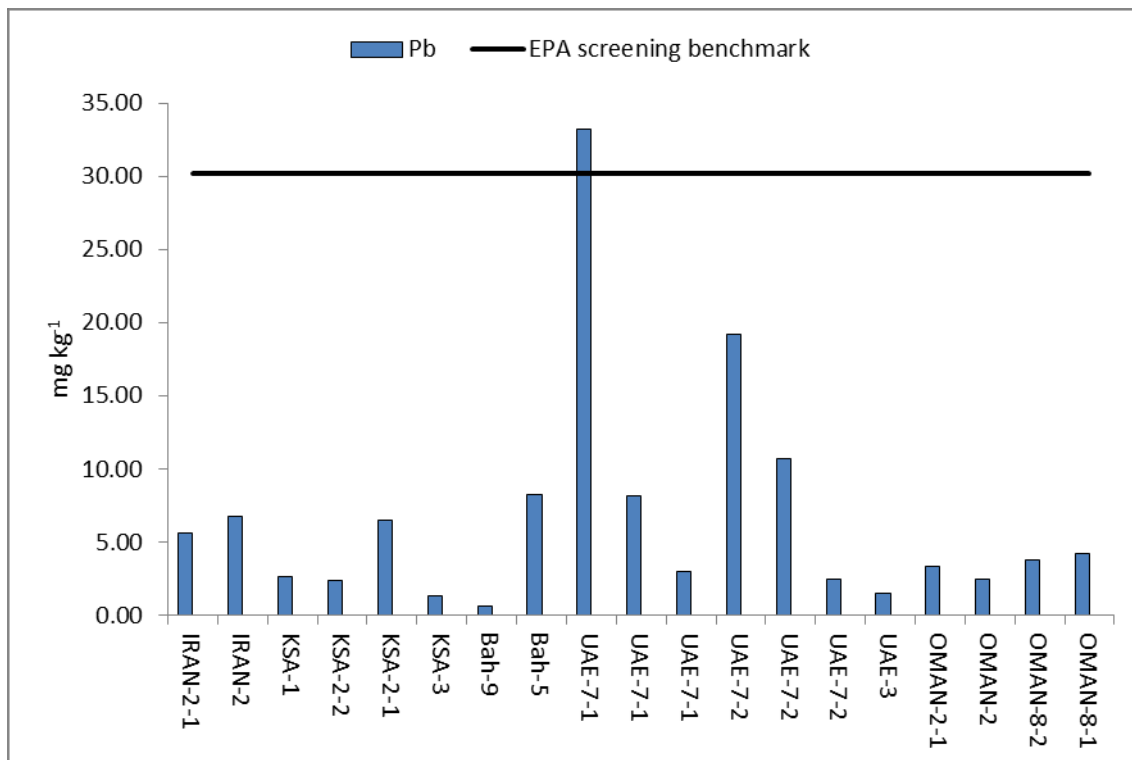


Figure 9. Lead concentrations in sediment samples

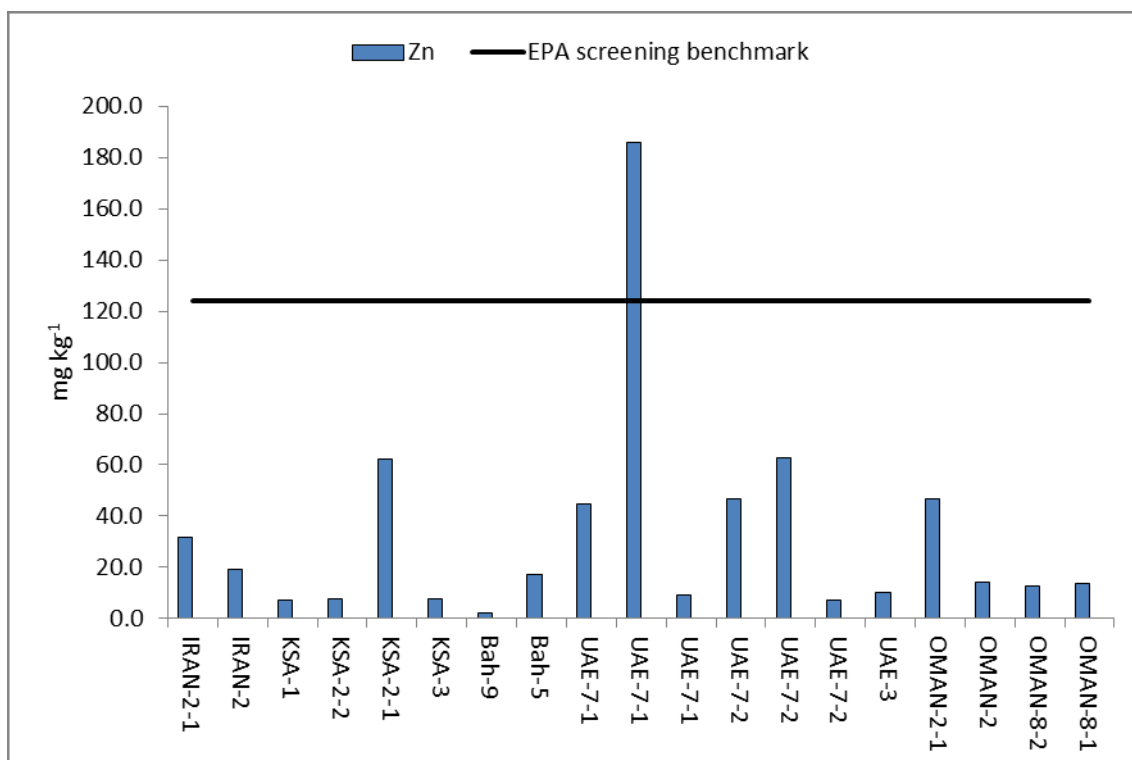


Figure 10. Zinc concentrations in sediment samples

The levels for monitored trace elements in sediments, were not exceptionally important and fell within the range reported previously (Basaham *et al.*, 1993; de Mora *et al.*, 2004).

The collected batch contained an important part of silica based (sand) and/or coarse material in addition to the finer sedimentary fraction. As silica generally does not contain any other trace elements, its presence in fact dilutes the sediment and generally the trace elements' concentrations are lower in comparison when only sedimentary fraction is analyzed.

To account for this factor the common practice is to normalize the trace element concentrations to a reference element considered as characteristic one for terrestrial material. The elements commonly used for this purpose are Al, Fe or Li. The chosen element should be found at high and relatively reproducible concentration in the sediment, and behaves conservatively in the marine environment.

As shown in the Table 5, most of the analyzed samples have more than 90% of sand, which is in good correlation with low Al and Fe results observed in the present study. Nevertheless, no clear correlation was found with any of the major elements and for this reason no further normalization was performed.

Table 5. Sediment Quality Guideline

CAS#	Analyte	Screening value (mg/kg)*	ERL ^{b,c}	ERM ^{b,d}
7440-38-2	Arsenic	7.24	8.2	70
7440-43-9	Cadmium	0.68	1.2	9.6
7440-47-3	Chromium	52.3	81	370
7440-50-8	Copper	18.7	34	270
7439-92-1	Lead	30.2	46.7	218
7439-97-6	Mercury	0.13	0.15	0.71
7440-02-0	Nickel	15.9	20.9	51.6
7440-22-4	Silver	0.73	1.0	3.7
7440-66-6	Zinc	124	150	410

Note: ^aEPA Marine Sediment Screening Benchmarks

www.epa.gov/reg3hwmd/risk/eco/btag/sbv/marsed/screenbench.htm (Macdonald *et al.*, 1996);

^b(Long *et al.*, 1995);

^cERL= Effect Range Low where effect are rarely observed (<10% of adverse effect reported if sediment <ERL);

^dERM= Effect Range Medium (<50% of adverse effect reported if sediment are <ERM).

The levels observed in the sediment samples were compared with values used by the Kuwait Environment Protection Agency of USA (KEPA) to evaluate sediment toxicity (Table 6). The screening benchmark value and the ERL value are concentrations were

effects are rarely observed and can be used to indicate sediments which do not represent a risk for the marine organisms, while ERM values are concentrations at which toxic effects are likely to occur. The EPA screening benchmarks and the ERM values (were needed) are also plotted for comparison in the Figures 3, 4, 5, 6, 7, 8, 9 and 10.

The observed levels of trace elements in sediment samples in this study are analyzed below on a country by country basis.

4.1.1 I.R. Iran

Two sediments were collected in Bushehr (IRAN-2) and Dayer (IRAN-2-1). Measured concentrations of most trace elements were bellow EPA screening benchmarks, except for Ni, Cr and As.

The concentrations of nickel in both samples were above the EPA's ERM. High levels of Ni were already reported in the same region (IAEA, 2008; Agah *et al.*, 2012). The levels observed along the Iranian coast are similar to the levels observed in the Sea of Oman. Nickel has a high natural background in this region and as stated before additional reason for this high level in the sediments could result from the natural mineralization of ophiolite rocks (De Mora *et al.*, 2004). The obtained Ni values in this study were also consistent with levels reported earlier (IAEA 1998, IAEA 2006, IAEA 2008).

Chromium concentrations measured in the two samples from I.R. Iran coast were also exceeding the EPA screening benchmark, but not the ERM value.

EPA screening limits for As was exceeded in sediment from Bushehr, but still bellow ERM. The observed levels for As were consistent with previous study. (IAEA 1998; IAEA 2006; IAEA 2008).

4.1.2 Saudi Arabia

Four sediment samples were collected along the coast of Saudi Arabia; except for Ni all measured concentrations of trace elements were below the screening benchmark of EPA and comparable with previous studies. Nickel values were ranging from 37.7 to 83 mg kg⁻¹ which is higher than levels reported earlier, (2.7 to 22.9 mg kg⁻¹ in 2005) especially for sample collected in Ras Tanura. Some high levels of Ni have been reported for some sample collected during 2002 and 2006 oceanographic cruise in the region of Jubail (49 and 100 mg kg⁻¹ in 2002 and 2006 respectively). Additional study is needed to conclude if the higher observed levels of Ni in the present study represent an increasing pollution trend or if they are artifacts linked to sample contamination during sampling.

4.1.3 Bahrain

The sediment samples were collected from two locations. Only Ni levels were above the screening limit, which was surprising when compared with previously published data (de Mora *et al.*, 2004; IAEA, 2005; and IAEA 2011).

The relatively high Pb concentrations observed previously in Askar (BAH-5), close to the BAPCO site (de Mora *et al.*, 2004 and IAEA, 2005), were not observed during this campaign. The difference from 70.9 mg kg⁻¹ in 2005 against 8.24 mg kg⁻¹ in this study validates once again the results observed in the 2011 campaign.

4.1.4 UAE

In total 7 samples were collected on the west side of U.A.E coast. Six of them were collected in the place of Umm Al-Quwain (UAE-7) which is also used as a sampling site in the frame of the inter-calibration exercise between Pearl and Rock oysters. Obtained results showed relatively high variation of the measured concentrations for all elements which can only partially be explained by difference in sediment composition (i.e. Al or Li content).

Some of the reported Pb values of the 2014 campaign (33 mg kg⁻¹ in UAE-7-1 station 1; 19.2 mg kg⁻¹ in UAE-7-2 Station 1) are significantly higher than the results reported for the same area in previous campaign. Chromium and Nickel levels were above the EPA screening benchmark for almost all samples and above ERM for Ni in 5 samples. High Cr and Ni concentrations have been reported earlier in Dubai (UAE-3) but not at Umm Al Quwain.

4.1.5 Oman

Six sediment were collected along the coast of Oman, two of them (OMAN-8, Mirbat and OMAN2-2, Khasab) could not be measured for the reasons already discussed before, since 100% of this samples were very coarse (grain size >1mm). These samples consisted of big stones and could not be considered for any trace element analysis.

Nickel concentrations measured in all stations exceed ERM values. Levels of Cr exceed EPA screening benchmark in all samples except in one sample from Qalhat. Two samples (Mina Al Fahal and Sohar) showed high level of arsenic (above screening benchmark value). The highest concentrations of Ni, Cr and As in this sampling campaign were found in Khasab (OMAN-2-1). The obtained results were comparable with results found in the previous campaign (IAEA, 2005). De Mora *et al.* (2004) reported some elevated Ni concentration in the Oman and eastern UAE coast probably related to the presence of ophiolite rich in nickel sulphide.

Table 6. Trace metal results in biota samples

Stations	Bivalve sp.	Ag mg kg ⁻¹	Al mg kg ⁻¹	As mg kg ⁻¹	Ba mg kg ⁻¹	Cd mg kg ⁻¹	Co mg kg ⁻¹	Cr mg kg ⁻¹	Cu mg kg ⁻¹	Fe mg kg ⁻¹	Hg mg kg ⁻¹	Li mg kg ⁻¹
Bah-5	Pearl Oyster	0.053	136	17.3	0.635	1.43	0.15	1.52	5.4	184	0.057	<0.4
Bah-9	Pearl Oyster	0.115	65	43.8	0.695	6.04	0.168	0.602	4.69	145	0.053	<0.4
IRAN-2	Rock Oyster	3.38	207	39.7	4.21	4.33	0.668	2.88	754	212	0.157	<0.4
IRAN-2-1	Rock Oyster	7.19	212	31.5	0.835	4.71	0.567	3.06	239	338	0.084	<0.4
IRAN-2-2	Rock Oyster	3.83	174	22.9	0.889	7.84	0.478	4.43	161	247	0.047	<0.4
Chiru	Rock Oyster	3.65	89	22.9	1.01	11.0	0.42	2.03	251	158	0.051	<0.4
IRAN-4	Rock Oyster	4.94	129	17.1	0.486	8.09	0.508	4.27	389	229	0.059	<0.4
IRAN-4-1	Rock Oyster	1.9	150	14.7	1.23	15.3	0.605	2.87	84.5	264	0.025	<0.4
IRAQ New Site	Pearl Oyster	0.457	319	35.2	24.2	21.9	0.963	1.71	11	405	0.144	<0.4
OMAN-8	Rock Oyster	2.7	26	26.1	<0.2	9.35	0.208	0.644	107	78	0.082	<0.4
OMAN-8-1	Rock Oyster	4.91	35.6	20	<0.2	8.59	0.233	0.717	391	88.7	0.056	<0.4
OMAN-8-2	Rock Oyster	2.65	43.5	19.3	0.369	18.8	0.367	0.944	156	141	0.046	<0.4
OMAN-2	Rock Oyster	3.2	25.9	15	<0.2	6.21	0.282	0.739	325	76.2	0.417	<0.4
OMAN-2-1	Rock Oyster	0.188	200	19.7	1.08	7.27	0.879	1.88	904	498	0.081	<0.4
OMAN-2-2	Rock Oyster	1.26	<10	20	<0.2	6.16	0.218	0.658	111	38.4	0.049	<0.4
KSA-3	Pearl Oyster	0.052	<10	37.8	0.335	4.57	0.109	0.472	4.89	81.4	0.045	<0.4
KSA-2-1	Pearl Oyster	<0.05	59.6	68.2	0.642	4.07	0.166	0.622	10.2	228	0.056	<0.4
KSA-2-2	Pearl Oyster	0.097	117	48	2.99	8.69	0.155	0.669	5.33	211	0.058	<0.4
KSA-1	Pearl Oyster	0.085	56.8	29.7	1.89	9.24	<0.1	0.521	4.31	124	0.049	<0.4
UAE-7-1 St.1	Rock oyster	5.87	36.9	34.7	0.682	2.85	0.243	0.877	289	125	0.071	<0.4
UAE-7-1 St.2	Rock oyster	8.34	38.8	28.7	1.57	3.15	0.259	1.33	304	186	0.079	<0.4
UAE-7-1 St.3	Rock oyster	4.58	31.4	31.3	0.422	2.59	0.195	0.55	225	120	0.069	<0.4
UAE-7-2 St. 1	Pearl Oyster	0.095	83.4	27.7	1.36	7.62	0.284	1.1	12.1	372	0.03	<0.4
UAE-7-2 St.2	Pearl Oyster	0.093	75.9	33.1	1.58	5.67	0.553	1.02	9.14	304	0.027	<0.4
UAE-7-2 St.3	Pearl Oyster	0.068	71.5	26.8	2.73	4.61	0.735	1.08	7.86	305	0.03	<0.4
UAE-3	Rock Oyster	0.169	61.9	17.5	0.369	4.91	1.3	1.96	276	188	0.046	<0.4

Table 6. Trace metal results in biota samples (Contd...)

Stations	Bivalve sp.	MeHg mg kg ⁻¹	Mn mg kg ⁻¹	Ni mg kg ⁻¹	Pb mg kg ⁻¹	Se mg kg ⁻¹	Sn mg kg ⁻¹	Sr mg kg ⁻¹	U mg kg ⁻¹	V mg kg ⁻¹	Zn mg kg ⁻¹
Bah-5	Pearl Oyster	0.009	7.13	0.618	1.35	3.52	<0.1	50.2	0.172	1.75	1519
Bah-9	Pearl Oyster	0.013	11	0.727	0.156	4.52	<0.1	56.8	0.191	3.19	2133
IRAN-2	Rock Oyster	0.052	4.81	4.36	0.986	2.44	<0.1	453	0.213	1.1	2961
IRAN-2-1	Rock Oyster	0.011	8.68	3.26	0.284	3.65	<0.1	132	0.209	1.37	2346
IRAN-2-2	Rock oyster	0.009	8.62	3.67	0.314	2.45	<0.1	238	0.156	0.865	824
Chiru	Rock Oyster	0.009	5.69	2.05	0.353	2.5	<0.1	121	0.192	0.951	859
IRAN-4	Rock Oyster	0.012	11.1	3.42	0.326	3.7	<0.1	179	0.155	0.849	861
IRAN-4-1	Rock oyster	0.002	6.92	3.73	0.554	2.41	<0.1	571	0.301	0.979	268
IRAQ New Site	Pearl oyster	0.023	24.5	3.38	0.185	4.83	<0.1	69.4	0.141	2.22	265
OMAN-8	Rock Oyster	0.026	3.77	0.976	0.146	2.85	<0.1	46.6	0.366	0.886	2267
OMAN-8-1	Rock Oyster	0.014	11.7	0.914	0.165	3.26	<0.1	56.6	0.174	1.09	4104
OMAN-8-2	Rock Oyster	0.018	16.2	1.12	0.077	3.25	<0.1	27	0.18	1.14	588
OMAN-2	Rock Oyster	0.373	10.3	0.933	0.109	2.76	<0.1	30.5	0.15	0.985	1450
OMAN-2-1	Rock Oyster	0.02	21.7	10.4	0.221	3.94	<0.1	26.8	0.212	1.74	2544
OMAN-2-2	Rock oyster	0.019	2.38	0.69	0.053	2.74	<0.1	23.4	0.08	0.7	967
KSA-3	Pearl Oyster	0.009	11.8	0.505	0.21	4.43	<0.1	121	0.153	1.16	2803
KSA-2-1	Pearl Oyster	0.019	22.7	0.549	0.461	4.08	<0.1	41.8	0.109	1.56	1937
KSA-2-2	Pearl Oyster	0.024	9.56	0.822	0.246	3.68	<0.1	81.5	0.15	2.8	1032
KSA-1	Pearl Oyster	0.026	10.4	0.59	0.243	3.77	<0.1	56.2	0.09	1.07	1035
UAE-7-1 St.1	Rock Oyster	0.012	4.36	4.27	0.18	3.43	<0.1	30.8	0.196	1.09	3411
UAE-7-1 St.2	Rock Oyster	0.01	4.93	1.05	0.321	3.67	<0.1	59.4	0.238	1.24	4239
UAE-7-1 St.3	Rock Oyster	0.013	3.83	0.484	0.132	3.11	<0.1	35.3	0.149	1.08	3384
UAE-7-2 St. 1	Pearl Oyster	0.01	35.2	2.59	0.506	4.28	<0.1	65.3	0.212	2.06	1736
UAE-7-2 St.2	Pearl Oyster	0.01	49.5	4.43	0.649	4.31	<0.1	57.6	0.184	1.8	1254
UAE-7-2 St.3	Pearl Oyster	0.011	13.4	5.5	0.862	4.29	<0.1	56.7	0.269	1.75	873
UAE-3	Rock Oyster	0.005	4.57	3.38	0.23	3.11	<0.1	89.9	0.211	0.922	5205

4.2 BIOTA

The results for trace metal in biota are shown in the Table 6.

In Figures 11 to 19 are presented the concentrations of trace elements in the sediment samples collected during the ROPME Mussel Watch 2014 campaign. In most cases, the interpretation of data must be treated with caution since only a small number of biota samples was analyzed, and trace elements' concentrations exhibit natural variation from sample to sample in function of age, season of sampling and sex.

In total, 26 biota samples were analyzed, all were Rock or Pearl oysters. It should be noted that different species will naturally have different concentration levels of trace elements. Levels already observed in the region are reported in the Tables 7 and 8. All obtained results are in accordance with the concentrations found in previous studies. As already reported the level of arsenic in bivalve from the ROPME region is high and of particular concern (de Mora *et al.*, 2004).

The levels of trace elements in the sediment samples are analyzed below on a country by country basis.

Table 7. Selected element concentration in pearl oysters from RSA

Analyte	Reported range (2000) ^a	Reported range (2005) ^b	Reported range (2011) ^c	Reported range (2014) ^d
As	21.0-45.7	14.4-68	18.6-48.8	17.3-68.2
Cd	2.7-10.0	1.56-7.95	1.3-7.3	1.43-21.9
Cr	0.29-2.4	0.33-4.83	0.27-2.2	0.472-1.71
Cu	3.13-17.3	2.48-5.33	3.7-5.64 (1068)	4.31-12.1
Hg	0.009-0.112	0.009-0.085	0.026-0.052	0.03-0.144
Ni	0.54-7.02	0.58-6.28	0.44-2.4	0.505-5.5
Pb	0.15-3.92	0.275-23	0.128-1.8	0.156-1.35
Zn	159-4290	654-2280	1310-3810	1265-2803

Note: ^a de Mora *et al.* (2004);
^b IAEA, 2005;
^c IAEA 2013;
^d This study
 () potential "artifact"

Table 8. Selected element concentration in rock oysters from RSA

Analyte	Reported range (2000) ^a	Reported range (2005) ^b	Reported range (2011) ^c	Reported range (2014) ^d
As	11.1-17.2	8.98-27.2	13.8-25.0	14.7-39.7
Cd	6.15-21.9	3.32-26.4	2.43-34.1	2.59-18.8
Cr	0.49-3.76	0.297-1.61	0.46-2.6	0.55-4.43
Cu	60.9-276	11-688	22.7-528	84.5-904
Hg	0.028-0.153	0.025-0.245	0.024-0.168	0.025-0.417
Ni	0.796-3.14	0.392-14.7	1.29-3.96	0.484-10.4
Pb	0.250-0.673	0.068-0.552	0.06-0.5	0.053-0.986
Zn	391-1614	308-2980	439-3650	268-5205

Note: ^a de Mora *et al.* (2004);
^b IAEA, 2005;
^c IAEA 2013.
^d This study

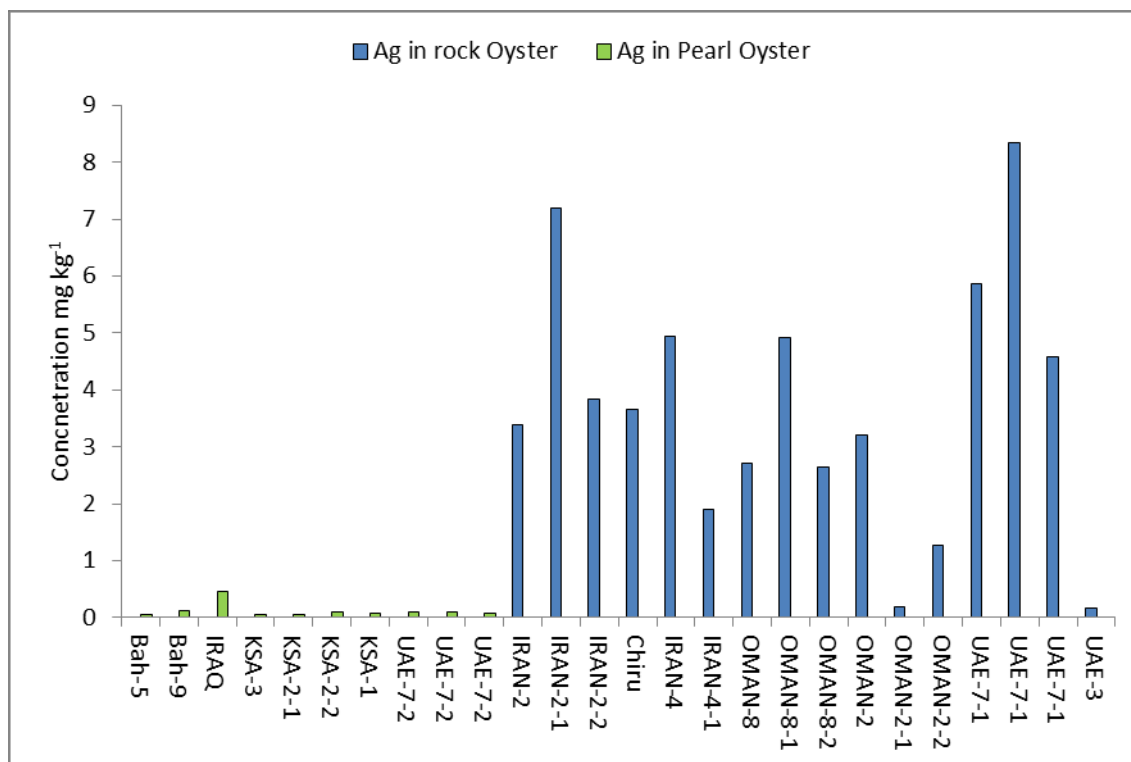


Figure 11. Silver concentrations in oyster samples

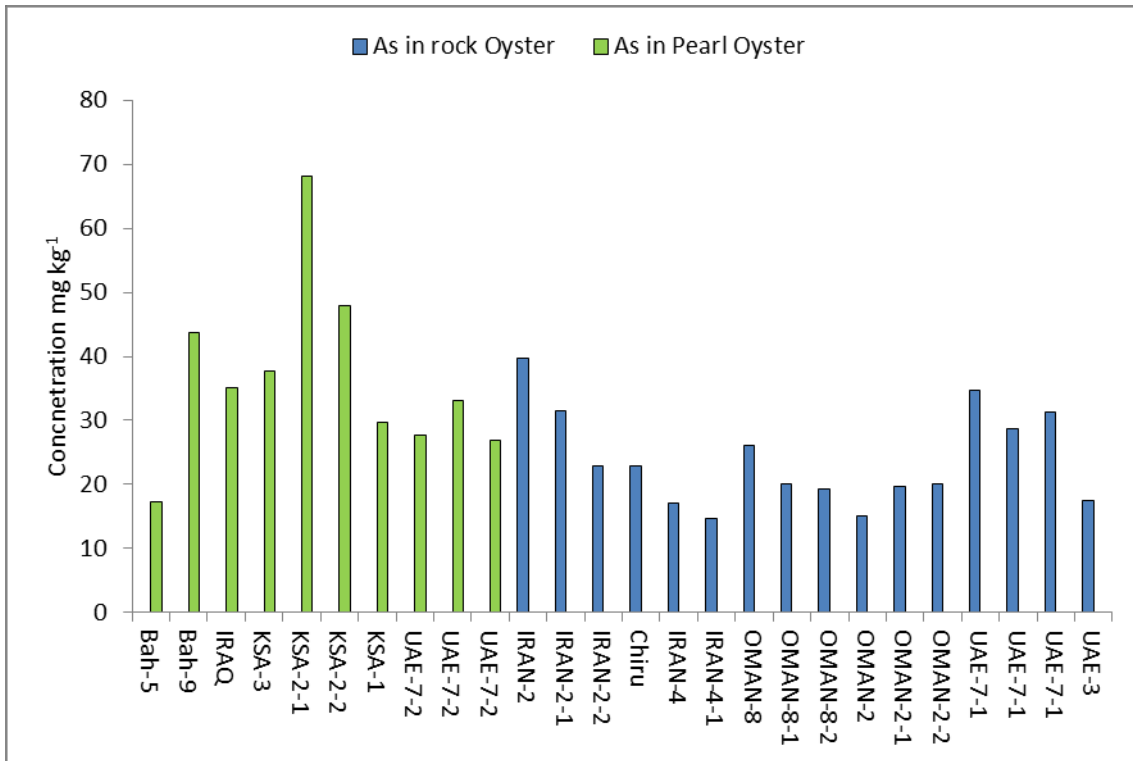


Figure 12. Arsenic concentrations in oyster samples

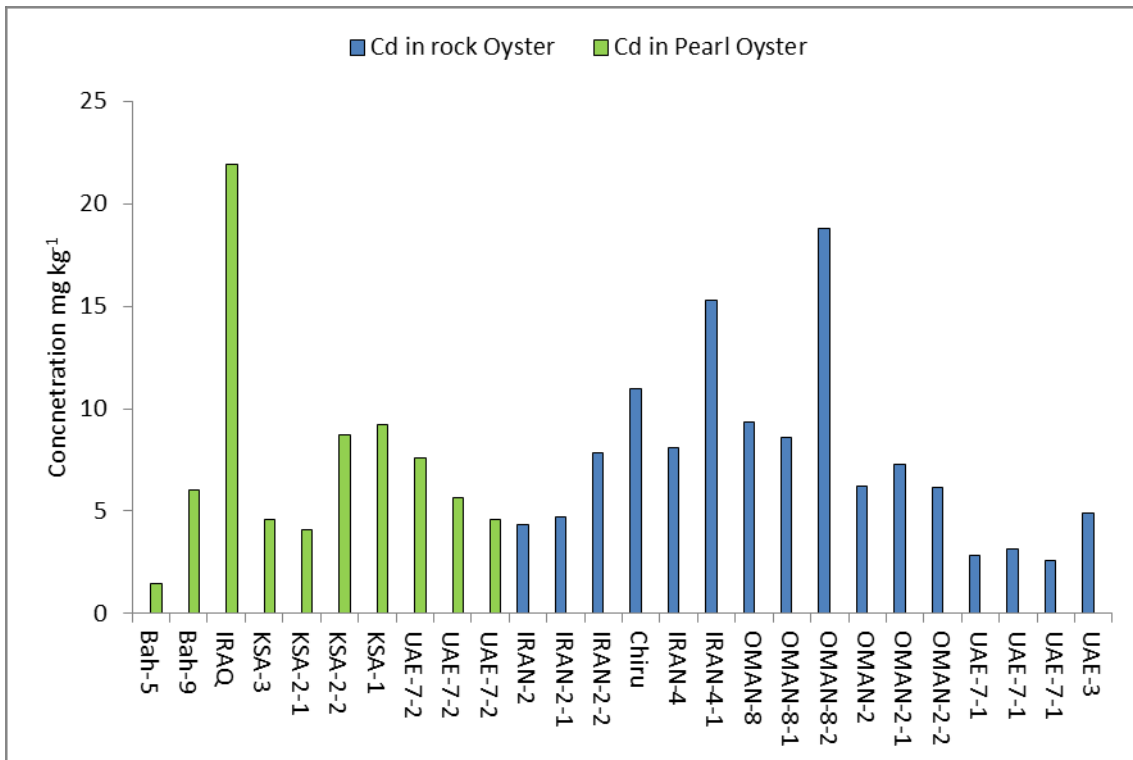


Figure 13. Cadmium concentrations in oyster samples

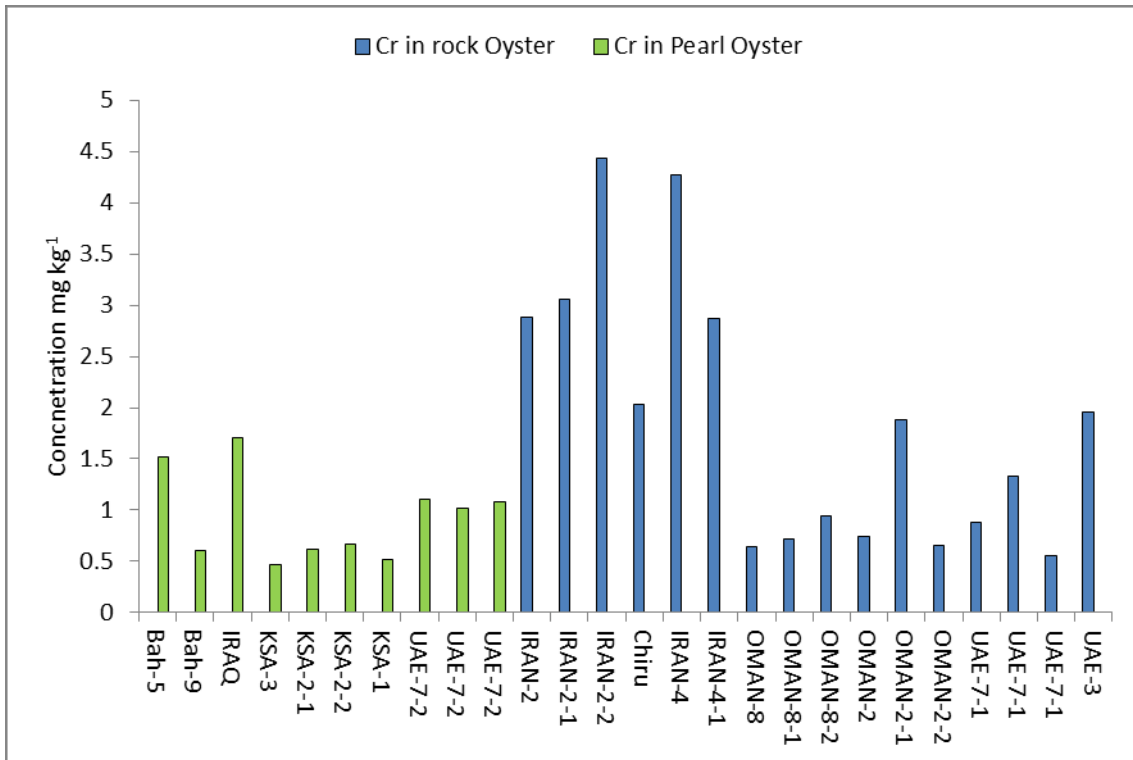


Figure 14. Chromium concentrations in oyster samples

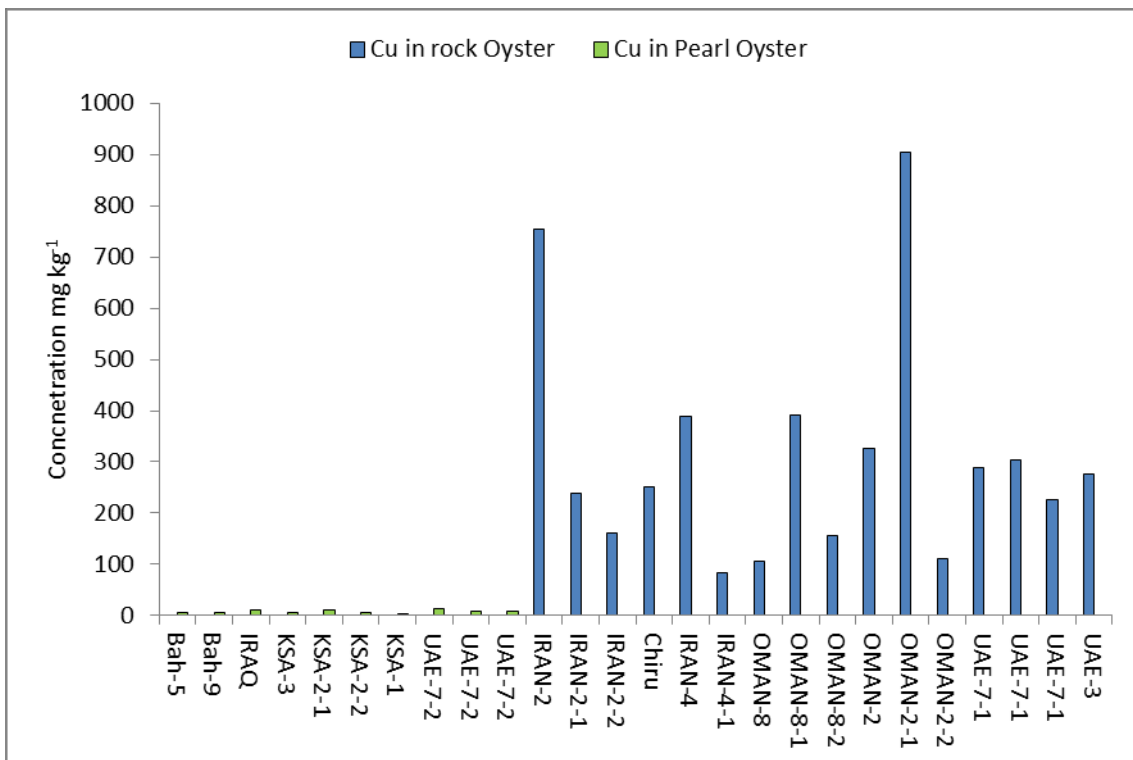


Figure 15. Copper concentrations in oyster samples

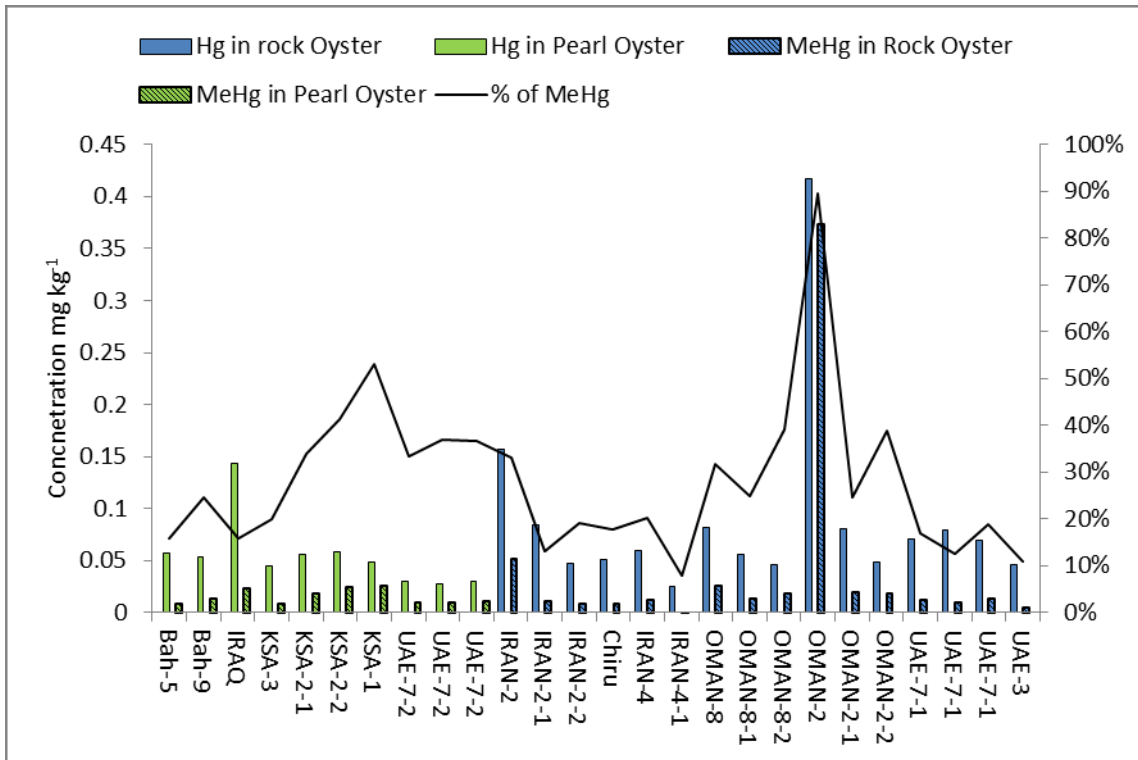


Figure 16. Mercury and methyl mercury concentrations in oyster samples

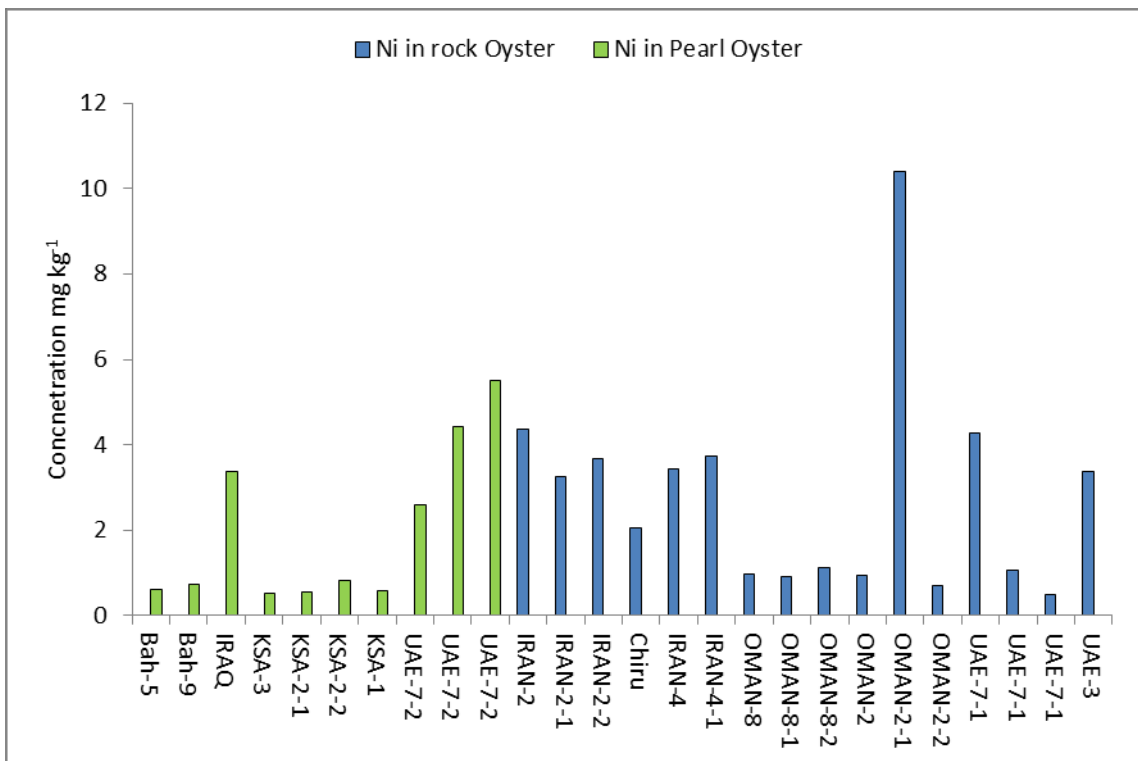


Figure 17. Nickel concentrations in oyster samples

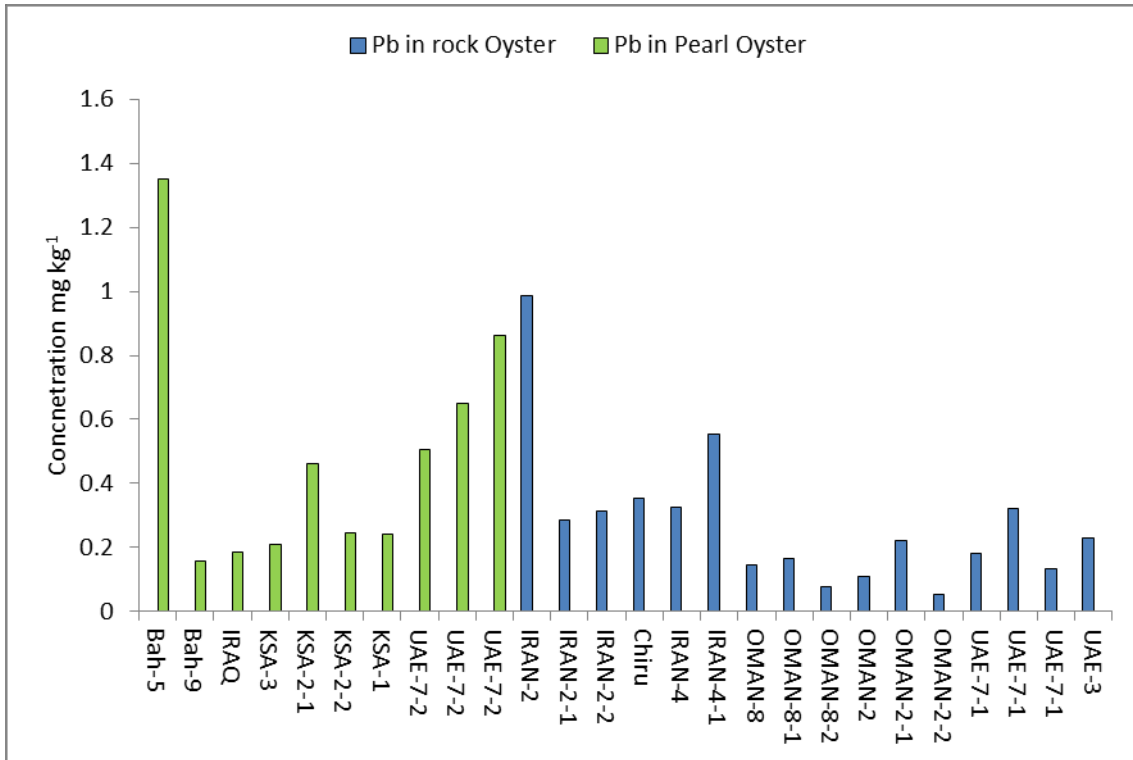


Figure 18. Lead concentrations in oyster samples

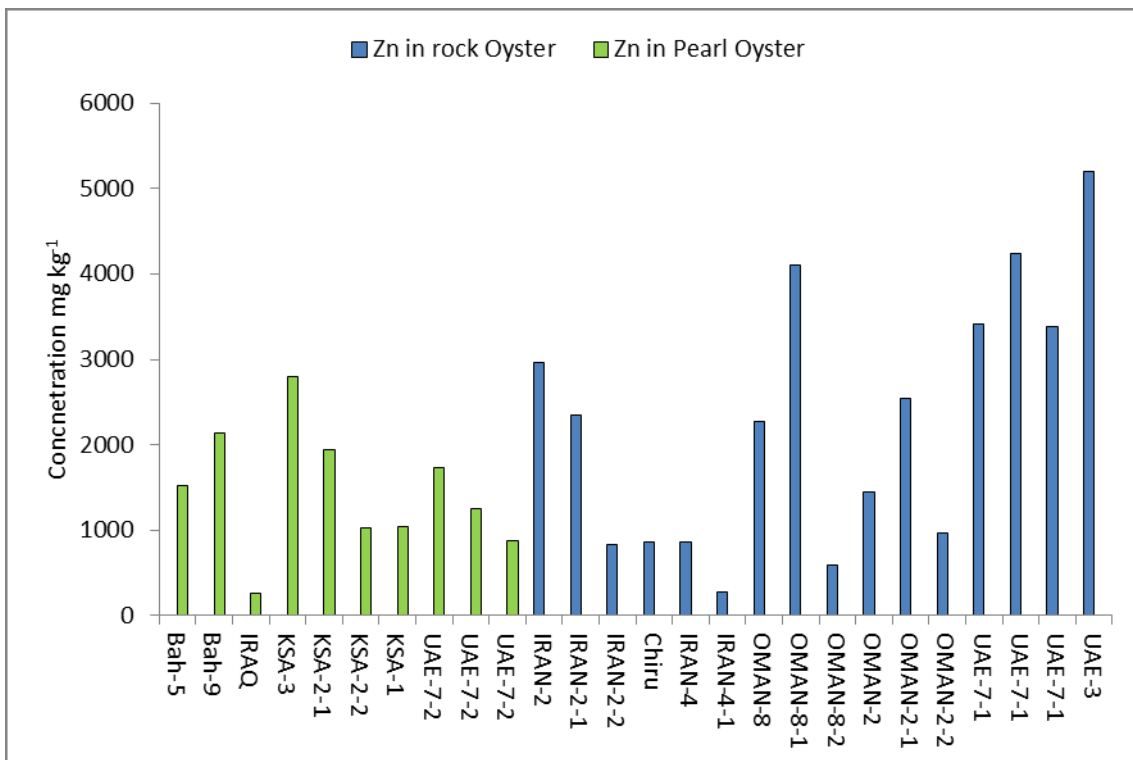


Figure 19. Zinc concentrations in oyster samples

4.2.1 I.R. Iran

Six rock oyster samples were collected along the coast of I.R. Iran. For most of the measured elements, the values observed were comparable with rock oysters collected in other stations of the RSA during the 2014 campaign. It can be noted that level of Cd in Qeshm Island (IRAN-4-1) was relatively high (twice the median), as it was also observed in the 2011 campaign (IAEA, 2013). Chromium concentrations in all sites in I.R. Iran were slightly higher compared to other sites (ranging from 2.03 to 4.43 mg g⁻¹ while the median is 1.60 mg kg⁻¹), which is in line with the results obtained in 2011. As in the 2011 campaign, the highest observed Cr concentration in Rock oyster was measured in Gavbandi (IRAN-2-2); named Parsian in 2011.

4.2.2 Saudi Arabia

Four pearl oysters were collected along the cost of Saudi Arabia. All values observed were comparable with the levels of other pearl oyster in the RSA. The highest As concentration found in pearl oyster during 2014 campaign was measured in Fanateer (KSA-2-1).

4.2.3 Iraq

Only one pearl oyster sample was collected from about 10 km offshore site in front of Shat Al Arab in Iraq. This sample exhibits the highest levels among the pearl oysters for Ag, Cd and Hg, while methyl mercury represents only 16% of the total mercury in the organism. In previous campaign no samples were collected from Iraq, and no GPS data are available in order to further compare those values with the concentration levels obtained from the sites in vicinity.

4.2.4 Bahrain

Two pearl oysters samples were collected along the coast of Bahrain. Concentrations levels in sample BAH-9, collected at Marwada were in good agreement with levels found in the same species collected in the RSA region during this sampling campaign.

As already observed in 2011, Askar (BAH-5) showed relatively high level of Pb and Cr. Measured levels are 2 to 4 times higher than concentrations calculated as a median for Cr and Pb respectively. The sample also exhibited the highest lead concentration observed during the 2014 campaign for the pearl oysters.

4.2.5 UAE

Four rock oysters and 3 pearl oysters samples have been collected. Triplicates samples from each species have been collected at Umm Al-Quwain for comparative study between species, which is discussed in a separate ROPME-IAEA Report.

With the exception of Ni; levels observed in the 7 oysters collected from 2 sites in UAE were generally in good agreement with levels observed in 2005 (IAEA, 2005) and earlier (de Mora, 2004; Fowler, 1993). The concentrations of Ni in the pearl oysters collected at Umm Al-Quwain were high in comparison with the levels observed in RSA for the same species.

4.2.6 Oman

Six rock oysters were collected along the coast of Oman during the 2014 campaign. Most of the measured elements were comparable with the previous results obtained for the region. The Cd concentration found in Qalhat (OMAN-8-2: 18.8 mg kg⁻¹) was about twice as high than in any other Oman's site, and was the highest Cd concentration found among rock oyster in the present study. Some high Cd concentrations were already reported for the same species along the coast of Oman, but sampled at different sites, e.g. Rasia (OMAN-9) during the 2005 campaign (26.4 mg kg⁻¹) and Masirah (OMAN-8-1: 34.2 mg kg⁻¹) in 2011.

It can also be noted that the highest concentration of Hg in oysters was found in the sample from Mina Al-Fahal (OMAN-2) site. This finding is similar to results obtained in 2011 campaign and the levels are still comparable with other previous mercury concentrations obtained for the region (de Mora *et al.*, 2004; IAEA, 2005). The percentage of methyl mercury in this sample was above 90%, which is somehow surprising for a bivalve species. During this campaign part of methyl mercury was between 8 to 50% for both types of oysters. Similar high methyl mercury percentage have already been found in Pearl oyster in Abu Dhabi port (IAEA, 1994), and could originate from local contamination.

5. CONCLUSION

The levels for the most of the trace elements observed in oysters are generally in agreement with levels reported in the previous study (de Mora *et al.*, 2004; Fowler *et al.*, 1993; IAEA, 2005; IAEA 2013) for the same species. Some relatively high levels were observed for As, Cd and Pb in some stations. The sample collected in Iraq shows significantly higher

levels for several elements but it is not clear if these results reflect a local pollution process, because this was the first time that samples were collected from this station. The continuation of sampling in the region will allow investigating if the enhanced trace element concentrations are consistent and if they are related to local pollution sources.

Overall the levels observed in sediments of the coastal zone of RSA collected during the ROPME Mussel Watch 2014 campaign are comparable with data obtained during previous studies (de Mora *et al.*, 2004; Fowler *et al.*, 1993; IAEA, 2005; IAEA 2013). It should be noted that the levels of Ni in the entire RSA region appear to be slightly increased in relation to the past. Continuation of monitoring is required to conclude if this is a real increasing trend or if it related to artifacts during the 2014 sampling campaign.

6. RECOMMENDATION

Despite the fact that most of the results observed in this study are in good agreement with the results from previous monitoring campaigns, additional investigations can be planned for the sites where higher concentrations of trace elements have been found. In order to obtain better evaluation of the level of contamination, an extensive and comprehensive sampling campaign could be envisaged, including the existing sampling stations for comparison purposes. In the present study, only few stations were common with previous sampling campaigns, which didn't allow the establishment of temporal contamination trends in many cases. Additional data on contaminants' concentrations will also allow the use appropriate statistical tools to better understand pollution processes in the region. It has to be underlined, that biological samples should be collected following rigorous standard operating procedures in order to obtain representatives and comparable samples with respect to species, size, gender, and spawning season. Also, sampling of sediments should be conducted in areas with relatively fine material, because sediment samples consisting entirely (or mainly) of coarse sand and shell fragments cannot be used for trace element analysis.

In addition, sampling (of biota and sediment) should be carried out by competent and trained staff and sampling protocols should be followed consistently and rigorously for the different steps involved: such as collection of samples, pre-treatment (dissection of organisms, freeze drying, etc.), transport and storage.

In the present study two results were considered as "potential artifact" but it was not possible to check this hypothesis because no duplicate samples were available. It is strongly recommended that samples are regularly collected in duplicates.

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