ROPME/GC-16/3

ROPME MUSSEL WATCH PROGRAMME 2014

Technical Report: No.4

RADIONUCLIDES SCREENING

Prepared by:

MESL/IAEA
Monaco, December 2015

For:

REGIONAL ORGANIZATION FOR THE PROTECTION OF THE MARINE ENVIRONMENT

ROPME/GC-16/3

REGIONAL ORGANIZATION FOR THE PROTECTION OF THE MARINE ENVIRONMENT

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FOREWORD

The Radiometrics Laboratory (RML) is one section of the International Atomic Energy Agency's Environment Laboratories (NAEL) in Monaco. Besides RML, NAEL has two other sections in Monaco: the Marine Environment Studies Laboratory (MESL) and the Radioecology Laboratory (REL) and one section in Seibersdorf, Vienna: the Terrestrial Environment Laboratory (TEL). IAEA's NAEL implements the Agency's Environment Programme.

For the last 40 years RML has been providing quality products which include the organization of inter-laboratory comparisons and proficiency tests, production of Reference Materials and Certified Reference Materials, development of radioanalytical methods and training. More than 45 radionuclide Reference Materials have been produced, including a wide range of marine sample matrices and radionuclide concentrations. RML also performs analyses of radionuclides in environmental samples, mostly of marine origin, in the framework of its programmatic activities carried out in collaboration with IAEA Member States laboratories. RML is active in the area of natural and anthropogenic radiotracer applications to marine environmental and oceanographic studies and in particular assists Member States in pollution assessment. RML also covers modelling of dispersion and transfer of radionuclides in the marine environment, dose assessment for marine exposure pathways and development of environmental databases. It runs low-level counting facilities in an underground laboratory in Monaco and provides advice and training for establishing or upgrading environmental analytical facilities.

1. INTRODUCTION

Under the ROPME Mussel Watch Programme, a survey was undertaken in February- July 2014 to screen for radionuclides in key coastal areas in Bahrain, I.R. Iran, Iraq, Oman, Saudi Arabia and the United Arab Emirates (UAE). The scope of the screening project was to provide a baseline assessment on the actual status of radioactivity along the RSA coast and characterize radionuclide distributions in the region. This report summarizes the results of measurements of radionuclides in the sediments and biota in the area using sediment and biota (bivalves) samples collected from the coastal zone of the ROPME Sea Area in 2014, and should be considered as a follow-up to previous ROPME-IAEA monitoring reports on radionuclides in the ROPME Sea Area [1].

The samples were collected by the Regional Organization for the Protection of the Marine Environment (ROPME) and sent through the Marine Environmental Studies Laboratory (MESL) of IAEA/NAEL to the Radiometrics Laboratory (RML), which carried out analyses on the determination of ^{40}K, ^{137}Cs, ^{210}Pb on the samples provided. MESL analyzed total Uranium, on the basis of which ^{235}U and ^{238}U were determined.

2. SAMPLING METHODOLOGY

Sediment and biota samples were collected by ROPME counterpart institutes from selected locations along the coast of Bahrain, I.R. Iran, Iraq, Oman, Saudi Arabia and the United Arab Emirates (UAE) in 2014 in the framework of the ROPME Mussel Watch Programme. Altogether 17 sediment samples and 22 biota samples were collected for radionuclides analyses. Table 1 summarizes the information received on sediment and biota samples collected in 2014 in the coastal areas of the RSA countries. The sampling stations location, names and code numbers are presented in Table 1 and Figures 1 and 2.

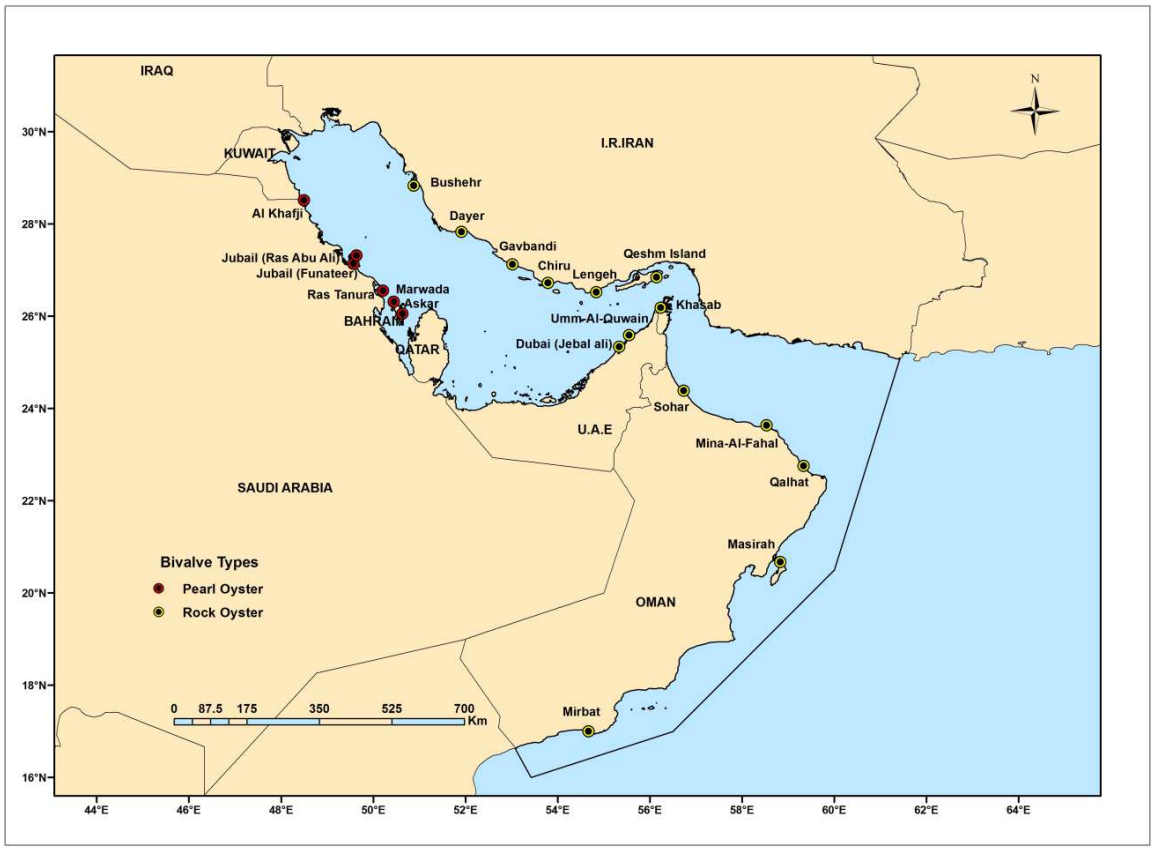

Figure 1. Sampling stations 2014 identified by name

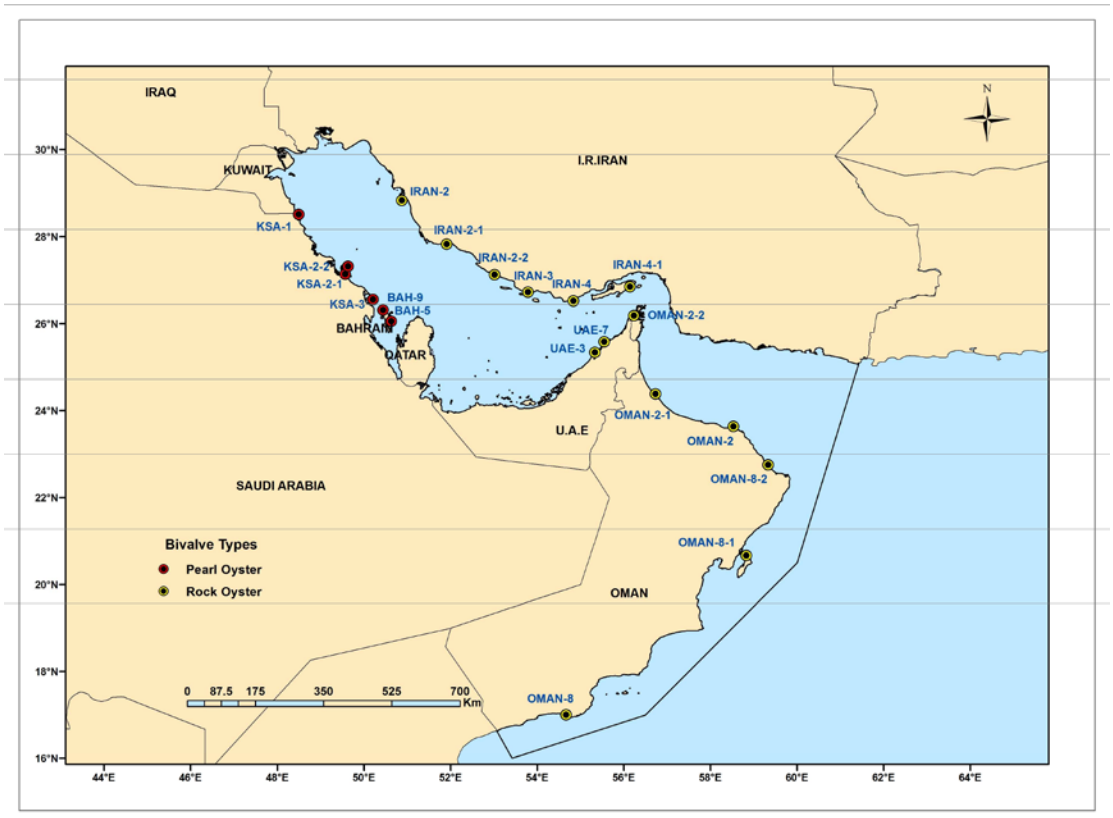

Figure 2. Sampling stations 2014 identified by code

Table 1. Sediment and biota 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	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. SAMPLE PROCESSING

Sediment samples were received dried and not sieved. Given that part of the samples contained shell debris and/or small stones, the decision was taken to sieve all samples through a 1000 µm mesh size sieve so as to improve sample homogeneity (and thus measurement result accuracy). This was possible since the quantity of sample was sufficient. No grinding was carried out as the samples were sandy.

Biota samples were received already freeze-dried. Most of them were grinded and homogenized, however six of the samples had to be further processed (grinded and homogenized) using a blender.

Following homogenization the samples were transferred into polyethylene containers in two calibrated geometries used for gamma spectrometric analyses and weighed.

4. METHODS

Sediment and biota samples were analyzed by high resolution gamma spectrometry in RML low-level underground counting facilities [2]. A Broad Energy Germanium (BEGe) and a well-type detector of 150% relative efficiency were used, having passive and respectively passive plus active cosmic veto shielding. Acquisition and basic spectrum processing was carried out using Gamma Vision ORTEC AMETEK © software [3]. Calibration was done using secondary volume standards traceable to standardized mixed gamma solutions QCYK8163 and QCYB40 and IAEA Certified Reference Materials IAEA-385 and IAEA-437 were used for internal quality control.

The specific activity at the time of sampling, the minimum detectable activity and the combined uncertainty were calculated [4]. The combined uncertainty takes into account the counting statistical uncertainty, the uncertainty in the mass of the sample, the uncertainty of the calibration procedure, the counting uncertainty of the background peak and uncertainties in decay data, where applicable. 1σ uncertainties are reported, expressed as % of the specific activity value. The coverage factor was taken as 1. Based on these values the end-user can easily estimate the uncertainties according to his/her purpose and quality criteria. For values with uncertainties higher than 45%, the limit of detection was reported.

All specific activities were decay-corrected to the date of sampling. On the time-scale of this sampling-analysis exercise, corrections are not significant for ^{40}K and U isotopes. ^{210}Pb is a member of the natural radioactive series of U-Ra and was considered in secular equilibrium with ^{226}Ra. Surface sediment will have a significant fraction of its ^{210}Pb content originating from atmospheric deposition (unsupported fraction), however the estimation of the two

fractions and of the specific activity at the time of sampling should be the object of a separate exercise, involving specific sampling sites and methods.

Counting times ranged between 2 and 9 days. However, for some of the samples the material available was not sufficient to detect ^{137}Cs and the combined uncertainty for various radionuclides was higher than for samples counted for longer times for previous campaigns. However, the detection limits and uncertainties are fit for the scope of screening and baseline study.

An estimate is given of U-238 in sediment based on results of ICP-MS analyses of total Uranium [5] and on the assumption of a natural isotopic composition of Uranium in the sample (99.2739% ^{238}U, 0.7205% ^{235}U, 0.0056% ^{234}U). The expanded uncertainty on U determination is 6% (coverage factor k=1).

5. RESULTS AND DISCUSSION

The results for sediments are presented in Table 2.

The levels of ^{137}Cs in sediments of the area are very low, as expected for the type of sediment analyzed (sandy, mixed with shell debris). No particular patterns can be observed. These results are corroborated by the levels measured in ^{40}K, also characteristic for sand and sandy sediments in the presence of shells debris. No particular observation can be made concerning the specific activities of the reported radionuclides as compared to similar samples elsewhere in the world ocean [6] or in the region [7 and following references up to 15], other than they are generally on the lower end of reported levels. Values also compare generally well with those obtained last year at proximate locations. No other anthropogenic gamma-ray emitting radionuclides besides ^{137}Cs were detected in the sediment samples. The available data do not suggest any specific source for the anthropogenic radionuclides found in the sediment samples analyzed, other than the well-known global sources. The results for ^{137}Cs and ^{238}U in sediments are presented in Figures 3 and 4.

Table 2. Activity concentrations of radionuclides in sediment samples collected in 2014 (Bq•kg^{-1} dry weight)

SAMPLE CODE	K-40		Cs-137		Pb-210		U-238	U-235
	Act Bq/kg	Unc %	Act Bq/kg	Unc %	Act Bq/kg	Unc %	Bq/kg	Bq/kg
BAH-5	67.5	7.1	0.31	25.8	26.0	7.7	38.3	1.77
BAH-9	14.9	12.1	<0.17		6.2	12.9	39.3	1.82
IRAN-2	83.5	6.2	0.26	30.8	17.9	8.4	20.0	0.92
IRAN-2-1	239	5.4	0.27	44.4	44.1	6.3	24.5	1.13
KSA-1	131	5.3	0.39	15.4	13.9	6.5	35.7	1.65
KSA-2-1 Fanateer	266	5.3	0.41	24.4	27.0	7.0	24.4	1.13
KSA-2-2	125	5.6	0.24	20.8	12.9	7.0	34.0	1.57
KSA-3	14.9	10.1	<0.17		12.1	5.8	28.2	1.30
OMAN-2	18.2	12.1	<0.15		14.1	8.5	16.8	0.78
OMAN-2-1	60.4	7.0	<0.16		7.1	12.7	11.7	0.54
OMAN-2-2	24.0	7.9	<0.08		12.6	29.4	-	-
OMAN-8	29.1	9.6	<0.15		18.0	11.7	-	-
OMAN-8-1	44.0	8.0	<0.18		12.0	10.0	27.5	1.27
OMAN-8-2	184	5.4	<0.05		17.8	16.9	20.0	0.92
UAE-3	34.0	6.8	<0.16		8.9	9.0	36.5	1.69
UAE-7-1-3	66.4	5.9	<0.15		9.9	9.1	34.3	1.59
UAE-7-2-3	63.5	5.8	<0.16		8.3	8.4	34.5	1.60

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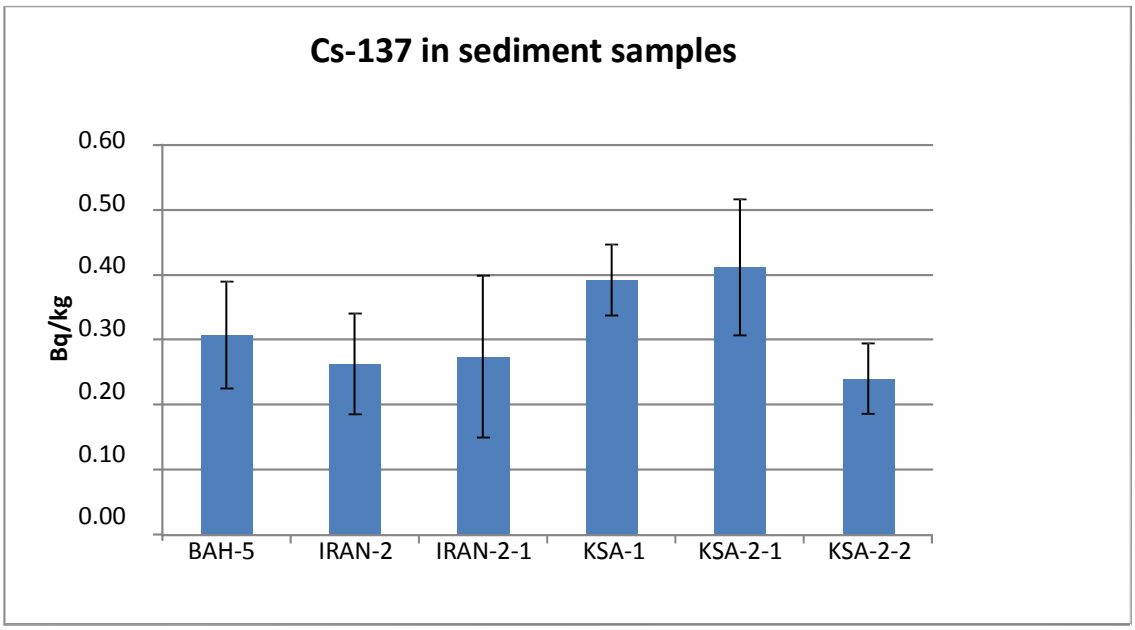

Figure 3. Cs-137 in sediment samples from the ROPME Sea Area

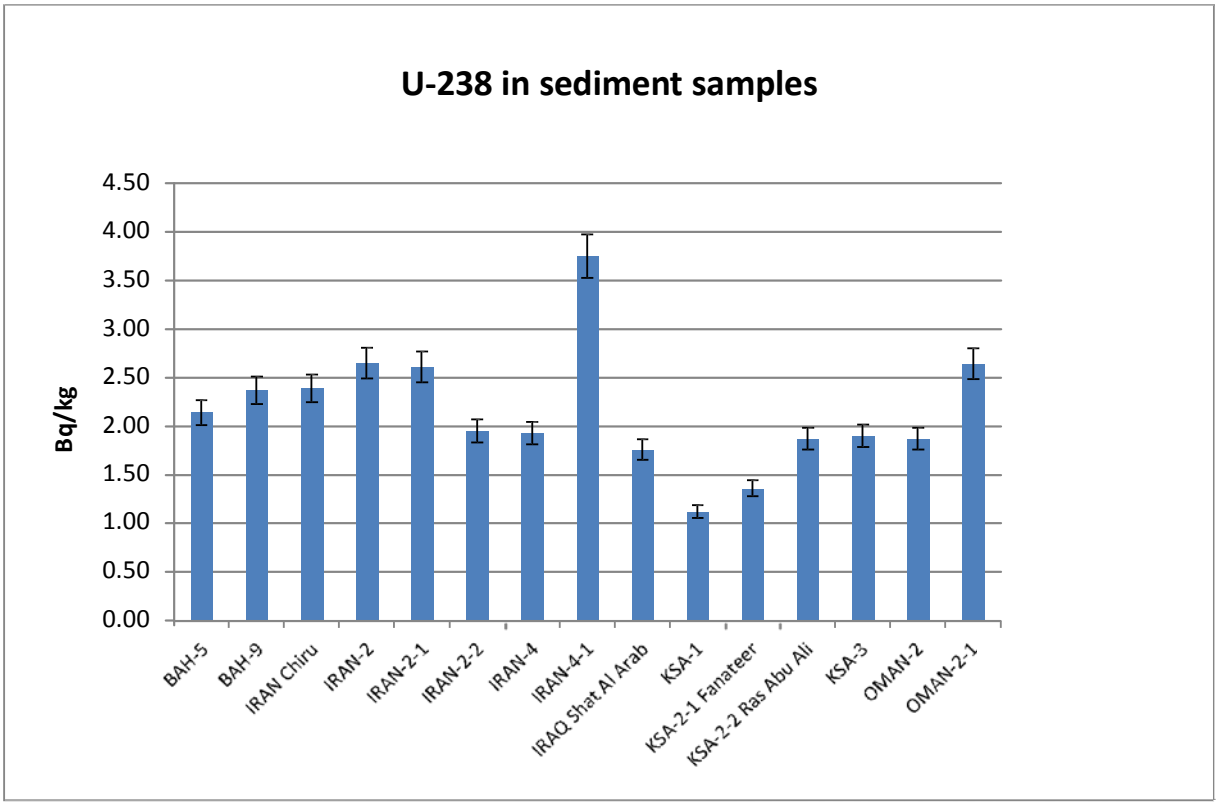

Figure 4. U-238 in sediment samples from the ROPME Sea Area

The results for biota are presented in Table 3.

Table 3. Activity concentrations of radionuclides in biota samples collected in 2014 (Bq•kg^{-1} dry weight)

SAMPLE CODE	K-40		Cs-137	Pb-210		U-238	U-235
	Act Bq/kg	Unc Bq/kg	Act Bq/kg	Act Bq/kg	Unc Bq/kg	Bq/kg	Bq/kg
BAH-5	345	5.5	<0.40	2.7	26	2.14	0.099
BAH-9	306	5.6	<0.47	4.0	15	2.37	0.110
IRAN Chiru	270	5.9	<0.49	2.7	33	2.39	0.11
IRAN-2	247	5.7	<0.53	2.5	24	2.65	0.123
IRAN-2-1	314	6.1	<0.46	<3.4		2.61	0.121
IRAN-2-2	278	5.8	<0.36	<2.6		1.95	0.090
IRAN-4	275	5.8	<0.34	4.1	24	1.93	0.090
IRAN-4-1	253	6.3	<0.60	4.0	30	3.75	0.174
IRAQ Shat Al Arab	394	5.6	<0.14	4.0	38	1.76	0.081
KSA-1	350	6.3	<0.58	3.3	36	1.12	0.052
KSA-2-1 Fanateer	412	6.6	<0.74	8.8	20	1.36	0.063
KSA-2-2 Ras Abu Ali	357	5.6	<0.51	5.1	18	1.87	0.086
KSA-3	356	5.9	<0.49	<3.6		1.90	0.088
OMAN-2	333	6.0	<0.18	3.3	45	1.87	0.086
OMAN-2-1	313	6.1	<0.73	5.6	21	2.64	0.122
OMAN-2-2	321	7.5	<0.97	8.8	27	1.00	0.046
OMAN-8	257	7.4	<0.25	<6.7		4.56	0.211
OMAN-8-1	269	5.6	<0.14	3.3	45	2.17	0.100
OMAN-8-2	326	5.5	<0.12	<3.1		2.24	0.104
UAE-3	232	6.5	<0.51	3.6	31	2.62	0.121
UAE-7-1-3	322	6.2	<0.62	4.1	32	1.86	0.086
UAE-7-2-2	254	15	<0.50	4.1	1	3.35	0.155

The activities of anthropogenic ^{137}Cs in the biota analyzed were undetectable with the amount of sample available even in the ultra-low level underground facility of the IAEA, and no other anthropogenic gamma-ray emitting radionuclides were detected in the samples. This further confirms that there is no significant local or regional source of contamination with gamma emitters. The activities of the natural radionuclides (^{40}K) were similar to those in other areas of the world ocean The ^{210}Pb activities were presented in Table 3 only for information purpose, because sample amounts, were insufficient for reliable analysis, in some cases values being under the minimum detectable activity. In this case it was not possible to prepare a calibration standard with the samples available, and therefore calculated self-attenuation corrections could not be experimentally validated. Nevertheless, Table 3 hints to relative variation of natural ^{210}Pb in bivalves, indicating either biological factors or local enhancements of natural radionuclides due either to natural or to technological processes (e.g. oil and gas, chemical or fertilizer industry). This should be further explored by analysis of Po-210 in marine biota, given that it represents the most significant radiological dose deliverer through the seafood ingestion pathway and is affected by a high natural variability. Note that for biota it is ^{210}Po and not ^{210}Pb that is of most interest. The results for and ^{238}U in biota are presented in Figure 5.

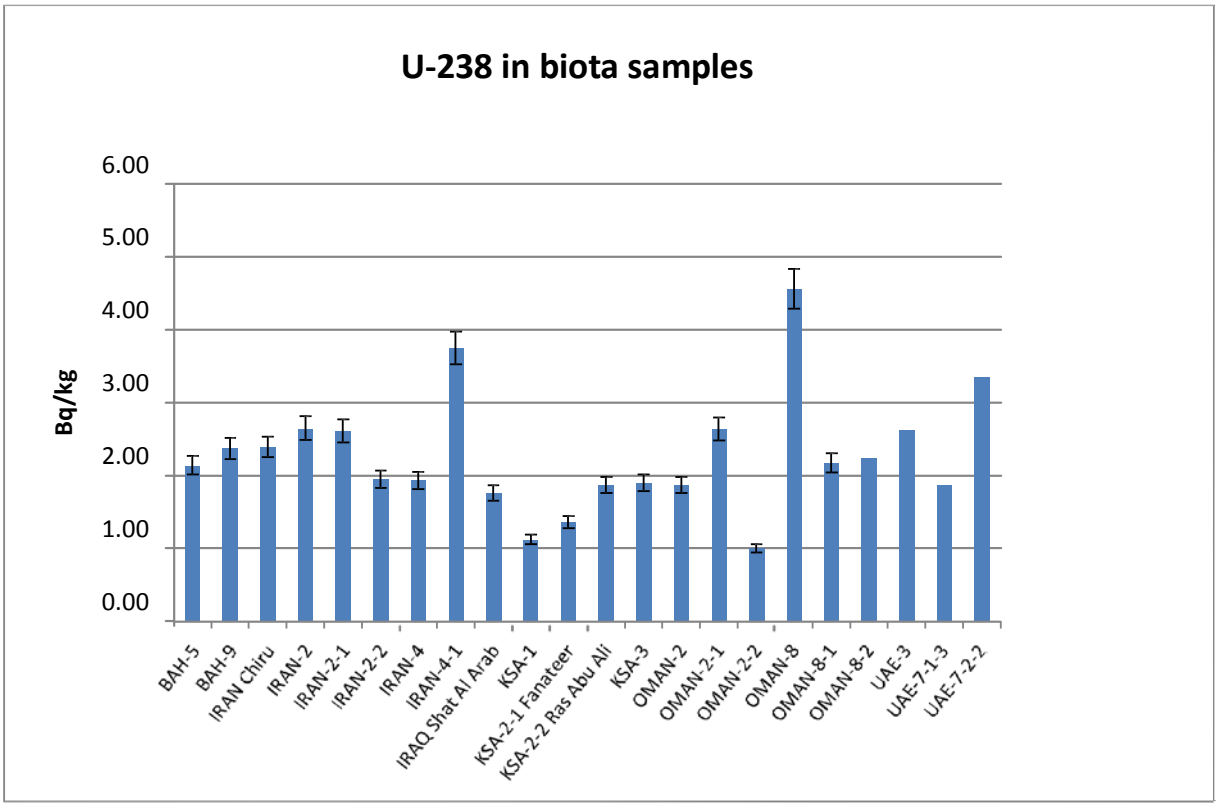

Figure 5. U-238 in biota samples from the ROPME Sea Area

6. CONCLUSIONS

The baseline assessment based on sediment and biota samples from the locations along the coast of the ROPME Sea Area did not reveal any increase of the radioactivity levels. The activities of anthropogenic radionuclides in sediment and biota were very low and those of natural radionuclides were similar to other areas of the world ocean. However, the number of samples analyzed was too small to be able to accurately represent the different regions of the RSA. A more thorough survey on the distribution of radioactivity in the RSA is required to collect more representative information for a comprehensive assessment.

7. RECOMMENDATIONS

Although the present results do not raise radiological concerns on radioactivity levels in the region, it is necessary to implement a more comprehensive assessment of the radioactivity in the ROPME Sea Area, collecting representative samples from more locations, including off-shore sediments (surface and cores samples), in an adequate number to allow for a robust statistical analysis of the results. Wherever it is possible, depending on the type of sediment, it is recommended to use a corer (e.g. Gemini corer, box corer, multi corer) in soft fine grain sediments, in order to study the historical deposition of sediments and contaminants over longer periods. This would allow also the radiometric dating of sediment layers. In addition, sampling (of biota and sediment) should be carried out by trained staff; sampling protocols should be followed consistently and rigorously for all the different steps involved including samples dissection, preparation, transportation and storage. Also, because radioactivity levels are generally low, larger quantities of samples have to be collected to allow for accurate results.

In order to have a more representative assessment of the level of radioactivity in the region, additional radionuclides have to be included in the analysis, such as NORMs (Pb-210/Po-210 in sediments, Ra-226 in seawater) and anthropogenic radionuclides (Cs-137, Plutonium isotopes (Pu), Am-241 in seawater, sediment and biota, Sr-90 in seawater and biota and Tritium in seawater). Strengthening Data Quality Assurance in the analysis of radionuclides in marine samples in the ROPME Sea Area should also be considered, in view of improving building regional capacity in the analysis of radionuclides in marine samples.

8. ACKNOWLEDGEMENTS

This was a collaborative project between the IAEA and ROPME, financially supported by both organizations. The Agency is grateful for the support provided to its Environment Laboratories by the Government of the Principality of Monaco. The IAEA Environment Laboratories in Monaco operates under an agreement between the IAEA and the Government of the Principality of Monaco.

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