ROPME/GC-15/3
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ROPME MUSSEL WATCH PROGRAMME 2011

Technical Report: No.4

RADIONUCLIDES SCREENING

Prepared by:

MESL/IAEA
Monaco, December 2013

For:

REGIONAL ORGANIZATION FOR THE PROTECTION OF THE MARINE ENVIRONMENT

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1. INTRODUCTION

Under the ROPME-IAEA Contaminant Screening Project, a survey was undertaken during February-March 2011 to screen for radionuclides activities at key coastal areas in Bahrain, Iran, Kuwait, Oman, Qatar, 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 in the ROPME Sea Area and identify potential abnormal distributions in the Region. This report summarizes the results of measurement of radionuclides in the offshore sediment samples collected during ROPME Oceanographic Cruise – Winter 2006, and in sediment and biota samples collected from nearshore areas during early 2011, within the framework of the Regional Mussel Watch Programme.

The samples were collected by the Regional Organisation for the Protection of the Marine Environment (ROPME) and sent through the Marine Environment 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, ^{235}U and ^{238}U on the samples provided

2. SAMPLING METHODOLOGY

Offshore sediment samples were collected during the ROPME Oceanographic Cruise – Winter 2006 and sediment and biota by the counterpart institutes from selected locations along the nearshore area of Bahrain, Iran, Kuwait, Oman, Qatar, Saudi Arabia and the United Arab Emirates (UAE) during 2011 in the framework of the ROPME Mussel Watch Programme. Surface sediment samples were collected by a grab sampler and were mostly sandy, containing shell debris, biota samples were collected from nearshore locations and consisted of Pearl Oyster (at Bahrain, Qatar and UAE stations), Rock Oyster (at Iran, Oman and UAE stations) and Asiatic Clam (at KSA stations). Altogether 29 sediment samples and 10 biota samples were collected for radionuclides analysis. Table 1 summarises the information on the sediment samples collected during ROPME Oceanographic Cruise – Winter 2006, while Table 2 summarises information on sediment and biota samples collected in 2011 in the nearshore areas of the ROPME Sea Area.

Further on in this report, samples will be identified by the codes written in bold in Tables 1 and 2 and Figures 1 and 2.

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Table 1: Identification of sediment samples collected during ROPME Oceanographic Cruise – Winter 2006

Station	Sampling Date	Depth (m)	Longitude	Latitude
ST1	9/3/2006	13	48° 29.000′	029° 21.000′
ST25	3/3/2006	67	50° 58.400′	027° 18.290′
ST51	22/2/2006	60	53° 05.650′	025° 48.625′
ST58	21/2/2006	75	53° 52.585′	025° 53.289′
ST07	8/3/2006	13	49° 52.049′	029° 52.106′
ST05a	6/3/2006	21.3	49° 05.508′	028° 08.501′
ST09a	6/3/2006	47.7	50° 24.200′	028° 51.200′
ST10a	2/3/2006	26	50° 23.700′	026° 59.800′
ST33	1/3/2006	14	50° 45.500′	026° 21.800′
ST27	1/3/2006	54	51° 57.000′	027° 29.200′
ST34	28/2/2006	14	51° 31.200′	026° 02.500′
ST49	22/2/2006	42	52° 54.000′	025° 26.090′
ST66	15/2/2006	42	54° 37.156′	025° 31.090′
ST70	14/2/2006	44	54° 57.957′	026° 32.104′
ST16a	9/2/2006	30	56° 39.300′	027° 01.400′
ST93	5/2/2006	67	56° 50.739′	024° 33.147′
ST98	3/2/2006	50	58° 36.914′	025° 26.801′
ST26a	2/2/2006	53	58° 46.100′	023° 31.000′

Table 2: Identification of nearshore sediment and biota samples collected during 2011

Member State	Sampling Date	Site		Coordinates		Biota Samples
		Code	Name	N	E	
Bahrain	Feb 2011	BAH-5	Askar #	26° 03′ 105	50° 37′ 805	Pearl oyster
I. R. Iran	Feb 2011	IRAN-4	Lenge Port #	26° 31′ 360	54° 49′ 742	Rock oyster
		IRAN-2	Bushehr # (Rostami port)	28° 50′ 063	50° 52′ 507	Rock oyster
Kuwait	Mar 2011	KUW-5 (Sediment only)	Doha#			---
Oman	Mar 2011	Oman-8	Mirbat #	17° 00′	54° 40′	Rock oyster
		Oman-2	Mina Al-Fahal #	23° 37′	58° 33′	Rock oyster
Qatar	Mar 2011	Doha-4-2	RasLaffan #	25° 53′	51° 36′	Pearl oyster
KSA	Mar 2011	KSA-3	Ras Tanura	26° 41′ 092	50° 04′ 083	Asiatic clam
		KSA-2	Ras Mishab #	28° 11′ 269	48° 37′ 846	Asiatic clam
UAE	Feb 2011	UAE-7-1-2	Dubai	25° 16′ 915	55° 17′ 520	Pearl oyster
		UAE-7-1-1	Dubai	25° 17′ 37”	55° 16′ 37”	Rock oyster

ROPME Contaminant Screening Reference Station

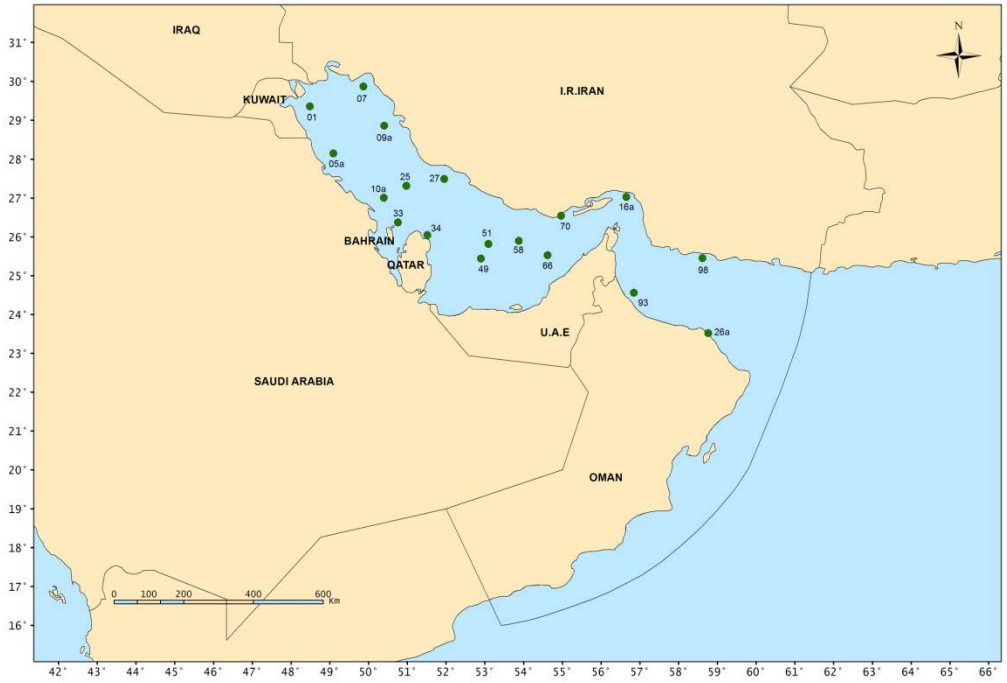


Figure 1: Offshore Sediment Sampling Stations during ROPME Oceanographic Cruise – Winter 2006

Figure 2: Mussel Watch Sampling Stations in RSA during 2011

3. SAMPLE PROCESSING

Sediment were received dried as bulk samples. Although the samples contained shell debris, the decision was taken not to sieve them, as the quantity of sample remaining after this would have been too small for the planned analyses. The first 4 samples in TABLE 1 were received readily ground. The rest was ground by RML using mortar and pestle. The samples were transferred into polyethylene containers in two calibrated geometries used for gamma spectrometric analyses and weighed.

Biota samples were received already freeze-dried and ground, so no additional pre-treatment was applied.

4. METHODS

Sediment and biota samples were analysed by high resolution gamma spectrometry in RML counting facilities underground and in the above-ground gamma counting laboratories in Monaco [1]. Well-type detectors of 50%, 150% and 200% efficiencies 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 and GESPECOR [2] was used for calculating corrections where required. 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 [3]. The combined uncertainty takes into account the counting statistical uncertainty, the uncertainty in the mass of the sample, the uncertainty of the calibration procedure and the counting uncertainty of the background peak, 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 the purpose and quality criteria. For values with uncertainties higher than 30%, the limit of detection was reported.

Given that no exact sampling dates were received for the February-March 2011 sampling campaign, all samples were decay-corrected to 15 February, respectively to 15 March 2011. For the rest of the samples the specific activities were decay-corrected to the given date of sampling. On the time-scale of this sampling-analysis exercise, corrections are not significant for ^{40}K and U isotopes. No decay-correction was performed for ^{210}Pb, member of the natural

radioactive series of U-Ra, this being equivalent to the whole activity being attributed to supported ^{210}Pb, 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, based on adequate samples, as mentioned above in the sampling methodology section.

Because of the very low levels of ^{137}Cs in some of the samples, counting times ranged between 1 and 20 days. Sediment samples contained a large fraction of shell debris, resulting in proper sediment samples being in too small quantity. Therefore an estimate is given of U-238 in sediment based on results of ICP-MS analyses of total Uranium [4] 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 12% (coverage factor k=2).

5. RESULTS AND DISCUSSION

The levels of ^{137}Cs in sediments of the area are very low, as expected for the type of sediment analysed (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 [5] or in the Region [6 and following references up to 14], other than they are generally on the lower end of reported levels. 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 analysed, other than the well-known global sources. The results for sediments and biota are presented in Tables 3 and 4 respectively. Figures 3 and 4 are showing the measurements of five radionuclides in sediments.

Table 3: Activity concentrations of Radionuclides in sediment samples collected during 2006 and 2011 ($Bq \cdot Kg^{-1}$ dry weight)

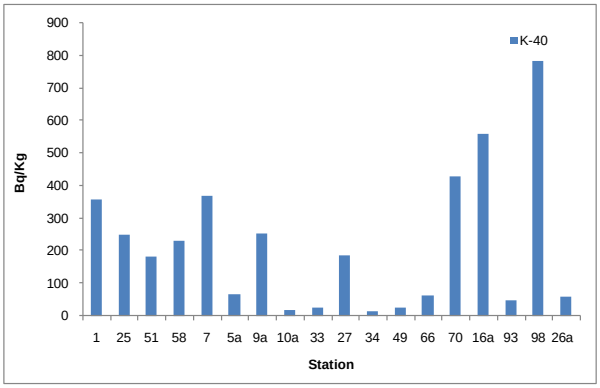
Stations	K-40 (Bq/kg)	%	Cs-137 (Bq/kg)	%	Pb-210 (Bq/kg)	%	U-238 (Bq/kg)	U-235 (Bq/kg)
2006 Samples								
ST1	358	2.8	1.7	14.2	41.9	5.8	27.0	1.3
ST25	251	2.6	1.6	8.9	39.3	3.6	49.3	2.1
ST51	184	2.8	1.6	10.5	28.3	5.5	39.6	1.9
ST58	230	2.8	1.4	14.0	35.2	5.7	50.5	2.4
ST07	370	2.7	3.9	6.7	56.3	4.5	32.6	1.5
ST05a	66.8	3.1	1.0	6.6	24.0	5.4		
ST09a	254	2.8	1.5	8.6	37.7	6.3	39.5	1.9
ST10a	17.4	3.8	0.17	15.2	8.4	8.8	12.6	0.6
ST33	25.9	3.9	0.44	10.6	18.9	6.8	34.1	1.6
ST27	186	3.2	0.85	25.4	30.1	7.2	42.9	2.0
ST34	16.0	4.8	0.66	24.0	15.1	7.8	29.5	1.4
ST49	25.0	3.3	0.26	10.0	9.2	7.8	17.4	0.8
ST66	61.8	3.8	1.9	11.0	21.6	7.6	35.0	1.6
ST70	430	2.7	2.5	10.0	51.2	5.1	38.6	1.8
ST16a	561	2.8	4.6	7.8	47.5	6.6	22.3	1.0
ST93	49.3	2.9	0.24	13.7	19.1	5.4	24.7	1.2
ST98	784	2.6	3.5	6.8	77.1	3.8	25.7	1.2
ST26a	61.4	3.0	0.31	12.8	24.3	5.1	28.4	1.3
2011 Samples								
BAH-5	70.0	3.0	0.19	21.6	15.8	8.1		
IRAN-4	259	2.6	0.63	8.9	25.1	6.0	32.4	1.5
IRAN-2	91.2	3.8	0.27	27.1	17.4	11.8		
KUW-5	75.4	3.6	0.20	25.5	9.5	14.7	41.3	1.9
Oman-2	130	2.7	0.11	24.0	7.7	11.3	18.1	0.9
DOHA-4-2	8.7	4.5	0.19	14.1	2.2	32.5		
KSA-3	52.3	3.1	0.35	12.7	10.1	8.2		
KSA-2	102	2.9	0.96	6.1	14.4	8.6		
UAE-7-1-2	101	3.9	<0.10		18.2	12.1		
UAE-7-1-1	52.7	3.5	0.22	20.3	12.5	9.9	65.9	3.1

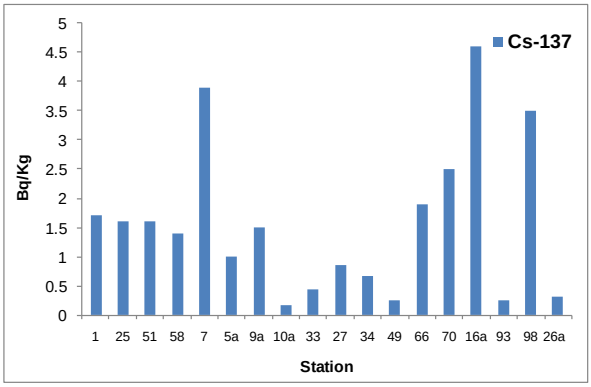
*U-238 and U-235 determined by ICP-MS (as per chapter 4) applying the conversion factors: 1 g Uranium = 12kBq with 99.237 % U-238 and 0.58kBq U-235 with 0.7205 % U-235 assuming the natural isotopic composition of uranium.

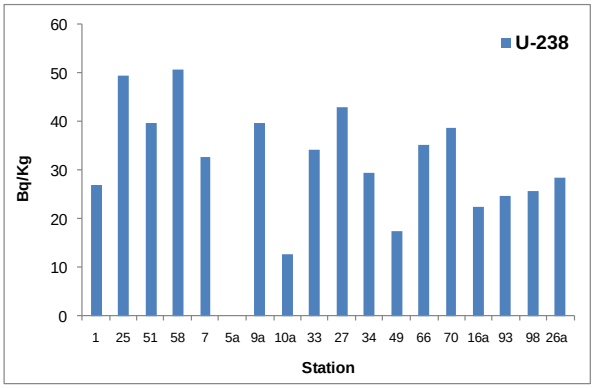
Table 4: Activity concentrations of Radionuclides in Biota samples collected during 2011 (Bq•Kg^{-1}dry weight)

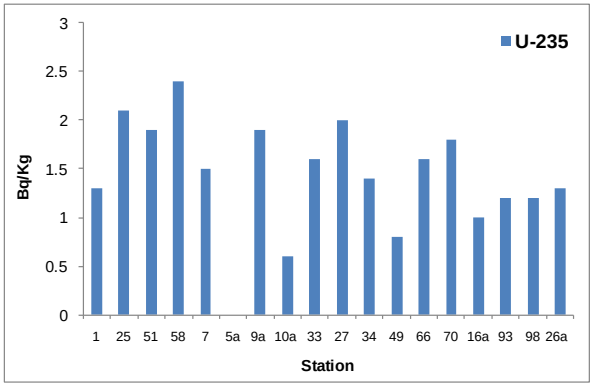
Stations	K-40 (Bq/kg)	%	Cs-137 (Bq/kg)	%	Pb-210 (Bq/kg)	%	U-238 (Bq/kg)	U-235 (Bq/kg)
BAH-5	377	2.6	< 0.10		3.7	18.2	2.32	0.08
IRAN-4	303	3.0	< 0.12		5.8	28.6	3.61	0.18
IRAN-2	289	2.8	0.13	29.7	5.0	20.3	0.82	0.04
OMAN-2	370	2.6	< 0.12		9.1	29.5	2.05	0.10
OMAN-8	379	3.2	< 0.12		16.8	18.5	1.50	0.07
DOHA-4-2	599	2.8	< 0.24		13.0	20.3	0.71	0.03
KSA-3	298	2.9	0.15	27.4	35.4	5.0	3.34	0.16
KSA-2	284	2.8	0.58	8.0	76.3	3.5	8.28	0.40
UAE-7-1-2	303	3.5	< 0.10		5,5	25.7	3.17	0.15
UAE-7-1-1	419	3.1	< 0.16		17.6	13.1	1.24	0.06

*U-238 and U-235determined by ICP-MS (as per chapter 4) applying the conversion factors: 1 g Uranium = 12kBq with 99.237 % U-238 and 0.58kBq U-235 with 0.7205 % U-235 assuming the natural isotopic composition of uranium.









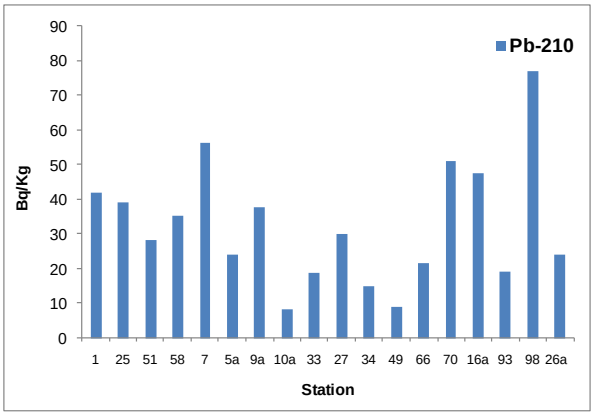


Figure 3: Levels of measured radionuclides in offshore sediments of the ROPME Sea Area during ROPME Oceanographic Cruise – Winter 2006

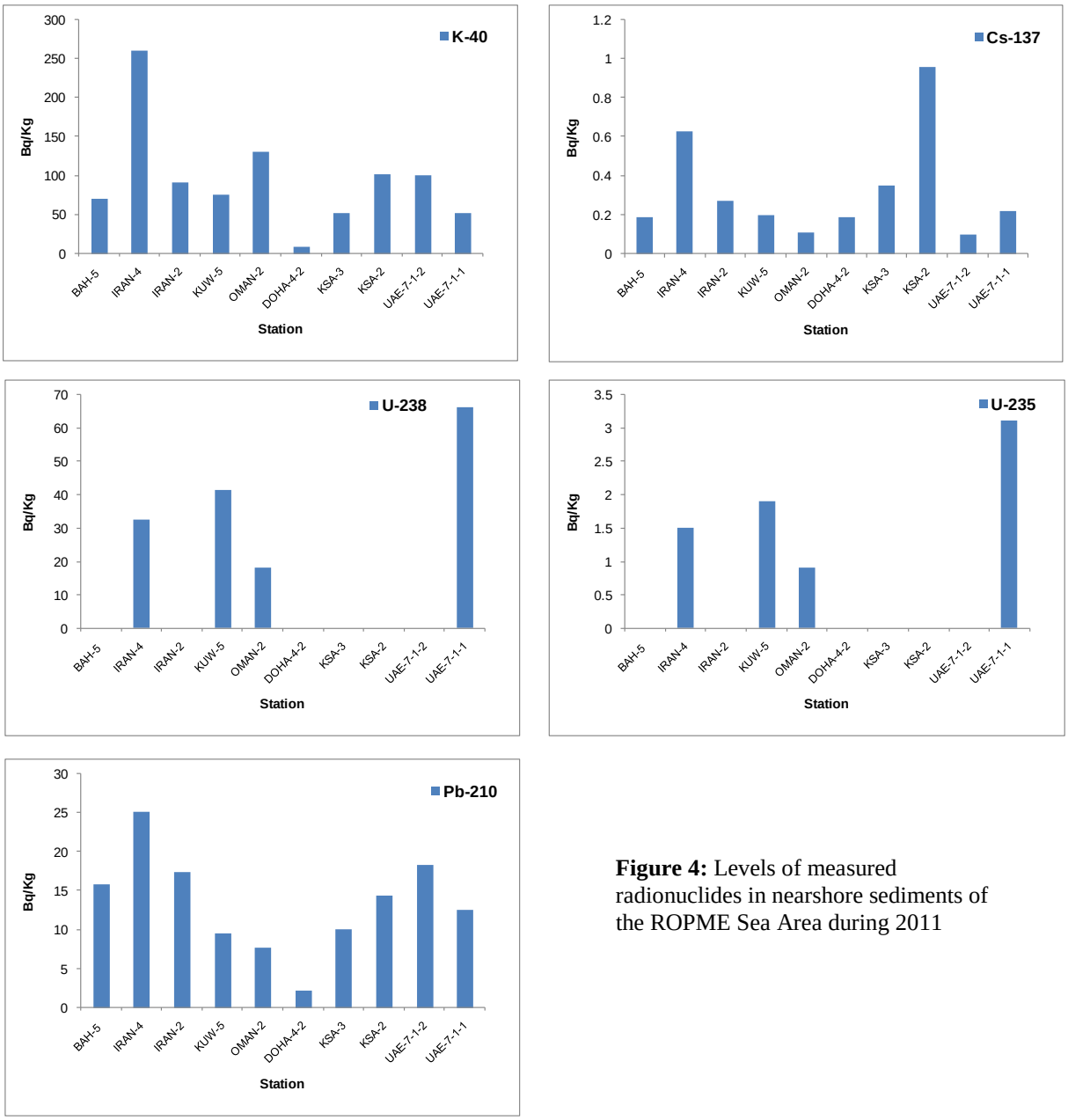


Figure 4: Levels of measured radionuclides in nearshore sediments of the ROPME Sea Area during 2011

The activities of anthropogenic Cs-137 in the biota analysed were very low 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 (K-40) were similar to those in other areas of the world ocean. The Pb-210 activities were presented in Table 4 only for information purpose, because sample amounts (ranging between 1g and 2.6 g), are totally insufficient for reliable analysis. 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 4 hints to relative variation of natural Pb-210 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 fertiliser 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 Po-210 and not Pb-210 that is of most interest. Figure 5 shows the measurements of five radionuclides in bivalves.

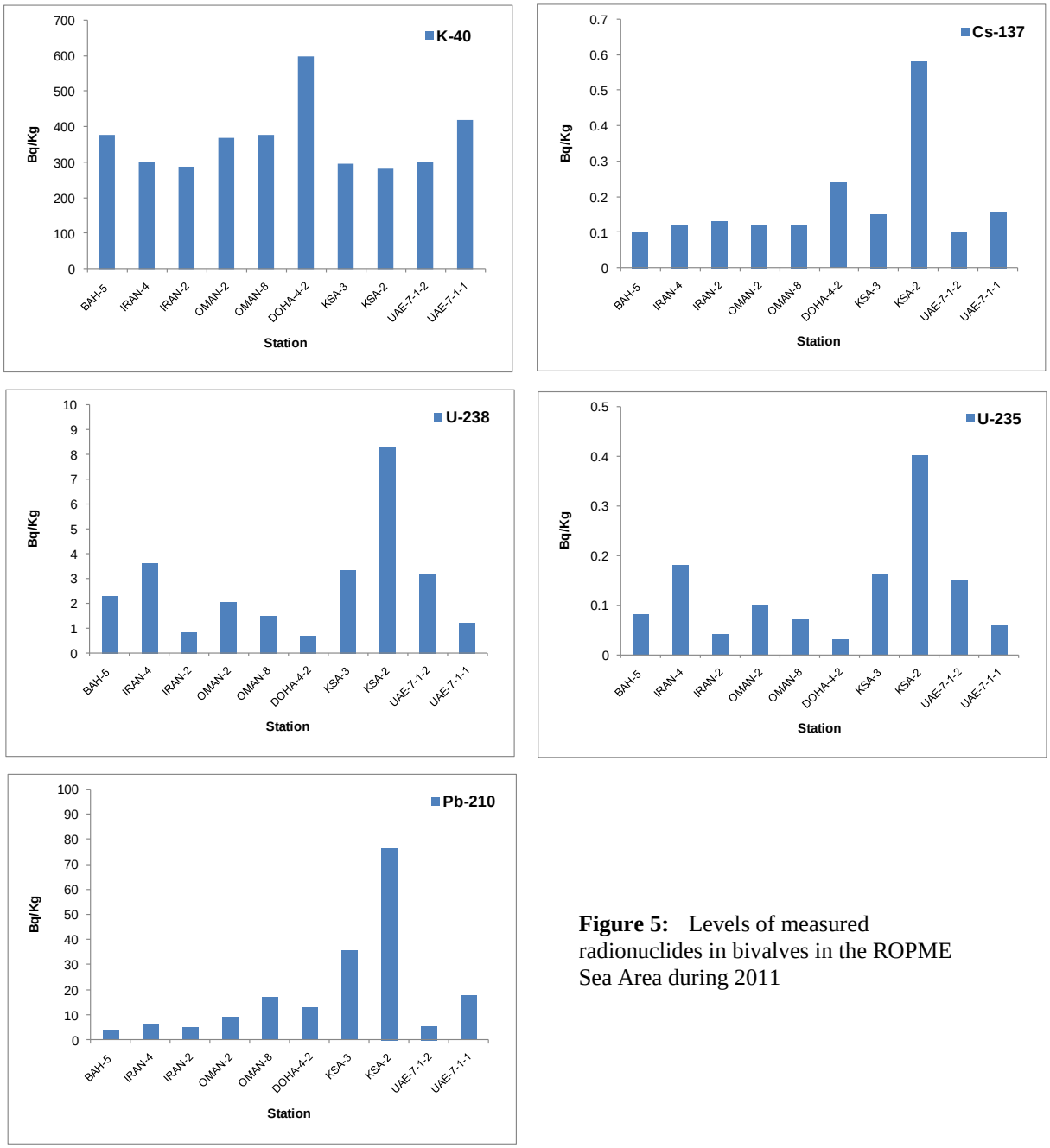


Figure 5: Levels of measured radionuclides in bivalves in the ROPME Sea Area during 2011

6. CONCLUSIONS

The baseline assessment based on sediment and biota samples from 11 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 analysed was too small to be able to accurately represent the different regions of the ROPME Sea Area. A more thorough survey on the distribution of radioactivity in the ROPME Sea Area 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 over longer periods. This would allow also the radiometric dating of sediment layers. Biological samples should be collected following rigorous standard operating procedures to make sure samples are representatives and comparable with respect to species, size, gender, and spawning season. In addition, sampling (of biota and sediment) should be carried out by competent and 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 of IAEA and ROPME, financially supported by both organizations. The Agency is grateful for the support provided by its Marine Environment Laboratory and the Government of the Principality of Monaco. The help rendered by Mr. Carlos Alonso and Beat Gasser for carbon analysis is highly appreciated with gratitude.

ROPME and MESL/IAEA extend their appreciation with gratitude for the logistic support offered by the ROPME National Focal Points and the efforts made by the National Mussel Watch Team in each Member State during sample collection.

9. REFERENCES

1. Povinec, P.P., Comanducci, J.F., Levy-Palomo I. IAEA-MEL's underground counting laboratory in Monaco - Background characteristics of HPGe detectors with anti-cosmic shielding. Appl Radiat Isot, **61**(2-3):85-93, Aug-Sep 2004.
2. Sima,O., Arnold,D., Dovlete,C.: GESPECOR. A versatile tool in gamma-ray spectrometry. Journal of Radioanalytical and Nuclear Chemistry, **248** 2(2001) 359-364.
3. Gilmore, G. and Hemingway, J. Practical Gamma-Ray Spectrometry. Ed. John Wiley & Sons Ltd, Chichester, England, 1995.
4. Godoy, M.L.D.P., Godoy, J.M., Roldão, L.A., Tauhata, L. Determination of total content and isotopic compositions of plutonium and uranium in environmental samples for safeguards purposes by ICP-QMS; Journal of Environmental Radioactivity, **100** (8), (2009) 613-625.
5. MARDOS, 1995. Sources of Radioactivity in the Marine Environment and their Relative Contributions to Overall Dose Assessment from Marine Radioactivity (MARDOS), Final report of a co-ordinated research programme. IAEA-TECDOC-838, Vienna, October 1995.
6. Pourahmad, J., Motallebi, A., Asgharizadeh, F., et *al*. Radioactivity concentrations in sediments on the coast of the Iranian province of Khuzestan in the Northern Persian Gulf, Environmental Toxicology, **23**(5) (2008) 583-590.
7. Abdi, M.R., Faghihian, H., Mostajaboddavati, M., Hasanzadeh, S., Kamali, M. Distribution of natural radionuclides and hot points in the coasts of Hormozgan, Persian Gulf, Iran. Journal of Radioanalytical and Nuclear Chemistry, **270** (2) (2006) 319–324.
8. Al-Kheliewi, A.S., Shabana, E.I. Activity concentration of some anthropogenic radionuclides in the surface marine sediments near the Saudi coast of the Arabian

(Persian) Gulf, Journal of Radioanalytical and Nuclear Chemistry, **274** (1) (2007) 207-212.

9. Abdi, M.R., Faghihian, H., Kamali, M., et *al*. Distribution of natural radionuclides on coasts of Bushehr, Persian Gulf, Iran. Iranian Journal of Science and Technology Transaction A, Science, **30** (A3) (2006) 259-269.
10. Al-Zamel, A.Z., Bou-Rabee, F., Olszewski, M., et *al*. Natural radionuclides and ^{137}Cs activity concentration in the bottom sediment cores from Kuwait Bay.Journal of Radioanalytical and Nuclear Chemistry, **266** (2) (2005) 269-276.
11. Al-Zamel, A.Z., Bou-Rabee, F., Al-Sarawi, M., A., et *al*. Determination of the sediment deposition rates in the Kuwait Bay using ^{137}Cs and ^{210}Pb, Nukleonika, **51**(2) (2006) S39-S44.
12. Saad, H.R., Al-Azmi, D. Radioactivity concentrations in sediments and their correlation to the coastal structure in Kuwait. Applied Radiation and Isotopes, **56(6)** (2002) 991-997.
13. Zare, M.R., Mostajaboddavati, M., Kamali, M., et *al*. ^{235}U, ^{238}U, ^{232}Th, ^{40}K and ^{137}Cs activity concentrations in marine sediments along the northern coast of Oman Sea using high-resolution gamma-ray spectrometry. Marine Pollution Bulletin, **64**(9) (2012) 1956-1961.
14. Al-Sulaiti, H., Regan, P.H., Bradley, D.A., et *al*. A preliminary report on the determination of natural radioactivity levels of the State of Qatar using high-resolution gamma-ray spectrometry. 11th International Symposium on Radiation Physics. Melbourne, Australia, Sep. 2009. Nuclear Instruments & Methods in Physics Research Section A, Accelerators Spectrometers Detectors and Associated Equipment, **619** (1-3) (2010).

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