THE IMPACT OF URANIUM NEAR A PHOSPHATE MINING PORT ON THE ENVIRONMENT IN THE NORTHERN GULF OF AQABA, RED SEA

Mohammad Wahsha[(1,2)*], Eman Al-Absi[(2)], Riyad Manasrah[(2)], Walid Al-Zyoud[(3)], Claudio Bini[(4)]

[(1)] Marine Science Station, The University of Jordan-Aqaba Branch, Jordan
[(2)] Faculty of Marine Sciences, The University of Jordan-Aqaba Branch, Jordan
[(3)] Department of Biomedical Engineering, School of Applied Medical Sciences, German-Jordanian University, Jordan
[(4)] Department of Environmental Sciences, Informatics and Statistics, Ca' Foscari University of Venice, Italy

*Corresponding author E.mail: m.wahsha@ju.edu.jo

Abstract

Uranium has three isotopes in nature, the ^{238}U, ^{235}U and ^{234}U. The presence of uranium isotopes in marine sediment at relatively high concentrations was the drive behind several studies to determine the radionuclides levels in marine ecosystems to assess the potentially negative effects on environment. This study determined the activity concentrations of uranium isotopes using alpha spectroscopy in marine sediment and seagrass from the northern Gulf of Aqaba. Samples were collected from a phosphate mining port located at the Jordanian coastline of the Gulf of Aqaba. The range of activity concentrations of alpha emitters in marine sediment of the phosphate port were (783.47 - 836.17, 29.43 - 30.43, and 804.56 - 847.80 Bq kg $^{-1}$) for ^{238}U, ^{235}U and^{234}U, respectively, where the average value in seagrass samples was 158.19 Bq kg $^{-1}$. Our results show that the determined levels of uranium radioactive isotopes are more than the internationally accepted limit by approximately two folds. In conclusion, raw phosphate dusts might be one of the main pollution sources for marine ecosystems in the Gulf of Aqaba.

Keywords: *Radioactivity, Gulf of Aqaba, sediment, alpha spectroscopy, uranium.*

Introduction

Jordan is rich in phosphate ore, which was discovered in 1894. The mining and production of phosphate started in1934 in Rusaifeh (Azhar, 2000). The phosphorus content of raw phosphate rock ranges from 30.81 to 33.90% (as P_2O_5) with the remainder consisting mainly of calcium (50.37-52.20%) as CaO and fluoride (3.53-3.99%). The marketable phosphate powder is exported through the port of Aqaba at the northern most part of the Gulf of Aqaba (Abu-Hilal, 1985), which is known as a major regional shipment center (second only to Suez and Jeddah) (Pilcher and Al-Moghrabi, 2000). Phosphate is usually transported onto ships by using one stationary, and two mobile ship loaders. The two docks can handle up to 8 million tons of rock phosphate per year (Abu Hilal et al., 2008). The Jordan Phosphate

DOI: 10.6092/issn.2281-4485/6600

Mines Company produces di-ammonium phosphate (DAP) and phosphoric acid per annum. Trivial amounts of sulphur and DAP are routinely spilled during loading operations for shipment (Pilcher and Al-Moghrabi, 2000). The fine sediment layers in port berth provide an evidence of receiving substantial amount of powder phosphate (Badran and Al-Zibdah, 2005). In fact, during shipping, transportation, storage, and loading, some phosphate is lost to the atmosphere, to the land around the storage areas, near the loading docks, and to the sea (Abu Hilal et al., 2008). The Jordanian phosphate powder is almost completely insoluble in seawater (Rasheed et al., 2005).

Wahbah and Zughul (2001) reported that the bulk of the sediment materials were of inorganic nature, derived from desert dust which is carried from Wadi Araba by the prevailing north winds, and partially from the dust of the exported raw phosphate. Phosphate is associated with the growth of grass and might cause death to coral colonies under stress conditions (Walker and Ormond, 1982). Phosphate has adverse effect on its surrounding environment as it is involved in reducing light intensity, inhibiting coral calcification, and increasing sediment load (Walker and Ormond, 1982; Islam and Tanaka, 2004).

It is well known that the natural phosphates contain various potentially toxic and radioactive elements that might be of environmental concern to the public (Ogunleye et al., 2002).

Natural radioactivity is present everywhere since the creation of earth (Salahel Din and Vesterbacka, 2012; Al-Absi et al., 2015). Therefore, several studies have investigated the levels of radionuclides in the environment. In marine environment, radionuclides are transferred through seawater by terrestrial radiation that originates predominantly from the upper 30 cm of the soil (Agbalagba et al., 2011, Padua et al., 2013) and from cosmic rays. Three primordial long-lived radionuclides are known as source of natural radioactivity; ^{238}U, ^{232}Th and ^{40}K (Al-Absi et al., 2015). Uranium has three naturally occurring isotopes; ^{238}U, ^{235}U and ^{234}U. The presence of uranium isotopes in marine sediment at relatively high concentrations (Al-Absi et al., 2016) has driven several studies to determine the levels of these radionuclides in marine ecosystems and subsequently to assess the potentially negative effects on environment. Uranium is found at high levels in marine sediment that contained large amounts of organic matter, phosphate, or both (Ordonez-Regil et al., 2013). Some studies have found that the most of uranium in marine environment came from sea water (Veeh, 1967; Sam et al., 2000). In a closed system, the equilibrium occurred between ^{234}U and ^{238}U (^{234}U/^{238}U is unity). In nature, disequilibrium is frequently found between these isotopes due to weathering processes. The ratio ^{234}U/^{238}U is ~1.15 in seawater whereas it is $\leq$ 1.0 in soil and sediment. Therefore, this disequilibrium is greater in seawater than in terrestrial samples (Ordonez-Regil et al., 2013).

The Gulf of Aqaba is the only seaport in Jordan, where quite a lot of activities are taking place in this sea and surrounding areas, such as tourism, dumping of litter due to lack of control and awareness, fishing, shipping for exportation processes, oil and hazardous material spills and phosphate industry (Ababneh et al., 2010).

This might represent a major source of contamination in marine environment. All previously mentioned activities and mainly the exportation of phosphate ore increases the levels of radionuclide contaminants taking into consideration that Jordan is considered as the fifth largest producer and the third largest exporter of phosphate rocks in the world (Al-Jundi et al., 2008; Ababneh et al., 2010).
The purpose of this study was to ascertain the effect of uranium on marine environment by the determination of the radioactivity associated with uranium content of the raw phosphate.

Materials and Methods

Study area

The Gulf of Aqaba is unique semi-enclosed water body located at the northern end of the Red Sea. It is located between the coordinates 28˚- 29˚30' N and 34˚30' -35˚ E. The maximum depth of the gulf is about 1800 m; its length is 180 km and its width ranges between 5 and 26 km (average of 16 km) (Al-Absi et al., 2016). The study area lies within the Jordanian coast of the gulf. Sediment and seagrass samples were collected from Phosphate area (PH) with coordinates 29˚30'01.31"N and 34˚59'31.04"E (Fig. 1)

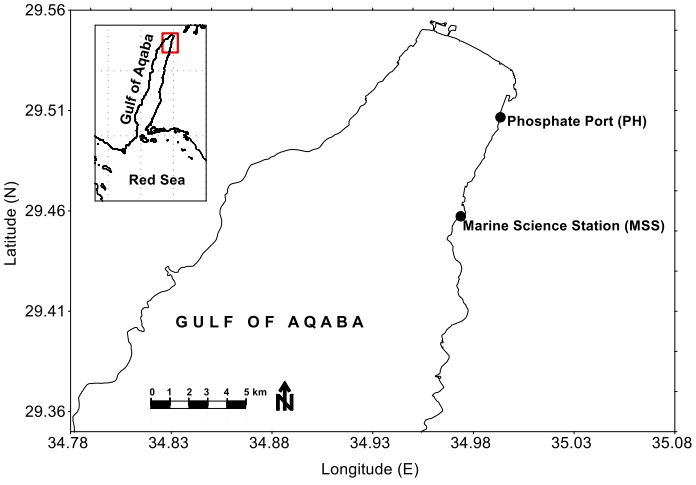

Figure 1
Map of sampling sites and study area in the northern Gulf of Aqaba

Sample collection and preparation

Twenty samples of sediment and seagrass were collected from two selected sites (the Marine Science Station "MSS" as a protected area and the Phosphate Port area "PH" as contaminated area) by scuba diving from the Gulf of Aqaba (Fig. 1). According to the procedures described by Benton Jones (2001) and Margesin and Schinner (2005), sediment samples were collected from the upper horizon at depth of approximately 25 cm. Each sediment sample was a composite of 5 subsamples collected in a given sector (4 m^2). Samples were taken at the site, mixed, packed in

DOI: 10.6092/issn.2281-4485/6600

containers, and then transported to the laboratory for further routine chemical and physical analysis. Seagrass samples were collected according to Benton Jones (2001) with minor modifications. At least six specimens of selected plant species (at the early vegetative phase and normal morphological appearance) were sampled at each site with their corresponding sediment clod. Samples were carefully packed in plastic bags and transported to the laboratory. Seagrass species were classified according to Edmund, et al (2003) as "*Halophila stipulacea*". All samples were dried in an oven at 105 °C overnight. They were crushed, homogenized and sieved through 63-100 µ mesh sieve. Then they became ash gradually at about 550 °C.

Analytical methods

Analytical methods consist of radiochemical separation and electroplating. Ash sediment samples (~2g) were spiked for chemical recovery and activity calculations by adding about 10µL of ^{232}U tracer. In this procedure, a sediment sample was weighed into a glass beaker of appropriate size and was mixed with 70% HNO_3 (30mL). The mixture was heated and stirred for about 3-4 hours. Furthermore, the leachable solution was centrifuged and the formed precipitate was dissolved in HNO_3. Subsequently, the solution was evaporated and the obtained residue was dissolved in 1M HNO_3 (70mL) and heated for 1hour. The solution was filtered (0.45µm pore size and 47mm diameter) into a beaker, washed by 1M HNO_3 (100mL) and heated again. An iron test was carried out by taking one drop from both NH_4SCN and the solution. The pH was adjusted to 8 by adding NH_3H_2O and as a result uranium salts were precipitated. These salts were digested by using the concentrated HNO_3 (5-10mL), heated at 200℃, and then evaporated. The residual was dissolved again by 8M HNO_3 (20mL). The sample was added to UTEVA resin containing 8M HNO_3 (10mL). Later, 0.1M HCl (20mL) was added to the resin. A volume of 2.5mL of $HNO_3$was also added to the sample and then evaporated. Another volume of 4mL of distilled water and 0.3M of H_2SO_4 with two drops of thymol blue indicator as well as concentrated NH_3 were all added to the residual (containing uranium) to adjust the pH to 2.1-2.4. Uranium was electroplated on stainless-steel discs for 1hour at 0.7A. A volume of 1mL of NH_3 H_2O was added and left for only one minute before switching off the electric current. Finally, the discs were removed and rinsed with acetone and dried to be ready for counting.

Alpha spectroscopy

The detector apparatus for alpha spectrometry system was configured using PIPS detector (Canberra, Industries, Meriden, CT) with surface area of 450 mm^2(23.9 mm diameter). The detector bias voltage was set at 39.5 V for all counting samples; the PIPS detector was connected to a Canberra alpha spectrometer (Model 7401) and a vacuum pump, which can evacuate down to 20 microns. Data were recorded with an analog-to-digital converter (ADC), which offers a resolution over a wide range of 2048 channel with a Canberra multichannel analyzer (MCA) model 2100. Genie 2000 is commercial software which consists of a comprehensive set of capabilities for acquiring and analyzing spectra from MCA. Its function includes MCA control, spectral display; basic spectrum analysis and reporting including

peak locate schemes, area calculation, background subtraction, nuclide identification, and activity calculation. Instrument was calibrated by using mixed source of $^{238+234}U$, ^{239}Pu and ^{241}Am (total activity of 376.9 dpm) and its counting efficiency was from 11-14%. All samples and background were counted around 70,000 s. The chemical recovery was 54%.

Results and Discussion

The characteristics of all sediment samples (depth below sea level, total organic, sediment type and color) are listed in Table 1. The total organic matter ranged between 1.81% at the upper horizon (0-12cm) and 1.64 % at the bottom (13-25cm) at the PH area, while at the MSS, it was 0.93 at the surface and 0.89% at the bottom. Moreover, the sediment type ranged between clay (PH) and sandy (MSS) and the color was gray to black in both horizons due the similarities in the physical, chemical, and geological properties of the marine sediments at that area.

Table 1. *Selected chemo-physical properties of the studied sediments at the phosphate port area (PH) and Marine Science Station (MSS) in the northern Gulf of Aqaba, Red Sea.*

Sample code	Depth below sea level (cm)	Total organic (%)	Sediment type	Color
PH-S	0 - 12	1.81	Clay	Gray to black
PH-B	13 - 25	1.64		
MSS-S	0 - 12	0.93	Sandy	Gray to black
MSS-B	13 - 25	0.85		

The activity concentrations of ^{238}U, ^{235}U, and ^{234}U in sediment and seagrass samples from phosphate area are summarized in Table 2. The lowest concentrations of total uranium were found at the surface layers of sediment (1618.46 Bq kg^{-1}), whereas the highest levels of total uranium (1713.40 Bq kg^{-1}) existed at the bottom layers of sediment (Table 2).

Table 2. *Activity concentration of ^{238}U, ^{235}U, and ^{234}U Bq kg^{-1}) in sediment and seagrass samples from phosphate port area (PH) and Marine Science Station (MSS) in the northern Gulf of Aqaba.* NM = not measured

Sample	^{238}U	^{235}U	^{234}U	Total U	$^{234}U/^{238}U$
Sediment					
PH (B)	836.17±124.46	29.43±4.75	847.80±126.18	1713.40	1.01
PH (S)	783.47±144.64	30.43±6.46	804.56±148.51	1618.46	1.03
MSS (B)	23.82±2.85	NM	NM		
MSS (S)	30.91±3.28	NM	NM		
Seagrass					
PH	158.19±15.92	NM	NM		
MSS	27.34±2.80	NM	NM		

The concentration of uranium proportionally increases with depth. This is due to the fact that uranium enters seawater from underwater geologic formations and it is likely that it has been constantly deposited on the seafloor. Moreover, values of uranium in sediment samples of the phosphate area were found to be higher than

DOI: 10.6092/issn.2281-4485/6600

the international accepted limit of 370 Bq kg^{-1} (Agbalagba and Onoja, 2011; El-Taher and Madkour, 2011; Alfonso et al., 2014; Komar et al., 2014; Ababneh et al., 2009). The $^{234}U/^{238}U$ activity ratio value was close or equal to 1.00, meaning that the radioactive equilibrium was occurring between ^{234}U and ^{238}U.
A tabulated comparison among this and other studies is shown in Table 3, which included the activity concentrations of natural and artificial radionuclides in marine sediments.

Table 3. *Comparison of uranium activity concentration in sediment samples between the present study and other studies worldwide.*

Location	^{238}U	Reference
The Gulf of Aqaba, Jordanian Coastline	11.3-676.7	Tsabaris et al. (2012)
The Gulf of Aqaba, Saudi Coastline, KSA	16.97	Salahel Din and Vesterbacka (2012)
Farasan Island, Southern Red Sea, KSA	35.46	DePaul (2010)
Red Sea Coastline, Egypt	22.7	Al-Zahrany et al. (2012)
Northern coast of Oman Sea	11.83-22.68	Al-Kheliewi et al. (2002)
East Coast of Tamilnadu, India	3.67	Avwiri et al. (2013)
Near shore of Vizag, South East India	19-48	Alfonso et al. (2014)
Red Sea, Aqaba	783.47-836.17	Present Study

The current data are consistent with our previously reported study by Al-Absi et al. (2016), which was conducted at the Jordanian coastline of the Gulf of Aqaba. However, other data from studies were conducted at the Red Sea in Egypt and Saudi Arabia showing variations due to the different anthropogenic activities in each country (Al-Trabulsy et al., 2011; El-Taher and Madkour, 2011; Al-Zahrany et al., 2012; Harb, 2008).

Conclusion

The obtained results show that the determined levels of uranium radioactive isotopes are more than the internationally accepted limit by approximately two folds. In conclusion, raw phosphate dust might be one of the main pollution sources for marine ecosystems. Further studies are definitely needed to provide additional information on various eco-toxicological approaches with the purpose of getting an educated estimate to the risk of adverse effects on human health and surrounding environment.

Acknowledgment
The authors wish to thank and appreciate the technicians at the *Jordan Atomic Energy Commission* for their help in samples analysis. In addition, exceptional thanks go to the staff and divers at the *Marine Science Station* for their help in sampling.

References

ABABNEH A.M., MASA'DEH M.S., ABABNEH Z.Q., AWAWDEH M.A., ALYASSIN A.M. (2009) Radioactivity concentrations in soil and vegetables from the Northern Jordan

Rift Valley and the corresponding dose estimates, Radiation Protection Dosimetry, 134(1): 30-37.
ABABNEH Z.Q., AL-OMARI H., RASHEED M., AL-NAJJAR T., ABABNEH A.M. (2010) Assessment of gamma-emitting radionuclides in sediment cores from the Gulf of Aqaba, Red Sea. Radiation Protection Dosimetry, 141(3):289–298.
ABU-HILAL A., RASHEED M., Ll-NAJJAR T. (2008) Potential environmental impact of dissolution of raw phosphate in sea water of the Gulf of Aqaba. Chemistry and Ecology, 24(1):51-59.
ABUHILAL A.H. (1985) Phosphate pollution in the Jordan Gulf of Aqaba. Marine Pollution Bulletin, 16:281-285.
AGBALAGBA E.O., ONOJA R.A. (2011) Evaluation of natural radioactivity in soil, sediment and water samples of Niger Delta (Biseni) flood plain lakes, Nigeria. Journal of Environmental Radioactivity, 102:667-671.
Al-ABSI E., Al-ABDULLAH T., SHEHADEH H., AI-JUNDI J. (2015) ^{226}Ra, ^{228}Ra, and ^{40}K activity concentration in some vegetables consumed in Jordan, and resultant annual ingestion effective dose. Radiation Protection and Environment, 38(1):29-34.
Al-ABSI E., MANASRAH R., WAHSHA M., Al-MAKAHLEH M. (2016) Radionuclides levels in marine sediment and seagrass in the Northern Gulf of Aqaba, Red Sea. Fresenius Environmental Bulletin, 25(9):3461-3474.
ALFONSO J.A., PEREZ K., PALACIOS D., HANDT H., LABRECQUE J.J., MORA A. VASQUEZ Y. (2014) Distribution and environmental impact of radionuclides in marine sediments along the Venezuelan coast. J RadioanalNucl Chem., 300:219-224.
AL-JUNDI J., AL-AHMAD N., SHEHADEH H., AFANEH F., MAGHRABI M., GERSTMANN U. (2008) Investigations on the activity concentrations of 238U, 226Ra, 228Ra, 210Pb and 40K in jordan phosphogypsum and fertilizers, Radiation Protection Dosimetry, 131(4):449-454.
AL-KHELIEWI A.S., SHABANA S.I., FAROUK M.A., AL-ZAHRANY A.A., AL-MASOUD F.I. (2002) Concentration of Man-Made Radionuclides in Marine Sediments at the Al-Khafji and Mneefa Coastal Areas in Saudi Arabia. The 6th Saudi Engineering Conference, KFUPM, Dhahran, 2:429-437.
Al-TRABULSY H.A., KHATER A.E.M., HABBANI F.I. (2011) Radioactivity levels and radiological hazard indices at the Saudi coastline of the Gulf of Aqaba. Radiation Physics and Chemistry, 80:343–348.
AL-ZAHRANY A.A., FAROUK M.A., AL-YOUSEF A.A. (2012) Distribution of naturally occurring radioactivity and 137Cs in the marine sediment of Farasan Island, Southern Red Sea, Saudi Arabia, Radiation Protection Dosimetry, 152:135-139.
AVWIRI G.O., EGIEYA J. M., ONONUGBO C. P. (2013) Radiometric assay of hazard indices and excess lifetime cancer risk due to natural radioactivity in soil profile in Ogba/Egbema/Ndonilocal government area of rivers state, Nigeria. Academic Research International, 4(5):54-65.
AZHAR M. (2000) Phosphate exports by Jordan. Arabic Studies Quarterly, 22(4):59-79.
BADRAN M., ALZIBDAH M. (2005) Environmental quality of Jordanian coastal surface sediment,Gulf of Aqaba, Red Sea. Ambioa Journal of the Human Environment, 8:609-614.
BENTON JONES J.R. (2001) Laboratory guide for conducting soil tests and plant analysis. CRC Press, New York, p: 363.
DEPAUL UNIVERSITY (2010) Radiation Safety Manual.

DOI: 10.6092/issn.2281-4485/6600

EDMUND P., GREEN FREDERICK T. (2003) World atlas of seagrasses. Publisher: University of California Press; First Edition, p: 310 .

EL-TAHER A. MADKOUR H.A. (2011) Distribution and environmental impacts of metals and natural radionuclides in marine sediments infront of different wadies mouth along the Egyptian Red Sea Coast. Applied Radiation and Isotopes, 69:550–558.

HARB S. (2008) Natural radioactivity and external gamma radiation exposure at the coastal Red Sea in Egypt. Radiation Protection Dosimetry, 130(3):376-384.

ISLAM M., TANAKA M. (2004) Impacts of pollution on coastal and marine ecosystems including coastal and marine fisheries and approach for management: a review and synthesis. Mar. Pollut. Bull., 48(78):624-49.

KOMAR D., ŠMUC N.R., BELAK Ž.L., MATESIC S.S., LOJEN S., KNIEWALD G., VRHOVNIK P., DOLENEC T., DOLENEC M. (2014) Geochemical characteristics and distribution of rare earth elements in Makirina Bay Sediments (N. Dalmatia, Republic of Croatia). GeologicaMacedonica, 28(2):127–137.

MARGESIN R., SCHINNER F. (2005) Manual for soil analysis — monitoring and assessing soil bioremediation, 1st ed. Springer, Heidelberg, Germany, pp: 359.

OGUNLEYE P.O., MAYAKI M.C., AMAPU I.Y. (2002) Radioactivity and heavy metal composition of Nigerian phosphate rocks: possible environment implications. J. Environ. Radioactivity, 62, 39-48.

ORDONEZ-REGIL E., ALMAZAN-TORRES M.G., SANCHEZ-CABEZA J.A., RUIZ-FERNANDE A.C. (2013) Presence of uranium and plutonium in marine sediments from gulf of tehuantepec, mexico. J Radioanal Nucl Chem 298, 981-986.

ORDONEZ-REGIL E., ALMAZAN-TORRES M.G., SANCHEZ-CABEZA J.A., RUIZ-FERNANDE A.C. (2013) Presence of uranium and plutonium in marine sediments from gulf of tehuantepec, mexico. J Radioanal Nucl Chem., 298:981-986.

PADUA J.Ch., BASIL ROSE M.R. (2013) Natural gamma radioactivity in the villages of kanyakumari district, Tamil Nadu, India. Radiation Protection Dosimetry, 156:42-48.

PILCHER N., AL-MOGHRABI S.M. (2000) The status of coral reefs in Jordan - 2000, Unpublished Technical Report. PERSGA.

RASHEED M., AL-ROUSAN S., BADRAN M. (2005) Phosphate enrichment in the northern Gulf of Aqaba: Regulation by carbonate sediments and impact on nitrogen elevation. Chemistry and Ecology, 21:199-208.

SALAHEL DIN K., VESTERBACKA P. (2012) Radioactivity levels in some sediment samples from Red Sea and Baltic Sea. Radiation Protection Dosimetry, 148(1):101–106.

SAM AL, AHAMED MMO, EL KHANGI FA, EL NIGUMI YO (2000) Uranium and thorium isotopes in some red sea sediments. Radiochim Acta, 883:307-312.

TSABARIS C., EVANGELIOU N., FILLIS-TSIRAKIS E., SOTIROPOULOU M., PATIRIS D.L., FLOROU H. (2012) Distribution of natural radioactivity in sediment cores from Amvrakikos Gulf (western Greece) as a part of IAEA's campaign in the Adriatic and Ionian seas. Radiation Protection Dosimetry, 150(4):474–487.

VEEH H. (1967) Deposition of uranium from the ocean. Earth Plant Sci Lett 3:145-150.

WAHBAH M., ZUGHUL M. (2001) Temporal distribution of chlorophyll a, suspended matter, and the vertical flux of particles in Aqaba (Jordan). Hydrobiologia, 459:147–156.

WALKER D.I., Ormond R.F.G. (1982) Coral death from sewage and phosphate pollution at Aqaba, Red Sea. Marine Pollution Bulletin, 13(1):21-25.