



CONCENTRATION OF MAN-MADE RADIONUCLIDES IN MARINE SEDIMENTS AT THE AL-KHAFJI AND MNEEFA COASTAL AREAS IN SAUDI ARABIA

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ABSTRACT

The present work is a part of a national project dedicated to establish marine radioactivity database of both natural and man-made radionuclides for the Saudi coasts of the Arabian Gulf and the Red Sea. Concentrations of Pu isotopes, ²⁴¹Am, ⁹⁰Sr, and ¹³⁷Cs radionuclides have been measured in marine sediment samples collected from 10 different locations along the Arabian Gulf coast at Al-Khafji and Mneefa areas. Pu isotopes, ²⁴¹Am, and ⁹⁰Sr were sequentially separated from all other components of the sample by anion exchange chromatography and prepared for counting. The alpha emitters were coprecipitated with Nd³⁺ as fluorides and mounted on a membrane filters for measurement by alpha spectroscopy while ⁹⁰Sr concentration was measured using liquid scintillation counting. Measurements of ¹³⁷Cs have been made using a hyper-pure germanium spectrometer. The activity concentrations of Pu isotopes, ²⁴¹Am, ⁹⁰Sr, and ¹³⁷Cs for all measured samples were <LLD - 0.056 Bq/kg, <LLD - 0.012 Bq/kg, <LLD - 0.041 Bq/kg, 0.02 - 0.14 Bq/kg, and <LLD - 5.69 Bq/kg dry weight respectively. The obtained results showed wide variation in the activity concentration of ¹³⁷Cs and ⁹⁰Sr depending on the type of the sediment. Results are discussed and compared with other reported data.

Keywords: *marine radioactivity, Pu isotopes, ²⁴¹Am, ⁹⁰Sr, ¹³⁷Cs, Al-Khafji, Mneefa*

المخلص

INTRODUCTION

The Arabian (Persian) Gulf is a 965 km long arm of the Indian Ocean. The Gulf is bounded by the Shatt al-Arab waterway in the north, and the Strait of Hormuz in the south, which connects it to the Gulf of Oman and the Indian Ocean. It is one of the most productive plankton water bodies in the world. Its low tidal displacement means that it has little discharge of its water into the Indian Ocean and thus little opportunity to flush out pollutants. The strait, which is 54 km wide at its narrowest point, is the choke point of the Gulf; through it the oil tankers and ships loaded with goods and radioactive materials pass so that any minor accident may affect the environmental marine life in this area. The Arabian Gulf is important as an international trade route connecting the Middle East to Africa, India and China.

The Kingdom of Saudi Arabia has more than 750 kilometers of coastline along the Arabian Gulf. This coastline is of great importance for the country. The desalination plants located on the Arabian Gulf play an important role in water supply for the Kingdom so any radioactive contamination may have a considerable influence on marine life as well as water quality in that area.

The importance of man-made radionuclides would have not been significant if some events had not occurred on our planet. Those events encompass nuclear weapons testing during fifties and sixties of last century, Chernobyl accident in the former USSR, nuclear power production reactors all over the world, transportation of high radioactive materials, nuclear fuel reprocessing plants, and many other nuclear accidents such as the SNAP-9A accident. The high level waste (HLW) shipment through oceans may threaten the environmental marine life if there is any leak or accident, otherwise the effect is minimal. This waste is a byproduct of extracting plutonium from spent nuclear fuel in French and British reprocessing plants. However, the contributions from fuel reprocessing plants, nuclear power plants, nuclear shipments or other sources, on a global scale are negligible and in the worst cases are detectable in limited areas in the vicinity of the source itself or on regional scale [Sam A. K. et al., 2000].

The Pu isotopes, ^{241}Am , ^{90}Sr , and ^{137}Cs are considered to be the most hazardous man made radionuclides due to their comparatively long half-life time and high radiological toxicity. There is a considerable number of literatures on the concentration of man-made radionuclides in marine environment, especially marine sediments and bio-organisms from different regions in the world [Guogang et al., 1998]. It has to be noted that no investigations have been carried out regarding marine environmental radioactivity in the Arabian Gulf.

Plutonium-238, which has a half-life of 87.7 years, is the isotope of choice for space missions because of its heat-producing capabilities. In 1964, a SNAP 9A (Systems for Nuclear Auxiliary Power) satellite failed to achieve orbit, re-entered the upper atmosphere and

incinerated. Its RTG (Radioisotopic Thermoelectric Generators) released its 2.1 pounds of plutonium 238 contents and an estimated 17 kilocuries (kCi) to the upper atmosphere. About 25 percent were deposited in the northern latitudes, with the remaining 75 percent settling in the Southern Hemisphere specifically southern Indian Ocean. Scientists later conducted samples around the world and found "SNAP-9A debris to be present at all continents and all latitudes [Hardy, E.P et al, 1972].

Another factor of importance is the Bushehr nuclear facility located on the other bank of the Arabian Gulf coast in Iran. This reactor might be considered as good incentives for conducting this kind of study. Before the reactor starts operation it is wise to take all necessary measurements so that any radioactive leakage that may happen in the future can be easily traced and detected.

EXPERIMENTAL METHODS AND PROCEDURE

A total of 10 samples of surface marine sediments as well as surface sea water were collected during May 2001 from 10 locations covering about 125 km of the Gulf Coast at Al-Khafji and Mneefa regions as shown in Fig.1. Locations of the collected samples were determined using a global positioning system (GARMIN GPS 100 SRVY II) which is a satellite based positioning and navigation system that provides precise position, velocity and time information. The uncertainty is ± 1.8 meter. Thus, for future reference, all collection sites can be predetermined by using the receiver's computed position to navigate to a location whose coordinates have been previously entered. A sediment sample was collected at a water depth ranging from 0 to 0.75 meter while other samples at depths ranging from 5 up to 25 meters. Due to the limited depth near the coast, which is a characteristic feature of the Arabian Gulf, samples were collected up to 7 kilometers from the shore. In tidal areas with shallow water sediment sampling was conducted by hand with assistance of a semi-cylindrical metallic, while deep-water bottom sediment samples were collected using 7 liters grab sampler. Concentration of deposited ^{137}Cs in sediment samples was determined by direct measurement of the gamma spectra of these samples after preparation in 0.5 liter marinelli beaker using a high resolution hyperpure germanium spectrometer. ^{137}Cs concentrations were determined using the 662 KeV gamma ray line. Other radionuclides of Pu isotopes, ^{241}Am , ^{90}Sr , and ^{137}Cs were analyzed using a combined procedure described by Moreno et al [Moreno J. et al., 1997]. Sediment samples were digested into a microwave oven. Sediment samples were ashed and six equal portions of mass 0.5 g each (total 3 g) were loaded into the 6 teflon vials of the microwave digestion oven. Six ml conc. HCl, 2 ml conc. HNO_3 and 2 ml conc. HF were added to each portion. The vials were sealed tightly and a digestion run of 30 minutes was carried out into the oven if any sample is not digested completely, additional acids are added and the digestion run should be repeated for complete digestion. The six digested fractions were combined together and spiked with ^{242}Pu and ^{243}Am radiotracers. Ten ml of strontium

carrier (1 mg/ml, as nitrate) were added and the solution was evaporated to dryness. The residue was converted to nitrate form by adding 5 ml of conc.HNO₃ and evaporated to dryness. The later evaporation process was repeated two times to ensure a complete conversion. The final residue was dissolved in 50 ml of 8M HNO₃ and filtered using a glass fiber filters and then submitted to the chemical separation procedure. Water samples (100 ml) were evaporated to dryness and (as in the soil samples) converted to nitrate form, dissolved in 50 ml of 8M HNO₃ and filtered. The sample was then submitted to the chemical separation procedure.

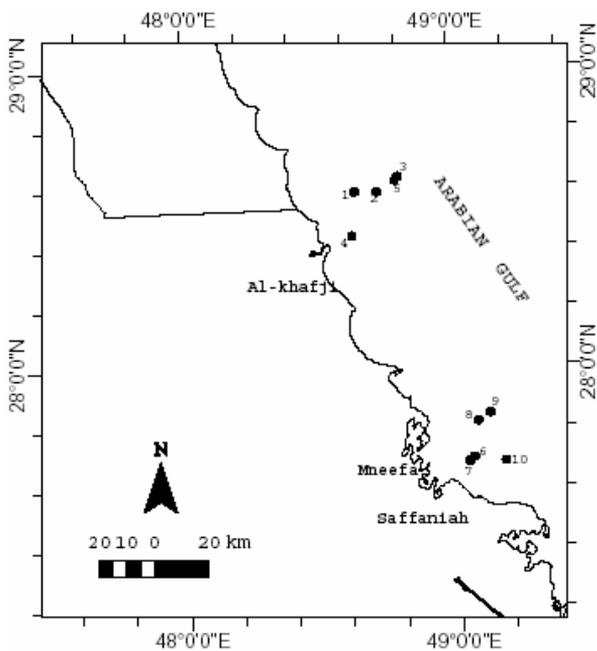


Figure . 1 Map showing the locations of the collected samples near Al-Khafji and Mneefa on the Arabian Gulf

Standard Reference Materials

²⁴²Pu and ²⁴³Am standard reference materials (purchased from the National Institute of Standards, NIST, USA, under the code numbers SRM 4334G and SRM 4332D respectively, were diluted and used as a spiking solutions in this study.

Separation of Plutonium

Before plutonium separation, the valence adjustment for possible plutonium isotopes in the sample (including the added radiotracer ^{242}Pu) was carried out to ensure complete mixing. Plutonium isotopes were separated by ion exchange chromatography using an anion exchanger (AG 1-8X, Cl-form) purified from possible thorium and stripped to get the pure plutonium fraction. The pure fraction of plutonium isotopes were prepared for measurement by precipitation with Nd^+ as fluorides [C.W. Sill, 1987, Shabana E.I. and Al-Shammari H.L., 2000], and filtered using 0.1 μm polypropylene membrane filter and mounted on stainless steel disk to get a very thin layer appropriate for alpha spectroscopic measurements and measured using high resolution alpha spectrometer.

The used alpha spectrometer was a Canberra Model 7404 “ Quad alpha “ spectrometer consisting of four 450 mm^2 silicon surface barrier detectors in four different vacuum chambers attached to a computer with necessary electronic devices and software to get four different alpha spectra representing the four different samples. Concentration of different alpha emitting radioisotopes namely Pu isotopes and ^{241}Am were determined from the peak areas of corresponding alpha groups

Separation of Americium-241

The effluent of the Pu separation column was evaporated and the residue was taken up in 2M HNO_3 and loaded into a 10 ml TRU-Spec column to separate americium. The later effluent contains possible strontium and was kept for strontium analysis. Americium and lanthanides were stripped with 4M HCl solution. Americium was purified from rare earth elements using a column packed with AG 1-X4 anion exchanger, Cl-form. The pure fraction of Americium isotopes was prepared for measurement by co-precipitation with Nd^+ as fluorides; and filtered using a 0.1 μm polypropylene membrane filter, mounted on stainless steel disk and measured using high resolution alpha spectrometer.

Separation of Strontium-90

For separation of strontium-90 [Moreno J. et al, 1997], three ml of 65% HNO_3 was added to the strontium containing effluent to get the sample in 3M acid solution. The sample was loaded into a column containing 3 g of Sr-spec. supported crown ether to separate strontium and stripping it by distilled water. For strontium source preparation, strontium was precipitated as oxalate from alkaline medium by adding 3ml of conc. ammonia solution. Then the precipitate was filtered, washed, dried and weighed for chemical recovery determination as strontium oxalate monohydrate, by gravity. The sample is then dissolved in 1 ml of 1M HNO_3 , mixed with 15 ml of optiphase “Hisafe” 3 LS cocktail and counted using liquid

scintillation counter. The ultra low-level liquid scintillation counter “Quantalus wallac “type model 1220 was used for ^{90}Sr counting.

RESULTS AND DISCUSSION

The activity concentrations of the transuranic isotopes, Pu isotopes, ^{241}Am , ^{90}Sr , and ^{137}Cs in the sediment samples collected from Al-Khafji area are presented in Table 1. For measurements of ^{238}Pu , the four detectors of the alpha spectrometer have shown some recoil contamination due to ^{222}Rn (5.490 MeV) which leads to higher background under ^{238}Pu energy peaks [(5.499 (71.6%) and 5.456 (28.3%)]. This increases the lower limit of detection. However, the low activity concentration and relatively higher detection limit for ^{238}Pu resulted in less precise results compared to those for $^{239+240}\text{Pu}$ and ^{241}Am .

The measured ^{238}Pu activity concentrations fall within the range of <LLD to 56 mBq/kg dry weight with an average value of 21.2 mBq/kg while the measured $^{239+240}\text{Pu}$ activity concentrations varied from <LLD – 8 mBq/kg with an average value of 5.2 mBq/kg. The observed concentration levels of ^{238}Pu in this area are appropriately comparable to the values reported for marine sediments from the Kara Sea [Hamilton, T. H. et al , 1994].

Table 1 Activity concentration (Bq/kg) of the radionuclides of interest in Al-Khafji sediment samples

Sample #	Lat. & Long.	Depth, m	^{90}Sr	^{137}Cs	^{238}Pu	$^{239+240}\text{Pu}$	^{241}Am
1	28 25 625N 48 32 388E	0	0.02 ± 0.01	0.05 ± 0.02	0.009 ± 0.006	0.006 ± 0.005	<LLD
2	28 25 625N 48 32 688E	8	0.11 ± 0.04	0.07 ± 0.02	0.011 ± 0.007	0.008 ± 0.07	0.018 ± 0.15
3	28 25 798N 48 32 977E	12	0.06 ± 0.03	0.05 ± 0.02	0.056 ± 0.038	0.008 ± 0.008	0.009 ± 0.009
4	28 26 035N 48 33 286E	18	0.03 ± 0.02	0.18 ± 0.03	<LLD	<LLD	0.041 ± 0.031
5	28 25 754N 48 33 872E	25	0.09 ± 0.02	<LLD	0.030 ± 0.027	0.004 ± 0.004	0.009 ± 0.009

The activity concentrations of the above man-made radionuclides are also measured in samples collected from Mneefa area (Table 2). The measured ^{238}Pu activity concentrations were found to range from 5 to 27 mBq/kg with an average value of 18.6 mBq/kg. The measured $^{239+240}\text{Pu}$ activity concentrations were ranging from <LLD to 12 mBq/kg with an

average value of 6.8 mBq/kg. The observed concentration levels of ^{238}Pu are comparable to those values found in Port Sudan [Sam A. K. et al., 2000]. The data analysis of Pu isotopes, ^{241}Am , ^{90}Sr , and ^{137}Cs of Al-Khafji and Mneefa of the Arabian Gulf indicate that all activity concentrations of the studied man made radionuclides were within the international limits.

Table 2 Activity concentration (Bq/kg) of the radionuclides of interest in Mneefa sediment samples

Sample #	Lat. & Long.	Depth, m	^{90}Sr	^{137}Cs	^{238}Pu	$^{239+240}\text{Pu}$	^{241}Am
6	27 35 412N 48 54 574E	0	0.03 ± 0.02	0.08 ± 0.02	0.017 ± 0.13	0.007 ± 0.005	<LLD
7	27 35 364N 48 54 519E	5	0.05 ± 0.02	4.91 ± 0.15	0.027 ± 0.025	0.009 ± 0.008	0.027 ± 0.019
8	27 35 850N 48 54 638E	10	0.14 ± 0.05	0.39 ± 0.04	0.020 ± 0.012	0.006 ± 0.005	0.019 ± 0.035
9	27 35 939N 48 54 800E	14	0.12 ± 0.02	5.69 ± 0.17	0.024 ± 0.023	0.012 ± 0.011	0.030 ± 0.030
10	27 36 297N 48 54 996E	15	0.02 ± 0.01	5.60 ± 0.16	0.005 ± 0.004	<LLD	0.007 ± 0.006

Comparative values of ^{238}Pu and $^{239+240}\text{Pu}$ activity concentrations in marine sediments from the literature are presented in Table 3. Although, there is a general lack of data in the literature on the Arabian Gulf radioecology, it may be concluded that the values of $^{239+240}\text{Pu}$ concentrations in Table 3 are much higher than those obtained from the Arabian Gulf which indicates that the fallout of nuclear testing and/or the Chernobyl accident of the former USSR have minor effect on that area or due to change in concentration with time due to environmental balance considerations. There is a time difference between the reported values and the present values.

Table 3 Levels of Pu isotopes from the literature (mBq/kg) comparing with Al-Khafji & Mneefa areas

Location	^{238}Pu	$^{239+240}\text{Pu}$	Reference No.
Kara Sea	10-60	370-1620	5
Ghazaouet Bay (Algeria)	20-50	300-600	10
NW Atlantic		680	11
Syrian coast (Latakia)		147 ± 25	12
Port Sudan (Sudan)	4.7-28.6	53-343	13
Al-Khafji	<LLD- 56	<LLD - 8	
Mneefa	5 - 27	<LLD - 12	

The activity concentrations of ^{90}Sr in the collected samples for Al-Khafji and Mneefa areas were 0.02 – 0.11 Bq/kg and 0.02 – 0.14 Bq/kg respectively (Tables 1 and 2). Thus all concentrations of ^{90}Sr fall within the international limits. Measurements of ^{137}Cs have depicted low levels ranging from <LLD to 0.18 Bq/kg for Al-Khafji and from <LLD – 5.69 Bq/kg for Mneefa. The relatively higher concentrations of cesium for Mneefa, compared with Al-Khafji, may arise from the fact that the nature and type of sedimentations are different for the two areas. The affinity of sediment for adsorption depends upon the nature and concentration of the surface adsorption sites. However, the activity concentration of ^{137}Cs in sediment of Al-Khafji and Mneefa are relatively low if compared with those for Port Sudan which falls in the range of 0.49 – 10.37 Bq/kg. [Sam A. K. et al, 2000]. The activity concentrations of ^{241}Am were <LLD – 0.041 Bq/kg for Al-Khafji and <LLD – 0.030 Bq/kg for Mneefa. These concentrations of ^{241}Am seem to be very low if compared with those of soil samples from the central region of Saudi Arabia, which vary from <LLD to 0.08 Bq/kg for plain areas and from 0.21 to 0.49 Bq/kg for closed depressions.

The activity concentration ratio of $^{238}\text{Pu}/^{239+240}\text{Pu}$ can be used to identify the source. This ratio was much higher from Chernobyl fallout than from other sources. The activity ratio $^{238}\text{Pu}/^{239+240}\text{Pu}$ in releases from nuclear fuel reprocessing plants, nuclear tests and weapon grade plutonium are about 0.25, 0.026 and 0.014, respectively compared to 0.47 in the Chernobyl fallout [Holm, E. et al, 1992]. The $^{238}\text{Pu}/^{239+240}\text{Pu}$ activity ratios ranged from <LLD to 7 for Al-Khafji and from 2 to 3.33 for Mneefa. This unexpected ratio might be due to the low accuracy and precision in the measurement of ^{238}Pu which came as a result of recoil contamination in the alpha spectrometer. Other studies found this ratio ranged from 0.02 to 0.07 in soil and plant samples [Guogang et al 1998 and Jia B. et al 1997]. According to this ratio, it is difficult to identify the source, but it may be due to the contribution of more than one source. The most probable sources are both Chernobyl fallout of plutonium isotopes and several decades of Pu fallout accumulation due to nuclear weapons testing. Releases from nuclear fuel reprocessing plants and weapons grade plutonium are expected to be minor or of negligible contribution.

CONCLUSION

The surface sediments from the Al-Khafji and Mneefa coastal areas in Saudi Arabia have very low activity concentrations of all studied man made radionuclides namely Pu isotopes, ^{241}Am , ^{90}Sr , and ^{137}Cs comparing with reported data from literature in different regions worldwide. It is recommended to measure, occasionally, the activity concentrations for all coastal areas along the west bank of the Arabian Gulf as well as the Strait of Hormuz due to its important location as a main gate of the Arabian Gulf.

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