WALAILAK JOURNAL
http://wjst.wu.ac.th Engineering and Physical Sciences

Gamma-Ray Measurements of Naturally Occurring Radioactive Materials in Sludge, Scale and Well Cores of the Oil Industry in Southern Iraq

Abdul Ridha HUSSAIN SUBBER*, Master Abdulla ALI and Walead Hamead AL-MOSAWY

Department of Physics, College of Education, University of Basra, Basra, Iraq

(*Corresponding author's e-mail: dabrhs@hotmail.com)

Received: 15 November 2012, Revised: 11 February 2013, Accepted: 10 March 2013

Abstract

Radioactivity of nuclides ^{238}U, ^{226}Ra, ^{232}Th and ^{40}K was measured in soil by γ-ray spectrometry using a NaI (Li) detector. A criterion was set in order to analyze sludge samples from oil fields and oil well-cores in southern Basrah, in the Iraq oil fields. More than 3 γ-ray energy peaks were used for the determination of ^{226}Ra and ^{232}Th activity concentrations to obtain results that are more accurate. Relationships between the measured radionuclides were discussed. Radionuclides ^{238}U and ^{226}Ra were found in disequilibrium with ratio of specific activities (^{238} U/^{226} Ra) less than unity for most of the sludge and core samples. The content of radioactive elements in the sludge, scale and well core is found within the range of other petroleum countries in the region.

Keywords: Gamma ray spectroscopy, oil sludge, oil well core, radium, NORM

Introduction

The oil and gas industry represents by far the largest industry in Iraq in terms of economical importance. Altogether, more than 40 oil fields are distributed in the country. The largest fields are in Basrah Governorate, which produces the largest waste by mass; from this industry as sludge and scale co-reduced with the oil and gas. The oil well-core is a solid sample of rock in the shape of a cylinder, taken from within the drilled oil or gas well. This core is a part of oil production waste that appears during the well drilling process. One problem with sludge waste is that it may contain elevated levels of Naturally Occurring Radioactive Materials (NORM). Uncontrolled disposal of these types of waste could lead to environmental pollution and thus eventually to radiation exposure of members of the public. This is a major challenge faced by oil producers and refineries, to safely dispose of oil sludge, scales, drilling well-cores and water generated during the processing of crude oil, as improper disposal could lead to environmental pollution, particularly soil and ground water contamination with toxic hydrocarbons, salt, and heavy elements. The presence of radioactive elements in the oily sludge and scale has been recorded in several works [1-9].

However, the largest generated volume of these wastes is water. The production water is usually separated from oil and disposed of by some means such as down an injection well or disposal well. Radioactive waste contains NORM, mainly from the natural radioactive series (^{238}U, ^{235}U and ^{232}Th), together with Potassium (^{40}K), or the production water, which contains mainly Radium isotopes which are alpha and gamma emitters. These radioactive isotopes are part of the natural radioactive series, with ^{226}Ra a daughter of ^{238}U and ^{228}Ra is a daughter of ^{232}Th and dissolves in production water when it contacts the rocks surrounding the oil well during crude oil production. Sludge, oily sediment that produced during the cleaning operation of oil separators storage tanks and other surface equipment, considered as the main

source of sludge contamination. Sludge is a mixture of residues left in the process of oil refining. It is made up of sand pumped up during the extraction of the oil, heavy hydrocarbons like paraffin. Scales are formed in the interior surface of ducts, pumps, and valves and also on the walls of separation and storage tanks. The other type of waste is the drilling waste (mud and well core), which comes out during the drilling operation. The concentrated sludge, scale and well-core after the industrial processes produces a highly concentration radioactivity, called Technologically Enhanced Naturally Occurring Radioactive Material (TENORM). The aim of the present work is to investigate the presence of gamma radioactivity in the sludge and oil well-core using gamma ray spectroscopy.

Materials and methods

Samples were collected from oil fields in the western south of the Basra Governorate, Iraq. Gamma surveys were done around pipelines and equipment at various locations, using a portable gamma detector, in order to identify the points in the process where gamma radiation was high enough to cause risk to the workers. The same was done around the barrels in the storage area located in the field of the maintenance unit. These barrels are filled with scale and sludge removed from the tanks and ducts during cleaning and maintenance operations. The survey in the laboratory was done with NaI (Li) 3×3, Spec Technologies, USA. The detector is shielded using 5 cm lead on all sides to reduce the background level of the system. Before measurement, the system was calibrated using ^{137}Cs and ^{60}Co gamma radioactive sources, which produce gamma energy at 662, 1173, 1334 keV, respectively. With these sources, it was possible to convert channel number to an energy scale. Sludge samples were taken either from inside the barrels before sending to the storage area, from the bottom of equipment opened for cleaning and maintenance or from the ground near crude oil main tanks. Scales were collected from the inside walls of ducts and used equipment and from barrels stored in the patio. Samples were taken also from the nearby separation units of oil, water, and sediment. The core samples collected during the drilling operation and from different depths starting from 100 up to 4000 m. The samples collected from different locations were each about 1 kg in mass. They were ground, homogenized and sieved by a crushing machine. The samples were then placed for drying at 110 °C for 24 h to ensure that moisture was completely removed. They were left undisturbed for 4 weeks, the time necessary for the secular equilibrium of the progeny from both the ^{238}U and ^{232}Th series. After that time, their radionuclide content was determined by gamma-ray spectrometry using a NaI detector. Counting time was at least 10 h, in order to accumulate enough counts under the peak and keep down the errors in the measurements; each measurement was repeated twice. The efficiency calculation of the system was carried out through different single-element radioactive sources, including, ^{109}Cd, ^{137}Cs, ^{57}Co, ^{60}Co, ^{22}Na and ^{54}Mn. Although the NaI gamma ray spectrometer has a poor energy resolution, it is suitable for the purpose of the present investigation, since its high efficiency and allows fast and precise intensity determination [10].

Both ^{226}Ra and ^{228}Ra were measured taking into account the condition of secular radioactive equilibrium between ^{226}Ra, ^{228}Ra and their direct progeny. The concentration values for ^{226}Ra were calculated by measuring the total counts under the 609.3 keV peak of ^{214}Bi. This higher energy peak was chosen instead of the 352 keV peak of ^{214}Pb to avoid problems with the auto-absorption of the lower energy gamma rays. The 186.2 keV line emitted by ^{226}Ra was not used in these measurements because it is too close to the 185.7 keV line from ^{235}U and the uncertainty in the measurement can be high.

The concentration values for ^{228}Ra obtained by integrating all the counts under the peak for the 911 keV gamma ray of the ^{228}Ac, one of its progeny. ^{228}Ra does not emit any gamma ray of significant energy to be able to measure directly, especially for low concentrations in the sample. The ^{232}Th concentration was obtained mainly from 911.20 and 2614.53 keV, while ^{40}K concentration was obtained by the 1460.83 keV peak. The count rate for each detected photopeak and activity for each of the detected nuclides were calculated. The specific activity in unit of Bq/kg is given as [11];

$$A_{Ei} = \frac{NP}{t_c I_\gamma(E_\gamma)\varepsilon(E_\gamma)M} \quad [Bq/kg] \tag{1}$$

where NP is the net peak counts, ε (Eγ) is the absolute full energy peak efficiency of the detector at this particular gamma-ray energy, t is the counting life time, $I_\gamma(E_\gamma)$ the number of gammas per disintegration of this nuclide for transition at energy E (branching ratio) and M the mass in kg of the sample. Under the assumption that the secular equilibrium reached between ^{232}Th, ^{238}U and their decay products, the measurement of gamma ray concentrations was done.

Radium equivalent activity

Radium equivalent activity (R_{aeq}) is used to assess hazards associated with materials that contain ^{226}Ra, ^{232}Th and ^{40}K in Bq/kg. which is, determined by assuming that 370 Bq/kg of ^{226}Ra or 260 Bq/kg of ^{232}Th or 4810 Bq/kg of ^{40}K produce the same γ dose rate. The R_{aeq} of a sample in (Bq/kg) can be calculated using the following equation [11];

$$Ra_{eq} = A_{Ra} + 1.43A_{Th} + 0.077A_K \tag{2}$$

Some isotopic ratios, especially those for the long-lived radionuclides of the U decay series, can be used as an indicator for the radioactive equilibrium/disequilibrium [12]. The most common isotopic ratios used in this work include ^{226}Ra/^{238}U and ^{238}U/ ^{40}K. Equilibrium is achieved if the activity ratio between parent/daughter or between daughter/daughter is equal to unity.

Results and discussion

Sludge and Scale Gamma Spectroscopy

The activity concentrations for different nuclides in Bq/kg for 14 locations are given in **Table 1**. The activity concentrations A_{Ra}, A_{Th} and A_K relate to ^{226}Ra, ^{232}Th and ^{40}K, respectively. From **Table 1**, it is clear that the concentration of U-238 is less than Th-232 ranging from 17 to 202 Bq/kg and 8 to 2089 Bq/kg, respectively. The maximum concentration of ^{226}Ra is 96452 ± 160 Bq/kg. The Ra_{eq} activity ranges from 57 in location L13 to 99721 Bq/Kg in location L1. These levels exceed the value of 370 Bq/kg considered acceptable for safe soil. This means that, the sludge is not suitable for plantations unless it is properly treated.

The mean values for all samples are; 87, 3822, 1215, 870, 868, for ^{238}U, ^{226}Ra, ^{232}Th, ^{228}Ra and ^{40}K respectively and the total mean value is 1372 Bq/kg. From **Table 1** it is found that the main radioactive element in sludge and scale is radium. This is due to the solubility of the element in the produced waters, which is brought to surface along with the oil and some sand to produce sludge. In comparison with the measurements in other petroleum producers for radioactivity concentrations, listed in **Table 2**, we find that our results are within this range.

Table 1 Specific activities in Bq/kg of some sludge and scale sample.

Sample No	Samples Name	^{238}U	^{226}Ra	^{232}Th	^{228}Ra	^{40}k	Ra_{eq}
L1	Central Degassing Station South	202±20	96452±160	1413±243	9315±152	16213±253	99721±259
L2	Southern Degassing Station	138±2	85931±140	1197±113	7623±96	14628±155	88769±344
L3	Qurenit Degassing Station	116±2	17623±207	976±163	7917±128	13876±222	20087±111
L4	Shamei Degassing Station	109±2	3290±215	2089±18	2211±10	489±19	6314±344
L5	Ratka Degassing Station	121±2	53261±730	11457±188	9213±145	14761±238	70781±276
L6	Central Degassing Station North	108±2	3890±315	7086± 35	6543± 45	619± 44	14070±98
L7	Second Degassing Station	56±3	2987±401	386±25	289±12	599±150	3385±85
L8	Thread Degassing Station	107±3	53260±876	1147±166	9813±123	14722±324	56034±112
L9	Fourth Degassing Station	96±3	42311±643	10122±113	8954±98	12863±182	57775±123
L10	Fifth Degassing Station	118±5	48321±722	9834±111	7822±93	13213±221	63401±253
L11	Sixth Degassing station	18±1	125±9	68±11	85±13	52±3	226±25
L12	Seventh Degassing station	31±2	3391±29	53±3	268±4	132±11	3477±88
L13	Eighth Degassing station	21±5	36±6	8±1	9±1	120±6	57±14
L14	Majnoon Central St.	17±7	38±4	8±2	10±2	117±6	58±11

Table 2 ^{238}U, ^{226}Ra, ^{228}Ra and ^{40}K activity concentrations (kBq/kg) for scale and sludge samples collected from different studies [13 and references therein].

Country/material	^{238}U	^{226}Ra	^{228}Ra	^{232}Th	^{40}K
Brazil/scale		19.1 - 323.0			
Brazil/sludge		0.36 - 367.0	4.0 - 23.5		
Algeria/scale		1.0-950			
Algeria/sludge		0.1 - 0.393			
Tunisia/scale		4.3 - 658			
Norway/sludge		0.3 - 32.3	0.3 - 33.5		
Various location		< 1000			
UK/scale		0.1 - 270	0.2 - 180		
UK/sludge		5.0 - 50.0	1 - 170		
Oman/sludge		1.1 - 5.67	0.47 - 0.92	0.11 - 0.61	
EUA/sludge		15000			
EUA/scale		26000			
USA/scale		10^4 - 10^6			
USA/sludge		Up to 10^6			
Iraq/sludge, scale present measurement	**0 - 0.202**	**0.125 - 96.5**	**0.05 - 9.81**	**0.01 - 11.45**	**0.04 - 56.3**

The well-core gamma spectroscopy

Typical well-core samples are shown in **Figure 1**. Samples were taken at regular intervals of 250 m, ground, dried and sieved in an isolated hood. The sample containers were well sealed and left for 4 weeks to reach equilibrium. The NaI scintillation counter used for NORM gamma ray concentration emitted from samples were collected using software UCS30 supplied by the manufacturer. The locations of oil wells and their codes are listed in **Table 3**.

Figure 1 Sample of the well core.

Table 3 Oil well locations in the oil fields in Basra Governorate and their codes used in the present work.

Sample number	Oil well name and location	Oil well code
WC1	*Rumailla* south southern west of Basra city	Ru-278
WC2	*Rumailla* north southern north of Basra city	Ru-277
WC3	*Ratawia* north of Basra city	Rt-11
WC4	*Tuba* north of Basra city	Tu-3
WC5	*Rumailla* north southern north of Basra city	R-7
WC6	West *Qurna* north of Basra city	WQ-31
WC7	*Zubair* west of Basra city	Zb-110
WC8	*Lahais* west of Basra city	Lu-22
WC9	*Nahr Umr* north of Basra city	NR-13
WC10	*Zubair* west of Basra city	Zb-122

The radioactivity concentrations, listed in **Table 4**, for 10 locations of the oil fields show a high amount of radium concentration in all 10 well cores, which is as expected, due to the high concentration of radon measured in the previous study [8].

Table 4 Radioactivity concentration of ^{238}U, ^{232}Th series and ^{40}K (Bq/kg) in well core (WC) samples from different locations in the oil fields of southern Iraq, taken at a depth of 4000 m.

Sample No	^{238}U	^{226}Ra	^{232}Th	^{228}Ra	^{40}K	Ra_{eq}
WC1	103±9	52600±463	5721±50	4312±70	18654±155	61386
WC2	82±7	41236±362	3256±28	3578±58	722±13	45947
WC3	65±6	32812±289	2712±23	3240±52	651±11	36740
WC4	52±4	28800±273	1113±9	1730±28	519±8	30431
WC5	49±4	19242±169	1432±12	1620±26	359±6	21316
WC6	67±6	36535±322	2238±19	3820±62	663±11	39786
WC7	57±4	33131±292	1120±19	1486±24	471±8	34768
WC8	44±4	18200±160	869±17	1413±22	357±6	19470
WC9	37±3	16221±143	636±6	1130±18	323±5	17154
WC10	36±3	17300±152	512±5	1444±23	212±3	18048

Figure 2 shows the summary of gamma spectroscopy results presented as a bar chart for the 10 wells. According to the high gamma ray concentration results, one has to pay attention to the protection of the workers in the field, when they deal with this TENORM in the oil industry. There are 2 kinds of exposures from the cores; the first one is the inhalation of radon gas (daughter of ^{226}Ra and ^{228}Ra) from the core rocks or the dust, the second is the external gamma radiation from bulk storage or thrown on the earth surface as waste materials. There is another concern of radioactive exposure, which is the inhalation of dust containing radioactive isotopes during equipment cleaning or bare contact with the core material.

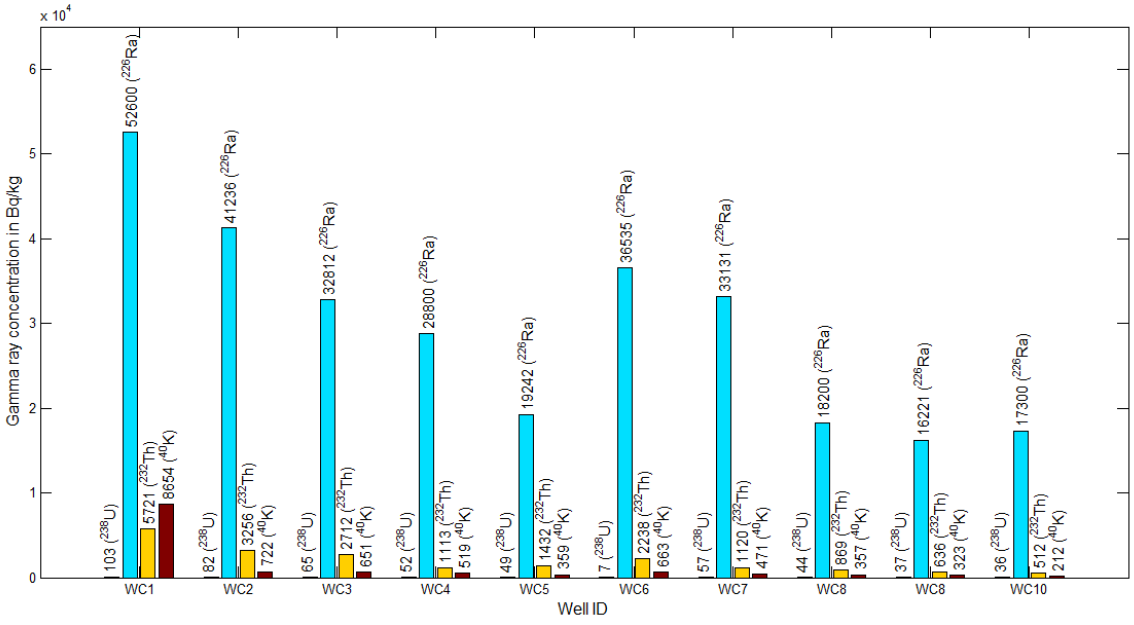

Figure 2 Gamma ray radioactivity of well-core samples.

Five oil well-cores samples (WC1, WC2, WC3, WC4 and WC5) were analyzed according to the depth from which the samples were collected with the results presented in **Figures 3 - 7**. The result shows a high concentration for ^{226}Ra compared with the other concentrations. The figures show also a trace of ^{238}U in all well-core samples. All the activities increase with depth, almost linearly, especially in the case of ^{226}Ra.

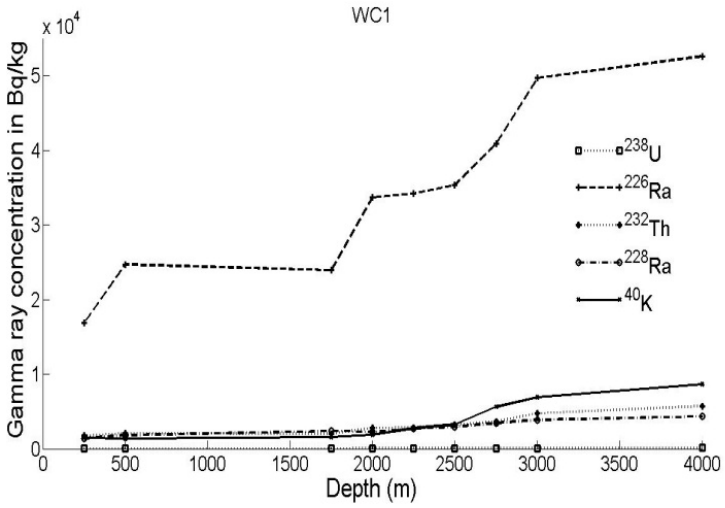

Figure 3 Gamma radioactivity concentration as a function of well core depth (WC1).

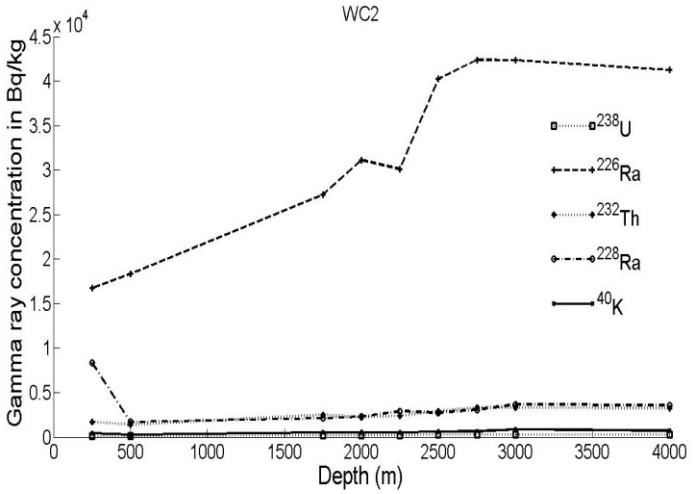

Figure 4 Gamma radioactivity concentration as a function of well core depth (WC2).

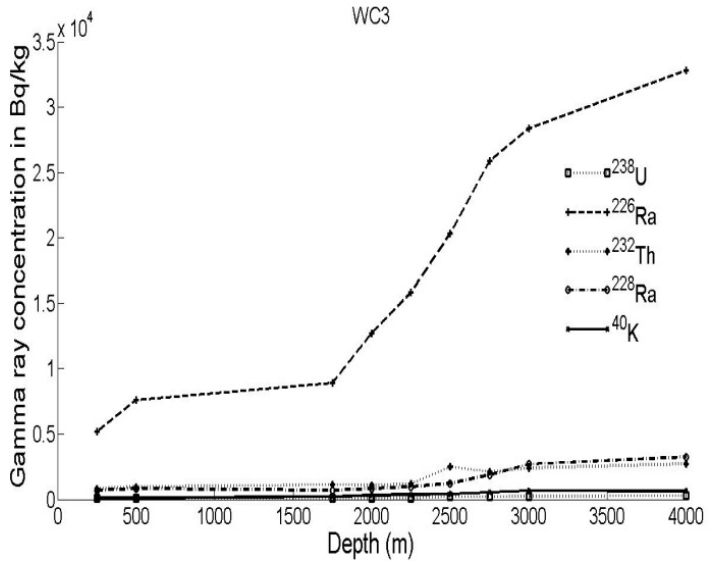

Figure 5 Gamma radioactivity concentration as a function of well core depth (WC3).

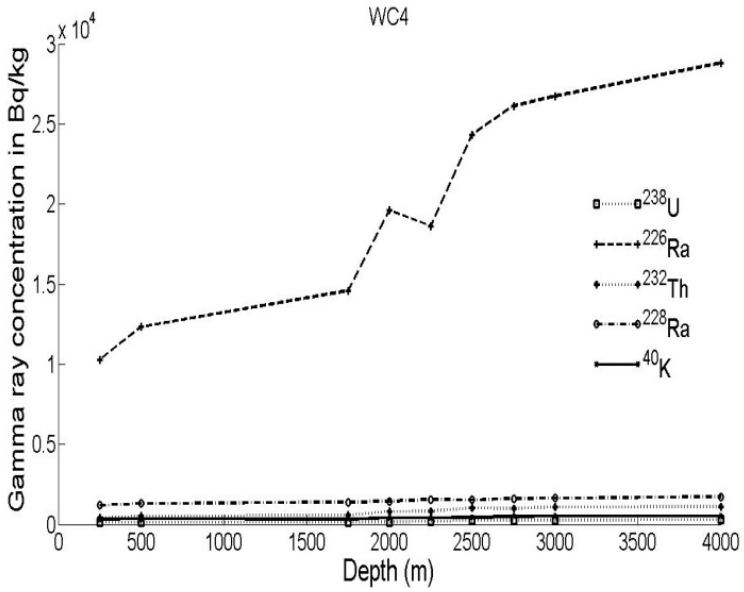

Figure 6 Gamma radioactivity concentration as a function of well core depth (WC4).

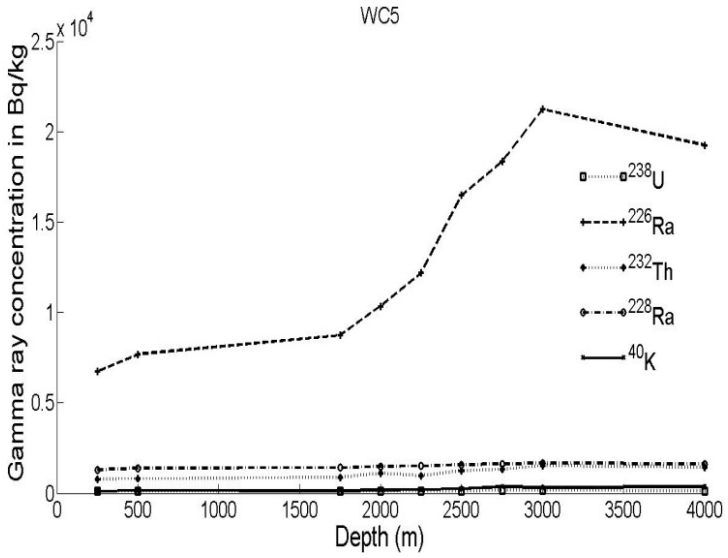

Figure 7 Gamma radioactivity concentration as a function of well core depth (WC5).

In order to observe a correlation between uranium, radium, thorium and potassium in the well core, graphs were plotted in **Figures 8 - 12**. Excellent correlation (0.9988) was found which indicates a strong evidence of a linear relationship between the activity concentration of ^{226}Ra and ^{238}U as shown in **Figure 10**, and correlation between ^{228}Ra and ^{232}Th (correlation coefficient 0.9698). A detailed analysis of the data indicates that there is some degree of positive correlation between the activity concentrations of ^{40}K with ^{238}U (R = 0.9242) and ^{226}Ra (R = 0.9298) in the core samples.

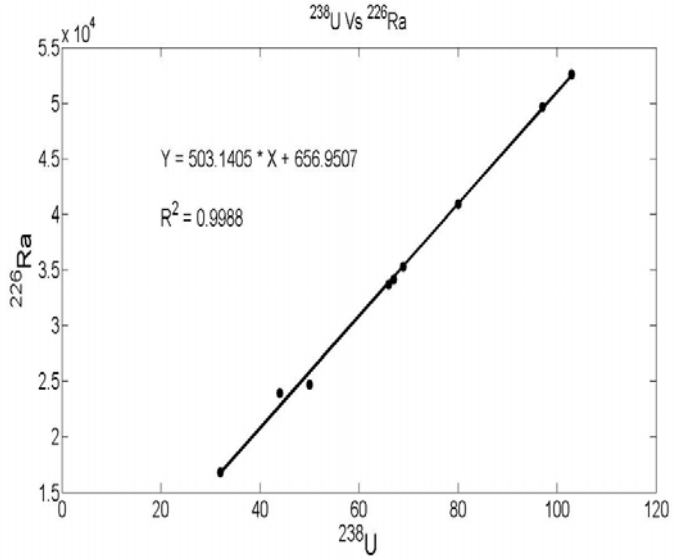

Figure 8 The correlation between ^{238}U and ^{226}Ra concentration in oil well-cores.

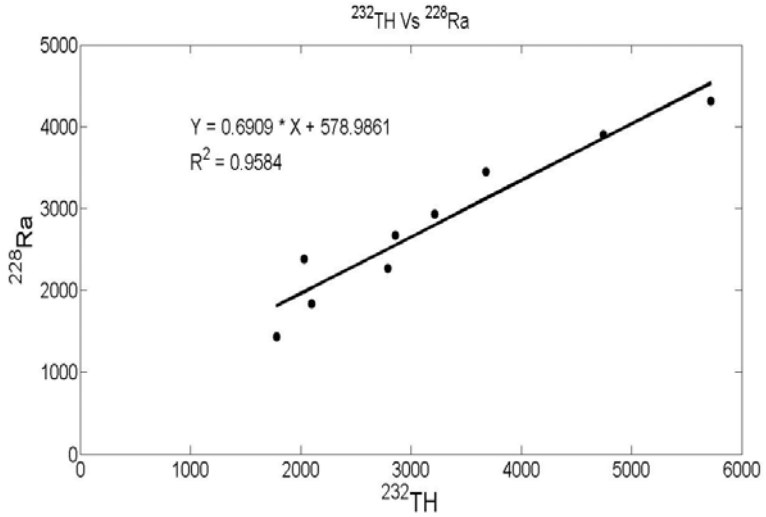

Figure 9 The correlation between ^{238}Ra and ^{232}Th concentration in oil well-cores.

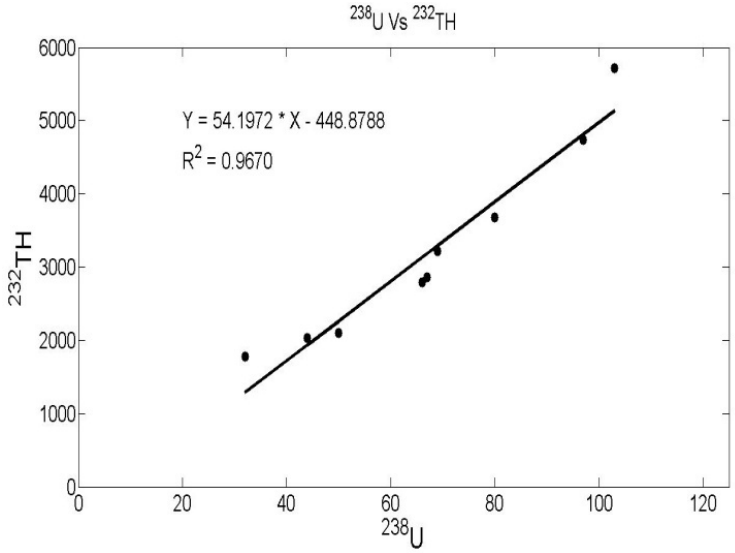

Figure 10 The correlation between ^{238}U and ^{232}Th concentration in oil well-cores.

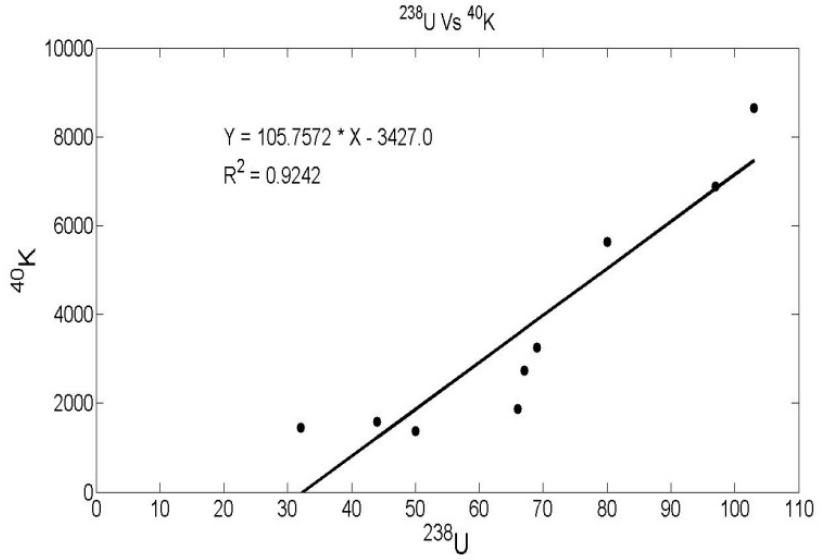

Figure 11 The correlation between ^{40}K and ^{238}U concentration in oil well-cores.

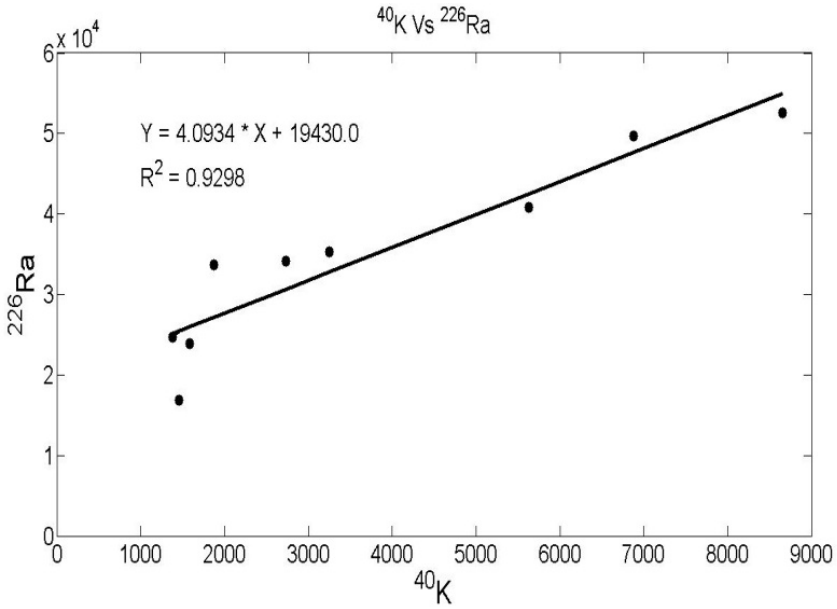

Figure 12 The correlation between ^{226}Ra and ^{40}K concentration in oil well-cores.

Potential environmental impact

The potential impact on the environment involves the effect of gamma radiation oily sludge on public health, livestock and crops. The results obtained in the present measurements do not indicate any immediate health hazard for the host communities. Some places however need further investigation, with a special emphasis on the control of ^{226}Ra and ^{222}Rn releases to prevent pollution of the environment with

these radionuclides. The flared ionizing radiations (radon gas) into the atmosphere precipitate upon condensing as rain water, thereby constituting radioactive rain water pollution. The growing concern amongst the population about the quality of their environment increases the significance of impact assessment of radioactive releases into the environment even if natural radionuclides occur.

Conclusions

The oil sludge, scale and well core material were successfully analyzed for radioactive elements, namely ^{238}U, ^{232}Th, ^{226}Ra and ^{40}K. The results clearly show that the radioactivity levels in both sludge and well core samples exceed the limits set by the EPA, but within the range found in nearby countries. Nevertheless, the health burden due to natural background radiation from oil production west on the inhabitants of these areas is high and hence carries significant health hazards. The data obtained in this study will serve as baseline data for the proper assessment of radiation exposure. Good correlation exists between the selected samples. The results also show symmetrical distribution of all studied radionuclides. We conclude that if no remedial steps are implemented, there will be long-term risks to the health of the workers in the fields. There are no standard methods for the clearance or disposal of such waste and more efforts are required to set up such methods.

References

[1] EO Chukwuocha and PI Enyinna. Radiation monitoring of facilities in some oil wells in Bayelsa and rivers states. *Sci. Afr.* 2010; **9**, 98-102.
[2] HB Pitta and ASN Rao. Gamma ray spectrometry of well cores for identification of Lithologies of pacific margin basins of India. *Arab. J. Sci. Eng.* 2011; **36**, 21-9.
[3] OGP, Guidelines for the management of Naturally Occurring Radioactive Material (NORM) in the Oil and Gas Industry 2008, International Association of Oil and Gas Producers, Publications, Report No. 412.
[4] AC Canoba, GA Gnoni and WA Truppa. Norm measurements in the oil and gas industry in Argentina. *In*: Proceeding of the 5th International Symposium on Naturally Occurring Radioactive Material, Sevilla España 2007, p. 19-22.
[5] AN Karen, P Smith, DL Blunt, P Gustavious and P Williams. An Assessment of the Disposal of Petroleum Industry NORM in Nonhaz Ardous Landfills. Institute Washington, DC, 1999.
[6] EA Pillay, M Fadhil, S Salih and MI Maleek. Radioactivity in oily sludge and produced waste water from oil: environmental concerns and potential remedial measures. *Sustainability* 2010; **2**, 890-901.
[7] ARH Subber, MA Ali and TM Salman. Radon concentration in oily sludge produced from oil refineries in the southern oil plant at Basra Governorate - Iraq. *Arch. Appl. Sci. Res.* 2011; **3**, 263-71.
[8] ARH Subber and MA Ali. Measurement of radon exhalation rate from core of some oil wells in Basra Governorate in the southern Iraq. *Adv. Appl. Sci. Res.* 2012; **3**, 563-71.
[9] International Association of Oil and Gas Producers. Guideline for the management of naturally Occurring Radioactive Material (NORM) in the Oil and Gas Industry. Report No. 412, 2008, p. 1-4.
[10] EPA Office of Compliance Sector Notebook Project, U.S. Environmental Protection Agency, Profile of the Petroleum Refining Industry, 1996, EPA/310-R-95-013, p. 1-146.
[11] OBS Karatepe and M Dogru. Assessment of natural radioactivity and radiological hazards in construction material used in Elazig Turkey. *Radiat. Meas.* 2011; **46**, 153-8.
[12] S Singh, A Rani and RK Mahajan. ^{226}Ra, ^{232}Th and ^{40}K analysis in soil samples from some areas of Punjab and Himachal Pradesh, India using gamma ray spectroscopy. *Radiat. Meas.* 2005; **39**, 431-9.
[13] F Bou-Rabee, AZ Al-Zamel, RA Al-Fares and H Bem. Technologically enhanced naturally occurring radioactive materials in oil industry (TENORM). A review. *Nukleonika* 2009; **54**, 3-9.