MEASUREMENT OF ENHANCED RADIUM ISOTOPES IN OIL PRODUCTION WASTES IN TURKEY

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HIGHLIGHTS

- Gamma dose rates of oil production equipment and waste were measured externally by survey meter.
- Activity concentrations of radium isotopes in oil production waste were determined by gamma ray spectrometers.
- Enrichment factors were calculated for radium isotopes in oil production wastes.

ABSTRACT

Gamma dose rates of oil production equipment and wastes were measured externally by survey meter. They were found to be between 0.2 μSv h^{-1} and 25.7 μSv h^{-1}. Activity concentrations of radium isotopes in crude oil, scale, sludge, contaminated soil and water samples were determined by gamma spectrometric method. Activity concentrations of ^{224}Ra, ^{226}Ra and ^{228}Ra in samples varied from MDA to 132,000 Bq kg^{-1}. Radium isotopes enriched up to 14,667 times in scale samples. The highest value of ^{226}Ra was found to be 35,122 ± 1,983 Bq kg^{-1} for sludge samples. Activity concentrations of a considerable number of samples were found to be higher than the exemption level recommended by IAEA. Measurement results revealed that oil production wastes caused soil contamination up to 70,483 Bq kg^{-1}. They may pose a radiological risk for workers and members of the public.

1. Introduction

The presence of naturally occurring radioactive materials (NORM) in oil and gas industry has been known since the beginning of 1900s (IAEA, 2003; Mc Lennan, 1904). Many studies have been reported for scale and sludge wastes originated from oil and gas industrial processes (API, 1992; Al-Masri et al., 1997). In these studies, ^{226}Ra activity concentrations have been found well above natural background levels. Moreover, the activity concentration of ^{226}Ra has been found to be 15 MBqkg^{-1} in a published scientific study (Jonkers et al., 1997).

The production quantities and radionuclide concentrations of NORMs depend on many parameters in particular geological structure of reservoir. Activity concentrations of NORMs may incompatible with each other even if samples are taken from different wells of same region. Therefore, each study contains original results concerning NORM information in oil industry.

Petroleum maintains its importance as one of the most prevalent energy sources in the today's world due to the continuous increase of its demand and production. Therefore, possible detrimental effects of petroleum origin NORM wastes to workers or members of public also keep its significance as a common radiological concern even today. Many institutions and researchers still work on the NORM problems in oil industry for this reason (Bassioni et al., 2012; Khodashenas et al., 2012).

^{238}U, ^{235}U and ^{232}Th decay series, ^{87}Rb and ^{40}K are known as primordial naturally occurring radionuclides. They are found on more or less in every material from Earth's crust or industrial wastes (IAEA, 2010). ^{226}Ra from ^{238}U series, ^{224}Ra and ^{228}Ra from ^{232}Th series and ^{40}K are frequently encountered radiologically significant radionuclides in oil and gas industry. Therefore, researchers mostly regard these radionuclides as significant in their studies.

Crude oil, formation water, and gas are found as a mixture in reservoir. The formation water contains many cations of calcium, strontium, barium, radium and their isotopes (IAEA, 2010). These isotopes are found as dissolved in the water and occurred in consequence of water-rocks interactions. When the liquid mixture reach to the surface, radionuclides can accumulate on the inner part of equipment as scale due to changed thermodynamic conditions (such as temperature, solubility, pressure, acidity etc.). Scale is a compound of sulphate and/or carbonate (Parmaksız et al., 2013). ^{238}U and ^{232}Th, which are parent radionuclides of natural radioactive series, have a low solubility in water. Therefore, they do not reach to the surface from reservoir through the oil-gas-water mixture. However, their decay product radionuclides (^{226}Ra, ^{224}Ra and ^{228}Ra) migrate to the surface through the oil-gas-water mixture. Thus, ^{226}Ra, ^{224}Ra, and ^{228}Ra are regarded as "unsupported radionuclides" in the oil and gas industry (Shawky et al., 2001). Many researchers have paid special attention about scale, sludge or produced water containing elevated activity concentrations in the oil industry (Parmaksız et al., 2013; Bakr 2010; Darko et al., 2012).

There is not a comprehensive study concerning NORMs generated from oil production industry in Turkey. However, it was known that high dose rates were detected from outer surface of some equipment of oil wells and their scrap metals generated in maintenance operations of oil production facilities. A recent study concerning sludge wastes gave an important hint about the possibility of having NORMs with high activity concentrations in oil production facilities in Turkey (Parmaksız et al., 2013). In the aforementioned study, enrichments of naturally occurring radionuclides were determined in residues of oil refineries.

According to the Environmental Protection Agency (EPA), petroleum industry generates approximately 260,000 metric tons NORM waste (produced water, scale, sludge, and contaminated equipment) in every year in the United States (EPA, 2013). The United States and Turkey produce 325.2 and 2.4 million tons of oil per year respectively (PIGM, 2013). Considering these data, it is estimated that the oil industry have produced approximately 19,000 metric tons of NORM waste in the last decade in Turkey.

Gamma dose rates of well components (scrap metals, production manifolds, separators, production lines etc.) were directly measured from the outer surface of the equipment by dose

rate meters in this study. Activity concentrations of ^{224}Ra, ^{226}Ra and ^{228}Ra radionuclides in water, contaminated soil, scale, and sludge samples collected from oil production facilities were determined by using gamma-ray spectrometers and finally results were discussed.

2. Material and method

2.1. Study Area

The study area is located in the southeast part of Turkey (Figure 1). The oil production is carried out in 26 different oil fields by using 209 oil wells in the region. In the country, approximately twenty percent of petroleum production is carried out in this region (Silkroad development agency, 2014). Four hundred cubic meters of natural gas are also produced per day in the region. It corresponds approximately one percent of natural gas production of the country.

Figure 1. Location of study area

Scale, which occurs in consequence of maintenance operations of equipment, is deposited in waste storage area. Many scrap metal equipment (production lines, pumps etc) contaminated by NORM are also deposited in the storage area. Sludge that is formed during oil production processes are deposited in warehouse and a portion of them is embedded in the ground without any radiation protection measures. Water, which rises to the surface by oil-gas-water mixture,or originates from production processes, is injected back into wells so as to enable pressure balance.

2.2. Dose rate measurements

There are many methods for measuring radiation. The most practical and widely used method among these is to measure of radiation dose rate by survey meter. It is very useful and convenient method for detecting radiation as initial examination tool. Therefore, dose rate measurements were performed primarily for the detection of radiation in this study. Commercially available Radiagem 2000 personal portable dose rate and survey meter was used for measurements. Ambient dose rates were measured initially in order to eliminate contributions

of terrestrial and cosmic radiation. Then, they were subtracted from dose rates of studied samples.

Radiagem 2000 personal portable dose rate and survey meter, which has a Geiger Mueller energy compensated detector, is suitable for gamma and X-ray measurements. It has a measurement range between 0.01 μSvh^{-1} and 100 $mSvh^{-1}$. Radiagem 2000 personal portable dose rate and survey meter has an energy range (International electrotechnical commission-IEC 60846) from 40 keV to 1.5 MeV. It has also a sensitivity of 0.83 c/s per μSvh^{-1}, an accuracy of ±15%, a response time range of 1 s to 10 s for average. Radiagem 2000 personal portable dose rate and survey meter has features of complete and automatic self-test when switching on and periodical control of main function when in use.

Radiagem 2000 personal portable dose rate and survey meter is calibrated periodically by the Secondary Standard Dosimeter Laboratory (SSDL) of the Çekmece Nuclear Research and Training Center (ÇNAEM). SSDL is a member of IAEA/WHO Network of SSDLs and continues its activities in Metrology Department of ÇNAEM of the Turkish Atomic Energy Authority (TAEK).

2.3. Sampling and sample preparation

Fifty-four samples (crude oil, water, scale, sludge and contaminated soil) were collected from the oilfield processing units and waste disposal sites. Crude oil and water samples were taken from processing units and separators. Scale samples were collected from waste sites, storage tanks, their scrap equipment generated in maintenance operations, and their residues accumulated on the inner surface of pipelines (Figure 2). Sludge samples were taken from barrels stored in processing units and final disposal sites (Figure 3).

Determination of activity concentration of radionuclides in soil is not an object of this study. However, sludge has poured around some wells and cause soil contamination. Sludge transforms into liquid phase from solid phase at temperature over 35 degrees. In the studied region, temperature mostly rises above 40 degrees in the daytime of summer. Maintenance operations of wells were performed a long time ago and sampling time coincided with the summer. Therefore, pure sludge samples could not be taken for some wells. Soil samples contaminated by sludge during maintenance operations were collected instead of sludge from around the wells. Soil samples were taken from 4-5 cm of surface soil because contamination (leakage) was not observed beyond the 4-5 cm surface soil.

Samples were put into 1 L plastic container, labelled, arranged as motionlessly transport and brought to Health Physics Department of the Sarayköy Nuclear Research and Training Centre. Two different sample preparation procedures were applied for samples in internal dosimetry laboratory.

Routine sample preparation procedure was applied for scale and contaminated soil samples. Initially, they were heated in a temperature controlled drying oven at 105ºC until their moisture was completely removed. Then, samples were filled into cylindrical plastic analysis containers,

which have 6cm diameter and 5cm height. They were weighed, hermetically sealed with parafilm and kept for at least 30 days to reach secular equilibrium between ^{226}Ra and its short half-life daughters (^{214}Pb and ^{214}Bi).

Figure 2. Scale accumulated on the inner surface of scrap equipment

Figure 3. Scrap equipment contaminated with sludge

For sludge, routine sample preparation procedures could not be applied properly because it was observed that sludge samples transform into the liquid phase from solid phase at temperature over 35 degrees. Plastic analysis container could not be used for measurements due to containing a small amount of organic impurities. The container's wall and insulating material were damaged from sludge. Thus, it was decided to use glassware material as analysis container. Autoclave container, which made of glass material, was used as analysis container for gamma spectrometric measurements.

2.4. Radioactivity measurements

Gamma Spectrometry Laboratory (GML) is one of two accredited laboratories capable of performing gamma spectrometric measurements in Turkey. GML has been accredited in 2009

and is audited annually by experts of Turkish Accreditation Agency (TURKAK) since then. The gamma-ray analyses were carried out by using commercially available gamma spectrometry systems equipped with germanium detectors (Canberra and Ortec branded). Their relative efficiencies range between 10% and 150%. Gammavision-32 and Genie-2000 software were used for data analysis. Features of the most used system in the study are given as follows: p-type HPGe detector having 451 cm^3 active volume and equipped with DSA-1000 multichannel analyser, 110% relative efficiency, 85:1 peak-to-Compton ratio and 2.1 keV and 1.3 keV energy resolutions at 1332.5 keV of ^{60}Co and 122 keV of ^{57}Co, respectively. In order to minimize the natural background radiation resulting from cosmic rays and building materials, detector is placed in a shield which is composed of 10cm lead thickness, 9.5mm steel outer housing, 1mm thick tin layer, 1.5mm thick copper layer.

^{241}Am, ^{137}Cs and ^{60}Co standard point sources were counted for energy calibration in order to identify radionuclides in spectrum. The energy calibration was performed by using an analytical function of energy curve obtained from counted spectrum peaks. Absolute efficiency calibration of gamma spectrometry system was determined with a counted spectrum of certified radioactive standard volume sources obtained from the International Atomic Energy Authority (IAEA). IAEA reference materials of RGU-1 (U ore), RGTh-1 (Th ore) and RGK-1 (K_2SO_4) were counted with the same size and geometry of samples. Activity concentrations of samples were determined by using comparative activity estimation method. Net count rates of samples was compared with net count rate of reference materials after subtraction of natural background count rate (Gilmore and Hemingway, 1995).

Activity concentrations of ^{226}Ra, ^{224}Ra and ^{228}Ra were calculated from gamma ray photopic of decay products instead of their own energies. Because of the overlap between 185.7 keV of ^{235}U and 186 keV of ^{226}Ra, activity concentration of ^{226}Ra was calculated from 295.2 keV and 351.9 keV gamma ray energies of ^{214}Pb and 609.3 keV gamma ray energy of ^{214}Bi. The ^{228}Ra content of samples was determined by using 338.3 keV and 911.2 keV peaks of ^{228}Ac. The ^{224}Ra was calculated from 238.6 keV of ^{212}Pb. Gamma ray spectrum of an analysed scale sample showing the locations of photopics are given in Figure 4.

Activity concentrations (A) of the samples were obtained from following formula (El-Taher, 2009):

$$A = N_p/[\varepsilon(E_\gamma) \times P_\gamma \times M] \qquad (1)$$

where, N_p is the net count rate, $\varepsilon(E_\gamma)$ is the efficiency for $E_\gamma$energy, P_γ is abundance of the γ-line in a radionuclide, M is mass of the sample in kilograms. The minimum detectable activity (MDA) values for samples were calculated as follows (Currie, 1968):

$$MDA = 1.64\sigma_n/[\varepsilon(E_\gamma) \times P_\gamma \times t \times M] \qquad (2)$$

In the equation, σ_n stands for standard deviation of background in the region of interest and equal square root of the number of count for the background spectrum, t denotes measurement time in seconds.

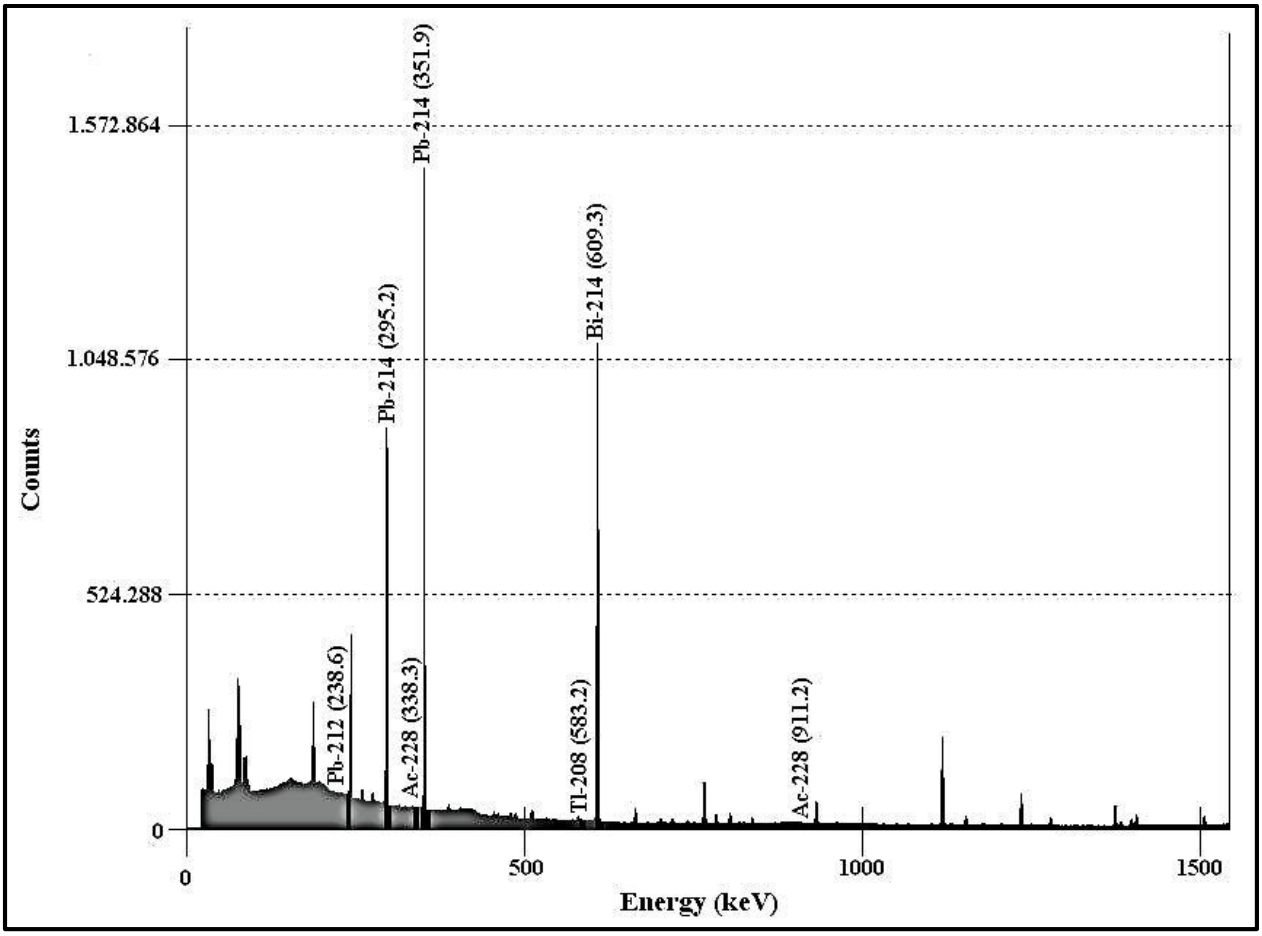

Figure 4. Gamma-ray spectrum of an analysed scale sample

3. Results and discussion

3.1. External gamma dose rates

Natural background dose rates were measured initially to determine contribution of terrestrial and cosmic radiation. Then, gamma dose rates of production equipment, scrap metal, scale, sludge and contaminated soil were measured externally and net dose rates were calculated by subtracting the contribution of natural background dose rates. Results were tabulated and given in Table 1. Majority of equipment could not be opened because of continuous production. Accordingly, dose rates were measured from outer surface of the equipment and an amount of dose rate contribution could not be measured by survey meters due to shielding of equipment. Considerable amounts of dose rates were detected although measurements were taken from the outer surface of the equipment.

The maximum dose rates reported in studies conducted in Algeria and Egypt was 100 μSvh^{-1} (Hamlat et al., 2001; El Afifi and Awward, 2005). Other studies conducted in the United

Kingdom and USA, maximum dose rate was found to be 300 μSvh^{-1} (Holland, 1998; Jonkers et al., 1997). Dose rates varied between 0.1 μSvh^{-1} and 6 μSvh^{-1} in studies carried out in Congo, Italy and Tunisia (Testa et al., 1994). Measurement results of this work were found to be within the expected range encountered in similar studies reported by IAEA (IAEA, 2003). Dose rates are consistent with the literature.

Table 1. External gamma dose rate ranges of this work and reported from similar studies

Location/ equipment	Gamma dose rate ranges (μSv h^{-1})	
	Present work	Similar studies' range (IAEA, 2003)
Down hole tubing, safety valves	up to 25.7	up to 300
Wellheads, production manifold	0.2-18.4	0.1-22.5
Production lines	0.2-3.0	0.3-4
Separators (scale, measured externally)	0.2-1.9	up to 15
Water outlets	0.2-0.4	0.2-0.5
Scrap equipment (externally)	0.8-3.0	-
Wellhead filter	7.8	-
Contaminated soil (with sludge)	0.2-18.7	-

3.2.Crude oil samples

Analysis results of crude oil samples collected from investigated region are presented in Table 2. The ^{224}Ra activity concentration of thirth-coded sample was found to be 3 ± 1 Bq kg^{-1}, others stayed below the level of MDA. The ^{226}Ra in crude oil samples ranged between MDA and 16 ± 3 Bq kg^{-1}. The maximum activity concentration of ^{228}Ra radionuclide in crude oil samples was found to be 9 ± 2 Bq kg^{-1}.

Table 2. Activity concentrations of crude oil samples

Crude oil	^{224}Ra (Bq kg^{-1})	^{226}Ra (Bq kg^{-1})	^{228}Ra (Bq kg^{-1})
1	<10	6 ± 2	<10
2	<11	16 ± 3	9 ± 2
3	3 ± 1	5 ± 1	2 ± 1
4	<7	<10	<7

Numbers given after "<" hypen indicate MDA values

In an Algerian work, ^{226}Ra in crude oil samples were given between 6 Bq kg^{-1} and 20 Bq kg^{-1} (Hamlat et al., 2001). Other studies conducted in US, activity concentrations of ^{226}Ra in crude oil were reported between 0.1 Bq kg^{-1} and 40 Bq kg^{-1} (Diyashev et al., 1994; Snavely, 1989). In an Egyptian work, the ^{226}Ra in crude oil were reported between 31 Bq l^{-1} and 2669 Bq l^{-1}(Bakr, 2010). In the recent study performed in Turkey, concentrations of all crude oil samples collected from refineries were found to be below the MDA (Parmaksız et al., 2013). According to UNSCEAR 2008 report, average concentrations of ^{226}Ra and ^{232}Th radionuclides in earth's crust

are 32 Bq kg^{-1} and 45 Bq kg^{-1} respectively (UNSCEAR, 2008). Radionuclide concentrations of crude oil samples were found to be compatible with similar studies and lower than average values of earth's crust as it is expected.

3.3. Scale samples

Scale accumulation of oilfield equipment is originated from precipitation of alkaline earth metal sulphates or carbonates according to the following chemical reactions (Attallah et al., 2012):

$$Ca^{+2} + CO_3^{-2} \rightarrow CaCO_3 \quad (3)$$
$$Sr^{+2} + SO_4^{-2} \rightarrow SrSO_4 \quad (4)$$
$$Ba^{+2} + SO_4^{-2} \rightarrow BaSO_4 \quad (5)$$

Therefore, activity concentrations of scale and sludge samples are much higher than crude oil and produced water samples. In this study, average ^{224}Ra, ^{226}Ra and ^{228}Ra concentrations in scales were found to be 123 Bq kg^{-1}, 20,614 Bq kg^{-1} and 129 Bq kg^{-1} respectively (Table 3). The ^{226}Ra was significantly higher in comparison with the other radionuclides. The highest ^{226}Ra in scale samples was measured as 132,000 ± 5,950 Bq kg^{-1}. Activity concentrations of ^{228}Ra in scale samples varied between MDA and 453 ± 28 Bq kg^{-1}.

Table 3. Activity concentrations of scale samples

Scale	^{224}Ra (Bq kg^{-1})	^{226}Ra (Bq kg^{-1})	^{228}Ra (Bq kg^{-1})
1	<10	10,670 ± 390	<10
2	64 ± 8	2,889 ± 88	79 ± 6
3	<3	756 ± 65	<3
4	<5	2,111 ± 88	<5
5	<6	3,292 ± 134	<6
6	<1	1,117 ± 34	<1
7	3 ± 1	40,969 ± 2,089	<2
8	<6	6,663 ± 267	<6
9	<4	1,319 ± 57	<4
10	3 ± 2	662 ± 20	9 ± 1
11	<1	774 ± 23	<1
12	<10	31,946 ± 974	<10
13	180 ±17	33,600 ± 1,452	138 ± 15
14	135 ± 15	33,600 ± 1,556	72 ± 12
15	159 ± 37	77,900 ± 3,600	193 ± 20
16	23 ± 13	6,250 ± 270	31 ± 10
17	3 ± 1	13 ± 2	3 ± 1
18	<15	168 ± 16	<1
19	502 ± 345	132,000 ± 5,950	453 ± 28
20	155 ± 19	34,500 ± 2,932	179 ± 19
21	121 ± 8	11,700 ± 600	132 ± 11

Activity concentration ranges of scales encountered in similar studies are presented in Table 4. It is clearly seen that radium concentrations in solid scales could reach to elevated levels (up to 3,700,000 Bq kg^{-1}) in oil and gas industry. The average radium concentration in scale was estimated to be 480 pCi g^{-1} (17,760 Bq kg^{-1}) by Environmental Protection Agency (EPA). Depending on the regional geology, it might reach up to 400,000 pCi g^{-1} (14,800,000 Bq kg^{-1}) according to EPA (EPA, 2013). In this study, the average activity concentration of ^{226}Ra in scale was calculated to be 20,613 Bq kg^{-1}. Accordingly, the result is compatible with similar studies encountered in literature.

Table 4. Activity concentration ranges of scale samples in similar studies

Country	^{226}Ra (Bq kg^{-1})	^{228}Ra (Bq kg^{-1})	Reference
Algeria	1,000-950,000		(Holland, 1998)
Australia	21,000-250,000	48,000-300,000	(APPEA, 2002)
Brazil	19,100-3,500,000	4,210-2,195,000	(Godoy and Cruz, 2003; Gazineu et al.,
Congo	97-151		(Testa et al., 1994)
Egypt	493-143,262	32-368,654	(Shawky et al., 2001; El Afifi, and Awwad, 2005; Abo-Elmagd et al., 2010)
Ghana	28-48	17-40	(Darko et al., 2012)
Italy	MDA(3)-2,890		(Testa et al., 1994)
Kazakhstan	510-51,000	200-10,000	(Kadyrzhanov et al., 2005)
Malaysia	114,300-187,750	130,120-206,630	(Omar et al., 2004)
Norway	300-32,300	300-33,500	(Lysabo et al., 1996)
Tunisia	31-658,000		(Testa et al., 1994; Heaton and Lamley, 1995)
Turkey	6-10	<MDA(2)	(Parmaksız et al., 2013)
UK	1,000-1,000,000		(EPF, 1987)
USA	15,400-3,700,000		(Scot, 1998; White and Rood, 2001)

3.4. Sludge samples

Analysis results of sludge samples collected from investigated region are presented in Table 5. Average ^{224}Ra, ^{226}Ra and ^{228}Ra in sludge samples were found to be 55 Bq kg^{-1}, 4,047 Bq kg^{-1} and 65 Bq kg^{-1} respectively. Activity concentrations of ^{226}Ra were determined to be higher than the other radionuclides for sludge samples. The highest value of ^{226}Ra was found to be 35,122 ± 1,983 Bq kg^{-1} for sludge samples.

A great number of analyses have been performed and data collected concerning naturally occurring radionuclides in sludge generated in oil and gas industry over the years. However, only a few reports and slightly more number articles have been published by this time. Activity concentration ranges of ^{226}Ra and ^{228}Ra radionuclides in sludge researches conducted various countries are given in Table 6. It is seen that concentrations of ^{226}Ra and ^{228}Ra in sludge range from less than MDA up to 413,000 Bq kg^{-1} in similar studies. In current study, activity

concentration results of ^{226}Ra and ^{228}Ra radionuclides were found within this range. Radium concentrations of scale are generally higher in comparison with sludge.

Table 5. Activity concentrations of sludge samples

Sludge	^{224}Ra (Bq kg^{-1})	^{226}Ra (Bq kg^{-1})	^{228}Ra (Bq kg^{-1})
1	<10	1,232 ± 41	<10
2	<7	14 ± 13	<8
3	51 ± 4	1,667 ± 95	65 ± 7
4	15 ± 3	1,810 ± 87	19 ± 3
5	<10	1,230 ± 65	<10
6	<2	621 ± 26	<7
7	10 ± 3	775 ± 35	6 ± 2
8	14 ± 9	870 ± 40	18 ± 5
9	<7	125 ± 10	<10
10	<8	<5	<10
11	178 ± 24	35,122 ± 1,983	188 ± 17
12	67 ± 6	3,950 ± 190	119 ± 11
13	<5	1,010 ± 47	<9
14	125 ± 27	21,171 ± 1,196	143 ± 14
15	14 ± 2	1,280 ± 110	15 ± 3
16	24 ± 4	988 ± 43	19 ± 4
17	53 ± 5	2,870 ± 140	59 ± 6
18	<1	4 ± 0.2	<1
19	<1	791 ± 24	<1
20	<10	1,360 ± 122	<2

Table 6. Activity concentration ranges of sludge samples in similar studies

Country	^{226}Ra (Bq kg^{-1})	^{228}Ra (Bq kg^{-1})	Reference
Australia	25,000	30,000	(APPEA, 2002)
Brazil	<LLD-413,000	<LLD-117,900	(Godoly and Cruz, 2003; Gazineu et al., 2005)
Egypt	5.3-18,000	1-13,250	(Shawky et al., 2001; Abo-Elmagd et al., 2010)
Ghana	2.8-47.5	2.6-55.8	(Darko et al., 2012)
Malaysia	6-560	4,520	(Omar et al., 2004)
Norway	100-4,700	100-4,600	(Lysabo et al., 1996)
Tunisia	66-453		(Testa et al., 1994)
Turkey	1.0-809.2	<MDA(0.2)-302.5	(Parmaksız et al., 2013)

LLD: Lower limit of detection

3.5. Contaminated soil samples

Removal from facility of scale and sludge containing naturally occurring radionuclides or equipment during maintaining or waste disposal processes can cause pollution in soil. Measurement results of soil samples contaminated by sludge is given in Table 7. Activity

concentrations of ^{226}Ra in contaminated soil samples varied between 24,793 ± 1,400 Bq kg^{-1} and 70,483 ± 2,137 Bq kg^{-1}. These results reveal an interesting inference regarding contaminated soil even though limited number of measurement results. The highest concentration of ^{226}Ra in soil samples was found to be approximately twice as much from sludge samples.

As stated in section 2.3, maintenance operations of wells were performed a long time ago from sampling. Sludge was poured to soil from mentioned wells and contaminated the soil.Thus, sludge sampling could not be performed for some wells due to lack of pure sludge. Instead of sludge, mixed soil samples contaminated by sludge were taken from 4-5 cm surface soil for previously mentioned wells. Due to the lack of the sludge samples, it is impossible to study radionuclide content of pure sludge or soil samples, or whether there is a radionuclide accumulation in soil or not. Measurement results indicated that some contaminated soil or sludge samples might have higher activity concentrations than that collected in current study. This study has also revealed a need concerning new, comprehensive and further studies on soil-sludge interactions and behaviours of radionuclides of sludge in the soil. In this study, chemical composition and organic content of soil and pedogenic processes should also be investigated.

Table 7. Activity concentrations of contaminated soil (by sludge) samples

Sample	^{224}Ra (Bq kg^{-1})	^{226}Ra (Bq kg^{-1})	^{228}Ra (Bq kg^{-1})
Contaminated soil-1	126 ± 10	24,793 ± 1,400	126 ± 13
Contaminated soil-2	<10	44,123 ± 1,343	<11
Contaminated soil-3	535 ± 33	70,483 ± 2,137	423 ± 34

3.6. Water samples

Activity concentrations of a facility-specific (not used commercially) a gasoline and five water samples collected from region were also presented in Table 8. For water samples, the highest ^{226}Ra and ^{228}Ra radionuclides were found to be 7.4 Bq kg^{-1} and 4.4 Bq kg^{-1} respectively. Concentrations are seen to be below detection limits for many of samples. For water (formation, produced or oilfield brine) samples, concentrations of ^{226}Ra and ^{228}Ra radionuclides encountered in similar studies are given in Table 9. Concentrations of ^{226}Ra in formation water, produced water or oilfield brine vary between 0.01 Bq l^{-1} and 217.5 Bq l^{-1}. Likewise, ^{228}Ra ranges from 0.05 Bq l^{-1} to 60.4 Bq l^{-1} for water samples as given in Table 9. In the present study, activity concentrations of ^{226}Ra and ^{228}Ra of water samples were found to be within expected range of literature.

Table 8. Activity concentrations of water and fuel samples

Sample	^{224}Ra (Bq l^{-1})	^{226}Ra (Bq l^{-1})	^{228}Ra (Bq l^{-1})
Water-1	4 ± 2	7 ± 2	<4
Water-2	<3	<4	<3
Water-3	<1	10 ± 2	<1
Water-4	<2	<3	<3
Water-5	<4	<5	<4
Gasoline (facility-specific)	3 ± 1	7 ± 2	4 ± 1

Table 9. Concentration ranges (or mean values) of water samples performed in similar studies

Country	^{226}Ra (Bq l^{-1})	^{228}Ra (Bq l^{-1})	Reference
Algeria (FW)	5.1-14.8		(Hamlat et al., 2001)
Australia (PW)	17 (Mean)	23 (Mean)	(APPEA, 2002)
Brazil (PW)	0.01-6	0.05-12	(Vegueria et al, 2002)
Congo (PW)	5.1 (Mean)		(Testa et al., 1994)
Egypt (FW, PW)	5-217.5	1.1-59	(Darko et al., 2012; Bakr, 2010)
Italy (PW)	0.2-2		(Testa et al., 1994)
Norway (FW, PW)	0.3-16	0.5-21	(Strad and Lysabo, 1998; NRPA, 2005; Eriksen et al., 2006)
Syria (PW)	9.9-111.2	8.8-60.4	(Al Masri, 2006)
Turkey (FW)	MDA(1.0)-4.5	<MDA(1.9)	(Parmaksız et al., 2013)
UK (PW)	1.7 (Mean)		(United Kingdom Off-Shore Operations Association, 1992)
USA (OB, PW)	0.15-60	0.7-30	(Snavely, 1989; Stephenson and Supernow, 1990; Swan et al., 2004; Zielinski and Budahn, 2007)

(FW): Formation water, (PW): Produced water, (OB): Oilfield brine

3.7. Exemption levels and enrichment factors for radionuclides in scale and sludge samples

10 Bq g^{-1}(10,000 Bq kg^{-1}) is the exemption activity levels of NORM for ^{224}Ra, ^{226}Ra and ^{228}Ra radionuclides as recommended in the International Basic Safety Standards for Protection against Ionizing Radiation and for the Safety of Radiation Sources (IAEA, 1996). Exemption activity levels were repeated for aforementioned radionuclides in interim edition of IAEA publication of Radiation Protection and Safety of Radiation Sources: International Basic Safety Standards (IAEA, 2011). For ^{224}Ra and ^{228}Ra radionuclides, activity concentrations in all sludge and scale samples are below of exemption activity levels of NORM recommended by IAEA. However, activity concentrations of ^{226}Ra were found to be higher than exemption activity levels for nine scale and two sludge samples.

Radionuclide concentrations of scale and sludge wastes resulting from maintaining operation in oil and gas industry widely depend on composition of crude oil as well as production processes. Crude oil, scale and sludge concentrations are given in Table 2, Table 3 and Table 5 respectively. For scale samples, mean enrichment factors were calculated to be 41 for ^{224}Ra, 2290 for ^{226}Ra and 23 for ^{228}Ra. For sludge samples, enrichment factors of ^{224}Ra, ^{226}Ra and ^{228}Ra were found to be 18, 450 and 12 respectively. Measurement results of crude oil, scale and sludge samples remaining under the detection limits were not taken into consideration in the enrichment factor calculations.

4. Conclusions

It has been observed that dose rates of oil production wastes reached up to 25.7 μSv h^{-1} and activity concentrations of naturally occurring radionuclides increased up to by 14,667 times as

132,000 Bq kg^{-1}. It was detected that oil production wastes caused to soil contamination up to 70,483 ± 2,137 Bq kg^{-1}. A considerable number of samples were found to be above the exemption activity level of NORM recommended by IAEA. Measurement results indicated that activity concentration of oil production wastes might pose a risk for workers and members of the public. Preventive precautions should be taken on time for protection against radiation in this context. Good operating practices should be focused on to minimize amount of radioactive waste and waste management should be applied to protect sector employee and members of public. Continual monitoring program can enable administration to decision making about radiological hazard potential of wastes. Educational program about radiation protection in oil and gas industry can prevent internal and external exposure of workers during maintenance or residue dispose operations.

5. Acknowledgements

This study was supported by Turkish Atomic Energy Authority and conducted within the scope of routine activities of Health Physics Department and Measurement and Instrumentation Department of Sarayköy Nuclear Research and Training Center.

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