



Radiological and elemental analysis of well cuttings from Rajian oil field, Potohar Basin, Pakistan

Zawwar Hussain Shah¹ · Naila Siddique² · Zafar Wazir³ · Nafeesa Batool⁴ · Muhammad Nusrat¹

Received: 10 November 2021 / Accepted: 9 April 2022 / Published online: 11 May 2022
© Akadémiai Kiadó, Budapest, Hungary 2022

Abstract

A study was undertaken to assess the trace elemental concentrations and changes in these elemental concentrations with well depth of Well-09 of Rajian Oilfield in the Potohar Basin using neutron activation analysis (NAA). Well cuttings and rock samples were provided by the Oil and Gas Company Limited Pakistan (OGDCL). Principal component analysis (PCA) was applied which was helpful in identifying and grouping the elements whose concentrations vary with depth. Activity concentrations and annual dose rates were measured by calculating naturally occurring radionuclides in Rajian Oilfield samples. Annual dose rates were found to be in the safe limits. Contamination indices; i.e., pollution index (PI), integrated pollution index (IPI), Geo accumulation index (I_{geo}) and enrichment factor (EF) were also calculated. Pollution level was found from low to moderate. Enrichment factors (EF) for Samples RJS7 and RJS10 were found to be extremely polluted in Hf, Rb, Sb, Sm, Ce, Sb and Sm.

Keywords Rajian oil field · Elemental analysis · Hydrocarbon exploration · Pollution indices

Introduction

A project was undertaken to investigate the elemental concentrations of well cuttings from Well no. 09 of Rajian Oilfields, Gujar Khan Pakistan. The main aim of the study was to investigate the variations in trace elements contents with varying well depths for different formations. It is first time that trace elemental profile of Potohar Basin has been measured. In petroleum geo-chemistry the study of trace elemental distribution in source rocks and sedimentary organic matter is a vital area of research [1–7] and such studies has been performed in many countries. Trace elemental composition is helpful in hydrocarbon exploration and environmental studies [8]. In oils, metal porphyrins are present in the form

of nickel porphyrins [9]. Other metals, such as vanadium and nickel are present in the form of chelates with pseudo-porphyrin structures [10]. The concentrations of trace elements in source rock and sedimentary organic matter and their relation with each other can be used in exploration of hydrocarbons [11]. Therefore, trace elemental data is used extensively in petrology and lithology. [1–4, 6–12]. Different techniques such as polarography, atomic absorption spectroscopy, calorimetric analysis, NAA, and optical emission spectroscopy have been used for the measurement of trace elements in Oilfield's soil and well cuttings but NAA has proven to be the most sensitive analytical technique for quantitative measurement of major, minor and trace elements in samples of diverse matrices [13–21]. Therefore, NAA was used in this work. The main purpose of the study was to estimate the concentrations and distribution of trace elements and their relationship, if any, as related to hydrocarbon exploration in various well cuttings (depths) and source formations of Rajian Oilfields, Chakwal in the Punjab province of Pakistan. Environmental geochemistry assessment of the research area was carried out by calculating Enrichment factor (EF), and different contamination indices like geo accumulation indices (I_{geo}), pollution indices (PI) and integrated pollution indices (IPI). Table 1 shows the detailed version of the collected samples.

✉ Zafar Wazir
zafar_wazir@yahoo.com

¹ Department of Physics, Riphah International University, Islamabad, Pakistan

² Chemistry Division, Directorate of Science, PINSTECH, PO Nilore, Islamabad 45650, Pakistan

³ Department of Physics, Ghazi University, Dera Ghazi Khan, Pakistan

⁴ Institute of Zoology, University of Punjab, Lahore, Pakistan

Table 1 Detailed description of the soil samples collected from Well No. 09 of Rajian Oilfields

No	Sample ID	Sample description	Site	Depth (m)	Well No	Formation
1	RJS1	SOIL	Rajian oil field	325	09	Chinji
2	RJS2	SOIL	Rajian oil field	669	09	Chinji
3	RJS3	SOIL	Rajian oil field	745	09	Kamlial
4	RJS4	SOIL	Rajian oil field	832	09	Kamlial
5	RJS5	SOIL	Rajian oil field	3374	09	Murree
6	RJS6	SOIL	Rajian oil field	3358	09	Chorghali
7	RJS7	SOIL	Rajian oil field	3460	09	Sakesar
8	RJS8	SOIL	Rajian oil field	3480	09	Nammal
9	RJS9	SOIL	Rajian oil field	3484	09	Patala
10	RJS10	SOIL	Rajian oil field	3488	09	Lokhart
11	RJS10A	SOIL	Rajian oil field	3498	09	Hangu
12	RJS11	SOIL	Rajian oil field	3508	09	Sardhai
13	RJS12	SOIL	Rajian oil field	3510	09	Warchha
14	RJS13	SOIL	Rajian oil field	3518	09	Dandot
15	RJS14	SOIL	Rajian oil field	3536	09	Tobra
16	RJS15	SOIL	Rajian oil field	3550	09	Bhaganwala
17	RJS16	SOIL	Rajian oil field	3558	09	Jutana
18	RJS17	SOIL	Rajian oil field	3598	09	Kussak
19	RJS18	SOIL	Rajian oil field	3680	09	Khewra

RJS Rajian oilfields soil

Naturally occurring radionuclides (NORMs)

The geological formations that contain oil and gas deposits also contain naturally-occurring radionuclides, which are mentioned as (NORMs) and may be brought to the surface during oil and gas production process [22]. Different rocks contain different concentrations of naturally occurring radionuclides (NORMs). Organic rich shale rocks contain highest concentrations of uranium, by weight; up to 1% U [23, 24]. Radiations are always present in the natural environment. Humans are exposed to ~80% of background radiations. Due to these mining and excavation activities in oil and gas regions, the risk of radiation exposure to the environment and human life needs to be monitored [25]. Contamination of the environment occurs mainly due to unregulated oil and gas production and transportation activities which lead to oil leakage and illegal disposal of contaminated materials and industrial discharges into water bodies. This large-scale contamination consists of radionuclide materials (NORMs) and technologically enhanced radioactive material (TENORM). As NORMs are linked with almost all minerals in the earth's shell, therefore the excavation process of such minerals may bring NORMS to the surface as TENORM and if not handled properly NORMs can penetrate into the earth surface water and then food, crops, vegetables etc. used by humans and animal [26]. Whole of the Potohar region has now

become the hub of oil and gas activities and employs a large number of people. However uncontrolled spills and activities have left the soil isolated and deserted. Naturally occurring radio nuclides mostly cause living organism to absorb radiations from ^{40}K , U^{226} , Th^{232} etc. [27, 28]. The contribution from anthropogenic radionuclides is minute in total dose. In the earth crust the average concentrations of uranium, thorium, and potassium are $2.7 \mu\text{g g}^{-1}$, $9\text{--}10 \mu\text{g g}^{-1}$, and 1.4% respectively. Sedimentary rocks contain relatively lower amounts of uranium ($1.5\text{--}2.2\%$) as compared to igneous rocks ($0.03\text{--}4.7 \mu\text{g g}^{-1}$) [27–30]. Many technological processes causing the spread of NORMs in the environment are mining and mineral treatment processes such as uranium mining and milling, phosphate rock, monazite/beach sands operations, mining/production of phosphoric acid, pyrochlore extracting mines and euxenite ores (columbium/tantalum), mines of copper, gold, tin, aluminum, beryllium, iron, lead, molybdenum, nickel, silver, titanium, zinc, zirconium, coal, fluor spar, granite and limestone. Industrial processes which contribute to NORMs include foundries using zircon sands, sand blasting with zircon sands, operations producing building materials from mine wastes, e.g., phosphor gypsum and phosphate slag, fertilizer manufacturers using phosphoric acid, procedures utilizing fly ash of coal mines, scrapyards exploiting polluted scrap of mines, foundries and smelters using contaminated scrap, operations using lignite, pumice, scoria and mineral wool, titanium dioxide from

ilmenite, tin smelting, processes utilizing pyrochlore in the making of special alloys, the generation of zirconia from baddeleyite, the production of glazes from zirconia, manufacture of catalysts and special glasses from rare earth elements, fly ash from electricity generation, metrology and oil and gas processing in oil/gas sector is 1000 Bq/g [32], facilities [31]. The specified activities of these materials are frequently greater than 1 Bq/g, and can reach upto 1000 Bq/g for some of the oil/gas scales and fly ash.

Geology of the study site

The area of study is Rajian Oilfields, Gujar Khan, as shown in Fig. 1; situated at about 60 km SE of Islamabad. It is located in the western lower Himalayan region of north Pakistan. Potohar sub basin is amongst world's most recognized oil regions, and is famous for its rich oil and gas resources. In 1915 the first oil well was drilled at Khaur. More than 150 oil wells were drilled in the region but are out of production now mainly due to presence of water in the molasses stores. In the north of Rajian Oilfields are Islamabad and Rawalpindi. Nearby roads are Lahore Grand Trunk Road and M2 motorway Islamabad [33–35]. The Rajian zone is thought to have a huge petroleum reservoir. Kohat–Potohar basin is situated in a significant part of the Himalayan chain in Pakistan and has proved to be the leading area for hydrocarbons.

The most productive source of hydrocarbon in the Potohar Basin is the Paleocene Patala shales. Fractured limestone in Sakesar Formation (Eocene age) and Lockhart Formation (Paleocene age), Arenaceous rock in Tobra Formation (Permian age), and Khewra sandstone (early Cambrian age) are plausible ponds rocks in the Potohar Basin. Inside the Rajian study area, the reservoir zone is Chorgali. To stop the seepage of hydrocarbons, drainage and further hydrocarbon migration, the existence of an impervious rock layer is essential. Fine-grained rocks, for example, shales, evaporate and clay-stone acts as a top cap rock. In the study area, the Murree Formation of Miocene age provides the hydrocarbons with a seal. Meanwhile, the Dandot and Kussak Formations are also possible closure rocks. [36–38].

Materials and methods

Sample collection

In the current work nineteen samples of soil at different well depths (325 to 3680 m) were collected from Well No.09 of Rajian Oilfields. Each sample was collected (100 ± 10 g) in a clean polythene bag. Samples consist of well cutting soil of non-uniform size. Samples were collected from different

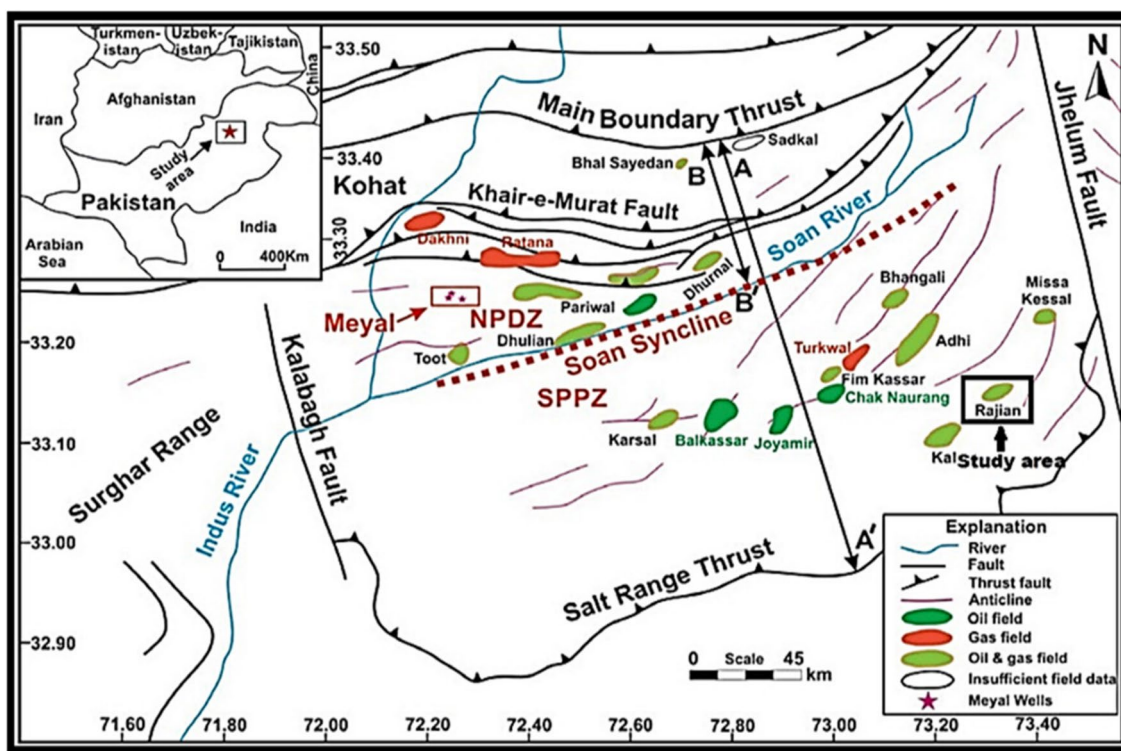


Fig. 1 Location and regional tectonic setting of Rajian Oilfields, Gujar Khan, Pakistan [35]

well depths and different geological formations shown in Table 1.

Sample preparation for INAA and radionuclide calculation

After crushing, grinding and sieving (0.125 mm; particle size less than 125 μm), homogenized soil samples were obtained. For analysis of these soil samples, 2 standard reference materials were used. The soil samples were screened to remove impurities such as rocks. All preventive measures were taken into account to avoid any contamination. For moisture removal the 20 to 40 g of soil samples were dried. In order to determine the elemental concentrations of the samples on dry weight basis the moisture contents of all the samples were obtained each sample was weighed and placed in a labeled glass vial. These vials were placed in an oven at 105 °C for 24 h. The vials were removed and reweighed after they had attained room temperature in a desiccator. The difference in the weights provided the moisture content of the samples which was found to range from 0.81 to 0.99%. For radionuclide analysis we used higher amount 15–35 g. For elemental analysis three ~ 100 mg triplicate samples were encapsulated in clean polythene capsules for irradiation. [40–42].

Multi-elemental analysis through NAA/Irradiation schemes at PARR- II

Four irradiation schemes were used for multi-elemental analysis of soil samples. For quantitative and qualitative analysis, the schemes were organized according to half-life and gamma energies of various isotopes [43–45]. Details of irradiation schemes used are given in Table 2.

The prepared samples were irradiated at the Miniature Neutron Source Reactor (MNSR) Pakistan Research Reactor-II (PARR-II). The reactor was run at 30 kW with a neutron flux of 1×10^{12} n/cm² sec. Gamma spectrometry system used consists of Canberra (AL-30) model high purity Germanium detector (HPGe) coupled to a PC built multichannel analyzer Inter technique via sensitive spectroscopy amplifier [46]. For data acquisition Gamma Vision, Version 6.01

(Advanced Measurement Technology, Inc.) software was used. The system has a resolution of 1.9 keV for 1332.5 keV peaks of ⁶⁰Co. The data collected by the multi-channel analyzer was further analyzed to find quantitative results with different in-house computer-based programs such as Gamma Cal, software which is written in visual basic [14, 47–49].

Calibration standards

Two standard reference materials (RMs) were used for quantitative analysis. Special care was taken to choose the RMs to match the sample matrix. It is also essential that the RM contain a large number of elements as certified values [41, 50]. Reference materials are given in Table 3.

Results and discussion

Measurement of radionuclides using gamma spectrometry

Reference Materials (RMs) were used to check the reliability of the results and for quality assurance purposes. In the current study the methods for the authentication of results are discussed below. [41, 50].

Quality assurance (QA)

The quality assurance (QA) of the analytical results was carried out using two RMs i.e., IAEA-S7 and IAEA SL1 [41, 50]. Experimental results were compared with certified data by calculating the Z-score values as stated by the following relation:

Table 3 Reference materials used in quantitative analysis by NAA

S. No	Standard	Details
1	IAEA-S7 [41]	Soil
2	IAEA-SL1 [50]	Lake Sediment

Table 2 The irradiation schemes used for characterization of Rajian Oilfields soil samples using INAA

Irradiation scheme	Elements	Irradiation time	Cooling time	Counting time
Sequential	Al, Ca, Cu, Ti, Mg, V	30 (s)	2 m	100 s
Short	Cl, K, Mn, Na	30 (s)	2 h	300 s
Intermediate	As, Br, Ga, K, La Na, Sb, Sm, U	1 (h)	2d	900 s
Long	Ba, Ce, Co, Cr, Cs, Fe, Eu, Hf, Hg, Ho, Lu, Mo, Nd, Rb, Sb, Sc, Se, Sm, Sn, Sr, Ta, Tb, Th, Yb, Zn, Zr	5 (h)	2–3 w	2 h

s, seconds; m, minutes; h, hours; d, days; and w, weeks

$$Z - \text{score} = \frac{(\text{Value}_{\text{Analyst}} - \text{Value}_{\text{Certified}})}{\sigma_{\text{Certified}}} \quad (1)$$

*where $\sigma_{\text{Certified}}$ represents uncertainty of 1σ measurement according to RM certificate [21].

Following three classes are defined based on Z-score values:

- 1) $Z\text{-score} \leq 2$ represents satisfactory performance
- 2) $2 < Z\text{-score} < 3$ indicates questionable performance
- 3) $Z\text{-score} \geq 3$ shows unsatisfactory performance

The Z-scores for IAEA-SL1 has been plotted in Fig. 2 and shows satisfactory performance for all the elements in IAEA-SL1 except the elements La and Sm which have values of z-scores greater than 3. Moreover, the z-score for Na also shows that the results for this element corresponding to SL-1 are questionable. The plot in Fig. 3 describes IAEA-S7 and Sm and Hf values using IAEA-S7 are unsatisfactory and are questionable.

Elemental profile

Elemental concentrations of all Rajian Oilfields samples were measured and are given in Table 4. In the 19 samples analyzed 17–23 elements were determined. Fewer elements were measured in RJS6, RJS15 and RJS16, while highest numbers of 23 elements were determined in RJS1, RJS2, RJS5, RJS10A and RJS11. Al, Ba, Fe, K, Mn, and Na were measured in higher amounts as these are always present in higher amounts in soil samples. Fifteen elements i.e., Al, As, Ce, Co, Cr, Fe, Hf, K, La, Mn, Na, Sc, Sm, Th, and V were determined in all samples. Eu, Cs, Rb, Yb and Sb detected in 17,16,13,13 and 12 samples respectively. Elements Ba, Sn, Sr were detected in 10 samples. Al, Fe, and Na were found to be in highest amounts; 4400–77,660, 6030–46,540, 1180–19,060 mg/kg respectively. Lowest amounts of these elements were measured in RJS7 and RJS6 while highest amounts of these elements were measured in RJS1 and RJS10A. Significant variations were observed in Al concentrations from 0.3 to 9.5% in RJS1, RJS12 and RJS13 which is due to high concentrations of barite in sedimentary rocks. Barite can commonly be found with alumina impurities.

Fig. 2 QA plot for IAEA SL1 (Lake sediment)

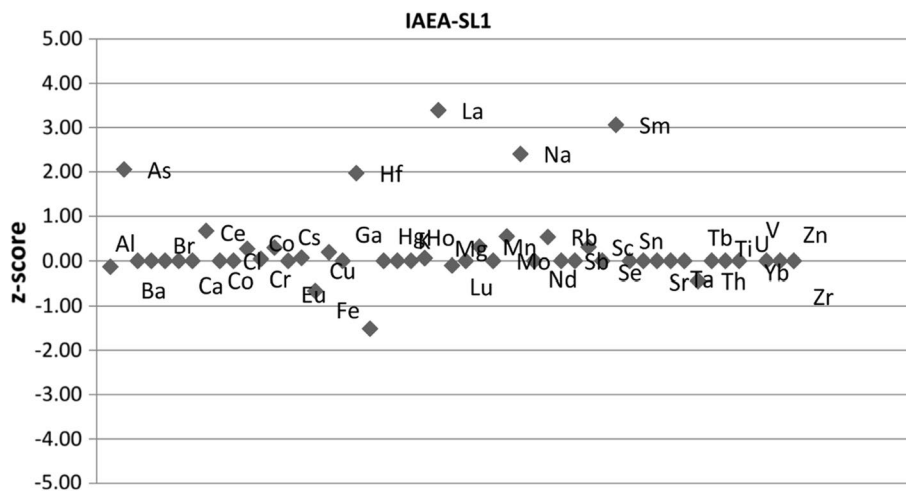


Fig. 3 QA plot IAEA S-7 (Soil)

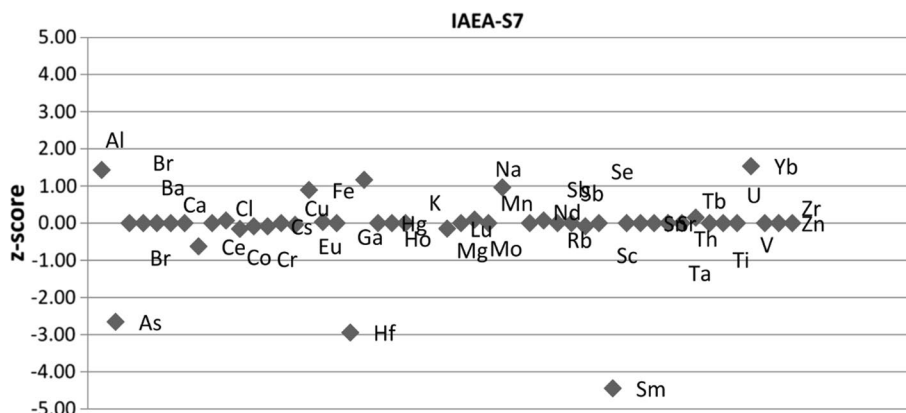


Table 4 Elemental composition of Rajjan Oilfields samples in µg/g on dry weight basis at 95% confidence interval

Element	RJS1	RJS2	RJS3	RJS4	RJS5	RJS6	RJS7	RJS8	RJS9	RJS10	RJS10A	RJS11	RJS12	RJS13	RJS14	RJS15	RJS16	RJS17	RJS18
Al (%)	9.5	6.9	6.22	6.57	7.94	0.98	0.54	4	7.1	1.27	7.68	7.13	8.62	8.1	5.68	6.5	4.97	5.61	0.3
As	19.13	13.68	1	9.72	18.4	3.47	7.71	10.8	13.15	5.36	8.72	13.59	8.66	8.09	13.56	5.52	8.11	7.51	5.09
Ba	58.93	121.8	268.53	253.05	1675.9	–	–	–	–	–	1263.7	1317.1	993.88	400.08	947.73	–	–	–	–
Ce	67.46	64.32	31.92	38.35	73.13	11.35	10.13	45.66	106.72	33.66	132.52	82.84	108.37	86.61	45.36	35.63	51.61	93.88	37.18
Co	13.14	10.62	6.35	8.49	12.67	2.46	2.12	10.81	18.67	4.69	22.13	14.56	20.35	20.69	14.23	9.48	14.09	10.45	5.25
Cr	100.5	88.89	108.44	104.36	107.05	15	33.17	74.6	139.62	42.57	97.49	89.33	79.62	81.76	68.52	43.96	124.7	86.39	42.47
Cs	14.99	9.62	2.89	4.85	8.98	0.57	0.56	2.09	3.43	1.09	3.13	2.1	–	–	–	2.67	2.71	2.76	2.13
Eu	1.25	1.05	0.82	0.85	1.46	–	–	0.73	1.43	0.44	1.77	1.47	2.22	2.01	1.26	1.43	0.95	1.23	0.68
Fe (%)	4.89	3.96	2.77	3.14	4.48	0.74	0.78	2.85	6.51	2.00	5.71	5.32	5.52	5.11	4.28	2.28	4.01	3.36	2.17
Hf	3.85	4.24	3.48	3.66	6.75	0.66	1.59	2.19	5.39	0.89	7.92	9.08	5.4	5.69	3.45	3.07	3.34	6.25	4.21
K (%)	6.31	6.41	5.49	4.78	7.13	0.93	0.53	4.17	6.13	1.60	7.50	7.30	6.64	6.41	6.42	7.46	5.11	1.78	5.65
La	32.14	28.63	17.99	18.07	36.33	6.99	5.92	23.3	37.65	14.01	74.06	57.39	89.44	79.82	41.29	37.13	22.17	43.19	22.71
Mn	834.3	894.28	684.08	674.08	682.2	517.4	67.66	195.78	163.97	362.7	1110.8	211.44	399.87	671.02	342.89	210.6	953.7	687.9	269.3
Na (%)	4.21	2.86	6.04	5.66	2.10	0.85	0.48	1.20	1.71	0.66	3.50	4.02	4.31	5.28	2.09	7.85	3.87	0.97	0.79
Rb	85.8	61.63	28.77	41.96	60.69	–	16.48	36.09	82.65	–	122.51	98.24	71.38	36.95	56.39	–	–	–	–
Sb	0.59	0.59	–	–	2.25	8.73	0.73	–	–	–	0.79	0.61	0.61	0.49	1.21	–	–	9.27	12.16
Sc	13.45	11.78	7.12	8.92	12.46	1.59	1.88	9.4	16.05	4.26	15.12	12.15	15	12.66	8.7	4.85	7.81	8.32	3.55
Sm	6.14	5.58	3.29	3.55	6.88	1.38	1.12	5.16	7.87	2.99	14.29	6.51	7.86	9.67	6.33	4.44	3.83	6.73	3.72
Sn	1.65	2.46	0.94	1.09	1.08	–	–	–	–	–	8.02	4.61	1.6	1.18	2.42	–	–	–	–
Sr	23.27	12.02	10.06	14.54	162.31	–	–	–	–	–	471.79	291.54	258.14	262.47	418.1	–	–	–	–
Th	13.24	10.74	6.12	7.58	13.63	1.4	1.53	6.29	13.53	4.1	15.62	12.91	15.03	12.62	9.35	5.58	7.28	13.85	7.25
V	107.2	73.11	84.01	97.50	113.37	26.97	16.49	98.39	126.86	35.66	79.00	75.27	79.25	75.21	87.8	61.6	76.64	55.07	26.07
Yb	1.48	1.74	0.87	1.37	3.33	–	–	1.38	3.18	1.05	2.82	2.48	1.71	2.61	1.68	–	–	–	–

Principal component analysis

The data obtained was tested using PCA (principal component analysis). PCA is a dimensionality reduction technique which is used to describe variance and covariance. PCA reduces the core of the data into very few components by showing the variation present in data set. When the numbers of input variables are large, then this technique is used. Here PCA was applied to a large data set of the studied 19 samples using inbuilt features in Origin software. The results obtained are shown below in Tables 5 and 6, respectively.

From Table 5 it is evident that first 2 principal components are enough to provide maximum information and account for 97.61% of the variance. This is clearly seen in Fig. 4 where the second point in the graph can be considered as elbow point.

Principal component 1 contains all the samples except RJS15, and RJS17. Principal component 3 mainly contains RJS15, and RJS17. Thus, the first factor we have the samples which were collected from upper depth i.e., from 325 to 3536 m depth of the Well No. 09 of Rajian Oilfields, whereas the second factor has samples collected from a depth of 3536 to 3580 m (Table 1). So, the samples from depth more than 3536 m were grouped together to keep difference from samples collected from lesser depth. If we look at vanadium (V) its concentrations as given in Table 4 are on the higher side in all samples but are low in samples RJS6, RJS7 and RJS18. The concentrations in RJS15 and RJS17 are almost the same. Higher vanadium concentrations can be a sign for the presence of hydrocarbon in soil samples from oilfields.

Figure 5 describes the loadings and the scores for components PC 1 and PC 2. All 19 points in the graph each representing a well sample is plotted as a scatter plot. Fe is found in higher amounts in samples like, RJS1-RJS11 while Na is found in higher concentrations in samples like, RJS1-RJS4, RJS12-RJS17. Overall, elements like Al, Fe, Na, K, Mn, Ba, were found in higher amounts.

From covariance matrix it can be seen that elements highly correlate with values greater than 0.7 in both components i.e., K measured in samples RJS13 and RJS17 is

Table 5 Eigen values of correlation matrix

No	Eigenvalue	Percentage of variance (%)	Cumulative (%)
1	17.8907	94.16	94.16
2	0.65495	3.45	97.61
3	0.44695	2.35	99.96
4	0.00495	0.03	99.99
5	0.00243	0.01	100.00

Table 6 Extracted eigen vectors

No	Samples ID	Coefficients of PC1	Coefficients of PC2
1	RJS1	0.23594	-0.06418
2	RJS2	0.23615	0.00492
3	RJS3	0.22394	0.27508
4	RJS4	0.22966	0.12184
5	RJS5	0.23487	-0.04734
6	RJS6	0.23444	-0.03586
7	RJS7	0.22994	-0.27706
8	RJS8	0.23466	-0.08469
9	RJS9	0.23064	-0.25553
10	RJS10	0.22961	-0.29172
11	RJS10A	0.2355	-0.10025
12	RJS11	0.2361	-0.06019
13	RJS12	0.23551	-0.10286
14	RJS13	0.23547	-0.0505
15	RJS14	0.23514	-0.0667
16	RJS15	0.2018	0.55114
17	RJS16	0.23572	-0.05512
18	RJS17	0.19078	0.54514
19	RJS18	0.22718	0.17964

covariant with Al in RJS1, RJS2, RJS5, RJS6, RJS7, RJS8, RJS9, RJS10, RJS10A, RJS11, RJS14 and RJS15 (Fig. 5).

In Table 7 comparison has been made between samples from the Potohar Basin from Rajian Oilfields considered as source rock formation (3680 m) and samples from Zealand and Yemen. Concentration of Al, Na and Fe are higher as compared to the other three regions of the world. Some elements like, Ce, Hf, K, La Sn, Sr, Th are present in Rajian Well No. 09 but missing in Yemen rock, North Cape coal, and Toko 1 sample C. Differences are may be

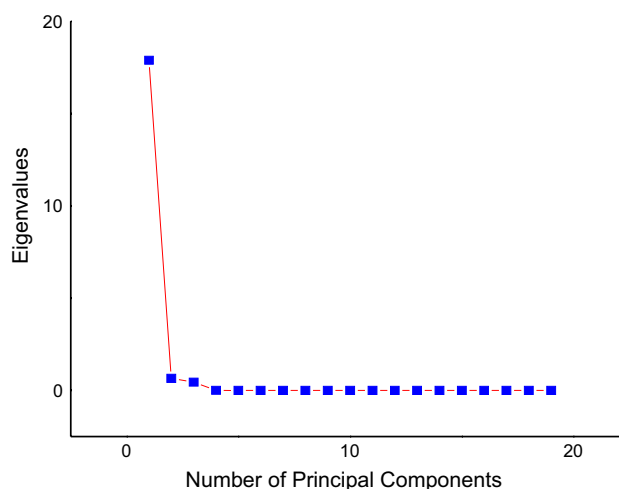


Fig. 4 Scree plot showing the sufficient number of PCAs and eigen values

Fig. 5 Bi plot of elements and samples by calculating covariance matrix

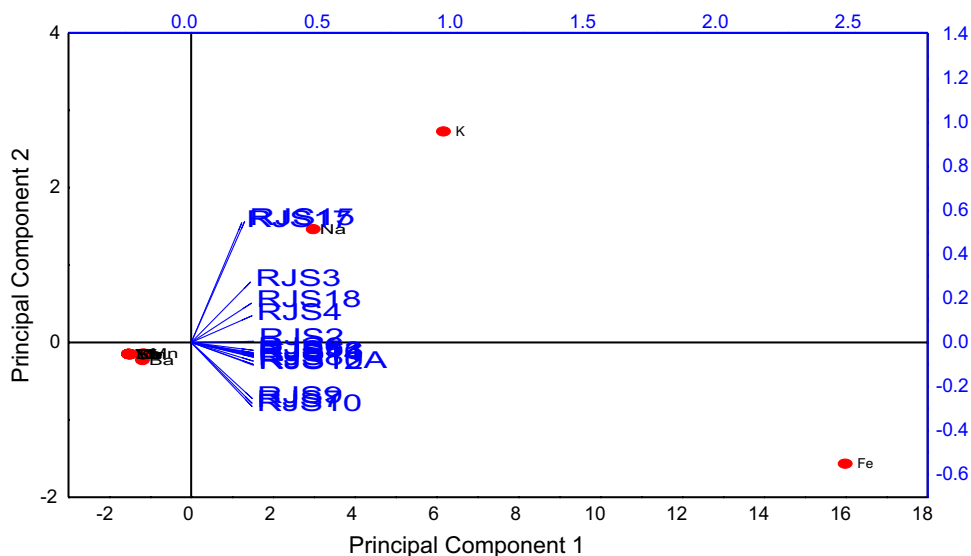


Table 7 Comparison of elemental composition of from Rajian Oilfields source rock with sample from Yemen and New Zealand Oilfields [65] (Concentrations in $\mu\text{g/g}$)

Element	Toko 1 sample C	North Cape coal	Yemen rock	Rajian Oilfields Well No. 09 (this study)
Al	503	525	1.19 (%)	0.3 (%)
As	13.16	0.62	1.75	5.09
Ba	–	–	–	–
Ce	–	–	–	37.18
Co	0.83	5.35	19.7	5.25
Cr	4.44	5.28	22.03	42.47
Cs	0.072	0.093	3.42	2.13
Eu	0.039	0.016	0.22	0.68
Fe	189.44	308.24	4653	2.17 (%)
Hf	–	–	–	4.21
K	–	–	–	5.65 (%)
La	–	–	–	22.71
Mn	1.636	3.693	135	269.3
Na	1951	1201	6154	7.9 (%)
Rb	–	–	–	–
Sb	0.055	0.128	0.33	12.16
Sc	0.16	0.04	2.1	3.55
Sm	0.21	0.02	0.88	3.72
Sn	–	–	–	–
Sr	–	–	–	–
Th	–	–	–	7.25
V	3.53	6.23	27.05	26.07
Yb	–	–	–	–

due to geological reasons as geological features differ from region to region. Most of the elements reported in “Toko 1 sample C” and “North Cape coal” samples have much lower amounts of elements determined than Rajian Oilfields Well No. 09 sample. Yemen rock has elemental composition

similar to the samples studied in this work. Concentrations of As, Sb, Mn, Sm has been found to be comparatively on the higher side in Rajian Well No.09 samples as compared to Yemen rock sample. However, the amounts of Cs, Eu, Sc and V are almost the same as in “Yemen Rock.”

Pollution contours study

Several indices like, Geo accumulation (I_{geo}), Enrichment factor (EF), pollution index (PI), and integrated pollution indices (IPI) were measured for the assessment of pollution level of the subject area in the present work. The following formula describes the EF as given by Taylor in 1964. For all pollution indices we used Upper Continental Crust data as background [66].

$$EF = (\text{Metal}/\text{Al}) \text{ sample}/(\text{metal}/\text{Al}) \text{ background} \quad (2)$$

Sutherland in 2000 [51] defined five classes of pollution level given in Table 8 based on EF values.

Pollution levels vary with in time and area. Generally regional background values are preferred. Solely with respect to Ba, Al, Ti, Mg, K, Ca, Na, Fe, Br, and Sc notable changes in background values arise with the type of soil [52, 53]. In soil the accumulation of heavy metal becomes an issue if concentrations are over two three orders of magnitude of the parental matter [54]. In this work geochemical standardization was accomplished with respect to Al. [16]. Complete description of each element with its EF is given in Table 9.

For most of the elements the enrichment factors were found to be from significant to extremely polluted category. Arsenic was found to be in minimal to very highly polluted category in all samples. Sr, and Na were found to be in minimal to significant range. Th, V and Sc were found to be in significant to very high limits in all samples. Samples RJS5, RJS6, RJS7, RJS10, RJS17 and RJS18 were found to be extremely polluted in Sb. Samples RJS7 and RJS10 were found to be extremely polluted in Hf, Rb, Sb, Sm and Ce, Sb and Sm.

Geo accumulation index (I_{geo})

I_{geo} is used to estimate contamination by using initial (preindustrial) and existing values [55]. It is calculated by the relation below.

$$I_{geo} = \ln \frac{C_n}{1.5} \times B_n \quad (3)$$

where, C_n = metal concentration.

B_n = metal (n) background geochemical concentration.

Table 8 Five categories of pollution level based on EF

Sr. No	EF level	Designated contamination category
1	EF < 2	deficiency to minimal enrichment
2	EF = 2–5	moderate enrichment
3	EF = 5–20	significant enrichment
4	EF = 20–40	very high enrichment
5	EF > 40	Extremely high enrichment

1.5 is a number which cuts the background variational effect in values.

Different classes of I_{geo} based on a scale of 1–6 given in Table 10.

The complete picture of the elements can be seen in Table 11 where their I_{geo} values are given (Table 12).

The I_{geo} results show that the study area is mostly unpolluted to moderately polluted. RJS5 is moderately polluted with Sb, whereas RJS6, RJS17 and RJS18 are strongly polluted with Sb.

Pollution and integrated pollution indices (PI & IPI)

For the assessment of heavy metal concentrations, Pollution index (PI) and Integrated pollution (IPI) index were calculated.

PI is the ratio of metal volume to the corresponding background value of the dust or soil sample given by the following relation [56, 57].

$$PI = C/S \quad (4)$$

where PI = pollution index.

C = measured value of each metal in mg/kg.

S = background value in mg/kg.

Mean PI value for each element is taken as IPI.

Pollution indices were calculated for Well No. 09 of Rajian Oilfields and are given in Table 13.

There are large variations from low to high in PI and IPI values for different elements the samples investigated. RJS6, RJS17 and RJS18 are highly polluted in Sb. IPI value of Sb is also greater than 2 while IPI values of Al, Eu, La, Sm, are between 1 and 2 which show moderate level of pollution.

Radionuclide (NORMS) result

Activity concentration

Human radiation exposure due to presence of naturally occurring radionuclides was calculated from the data given in Table 14.

Activity concentrations (Bq/kg) of the radionuclide

The activity concentrations were calculated by Mokobia and Jibiri [61, 62] from the area under the peaks.

$$C (\text{Bq} \cdot \text{kg}^{-1}) = k C_n \quad (5)$$

C (Bq. kg^{-1}) is the sample concentration.

C_n is the count rate under corresponding Peak

Table 9 EF with respect to Al for the elements in Rajjan Oilfield Well No. 09

Elements	Al	As	Ce	Co	Cr	Cs	Eu	Fe	Hf	K	La	Mn	Na	Rb	Sb	Sc	Sm	Sr	Th	V
RJS1	1.00	3.19	11.24	7.97	11.46	32.11	13.08	10.68	7.63	6.64	10.88	11.31	4.42	10.72	15.44	10.08	13.72	0.76	13.23	13.23
RJS2	1.00	3.15	14.79	8.90	14.00	28.44	15.26	11.83	11.58	9.29	13.38	16.74	4.15	10.63	21.22	12.19	17.20	0.54	14.82	14.82
RJS3	1.00	0.26	8.14	5.90	18.95	9.49	13.11	9.08	10.56	8.82	9.33	14.21	9.71	5.50	20.09	8.17	11.24	0.51	9.36	9.36
RJS4	1.00	2.35	9.26	7.46	17.26	15.05	12.89	9.95	10.50	7.28	8.87	13.25	8.61	7.60	19.02	9.70	11.51	0.69	10.99	10.99
RJS5	1.00	3.68	14.62	9.23	14.66	23.09	18.34	11.75	16.05	8.98	14.76	11.10	2.65	9.10	70.93	11.21	18.44	6.39	16.34	16.34
RJS6	1.00	5.63	18.39	14.50	16.65	11.83	5.11	15.73	12.63	9.52	23.04	68.26	8.76	6.08	2228.27	11.62	30.01	–	13.61	13.61
RJS7	1.00	22.69	29.81	22.74	66.82	21.06	9.27	30.25	55.74	9.91	35.38	16.20	9.04	36.35	338.54	24.87	44.01	–	27.08	27.08
RJS8	1.00	4.29	18.11	15.63	20.26	10.68	18.27	14.80	10.31	10.42	18.79	6.32	3.01	10.74	31.24	16.78	27.41	–	14.97	14.97
RJS9	1.00	2.94	23.84	15.19	21.36	9.85	20.10	19.09	14.32	8.63	17.09	2.98	2.42	13.85	17.59	16.13	23.57	–	18.14	18.14
RJS10	1.00	6.68	41.94	21.27	36.33	17.48	34.40	32.57	13.22	12.29	35.47	36.79	5.24	4.67	98.13	23.87	50.00	–	30.65	30.65
RJS10A	1.00	1.80	27.38	16.65	13.79	8.31	23.06	15.46	19.46	9.75	31.10	18.68	4.53	18.99	25.69	14.06	39.57	19.19	19.36	19.36
RJS11	1.00	3.02	18.42	11.79	13.60	5.74	20.64	15.49	24.01	10.23	25.93	3.83	5.63	16.38	21.45	12.15	19.41	12.76	17.22	17.22
RJS12	1.00	1.60	19.96	13.65	10.04	1.18	25.76	13.33	11.82	7.71	33.47	5.99	5.00	9.86	17.72	13.26	19.41	9.36	16.61	16.61
RJS13	1.00	1.58	16.98	14.77	10.97	1.26	24.79	13.13	13.27	7.92	31.79	10.71	6.48	5.43	15.24	11.16	25.42	10.13	14.84	14.84
RJS14	1.00	3.79	12.67	14.48	13.11	1.80	22.11	15.70	11.44	11.31	23.44	7.80	3.69	11.81	53.16	10.94	23.68	22.99	15.68	15.68
RJS15	1.00	1.35	8.71	8.44	7.36	8.39	22.09	7.31	8.94	11.51	18.45	4.19	12.10	0.92	19.26	5.33	14.55	–	8.19	8.19
RJS16	1.00	2.59	16.48	16.39	27.27	11.13	19.08	16.80	12.68	10.29	14.39	24.79	7.79	1.20	25.15	11.23	16.42	–	13.95	13.95
RJS17	1.00	2.13	26.55	10.76	16.73	10.04	21.92	12.47	21.03	31.71	24.83	15.84	1.74	1.06	413.05	10.59	25.52	–	23.50	23.50
RJS18	1.00	2.74	20.04	10.30	15.68	14.75	23.09	15.39	27.00	19.20	24.87	11.81	2.68	2.02	1032.40	8.60	26.90	–	23.43	23.43

Table 10 Geo accumulation categories for pollution assessment

Sr.No	Igeo Level	Defined contamination class
1	$I_{geo} \leq 0$	Not polluted
2	$0 < I_{geo} < 1$	Not polluted – moderately polluted
3	$1 < I_{geo} < 2$	Moderately pollution level
4	$2 < I_{geo} < 3$	Moderate to strong pollution level
5	$3 < I_{geo} < 4$	Strong pollution level
6	$4 < I_{geo} < 5$	Strong – very strong pollution level
7	$I_{geo} > 5$	Very strong pollution level

$$k = 1/\varepsilon p_{\gamma} M_s \quad (6)$$

ε is the detector efficiency at specific gamma energy.

p_{γ} is the absolute transition probability of specific gamma energy.

M_s is the mass of sample in kg.

The minimum detection limit/detectable activity in a sample, was calculated using the following equation [61, 62]

$$DL \text{ (Bq.Kg}^{-1}\text{)} = 4.65\sqrt{C_b/t_b \cdot k} \quad (7)$$

where C_b and t_b is the net background count in corresponding peak and background counting time (s) respectively.

k is the factor that converts counts per second to activity concentrations.

The results of the activity concentrations (Bq/kg) of the radionuclide are presented in the Table 14.

Outdoor exposure is measured for γ -rays discharged by terrestrial materials and for time of outdoor stay. For the calculation of outdoor exposure, radiation indices, radium equivalent activity (Ra_{eq}), outdoor external dose (D_{out}) and annual outdoor effective dose (E_{out}) were calculated. Moreover, for the calculation of indoor radiation threat, indoor external dose (D_{in}) and annual indoor effective dose (E_{in}) were calculated. The methods for these dose calculations are given below. Radium equivalent activity (Ra_{eq}) was calculated using the following equation [58].

$$Ra_{eq} = \left(\frac{A_{Ra}}{370} + \frac{A_{Th}}{259} + \frac{A_K}{4810} 370 \right) \quad (8)$$

where A_{Ra} , A_{Th} and A_K are the activities of Ra, Th and K as given in Table 14.

The assessment of Outdoor External Dose (D_{out}) in $nGy h^{-1}$ was done using the following equation [59].

$$D_{out} = 0.462A_{Ra} + 0.604A_{Th} + 0.0417A_K \quad (9)$$

Annual Outdoor Effective Dose (E_{out}) was calculated using the equation below [59].

$$E_{out} = D_{out} \times 1.22 \times 10^{-3} \text{ (mSvy}^{-1}\text{)} \quad (10)$$

Risk assessment for indoor activities

EC in (1999) gives the relation for Indoor Effective Dose (D_{in}).

$$D_{in} = 0.92A_{Ra} + 1.1A_{Th} + 0.08A_K \quad (11)$$

Annual Indoor Effective Dose (E_{in}) was assessed according to the expression [59].

$$E_{in} = D_{in} \times 4.905 \times 10^{-3} \text{ (mSvy}^{-1}\text{)} \quad (12)$$

Undue life time cancer risk (ELCR)

The undue life time cancer risk was calculated using the following relation.

$$ELCR_{out} = E_{out} \times LE \times RF \quad (13)$$

$$ELCR_{in} = E_{in} \times LE \times RF \quad (14)$$

where $ELCR_{out}$ and $ELCR_{in}$ are the excessive life time cancer risks for outdoor and indoor exposures respectively. LE is the life time expectancy and is taken as 66 years. RF is the fatal risk factor per Sievert and is 0.05 as per (ICRP, 1991) [60].

The radiation indices of ^{226}Ra , ^{232}Th and ^{40}K were calculated using the data given in Table 14. The existing oil and gas fields are of ancient origin including and contain products of the ^{238}U , ^{235}U , ^{232}Th decay series; i.e., ^{40}K , ^{87}Rb and ^{226}Ra are the decay products of ^{238}U . The average radionuclide concentrations of Rajian Oilfields Well No.09 are 8.312, 7.308, 131.67 Bq/kg for ^{226}Ra , ^{232}Th and ^{40}K respectively. The activity concentration values of the radionuclides are independent of the well depth, as rock formation radionuclides content depends on the geology of the area.

Health hazards estimation

From Table 15 it can be seen that D_{out} and D_{in} values vary from 1.34 to 80.00 and 2.57–59.00 $nGy h^{-1}$, respectively. Other values E_{out} , E_{in} , $E_{out} + E_{in}$ ($mSv \cdot y^{-1}$) and $ELCR_{out} \cdot 10^{-3}$, $ELCR_{in} \cdot 10^{-3}$ are given in Table 15. It is evident from many previous studies that radioactivity is higher in soil samples taken from oil well cuttings and oil samples than non-oil samples/sites [63, 64]. IAEA set a safety standard of 10,000 Bq/kg for radionuclide activity level, beyond this limit is considered a threat to human health and environment. At the end of the Table 15, a comparison has been made for naturally occurring radionuclides between average values of Rajian Well No. 09 and world average. Overall, the effective absorbed average dose rates/values for Well

Table 11 Geo-accumulation indices of component elements of Rajian Oilfields Well No.09

Elements	Al	As	Ce	Co	Cr	Cs	Eu	Fe	Hf	K	La	Mn	Na	Rb	Sb	Sc	Sm	Sr	Th	V
RJS1	-3.98	1.41	-0.49	-0.98	-0.46	1.03	-0.27	-0.56	-1.05	-1.24	-0.53	-0.48	-1.83	-0.55	-0.03	-0.64	-0.20	-4.37	-0.25	-0.44
RJS2	-4.44	0.93	-0.56	-1.29	-0.63	0.39	-0.51	-0.88	-0.91	-1.23	-0.70	-0.38	-2.39	-1.03	-0.03	-0.83	-0.34	-5.32	-0.55	-0.99
RJS3	-4.59	-2.85	-1.57	-2.03	-0.35	-1.35	-0.88	-1.41	-1.19	-1.45	-1.37	-0.76	-1.31	-2.13	-0.26	-1.56	-1.10	-5.58	-1.36	-0.79
RJS4	-4.51	0.43	-1.30	-1.61	-0.40	-0.60	-0.82	-1.20	-1.12	-1.65	-1.36	-0.78	-1.41	-1.59	-0.26	-1.23	-0.99	-5.05	-1.05	-0.58
RJS5	-4.24	1.35	-0.37	-1.03	-0.37	0.29	-0.04	-0.69	-0.24	-1.07	-0.36	-0.77	-2.83	-1.05	1.91	-0.75	-0.04	-1.56	-0.21	-0.36
RJS6	-7.26	-1.05	-3.06	-3.40	-3.20	-3.69	-4.91	-3.28	-3.60	-4.01	-2.73	-1.17	-4.13	-4.66	3.86	-3.72	-2.35	-	-3.49	-2.43
RJS7	-8.12	0.10	-3.22	-3.61	-2.06	-3.72	-4.91	-3.20	-2.32	-4.81	-2.97	-4.10	-4.94	-2.94	0.28	-3.48	-2.66	-	-3.36	-3.14
RJS8	-5.23	0.59	-1.05	-1.26	-0.89	-1.81	-1.04	-1.34	-1.86	-1.85	-1.00	-2.57	-3.64	-1.80	-0.26	-1.16	-0.45	-	-1.32	-0.56
RJS9	-4.40	0.87	0.18	-0.48	0.02	-1.10	-0.07	-0.15	-0.56	-1.29	-0.30	-2.82	-3.13	-0.61	-0.26	-0.39	0.16	-	-0.22	-0.20
RJS10	-6.88	-0.43	-1.49	-2.47	-1.70	-2.75	-1.78	-1.85	-3.15	-3.26	-1.73	-1.68	-4.49	-4.66	-0.26	-2.30	-1.24	-	-1.94	-2.03
RJS10A	-4.29	0.28	0.49	-0.23	-0.50	-1.23	0.24	-0.34	0.00	-1.00	0.67	-0.06	-2.11	-0.04	0.40	-0.47	1.02	-0.02	-0.01	-0.88
RJS11	-4.39	0.92	-0.19	-0.83	-0.63	-1.87	-0.03	-0.44	0.19	-1.04	0.30	-2.46	-1.90	-0.36	0.03	-0.79	-0.11	-0.72	-0.29	-0.95
RJS12	-4.12	0.27	0.20	-0.35	-0.79	-3.88	0.57	-0.38	-0.56	-1.18	0.94	-1.54	-1.80	-0.82	0.03	-0.39	0.16	-0.89	-0.07	-0.88
RJS13	-4.21	0.17	-0.13	-0.33	-0.76	-3.88	0.42	-0.50	-0.48	-1.23	0.78	-0.79	-1.52	-1.77	-0.28	-0.73	0.46	-0.87	-0.32	-0.95
RJS14	-4.72	0.91	-1.06	-0.87	-1.01	-3.88	-0.26	-0.75	-1.21	-1.22	-0.17	-1.76	-2.84	-1.16	1.01	-1.27	-0.16	-0.20	-0.75	-0.73
RJS15	-4.53	-0.38	-1.41	-1.45	-1.65	-1.46	-0.07	-1.66	-1.37	-1.01	-0.32	-2.46	-0.93	-4.66	-0.26	-2.12	-0.67	-	-1.50	-1.24
RJS16	-4.92	0.17	-0.87	-0.88	-0.15	-1.44	-0.66	-0.85	-1.25	-1.55	-1.07	-0.28	-1.95	-4.66	-0.26	-1.43	-0.88	-	-1.11	-0.92
RJS17	-4.74	0.06	-0.01	-1.31	-0.68	-1.41	-0.29	-1.10	-0.35	0.25	-0.11	-0.76	-3.94	-4.66	3.95	-1.34	-0.07	-	-0.19	-1.40
RJS18	-5.67	-0.50	-1.35	-2.31	-1.70	-1.79	-1.14	-1.73	-0.92	-1.41	-1.03	-2.11	-4.25	-4.66	4.34	-2.57	-0.92	-	-1.12	-2.48

Table 12 PI and IPI classes of Pollution level

Sr. No	PI class	Designated pollution level	IPI class
1	$PI \leq 1$	Low	$IPI \leq 1$
2	$1 < PI \leq 3$	Moderate	$1 < IPI \leq 2$
3	$PI > 3$	High	$IPI > 2$

No. 09 Rajian Oilfield are less than the world averages and therefore do not affect the oil field workers' health and the environment. Moreover, use of this soil is safe for construction purposes.

Conclusion

Well cuttings and source rock extracts of Rajian Oilfields Well No. 09 in the Potohar Basin were studied using NAA. Moreover, naturally occurring radionuclides were also measured in these samples. NAA established the heavy metals, major, minor, trace and toxic elemental composition with concomitant measurement of their amounts in Rajian Oilfields samples. Maximum of 23 elements were identified. Various pollution indices like PI, IPI, Igeo indicated that the depth samples were low to highly polluted. EF values for V and Sc were very high at all depths which are expected in well cuttings. This study also provided information about

Table 14 The activity concentration (Bq/kg) of the radionuclide in Rajian Oilfield Well No. 09 On dry weight basis at 95% confidence interval

Sample	Ra226 Mean	Th232 Mean	K40 Mean
RJS1	ND	4.30 ± 6.54	97.65 ± 3.75
RJS2	ND	ND	168.94 ± 6.48
RJS3	ND	ND	88.03 ± 3.38
RJS4	5.41 ± 11.13	5.36 ± 8.04	87.66 ± 3.36
RJS5	ND	ND	173.80 ± 6.67
RJS6	ND	ND	38.83 ± 1.49
RJS7	9.07 ± 14.29	ND	0.91 ± 0.03
RJS8	ND	26.69 ± 40.04	112.42 ± 4.31
RJS9	16.25 ± 25.61	5.03 ± 7.65	237.56 ± 9.11
RJS10	ND	ND	32.12 ± 1.23
RJS10A	1.63 ± 2.57	7.87 ± 11.97	210.79 ± 8.09
RJS11	ND	4.37 ± 6.64	89.69 ± 3.44
RJS12	ND	5.86 ± 8.91	201.63 ± 7.74
RJS13	ND	ND	172.18 ± 6.61
RJS14	ND	5.04 ± 7.66	125.54 ± 4.82
RJS15	9.20 ± 10.63	4.07 ± 6.18	185.84 ± 7.13
RJS16	ND	ND	104.56 ± 4.01
RJS17	ND	4.49 ± 6.83	228.08 ± 8.75
RJS18	ND	ND	145.56 ± 5.58

where ND denotes not detected

Table 13 Pollution and integrated pollution indices (PI & IPI)

Elements	Al	As	Ce	Co	Cr	Cs	Eu	Fe	Hf	K	La	Mn	Na	Rb	Sb	Sc	Sm	Sr	Th	V
RJS1	0.10	3.99	1.07	0.76	1.09	3.06	1.25	1.02	0.73	0.63	1.04	1.08	0.42	1.02	1.47	0.96	1.31	0.07	1.26	1.11
RJS2	0.07	2.85	1.02	0.61	0.97	1.96	1.05	0.82	0.80	0.64	0.92	1.16	0.29	0.73	1.46	0.84	1.19	0.04	1.02	0.75
RJS3	0.06	0.21	0.51	0.37	1.18	0.59	0.82	0.57	0.66	0.55	0.58	0.88	0.60	0.34	1.25	0.51	0.70	0.03	0.58	0.87
RJS4	0.07	2.03	0.61	0.49	1.13	0.99	0.85	0.65	0.69	0.48	0.58	0.87	0.57	0.50	1.25	0.64	0.76	0.05	0.72	1.01
RJS5	0.08	3.83	1.16	0.73	1.16	1.83	1.46	0.93	1.27	0.71	1.17	0.88	0.21	0.72	5.63	0.89	1.46	0.51	1.30	1.17
RJS6	0.01	0.72	0.18	0.14	0.16	0.12	0.05	0.15	0.12	0.09	0.23	0.67	0.09	0.06	21.82	0.11	0.29	–	0.13	0.28
RJS7	0.01	1.61	0.16	0.12	0.36	0.11	0.05	0.16	0.30	0.05	0.19	0.09	0.05	0.20	1.83	0.13	0.24	–	0.15	0.17
RJS8	0.04	2.25	0.72	0.63	0.81	0.43	0.73	0.59	0.41	0.42	0.75	0.25	0.12	0.43	1.25	0.67	1.10	–	0.60	1.01
RJS9	0.07	2.74	1.69	1.08	1.52	0.70	1.43	1.36	1.02	0.61	1.21	0.21	0.17	0.98	1.25	1.15	1.67	–	1.29	1.31
RJS10	0.01	1.12	0.53	0.27	0.46	0.22	0.44	0.41	0.17	0.16	0.45	0.47	0.07	0.06	1.25	0.30	0.64	–	0.39	0.37
RJS10A	0.08	1.82	2.10	1.28	1.06	0.64	1.77	1.19	1.50	0.75	2.39	1.44	0.35	1.46	1.97	1.08	3.04	1.47	1.49	0.81
RJS11	0.07	2.83	1.31	0.84	0.97	0.41	1.47	1.11	1.71	0.73	1.85	0.27	0.40	1.17	1.53	0.87	1.39	0.91	1.23	0.78
RJS12	0.09	1.80	1.72	1.18	0.87	0.10	2.22	1.15	1.02	0.66	2.89	0.52	0.43	0.85	1.53	1.14	1.67	0.81	1.43	0.82
RJS13	0.08	1.68	1.37	1.20	0.89	0.10	2.01	1.06	1.07	0.64	2.57	0.87	0.52	0.44	1.23	0.90	2.06	0.82	1.20	0.78
RJS14	0.06	2.82	0.72	0.82	0.74	0.10	1.26	0.89	0.65	0.64	1.33	0.44	0.21	0.67	3.02	0.62	1.35	1.31	0.89	0.91
RJS15	0.06	1.15	0.57	0.55	0.48	0.54	1.43	0.47	0.58	0.75	1.20	0.27	0.79	0.06	1.25	0.35	0.94	–	0.53	0.63
RJS16	0.05	1.69	0.82	0.81	1.36	0.55	0.95	0.83	0.63	0.51	0.72	1.23	0.39	0.06	1.25	0.56	0.82	–	0.69	0.79
RJS17	0.06	1.57	1.49	0.60	0.94	0.56	1.23	0.70	1.18	1.78	1.39	0.89	0.10	0.06	23.18	0.59	1.43	–	1.32	0.57
RJS18	0.03	1.06	0.59	0.30	0.46	0.43	0.68	0.45	0.80	0.57	0.73	0.35	0.08	0.06	30.40	0.25	0.79	–	0.69	0.27
IPI	0.06	1.99	0.97	0.67	0.87	0.71	1.11	0.76	0.81	0.60	1.17	0.68	0.31	0.52	5.46	0.66	1.20	–	0.89	0.76

Table 15 Absorbed and effective dose rates, outdoor and indoor absorbed and effective dose rates and health hazards

Sample	D_{out} (nGy.h ⁻¹)	D_{in} (nGy.h ⁻¹)	E_{out} (mSv.y ⁻¹)	E_{in} (mSv.y ⁻¹)	$E_{out} + E_{in}$ (mSv.y ⁻¹)	$ELCR_{out} \times 10^{-3}$	$ELCR_{in} \times 10^{-3}$	$ELCR_{total} \times 10^{-3}$
RJS1	6.66	12.54	0.01	0.06	0.07	0.03	0.20	0.23
RJS2	7.04	13.51	0.01	0.07	0.07	0.03	0.22	0.25
RJS3	3.67	7.04	0.00	0.03	0.04	0.01	0.11	0.13
RJS4	9.39	17.89	0.01	0.09	0.10	0.04	0.29	0.33
RJS5	7.25	13.90	0.01	0.07	0.08	0.03	0.23	0.25
RJS6	1.62	3.11	0.00	0.02	0.02	0.01	0.05	0.06
RJS7	4.23	8.41	0.01	0.04	0.05	0.02	0.14	0.15
RJS8	20.81	38.35	0.03	0.19	0.21	0.08	0.62	0.70
RJS9	20.45	39.48	0.02	0.19	0.22	0.08	0.64	0.72
RJS10	1.34	2.57	0.00	0.01	0.01	0.01	0.04	0.05
RJS10A	14.30	27.02	0.02	0.13	0.15	0.06	0.44	0.49
RJS11	6.38	11.98	0.01	0.06	0.07	0.03	0.19	0.22
RJS12	11.95	22.58	0.01	0.11	0.13	0.05	0.37	0.41
RJS13	7.18	13.77	0.01	0.07	0.08	0.03	0.22	0.25
RJS14	8.28	15.59	0.01	0.08	0.09	0.03	0.25	0.29
RJS15	14.46	27.81	0.02	0.14	0.15	0.06	0.45	0.51
RJS16	4.36	8.37	0.01	0.04	0.05	0.02	0.14	0.15
RJS17	12.22	23.19	0.01	0.11	0.13	0.05	0.38	0.42
RJS18	6.07	11.64	0.01	0.06	0.06	0.02	0.19	0.21
Average (this study)	8.82	16.78	0.01	0.08	0.09	0.04	0.27	0.31
World average	84.00	59.00	0.07	0.41	0.52	0.29	1.16	1.45

variation in trace elements concentration with changing well depth. PCA results showed that upper and depth samples belong to different categories. However, there is no clear evidence to show correlation of presence of oil with elemental concentrations of source rocks.

Recommendations

NAA may be used for the analysis of the rock extracts from different Oilfields in Pakistan and relationship can be established between elements by comparing the elemental concentration of the elements of source rocks of different Oilfields.

Acknowledgements The technical assistance of Reactor Operations Group (ROG) and Health Physics Division (HPD) at PINSTECH is greatly acknowledged. The assistance and cooperation of the NAA/MNSR Lab's personnel in carrying out this research at PARR-II is greatly appreciated. The financial support from HEC NRPU Project no 15785, Ghazi University is highly appreciated.

References

1. Filby RH (1994) Origin and nature of trace element species in crude oils, bitumens and kerogens. *Geol Soc Londn Special Publ* 78:203–219
2. Alberdi-Genolet M, Tocco R (1999) Trace metals and organic geochemistry of the Machiques Member (Aptian–Albian) and La Luna Formation (Cenomanian Campanian). *Venezuela Chem Geol* 160:19–38
3. Akinlua A, Torto N, Ajayi TR, Oyekunle JAO (2007) Trace metal characterisation of Niger Delta kerogens. *Fuel* 86:1358–1364
4. Tribouillard N, Algeo TJ, Lyons T, Riboulleau A (2006) Trace metals as paleo-redox and paleo-productivity proxies: an update. *Chem Geol* 232:12–32
5. Galarraga F, Llamas JF, Martinez A, Martinez M, Marquez G (2008) Reategui K. V/Ni ratio as a parameter in palaeo-environmental characterization of non-mature medium-crude oils from several Latin American basins. *J Petrol Sci Eng* 61:9–14
6. Akinlua A, Adekola SA, Swakamisa O, Fadipe OA, Akinyemi SA (2010) Trace element characterisation of Cretaceous Orange Basin hydrocarbon source rocks. *Appl Geochem* 25:1587–1595
7. Jegede TO, Adekola SA, Akinlua A (2018) Trace element geochemistry of kerogens from the central Niger Delta. *J Pet Explor Prod Technol* 8:999–1007
8. Oluwole AF, Asubiojo OI, Nwachukwu JI, Ojo JO, Ogunsola OJ, Adejumo JA, Filby RH, Fitzgerald S, Grimm C (1993) Neutron activation analysis of Nigerian crude oils. *J Radioannal Nucl Chem* 168:145–152

9. Nikolay M, Dmitry M, Guzalia A, Alvira T, Svetlana Y, Makhmut RY (2020) Preparative-scale purification of petroleum vanadyl porphyrins by sulfuric acid loaded macroporous silica. *J Porphyrins Phthalocyanines* 24(4):528–537
10. Lewan M, Maynard JB (1982) Factors controlling enrichment of vanadium and nickel in the bitumen of organic sedimentary rocks. *Geochim Cosmochim Acta* 82:90377–90385
11. Hitchon B, Filby RH, Shah KR (1975) Origin and nature of trace element species in crude oils, bitumens and kerogens: implications for correlation and other geochemical studies. *Geol Soc Londn Special Publ* 78:203–219
12. Galarraga F, Llamas JF, Martinez A, Martinez M, Marquez G, Reategui K (2008) V/Ni ratio as a parameter in palaeoenvironmental characterization of non-mature medium-crude oils from several Latin American basins. *J Petrol Sci Eng* 61:9–14
13. Bergerioux JL, Galinier L, Zikovskiy L (1979) Determination of trace element pathways in a petroleum distillation unit by instrumental neutron activation analysis. *J Radioanal Chem* 54(1–2):255–265
14. Zaidi JH, Qureshi IH, Arif M, Fatima J (1995) Input of missing trace elements in some IAEA/NBS biological certified reference materials using INAA. *J Radioanal Chem* 196:125–133
15. Jiang DZ, Teng EJ, Liu YL (1996) The contribution of difference on the element background values in soils and the analysis of variance of single factor on soil groups. *Environ Monit Assess* 2:21–24
16. Blaser P, Zimmermann S, Luster J, Shotyk W (2000) Critical examination of trace element enrichments and depletions in soils: As, Cr, Cu, Ni, Pb, and Zn in Swiss forest soils. *Sci Total Environ* 249(1–3):257–280
17. Zhang J, Liu CL (2002) Riverine composition and estuarine geochemistry of particulate metals in China – weathering features, anthropogenic impact and chemical fluxes estuarine. *Coastal Shelf Sci* 54:1051–1070
18. Adeyemo D, Umar I, Jonah S, Thomas S, Agbaji E, Akaho E (2004) Trace elemental analysis of Nigerian crude oils by INAA using miniature neutron source reactor. *J Radioanal Chem* 261:229–231
19. Szczepaniak K, Biziuk M (2005) Some applications of neutron activation analysis: a review. *J Radioanal Chem* 265:141–150
20. Gonzales-Macias C, Schifter I, Lluch-Cota DB, Mendez-Rodriguez L, Hernandez VS (2006) Distribution, enrichment and accumulation of heavy metals in coastal sediments of Salina Cruz Bay, Mexico. *Environ Monit Assess* 118:211–230
21. Shakhshiro AA, Trinkl A, Torvenyi E, Zeiller T, Benesch, Sansone U (2006) Proficiency test on the determination of major, minor and trace elements in ancient Chinese Ceramic, Seibersdorf, Austria. In: IAEA/AL/168, Report on the IAEA-CU-2006-06
22. Escot (1984) Occupational exposures in petroleum refining: crude oil and major petroleum fuels. *Chem Abstr Services Reg. No.:* 8002-05-9
23. Fowzia H, Abdullah, Hasan S, Ameenah F (2008) An investigation of naturally occurring radioactive material (NORM) in oilfields and oil lakes in Kuwait. *J Open Petro. SPE*-11156
24. Brad F, Jan B, Kyle B, Greg B, Angela G, Brad I, Zoe J, Mark L, Randall M, Scott M, Michael M, Hugh M, Lucia R, Chris U, Hai Z (2002) Tectono-stratigraphic development and hydrocarbon reservoir quality on a convergent margin: East Coast, North Island, New Zealand. *APPEA J* 49(2):600–600
25. Israel NYD, Cynthia FI, Neda SS, Mark PT (2019) Human exposure and risk associated with trace element concentrations in indoor dust from Australian homes. *Environ Int* 133:105125
26. Babatunde BB, Sikoki FD, Avwiri GO, Chad-Umoreh YE (2019) Review of the status of radioactivity profile in the oil and gas producing areas of the Niger delta region of Nigeria. *J Environ Radioact* 202:66–73
27. Kathren RL (1998) NORM sources and their origins. *Apple Radiant Isot* 49:149–168
28. Wasim M, Ali M, Daud M (1992) Classification of surface and deep soil samples using linear discriminant analysis. *Nucleus* 52(2):85–87
29. Bethesda, MD (2009) NCRP Report No. 160: ionizing radiation exposure of the population of the United States. National council on radiation protection and measurements. *J Radiol Prot* 29: 465
30. Bowen HDM (1979) Environmental chemistry of the elements. Academic Press, London
31. Valkovic V (2019) Technologically modified exposure to natural radiation. In: Radioactivity in the environment, 2nd edn. Zagreb, Croatia, pp. 31–62
32. Ali MMM, Zhao H, Li Z, Maglas NNM (2019) Concentrations of TENORMs in the petroleum industry and their environmental and health effects. *RSC Adv* 9:39201
33. Khan MA, Riaz A, Raza HA, Arif K (1986) Geology of petroleum in Kohat-Potwar depression, Pakistan. *Geo Sci World AAPG Bull* 70(4):396–414
34. Muhammad R, Pimentel N, Tehseen Z, Shahid G (2019) 2D seismic interpretation of the Meyal Area, Northern Potwar Deform Zone, Potwar Basin, Pakistan. *J Open Geosci* 11:16
35. Naveed A, Sikandar K, Eisha FN, Zhi HZ, Abdul LA (2021) Seismic data interpretation and identification of hydrocarbon-bearing zones of Rajian Area, Pakistan. *J MDPI Minerals* 11(8):891
36. Gee ER, Gee DG (1989) Overview of the geology and structure of the Salt Range, with observations on related areas of northern Pakistan. *Geol Soc Am Spec Pap* 232:95–112
37. Ghazi S, Ali A, Hanif T, Sharif S, Arif J (2010) Larger benthic foraminiferal assemblage from the early Eocene Chor Gali formation, Salt Range. *Pakistan Geol Bull Punjab Univ* 45:8391
38. Sameeni SJ, Nazir N, Abdul-Karim A, Naz H (2009) Foraminiferal biostratigraphy and reconnaissance microfacies of Paleocene Lockhart Limestone of Jabri area, Hazara, northern Pakistan. *Geol Bull Punjab Univ* 44:85–96
39. Daud F, Khan GN, Ibrahim M (2011) Remaining hydrocarbon potential in Pakistan - a statistical review. In: Distribution of source rocks and reservoir facies, OMV Pakistan (Exploration) GmbH. pp. 1–14
40. Mashireva LG, Gonsales AG, Zimina KI, Zhilkin VV (1975) Experience in use of atomic-absorption method for analysis of petroleum products. *J Radioanal Chem* 11:319–321
41. Pszonicki L, Hanna AN, Suschny O (1984) Report on Intercomparison IAEA/Soil-7 for the determination of Trace Elements in soil. In: IAEA/RL/112
42. Kang S, Lee J, Kima K (2007) Biosorption of Cr (III) and Cr (VI) onto the cell surface of *Pseudomonas aeruginosa*. *Biochem Eng J* 36:54–58
43. Lesmana SO, Febriana N, Soetaredjo FE, Sunarso J, Ismadji S (2009) Studies on potential applications of biomass for the separation of heavy metals from water and waste water. *Biochem Eng J* 44:19–41
44. Loska K, Wiechula D, Korus I (2004) Metal contamination of farming soils affected by industry. *Environ Int* 30:159–165
45. Bakr MA, Elattar AL, Salama S, Ahmed MH, Zahran EM (2018) NAA for trace elemental analysis of sludge samples from different oil sites in the Egyptian Eastern Desert. *J Rad Nucl Appl* 3:163–170
46. Federico CA, González OL, Fonseca ES, Martin IM, Caldas LVE (2010) Neutron spectra measurements in the south Atlantic anomaly region. *Radiat Meas* 45(10):1526–1528
47. Tribovillard N, Algeo TJ, Lyons T, Riboulleau A (2006) Trace metals as paleoredox and paleoproductivity proxies: an update. *Chem Geol* 232:12–32

48. Waheed S, Waseem M, Rahman A, Ahmad S (2001) Estuarine sediment as proposed reference material for environmental studies. *Geostand Geoanal Res* 25:137–143
49. Ahmad S, Zaidi JH, Rahman A, Qureshi IH, Saleem M (2001) Transfer of inorganic elements in air and their enrichment in ash during coal combustion. *Toxicol Environ Chem* 83:13–23
50. Waheed S, Rahman A, Siddique N, Ahmad S (2007) Rare earth and other trace element content of NRCC HISS-1 sandy marine sediment reference material. *Geostand Geoanal Res* 31(2):133–141
51. Dybozynski R, Suschny O (1979) Final report on the Intercomparison Run SL-1, IAEA Lab. Seiberdorf, IAEA/RL/64
52. Sutherland RA (2000) Bed sediment associated trace metals in an urban stream, Oahu, Hawaii. *Environ Geol* 39:611–627
53. de Souza RM, Meliande ALS, da Silveira CLP, Aucelio RQ (2006) Determination of Mo, Zn, Cd, Ti, Ni, V, Fe, Mn, Cr and Co in crude oil using inductively coupled plasma optical emission spectrometry and sample introduction as detergentless microemulsions. *Microchem J* 82:137–141
54. Rubio B, Nombela MA, Vilas F (2000) Geochemistry of major and trace elements in sediments of the Ria de Vigo (NW Spain): an assessment of metal pollution. *Mar Pollut Bull* 11:968–980
55. Taylor SR (1964) Abundance of chemical elements in the continental crust: a new table. *Geochim Cosmochim Acta* 28:1273–1285
56. Muller G (1969) Index of geo-accumulation in sediments of the Rhine River. *Geo J* 2:108–118
57. Williams TR (1972) Analytical methods for atomic absorption spectrophotometry (Perkin Elmer Corp.). *J Chem Edu* 49(4):1315–1316
58. Tokalioglu S, Kartal S (2006) Multivariate analysis of the data and speciation of heavy metals in street dust samples from the organized industrial district in Kayseri (Turkey). *J Atmos Environ* 40:2797–2805
59. Beretka J, Matthew PJ (1985) Natural radioactivity of Australian building materials, industrial wastes and by-products. *Health Phys* 48(1):87–95
60. Sources and effects of ionizing radiation (United Nations Scientific Committee on the Effects of Atomic Radiation), (UNSCEAR) Report Vol. I, to the General Assembly, with scientific annexes 2000
61. ICRP Publication 60 (1991) *Ann. ICRP* 21, 1-3
62. Mokobia CE, Adebisi FM, Akpan I, Olise FS, Tchnokossa P (2006) Radioassay of prominent nigerian fossil fuels using gamma and TXRF spectroscopy. *Fuel* 85:1811–1814
63. Jibiri NN, Emelue HU (2008) Soil radionuclide concentrations and radiological assessment in and around a refining and petrochemical company in Warri, Niger Delta, Nigeria. *J Radiol Prot* 28(3):361–368
64. Smith KP, Blunt DL, Williams GP, Arnish JJ, Pflingston MR, Herbert J (1999) Assessing the disposal of wastes containing NORM in nonhazardous waste landfills. In: international petroleum environmental conference, Houston, TX (United States). Vol 20, pp. 16–18 Nov 1999
65. Avwiri GO, Enyinna PI, Agbalagba EO (2007) Terrestrial radiation around oil and gas facilities In Ughelli Nigeria. *J Appl Sci* 7(11):1543–1546
66. Nusrat M, Naila S (2021) Neutron activation analysis and gamma spectrometry of Shawa oil well of Kohat basin, Pakistan. *Environ Earth Sci* 81(1):10126–10136
67. Rudnick RL, Gao S (2003) Composition of the continental crust, treatise on geochemistry. *Treat Geochem* 3:1–64

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.