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A century of oil and gas exploration in Albania: Assessment of Naturally Occurring Radioactive Materials (NORMs)

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ABSTRACT

The Naturally Occurring Radioactive Materials (NORMs) that are potentially generated from oil and gas extractions in Albania have been disposed of without regulations for many decades, and therefore, an extensive survey in one of the most productive regions (Vlora-Elbasan) was performed. A total of 52 gamma ray spectrometry measurements of soil, oil-sand, sludge, produced water and crude oil samples were performed. We discovered that relatively low activity concentrations of ^{226}Ra, ^{228}Ra, ^{228}Th and ^{40}K, with concentrations of 23 ± 2 Bq/kg, 23 ± 2 Bq/kg, 24 ± 3 Bq/kg and 549 ± 12 Bq/kg, respectively, came from the oil-sands produced by the hydrocarbon extraction of the molasses formations. The mineralogical characterizations and the ^{228}Ra/^{40}K and ^{226}Ra/^{40}K ratios of these Neogene deposits confirmed the predictions of the geological and geodynamic models of a dismantling of the Mesozoic source rocks. The average activity concentrations (±standard deviations) of the radium isotopes (^{226}Ra and ^{228}Ra) and of the ^{228}Th and ^{40}K radionuclides in soil samples were 20 ± 5 Bq/kg, 25 ± 10 Bq/kg, 25 ± 9 Bq/kg and 326 ± 83 Bq/kg, respectively. Based on the measurements in this study, the future radiological assessments of other fields in the region should be strategically planned to focus on the oil-sands from the molasses sediments. Disequilibrium in the ^{228}Ra decay segment was not observed in the soil, sludge or oil-sand samples within the standard uncertainties. After a detailed radiological characterization of the four primary oil fields, we concluded that the outdoor absorbed dose rate never exceeded the worldwide population weighted average absorbed dose rate in outdoor air from terrestrial gamma radiation.

1. Introduction

The exploration for and the production of petroleum in Albania began in the second decade of the 20th century in the Vlora-Elbasan Region, which is characterized by Neogene clastic deposits. The primary oil extraction technique in Albania is the use of beam pumps, which exploit the pressure of the gas in the reservoir, forcing the oil out and into the well. Recently, several secondary recovery techniques, such as water and steam injection, were used in the pilot wells in the area, leading to an increase in the oil production rate. Moreover, in the future, the use of unconventional methods of shale gas extraction such as "fracking" is also likely. All of these techniques cause the Naturally Occurring Radioactive Materials (NORMs) to rise to the surface as part of the flow back and the production of brine. In general, in the oil and gas industry, the contamination of the oil equipment and the oil field area with NORMs (e.g., scale, sludge and produced water) demands specific attention.

Several environmental studies showed that the release of the produced water into the surroundings of the oil wells, into the decantation plants and into the oil spillage sites resulted in serious soil, water and air contamination with BTEX (acronym for Benzene, Toluene, Ethylbenzene, and Xylene), volatile organic compounds or crude oil (REC, 2000; Beqiraj et al., 2010; Guri et al., 2013). However, after a century of oil exploration in Albania with poor regulatory control, particularly in the early years of the oil exploration, the risk of soil contamination from NORMs requires investigation. According to the CD 2013/59/EURATOM (2014) directive, the industrial processes that involve NORMs should be

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identified and monitored by countries to assess the exposure of workers and members of the public to radioactivity.

The NORMs produced by the oil and gas industry are residues that are enriched with the radium isotopes that originated from the uranium and thorium in the reservoir rocks. Moreover, whereas both uranium and thorium are in the hydrocarbon reservoir rocks and are essentially insoluble under the reducing conditions, the progenies ^{226}Ra and ^{228}Ra of these isotopes concentrate in formation waters. Thus, the ^{226}Ra and ^{228}Ra are unsupported by the long-lived uranium and thorium parent radionuclides, and because of half-lives of 1600 y and 5.75 y, respectively, the ^{226}Ra and ^{228}Ra tend to accumulate in the formation waters. The produced water (i.e., water brought to the surface) contains various cations in solution, such as barium, calcium, and strontium, in addition to the sulfate and carbonate anions, with which the radium can co-precipitate as radium sulfates or radium carbonates. The effect of the co-precipitation is the formation of scales in oil and gas equipment for which the ^{226}Ra and ^{228}Ra specific activities are as high as 1500×10^4 Bq/kg and 280×10^4 Bq/kg, respectively, although highly variable concentrations are typically observed (Xhixha et al., 2013). Furthermore, sludge wastes (i.e., a mixture of crude oil, oil-sand and soil) are also generated, which have slightly lower activity concentrations than the scales, with values up to 350×10^4 Bq/kg and 205×10^4 Bq/kg for the ^{226}Ra and the ^{228}Ra (Xhixha et al., 2013), respectively. However, to date, no study has been performed on the oil-sand wastes produced during heavy oil extraction.

This study is the first to investigate the radioactivity concentrations in the soils, oil-sands, sludges, crude oil and produced waters from the KUçova (KU), MArinza (MA), BAllsh (BA) and HEkali (HE) oil fields. This original data set will provide the baseline information for the possible contamination caused by the oil-sands. The geological framework and mineralogical analyses provided an exhaustive interpretation of the radiometric data, and these analyses allowed for the assessment of the effects of the activities of the oil industry in the four oil fields on the environment and on humans. Moreover, these results may lead to the implementation in the Albanian legislature of the European recommendations regarding the "Basic Safety Standards for the protection against dangers arising from exposure to ionizing radiation (CD 2013/59/EURATOM, 2014)".

2. Materials and methods

2.1. Geological setting of the study area

Albania is part of the Alpine Mediterranean Mountain belt and is subdivided into two groups of tectonic units with NNW–SSE orientation: the Inner Units, which are characterized by intense deformations comprised of ophiolites and metamorphic rocks, and the Outer Units, which are composed of regional thrusts that involve the sedimentary rocks of the Triassic to Pliocene age (Prifti and Muska, 2013). The primary rocks that characterize the units of the two groups, according to the tectonic scheme, are shown in Fig. 1. A major transfer zone, i.e., the Vlora-Elbasan lineament, along which most of the oil and gas fields occur, affects the Outer Units (Roure et al., 2010).

The onshore petroleum extraction in Albania is primarily located in the IONian unit (ION) and in the Durrës Basin, also referred to as the Peri-Adriatic Depression (PAD). The ION is an unbroken, elongated tectonic unit (ca. 60–70 km long × 60 km wide) that extends continuously southward into Greece. In the ION, two primary tectonic phases are recognized (i.e., the Middle Miocene and the Miocene-Pliocene), which form large anticlines and synclines that are cut by major high-angle reverse faults (Robertson and Shallo, 2000).

The exposure in the ION begins with the evaporites and then passes upward into the shallow-marine platform carbonates (limestone and dolomites) of the Late Triassic–Early Jurassic age. This succession culminates in a hard-ground (ancient lithified seafloor) that is overlain by pelagic carbonates and cherts (Middle–Late Jurassic to Eocene age, with a thickness of 2.5–4 km) and by terrigenous turbidites (Late Eocene–Early Miocene age, with a thickness of approximately 4–6.5 km). The Paleogene units are disconformably overlain with Neogenic sediments. The PAD is filled by molasses mega-sequences of conglomerates, sandstone and clastic limestones, with clays, shale, coal and gypsum at the top. The thickness of the molasses deposits increases from the southeast to the northwest, reaching a maximum of 5 km in thickness (Silo et al., 2013).

According to Silo et al. (2013), six potential source rocks of hydrocarbons are recognized within the Mesozoic limestone stratigraphic column of the ION. The primary source rocks are the Triassic bituminous dolomite at the bottom, the lower Jurassic schists and the other Jurassic source rocks. The Cretaceous shales are also found under the thrust synclines, shales that could be exploited as hydrocarbon generators in the future.

The migration of the crude oil from the Mesozoic limestone toward the Neogene reservoirs resulted from successive episodes driven by the aforementioned tectonic structures. The oil currently explored in the Neogenic molasses sediments is the product of a secondary migration from the underlying limestone (ION). The hydrocarbons are generally accumulated in the stratigraphic traps of the clastic deposits of the PAD. Because these phenomena evolved over geological time with different horizontal and vertical distributions, each reservoir displays unique characteristics caused by the local geochemical conditions.

2.2. Sample collection

2.2.1. Kuçova oil field

The Kuçova (KU) oil field is located in the central eastern part of the Durrës Basin and extends along a flat surface of approximately 14 km^2. Covered by alluvial sediments, the area was investigated with 21 soil samples (Fig. 2 (KU)), collected at a depth of 0–10 cm, to characterize the terrestrial component of the outdoor absorbed dose rate. According to the USDA Soil Taxonomy, the textural characteristics of the soil samples overall were sandy (percentage of sand >50% for most of the samples) with medium amounts of silt (approximately 30%) and low amounts of clay (<20%).

The hydrocarbon reservoir is set in the Driza, Gorani, Kuçova and Polovina members of the Tortonian-Messinian molasses sediments (PAD). In particular, the oil that is extracted is accumulated in sand lenses (Fig. 3 sect. AA′) (extending from 100 to 1500 m) that are sealed with shales (Sejdini et al., 1994) with a large amount of clay (Prifti and Muska, 2013). The depth of the reservoir has a range that varies from the surface down to 1500 m.

The KU oil field was discovered in 1928, and the Bankers Petroleum Ltd., a Canadian company with the full rights to develop the oil field, declared in 2013 that there are approximately 297 million barrels of Original Oil in Place (OOIP). The oil extracted is characterized by API gravity values and sulfur contents in the ranges of 14–22° and 4–5%, respectively (Sejdini et al., 1994; Prifti and Muska, 2013). During the periodic pipe cleaning process, we collected 10 samples of oil-sand from three different operating wells (500–1000 m depth) and 3 samples of sludge from the surrounding areas. Furthermore, the produced water and the crude oil were collected in polyethylene bottles directly from the decantation plants.

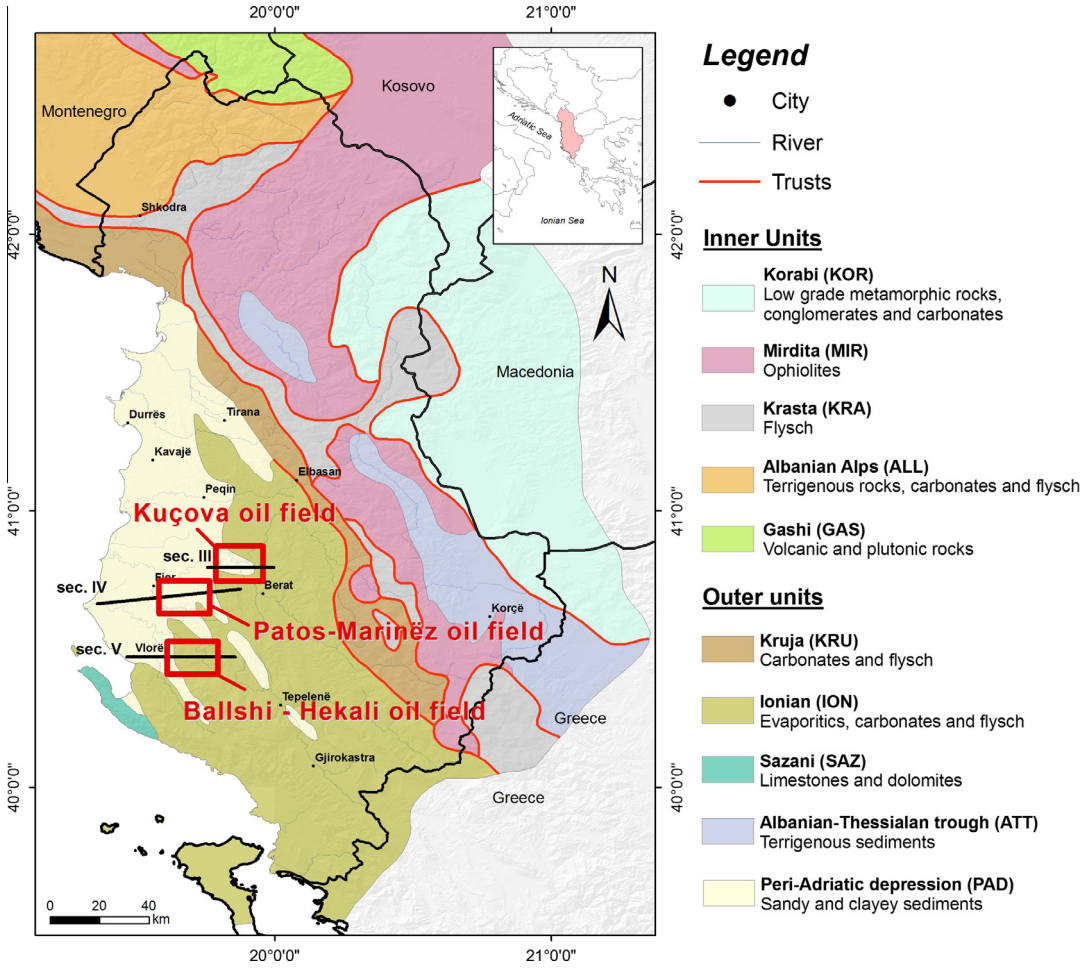

Fig. 1. Simplified geological map of Albania modified from Havancsák et al. (2012). The labels refer to the geological units. The red squares represent the locations of the sample areas; the solid black lines show the sections (not to scale).

2.2.2. Marinza oil field

The Marinza (MA) oil field, located in the southeastern part of the Durrës Basin, is the northern part of the Patos-Marinza oil field system that extends for 5 km WE and for 14 km NS. The wide plain is covered by alluvial sediments, which were investigated for radiological assessment with 3 soil samples (Fig. 2 (MA)); the soils were classified with a texture of clay-loam with sand <40% (a lower percentage than the Kuçova soil), clay at 35% and silt at 25%.

The Driza, Gorani, and Marinza members of the Tortonian-Messinian molasses formation (PAD) are the primary hydrocarbon reservoirs. The multiple layers of unconsolidated fine grain sandstone are located at a depth that ranges from 900 to 2000 m. The depositional environment is a marine environment with fluvial-channel and shore face deposits. In some cases, the underlying fractured carbonates (ION), which are located below a major unconformity (Fig. 3 sect. BB'), are the oil reservoirs (Weatherill et al., 2005; Sejdini et al., 1994). The Patos-Marinza oil field was discovered in 1929, and the amount of OOIP is approximately 5.4 billion barrels, according to the 2013 data reported by Bankers Petroleum Ltd.

The two separate fields (Patos in the south and Marinza in the north) have productive sands at different depths, i.e., 0–1200 m for Patos and 1200–1800 m for MA. The oil extracted is characterized by an API gravity value range of 3–33° and by a sulfur content range of 2–7% (Weatherill et al., 2005; Prifti and Muska, 2013). We collected 1 sludge sample and 1 oil-sand sample from each of the two investigated wells (2000 and 2500 m depths) in the MA oil field.

2.2.3. Ballsh–Hekali oil field

The Ballsh–Hekali oil field system is located in a hilly area 29 km SE of Fieri. The radiological assessment of the two distinct fields, Ballsh (BA) and Hekali (HE), was performed with the collection of 3 and 5 soil samples, respectively (Fig. 2 (BA) and (HE)). The soil textures were classified as sand or loamy sand with sand >80%, clay <10% and silt at 20%.

The reservoirs are restricted to the Paleocene–Eocene carbonate rocks (ION) and have a depth range of 1000–3000 m. The geological structure is two superposed faulted anticlines (Fig. 3 sect. C-C'), and the oil stratigraphic column has a thickness greater than 550 m (Sejdini et al., 1994). The BA and the HE oil fields were discovered in 1966, and the OOIP is approximately 440 million barrels (Sejdini et al., 1994). The extracted oil is characterized with API gravity values of 2–30° and sulfur contents of 3–7.5% (Prifti and Muska, 2013). For the radiological characterization, 2 samples of sludge were collected from an operative well of the BA oil field.

2.3. Sample preparation and measurements

2.3.1. HPGe gamma ray spectrometry measurements

The samples were homogenized to a grain size of less than 2 mm and were dried for at least 24 h at 105 °C until a constant weight was achieved. The produced water and crude oil samples were collected in polyethylene bottles directly from the decantation plants at the KU oil field. The samples were then transferred

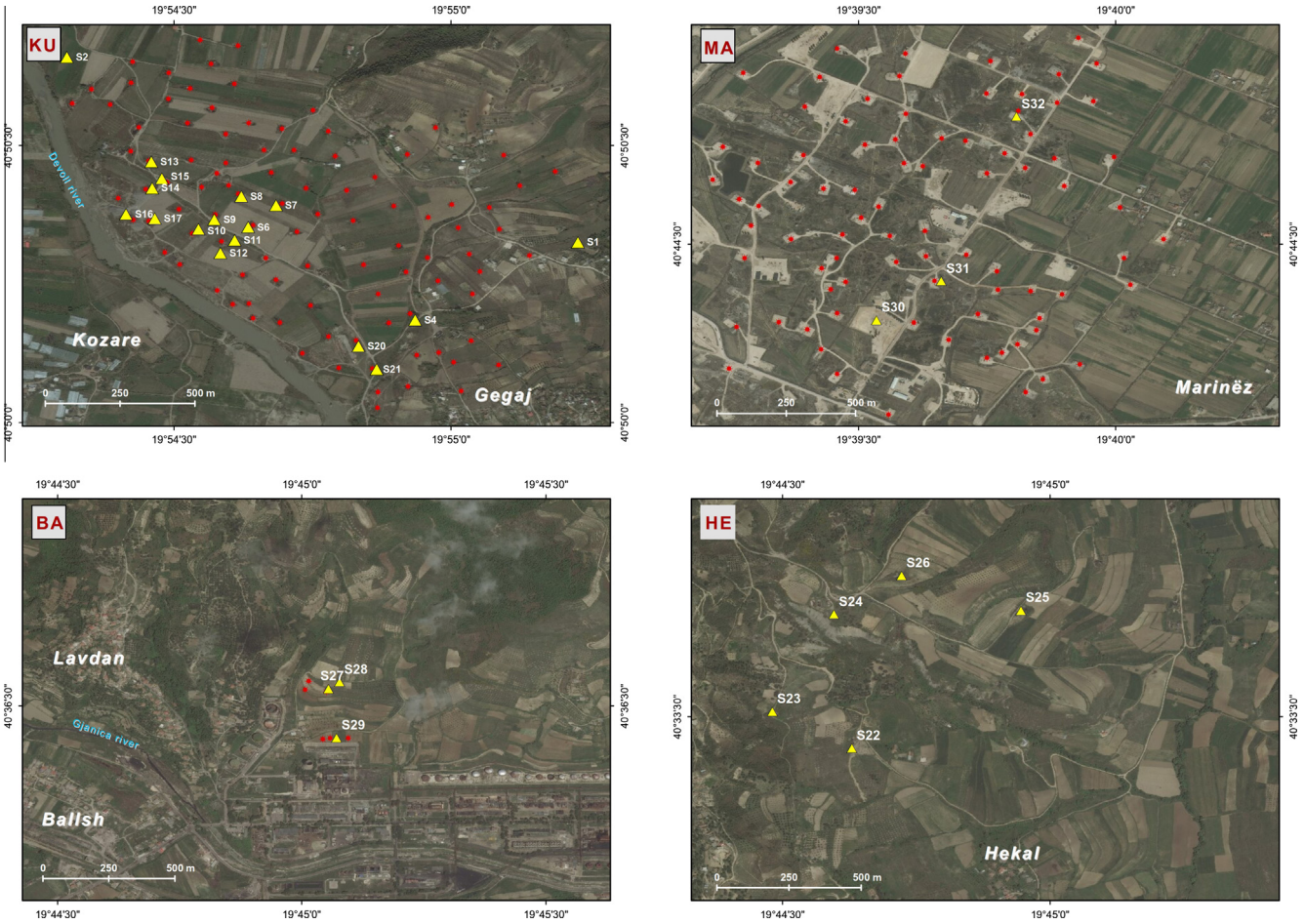

Fig. 2. Approximate locations of the oil wells (red stars) and the soil samples collected in the study area (yellow triangles). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

into cylindrical polycarbonate boxes with a volume of 180 cm^3, sealed hermetically and left undisturbed for at least four weeks before the measurements with a HPGe gamma spectrometer to establish a radioactive equilibrium in the ^{226}Ra decay chain segment.

The samples were measured using the MCA_Rad system described in Xhixha et al. (2013). The fully automated spectrometer consisted of two 60% relative efficiency coaxial p-type HPGe gamma ray detectors with an energy resolution of ~1.9 keV at 1332.5 keV (^{60}Co). The absolute full energy peak efficiency of the MCA_Rad was calibrated using certified standard point sources (^{152}Eu and ^{56}Co). The overall uncertainty in the efficiency calibration was estimated to be less than 5%. A certified reference material that contained contaminated bulk soil from a Syrian oil field (IAEA-448) was used for the quality control. In general, the ^{226}Ra, ^{228}Ac, ^{212}Pb, ^{208}Tl and ^{40}K activity concentrations were within 3–10% of the reference values.

The radionuclides studied in this work were ^{226}Ra, ^{228}Ra, ^{228}Th and ^{40}K, which were analyzed by different gamma lines (Santawamaitre et al., 2014). The presence of ^{137}Cs in the soils was also investigated as a proxy for the Chernobyl fallout. The ^{226}Ra activity concentration was determined by analyzing the two primary gamma emissions of the radon progenies, ^{214}Pb (at 352 keV) and ^{214}Bi (at 609 keV), and calculating the weighted average. The ^{228}Ra activity concentration was determined through the direct progeny ^{228}Ac, which produced gamma emissions at 338 keV and 911 keV. The ^{228}Th activity concentration was determined by analyzing the two primary gamma emissions of the radon progenies, ^{212}Pb (at 239 keV) and ^{208}Tl (at 583 keV). The activity concentrations of ^{40}K and ^{137}Cs were determined from the gamma emissions at 1460 keV and 662 keV, respectively. The acquisition time was set to 4 h for the soil, oil-sand and sludge samples and to 24 h for the produced water and the crude oil samples.

2.3.2. X-ray diffractometry measurements

Before the mineralogical analysis, the samples were dried at 50 °C for several hours and then were gradually ground on an agate mortar to preserve the crystalline structure of the minerals. The XRD patterns of oriented and random samples were recorded using a GNR APD2000PRO diffractometer, with Cu Kα radiation and a graphite monochromator, which operated at 40 mA and 40 kV. The X-ray diffractometry of 5 samples was conducted with the divergence and the scatter slits set at 1° and the receiving slit set at 0.2 mm. The step size and the counting time were 0.03° (2θ) and 3 s/step, respectively. A quasi-random orientation of powder samples was obtained by filling a side-entry aluminum holder. The XRD patterns were processed with the SAX Analysis software, and the identification of the minerals was based on the comparison with the PDF-2 reference data from the International Center for Diffraction Data (ICCD, 2013). A semi-quantitative analysis of the minerals identified by the XRD was calculated based on chemical analyses, with thermogravimetric data related to the volatile components and to the Reference Intensity Ratio method.

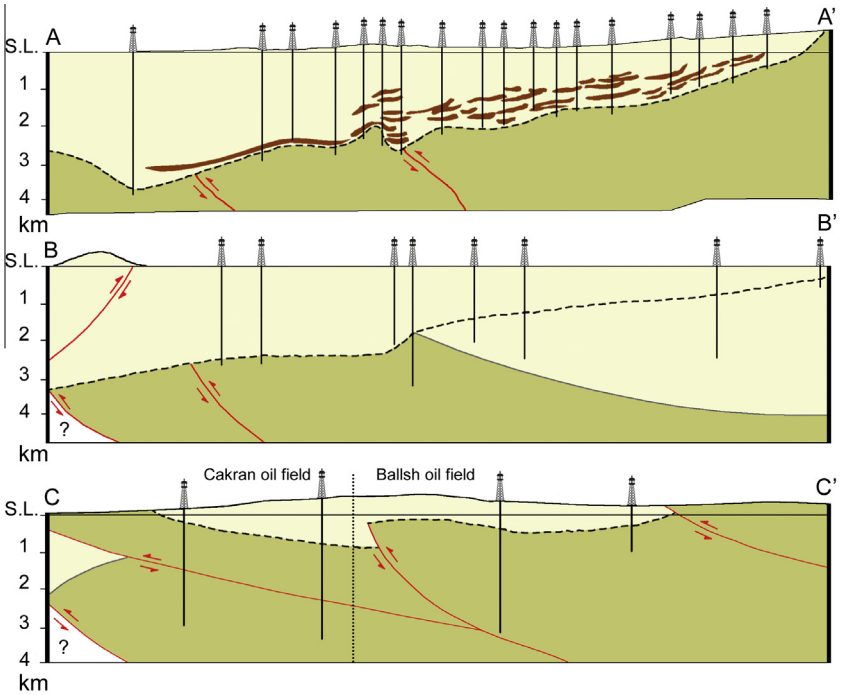

Fig. 3. Cross sections of (a) A-A′ in the KU oil field, (b) B-B′ in the MA oil field and (c) C-C′ in the BA–HE oil field (horizontal dimensions are not to scale), modified from Silo et al. (2013), and obtained from the seismic lines shown in Fig. 1. The colors of the sections are consistent with those of Fig. 1 and correspond to the PAD (yellow) and ION (green) zones. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3. Results and discussion

3.1. Activity concentrations in soil samples

The activity concentrations of the ^{40}K, ^{226}Ra and ^{228}Ra and ^{228}Th with $\pm1\sigma$ uncertainty (in Bq/kg) in the soil, oil-sand and sludge samples are shown in Appendix A. In Table 1, the average activity concentrations at $\pm1\sigma$ and the ranges for the soil, sludge and oil-sand samples from the different oil fields are shown. The overall averages of the activity concentrations (±standard deviation) of ^{40}K, ^{226}Ra, ^{228}Ra and ^{228}Th in the soil samples were 326 ± 83 Bq/kg, 20 ± 5 Bq/kg, 25 ± 10 Bq/kg and 25 ± 9 Bq/kg, respectively. The soil sample concentrations were lower than or comparable with the global median activity concentrations of ^{40}K, ^{238}U and ^{232}Th, which are 400 Bq/kg, 35 Bq/kg and 30 Bq/kg (UNSCEAR, 2000), respectively. Moreover, we compared our results with the data from several studies on the activity concentrations in soil samples from oil fields (Table 1). These data were highly variable, which could be attributed to the natural features, such as the geological and geochemical characteristics of the different areas, and to human activities, such as the contamination caused by the scales and the sludges. In a case study on natural radioactivity in Qatar (Al-Sulaiti et al., 2012), the high concentration of ^{226}Ra in the soil samples was from the NORM associated with the oil and gas extraction processes. In our study, although most soil samples were contaminated with crude oil and most likely, produced water, we did not observe any obvious radiological contamination. Radiological contamination was most likely not detected because the samples of produced water and crude oil had the minimum detectable activities (MDA) for all radionuclides, corresponding to 0.4, 1.1, 0.4 and 1.4 Bq/kg for ^{26}Ra, ^{228}Ra, ^{228}Th and ^{40}K, respectively.

The radium isotopes are generally unsupported in formation water, and because a fraction of the isotopes precipitate with oil-sands during oil extraction, an increase in the concentration and disequilibrium in the decay chain can occur. The disequilibrium in the ^{228}Ra decay segment was studied with the ratio of the activity concentrations of ^{228}Th and ^{228}Ra (Appendix B). We observed ratios that were systematically greater than unity; however, these ratios were not strong evidence of disequilibrium within the standard uncertainties. The ratios of the activity concentrations of ^{228}Ra and ^{228}Th for the soil, sludge and oil-sand samples (the last is discussed below) and the corresponding values of goodness of fit, expressed as reduced χ^2 in the parentheses, were 1.02 ± 0.07 (χ^2 = 0.5), 0.99 ± 0.20 (χ^2 = 3.9) and 1.05 ± 0.09 (χ^2 = 1.6), respectively. In this case, we also observed ratios close to unity for both the sludge and the oil-sand samples. However, for issues of environmental legacy, only the ^{226}Ra is a long-term concern because, after 25 years, approximately only 5% of the ^{228}Ra remains, but the evaluation of the secular equilibrium conditions was beyond the capacity of the MCA_Rad system.

The highest concentrations of ^{40}K, ^{226}Ra, ^{228}Ra and ^{228}Th were systematically observed in the HE oil field, whereas the lowest concentrations were in the KU oil field. The KU and MA oil fields are in the same hydrographic basin, located in the upstream and the downstream sectors of the basin, respectively, which was confirmed by the presence of round pebbles with dimensions in the range of centimeters in the KU oil field that were not present in the fine grain soils of the MA oil field. Therefore, the higher concentrations of ^{228}Ra and ^{228}Th in the sediments of the MA oil field than those in the sediments of the KU oil field might be correlated with a selective mechanical deposition, which was also observed in placer deposits. Moreover, as reported by Ostrosi et al. (1998), heavy mineral placers are exploited along the shore of the Adriatic Sea. However, the higher activity concentrations in the HE oil field could be a consequence of either different host rocks or differences in the geomorphological structure (slope debris) compared with the KU and MA oil fields. Additionally, the genetic processes of soils that originated on carbonate substrates tend to enrich the sediments, in particular, with uranium and thorium; this process might be the cause for the relatively high activity in the soils from the HE oil field (Greeman et al., 1999).

Table 1
Average activity concentrations (±1σ) for ^{40}K, ^{226}Ra, ^{228}Ra and ^{228}Th in soil, oil-sand and sludge samples for different oilfields studied in Albania are reported together with the average (±1σ), absorbed dose rates (*DR*) and annual effective dose rates (*AEDR*). Average activity concentrations (±1σ) and ranges for ^{40}K, ^{226}Ra, ^{228}Ra and ^{228}Th in soil samples compared with those from oilfields reported in different studies.

Sample type	Country (Author)		No.	^{40}K (Bq/kg)	^{226}Ra (Bq/kg)	^{228}Ra (Bq/kg)	^{228Th} (Bq/kg)	DR (nGy/h)	AEDR (mSv/y)
Soil	Albania	KU	21	297 ± 48	17 ± 2	19 ± 5	20 ± 5	32 ± 5	0.04 ± 0.01
		MA	3	360 ± 42	19 ± 3	33 ± 6	29 ± 5	44 ± 5	0.05 ± 0.01
		BA	3	253 ± 75	21 ± 7	29 ± 8	29 ± 9	38 ± 11	0.05 ± 0.01
		HE	5	472 ± 41	30 ± 1	42 ± 6	40 ± 4	58 ± 4	0.07 ± 0.01
	Albania (this study)		32	**326 ± 83** (204–535)	**20 ± 5** (12–32)	**25 ± 10** (11–51)	**25 ± 9** (11–44)	**38 ± 11** (32–58)	**0.05 ± 0.01** (0.04–0.07)
	Tunisia (Hrichi et al., 2013)		1	176 ± 1	9 ± 0.1	11 ± 0.1[a]	18 ± 0.2	0.022	
	Kuwait (Abdullah et al., 2008)		47	(191–296)	(12–25)	(9–16)[a]		–	–
	Nigeria (Avwiri and Ononugbo, 2012)		12	**263 ± 10** (134–395)	**30 ± 1** (16–52)	**17 ± 1**[a] (10–34)	**35** (23–47)	**0.04** (0.03–0.06)	
	Nigeria (Jibiri and Amakom, 2011)		9	**129 ± 70** (MDA–248)	**76 ± 34** (30–122)	**21 ± 6**[a] (12–29)	**53 ± 18** (25–73)	**0.06 ± 0.02** (0.03–0.09)	
	Canada (Saint-Fort et al., 2007)		21	–	(10–10 × 10^3)	(7–260)	(MDA–10)	–	–
	Egypt (Shawky et al., 2001)		4	(MDA–45 × 10^3)	(18 × 10^3–438 × 10^3)	(35 × 10^3–987 × 10^3)	(MDA–9 × 10^3)	–	–
Sludge	Albania	–	3	348 ± 115	19 ± 4	22 ± 4	23 ± 6	36 ± 8	0.04 ± 0.01
		MA	1	314 ± 18	18 ± 3	22 ± 6	25 ± 3	35 ± 6	0.04 ± 0.01
		BA	2	175 ± 89	20 ± 11	21 ± 7	13 ± 1	29 ± 3	0.04 ± 0.01
Oil-sand	Albania	KU	10	549 ± 12	23 ± 2	23 ± 2	24 ± 3	47 ± 2	0.06 ± 0.01
		MA	2	366 ± 49	12 ± 2	14 ± 4	12 ± 4	29 ± 2	0.04 ± 0.01

[a] Reported as ^{232}Th.

The ^{137}Cs was only in the soil samples and the concentrations were highly variable: the average concentrations were 6 ± 4 Bq/kg in the KU oil field, 14 ± 6 Bq/kg in the BA oil field, 9 ± 9 Bq/kg in the HE oil field and 15 ± 7 Bq/kg in the MA oil field. Moreover, for undisturbed soils with a high presence of minerals, the vertical migration of ^{137}Cs was comparatively slow, and a greater fraction of activity concentration was expected in the top-soil (0–10 cm) (UNSCEAR, 2008). The absence of ^{137}Cs in the oil-sands could be used to discriminate those samples from the soil samples with the tracer.

The activity concentration ratios (±1σ uncertainty) for ^{228}Ra/^{226}Ra, ^{226}Ra/^{40}K and ^{228}Ra/^{40}K (Fig. 4) (hereafter, assuming secular equilibrium, as Th/U, U/K and Th/K, respectively) are summarized in Appendix B. The ratios were studied to understand the hidden geochemical patterns of the analyzed samples. In general, the activity concentration ratios in the soil samples showed a specific signature (confirmed at ±1σ) over the oil field reservoirs, which allowed us to attribute a clastic sedimentary origin to the reservoirs (primary constituents of the PAD unit, see Fig. 1). Moreover, the measured activity concentration ratios of Th/U, U/K and Th/K were comparable with the average activity concentration ratios in sandstone, which are 1.06, 0.062 and 0.068, respectively, and in shale, which are 1.07, 0.055 and 0.058, respectively (Van Schmus, 1995). This comparison was reasonable because the soils originated in the alluvial deposits overlaying the PAD unit.

The oil-sand samples (discussed later) also had similar ratios (Fig. 4); a collective interpretation of the results from the oil-sands was relatively complex because of their different lithological origins. For the MA oil field, the activity concentration ratios (Appendix B) indicated an increase in Th and K compared with an average carbonate rock, which were characterized by Th/U, U/K and Th/K values equal to 0.25, 0.32 and 0.082, respectively (Van Schmus, 1995). This result could be ascribed to the lithological characteristics of the MA reservoir rock, which has a significant amount of terrigenous minerals (ION unit described in Fig. 1). For the KU oil field, the activity concentration ratios were particularly similar to sandstone rocks (Van Schmus, 1995), and the slight difference could be attributed to the highly heterogeneous composition of the sandstone rocks.

3.2. Activity concentrations in the sludge samples

The averages of the activity concentrations of ^{40}K, ^{226}Ra, ^{228}Ra and ^{228}Th in the sludge samples were comparable, within the uncertainty, for all of the oil fields (Table 1). Because the sludge was a mixture of crude oil, oil-sand and soil, the variability in the activity concentrations of the sludge was difficult to interpret because the variability was dependent on the fractions in the mixture. However, a significant fraction of crude oil in the mixture would decrease the radioactivity level because the concentrations of radionuclides were very low in crude oil. In the sludge samples from the KU oil field, we observed a slight increase in the activity concentrations of ^{40}K, ^{226}Ra, ^{228}Ra and ^{228}Th compared with the soil samples; this increase was most likely caused by the relatively high concentrations of oil-sand in the sludge samples. This assumption was confirmed in the MA oil field in which we observed a slight decrease in the activity concentrations of ^{40}K, ^{226}Ra, ^{228}Ra and ^{228}Th compared with the soil samples because of the relatively low concentrations of oil-sand in the sludge samples.

3.3. Activity concentration in the oil-sand samples

The activity concentrations of ^{40}K, ^{226}Ra, ^{228}Ra and ^{228}Th in the oil-sand samples from the KU and the MA oil fields differed significantly (within 2σ uncertainty) (Table 1). The two oil fields were

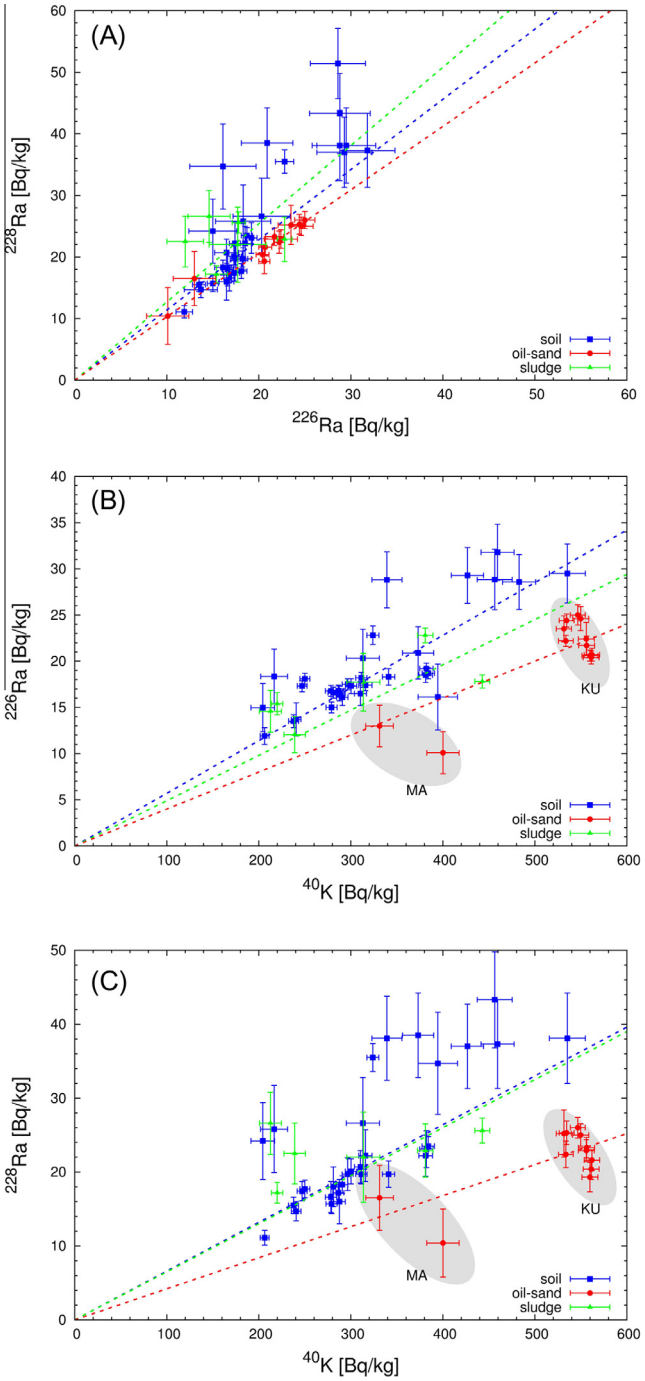

Fig. 4. (A) ^{228}Ra/^{226}Ra, (B) ^{226}Ra/^{40}K and (C) ^{228}Ra/^{40}K activity concentration ratios for soil (blue), oil-sand (red) and sludge (green) samples. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

easily recognized using the patterns of the ^{226}Ra/^{40}K and ^{228}Ra/^{40}K ratios (Fig. 4b and c). The discrimination between the two oil fields was also achieved with the mineralogical analysis (Table 2) of the oil-sand samples collected in the different wells from the KU and the MA oil fields. These results confirmed that the KU oil field reservoir was located in sandy lenses that were in the PAD (absence of dolomite and very low calcite, in addition to the presence of muscovite and chlorite and an increase in the K-feldspar), whereas the MA oil field reservoir was located in the fractured limestones of the ION (presence of calcite and dolomite) (see Fig. 1). This interpretation was also supported by the higher radioactivity content of the KU oil field samples (more radioactive sandy lenses) than that in the samples of the MA oil field (less radioactive limestones) (Fig. 4).

The KU oil-sand samples were characterized by a significant terrigenous content (deep-sea sediments transported to the oceans by rivers from land sources) composed of quartz, feldspars, mica, chlorite and a very low amount of calcite. The chlorite and muscovite minerals confirmed the geodynamic model that predicted a dismantling of the magmatic rocks of the Inner Units. In particular, the chlorite could be formed by the alteration of other silicate minerals that contained Mg and Fe (e.g., olivine, augite (pyroxene), hornblende, and biotite), which is typical of ophiolitic suites (deep-sea marine sediments overlying, from top to bottom, pillow basalts, sheeted dikes, gabbro, dunite, and peridotite). The percentages of Quartz, Feldspar and Lithics (QFL) (plotted in the ternary diagram of Fig. 5) measured in the 3 samples of the KU oil-sand were comparable with those reported in Dickinson (1985), which corresponded to the mineralogical signatures typical of terrigenous Cenozoic sandstones deposited in different sites. Referring to the QFL triangle of Dickinson (1985), we affirmed that the oil-sand samples were related to a source rock environment, such as a "dissected arc", which was connected to the exposure of volcanic and basement rocks (in this case, the ophiolitic rocks of the Inner Unit). The reservoir was formed by sands that contained many minerals of magmatic derivation (muscovite, chlorite and feldspars), and therefore, the higher amounts of radionuclides in the KU samples than in the MA samples was confirmed.

In the MA oil field, the depth provenance of the oil-sand was greater than that of the KU oil-sand samples because of the geological structure and the existence of deep stratigraphic traps. In particular, the MA oil-sand samples came from a reservoir that is located near a planar discontinuity called a "major unconformity" (dashed line in Fig. 3 Sect. BB′). The higher calcite content (Table 2) of both the MA oil-sand samples indicated that the reservoir is located in the carbonate source rock (ION) or near the interface with the overlying molasses sediments (PAD) (see Fig. 1). The data from the MA and the KU in the QFL (Quartz, Feldspar and Lithics) confirmed our analysis. In particular, the MA oil-sands were the result of recycled orogens. The deformation and the uplift of supracrustal strata included sedimentary and volcanic rocks exposed in varied fold-thrust belts of the orogenic regions. The lower radioactivity content was perfectly consistent with the geodynamic framework and the mineralogical nature of the oil-sand reservoir. In particular, the source rock with the high calcite content, which is typical for the ION, lacked radionuclides, and therefore, the extracted oil-sands were a negligible source of NORM.

4. Radiological assessment

The absorbed dose rate (*DR*) in air from external gamma radiation at 1 m above ground-level caused by the presence of uniformly distributed natural radionuclides in the measured soils was calculated according to UNSCEAR (2000):

$$DR\ (\mathrm{nGy/h}) = 0.0417A_{\mathrm{K}} + 0.462A_{\mathrm{U}} + 0.604A_{\mathrm{Th}} \quad (1)$$

where A_{K}, A_{U}, and A_{Th} are the activity concentrations (in Bq/kg) for ^{40}K, ^{238}U (as ^{226}Ra) and ^{232}Th (as ^{228}Ra), respectively. Secular equilibrium was assumed for the dose calculation. The average outdoor absorbed dose rate (at $\pm 1\sigma$ uncertainty) in the KU oil field area was 32 ± 5 nGy/h; in the MA oil field, 44 ± 5 nGy/h; in the BA oil field, 38 ± 11 nGy/h; and in the HE oil field, 58 ± 4 nGy/h (Table 1). The calculated outdoor absorbed dose rates ranged from 21 (KU) to 64 nGy/h (HE). These dose rates were lower than or comparable with the population weighted average absorbed dose rate in

Table 2
Mineral percentage content measured by X-ray diffractometry and activity concentration measured by the MCA_Rad system for oil-sand samples collected in the KU and MA oilfield. The uncertainty associated to the mineralogical analysis is approximately 10–15% for Quartz and 20–30% for the other minerals (minerals estimated with an uncertainty greater than 30% are reported as <5). The Limit of Detection (LD) for XRD measurements is 1%.

Sample ID	Qtz	Pl	Kfs	Cal	Dol	Ms	Chl	^{40}K (Bq/kg)	^{226}Ra (Bq/kg)	^{228}Ra (Bq/kg)	^{228Th} (Bq/kg)
KU_OS1	40	20	6	<5	<LD	15	7	534 ± 8	22 ± 1	22 ± 2	25 ± 2
KU_OS5	44	20	13	<5	<LD	8	8	547 ± 8	25 ± 1	26 ± 1	29 ± 2
KU_OS6	43	20	8	<5	<LD	10	6	560 ± 9	21 ± 1	19 ± 2	21 ± 1
MA_OS1	60	12	8	12	<5	<LD	<5	331 ± 15	13 ± 2	16 ± 4	9 ± 2
MA_OS2	55	11	8	20	<5	<5	<LD	400 ± 18	10 ± 2	10 ± 5	14 ± 2

Qtz – Quartz, Pl – Plagioclase, Kfs – K-Feldspar, Cal – Calcite, Dol – Dolomite, Ms – Muscovite, and Chl – Chlorite.

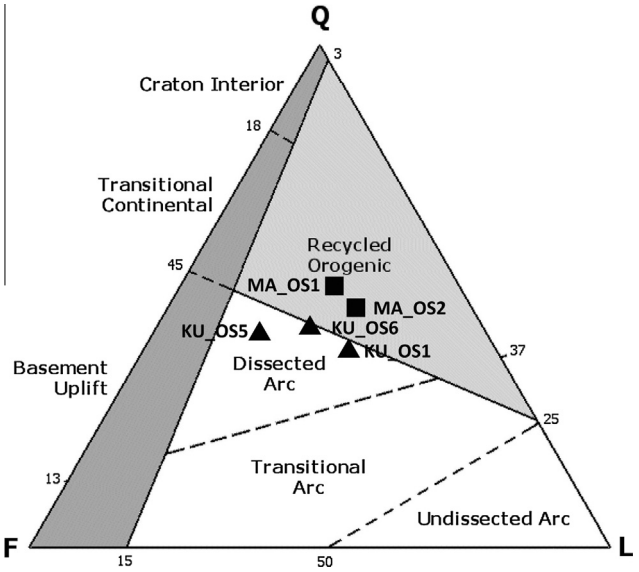

Fig. 5. Quartz, Feldspar and Lithics ternary diagram after Dickinson (1985). The oil-sand plot is primarily in the dissected arc and recycled orogenic fields for KU (triangles) and MA (rectangles) oil fields, respectively.

outdoor air from terrestrial gamma radiation (60 nGy/h) (UNSCEAR, 2000).

The average outdoor absorbed dose rates (at ±1σ uncertainty) from the sludge and the oil-sand samples are reported in Table 1, which ranged between 27 and 50 nGy/h. Assuming the worst-case scenario in the KU oil field, which corresponded to oil-sands uniformly distributed over the topsoil, the absorbed dose rate was estimated to increase on average 50%, i.e., to a maximum value of 47 ± 2 nGy/h. With the same scenario, we observed a decrease in the absorbed dose rate for the other oil fields. Therefore, the radiation exposure to workers in the oil and gas industry was negligible from increased gamma dose rates, despite the relatively higher radioactivity content in the oil-sand residues in the KU oil field.

The radiological hazard for workers and populations living in the oil field areas was evaluated as the Annual Effective Dose Rate (*AEDR*). The evaluation of the *AEDR* was performed using an outdoor time occupancy factor equal to 20% and a conversion factor of 0.7 (Sv/Gy), which accounted for the biological effectiveness of the dose rate in causing damage to human tissues.

$$AEDR\ (\mathrm{mSv/y}) = DR \times 10^{-6}(\mathrm{mGy/h}) \times 8760(\mathrm{h/y}) \times 0.7(\mathrm{Sv/Gy}) \times 0.2 \quad (2)$$

The results of the radiological assessment are summarized in Table 1. The annual outdoor effective dose rate of 0.05 ± 0.01 mSv/y that was associated with the radioactive content in the soils was lower than the worldwide annual effective dose value of 0.07 mSv/y, as reported by UNSCEAR (2000). For the worst-case scenario described above, we predicted an increase in the *AEDR* of approximately 0.02 ± 0.01 mSv/y for the KU oil field; a value that was negligible because of the recommended excess limit of an effective dose for the local population (1 mSv/y). Therefore, in the KU, MA, BA and HE oil fields, radiological contamination was not a concern.

5. Conclusions

This study was the first screening campaign for the identification and the monitoring of oil and gas industry processes that involved NORMs. Accordingly, the KU, MA and BA–HE oil fields were chosen as pilot study areas in which secondary recovery techniques for oil extraction were recently introduced. In particular, the radioactivity of soil (N = 32), sludge (N = 6), oil-sand (N = 12), produced water (N = 1) and crude oil (N = 1) samples was measured using gamma ray spectrometry. The results provided baseline information for the local environmental legacy policies and for the implementation of EU legislation.

The average activity concentrations (±standard deviations) of ^{40}K, ^{226}Ra, ^{228}Ra and ^{228}Th in the soil samples collected in the primary oil fields in Albania were 326 ± 83 Bq/kg, 20 ± 5 Bq/kg, 25 ± 10 Bq/kg, 25 ± 9 Bq/kg and 6 ± 4 Bq/kg, respectively. The results for the soil samples were comparable with the data that were reported in several studies on activity concentrations in soil samples from oil fields. The activity concentrations in the soil samples were highly variable, which could be attributed primarily to the geological and geochemical characteristics of the different areas, and secondarily, to effects most likely from human activities, such as the release of oil-sands and sludges. The radiological effect caused by the soils contaminated with crude oil and produced water surrounding the Albanian oil fields was negligible; the activity concentrations in the produced water and the crude oil samples were very low (below the MDA). Geological and geochemical arguments were used to describe the activity concentrations in the different oil fields. The higher radioactivity content in the soils from the HE oil field than that from the soils of the KU oil field was attributed to both the carbonate origin of the host rocks and the different geomorphological structure. Moreover, previous studies confirmed that soils that originated on carbonate substrates tended to enrich the sediments with uranium and thorium. For the KU and MA oil fields, which are part of the same hydrographic basin, the increasing trend for the activity concentrations of the thorium progenies indicated selective deposition and as supported by studies in the literature, the occurrence of heavy placer deposits along the shore of the Adriatic Sea. According to the Th/U, U/K and Th/K ratios, the origin of the soil samples was reasonably connected to the alluvial deposits overlaying the PAD unit.

The activity concentrations in the sludge samples were reasonably understood when considering that the sludges were mixtures of soil, crude oil, and oil-sand. This study was the first to report on the activity concentrations in the oil-sand samples generated

during heavy oil extraction. The average activity concentrations of the oil-sand samples measured in the KU and MA oil fields differed at the 2σ level and were 549 ± 12 Bq/kg (^{40}K), 23 ± 2 Bq/kg (^{226}Ra), 23 ± 2 Bq/kg (^{228}Ra) and 24 ± 3 Bq/kg (^{228}Th) in the KU oil field and were 366 ± 49 Bq/kg (^{40}K), 12 ± 2 Bq/kg (^{226}Ra), 14 ± 4 Bq/kg (^{228}Ra) and 12 ± 4 Bq/kg (^{228}Th) in the MA oil field. Based on the mineralogical analysis of the oil-sand samples, we confirmed the geophysical evidence in the literature on the origin of the oil field reservoirs: the sandy lenses located in the PAD unit for the KU oil field, and the fractured limestone located in the ION unit for the MA oil field. Moreover, the KU oil-sand samples were characterized by terrigenous contents with very low amounts of calcite, and the presence of chlorite and muscovite minerals confirmed the geodynamic model that predicted a dismantling of magmatic rocks in the Inner Unit. The MA oil-sands confirmed the connection to the geological structure because of the higher amount of calcite. These different origins of the oil fields were also confirmed with the activity concentration results because the KU samples contained many minerals from the magmatic deviation that showed higher activity concentrations of ^{40}K, ^{226}Ra, ^{228}Ra and ^{228}Th than the MA samples, which originated from carbonate rocks with a lower radioactive content. Based on this geological framework, the future radiological assessments of other fields in the region can be strategically planned to focus on the oil-sands from the Neogene molasses deposits.

The absorbed dose rate and the annual effective dose rate were calculated to assess the radioactive exposure of workers and members of the public from the NORMs produced in the oil and gas industry, in compliance with an EU recommendation. Assuming the worst-case scenario, i.e., sludge and oil-sands uniformly distributed over the topsoil, the absorbed dose rate and the *AEDR* of the KU oil field were estimated to increase on average by a maximum of 50%, i.e., to maximum values of 47 ± 2 nGy/h and 0.06 ± 0.01 mSv/y, respectively. In the other oil fields, the effects of the industrial processes were negligible. Based on the worldwide annual effective dose of 0.07 mSv/y associated with the radioactive content in soils and on the recommended excess limit of an effective dose for the local population of 1 mSv/y, we concluded that radiological contamination was not a concern in the KU, MA, BA and HE oil fields.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemosphere.2015.05.018.

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