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RADIOLOGICAL IMPACT ASSESSMENT ON BEHALF OF OIL/GAS INDUSTRY

Elena Botezatu, C. Grecea

Institute of Public Health Iaşi

Abstract. Aim: to assess the radiological impact of oil and gas industry on the environment and population. **Material and Methods**: Since 1999 we made environmental monitoring of radioactivity in the surrounding of six oil fields in Bacău and Brăila districts. The ground and surface water samples originating from oil areas and the formation water samples arising from oil wells, water injection wells and treating stations were analysed for their radium-226 content. **Results and discussion:** Radium-226 concentrations from 0.005 Bq/l up to more 10 Bq/l were found in the formation water samples. In production equipment, we found the highest concentrations of radium reaching up to 9000 Bq/kg in scale and much lower (300 Bq/kg) in sludge. Measurements in soil and vegetation had clearly shown somewhat higher local activity values for radium-226 content related to accidental discharges of oil-field brines. **Conclusion:** From the radiological point of view, the situation does not pose any immediate concern, but the high radium-226 content of oil field formation waters could lead to environmental pollution.
Key words: radioactivity, natural radionuclides, oil and gas industry

Rezumat. Obiectiv: evaluarea impactului radiologic al industriei extractive de petrol şi gaze asupra mediului şi populaţiei. **Material şi metodă:** Începând din 1999 s-a efectuat determinarea radioactivităţii naturale în probe de mediu prelevate din judeţele Bacău şi Brăila unde există 6 schele petrolifere. **Rezultate şi discuţii:** Conţinutul de radiu-226 al apelor de zăcământ este mult mai mare (până la 2 ordine de mărime) decât al apelor de suprafaţă sau de profunzime din aceleaşi zone. Valorile se situează în domeniul 0,005 – 10,25 Bq/l, cu valorile cele mai mari pentru judeţul Bacău. Concentraţiile de radiu-226 ating valori de 9000 Bq/kg în crusta de pe instalaţii şi 300 Bq/kg în nămolul din staţiile de tratare. Determinările conţinutului de radiu-226, efectuate pentru sol şi vegetaţie spontană, au relevat unele valori locale mai mari pentru zonele cu deversări accidentale de apă de zăcământ sau în zonele de depozitare şi curăţire a instalaţiilor dezafectate. **Concluzie**: Din punct de vedere radiologic situaţia prezentă nu ridică probleme imediate, însă potenţialul de poluare a zonelor petrolifere cu radiu-226 există.
Cuvinte cheie: radioactivitate, radionuclizi naturali, industria de petrol şi gaze

INTRODUCTION

The mining, milling and industrial use of naturally occurring radioactive materials (NORM) covers a range of mineral resources and industrial activities. The main so non-nuclear industries include phosphoric acid and fertilizer production; iron and steel production; coal and gas fired power plants; coal tar processing; extraction of coal, oil and gas; building materials industry; mineral sand; titanium pigment production, and uranium and thorium mining (1,2,3). There are no radiological

controls on the operation of these industries or restrictions on how waste is discharged (to the atmosphere, to landfill or being sold) which relate to its radionuclide content.

Radionuclides are known to be associated with organic materials in nature. Therefore, oil, gas and oil field brines frequently contain radioactive materials (4).

These materials accumulate in piping used to remove and process petroleum and natural gas.

Radioactivity in oil and gas production and processing equipment is of natural origin (5,6,7). Naturally occurring radioactive elements such as uranium, radium, and radon are dissolved in very low concentrations during normal reactions between water and rock or soil. Ground water that coexists with deposits of oil can have unusually high concentrations of dissolved constituents that build up during prolonged periods of water/rock contact. Uranium and thorium compounds are mostly insoluble, therefore remain in the underground reservoir and as oil and gas are brought to the surface. Many oil-field brines are particularly rich in chloride, enhancing the solubility of other elements including the radioactive element radium. Radium concentrations tend to be higher in more saline water (8). Some of this saline, radium-bearing water is also extracted with the oil and gas. Some radium and radium daughter compounds are slightly soluble in water and may become mobilized when this production water is brought to the surface.

Since in the Eastern Romania there are two oil regions in Bacău and Brăila counties, which represent about 25% from Romanian oil-field exploitation (over 10,000 wells) we aimed to the assessment of radium-226 content of oil-field waters and possible pollution of these zones with this radionuclide.

The objective of this study was to assess the radiological impact on the environment and population of the oil/gas industry that is non-nuclear industry but uses and can produce materials, with an enhanced content of naturally occurring radionuclides.

MATERIAL AND METHODS

The ground and surface water samples (87) originating from oil areas and the formation water samples (1200) arising from oil wells, water injection wells and treating stations were drawn and analysed for their radium-226 content. The method used for the determination of the radium-226 content in water collects the radon-222 gas product of the decay of radium-226. Its radioactivity is measured by alpha rays measurement in a scintillating chamber and extrapolated back to the concentration of radium-226. The combined standard uncertainty varied in the range 0.01–0.11 Bq/l and the limit of detection was of 0,003 Bq/l.

The oil and gas production may produce radioactive pipe scale (a residue left in pipes from drilling oil wells) and sludge (that leaves sites and equipment contaminated), therefore we sampled scale and sludge. All these solid samples (60) were dried at 105^0C and after grinding were passed through 12-mesh sieve. The sieved samples were placed in the plastic Marinelli beaker and stored for 30

days to allow build up and reach radioactive equilibrium of radon and its daughters. After this period those samples were measured for their radium content. High-resolution gamma spectrometry techniques carried out in conformity with the current national standards and settlements were applied.

RESULTS AND DISCUSSION

The formation water must be separated and then disposed, usually by return to depth in an injection well. The present NORM in oil and gas production streams occasionally accumulates as scale or sludge in tubing and surface equipment. NORM radioactivity levels in produced water; scale and sludge usually are characterized in terms of radium activity level (Radium-226 and Radium-228).

Because the activity level of ^{226}Ra usually is three times that of ^{228}Ra, Radium-226 is the primary isotope of concern with respect to long term radiological concerns in environmental impact (6,8).

Radium-226 concentrations from 0.005 Bq/l up to more 10 Bq/l were to be found in the formation water samples arising from oil wells, water injection wells and treating stations (table 1). One should remark that 80% of samples exceeded the specific admitted activity of 0.88 Bq/l in Romania for surface water. We must give this problem our careful consideration taking into account that these formation waters are not reinjected in all situations, being accidentally discharged into watercourses and into cultivated or meadow lands.

Table 1. Activity concentration of ^{226} Ra in water samples originating from oil areas

DISTRICT	OIL FIELD	Water type	Radium-226 (Bq/L)	
			Range	Average ± SD
BACĂU	MOINESTI	Formation water	0.07 – 10.24	3. 72 ± 1.99
	MODARZAU	Formation water	0.17 – 4.45	2.53 ± 1.62
	ZEMES	Formation water	0.15 - 4.39	1.72 ± 1.53
	MOINESTI, ZEMES, MODARZAU	Ground and surface water	0.003 – 0.199	0.053 ± 0.039
BRĂILA	BORDEI VERDE	Formation water	0.052 – 0.077	0,067 ± 0,008
	OPRISENESTI	Formation water	0.005 – 0.019	0,009 ± 0.005
	IANCA	Formation water	0.034 – 5.05	1.70 ± 2.05
	BORDEI VERDE, OPRISENESTI, IANCA	Ground and surface water	0.007 – 0.127	0.044 ± 0.032

The radium-226 concentrations of the ground and surface water in the same territory were much smaller than that in oil-fields water, for the time being.

At oil-field sites the pipes and tanks that handle large volumes of this "produced water" can become coated with scale deposits that contain radium. Radium-bearing scale is the type of "diffuse NORM waste" that commonly occurs in the oil industry (7,9-12). When radium substitutes into the barium sulfate or calcium carbonate scale, it causes the scale to become

radioactive. Once formed, the barium sulfate scale is nearly impossible to dissolve. Mineral deposits in the form of radioactive scale and sludge can be progressively formed in production tubular and surface processing and transportation equipment. Since the radium concentrations in the original formation are highly variable, the concentrations that precipitate out in sludge and as scale on internal surface of oil and gas production and processing equipment are also variable. The scale is relatively insoluble and may vary in thickness from a few millimeters to more than 2 cm. NORM-contaminated scales and sludge is found in production equipment, such as wellheads, heaters treaties, and storage tanks, as well as the pipe connecting the equipment. We found the highest concentrations of radium reaching up to ten thousand of Bq/kg in scale deposited in wellhead piping and in production tubing near wellhead. There was a decrease of this concentration of radium deposited in separators (up to one order of magnitude), the lowest value being found in heaters/treaties.

Some of the solids in the original product stream are removed in the separator, the treatment equipment and tanks and accumulate there as sludge. Radium-226 concentrations in sludge were much lower than concentrations in pipe scale (table 2).

Table 2. Activity concentration of ^{226}Ra in scale and sludge samples

Type of sample	Radium-226 (Bq/kg) Range	Average
SCALE	287 – 9260	3200 ± 1310
SLUDGE	21 – 330	120 ± 67

Radium-226 dominates sludge and pipes scale accumulations, while deposits on interior surfaces of gas plant equipment are predominantly Lead-210 with its decay product Polonium-210, up to 3000 Bq/kg. Therefore, all the oil field equipment must be surveyed for the presence of enhanced natural radioactivity. The only way to remove the scale is to drill it out or otherwise physically remove it. Some scale is removed at the well site during work over operations. As a result, NORM contamination was found on the ground where work over operations have been conducted to remove scale, either at the well site or at a remote pipe-cleaning yard. Most scale is recovered from equipment when this is sent to a facility for cleaning. More external gamma exposure and dust inhalation occurs for workers when contaminated scale or sludge is cleaned from the inside surfaces of equipment during well work over operations (10).

Measurements in soil and vegetation had clearly shown somewhat higher local activity values for radium-226 content related to accidental discharges

of oil-field brines. Local activities up to about 300 Bq/kg of soil and the relatively higher external dose rates up to 400 nGy/h, (two times natural radiation background) were associated with these areas around formation water discharge and handling system and descaling of pipes.

The activity concentration values in soil, surface water and spontaneous vegetation originated in oil field areas are reported in table 3 comparatively with usual values for Romania.

- The concentrations of uranium, thorium and potassium in the upper 5cm layer of soil were generally higher in the surroundings of the investigated oil fields and wells but were comparable to the representative values for the Romania (13,14).

The average value of annual absorbed dose rate in air from terrestrial gamma radiation (mGy/y) related to this non-nuclear industry is of 0.61, smaller than those related to the other non-nuclear industries (0.72 for Coal Fired Power Plants and 0.64 for Phosphate Fertilizer Plant) (15). These values, even higher, are comparable with the annual average absorbed dose rate in air from terrestrial gamma radiation in Romania is of 0.52 mGy/y (16).

Table 3. Typically encountered activity concentration of natural radionuclides associated with oil and gas industry

Component of Environment	Industry	Activity mass concentration (range)			
		^{238}U	^{226}Ra	^{232}Th	^{40}K
Soil Bq/kg	Oil-field	2.4 – **120**	60 – **330**	8 – 87	53 - 960
	Usual values	8 – 60	8 – 72	11 – 75	250 - 1100
Surface water mBq/l	Oil-field	0.043 – 1.1	23 – 45	0.2 – 8.0	221 - 899
	Usual values	0.35 – 18.5	1.8 – 22.5	1.5 – 12.2	25 - 670
Spontaneous vegetation Bq/kg	Oil-field	0.2 - 55	3.7 – 59.2	0.05 – 0.12	710 - 1100
	Usual values	0.7 - 48	1.8 – 18.7	1.6 – 3.5	350 - 640

- The natural radioactivity levels for thorium-232 and potassium-40 detected in surface water are generally comparable to those found in the other zones of Romania. The values of radium-226 are little higher than the corresponding concentrations found generally in Romanian surface waters (13-16). One should remark that the values for neither of the analysed groups of samples exceeded the level for specific admitted activity in Romania even for fresh water, for any of the natural radioelements under investigation.
- The vegetation samples showed somewhat higher local activity values for radium-226 content of up to 62

Bq/kg, related to accidental discharges of formation water areas being much higher than that determined in other areas (14).

CONCLUSIONS

- The natural radioactivity levels in the oil field environmental media, which could represent a risk for the people living in the areas influenced by this non-nuclear industry, do not indicate an increase in the natural radiation background.
- From a radiological point of view, the situation does not pose any immediate concern. Some places however need further investigations, with special emphasis on the control of ^{226}Ra releases to prevent from polluting the environment with this radionuclide.
- The growing concern amongst the population about the quality of their environment increases the significance of impact assessment of radioactive releases into the environment even if natural radionuclides occur.

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