Investigation into Natural and Anthropogenic Radionuclide Contamination on the Absheron Peninsula, Azerbaijan - 10208

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ABSTRACT

The Absheron peninsula in Azerbaijan has a long history of oil and gas exploration, transport, and processing. The region surrounding the capital, Baku, has played a critical role in past conflicts, in particular in the two World Wars, and it continues to play a critical role in providing fossil fuels to Europe. However, the urgency of providing oil and gas, coupled with less stringent environmental controls in the past, has led to considerable contamination of the soil and water in the region with naturally occurring radioactive materials (NORM) as well as heavy metals and organic materials. In addition, the malfunction of the Chernobyl nuclear power reactor in Ukraine has contributed to the environmental burden in the region.

Radiometric surveys, performed at two abandoned iodine separation plants, have shown radiation levels two to three orders of magnitude above background levels. These elevated radiation levels are mainly due to Ra-228 and Ra-226 with lower contributions from U-238 and U-235. More detailed analysis of one specific sample showed a general decrease in Ra-226 and Ra-228 concentration with depth.

INTRODUCTION

Azerbaijan has long been considered as one of the leading oil and gas producing nations. Currently, 35 leading oil companies, representing 15 nationalities, are involved in exploration in 22 areas in this country. In addition, Azerbaijan continues to serve as a hub for the transportation of hydrocarbon resources to international markets.

The oil and gas industry in Azerbaijan has a long history [1]. Ancient historians described the shipping of oil, from the territory currently identified as Azerbaijan to Iran, as early as the third and fourth century. Information on the extraction of oil on the Absheron peninsula has been published by many Arabian and Iranian authors, for example, by Ibn Miskaveykh and Abu Dulafa in the 10^{th} century, by Yakut al Khamavi in the 13^{th} century, and by Khamdullah Qazvini in the 14^{th} century. In the 17^{th} century, oil from the Baku region attracted the attention of European countries. In the first quarter of the 18^{th} century, the Russian Czar, Peter the Great, became interested in the Baku region as a starting point for the development of trade with East. He was attracted especially to the so-called "white oil" that had been extracted in the Baku region for many years [2]. Azerbaijan played a crucial role during the World War II by supplying large quantities of oil to the former Soviet Union. In 1941, 23.5 million metric tons were extracted, representing 71.4 % of all the oil extracted in the former USSR.

The capital of Azerbaijan, Baku, located on the oil-rich Absheron peninsula, has long been functioning as a centre that brings together ancient oil-extracting traditions, current research and development in drilling, and extracting both oil and gas. However, the intense industrial activities, the urgency to extract oil, dictated by the war effort, and less stringent environmental standards have left a legacy of contamination in the district. To add to the level of contamination, along with the development of oil production,

refineries and various industrial enterprises, including the separation of iodine, and numerous chemical plants were created in Azerbaijan. After disorder in the Soviet Union, some of these factories stopped the activities. But, the environmental problems resulting from these activities are still of great concern. The use of obsolete technological processes and equipment over the years has led to the release of large quantities of a variety of waste into the environment. As a result, surface waters, soil, and the atmosphere have become polluted, numerous artificial lakes and swamps are polluted with oil, and emissions from outmoded equipment and a poorly maintained system of pipes to transport the oil and gas have contributed to the environmental burden.

Because of increased environmental awareness, the current Azeri government has initiated a number of projects to identify contaminated regions, to quantify the extent of contamination, and to develop and implement remedial action programs. Of particular importance to these initiatives is the presence of naturally occurring radioactive material (NORM), which are contaminants produced during oil extraction and refining processes. Preliminary investigations have shown U-235, U-238, Th-232, and K-40 levels that present unacceptable hazards to both the environment and the general public [3–9]. These projects are carried out with scientific and financial cooperation and support from a number of international organizations and funds [3, 4, 10-12]. Within these programs, the Project "Radio ecological survey of the soil of the territory of Baku City of the Absheron peninsula" is coordinated by Baku State University. The main purpose of this project is to perform radiometric surveys of soil, surface water, and marshy areas in the vicinity of Baku to: (1) identify sources of harmful radiation; (2) determine radionuclide composition and radioecological parameters, including activity, energy of radiation of these sources; and (3) estimate radioecological impact of the extent of the contamination.

When oil is separated from subsurface waters, NORMs such as uranium, thorium, and their daughter products are also extracted. These waters also contain alkali elements such as sodium and potassium, alkaline earth elements such as calcium, strontium, barium, and radium, and halides including iodine. Once the oil has been separated from the subsurface water, the water is disposed of in artificial lakes. Over time, NORMs accumulate in surface water and soil, giving rise to radiation levels as high as 1000 μR/h. The decay of uranium and thorium into radium and radon isotopes also presents a hazard to personnel who work on the oil extraction platforms.

The recovery of iodine for commercial purposes has exacerbated the environmental problem. When iodine was isolated, it was absorbed on activated charcoal in the presence of an acidic solution, then oxidized with $KMnO_4$, Cl_2, NaClO, $NaClO_3$, $KClO_3$, H_2O_2 or $NaNO_2$ [10]. The activated charcoal, now contaminated with NORM, was disposed of on the surface area around the iodine separation facilities. The sites are still contaminated and pose a health risk for those who live nearby. For example, although the sites are surrounded by security fences, local residents can be exposed to contaminants when they use materials from the sites for cooking or heating fuel in their homes.

The two main objectives of this research are: (1) to determine the levels of contamination at a number of sites, which have previously been identified as problematic; and (2) to survey soil, water, and sediment in locations that have shown elevated levels of radiation.

EXPERIMENTAL

The locations of the three sites under investigation are shown in Fig. 1. The distance between the Ramani and Surakani sites is ~ 7 km. Radiation levels were measured at a distance of 50 cm from the surface using a scintillation gamma dosimeter (MKC-AT1125) equipped with a NaI(Tl) crystal. The exact geographical location of the readings and subsequent sampling sites were measured using a GPS instrument (eTrex Legend Cx, Garmin) with a resolution of 0.1" or 5 m. Three separate readings were taken at each location and averaged for this report. Radiation readings were also taken at a distance of 10 m from the perimeter of the sites. Soil and sediment samples were taken from each corner and from the centre of selected 100 cm x 100 cm rectangular quadrats. The samples were thoroughly mixed, then dried for 5 hours at a temperature of 105°C. The dried samples were stored in hermetically sealed Marinelli beakers for one month to allow daughter isotopes to grow and reach a secular equilibrium. The samples were then counted by gamma spectrometry using an ORTEC spectrometer with an HPGe detector.

Figure 1: Location of the Ramani site (R), two sampling locations at the Surakhani site (S-1; S-2), and the capital of Azerbaijan, Baku

RESULTS AND DISCUSSION

The Ramani and Surakhani sites contain large volumes of activated charcoal in three and six distinct locations, respectively. The volumes and masses of this material were estimated based on the surface area that these volumes cover, the average height of the piles of charcoal, and a density of 600 kg/m^3 of the material sampled. These estimates are presented in Table I.

Table I. Estimated quantities of activated charcoal waste at the Ramani and Surakhani sites

Location	**Area** (m^2)		**Volume** (m^3)		**Mass** (metric tons)	
	Ramani	Surakhani	Ramani	Surakhani	Ramani	Surakhani
A	1521	5460	2282	6552	1370	3931
B	2095	4612	3143	4612	1890	2767
C	2475	5008	2723	12520	1630	7512
D	-	152	-	61	-	37
E	-	420	-	126	-	76
F	-	323	-	48	-	29
Total	6091	15975	8148	23919	4890	14352

The radionuclide concentrations of the activated coal samples from the Ramani and Surakhani sites were determined by gamma spectrometry and are shown in Table II.

Table II. Radionuclide concentrations in activated charcoal samples from the Ramani and Surakhani sites

Sample Location (waste)	**Depth** (m)	**U-235** (Bq/kg)	**U-238** (Bq/kg)	**Ra-226** (Bq/kg)	**Ra-228** (Bq/kg)	**A_{eff}** (Bq/kg)
Ramani						
M7 (A)	0.0	167±5	3480±15	5019±19	811±11	6081±24
M12 (B)	0.0	84±2	1743±12	4111±19	680±11	5002±24
M25 (C)	0.0	284±6	5928±27	9452±30	576±11	10207±33
M25 (C)	0.60	174±5	3623±16	7120±25	445±16	7703±33
M41	0.0	3371±443	70360±9260	138250±3350	9573±125	150790±3353
Surakhani						
N12 (I)	0.0	82±2	1709±15	8003±41	2974±32	11899±59
N17 (II)	0.0	150±5	3129±19	8510±31	1252±18	10150±39
N23 (III)	0.0	170±6	3553±21	8984±30	963±19	10246±39
N23 (III)	0.30	179±6	3744±23	11876±46	979±31	13158±61
N23 (III)	0.60	164±5	3421±19	10176±47	718±32	11117±63
N24 (IV)	0.0	182±7	3797±22	10523±49	951±33	11769±65
N31 (V)	0.0	71±3	1473±12	6325±24	798±14	7370±30

The dose rate near the wastes was in the range of 38-163 μR/h, and 102-240 μR/h near the centre. At a distance of 10 m from the perimeter, the dose rate remained relatively high, i.e., 12-25 μR/h, compared to background readings of 5-8 μR/h. During these dose rate measurements, the activity of radon isotopes was below the limit of detection of the instrument (<20 Bq/m^3), presumably because of dilution in the atmosphere or dispersion by the wind. However, under confined conditions, radon emanation would be expected to lead to unacceptably high values; and thus unsafe working conditions. This point should be considered in plans for eventual disposal and handling of the activated charcoal, and also with respect to any unauthorized use of this material as fuel for heating or cooking.

Results obtained for water samples showed the presence of U-235, U-238, Ra-226, and Ra-228, including decay products. Ra-226 and Ra-228 concentrations in the groundwater associated with oil were less than 10 Bq/L, and that of K-40 was less than 30 Bq/L. The high radionuclide concentrations in the activated charcoal are attributed to the high sorptive capacity of this material. It should be noted that, with the exception of K-40, the concentration of NORM in unpolluted soils, taken near Baku State University and near the Heydar Aliyev international airport, are lower than 100 Bq/kg.

Although the measured uranium concentration in the groundwater was also very low, uranium is expected to have been sorbed on the activated charcoal over the years, resulting in relatively high U-235 and U-238 concentrations. The absence of K-40 in the activated charcoal can be explained by the high solubility of the salts that it forms. Any sorbed potassium would have been leached from the charcoal by rainwater over the years.

To estimate the radiological health hazard of the activated charcoal, its activity was evaluated on the basis of Russian standards, which are applied to construction materials containing NORMs. This standard is based on the calculation of the effective activity, $A_{eff.}$ [13]. A_{eff} and its standard deviation were calculated using the following equations:

$$A_{eff} = A_{Ra226} + 1.31A_{Th232} + 0.085A_{K40} \quad \text{(Eq. 1)}$$

$$\sigma_{A_{eff}} = \sqrt{\sigma^2_{A_{Ra226}} + 1.7\sigma^2_{A_{Th232}} + 0.007\sigma^2_{A_{K40}}}$$

The classification of these waste categories are shown in Table III. (Eq. 2)

Table III. Categories of industrial waste at the OGC enterprises

Waste Category	**Effective Activity (A_{eff}),** Bq/kg	**Gamma Radiation Dose Rate** μR/h
I	$A_{eff} \leq 1500$	≤70
II	$1500 < A_{eff} \leq 10000$	70-440
III	$A_{eff} > 10000$	>440

Note: Gamma radiation dose rate is measured at a distance of 0.1 m from the surface of the waste

The radiation measurements and the radiometric results for soil, solid waste, and sediments sampled from the S-2 location at the Surakhani site are presented in Table IV.

Even though the radiation levels of samples 5, 9, 10, 14, 15, and 16 were similar to background levels, these samples were included in the gamma spectrometric analysis to ascertain if a relationship exists between radiation levels and radionuclide concentrations.

The results show that the highest level of radioactive contamination was observed in samples taken from soils in the vicinity of borehole pipes and around channels used to discharge groundwater that was pumped from the geological formations with the oil (samples 1, 2, 6, 7, 12). The levels of the NORM were, typically, two orders of magnitude higher than those of background samples. This observation can be explained by the fact that, as the groundwater reaches the surface, the pressure and temperature decrease. This causes the alkaline earth element and the carbonate and sulphate anions concentrations to exceed their respective solubility product leading to the precipitation of mixed calcium and magnesium sulphates and carbonates with the co-precipitation of trace quantities of radium on the inner walls of pipes, valves, pumps, and separators, and in the channels used to discharge the groundwater. Clays and other phyllosilicates in the soil also serve as ion exchange media for the preferential sorption of alkaline earth metal ions, including radium. However, there are some exceptions: sample 10, representing sediment from one of the channels, did not show elevated levels of NORM or potassium. A sample taken from a dry lake (sample 8) also showed negligible levels of NORM and no detectable level of K-40.

Referring to Table III, five areas represented by samples 3, 4, 8, 11, and 13 fall into Waste Category 1, while four areas, represented by samples 1, 2, 7, and 12 fall into Waste Category II and one area, represented by sample 6, falls into Waste Category III. There are no health and safety restrictions for handling wastes in Category I, including their collection, temporary storage, transportation, and burial with common industrial waste at designated disposal sites in the region. Handling, transportation, and eventual disposal of material that falls into Waste Category II is governed by regulations developed by the Organization for State Sanitary - Epidemiological Control of the Republic of Azerbaijan to protect worker health and address radiation safety. Material classified as Waste Category III requires adherence to the Special Rules on Providing of Radiation Safety for low-activity material, as accepted by the Republic of Azerbaijan.

Table IV. Radiation measurements and radionuclide concentrations in soil, solid waste, and bottom sediment samples from various locations at the Surakhani site

No	Sample	Coordinates	**DR** μR/h	Radionuclide concentrations, Bq/kg			
				K-40	**Ra-226**	**Ra-228**	**A_{eff}**
1	Waste from borehole pipes	40° 24' 37.6" N 50° 01' 01.4" E	115	1021±245	3699±285	1861±153	6209±349
2	Waste from borehole pipes	40° 24' 37.5" N 50° 01' 00.3" E	210	1416±406	6526±686	1018±128	7975±707
3	Soil	40° 24' 35.9" N 50° 00' 54.4" E	150	496±112	1108±87	34.4±8.3	1197±88
4	Soil	40° 24' 36.6" N 50° 00' 54.5" E	40	126±67	395±37	210±23	679±48
5	Soil	40° 24' 30.8" N 50° 01' 09.4" E	9	315±60	35.4±4.2	25.6±4.4	97±12
6	Soil	40° 24' 59.2" N 50° 00' 47.6" E	150	2383±896	11490±1226	278±81	12063±1233
7	Soil	40° 24' 58.6" N 50° 00' 47.6" E	87	439±123	2511±189	52±11	2618±190
8	Salt from dry lake bottom	40° 24' 58.4" N 50° 00' 47.6" E	50	–	63±12	17.3±7.2	85±16
9	Soil	40° 24' 55.1" N 50° 00' 47.6" E	11	224±46	38.5±5.5	18.6±3.9	83±8
10	Bottom sediment	40° 24' 54.1" N 50° 00' 47.2" E	10	112±33	27.3±4.6	10.2±3.3	51±7
11	Soil	40° 24' 53.7" N 50° 00' 48.8" E	160	1394±257	50.4±9.8	55.6±10.4	247±27
12	Soil	40° 24' 52.9" N 50° 00' 48.9" E	230	1502±267	6254±459	112±18	6533±460
13	Soil	40° 24' 56.2" N 50° 00' 50.9" E	43	346±97	1189±93	18.2±7.2	1243±94
14	Soil	40° 25' 31.1" N 50° 01' 19.5" E	5	128±26	17.5±2.8	9.9±2.2	42±5
15	Soil	40° 25' 31.8" N 50° 01' 23.7" E	5	226±47	24.9±4.5	17.1±3.9	67±8
16	Soil	40° 25' 33.4" N 50° 01' 18.9" E	10	138±59	35.8±8.9	36.6±9.0	96±16

Ideally, and for reasons of expediency, an assessment of the level of contamination and its distribution should be made by surveys using radiation detectors. However, as the results in Table IV and in Fig. 2 indicate, there is no direct correlation between the measured radiation (μR/h) and radionuclide concentrations (Bq/kg).

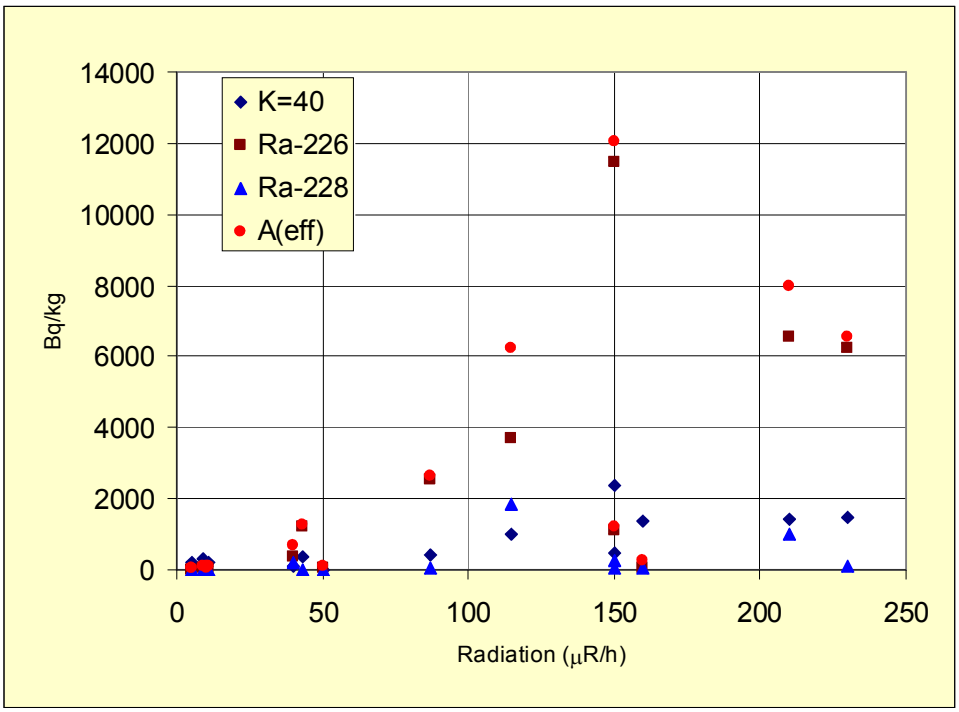

Figure 2: Relationship between radiation measurements and measured radionuclide concentrations

This observation is not unexpected because the soils and sediments are not homogeneous, and radiation from subsurface soils can be expected to be attenuated by overlying soils.

To obtain information on the vertical distribution of Ra-226 and Ra-228, a ~72-cm soil core (Fig. 3) was taken from the location with the highest observed radionuclide concentration, represented by sample 6 and with coordinates of 40° 24’ 59.2” N and 50° 00’ 47.6” E. Using a Multicorer, this sample was taken from the bottom of a channel through which groundwater had been flowing for a number of years. The core was cut into 4-cm thick slices. Each slice was homogenized after it was dried and hermetically sealed for one month to allow secular equilibrium to be reached. The Ra-226 and Ra-228 concentrations were obtained by gamma spectrometry using the 351.6 and 911 kev photopeaks, respectively.

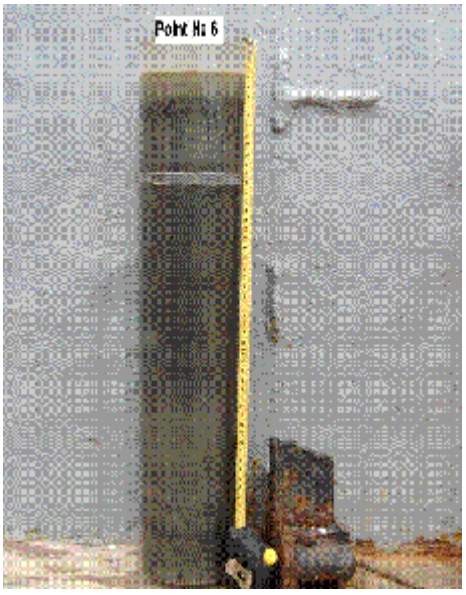

Figure 3: Soil core taken from 40° 24’ 59.2” N and 50° 00’ 47.6” E, represented by Sample 6 in Table IV

The concentrations for Ra-226 and Ra-228 as a function of depth are shown in Fig. 4.

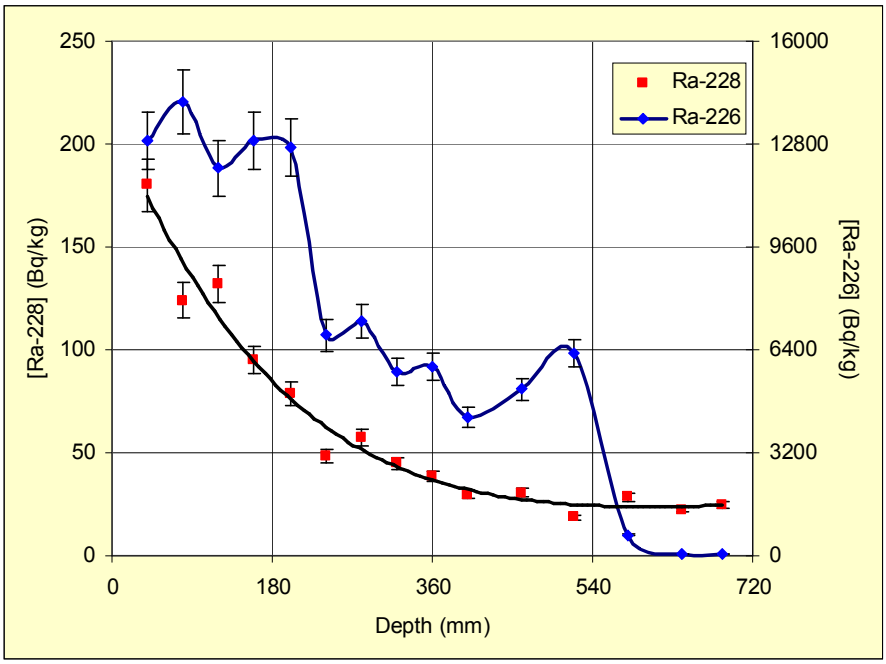

Figure 4: Radionuclide concentrations for Ra-226 and Ra-228 as a function of depth for core shown in Fig. 3

The groundwater that is co-extracted with the oil flows in the channels from where the sediment core was taken. The radium in this groundwater is sorbed onto the soil particles or incorporated in the sediments that have built up over the years. The sedimentation rate in these channels depends on a number of factors, including volume and flow velocity of the groundwater and has been reported as 5-50 mm/a [4, 6-8]. The results shown in Fig. 4 indicate that the concentration of Ra-228 decreases smoothly as a function of depth. If it can be assumed that the flux of Ra-228 into the channel, and hence incorporated into the sediments has been constant over the years, the relationship between Ra-228 concentration and depth is similar to a decay curve and can be used to date the sediments. Converting the standard relationship describing radioactive decay,

$$A = A_0 \cdot e^{-\lambda \cdot \Delta t} \qquad \text{(Eq. 3)}$$

into

$$\Delta t = \frac{\ln \frac{A}{A_o}}{-\lambda} = \frac{\ln \frac{30}{180}}{-\frac{\ln 2}{5.75\ a}} = 15\ a \qquad \text{(Eq. 4)}$$

This corresponds to an average rate of sedimentation of 500 mm/15a = 33 mm/a. However, this calculation does not take into account any background Ra-228 in these sediments. If a background concentration of 20 Bq/kg is assumed for this isotope, the age of the sediment at a depth of 50 cm would increase to 23 years and an average sedimentation rate of 20 mm/a. Both values are in agreement with the range reported in the literature.

By contrast, the profile for Ra-226 is not nearly as smooth as that for Ra-228. Close inspection of this curve shows two distinct decreases in Ra-226 concentration, one at a depth of ~200 mm and another at a

depth of ~560 mm. The half life of Ra-226 is 1600 years, and no appreciable decay would have occurred over the past 50–100 years. The average Ra-226 concentration at the depth interval of 0-200 mm is 13,000 Bq/kg; at the depth interval of 200-500 mm, the average concentration decreased to 5,500 Bq/kg, and to 50 Bq/kg at a depth greater than 500 mm. The concentration profile for Ra-226 can then be used, together with the sedimentation rate calculated from the Ra-228 results, to date the flux of the Ra-226 from the groundwater into the channel and then into the sediments. This would suggest that the upper layer of the sediment with the highest Ra-226 concentration was deposited from 1999 to 2009, and the sediment containing ~500 Bq/kg Ra-226 was deposited between 1984 and 1999. No evidence of any groundwater in the channel is evident prior to 1984.

CONCLUSIONS

1. The radiation levels at the Ramani and Surahani sites, in which the abandoned iodine separation plants are located, are two to three orders of magnitude higher than background levels.
2. The most likely source of the contamination is the subsurface water that was extracted as part of the oil recovery program. This water served as feedstock for the separation of iodine. Activated charcoal was used in the iodine separation process and was discarded at the two sites when operation at these facilities ceased and sites were essentially abandoned.
3. Activated charcoal inadvertently served as a sorbent for NORM.
4. Radium is thought to have been co-precipitated with alkaline earth elements as carbonates or sulphates.
5. There is no correlation between measured radiation levels and concentration of NORM.

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