Environmental impact of some NORM industries in Mexico

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Abstract

Industrial activities associated with metal mining, extraction and processing of oil and gas, power generation using fossil fuels, among others, may concentrate natural radionuclides in various products, by-products and wastes. Radiological implications of naturally occurring radioactive materials (NORM) generated by human activities need to be taken into account to control exposure to workers, public and the environment.
Concerning these types of industries in Mexico, in this work we present the radiometric characterization of different materials with naturally occurring radioactive contents; wastes generated by silver mining in Xichú, environmental soils affected by and an industrial complex (oil refining, power generation and manufacture of agrochemicals) in Salamanca and produced waters from the oil and gas industry in Monclova. The activity concentrations of radionuclides from the natural series ^{238}U and ^{232}Th, besides ^{40}K in the analysed samples have been determined by gamma-ray spectrometry and alpha-particle spectrometry.
The levels of radioactivity found in Xichú and Salamanca are of the order of the values found in soils not affected by human activities, indicating that the NORM environmental radiological impact of these industries is very low. On the other hand, the activity concentrations of natural radionuclides, mainly ^{226}Ra and ^{228}Ra, in produced waters from Monclova showed values up to a thousand times higher than those found in natural waters, with a variable radiological impact in the region. A periodic radiometric monitoring is required to ensure a proper control of the produced waters and limit the potential radiological environment contamination.

Introduction

For several decades, international studies have shown that exposure to natural radiation sources is modified by human practices. This has led to a growing interest in control of radioactivity in the environment around different industrial activities. Industrial activities associated with metal and non-metal mining, processing of ores, production of oil and gas, power generation using fossil fuels, among others, may generate Naturally Occurring Radioactive Materials (NORM), increasing the potential for exposure of workers, public and environment in comparison with the unaltered situation (IAEA, 2003).Therefore, these industrial activities are considered as NORM industries.

Natural radionuclides, including ^{40}K and decay products from the natural series of ^{238}U and ^{232}Th are presents in significant amounts in many raw materials used by NORM industries. When the levels of natural radionuclides are concentrated in products, by-products or wastes as a result of an industrial process, radiological implications need to be taken into account to control exposure to workers, public and the environment. The presence of technologically enhanced NORM at industrial activities may contribute to internal/external doses in humans, particularly during maintenance activities. Although each country establishes its own NORM regulations, exemption levels of 10 kBq/kg for ^{40}K and 1 kBq/kg for all radionuclides of the natural series of ^{238}U and ^{232}Th, are recommended for proper control of NORM (IAEA, 2014).

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For example, in mining and processing of Cu in Arizona (United States of America), increases in natural radionuclide levels have been found in solutions and residues from solvent extraction processes, affecting surface water sources and underground mining near the mines (USEPA, 1999). Aluminum processing and refining (bauxite) generates several million tons worldwide of tailings (bauxite tailings) with a high content of natural radionuclides. Typical values of 232Th in tailings areof the order of 100 to 3000 Bq/kg (IAEA, 2013).However, NORM levels in the mining industry vary greatly according to the geological conditions of the region, the type of ore exploited, among others, so that a radiometric evaluation is necessary for each specific case.

Likewise, exploration, extraction and production of fossil fuels including oil, gas and coal are also considered NORM industries. In the deposits of these natural resources, rock formations usually contain significant amounts of natural radionuclides. In the oil industry, during the production processes a mixture of oil, gas and water is drawn through a piping system from a well. In the rock formations present in the production well are radionuclides of the ^{238}U and ^{232}Th series. Although uranium and thorium do not mobilize from the rock formations present in the rock formations, the decay products ^{226}Ra, ^{228}Ra and ^{210}Pb do have mobility and are thus extracted and concentrated in the produced water, sludge and crusts of the pipes. These NORM by-products and wastes usually contain high concentrations of radioactive content (NRPA, 2004; OGP, 2008).

Thus, it is important for industries and regulatory bodies to understand where and when high concentrations of NORM are present in a given process, to manage NORM generated in a way that ensures the protection of human health and the environment.

In Mexico there are important activities that can be classified as NORM industries. Globally, Mexico is one of the largest producers of oil, gas, silver, copper, gold, lead, zinc, among other natural resources. However, in the country there are few studies on the radiological impact that the NORM industries generate when exploiting these natural resources.In this work we present the radiometric characterization of different materials with naturally occurring radioactive contents; wastes generated by silver mining, produced water from the oil and gas industry and soils affected by an industrial complex.

Materials and Methods

Samples

In this work a total of 37 samples were collected, including, wastes, soils and sediments from three different regions of Mexico influenced by several NORM industries. In Figure 1 a map of the regions of Mexico where samples were collected is presented.

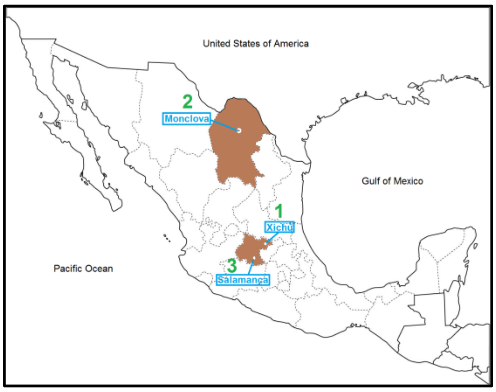

Figure 1.*Map of the regions from Mexico where samples were collected.*

The samples from each region are described below:

1. Mine wastes from Xichú. Samples of mine tailings generated by silver, gold and copper mining activities and also sediment from Xichú River in Guanajuato were collected. High amounts of mine wastes enriched with potentially toxic elements (As, Pb, Fe) are abandoned along Xichú River, representing a potential risk for environment and health from nearby population.

2. Produced water from Monclova. Samples of produced water from two different oil and gas water treatment stations were collected in Coahuila. Collected samples are a mixture produced waters obtained as a by-product after separation from oil and gas from several gas wells. In this region produced water is reinjected to depleted wells and may represent a radiological issue for workers during maintenance activities or potential releases to environment.

3. Soils from Salamanca. Samples of soils affected by an industrial complex were collected. Activities associated with oil refining, power generation by combustion of gas and fuel oil, and also manufacture of agrochemicals are carried out inside the industrial complex. Soils around the industrial complex have been influenced by contamination released from the industrial complex for several decades. Salamanca is considered as one of the most highly contaminated zones of the country (SEMARNAT, 2013).

All solid samples were collected form the first 10 cm in points selected randomly according to potential influence from NORM activities. About 1 kg of solid samples were transported in sealed plastic bags to laboratory, dried, grounded and sieved for further analysis. Liquid samples were transported in 5 L plastic bottles and kept in fresh environment (22 °C) until further analysis.

Radiometric techniques

Samples were characterized radiometrically by gamma-ray spectrometry and alpha-particle spectrometry.Proper aliquots of the samples were taken and treated according to the required methodology by each technique. A detailed description from the methods used in this work for the determination of the radionuclides of interest may be found elsewhere (Lehritani, 2012;Mantero, 2015; Mandujano-García, 2016). Briefly,

Samples were vacuum sealed in adequate containers. Solid samples were packed in Petri dishes and liquid samples were packed in 1 LMarinelly beakers. All samples were stored for 30 days before measurement. In this way, secular equilibrium between ^{226}Ra and their short half-life daughters was ensured.The samples were measured in a spectrometric system consisting of a Canberra hyperpure germanium detector HPGe type XtRa (extended range), with a relative efficiency of 37% and resolution of 1.77 keV for the 1.33 MeV photopeak of ^{60}Co. The detector is shielded by 10 cm of old lead, lined with a 5 mm layer of Cu, and, additionally, has an anticoincidence device (organic scintillator) to reduce background radiation levels and increase the sensitivity in the environmental gamma radiation measurements.

Efficiency calibration was performed for each type of geometry. For solid samples, reference standards materials: IAEA-RGU1 and IAEA-RGTH1, were used for energy peack efficiency determination. To determine the activity concentration of ^{226}Ra the values obtained from the main gamma emission of their descendants in secular equilibrium were averaged: ^{214}Pb (295 and 352 keV) and ^{214}Bi (609, 1120 and 1764 keV), which were consistent considering associated uncertainties (1-σ) throughout the measurement process. The effects of sum coincidence for efficiency determination can be neglected due to the use of reference materials with the same radionuclides of interest. For the low energy emissions of ^{210}Pb (46.5 keV) corrections were applied due to differences in self-absorption between the real and reference samples, following the methodology described by Cutshall (Cutshall et al., 1983). In the case of liquid samples a CIEMAT mixed nuclides solution with multi-gamma emissions in the range of 59.5-1836.5 keV was used for efficiency calibration.

On the other hand, ^{238}U, ^{234}U, ^{230}Th and ^{232}Th radionuclides were determined by alpha spectrometry. In this technique, radionuclides of interest must be isolated from the matrix by applying a radiochemical process consisting of three stages: pre-concentration of actinides, separation and purification of the elements of interest, and preparation of alpha particle sources for measurement. The methodology of the radiochemical process followed in this work is well described by Lehritani (Lehritani et al, 2012).

Results and Discussion

Activity concentration values of radionuclides from ^{238}U and ^{232}Th natural series were measured via alpha spectrometry and gamma-ray spectrometry. Figure 2 shows the results obtained for the activity concentration of radionuclides from the U and Th natural series in the samples from Xichú.

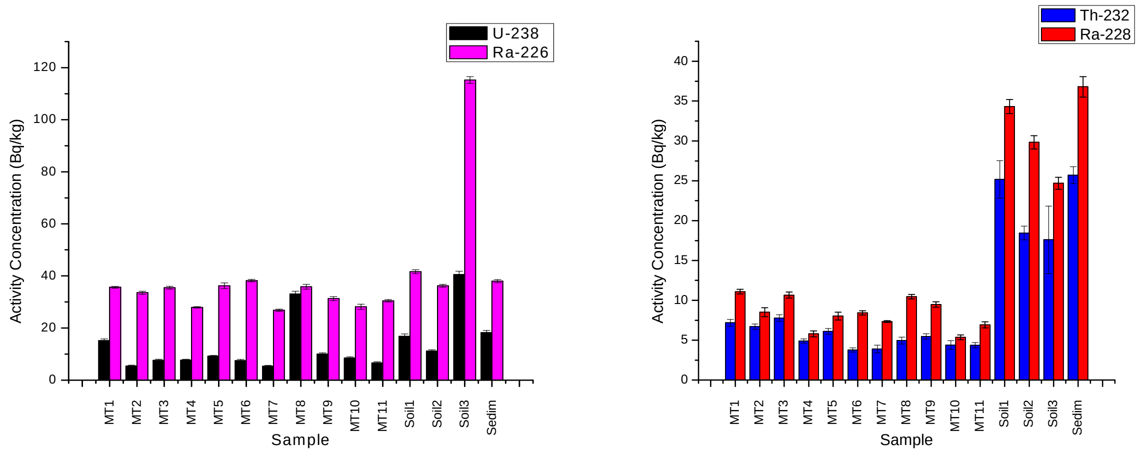

Figure 2.*Activity concentrations (Bq/kg) of radionuclides from the U and Th natural series in mine tailings from Xichú. Uncertainties correspond to 1-σ.*

Samples of mine tailings from Xichú (MT1-MT-11) presented levels of activity concentration in the range of 4-38 Bq/kg for both series. These levels are very similar to the values found in the soil and sediment collected in the surroundings. Also, the activity concentration levels of the analysed samples are in the order or lower than world average environmental soils: 20-40 Bq/kg(UNSCEAR, 2000). The low levels indicate that U-238 and Th-232 radionuclides mobilize to other stages of the mining activities. The results as a whole clearly indicates that mine wastes under analysis do not constitute any radiological problem either form a public or environmental point of view.

In the same way, the results of the activity concentration levels of natural radionuclides measured in soils from Salamanca are presented in Figure 3. Measurements of activity concentration of radionuclides from ^{238}U and ^{232}Th natural series presented values in the range of 10-82 Bq/kg for both series. Activity concentrations of ^{238}U are similar than the values found in unaltered soils from North America; mean natural radionuclide content in soils from United States of America and Costa Rica are 35 and 46 Bq/kg respectively. The obtained results indicated that there is not clear anthropogenic increments in the levels of NORM in the analyzed soils.

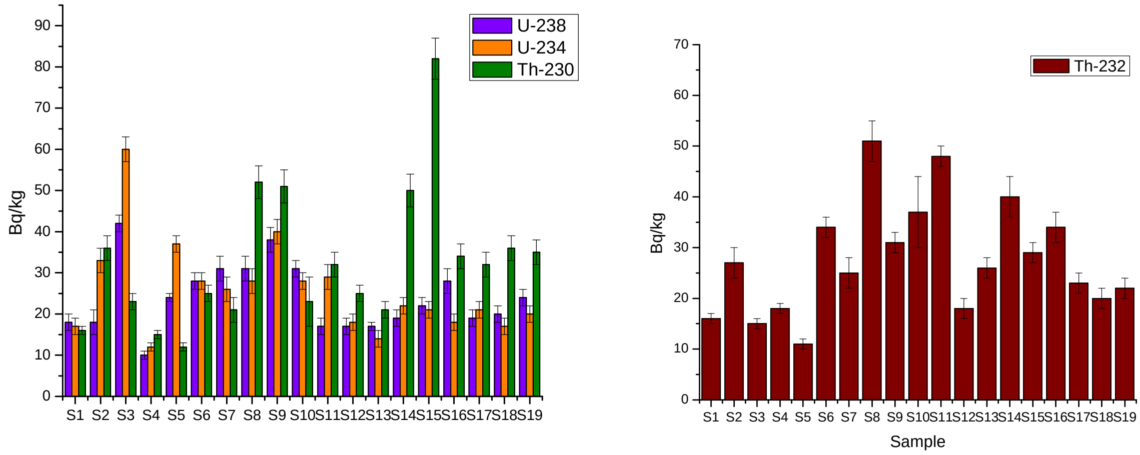

Figure 3.*Activity concentrations (Bq/kg) of radionuclides from the U and Th natural series in mine tailings from Xichú. Uncertainties correspond to 1-σ.*

Moreover, results of activity concentration levels measured in the samples of produced waters from Monclova are compiled in Table 1. The obtained activity concentration values in the analysed produced water samples are quite variable but in the order found in other oil and gas regions of the world: 0.002-1200 Bq/L for ^{226}Ra (OGP, 2008).

Table 1.*Activity concentrations (Bq/L) of radionuclides from the U and Th natural series in produced water from Monclova, Mexico. Relative uncertainties correspond to 10% .*

Radionuclide	**Station A Activity Concentration (Bq/L)**	**Station B Activity Concentration (Bq/L)**
^{238}U	0.046	0.001
^{234}U	0.074	0.005
^{226}Ra	1.0	15.5
^{210}Po	0.017	0.470
^{228}Ra	<0.30	2.4

The results of the analysed produced water samples show that both stations could be considered NORM due to the activity concentration levels clearly higher than the found ones in natural surface/ground waters. In particular, levels of Ra-isotopes are quite high, while U-isotopes are clearly lower. Produced water samples from Station B contain higher concentration activities of ^{226}Ra and ^{210}Po than Station A samples. Both samples present a high ^{234}U/^{238}U disequilibrium.

Conclusions

After all measurements of samples associated with NORM industries in Mexico, the results lead to the following conclusions:

The levels of radioactivity found in Xichú and Salamanca are of the order of the values found in soils not affected by human activities, indicating that the NORM environmental radiological impact of these industries is very low.

On the other hand, radiometrical characterization of produced waters from Monclova, shows that Ra isotopes presented a high activity concentration very depending from station to station, indicating that the radiological impact of the produced waters for the Mexican gas industry can be quite variable; a more extensive monitoring for each station is needed for a proper radiological management of the produced waters.

It is recommended to continue this kind of studies to other regions of the countries affected by these and other types of NORM industries, in order to increase the information about the levels of natural radionuclides and their radiological implications to environment and health population.

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