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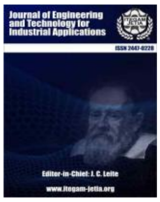

RESEARCH ARTICLE OPEN ACCESS

DETERMINATION OF NATURALLY OCCURRING RADIOACTIVE MATERIALS-NORM (RA-226, RA-228) IN SYNTHETIC FLOWBACK DEVELOPED AT LABORATORY SCALE FROM ROCKS OF THE LA LUNA-1 WELL, COLOMBIA, AND BENCHMARKING WITH MARCELLUS AND EAGLE FORD SHALE PLAYS

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ABSTRACT

The current decade has been characterized by significant changes in global energy, among which the development of new hydrocarbon deposits, including Unconventional, stand out. In Colombia, the need for exploration of these deposits has been evidenced by the lack of reserves of conventional. One of the main problems identified in the production of these resources is the perception of direct negative effects on the environment, including water as a resource. As part of efforts aimed at identifying potential effects on future production of source rock deposits in Colombia, experiments have been conducted to detect the presence or increase of radioactive elements in the flowback water from hydraulic fracturing fluids, which is one of the main issues identified in currently producing fields in world. Samples from La Luna-1, the first stratigraphic Shale Gas/ Oil Well in Colombia were used. This experimental research was intended to obtain measurements of “NORM Test with Lower Detection Limits” from a synthetic flowback from the digestion of rock samples and fracture fluids (slick water) including HCl at 15%. The results show low concentrations of NORM from synthetic flowback; to contextualize this data was carried a benchmarking with two important unconventional deposits, Marcellus and Eagle Ford Shales.

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I. INTRODUCTION

According to the National Hydrocarbons Agency (2021) [1], Colombia currently has 2041 million barrels (Mbls) of crude oil (proven reserves), from which 300 Mbls are produced annually, with remaining production expected to last approximately 5 more years. On the other hand, an estimated 3163 Gcf are the remaining proven gas reserves, from which 400 Gcf are produced annually. According to the foregoing, Colombia has approximately 8 years of gas reserves left to be produced. Therefore, there is an obvious need to increase or incorporate new conventional reserves, increase production from recovery techniques, and venture into the exploration and exploitation of unconventional resources. Ecopetrol is currently carrying out studies focused on the identification of potential unconventional resources in Colombia; hence, the company has conducted a well campaign in the Middle Magdalena Valley (MMV) aimd at defining areas for possible shale gas/oil production.

“Natural gas is poised to enter a golden age, but will do so only if a significant proportion of the world’s vast resources of unconventional gas – shale gas, tight gas and coalbed methane – can be developed profitably and in an environmentally acceptable manner. The technologies and know-how exist for unconventional gas to be produced in a way that satisfactorily meets these challenges, but a continuous drive from governments and industry to improve performance is required if public confidence is to be maintained or earned" [2]. A key guideline at Ecopetrol is to ensure that procedures and processes for exploitation of resources, in this case, unconventional, are carried out in accordance with national and international standards, including zero environmental impact and responsible use of water.

A major concern in the production of Shale gas/oil is the presence or increase of radioactive elements derived from the interaction of La Luna Formation fluids with brines from source rocks. An experiment in the MMV is propose to simulated such interaction as it would occur in bottom hole conditions. Therefore, the goal of this study is to identify from a laboratory scale experiment, obtaining a synthetic fluid resulting from HCl [15%] digestion and subsequent slick water addition from rock samples from the La Luna-1 Well, if it presents radioactive elements of natural origin and in what proportion, this fluid will be characterized based on the "NORM Test with Lower Detection Limits", which identifies the amount of naturally occurring radioactive materials.

Given the importance of the topic for the scientific community and the community in general, it is necessary to approach the subject from the recognition of the hydraulic fracturing technique, the fluids that are generated, among them the flowback and associated to these the NORM, identifying how these radioactive elements originate. Finally, in order to understand the data generated with the synthetic fluid, it is necessary to make a benchmarking with two unconventional reservoirs, the first (Marcellus Shale) for its trajectory in the process and the second (Eagle Ford Shale) for being analogous to the La Luna Formation, one of the Formations of interest for the unconventionals in Colombia.

I.1 LOCATION

This study was carried out in the La Luna-1 Well, which is the first stratigraphic shale gas/oil well in Colombia. It is situated near the Cira-Infantas Field, MMV basin, with coordinates, 1,249,953.0m N/1,031,363.5m E, in the department of Santander (Figure 1).

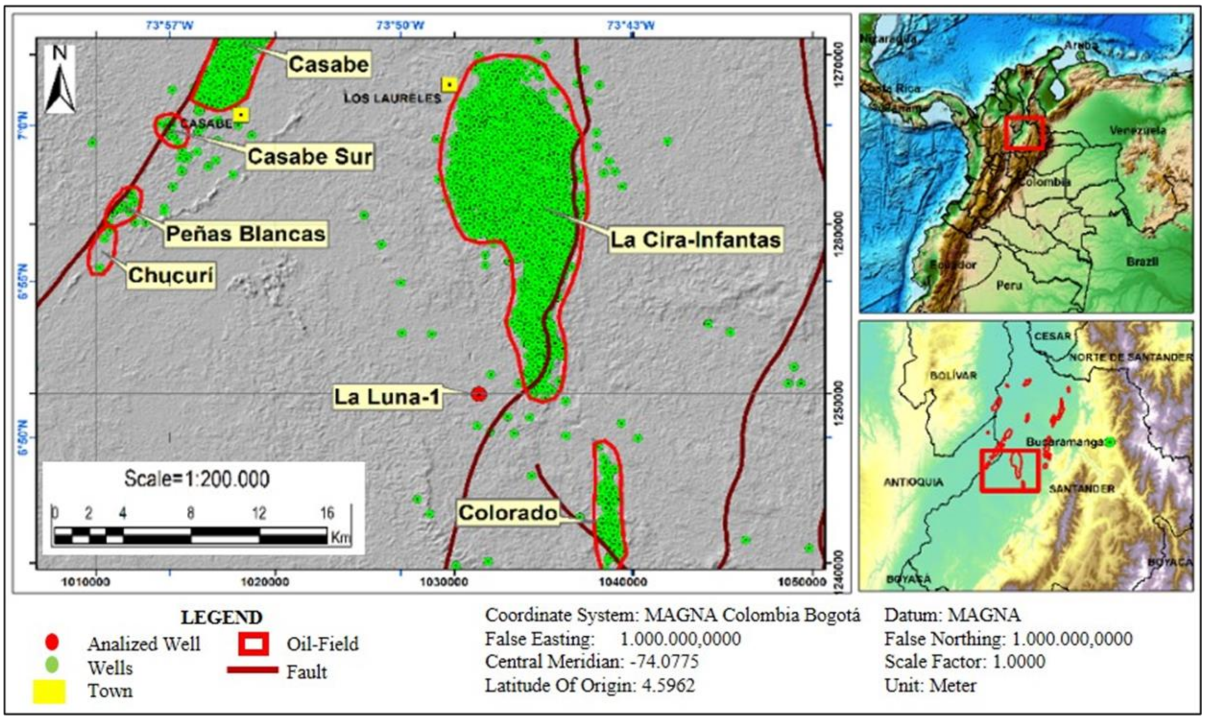

Figure 1: Location of the study area and La Luna-1 well in the Middle Magdalena Valley.
Source: Authors, (2021).

II. UNCONVENTIONAL DEPOSITS

Unconventional and conventional hydrocarbons are compositionally and genetically identical; they only differ in that the latter has migrated to a permeable reservoir rock (conventional reservoir), and the former remains in the source rock where shale gas/oil is generated or has migrated to a very compacted reservoir rock (tight gas) (Figure 2). Source rocks and tight rocks that contain hydrocarbons are called unconventional reservoirs [3].

These unconventional deposits are described as sedimentary rocks of very fine grain with low permeability, which limit the flow of fluids. As gas and oil are distributed in millions of microscopic pores that, unlike conventional reservoirs, are not interconnected and, therefore, cannot move inside the formation. Consequently, it is necessary to artificially generate pathways for fluid flow in the well [4].

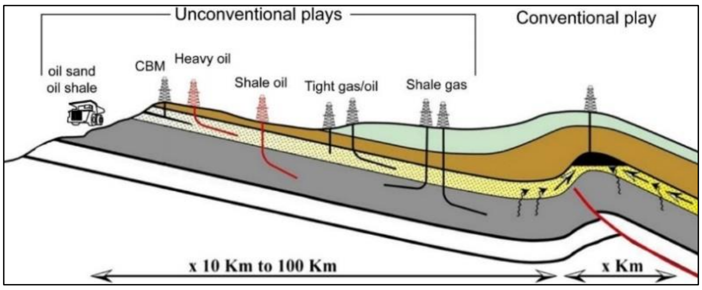

Figure 2: Generalised petroleum system for conventional and unconventional deposits.
Source: [5].

The interest in the MMV is related to the trapped hydrocarbons in the shale gas/oil source rock. The main targets are the Olini Group (Upper Lidita, Lower Lidita), the La Luna

Formation (Galembo and Salada members) and the Tablazo Formation [6]. The risked, technically recoverable shale gas and shale oil resources in the combined Cretaceous La Luna and Tablazo shales of the Middle Magdalena Valley Basin are estimated to be 18 Tcf and 4.6 billion barrels, out of risked shale gas and shale oil in-place of 135 Tcf and 79 billion barrels. By comparison Ecopetrol has estimated the MMV Basin has 29 Tcf of shale gas potential [7].

II.1 TECHNICAL REQUIREMENTS FOR THE EXPLOITATION OF SOURCE ROCK DEPOSITS

The hydraulic stimulation technique, also called hydraulic fracturing or fracking, was developed almost 80 years ago, with the purpose of improving the permeability of specific deposits. This technique consists in opening tiny fibres of the source rock, where the hydrocarbons were generated and sealed over time by injecting fluids into the rock (water and sand 99.5% plus highly diluted chemicals 0.5%) (Figure 3) [4].

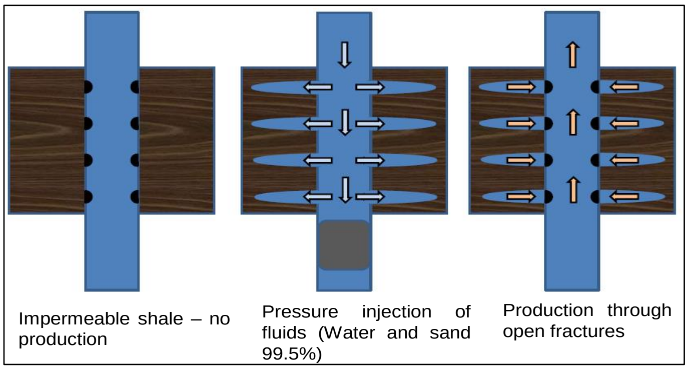

Figure 3: Diagram displaying the drilling design of shale gas/oil deposits.
Source: [3].

For the exploitation of unconventional hydrocarbons, drilling must be carried out horizontally throughout the formation for hydraulic fracturing; this technique is developed in several stages. Horizontal drilling enables access to a wider surface of the source rock layer throughout the length of the deposit, thus, maximizing the amounts of shale gas/oil that can be recovered [8]. Further, horizontal drilling allows for multiple wells from a single wellpad, reducing surface footprint and capital investment, and improving shale gas/oil production and efficiency [9]; (Figure 4); hence, it is possible to maximize the Stimulated Reservoir Volume (SRV).

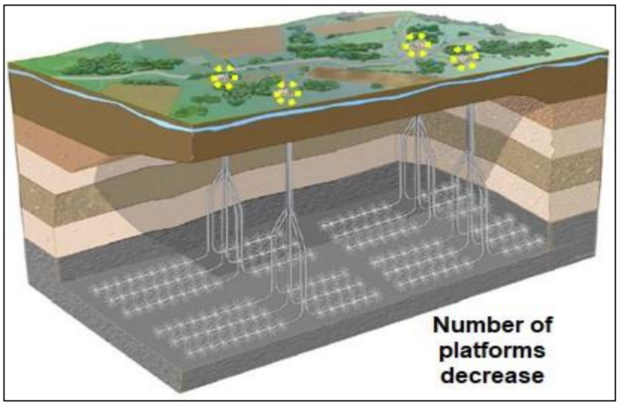

Figure 4: Diagram displaying the paddrilling.
Source: [10].

Thus, a high-conductivity zone is artificially constructed within the rock to allow flowing of hydrocarbon from the reservoir to the wellbore. Quite often, before the main hydraulic fracturing operation, it is necessary to pump an acid treatment, usually 15% HCl, intended to clean the perforations and reduce the frictional pressure losses in the near-wellbore zone to thus reduce fracture pressure (this condition was simulated in this experimental protocol).

In conventional reservoirs (reservoir rock), hydrocarbons are stored in the porous rock matrix, which petrophysical properties allow the flow or movement of hydrocarbons and water from the reservoir to the wellbore for subsequent production to the surface, due to the thrust exerted by reservoir pressure. These wells are mostly vertical or deviated, which once drilled and completed can produce hydrocarbons without the need to use the hydraulic fracturing technique; nonetheless, this is widely used worldwide and in Colombia to accelerate production and to solve several production loss issues relative to various mechanisms of formation damage occurring throughout the productive life of the assets [11].

On the other hand, in unconventional reservoirs (source rock), the situation is different, as it is necessary to manage production of the hydrocarbon that did not migrate and was trapped in small pores in the rock. In the source rock, the porosity is very low and these small pores are not interconnected, so the permeability is almost zero (nano-darcies), and that is why in this type of reservoir it is essential to apply the hydraulic fracturing technique (Table 1) to create a network of complex fractures to contact the pores where the hydrocarbons are deposited, and thus create the reservoir in an artificial manner that enables profitable production.

Table 1: Hydraulic Fracturing Objectives in Conventional and Unconventional Reservoirs.

Conventional Reservoirs	Unconventional Reservoirs
To accelerate production	To artificially create the reservoir (VRS) to maximize rock contact and enable hydrocarbon production
Develop additional reserves	
Extend the productive life of assets	
Overcome formation damage	
Mitigate sanding problems	
Reduce organic scale precipitation problems	

Source: [11].

II.1.1 Fracture Fluids

The fracture fluids used are a mixture of water, chemicals and proppants (solid substances, such as sand) injected into the shale at high pressure in a well. This process creates a network of small fractures, held open by propagators, allowing oil or gas to flow into the well. Fracture fluids must achieve three main objectives: create a fracture, distribute the proppant and return to the surface avoiding damage of the conductivity of the proppant package [8].

The fluid is used to transmit enough high pressure from the surface to the well and to fracture the rock and place the proppant in the formation. Figure 5A shows the composition of the fracture fluid, which concentration of chemicals is very low. The purpose of the fluid includes mainly: control of bacterial growth, inhibition of clay, gelling agents, surfactants (interfacial tension reducers), emulsion prevention, pH buffer, scale inhibition, friction reduction, gel breakers, and crosslinkers, [13].

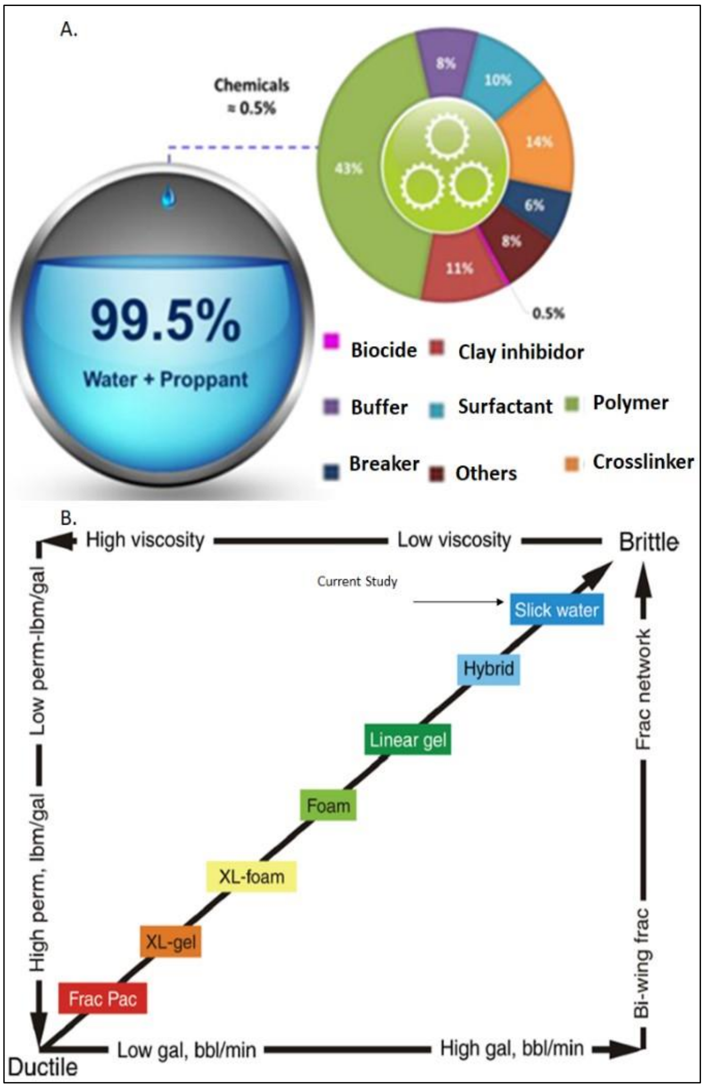

Figure 5: (A) Fluid composition of shale gas/oil fracturing. Water and sand (99,5%), plus additional extremely diluted chemicals (0,5%). (B) Classification of fracturing fluids according to their rock geomechanical characteristics.
Source: [8], [14].

Different types of fracture fluids are used in hydraulic fracturing for unconventional reservoirs, according to the characteristics of the target rocks [14]. For this study, the slick water (SW) fluid was used. This fluid is described as having low viscosity mainly composed by water and other chemical additives of very low concentration such as biocides, clay controllers, friction reducers, and surfactants. It is suitable for use with fragile rocks with very low permeability, and rocks that hold pre-existing fractures (Figure 5B), as this enables the creation of denser and more complex fracture networks [15][16].

II.1.2 Flowback

As they pass through the shale, fracking fluids dissolve many substances trapped naturally in the rock. The substances include particles of naturally occurring radioactive material (NORM), such as potassium (K) and radium (Ra). By dissolving chemicals trapped in the shale, the injected fluids can also become very salty. Some will return via the well to the surface and if they do so, are known as flowback fluids. Understanding their chemical composition is crucial to assessing whether they might have any impact on human health or the wider environment. [12].

II.2 RADIOACTIVE MATERIALS OF NATURAL ORIGIN - NORM

All elements naturally found in the Earth's crust have different concentrations. However, only eight of them, namely oxygen (O), silicon (Si), aluminum (Al), iron (Fe), calcium (Ca), sodium (Na), magnesium (Mg) and potassium (K) - correspond to 98.5% (Figure 6A). Uranium and Thorium are relatively rare elements that form natural radioactive series (Figure 6B).

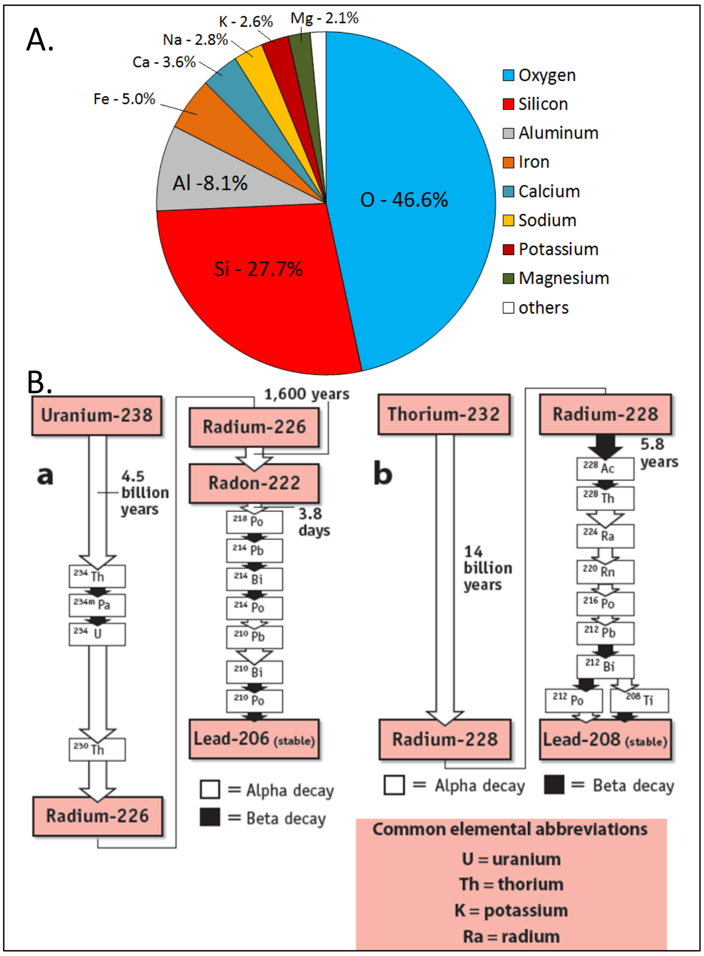

Figure 6: A. Main elements of continental crust. B. Decay sequence that leads to the main elements associated to radioactivity by decay a) U-238 and b) Th-232. Example for the shale gas of Marcellus, United States, one of the main source rocks for unconventional gas.
Source: [17], [18].

Naturally occurring radioactive materials (NORM) are defined as materials that may contain any of the primary radionuclides or radioactive elements as they occur in nature, such as radium, uranium, thorium, potassium and its respective decomposition radioactive products. Energy and emitted particles as radioactive material disintegrate to achieve stable (Figure 6B; [19]). NORMs exist in all natural media and are widely distributed in the earth's crust, water, and air. It has been proven that mineral and hydrocarbon extraction processes produce some radioactive waste [20].

The components of the Earth's crust have radioactivity due, fundamentally, to the presence of radionuclides of the three natural radioactive series (from U-238, Th-232 and U-235) and to K-40, which were formed at some stage prior to the formation of the solar system. Since then, these components started to disintegrate, thus, decreasing their concentration on Earth. Hence, in addition to original radioactive elements, the decay elements or products are also presented (Figure 6B). Uranium and Thorium generate very long radioactive families and Potassium is part of seawater salt and all living things. Basically, it is impossible to find a material or an environment in the Earth that is not radioactive; all of them are, to a greater or lesser extent, even ourselves [21].

II.2.1 Radioactive Materials of Natural Origin Technologically Enhanced - TENORM

Some of the injected fluids can dissolve NORM in shale deposits and transport them to the surface (TENORM); radioactive drilling wastes are identified as a form of TENORM (technologically enhanced naturally occurring radioactive material), which are a form of NORM that have been concentrated or placed for human exposure by anthropogenic means [20].

"Technologically Enhanced" means that the radiological, physical and chemical properties of the radioactive material have been further concentrated or altered as they have been processed, benefited or altered in a way that increases the potential for human and/or environmental exposure [19]. As previously mentioned, the shales must be hydraulically fractured to extract the hydrocarbons; this fracture requires high-pressure injection of fluid into the rock. Some of the injected fluids can dissolve the naturally occurring radioactive substances in the shale and transport them to the surface (Figure 7A).

Following the hydraulic fracturing, a mixture of oil, gas and formation water is pumped to the surface, where the water is separated from the gas and stored in tanks where it undergoes processes that concentrate the minerals present in it (Figure 7B). In addition to ions such as barium, strontium or bromine, these may include low concentrations of heavy metals and radioactive isotopes such as Ra-226 and Radio-228.

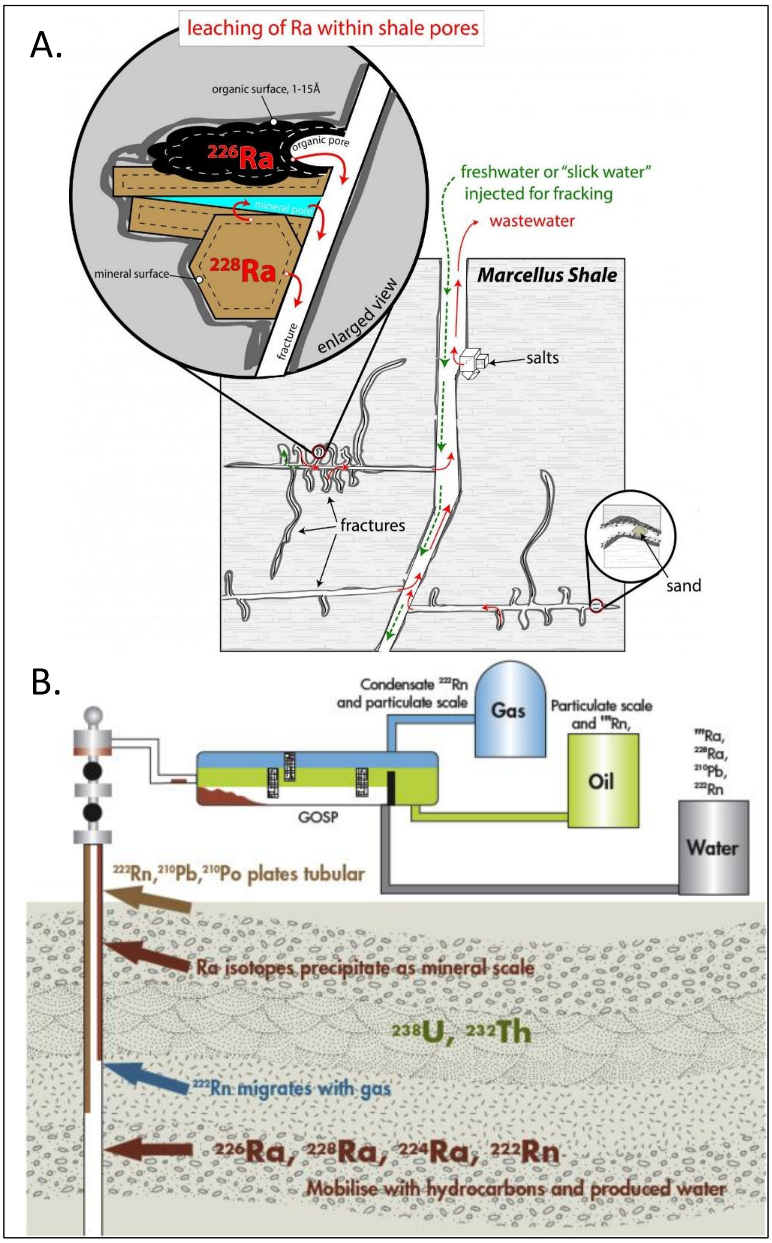

Figure 7: A. Fracturing involves the injection of fluid into the rock at high pressures; some of the injected fluids can dissolve the radioactive substances (Ra-226 and Ra-228) naturally found in the shale and transport them to the surface. B. A mixture of oil, gas and formation water is pumped to the surface; water is then separated from the gas and stored in tanks where it can undergo processes that concentrate the minerals present in it.

Source: [22], [23].

II.2.2 Radioactive Materials in Sedimentary Rocks

Sedimentary rocks were formed from igneous, sedimentary or metamorphic rocks. The amount of uranium and thorium present in sedimentary rocks is directly or indirectly related to igneous rocks. These radioelements are removed, by erosion and partial deposition due to their high density near the source rock or during transport, until they reach the sedimentary basin. When the radioactive elements are dispersed, sedimentary rocks generally contain less uranium and thorium than the source rock. A sedimentary rock affected by erosion results in less active sediments and, generally, each sedimentation cycle provides more rocks with less radioactive elements. Therefore, uranium and thorium from sedimentary rocks are, in most cases, in a diffuse state [24].

Among the different radioactive isotopes that can be found in rock formations, their ability to concentrate and come into contact with different materials depends on their mobility.

II.2.3 Uranium

Under reducing conditions, the uranium ion precipitates as complex primary oxides with organic matter or as insoluble hydroxides of iron or manganese. Under oxidizing conditions, secondary uranium minerals precipitate by evaporating uranium containing solutions and can form phosphates, arsenates, vanadate, and silicates, with copper, calcium, potassium and other metals.

In humid climates, uranium is transported by groundwater; however, the amount accumulated in seawater and carried by rivers is very low (Figure 8A). Most of the uranium precipitates as soon as it finds enough reducing conditions for conversion from U2+ to U4+. These conditions are due to organic matter, which can be found both on the bottom of the restricted sedimentary basins, and in sediments where waters with uranium content circulate. Moreover, uranium is usually associated with coal, fossil wood, bituminous shales, oil and asphaltite. The form of uranium in these cases is either very finely subdivided UO2, or oxide in amorphous state.

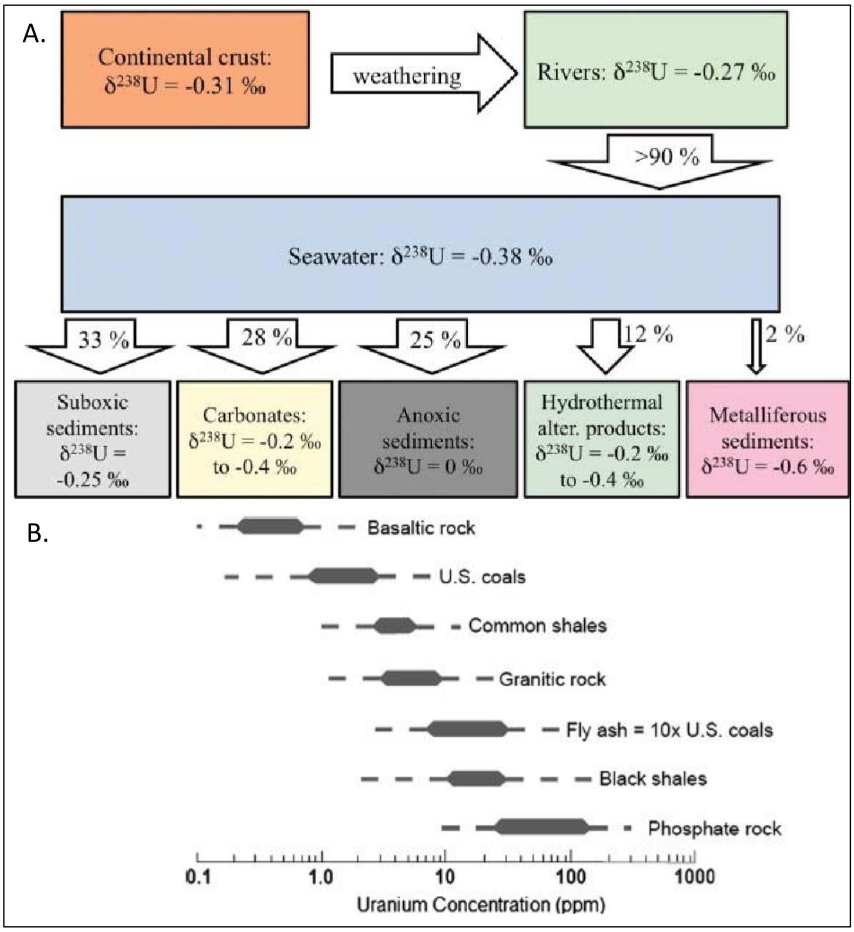

Figure 8: A. Uranium present in the continental crust showing its distribution in different environments. B. Amount of uranium in sedimentary and other types of rocks.
Source: [25], [26].

Black shales contain trace levels of U-238, U-235, K-40 and Th-232 in higher concentrations than those found in grey shales, sandstones or limestones, which are less rich in organic matter. This occurs because: 1) U-238 and U-235 bind better to organic matter, such as algae that die and settle at the bottom of the ocean; and 2) K-40 and Th-232 bind better to clays, which make up much of the sediment at the bottom of the ocean. Finally, as "black shales" contain more organic matter and clays, they are generally more radioactive than other shales or sedimentary rocks [18], (Figure 8B, Figure 9). Black shales and marine phosphates are enriched with uranium and can often contain more 100 parts per million (ppm) [26].

II.2.4 Radium

The decomposition of uranium leads to the formation of radium (decayed isotope). Radium, it is usually found where uranium is produced, including rocks, soil and groundwater. However, sometimes radium can be found far from its uranium parent in the ground or in groundwater. These include soils derived from carbonated rocks, such as limestone, which is generally not enriched in uranium. During the soil formation process, carbonates leaked resulting in enriched clay with residual materials, which include uranium. In addition, unlike uranium, radium is soluble in acidic or chloride-rich water [27, 28]. Reduced water can transport dissolved radium, just as hydrogen peroxide can transport the uranium in solution away from the area of origin.

The U-238 and Th-232 are part of the rock matrix and are linked to it, being essentially insoluble in the formation fluids under the typical anoxic conditions of black shales; however, the radius (decay product of U and Th) is easily dissolved and transported. The radius occurs naturally within black shales. Among radio isotopes, two of them, Ra-223 and Ra-224, have a short half-life (few days), while the average life of the other two isotopes, Ra-226 and Ra-228, is 1,622 and 5,75 years respectively. If they are dispersed in the environment, they will either endure for long periods or result in high doses. Examples of radium-containing water include wastewater from acid mines or brine waters associated with the extraction of oil, gas and methane [28].

Figure 9 summarizes radioactivity for sedimentary rocks according to the type of rock, with marine organic matter being the one with the highest radioactivity.

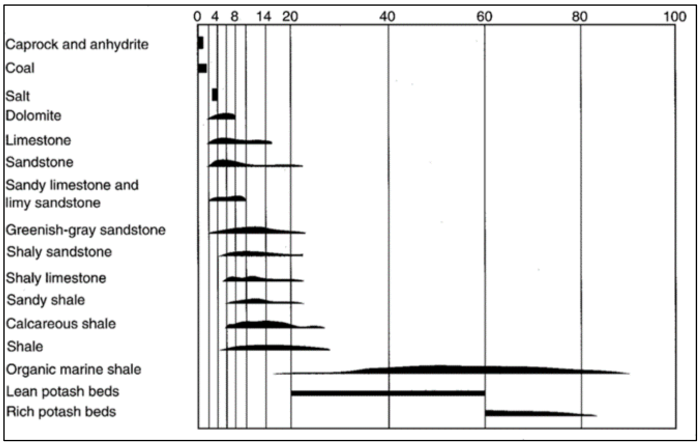

Figure 9: Relative radioactive distribution for several types of sedimentary rocks.
Source: [29].

Several studies have shown the adsorption of Ra in organic matter. Their results suggest that Ra can be strongly adsorbed by organic material. It has been determined that the adsorption affinity of organic matter and clays is mainly due to its cation exchange capacity (CEC). It has also been identified that organic matter adsorbs approximately 10 times more Ra-226 than clays (Figure 9).

Organic matter is incorporated into the sediment in the following cases: 1. absorbed in mineral particles (clays and others), 2. dissolved in gel form into the pores of sediments and 3. by cellular material of organisms (phyto and zoo plankton) incorporated directly into the sediment.

In Figure 10, A) Shales are typically composed of clay minerals, quartz and calcium carbonate. Some shales contain organic matter, which, when heated sufficiently, will release gas, such as methane. NORM is commonly stuck (adsorbed) to the surface of the organic matter. B) In shale gas production, a well is drilled down into gas-rich shales, usually buried at depths of 1.5 km or more. A horizontal well is drilled into the shale, and fracking fluids forced into the rock at high pressure through holes in the well casing. The flowback fluid carries gas back up the well to the surface, but also picks up and transports some particles of NORM. [12].

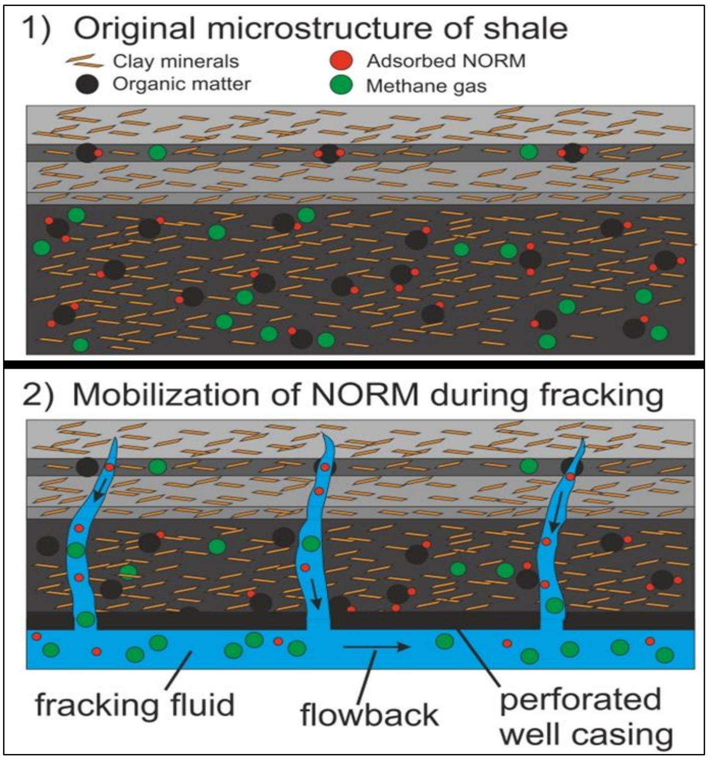

Figure 10: NORM schematic diagram in shales.
Source: [12].

According to the information gathered by [30] although the first reports of NORM associated with oil and natural gas appeared in 1904 and, at least since the 1930s, the presence of radionuclides in oil reservoirs has been known. However, it was not until the 1980s, when NORMs were detected in British North Sea oil and gas operations, that knowledge of their presence became public. The U.S. oil and gas industry became aware of specific sources of NORM in 1986, when barium sulfate scale containing elevated levels of Radium-226 and Thorium-232 was discovered in pipelines being removed from a well in Mississippi.

Since unconventional gas development has the potential to generate large quantities of residues containing Ra-226 and Ra-228 in both solid and liquid form, a full analysis of the public exposure pathways should be performed as a prerequisite to the start of activities. Thus, wastewater contains heavy and radioactive metals that will include, mostly Ra-228 and Ra-226, which are soluble in water and may imply a health risk [30].

Both, the speed and scope of the natural gas drilling boom in the USA, have led to greater scrutiny of radioactive exposure and waste management issues [20]. This is currently focused on the formations with the highest production worldwide; however, in countries that are beginning the exploration of unconventional hydrocarbons, additional studies are required to support their exploitation to avoid direct impact for the people and the environment. Such is the case of Colombia, where Ecopetrol is currently analyzing the viability of the exploitation of this resource. This experiment is a great input to study the potential impact.

III. MATERIALS AND METHODS

The experimental procedure is performed with the purpose of reproducing the physicochemical conditions that exist during the hydraulic fracturing process, which reproduce flowback waters. Currently, the NORM-TENORM present in these waters is being monitored in the deposits with highest production all over the world. The procedure to understand the interaction between rock and fluid formations and fracturing fluids was carried out in the Optimization Laboratory for Production and Improved Recovery, in the experimental area of Production Chemistry at the Ecopetrol S.A, Innovation and Technology Center - Colombian Petroleum Institute (ICP), using samples from the La Luna-1 Well (Table 2), which sedimentological characterization is shown in the stratigraphic column, Figure 11.

Table 2: Sample intervals from the La Luna-1 well. Source:Authors

Sample number	Identification	La Luna-1 Well Fm/Member	Depth (ft)
1	QP-18-149-11	Upper Lidita Fm (Kls)	9854.42
2	QP-18-149-12	Lower Lidita Fm (Kli)	10486.50
3	QP-18-149-13	Galembo Member	10854.83
4	QP-18-149-14	Salada Member	11892.50
5	QP-18-149-15	Tablazo Fm (Kt)	14755.83

Source: Authors, (2021).

Rock samples from the La Luna-1 Well (Table 1.), iron mortar, sieve mesh #10 and #18 grain size >1mm and <2mm, Slick Water, HCl [15%], oven, schott bottles, and nitric acid was the materials used.

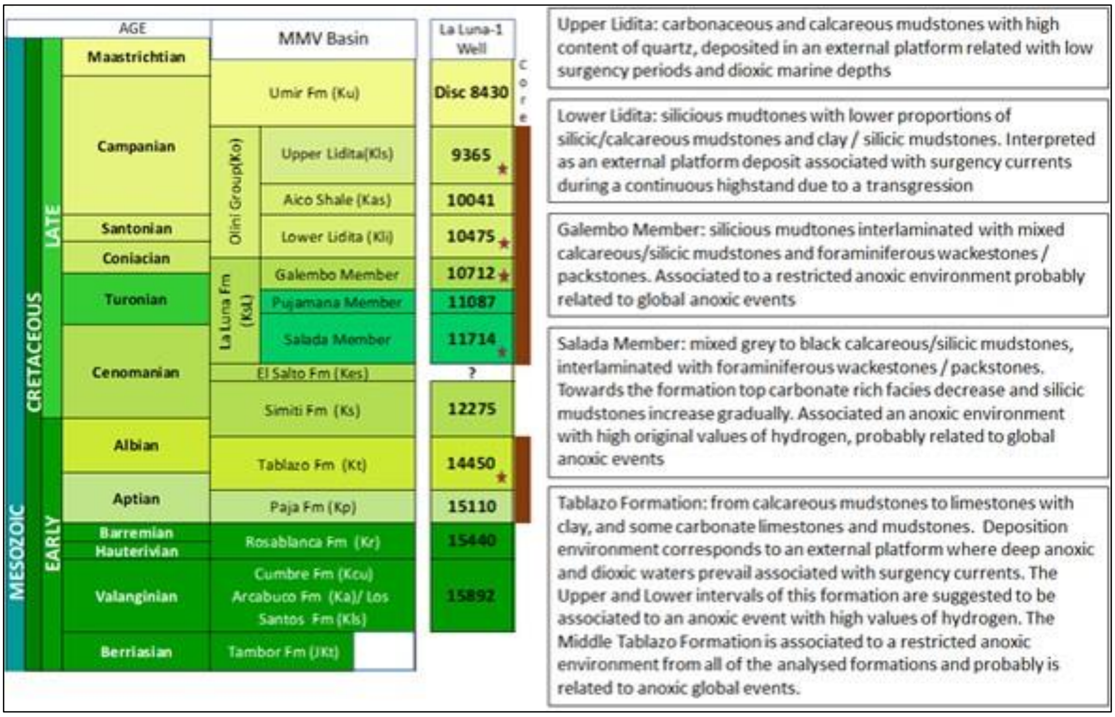

Figure 11: Stratigraphic column from the Cretaceous interval, Middle Magdalena Valley. The intervals are shown in red, and the star represents the interval NORM sample. Modified from.
Source: [6], [31].

III.1 EXPERIMENTAL DEVELOPMENT

1. Sampling: sampling of approximately 120 g of rock for each interval of interest (Figure 12).

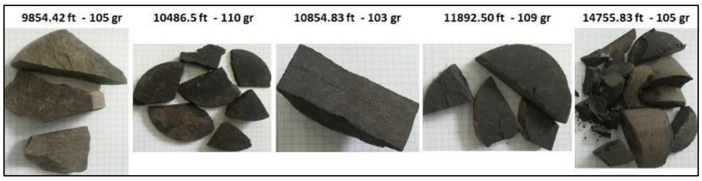

Figure 12: Selected samples for the NORM analysis in the Cretacic interval, MMV.
Source: Authors, (2021).

2. Mash: For this procedure, an iron mortar was used, the samples are mashed seeking a grain size that allows best rock-fluid interaction, so as to have greater contact with the fluids.

3. Sieve: Sieves # 10 and 18 (ASTM) were used; the screened sample is larger than 1 mm and smaller than 2 mm. After screening, 100 g of the samples were weighed (Figure 13).

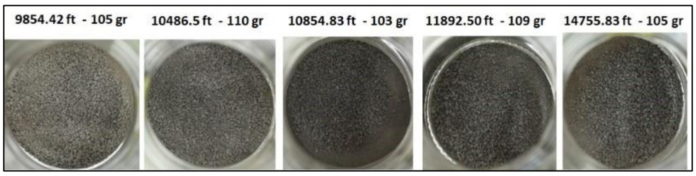

Figure 13: Sieve samples for the NORM analysis in the Cretacic interval, MMV.
Source: Authors, (2021).

4. Acid digestion: The samples were placed in a schott bottle where 0.5 ml of [15%] HCl per gram was added. Thus, for 100 g, 50 ml of [15%] HCl were added, in order to simulate the previous treatment of acidification fracturing (Well stimulation operation

where an acid, usually hydrochloric [HCl], is injected into a carbonate formation at a higher pressure than the formation fracture pressure). The circulating acid tends to truncate the fracture faces according to a non-uniform pattern, forming conductive channels that remain open without a supporting or propping agent after the fracture is closed [32].

Pumping a volume of acid prior to fracturing (pre-flow) is an operational practice in hydraulic fracturing that is intended to clean perforations and reduce frictional pressure losses in the near-wellbore zone to ensure the success of the operation. Because a high reaction rate acid is required to dissolve part of the calcareous fraction present in the shale in the near-wellbore zone, the industry, based on the experience of unconventional reservoir development in the United States, has standardized the use of 15% HCl. However, in practice, 15% HCl is pumped as a general rule and it is not a concentration that is defined for each particular well or depending on the mineralogy of each zone or interval.

Based on the foregoing, from an operational and practical point of view, what the protocol used tried to represent was precisely the fact that most likely in Colombia pre-flows with HCl at 15% will also be used and thus determine what could be the concentration of the different parameters in the flowback, as the mineralogical compositions of the rock vary.

The scenario where acidic preflow pumping is used represents the most critical scenario from the perspective of maximum concentration of the different ions or parameters in the flowback. However, in scenarios where, due to operational issues, the use of acid pre-flows is not necessary, it is expected to have lower concentrations of the different parameters in the flowback, the expected concentrations of some ions could be lower than those identified.

5. The digested samples with HCl at [15%] were placed in an oven at 90 ° C, where they were left for interaction for nearly 45 minutes - temperature and approximate time for this treatment.

6. After 45 minutes, the samples were removed from the oven, and 1 liter of the slick water was added, emulating hydraulic fracturing. The fluid is composed, concentration per liter:

Water	Base fluid	982.5 ml
KCl	Clay inhibitor	22.454 g/l
Cla-Web	Clay inhibitor of clays	2 ml
LoSurf 300M	Surfactant	2 ml

From the left-over fluid from the latter mix, the pH is calculated previous to stirring (Table 3).

Table 3: Calculated pH from rock digestion of HCl-Slick Water in the La Luna-1well.

ID Sample Lab ICP	Depth	Formation	pH
QP-18-149-11	9854.42’	Upper Lidita	6.36
QP-18-149-12	10486.50’	Lower Lidita	6.28
QP-18-149-13	10854.83’	Galembo	6.25
QP-18-149-14	11892.50’	Salada	6.22
QP-18-149-15	14755.83’	Tablazo	6.40

Source: Authors, (2021).

7. This fluid-rock interaction, which occurs on a large scale in the hydraulic fracturing process, is taken to the oven for 30 days at a temperature of 90°C (the schott bottle lid must be tightly secured to prevent the evaporation of fluids).

8. After 30 days, the samples are reduced, shaken and decanted (Figure 14). The fluid (1-liter, minimum amount required by the laboratory) is separated from the solid fraction of the rock and transferred to a bottle, adding 0.5 ml of nitric acid to preserve the sample in a liquid state (this is according to the Pace Analytical laboratory specifications). Finally, the five fluid samples (equivalent to the return fluid) were sent to the Pace Analytical laboratory in order to measure either the radioactive materials of NORM or the potential TENORM.

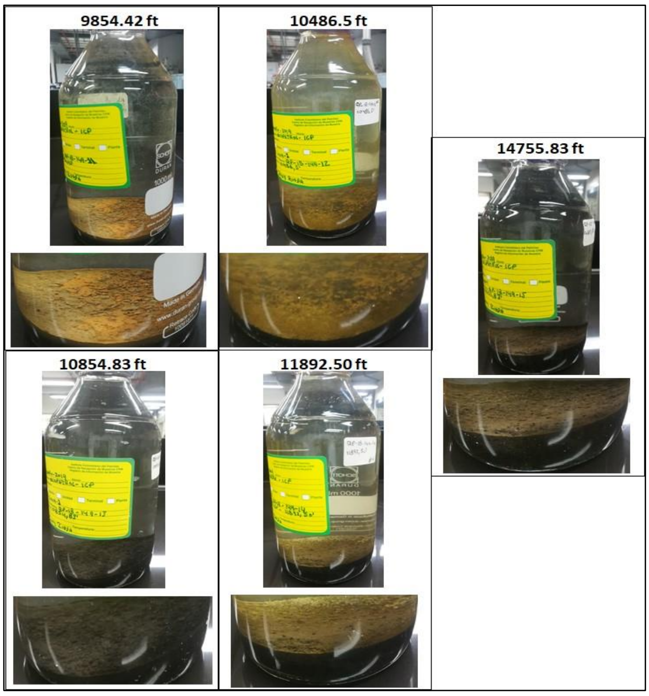

Figure 14: Digestion sample result: sieve sample (1-2mm) + HCl {15%} + Slick water, day 30.
Source: Authors, (2021).

IV. RESULTS AND DISCUSSIONS

The analysis of fluid samples was carried out in the Pace Analytical laboratory located in Pennsylvania, USA. The laboratory followed the EPA 903 and EPA 904 nomenclature, which describes the procedure to measure Radio-226 and Radio-228 isotopes respectively according to the United States Environmental Protection Agency [33]. Table 4 displays the results obtained, which units are presented in pCi/L.

Where. Act: Activity/ Unc: Uncertainty: For Safe Drinking Water Act (SDWA) analyses, the reported Unc. Is the calculated Count Uncertainty (95% confidence interval), using a coverage factor of 1.96. For all other matrices (non-SDWA), the reported Unc. is the calculated Expanded Uncertainty (aka Combined Standard Uncertainty, CSU), reported at the 95% confidence interval, using a coverage factor of 1.96./ MDC: Minimum Detectable Concentration/ Carr: C: Carrier Recovery (%)/Trac: T: Tracer Recovery (%).

Table 4: Isotopic results of Ra-226 and Ra-228, for the experimental return fluid from the La Luna-1 Well in the MMV, Colombia.

ID Sample Lab ICP	ID Sample Lab EHS	Depth	Formation	Parameter	Method	Results Act ± Unc (MDC) Carr Trac	Units
QP-18-149-11	BO1902506.001	9854.42’	Upper Lidita	Ra-226	EPA 903.0	7.27 ± 1.85 (1.25) C:NA T:65%	pCi/L
QP-18-149-12	BO1902505.001	10486.50’	Lower Lidita	Ra-228	EPA 904.0	17.7 ± 3.39 (0.845) C:73% T:79%	pCi/L
QP-18-149-13	BO1902506.002	10854.83’	Galembo	Ra-226	EPA 903.0	35.2 ± 5.36 (1.64) C:NA T:35%	pCi/L
QP-18-149-14	BO1902505.002	11892.50’	Salada	Ra-228	EPA 904.0	8.53 ± 1.75 (0.828) C:73% T:85%	pCi/L
QP-18-149-15	BO1902505.003	14755.83’	Tablazo	Ra-228	EPA 904.0	2.22 ± 0.753 (1.13) C:69% T:81%	pCi/L

Source: Authors, (2021).

IV.1 NORM REGULATIONS

Compared to conventional hydrocarbon exploitation, on average, the concentrations of NORM in the water produced during unconventional methods can have a factor of approximately 1.5 higher than the water produced during conventional methods. So far, the reported concentration ranges are still within the reported ranges for conventional wells [34].

According to the International Commission for Radiation Protection (ICRP) and the International Atomic Energy Agency (IAEA) which raises the Basic Safety Standards (BSS), synchronized with the legislation of the European Union (EU), the extraction and processing of raw materials that involve exposure due to radioactive material, including the oil and gas industry, are treated as a practice in a planned exposure situation. The EU includes the oil and gas industry in a "list of 16 different industrial sectors involving NORM."

The ICRP stated that "natural radiation sources (e.g. NORM) can legitimately be completely excluded from the scope of their recommendations once the activity concentration of each NORM is less than 1 Bq [NORM] / g". This statement was implemented as per basic safety standards of the IAEA – EU, which states that "exemptions or authorization values for solid-state NORM-materials in secular equilibrium with their progeny" for members of the Th-232 decay series and U-238 will be 1 Bq [NORM] / g, which are equivalent to 27,03 pCi /g. Consequently, a substance or material with a concentration of NORM activity greater than 1 Bq/g, where the NORM must be a member of the Th-232 or U-238 decomposition series, can be defined as NORM.

The different chains of the oil and gas industry that produce solid materials with activity concentrations lower than those mentioned above, will be out of extend. However, for higher activity concentrations, the BSS provides a list of exempt activity concentrations. The BSS does not provide general exempt concentrations for crude oil/water and natural gas. When the composition and salinity can be the determining factor for the production of water at large, the values provided for production water with concentrations below 10 Bq [Ra-228] / L, 10 Bq [Ra-226] / L can be treated as exempted, which are equivalent to 270 pCi / L [34]. According to the United States Nuclear Regulation Commission, the discharge limit for industrial effluents must be 60pCi / L. According to international standards such as the EPA, and national regulations for water quality in Colombia (NTC 813), the maximum limits for drinking water are equivalent to Ra-226, Ra-228 of 5 pCi/L.

According to the foregoing regulations and the results shown in Table 4 in synthetic flowback, the effluents generated would be treated as radioactive waste materials as they exceed 1 Bq [NORM] / g. Nonetheless, it is also suggested that they would be under the limits to be treated as exempt, as they are below 270 pCi / L, both for Ra-226 and Ra-228.

IV.2 COMPARISON BETWEEN THE RESULTS OBTAINED FROM THE LA LUNA-1 WELL AND A STANDARD WORLDWIDE SITE

In order to understand the results obtained from the La Luna-1 Well with respect to the NORM content, some parameters must be considered. One of the most important is the deposition environment of the rocks, which is directly associated with the content of TOC, Ro, Salinity and NORM of the intervals of interest, associated with the gamma ray log. Moreover, it is necessary to have a reference from another perspective, thus, the Marcellus Shale Play will be used, which one of the main shale gas/oil deposits worldwide (NORM deposits are widely distributed; Figure 15A, 15B) and is part of the deposits with the highest production in North America (Figure 15C, 15D).

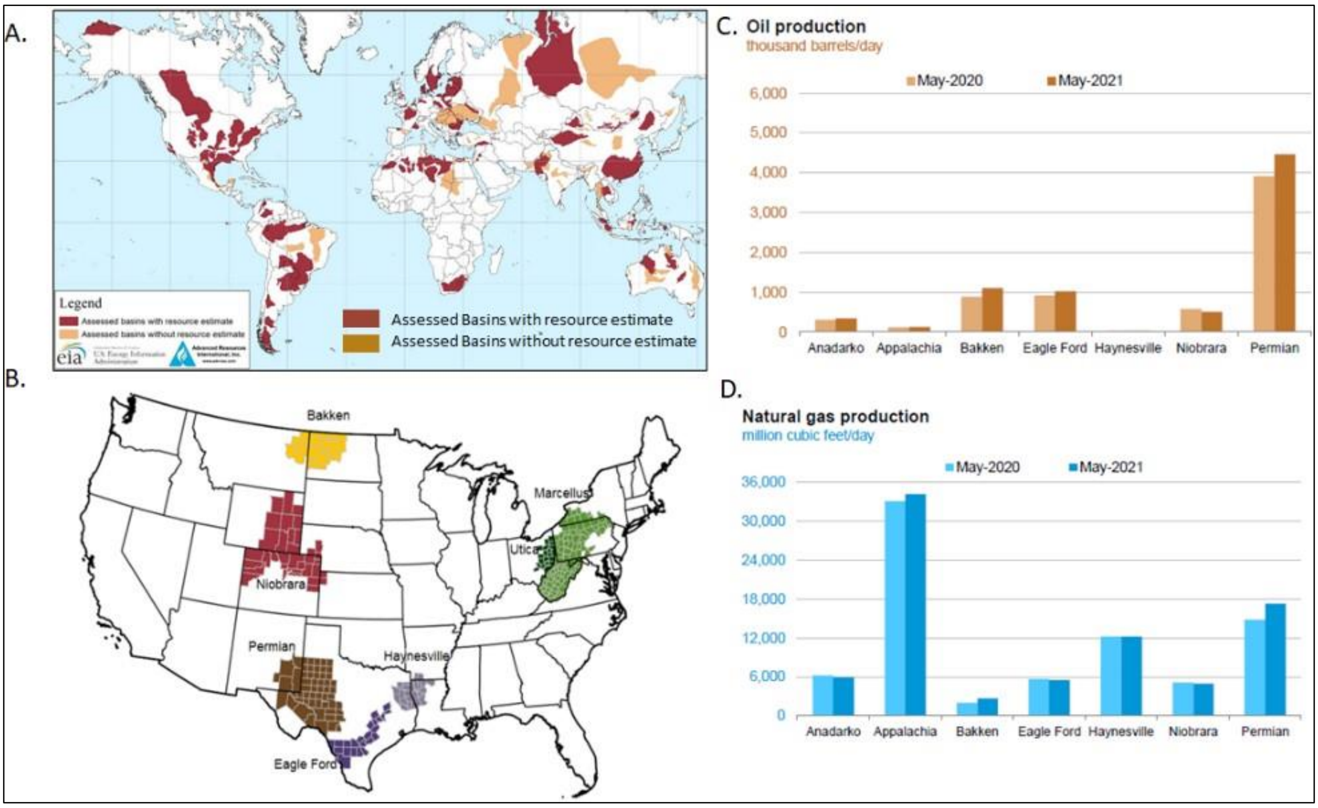

Figure 15: A. Global map of the evaluated basins with shale gas/oil formations.
B. Main productive basins of shale gas/oil in USA. C and D Resources from Marcellus Shale.
Source: [35], [36].

Table 5, figures 16 and 17, show data from the formations of interest in Colombia and the Marcellus Formation in the United States. Table 5 shows the global paleogeography established by Blakey Ron (2013) [37], identified to be Cretaceous, where the rocks in the VMM were deposited in an open shallow marine environment, under dysoxy and anoxic periods during cycles of major transgressions and regressions [38, 39].

Sediments rich in organic carbon are associated to oceanic anoxic events where large amounts of organic matter was generated and preserved [40]. These events are believed to represent important disturbances in the global carbon cycle [41, 42]. The Cretaceous is a period where organic rich sediments were extensively distributed all over the world in deep and shallow marine environments [43, 44].

Table 5: Comparison between the MMV basin and the Marcellus Formation (Located in the Appalachian basin, USA).

Formations of interest		Age	Environment of formation	Paleogeography, Blakey 2013.	TOC (%)			Ro (%)	Porosity (%)			NORM (pCi/L) (See Figure 17)
					Max	**Avr**	**Min**	**Avr**	**Max**	**Avr**	**Min**	
Olini Group	**Upper Liditas**	Upper Cretaceous - Campanian	Deposited in an external platform possibly associated with few periods of surgency with marine dioxic depths		4,90	3,24	1,20	0,65	10,81	7,00	0,81	7.27±1.85
	Lower Liditas	Upper Cretaceous - Santonian	Interpreted as a platform external deposit associated with surgency currents during a highstand followed by a transgression		5,02	4,12	3,30	0,72	17,77	12,18	8,71	17.7±3.39
La Luna Fm	**Galembo Member**	Upper Cretaceous - Coniacian	Associated to a restricted anoxic environment, probably related to global anoxic events		8,95	5,08	2,76	0,76	20,29	13,23	8,30	35.2±5.36
	Salada Member	Upper Cretaceous - Turonian	Associated to an anoxic environment, with high original values of hydrogen, probably related to global anoxic events		8,13	3,57	0,35	0,92	14,70	8,30	4,68	8.53±1.75
Tablazo Fm		Lower Cretaceous - Albian	External platform where anoxic and dioxic deep water conditions prevail with influence of current surgency deposits. The intervals of Lower and Upper Tablazo are suggested to be related to an anoxic environment with high hydrogen original values.		26,50	5,10	0,28	1,38	15,90	8,80	2,40	2.22±0.753
Marcellus FM		Middle Devonian	The paleogeographic reconstruction shows that system is rich in relation to the deposition of organic matter which took place in a three-way packing, almost closed. This geometry created a restriction in the marine circulation of the Appalachian basin during the middle Devonian		20,00	6,50	1,00	0.5/ 3.5	15,00	6,00	5,00	Depends on the analysed place, varying from 27 up to 13000

Source: [45], [6], [31].

For the Middle Magdalena Valley, in the La Luna-1 Well, Uranium is the element that contributes the most to the total gamma ray (Figure 16). On average, it corresponds to concentrations of 25 ppm, except for the Salada Member of the La Luna Formation, where some intervals reaching 80-100 ppm are observed. This follows maximum TOC values, greater deepening of the basin, and the lower contribution of terrestrial sediments. For the Salada Member specifically, Uranium enrichment could be produced by its incorporation into the sea through hydrothermal solutions associated with the subduction zone and the volcanic activity of the Early Cretaceous during the initial stages of the MMV basin, which is supported by the occurrence of volcanic ash layers in the Salada Member from the La Luna-1 Well [46].

According to Gomez (2014) [46], Uranium from the Salada Member was incorporated into the sediments by different mechanisms: 1) fixed to organic matter, 2) precipitated as uraninite evidenced by high contents of pyrite (obtained from DRX) and abundance of pyrite nodules (identified in the core), 3) chemically linked to phosphate nodules, as evidenced by the greater abundance of phosphate nodules in the Lower Salada Member (observed in the core and outcrops), and 4) being part of heavy minerals, such as apatite, also evidenced in the description of the core.

The concentration of Uranium in the Marcellus Formation varies from 8 to 53 ppm (Figure 16), and in some studies it has been reported up to 100 ppm [47]. According to Taylor (2013) [48], the deposition of black shale from the Marcellus Formation took place when the basins were deeper, more restricted, and received less sediment. Furthermore, different authors have also proposed that Black Shale was deposited in an epicontinental sea of a shallow basin (Table 5), which enabled the preservation of organic material under anaerobic conditions in an almost closed environment where ocean circulation was restricted due to paleoclimatic and paleogeographic limitations. With regard to the Marcellus Formation, the enrichment or high concentration of metals in the shale has been identified, where the total organic carbon concentration generally increases. It is suggested that this is likely due to the conditions that favor the preservation of organic matter during the shale and during the deposition of metals in a reduced state [47].

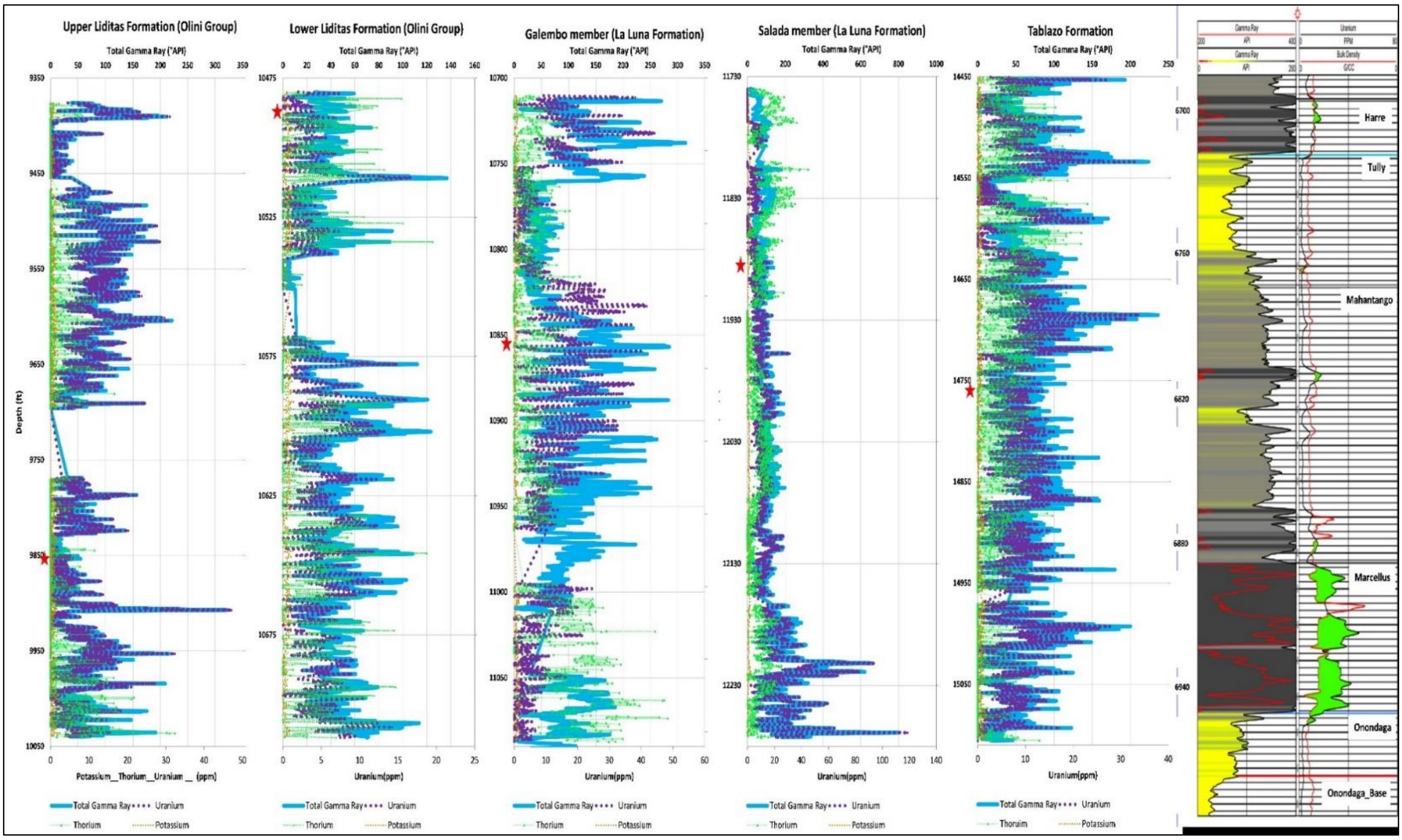

Figure 16: Core Gamma Ray Log obtained for the La Luna-1 well cores (Potassium, Thorium, Uranium and total Gamma Ray). From left to right, Upper Liditas fm, Lower Liditas fm, Galembo Member, Salada member, Tablazo fm, Marcellus Fm. (The curve of gamma ray is plotted in two tracks, from 0 to 200 API, and when Gamma ray exceeds 200 API it is indicated by the red line in the second track).

Source: [49], [6], [31].

The values that have been reported for the Marcellus Formation in Flowback water for the Ra-226 range from 551 to 25500, and average 8490 pCi / l [50] (Figure 17). Experimentally, the highest value for the MMV was 35.2 pCi / l (Figure 17). According to the regulations, the NORM values for the Marcellus Formation are higher than the exception level. Thus, the higher Marcellus values and lower MMV values are determined by the formation conditions for each respective reservoir. However, it is necessary to pursue the analyses, either at laboratory or pilot scale, in order to obtain thorough knowledge of the different parameters that may increase the NORM contents in the formations of interest. The Marcellus has elevated NORM levels because it is generally more organic-rich than other shales and radioactive elements bond to organic matter [18].

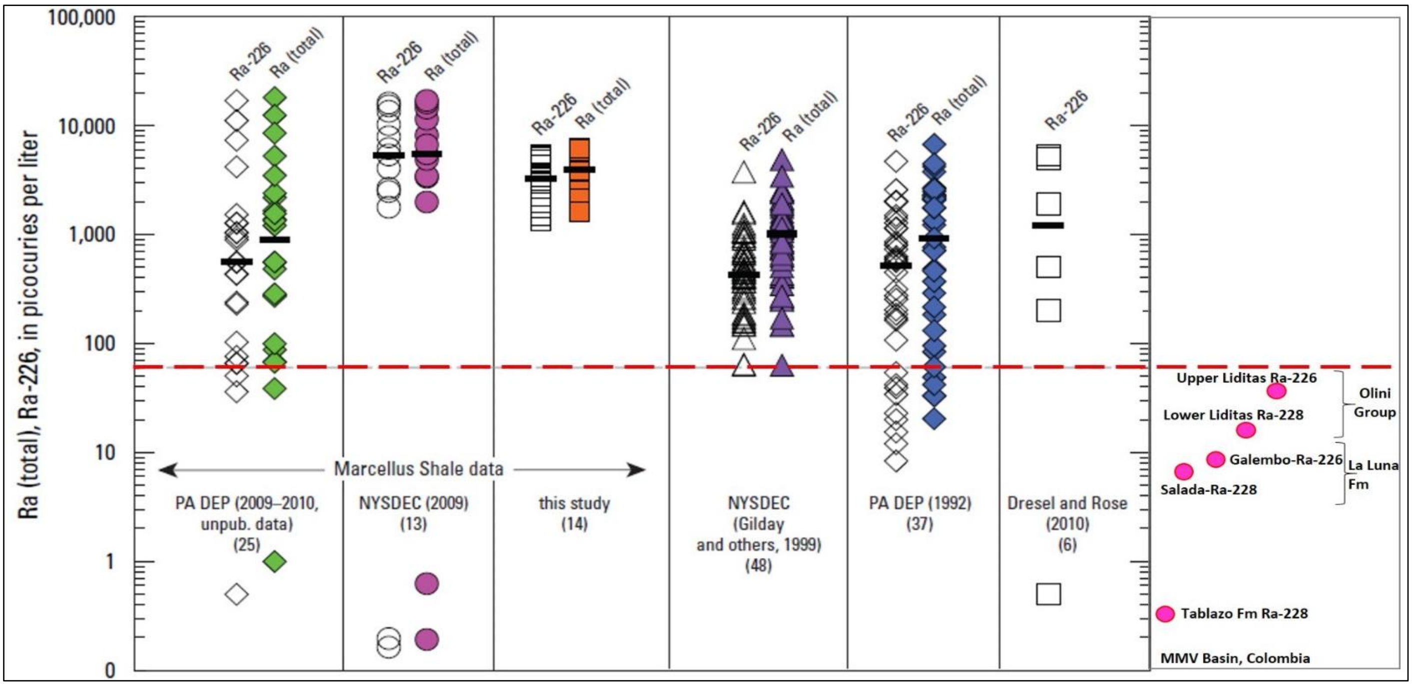

Figure 17: Comparison of data of total Ra-226 (Ra-226 + Ra-228) and Ra-226 in return waters for the Marcellus shale gas deposits and the Olini Group, the La Luna Formation, and the Tablazo Formation as the potential deposits in Colombia. In the case of Marcellus, the number of points in each data set is shown in brackets and the average value is plotted as a black line. For reference purposes, the dotted line shows the discharge limit to industrial effluents (60 pC/l) for Ra-226, according to the U.S. Nuclear Regulatory Commission (http://www.nrc.gov/reading-rm/doc-collections/cfr/part020/appb/Radium-226.html).
Source: Adapted from [51].

IV.3 COMPARISON WITH HYPOTHETICAL ANALOGUE

A foreign formation similar to a Colombian formation must be identified to correlate the physic chemical features of the flowback [52]. According to some data [52, 53] it was determined that the La Luna formation located in the Magdalena Valley (VMM) and the Shale Eagle Ford, showed similarities in their petrophysical and geologic features; in order to establish the similarities, the following features were taken into account: permeability, porosity, TOC, type of hydrocarbons, type of kerogen, temperature and vitrinite reflectance (Ro) [52].

The Eagle Ford formation consists of organic-rich calcareous mud rock with mineralogy ranging from 40-90% carbonate minerals, 15-30% clay, and 15-20% silica (quartz). The total-organic-carbon content (TOC) ranges from 2-12%, thermal maturity (%Ro) 0.45-1.4%, API gravity 28-62°, porosity 8-12%, and pressure gradient 0.5-0.8+ (psi/ft), Depth 6500ft-14000 ft, Thickness 75ft-300ft [54].

The Eagle Ford Shale is a hydrocarbon-producing geological formation of significant importance due to its capability of producing both natural gas and more oil than other traditional shale play, the shale play trends across Texas from the Mexican border into East Texas [55] (Figure 15A, 15B). It was deposited approximately 93 million years ago in a marine continental shelf environment [56] (Figure 18), during a period of enhanced volcanism, which resulted in an abrupt rise in temperature due to an influx of CO2 into the atmosphere, OAE2 Oceanic Anoxic Event [42, 57]. In short, deposition occurred mostly under the influence of: An oxic-suboxic water column before or after the onset of an OAE, an anoxic and possibly sporadically euxinic water column during the onset of an OAE A euxinic water column with available H2S during the late phase of an OAE [57].

Figure 18: Paleogeographic reconstruction of North America during the Late Cretaceous. Eagle Ford deposition is shown.
Source: [37].

The formation is divided into two units: an upper unit, characterized by interlayered light and dark gray calcareous mudrock deposited during a regressive interval (sea level falling), and a lower unit of mostly dark gray mudstone deposited during a transgressive interval (from rises in sea levels) [56].

Based on chemostratigraphic data, changing paleoceanographic conditions were documented, anoxic conditions associated with the Lower Eagle Ford Formation, suboxic conditions associated with most of the upper Eagle Fords, and then a return to normal marine conditions at the top of the Eagle Ford Formation. The high TOC content of the lower Eagle Ford was most likely caused by high productivity which in turn drove conditions to anoxia [58].

According to Fertl et al 1980 [59] and recent studies, this formation may vary from a typical dark, organic-rich shale response (i.e., high potassium, excessively high uranium, and high thorium) to a response of low potassium, low thorium, and excessively high uranium in the brittle, calcareous, fractured, and often productive Eagle Ford formation. Uranium concentrations ranging as high as 7 to 15 ppm are frequently observed [56]. In the Upper Eagle Ford, the Uranium values are highly scattered, although ranging from near 0 up to near 30 ppm [60]. The lower Eagle Ford is characterized by high gamma-ray values (90 to 135 API units), predominantly from high U, and many ash beds marked by Th and an upward-coarsening trend; the upper Eagle Ford Formation, interpreted as part of the high-stand systems tract, is characterized by generally low gamma-ray values (45 to 75 API units) with decrease in U and rarely Th, and an upward-fining trend [61, 62].

IV.3.1 Reported Norm and Regulations in the Eagle Ford Shale Region

Once the shale Eagle Ford formation was identified as the foreign formation analogue to the Colombian La Luna, it is assumed that the physic chemical composition of the flowback resulting from this formation in the United States is the base composition of the flowback in a non-conventional reservoir in the Colombian area [52].

The Eagle Ford Shale is 50 miles wide and 400 miles long; it has been a significant source of both gas and oil production ever since Petrohawk drilled its first wells in 2008 [63]. The increase in drilling activity could be an issue, because chemicals that flow back out of oil and gas wells during extraction could potentially cause groundwater contamination with toxic materials [63]. Due to the significant amount of oil and gas production, Texas has some of the most comprehensive laws and regulations in the country [55].

Jurisdiction over oil and gas NORM waste is split between the Texas Department of State Health Services (DSHS) and the Railroad Commission. The DSHS regulates the possession, use, transfer, transport, and storage of NORM, and the Railroad Commission regulates the activities associated with disposal of oil and gas NORM waste [55].

IV.3.2 Limits From Texas Regulations for Control of Radiation (Above Background)

Texas uses the term NORM instead of TENORM, under both the general radiation provisions and the oil and gas NORM disposal provisions. Texas defines NORM as "[naturally occurring radioactive] materials not regulated under the AEA whose radionuclide concentrations have been increased by or as a result of human practices," which often meets the definition of TENORM. Oil and gas NORM waste disposal limits: [64].

For protection of general public:	100 mRem/yr
For radium in water:	30 pCi/liter
For radium in drinking water:	5 pCi/liter
Uranium	30 µg/l
Alpha particles	15 pCi/l

Considering that the levels are typically so low, NORM in produced waters and natural gas is not a problem in Texas, unless it becomes concentrated in some manner. Through temperature and pressure changes that occur in the course of oil and gas production operations, radium 226 and 228 found in produced waters may co-precipitate with barium sulfate scale in well tubulars and surface equipment. Concentrations of radium 226 and 228 may also occur in sludge that accumulates in oilfield pits and tanks. These solids become sources of oil and gas NORM waste [55]. This is explained by the behavior of the Radium, although Ra prefers the aqueous phase, leading to somewhat naturally enhanced concentrations, Ra will follow the aqueous produced water stream, and because Ra is chemically similar to barium (Ba), strontium (Sr), calcium (Ca) and magnesium (Mg) becomes incorporated in group II sulfate or carbonate deposits and scale [34].

Drinking water supplies come from several sources including surface water and aquifers. To identify possible affectation by radioactivity in water, such as Ra 226, numerous studies have been conducted in Texas about aquifers of this region. The Gulf Coast aquifer region has a history of uranium mining and several mines are active today. Currently, all the active mines obtain Uranium using in-situ methods whereby they inject fluids into the ground to dissolve the minerals, which are then brought to the surface in the fluid and sent for processing [65]. A 1989 survey showed the average radium-226 concentration in uranium-mine overburden to be about 0.9 kBq/kg (25 pCi/g) [66]. Very high in-situ gamma radiation from potassium-40, thorium, and uranium have been observed [59, 60].

At the surface, the RRC reports that one Eagle Ford drilling field in Wood County documented radiation greater than 500 microroentgen/hour (µR/hr); these contamination cases are related to historical uranium mining and waste disposal. Additionally, some records indicate concentrations above the EPA MCL (from 0.0 to 1120 pCi/l) Figure 19A, but it is unclear whether these last data points were taken in response to a contamination event, or whether they represent unaffected background data [63]. Figure 19B, shows the Map of some counties considered: those in dark gray counties had Ra-226 over the legal limit and those in light gray counties consistently had Ra-226 under the legal limit set by the US EPA, while those in white had no reported values. Excess figures varied from 1 to 195 times for all water systems within the county [65].

According to some studies [63], in light of the potential for groundwater contamination to occur in the Eagle Ford shale region, it is worth assessing the strength of existing background water quality datasets in accurately predicting a regional baseline of water quality. "Background" water or baseline quality refers to the chemical characteristics of water before a change introduced to the water body that could affect its chemical characteristics. Further, oil and gas companies (industry) are aware of the opportunity for landowners to falsely claim that contamination has occurred when water quality problems already exist. On the other hand, landowners have been unable to obtain compensation for groundwater remediation when no comparison to background water quality is available to indicate the source of contamination.

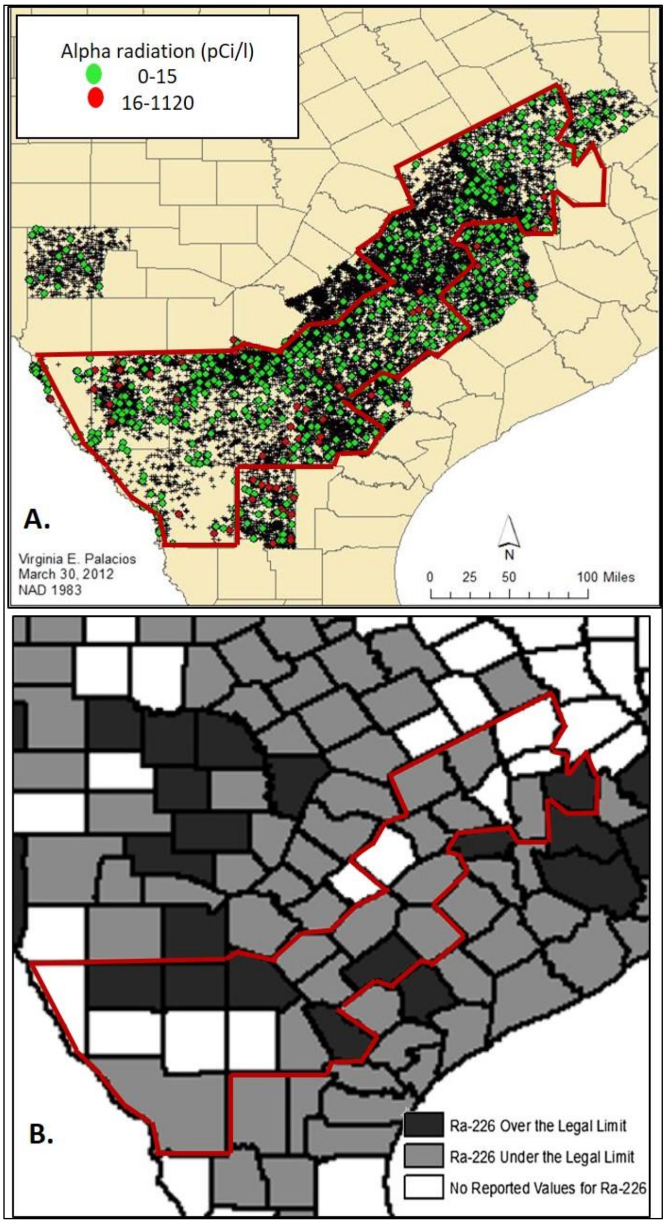

Figure 19: A. Alpha particle concentrations in the counties of interest. Red points represent values greater than the EPA MLC. B. Map of the counties considered: those in dark gray counties had Ra-226 over the legal limit and those in light gray counties consistently had Ra-226 under the legal limit set by the US EPA, while those in white had no reported values.
Source: [63], [65].
*Note in red the Eagle Ford boundaries.

V. CONCLUSIONS

The methodology simulated at laboratory scale the possible scenarios of rock-fluid contact (fracturing fluid) that occur in the hydraulic fracturing process (contact time, in this case with acid preflow), to obtain "synthetic flowback" samples. This fluid was called synthetic because although it used real rock samples from the La Luna formation, it is obtained in laboratory conditions; the importance of this experiment was to estimate or have indications of what could be the expected concentrations of NORM in this flowback in order to make risk management and mitigation plans based on this data for the possible development of unconventionals in Colombia.

Based on the results obtained from the synthetics flowbacks in the Geologic formations of interest of the La Luna-1 well in the MMV basin in Colombia to identify NORM in flowback water, would be treated as Radioactive Waste Materials, as they exceed 1 Bq [NORM] / g, nevertheless, they are below the limits to be treated as exempted as they are below 270 pCi / L, both for the Radio-226 as for the Ra-228. However, it is necessary to pursue the analyses, either at laboratory or pilot scale, in order to obtain thorough knowledge of the different parameters that may increase the NORM contents in the formations of interest.

Uranium and Radium 226 values measured in the La Luna-1 Well compared to the measured averaged values in the Marcellus Formation are present in lower concentrations, suggesting that the NORM enrichment in the Marcellus Formation and the low NORM values in Colombia are related to the content of uranium according to this results.

Uranium and Radium 226 values measured in the La Luna-1 Well compared to the measured averaged values in the Eagle Ford Formation exist in lower concentrations; however, it is not clear whether data from Eagle Ford were taken in response to an Oil and gas industry contamination event, or other influence such a uranium mining.

It is advisable to conduct a “Background” water or baseline quality assessment in the Middle Magdalena Valley Basin, intended to identify if another factor exists that could increase contamination in surface and underground water, as it occurred in the Eagle Ford Shale Play.

VI. AUTHOR’S CONTRIBUTION

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Methodology: Javier Perez and Jose Manuel Usuriaga.
Investigation: Jenny Paola Rueda.
Discussion of results: Jenny Paola Rueda, Javier Perez, Jose Manuel Usuriaga and Alvaro Villar Garcia.
Writing – Original Draft: Jenny Paola Rueda.
Writing – Review and Editing: Jenny Paola Rueda, Javier Perez, Jose Manuel Usuriaga and Alvaro Villar Garcia.
Resources: Jenny Paola Rueda, Javier Perez, Jose Manuel Usuriaga and Alvaro Villar Garcia.
Supervision: Javier Perez and Jose Manuel Usuriaga.
Approval of the final text: Jenny Paola Rueda, Javier Perez, Jose Manuel Usuriaga and Alvaro Villar Garcia.

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