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PhD THESIS - SUMMARY

STUDIES AND RESEARCH ON RADIUM IN GROUNDWATER

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INTRODUCTION

Distribution and behavior of radium isotopes in groundwater are important topics both from a practical and a scientific point of view. The practical importance comes from human health risks associated both with the ingestion of radium and the inhalation of radon or of decay products thereof.

The scientific importance largely derives from the potential applications of radium isotopes in tracing the mechanisms and rates of interaction on water-soil and water-rock surface and the transport mechanisms of the various elements in aquifers.

. Therefore the objective of this paper is to study the radium geochemistry, its generation and migration in nature, but especially in natural groundwaters, particularly in groundwaters from mine galleries and mineral water bottled and consumed in Romania.

The first part of the paper is a comprehensive documentary study from the technical literature on radium and its radioactive progeny, especially the radioactive gas, the radon, its presence in the soil, but especially in groundwater, the factors influencing its migration into groundwater and the danger posed to the population.

The second part of the paper presents the way of groundwater sampling, the characteristics of the geographic area where they were taken from, the experimental methods used by the author to measure the concentration of radium in groundwater, the results and their reporting to other measurements of radium mentioned in various international studies.

The first chapter is an introductory chapter presenting the physical and chemical properties of the element radium, summarizing data about its origin and generation. The table summarizing the main features of all known isotopes of radium at the time of writing this paper may be of interest.

In the second chapter of the thesis describes the mechanisms of radioactive decay and the main characteristics of the three natural decay series. In addition to the head of the radioactive series from where the entire radioactive chain is generated and the final stable element of the series, each of the three series also has an element called radium, generating the only gaseous element of that series, that is the radon. The decay schemes are presented for all three radioactive series, half-lives and the modality of decay for each series component, the energy and the abundance of emitted radiation.

If from the point of view of a radioactive decay the elements are in secular equilibrium, there are many situations in nature where a radioactive disequilibrium occurs between these elements. The description of the radioactive disequilibrium, the mechanisms and processes influencing this disequilibrium are described in the third chapter of the thesis. The focus was on the radioactive disequilibrium manifested in soil, rocks, but especially in groundwater.

The fourth chapter of the thesis contains elements of radium and radon geochemistry in different types of soils and natural waters. The main physical and chemical properties of radon are summarized and its way of generating from the parent element, the radium. It is also described the phnomenon of transport from the place of formation, in the mineral grain of soil, in rock or building material, towards the atmosphere or indoor air, but also in groundwater.

There are also presented the results of several studies conducted both domestically and worldwide on the presence of radium and radon in different types of soils and rocks within the territory of many countries, but also in different types of soils and natural waters crossing the rocks and soils in question. There are references regarding the way in which the radium and the radon derived from ingested water penetrate inside the body, but also regarding the accumulation of these two radionuclides in different organs.

The fifth chapter of the thesis presents the elements related to the migration of the radium in groundwater, its main entry ways into the groundwater and the main migration routes through the terrestrial hydrosphere. Thus, it is highlighted the modality of releasing the radium from wastewater coming from uranium and phosphate primary processing, from mine drainage waters, from the springs of radioactiv water, from rocks washed of groundwater, etc. Last, but not least the factors with a significant influence on the migration of radium in groundwater are mentioned, such as the absorption and desorption on minerals, ion exchange processes, precipitation in aqueous solutions, colloidal transport and particle transport, oxidation-reducing environments and groundwater pH, the salinity thereof.

The sixth chapter contains the results obtained by the author and the staff he was part of during the study on the presence of radium in groundwater from the mine galleries, located in Rodna, Gutâi and Maramureș Mountains, mountainous regions in the north and north-western part of Romania. For this study there were selected only mine galleries where any kind of human activity has been suspended for several years so that human activity should not influence the results of radium measurement in groundwater.

Seeing that the abundance of radium in soil and rocks varies by their geological characteristics, it was presented such a description of the regions where the waters coming from the mine galleries included in this study were taken from .

Based on the fact that between the radium and its decay product, the radon, a state of secular equilibrium state is achieved, an indirect method for radium measuring was used. First, it was determined the radon concentration in samples of groundwater with a method based on the scintillation produced by the Lucas cells, then given the state of secular equilibrium between the radium and the radon in water, the radium concentration in the samples in question was determined. It was also shown the principle underlying the method for the radon measuring (radium implicitly, with which it achieved the secular equilibrium), the sampling modality and preparation of water samples, the composition and role of each element on the experimental scheme, the results obtained. Starting from the two Lucas cell variants two experimental methods of making the measurement equipment for the radon concentration in groundwater were presented.

The method involving the use of the Lucas cell type, with a the useful volume of 145 ml, led to the determination of radium present in 23 different types of bottled mineral water and offered for public consumption in Romania. The results are presented in chapter seven of the paper. Two, three or five separate determinations in one year were performed for each type of bottled mineral water .

Given the reported level of consumption of bottled mineral water from Romania, the conversion factor of the radiation dose, it was estimated the effective dose due to the ingestion of mineral water by the population of our country by various age groups. The chapter also contains these values of the effective dose due to the consumption of mineral water.

We also present in a comparative way, numerous literature data on radium concentrations measured in bottled mineral water and the collective or effective doses due to the consumption of these waters throughout the world.

The final part of the thesis is the conclusions drawn from the results and considerations related to the issues remained open, issues due to the radium present in groundwater.

1 - **RADIUM – GENERAL DATA**

1.1 - ***Radium: description and discovery***

The radium is a chemical element with the symbol Ra and the atomic number 88 hovering in the periodic table of elements in the second group and the seventh column. The radium is an alkaline – earth metal, which is pure white, but it readily oxidizes on exposure to air, becoming black. As part of the second group of the periodic system of elements the radium has the characteristics of this group of metals: they are generally white, they are malleable, extrudable, it lends itself to machining, it can be drawn in the form of bars or plates, they are less reactive than the alkaline earths in the first group of the periodic system, and their melting and boiling points are higher than these.

In nature, the radium is found in uranium ores in very small quantities, about seven grams per ton of uraninite. The radium is not necessary for living bodies, and it has adverse effects on health when it is incorporated in the biochemical processes because of its radioactivity and chemical reactivity.

The radium (Latin radius - radius), was discovered by Marie Skłodowska - Curie and her husband Pierre on December 21, 1898, in a sample of uraninite. The Curies announced their discovery at the French Academy of Sciences on December 26, 1898. The name of radium comes from 1899, from the french word radium, formed by the latin radius, ray, so named for its power to emit energy in the form of rays.

1.2 - ***Radium – Physical characteristics***

The radium atom has a radius of 1.43 angstroms, a number of 88 electrons revolving around a core where there is a number of 88 protons and 138 neutrons, if the isotope is Ra-226 (Stwertka, A ., 1998). The radium has similar properties to his more stable counterpart, the barium.

Pure radium is a white, silvery metal, which melts at 700 ° C and boils at 1737 ° C, similar to the barium. The radium has a density of 5.5 g/cm3; the radium - barium density ratio is comparable to the radium - barium atomic mass ratio, which makes that these elements have very similar centered cubic structures (Kirby, H. W, 1964).

1.3 - ***Radium - Chemical characteristics and compounds***

The radium is the heaviest known alkaline earth metal and its chemical properties are especially similar to the barium. When exposed to air, the radium reacts violently with it, forming the radium nitride, which causes darkening of this white metal. It exhibits only the +2 oxidation state in solution. The radium ions do not form chemical complexes easily, due to the highly basic character of the ions. Most radium compounds co-precipitate with all barium, most strontium, and most lead compounds, and they are ionic salts. The radium ion is colorless, forming white radium salts when freshly prepared (Kirby, H. W, 1964).

The radium compounds burn with a red - purple flame and give a characteristic spectrum. Like other alkaline – earth metals, the radium reacts violently with water to form radium hydroxide and it is slightly more volatile than barium (Holden, N., E., 2004). Due to its geologically short half-life and intense radioactivity, the radium compounds are quite rare, being found almost exclusively in uranium ores.

The radium can be dissolved in solutions having a varied pH values from the acid (pH = 3) to the base ones (pH = 10). Dissolved radium is a double ionized state, Ra^{2+} (Smith, B., 2006). The radium chloride, the radium bromide, the radium hydroxide, and the radium nitrate are soluble in water, with solubilities slightly lower than the chloride and barium bromide, and greater than the barium nitrate. The radium hydroxide is more soluble than the hydroxides of other alkaline earth metal, of actinium and thorium, and more basic than the barium hydroxide. The insoluble radium compounds include the radium sulfate, the radium chromate, the radium iodate, the radium carbonate, and the radium tetrafluoroberyllate. The radium sulfate is the most insoluble known sulfate (Kirby, HW, 1964).

1.4 - Radium isotopes

The radium has 25 different known isotopes, four of which are found in nature, the isotope Ra-226 being the most common. The radium has no stable isotopes, all presenting the phenomenon of radioactive decay. The Ra-223, Ra-224, Ra-226 and Ra-228 isotopes are generated naturally as a result of the decay of uranium (U-238) and thorium (Th-232). All radium isotopes of are highly radioactive, the most stable isotope is radium-226, which has the highest half-life of 1600 years and decays into radon, which is a natural gas. The following is Ra-228, a product of Th-232 decay with a half-life of 5.75 years (Stwertka, A., 1998).

Of these four isotopes of radium in nature, the most abundant are the radioisotopes Ra-226 andRa-228, having the highest half-lives of 1600 years, respectively, 5.75 years (Table 1.1).

Table 1.1 – ***Radium natural isotopes***

ISOTOPE	**HALF - LIFE**	**DECAY MODE**	**DECAY SERIES**	**PARENT NUCLIDES**	**DAUGHTER NUCLIDES**
Ra-228	5,75 years	Beta	Th-232	Th-232	Ac-228
Ra-226	1600 years	Alfa, gamma	U-238	Th-230	Rn-222
Ra-224	3,66 days	Alfa, gamma	Th-232	Th-228	Rn-220
Ra-223	11,44 days	Alfa, gamma	U-235	Fr-223	Rn-219

From the point of view of the health of the human body, these two isotopes of radium have the most important impact, having the highest radiotoxicity, and once inside the body, they tend to be accumulated in the bones. The behavior of radium within the human body is similar to that of calcium.

To date, 34 isotopes of radium have been synthesized, ranging from a mass number of 202 to 234. At least 12 nuclear isomers have been reported; the most stable of them is Ra - 205m, with a half-life of 180 ms.

2 – THE CHARACTERISTICS OF RADIOACTIVE SERIES

Although there are natural radioactive elements of the different, most were seen as coming from heavy elements U and Th which otherwise have no stable isotopes. All radioactive elements between Bi-83 (the last element in the periodic table that still has stable isotopes) and U-92 are grouped into three radioactive families called natural radioactive series.

In a radioactive series, from a parent nuclide, it results by decay a different nuclide called "daughter nuclide" or "secondary element", called the generator element, ", which in turn is itself radioactive nuclide becoming the parent nuclide or the generator element for another nuclide, etc.

This can be represented by the formula

$$1\xrightarrow{\lambda_1}2\xrightarrow{\lambda_2}3$$

where λ_1 and λ_2 are the decay constants for the two "parent" nuclides.

All the three natural series present in the earth's crust have as common characteristics the fact that they start with one head of series with a lengthy half life, being contemporaries of the Earth ($T_{1/2} = 4.468 \times 10^9$ years for U-238, $T_{1/2}$=1,4 x10^{10} years for Th-232 and $T_{1/2}$=7,0 x10^8 years for U-235), and the fact that they end with an isotope of lead (Pb, 82) which is one of the most stable elements from the periodic system.

Table 2.1. presents the heads of series with stable nuclide results and half-life of the head of series.

It can be noticed that in the last line of this table has also been introduced the series of 4n +1 type which, because a small half-life (2.14 million years) is no longer found in nature. The entire Neptunium series can however be produced artificially (Lederer, MC, 1978).

Table 2.1 - ***Main characteristics of the radioactive series***

Name of series	**Type series**	**Final nuclide**	**Head of series**	**$T_{1/2}$ (years)**
Thorium	4n	Pb-208	Th-232	1,41x10^{10}
Uranium	4n+2	Pb-206	U-238	4,47x10^9
Actinium	4n+3	Pb-207	U-235	7,04x10^8
Neptunium	4n+1	Bi-209	Np-237	2,14x10^6

It can be noticed that in the last line of this table has also been introduced the series of 4n +1 type which, because a small half-life (2.14 million years) is no longer found in nature. The entire Neptunium series can however be produced artificially (Lederer, MC, 1978).

Apart from the head of series and final stable element, each radioactive series has a gaseous radioactive element (emanation). Thus, for the Uranium series (U-238) the gaseous element is radon Rn-222, for the Th series (Th-232) the gaseous element is the Thoron Rn-220 and from the actinium series (U-235) the gaseous element is the Action Rn-223.

Another feature of the radioactive series is that the radioactive components are in secular equilibrium. In this case, the number of nuclei for all descendants decreases in the same way to that of the head of the series, and the activity is the same for each nuclide, equal to that of the head of the series. This property of radioactive series is used in practice to estimate the concentrations of radionuclides in the series in question. If the secular equilibrium is assumed, it is enough to determine the specific activity for a single element of the series, seeing that its activity is equal to any element of the series.

The nuclei of these series are obtained from the head of the series through a series of alpha and beta decays (+ or -). From driving laws we know that the mass number A decreases by 4 to alpha decay and beta decay remains unchanged. It follows that the difference between the mass numbers of two nuclei in the series differ by a multiple of 4. Thus four radioactive series can be imagined as starting from the same area of the nearly stable nuclei with the mass above 230; they are characterized by mass numbers of the form (4n+0), (4n+1), (4n+2) and (4n+3), where *n* is a natural number.

In each radioactive series there are ramifications caused by the competition between α decay and β decay. In the series with an even number (4n and 4n +2 form), the main branch is given by the sequence α - β - β - α, while in the odd series (4n + 1 and 4n +3 form) the main branch is given by the sequence α - β - α - β. The main branches have the highest relative abundance.

3 – THE NATURAL RADIOACTIVE SERIES DISEQUILIBRIUM

3.1 Generating the mechanism of radioactive disequilibrium

The radioactive disequilibrium occurs when a radioactive decay product is more mobile than the other. This disequilibrium can be observed especially at the boundary between two media, such as the liquid/solid, gas/solid and solid/solid boundary. The different mobility of radionuclides induces their transport from the place of training, transport implying a fluid, either water or air. In both cases the radionuclide may exist either in solution or associated with the solid particles. Besides, solutions and precipitates are by far the most important in the development of radioactive disequilibrium, and most examples of radioactive disequilibria observed in nature have their origin in the hydrosphere. The groundwater and aquifer environments where water and minerals are intimately mixed are of particular importance.

The radioactive disequilibrium is induced by a number of mechanisms that are specific to the radioactive decay, but also a number of physical or chemical processes specific for radionuclide transport agent (water or air), and the radionuclide itself.

3.1.1 - **Decay recoil**

The recoil is the process by which a daughter radionuclide can be physically removed from the site of the parent radionuclide by decay. This can lead to a direct transfer of the radionuclide daughter from the mineral surface in solution or the transfer of the daughter radionuclide to another place of the mineral. This can cause subsequent loss of the daughter radionuclide in solution because the matrix is now damaged and thus the daughter radionuclide can be easily trained on minerals.

In geochemical systems, the recoil movement can be a significant process in measuring disequilibrim where there are elements of small aggregation states such as microcrystals from volcanic rocks in clay soils, the precipitates disseminated in aquifer, or where the gradients of concentration are high between two adjacent phases, such as the radioactive mineral grain in contact with the groundwater.

3.1.2 - ***Chemical transformation***

In the chemical transformation, the decay process can produce a daughter radionuclide whose geochemical characteristics significantly differ from those of the parent radionuclide. A good example is Ra-226 and the daughter radionuclide Rn-222, and a radionuclide of "nephew" type. In the sulphate rich groundwater, for example, Ra-226 can be present as $Ra_{226}SO_4$ and thus may be co-precipitated in gypsum (as $CaRa_{226}S0_4$) or barite (barium salt $BaRa_{226}S0_4$) (Alexander, R., 2003). However, after the decay, Rn-222 the daughter radionuclide in gaseous form, usually diffuses from mineral structure, when it can be transported in groundwater where it decays through a series of daughter radionuclides giving rise to Pb-210 which is relatively insoluble.

3.1.3 - ***Advection***

Advection is the process by which associated radionuclides, for example, with dissolved or colloidal species are transported by mass movement of groundwater and cause the radioactive disequilibrium by transporting radioactive radionuclides away from where they were released from the particles of material. The pressure gradients of groundwater flow can occur from variations in the hydraulic pressure (due to variations in the height of the body of water, for example), and from variations in the density associated with salinity and temperature contrasts.

3.1.4 - ***Dispersion***

The solutions tend to occupy the entire volume of water through a movement in all directions. This phenomenon is called hydrodynamic dispersion. The dispersion causes a dilution of the solution and its radioactive contents due to spatial variation of groundwater flow velocity and mechanical mixing during fluid advection.

Dispersion can cause some radionuclides (in dilute) to move faster than the average speed of groundwater flow. This can be significant for radionuclides with a half-life relatively small: if some radionuclides arrive relatively quickly in an environment, due to dispersion, they will cause a higher radioactivity in the medium and will induce more pronounced radioactive disequilibrium in the environment they left.

Dispersion is the most important mechanism responsible for the dilution of groundwater, but it is generally less important in surface water and air.

3.1.5 - ***Diffusion***

Diffusion is the process by which radionuclides migrate to lower chemical potential gradients. Diffusion causes a spread of transported solutes or colloids. The rate of diffusion is determined by the magnitude of the concentration gradient, and also the diffusion coefficient of each solution. The diffusion coefficient is itself a function depending on the intrinsic properties of the chemical species in question, but also on the properties of the rocks such as the tortuosity of the pore space, properties of groundwater and, in particular, their temperature, and properties of the diffusion species, such as electric charge and the load size.

3.1.6 - ***Coupled physical processes***

In addition to the direct processes of advection, diffusion, and dispersion a number of coupled processes, which include electrical, chemical and thermal osmosis, thermal diffusion, hyperfiltration and electrophoresis, can carry water from the pores and radionuclides from solutions in response to temperature pressure, concentration gradients of the solution and electric potential (Alexander, R., 2003). Although such coupling is generally negligible for most practical applications, some of these processes, including chemical osmosis and hyperfiltration, can be significant in clay sediments in the case where the double overlapping diffusion layer of clay acts as a semipermeable membrane.

3.1.7 - ***Selective leaching***

One of the most common processes inducing a radioactive disequilibrium is the selective solubilization of the groundwater through dissolution of the solid mineral. Some of the elements of the uranium series are more soluble than others under the same conditions specified by the oxidation potential, pH, etc.. The result is an excess of elements belonging to the radioactive series, in hydrosphere, and a lack of such elements in solids. The dissolved elements in water produce by decay other daughter elements which can be much less soluble than the items they come from.

3.1.8 - A***bsorption***

Absorption includes all solution – rock interactions, interactions causing a slow migration of radionuclides in groundwater. The absorption capacity of the rock depends on the chemical properties of the groundwater as well as those of rock. Since some chemical reactions are relatively slow, absorption can be described as a function of time.

The tendency of dissolved radionuclides in the groundwater to be absorbed by the solid phase of aquifer can be characterized by empirically determined measure, called distribution coefficient K_d defined as the ratio of the isotope absorbed and dissolved. This measure, the distribution coefficient, is the simplest way to express the phenomenon of radionuclides absorption in groundwater.

3.1.9 - ***Ion exchange***

The ion exchange process is one of the possible absorption procesess with an important role for the radionuclide cationic. The most important mechanism to slowdown the transport of radionuclides in groundwater systems is the ion exchange and precipitation. The ion exchange applies primarily to cations and although to anions it may become a slowing process of transport and thus a process of influencing the radioactive disequilibrium.

The ionic charges on the outer surface of the minerals come from the cationic substitutions of the crystal lattice and the surface ionic dissociation. The ions in the outer layer can be negative or positive, depending on the pH - of the medium nearby. At low pH, the positive ions will prevail while at neutral or higher pH, the negative ions will prevail (Freeze, RA, 1979). Most groundwater systems have a neutral pH, with a tendency to increase. Therefore the ions in the outer layer will be mostly negative (cation).

3.1.10 - ***Precipitation***

The changes in temperature, pH and other chemical constituents of groundwater will cause precipitation (separation) of dissolved radionuclides in groundwater. The solubility of many radionuclides varies directly with the temperature and the acidity level of groundwater can also be affected by solubility (Sposito, G., 1981). In contrast to the formation of chemical complexes, which is always an equilibrium process, the precipitation process is not an equilibrium or metastable process.

The co-precipitation refers to a group of processes by means of which more dissolved constituents precipitated in the groundwater at the same time.

3.1.11 - ***Formation of natural colloids***

Colloidal particles having a diameter of up to 0,5 μm, remain suspended in solution for a long period of time and can migrate with the groundwater. The particles containing radionuclides can be formed by the absorption of dissolved radionuclides in water on non-radioactive particles. In order to estimate the amount of radionuclides which can be carried by the colloidal suspension, several aspects must be taken into account: the size of the colloidal particles, the rate of absorption of the radionuclides on the colloidal particles, the stability of the these colloids and the filtration or particles absorption degree by the rocks structure through which the groundwater passes.

Radiocolloids are credited as having a significant role in the transport of radionuclides through various aquifers media and thus to induce a radioactive disequilibrium in this environments (Avogadro, A., 1982).

3.1.12 - ***Biofixation***

Biofixation is a mechanism affecting transport of radionuclides due to microbial attachment (West, J., M., 1984). The radionuclides can be fixed and/or move on the microorganisms in the environment. The immobilization may occur when the radionuclides are incorporated into the structure of the micro-organisms cells or plant, which are relatively stationary. Also radionuclides can be transported by forming biocolloids as bacteria, spores and viruses.

3.1.13 - ***Radionuclide interactions with natural organic matter***

In some cases, organic matter can play a significant role in inducing a radioactive disequilibrium of radionuclides present in environments aquifers (Leventhal, J. S., 1979). The interactions of radionuclides with organic matter influences their transport by:

- Mobilization – the decomposition of organic matter increases the pressure of CO2 in groundwater and soil and mobilizes some radionucizi, eg uranium.
- Transport - the uranium may be carried as a bicarbonate anion or an organic complex soluble in groundwater.
- Concentration - the humic acid can concentrate the uranium found in groundwater. It may precipitate in water when it becomes more acidic. The concentration factor may rise to 10 000 times if the groundwater contains organic matter.

3.1.14 - ***Anion exclusion***

The negative charge present on many mineral surfaces may reject ions near those areas. This exclusion may limit the diffusion of these ions in the mineral matrix, thus allowing anions to move at a greater speed than the movement of water through the centre of mineral matrix fractures or intergranular pore space away from the negatively charged surfaces. The same phenomenon can restrict the entry of anions in the pores smaller than the intergranular ones. This process is important for the transport of radionuclides because the negatively charged radiocolloids could move faster than the average speed of groundwater.

3.1.15 - C***omplex organic formation***

The natural organic colloids can act as an absorber for the radionuclide in the absorption/desorption process and the cation exchange. Due to the existence of a large outer surface per mass unit and the association of anionic surface with the colloidal organic matter, radionuclides have a high potential to be absorbed. If the absorption takes place on the mobile colloidal matter then the radionuclides will be transported along with it.

The size of organic complexes consisting of the radionuclides with the organic material increases aalong with the increasing pH and the concentration of humic substances.

4 – **RADIUM GEOCHEMISTRY IN WATER AND SOIL**

The radium has four naturally occurring isotopes: Ra-223, Ra-224, Ra-226 and Ra-228. Out of these, the great majority of information about their behavior in different environmental factors is available for the isotopes Ra-226 and Ra-228. The most abundant natural isotope of the radium are Ra-226 and R-228, with half-times of 1600 years, respectively, 5.75 years.

In less saline groundwater, the Ra-226/Ra-228 abundance ratio varies in a very wide value range. In this way, values of this ratio between 0.07 and 41have been identified. In saline groundwater the Ra-226/Ra-228 abundance ratio varies much less, with values between 0.44 and 4 (Vesterbacka, P., 2005).

Ra-226, Th-230 nuclide follower is generally found in natural waters, in excess compared to the parent nuclide due to higher solubility of the radium compared to that of thorium and the diffusion from sediments into the water column located above them. It is collected from the water especially by the silicon impurities, but it is redissolved in depth.

In fresh waters, the radium is found in highest concentrations in limestone regions, where it is more soluble.

In soils and sediments, Ra-226 is generally in excess compared to Th-230, and more in excess than the U-238 because both are deposited by ion exchange on the clay and organic compounds from the water entered in the ground or by preferential removal of the U-238 from the ground or precursor rock.

The Ra-228 isotope (derived from the Th-232), is also in excess compared to the parent nuclide in natural waters. In this case too, the excess is mainly due to diffusion from the sediments.

The radium concentration in the groundwater depends primarily on its concentration in the layers of rocks penetrated by groundwater and on a number of mechanisms that affect the water transport of radium (absorption - desorption, precipitation - dissolution, formation of chemical complex). These processes are associated with the chemical composition of groundwater.

The radium dissolved as radium ion double ionized can be absorbed by soil particles through ion exchange. The extent of this interaction for a wide range of chemical conditions of the water and soil properties can be quantified by using the distribution of the K_d coefficient, defined as the ratio of isotopes of radium absorbed on the soil particles and the concentration of the radium isotopes dissolved in water (Smith, B., 2006):

$$K_d\left(\frac{l}{kg}\right)=\frac{C_a}{C_d}$$

where C_a - concentration of absorbed radium isotopes (Bq/kg)

C_d - the concentration of radium isotopes dissolved in water (Bq/l)

A large distribution of K_d coefficient means more radioisotopes absorbed on solid particles and less water.

The radium is known to be readily absorbed by clays and oxidized minerals present in the soil, especially in terms of water with neutral and alkaline properties. The absorption of radium is the strongest of all alkaline – earth metals.

The pH level of the water - soil system can have a strong effect on the absorption of cationic species such as radium. When an ion is absorbed on the ground particle, it is typically released as a hydrogen ion (H^+). This release is facilitated by the alkaline conditions of the system and it is inhibited by its acidic conditions. The radium will thus become more mobile in soils and acidic water. This effect becomes much more powerful when the decrease of the soil or water pH occurs in the presence of organic acids.

The radium is chemically similar to calcium, and it is absorbed from soil by plant, reaching to humans through food. The amount of calcium in the soil influences the rate of radium absorption by plants. A portion of the ingested radium is transferred in the small intestine to the body and it is attached to the bones. The skeletal system includes between 70-95% of the total radium content found in the whole body.

5 – RADIUM MIGRATION IN GROUNDWATER

5.1 – The radium migration paths in hydrosphere

The radium can occur in groundwater from natural sources as a result of the interaction of groundwater with different natural materials containing radium, such as rocks, soil, minerals and other raw materials. The concentration of radium and its parent nuclides in groundwater is affected by the availability and solubility of rocks nuclides entering the groundwater and rock permeability, the presence of materials with ionic character, medium acidity, etc.. All these parameters vary greatly and can explain the variation in concentrations of radium in groundwater.

The radium and other natural radionuclides can also be indirectly released into groundwater by exploiting radioactive ores (eg, U, Th) that are part of the nuclear fuel cycle. This is also true for the operation and processing of other conventional mineral of commercial importance, such as phosphate minerals, copper, gold, lignite, coal and other minerals - due to the presence of the uranium and its disintegration products with a long half life.

Geothermal springs and geothermal energy production are other sources of radium in groundwater. The radium is slightly soluble and therefore it can easily penetrate into the groundwater and be co-precipitated with Ba and Ca salts and then deposited on the internal surfaces of the drilling and production equipment, as well as the production of oil and natural gas. The sludge formed by precipitation and settling, and their arrangement as well as deposits in various waste storage facilities have a long-term high potential for the transport of radionuclides in groundwater, if there is no adequate barrier.

A relatively recent situation generating concern is the use of water mixed with sand and chemicals at high pressure to fracture rock formations and release natural gas, a process known as hydraulic fracturing. Much of the injected water may reappear in the first weeks of the process. This water can contain high activity thereof, of up to 620 Bq/l Ra-226 and 95 Bq/l Ra-228 (Rowan, EL, 2011).

Acid mine waters or acidic waters generally constitute another source of radium contamination due to the higher solubility of radionuclides at low pH. Such high concentrations have been reported radionuclides frequently occurred in such waters.

The main routes of radium migration in the earth's hydrosphere are shown in Fig.5.1.

This migration paths are a complex of factors, where there is a large number of possible combinations.

The radium released by these processes contaminates groundwater and surface water, where it can undergo various transformations, it can be fixed on aquifer, sediment stored or transported by sea. Radium migration involves a combination of natural processes which are not, however, strongly influenced by humans. The Transport through surface water is sensitive to changes induced by industrial or municipal contamination of these waters and their use for technological or irrigation purposes.

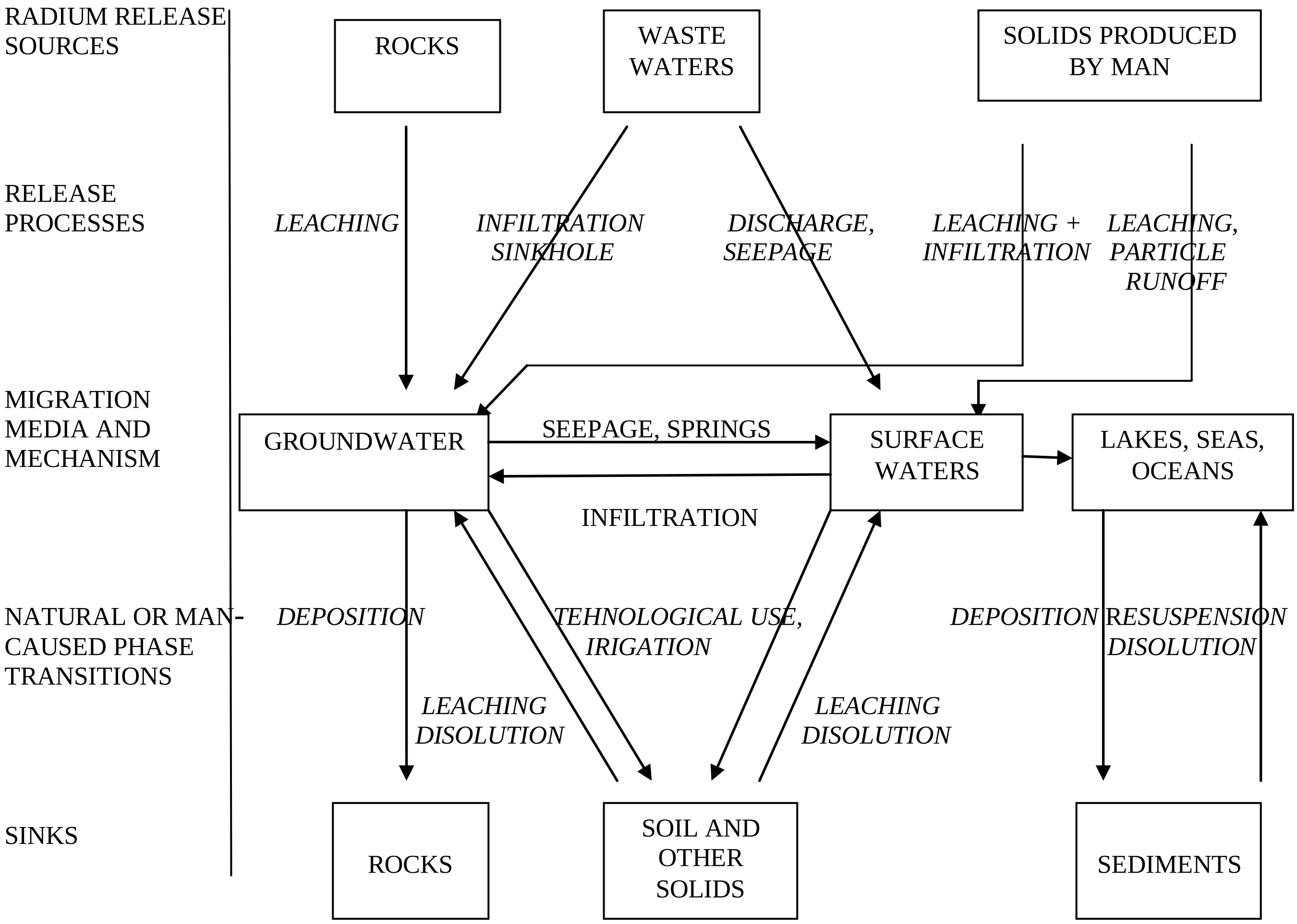

Fig. 5.1 - Radium migration paths in hydrosphere

5.2 – **Radium release in groundwater**

The radium can enter in the groundwater on several ways such as decay of the parent dissolved in water, the recoil of the parent isotope alpha decays of mineral, desorption from the aquifers surface, dissolution of solids, ion exchange and leaching of the crystal structure as a result of their damage after a decay (Dickson, B. L., 1990).

Tiny fragmentation of minerals containing radium can provide a continuous supply of radium over an aquifer. The primary minerals containing U and Th have isotopes of radium in secular equilibrium with their parents decay series, as well as other minerals with a large enough life time, more than 10^5 years. In this case, the radium nuclides will have an activity input rate of groundwatwer equal to the decay series heads activity rate, for example U-238/Ra-226 = 1. The minerals having a lower life time, which are rich in Th-232 and also incorporate nuclides of Th230 from U-238 series will have Ra-228 and Ra224 isotopes nearly in secular equilibrium with Th-232 but the Ra-226 content will be much lower. Thus, the radium isotopes of different decay series can be released into groundwater with different rates, depending on the rate of release in the same water seeded. Instead, the nuclides that are released into the groundwater at the same rate, will have different rates of elimination of those waters based on the specific behavior of each groundwater (Carvalho, F. 2014).

The contribution of radium for underground water of the parent nuclide decay dissolved in water is generally negligible because thorium isotopes are almost insoluble in groundwater (Langmuir, D., 1980).

However, the contribution of radium in groundwater coming from the thoryum decay absorbed on the surface of aquifer can be significantly (Davidson, E.M., 1986).

The entry of radium in water from mineral pore by alpha decay recoil of parent nuclides depends on their activity and location relative to the solid – fluid interface. The size of recoil nucleus is of the order of 0.02 to 0.05 μm in most mineral structure (Fleischer, RL, 1975), such that the atoms of radium may be removed from solids in the fluid of pores if thorium atoms, the parent element, lies at a distance of 0.02 to 0.05 μm to mineral-fluid interfaces. In addition, the damage caused by the recoil energy of the mineral matrix structure could increase from leaching of radium solid contribution in groundwater.

High levels of radium in groundwater require certain radium sources (eg, U, Th) and mechanisms to its solubility limit, which should not be significant. Uranium and thorium are present in the mineral structure or absorbed on mineral surfaces. The uranium decay propels the thorium nuclides in solution. This may, in turn, release the radium directly into groundwater.

The thorium is highly insoluble, and it is strongly absorbed on the surfaces of the negatively charged minerals, such as silicate minerals (Langmuir, D., 1980). The thorium decay present on mineral surface can generate significant amounts of radium in solution. The decay reactions tend to weaken the chemical bonds that keep the nuclides in the matrix, thus increasing the potential of the leaching solution (Fleischer, RL, 1980).

5.3 – **Radium release in mine drainage waters**

The mine water generated in the mine galleries and released into surface water contain different radionuclides, including radium, due to the interaction of water with rocks and soil it runs across. The chemical and radiological composition of mine water varies by location and is dependent on the geochemistry of the ore and the surrounding area.

The features and chemical composition of drainage waters are variable and depend on the mineral extracted by mining, geological and hydrological environment, mining methods and steps.

The radium in the form of particles in the mining water is mainly radium bound to suspended particles or radium absorbed on the scattered rocks. A good correlation was found between the particle content of radium and the suspended solids in mining waters from an underground mine (Sebesta, F., 1981).

The human activity of extraction and processing of various minerals can also cause a transfer of radium from groundwater in the surface waters and then in sediment. Large amounts of Ra-226are released into the environment with waste water from coal mines. This waste water with barium containing in the form of Ra^{2+} and Ba^{2+} mixed with natural water which in turn contains SO_4^{2-}, lead to the co-precipitating of Ra and B, which will be found in the different deposits and sediments. Large quantities of these sediments have been observed in some mines, on the collection channels of these waters and at the bottom of tailings.

5.4 - **Factors influencing the migration of radium in groundwater**

5.4.1- ***Ion exchange processes***

The ion exchange and absorption processes are particularly important in determining the rate of transport of radium in any type of groundwater-soil system. The cation exchange equilibrium is dominated by:

(a) Coulomb interactions between the cation (in various stages of hydration) and the fixed groups of exchanger material;

(b) ion hydration effects caused by ion-dipole interactions with water molecules (Eisenmann, G., 1962).

When the ion hydration effects predominates the short-range hydration ions tend to move ions with large range of hydration and the batch absorption affinity (or ion exchange), follows the order:

$$Ra^{2+} > Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+} > Be^{2+}$$

because Ra^{2+} is the smallest hydrated ion (Essington, ME, 2003).

5.4.2 - ***The precipitation of barite***

The radium can be precipitated in solution by the Ca and Ba minerals. The barium is the most important factor controlling the concentration of radium in groundwater. In the presence of the sulphate ions, the precipitation reaction is given by the relation

$$Ba^{2+} + Ra^{2+} + 2SO_4^{2-} = BaRa(SO_2)4$$

The most common mineral that precipitates from groundwater and incorporates radium is barite, $BaSO_4$ (Langmuir, D., 1985). It thus controls the concentration of barium in groundwater. Although the barite precipitation of radium causes its removal from solution, subsequent dissolution of barite as a result of geochemical conditions change, can become a source of radium in groundwater. Also precipitation on gypsum may remove radium from solution.

5.4.3 – ***Absorption***

Absorption exerts a strong control over the radium diluted in groundwater, in terms of type of substance, solution composition and temperature. Ra-226 desorption potential of the surface depends on the ionic strength of the water increasing along with the increase of the ionic strength. Thus, higher concentrations of Ra-226 are generally in salt solution than in the diluted water. Best absorption of radium is generally on Fe and Mn oxyhydroxide and clay (Vengosh, A., 2009).

The absorption and desorption take place very rapidly, in time intervals from the order of seconds to hours (Langmuir, D., 1985; Gonneea, ME, 2008).

5.4.4- ***Colloidal transport and transport of mineral particles***

Colloids present in groundwater absorb various radionuclides present and increase their migration speed through the water. Colloid compositions vary widely and may include the addition of clay and inorganic constituents such as Fe and Mn oxyhydroxide organic colloids and microorganisms. Colloids have usually large area for the formation of chemical complexes, and ion exchange reactions and efficiently carry a variety of building blocks.

The radium can be easily attached to the colloids due to its high affinity to surfaces, so that both the as colloids and clay particles and iron hydroxide can play a role in the transport of the radium (Short, S.A., 1988).

5.4.5 - ***The*** r***edox environment and pH of the groundwater***

The radium is present in one oxidation state, as Ra^{2+} , and thus it is not affected by the changes of redox environments type from aquifer. However, other kinds of minerals that have an impact on the behavior of Ra may be affected. Under reducing conditions, sulfate ions can be reduced, so that the barite saturation is not reached.

For some groundwater in Brazil, with very low pH values, high concentrations of Ra-226 and Ra-228 were determined (Almeida, RMR,). This was because of the decreased absorption on the iron oxyhydroxide surface, which has a positive charge at a low pH. Under anoxic conditions, the compounds of Fe and Mn are dissolved, and thus are not available for the radium absorption.

5.4.6 - ***The salinity of groundwater***

The behavior of radium in saline waters was generally explained by the processes of absorption on minerals present in groundwater and is influenced by:

- Competition on absortion surfaces of other, more abundant cations;

- Dissolution of constituents based on Fe and Mn in anoxic saline waters, reducing the availability of absortion surface;
- Increase of mineral surface due to decrease in pH;
- Increasing stability of inorganic complexes such as chlorides;
- increased Solubility of sulfate mineral that leads to an increase in radium, but also to limit its release into water as a result of precipitation of respective sulphates;
- The presence of dissolved organic complexes (Carvalho, F., 2014).

6 - DETERMINATION OF RADIUM IN MINE WATER FROM THE NORTH OF TRANSYILVANIA, ROMANIA

Mining activities, regardless of raw material extracted from the earth's crust (iron ore, coal, nonferrous ore, uranium, etc.) result in bringing to the surface large quantities of sterile. Both raw material and tailings resulted can have powerful effects of damaging the terrestrial environment. Although mining activity itself has been closed, different materials can still reach the earth's surface, (mine water in particular) and may keep on damaging the environment. In addition to various substances that reach the surface, under different chemical and physical forms, substances with radioactive containing can cause an increase in the natural radioactivity concentration of different environmental factors, with respect to the natural radiation dose received by the human body. (UNSCEAR, 2000).

Among the natural radioactive elements, uranium and thorium have an important role, especially their decay products, such as Ra-226, Ra-228, Rn-222, Pb-210 and Po-210, most of them being alpha emitting nuclides (Lehto & Hou, 2011). The Ra-226 plays an important role in internal human body contamination, if it is ingested, due to: the alpha particle emission, its long half-life of 1602 years and also because its short lived daughters.

The occurrence of radium into the groundwater, as well as other chemical compounds, is due to the interaction of water with ground rocks with which it comes into contact, process influenced by many factors, such as its solubility and way of radioactive decay. Radium, occurring after an alpha decay is dislodged from the crystal lattice of minerals and it is accumulated in the free spaces of the rocks where it can more easily enter into direct contact with groundwater. Radium concentration in groundwater depends on its concentration in the soil, physical and chemical properties of water and soil, the nature and structure of the pores in the rocks system and last but not least, the physical - chemical properties of radium.

Once inside the body, from food and water, Ra-226 tends to be accumulated in bones. Over 70% of radium from human body is contained in bones and teeth, the remaining fraction being fairly distributed evenly in soft tissues (Lloyd, 1961). Radium metabolic behavior inside the human body is similar to calcium. At the same time, Ra-226 acts as parent for Rn-222, which is a radioactive gas easily inhaled by humans, being the second leading cause for lung cancer occurrence, after smoking. (Baias et al., 2010; Cosma et al., 1997, Cosma et al., 2009).

Therefore, it is important to measure the Ra-226 concentration from water to protect human health.

The following are the results of determining the concentration Ra-226 in mine waters, waters coming naturally from the closed mine galleries, where the operating activities have been halted for several years. There were selected only mine galleries where any kind of economic and human activity, in general, has been suspended for several years so that these activities do not influence the measurement results of radium in groundwater.

The chosen study area is the mountains of the north and north - western part of Romania. In this area, there had been over the centuries, intense mining activities. In Gutâi Mountains, Rodna and Maramures Mountains, polymetallic ores with high content of lead, zinc, silver, gold, copper, antimony were exploited. These mining activities are currently stopped and the mine galleries are in various closing stages.

Once the flowing water is out of the mine galleries, it can reach directly the environment, or, it may pass, in advance, through a treatment plant and then is discharged into the environment. Note that the purpose of the mine water treatment is not to decrease the natural radionuclides concentration, but to reduce the contained water with chemical elements that can reach the surface water.

There were water samples collected from 19 underground mine galleries from Gutâi, Rodna and Maramureș Mountains (Fig. 1).

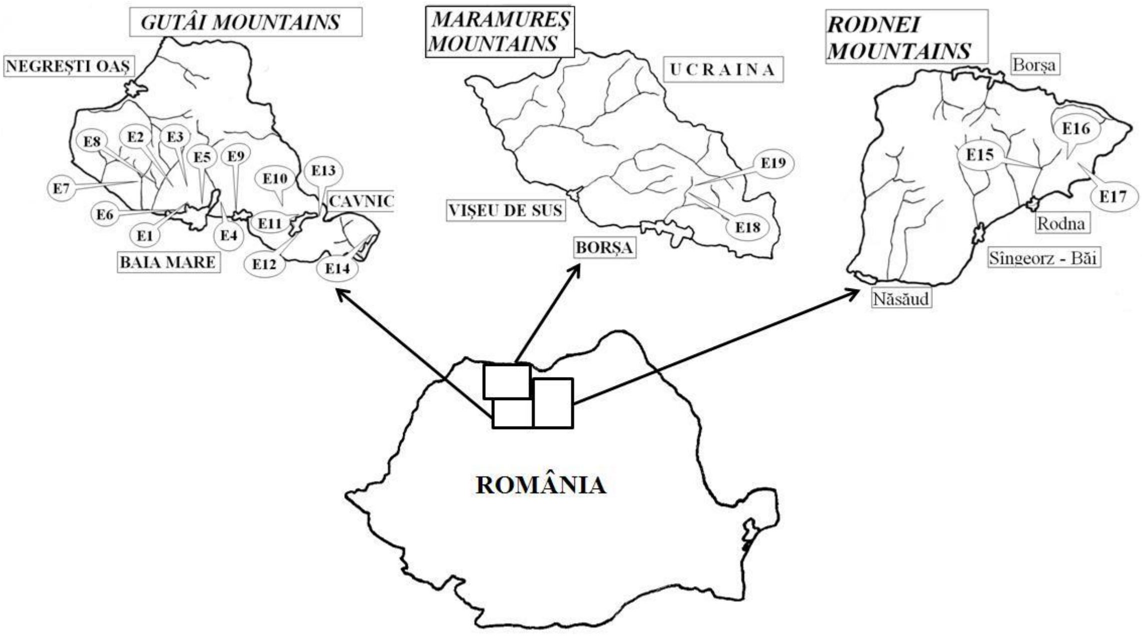

Figure 1. Study area – Gutai, Rodna and Maramures Mountains - and locations of groundwater sampling, E1 - E19.

6.1 - **Methods used for radium measuring in groundwater**

The water samples were taken right out of the gallery, in PET containers, hermetically sealed, with volume of 2l and 2,5 l. After the harvest, an amount of 2 mm^3 hydrochloric acid was added to each container with the water sample to prevent radium accession to the walls of the container, to inhibit the biological activity during water storage containers and to avoid any non homogenous distribution of the radium in the collected water sample. All mine water samples were collected in April and May 2012.

The water samples were taken only from those mine galleries where there was a strong and steady water flow from the inside gallery, avoiding galleries with pool water, because of the possibility of water intake from outside the mines. In most mine galleries the water was flowing naturally, but in some, the water came through mounted pipes, for cleaning, before discharging into the environment. All the galleries from which the samples were taken have not had any operating activities for at least five years.

The principle underlying the determination of Ra-226 concentration in water samples is based on the secular equilibrium between Ra-226 and its decay product Rn-222.

The radioactive decay of Ra-226 to Rn-222 and Po-218 is expressed by (1) (Cosma, C., 1996):

$${}^{226}_{88}Ra \xrightarrow[1600\ ani]{} {}^{222}_{82}Rn \xrightarrow[3{,}82\ zile]{} {}^{218}_{84}Po \qquad (1)$$

Thus, for a time *t* much smaller than the half-life of the Ra-226 ($T_{1/2}$ (Ra) = 1600 years), and noting the decay constant with λ_{Ra}, the number of atoms of radium at time *t* is

$$N_{Ra}\,(t) = N_{0Ra}\, e^{-\lambda_{Ra} t} \cong N_{0Ra} = constant \qquad \text{for} \quad t \ll T_{\frac{1}{2}}(\text{Ra})$$

namely the radium activity is constant.

$$\Delta_{Ra} = \lambda_{Ra} N_{Ra} \cong \lambda_{Ra} N_{0Ra} = constant \qquad (3)$$

Also at time *t* the atom number of radium resulted from the decay of radon is

$$N_{Rn} \approx N_{Ra} \frac{\lambda_{Ra}}{\lambda_{Rn}} \left(1 - e^{-\lambda_{Rn} t}\right) \qquad (4)$$

where λ_{Rn} is the decay constant of radon.

For a time *t* greater than the half life of radon ($T_{1/2}$ = 3.82 days), then $e^{-\lambda_{Rn} t} \approx 0$, and the relation (4) becomes

$$N_{Rn} = N_{Ra} \frac{\lambda_{Ra}}{\lambda_{Rn}} \qquad \text{or} \quad \lambda_{Rn} N_{Rn} = \lambda_{Ra} N_{Ra} \qquad (5)$$

Well, at time *t* the radon activity $\Delta_{Rn} = \lambda_{Rn} N_{Rn}$ is equal to the radium activity.

$$\Delta_{Ra} = \lambda_{Ra} N_{Ra}, \qquad \text{so} \qquad \Delta_{Rn} = \Delta_{Ra} \qquad (6)$$

In this case the secular equilibrium is reached after a period of 30 days, so that the water samples taken were kept sealed for more than 30 days to achieve the secular equilibrium between the radium and the radon radionuclides present in these samples. Measuring the activity of the radon present in the samples is practically determined the activity of the radium, considering that between the radon and the radium from these samples the secular equilibrium was performed (Moldovan, M., 2009).

Determining the radium Ra-226 concentration is based on the collection of radon, the decay product of radium present in the water samples, and its measurement in two ways, by scintillation, using different Lucas cells of different volumes, 1000 ml and 145 ml .

6.1.1- ***Radium measurement using large Lucas cells (1000 ml)***

For the first method, the measuring device is composed from a Lucas cell, with a volume of 1000 ml, attached to a photomultiplier connected to a single-channel analyzer (Fig. 2).On its inner surface, the Lucas cell has a thin layer of zinc sulfide, which converts the kinetic energy of the alpha particles at the moment of the impact with it, in radiation of light. This radiation passes through a window located at the top of the Lucas cell, into a photomultiplier tube, which is closely related to it. The signal is generated by the photomultiplier and then recorded, using a single channel analyzer.

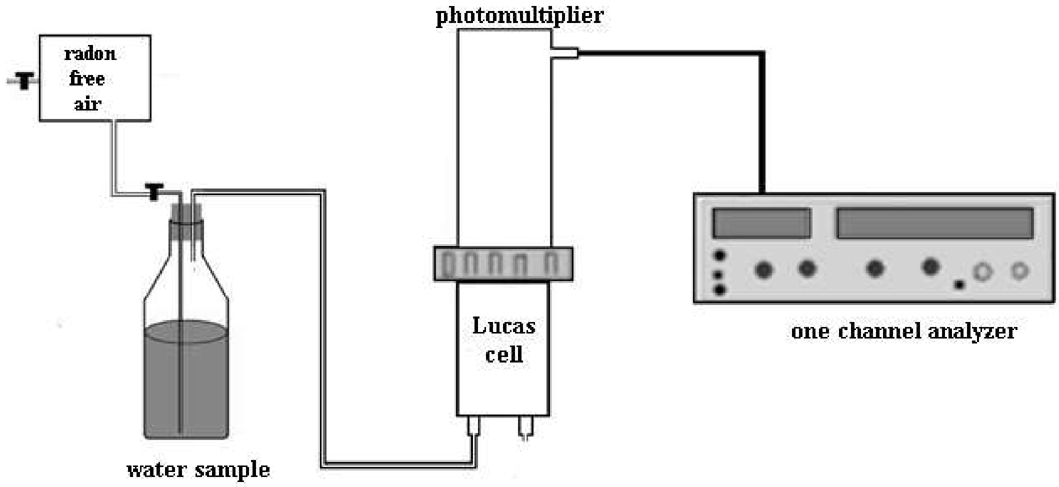

***Fig. 6.2. 1000 ml Lucas cell method scheme*.**

After achieving the secular equilibrium, the radon gas is extracted from the water sample, and it is transferred into a Lucas cell (scintillation camera), with a useful volume of 1000 l, with the air evacuated in advance.

Extracting the radon from the water is done by bubbling old air which no longer contains any radon. To eliminate the presence of radon from the air bubbling the water sample and to prevent the introduction of natural radon from the air of the workroom, the transfer of radon from the sample inside the cell Lucas was done by using a quantity of air closed earlier, in a large container, where the radon disappeared by radioactive decay, due its low half-life (3.82 days). The alpha radiations produced by the decay of radon extracted from water cause flickering on the impact with the inner layer of Lucas cells, scintillations which are then amplified by the photomultiplier and measured by the single-channel analyzer. The measuring time was set to 100 seconds.

The radon concentration in water for the above described method is (Begy et al., 2012):

$$C_{Rn}\left({}^{Bq}/_{l}\right) = C_{Luc}\left(k + \frac{V_A}{V_W}\right) \qquad (7)$$

where: C_{Rn} - radon concentration in water;

$C_{Luc} = \frac{N_S - N_B}{\varepsilon \cdot t \cdot e^{-\lambda_{Rn} t}}$ (3) – Lucas cell radon concentration;

k –the coefficient of radon solubility in water (Ostwald coefficient);

V_A - the air volume in the measurement system ($V_A + V_D = V_S$),

where: - V_S - connecting tubes volume,

V_D - Lucas cell volume;

$V_W = 0.5$ l - water sample volume;

N_S - sample pulses number recorded by the analyzer

N_B - background pulses number recorded by the analyzer;

ε - Lucas cell efficiency;

$t = 100$ sec. - measurement time;

λ_{Rn} - radon decay constant.

The measurement of water samples was done by using a set of 5 Lucas cells (1 liter volume) with efficiency between 66-87%, determined by the introduction of a known amount of radon in each Lucas cell. The limit of quantification (determination) for the 1000 ml Lucas cells is 20 mBq/l.

The coefficient of radon solubility in water for a room temperature (thus the water temperature) of 20 ° C, is 0.254 (Clever, H.L., 1979), while for other temperatures the following relation can be used (Hunyadi, I., 1999)

$$.\ k = 0{,}105 \cdot 0{,}405 e^{-0{,}0502 \cdot T} \qquad (8)$$

The measurement results are listed in Table. 6.2.

6.1.2 - ***Radium measurement using small Lucas cells (145 ml)***

In the case of the second method, mine water samples were also obtained from the original samples and stored as stated above. The radon from water was measured using Lucas cells of 145 ml and the LUK-3A type of device, specially adapted for measuring radon in water. The measuring equipment, called LUK-VR, includes a 500 ml volume scrubber where a known amount of water sample (300 ml) is transferred (fig. 6.3).

The air with radon content above the water in the scrubber, with volume V_a and the radon concentrațion A_a, is transferred through the rubber tubes, provided with two check valves, into the scintillation room (Lucas cells). Scintillation camera is inside the device LUK - 3A, jointed to a photomultiplier.

Before the measurement, the water sample was brought to the room temperature and, through a vigorous stirring, for one minute, the balance between the radon from the water and the radon from the air above was achieved. The scrubber was connected on one side to the Lucas cell, previously evacuated by means of a pump and closed by a valve, and on the other side to a Janet syringe

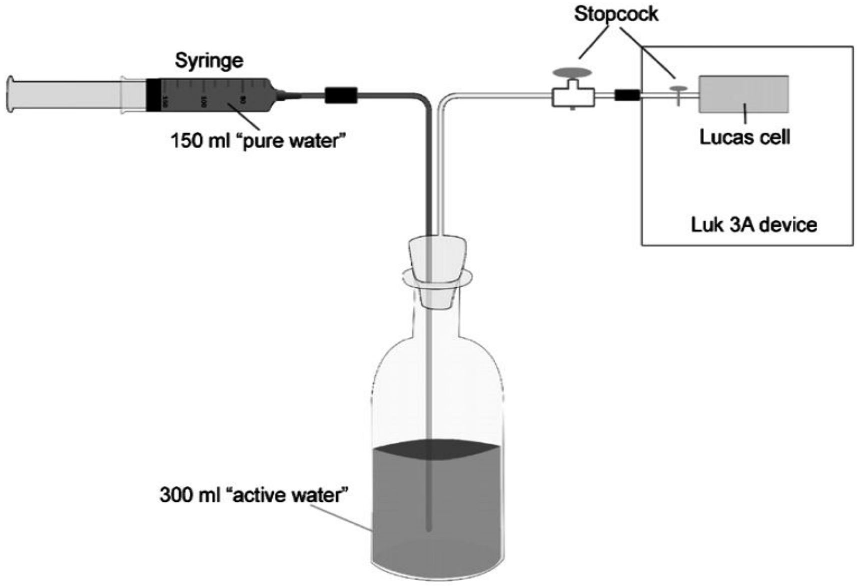

Fig. 6.3 145 ml Lucas cell method scheme

containing a quantity of 150 ml of radon free water. By opening the Lucas cell coupling valve and introducing the water from the Janet syringe, the air containing radon from the scrubber passes into the Lucas cell, which has a volume of 145 ml due to the pressure drop. The Lucas cell is jointed to a photomultiplier tube which helps counting the scintillations from the cell. Radon progenies are prevented to enter the volume of the Lucas cell by inserting a filter between this and scrubber with the water sample.

The Lucas cells activity measurement was made by directly jointing the cells to a photomultiplier included into the LUK-3A device and then to a pulse counter.

The ratio of the radon concentration A_w remained in the water of the scrubber, which the volume V_w and the radon concentration A_a above the water, in the air with volume V_a, is given by the solubility coefficient (Permyakov, V.M., 1963):

$$\alpha = \frac{A_w}{A_a} \frac{V_a}{V_w} \qquad (1)$$

where α is the solubility coefficient of radon in water.

The radon concentration remained in water A_w can be written as a difference between the radon concentration in the original water sample A and the radon concentration that came out of the water A_a and occupied space above the water, that

$$A_w = A - A_a \qquad (2)$$

Then the equation (1) becomes, after transformation and taking into account of the solubility coefficient values , the ambient temperature in which measurements were made, the volume occupied by air (scrubber hose connection, Lucas cell), the volume of water sample, and the time elapsed since the introduction of air into the Lucas cell and start measuring:

$$A(\mathrm{Bq/l}) = 5{,}3 \times N\ (\mathrm{imp/s}) \qquad (3)$$

where A is the radon concentration in the water, and N is the pulse number given by the counter.

The efficiency of detection is 1.46 counts/Bq for 15 minutes time of delay between filling the Lucas cell with air and starting the measurement. A constant efficiency of 1.24 counts/Bq was used, determined by a five minutes measurement, which started after 2 minutes from transferring the air from the scrubber into the Lucas cell. This constant was found using a standard solution of radium chloride $RaCl_2$ (STANDARD 12051 ARE, Romania). The decrease in the delay time allowed an increase in the number of samples analyzed per hour.

6.2 - Results and discussions

The measurement results of Ra-226 concentration from 19 samples of groundwater mining using both measurements protocols described above are listed in Table 6.1. The determined detection limit is 20 mBq/l for large Lucas cells (1 000 ml) and 50 mBq/l for small Lucas cells, 145 ml.

The relatively large differences occurred between the measured values by the two methods described, with Lucas cell of 1 000 ml, respectively, of 145 ml, is due to measurement errors and statistical errors involved. The mean difference between the two methods used is about 18%.

The lowest values of the measured radium concentration by the two methods, were found in mine water from Baia Sprie – Boului Gallery in Maramures County, both under the detection limit of used methods.

The highest values of radium concentration were 510 mBq/l for the 1000 ml Lucas cell method and 501 mBq/l for the 145 ml Lucas cell method. These values were determined for the mine water coming from Nistru - Gallery in Maramureș County.

The average measures of radium concentration by both methods are 138mBq/l for the 1000 ml Lucas cells method and 171 mBq/l for the 145 ml Lucas cells method.

Only in four analyzed samples (E4, E7, E8, and E12), representing 21% of all samples, the determined values of radium concentrations were higher than the value established in the U.S. as the maximum permissible value for radium in drinking water, 185 MBq/l (US EPA, 2000). The remaining amounts of radium concentrations were below this value representing a percentage of 79% of the total number of analyzed samples.

The radium concentration values measured by the two methods are comparable in what concerns the magnitude with the values of radium concentrations measured in the mineral waters from Transylvania, using the cells LUK - VR.

The values of the radium from the studied mine waters are lower than the values measured in other countries still in water taken from the mine galleries. Thus in Poland, the values of radium Ra-226 of 62.76 Bq/l and Ra-228 of 34.67 Bq/l were measured in groundwater from coal mines, water containing barium. In other waters, wherein the barium content was very low, the measured values for Ra-226 were 3.45 Bq/l for Ra-226, and 5.1 Bq/l for Ra-228 (Chalupnik, S., 2005).

Table 6.1 - Radium concentration from mine water measured with two methods.

Water samples - name and location	**Radium concentration (mBq/l)**	
	Lucas cell (1000 ml)	Lucas cell (145 ml)
E1 - Baia Mare –SCHWEITZER Gallery	**150** ±15	**186** ±30
E2 - Baia Mare – Valea Rosie Gallery 1	**70** ±4.9	**75** ±7
E3 - Baia Mare – Valea Rosie Gallery 2	**98** ±7	**98** ±8
E4 - Baia Mare –Mina Herja Gallery	**410** ±40	**463** ±51
E5 - Baia Mare –Dealu Crucii Gallery	**51** ±5	<50
E6 - Baia Mare –Sasar Gallery	**112** ±10	**122** ±11
E7 - Nistru – The Village Gallery	**510** ±40	**501** ±46
E8 - Baita – Purge Station Gallery	**212** ±21	**254** ±31
E9 - Baia Sprie –Boului Gallery	<20	<50
E10 - Suior – Mining Gallery	**116** ± 12	**148** ±25
E11 - Cavnic –REINER (Hospital) Gallery	**141** ±15	**113** ±23
E12 - Cavnic – Flotation Station Gallery	**325** ±30	**286** ±27
E13 - Cavnic –ROATA Gallery	**72** ±6	**70** ±7
E14 - Baiut – The Village Gallery	**45**±4	**50** ±6
E15 - Valea Vinului –Izvorul Rosu Gallery	**74** ±6	**66** ±8
E16 - Valea Blaznei Gallery	**60** ±6	<50
E17 - Valea Mare –Faget Mine Gallery	**57** ±6	**69** ±7
E18 - Baia Borsa –EMERICH Gallery	**53** ±4	**59** ±6
E19 - Baia Borsa –23 August Gallery	**56** ±5	<50
Average	**138**	**171**

The results obtained in this study lead to the conclusion that the activity of radium in the waters from the studied mine galleries, galleries currently closed and located in the northern part of Transylvania, Romania, poses no significant risk to the environment.

Therefore the low concentration of radium measured in mine waters in the study area does not present a significant risk for the health of people using contaminated surface water coming from the mine water from the studied mining galleries.

7- DETERMINING RADIUM CONCENTRATION IN BOOLTED MINERAL WATERS OF ROMANIA

7.1 - **Introduction**

Radium-226 and its daughter products are responsible for a major fraction of the internal dose received by humans from naturally occurring radionuclides. Many mineral springs contain relatively high concentrations of radium and radon. The Ra-226 values in mineral water, determined and published values were more over the reported values for public water supplies (Eisenbud, M., 1997).

Bottled mineral waters have always been regarded as a voluptuary good, something between a soft drink and a dietary or medical aid with a limited importance in the human diet. Nowadays the consumption of bottled mineral waters has become very popular. A considerable segment of the population drinks almost only mineral water as drinking water, which is about 1 l/day. As it is known, some kinds of mineral waters contain naturally occurring radionuclides in higher concentration than the usual drinking water.

In the last years, consumption of bottled mineral water has widely increased in all countries as well as in Romania. For example, during 1990-2000, mineral water consumption increased by 50 % in Germany and by 130 % in U.S.A.

In Romania there are over 2,000 mineral springs whose chemical diversity reflects very complex geological conditions that have influenced their genesis. Most springs present carbonated mineral water, whose origin is related to post volcanic phenomena associated to the Neogene magmatism. The Carpathian volcanic phenomena are particulary manifested on one of the largest areas in Europe.

The most important mineral deposits from Romania, subject to bottling, are situated in mountainous areas and in depressions away from sources of pollution characteristic to industrial areas or to areas where an intensive agriculture is practised.

Following the collecting rock lithology it is found that over 45% of natural mineral water accumulations are related to carbonate rocks (limestone, calcareous conglomerate), roughly 25% are located in pyroclastics and andesite, 25% in detrital sedimentary deposits and 5% in sandstones and crystalline schists (Feru, A., 2012).

Despite the high potential mineral resources and the long tradition regarding their consumption, during 2011 Romania produced slightly less than 1.1 billion liters of mineral water, which means an average consumption of 58 liters per capita.

Bottled mineral water is groundwater from natural springs or wells of different depths. The concentrations of Ra-226 in bottled mineral waters commercially available in Romania were determined, concentrations measured using a method that uses Lucas cell. Samples sprayer of mineral water bottled in different years were investigated (2006-2007). Based on the average values of concentration and an average consumption of 1 liter/day, the internal doses that could be attributed to the use of this type of water were estimated.

7.2 - Methods of measurement and assessments

Generally, Ra-226, the direct forerunner of radon Rn-222, is in secular equillibrium with the latter. The principle that underlies the determination of the Ra-226 concentration of mineral waters is to achieve secular equilibrium between this and its decay product Rn-222 dissolved in water. The working method is the one with small Lucas cell described in Chapter 6, Section 6.2.2 – Radium measuring using small Lucas cells (145 ml). Thus, in the case of determinining the radium from the mineral water when achieving a radioactive equilibrium, the concentration of radon in the water is considered equal to the concentration of radium dissolved in the water sample. Practically, measuring the concentration of radon in water is thus measured the radium concentration.

The radon concentration is equal to the radium concentration, this happens after a period of 30 days when the radium can be considered in secular equilibrium with the radon. In all the used calculations we will refer to the radon concentration measurement which is actually the concentration of radium.

The radon in water was measured using a LUK-3A device specially adapted for the radon measurement in water. This equipment called LUK-VR, (Figure 6.2) consists of a 500 ml scrubber where a known quantity of water (300 ml) is introduced. Before measuring, the water temperature was brought to the room temperature.

A volume of two liters of mineral water was evaporated to a volume of 0.5 l, then it was sealed for a month in glass bottles. The radon in equilibrium with the radium was then measured according to the method described in paragraph 6.2.2. Considering all types of errors (statistics, measurement) of about 25%, the detection limit for the measurement of the radium in water was set at 0.05 Bq/l.

7.3 - ***Results and discussions***

The radium concentration was determined for 23 types of bottled mineral water available in Romania, and two, three or five measurements (the last number in parenthesis) were made for each type of water individually for a period of 12 months. The measured values are shown in Table 7.1. The distribution of radium concentration values in the different types of bottled mineral water is shown in Fig. 7.2.

In twelve cases the ^{226}Ra concentration is less than 100 mBq l^{-1}, the characteristic value for the mineral drinking water in Romania (Begy, R., 2006; . Botezatu, E., 2005). In other eleven samples the ^{226}Ra concentration is more than 100 m Bq^{-1}. In all cases the ^{226}Ra concentration is less than 500 m Bql^{-1}. Of all the measured mineral waters only two measured values were under the detection limit of the measuring system, so the concentration of radium could not be specified for them.

There are four manufacturers who in 2008 had about 55% of the production and distribution of bottled mineral water. They are: A - Borsec with 20 %, F - European Drinks with 17%, R - Dorna with 10% and D - Perla Harghitei with 8% (Feru, A., 2012).

As it can be seen from table 7.1, only two types of water belonging to big producers have a radium concentration of over 100 mBq/l.

If the consumption rate of mineral water is of 1 liter/day, assessing the effective dose due to ingested radium in one year is obtained by multiplying the radium concentration in mineral

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Table 7.1 – Radium activity in bottled mineral water from Romania

Type of water (number of samples)	Ra-226 concentration (mBq/l)				
	Arithmetic average	Minimum	Maximum	Standard Deviation	Mean value
Borsec (5)	132.8	108	156	18.4	132
Tuşnad (5)	116.8	100	136	14.8	120
Borşa (5)	119.2	116	104	12.7	116
Perla Hraghitei (2)	84	80	88	5.6	86
Steaua Nordului (3)	130.6	116	148	16.1	128
Izvorul Minunilor (3)	198.4	172	228	21	196
Bucovina (3)	440.8	404	476	33.1	440
Izvorul Harghitei (3)	84	60	96	16.3	90
Biborţeni (3)	185.3	168	208	20.5	180
Alpina Borşa (3)	158.6	148	172	12.2	156
Roua (3)	61.3	52	72	10	60
Carpatica (3)	77.3	60	88	15.1	84
Cristalul Munţilor (3)	62.6	56	68	6.1	64
Briza Lipovei (3)	443.2	360	488	49.5	452
Vitalinea (3)	69.3	64	76	6.1	68
Gura Căinarului (3)	96	92	100	4	96
Dorna (3)	94.6	88	100	6.1	96
Cezara (3)	277.3	252	296	22.7	284
Aquatique (3)	349.3	332	368	18	348

Zizin (3)	78.6	72	84	6.1	80
Stânceni (2)	62	60	64	2.8	61
Poiana Negri (3)	<LD				
Izvorul Alb (3)	<LD				

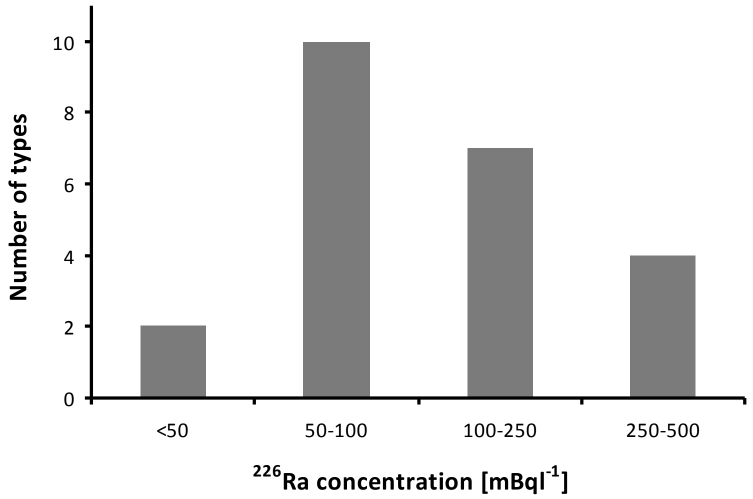

Fig. 7.2 - *The distribution of radium concentration values in the different types of mineral water*

water with the appropriate dose conversion factor, according to the relation

Effective dose (mSv/y) = Radium activity (Bq/l) x conversion factor (Sv/Bq) x
Annual water consumption (l/y) x 1000

The calculations used the conversion factors listed in Table 7.3.

Table 7.3 – Dose conversion factors

Organisation	**Age group**	**conversion factor (Sv/Bq)**
OMS	adults	2,2x10^{-7}
AIEA	2 – 7 years 7 – 12 years 12 – 17 years adults	6,2x10^{-7} 8x10^{-7} 1,5x10^{-6} 2,8x10^{-7}

Table 7.4 shows the annual effective dose due to radium, for different age groups, assuming a daily consumption of 1 l/day of mineral water, with more than 100 mBq/l radium-226 concentration. In calculating the annual effective dose only the 11 mineral waters of the studied ones were considered, for which the radium concentration was higher than 100 mBq/l. At the moment of doing the measurements this was the value recommended by World Health Organization (WHO), regarding the consumption of bottled mineral water (WHO, 1993).

This has been changed by the recent recommendations of WHO, where the suggested annual committed effective dose caused by water consumption is less than 0.1 mSv. The latter value is recommended by the European Union (Council Directive 98/83/EC, 1998). Using the dose conversion factors from the standards of the International Atomic Energy Agency (IAEA) this value means 489 mBq/l of – 226 radium for 2 l/day water consumption for adults. In the case of the age group 12–17 years, the value of 0.1 mSv results from 91 mBq/l radium concentration.

Different rates of mineral water consumption will determine proportionally different doses. In several countries the concentration of radium-226 contained in the drinking water is restricted to 100 mBq/l.

The ^{226}Ra average activity concentration measured in bottled mineral waters from Romania presented in this paper (155,7 mBq l^{-1}) is similar to that determined in bottled mineral waters from Argentina, 180 mBq/l (Bomben, A. M., 1996). Another study (Sanchez, AM, 1999) shows a concentration of radioactivity Ra-226 in 43 samples of bottled mineral waters consumed in France, Portugal and Spain ranging from 60 to 1.860 mBq/l. In the 35 samples of bottled mineral water analyzed in Brazil there were similar average activity concentrations of ^{226}Ra obtained, with an arithmetic mean of the activity ranging from 2.2 to 647 mBq/l (de Oliveira, J., 2001).

Considering the average value of the Ra-226 activity of 155.7 mBq/l in bottled mineral waters from Romania, its appropriate effective dose is 0.067 mSv/year. This value represents less than 2.8% of the average effective dose annually attributable to the natural background radiation for people in Romania. The collective dose due to the consumption of this water was evaluated to 66 manSv. For this calculation it was considered that the Romanian production of bottled mineral water is about 1.1x10^9 l/ year.

Table 7.4: The estimated effective dose for different age groups due to radium contained in a volume of 1 liter of bottled mineral water drunk in one day, the estimated dose using conversion factors of ingested dose IAEA (1995) and WHO (1993)

Water type	Annual effective dose (mSv)				
	IAEA (1995)				WHO (1993)
	Age group 2-7 years	Age group 7-12 years	Age group 12-17 years	Adults	Adults
Borsec	0.030	0.038	0.072	0.013	0.010
Tuşnad	0.026	0.034	0.064	0.011	0.009
Borşa	0.027	0.035	0.065	0.012	0.009
Steaua Nordului	0.030	0.038	0.071	0.013	0.01
Izvorul Minunilor	0.045	0.058	0.108	0.020	0.015
Bucovina	0.099	0.128	0.241	0.045	0.035

Biborţeni	0.041	0.054	0.101	0.018	0.014
Alpina Borşa	0.035	0.046	0.087	0.016	0.012
Briza Lipovei	0.100	0.129	0.242	0.045	0.035
Cezara	0.062	0.080	0.151	0.028	0.022
Aquatique	0.078	0.101	0.191	0.035	0.028

In recent years the consumption of mineral water in Romania has increased to a great extent. In the great majority (52%) of mineral water the ^{226}Ra concentration does not exceed the 100 mBq/l value.

The expected doses from consumption of mineral water in Romania are insignificant compared to other natural sources of radiation (such as radon in indoor air, K-40, etc.).

According to the results presented above, it is obvious that radium activity measured in mineral water does not pose any significant risk to people who consume this mineral water. The concentrations and the effective doses due to intake of ^{226}Ra in bottled mineral drinking water are similar to the results presented in the works published in other parts of the world (Kovacs, T., 2003; Amrani, D., 2002; Bettencourt, A.O., 1988).

In Hungary, in another study it was obtained the mean value of radium concentration of 185 mBq/l, in bottled mineral water and drinks obtained from these waters (Somlai, J.,, 2002). The purpose of these measurements was to determine whether mineral waters bottled in Hungary are below the recommended WHO limit. A controlled and limited consumption is proposed for the water with higher concentrations.

In Italy both the concentration of radium (41 mBq/l) and the dose of 21 of bottled mineral waters were determined, resulting an average dose of 0.26 × 10-2 mSv/year (Rusconi, R., 2004). Apart from determining the dose to which the population is exposed from the consumption of these water, the purpose of these measurements was also to find a correlation between the radium concentration and the chemical composition of water.

In Spain the radium activity was determined in most mineral water by alpha spectrometry, obtaining an average value of 180 mBq/l (Bayes, J.C., 1996). The equivalent dose obtained in this study does not exceed 5 mSv/year which is also the limit governed by the laws of Spain.

For a total of 43 types of mineral water from France, Portugal and Spain, the radium concentration measured by alpha spectrometry ranged between 0.06 Bq/L and 1.86 Bq/l and a mean dose of 9.5×10^{-2} mSv/year (Sanchez, A.M, 1999). This study led to the conclusion that there is a close connection between the radium content of water and the origin of water. The mineralization of this water occurs at great depths, which are also enriched with radium.

In Brazil, the radium concentration of 17 samples of bottled and sold mineral water had an average value of 63 mBq/l, with a maximum of 647 mBq/l, the estimated annual dose being of 1.3×10^{-2} mSv/year . The collective dose due to the consumption of mineral water was set at 90 man x Sv (de Oliveira, J., 2001).

In Argentina, an average value of 180 mBq/l for the radium concentration measured in most bottled mineral water, had an assessed collective dose of 1.4 man Sv and an effective dose of 0.4 μ Sv per year (Bomben, AM , 1996).

CONCLUSIONS

The principle of the secular equilibrium existing between nuclides of radium Ra-226 and radon Rn-222 present in water samples taken was considered in order to determine the concentration of radium in groundwater.

From the category of groundwater the water of the mine galleries in northern Transylvania, Romania, and the mineral waters bottled and sold all over Romania were selected for this study.

The Determination of radium Ra-226 concentrațion is based on the collection of radon, as the product of the radium decay present in the water samples, and its measurement by two ways, by scintillation, using different volumes of Lucas cell, 1000 ml and 145 ml.

When measuring radium in the water samples a method based on Lucas cells with useful volume of 1000 ml has been developed, where it was also used a set of 5 cells with efficiency between 66-87%, efficiency determined by placing in each Lucas cell a known amount of radon. The limit of detection for determination of the radon using the Lucas cell of 1 000 ml is 20 mBq/l. The measuring time was set to 100 seconds.

A method of measuring the radon in water based on dedicated equipment was perfected, used in several laboratories in the world (LUK 3A-VR) and is based on the Lucas cell technique with the net volume of 145 ml, and on achieving balance between the radon dissolved in water and the air above the water.

By recalibration of the system, the time required to measure a sample from 20 minutes to 5 minutes was reduced allowing the measurement of a greater number of samples in a reasonable time.

There were references made in the thesis about the measurements: the recalibration equipment, the recipient where the sample is taken, the transfer proof scrubber, the precision of the measurements, including the detection limit (50 mBq/l).

The Water samples were collected from the 19 mine galleries where the operating activity or the performance of some specific activities and conservation closure of a mine galleries had been suspended for several years so that the water to be as characteristic as possible to the natural state of these waters and this should not be influenced by inside human activities.

At the time of sampling there were treatment plant for water of the mine galleries in only two cases, the samples noted in the table of E8 and E15, stations built for reasons of increased concentrations of other chemicals in the water, not for the radioactive content ones. Almost any method used to mine wastewater with high content of hazardous chemicals will indirectly contribute to a decrease in the concentration of radium in the mine water discharged in rivers. In case of increasing concentrations of containing radioactive substances, in these treatment plants or those expected to be built in the future, we can apply a method of removing radioactive substances (radium, for example) in groundwater from galleries mine.

The lowest values of the measured radium concentration by the two methods, were found in mine water from Baia Sprie – Boului Gallery in Maramures County, both under the detection limit of used methods.

The highest values of radium concentration were 510 mBq/l for the 1000 ml Lucas cell method and 501 mBq/l for the 145 ml Lucas cell method. These values were determined for the mine water coming from Nistru - Gallery in Maramureș County.

The average measures of radium concentration by both methods are 138mBq/l for the 1000 ml Lucas cells method and 171 mBq/l for the 145 ml Lucas cells method.

In order to estimate population exposure to mineral water consumption the radium content of mineral waters was measured using Lucas cell method based on the volume of 145 ml and the dose due to ingestion of radium was calculated for 23 types of Romanian bottled mineral water.

In twelve cases the Ra-226 concentration is less than 100 mBq/l, and in the other eleven samples the Ra-226 concentration is more than 100 mBq/l. In all cases the Ra-226 concentration is less than 500 mBq/l. Of all the measured mineral waters only two measured values were under the detection limit of the measuring system, so the concentration of radium could not be specified for them.

The doses due to the radium received by the consumption of that mineral waters are comparable to those in other European countries and represent a minor contribution (2.8%) from the natural exposure to radiation (2.4 mSv/year) compared to the exposure to the indoor radon (1.3 mSv/year). The Collective dose is 66 manSv.

The radium concentrations values in the mine groundwater, measured by the two methods are comparable in order of magnitude with the radium concentrations measured values in the mineral waters in Romania, using the LUK – VR cells.

The results obtained in this study lead to the conclusion that the activity of radium present in the waters of the studied mine galleries, galleries currently closed and located in the northern part of Transylvania, Romania, does not pose a significant risk to the environment or the health of the persons using surface water where the mine water from the studied mining galleries are discharged.

The doses due to the radium present in mineral water consumption in Romania are insignificant compared to the natural sources of radiation (such as the radon in indoor air, K-40, etc.)

According to the results presented above, it follows that the radium activity measured in the studied mineral water does not pose a significant risk to the population who consume this mineral water. The concentrations and the effective doses due to the intake of Ra-226 content in the bottled mineral water are similar to the results presented in some papers published in other parts of the world.

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