

Geochemistry of Natural Radionuclides Associated with Acid Mine Drainage (AMD) in a Coal Mining Area in Southern Brazil

Juliana A. Galhardi, Daniel M. Bonotto

Abstract—Coal is an important non-renewable energy source of and can be associated with radioactive elements. In Figueira city, Paraná state, Brazil, it was recorded high uranium activity near the coal mine that supplies a local thermoelectric power plant. In this context, the radon activity (Rn-222, produced by the Ra-226 decay in the U-238 natural series) was evaluated in groundwater, river water and effluents produced from the acid mine drainage in the coal reject dumps. The samples were collected in August 2013 and in February 2014 and analyzed at LABIDRO (Laboratory of Isotope and Hydrochemistry), UNESP, Rio Claro city, Brazil, using an alpha spectrometer (AlphaGuard) adjusted to evaluate the mean radon activity concentration in five cycles of 10 minutes. No radon activity concentration above 100 Bq.L^{-1} , which was a previous critic value established by the World Health Organization. The average radon activity concentration in groundwater was higher than in surface water and in effluent samples, possibly due to the accumulation of uranium and radium in the aquifer layers that favors the radon trapping. The lower value in the river waters can indicate dilution and the intermediate value in the effluents may indicate radon absorption in the coal particles of the reject dumps. The results also indicate that the radon activities in the effluents increase with the sample acidification, possibly due to the higher radium leaching and the subsequent radon transport to the drainage flow. The water samples of Laranjinha River and Ribeirão das Pedras stream, which, respectively, supply Figueira city and receive the mining effluent, exhibited higher pH values upstream the mine, reflecting the acid mine drainage discharge. The radionuclides transport indicates the importance of monitoring their activity concentration in natural waters due to the risks that the radioactivity can represent to human health.

Keywords—Radon, radium, acid mine drainage, coal

I. INTRODUCTION

COAL is an important source of non-renewable energy and can be associated with radioactive elements [1]. According to [2], main environmental impacts associated with coal mining activity arise from the disposal of solid waste on the ground, giving rise to acid mine drainage (AMD) that leaches toxic metals to the soil and groundwater - including radioactive isotopes [3], this way increasing the human exposure to radioactivity.

J. A. Galhardi is with the Geosciences and Environment Graduated Program, Rio Claro, SP 13506-900 Brazil (phone: 55(19)981370898; e-mail: julianagalhardi@Yahoo.com.br).

D. M. Bonotto is with Department of Petrology and Metallogeny, UNESP-University of São Paulo State, Rio Claro, SP 13506-900 Brazil (e-mail: danielmarcosbonotto@gmail.com.br).

This investigation was performed under a financial support from CNPq.

In Brazil, coal represents the largest source of non-renewable fuel to electricity generation and the largest reserves take place in the states of Rio Grande do Sul, Santa Catarina and Paraná [2].

In the city of Figueira, state of Paraná, the coal exploitation supplies a local thermal power plant and is part of the largest coal reserve in the State, wherein the occurrence of uranium and thorium have been recorded with levels of 28 and 8 ppm, respectively [4].

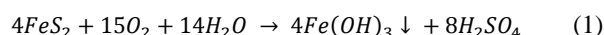
Coal from this region has high pyrite content, which is responsible for environmental problems in soil, water and air because of the AMD generation. In this context, the objective of this research was to promote an assessment of the ^{222}Rn (by ^{226}Ra decay in the ^{238}U natural series) and ^{226}Ra geochemical behavior associated with the AMD generation in a coal mine located at Figueira city, Paraná State, Brazil.

A. Radiochemical and Environmental Aspects Associated with Coal Mining

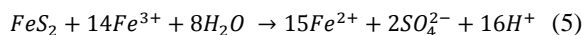
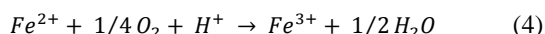
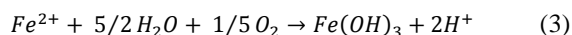
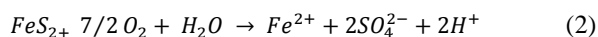
The main environmental impacts resulting from the coal mining and beneficiation come from the solid waste disposal that induce the AMD generation due to sulfides minerals oxidation and subsequent acid solution production. It accelerates the toxic metals leaching, allowing the dispersion of contaminants into the environment. Radiological impact can also occur, since the effluents may contain radionuclides which, once released in the environment, can cause severe damage to biota.

The main sulfide minerals occurring in bituminous coal are pyrite (FeS_2) and marcasite (FeS_2). Pyrrhotite (FeS), arsenopyrite (FeAsS), chalcopyrite (CuFeS_2) and other sulfide minerals containing Fe, Cu, As, Sb, Bi, Se and Mo can also produce acidic solutions, however, they are not common in coal horizons [5].

Iron ions and sulfate molecules predominating in the AMD are associated with jarosite, schwertmannite and iron hydroxides [6], but pyrite is the main responsible for the AMD generation. The overall reaction can be given as:



AMD solutions can exhibit pH below 3 and act as an effective metal leaching in the mining environment. The chemical and biochemical reactions that result in the acidic wastewater generation can be represented by this reaction sequence [7]:



At first, pyrite weathering reaction includes oxidation by oxygen (1). Sulfur is oxidized to sulfate and ferrous iron (Fe^{2+}) is released. Two moles of acidity (H^+) are generated for each mole of oxidized pyrite (2).

Metals are released during the early stages of pyrite oxidation and can be combined with alkaline materials, which are present in the host rock or tailings and can form metallic precipitates in the solution (3).

The next reaction is the iron hydrolysis with the generation of two moles of acidity. Part or almost all of the iron content in solution can precipitate as $Fe(OH)_3$ or related minerals. This precipitate is pH dependent: solids will be formed for $pH \geq 3.5$, whereas little or no solids will precipitate at $pH < 3.5$. Most of the dissolved iron in solution at pH 3.5 occurs as Fe^{2+} due to the relative Fe^{3+} insolubility.

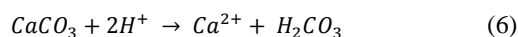
Once pH decreases, metal precipitates can return to solution if there is no alkalinity available in the tailings. This reaction consumes one mole of acid (4). Several species of sulfur and iron oxidizing bacteria increase the oxidation rate of ferrous iron to ferric iron. This reaction rate is pH dependent, with a slow speed under acidic conditions (pH 2-3) due to the bacteria unavailability, but it is several orders of magnitude faster at pH values around 5. This reaction usually determines the overall rate of the AMD generation.

The hydrolysis (3) hardly occurs at $pH \leq 2.3$. However, the third reactions step indicates that pyrite can oxidize (5) accompanying the Fe^{3+} concentration increase, where the ferric iron is the oxidizing agent. This step is cyclical and occurs quickly until the ferric iron or pyrite becomes exhausted.

The Fe^{+3} chemistry is governed by combined effects of the Fe^{2+} bacterial oxidation, Fe^{3+} reduction by pyrite and the complexes formation with iron sulfate and hydroxyl as the process proceeds and the solution pH decreases below 2.5. The reactions proceed to the sulfate depletion.

Carbonated minerals dissolution may also happen in addition to these reactions, consuming H^+ and neutralizing the acidity. If the water flowing in contact with pyrite is alkaline, the above described reactions can be inhibited so that little or no AMD is produced. On other hand, since the AMD is generated, its interaction with alkaline materials can neutralize the acidity and promote the iron, aluminum and other metals removal from solution. Therefore, water with high sulfate and low iron contents can indicate AMD previously generated and controlled along the time [5].

Calcite and dolomite are the main minerals providing alkalinity in surface water and groundwater, occurring near the coal horizons. An initial reaction with an acid solution can be described as:



One major environmental problem associated with coal mining is the radionuclides release into water, soil or atmosphere. The nuclear industry interest in finding uranium resources since the 1940s and 1950s has provided several studies on coal deposits. All fossil fuels contain natural levels of radionuclides and their decay products or precursors. Coals contain an approximate range of 12 to 24 $Bq.Kg^{-1}$ of ^{238}U and 12 to 17 $Bq.Kg^{-1}$ of ^{232}Th [8]. According to [9], medium activity concentrations of ^{40}K , ^{238}U and ^{232}Th in coal are 50, 20 and 20 $Bq.Kg^{-1}$, respectively, based on coal analysis performed in 15 countries.

It was found in coal from Rio Bonito Formation in Figueira city concentrations ranging from 813 to 2,609 $Bq.Kg^{-1}$ for ^{238}U and from 22 to 40 $Bq.Kg^{-1}$ for ^{232}Th . They concluded that the coal combustion in the fuel increases the natural radionuclides concentration in particulate matter by a factor of 5 to 10 times [8]. The ash produced in the thermal plant in the same city exhibited high ^{238}U , ^{226}Ra and ^{210}Pb activity concentration, reporting in topsoil (0-2 cm) these values: $^{238}U = 36-138 Bq.kg^{-1}$; $^{226}Ra = 35.2-122 Bq.kg^{-1}$; $^{210}Pb = 52.4 Bq.kg^{-1}$; $^{40}K = 120-563 Bq.kg^{-1}$ [10].

One of the most problematic radionuclide is radon gas, that can accumulate in the ground waters or in underground mine environment. Radon (^{222}Rn , half-life 3.8 days) is a naturally occurring volatile noble gas formed from the normal radioactive decay series of ^{238}U . Radon (^{222}Rn , half-life 3.8 days) is a naturally occurring volatile noble gas formed from the ^{238}U radioactive decay series. It is colorless, odorless, tasteless, chemically inert and radioactive gas produced continuously in rocks and soils through ^{226}Ra α -decay, with some atoms escaping to the surrounding fluid phase, such as groundwater and air.

^{222}Rn decays to stable lead according to the sequence: ^{222}Rn (3.83 d, α) \rightarrow ^{218}Po (3.05 min, α) \rightarrow ^{214}Pb (26.8 min, β) \rightarrow ^{214}Bi (19.7 min, β) \rightarrow ^{214}Po (0.16 ms, α) \rightarrow ^{210}Pb (22.3 a, β) \rightarrow ^{210}Bi (5 d, β) \rightarrow ^{210}Po (138.4 d, α) \rightarrow ^{206}Pb .

Radium is a radioactive and alkaline metal that occurs naturally in the Earth's crust and is found in minerals and rocks that have uranium and thorium in its composition, whereby can be transferred to the air, water and soil by weathering processes. When incorporated into blood by absorption from the gastrointestinal or respiratory tract lungs, the isotopes ^{228}Ra (half-life of 5.75 years) and ^{226}Ra (half-life of 1,622 years) exhibit a similar behavior to calcium [11]. More than 70% of ^{226}Ra can be fixed in bones, whereas the remainder fraction is evenly distributed on soft tissues [9].

The immediate decay product of ^{226}Ra is the noble gas ^{222}Rn , an alpha emitter whose activity in groundwater is generally high, resulting in a high mobility and transfer rate from the aquifer matrix to the water, if it is not readily lost to decay from non-retentive materials [11].

However, in minerals or in solid particles dissolved in water, the ^{222}Rn may not escape before decay, generating a chain of short lived daughter nuclides. ^{222}Rn is considered the most important radon isotope responsible for the radioactivity

in water due to its longer half-life (3.8 days) compared to other radon isotopes.

In fact, the ^{222}Rn proportion in groundwater depends on the presence of ^{226}Ra , its parent in the ^{238}U radioactive decay series with which it comes into radioactive equilibrium in about 25.6 days. Once inhaled, radon can be retained in the lungs in the form of its decay products, ^{210}Pb and ^{210}Po , increasing the risk of lung cancer occurrence. When ingested, radon is transported from the digestive system into the blood, eventually to the bloodstream through the lungs, from which a large portion is exhaled [12]. High concentrations of ^{222}Rn in water indicate the presence of their parents, ^{238}U and ^{226}Ra , in the water-rock system, which may also represent severe risks to human health.

Many countries adopted the standard quality on the radionuclide activity recommended by the World Health Organization [13], which is equivalent to the activity concentrations of 0.5 Bq.L^{-1} for alpha activity and 1 Bq.L^{-1} for beta activity. Maximum permitted levels of radioactivity are also established for some radionuclides present in water for human consumption, in which, for ^{226}Ra , the limit is 1 Bq.L^{-1} and for ^{222}Rn , it was proposed that the radiological control should be implemented if its concentration exceed 100 Bq.L^{-1} [14]. The World Health Organization revised the guideline for the radon activity concentration in waters for human supply. In this case, according to [13], it is more appropriated to measure the radon in the air wherein the reference level for radon concentration in indoor air is 100 Bq/m^3 in dwellings.

Mining is the most common industrial activity associated with radon exposure, as it occurs in crushing and processing plant, in which fine particles of metals and other elements, including radioactive, are produced after physical and chemical processes. The waste originated from these activities is generally disposed on the ground, giving rise to metals and toxic elements leaching, including the radon emission.

The coal burning for electricity generation is another important way of releasing radionuclides to the environment. In thermal power plants, coal burning is carried out in furnaces in $1,700^\circ\text{C}$ and, depending on the emission control system, a proportion of fly ash and gases are released into the atmosphere, carrying on together toxic elements.

It was reported that, in general, the coal burning for supplying one gigawatt can cause the release of ashes and gases containing about $109\text{-}1011 \text{ Bq.y}^{-1}$ of both ^{220}Rn and ^{222}Rn [15]. It has been also found high radon levels in air in the coal mine at Figueira city [16] but, until now, no radon data in waters have been reported.

II. STUDIED AREA

Figueira city is located in the northeast of Paraná State, Brazil (Fig. 1).

The studied area is located in Paraná sedimentary basin, an intracratonic basin evolved along the South American Platform and deposited on the Crystalline Basement, gathering a set of rocks older than 650 Ma [17].

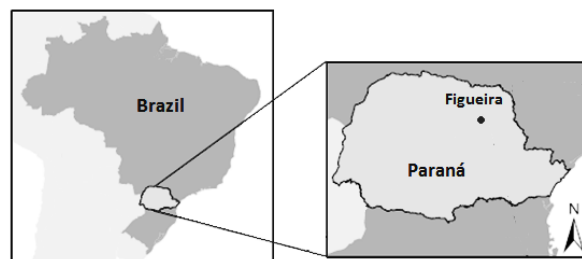


Fig. 1 Location of Figueira city in Brazil

The Paraná basin covers an area of approximately $1,600,000 \text{ km}^2$ over the states of Mato Grosso, Mato Grosso do Sul, Goiás, São Paulo, Paraná, Santa Catarina and Rio Grande do Sul, in Brazil, and territories of Argentina, Uruguay, and Paraguay.

It was proposed that Paraná Basin stratigraphy is given by six super-sequences: Rio Ivaí (Ordovician-Silurian), Paraná (Devonian), Gondwana I (Carboniferous-Eotriassic), Gondwana II (Meso-Neotriassic), Gondwana III (Neo-Jurassic-Early Cretaceous) and Bauru (Late Cretaceous) [18], [19].

The regional geology of the investigated area is related to the Gondwana I Supersequence, whose outcropping stratigraphic units of Permian age belong to the Itararé Group, Guatá Subgroup (Rio Bonito and Palermo formations) and Passa Dois Group (Irati, Serra Alta and Teresina formations) [20], [21]. Diabase dikes of Serra Geral Formation also occur in the area.

The coal in the studied area is at Rio Bonito formation (Fig. 2 (a)) and is constituted by plant debris and reworked material concentrated by marine agents [22]. The coal horizon thickness varies between 0.50 and 0.65 m and its occurrence depth is variable (38-75 m) [23]. Previous analysis indicate humidity = 6%; volatile matter = 28.8%; carbon = 32.5%; ash content = 38.7%; sulfur content = 4-12%; calorific power = $4300 \text{ kcal.kg}^{-1}$. Such composition classifies it as bituminous coal [20].

The solid wastes generated in the beneficiation process are disposed in two tailings pile (Fig. 2 (b)). The material aggregate waste has been produced over the last 50 years. Calcium carbonate has been added in the tailings during the disposal of this material in order to neutralize the acidity generated in the reject dumps (Fig. 2 (c)). The acid effluent is drained to a tank where, after a period of time, it returns to the industrial process (Fig. 2 (d)).

III. MATERIAL AND METHODS

The samples in this study were collected in August 2013 (monthly rainfall = 1.1 mm) and February 2014 (monthly rainfall = 341.6 mm) in order to allow the results comparison in different climatic conditions. Groundwater, river water and acid effluent samples were collected and preserved in polyethylene bottles for major cations and anions analysis and in amber glass flask for radon and radium analysis.



Fig. 2 Outcrop of coal in Rio Bonito Formation in Figueira, outside the mine site a); Coal reject dump and sedimentation pond b); Coal reject dump with CaCO₃ addition c) and Effluent generated from the coal rejects d)

Analysis of dissolved oxygen (DO), temperature (T) and pH were performed *in situ* using portable devices. Once collected, samples were sent to LABIDRO - Laboratory of Isotopes and Hydrochemistry of the Department of Petrology and Metallogeny of the Institute of Geosciences and Exact Sciences, UNESP, Rio Claro. Chemical analysis was performed using a Hach spectrophotometer Model DR 2000 [24].

The technique used to quantify ²²²Rn and ²²⁶Ra was alpha spectrometry with an Alpha Guard PQ2000PRO (Genitron GmbH) device equipped with an appropriate drive (Aquakit) [25]. The spectrometer consists in an ionization chamber that measures radon in a system consisting of two glass containers where the radon degassing contained in the sample occurs. Indoors, the samples were monitored by Alpha Guard in five cycles of 10 min. The determination of the radon concentration in water samples was done by:

$$1000 c_w = c_a \left[k + \left(\frac{V_{SY} - V_{SA}}{V_{SA}} \right) \right] - C_0 \quad (7)$$

where: c_w = radon concentration in water (Bq.L⁻¹); c_a = measured value (Bq/m³); C_0 = zero level (0 Bq/m³); V_{SY} = system volume (1122 mL); V_{SA} = water sample volume (100 mL); k = Radon distribution coefficient between air and liquid phase (0.16).

The radon decay between collection and analysis has been also corrected by:

$$C_{wr} = C_w \times e^{D.t} \quad (8)$$

where: C_{wr} = corrected radon concentration (Bq.L⁻¹); C_w = radon concentration measured in the water sample (Bq.L⁻¹); D = radon decay constant; t = time elapsed between sampling and analysis.

A period of 25 days is needed for ²²²Rn to reach radioactive equilibrium with ²²⁶Ra. After this time, the same procedure was used for ²²⁶Ra analysis by alpha counting. For cleaning purposes, the Alpha Guard system was coupled to an activated charcoal filter to remove the radon of the system, after processing each sample.

Groundwater (P1-P8) and effluent samples (E1, E2) were collected in the coal mining area, whereas the samples from Ribeirão das Pedras stream (RP1, RP2) and Laranjinha River

(L1, L2) were collected near the coal mine, upstream and downstream of the area.

IV. RESULTS AND DISCUSSION

The results obtained are shown in Tables I-IV. Tables II and IV indicate that there is none radon activity concentration above 100 Bq.L⁻¹ (Table II) as previously proposed by WHO (2008). In the first sampling period (August 2013), the groundwater exhibited an average radon activity concentration of 10.39 ± 1.38 Bq.L⁻¹, whereas for radium it was 0.22 ± 0.09 Bq.L⁻¹. The river water exhibited radon and radium activity concentration of 0.96 ± 0.35 Bq.L⁻¹ and 0.23 ± 0.09 Bq.L⁻¹, respectively. The effluents exhibited mean radon and radium activity concentration of 3.50 ± 0.82 Bq.L⁻¹ and 0.17 ± 0.08 Bq.L⁻¹, respectively.

The major cations and anions in Tables I and II indicate for groundwater a predominance of bicarbonated, sulfated or chlorinated sodic waters. Waters from both Ribeirão das Pedras stream and Laranjinha River can be classified as bicarbonated sodic. The same classification was verified in the second sampling period (February 2014).

The iron and aluminum concentration was higher in E2 (with CaCO₃ addition) than in E1 (without CaCO₃ addition as a pH control). Although no carbonate was added to the pH control in E1, it may be expected a lower AMD generation and metals leaching as it is an older pile.

The samples P3, P4, P5 and E2 exhibited high levels of dissolved iron and sulfate and a low pH value, indicating AMD generation in a higher scale than in the other samples. In the case of the groundwater samples, it also indicates generation and percolation of acid effluents into the aquifer.

The samples P2, P6, P7 and P8 exhibited high sulfate values and low iron content, indicating that AMD was generated, despite its control in the present days.

The samples collected downstream the mine (RP1 and L2) exhibited lower pH and higher dissolved sodium, potassium, magnesium, aluminum, sulfate and phosphate content than in the samples collected upstream the mine, maybe due to the effluent discharge closer to the river.

The temperature exhibited significant correlation with conductivity (0.79), dissolved oxygen (-0.87), sodium (0.89), calcium (0.84), magnesium (0.89) and bicarbonate (0.91). Sodium showed significant correlation with potassium (0.72), calcium (0.98), magnesium (0.99) and bicarbonate (0.98).

Bicarbonate exhibited significant correlation with calcium (0.98) and magnesium (0.99). These relationships can be associated with weathering processes and elements and compounds dissolution/leaching by water that is catalyzed by the temperature increase and pH decrease.

TABLE I
PHYSICAL-CHEMICAL PARAMETERS AND MAIN DISSOLVED CATIONS MEASURED IN THE SAMPLES COLLECTED IN AUGUST 2013

Sample	T (°C)	Suspended solids (mg.L ⁻¹)	pH	Na ⁺ (mg.L ⁻¹)	K ⁺ (mg.L ⁻¹)	Ca ²⁺ (mg.L ⁻¹)	Mg ²⁺ (mg.L ⁻¹)	Ba ²⁺ (mg.L ⁻¹)	Al ³⁺ (mg.L ⁻¹)	Fe ²⁺ (mg.L ⁻¹)	Fe ³⁺ (mg.L ⁻¹)	Si ²⁺ (mg.L ⁻¹)
P1	20.50	63.00	5.34	4.39	0.8	11.28	2.0	1.5	1.3	0.01	3.0	19.6
P2	20.70	3239.00	3.71	127.0	11.7	8.0	4.32	4.5	2080.0	4.2	6.1	15.5
P3	20.70	2097.00	3.80	17.5	0.74	2.0	0.38	52.5	1067.0	18.0	566.0	105.6
P4	21.50	993.00	2.94	54.6	10.0	1.0	5.0	285.0	2542.0	22.4	988.0	0.00
P5	20.30	431.00	3.21	22.8	41.0	26.16	2.0	117.0	44.85	3.5	131.0	0.7
P6	22.50	1364.00	4.03	35.22	2.32	1.0	1.42	4.0	1090.0	1.84	20.3	21.3
P7	21.20	53.40	3.72	103.0	16.1	33.2	2.0	3.0	4.0	0.01	1.45	18.3
P8	24.90	373.00	6.04	859.0	49.7	196.0	1400.0	45.0	1.3	0.05	2.75	1.7
RP1	17.10	12.00	6.95	9.74	2.7	2.0	3.28	3.0	1.3	0.01	0.01	17.6
RP2	16.50	2.00	7.26	5.1	2.66	2.0	3.04	4.7	0.96	0.01	0.14	14.6
L1	18.50	19.00	7.04	3.07	2.24	1.0	0.24	2.0	12.5	0.01	0.3	12.7
L2	17.30	86.00	6.88	3.21	2.26	10.0	4.6	1.5	0.07	0.0	0.35	11.9
E1	26.10	292.00	6.24	144.0	26.0	1.0	1.36	5.0	1.0	0.02	21.98	11.9
E2	27.85	259.00	4.01	96.10	28.50	38.00	1.00	120.0	1317.50	26.00	2824.00	0.00

TABLE II
MAIN DISSOLVED ANIONS AND RADIONUCLIDES ACTIVITY CONCENTRATION MEASURED IN THE SAMPLES COLLECTED IN AUGUST 2013

Sample	Cl ⁻ (mg.L ⁻¹)	HCO ₃ ⁻ (mg.L ⁻¹)	SO ₄ ²⁻ (mg.L ⁻¹)	NO ₃ ⁻ (mg.L ⁻¹)	PO ₄ ³⁻ (mg.L ⁻¹)	²²² Rn (Bq.L ⁻¹)	²²⁶ Ra (Bq.L ⁻¹)
P1	1.3	50.0	4.0	1.5	4.0	44.73 ± 3.23	0.31 ± 0.13
P2	2.1	25.0	7875.0	5.0	1.2	1.22 ± 0.72	0.12 ± 0.06
P3	1.6	20.0	4521.0	64.0	5.2	1.73 ± 0.89	0.37 ± 0.13
P4	6.2	30.3	12375.0	580.0	0.4	4.06 ± 0.89	0.15 ± 0.08
P5	0.9	15.0	1250.0	82.0	0.4	7.85 ± 1.21	0.2 ± 0.09
P6	1.4	70.0	3980.0	2.5	0.4	12.67 ± 1.62	0.18 ± 0.08
P7	2.1	15.0	200.0	1.5	0.8	9.59 ± 1.87	0.12 ± 0.07
P8	3.0	860.0	11250.0	1.5	0.0	1.26 ± 0.62	0.3 ± 0.11
RP1	1.8	18.0	33.0	1.5	1.6	0.8 ± 0.26	0.23 ± 0.09
RP2	3.7	29.0	6.0	2.0	0.4	1.37 ± 0.42	0.22 ± 0.09
L1	1.5	42.0	14.0	2.5	0.2	0.84 ± 0.42	0.14 ± 0.07
L2	1.8	22.0	16.0	2.5	0.4	0.83 ± 0.31	0.31 ± 0.11
E1	0.2	4.0	4900.0	0.3	0.08	2.24 ± 0.66	0.18 ± 0.08
E2	2.25	1.0	9500.0	54.0	0.03	4.06 ± 0.9	0.15 ± 0.08

TABLE III
PHYSICAL-CHEMICAL PARAMETERS AND MAIN DISSOLVED CATIONS MEASURED IN THE SAMPLES COLLECTED IN FEBRUARY 2014

Sample	T (°C)	Suspended solids (mg.L ⁻¹)	pH	Na ⁺ (mg.L ⁻¹)	K ⁺ (mg.L ⁻¹)	Ca ²⁺ (mg.L ⁻¹)	Mg ²⁺ (mg.L ⁻¹)	Ba ²⁺ (mg.L ⁻¹)	Al ³⁺ (mg.L ⁻¹)	Fe ²⁺ (mg.L ⁻¹)	Fe ³⁺ (mg.L ⁻¹)	Si ²⁺ (mg.L ⁻¹)
P1	25.2	786.0	5.45	2.21	0.92	2.8	1.0	4.5	0.1	0.02	0.27	19.0
P2	23.7	1519.0	5.59	22.9	17.8	1.0	15.4	3.0	0.01	0.02	0.05	18.7
P3	24.5	1540.0	4.1	15.0	3.6	16.0	12.0	3.0	0.2	0.2	1.0	15.0
P4	24.3	1951.0	3.25	135.0	5.7	28.0	80.0	0.0	4100.0	910.0	520.0	60.0
P5	24.2	7435.0	4.46	24.3	25.2	240.0	100.0	120.0	80.0	72.0	116.0	21.1
P6	26.4	519.0	4.5	27.0	4.6	10.0	6.0	4.5	0.2	2.0	7.0	8.0
P7	23.3	29.0	3.9	89.0	3.2	6.0	6.0	3.0	0.1	3.0	4.0	6.0
P8	25.00	280.0	6.63	1009.0	36.4	0.4	0.2	1.5	0.0	28.0	57.0	5.8
RP1	25.00	52.0	6.4	14.2	6.92	0.6	1.2	3.0	0.04	0.01	0.16	14.8
RP2	25.7	22.0	7.38	13.6	8.4	22.0	7.0	1.5	0.0	0.01	0.38	17.3
L1	26.7	5.0	7.59	3.97	3.16	11.6	4.0	4.5	0.1	0.01	0.41	15.9
L2	26.5	49.0	6.6	4.19	3.44	12.0	2.02	1.5	0.14	0.01	0.4	16.2
E1	26.4	175.0	4.3	304.0	34.5	720.0	1240.0	120.0	1132.0	1300.0	790.0	3.1
E2	28.3	51.0	5.91	174.0	79.2	1.0	198.0	4.5	54.0	39.8	330.2	10.9

TABLE IV
MAIN DISSOLVED ANIONS AND RADIONUCLIDES ACTIVITY CONCENTRATION MEASURED IN THE SAMPLES COLLECTED IN FEBRUARY 2014

Sample	Cl ⁻ (mg.L ⁻¹)	HCO ₃ ⁻ (mg.L ⁻¹)	SO ₄ ²⁻ (mg.L ⁻¹)	NO ₃ ⁻ (mg.L ⁻¹)	PO ₄ ³⁻ (mg.L ⁻¹)	²²² Rn (Bq.L ⁻¹)	²²⁶ Ra (Bq.L ⁻¹)
P1	10.8	20.0	1.5	1.8	0.2	41.15 ± 3.27	0.20 ± 0.1
P2	2.1	30.0	607.5	2.0	0.4	0.89 ± 0.41	0.19 ± 0.1
P3	7.8	15.0	175.0	1.0	2.0	1.58 ± 0.81	0.41 ± 0.14
P4	17.7	0.00	14400.0	0.00	0.2	3.94 ± 1.05	0.28 ± 0.12
P5	14.1	0.00	1550.0	28.5	0.4	8.56 ± 1.28	0.37 ± 0.15
P6	6.9	15.0	360.0	1.0	4.0	17.76 ± 2.02	0.43 ± 0.17
P7	4.5	10.0	320.0	0.5	3.0	5.68 ± 1.11	0.61 ± 0.23
P8	3.6	420.0	8300.0	0.00	0.4	0.7 ± 0.12	0.28 ± 0.12
RP1	0.00	30.0	46.0	2.5	0.2	0.78 ± 0.31	0.25 ± 0.13
RP2	4.8	60.0	30.0	2.5	0.4	0.82 ± 0.28	0.21 ± 0.11
L1	3.9	75.0	3.0	2.5	0.2	0.56 ± 0.4	0.24 ± 0.12
L2	4.8	70.0	12.0	3.5	0.8	0.43 ± 0.21	0.12 ± 0.09
E1	7.2	5.0	14700.0	160.0	0.2	8.92 ± 1.48	0.22 ± 0.11
E2	1.8	3.0	3400.0	5.0	0.2	5.43 ± 1.61	0.45 ± 0.17

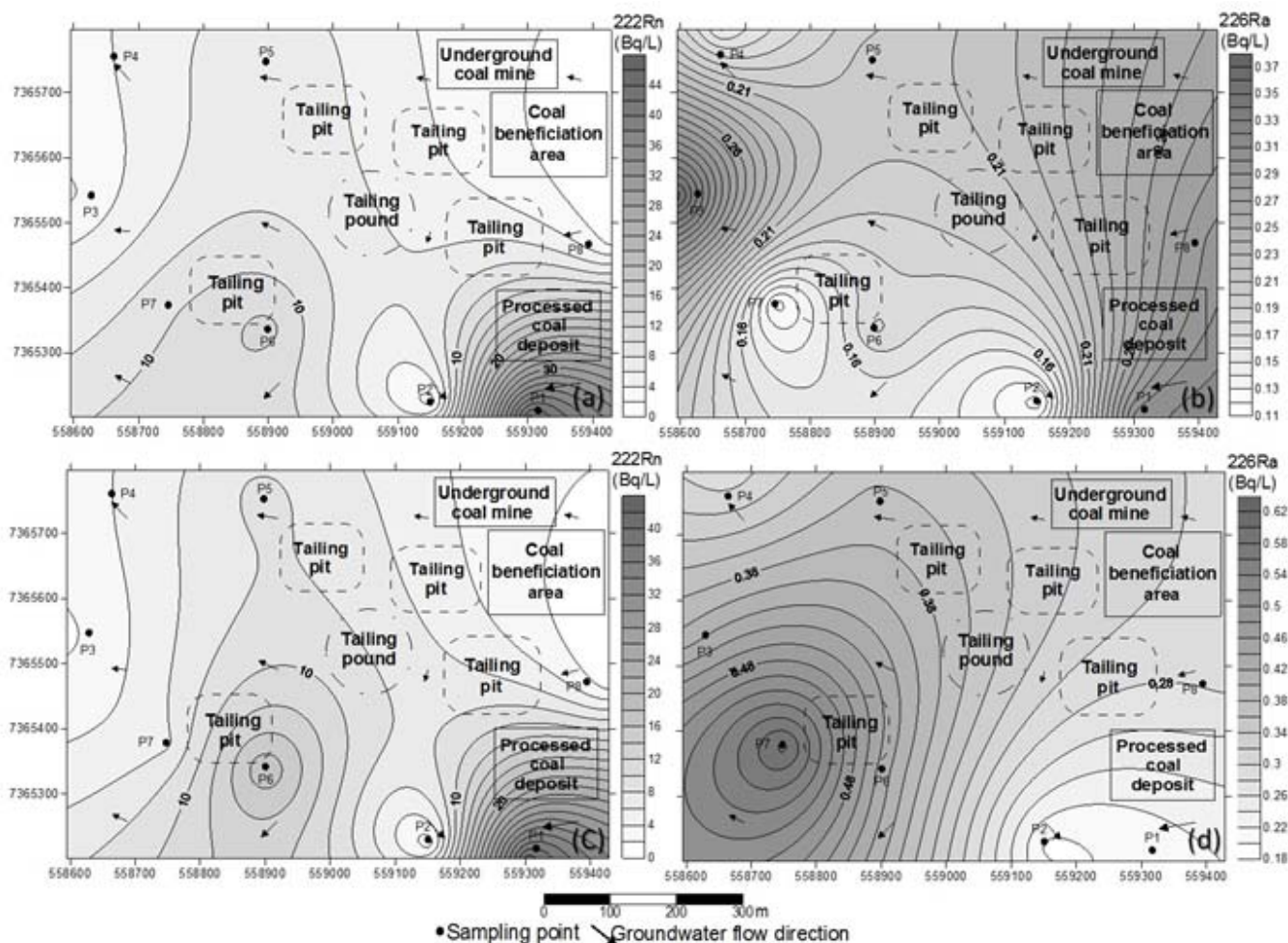


Fig. 3 ²²²Rn activity concentration distribution (August 2013) (a); ²²⁶Ra activity concentration distribution (August 2013) (b); ²²²Rn activity concentration distribution (February 2014) (c) and ²²⁶Ra activity concentration distribution in the studied area (February 2014) (d)

Chemical and radiochemical parameters analyzed in February 2014 are shown in Tables III and IV. In this rainy month, the mean radon and radium activity concentration in groundwater was 10.03 ± 1.23 Bq.L⁻¹ and 0.35 ± 0.14 Bq.L⁻¹, respectively; in river water, it was 0.65 ± 0.30 Bq.L⁻¹ and 0.21

± 0.11 Bq.L⁻¹, respectively; in the effluents, it was 17.67 ± 2.15 Bq.L⁻¹ and 0.46 ± 0.17 Bq.L⁻¹, respectively.

Radon exhibited lower value for groundwater and river water samples in the rainy than in the dry month, probably due to the higher dilution rate. The opposite relation was verified

in the case of the effluents, maybe due to the higher leaching rate in the reject dumps that mobilized more radon and radium atoms.

Radium exhibited significant correlation with suspended solids (0.96). The pH showed significant correlation with silica (-0.92) and chloride (-0.89). Suspended solids correlated with calcium (0.99), barium (0.97), and nitrate (0.97). Calcium correlated with conductivity (0.99), barium (0.99), and nitrate (0.99). Aluminum correlated with ferrous iron (0.99), ferric iron (0.98), and silica (0.96). These relationships can also be associated with the elements and compounds leaching during the interactions of rainwater, river water and groundwater with the rocks soils, and solid wastes occurring in the area.

Samples P2, P3, P6 and P7 exhibited high sulfate values and low iron concentration, possibly indicating an AMD neutralization. The opposite was verified in the case of the samples P4, P5 and P8.

Fig. 3 illustrates the ^{222}Rn (Fig. 3 (a)) and ^{226}Ra (Fig. 3 (b)) distribution in groundwater in August 2013 and the ^{222}Rn (Fig. 3 (c)) and ^{226}Ra (Fig. 3 (d)) distribution in February 2014, whereby it may be concluded that the groundwater flow contributes to the radon and radium transport, as the activity concentration of these radionuclides exhibited elevated values in areas where the groundwater movement direction is preferred (next to P1 and P3).

In both sampling periods, the pH was below 4 for most of the samples. The concentrations of iron and aluminum, as well as sulfate, were quite high in several monitoring points in both months sampling, reflecting that the acid waste generation is occurring, where the percolation of these effluents can be reaching the aquifer and water resources.

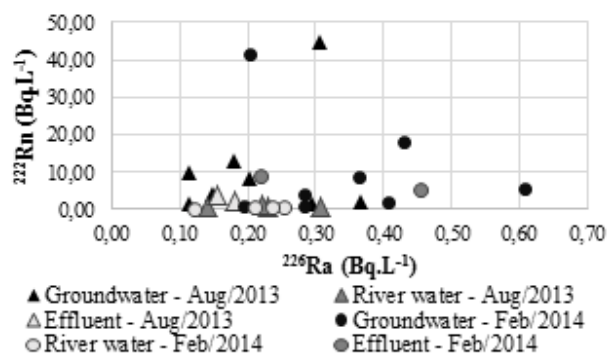


Fig. 4 ^{222}Rn versus ^{226}Ra for the total samples

There is no significant correlation between the radon and radium activity concentration in both sampling periods. In both months, it was not verified a large difference between the radon and radium levels, as illustrated in Fig. 4.

The average radon activity concentration in groundwater was higher than in river water and the effluents, possibly due to the uranium and radium accumulation in the aquifer layers that favors the radon trapping. The lower values in the river water samples can indicate dilution and the intermediate value in the effluents may indicate the occurrence of radon absorption in the coal particles of the reject dumps. The results

also indicate that the radon activities in the effluents increase with the sample acidification, possibly due to the higher radium leaching and the subsequent radon transport through the drainage flow.

Waters of Laranjinha River, which supplies the city, and Ribeirão das Pedras stream, its tributary that receives the mining effluent, exhibited higher pH values upstream the mine, reflecting the acid mine drainage discharge. The radionuclides transport indicates the importance of monitoring their activity concentration in natural waters due to the risks that the radioactivity can represent to the human health.

V.FINAL CONSIDERATIONS

Radon is a critic radionuclide in terms of health damage. Its monitoring is important not only in the atmosphere of closed environments but also the investigation of its activity concentration acquires importance in terms of water used for human supply. The radionuclides transport in natural waters verified in this research indicates the importance of monitoring their activity concentration in natural waters due to the risks that the radioactivity can represent to the human health. In the case of a coal mining area, the AMD generation and the rate of the acidity released to the solutions which can be in contact with natural waters is also a critic aspect of radiochemical contamination. It became also important the monitoring of the AMD generation seasonally, as well as to adopt control measures to avoid the generation of acids waste.

REFERENCES

- [1] F. A. Balogun, C. E. Mokobiab, M. K Fasasia and F. O. Ogundarec, "Natural radioactivity associated with bituminous coal mining in Nigeria", *Nuclear Instruments and Methods in Physics Research*, vol. 505, pp. 444-448, 2003.
- [2] D. A. Fungaro and J. C. Izidoro, "Remediação da drenagem ácida de mina usando zeólitas sintetizadas a partir de cinzas leves de carvão", *Quim. Nova*, vol. 29, no. 4, p. 735-740, 2006.
- [3] United States Environmental Protection Agency (USEPA), "Office of Solid Waste: Human health and environmental damages from mining and mineral processing wastes", USEPA: Washington, 1995.
- [4] H. M. Fernandes, M. A. Pires do Rio, L. H. S. Veiga and E. C. S. Amaral, "Environmental radiological problems associated to non-uranium mining and milling industries", in *4º Encontro Brasileiro sobre Aplicações Nucleares*. Poços de Caldas, 1997.
- [5] G. H. Berghorn and G. R. Hunzeker, "Passive Treatment Alternatives for Remediating Abandoned Mine Drainage", *Remediation Journal*, vol. 11, no. 3, pp. 111-127, 2001.
- [6] T. Arnold, N. Baumann, E. Krawczyk-Bärsch, S. Brockmann, U. Zimmermann, U. Jenk and S. Weib, "Identification of the uranium speciation in an underground acid mine drainage environment", *Geochimica et Cosmochimica Acta*, vol. 75, pp. 2200-2212, 2011.
- [7] A. Al-Hashimi, G. J. Evans and B. Cox, "Aspects of the permanent storage of uranium tailings", *Water, Air, and Soil Pollution*, vol. 88, pp. 83-92, 1996.
- [8] M. Flues, I. M. C. Camargo, P. S.C. Silva and B. P. Mazzilli, "Radioactivity of coal and ashes from Figueira coal power plant in Brazil", *Journal of Radioanalytical and Nuclear Chemistry*, vol. 270, no.3, pp. 597-602, 2006.
- [9] United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR), "Sources, Effects and Risks of Ionizing Radiation", United Nation: New York, 1988.
- [10] V. P. Campaner, "Dispersão geoquímica elementar e isotópica na atmosfera e no solo em área com atividade minerária e termoelétrica a carvão", Universidade Estadual de Campinas: Campinas, 2013.
- [11] International Atomic Energy Agency (IAEA), "The environmental behavior of radium", IAEA: Vienna, 1990.

- [12] United States Environmental Protection Agency (USEPA), “*Radon in drinking water health risk reduction and cost analysis*”, USEPA: Washington, 1999.
- [13] World Health Organization (WHO), “*Guidelines for drinking water quality*”, 4th ed., WHO Press: Geneva, 2011.
- [14] World Health Organization (WHO), “*Guidelines for drinking water quality*”, 3rd ed., WHO Press: Geneva, 2006.
- [15] M. S. Baxter, “Environmental radioactivity: a perspective on industrial contributions”. IAEA Bulletin, v. 35, n. 2, p. 33–38, 1993.
- [16] L. H. S. Veiga, V. Melo, S. Koifman and E. C. S. Amaral, “High radon exposure in a Brazilian underground coal mine”, *J. Radiol. Prot.*, vol. 24, pp. 295–305, 2004.
- [17] M. A. Iritani and S. Ezaki, “*As águas subterrâneas do Estado de São Paulo*”, Secretaria do Estado de Meio Ambiente: São Paulo, 2008.
- [18] E. J. Milani, “*Evolução tectono-estratigráfica da Bacia do Paraná e seu relacionamento com a geodinâmica fanerozóica do Gondwana Sul-Occidental*”, Universidade Federal do Rio Grande do Sul: Porto Alegre, 1997.
- [19] E. J. Milani, J. H. G. Melo, P. A. Souza, L. A. Fernandes and A. B. Franca, “Bacia do Paraná”, *Boletim Geociências da Petrobrás*, vol. 15, no. 2, pp. 265-287, 2007.
- [20] M. S. S. Shuqair, “*Estudo da contaminação do solo e água subterrânea por elementos tóxicos originados dos rejeitos das minas de carvão de Figueira no Estado do Paraná*”, Universidade de São Paulo, IPEN: São Paulo, 2002.
- [21] L. A. Bizzi, C. Schobbenhaus, R. M. Vidotti and J. H. Gonçalves, “*Geologia, Tectônica e Recursos Minerais do Brasil*”, CPRM: Brasília, 2003.
- [22] A. A. Zacharias and M. L. Assine, “Modelo de preenchimento de vales incisivos por associações de fácies estuarinas, Formação Rio Bonito no Norte do Estado do Paraná”, *Revista Brasileira de Geociências*, vol. 35, no. 4, pp. 573-583, 2005.
- [23] Agência Nacional de Energia Elétrica (ANEEL), “*A Situação da Produção de Carvão Mineral no Estado do Paraná em Relação a Nota Técnica 034/2011*”. ANEEL, Curitiba, 2011.
- [24] HACH, “*Water Analysis Handbook*”, Ed. Hach Company: Colorado, 1992.
- [25] Genitron, “*Alpha Guard PQ2000/MC50 - Multiparameter Radon Monitor*”, Genitron Instruments: Frankfurt, 2000.