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Influence of Phosphogypsum Stacks on the Distribution of Natural Radionuclides in Surface and Subsurface Waters in the City of Imbituba, SC, Brazil

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Abstract This study aimed to chemically and radiologically characterize the water resources influenced by a phosphogypsum stack in Imbituba, SC, Brazil and to identify the annual intake by ingestion. Surface water was collected at six points downstream of the phosphogypsum stack. Subsurface water samples were collected from a piezometer in the stack area. These samples were analyzed using a radiochemical method to determine the natural radionuclide content and an inductively coupled plasma optical emission spectrometry to determine the concentration of selected metals. The concentrations of radionuclides were also compared with current standards. The radionuclide concentrations in the surface waters samples were lower or similar to those found in other studies. The effective dose resulting from water ingestion is below the recommended reference levels for drinking water. Samples collected exhibited no increase in radioactivity, under the influence of phosphogypsum stacks.

Keywords Radiochemical method · ICP-OES · Intake by ingestion

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1 Introduction

The industrialization process in Brazil that has occurred over the last few decades has had a notable impact on coastal areas, resulting in intense contamination of the coast with the byproducts of industrialization (Lacerda et al. 2007). Within this context, the discharge of radionuclides and metals into the water can stem from both natural and artificial sources. The primary natural sources of radionuclides and metals are the Earth's crust (mainly rocks and minerals) and the atmosphere. Subject to a continuous process of weathering associated with erosion and leaching due to the action of wind and water, both rocks and minerals release radioactive elements and metals, which are subsequently carried to the ocean (Joseph et al. 1971).

Artificial radionuclides enter the environment as the result of anthropogenic activities, such as the use of nuclear reactors, mining, discharge of radioactive material straight into rivers and seas, accidental releases of liquid effluents from nuclear sources, and nuclear

explosive tests, which can raise the levels of radioactivity in the environment, consequently increasing the radiation dose to the individuals exposed. Metals enter the environment due to various human activities that generate substances, residues, and effluents with the potential to contaminate the environment.

The city of Imbituba is located on the southern coast of Brazil, in the state of Santa Catarina, 90 km away from the capital city, Florianópolis (Fig. 1). A phosphogypsum deposit occupies an area of approximately 7 ha adjacent to the city's port. The stack reaches 10 m in height and contains approximately 500,000 tons of stacked phosphogypsum. There is a stream alongside the stack and a piezometer installed in the stack area. The radionuclide concentrations in the stack were determined to be 98 Bq kg^{-1} for ^{226}Ra, 68 Bq kg^{-1} for ^{228}Ra, and 278 Bq kg^{-1} for ^{210}Pb (Borges 2011).

Based on the possibility of a one-off contamination, the aim of this work was to chemically and radiologically characterize the surface water samples collected along the Imbituba stream and subsurface water samples collected in the piezometer and to investigate the impact of the final disposal of phosphogypsum on the nearby surface and subsurface waters. Additionally, this worked aimed to calculate the annual dose resulting from ingestion of such waters.

2 Materials and Methods

2.1 Water Sampling

In May 2008, six surface water samples were collected from six georeferenced points along a stream located beside the phosphogypsum stack in the city of Imbituba, SC, Brazil (Fig. 2). Additionally, water from a piezometer in the phosphogypsum stack area was sampled; the average depth of which was estimated to be 5 m.

The surface water samples were collected in 2-L polyethylene bottles directly from the stream. The samples were transferred to polyethylene flasks and acidified with nitric acid P.A. to pH <2 to minimize the biological activity and to avoid the desorption of metals into the walls of the plastic. The treated samples were kept refrigerated during transportation to the Laboratory of the Geochemical Department of the UFF and were immediately filtered twice using disposable 0.45 μm pore size cellulose acetate microfilters.

2.2 Determination of Metals in the Water Samples

As this work involves the study of chemical elements in trace concentrations in water, procedures based on clean techniques that are internationally validated (USEPA 1999) were adopted. Such procedures aim to decrease possible contamination during all sample processing stages, from the collection of the samples to the final moment of analysis (Sodré 2005).

The materials used in the analysis of this study were left to soak for 1 day in *Extran* 5 % in a plastic recipient with a lid. Subsequently, the flasks were rinsed with running water and then with distilled water. The flasks were left submerged for another day in a 10 % nitric acid (HNO_3). Finally, the flasks were washed with Milli-Q water, dried, and analyzed or stored in plastic bags (Sodré 2005).

All reagents used in this work were of analytic grade. Ultrapure water, such as Milli-Q (Millipore), was used in the preparation of all solutions that were part of a trace element analysis.

Inductively coupled plasma optical emission spectrometry (ICP-OES) is widely used in environmental analyses because it allows rapid, simultaneous multielement analyses, with high sensitivity and precision in a broad linear dynamic band (Harris 2005; Skoog 2002). ICP-OES has been used in Brazil since the 1970s (Petry 2005).

2.3 Determination of Radionuclide Activity and Concentration in Water Samples

The radionuclide determinations were carried out in the Institute of Radiation Protection and Dosimetry (IRD). To determine the ^{210}Pb levels, a stable lead tracer in nitrate form was used. After the purification processes, a lead chromate precipitate was obtained (Lauria and Godoy 1988).

The radium isotopes were coprecipitated as $Ba(Ra,Pb)SO_4$ by the addition of H_2SO_4 and $BaCl_2$ in a 1-L sample. The barium sulfate of radium was dissolved with nitriloacetic acid and reprecipitated with the addition of acetic acid until the solution reached pH 4.5–5.0, whereas ^{210}Pb remained in its aqueous phase. The solid and aqueous phases were separated by centrifugation, and $Ba(Ra)SO_4$ was purified by dissolution with EDTA at pH 10. Next, the sulfate was precipitated again and filtered using Whatman 44 (d=28) filtering paper and forced

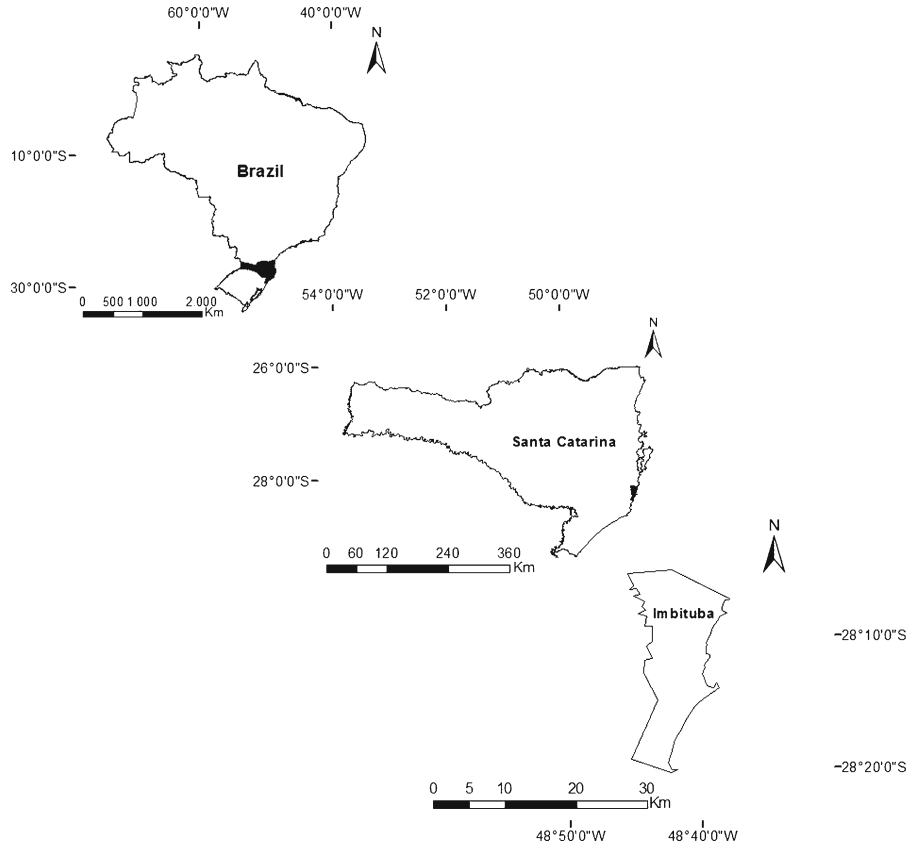

Fig. 1 Geographic location of Imbituba, SC

filtration. The precipitate was washed with 5 mL of ultrapure H_2O (Milli-Q) and dried in a hotbed at 80 °C for 30 min. The filtering paper containing the precipitate was placed on a stainless steel plate, and its edges were attached with the aid of a PVC ring (Godoy 1990).

We waited at least 21 days after the precipitation to begin sample radionuclide activity counting. The

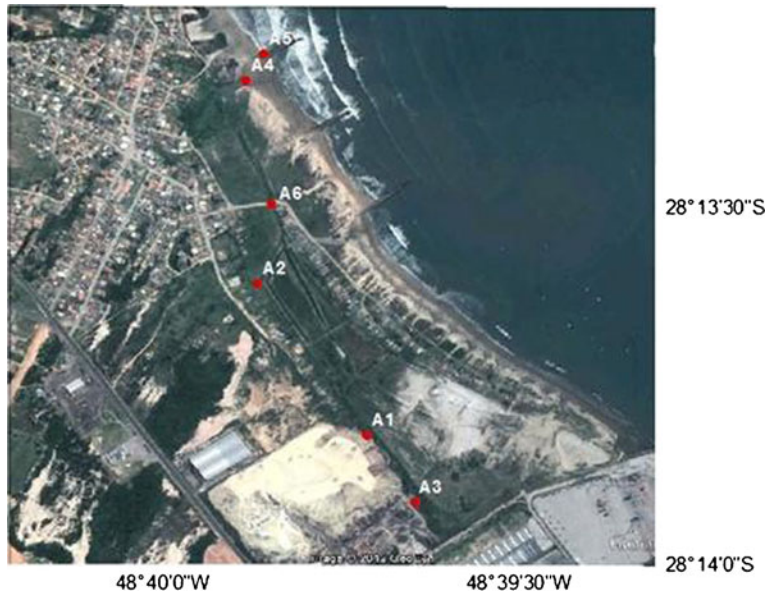

Fig. 2 Location of the water sample collection points in the stream in Imbituba, SC

activity was counted using a Berthold LB 770–1 model proportional α and β detector of low background radiation. First, the α count was conducted for 100 min, and then, the samples were covered with filter paper and the β count was conducted for 400 min.

This method of analysis is routinely used in the IRD's laboratories, and the analysis method performance is periodically tested via participation in interlaboratory comparison exercises conducted by different organizations, such as the EML/USDOE in NewYork, the MAPEP/RESL/USDOE in Idaho Falls, and the PNI/IRD/CNEN in Rio de Janeiro (Vianna et al. 1998).

2.4 Statistical Analysis

Given the complexity and the large variance usually observed in environmental studies (Einax and Soldt 1999), the use of multivariate statistical methods is frequent reported in the literature. The purpose of these methods is to identify and differentiate the natural levels of anthropic contamination and to evaluate and identify pollution sources.

To determine which of these parameters contributed the most to such characterization in the present samples and how they might be related, the cluster analysis method was used. The analyses were conducted using STATISTICA 7 (Copyright© 1984–1987, StatSoft, Inc. 2300 East 14th Street Tulsa, OK 74104, USA).

3 Results and Discussion

Table 1 lists the results for the average activity of ^{226}Ra, ^{228}Ra, and ^{210}Pb in the water samples collected from the stream in Imbituba, SC, Brazil. The associated errors pertain to the standard deviation of the duplicate measurements.

Table 1 Activity of ^{226}Ra, ^{228}Ra, and ^{210}Pb in water samples. (Bq L^{-1})

Sampling points	^{226}Ra	^{228}Ra	^{210}Pb
A1	0.006±0.002	0.040±0.01	0.077±0.007
A2	0.033±0.005	0.110±0.01	0.135±0.007
A3	0.011±0.003	0.010±0.001	0.023±0.005
A4	0.008±0.002	0.020±0.001	0.022±0.003
A5	0.012±0.003	0.068±0.007	0.062±0.005
A6	0.013±0.003	0.030±0.001	0.015±0.003
A7	0.009±0.003	0.014±0.006	0.040±0.005

The ^{226}Ra concentration in the water was within the limits if compared with the range of values reported for superficial waters, 0.0074–0.222 Bq.L^{-1} (IAEA 1990). The samples taken from point A2 presented activities that were higher than those found in the other point samples. This difference may be associated with the contribution of effluents discharged at that point.

The activities of ^{226}Ra, ^{228}Ra, and ^{210}Pb in the water of the Imbituba stream were average when compared with the activity values of the subsurface piezometer water samples, with the exception of point A2. These results indicate no evidence of contamination of the water by the phosphogypsum stacks. Santos (2002) determined the activity for these radionuclides in water from wells in the area of the phosphogypsum stacks in the city of Cubatão in Brazil and in reference wells previously determined to be natural for the region and found average values of 0.057 Bq L^{-1} for ^{226}Ra, 0.069 Bq L^{-1} for ^{228}Ra, and 0.024 Bq L^{-1} for ^{210}Pb for the reference wells and 1.5 Bq L^{-1} for ^{226}Ra, 6.0 Bq L^{-1} for ^{228}Ra, and 2.1 Bq L^{-1} for ^{210}Pb for the stack region wells.

The values obtained in this work from the piezometer samples (A7) are lower than those found by Santos (2002) for the reference wells in Cubatão, and they are within the low range of values of ^{226}Ra and ^{228}Ra determined for the groundwater in Brazil ranging from 0.01 to 3.79 Bq.L^{-1} and from 0.002 to 3.80 Bq. L^{-1}, respectively (Godoy and Godoy 2006).

Silva (2004) conducted a radiological characterization for these same radionuclides in the rivers and estuary of the city of Santos for surface waters and found maximum values of 0.034 Bq L^{-1} for ^{226}Ra, 0.031 Bq L^{-1} for ^{228}Ra, and 0.0066 Bq L^{-1} for ^{210}Pb adjacent to the phosphogypsum stack in Cubatão. With the exception of ^{228}Ra and ^{210}Pb values from the point A2 Imbituba sample (downstream from the stack) that presented values greater than those of Cubatão, the other surface water sampling points evaluated in this work presented radionuclides values that were lower or similar to those found in the surface waters of Cubatão. The results from point A2 might be explained by the discharge of effluents at point A2 contributing to the increase of radionuclide concentrations in the related samples.

In an evaluation of other studies in the literature focused on environments altered by phosphogypsum,

Table 2 Physical–chemical parameters and concentration (μg kg^{-1}) of Zn, Cu, and Mn in the stream of Imbituba, SC

Sampling points	Salinity	pH	Zn	Cu	Mn
A1	3.4	1.48	350	50	1,916
A2	3.4	2.29	1,033	632	2,538
A3	4.1	3.22	280	19	1,327
A4	3.3	2.44	474	65	2,170
A5	40.3	5.85	37	11	344
A6	3.6	1.82	699	97	3,063
A7	2.1	4.70	69	31	1.14
Investigation[a]	–	–	1050[a]	2000[a]	400[a]

[a] Values calculated based on risk to human health, according to the scope of this Resolution. They differ from the acceptance standards for human consumption defined in Ordinance No. 518/2004 of the Ministry of Health (Table 5) and from the maximum values allowed for human consumption defined in Exhibit I of CONAMA Resolution No. 420/2009

we observed that the ^{228}Ra activity in the waters of the Imbituba stream (point A2) was greater than the values reported by Carvalho (1997) in Tagus Estuary in Portugal (0.00058–0.0081 Bq L^{-1}), by Choukri et al. (2002) for the Moulouya River in Morocco (0.012 to 0.026 Bq L^{-1}) and by Pelegrina and Martinez-Aguirre (2001) for estuaries of the Tinto and Odiel Rivers in Spain (0.0018–0.0143 Bq L^{-1}). On the other hand, the other points evaluated in this study presented values close to the values in the aforementioned works.

The radionuclides concentrations identified in this study were compared with the pertinent standards in Brazil. The Brazilian State Ministry of Health, as an amendment to Ordinance No. 2914/MS/GM, on December 12, 2011 approved national rules and standards of drinkability for water intended for human consumption.

The screening levels for drinking water intended to be supplied to humans must comply with the following radioactive characteristics:

- The reference value for the total alpha radioactivity (including ^{226}Ra) is 0.5 Bq L^{-1}.
- The reference value for the total beta radioactivity is 1 Bq L^{-1}.

The concentrations of radionuclides determined in the waters of Imbituba, SC, Brazil, were compared with the values of the abovementioned ordinance (MS 2011) for the total alpha and beta activities. If we assume that the entire alpha activity present in the water results from the ^{226}Ra activity, we can state that the maximum value obtained for the radionuclide, 0.033 Bq L^{-1}, is much lower than the 0.5 Bq L^{-1} reference value established in the ordinance.

Similarly, the ^{228}Ra and ^{210}Pb present in the water can be considered the limiting beta-emitting radionuclides from a radiotoxicity viewpoint. The sum of the maximum concentrations of these radionuclides in the present study, 0.245 Bq L^{-1}, is also lower than the ordinance reference value of 1 Bq L^{-1} for the total beta activity.

Table 2 lists the physical–chemical parameters analyzed in the Imbituba water samples. The metals

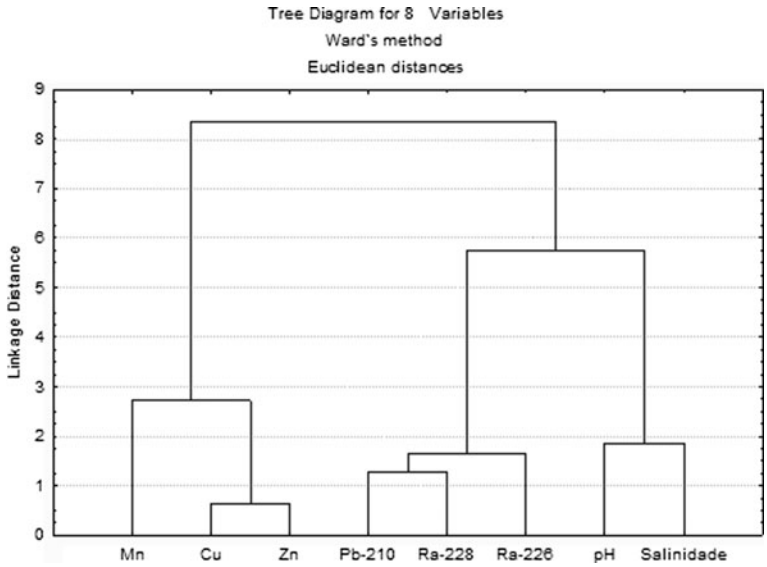

Fig. 3 Dendrogram of the chemical parameters analyzed in the water

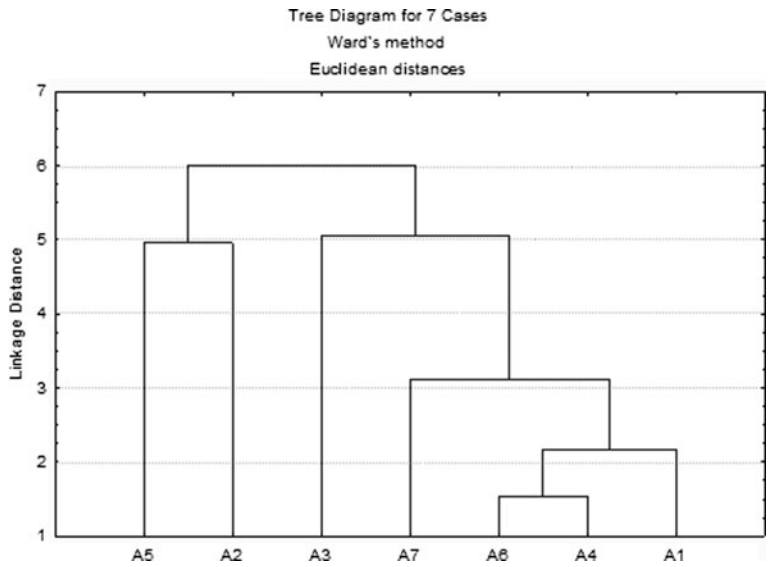

Fig. 4 Dendrogram of the collection points analyzed in Imbituba

analyzed herein are used in industry and are thus some of the most studied from the toxicological viewpoint. In addition, the elements are classified as essential for humans because related deficiencies cause health issues, but excesses of these metals can lead to lethal toxicity.

In addition to the elevated radionuclide concentrations, the point A2 water samples presented the greatest concentrations of metals, which is likely associated with the release of effluents at the sample point.

The pH determined in the stream varied l from 1.5 to 5.8, and we can observe that the points close to the stack presented greater acidity. The acid pH observed close to the stack is most likely due to the presence of phosphoric, sulfuric, and fluoridric acids residues of the phosphogypsum used in the dissolution of the phosphatic rock. According to Silva (2001), the average pH found in the tested Cubatão waters was 3.2.

The concentration of metals in the water decreases with the increase of pH, which is in accordance with other studies (Grassi et al. 1997 and Sposito 1984). In general, the solubility of the metals increases reductions in pH. The dissolved metals evaluated in the waters of Praia do Porto (A5) and in the piezometer (A7) presented the lowest concentrations, which likely is a consequence of the increased pH at those points. The low levels of Zn, Cu, and Mn at the Praia do Porto sample point is also related to carbonate dilution effects.

Pelegrina and Martinez-Aguirre (2001), while studying the Tinto and Odiel Rivers in Spain (Cu concentration of 10–1,800 mg L^{-1} and Zn concentration of 61–2,300 mg L^{-1}), and Paul (2001), while studying the Peryar River in India (Cu concentration of 5–51 mg L^{-1} and Zn concentration of 82–1,130 mg L^{-1}), in regions that also house industrial complexes for the production of phosphoric acid, found concentrations of Cu and Zn similar to those recorded in environments influenced by phosphogypsum in Imbituba, SC, Brazil.

We observed that the Mn concentrations obtained in this work were much higher than the investigation amounts determined by Resolution No. 420/2009 of CONAMA. These results demonstrate that the aquatic compartment of the stream in Imbituba was altered due to the high levels of the metal. On the other hand, the Zn and Cu concentrations were below the Investigation Amounts (CONAMA 2009).

Figure 3 shows the clusters formed by the elements and considering all the sampling points analyzed herein. Group I is defined by the concentration of the

Table 3 Actual dose resulting from water consumption (mSv y-1)

Sampling points	^{226}Ra	^{228}Ra	^{210}Pb	Total
A1	1.2×10^{-3}	2.0×10^{-2}	3.9×10^{-2}	6.0×10^{-2}
A2	6.7×10^{-3}	5.5×10^{-2}	6.8×10^{-2}	1.3×10^{-1}
A3	2.2×10^{-3}	5.0×10^{-3}	1.1×10^{-2}	1.9×10^{-2}
A4	1.6×10^{-3}	1.0×10^{-2}	1.1×10^{-2}	2.3×10^{-2}
A5	2.4×10^{-3}	3.4×10^{-2}	3.1×10^{-2}	6.8×10^{-2}
A6	2.6×10^{-3}	1.5×10^{-2}	7.5×10^{-3}	2.5×10^{-2}
A7	1.8×10^{-3}	7.0×10^{-3}	2.0×10^{-2}	2.9×10^{-2}

metals evaluated, indicating that the behaviors of the elements in the water have greater similarity among themselves if compared to the elements of group II. Cu and Zn form a subgroup probably because they presented a behavior different from Mn.

Group II consists of two subgroups, one encompassing salinity and pH, and another formed by the natural radionuclides, which presented a greater similarity within each subgroup. These results indicate that the variation of salinity and pH can influence the flow of the natural radionuclides in the Imbituba stream waters.

Figure 4 shows the clusters formed by the collection points. Two similarity groups were formed, one consisting of points A5 and A2, and another encompassing the other points. In this type of analysis, the shorter the distance between the points, the greater the similarity. In this case, it is notable that there is greater similarity between points A6, A4, and A1, which is probably associated with the greater influence of the phosphogypsum stack on those points.

Points A5, A2, and A3 were less similar, which is most likely associated with the highly variable concentrations of radionuclides and metals of those points, in addition to high variations in chemical parameter values. Point A2 presented the greatest concentrations of all elements. A3 and A5 presented the lowest concentrations of metals and some radionuclides.

Based on the concentrations of ^{226}Ra, ^{228}Ra, and ^{210}Pb determined in the Imbituba water samples, the actual ingestion doses of such water were estimated (Table 3). The doses were calculated considering a daily ingestion rate of 2 L. The conversion factor of an actual effective dose was obtained from CNEN standard NE 3.01 (CNEN 2005) and considering the metabolism of a grown person and an interval of time for the integration of the actual dose of 50 years after an acute incorporation of the relevant radionuclides. The final results of the effective dose resulting from water ingestion are below the reference levels for exposure due to radionuclides in drinking water of 1 mSv year^{-1}, recommended by International Atomic Energy Agency (IAEA 2011). In all of the water sample points, radionuclides ^{228}Ra and ^{210}Pb contributed the most to the total dose.

The ingestion reference levels pertained to the ingestion of drinking water and were purposefully conservative, a decision which was made in this radiological impact evaluation to favor individual safety. Thus, it can be concluded that exposure via ingestion of the water does not present a critical health risk because it involves doses below the dose reference level of 1 mSv year^{-1} and in consequence the Imbituba phosphogypsum stack has little influence on the health risk for the population due consumption of local waters.

4 Conclusions

The concentrations of natural radionuclides in the surface waters were at the same levels compared with the values of the piezometer subsurface water samples. The radionuclide values in the surface waters of point A2 in Imbituba were greater than the other sampling points, which probably occurred due to the discharge of effluents at the sampling point. However, the values were quite lower than the maximum limits allowed in waters.

With the exception of point A2, for the other sampling points evaluated (A1, A3, A4, A5, and A6), the radionuclides in the surface waters were at the same levels as in the works found in the national and international literature.

Mn was present in the majority of the sampling points in amounts above the investigation level of resolution 396/2008 of CONAMA. The Zn and Cu concentrations were below the relevant CONAMA levels.

Cluster analysis was used to examine the concentrations of the elements analyzed. Two groups were identified: Group 1 (Zn, Cu and Mn) and group 2 (^{226}Ra, ^{228}Ra, and ^{210}Pb). The concentration of the group 2 elements was also determined to be related to the salinity and the pH of the water samples.

An assessment of the stream water and the piezometer sample water in the area of the Imbituba phosphogypsum stack indicates that the related ingestion doses are below the specific recommended reference level.

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