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THEMATIC ISSUE

Ra and Rn isotopes as natural tracers of submarine groundwater discharge in the patagonian coastal zone (Argentina): an initial assessment

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Abstract

Submarine groundwater discharge (SGD) is herein recognized as a significant pathway of material transport from land to the coastal SW Atlantic Ocean and thus, it can be a relevant factor affecting the marine biogeochemical cycles in the region. This paper focuses on the initial measurements of ^{226}Ra, ^{228}Ra and ^{222}Rn made in Patagonia's coastal zone of Chubut and Santa Cruz provinces (42°S–48°S, Argentina). ^{226}Ra activity ranged from 2.9 to 73.5 dpm 100 L^{-1}, and ^{228}Ra activity ranged from 11.9 to 311.0 dpm 100 L^{-1} in groundwater wells. The radium activities found in Patagonia's marine coastal regions and adjacent shelf indicate significant enrichment throughout the coastal waters. Groundwater samples presented the largest ^{222}Rn activity and ranged from 2.66 to 1083 dpm L^{-1}. Conversely, in the coastal marine environment, the ^{222}Rn activity ranged from 1.03 to 6.23 dpm L^{-1}. The Patagonian coastal aquifer showed a larger enrichment in ^{228}Ra than in ^{226}Ra, which is a typical feature for sites where SGD is dominant, probably playing a significant role in the biogeochemistry of these coastal waters.

Keywords Radium · Radon · Submarine groundwater discharge · Patagonia's coastal zone · SW Atlantic Ocean

Introduction

Submarine groundwater discharge (SGD) is defined as a submarine inflow of fresh and brackish groundwater (i.e., seawater–freshwater mixtures and/or recirculated seawater) from land into the sea, and it is regulated by several forcing mechanisms, which cause the hydraulic gradient required to establish the water flux (Burnett et al. 2003; Santos et al. 2012). SGD is a complex hydrological process which frequently occurs in the continent–ocean interface and plays an important role in coastal hydrological and biogeochemical processes. During the last decades, SGD has become recognized as an important pathway of dissolved material transport (e.g., Moore 1999; Burnett and Dulaiova 2003). From a chemical point of view, the SGD is a potential transport vector of dissolved inorganic nutrients, carbon, trace elements and gases to coastal waters (Moore 2006; Swarzenski et al. 2006). Although not as obvious as the riverine contribution, which discharges about 36 × 10^{12} m^3 year^{-1} to world oceans (Milliman and Farnsworth 2011), SGD flows directly into the sea and appears to be 3–4 times greater (120 × 10^{12} m^3 year^{-1}) than riverine fluxes into oceans (Kwon et al. 2014). Clearly, such continental contributions

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of nutrients may affect the biogeochemical cycles in coastal environments (e.g., Garcia-Solsona et al. 2010; Godoy et al. 2013).

SGD can enter to the sea within the coastal zone and/or several tens of kilometers offshore, depending on the hydrogeological characteristics of each site (Kroeger and Charette 2008). The assessment of such fluxes is, therefore, difficult (Burnett and Dulaiova 2003). However, there has been a significant interdisciplinary effort to better understand the origin of SGD, and to assess its fluxes in different hydrogeological environments (Povinec et al. 2008).

The most useful methods for identifying coastal sites with SGD involve the measurement of certain geochemical tracers. The most widely used are: Cl^-, water temperature, radioactive (^{3}H, ^{222}Rn, ^{223}Ra, ^{224}Ra, ^{226}Ra and ^{228}Ra) and stable isotopes (^{2}H and ^{18}O) (Moore 2003; Burnett et al. 2003; Windom et al. 2006; Santos et al. 2009; Peterson et al. 2010; Schmidt et al. 2011; Swarzenski et al. 2017). The coastal seawater column tends to integrate natural tracers coming into the system via groundwater pathways. Therefore, some major and minor elements may be strongly influenced either by the direct discharge of ground fresh water into the sea or by chemical reactions occurring during the circulation of seawater through a coastal aquifer (Zektzer et al. 1973; Moore 1999).

The rivers that drain Patagonia's eastern Atlantic seaboard export major and trace elements, nutrients and sediments, thus playing a significant role in maintaining a rich biological structure all along Patagonia's coastal zone (Depetris et al. 2005). Scientific information on the likelihood of SGD in the region is, however, scarce or nonexistent, and its subsequent biogeochemical role is, at best, speculative. This paper brings into focus the measurements and qualitative aspects of ^{226}Ra, ^{228}Ra and ^{222}Rn measurements in Patagonia's coastal zone of Chubut and Santa Cruz provinces (42°S–48°S, Argentina). These are the first measurements of natural radioisotopes tracers made in Patagonia and constitute an initial reconnaissance. More work is required to translate these measurements into rates of SGD flowing into this significant portion of Patagonia's coastline.

Study area

The Argentine provinces of Chubut and Santa Cruz are located in Patagonia (between 42°S and 52°S) (Fig. 1). The coastal areas of both provinces exhibit low atmospheric precipitations (~ 240 mm $year^{-1}$) (EMC 2014) which, in addition to high evaporation and evapotranspiration (2000 mm·$year^{-1}$), results in a markedly arid climate. Average annual temperature is 13.4 °C with a mean minimum of 6.4 °C in July (winter) and a mean maximum of 20.4 °C in January (EMC 2014). The average annual relative humidity is 40%, which further promotes soil dryness. Spring is the season with the largest W and SW wind speeds, with an annual average speed of 16.6 km h^{-1}, and a recorded maximum of ~ 90 km h^{-1} (EMC 2014). These conditions stimulate oxygenation and vigorous mixing in the water column of the coastal zone.

The Chubut province is in central Patagonia, and it is dissected by the west-flowing Chubut river, which is approximately 800 km long. It covers a drainage area of ~ 40,000 km^2 (Depetris et al. 2005; Milliman and Farnsworth 2011). Its mean discharge is ~ 50 m^3 s^{-1}, and the

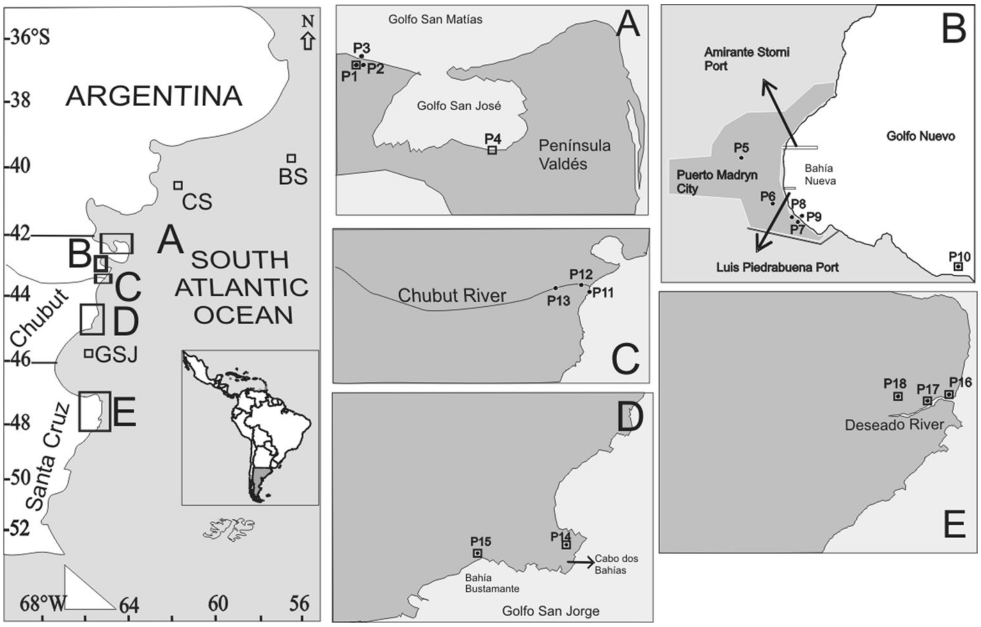

Fig. 1 Map showing the studied area in Chubut and Santa Cruz provinces in the Patagonian coastal zone from Argentina. Dots and squares are indicating the sites in which the ^{222}Rn and $^{226-228}$Ra activities were measured, respectively

sediment flux delivered to the Atlantic Ocean has been estimated in ~ 49×10^9 g year^{-1} (Depetris et al. 2005). Most heavy metal concentrations found in bed sediments, in suspended matter, and in the dissolved load of the Chubut River—as well as in the remaining Patagonian rivers—are comparable to those reported in the international literature for non-polluted rivers (Gaiero et al. 2002). Moreover, the material sources, chemical weathering and denudation in the Chubut River drainage basin have been studied by Pasquini et al. (2005).

Bahía Nueva is located on the western edge of *Golfo Nuevo* (Fig. 1). Marine currents are weak inside the Gulf and have an average speed < 2.5 cm s^{-1} (Tonini et al. 2006). The observed semi-diurnal tide amplitude is 4.13 m (SHN 2015). Nitrogen is the limiting element for the primary production within the gulf (Charpy-Roubaud et al. 1982). Concerning productivity, the highest phytoplankton abundance (6.6×10^6 cel L^{-1}) was found in coastal sites of *Bahía Nueva* during spring–summer and these showed a heterogeneous spatial distribution (Santinelli et al. 2002). These maximum abundances were associated with high nutrient concentration and salinity, along with low temperature and dissolved oxygen (Santinelli et al. 2002). Harmful phytoplankton has been detected in *Bahía Nueva*. These organisms produce paralyzing toxins, cause clogging of fish gills, and/or decreases in the relative level of dissolved oxygen in the Bay (Esteves et al. 1992; Santinelli et al. 2002; Sastre et al. 2007). The main species of potentially harmful phytoplankton found in *Bahía Nueva* are diatoms (as *Pseudo-nitzschia pseudodelicatissima* and *Pseudo-nitzschia australis*); Dinoflagellates (as *Alexandrium tamarense*; *Prorocentrum micans*; *Dinophysis acuminata*); and Silicoflagellates (as *Dictyocha fíbula* and *Distephanus speculum*) (Esteves et al. 1992; Sastre et al. 2007).

Along Chubut's coastline, there are several protected marine areas established to preserve its biodiversity. Between them, peninsula *Valdés*, located 100 km north of the city of Puerto Madryn, was designated Natural Heritage of Humanity (UNESCO 1999) and Biosphere Reserve (UNESCO 2014). The northern *Golfo San Jorge* (*Cabo dos Bahías*), is one of Patagonia's most productive marine coastal areas. In 2008, it was established as a Coastal Marine Park in order to maintain biodiversity and natural resources. In the ocean, facing peninsula *Valdés* and *Cabo dos Bahías*, oceanographic fronts are partly responsible for supporting a significant marine biodiversity.

South of Chubut, the Deseado (~ 47°S) is another river draining the Patagonian Atlantic seaboard, in the Argentine Province of Santa Cruz. This 615 km-long Andean river originates in the proglacial Buenos Aires Lake (NW corner of Santa Cruz Province), and flows eastward toward the SW Atlantic. On the way to its outflow, its water is tapped for irrigation. The river sometimes disappears under arid and permeable terrains, to re-emerge before reaching a deep-water natural harbor, at Puerto Deseado in Santa Cruz's coastline. The river's outlet has become submerged and inundated by sea water, forming an estuary. In 1977, this area was set aside as a nature reserve, the *Reserva Natural Ría Deseado*.

The geology of the area consists mainly of Tertiary (Puerto Madryn and Gaiman Formations) and Quaternary sediments (Haller et al. 2001; Alvarez et al. 2009). The thickness of the Puerto Madryn Formation (Holocene) strata is extremely variable, reaching ~ 150 m. The Gaiman Formation (Miocene) reaches greater depths; the impermeable beds consist of compact silts and clays with abundant volcanic ash. Quaternary sediments are represented by shingle layers (often thick) of glacifluvial origin—referred to as *rodados patagónicos or Patagonian pebbles*—as well as other sediments of eolian, alluvial, and colluvial origin (Alvarez et al. 2009). More geologic information on this area and the entire Patagonian region can be obtained elsewhere (e.g., Gaiero et al. 2004, 2006).

The biogeochemical output and typology of the rivers draining Patagonia's Atlantic seaboard was studied by Depetris et al. (2005) and Pasquini and Depetris (2007) and reviewed by Depetris and Pasquini (2008). Historical Chubut river discharge series did not show significantly increasing or decreasing trends (period 1943–2003). In recent decades, however, the system shows a statistically significant decreasing discharge trend. Deseasonalized hydrological series show a faint signal coherent with El Niño-Southern Oscillation (ENSO) events in the Pacific Ocean. Such connection may be attributable to greater snow accumulation along the Andes during ENSO events (Pasquini et al. 2008). There is, however, a lack of information in the studied area, which links SGD with nutrient fluxes and primary production.

Materials and methods

Isotopic approach

The measurement of a range of isotopic tracers at the groundwater–ocean interface and in the coastal ocean provides a method that can be used to produce integrated flux estimates of groundwater discharge. For selecting the most appropriate groundwater tracer in a certain system one should consider several factors including, (1) the tracer's enrichment factor in groundwater relative to surface water, (2) its reactivity in the environment, and (3) the identification of other sources and sinks if a natural tracer is being used (Peterson et al. 2010).

Several investigators have assessed the magnitude of SGD fluxes into the coastal zone using radon and radium isotopes, such as ^{222}Rn and $^{223–224–226–228}$Ra (Swarzenski et al. 2006; Burnett and Dulaiova 2006; Burnett et al. 2008). ^{222}Rn is a non-reactive isotope and is a daughter isotope of ^{226}Ra. The concentration of radon can be used in conjunction with radium isotopes to estimate SGD because high levels of radon are the result of radium decay in the sediments through which groundwater flows. In contrast, radon in seawater is supported only by the (low) content of radium in water itself and from a thin layer of sand and sediments at the seafloor (i.e., radon diffusion). Naturally occurring ^{222}Rn is a reliable natural tracer of groundwater discharge because it is chemically conservative and typically 2–3 orders of magnitude higher in groundwater than in surface waters (Burnett and Dulaiova 2003; Burnett et al. 2010; Peterson et al. 2010).

Likewise, groundwater also tends to have a larger content of radium than seawater. Hence, radon and radium can be used together to trace the groundwater supply to the sea (Schlüter 2002). Radionuclides have been used for quantification of SGD in several regions of Brazil (Windom et al. 2006; Burnett et al. 2008) and in other regions of the world with different tidal regimes, coastal circulation and continental contributions (Moore 2010; Charette 2015). Radium isotopes have also been shown to be very useful tracers of processes occurring in the continental shelf, including the assessment of mixing rates and SGD magnitudes (Moore 1996). In addition, radon was applied to quantify SGD not only in coastal environments (Burnett et al. 2006) but also in lagoons (Santos et al. 2008), rivers, and canals (Chanyotha et al. 2014).

The strategy for using radium isotopes in SGD studies is based on the fact that radium is largely particle-bound in fresh water but desorbs from particles in contact with salty water. The discovery of high ^{226}Ra activities (half-life = 1600 y) in the coastal ocean which could not be explained by input from rivers or sediments, coupled with the measurement of high ^{226}Ra in salty coastal aquifers, led to the hypothesis that SGD was responsible for the observed elevated activities. These increased ^{226}Ra activities, which have been measured along many coasts, provided the primary evidence for large SGD fluxes to the coastal ocean (Moore 2003). More recently, the inventory of ^{228}Ra (half-life = 5.75 year) in the upper kilometer of the Atlantic Ocean has been used as a proxy for the total SGD input to the Atlantic Ocean (i.e., after other sources of ^{228}Ra were evaluated) (Moore and Shaw 2008). The sources that supply radium to the coastal region include ocean waters, river water, desorption of sediment from rivers, land erosion, and SGD (Moore 1996).

In many coastal environments, the monitoring of ^{222}Rn in the water column is used to estimate SGD by measuring in situ activities. The main principle of using continuous radon measurements to decipher rates of SGD is converting the changes observed in ^{222}Rn inventories to fluxes of ^{222}Rn. This is accomplished by monitoring coastal waters at a fixed location, making allowances for tidal height changes, and for losses due to atmospheric evasion and mixing offshore with low-concentration waters. Assessment of possible time-dependent trends of radon is important because groundwater flow is known to be extremely variable in some cases even reversing the flow direction in response to external forcing (tides, changes in water table height, etc.).

An example of the combined use of these tracers was presented by Peterson et al. (2008) who used both techniques to estimate SGD in the Yellow River Delta. Due to the intrinsic properties of each of these elements, it was decided—for this pioneering study of the Patagonian region—to implement a sampling strategy that would provide a wide evaluation on the distribution and activity of both tracers. Therefore, the objective of this work is not to consider the pros and cons of each tracer but to obtain, instead, the best and most complete data set so that in the ongoing study (i.e., the determination of SGD), either technique may be used separately or both of them together.

Due to logistic limitations, this preliminary isotopic evaluation focuses on the activities of long-lived radium. Future studies will include short-lived radium isotopes, which are advantageously used not only for the evaluation of the SGD, but also to determine the age of water masses and the mixing rate of coastal and oceanic waters.

The measurements of ^{222}Rn are most often taken in situ for both, point and time series sampling. This analytical advantage allowed reaching a larger number of sampling stations, expanding the sampling network for the continued study of SGD.

Sampling and analytical methods

Surface and groundwater was sampled at the end of the austral summer of 2011. Sampling of the coastal aquifer (i.e., groundwater of the coastal zone) was accomplished by pumping water from permanent wells. A push-point piezometer system was also used to sample groundwater along the beach of the Patagonian coast, down to a maximum depth of a meter or two. Sampling sites along the Patagonian coast were sufficiently spaced to be representative (Fig. 1). Offshore seawater samples were collected along Chubut province's coastline during a cruise on board of the R/V "Puerto Deseado."

Temperature, dissolved oxygen, pH, salinity, conductivity, total dissolved solids (TDS), and redox potential (Eh) were measured in situ using a multi-probe sensor (YSI MPS-556).

The activity of long-lived radium isotopes, ^{226}Ra and ^{228}Ra was determined in water from 11 stations: permanent wells (*Esperanza* (P1), *Cabo dos Bahías* (P14), *Bustamante* (P15) and Ría *Deseado* (P17, P18), in piezometric wells

(Fracaso, P4), in marine coastal zone (Puerto Madryn (P10) and *Ría Deseado,* P16) and in three locations at the shelf off Patagonia. For radium isotopic analyses, 4–10 L samples were collected from permanent wells and beach piezometers by means of a peristaltic pump. About 50 L of surf zone water was collected using a clean bucket, and 200 L samples offshore water from 3 to 5 m depth were collected with a submersible pumping system. These samples were immediately processed by passing through manganese oxide-coated fibers to retain radium (Moore 1976). Later, at the University of South Carolina (USA), radium was leached from the fibers and ^{226}Ra and ^{228}Ra were measured by gamma spectrometry (Moore 1984).

Activities of ^{222}Rn in water were measured continuously in the field using a modified RAD-7 (Durridge Company Inc.) radon-in-air monitor (Burnett et al. 2001). Surface water (0.5 m below the surface) was pumped to an air/water equilibrium exchanger system. In this system, the headspace air is circulated to the RAD-7 for analysis of ^{222}Rn activity in the air, and recycled back to the exchanger, creating a closed air loop. Applying a temperature-dependent solubility coefficient for ^{222}Rn, it was possible to convert the measured radon in air to the corresponding value in the water. Each data point attained represents an integrated value over 30–60 min, depending upon the desired measurement uncertainty.

Groundwater samples for ^{222}Rn were collected using a peristaltic pump and measured using a RAD-H_2O system (Big Bottle) that uses the internal pump of the RAD-7 to spurge radon from a 4 L volume and circulate it to the counter for measurement.

Results and discussion

Physicochemical water characteristics

The physical and chemical characteristics of the water from the sampled sites are shown in Table 1. Dissolved oxygen level was near saturation at all the sites where surface water samples were measured. However, in groundwater samples dissolved oxygen ranged from 4.3 (P11) to 8.9 (P17) mg L^{-1}. Neutral or slightly alkaline pH was measured in situ and varied from 6.9 to 8.9, 6.9 to 7.9, 7.0 to 8.2 in permanent wells, piezometric wells and, coastal marine zone and Atlantic Ocean, respectively. The highest thermal amplitude and the lowest temperatures were observed in groundwater samples (ranging between 11.5 and 23.2 °C), while in other surface water sites (Coastal Marine and Atlantic Ocean) the temperature was 13.1–18.0 °C. In all cases, conductivity was highly correlated with TDS ($R^2 = 0.984$, $p < 0.001$). In groundwater samples the redox potentials ranged from 180 (P4) to 337 (P1) mV, with persistent aerobic conditions; conductivity levels ranged from 744 (P2) to 54,160 (P4) µS cm^{-1}. High values (13,900 µS cm^{-1}) were obtained in surface water from a Puerto Madryn lagoon, which was supposed to be fresh water. Values > 39,000 µS cm^{-2} were registered in seawater from the coastal marine zone and in oceanic water. It is worth emphasizing that conductivity measurement in groundwater wells were always lower than the seawater sampled in the coastal zone.

Radium isotopes

In groundwater samples, ^{226}Ra activity ranged from 2.9 to 73.5 dpm 100 L^{-1} and ^{228}Ra activity presented the same tendency and, ranged from 11.9 to 311 dpm 100 L^{-1} (Table 2). Some wells exhibited high salinity (40.95 in P4), which can account for the large variability in the activities because increased dissolved salt concentrations promotes, by ion exchange, desorption of ^{226}Ra and ^{228}Ra in the sediments. The highest ^{228}Ra activity (311 dpm 100L^{-1}) was found in groundwater with low salinity (4.66 ups) from *Cabo dos Bahías* (P14) (Fig. 2). Also, in groundwater from beach well (P4) with high salinity (40.95 ups), a high ^{228}Ra activity (243 dpm 100 L^{-1}) was found. Finally, values between 3 and 20 dpm 100 L^{-1} were found in seawater from SW Atlantic Ocean.

This trend was also observed in other studies conducted in coastal regions of South America. Windom et al. (2006), in a region of southern Brazil well-known by the occurrence of SGD, found high Ra activities in groundwater as a result of the mixing process of fresh/salt water in permeable sediments. Furthermore, they observed that the activities of ^{228}Ra were higher than the activities of ^{226}Ra. This same feature was found in the coastal region of Patagonia. Moore (2003) showed that aquifers which are rapidly flushed with salty water, contain much higher activities of ^{228}Ra than ^{226}Ra.

The radium values found in marine coastal regions and adjacent shelf clearly indicate radium enrichment in the Patagonian coast (Table 2). This may be related to the nature of the sediment, to terrigenous sediment supply or even to the mentioned circulation of fresh/salt water in the permeable sediments of the buried estuary. In many regions worldwide, radium showed a similar enrichment, attributed to the occurrence of SGD (Niencheski et al. 2007).

In the specific case of Patagonia (without considering wind-blown cliff material), the atmospheric contribution represents a minimum of 90% of the mass of Patagonian sediments delivered to the ocean as compared with the riverine pathway. However, it can be even more important in some exceptional situations, like the two large explosive eruptions of the Hudson (1991) (Gaiero et al. 2003, 2004), and the Chaitén volcanoes (2008), both located in Patagonia's Andes. In addition, Gaiero et al. (2003) have estimated

Table 1 Physical and chemical characteristics of groundwater from wells, surface water from rivers, marine coastal zone and South Atlantic Ocean

Origin	Site	Date March 2011	N°	Lat “S”	Long “W”	Depth (m)	Temp. (°C)	Cond. (μS cm^{-1})	T.D.S. (g L^{-1})	D.O. (mg L^{-1})	D.O. (%)	pH	Eh (mV)
Ground water permanent well	Puerto Madryn	11	P6	42°46′55.42	65°01′03.85	2	21.2	1358	0.8	6.9	71	7.7	268
	Esperanza 1	13	P1	42°08′20.89	64°57′43.42	20	18.0	5933	4.4	8.2	89	7.0	337
	Esperanza 2	13	P2	42°08′14.44	64°57′50.35	10	19.1	744	0.5	5.7	61	8.9	295
	Playa Unión	14	P11	43°20′24.34	65°03′40.33	18	18.8	34,030	25.1	4.3	53	6.9	276
	Cabo dos Bahías	24	P14	44°53′50.87	65°39′36.45	7	13.6	6499	5.4	5.9	58	7.3	232
	Puerto Deseado 1	21	P17	47°38′40.10	66°02′41.70	12	11.5	1824	1.6	8.9	101	7.8	274
	Puerto Deseado 2	21	P18	47°43′28.45	65°55′24.95	18	18.4	8260	6.1	8.4	93	7.1	245
	Bustamante	23	P15	45°06′54.83	66°32′45.92	1	16.6	4929	3.8	8.8	98	7.8	226
Groundwater Beach (Piezometric well)	Fracaso	19	P4	42°25′35.85	64°07′12.09	1	19.2	54,160	39.6	7.1	99	6.9	180
	Puerto Madryn 1	10	P7	42°47′01.88	65°00′22.55	0	23.2	47,544	29.6	7.2	97	7.9	287
	Puerto Madryn 2	10	P8	42°47′01.88	65°00′22.55	0	21.6	46,778	32.3	7.6	98	7.6	240
	Puerto Madryn 3	10	P9	42°47′01.88	65°00′22.55	0	23.2	51,580	30.1	8.6	101	7.9	287
Surface Fresh water	Chubut River-Rawson	14	P12	43°18′23.57	65°05′31.44	0	17.0	312	0.2	11.8	122	8.0	276
	Chubut River-Gaiman	14	P13	43°17′32.42	65°29′44.77	0	16.2	263	0.2	9.8	100	8.3	262
	Puerto Madryn Lagoon	11	P5	42°46′46.82	65°01′54.16	0	23.2	13,917	7.3	8.2	89	8.0	258
Marine coastal zone	Puerto Madryn Ocean	15	P10	43°50′06.74	65°52′29.52	0	15.0	44,699	31	7.9	96	7.8	290
	Ría Deseado	21	P16	47°45′20.45	65°54′08.86	0	13.1	39,151	33	8.0	95	7.8	305
South Atlantic Ocean	Esperanza Ocean	13	P3	42°08′20.89	64°57′43.42	0	18.0	59,330	4.4	8.2	112	7.0	337
	Golfo San Jorge	19	GSJ	42°32′03.73	67°03′16.01	0	16.9	51,665	32.1	9.4	110	8.2	320
	continental Shelf	26	CS	42°08′20.89	64°57′43.42	0	17.3	50,748	33.2	9.8	113	8.2	315
	Break shelf	27	BS	42°08′20.89	64°57′43.42	0	18.0	52,869	32.9	10.6	116	8.0	282

Table 2 ^{226}Ra and ^{228}Ra activity measured in water from wells, piezometric wells, marine coastal zones and, South Atlantic Ocean

Origin	Site	Date March 2011	N°	Salinity	^{226}Ra (dpm 100 L^{-1})	^{228}Ra (dpm 100 L^{-1})	228/226 A. R.
Groundwater permanent well	Esperanza 1	13	P1	3.75	11.2	30.3	2.7
	Cabo dos Bahías	24	P14	4.66	73.5	311	4.2
	Puerto Deseado 1	22	P17	1.27	2.9	11.9	4.2
	Puerto Deseado 2	22	P18	5.33	19.5	25.4	1.3
	Bustamante	23	P15	3.20	25.9	61.4	2.4
Groundwater beach well	Fracaso	19	P4	40.95	50.1	243	4.9
Marine coastal zone	Puerto Madryn Ocean	15	P10	34.61	48.1	86.9	1.8
	Ría Deseado	21	P16	33.29	7.3	8.6	1.2
South Atlantic Ocean	Golfo San Jorge	18	GSJ	33.046	14.2	20	1.4
	Continental shelf	26	CS	33.061	15.8	6.5	0.4
	Break shelf	27	BS	33.328	20.8	3.1	0.1
Atlantic Ocean North	Ocean	–	–	–	5–22	0–6	Charette et al. (2015)
South of Brazil	Surf zone	–	–	–	6.16–8.87	14.9–24	Windom et al. (2006)
South of Brazil	Beach well	–	–	–	7.1–68.8	40.7–256	Windom et al. (2006)

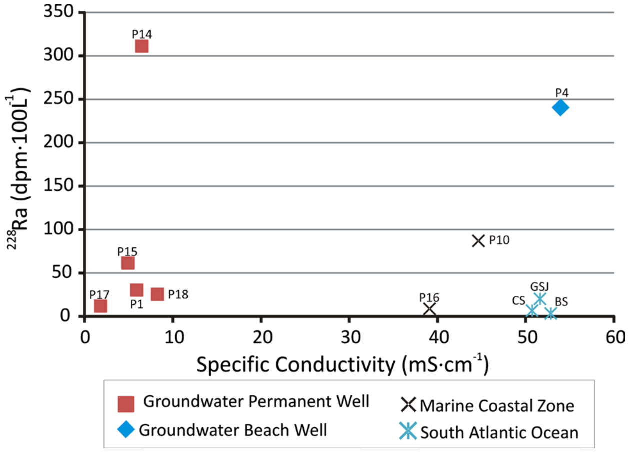

Fig. 2 Relationship between ^{228}Ra activity and specific conductivity in groundwater from permanent and beach wells as well as, in seawater from coastal zone and South Atlantic Ocean

that the sediment mass supplied by eight Patagonian rivers to the South Atlantic shelf is approximately 2.0×10^6 T year^{-1}. Specifically, the Chubut River makes a small contribution to the total suspended particulate material, which is similar to other Patagonian rivers (Gaiero et al. 2003).

Another potential source of radium that could increase its total concentration is fine-grained mud present in the coastal zone (Rodellas et al. 2015). Marine coastal sediment from *Bahía Nueva*, however, (i.e., in front of Puerto Madryn) is mainly sandy (> 50% of the mass of the 63 μm to 2 mm grain-size range), whereas the gravel proportion (> 2 mm) may range between 25 and 62%, and the fine grain-size fraction (silt–clay < 63 μm) can reach 36% by weight (Gil et al. 2014). Therefore, sediment would not contribute to increased radium activity in the studied area because these textural characteristics prevailing in the bottom sediments lead to the hypothesis that the radium supplied by sediments is relatively unimportant. Thus, the presumption that the continental groundwater is mainly responsible for sustaining the high radium activity prevails. Such activity is likely increased by the circulation in the buried estuary. This conjecture stimulates the sustained investigation of, not only the long-lived isotopes, but also the ^{223}Ra and ^{224}Ra isotopes, seeking to obtain an improved evaluation of the SGD by means of the radium quartet.

Radon isotopes

The data obtained with radium isotopes stimulated the investigation of radon activity in the coastal environment, in order to identify its possible sources or sinks. Although this element is not chemically reactive other ocean components (e.g., 4 m-tides, waves, and buoyancy), which may alter radon activity along the coast, should be considered as radon sinks. Any increase in the ^{222}Rn activity in the beach area, higher than the isotopic parental activity, could indicate the presence of an advective process (Burnett and Dulaiova 2003).

Groundwater samples presented the largest ^{222}Rn activity and it ranged from 2.66 to 310 dpm L^{-1} in *Golfo Nuevo* (Fig. 1b), 722 dpm L^{-1} in Puerto Deseado (Fig. 1e) and reaching more than 1000 dpm L^{-1} at *Cabo dos Bahías* (Fig. 1d) (Table 3). According to the literature, studies carried out in *Serra Geral* and *Botucatu* Formation (Brazil) presented an average ^{222}Rn activity of 600 dpm L^{-1} in

Table 3 Activities of ^{222}Rn in water of Chubut River, wells and marine coastal zone from Chubut and Santa Cruz provinces

Origin	Site	Date March 2011	N°	^{222}Rn (dpm·L^{-1})	Uncertainty (dpm·L^{-1})
Groundwater permanent well	Puerto Madryn	11	P6	310	18
	Esperanza 1	13	P1	264	15
	Esperanza 2	13	P2	402	20
	Playa Unión	14	P11	262	16
	Cabo dos Bahías	24	P14	1084	44
	Puerto Deseado 1	22	P17	594	31
	Puerto Deseado 2	22	P18	722	35
	Bustamante	23	P15	243	20
Groundwater beach well	Puerto Madryn 1	10	P7	66.5	8.3
	Puerto Madryn 2	10	P8	24.1	4.8
	Puerto Madryn 3	10	P9	2.66	1.81
Surface fresh water	Chubut River—Rawson	14	P12	10.9	2.2
	Chubut River—Gaiman	14	P13	14.8	2.6
	Puerto Madryn Lagoon	11	P5	4.7	2.4
Marine coastal zone	Esperanza Ocean	23	P3	1.03	0.75
	Puerto Madryn Ocean	15	P10	2.47	2.01
	Ría Deseado	21	P16	6.23	3.77

groundwater obtained from 34 wells (Bonotto and Bueno 2008; Bonotto 2011). In addition, other studies conducted in permanent groundwater wells in *Rio Grande do Sul State* (Southern Brazil) reported an average value of 380 dpm L^{-1} (Santos et al. 2008), which was similar to 360 dpm L^{-1} reported in this study. In surface fresh water, ^{222}Rn activity reached 4.74 dpm L^{-1} in Puerto Madryn's pond and 1484 dpm L^{-1} in the Chubut River.

As expected, a lower ^{222}Rn activity was found in the coastal marine environment (1.03–6.2 dpm L^{-1}). The ^{222}Rn activities measured in Patagonia were significant when compared with the values found in Southern Brazil (0.25–0.47 dpm L^{-1}, Andrade 2010) and Uruguay (0.30 ± 0.10 dpm L^{-1}).

The fact that the beach region, with intense hydrodynamic processes, presents a high ^{222}Rn activity indicates that the SGD may be active in maintaining such activity. Similar ^{222}Rn activities were used in other studies as evidence of intense SGD (Cable et al. 2004; Burnett et al. 1996; Burnett and Dulaiova 2003, 2006).

Finally, the radon results reported in this study show that permanent wells close to the beach have shown the highest ^{222}Rn activities and lowest specific conductivity levels (Fig. 3). Moreover, in the marine coastal environment, the activity of ^{222}Rn was higher than those found for the southern region of Brazil and Uruguay. This leads to the speculation that these high activities are a consequence of the contribution of either the sediments themselves or the action of the SGD, enhanced by tidal pumping.

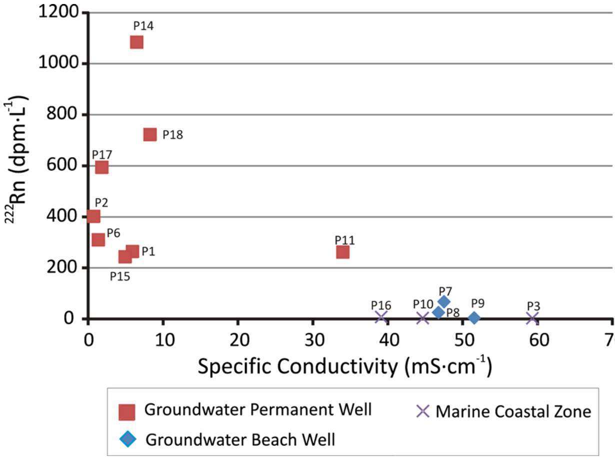

Fig. 3 Relationship between ^{222}Rn activity and specific conductivity in groundwater from permanent and beach wells and seawater from coastal zone of Chubut and Santa Cruz provinces in the Argentina Patagonian

Conclusion

Salinity, radon and radium isotopes are useful tracers in this environment, showing water flowing across the sediment–water interface and into the overlying water column, regardless of composition. Our data set includes riverine freshwater, terrestrial groundwater and saline, recirculated seawater.

The dataset suggest that SGD can be an important process in this particular stretch of Patagonia's coastal region, where the hydraulic gradient certainly is the main driving force that results in fresh, terrestrial aquifer waters discharging at the coastline. Other driving forces that control recirculated seawater, as tidal pumping and wave setup, are very significant.

As SGD causes both positive and negative effects in the biogeochemical cycles of the coastal environments, we suggest that measurements of radium and radon isotopes should continue to be obtained, in both high resolution time series and horizontal offshore transects, to allow quantifying the offshore transport rates of discharged continental groundwater. Considering that the SGD has important implications in the biogeochemical cycles of coastal environments, future studies in this region should complement isotopic measurements with determinations of inorganic nutrients, iron, carbon, rare earth elements, and toxic metals.

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