Environmental Earth Sciences (2021) 80:109
https://doi.org/10.1007/s12665-021-09388-x

THEMATIC ISSUE

Variability of ^{222}Rn in the sandy aquifer of Buenos Aires coast

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Received: 28 November 2019 / Accepted: 14 January 2021 / Published online: 31 January 2021

Abstract

^{222}Rn is widely used as a tracer to detect and calculate submarine groundwater discharge in coastal zones, rivers and lakes. Relatively few investigations, however, have used this element for other applications in hydrogeology. We analyze the relationship between ^{222}Rn activity in groundwater and variations in the water cycle in the sandy aquifer of Buenos Aires coast, Argentina. Groundwater levels, electrical conductivity and ^{222}Rn activity were measured in situ in wells in March 2016 and November 2018, representing two different hydrological conditions. Groundwater flow maps were drawn, hydrological gradients and flux velocities were calculated. An inverse correlation between ^{222}Rn activity and recharge conditions was found. Lower water surplus shows higher ^{222}Rn activity and vice versa, potentially due to dilution of high ^{222}Rn activity water with 'newer' lower activity recent recharge. A variability in ^{222}Rn spatial distribution was identified along the sand dune barrier. A correlation between ^{222}Rn and groundwater electrical conductivity was not observed.

Keywords Radon · Hydrological cycle · Sand dune barrier · Buenos Aires

Introduction

^{222}Rn is considered to be an important tracer of hydrogeological processes. One of its more common roles is as a tracer to detect and calculate submarine groundwater discharge (SGD) in coastal zones, rivers and lake systems (i.e., Burnett and Dulaiova 2003; Burnett and Dulaiova, 2006; Burnet et al. 2008; Rapaglia et al. 2015; Carretero et al. 2019; Wang et al. 2019). Meanwhile, Hamada (2000) proposed a method for estimating groundwater flow rate using ^{222}Rn decay in a well. Schubert et al. (2011) took the approach introduced by Hamada (2000) and made modifications to the theoretical framework and equations so they can be applied to higher flow velocities. Mayer et al. (2016) attempted to highlight the effects of aquifer heterogeneity and the freshwater/saltwater interface by repeating the experience of Schubert et al. (2011) at three depths. Kafri (2001) presented cases from Israel employing the decay rate of radon along the flow path to assess groundwater flow velocities.

There are currently little data published regarding radon and its spatial and temporal variability in groundwater related to the water cycle. Kasztovszky et al. (2000) studied the variation of ^{222}Rn activity in groundwater in an area of Northeastern Hungary. These authors found that the observed radon activity of some wells show unpredictable variability both in space and time. ^{222}Rn activity in water and soil were strongly modified by some external conditions, the most significant of which was the variation of air pressure. Mullinger et al. (2009) demonstrated that in an area of the United Kingdom, seasonal changes in water table elevation lead to variable radon activity in groundwater. ^{222}Rn activity in shallow piezometers was found to respond to both seasonal changes in the water table and individual

This article is a part of the Topical Collection in Environmental Earth Sciences on "Advances in Environmental Geochemistry" guest edited by Dr. Eleanor Carol, Dr. Lucia Santucci and Dr. Lia Botto.

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rainfall events. Ball et al. (1991) studied the role of soil type and climate variables (wind, atmospheric pressure, relative humidity). They found that pore-sealing effects of moisture near the surface can result in temporary entrapment of radon in soil gases, with a significant increase in the total gamma activity. Hoehn and Gunten (1989) measured the radon activity in groundwater as a tool to assess infiltration from surface waters to aquifers.

As was stated above, the application of ^{222}Rn measurements in case studies not focused on SGD estimations are limited; the relationship between ^{222}Rn activity and the hydrological cycle is not widely addressed. The aim of this work was to analyze the relationship between ^{222}Rn activity in groundwater and variations in the water cycle in the sandy aquifer of the Buenos Aires coast, Argentina. Novel data are presented, which may shed some light on hydrogeological processes in the study area.

Study area

The study area (Fig. 1) lies in the sandy coast of Buenos Aires Province, Argentina, which includes the districts of Partido de La Costa (PDLC) (northern sector) and Partido de Pinamar (southern sector). These districts constitute one of the most important tourist destinations in the country.

The drinking water supply depends exclusively on groundwater sources. As most of the localities in the PDLC do not have a centralized drinking water supply, domestic wells provide water without treatment for the majority of the population. Only a small percentage of the inhabitants of San Clemente del Tuyú, San Bernardo and Mar de Ajó are connected to a local water supply network. In Pinamar, the population is served by means of a system operated through a sanitation service provider.

The climate of this coastal region can be described as humid temperate and is marked by a dry season which coincides—in the southern hemisphere—with the coldest months (April–September) and a rainy season during the warmest months (October–March). The mean annual precipitation fluctuates between 900 and 1000 mm, with 60% of the precipitation occurring during months with higher evapotranspiration. Therefore, contrary to logical thought, the highest groundwater recharge values can be found in the dry season (Carretero and Kruse 2012). Such recharge is driven by the precipitation surplus (precipitation minus evapotranspiration), rather than the overall precipitation.

The sand dune barrier system has a width ranging from 2 to 4 km. To the west, it borders the continental plain, which is characterized by heights below 2 m a.s.l. (meters above sea level) and by the predominance of silty and clayey materials. In the northern area, this environment is characterized by gullies oriented in a southeast–northwest direction draining towards the Samborombón Bay. The continental plain landscape is prone to flooding, with clayey soils (Vertisols) (Soil Survey Staff 2014).

In the north, the dunes in the barrier are between 2 and 11 m a.s.l., whereas to the south the dunes reach topographic heights between 35 and 40 m a.s.l. In this environment, soils are sandy, with no horizon development, excessively drained and unstable. The soil development depends on the stability of the sand accumulations and, in general, soils are Typic Torripsamments and Quartzipsamments (Soil Survey Staff 2014).

The hydrogeological system is composed of five hydrofacies. Hydrofacies A, C and E are aquifer units, whereas hydrofacies B and D are aquitard units and occur in between the former (Fig. 2a).

In the PDLC, hydrofacies A and C (combined thicknesses less than 12 m) are the aquifer units that supply water to the population (Fig. 2b). Hydrofacies D constitutes the hydrogeological basement which consists of a clayey complex in this area. The water table depths oscillate from 1 to 3 m b.g.l (meters below ground level) (Carretero 2011).

In Pinamar, the system is formed by three aquifer layers A, C and E whose exploited thickness is between 20 and 45 m. The water supply is obtained from these three aquifer layers, constituting—depending on the occurrence and composition of the less permeable layers (aquitards)—a hydraulically interconnected system. In Pinamar, the water table is at a depth of over 6 m b.g.l. (Rodrigues Capitulo 2015) which is more than twice the water table depth in PDLC.

The groundwater flow path corresponds to equipotential curves parallel to the coastline. It is separated by a groundwater divide which coincides with the maximum topographic height and has a hydraulic gradient that ranges from 1 to 4 m/km. From the divide, groundwater flows into two directions, towards the east (sea) and towards the west (continent). Two interfaces were recognized, a freshwater–brackish water interface towards the continental plain and a freshwater–saltwater interface towards the sea. The geomorphological environment determines the aquifer hydrodynamic and hydrochemical behavior. Groundwater In the sand dune barrier mainly consists of the Ca-HCO_3 and Na-HCO_3 types, and exhibits low salinity (TDS < 1500 mg/L). In the continental plain, groundwater is of the Na-Cl type and shows high salinity (TDS > 3000 mg/L) (Carretero et al. 2013).

In the PDLC, a chemical zonation and a vertical gradient of electrical conductivity, which increases abruptly at a depth of 5–7 m, was found. This phenomenon limits the thickness of the aquifer related to groundwater quality.

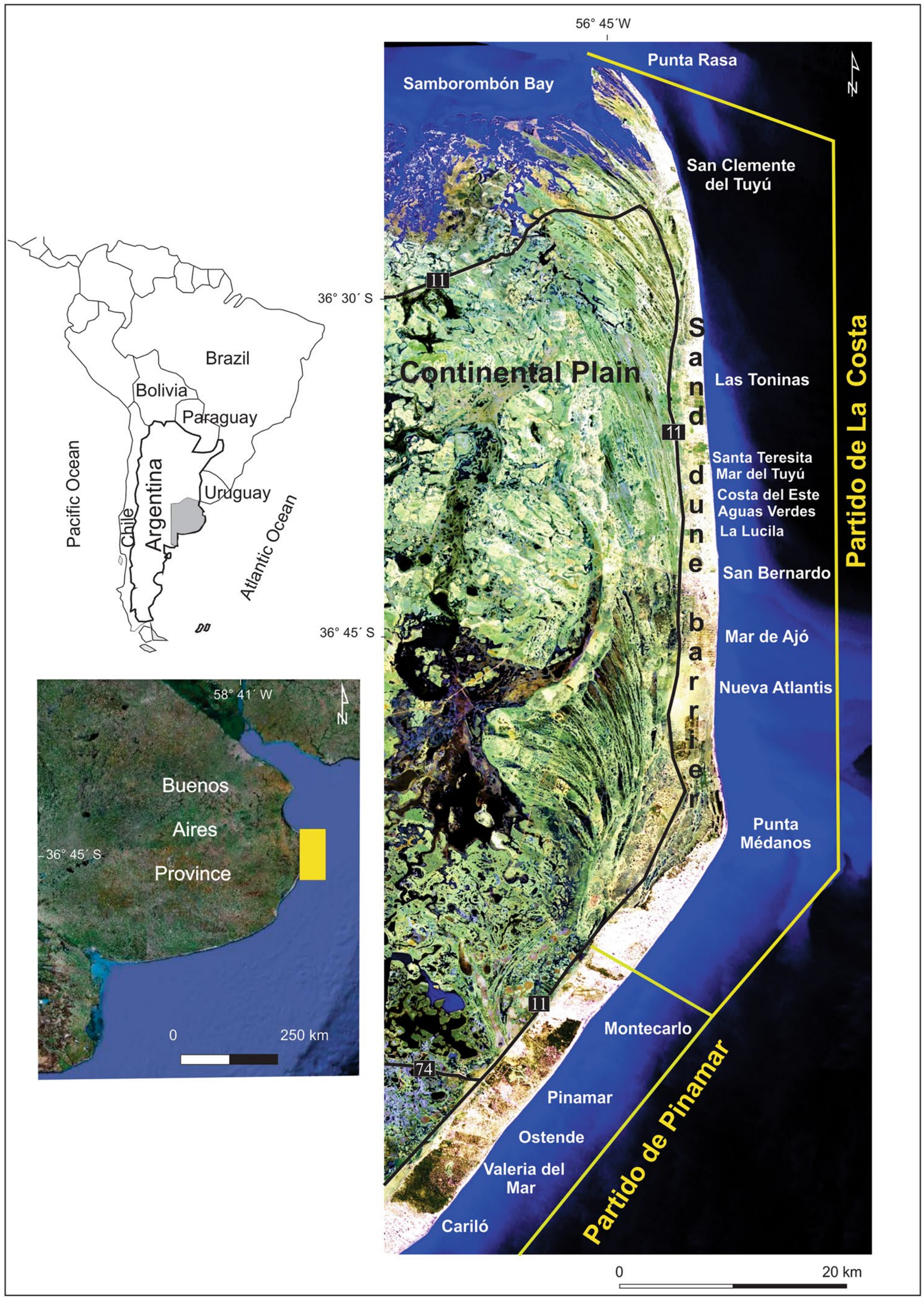

Fig. 1 Study area, showing the localities along the PDLC and Pinamar and the geomorphological environments

A similar pattern is not observed in the aquifer system of Pinamar, which is defined by a thick, high-quality aquifer.

Isolated occurrences of salinization processes can be recognized, both in the northern sector (Santa Teresita) and in the southern sector (Pinamar, Valeria del Mar and Cariló). These processes are related to the intensive extraction of the groundwater, which can be verified by the major increase in electrical conductivity values in wells close to the coastline.

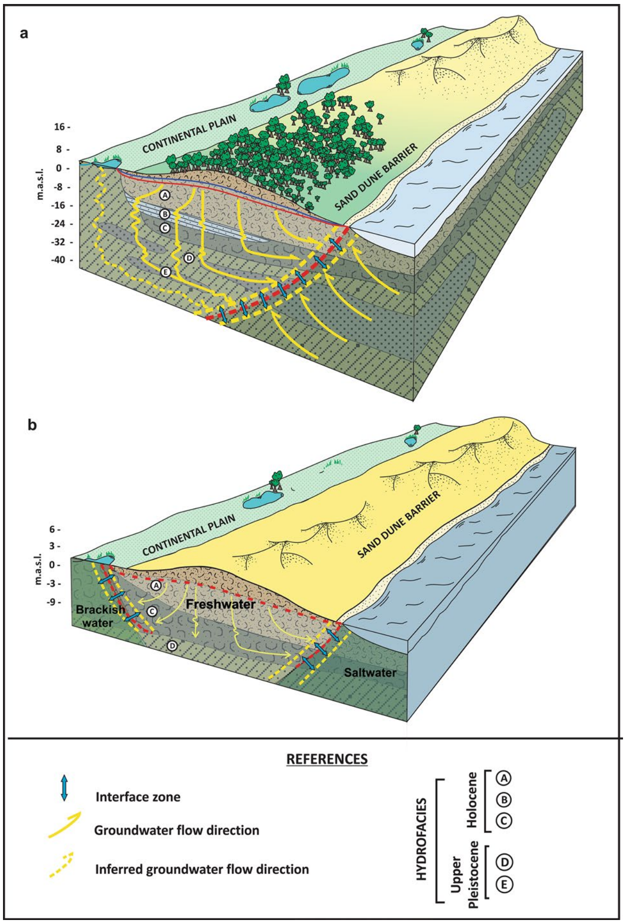

Fig. 2 Hydrogeological and geomorphological scheme for **a** Pinamar; **b** PDLC

Materials and methods

In March 2016 and November 2018, field work was carried out in the coast of Buenos Aires province. Piezometers in the PDLC were evaluated in both sampling campaigns, but Pinamar wells were only included in the field campaign of 2018.

Wells located in the main groundwater recharge area, discharge area and areas affected by saltwater intrusion were selected (Fig. 3). The analyzed wells are part of a monitoring network which comprises wells drilled into the phreatic aquifer between 3 and 6 m deep. Wells identified as PR (Fig. 3) are exploratory boreholes and were drilled covering the total thickness of the aquifer (12 m).

Groundwater depth, electrical conductivity (EC) and ^{222}Rn activity were measured in situ. ^{222}Rn activity was counted using a Durridge radon-in-air detection system (RAD7) modified to measure radon in water via gas exchange (Burnett and Dulaiova 2003) through a 3 M Liqui-Cel mini-module membrane filter, which allows the separation of ^{222}Rn from the water passing through the filter. The gas enters the RAD7 system. Water was pumped into the mini-module via a peristaltic pump at a rate of 0.5–0.8 L/min. Well water was pumped through a mini-module until an equilibrium activity was reached in the detector (~ 35 min).

To evaluate the hydrological conditions for each field site, a daily water balance (Thornthwaite and Mather 1955) was performed via the calculation of the water surplus. Data correspond to daily precipitation from a meteorological station located in San Clemente del Tuyú for the periods April

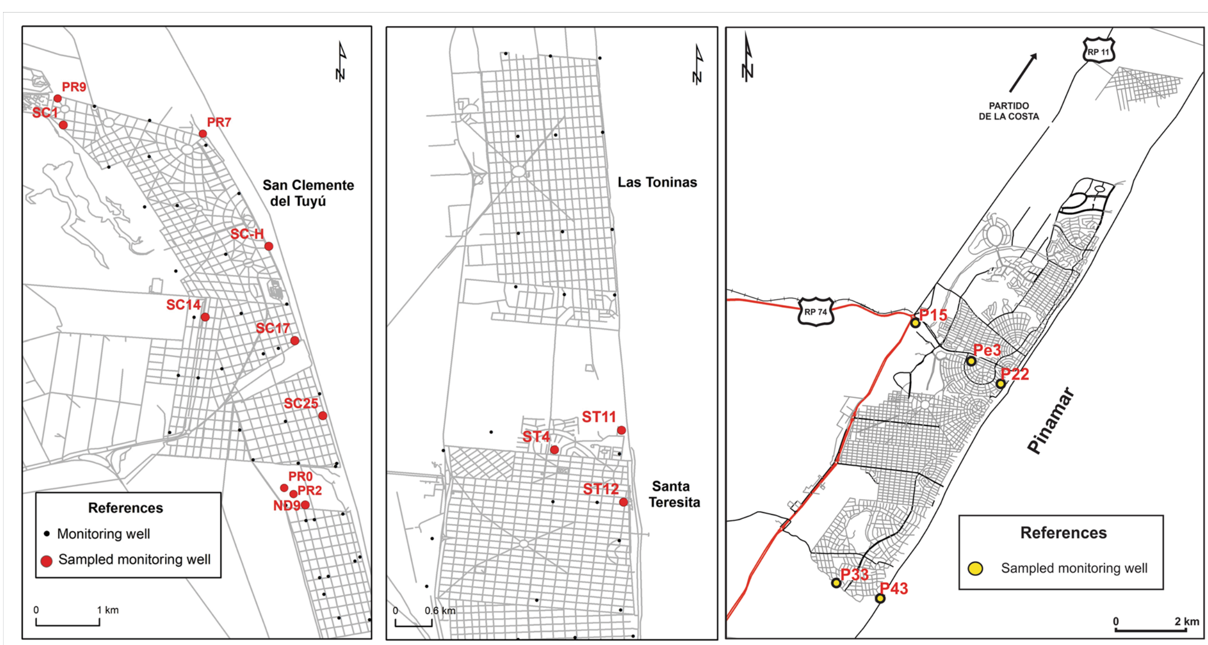

Fig. 3 Sampling area: well location

2015–March 2016 and April 2018–March 2019. The daily mean reference evapotranspiration (Et_o) was determined according to the FAO Penman–Monteith method (Allen et al. 1998). The water balance was calculated using the AGROAGUA v.5.0 software (Forte Lay et al. 1995), which performs daily water balances and continuously monitor soil water storage, using daily rainfall, daily potential evapotranspiration and soil field capacity variables. In the case of immature, sandy soils with sparse vegetation and an effective depth for the water balance of 0.25 m—which characterize the coastal sand dune barrier—,a field capacity of 40 mm was assigned.

Due to the characteristics of the soil (high permeability of sediments) (Sala et al. 1976), no surface runoff processes can be observed, and it is considered that the water balance surplus is transformed directly into effective recharge to the aquifer (common in sandy barrier environments).

Results

Water balance

The water balance shows that, for both hydrological cycles (2015–2016 and 2018–2019), rainfall mainly occurs during the cold season (> 70%), which is not coincident with the normal pattern. In other words, even though there is commonly a greater surplus in the cold season due to lower evapotranspiration, it has been augmented here due to higher than normal precipitation (Table 1). The hydrological conditions during the two sampling campaigns were very different. For the warm season of the hydrological cycle 2015–2016, the water surplus value (March 2016) is 7 mm. Meanwhile, water surplus reaches 324 mm during the cold season of the hydrological cycle 2018–2019, which is representative

Table 1 Results of the water balance for the hydrological years considering cold and warm seasons

		Month	P[a] (mm)	PET[b] (mm)	AET[c] (mm)	Surplus (mm)
Hydrological year 2015–2016	**Cold season**	Apr-15	34	67.8	24.1	0
		May-15	140	49	37.4	88.7
		Jun-15	0	37.1	18.3	0
		Jul-15	70	37.2	11.3	29.7
		Aug-15	236	48.9	42.6	205
		Sep-15	15	58.2	26.5	0
		Total season	**495**	**298**	**160**	**324**
	Warm season	Oct-15	42	65.1	42.8	0
		Nov-15	24	63	24.6	0
		Dec-15	45	63	26.2	7
		Jan-16	0	65.5	19.9	0
		Feb-16	37	64.3	25.7	0
		Mar-16	38	75.3	40.9	0
		Total season	**186**	**396.2**	**180.1**	**7**
		Total year	**681**	**694**	**340**	**331**
Hydrological year 2018–2019	**Cold season**	Apr-18	157	67.7	51.4	102.3
		May-18	158	51	39.3	100.5
		Jun-18	10	36.6	26.7	0
		Jul-18	103	37.7	30	64.4
		Aug-18	13	50.3	30.6	0
		Sep-18	105	58.3	24.9	56.6
		Total season	**546**	**302**	**203**	**324**
	Warm season	Oct-18	10	65	31	0
		Nov-18	45	64	36	7
		Dec-18	72	66	40	10
		Jan-19	71	66	46	51
		Feb-19	10	61	12	0
		Mar-19	152	73	54	91
		Total season	**360**	**395**	**219**	**159**
		Total year	**906**	**697**	**422**	**483**

[a]*P* precipitation, [b]*PET* potential evapotranspiration, [c]*AET* actual evapotranspiration

The total values are in bold. Also the month March-16 and Nov-18 when the samples were taken of the November 2018 survey. Hence, the March 2016 data represent the lowest water levels of the year and the November 2018 data represent the highest water levels. The total surplus for the cold season and October–November 2018 is of 331 mm. Usually October and November, in every hydrological year, are the months which present the highest water table level as consequence of the highest recharge during the prior cold season. On the contrary, March, at the end of the warm season, presents the lowest water table level due to higher evapotranspiration and lower recharge.

Hydrodynamics

The groundwater flow maps reflect the hydrological characteristics of the region. The water table contour maps show that the isophreatic curves increase from north to south. Two main directions of regional discharge can be observed, towards the west to the continental plain and, towards the east, to the sea (Fig. 4).

In March 2016, the water table contour maps for the localities of the PDLC show that in San Clemente (Fig. 4) the curves fluctuate between 0.5 and 2 m a.s.l. The highest water table heights are detected in the southern area of the town. Las Toninas is characterized by water levels between 1.5 and 3 m a.s.l. In Santa Teresita, the highest water level was found to be 1.5 m a.s.l. In general, this town shows the lowest water levels and there are sections along Coastal Avenue with curves below mean sea level, where saltwater intrusion process was detected.

For the PDLC, the calculated average hydraulic gradient is 0.0012, whereas an effective velocity of 0.24 m/day was estimated.

In November 2018 (Fig. 4), the maps drawn for San Clemente show that water table level fluctuates between 1 and 3 m a.s.l., also with the highest water table heights in the southern sector of the town. In las Toninas and Santa Teresita, the curves fluctuate between 1 and 4.5 m a.s.l. The average hydraulic gradient is of 0.0016 and the effective velocity of 0.32 m/day.

Pinamar is characterized by water levels between 1 and 13 m a.s.l. with some values below mean sea level associated to pumping wells close to the coastline (Fig. 5). An average hydraulic gradient of 0.004 and an effective velocity of 0.88 m/day were calculated.

Variation in electrical conductivity

Electrical conductivity (EC) values were, in general, lower than 2000 µS/cm with the exception of wells related to the interface between fresh water and salt/brackish water or in wells affected by saltwater intrusion.

In the sand dune barrier, changes in EC between samplings were heterogeneous (Table 2). According to water balance results, lower EC values would be expected in November 2018 when compared to March 2016, due to a dilution process caused by a greater water surplus and recharge. However, this was not necessarily the case; wells SC25, SC14, SC-H and ST12 all show an increase in EC, while wells SC1, SC17, ND9, ST11 and ST4 show a decrease in EC concentration. ST12 is affected by saltwater intrusion, and SC1 is influenced by brackish water from the bay, hence these two wells cannot be taken into consideration for the comparison.

Wells ND9 and ST14 are located in the main recharge area of the sand dune barrier and they show a decrease in EC values, which is expected with higher recharge, but elsewhere, the wells in the discharge sector show both increases and decreases in EC, hence it can be said that the effect of recharge on EC is inconclusive.

Variation in ^{222}Rn activity

^{222}Rn and its relationship with water cycle conditions and environmental settings

Radon in aquifers reaches 99% of its steady state activity in 25 days or less (Hoehn et al. 1992) and hence, in many cases, we can say that radon is in steady state and the only changes in the radon activity are due to dilution with new precipitation. The average ^{222}Rn activity for March 2016 in the PDLC was 11023 ± 1326 Bq/m^3 while in November 2018, it was 5502 ± 958 Bq/m^3. In Pinamar, ^{222}Rn activity is more homogeneous with an average value of 1600 ± 569 Bq/m^3 and is the lowest in the study area.

^{222}Rn activity in our study area does not seem to be affected by high salinity, suggesting that the high salt content groundwater have reached equilibrium with the surrounding sediments (wells SC1, SC12, P43).

When comparing the hydrogeological and radon data from March 2016 with November 2018, a clear pattern is observed. During March 2016 (low aquifer recharge), we find higher ^{222}Rn activity (average values of 11023 ± 1326 Bq/m^3) associated with lower effective velocities (0.24 m/day). Meanwhile in November 2018 (high water surplus), higher effective velocities (0.32 m/day) corresponded to lower ^{222}Rn activity (average values of 5502 ± 958 Bq/m^3).

Higher water tables are also associated with the higher water surplus (331 mm) that was observed during this sampling period.

In the case of Pinamar, the highest effective velocity (0.88 m/day) was observed, which led to the lowest ^{222}Rn activity (average values of 1600 ± 569 Bq/m^3). These observations are important for understanding the utility of ^{222}Rn in mass balance analyses.

Meanwhile within the PDLC itself, different ^{222}Rn activities were observed for each sampling campaign according to well location. In the sand dune barrier, transitional to the

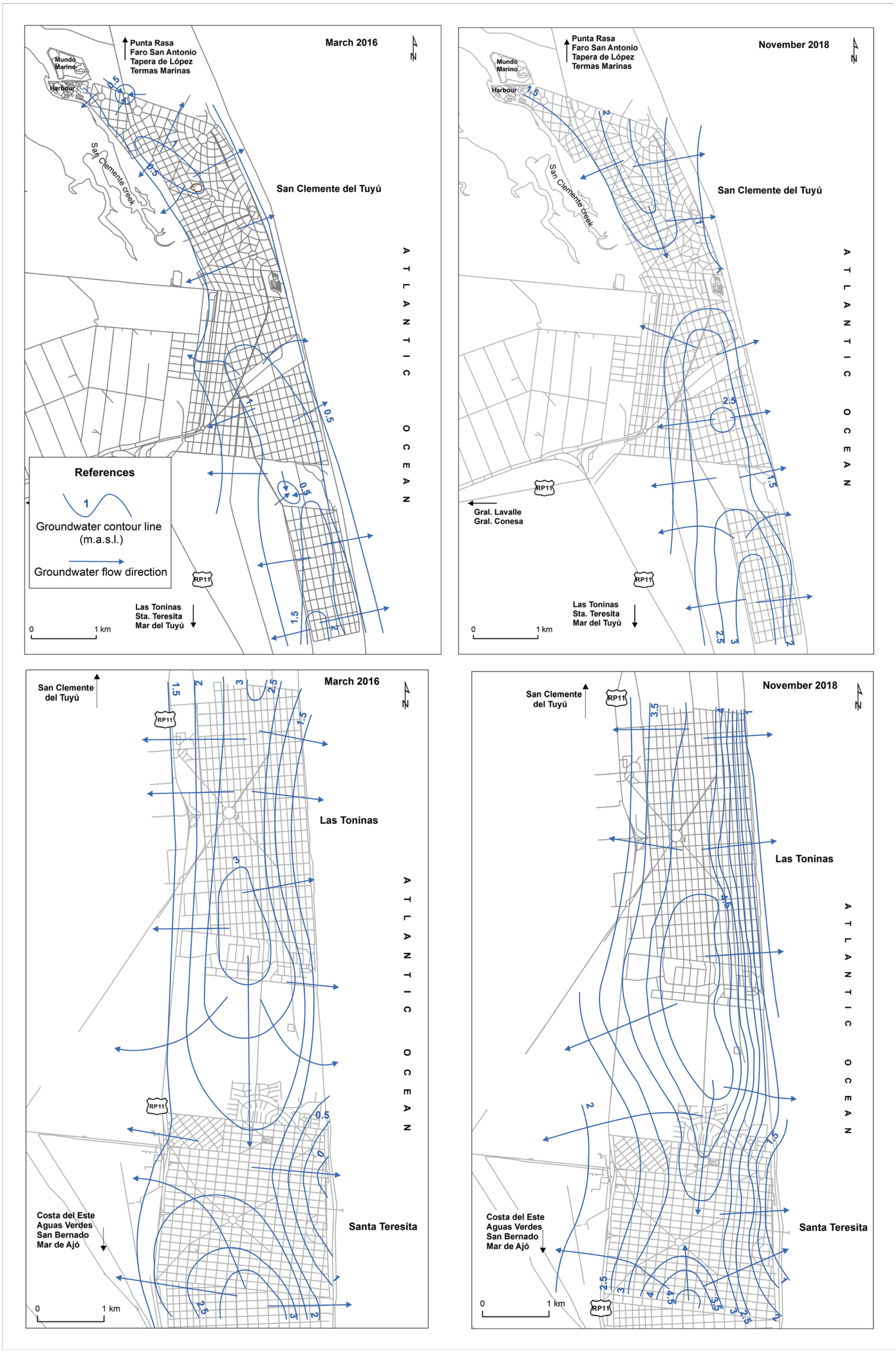

Fig. 4 Groundwater flow maps for the PDLC in March 2016 and November 2018

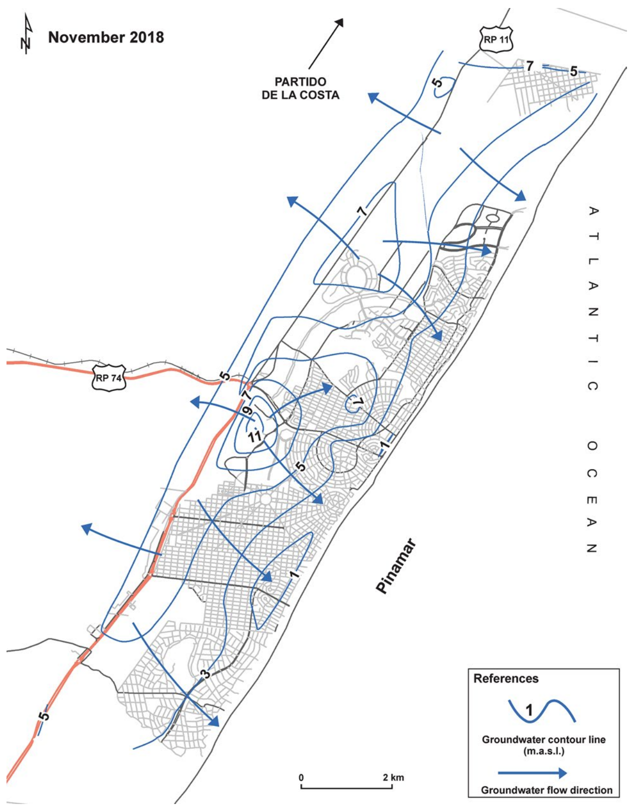

Fig. 5 Groundwater flow maps for Pinamar in November 2018

coastal plain environment (Fig. 6a, b), in March 2016, radon activity was 9750 ± 1250 Bq/m^3 whereas in November 2018, it was of 7000 ± 1096 Bq/m^3, a decrease of 28%.

Separating the sand dune barrier into the discharge and recharge areas, we see a further distinction. The discharge area is characterized by a higher average ^{222}Rn activity in both seasons, even though a decrease from 10590 ± 1281 Bq/m^3 (March 2016) to 5920 ± 998 Bq/m^3 (November 2018) is registered, which means a reduction of 44%. For 2016, ^{222}Rn values are more widely distributed while in 2018 they seem to be more clumped together. Note, well SC25 presented the highest value in both sampling campaigns (Fig. 6e, f).

In the sand dune barrier, in the main recharge area, during the first sampling campaign, the average ^{222}Rn activity was 8920 ± 1010 Bq/m^3, whereas it was significantly lower during the second sampling period (1973 ± 478 Bq/m^3). This represents a reduction of 78% in ^{222}Rn activity between both sampling periods. In this environment, the ^{222}Rn decrease was the highest. This is the largest decrease in radon seen along the PDLC.

In Pinamar, average ^{222}Rn activity for the continental plain, and the sand dune recharge and discharge to the sea sectors are 1420 ± 541, 1680 ± 581 and 1610 ± 572 Bq/m^3, respectively, showing a more homogeneous distribution than in the PDLC.

Variation with depth

In the northern sector of the PDLC, the aquifer thickness is limited by a chemical zonation and a vertical gradient of

Table 2 Field data for the sampled wells in March 2016 and November 2018

	Well	Depth (m)		EC (μS/cm)		^{222}Rn (Bq/m^3)		Environment/observations
		Mar-16	Nov-18	Mar-16	Nov-18	Mar-16	Nov-18	
PDLC	SC25	1.66	1.20	805	1047	18000 ± 1800	9780 ± 1320	
	SC1	1.03	0.37	18,772	12,260	11000 ± 1300	8700 ± 1210	Sand dune barrier transitional to the coastal plain. Influenced by brackish water
	SC17	1.69	1.13	818	775	1630 ± 580	6220 ± 1050	Sand dune barrier—discharge to the sea
	SC14	1.32	1.10	1122	1906	8500 ± 1200	5300 ± 982	Sand dune barrier transitional to the coastal plain
	SC-H			913	1365	4630 ± 874	7810 ± 1190	Sand dune barrier—discharge to the sea
	ND9	2.04	0.88	1762	1562	11500 ± 1400	4710 ± 925	Sand dune barrier. Main recharge sector
	ST12	4.00	3.25	30,600	31,600	13250 ± 1500	1320 ± 526	Sand dune barrier—discharge to the sea. Affected by saltwater intrusion
	ST11	2.02	1.37	787	759	15440 ± 1630	4470 ± 906	Sand dune barrier—discharge to the sea
	ST4	3.70	2.11	2033	2020	15260 ± 1630	1210 ± 509	Sand dune barrier. Main recharge sector
Pinamar	P15		2.03		1414		1420 ± 541	Sand dune barrier transitional to the coastal plain
	Pe3		6.69		353		1320 ± 526	Sand dune barrier. Main recharge sector
	P43		1.56		5320		1730 ± 590	Sand dune barrier—discharge to the sea. Affected by saltwater intrusion
	P22		4.5		623		1490 ± 553	Sand dune barrier—discharge to the sea
	P33		7.48		577		2040 ± 636	Sand dune barrier. Main recharge sector

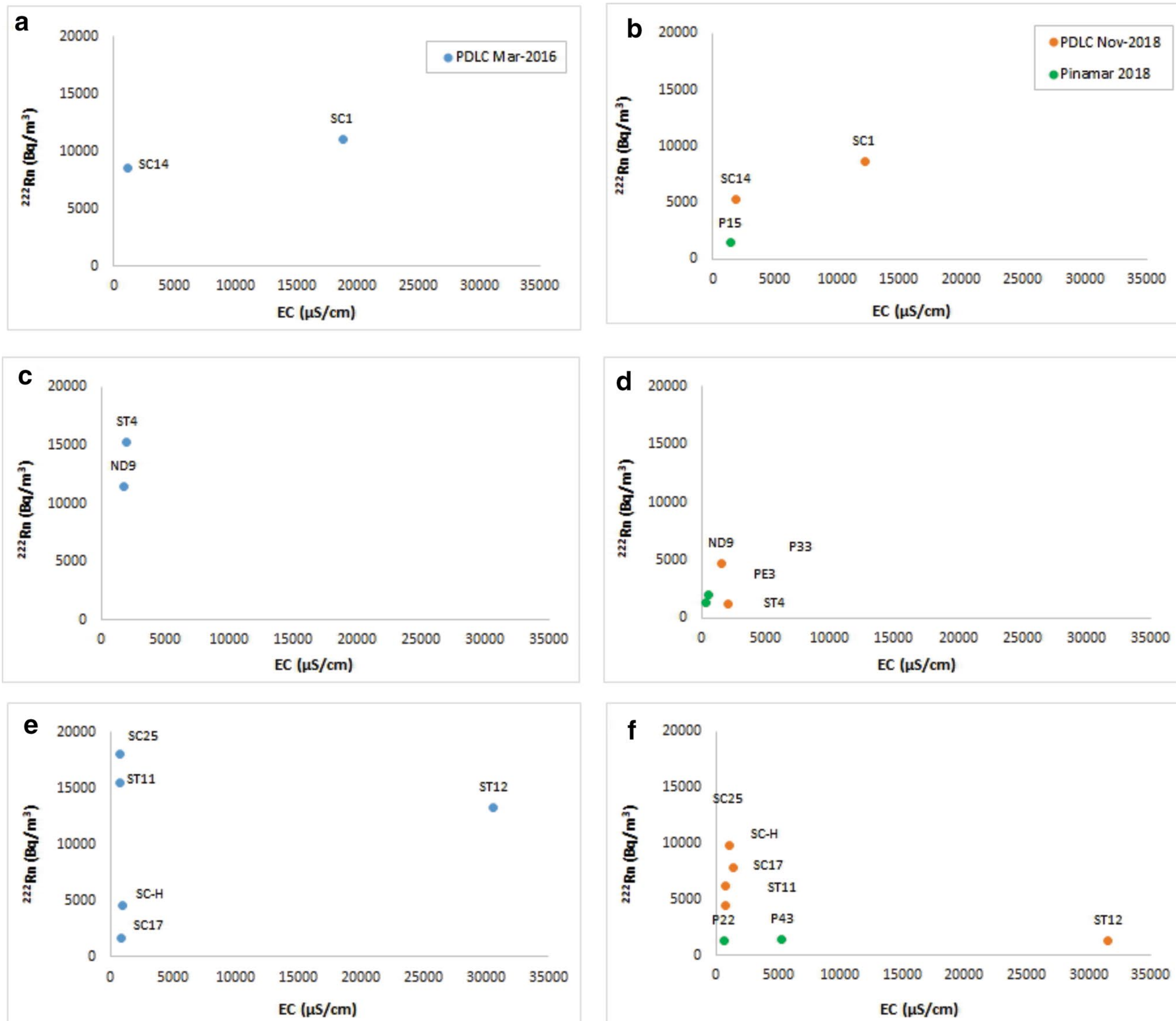

Fig. 6. ^{222}Rn activity vs EC for both sampling dates and according to the well location. **a**, **b** Sand dune barrier transitional to the coastal plain. Influenced by brackish water; **c**, **d** Sand dune barrier, main recharge sector; **e**, **f** Sand dune barrier, discharge to the sea

Table 3 Samples taken in November 2018 in wells with chemical zonation

Well	Sample #	Sampling depth (m b.g.l.)	EC (µS/cm)	T (°C)	^{222}Rn (Bq/m^3)	Environment/observations
PR9	PR9 (1)	1.5	5400	19.8	4530 ± 914	Sand dune barrier transitional to the coastal plain. Influenced by brackish water
	PR9 (2)	7.5	38,400	18.5	3690 ± 833	
PR7	PR7 (1)	1.5	610	17.9	4420 ± 907	Sand dune barrier. Discharge to the sea
	PR7 (2)	7.5	34,100	17.5	2940 ± 751	
PR0	PR0 (1)	2	2410	22.6	2160 ± 654	Sand dune barrier. Main recharge sector
	PR0 (2)	9.5	16,900	21.5	1900 ± 618	
PR2	PR2 (1)	2	1766	22.4	1900 ± 618	Sand dune barrier. Main recharge sector
	PR2 (2)	9.5	18,750	21.5	4050 + 866	

electrical conductivity, which increases abruptly at a depth of 5–7 m. ^{222}Rn was measured in both chemical zones and the results are shown in Table 3.

Higher ^{222}Rn activities were found in the shallow samples, except for well PR2, showing an inverse correlation between ^{222}Rn and EC. Decrease in ^{222}Rn activity from shallow to deep samples in well PR9 was of 19%, for well PR7 was of 33% and for PR0 was of 12%. ^{222}Rn activity increases 113% from shallow to deep groundwater in PR2.

The correlation between shallow groundwater ^{222}Rn activity and the geomorphological environment location of the wells is also observed in these wells. Lower values were measured in the recharge zone (~ 2000 Bq/m^3) and higher values in the discharge areas (~ 4500 Bq/m^3).

Discussion

EC variability

According to the results of the water balance, it would be expected that EC in November 2018 were lower than in March 2016 due to a dilution process because of a greater water surplus. This phenomenon had been previously observed in the sand dune environment by Carretero et al. (2013) where samples from October 2006 (warm season, EC = 1279 µS/cm) and July 2008 (cold season, CE = 961 µS/cm) were analyzed. Average EC values show that concentration in July 2008 was 25% lower than in October 2006, however, if taking into consideration later sampling (not published), a great variability is shown in the sand dune barrier.

The average EC in different years of sampling during the cold season (July 2008 = 961 µS/cm, July 2009 = 981 µS/cm and July 2013 = 1281 µS/cm) shows a variability that fluctuates between 2 and 33%. If the average EC value in the warm season (March 2010 = 1101 µS/cm) is included in the comparison, the difference oscillates from 12 to 14% with EC concentrations in March 2010 higher than in July 2008 and 2009, and lower than in July 2013. Surplus from the water balance before March 2010 sampling was of 154 mm while the average for the months of July was of 32 mm. Therefore, it should be expected that EC in March 2010 were lower due to dilution but it was not the case. Hence, EC concentration may not be dependent of seasonal changes.

A possible explanation to this lack of correlation could be the variability of EC in the rainfall that recharges the aquifer. Electrical conductivity has been measured in individual rain events between April-15 and April-19 in which a great heterogeneity has been observed. There are values ranging from 5 to 2950 µS/cm with an average of 336 µS/cm. Such a large range of EC values could seem unreasonable, but they have been observed in several areas. For instance, in Zadar, Croatia (Lekouch et al. 2010), EC in rain ranges from 6 and 4980 µS/cm with a mean EC of 132 µS/cm. Rain values ranging from 5.5 to 389 µS/cm with a mean value of 50.7 µS/cm were measured in the coastal zone of Bordeaux, France (Beysens et al. 2006). Meanwhile in the coastal zone of Hong Kong, according to the research by Sequeira and Lung (1995), the mode is around 15–20 µS/cm, but there are extreme values of 525 µS/cm. Along the Korean peninsula, maximum rain EC concentrations are up to 400 µS/cm, and the mode is represented for values lower than 400 µS/cm (Lee et al. 2000). Therefore, EC in rain samples in Buenos Aires coastal area are within the range of concentration mentioned for rainfall in other regions.

If the precipitation prior to the sampling campaigns in March-16 and November-18 are taken into consideration, some observations can be made. The average EC of rain samples collected between October-15 and March-16 is 153 µS/cm. The rain event in March-16 shows an EC value of 461 µS/cm. On the other hand, the average EC for the precipitation events during the cold season before the November-18 sampling campaign is 11 µS/cm. However, if we focus on the rain events that occurred close to the groundwater sampling date, much higher values are observed. On October-18, an individual rain event with an EC of 2950 µS/cm was detected and in November-18, two rain events with an EC of 910 and 659 µS/cm were measured. The average EC of these three rainfall events before the groundwater sampling is of 1506 µS/cm which could explain the higher EC values obtained in groundwater in this period.

On the other hand, in the continental plain environment, average EC in October 2006 (4237 µS/cm) was significantly lower than in July 2008 (6685 µS/cm) (Carretero et al. 2013) leading to an overall increase of 44%. The connection of this environment with the Samborombón Bay through tidal channels and the tidal influence are factors that could modify the groundwater chemical composition, concealing any seasonal effects. In addition, the area is affected by storm surges locally known as southeasters (D'Onofrio et al. 2008), which are strong winds from the east–southeast direction that cause an additional mean water level rise and the advance of the brackish water from the bay towards the continental plain, modifying the concentration of the chemical components and, consequently, the groundwater. Saltwater intrusion into coastal aquifers via marine flooding is a well-known phenomenon where there is a strong hydrological connection between the coastal aquifer and the sea.

In the continental plain part of the aquifer, average EC during the same months considered in the analysis of the sand dune barrier is more homogenous between seasons (July 2008 = 6685 µS/cm, July 2009 = 9153 µS/cm and July 2013 = 8768 µS/cm, March 2010 = 7230 µS/cm). Sample SC1, collected in the continental plain for the present study shows a higher EC value in March 2016.

No correlation between ^{222}Rn activity and EC was observed in this work. Radon activity seems to present an inverse correlation with the variations in the water cycle conditions. The lack of correlation between radon and EC in groundwater was also observed by Srilatha et al. (2014) in two districts in India. On the other hand, Akawwi (2014) studied the ^{222}Rn activity in the groundwater along Eastern Jordan Rift and found a negative correlation between radon and EC. A positive correlation has been observed between the ^{222}Rn activity and EC in thermal springs in Turkey by Tabar and Yakurt (2014), but the correlation coefficient was weak ($r=0.31$). Radolić et al. (2005) have not found any correlation between the radon variation and EC in geothermal water of Croatia.

According to the literature, positive, negative or no correlation between radon and EC has been reported. Thus, this relationship seems to be unclear but none of the authors explain the reason for this phenomenon.

^{222}Rn variability along the sand dune barrier

Three types of ^{222}Rn variability along the sand dune barrier have been observed: variations related to the water cycle condition, variations according to well's location related to recharge or discharge zones and variations between the different districts (PDLC vs Pinamar).

In the first case, there would be an inverse correlation between ^{222}Rn activity and groundwater flux velocity which is directly related to recharge conditions. Lower water surplus shows higher ^{222}Rn activity and vice versa. This behavior is best explained by dilution processes of high ^{222}Rn activity water with 'newer' lower activity recent precipitation. This was seen in other studies, which investigate directly the geochemical behavior of ^{222}Rn in groundwater (Cho and Choo 2019). Thus, it is important to note that if SGD is calculated based on the ^{222}Rn end member activity and this activity changes with wet and dry periods, one can under or overestimate SGD based on the end member activity chosen.

In the second case, the changes in ^{222}Rn activity could be explained by the aquifer hydrodynamics. The recharge area presents the lowest ^{222}Rn values compared with the discharge sectors. This could be supported by the fact of in the recharge sector the highest hydraulic heads are found and they are associated with the highest specific velocities in the sand dune. This may also be due to the fact that the groundwater here is diluted with new low radon surface water. Discharge zones are associated with lower specific velocities and present higher ^{222}Rn activities.

In the third case, ^{222}Rn variations are more difficult to explain. The mineralogy and sedimentological characteristics of the sand dune barrier in the aquifer are quite similar for both districts, therefore, these factors would not explain the ^{222}Rn variability. The main difference between these two locations is the aquifer thickness and consequently the hydraulic gradient and the effective velocity. In November 2018, in Pinamar, the effective velocity was calculated to be 0.88 m/day whereas in the PDLC it was of 0.32 m/day, being almost 3 times lower. Average ^{222}Rn activity in Pinamar was of 1600 ± 569 Bq/m^3 whereas in the PDCL it was of 5502 ± 958 Bq/m^3 being around 3 times higher. Thus, a higher effective velocity would lead to a higher discharge rate, removing ^{222}Rn from the system.

^{222}Rn variability with depth

Due to the water table shallowness and the lack of soil development (Ball et al. 1991), atmospheric degassing may occur. However, data are not consistent with this theory as ^{222}Rn activities are higher in the shallowest samples.

Mayer et al. (2016) observed different ^{222}Rn activities (wells with 10000–11000 Bq/m^3 and wells with 9000 Bq/m^3) and explained these variations suggesting that a lower activity is probably due to the larger sediment grains and the overall lack of fine sediments found near these wells. This would imply that in areas of larger sediment grains there is a lower surface area and consequently a lower amount of adsorbed ^{226}Ra (and thus also lower ^{222}Rn) for the same water volume. If this theory would explain our own results, then all wells should have to exhibit lower ^{222}Rn activities in the shallower samples. Besides, the differences in grain size in our area are not as great as they described in their paper. These authors are referring to gravels or coarse-grain sands and in this study, the aquifer is composed by fine-grained sands on the top and fine to very fine-grained sands with some clay content on the bottom. There are no significant differences between the sedimentary profiles of PR2 and the other boreholes that could explain the inversion of the ^{222}Rn values in this well. A general profile is presented in Table 4.

Surbeck and Voelkle (1988), referring to the mechanism of ^{222}Rn emanation, mentioned that the specific activities for the U and Th series are dependent upon grain size, since only radon produced near the surface of a grain can escape. Hence, radon activity is inversely correlated to grain size. In our case study, grain size at the depth where the deep samples were taken is smaller but the ^{222}Rn activity is lower, therefore, it is likely that grain size is not the only factor controlling ^{222}Rn activity here.

According to Hoehn and Von Gunten (1989), a microstructural view of the emanation process of radon in granular aquifers indicates that the grain size distribution, the alteration of grain surfaces, and the pore water content seem to be the controlling factors for the radon transport. As an inert gas, radon is quite susceptible to migration. It

Table 4 Stratigraphic profile for an exploratory borehole adapted to the stratigraphy recognized in the area and its relationship with the hydrological behavior

	Depth (m b.g.l.)	Lithology	Stratigraphy[a]	Environment	Hydrological behavior	Water EC[b] (µS/cm)
1	2	Light-colored sand with shell fragments	PMFm	Modern sand dunes	Aquifer	< 2000
2	3.5	Light-colored sand with shell fragments				
3	5	Dark-colored sand with shell fragments	P17Fm MDAF	Barrier developed through spit accretion		
4	6.5	Dark-colored sand with shell fragments				
5	8	Dark-colored sand with shell fragments				
6	9.5	Dark-colored, fine-grained sand, very clayey, with fine shell fragments	P8Fm DRSF/ La Victoria Facies	Tidal plains and marshes/ lagoon deposits		> 10,000
7	11	Clayey sand with shells			Aquitard/aquiclude	
8	> 11	Grey clay with fragments of coarse shells (5 mm)				

[a]Punta Médanos Formation (PMFm), the Pozo No. 17 Formation (P17Fm)—represented by the Mar de Ajó Facies (MDAF)—and the Pozo No. 8 Formation (P8Fm), with its Destacamento Río Salado Facies (DRSF)

[b]*EC* electrical conductivity

can diffuse from grain surfaces or nanopores to intergranular space. In water-saturated aquifers, the contribution of diffusion to the radon transport in groundwater depends on the flow velocity. The average hydraulic conductivity (K) values obtained for fine-grained sands on the top was 22 m/day and 15 m/day for the fine to very fine-grained sands with some clay content on the bottom. Therefore, in our case, a lower K could lead to a lower radon transport and might be a possible reason to explain the lower radon activity in the deeper samples.

On the other hand, Sexsmith (1996) mentioned that iron and manganese oxides are important sorbents for uranium. The most common occurrence of elevated Ra throughout the USA reported by Szabo et al. (2012) occurred in anoxic water with high concentrations of Fe or Mn, and in some places, where high concentrations of the competing ions Ca, Mg, Ba and Sr, and occasionally of dissolved solids, K, SO_4 and HCO_3 was observed. This is an important fact to be taken into consideration due to the fact that in the study area high iron and manganese concentrations in groundwater were recognized (Carretero and Kruse 2015). These elements are derived from pyroxenes, amphiboles, biotites, Fe oxides and oxyhydroxides, as well as the volcanic groundmass stained by iron hydroxides that compose the sand dunes which constitute the phreatic aquifer. However, this should not affect ^{222}Rn activity as the ^{222}Rn is in a gaseous state and not sorbed onto the manganese or iron.

At the sight of these observations and the results obtained in this work, future efforts should be directed toward the study of sediments grain size, mineralogy and natural radioactivity of the aquifer sands.

Conclusions

The coastal barrier system of the Buenos Aires Province in Argentina is marked by several interesting hydrogeological characteristics, which take on extreme importance due to the fact that groundwater constitutes the only freshwater resource available. One of the more interesting characteristics of this region is that groundwater recharge is the greatest in the dry season (winter) when evapotranspiration is the lowest, and groundwater recharge is the lowest in the wet season (summer) when evapotranspiration is the highest. Logic indicates that groundwater recharge would always be the greatest during the wet season, but in this case, the wet season also corresponds to hot summer days.

As these hot summer days coincide with the peak tourist season (in which the local population can increase tenfold, low recharge is coupled with higher consumption rates, which can lead to serious saltwater intrusion problems during the wet season.

^{222}Rn activity in the PDLC sand dune aquifer shows variations over time. An inverse correlation between ^{222}Rn and aquifer recharge can be inferred. Sampling under scarce water surplus conditions presents higher ^{222}Rn values while during higher water surplus conditions ^{222}Rn activity is reduced most likely due to dilution from precipitation infiltrating into the freshwater lens. Groundwater in Pinamar shows the lowest ^{222}Rn activity which would indicate a spatial variability along the sand dune barrier. ^{222}Rn activity, therefore, could be an indicator of recharge and vice versa.

No correlation between ^{222}Rn values and EC was observed. In the PDLC, there is a relationship between ^{222}Rn activity and the geomorphological environment location of the wells but this phenomenon is not observed in Pinamar.

A possible relationship between ^{222}Rn activity and the aquifer thickness, hydraulic gradient and flux velocity could be considered. We observed high values of ^{222}Rn activity in March 2016 during a period with low recharge and effective velocities, while low values of ^{222}Rn activity were associated with high groundwater recharge and high effective velocities. On the other hand, at Pinamar, the registered values of these parameters were of 0.004 and 0.88 m/day, coincident with the lowest ^{222}Rn activity. An aquifer thickness of 42 m in Pinamar could be responsible for the higher flux velocity and a faster discharge process that could lead to a reduction in ^{222}Rn activity. This is particularly interesting when trying to utilize ^{222}Rn activity mass balance to quantify groundwater flow, in a location in which the endmember activity is variable in space and time.

The correlation between climatic conditions, aquifer hydraulic parameters and ^{222}Rn was previously mentioned in the literature. The results obtained in this work could confirm this theory and constitute a valuable contribution to the knowledge of the sand dune aquifer of Buenos Aires coast.

In addition to local knowledge of the hydrogeological properties of the local sand dune barrier system, the results herein may have important implications for wider radon-based groundwater studies. The endmember activity is critical to the quantification of groundwater flow when using radon mass balance as a tool. Therefore, a better understanding of the temporal and spatial variability of the radon endmember activity may help in the further advance the field of SGD research.

Acknowledgements This work was supported by the Agencia Nacional de Promoción Científica y Tecnológica, Grant number PICT 2016–2522, 2017–2020 and Universidad Nacional de La Plata, Grant number PPID/N021, 2017–2018. The authors would like to thank the Cooperativa de Provisión de Obras y Servicios Públicos de San Clemente del Tuyú Ltda. for their collaboration as well as the reviewers and editors for the valuable comments that improved the quality of the manuscript.

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