# Radon as an indicator of submarine groundwater discharge in coastal regions

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This article reviews the various available methodologies to estimate submarine groundwater discharge (SGD) and demonstrates the utility of radon with a case study. An attempt has been made to identify the existence of submarine groundwater discharge (SGD) and semi-quantitatively estimate its rate in the coastal area of Vizhinjam, Thiruvananthapuram, Kerala. Natural <sup>222</sup>Rn (half-life = 3.8 days) was used as a tracer of SGD because of its conservative nature, short half-life, easiness in measurement and high abundance in groundwater. An in situ radon (<sup>222</sup>Rn) monitoring study conducted in this region indicated comparatively higher <sup>222</sup>Rn activities (average: 14.1 ± 1.7 Bq/m<sup>3</sup>) in the coastal waters revealing significant submarine groundwater discharge. The SGD may be a combination of fresh groundwater and recirculated seawater that is controlled by the hydraulic gradient in the adjacent aquifer and varying tidal conditions in the coastal waters. Using a transient <sup>222</sup>Rn mass balance model for the coastal waters, SGD rates were computed and the average value was found to be  $10.9 \pm 6.1$  cm/day. These estimates are comparable with those reported in the literature. In general, identification and estimation of submarine groundwater discharge is important in the Indian context because of the possibility of large amounts of groundwater loss through its long coastline, that can be judiciously exploited to cater to the present water requirements for drinking and irrigation purposes.

**Keywords:** Coastal water, mass balance, radon, submarine groundwater discharge.

MANY parts of India are currently facing severe water crisis and this is likely to increase in the coming years because of the variability in monsoons and increased demand due to population growth. Because the monsoons are confined only to a few months, groundwater is the only reliable source of water for the rest of the year in many places. In the recent years, water conservation measures are widely being practised to alleviate the ever declining groundwater levels. Although peninsular India, with a coastline of about 7000 km, receives abundant monsoon rains (more than 1500 mm), water scarcity is severe in many coastal regions. One of the reasons for the water shortage is the quick surface runoff through the rivers and streams during the monsoon seasons due to steep topography. Another possible cause may be the significant water loss in the coastal regions as submarine groundwater discharge (SGD) – which has not attracted much attention of the scientific community till now.

SGD is defined as the flow of terrestrially derived groundwater and recirculated seawater through the underlying sediments in the seabed into the coastal water<sup>1</sup>. The mechanisms and the driving forces for the above two components are quite different: the terrestrial component is driven by the hydraulic gradient of the groundwater in the land whereas the marine component is controlled by the local oceanographic conditions such as wave set up, tidally driven oscillations, current-induced pressure gradients and convective circulation of water (thermal or density driven) from the bottom sediments. Although these terrestrial and marine driving forces are often superimposed, their relative contributions are difficult to determine. Groundwater discharge, either in the form of concentrated or diffused discharge, could be as large as half the total annual river flow<sup>2</sup>. SGD also acts as pathways of large concentrations of nutrients, metals, organic compounds and inorganic carbon from the continents to the ocean. Even SGD from pristine aquifers can be a source of nitrates and other nutrients to the oceans, as their concentrations are much higher than seawater<sup>3</sup>. The magnitude of SGD and its generation mechanisms are indeed poorly understood mainly because of the nonavailability of accurate measurement techniques and many times, the sources are invisible, slow moving, and spatially and temporally variable.

Conventionally, it is estimated as a residual term in the computation of basin/aquifer scale water balance<sup>4,5</sup>, from numerical modelling of groundwater flow<sup>6,7</sup>, by applying Darcy's law on the hydraulic parameters measured from nested pieozometers installed in the coastal areas<sup>8,9</sup> or by *in situ* measurements conducted in the sea bottom using seepage meters<sup>10–12</sup>. Due to uncertainties in the estimation of water balance terms<sup>13</sup>, limitations in obtaining information about the aquifer heterogeneities in the case of hydraulic measurements from piezometers and groundwater modelling and difficulties in accounting the recirculation of seawater, the SGD rates obtained from these

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methods are sometimes ambiguous; however, they could be used as first-hand estimates<sup>14</sup>. Whereas seepage meter measurements are labour intensive, difficult to install in rough sea conditions and they provide only point information. Despite that, the use of seepage meters showed consistent and reliable results in some studies<sup>9,15</sup>. Tracer techniques, including the use of naturally occurring isotopes, on the other hand, provide a convenient way of assessing the SGD, as they integrate the water fluxes over various spatial and temporal scales.

Because of the distinction in geochemical constituents such as salinity, barium, ceasium, phosphate, ammonia, methane, etc. and some isotopic ratios such as  $^{234}U/^{238}U$ ,  $^{87}Sr/^{86}Sr$ , etc. in groundwater and seawater, they could be used to identify fresh groundwater discharges  $^{16,17}$ . However, measurements of isotopes in the uranium–thorium decay series have an additional advantage of tracing and quantifying the brackish water SGD fluxes as well, which have more impact on coastal environments. The most commonly used isotopes for SGD studies include the quartet of radium isotopes having half lives ranging from 3.66 days ( $^{224}Ra$ ) to 11.4 days ( $^{223}Ra$ ) to 5.7 years ( $^{228}Ra$ ) to 1600 years ( $^{226}Ra$ ) and radon isotope,  $^{222}Rn$  (half-life = 3.83 days) which are derived from the radioactive decay series of thorium in the sediments.

The observed enrichment of radium isotopes in groundwater relative to the surface water bodies because of greater contact with the sediments helps to understand the groundwater-seawater interactions occurring in a wide range of time scales. Radium tends to desorb from the sediments with increasing salinity whereas the parent thorium is retained, thus, sediments act as a constant source of radium to the coastal waters<sup>2</sup>. Accounting for the removal of radium from coastal regions by tidal flushing, SGD rates can be estimated using radium mass balance. Several recent studies used this approach to quantify SGD<sup>18,19</sup> and its seasonality<sup>20</sup>, identify density driven SGD<sup>21</sup> and estimate radium fluxes to the oceans<sup>16</sup>. In conjunction with biogeochemical assays, they could be used to estimate nutrient<sup>22,23</sup> and silicate<sup>24</sup> fluxes associated with SGD, understand eutrophication<sup>25,26</sup> and occurrence of algal blooms, red tides<sup>27</sup>, etc. Since the flushing time of shallow aquifers is shorter compared to the deep confined aquifers, they have more activities of <sup>228</sup>Ra than <sup>226</sup>Ra because of the comparatively shorter half-life, hence, measurement of these isotopes in the marine waters helps to quantify the relative contributions of SGD from the individual aquifers<sup>19,28</sup>. Measurement of  $^{224}$ Ra and <sup>223</sup>Ra is also useful in determining the horizontal eddy diffusivity coefficients and coastal mixing rates<sup>29</sup>, shelf water residence times<sup>30</sup>, identification of coastal plumes derived from rains<sup>31</sup> and rivers<sup>32</sup>, etc.

Natural radon is an excellent tracer for identifying areas of significant groundwater discharge because of its conservative nature, short half-life, high abundance in groundwater compared to surface water and easiness in measurement. <sup>222</sup>Rn activities in groundwater are often 2-4 orders of magnitude higher than those of seawater, hence, even after large dilutions in the coastal waters, they can be detected at very low concentrations<sup>33</sup>. <sup>222</sup>Rn is particularly useful in locating submarine freshwater springs as radium may not enrich under such conditions. One of the limitations of <sup>222</sup>Rn is that, being an inert gas, it escapes into the atmosphere. From the continuous monitoring of <sup>222</sup>Rn in coastal waters, it is possible to quantify  $SGD^{18,34-36}$ . Some of the recent studies use <sup>222</sup>Rn to identify freshwater SGD<sup>37</sup> and tidal pumping of seawater<sup>38</sup>. A recent inter-comparison exercises that employed hydrogeologic and various tracer methods for the quantification of SGD have helped improve the understanding of SGD generation processes and recommended the use of multiple tracers for obtaining confidence in these estimates  $9,3\bar{9}-41$ .

In the Indian scenario, most of the studies conducted in the coastal regions are concentrated on water quality aspects including seawater intrusion in aquifers<sup>42–45</sup>. No reliable data exists about submarine groundwater discharge in the Indian sub-continent. A few studies conducted in the Bengal basin using barium, <sup>226</sup>Ra and <sup>87</sup>Sr/<sup>86</sup>Sr indicate substantial groundwater discharge into the Bay of Bengal through the Ganga–Brahmaputra river systems<sup>16,17</sup>. SGD is suspected from a recent hydrogeological and groundwater modelling study conducted in the shallow aquifers of Vizhinjam, Kerala<sup>46</sup>. Hence, an attempt has been made in the present study to identify the existence of SGD and semi-quantitatively estimate its rate in the coastal waters of Vizhinjam, Thiruvananthapuram, by the *in situ* monitoring of dissolved <sup>222</sup>Rn in water.

#### The study area

The study area is located in the southwest coast of India between latitudes  $8^{\circ}19'-23'N$  and  $76^{\circ}59'-77^{\circ}03'E$  which is about 16 km south of Thiruvananthapuram (Figure 1).



Figure 1. Location map of study area showing sampling points.

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In the coastal region, water depth of about 9-10 m is attained at less than 0.5 km from the shore and this continental shelf is the steepest shelf in the west coast of India. It is a microtidal coastal region having semidiurnal tides with tidal ranges less than 1 m. Bedrock and lateritic cliffs are exposed at the shorelines, whereas irregular rock surfaces are encountered at certain shallow depths. Beach profiles show change in morphology from sandy, lateritic to rocky indicating sediment accretion and erosion at short distances alongshore. The average annual rainfall exceeds 2300 mm, more than 70% occurs during the summer monsoon (June to September) and the remaining in winter monsoon (October to December). The seasonal reversal of wind circulation pattern has an important bearing on the hydrography of this region<sup>47</sup>. The winds are strong and change their direction from south to east during March to July. It weakens in September and October and blows towards north-northwest. Alongshore currents are stronger during March to September and flow in south-southeast direction whereas cross shore currents become stronger towards north during November to January<sup>47,48</sup>.

The continental region is generally covered by Holocene unconsolidated sediments known as red Teri sands and occasional exposures of Tertiary sediment sequence which is partially covered by loose sand and clay intercalations of recent marine origin. They are conformably underlain by Precambrian crystalline rocks comprising Khondalite suite of rocks. Neotectonic disturbances are reflected by the development of sea cliffs and large scale deposition of red sands over loose unconsolidated sands in the coastal region<sup>49</sup>. The top unconsolidated sediment sequences in the area forms the phreatic aquifer which is being tapped for domestic purposes. Fracture flow occurs in the basement rock.

#### Field monitoring survey

A field monitoring survey was carried out in Vizhinjam coast during the last week of November 2007. Using a depth sampler, seawater samples were collected at a depth interval of 1 m from various locations and measured for physical parameters such as temperature, electrical conductivity (EC) and pH using portable conductivity (EUTECH Cyberscan CON 11 Make) and pH (EUTECH Cyberscan pH 11 Make) meters respectively. In order to accurately measure a wide range of electrical conductivities (fresh water to saline water), a multi-point calibration procedure was adopted for the conductivity meter. The sampling locations are shown in Figure 1. Groundwater samples were also collected from the adjacent continental areas and measured for the given physical parameters. Because of the existence of lateritic cliffs on the northern part of the coastal area, not many wells exist in this region for groundwater sampling.

Because the <sup>222</sup>Rn concentrations in surface waters are low and due to its short half-life, large volumes of water are required for the measurement of <sup>222</sup>Rn and hence *in situ* monitoring is highly essential. For the present study, a radon monitoring system similar to that developed by Burnett *et al.*<sup>50</sup>, was set up using a radonin-air monitor.

For the in situ measurement of <sup>222</sup>Rn in the coastal region, seawater was continuously pumped from 1 m above the sea bed using a peristaltic pump and sprayed as a jet into an air-water exchanger (Figure 2a). The radon thus stripped out from the water is circulated through a closed air-loop via a desiccant tube into a <sup>222</sup>Rn counting system. Photograph of continuous field <sup>222</sup>Rn monitoring is given in Figure 2 b. The purpose of the desiccant is to absorb moisture, as detection efficiency decreases at higher humidity. The equilibrium of <sup>222</sup>Rn between the liquid and gaseous phase is established within 30 min<sup>51</sup>. The radon monitor (RAD-7; Durridge make) uses a highelectric field above a silicon semiconductor detector at ground potential to attract the positively charged polonium daughters,  ${}^{218}Po^+$  (half-life = 3.1 min; alpha energy = 6.00 MeV) and  ${}^{214}Po^+$  (half-life = 164  $\mu$ s; alpha energy = 7.67 MeV), which are counted as a measure of <sup>222</sup>Rn concentration in air. An air filter at the inlet of the radon monitor prevents dust particles and charged ions from entering into the alpha detector. The ions are collected in energy specific windows which eliminate interference and maintain very low background. <sup>222</sup>Rn activities are expressed in Bq/m<sup>3</sup> (disintegration per second per m<sup>3</sup>) with  $2\sigma$  uncertainties. In order to get acceptable precision, <sup>222</sup>Rn activity at each location was counted for two hours (three cycles of counting) after attaining equilibrium. At room temperature, as the radon in air is about four times more than that in water at equilibrium, the measured radon concentrations in air are corrected accordingly<sup>52</sup>.

Extensive <sup>222</sup>Rn monitoring survey could not be done in the coastal waters due to rough sea conditions prevailing in the area because of the influence of northeast monsoon depressions.

Groundwater samples were collected in 250 ml glass bottles using a low discharge sampling pump. The <sup>222</sup>Rn concentrations were directly measured within six hours of sample collection using a radon monitor by stripping radon via bubbling air in a closed loop. <sup>222</sup>Rn activity is then counted for 40 min (four cycles of counting) after attaining equilibrium. All <sup>222</sup>Rn activities are corrected for the radioactive decay with respect to the sampling time.

### **Results and discussion**

The measured physical parameters and <sup>222</sup>Rn activity in the coastal waters of Vizhinjam area during the field

#### **RESEARCH ARTICLES**



Figure 2. *a*, Schematic sketch of surface water <sup>222</sup>Rn monitoring system; *b*, *In situ* measurement of <sup>222</sup>Rn in coastal water.

Table 1. Measured physical parameters and radon activity in the Vizhinjam coastal water

ID no.	Latitude	Longitude	Temp (°C)	EC (µS/cm)	pН	Radon activity (Bq/m <sup>3</sup> ) $\pm 2\sigma$
SR1	8°21′49″	77°00′13″	29.1	52400	8.13	$14.6 \pm 4$
SR2	8°22′01″	77°00′06″	28.9	52700	8.13	$13.3 \pm 4$
SR3	8°22′35″	76°59′20″	28.8	55300	8.18	$11.7 \pm 3$
SR4	8°22′37″	76°59′31″	29.1	54800	8.17	$15.0 \pm 4$
SR5	8°22′32″	77°59′31″	28.8	53800	8.17	$16.0 \pm 4$

Table 2. Measured physical parameters and radon activity in groundwater, Vizhinjam area

ID no.	Location	Туре	Depth (m)	Temp (°C)	$EC \; (\mu S/cm)$	pН	Radon activity (Bq/m <sup>3</sup> ) $\pm 2\sigma$
G1	Karimkulam	SW	5	29.9	787	7.41	$2280\pm230$
G2	Kochuthura	SW	5	27.2	998	7.30	$1120 \pm 270$
G3	Pallom	SW	6	28.6	734	6.71	$7200 \pm 1750$
G4	Pulluvila	SW	6		180	7.33	$1480 \pm 550$
G5	Pulluvila	DW	30	27.3	1335	7.37	$8580 \pm 1600$
G6	Adimalathura	SW	6	29.1	225	5.65	$8630 \pm 780$
G7	Adimalathura	SW	5	27.2	573	7.20	$5300 \pm 860$
G8	Karchal	SW	7	30.1	382	7.20	$11,800 \pm 1100$
G9	Chappat	SW	6	27.5	245	6.91	$1960 \pm 250$
G10	Vizhinjam	SW	5	27.9	456	7.24	$1470 \pm 220$
G11	Vizhinjam	SW	10	27.6	424	7.31	$1240\pm210$

SW, Shallow well; DW, Deep well.

study in November 2007 are given in Tables 1 and 2. It is seen that the groundwater temperature varies from 27.2°C to 30.1°C, whereas coastal waters have a uniform temperature of about 28.9°C. The pH measurements show that groundwater is acidic to neutral, whereas coastal water is alkaline. Electrical conductivity of coastal groundwater ranges from 180 to 1335  $\mu$ S/cm. This shows that the groundwater is fresh and the seawater interface is lying within the coastal zone. Hence, presently there is no seawater intrusion in this region, which is mainly controlled by the hydraulic gradient and the coastal topography (lateritic cliffs).

Vertical profiles of temperature and electrical conductivity at various locations in the Vizhinjam coastal waters during November 2007 are shown in Figure 3. Temperature profiles at various locations are almost similar (variation is less than  $0.7^{\circ}$ C) and they are uniform throughout the water column. This indicates that a well mixed condition prevails in this region during the winter season. The observed northeast monsoon surges may also be responsible for the horizontal and vertical mixing. The average electrical conductivity in the coastal region is about 54,100 µS/cm, which is 10,000 µS/cm lower than the average electrical conductivity measured at Alappuzha coast located at about 150 km north of the study area in the Arabian Sea<sup>53</sup>. The comparatively lower electrical conductivity in the Vizhinjam coastal water can be attributed to submarine groundwater discharge as there is no major river in this area. The electrical conductivity profiles show slight reduction in conductivity in the superficial waters at locations S5 and S6 and in bottom waters at locations S3 and S4. This reduction in electrical conductivity could be an indication of existence of localized groundwater discharge points.

Groundwater samples collected from the shallow aquifer exhibit higher <sup>222</sup>Rn activities than in coastal waters (Figure 4). They are enriched in <sup>222</sup>Rn activities by two orders of magnitude. The average <sup>222</sup>Rn activity in the Vizhinjam coastal water is about  $14.1 \pm 1.7$  Bq/m<sup>3</sup> whereas in groundwater it is about  $4640 \pm 3830$  Bq/m<sup>3</sup>. Considerable spatial variation in <sup>222</sup>Rn activities is observed in groundwater whereas coastal water does not show significant variation in activities. The large difference in activities among these end members helped in using <sup>222</sup>Rn as an indicator of groundwater discharge into the sea.

A close observation of the groundwater <sup>222</sup>Rn data along with the geological and structural features of the area



Figure 3. Vertical profiles of water temperature (a) and electrical conductivity (b) in Vizhinjam coastal waters during November 2007.



Figure 4. Comparison of <sup>222</sup>Rn activities in groundwater and coastal waters, Vizhinjam, Kerala.

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reveal that high <sup>222</sup>Rn activities (more than 3000 Bq/m<sup>3</sup>) are associated with the location of lineaments (Figure 1). Because the lineaments are geologically weak zones, the <sup>222</sup>Rn from the crust/mantle may be escaping into the atmosphere through these zones. Therefore, these high <sup>222</sup>Rn values are neglected for better statistical precision and an average value of the remaining data, i.e.  $1620 \pm 440$  Bq/m<sup>3</sup> is considered as a representative <sup>222</sup>Rn activity in the groundwater for calculation of SGD rates.

Radon activity in offshore water, where the influence of SGD is considered to be minimum, is generally taken as the natural background <sup>222</sup>Rn activity in seawater. Natural <sup>222</sup>Rn activity in seawater comes from radioactive decay of <sup>226</sup>Ra present in the sediment and water. High natural radioactivity of <sup>232</sup>Th and <sup>226</sup>Ra in beach sediments of Chavara, Kollam district, Kerala<sup>54</sup> is reported. However, we have not observed any high concentrations of <sup>222</sup>Rn in the coastal waters of Vizhinjam. Due to rough sea weather conditions prevailing during field study, radon activities could not be measured in offshore waters. A radon survey conducted in offshore waters of Alappuzha, Kerala<sup>53</sup> indicated an average <sup>222</sup>Rn activity of about  $5 \pm 5$  Bq/m<sup>3</sup> whereas the measured average <sup>222</sup>Rn activity in the shallow aquifer is  $1850 \pm 600$  Bq/m<sup>3</sup>. Hence, the <sup>222</sup>Rn activity in offshore waters of Alappuzha is considered as the background activity in Vizhinjam. The relatively higher <sup>222</sup>Rn activities in Vizhinjam coastal waters compared to offshore values show significant SGD. Results of <sup>222</sup>Rn and electrical conductivity measurements indicate that SGD in this region may be a combination of fresh groundwater and recirculated seawater which is governed by hydraulic gradient in the adjacent aquifer and varying tidal conditions in coastal waters.

Algal blooms are visually observed in the Vizhinjam coastal waters during field survey (Figure 5). Occurrence of red tide of *Noctiluca miliaris* is reported<sup>55</sup> in this region subsequent to a 'stench event' at the southern Kerala coast during 2004 which is suspected to be caused by eutrophication followed by upwelling. Algal blooms and



Figure 5. Algal blooms observed during the field survey.

outbreak of red tides are often associated with SGD, as they are the pathways of nutrients from the aquifer to the coastal region<sup>27</sup>. Hence, it can be said that the frequent outbreak of red tide in this region could be because of SGD.

#### Estimation of submarine groundwater discharge

Because <sup>222</sup>Rn is highly enriched in groundwater, SGD can be calculated using <sup>222</sup>Rn mass balance in the coastal water. The general steady state <sup>222</sup>Rn mass balance equation for coastal water can be written as:

$$\Psi_{\text{SGD}} \times C_{\text{GW}}^{^{222}\text{Rn}} \times A_{\text{Bott}} + F_{\text{Diff}}^{^{222}\text{Rn}} = I_{\text{CW}}^{^{222}\text{Rn}} \times \lambda_{2^{22}\text{Rn}} + C_{\text{EX}}^{^{222}\text{Rn}} \times V_B \times \lambda_{\text{Mix}} + F_{\text{Atm}}^{^{222}\text{Rn}},$$
(1)

where  $\Psi_{\text{SGD}}$  is the seepage rate of submarine groundwater (m/d);  $C_{\text{GW}}^{^{222}\text{Rn}}$  the average  $^{222}\text{Rn}$  activity in groundwater (Bq/m<sup>3</sup>);  $A_{\text{Bott}}$  the bottom area of the bay (m<sup>2</sup>);  $F_{\text{Diff}}^{^{222}\text{Rn}}$  the diffusive flux of  $^{222}\text{Rn}$  from the bottom sediments (Bq/day);  $I_{\text{CW}}^{^{222}\text{Rn}}$  the  $^{222}\text{Rn}$  inventory in the coastal water (Bq);  $\lambda_{^{222}\text{Rn}}$  the radioactive decay constant of  $^{222}\text{Rn}$  (per day);  $C_{\text{EX}}^{^{222}\text{Rn}}$  difference in  $^{222}\text{Rn}$  activity between coastal water and open sea (Bq/m<sup>3</sup>);  $V_{\text{B}}$  the volume of the coastal water (m<sup>3</sup>);  $\lambda_{\text{Mix}}$  the exchange rate between coastal water and open sea (per day);  $F_{\text{Atm}}^{^{222}\text{Rn}}$ the atmospheric  $^{222}\text{Rn}$  evasion flux across air–sea interface.

The left side of the equation represents various <sup>222</sup>Rn input fluxes into the coastal waters such as from the submarine groundwater flow and diffusion from the bottom sediments, whereas terms on the right side represent the <sup>222</sup>Rn outflow fluxes such as the loss due to radioactive



**Figure 6.** *a*, Temporal variation of  $^{222}$ Rn and *b*, estimated SGD rates in Vizhinjam coastal waters during 27 November 2007 ( $^{222}$ Rn activities and SGD rates are expressed as integrated values for a 2 h period).

decay in the coastal waters, mixing with open ocean (offshore water) and evasion into the atmosphere.

Temporal variation of <sup>222</sup>Rn decay in coastal water and diffusion from bottom sediments can generally be insignificant in many cases<sup>38</sup>. Hence these terms can be avoided. Other components such as atmospheric evasion and mixing with offshore waters will vary depending upon the local hydro-meteorological conditions such as wind speed, waves, etc. Because the water was sampled about 1 m above the seabed, the measured <sup>222</sup>Rn activities may be less affected by the fluctuation in wind speed and waves. Also, being a microtidal coastal region, the tidal watermass exchange time can be more than 12 h. Hence, terms on atmospheric evasion and offshore water mixing can be neglected for a semi-quantitative calculation of SGD. Hence, the observed higher activities in coastal waters can be attributed only to submarine groundwater discharge.

Therefore, eq. (1) reduces to:

$$\Psi_{\text{SGD}} \times C_{\text{GW}}^{^{222}\text{Rn}} \times A_{\text{Bott}} = I_{\text{CW}}^{^{222}\text{Rn}} \times \lambda_{^{222}\text{Rn}}.$$
 (2)

Radioactive decay constant of <sup>222</sup>Rn is calculated as:

$$\lambda_{222\,\rm Rn} = \frac{\ln 2}{t_{1/2}},\tag{3}$$

where  $t_{1/2}$  is the half-life of <sup>222</sup>Rn (3.83 d).

<sup>222</sup>Rn inventory in coastal water is given by:

$$I_{\rm CW}^{^{222}\rm Rn} = C_{\rm EX}^{^{222}\rm Rn} \times A_{\rm Bott} \times y, \tag{4}$$

where *y* is the average depth of the coastal area ( $\sim 8$  m).

 $C_{\text{EX}}^{^{222}\text{Rn}}$  is the unsupported or excess  $^{^{222}\text{Rn}}$  calculated as the difference between the measured  $^{^{222}\text{Rn}}$  activity in the coastal water and the  $^{^{222}\text{Rn}}$  derived from the *in situ* decay of  $^{^{226}\text{Ra}}$ . Measured  $^{^{222}\text{Rn}}$  activity in open ocean can be taken as  $^{^{222}\text{Rn}}$  derived from  $^{^{226}\text{Ra}^{33}}$ . Therefore, for the present calculation, measured  $^{^{222}\text{Rn}}$  activity (5 ± 5 Bq/m<sup>3</sup>) in offshore waters of Alappuzha<sup>53</sup> is considered as the  $^{^{222}\text{Rn}}$  derived from the *in situ* decay of  $^{^{226}\text{Ra}}$ .

Equation (2) cannot be directly used to estimate SGD because, in actual conditions, the <sup>222</sup>Rn fluxes in the coastal water will vary with tidal conditions and steady state conditions are not valid.

Burnett and Dulaiova<sup>33</sup> continuously measured <sup>222</sup>Rn in the sea over a period of time and any change in the calculated time dependent <sup>222</sup>Rn inventories were converted into fluxes.

Therefore, for the transient condition, eq. (2) can be modified as:

$$\Psi_{\rm SGD} \times C_{\rm GW}^{^{222}\rm Rn} \times A_{\rm Bott} = \frac{\Delta I_{\rm CW}^{^{222}\rm Rn}}{\Delta t},\tag{5}$$

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where  $\Delta I_{CW}^{^{222}Rn}$  is the change in  $^{222}Rn$  inventories between two consecutive measurements and,  $\Delta t$  the time interval (generally 2 h).

Assuming the observed variation in <sup>222</sup>Rn activities in coastal water is not due to aquifer heterogeneity but because of temporal variation in <sup>222</sup>Rn fluxes (Figure 5 *a*), SGD rates are estimated using eq. (5) and shown in Figure 5 *b*. The estimated average SGD rate is found to be  $10.9 \pm 6.1$  cm/day. These are the absolute minimum values, as the inclusion of atmospheric evasion term will only increase the SGD rates. The reported significant SGD rates are typically in the range of 10–100 cm/day<sup>33</sup>.

#### Conclusion

The importance of SGD in the catchment water balance is recognized in the Indian context. Available methods to understand SGD are briefly reviewed in the present article. Radium and radon isotopes are found to be excellent tracers of SGD compared to other conventional methods as they can provide information on coastal processes occurring on a wide range of temporal and spatial scales.<sup>222</sup>Rn is particularly useful in SGD studies because of its conservative nature, easiness in measurement, high abundance in groundwater compared to surface water, possibility for *in situ* measurement and its decay rate comparable with the time scales of many coastal processes.

A field <sup>222</sup>Rn monitoring study conducted in November 2007 in coastal areas of Vizhinjam and Thiruvananthapuram, revealed significant SGD into the coastal waters through the seafloor. The SGD in this region is thought to be a combination of fresh groundwater and recirculated seawater which is governed by the hydraulic gradient in the adjacent aquifer and varying tidal conditions in coastal waters. A first-hand estimate of SGD rate is computed from the <sup>222</sup>Rn mass balance in the coastal waters and is found to be  $10.9 \pm 6.1$  cm/day.

Further studies are in progress by applying various radium isotopes and deployment of seepage meters. Effect of atmospheric evasion of <sup>222</sup>Rn and mixing with offshore waters on SGD estimates will also be evaluated.

In general, submarine groundwater discharge studies help to plan for optimum groundwater exploitation of coastal aquifers keeping the seawater interface well within the coastal zones. Also, ideal sites for construction of subsurface barriers to arrest groundwater discharge could be explored.

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