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Spatial Distribution of Submarine Groundwater Discharge and Associated Nutrients within a Local Coastal Area

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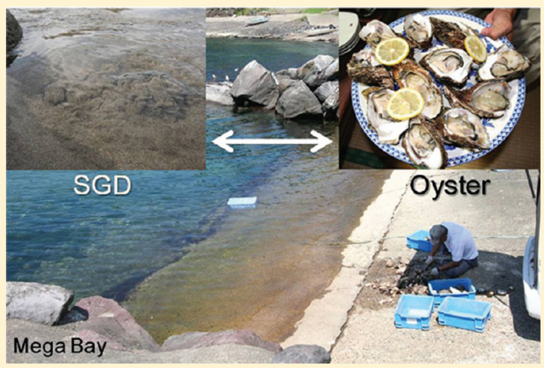
ABSTRACT: To understand the local-scale distribution of submarine groundwater discharge (SGD) and dissolved nutrients, a multiple-detector ^{222}Rn monitoring survey was undertaken along the Mt. Chokai volcanic coast in northern Japan. The surveys revealed that the highest SGD (calculated to be 6.2×10^4 m^3 d^{-1}, within an area of 2×10^4 m^2) with the greatest nutrient fluxes (sum of NO_3^-, NO_2^-, and NH_4^+ (DIN): 9.2×10^2 mol d^{-1}; PO_4^{3-} (DIP): 56 mol d^{-1}) is present at the edge of the youngest volcanic lava flow in the area. Recharged groundwater transports nutrients through porous volcanic flows and discharges as SGD near shore. Our results demonstrate that the spatial distribution of SGD in the study area is closely regulated by the local geology and topography. Furthermore, we show that continuous ^{222}Rn monitoring with a multidetector system at boat speeds of 1−2 knots provides details at a scale one order of magnitude greater than has been reported previously. In addition, the results of our study suggest that SGD-borne DIP may play an important role in the important local oyster production.



1. INTRODUCTION

Submarine groundwater discharge (SGD) is important as a major pathway for freshwater and nutrient loads from land to ocean.[1−5] In the last two decades, knowledge has accumulated on the distribution of SGD and fluxes of freshwater and nutrients through SGD at many locations.[6−8] Various natural tracers of SGD (e.g., temperature, salinity, CH_4, and radium and radon isotope tracers) have been applied to quantify local to regional SGD fluxes.[9−13] Radon (^{222}Rn), a naturally occurring radioactive gas that is typically 2−3 orders of magnitude higher in groundwater than surface waters, is a powerful tracer of groundwater inputs to oceans.[14] The methodology of continuous ^{222}Rn monitoring surveys has been developed in the last 10 years as a novel tool allowing visualization of spatial SGD distribution along coastlines.[9,15−18] The method has been successfully applied in 100-km scale study areas.[12,19,20] However, the variability of this method at a scale of only a few kilometers means that the role of local-scale distribution patterns of SGD and associated nutrient fluxes has not yet been clarified due to the lack of test studies on this scale.

Volcanic mountain coastlines have a high potential for SGD worldwide.[3,8,21] The Chokai Quaternary volcano (2236 m) is the highest peak in northern Japan and is located on the Sea of Japan coast.[22,23] The annual rainfall in this area is about 2000 mm. Abundant spring discharges are present around the foot of the mountain at the terminus of volcanic lava flows[24] (Figure 1a). Importantly, streamwater discharges are absent at the foot of the mountain along a 11-km stretch of the western coastline (Figure 1b). The topography of this western coastline area is created by several andesitic lava flows that are oriented toward the sea[25] (Figure 1b). Among the several lava flows, the "Saruana" (meaning "monkey cave" in Japanese) lava flow is unique in terms of its age (3 ka), very young compared with the other lava flows (0.16−0.1 Ma), and its porous nature with clinker commonly present and an unweathered surface.[25] The mountain coastline displays sharp contrasts between small peninsulas (of down-flowing lava flows) and local bays (between these lava flows) (Figure 1b). The coastal sea bottom is composed basically of andesitic rocks, and sandy beaches are limited along this mountain coastline except for the Kamaiso sandy beach (Figure 1c), the sands of which were largely transported from southern rivers.

There are five recognized spring sites along this coast at accessible locations from the land (Figure 1b). Each of them is

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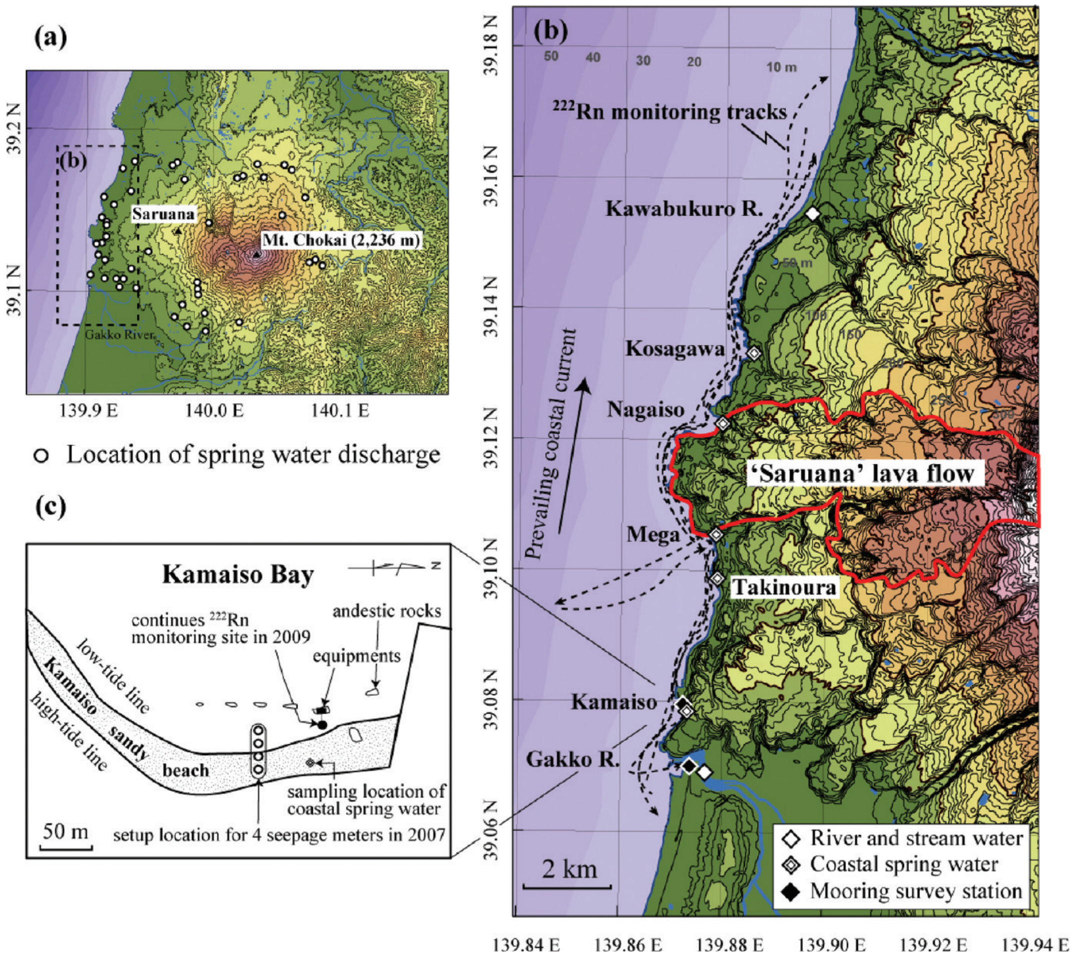

Figure 1. Map showing (a) spring water distribution around the foot of the Mt. Chokai, (b) continuous ^{222}Rn monitoring tracks, ^{222}Rn mooring stations, and sampling locations for chemical analysis, and (c) mooring setup location in Kamaiso beach.

located around the perimeter of the toe of the individual lava flows implying that the recharged groundwater flow pathways are regulated by the flow orientations. However, access to the coast line from land is limited making it difficult to observe the occurrence and size of the springs as well as disseminated SGD along the shoreline. For instance, there is no access to the volcanic cliff coast between Mega and Nagaiso Bay and between Kosagawa Bay and Kawabukuro River (Figure 1b). Interestingly, Mega Bay is famous for its high-quality natural oysters. Local fishermen believe that the production of these oysters is linked with the spring discharges that they have observed within this bay. Fishermen also perceive that oysters from stream-fed bays nearby do not produce comparable quality oysters. However, there is no scientific evidence verifying any connection between oyster production and quality with SGD.

The aim of this study was to investigate the relationship between the coastal distribution of SGD and the local-scale coastal geology and topography. In addition, we wanted to test the use of the continuous ^{222}Rn monitoring approach within a study site of only a few kilometers. We considered that the Chokai volcanic coast, with abundant springs and variable geology, is an ideal test area. As a secondary objective, we also looked at the potential impact of SGD on local marine production by comparing the distribution patterns of SGD and associated nutrients along the coastline.

2. EXPERIMENTAL SECTION

The activity concentrations of ^{222}Rn (half-life = 3.8 d) in water were measured using portable continuous Rn-in-air monitors (RAD7: Durridge Company) interfaced with an air–water exchanger. The properties of this equipment and the principles of ^{222}Rn measurement are described in detail in Burnett et al.[15] The continuous ^{222}Rn monitoring surveys were performed on a boat along the Chokai volcanic coastline as well as offshore transects (Figure 1b). Along the shoreline, the activities of ^{222}Rn in seawater were measured continuously, tracking close to the coast (~200 m from the coastline at a water column depth of around 3–8 m; Figure 1b). The one-way length of the tracking route averaged 12.92 km (n = 4). All monitoring surveys were conducted during flood tide in two periods, July 21–23, 2009 and August 19 and 21, 2010.

In 2009, we monitored ^{222}Rn along the coast twice (July 21 from north to south and July 22 from south to north) traveling at a boat speed of 4 knots, a speed that has been commonly applied in previous investigations along a 100-km scale study area.[12,19,20] We also traveled on July 23 from land to offshore and returned along the similar route at the same speed (Figure 1b). During July 19–23, there was no rain on the 19th and 20th. From 10:00 July 21 (after the "north to south" ^{222}Rn monitoring survey) until 10:00 the next day there was intermittent rain in the area (total amounts account for 7 mm d^{-1}). In 2010, to examine spatial ^{222}Rn variations in more

Table 1. Analytical Data for Spring and River Waters from the Chokai Area, Northern Japan

sampling site	year	^{222}Rn dpm L^{-1}	salinity ‰	$^{a}NO_3^-$ μmol	$^{b}NO_3^-$ μmol	$^{b}NO_2^-$ μmol	$^{b}NH_4^+$ μmol	^{b}DIP (PO_4^{3-}) μmol	^{b}DIN μmol
				coastal spring					
Kamaiso	2009	1409 ± 95	0.019	12					
	2010	1332 ± 120	0.076	19	11.0	0.09	0.63	1.14	11.7
Takinoura	2009	2077 ± 131	0.068	13					
	2010	1718 ± 169	0.094	18	13.0		1.04	0.81	14.0
Mega	2009	1086 ± 24	0.061	13					
	2010	897 ± 97	0.029	24	15.0	0.06	0.69	0.87	15.8
Nagaiso	2009	446 ± 57	0.053	17					
	2010	1370 ± 117	0.037	21	16.1	0.02	0.90	0.87	17.0
Kosagawa	2009	1423 ± 78	0.033	9					
	2010	1557 ± 191	0.057	18	11.4	0.33	0.80	0.81	12.5
median value		*1390*	*0.053*	*16*	*14.0*	*0.1*	*0.8*	*0.9*	*14.9*
				river water					
Gakko	2009	36 ± 13	0.031	17					
	2010	157 ± 12	0.037	22	9.1	0.19	7.12	0.21	16.4
Kawabukuro	2009	180 ± 42	0.015	7					
	2010	96 ± 13	0.022	14	7.2	0.01	2.97	0.65	10.2
median value		*127*	*0.026*	*15*	*8.2*	*0.1*	*5.0*	*0.4*	*13.3*

^{a}Measured by ion chromatography. ^{b}Measured by auto nutrient analyzer.

detail than we did in 2009, we monitored ^{222}Rn with a slower boat speed of only 1−2 knots on August 19 from south to north and on August 21 from north to south. Coastal water visibility along the survey track was low on August 19 due to suspended materials resulting from swollen river discharge transported from the south via the prevailing coastal currents (Figure 1b) triggered by strong regional rainfall (14 mm h^{-1}) the previous day. During the monitoring survey of August 21, water visibility was again clear after two fine days. Seawater samples for nutrient analysis were collected at 10 min intervals in both travel directions.

For continuous ^{222}Rn monitoring on a boat, we applied a multidetector system by connecting three RAD7s in parallel.[17] Selected measurement intervals, depth of water pumping, and pumping rate were 10 min, 0.5 m from the water surface, and within 5−10 L min^{-1}, respectively. The uncertainty of the ^{222}Rn measurements was estimated by counting statistics and expressed as two-sigma values. The minimum time required to establish a new air−water equilibrium for the multidetector system at such water flow rates is estimated at 20−25 min.[17] This fact allows us to obtain ^{222}Rn counts that can be used to examine the relative changes of ^{222}Rn concentrations along the coastline while it does not always represent the absolute ^{222}Rn concentrations in water at each measurement point. It has been previously shown that ^{222}Rn counts obtained by the multidetector system represent radon activities approximately 10−20 min past the actual measurement site (depending upon air and water flow rates) due to a delay in response caused by the time required to reach a new air−water equilibrium.[20] Therefore to get the "most accurate" ^{222}Rn counts for each site we normalized the measured ^{222}Rn data by time shifting 10 min (one cycle) which seemed more appropriate with our high water flow rates.

To estimate the SGD flux, we set up a mooring at the northern part of the sandy beach in the small embayment of Kaimaiso during July 21−23, 2009 (Figure 1c). We confirmed that there is no visible point source SGD from the seabed, suggesting that submarine groundwater is seeping through bottom sediments. Other bays are characterized by andesitic rocks with point source SGD discharges. Another mooring was deployed during the same period in the mouth of the Gakko River (Figure 1b), where there is a mixture of surface and groundwater flows through the sandy bottom. For these mooring stations, we measured ^{222}Rn activity concentrations using a single RAD7 monitor and the water depth by using an Onset Water Level Sensor for each site following the approach described by Burnett et al.[15] We also monitored ^{222}Rn concentrations in the air during the same period using another RAD7 monitor.

On July 24, 2009 and August 22, 2010, coastal spring and river waters were sampled for ^{222}Rn, major ions, and nutrient analysis, with samples of each stored in 250-mL glass bottles, 50-mL polyethylene bottles, and 10-mL plastic tubes (two tubes for each site), respectively. The ^{222}Rn concentrations were measured with a single RAD7 monitor with a RAD-AQUA accessory. To estimate the offshore ^{226}Ra activity, 20 L of seawater was collected at a location 3000 m offshore on July 23, 2009 during the ^{222}Rn monitoring survey. The seawater was passed through a "Mn fiber" adsorber in a gas-tight cartridge. After waiting for ingrowth of ^{222}Rn in the sealed cartridge, ^{226}Ra activity was measured using a RAD7 following the method described in Kim et al.[26] and Dimova et al.[27] Salinity was measured along the same tracking route on August 14, 2011 using a salinity sensor (RINKO-Profiler, ASTD102, Japan). Although we cannot use this salinity data collected during the 2011 survey to compare to the radon results in 2009 and 2010, it is still helpful to understand general salinity patterns along the coastal line.

All the samples collected for chemical analysis were filtered through ADVANTEC 0.2-μm cellulose-acetate filters before storing in the field. Filtered samples for nutrient analysis were frozen until analysis in the laboratory. Four nutrient (NO_3^-, NO_2^-, NH_4^+, and PO_4^{3-}) concentrations were analyzed by ion chromatography (Compact IC 761, Metrohm, Switzerland) and auto nutrient analyzer (SWAAT, BLTEC, Japan), respectively. Although NO_3^- concentrations were determined by two instruments (ion chromatography and auto nutrient analyzer), the following discussion uses the data determined by auto nutrient analyzer, which has a higher precision. We

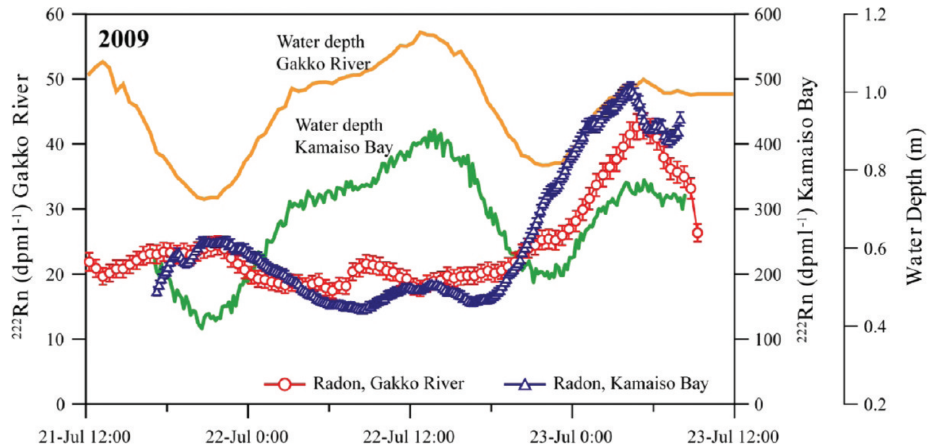

Figure 2. ^{222}Rn time-series from the mooring survey at Kaimaiso Bay and the mouth of the Gakko River. Locations of the two mooring stations are shown in Figure 1.

defined DIN as the sum of NO_3^-, NO_2^-, and NH_4^+ and DIP as PO_4^{3-}.

3. RESULTS AND DISCUSSION

3.1. SGD Fluxes and Patterns. Analytical results for salinity, ^{222}Rn, and nutrients in spring and river waters are shown in Table 1. ^{222}Rn concentrations of the coastal spring waters ranged between 446 and 2077 dpm L^{-1} (Table 1) with a median value of 1390 dpm L^{-1} (n = 10). River water samples were also elevated in ^{222}Rn relative to most surface waters (36–180 dpm L^{-1} with a median value of 127 dpm L^{-1}; n = 4), suggesting that much of the water originated from inland spring waters. However, in the mountain coastal zone in areas without any river water discharges, increased ^{222}Rn activities in seawater are likely due to increased SGD contributions. Very high ^{222}Rn activities (up to 500 dpm L^{-1}) were observed in the mooring survey at Kamaiso Bay (Figure 2). This is about 10 times higher than the concentration measured at the mouth of the Gakko River. Time-dependent changes in ^{222}Rn concentrations for the two different mooring stations showed patterns similar to each other, and were not always synchronized with the tidal pattern as often seen in some other areas[14] (Figure 2). These results suggest that the SGD in this area is not simply driven by the usual tidal pumping effects,[9,28–30] but is caused by a significant hydraulic gradient due to the steep topography, transmissive nature of the volcanic rock, and the abundant rainfall in this area.[29] Radon monitoring over longer time periods is needed to understand the detailed discharge mechanism of groundwater in the Chokai area.[31]

Variations in the time-series ^{222}Rn record from the mooring survey were used to estimate the SGD flux by a non-steady-state mass balance with the unknown term being radon supplied by fluid advection through sea bed,[16,29] which is expressed in the following equation:

$$J_{benthic} + \lambda I_{Ra} - \lambda I_{Rn} - J_{atm} \pm J_{hor} = 0$$

where $J_{benthic}$ represents the combined advective and diffusive flux of radon to the overlying water column, λ is the decay constant of ^{222}Rn (0.181 d^{-1}), I is the inventory (multiplying measured excess ^{222}Rn activity (dpm m^{-3}) by the monitored water depth (m) = (dpm m^{-2})) of either ^{226}Ra or ^{222}Rn, λI_{Ra} and λI_{Rn} account for the production and decay of radon in the water column, J_{atm} is the flux of radon to the atmosphere, and J_{hor} is the horizontal mixing of radon into or out of the study area.

Radon inventories were calculated for each 10 min interval. "Excess" (unsupported) ^{222}Rn activities in the water column were estimated by subtracting the single measured ^{226}Ra concentration of seawater collected 3000 m offshore (356 dpm m^{-3}). We considered loss of ^{222}Rn by radioactive decay negligible within 10 min measurement intervals. J_{atm} was determined based on molecular diffusion and turbulent transfer models[32,33] using measured atmospheric ^{222}Rn data and temperature and wind speed data from Japan Meteorological Agency reports. During the mooring survey period, these values ranged from 0.00 to 0.65 dpm L^{-1}, 19.3–23.6 °C, and 0.0–3.6 m sec^{-1}, with mean values of 0.24 dpm L^{-1}, 20.6 °C, and 1.4 m sec^{-1} (n = 273), respectively. The offshore mixing term, J_{hor}, was estimated under the assumption that horizontal seawater mixing can be simplified by a two end-member linear mixing between coastal and offshore seawaters. We assumed that the absolute values of the apparent negative fluxes, when mixing was not considered, account for the mixing losses for different periods. The ^{222}Rn concentration of offshore seawater was estimated to be 1000 dpm m^{-3}, by using the lowest ^{222}Rn concentration encountered during the ^{222}Rn monitoring surveys along the offshore transects. To convert radon flux estimates to water flux, we simply divide by measured ^{222}Rn concentration in spring water of Kamaiso Bay (1409 dpm L^{-1}) for both Kamaiso Bay and Gakko River data. We assumed that advective flux of radon from the sediment dominates the total flux, and diffusive flux was ignored in our calculations. The final estimated uncertainties of the calculated SGD flux become over 100% when the water flux is smallest but the precision is better than 7% with higher flux values. Detailed explanations of the calculations and corrections for estimating SGD flux from moorings are provided by Burnett and Dulaiova[16] and Burnett et al.[29]

Our discharge estimates based on the above ^{222}Rn model yielded average SGD fluxes for the mooring sites in the mouth of the Gakko River and north of Kamaiso Bay of 0.019 and 0.389 m^3 m^{-2} d^{-1} with maximum values of 0.10 ± 0.01 and 2.18 ± 0.16 m^3 m^{-2} d^{-1}, respectively. Considering that the groundwater potential during the May to August snow melting and rainy season is commonly highest in northern Japan, it is likely that our estimated values would be the maximum encountered throughout the year. The SGD fluxes in Kamaiso

Bay have previously been measured by automated seepage meters[11] at four different sites across the coastline (Figure 1c) from 12:00 August 21 to 0:00 August 23, 2007 in 10 min intervals. The average SGD flux in the center of Kamaiso beach was estimated to be very high at 1.8 ± 0.3 m d^{-1} with the minimum value of 0.9 ± 0.1 m d^{-1}. Although these results were taken by a different measurement approach and a different year, it is suggested that this location is characterized by significant groundwater discharge, much higher than in many other areas of the world.[6]

The results of the continuous ^{222}Rn monitoring surveys are shown in Figures 3 and 4. The characteristic ^{222}Rn pattern along the coastline in all the surveys is somewhat of an "M-shaped" ^{222}Rn pattern with the highest ^{222}Rn peaks in two coastal areas (Figure 3), which suggests these areas have elevated SGD at least during summer time. As expected, ^{222}Rn activities dramatically decreased as we moved offshore (Figure 4). There are four possible reasons for variations in ^{222}Rn along the coastline as well as among four different sampling tracks: (1) tidal variations, (2) variable amounts of SGD along the coast, (3) subterranean mixing and discharge of recirculating seawater with high ^{222}Rn concentrations, and (4) dilution by rainfall and surface waters. Of these possibilities, case (3) is considered less important since the ^{222}Rn patterns generally inversely correspond with salinity patterns (Figure 3b) and this area is known to have many fresh water springs. Considering the constant "M-shaped" ^{222}Rn pattern, and that all surveys took place on a flood tide, case (2) is likely the main reason, although tidal effects, case (1), cannot be dismissed as tidal pumping is known to drive SGD.[9,28−30] Case (4) is the probable reason for ^{222}Rn decline in the south coast in the survey on July 22, 2009 (Figure 3a; south to north) and for overall low ^{222}Rn concentration level in the survey on August 19, 2010 (Figure 3b; south to north) after river flood event due to heavy rainfall. Overall, it can be concluded that the observed variation in ^{222}Rn concentrations along the Mt. Chokai coast is mainly due to differing degrees of SGD contributions to the ocean.

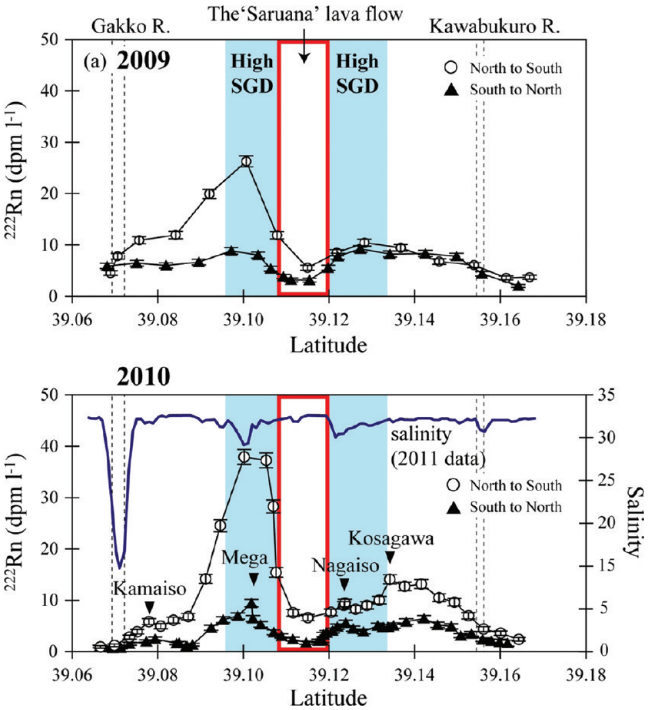

Figure 3. Results of a continuous ^{222}Rn monitoring survey traveling along the coastline (a) in 2009 and (b) in 2010. Panel (b) also shows the salinity profile obtained from the 2011 survey.

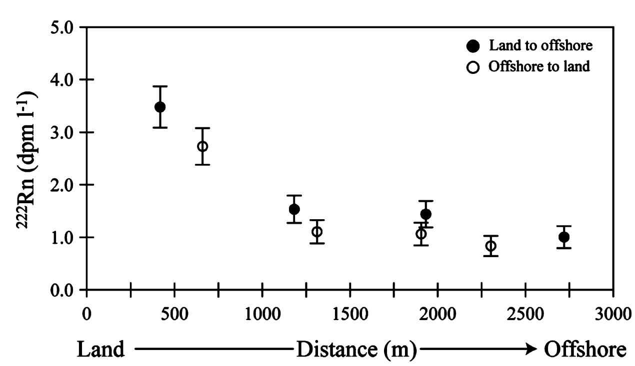

Figure 4. Results of a continuous ^{222}Rn monitoring survey in 2009 traveling by a return route between the land and offshore.

3.2. Significance of the Discharge Pattern of Submarine Groundwater. Careful examination of the "M-shaped" distribution of ^{222}Rn activities along the coastline (Figure 3) is a key to understanding the SGD discharge pattern in relation to the area's hydrology, geology, and topography. For example, the survey results from August 21, 2010 along the coastline from north to south showed ^{222}Rn activities ranging from 1 to 38 dpm L^{-1} (Figure 3b). At the southern end of the sampling track, south of the Gakko River, seawater had ^{222}Rn concentrations lower than 1 dpm L^{-1} (Figure 3b), confirming that there is almost no SGD contribution from the coastal zone in this area. Radon concentrations around the mouth of the Gakko River still showed low but somewhat elevated values below 5 dpm L^{-1}. Concentrations increased slightly (up to 6 dpm L^{-1}) at Kamaiso Bay, where a high SGD was observed in the mooring survey. The highest peak of ^{222}Rn concentrations (38 dpm L^{-1}) was observed around Takinoura and Mega Bay, where two spring sites exist on the coast (Figure 1b). There are no significant ^{222}Rn peaks around the seaward end of the Saruana volcanic lava flow toe (Figure 3b). Instead, the second highest ^{222}Rn peak (14 dpm L^{-1}) was observed on the northern side-end of this lava flow at just around Nagaiso and Kosagawa Bay (Figure 3b).

These results show that the Saruana lava flow is the prime aquifer transporting recharged groundwater to the sea on the Mt. Chokai shoreline. Furthermore, this pattern shows that the groundwater flow does not reach the end of the volcanic toe but rather discharges to the sea through the topographically shortest route along the sides of the lava flow. As mentioned previously, Mega Bay is located at the southern end of the Saruana volcanic lava flow. It seems likely that abundant groundwater flows through the young and porous volcanic lava flows in this area create the largest SGD zone near Mega Bay. There is no access to check the existence of coastal springs along the volcanic cliff coast between Kosagawa Bay and the Kawabukuro River (Figure 1b). However, some high ^{222}Rn concentrations up to 10 dpm L^{-1} were observed along this part of the coast, suggesting the presence of a series of SGD discharges along this area, probably through joints or breaks in the volcanic rocks. The concentrations decrease to less than 5 dpm L^{-1} north of the Kawabukuro River, suggesting that there are no significant SGD contributions in that area.

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Continuous ^{222}Rn monitoring surveys along the Mt. Chokai volcanic coast have demonstrated that the distribution pattern and amounts of SGD are clearly linked with changing geology and topography at the coast. The pathways of recharged groundwater flow are suggested to be regulated by the orientation of the lava flows. In our local-scale (few kilometers) survey area, ^{222}Rn continuous monitoring using a multidetector system[17] with a boat speed of 4 knots can display only a rough SGD pattern along the coastline (Figure 3a). However, with boat speeds of 1−2 knots, the ^{222}Rn monitoring was able to point out exact locations of local SGD zones regardless of travel direction (Figure 3b). We note that in the 2010 survey the SGD signal around Kosagawa Bay was not detected on August 19 (south to north); but was found on August 21 (north to south) (Figure 3b). This was likely due to slightly different boat paths between two tracks. Nonetheless, our results clearly demonstrate the advantageous utility of this technique for locating more precise SGD locations and providing an idea of the relative importance of SGD at each location (Figure 3b). In addition, such surveys can reveal the presence of inland groundwater sources on a precise scale, which are sometimes difficult to observe from the land-side. The approach taken here should be applicable not only to other young volcanic coasts, but also to many other regions having contrasting geological and topographical characteristics.

3.3. Potential Impact of SGD on Local Marine Production. The distribution of nutrient concentrations along the coastline is shown in Figure 5. Similar patterns, similar to the "M radon pattern" shown earlier, were observed for NO_3^-, NO_2^-, and PO_4^{3-}, while NH_4^+ showed a more variable signature. High NO_3^-, NO_2^-, and PO_4^{3-} concentrations were observed at the mouth of the Gakko River, in Mega Bay, and north of Nagaiso Bay (Figure 5a, b, d). It is clear that river and spring waters with relatively high NO_3^- concentrations (7.2−16.1 μmol with a median value of 11.4 μmol, $n = 7$), NO_2^- (0.01−0.33 μmol with a median value of 0.07 μmol, $n = 6$), and PO_4^{3-} (0.21−1.14 μmol with a median value of 0.81 μmol, $n = 7$) (Table 1) are the major sources of these nutrients to the coastal sea. Notably low NH_4^+ concentrations were present in the coastal waters on Aug 21, 2010 in the area between the southern end of sampling and Mega Bay (Figure 5c), while almost constant concentrations or no clear patterns were seen in other areas on both sampling days. Ammonium is the most abundant (up to ~6 μmol) nitrogen species in this area (Figure 5). Because the spring water in this area is not enriched in NH_4^+ (0.63−1.04 μmol with a median value of 0.8 μmol, $n = 5$), other sources such as river water (e.g., Gakko River: 7.12 μmol) might be the origin of the NH_4^+ in coastal seawater.

On the DIN vs DIP diagram (Figure 6), spring water samples from the Chokai area generally plot in the compositional field near the Redfield ratio.[34] This suggests that the SGD in this area has a nutrient balance which is advantageous for phytoplankton uptake. In contrast, the coastal seawater samples generally plot in the compositional field with significantly higher DIN/DIP values. Overall the sampled coastal seawater is enriched in nitrogen and depleted in phosphorus in terms of biocompatibility. Important exceptions are the samples of SGD-affected coastal seawater which tend to plot on the compositional field with lower DIN/DIP ratios with higher DIP (Figure 6) than the general seawater samples. In general, NH_4^+ is the first nutrient consumed during biological uptake.[35] The observed depressions in NH_4^+ along the southern coastal area

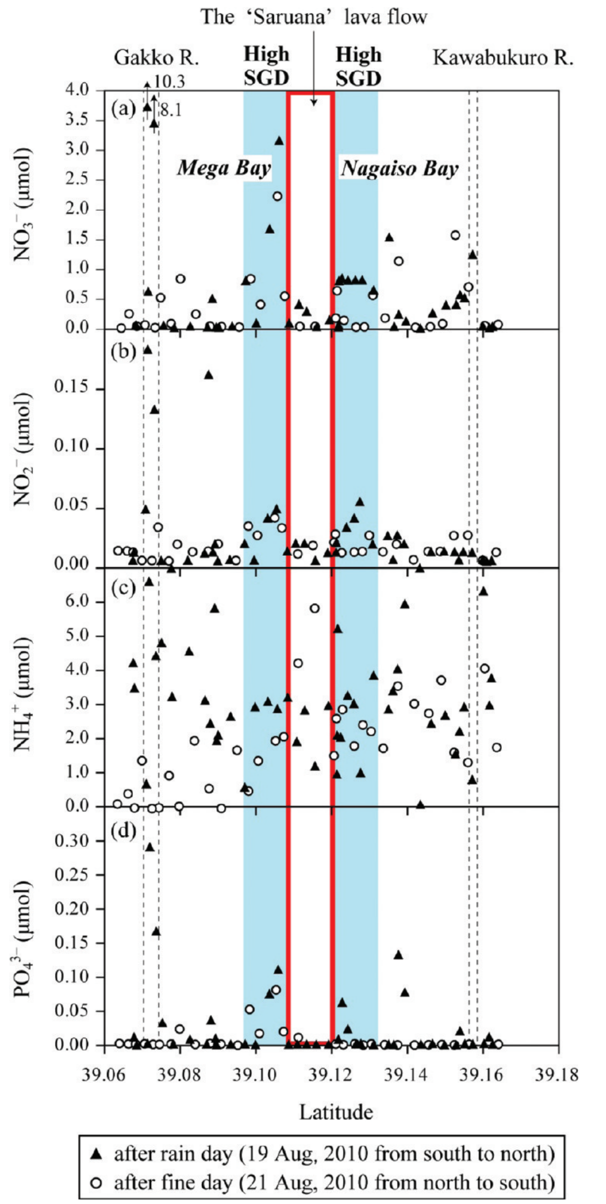

Figure 5. Nutrient (NO_3^-, NO_2^-, NH_4^+, and PO_4^{3-}) concentrations in coastal seawater collected along the coastline.

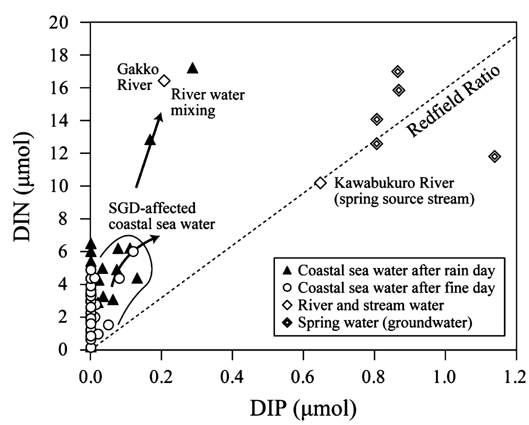

Figure 6. Relationship between DIN vs DIP for water samples from the Chokai coastal area. Lines indicate typical nutrient stoichiometry for marine diatoms from Redfield.[34].

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cannot be simply attributed to the decline of NH_4^+ supply from the source because seawater along the northern coastal area did not show any change in NH_4^+ range. So it is possible that it may be attributable to NH_4^+ removal by plankton activity associated with of the availability of PO_4^{3-}, transported though submarine groundwater and river water discharges.

According to the precise continuous ^{222}Rn monitoring survey on August 21, 2010 (Figure 3b), the ^{222}Rn concentration level near Mega Bay is about eight times higher than that around Kamaiso Bay. If we consider the area of the SGD discharges in both bays to be similar to each other (estimated at about 2×10^4 m^2) and that the observed ^{222}Rn concentrations in the continuous monitoring survey correspond to the relative amounts of SGD at each location, the SGD in Mega Bay can be roughly estimated at 6.2×10^4 m^3 d^{-1}, by multiplying the estimated SGD flux in Kamaiso Bay (0.389 m^3 m^{-2} d^{-1}) by a factor of 8 and area (2×10^4 m^2). This value is one order smaller than that of average river discharges of the Gakko River (4.1×10^5 m^3 d^{-1}) or 5−6 times larger than the Kawabukuro River (1.1×10^4 m^3 d^{-1}) discharge in July (Uza Town Office data). If we extrapolate the maximum SGD flux value of Kamaiso Bay (2.18 m^3 m^{-2} d^{-1}) in the above calculation, the SGD in Mega Bay is estimated to be 3.4×10^5 m^3 d^{-1}.

Median concentrations of NO_3^-, NO_2^-, NH_4^+, DIN, and DIP for the source waters (spring waters) are 14.0, 0.1, 0.8, 14.9, and 0.9 μmol, respectively (Table 1). Using the calculated SGD flux value of 6.2×10^4 m^3 d^{-1}, the fluxes of these nutrients in Mega Bay through SGD are calculated to be approximately 868, 6, 50, 924, and 56 mol d^{-1}, respectively. These values are lower than those calculated for Gakko River (3362, 41, 2050, 5453, and 164 mol d^{-1}, respectively) with an estimated river water discharge of 4.1×10^5 m^3 d^{-1}. However, the DIP flux from SGD into Mega Bay (56 mol d^{-1}) is still significant, accounting for up to one-third of that of Gakko River. Given that Mega Bay is considered the best location for high-quality oysters in the area, we suggest that SGD with moderately enriched PO_4^{3-} may be an important factor providing an environment for the type of phytoplankton productivity that drives high quality oyster production.

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Notes

The authors declare no competing financial interest.

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