J Radioanal Nucl Chem (2016) 307:1865–1870
DOI 10.1007/s10967-015-4580-9

Autonomous long-term gamma-spectrometric monitoring of submarine groundwater discharge trends in Hawaii

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Received: 4 June 2015 / Published online: 27 October 2015

Abstract We developed a fully autonomous underwater gamma-spectrometer for long-term coastal submarine groundwater discharge (SGD) monitoring. The instrument represents a significant improvement over previous submarine gamma-spectrometers in that it is very robust, has high sensitivity allowing high temporal resolution, and is completely autonomous. Here we describe the technical parameters of the new instrument as well as data collected over its 9-month deployment in Kiholo Bay, HI, USA. We also present methods to convert the measured activities to SGD rates. In Kiholo Bay, the derived SGD matched previous estimates but in addition it revealed previously undocumented short- and long-term patterns in SGD.

Keywords Submarine groundwater discharge · Long-term SGD monitoring · Radon · Underwater gamma-spectrometry

Introduction

Long-term trends of submarine groundwater discharge (SGD) are affected by changes in terrestrial and marine driving forces of the coastal hydraulic gradient. These can be tidal and daily variations, seasonal changes as well as processes with time scales of years and decades [1]. Radon as an SGD tracer has been proven to work as an appropriate tracer for long-term monitoring [2, 3]. However, the well-established method of radon time-series monitoring using the RAD-Aqua (Durringe, Inc) instrument is only feasible in settings where power is available and the instrument can be protected from the weather and corrosiveness of the marine environment. The power requirements are mostly driven by the need to actively pump coastal water at >1 L min^{-1} into an air–water exchanger. Passive air–water exchangers such as the Water Probe (Durridge, Inc) have been introduced to eliminate the need for active pumping but those do not provide the required temporal resolution of radon measurements that would reveal the tidal variations in the SGD signature. Other technologies have been developed and applied for SGD studies, such as underwater High Purity Germanium detectors [4, 5] and underwater Sodium Iodine detectors [4, 6–8]. These measure a full spectrum of gamma-rays and are able to selectively detect the ^{214}Bi isotope which is a great-grand daughter of ^{222}Rn. These studies laid ground to the applicability of gamma-spectrometry for SGD.

This paper introduces a new autonomous gamma-spectrometer system for radon monitoring and investigates the applicability of a well-established coastal radon mass-balance [9] for long-term SGD calculation.

Experimental

Technical parameters of the SGD Sniffer

The underwater autonomous gamma-spectrometer named SGD Sniffer consisted of a 7.6×7.6 cm NaI(Tl)

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scintillation detector (Alpha Spectra, Inc.) connected to a 14-pin photo multiplier tube base with integrated bias supply, preamplifier, and multi channel analyzer with digital signal processing (digiBASE^{TM}, Ametek. Inc) operated by a mini PC (Lippert Cool RoadRunner LX-800). The system was housed in a 0.95 cm thick Delrin housing manufactured at the SOEST Engineering Support Facility of the University of Hawaii. Delrin was selected for housing material as it provided desired thermal isolation and was rugged enough to withstand possible impacts while deployed at sea. The housing was purged with nitrogen gas to prevent water condensation. The gamma-ray attenuation of the housing was measured to be $\sim$10 % at 661 keV using a ^{137}Cs source, which was acceptable for our application. The instrumentation was powered by four Li-ion batteries (14.4 V, 95 Whr) connected to a battery management module (both Ocean Server Technology, Inc.) that was charged by four solar panels (Ganz GSP-30). The batteries stored enough power to run the system for 20 days before the computer would shut down in case the panels were not able to recharge the batteries due to low solar input. The system was mounted on a 1.05 $\times$ 1.05 $\times$ 0.69 m floating aluminum frame and moored at a selected coastal location (Fig. 1).

The measurement was controlled by the mini PC using a free code (GPL-3) based on the lidbase C-library for Ortec digiBASE access from Linux user space (sourceforge.net) that was adapted for the digiBASE firmware version used. Recorded spectra were stored in the memory of the mini PC and retrieved every 3–6 months during maintenance visits to the buoy. The downloaded spectra were processed in batch mode by a perl script using Fityk software [10] for peak area determination. Only the 609 and 1460 keV lines were evaluated to determine ^{222}Rn and ^{40}K content in the water. The SGD Sniffer was also outfitted with salinity and temperature sensors (CTD diver, Schlumberger Inc.).

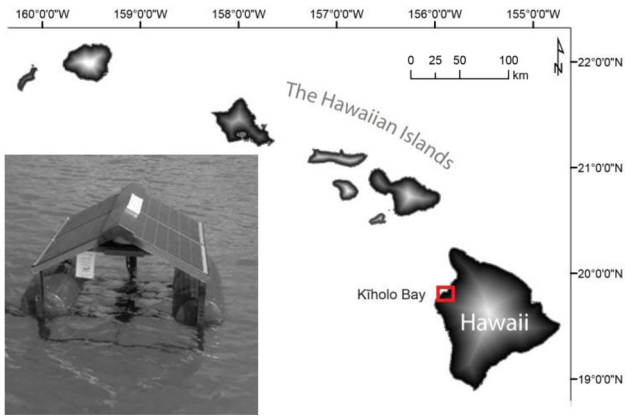

Fig. 1 The SGD Sniffer was deployed in Kiholo Bay, HI between March and November 2014

Principle of measurement

Groundwater is highly enriched in radon, which is soluble in water and is chemically inert. Radon cannot be directly measured via gamma-spectrometry, only its decay products ^{214}Pb ($T_{1/2}$ = 26.8 min) and ^{214}Bi ($T_{1/2}$ = 19.9 min) have strong gamma-rays applicable for ocean monitoring. However, because of the relatively long half-life of these daughter isotopes, we expect that radioactive equilibrium between ^{222}Rn and ^{214}Bi would be established in approximately 3 h. This is an undesirable effect as monitoring tidal scale variations of SGD requires a better measurement response time. Fortunately, in systems where geochemical reactions in the subterranean estuary do not remove Pb and Bi from the groundwater, the discharging water has ^{214}Pb, ^{214}Bi, and ^{222}Rn close to radioactive equilibrium. For our setting this was investigated by a combined measurement of ^{222}Rn by alpha spectrometry via ^{218}Po and of ^{214}Bi by gamma-spectrometry. For this test, we deployed a RAD-Aqua continuous radon monitor alongside the SGD Sniffer for a period of 2 days and the water intake for the RAD-Aqua was positioned at the same depth as the detector. When equilibrium between ^{214}Bi and ^{222}Rn was confirmed, the 609 keV-derived activities measured by the gamma-spectrometer were used as radon activities.

Water column radon and salinity distribution

In order to use measured radon activities to calculate SGD, we had to estimate how the radon measured in the surface represented whole water column radon inventories. Our approach was, after establishing a strong negative correlation between salinity and radon activities, to use salinity to characterize groundwater plume thickness in which we assumed homogenous radon distribution. During our site visits in March and May 2014 we collected vertical salinity depth profiles using a YSI multiparameter sonde (V2-2) on a transect traversing the lagoon.

Study site

The SGD Sniffer was deployed in Kiholo Bay, HI, USA between March 13 and November 23, 2014. The Kiholo watershed is located on the flanks of the Hualalai volcano (Fig. 1). The coastal aquifer consists of an unconfined basal lens in the flank lavas and the upstream watershed has high-level, unconfined, dike-impounded aquifers. Near the coast the watershed receives a mean annual rainfall of only 255 mm [11] but higher precipitation rates (1222 mm) at higher elevations of the watershed contribute significant recharge to the aquifers [12]. Due to the high permeability of lava flows the watershed does not have any perennial streams.

Kiholo Bay consists of an open bay area effectively flushed with the open ocean and a lagoon, which has a more restricted estuarine circulation. The total coastline length is about 1000 m. There is no surface runoff into Kiholo Bay and freshwater is delivered into the bay in the form of brackish SGD. It has been shown that the coastal aquifer has a very wide (km's) salinity transition zone and salinity in the surface of the aquifer 100–200 m inland is ~2 [13]. Groundwater discharges to the bay via well-constrained conduits such as lava tubes as well as diffuse seepage [14, 15]. Previously identified SGD into the bay was estimated to be 7100 m^3 day^{-1} [16]. Other studies have shown that about 4600 m^3 day^{-1} discharges in the open bay [15] and 200–2900 (mean 2100) m^3 day^{-1} in the lagoon [13].

The SGD Sniffer was deployed in Kiholo Bay lagoon, 50 m from the shoreline where water depth is 3 m (Fig. 1). The SGD Sniffer frame floated on the water (Fig. 1) and the frame bottom with the detector was positioned 0.3 m below the water surface to capture the radioisotopic signature of the buoyant groundwater plume. This setting assured that radiation from the benthic substrate would not interfere with water column measurements.

Results and discussion

Detector efficiency calibration

The SGD Sniffer was calibrated in the laboratory by submerging the instrument in a center of a 1 m diameter 1 m tall plastic cylinder filled with tap water with ^{222}Rn activity of 1000 Bq m^{-3} equilibrated for 3 h. The instrument was run for a period of 24 h with 1-h integrated measurement intervals. Radon activity was checked periodically throughout the experiment by a RAD-H_2O system (Durridge, Inc.). This geometry was selected based on estimates that within 0.5 meters of water thickness 99 % of the 609 keV gamma-rays would get attenuated. This assured that our calibration geometry properly mimicked field settings where an "infinite" thickness of water surrounded the detector. This calibration experiment resulted in a detection efficiency of $1.7 \pm 0.4 \times 10^{-4}$ counts s^{-1} Bq^{-1} m^{-3} for the 609 keV of ^{214}Bi.

We performed a field calibration by deploying a RAD-Aqua continuous radon monitor along the SGD Sniffer in Kiholo Bay for a period of 2 days. Both systems were set to record simultaneously at 1-h resolution. These measurements resulted in a detection efficiency of $1.7 \pm 0.7 \times 10^{-4}$ counts s^{-1} Bq^{-1} m^{-3} for 609 keV of ^{214}Bi. The relatively large uncertainty of the efficiency is due to the relatively low ^{214}Bi activities in the natural water resulting in low count rates than what would be achieved with water spiked with a ^{226}Ra tracer. Salinity recorded during this period by the CTD diver was used to derive detection efficiency for ^{40}K assuming conservative potassium behavior with salinity and ^{40}K natural abundance of 0.012 %. Detection efficiency for 1460 keV of ^{40}K was $1.6 \pm 0.2 \times 10^{-5}$ counts s^{-1} Bq^{-1} m^{-3}.

Coastal radon inventories

Radon activities throughout the deployment period between March and November 2014 ranged from 44 to 1900 Bq m^{-3} (Fig. 2). The average 1-sigma relative measurement uncertainty was 29 ± 18 %. 44 Bq m^{-3} was the lowest activity that the SGD Sniffer was able to detect, in 13 % of the spectra the peak evaluation procedure was not able to resolve a peak for the 609 keV line. Due to lower sensitivity, it was impossible to determine the true background of the in situ measurement geometry as no ocean water occurs without a presence of traces of radon, consequently no MDA has been calculated for the method. We assumed negligible background contribution from the bottom sediments as attenuation of gamma-rays to 99 % of original intensity was 0.5 m of seawater for 609 keV and 0.8 m for the 1460 keV gamma-line.

The 24-h average radon activities spanned from 66 to 1200 Bq m^{-3} (Fig. 2a) and the 9-month average radon activity was 441 Bq m^{-3} with a standard deviation of this average of 304 Bq m^{-3}. The large standard deviation of the average indicated large variability in radon activities that was apparent during each tidal cycle. The activity range within one tidal cycle spanned as much as 1000 Bq m^{-3}. These radon variations showed a strong negative correlation with tidal height (Fig. 2b), high activities were always observed at low tide (both, lower low and higher low tides) and activities decreased at high tide, independently of neap and spring tides, or seasons. The reason was that during low tide, the hydraulic gradient between the coastal aquifer and the ocean was larger than at high tide, resulting in higher SGD and therefore larger radon flux. Also, at low tide there was less dilution than at high tide when flooding ocean waters diluted the chemical signature of SGD. This dynamics also compared very well to the RAD-Aqua record (Fig. 3). In fact, we found that the gamma-spectrometric measurement did not show any shifts in time in the appearance of maxima of ^{214}Bi activities throughout the tidal cycle compared to ^{218}Po measurement by alpha-spectrometry using the RAD-Aqua, suggesting radioactive equilibrium between ^{222}Rn and ^{214}Bi in the discharging groundwater.

Previous studies using coastal radon mass balances assumed SGD from the coastline and benthic environment into a well mixed water column, and calculated coastal radon inventories by multiplying measured activities with

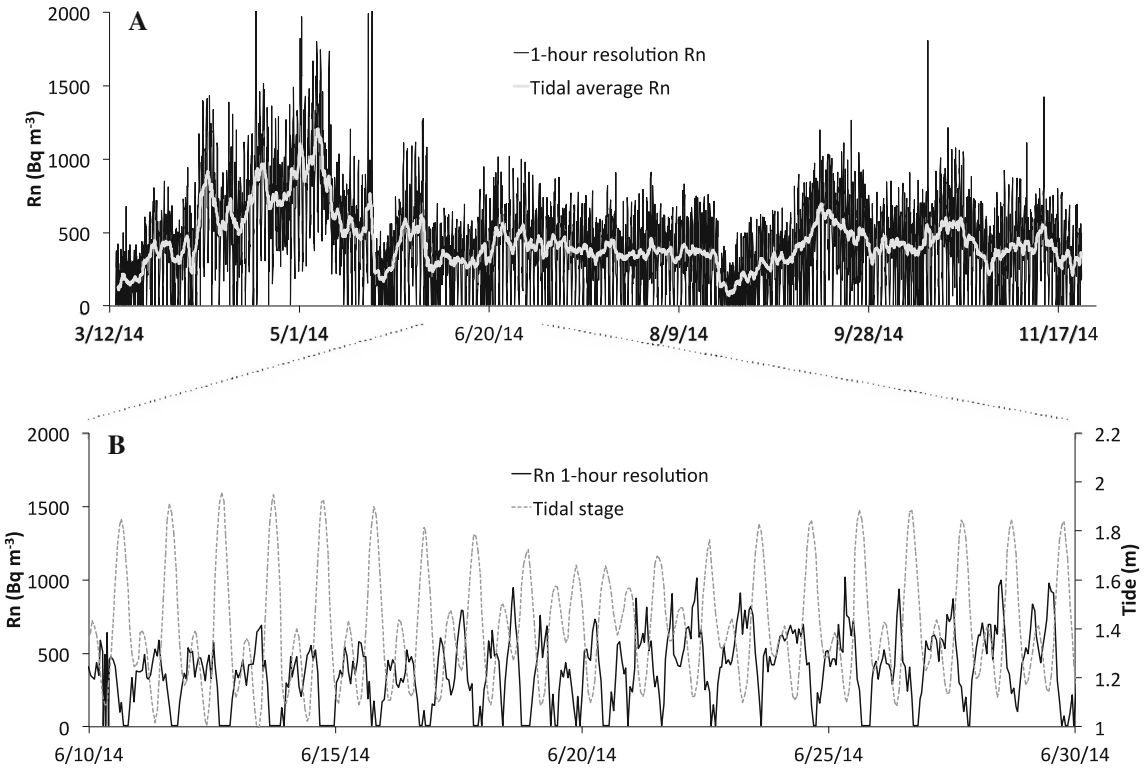

Fig. 2 **a** Radon activities recorded by the SGD Sniffer in Kiholo Bay, HI at hourly resolution (*black line*) and running averages over a tidal cycle (*gray line*). **b** Radon was negatively correlated with tidal stage (*gray dotted line*) throughout the deployment

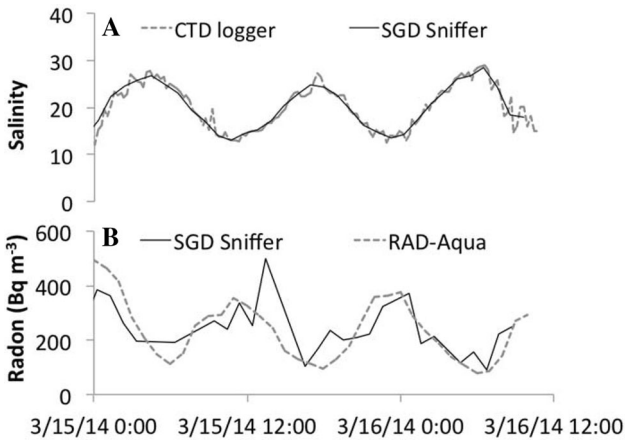

Fig. 3 **a** Salinity in coastal surface water measured by a salinity probe (*dashed line*) and calculated based on the ^{40}K activity determined by the SGD Sniffer (*solid line*). **b** Radon in coastal surface water measured via the RAD-Aqua radon in-air monitor (*dashed line*) and through ^{214}Bi using the SGD Sniffer (*solid line*)

total water depth [9]. This approach was not applicable in our situation where the buoyant groundwater plume was of finite and variable thickness less than the water column depth. The stratification of the water column needed to be characterized but due to the low sensitivity and a required minimum 1-h measurement time of the SGD Sniffer it was impractical to use it to measure a radon depth-profile. We used salinity to characterize the water column vertical structure. Based on two depth surveys performed in March and May 2014 we found that the buoyant groundwater plume thickness was $\sim$1 m at the SGD Sniffer location and the plume extended across the entire lagoon. The plume surface experienced lower salinity at low tide than at high tide but its total thickness did not change significantly during the observed periods. We acknowledge that actual plume thicknesses over the 9-month deployment probably varied with SGD inputs as well as mixing of currents and wind speed, and a more detailed study would be required to derive its dynamics. For our radon inventory calculations we therefore compared two simplified scenarios (1) assumed a constant 1-m plume thickness, and (2) varied plume thickness by normalizing it to tidal height. The difference between the resulting radon inventories for the two scenarios was 22 %.

SGD trends

The measured coastal radon inventories were used to calculate SGD following methods described in [9, 17]. We derived a transient coastal radon mass balance, which in comparison to the one presented in [17] neglected benthic inputs by diffusion because the groundwater plume was

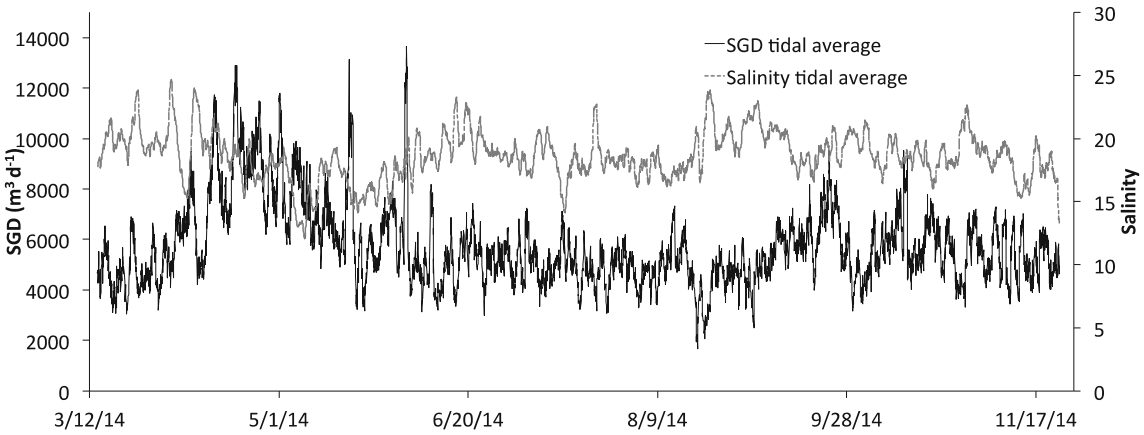

Fig. 4 Tidally averaged SGD (*black line*) and salinity (*gray line*) measured in the surface coastal ocean in Kiholo Bay, HI

isolated from the bottom sediments, and it also neglected radioactive decay because the residence time of the groundwater plume was significantly shorter than the time scale of radon decay. The following equation was applied:

$$F_{\mathrm{SGD}} = \frac{\frac{(A - A_{\mathrm{ocn}} - A_{\mathrm{Ra}}) * z_{\mathrm{pl}}}{T} + k(A - \alpha A_{\mathrm{atm}}) + F_{\mathrm{mix}}}{A_{\mathrm{gw}}} \quad (1)$$

where F_{SGD} is groundwater discharge ($m^3\ m^{-2}\ day^{-1}$), A, A_{gw}, A_{ocn}, A_{atm} are radon activities ($Bq\ m^{-3}$) measured in coastal surface water, groundwater, offshore ocean, and the atmosphere, respectively, A_{Ra} is coastal dissolved ^{226}Ra activity, z_{pl} is the groundwater plume thickness (m), T is the coastal radon measurement interval (day), k is the gas diffusion coefficient ($m\ day^{-1}$), α is the radon gas solubility coefficient, and F_{mix} is radon loss by lateral mixing ($Bq\ m^{-2}\ day^{-1}$).

To derive the radon gas transfer velocity and solubility coefficient we used wind speed measured at a nearby meteorological station (Kawaihae station, National Weather Service), and salinity and temperature measured by the SGD Sniffer. The wind speed varied from 0 to 15 $m\ s^{-1}$ and salinity from 8 to 32 during the measurement period. Other parameters used in the coastal radon mass balance were offshore ^{222}Rn contribution, which was assumed to be radon in equilibrium with offshore dissolved ^{226}Ra (1 $Bq\ m^{-3}$ [18]), in situ radon production by ^{226}Ra decay (1.5 $Bq\ m^{-3}$ Dulaiova, unpublished data), and groundwater as well as atmospheric ^{222}Rn activities measured at the site. Two versions of the mass balance were calculated based on the two scenarios of groundwater plume thickness z_{pl} 1) constant, 1-m thickness and 2) tidally normalized variable thickness. Final F_{SGD} ($m^3\ m^{-2}\ day^{-1}$) was converted to total volumetric discharge ($m^3\ day^{-1}$) by multiplying F_{SGD} by the plume area, which was determined during a coastal survey [19] detailed in [13].

Daily average SGD estimates varied from 1600 to 13,700 $m^3\ day^{-1}$ (Fig. 4) with a 9-month average flux of $5700 \pm 1600\ m^3\ day^{-1}$. The period of highest SGD occurred between mid-April and mid-May 2014 (8200 $m^3\ day^{-1}$) and the lowest groundwater fluxes were observed in the second half of August 2014 (3500 $m^3\ day^{-1}$). These intervals were within wet and dry periods, respectively, suggesting seasonality in SGD. The mass balance using tidally normalized groundwater plume thickness resulted in SGD fluxes 20 % higher then the constant thickness scenario.

Conclusions

We have demonstrated that the SGD Sniffer is well-suited for long-term autonomous SGD monitoring. While it has a lower sensitivity than the well-established RAD-Aqua method, its advantage is that it is capable of operating in remote areas without any maintenance requirements. Radon data collected by the instrument were converted to SGD providing information on long-term trends and dynamics of groundwater discharge. The derived SGD was comparable to previous findings of 7100 $m^3\ day^{-1}$ [16] and in addition, our measurements revealed the highly dynamic nature of SGD on short, tidal time scale as well as long-term seasonal changes. The promise of this instrument is in a longer-term monitoring possibility to help understand driving forces behind SGD from the terrestrial as well as the marine environment. Expected future precipitation changes and sea level rise are two examples that may possibly lead to changes in SGD magnitude and dynamics. The SGD Sniffer was developed to record such changes.

Acknowledgments The authors are grateful to Hui Aloha Kiholo for their support. This publication was made possible in part by support from the Hawai'i EPSCoR Program under National Science Foundation award number EPS-0903833. Its contents are solely the responsibility of the authors and do not necessarily represent the official views of NSF. We thank for the contribution of EPSCoR participants Craig Glenn, Joe Fackrell, and Samuel Wall. The paper was also funded in part by a grant from the National Oceanic and

Atmospheric Administration, Project #R/IR-19, which is sponsored by the University of Hawaii Sea Grant College Program, SOEST, under Institutional Grant No. NA09OAR4170060 from NOAA Office of Sea Grant, Department of Commerce. The views expressed herein are those of the authors and do not necessarily reflect the views of NOAA or any of its sub-agencies. UNIHI-SEAGRANT-JC-13-15.

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