Non-conservative behavior of fluorescent dissolved organic matter (FDOM) within a subterranean estuary

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Abstract - The role of submarine groundwater discharge (SGD) in releasing fluorescent dissolved organic matter (FDOM) to the coastal ocean and the possibility of using FDOM as a proxy for dissolved organic carbon (DOC) was investigated in a subterranean estuary in the northeastern Gulf of Mexico (Turkey Point, Florida). FDOM was continuously monitored for three weeks in shallow beach groundwater and in the adjacent coastal ocean. Radon (^{222}Rn) was used as a natural groundwater tracer. FDOM and DOC correlated in groundwater and seawater samples, implying that FDOM may be a proxy of DOC in waters influenced by SGD. A mixing model using salinity as a seawater tracer revealed FDOM production in the high salinity region of the subterranean estuary. This production was probably a result of infiltration and transformation of labile marine organic matter in the beach sediments. The non-conservative FDOM behavior in this subterranean estuary differs from most surface estuaries where FDOM typically behaves conservatively. At the study site, fresh and saline SGD delivered about 1800 mg d^{-1} of FDOM (quinine equivalents) to the coastal ocean per meter of shoreline. About 11% of this input was related to fresh SGD, while 89% were related to saline SGD resulting from FDOM production within the shallow aquifer. If these fluxes are representative of the Florida Gulf Coast, SGD-derived FDOM fluxes would be equivalent to at least 18% of the potential regional riverine FDOM inputs. To reduce uncertainties related to the scarcity of FDOM data, further investigations of river and groundwater FDOM inputs in Florida and elsewhere are necessary.

Keywords: sandy beach, permeable sediments, coastal aquifers, seepage, fluorescence.

1. Introduction

Submarine groundwater discharge (SGD) is considered a significant source of nutrients to the coastal ocean and can enhance the productivity of coastal waters (Moore, 2010). A large fraction of these nutrients may reach the sea associated with dissolved organic matter (DOM). Closing coastal biogeochemical budgets may require the quantitative determination of nutrient and DOM release through SGD. In some cases, SGD volumetric inputs can be comparable or higher than the total river discharge (Kwon et al., 2014; Moore, 1996; Santos et al., 2014), while in other regions, SGD may represent a only minor source of water to the coastal ocean (Bokuniewicz, 1980; Godoy et al., 2013). Nutrient concentrations in coastal groundwater can be several orders of magnitude higher than in nearshore surface waters (Kroeger and Charette, 2008; Slomp and Van Cappellen, 2004), highlighting the potential role of SGD as significant driver of biogeochemical processes, even where SGD is a minor volumetric source of water to the coastal ocean.

Coastal aquifers and beach sands function as biogeochemical reactors, mobilizing nutrients and releasing DOM from sediments (Anschutz et al., 2009). Where freshwater and seawater mix in the aquifer, biogeochemical processing of organic matter and inorganic constituents may be accelerated (Santos et al., 2009b). The release of solutes, and the processing of nutrients (Erler et al., 2014; Slomp and Van Cappellen, 2004), metals (Charette and Sholkovitz, 2006; Jeong et al., 2012), and carbon (Cai and Wang, 1998; Cyronak et al., 2013; Stewart et al., 2015) associated with SGD have been described in the literature. The long residence time of water in subterranean estuaries compared to that in surface estuaries may increase the effects of biogeochemical reactions that influence the chemical signature of fresh groundwater prior to discharge into the coastal ocean (Riedel et al., 2011; Santos et al., 2008).

Compared to information regarding inorganic nutrients in subterranean estuaries (STEs), our knowledge on the role of organic constituents in SGD is scarce (Kim et al., 2012). DOM from terrestrial sources seeps into groundwater, and high concentrations of dissolved organic carbon (DOC) have been observed in subterranean estuaries and shallow coastal groundwaters (Goni and Gardner, 2003; Kim et al., 2013; Santos et al., 2015; Santos et al., 2008; Santos et al., 2012; Seidel et al., 2014; Stewart et al., 2015). DOM contains degradable substrates that support growth of heterotrophic microbes (Williams and Yentsch, 1976) and is often quantified as DOC. Because the analysis of DOC requires discrete samples, observations at high temporal and spatial resolution are difficult to obtain. This is problematic because shallow STEs may be highly dynamic and strongly affected by short term fluctuations driven by tides and rain events (Santos et al., 2011; Smith et al., 2008). A method for the rapid in-situ detection of DOC therefore is useful for elucidating its temporal and spatial dynamics. Fluorescent dissolved organic matter (FDOM) may be a proxy for DOC (Fichot and Benner, 2011; Spencer et al., 2007). FDOM can be determined via its fluorescence, thereby permitting high resolution time series observations. Possible sources of FDOM to coastal aquifers include the decomposition of terrestrial or marine plant materials (Nakane et al., 1997; Uchida et al., 2000), anthropogenic input (Azevedo et al., 2000; Mostofa, 2005), and by-products of primary or bacterial production (Carder et al., 1989; Del Castillo et al., 2000).

Owing to its dynamic nature and the difficulties associated with sampling and quantification, the role of SGD on coastal biogeochemical processes is still poorly understood. In this paper, we assess whether FDOM can function as a proxy for DOC, and investigate the potential role of the SGD as a source of FDOM to the ocean in the Florida Gulf of Mexico coast. We use radon-derived SGD rates to estimate the flux of FDOM from the subterranean estuary to the coastal ocean. Radon (^{222}Rn) is a natural tracer now widely

used for quantifying SGD and has been successfully applied to calculate nutrient (Burnett et al., 2009), carbon (Atkins et al., 2013), greenhouse gases (Call et al., 2015; O'Reilly et al., 2015) and trace metal (Santos et al., 2011) inputs via groundwater pathways. Radon is continuously released from aquifer minerals through the radioactive decay of ^{226}Ra , which in turn is a product of the longer-lived parent ^{238}U (Swarzenski, 2007). The short half-life of 3.8 days makes ^{222}Rn a good tracer for recent groundwater inputs into coastal waters.

2. Materials and Methods

2.1 Study site

The study site was located on the northeastern coast of the Gulf of Mexico (Turkey Point, Florida, USA). Several studies on SGD have been conducted in this area (Burnett and Dulaiova, 2003; Cable et al., 1996; Li et al., 2009; Moore, 2003; Mwashote et al., 2010; Santos et al., 2009a), including studies on the biogeochemistry of the subterranean estuary (Santos et al., 2008; Santos et al., 2009b; Santos et al., 2011). This subterranean estuary releases diffuse fresh and saline groundwater through an unconfined shallow aquifer and submarine springs from the deeper, confined Floridian Aquifer. Even though fresh groundwater accounts for only ~5% of the total SGD volume, SGD is an important pathway of nutrients as a result of biogeochemical processes in the subterranean estuary (Santos et al., 2009b). The annual precipitation in this area is on average ~1500 mm with maximum rainfall occurring between June and October. The water depth is only ~2 m as far as 1,000 m off shore, and the average tidal range is about 1.0 m (Lambert and Burnett, 2003). The upper meter of the sublittoral sediment consists of sand and muddy-sand beneath it until carbonate rock substrate is reached at around 5 m below the surface. Groundwater temperature in the

shallow subterranean estuary (<3 m) fluctuates from a minimum of 21°C in winter and 25°C early in the fall. The seawater temperature ranges from around 30°C in the summer to 14°C in the winter. The concentrations of DOC in shallow beach groundwater are highly variable and can exceed 1000 µM (Santos et al., 2008).

2.2. Experimental approach

Groundwater in the subterranean estuary and adjacent coastal waters were continuously monitored for FDOM, salinity, pH, and temperature from 22 September to 13 October 2007. Radon (^{222}Rn) was monitored in seawater but not in beach groundwater. For these measurements, seawater was continuously pumped from 300 m offshore and 1.6 m depth in the coastal Gulf of Mexico. In addition, discrete water samples were taken hourly over one complete tidal cycle on 28 September 2007 for analysis of DOC. Groundwater samples were drawn from a 0.5 m deep well, which was located 2.3 m inland of the high tide mark. Previous studies indicated that this is the most dynamic location of the subterranean estuary in terms of salinity fluctuations (Santos et al., 2008; Santos et al., 2009b).

Two FDOM sensors were deployed over the three-week study period. One was installed in the well, and the other was connected to the end of the seawater pipe in the FSU coastal and marine laboratory. Groundwater FDOM was measured with a WET Labs ECO 3 sensor that simultaneously determines FDOM and chlorophyll-a fluorescence. Seawater FDOM was measured by a WET Labs ECO Fluorometer, equipped with a copper brush wiper to prevent biofouling. The sensors were calibrated by the manufacturer using quinine dihydrate and the FDOM concentration is expressed in ppb ($\mu\text{g L}^{-1}$) of quinine. The excitation/emission wavelengths used in these devices are 370/460 nm for FDOM and 470/695 nm for chlorophyll-a. Both sensors were configured to measure FDOM (and chlorophyll-a in the well) at 5-minute time steps. While the fluorescence signal is from both

dissolved and particulate compounds, we assume that dissolved compounds dominate the local FDOM pool.

A CTD (conductivity, temperature and depths) probe was deployed in the well and in the seawater outlet to continuously measure salinity and temperature, and water level in the well. Precipitation data were obtained online (www.wunderground.com) from a weather station located at Alligator Point, about 10 km away from our study site. In addition to continuous in situ monitoring, salinity, temperature, and pH were measured with a handheld YSI-85 probe immediately after collection of the discrete samples. The concentration of ^{222}Rn was recorded at a sampling rate of 1 hour in the seawater outlet of the marine laboratory using a RAD-7 instrument (Santos et al., 2009a). SGD rates were estimated based on a non-steady state radon mass balance model explained elsewhere (Burnett and Dulaiova, 2003). All FDOM and DOC data reported here are original, while some of the radon dataset has been discussed in detail in a companion paper (Santos et al., 2009a).

Samples for DOC were collected hourly from the well and the Gulf Mexico over a 15-hour period on 28 September 2007. Water was drawn from the well through acid-cleaned Teflon tubing using a polyethylene syringe. The tubing was thoroughly flushed with groundwater before sampling. Samples from the Gulf of Mexico were directly taken from the seawater outlet in the laboratory, through which seawater was continuously flowing. Immediately after sampling, the water was filtered through disposable 0.7 μm Whatman GF/F syringe filters (sample-cleaned), acidified with HCl (analytical grade) to pH 2 to remove inorganic carbon, and fire-sealed into pre-muffled (500°C) glass ampoules. DOC was analyzed using a Shimadzu TOC- V_{CPH} total organic carbon analyzer with a detection limit of 5 μM and analytical uncertainties better than 5%. We included deep sea reference samples distributed by Dennis Hansell of the University of Miami as external reference in the measurements and obtained results comparable within a 5% margin.

3. Results

FDOM concentrations in groundwater were on average 5.5-fold higher than those in seawater, and the FDOM variability in the groundwater (relative standard deviation = 12%) also exceeded the variability in seawater (relative standard deviation = 7%; Table 1). In the groundwater, salinity ranged from 2.5 to 35.4, while salinity in the seawater ranged from 33.8 to 36.4. The average temperature in the groundwater was only slightly different than that in the seawater. Freshening of the groundwater, driven by a 26 mm rain event at the beginning of the 3-week time series experiment, was associated with a maximum in FDOM concentration in the groundwater (Fig. 1). During the rain event, water level, FDOM concentration, and chlorophyll-a concentration were comparably higher than the respective averages, while temperature did not show any changes. No additional rainfall events were observed during the rest of our study. Although the freshening effect in the seawater was not as pronounced as in the groundwater, the minimum recorded seawater salinity coincided with a maximum water level as well as maximum FDOM concentration (Fig. 2).

Discrete sampling (15 hours) of seawater revealed higher DOC concentrations at low tide when salinity was slightly lower (Fig. 3). Discrete sampling in groundwater (Fig. 3) also showed higher DOC concentrations at low tide when salinity dropped. Radon-derived SGD rates did not show clear variations following the rain event because fresh SGD accounts for only a minor fraction of the total SGD traced by radon at this site (Santos et al., 2009a).

4. Discussion

4.1. FDOM behavior in the subterranean estuary

Simple conservative mixing between the fresh groundwater end-member and the seawater end-member could not explain the FDOM distribution in the shallow groundwater in the beach (Fig. 4). There are at least three potential sources of DOM to this groundwater: (1) terrigenous DOM of vascular plant origin, i.e. soils of the adjacent pine forest may contribute to the high FDOM in fresh groundwater, (2) marine sources; i.e. phytoplankton degradation in groundwater with high salinities or leaching of seagrass debris, and (3) desorption of organic matter from beach sediments during the infiltration of high pH seawater into the shallow aquifer (Komada et al., 2004). Soil-derived DOM contains more aromatic groups and is often associated with higher FDOM than marine-derived DOM (Esteves et al., 2009). We also noticed that there was seagrass debris accumulating on the beach at the high tide line during sampling, which could be another potential source of DOM (Stabenau et al., 2004) supporting FDOM production for several weeks after seagrass stranding events.

Interestingly, the FDOM concentrations in saline groundwater (~100 ppb) were about 4-fold higher than the FDOM concentrations in seawater (~28 ppb) with approximately the same salinity (~34). This implies effective FDOM production soon after seawater infiltrates the beach sediments at high tide. Based on the shape of the FDOM vs. salinity plot (i.e., steeper slopes at high salinities; Fig. 4), this increase in FDOM may be related to breakdown of labile marine organic matter. As saline groundwater ages and mixes with fresh groundwater, the remaining organic matter likely becomes more refractory, potentially preventing further FDOM production at lower salinities. As a result, the increase in FDOM from ~150 ppb at salinity 25 to 200 ppb at salinity 0 appears to be related to conservative mixing between fresh groundwater and brackish groundwater already enriched in FDOM. The

breakdown of labile marine organic matter and long residence times probably contributed to the higher FDOM in saline groundwater, as suggested for DOC concentrations and specific molecular constituents in tidal flat sediments (Seidel et al., 2014). While no observations are available on the fresh groundwater FDOM endmember, the variability in low salinity samples was narrower than the variability in high salinity samples.

The observed FDOM production in the high salinity region of the subterranean estuary is consistent with a previous study reporting DOC production in the same region (Santos et al., 2009b). Some surface estuaries may also exhibit DOM production along the mixing gradient as in a system in the Everglades fringed by mangroves (Cawley et al., 2014). However, most previous surface estuary investigations revealed that DOM and FDOM often behave conservatively. For example, Yamashita et al. (2011) demonstrated that DOC and “humic-like” FDOM behaved conservatively in Liverpool Bay. Del Castillo et al. (2000) made similar conclusions for FDOM on the West Florida Shelf. The implied contrast between surface and subterranean estuaries is likely related to longer residence times in beach groundwater than in surface estuarine waters (Moore, 1999), higher microbial activity in beach sands than in the water column (Wild et al., 2006), and the constant input of marine organic matter and oxygen into the beach associated with tidal pumping (Billerbeck et al., 2006; Santos et al., 2009b). Combined, these processes make subterranean estuaries and beach sands effective bioreactors that can consume large amounts of particulate organic matter and release dissolved products such as DOM.

A positive correlation was observed between FDOM and chlorophyll-a in the well ($p < 0.05$; Fig. 5). This supports our suggestion that the degradation of marine DOM was a main factor behind the non-conservative FDOM behavior observed in groundwater with salinities >25 . The intrusion of labile, algal-derived DOM into the subterranean estuary may concurrently increase chlorophyll-a and FDOM. In contrast, terrigenous soil-derived DOM

does not contain chlorophyll-a but has high FDOM. The observed relationship between FDOM and chlorophyll-a therefore implies the presence of labile plant-derived biomass in the groundwater, which would be consistent with recent phytoplankton or seagrass as major sources of DOM. In addition, the increase in FDOM in groundwater following the rain event occurred on time scales of hours, while the transport of fresh groundwater from the pine forest to the beach occurred on time scales of a few weeks (Santos et al., 2009b). Therefore, it is more likely that the observed FDOM production is caused by tidally-driven infiltration of marine organic matter at high tide rather than the horizontal transport of terrestrial organic matter from the pine forest. The high dissolved nitrogen and phosphorus concentrations (Santos et al., 2009b) may contribute to fuel subsurface microbial activity and the apparent production of FDOM and DOC in this subterranean estuary.

4.2 FDOM as a proxy for DOC

In spite of the scatter that is likely related to the narrow concentration ranges, FDOM and DOC concentrations were correlated both in the coastal Gulf of Mexico waters and beach groundwater ($p < 0.05$; Fig. 6). Therefore, it may be possible to estimate SGD-derived DOC fluxes at this site from the fluorescence measurements. The FDOM/DOC ratios were consistently higher in the groundwater (~ 0.14) than in the coastal waters (~ 0.10). This indicates high fluorescence components in groundwater DOM of possibly terrestrial origin and a low fluorescence background in the nearshore waters. The lower FDOM/DOC ratio in the Gulf of Mexico waters may be attributed to a primarily marine source of DOM (Esteves et al., 2009), or to photodegradation, which can be a major sink of FDOM (Andrews et al., 2000). The use of optical properties of DOM as a proxy of DOC concentrations and sources has been explored previously (Kowalczyk et al., 2010). Significant correlations between FDOM and DOC concentration have been reported in several coastal systems (Huguet et al.,

2010) including shallow sediment porewaters (Burdige et al., 2004). As observed in this study, FDOM/DOC ratios are source-specific, but photodegradation in surface waters and seasonality may cause deviations of the groundwater source on larger spatial and temporal scales. Longer term investigations would be warranted to assess changes in the FDOM/DOC ratios in coastal seawater and groundwater.

4.3 SGD as a source of FDOM to the Gulf of Mexico

FDOM fluxes to the coastal ocean were estimated by multiplying the SGD rate by the groundwater FDOM endmember concentration (Table 2). SGD rates are available from a radon mass balance that includes a combination of both freshwater and seawater (Santos et al., 2009a). At Turkey Point, about 95% of the SGD is related to saline water recirculation through the beach face and the remaining is fresh SGD (Santos et al., 2009a). We assume that the endmember FDOM concentration in fresh SGD is equivalent to the FDOM values observed in fresh beach groundwater (~205 ppb), while the saline SGD FDOM endmember was defined as the difference between average seawater concentration (~28 ppb) and saline beach groundwater concentrations (~100 ppb). This approach of estimating the saline SGD endmember concentration provides an estimate of the net FDOM production released during seawater recirculation in beach sediments and is consistent with previous studies at the same site (Santos et al., 2009b) and elsewhere (Beck et al., 2010). In spite of the higher endmember concentration in fresh groundwater, the FDOM fluxes associated with saline SGD (or seawater recirculation in beach sediments) were about 8-fold higher than those associated with fresh SGD. The radon-derived SGD rates used in this study represent only a narrow seepage face stretch of about 200 m off the beach (Santos et al., 2009a). Therefore, our estimates should be seen as minimum values because saline and fresh SGD are likely to occur

further offshore as observed near our study site (Cable et al., 1997; Moore, 2003) and elsewhere in Florida (Liu et al., 2014; Smith and Swarzenski, 2012).

If the FDOM flux via SGD in our study is assumed to be representative of the entire Gulf Coast of Florida (shoreline linear length approximately 1200 km), the total SGD FDOM flux to the Florida Gulf Coast would be equivalent to $\sim 2200 \text{ kg d}^{-1}$. This is probably a conservative value because our SGD-flux estimate ignores offshore SGD and coastal embayments that would extend the shoreline length. Putting these values in perspective is difficult because concentrations of FDOM in nearby rivers are unavailable. We have used the same sensor described here in the Suwanee River and found FDOM values of 140 ppb (author's unpublished data). Considering an average freshwater river discharge to the Florida Gulf Coast of about $1000 \text{ m}^3 \text{ s}^{-1}$ (the approximate sum of the Apalachicola River and Central Florida Rivers discharges) (Hu et al., 2006), and assuming the Suwanee River concentration is representative of the Florida Gulf Coast, a river-derived FDOM flux of $12,000 \text{ kg d}^{-1}$ could be delivered to the Florid Gulf Coast. This value is about 6-fold greater than the estimated SGD-derived FDOM flux. Although these back of the envelope calculations are subject to large uncertainties owing to the scarcity of data and short-term measurements, they suggest that SGD is not a negligible source of FDOM to the nearshore Gulf of Mexico and demonstrate the need for further studies addressing both SGD and river inputs in detail.

To further evaluate whether the observed FDOM production in the STE is large enough to be reflected in the nearby coastal ocean, we assessed correlations between the radon-derived SGD rates and FDOM concentrations in seawater (Fig. 7). The large scatter was somewhat reduced when we removed daily trends and restricted our correlation analysis to tidal time scales (Fig. 7b). For this purpose we calculated one-day moving averages for FDOM in the coastal ocean and ^{222}Rn -derived SGD, and subtracted these “background” values from the individual hourly data. While a broad scatter was still observed, the detrended

FDOM and SGD rates were positively correlated (Fig. 7). The weak correlation ($r^2 = 0.07$), implies a low regional FDOM contribution from SGD relative to other processes driving FDOM in seawater. In addition, photobleaching may occur rapidly after FDOM reaches coastal waters and dampen FDOM intensity (Blough and Del Vecchio, 2002).

4. Conclusions

FDOM values in beach groundwater from northern Florida were highly variable over tidal time scales and much higher than in the adjacent Gulf of Mexico. FDOM was not only introduced to shallow groundwater from a nearby pine forest but also produced within the subterranean estuary from marine DOM sources. The observed FDOM distribution could only be explained by biogeochemical processes within the subterranean estuary, releasing FDOM to solution primarily at groundwater salinities higher than ~25. Subterranean estuaries may thus differ from surface estuaries, where FDOM often behaves conservatively. Local FDOM production within subterranean estuaries thus may have to be considered when calculating the flux of DOM to the coastal ocean via groundwater and porewater pathways. FDOM may be used as a proxy of DOC not only in surface waters, but also in beach groundwater. SGD delivered about 1800 mg d^{-1} of FDOM to the coastal ocean per meter of shoreline at the study site. If extrapolated to the Florida Gulf Coast, these SGD fluxes would be equivalent to about 18% of the potential regional riverine inputs. Considering the large uncertainties associated with these extrapolations, additional investigations should focus on larger spatial and longer temporal scales to assess whether SGD is an important regional source of DOM.

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Table 1: Average (Avg) $\pm$ standard deviation (St. Dev.) of selected parameters during the 3-week long time series in groundwater and seawater.

		Groundwater			Seawater		
FDOM, ppb	Avg. $\pm$ St. Dev	156	$\pm$	19	28	$\pm$	2
	Min. - Max.	98	-	234	22	-	34
DOC, μM	Avg. $\pm$ St. Dev	722	$\pm$	42	294	$\pm$	42
	Min. - Max.	634	-	777	272	-	340
Temp, $^{\circ}\text{C}$	Avg. $\pm$ St. Dev	26	$\pm$	1	29	$\pm$	2
	Min. - Max.	24	-	27	25	-	33
Salinity	Avg. $\pm$ St. Dev	28	$\pm$	6	35	$\pm$	1
	Min. - Max.	3	-	34	34	-	36
Chl-a, mg L^{-1}	Avg. $\pm$ St. Dev	7	$\pm$	2	na		
	Min. - Max.	3	-	12			
Water Level, cm	Avg. $\pm$ St. Dev	28	$\pm$	12	17	$\pm$	28
	Min. - Max.	11	-	65	-71	-	73
^{222}Rn , dpm m^{-3}	Avg. $\pm$ St. Dev	na			4843	$\pm$	1005
	Min. - Max.				2013	-	6935

Table 2: Fluxes of FDOM (quinine equivalents) from fresh and saline groundwater to coastal Gulf of Mexico. The SGD rates were obtained from a radon mass balance model and are shown in units of m^3 per meter of shoreline per day assuming a 200-m wide seepage face (Santos et al., 2009a).

	FDOM Endmember mg m^{-3}	SGD rates $\text{m}^3 \text{m}^{-1} \text{d}^{-1}$	SGD-derived FDOM Flux $\text{mg m}^{-1} \text{d}^{-1}$
Fresh SGD	205	1	205
Saline SGD	73	22	1606
Total	-	23	1811

Figure 1: Results of the three-week time series in the 0.5-m deep beach groundwater well located at the high tide mark in northern Florida. The data gap was caused by necessary instrument maintenance.

Figure 2: Results of the three-week time series measurements in the adjacent coastal seawater.

Figure 3: Fifteen-hour time series in the seawater (left panel) and groundwater (right panel).

Note the different Y axis scales to highlight temporal trends.

Figure 4: Mixing diagram for FDOM in the beach groundwater. The dashed line indicates conservative mixing of seawater and fresh groundwater, while the solid line indicates conservative mixing between saline groundwater and fresh groundwater. Nearly all the groundwater observations plot above these theoretical conservative mixing lines implying FDOM production within the subterranean estuary. The arrows indicate the zone of FDOM production (i.e., saline groundwater) and the zone of apparent conservative mixing within beach groundwater.

Figure 5: Correlation between FDOM and chlorophyll-a in the groundwater. The color gradient of data points indicates salinity.

Figure 6: FDOM versus DOC in groundwater (A) and seawater (B). The dashed lines show the 95% confidence intervals of the slope. The equation describing the DOC vs. FDOM relationships in groundwater and seawater were $\text{DOC} = -315 \pm 394 + 6.9 \pm 2.6 \text{ FDOM}$, and $\text{DOC} = -2 \pm 128 + 9.6 \pm 4.1 \text{ FDOM}$, respectively, with uncertainties representing standard errors.

Figure 7: Scatter plot of FDOM in seawater and ^{222}Rn -derived SGD before detrending (A) and after detrending and zero averaging the data (B). The data passed a test for normal distribution (normal probability plot).