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What Is the Role of Fresh Groundwater and Recirculated Seawater in Conveying Nutrients to the Coastal Ocean?

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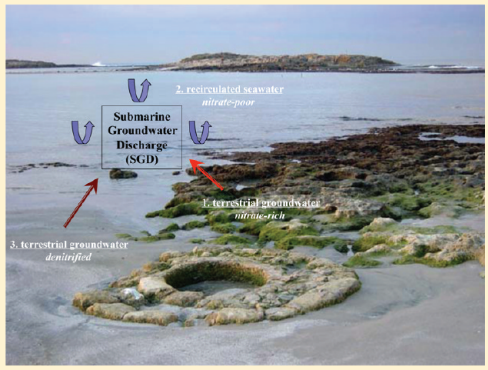
ABSTRACT: Submarine groundwater discharge (SGD) is a major process operating at the land−sea interface. Quantifying the SGD nutrient loads and the marine/terrestrial controls of this transport is of high importance, especially in oligotrophic seas such as the eastern Mediterranean. The fluxes of nutrients in groundwater discharging from the seafloor at Dor Bay (southeastern Mediterranean) were studied in detail using seepage meters. Our main finding is that the terrestrial, fresh groundwater is the main conveyor of DIN and silica to the coastal water, with loads of 500 and 560 mol/yr, respectively, per 1 m shoreline. Conversely, recirculated seawater is nutrient-poor, and its role is mainly as a dilution agent. The nutrient loads regenerated in the subterranean estuary (sub-bay sediment) are relatively small, consisting mostly of ammonium (24 mol/yr). On the other hand, the subterranean estuary at Dor Bay sequesters as much as 100 mol N/yr per 1 m shoreline, mainly via denitrification processes. These, and observations from other SGD sites, imply that the subterranean estuary at some coastal systems may function more as a sink for nitrogen than a source. This further questions the extent of nutrient contributions to the coastal water by some subterranean estuaries and warrants systematic evaluation of this process in various hydrological and marine trophic conditions.



INTRODUCTION

Submarine groundwater discharge (SGD) is now commonly recognized as a major conveyor of dissolved matter between land and the sea. Main driving forces include the hydraulic gradient of the coastal aquifer as well as tidal forcing and wave setup. Usually, most of the discharging water is recirculated seawater, with its proportion depending on local hydraulic conditions, though in karstic, and some volcanic and glacial areas, it is composed principally of fresh meteoric water. Several papers have established the important role of the recirculated seawater in the transport of solutes from aquifers to the coastal water. Moore[1,2] established the term "subterranean estuary" (hereafter, STE) for the aquifer zone, where recirculating seawater mixes with fresh groundwater, and where water−rock interaction affects the mobility of constituents, including nutrients, toward the sea. Several follow-up studies concluded that both fresh and saline SGD can carry large loads of nutrients to the coastal seawater (e.g., 3−7). In most of these works, nutrient concentrations measured in onshore wells were multiplied by offshore groundwater discharge (measured by geochemical tracers or by seepage meters) to derive fluxes (e.g., 3−5,7).

In this paper, we show that while fresh SGD is undoubtedly a major supplier of nutrients to the sea, the recirculated seawater component of SGD can often be relatively nutrient-poor, thus limiting its role as a biogeochemical conveyor and its impact on coastal water ecology. Moreover, it is shown that the STE may actually act more as a trap for nitrates supplied by the fresh groundwater.

HYDROGEOLOGY AND SGD BACKGROUND

Dor Bay is located at the southern Carmel coastal plain along the southeastern oligotrophic Mediterranean coast (Figure 1). In this area, direct discharge to the sea (SGD) is from a Quaternary sandstone aquifer (Figure 2; [8]), which is mainly composed of up to 40 m thick calcareous sandstone (locally called "Kurkar"), which forms 2−3 north−south oriented topographic ridges at the surface (Figure 2). The depressions between the ridges are filled with clays, which are overlain by Holocene loose sands that form local small unconfined aquifers. The enclosure of the Dor Bay was created by the partly submerged western Kurkar ridge

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(Figure 1). The Kurkar and the sand are both exposed at the bay floor (proportions of 30:70, respectively) such that the semi-confined Kurkar unit discharges to the sea both directly and through breaches in the overlaying clay and the sand.

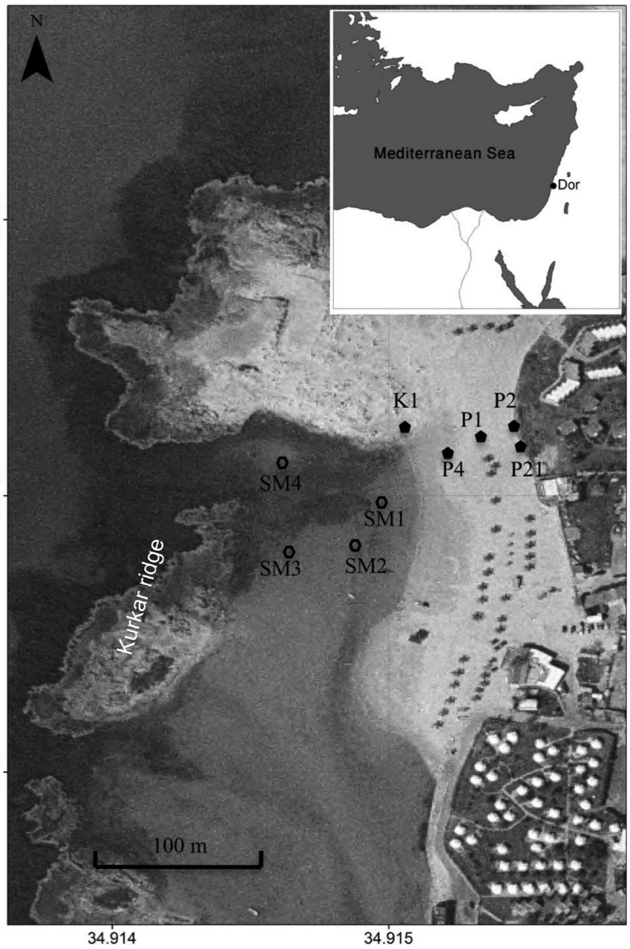

Figure 1. Air photo of the Dor Bay area. Dark-colored areas in the bay are where the calcareous sandstone ("Kurkar") is exposed, while light-colored areas are sand covered. Locations of the piezometers (K1, P1−4, and P21) and main seepage meters (SM1−4) are indicated. The inset is a location map of Dor.

Previous reports on SGD in Dor Bay,[9,10] based on radon activities and short-lived radium isotopes in groundwater and in the water discharging from the bay floor, indicated that fresh water was mainly discharging from the Kurkar semi-confined unit, while seawater circulation was restricted to the phreatic sand unit. The exclusive fresh water discharge and the absence of seawater circulation in the Kurkar is due to its larger hydraulic gradients.[10] Discharge from the bay floor was very variable even on a 1-m scale and varied between 0 and 50 cm/d. Multiannual average fresh water discharge is estimated at 3.5 cm/d. The salinity of discharging water changed between the Kurkar area, where discharge was usually of low-salinity[2,3] brackish water, and the sand-covered areas of the bay with salinities of 15−37 (5−60% fresh water[10]).

■ FIELD AND ANALYTICAL METHODS

Onshore groundwater was sampled from several piezometers located in the sand (P1, P2, P4) and in the Kurkar (K1 and P21, Figure 1) 5−55 m from the high tide line, 10−20 cm below the water table. Water discharging from the sandy bay floor was sampled via seepage meters, which were installed in several locations in the bay (Figure 1). The seepage meters were conical, 30 cm high, and 50 cm in diameter, with a 4-L flexible collection bag attached to a threaded pipe nipple at the top of the meter. The collection bag was prefilled with 0.5 L water to reduce artifacts due to bag expansion. Due to its hard nature, no seepage meters could be installed directly on the Kurkar calcareous sandstone. Seepage meter water was sampled either from the meters' collection bags or via direct pumping from the meters. Water sampling for nutrients started 2 days after installation, to ensure flushing of the meters by the advecting water, and lasted for 36−48 h. Collection bags were changed every ca. 2 h, and the net volumes collected were mostly 2−2.5 L. We used water samples only from those meters that showed a discharge of >10 cm/d, implying water residence time of <1 day in the meters, as to avoid water stagnation.

Salinity was measured in situ using YSI 6600 probe and PC6600 software or by a DELTA-OHM HD2156.2 conductivity meter. Samples for nutrients were kept frozen until analysis. Nutrients, including ortho-phosphate, nitrate + nitrite (hereafter referred as nitrate), silicic acid (hereafter referred as silica) and ammonium, were determined using a segmented flow Skalar SAN^{plus} System Instrument as detailed in ref 11.

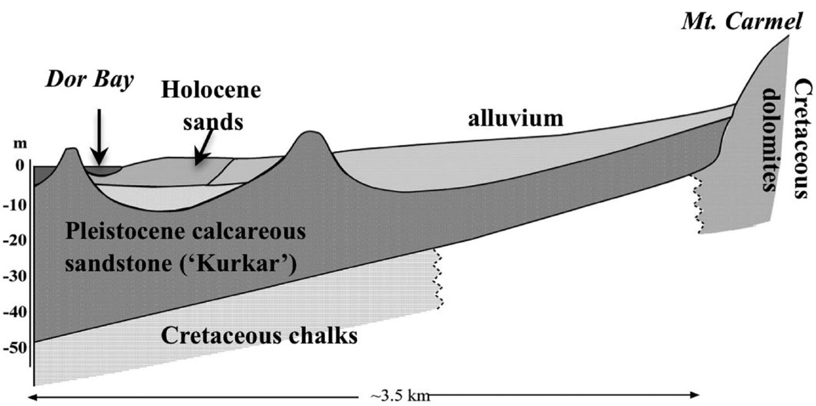

Figure 2. Schematic cross section through the main geological units in the Carmel coastal plain (after Michelson, 1970).

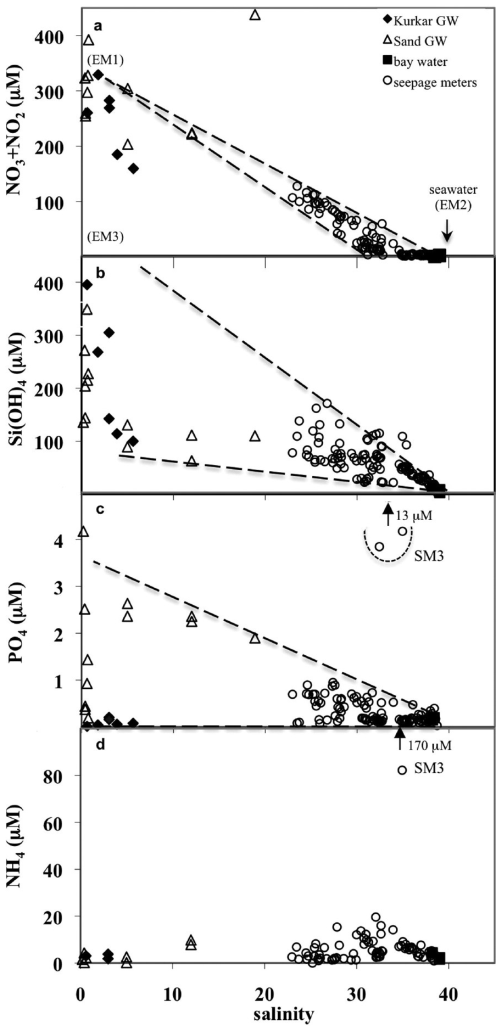

Figure 3. Nutrient concentrations against salinity in groundwater, bay water ("seawater"), and water discharging from Dor Bay floor through seepage meters: (a) nitrate; (b) silica; (c) phosphate; (d) ammonium. Dashed lines in a−d are mixing lines between possible end-members (EM), as defined by the spectrum of seepage meter water compositions. The water with exceptionally high PO_4 (4−13 μM) and NH_4 (up to 170 PO_4) were sampled from seepage meter SM3 in May 2008.

■ RESULTS

Nutrient concentrations sampled during February and June 2007 and May 2008 are presented in Figure 3a−d together with salinity. The eastern Mediterranean is an oligotrophic sea, with typical nitrate and phosphate concentrations much less than 100 nM in surface seawater.[11] Observed nitrate and silica concentrations in Dor Bay water are somewhat higher, but usually constrained to <3 and <5 μM, respectively, while phosphate is indistinguishable from the eastern Mediterranean. On the other hand, Dor groundwater carries relatively high concentrations of nutrients. Average concentrations in onshore groundwater were 280 and 210 μM of nitrate and silica, respectively (Figure 3a and b). This is true also for onshore saline groundwater, with up to 438 μM nitrate in one water sample with a salinity of 19, which was taken from the close to shore piezometer P4 (Figure 3a). While the variability in nutrient concentration was relatively large, there were no apparent systematic temporal or spatial trends. Concentrations in the Kurkar groundwater were similar to those measured in the sand (Figure 3a and b), except for PO_4, which was very low (lower than in seawater) in the Kurkar (Figure 3c).

Nitrate and silica concentrations in groundwater discharging from the bay floor (sampled from the seepage meters) were between those of bay water and onshore groundwater (0−128 μM and 2−120 μM, respectively). The phosphate in the discharging water was relatively low, though mostly higher than both in bay water and in the Kurkar groundwater (0−0.95 μM, Figure 3c). When plotted against salinity, nitrate shows mixing between nitrate-poor saline water and nitrate-rich fresh or slightly brackish groundwater (Figure 3a). Moreover, while the groundwater from both the Kurkar and the sand shows a wide variability of nitrate content, all discharging waters point to a very well-defined end-member composition in the upper range of the fresh groundwater spectrum (∼330 μM).

Silica in the discharging water shows a similar pattern (Figure 3b), although the data are more scattered and does not allow the definition of a uniform groundwater endmember composition. The phosphate data are also scattered (Figure 3c); however, concentrations are clearly constrained between a phosphate-poor mixing line that connects seawater and the Kurkar groundwater and another mixing line that connects seawater and phosphate-rich sand groundwater (Figure 3c). This is except for the samples that were taken from seepage meter SM3 in May 2008, which yielded very high PO_4 concentrations (4−13 μM, Figure 3c), which came together with strong H_2S odor. It is considered as an exceptional case, which may be related to the decomposition of locally buried organic matter.

Ammonium was quite low in both bay water and in onshore groundwater (≤4 μM, Figure 3d). However, in the saline groundwater of P4 it was relatively high (8−10 μM). The water discharging from the bay floor shows a wide range of concentrations, with most samples showing higher than groundwater concentrations (up to 20 μM, Figure 3d), albeit still 1 order of magnitude lower than the nitrate concentrations in these samples (Figure 3a). Similar to the phosphate, samples taken from SM3 in May 2008 yielded very high NH_4 concentrations (up to 171 μM, Figure 3d), which are considered as an outlier in this study.

■ DISCUSSION

Nutrient Transport between Land and Sea. Coastal aquifers facilitate the interaction of nutrient-rich groundwater with nutrient-poor seawater. This is especially important in oligotrophic settings, such as the eastern Mediterranean, where the nitrate content of seawater is typically <100 nM.

On a nitrate−salinity diagram (Figure 3a), the water discharging from the bay floor appears to plot along a mixing line between a nitrate-rich (∼330 μM) fresh groundwater endmember (hereafter, EM1) and a nitrate-poor saline component, implying that nitrates are being carried to the sea solely with the fresh groundwater and that the mixing with recirculated seawater acts just as a dilution agent. However, on the nutrient-poor side, the endmember composition is not well-defined, but spans a salinity range between 31 and 39 (Figure 3a). Actually, one can identify ternary rather than binary mixing, where on the nutrient-poor side there are two unique endmembers. The first (EM2) is characterized by eastern Mediterranean seawater salinity (∼39), thus it is identified as recirculated seawater. The other endmember has a lower salinity, and in the context of Dor Bay it should be a nutrient-poor fresh or slightly brackish groundwater component (EM3, Figure 3a). The absence of any discharging water outside the triangle defined by EM1−EM2 and the low nutrient-salinity 31 point (Figure 3a)

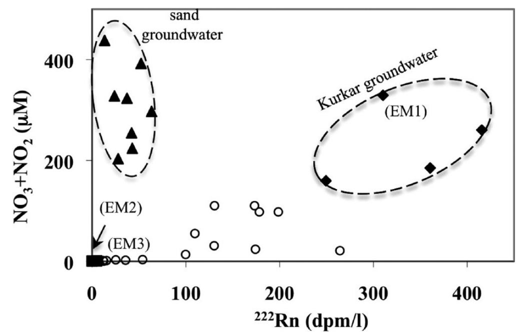

Figure 4. Nitrate concentration against radon activity (from ref 10) in Dor Bay water.

suggests that there is no simple mixing between all end-members, which would produce more scatter. Rather, it seems that the mixing occurs in two steps. First, there is mixing between the two nutrient-poor end-members (EM3 and EM2) to create the 31−39 salinity low-nutrient end, and then this compositional spectrum mixes with the nutrient-rich EM1 water.

The nitrate-poor nature of EM3 cannot be attributed to an onshore fresh groundwater component, because there are no onshore groundwater samples with $NO_3 + NO_2 < 160\ \mu M$. We also consider highly unlikely the possibility that the low nitrate is due to reduction within the seepage meter. This is because of the high flushing rate (water residence time of less than 1 day in the meters), the relatively short deployment period (3−4 days) and since within-meter reduction would produce a scatter rather than the clear pattern observed in Figure 3a. Thus, it is suggested that the low nitrate in EM3 is caused by the removal of nitrate en route to the sea within Dor Bay sediment, probably mainly via denitrification (e.g., 12−14). Removal could also occur via dissimilatory nitrate reduction to ammonium (DNRA[15]). However, though being higher than in onshore groundwater (Figure 3d), ammonium concentrations in the discharging water (average of 5 μM) could account for just a small part of the missing nitrate. We further hypothesize that EM3 groundwater has a relatively long residence time in the sub-bay sediment, while the nitrate-rich EM1 groundwater flows relatively fast, thus is less amenable to denitrification (e.g., 16).

It was previously shown[10] by means of radon and salinity that the main source of the fresh water discharging to the bay is the semi-confined calcareous sandstone Kurkar unit (Figure 2). Following this, we suggest that the EM1 water derives from the Kurkar unit, while the low nitrate, EM3 endmember is denitrified groundwater from the overlaying sand unit (Figure 2). This is evident in Figure 4, where the low radon water (<60 dpm/L) discharging from the bay floor are all nitrate-poor, probably due to denitrification of the similarly low radon albeit nitrate-rich sand groundwater, while samples with higher activities mostly lie on a mixing line between the above and the (nutrient and Rn-rich) Kurkar groundwater. The selective denitrification of the sand groundwater (except for one seepage meter sample with typical Kurkar radon activity of 264 dpm/L but low nitrate, Figure 4) probably occurred due to its long residence time in the sub-bay sediment, a result of the relatively low hydraulic gradient in this unit.[10] During this slow flow, the sand groundwater also mixes with seawater to a variable degree (salinity of 31−39). On the other hand, the higher hydraulic gradient in the semi-confined Kurkar[10] allows a faster flow to the sea, which is short enough to avoid denitrification. The lithologic differences between the units could also affect the denitrification process. While the sand unit is granular and may develop a convenient substrate for the denitrifying microbes, the Kurkar is a lithified calcareous sandstone with pseudokarstic nature and the flow is more in focused conduits with higher water/rock ratios. Therefore, the microbially mediated denitrification may be less effective in the latter. It should be noted that the difference in the radon activity in the water of the two units (Figure 4) is source-dependent[10] and is not related to the different travel time in the sediment.

Therefore, it seems that the spectrum of compositions observed in Figure 3a is produced in three stages. In the first, the sand groundwater undergoes denitrification (and DNRA), producing EM3. This is followed (2nd stage) by mixing with low-nitrate reticulating seawater (EM2). Then in the final stage, the nitrate-rich Kurkar groundwater (EM1) discharges through breaches in the overlaying clay unit and through the sand and mixes with the low nutrient EM3−EM2 mixed water (Figure 5a).

According to the nitrate and salinity distributions (Figure 3a), the average proportions of the three endmembers in the discharging water are 9%, 79%, and 12% for EM1, EM2, and EM3, respectively. However, the calcareous sandstone (the Kurkar) is exposed at 30% of the bay floor (Figure 1). The discharge at this area is solely of the EM1 Kurkar groundwater,[10] which produces corrected discharge proportions for the whole bay of 36%, 56%, and 8%, respectively.

Silica in the water discharging from the bay floor also roughly shows mixing between silica-rich fresh water and silica-poor seawater. Unlike nitrate, the discharging water does not point to unique groundwater end-member silica compositions (Figure 3b), implying that the groundwater is heterogeneous in terms of silica. Some of the samples lie above the possible mixing zone with observed groundwater compositions. This could either be due to an undetected very silica-rich groundwater or due to a slight enrichment with silica in the STE.

Phosphate is very low in the Kurkar groundwater (EM1), probably due to phosphate removal by water−rock interaction and/or by iron oxide precipitation. The higher phosphate in the discharging water (seepage meters, Figure 3c) could be attributed to the mobilization of phosphate in the STE by recirculated seawater. However, the restriction of phosphate concentrations between the mixing lines of seawater with EM1 and EM3 (Figure 3c) suggests that mixing is the dominant process and that the high phosphate is mainly derived from the sand fresh groundwater.

To summarize (Figure 5a), the discharge of groundwater to Dor Bay includes a mixture of (EM1) fresh Kurkar groundwater (nitrate- and silica-rich, phosphate- and ammonium-poor), (EM2) recirculated seawater (nitrate-, silica-, and phosphate-poor), and (EM3) denitrified fresh sand groundwater (nitrate-poor, high silica, phosphate, and ammonium).

Lower nutrient (particularly nitrogen) loads in recirculated seawater compared with the fresh discharge have been reported at other SGD sites, e.g. the Ria Formosa,[17] Yucatan,[18] the Indian River Bay and the Chincoteague Bay,[12] and Waquoit Bay.[19] In a work from Tampa Bay, where saline water was found to carry significant amount of nitrogen, the water was actually a mixture of recirculated seawater and fresh water (e.g., 7). On the other hand, a detailed study of pore water from the northeastern Gulf of Mexico[20] clearly indicated that offshore recirculated seawater in this area is nutrient-rich. It was further shown that the nutrient source in this case was the remineralization of marine organic matter in the STE (20; Figure 5b).

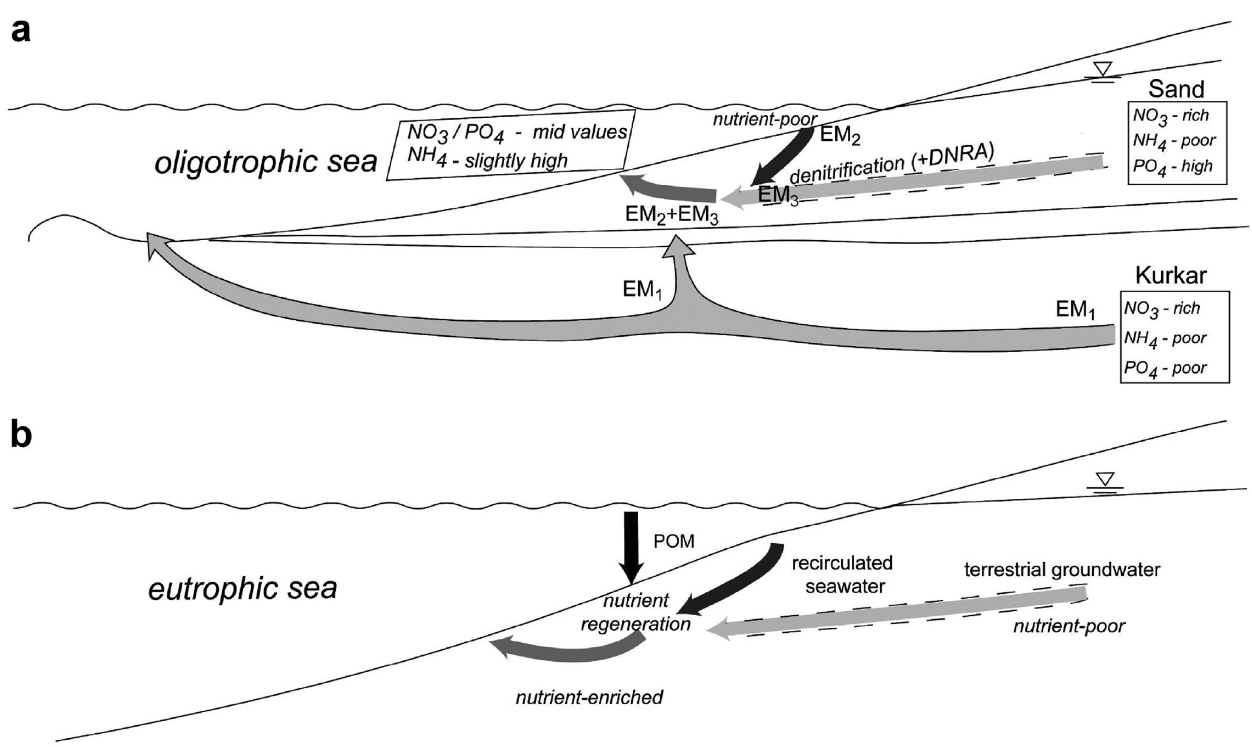

Figure 5. Different scenarios of nutrient transport to the sea by SGD: (a) the Dor-like model, where nutrients mainly derive from land, and the STE's role is mainly as a sink for nitrates; (b) the Gulf of Mexico model, where nutrients are mainly of marine origin.

The difference between the Gulf of Mexico site and the Dor-style sites is in the provenance of the nutrients. Unlike the Gulf of Mexico site, at Dor and the other above-mentioned sites most nutrients are land-derived (Figure 5a), similar to karstic and volcanic areas (e.g., 21−25), where nutrients are mainly transported by point source fresh groundwater. The only nutrient that clearly originates in the STE of Dor Bay is ammonium, which is relatively high in the discharging water (Figure 3d), probably due to regeneration via reduction of some of the sand groundwater nitrate to ammonium (DNRA[15]). Nevertheless, the main impact of the Dor Bay STE on the discharging water composition is the nitrogen removal from the sand groundwater (denitrification), which is larger than the ammonium production (see fluxes below).

The nutrient-poor nature of the recirculated seawater at Dor Bay and other SGD sites could be the result of a shallow, short-term circulation of seawater in the sediments.[26] This shallow circulation is likely forced by tidal pumping or wave setup (e.g., 27) rather than by a seasonal shift of the fresh-saline water interface.[28] Alternatively, the nutrient-deficiency in the recirculated seawater could be the result of the organic-poor nature of the coastal sediments.

Based on the above, we suggest that large fluxes of nutrients should not be a priori assumed at all SGD sites where high concentrations of nutrients were observed in onshore groundwater. Rather, nutrient concentrations should be measured directly in the discharging water or in offshore porewater (e.g., 17,20,29). This should be checked in various SGD salinities, climate and hydrological conditions, anthropogenic stress, and marine trophic conditions.

Nutrient Fluxes and Sinks at Dor Bay. The definition of the EM1 endmember as the ultimate source of nitrates to the Dor Bay is convenient when trying to calculate the fluxes of nutrients to the bay. Assuming a concentration of 330 μM nitrate in the discharging Kurkar water and an average Kurkar groundwater (EM1) discharge of 3.5 cm/d (see above) into the 120-m-wide Bay, we arrive at a flux of 506 mol/yr of nitrate per 1 m shoreline at Dor Bay. The flux of ammonium is relatively small. With a total (fresh + saline) discharge of 10 cm/d (since EM1 is just 36% of the total discharge, see above) and an average concentration of 5.4 μM in the discharging water (Figure 3d), the NH_4 flux is 23.7 mol/yr, which completes the DIN flux to 530 mol N/yr (= 7.41 kg/yr) per 1 m shoreline.

Similarly, assuming a rough average concentration of 300 μM silica in both the EM1 and the EM3 endmembers (Figure 3b) and using the specific discharge of 3.5 cm/d for EM1 and 0.8 cm/d for EM3 (based on the EM1/EM3 discharge ratio of 36:8, calculated above), we derive a flux of 560 mol Si/yr per 1 m shoreline. The loads of PO_4 are relatively low due to their low concentration in the Kurkar groundwater (EM1). With an average concentration in the discharging water of 0.3 μM (Figure 3c), this translates into a flux of 1.3 mol/yr per 1 m shoreline.

Last, the STE at Dor appears to be a filter for land-derived nitrate, whereby sand groundwater undergoes almost complete denitrification (and possibly DNRA) en route to the sea. The average nitrate concentration in the sand fresh groundwater is 295 μM (Figure 3a), while only 0−5 μM in the denitrified EM3 water. With an EM3 discharge of 0.8 cm/d, this amounts to 103 mol N/yr per 1 m shoreline, which is 17% of the total nitrate transported by the fresh groundwater. This is about 4.6 times the nitrogen supplied by the STE (ammonium), which means that at Dor Bay the STE is a sink for terrestrial nitrogen (see a similar conclusion for Waquiot Bay in 14).

The cycling of nitrogen species within different types of subterranean estuaries should be carefully studied, especially in light of the expected climate change and sea level rise, which may impact the residence time of terrestrial fresh groundwaters in the subterranean estuary, thereby affecting their vulnerability to various inputs or sequestration processes.

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