

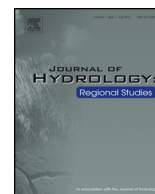


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Hydrogeologic controls on chemical transport at Malibu Lagoon, CA: Implications for land to sea exchange in coastal lagoon systems

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ABSTRACT

Study region: Hydrogeologic controls on seasonal land/sea exchange are investigated in Malibu, California, USA.

Study focus: An assessment of regional groundwater/surface water exchange and associated biogeochemical transport in an intermittently open, coastal lagoon in California is developed using naturally occurring U/Th-series tracers.

New hydrological insights for the region: Nearshore lagoons that are seasonally disconnected from the coastal ocean occupy about 10% of coastal areas worldwide. Lagoon systems often are poorly flushed and thus sensitive to nutrient over-enrichment that can lead to eutrophication, oxygen depletion, and/or pervasive algal blooms. This sensitivity is exacerbated in lagoons that are intermittently closed to surface water exchange with the sea and occur in populous coastal areas. Such estuarine systems are disconnected from the sea during most of the year by wave-built barriers, but during the rainy season these berms can breach, enabling direct water exchange. Using naturally-occurring ²²²Rn as groundwater tracer, we estimate that groundwater discharge to Malibu Lagoon during open berm conditions was one order of magnitude higher (21 ± 17 cm/day) than during closed berm conditions (1.8 ± 1.4 cm/day). The SGD (submarine groundwater discharge) into nearshore coastal waters at the SurferRider and Colony Malibu was 4.2 cm/day on average. The exported total dissolved nitrogen (TDN) through the berm during closed berm was 1.6×10^{-3} mol/day, whereas during open berm (exported by the Creek) was 3.5×10^3 mol/day. Although these evaluations are specific to the collection campaigns the 2009 and 2010 hydro years, these two distinct hydrologic scenarios play an important role in the seasonality and geochemical impact of land/sea exchange, and highlight the sensitivity of such systems to future impacts such as sea level rise and increasing coastal populations.

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1. Introduction

Eutrophication impairs estuarine biological resources on a global scale, with demonstrated links between anthropogenic changes in watersheds, increased nutrient loading to coastal waters, elevated estuarine primary production, harmful algal blooms, hypoxia, and impacts on aquatic food webs (Valiela et al., 1990; Slomp and Van Cappellen, 2004; Paerl et al., 2003; Panuelas et al., 2013; Rodellas et al., 2015). Over the past 50 years, there has been a substantial increase in nutrient loading to the coastal zone, resulting in persistent algal blooms, hypoxia (and anoxia), and microbial and bacterial manifestations (Buckley and Nixon, 2001; Conley et al., 2009; Izbicki et al., 2012; Izbicki, 2014; Panuelas et al., 2013). Understanding the factors controlling estuarine biogeochemical response to enhanced nutrient loads is critical to successfully mitigate the effects of eutrophication. The biological response of estuaries to nutrient loading is complex, varying greatly as a function of physiographic setting, tidal regime, timing and magnitude of freshwater inputs etc. (NAS, 2000). To date, the majority of research on eutrophication in estuaries has focused on deep water estuaries and embayments where aquatic primary production is typically dominated by phytoplankton. Less data are available for shallow coastal lagoons which are connected to the ocean at least intermittently by a restricted inlet or barrier island (Kjerfve, 1994) and where most of the primary production is carried out by angiosperms such as *Ruppia maritima*, epiphytic algae, drift and attached macroalgae, and microphytobenthos (Buckley and Nixon, 2001). Biogeochemical controls on nutrient cycling in these systems are complicated by the extreme variability in lagoon hydrodynamics, particularly with respect to the timing and duration of inlet closures relative to freshwater flows, sediment and nutrient loads. Among coastal lagoons with intermittent inlet closures, the salinity regime and dominant primary producer communities are highly variable, both seasonally and inter-annually, and in turn significantly influence the cycling and ultimate fate of nitrogen (N) and phosphorus (P) within the lagoon (e.g., Flores-Verdugo et al., 1988).

In southern California, which has a Mediterranean climate with distinct wet and dry seasons, peak freshwater flows during the wet season often cause the sandbars at the tidal inlets of intermittently tidal coastal lagoons to breach, allowing full tidal exchange for that typically extends from November to April (Ambrose and Orme, 2000). During the dry season, runoff declines, inlets close for lengths of time varying from two to six months or longer depending on the hydrological condition, and submarine groundwater discharge (SGD) is the only pathway for water and material fluxes from the lagoon to the coastal ocean. The quality of SGD in these systems depends on geochemical processes in the lagoon water column and sediments, but in systems that may have been naturally hyper-saline during the dry season, urban freshwater and associated nutrient flows can cause lagoons to be brackish to fresh during inlet closure with dramatic impacts on lagoon ecosystems to coastal waters. It is during the time period of inlet closure that indicators and effects of eutrophication are most visible and severe. The effects include overgrowth of brackish water submerged aquatic vegetation (SAV) such as *Ruppia maritima* blooms of green, mat-forming algae such as *Rhizoclonium hookeri*, dense benthic diatom and cyanobacterial mats, low dissolved oxygen (DO), and fish kills (Rizzo and Christian, 1996; Ambrose and Orme, 2000). SGD fluxes to coastal waters likely are also impacted by changes in lagoon biogeochemistry. During the wet season, it is commonly assumed that anthropogenic nutrient inputs are flushed into the coastal ocean, rather than retained within the lagoon, so common management strategies to control lagoon eutrophication have focused on identifying nutrient sources to the lagoon during the dry season.

The objectives of the study were to: (1) evaluate the seasonal patterns in groundwater fluxes into Malibu Lagoon and adjacent coastal waters during contrasting hydrological conditions (wet and dry seasons); (2) examine how the development and breaching of the seasonal berm may impact regional hydrology and associated geochemical signatures, and (3) evaluate episodic SGD versus surface runoff-derived loadings to coastal waters.

2. Study site

Malibu Lagoon is a 0.075 km² brackish lagoon situated at the base of the 282-km² Malibu Creek Watershed, the second largest watershed that drains into Santa Monica Bay, California. The Malibu Creek Watershed encompasses a mix of high intensity land-use types that are located in the upper watershed and natural habitat in the narrow, lower portion of the watershed where the creek drains through the Santa Monica Mountains and flows into the sea (Izbicki, 2014). Lower Malibu Creek is tidal and surrounded by municipal and residential infrastructure (Fig. 1). The climate of Southern California is often dry with episodic precipitation events. Intense precipitation events during the rainy season (November–April) quickly spike stream flows and such burst in river discharge results in breaching the seasonal sand barrier located at the terminus of the lagoon. During the dry season, longshore transport of sand builds a berm across the seaward extension of the lagoon and effectively restricts surface water exchange from the lagoon to the Pacific Ocean. During closed berm conditions, lagoon water levels rise and salinity in the brackish lagoon drops as the freshwater inputs from urban runoff in the watershed are impounded. Seasonal storm flows can contribute a large proportion of the overall annual nutrient load to southern California estuaries and coastal ocean (Ackerman and Schiff, 2003; Ambrose and Orme, 2000) and during winter months, an inland publically owned treatment works (POTW) discharges treated wastewater directly to Malibu Creek which flows into Malibu Lagoon. During summer months, creek discharge and suspended sediment transport are generally lower, and POTW effluent is not discharged into Malibu Creek; at these times urban runoff and groundwater seepage are the main source of freshwater inputs to the lagoon and so nutrient loads are generally lower than in winter (Ambrose and Orme, 2000).

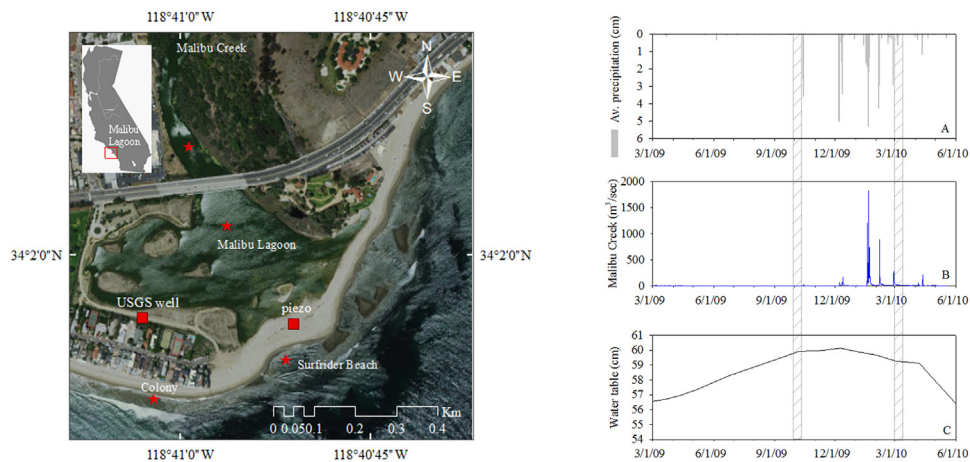


Fig. 1. Left panel shows the location of Malibu Lagoon, CA; stars identify sampling locations and squares identify the location of the temporal piezometer installed during sampling. Right panel consists of (A) 15-min average precipitation in the Malibu Creek Watershed during this study, (B) 15-min average Malibu Creek discharge, and (C) water table fluctuations in observation well, (USGS station #340155118410201001S) located SW of the lagoon near the Malibu Colony sampling site. Both the Malibu Creek flow regime and the lagoon water table respond quickly to precipitation events. Vertical bars across the three graphs highlight the two sampling campaigns during closed berm (July 2009) and open berm (April 2010) conditions.

Table 1

Model parameters for all of the study sites and discharge rates. gw = groundwater; sw = surface water.

Research site ID	^{222}Rn in sw $\times 10^3$ (dpm/m ³)	^{222}Rn in gw $\times 10^3$ (dpm/m ³)	^{226}Ra (dpm/m ³)	Water depth (m)	Wind speed (m/s)	Salinity lagoon	gw flux (cm/day)
Upper Lagoon							
- 2009 (closed)	26.1 ± 12 n = 225	1136 ± 160 n = 8	200 ± 50	0.45 ± 0.01 n = 225	2.7 ± 1.8 n = 225	14.6 ± 1.6 n = 225	2.8 ± 5.5
- 2010 (open)	251 ± 150 n = 166	911 ± 474 n = 9	200 ± 50	2.2 ± 0.3 n = 166	1.76 ± 2.2 n = 166	Surface: 16.9 ± 6 Bottom: 17.9 ± 9	33 ± 13
Lower Lagoon							
- 2009 (closed)	16.3 ± 5 n = 66	1136 ± 160 n = 8	200 ± 50	0.25 ± 0.01 n = 66	2.7 ± 1.8 n = 66	14.2 ± 1.4 n = 66	1.6 ± 1.7
2010 -(open)	125 ± 74 n = 183	911 ± 474 n = 9	200 ± 50	1.24 ± 0.3 n = 183	1.76 ± 2.2 n = 166	Surface: 20.4 ± 3 Bottom: 20.6 ± 2	9.4 ± 4
Sea sites (offshore bottom waters)							
- 2009 (closed)						Bottom:	
Surfrider Beach	15 ± 15 n = 85	1136 ± 160 n = 8	200 ± 50	1.0 ± 0.4 n = 85	0.14 n = 155	32.3 ± 2 n = 85	4.2 ± 7.7
Colony	6.7 ± 4.5 n = 47	1136 ± 160 n = 8	200 ± 50	1.3 ± 0.5 n = 47	0.14 n = 155	Bottom: 20.2 ± 9.5 n = 47	4.8 ± 7.3

3. Field methods and radon mass-balance models

To assess the significance of groundwater derived material fluxes to Malibu Lagoon and nearshore coastal waters, we used radon (^{222}Rn , $t_{1/2} = 3.8$ d) as a groundwater tracer and analyzed dissolved constituents in groundwater, lagoon water and seawater during high and low creek flow conditions. We also used electrical resistivity tomography (ERT) to better understand the pathways of subsurface material fluxes towards the coast during closed berm. Auxiliary water parameters (e.g. temperature, conductivity and groundwater and surface water levels) were collected during all sampling campaigns to support the main data interpretation.

3.1. Radon measurements in surface and groundwater and specific tracer models used to calculate groundwater fluxes

Evaluation of groundwater discharge was based on the mass-balance of ^{222}Rn in the water column. To construct a mass-balance model, we collected continuous time-series of ^{222}Rn concentrations in surface water (i.e. surface water end-member of lagoon and coastal waters) using a RAD AQUA system by Durrigge Inc. (Table 1). A detailed description of the principles of this technique can be found elsewhere (Burnett et al., 2001; Lane-Smith et al., 2002; Dulaiova et al., 2005; Swarzenski et al., 2006). In this approach surface water is collected from the top 30–40 cm layer and ^{222}Rn readings are acquired in 30-min intervals. The length of this data acquisition assured analytical uncertainty below 5%. Radon in

groundwater (i.e., groundwater end-member) was measured using in two different ways: (1) using grab-sampling protocol RAD H2O (http://www.durridge.com/products_rad_h2o.shtml) where 200-mL groundwater samples were collected from multiple observation wells in the Malibu Watershed; and (2) using the continuous measurement technique RAD AQUA (described above) by sampling a 2.7-m deep piezometer that was permanently deployed on the berm (Fig. 1). When grab sampling was used, each groundwater well was first purged for three volumes and then sampled for ^{222}Rn in duplicate; thus reported uncertainties ($\pm 2\sigma$) were based on the averages of the duplicate samples. To calculate groundwater advection rates to Malibu Lagoon and to the coastal waters (i.e. SGD) adjacent to Surfrider Beach and Malibu Colony, we used mean ^{222}Rn concentrations observed in groundwater for each hydrological scenario (e.g. dry and wet season). To calculate groundwater discharge we used two different models depending on the hydrological and morphological conditions in the lagoon. Mass-balance calculations for closed berm conditions were based on a steady state model following Dimova and Burnett (2011), whereas for open berm conditions (or tidally modulated ^{222}Rn inventories), we used a non-steady state model following Burnett and Dulaiova, 2003. Descriptions of each model variation follow in Section 3.5. *Radon mass-balance models*

3.2. Salinity and water levels

Specific conductivity and water depth measurements during time-series were obtained using CTD Divers (Solinst®). During open berm the lagoon was tidally influenced and CTD divers were deployed both at the bottom and near the surface (sensors attached to the radon intake submersible pump) to monitor possible water column stratification. The frequency of data collection was in 2-min intervals with level logger accuracy of $\pm 0.05\%$. To convert specific conductivity to salinity, we used temperature records of each data set.

3.3. Nutrient and trace metal analyses

During 12-h hourly sampling event at open berm conditions, grab samples of surface water, groundwater and sea-water were collected and analyzed for a suite of nutrients (NH_4^+ , SiO_4 , PO_4^{3-} , $[\text{NO}_3^- + \text{NO}_2^-]$, total dissolved N (TDN)) as well as for select trace elements (Mo, Ba, Re, V, Fe, Cs, U, Cr, and Mn) as described previously in Swarzenski et al., (2007). Dissolved inorganic nitrogen (DIN) was calculated as the sum of NH_4^+ and $[\text{NO}_3^- + \text{NO}_2^-]$, and dissolved organic nitrogen (DON) was calculated as the difference between TDN and DIN. All samples (50 mL) were filtered through a $0.45\ \mu\text{m}$ PES (polyethersulfone) membrane filter in the field and kept on dry ice during transportation to the laboratory for analysis. Nutrients were analyzed at the Woods Hole Oceanographic Institution (WHOI) Nutrient Laboratory (<http://www.whoi.edu/sbl/liteSite.do?litesiteid=1671&articleId=2922>) via flow injection analysis for NH_4^+ , SiO_4 , PO_4^{3-} , and $[\text{NO}_3^- + \text{NO}_2^-]$, with precisions better than 1%. Trace element concentrations were determined by high-resolution inductively coupled plasma mass spectrometry (HR-ICP-MS) at the University of Southern Mississippi (Center for Trace Analysis, University of Southern Mississippi; <https://www.usm.edu/marine/research-ceta-center-trace-analysis>). Precision of the heavy metal analyses, as assessed by repeated analysis of a standard, was better than 5% for all elements except Re for which the uncertainty was 14%. Accuracy was assessed by analysis of NASS 5 as well as a spiked seawater sample; recoveries were typically $100 \pm 10\%$.

During closed berm we did not perform the detailed water chemistry sampling as during open berm, but lagoon and groundwater samples from 12-h time-series samples were analyzed for dissolved organic carbon (DOC) and for total nitrogen (TN) during a full tide cycle.

3.4. Land-based and marine electrical resistivity surveys

During closed berm electrical resistivity measurements were carried out in the field both in marine mode (i.e. continuous resistivity profiling (CRP)), and in land-based mode using AGI SuperSting instrumentation. In the CRP mode an 11-electrode cable was towed behind a boat surveying nearshore areas of the Surfrider Beach. The land-based array was run with a 56-electrode cable, with electrodes spaced 2 m apart using a dipole–dipole configuration. Both data sets were processed and interpreted using EarthImager (AGI Inc.), similar to Swarzenski et al. (2006, 2007) and Dimova et al. (2012).

3.5. Radon mass-balance models

Radon mass-balance models were used to evaluate groundwater discharge and were adapted for each lagoon morphological stage (i.e. open and closed berm), and for each season and site. During open berm i.e., tidally influenced conditions, we used a non-steady state approach. In this approach, radon inventories in the water column were calculated over 30-min intervals and excess radon delivered by SGD was quantified as the difference between two consecutive measurements (Burnett and Dulaiova, 2003; Swarzenski et al., 2006, 2007). The non-steady state model was also used to calculate SGD at the two offshore sites (Fig. 1) during closed berm conditions. To calculate discharge into Malibu Lagoon during closed berm conditions, we used a steady state model developed by Cable et al. (1996) and further refined for lakes by Dimova and Burnett, (2011), where average excess radon delivered via groundwater was calculated by balancing observed radon inventories in the water column against atmospheric and decay losses. Groundwater discharge in both hydrological scenarios was calculated by dividing the net excess radon fluxes by site-specific radon concentrations in the local groundwater

Table 2A
closed berm.

sample ID	^{222}Rn in gw 2009“closed berm” ($\times 10^3$ dpm/m 3)
CCPC	949 \pm 134
P-9	1345 \pm 198
SMBRP-12	650 \pm 141
15/171S-3293	846 \pm 158
SMBRP-2	1222 \pm 189
CCPNE	1368 \pm 160
CCPE	1050 \pm 139
CCR-1	1658 \pm 163
av. GW end-member “closed berm”	1136 \pm 325

Table 2B
open-berm.

	^{222}Rn in gw 2010“open-berm” ($\times 10^3$ dpm/m 3)
CCPC	1383 \pm 155
340205118410101	838 \pm 67
CCPSW	1520 \pm 68
340210118405401	1198 \pm 29
C1	744 \pm 459
SMBRP-3C	1283 \pm 51
MC old shallow seep	76 \pm 42
max 9 ft. piezo	710 \pm 11
av. 9 ft piezo	451 \pm 97
av. GW end-member (“open-berm”)	911 \pm 474

(i.e. the groundwater end-member). Radon concentrations in groundwater were averages of the two sampling methods, from grab well samples and from the piezometer deployed on the berm which collected 10-min interval measurements and were season-specific (Table 2A). Dissolved ^{226}Ra (direct parent of ^{222}Rn) in surface waters was assessed using procedures described by Peterson et al. (2009). Reported uncertainties of the advection rates into Malibu Lagoon are based on averages of two RAD AQUA deployments (one each in the upper and lower lagoon) and thus reflect both temporal and spatial variability within the lagoon.

4. Results

The influence of the hydrological regime of Malibu Creek on the material exchange through a permeable, transient beach barrier was examined during two contrasting hydrological scenarios: (1) a low creek flow regime, during which the coastal lagoon was closed and a sandbar constrained the direct exchange of water and associated constituent exchange with the adjacent ocean; and (2) a high creek flow regime, during which the lagoon exchanged material freely with the ocean via direct surface and groundwater discharge and tidal exchange (Fig. 1A, B and C). Herein, we will refer to case (1) as the “closed berm” scenario and case (2) as the “open berm”, or tidally-influenced scenario. In this particular study, the second scenario was examined 2 days after a storm event that caused to breach the berm, thus the results should be interpreted as post-storm fluxes or a flushing event.

4.1. Closed berm (low flow of Malibu creek)

4.1.1. Groundwater measurements during closed berm

Salinity and ^{222}Rn in groundwater from a 2.7-m deep piezometer deployed on the sandbar (berm) did not vary significantly during a full tide cycle (Fig. 2A). Over the 12-h observation period the average ^{222}Rn concentration in groundwater was $45.2 \pm 6 \times 10^3$ dpm/m 3 ($n = 26$) whereas the average salinity was 25.6 ± 0.3 ($n = 26$). Groundwater grab samples were also collected from eight monitoring wells within the Malibu Watershed; the average ^{222}Rn concentration from these wells was $1136 \pm 325 \times 10^3$ dpm/m 3 ($n = 7$) (Table 2A).

DOC and TN were measured in groundwater samples collected from the 2.7-m deep piezometer in 12-h time-series during a full tide cycle. On average DOC was $200 \pm 8 \times 10^{-3}$ mol/m 3 ($n = 11$) whereas the average TN was 38.6 ± 6 $\mu\text{mol}/\text{m}^3$ ($n = 11$).

4.1.2. Lagoon measurements and groundwater fluxes estimates during closed berm

A boat survey performed during closed berm within Malibu Lagoon did not reveal particular spatial pattern of ^{222}Rn , but concentrations varied over more than an order of magnitude, $2.7\text{--}37 \times 10^3$ dpm/m 3 (Fig. 3A). On the other hand, salinities were relatively constant throughout the lagoon, 12.0–12.9 (Fig. 3B). To monitor temporal variability in groundwater

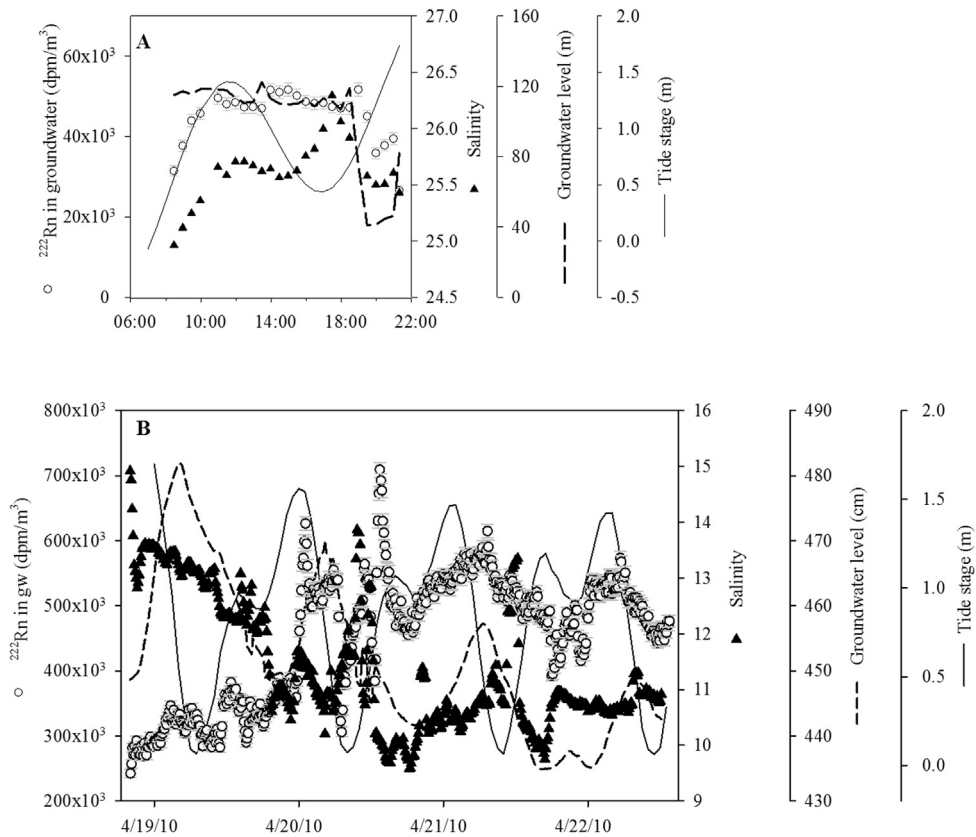


Fig. 2. Variations in salinity and radon in 2.7-m piezometer installed at the sand bar during (A) closed- and (B) open berm conditions. Top plot shows that radon and salinity in the groundwater were independent of the tidal variations, whereas during open berm conditions, the record shows tidal modulations of radon concentrations in groundwater (B).

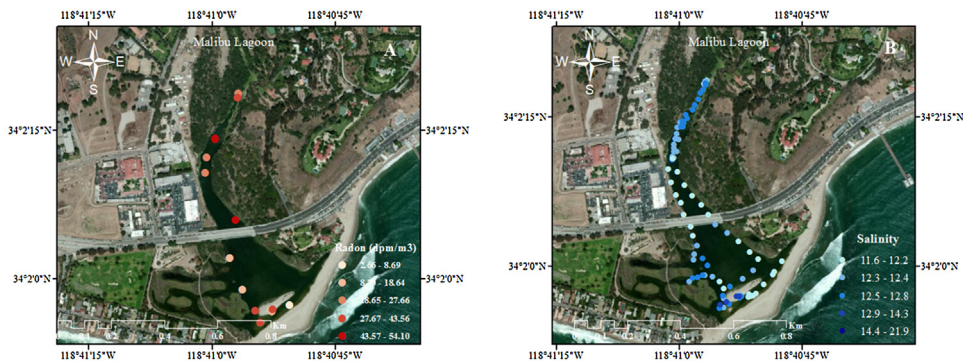


Fig. 3. Radon (left panel) and salinity (right panel) survey results during closed berm conditions. Radon distribution (left panel) did not show a specific pattern whereas salinity (right panel) on average was higher nearshore and upstream Malibu Creek compared to mid-lagoon.

discharge, continuous ^{222}Rn measurements were obtained simultaneously in the (1) upper lagoon and (2) lower lagoon. The salinities and lagoon water depths in the upper and lower part of the lagoon did not change noticeably with the tide: in the upper and lower lagoon salinity was 14.6 ± 1.6 ($n = 225$) and 14.2 ± 1.4 ($n = 66$), respectively and water depths were 0.45 ± 0.01 m ($n = 225$) and 0.25 ± 0.01 m ($n = 66$) (Table 1, Fig. 4A and B). However, ^{222}Rn concentrations in the upper lagoon were on average 40% higher ($26.1 \pm 12 \times 10^3$ dpm/m³, $n = 225$) compared to the lower lagoon ($16.3 \pm 5 \times 10^3$ dpm/m³, $n = 66$). Wind speed in the lagoon area was in the normal range at the beginning of the monitoring period but increased intensity towards the end. This affected the ^{222}Rn inventories in the lagoon water column; we observed an overall decreasing trend (Fig. 4B). This atmospheric loss was accounted for in the mass-balance model. Based on a steady state ^{222}Rn mass-balance model specific discharge into the upper lagoon was 2.8 ± 5.5 cm/day ($n = 225$) and 0.8 ± 1.5 cm/day ($n = 66$) into the lower lagoon (Table 1).

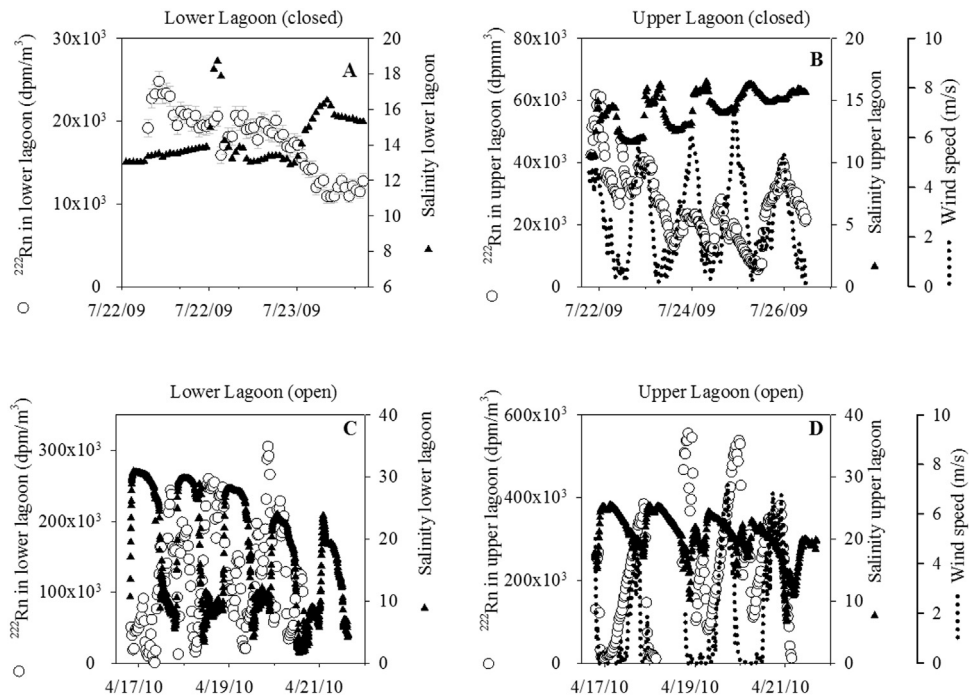


Fig. 4. Radon (open circles) and salinity (triangles) time-series of lagoon water during closed berm (top plots) and open berm (lower plots) conditions. Longer deployment (B) in the upper lagoon shows a decrease in ^{222}Rn concentrations in surface water due to an increase of wind speed in the study area (dotted line). Both ^{222}Rn and salinity during open berm conditions were much higher compared to closed berm and were strongly modulated by tide.

4.1.3. Resistivity measurements during closed berm

A 56-electrode ERT array was deployed at Surfrider Beach across the berm (perpendicular to the shore) to image subsurface pore water distribution and potential groundwater-seawater exchange during both low tide and high tide. The images showed contrasting stratified sediment-water interfaces (Fig. 5A and B). We found a well-developed three-layer subsurface structure: a top more saline (~ 32) layer which, overlaid less saline (12) and moderately saline (22) saturated sediment layers. Although this layered structure was preserved during both low and high tide, it was more pronounced during low tide (Fig. 5A). In the following discussion, we use the term “shallow seep” to refer to SGD detected ~ 30 m offshore, near the groundwater piezometer that was screened within the more saline layer. We use the term “deep seep” to describe SGD associated with the less saline layer detected ~ 40 m offshore (Fig. 5)

Continuous resistivity profiling (CRP) of the water column from a shore-parallel boat survey revealed a relatively uniform water column (Fig. 6, B–B’), while CRP results within the lagoon showed stratification, with a low resistivity layer (i.e., saltier water) near the sediment-water interface compared to the top layer profile (Fig. 6, transect A–A’).

4.1.4. Seawater measurements and SGD estimates closed berm

During closed berm seawater measurements and SGD estimates were performed at two sea sites: Surfrider Beach and Malibu Colony (Fig. 1). Seawater in both locations was collected by deploying a long pvc tubing along the ocean floor approximately 30 m offshore at Surfrider, and 40 m at Colony. Using this sampling set up at each site we collected continuous data for ^{222}Rn and salinity in bottom waters (Fig. 7, Table 1). Seepage water with a high salinity (32.3 ± 2 , $n=85$) and high ^{222}Rn ($15 \pm 15 \times 10^3$ dpm/m 3 , $n=85$) signature was detected at the ocean floor during the ~ 17 -h offshore deployment at Surfrider Beach (Fig. 7A and C, Table 1). A diluted brackish lens ($20.2 \pm 9.5 \times 10^3$ dpm/m 3 , $n=47$) of relatively high ^{222}Rn ($6.7 \pm 4.5 \times 10^3$ dpm/m 3 , $n=47$) was detected as a deeper seepage during the shorter (~ 22 -h) deployment (Fig. 7B and D, Table 1) at the Colony offshore sampling site which is located about 0.5 km west of the Malibu Lagoon (Fig. 1). At both sites the ^{222}Rn signal was tidally modulated whereas salinity did not show such strong dependence on the tide stage (Fig. 7). Based on a non-steady state ^{222}Rn model (i.e. for tidally modulated surface water ^{222}Rn inventories) the SGD rate from offshores shallow seep the Surfrider site was 4.2 ± 7.7 cm/day compared to 4.8 ± 7.3 cm/day at the deep seep at the Colony site (Table 1). SGD fluxes calculated in 30-min increments show that both sites were strongly affected by tide (Fig. 7 E and F). Despite the fact that the specific groundwater fluxes were essentially the same at both sites, these seeps were distinguished by different saturated sediment layers and different salinity and ^{222}Rn signatures (Table 1). This was also confirmed by the ERT images and CRP in the water column (Figs. 5 and 6)

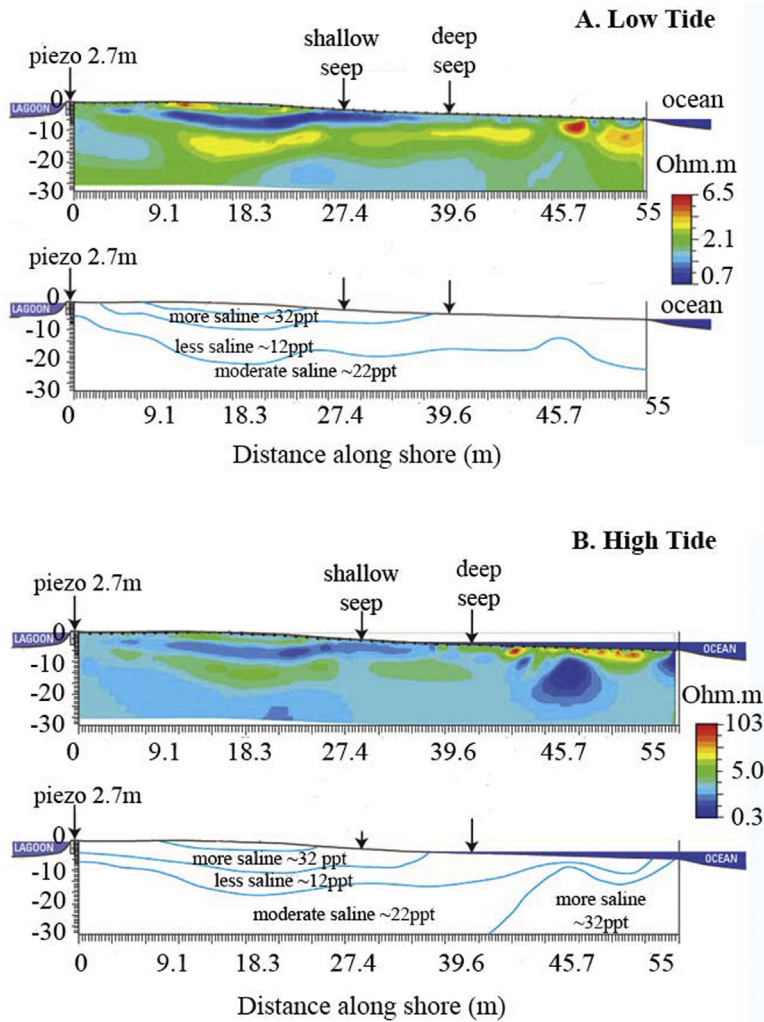


Fig. 5. 56-electrode, land-based ERT images during (A) low tide and (B) high tide conditions. ERT images were produced using a dipole-dipole configuration and the cable was placed perpendicular to the shore (i.e., across the sand bar) during closed berm conditions. Based on these images, we speculate that there are two areas of groundwater seepage: (1) shallow seepage that originates at the ocean-side of the berm (~30 m from the deployed piezometer) and is representative of the hydraulic connection between the lagoon and ocean and it is more saline (~32) compared to (2) deep seepage area with lower salinity (~12) at about 40 m offshore. The signature of this fresher pore water was less evident during high tide (B). (modified from Izbicki, 2014).

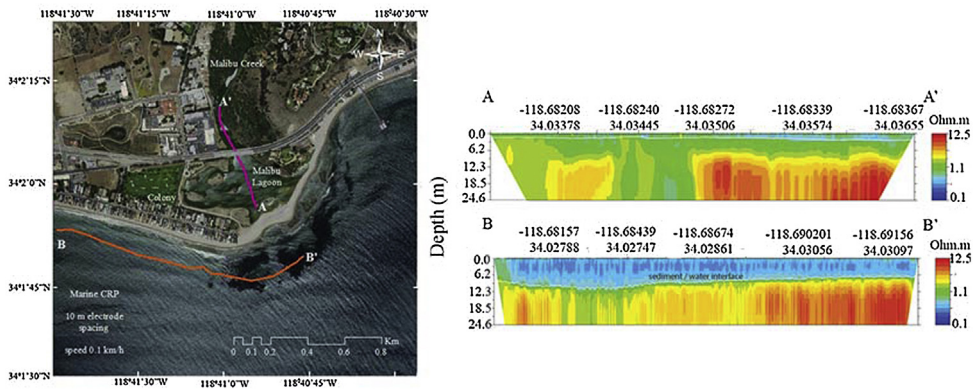


Fig. 6. Continuous resistivity profiles (CRP) in offshore coastal waters near Surferider and Colony Beach and within Malibu Lagoon during closed berm conditions. Left panel shows a map of two transect lines. Images from transects A–A' (shore-perpendicular) within the lagoon and B–B' (shore-parallel) are shown on the right panel. White lines in both images identify the sediment-water interface.

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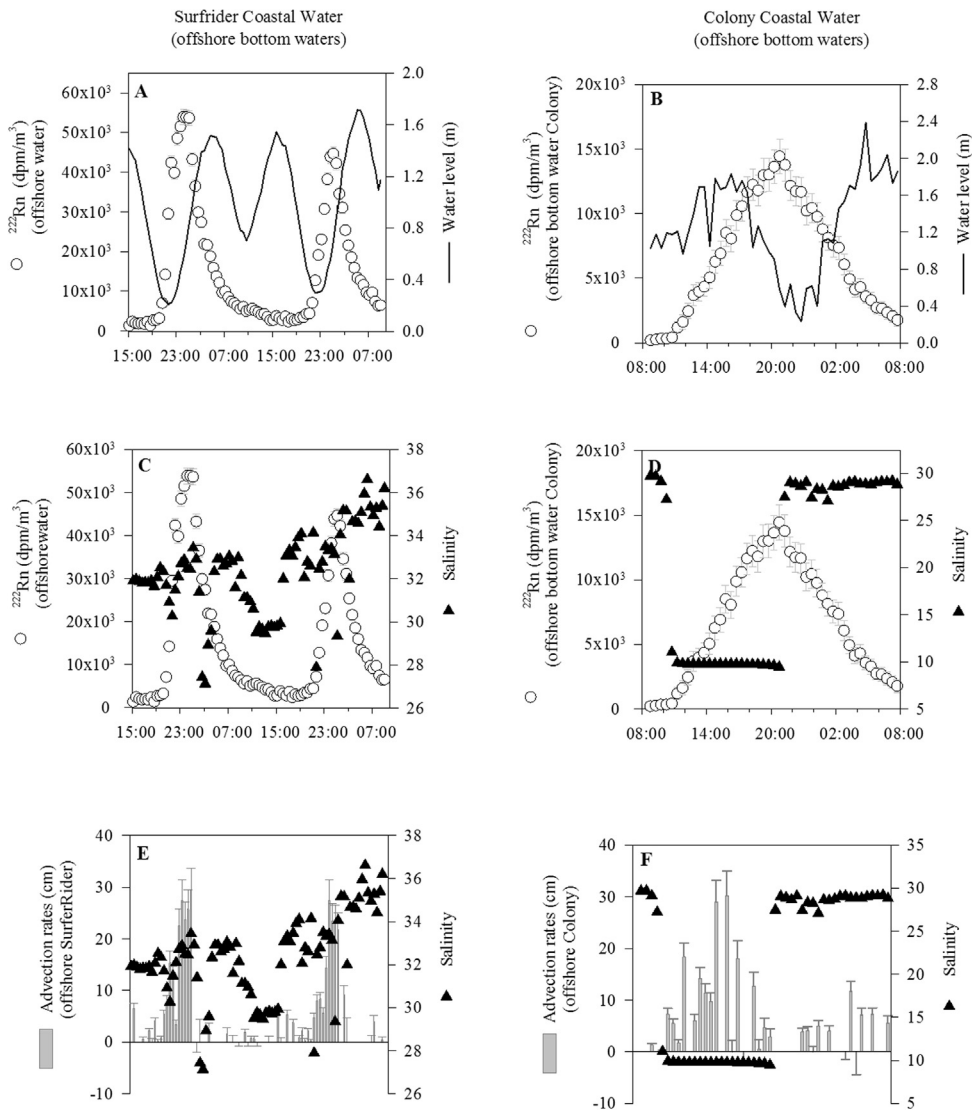


Fig. 7. Offshore, time-series at Surfrider Beach and at the Malibu Colony, NW of Malibu Lagoon during closed berm. Top panels A and B show variations in ²²²Rn concentrations detected in offshore bottom waters (the water intake was placed near the seafloor); middle panels C and D depict salinity variations versus radon changes; lower panels E and F show calculated offshore ASGD during closed berm. It was evident that the SGD fluxes were brackish to saline as detected by the ERT images (Fig. 5).

4.2. Open berm (high flow of Malibu creek)

Groundwater from the same 2.7-m deep piezometer (which was installed at the berm earlier during closed berm), lower lagoon water and seawater were sampled concurrently in a 12-h sampling event during falling tide. All waters samples were analyzed for: ²²²Rn, dissolved inorganic nitrogen (DIN as NH₄⁺, [NO₃⁻ + NO₂⁻]), TDN, PO₄⁺, SiO₄, and a full suite of major (Fe³⁺, Mn⁵⁺) and trace metals (Table 3).

4.2.1. Groundwater measurements during open berm

Radon concentrations in groundwater during open berm varied with the tide (Fig. 2B). Spatial ²²²Rn variations in groundwater were also observed in nearby groundwater wells within the Malibu Watershed (Table 2B). To calculate groundwater discharge to the lagoon, we used an average ²²²Rn value of 911 ± 474 × 10³ dpm/m³ (Table 2B), combining data from the time-series four-day piezometer record and the wells.

Results from DIN analyses show that the dominant DIN form in groundwater was ammonia (NH₄⁺) with an average concentration of 68 ± 13 μM (n = 11), whereas the oxidized N- forms ([NO₃⁻ + NO₂⁻]) were mostly below the detection limit (<0.5 μM), with an overall average of 3 ± 4 μM (using a value of ½ the detection limit for below-detection samples). Phosphorus was measured as orthophosphoric acid (i.e. dissolved PO₄³⁻) and it was 18 ± 3 μM (n = 11). Dissolved silica (as SiO₄)

Table 3

Nutrient concentrations from 12-h time-series grab sampling during “open berm” conditions. All concentrations are in μM with standard deviations of mean values $\pm 2\sigma$.

Water type # samples	NH ₄	NO ₃ + NO ₂	DIN	DON	TDN	PO ₄ (acid.)	SiO ₄	Fe	Mn
Groundwater (n = 11)	68 ± 13	3 ± 4	68 ± 13	28 ± 13	96 ± 4	18 ± 3	340 ± 33	45343 ± 13396	25687 ± 4249
Lagoon water (n = 7)	7 ± 13	7 ± 2	14 ± 5	26 ± 6	40 ± 8	8 ± 2	270 ± 24	250 ± 261	827 ± 196
Ocean water (n = 12)	2 ± 1	2 ± 1	3 ± 2	9 ± 3	13 ± 2	2 ± 3	18 ± 10	89 ± 59	39 ± 21

was elevated, $340 \pm 33 \mu\text{M}$ (n = 11) which is typical for groundwater. Heavy metal concentrations, i.e. Fe³⁺ and Mn⁵⁺, were very high too, $\sim 45 \pm 13 \text{ mM}$ (n = 11) and $26 \pm 4.2 \text{ mM}$ (n = 11) respectively (Table 3).

4.2.2. Lagoon measurements and groundwater flux estimates during open berm

Radon concentrations in lagoon waters were much higher during open berm compared to closed lagoon conditions (Table 1). In the upper lagoon the average ²²²Rn concentration was $251 \pm 150 \times 10^3 \text{ dpm/m}^3$ (n = 166), whereas ²²²Rn in the lower part of the lagoon was $125 \pm 74 \times 10^3 \text{ dpm/m}^3$ (n = 183), which is about half the concentration observed in the upper lagoon within only 0.6 km distance between the moorings (Fig. 1). On average, ²²²Rn in upper lagoon was considered extremely high for natural waters, the measure levels were about 27% of ²²²Rn in groundwater. The average depth at both the lower and upper lagoon locations was higher compared to closed conditions, $2.2 \pm 0.3 \text{ m}$ (n = 166) and $1.24 \pm 0.3 \text{ m}$ (n = 183), respectively (Table 1). Salinities at both sites were similar, ~ 17.0 in the upper lagoon and 20.4 in the lower lagoon, and were generally higher compared to the typical closed berm salinity of ~ 14 . CTD sensors at the bottom and surface of each ²²²Rn mooring showed slight stratification in the relatively shallow water column in both locations. Wind speed did not change significantly throughout the monitoring (Table 1; Fig. 3A and C).

Using a non-steady state ²²²Rn mass balance model (i.e. for tidally influenced ²²²Rn inventories in the water column) and groundwater end-member $911 \pm 474 \times 10^3 \text{ dpm/m}^3$, groundwater fluxes to the upper lagoon were $33 \pm 13 \text{ cm/day}$, whereas to the lower lagoon section, groundwater flux rates were $9.4 \pm 4 \text{ cm/day}$. Note that reported flux uncertainties are due to non-steady state conditions and are result of tidal fluctuations during the time-series deployments, not a result of the analytical precision of the groundwater tracer measurements.

DIN in lagoon water averaged $14 \pm 5 \mu\text{M}$ (n = 7), of which 50% ($7 \pm 2 \mu\text{M}$) was [NO₃⁻ ± NO₂⁻] and 50% NH₄⁺ ($7 \pm 3 \mu\text{M}$). DON in lagoon samples was $26 \pm 6 \mu\text{M}$ (n = 7) which was statistically the same as the average value in groundwater $28 \pm 13 \mu\text{M}$ (n = 11). Dissolved silicate in lagoon water was unusually high, the average value was $270 \pm 24 \mu\text{M}$ (n = 11), which was 70% of that detected in groundwater, $340 \pm 33 \mu\text{M}$ (n = 11), Table 3. However, PO₄³⁻ was $8 \pm 2 \mu\text{M}$ (n = 7), which is $\sim 40\%$ lower than groundwater $18 \pm 3 \mu\text{M}$ (n = 11). Compared to groundwater, dissolved Fe and Mn decreased two orders of magnitude to levels of $250 \pm 261 \mu\text{M}$ (n = 7) and $827 \pm 196 \mu\text{M}$ (n = 7) respectively, an indication of sharp change in redox conditions (Table 3). We did not monitor Eh during this sampling campaign to firmly confirm this shift.

4.2.3. Seawater measurements open berm

Strong winds (up to 7.2 m/s) and an unusually large swell event during this sampling campaign prevented deploying ²²²Rn continuous time-series instruments at the offshore sites that were previously examined during closed berm conditions. However, grab samples of seawater at the Surfriider Beach were collected during the 12-h sampling event described above (Table 3). DIN in seawater was more than twenty times lower compared to groundwater, $3 \pm 2 \mu\text{M}$ (n = 12), which included both NH₄⁺ ($2 \pm 1 \mu\text{M}$) and [NO₃⁻ ± NO₂⁻] ($2 \pm 1 \mu\text{M}$). DON was three times higher, $9 \pm 3 \mu\text{M}$ (n = 12), than DIN. Dissolved Fe and Mn dropped another order compared to lagoon waters and were $89 \pm 59 \mu\text{M}$ (n = 12) and $39 \pm 21 \mu\text{M}$ (n = 12) respectively. The same was observed for dissolved silicate, $18 \pm 10 \mu\text{M}$ (n = 12). Silicate concentrations in seawater were only 5% of the observed levels in groundwater. Phosphate was on average $2 \pm 3 \mu\text{M}$ (n = 12) which was in the same order of magnitude compared to lagoon water ($8 \pm 2 \mu\text{M}$), Table 3.

In summary, our results show that, as to be expected, materials' concentrations decreased while transitioning from groundwater through lagoon system to ocean. Based on our observations the lagoon chemistry was much more like groundwater than ocean chemistry. This may be due to the fact that our sampling captured a flushing event; we sampled only 2 days after the berm was breached.

5. Discussion

Results from two sampling events during closed and open berm at Malibu Lagoon show that the magnitude of groundwater discharge and material fluxes into Malibu Lagoon are influenced strongly by the local hydrological and coastal morphological conditions. The geomorphological set up of the coastal lagoon and the local topographic and hydraulic gradients in the Malibu Watershed also determine the degree of seawater circulation within the lagoon and the water chemistry within the creek-lagoon-ocean reach. The transition in water chemistry follows the switch between tidally-influenced salt wedge during open berm to diffusive behavior when closed.

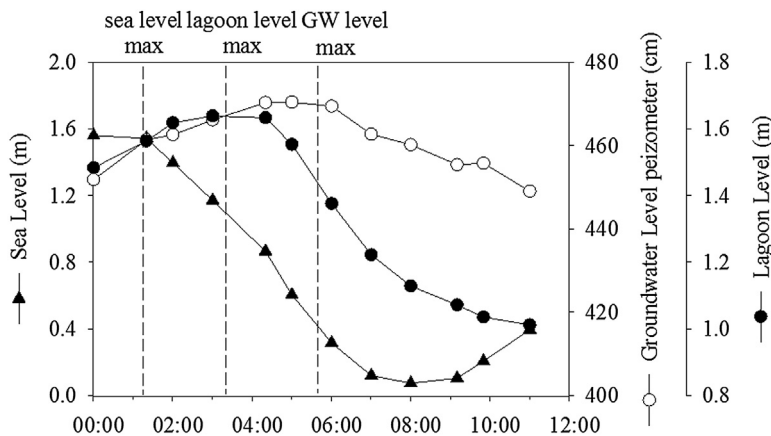


Fig. 8. Groundwater, lagoon level, and sea level changes during open berm conditions (April 2010). A complex interplay between sea level fluctuations, groundwater table and lagoon levels determine the observed aqueous geochemistry in these three water bodies.

5.1. Groundwater-surface water exchange

During open berm groundwater advective fluxes to Malibu Lagoon were on average one order of magnitude (21 cm/day) higher compared to closed berm conditions (2.2 cm/day). Observed differences in discharge, during both closed and open berm, upstream and downstream from the Malibu Creek are natural; Malibu Lagoon is part of the Malibu Creek Watershed, which is situated in the foothills of the Santa Monica Mountains, and steeper gradients upstream would enhance both surface runoff and groundwater discharge (Fig. 1). Using an average lagoon area of $7.5 \times 10^4 \text{ m}^2$, groundwater discharge to Malibu Lagoon during open berm was $1.6 \times 10^4 \text{ m}^3/\text{day}$, whereas under the same conditions, the average Malibu Creek discharge was $90 \times 10^3 \text{ m}^3/\text{day}$ (station# USGS 11105510 MALIBU C A MALIBU CA, <http://nwis.waterdata.usgs.gov/ca/>). Thus during open berm, groundwater discharge to Malibu Lagoon was about 18% of Malibu Creek's discharge. During closed berm the stream discharge was below the detection at the USGS gaging station i.e., showing zero discharge and our calculations indicate that the groundwater flux was one order of magnitude lower as well, averaging 1.8 cm/day or $\sim 1.4 \text{ m}^3/\text{day}$ (Table 1). It should be noted that the results for open berm are representative of a surge of groundwater discharge in response to the rapid change in hydraulic gradient, because the berm had breached only two days before our sampling. Such a sudden transition from lagoon to estuarine hydraulics (but on a much larger scale) occurs during routine dam releases in many dammed river systems around the world. For example, similar behavior for hydraulic head was also observed in a controlled dam release in the Yellow River estuary by Xu et al. (2014), where elevated river levels significantly (more than 10 times) enhanced groundwater discharge to the estuary. Xu et al. (2014) observed that the high Yellow River discharge during the controlled dam release resulted in an elevated hydraulic head in the river water and the corresponding pressure potentially drove more groundwater discharge to the estuary. A 4-day record of groundwater level (from a 2.7-m piezometer) and tide stage (http://tidesandcurrents.noaa.gov/sltrends/sltrends_station.shtml?stnid=9411340, Santa Barbara) shows a gradual decrease of groundwater levels since the berm breached just few days before our sampling event. Parallel to this groundwater table trend salinity in groundwater decreased from ~ 14.5 to 11, whereas on average ^{222}Rn doubled from $250 \times 10^3 \text{ dpm}/\text{m}^3$ due to about $500 \times 10^3 \text{ dpm}/\text{m}^3$ (Fig. 2B). These general trends are indication of an overall increase in groundwater discharge to the increase in discharge observed by Xu et al. (2014). On short-time scales (hours), during open berm the water table in the lagoon area is controlled mainly by tidal fluctuations, although there was a 2-h time lag (Fig. 2B, Fig. 8). On the other hand the peak of lagoon water level occurred about 40 min before the groundwater maximum which is most likely due to water contribution from Malibu Creek (Fig. 8).

We did not have an extensive record reflecting the hydrodynamics during closed berm conditions and thus we cannot make similar deductions about the timing and magnitude of groundwater-surface water exchange. However, based on ERT images collected during low and high tide as well as from water chemistry (Fig. 6), we are certain that the ocean-groundwater exchange was facilitated through a multi-layer subsurface structure (shallow and deep seeps) through the berm (Fig. 5). However, the magnitude of these water and constituent fluxes were much lower compared to open berm.

5.2. Geochemistry and material fluxes through the creek-lagoon-ocean system

Although we did not perform laboratory experiments to assess the kinetics of geochemical transformations within the lagoon system, our data indicate that the complex timing and energetics of groundwater, creek water and lagoon water mixing during open and closed berm in the lagoon area must play an important role in the aqueous geochemistry of surface water and groundwater. The two examined scenarios were dramatically different not only based on groundwater fluxes, but also based on material inventories within the analyzed waters and calculated fluxes.

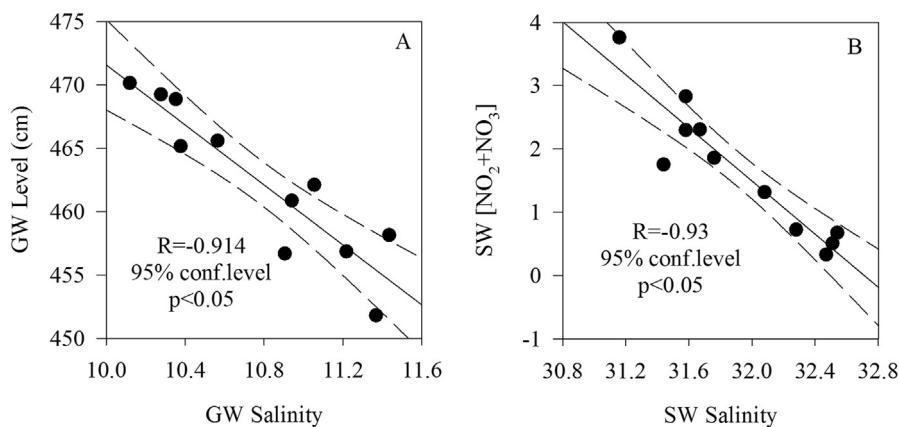


Fig. 9. Plot A shows significant between groundwater (GW) levels and salinity suggesting strongly that groundwater discharge to Malibu Lagoon was fresh during open berm. Reverse correlation of salinity and oxidized N- in seawater suggests that N- was delivered to coastal waters by fresh water discharge.

A strong linear correlation ($R^2 = 0.84$ and $R = -0.914$ at 95% confidence level, $p < 0.05$) between groundwater level and salinity in groundwater during the 12-h sampling event indicated that groundwater discharged to the lagoon was mostly fresh (Fig. 9A). The total dissolved N- (TDN) in groundwater was about 29% DON and 71% DIN, with NH_4^+ comprising almost 100% of the DIN pool (Table 3). This high concentration in combination with calculated high groundwater fluxes suggests that groundwater must be a significant source of NH_4^+ to the lagoon water column. To evaluate the magnitude and understand the significance of these fluxes, we calculated a simple NH_4^+ mass-balance in lagoon waters. We treated the system as a box with: an “in flux” equal to ~ 1.1 mol/day (groundwater discharge 1.6×10^4 m³/day multiplied by the NH_4^+ groundwater concentration of 68×10^{-6} mol/m³) and an “out flux” equal to 0.63 mol/day (Malibu Creek discharge 90×10^4 m³/day multiplied by the NH_4^+ lagoon concentration of 7×10^{-6} mol/m³). This mass-balance resulted in a “net” +0.46 mol/day NH_4^+ . At average residence time of lagoon water was about 1.4 days (based on a water balance using Malibu Creek discharge), and the total gained inventory of NH_4^+ from groundwater to lagoon water was 0.66 mol. This is about 73% of the total measured NH_4^+ lagoon inventories of 0.91 mol (calculated by multiplying NH_4^+ concentration in the lagoon by lagoon’s volume 1.3×10^3 m³). Although, these calculations assume conservative NH_4^+ behavior (which we know is not the case), such estimate gives a better idea of the significant role groundwater has on NH_4^+ fluxes to the lagoon and on the aqueous chemistry during open berm. Similar high NH_4^+ concentrations (500–2000 μM) in pore water extracted from sediment were observed by Sutula et al. (2004) at several locations upstream of Malibu Lagoon during open berm. Additionally, Sutula et al. (2004) and others (e.g., Thursby and Harlin, 1984) examined the uptake of NH_4^+ by *R. maritima*, a brackish water aquatic plant that is seasonally abundant in Malibu Lagoon, and found that their roots have a higher affinity for NH_4^+ than for NO_3^- . One could speculate that perhaps adoptive mechanisms of N-uptake were acquired by *R. maritima* to adjust to high reduced N-, and highlights the ecological importance of the NH_4^+ sources in such aquatic systems.

Although we do not have a record of the *Eh* of pore water, elevated concentrations of the reduced form of N- were likely due to anoxic conditions in the sediment. As other studies have shown, anaerobic conditions appeared to enhance the mobility of particle reactive elements, such as NH_4^+ and trace metals, as documented by mM concentrations of dissolved (< 0.45 μM) Fe and Mn in groundwater (Table 3). For example, enhanced metal mobility in coastal aquifer systems has been documented elsewhere by Ganguli et al., 2014 and is of particular concern at Malibu Lagoon, where coastal groundwater discharge is a documented source of bioaccumulative methylmercury (MeHg) to nearshore seawater (Ganguli et al., 2012).

As a result of the described mechanism of accumulation of NH_4^+ in the lagoon, the DIN in Malibu Lagoon water during open berm was 50% NH_4^+ and 50% $[\text{NO}_3^- + \text{NO}_2^-]$ in composition. We expect that the source of $[\text{NO}_3^- + \text{NO}_2^-]$ in lagoon water was a combination of surface water runoff from the upgradient watershed as well as the biological oxidation (i.e., nitrification by aerobic bacteria) of NH_4^+ transported by groundwater discharge to the overlying water column. The observation that reduced N- (NH_4^+) comprised half of the DIN present in the oxic open lagoon water provides additional evidence of a proximal source of NH_4^+ (i.e., groundwater discharge into shallow lagoon waters). The $[\text{NO}_3^- + \text{NO}_2^-]$ present in open lagoon water was apparently transported offshore, as evidenced by a strong reverse correlation ($R^2 = 0.87$ and $R = -0.93$ at 95% confidence level, $p < 0.05$) between nearshore seawater salinity and $[\text{NO}_3^- + \text{NO}_2^-]$ concentrations (Fig. 9B), with increased $[\text{NO}_3^- + \text{NO}_2^-]$ when seawater became fresher. This trend, combined with a $\text{NH}_4^+ : [\text{NO}_3^- + \text{NO}_2^-]$ ratio of 1:1 in both open lagoon water and seawater, suggests lagoon water was the source of DIN in the coastal marine system. The relatively lower ocean water average DIN concentration (1.7 μM) relative to open lagoon water (7 μM) is probably due to dilution when the water masses mixed.

We do not have detailed water chemistry analyses during closed berm conditions and thus our conclusions for the dry season are more speculative. However, TC and TN (C/N ratios) in groundwater and seawater showed a reverse correlation during a full tide cycle (Fig. 10) and high C/N ratios during low tide suggests the release of excess nutrients can be delivered by either: (1) groundwater discharge through the sandbar or/and (2) *in-situ* respiration of organic material in seawater.

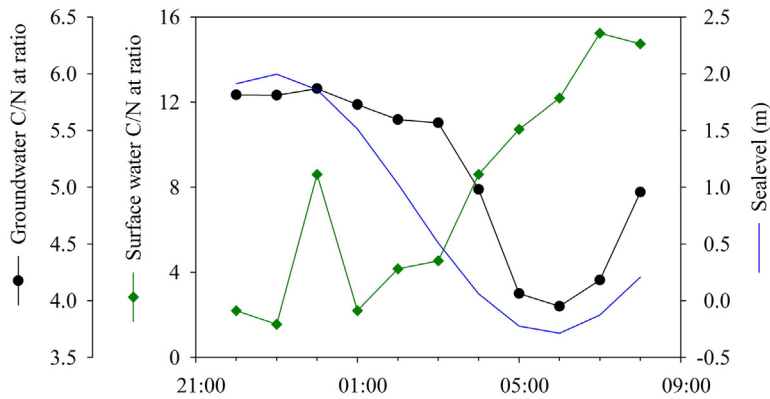


Fig. 10. Groundwater and seawater C/N ratio dependence on tidal variations during closed berm conditions in Surfer Rider Beach. C/N in seawater increased threefold during low tide suggesting that tidal pumping plays an important role in the delivery of nutrients to coastal waters during closed berm.

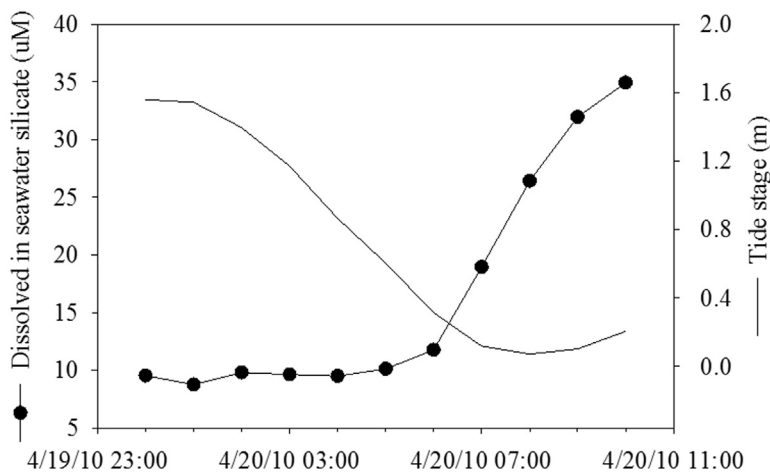


Fig. 11. Variation of dissolved silicate in seawater versus tide stage during open berm. Si was delivered to coastal waters through surface water. However, most of the surface water had strong groundwater signature.

Because the low tide sampling event occurred at night (Fig. 10) and the calculated groundwater seepage through the sandbar was notably low during closed berm conditions, we hypothesize that the second mechanism (i.e., respiration of organic material) is likely the dominant mechanism of nutrient regeneration in the water column. N-limited waters during flood tide (daylight) support fast photosynthesis rates with nutrient consumption. However, more detailed analyses of the kinetics during closed berm conditions are necessary to delineate the actual contribution of hydrological factors versus rates of biochemical transformations in the sediment and seawater that resulted in the observed changes.

5.3. Comparing constituent fluxes to Malibu lagoon and to the coastal zone during open and closed berm conditions

We calculated groundwater nutrient fluxes to Malibu Lagoon by multiplying respective average nutrient concentrations in groundwater (Table 3) by the average ²²²Rn-derived groundwater flux (Table 1). Based on these data, the TDN flux delivered by groundwater to Malibu Lagoon during the open regime was 1531 mol/day, whereas DIN was 1088 mol/day (virtually all of which occurred as NH₄⁺ at 1076 mol/day) and DON was 444 mol/day. Because we could not obtain a time-series record of ²²²Rn in seawater during open berm, we used dissolved silicate (SiO₄) as a conservative groundwater tracer in seawater. Previous studies have shown that groundwater typically is highly enriched in dissolved SiO₄ relative to surface water (Null et al., 2012; Swarzenski and Izbicki, 2009). Similarly, in this study we found that the average SiO₄ concentration in groundwater during our 12-h sampling event during open berm, was 20 times higher than in seawater (Table 3). Thus, we suggest that any enrichment of SiO₄ in the seawater was likely due to groundwater inputs. A reverse correlation (Fig. 11) between sea level and SiO₄ concentrations in seawater confirms that SiO₄ was delivered to the coastal ocean during low tide, i.e. via tidal pumping. Similar to most of the DIN, we suggest that the source of SiO₄ to nearshore water at Surfrider Beach is Malibu Lagoon via Malibu Creek. Indeed, our results show that the average SiO₄ concentration in lagoon water was only ~20% lower than that of groundwater (Table 3). This finding suggests that ~80% of the lagoon water is ultimately of groundwater origin (i.e. result of groundwater discharge to the lagoon). This is also consistent with the very high ²²²Rn concentrations detected

during time-series deployments in the upper and lower lagoon as well as the high calculated groundwater discharge rates during open berm conditions (Table 1). Conservative mass-balance of NH_4^+ in lagoon water column (presented above) also suggested that 73% of the total NH_4^+ in lagoon water is from groundwater. Based on these lines of evidence, we speculate that during open berm conditions the ultimate source of most nutrients to nearshore coastal waters off Surfrider Beach (including $[\text{NO}_3^- + \text{NO}_2^-]$) are most likely from groundwater discharge to Malibu Lagoon followed by export out of the lagoon by advection and tidal exchange.

To calculate net constituent fluxes to the nearshore waters adjacent to Malibu Lagoon, we assumed that: (1) during open berm conditions, surface water runoff via Malibu Creek transported the majority of terrestrial constituents to the coastal ocean and thus net material fluxes exported to the coastal zone were calculated by multiplying constituent concentrations in lagoon water by Malibu Creek's discharge at the time of collection; and (2) during closed berm conditions, the source of nutrients and trace metals was subsurface seepage at the beach face through the sandbar and offshore exported nutrient fluxes were calculated by multiplying the SGD rates from offshore deployments with the nutrient concentrations in pore water that was detected by ERT land-based imaging (Fig. 5). Based on a Malibu Creek discharge of $90 \times 10^3 \text{ m}^3/\text{day}$ and concentrations of nutrients and trace metals measured in surface Lagoon water, the TDN exported via Malibu Creek to the ocean during open berm conditions was 3600 mol/day of which the dominant N-form was DON, 2300 mol/day, i.e., about 65% of TDN. The highest nutrient flux by far is Mn ($\sim 74 \text{ kmol/day}$) followed by SiO_4 ($\sim 24 \text{ kmol/day}$) and Fe ($\sim 22 \text{ kmol/day}$). During closed berm conditions, the average SGD to Surfrider Beach was $4.2 \pm 7.7 \text{ cm/day}$, and the TDN flux was $1.6 \pm 2.7 \text{ mmol/day}$. This shows that N-fluxes delivered by SGD during closed conditions are insignificant (6 orders of magnitude smaller) compared to open conditions. However, most of the Malibu Creek water during open conditions originates from groundwater (i.e., gaining stream) and thus these fluxes to the ocean are in fact groundwater-derived.

6. Conclusions

Malibu Lagoon is seasonally separated from the coastal ocean by a permeable beach barrier and transitions periodically from lagoonal (closed berm/dry season) to estuarine conditions (open berm/wet season). In this study, we examined the magnitude of constituent export through Malibu Lagoon in both lagoonal and estuarine scenarios. We found that during the wet season when Malibu Lagoon is open to the coastal ocean, groundwater discharge at the mouth of the lagoon is one order of magnitude higher compared to the dry season, when the beach barrier separates the lagoon from the coastal ocean. DIN in groundwater occurred primarily as NH_4^+ and we estimate that $\sim 50\%$ of it was transported from the upgradient watershed and with the remaining $\sim 50\%$ produced within the lagoon sediments. This NH_4^+ appeared to be advected to the (open) lagoon via groundwater discharge, and then exported to the ocean in surface water exchange through the mouth of the lagoon at a rate of 1076 mol/day. We suggest that NH_4^+ is then oxidized and we found that the dominant N-form in seawater is $[\text{NO}_3^- + \text{NO}_2^-]$. Elevated, Mn ($\sim 74 \text{ kmol/day}$) and SiO_4 ($\sim 24 \text{ kmol/day}$) Fe ($\sim 22 \text{ kmol/day}$) fluxes during open berm conditions were measured as well. Nutrient fluxes (e.g., TDN) during closed berm conditions were several orders of magnitude lower compared to open berm conditions, and thus considered insignificant. However, note that the large flux estimates for the open berm scenario are based on data collected shortly after a berm breach at the end of the wet season (April 2010) and may have captured a pulse of groundwater discharge. It is possible both groundwater and material fluxes are lower when the system is at base-flow conditions. Our findings suggest that such groundwater pulses following berm breaches may deliver substantial fluxes of redox sensitive chemicals, such as metals and particle reactive nutrients. During the low flow regime, the recycling of nutrients within the seawater column may play a more important role in the release of nutrients compared to SGD. However, a more detailed geochemical analyses during closed berm conditions is required to delineate the actual contribution of hydrological factors versus rates of biochemical transformations in the sediment and seawater to account for the observed changes. Large seasonal variability in constituent fluxes likely occur at other coastal lagoons and perhaps in areas where large rivers are regulated upstream by dams that mimic the natural conditions in seasonally dynamic coastal lagoon systems. Understanding the interplay of groundwater-surface water interaction is a critical point in managing coastal waters.

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