From soil to sea: the role of groundwater in coastal critical zone processes

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Near coasts, surface water–groundwater interactions control many biogeochemical processes associated with the critical zone, which extends from shallow aquifer to vegetative canopy. For example, submarine groundwater discharge delivers a significant fraction of weathering products such as silica and calcium to the world's oceans. Owing to changing fertilizer and land use practices, submarine groundwater discharge is also responsible for high nitrogen loads that drive eutrophication in marine waters. Submarine groundwater discharge is generally unmonitored due to its heterogeneous and diffuse spatial patterns and complex temporal dynamics. Here, we review the physical processes that drive submarine groundwater discharge at various spatial and temporal scales and highlight examples of interdependent critical zone processes. Like the inland critical zone, the coastal critical zone is undergoing rapid change in the Anthropocene. Disturbances include warming air and sea temperatures, sea-level rise, increasing storm severity, increasing nutrient and contaminant inputs, and ocean acidification. In a changing world, it is more important than ever to understand complex feedbacks between dynamic surface water-groundwater interaction, rocks, and life through long-term monitoring efforts that extend beyond inland rivers to coastal groundwater. © 2016 Wiley Periodicals, Inc.

INTRODUCTION

The flow of river water and groundwater influences global biogeochemical cycles by delivering solutes from the continents to the oceans.[1] As water flows through the critical zone (the water table aquifer, soils, and vegetative canopy where water, rock, and life interact[2]), it facilitates chemical transformations and transports dissolved chemical products to the ocean. There, solutes can be released to the atmosphere, taken up by biota, or eventually deposited on the ocean floor. For most of geologic history, solid and solute loads from land to sea have consisted only of rock weathering products and organic substances. In the Anthropocene, human activities have accelerated the weathering cycle and introduced new chemicals to these flows. Contaminants include heavy metals, excess nutrients, and synthetic organic chemicals[3,4] such as flame retardants and pharmaceuticals.

The transfer of water and dissolved solids from land to sea affects coastal water quality and ecosystem health. Rivers collect continental solutes and solids and deliver them to points along the coast. The world's 10 largest rivers drain 92% of all continental landmass.[5] It is no surprise that these point sources of continental waste exert a disproportionate influence on coastal water quality within hundreds of

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kilometers of their mouths. However, a large portion of the global coast is uninfluenced by large rivers and instead drains to the shoreline or to small, unmonitored creeks.[6] These coastal catchments are often densely populated (almost one quarter of the global population lives near the coast[7]). In these areas, direct groundwater discharge can play a large role in solute export from land to sea.[6]

Submarine groundwater discharge includes a fresh component that originally recharged on continents, as well as a saline component that originally recharged through the seabed (Figure 1). The mixing zone between fresh and saline groundwater in coastal aquifers is often termed the 'subterranean estuary' in oceanography literature, due to its importance in chemical reactions and subsurface ecology.[8] As groundwater circulates through coastal aquifers, it incorporates dissolved solids, and it also interacts with microbial communities that transform groundwater chemistry. The residence time of groundwater in the subsurface, chemical composition of sediments or rocks and microbial activity together determine the ultimate chemistry of discharging groundwater. The patterns and rates of groundwater flow near coasts are important for three reasons: discharging groundwater can influence surface water quality, groundwater chemistry controls geochemical and ecological processes in the subsurface, and fresh groundwater is an important water resource for coastal communities.[1]

The contribution of groundwater discharge to the chemical budgets of coastal waters has traditionally been overlooked for multiple reasons. Hidden in the subsurface, groundwater is both easy to ignore and hard to measure.[9] Unlike the discharge of river water, groundwater discharge to the coast is heterogeneous and diffuse. Groundwater delivers solutes to broad discharge zones offshore, while rivers deliver solutes to discrete points. Because rivers collect water from readily delineated catchments, the catchment serves as a convenient system with one primary outlet for monitoring integrated chemical signals associated with critical zone processes. By focusing on rivers and their catchments, however, we overlook the coastal critical zone. In the Anthropocene, it is more imperative than ever that we understand changes to the coastal critical zone, where human activities are most densely concentrated. In order to do so, we must understand groundwater discharge, which is responsible for draining much of the coastal critical zone.

In this review, we argue for the need to integrate coastal critical zone and near-shore research and extend our current view of the critical zone to
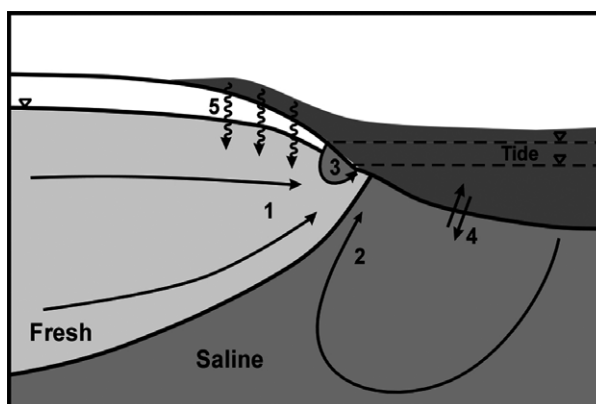
FIGURE 1 | Physical processes that drive coastal surface water-groundwater exchange and solute transport. 1: Fresh submarine groundwater discharge. 2: Deep, density-driven circulation of saline groundwater. 3: Shallow exchange of saline groundwater due to tides and swash. 4: Subtidal exchange of saline groundwater due to hydraulic head gradients associated with interactions of currents and waves with the sediment-water interface. 5: Onshore infiltration of saline water due to storm surge.

subaqueous environments. We also highlight the sensitivity of the coastal critical zone to anthropogenic disturbance. We divide our review according to the major hydrological processes that drive submarine groundwater discharge, which operate across a diverse range of timescales and length scales (Figure 1). While previous review papers have examined these hydrodynamic processes in greater detail,[8–10] our goal is to use a systems-based approach to evaluate their impact on the coastal critical zone, with a particular focus on biogeochemical cycles involving carbon, nutrients, and contaminants. For each submarine groundwater discharge process, we highlight one or more representative critical zone biogeochemical processes that depend on it. We also discuss potential responses to anthropogenic disturbance. We conclude by identifying research opportunities and monitoring needs for the coastal critical zone.

FRESH SUBMARINE GROUNDWATER DISCHARGE

Physics
All fresh submarine groundwater discharge originates from recharge on land (Process 1 in Figure 1). The rate of fresh groundwater discharge generally decreases exponentially with offshore distance.[11] Most fresh groundwater discharge is therefore focused within tens of meters of the shoreline and has residence times on the order of years to

decades.[12,13] In volcanic rocks and karst, conduits can transmit fresh groundwater to springs farther offshore.[14] Relatively old groundwater can also discharge to the continental shelf from fresh aquifers that were recharged during previous sea-level lowstands.[15]

The rates of fresh groundwater discharge depend on many factors, including sediment or rock permeability and onshore recharge patterns. Spatial patterns of fresh groundwater discharge are often highly heterogeneous at scales ranging from meters to kilometers. At the scale of meters, relatively permeable channel fill deposits in sedimentary rocks or fracture networks in crystalline rocks tend to focus fresh groundwater discharge offshore.[16–18] At the scale of tens to thousands of kilometers, onshore recharge rates can vary due to changes in land use and the proportion of impermeable cover or changes in net precipitation across climatic gradients. These variations in recharge rates directly control the supply of fresh groundwater to the coast.

Recharge rates also vary temporally over individual storm events, seasons, and geological timescales. An increase in recharge elevates the water table onshore, driving an offshore increase in fresh submarine groundwater discharge. Menning et al.[19] observed an increase in fresh groundwater discharge to a Florida estuary in response to a hurricane. Michael et al.[20] identified seasonal dynamics in fresh (and saline) submarine groundwater discharge that lag seasonal dynamics in water table elevation by several months. Anderson and Emanuel[21] showed that groundwater discharge rates in coastal catchments were strongly correlated with interannual climate oscillations such as the El Niño Southern Oscillation (ENSO). Seasonal and decadal signals in submarine groundwater discharge may be associated with chemical loading signals to coastal waters.[20]

Role of Fresh Submarine Groundwater Discharge in Rock Weathering

The direct discharge of fresh groundwater from land to sea plays an important role in many critical zone processes, including rock weathering (Figure 2). In both inland and coastal watersheds, chemical weathering reactions and rates depend on a suite of variables related to solid phase and aqueous geochemistry, hydrogeology, climate, and biology. These include physical/climatic factors such as temperature, precipitation, solution residence time, aquifer parent material mineralogy, grain size, and hydraulic conductivity; biological factors such as microbial processes, root exudates, and uptake; and
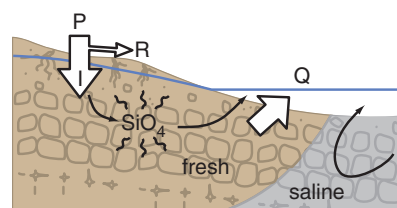
FIGURE 2 | In young permeable volcanic islands, most precipitation (P) infiltrates (I) and transports subsurface weathering products to the coast through submarine groundwater discharge (Q). River flow (R) represents a small component of water and solute fluxes. Weathering along groundwater flow paths produces base cations and clay minerals in conjunction with alkalinity and consumes CO_2 and acidity. Example silicate weathering reactions include potassium feldspar (felsic silicate) weathering: ($KAlSi_3O_8(s) + CO_2(g) + 1.5H_2O \rightarrow 0.5Al_2Si_2O_5(OH)_4(s) + K^+ + HCO_3^- + 2H_4SiO_4°$), and olivine (mafic silicate) weathering: ($Mg_2SiO_4(s) + 4H_2O + 4CO_2(g) \rightarrow 2\,Mg^{2+} + H_4SiO_4° + 4HCO_3^-$).

aqueous geochemical factors including pH, redox chemistry, and organic ligand concentration and class. Indeed, a vast array of recent literature reviews address chemical weathering in the critical zone from the perspectives of watershed and soil geochemistry (e.g., Brantley et al.,[2] Anderson et al.,[22] Perdrial et al.[23]). However, these processes are rarely considered in coastal settings, where mineralogical transformation or dissolution of freshwater aquifer materials dictates subterranean fluxes of solutes from land to sea. The impact of these solute fluxes on receiving water quality, biogeochemical cycling, and ecosystem health is likely profound.

Weathering budgets for coastal watersheds are difficult to calculate via mass balance, as there are diffuse boundaries regarding both inputs and outputs. Submarine fluxes of weathering-derived products have historically been estimated via back calculation from geochemical budgets, where other components of the budget are thought to be better constrained.[9] Yet due to long residence times, there is the potential for extensive chemical weathering to occur and for weathering-derived fluxes to constitute a significant component of solute loads to the ocean. For example, the input of calcium to the ocean from submarine groundwater discharge, which is mostly derived from chemical weathering processes in coastal aquifers, has been estimated to be anywhere from 40 to 120% of riverine input.[9,24] These estimates confirm that (1) submarine groundwater discharge flux of chemical weathering-derived solutes is a highly significant term for marine geochemical budgets and (2) estimates are extremely poorly constrained and dependent on assumptions inherent to estimates of other processes (e.g., riverine flux,

cycling, and residence time in the marine environment).

Some recent work has directly quantified chemical weathering rates in these environments using water balance and groundwater solute measurements.[25,26] Rad et al.[25] found that submarine groundwater discharge was responsible for the majority of the total weathering-derived solute flux for the islands of Martinique (90%), Guadeloupe (60%), and Reunion (75%). Submarine weathering flux rates were 2–5 times higher than corresponding fluxes from surface water, and were associated with some of the highest measured silicate weathering rates worldwide. This was due to both an abundance of soluble silicate minerals and rapid high-temperature dissolution of minerals due to hydro-thermal water–rock interactions on these volcanic islands. An important implication is that global volcanic islands could contribute anywhere from 23 to 31% of the silicate weathering flux transported from global continental rivers, although they only constitute 9% of the silicate rock area.

Subsequent work on the Hawaiian Islands by Schopka and Derry[26] further confirmed that submarine groundwater discharge is the dominant flux of weathering-derived solutes on this basaltic island chain based on measurements of Hawaiian groundwater chemistry (dissolved silica and alkalinity) coupled to water balance estimates (Figure 2). For the youngest (recently crystallized magma) systems, essentially all of the weathering solute flux was derived from submarine groundwater discharge. In older systems, less of the total island flux of weathering solutes was conveyed by submarine groundwater discharge, though it was still the dominant source for all systems studied. Furthermore, both of these recent studies suggest that groundwater-derived consumption of CO_2 due to silicate weathering is systematically underestimated. Weathering along coastal groundwater flow paths, particularly in volcanic island systems, needs to be considered as an important CO_2 sink in global budgets.

Another related component of chemical weathering reactions in these aquifers that is important to the marine system is the production of alkalinity as a byproduct of silicate or carbonate dissolution and CO_2 consumption. As such, the alkalinity inputs via submarine groundwater discharge could potentially buffer coastal systems to ocean acidification.[27] Indeed, Moore et al.[28] confirmed that the submarine groundwater discharge impacts the concentration and distribution of alkalinity in coastal waters of the Wadden Sea. Cyronak et al.[29] further suggest that submarine groundwater discharge fluxes of

carbonate weathering-derived alkalinity could impact how susceptible coral reef systems are to ocean acidification, but that the potential impact is highly variable in both time (tidal cycle) and space (hydrogeology). In coastal lagoons, submarine groundwater discharge was always observed to be a net source of alkalinity, whereas in unconsolidated high hydraulic conductivity sediments, tidal pumping impacted whether the interface was a net source or sink of alkalinity. Clearly, the role of submarine groundwater discharge-derived alkalinity varies across coastal environments. Understanding how this relates to risk assessment for marine ecosystems that are sensitive to acidification would be a fruitful avenue for future research.

Nutrient Fluxes from Land to Sea in Fresh Submarine Groundwater Discharge

Fresh submarine groundwater discharge plays an important role in other critical zone processes, particularly through its large influence on nutrient supply to coastal waters. Large nutrient inputs can increase primary productivity in coastal waters and lead to algal blooms.[30] Harmful algal blooms are particularly problematic because they can drive hypoxia, deteriorate marine ecosystems, and impact fishing and tourism revenues.[31] Here, we focus on inputs of nitrogen, the limiting nutrient for algal growth in many coastal marine waters,[30] but groundwater also transports phosphorus, silica, and other micronutrients.[1,14,32] Numerous studies have linked groundwater sources of nitrogen with high productivity and harmful algal blooms.[33–35] While both fresh and salty submarine groundwater discharge deliver nitrogen to coastal waters, the component in fresh groundwater discharge is the only external or 'new' input. Nitrogen in fresh groundwater is land derived, whereas nitrogen in saline groundwater is generally regenerated from mineralization of organic matter in aquatic sediments.[36]

Human activities disproportionately alter dissolved inorganic nitrogen (DIN) in fresh submarine groundwater discharge. Anthropogenic sources of DIN include fertilizers and leaky septic tanks.[37] In developed areas, DIN concentrations in groundwater can greatly exceed surface water concentrations, resulting in large chemical fluxes from groundwater, even when fluid fluxes are relatively small.[8] For example, fresh groundwater discharge to Tampa Bay is approximately 50% of stream flow but supplies approximately the same total dissolved nitrogen load.[38] In a subestuary of the Chesapeake Bay, groundwater is highly enriched in DIN relative to

surface water, and Charette and Buesseler[39] showed that area-adjusted DIN loads from groundwater are comparable to average DIN loads for the entire Chesapeake Bay. Furthermore, N:P ratios in coastal groundwater are typically greater than river water or the Redfield ratio. Thus, fresh groundwater discharge can potentially shift coastal primary production toward P-limitation rather than N-limitation.[32]

Nitrogen can be removed along groundwater flow paths through coupled nitrification–denitrification or anammox processes. Nitrogen transformations partly depend on distributions of organic matter and permeability at both small and large scales.[40,41] For example, denitrification requires a supply of labile organic carbon and absence of oxygen, which sometimes occur in coastal aquifers. Removal of DIN can be limited in permeable, mineral-rich aquifer materials where organic matter content is low and travel times are faster than reaction timescales.[42] Yet Kroeger and Charette[43] showed that even in relatively organic C-poor aquifer materials, most (~65%) of DIN in fresh groundwater is removed over a relatively small region near the seepage zone. If shallow groundwater flow paths intersect organic-rich coastal wetland soils, N removal can be even more efficient.[44] Thus, coastal aquifers perform an important ecological service by attenuating anthropogenic N loads to coasts.

# DENSITY-DRIVEN SALINE GROUNDWATER DISCHARGE

Physics

Variations in groundwater density due to salinity and temperature drive large-scale circulation of seawater through offshore aquifers. The angled density gradient between fresh and saline groundwater creates a cell of circulation and discharge along the freshwater–saltwater interface (Process 2 in Figure 1). In a homogeneous aquifer, saltwater flows into the aquifer offshore, circulates downward and landward, and flows up along the offshore portion of the interface.[45–48] Geothermal gradients similarly drive circulation across the continental shelf break or

carbonate platforms (Figure 3). The geothermal gradient is steeper above the shelf or platform interior than the slope, which promotes recharge of cold, saline water on the slope and discharge of warm, brackish water across the shelf or platform top.[49,50] In thick aquifers, groundwater flowpaths and residence times may be long, perhaps tens of kilometers and decades to tens of thousands of years.[51] The water–rock interactions along these deep paths of varying salinity and temperature can transform the chemistry of the inflowing seawater such that the resulting discharge may impact the composition of the ocean; and further, reaction processes may alter the composition and hydraulic properties of the aquifer matrix.

The discharge rates driven by these mechanisms vary widely. Similarly to fresh discharge, circulation rates are affected by aquifer permeability. However, the nature of the flow system is dependent on the distribution of temperature and salinity, which can be complex, particularly in the case of salinity. More extensive freshwater–saltwater interfaces, occurring where fresh discharge rates are low and mixing is high, tend to drive greater circulation until gradients become so low that free convection breaks down.[48] In aquifers with large-scale heterogeneity, density gradients within mixing zones can have complex structure. Models predict that saltwater circulation driven by salinity gradients can easily exceed fresh discharge, even by orders of magnitude, particularly where landward hydraulic gradients are low and heterogeneity is substantial.[48,52]

Role of Density-Driven Saltwater Circulation in Carbonate Diagenesis

Diagenetic water–rock reactions, such as calcite dissolution and dolomitization that occur along saltwater circulation flowpaths, have the potential to alter atmospheric CO_2 levels and the chemistry of the ocean over geologic time.[54] In freshwater–saltwater interfaces, mixing of fresh groundwater and seawater that is supersaturated with respect to calcite results in groundwater that is undersaturated, leading to enhanced calcite dissolution in mixing zones.[8,55,56]
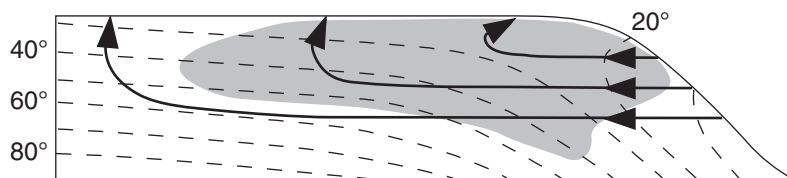
FIGURE 3 | Idealized isotherms (dashed lines) and convection patterns (solid lines) in a carbonate platform. Gray zone illustrates approximate region of maximum dolomite precipitation, after Whitaker and Xiao.[53]

This dissolution has been observed in the field,[57,58] though precipitation of calcite has also been shown in laboratory column experiments.[59] Reactive transport modeling has demonstrated that dissolution rates and locations within the mixing zone are dependent on groundwater fluxes, aquifer properties, and endmember chemistry.[60,61] The enhanced porosity due to carbonate dissolution can increase permeability, creating a feedback between flow and reaction that causes the mixing zone to move inland.[61] This seawater intrusion, accelerated by groundwater withdrawals, reduced recharge, and sea-level rise,[62,63] can result in ion exchange that reduces pH and further enhances calcite dissolution.[64] These dissolution processes supply significant amounts of dissolved inorganic carbon (DIC) to both fresh and saline coastal groundwater,[65] comprising part of the DIC load to the ocean that has been implicated as a significant component of the carbon cycle.[66,67]

Saline convection driven by geothermal gradients is also considered a primary mechanism for dolomitization of carbonate platforms (Figure 3). Dolomitization, or the replacement of calcite by dolomite, is a major diagenetic process in carbonates that is relatively poorly understood. Although dolomite is abundant in ancient carbonates,[68] it is surprisingly resistant to precipitation in the laboratory under near-surface temperatures.[69] Geothermal convection of saline water may explain the widespread occurrence of massive dolomites in the rock record. Convection acts as a long-term pump that delivers magnesium-rich seawater to platform interiors, where warmer temperatures may relieve the kinetic limitations on dolomitization[70,71] (Figure 3). As water warms along flowpaths toward the platform interior, the reaction rate for dolomitization abruptly increases, and dolomitization may become transport limited rather than kinetically limited. Steady, long-term convection is needed to sustain the dolomitization process. In the absence of advective transport, dolomitization effectively removes magnesium from pore water, and dolimitization is limited to a thin, armored zone.[72]

Field observations and numerical experiments generally support the role of saltwater convection in dolomitization. Field evidence includes geochemical analyses of brackish submarine springs, which are both depleted in magnesium and enriched in calcium offshore of Florida and Italy.[73–75] Fanning et al.[73] estimated that more than 140 m^3 of dolomite could be produced annually along flowpaths that discharged to the single vent they sampled. Numerical simulations that link fluid flow, heat flow, and reactive solute transport show that dolomitization occurs along recirculating saline groundwater flow paths. Early generations of models typically predicted diffuse precipitation of dolomite within a broad region of the platform interior where temperatures are warm (50–80°C).[76,77] At greater temperatures and depths, dolomitization is reduced due to slow circulation, which limits magnesium transport. At lower temperatures and shallower depths, transport rates are high, but the kinetic limitation is severe. More recent models that span longer timescales show that shallower regions within the platform margin also dolomitize due to nonlinear feedbacks between porosity, permeability, and dolomitization, which enhance circulation of magnesium (Figure 3). As a result, significant dolomitization can occur between 20 and 40°C and at depths less than 500 m.[53]

Permeability and reactive surface area, which are often inversely related, have a large influence on the regions and rates of dolomitization. For example, highly porous and permeable carbonates with lower reactive surface area have slower dolomitization rates, and dolomitization is restricted to warmer regions of the platform interior. Relatively impermeable mudstones restrict circulation and limit dolomitization to the shallow platform margin.[53] Permeability heterogeneity influences dolomitization rates and patterns by focusing solute and heat transport along conductive layers and may be responsible for concentrated dolomitization of thin beds as observed in some outcrop studies.[76] Platform geometry also influences the extent of dolomitization through controls on geothermal convection and temperature patterns.[53] These models suggest that complete dolomitization requires millions of years, depending on temperature and formation properties.[53,76,77] Other models suggest that dolomitization rates can be faster in the shallow platform if evaporation of seawater leads to brine reflux.[78] The greater brine density drives rapid convection, and the greater magnesium:calcium ratio within the brine water also accelerates dolomitization.

INTERTIDAL SURFACE WATER–GROUNDWATER EXCHANGE

Physics within Unvegetated Beach Environments

The run-up of seawater onto beaches as a result of wave and tide action produces a zone of circulation and mixing in the intertidal zone of beach aquifers (Process 3 in Figure 1). Although small in size relative to deeper saltwater–freshwater interfaces in coastal aquifers, these intertidal mixing zones can have a
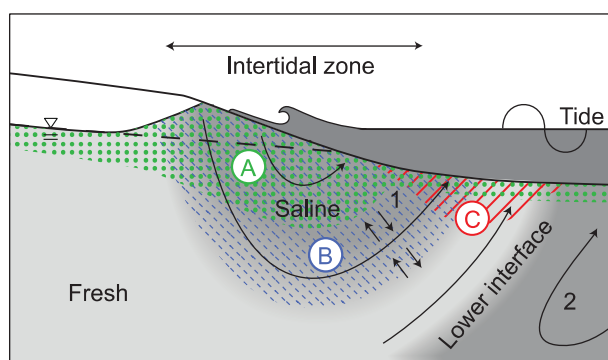
FIGURE 4 | Mechanisms of fresh and saline groundwater flow in the intertidal beach zone.[80] Solid black lines represent flow paths (1: saltwater exchange driven by tides and wave setup, 2: density-driven saltwater exchange). Gray shading represents salinity. Colors indicate key geochemical zones (A: high dissolved oxygen in shallow swash zone, B: high pH in saline pore waters, C: transient zone where high pH, oxygenated saltwater mixes with anoxic, Fe(II) rich freshwater to form Fe(oxy)hydroxides within the Fe curtain.

proportionally much larger effect on solute fluxes because they are highly reactive and situated adjacent to the zone of greatest submarine groundwater discharge. Infiltrating seawater introduces oxygen, sulfate, organic carbon, and other dissolved and particulate matter to the shallow beach aquifer (Figure 4). As these migrate downward and seaward, they mix with fresh groundwater below, which tends to be low in oxygen and high in solutes such as iron and nitrate. Resulting reactions alter solute concentrations in groundwater prior to discharge to the ocean (Figure 4).

The residence time of seawater in the intertidal zone usually ranges from days to several weeks.[20,79–81] Circulation rates tend to vary inversely to the landward hydraulic gradient[80–82] and beach slope,[79,83] and increase with permeability,[84] tidal amplitude,[79,80,85] and wave energy.[86] Although highly variable, discharge from intertidal circulation cells can be more than an order of magnitude larger than fresh submarine groundwater discharge in some environments.[87]

Iron Cycling within Beach Environments

The strong redox gradients and continuous supply of reactants in the intertidal mixing zone create an environment conducive to dynamic cycling and partitioning of redox-sensitive elements such as iron (Fe) across both time and space. Dissolved Fe is a critical micronutrient essential to phytoplankton populations,[88] and its ubiquitous secondary iron (hydr)oxide and sulfide minerals can govern the

residence time, mobility, and bioavailability of many nutrients and pollutants at reactive interfaces.[89,90] Because both fresh and saline groundwater flow is focused through this zone of intertidal mixing, the behavior of Fe impacts the sequestration, release, and residence time of many terrestrially derived nutrients and pollutants in transit to the coastal ocean.

While Fe cycling in fine-grained cohesive sediments has been well described in the marine literature (as of the writing of this article, Froelich et al.[91] has 1723 citations in Web of Science), the more dynamic and variable behavior of Fe in permeable aquifers beneath much of the coast has only recently been examined (e.g., Charette and Sholkovitz[92]). In these systems, the advective mixing of biogeochemically distinct water masses from both marine and terrestrial environments (Figure 4) has a dramatic impact on the chemical form, concentration, distribution, and cycling of Fe, a critical result of which is the generation of an underground veneer of secondary iron minerals termed 'the iron curtain.'[92] Typically, the Fe curtain is visibly identifiable as a zone of sand grains that are coated in yellow, red, and orange Fe (III) precipitates, the formula of which is nominally assumed to be either $FeOOH$ (goethite and/or lepidocrocite) or $Fe(OH)_3$ (ferrihydrite) or some combination of the two of varying degrees of crystallinity.[93–95] Few studies have actually used direct methods capable of distinguishing the speciation of Fe oxide phases associated with the Fe curtain. However, Charette et al.[93] detected all three phases in varying proportion through Fe EXAFS analysis of multiple samples across this interface in Waquoit Bay (Cape Cod, MA). Such mineralogical composition is in fact typical of other aqueous systems undergoing redox fluctuations in this pH range and would be anticipated in oxidizing coastal aquifers (e.g., Cornell[89]).

The Fe curtain forms where mixing occurs between relatively reduced, acidic, Fe(II)/nitrate-rich fresh groundwater and Fe-poor, relatively oxidized, circumneutral pH, sulfate- and reactive organic carbon-rich marine water (Figure 4). The nature of mixing and the number of biogeochemically distinct water masses that produce components of the Fe curtain may vary. Yet the principle reaction governing its initial formation is the oxidation of dissolved ferrous iron, which is generally followed by rapid precipitation of Fe(III) (hydr)oxides.[94,96,97] The oxidation of terrestrially derived Fe(II), usually sourced in reducing fresh groundwater (Figure 4), has been attributed to both the redox-driven interaction with dissolved oxygen in marine or freshwater masses[92] as well as dramatic rise in pH as acidic

terrestrial water mixes with circumneutral marine waters.[97] Both mechanisms are likely important, and their relative importance presumably depends on the severity of chemical gradients, as well as the concentration and speciation of dissolved Fe. Further complicating matters is the fact that Fe(II) oxidation can occur under biotic or abiotic control.[98] McAllister et al.[94] suggested that microbially mediated Fe(II) oxidation drives Fe curtain formation at Cape Shores, DE. Similar to pH and abiotic oxidation of terrestrial Fe(II), microbial influence on Fe curtain formation is likely ubiquitous, with its relative importance varying across and within coastal aquifers.

Of additional importance to understanding the structure and composition of the Fe curtain are redox dynamics near the sediment-water interface where fresh groundwater discharges. In this environment, steep gradients can occur in the bioavailability of carbon, as the carbon associated with marine phytoplankton populations tends to be labile, particularly relative to the refractory nature of terrestrial-derived dissolved organic carbon present in deep groundwater. Benthic microbial consumption of this reactive organic matter facilitates the development of a more reducing interface that is also proximal to a source of sulfur, marine sulfate. Under these conditions, adjacent Fe(oxy)hydroxides of the perimeter of the Fe curtain are no longer stable and redissolve, producing additional aqueous Fe(II), while sulfate is reduced to sulfide species. This creates conditions conducive to the formation of reduced amorphous to crystalline Fe sulfide phases, in this case often observed as black veneers of FeS of likely varying crystallinity. McAllister et al.[94] suggested that these secondary minerals, which behave very differently from Fe(hydr)oxides in the environment, should also be considered part of the Fe curtain. These reactions are also typically mediated by Fe and SO_4 reducing bacteria,[99] further suggesting the profound impact of microbial populations in the composition and configuration of the Fe curtain.

The composition and configuration of the Fe curtain, as well as the solute fluxes that it controls, may be highly impacted by hydrodynamic variability across multiple timescales associated with waves, tides, storms, seasons, interannual precipitation trends, sea-level rise, and climate change.[20,95,100,101] Indeed, McAlister et al.[94] observed seasonal variability in the spatial distribution of critical solutes such as oxygen, Fe(II), nitrate, sulfide, and marine carbon that is consistent with dynamics of the mixing zone itself (i.e., Heiss and Michael[80]). They proposed that seasonal contraction and expansion of the Fe curtain occurs due to fluctuating interfaces associated with seasonal freshwater gradients. The Fe curtain advances toward the ocean during the summer and toward land during the winter. Additionally, during three successive hydrologic years, Roy et al.[101] observed dramatic differences in the size of the seepage face in Indian River Lagoon, FL, which were associated with Fe curtain dynamics. They measured less Fe(oxy)hydroxide dissolution under drier conditions and contend that interannual changes in precipitation could cause dramatic variability in the spatial configuration of the Fe curtain, as well as the flux of Fe(II) to the coastal ocean. This would also presumably affect the formation and distribution of FeS phases along the margins of the Fe curtain. On longer timescales at the same site, Roy et al.[95] suggested that sea-level rise would also have a dramatic effect on the extent of the Fe curtain. They posited that landward migration would provide a labile marine carbon source to new, vadose zone-derived Fe(oxy)hydroxides in this previously fresh region of the aquifer, which would promote transformation from Fe(oxy)hydroxide to FeS and release significant Fe(II) to the coastal system. These studies all illustrate the pressing need to better constrain the variability in the composition and structure of the Fe curtain in time, space, and in response to different hydrodynamic drivers.

Because the Fe curtain occupies the interface between aqueous terrestrial contaminants and the coastal marine ecosystem, the dynamics outlined above may have significant impacts on both nutrient and pollutant fluxes to the coastal ocean. Both Fe(II) sulfide and Fe(III) (hydr)oxide sequester and release contaminants and pollutants depending on biogeochemical conditions. For example, studies in Waquoit Bay have demonstrated marked enrichment of both As and PO_4, both of which have a strong and well-established affinity for Fe(oxy)hydroxides at pH ranges typical of beach aquifers where the Fe curtain forms.[102,103] Interestingly, As concentrations in some zones were extremely high even though As contamination in local groundwater was not evident, suggesting that beach aquifers can serve as sites for As accumulation over time. Jung et al.[103] proposed that the high concentrations of As present in ferrihydrite-rich sediments of Waquoit Bay had accumulated over thousands of years. Their data also suggest that zones within the Fe curtain that are dominated by amorphous Fe(III) phases tend to be more enriched in As and P relative to more crystalline Fe (hydr)oxide mineral assemblages. Thus, even within the oxidized component of the Fe curtain, there could be dramatic variability in the ability of Fe

phases to scavenge bioavailable As. Furthermore, since it is well-known that amorphous nanoparticulate Fe(oxy)hydroxides such as ferrihydrite are the least stable Fe(hydr)oxide over time, those concentrated As pools in the sediment are not necessarily immobilized for the long term. Any of the previously mentioned drivers of hydrodynamic variability and related interface migration could remobilize the nutrients and pollutants associated with these phases. Indeed, Johnston et al.[104] observed elevated concentrations of As due to reductive dissolution of Fe (hydr)oxides on flood tides in coastal Australia, suggesting that As sorbed to Fe (hydr)oxide surfaces can be remobilized under flooding conditions. Again, this suggests that additional research is warranted to determine how Fe curtain and related solutes respond under sea-level rise and climate change as coastlines rapidly change.

Physics of Vegetated Intertidal Zones

Where vegetation can establish within the intertidal critical zone, mangrove species dominate in warm waters, and nonarboreal, salt-tolerant plant species dominate in cooler waters.[105] Both mangrove and salt marsh communities are effective at sequestering carbon and therefore these environments play an important role in the global carbon cycle. Here, we limit our review to salt marshes but refer the interested reader to Kristensen et al.[106] and Alongi[107] for reviews of hydrologic, biogeochemical, and ecological processes within mangroves.

The primary morphologic units within salt marshes are tidal creeks, levees, low marsh, and high marsh (Figure 5(a)). Water exchange among morphologic units depends strongly on tides.[108] As tides rise, creek water flows laterally into marsh sediments, and when tides are high enough to overflow natural

levees, recharge occurs vertically over the low marsh. During ebb tide, groundwater discharges from the low marsh to creeks,[109,110] resulting in export of associated solutes.[188] Gradients in tidal flushing and groundwater discharge across morphologic units drive steep gradients in pore water salinity and biogeochemistry.[111,112] Tidal flushing is greatest near creek banks, and corresponding salinities tend to be similar to creek water, which ranges from oligohaline (starting at 0.5 ppt) to polyhaline (up to 30 ppt) depending on hydrologic connectivity with the open ocean and upland rivers.[113] With increasing distance from creek banks, salinity of low marsh pore water often increases due to decreasing tidal exchange and the concentrating effects of evapotranspiration.[105] Although traditionally thought to play a small role in water and solute budgets,[114] groundwater discharge from marshes has been increasingly shown as an important source of nutrients, carbon, and other solutes to the ocean (e.g., Krest et al.[115]; Porubsky et al.[116]). Tobias et al.[44] showed that regional groundwater flow can influence low marsh salinities. During spring in particular, precipitation and snowmelt promote high discharge rates and limit exchange associated with tidal inundation. Thus, groundwater seasonally plays a major role in solute export from the low marsh zone. In the high marsh zone and other rarely inundated areas, groundwater is a key component of water and solute budgets year-round.[44,117]

Salt marsh soils typically include sand, silt, and clay. Proportions vary geographically as well as locally across creek, low marsh, and high marsh settings.[105] Soils can contain large amounts of peat and substantial amounts of organic carbon. Much of the carbon originates in place through growth of roots and rhizomes.[105] Hydraulic conductivities in salt marsh soils are similar to fine sand,[111] due in part to
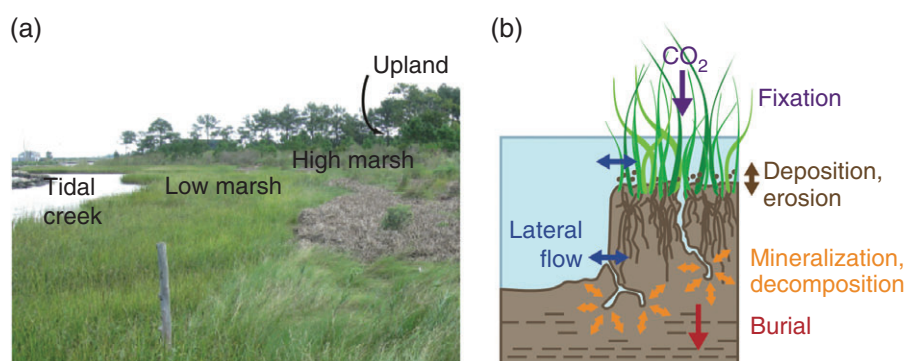
FIGURE 5 | (a) Salt marsh environments. (b) Salt marshes fix atmospheric carbon. A portion is sequestered through burial, while another portion is decomposed or mineralized and exported as dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC) to surrounding estuary and coastal waters via surface water and groundwater flow.

highly connected networks of macropores created by crabs and other fauna.[111] Burrows, hollow stems, and rhizomes of Spartina (the dominant plant genus in global salt marshes) transfer oxygen to soils and create orange oxidized zones.[105] Matrix pore water is less mobile and tends to be reducing. Anaerobic soils often contain high levels of H_2S and organic matter with low pH.[118,119] Oxygen is removed within millimeters of burrows due to sulfide and methane oxidizers.

Carbon Dynamics in Salt Marshes

The vegetated coastal critical zone plays an important role in carbon dynamics. The carbon sequestered in salt marshes and other vegetated marine ecosystems (mangroves and seagrass beds) is called 'blue carbon.' Salt marsh vegetation fixes atmospheric carbon, and a portion of that carbon is eventually buried in underlying sediments (Figure 5(b)). However, a large portion is decomposed or mineralized and then offgassed or exported as DOC and DIC in discharging groundwater to surrounding estuaries and open oceans. Erosion also leads to export of particulate organic carbon. Lateral carbon transfers between salt marshes and coastal waters are difficult to constrain, given the dynamic influence of tides and storms on solute and sediment transport.[120] Salt marshes were traditionally considered net exporters of organic carbon to shallow coastal waters,[121,122] but studies have shown evidence of net import too.[123,124] Where microtopography is favorable, salt marshes trap carbon from estuaries and open oceans during tidal inundation.[122] Thus, the carbon sequestration footprint of salt marshes can be larger than their areal extent.[125] Tidal range is one factor that influences the balance between burial of local and laterally imported carbon.[126] Lateral carbon exchange in salt marshes directly influences their importance as a carbon sink and is a key area for continued research.

Carbon sequestered in the living biomass of salt marshes has a residence time on the order of decades, while carbon in salt marsh soils can be sequestered for millennia.[127] Unlike terrestrial soils, salt marsh soils do not have a limit in their ability to sequester carbon because they accrete vertically as long as the ecosystem is healthy (Figure 5(b)). Thus, the rate of the carbon sequestration and the size of the carbon pool can steadily increase over time.[128] Total global carbon sequestration rates are estimated at 218 +/–24 g C/m^2/year in salt marshes, though site-specific measurements range widely from 18–1713 g C/m^2/year. For comparison, rates of carbon accumulation in terrestrial forest soils only range from 0.7–13.1 g C/m^2/year.[125] Although their global area is substantially less than temperate forests, salt marshes bury 5–87 Tg C/year globally, while temperature forests bury 53 Tg C/year.[125]

Unfortunately, salt marshes are globally in decline, and their carbon sequestration potential is under threat. One quarter of salt marshes has been lost since the 1800s, and the annual loss rate by area is 1–2%.[127,129] Pendleton et al.[130] estimated that global salt marsh degradation emits 0.06 Pg CO_2 year^{-1}, and the global economic impact of this new carbon source to the atmosphere is $2.6 billion per year. Pressures on salt marshes include dredging, filling, diking, draining, and eutrophication. Drainage releases carbon by exposing sediments to oxygen, which increases microbial activity and exposes carbon stocks to rapid decay by aerobic respiration. The effects of eutrophication remain unclear. Nitrogen fertilization stimulates decomposition of recalcitrant organic matter.[131] However, salt marshes are generally nitrogen limited,[122] so nitrogen fertilization may also increase carbon fixation and rates of sediment accretion.[132]

The response of salt marshes to rising and warming seas is also uncertain. Rapid sea-level rise floods and erodes salt marshes.[133] Mudd et al.[134] showed that carbon accumulation can keep pace with sea-level rise until a critical threshold where drowning occurs. The critical rate of sea-level rise depends on inorganic sediment supply and hydrologic conditions. Numerical models predict that salt marsh accumulation will keep pace with sea-level rise for the first half of the 21st century and then decline,[135] though marsh resiliency may be underestimated.[136] The carbon sequestration rate may also decline with warmer air and sea surface temperatures. Although primary productivity increases with temperature, the increase may be offset by faster mineralization rates of organic matter in soils.[137] As the flow of surface water and groundwater mediates carbon release rates from salt marshes through physical and biogeochemical effects, determining future salt marsh responses to disturbance will require integrated research across scientific disciplines.

CURRENT AND WAVE PUMPING IN SUBTIDAL ZONES

Physics

The interactions of waves and currents with a permeable bed pumps saline water across the sediment-water interface in the subtidal zone[10] (Process 4 in Figure 1). These exchange mechanisms are particularly important in estuaries and sandy regions of the

continental shelf above the storm wave base where water energy can be high.[138,139] Although these exchange mechanisms result in no net water input to the global oceans, they are responsible for turning over a large ocean water volume through microbially active sediments and for mixing oxygen-rich surface water with reducing pore waters. In fact, the entire global ocean volume exchanges through permeable sediments once every 3000 years, while the world's rivers replace the global ocean volume only once every 36,000 years.[10]

The interactions of currents with ripples and other topographic features such as burrow vents create pressure gradients along the bed that drive surface water-pore water exchange.[140,141] Specifically, currents are deflected upward over the stoss face of a ripple, forming a zone of high pressure where surface water downwells into the bed. Downstream of the lee face, a zone of low pressure forms and creates a zone of upwelling.[142] If the current oscillates due to wave action, the zone of low pressure and upwelling is located at the ripple crest[143] (Figure 6(a)). The depths of surface water-pore water exchange are typically on the order of the bedform wavelength. Exchange rates increase with current or wave height, bedform steepness, and permeability of the sediment.[142,143] Residence times can range from seconds to weeks.[144] If currents are sufficient to mobilize sediment, bedform migration rapidly exchanges surface water and pore water. A more detailed review is available in Santos et al.[10]

Carbon Cycling in Sandy Subtidal Sediments

Current and wave pumping directly influence carbon cycling and diagenesis of organic matter on continental shelves. Efficient organic carbon sequestration requires a low residence time in oxygenated sediments, which can be achieved by a fast burial rate or a thin aerobic layer. In sandy estuarine and shelf sediments, wave and current pumping can substantially increase the aerobic zone thickness,[145] which leads to rapid degradation of organic matter deposited in sediments. Traditionally, the low organic matter content of sandy aerobic sediments was thought to correspond with low productivity and respiration rates, but current estimates suggest that up to three-quarters of total shelf sediment respiration may occur in sandy sediments.[146] Webb and Theodor[147] first observed benthic exchange in sandy marine sediments and speculated that productivity and respiration could be high if fluxes of dissolved and particulate organic matter were high. Later field observations confirmed high mineralization rates in shelf sediments with low organic matter content.[148–150] Shum et al.[151,152] first used reactive transport models to show that wave pumping is an efficient mechanism for delivering organic matter and dissolved oxygen to microbially active sediments. The presence of a rippled bed substantially increases the depth of oxygen penetration (particularly beneath ripple troughs) and increases rates of oxygen consumption and carbon mineralization. In general, steeper ripple slopes and more permeable sediments lead to faster mineralization. Cook et al.[153] showed that virtually all sediment organic matter was oxidized in subtidal sediments beneath a rippled bed, and aerobic respiration was the dominant metabolic pathway. By comparison, in a flat bed with less advective exchange and more organic matter, mineralization rates were higher but proceeded mainly through sulfate reduction. Winter storms maintained this process over annual cycles by resuspending sediments and rejuvenating the supply of sulfate.

Ripple features and wave energy vary over seasons and storms, and seasonal algal blooms alter the supply of organic matter. Thus, mineralization rates and the depth of the redox front in sandy shelf
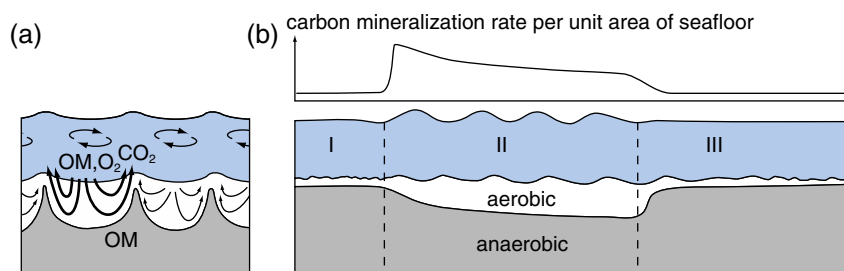
FIGURE 6 | (a) Exchange of salt water through shallow, microbially active subtidal sediments enhances delivery of oxygen and organic matter (OM), which increases OM mineralization. (b) I. Under calm conditions, the aerobic zone is thin and the carbon mineralization rate per unit area of seafloor is low. II. An increase in wave energy mobilizes sediments, which leads to bedform organization, deepening of the aerobic zone, exposure of labile OM to oxidants, and increased carbon mineralization. III. When calm conditions resume, bedform-current interaction ceases, the aerobic zone contracts, and carbon mineralization declines.[138]

sediments are expected to be highly dynamic (Figure 6(b)). For example, Riedl et al.[145] suggested that seasonal declines in wave energy should shift the redox front downward in deep outer shelf environments and subject biomes to stagnation stress. Precht and Huettel[138] further emphasized the importance of bedform topography for both the depth of the redox front and the flux of solutes across the sediment–water interface. Specifically, periods of high wave energy mobilize sediments and form ripples, leading to a rapid flush of accumulated metabolites (Figure 6(b)). As waves interact with ripples, the depth of oxygen penetration into sediments increases and may reach a steady state. Once wave energy declines, solute exchange rates and the depth of oxygen penetration similarly decline. Bioturbative flattening of ripples contributes to further stagnation of pore water, accumulation of metabolites, and depletion of dissolved oxygen (Figure 6(b)). Additional seasonal factors such as bottom water temperature may also drive episodic pore water exchange through controls on buoyancy. These seasonal exchange dynamics are particularly important for surface water quality, because episodes of anoxic pore water release have been shown to contribute to surface water hypoxia.[154]
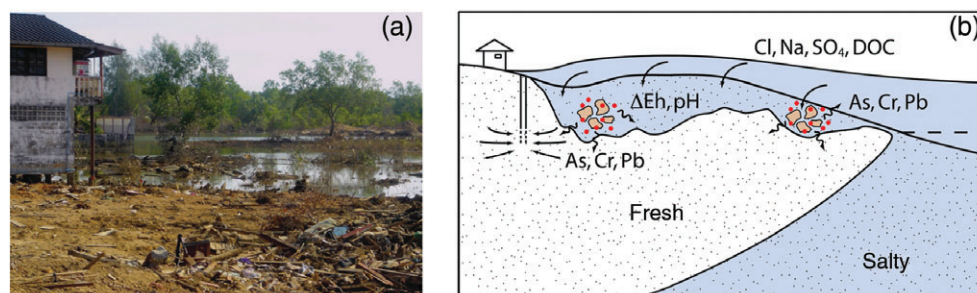
OCEAN SURGES

Physics

Storms, tsunamis, and other disturbances can cause ocean water to surge and flood the coastal critical zone (Figure 7). Recent events such as Hurricane Sandy in the eastern USA and the 2011 Tohoku tsunami in Japan illustrate their potentially wide-reaching and destructive effects. A portion of floodwater infiltrates the coastal aquifer during and after surges (Figure 1), introducing salt and other ocean- and surface-derived solutes. While ocean surge floodwaters may retreat in hours or days, saltwater retained in surface depressions may cause prolonged infiltration and salinization (e.g., Figure 4 (c) in Chidambaram et al.[155]). The resulting unstable density gradient in which denser saltwater overlies less dense freshwater can lead to density-driven convection and downward movement of seawater (e.g., Yu et al.[156]; Kooi et al.[157]).

Compared to other land–ocean exchange mechanisms, subsurface effects of ocean surges are understudied, yet they can have important short- and long-term impacts on groundwater flow and salinity distributions. Over long time periods, exposure to periodic surge inundation has been shown to control the morphology of the subsurface mixing zone on barrier islands.[158] More severe episodic events also have important impacts. Field monitoring of aquifer recovery after the 2004 Indian Ocean tsunami indicates that elevated salinity may persist for years after an episodic event and extend to depths of tens of meters.[159,160] These findings are supported by laboratory[161,162] and modeling studies.[163,164] Ocean surges disrupt freshwater lenses on small islands that are critical for water resources,[165] and effects may persist for years even on highly permeable carbonate atolls.[166] Observations after Supertyphoon Haiyan in the Philippines demonstrate that flushing processes are complex and affected by stratigraphic features,[167] and simulations of island inundation point to the importance of topographic depressions[168,169] and hydrogeologic setting.[170]

The fluxes of water through coastal aquifers driven by ocean surges are not well quantified. Only a handful of studies have modeled both surface water and groundwater dynamics in a way that can realistically estimate infiltration rates (e.g., Yang et al.[171]; Yu et al.[169]), but the focus of all of these studies is salinity evolution rather than flux. Nearly all of the modeling studies conducted to date are based on site-specific simulations that do not encompass the range

FIGURE 7 | Effect of ocean surges on the critical zone. (a) Photograph of coastal Thailand 3 weeks after the 2004 Indian Ocean tsunami. Saline floodwater is still visible in surface depressions. (b) Schematic of infiltration of saline floodwater into a fresh aquifer and associated changes in chemistry and mobilization of trace metals.

of topographic, subsurface, and surge conditions that occur along world coastlines. Thus further study is needed to understand the potential effects of ocean surges on critical zone processes.

Contaminant Mobilization

In addition to uncertainty about physical impacts of ocean surges on coastal aquifers, little is known of their biogeochemical effects. One concern with important implications for human and critical zone health is the impact of storm surges on mobilization of sediment-bound contaminants (Figure 7(b)). Dense populations in coastal zones and legacy industrial activity have contaminated soils along many world coastlines. Although the highest concentrations may be localized near sources, even relatively pristine areas such as coastal marshes often have high levels of metals and organic contaminants due to redistribution by transport and long-term build up of contaminated sediments or water (e.g., Personna et al.[172]). Benthic sediments submerged in coastal areas are also repositories of toxic contaminants, either deposited directly with the sediment or accumulated by immobilization from the water column (e.g., Hart[173]). Indeed, after Hurricane Katrina in August 2005, elevated metal concentrations were observed in urban floodwater,[174] as were high concentrations of pathogenic bacteria.[175] A study of New Jersey soils inundated by Hurricane Sandy showed elevated levels of As, Pb, Cu, Cr, and Fe in pore water within a few days, with effects lasting at least a year in some cases.[172]

Ocean surges can mobilize heavy metals due to a combination of effects on salinity, pH, and redox chemistry (Figure 7). Infiltrating seawater raises the ionic strength of aquifer sediments and pore water and causes ion exchange with the sediments (e.g., Andersen et al.[176]). At near-neutral pH, Wong et al.[177] showed that short-term exposure of benthic sediments to seawater caused rapid release of Cu, Fe, Mn, and Ni due to competitive exchange of metal cations. However, increasing ionic strength was shown to have a minor effect on mobilization of Cd, Cu, Pb, and Zn from marine sediments compared to physical disturbance and pH changes.[178] These processes interact, as displacement of protons due to ion exchange can change pH.[179,180] Wong et al.[180] showed experimentally that exposure of coastal lowland acid sulfate soils to seawater drives ion exchange and increases acidity, resulting in a pulsed release of Al, Fe, Ni, Mn, and Zn. An increase in pH due to exposure of reduced sediments to oxygenated seawater was shown to mobilize U from sediments from a coastal nuclear site in the UK.[179]

Redox shifts in either direction can mobilize contaminants, depending on the antecedent conditions and the contaminants present. Surge inundation can lower redox potential and enhance reduction in two ways. First, an influx of labile organic carbon in floodwater can promote microbial respiration. Second, flood conditions, particularly in surface depressions, and high water tables resulting from infiltration can limit the penetration of oxygen. Both of these processes can have cascading impacts on redox-driven processes in sediments that could facilitate contaminant release. Resulting reductive reactions, such as dissolution of Fe and Mn oxides, can release associated toxic metal(loid)s such as As, Al, U, Th, Cd, Ni, and Zn.[181–183] High concentrations of these metals can be associated with Fe and Mn oxides due to both sorption and coprecipitation.[103,184] Surges can also expose anoxic sediments to oxygen by physical disturbance, by infiltration of floodwater, or by greater penetration of surface water into benthic sediments.[178,181,185] More oxic conditions can also mobilize trace metals associated with sulfide phases, as observed in wetland sediments.[186] Oxidation of sulfide minerals and associated lowering of pH have been shown to alter soil organic carbon consumption rates and associated biogeochemical reactions in salt marshes.[187]

The impact of ocean surges on contaminant mobilization is a complex function of the contaminant, the sediment, *in situ* pore water chemistry, floodwater chemistry, and resulting biogeochemical reactions in coastal critical zones. Furthermore, the processes that initially mobilize contaminants may be different than those that govern longer-term cycling and transport.[180,181] Future study involving field observations, laboratory experimentation, and modeling are required to gain a better understanding of the mechanisms that may mobilize and transport contaminants from coastal sediments as a result of periodic and episodic ocean surge events.

CONCLUSION

Groundwater plays an important role in many widespread critical zone processes, including rock weathering, carbon release and sequestration, and contaminant and nutrient transport and cycling. These critical zone processes behave uniquely near coasts because salinity in coastal aquifers is highly variable and influences fluid flow and biogeochemistry. Additionally, hydrologic forcing from both

marine and terrestrial boundaries drives dynamics in biogeochemical reactions and transport over spatial scales from ripples to continental shelves and over timescales from waves to glacial cycles.

Coastal responses to climate change also differ from inland responses, though there are similarities. Both coastal and inland systems will be impacted by warming water temperatures, changing precipitation patterns, and increasing storm severity. Rising temperatures will likely accelerate carbon mineralization and mineral weathering, albeit to different degrees in coastal and inland systems. Erosion and flooding will mobilize terrestrially derived nutrients and contaminants with more severe storms. Unique to coastal systems, ocean acidification could further enhance chemical weathering and carbon mineralization rates in shallow aquifers. Additionally, sea-level rise is certain to have a powerful impact on the coastal critical zone, with potential to alter the spatial configuration and the related stability and distribution of the hydrodynamic and biogeochemical interfaces highlighted in our review, with far reaching potential ramifications for estuarine and marine ecology, water quality, and ecosystem services.

Perhaps due to its unique hydrodynamic and biogeochemical setting and sensitivity to global change, the coastal interface is disproportionately important in many geochemical cycles and budgets relative to its areal extent. We have presented only a subset of examples in this review. For example, groundwater-derived consumption of CO_2 due to silicate weathering in coastal aquifers is likely a significant component of the weathering carbon sink: the silicate weathering flux from groundwater in volcanic islands is 23–31% that of rivers. Nitrogen loads from fresh groundwater discharge often rival riverine loads. Salt marshes facilitate the development of concentrated and potentially reactive pools of nutrients, contaminants, and carbon relative to headwater catchments. Considering the importance of these processes as well as the density of human populations in coastal zones and their reliance on coastal ecosystem services, it is essential that coasts be viewed as an integral component to the critical zone.

Despite their importance, the biogeochemical and hydrodynamic processes operating across time and space in the coastal critical zone remain, in many cases, poorly constrained. Many critical zone research efforts are focused on inland, headwater settings, where rivers and streams can conveniently be used to monitor integrated geochemical and hydrologic processes over catchment scales. Coastal catchments require more distributed monitoring networks capable of measuring the diffuse and transient material fluxes across the land–sea interface and capturing a broader range of cyclic and episodic temporal change. Coastal biogeochemical cycles are tightly coupled to hydrologic dynamics along active mixing interfaces within and between surface and subsurface environments. Long-term monitoring networks across these interfaces are needed to improve our understanding of the feedbacks between coastal hydrodynamics and biogeochemistry, and to better predict the impacts of environmental change on the coastal critical zone. Networks such as those established by the Critical Zone Observatories funded by the US National Science Foundation are an applicable framework for achieving these goals, particularly when adapted to capture unique coastal processes. Groundwater and surface water monitoring networks should span salinity, redox, and other geochemical gradients, allowing for movement through time in response to physical forcing. Deployment of rapidly evolving sensor technology across these interfaces that resolve the short-term hydrodynamic and biogeochemical processes characteristic of the coastal critical zone, such as waves and tides, would provide powerful insights. Such sensor networks would capture the linked biogeochemical and hydrodynamic responses to stochastic disturbance, both of which can be missed, masked, or mischaracterized using traditional sampling protocols. An array of options are possible to build on and connect existing research infrastructure between coastal and headwater systems, thereby developing a more holistic global monitoring network spanning multiple critical interfaces from headwaters to the coastal ocean. Linking these environments will likely become increasingly necessary for the global research community in the age of the Anthropocene.

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