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Biogeochemical sulfur cycling in the bar-built Pescadero Estuary: Interdisciplinary investigations into near-annual fish mortality events

by

Chandra Mercedes Richards

A dissertation submitted in partial satisfaction of the

requirements for the degree of

Doctor of Philosophy

in

Environmental Science, Policy, and Management

in the

Graduate Division

of the

University of California, Berkeley

Committee in charge:

Professor Céline E. Pallud, Chair

Professor Stephanie M. Carlson

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Biogeochemical sulfur cycling in the bar-built Pescadero Estuary: Interdisciplinary investigations into near-annual fish mortality events

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Abstract

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Natural and human impacts on geochemical redox cycling and biodiversity in estuaries have long been a global concern. In estuarine systems, sulfur (S) is a macroelement of great environmental importance. The production and oxidation of hydrogen sulfide (H_2S) are highly impacted by biogeochemical and physical conditions, including redox conditions and pH. For decades, hydrogen sulfide (H_2S) has been recognized as a major contaminant in estuarine systems due to its direct (toxicity) and indirect (oxidative) effects on aquatic and sediment life. Mass mortality events of fish and migratory birds have occurred in various coastal ecosystems, including bar-built estuaries, which serve as major ecological habitats and as water-purifying marshlands. In this dissertation, I develop an integrated and comprehensive understanding of the geochemical and biological transformations involved in the sulfur redox cycling at the interface of the hydrosphere and pedosphere in a northern California bar-built estuary (Pescadero Estuary, CA) and their consequences on water quality. Fish kills have been more regular and severe at Pescadero than at other nearby California bar-built systems. Across scientific disciplines and spatial and temporal scales, I begin by illustrating the temporal evolution in geochemical conditions in water and sediment from closed to open state to accentuate the decline in water conditions as the estuary opens. I then examine the major anaerobic respiration pathways controlling the biogeochemical cycling of sulfur and its effects on iron (Fe) cycling and pH. Finally, using flow-through reactor experiments and slurry incubations, I investigate the biogeochemical mechanisms that control the production, precipitation, and re-oxidation of hydrogen sulfide in water and sediment.

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Common in Mediterranean climates (e.g. United States, South Africa, Australia, Europe), intermittent estuaries have received little research attention, which lacks in information on the geochemistry of the systems. In California, bar-built estuaries represent about 75% of over 400 estuaries along the Pacific coastline and function as critical refuges to migratory and endangered fish communities, including federally-threatened steelhead trout (*Oncorhynchus mykiss*). An established watershed spanning centuries of human use, the bar-built Pescadero Estuary has, however, been afflicted by near-annual fish mortality events of steelhead trout since 1995, occurring with the natural or anthropogenic opening of the sandbar barrier. In Chapter 1, I tracked the temporal and spatial evolution of water and sediment geochemical conditions from closed to open state to highlight the decline in water conditions between states, specifically acidification. This extensive sampling campaign was feasible for this relatively small system and illustrated that the northern tributary, Pescadero Creek, showed a significant departure in geochemical conditions from the rest of the Estuary; this implied that it may be considerably less susceptible to fish die-offs than the rest of the Pescadero Estuary.

Using this large-scale interpretation of the Pescadero Estuary, I chose four contrasting study to investigate in more details biogeochemical redox cycling of sulfur and iron in sediment during the closed and open states. The speciation and cycling of sulfur are largely driven by microbial activity and redox conditions. The analysis of Pescadero Estuary pore water profiles confirmed that microbial sulfate reduction to hydrogen sulfide is the dominant anaerobic respiration pathway in both the closed and open states. Moreover, the absence of nitrate and presence of reduced ferrous iron confirmed suboxic, reducing conditions in water and the steady production of acid-volatile sulfides (AVS) and iron sulfides in sediment. Additionally, I observed that iron reduction and sulfate reduction occur concomitantly. In Chapter 3, I corroborated that sulfate reductive processes predominate in the Pescadero Estuary, with greater rates in the closed state than in the open state and also in fine-grained sediments than in coarse-grained sediments. Despite higher values than the EPA-defined criterion for aquatic life, the low concentrations of aqueous hydrogen sulfide imply that it cannot solely cause fish deaths. The majority of aqueous sulfide precipitates as metal sulfides in sediment, who could indirectly be implicated in fish die-offs in the transition from closed to open state upon re-oxidation.

The coupled interactions between physical state, sediment conditions, water quality, and overall estuarine health are complex. Linked to climatic conditions and water inflows from ocean and freshwater, the transitional period from closed to open state is characterized by sediment resuspension and mobilization of sediment metal sulfides into the water column where they can be oxidized. In Chapter 4, I demonstrated the oxidative effects of Pescadero Estuary sediments on water conditions using slurry incubation resuspension experiments. I confirmed that aqueous hydrogen sulfide concentrations were low and oxidized quickly (<1 day) and therefore cannot be responsible for fish kills, consistent with the results from Chapter 3. In contrast, the oxidation of sediment AVS was slower, and resulted in their complete removal in six days, with large contents of sulfur released from sediment to water. The oxidation of AVS leads to severe acidification and release of metals (iron, manganese, and zinc) to water. The aqueous metal concentrations reached were greater than the EPA-defined maximum criteria for aquatic life, indicating a potential link to poor fish health.

The integration of scientific knowledge across spatial, environmental, and ecological scales is rarely attempted, thus limiting our mechanistic understanding of sulfur cycling and the causal reasons for mortality events in bar-built estuaries globally. The role of sediment and its impacts on ecosystem health, water quality, and aquatic life due to natural and anthropogenic causes is particularly important. This work is the first to examine the natural, direct and indirect effects of hydrogen sulfide at the interface of water and sediment and across spatial and temporal scales in a bar-built estuary. It is also the first to undertake an extensive sampling campaign to pinpoint the temporal evolution of geochemical conditions. As a comprehensive examination of a complex, environmental problem, this study represents an important advancement in the fields of water, soil, and estuarine science. The management and remediation of intermittent systems depends on our ability to predict estuarine conditions, which will be also be used for similar estuaries along the California coast and to meet policy criteria for water quality. Further development of sulfur cycling across scientific disciplines, landscape types, and coastal environments will be achievable to minimize the likelihood of fish mortality events.

Dedication

This dissertation is dedicated to my mother, Mercedes Tharam Richards.

You inspire me every day.

"It is not important what you do, but what is important is that you love what you do."

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Richards, C. M. and Pallud C., 2013. Kinetics of microbial Fe(III) reduction in Colorado subalpine wetland soils. *American Chemical Society 245th National Meeting & Exposition*, New Orleans, LA, USA, Poster.

Invited Lectures:

Richards, C. M., 2016. Understanding the impacts of physical hydrodynamics on estuarine sediments, water quality, and near-annual fish kills in the bar-built Pescadero Estuary. *Smithsonian Environmental Research Center Seminar*, Edgewater, MD, USA.

Richards, C. M., 2016. A biogeochemical study of sulfur cycling in the bar-built Pescadero Estuary: Interdisciplinary investigations into near-annual fish kills. *University of California, Berkeley, Environmental Science, Policy, and Management Seminar Series*, Berkeley, CA, USA.

Richards, C. M., 2015. Hydroclimates: Biogeochemical impacts of flooding, drainage, and drought in California bar-built estuaries. *University of California, Berkeley, Climatology Seminar Series*, Berkeley, CA, USA.

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Introduction

Bar-built estuaries, also called temporarily open and closed estuaries or intermittent estuaries, are dynamic coastal environments located at the confluence of fresh and saline water. Unlike most estuaries that remain open all year long, intermittent estuaries are characterized by the presence of a sandbar barrier at the estuary's mouth during dry periods, which physical separates the estuary from the ocean. During this closed state, the bar-built estuaries operate like lagoonal systems, during which limited mixing and low freshwater inflows lead to brackish water and anoxic, reducing conditions (Cooper, 2001). The opening of the estuary's mouth is caused by natural (heavy rainfall combined with strong tidal action and high freshwater inflows) or anthropogenic breach events, leading to severe flooding of the estuary and sediment resuspension (Gillanders et al., 2011). The removal of the sandbar barrier returns the estuary to the open state, which is characterized by daily drainage and flushing with saline, oxic, nutrient-rich marine water (Whitfield et al., 2012). Common in regions with Mediterranean climates with wave-dominated coasts (Williams and Stacey, 2015), bar-built estuaries are widespread around the world, representing 50% of estuaries in Australia (Griffiths and West, 1999; Roy et al., 2001), 70% in South Africa (Cooper, 2001; Whitfield et al., 2008; Whitfield et al., 2012), 18% of the North American coastline (Barnes, 1980), including over 75% in California (Emmett et al., 2000).

The Pescadero Estuary is the largest (1.3 km^2) California bar-built estuary between San Francisco and Santa Cruz, and has experienced near-annual fish kills since 1995 (Smith, 2004; Sloan, 2006; Smith, 2009; Atkinson, 2010; Merz et al., 2011; Volpi, 2014). Of the watersheds listed on the California 303(d) list for impaired water bodies, Pescadero Estuary has not satisfied EPA guidelines for water quality due to excessive siltation and sedimentation nor as a suitable aquatic habitat for sensitive fish species since 1998 (US-EPA, 1998). It has been labeled as an important fish habitat and wildlife refuge in northern California for its migratory and breeding use by more than 2,000 species, including federally-threatened steelhead trout (*Oncorhynchus mykiss*) (Volpi, 2014). Receiving roughly 90% of its annual precipitation between November and April, the Pescadero watershed drains 210 km^2 (Phillips and Rojstaczer, 2001) and has supplied agricultural and municipal water to thousands in the San Mateo County. However, the open water channels associated with the Pescadero Estuary have declined by over 50% in the last century due to land reclamation for agricultural purposes (Viollis, 1979; Bozkurt-Frucht, 2013). Hydrogen sulfide has been detected for decades, even prior to the first reported fish kill in 1995 (Viollis, 1979).

Bar-built estuaries are productive systems of great ecological value, acting as nurseries and rearing habitats for a diversity of organisms, including birds, fish, and invertebrates (Pollard, 1994; Emmett et al., 2000; Griffiths, 2001; Gladstone et al., 2006; Hayes et al., 2011). However, many bar-built estuaries exhibit symptoms of poor health, including low dissolved oxygen levels, build-up of contaminants, metals, and waste materials in sediment and water, and ecological damage to aquatic ecosystems, leading to species migration, disease, and/or mortality (Griffiths and West, 1999; Whitfield et al., 2012). The dramatic opening event – when the system transitions from

closed lagoon to open estuary – specifically has been associated with fish mortality events that have been observed repeatedly in bar-built estuaries globally (Whitfield, 1995; Swinker et al., 2001; Luther et al., 2004; Thronson and Quigg, 2008; Wong et al., 2010)).

With over half of the world's population living along a coastline (Small and Nicholls, 2003), the causal reasons for poor health in all estuaries are believed to be partially anthropogenic. Sulfur (S) is among the major elements that is highly impacted by both human and natural activities, especially redox conditions and pH (Goldhaber, 1997; Doney et al., 2007). Sulfur is an ecological, versatile, and essential macronutrient in estuarine systems and its speciation and cycling are largely driven by microbial activity and redox conditions (Thamdrup et al., 1994; Goldhaber, 1997; Bianchi, 2007). In estuarine systems, sulfur predominates as the non-toxic, water-soluble oxyanion, sulfate (SO_4^{2-}) (Howarth, 1984). In anoxic estuarine and marine sediments, sulfate reduction is the dominant anaerobic respiration pathway, coupling the oxidation of organic matter with sulfate reduction to aqueous hydrogen sulfide (H_2S) (Jørgensen, 1977; Kostka et al., 2002; Billon et al., 2002). The poorly-soluble hydrogen sulfide undergoes volatilization under acidic conditions or precipitation in sediment with aqueous metals to form insoluble metal sulfides and potentially leading to acid sulfate soils (Thamdrup et al., 1994). Under hypoxic or oxic conditions, hydrogen sulfide and metal sulfides are chemically and microbially oxidized, resulting in severe oxygen consumption, acidification, and metal release to water (Aller and Rude, 1988; Simpson et al., 1998; Schippers and Jørgensen, 2002; Jørgensen and Nelson, 2004; Rickard and Morse, 2005; Burton et al., 2006).

Hydrogen sulfide directly and indirectly threaten conditions in bar-built estuaries, leading to decreased water quality, contaminated sediments, and mass mortality events of keystone species (Bagarinao, 1992; Chapman and Wang, 2001). Hydrogen sulfide is highly toxic to aquatic species and humans by entering through both circulatory and respiratory systems and inhibiting physiological functioning necessary for cellular respiration and signal transmission (Beauchamp et al., 1984; Bagarinao and Lantin-Olaguer, 1998). In water, fish are stressed and susceptible to disease by hydrogen sulfide concentrations above the safe water quality criteria of 58 nM for aquatic life (Wang and Chapman, 1999; US-EPA, 2016). Moreover, sediments with metal sulfides, or acid sulfate soils, are of further international concern due to their oxidative products, which far surpass the safe water quality criteria for aquatic life (US-EPA, 2016) and jeopardize fish survival (Sammut et al., 1996; Wilson et al., 1999; Powell and Martens, 2005).

The near-annual fish die-offs at the Pescadero Estuary occur during the transition from closed to open state are more severe at Pescadero than other nearby bar-built estuaries along the California coast (Sloan, 2006; Martin et al., 2007; Smith, 2009; Atkinson, 2010). However, the problem of fish kills in intermittent estuaries is not only recurrent in California: fish mortality events have been observed in other regions with Mediterranean climates and has been often linked to the direct and indirect effects of hydrogen sulfide and the transition between closed and open states (Bennett et al., 1985; Becker et al., 2009). The cause of widespread fish mortalities in the Pescadero Estuary has been associated with anoxia, hydrogen sulfide toxicity, acid sulfate soils, acidification, salinity, and fine particle suspension (Sloan, 2006; Smith, 2009). While anoxia is believed to be the main cause of die-offs (Smith, 2009), the physiological functioning of fish in the Pescadero Estuary may be severely impaired by their exposure to hydrogen sulfide, whose

concentrations (8-41 µM; Bostick et al., 2004) are elevated enough to be danger to fish. Moreover, the severe oxidative effects of acid sulfate soils may be lethal to fish residing in the Pescadero Estuary.

To understand the production and environmental effects of hydrogen sulfide in complex bar-built systems, it is important to measure the biogeochemical kinetic rates of sulfate reduction, hydrogen sulfide release to water, and sulfide re-oxidation that are ultimately dependent on redox conditions. The use of flow-through reactor experiments preserves pore structure and spatial biogeochemical distributions and may best mimic the undisturbed sediment layer (Pallud et al., 2007), whereas slurry incubations may best represent re-suspended sediments in the water column in the open state (Cantwell et al., 2002). Moreover, it is also necessary to study the temporal evolution of geochemical conditions in water and sediment as the estuary transitions between states to assess ecological health for water resources and management purposes. These multifaceted analyses have not been widely performed and may be feasible in small bar-built systems to pinpoint sulfur transformations as shaped by redox conditions and climatic events.

In this dissertation, I investigate the biogeochemical redox cycling of sulfur in water and sediment across spatial and temporal scales in the bar-built Pescadero Estuary in northern California. More specifically, the objectives were to identify dominant mechanisms and quantify sulfur cycling as the Pescadero Estuary opens and closes and as the adjacent marshlands are flooded and drained and link these conditions to fish mortality events. In Chapter 1, I begin by highlighting the temporal evolution of geochemical conditions from closed to open state and identify spatial regions that are geochemical vulnerable to increased fish mortality events. This first chapter characterizes geochemical and physical conditions in water and sediment between closed and open states across thirty-two sites in the Pescadero Estuary. In Chapter 2, I then examine dominant anaerobic respiration processes in sediment using sediment pore water with depth at four key sites on a gradient from ocean to freshwater. In this pore water analysis, I evaluate how geochemical sulfur redox cycling is controlled and cycles iron, carbon, and protons in sediment. In Chapter 3, to explore microbial sulfate reduction as the dominant anaerobic process in the Pescadero Estuary in closed and open states, I follow with kinetic rate measurements of sulfate reduction, sulfide export to water, and sulfide precipitation in sediment. This third chapter includes the use of flow-through reactors on intact sediment cores from four sites in the closed state and open state. Finally, in Chapter 4, to understand the direct, oxidative effects of acid sulfate soils on water conditions, I performed slurry incubations containing sediment from four sites. In the sediment resuspension experiments, I measured potential rates of water and sediment sulfide oxidation, acidification, and metal (iron, manganese, zinc) release.

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Chapter 1

Temporal evolution in water quality in a bar-built estuary (Pescadero, California): Geochemical investigations of sulfur redox cycling as a main driver of poor conditions

Abstract – Bar-built estuaries are coastal environments defined by the partial closure of the estuary with a sandbar barrier at the estuary mouth (closed state). Reopening the estuary to the ocean by natural events (rainfall) or anthropogenic influences, the transition to open state often induces poor physical effects, including increased water mixing and sediment resuspension, that directly result in the oxidation of sediment acid-volatile sulfides (AVS). The acidification and release of metals directly associated with AVS oxidation are believed to drive poor water quality and fish mass mortality events in the Pescadero Estuary (CA); however, the temporal evolution and spatial distribution of geochemical water and sediment conditions are poorly understood. I characterized physical and geochemical conditions of water and sediment at thirty-two sites spanning the Pescadero Estuary over a one-year period to investigate sulfur redox cycling as a main driver of poor water conditions in the transition from closed to open state and to identify spatial regions that are geochemically vulnerable to increased mortalities. I showed that the transition from closed to open state is the physical driver of poor water conditions, specifically decreases in pH and increases in hydrogen sulfide and iron concentrations, which are indirectly worsened by the oxidative effects of aqueous hydrogen sulfides and sediment metal sulfides (i.e. acute toxicity, anoxia, and acidification). Aqueous hydrogen sulfide concentrations were low (6.3 ± 0.4 µM) in both closed and open states, yet significantly higher than the recommended thresholds for aquatic life. This spatial analysis further highlighted that the northern tributary, Pescadero Creek, maintains low average sulfate concentrations (7.5 ± 3.0 mM), AVS contents (8.8 ± 5.6 mmol kg^{-1}), and organic matter contents ($0.9\pm0.7\%$), suggesting that it is more chemically stable than the rest of the estuary and that the geochemical effects of sulfate reduction, sulfide precipitation, and sulfide re-oxidation are less severe there. However, significantly higher AVS contents (19-24 mmol kg^{-1}) could be re-oxidized from estuarine sediments at the River Confluence and Butano Creek regions, resulting in severe acidification and metal release in the transition from closed to open state.

1. Introduction

Bar-built estuaries, also called temporarily open/closed estuaries (TOCEs), are dynamic coastal environments located between marine and freshwater sources (Chapman and Wang, 2001; Hu et al., 2004). Unlike permanently open estuaries that are connected to the ocean all year long, bar-built estuaries have a closed state, in which they are separated from the ocean for extended periods by a sandbar barrier. Through high rainfall and wave events or artificial means to restore connectivity, the sandbar is breached, leading to the open state (Becker et al., 2009). The timing of estuaries' opening is usually driven by climate, with typically high precipitation in the summer

in Australia, such as for the bar-built Surrey Estuary and the Richmond River Estuary (Becker et al., 2009; Wong et al., 2010), and in the winter for bar-built estuaries in North America (Behrens et al., 2013). TOCEs are ubiquitous, representing about 18% of the North American coastline (Barnes, 1980), 45-50% of estuaries in southern Australia (Griffiths and West, 1999; Roy et al., 2001), and 70% of estuaries in South Africa (Whitfield et al., 2008; Whitfield et al., 2012).

In recent decades, fish mortalities have been observed in bar-built estuaries around the world (Whitfield, 2005; Sloan, 2006; Whitfield et al., 2008; Becker et al., 2009; Wong et al., 2010), with many directly linked to biogeochemical (e.g., deoxygenation) events spared by physical (e.g., rainfall and flooding) events. Regular fish and invertebrate kills have occurred in several of California's bar-built estuaries, including the Pescadero Estuary (Sloan, 2006; Largier et al., 2015), Rodeo Lagoon (Martin et al., 2007), and San Gregorio Lagoon (Atkinson, 2010; Kerbavaz and Rischbieter, pers. comm.), where imperiled salmonid fish have been among the killed organisms (Sloan, 2006). Fish mortalities are often associated with the transition from closed to open state, and are positively correlated with the length of the closed state, as observed in California (Sloan, 2006; Smith, 2009) and elsewhere (Gladstone et al., 2006; Whitfield et al., 2008; Becker et al., 2009).

Fish kills are repeatedly linked to hypoxia and/or anoxia (<5 ppm dissolved oxygen) high hydrogen sulfide concentrations (>50 µM), severe acidification (pH < 6.5), nutrient loadings, and elevated dissolved metal concentrations in estuarine waters (Bagarinao and Lantin-Olaguer, 1998; Luther et al., 2004; Thronson and Quigg, 2008; Becker et al., 2009; Wong et al., 2010). Hydrogen sulfide influences water and sediment conditions in three ways, acting as a (1) direct toxic pollutant, (2) detoxification agent via metal precipitation, and (3) indirect agent of deoxygenation, acidification, and metal dissolution (Chapman and Wang, 2001). Water temperature is also a major contributor to habitat quality for estuarine species, in which higher values (>22 °C) result in lower dissolved oxygen concentrations (<9 ppm) (Wong et al., 2010), therefore indirectly affecting fish survival. In addition to poor geochemical conditions in water, Whitfield (2005) implies that kills may also be attributed to suspended or fine particles that clog fish gills.

Among the California TOCEs affected by fish mortality events, Pescadero Estuary (Figure 1.1) has been afflicted by reoccurring, near-annual kill events of federally-endangered steelhead trout since 1995, occurring in the transition from closed to open state (Sloan, 2006). Although not unique to the Pescadero Estuary or to California, these kill events have been more regular in Pescadero than in nearby estuaries on the California Coast. Based on this regularity, Pescadero can act as a model for other TOCE systems with similar hydrodynamic, geochemical, and ecological patterns. Recent studies on the physical, biological, and geochemical interactions in the Pescadero Estuary have focused on understanding its hydrodynamic interactions (Williams and Stacey, 2015), sediment geomorphology (Clarke et al., 2014), and geochemistry, with a focus on arsenic (Bostick et al., 2004) and sulfur cycling (Richards and Pallud, 2016). Dissolved oxygen concentrations throughout the main Pescadero channels range from normoxic levels (>5 mg L^{-1}) to hypoxic (3-5 mg L^{-1}) and anoxic (<3 mg L^{-1}) levels, with higher values near the air/water interface (Jankovitz, 2014). Furthermore, aqueous hydrogen sulfide concentrations range up to 45 µM, and water pH values are mildly acidic to moderately alkaline in the main channels of the estuary (Jankovitz, 2014; Jankovitz, 2015; Richards and Pallud, 2016). Sediments in the Pescadero Estuary have a

high potential for the production of metal sulfides under waterlogged conditions (Richards and Pallud, 2016). Sulfide minerals, specifically mackinawite and pyrite, predominate at Pescadero in the North Marsh and are maintained by high hydrogen sulfide concentrations and sulfate concentrations in the pore water (Bostick et al., 2004) and overlying water (Largier et al., 2015). The disturbance of sulfide-rich sediments can occur with natural precipitation and flood events (Sammut et al., 1996; Wilson et al., 1999) or anthropogenic influences (dredging, manual re-opening) (Powell and Martens, 2005). Suggested to drive fish kills at Pescadero (Sloan, 2006; Largier et al., 2015), these disturbances can induce sulfide mobilization, re-oxidation, and dissolution (Powell and Martens, 2005; Wong et al., 2010), potentially leading to deoxygenation, acidification, and metal toxification of estuarine waters, as observed elsewhere (Eyre et al., 2006; Burton et al., 2006; Wong et al., 2010).

This study explores the monthly geochemical evolution of sulfur redox cycling in water and sediment throughout the bar-built Pescadero Estuary to highlight the temporal evolution in the transition from closed to open state and identify spatial regions that are geochemically vulnerable to increased kill events. More specifically, I characterized geochemical and physical conditions of water (i.e. dissolved oxygen, sulfate, hydrogen sulfide, iron concentrations and pH) and sediment (i.e. sulfide and iron contents, pH, and texture) at thirty-two sites spanning the Pescadero Estuary over a one-year period as the estuary transitions between closed and open states. These results show that the transition from closed to open state is the critical step leading to poor water conditions, specifically decreased pH values and increases hydrogen sulfide and iron concentrations, and that the northern tributary, Pescadero Creek, is chemically stable and therefore less affected by geochemical redox cycling than the other regions of the estuary, whose higher AVS contents render them susceptible to severe conditions in the open state.

2. Material and Methods

2.1. Field site

The Pescadero Estuary is a macrotidal and intertidal bar-built estuary located along the Pacific Coast in California, USA (Figure 1.1). The Mediterranean hydroclimate at Pescadero is characterized by an average annual rainfall of 73.5 cm with a pronounced colder wet season extending from November to April and warmer dry season from May to October (US Climate Data 2016). The source of Pescadero's freshwater derives from its two tributaries, the Pescadero Creek and the Butano Creek (Figure 1.1) through stream inflow rates of 0.34 m^3 s^{-1} and 0.17 m^3 s^{-1}, respectively (Sloan, 2006). The water column is shallow (<3 m) at high tide and salinity-stratified (Williams and Stacey, 2015). Pescadero sediment encompasses a variety of textures ranging from silt loams to sandy loams (Richards and Pallud, 2016).

Pescadero is closed for 3 to 10 months per year, beginning in spring or summer months and has opened up to four times per year since 1985, typically beginning during the California rainfall season in November (Sloan, 2006; Smith, 2009; Volpi, 2014; Largier et al., 2015; Williams and Stacey, 2015; Richards and Pallud, 2016). This study period ranged from September 2014 to August 2015. During that period, the estuary was closed in September and November 2014, opened
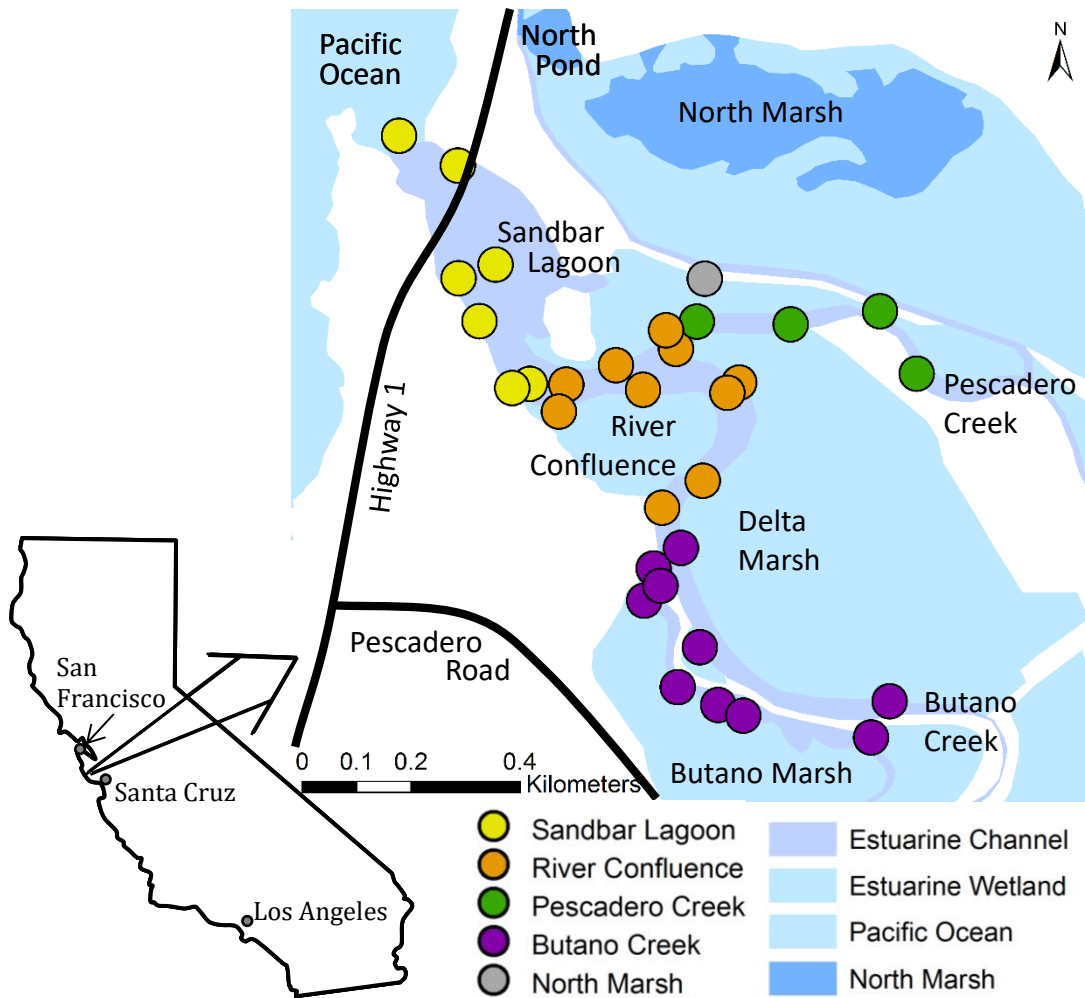
Figure 1.1. The Pescadero Estuary in California with the location of the thirty-two littoral sites sampled for water and sediment in 2014-2015. With the exception of the site adjacent to the North Marsh (gray), sites were separated into four segments, as represented by the Sandbar Lagoon sites (yellow), the River Confluence sites (orange), the Pescadero Creek sites (green), and the Butano Creek sites (purple).

in December 2014 after heavy precipitation (5.4 cm, as estimated for Half Moon Bay, CA) (US Climate Data, 2016) and remained open through early spring (March 2015) (Figure 1.2). After a brief closure in April 2015, the estuary re-opened in May and closed again in August at the end of the study period.

2.2. Sampling campaign

Overlying water (one meter below the surface) and surface sediment (20-40 cm below the water column) samples were collected monthly between September 2014 and August 2015 at thirty-two sites along the littoral of the Pescadero Estuary (Figure 1.1). These sites covered the

entire span of the estuary, ranging from the confluence with the Pacific Ocean to the Butano Creek on the south end and the Pescadero Creek on the north end. With the exception of the North Marsh site, all sites belong to four segments within the estuary: Sandbar Lagoon, River Confluence, Pescadero Creek, and Butano Creek (Figure 1.1). All bulk water and sediment samples were stored at 4°C under anoxic conditions until analyses of geochemical and physical properties.

2.3. Water analyses

Water temperature, conductivity, and dissolved oxygen concentrations were measured monthly *in situ* at the thirty-two sites at a depth of 1 m below the water level using an OAKTON CON6/TDS 6 hand-held conductivity/TDS/temperature probe and meter and Orion standard epoxy DO probe with an Orion 3-STAR meter, respectively. Temperature and conductivity were measured over the full sampling period, while dissolved oxygen was measured only between April 2015 and August 2015.

Sulfate and chloride concentrations in water samples were measured on a Dionex ion chromatograph (IC) (ICS-1000 system; IonPac analytical column, AS18/AG18; suppressor, ASRS 300, 4 mm) supplied with a hydroxide eluent (27.5 mM NaOH) at a flow rate of 1.0 mL min^{-1}. Salinity was calculated using conductivity and temperature data following Müller (1999). Total hydrogen sulfide concentrations in water samples were measured from potentials with an Ionplus Sure-Flow silver-sulfide selective pH/ISE electrode and Thermo Scientific meter following 1:1 dilution with a sulfide anti-oxidant buffer (SAOB) of 1 M sodium hydroxide (NaOH) and 0.1 M ethylenediaminetetraacetic acid (EDTA). Total iron concentrations in water samples were measured *via* the ferrozine method using a Thermo Spectronic spectrophotometer at 562 nm (Stookey, 1970). Water pH was determined using a pH/ATC Sartorius ATC combination electrode and Denver Instrument meter. Following filtration and subsequent 1:1 dilution with water, dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC) concentrations were measured using an O-I-Analytical analyzer.

2.4. Sediment analyses

Acid-volatile sulfide (AVS), and total iron (Fe$_{tot}$) extractions were achieved using an acid extraction method (van Griethuysen et al., 2002), in which sediment (1-2 g) is stirred with 1 M hydrochloric acid (20 mL) in a sealed extraction chamber for two hours with a SAOB trap described above. Using a Thermo Spectronic spectrophotometer, AVS and Fe$_{tot}$ contents were then measured colorimetrically *via* the methylene blue method at 670 nm (Simpson, 2001) and ferrozine method at 562 nm (Stookey, 1970), respectively. Organic carbon and total nitrogen contents were determined using a CE Instruments Elemental Analyzer on air-dried sediment following the removal of inorganic carbon with 0.5 M FeSO$_4$-H$_2$SO$_4$ acid digestion solution at room temperature. Sediment pH was measured in a suspension of dry sediment (10 g) in a CaCl$_2$ solution (10 mL) (Thomas, 1996), as described above for water. Mean grain size and sand, silt, and clay percentages were measured on oven-dried sediment, following organic matter and carbonate removal with 35%

hydrogen peroxide and 1 M hydrochloric acid, respectively; all values were measured using a LISST-Portable|XR Sequoia Scientific Particle Size Analyzer.

2.5. Statistical analyses

The statistical significance between months for water and sediment characteristics were determined by one-way ANOVA with a significance threshold of $P = 0.05$. Correlations between water and sediment characteristics were evaluated using Pearson's correlation coefficient with a correlation threshold of $r = \pm 0.9$. Reported uncertainty ranges are ± 1 standard deviation unless otherwise stated. The statistical analysis was performed with the EZAnalyze package.

2.6. Spatial data analyses

All geochemical variables were compiled and integrated into maps in the geographic information system (GIS) software, ArcGIS (ESRI, Inc.), over the California Wetlands Basemap (U.S. Fish & Wildlife Services, 2014). The map scale and area are 1:7181 and 2.15 square kilometers, respectively. All maps were adapted to a coordinate system of WGS 1984 Web Mercator Auxillary Sphere with Mercator Auxillary Sphere projection, WGS 1984 datum, and meter units. The unit value ranges for all variables were divided into five equal parts for comparison of the spatial distributions across all temporal scales.

3. Results

3.1. Average characteristics of Pescadero water

All water variables showed significant differences between closed and open states. Conductivity, salinity, as well as concentrations of sulfate, total hydrogen sulfide and chloride showed significantly lower average values in the closed state than in the open state. The opposite was true for concentrations of total iron, DOC and DIC, as well as pH (Table 1.1).

With the exception of July 2015, Pescadero water temperatures reflected the evolution in air temperatures observed for the closest town with climate data (Half Moon Bay, CA, 28.4 km away) (US Climate Data, 2016) (Figure 1.2a). Average water temperatures at Pescadero decreased from 24.7 to 16.7°C during the first closed state period (September-November 2014), then slowly increased to 28.6°C in August 2015, despite a sharp surge in July 2015 (Figure 1.2a). Average conductivities at all sites and months ranged from 0.2 to 47.2 mS cm^{-1}, with higher average values in the open state (21.0±9.3 mS cm^{-1}) than in the closed state (9.5±2.7 mS cm^{-1}) (Table 1.1). The two transitions from closed to open states were characterized by 3- to 9-fold increases in average conductivity. The highest average conductivity values were observed in summer (May-July, open state), in which the largest variability was also observed (Figure 1.2b). Salinity in the estuary was mildly to heavily brackish and showed a similar temporal evolution to conductivity, with significantly lower values (1.8-8.0‰) in the closed state and higher, more fluctuating values (8.4-23.8‰) in the open state, with the highest values observed in July 2015 (Figure 1.2c). Dissolved

Table 1.1. Water and sediment characteristics in the Pescadero Estuary system. Values are presented as averages ±standard deviations for the thirty-two study sites for the September 2014 to August 2015 period, except for DO where values were obtained only for the April 2015 and August 2015 period. nm means not measured.

Variable	Average	Closed state average	Open state average
Water			
Temperature (°C)	21.1±2.8	21.8±1.9	21.0±3.1
Conductivity (mS cm^{-1})	17.1±7.8	9.5±2.7	21.0±9.3
Salinity (‰)	11.5±5.6	5.7±1.7	14.3±6.9
DO (mg L^{-1})	6.2±1.4	nm	nm
[Cl$^-$] (mM)	220.1±72.6	166.4±19.8	227.4±94.0
[SO$_4^{2-}$] (mM)	11.8±4.5	5.9±0.8	13.8±6.0
Cl$^-$/SO$_4^{2-}$ ratio	17.5±1.7	24.0±2.0	15.5±1.5
[H$_2$S] (µM)	6.3±0.4	5.3±0.3	7.3±0.4
[Total Fe] (µM)	4.6±2.6	5.5±2.1	3.8±2.7
pH	7.8±0.3	8.3±0.2	7.6±0.3
DIC (mg L^{-1})	30.8±4.9	36.3±4.7	28.5±5.5
DOC (mg L^{-1})	3.5±1.1	5.6±0.9	3.2±1.3
Sediment			
AVS (mmol kg^{-1})	16.9±15.0	15.6±10.9	17.7±17.4
Total Fe (mmol kg^{-1})	60.8±24.0	59.7±25.9	62.0±23.5
pH	7.2±0.5	7.5±0.4	7.1±0.4
Organic C (%)	2.0±1.8	2.7±2.4	1.7±1.5
Total N (%)	0.17±0.14	0.22±0.18	0.15±0.12
C$_{org}$/N (mol mol^{-1})	10.5±3.4	11.2±3.7	10.0±3.2

oxygen concentrations averaged throughout the estuary were oxic (8.3-8.9 ppm) in late spring (April-May 2015), then slowly declined to 5.7±1.7 ppm by July 2015 and plummeted to hypoxic values (1.2±0.2) as the estuary closed (August 2015) (Figure 1.2d).

Average chloride concentrations were characteristic of mildly to strongly brackish conditions, ranging from 17.9 to 497 mM. They showed a similar temporal evolution to conductivity and salinity, with significantly lower average values (166±20 mM) in the closed state (with the exception of August 2015 that had the highest value), and higher, more fluctuating average values in the open state (Figure 1.3a). Averaged over all sites, the two transitions from closed to open state were characterized by 3- to 11-fold increases in chloride concentrations. Average chloride concentrations exhibited moderate positive correlations with conductivity (r = 0.68, P < 0.05), salinity (r = 0.62, P < 0.05), and a strong positive correlation with sulfate concentration (r = 0.85, P < 0.001). Molar chloride to sulfate ratios ranged from 5.8 to 34.9, with significantly higher
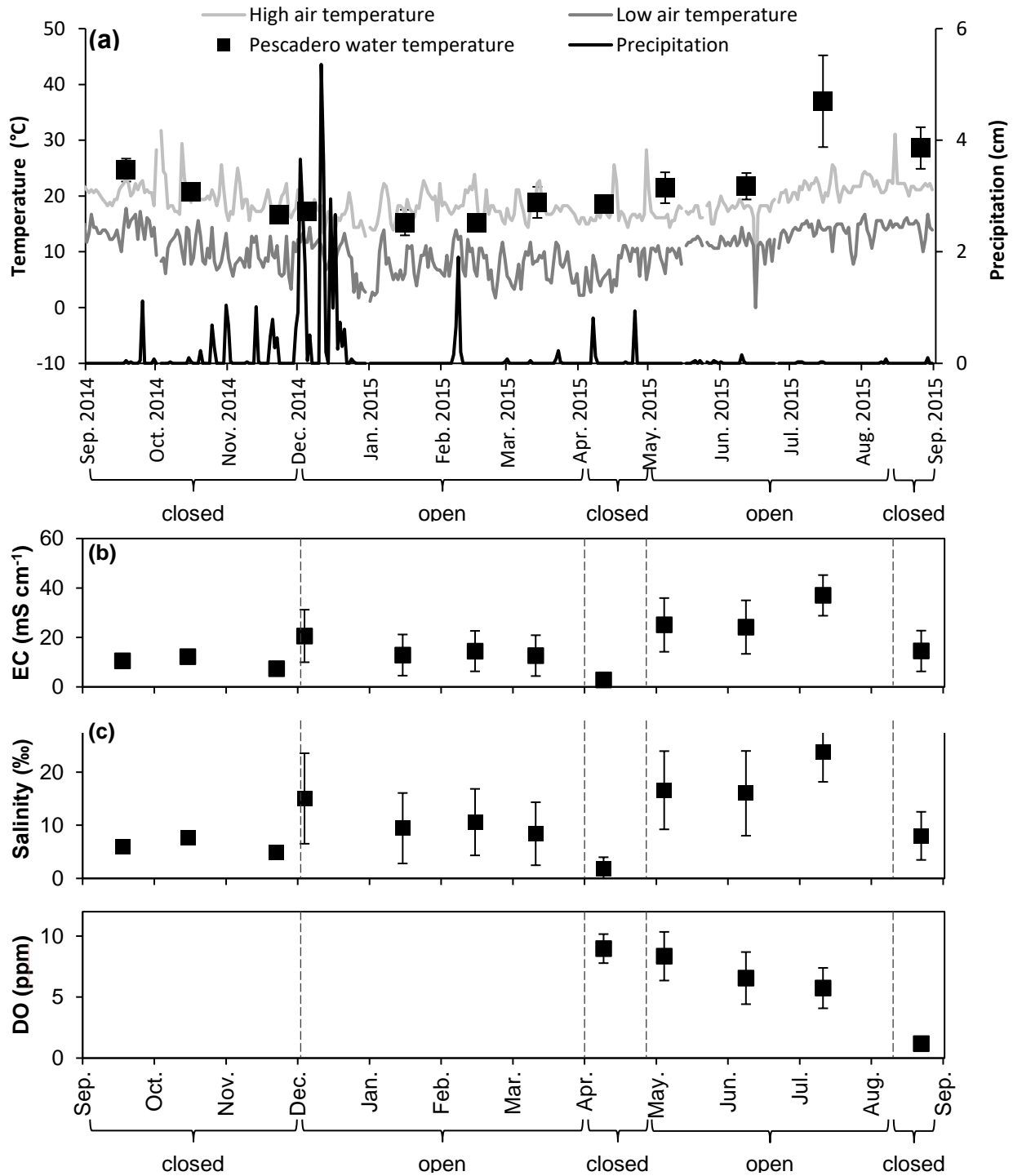
Figure 1.2. In situ **(a)** water temperatures combined with U.S. Climate Data of high and low air temperatures and precipitation observed for Half Moon Bay, CA, **(b)** conductivity (EC), **(c)** salinity, and **(d)** dissolved oxygen (DO) concentration measured between September 2014 and September 2015. Values are presented as averages for the thirty-two study sites. Error bars indicate standard deviation; when not visible, they fall within the size of the symbols.

average values (24.0±2.0) in the closed state (with the exception of April 2015 that had the lowest
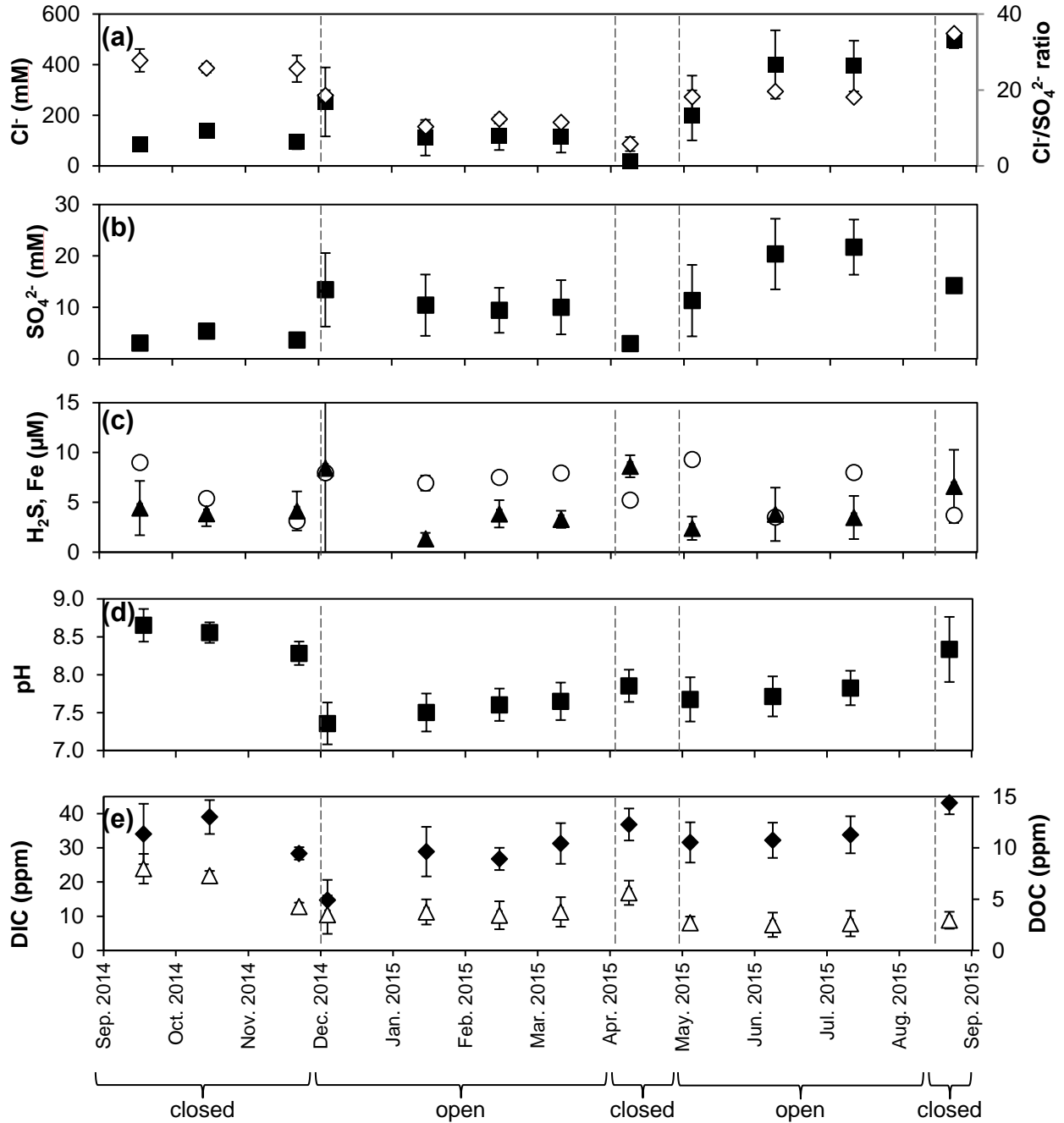
Figure 1.3. Geochemical aqueous **(a)** chloride concentration (squares) and chloride to sulfate ratio (diamonds); **(b)** sulfate concentration; **(c)** total hydrogen sulfide (circles) and total iron (triangles) concentrations; **(d)** water pH; and **(e)** dissolved inorganic carbon (diamonds) and dissolved organic carbon (triangles) concentration measured monthly between September 2014 and September 2015. Values are presented as averages for the thirty-two study sites. Error bars indicate standard deviation; when not visible, they fall within the size of the symbols.

value) than in the open state (15.5±1.5) (Figure 1.3a). Molar chloride to sulfate ratios decreased in the first transition from closed to open state yet increased in the second transitional period due to

the lowest ratio (5.8±1.8) observed in April 2015.

Average sulfate concentrations also showed a similar temporal evolution to salinity, with significantly lower values in the closed state (5.9±0.8 mM) than the open state (13.8±6.0 mM) (Table 1.1, Figure 1.3b). Sulfate concentration exhibited strong positive correlations with conductivity (r = 0.87, P < 0.001) and salinity (r = 0.87, P < 0.001). Both average total aqueous hydrogen sulfide concentrations and average total iron concentrations were low (<60 µM), with respective average ranges of 3.5-9.3 µM and 1.4-8.6 µM (Table 1.1, Figure 1.3c). Average iron concentrations in the closed state (5.5±2.1 µM) were significantly higher than in the open state (3.8±2.7 µM), whereas the opposite trend was observed for average hydrogen sulfide concentrations (Table 1.1). Water pH values were slightly alkaline (7.9-8.7) in the closed states (September-November 2014, August 2015) and circumneutral (7.4-7.8) in the open states (Figure 1.3d). In both transitions from closed to open states, average water pH showed a significant decrease by 0.2-1.0 units (Figure 1.8).

Average DOC concentrations at all sites and times fluctuated between 0.7 and 11.8 ppm and decreased in the transition from closed to open state, with significantly higher values in the closed state (5.6±0.9 ppm) than in the open state (3.2±1.3 ppm) (Table 1.1). DOC concentrations showed moderate negative correlations with conductivity (r = -0.60, P < 0.05), chloride concentration (r = -0.60, P < 0.05), salinity (r = -0.63, P < 0.05), sulfate concentration (r = -0.77, P < 0.01), and a moderate positive correlation with water pH (r = 0.70, P < 0.05). Average DIC concentrations ranged from 8.8 to 55.7 ppm, with values approximately an order of magnitude larger than average DOC concentrations (Table 1.1; Figure 1.3e). Similar to DOC, average DIC values were significantly higher in the closed state (36.3±4.7 ppm) than in the open state (28.5±5.5 ppm) (Table 1.1), yet no trends were observed in the transition between states. The lowest and highest average DIC values were observed in December 2014 (open state) and August 2015 (closed state), respectively. DIC also exhibited a moderate positive correlation with water pH (r = 0.65, P < 0.05).

3.2. Average characteristics of Pescadero sediment

The concentrations of acid-volatile sulfides present in sediment, or AVS sediment contents, fluctuated widely among sites and times, reaching up to 125 mmol kg^{-1} sediment and showed no significant differences between closed and open states (Table 1.1; Figure 1.4a). The lowest observed AVS contents (8.2 mmol kg^{-1}) were measured in April 2014, during which the estuary was closed following a four-month open period; however, the greatest temporal variability was observed in the open state (February-March 2014). Total sediment iron contents also fluctuated heavily, ranging from 4.3 to 178.4 mmol kg^{-1} sediment and averaging 60.8±24.0 mmol kg^{-1} at all sites over the year-long period (Table 1.1; Figure 1.4a). Similar to AVS content, total iron contents showed no significant differences between closed and open states. Sediment pH values recorded at all study sites and times ranged widely from strongly acidic (4.9) to strongly alkaline (8.9) (Table 1.1). Sediment pH was significantly higher in the closed state (7.5±0.4), than the open state (7.1±0.4) (Figure 1.4b).

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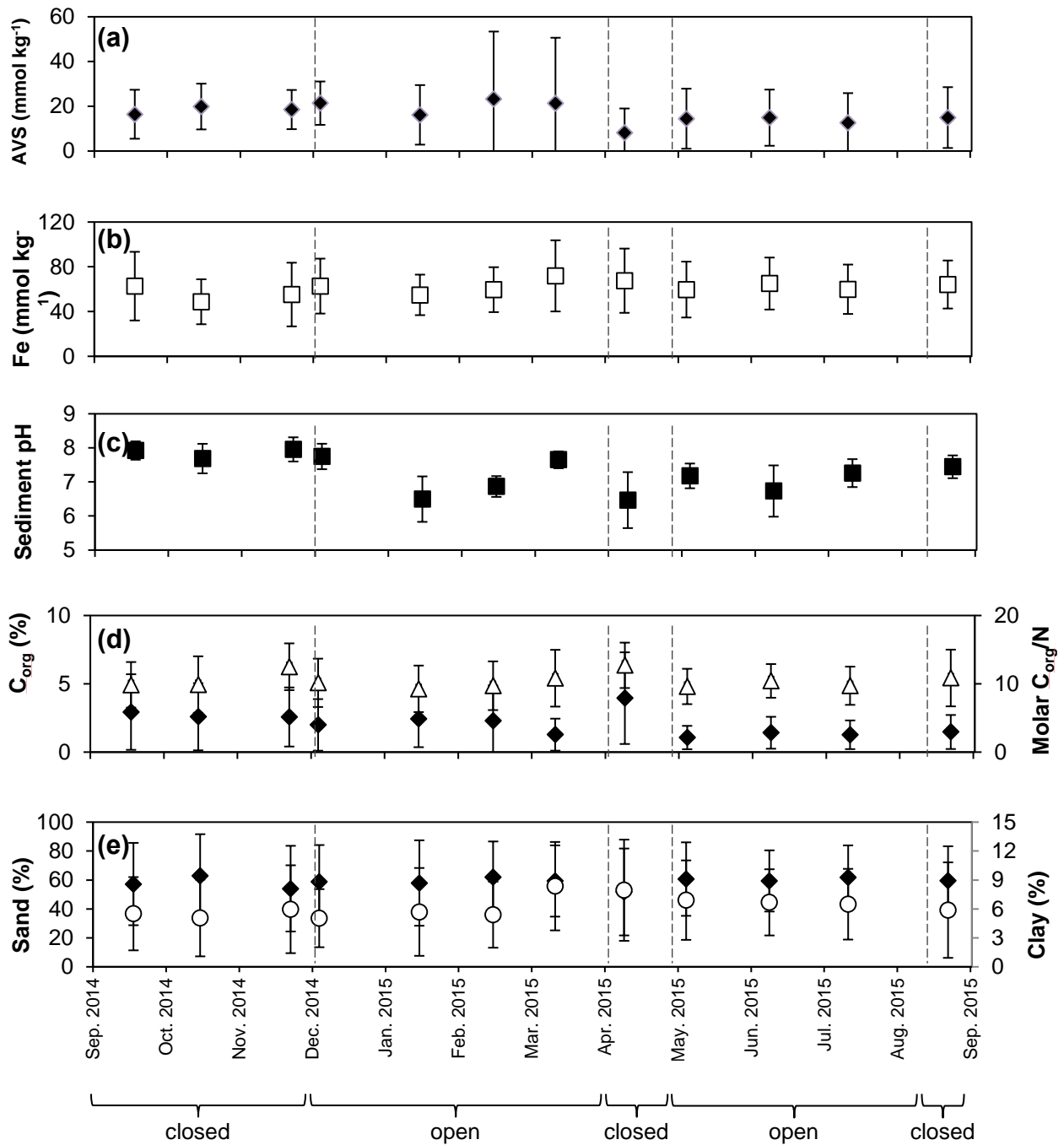
Figure 1.4. Geochemical sediment **(a)** acid-volatile sulfide (diamonds) and total iron (squares) contents; **(b)** pH; **(c)** organic carbon content (diamonds) and molar C_{org}/N (triangles); and **(d)** sand (diamonds) and clay (circles) contents measured monthly between September 2014 and September 2015. Values are presented as averages for the thirty-two study sites. Error bars indicate standard deviation; when not visible, they fall within the size of the symbols.

Total sediment organic carbon content varied between 0.4 and 28.9%, with significantly higher values observed in the closed state ($2.7\pm2.4\%$) than in the open state ($1.7\pm1.5\%$) (Table 1.1;

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Figure 1.4c). Average sediment C_{org} content showed moderate negative correlations with conductivity (r = -0.76, P < 0.01), chloride concentration (r = -0.69, P < 0.05), salinity (r = -0.74, P < 0.01), and sulfate concentration (r = -0.768, P < 0.01) recorded in water, and a moderate positive correlation with water DOC concentration (r = 0.72, P < 0.01). Total sediment N content were on average an order of magnitude lower than sediment C_{org} content and showed a similar trend with significantly higher values in the closed state (0.22±0.18%) than in the open state (0.15±0.12%) (Table 1.1). Average sediment N content exhibited a strong positive correlation with sediment C_{org} content (r = 0.99, P < 0.001), a moderate positive correlation with DOC concentration (r = 0.72, P < 0.01), and moderate negative correlations with conductivity (r = -0.74, P < 0.01), chloride concentration (r = -0.70, P < 0.05), salinity (r = -0.72, P < 0.01), and sulfate concentration (r = -0.75, P < 0.01) in water. With no significant differences between states, molar C_{org}/N ranged from 0.4 to 28.9 (Table 1.1; Figure 1.4c) and showed moderate negative correlation with average hydrogen sulfide concentration in water (r = -0.61, P < 0.05).

3.3. Spatial and temporal variability in water characteristics

Little inter-site variability of all geochemical variables was observed for the closed state, whereas more pronounced spatial variability was observed during the open state. Dissolved oxygen concentrations showed limited spatial differences throughout the estuary for both states; however, values were markedly lower at the Butano Creek sites between July and August 2015 (Figure 1.5).

Compared to other sites at the same times, higher sulfate concentrations (>20 mM) were observed in the Butano Creek region in December 2014; however, higher sulfate concentrations (>18 mM) were observed in the Sandbar Lagoon and North Marsh sites in January 2015 (Figure 1.6). The Pescadero Creek region had consistently low sulfate concentrations (<12 mM) for the full sampling period, except for June 2015 (open). Gradients in sulfate concentration and also salinity (Supp. Figure 1.14) from marine to freshwater sites for sulfate concentration were first observed in July 2015, three months after the estuary re-opened in May. Contrary to sulfate concentrations, total hydrogen sulfide concentrations showed very little spatial variation throughout the estuary (Figure 1.7). Hydrogen sulfide also exhibited minimal temporal variations with values significantly increasing in the transitions between closed and open states from 3.1-5.2 µM to 8.0-9.3 µM.

Similar to hydrogen sulfide concentration, the spatial variations in water pH were minimal (Table 1.2); however, temporal variations were high. In both transitions from closed to open state, during which there was the highest temporal variability, water pH values reached the lowest, yet circumneutral values in December and May (7.4-7.7), with both circumneutral and slightly acidic values (6.7-7.7) scattered along the River Confluence and Butano Creek (Figure 1.8). With few exceptions, water pH was very homogenous throughout the estuary, decreasing from slightly or moderately alkaline to slightly acidic or circumneutral values from closed to open states. Moreover, despite circumneutral pH in the bulk of the estuary between March and July 2015,

several scattered sites display moderately alkaline water. The Pescadero Creek had relatively stable, circumneutral values throughout the sampling period.

Table 1.2. Water and sediment characteristics of four regions in the Pescadero Estuary system. Values are presented as averages ±standard deviations for each of the spatial regions for the September 2014 to August 2015 period, except for DO where values were obtained only for the April 2015 and August 2015 period.

Variable	Sandbar Lagoon	River Confluence	Pescadero Creek	Butano Creek
Water				
Temperature (°C)	22.9±1.3	21.9±1.6	19.3±2.2	19.9±2.3
Conductivity (mS cm^{-1})	21.1±3.8	18.1±6.8	10.0±6.8	17.4±6.4
Salinity (‰)	13.8±2.9	11.9±5.0	6.5±4.8	12.1±4.7
DO (mg L^{-1})	6.7±0.7	6.2±0.9	6.3±0.8	5.5±1.8
[Cl$^-$] (mM)	267.9±40.3	223.4±60.5	142.8±59.2	225.2±47.7
[SO$_4^{2-}$] (mM)	14.9±3.2	12.0±3.7	7.5±3.0	11.6±2.9
Cl$^-$/SO$_4^{2-}$ ratio	17.8±1.0	17.6±1.5	15.4±2.1	18.0±0.6
[H$_2$S] (µM)	6.2±0.5	6.4±0.4	6.3±0.1	6.4±0.2
[Total Fe] (µM)	4.3±1.7	5.2±3.6	4.0±1.2	4.6±1.4
pH	7.9±0.1	7.8±0.2	7.8±0.1	7.7±0.2
DIC (mg L^{-1})	30.4±1.7	32.1±4.4	32.9±2.0	28.7±2.9
DOC (mg L^{-1})	2.8±0.5	3.3±0.9	3.3±0.7	4.1±1.0
Sediment				
AVS (mmol kg^{-1})	9.0±9.8	19.9±13.3	8.8±5.6	23.4±15.4
Total Fe (mmol kg^{-1})	41.3±23.5	66.8±18.0	65.8±12.7	65.6±26.6
pH	7.4±0.4	7.2±0.4	7.2±0.3	7.1±0.4
Organic C (%)	0.6±0.7	2.0±1.3	0.9±0.7	3.5±1.8
Total N (%)	0.06±0.05	0.17±0.10	0.08±0.04	0.29±0.14
C$_{org}$/N (mol mol^{-1})	8.8±4.4	11.0±2.3	10.2±3.6	11.6±1.7
Mean grain size (um)	171.1±96.8	66.2±41.6	80.8±31.3	39.7±32.3
Sand (%)	82.6±15.8	59.1±19.3	69.5±12.2	39.1±22.6
Silt (%)	14.4±13.4	35.1±16.9	25.0±10.2	51.9±19.3
Clay (%)	3.0±2.6	5.7±2.8	5.5±2.7	9.1±4.0
Texture	Sand, sandy loam	Sandy-silt loam	Sandy loam	Sandy-silt loam
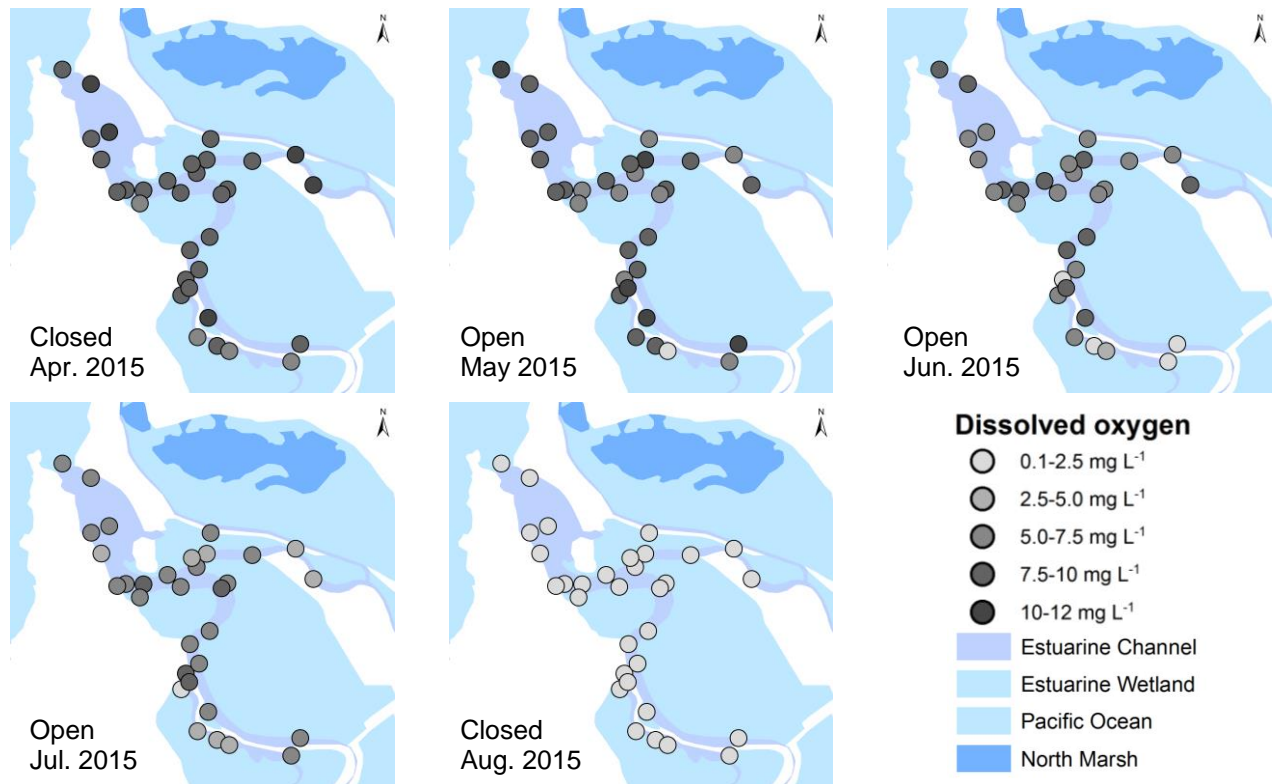
Figure 1.5. A spatio-temporal evolution of water dissolved oxygen concentration (mg L^{-1}) sampled at the Pescadero Estuary in 2014-2015 for thirty-two littoral sites. The estuary was closed in September-November 2014 and April and August 2015.

3.4. Spatial and temporal variability in sediment characteristics

The sediment texture throughout the estuary ranged from medium-textured (silt loam and loam) in the Butano Creek, to coarse-textured (sandy loam and sand) closer to the ocean, including the Sandbar Lagoon and Pescadero Creek (Figure 1.9). More specifically, the medium-textured sediments had lower average grain sizes (5.9-68 µm), higher clay contents (5.0-23.2%), and lower sand content (0.8-50.4%), than the coarse-textured sediments with average grain sizes of 34-357 µm, clay contents of 0.2-13.7%, and sand contents of 45.1-99.4%. The sediment's textures at all sites fluctuated slightly over time (data not shown) and between closed and open states, especially along the littoral of the Pescadero channels (Figure 1.4d-e; Figure 1.9).

Sediment AVS contents showed no discernible spatial trends, except for consistently low values (<30 mmol kg^{-1}) at the Sandbar Lagoon and Pescadero Creek sites and higher values (>40 mmol kg^{-1}) at the North Marsh and Butano Creek sites (Figure 1.10). Sediment iron contents showed generally higher values (>35 mmol kg^{-1}) at all sites than at the Sandbar Lagoon and Pescadero Creek sites (Figure 1.11). The Butano Creek and North Marsh sites exhibited iron contents up to 180 mmol kg^{-1}. In both AVS and iron contents, the Pescadero Creek sites
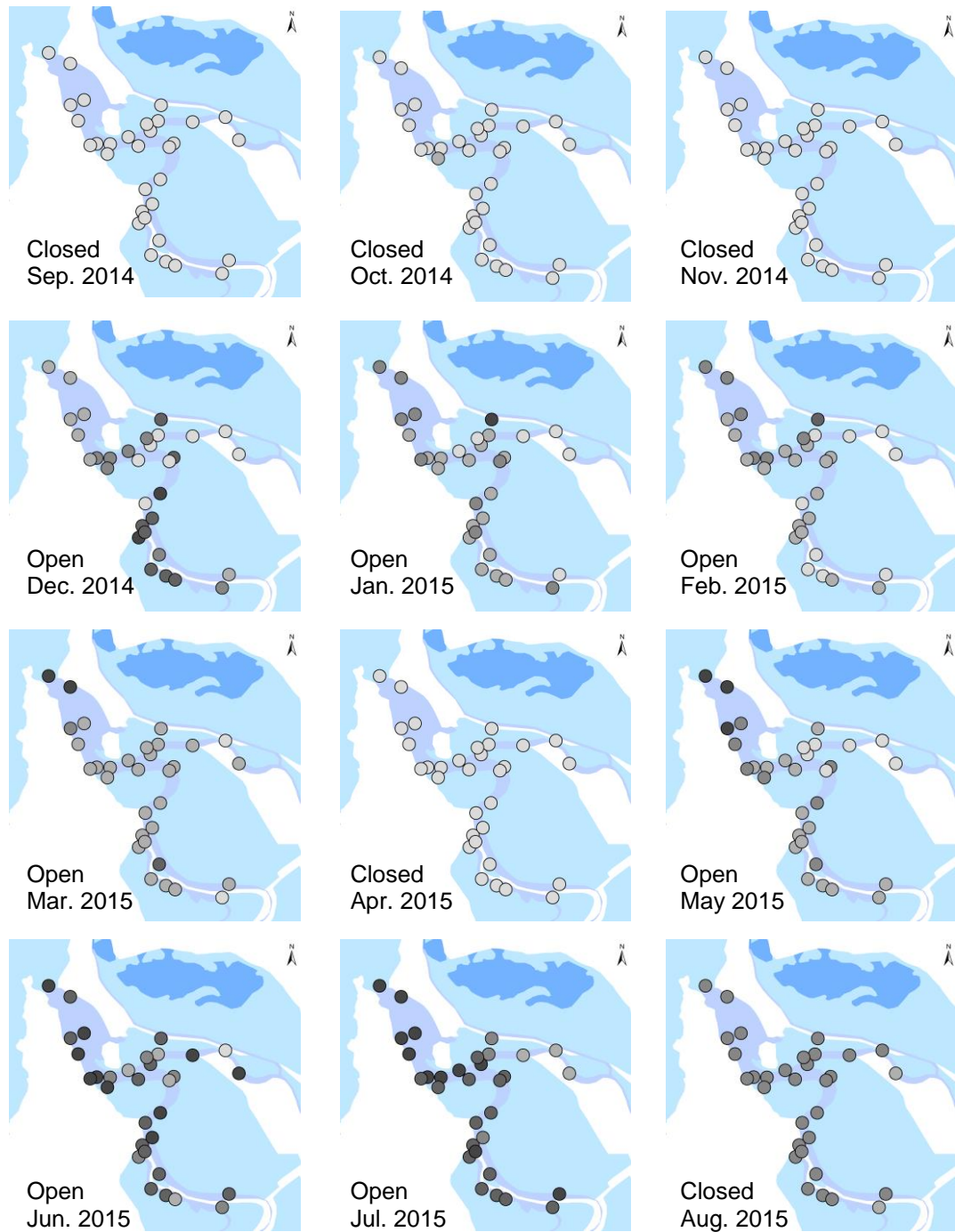
Figure 1.6. A spatio-temporal evolution of water sulfate concentration (mM) measured at thirty-two sites in the Pescadero Estuary in 2014-2015. The estuary was closed in September-November 2014 and April 2015.

consistently exhibited low spatial variability, while the Butano Creek and Sandbar Lagoon sites
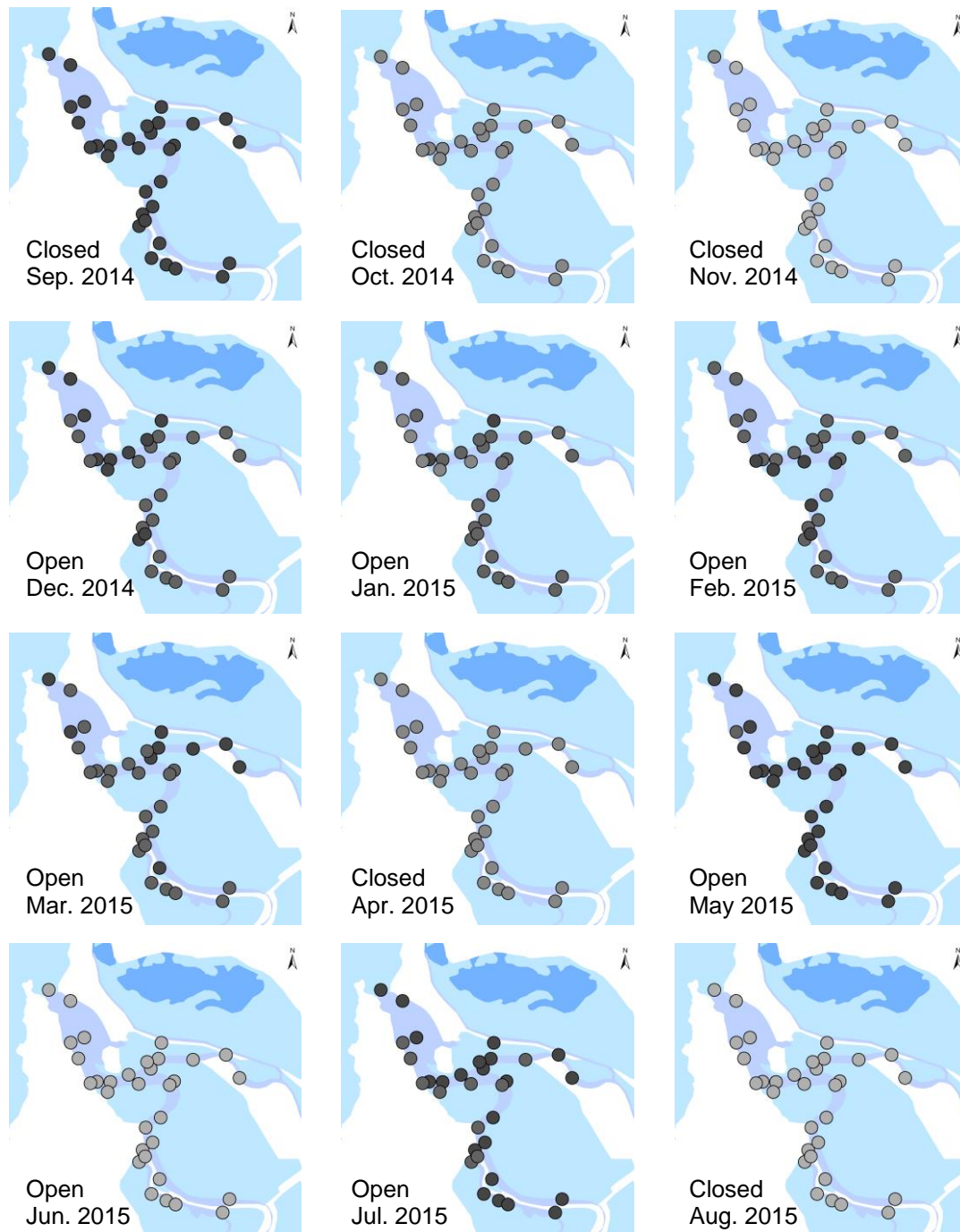
Figure 1.7. A spatio-temporal evolution of water hydrogen sulfide concentration (μM) measured thirty-two sites in the Pescadero Estuary in 2014-2015. The estuary was closed in September-November 2014 and April 2015.

Hydrogen sulfide
○ 0.1-2 μM
◔ 2-4 μM
◑ 4-6 μM
◕ 6-8 μM
● 8-12 μM

Estuarine Channel
Estuarine Wetland
Pacific Ocean
North Marsh

exhibited high spatial variability (Table 1.2).
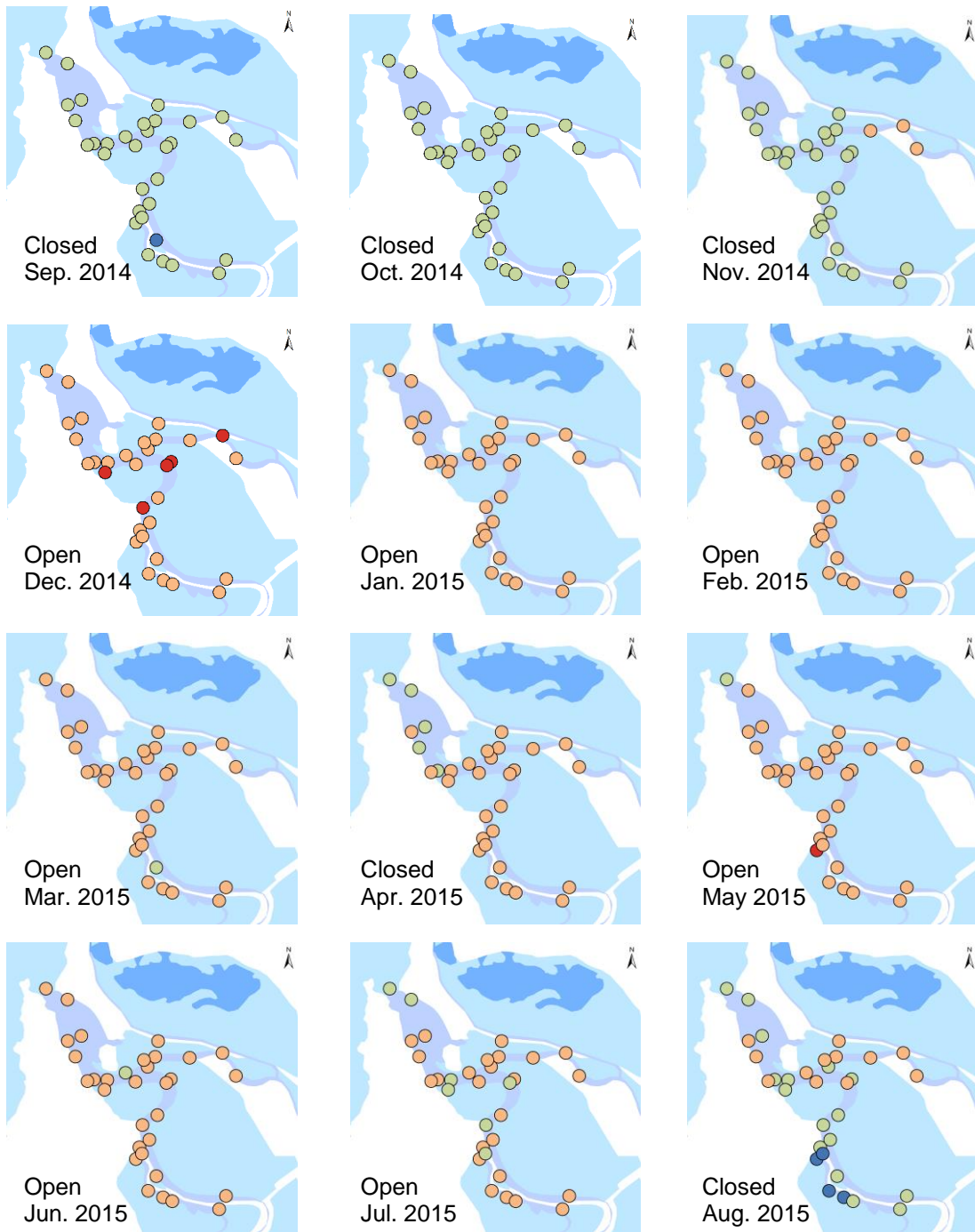
Figure 1.8. A spatio-temporal evolution of water pH measured at thirty-two sites in the Pescadero Estuary in 2014-2015. The estuary was closed in September-November 2014 and April 2015.

Water pH
- 🔴 6-7
- 🟠 7-8
- 🟢 8-9
- 🔵 9-10

- Estuarine Channel
- Estuarine Wetland
- Pacific Ocean
- North Marsh

Sediment pH values generally showed slightly lower values in the Butano Creek and River
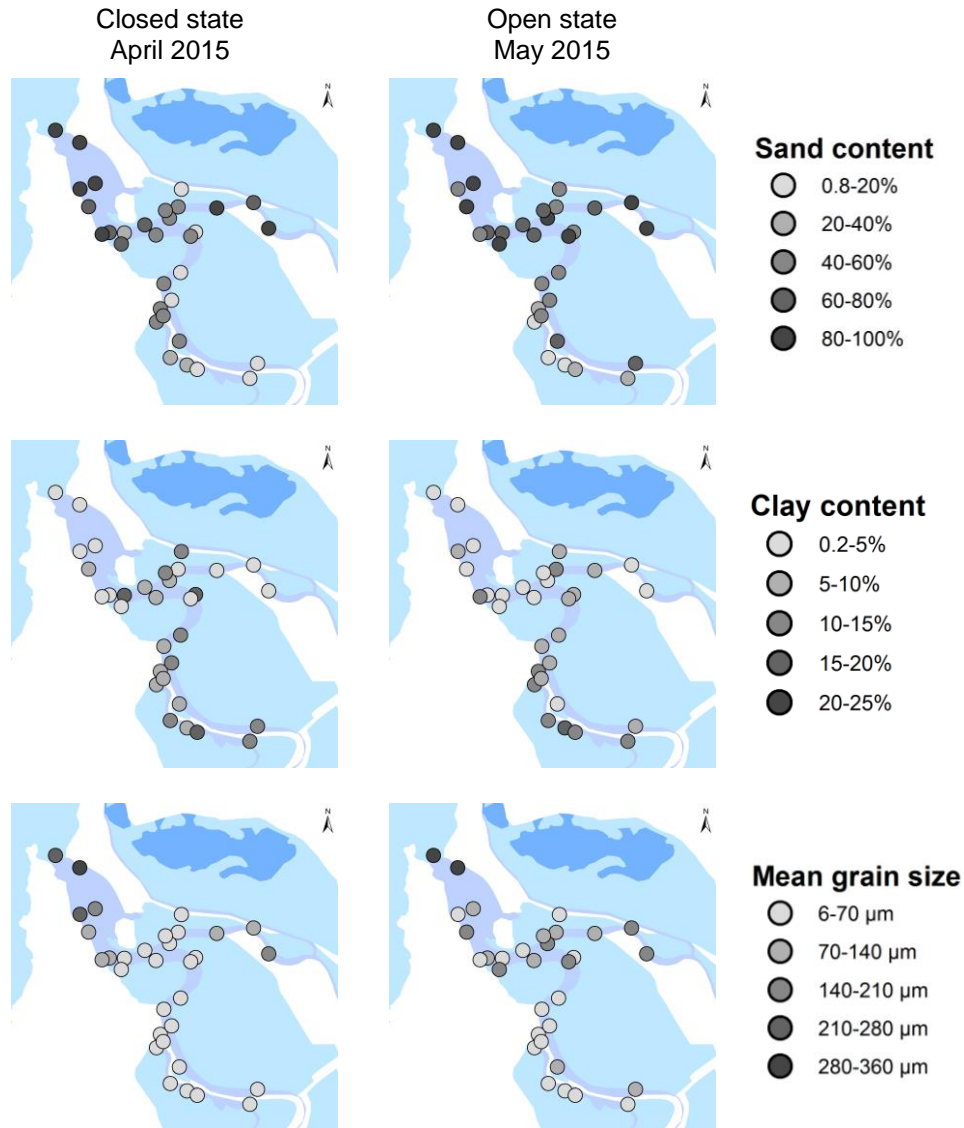
Figure 1.9. Geospatial images of sand content, clay content, and mean grain size as measured in the closed state (April 2015) and open state (May 2015). Particle size distributions were measured monthly at all thirty-two sites; however, one point representative of each state is shown here.

Confluence sites in the closed state than in other regions (Figure 1.12). Contrary to water pH, sediment pH showed spatial variation throughout the estuary with slightly to moderately alkaline (7.7-8.0) values in 2014 and low spatial variability at the Pescadero Creek and Sandbar Lagoon sites (Table 1.2). However, a month after the estuary re-opened in January 2015, sediment pH sharply dropped to strongly acidic to circumneutral values (5.0-7.5) in the Sandbar Lagoon and Pescadero Creek regions, with overall higher spatial variability than at the other sites (Figure 1.12). The same sharp decrease in pH was observed in June 2015 after a shorter closed period, however,

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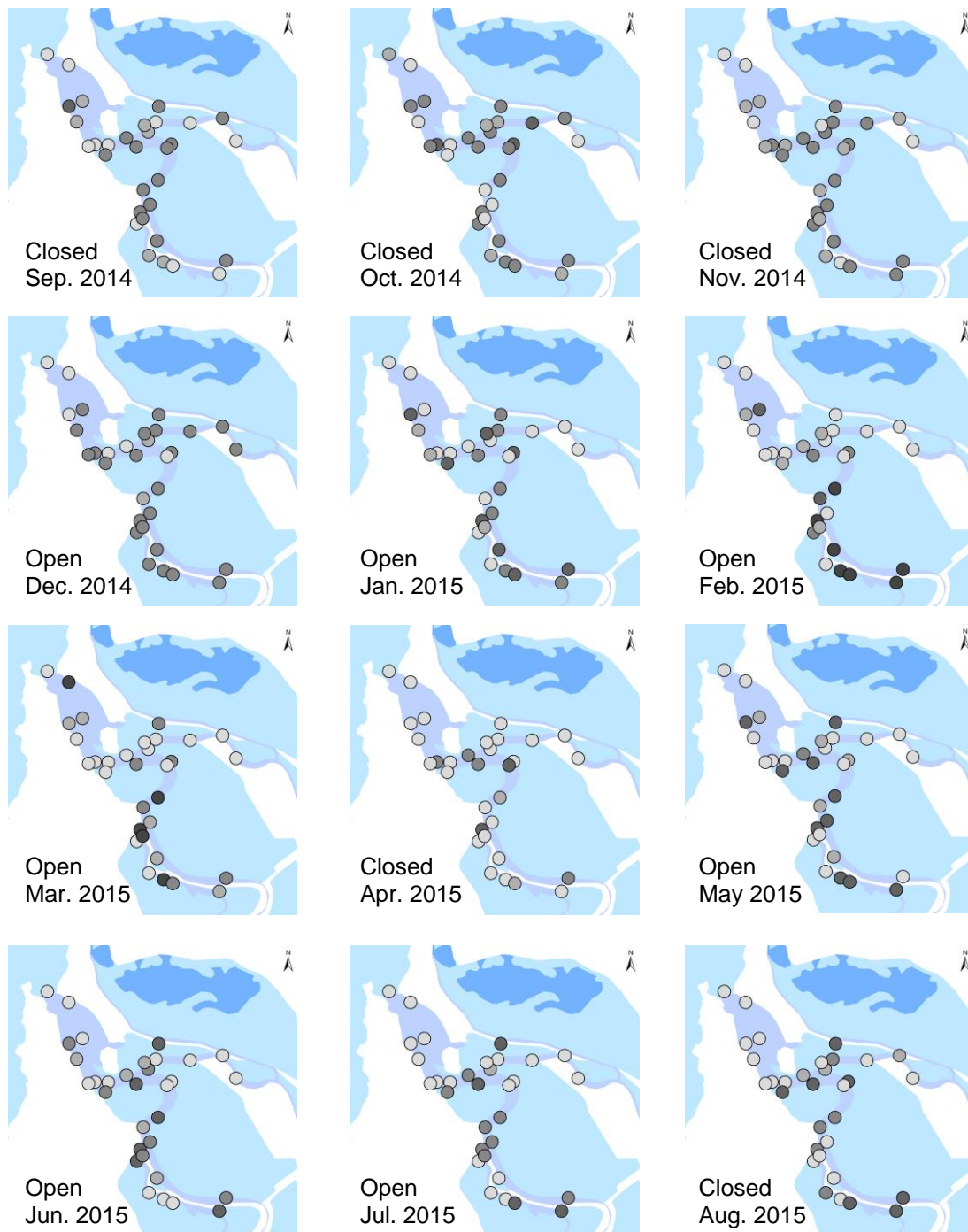
Figure 1.10. A spatio-temporal evolution of sediment AVS content (mmol kg^{-1}) measured at thirty-two sites in the Pescadero Estuary in 2014-2015.

Acid-volatile sulfide
- 0.1-10 mmol/kg
- 10-20 mmol/kg
- 20-30 mmol/kg
- 30-40 mmol/kg
- 40-50 mmol/kg

- Estuarine Channel
- Estuarine Wetland
- Pacific Ocean
- North Marsh

with the lowest values observed at the River Confluence and Delta Marsh sites. Total sediment
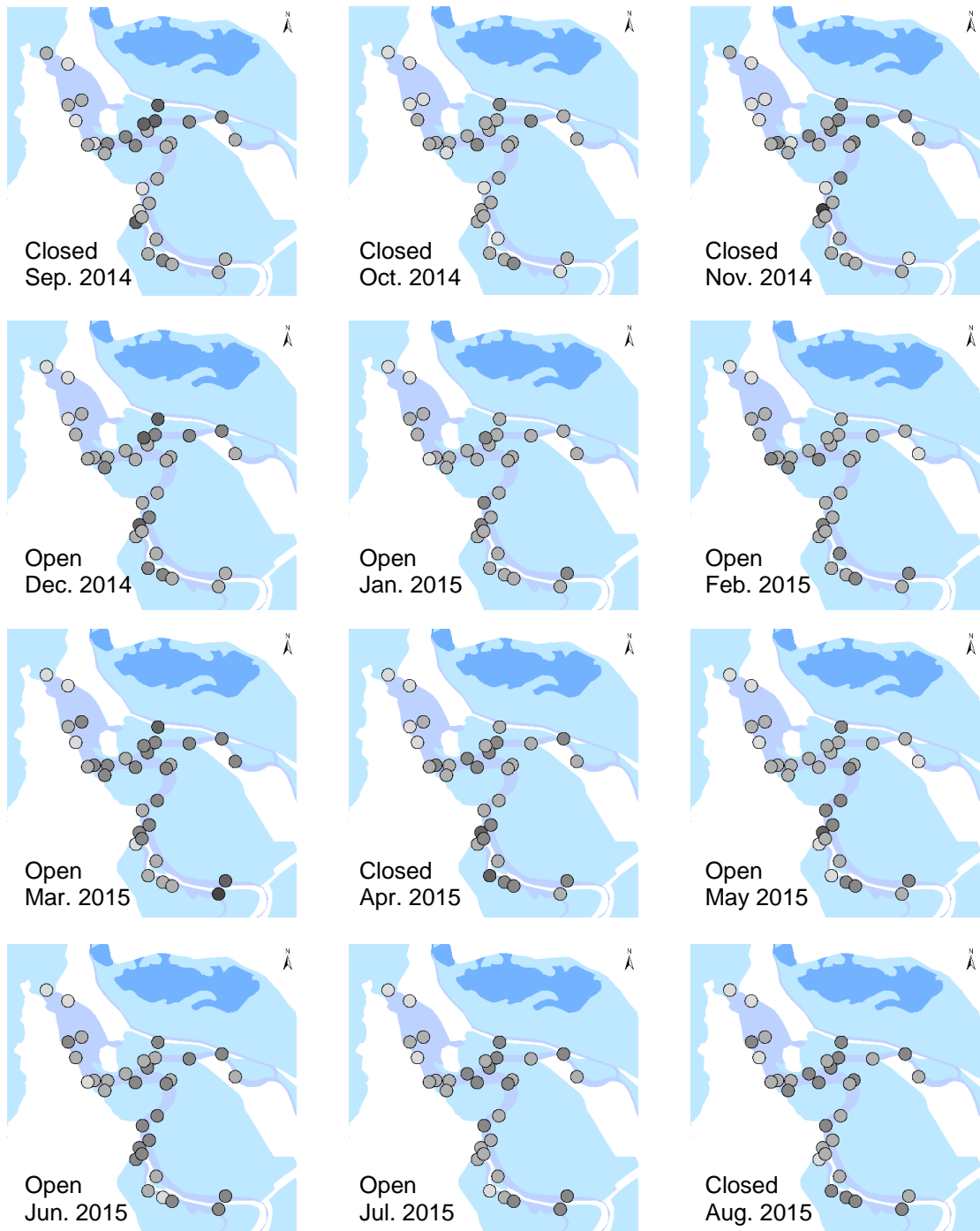
Figure 1.11. A spatio-temporal evolution of sediment iron content (mmol kg^{-1}) measured at thirty-two sites in the Pescadero Estuary in 2014-2015.

Total iron

- ◯ 4-35 mmol/kg
- ◔ 35-70 mmol/kg
- ◕ 70-105 mmol/kg
- ◕ 105-140 mmol/kg
- ● 140-180 mmol/kg

Estuarine Channel
Estuarine Wetland
Pacific Ocean
North Marsh
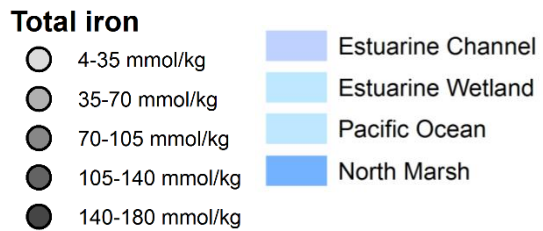
organic carbon and nitrogen contents exhibited consistently higher values (>3% and >0.2%) at the
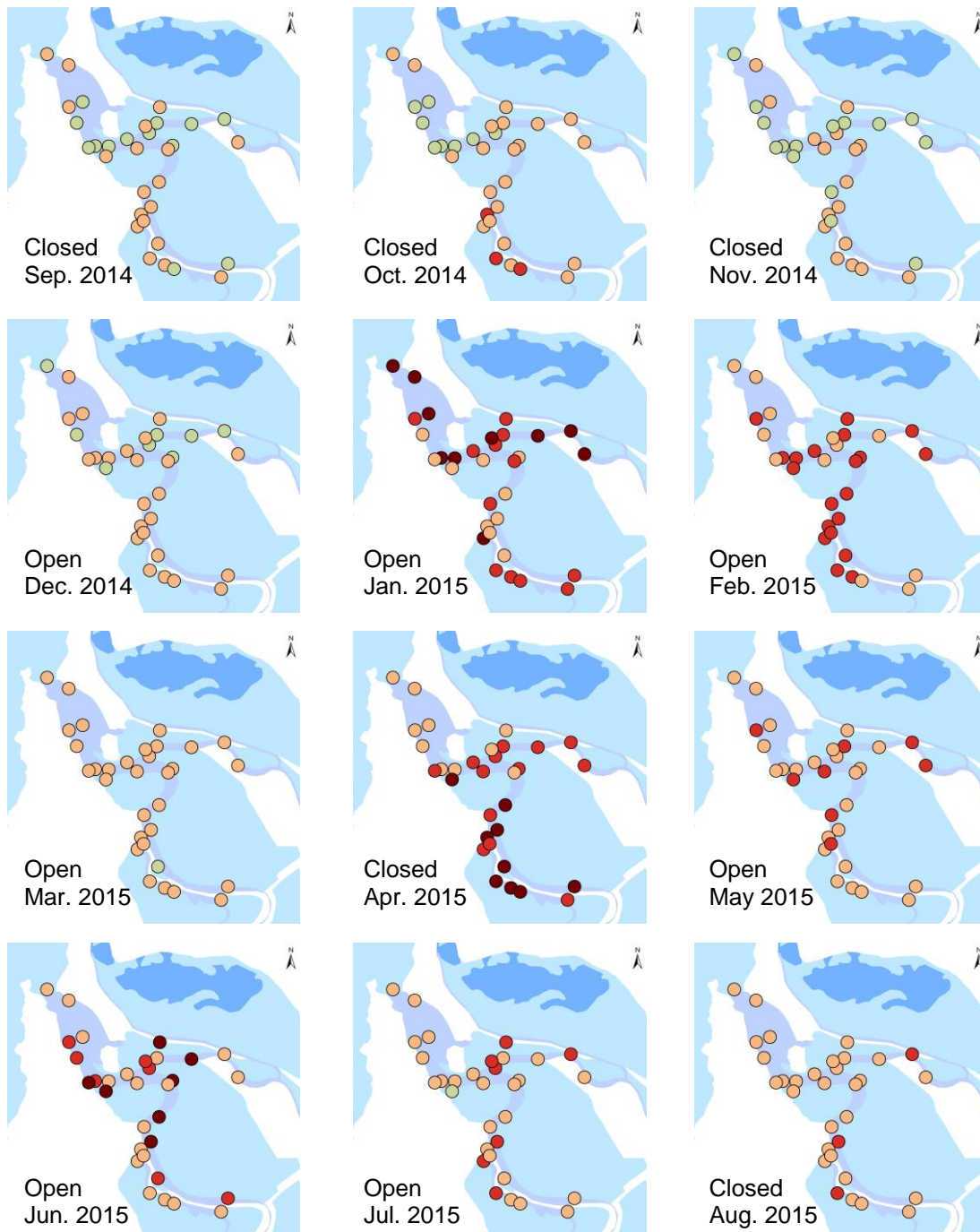
Figure 1.12. A spatio-temporal evolution of sediment pH measured at thirty-two sites in the Pescadero Estuary in 2014-2015.

Sediment pH
- 4.9-6
- 6-7
- 7-8
- 8-9

- Estuarine Channel
- Estuarine Wetland
- Pacific Ocean
- North Marsh

Butano Creek sites, where the highest spatial and temporal variability were also observed (Figure
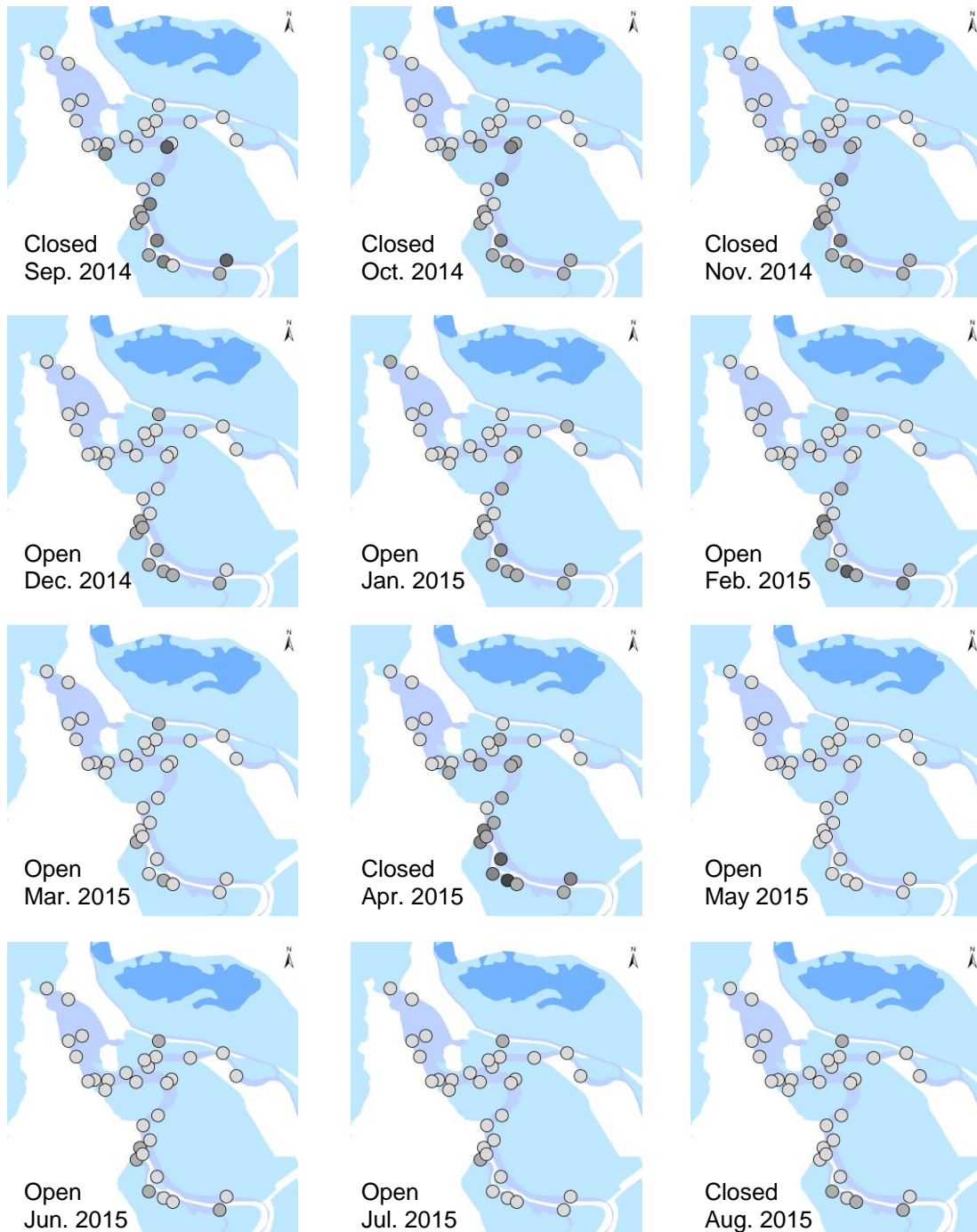
Figure 1.13. A spatio-temporal evolution of sediment organic carbon content (%) measured at thirty-two sites in the Pescadero Estuary in 2014-2015.

1.13). Conversely, the Pescadero Creek and Sandbar Lagoon sites comprised of low total carbon

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contents (<1%) and nitrogen contents (<0.01%), both with low spatial variability (Table 1.2).

Altogether, sediments from the Pescadero Creek sites are sandy loams with low clay contents (5.5±2.7%) and silt contents (25.0±10.2%) characterized by low AVS contents (8.8±5.6 mmol kg^{-1}), high iron contents (65.8±12.7 mmol kg^{-1}), low organic carbon contents (0.9±0.7%), and low nitrogen contents (0.08±0.04%). Furthermore, Sandbar Lagoon sites are comprised similarly, as sand and sandy loam sediments with low AVS contents (9.0±9.8 mmol kg^{-1}), yet lower iron, organic carbon, and nitrogen contents than the Pescadero Creek sites. Conversely, the Butano Creek and Marsh and River Confluence sites are categorized as sandy loams and silt loams with higher AVS, iron, organic carbon, and nitrogen contents than the Pescadero Creek sites.

4. Discussion

4.1. Temporal differences of geochemical conditions in the Pescadero Estuary

The three closed states were characterized by similar water characteristics that contrast with the open state conditions. Those include alkaline pH, as well as mildly brackish salinity, high chloride to sulfate ratios (>25), low average concentrations of sulfate (<5.9 mM), hydrogen sulfide (<5.3 µM), and chloride (<167 mM), but high average concentrations of total iron (>5.5 µM), DIC (>36.3 ppm), and DOC (>5.6 ppm). In contrast, no specific set of sediment variables characterized the closed or open states, even as sediment conditions varied over time.

The salinity and chloride concentrations in Pescadero water were characteristic of bar-built estuaries, with mildly brackish conditions in the closed states and moderately to strongly brackish conditions in the open states. The difference is due to the absence of mixing with marine saline water and rainfall dilutions in the closed state, whereas mixing between estuarine water and ocean saline water occurs in the open state. The lower salinity and sulfate and chloride concentrations observed in the estuary in the April 2015 closed state were due to dilution by the late periods of intermittent rainfall (Figure 1.2a).

The alkaline pH, low sulfate concentrations, and high DIC concentrations in water consistently observed in the closed states indicate that microbial sulfate reduction, which consumes sulfate, produces hydrogen sulfide and causes basification (Hines et al., 1989; Duarte et al., 2013) could be an important process in Pescadero sediment. Low concentrations of competing terminal electron acceptors, such as DO (Largier et al., 2015), nitrate (Laverman et al., 2012), and iron oxides (Bostick et al., 2004; Richards and Pallud, 2016) support this hypothesis. The decrease in aqueous hydrogen sulfide concentrations observed consistently in the three closed states suggests that the hydrogen sulfide precipitates in sediment as metal sulfides and/or is chemically converted from aqueous to gaseous form as water pH shifts to circumneutral values. Concentrations of sulfate, dissolved oxygen (DO), and aqueous metals, as well as organic matter content, and pH in water and sediment all directly control hydrogen sulfide concentrations in water. In contrast, I observed an increase in aqueous total iron concentrations, suggesting that while iron reduction occurs in parallel with sulfate reduction in the closed state, as observed elsewhere (Sørensen, 1982; Thamdrup et al., 1994), sulfate reduction and organic matter oxidation may be the rate-limiting steps in forming sulfide precipitates (Berner, 1984; Morse et al., 1987; Schoonen, 2004). The

elevated DIC concentrations observed in the closed state also corroborate the hypothesis, as it suggests the presence of carbon dioxide and carbonates, the latter being products of anaerobic respiration processes under anoxic conditions (Canfield and Des Marais, 1993). Sediment organic carbon and nitrogen contents were nearly twice as large in the closed state due to increases in vegetative organic matter (Thornton and McManus, 1994) than in the open state, in which organic matter is derived from fresh, labile phytoplankton biomass (Cloern et al., 2002).

The molar ratio of chloride concentration to sulfate concentration (Cl^-/SO_4^{2-}) reflects the relative importance of reduction and oxidation of sulfur (Hines et al., 1989), in which higher values generally indicate a predominance for reduction of sulfate and lower values indicate a predominance for oxidation of metal sulfides to sulfate. Rainfall, tidal flushing, and evaporation should input both chloride and sulfate equally into the system, therefore the ratio should be unaffected by these factors. The higher Cl^-/SO_4^{2-} ratios (>25) observed in the 2014 closed state and in the September 2015 closed state (Figure 1.3) can be attributed to anoxia, as observed here (Jankovitz, 2015) and elsewhere (Becker et al., 2009), and higher potentials for sulfate reduction (Richards and Pallud, 2016). However in the short April 2015 closed state, the lower ratios are controlled by oxic water conditions, despite decreased mixing and potentially higher sulfate reduction rates than in the open state (Richards and Pallud, 2016).

The transitions from closed to open state were characterized by increases in water hydrogen sulfide concentrations, decreases in water pH, decreases in chloride to sulfate ratio, and slow decreases in sediment pH. The extent of those changes was proportional to the length of the closed state that preceded the transitions. During the transition from closed to open state, a rapid re-suspension of sediment into the water column occurs due to increased infragravity motions and tidal flows (Williams and Stacey, 2015). This sediment re-suspension leads to a mixing of sediment pore water and overlying water column, and consequently, to a sharp increase in aqueous hydrogen sulfide concentrations, despite low release rates of hydrogen sulfide from sediment to water (Richards and Pallud, 2016). This rapid sediment re-suspension at Pescadero also leads to oxidation sediment metal sulfides, which explains the observed decrease in water pH, similarly to what has been observed here and elsewhere (Powell and Martens, 2005; Johnston et al., 2009). Furthermore, the increase in iron concentration in the first transitional period indicates that the oxidation effects resulting in acidification also lead to increased metal dissolution, as observed elsewhere (Du Laing et al., 2009). The lower iron concentrations observed in the second transitional period may be due to mildly alkaline water pH values and oxic conditions, where insoluble iron oxides predominate (Byrne and Kester, 1976; DeLaune and Patrick, Jr., 1981). Furthermore, decreased water pH values and increased sulfate concentrations observed in the transitions from closed to open states could also be the result of the oxidation of hydrogen sulfide and metal sulfides, but this is hard to separate from the effects of the influx of sulfate-rich water into the estuary. The first transition from closed to open state was characterized by decreased chloride to sulfate ratios (from 26 to 18) due to increased chloride concentrations, lower potentials for sulfate reduction, and higher potentials for sulfide oxidation. Conversely in the second transitional period, I observe an increase in ratio (from <10 to 16) because the April 2015 closed state had higher sulfate concentrations coupled with higher water temperatures, and subsequently higher evaporation and lower water levels (Williams and Stacey, 2015), which are also both suggestive of potentially high oxidation rates of metal sulfides.

Tidally-driven sediment re-suspension that occur in the open state seem to drive the conditions observed in the overlying water. The mildly acidic and circumneutral water pH values observed in the open state reflect the mixing between alkaline marine water and acidic sulfide-rich sediments. The elevated aqueous dissolved oxygen concentrations measured in the open state result from the daily tidal flushing of estuarine water, as observed elsewhere on small bar-built systems (Taljaard et al., 2009; Whitfield et al., 2012). Chloride to sulfate ratios generally varied around that of seawater (~19.4) due to the predominance of oxidation over reduction (Williams and Stacey, 2015). However, sulfate and chloride concentrations, salinity, and chloride to sulfate ratios measured in the first open state (December-March) were lower than those of the second open state (May-July) and lower than marine values, which may be attributed to lower influxes of marine water into the estuarine system, due to shallow water levels in December-March than in May-July. The lack of precipitation combined with higher air and water temperatures resulted in lower water levels across the estuary, which may have been worsened by the California drought that persists throughout 2015 (Mao et al., 2015). Aqueous iron concentrations were also lower (<3.8 µM) in both open states than in the closed states, suggesting that oxidizing conditions in the open state converted iron from aqueous forms (i.e. ferrous iron) to insoluble ferric iron, the latter which has been observed along the Pescadero channels and is supported by the elevated DO concentrations (Jankovitz, 2015).

4.2. Spatial differences of physical and geochemical conditions in the Pescadero Estuary

Compared to the other sites in the estuary, the Pescadero Creek is characterized by mildly alkaline, cooler water with lower sulfate (7.5±3.0 mM), chloride (142.8±59.2 mM), and total iron (4.0±1.2 µM) concentrations, salinity (6.5±4.8‰), and molar chloride to sulfate ratios (15.4±2.1) (Supp. Figure 1.15). This spatial analysis suggest that potential sulfate reduction and sulfide precipitation rates may be severely limited in the Pescadero Creek by lower sulfate and iron concentrations, cooler temperatures, and the predominance of oxidation over reduction. Average hydrogen sulfide, DIC, and DOC concentrations and pH were consistently similar (6.2-6.4 µM, 28-33 ppm, 2.8-4.1 ppm, and 7.7-7.9) across all sites, indicating no spatial variability for those geochemical conditions.

The results indicate that high sediment AVS contents, and consequently sulfide precipitation, are controlled by both high sediment organic carbon content and iron content, as observed at the Butano and River Confluence regions. This corroborates previous observations on a range of sediments by Berner (1984) and Billon et al. (2001). Sulfide precipitation in the Sandbar Lagoon and Pescadero Creek regions is limited by low organic matter contents, resulting in part from their coarser texture, which can also limit sediment iron content (Morse, 1999). Consequently, the effects of sediment re-suspension, specifically acidification and subsequent metal dissolution into water, are likely to be less severe in the Pescadero Creek and Sandbar Lagoon regions than in the rest of the estuary. The Pescadero Creek showed low spatial variability in its geochemical characteristics, which could indicate it is more chemically stable than the other regions in the Pescadero Estuary.

4.3. Implications of water and sediment conditions for estuarine and fish health

The oxidation of metal sulfides precipitated in sediments upon sediment re-suspension can be coupled with the reduction of oxygen or ferric iron, and can severely affect both water and sediment conditions through deoxygenation, acidification, and metal release to water (Simpson et al., 1998; Schippers and Jørgensen, 2002; Burton et al., 2006; Du Laing et al., 2009). I performed simple calculations of sulfide oxidation in Pescadero sediments to demonstrate its severe consequences on dissolved oxygen concentration and pH. For instance, the oxidation of mackinawite (FeS), a major iron sulfide phase at Pescadero (Bostick et al., 2004) is:

$$FeS\ (s) + 9/4\ O_2 + 5/2\ H_2O \rightarrow Fe(OH)_3 + SO_4^{2-} + 2H^+ \qquad (R1).$$
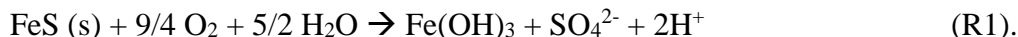
At an average Pescadero concentration of 10 mmol FeS kg^{-1} sediment, FeS requires 2.25 moles of dissolved oxygen and produces 2 moles of protons. Considering oxic conditions (DO concentration = 10 ppm), a kilogram of mackinawite-rich sediment would deplete 32 L of oxic pore water and potentially convert the sediment environment to extremely acidic (pH<1). Therefore, the highest concentration of mackinawite (such as 72 mmol FeS kg^{-1} sediment using the maximum Fe content) would deplete a larger volume of oxic water (~231 L) with the same final pH as above, whereas under suboxic conditions (DO ~ 4 ppm) and 72 mmol FeS kg^{-1} sediment, even larger volumes of water (~576 L) would be depleted of oxygen. These assumptions disregard ferric iron as a terminal electron acceptor and sulfate reduction, both of which occur in the open state and can further lower water and sediment pH and increase metal dissolution, respectively (Luther et al., 1992; Bottrell et al., 2000; Richards and Pallud, 2016).

The conditions observed here in the open state, specifically as gauged by dissolved oxygen (6.9±1.1 µM), hydrogen sulfide (7.3±0.4 µM), and iron (3.8±2.7 µM) concentrations and slightly alkaline pH (7.6±0.3), are highly variable compared to the water conditions in estuaries affected by fish kills (Allanson, 2001; Luther et al., 2004; Becker et al., 2009; Wong et al., 2010). Fish mass mortalities often occur after extended closed periods of an estuary lacking in freshwater inflows (Whitfield, 2005); however, the results cannot confirm if limited inflows (Sloan, 2006) and prolonged closed state periods (Volpi, 2014) directly result in hypoxic or anoxic conditions at Pescadero. In contrast, I observe oxic conditions in the open state, whereas Becker et al. (2009) observed hypoxic and anoxic conditions (<5 mg L^{-1}) in the water column for six days following an artificial opening of a southern Australian bar-built estuary, leading to exposed sediment and a major kill. Similarly, Wong et al. (2010) measured hypoxic conditions (<4 mg L^{-1}) and also mildly acidic to alkaline water pH (6.0-7.9) and high aqueous iron concentrations (1.4-48.3 µM) in marshland floodwaters as the Richmond River Estuary (eastern Australia) drained its sulfide-rich sediments following a flood event. These pH values are consistent with the values observed here, whereas their aqueous iron concentrations are up to an order of magnitude larger. Sammut et al. (1996) observed low pH values (1.8-7.2) resulting from the oxidation of sediment sulfides in Australian metal-rich waters during and following severe floods; the circumneutral pH values are higher by 0.2-6.9 units. Additionally, observed hydrogen sulfide concentrations in the KwaZulu-Natal Estuary (South Africa) ranged up to 294 µM in bottom water (Allanson, 2001) and are two orders of magnitude larger than observed here. In contrast, the DO (1.6-5.7 mg L^{-1}) and hydrogen sulfide concentrations (3-10 µM) and circumneutral pH (6.5-7.7) reported by Luther et al. (2004)

following a 2000 fish kill in Delaware bays (USA) are closely aligned with these values. In agreement with Sammut et al. (1996), I can conclude that fish deaths globally are directly linked to a range of poor geochemical conditions in water and sediment that are indirectly driven by physical (i.e. rainfall and flooding) events in bar-built estuaries globally.

The results show that many water indicators reach values that are beyond optimal for fish or aquatic life. Temperatures in late summer months (September 2014, July-August 2015) exceeded tolerable conditions for anadromous fish (<21 °C) (Stenhouse et al., 2012), indicating a decline in water conditions. Hypoxic (<5 mg L^{-1} dissolved oxygen) water was observed in the summer months of 2015, whereas the tolerable water conditions for a variety of anadromous fish are defined as oxic (>5 mg L^{-1} dissolved oxygen) (Barton, 1996; Bagarinao and Lantin-Olaguer, 1998). I observed many smaller steelhead trout jumping out of the water between June and August 2015 in the open state, possibly in reaction to the low DO levels in water. Mildly acidic conditions were observed in Pescadero water following the transitions from closed to open state, which is lower than the permissible limits of 6.5-8.5 for a variety of anadromous fish (Barton, 1996; Bagarinao and Lantin-Olaguer, 1998). Consequently, I show that poor water conditions encompass, more specifically, warm (>21°C), moderately acidic (<6.5) water with hydrogen sulfide (>0.06 µM) concentrations that exceed the chronic water quality concentrations. Moreover, aqueous hydrogen sulfide concentrations far exceeded the chronic water quality recommended concentration for aquatic life (0.06 µM; US-EPA, 2016) over the entire sampling campaign. Hydrogen sulfide is directly toxic to fish by inhibiting their enzymatic activity and physiological function, leading to asphyxiation, reproductive disturbances, disease, and mortality (Oseid and Smith, 1974; Bagarinao, 1992; Bagarinao and Lantin-Olaguer, 1998). Higher aqueous hydrogen sulfide concentrations (>4 µM) and slightly lower water pH values observed in the open state than the closed state indicate that water conditions are potentially more severe for steelhead trout in the open state.

The sediment AVS and iron contents are non-bioavailable and non-toxic for invertebrates compared to aqueous hydrogen sulfide or iron concentrations (Di Toro et al., 1992; Allen et al., 1993; Wang and Chapman, 1999). However, the high silt and clay contents (41-61%) observed in the Butano Creek and River Confluence regions, may also be partly responsible for fish deaths. These implications are consistent with Newcombe and Jensen (1996), who concluded that fine suspended sediment can be easily ingested, triggering fish cell and tissue damage inside the body. In contrary, Servizi and Martens (1991) suggested that the lethal tolerance of coho salmon to suspended sediments decreases as the average particle size of suspended sediments increases, due to increased difficulties in clearing larger particles from the gills. These conflicting results suggest that all sediment particle sizes are physical deleterious for fish. Furthermore, sediment grain size distribution is a significant factor influencing sediment metal concentrations and absorptive capacities of clay sediments compared to their sand counterparts (Chapman and Wang, 2001). Sediment metal concentrations indirect control aqueous metal concentrations through dissolution, precipitation, and therefore influencing water quality for fish.

5. Conclusions

The result show that the transition from closed to open state leads to poor water conditions, specifically low pH driven by the indirect, oxidative effects of aqueous hydrogen sulfide and sediment metal sulfide precipitates. While low dissolved oxygen concentrations are also an indirect effect of sulfide oxidation, I do not observe this here in the transitional period. In contrast, aqueous hydrogen sulfide concentrations are significantly higher than the recommended levels for aquatic life, however do not significantly worsen in the transition between states during which fish kills are observed.

The results also show that not all the estuary is similarly affected and that the Northern tributary, Pescadero Creek, is characterized by a slight decline in water conditions than the rest of the estuary. The Pescadero Creek region maintains significantly lower sulfate concentrations, AVS contents, and organic matter contents, and, as a result, is more chemically stable as the geochemical effects of sulfate reduction, sulfide precipitation, and sulfide re-oxidation, are minimal compared to the rest of the Pescadero Estuary. However, the higher AVS contents observed in the River Confluence and Butano Creek regions can result in severe acidification and metal release to water if re-oxidized during sediment resuspension events.

The recent cyclic effects of El Niño/Southern Oscillation (ENSO) phenomena along the Pacific Coast have altered precipitation and wave events, and more specifically the timing and magnitude of closed and open state (Behrens et al., 2013). The natural, rainfall-influenced re-opening of the Pescadero Estuary has occurred more frequently ($\geq$3 times per year) in the last six years than prior to 2010, during which the re-opening averaged once per year (Sloan, 2006; Volpi, 2014; Richards and Pallud, 2016). Drought and decreased rainfall events are predicted to lower the timing and frequencies of river flow, tidal flushing, and other sediment re-suspension events, leading to slightly alkaline, warm (>21 °C), water with mildly to moderately brackish (16-24‰) salinities, moderately oxic (5.5-8.5 mg L^{-1}) levels, and high sulfate (>11 mM) concentrations, as observed here in the summer open state period.

Furthermore, with the onset of climate-induced factors, specifically increases in water and air temperatures observed here, atmospheric carbon dioxide, and ocean acidification, estuarine water at the sediment interface may become more oxygen-depleted, leading to higher potential sulfate reduction rates and subsequent more acidic waters in the open state than currently observed here. Constriction by a cliff structure at the estuary's mouth as coupled with sea level rise may constrict re-opening, drainage, and flushing, as observed at Pescadero (Williams and Stacey, 2015) and in other North American estuaries (Geyer, 1997; Wong et al., 2010), so the direct and indirect effects of changing hydrodynamics on fish may not be as severe in the future. However, increased rainfall events and storm surges may increase the frequency of mouth re-openings and increase sediment re-suspension, as observed elsewhere (Gillanders et al., 2011), therefore worsening water conditions, health of steelhead trout, and generally the overall state of Pescadero Estuary. Despite limiting closure periods and increasing flushing, increased opening events may also worsen water conditions, proving it difficult to potentially save steelhead trout from the indirect effects of sulfide re-oxidation at Pescadero.

6. Acknowledgements

7. References

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Supplementary Figure 1.14. A spatio-temporal evolution of salinity measured at thirty-two sites in the Pescadero Estuary in 2014-2015.

Salinity
- 0.5-7‰
- 7-14‰
- 14-21‰
- 21-28‰
- 28-35‰

Estuarine Channel
Estuarine Wetland
Pacific Ocean
North Marsh
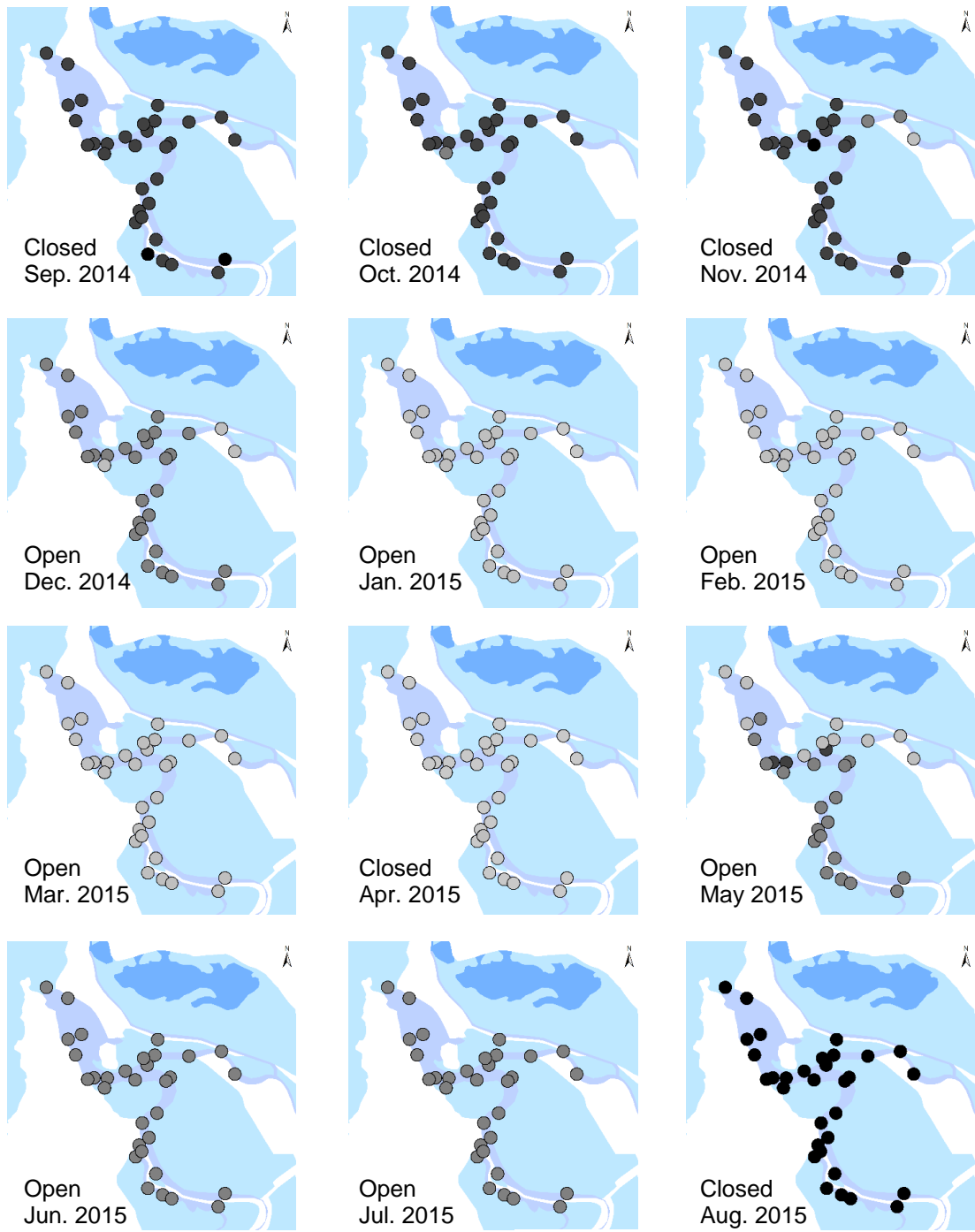
Supplementary Figure 1.15. A spatio-temporal evolution of molar chloride to sulfate ratios calculated for the thirty-two sites across the Pescadero Estuary in 2014-2015.

Cl^-/SO_4^{2-} ratio

- 0-8
- 8-16
- 16-24
- 24-32
- 32-40

Estuarine Channel
Estuarine Wetland
Pacific Ocean
North Marsh

Chapter 2

The predominance of sulfur geochemical redox cycling in a northern California bar-built estuary (Pescadero, CA)

Abstract – Bar-built estuaries are coastal watersheds that are defined by their physical characteristics, or more specifically, a sandbar barrier at the mouth of the estuary, which is reopened to the ocean with heavy rainfall, flooding, and tides. The transitional period from closed to open state has considerable impacts on physical conditions in the estuary, which through tidal mixing and sediment resuspension, can strongly affect geochemical conditions of sulfur and iron constituents in sediment and sediment pore water, worsen water quality, and cause fish mortality events. In the bar-built Pescadero Estuary (CA), near-annual fish mortality events are suspected to result from the oxidation of acid-volatile sulfides (AVS), whose direct effects lead to acidification and metal release in sediment pore water and the surrounding environment. I investigated the spatial and temporal evolution of sediment pore water to determine the dominant respiration processes in Pescadero sediment and understand the biogeochemical effects of redox cycling on pH. Using diffusion chambers containing anoxic water, I measured sediment pore water concentrations (including sulfate, hydrogen sulfide, and iron concentrations) at four Pescadero sites representing a gradient from ocean to freshwater in the closed state and open state. The pore water profiles exhibited the presence of sulfate, hydrogen sulfide, and ferrous iron and absence of nitrate, which is indicative of suboxic, reducing conditions. The predominance of hydrogen sulfide over ferrous iron implies that microbial sulfate reduction is the dominant anaerobic respiration pathway. This is in conflict with the redox tower, in which iron reduction predominates before sulfate reduction. The microbial and abiotic reduction of ferric iron oxides is shown to be mediated by hydrogen sulfide and/or sulfate-reducing bacteria to form ferrous iron and iron sulfide precipitates in sediment. The effects of sulfur and iron cycling on pH are two-fold: first, reductive processes cause basification, leading to circumneutral to mildly alkaline pH, and secondly, the oxidation of iron sulfides can cause acidification to significantly lower pH values than the oxidation of aqueous hydrogen sulfides can. However, the oxidative effects of iron sulfide precipitates are minimal in pore water due to mixing with alkaline marine water and buffering by DIC. Dominant in Pescadero Estuary sediments, the re-cycling of sulfur controls both iron cycling and the production of iron sulfide precipitates, whose effects on pH are minimal across a range of fine- and coarse-grained sediments with varying AVS contents.

1. Introduction

Located at the interface between terrestrial, freshwater, and marine ecosystems, bar-built estuaries are productive ecosystems characterized by the aperiodic formation of a sandbar at the estuary's mouth, separating it from the ocean during periods of low rainfall (Haines et al., 2006; McKenzie et al., 2011). Bar-built estuaries are universal: they are prevalent in Australia (Griffiths and West, 1999; Roy et al., 2001), South Africa (Largier and Taljaard, 1991; Whitfield et al.,

2012), and North America (Behrens et al., 2013). Representing over 50% of estuaries along the conterminous West Coast (Emmett et al., 2000), these estuaries often develop in Mediterranean climate environments and wave-dominated coasts with seasonal cycles of drought and precipitation (Roy et al., 2001; Gillanders et al., 2011; Behrens et al., 2013). Bar-built estuaries are defined by their physical structure, specifically the presence or absence of a sandbar barrier at the estuary's mouth (Potter et al., 2010). During the closed state, stratifications of dissolved oxygen and salinity dominate during the lagoon (Largier and Taljaard, 1991; Stanley and Nixon, 1992). Combined with limited mixing, these redox stratifications lead to anoxic or hypoxic (dissolved oxygen concentrations less than 0.2 mM) and highly brackish conditions of the bottom water, in contrast with the oxic, mildly brackish conditions of the surface water (Koretsky et al., 2005). However, with heavy rainfall, flooding, and tides, the sandbar barrier is washed away, transitioning the estuary from closed to open state, where periodic mixing and flushing predominate (Gale et al., 2007; Williams and Stacey, 2015). The two physical states, and the transitional period between them, can have considerable impacts on physical mixing, water quality, and biogeochemical sediment and pore water conditions (Behrens et al., 2013). In recent decades, these intermittent systems have received increased attention globally due to increased contaminations of water and sediment, leading to fish mortality events in intermittent estuaries around the globe, including in Australia (Surrey Estuary: Becker et al., 2009; Richmond River Estuary: Wong et al., 2010), South Africa (Seekoei Estuary: Whitfield, 1995; Mdloti Estuary: Whitfield et al., 2012), and the United States (Pescadero Estuary: Richards and Pallud, 2016).

Bar-built estuaries are sensitive transition zones and vulnerable to fluctuations in geochemical conditions, often due to physical hydrodynamics, seasonal phases, climatic conditions, and/or anthropogenic disturbances (Luther et al., 2004; Eyre et al., 2006; Wong et al., 2010; Kennison and Fong, 2014). In many estuaries and coastal ecosystems, 20-40% of the total processes in anoxic sediments are dominated by microbial sulfate reduction (Al-Raei et al., 2009); the anaerobic, redox process converts sulfate, the innocuous, marine-derived terminal electron acceptor (TEA), to the highly toxic, odorous hydrogen sulfide (Pallud and Van Cappellen, 2006). Microbial sulfate reduction is the predominant anaerobic process coupled to the oxidation of riverine-based dissolved and particulate organic matter substrates, accounting for over than 50% of organic carbon mineralization (Canfield et al., 1993; Koretsky et al., 2005; Weston, Dixon, et al., 2006; Al-Raei et al., 2009). The reduction of competing TEAs, such as nitrate, ferric iron oxides, and manganese oxides, are also thought to be dominant redox processes in bar-built estuaries; however, relative to sulfate, their low concentrations in coastal watersheds indicates that sulfate reduction may predominate (Whitmire and Hamilton, 2005). However, the presence of aqueous reduced species, specifically hydrogen sulfide and ferrous iron, suggests that iron sulfide precipitation in sediment is potentially an important sink for hydrogen sulfides (Rickard and Morse, 2005).

In bar-built estuaries, the transition from closed to open state may result in the sudden resuspension of acid-volatile sulfides and metal sulfides from sediment to water, resulting in elevated hydrogen sulfide and metal concentrations and acidic pH values in the overlying water column (Bush et al., 2004; Burton et al., 2006). These conditions may be attributed to oxidizing conditions, the abundance of sulfide-oxidizing microorganisms, organic matter availability, and ample terminal electron acceptors (i.e. oxygen, iron oxides) (Thouvenot-Korppoo et al., 2012).

During high tide in the open state, the estuary is fully filled, potentially leading to anoxia and anaerobic reductive processes, such as observed in the closed state (Richards and Pallud, 2016). Conversely during low tide, the estuary is full draining, leading to re-oxidation and/or volatilization of hydrogen sulfide and its metal precipitates at the water-sediment interface, as observed elsewhere (Goldhaber, 1997; van Griethuysen et al., 2002; Burton et al., 2006). The transitional period between high and low tide in the open state may also lead to re-suspension of sulfide-rich sediment and its pore water into the water column (Bush et al., 2004; Maddock et al., 2007), thus leading to potentially lower pH and higher metal concentrations in pore water.

Hydrogen sulfide concentrations in water, sediment, and sediment pore water, are rarely measured simultaneously. The geochemical conditions and controls over hydrogen sulfide production of hydrogen sulfide are also important prerequisites to understanding the direct and indirect effects on estuarine ecosystems, ecological communities, and causal reasons for fish die-offs (Tobler et al., 2006). Reflecting the balance between production, consumption, and transport processes, substrate concentrations in sediment pore water allow us to pinpoint dominating TEA processes such as denitrification, iron reduction, sulfate reduction, and methanogenesis (Koretsky et al., 2005; Weston et al., 2006). Moreover, pore water concentrations of hydrogen sulfide are likely significantly greater than their water column counterparts (Kuwabara et al., 1999), indicating that their direct release to the water column, may have severe implications on water conditions and fish habitats by contributing to direct toxicity, indirect oxygen removal, and indirect acidification upon oxidation. Hydrogen sulfide also adversely affects the respiratory and physiological systems of fish. It is lethal for milkfish and tilapia at 30-115 µM after 2-4 hours under hypoxic, acidic conditions (Bagarinao and Lantin-Olaguer, 1998).

The largest intermittent estuary between San Francisco and Santa Cruz, CA, Pescadero Natural Marsh Preserve (Figure 2.1) has been experiencing near-annual fish mortality events since 1995, typically occurring with the breach of the sandbar barrier that separates the estuary from the Pacific Ocean (Swenson, 1999; Smith, 2004; Allen et al., 2006; Sloan, 2006). After a long closure period, the first opening occurred on February 4, 2014, resulting in a major die-off of federally-threatened steelhead trout and other resident fish (E. Huber, personal communication). This open state period was followed by two cycles of closure/opening that tracked rainfall patterns for the remainder of 2014 and throughout 2015. In closed and open states, hydrogen sulfide concentrations and pH in the overlying water ranged 2-9 µM and 5.1-8.6, respectively (Richards and Pallud, 2016), indicating a range of geochemical conditions for microbial sulfur and iron redox cycling.

I investigated the spatial and temporal variability of sediment pore water in intermittent Pescadero Estuary during both the closed and open states to identify dominant anaerobic redox processes and understand how geochemical sulfur redox cycling is controlled and cycles iron, carbon, and protons in sediment. In particular, I measured the pore water concentrations of major geochemical constituents (including sulfate, hydrogen sulfide, and iron concentrations) at four littoral sites along a salinity gradient during both the closed and open states. The results demonstrate that the dominant anaerobic process in Pescadero sediments is microbial sulfate reduction, which is controlled by sulfate and DOC concentrations and produces elevated hydrogen sulfide concentrations in both states. Moreover, through microbial and abiotic pathways, the re-

cycling of sulfur controls the production of ferrous iron and iron sulfide precipitates and shifts in pH toward alkaline or acidic values resulting from reductive or oxidative processes, respectively.
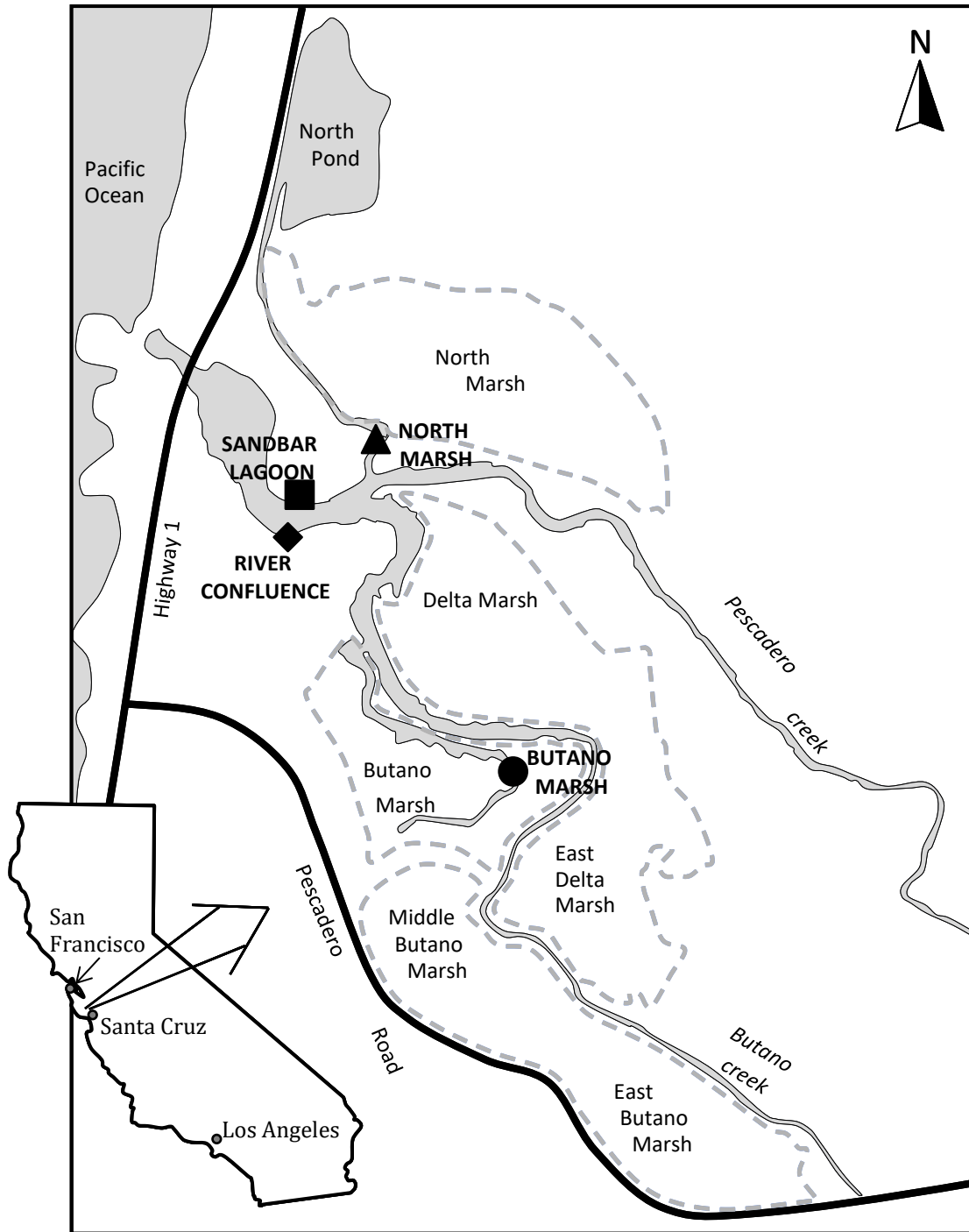
Figure 2.1. Map showing the location of the Pescadero Estuary in California and of the four littoral sites sampled for sediment pore water between November 2014 and November 2015. The sites are comprised of the Sandbar Lagoon (square), North Marsh (triangle), River Confluence (diamond), and Butano Marsh (circle).

2. Materials and Methods

2.1. Study site

I compared pore water profiles at four sites along the littoral zone of the Pescadero Estuary representing a gradient from the most marine region of the system to freshwater tributaries (Figure 2.1). All sites have been affected by fish die-offs during breaching events (transitions from closed to open state) since 1995. Each site was investigated during closed and open states in November 2014 and May 2015, respectively. The estuary was closed for about five months prior to sampling in the closed state and open for one month prior to sampling in the open state. The Sandbar Lagoon site (N37.26330°, W122.40780°) is located directly along the channel adjacent to the marshland and is the closest site to the ocean. The River Confluence site (coordinates: N37.26293°, W122.40913°) is located in a shallow marshy inlet near the separation of the Butano and Pescadero Creeks, and the North Marsh site (N37.26486°, W122.40673°) is located in an inlet adjacent to the North Marsh. The farthest site from the ocean is the Butano Marsh site (N37.25937°, W122.40633°) and is located in the southern channel of the Butano Creek.

2.2. *In situ* pore water sampling

Pore waters were sampled using dialysis samplers (Hesslein, 1976; Mayer, 1976), also known as 'peepers'. The peepers were 36 cm long, 25 cm wide, and 5 cm thick, and included a removable stainless steel handle for easy retrieval and a triangular base to facilitate submersion into wet sediments. They were constructed of low-density polyethylene with 22 equally spaced (0.5 cm intervals) 60-mL chambers ($1\times20\times3$ cm). The chambers were initially filled with deoxygenated, deionized water and covered with a 0.45 µm nitrocellulose membrane and the peepers were kept in anoxic conditions when transported to the field. At each site, a meter near the shoreline, peepers were quickly inserted into the unvegetated part of the sediment to prevent oxygenation and were left to equilibrate with the surrounding pore water for 8-10 weeks. Upon retrieval, the peepers were immediately placed in a N_2-flushed box and transported to the laboratory where they were transferred in a N_2/H_2 (96-4%) glove bag. Pore waters were extracted from the chambers, filtered, and transferred into vials until processing. The peepers were deployed at the four study sites in the Pescadero Estuary in September 2014 (closed state) and March 2015 (open state).

2.3. Overlying water and surface sediment sampling

Overlying water and surface sediment was collected in November 2014 (closed state) and May 2015 (open state) at all four sites. Overlying water was collected one meter below the air-water interface, and surface sediment samples were collected 20-50 cm below the water column. All water and sediment samples were stored at 4°C under anoxic conditions until analyses of geochemical and physical characteristics.

2.4. Pore water analyses

Sulfate (SO_4^{2-}), chloride (Cl^-), and nitrate (NO_3^-) concentrations were measured using an ion chromatograph (Dionex chromatography system, ICS-1000; analytical and guard columns, AS18/AG18) supplied with a hydroxide eluent (27.5 mM NaOH) at a flow rate of 1.0 mL min^{-1}. Hydrogen sulfide (H_2S) concentrations were measured with a pH/ISE electrode (Ionplus Sure-Flow silver/sulfide selective electrode) after mixing 2 mL of pore water with 2 mL of sulfide anti-oxidant buffer (SAOB) trap of 1 M sodium hydroxide (NaOH) and 0.1 M ethylenediaminetetraacetic acid (EDTA). Detection limits for the IC and sulfide electrode were 30 and 0.03 µM, respectively. Dissolved ferrous (Fe^{2+}) and total iron concentrations were measured spectrophotometrically at 562 nm using the ferrozine colorimetric method (Stookey, 1970) after mixing 0.5 mL pore water with 50 µL of water or 1 M hydroxylamine hydrochloride, respectively. Dissolved ferric iron (Fe^{3+}) concentrations were subsequently calculated as the difference of total iron and ferrous iron concentrations. Following 1:4 dilution with water, dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC) were measured using a TOC analyzer (O-I Analytical, Model 1010). Water pH was measured using a pH/ATC electrode (high performance glass-body Sartorius ATC combination electrode) and meter.

2.5. Overlying water and sediment analyses

Overlying water characteristics were measured as mentioned above for concentrations of sulfate, chloride, nitrate, hydrogen sulfide, dissolved iron, DIC, and DOC. Using a method adapted from Simpson et al. (1998) and van Griethuysen et al. (2002), sediment acid-volatile sulfide (AVS) and iron (Fe) contents were extracted from anoxic, dried sediment stirred for two hours with 1 M hydrochloric acid in a sealed extraction chamber with a SAOB trap (described in the previous section) to equilibrate soluble sulfide in the SAOB trap and soluble iron in the acid fraction. Sediment AVS and iron content were measured colorimetrically with the methylene blue method at 670 nm (Simpson, 2001) and the ferrozine method at 562 nm (Stookey, 1970), respectively. Sediment organic carbon and total nitrogen contents were measured using a CE Instruments elemental analyzer on air-dried samples following inorganic carbon removal with 1 mL of 0.5 M $FeSO_4$-H_2SO_4 acid digestion solution over heat.

Mean sediment grain size and sand and clay percentages were determined on 5 g air-dried sediment in 20 mL water, following organic matter and carbonate removal with 20 mL of 35% hydrogen peroxide and 20 mL of 1 M hydrochloric acid, respectively using a LISST-Portable|XR Sequoia Scientific Particle Size Analyzer. Soil texture was determined from sand and clay percentages using the USDA Soil Texture Calculator (USDA, 1996).

2.6. Statistical analyses

The statistical significance of differences among sites and between open and closed states was determined by two-way (repeated measures) ANOVA with a significance threshold of alpha

= 0.05. Correlations between pore water variables were evaluated using Pearson's correlation coefficient with a correlation threshold of r = ±0.7. Reported uncertainty ranges are ±1 standard deviation unless otherwise stated. The statistical analysis was performed with the EZAnalyze package.

3. Results

3.1. Geochemical pore water characteristics of the closed state

Across all sites and depths in the closed state, pore water sulfate concentrations ranged from 0.02 mM to 5.7 mM (Figure 2.2), with higher average pore water concentrations in surface sediment than in bottom sediment. At the North Marsh, River Confluence, and Butano Marsh sites, pore water sulfate concentrations values generally decreased from 3.3-4.9 mM to <1 mM below 15 cm depths. However, at the Sandbar Lagoon site, pore water sulfate concentrations fluctuated with depth between 1.4 and 5.7 mM in the closed state (Figure 2.2a). Pore water sulfate concentrations in surface sediment were significantly larger at the North Marsh site than at the Butano Marsh site (Figure 2.2c-d).

An order of magnitude lower than sulfate concentrations, total hydrogen sulfide pore water concentrations ranged from 1.5 µM to 360 µM in the closed state in all four sampling sites (Figure 2.2). Low hydrogen sulfide concentrations (<80 µM) were observed at the Butano Marsh, North Marsh, and Sandbar Lagoon sites; values spiked to greater than 180 µM below 6 cm depths. Hydrogen sulfide concentrations were significantly lower at the North Marsh and Butano Marsh sites than at the River Confluence site in surface and bottom sediment, the latter where the highest value (>260 µM) were observed in the closed state (Figure 2.2b).

Pore water ferric iron and ferrous iron concentrations ranged up to 25 µM and 355 µM in the closed state, respectively (Figure 2.3). Pore water dissolved ferric iron concentrations in the closed state were the highest at the North Marsh and Butano Marsh sites and lowest at the River Confluence site (<8 µM) in surface and bottom sediment (Figure 2.3c-d), but were not significantly different between sites in surface sediment. Pore water ferrous iron concentrations in the closed state were significantly higher at the North Marsh site than at the Butano Marsh and River Confluence sites and significantly lower (<6 µM) at the River Confluence site than North Marsh and Butano Marsh sites (Figure 2.3). Ferrous iron concentrations significantly increased at the North Marsh and Butano Marsh sites between surface and bottom sediment (Figure 2.3c-d).

Pore water pH values were circumneutral to mildly alkaline (7.2-8.5) at all sites in the closed state, with slight deviation toward circumneutral values with depth (Figure 2.3). Pore water pH values fluctuated with depth from circumneutral (~7.5) to mildly alkaline (~8.0) at the Sandbar Lagoon site (Figure 2.3a), whereas values decreased with depth from slightly alkaline (8.0-8.3) to circumneutral (7.3-7.4) at the remaining three sites in the closed state (Figure 2.3b-d). Pore water pH values at the River Confluence site were significantly higher in bottom sediment than in bottom sediment at all other sites. Chloride concentrations in pore water ranged between 60 mM and 230 mM corresponding to mildly brackish (8-10‰) in the closed state, with average values slightly
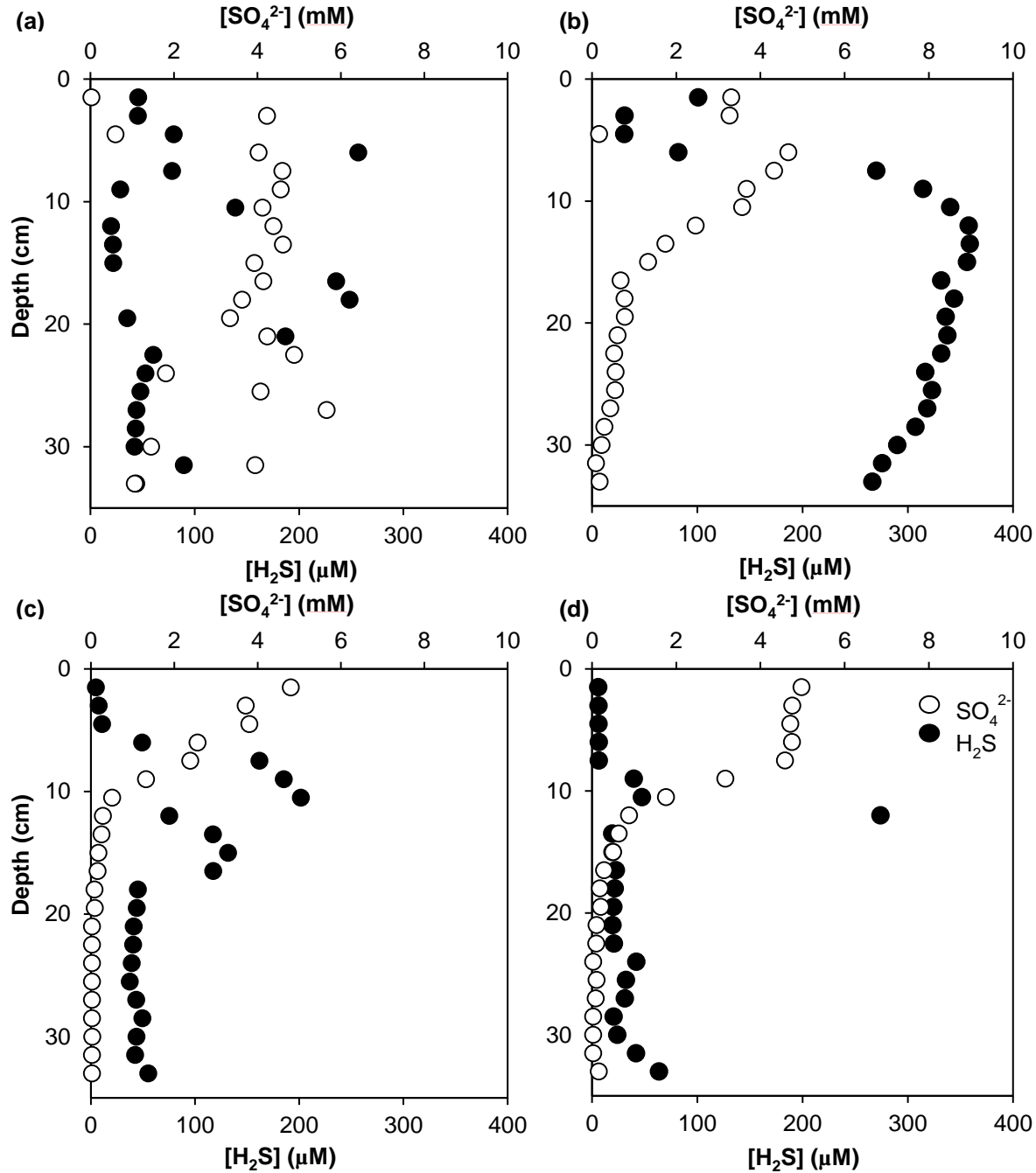
Figure 2.2. Depth profiles of sulfate concentration (white circles) and total aqueous hydrogen sulfide concentration (black circles) in sediment pore water sampled during the Pescadero Estuary closed state (November 2014) for the (**a**) Sandbar Lagoon site, (**b**) River Confluence site, (**c**) North Marsh site, and (**d**) Butano Marsh site.

increasing with depth (Figure 2.4). Pore water chloride concentrations were significantly greater (134-228 mM) at the Butano Marsh and North Marsh sites than the Sandbar Lagoon and River Confluence sites (83-166 mM) in both surface and bottom sediment.
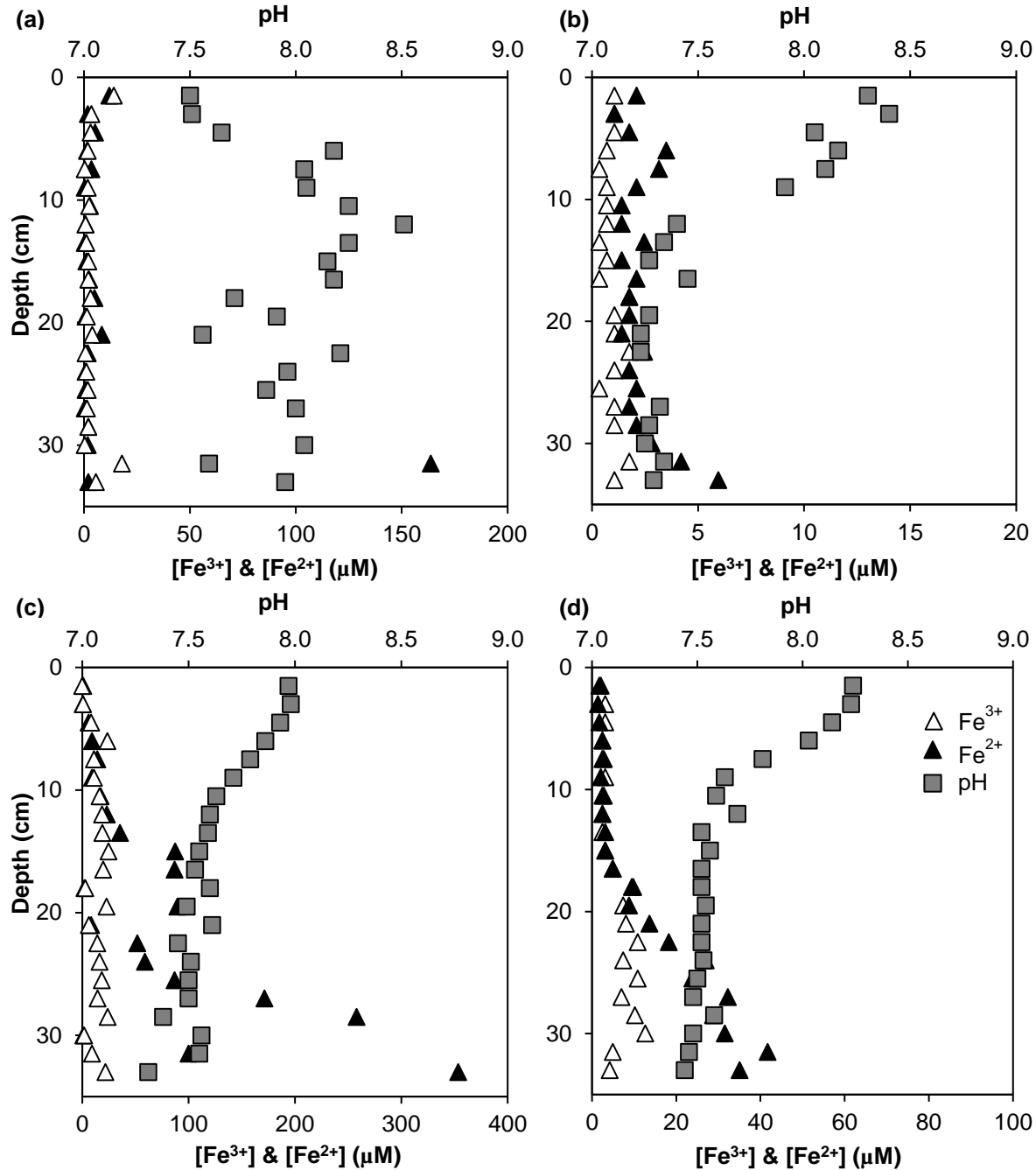
Figure 2.3. Depth profiles of dissolved ferric iron concentration (white triangles), dissolved ferrous iron concentration (black triangles), and pH (gray squares) in sediment pore water sampled during the Pescadero Estuary closed state (November 2014) for the (**a**) Sandbar Lagoon site, (**b**) River Confluence site, (**c**) North Marsh site, and (**d**) Butano Marsh site.

Pore water dissolved organic carbon (DOC) concentrations ranged from 11 to 38 mg L^{-1} (Figure 2.4). DOC concentrations were significantly lower (<17.5 mg L^{-1}) at the Sandbar Lagoon
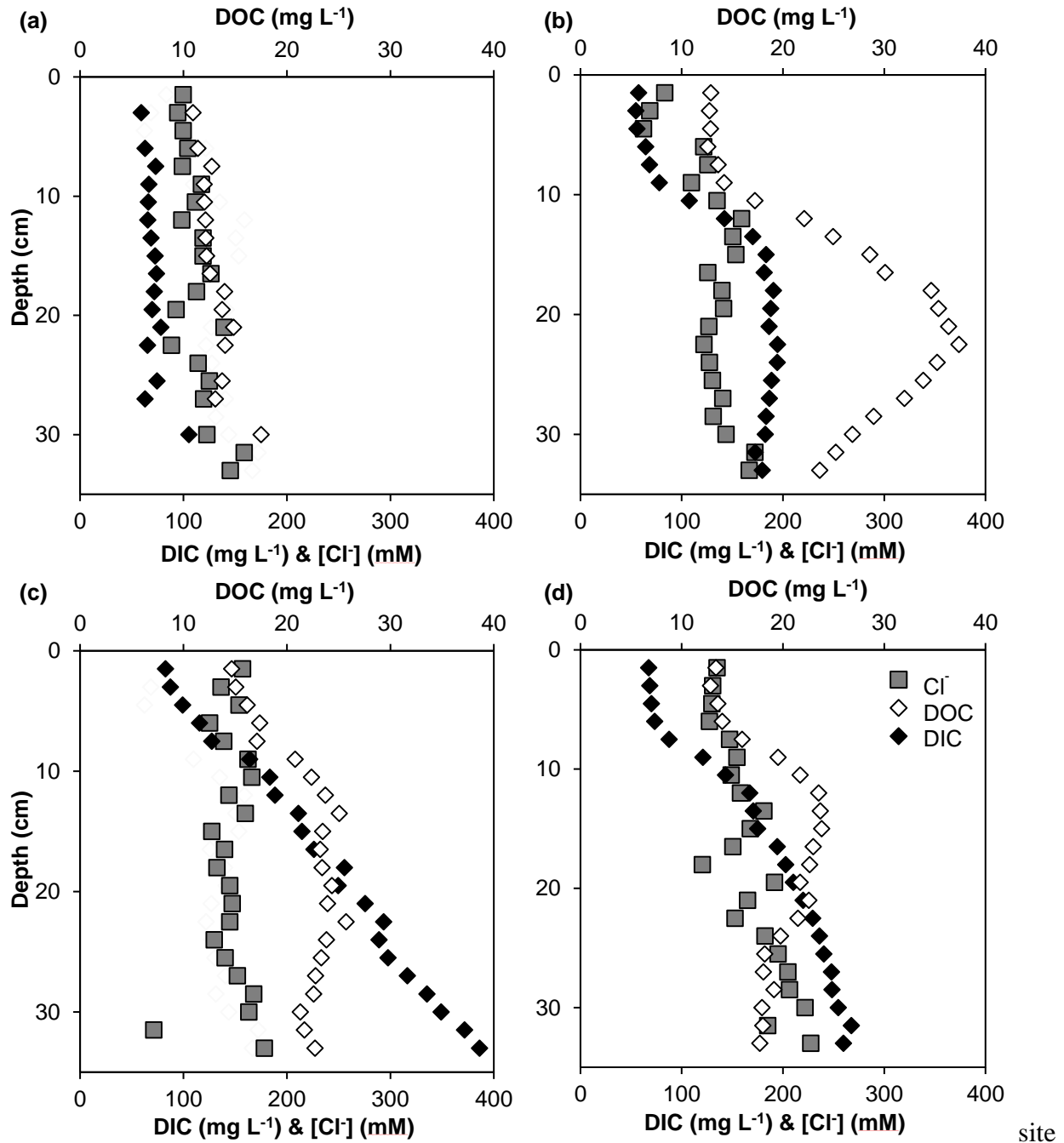
Figure 2.4. Depth profiles of chloride concentration (gray squares), dissolved organic carbon concentration (white diamonds), and dissolved inorganic carbon concentration (black diamonds) in sediment pore water sampled during the Pescadero Estuary closed state (November 2014) for the (**a**) Sandbar Lagoon site, (**b**) River Confluence site, (**c**) North Marsh site, and (**d**) Butano Marsh site.

than at all other sites. In surface sediment, DOC was largest at the Butano Marsh and North Marsh sites (16-19 mg L^{-1}). In bottom sediment, DOC peaked around 18-23 cm depths at the River

Confluence site to the largest values observed (>12 mg L^{-1}) in the closed state (Figure 2.4b). An order of magnitude lower than DOC, pore water dissolved inorganic carbon (DIC) concentrations fluctuated between 55 mg L^{-1} and 387 mg L^{-1} at all sites and increased with depth (Figure 2.4). DIC concentrations were significantly larger at the Butano Marsh and North Marsh sites than at all other sites. The Sandbar Lagoon site was characterized by the lowest pore water DIC concentrations (<70 ppm) in the closed state (Figure 2.4a). In the closed state, DOC was negatively correlated with pH (r = -0.76, P < 0.001), and DIC was negatively correlated with sulfate concentration (r = -0.80, P < 0.001).

3.2. Geochemical pore water characteristics of the open state

Pore water sulfate concentrations in the open state ranged from 0.05 mM to 17 mM and were significantly higher at the River Confluence site, followed by the Sandbar Lagoon site and North Marsh site (Figure 2.5). Sulfate concentrations at the Sandbar Lagoon site decreased with depth from 17 mM in surface sediment to <5 mM below 20 cm depths in the open state (Figure 2.5a). Pore water sulfate concentrations at the North Marsh and Butano Marsh sites decreased from 7.9-10.5 mM to <1 mM below 15 cm depths (Figure 2.5c-d). Conversely, at the River Confluence site, sulfate concentrations fluctuated between 6 and 13 mM in the open state (Figure 2.5b). Sulfate concentrations were significantly higher (>8 mM) at the River Confluence and Sandbar Lagoon sites in open state surface sediment than in the closed state surface sediment.

With behavior varying by site, total hydrogen sulfide concentrations in pore water ranged from 35 µM to 314 µM in the open state (Figure 2.5). In comparison to the closed state, pore water hydrogen sulfide concentrations in the open state were lower (~35 µM) above 27 cm depths and higher (~180 µM) below that at the Sandbar Lagoon site (Figure 2.5a). The River Confluence site fluctuated between 45 µM and 155 µM in surface sediment yet increased from 43 µM to 150 µM in bottom sediment (Figure 2.5b). At the North Marsh and Butano Marsh sites, hydrogen sulfide concentrations increased up to 130 µM below 7 cm depths in the open state (Figure 2.5c-d). Pore water hydrogen sulfide concentrations significantly increased at the North Marsh site from the closed to open state in surface and bottom sediment and at the River Confluence and Butano Marsh sites in bottom sediment.

With fluctuating values in the open state, dissolved ferric iron concentrations in pore water ranged up to 188 µM (Figure 2.6). In surface sediment, ferric iron concentrations ranged up to 105 µM and did not change significantly from closed to open state. In bottom sediment, ferric iron concentrations significantly decreased at the North Marsh site between closed and open state yet significantly increased at the River Confluence site (Figure 2.6b-c). Ferric iron concentrations were significantly lower in surface sediment than in bottom sediment, where the Sandbar Lagoon site had significantly lower concentrations (<10 µM) than the River Confluence site (Figure 2.6a-b).

In the open state, pore water ferrous iron concentrations fluctuated up to 400 µM at the River Confluence and North Marsh sites (Figure 2.6). Ferrous iron concentrations did not change significantly from closed to open state in surface sediment yet significantly increased between
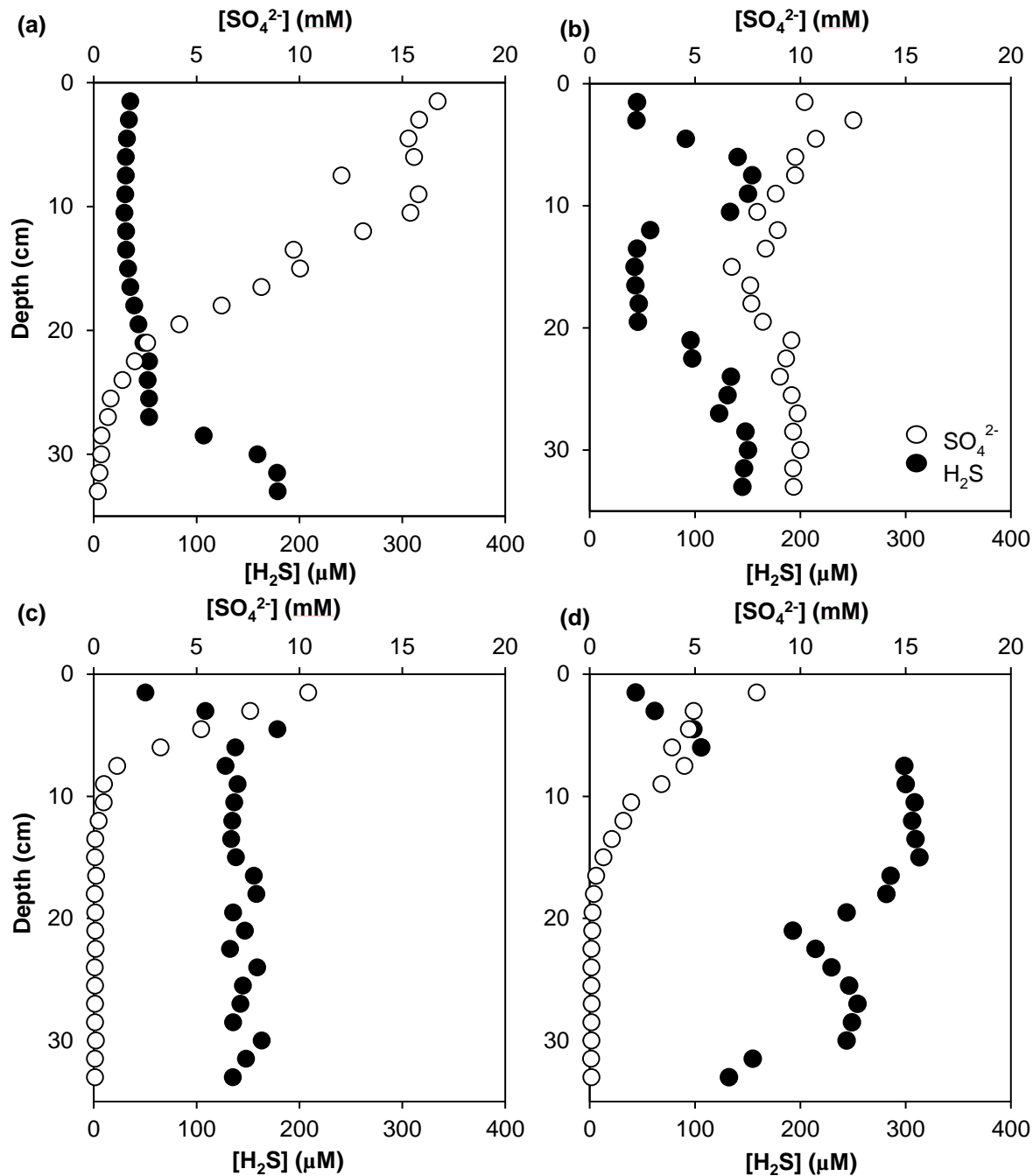
Figure 2.5. Depth profiles of sulfate concentration (white circles) and total aqueous hydrogen sulfide concentration (black circles) in sediment pore water sampled during the Pescadero Estuary open state (May 2015) for the (**a**) Sandbar Lagoon site, (**b**) River Confluence site, (**c**) North Marsh site, and (**d**) Butano Marsh site.

states at the Sandbar Lagoon and River Confluence sites in bottom sediment. Pore water ferrous iron was significantly greater at the River Confluence site than the Butano Marsh site in bottom
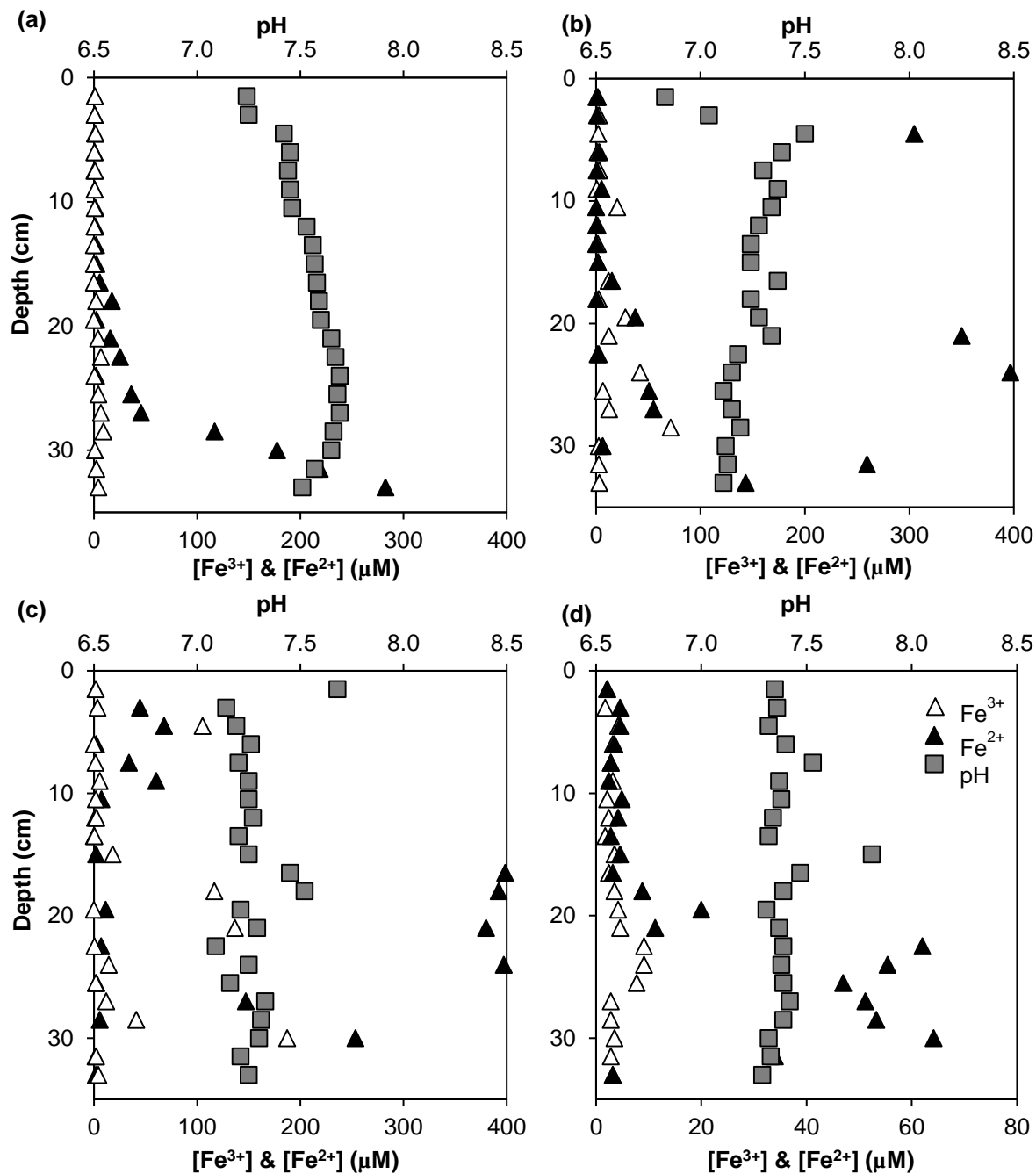
Figure 2.6. Depth profiles of dissolved ferric iron concentration (white triangles), dissolved ferrous iron concentration (black triangles), and pH (gray squares) in sediment pore water sampled during the Pescadero Estuary open state (May 2015) for the (**a**) Sandbar Lagoon site, (**b**) River Confluence site, (**c**) North Marsh site, and (**d**) Butano Marsh site.

sediment (Figure 2.6). The highest ferric iron and ferrous iron concentrations (187 and 400 µM) were observed at the North Marsh site in bottom sediment in the open state.
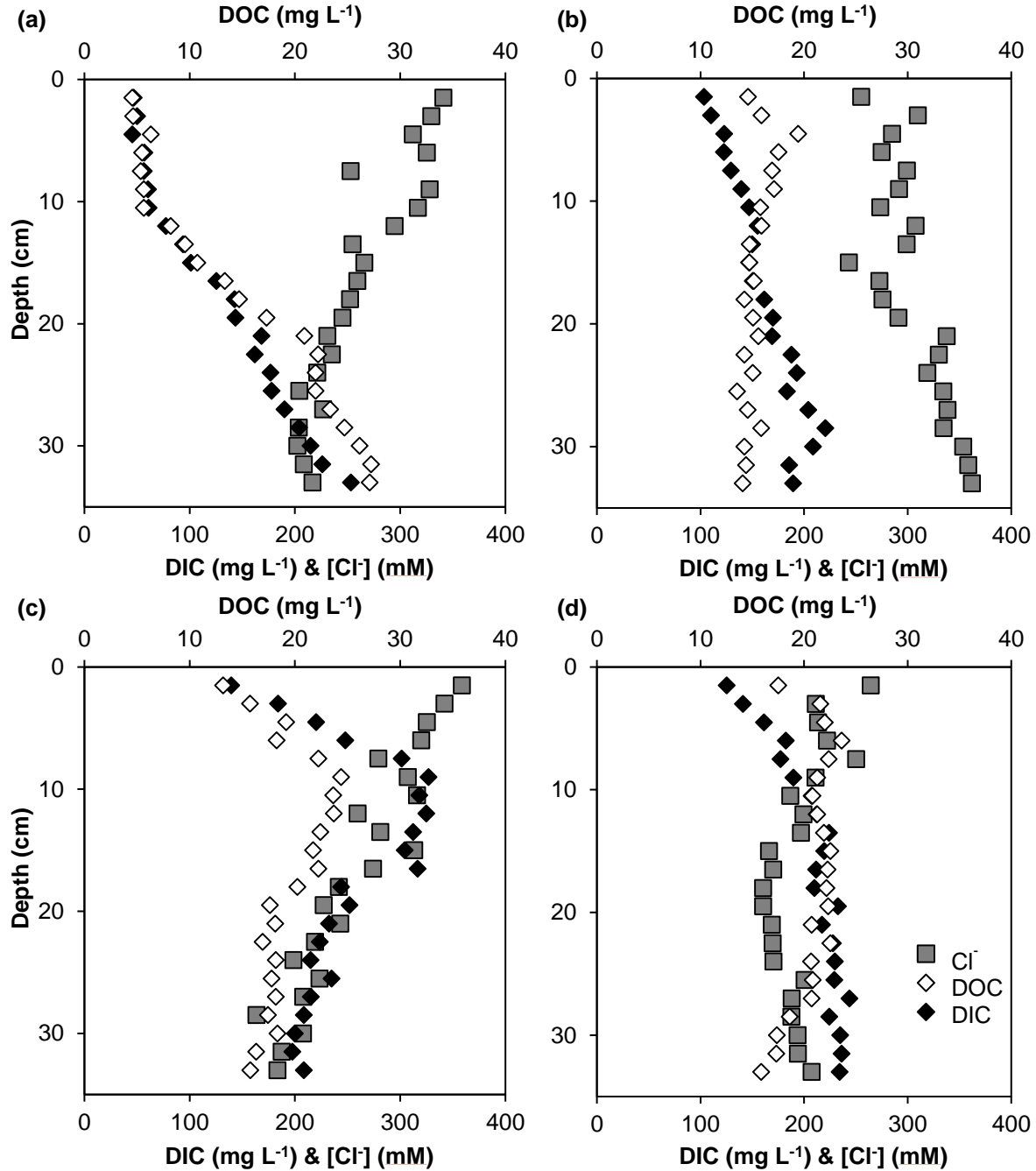
Figure 2.7. Depth profiles of chloride concentration (gray squares), dissolved organic carbon concentration (white diamonds), and dissolved inorganic carbon concentration (black diamonds) in sediment pore water sampled during the Pescadero Estuary open state (May 2015) for the (**a**) Sandbar Lagoon site, (**b**) River Confluence site, (**c**) North Marsh site, and (**d**) Butano Marsh site.

Pore water pH was significantly lower in the open state than in the closed state, with circumneutral to slightly alkaline values (6.8-7.8) that remained constant with depth in the open state (Figure 2.6). In surface sediment, pore water pH was significantly greater at the Sandbar

Lagoon site than at the River Confluence site, where the lowest pH value was observed (Figure 2.6b). In bottom sediment, pH values were lowest (<7.4) at the River Confluence site, followed by the Butano Marsh and North Marsh sites (Figure 2.6c-d). Pore water pH decreased significantly from the closed to open state at all sites and depths. Pore water chloride concentrations were significantly higher in the open state than the closed state, ranging from 160 mM to 362 mM (Figure 2.7) corresponding to moderately brackish salinities (15-19‰). Chloride concentrations significantly decreased with depth at the Sandbar Lagoon, North Marsh, and Butano Marsh sites from 264-342 mM to 183-216 mM (Figure 2.7). Conversely, pore water chloride concentrations significantly increased with depth from 255 mM to 362 mM at the River Confluence site in the open state (Figure 2.7b). Pore water chloride concentrations were significantly higher at the Butano Marsh and Sandbar Lagoon sites than the remaining sites in surface sediment and significantly greater at the River Confluence site than all other sites in bottom sediment. Chloride concentration in the open state was positively correlated with sulfate concentration (r = 0.75, P < 0.001).

Pore water DOC concentrations ranged between 4 and 28 mg L^{-1} in the open state, with the highest values observed at the North Marsh site in surface sediment and Sandbar Lagoon site in bottom sediment (Figure 2.7). The lowest DOC concentrations were observed at the Sandbar Lagoon site in surface sediment (Figure 2.7a) and at the River Confluence site in bottom sediment (Figure 2.7b). In comparison to the closed state, DOC concentrations were significantly greater in open state surface sediment at the North Marsh site and significantly lower in open state surface sediment at the Sandbar Lagoon site. In bottom sediment, DOC concentrations significantly decreased at the River Confluence and Butano Marsh sites from closed to open state and significantly increased at the Sandbar Lagoon site between states. DOC concentrations at the Sandbar Lagoon increased with depth from 4.5 mg L^{-1} in the open state, yet remained constant at the remaining sites. Pore water DIC concentrations ranged between 45 mg L^{-1} and 330 mg L^{-1} in the open state (Figure 2.7), with the smallest values (<100 and <254 mg L^{-1}) observed at the Sandbar Lagoon site in surface and bottom sediment, respectively (Figure 2.7b). Pore water DIC concentrations were largest at the North Marsh site, followed by the Butano Marsh site in surface and bottom sediment (Figure 2.7c-d). In surface sediment, DIC concentrations significantly increased from closed to open state at all sites except for at the Sandbar Lagoon site, where values remained constant. In bottom sediment, DIC concentrations significantly increased between states only at the Sandbar Lagoon site. DOC concentration was negatively correlated with sulfate concentration (r = -0.83, P < 0.001) and positively correlated with DIC concentration (r = 0.75, P < 0.001). DIC concentration was negatively correlated with sulfate concentration (r = -0.82, P < 0.001).

Sediment pore water composition averaged for the four study sites at Pescadero varied significantly between closed and open states and between surface sediment (<12 cm) and bottom sediment (>12 cm) (Table 2.1). Average pore water sulfate concentrations were significantly higher in surface sediment than bottom sediment, while average hydrogen sulfide, ferric iron, ferrous iron, DOC, and DIC concentrations were higher in bottom sediment in both closed and open states (Table 2.1). Pore water chloride concentrations were higher in bottom sediment than surface sediment in the closed state, yet the opposite trend was observed in the open state (Table 2.1). Average sulfate, hydrogen sulfide, ferric iron, ferrous iron, chloride, and DIC concentrations were significantly higher in the open state than in the closed state, while the opposite trend was

Table 2.1. Pore water characteristics in the Pescadero Estuary system. Values are presented as averages ±standard deviations of the surface sediment pore water (<12 cm) and bottom sediment pore water (>12 cm) in the closed state (November 2014) and open state (May 2015) at all sites. bdl means below detection limits (30 µM).

Variable	Closed state	Open state
Surface sediment pore water (<12 cm)		
$[SO_4^{2-}]$ (mM)	3.2±1.6	8.1±5.2
$[H_2S]$ (µM)	103.4±111.3	112.8±86.7
$[NO_3^-]$ (µM)	bdl	bdl
$[Fe^{3+}]$ (µM)	5.3±8.5	5.7±18.5
$[Fe^{2+}]$ (µM)	4.4±5.3	17.8±55.1
pH	7.9±0.4	7.3±0.2
$[Cl^-]$ (mM)	125.1±27.5	283.3±46.2
DOC (mg L^{-1})	15.4±4.0	15.9±6.6
DIC (mg L^{-1})	93.3±40.3	154.4±83.4
Bottom sediment pore water (>12 cm)		
$[SO_4^{2-}]$ (mM)	1.1±1.6	3.1±4.1
$[H_2S]$ (µM)	123.5±124.8	140.1±76.6
$[NO_3^-]$ (µM)	bdl	bdl
$[Fe^{3+}]$ (µM)	6.8±7.1	29.1±109.5
$[Fe^{2+}]$ (µM)	33.9±66.0	91.0±133.1
pH	7.5±0.4	7.4±0.2
$[Cl^-]$ (mM)	146.9±31.4	239.0±58.2
DOC (mg L^{-1})	22.4±6.6	18.5±4.0
DIC (mg L^{-1})	195.2±83.9	204.2±44.4

observed for average pore water pH. Average pore water DOC concentrations were significantly higher in the closed state than in the open state at all sites except for the Sandbar Lagoon site in bottom sediment (Table 2.1). Pore water nitrate concentrations were below detection limits (30 µM) at all depths, sites, and states (Table 2.1).

3.3. Geochemical overlying water characteristics in closed and open states

Sulfate concentrations in the overlying water were highest in the closed state at the Butano Marsh site, followed by the Sandbar Lagoon site and North Marsh site (Table 2.2a). Sulfate concentrations increased at all sites in the open to 6.4-16.7 mM, with the smallest values (6.5-7.7 mM) observed at the Butano Marsh, North Marsh, and Sandbar Lagoon sites. Hydrogen sulfide concentrations in the overlying water were significantly lower in the closed state (3.1-3.5 µM) than in the open state (9.2-9.4 µM), with no significant differences between sites (Table 2.2a).

Table 2.2. Geochemical (**a**) overlying water and (**b**) surface sediment characteristics at the Sandbar Lagoon, River Confluence, North Marsh, and Butano Marsh sites in the closed state (November 2014) and open state (May 2015) at the Pescadero Estuary. Values are presented as averages ±standard deviations, as compiled from Chapter 1. bdl means below detection limits (30 µM).

(a)

Site	$[SO_4^{2-}]$ (mM)	$[H_2S]$ (µM)	$[NO_3^-]$ (µM)	[diss. Fe] (µM)	pH	$[Cl^-]$ (mM)	DOC (mg L^{-1})	DIC (mg L^{-1})
Closed state								
Sandbar Lagoon	4.0±0.1	3.5±0.2	bdl	2.8±0.2	8.3±0.1	103.4±0.4	4.3±0.2	27.9±1.6
River Confluence	1.9±0.1	2.7±0.2	bdl	3.2±0.2	8.2±0.1	55.4±0.5	3.9±0.1	25.3±1.1
North Marsh	3.8±0.1	3.4±0.2	bdl	5.4±0.3	8.3±0.1	98.8±0.5	4.4±0.1	28.3±1.7
Butano Marsh	4.2±0.2	3.1±0.2	bdl	2.5±0.2	8.5±0.1	115.9±0.8	4.7±0.1	29.8±1.2
Open state								
Sandbar Lagoon	7.7±0.2	9.6±0.4	bdl	2.5±0.2	7.7±0.1	240.5±1.0	2.2±0.1	29.4±2.1
River Confluence	16.7±0.2	9.4±0.4	bdl	1.4±0.2	7.7±0.1	290.6±1.3	2.5±0.1	31.7±1.6
North Marsh	7.6±0.1	9.2±0.4	bdl	2.1±0.2	8.0±0.1	85.8±0.4	3.0±0.1	39.8±3.5
Butano Marsh	6.4±0.1	9.2±0.4	bdl	4.7±0.3	7.1±0.1	151.0±0.7	3.6±0.2	27.0±2.3

(b)

Site	AVS content (mmol S kg^{-1})	Fe content (mmol kg^{-1})	pH	C_{org} content (wt%)	N content (wt%)	C_{org}/N
Closed state						
Sandbar Lagoon	16.1±2.4	27.1±0.9	8.0±0.1	1.04±0.10	0.08±0.01	13.4±0.2
River Confluence	27.1±3.7	36.0±0.9	8.2±0.1	1.51±0.07	0.17±0.01	9.1±0.2
North Marsh	22.0±1.3	74.5±1.5	8.0±0.1	2.21±0.05	0.16±0.01	13.6±0.1
Butano Marsh	26.1±5.3	41.6±0.9	8.0±0.1	5.19±0.13	0.40±0.02	12.9±0.3
Open state						
Sandbar Lagoon	6.2±3.6	51.9±1.1	7.2±0.1	0.68±0.08	0.08±0.01	8.8±0.1
River Confluence	33.0±4.9	54.3±0.5	6.9±0.1	0.40±0.02	0.04±0.01	10.2±0.1
North Marsh	31.8±2.4	75.9±1.3	7.2±0.1	2.98±0.06	0.26±0.02	11.7±0.4
Butano Marsh	31.0±3.8	36.4±0.4	7.3±0.1	1.55±0.08	0.14±0.01	11.3±0.3

Hydrogen sulfide concentrations were also lower in the overlying water than in pore water. Nitrate concentrations were below detection limits at all sites and states (Table 2.2a). Compared to pore water values, total dissolved iron concentrations remained low in the closed state (2.5-5.4 µM) and

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Table 2.3. Physical surface sediment characteristics at the Sandbar Lagoon, River Confluence, North Marsh, and Butano Marsh sites in the closed state (November 2014) and open state (May 2015) at the Pescadero Estuary. Values are presented as averages ±standard deviations, as compiled from Chapter 1.

(c)

Site	Closed state			
	Mean grain size (µm)	Clay (wt%)	Sand (wt%)	Texture
Sandbar Lagoon	83.8±7.9	2.1±0.7	77.7±5.3	Sandy loam
River Confluence	59.7±12.7	3.2±0.9	62.6±5.2	Sandy loam
North Marsh	63.3±4.5	2.9±0.2	71.3±2.7	Sandy loam
Butano Marsh	21.8±11.5	10.2±1.2	30.6±4.8	Silt loam
Open state				
Sandbar Lagoon	69.3±11.7	4.2±1.3	73.1±6.3	Sandy loam
River Confluence	144.4±17.4	2.3±0.1	85.8±0.3	Sandy loam
North Marsh	32.0±0.6	8.8±0.3	43.6±1.0	Loam
Butano Marsh	18.7±0.9	11.1±0.7	24.3±0.6	Silt loam

open state (1.4-4.7 µM) (Table 2.2a). Iron concentrations were highest at the North Marsh site in the closed state and highest at the Butano Marsh in the open state. Overlying water pH values were mildly alkaline (8.2-8.5) in the closed state and significantly decreased to circumneutral to mildly alkaline values (7.1-8.0) in the open state (Table 2.2a). Over both sites, the highest and lowest pH values were observed at the Butano Marsh in the closed state and open state, respectively.

Chloride concentrations in the overlying water significantly increased from 55-116 mM in the closed state to 151-291 mM at the Sandbar Lagoon, River Confluence, and Butano Marsh sites (Table 2.2a). Overlying water chloride concentrations decreased at the North Marsh site between states. At all sites, chloride concentrations corresponded to mildly brackish (3-7‰) and moderately brackish (11-25‰) salinities in the closed and open state, respectively. DOC concentrations in the overlying water significantly decreased from 3.9-4.7 mg L^{-1} in the closed state to 2.2-3.6 mg L^{-1} in the open state, with no significant differences among sites (Table 2.2a). DIC concentrations significantly increased from 25.3-28.3 mg L^{-1} in the closed state to 29.4-39.8 mg L^{-1} in the open state at the Sandbar Lagoon, River Confluence, and North Marsh sites (Table 2.2a). At the Butano Marsh sites, DIC decreased slightly to the lowest value (27 mg L^{-1}) observed in the open state.

3.4. Physical and geochemical characteristics of surface sediment in closed and open states

In both closed and open state, surface sediments at the four study sites ranged from a medium-textured silt loam at the Butano Marsh site, with average grain sizes of 18-22 µm, to coarse-textured sandy loams at the River Confluence and Sandbar Lagoon sites, with higher

average grain sizes of 63-86 µm (Table 2.3). The Butano Marsh sediment had higher clay contents (10-12%) and lower sand contents (24-31%) than its coarse-textured counterparts, whose sediment clay and sand contents ranged 2.1-4.2% and 62-86%, respectively. With lower clay contents (<9%) and sand contents (>43%), the North Marsh sediment ranged from a coarser-textured sandy loam of 63 µm grain size in the closed state to a finer-textured loam of 32 µm grain size in the open state. The highest sand contents (>73%) were observed at the Sandbar Lagoon site in the closed state and River Confluence site in the open state.

At all sites, AVS contents ranged 6-33 mmol kg^{-1}, with the largest values observed in the open state at the River Confluence and North Marsh sites (Table 2.2b). AVS contents increased from 22-27 mmol kg^{-1} in the closed state to 31-33 mmol kg^{-1} in the open state at the River Confluence, North Marsh, and Butano Marsh sites yet decreased between states at the Sandbar Lagoon site. Sediment iron contents increased from closed state (24-75 mmol kg^{-1}) to open state (51-76 mmol kg^{-1}) at the Sandbar Lagoon, River Confluence, and North Marsh sites (Table 2.2b). Conversely, sediment iron contents decreased at the Butano Marsh site from closed to open state. Sediment pH was mildly alkaline (8.0-8.2) in the closed state and circumneutral (6.9-7.3) in the open state (Table 2.2b). The lowest sediment pH value was observed at the River Confluence site in the open state.

Sediment organic carbon contents ranged between 0.4% to 5.2%, with the highest values observed at the Butano Marsh site in the closed state and the North Marsh site in the open state (Table 2.2b). From closed to open state, organic carbon contents decreased at the Sandbar Lagoon, River Confluence, and Butano Marsh sites yet increased at the River Confluence site. Sediment nitrogen contents decreased slightly from 0.17-0.40% in the closed state to 0.04-0.14% in the open state at the River Confluence and Butano Marsh sites (Table 2.2b), yet did not change significantly between states at the other two sites. The largest sediment nitrogen contents (>0.26%) were observed at the Butano Marsh and North Marsh sites. Molar C_{org}/N ranged 9.1-13.6 in the closed state, with the highest values (>13) observed at the Sandbar Lagoon and North Marsh sites (Table 2.2b). In the open state, molar C_{org}/N ranged 8.8-11.7, with the highest values observed at the North Marsh and Butano Marsh sites.

4. Discussion

The Pescadero Estuary along the California coast is a bar-built estuary that cycles between closed and open states. The transitions from closed to open state in the Pescadero Estuary is often associated with hydrogen sulfide and fish-kill events. The sediment pore water investigations of geochemical sulfur and iron redox cycling during both states found that microbial sulfate reduction predominates, leading to sulfur-driven iron redox cycling and iron sulfide precipitation. Below, I discuss each result in turn as well as the biogeochemical controls over sulfate and iron reduction and sulfide precipitation in sediment and the implications of sulfur and iron redox cycling on pH.

4.1. Co-occurrence of anaerobic respiration pathways in closed and open states

The closed state sediment pore water conditions were characterized by mildly alkaline pH (7.9±0.4), mildly brackish salinity (8.0‰), and low average concentrations of sulfate (<5.0 mM), chloride (<166 mM), and DIC (<189 ppm). In addition, the bottom sediment was also characterized by significantly higher average concentrations of ferrous iron (33.9 µM) and DOC (22 ppm). The closed state pore water conditions contrast with the open state pore water, which was characterized as circumneutral (7.3±0.2) with moderately brackish salinity and higher average concentrations of sulfate, chloride, and DIC. The closed state characteristics are consistent with that of permanently closed estuaries and coastal lagoons, where marine inputs of alkaline, saline, sulfate-rich water are restricted (Tagliapietra et al., 2009; Whitfield et al., 2012). In contrast, the open state characteristics are consistent with permanently open estuaries, where alkaline, saline, sulfate-rich water is widely accessible (Whitfield, 1992; Allen et al., 2006; Tagliapietra et al., 2009), therefore driving the correlation observed between chloride and sulfate pore water concentrations.

However, similar to the closed state, the trends in sulfate and DOC concentrations with depth in both states indicate that sulfate reduction is a dominant process in sediment, leading to the production of DIC and explaining the negative correlation between the two. Hydrogen sulfide, ferrous iron, and DIC concentrations also dominate in sediment pore water, further confirming the predominance of anaerobic respiration processes at the Pescadero Estuary during both the closed and open states. Relative to sulfate concentration, low nitrate concentrations corroborate that nitrate reduction is not a dominant process in Pescadero littoral sediments and that redox conditions are suboxic (Chapelle et al., 2009). The presence of sediment iron up to 75 mmol kg^{-1} and pore water ferrous iron suggest that iron reduction may also predominate as an anaerobic process in Pescadero Estuary sediments. However, due to higher sulfate availability, sulfate reduction may be more favorable than iron reduction, as observed elsewhere in freshwater sediments (Hansel et al., 2015). As reductive constituents, hydrogen sulfide and ferrous iron pore water concentrations are subsequently higher in bottom sediment than surface sediment, indicating that anaerobic respiration pathways such as sulfate reduction and ferric iron reduction often occur simultaneously (Canfield and Des Marais, 1993; Weston et al., 2006; Jørgensen and John Parkes, 2010). Unlike sulfate reduction which is strictly a microbial process, the pore water profiles cannot predict if ferrous iron is produced through biotic and/or abiotic pathways (Koretsky et al., 2003).

Past hypoxic (<0.2 mM) and anoxic conditions in Pescadero water (Sloan, 2006) corroborate the predominance of anaerobic respiration processes over aerobic respiration at the Pescadero Estuary. Moreover, there may be insufficient dissolved oxygen (<4 mM) during both states to fully remove hydrogen sulfide and ferrous iron as they are produced, explaining their presence in pore water in closed and open states. A mass balance analysis of aqueous hydrogen sulfide oxidation coupled with dissolved oxygen as a terminal electron acceptor reveals a 1:2 molar ratio of hydrogen sulfide to dissolved oxygen (Chen and Morris, 1972), in which the oxidation of aqueous hydrogen sulfide can deplete up to 0.7 mM and 0.6 mM of dissolved oxygen in sediment pore water in the closed and open states, respectively. Moreover, the oxidation of dissolved ferrous iron can deplete up to 0.1 mM of dissolved oxygen in both states, as determined by a 4:1 mass balance molar ratio of iron to oxygen (Burke and Banwart, 2002). Despite low values in the

overlying water, hydrogen sulfide and ferrous iron concentrations in pore water are sufficiently large to fully remove dissolved oxygen from sediment, leading to anoxic conditions.

However, in agreement with Chapelle et al. (2009), I can distinguish sulfate reduction from iron reduction using Fe^{2+}/H_2S molar ratios as calculated from plots of H_2S vs. Fe^{2+} (Figure 2.8). Fe^{2+}/H_2S molar ratios of <0.5 indicate that sulfate reduction predominates, while molar ratios of
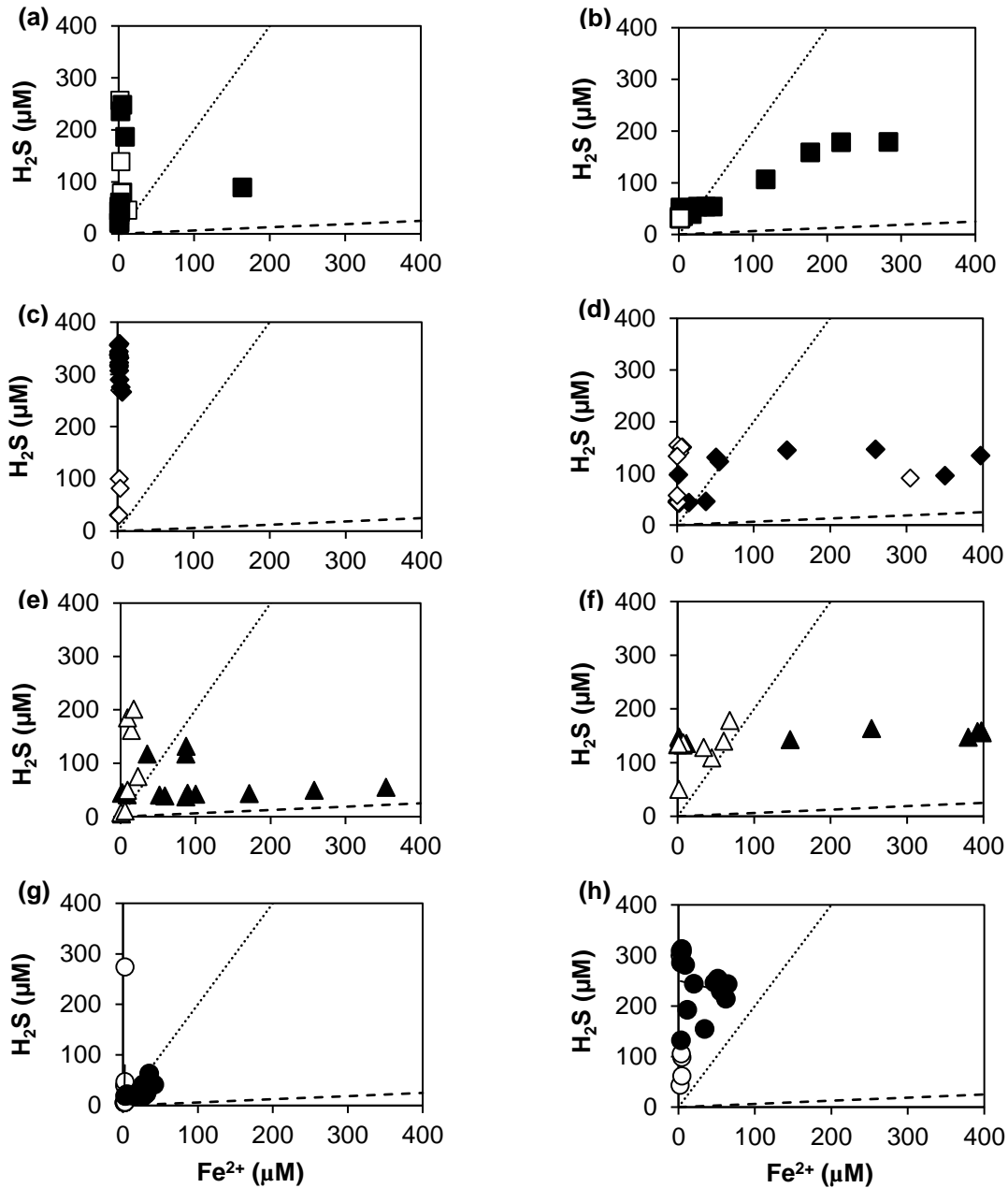
Figure 2.8. Pore water concentrations of H_2S vs. Fe^{2+} in surface sediment (open symbols) and bottom sediment (closed symbols) in the Pescadero Estuary closed state (November 2014) (**a, c, e, g**) and open state (May 2015) (**b, d, f, h**) for the (**a-b**) Sandbar Lagoon site (squares), (**c-d**) River Confluence site (diamonds), (**e-f**) North Marsh site (triangles), and (**g-h**) Butano Marsh site (circles). The dotted and dashed lines represent Fe/H_2S ratios of 0.5 and 16.

>16 indicate that iron reduction predominates and ratios between 0.5 and 16 involve simultaneous sulfate and iron reduction (Chapelle et al., 2009). Iron reduction did not predominate at any of the sites in closed or open states. The surface sediments at all sites in the closed and open states are dominated by sulfate reduction, where molar ratios are low (<0.5). However, bottom sediments in the closed state varied between sites, ranging from predominantly sulfate reduction at the River Confluence and Sandbar Lagoon sites to simultaneous sulfate and iron reduction at the Butano Marsh and North Marsh sites. Similarly, bottom sediment in the open state also varied between sites, ranging from sulfate reduction at the Butano Marsh site to a combination of sulfate and iron reduction at the three other sites. This analysis confirms that microbial sulfate reduction dominates as the major anaerobic respiration process in the Pescadero Estuary sediments in the closed state, whereas simultaneous sulfate and iron reduction predominate in the open state across surface and bottom sediments.

4.2. Controls over sulfate reduction and sulfide precipitation

Sulfate reduction is controlled by sulfate and organic carbon substrates; DOC concentrations are roughly equivalent with depth within the Pescadero Estuary, suggesting that microbial sulfate reduction is limited by the concentration of sulfate, and not DOC in this system. Moreover, SRB activity and growth are likely at a maximum due to high hydrogen sulfide concentrations, circumneutral to slightly alkaline pH, and reducing conditions, as measured and estimated in the Pescadero Estuary and elsewhere in mine sediments (Fortin et al., 1996). Under reducing conditions, sulfate removal is coupled with increases in DOC as observed at Pescadero and is in agreement with Knorr (2013), who found a negative correlation between pore water sulfate and DOC concentrations. The depth threshold for which I observe no sulfate due to reduction is dependent on physical (ex. estuary state, sediment particle size composition, depth, rain fall events, transport limitations) (Goldhaber et al., 1977; Chapelle and Lovley, 1992), geochemical (ex. available organic matter substrates, temperature, pressure) (Goldhaber and Kaplan, 1976; Boudreau and Westrich, 1984; Al-Raei et al., 2009), and biological (ex. SRB abundance and activity) (Widdel and Bak, 1992; Fauque, 1995) differences. For instance, potentially due to their geochemical similarities, I observe complete sulfate removal (i.e. reduction) at similar depths (9-15 cm) at the North Marsh and Butano Marsh sites in both the closed and open states. This may be attributed to similar geochemical (i.e. DOC concentrations (15-25 mg L^{-1}) and organic carbon contents (1.5-5.2%) in sediment) and physical (mean grain size, clay and sand contents) conditions. However, I observe sulfate reduction at lower depths (>27 cm) at the Sandbar Lagoon site in the open state, yet no complete removal at the same site in the closed state; this may be due to lower DOC concentrations and low sediment organic carbon substrates (<1.1%). I also observe the opposite trend for the River Confluence site with complete sulfate removal in bottom sediment pore water in the closed state but not in the open state, confirming that physical and geochemical differences can shape sulfur cycling in bar-built estuaries.

The presence of aqueous hydrogen sulfide and ferrous iron, especially in larger average concentrations (>34 μM) than sulfate and ferric iron concentrations, and of sediment AVS and iron contents suggest a solid-phase sink for sulfur and iron to iron sulfide precipitates in sediment in the Pescadero Estuary. Relative to hydrogen sulfide concentrations, the low ferrous iron

concentrations indicate that it is often the limiting reagent in iron sulfide precipitation as a dominant pathway (Neal et al., 2001; Ulrich and Sedlak, 2010). A mass balance analysis of sulfur in pore water in surface sediments (<12 cm) indicate that up to 37% of produced hydrogen sulfide remains in pore water relative to sulfate concentration, reflecting that the remainder (>63%) likely precipitates in sediment. The black deposits observed on all nitrocellulose membrane filters likely correspond to iron monosulfide (FeS) and other metal sulfide precipitates, as observed elsewhere (Hyacinthe and Van Cappellen, 2004). While the hypothetical explanations do not account for diffusion to the bulk water column or volatilization (which, based on pore water pH is minor), these estimates confirm the sheer magnitude of sulfide precipitation into sediment at Pescadero (Richards and Pallud, 2016). Furthermore, the ample sulfate and hydrogen sulfide in open state pore water and AVS in sediment verify that sulfur is repetitively reduced and oxidized.

The low average concentrations of DOC (<15 ppm), DIC (<130 ppm), hydrogen sulfide (<85 µM), and ferrous iron (<44 µM) observed at the Sandbar Lagoon site in both open and closed states suggest that sulfate reduction and sulfide precipitation are more limited there than at the other three study sites. The low AVS contents (<16 mmol kg^{-1}) corroborate limited sulfide precipitation there. The presence of sulfate in bottom sediment pore water further supports that reduction rates are lower in the closed state than in the open state, where no sulfate is observed below a depth of 25 cm. This is consistent with the previous observations (Richards and Pallud, 2016) at the Sandbar Lagoon site, where greater maximum sulfate reduction rates were observed in open state than the closed state.

Sulfate reduction at the nearby River Confluence site may be limited by hydrogen sulfide, whose higher concentrations may not be conducive for SRB activity (Reis et al., 1992); however sulfate reduction is not limited by DOC, which is also highest (25.1±9.0 mg L^{-1}) at that site. Moreover, iron sulfide production is limited by ferrous iron which is lowest (<5 µM) there. In contrast, the relatively constant sulfate concentrations (9.3±1.2 mM) and lower hydrogen sulfide concentrations (<155 µM) observed at the River Confluence site in the open state indicates that suboxic conditions and sulfate-rich marine water ultimately control sulfur cycling observed in the pore water column. In combination with low ferrous iron concentrations (2.3±1.1 µM) in the closed state, sediment iron contents are not as high there as at the North Marsh and Butano Marsh.

The observed sulfate and DOC concentrations and organic carbon at the North Marsh and Butano Marsh sites indicate that sulfate reduction is not limited there in the closed state. Furthermore, the mildly alkaline pore water pH and lower hydrogen sulfide concentrations in the closed state are also conducive to SRB growth and activity at those sites (Reis et al., 1992; Fauque, 1995). The high sediment contents of AVS (>22 mmol kg^{-1}) and iron (>36 mmol kg^{-1}) suggest no potential limitations on sulfide precipitation at the North Marsh and Butano Marsh sites in both closed and open states, as previously observed in the Pescadero Estuary (Richards and Pallud, 2016). Increases in sulfate, DOC, DIC, hydrogen sulfide, and ferrous iron concentrations in the open state indicate no limitations on sulfate reduction nor sulfide precipitation at the North Marsh and Butano Marsh sites, whose AVS contents increase from closed to open state.

The similar chloride concentrations observed across the closed state hints at constant diffusion into bottom sediment pore water and therefore no limitations on diffusion at all sites; despite larger concentrations and variable trends, constant diffusion is also suggested for the open

state. Chloride is a conservative element, with solely marine inputs, and chloride depth profiles are spatially molded by marine saline water, riverine fresh water, and vertical density stratifications (Allen et al., 2006). The similar patterns of chloride and sulfate decreasing with depth in the open state suggests both hydrological (i.e. dilution by rainfall) and biogeochemical processes (i.e. reduction), explaining the correlation between the two.

The trend of larger values nearer to the ocean and smaller values farther from the ocean is observed for pore water sulfate in both states but not for chloride in the closed state. In fact, average chloride concentrations in the closed state are higher (156.0 ± 29.1 mM) at the North Marsh and Butano Marsh sites, which are farthest from the ocean, than at the Sandbar Lagoon and River Confluence sites (121.9 ± 24.6 mM). This is attributed to the fact that sediments from North Marsh and Butano Marsh have higher clay contents and lower average grain sizes than the other two sites (Richards and Pallud, 2016), and consequently could retain greater concentrations of salts. Moreover, these fine-grained sediments have a higher propensity to retain greater concentrations of metal sulfides and heavy metals (Morse, 1999), suggesting that these sites have greater AVS and iron contents than sites with coarse-textured sediments.

4.3. Sulfur-fueled iron redox cycling

The Fe^{2+}/H_2S molar ratios showed that iron reduction predominates at the North Marsh site and operates simultaneous with sulfate reduction at the Sandbar Lagoon and River Confluence sites (Figure 2.8). While microbial sulfate reduction is the dominant anaerobic respiration pathway in Pescadero Estuary sediments, both microbial and abiotic iron reduction are also dominant pathways despite their higher position on the redox tower (Coleman et al., 1993; Weber et al., 2006; Melton et al., 2014; Hansel et al., 2015). The abiotic reduction of ferric iron oxides to ferrous iron by bisulfide (HS^-) suggested by Hansel et al. (2015) may possibly occur at Pescadero due to high bisulfide concentration (up to 264 µM) at the circumneutral to mildly alkaline pH values observed in the closed and open states. Iron concentrations at all sites in the closed states are low (<70 µM) due to abiotic reduction of ferric iron oxides by hydrogen sulfide to iron sulfide precipitates in sediment, preventing the release of both constituents to overlying water (Melton et al., 2014). In bottom sediment where sulfate is largely absent, the high ferrous iron and DIC concentrations imply the oxidation of organic matter substrates coupled with Fe(III) reduction and explains the negative correlation observed between DIC and sulfate. This is consistent with Chapelle and Lovley (1992) who found a positive correlation between DIC and ferrous iron.

The high ferrous iron concentrations observed at all four study sites in bottom sediment suggest that sulfate-reducing bacteria (SRB) reduce iron oxides in subsurface environments, as observed in deep coastal sediments (Lovley et al., 1993), leading to the production of iron sulfides in the Pescadero Estuary and also in mine sediments (Fortin et al., 1996). Moreover, the higher ferrous iron concentrations observed in bottom sediment than in surface sediment indicates that SRB may enzymatically reduce ferric iron oxides in the absence of sulfate and is consistent with Li et al. (2006) and Hansel et al. (2015). Compared to the River Confluence site, the lower sediment AVS contents and higher DIC concentrations observed at the North Marsh and Butano

Marsh sites suggest that sulfate-reducing bacteria drive the microbial reduction of iron through enzymatic reaction, forming siderite ($FeCO_3$) instead of iron sulfides (Coleman et al., 1993).

Compared to the closed state, the open state was also characterized by slight increases in ferric iron and significant increases in ferrous iron, which may be attributed to oxidizing conditions that couple iron sulfide oxidation with ferric iron oxide reduction, producing sulfate (Schippers and Jørgensen, 2002). Relative to ferrous iron, the low ferric iron concentrations may be due to low water solubility and mildly alkaline pH values (Byrne and Kester, 1976; DeLaune and Patrick, Jr., 1981); however, the high iron contents indicate that ferric oxides are widely available in Pescadero sediment. Moreover, in agreement with Hansel et al. (2015), these results demonstrate that the microbial re-cycling of sulfur species drives the redox cycling of iron, reinforcing the interplay between iron and sulfur in estuarine sediments.

4.4. The effects of sulfur and iron redox cycling on pH

The circumneutral to mildly alkaline pH (7.2-8.5) observed in the closed state at all sites indicates that microbial sulfate reduction and iron reduction consume protons and cause basification (Hines et al., 1989; Chapelle et al., 2009; Duarte et al., 2013). Mass balance analysis shows that hydrogen sulfide production and ferrous iron production consume protons in 2:1 molar ratios of protons to hydrogen sulfide and ferrous iron (Chapelle et al., 2009). These ratios indicate that pore water pH can potentially increase by up 2 units, leading to the alkaline values observed in the closed state.

After nearly nine months in the closed state, Pescadero Estuary reopened in December 2015, altering the geochemistry of the sediment pore water. Compared to the closed state, the open state was consistent with observed surface sediment increases in sulfate concentration up by ~5 mM, chloride concentration by ~158 mM, salinity by 10‰, total iron by up to 100 µM, and decreases in pH by <1 unit across all four sites. Higher sulfate and chloride concentrations observed in the open state than the closed state partly result from the influx of sulfate-rich, saline marine water during the open state. However, increases in sulfate and dissolved iron concentration and decreases in pH may collectively be attributed to the oxidation of aqueous hydrogen sulfides and metal sulfides in sediment (Schippers and Jørgensen, 2002; Burton et al., 2006; Burton et al., 2009; Morgan et al., 2012).

The oxidation of aqueous hydrogen sulfide and dissolved iron produce 2:1 and 8:1 molar ratios of protons to hydrogen sulfide and dissolved iron (Chen and Morris, 1972), potentially leading to zones of moderately acidic pore water pH values. Yet, despite their removal of oxygen and production of acid, iron sulfide precipitates have more critical effects on estuarine conditions than their aqueous counterparts (Simpson et al., 1998; Maddock et al., 2007; Hong et al., 2011). The oxidation of mackinawite (FeS) or pyrite (FeS_2) as coupled with oxygen reduction produces 2:1 protons to the iron sulfide, whereas the oxidation of both iron sulfides coupled with ferric iron reduction produces 8:1 or 16:1 protons to mackinawite or pyrite, respectively (Taylor et al., 1984; Moses et al., 1987; Schippers and Jørgensen, 2002; Jørgensen et al., 2009), leading to strongly acidic pore water. Moreover, acidification exacerbates sulfide toxicity (Wang and Chapman, 1999) and increases metal dissolution (Cusimano et al., 1986; Burton et al., 2006; Weber et al., 2006),

leading to further sulfide re-oxidation and severe oxygen consumption, leading to anoxia (Sammut et al., 1996; Bush et al., 2004). Since the presence of hydrogen sulfide and ferrous iron in the open state indicates suboxic conditions, I suggest that iron sulfide oxidation coupled with ferric iron reduction predominates in the Pescadero Estuary.

The influx of alkaline marine water in the open state may buffer the potentially acidic pore water resulting from metal sulfide oxidation, leading to the circumneutral values observed in the Pescadero Estuary at all four sites. DIC acts as a buffering agent for acidic pore water resulting from sulfide oxidation, therefore potentially lowering its concentration in pore water. Riverine and intertidal marsh inputs of DIC into the Pescadero Estuary may explain the pore water increases in DIC from closed to open state. In contrast with salinity, I observe a gradient in DIC concentrations, increasing from ocean to freshwater, which act as evidence of freshwater plumes into Pescadero Estuary during the transition from closed to open states. The higher average DIC concentrations (>170 mg L^{-1}) observed at the North Marsh and Butano Marsh sites may explain small decrease in pore water pH (by ~0.3 units) at those sites. The lower DIC concentrations (<130 mg L^{-1}) observed at the Sandbar Lagoon site may also explain the larger decrease (by ~0.5 units) observed there. Combined with the influx of alkaline marine water, the circumneutral pH values in surface and bottom sediment pore waters, however, suggest a balance between anaerobic sulfate and iron reduction and iron sulfide oxidation that cause basification (Duarte et al., 2013) and acidification (Simpson et al., 1998; Burton et al., 2006), respectively.

5. Conclusions

Sulfur cycling in the bar-built Pescadero Estuary is a biogeochemical cycle driven by redox processes and also in part by ion transport exchange with fresh and marine water, carbon mineralization, and metal cycling. The ample pools of dissolved organic and inorganic carbon and sediment organic substrates reveal no constraints on the oxidation of organic matter substrates for redox cycling. At Pescadero, sulfate reduction is the dominant anaerobic respiration pathway; this chemically reduced constituent (H_2S) and microbial reducers are believed to drive iron reduction. The sediment pore water analyses measured in the Pescadero Estuary during the closed and open states show that both microbial sulfate and iron (III) reduction occur mutually to form their reduced counterparts. The absence of nitrate and presence of hydrogen sulfide and ferrous iron indicate hypoxic or anoxic, reducing conditions. In combination, these reduced constituents form iron sulfide precipitates, as observed in the Pescadero Estuary (Richards and Pallud, 2016) and in coastal marine sediments (Canfield et al., 1993; Thamdrup et al., 1994; Charette and Sholkovitz, 2006). The oxidative effects of iron sulfide precipitates are much more severe for pH and metal concentrations than observed in the study system (Burton et al., 2006; Hong et al., 2011). In the Pescadero Estuary, I show the increase in pore water pH due to reductive processes and decrease in pore water pH due to oxidative processes, the latter which can be achieved with iron oxides under suboxic conditions.

These pore water profiles point to spatially and temporally (seasonally) cyclic variations in the cycling of sulfur, iron, and carbon in sediment, as dominated by sulfate reduction and sulfide oxidation. Occurring in the open state, the oxidation of aqueous sulfides and sulfide precipitates

indirectly results in suboxic, circumneutral conditions with large metal concentrations up to 100 µM. Compared to the oxidative effects of iron sulfide precipitates, the oxidative effects of aqueous hydrogen sulfide are minor. However, the effects in pore water pH are minimal due to mixing with alkaline ocean water and the high buffering capacity of DIC, whose pore water values show a gradient from freshwater and fine-grained sediments to ocean and coarser-grained sediments, ultimately limiting pH damage to vulnerable regions of the bar-built system.

6. Acknowledgements

7. References

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Chapter 3

Kinetics of sulfate reduction and sulfide precipitation rates in sediments of a bar-built estuary (Pescadero, California)

Abstract – The bar-built Pescadero Estuary in Northern California is a major fish rearing habitat, though recently threatened by near-annual fish kill events, which occur when the estuary transitions from closed to open state. The direct and indirect effects of hydrogen sulfide are suspected to play a role in these mortalities, but the spatial variability of hydrogen sulfide production and its link to fish kills remains poorly understood. Using flow-through reactors containing intact littoral sediment slices, I measured potential sulfate reduction rates, kinetic parameters of microbial sulfate reduction (R_{max}, the maximum sulfate reduction rate, and K_m, the half-saturation constant for sulfate), potential sulfide precipitation rates, and potential hydrogen sulfide export rates to water at four sites in the closed and open states. At all sites, the Michaelis-Menten kinetic rate equation adequately describes the utilization of sulfate by the complex resident microbial communities. I estimate that 94-96% of hydrogen sulfide produced through sulfate reduction precipitates in the sediment and that only 4-6% is exported to water, suggesting that elevated sulfide concentrations in water, which would affect fish through toxicity and oxygen consumption, cannot be responsible for fish deaths. However, the indirect effects of sulfide precipitates, which chemically deplete, contaminate, and acidify the water column during sediment re-suspension and re-oxidation in the transition from closed to open state, can be implicated in fish mortalities at Pescadero Estuary.

1. Introduction

At the interface between terrestrial, freshwater, and marine ecosystems, intermittent, or bar-built, estuaries, are dynamic environments characterized by the aperiodic formation of a sandbar at the estuary's mouth separating it from the ocean during periods of low rainfall (McKenzie et al., 2011). Intermittent estuaries constitute 13% of the world's coastline and are common in Mediterranean climate regions, representing about 70% of South African estuaries (Whitfield, 1992; Lawrie et al., 2010), 49% of southeast Australian estuaries (Griffiths and West, 1999; Roy et al., 2001), and 18% of the North American coastline (Barnes, 1980), including 75% of estuaries along the California coast (Emmett et al. 2000; Fong and Kennison 2010). Intermittent estuaries function as productive watersheds with high biotic diversity (Bianchi, 2007) and riparian zones to reduce nutrient and contaminant loads (Naiman and Decamps, 1997; Verhoeven et al., 2006). Such spatially and temporally complex systems are also productive nursery habitats and breeding grounds for economically and ecologically important aquatic species (Gillanders et al., 2011; Seghesio, 2011). However, intermittent estuaries frequently experience dramatic changes in physical, biological, and geochemical conditions that can be stressful for their inhabitants (Pollard, 1994; Griffiths, 2001). During the open state, tides carry marine water into the estuary, whereas during the closed state, the estuarine channel is flooded with freshwater and transforms into a

lagoon (Whitfield et al., 2008). During the closed state, the epilimnion is characterized by oxic freshwater with high densities of fish, that with depth, transitions to a hypoxic or anoxic, brackish hypolimnion (Breitburg, 2002; Whitfield et al., 2008; Seghesio, 2011). The opening of the estuary's mouth is caused by an anthropogenic (artificial) or natural (rainfall) breach of the sandbar, leading to drainage of the estuary (Roy et al., 2001), water mixing, sediment re-suspension (Breitburg, 2002; Gillanders et al., 2011), and tidal flushing (Demers et al., 1987; Griffiths and West, 1999).

In intermittent estuaries around the world, the transition from closed to open state is often accompanied by fish kills (Bennett et al., 1985; Whitfield, 1995; Sloan, 2006; Martin et al., 2007; Becker et al., 2009; Atkinson, 2010). Although there are multiple causes to the kill events (Whitfield 1995), including salt, pH, and temperature stresses, the fish kills may result from the indirect (removal of dissolved oxygen) and direct (acute toxicity) effects of hydrogen sulfide; however, these are rarely studied collectively (Bagarinao and Lantin-Olaguer, 1998; Luther et al., 2004). Moreover, the effects of anoxia and hydrogen sulfide generally occur jointly and therefore are difficult to isolate (Diaz and Rosenberg, 1995). Oxygen depletions adversely influence physical habitat availability, osmoregulation, reproductive capacity, and susceptibility to disease for many fish (Bennett et al., 1985; Borsuk et al., 2001). Hydrogen sulfide in seawater adversely affects fish physiology and respiratory systems and is lethal for steelhead counterparts, milkfish, and tilapia at concentrations above 30µM after 2 hours (Bagarinao and Lantin-Olaguer, 1998).

A "fast-acting labile and non-cumulative poison" (Bagarinao and Lantin-Olaguer, 1998), hydrogen sulfide is a predominant sulfur form under acidic and highly reducing conditions and is acutely toxic (Beauchamp et al., 1984; Reiffenstein et al., 1992). Hydrogen sulfide is produced through microbial sulfate reduction, which couples the oxidation of organic matter with the reduction of sulfate to hydrogen sulfide (Boudreau and Westrich, 1984; Howarth, 1984). Electron donors for sulfate reducers range from H_2 to acetate, lactate, and pyruvate, compounds ubiquitous in anoxic environments (Widdel, 1988). The produced hydrogen sulfide can undergo volatilization under acidic conditions, dissociation to bisulfide (HS^-) and sulfide (S^{2-}) under alkaline conditions, or precipitation into poorly mobile metal sulfides (FeS, FeS_2, As_2S_3, and ZnS) (Morse et al., 1987; Reiffenstein et al., 1992; Billon et al., 2001). Chemical and biological sulfide oxidation occurs in oxic and suboxic environments, coupling the oxidation of hydrogen sulfide and metal sulfides with the reduction of dissolved oxygen, nitrate, or iron oxides in re-suspended sediments, leading to severe acidification (Wilson et al., 1999; Burton et al., 2006; Du Laing et al., 2009) and toxification of the pore water and water column (Luther et al., 1982; Thamdrup et al., 1994; Schippers and Jørgensen, 2002). The combined effects of hydrogen sulfide can be implicated in fish kills through direct acute toxicity, indirect removal of dissolved oxygen, and indirect re-oxidation of hydrogen sulfide and its metal precipitates, which lead to sediment contamination, further oxygen depletion, and severe acidification (Bagarinao and Lantin-Olaguer 1998).

In order to develop and calibrate predictive models of hydrogen sulfide export to water, data on sulfate reduction rates and kinetics, specifically sulfate half-saturation concentrations (K_m) and maximum reduction rates (R_{max}), that are relevant to field conditions are required. In marine sediments with high sulfate concentration (23-30 mM), K_m values for sulfate range broadly from 0.1 to 3 mM (Roychoudhury et al., 2003; Pallud and Van Cappellen, 2006), which contrasts starkly

from the K_m values observed for freshwater sediments (0.02-0.18 mM) where sulfate concentrations are lower (0.01-0.8 mM) (Smith and Klug, 1981; Roden and Tuttle, 1993; Urban et al., 1994; Pallud and Van Cappellen, 2006; Tarpgaard et al., 2011). The low K_m values derived from freshwater sediments suggest that their inhibiting sulfate-reducing bacteria hold a high affinity for sulfate and are notably adaptive to sulfate (Tarpgaard et al., 2011). Interestingly, the highest K_m values (3.5-7.5 mM) reported for natural environments were measured on coastal aquifer sediments with low sulfate concentration (1.1-1.4 mM) using slurry incubations (Roychoudhury and McCormick, 2006). The R_{max} reported for sulfate reduction in sediments range by 5 orders of magnitude, reflecting, in part, the use of three different experimental approaches to determine them. The R_{max} range from 0.96 to 127 nmol cm^{-3} h^{-1} for an array of freshwater surface sediments (Smith and Klug, 1981; Urban et al., 1994; Pallud and Van Cappellen, 2006; Roychoudhury and McCormick, 2006) and from 0.003 to 118.6 nmol cm^{-3} h^{-1} for estuarine and marine surface sediments (Boudreau and Westrich, 1984; Roden and Tuttle, 1993; Roychoudhury et al., 1998; Roychoudhury et al., 2003; Pallud and Van Cappellen, 2006; Tarpgaard et al., 2011).

I investigated the temporal and spatial variability in sulfate reduction kinetics in sediment and hydrogen sulfide export to water in the Pescadero Estuary (USA), where fish kills occur almost annually with the aperiodic breaching of the sandbar closure (Swenson, 1999; Smith, 2004; Sloan, 2006). Specifically, I measured the kinetics of microbial sulfate reduction and potential hydrogen sulfide export rates using flow-through reactor experiments containing intact slices of sediments from the closed and open states. I also measured the major physical, biological, and geochemical water and sediment characteristics in both states at four littoral sites that constitute a gradient from the ocean to freshwater regions of the estuary, including the Butano Marsh where most of the fish kills were observed in the past. The results indicate a very high potential for sulfate reduction throughout the estuary, with only a minor potential export of hydrogen sulfide to water, yet sulfide precipitation in sediment can have adverse implications for both sediment and water in the Pescadero Estuary.

2. Materials and Methods

2.1. Study sites

Pescadero Estuary is the largest coastal bar-built estuary (1.3 km^2) between San Francisco and Santa Cruz (Figure 3.1). The Pescadero-Butano watershed is an intricate spawning habitat and critical nursery to native, migratory, and endangered communities of fish wildlife, including tens of thousands of near-threatened Pacific steelhead trout (Viollis, 1979; Allen et al., 2006). Although not unique to Pescadero, these critical kill events have been more regular there than in other nearby California estuaries (Sloan, 2006; Martin et al., 2007; Atkinson, 2010; Merz et al., 2011). As a result, in 1998, Pescadero was included in the California Clean Water Act section 303(d) list of impaired waters for its environmental impairments to the steelhead trout population (US-EPA, 1998). Situated at the confluence of the Pescadero and Butano Creeks (Figure 3. 1), the estuary is a complex ecosystem bordering a wooded riparian zone inhabited by coastal scrub plant communities (Bozkurt-Frucht, 2013). With agricultural development, Pescadero suffered state-mandated drainage, channelization, logging, and sedimentation in the 18th and 19th centuries
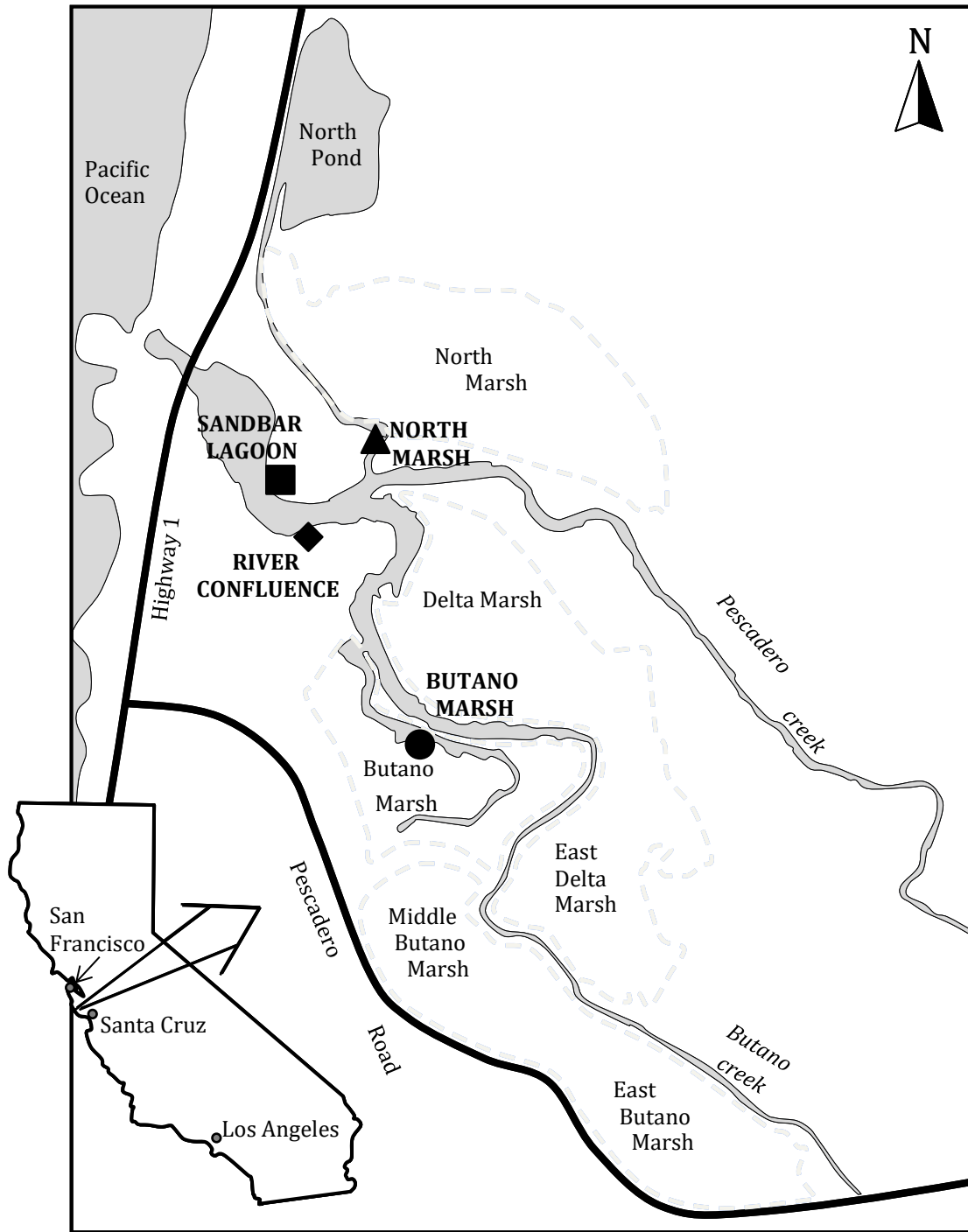
Figure 3.1. Map showing the location of the Pescadero Estuary in California and of the four littoral sites sampled in August 2013 (closed state) and February 2014 (open state). The sites are comprised of the Sandbar Lagoon (square), North Marsh (triangle), River Confluence (diamond), and Butano Marsh (circle).

(Viollis, 1979), followed by urban development, poor operational practices, specifically severe drainage and channelization, and inconsistent hydrological and geomorphological management in

the 1980s and 1990s (Coats et al., 1989).

Sulfate at Pescadero Estuary originates from the Pacific Ocean, entering in the open state at high concentrations (24-28 mM) in the overlying water (Howarth, 1984; Bianchi, 2007) and decreasing to low concentrations (0.5-6 mM) in the closed state. Sulfate concentrations in sediment pore water have not been reported yet for Pescadero Estuary; however, they are likely an order of magnitude lower than in the overlying water, as observed in range of freshwater to marine sediments (Goldhaber and Kaplan, 1976; Holmer and Kristensen, 1996; Marvin-DiPasquale et al., 2003; Weston et al., 2006). Sulfate reduction is thought to be the dominant terminal electron accepting process in Pescadero sediment, due to low dissolved oxygen, nitrate (NO_3^-), and iron oxide concentrations (i.e. less than 156 µM, 20 µM, and 519 mmol kg^{-1}, respectively) (Jørgensen, 1982; Bostick et al., 2004; Sloan, 2006; Laverman et al., 2012).

Four sampling sites that span the estuarine region and represent a salinity gradient were compared around the littoral zone of Pescadero Estuary (Figure 3.1) during the estuary's closed and open states. The Sandbar Lagoon site (coordinates: N37.26393°, W122.40937°) is the closest site to the ocean and sandbar. The River Confluence site (N37.26293°, W122.40913°) is located in a shallow marshy inlet near the separation of the Butano and Pescadero Creeks. The North Marsh site (N37.26486°, W122.40673°) is located in an inlet adjacent to the eponymic marshland, and the Butano Marsh site (N37.25937°, W122.40633°) is located in the south channel of the Butano Creek in the estuary. Since 1995, fish die-offs have occurred in the River Confluence, North Marsh, and Butano Marsh sites.

2.2. Field sampling

Sediment and overlying water were sampled at the four study sites in August 2013 (four months after the estuary closed) and February 2014 (less than a month after the estuary opened). At each site, four intact cores (4.7 cm inner diameter, 2 cm length) of surface sediment were collected in Plexiglas rings about a meter from the shoreline in the non-vegetated channel in water depths of 30-55 cm. Overlying water was collected at each of the sampling sites before sediment sampling. All samples were transported and stored at 4°C in sealed anoxic bags until the analyses and experiments were performed.

2.3. Physical and geochemical characterization of the overlying water

Water pH was measured using a pH/ATC electrode (high performance glass-body Sartorius ATC combination electrode) and meter (Denver Instrument, Model 215). Conductivity was measured with an OAKTON CON6/TDS 6 hand-held conductivity/TDS meter (Eutech Instruments, USA). Chloride and sulfate concentrations were measured using a Dionex ion chromatograph (IC) (electrochemical detector, ED40; analytical column, AS23/AG23; anion self-regenerating suppressor, ASRS-I, 4 mm) supplied with a carbonate eluant (7.2 mM Na_2CO_3 and 1.28 mM $NaHCO_3$) at a flow rate of 1.0 mL min^{-1}. Total hydrogen sulfide concentration (2 mL solution combined with a sulfide anti-oxidant buffer (SAOB) trap of 1 M sodium hydroxide (NaOH) and 0.1 M ethylenediaminetetraacetic acid (EDTA)) was measured from potentials with

a pH/ISE electrode (Ionplus Sure-Flow silver/sulfide selective electrode) and meter (Thermo Scientific Orion Star A324). Detection limits for the IC and hydrogen sulfide electrode were 30 and 0.1 µM, respectively.

2.4. Physical, geochemical, and biological characterization of the sediment

Sediment dry bulk density (ρ_d) was calculated after drying a known volume of sediment for 24 hours at 105°C. Porosity (φ) was calculated from the dry bulk density and particle density (ρ_s estimated at 2.65 g cm^{-3}) as 1-(ρ_d/ρ_s). Sediment pH was measured as described above after 5 g sediment were suspended in a 10 mL solution of 10 mM CaCl$_2$ (Thomas, 1996). Total organic carbon (C_{org}) content and total nitrogen (N) content were measured on 30 mg of air-dried sediment samples after removal of inorganic carbon with 0.5 M FeSO$_4$-H$_2$SO$_4$ acid digestion solution over heat, followed by analysis using a NC 2100 Elemental Analyzer (CE instruments, USA). Mean particle size, as well as clay, silt, and sand percentages were obtained using a LISST-Portable|XR Particle Size Analyzer (Sequoia Scientific, USA) on 5 g oven-dried sediment samples following organic matter and carbonate removal with 3 mM hydrogen peroxide and 1 M hydrochloric acid, respectively. All measurements were performed in triplicate. Sediment porewater sulfate concentrations were measured on wet sediment by Delta Environmental Labs, LLC (Benicia, CA) using an EPA-certified method (SM 4500-SO4 E); the detection limit was 0.21 mmol kg^{-1}.

Total iron (Fe$_{tot}$) and acid-volatile sulfide (AVS) were extracted from sediments using a protocol adapted from Lovley and Phillips (1986), Simpson (2001), and van Griethuysen et al. (2002). This acid extraction method solubilizes various metal sulfides from sediments, primarily iron (II) sulfides (ex. crystalline and amorphous FeS), greigite (Fe$_3$S$_4$), pyrite (FeS$_2$), and heavy metal sulfides (Morse and Cornwell, 1987; Rickard and Morse, 2005). Anoxic, dried sediment samples (1-2 g) were combined with 20 mL of 1 M hydrochloric acid (HCl) sealed in an extraction chamber with a sulfide anti-oxidant buffer (SAOB) trap of 1 M NaOH and 0.1 M EDTA. After stirring for 2 hours at 21°C to allow equilibration of soluble iron in the acid fraction and soluble sulfide in the SAOB trap, total iron concentration was measured spectrophotometrically (Thermo Spectronic, 20 Genesys) with the ferrozine colorimetric method (Stookey, 1970) at 562 nm following 1:10 dilution with 1 M HCl (Porsch and Kappler, 2011), whereas the AVS concentration in the SAOB trap solution was measured with the methylene blue colorimetric method at 670 nm (Simpson, 2001). All measurements were performed in triplicate.

The abundance of sulfate-reducing bacteria (SRB) in sediment was estimated by the most probable number (MPN) method (Woomer, 1994) using the protocol of Pallud and Van Cappellen (2006). Five grams of wet sediment were suspended in 50 mL sterile brackish solution (342 mM NaCl, 32 mM MgCl$_2$) and shaken. Tenfold dilution series (eight replicates) were made directly in 96-well microtiter plates, using sodium sulfate as the electron acceptor and both acetate and lactate as electron donors. The culture medium consisted of 222 mM NaCl, 10 mM MgCl$_2$·6H$_2$O, 1 mM CaCl$_2$·2H$_2$O, 1.5 mM KH$_2$PO$_4$, 5 mM NH$_4$Cl, 4 mM KCl, 28 mM Na$_2$SO$_4$, 0.1 g L^{-1} yeast extract, 0.5 mg L^{-1} resazurine, 1 mL trace elements solution; the pH was adjusted to 7.0 followed by sterile addition of 30 mM NaHCO$_3$, 5 mM NaC$_2$H$_3$O$_2$, 5 mM NaC$_3$H$_6$O$_3$, and 1 g L^{-1} crystalline Na$_2$S$_2$O$_4$. A strong reducing agent, 0.5 mM mercaptoacetic acid, and 0.2 mM FeSO$_4$ were added to the

medium before dispensing it into well plates. The microtiter plates were incubated under anoxic conditions at 26°C in the dark for six weeks. The presence of sulfate-reducing bacteria was scored positive upon precipitation of black FeS as an indicator of hydrogen sulfide production.

2.5. Flow-through reactor (FTR) experiments

Flow-through reactor (FTR) experiments were performed in duplicate to measure the potential steady-state sulfate reduction rates (SRR) and hydrogen sulfide export rates (SER) in response to increasing sulfate concentrations and the kinetics of sulfate reduction. Each Plexiglas FTR cell (4.7 cm ID, 2 cm L) contained an intact core of sediment, with 0.2 µm pore size hydrophilic PVDF filters and glass fiber filters at each end. The reactors were sealed with Plexiglas caps kept in place using steel screws, while O-rings prevented leakage. The experiments were conducted inside a glove box under anoxic conditions (97% N_2, 3% H_2) at constant temperature (25°C). An inflow solution was supplied to the reactors at constant volumetric flow rate (1.9±0.5 mL h^{-1}) with a peristaltic pump. Each FTR was supplied with six successive inflow sulfate concentrations for four days each to reach steady-state of sulfate in the outflow. The inflow solutions (pH 7) contained sodium sulfate (Na_2SO_4) (concentrations: 0.2, 0.5, 1.0, 2.0, 3.0, 4.0 mM) and 34 mM (closed state) or 76 mM (open state) NaCl to simulate the salinity conditions of Pescadero water. The inflow sulfate concentrations were chosen to cover field values, and the highest concentrations were well above previously-reported K_m for sulfate in freshwater to marine sediments (Roychoudhury et al., 2003; Pallud and Van Cappellen, 2006; Tarpgaard et al., 2011) in order to reach maximum rates of sulfate reduction. Inflow solutions were purged with O_2-free N_2. Outflow samples were collected for 6 hours in tubes pre-filled with 2 mL of sulfide trap solution (46 mM zinc acetate) to prevent hydrogen sulfide re-oxidation. Anions (Cl$^-$ and SO_4^{2-}) and hydrogen sulfide concentrations in outflow samples were analyzed using an IC and sulfide electrode, respectively as described earlier for water samples. Sulfate and hydrogen sulfide breakthrough curves (outflow concentrations as a function of time) were used to determine steady-state sulfate reduction rates (SRR) and sulfide export rate (SER), as described below. Detailed descriptions of the flow-through reactor (FTR) design and the determination of potential rates can be found elsewhere (Roychoudhury et al., 1998; Laverman et al., 2006; Pallud and Van Cappellen, 2006; Pallud et al., 2007).

2.6. Determination of potential steady-state sulfate reduction rates, sulfide export rates, and sulfide precipitation rates

Potential steady-state sulfate reduction rates (SRR) were calculated as:

$$SRR = \frac{(C_{out} - C_0) \cdot Q}{V} \qquad (1),$$

where C_{out} is the steady-state outflow sulfate concentration, C_0 represents the imposed inflow sulfate concentration, Q is the volumetric flow rate, and V is the volume of sediment in the FTR. The SRR obtained with the FTR are referred to as "potential" rates because they correspond to

sulfate reduction activities when the sole terminal electron acceptor supplied to the sediment microbial community is sulfate (Pallud and Van Cappellen, 2006).

Potential steady-state hydrogen sulfide export rates (SER), which represent the fraction of hydrogen sulfide exported from the sediment in the FTR outflow, were calculated as:

$$SER = \frac{C_{out} \cdot Q}{V} \tag{2},$$

with C_{out} representing the average outflow hydrogen sulfide concentration.

Due to highly insoluble precipitates of metal sulfide in sediment, sulfide precipitation rates (SPR), which represent the rates of sulfide precipitation in sediment, were estimated with reaction stoichiometry by first calculating the amount of hydrogen sulfide produced from the SRR measurements, followed by calculation of the difference between SRR and measured SER to estimate the amount of hydrogen sulfide retained in sediment.

2.7. Kinetic parameters of sulfate reduction

The dependence of SRR on the sulfate concentration follows the Michaelis-Menten rate equation in freshwater to marine sediments (Pallud and Van Cappellen, 2006):

$$SRR = \frac{R_{max} C}{K_m + C} \tag{3},$$

where R_{max} is the maximum sulfate reduction rate, K_m is the half-saturation constant of sulfate, and C is the variable sulfate concentration. Pallud et al. (2007) showed that the average steady-state sulfate concentration in the FTR can be approximated as the midpoint between inflow and outflow concentrations when less than 50% of the sulfate provided is consumed, which is the case here. The rate parameters R_{max} and K_m were obtained for each FTR experiment from the steady-state SRR calculated with Eq. (3), and the average, steady-state sulfate concentrations by performing a non-linear regression fit of the Michaelis-Menten expression to the data, using the KaleidaGraph software.

2.8 Statistical analysis

The statistical significance of differences between sites for water and sediment characteristics, reaction rates, and kinetic parameters was determined by one-way ANOVA with a significance threshold of alpha = 0.05. Correlations between water and sediment characteristics, reaction rates, and kinetic parameters were evaluated using Pearson's correlation coefficient with a correlation threshold of r = ±0.9. Reported uncertainty ranges are ±1 standard deviation unless otherwise stated. The statistical analysis was performed with the EZAnalyze package.

3. Results

3.1 Physical and geochemical water characteristics

The physical and geochemical characteristics of the water sampled at the four study sites in the closed and open states are shown in Table 3.1 and Figure 3.2. Water sulfate concentrations ranged between 0.5 and 1.1 mM in the closed state, with the lowest values observed at the Sandbar Lagoon and Butano Marsh sites and the highest values at the North Marsh and River Confluence sites. Water sulfate concentrations were larger during the open state, ranging from 1.0 mM at the River Confluence site to 9.3 mM at the North Marsh site (9.3 mM) (Figure 3.2). Total hydrogen sulfide concentrations in water were lower in the open state (0.6-0.8 µM) than in the closed state, when they vary greatly from 1.1 to 41.1 µM. Chloride concentration ranged between 31.7 and 56.1 mM in the closed state, with the lowest values observed at the North Marsh, Butano Marsh, and River Confluence sites, but were slightly higher in the open state, ranging between 28.0 and 255.4 mM. Chloride concentration in the open state was positively correlated with sulfate concentration ($r = 0.95$, $P < 0.05$). Similarly, conductivity ranged from 10.4 to 17.3 mS cm^{-1} in the closed state, with the highest value observed at the Sandbar Lagoon site, as compared to 9.1 to 19.3 mS cm^{-1} in the open state, with the highest values observed at the North Marsh and Sandbar Lagoon sites. Water chloride concentration and conductivity, which are both indicators of salinity and positively correlated in the closed state ($r = 0.98$, $P < 0.05$) showed a decreasing trend observed on a gradient from the Pacific Ocean to the Butano Creek. Water pH varied only slightly between sites and was circumneutral in the closed state (6.7-7.3) and slightly alkaline in the open state (7.7-8.2).

3.2. Physical, geochemical, and biological sediment characteristics

The physical, geochemical, and biological characteristics of the sediment sampled at the four study sites in the closed and open states are shown in Table 3.1 and Figure 3.2. The sediments ranged in texture from silt loam, with an average grain size of 9-15 µm, high clay content (>11%), and low sand content (<22%) at the Butano Marsh site, to sandy loam, with an average grain size of 36-74 µm, low clay content (<7%), and high sand content (>52%) at the Sandbar Lagoon site. The sediment's texture at the remaining sites changed over time, with a finer texture observed during the open state than the closed state for the North Marsh, and an opposite trend observed for the River Confluence site. In the closed and open states, sand content was positively correlated with average grain size (closed: $r = 0.99$, $P < 0.01$; open: $r = 0.97$, $P < 0.05$). Sediment porosity was similar in the closed and open states, ranging from 0.58 to 0.84. In the closed state, sediment porewater sulfate concentration ranged from below detection limit for the North Marsh and River Confluence sites to 1.4 mmol kg^{-1} dry sediment at the Butano Marsh site. Acid-volatile sulfide (AVS) content in sediment ranged from 49.7 mmol kg^{-1} dry sediment at the Sandbar Lagoon site to 87.2-89.8 mmol kg^{-1} dry sediment at the North Marsh and Butano Marsh sites in the closed state; however, AVS content decreased to 8.6-29.6 mmol kg^{-1} dry sediment in the open state. In the closed state, AVS content was negatively correlated with chloride concentration ($r = -0.99$, $P < 0.001$) and conductivity ($r = -0.99$, $P < 0.05$). Conversely, in the open state, AVS content was
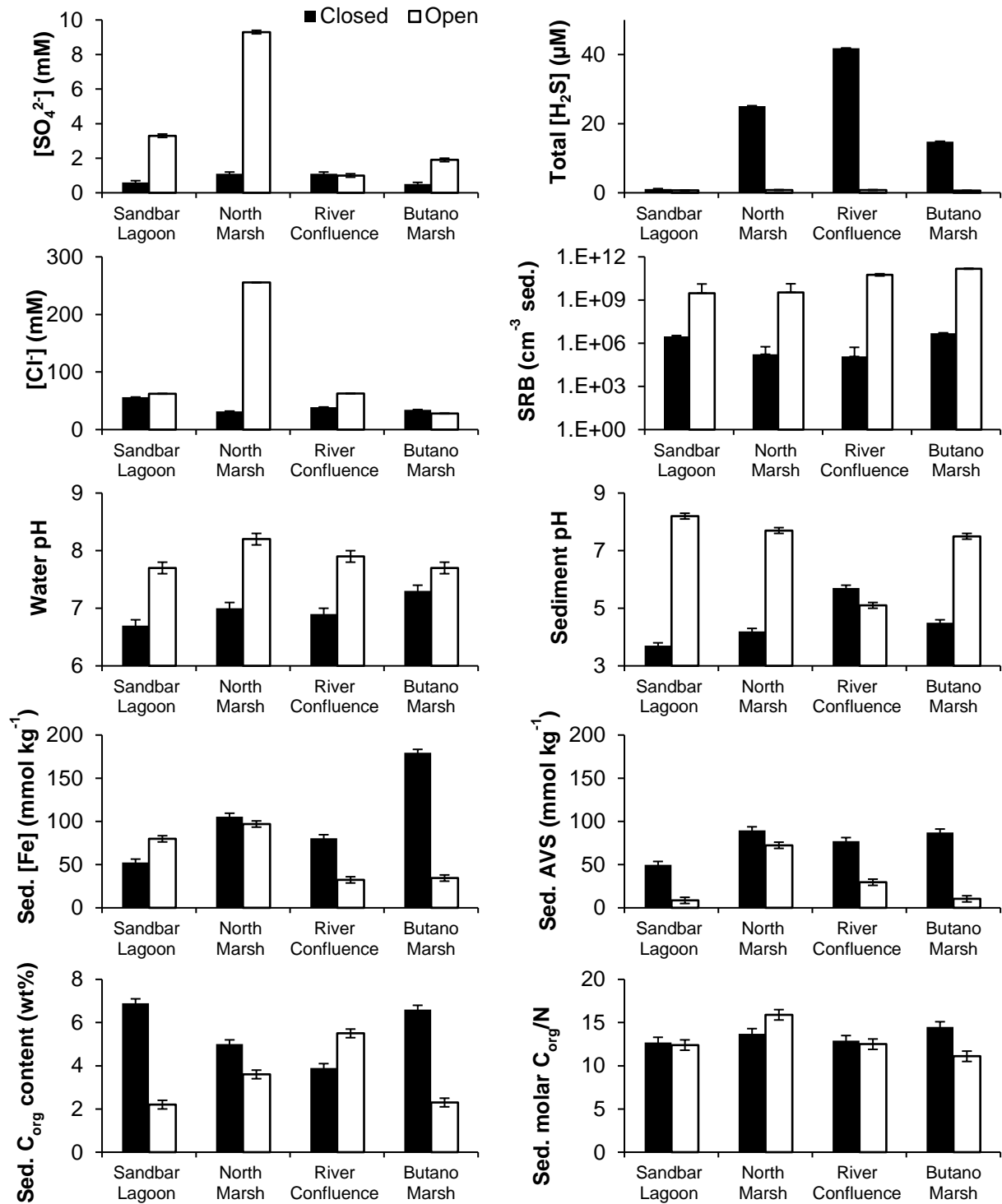
Figure 3.2. Geochemical and biological water and sediment characteristics of the four study sites in the closed state (August 2013) (solid bars) and open state (February 2014) (white bars). Error bars indicate standard deviation; when not visible, they fall within the size of the symbols. Sed. indicates sediment characteristics.

positively correlated with chloride concentration ($r = 0.96$, P < 0.05) and water pH ($r = 0.99$, P <

Table 3.1. Physical and geochemical water and sediment characteristics of the four study sites in the closed state (August 2013) and open state (February 2014). nd indicates no data. bdl indicates measurements below detection limits.

Site	Water		Sediment					
	Conductivity (mS cm^{-1})	[SO$_4^{2-}$] (mmol kg^{-1})	N content (wt%)	Porosity (%)	Mean grain size (µm)	Clay (wt%)	Sand (wt%)	Texture
Closed state								
Sandbar Lagoon	17.3±0.3	0.49 ±0.02	0.54±0.03	0.67	74.0±20.6	2.9±0.9	78.1±6.5	Sandy loam
North Marsh	11.2±0.2	bdl	0.36±0.02	0.71	48.1±12.5	3.5±0.9	50.3±2.7	Loam
River Confluence	12.7±0.2	bdl	0.30±0.01	0.65	10.6±0.7	11.1±0.2	7.8±2.7	Silt loam
Butano Marsh	10.4±0.2	1.4 ±0.06	0.46±0.03	0.82	14.9±2.6	13.0±0.8	21.8±5.3	Silt loam
Open state								
Sandbar Lagoon	19.3±0.1	nd	0.17±0.01	0.58	36.5±8.7	7.1±1.5	52.9±10.3	Sandy loam
North Marsh	18.6±0.1	nd	0.23±0.02	0.70	17.7±4.0	7.8±1.2	23.0±8.8	Silt loam
River Confluence	16.8±0.1	nd	0.44±0.02	0.84	63.2±41.8	4.1±2.8	69.4±22.6	Sandy loam
Butano Marsh	9.1±0.1	nd	0.21±0.01	0.70	9.9±0.1	11.8±0.4	5.3±0.7	Silt loam

0.01). Total iron content ranged from 52.4 to 179.4 mmol kg^{-1} dry sediment in the closed state and
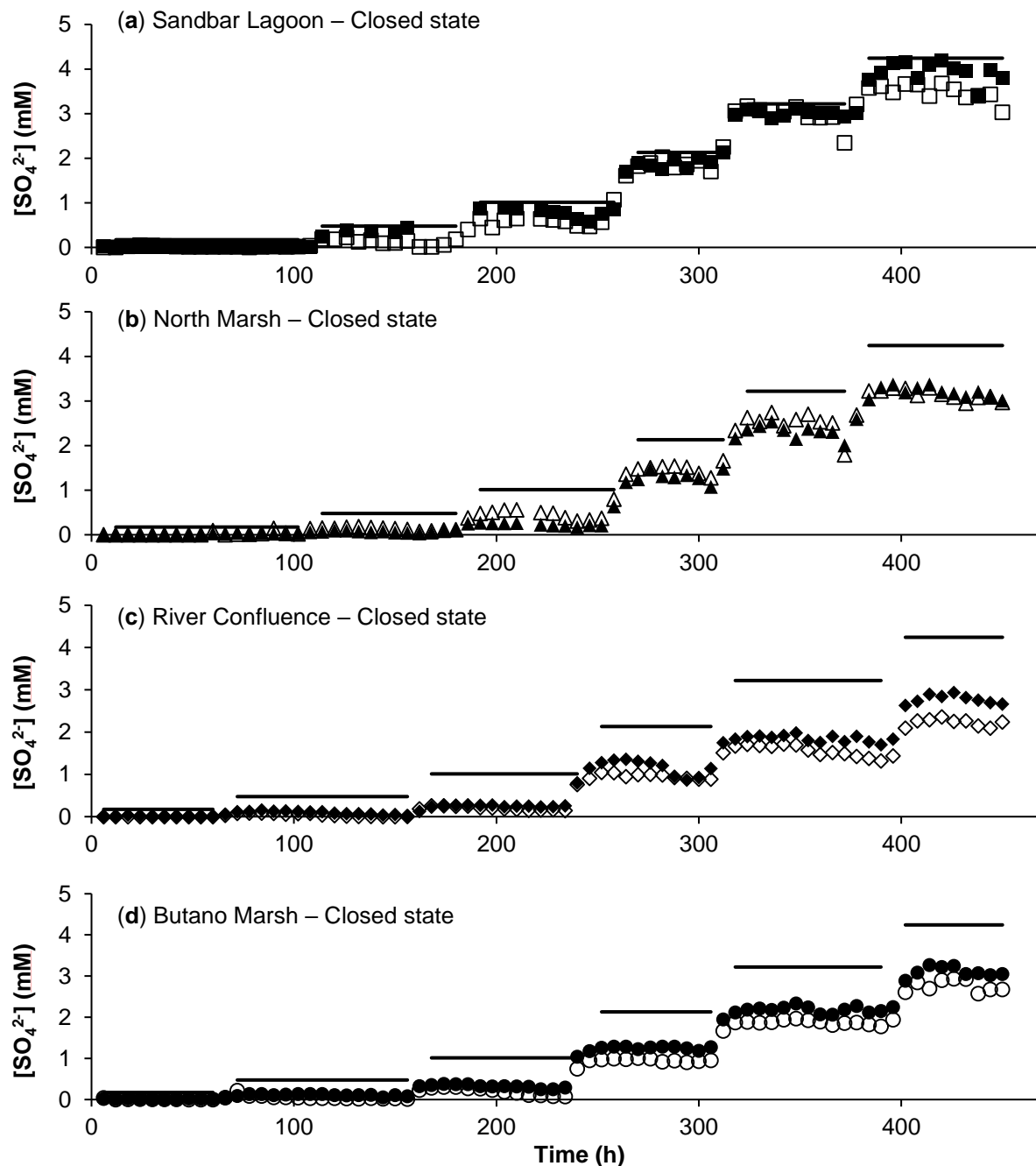
Figure 3.3. Sulfate breakthrough curves obtained from flow-through experiments performed on sediment sampled during the Pescadero Estuary closed state for the (**a**) Sandbar Lagoon site, (**b,**) North Marsh site, (**c**) River Confluence site, and (**d**) Butano Marsh site. Open and closed symbols represent duplicate experiments. The black lines represent inflow sulfate concentrations. Experiments were performed at a flow rate of 1.9 ±0.5 mL h^{-1}, in anoxic conditions, and at 25°C.

from 32.4 to 97.0 mmol kg^{-1} dry sediment in the open state. Total sediment iron content was positively correlated with water pH ($r = 0.99$, $P < 0.01$) in the closed state. Sediment pH was
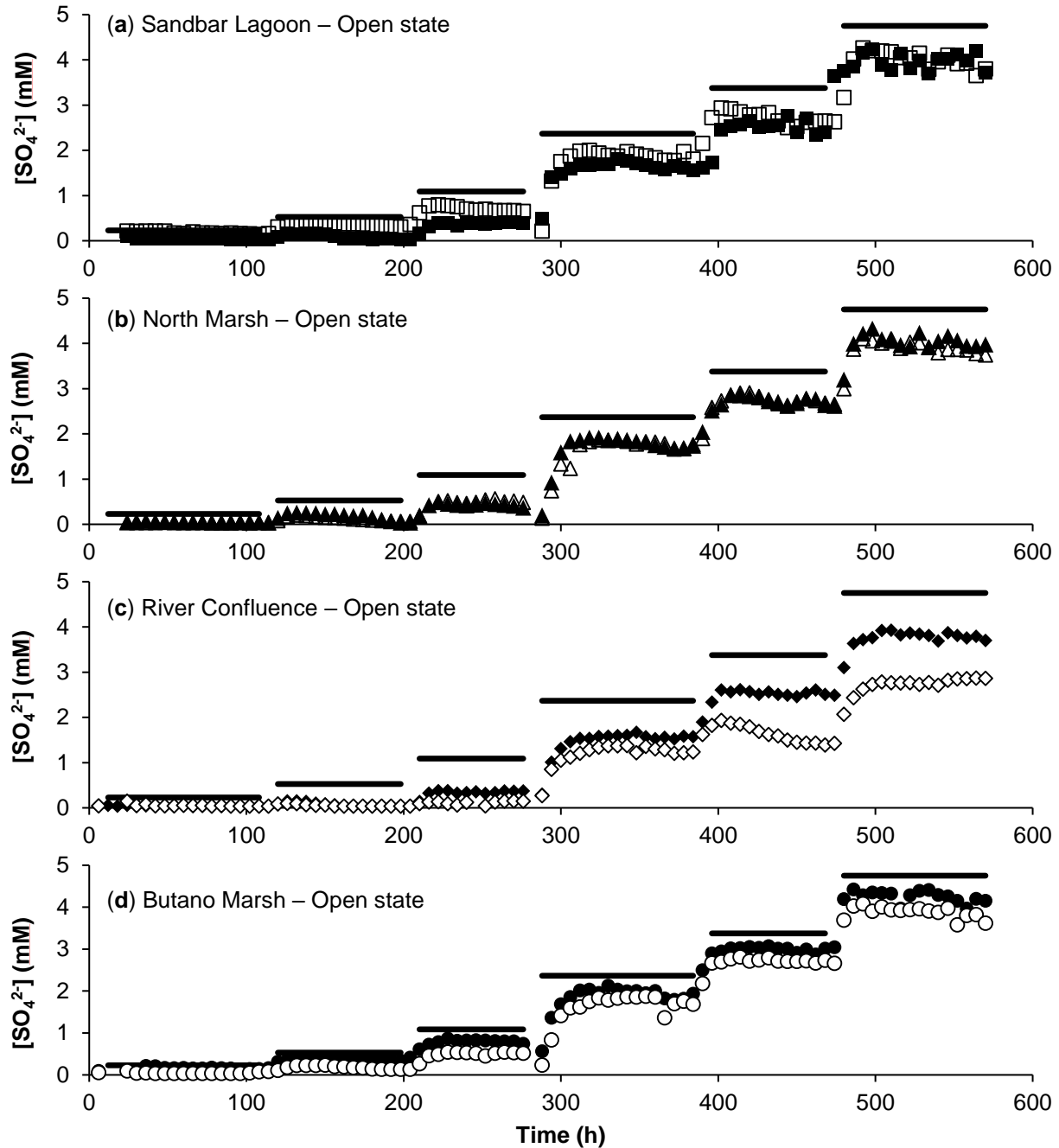
Figure 3.4. Sulfate breakthrough curves obtained from flow-through experiments performed on sediment sampled during the Pescadero Estuary open state for the (**a**) Sandbar Lagoon site, (**b**) North Marsh site, (**c**) River Confluence site, and (**d**) Butano Marsh site. Open and closed symbols represent duplicate experiments. The black lines represent inflow sulfate concentrations. Experiments were performed at a flow rate of 1.9 ±0.5 mL h^{-1}, in anoxic conditions, and at 25°C.

strongly to moderately acidic (3.7-5.7) in the closed state and was positively correlated with total hydrogen sulfide concentration in water ($r = 0.99$, $P < 0.05$). However, it was mildly alkaline (7.5-
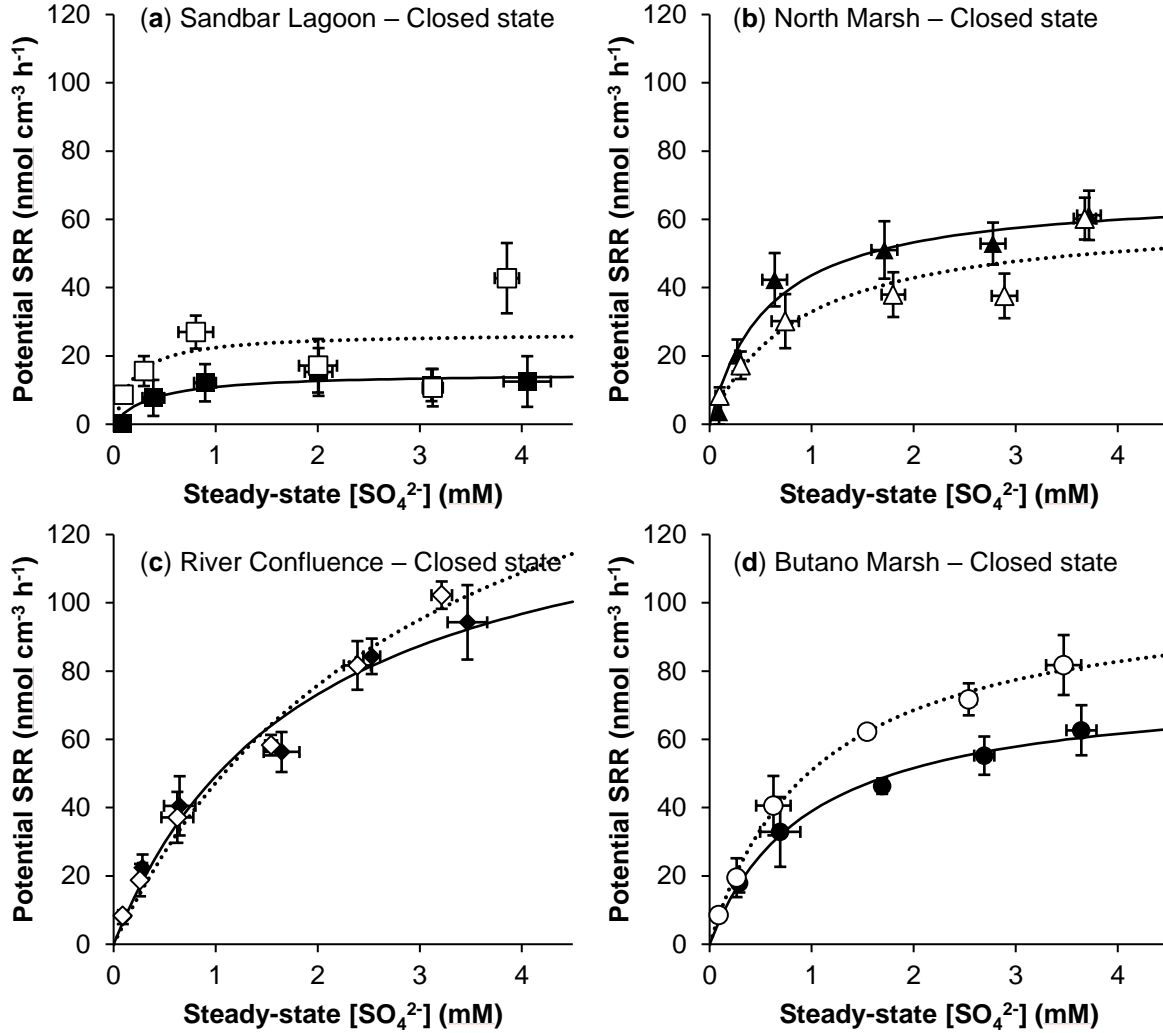
Figure 3.5. Steady-state potential sulfate reduction rates (SRR) measured at 25°C in continuous flow-through reactors as a function of the average sulfate concentration in the reactor in the 0-2 cm depth sediment cores of the (**a**) Sandbar Lagoon site, (**b**) North Marsh site, (**c**) River Confluence site, and (**d**) Butano Marsh site during the Pescadero Estuary closed state. Open and closed symbols represent duplicate experiments. The lines (solid for closed and dotted for open symbols, respectively) correspond to the Michaelis-Menten kinetic rate expression (**Equation 3**), calculated using R_{max} and K_m obtained from a direct fit of the Michaelis-Menten model. Error bars indicate standard deviation; when not visible, they fall within the size of the symbols.

8.2) at all sites in the open state, except for the River Confluence site where it was moderately acidic (5.1).

Total sediment organic carbon (C_{org}) content ranged from 3.9 to 6.9% in the closed state and from 2.2 to 5.5% in the open state. Total sediment nitrogen (N) content was one order of magnitude lower than total sediment C_{org} content, ranging from 0.30 to 0.54% and from 0.17 to 0.44% in the closed and open states, respectively. In the closed state, sediment C_{org} content was positively correlated with total sediment N content ($r = 0.96$, $P < 0.05$) and negatively correlated
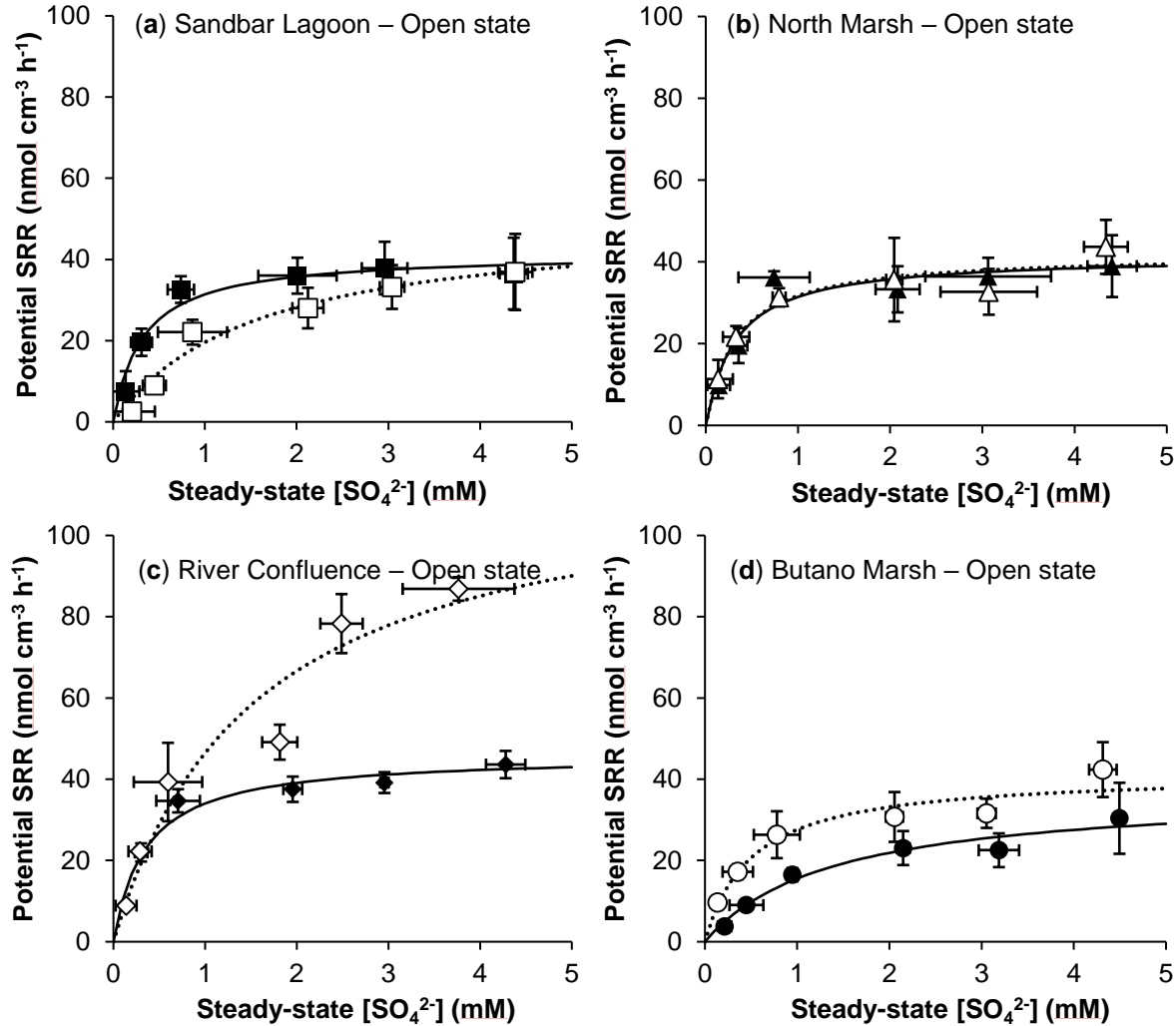
Figure 3.6. Steady-state potential sulfate reduction rates (SRR) measured at 25°C in continuous flow-through reactors as a function of the average sulfate concentration in the reactor in the 0-2 cm depth sediment cores of the (**a**) Sandbar Lagoon site, (**b**) North Marsh site, (**c**) River Confluence site, and (**d**) Butano Marsh site during the Pescadero Estuary open state. Open and closed symbols represent duplicate experiments. The lines (solid for closed and dotted for open symbols, respectively) correspond to the Michaelis-Menten kinetic rate expression (**Equation 3**), calculated using R_{max} and K_m obtained from a direct fit of the Michaelis-Menten model. Error bars indicate standard deviation; when not visible, they fall within the size of the symbols.

with total hydrogen sulfide in water (r = -0.96, P < 0.05). In the closed state, total sediment N content was also negatively correlated with total hydrogen sulfide in water (r = -0.99, P < 0.05) and sediment pH (r = -0.99, P < 0.01). However, in the open state, sediment N content was positively correlated with total C_{org} content (r = 0.99, P < 0.05) and negatively correlated with sediment pH (r = -0.99, P < 0.01). Molar C_{org}/N ranged from 11.1 to 15.9 in the open and closed states and was positively correlated with chloride concentration (r = 0.99, P < 0.05) in the open

state. Molar C_{org}/N was positively correlated with porosity ($r = 0.95$, P < 0.05), total iron content ($r = 0.97$, P < 0.05), and water pH ($r = 0.96$, P < 0.05) in the closed state.

The abundance of sulfate-reducing bacteria (SRB) in sediments varied by one order of magnitude between sampling sites, ranging between 1.2×10^5 and 4.9×10^6 cm^{-3} sediment in the closed state and 3.0×10^9 and 1.5×10^{11} cm^{-3} sediment in the open state (Table 3.1). The highest SRB abundance in both open and closed states was observed at the Butano Marsh site. In the closed state, the logarithm of SRB densities was negatively correlated with water sulfate concentrations ($r = -0.99$, P < 0.01) and positively correlated with total sediment C_{org} content ($r = 0.96$, P < 0.05).

3.3. Sulfate reduction rates (SRR) and kinetics of sulfate reduction

Sulfate breakthrough curves obtained from duplicate flow-through reactor (FTR) experiments for the closed and open states in response to six inflow sulfate concentrations are shown for the four study sites in Figure 3.3 and Figure 3.4. For all study sites and for the six different inflow sulfate concentrations, the outflow sulfate concentrations reached steady-state within 24 hours after the inflow sulfate solution had been supplied to the reactors, although slightly less quickly for experiments run with closed state sediments than open state sediment (18-24 hours or 1.2-2.1 pore volumes versus 12-18 hours or 1.5-1.9 pore volumes). In all study sites, potential SRR increased with increasing pore water sulfate concentration supplied, following Michaelis-Menten rate kinetics (Figure 3.5 and Figure 3.6). Repeatability, as calculated from Cronbach's alpha, was excellent (>0.9) to good (0.8-0.9) between duplicate experiments at each site in the closed and open states.

The range of both R_{max} and K_m values was larger in the closed state than the open state. In the closed state, the average R_{max} values varied by a factor of seven between sites, ranging from 20.9 to 167.6 nmol SO_4^{2-} cm^{-3} h^{-1}, whereas in the open state, average R_{max} values ranged from 41.7 to 81.8 nmol SO_4^{2-} cm^{-3} h^{-1} (Table 3.2). The River Confluence site had the largest R_{max} values observed in both closed and open states (Figure 3.7). In the closed state, the lowest value was observed at the Sandbar Lagoon site, followed by the North Marsh site and the Butano Marsh site. However, the open state showed the contrary, in which the lowest value was observed at the Butano Marsh site, followed by the North Marsh site and Sandbar Lagoon site. The K_m values varied by almost an order of magnitude between sites in the closed state, ranging from 0.28 to 2.5 mM SO_4^{2-} and exhibited a strong positive correlation with R_{max} ($r = 0.99$, P < 0.05). In the open state, average K_m values ranged from 0.32 to 0.96 mM SO_4^{2-} (Table 3.2), with the lowest value observed at the North Marsh site, followed by the River Confluence site, Butano Marsh site, and Sandbar Lagoon site (Figure 3.7). Despite no correlation with R_{max}, these values exhibited negative correlation with chloride concentration ($r = -0.99$, P < 0.05) in the open state.

3.4. Potential hydrogen sulfide export rates (SER) and sulfide precipitation rates (SPR)

For the four study sites in the closed and open states, hydrogen sulfide was detected in the outflow solutions of the flow-through experiments (breakthrough curves not shown). These

Table 3.2. Kinetic parameters, R_{max} and K_m, averaged for duplicate experiments of the four study sites in the closed state (August 2013) and open state (February 2014).

Site	Average R_{max} (nmol cm^{-3} h^{-1})	Average K_m (mM)
Closed state		
Sandbar Lagoon	20.9±5.5	0.28±0.28
North Marsh	64.9±9.1	0.72±0.35
River Confluence	167.6±13.1	2.49±0.87
Butano Marsh	90.5±3.7	1.01±0.12
Open state		
Sandbar Lagoon	46.2±4.9	0.96±0.32
North Marsh	41.7±3.4	0.32±0.11
River Confluence	81.8±13.7	0.94±0.43
Butano Marsh	39.3±4.1	0.95±0.31
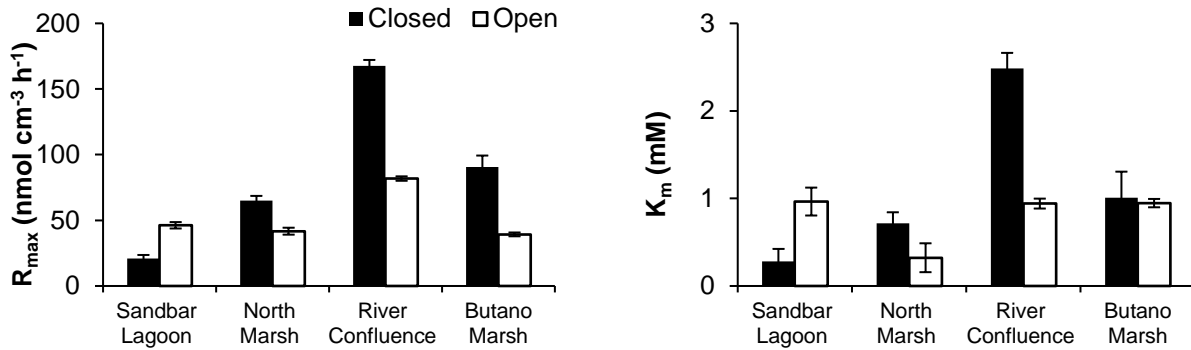
Figure 3.7. Michaelis-Menten kinetic rate parameters, R_{max} and K_m of the four study sites in the closed state (August 2013) (solid bars) and open state (February 2014) (white bars). All values are averaged for duplicate experiments at 25°C in continuous flow-through reactors in the 0-2 cm depth sediment cores. The R_{max} and K_m averaged for duplicate experiments are summarized in **Table 2**. Error bars indicate standard error; when not visible, they fall within the size of the symbols.

concentrations ranged up to maximums of 180.5-307.4 µM at all sites in the closed state as compared to maximums of 52.1-113 µM at all sites in the open state, when the inflow sulfate concentrations were well above their respective K_m values. However, in contrast to sulfate, outflow hydrogen sulfide concentrations were fairly variable and never reached steady-state. In all study sites, potential hydrogen sulfide export rates (SER) increased with increasing pore water sulfate concentration, ranging from 0.09 to 10.9 nmol cm^{-3} h^{-1} in the closed state, and from 0.5 to 2.5 nmol cm^{-3} h^{-1} in the open state. SER were the highest at the River Confluence and Butano Marsh sites in both closed and open states (Figure 3.8 and Figure 3.9). The SER values were an order of magnitude smaller than SRR, indicating that 1-35% and 2-9% of the hydrogen sulfide produced through sulfate reduction was exported from the sediment to the porewater during the experiments.
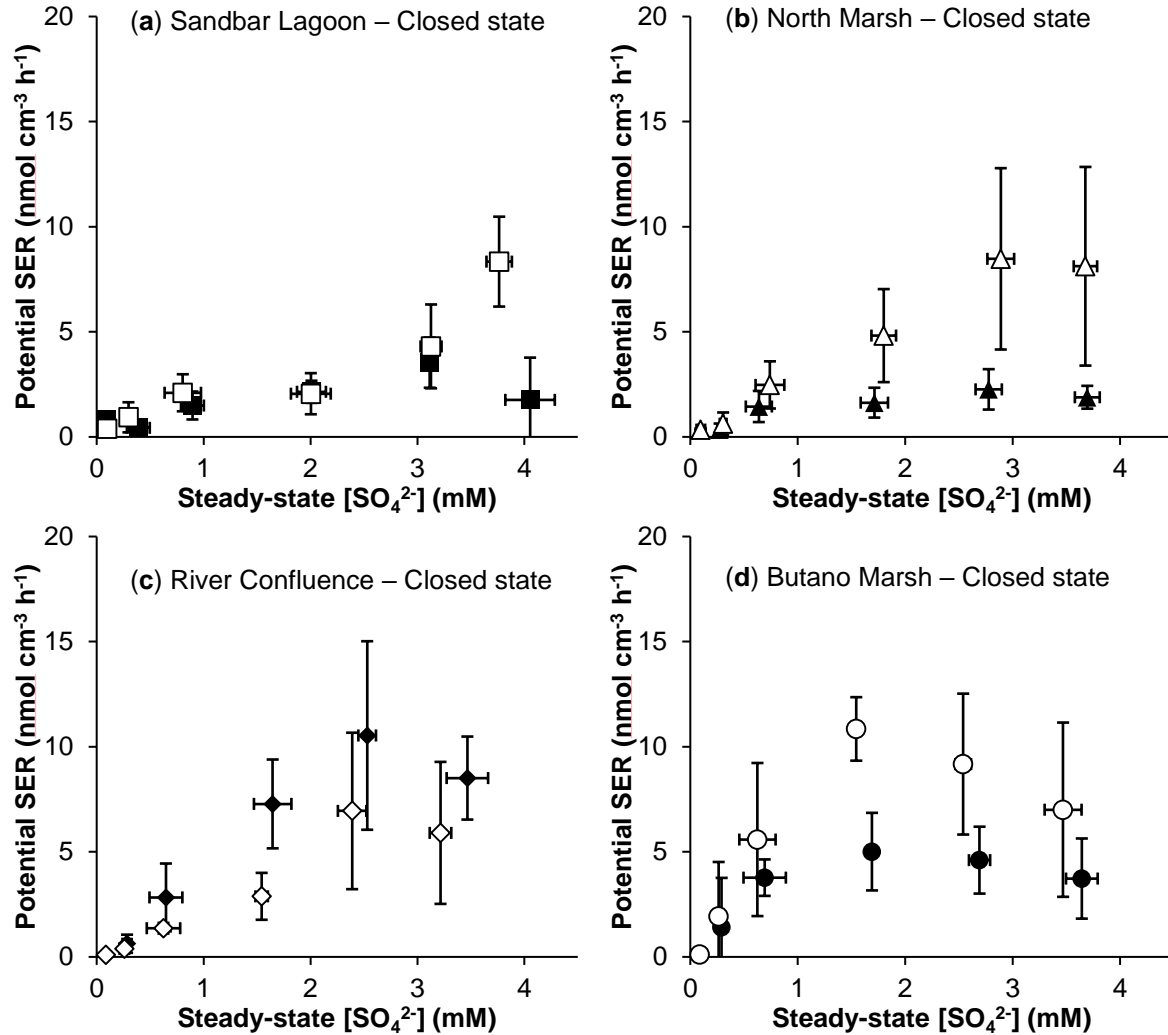
Figure 3.8. Average, potential hydrogen sulfide export rates (SER) measured in 0-2 m depth sediment cores of the (**a**) Sandbar Lagoon site, (**b**) North Marsh site, (**c**) River Confluence site, and (**d**) Butano Marsh site during the Pescadero Estuary closed state. Rates were measured at 25°C in continuous flow-through reactors as a function of the average sulfate concentration in the reactor. Open and closed symbols represent duplicate experiments. Error bars indicate standard deviation; when not visible, they fall within the size of the symbols.

Similar to SER, potential sulfide precipitation rates (SPR) measured in experiments with sediments from all study sites increased with increasing pore water sulfate concentration. SPR ranged from 3.8 to 91.1 nmol cm^{-3} h^{-1} in the closed state (Figure 3.10) and 4.6 to 62.8 nmol cm^{-3} h^{-1} in the open state (Figure 3.11). In both states, SPR was the lowest at the Sandbar Lagoon site, followed by the North Marsh site, the Butano Marsh site, and the River Confluence site. At all sites, SPR represented 65-99% and 91-98% of the hydrogen sulfide produced through sulfate reduction in the closed and open states, respectively.

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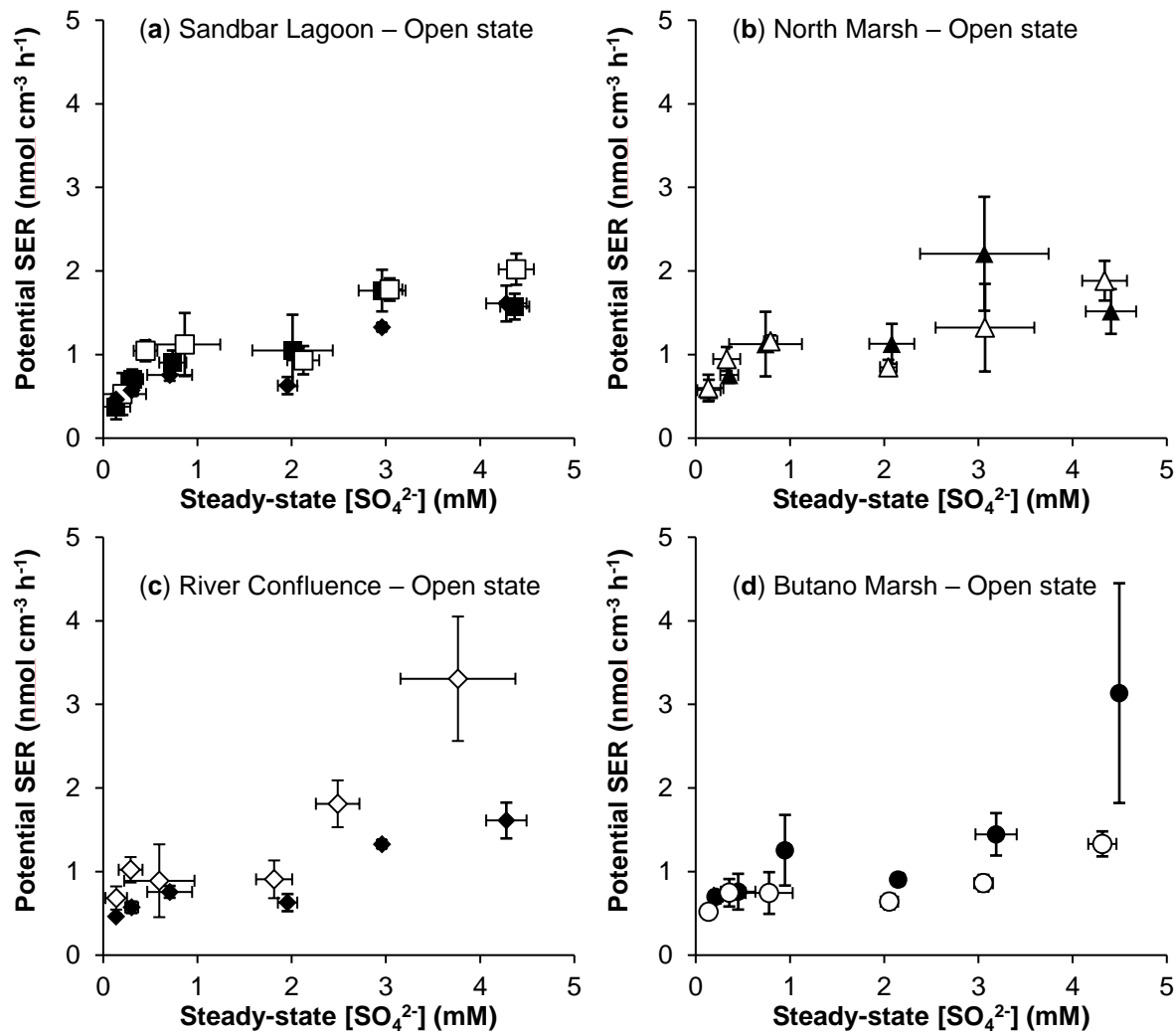
Figure 3.9. Average, potential hydrogen sulfide export rates (SER) measured in 0-2 cm depth sediment cores of the (**a**) Sandbar Lagoon site, (**b**) North Marsh site, (**c**) River Confluence site, and (**d**) Butano Marsh site during the Pescadero Estuary open state. Rates were measured at 25°C in continuous flow-through reactors as a function of the average sulfate concentration in the reactor. Open and closed symbols represent duplicate experiments. Error bars indicate standard deviation; when not visible, they fall within the size of the symbols.

4. Discussion

4.1. Differences in Pescadero Estuary water and sediment conditions between closed and open states

Our results corroborate that chloride concentration is the predominant constituent influencing conductivity in estuarine water (Hem, 1982). The lower water sulfate concentrations, pH, and salinity observed here in the closed state than in the open state indicate limited interactions
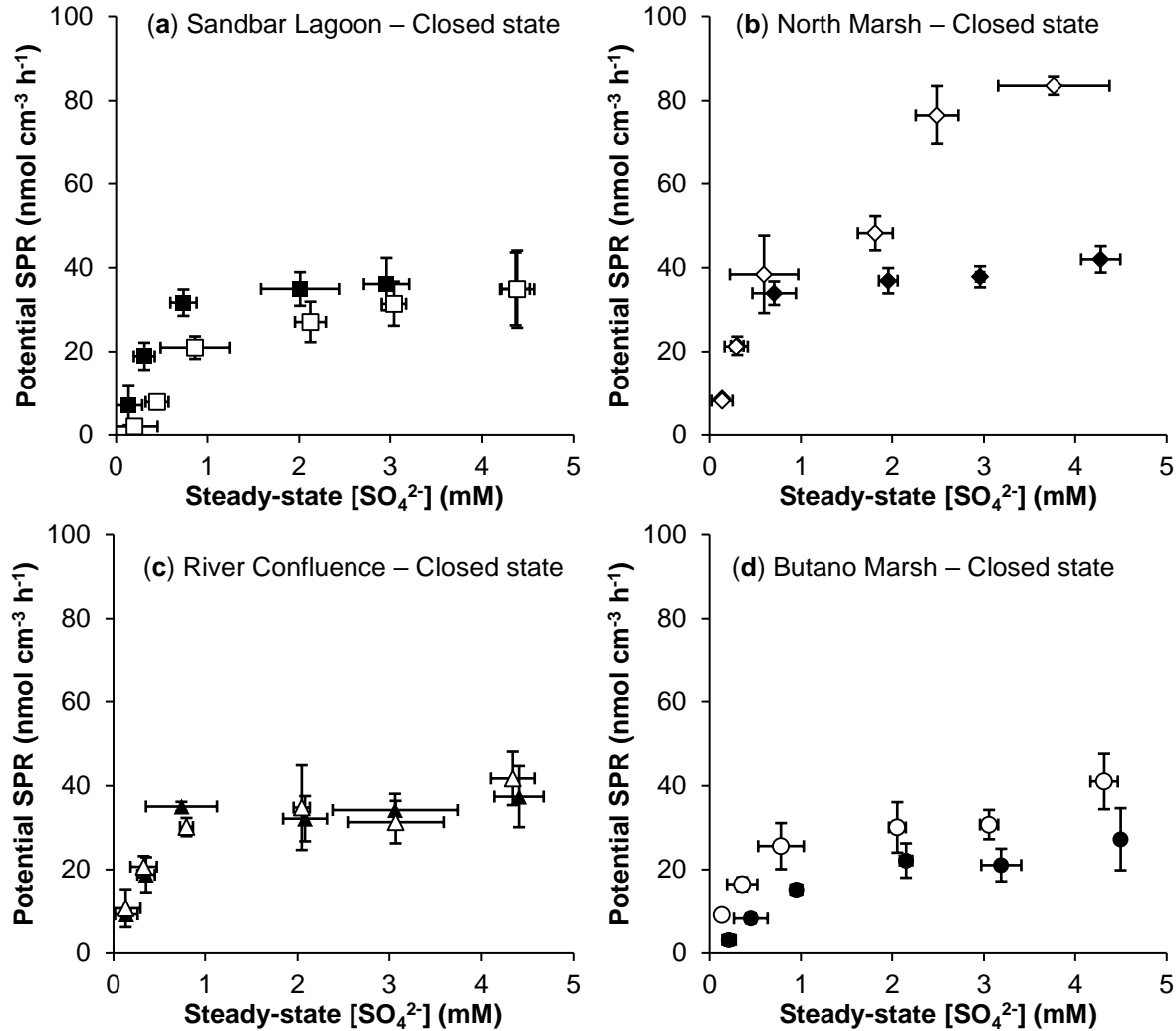
Figure 3.10. Average, potential sulfide precipitation rates (SPR) measured in 0-2 cm depth sediment cores of the (**a**) Sandbar Lagoon site, (**b**) North Marsh site, (**c**) River Confluence site, and (**d**) Butano Marsh site during the Pescadero Estuary closed state. Rates were measured at 25°C in continuous flow-through reactors as a function of the average sulfate concentration in the reactor. Open and closed symbols represent duplicate experiments. Error bars indicate standard deviation; when not visible, they fall within the size of the symbols.

between the bar-built lagoon and the ocean during the closed state. However, higher sulfate concentrations, pH and salinity in water during the open state can be attributed to ample mixing with marine water (28 mM sulfate, pH 8.5, and salinity 35‰). A salinity gradient was observed from the Pacific Ocean to the Butano Creek during the closed state, as a result of freshwater dilution from the Butano tributary.

On the other hand, heavy mixing of water and sediment, marine water flushing, and freshwater dilution that occur daily during the open state led to a lack of spatial gradients for any
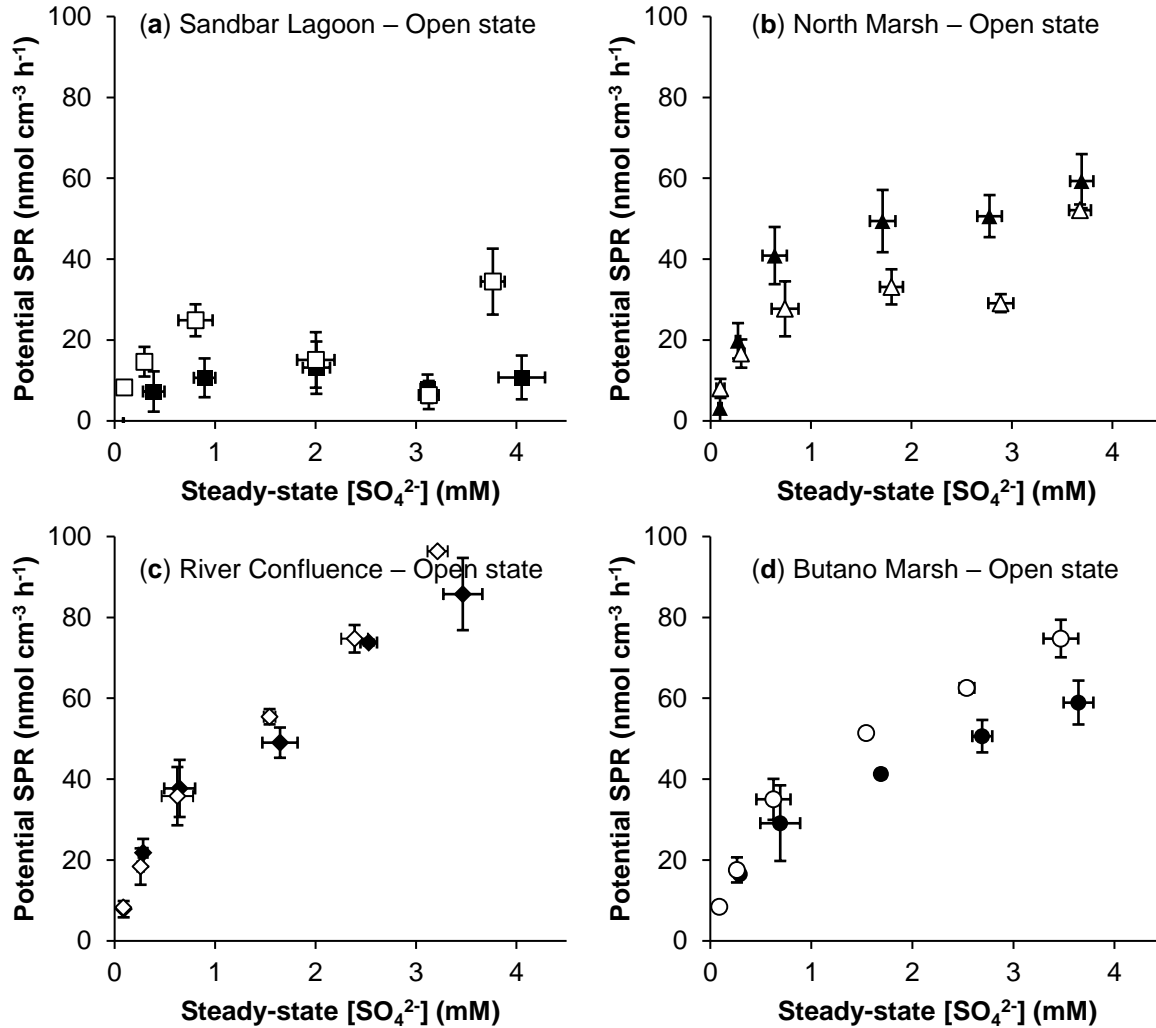
Figure 3.11. Average, potential sulfide precipitation rates (SPR) measured in 0-2 cm depth sediment cores of the (**a**) Sandbar Lagoon site, (**b**) North Marsh site, (**c**) River Confluence site, and (**d**) Butano Marsh site during the Pescadero Estuary open state. Rates were measured at 25°C in continuous flow-through reactors as a function of the average sulfate concentration in the reactor. Open and closed symbols represent duplicate experiments. Error bars indicate standard deviation; when not visible, they fall within the size of the symbols.

of the water or sediment variables measured during the open state. The lack of spatial gradients also explains the mildly alkaline water pH values characterizing the estuary's open state, which result from the mixing of alkaline oceanic water with acidic, oxidized estuarine sediments. The large variability in sediment texture between states also confirms that both heavy mixing and flushing of the water and sediment (i.e. sediment re-suspension) occurs as the estuary transitions from closed to open state.

Despite sulfate being present in higher concentrations during the open state than the closed state, hydrogen sulfide concentrations in the overlying water showed an opposite trend, which is

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suggestive of limited *in situ* sulfate reduction and/or higher sulfide precipitation rates in sediment during the open state. At all sites in the closed state, the circumneutral water pH values suggest equal partitioning between aqueous hydrogen sulfide and bisulfide (Morse et al., 1987), whereas the strongly to moderately acidic sediment pH values imply that the reduced soluble sulfur exists predominantly (>95%) as aqueous hydrogen sulfide. However, the water and sediment pH values in the open state suggest a decrease in aqueous hydrogen sulfide concentrations, with the majority (76-94%) of reduced soluble sulfur present as bisulfide and the minority (<24%) present as aqueous hydrogen sulfide.

Our observations that AVS concentrations in sediment were significantly larger than sediment sulfate concentrations and water hydrogen sulfide concentrations suggests, based on stoichiometric analysis, that hydrogen sulfide accumulates in sediment at all sites in both closed and open states. Although sulfide oxidation is accompanied by a pH decrease (Schippers and Jørgensen, 2002; Luther et al., 2004; Burton et al., 2006) as observed previously at Pescadero (Sloan, 2006), I did not observe a decrease in water nor sediment pH due to the influx of alkaline marine water. The temporal and spatial variability in sediment AVS, in addition to the low potential rates of hydrogen sulfide export from sediment to water, indicate that sulfide precipitation in sediment is a major sink for the sulfide produced *via* sulfate reduction at Pescadero. Sulfide precipitation in Pescadero sediment will be partly controlled by the extent of microbial sulfate reduction coupled to organic matter oxidation, and therefore is influenced in part by sediment organic matter content, in addition to total iron content and pH that control metal solubility, and redox conditions.

Sediment C_{org} and N contents were about twice larger in the closed state than in the open state, due to the replacement of terrestrial vascular pools of organic matter to labile marine pools of organic matter as the estuary transitions from closed to open state. This contradicts previous observations in open intermittent estuaries, where increases in flow and flooding during the open state have been shown to increase the sediment organic matter content compared to the closed state (McKenzie et al., 2011). Conversely, as the estuary transitions from closed to open state, increases in organic content may be due to particulate matter loading and outflow discharges. The sites exhibit similar C_{org}/N during the closed and open states, with average values of 13-13.4, which is consistent with that of estuarine (9-20) (Thornton and McManus, 1994; Cloern et al., 2002) and lacustrine sediments (11-15) (Meyers and Ishiwatari, 1993; Sampei and Matsumoto, 2001). Additionally, the values are slightly greater than the average calculated at Pescadero from Volpi (2014) (9.2±0.8) during the closed state but are about three times larger than the value reported by Laverman et al. (2012) during the open state, which indicates that sediment characteristics cannot pinpoint explicit trends between closed and open states. The C_{org}/N values suggest that the organic matter may derive from autochthonous biomass, specifically littoral marsh vegetation (25-400) and phytoplankton (5-8) (Thornton and McManus, 1994). However, the observations suggest that the highest abundance of decomposed organic matter is detectable during the closed state, whereas the open state may be largely characterized by high inputs of fresh algal detritus (Cloern et al., 2002).

The higher abundance of SRB in the open state compared to the closed state may be attributed to the differences in water sulfate and hydrogen sulfide concentrations and in sediment

pH and organic matter pools. In the closed state, the higher hydrogen sulfide concentrations in water and acidic sediment pH could have inhibited SRB growth, whereas in the open state, the mildly alkaline sediment pH and lower hydrogen sulfide concentrations were more conducive to SRB growth (Reis et al., 1992; Fauque, 1995). Additionally, the availability of fresh phytoplanktonic biomass in the open state may be more conducive for SRB than organic matter derived from marsh vegetation in the closed state, suggesting that the quantity and quality of organic matter pools are key factors controlling SRB communities. Even though *in situ* SRB activity is expected to be lower in the open state due to lower temperature and higher dissolved oxygen, as well as limited C_{org} and N contents in sediment, the increase in sulfate concentration in water and decrease in AVS in sediment suggest SRB communities may be larger and more diverse in the open state (Purdy et al., 2001).

4.2. Spatial heterogeneity and kinetic parameters of sulfate reduction

Our results indicate a potential for sulfate reduction at all study sites, in which the Michaelis-Menten rate equation (Equation 3) effectively described the consumption of sulfate by the resident microbial communities. Furthermore, the consumption of sulfate in FTR experiments was observed immediately upon its addition, implying the presence of active sulfate-reducing microorganisms in sediment from all study sites, both during the closed and open states.

A lack of correlation between sediment and water characteristics and the kinetic parameters of sulfate reduction indicates that the majority of investigated characteristics cannot be used as predictors of maximum sulfate reduction rates or half-saturation constants in Pescadero sediments. The R_{max} values measured for all sites were, interestingly, not correlated with *in situ* salinity but were correlated with sand content in the closed state and also with sediment pH and sediment N content in the open state.

Our R_{max} measurements show that the potential for sulfate reduction is high in Pescadero sediments, as the values are generally larger than values reported earlier for surface sediments (Table 3.3), including measurements performed using slurry incubations, which overestimate rates compared to measurements on intact sediment cores (Laverman et al., 2006; Pallud and Van Cappellen, 2006). Pescadero Estuary is a productive ecosystem richer in organic matter than other littoral systems, which may explain the large R_{max} values observed. Yet, reported R_{max} values for estuarine sediments range broadly from 45.5 to 208.3 nmol cm^{-3} h^{-1} for freshwater to saltmarsh sediments (Roychoudhury et al., 2003; Pallud and Van Cappellen, 2006) and sediment contaminated with petroleum hydrocarbons (Roychoudhury and McCormick 2006). The observations that R_{max} was larger and varied more in near-freshwater sediments during the closed state than in the estuarine/marine sediments during the open state may be attributed to higher organic matter content and lower salinity that are favorable for SRB activity and growth. With the exception of the values measured in sediment of a contaminated aquifer (Roychoudhury and McCormick, 2006), the kinetic values in the closed and open state are 1-2 orders of magnitude larger than that of sediment at lower depths, as observed in marine sediments (Boudreau and Westrich, 1984; Tarpgaard et al., 2011), which can be attributed to low organic matter content at deeper depths (Table 3.3).

Table 3.3. Kinetic parameters of microbial sulfate reduction as measured on sediments from natural environments under various experimental methods. CI, SI, and FTR represent core incubations, slurry incubations, and flow-through reactors as experimental methods, respectively.

R_{max} (nmol cm^{-3} h^{-1})	K_m (mM)	[SO$_4^{2-}$] (mM)	Sediment depth (cm)	Temperature (°C)	Salinity	Sediment origin	Method	Reference
13.2	0.068	0.23	0-8	10	Freshwater	Eutrophic lake	CI	Smith and Klug (1981)
5.7	0.042	0.5-1.7	0-10	25	Freshwater	Estuarine	CI	Roden and Tuttle (1993)
11	0.020	0.03	0-10	4-23	Freshwater	Seepage lake	SI	Urban et al. (1994)
0.96-3.9	1.24-3.17	0.3-0.5	0-10	59-70	Freshwater	Hydrothermal springs	SI	Roychoudhury (2004)
10.7-45.5	0.10-0.18	0-0.8	0-8	21	Freshwater	Intertidal marsh	FTR	Pallud and Van Cappellen (2006)
31-127	0.5-4.8	0-0.8	0-15	21	Freshwater	Intertidal marsh	SI	Pallud and Van Cappellen (2006)
208.3	3.5-7.5	1.1-1.4	250-300	17-22	Freshwater	Contaminated aquifer	SI	Roychoudhury and McCormick (2006)
17.5-31.1	0.92-0.95	0.5-1.7	0-10	25	Brackish	Estuarine	CI	Roden and Tuttle (1993)
3.7-7.6	0.37-0.87	4-5	0-8	21	Brackish	Intertidal marsh	FTR	Pallud and Van Cappellen (2006)
4-16	1.5-4.9	4-5	0-15	21	Brackish	Intertidal marsh	SI	Pallud and Van Cappellen (2006)
4.3	1.62	1.00	50-100	21	Saline	Marine	SI	Boudreau and Westrich (1984)
5.3	0.24	23	5-9	15.5	Saline	Tidal creek	FTR	Roychoudhury et al. (1998)
118.6	0.20	27-31	3-5	25	Saline	Saltmarsh field	FTR	Roychoudhury et al. (2003)
17.8-32.0	0.10-0.33	8-22	0-8	21	Saline	Intertidal marsh	FTR	Pallud and Van Cappellen (2006)
13-40	0.4-2.8	8-22	0-15	21	Saline	Intertidal marsh	SI	Pallud and Van Cappellen (2006)
0.003-0.91	0.002-0.63	0.1-24	6-20	15	Saline	Saline shelf	SI	Tarpgaard et al. (2011)

The half-saturation constant for sulfate, K_m showed no correlation with any water and

sediment characteristics in the closed state, and a negative correlation with chloride concentration in the open state. However, K_m values were positively correlated with R_{max} values, linking low affinity for sulfate with high potential rates of sulfate reduction. The results also indicate a high affinity for sulfate in sediments characterized by low hydrogen sulfide content (<15 mmol kg^{-1}) and low C_{org}/N (<12.5), which is evocative of SRB communities operating over a range of sediment conditions.

The K_m values measured in the closed (0.28-2.49 mM) and open (0.32-0.96 mM) states exhibited the same trend as R_{max} values, in which open state sediments displayed a smaller, lower range than closed state sediments. Based on these measurements and limited literature data sets (Table 3.3) (Tarpgaard et al., 2011), K_m values for natural SRB communities in estuarine sediments generally range from 0.92 to 0.95 mM (Roden and Tuttle, 1993), which is slightly larger than the range estimated by Pallud and Van Cappellen (2006) using flow-through reactors. Although consistent with values reported for slurry incubations on freshwater and brackish sediments (Roychoudhury, 2004; Pallud and Van Cappellen, 2006), the measurements exceed the range of K_m values reported in saltmarsh and freshwater to marine surface sediments using flow-through reactors (Roychoudhury et al., 1998; Roychoudhury et al., 2003). The K_m values also exceed the values measured using core incubations on freshwater sediments (Smith and Klug, 1981; Roden and Tuttle, 1993; Urban et al., 1994) but were lower than the K_m values reported by Roychoudhury and McCormick (2006) for freshwater aquifer sediments. These differences in K_m values can be attributed to sediment reactive and bioavailable organic matter substrates and SRB activity. The lack of correlation between K_m and *in situ* salinity indicate that a diverse SRB microbial community that includes organisms with both high and low uptake affinities for sulfate is present in Pescadero sediments, as observed by Pallud and Van Cappellen (2006) and Tarpgaard et al. (2011) in estuarine and marine systems, respectively. With continually fluctuating sulfate conditions at Pescadero on smaller (closed and open states) and larger (annual) temporal scales, microorganisms adapt by developing such a complex and mixed community of sulfate reducers with both low and high affinity uptake system for sulfate. Even though Purdy et al. (2001) proposed that SRB in freshwater environments develop higher uptake affinities for sulfate than SRB in marine environments in order to cope with low *in situ* sulfate concentrations, the microbial communities in the sediments may not need to develop an uptake system of both high and low affinities (Tarpgaard et al., 2011). A limited uptake system of high or low affinities is consistent with what has been observed in pure cultures (Ingvorsen and Jorgensen, 1984; Okabe et al., 1992; Dalsgaard and Bak, 1994; Sonne-Hansen et al., 1999; Moosa et al., 2002) or in core incubation experiments (Smith and Klug, 1981; Boudreau and Westrich, 1984; Roychoudhury, 2004).

Possibly, the half-saturation concentration for sulfate in relation to *in situ* sulfate concentration in the overlying water is more informative of the potential *in situ* rates. During the estuary closed state, the *in situ* sulfate water concentrations for the Sandbar Lagoon and North Marsh sites are 2.3 times greater than the half-saturation constants for sulfate, K_m. At those sites, this suggests that *in situ* sulfate reduction is not limited by sulfate availability in the overlying water and that the SRB communities could be operating near the maximum potential rate, R_{max}. An opposite trend is observed for the River Confluence and Butano Marsh sites, where *in situ* sulfate reduction is limited by sulfate availability and, consequently, *in situ* SRB communities operate well below R_{max}. In the open state, the half-saturation constants, K_m, at the Sandbar

Lagoon, River Confluence, and Butano Marsh sites are 1.2-5 times greater than the *in situ* sulfate concentration in the overlying water. This confirms that *in situ* SRB communities operate well below R_{max} in the open state and that *in situ* sulfate reduction is surprisingly limited by sulfate availability at these sites. The opposite trend is observed for the North Marsh site, in which *in situ* sulfate concentration in water is nearly 6 times greater than the half-saturation constant for sulfate.

4.3. Implications for sulfur cycling and fish kills in the Pescadero Estuary

The detection of hydrogen sulfide in outflow solutions from all FTR experiments indicates that hydrogen sulfide could be released to porewater under *in situ* conditions as well. However, these export rates best represent maximum rates due to the constant flushing of the reactors. Based on sulfur mass balance calculations throughout the FTR experiments, I estimate that 94-96% of the hydrogen sulfide produced through sulfate reduction precipitates in the sediment, whereas the remaining 4-6% of the hydrogen sulfide produced is exported to water. The potential for hydrogen sulfide export from sediment to the overlying water is consequently minor in the four study sites that span the Pescadero Estuary, thus preventing aqueous hydrogen sulfide concentrations from reaching toxic levels that pose an environmental hazard to fish in the closed state. On the other hand, the potential for sulfide precipitation is very high in the Estuary's sediments, leading to a large pool of precipitation sulfide minerals in sediments. When the estuary transitions from closed to open state, re-oxidation of the precipitated sulfide minerals could lead to decreased dissolved oxygen concentrations, increased hydrogen sulfide concentrations, and decreased pH as observed in other estuarine sediments (Simpson et al., 2000; Burton et al., 2006; Maddock et al., 2007), which could have direct detrimental effects on the fish populations.

Kaplan et al. (1963) and Howarth (1984) observed a large variability in the fraction of sulfide that precipitate in coastal marine sediments, with 5-94% of the hydrogen sulfide potentially produced *via* sulfate reduction precipitating as pyrite. The highest value (94%) predicted for a California coastal salt marsh peat (Howarth, 1984) may be attributed to surface sediment with high organic matter content and iron content. The total iron and AVS contents measured in sediments at the end of the FTR experiments showed values up to 80.5 mmol Fe kg^{-1} and 16.2 mmol H_2S kg^{-1} dry sediment in the closed and open states, suggesting a remarkably high iron content to precipitate the majority of sulfide produced. To quantitatively assess the importance of microbial sulfate reduction and hydrogen sulfide export at Pescadero, I compared the measured sulfate reduction rates with sulfate fluxes in the estuary and integrated this over the sediment surface in a simple calculation on the higher end of potential values at Pescadero. Considering sediment to a depth of 10 cm, where the majority of sulfate reduction is likely to occur (Jørgensen and John Parkes, 2010), and assuming that the water-sediment interface is equal to the estuary's drainage size (210 km^2) and that sulfate reduction predominates in the lower half of the Estuary, this effectively corresponds to sediment volume of 0.011 km^3. Taking into account the stream flow from the Butano River into the estuary of 1.1 m^3 h^{-1} (Sloan, 2006; Volpi, 2014) and water sulfate concentrations of 6-28 mM, this information suggests that the total sulfate input to this region is approximately $(0.7-3.1) \times 10^1$ mol h^{-1} in the open state. If I first consider the sulfate sink in the closed state, the maximum sulfate removal rates for the entire estuary are $(1.5-5.7) \times 10^5$ mol h^{-1},

given R_{max} of 20.9-168 nmol cm^{-3} h^{-1}, low sulfate concentrations of 0.5-1.1 mM, unlimited organic carbon substrates, and complete anoxia of top sediment. Similarly, with maximum potential SER of 0.4-2.9 nmol cm^{-3} h^{-1} and SPR of 13-48 nmol cm^{-3} h^{-1} in the closed state, this corresponds to maximum hydrogen sulfide export rates of $(1.5-4.4) \times 10^4$ mol h^{-1} and sulfide precipitation of $(1.5-5.2) \times 10^5$ mol h^{-1} for the entire Pescadero Estuary. This shows that the maximum potential SRR and SPR at Pescadero in the closed state are likely four orders of magnitude greater than the flux of sulfate into the region in the open state. It also implies that the estuary is a major sulfate sink *via* reduction as a dominant pathway and a major source of sulfide precipitates, with re-oxidation as a dominant pathway when exposed to oxygen. Furthermore, the maximum potential sulfate removal, hydrogen sulfide export, and sulfide precipitation rates for the open state, given higher sulfate concentrations of 6-28 mM, unlimited organic carbon substrates, and complete anoxia, are: $(4.5-9.0) \times 10^5$ mol h^{-1}, $(1.3-1.8) \times 10^4$ mol h^{-1}, and $(2.8-4.3) \times 10^5$ mol h^{-1}, respectively. In terms of the estuary's functioning, this likely implicates high levels of microbial productivity and rapid exchange of sulfur from the water to sediment interface. When compared to sulfate reduction or sulfide precipitation rates that are two orders of magnitude larger in the closed and open states, the hydrogen sulfide export pathway is negligible. This indicates that hydrogen sulfide export to water during the closed and open state is too low to pose a threat to fish and other aquatic life at Pescadero. However, during the transition from closed to open state when sediments are re-suspended and re-oxidized, issues may arise with hydrogen sulfide when rapidly mixed into the water column.

In the closed state, sulfate reduction is limited by low sulfate concentration in the water and by the activity of culturable SRB in the closed state, as controlled by acidic sediment pH values. On the other hand, the higher sulfate concentrations in water and abundance of SRB suggest that potential sulfate reduction is higher in the open state than the closed state. However, sediment organic matter content is a key driver of sulfate reduction, with higher contents and subsequent higher observed maximum rates in the closed state than in the open state. High sulfate reduction rates in the closed state can have severe implications for water quality via one reaction pathway: sulfide precipitation in sediment. Since hydrogen sulfide concentrations in water and low export rates are low in both closed and open states, it is unlikely that hydrogen sulfide is responsible for fish kills as the estuary transitions from closed to open state. While sulfate reduction in the open state is limited to the anoxic sediment below the surface, it is also constrained by the lower organic matter content. However, sulfide precipitation into sediment is also a dominant pathway in the open state, regardless of lower rates that suggest that reduction and oxidation likely occur together. Sulfide precipitation in sediment can have greater, deleterious implications for water quality and Pescadero fish when sulfide minerals are mobilized and re-suspended into the water column as the estuary opens. As the marshlands are drained, oxidation mechanisms, which predominate on sulfide-rich surface sediment, can result in an immediate decrease in dissolved oxygen concentration and pH.

5. Conclusions

This study investigated potential rates of microbial sulfate reduction, hydrogen sulfide export to water, and sulfide precipitation in sediment on intact sediment cores sampled during the

closed and open states at Pescadero Estuary. I observed spatial differences in the kinetic parameters for sulfate reduction and hydrogen sulfide export rates, both of which were highest at the River Confluence, Butano Marsh, and North Marsh sites in the closed state, which are predominant locations of fish kills. This implicates hydrogen sulfide production, specifically precipitation in sediment, as a dominant spatial and temporal pathway in which sulfide precipitates could indirectly affect water quality and aquatic life during re-oxidation. However, the potential for hydrogen sulfide export from sediment to the overlying water is minor throughout Pescadero Estuary, thus preventing aqueous hydrogen sulfide concentrations from possibly reaching toxic levels that pose an environmental hazard to fish in the closed state. Therefore, sulfate reduction and sulfide precipitation are the major sulfur processes controlling hydrogen sulfide toxicity, anoxia, and acidification in both states and may be implicated in fish mortalities in the transition from closed to open state at Pescadero.

6. Acknowledgments

7. References

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Chapter 4

Effects of sediment resuspension on the oxidation of acid-volatile sulfides and release of metals (Fe, Mn, Zn) in estuarine sediments (Pescadero, CA)

Abstract – Bar-built estuaries are unique ecosystems characterized by the presence of a sandbar barrier, which separates the estuary from the ocean for extended periods, and which reopens to the ocean with heavy rainfall and freshwater inflows. The physical effects associated with the transition from closed to open state, specifically water mixing and sediment resuspension, often indirectly worsen water quality conditions, and are suspected to drive near-annual fish kills at the Pescadero Estuary in northern California. The direct, oxidative effects of sediment acid-volatile sulfides (AVS), specifically acidification and metal release, are believed to stress fish, yet their oxidative pathways, release of acid and metals, and link to fish kills remain poorly understood. Using slurry incubations containing sediment from four sites distributed around the Pescadero Estuary, representing a gradient from the Pacific Ocean to freshwater tributaries, I measured maximum rates of aqueous hydrogen sulfide oxidation, sediment AVS oxidation, sulfate production, and acidification, as well as maximum release rates of iron (Fe), manganese (Mn), and zinc (Zn) to water. I estimated AVS oxidation rates of 8.2-21.4 mmol S kg^{-1} d^{-1}, which were three orders of magnitude higher than aqueous hydrogen sulfide oxidation rates, 6.2-25.6 µmol S kg^{-1} d^{-1}. I also suggest that aqueous hydrogen sulfide cannot be responsible for the observed fish kills due to its limited oxidative effects on pH and metal concentrations. However, the oxidative effects of AVS were severe, decreasing pH by X units to strongly acidic or moderately acidic values and releasing aqueous Fe, Mn, and Zn up to 11.2 mM, 0.46 mM, and 88 µM, respectively, indicating a direct link between sediment resuspension and poor water quality conditions for fish in the Pescadero Estuary.

1. Introduction

Bar-built estuaries, also called temporarily open/closed estuaries, are characterized by the presence of a sandbar barrier, which forms at their mouth during dry seasons and under low river flow and wave conditions, separating the estuary from the ocean for extended periods of time (Perissinotto et al., 2010). Typically most common in the southern hemisphere (James et al., 2007; Perissinotto et al., 2010), especially South Africa (Whitfield and Bate, 2007) and Australia (Roy et al., 2001; Potter et al., 2010), bar-built estuaries can also be dominant in Mediterranean climatic zones of the northern hemisphere, such as California (USA), where they comprise 75% of the estuaries (Emmett et al., 2000). Increasing freshwater inflows or heavy rainfall can lead to the breaching of the sandbar barrier and the opening of the estuaries' mouth, leading to drainage of the estuary (Roy et al., 2001), water mixing, sediment resuspension (Breitburg, 2002; Gillanders et al., 2011), and tidal flushing (Demers et al., 1987; Griffiths and West, 1999). Artificial breaching of bar-built estuaries has also been undertaken, often in response to long periods of closure and decreases in productivity and water quality (Whitfield et al., 2012). However, the physical opening

events of the estuaries' mouth often worsens water and sediment geochemical conditions (Bagarinao and Lantin-Olaguer, 1998; Johnston et al., 2009; Wong et al., 2010), particularly for many fish species that use the ecosystems as breeding grounds and nurseries (Allen et al., 2006; Moore, 2011). The breaching of bar-built estuaries and the transition from closed to open state has led to mass mortality events for fish around the world (Bennett et al., 1985; Whitfield, 1995; Sloan, 2006; Martin et al., 2007; Becker et al., 2009; Atkinson, 2010; Wong et al., 2010), including almost yearly kill events of imperiled steelhead trout for the past 20 years in the Pescadero Estuary (CA, USA) (Largier et al., 2015). Regular kills of federally-threatened salmonid fish have also occurred in nearby California bar-built estuaries, including San Gregorio Lagoon (Atkinson, 2010) and Rodeo Lagoon (Martin et al., 2007); however, these events have been more regular at Pescadero than in nearby estuaries along the Pacific Coast.

The regular changes between closed and open states in bar-built estuaries lead to more variable and complicated physico-chemical dynamics than in permanently open estuaries (Perissinotto et al., 2010). In the closed state, these estuaries behave like lagoons where water mixing and flushing are limited (Behrens et al., 2013). Combined with steady freshwater inflows into the lagoon, prolonged mouth closure often leads to stratified conditions of anoxia or hypoxia (low dissolved oxygen concentrations, <5 mg L^{-1}), which are favorable for sulfate reduction coupled with organic matter oxidation leading to the production of hydrogen sulfide (H_2S) (Goldhaber and Kaplan, 1976; Boudreau and Westrich, 1984). Part of this produced aqueous hydrogen sulfide undergoes precipitation with iron (Fe), manganese (Mn), zinc (Zn), or other trace metals to form solid acid-volatile sulfides (AVS) and metal sulfides in sediment (Morse and Cornwell, 1987; Allen et al., 1993). Composed primarily of mackinawite (FeS), amorphous FeS, pyrite (FeS_2), and greigite (Fe_3S_4), acid-volatile sulfides (AVS) are defined largely as the solid-phase sulfides in sediment that are soluble in acid, releasing hydrogen sulfide upon extraction (Morse and Cornwell, 1987; Rickard and Morse, 2005; Johnston et al., 2009).

The disturbances associated with the transition from closed to open state are suspected to negatively affect sediment conditions and water quality. Often driven by natural (ex. heavy rainfall, tidal currents, estuary flushing) and/or anthropogenic (ex. dredging) events, periodic sediment resuspension and mixing could lead to acid-volatile sulfides oxidation through exposure of anoxic sediments to oxic conditions, causing increased microbial activity, oxygen depletion, and severe acidification of water, such as observed for acid-sulfate soils globally (Sammut et al., 1996; Wilson et al., 1999; Schippers and Jørgensen, 2002; Wong et al., 2010; Hong et al., 2011). In addition, sediment resuspension in estuarine systems has been shown to release metals (ex. iron, manganese (Mn), zinc (Zn), aluminum, cadmium, copper, and nickel) to the water; however, this is largely dependent on the severity of oxidative effects of metal sulfides, specifically acidification (Hirst and Aston, 1983; Simpson et al., 1998; Simpson et al., 2000; Eggleton and Thomas, 2004; Burton et al., 2006; Hong et al., 2011), which ultimately controls the toxicity of these metals for water quality (Di Toro et al., 1996).

I investigated the effects of sediment resuspension on water conditions in a California bar-built estuary, the Pescadero Estuary (USA), where fish mortality events of federally-threatened juvenile steelhead trout have been observed almost annually (Largier et al., 2015) and up to four days following a transition from closed to open state (Viollis, 1979; Sloan, 2006; Volpi, 2014).

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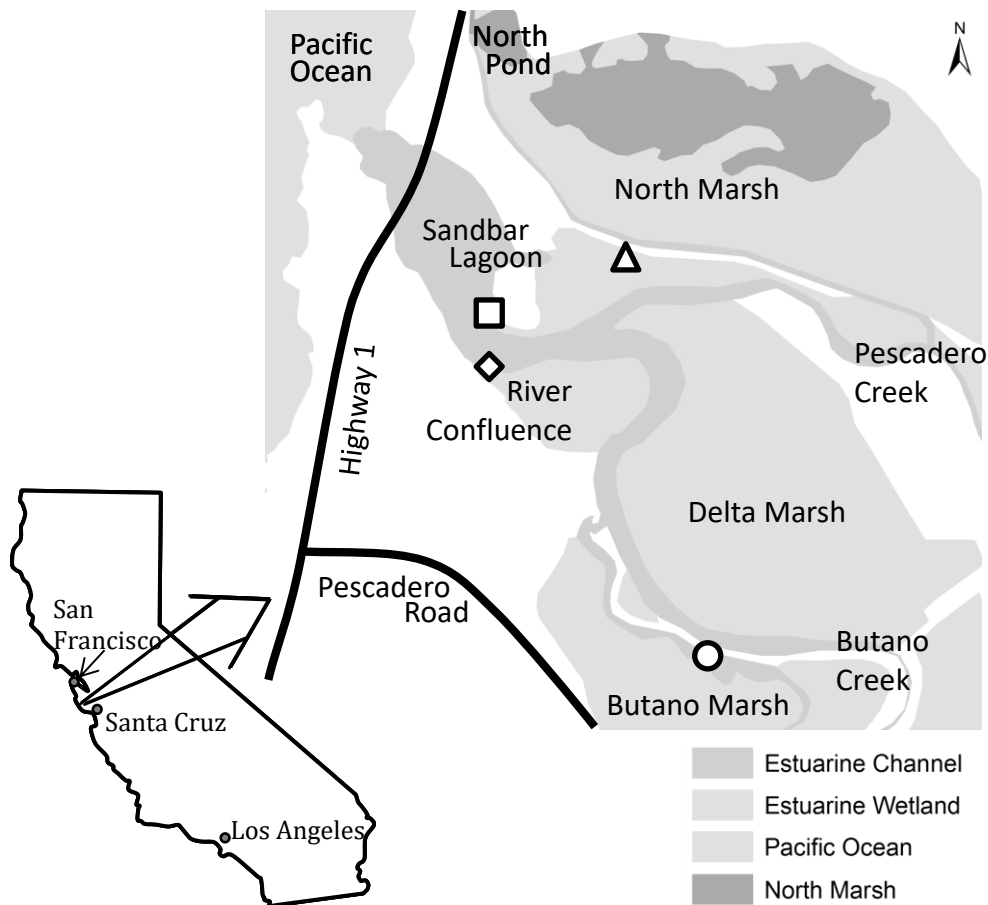
Figure 4.1. The Pescadero Estuary in California with the location of the four littoral sites, more specifically the North Marsh site (triangle), the Butano Marsh site (circle), the River Confluence site (diamond), and the Sandbar Lagoon site (square), sampled for sediment experiments in June 2015.

More specifically, I measured the effects of sediment mixing and oxygenation on sulfide oxidation and water acidification, as well as on the release of sulfide and metals to water in sulfide-rich sediment sampled at four littoral sites within the estuary spanning a gradient in salinity and sulfate concentration from ocean to freshwater tributaries. My results illustrate a sharp decrease in pH coupled with decreases in sediment and water sulfide concentrations and increases in metal (Fe, Mn, Zn) concentrations upon sediment resuspension, with high oxidation rates of acid-volatile sulfides throughout the Pescadero Estuary that are potentially greater than at other sites impacted by fish kills.

2. Methods

2.1. Sampling sites

Sediments from the Pescadero Estuary (San Mateo County, USA) were sampled two months after the estuary opened in June at four sites representing a gradient from the most marine region of the system, called Sandbar Lagoon, to freshwater tributaries (Figure 4.1). At each site, sediment samples were collected from the water/sediment interface down to a depth of 10 cm about a meter from the shoreline in the non-vegetated channel in water depths of approximately 30 cm. All samples were collected with a hand shovel, immediately placed in an anoxic glass sealed container, and transported to the laboratory where they were stored in the dark at 4°C until use.

2.2. Slurry incubations

Batch slurry incubations were prepared in duplicate in serum bottles, using 150 g of saturated wet sediment and 175 mL deionized water adjusted to pH 8.7 in order to mimic field conditions (Richards and Pallud, 2016). The slurries were continuously bubbled with air and stirred for eleven days to maintain oxic conditions and to ensure the sediment stayed in suspension. Slurry pH was measured daily. In addition, slurries were sampled daily for water analyses. The sub-samples were immediately centrifuged and the supernatant was filtered through a 0.20 µm nitrocellulose filter prior to analyses of sulfate, chloride, nitrate, ferrous iron, ferric iron, and hydrogen sulfide concentrations. Additionally, samples were taken on days 0, 3, 6, and 11 to determine sediment iron and acid-volatile sulfide contents, and on days 0 and 11 to measure sediment organic carbon and nitrogen contents. Finally, sediment texture and mean grain size were measured at the completion of the experiment.

2.3. Analyses of liquid samples

Water pH was determined using a pH/ATC electrode (high performance glass-body Sartorius ATC combination electrode) and meter (Denver Instrument, Model 215). Aqueous ferric and ferrous iron concentrations were measured spectrophotometrically at 562 nm using the colorimetric ferrozine method (Stookey, 1970). Total aqueous iron was calculated as the sum of ferric and ferrous iron concentrations. Chloride, sulfate, and nitrate concentrations were determined using ion chromatography. Total hydrogen sulfide concentrations were determined after combining 1.5 mL sample with 1.5 mL of a sulfide anti-oxidant buffer (SAOB) solution of 1 M sodium hydroxide and 0.1 M ethylenediaminetetraacetic acid (EDTA) using potentials with a pH/ISE electrode (Ionplus Sure-Flow silver/sulfide selective electrode) (detection limit 2 µM). Using an EPA-certified method (EPA 200.7), aqueous arsenic (As), manganese (Mn), and zinc (Zn) concentrations were measured via inductively coupled plasma-atomic emission spectrometry (ICP-AES) at Delta Environmental Laboratories, LLC (Benicia, CA).

2.4. Sediment analyses

Sediment total iron and acid-volatile sulfide (AVS) were extracted using a method adapted from Simpson et al. (1998) and van Griethuysen et al. (2002), in which anoxic, dried sediment was stirred for two hours with 1 M hydrochloric acid in a sealed extraction chamber with a SAOB trap

(described in section 2.3). After equilibration of soluble sulfide in the SAOB trap and soluble iron in the acid fraction, iron and AVS contents were measured colorimetrically *via* the ferrozine method at 562 nm (Stookey, 1970) and the methylene blue method at 670 nm (Simpson, 2001), respectively. Using an EPA-certified method (EPA 6010B), sediment arsenic and zinc contents were measured via ICP-AES at Delta Environmental Laboratories, LLC (Benicia, CA). Sediment organic carbon and total nitrogen contents were measured using a CE Instruments Elemental Analyzer on air-dried samples following inorganic carbon removal with 0.5 M $FeSO_4$-H_2SO_4 acid digestion solution over heat.

Mean sediment grain size and sand and clay percentages were determined on 5 g air-dried sediment in 20 mL water, following organic matter and carbonate removal with 35% hydrogen peroxide and 1 M hydrochloric acid, respectively using a LISST-Portable|XR Sequoia Scientific Particle Size Analyzer. Soil texture was determined from sand and clay percentages using the USDA Soil Texture Calculator (USDA, 1996).

2.5. Potential reaction rates

Potential rates of aqueous hydrogen sulfide oxidation (SOR, in μmol S kg^{-1} d^{-1}), of sediment acid-volatile sulfide oxidation (SSOR, in mmol S kg^{-1} d^{-1}), of water sulfate production (SPR, in mmol S kg^{-1} d^{-1}), and of slurry acidification rate (AR, in μmol H$^+$ kg^{-1} d^{-1}) were calculated from the decrease in aqueous hydrogen sulfide, decrease in sediment acid-volatile sulfide content, initial increase in aqueous sulfate concentration, and initial decrease in aqueous protons with time, respectively. Potential rates of aqueous iron release (FeReR, in mmol kg^{-1} d^{-1}), of aqueous manganese release (MnReR, in μmol kg^{-1} d^{-1}), and of aqueous zinc release (ZnReR, in μmol kg^{-1} d^{-1}) were calculated from the increase in concentration of dissolved total iron, manganese, and zinc with time, respectively.

2.6. Statistical analyses

The statistical significance and correlations between all geochemical water variables were evaluated by one-way ANOVA with a significance threshold of alpha = 0.05 and Pearson's correlation coefficient with a correlation threshold of r = ±0.9. Significance between variables with correlations below r = ±0.6 were not reported. Reported uncertainty ranges are ±1 standard deviation unless otherwise stated. The statistical analysis was performed with the EZAnalyze package.

3. Results

3.1. Characterization of the four study sites

Table 4.1. Sediment **(a)** physical characteristics, **(b)** geochemical characteristics measured at the four study sites during the estuary's open state (June 2015). All values are averages ± standard deviations. bdl means below detection limits, which were 0.03 mmol kg^{-1} for sediment As content, respectively.

(a)

Site	Sediment		
	Mean grain size (μm)	Clay (wt%)	Sand (wt%)
Sandbar Lagoon	19.1±1.9	10.8±0.4	22.1±2.3
River Confluence	38.2±10.6	8.1±1.3	39.5±9.2
North Marsh	10.0±1.4	14.7±0.6	10.1±3.2
Butano Marsh	17.7±2.4	9.9±0.6	21.8±3.2

(b)

Site	Sediment							
	AVS content (mmol S kg^{-1})	Fe content (mmol kg^{-1})	pH	As content (mmol kg^{-1})	Zn content (mmol kg^{-1})	C_{org} content (wt%)	N content (wt%)	C_{org}/N
Sandbar Lagoon	38.7±4.5	31.9±0.3	7.4±0.1	0.05±0.02	0.83±0.02	1.49±0.01	0.14±0.01	10.8±0.1
River Confluence	34.3±8.1	17.2±0.1	8.0±0.1	bdl	0.87±0.02	1.37±0.13	0.14±0.01	10.0±0.9
North Marsh	61.4±1.4	30.3±0.1	7.7±0.1	0.07±0.02	1.17±0.02	2.99±0.06	0.20±0.01	14.5±0.1
Butano Marsh	54.9±1.5	19.1±0.8	7.1±0.1	0.07±0.02	1.30±0.02	5.28±0.15	0.39±0.01	13.4±0.2

The sediment of the four study sites were medium-textured silt loams, with clay and sand contents ranging from 8.1 to 14.7% and from 10.5 to 39.5%, respectively (Table 4.1). However,

Table 4.2. Sediment pore water geochemical characteristics measured at the four study sites during the estuary's open state (June 2015). All values are averages $\pm$ standard deviations. bdl means below detection limits, which were 30 μM, 0.8 μM, and 2.0 μM, for pore water NO_3^-, Zn, and As concentrations, respectively.

Site	Sediment pore water						
	$[SO_4^{2-}]$	$[H_2S]$	$[NO_3^-]$	$[Cl^-]$	[Mn]	[Zn]	[As]
	(mM)	(μM)	(μM)	(mM)	(μM)	(μM)	(μM)
Sandbar Lagoon	5.7$\pm$0.1	17.5$\pm$1.4	bdl	63.2$\pm$0.7	92.0$\pm$15.1	1.4$\pm$0.8	bdl
River Confluence	2.2$\pm$0.2	11.0$\pm$0.6	bdl	56.5$\pm$7.6	14.3$\pm$5.0	bdl	bdl
North Marsh	0.1$\pm$0.1	23.4$\pm$0.8	bdl	52.3$\pm$2.7	37.3$\pm$8.5	bdl	bdl
Butano Marsh	2.4$\pm$0.2	7.6$\pm$0.2	bdl	88.2$\pm$5.8	58.8$\pm$6.4	0.9$\pm$0.1	bdl

the sediment of the River Confluence site was coarser than the three other sites, with 2-4 times significantly higher mean grain size and sand content (Table 4.1). The North Marsh site had the largest clay contents, with values 1.4-1.8 times significantly higher than at the other sites. Mean grain size was positively correlated with sand content ($r = 0.99$, $P < 0.001$) and negatively correlated with silt content ($r = -0.99$, $P < 0.001$) and clay content ($r = -0.89$, $P < 0.01$).

Pescadero sediments at the four sites were rich in acid-volatile sulfides (AVS), with contents ranging from 34.3 to 61.4 mmol kg^{-1} sediment (Table 4.1), with the highest values observed at the North Marsh and Butano Marsh sites. Total iron content in sediment ranged between 17.2 and 31.9 mmol kg^{-1} at all sites, with the lowest values observed at the River Confluence and Butano Marsh sites (Table 4.1). Sediment iron content was positively correlated with pore water hydrogen sulfide concentrations ($r = 0.86$, $P < 0.01$). Circumneutral sediment pH values (7.1-7.4) were observed at the Butano Marsh and Sandbar Lagoon sites, whereas mildly alkaline pH values (7.7-8.0) were observed at the River Confluence and North Marsh sites (Table 4.1). Sediment arsenic and zinc contents ranged from below detection limits to 0.07 mmol kg^{-1} and 0.8 to 1.3 mmol kg^{-1}, respectively, with the largest values observed at the North Marsh and Butano Marsh sites (Table 4.1). Both sediment organic carbon and nitrogen contents increased by factors of 3.9 and 2.8, respectively, along the estuarine gradient, with the lowest values reported for the two sites the closest to the ocean, Sandbar Lagoon and River Confluence, and the highest values reported for the site with the highest freshwater influence, Butano Marsh (Table 4.1). Sediment nitrogen content was positively correlated with sediment organic carbon content ($r = 0.99$, $P < 0.001$) and negatively correlated with sediment pore water pH values ($r = -0.74$, $P < 0.05$). Sediment molar C_{org}/N followed a similar trend along the estuarine gradient, with lower values in the Sandbar Lagoon and River Confluence sites and the lowest at the North Marsh and Butano Marsh sites (Table 4.1). Sediment molar C_{org}/N was positively correlated with acid-volatile sulfide content ($r = 0.96$, $P < 0.001$).

Sediment pore water sulfate concentrations ranged from 0.1 mM at the North Marsh site up to 5.7 mM at the Sandbar Lagoon site and showed no correlation with chloride concentrations,
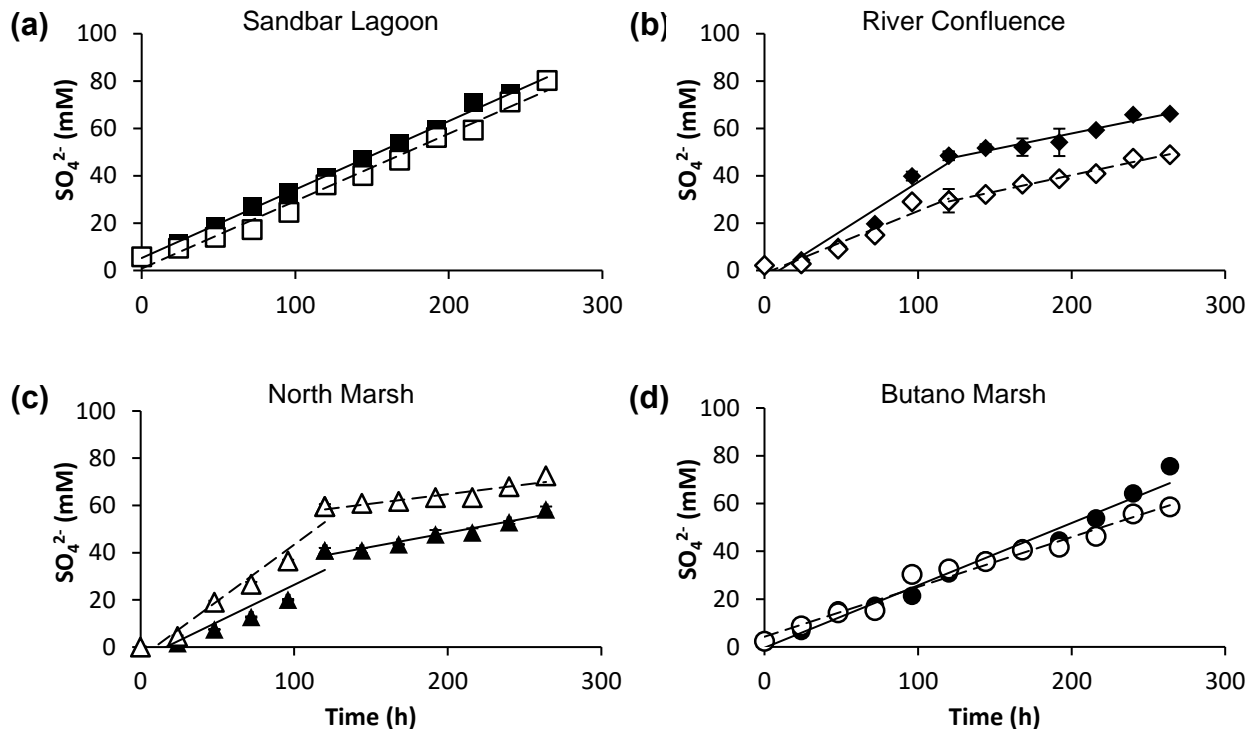
Figure 4.2. Sulfate concentration measured in slurry incubations at the **(a)** Sandbar Lagoon (squares), **(b)** River Confluence (diamonds**), (c)** North Marsh (triangles), and **(d)** Butano Marsh (circles) sites. Open and closed symbols represent duplicate slurry experiments. The dashed and solid lines represent linear regression for open and closed symbols, respectively. Error bars indicate standard deviation; when not visible, they fall between the size of the symbols.

which were the highest (88.2 mM) at the Butano Marsh site, and were in a similar range (52.3-63.2 mM) for the three other sites (Table 4.2). Sediment pore water manganese concentrations ranged from 14.3 µM at the River Confluence site up to 92.0 µM at the Sandbar Lagoon site (Table 4.2). Sediment pore water zinc concentrations ranged from below detection limits to 0.9-1.4 µM at the Sandbar Lagoon and Butano Marsh sites (Table 4.2). Sediment pore water nitrate and arsenic concentrations were below detection limits at all four sites (Table 4.2).

3.2. Evolution of water and sediment slurry conditions over time

Sulfate concentrations increased in all slurry incubations up to 19 mM after two days and up to 60 mM after five days, reaching concentrations 10 times higher than initial values by the end of the experiments (Figure 4.2). For the Sandbar Lagoon and Butano Marsh sites, sulfate concentrations increased linearly over the eleven-day experimental period, reaching final values of 80-81 mM and 58-76 mM, respectively. However, the evolution of sulfate concentration over time was different in the North Marsh and River Confluence sites, where the increase in sulfate concentrations was initially fast but slowed down after the first five days, reaching final values of 58-73 mM and 48-67 mM, respectively. Sulfate concentrations values were negatively correlated with pH over the course of the experiments (r = -0.89, P < 0.001).
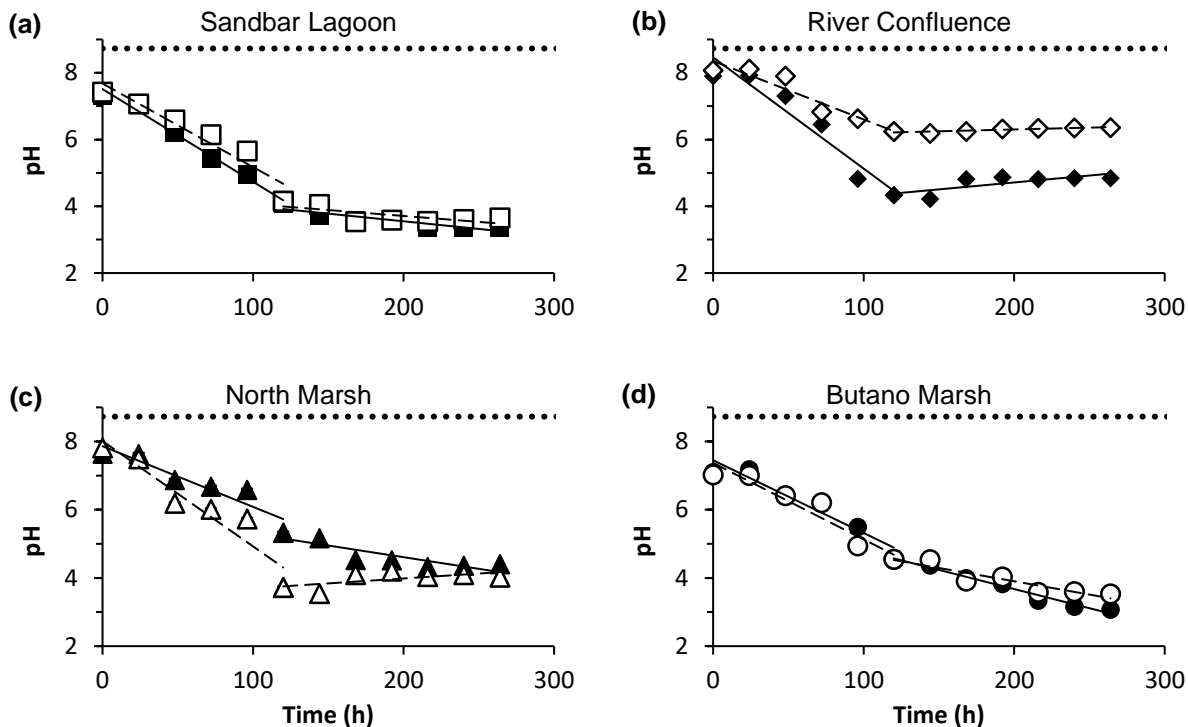
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Figure 4.3. pH measured in slurry incubations at the **(a)** Sandbar Lagoon (squares), **(b)** River Confluence (diamonds), **(c)** North Marsh (triangles), and **(d)** Butano Marsh (circles) sites. Open and closed symbols represent duplicate slurry experiments. The dashed and solid lines represent linear regression for open and closed symbols, respectively. Error bars indicate standard deviation; when not visible, they fall between the size of the symbols.

For all study sites, pH decreased dramatically over the eleven-day experimental period by 2 to 4 pH units, with the largest declines observed at the Sandbar Lagoon and Butano Marsh sites (Figure 4.3). After five days, the pH values began to equilibrate near strongly to mildly acidic values at the River Confluence and North Marsh sites (4.2-6.1 and 3.7-5.4, respectively) and near strongly acidic values at the Sandbar Lagoon and Butano Marsh sites (3.3-3.8 and 3.0-3.5, respectively). Sulfate concentration and pH were generally consistent between duplicate slurries at the Butano Marsh and Sandbar Lagoon sites over the eleven-day experiments, respectively, whereas duplicate slurries were less consistent at the River Confluence and North Marsh sites. At all sites, aqueous hydrogen sulfide concentrations decreased sharply to less than 2 μM (below the detection limit) after one day, where it remained for the rest of the experiments (Figure 4.4).

The study sites showed an increase in aqueous ferrous iron concentrations starting at days 4-6 of the slurry experiments, reaching values up to 9.3-11.2 mM after 11 days with the exception of the River Confluence site, which showed a very limited and temporary increase in aqueous ferrous iron concentrations over the duration of the experiment (Figure 4.5a-d). Ferrous iron concentrations were positively correlated with sulfate concentration (r = 0.77, P < 0.001) and negatively correlated with pH (r = -0.75, P < 0.001). Total aqueous iron concentrations were negatively correlated with pH (r = -0.74, P < 0.001) and positively correlated with sulfate
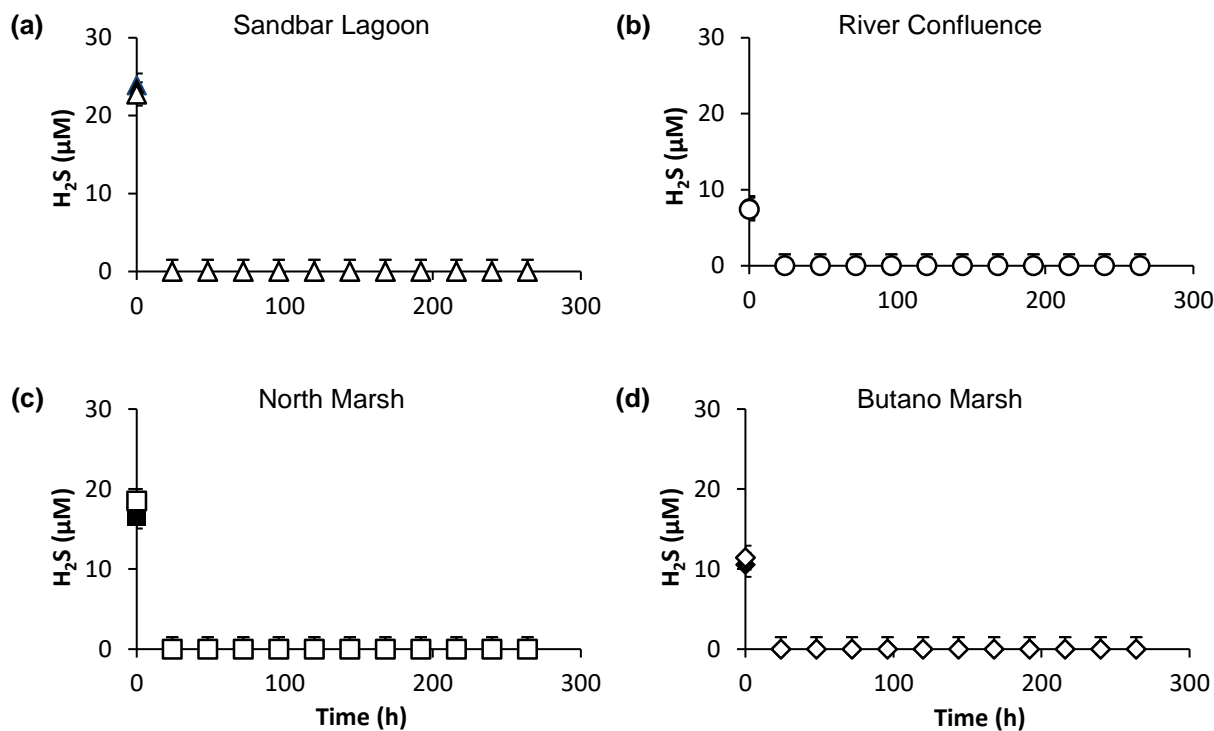
Figure 4.3. Aqueous hydrogen sulfide concentration measured in slurry incubations at the **(a)** Sandbar Lagoon (squares), **(b)** River Confluence (diamonds), **(c)** North Marsh (triangles), and **(d)** Butano Marsh (circles) sites. Open and closed symbols represent duplicate slurry experiments. The dashed and solid lines represent linear regression for open and closed symbols, respectively. Error bars indicate standard deviation; when not visible, they fall between the size of the symbols.

concentration ($r = 0.81$, $P < 0.001$). An order of magnitude lower than ferrous iron concentrations, aqueous ferric iron concentrations also started to increase after day 4 of the experiments. Increases were limited in the Sandbar Lagoon and Butano Marsh sites, reaching maxima of 0.2 and 0.4 mM, respectively, and slightly higher, reaching maxima of 0.6 and 1 mM at the River Confluence and North Marsh sites, respectively (Figure 4.5e-h). Aqueous manganese concentrations increased after day 4 of the experiments, fluctuating steadily up to 0.2 mM at the Butano Marsh site and up to 0.4 mM at all other sites (Figure 4.6a-d) and were an order of magnitude lower than ferrous iron concentrations. One order of magnitude lower than aqueous manganese concentrations, aqueous zinc concentrations also increased after day 4 of the incubations (Figure 4.6e-h). Zinc concentrations ranged up to 62-79 µM at the Butano Marsh and Sandbar Lagoon sites and 44-65 µM at the North Marsh, yet up to 39 µM at the River Confluence site. Zinc concentrations were negatively correlated with pH ($r = -0.81$, $P < 0.001$) and positively correlated with total aqueous iron concentration ($r = 0.73$, $P < 0.001$) and sulfate concentration ($r = 0.86$, $P < 0.001$). Aqueous arsenic concentrations were below detection limits over the duration of the incubations at all sites (data not shown).

The slurry acid-volatile sulfide (AVS) contents steadily decreased, reaching zero between 1 and 3 days at the Butano Marsh site and between 3 and 6 days at the other sites (Figure 4.7a-d).
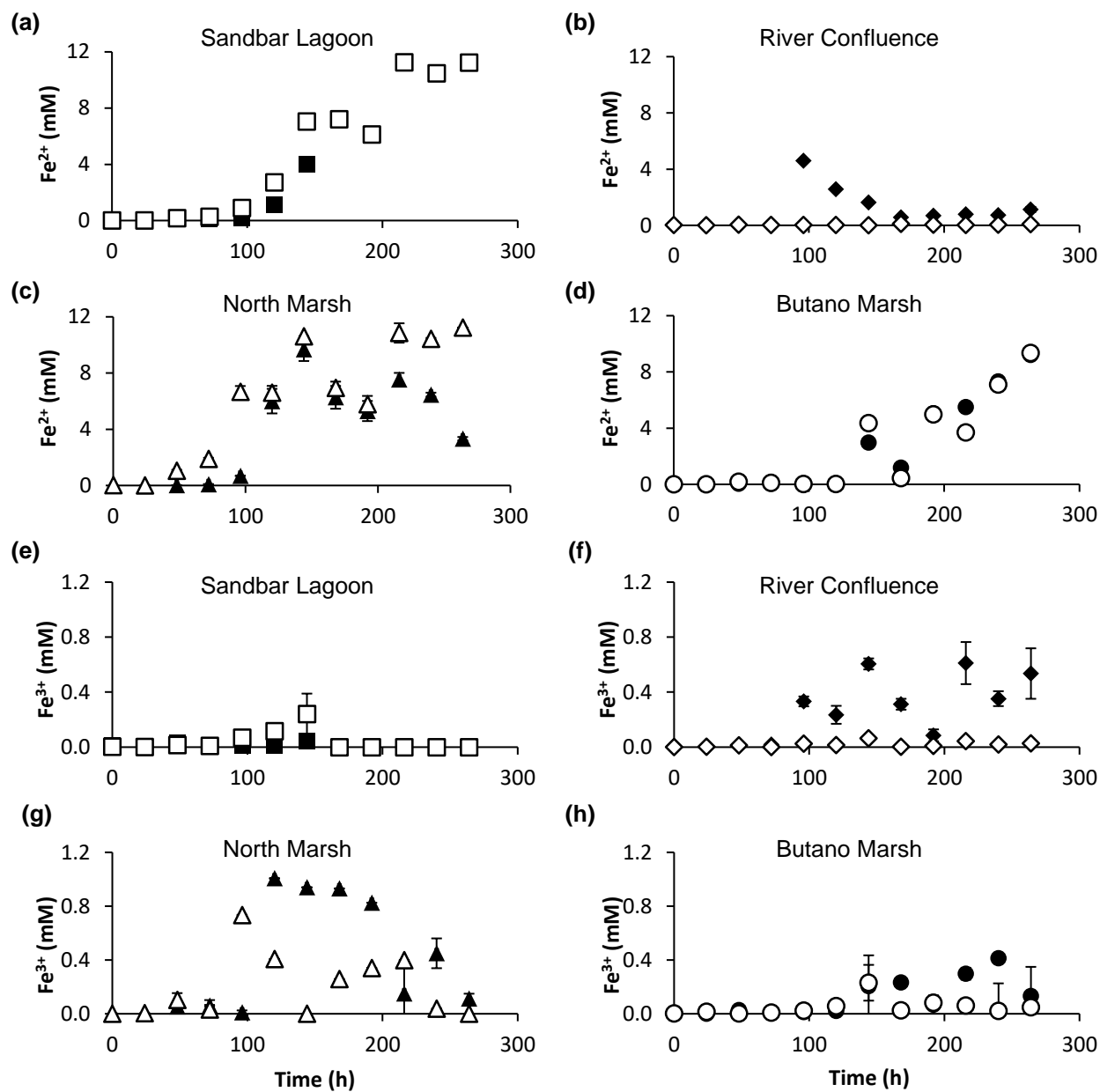
Figure 4.5. (a-d) Ferrous iron concentration and **(e-h)** ferric iron concentration measured in slurry incubations at the Sandbar Lagoon (squares), River Confluence (diamonds), North Marsh (triangles), and Butano Marsh (circles) sites. Open and closed symbols represent duplicate slurry experiments. Error bars indicate standard deviation; when not visible, they fall between the size of the symbols.

Over the course of the eleven-day experiments, sediment iron contents equilibrated to a lower range of 6.8-16 mmol kg^{-1} (Figure 4.7e-h). Sediment organic carbon contents and sediment nitrogen contents ranged 0.9-5.3% and 0.1-0.4%, respectively, and did not change significantly over the eleven-day incubations (data not shown). Sediment molar organic carbon to nitrogen
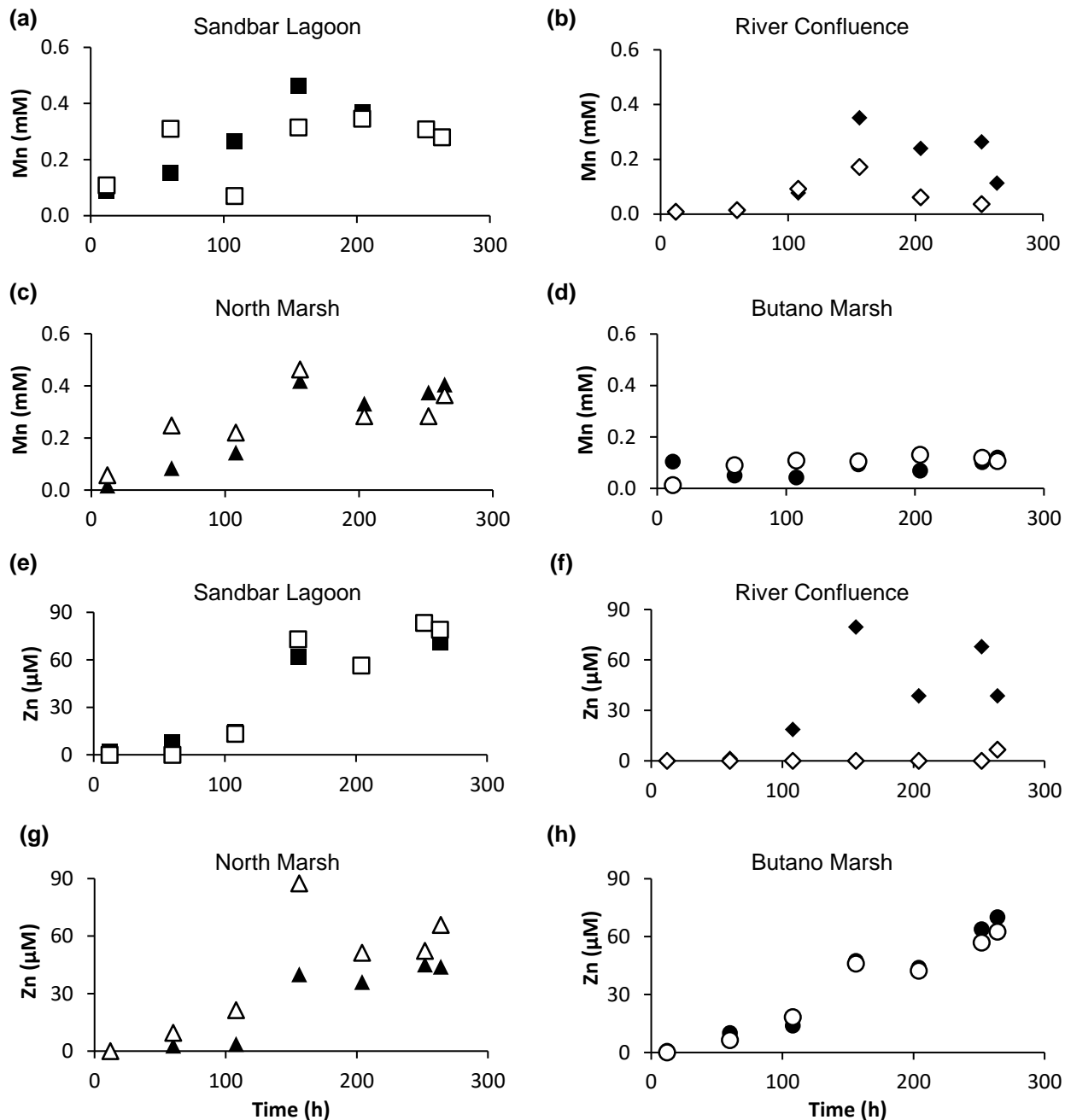
Figure 4.6. (a-d) Aqueous manganese concentration and **(e-h)** aqueous zinc concentration measured in slurry incubations at the Sandbar Lagoon (squares), River Confluence (diamonds), North Marsh (triangles), and Butano Marsh (circles) sites. Open and closed symbols represent duplicate slurry experiments. Error bars indicate standard deviation; when not visible, they fall between the size of the symbols.

ratios increased significantly at the River Confluence and Sandbar Lagoon sites from 10.0-10.8 to 12.6-13.9 but did not change significantly at the North Marsh and Butano Marsh sites, where the highest values (13.4-16.7) were observed (data not shown).
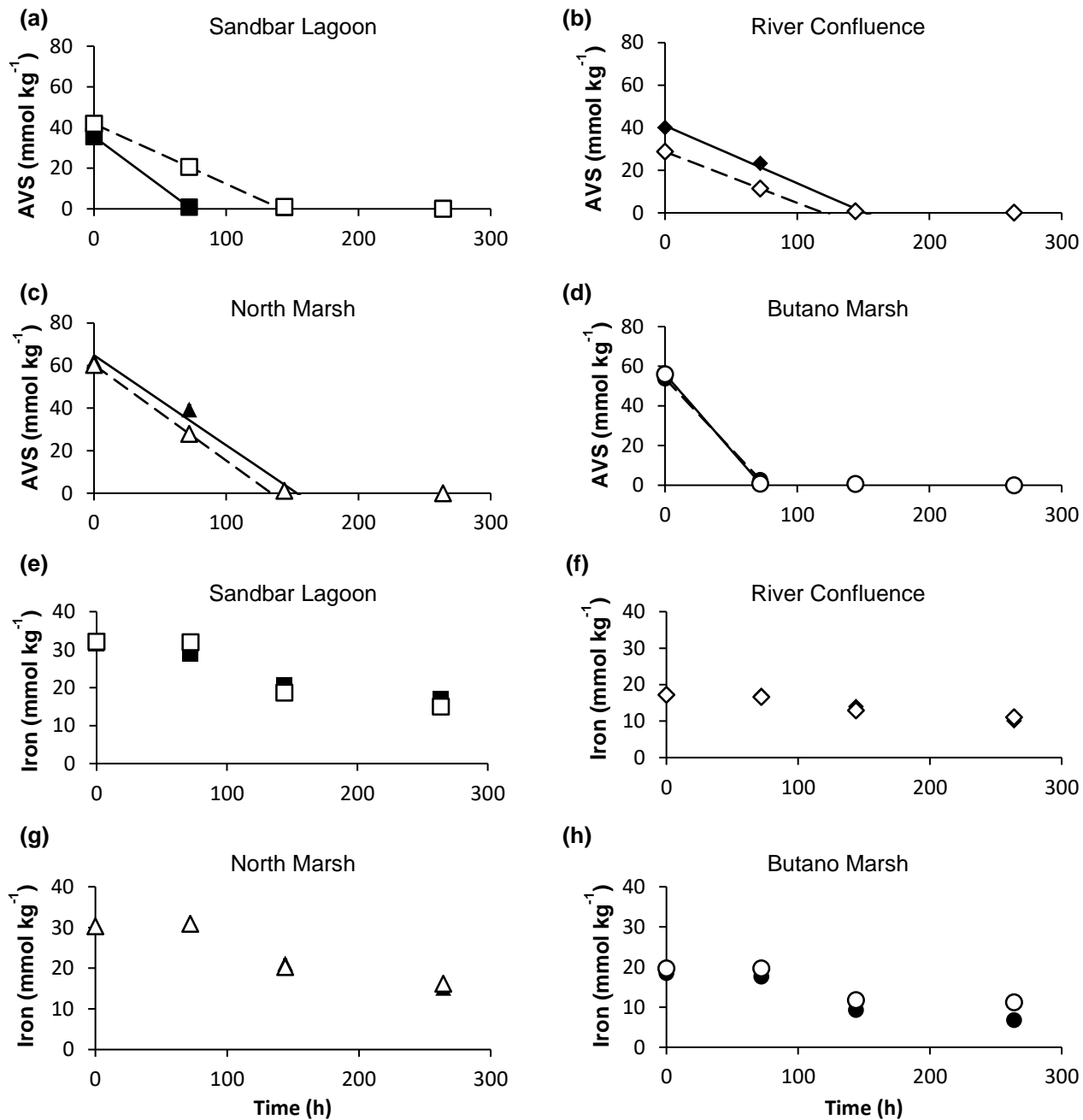
Figure 4.7. Sediment **(a-d)** acid-volatile sulfide content and **(e-h)** iron content measured in slurry incubations at the Sandbar Lagoon (squares), River Confluence (diamonds), North Marsh (triangles), and Butano Marsh (circles) sites. Open and closed symbols represent duplicate slurry experiments. The dashed and solid lines represent linear regression for open and closed symbols, respectively. Error bars indicate standard deviation; when not visible, they fall between the size of the symbols.
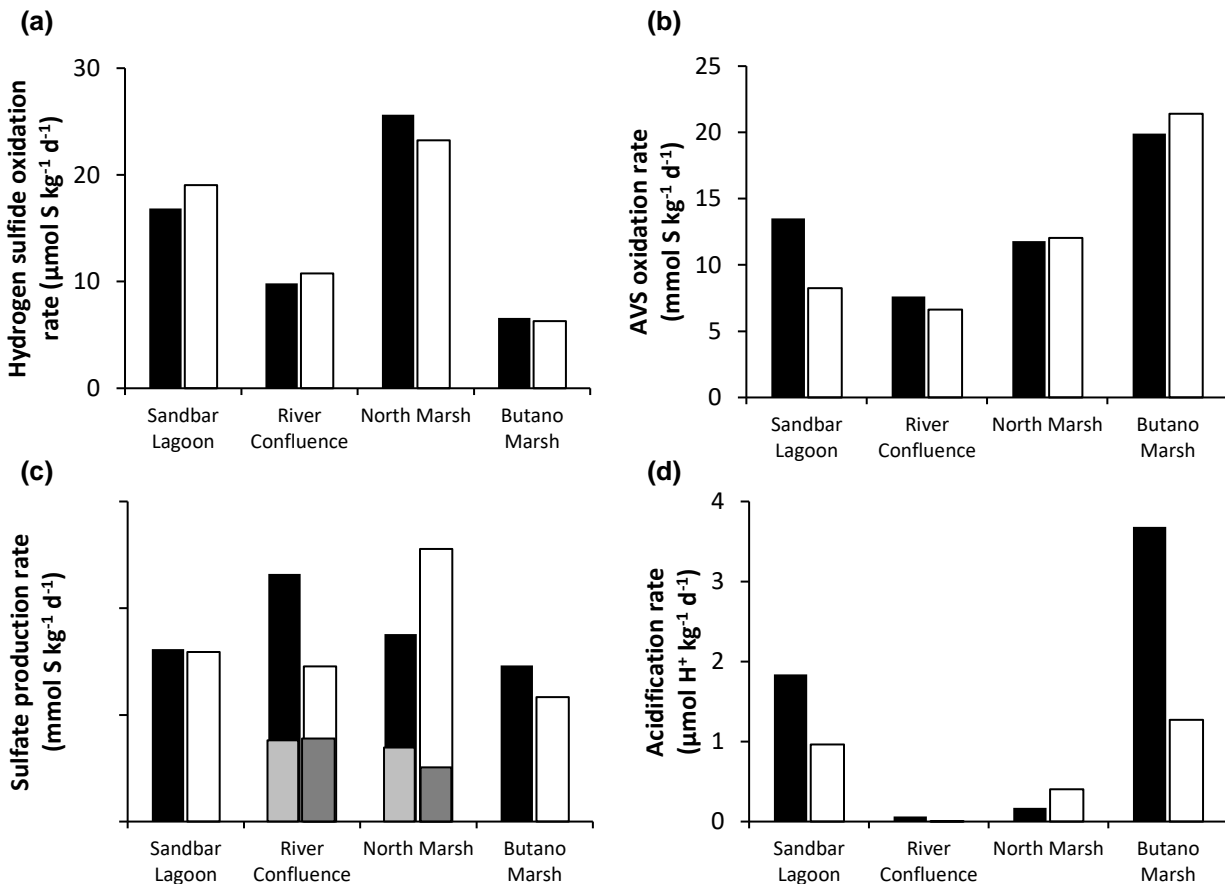
Figure 4.8. (a) Aqueous hydrogen sulfide oxidation rates (SOR), **(b)** sediment acid-volatile sulfide (AVS) oxidation rates (SSOR), **(c)** sulfate production rates (SPR), and **(d)** acidification rates (AR) calculated for the Sandbar Lagoon, River Confluence, North Marsh, and Butano Marsh sites. Open and closed symbols represent duplicate slurry experiments. The grey symbols represent the second period of lower SPR. All rates estimated here for all sites are an underestimation of the *in situ* rates.

3.3. Sulfide oxidation rates, sulfate production rates, and proton production rates

Since aqueous hydrogen sulfide dropped to 0 after the first day, the measured aqueous hydrogen sulfide oxidation rates (SOR) were minimal estimates of the real rates. SOR ranged from 6.3 to 25.6 μmol kg^{-1} d^{-1}, with the highest values observed at the North Marsh and Sandbar Lagoon sites (Figure 4.8a) and exhibited strong positive correlations with sediment iron content ($r = 0.86$, $P < 0.01$) and clay content ($r = 0.81$, $P < 0.05$). Sediment AVS oxidation rates (SSOR) were greatest at the Butano Marsh site (19-22 mmol kg^{-1} d^{-1}) and lowest at the River Confluence site (6-7 mmol kg^{-1} d^{-1}) (Figure 4.8b). The North Marsh and Sandbar Lagoon sites exhibited similar, yet lower SSOR (8.2-14 mmol kg^{-1} d^{-1}). SSOR showed a negative correlation with pH ($r = -0.87$, $P < 0.006$) and positive correlations with chloride concentration ($r = 0.81$, $P < 0.016$), sediment organic carbon content ($r = 0.92$, $P < 0.001$), and sediment nitrogen content ($r = 0.93$, $P < 0.001$).

120
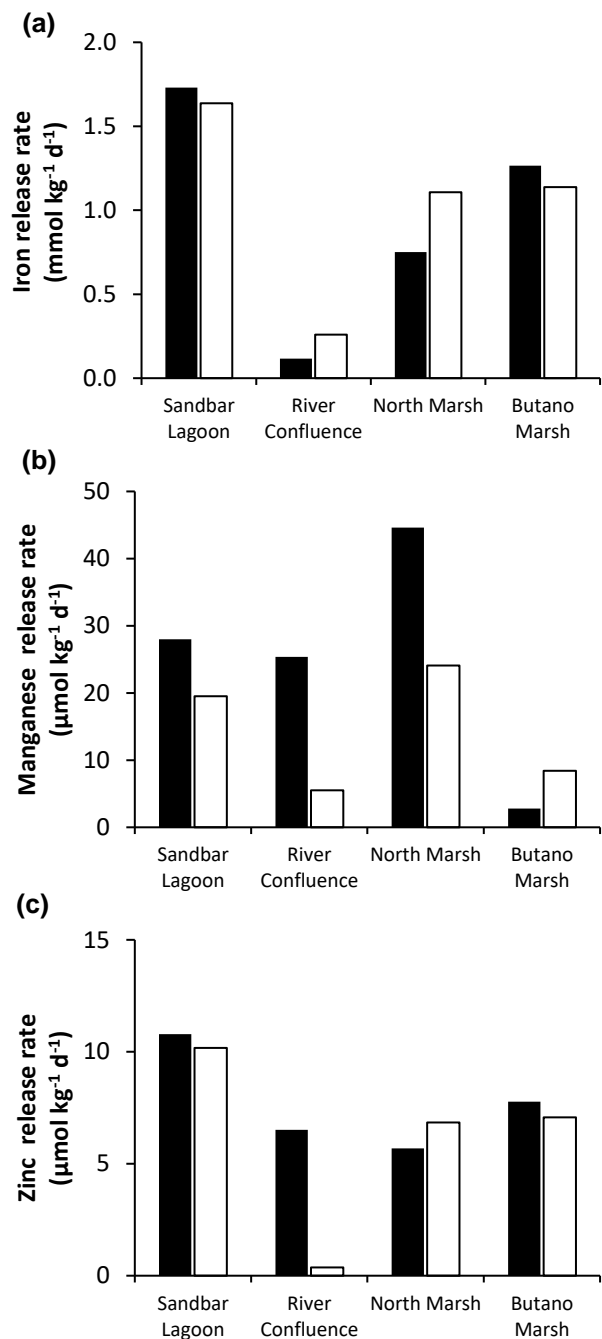
Figure 4.9. (a) Aqueous iron release rates (FeReR), **(b)** aqueous manganese release rates (MnReR), and **(c)** aqueous zinc release rates (ZnReR) calculated for the Sandbar Lagoon, River Confluence, North Marsh, and Butano Marsh sites. Open and closed symbols represent duplicate slurry experiments. All rates estimated here for all sites are an underestimation of the *in situ* rates.

Sulfate production rates (SPR) varied between 5.2 and 12.8 mmol kg^{-1} d^{-1} at all sites, with similar SPR at the Sandbar Lagoon and Butano Marsh sites (Figure 4.8c). Conversely, SPR were

the largest (7.3-11.6 mmol kg^{-1} d^{-1}) in the first 120 hours at the North Marsh and River Confluence sites, yet decreased to 2.4-3.8 mmol kg^{-1} d^{-1} for the remainder of the experiment. The slurry acidification rates (AR) ranged up to 3.7 µmol kg^{-1} d^{-1}, with the highest average values observed at the Butano Marsh and Sandbar Lagoon sites (1.0-3.7 µmol kg^{-1} d^{-1}) and values an order of magnitude lower at the River Confluence and North Marsh sites (0.002-0.4 µmol kg^{-1} d^{-1}) (Figure 4.8d). AR exhibited positive correlations with SSOR (r = 0.71, P < 0.05) and chloride concentration (r = 0.83, P < 0.01) and a negative correlation with pH (r = -0.79, P < 0.05).

Aqueous total iron release rates (FeReR) ranged from 0.1 to 1.7 mmol kg^{-1} d^{-1}, with the highest values observed at the Sandbar Lagoon site, followed by the North Marsh and Butano Marsh sites (0.8-1.3 mmol kg^{-1} d^{-1}) (Figure 4.9a). FeReR were negatively correlated with pH (r = -0.72, P < 0.05) and positively correlated with pore water manganese concentration (r = 0.80, P < 0.05). Aqueous manganese release rates (MnReR) varied between 2.8 and 44.6 µmol kg^{-1} d^{-1}, with the lowest values observed at the Butano Marsh site and the highest value observed at the North Marsh site (Figure 4.9b). MnReR were positively correlated with pore water hydrogen sulfide concentration (r = 0.79, P < 0.05) and SOR (r = 0.81, P < 0.05) and also negatively correlated with pore water chloride concentration (r = -0.76, P < 0.05). Aqueous zinc release rates (ZnReR) were the greatest at the Sandbar Lagoon site (10-11 µmol kg^{-1} d^{-1}), followed by the North Marsh and Butano Marsh sites (5.8-7.8 µmol kg^{-1} d^{-1}) (Figure 4.9c). ZnReR were positively correlated with FeReR (r = 0.81, P < 0.05). Average aqueous iron, manganese, and zinc release rates were the lowest at the River Confluence site (Figure 4.9).

4. Discussion

4.1. Oxidation of Pescadero sulfidic sediments

The decreases in aqueous hydrogen sulfide concentrations, sediment AVS content, sediment iron content, and pH as well as increases in sulfate, aqueous ferrous iron, aqueous ferric iron, aqueous manganese, and aqueous zinc concentrations observed upon sediment resuspension are consistent with the oxidation of sulfide-rich sediments. A complete oxidation of aqueous hydrogen sulfide was observed in less than one day, which is fast compared to the complete oxidation of AVS, which occurred at all sites by the sixth day. While the potential rates measured here for SSOR and SOR are sometimes an underestimation of the real rates, SSOR were generally two to three orders of magnitude greater than SOR, indicating that AVS oxidation is faster. Due to low concentrations, aqueous hydrogen sulfides oxidized quickly, whereas AVS oxidized slowly, resulting in greater sulfur loss from sediment; this is contrary to the slurry incubations on anoxic estuarine sediments rich in metal sulfides performed by Simpson et al. (1998), who attributed higher SOR than SSOR due to the presence of catalytic metal ions.

In the slurries, aqueous hydrogen sulfide is consumed in less than 1 day at all sites. The oxidation of aqueous hydrogen sulfide by dissolved oxygen follows:

$$H_2S \text{ (aq)} + 2O_2 \rightarrow SO_4^{2-} + 2H^+ \hspace{3cm} \text{(R1),}$$

producing one mole of sulfate and two moles of proton per mole of hydrogen sulfide (Chen and Morris, 1972). For the slurries where aqueous hydrogen sulfide ranged from 7.6 to 23.4 µM, it could result in a proton concentration of 15-47 µM at all sites, which would lead to pH values of 4.3-4.8 given excess oxygen and no other geochemical constituents in the slurry. However, due to the moderately alkaline pH in the first few days of the slurries and potentially high buffering capacity of estuarine sediments elsewhere (Schippers and Jørgensen, 2002; Atkinson et al., 2007), I suggest that the oxidation of aqueous hydrogen sulfide had little to no effect on water sulfate concentrations and pH in the experiments. A mass balance analysis of sediment AVS oxidation rates (SSOR), aqueous sulfide oxidation rates (SOR), and sulfate production rates (SPR) shows that for every 0.8-2.8 millimoles of sulfide oxidized from water and sediment, 0.1-1.0 millimoles of sulfate are produced in the first day. If I remove SOR from the mass balance analysis following aqueous hydrogen sulfide removal in the first day, I observe the same trend, indicating that the primary source of oxidized sulfur derives from insoluble sulfides rather than from its dissolved counterpart, as observed by Aller and Rude (1988) for surficial marine systems. In all, these mass balance calculations showed that the changes in sulfate concentrations and pH in the slurry aqueous phase are due to the oxidation of sediment AVS.

AVS constituents, iron monosulfide (FeS) and pyrite (FeS_2), can be oxidized by terminal electron acceptors such as dissolved oxygen or Fe-oxides. The oxidation of FeS by both terminal electron acceptors is:

$$FeS\ (s) + 9/4\ O_2 + 5/2\ H_2O \rightarrow Fe(OH)_3 + SO_4^{2-} + 2H^+ \qquad \text{(R2) and}$$

$$FeS\ (s) + 8Fe^{3+} + 4H_2O \rightarrow SO_4^{2-} + 9Fe^{2+} + 8H^+ \qquad \text{(R3)},$$
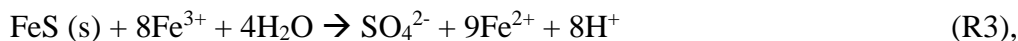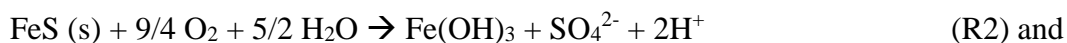
producing one mole of sulfate and up to eight moles of protons per mole of iron monosulfide. Similarly, the oxidation of FeS_2 by both terminal electron acceptors is:
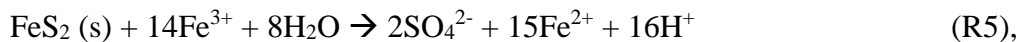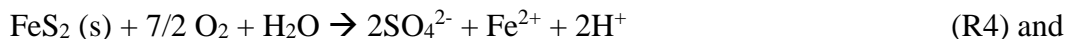
$$FeS_2\ (s) + 7/2\ O_2 + H_2O \rightarrow 2SO_4^{2-} + Fe^{2+} + 2H^+ \qquad \text{(R4) and}$$

$$FeS_2\ (s) + 14Fe^{3+} + 8H_2O \rightarrow 2SO_4^{2-} + 15Fe^{2+} + 16H^+ \qquad \text{(R5)},$$

producing 2 moles of sulfate and 2-16 moles of protons per mole of pyrite (Taylor et al., 1984; Moses et al., 1987; Schippers and Jørgensen, 2002).

The decrease in sediment AVS by day 6 of the incubation was accompanied by the production of 0.7-1.4 moles of sulfate and 0.03-6.1 micromoles of protons per mole of AVS consumed during oxidation, suggesting that the mackinawite oxidation pathways (R2-3) predominate at all sites. Moreover, aqueous total iron concentrations increased to 12 mM and sediment iron contents decreased only when the slurry pH values dropped below 6.6 after one to three days, indicating the release of iron from sediment to water under acidic conditions upon sediment sulfide oxidation (R1-4). Despite oxidizing conditions, aqueous ferric iron concentrations were an order of magnitude lower than aqueous ferrous iron due to their poor solubility and precipitation as Fe-oxides (Byrne and Kester, 1976; DeLaune and Patrick, Jr., 1981). The decrease in slurry pH below 6.6 was also accompanied by an increase in aqueous manganese and zinc concentrations up to 0.5 mM and 87.5 µM, respectively, indicating the release of both metals under acidic conditions. Metal release during sediment re-suspension is largely pH-

dependent such that metal solubility may be attributed to acidification resulting from elemental sulfur oxidation, as observed elsewhere (Burton et al., 2006; Hong et al., 2011). The correlation between metals (iron and zinc) and sulfate concentration also show that sulfide oxidation was the predominant process releasing metals to water.

Our results show that sulfide oxidation of Pescadero Estuary sediments, as measured here by SOR (6.3-25.6 μmol kg^{-1} d^{-1}), SSOR (8.2-21.4 mmol kg^{-1} d^{-1}), SPR (5.8-12.8 mmol kg^{-1} d^{-1}) and AR (0.002-3.8 μmol kg^{-1} d^{-1}), has the potential to occur at rates higher than observed elsewhere on natural sulfidic sediments (Taylor et al., 1984; Lee et al., 2000; Burton et al., 2006; Jørgensen et al., 2009; Hong et al., 2011; Vaclavkova et al., 2014). Lee et al. (2000) measured SSOR of 0.02-1.5 mmol kg^{-1} d^{-1} and 0.02-0.2 mmol kg^{-1} d^{-1} with slurry incubations on California mudflat surface (<0.5 cm) and subsurface (0.5-7.5 cm) sediments, respectively, which is one to three orders of magnitude lower than observed here. Their low SSOR are potentially due to low AVS contents, which ranged from 0.5 to 35 mmol kg^{-1} (Lee et al., 2000). Hong et al. (2011) observed SSOR of 6.2 mmol kg^{-1} d^{-1} with slurry incubations on riverine sediments, which is on the lower end of values observed here despite similar sediment AVS contents (42.3 mmol kg^{-1}). Using anoxic groundwater sediments with pyrite (82.6 mmol kg^{-1}) from natural or amended batch reactors, Jørgensen et al. (2009) measured sulfate production rates (SPR) of 1.1-5.8 μmol kg^{-1} d^{-1}, values which are three orders of magnitude lower than measured here potentially due to reducing conditions. Additionally, Vaclavkova et al. (2014) calculated SPR of 0.7-43 μmol kg^{-1} d^{-1} using brackish estuarine sediments with AVS contents of 2-200 mmol kg^{-1} in reactor incubations coupled with nitrate as an oxidant. Conversely on pure pyrite in bacterially-mediated wet and dry experiments, Taylor et al. (1984) estimated SPR of 0.01-0.5 mmol kg^{-1} d^{-1} and 1.5-7.9 mmol kg^{-1} d^{-1} under anaerobic and aerobic conditions, respectively, which are generally lower than the values observed here, indicating that oxic conditions are necessary to achieve higher rates. With complete removal of AVS (220 mmol kg^{-1}) from Australian flood plain sediments in under 24 hours in sediment suspension experiments, Burton et al. (2006) observed SPR of 2.0 mmol kg^{-1} d^{-1} and a pH decrease of 0.18 pH d^{-1}, which were 2.9-6.5 and 1.2-2.8 times lower than observed in the Pescadero system.

Furthermore, I also show that the release of iron, manganese, and zinc from oxidized Pescadero sediments, as measured here by FeReR (0.1-1.7 mmol kg^{-1} d^{-1}), MnReR (2.8-44.6 μmol kg^{-1} d^{-1}), and ZnReR (0.4-10.8 μmol kg^{-1} d^{-1}), has the potential to occur at rates higher than observed elsewhere on natural sulfidic sediments (Simpson et al., 2000; Burton et al., 2006; Hong et al., 2011). Burton et al. (2006) observed FeReR of 33.8 μmol kg^{-1} d^{-1}, MnReR of 14.0 μmol kg^{-1} d^{-1}, and ZnReR of 4.1 μmol kg^{-1} d^{-1}, which were generally lower than observed here. From riverine sediments, Hong et al. (2011) showed the release of manganese and zinc, with estimates of MnReR and ZnReR up to 2 μmol kg^{-1} d^{-1} and 1 μmol kg^{-1} d^{-1}, respectively, which were on the lower end of values measured here, despite higher sediment zinc contents (8.5 mmol kg^{-1}) than observed here. In contrast, the short-term resuspension experiments on intertidal sediments performed by Simpson et al. (2000) did not release iron, manganese, and zinc from sediment, despite significantly higher sediment iron, and zinc contents (123 mmol kg^{-1} and 18.9 mmol kg^{-1}) than observed here; the circumneutral pH values observed there confirm the dependency of metal release on pH.

The oxidation, production, and release rates observed here may be an overestimation of field values due to the unlimited supply of dissolved oxygen and physical stirring during the slurry incubations, the latter which also disrupts the geochemical and microbial structure of sediments while limiting transport restrictions (Pallud and Van Cappellen, 2006; Pallud et al., 2007). However, slurry incubations may best represent the conditions of Pescadero as it transitions from closed to open state due to the daily, severe tidal flushing of estuarine water with marine water (Williams and Stacey, 2015).

4.2. Geochemical controls on sulfide oxidation pathways

The molar AVS/iron ratios ranged from 1 to 3 at the beginning of the slurry incubations. The ratio of 1 calculated for the Sandbar Lagoon site indicates that mackinawite (FeS, ratio of 1) is the predominant iron sulfide form present there, whereas the ratios of 2 calculated for the North Marsh and River Confluence sites indicate that pyrite (FeS_2, ratio of 2) is potentially the major iron sulfide form present. The higher ratio of 3 observed at the Butano Marsh site points to the presence of an assortment of iron sulfides, which is consistent with the observation of various metal sulfides, including FeS, FeS_2, arsenopyrite (FeAsS), and arsenic trisulfide (As_2S_3) in the nearby location of North Pond (Bostick et al., 2004). However, ferrous iron monosulfides (FeS), which are sensitive to oxidation (Rickard and Morse, 2005), may possibly dominate AVS over pyrite in Pescadero surface sediments (Bostick et al., 2004).

Our rate balance analysis of AR/SSOR ratios also indicate that both dissolved oxygen and ferric iron were utilized as oxidants as coupled with sulfide oxidation at all four sites. More specifically, R2-3 predominate at the Sandbar Lagoon site and R4-5 predominate at the other three sites. Microbial nitrate reduction has also been shown to be coupled with sediment AVS oxidation (Aller and Rude, 1988; Goldhaber, 1997; Schippers and Jørgensen, 2002; Vaclavkova et al., 2014), following:

$$FeS\ (s) + 9/5\ NO_3^- + 8/5\ H_2O \rightarrow Fe(OH)_3 + SO_4^{2-} + 9/10\ N_2 + 1/5\ H^+ \qquad (R6)\ and$$

$$FeS_2\ (s) + 3NO_3^- + 2H_2O \rightarrow Fe(OH)_3 + 2SO_4^{2-} + 3/2\ N_2 + H^+ \qquad (R7);$$
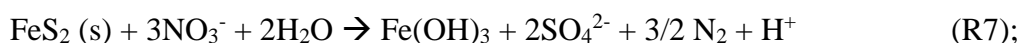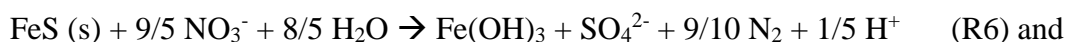
however, nitrate was not detected in Pescadero porewater, indicating that it cannot be an important oxidant here.

The observation that sulfate is still produced and pH is still decreasing once all AVS are removed (i.e. after day six) also implies the presence and potential oxidation of other more stable metal sulfides, such as As_2S_3 and FeAsS observed in the North Pond at Pescadero (Bostick et al., 2004) or other polysulfides. Despite high stability compared to mackinawite, pyrite and greigite oxidation may also be a fast process, catalyzed by electrons shuttling between ferrous and ferric iron (Jørgensen and Nelson, 2004), which explains their inclusion as AVS.

Further mass balance calculations of molar rate ratios can elucidate which oxidation pathway predominates at each of the sites. More specifically, the molar ratio of SPR/SSOR (i.e. sulfate produced to AVS oxidized) for up to six days during which AVS was fully oxidized can

elucidate which oxidation reaction predominates, where a value of 1 indicates that FeS (*via* R1 and R2) predominates and a value of 2 indicates that FeS_2 (*via* R3 and R4) predominates. A rate balance analysis of SPR/SSOR ratios revealed a value of 1 at the Sandbar Lagoon site, confirming that FeS predominates there. These molar ratios further corroborate a mixture of FeS and FeS_2 at the North Marsh, Butano Marsh, and River Confluence sites.

These calculations reveal the near-complete transformation (>96%) of water and sediment sulfides to sulfate by day 6 at the River Confluence and Sandbar Lagoon sites, yet lower removal rates of sulfides (56-71%) at the North Marsh and Butano Marsh sites. The incomplete transformation of sulfides to sulfate implies the production of elemental sulfur (Fuseler and Cypionka, 1995; Billon et al., 2001; Burton et al., 2006) or other intermediate reduced species, such as polysulfides that could react with AVS to produce pyrite (Rickard and Morse, 2005).

While the SSORs alone do not indicate which oxidative pathway (R2-5) predominates in Pescadero sediments, or more generally in sulfide-rich environments, the results show that AVS oxidation is coupled with iron release from sediment. Further mass balance of iron transformation showed a decrease in sediment iron contents by 0.9 to 2.6 millimoles and an increase in total aqueous iron concentrations by 0.7 to 2.0 millimoles over the course of the eleven-day experiment. Moreover, the results show that AVS oxidation is coupled with manganese and zinc release from sediment. Similarly, mass balance of zinc transformation showed a release of 1.1-24 micromoles from sediment to increases of 6.7-13.8 micromoles in water. Aqueous manganese concentrations also increased by 6.4-71 micromoles in water; however, aqueous arsenic was absent from slurry incubations, suggesting that the chemical forms of sulfide in sediment are not consistent with arsenopyrite or arsenic trisulfide, as suggested by Bostick et al. (2004) for the North Pond. Instead, manganese sulfide (MnS) and zinc sulfide (ZnS) may predominate over arsenic sulfides in sediments in Pescadero's main channels, or in the structure of sulfide crystals, as observed elsewhere in estuarine sediments (Luther et al., 1980). However, I do not observe the release of aqueous arsenic in slurry incubations, suggesting that they are not promptly oxidized or widely prevalent in Pescadero sediments. In all, I demonstrate the transformation or release of iron, manganese, and zinc from sediment to water as coupled with AVS oxidation and proton production.

I observed some spatial differences in SSORs in the Pescadero Estuary, with higher rates at the two sites located the farthest from the ocean, North Marsh and Butano Marsh. The higher sulfide removal potential of those two sites could be attributed to their higher sediment AVS, organic carbon, and nitrogen contents and finer textures, all of which have the potential to drive redox reactions R1-5. Goldhaber and Kaplan (1976) suggest a tendency for sediments with high organic carbon contents to be associated with high reduced sulfur (i.e. pyrite) contents, confirming the positive trend observed here between AVS and organic carbon contents. Furthermore, Eggleton and Thomas (2004) assert that fine-grained sediments with higher sorptive capacities generally accumulate higher contaminant contents than their coarse-grained counterparts, therefore corroborating the positive trends between metal contaminant (i.e. AVS or other sulfide complexes) content and mean grain size.

Of the four sites, the River Confluence site has the lowest average rates of sulfide oxidation (SSOR), acidification (AR), and metal release, which could result from the low AVS and metal

contents and aqueous hydrogen sulfide concentrations observed there. These rates also indicate that the oxidative effects of AVS (i.e. acidification and metal release) are less severe there than at the other sites. Despite the largest difference in proximity from the ocean, the Sandbar Lagoon and Butano Marsh sites have the largest SSOR, AR, FeReR, and ZnReR, which may be attributed to greater AVS fractions of the more soluble mackinawite than other divalent AVS than at the remaining two sites. This difference in AVS composition may explain the spatial difference in rates across the estuary, as also suggested elsewhere for anoxic sediments subjected to oxic conditions (Hong et al., 2011). However, also in agreement with Hong et al. (2011), oxidation and release rates are a consequence of many interrelated biogeochemical processes, indicating that the magnitude or severity of effects can vary under different spatial, physical, and geochemical conditions such that I cannot accurately predict geochemical rates nor shifts toward poor water conditions.

4.3. Implications of the direct and indirect oxidative effects of sulfide-rich sediments

The changes in water conditions caused by sulfide oxidation when the sediment is stirred and oxygenated as the estuary opens, specifically the decrease in pH and the release of iron, manganese, and zinc, are potentially severe enough to cause fish kills at all sites at Pescadero. The maximum aquatic life criteria for water pH and aqueous hydrogen sulfide are 6.5-8.5 and 0.06 µM; the maximum criteria for the aqueous concentrations of iron, zinc, and arsenic are 28 µM, 1.2-1.8 µM, and 0.9-4.5 µM, respectively in fresh to salt water systems (US-EPA, 2016). The cardiovascular system of steelhead trout is heavily affected by hydrogen sulfide toxicity, with 48-hour lethal and LC50 thresholds of 0.2 µM and 0.4 µM, respectively (Dombkowski et al., 2004). In addition to pH stress, steelhead trout in moderately acidic pH environments (<5.5) have been shown to have higher plasma cortisol levels (Barton et al., 1985) and subsequently increased susceptibilities to other compounding stressors, such as anoxia and hydrogen sulfide. Their sperm motility has been found to be negligible at extracellular pH values below circumneutral values (<7.7) (Ingermann et al., 2003). With 96-hour LC50 thresholds of 1-10 µM under acidic to circumneutral pH conditions (4.7-7.0) for small steelhead trout, zinc has been observed to cause excess mucus secretion and accumulation and necrotic damage (Cusimano et al., 1986).

The presence of AVS is consistent with low aqueous metal concentrations, as observed in the Pescadero Estuary and other estuarine sediments (California: Lee et al., 2000; Australia: Powell and Martens, 2005; France: Audry et al., 2007) and is believed to reduce metal bioavailability, solubility, and toxicity (Di Toro et al., 1992; Simpson et al., 1998; Burton et al., 2005; Rickard and Morse, 2005). Sulfide oxidation effects are also compounded by the reduction of Fe-oxides that follows, resulting in greater iron release from insoluble to soluble forms (Aller and Rude, 1988; Thamdrup et al., 1994; Schippers and Jørgensen, 2002).

In the incubations, aqueous hydrogen sulfide concentrations quickly decreased from <25 µm to below detection limits, indicating that hydrogen sulfide is quickly removed from water under *in situ* conditions. Consequently, the low *in situ* aqueous concentrations of hydrogen sulfide coupled to its fast oxidation confirm that direct toxicity to fish due to high aqueous hydrogen

sulfide concentrations are not likely to occur as the Pescadero Estuary transitions from closed to open state. This is consistent with the conclusions of Richards and Pallud (2016).

The oxidation of sediment sulfides resulted in significant iron, manganese, and zinc release from sediment to water under acidic (pH<6.6) conditions, which occurred after two to three days at all sites. Furthermore, the increases in aqueous iron concentrations in the slurries over time (up to 11 mM) indicate that there is a high potential for surface water contamination with iron or more toxic metals than iron, such as zinc and manganese, which also form metal sulfides (Giblin, 2009) and have been observed here and in the North Pond sediments (Bostick et al., 2004) and also copper and nickel, as observed elsewhere (Cooper and Morse, 1998; Simpson et al., 1998; Du Laing et al., 2009; Morgan et al., 2012). The dissolution of iron and zinc released 35-54% and 1-14% of their sediment contents, respectively. Using sediment manganese contents from North Pond sediments (0.5-1.1 mmol kg^{-1}) (Bostick et al., 2004), I estimate that the slurry incubations released similar percentages of manganese to water, resulting in the aqueous concentrations observed here (0.1-0.5 mM). With stressful thresholds for aquatic life (US-EPA, 2016), these metals could individually or jointly kill fish. In contrast, aqueous arsenic was not detected in water, demonstrating that it does not have a significant effect on water conditions nor fish health.

The sharp decreases in pH down to 3.1 over the course of the experiment also participates in decreasing water conditions upon sediment resuspension. Moreover, severe acidification (pH<6.6) increases dissolution rates of iron, manganese, zinc, as observed here, and also of other heavy metals, as observed elsewhere (Cusimano et al., 1986), indicating a direct correlation between the two. Subsequent aqueous iron, manganese, and zinc concentrations are highest (11 mM, 0.5 mM, and 83 µM, respectively) after 6 days of Pescadero sediment resuspension, during which pH values are lowest. Furthermore, the values observed for pH and aqueous iron, manganese, and zinc concentrations at this timescale are beyond the maximum aquatic life criteria (US-EPA, 2016), indicating that the indirect effects of sulfide oxidation could potentially be deleterious for steelhead trout and other fishes at the Pescadero Estuary.

The oxidation effects of precipitated sulfide minerals imply that dissolved oxygen concentrations may also be consumed, as observed elsewhere (Simpson et al., 2000; Burton et al., 2006; Maddock et al., 2007), leading to anoxic and/or hypoxic conditions that are also individually detrimental for fish (Diaz and Rosenberg, 1995; Bagarinao and Lantin-Olaguer, 1998; Luther et al., 2004). Sulfate concentrations measured in the slurry incubations (up to 81 mM) were nearly three times larger than seawater values (Howarth, 1984; Bianchi, 2007). Coupled with a high potential for sulfate reduction to occur in the open state (Richards and Pallud, 2016) and potentially anoxic and/or hypoxic conditions, these concentrations indicate that sulfate-reducing microorganisms may be operating at near-maximum rates, leading to greater sediment AVS contents when the estuary is filled and worse water conditions (i.e. severe acidification and metal dissolution) when the estuary is drained.

5. Conclusions

Overall, I demonstrate that sediments from the Pescadero Estuary are acid-sulfate sediments (ASS), whose direct (i.e. acute hydrogen sulfide toxicity) and indirect, oxidative effects

have severe implications for water and sediment conditions. Both AVS and aqueous hydrogen sulfide have larger oxidative rates at the Pescadero Estuary than observed at other estuarine sites impacted by ASS and fish mortality events. Sediment AVS predominates over aqueous hydrogen sulfide in concentration, indicating that aqueous hydrogen sulfide cannot be responsible for fish deaths during sediment resuspension in the transition from closed to open state at the Pescadero Estuary. However, the experiments show that sediment AVS drives the rapid release of protons, iron, manganese, and zinc from sediment to the water column to concentrations greater than the stressful or lethal thresholds for steelhead trout and other fish, indicating a toxic effect on water conditions at the Pescadero Estuary.

6. Acknowledgements

7. References

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Conclusions

The production of hydrogen sulfide (H_2S) and sulfide precipitates and oxidation of acid-volatile sulfides (AVS) are major issues concerning coastal environments globally (Chapman & Wang, 2001; Powell & Martens, 2005; Thamdrup et al., 1994). AVS and other metal sulfides is known to reduce metal toxicity (Di Toro et al., 1992; Simpson et al., 1998), indicating a positive effect on water conditions in estuaries. However, in combination with persistent hydrogen sulfide production and toxicity, the indirect, oxidative effects of AVS are continuous, leading to poor water quality (Burton et al., 2006; Johnston et al., 2009; Sammut et al., 1996; Wilson et al., 1999) and fish mortality events in estuaries across the globe (Bush et al., 2004; Luther et al., 2004). Due to their global production, there appear to be few studies regarding the complete removal or containment of AVS in estuarine environments, indicating that there are many opportunities for management practices to limit the deleterious effects of AVS on watershed**s**. Culminating in this comprehensive analysis, a better biogeochemical understanding of sulfur redox cycling in a heavily impacted and complex bar-built estuary (Pescadero, CA) may yield new approaches to reduce fish mortality events and this and other intermittent estuaries. Towards this end, I conducted four studies, the results of which are described below.

In my first chapter, I illustrated the decline in water conditions, specifically pH, in the transition from closed to open state in the intermittent Pescadero Estuary. The physical opening events in this system are directly linked to increased water mixing and sediment resuspension (Williams and Stacey, 2015). Given that fish mortality events are consistently associated with the transitional period from closed to open state (Becker et al., 2009; Bennett et al., 1985; Sloan, 2006), it appears that limiting the physical opening events may potentially limit the severity of the kill events. In contrast, increased closure periods eliminate threatened (migratory and anadromous) steelhead trout from migrating to freshwater without a connection to the Pacific Ocean. Closed states also are unhealthy for water conditions, specifically due to low water mixing and hypoxic conditions (Sloan, 2006; Whitfield et al., 2008), indicating no straightforward restorative solution of a permanently closed or permanently open system on ecological and geochemical scales. The opening chapter highlighted spatial differences, in which the Pescadero Creek region maintains more geochemically-stable conditions than the rest of the Pescadero Estuary. The water and sediment characteristics of the other Pescadero Estuary regions are a significant departure from the coarse-grained Pescadero Creek sediments with significantly lower sulfate concentrations and sediment AVS and organic carbon contents. The sediment conditions observed in the other regions suggest that the effects of sulfate reduction, sulfide precipitation, and sulfide re-oxidation on pH and metal release can be much more severe there. As a result, endangered steelhead trout may be safer in the Pescadero Creek than the second major tributary to the estuary, Butano Creek, or the main channels.

My second chapter elucidated sulfur and iron redox cycling in the closed and open state at four Pescadero Estuary sites on a gradient from ocean to freshwater, and more specifically the dominant anaerobic respiration processes in sediment. The pore water profiles of reduced sulfur

and iron constituents, hydrogen sulfide and ferrous iron, showed that microbial sulfate reduction is the dominant anaerobic respiration process in Pescadero Estuary sediments in both states. The suboxic, reducing conditions in sediment pore water also indicated that iron reduction may be driven by microbial and/or abiotic means in conjunction with sulfate reduction. The coupled production of hydrogen sulfide and ferrous iron leads to the formation of iron sulfide precipitates across a range of coarse- to fine-grained sediments in the Pescadero Estuary. The reductive processes caused basification, as observed by the circumneutral to mildly alkaline values in the closed and open state. In contrast, oxidative processes caused severe acidification in the open state, however were balanced by alkaline marine water, buffered by dissolved inorganic carbon, and limited to slightly lower pH values due to reductive processes occurring simultaneously.

In my third chapter, I identified higher maximum potential rates of microbial sulfate reduction, sulfide export to water, and sulfide precipitation in sediment in the closed state than in the open state. I also discovered that potential rates were higher in fine-grained sediments, including the River Confluence, Butano Marsh, and North Marsh sites, where higher organic carbon contents and SRB abundances were observed. Compared to sulfate reduction and sulfide precipitation rates, rates of hydrogen sulfide export to water were negligible, exposing the rapid exchange of sulfur from water to sediment in both closed and open states. Concentrations of the poorly-soluble hydrogen sulfide were low, therefore suggesting that it cannot be solely responsible for fish mortality events. My analysis indicated that maximum potential rates of sulfate reduction and sulfide precipitation in the closed state were four orders of magnitude greater than the flux of sulfate in the open state, implying that the Pescadero Estuary is a major source of metal sulfides in sediment. In all, with AVS contents up to 90 mmol S kg^{-1}, sediment metal sulfides may be damaging for water conditions and fish during physical events directly resulting in their fast re-oxidation, consumption of oxygen, and acidification. This chapter has been published in the peer-reviewed journal, Water Research (Richards and Pallud, 2016).

Finally, the fourth chapter demonstrated that the oxidative effects of Pescadero Estuary sulfide-rich sediments on water conditions are severe enough to cause poor water conditions and potentially lead to fish mortality events. Similar to the values measured in the closed and open states of the first chapter, hydrogen sulfide concentrations were low in slurry incubations and their oxidation rates were low (<30 µmol S kg^{-1} d^{-1}) across all sites. However, with complete removal of AVS after six days, rates of AVS oxidation ranged up to 22 mmol S kg^{-1} d^{-1} and were three orders of magnitude greater than that of their aqueous counterparts. The oxidative effects of AVS reduced pH to strongly acidic and moderately acidic values that do not align with circumneutral values preferred by fish. The slurry incubations also confirmed a dependency of metal release on pH, such that metal concentrations increased significantly below circumneutral pH values (<6.6). Aqueous concentrations of iron (Fe), manganese (Mn), and zinc (Zn) rose to 12 mM, 0.6 mM, and 90 µM, respectively, which were all an order of magnitude or greater than the EPA-defined maximum criteria for aquatic life (US-EPA, 2016).

From a larger analysis of the watershed to an in-depth interpretation of the water and sediment interactions, the profound evidence presented here on the Pescadero Estuary confirms that both physical and biogeochemical influences control sulfur redox cycling, leading to poor water and sediment conditions. In the closed state, low water mixing and microbial sulfate

reduction are physical and biogeochemical precursors to hydrogen sulfide production and sulfide precipitation in sediment. The transition from closed to open state physically drives water mixing and sediment resuspension (Gillanders et al., 2011) of sulfide-rich sediments, leading to acidic, metal-rich water across the main channels of the Pescadero Estuary. These effects are spatially-dependent, however, resulting in poorer water and sediment conditions in the fine-grained sediments of the Butano Creek region and main channels than in the coarse-grained Pescadero Creek region. In both closed and open states, hydrogen sulfide remains omnipresent, in concentrations up to 42 µM – i.e. two to three orders of magnitude greater than the maximum aquatic life criterion for the odorous chemical (58 nM) (US-EPA, 2016). With contents ranging up to 90 mmol kg^{-1} across the estuary, AVS and other metal sulfides may indirect exacerbate water conditions for fish. Consistent with Sloan (2006) and Smith (2009), the acute toxicity of hydrogen sulfide, combined with anoxic, acidic water conditions with high aqueous metal concentrations are believed to produce unfavorable water conditions and, ultimately, fish mortality events in the Pescadero Estuary.

The consistent association of fish mortality events with anoxia, hydrogen sulfide, and acidification in the Pescadero Estuary indicate that the geochemical conditions in water and sediment have not changed significantly in the last decade (Viollis, 1979; Sloan, 2006; Smith, 2009). However, physical influences have shifted significantly, including the dynamics of the sandbar barrier which are influenced by climate, tides, and wave action (Williams and Stacey, 2015). The Pescadero Creek region is shallow compared to the Butano Creek region and main channels, indicating further physical differences. Compared to the regular occurrence of kills between 1995 and 2005, the last two major mortality events were in February 2014 and October 2016, which may be due to direct drought effects (Mao et al., 2015), specifically limited precipitation events leading to lower water levels and limited sediment resuspension. Differences in the magnitude of kill events among years may also be attributed to fewer juvenile steelhead trout in the Pescadero Estuary in some years than others. Despite a shift in climatic conditions and physical dynamics, the root of the problem is the natural microbial reduction of sulfate to hydrogen sulfide at the interface of water and sediment in the Pescadero Estuary. Due to high influxes of sulfate and organic matter from ocean and riverine sources, respectively, hydrogen sulfide and metal sulfides will always be in abundance in estuarine environments. Remedial methods, including tidal inundation, acid suppression, and buffering techniques, may alleviate the problem; however, the intermittent intrusion of marine water must be avoided to inhibit sulfate reduction (Powell and Martens, 2005). A permanently closed system eliminates the potential for the estuary to be used as breeding grounds for marine and anadromous fishes and therefore is implausible. The management and remediation of Pescadero Estuary as a valuable watershed and sensitive fish habitat is a constant challenge, especially in meeting policy criteria for both water quality and ecological purposes. Environmental and ecological solutions will be attained upon development of our biogeochemical knowledge of sulfur cycling across scientific disciplines and complex estuarine ecosystems.

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