Safeguarding from Sulfide: Can Pescadero Estuary be restored?

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Introduction

Intermittent estuaries are dynamic environments characterized by the aperiodic formation of a sandbar at the estuary's mouth (*1*). Common on the California coast (*2*), these spatially and temporally complex systems act as productive watersheds, riparian zones, and nursery habitats for ecologically and economically important species. However in recent years, 67% of estuaries in the U.S. have degraded due to eutrophication, dissolved oxygen (DO) depletion, and disease (*3*). In intermittent estuaries globally, fish kills are often associated with the transition from closed to open, likely resulting from the direct and indirect effects of hydrogen sulfide (H_2S), a product of microbial sulfate (SO_4^{2-}) reduction under anoxic conditions (*4*).

Since 1995, fish kills have occurred nearly annually with the aperiodic breach of the sandbar in the Pescadero Estuary located on the California coast (Fig. 3), leading to its inclusion on the CA Clean Water Act list of impaired waters (*5*). The cause, though unclear, is likely an environmental issue relating to poor water quality (*6*). In order to understand the effects of the estuary biogeochemical dynamics on water quality, we investigated the spatial heterogeneity of microbial sulfate reduction in sediment and hydrogen sulfide release to water and the variables controlling these biogeochemical processes in the closed and open states at Pescadero (Fig. 5).

Hypotheses: In the closed state, microbial SO_4^{2-} reduction increases due to low DO, increasing H_2S in the water column and iron sulfide precipitates in sediment. In the open state, microbial SO_4^{2-} reduction decreases slightly as the estuary is drained and iron sulfide precipitates are oxidized, further depleting DO in the water column. Long periods of closed state, coupled with breaching events, worsen water quality and increase fish kill events.

Effects of Hydrogen Sulfide in Intermittent Estuaries

Closed State

1. Indirect removal of dissolved oxygen
   - Stressful, lethal levels observed for fish
2. Direct acute toxicity
   - Lethal >10μM after 24-96 hours for fish
3. Metal sulfide precipitation in sediment

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Open State

1. Re-suspension and mixing into water column as the estuary drains
2. Metal sulfide oxidation
3. Severe acidification and DO depletion in sediment and water

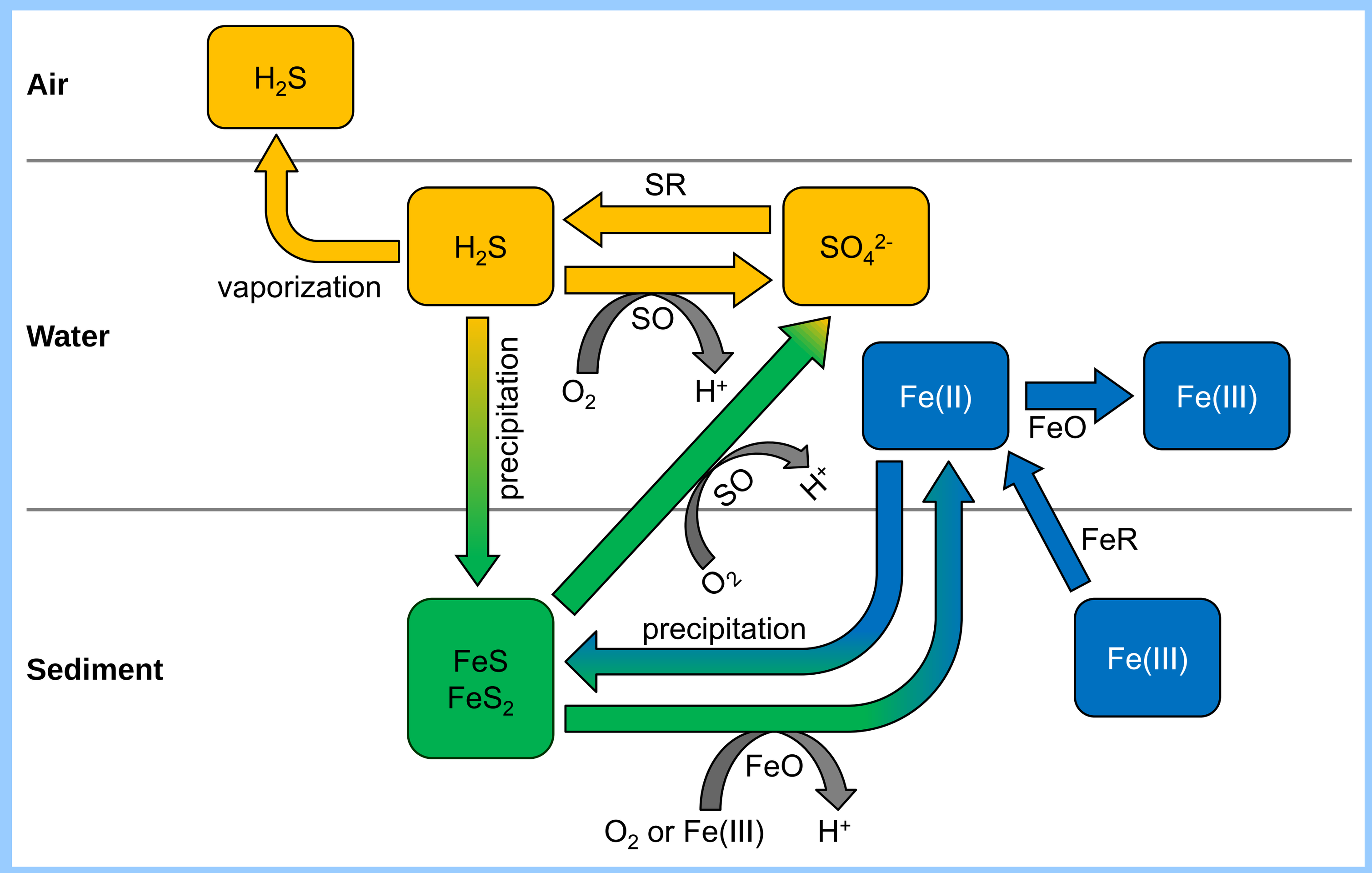

Figure 1. Basic schematic of biogeochemical processes in intermittent estuaries, such as Pescadero Estuary. Key processes include: sulfate reduction (SR), sulfide oxidation (SO), iron reduction (FeR), and iron oxidation (FeO).

Laboratory Analyses

- ***Water geochemical characteristics***: pH, conductivity; [SO_4^{2-}], [H_2S], [Cl^-]
- ***Sediment physical characteristics***: porosity, dry bulk density, mean grain size, texture; sand, silt, clay contents
- ***Sediment geochemical characteristics***: pH, C_{org}/N; total Fe, SO_4^{2-}, H_2S, C_{org}, N contents
- ***Microbiological counts***: enumeration of sulfate-reducing microorganisms
- ***Flow-through reactor experiments***: Input SO_4^{2-} solutions (with Br^- and adjusted with Cl^- to mimic site) into undisturbed *in situ* sediment cores to measure outflow concentrations of ions in solution over time via ion chromatography.

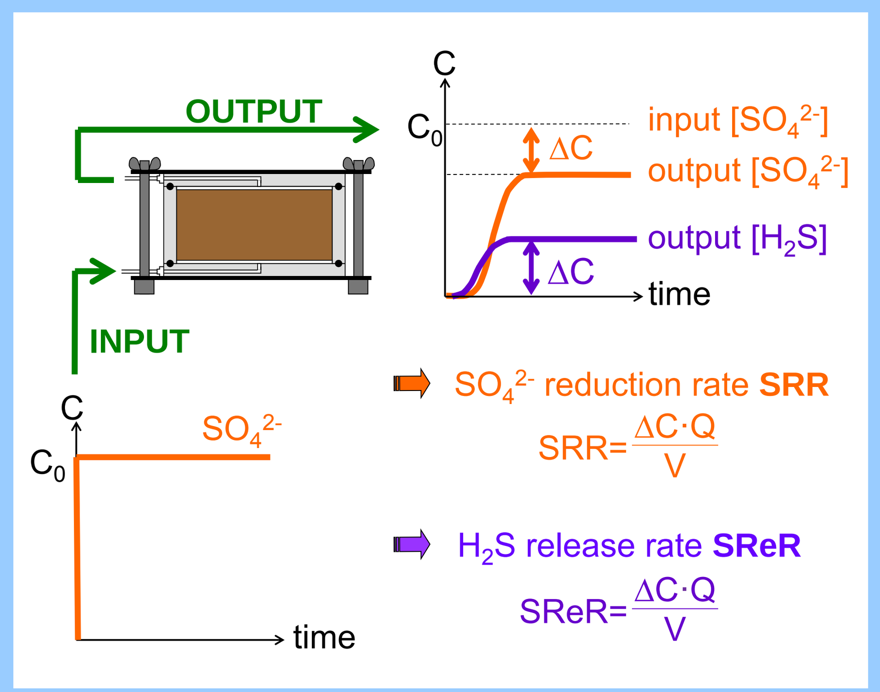

Figure 2. Schematic of flow-through reactor experiments and rate calculations. For SRR, ΔC is the change in sulfate concentration (mM), Q is the volumetric flow rate (mL h^{-1}), and V is the volume of the sediment slice (cm^3). For SReR, ΔC is the output hydrogen sulfide concentration.

Study Site: Pescadero Natural Marsh Preserve

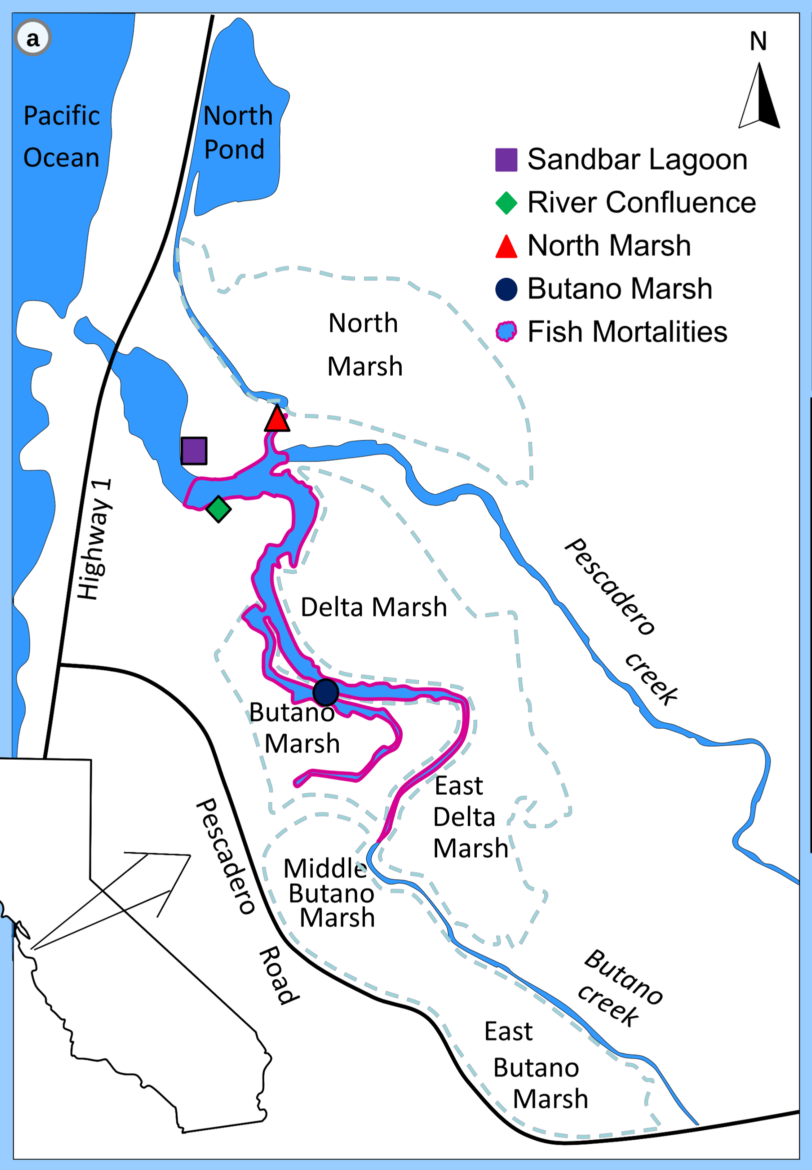

Figure 3. *a*) Pescadero Estuary (CA), and location of the four sites sampled in August 2013 (closed state) and February 2014 (open state). *b*) Federally-threatened steelhead trout with sulfide-rich sediments in their mouths and gills, after a natural breaching event.

Results

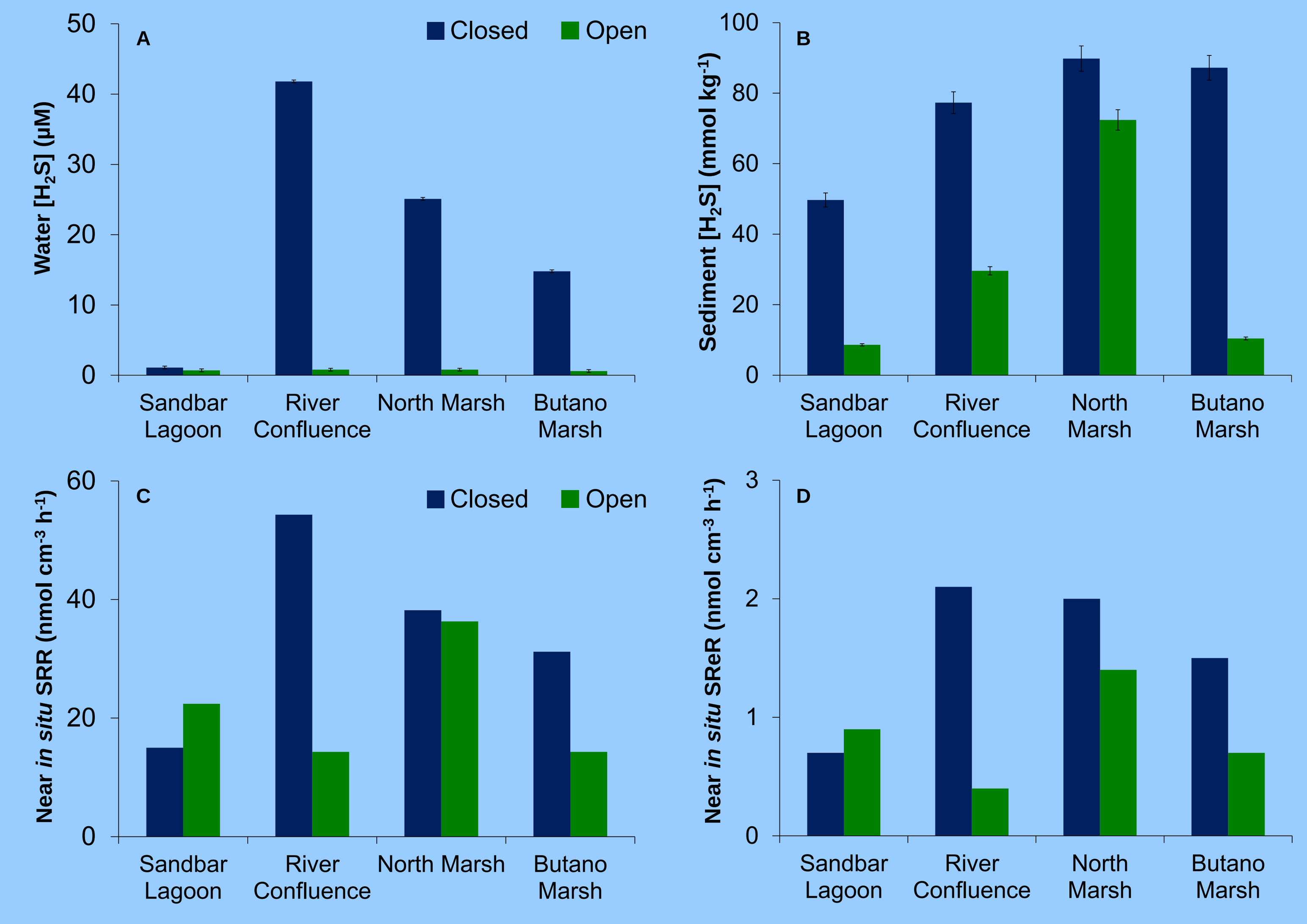

Figure 4. Geochemical characteristics and near *in situ* rates at four Pescadero sites in the closed and open states: a) water H_2S concentration; b) sediment H_2S content; c) near *in situ* SRR; d) near *in situ* SReR. The sites exhibit a salinity gradient from the Pacific Ocean to the Butano Creek.

Physical Dynamics

Figure 5. The mouth of the Pescadero Estuary in the closed and open states.

Discussion

In the closed state:
- Sulfate reduction occurs in sediment at all sites in the closed state, as enhanced by high [SO_4^{2-}] and anthropogenic and natural loads of organic matter.
- Based on mass balance calculations, the majority of hydrogen sulfide precipitates in sediment, since near *in situ* SReR represent 4-6% of their near *in situ* SRR counterparts (Fig. 4C,D).
- Near *in situ* SRR (1.9-12 × 10^5 mol h^{-1}) and estimated hydrogen sulfide precipitation rates (1.8-11 × 10^5 mol h^{-1}) are two orders of magnitude greater than the SO_4^{2-} flux (5.4-12 × 10^3 mol h^{-1}) into the estuary (Fig. 3).

In the open state:
- Water and sediment [H_2S] undergo volatilization and chemical or biological oxidation in surface, oxic sediments.
- Sulfate reduction is limited to anoxic sediments at lower depths.
- Estimated hydrogen sulfide precipitation rates are limited due to rapid re-oxidation of metal sulfides.

Transition from closed to open state:
- As the marshland drains, the variations in near *in situ* SRR and SReR suggest that both oxidation and reduction processes occur together.
- H_2S oxidation may be responsible for the increase in near *in situ* SRR at the Sandbar Lagoon site.
- Spatio-temporal heterogeneity between sites suggests that fish may be affected low dissolved oxygen and high potentials for sulfate reduction to hydrogen sulfide precipitation in the River Confluence, North Marsh, and Butano Marsh.

This research can be highlighted as the first to measure kinetic rate expressions at Pescadero for microbial sulfate reduction in sediment and hydrogen sulfide release to water on intact soils and sediments that contain natural, complex microbial communities.

Predictions for Pescadero

It is unclear whether any coastal management will increase estuarine health at Pescadero.

Biological response of aquatic species: Fish avoid shallow regions and bottom anoxic water at Pescadero; they typically swim in surface, normoxic water. During the breaching event, they gasp for DO, instead taking acidic water and sulfide-rich sediment into their bodies.
Ocean and estuarine physical dynamics: A cliff at the estuary's mouth limits breaching events.

- **Mitigation possibility**: keep Pescadero open to continually flush the estuary, oxidize metal sulfides, and limit H_2S production (decade-long process)
  - Intervention: CA Dept. of Fish and Wildlife removes fish from Pescadero prior to any mitigation practices.
  - Research: San Francisco Regional Water Quality Board continues monthly biogeochemical water and sediment testing

The effects of climate change, specifically temperature, estuarine mouth geomorphology, and sea level, likely worsen estuaries globally. With the expected decrease in the estuary's size, the substantial build-up of metal sulfides would lead to higher frequencies of spatially extensive and severe fish kills. It is probable that damages to Pescadero are highly irreversible, so it may not ever return to its pre-existing wetland conditions.

Conclusions

This study investigated microbial sulfate reduction, hydrogen sulfide release, and hydrogen sulfide precipitation using flow-through experiments on intact sediment cores of Pescadero Estuary in the closed and open states. FTR experiments revealed a link between near *in situ* rates and field concentrations of SO_4^{2-} and H_2S. Consistent with our hypotheses, sulfate reduction predominates in the closed state, only outweighed slightly by hydrogen sulfide oxidation pathways in the open state.

Acting as a unique marshland, wildlife habitat, and water supply for agricultural and municipal use, the protection of our intermittent estuaries is a high priority for ecological health; hence, this study is essential because it uses fundamental and innovative soil research to advance our understanding of sensitive global ecosystems. Furthermore, this interdisciplinary research advances our ability to predict and evaluate wetland sediments for their vulnerability to environmental change, directly offer simplified descriptions of estuarine conditions and fish kills in Pescadero that can be used predictively in the management of this system, and, more generally, other small California coastal estuaries.

Acknowledgments

We acknowledge undergraduate field and laboratory assistance from Kyle Carbajal, James Hake, Hoai Ngo, and Vu Ngo. We would like to thank Heather Dang (Silver Lab) for assistance with the C:N analyzer, Stephanie Carlson and Mark Stacey for their collaborations, and fellow Pallud Lab members, Kathrin Schilling, Sarick Matzen, and Linden Schneider for their advice during the study. This research was supported by SeaGrant and the UC Berkeley Department of Environmental Science, Policy, and Management.

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