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# Inorganic chemical oxygen demand of re-suspended sediments in a bar-built lagoon

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# INORGANIC CHEMICAL OXYGEN DEMAND OF RE-SUSPENDED SEDIMENTS IN A BAR-BUILT LAGOON

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Master of Science

by
Keenan A. Smith
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The Designated Thesis Committee Approves the Thesis Titled

INORGANIC CHEMICAL OXYGEN DEMAND OF RE-SUSPENDED SEDIMENTS
IN A BAR-BUILT LAGOON

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APPROVED FOR THE DEPARTMENT OF BIOLOGICAL SCIENCES

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# ABSTRACT

## INORGANIC CHEMICAL OXYGEN DEMAND OF RE-SUSPENDED SEDIMENTS IN A BAR-BUILT LAGOON

by Keenan A. Smith

Rapid dissolved oxygen (DO) depletion, caused by inorganic chemical oxygen demand (COD) of re-suspended sediment compounds, has been documented in few studies, yet fish kills occur often from the process. Pescadero Lagoon, California, USA, a bar-built lagoon that suffers annual fish kills caused by rapid mixing-induced hypoxia upon sandbar breach, was studied to investigate the potential for COD of re-suspended sediment to deplete oxygen. In-situ chamber mixing trials demonstrated that re-suspended sediment can exert powerful oxygen demand on receiving waters. Surface DO depletion upon bar breach was too severe to be explained solely by mixing of the anoxic hypolimnion into the water column, and the depletion was too rapid to be attributed to biochemical oxygen demand (BOD), making COD of re-suspended sediment the likely direct cause. Sedimentous iron and sulfur compounds that exert COD are reduced under anoxic conditions created by water column stratification and BOD of heterotrophic bacteria.

# ACKNOWLEDGEMENTS

It takes a village to raise a thesis, so many people deserve recognition for their generous contributions toward the realization of this study.  First, I would like to thank my wife, Nicole, for the many cold nights she spent in the marsh and her unending capacity for understanding and support.  Many thanks to Dr. Shannon Bros-Seemann for her tireless help in experimental design, thesis composition, and instruction in the entire scientific process, generally.  Thanks to Sarah Piramoon and Carole Foster, the elite few who were generous enough to brave the cold, wet nights and sleep deprivation in the marsh to help collect the data.  Gratitude goes out to Rebecca Sloan, who provided the inspiration and initial direction for the study both directly and through years of prior research in Pescadero Marsh.  Thanks to Joanne Kerbavaz and CA State Parks for providing funding and all of the equipment that made this study possible.  Thank you to Dr. Jerry Smith for lending his vast knowledge of Pescadero Marsh and for many semesters of instruction on all things aquatic.  Many thanks to Dr. Kristy Morris and the Shennan Lab at UC Santa Cruz for so graciously allowing me to make a mess in the lab on countless occasions and for instructing me in BOD theory and lab technique.  Finally, thanks to SJSU for providing partial funding through the Arthur and Karin Nelson Research Fellowship.

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## INTRODUCTION

Booming human populations, with accompanying water use, land alteration, and nutrient, sewage, and toxic chemical release, have increased stress on aquatic systems, making fish kills more prevalent (Sklar and Browder 1998, Scott et al. 1999, Thronson and Quigg 2008). In many systems, low dissolved oxygen (DO) has been implicated as the primary factor of fish mass mortality events (Portnoy 1991, D'Avanzo and Kremer 1994, Mallin et al. 1999, Mallin et al. 2002, Thronson and Quigg 2008). Hypoxia (low DO, generally <2-3 mg/L) and anoxia (absence of DO) disrupt aquatic organism growth, behavior, reproduction, and community structure, and if low DO levels are prolonged or acute, then significant mortality will result (Kramer 1987, Breitburg 1992, Rahel and Nutzman 1994, Diaz and Rosenberg 1995, Breitburg et al. 1997).

In many cases describing hypoxia-induced kills, the hypoxia is attributed to biochemical oxygen demand (BOD), in which heterotrophic bacteria of the sediment and water column consume DO in the process of breaking down carbon (Portnoy 1991, D'Avanzo and Kremer 1994, Mallin et al. 1999, Mallin et al. 2002). This process is largely dependent upon the availability of organic matter (OM) to the bacteria, so if there is a large influx of OM into the system, or nutrients to fuel the production of OM, there will likely be a proliferation of bacteria and an accompanying drop in DO (Taft et al. 1980).

Some studies show hypoxia/anoxia as a result of an influx of OM into the system from severe storm event runoff (Portnoy 1991, Tilmant et al. 1994, Mallin et al. 1999).

Other studies describe hypoxia in the absence of a mixing event, caused by BOD from decomposing aquatic plants whose growth was stimulated by nutrient-rich sewage discharge and agricultural runoff (D'Avanzo and Kremer 1994, Nixon 1995, Kemp et al. 2005). Finally, in estuarine environments, a few studies have documented hypoxia in the estuarine turbidity zone, where opposing tidal and fluvial flows keep sediment suspended for sufficient time to allow sediment-attached bacteria to exert oxygen demand (Uncles et al. 1998, Talke et al. 2009).

However, in some systems that experience sediment re-mobilization due to a mixing event, oxygen depletion may occur too rapidly to be explained by BOD alone. The effect of organic BOD on DO levels is a slow process (several hours to days) compared to oxygen depletion caused by abiotic chemical oxygen demand (COD) of reduced inorganic compounds, such as iron and sulfur (Graczyk and Sonzogni 1991, Baird and Smith 2002). The process of COD begins when sedimentous ferric iron and sulfates, among others, are reduced to ferrous and sulfide compounds under hypoxic/anoxic conditions (i.e. in the hypolimnion of stratified or stagnant systems) (Cole 1994, Baird and Smith 2002). When those compounds are then introduced to oxygenated water during a mixing event in which sediment is mixed into the water column, they have the potential to exert a rapid and substantial oxygen demand during oxidation (Pamatmat 1971, Baird and Smith 2002).

Few studies have implicated re-suspension of iron and sulfur compounds as the primary cause of DO depletion and the accompanying mortality event. Although they did not posit the specific chemical mechanisms involved, Kreutzberger et al. (1980)

recognized the enormous potential for rapid oxygen demand from re-suspended sediments in their studies of the lower Milwaukee River, Wisconsin. They implicated bed sediment, re-suspended by combined sewer overflow discharge points, as the cause of rapid DO depletion. Graczyk and Sonzogni (1991) also reported rapid DO decreases to near-zero levels in several southern Wisconsin streams. They found that the DO depletion corresponded closely with the hydrograph during storm runoff events and listed reduced inorganic chemicals of the sediments as one of a few possible contributors to oxygen loss. In a few unpublished reports, Lee and Jones-Lee (2003, 2004c) and Lee (2003) attributed a rapid drop in DO levels and subsequent fish kills in tidal sloughs along the San Joaquin River and the Sacramento/San Joaquin Delta to the oxygen demand from ferrous sulfide precipitates that had accumulated in the city's storm sewers. Lee and Jones-Lee (2007) suggested that the rapid depletions of DO in the Upper Newport Bay watershed (Orange County, CA), the Trinity River in Dallas, TX, and Black Earth Creek, west of Madison, WI were due to oxygen demand from re-suspended ferrous sulfide.

Pescadero Lagoon, a seasonal bar-built lagoon approximately sixty-four km (forty mi) south of San Francisco, CA, is an ideal system in which to study the potential effects of re-suspended sediment on water DO content. The lagoon experiences annual fish kills (Table 1) that were attributed to low DO levels (Sloan 2006), and continuously-monitoring sonde data from previous years showed rapid DO depletion throughout the water column upon sandbar breach (CA State Parks *unpublished data*). When the sandbar breaches, the stratified water column quickly mixes, and a large amount of

*Table 1: History of fish and invertebrate kills in Pescadero Lagoon and dates of sandbar closure and breach. Courtesy of California State Parks, 2009.*

| Year | Date Bar Formed | Bar Breach | Sandbar Citation | Fish Kill | Species Observed | # Steelhead | Kill Citation |
|---|---|---|---|---|---|---|---|
| 1983 |  | ~Nov. 10 | Curry et al. 1985 | None reported |  |  |  |
| 1985 | Late April | Unknown | J. Smith 1990 | None reported |  |  |  |
| 1986 | Mid July | Oct. 31 (art breach) | J. Smith 1990 | None reported |  |  |  |
| 1987 | Late March | Unknown | J. Smith 1990 | None reported |  |  |  |
| 1988 | Late May | Unknown | J. Smith 1990 | None reported |  |  |  |
| 1989 | May 28 | summer art. Breach | J. Smith 1990 | None reported |  |  |  |
| 1990 | Late Sept. | After Jan. 19 | J. Smith 1991 | None reported |  |  |  |
| 1991 | Unknown | Unknown | None | None reported |  |  |  |
| 1992 | Unknown | Unknown | None | None reported |  |  |  |
| 1993 | Dec. (art. Open Aug.) | Jan. | J. Smith 1997 | None reported |  |  |  |
| 1994 | Mid May | Nov. | J. Smith 1997 | None reported |  |  |  |
| 1995 | Oct. | Dec. 8 | Parks Report | YES | SH, SB, SF, C[a] | Unknown |  |
| 1996 | Late Aug | Early Nov. | J. Smtih 1997 | None reported |  |  | Parks Report 1995 |
| 1997 | Unknown | Unknown | None | YES |  |  | SWH 01 |
| 1998 | Unknown | Unknown | None | None reported |  |  | N. Beck |
| 1999 | No closure | No closure | N. Beck | None reported |  |  | Simms |
| 2000 | Unknown | Unknown | None | None reported |  |  | Simms |
| 2001 | Mid June | Nov. 14 | SHG[b] 01 & 02 | YES | SH[a] | >30 | Simms |
| 2002 | Sept. 18 | Dec. 2 | SHG[b] 02 | YES | C, SF[a] |  | SHG[b] 01 |
| 2003 | Sept. 14 | Dec. 1 | J. Smith 2004 | YES | SH, C[a] | ~300 | D. Sicular |
| 2004 | Apr. 30 | May 15 | T. Frahm | None reported |  |  |  |
| 2004 | Oct. 5 | Dec. 5 | T. Frahm | YES | SH,C,SB,SF,SS,S[a] | 63 | R. Sloan |
| 2005 | Oct. 10 | Dec. 4 | T. Frahm | YES | SH, C[a] | 64 | R. Sloan |
| 2006 | Oct. 23 | Nov. 25 | T. Frahm | YES | SH, C, S, SB[a] | 170 | J. Kerbavaz |
| 2006 | Dec. 16 | Dec. 29 | T. Frahm | None reported |  |  |  |
| 2007 | Oct. 19 | Jan. 3 | T. Frahm | YES | SH, C, SB, SS, S, SF[a] | 6 | R. Sloan |
| 2008 | Sep. 11 | Dec. 29 | CSP ranger | YES | SH, C, SS, S[a] | 8 | K. Smith |

[a] SH = steelhead, SF = Starry flounder, C = Crab, DC = dungeness crab, SB = stickleback, SS = staghorn sculpin, S = jacksmelt or topsmelt

[b] SHG = Swanson Hyrdrology and Geomorphology

sediment and organic detritus (hereafter referred to simply as sediment) is re-suspended (Sloan 2006).

In the Pescadero system, there is evidence that the fish kills are linked to various recent modifications of the marsh. In 1993, a restoration project was implemented by the California State Parks System to increase hydraulic connectivity to certain areas of the marsh, while isolating others. Separately, but at the same time, California Department of Transportation (CDOT) replaced the Highway 1 bridge that runs over the mouth of Pescadero Lagoon, altering the mouth's shape. Prior to the restoration work and bridge replacement, no fish kills were documented (Table 1), and water quality was generally good (Smith 2004). However, after the modifications, fish kills have been reported in ten of the last fifteen years (Table 1) and water quality suffers as a result of increased salinity stratification (Smith 2004). Smith (2004) attributes the deteriorated water quality and resultant fish kills to the delayed timing of sandbar formation caused by either the CA State Parks restoration effort and/or the CDOT bridge replacement. The post-1993 sandbar typically forms two to four months later in September or October (Table 1). With the sandbar now not in place until late in the dry season, when flows are low, there is less freshwater inflow and a larger saltwater component to drive stratification and induce bottom water anoxia.

In the post-1993 Pescadero system, there are two competing hypotheses for the mechanism of DO depletion that occurs after the bar breaches. During the two months or so that the bar is in place, the lagoon becomes strongly density-stratified for salinity and temperature; an anoxic hypolimnion develops as a result of constant DO depletion from BOD and the isolation from surface mixing. The first possibility is that simple mixing of the anoxic bottom water into the oxygenated surface water may have diluted the oxygen levels. If a simple mixing of the strata was the cause, then one would expect the resultant mixture to be a mass-balanced mean DO of the pre-bar-breach water column.  The second possible explanation is that the oxygen depletion may have been the result of re-suspended oxygen-binding ferrous and sulfide compounds from the sediments that subsequently precipitate.  If this were occurring, one would expect to see a drop in DO larger than could be explained by a simple mixing of the water strata; any drop in excess of a simple strata mixing would be attributed to the sediment and its chemical compounds.

If it is found that the re-suspended sediments do play a role in oxygen depletion, then the next step is to determine whether the driving process behind the depletion is BOD, exerted by sediment bacteria suspended by the mixing, or COD, exerted by re-suspended, reduced sediment compounds.  For this distinction, time, among other things that will be discussed later, can be a guiding factor.  If the drop occurs within several hours to days, that would suggest BOD, while seconds to a few hours would support COD.

This study consisted of two major components.  One component consisted of in-situ water chamber mixing experiments, intended to test the competing hypotheses for the mechanisms of DO depletion after bar breach by mimicking the bar breach mixing event. The other component consisted of water quality monitoring of Pescadero Lagoon over the course of one sandbar cycle, from formation to breach, with high time resolution monitoring bracketing the bar breach event.

## STUDY LOCATION

Pescadero Marsh is a human-modified 1.3 k$^2$ (320 acre) coastal wetland at the confluence of Butano and Pescadero Creeks (Fig. 1).

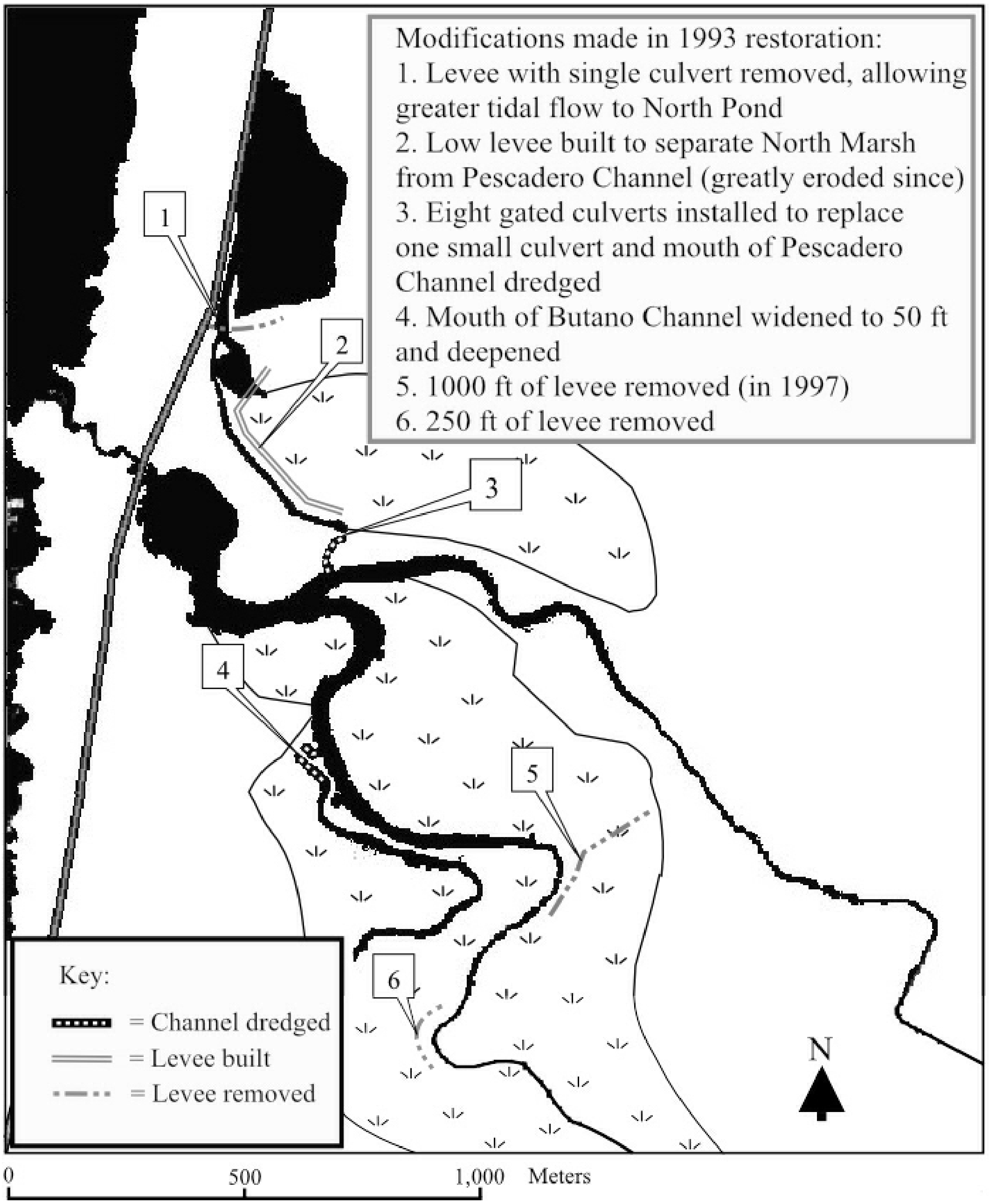

Modifications made in 1993 restoration:
1. Levee with single culvert removed, allowing greater tidal flow to North Pond
2. Low levee built to separate North Marsh from Pescadero Channel (greatly eroded since)
3. Eight gated culverts installed to replace one small culvert and mouth of Pescadero Channel dredged
4. Mouth of Butano Channel widened to 50 ft and deepened
5. 1000 ft of levee removed (in 1997)
6. 250 ft of levee removed

*Figure 1: Modifications made on the marsh. Modified from Sloan 2006.*

In the early 1900’s, a series of levees were built to restrict water flow for agricultural purposes (Viollis 1979). As part of a restoration effort in 1993, portions of the upstream Butano Marsh levees were removed to increase freshwater input during storm runoff into Butano Marsh in the south. In the north part of the marsh complex, eight large corrugated pipes replaced a single small pipe in the levee separating Pescadero Creek from Pescadero Channel to increase tidal flow to North Pond. A low levee was added in an attempt to isolate North Marsh from Pescadero Channel. Finally, a small portion of Butano Channel, at its confluence with Butano Creek, was dredged and widened to increase depth and flow capacity. Additionally, in the unrelated CDOT bridge replacement at the lagoon’s mouth, the bridge span was increased and the number of piers in the mouth was reduced.

Pescadero marsh, in its current state, has four major arteries: Pescadero Creek, Pescadero Channel, Butano Creek, and Butano Channel (Fig. 2). All range between 1-2 m (3-6 ft) deep and the channels are about 12 m (40 ft) across, while the creeks average about 30 m (100 ft) across. Butano Channel drains the Butano marshes and empties into lower Butano Creek, while Pescadero Channel drains North Marsh and North Pond, which is less than 1 m deep, and empties through several large corrugated pipes into lower Pescadero Creek. Butano Creek and Pescadero Creek join about 609 m (2,000 ft) upstream from the mouth of the lagoon. These waterways are surrounded by elevated saltmarsh that becomes submerged sometime after the bar is closed.

Currently, Pescadero and Butano Creeks drain a 210 $k^2$ (51, 892 acre) watershed (Sloan 2006). Flows in Pescadero Creek range between averages of 0.11 $m^3$/s (4 $f^3$/s)

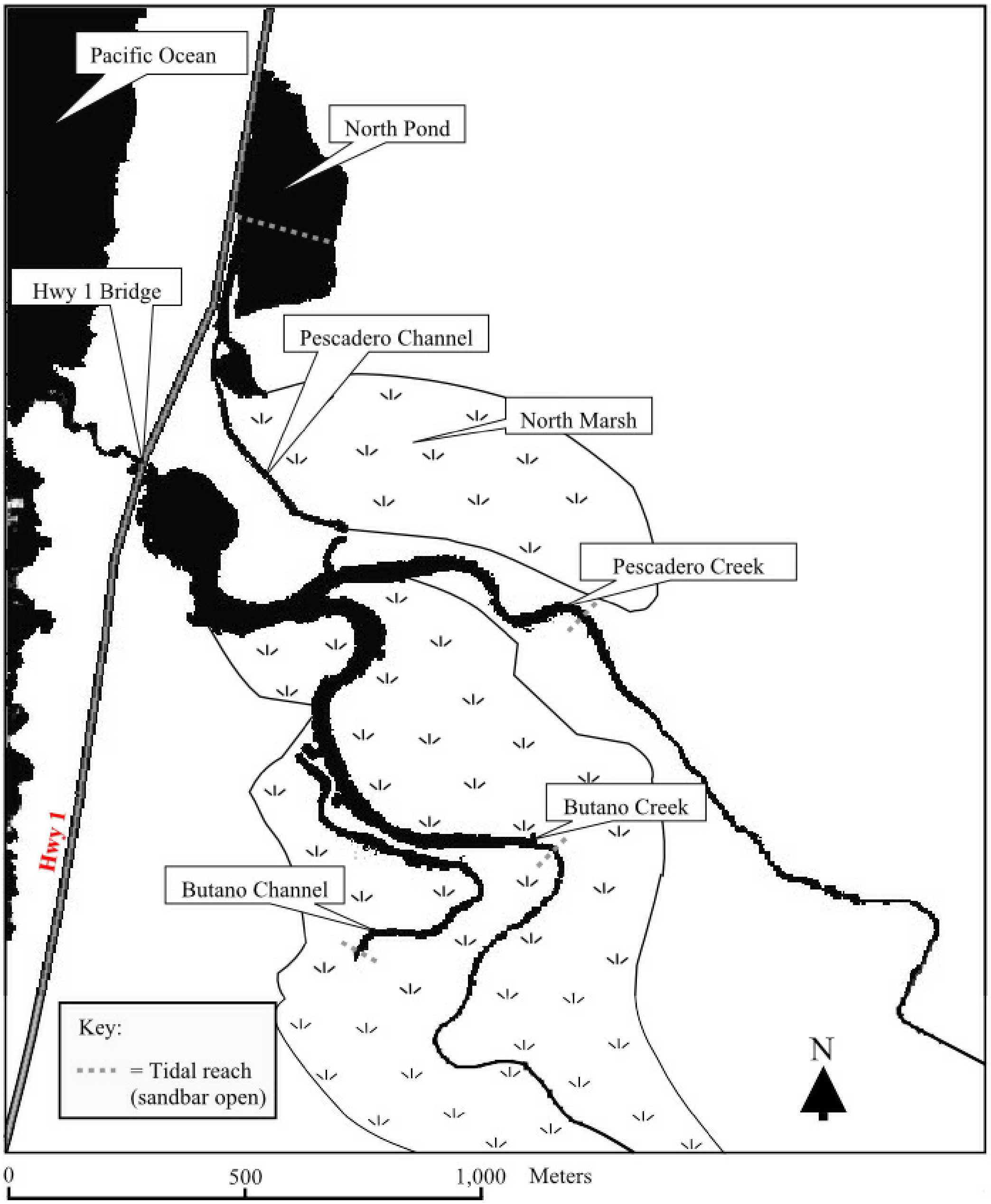


*Figure 2: Pescadero Marsh. Area of inundation shown for when the sandbar is open (black) and closed (marsh pattern). Tidal reach when the sandbar is open is indicated by gray dotted lines.*

during the driest months (Jul-Oct) and 3.11 $m^3/s$ (110 $f^3/s$) during the wettest months (Dec-Mar) (USGS). Flow data is not available for Butano Creek, due to the absence of a stream gage, but it is estimated to be slightly less than that of Pescadero Creek. When the sandbar is open, Pescadero marsh receives substantial tidal influence with tidal water typically reaching approximately 1,300 m (0.8 mi) up Pescadero Creek and 1,600 m (1 mi) up Butano Creek (Fig. 2). When the sandbar closes, the lagoon slowly fills by freshwater river inflow and saltwater overwash of the sandbar, causing the lagoon water to back up into the channels and inundate the surrounding marsh (Fig. 2). The surface substrate is coarse beach sand up to about 213 m (700 ft) from the mouth, at which point the substrate in the creeks becomes a mixture of sand and silt. Substrate in Pescadero and Butano Channels is fine silt. The Pescadero-Butano watershed consists of one third timber land, one third agricultural land, and one third protected land (Sloan 2006).

## METHODS

### Water Quality Monitoring (Sandbar in Place)

To assess the rate of change in DO concentration while the sandbar was in place, water chemistry was monitored from September 2008 to January 2009. Vertical profiles of DO, salinity, and temperature, were measured at depth increments of 0.25 m at bi-monthly intervals at seven study sites throughout the marsh (Fig. 3). To enable year to year comparisons, study site locations were chosen based on sites from previous studies of the lagoon (Smith 1990, Smith 2004, Sloan 2006). Profiles were measured using a YSI 85 handheld probe. Turbidity was measured using a secchi disk. Water samples for $BOD_4$ lab analysis were collected at the surface and bottom of the water column at each site during these samplings as well, using a 1L Van Dorn sampling bottle for the bottom

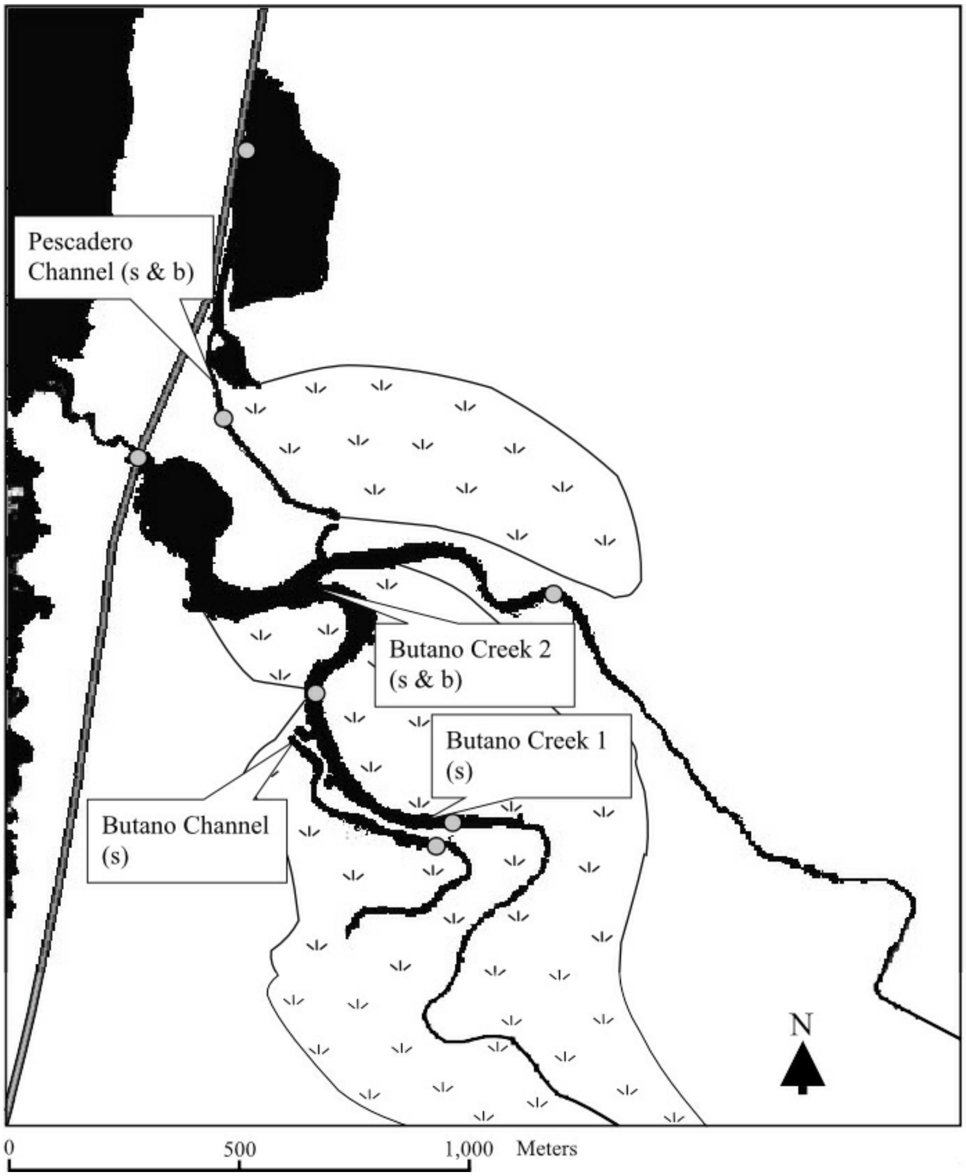


*Figure 3: Bi-monthly water quality sampling sites (gray circles) and continuously-monitoring sonde sites (white boxes); the presence of a surface (s) or a bottom (b) sonde is indicated in parentheses.*

samples. Because the majority of the oxygen demand in a given sample is expressed in the first four days and only roughly 10% or less of the total BOD occurs during the fifth day (Baird and Smith 2002), four-day incubations were used instead of the sewage-treatment-standard five days in order to shorten incubation times. Aside from incubation time, analyses of BOD followed standard protocols described by the American Public Health Association (APHA 2005). Because many of the parameters measured can experience dramatic diel fluctuations as well as fluctuations from tidal cycling (for samplings that occurred when the bar was open), each site was sampled four times over a twenty-four hour period (resulting in each site being sampled approximately every six hours).

### Water Quality Monitoring (Sandbar Breach)

In order to confirm the occurrence in the study year of hypoxic/anoxic conditions upon bar breach, six Hach 4a continuously-monitoring sondes, set to take readings every thirty minutes, were anchored at four informative locations throughout the marsh (Fig. 3). Sonde placement decisions were made based on prior years' sonde data, with sondes being placed in areas of the lagoon where water quality suffers most after bar breach (Rebecca M. Sloan pers. comm.). Butano Creek and Butano Channel were of special interest and each received sonde coverage, because lower Butano Creek, downstream of the Butano Channel confluence, is where the majority of fish carcasses are typically found (CA State Parks *unpublished data*). No sondes were set in Pescadero Creek, due to its lack of fish carcasses and better water quality (CA State Parks *unpublished data*). Two of the sites, Butano Creek 1 and Butano Channel, had only a surface sonde each. The other two sites, at the confluence and at Pescadero Channel, had both a surface and a bottom sonde each. The surface sondes were kept afloat (with the probe about three inches below the surface) using Styrofoam float material. Bottom sondes were fitted with a weight and allowed to rest on the substrate. Both surface and bottom sondes were tethered to a pole driven into the substrate. Sondes were inspected and batteries were replaced approximately every two weeks.

### Carcass Survey

A carcass survey was conducted at the first low tide after the bar break (Fig. 4). Fish were identified to species, counted, and standard lengths were measured to five-cm (two-in.) groupings. Crabs were counted, but no length measurements were taken.

### Chamber Mixing Experiment

To determine if re-suspended sediment could play an important role in post-bar-break oxygen depletion, two treatments were performed: One with re-suspended sediment (referred to as Strata Plus Sediment) and one without re-suspended sediment (Strata-only). These were conducted on November 8, 2009, when the lagoon was well stratified and a hypoxic bottom layer was present. The treatments were performed using in-situ mixing chambers that were designed to mimic the mixing that occurs when the sandbar breaks and to quantify the various parameters of the resulting mixture. One five-minute trial was conducted for both treatments at three representative sites throughout the lagoon complex (Fig. 5).

In the Strata-only mixing treatment, a 1.8-m (6-ft) tall, 10-cm (4-in.) diameter plastic pipe and another 1.8-m tall, but slightly smaller-diameter pipe was used (Fig. 6).

*Figure 4: Fish and invertebrate carcass locations for 2008 on the first low tide after bar breach. Star = steelhead trout; square = staghorn sculpin; triangle = top smelt; oval or circle = dungeness crabs (oval indicates multiple individuals and is labeled with the number, while circle indicates a single crab).*

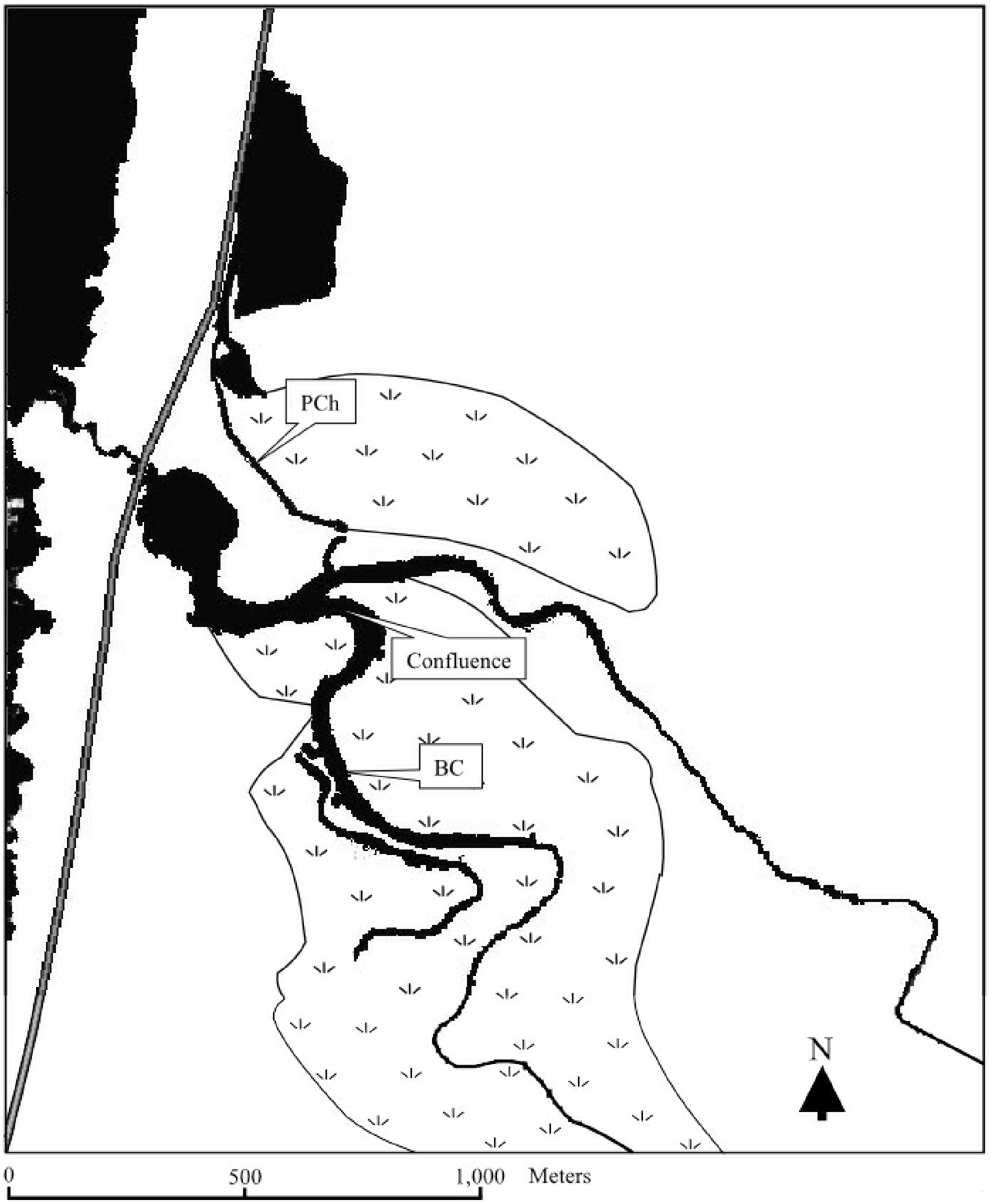


*Figure 5: In-situ chamber mixing experiment sites. A Strata-only and a Strata Plus Sediment mixing treatment was performed at each of three sites: Pescadero Channel (PCh), Pescadero and Butano Creeks confluence (Confluence), and Butano Creek (BC).*

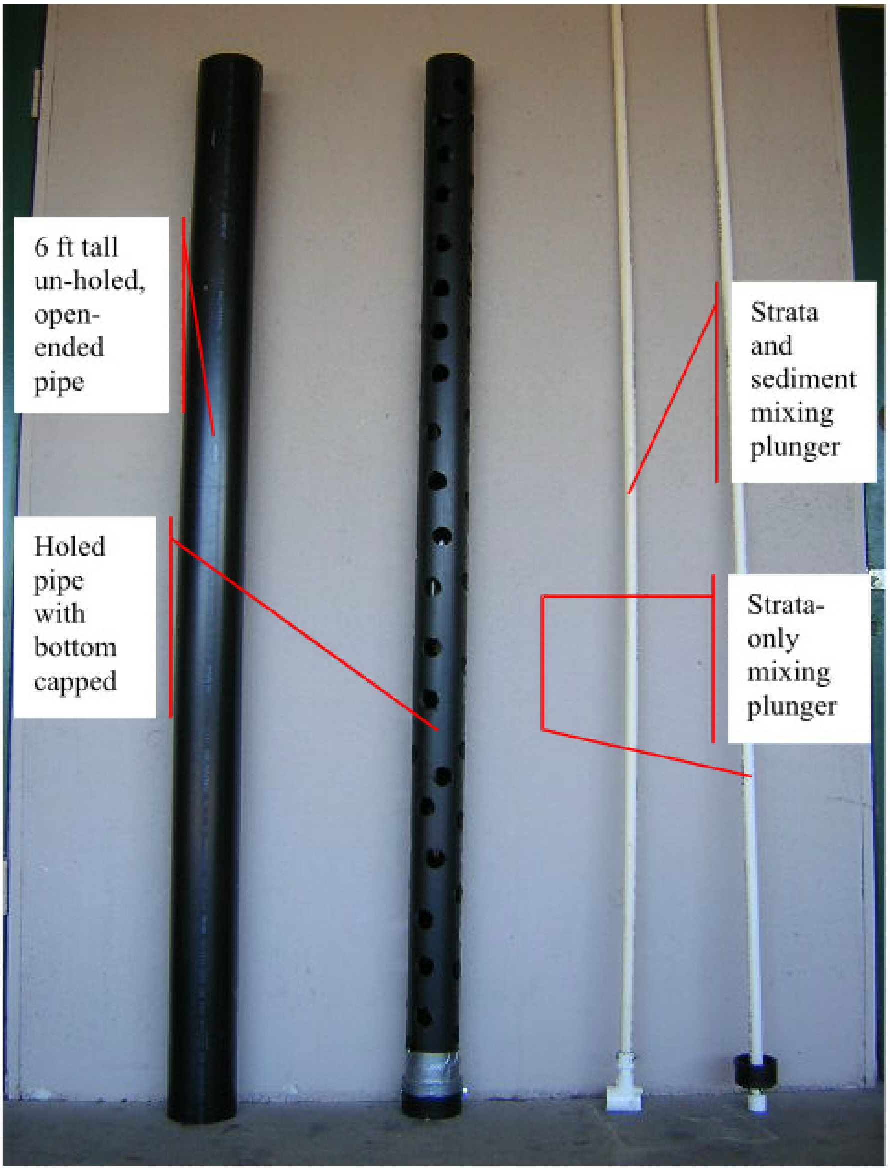


*Figure 6: Strata and sediment mixing experiment equipment creates an isolated column of water with the same stratification as the surrounding lagoon water, so that the effects on DO of different mixings (Strata-only and Strata Plus Sediment) can be evaluated. The equipment is intended to mimic what occurs upon sandbar breach.*

The pipe of slightly smaller diameter was drilled with many 3.2 cm (1.25 in.) holes all around it along its entire length and was fitted with a cap on the bottom end. The purpose of the holes was to allow the water to enter the pipe as it was carefully lowered down, so as not to disturb the water strata. The bottom cap on the pipe was to prevent any sediment from entering the pipe when its bottom touched the substrate. This holed pipe was slowly lowered vertically into the water in order to keep the existing water strata intact (this was confirmed using the YSI probe). Once that pipe was resting on the bottom, with its top extending above the water's surface, the other, slightly larger pipe with no holes drilled in it was lowered over top, so that the holed pipe was enclosed within the un-holed pipe. This resulted in a chamber containing an isolated column of water that had the same stratification as the lagoon water outside the chamber. Then a "plunger," made of a long, small diameter (2.5 cm) PVC pipe with a circular plastic cup on the end that was roughly the same diameter as the interior space of the chamber, was used to completely mix the water inside the pipes, taking care not to disturb the water's surface. (Complete mixing of the strata by this procedure was confirmed with the YSI probe prior to the beginning the experiment). After mixing, the YSI probe was quickly lowered down about a quarter meter (10 inches) into the water in the pipes and readings were recorded every minute for five minutes. These data were compared to the vertical profile taken just before each trial.

For the Strata Plus Sediment treatment, sites were selected to be near the corresponding Strata-only experiment locations, but sufficiently distant (approximately 9m, or 30 ft, up or downstream) to avoid any disturbance of the strata caused by the Strata-only mixing trial. At these locations, only the un-holed, un-capped pipe was lowered vertically into the water, so that one end of the pipe rested on the substrate and the other end extended out of the water. Again, this was done slowly to avoid disturbing the water strata. A different plunger, with the addition of a sediment disturbing attachment that digs up the top 3 cm (>1 in.) or more of sediment, was used to mix the strata and re-suspend sediment up into the pipe. After disturbing the bottom sediment and mixing it up into the water column within the pipe, the DO was recorded each minute for five minutes and compared to the vertical profile taken before the experiment. Any additional depletion in DO compared to the Strata-only treatment for that location, could be attributed to the re-suspended sediment. Additionally, the time required for the sediment to exert its effects on DO could instruct on the process driving the DO depletion (i.e. BOD or COD).

### Statistical Analyses

A one-way ANOVA with repeated measures was used to determine if the resulting oxygen levels differed between the Strata-only and Strata Plus Sediment treatments (Zar 1999). The independent variable was sediment (Strata-only or Strata Plus Sediment). The measurements were the differences between pre- and post-mix DO values over five minutes with one-minute intervals. Time was the repeated measure.

## RESULTS

Bi-monthly profiles showed that water quality parameters in the lagoon progressed in a steady, predictable manner during bar closure, prior to the breach (Fig. 7, Fig. 8, Fig. 9). Stratification occurred across the vertical salinity and temperature gradients and

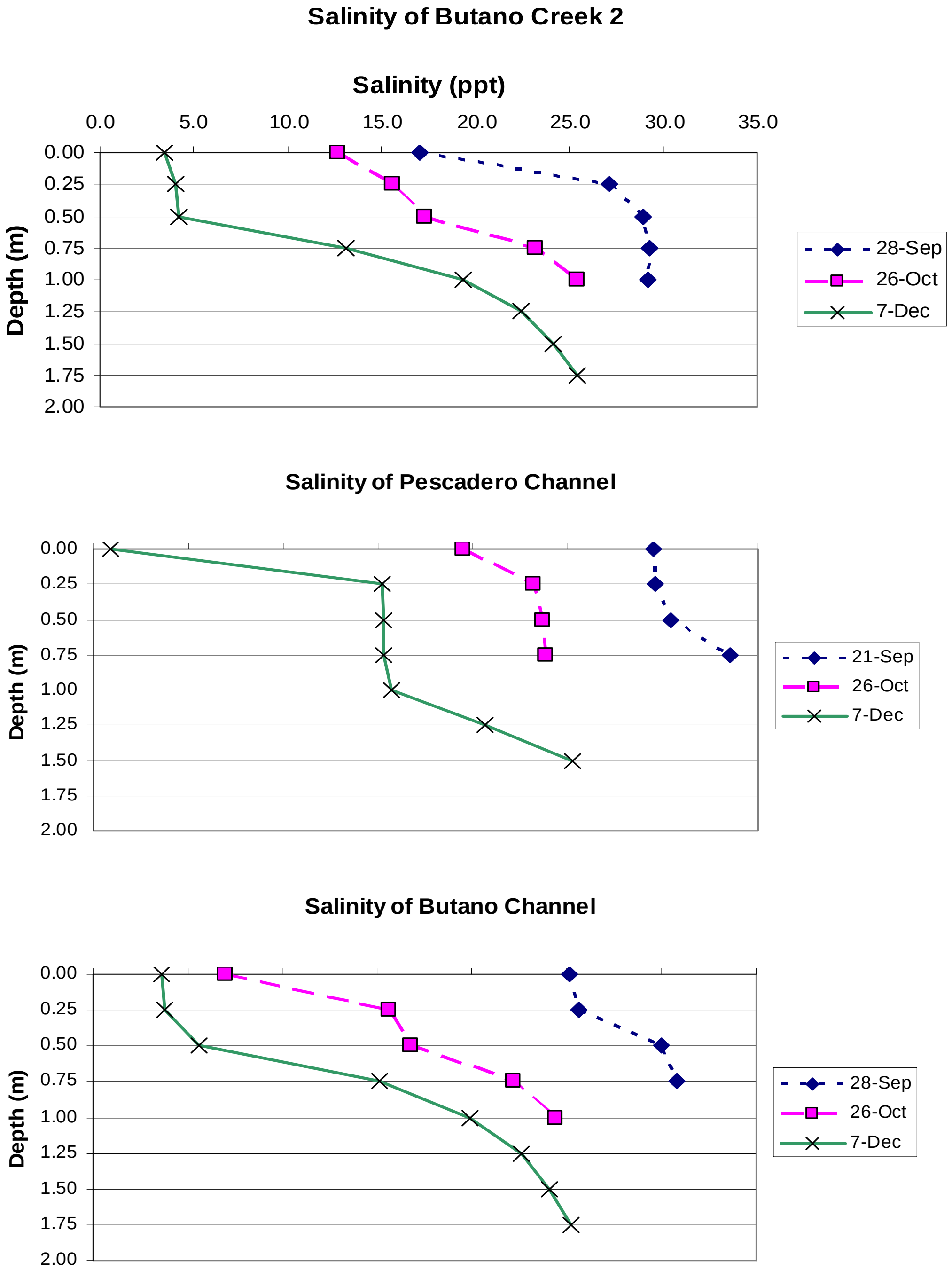


*Figure 7: Salinity profiles of three selected sites showing the progression of salinity stratification during bar closure. Collected shortly after bar closure (21 or 28-September, diamond), mid-way through bar-closed period (26-Oct, square), and just before bar breach (7-Dec, X).*

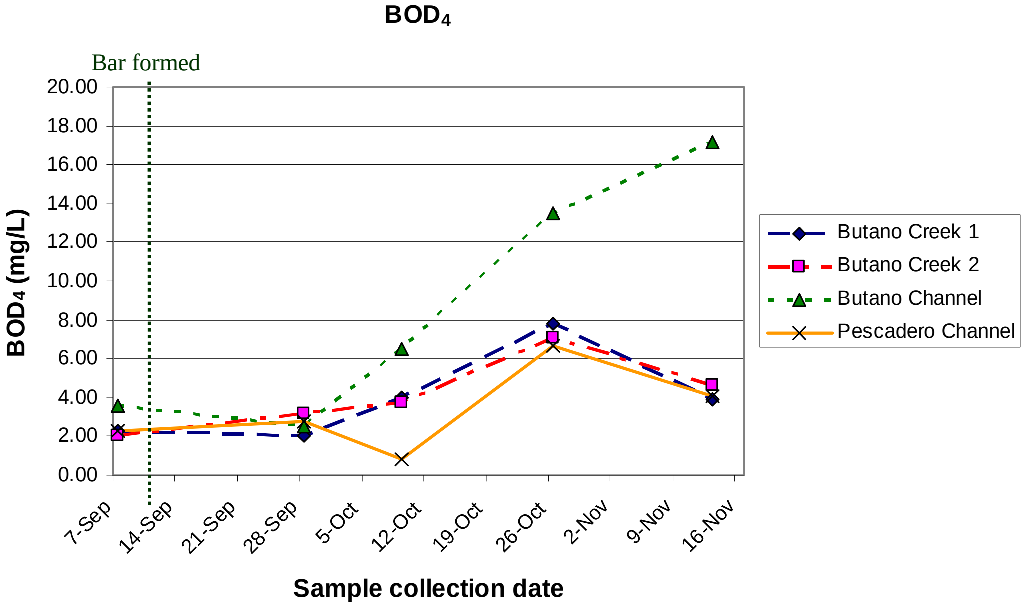


*Figure 8: $BOD_4$ values (mg/L) for bottom water samples collected at sites Butano Creek 1 (diamond), Butano Creek 2 (square), Butano Channel (triangle), and Pescadero Channel (X) in 2008. The sandbar closed on September 11, 2008 (vertical dotted line).*

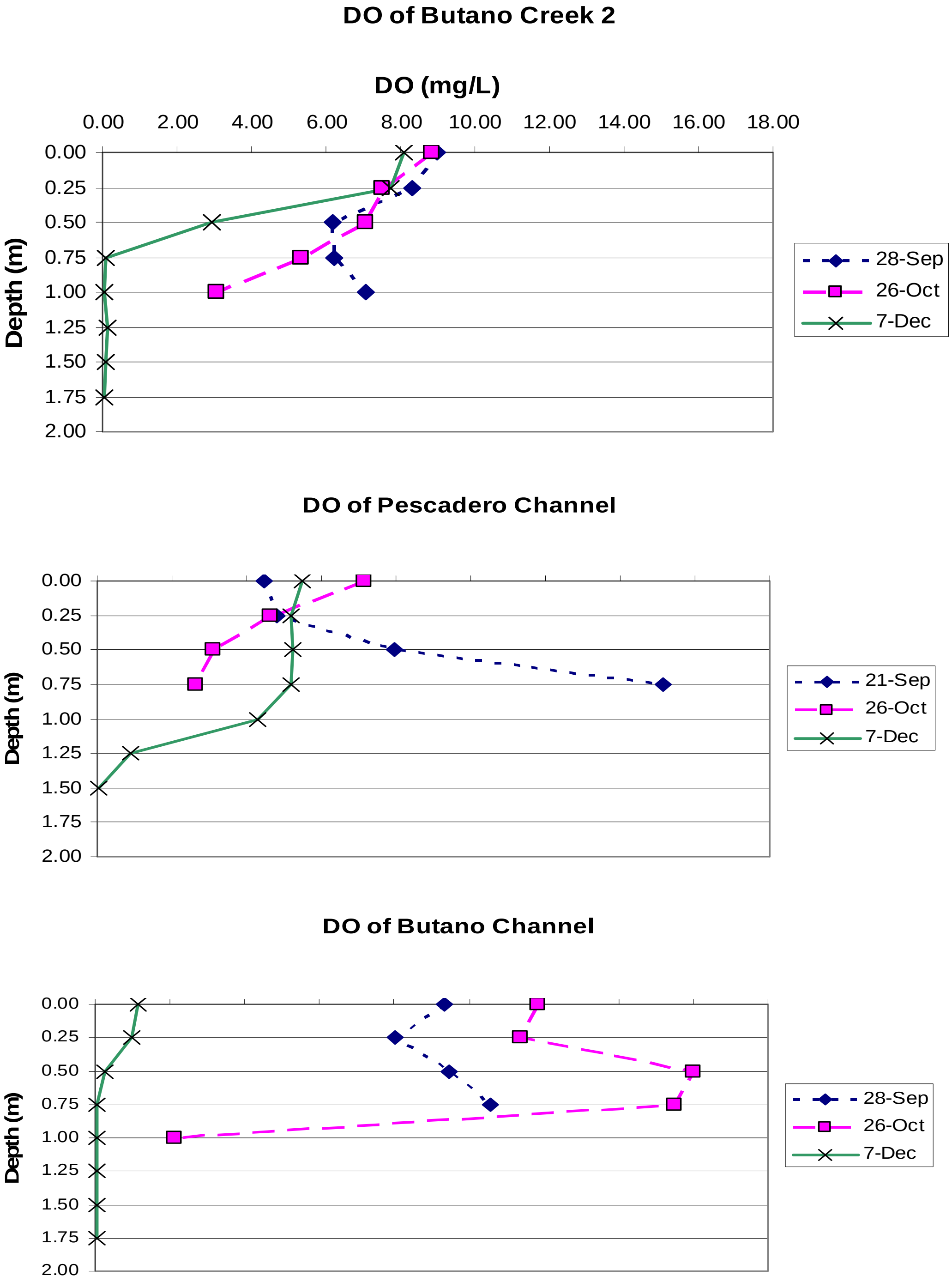


*Figure 9: DO profiles of three selected sites showing the progression of oxygen depletion during bar closure. Collected shortly after bar closure (21 or 28-September, diamond), mid-way through bar-closed period (26-Oct, square), and just before bar breach (7-Dec, X).*

increased in strength over time.  With increasing BOD, hypolimnion oxygen content steadily declined over time and the oxycline steadily rose with occasional slight disruptions due to oxygen infusion from high winds or tidal input over the bar (in the lower lagoon).  Butano Channel suffered the largest degradation in water quality during the bar-closed period (Fig. 9).  The lagoon level rose with an early inflow of rain runoff.

As expected, the sandbar breach in 2008 resulted in deteriorated water quality. The sandbar formed on September 11, 2008 and breached at approximately 15:00 on December 29, 2008 (CA State Parks Ranger pers. comm.).  The breach caused a rapid and complete mixing of the water column (Fig. 10) as the water drained out of the mouth.

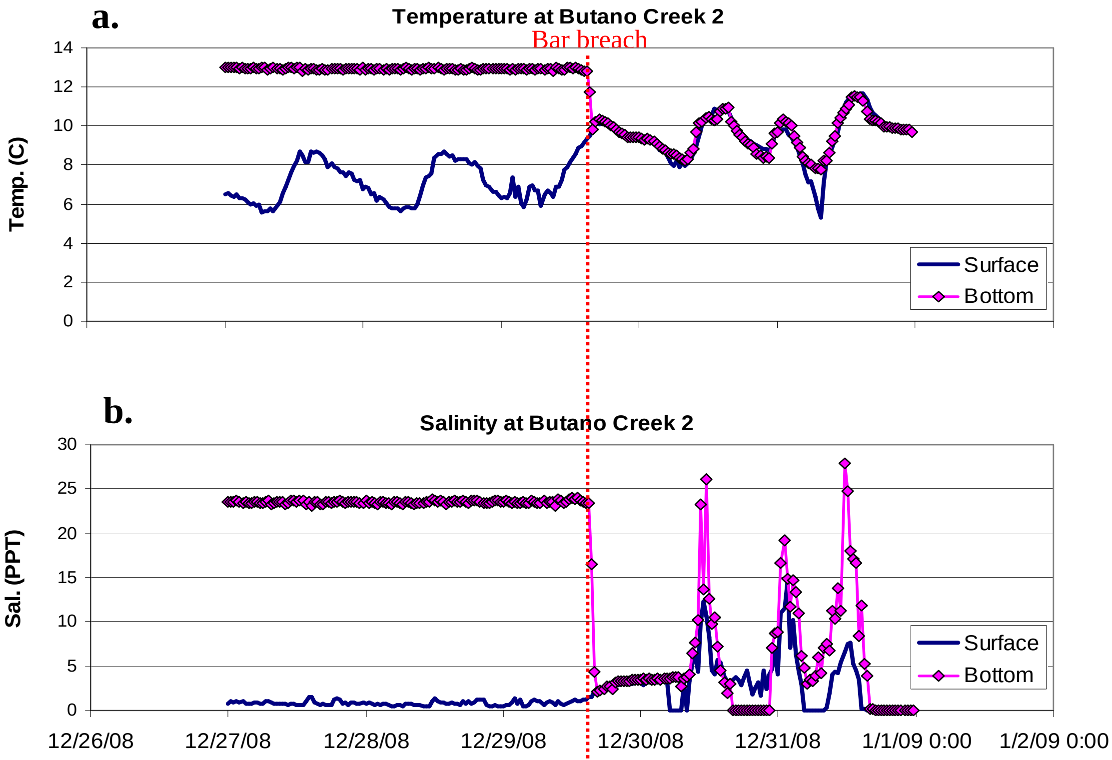


*Figure 10: Surface and bottom temperature (a) and salinity (b) before and after bar breach at Butano Creek 2 sonde site.*

A large amount of sediment was re-suspended upon bar breach, immediately resulting in highly-turbid water (CA State Parks Ranger pers. comm.). Secchi depths recorded approximately 25 hrs after bar breach at selected bi-monthly sampling sites still registered an average of 29 cm (<1 ft), compared to 70 cm (2.3 ft) depths recorded before bar breach.

Upon bar break, the surface DO dropped immediately and substantially at all sites (Fig. 11). In Butano Creek, surface DO levels dropped by 6% in less than 30 minutes, 27% by 1 hour, 43% by 1.5 hours, and 62% by 2 hours after the bar break. The surface DO dropped from a pre-breach 9-10 mg/L to less than 3 mg/L (hypoxic) within 2 hours and 15 minutes and then continued to drop to below 1 mg/L levels by 3.5-4 hours after bar break. The DO levels then stabilized around 3 mg/L for 20-30 hours (the downstream area having the slowest recovery time). In Butano Channel, which drains slightly slower, the DO levels dropped from 10 mg/L to below 3 mg/L within 4 hours and then remained under 2 mg/L for about 31 hours after break. Oxygen depletion in Pescadero Channel was much less severe, never dropping below 3.5 mg/L for any substantial period of time. Pescadero Creek, Butano Creek, and Butano Channel were drained within 7 hours of the breach, while Pescadero Channel, which drains through the culverts, was not drained until another 8 hours (Fig. 12). Although the draining time was partially obscured by an incoming tide, the area at the confluence drained from a depth of 4.33 m to approximately 2 m at a rate of 33.3 cm/hr, while Pescadero Channel drained from a depth of 3.43 m to 1.74 m at a rate of 11.3 cm/hr (Fig. 12).

The conditions after bar breach throughout most of the lagoon were severe enough

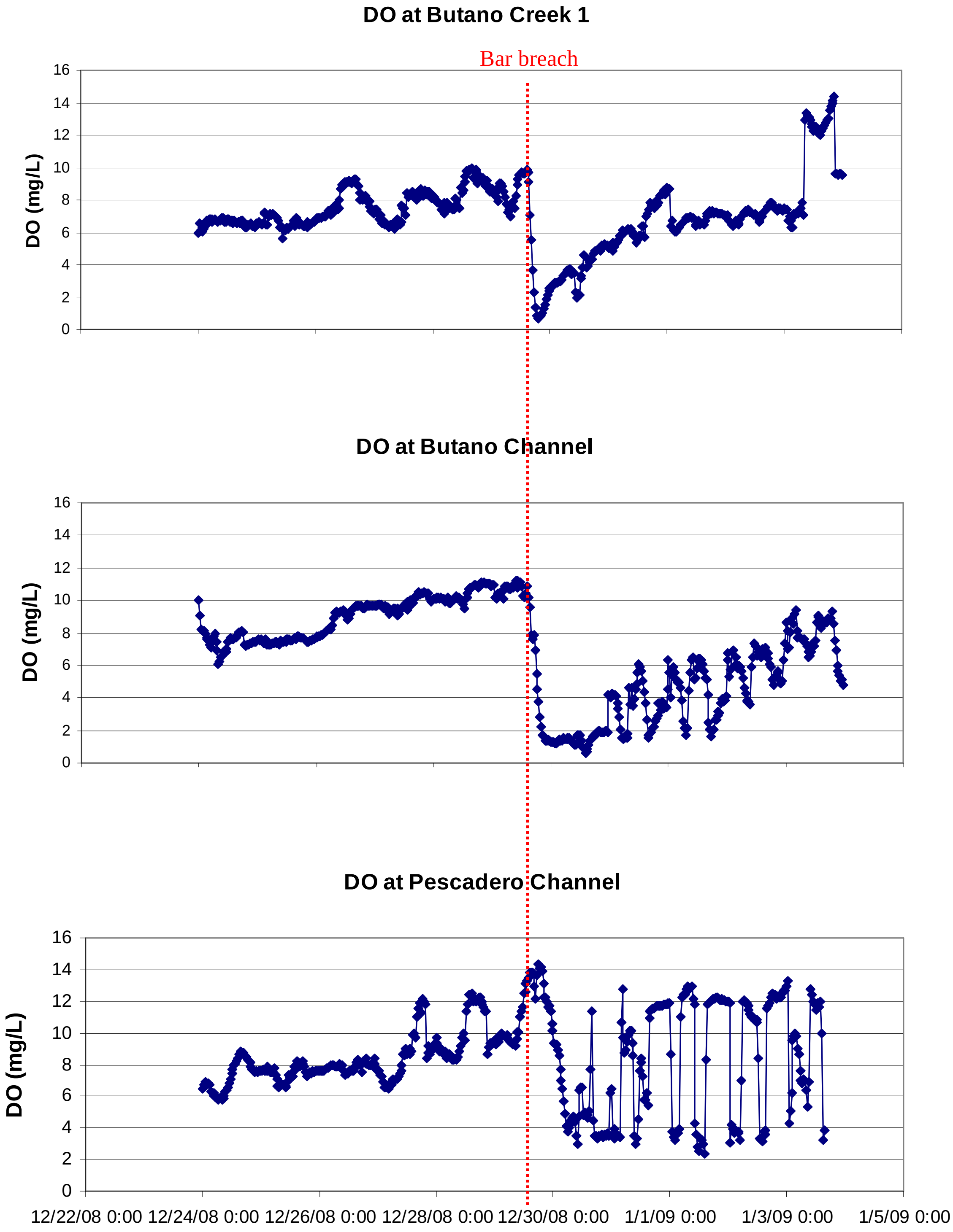


*Figure 11: Dissolved oxygen of lagoon surface water for three selected sonde sites before and after the sandbar breach.*

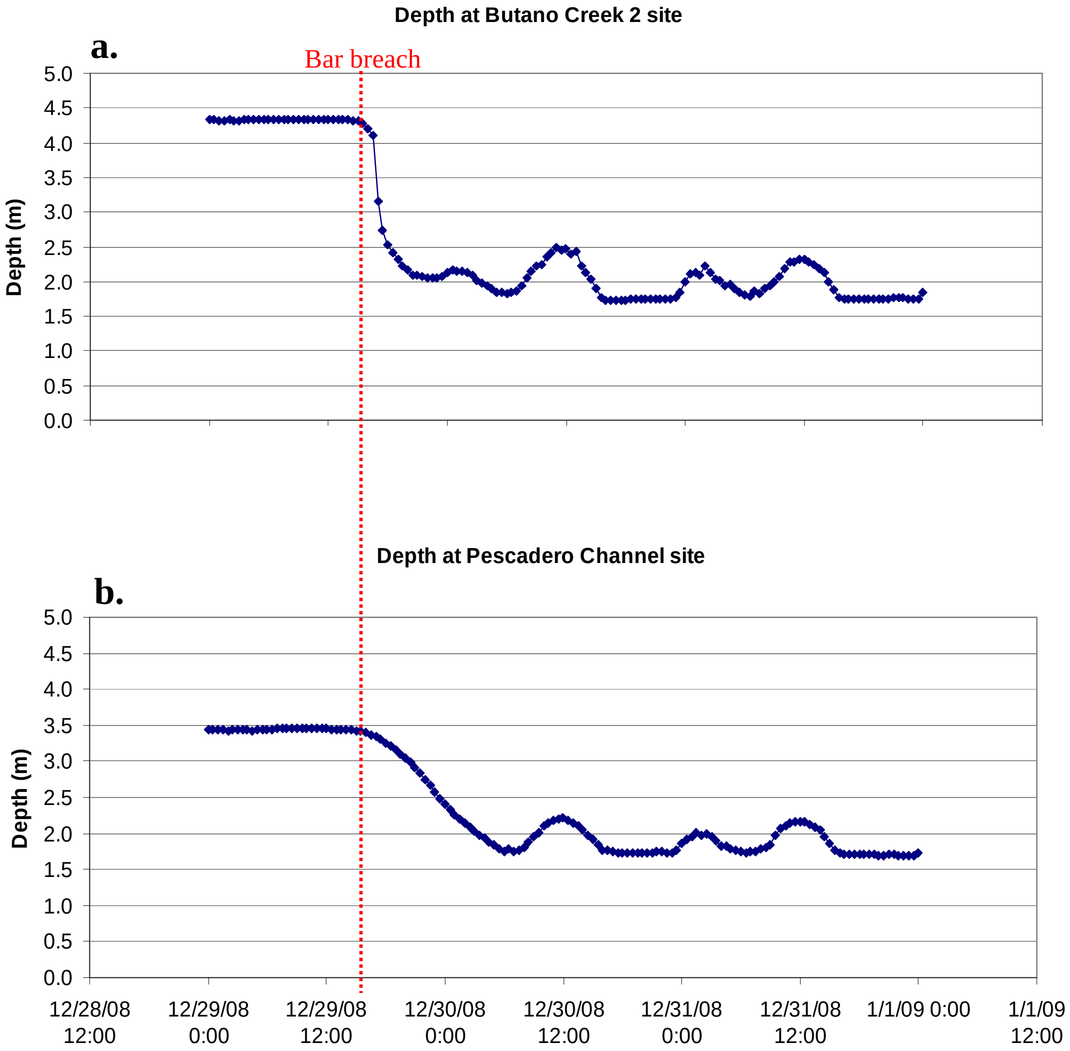


*Figure 12: Lagoon depth at sonde sites Butano Creek 2 (a) and Pescadero Channel (b) before and after bar breach.*

in level and duration to cause a fish kill (Fig. 4, Fig. 11). Eight steelhead trout (mostly 1+), 5 adult staghorn sculpin, 1 topsmelt, and 100 dungeness crabs were found dead or moribund throughout the marsh at the first low tide after the break. Most of the fish carcasses (79%) were found in lower Butano Creek, upstream of the Pescadero-Butano confluence, while most of the crab carcasses (79%) were found in the main, lower embayment. No carcasses were found in Pescadero Creek or Pescadero Channel.

Post-breach DO depletion could not be attributed to only a mixing of the stratified water column (Table 2).

*Table 2: Repeated Measures 1-Way ANOVA. Treatment has two levels (Strata Only and Strata plus Sediment). Time is the repeated measure (1, 2, 3, 4 and 5 min). Measured variable is the difference between pre-mix and post-mix DO (mg/L) for each of the five time periods.*

| | | df | SS | MS | F | p-value |
|---|---|---|---|---|---|---|
| Treatment | | 1 | 80.461 | 80.461 | 26.721 | 0.007 |
| | Error | 4 | 12.045 | 3.011 | | |
| Time | | 5 | 17.798 | 3.560 | 28.055 | <0.001 |
| | Error | 20 | 2.538 | 20 | 0.127 | |

The Strata Plus Sediment treatment exhibited significantly, and substantially, lower DO after mixing than the Strata-only treatment (Fig. 13, Table 2).

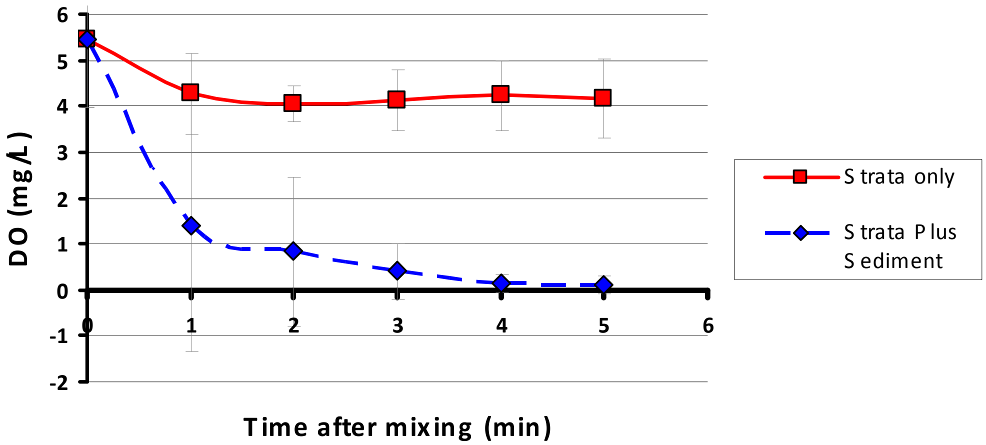


*Figure 13: Dissolved oxygen of water inside the mixing chamber at one-minute intervals after Strata-only mixing (square) and Strata Plus Sediment mixing (diamond). The vertical bars at each data point represent 95% confidence limits.*

In the Strata Plus Sediment treatments, DO levels dropped at all sites by 97% or greater, to near zero, within five minutes. In the Strata-only treatments, the largest drop seen was

30% and the lowest oxygen level recorded was 3.9 mg/L (dropped from 4.8 mg/L), with most sites stabilizing at over 4 mg/L. The oxygen levels that resulted from the Strata-only mixings were very close to the mass-balanced means of the corresponding pre-mixing strata, with the exception of the Confluence site, which resulted in slightly higher levels (Table 3). The mixings produced consistent results at all sites, despite very different initial conditions (Fig. 14).

The vertical pre-break profile at the Pescadero-Butano Creek confluence, taken on December 7, 2008, twenty-two days before the bar break, was similar to the profile taken at that site immediately before the mixing trials on November 8, 2008 (Fig. 15). The oxyclines on the two dates were within 0.25 m to 0.50 m of each other, differences commonly seen even within the diel cycle as a result of photosynthesis/respiration.

## DISCUSSION

During the approximately three and a half months that the sandbar was closed in 2008, the water became strongly stratified by salinity and temperature, BOD increased, and an anoxic bottom layer was produced. When the sandbar breached, a mixing event occurred, accompanied by a rapid DO depletion throughout the entire water column and a resultant fish kill.

The results of the chamber mixing experiment show that re-suspended sediment plays a dominant role in the bar break oxygen depletion in the Pescadero system. In the Strata-only treatment, the post-mixing oxygen levels were essentially mass-balanced

*Table 3: Pre-mixing profiles and Strata-only mixing results for Pescadero Channel (a), Butano Creek (b), and the Confluence (c) mixing sites. The results of the Strata-only mixings are very close to a mass-balanced mean of the corresponding pre-mixing vertical profiles. Note that the left-side columns within each site's tables display different information (the first displays probe depth, while the second displays time after mixing).*

**a.**

**Pescadero Channel**

| Pre-mix vertical profile | | |
|---|---|---|
| Probe depth (m) | Water temp | DO (mg/L) |
| 0.00 | 15.9 | 5.1 |
| 0.25 | 16.3 | 4.8 |
| 0.50 | 15.9 | 3.9 |
| 0.75 | 15.8 | 3.2 |
| 1.00 | 15.8 | 2.3 |
| **Mean:** | **15.9** | **3.9** |

| Strata-only mixing | | |
|---|---|---|
| Time after mixing (mins | Water temp | DO (mg/L) |
| 0 | 16.3 | 4.8 |
| 1 | 15.9 | 3.9 |
| 2 | 15.9 | 3.9 |
| 3 | 15.9 | 3.9 |
| 4 | 15.9 | 4.0 |
| 5 | 15.9 | 3.8 |

**b.**

**Butano Creek**

| Pre-mix vertical profile | | |
|---|---|---|
| Probe depth (m) | Water temp | DO (mg/L) |
| 0.00 | 14.9 | 5.9 |
| 0.25 | 14.9 | 5.9 |
| 0.50 | 13.9 | 0.6 |
| 0.75 | 14.9 | 3.9 |
| **Mean:** | **14.7** | **4.1** |

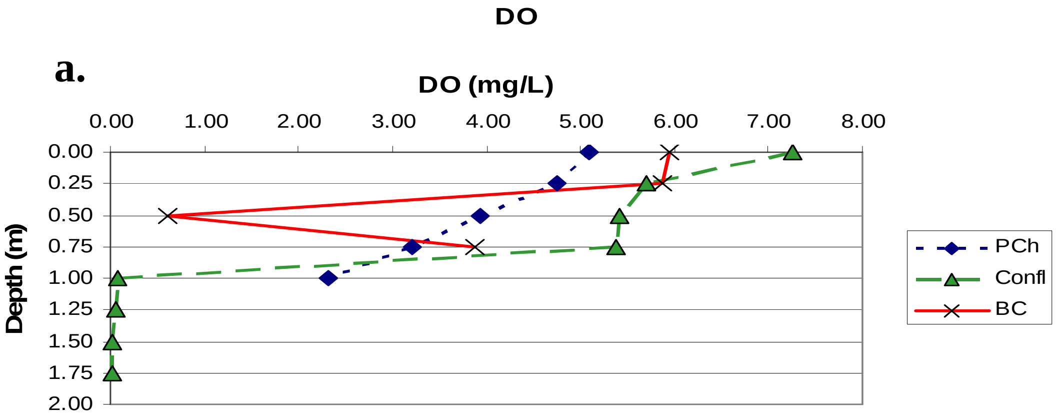
| Strata-only mixing | | |
|---|---|---|
| Time after mixing (mins | Water temp | DO (mg/L) |
| 0 | 14.9 | 5.9 |
| 1 | 14.7 | 4.3 |
| 2 | 14.7 | 4.2 |
| 3 | 14.7 | 4.1 |
| 4 | 14.7 | 4.2 |
| 5 | 14.7 | 4.2 |

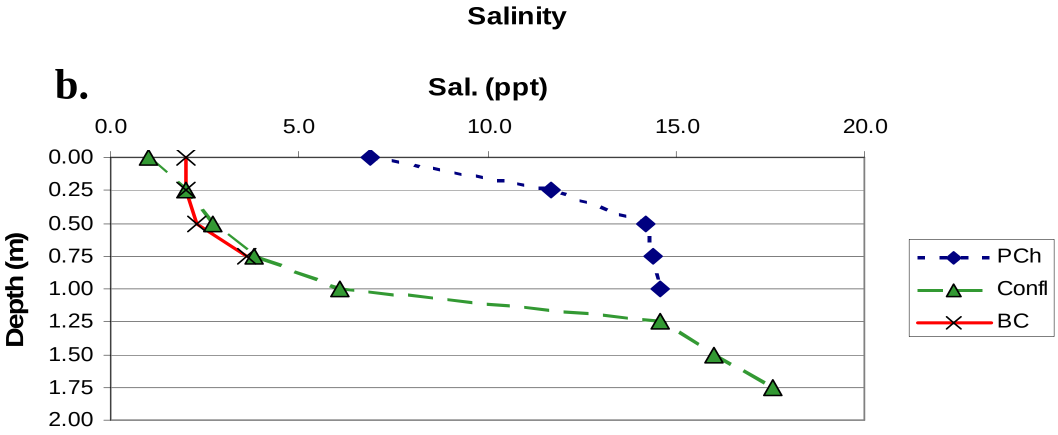
**c.**

**Confluence**

| Pre-mix vertical profile | | |
|---|---|---|
| Probe depth (m) | Water temp | DO (mg/L) |
| 0.00 | 14.4 | 7.3 |
| 0.25 | 14.7 | 5.7 |
| 0.50 | 14.7 | 5.4 |
| 0.75 | 14.9 | 5.4 |
| 1.00 | 15.4 | 0.1 |
| 1.25 | 16.2 | 0.1 |
| 1.50 | 16.3 | 0.0 |
| 1.75 | 16.6 | 0.0 |
| **Mean:** | **15.4** | **3.0** |

| Strata-only mixing | | |
|---|---|---|
| Time after mixing (mins | Water temp | DO (mg/L) |
| 0 | 14.7 | 5.7 |
| 1 | 14.9 | 4.6 |
| 2 | 14.9 | 4.2 |
| 3 | 15.0 | 4.4 |
| 4 | 14.8 | 4.6 |
| 5 | 14.8 | 4.5 |





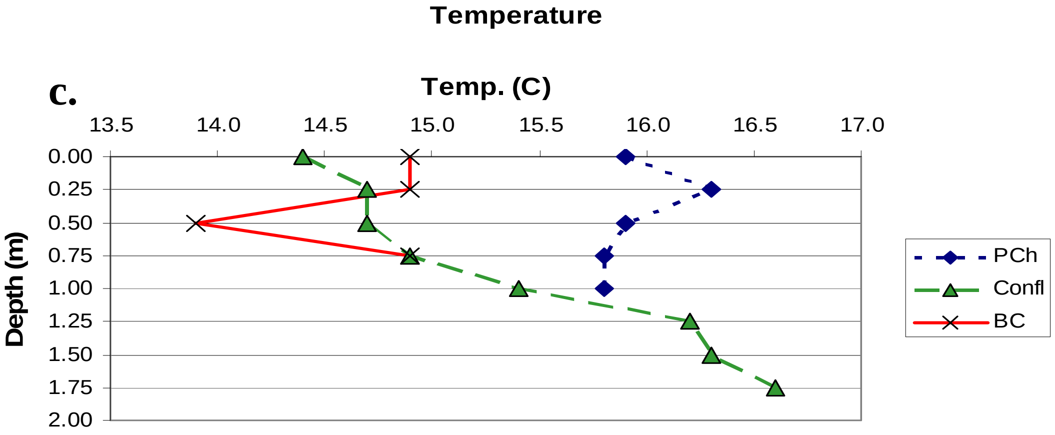


*Figure 14: Dissolved oxygen (a), salinity (b), and temperature (c) profiles taken on November 9, prior to mixing at the three mixing experiment sites: Pescadero Channel (diamond), Confluence (triangle), and Butano Creek (X). These illustrate the great variance in the profiles of the three sites, yet the outcomes of all the mixings were similar.*

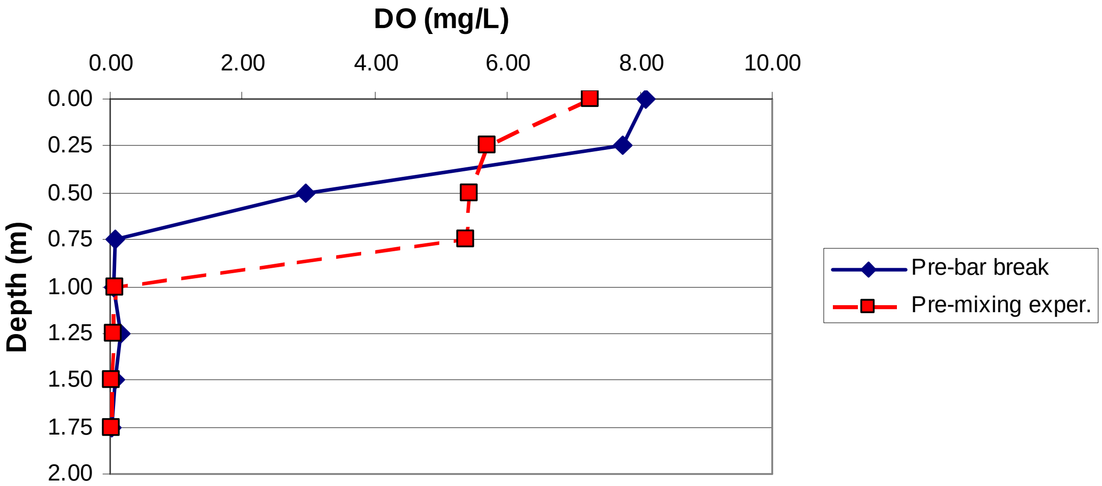


*Figure 15: Last vertical DO profile taken before bar break at the Pescadero-Butano Creeks confluence (twenty-two days before bar break) (diamond). That profile is similar to the DO profile (square) taken from the same area during the strata/sediment mixing experiments one month prior, suggesting that a mixing of the water columns represented in each graph would yield similar results.*

means of their corresponding pre-mixing vertical profiles (with the exception of the Confluence trial, which resulted in slightly higher than mean oxygen levels probably due to an incomplete mixing of the strata). The resultant oxygen levels for the Strata-only treatment (3.9 mg/L or greater) were not low enough to cause fish mortality on their own (1-3 mg/L for trout) (USEPA 1986). However, with the addition of sediment, the resulting oxygen levels (near zero) alone would cause acute mortality. The results were consistent, despite high variance in initial vertical water column profiles.

The pre- and post-sandbar-break oxygen data show that the DO depletion upon bar break was too severe (to less than 1 mg/L at the surface in some places) to be explained only by a simple mixing of the pre-break strata. Therefore, there is an additional oxygen-demanding factor involved. As shown by the results of the chamber mixing experiment, re-suspended sediment exerts oxygen demand powerful enough on waters exposed to the plume to account for the DO levels seen after the bar breach. It was also shown, by observation and by secchi measurements, that substantial sediment was re-suspended throughout the entire water column after bar break.

The results of the mixing experiment can be applied to the actual bar-break mixing event itself. The pre-mix profiles seen in the mixing experiment were similar to the profiles recorded before bar breach, suggesting that the outcome of the chamber mixings and the outcome of the mixing that occurs after bar breach will also be similar. The application of the mixing experiment results to the bar breach is further supported by the fact that, although the vertical profiles recorded before the mixings differed greatly between the three sites, they all resulted in the same conclusion: When sediment was re-suspended, the oxygen fell to near zero.

BOD and COD are two possible mechanisms by which the re-suspended sediment might exert oxygen demand on receiving waters. Time can indicate which process was at work. Oxygen depletion due to BOD is slower to occur. The typical domestic wastewater BOD reactions are about 70% completed after five days (Lee and Jones-Lee 2007). When deprived of oxygen or food (primarily carbon), the heterotrophic bacteria of the sediment that exert BOD will enter a state of endogenous respiration, maintaining only critical life functions (Baird and Smith 2002); in Pescadero Lagoon, with the bar closed and the water column stratified, oxygen at the sediment-water interface is almost non-existent. Once the oxygen or food is reintroduced (e.g. when oxygenated surface waters mix with sediment after sandbar breach) there is up to a two-hour lag time required for the bacteria to acclimate to the new conditions before normal cell growth and reproduction can resume and substantial oxygen consumption begins (Baird and Smith 2002). The length of this lag time depends on how long the bacteria experienced resource deprivation, with longer lag times associated with longer deprivation times (Baird and Smith 2002); in Pescadero lagoon, this deprivation time was about two months. With BOD starting its substantial oxygen consumption within several hours to days, it is unlikely that the immediate DO depletion that occurred minutes after bar breach was a result of BOD. It is therefore proposed that COD, which acts in seconds to minutes, is most likely the cause of the immediate oxygen depletion after bar break.

However, hypoxia persisted for twenty to thirty hours after bar breach at most sites, so a mechanism must be proposed for this longer-term period of hypoxia as well. Hypoxia as a result of BOD from re-suspended sediment has been documented in estuarine systems (Uncles et al. 1998, Talke et al. 2009). In these instances, heterotrophic bacteria attached to the substrate is suspended into the water column and attenuated by opposing tidal and river forces, the interface of which is termed the estuarine turbidity zone (Uncles et al. 1998, Talke et al. 2009). These studies demonstrated how the residence times in the estuarine turbidity zones of their respective systems (seven to eleven days in the Humber-Ouse estuary studied by Uncles et al.) are long enough for the suspended bacteria to exert oxygen demand and cause a mobile zone of hypoxia/anoxia that advances and recedes with the tide.

The twenty- to thirty-hour time span of hypoxia that occurred in Pescadero

Lagoon, while not seven to eleven days (Uncles et al. 1998), is theoretically sufficient time for BOD-exerting bacteria to have become acclimated and mobilize to a state of substantial oxygen consumption. However, flushing times of Pescadero Lagoon preclude the possibility. The majority of the lagoon, with the exception of Pescadero Channel, completed draining within about seven hours after bar breach. The individual oxygen-demanding bacteria at any given location throughout the lagoon would theoretically have flushed with the exiting water, thus lacking the necessary time to exert meaningful oxygen demand.

It is more likely that as the water exited additional layers of sediment, containing reduced iron and sulfur compounds of COD, were uncovered and suspended up into the water column. Additionally, two tidal influxes occurred during the twenty to thirty hours after bar breach, and by the same mechanism they likely contributed additional COD over that time period. Once all readily-mobile substrate had been suspended and its ferrous sulfide had been oxidized, the DO returned to healthy levels by surface mixing with the air and by tidal/fluvial flushing.

Although this paper implicates COD, rather than BOD, as the direct cause of oxygen depletion upon bar break, BOD is still a major factor in the depletion event. Indeed, during bar closure when the water is stratified, BOD is the primary mechanism that creates the anoxic bottom water allowing the formation of reduced COD compounds. Therefore, BOD is a major player in the COD process and should not be overlooked as the indirect cause of low DO levels caused by re-suspended sediment.

COD, as it pertains to deterioration of water quality in freshwater and estuarine systems, may be more common than the literature reflects. COD's potentially short-lived effects may elude many conventional sampling efforts, especially in quickly-flushed lotic systems. Several studies have documented hypoxia/anoxia in waterways or bays as a result of high organic-matter-containing storm water runoff and mixing due to a hurricane or severe storm event (Portnoy 1991, Tilmant et al. 1994, Valiela et al. 1996, Mallin et al. 1999, Luther III et al. 2004). However, presumably due to the unpredictable nature of storms and the difficulty of sampling in inclement weather, data collection was not begun in some studies until days after the storm event subsided (Tilmant et al. 1994). Therefore, while low DO levels that persisted for weeks to months were likely correctly attributed to BOD of runoff, it is possible that there was an initial inorganic sediment oxygen demand component at work during the storm's high flows. This might have contributed to resultant fish kills in certain systems. Authors of other studies of runoff-induced hypoxia either did not collect, or did not report, DO data with a detailed enough time resolution to detect COD oxygen depletion, so it is unknown whether that process occurred in those instances as well (Mallin et al. 1999, Luther III et al. 2004).

Systems in which COD should be considered when studying the causes of low DO fish kills will share certain characteristics (note: these proposed characteristics are only theoretical): First, anoxic bottom waters and/or sediment will be present. Anoxia affects redox conditions, causing the creation of ferrous iron and sulfide/polysulfide species in the sediment that drive COD. This hypolimnic anoxia need not be permanent to create reduced COD compounds and resultant oxygen depletion, so long as it occurs up to the point of mixing. Anoxic conditions are typical for many streams, lakes, and reservoirs during the low-flow summer months, when systems tend to stagnate and higher temperatures drive increased stratification and anoxia.  Sub-surface sediment layers are often anoxic even if the overlying water is not.  Second, in addition to anoxic bottom waters and/or sediment, the system must experience a mixing event.  The sediment, and its reduced COD compounds, must somehow be re-suspended and introduced to the oxygenated surface water to deplete oxygen.  This can be achieved by a severe storm runoff event, a wind mixing event, or sandbar breach.  Stronger, longer, or back-to-back mixing events can lead to more and deeper sediment being re-suspended and more oxygen depletion.  Third, a system that experiences substantial oxygen depletion by COD will likely be shallow.  Severity and area of oxygen depletion likely depend on how much of the water column is exposed to the oxygen-starved sediment.  Shallower systems, where re-suspended sediment will mix into a larger portion of the water column, will likely be more susceptible to COD-driven fish kills.

DO depletion, caused by a mixing event and resultant COD, can be reduced or managed in a few ways.  Steps could be taken to prevent or break up the anoxic hypolimnion that contributes to the formation of COD compounds.  This could be attempted in various ways, depending on the individual characteristics of each system.  For instance, if a system suffers from eutrophication and resultant BOD, then measures to decrease nutrient loading may be in order.  Bubbling aerators or vertical water column mixers are commonly applied to break up stratification; however these would have limited effectiveness in a system with branched, complex channels, such as Pescadero Lagoon.  In the case of Pescadero Lagoon, the salt wedge plays a large role in density stratification (Sloan 2006). As Smith (2004) suggested based on pre- and post-restoration water quality studies, reducing salinity by allowing freshwater conversion (saltwater is slowly forced out through the sandbar by inflowing freshwater) would correct many water quality issues. This might be accomplished by altering the mouth or levee system in order to restore the earlier pre-restoration sandbar formation/breach timing that allowed the system to freshwater convert in wetter years (Smith 2004).

In addition to eliminating bottom water anoxia, reducing the strength of the mixing event may help decrease the occurrence of COD. If the amount of sediment that is re-suspended is reduced or the portion of the water column exposed to the plume is reduced, then the effects will likely be less severe. This appears to be supported in the Pescadero system by the fact that Pescadero Channel, which took more than twice as long to drain as the rest of the lagoon, never suffered hypoxia for any substantial period of time. The now-deteriorated corrugated pipes that release Pescadero Channel into Pescadero Creek constrict the flow and likely substantially slow the exit of water. This, in turn, probably reduces the amount of channel sediment that is re-suspended.

COD-driven oxygen depletion can be immediate and severe and can contribute to mass aquatic organism mortality. However, because of its potentially brief period of occurrence that eludes many sampling efforts, it may be greatly underrepresented in the literature. Future research should focus on the prevalence of COD-induced hypoxia in aquatic systems.

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