

# **Restoration of the Salton Sea**

## **Volume 1: Evaluation of the Alternatives**

### **Appendix 1E: Salton Sea Sediment and Water Oxygen Demands**

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# **PART I – SALTON SEA SEDIMENT AND WATER OXYGEN DEMANDS**

**June 14, 2005**

**Updated on August 3, 2005**

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The report is submitted in support of the Feasibility Study of Salton Sea Restoration Alternatives.

## **Materials and Methods**

Sediment cores and bottom water were collected from the five locations in the Salton Sea on June 1, 2005. Due to rough conditions on the sea, we were able to sample only the north basin and a point near the mid-Sea. Sampling locations are given in Table 1 and accompanying map (Fig. 1).

Sediment samples were collected with an Ekman dredge; the center of the material was then cored into 6.3 cm diameter x 30 cm Lucite tubes to a depth of 10 cm ( $\pm 2$  cm). The sediment was covered with bottom water collected just above the sediment using a 2L Van Doren sampler. The tubes were completely filled with water and stoppered, leaving no head space. Three cores were collected at each site and one site (2-1) had 4 replicates. An additional 20 L of bottom water was collected near site 12-1 for determination of water oxygen demand (WOD).

Upon returning to the lab, the cores were placed in temperature-controlled water bath ( $28 \pm 0.3$  °C). The incubation temperature of 28 °C was chosen because it is the estimated average summer temperature of the Sea. A set of three columns containing only bottom water (no sediment) were incubated to determine the WOD. The overlying water in each column was aerated with room air for approximately 10 minutes until the dissolved oxygen concentration stabilized. Dissolved oxygen (DO) was measured with a YSI Model 55 DO meter. The columns were sealed using rubber stoppers with zero headspace, incubated in the dark, and DO measured after 0.0, 1.4, 3.7, 8.7, 17.2, and 20.3 hours.

After 20 hours of incubation, the DO concentrations in most of the samples had fallen to < 1 mg/L, so the overlying water was re-aerated, stoppered, and DO measured again periodically over time. When the DO had fallen to <1 mg/L in most of the columns, the overlying water was aerated a 3<sup>rd</sup> time. DO was monitored for total of 90 hours.

Sulfide concentration ( $\text{H}_2\text{S}_{\text{aq}} + \text{HS}^- + \text{S}^{2-}$ ) was determined periodically during the incubation, especially when D.O. values dropped below 1 mg/L. For sulfide analysis, water samples from the columns were pipetted (2.5 mL) from 8 cm below the surface immediately after opening and the sample mixed with 2.5 mL of an antioxidant buffer solution (AOB). The AOB was made with 40 g NaOH, 160 g sodium salicylate, and 36 g ascorbic acid, and brought to 1 liter with de-aired, deionized water. Sulfide standards were prepared by dissolving reagent grade  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  in a 50:50 mixture of AOB and de-aired, deionized water. The AOB solution serves two purposes: it protects the sulfide from oxidation, and the high pH converts all of the  $\text{H}_2\text{S}_{\text{aq}}$  and  $\text{HS}^-$  into  $\text{S}^{2-}$ . The concentration of total  $\text{S}^{2-}$  was determined with an Orion IonPlus silver/sulfide specific ion electrode on a Fisher Accumet mV meter.

Following each sampling and DO measurement, the columns were topped-off with 2 to 4 mL of incubated Salton Sea bottom water to ensure no air bubble in the headspace of the columns.

## Results

Figure 2 shows the loss of dissolved oxygen in the overlying water for the cores and water blanks following the first aeration. Linear regression calculations of the DO vs. time plots were used to calculate the water and sediment oxygen demands. In general, the regression plots were restricted to DO values >1.0 mg/L due to the slow oxygen consumption at very low DO concentrations. This is standard procedure for SOD measurements (Arega and Lee, 2005).

Table 2 and Figure 3 show the average water oxygen demand (WOD) rates over the three aerations. Of particular note is the accelerating rates measured for the WODs. This acceleration can be seen in Figure 2 during the first incubation period. The “water only” curve shows an increase in slope with time. The rate of oxygen consumption increased continuously during the whole incubation period, which included three separate aerations. The reason for this increase in water oxygen demand with time is unclear, although it may be due to the development an aerobic microbial population living on the dead anaerobic microbes and dissolved organic matter in the bottom water.

Figure 4 shows the average change in DO and sulfide concentration in the overlying water for all 16 sediment cores. Table 3 shows the best-fit lines for the

DO vs. time for all of the columns following the first aeration. Sediment oxygen demands (SOD) were calculated from the slopes of the DO loss curves for individual column, and corrected for the WOD rate. Similar calculations were done for the following the other two aeration periods.

Table 3 shows there was high variability among the replicates at several of the sites. In particular, a few cores had very high oxygen consumption rates, which were consistent for all three aeration periods. This high variability may be attributed to the less-than-perfect core collection procedure. Because of the rough conditions on the Sea during sampling, only a few of the columns remained intact and unmixed with the surface sediment on top of the core. The exceedingly high oxygen demands observed in a few of the columns could be due to the mixing that occurred during column assembly.

Table 4 shows the average SOD values for all 16 sediment cores for each of the three aeration events. The SOD values decreased with time and successive aeration due to the continuously increasing WOD values. Because of this unusual behavior of the water-only incubations, we recommend using the SOD values for the first aeration and incubation period (Tables 3 and 4). SOD values for the first incubation ranged from  $21 - 584 \text{ mg m}^{-2} \text{ h}^{-1}$  ( $0.5 - 14 \text{ g m}^{-2} \text{ d}^{-1}$ ), with an average of  $112 \text{ mg m}^{-2} \text{ h}^{-1}$  ( $2.7 \text{ g m}^{-2} \text{ d}^{-1}$ ).

Recently, Arega and Lee (2005) reported SOD values from eutrophic coastal bays around Hong Kong that ranged from  $96 - 254 \text{ mg m}^{-2} \text{ h}^{-1}$ . SOD values in the Neuse River estuary, North Carolina, ranged from  $16 - 74 \text{ mg m}^{-2} \text{ h}^{-1}$  (Fear et al., 2004). The SOD values we measured are well within the ranges observed in eutrophic, estuarine systems.

Steeby et al. (2004) measured the SOD in 45 commercial catfish ponds in northwest Mississippi using *in situ* respirometry. The SOD values ranged from 63 to 1,038 with a mean of  $359 \text{ mg m}^{-2} \text{ h}^{-1}$ . The authors said these SOD values were greater than previously reported for other catfish ponds but were similar to SOD in semi-intensive marine shrimp ponds. Some of the cores from our study had SOD values similar to those reported for aquaculture ponds and significantly higher than those reported for other natural systems, indicating the high productive of the Salton Sea.

It should be pointed out that our SOD measurements were made on quiescent systems. It has been recognized for some time that the flow velocity above a sediment can have a significant effect on the SOD measurement, even when no sediment resuspension has been observed (Arega and Lee, 2005, and references therein). Higher SOD values associated with water flow above the sediments could have important implications for the modeling of mixing events at the Sea.

Figure 4 shows release of total sulfide from the sediments into the overlying water column when DO concentrations dropped to  $<1.0 \text{ mg/L}$ . The high SOD rates

measured for the Salton Sea sediments can be attributed to both biotic and abiotic reactions. The abiotic reactions include the scavenging of dissolved oxygen by hydrogen sulfide and bisulfide ion released from the sediment pore water.

In addition, the oxidation of iron monosulfide minerals (FeS) was observed during the incubation of the cores. Many of the cores, especially from site 2-1, contained a lot of black FeS minerals. At site 2-1, the surface layer of the sediments had a coating of this black material. Exposure to oxygen converted this black surface layer to tan/brown within a day or two. Following the incubation, the columns were allowed to react with atmospheric oxygen and an orange coloration could be seen on the surface of a few of the sediments. It appears that the oxidation of FeS to  $\text{Fe}(\text{OH})_3$  and  $\text{SO}_4^{2-}$  had occurred.

High SOD and WOD found in the Salton Sea will have important effects on oxygen concentration within the water column, particularly on windy days when bottom water and sediments are mixed into the upper portions of the lake.

## References

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- Fear, J., T. Gallo, N. Hall, J. Loftin, and H. Paerl. 2004. Predicting benthic microalgal oxygen and nutrient flux responses to a nutrient reduction management strategy for the eutrophic Neuse River estuary, North Carolina. *Estuarine Coastal & Shelf Sci.* 61: 491-506.
- Steeby, J.A., J.A. Hargreaves, and C.S. Tucker. 2004. Factors affecting sediment oxygen demand in commercial channel catfish ponds. *Journal of World Aquaculture Society* 35:322-334.

Table 1.—Sites sampled at the Salton Sea on June 1, 2005

Sample Site	Coordinates		Depth (ft)
	Latitude	Longitude	
2-1	33.5001	116.050	11
4-1	33.4585	116.000	39
4-3	33.4595	115.900	43
7-1	33.3932	116.025	16
12-1	33.2916	115.858	24

Table 2.—Average water oxygen demand (WOD) rates (m) over three aerations. Values determined in three replicate core tubes filled only with 0.87 L of bottom water collected at 30 ft. Columns were aerated three different times (I, II, III). s.d. = standard deviation.

Aeration	WOD rate
	(mg L <sup>-1</sup> hr <sup>-1</sup> )
	Average ± s.d.
I	0.15 ± 0.01
II	0.47 ± 0.02
III	1.22 ± 0.25
Global Average	0.61 ± 0.09



Table 3.—Best fit line equations applied to data from the first aeration of water/sediment cores. For the equations  $y = -mx + b$ ,  $y$  is DO,  $mg\ L^{-1}$ ;  $m$  is SOD rate,  $mg\ L^{-1}\ hr^{-1}$ ;  $x$  is time, hours; and  $b$  is the  $y$  intercept,  $mg\ L^{-1}$  DO. SOD rates were calculated as follows:  $(m_{water+sediment} - m_{water}) * (V/A)$  where  $m_{water}$  is the rate of DO loss from water alone,  $m_{sediment+water}$  is the rate of DO loss from water/sediment cores,  $V$  is core water volume, and  $A$  is the surface area of the water/sediment interface

Sample Site	Core Replicate	Core Sediment Depth (cm)	Approximate Core Water Volume (L)	Best fit line		SOD rates
				$y = -mx + b$	$r^2$	
2-1	A	8	0.609	$y = -0.721x + 6.37$	0.99	104
	B	13	0.443	$y = -0.664x + 5.91$	0.95	68
	C	9	0.575	$y = -0.731x + 6.59$	0.99	100
	D	6	0.675	$y = -0.333x + 6.42$	1.00	37
4-1	A	11	0.509	$y = -1.441x + 5.44$	1.00	64
	B	12	0.476	$y = -1.667x + 6.30$	1.00	217
	C	11	0.509	$y = -3.957x + 5.85$	1.00	584
4-3	A	9	0.575	$y = -0.641x + 5.30$	0.91	85
	B	9	0.575	$y = -0.375x + 5.79$	0.94	39
	C	9	0.575	$y = -0.272x + 6.44$	1.00	21
7-1	A	11	0.509	$y = -1.568x + 6.30$	1.00	217
	B	12	0.476	$y = -0.474x + 5.92$	0.99	46
	C	11	0.509	$y = -0.668x + 5.16$	0.74	79
12-1	A	11	0.50902	$y = -0.358x + 6.11$	0.99	32
	B	10	0.542	$y = -0.343x + 5.75$	0.97	31
	C	9	0.575	$y = -0.572x + 5.98$	0.98	73

Table 4.—Average sediment oxygen demand (SOD) for all three aerations of the water/sediment core samples. The SOD rates decreased with each aeration (I, II, III) due to the increasing WOD.

SOD rate	
(mg m <sup>-2</sup> hr <sup>-1</sup> )	
Aeration	Average ± s.d.
I	112 ± 139
II	106 ± 122
III	12 ± 120
Grand Average	77 ± 133

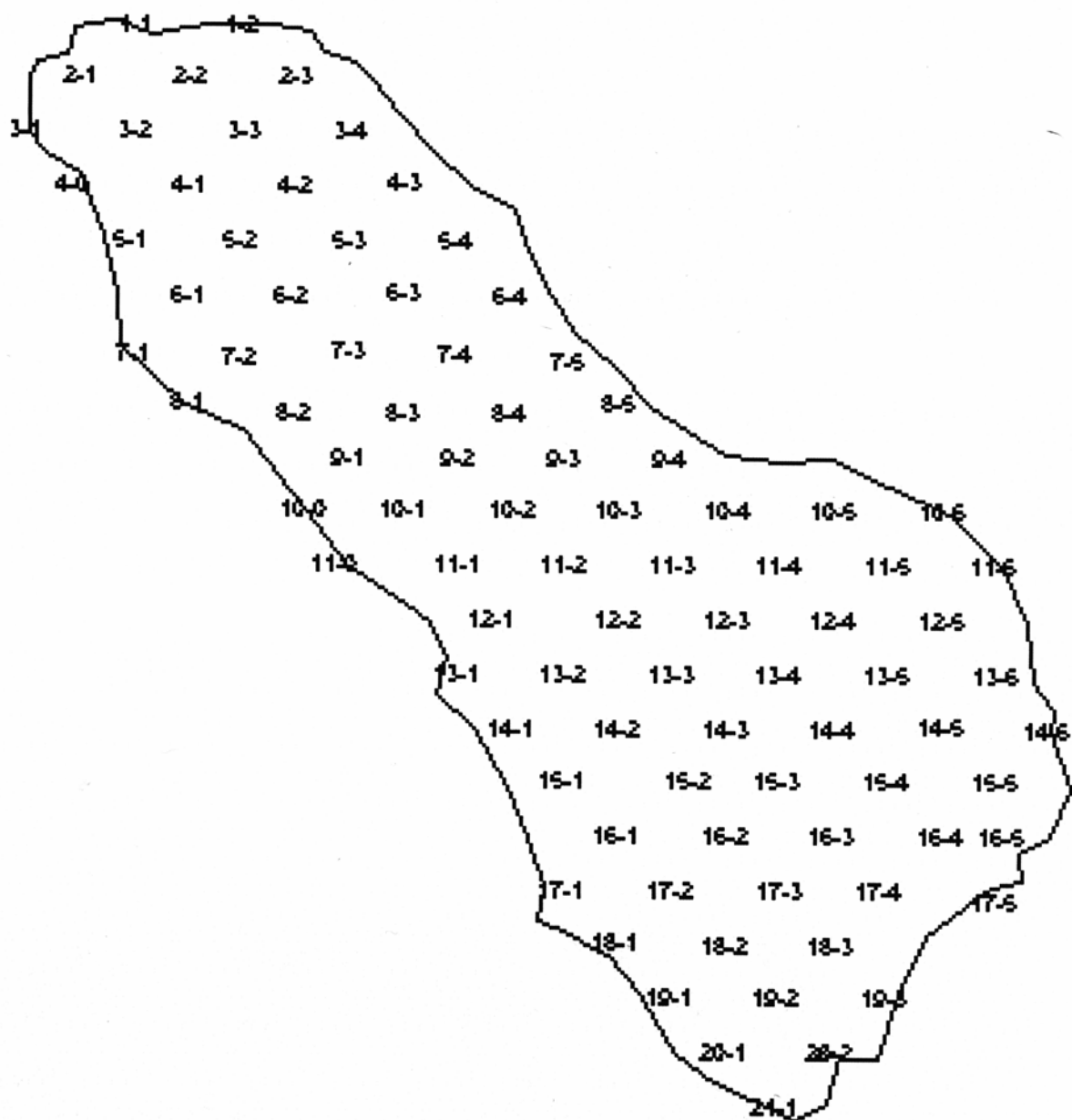


Figure 1.—Sampling locations on the Salton Sea. Refer to Table 1 for the sites sampled for this study.

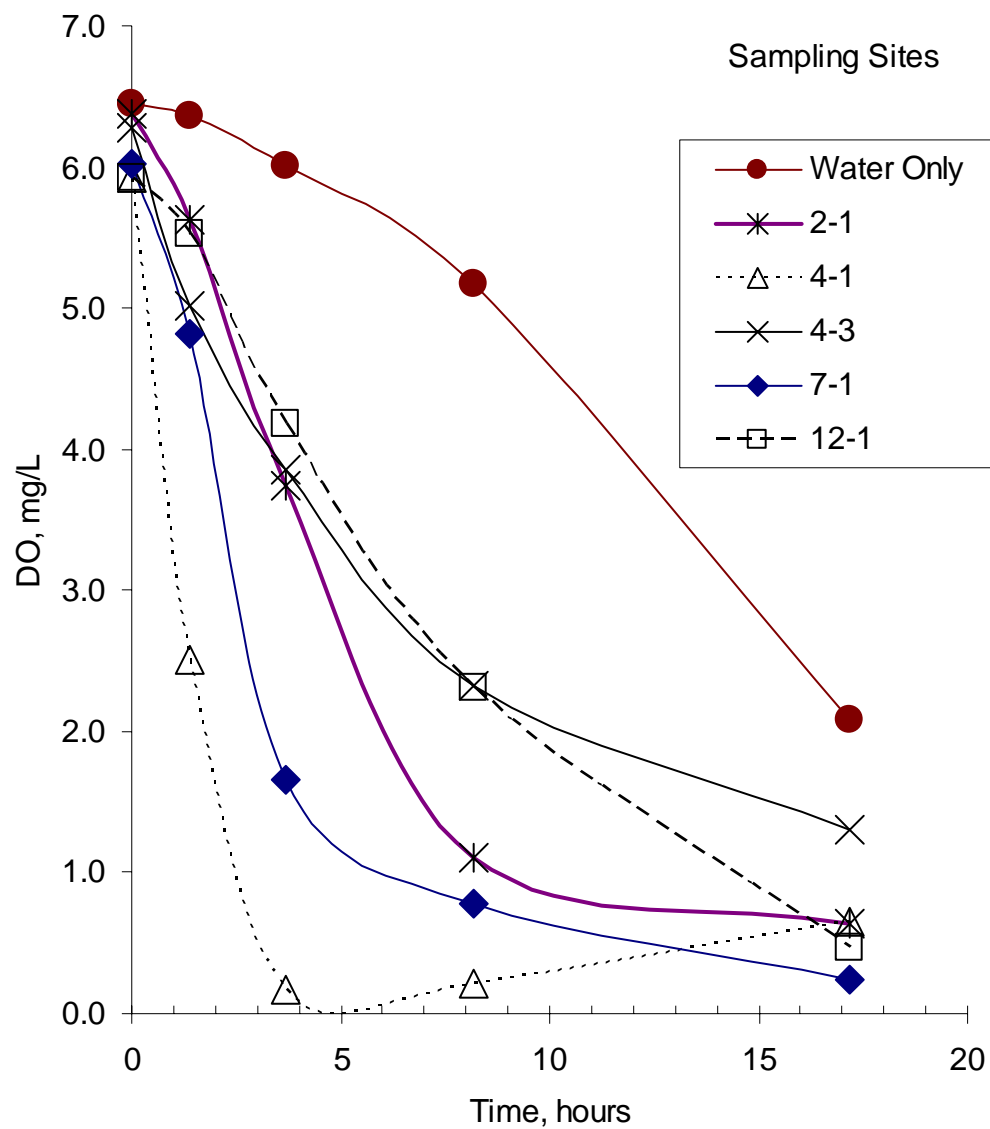


Figure 2.—Dissolved oxygen measurements on the sediment cores and water blanks following the first aeration of the overlying water. Points are averages of 3 or 4 replicates.

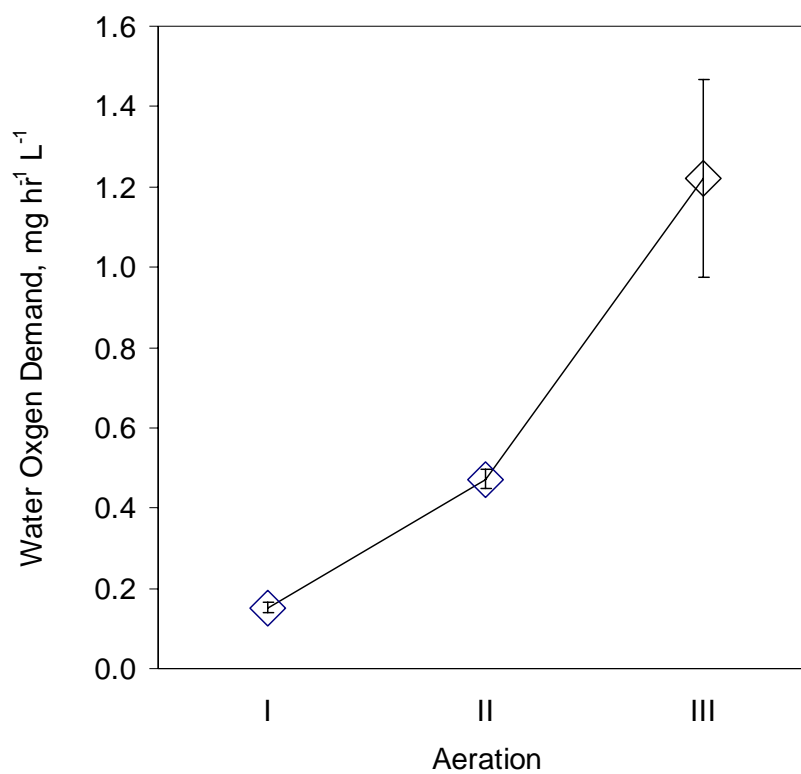


Figure 3.—Average water oxygen demand (WOD) rates over three aerations. Values determined in three (or four) replicate core tubes filled only with 0.87 L of bottom water collected at 30 ft.

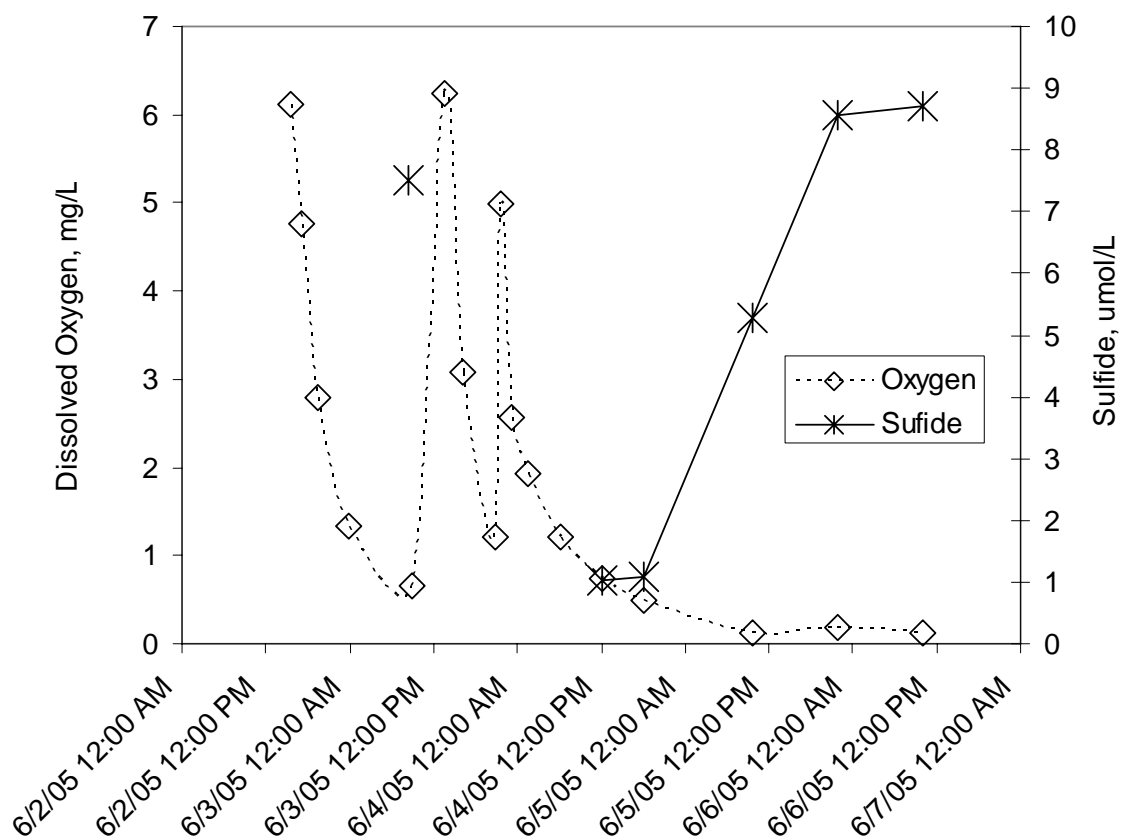


Figure 4.—Dissolved oxygen and sulfide concentration over time in Salton Sea sediment cores. The data are averaged from 16 core columns.

# PART II – SALTON SEA SEDIMENT AND WATER OXYGEN DEMANDS

Update: August 3, 2005

## More on Hydrogen Sulfide and SOD

On June 1, 2005 we collected sediments from the Salton Sea and extracted the sediment pore water for analysis. The average sulfide concentration (n=10) in the pore water 0.13 mM (4.2 mg/L). These were the samples we used for the SOD measurements presented above. In addition to the undisturbed sediment cores, we also measured SOD values in mixed sediment suspensions.

On July 6, 2005 we resampled the sediments and measured an average pore water sulfide concentration of 1.4 mM (44 mg/L), with a range from 0.5 to 3.8 mM (16 to 122 mg/L) for n = 11. In one month (June 1 to July 6), the average sulfide concentration of the pore water had increased 10-fold due to increasing water temperature and organic matter inputs to the sediments. Thus, the SOD values for samples collected on June 1, 2005 will be low compared to mid to late summer time values. SOD analyses were not measured on the July 6 samples. However, based on the pore water sulfide concentrations, oxygen demand can be estimated.

If the sediment pore water diffuses into the overlying sea water, or is mixed by turbulent flow, the sulfide will rapidly react with oxygen to form sulfate:



For the July 6<sup>th</sup> samples, this oxidation reaction has the potential to consume 90 mg O<sub>2</sub> if a liter of pore water is released to the overlying sea water. Under these conditions, low to zero dissolved oxygen (DO) can be expected in the sea, and there is sufficient sulfide released to outgas from the lake.

Dissolved sulfide is highly toxic to aquatic life. According to the MSDS for hydrogen sulfide in solution, the 96 hour median toxic level (TLm) for aquatic sowbug (*Asellus* sp) is 0.11 mg/L, for Gammarus (scud shrimp) 0.84 mg/L, for bluegill sunfish 0.05 mg/L, and for fathead minnow 0.01 to 0.55 mg/L.

[[http://www.eecs.umich.edu/ssel/MSDS/Hydrogen\\_Sulfide.pdf](http://www.eecs.umich.edu/ssel/MSDS/Hydrogen_Sulfide.pdf)]

Hydrogen sulfide gas is 18% heavier than air, so there is a tendency for it to accumulate in low-lying areas, and when released, to travel near the ground. If persistent stratification occurred at the sea and hydrogen sulfide accumulated in the hypolimnion of the lake to a concentration of 44 mg/L (average porewater concentration on July 6, 2005), an overturning of the lake could release

a significant amount of gas, in addition to consuming all of the oxygen in the lake and killing much of the aquatic life. An atmospheric concentration of 1,400 mg/m<sup>3</sup> H<sub>2</sub>S is reported to cause immediate respiratory arrest (Collins and Lewis, 2000). The toxicity of lower concentrations depends on exposure time and the sensitivity of the individual. It is likely that a mixing event that releases H<sub>2</sub>S from displaced bottom-water would coincide with a major wind event. Thus, toxic concentrations of H<sub>2</sub>S gas that could kill animals downwind of the lake seem unlikely. However, concentrations could be high enough to cause headaches and nausea in sensitive individuals.

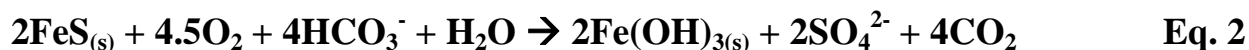
## SOD Measurements on Suspended Sediments

Refrigerated sediments from the June 1, 2005 sampling date were weighed into 520 mL of aerated, deionized water and the dissolved oxygen recorded every minute for up to 3 hours. Approximately 7.5 g of wet sediments were placed into the well-mixed flasks with no head-space. The dissolved oxygen probe was secured in the flask and the opening sealed with parafilm to exclude room air. Replicates (labeled A and B) were collected in the field and treated as unique samples throughout the tests. For each sample, three separate portions of the wet sediments were placed in tin crucibles for water content analysis by drying in the oven at 105°C overnight. The water content of the sediments was used to calculate the oxygen demand of the solid phase (sediments) on a dry weight basis. It also allowed us to determine the contribution of the pore water to the total SOD.

Figures 5A and 5B show the loss of dissolved O<sub>2</sub> in the suspensions over time for replicated runs. The oxygen loss did not fit first-order kinetics expressions suggesting a complex series of reactions are involved in the oxygen loss. Some of these reactions include the oxidation of pore water sulfide, oxidation of FeS minerals, and bacterial respiration.

Using the oxygen loss after 60 minutes, we calculated the SOD values for the sediment (dry weight basis). The SOD measurements were corrected for the pore water (PW) oxygen demand based on the sulfide concentration of the pore water, the pore water content of the wet sediment, and Equation 1. The average SOD for the sediments was 0.62 mg O<sub>2</sub>/g dry sediment (Table 5, column 3).

The sulfide content of the PW was relatively low on June 1, so the PW oxygen demand was less than 8% of the total oxygen demand of the wet sediment (Table 5, column 4). The oxidation of iron monosulfide minerals (FeS) to Fe(III)-hydroxides (Fe(OH)<sub>3</sub>) was observed during the measurements (black mud turned yellow-brown) suggesting this may have been the dominant oxygen demand in this study. The reaction is as follows:



In an earlier study we measured the average FeS content of Salton Sea sediments at 1.0 mg Fe/g dry sediment, with a range of 0.11 to 2.4 mg Fe/g dry sediment (DeKoff et al., submitted). If the FeS reacts with O<sub>2</sub> as given in Eq. 2, the oxygen demand of the sediment solid phase would



average 1.3 mg O<sub>2</sub>/g dry sediment. This “potential SOD” is approximately double the measured SOD of 0.6 mg O<sub>2</sub>/g dry sediment measured. This demonstrates that the SOD values we report in Table 5 can be attributed to the oxidation of FeS minerals.

DeKoff et al. also reported the concentrations of other iron sulfide minerals including pyrite (FeS<sub>2</sub>) and greigite (Fe<sub>3</sub>S<sub>4</sub>) in Salton Sea sediments. Both of these minerals react more slowly with O<sub>2</sub> compared to the FeS solids, which occurs as both amorphous FeS and crystalline phases (mackinawite). DeKoff et al. estimated that 7,000 metric tons of iron sulfide minerals are precipitating in the Salton Sea annually. Total iron sulfide content of the sea sediments averaged 1.1% (dry weight). Oxidation of exposed sea sediments will result in a long term oxygen demand due to the reaction of these iron sulfide solids.

If we assume the pore water had 10 times more sulfide (as found in the July 6 samples), then the PW oxygen demand increases to 24% of the total sediment demand (Table 5, column 5). Resuspension of sediments and mixing of pore water into the overlying water have the potential to impose a significant oxygen demand on the water in the sea. In the early summer (June) the solid phase oxygen demand dominated the SOD. As pore water sulfide concentrations increased later in the summer (July), the entrained pore water contributed approximately 45% of the total sediment oxygen demand in some locations.

## Conclusions

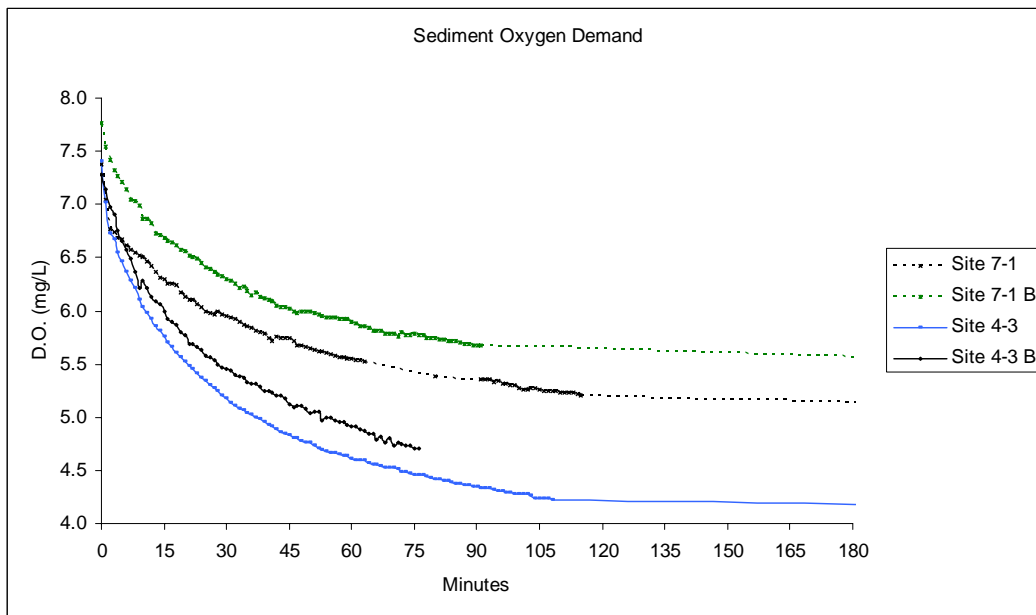
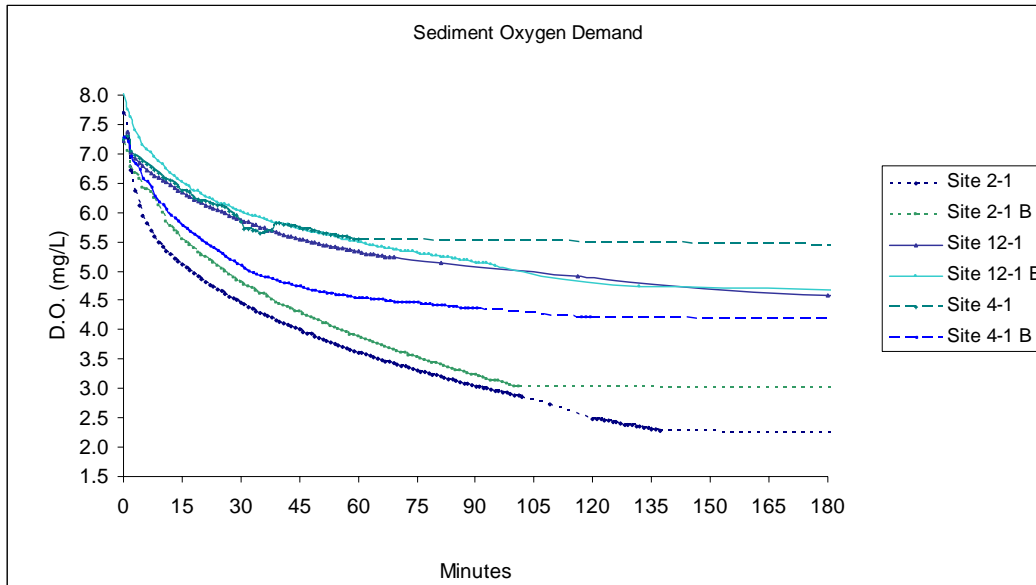
Disturbances to the sediments of the Salton Sea will impose a large oxygen demand on the water. Dike construction to isolate portions of the sea for shallow water habitat or a marine lake or could cause local oxygen sags that could spread to larger areas of the sea as the suspended solids are moved by currents.

## References

- Collins, J. and D. Lewis. 2000. Hydrogen sulfide: Evaluation of current California air quality standards with respect to protection of children. California Air Resources Board California, Office of Environmental Health Hazard Assessment. Available at: <http://www.arb.ca.gov/ch/ceh/aqstandards/OEHHAH2SContractorReport091200.pdf>
- DeKoff, J., M. A. Anderson, C. Amrhein. Geochemistry of iron in the Salton Sea, submitted to *Hydrobiologia* on May 1, 2005.

Table 5.—Sediment oxygen demand for sediment suspensions

Site	Solids content of sediments (% dry wt)	SOD (60 min) mg O <sub>2</sub> /g sediments (dry wt)	PW O <sub>2</sub> demand to the total O <sub>2</sub> demand (percent)	July 6 PW O <sub>2</sub> demand (based on PW S <sup>2-</sup> ) Percent of total O <sub>2</sub> demand
2-1 A	50%	0.47	<1%	5%
2-1 B	50%	0.37	<1%	5%
4-1 A	15%	0.91	4.5%	30%
4-1 B	21%	0.69	7.9%	46%
4-3 A	17%	1.13	4.7%	37%
4-3 B	16%	0.90	2.2%	18%
7-1 A	19%	0.67	1.0%	9%
7-1 B	29%	0.43	1.4%	12%
12-1A	21%	0.59	3.9%	29%
12-1B	15%	0.92	7.4%	44%



Figures 5A and 5B.—Sediment oxygen demand of suspended sediments collected from the Salton Sea on June 1, 2005.