Lake and Reservoir Management 23:637-652, 2007

Sulfide irruptions and gypsum blooms in the Salton Sea as detected by satellite imagery, 1979-2006

Mary A. Tiffany[1], Susan L. Ustin[2] and Stuart H. Hurlbert[1]
[1]Department of Biology and Center for Inland Waters,
San Diego State University, San Diego, CA 92182-4614, USA

[2]Department of Land, Air and Water Resources,
University of California, Davis, Davis, CA 95616-8527, USA

Abstract

Tiffany, M.A., S.L. Ustin and S.H. Hurlbert. 2007. Sulfide irruptions and gypsum blooms in the Salton Sea as detected by satellite imagery, 1979-2006. Lake Reserv. Manage. 23:637-652.

Bright pale-green surface waters, locally called "green tides," are visible to the naked eye and satellite sensors in patches at the Salton Sea, usually between May and November. These were studied using satellite remote sensing and by direct sampling. Algal blooms are ruled out as a cause as phytoplankton abundance, and chlorophyll concentrations were lower within the patches than in surrounding areas. The presence of abundant microscopic gypsum ($CaSO_4 \cdot 2H_2O$) crystals in surface waters suggests that scattering from this precipitating salt produces the intense signals. Biogeochemical factors include: the decomposition of organic matter, resultant anoxia and production of hydrogen sulfide by sulfate-reducing bacteria at depth, and oxidation back to sulfate and precipitation of gypsum during wind-induced overturn events. Sulfide concentrations following one such event in September 2005 ranged from 0.3 to 2.7 mg l^{-1} at the surface and 1.2 to 25 mg l^{-1} in bottom waters. Gypsum crystals occurred at densities up to 40,000 ml^{-1} in surface water on that date, most 20-30 µm in length with some as long as 190 µm. From 1998 to 2006, gypsum blooms appear to have increased in intensity and duration implying an increase in sulfide irruptions and anoxia in surface waters. As much as 97 percent of the lake was affected in early summer of 2003 and 75-80 percent in summers of 2005 and 2006. Events lasted for months at a time during these years. This intensification is likely due to the decline in abundance of a planktivorous fish, a hybrid tilapia, the California Mozambique mouthbrooder, leading to increased algal productivity, more severe anoxia and higher levels of dissolved hydrogen sulfide. Gypsum blooms seem to have occurred at least as far back as the 1970s, and are associated with frequent mass mortalities of fish, plankton and benthos.

Key words: tilapia, fish kills, remote sensing, sulfide, anoxia

Introduction

During October 20 to November 3, 2003 the most disastrous wildfires in the history of southern California and northern Baja California burned ~300,000 ha, destroyed 3,361 homes and businesses, and left 26 people dead in the US alone (Johnson 2004; Keeley *et al.* 2004). Smoke from these blazes wafted far out over the Pacific Ocean pushed by strong, dry winds from the northeast, known locally as Santa Anas (Fig. 1). These winds always increase the danger of the wildfire season in California and also often lead to upwelling in the Southern California Bight (Hu and Liu 2003).

Limnologists viewing this satellite image, however, might have been more intrigued by large patches of bright green water in the Salton Sea. These are called "green tides" by local residents and, it turns out, were the result of wind-driven upwelling in that water body. The Salton Sea is located in the southeastern corner of California and lies within the Coachella and Imperial Valleys. It has an area of ~980 km^2 and a mean depth of ~8 m. Well below sea level and fed by both agricultural and municipal wastewaters, it has become saline since its accidental formation in 1905. This is primarily due to its lack of outlet and high evaporation rates but also to diffusion of salts from sediments (Wardlaw and Valentine 2005). Most of the salts in the Salton Sea are ultimately derived from the Colorado River. Therefore, its proportions of salts are somewhat different from those of the ocean. Additionally the lake is about 25 percent saltier than the ocean. Calcium levels are at 944 mg l^{-1} and sulfate at 10,500 mg l^{-1}

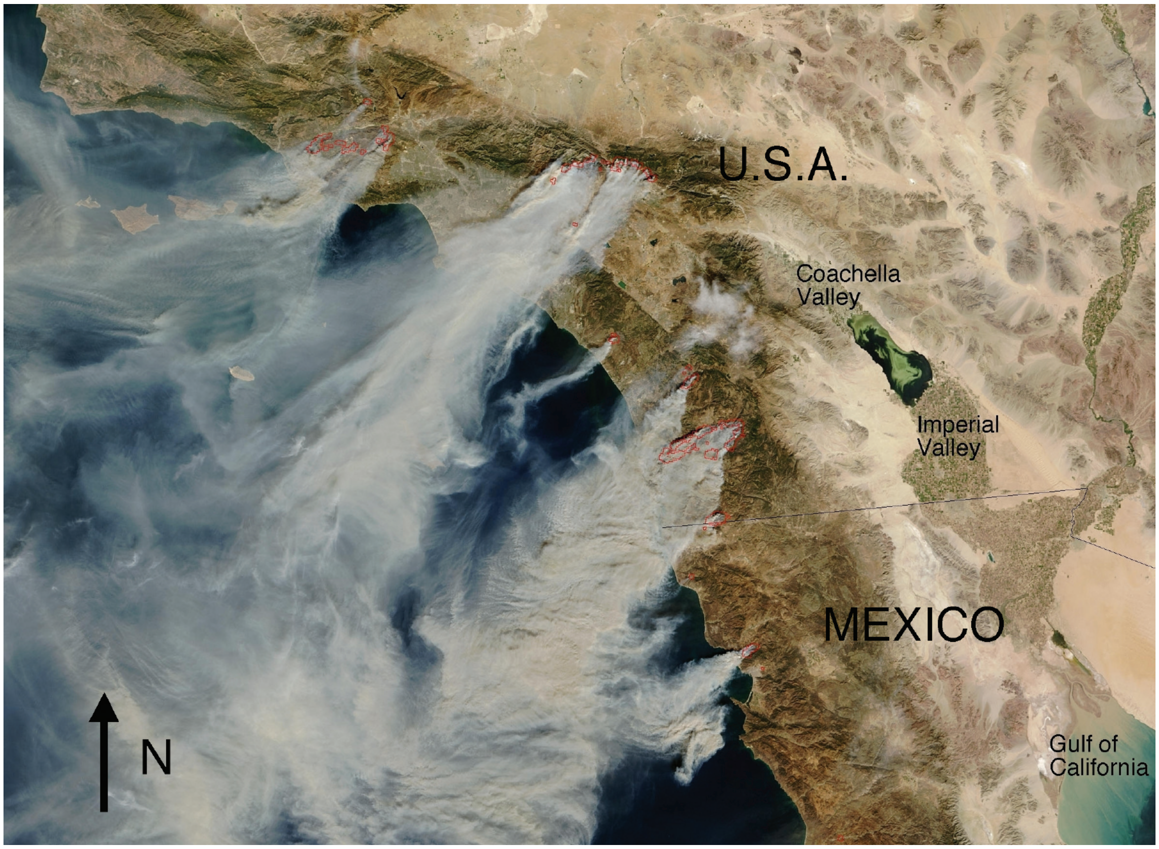

Figure 1.-Fire on land, gypsum in the water. MODIS (Aqua) true color image on 26 Oct 2003 showing major fires in southern California and Baja California. Note bright green patches in the Salton Sea. Red markings show sites of thermal signals (fires).

(Holdren and Montaño 2002). It is at saturation with respect to calcium sulfate (gypsum) and calcium carbonate, which have long been precipitating out in the Salton Sea (Hely *et al.* 1966; Tostrud 1997; Holdren and Montaño 2002; Schroeder *et al.* 2002; Wardlaw and Valentine 2005) and are abundant in the sediments (Schroeder *et al.* 2002; Dexter *et al.* 2007). At times, especially in the warmer months, surface water in the middle of the lake has extremely low oxygen content along with high sulfide levels (Watts *et al.* 2001). Watts *et al.* (2001) suggested that gypsum crystals in surface waters, precipitating as sulfide oxidizes back to sulfate, turn the water a bright green. These inorganic crystals primarily scatter rather than absorb light; the index of refraction of gypsum is ~1.13-1.15 (Nesse 2004) relative to water (Mobley 1994) so gypsum crystals suspended in water would make good scatterers of impinging light (Stramski *et al.* 2004). It is this index that determines scattering characteristics of particles in a medium (Mobley 1994). Other things being equal, mineral particles of high refractive index backscatter light ~30 times more than do "soft" organic particles (Stramski *et al.* 2001).

Sulfide events are likely of immense importance to the ecosystem of this lake due to resultant mortality of fish, plankton and benthos (Tiffany *et al.* 2002; Caskey *et al.* 2007; Tiffany *et al.* 2007a, b). The strong odor of hydrogen sulfide and/or other volatile organic sulfur compounds and presence of gypsum crystals in the water column were also noted in March 2005 when a mass mortality of benthic invertebrates occurred (Dexter *et al.* 2007).

The three primary objectives of this study were: to document the spectral signature of Salton Sea in the visible and near-infrared wavelengths within green patches to distinguish them from algal-laden waters; to determine the seasonal and interannual variation in duration and spatial extent of green water events; and to relate these variations to water temperature, plankton and tilapia populations. The tilapia species present is the California Mozambique mouthbreeder, an *Oreochromis mossambicus* Peters x *O. urolepis honorum* (Trewavas) hybrid (Costa-Pierce and Doyle 1997).

Materials and methods

This paper is based almost entirely on available satellite data using imagery from four satellite sensors. But, in addition, we made a number of measurements during a particular "green tide" event. Remote sensing data for the Salton Sea has been available since the first ocean color satellite was launched in late 1978. These sensors are compared by Whitehouse and Hutt (2006). Satellite observations are probably limited to the upper meter or two in this turbid lake as the Secchi depth varies from 0.5 to ~2 m (Watts *et al.* 2001). Cloud-free days are common in the Salton Sea region, permitting frequent observation of the lake surface. Ground-truth data to accompany satellite imagery is relatively scarce and mostly available from 1997-1999. Sampling during a "green tide" event in 2005 was undertaken to resolve the origin of this phenomenon by measuring temperature, chlorophyll *a* (chl-*a*), oxygen and sulfide concentrations and gypsum crystal abundance, both within and outside of green patches.

Anecdotal reports of "green tides" exist from the 1960s and 1970s (Watts *et al.* 2001). The CZCS (Coastal Zone Color Scanner) was a prototype sensor, the first intended to measure ocean color and operated from 1979-1985. We used data from this sensor to obtain information on the extent of "green tides" from this time period. Many of the images covered the west coast of North America and included the Salton Sea. Resolution was 0.825 km^2 and the four visible wavebands were centered at 443, 520, 550 and 670 nm with 20 nm bandwidths and a broad near-infrared band at 760 with bandwidth 100 nm. Over time the radiometric sensitivity declined so that data from years before 1981 is the most useful (Gordon *et al.* 1983; Evans and Gordon 1994). The signal from the CZCS sensor was 8 bit digitized with direct counts of from 0 to 255 for each pixel. Saturation of the signal, where the energy flux exceeds the sensitivity range of the detector, occurred above counts of 255 (Gordon 1981). Most land pixels exceeded this value in the 550 nm waveband. This precluded normalization of level 1 data with a land pixel. Instead, level 1A images (raw radiance counts) were plotted at all wavelengths on 15 Aug 1979 during a typical bright signal event. All available images from 1979-1985 were then similarly examined for any unusual signals.

SeaWiFS (Sea-viewing Wide Field-of-view Sensor) was used to calculate the intensity of radiances in the Salton Sea at various wavebands and the area of the lake with elevated radiances in the green waveband (555 nm). This sensor has provided nearly daily coverage of ocean color from its launch in late 1997 to the present (2007) and was primarily intended to provide information on chlorophyll concentrations in the open ocean. It traverses the Salton Sea region from north to south at about the same time each day (~noon). The resolution is ~1.1 km^2 (Hooker *et al.* 1992). The visible wavebands for SeaWiFS are 412, 443, 490, 510, 555 and 670 nm with bandwidth of 20 nm and the near-infrared bands are at 765 and 865 nm with bandwidth of 40 nm. Production of Level 2 images (normalized water-leaving radiances, atmospherically corrected) uses an algorithm that assumes zero water-leaving radiances for the NIR bands at 765 and 865. This produces negative water-leaving radiances for many coastal or turbid waters, especially at shorter wavelengths (Ruddick *et al.* 2001). When processed to level 2, many or even most of the pixels within an image of the Salton Sea have negative values (Tiffany *et al.* 2007a). Thus, we chose to process images only from level 1A (raw radiances) to level 1B (calibrated and geolocated- but not atmospherically corrected) using the image analysis package SeaDAS (SeaWiFS Data Analysis System).

Level 1A SeaWiFS data are very large files. Due to limitations on the size of the hard drive used, the first step was to use the subscene feature of SeaDAS to circumscribe a region around the Salton Sea. The two points used were 33.9°N 116.7°W and 32.7°N 115°W. The images that resulted varied in size from ~200-400 kb depending on the viewing angle of the sensor. Those images < 260 kb, as when the Salton Sea region was at the edge of a swath, were deemed to have too few pixels for analysis and were disregarded. Dates with clouds were eliminated by inspecting each image at bandwidth 865 nm and rejecting those where clouds occluded any part of the surface of the lake.

Images were then processed to level 1B with an orthographic projection centered at 33.3°N and 115.83°W and normalized to a pixel at 33.20°N and 115.93°W. A relative radiometric normalization technique (Yuan and Elvidge 1996) was employed using a bright nearby terrestrial pixel (~1.1 km^2). This was chosen to be ~9 km away from the southeastern shore, far from human habitation or roads, and where the vegetation likely does not change seasonally (red dot in Fig. 5B). At 555 nm the value of this pixel was usually in the range of 13-17 $mW\ cm^{-2}\ \mu m^{-1}\ sr^{-1}$ in summer and 8-10 $mW\ cm^{-2}\ \mu m^{-1}\ sr^{-1}$ in winter. By normalization to a "pseudo invariant" land pixel (Schott *et al.* 1998), seasonal changes in illumination, daily changes in meteorological factors such as aerosols and ozone, and effect of sensor angle are accounted for, assuming they are constant within the region of interest. For each image all pixels were adjusted by a ratio so that the terrestrial pixel had a value of 15 $mW\ cm^{-2}\ \mu m^{-1}\ sr^{-1}$, chosen as it is a typical summer value at this latitude and longitude when events of most interest occur.

Histograms of radiances emitted at 555 nm sometimes showed a bimodal distribution with peaks at about 3.5-4 $mW\ cm^{-2}\ \mu m^{-1}\ sr^{-1}$ (dark water) and another at ~7-9 $mW\ cm^{-2}\ \mu m^{-1}\ sr^{-1}$ (Fig. 2). To compute the percent of the lake area brighter than 5 $mW\ cm^{-2}\ \mu m^{-1}\ sr^{-1}$ on a given date the perimeter of the lake was manually traced using the SeaDAS annotation/blotch function, avoiding land pixels as much as possible, and a histogram was produced using 9 bins and the blotched area. A total of 1,020 dates with suitable cloud-free images were analyzed from 1998-2006.

MODIS (Moderate Resolution Imaging Spectroradiometer) was used to illustrate true color images on certain dates. It consists of two sensors (Terra, launched in late 1999 and Aqua, launched in 2002). These are multi-use sensors intended for both terrestrial and aquatic uses. MODIS also has thermal bands allowing the measurement of sea surface temperature (SST). MODIS true color image composites with a resolution of are produced using three visible bands: blue, green and red (479, 565 and 670 nm), with resolutions of 500 m^2, 500 m^2 and 250 m^2 respectively, and posted on the MODIS Rapid Response website.

On 3 Sep 2005 sampling was carried out along two transects in the lake, one from north to south and one along the northwest-southeast axis of the lake (eight stations, Table 1, Fig. 5B). Suitable transect locations including both green and brown water were selected by observation from an ultralight aircraft on the day of sampling. Gypsum crystals were enumerated from 0-3 m integrated water samples and counted using settling tubes and an inverted microscope as for phytoplankton (Tiffany *et al.* 2007a) within 24 h. Gypsum crystals were briefly rinsed in deionized water to remove dissolved salts, collected on a stub and air-dried. Crystals were imaged by scanning electron microscopy (SEM) using a Hitachi S-2700 at an accelerating voltage of 10 KV. For comparison, crystals in 0-3 m surface samples were also counted for six of the same stations, collected on 4 May 2005, a date without green waters. 500 ml samples were collected from the 3 Sep 2005 integrated samples to determine chlorophyll *a*, stored at -80 °C and analyzed in the laboratory using a Turner Designs Model 10 fluorometer. Samples for sulfide analysis were taken at 2 m depth intervals starting at the surface. They were immediately preserved 1:1 with SAOB (sulfide anti-oxidant buffer, Orion™) to prevent oxidation before analysis. Sulfide concentrations were measured using an OrionTM silver/sulfide electrode using Na_2S as the standard solution. SeaWiFS and MODIS images were also obtained for this date as well as from the previous day. Temperature, oxygen and conductivity profiles on 3 Sep 2005 were measured with a YSI 85 probe as described in Watts *et al.* (2001).

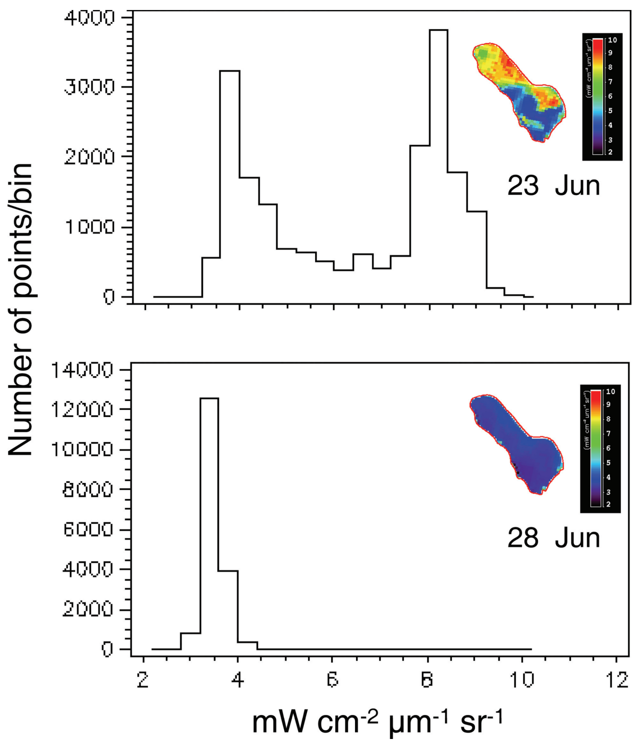

Figure 2.-Rationale for using radiances > 5 mW cm^{-2} μm^{-1} sr^{-1} at 555 nm to indicate gypsum blooms. Histograms of radiance values over surface of the Salton Sea for level 1B SeaWiFS images, on two dates in June 2003, using 20 bins. Note bimodal distribution on earlier date, typical for gypsum blooms.

Table 1.-Locations of stations, 5 May and 3 Sep 2005.

Station	Latitude	Longitude
S-1	33° 25.00'	115° 55.00'
S-2	33° 21.00'	115° 51.00'
S-3	33° 18.00'	115° 48.00'
T-1	33° 29.17'	115° 55.00'
T-2	33° 28.33'	115° 55.00'
T-7	33° 23.25'	115° 55.00'
T-9	33° 21.58'	115° 55.00'
T-11	33° 20.00'	115° 55.00'

Results

Spectral signatures: bloom vs. non-bloom conditions

Images from MODIS and SeaWiFS are compared for two representative dates in 2006 (Figs. 3A, B). The earlier date, 22 Jul showed no green patches in MODIS true color images (Fig. 3A). Green water appeared by 28 Jul (not shown). On 2 Aug a bright swath of green water covered > 80 percent of the lake surface, especially evident in true color at the northern half of the lake (Fig. 3A). On 3 Aug discovery of a die-off of ~1 million fish in the north end of the Salton Sea made news headlines (Boxall 2006). It is likely their demise occurred several days earlier but they were not observed until washing up on the shoreline.

Analysis of level 1B SeaWiFS images for the six visible wavebands and the shortest near-infrared band (765 nm) showed interesting patterns using these two dates as exemplars. During most of the year the lake exhibits fairly even radiances over its entire area and for all wavelengths (*e.g.*, 21 Jul 2006, Fig. 3B). Images are intense in the shorter wavelengths because they are not atmospherically corrected. On

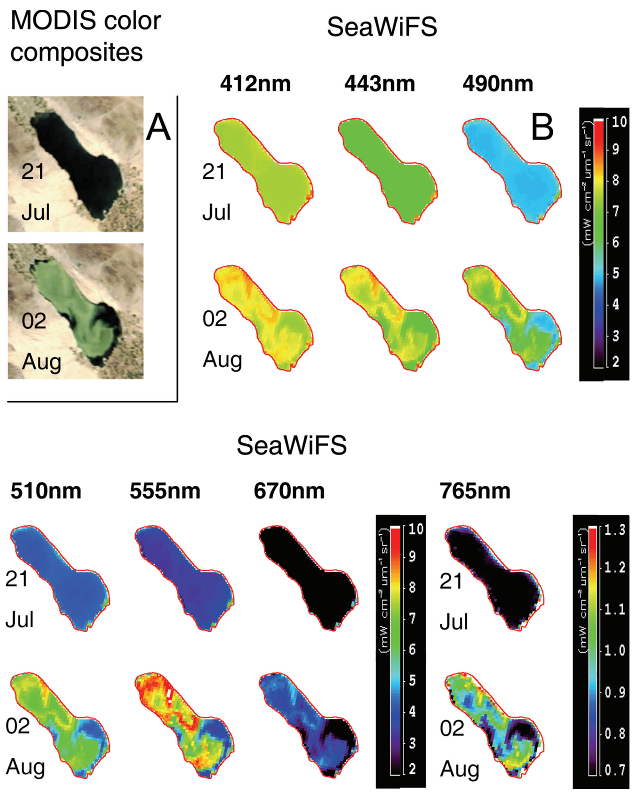

Figure 3.-Gypsum blooms detected at various wavebands, MODIS and SeaWiFS images, 2006. A. MODIS true color images for two dates, 12 days apart, one with no green tide (21 Jul) and one with an extensive green tide (2 Aug). B. SeaWiFS images plotted for seven wavebands on the same two dates. Note change of scale for the 765 nm band. Units are mW cm^{-2} μm^{-1} sr^{-1}.

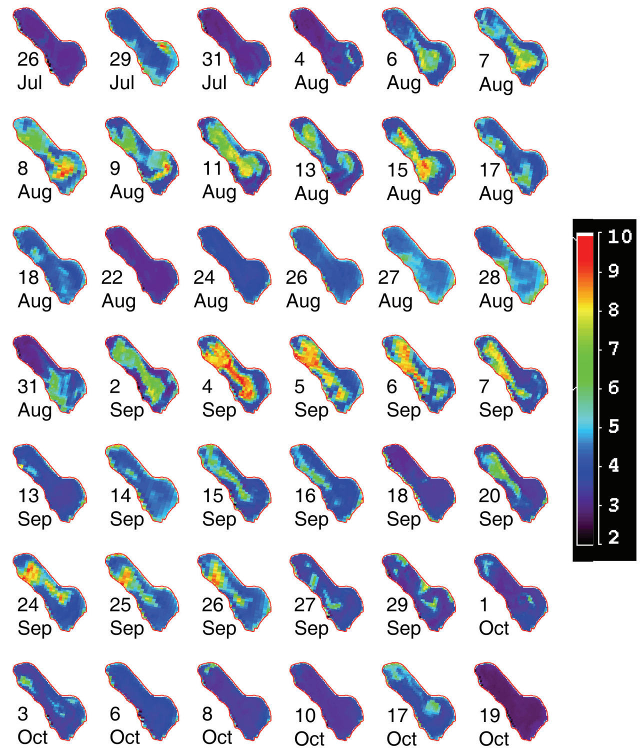

Figure 4.-Waxing and waning of "green tides" for late July to mid-October, 1999. SeaWiFS images for irradiances at 555 nm. Units are mW cm^{-2} μm^{-1} sr^{-1}.

some dates, especially from May-October (*e.g.*, 2 Aug 2006, Fig. 3B), bright patches appear at all wavelengths, especially apparent at the 555 nm green bandwidth. On several dates the radiance exceeded 9 mW cm^{-2} μm^{-1} sr^{-1} at 555 nm, but any radiance over 5 mW cm^{-2} μm^{-1} sr^{-1} is readily apparent on the images. On the other hand, on dates with green patches the portions of lake area lying outside them resemble those on dates lacking bright green water. Increases in radiance from that of surrounding water of ~1-2 mW cm^{-2} μm^{-1} sr^{-1} were found for 412-490 nm, up to 6-7 mW cm^{-2} μm^{-1} sr^{-1} for the 510 and 555 nm bands, ~2 mW cm^{-2} μm^{-1} sr^{-1} for the 670 nm band, and, interestingly, as much as 0.4 mW cm^{-2} μm^{-1} sr^{-1} in the NIR band at 765 nm. Water-leaving radiances from the NIR bands are usually assumed to be negligible as pure seawater absorbs very strongly at those wavelengths (Morel 1974; Smith and Baker 1991; Pegau and Zaneveld 1993).

Waxing and waning of blooms in 1999

At least three major "green tide" events occurred in 1999, a year for which we have information on physical and biological factors (Fig. 4). We chose to examine the 555 nm images (green) because this wavelength had the strongest signal. There were slightly elevated signals over a small portion of the lake on 29 Jul–4 Aug but the first major event began on 6 Aug, dissipating by 18 Aug. Reappearance of green water began on 27 Aug, intensified greatly by 4 Sep, and then was entirely gone by 18 Sep. The last major event of 1999 started about 20 Sep and faded by 3 Oct. Before 29 July and after Oct 17 there was no indication whatsoever of "green tides." The spatial patterns shown in the images indicates the brightest green water, up to 8 or 9 mW cm^{-2} μm^{-1} sr^{-1}, was generally in mid-lake although there were dates when green water was close along the shore, especially in the northwest portion of the lake (*e.g.*, 5 Sep, Fig. 4). The events lasted from a day or two to almost two weeks.

Spatial covariation of sulfide and crystals

Sulfide concentrations on 3 Sep 2005 seemed to co-vary with gypsum crystal abundance. Higher concentrations of crystals were found at those stations with high surface sulfide

Table 2.-Chlorophyll, oxygen and gypsum crystal concentrations on two dates, one with green tides and one without.

Water type and Station no.	Chl *a* 0-3 m (µg l^{-1})	Gypsum crystals 0-3 m (no. ml^{-1})	Dissolved O_2 (mg l^{-1}) at ~10 cm	Surface sulfide mg l^{-1}
		5 May, 2005		
No green water				
S-1	129	67	12	*
S-2	108	8	11.1	*
S-3	69	12	9.7	*
T-1	113	23	9.7	*
T-2	101	5	17.8	*
T-7	78	13	9.5	*
		3 Sep, 2005		
Inside green patch				
S-1	25	13100	0.06	2.65
T-1	10	40800	0.02	1.26
T-2	24	18100	0.07	1.2
T-7	22	11200	0.07	0.74
On boundary of patch				
S-3	22	8900	4.4	1.1
T-9	33	8000	3.8	0.44
Outside green patch				
S-2	42	4100	5.4	0.3
T-11	67	2300	16.9	0.28

* Not measured

concentration and green water (11,200-40,800 crystals ml^{-1}) and lowest at stations with low surface sulfide outside green water (2,300-4,100 ml^{-1}), with stations on the boundary being intermediate in both regards (Table 2).

The MODIS true color image from that date (Fig. 5A) shows two swirling patches of green water, one in each basin, separated by darker waters. While flying over the northerly patch of green water at ~300 m above the lake, the odor of hydrogen sulfide or other sulfur compounds was noted, evidently escaping from the water, and sharp demarcations of green vs. dark brown water were observed. In the north-eastern sector of the lake, green waters were close to shore. On this date several hundred brown pelicans (*Pelecanus occidentalis* Linnaeus) and a few white pelicans (*Pelecanus erythrorhynchos* Gmelin) were observed to be intensively feeding in a narrow nearshore strip of water about 10 km south of the Salton Sea State Recreation Area headquarters (just to the east of station T-2, Fig. 5B) where tilapia were swimming at the lake surface, presumably seeking refuge from anoxic, sulfide-laden waters.

Analysis of the SeaWiFS image on 3 Sep 2005 showed 61 percent of surface of the lake was brighter than 5 mW cm^{-2} μm^{-1} sr^{-1} in the 555 nm waveband and nearly 18 percent was brighter than 7 mW cm^{-2} μm^{-1} sr^{-1} (Fig. 5B). This particular event lasted over a month starting on 12 Aug and ending

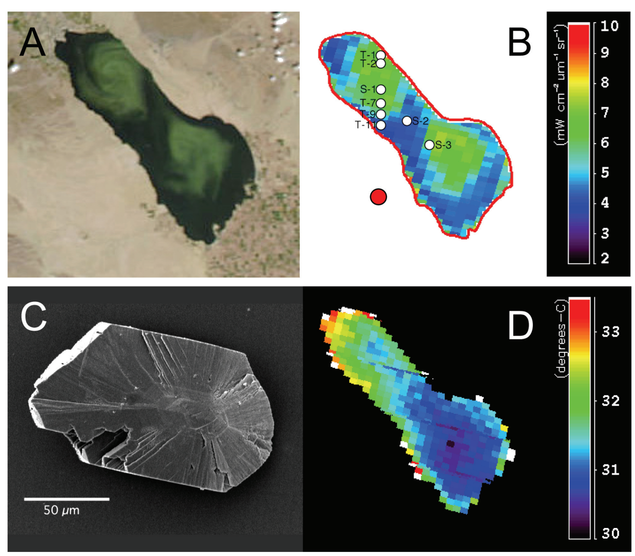

Figure 5.-State of the Salton Sea on 3 Sep 2005. A. MODIS true color image. B. SeaWiFS image showing station locations. Red dot shows location of "pseudo invariant" terrestrial pixel used to normalize SeaWiFS images. Units are mW cm^{-2} μm^{-1} sr^{-1}. C. Gypsum crystal from the Salton Sea in SEM, scale bar = 50 µm. D. MODIS Sea Surface Temperature (°C, SST) for 2 Sep 2005.

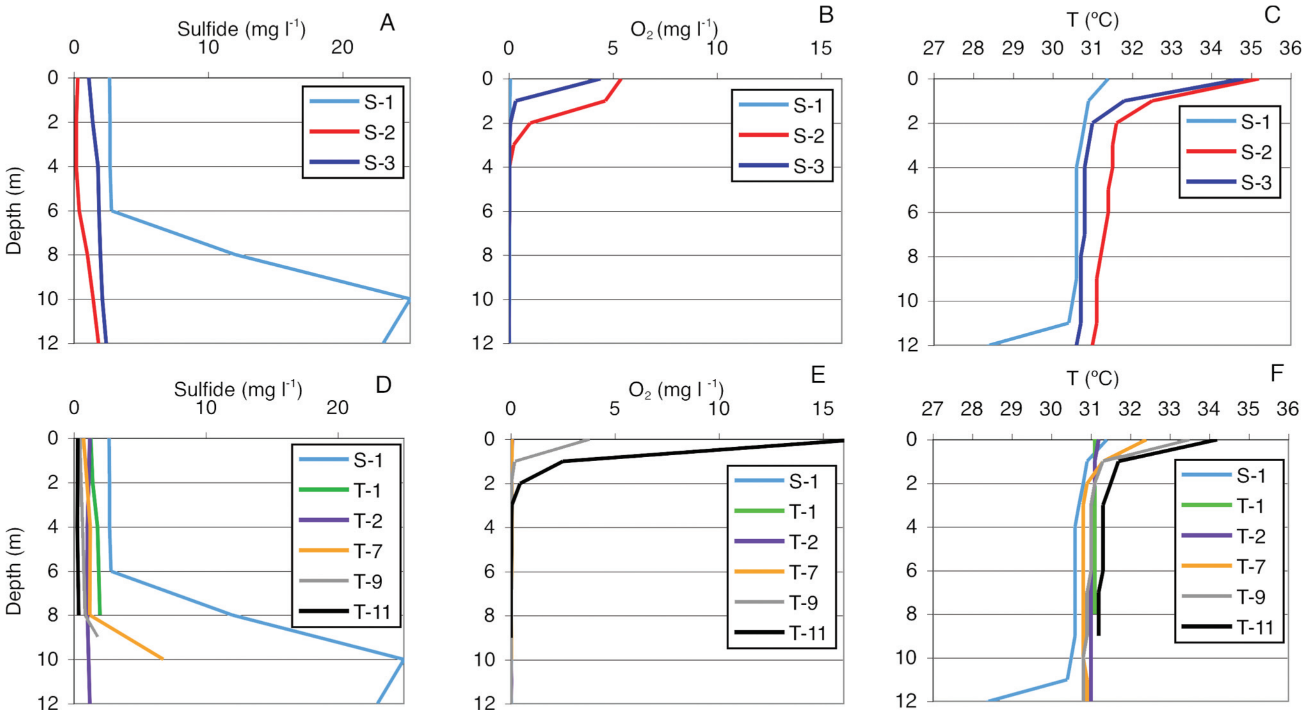

Figure 6.-Depth profiles for sulfide (A, D) and oxygen (B, E) concentrations and for temperature (C, F) along two transects, 3 Sep 2005. Locations of transects and stations are shown in Figure 5.

14 Sep (Fig. 7). Stations S-3 and T-9 were near the edge of green patches and stations S-2 and T-11 were completely outside them (Fig. 5B).

A MODIS SST image from the previous day showed possible upwelling (cooler waters) in the center of the southern basin extending somewhat to the north (Fig. 5D).

Numerous crystals of gypsum from ~20 µm to 190 µm in length (Fig. 5C) were observed by us in surface water samples (Table 2). Small particles scatter visible light more efficiently than larger ones and the possibility of multiple scattering events exists, increasing the effect (Clark 1999). Concentrations ranged from 5-67 crystals ml^{-1} on 4 May 2005, a date with no green water, and 2,300-40,800 ml^{-1} during the gypsum bloom on 3 Sep 2005. The highest concentrations in September were in green water and the lowest in brown water (stations S-2 and T-11).

Chlorophyll *a* concentrations were ~2-3 fold higher at stations S-2 and T-11, outside the green water, than at the other stations (Table 2). The lowest chlorophyll concentration was at station T-1, well within a green patch, and the highest at T-11, outside it.

Sulfide and oxygen concentration and temperature profiles are shown for the two transects (Fig. 6). Conductivity measurements showed there was no halocline present at any station (not shown). The transect along the axis of the lake consisted of the same stations used in the 1997-1999 limnological survey (S-1, S-2 and S-3, Fig. 5B). The highest concentration of sulfide, 25 mg l^{-1}, was found at station S-1, at 10 m depth (Figs. 6A, D). Since the concentration of dissolved sulfate (SO_4^{-2}) is presently at ~10,500 mg l^{-1} (Holdren and Montaño 2002), sulfide represented only ~1 percent of total sulfur at this depth. At this station, at 6 m depth and shallower, the sulfide concentrations decreased to about 2.7 mg l^{-1}. At S-2, outside of green water, sulfide was very low except below 6 m (Fig. 6A). At S-3, on the edge of the southerly green water patch, surface sulfide was 1-1.5 mg l^{-1}, increasing slightly to 2.4 mg l^{-1} at 12 m. Oxygen concentrations showed the reverse trends (Fig. 6B). Anoxia prevailed in the entire water column at S-1 whereas at stations S-2 and S-3 surface waters contained up to 5 mg l^{-1} (Table 2) dropping to very low levels below 1-3 m (Fig. 6B).

Along the north-south transect a similar pattern was observed. S-1 had the highest surface sulfide concentration while station T-11, which was outside of green water, had the lowest (Fig. 6D). Station T-7, the station closest to S-1, had high sulfide below 8 m. Only stations T-9, at the edge of the green water and T-11 outside it had measurable oxygen content at and above 3 m, with surface water at T-11 registering the highest concentration at 16.9 mg l^{-1}. The high oxygen concentration at T-11 was likely due to photosynthetic input

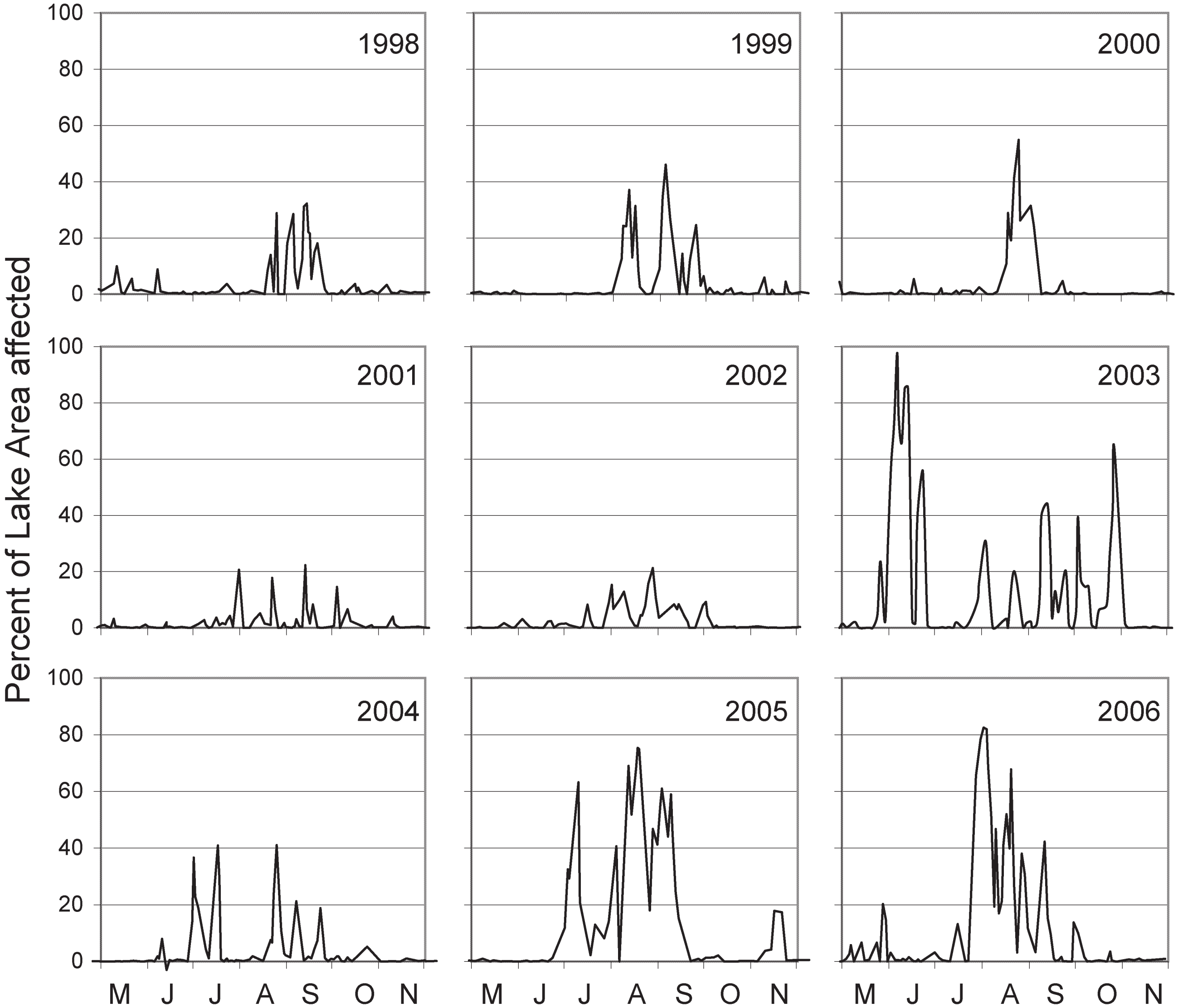

Figure 7.-Areal extent of "green tides" during 1998-2006 as detected with SeaWiFS imagery. Percent of lake surface with radiance > 5 mW cm^{-2} μm^{-1} sr^{-1}.

of the abundant algae there. Again, all stations were anoxic below 3 m (Fig. 6E).

Temperature profiles (Figs. 6C, F) were nearly isothermal, at about 31 °C, from 2 m to the bottom at all stations except S-1 where water below 11 m was about 3 °C colder than the rest of the water column, dipping to 27.6 °C. The top 1 m at all stations tended to be several degrees warmer than the rest of the water column, likely due to solar insolation that day.

Areal extent of gypsum blooms, 1998-2006

The areal extent of gypsum blooms showed interesting patterns in the Salton Sea during the nine year period, 1998-2006 (Fig. 7). First, there were no gypsum signals during the cold water months December-April (not shown). Second, there was a general tendency for an increase in the temporal and spatial extent of gypsum "green tides" over this interval. The percent of lake with green water was extremely variable during the warm part of the year.

"Green tides" during those years for which we have limnological data (1998 and 1999) mostly occurred in August and September and the areal extent of green waters never exceeded ~30 percent of the lake in 1998 or ~40 percent in 1999. In 2000 only one major event occurred lasting from 17 Aug to 4 Sep peaking at > 50 percent of the lake surface. 2001 and 2002 were rather quiescent years; at no time was

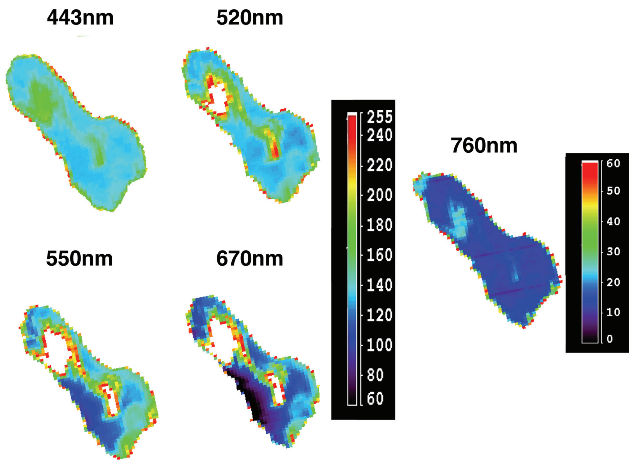

Figure 8.-CZCS raw radiance count images from 15 Aug 1979. Images for four visible wavebands (443, 520, 550 and 670 nm) and one in the near-infrared (760 nm) (note change in scale). Units are mW cm^{-2} μm^{-1} sr^{-1}.

the area of the lake affected by more than ~20 percent green water.

The year with the most intense "green tides" was 2003, when they began in late May and continued until late October. According to the criterion of > 5 mW cm^{-2} μm^{-1} sr^{-1} signaling a "green tide," the most extreme date occurred on 6 Jun when ~97 percent of the lake was affected. "Green tides" occurred multiple times during that summer, waxing and waning irregularly. In late October 2003 > 60 percent of the lake was green (Figs. 1 and 7).

In 2004 "green tides" began in June and ended for the most part by late September, and green water was limited to ~40 percent of the lake surface. In 2005 and 2006 large areas of lake were affected, > 60-80 percent of the lake at times, and events were of long duration. From mid-June to September, 2005 there were only a few dates with < 20 percent green water and during July-September 2006 another long event occurred. In 2005 a gypsum bloom was observed as late as mid-November.

Evidence for gypsum blooms, 1979-1985

Analysis of CZCS data demonstrates that similar green water events occurred in the past. Information from 1979 proved the most useful as it had the greatest temporal coverage and the sensor was not yet compromised. Four events seem to have occurred in 1979 (7 Jun-6 Jul, 14 Aug-26 Aug, 30 Aug-1 Sep, 27 Sep-15 Oct). During these intervals bright patches appeared, mostly in the center of the lake (Fig. 8). As was the case for the SeaWiFS images, the green and red bands (555 and 670 nm) exhibited especially bright radiances, often exceeding the sensitivity of the sensor (white areas in Fig. 8). This indicates a mineral rather than an algal pigment signal.

As in the SeaWiFS spectral signatures in 1998-2006, there is an elevated signal in the near-infrared (760 nm) within the patch (shown for 15 Aug 1979, Fig. 8). Similar events were seen in following years: three in 1980 (in May, August-September and October), one in 1981 (September), two in 1982 (August-early September and another in mid September), and two in 1983 (July and August). Images were scarce and somewhat unreliable after 1981, but in every year during 1979-1983 at least several intervals of patchy bright green water occurred, generally in summer and fall. Anecdotal reports of "green tides" extend back decades, often associated with fish kills, and smart Salton Sea fishermen have long advised newcomers to fish in brown waters and not in green.

Discussion

Gypsum crystal formation

Precipitation of gypsum crystals has been directly observed in this study during sulfide irruptions. The mechanism of their formation appears to be as follows. In late spring-summer hydrogen sulfide, which at the pH range of ~7.6-8.3, typical for that of the Salton Sea (Watts *et al.* 2001), is probably mostly in the form of HS^- (Millero 1986). Sulfide accumulates in bottom waters by the decomposition of organic matter and by the action of sulfate-reducing bacteria (*e.g.*, *Desulfovibrio* spp.) that operate in anaerobic conditions with the presence of sulfate and suitable organic matter (Ivanov 1964; Brock and Madigan 1991). Pyrite and other iron sulfides are likely forming in the Sea within its anoxic basins (deKoff *et al.* 2007) but, due to the flux of sulfate from the sediments (Wardlaw and Valentine 2005), abundance of gypsum in the sediments (Walker 1996; Dexter *et al.* 2007) and low dissolved iron concentration (8.3-65 µg l^{-1}; Holdren and Montaño 2002), sulfate is likely never depleted in the water column. In fact, total sulfur may be slightly higher in the hypolimnion during stratification due to influxes of sulfur from dead organic material sinking from the epilimnion and sulfate or sulfide emanating from the sediments. When exposed to oxygen after mixing or upwelling events, sulfide is oxidized back to sulfate both by sulfur-oxidizing bacteria and by direct reaction with molecular oxygen, with the overall reaction of:

$HS^- + 2O_2 \rightarrow SO_4^{-2} + H^+$ (Chen and Morris 1972; Zopfi *et al.* 2004).

Intermediate products, sulfite (SO_3^{-2}), thiosulfate ($S_2O_3^{-2}$) and elemental sulfur (S°) may be involved (Zopfi *et al.* 2001, 2004); but nothing is presently known of these in the Salton Sea. Microscopic crystals of gypsum are formed and grow *in situ* because the calculated saturation index for gypsum is positive (Holdren and Montaño 2002). Numerous crystals in the range of 2-8 μm in length and confirmed to be gypsum by X-ray analysis, were observed in green waters on 20 Aug 2006 (K. Reifel and B. Swan, unpublished data). No elemental sulfur was observed. Days are sometimes required to fully oxidize the sulfide, as the concentration of sulfide can be sufficient to completely deoxygenate surface waters after a mixing event (Watts *et al.* 2001). Conditions of high sulfide levels and surface anoxia or hypoxia are not detectable in satellite images; but presence of gypsum blooms serves as an indicator of them. Presumably, as the crystals grow they eventually sink out of the water column, as the specific gravity of gypsum (2.32, Berry *et al.* 1983) exceeds that of water and accumulate in the sediments. When this occurs the green color dissipates. A dynamic between winds, turbulence, upwelling and currents, resultant sulfide irruptions and anoxia, production, growth and sinking of gypsum crystals and mortality and sedimentation of pigment-bearing phytoplankton leads to the complex swirling patterns seen in satellite images or from aircraft. At times the patterns reflect the wind-induced counter-clockwise gyres, especially in the southern basin (Cook *et al.* 2002). Horizontal crusts of gypsum occur in and on Salton Sea bottom sediments, suggesting that gypsum forms and accumulates episodically (Dexter *et al.* 2007).

Neither phytoplankton nor silt

Two other types of particles in the water column might be considered possible sources for the green signals in satellite imagery. These are algal cells and silt and clay brought in by rivers.

Logically, the first impression one might have upon encountering very green water is that it is caused by an algal bloom, possibly of chlorophytes or cyanobacteria. However, during 1997-1999, phytoplankton was least abundant at times of green waters presumably as a result of being killed off by sulfide (Tiffany *et al.* 2007a). Another argument against algal blooms as a cause of green waters is their spectral signature. Due to their chlorophyll pigments, photosynthetic algae absorb light in the red and blue wavelengths (Kirk 1983). The dramatic signal in the red waveband (670 nm) and unusual signal in the near-infrared (765 nm) (Fig. 3) during "green tides" are not typical of an algal bloom.

Allochthonous silt or clay brought in from rivers might conceivably produce a signal. However, riverine input of silt is more-or-less continuous throughout the year (Holdren and Montaño 2002) while the green signals in the Salton Sea are episodic, confined to the warm months. Also, in satellite imagery there is usually a wide gap between green water and the river mouths. Much of the silt brought in to the Salton Sea is likely quickly deposited at or near the river deltas (Holdren and Montaño 2002). Thus, it appears that suspended silt from rivers does not account for the bright green signals in the Salton Sea.

Primary productivity and influence of tilapia

The apparent increase in frequency and duration of gypsum blooms from 2003-2006 may be primarily due to the dramatic post-2000 decrease in the abundance of planktivorous tilapia (Caskey *et al.* 2007). Tilapia grazing affects both the standing biomass and the species composition of the phytoplankton of the Salton Sea (Tiffany *et al.* 2007a). These fish can feed directly upon algae (Mironova 1969) and were shown to reduce phytoplankton by 28-92 percent in an experiment using Salton Sea microecosystems (González 1997). In the lake itself, as the tilapia population decreased over the period 1997-1999, the abundance of larger cells increased, though not that of total phytoplankton (Tiffany *et al.* 2007a). By 2005, however, the total spring phytoplankton abundance had increased 2-5 fold from 1997-1999 levels, probably due to a release from grazing pressure on phytoplankters, and the species composition had shifted radically (Anderson *et al.* 2007).

Higher algal production following the tilapia crash probably led to more organic matter decomposing at depth, earlier and more severe anoxia and an increase in the pool of accumulated hydrogen sulfide. If the frequency of warm season mixing events remained roughly the same over this period of years (1998-2006), then the number of mixing events that brought *large* amounts of hydrogen sulfide into surfaces waters would have increased. This appears to have led to increased gypsum formation as detected by satellite imagery and greater persistence and intensity of its signals.

Temperature effects

Water temperature affects sulfide events and their gypsum signals by influencing rates of decomposition of organic matter, of sulfide production at depth, and of reaction of sulfide with molecular oxygen, and also by affecting water viscosity. These effects account for why gypsum forms primarily in summer and no "green tides" are seen between November and April, the coldest months.

In winter, the lake is cold (~14-16 °C) and well oxygenated (Watts *et al.* 2001). Decomposition of organic material (mostly dead algal cells) is slow and does not result in the accumulation of sulfide because oxygen is present. Once stratification sets in, organic matter decomposes in bottom waters and depletes the oxygen in them. Rates of decomposition and of sulfate reduction decrease with decreasing temperature (Jørgensen *et al.* 1979; Wieland and Kühl 2000). Thus, while the water is still cold in spring, sulfide probably accumulates only slowly at depth. However, this polymictic lake mixes frequently in the spring and summer during wind events, and this injects heat into the bottom waters. During periods of stratification between mixing events in summer, decomposition is accelerated as waters are at ~25-30 °C and anoxia develops and sulfide builds up rapidly. However, oxygen is less soluble in warmer water (Wetzel 2001). This will favor a slower conversion of sulfide to sulfate in summer, if oxygen in surface waters is generally close to 100 percent saturation.

The rate of sulfide oxidation, the reaction occurring in surface waters after sulfide irruptions, also increases as temperature rises (Jørgensen *et al.* 1979), but, according to Watts *et al.* (2001) there can be a surplus of sulfide in the deoxygenated waters in summer after overturn as the water is stripped of oxygen in the entire water column. Few living phytoplankters are present after sulfide irruptions to photosynthesize and produce oxygen (Tiffany *et al.* 2007a). It appears to take days to convert surface dissolved sulfide to sulfate in the Salton Sea even though, in the presence of even a low oxygen concentration, sulfide has a half-life of only ~5-40 minutes (Jørgensen *et al.* 1979; Millero 1991). Thus, given the high levels of sulfide and near absence of oxygen in upwelled waters, diffusion of oxygen into the lake could be the limiting factor for sulfide oxidation near the surface of the Salton Sea.

Gypsum signals will be strongly a function of how long crystals, once formed, remain in surface waters. This in turn will be a function of viscosity. The viscosity of water decreases with increasing temperature (Wetzel 2001) and that for ocean water at 40 g l^{-1} is 1.23 cP (centipoise) at 14 °C and 0.86 cP at 30 °C (Dorsey 1940). It changes little with pressure for the depths typical of the Salton Sea (Stanley and Batten 1969). Surface temperatures in the Salton Sea vary from ~14-36 °C (Watts *et al.* 2001). By Stokes's law the velocity of sinking particles in still water varies inversely with viscosity and directly with the difference in density between the particle and the surrounding water (Wetzel 2001). This implies that gypsum crystals should sink ~50 percent faster in summer than in winter. That the crystals can be observed in surface water is likely a result of both their continuous formation and the turbulence of surface waters. When winds abate, the crystals likely quickly sink. This provides a likely explanation for the strong gypsum signals often dissipating within a day or two.

In the range of ambient temperature of the Salton Sea, the solubility of gypsum varies little with temperature so this probably is not an important factor in determining gypsum precipitation (Schaffer 1967; Ostroff and Metler 1966).

Phytoplankton interference

Phytoplankton cells are particles containing pigments: chlorophyll, carotenoids, xanthophylls and others. They absorb visible light in order to photosynthesize, especially in the blue and red, attenuating light (Kirk 1983). When phytoplankters are abundant, they will absorb or scatter much of the light in the surface water. This would likely obscure the gypsum signal when both crystals and phytoplankton are abundant.

There were three dates where we documented the presence of crystals in water samples. Only when algal abundance was low were we able to detect gypsum blooms by satellite imagery. On 14-17 Mar 2005, the odor of hydrogen sulfide was noted over the entire Salton Sea, pileworms (*Neanthes succinea* Frey and Leuckart) were nearly absent from the sediments, and water samples from the southwestern corner of the lake contained gypsum crystals (Dexter *et al.* 2007). That this major event was not detected by satellite imagery is likely due to masking by the great abundance of phytoplankton present then. Chlorophyll *a* concentrations were ~70-120 µg l^{-1} in April and May of that year (Anderson *et al.* 2007). Intense gypsum signals did not appear until mid-June of 2005, perhaps due to lower density of phytoplankton by then. Gypsum crystals were low in abundance in April and May of 2005, phytoplankton was abundant, and no gypsum signal was detected in satellite imagery.

More-or-less continuous spates of green water occurred in 2005 from late June to September (Fig. 7). Gypsum crystals probably precipitated throughout these months. Gypsum crystal abundance outside green patches was a fraction of that within them in Sep 2005, but they were still numerous. They may have formed during previous sulfide irruptions and been maintained in suspension by turbulence. Lack of a gypsum signal there might have been due to the concentration of crystals being too low to produce a detectible signal, but more likely the high phytoplankton abundance masked the signal from the crystals.

Sulfide: fish, plankton and benthos kills

Sulfide is well known to be toxic to aerobic aquatic organisms (Bagarinao 1992). With the exception of a few sulfide-tolerant organisms, overturns or upwelling and green water with associated sulfide in the Salton Sea are associated with mortality of plankton, benthos and fish.

Bagarinao and Lantin-Olaguer (1999) found that the LC_{50} (dose that causes 50 percent mortality) for tilapia (*Oreochromis mossambicus* Peters) at 2 h was ~6.3 mg l^{-1} S^{-2} and the LC_{50} for 24-96 h was ~2 mg l^{-1}. Clearly fish cannot survive long at sulfide levels such as those found below 6 m at stations S-1 and T-7 on 3 Sep 2005 (6.8-25 g l^{-1}). Fish could escape lethal waters such as these by finding refuge at the surface but apparently, at times, even surface waters in mid-lake have deadly concentrations of hydrogen sulfide (up to 2.7 g l^{-1}), along with hypoxia or anoxia which make matters even worse. The other alternative for fish is to congregate in the often better-oxygenated waters near the shoreline during the warmer part of the year (Riedel *et al.* 2002; Caskey *et al.* 2007). Even this refuge becomes compromised when, due to wind patterns, currents or upwelling, sulfide-rich waters come on to shore, as they appear to do in many of the satellite images (*e.g.*, 4-6 Sep 1999, Fig. 4). Then millions of fish may die, causing immense rafts of rotting carcasses to wash ashore.

The locations of fish kills in May and July of 2001 were directly linked to sites of upwelling caused by winds (Marti-Cardona *et al.* 2007). On 8 May a fish kill numbering 442,000 individuals was reported in the northwest corner of the lake, precisely where elevated gypsum signal was located in a SeaWiFS image for 9 May (Fig. 9A). On 29 May another large die-off of over 1,200,000 occurred in the northeast sector, again just where we document a strong gypsum signal (Fig. 9B). On 30 Jul the green tide was at the southwest corner of the lake, the site of a fish kill numbering 1,800,000 (Fig. 9C). On all three dates the gypsum signal were close to shore. The same phenomena that lead to summer fish kills (anoxia and elevated sulfide) also provide us with gypsum signals.

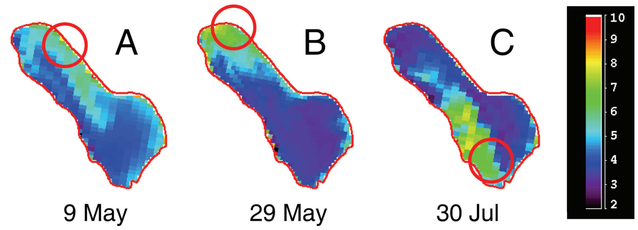

Figure 9.-Sites of documented fish kills and in 2001 (from Marti-Cardona *et al.* 2007: red circles). SeaWiFS images at 555 nm. A. Fish kill (442,000) on 8 May and gypsum signal on 9 May. B. Fish kill (1,200,000) and gypsum signal on 29 May. C. Fish kill (1,800,000) and gypsum signal on 30 Jul. Units are mW cm^{-2} µm^{-1} sr^{-1}.

Plankton also is killed by persistent high levels of sulfide in the Salton Sea. Dramatic drops in metazooplankton abundance were observed in 1997-1999, especially adversely affecting the copepod, *Apocyclops dimorphus* Kiefer (Tiffany *et al.* 2002). Phytoplankton, other than a tolerant euglenoid species, experienced orders of magnitude drops in abundance in green sulfide-laden waters (Tiffany *et al.* 2007a). Ciliates were similarly affected except for an anaerobic ciliate, *Sonderia* sp. (Tiffany *et al.* 2007b). The dominant benthic invertebrate, a polychaete worm (*Neanthes succinea*), is adversely affected by anoxia and sulfide (Detwiler *et al.* 2002; Dexter *et al.* 2007) and some of our sulfide measurements at depth are at lethal levels. When anoxic sulfide-laden waters are advected onshore, even nearshore environments can prove deadly for invertebrates as well as fish (Dexter *et al.* 2007).

Similar events in other locales

Few water bodies on the planet have spectral signatures similar to those during gypsum blooms in the Salton Sea, or water-leaving radiances as high. Three waterbodies have, however, been documented to experience high surface sulfide concentrations along with a change in water color. These are the coastal waters off Namibia, at the head of Tokyo Bay, Japan, and a small lake in Croatia.

Satellite images of the region of the Pacific Ocean off the coast of Namibia at times resemble the green waters of the Salton Sea. Unusual bright turquoise signals extending over as much as 20,000 km^2 have been observed in Namibian waters, coupled with anoxia and high levels of hydrogen sulfide (Weeks *et al.* 2004; Bakun and Weeks 2004). These events are associated with fish kills and lobsters stranding themselves on beaches to avoid the conditions. H_2S accumulates at depth after blooms of phytoplankton sink and decay into a "sludge." Sulfide concentrations of as high as 0.6 mg l^{-1} at the surface and 3.4 mg l^{-1} at 13 m were observed in these milky waters. Weeks *et al.* (2004) observed elemental sulfur granules, in concentrations up to 1.8 µM, that form after oxidation of sulfide brought up by upwelling. These are highly reflective and readily visible by satellite imagery (Weeks *et al.* 2004). When we examined SeaWiFS images from this region during these events we found an increase in intensity of the green and red wavebands, similar to that seen in Salton Sea images. Absorption of blue light by CDOM (colored dissolved organic matter) is likely much less a factor than at the Salton Sea as it is probably much lower in concentration. Chlorophyll *a* concentrations cannot be estimated using standard algorithms during these precipitation events due to interference by sulfur particles (Weeks *et al.* 2004) but can be estimated when they are not present.

In the Tokyo Bay, milky blue-green waters associated with fish kills have been noted since the 1950s in summer and fall following upwelling of sulfidic waters (Nanba *et al.* 2001). A strong optical signal centered near 550 nm has been attributed to a combination of colloidal elemental sulfur and manganese-rich particles that accumulate after oxidation of upwelled waters (Takeda *et al.* 1991).

Lake Rogoznica, a eutrophic, meromictic coastal salt lake in Croatia, experienced an overturn event in 1997 when the halocline that is usually present (Ciglenečki *et al.* 1996, 2005) disappeared. Sulfide levels in surface waters increased, accompanied by anoxia, and the lake appeared milky white due to elemental sulfur particles (Kršinić *et al.* 2000; Barić *et al.* 2003). Plankton populations experienced severe mortality and, because the entire lake became sulfidic, did not recover quickly.

Even if sulfide were to be completely oxidized to sulfate in the three marine systems described above, sulfate and calcium concentrations are well below saturation (seawater has ~2,811 mg l^{-1} SO_4^{-2} and ~427 mg l^{-1} Ca^{+2}; Millero 2006), about one fourth and one half, respectively, those of the Salton Sea, so precipitation of gypsum is highly unlikely.

Chlorophyll estimates impossible from satellite imagery

Chlorophyll *a* concentrations are often used as a proxy for algal productivity (Schalles 2006) and estimation of these is a primary purpose for ocean color satellites. Waters have historically been classified as Case 1 (open water, low chlorophyll) or Case 2 (coastal, turbid, high chlorophyll) (Morel and Prieur 1977). Semi-analytical algorithms have been developed to estimate surface chlorophyll concentrations for Case 1 waters (O'Reilly *et al.* 1998). Attempts to develop algorithms for Case 2 waters have usually been site specific (Ruddick *et al.* 2001; Darecki *et al.* 2003; Li *et al.* 2004; Pozdnyakov *et al.* 2005). The study of optics in the Salton Sea will be complex due to sporadic precipitation of gypsum, suspended sediment input from rivers, and very high chlorophyll concentrations. Water transparencies (Secchi Disk readings) and light attenuation are not always a simple function of chlorophyll concentrations, especially during phytoplankton crashes (Swan *et al.* 2007). The lake likely also has large concentration of colored dissolved organic matter (CDOM), affecting the optics by strong absorption in the blue wavelengths (K. Reifel and B. Swan, unpublished data). Prospects to measure chlorophyll *a* by satellite appear bleak but, because of their characteristic spectral signatures, most gypsum blooms can readily be tracked.

Far-red light and an unusual cyanobacterium

Sporadic bright signals in the red (670 nm) and dim ones in near-infrared (765 nm) suggest that during gypsum blooms there is an unusually elevated amount of light available in surface waters throughout the far-red part of the spectrum. Apparently gypsum crystals scatter light efficiently in the red wavelengths. A free-living cyanobacterium, similar to *Acaryochloris marina* Miyashita and Chihara, associated with ascidians, was recently discovered in the Salton Sea (Miller *et al.* 2005). It uses chlorophyll *d* rather than chlorophyll *a* as its primary photosynthetic pigment. Chlorophyll *d* in *Acaryochloris marina* harvests light efficiently in the far-red, at ~716 nm (Miyashita *et al.* 1997), light that appears to be enriched in the Salton Sea. This suggests that this cyanobacterium may be adapted to the unusual light regime present during frequent gypsum blooms of the Salton Sea, allowing it to live in a free condition.

Conclusions

Hypoxia and anoxia in coastal and inland waters are growing problems worldwide, possibly due to human activities and increasing population (Diaz 2001; Rabalais *et al.* 2002; Grantham *et al.* 2004). When anoxia extends to surface waters, aerobic organisms of entire water column are adversely affected, particularly if high levels of sulfide are also present. Low oxygen content and/or high levels of hydrogen sulfide in surface waters do not have a spectral signature. The Salton Sea, however, has provided an unusual opportunity to investigate these phenomena as gypsum crystals that form subsequent to sulfide irruptions do have a strong optical signature. When these are abundant their presence is an indicator for poor water quality even though their absence does not necessarily indicate good water quality. Duration and intensity of gypsum blooms appear to have increased since 2002, implying a worsening of conditions at the lake. MODIS true color images and sea surface temperature are available within a day or two of collection and might be used to anticipate the location of fish kills by detection of, respectively, gypsum blooms and upwelling. Plans to rehabilitate the Salton Sea should take its sulfur biogeochemistry and mixing patterns into account.

Acknowledgments

Ocean color data used in this study were produced by the SeaWiFS Project at Goddard Space Flight Center. SeaWiFS and CZCS data were obtained from the Goddard Earth Sciences Distributed Active Archive Center under the auspices of the National Aeronautics and Space Administration (NASA). Use of this data is in accord with the SeaWiFS Research Data Use Terms and Conditions Agreement. The use of MODIS true color images was accorded by NASA/GSFC, MODIS Rapid Response. We thank Lisa Thurn and Richard Bizzoco for assistance with sulfide measurements and Charles Trees for chlorophyll analyses. We are also grateful to Brandon Swan and Kris Reifel for field assistance and Bryan Brinegar for boat and ultralight aircraft logistics on 3 Sep 2005. Two anonymous reviewers improved the manuscript. This work was supported by NASA Headquarters under the Earth System Science Fellowship Program Grant NNG05GB55H to M. Tiffany.

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