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Sources of Oxygen Demand in the Lower San Joaquin River, California

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ABSTRACT: Dissolved oxygen concentration below 5 mg l^{-1} has characterized the lower tidal portion of the San Joaquin River downstream of Stockton, California, during the summer and fall for the past four decades. Intensive field research in 2000 and 2001 indicated low dissolved oxygen concentration was restricted to the first 14 km of the river, which was deepened to 12 m for shipping, downstream of Stockton. The persistent low dissolved oxygen concentration in the shipping channel was not caused by physical stratification that prevented aeration from vertical mixing or respiration associated with high phytoplankton biomass. The low dissolved oxygen concentration was primarily caused by nitrification that produced up to 81% of the total oxygen demand. Stepwise multiple regression analysis isolated dissolved ammonia concentration and carbonaceous oxygen demand as the water quality variables most closely associated with the variation in oxygen demand. Between these two sources, dissolved ammonia concentration accounted for 60% of the total variation in oxygen demand compared with a maximum of 30% for carbonaceous oxygen demand. The Stockton wastewater treatment plant and nonpoint sources upstream were direct sources of dissolved ammonia in the channel. A large portion of the dissolved ammonia in the channel was also produced by oxidation of the organic nitrogen load from upstream. The phytoplankton biomass load from upstream primarily produced the carbonaceous oxygen demand. Mass balance models suggested the relative contribution of the wastewater and nonpoint upstream load to the ammonia concentration in the shipping channel at various residence times was dependent on the cumulative effect of ammonification, composition of the upstream load, and net downstream transport of the daily load.

Introduction

Frequent low dissolved oxygen concentration (< 5 mg l^{-1}) characterized a 14 km reach of the river in the lower tidal portion of the San Joaquin River downstream from Stockton, California, during the summer and fall since the 1960s (Bain and Pierce 1968; McCarty 1969; U.S. Army Corp of Engineers [U.S. ACE] 1988). This portion of the San Joaquin River is called the Stockton Deep Water Channel (Channel). The Channel was initially developed for shipping in the 1870s in response to agricultural and industrial growth and was deepened to 12 m and widened to 80–200 m in the 1980s (U.S. ACE 1988). The San Joaquin River is one of the two major rivers that form the northern San Francisco Bay Estuary (NSFE) and drain about 40% of the water in California. NSFE is generally characterized as a nutrient replete estuary with high to hypereutrophic chlorophyll *a* (chl *a*) concentration and infrequent hypoxia (National Oceanic and Atmospheric Administration 1998). The low dissolved oxygen concentration in the lower San Joaquin River is of concern ecologically because of its potential effect on the health of the ecosystem and estuarine production. In general, dissolved oxygen concentration at $<50\%$ saturation can adversely impact fish production through a suite of factors that effect mortality, growth rate, behavior, food web processes, and reproductive success (Breitburg 2002). Low dissolved oxygen is also a potential block to upstream migration of fall run Chinook salmon (*Oncorhynchus tshawytscha*), an endangered species in this estuary. Initial studies suggested these salmon did not migrate upstream when dissolved oxygen was below 6 mg l^{-1} (Hallock et al. 1970). This problem has become a greater concern in NSFE since the spring of 2003 when anoxia and fish kills characterized the Channel.

Initial research in the 1960s identified the five major controlling factors for the low dissolved oxygen in the Channel to be the channel morphology, the load of oxygen demanding substances from the Stockton wastewater treatment plant, the load of oxygen demanding substances from nonpoint sources upstream, streamflow, and environmental conditions (Bain and Pierce 1968). Calculations suggested that the wastewater treatment plant and upstream load contributed equally to the oxygen demand (Bain and Pierce 1968). Management actions in the 1970s to improve water quality conditions included an upgrade of the wastewater treatment plant to reduce organic matter load and placement of barriers upstream to enhance stream-

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flow in the main stem of the San Joaquin River (U.S. ACE 1988). These actions did not eliminate the occurrence of low dissolved oxygen concentrations (Hayes and Lee 2000).

Numerous attempts were made to predict dissolved oxygen concentration for management purposes using coupled hydrodynamic and water quality models (DiToro et al. 1971; U.S. ACE 1988; Chen and Tsai unpublished material). Insufficient information on the magnitude and variability of controlling factors has limited model predictions. All of these modeling efforts were hampered by the need to predict small changes in dissolved oxygen in a highly variable environment (U.S. ACE 1988).

The current conceptual model (Lee and Jones-Lee 2003) is essentially unchanged from that in the 1970s (U.S. ACE 1988). Low surface to volume ratio, high water temperature, and long residence time coupled with the load of oxygen demanding substances from nonpoint sources upstream and the wastewater treatment plant create high oxygen demand in the summer and fall. The relative importance of these factors to oxygen depletion remains uncertain.

Both low dissolved oxygen concentration (hypoxia) and anoxia are major and increasing problems in estuarine environments, such as the Chesapeake Bay (Seliger et al. 1985), and coastal environments, such as the Gulf of Mexico (Rabalais and Turner 2001), where anthropogenic impacts are high. In many of these regions oxygen depletion is associated with nutrient loading (Carpenter et al. 1998) and the subsequent growth and decomposition of phytoplankton biomass under stratified conditions (Officer et al. 1984). Excess nutrient loading is a common problem worldwide and is primarily caused by nonpoint source loads associated with agriculture and animal feeding operations (Howarth et al. 2002; Paerl et al. 2002). Conceptual models that focus on nutrient loading and associated phytoplankton growth are generally not applicable to NSFE because macronutrient concentrations are not limiting and phytoplankton growth is controlled by turbidity from suspended sediments (Cloern 2001); tributary loading was the largest source of total organic carbon to NSFE (Jassby and Cloern 2000).

Pilot research in 1999 demonstrated oxygen concentration in the lower San Joaquin River could decrease to 2 mg l^{-1} and had a larger geographical extent downstream than previously measured (Lehman and Ralston 2001). A multidisciplinary research program was conducted in 2000 and 2001 to fully characterize the oxygen depletion and quantify the current sources of oxygen demand in the Channel during the summer and fall. This paper describes the relative contribution of in situ phytoplankton growth and the upstream load of inorganic and organic oxygen demanding substances to oxygen depletion. Research objectives were achieved via an intensive field program that combined continuous and discrete water quality monitoring with in situ and laboratory bioassay experiments.

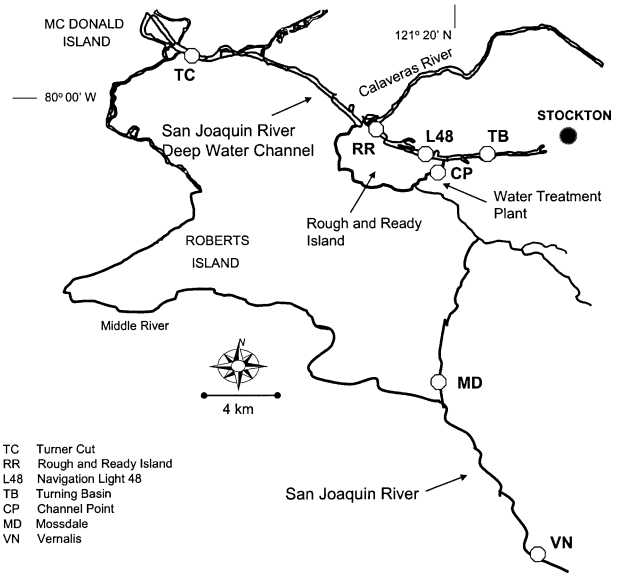

Fig. 1. Map of sampling stations in the San Joaquin River.

Materials and Methods

Site Description

Dissolved oxygen concentration less than 5 mg l^{-1} occurs in a 14-km reach within the lower tidal portion of the San Joaquin River just downstream of Stockton between Navigation Light 48 (L48) and Turner Cut (TC; Fig. 1). This reach of the river was enlarged to a 12-m depth and 80–200 m width to create the Channel. The natural river channel averages 5-m deep and 121 m wide and extends upstream of L48 for approximately 120 km to the headwaters of the Merced River in southern California. The river downstream of Vernalis is a freshwater tidal zone and forms the eastern boundary of the NSFE. Net streamflow during the summer ranges between 150–800 m^3 s^{-1} upstream of the Channel. Tidal stage downstream of Stockton varies by 1.2 m and is accompanied by tidal flows that reach 2,400 m^3 s^{-1} at Rough and Ready Island (RR).

Continuous Monitoring

Continuous water quality measurements were made with a Schneider multiparameter water quality monitoring system in which probes were ex-

posed to water pumped from 1-m depth at RR and Mossdale (MD) by the California Department of Water Resources (Fig. 1). Chl *a* fluorescence was measured with a Turner 10 fluorometer and calibrated with chl *a* concentration determined from laboratory analysis of extracted samples. Water quality probes were automatically cleaned each day at midnight and values were verified every 10 d. The sampling error associated with the dissolved oxygen probe was 0.15–0.20 mg l^{-1}. Continuous measurements were made of solar irradiance using an Eppley pyroheliometer and of streamflow using a SONTEK acoustic Doppler continuous profiler at RR. Streamflow data was also available from an additional ultrasonic velocity meter (UVM) streamflow monitor upstream of Channel Point (CP) operated by the U.S. Geological Survey, Sacramento. Missing streamflow data at CP in 2001 were estimated from linear statistical relationships among streamflow gauges in the region (Jones and Stokes Associates 2002).

Discrete Water Sampling

Vertical profiles were conducted at semimonthly to monthly intervals from July 27 to November 16, 2000, and June 26 to October 3, 2001. Specific conductance, water temperature, dissolved oxygen concentration, and chl *a* fluorescence were measured continuously from surface to bottom with a freshly calibrated YSI 6600 water quality monitor. Light extinction was also measured at 0.5-m depth intervals with a LiCOR spherical quantum sensor.

Surface and bottom discrete water samples were collected following the vertical profiles for measurement of dissolved ammonia-nitrogen, nitrate-nitrogen plus nitrite-nitrogen, soluble reactive phosphorus, chl *a,* phaeophytin, total and dissolved organic carbon, volatile suspended solids (VSS), total Kjeldahl nitrogen concentration (TKN), and biochemical oxygen demand (BOD) concentration. Non-ammonia TKN is commonly referred to as total organic nitrogen and was calculated as TKN concentration minus dissolved ammonia concentration. Water samples for all discrete water quality analyses were collected using a Van Dorn water sampler and were stored on ice or frozen as appropriate until laboratory analysis (U.S. Environmental Protection Agency [U.S. EPA] 1983; American Public Health Association [APHA] et al. 1998). Dissolved oxygen and chl *a* concentration for 1970–2001 used in the analysis were obtained from the California Department of Water Resources (California Department of Water Resources unpublished data). The total ammonia concentration, TKN, and chl *a* concentration in the Stockton wastewater treatment plant discharge was measured by Stockton, California (City of Stockton unpublished data). It was assumed that the total ammonia concentration from the wastewater treatment plant was primarily dissolved ammonia and biologically readily available.

BOD was measured in laboratory assays as the change in oxygen concentration over a 10-d interval in 300 ml borosilicate glass (BOD) bottles at 20°C (APHA et al. 1998). BOD was partitioned into carbonaceous biochemical oxygen demand (CBOD) measured in companion samples treated with nitrification inhibitor (APHA et al. 1998) and nitrogenous biochemical oxygen demand (NBOD), which was calculated as BOD minus CBOD.

The ammonification of chl *a* to dissolved ammonia was determined for water samples collected during the initial phase of a phytoplankton bloom at MD. Replicate water samples were placed into BOD bottles and incubated for 30 d at 20°C in the dark. Dissolved oxygen, chl *a,* and dissolved ammonia concentration were measured at 5-d intervals during the incubation period from replicate bottles. The ammonification of chl *a* was estimated as the ratio of the change in dissolved ammonia and chl *a* concentration over time.

Plankton Production Rate

Net plankton production and respiration rates were measured by the dissolved oxygen light and dark bottle incubation technique conducted at monthly or semimonthly intervals between TC and L48 (Vollenweider 1974). Water samples were overflowed three times into replicate 300 ml light and dark BOD bottles, stoppered, and incubated for 24 h. In 2000, bottles were incubated in situ at 1-m depth at RR. In 2001, bottles were incubated in an open-air continuous flow through incubator that used ambient surface irradiance and river water pumped from 1-m depth to produce both the natural pattern of diel irradiance and water temperature at RR. Water temperature in the chamber was within 0.5°C of the water temperature at 1-m depth. Diel changes in surface irradiance and chamber light were continuously monitored with an Eppley pyroheliometer and calibrated with a LiCor spherical quantum sensor.

Dissolved oxygen concentration was measured by Winkler titration (APHA et al. 1998) in 2000 and a YSI 5000 dissolved oxygen meter fitted with a BOD bottle dissolved oxygen probe and attached stirrer in 2001. Measurements with the dissolved oxygen probe were usually within 0.2 mg l^{-1} of Winkler titration values. Samples for Winkler titration were fixed in the field by addition of magnanous sulfate and kept at 4°C and in the dark until titration within 24 h. Addition of alkaline azide and sulfamic acid just before titration reduced the in-

terference of organic material on the analysis (APHA et al. 1998; Carignan et al. 1998).

The net plankton production rate measurement described both phytoplankton and bacterial growth and respiration and was strongly influenced by the respiration of nitrifying bacteria. The respiration from nitrifying bacteria was estimated as the product of the NBOD to BOD ratio from companion laboratory assays and the in situ plankton respiration for each water sample. Phytoplankton (phytoplankton plus non-nitrifying bacteria) respiration rate was estimated by the plankton respiration rate minus the respiration rate of nitrifying bacteria. Net phytoplankton production rate was estimated by the net plankton production rate plus the respiration rate of nitrifying bacteria.

Net Downstream Transport

Net downstream transport in the Channel was calculated as the net tidal day load at CP minus the net tidal day load at RR. Net tidal day load (kg d^{-1}) was calculated as the integrated sum of the concentration of each water quality constituent (mg l^{-1}) multiplied by the streamflow (m^3 s^{-1}) measured over 24 h. Concentrations were determined from water samples collected on ebb (2 tides) and flood (2 tides) tide during spring and neap tidal regimes at semimonthly intervals by ISCO automatic water samplers. Water samples were kept at 4°C after collection and processed within 24 h for laboratory analyses as described for discrete samples above (U.S. EPA 1983; APHA et al. 1998).

Mass Balance Model

A simple mass balance model was developed to determine the relative contribution of dissolved ammonia from upstream and the wastewater treatment plant to the ammonia concentration in the Channel at different residence times. Daily inorganic and organic nitrogen load from upstream was estimated from weekly to biweekly measurements of dissolved ammonia and TKN at MD plus continuous streamflow upstream of CP. MD was upstream of the tidal influence of the Channel and downstream of major tributaries. Daily inorganic and total organic nitrogen load from the wastewater treatment plant was estimated from daily dissolved ammonia concentration, biweekly TKN concentration, and daily discharge flow measured by Stockton. Missing TKN data were estimated using a linear interpolation; this probably had little impact on the nitrogenous load estimate because TKN load varied little over the season upstream and total organic nitrogen load was small at the wastewater treatment plant.

The percentage contribution of dissolved ammonia in the Channel from upstream or the wastewater treatment plant at each residence time was calculated from the sum of the direct dissolved ammonia load plus the indirect dissolved ammonia load produced from ammonification of the total organic nitrogen each day. The daily residual (unoxidized) total organic nitrogen was tracked and included in the estimate of total organic nitrogen available for ammonification on the subsequent day. The rate of ammonification was adjusted to ambient water temperature assuming a linear curve. The percentage contribution of the upstream load and wastewater treatment plant to the dissolved ammonia in the Channel at residence times between 1 and 25 d was evaluated by combining successive days in the season.

Two model scenarios were examined in order to set upper and lower bounds on the relative contribution of the wastewater treatment plant and upstream load to dissolved ammonia concentration in the Channel. Model run 1 assumed all of the total organic nitrogen oxidized at the maximum ammonification rate of chl *a* and the ammonia load (AL) in kg d^{-1} over a residence time of n days was computed as:

$$\Sigma\, AL_n = DA_n + (r)(ON_n) + (r)(RON_{n-1}) \quad (1)$$

Where DA_n was the dissolved ammonia load on day n, $(r)(ON_n)$ was the dissolved ammonia load from the oxidation of total organic nitrogen (ON_n) on day n based on the ammonification rate r for chl *a,* and $(r)(RON_{n-1})$ was the dissolved ammonia load from ammonification of the residual total organic nitrogen (RON_{n-1}) from the preceding day.

Model run 2 assumed only the percentage of the total organic nitrogen load composed of chl *a* (pchl) oxidized at the maximum ammonification rate for chl *a* and the dissolved ammonia load over a residence time of n days was computed as:

$$\Sigma\, AL_n = DA_n + (r)(pchl)(ON_n) + (r)(pchl)(RON_{n-1}) \quad (2)$$

Significant difference between the percentage of the dissolved ammonia in the Channel contributed by the wastewater treatment plant and the upstream load at MD at each water residence time was identified using the Wilcoxon Mann-Whitney nonparametric test.

Results

Physical and Chemical Conditions

Minimum dissolved oxygen concentration in bottom waters was often below the U.S. Environmental Protection Agency water quality criteria of 5 mg l^{-1} within a 14-km reach of the San Joaquin River between the Turning Basin (TB) and TC

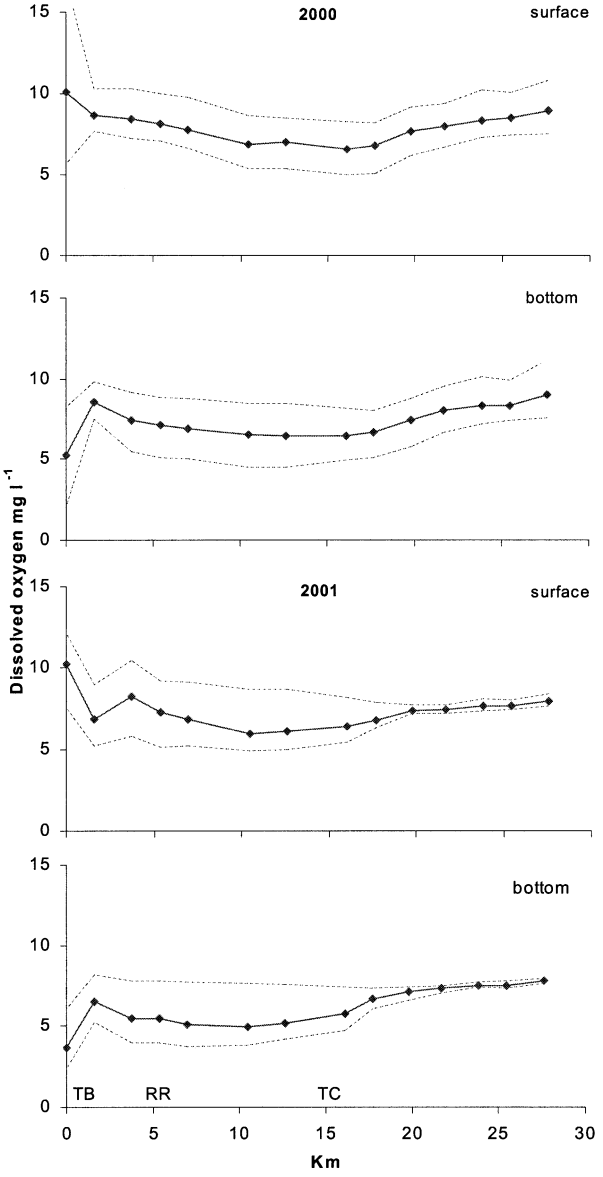

Fig. 2. Longitudinal profile of dissolved oxygen concentration at depths of 1 m and 1 m from the bottom downstream from Stockton, California, near the Turning Basin (TB).

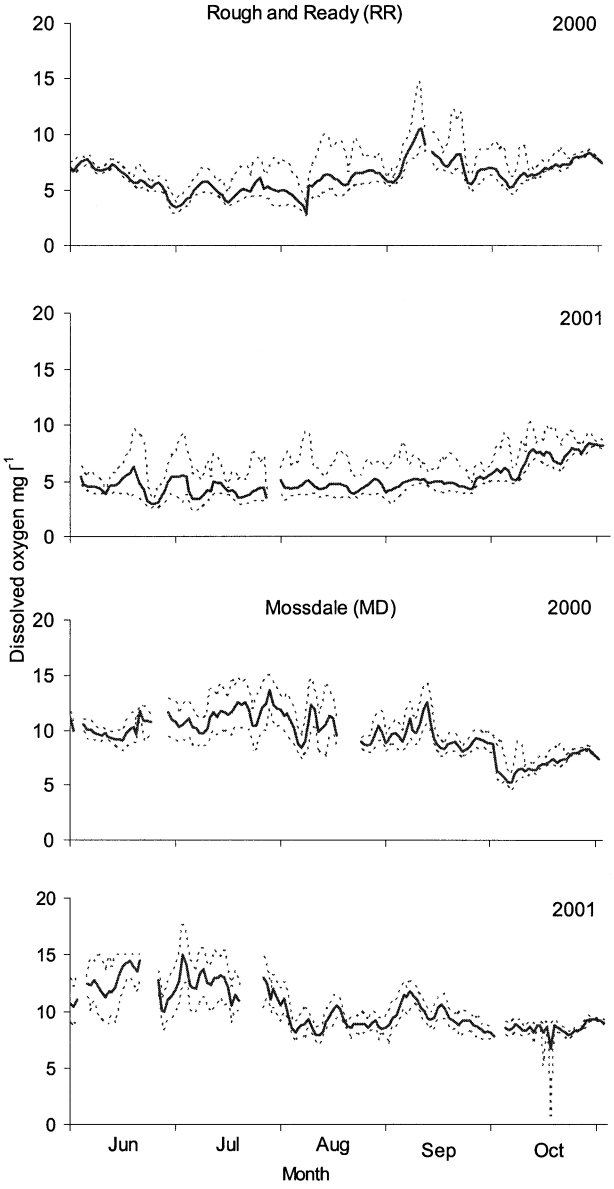

Fig. 3. Daily mean, maximum and minimum dissolved oxygen concentration in the Stockton Deep Water Channel (Channel) at Rough and Ready Island and Mossdale in 2000 and 2001.

downstream of Stockton during midday (Fig. 2). The most severe oxygen depletion occurred near RR and was lower in the dry year 2001 than the wet year 2000. Continuous monitors near the surface at RR indicated daily dissolved oxygen minima were 1 to 2 mg l^{-1} below 5 mg l^{-1} between July and September (Fig. 3). These values contrasted with daytime values that were above 5 mg l^{-1}. Low values persisted longer in the dry year 2001 than the wet year 2000. The low dissolved oxygen concentration in the Channel contrasted with the high to above saturation dissolved oxygen concentration in the natural, shallow river channel upstream of the Channel near MD. Here dissolved oxygen concentration was often near 10 mg l^{-1} throughout the day between June and September and little difference occurred between the wet and dry years 2000 and 2001.

The frequency of dissolved oxygen concentration below 5 mg l^{-1} has not decreased over the past three decades in the Channel. Semi-monthly to monthly discrete sampling during the summer and fall by the California Department of Water Resources suggested the average percent frequency of values below 5 mg l^{-1} between TC and L48 near

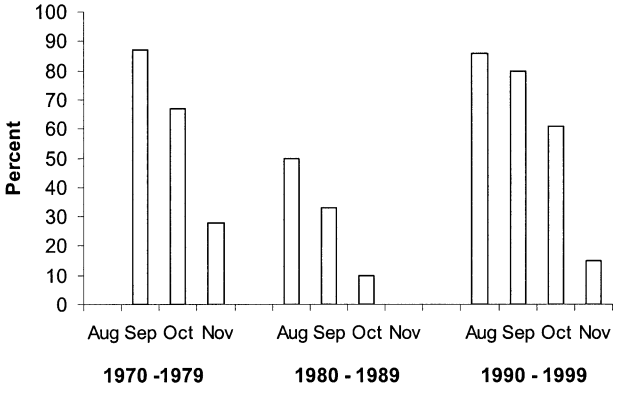

Fig. 4. Average frequency of dissolved oxygen concentration below 5 mg l^{-1} measured in the Stockton Deep Water Channel during semimonthly longitudinal profiles between 1970 and 1999.

midday was similar in the 1970s and 1990s (Fig. 4). The relatively low percent frequency in the 1980s was probably a function of the high streamflow during these years that facilitated aeration and dilution. The decrease in chl *a* concentration by a factor of four since the 1970s suggested live phytoplankton biomass contributed little to oxygen depletion (Fig. 5).

Causes of Oxygen Demand

Persistent stratification of the water column that prevented aeration by vertical mixing was not the cause of low dissolved oxygen concentration near the bottom of the Channel. Vertical stratification was weak and transient even during the fall months of September and October when the stratification was the strongest due to low streamflow (Fig. 6). Dissolved oxygen was sometimes higher near the surface due to photosynthesis. Specific conductance was nearly constant with depth and water temperature commonly decreased from surface to bottom by only one or two degrees. A strong gradient in water temperature accompanied by a decrease in dissolved oxygen concentration was sometimes measured in the late afternoon, but was gone by the next morning (Litton 2003).

Oxygen demand from in situ phytoplankton respiration was also not the primary source of oxygen demand (Fig. 7). The net daily oxygen demand from phytoplankton growth was positive or only slightly negative in 2000 and 2001 and averaged 0.08 mg l^{-1} and 0.29 mg l^{-1}, respectively. Net oxygen demand was associated with an increase in total organic carbon through the production of chl *a* in the photic zone at the rate of 40 ± 14 kg d^{-1} in 2000 and 41 ± 12 kg d^{-1} in 2001. This organic carbon production was small compared with the potential chl *a* load from upstream computed from

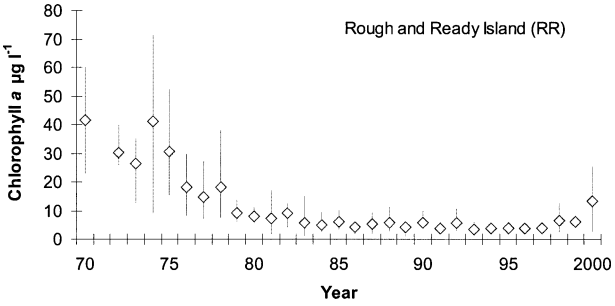

Fig. 5. Average, maximum and minimum chlorophyll *a* concentration measured at Rough and Ready Island between July and November from 1970 to 2001.

chl *a* at MD that averaged 89 ± 61 kg d^{-1} in 2000 and 87 ± 35 kg d^{-1} in 2001.

Although in situ phytoplankton growth positively contributed to the dissolved oxygen, the net plankton oxygen demand was usually negative and averaged −0.24 mg l^{-1} for both years. The average loss of oxygen in the water column was higher in the dry year 2001 at −3.48 g O_2 m^{-2} d^{-1} than the

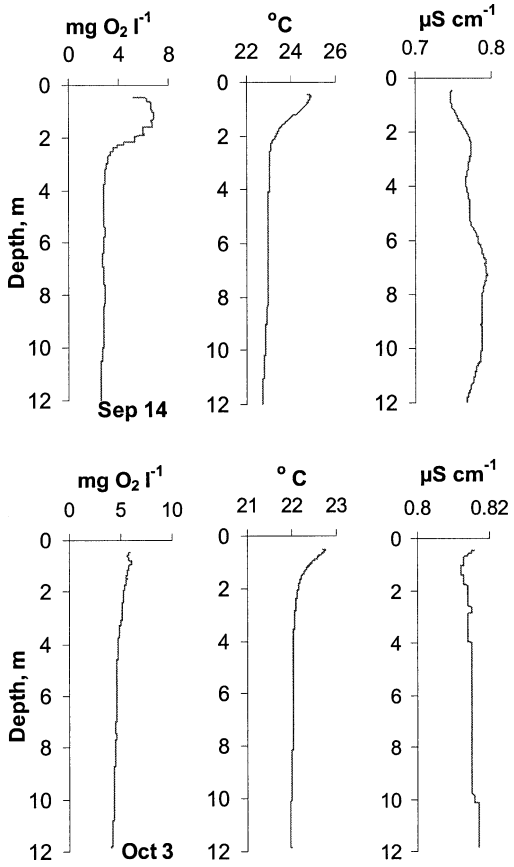

Fig. 6. Vertical profiles of dissolved oxygen concentration, water temperature and specific conductance at Rough and Ready Island in 2001.

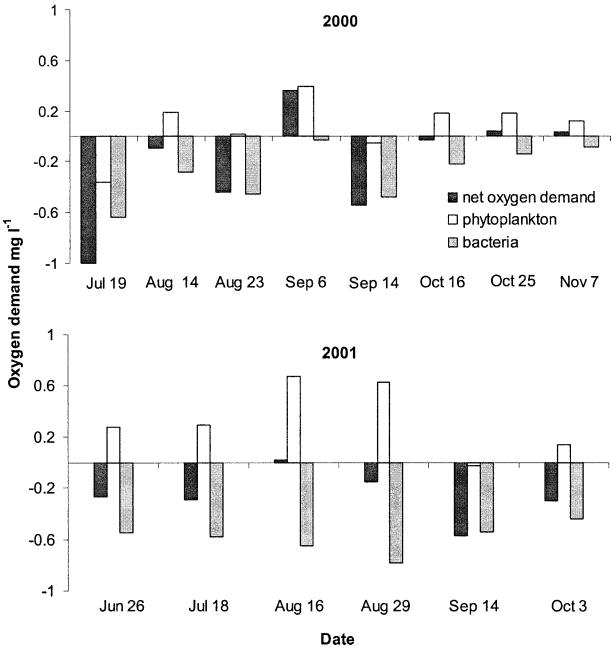

Fig. 7. Net, phytoplankton and bacterial oxygen demand in the Stockton Deep Water Channel in 2000 and 2001 based on in situ production rate measurements.

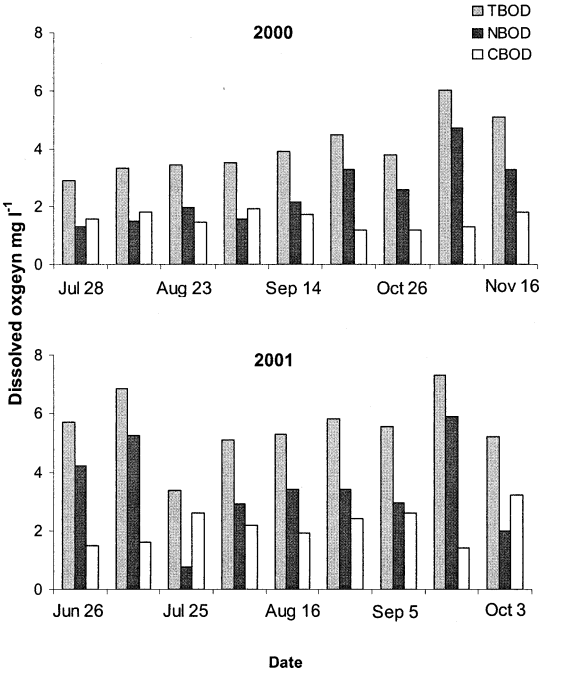

Fig. 8. Average total (TBOD), nitrogenous (NBOD), and carbonaceous (CBOD) oxygen demand determined from laboratory assays during 2000 and 2001.

wet year 2000 at -2.52 g O_2 m^{-2} d^{-1}. These negative oxygen demand values were strongly influenced by the loss of oxygen from respiration of nitrifying bacteria that used an average of 0.29 mg O_2 l^{-1} d^{-1} in 2000 and 0.59 mg O_2 l^{-1} d^{-1} in 2001.

Laboratory BOD tests confirmed that nitrification was the major source of oxygen demand in both 2000 and 2001. Average BOD ranged from 3 to 7 mg l^{-1} between June and November and up to 81% of this oxygen demand was caused by NBOD (Fig. 8). The percentage NBOD varied seasonally but always paralleled the change in BOD. The percentage NBOD was also similar among years even though the BOD was higher in the dry year 2001 than the wet year 2000. CBOD accounted for 30–50% of the total oxygen demand and did not vary with BOD.

Both BOD and NBOD varied closely with dissolved ammonia concentration, but not organic carbon or nitrogen variables (Table 1). The strong association between dissolved ammonia concentration and both BOD and NBOD was supported by the high correlation of BOD with TKN. Neither BOD nor NBOD were strongly correlated with organic carbon variables such as total organic carbon, dissolved organic carbon, and VSS (Table 1). BOD and chl *a* concentration were significantly correlated in 2001 but not 2000 and NBOD was poorly or negatively correlated with chl *a* concentration in both years. The strong correlation between CBOD and chl *a* concentration and the weak correlation between CBOD and total organic nitrogen concentration suggested live phytoplankton biomass was an important contributor to carbon oxidation processes. The importance of live phytoplankton biomass to CBOD was supported by the significant correlation between total organic carbon and total pigment concentration.

Stepwise multiple regression analysis conducted with the chemical variables measured in this study isolated dissolved ammonia followed by CBOD as the variables that accounted for the largest percentage of the variation in BOD (Table 2). These two variables described 73% and 93% of the variation of BOD in 2000 and 2001, respectively, and 83% of the variation for both years combined. Between these two variables, dissolved ammonia accounted for the largest percentage of the variation in BOD at 60% and was similar for both years. CBOD accounted for up to 30% of the variation in BOD and differed by a factor of 10 between the two years. Most of the CBOD was probably derived from phytoplankton carbon because substitution of total pigment concentration (chl *a* plus phaeophytin) for CBOD in the regression only decreased the coefficient of determination (R^2) by 5%.

The importance of dissolved ammonia concentration to the daily variation in BOD and NBOD was not surprising given the high dissolved ammonia concentration and the nearly stable water

TABLE 1. Pearson correlation coefficients among biochemical oxygen demand and water quality variables in the Stockton Deep Water Channel (Channel) for 2000 and 2001. Coefficients were significant at the 0.01 level (bold type) and 0.05 level (regular type) or nonsignificant (italicized type).

Comparisons	Year	
	2000	2001
Total BOD	n = 92	n = 85
total BOD and nitrogenous BOD	**0.92**	**0.86**
total BOD and dissolved ammonia	**0.77**	**0.78**
total BOD and total Kjeldahl nitrogen	**0.63**	**0.75**
total BOD and total organic nitrogen	*0.00*	**0.41**
total BOD and carbonaceous BOD	**0.33**	**0.62**
total BOD and chlorophyll *a* concentration	*−0.15*	**0.59**
total BOD and total organic carbon	**0.55**	0.24
total BOD and dissolved organic carbon	**0.46**	**0.41**
total BOD and volatile suspended solids	*0.06*	**0.36**
Nitrogenous BOD		
nitrogenous BOD and dissolved ammonia	**0.86**	**0.93**
nitrogenous BOD and total Kjeldahl nitrogen	**0.58**	**0.82**
nitrogenous BOD and total organic nitrogen	*−0.16*	**0.34**
nitrogenous BOD and chlorophyll *a* concentration	**−0.41**	*0.08*
nitrogenous BOD and total organic carbon	**0.66**	0.22
nitrogenous BOD and dissolved organic carbon	**0.55**	**0.36**
nitrogenous BOD and volatile suspended solids	*−0.13*	0.20
Carbonaceous BOD		
carbonaceous BOD and chlorophyll *a* concentration	**0.57**	**0.81**
carbonaceous BOD and total organic nitrogen	**0.37**	**0.28**
total organic nitrogen and total pigment	**0.57**	**0.28**

quality conditions in the Channel during the summer. Dissolved ammonia concentration averaged 0.40 mg l^{-1} in both years and reached as high as 1.10 mg l^{-1}. By stoichiometry, oxidation of this ammonia required 4 times as much oxygen at 4.57 mg oxygen (mg ammonia)$^{-1}$ or 1.8 mg oxygen l^{-1}. The study reach also contained an average of 18.9 μg l^{-1} of chl *a* plus phaeophytin that was equivalent to 0.76 mg l^{-1} of carbon based on a carbon to chl *a* ratio of 40. Oxidation of this phytoplankton carbon based on Redfield ratios (Redfield 1958) required only 1.25 mg oxygen (mg algal biomass)$^{-1}$ or 0.95 mg oxygen l^{-1}, half of that needed for dissolved ammonia.

Sources of Dissolved Ammonia

Major sources of dissolved ammonia included the dissolved ammonia and organic nitrogen load from the wastewater treatment plant just upstream of the Channel and nonpoint sources farther upstream. Dissolved ammonia concentration in the wastewater treatment plant discharge was high and averaged 12.5 ± 9.2 mg l^{-1} in 2000 and 13.6 ± 4.3 mg l^{-1} in 2001. The average flow rate of the discharge was fairly stable at 10 m^3 s^{-1} between June and November and produced an average dissolved ammonia load of 1,218 ± 1,115 kg d^{-1} in 2000 and 1,325 ± 772 kg d^{-1} in 2001. The wastewater treatment plant also discharged a small amount of total

TABLE 2. Stepwise multiple regression equations that explained the variation in biochemical oxygen demand with dissolved ammonia concentration and carbonaceous BOD (CBOD) for the Stockton Deep Water Channel (Channel) during 2000 and 2001.

Year	n	Variable	Parameter Estimate	Standard Error of Estimate	% Variance	t Value	Probability	F Value	Adj. R-square
2001	85	intercept	1.00	0.15		6.51	<0.01	446.32	0.91
		ammonia	4.98	0.22	0.60	22.58	<0.01		
		CBOD	1.08	0.06	0.31	17.75	<0.01		
2000	100	intercept	1.10	0.24		4.50	<0.01	137.25	0.73
		ammonia	3.90	0.25	0.60	15.60	<0.01		
		CBOD	1.00	0.13	0.17	7.80	<0.01		
2000 and 2001	186	intercept	0.80	0.14		5.80	<0.01	458.55	0.83
		ammonia	4.40	0.18	0.53	23.96	<0.01		
		CBOD	1.18	0.06	0.31	18.96	<0.01		

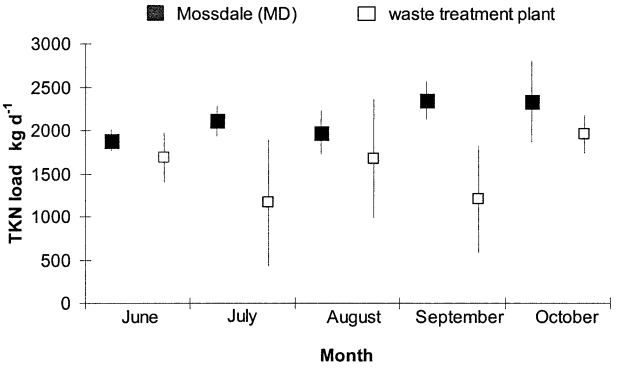

Fig. 9. Comparison of the average daily load of total Kjeldahl nitrogen into the Stockton Deep Water Channel from the Stockton Wastewater Treatment Plant and Mossdale (MD) upstream in 2001.

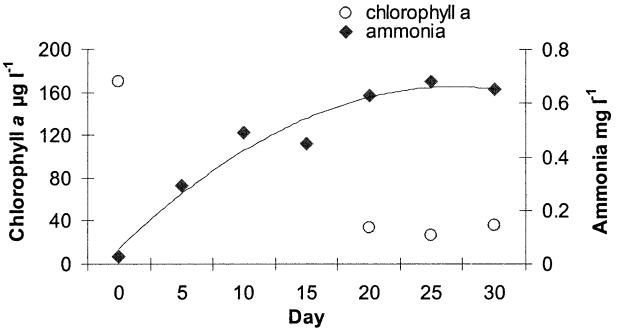

Fig. 10. Ammonification rate associated with the oxidation of chlorophyll *a* in laboratory biochemical oxygen demand assays conducted at 20°C with water samples collected during a phytoplankton bloom at Mossdale.

organic nitrogen that oxidized to ammonia. This load averaged 122 ± 131 kg d^{-1} in 2000 and 264 ± 189 kg d^{-1} in 2001. The monthly average TKN load from the wastewater treatment plant due to these two ammonia sources averaged 1,340 kg d^{-1} in 2000 and 1,589 kg d^{-1} in 2001 and was similar among months between June and October in 2001 (Fig. 9).

The monthly average TKN load was significantly higher ($p < 0.05$) for MD than the wastewater treatment plant in July through September because of the high total organic nitrogen load (Fig. 9). The dissolved ammonia load was low. Dissolved ammonia concentration averaged 0.24 ± 0.22 mg l^{-1} for both years and was associated with an average daily load of 180 ± 246 kg d^{-1} in the dry year 2000 and a higher load of 446 ± 336 kg d^{-1} in the wet year 2001. This dissolved ammonia load was less than 30% of the wastewater treatment plant load. The potential dissolved ammonia load from full oxidation of the upstream organic nitrogen load was much higher than that from the wastewater treatment plant. Total organic nitrogen concentration averaged 0.68 mg l^{-1} in 2000 and 1.12 mg l^{-1} in 2001 at MD and was associated with a total organic nitrogen load from 823 to 4,426 kg d^{-1} in 2000 and from 1,439 to 3,262 kg d^{-1} in 2001. The combined dissolved ammonia and total organic nitrogen load produced an average TKN load of 3,621 kg d^{-1} in 2000 and 2,208 kg d^{-1} in 2001. This TKN load was about two times higher than that from the wastewater treatment plant.

The relative contribution of the wastewater treatment plant and upstream load to the dissolved ammonia concentration and the subsequent oxygen demand from nitrification was strongly influenced by the ammonification of chl *a* that was 0.15 mg N (mg chl *a*)$^{-1}$ l^{-1} d^{-1} at 20°C (Fig. 10). If only a linear correction for water temperature was applied to the rate of ammonification, then the combined dissolved ammonia load from the direct addition of dissolved ammonia plus the decomposition of total organic nitrogen was significantly higher ($p < 0.01$) for the wastewater treatment plant than upstream at MD on a daily basis in the Channel (Table 3). This occurred even though the daily organic nitrogen load from upstream was significantly higher than the wastewater treatment plant, because the ammonification rate was too slow on a daily basis to release as much dissolved ammonia as the direct dissolved ammonia load from the wastewater treatment plant. This may partially explain why the weekly average wastewater treatment plant load was significantly correlated with both the dissolved ammonia concentration ($r = 0.56$, $p < 0.01$, $n = 32$) and NBOD ($r = 0.74$, $p < 0.01$, $n = 32$) at RR. Neither the weekly average total organic nitrogen load nor dissolved ammonia load at MD were significantly correlated with the dissolved ammonia or NBOD at RR.

As the water residence time increased in the Channel, the relative contribution of the upstream load to oxygen demand by nitrification increased because there was more time for the accumulated organic nitrogen load to oxidize to dissolved ammonia. In model run 1, it took a residence time of about 10 d for the percentage of the accumulated dissolved ammonia load from upstream to exceed the accumulated dissolved ammonia load from the wastewater treatment plant (Table 3). The assumption in model run 1 was that all of the organic nitrogen was oxidized to dissolved ammonia at the maximum rate measured for the ammonification of chl *a*. Chl *a* concentration only contributed 13–43% of the total organic nitrogen load at MD between July and October in 2001 (Fig. 11). As a result, the conversion of total organic nitrogen to dissolved ammonia probably represented an upper

TABLE 3. Comparison of the percent dissolved ammonia in the Stockton Deep Water Channel (Channel) contributed by the Stockton Wastewater Treatment Plant (WTP) and upstream at Mossdale (MD) for different residence times. Model run 1 included a seasonal adjustment for water temperature on oxidation rate and model run 2 added an adjustment for the percentage chlorophyll *a* concentration in the total organic nitrogen load.

Model	Residence Time Day	MD Median Percent	Percentile		WTP Median Percent	Percentile		Significant Difference Level	Sample Size n
			10th	90th		10th	90th		
Run 1	1	38	16	52	62	0	72	<0.01	102
	5	49	40	56	51	18	56	ns	20
	10	55	42	57	45	29	49	<0.02	10
	15	61	45	61	39	35	46	<0.04	7
	20	58	50	62	42	33	46	<0.04	5
	25	58	56	59	42	38	43	ns	4
Run 2	1	34	6	47	66	0	83	<0.01	102
	5	38	15	47	62	35	70	<0.01	20
	10	43	26	45	57	46	69	<0.01	10
	15	42	31	46	58	46	64	<0.02	7
	20	38	35	45	62	48	63	<0.05	5
	25	41	34	44	59	49	61	ns	4

limit of the contribution of the upstream load to dissolved ammonia.

The wastewater treatment plant was the primary source of dissolved ammonia with residence times from 1 to 25 d when the total organic nitrogen load was adjusted to include only the chl *a* concentration (Table 3). Model run 2 probably represented the lower limit of the impact of ammonification on the release of dissolved ammonia. This lower limit was probably closer to the actual value because the total organic nitrogen load primarily consisted of highly oxidized phytoplankton biomass that could not be identified as phytoplankton by pigment analysis (Fig. 11). The total organic carbon to organic nitrogen molar ratios of 4 to 6 confirmed the suspended organic material at MD was similar to the range of 5 to 8 that characterize phytoplankton (Redfield 1958).

Water temperature was probably not a significant source of daily variation in the nitrification rate during most of the summer season. Water temperature hovered near 25°C most of the summer and varied by only one to two degrees each day. The largest change in water temperature occurred at the beginning of the season in June and the end of the season in October when water temperature was close to 20°C.

The greatest uncertainty in the contribution of the wastewater treatment plant and upstream load to the oxygen demand was associated with material transport from upstream. The wastewater treatment plant was only 3 km from the Channel and the average net tidal day dissolved ammonia transport of 1,382 ± 1,072 kg d^{-1} at CP suggested that most of the 1,422 ± 472 kg d^{-1} dissolved ammonia load from the wastewater treatment plant entered the Channel in 2001. Greater uncertainty was associated with the transport of inorganic and organic material from farther upstream. The significantly ($p < 0.05$) lower chl *a* concentration at CP than MD suggested there was a loss of live phytoplankton biomass with downstream transport over the 24 km that separates these stations (Fig. 12). Higher ($p < 0.05$) average phaeophytin concentration of 36.9 ± 24.5 μg l^{-1} at CP than of 17.6 ± 4.6 μg l^{-1} at MD suggested decomposition of organic matter

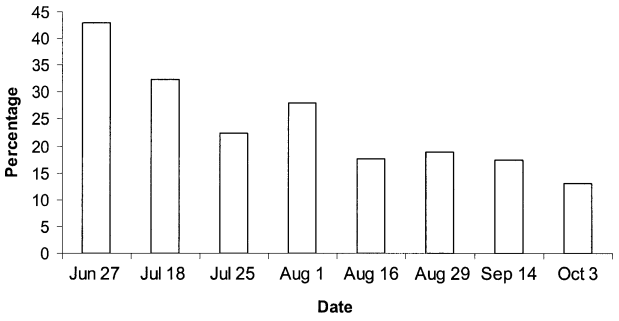

Fig. 11. Percent chlorophyll *a* composition of the total organic nitrogen load at Mossdale in 2001.

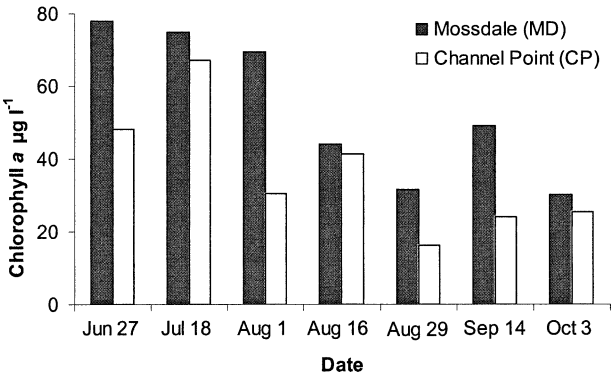

Fig. 12. Comparison of chlorophyll *a* concentration measured at Mossdale and Channel Point in 2001.

TABLE 4. Percent retention of material loads between Channel Point and Rough and Ready Island in 2001. Percent retention was calculated as the difference between weekly average net tidal day load measured at Channel Point and Rough and Ready Island.

	Chlorophyll *a*		Total Organic Nitrogen		Dissolved Ammonia		Total BOD	
Week	Net Transport kg d^{-1}	Percent Retention	Net Transport kg d^{-1}	Percent Retention	Net Transport kg d^{-1}	Percent Retention	Net Transport kg d^{-1}	Percent Retention
June 3	49	91	903	50	−61	−17	7,489	61
June 10	25	89	988	64	72	20	6,287	69
July 1	8	19	−389	−37	8	1	−206	−1
August 12	8	27	−181	−11	418	32	−1,166	−11
August 19	28	85	1,054	77	787	69	8,025	73
September 9	13	51	791	37	333	44	4,166	37
September 16	41	77	1,226	49	782	50	4,638	34
October 7	32	47	1,112	47	3,056	84	10,186	52
Median	27	64	946	48	375	38	5,462	44
10th percentile	8	19	−389	−37	−61	−17	−1,166	−11
90th percentile	34	86	1,068	54	783	55	7,623	63

also occurred during downstream transport. As a result, the upstream total organic nitrogen load calculated for MD probably represented the maximum potential contribution from upstream.

Net material transport between CP and RR confirmed the daily retention of oxygen demanding substances needed to facilitate the release of dissolved ammonia through oxidation. On average, 61% of the chl *a* was retained in the Channel. The average percentage retention of total organic nitrogen, BOD, and dissolved ammonia was lower at 35–39% and more variable than chl *a* (Table 4). The similar and short retention times of BOD and dissolved ammonia reinforced the potential influence of dissolved ammonia load on BOD. The relatively short retention time of total organic nitrogen but long retention time of chl *a* reinforced the importance of live phytoplankton biomass to oxygen demand processes.

Discussion

Physical Conditions

Stratification was not a controlling factor for oxygen depletion in the Channel as is common in many estuaries, fjords, lakes, and coastal regions (Seliger et al. 1985). The weak vertical temperature and salinity gradient suggested insufficient surface diffusion, and vertical mixing caused the low dissolved oxygen concentration throughout the water column and bottom minimum. Insufficient surface diffusion and vertical mixing were also a common cause of oxygen depletion near the bottom of Virginia estuaries (Kuo and Neilson 1987), Chesapeake Bay (Officer et al. 1984), and the Gulf of Mexico (Rabalias and Turner 2001). The low dissolved oxygen concentration in these ecosystems was caused by strong gravitational circulation and an associated steep pycnocline that prevented replenishment of respired oxygen in the bottom layer by vertical mixing (Officer et al. 1984). A physically induced vertical gradient in dissolved oxygen concentration was sometimes measured in the Channel in association with high water temperature in the late afternoon, but it disappeared by morning (Litton 2003). This transient to weak physical stratification probably accounted for the relatively low severity and short persistence of oxygen depletion in the Channel compared with Chesapeake Bay and the Gulf of Mexico. It also suggested biological rather than physical processes dominated net ecosystem metabolism similar to nearby San Francisco Bay (Kemp et al. 1997).

Phytoplankton Production Rate

The finding that respiration of organic matter from in situ phytoplankton growth was not the primary cause of oxygen demand in the Channel differed from estuaries in the Chesapeake Bay and the Gulf of Mexico where the oxidation of phytoplankton biomass from in situ phytoplankton growth was sufficient to cause heterotrophy (Kemp et al. 1997; Rabalais and Turner 2001). The difference was partly a function of the low net phytoplankton production rate in the Channel. Chl *a* concentration ranged from 1,000 to 2,000 mg m^{-2} and was associated with a primary production rate from 15 to 427 mg C m^{-2} h^{-1} in the Susquehanna River estuary of Chesapeake Bay (Malone 1992). This was at least two times higher than the chl *a* concentration of 33 to 698 mg m^{-2} and phytoplankton production rate of 65 to 146 mg C m^{-2} h^{-1} in the Channel. Phytoplankton growth in the Channel is limited by high concentrations of inorganic suspended solids that create light-limiting conditions (Jassby et al. 2002).

These light-limiting conditions reduced the impact of eutrophication on oxygen depletion in the Channel compared with Chesapeake Bay. A long-term increase in the eutrophication of east coast estuaries was associated with an increase in the dis-

solved inorganic nitrogen to total organic carbon ratio (Cooper and Brush 1991). The addition of dissolved inorganic nitrogen fuelled phytoplankton growth and the resulting respiration of organic matter increased the severity and extent of oxygen depletion over time (Nixon et al. 1995). Dissolved inorganic nitrogen has also increased in the lower San Joaquin River by a factor of 2 since the 1970s (Lehman 1996). The increase in inorganic nitrogen did not appear to enhance the chl *a* concentration or oxygen demand because both have decreased since the 1970s. In general, macronutrient concentrations were at least an order of magnitude higher than limiting values throughout NSFE since the 1970s (Jassby et al. 2002).

The largest load of phytoplankton biomass into the Channel came from phytoplankton growth upstream. The daily flux of live phytoplankton biomass measured as chl *a* from upstream was a factor of 2 higher than the chl *a* load from daily phytoplankton growth in the photic zone. The live phytoplankton load from upstream was accompanied by a large load of phytoplankton biomass in various stages of oxidation. This oxidized phytoplankton biomass included detrital phytoplankton measured as phaeophytin and an even larger load of highly decomposed phytoplankton that could not be identified as phytoplankton by pigment concentration. Both carbon to nitrogen molar ratios and stable isotope ratios of organic material in the San Joaquin River just upstream of MD confirmed that most of the suspended organic matter in the river was of phytoplankton origin (Kratzer et al. 2003). The upstream phytoplankton load contributed directly to the oxygen demand upon entry into the Channel because a high settling rate at the junction of the San Joaquin River and the Channel of 1.7 m h^{-1} caused this load to immediately settle to the bottom where only respiration processes occurred (Litton 2003). Full oxidation of this phytoplankton load was facilitated by the long residence time.

Nitrification

Nitrification associated with the presence of high dissolved ammonia concentration was the primary cause of oxygen demand in the Channel during 2000 and 2001. Nitrification was also identified as an important cause of oxygen demand during the 1960s (McCarty 1969). Nitrification can directly control oxygen demand in the water column when ammonia concentration is high (Berounsky and Nixon 1993; Brion et al. 2000). Ammonia concentration reached 1.0 mg l^{-1} and was associated with an average nitrification rate of 0.06 to 0.12 mg N l^{-1} d^{-1}. This nitrification rate was within the range of values measured in the Mississippi River (0.09–0.14 mg N l^{-1} d^{-1}; Pakulski et al. 1995), the Seine River (0.02–0.91 mg N l^{-1} d^{-1}; Brion et al. 2000), and Narragansett Bay (0.01–0.15 mg N l^{-1} d^{-1}; Berounsky and Nixon 1993). The oxygen demand in the sediments was small at 0.3 to 0.8 g oxygen m^{-2} d^{-1} and has not changed significantly from the values measured in the 1980s of 1 g oxygen m^{-2} d^{-1} (U.S. ACE 1988; Litton 2003). Sediment trap studies confirmed that most of the oxygen demand occurred in the aqueous phase in the Channel (Litton 2003). Nitrification in the sediment is commonly low in large river areas like the Channel with a small surface to volume ratio (Berounsky and Nixon 1993).

The importance of dissolved ammonia load to oxygen demand contributed to our growing knowledge of the different effects of nutrient load on estuarine environments. Coastal systems where light is a limiting factor do not react to nutrient load in the traditional limnological fashion in which nutrient load controls oxygen demand through its influence on local phytoplankton carbon growth (Cloern 2001). The importance of the direct impact of dissolved ammonia on oxygen demand was initially developed in the 1880s, but subsequent research often focused on the many regions where eutrophication was the controlling factor for oxygen demand (Nixon and Pilson 1983). The direct impact of dissolved ammonia concentration on oxygen demand is still important for coastal regions where dissolved ammonia comprises most of the dissolved inorganic nitrogen (Nixon and Pilson 1983) and rivers that directly receive wastewater (Brion et al. 2000). The direct impact of dissolved ammonia load on oxygen demand may also increase in the future for coastal regions with the increase in dissolved ammonia load from atmospheric deposition resulting from fertilizer application and animal feeding operations (Howarth et al. 2002; Paerl et al. 2002). Atmospheric deposition may also be important in the San Joaquin River where recent stable isotope analysis identified both animal and human waste as the major source of nutrients in the upper river (Kratzer et al. 2003).

This study also demonstrated some of the potential problems associated with application of ultimate oxygen demand (30-d BOD) to quantify the sources of oxygen demand because it does not incorporate the sequential influence of source loads and their different oxidation rates on daily oxygen demand. Like most estuaries the combined inorganic and organic nitrogenous load from nonpoint sources upstream was many times higher than the point source load from the local wastewater treatment facility (Carpenter et al. 1998; Howarth et al. 2002). As a result, wastewater treatment facilities

are generally considered to be less important to oxygen demand in coastal systems than nonpoint sources (Howarth et al. 2002). Yet, dissolved ammonia concentration from the wastewater treatment plant was a major source of oxygen demand in the Channel when daily ammonification rate was included in the mass balance model. McCarty (1969) first identified the influence of different oxidation rate processes on the relative importance of wastewater treatment plant and upstream nonpoint organic load to the oxygen depletion in the Channel in the 1960s. In his research short-term oxidation rates in BOD assays were higher for the wastewater treatment plant than nonpoint sources upstream. The importance of oxidation rate was further supported by recent predictive models in which nitrification rate and oxidation rate of organic nitrogen had the largest impact on model predictions (Chen and Tsai 2002).

Perhaps the most important factor affecting the magnitude of the carbonaceous and nitrogenous oxygen demand from organic material in the Channel was the composition of the load. Live phytoplankton biomass decomposed quickly compared with more oxidized detrital and organic matter and accounted for more of the short-term oxygen demand. The combined chl *a* and phaeophytin concentration accounted for nearly all of the variation in CBOD even though these pigments accounted for only a small percentage of the total organic matter. The combined chl *a* and phaeophytin pigment concentration also accounted for over 90% of the variation in BOD in the upper San Joaquin where dissolved ammonia concentration was low (Foe et al. 2002). The reactivity of the pigment load was more dependent on the chl *a* concentration than phaeophytin concentration because chl *a* concentration oxidized at a faster rate than phaeophytin (Litton 2003). The importance of live phytoplankton biomass to oxygen demand was supported by research in the Chesapeake Bay where new phytoplankton production contributed more to oxygen demand than more highly decomposed riverine carbon (Kemp et al. 1997).

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