Dissolved oxygen dynamics in a eutrophic estuary, Upper Newport Bay, California

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Abstract

Eutrophication often causes hypoxia in estuarine and coastal systems, but the mechanisms that control hypoxic events vary among estuaries and are often difficult to discern. This study monitored surface and bottom dissolved oxygen (DO) in the Upper Newport Bay (UNB), a tidally-mixed estuary in southern California subject to anthropogenic nutrient loading, eutrophication and hypoxia. The goal of this study was to identify the environmental factors regulating DO dynamics. Six hypoxic events occurred between June and November and were associated with a combination of low solar radiation, increased freshwater discharge following precipitation, and enhanced haline stratification during reduced tidal range periods. At the head of the estuary, high macroalgal biomass and pronounced haline stratification resulted in high DO in the surface layer and low DO in the bottom layer. Oxygen-rich and oxygen-poor waters were transported down-estuary by ebb tides, resulting in DO heterogeneity throughout the UNB. Cross-wavelet analysis illustrated the down-estuary propagation of high/low DO signal correlated with the phases of diurnal photosynthetic and semi-diurnal tidal cycles.

Introduction

In this study, the dissolved oxygen (DO) dynamics in the Upper Newport Bay (UNB), a tidally-mixed eutrophic urban estuary in southern California were analyzed with respect to anthropogenic nutrient loading, eutrophication, and hypoxia. The patterns and mechanisms of hypoxia in small, well-mixed estuaries on the US West coast have not been documented or studied as well as in large estuaries on the US East coast.

Dissolved oxygen concentration is an important water quality parameter in estuarine environments because low DO concentrations can be physiologically stressful or lethal to aquatic organisms (Breitburg *et al*. 1997). Hypoxic and anoxic conditions can have a severe impact on the behavior of marine animals and on the structure and function of benthic communities including macroinvertebrates (Diaz and Rosenberg 1995, Gamenick *et al*. 1996), meiofauna (Steyaert *et al*. 2007), and fish (Pichavant *et al*. 2001, Wu *et al*. 2003, Ripley and Foran 2007). Detecting hypoxia is difficult because DO is exceptionally variable over short time scales, i.e., less than a day, due to variable rates of oxygen production and consumption, which fluctuate in response to different environmental factors.

Oxygen balance in aquatic environments is often adversely affected by eutrophication, defined as an increase in the rate of supply of organic matter to an ecosystem typically resulting from anthropogenic nitrogen discharge (Nixon 1995). Increase in the biomass of primary producers enhances the rates of oxygen production and consumption and magnifies the amplitude of DO fluctuations. Margalef (1974) noted that eutrophication is "...the enrichment of waters with nutrients at a rhythm which cannot be compensated by their definite elimination by total mineralization, in such a way that the degradation of the organic material produced causes a severe depletion in the concentration of oxygen in deep waters." Eutrophication resulting from anthropogenic nitrogen flux has been documented in many coastal and estuarine systems worldwide including such large systems as the Gulf of Mexico (Alexander *et al*. 2000, Krug and Merrifield, 2007) and Chesapeake Bay (Boesch *et al*. 2001, Kemp *et al*. 2005), other large estuaries (Paerl *et al*. 2006) and numerous small estuarine systems (Tappin 2002, Verity *et al*. 2006).

In shallow estuaries, nutrient enrichment often

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results in macroalgal blooms (Sfriso *et al*. 1987,1992; Valiela *et al*. 1992; Raffaelli *et al*. 1999). Dense macroalgal mats dramatically change intertidal and shallow habitats (Raffaelli, 1999), affecting benthic communities including invertebrate density and faunal composition (Raffaelli *et al*. 1991, Ahern *et al*. 1995, Norkko and Bronsdorff 1996, Thiel and Watling 1998, Cardoso *et al*. 2004), and foraging behavior of fish (Isaksson *et al*. 1994, Pichavant *et al*. 2001) and shorebirds (Murias *et al*. 1996, Cabral *et al*. 1999, Lopes *et al*. 2006). Macroalgal mats significantly decrease near-bottom current velocities, reducing sediment erosion and enhancing sediment deposition (Romano *et al*. 2003). High macroalgal biomass results in increased photosynthetic oxygen production, but this increase is often outpaced by increased oxygen consumption because macroalgae release large amounts of dissolved organic matter, which enters the microbial food web (Alber and Valiela 1994) and increases biological oxygen demand (D'Avanzo and Kremer 1994) resulting in hypoxia and/or anoxia.

In part, frequency and severity of hypoxic events in estuaries depend on physical factors controlling the rates of photosynthesis, oxygen consumption, and ventilation (Mee 1988). Photosynthetic rate depends on available light, which fluctuates at different time scales, from diurnal to seasonal. Oxygen flux from the atmosphere through the water column to bottom layers is regulated by vertical mixing, which is in turn determined by water column stratification, vertical profiles of temperature and salinity, and wind and tidal mixing. Haline stratification depends on freshwater discharge, while thermal stratification is regulated by insolation and heat flux through the water surface. Factors that affect stratification and hypoxia fluctuate at different time scales, from semi-diurnal to seasonal and interannual. The physical characteristics of each estuary (e.g., size, aspect, tidal range, depth) further influence spatial and temporal patterns of hypoxia.

Water residence time is a useful indicator of mixing in semi-enclosed basins and is generally negatively correlated with oxygen flux and positively correlated with the frequency and severity of hypoxia. Residence time of bottom water in large, relatively deep and stratified estuaries with chronic hypoxia problems (e.g., Chesapeake Bay on the US East Coast) is measured in months (Kemp *et al*. 2005). Theoretically, well-mixed estuaries with short bottom water residence time are assumed to be immune from extended hypoxia (Verity *et al*. 2006). However, recent observations have shown that under continuous anthropogenic stress even small estuaries characterized by short residence time can be subject to gradual decreases of DO and eventual hypoxia (Verity *et al*. 2006). This idea is confirmed by comparative analysis of ecosystem metabolism in different estuarine systems in the USA that showed that in larger estuaries DO is more balanced than in smaller systems that trend toward heterotrophy and hypoxia (Caffrey 2004).

Many small well-mixed estuaries are characterized by spatial and temporal heterogeneity, which limits the use of linear models, such as those based on diurnal productivity-related DO rhythms, to accurately predict hypoxic events. Modelers must develop approaches that are more sophisticated to relate temporal and physical features to hypoxia in these estuaries. These new models would better serve scientists and managers in their attempts to address the causes of hypoxia, especially in estuaries located in heavily populated areas such as southern California.

The goal of this study was to investigate the occurrence and extent of hypoxic events in a small, tide-dominated urban estuary to determine 1) which factors most influence hypoxia, and 2) ways in which statistical approaches can be applied to investigate these complicated patterns. In this study, special attention was paid to the role of water column stratification and horizontal tidal mixing regulating DO spatial heterogeneity.

Methods

Study Site

The UNB is located in southern California between Los Angeles and San Diego (Figure 1). It is ~5.5 km in length, area ~400 ha, average mean low water (MLW) depth <1 m, tidal range up to 2 m (mean tidal range 1.16 m) and includes ~100 ha of salt and freshwater marsh. According to the classification suggested by Roy *et al*. (2001), the UNB is a tide-dominated estuary: the tidal range is similar to that of the open ocean, and tides in the UNB are more important than waves in moving water and sediment. The main freshwater inflow to the UNB is from San Diego Creek (SDC), which drains 85% of the 400-km^2 watershed. The SDC discharges an average of $27.6 \cdot 10^3$ m^3 day^{-1}; the second largest freshwater source, Santa Ana Delhi Channel, discharges ~$6 \cdot 10^3$ m^3 day^{-1} (McLaughlin et al. 2007).

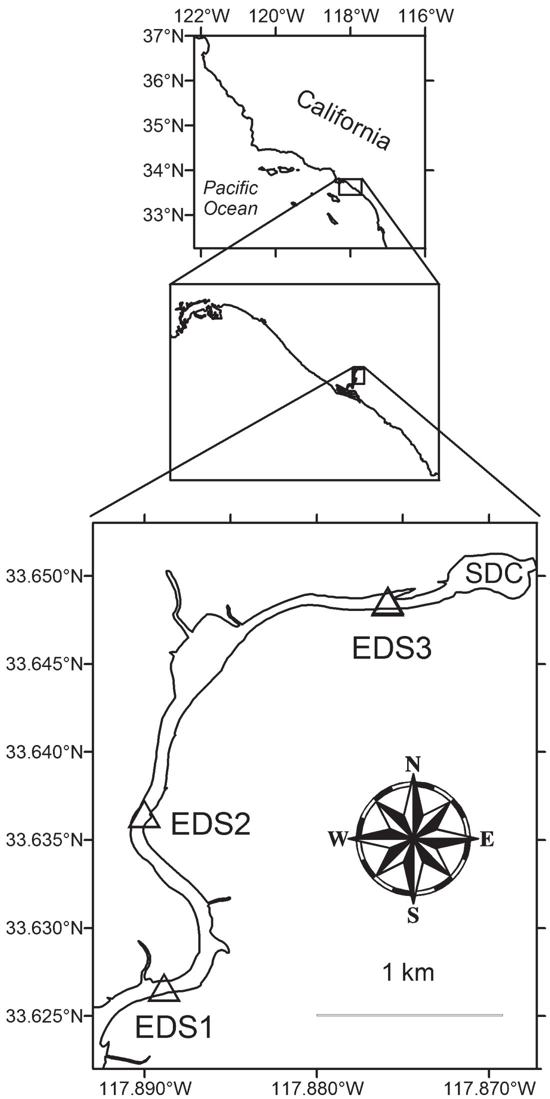

Figure 1. Location of three sondes (EDS1, EDS2, and EDS3) in the Upper Newport Bay estuary in southern California. SDC is the location of San Diego Creek mouth.

The main channel of the UNB is wide with extensive broad mudflats and shallow areas; however, the center of the channel is routinely dredged to 5 m below sea level for sediment retention and navigational purposes. The UNB is separated from the Pacific Ocean by Lower Newport Bay (LNB), which has been dredged and developed into a marina with no natural wetland area remaining.

The UNB is classified as eutrophic because it is subject to both point and non-point nutrient sources (which have not been well studied yet) discharged from surrounding urbanized areas (Kamer *et al*. 2001, Kamer and Stein 2003, Boyle *et al*. 2004). Intensive macroalgal growth in the intertidal zone (green algae *Ulva* spp. and red algae *Ceramium* spp.) occurred during the study period (June-December 2005). Macroalgal coverage estimated from aerial photography increased from 37% in July to 57% in September and 80% in October (Nezlin *et al*. 2007). In the beginning of the study period (July) macroalgal abundance was higher at the head of estuary (55%) than down-estuary (19%), although in the end (October) macroalgal coverage was evenly high throughout UNB (74-88%).

The UNB is a warm basin with high diurnal variability (Table 1). Warm waters are associated with low oxygen saturation and intensive respiration and organic matter decomposition rates. In the surface layer at the head of estuary, SDC discharge resulted in significantly lower salinity than down-estuary (Table 1). At the same time, the mean surface temperature at the head of estuary was warmer than near the bottom and down-estuary, indicating that high DO there couldn't be attributed to high DO saturation resulting from cold freshwater inflow. High DO in warm water suggested supersaturation conditions caused by photosynthesis, indicating macroalgae (concentrated at the head of estuary) as a critical factor of oxygen balance in the UNB.

Data Collection

Water column DO (mg O_2 L^{-1} and % saturation), temperature (T, ºC), conductivity (transformed to salinity (S, psu)), depth (m) and pH were continuously monitored in surface and bottom waters at three sites in the UNB (Figure 1): EDS1 at the seaward end of the estuary, EDS2 mid-estuary, and EDS3 at the head. Two YSI 6600 Extended Deployment System (EDS) sondes were deployed at each station; one sonde collected data 0.5 m from the surface and the other collected data 0.5 m from the bottom. Data were collected at 30-minute intervals from June 15 to December 28, 2005. Sondes were inspected, checked for drift, and recalibrated; data were downloaded on a bi-weekly schedule. Water density (Sigma-T) was calculated from water temperature, salinity, and depth using conventional UNESCO International Equation of State IES80 (Pond and Pickard 2000). The index of water column stratification was defined as the difference between Sigma-T in the bottom and surface layers.

Prior to deployment, conductivity, DO, and pH sensors on each sonde were calibrated, and accuracy was checked by measuring standards. Standards were also measured after deployment to determine

Table 1. Temperature, salinity, and dissolved oxygen in the surface and bottom layers at three UNB stations during June-December 2005. sd=standard deviation.

Sonde	Layer	Temperature (T)		Salinity (S)		Dissolved oxygen (DO)	
		Mean ± sd	Diurnal Variations	Mean ± sd	Diurnal Variations	Mean ± sd	Diurnal Variations
EDS3 (head of estuary)	Surface	22.16 ±3.58	3.78 ±1.87	22.58 ±4.42	9.91 ±4.37	9.07 ±2.83	7.56 ±2.79
	Bottom	20.05 ±2.86	1.71 ±0.86	31.09 ±2.23	3.40 ±3.64	4.67 ±2.22	4.43 ±3.33
EDS2 (mid-estuary)	Surface	20.89 ±3.47	2.94 ±1.28	29.04 ±3.27	6.18 ±2.82	7.05 ±2.15	4.10 ±1.68
	Bottom	20.05 ±2.86	1.71 ±0.86	31.43 ±1.32	2.10 ±1.02	5.29 ±1.12	2.04 ±1.01
EDS1 (mouth of estuary)	Surface	20.35 ±3.15	2.64 ±1.26	30.78 ±2.50	4.63 ±2.03	6.42 ±1.62	3.06 ±1.52
	Bottom	19.16 ±2.62	1.79 ±0.99	31.91 ±1.83	2.36 ±1.12	5.95 ±1.63	1.86 ±0.94

instrument drift (in %): Drift = 100 · ((Measured value of standard - Known value of standard)/(Known value of standard)). Drift of 20% or less was considered acceptable and the data used for analysis; data for drift greater than 20% were rejected.

Freshwater Residence Time

The analysis of freshwater residence time (T_r) in the UNB was based on the assessment of freshwater replacement time (Ketchum, 1951), i.e., the ratio of the input of freshwater (Q_f) to the volume of freshwater in the estuary (V_f ; D'Avanzo *et al*. 1996, Geyer 1997):

$$T_r = V_f / Q_f \qquad (1)$$

The volume of freshwater (V_f) can be calculated using 3D integration from the salinity (S) if the salinity outside the estuary (S_0) is relatively uniform in time:

$$V_f = \iiint (S_0 - S)/S_0 \bullet dxdydz \qquad (2)$$

This approach includes a segmentation of the estuary and a summation of the segment volumes multiplied by freshwater concentration. Due to the elongated shape of the UNB, we assumed that the three volume segments attributed to EDS1, EDS2, and EDS3 were nearly equal and used a simplified form of Equation 2, where S was estimated as a daily average of all salinity measurements at six locations (surface and bottom at EDS1, EDS2, and EDS3), and the total UNB water volume (V_{tot}) was used instead of integration:

$$V_f = V_{tot} \bullet (S_0 - S)/S_0 \qquad (3)$$

Brackish water at the seaward end of the UNB mixes not with ocean water but with water from LNB, which is lower in salinity than the ocean. Analyzing statistical relationship between V_f and S, the present study accounted for the time period during which freshwater from SDC mixes with salt water, resulting in a time lag between SDC discharge and changes in UNB salinity. To analyze this process, the study calculated time-lagged correlations between daily SDC discharge and UNB salinity (S) separately for EDS3 (surface); EDS3 (surface and bottom); EDS2 and EDS3 (surface); EDS2 and EDS3 (surface and bottom); EDS1, EDS2 and EDS3 (surface); and EDS1, EDS2 and EDS3 (surface and bottom). This study considered linear correlations between V_f and S in Equation 3 independent of S_0 because the right side of Equation 3 includes a linear transformation of S with S_0 as a constant. After the best time-lagged correlation between Q_f and S was found, the time lag and the coefficients of linear regression were used to transform S into V_f using Equation 3 and substituting Equation 3 into Equation 1:

$$S = S_0 - [S_0 \bullet \mathrm{T}_{rm} / V_{tot}] \bullet Q_f \qquad (4)$$

As such, the intercept of the linear regression equation between S and Q_f is S_0 (i.e., the salinity outside the UNB) and the slope is the product of S_0 and water residence time averaged for the entire observed period (T_{rm}) divided by UNB water volume (V_{tot}). To obtain the T_r time-series, the time-series of salinity averaged over daily intervals for the entire UNB (S) and the daily averaged SDC discharge (Q_f) were smoothed with a seven-day sliding window; then S was transformed into V_f using Equation 3 and V_f was transformed into T_r using Equation 1.

Time Series Analysis

Time-series analysis was performed on daily and hourly time scales. To analyze the correlations between the measured parameters and the environmental factors, T, S, DO, and stratification index were averaged to daily values. The goal of this averaging was to remove diurnal and tidal variability. When two variables oscillate with similar frequencies (e.g., diurnal or tidal), the correlation coefficient between them is high and significant, indicating nothing but a similarity of dominating frequencies. Daily averaged time series avoid this problem. The daily parameters were analyzed against the following environmental factors: mean (daily averaged) tidal water level and tidal range (the daily difference between maximum and minimum tidal levels) obtained from tidal model JTides 5.2 (http:// www.arachnoid.com/ JTides), freshwater discharge from SDC measured just upstream of the discharge into the UNB, solar radiation, air temperature, and wind speed measured 15 km from the UNB at California Irrigation Management Information System (CIMIS) station #75 at Irvine (33º41'19"N; 117º43'14"W). The tidal data calculated by JTides model were compared to the sonde depth data: the correspondence was almost perfect excluding some periods attributed to sensor malfunction.

Stratification strength and contribution of T and S to the density gradient at different stations were analyzed from the correlations between T, S, Sigma-T, and DO in the surface and bottom layers. High correlations with zero time lag indicate low stratification and intensive vertical mixing. In contrast, low or negative correlations indicate that the water column is stratified and the surface and bottom layers fluctuate independently. These correlations were compared to the index of stratification, i.e., the difference between Sigma-T in the bottom and surface layers.

Hourly datasets were analyzed to reveal the influence of non-linear interaction between diurnal photosynthetic and semi-diurnal tidal cycles on DO. All measurements obtained during each one-hour interval (typically two measurements per hour) were averaged and attributed to hourly intervals. The resulting dataset consisted of 24 variables (4 parameters: T, S, DO, and pH at 6 stations each (3 sondes and 2 depths)) and 4701 hourly observations (starting at 16:00 June 15, 2005, and ending at noon December 28, 2005). The methods of multivariate statistical analysis included missing data reconstruction and cross-wavelet transform.

One of the goals of this study was to find and test a statistical method illustrating the relationship between the diurnal tidal phase and DO. For this purpose we used a cross-wavelet transform, which requires filling gaps in the data set that occurr due to sensor malfunction or data rejection. Conventional methods of filling missing data include zero padding or linear interpolation. For wavelet analysis, these data filling methods of interpolation are undesirable, because they substantially disturb the frequency patterns of the analyzed time-series. To fill gaps in the dataset, this study used the novel method suggested by Beckers and Rixen for data recovery in satellite imagery (Beckers and Rixen 2003; Alvera-Azcarate *et al*. 2005, 2007). According to this method, missing data were reconstructed on the basis of their correlations with the data measured simultaneously (different parameters measured at the same location and the data measured at other locations) using an iterative procedure. First, the missing data in each column (i.e., variables) were replaced by the column mean. Next, at each iteration step, the data matrix was decomposed into a complete set of empirical orthogonal functions (EOF), the number of which was equal to the number of variables (i.e., 24). In accordance with the fundamentals of Principal Component Analysis (PCA; Preisendorfer 1988), the leading EOF modes contain maximum of variance, while the trailing EOF modes contain mostly noise. The product of factor loadings and several (significant) leading EOF modes results in a new matrix with principal features similar to the initial data matrix and a substantial amount of noise eliminated. The missing values from the initial data matrix were then replaced with corresponding values from the new matrix; the resulting matrix was decomposed again, and the process was repeated until the matrices converged. The number of "significant" EOF modes used in the iterative process was estimated from a series of experiments using between 1 and 24 significant EOF modes. For each reconstructed data set, 50 randomly selected points were added to the set of missing data; the mean difference (rms) between these 50 values and the corresponding newly estimated values was used to measure the accuracy of missing data filling. This process resulted in 15 EOF modes being used to fill data gaps; the other 9 EOF modes contained mostly noise. The result is a continuous data series that is suitable for subsequent wavelet transform; in total, 16.3% of data were reconstructed. The reconstructed data were analyzed with extra care because they were not actual measurements. Notably, the reconstructed data reflected variations relevant to the entire system being studied.

The covariance between the reconstructed DO time-series and the tidal level time-series in the UNB was analyzed using cross-wavelet transform. Standard methods of statistical analysis (e.g., linear time-lagged correlation models) were inapplicable because the covariance between tides and DO repeatedly changed its sign depending on the DO signal (i.e., oxygen-rich or oxygen-poor waters) transported up- and down-estuary by tidal flows. Wavelet transform is a relatively new computational method for signal processing (Torrence and Compo 1998) focused on temporal (or repeating) patterns in the data. The software for MATLAB was produced by Aslak Grinsted (Jevrejeva *et al*. 2003, Grinsted *et al*. 2004, Moore *et al*. 2005). In essence, the wavelet transform takes the one-dimensional function of time and expands it into a two-dimensional space consisting of time and scale. For each location (surface and bottom of EDS1 - EDS3), the cross-wavelet power spectrum (W_{xy}) of two time-series (DO and tidal level) was calculated and the real part of the complex W_{xy} vector for semi-diurnal (i.e., tidal) frequency domain was extracted. Statistical significance was estimated against a red noise model (Torrence and Compo 1998). Positive W_{xy} indicated low (ebb) tides correlated with low DO; during these ebb tides, oxygen-poor waters were transported down-estuary. In contrast, negative W_{xy} indicated ebb tides transporting down-estuary oxygen-rich waters. The periods of positive/negative W_{xy} were compared to the diurnal phase of tidal cycle in the UNB.

Results

Spatial Heterogeneity of DO

Stratification and associated bottom anoxia/hypoxia in the UNB were spatially heterogeneous over our study period. High DO in the surface layer and low DO near the bottom were observed at the head of estuary, where macroalgal coverage was high during the entire observed period (Figure 2a). Down-estuary, the difference between DO in the surface and bottom layers was less evident (Figure 2b,c). Photosynthetic oxygen production in well-illuminated surface layers resulted in DO >7 - 10 mg L^{-1}. In the bottom layers, DO was lower (~5 - 6 mg L^{-1}).

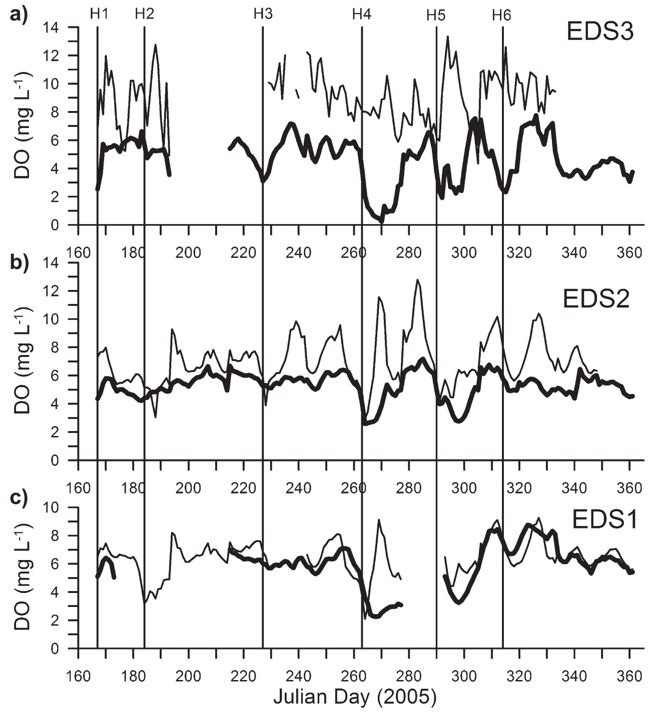

Figure 2. Dissolved oxygen (DO) in surface (thin line) and bottom (thick line) layers at the head of estuary (a), mid-estuary (b) and the mouth of estuary (c). Vertical lines indicate the beginning of six hypoxia events starting on Julian days 167 (H1), 184 (H2), 227 (H3), 263 (H4), 290 (H5), and 314 (H6).

DO in the bottom layer at head of estuary (Figure 2a) was comparable with DO observed mid-estuary and at the seaward end of the estuary (Figure 2b,c), excluding several periods of pronounced hypoxia (see below).

Water Residence Time

The mean water residence time in the UNB was short (<2 days) and the freshwater discharged to the UNB commingled with water from the LNB, which had salinity (~30 psu) lower than the coastal ocean (33.4 - 33.6 psu). The residence time and salinity in the UNB were derived from the coefficients of linear regression (Equation 4) between the SDC discharge (Q_f) and salinity (S) in the UNB one day later (intercept = 29.95; slope = -1.714; R^2 = 0.335). Taking into account the UNB water volume ($2.8 \cdot 10^6$ m^3 at the mid tidal level, $1.6 \cdot 10^6$ m^3 at lower low and $5.0 \cdot 10^6$ m^3 at higher high tidal levels; B. Sanders, personal communication), mean residence time (T_{rm}) in the UNB was 44 hours (1.8 days), and ranged from 25 to 79 hours (1.0 - 3.3 days).

The time-series of T_r obtained from S and Q_f

show several periods when T_r exceeded four to five days (Figure 3a). The most pronounced periods of longer than normal residence time (e.g., mid-June, mid-August, and the end of October) coincided with neap tides (Figure 3d) and were associated with hypoxic events in different parts of the UNB (Figure 2). At the same time, during many days T_r was near zero; this could be explained by relatively small discharge of freshwater (~$30\cdot10^3$ m^3 day^{-1}) into a larger seawater volume (~$1.6\cdot10^6$ m^3).

Freshwater discharged from SDC mixed with saline water over the entire UNB area during a short (approximately one-day) period following discharges from the watershed. During this period, only a small portion of discharged freshwater was retained in the surface layer at the head of the estuary. This was evident from the inverse relationship between the salinity in the UNB and the SDC discharge (Table 2). This correlation was highest when the salinity was averaged over the entire UNB when the time lag between salinity effects and SDC discharge was one day. In theory, slower mixing in an estuary should result in a higher correlation between the freshwater discharge and the salinity in the surface layer of the area closest to the freshwater source. However, no significant correlation was observed between SDC discharge and salinity in the surface layer at the head of estuary (EDS3), indicating that freshwater was not retained in the region closest to the SDC mouth.

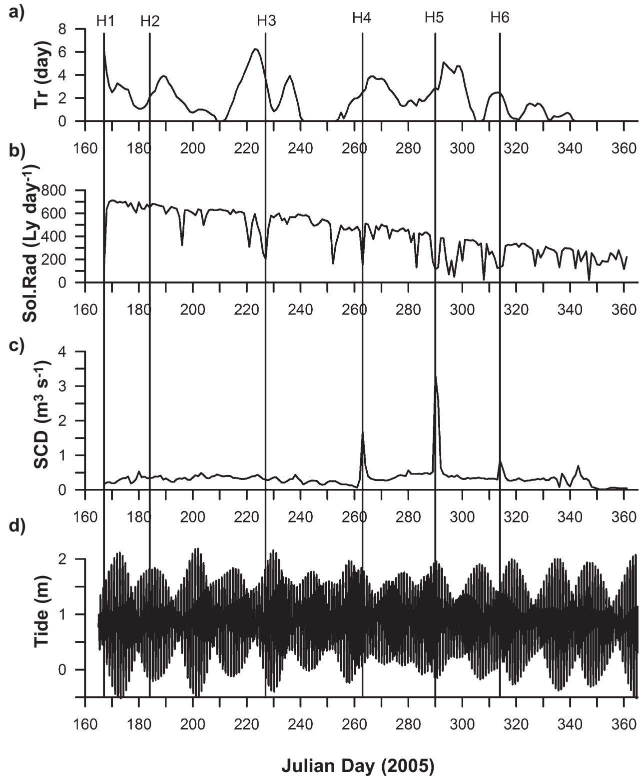

Figure 3. Water residence time (a), solar radiation (b), San Diego Creek discharge (c), and tides (d) in the UNB during June-December 2005. Vertical lines indicate the beginning of six hypoxia events starting on Julian days 167 (H1); 184 (H2); 227 (H3); 263 (H4); 290 (H5); and 314 (H6). The water residence time (T_r) was calculated using Equations 3 and 1 from the daily averaged salinity (S) and SDC discharge (Q_f) smoothed with a seven-day sliding window.

Stratification and DO

Stratification was stronger at the head of estuary (EDS3) than in mid-estuary and down-estuary regions. Correlations between surface and bottom T, S, Sigma-T, and DO were lower at EDS3 than at EDS1 and EDS2 (Table 3). The difference between surface and bottom Sigma-T, which is also an index of water column stratification, was highest at the head of estuary (EDS3) and decreased down-estuary (Figure 4).

Correlations between surface and bottom T and S indicate that water column vertical stratification was more influenced by salinity than temperature (Table 3). Mid-estuary and at the seaward end, T in

Table 2. Maximum time-lagged correlations between San Diego Creek (SDC) freshwater discharge and salinity averaged over different stations. Only significant correlations (p >0.95) are shown.

Stations	Maximum Correlation Coefficient	Maximum Correlation Time Lag
EDS3 (surface)	-	-
EDS 3 (surface and bottom)	-0.2767	4 days
EDS2 and EDS3 (surface)	-0.4337	1 day
EDS2 and EDS3 (surface and bottom)	-0.4925	1 day
EDS1, EDS2, and EDS3 (surface)	-0.5166	1 day
EDS1, EDS2, and EDS3 (surface and bottom)	-0.5736	1 day

Table 3. Maximum time-lagged correlations between temperature (T), salinity (S), water density (Sigma-T), and dissolved oxygen (DO) in the surface and bottom layers at three stations. Only significant correlations (p >0.95) are shown. In brackets the time lag of maximum correlation; positive time lags indicate that the surface time-series lead the bottom one.

Sonde #	Location	T	S	Sigma-T	DO
EDS3	Head of Estuary	+0.340 (-6 days)	-0.243 (-14 days) -0.230 (+1 day)	-0.233 (+1 day)	- -
EDS2	Mid Estuary	+0.983 (0 days)	-0.253 (-3 days) -0.236 (+4 days)	+0.324 (+0 days) +0.337 (+10 days)	- -
EDS1	Mouth of Estuary	+0.962 (0 days)	+0.261 (+0 days) +0.396 (+12 days)	+0.477 (+0 days) +0.504 (+12 days)	+0.514 (+1 day) -

the surface and bottom layers was highly correlated with zero time lag, indicating that thermal stratification was low. In contrast, the correlation between surface and bottom S was low at the seaward end and negative at the head and mid-estuary, indicating pronounced haline stratification.

Stratification at the head of estuary was strong and persistent; it did not exhibit prompt responses to physical factors such as freshwater runoff and/or tidal flows, which regulated stratification down-estuary. Correlations among SDC discharge, tidal range, mean tidal water level, and stratification index (the difference between surface and bottom Sigma-T) were low and insignificant at EDS3 in contrast to EDS2 and EDS1 (Table 4), where the influence of these factors on stratification was greater. Positive correlation between the mean tidal water level and stratification at EDS1 and EDS2 may be due to horizontal inflow of saline ocean water to the bottom layers during high tides; however, the influence of this inflow decreases with distance up-estuary. The negative correlation between stratification and tidal range at EDS1 and EDS2 indicates that tidal mixing had eroded vertical stratification. This was not the case at the head of estuary (EDS3), where stratification was always strong. At all stations, low correlation coefficients between wind speed and stratification index showed that the influence of wind on stratification in the UNB was weak.

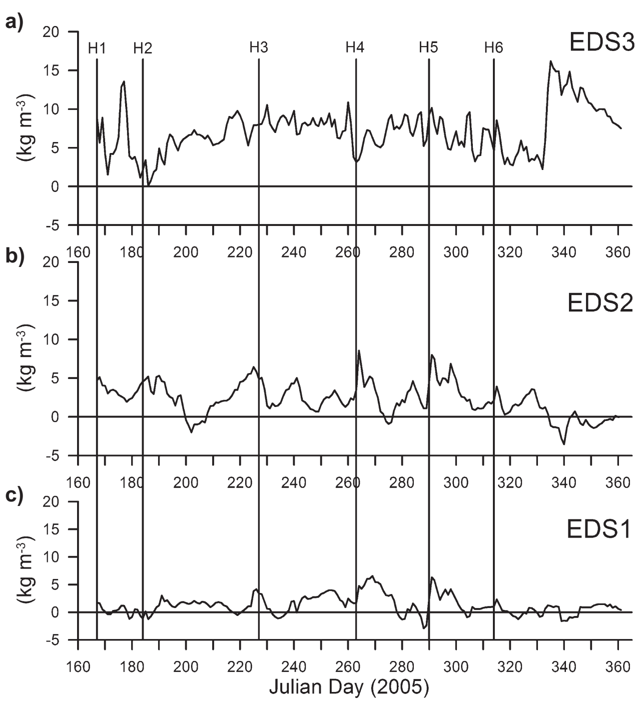

Figure 4. Stratification index (the difference between the bottom and surface water density (Sigma-T)) at the head of estuary (a), mid-estuary (b), and the mouth of estuary (c). Vertical lines indicate the beginning of six hypoxia events starting on Julian days 167 (H1), 184 (H2), 227 (H3), 263 (H4), 290 (H5), and 314 (H6).

High stratification prevented ventilation and resulted in low DO in the bottom layer (Table 5). The stratification index was inversely correlated with bottom layer DO concentrations throughout the estuary. At the head of estuary, high stratification resulted in high surface water DO, suggesting that oxygen produced by photosynthesis remained in the surface layer rather than mixing throughout the water column. In contrast, at the seaward end of the estuary and mid-estuary surface DO was negatively correlated with the stratification index, indicating that in these regions macroalgal biomass was lower and that DO in the surface layer was less influenced by photosynthesis.

Solar Radiation and DO

Solar radiation was significantly correlated with

Table 4. Maximum time lag correlations between environmental factors and stratification defined as the difference between surface and bottom Sigma-T. Only significant correlations ($p > 0.95$) are shown. The time lag of maximum correlation is shown in brackets; positive time lags indicate that the environmental factor was leading the stratification index.

Sonde #	Location	SDC Discharge	Wind	Tidal Range	Mean Tidal Water Level
EDS3	Head of Estuary	-	-0.165 (+1 day)	+0.191 (+3 days)	-
EDS2	Mid Estuary	+0.418 (+1 day)	-	-0.304 (+1 days)	+0.392 (-1 days)
EDS1	Mouth of Estuary	+0.279 (+1 day)	-0.198 (+1 day)	-0.211 (+2 days)	+0.432 (-1 days)

DO concentrations in the bottom layer at the head of estuary and to a lesser extent mid-estuary (Table 5). No significant correlation was observed in the surface layer and at the seaward end of the estuary.

Hypoxic Events

Hypoxic events were defined as periods when either the DO daily average was ≤3 mg L^{-1} or any observation during the 24-hour period was ≤1 mg L^{-1}. In total, 6% of all the DO measurements were <3 mg L^{-1}. Hypoxia was more prevalent at the head of the UNB, where 18% of bottom layer measurements were <3 mg L^{-1}.

Six hypoxic events were observed from June to December 2005 (Figure 2). All of these events seemingly resulted from one or more of three environmental factors: low solar radiation (resulting in reduced oxygen production via photosynthesis), increased freshwater discharge (resulting in enhanced haline stratification, which prevents ventilation of bottom waters), and sluggish bottom water ventilation due to stratification often occurring during neap tidal phase (Figure 3). The most intense hypoxic events in the UNB occurred in the second half of September and mid-October, following rain events and increases in freshwater flow from SDC.

Hypoxia occurred in the bottom layer at EDS3 in mid-June, during the start of our observations (Figure 2; H1: Julian day 167, daily average DO [mean ±sd] 2.5 ±1.41 mg L^{-1}, DO minimum 0.77 mg L^{-1}), and mid-August (Figure 2; H3: Julian day 227, daily average DO 3.11 ±1.14 mg L^{-1}, DO minimum 1.91 mg L^{-1}). Both events coincided with low solar radiation (129 langleys (Ly) day^{-1} in mid-June and 202 Ly day^{-1} in mid-August vs. normal ~600 - 700 Ly day^{-1}; Figure 3b), neap tides (Figure 3d) and relatively long water residence times (Figure 3a).

Another hypoxic event was observed in the surface layer at EDS1 (bottom data were missing) in the beginning of July (Figure 2; H2: Julian day 184). During that period, the daily average DO was 3.18 ±1.00 mg L^{-1}, but there were several instances where the hourly average DO was less than 1 mg L^{-1} (minimum 0.51 mg L^{-1}). This hypoxia could not be explained by neap tide or low insolation. However, during that period mid-estuary stratification was higher than normal (Figure 4; EDS2). This may have led to insufficient ventilation of the bottom layer, producing hypoxic waters that were transported down-estuary and detected by EDS1 (Figure 2).

The most pronounced period of hypoxia started on September 20 (Figure 2; H4: Julian day 263). Over a two-week period, the daily average DO concentrations measured by EDS3 bottom were

Table 5. Maximum time-lagged correlations between dissolved oxygen (DO) and the density stratification index defined as the difference between surface and bottom water density (Sigma-T) and solar radiation. Only significant correlations ($p > 0.95$) are shown. The time lag of maximum correlation is shown in brackets; positive time lags indicate that stratification or solar radiation lead DO.

Sonde #	Location	Stratification		Solar Radiation	
		Surface	Bottom	Surface	Bottom
EDS3	Head of Estuary	+0.526 (+11 days)	-0.159 (+0 days)	-	+0.327 (+1 days)
EDS2	Mid Estuary	-0.372 (+7 days)	-0.354 (+4 days)	-	+0.162 (+2 days)
EDS1	Mouth of Estuary	-0.199 (+9 days)	-0.434 (+4 days)	-	-

<1 mg L^{-1}. Both surface and bottom DO concentrations also decreased at EDS1 and EDS2. This hypoxic event likely resulted from low solar radiation, an increase in freshwater discharge from SDC (by 1.7 $m^3 s^{-1}$) associated with a rain event, and a neap tide series (Figure 3). Precipitation was relatively insignificant (0.1 cm during the two-day rainstorm starting September 19), but on September 20 the San Joaquin Marsh water treatment wetland facility (located just above the confluence of SDC with the UNB) stopped operations and untreated surface water flowed directly to the UNB. Subsequent settling and oxidation of organic matter associated with the freshwater discharge may have contributed to the hypoxia, which propagated down the estuary as a result of horizontal tidal mixing. At the same time, the upper layer at the head of estuary was not affected by hypoxia because the freshwater discharge and salinity gradient (20 - 25 psu in the upper layer vs. 30 - 33 psu near the bottom) stratified the water column and isolated the surface layer from the bottom.

The next hypoxic event occurred in mid-October (Figure 2; H5: starting Julian Day 290) and followed heavy rain, when solar radiation was low, precipitation was 1.5 cm and freshwater discharge from SDC exceeded 3.3 $m^3 s^{-1}$ (vs. normal 0.2 - 0.4 $m^3 s^{-1}$; Figure 3c). Hypoxia affected bottom waters at EDS3 and both surface and bottom waters at EDS2 (no data on EDS1). Surface waters at the head of estuary were isolated from the bottom layer by haline stratification and DO concentration was even higher than normal (Figure 2; EDS3), possibly due to increased algal productivity in response to increased nutrient availability. Solar radiation was low (Figure 3b), which seemingly decreased photosynthesis in the bottom layer and enhanced hypoxia. Tidal range was high (Figure 3d), resulting in intensive horizontal mixing and propagation of hypoxic waters down-estuary, where they affected both surface and bottom layers.

The last hypoxic event at EDS3 was observed in mid-November (Figure 2; H6: Julian Day 314). This event slightly affected both surface and bottom layers at EDS1 and EDS2. This event was preceded by a small rainstorm (precipitation 0.5 cm, SDC discharge 0.86 $m^3 s^{-1}$; Figure 3c) and several days of low solar radiation (Figure 3b). Tidal range was high (Figure 3d), stimulating horizontal mixing and propagation of hypoxic waters down-estuary.

Tidal transport of DO

Spatial heterogeneity of DO in the UNB was associated with an intricate pattern of DO dynamics, when both oxygen-rich and oxygen-poor waters were generated at the head of estuary and transported down-estuary by ebb tides. Daytime/afternoon ebb tides often, but not always invariably, transported down-estuary oxygen-rich waters, while nighttime/early morning ebb tides were primarily associated with oxygen-poor (hypoxic) waters. This was evident in W_{xy} between tides and DO for the 0.5-day frequency domain (Figure 5), and the diurnal

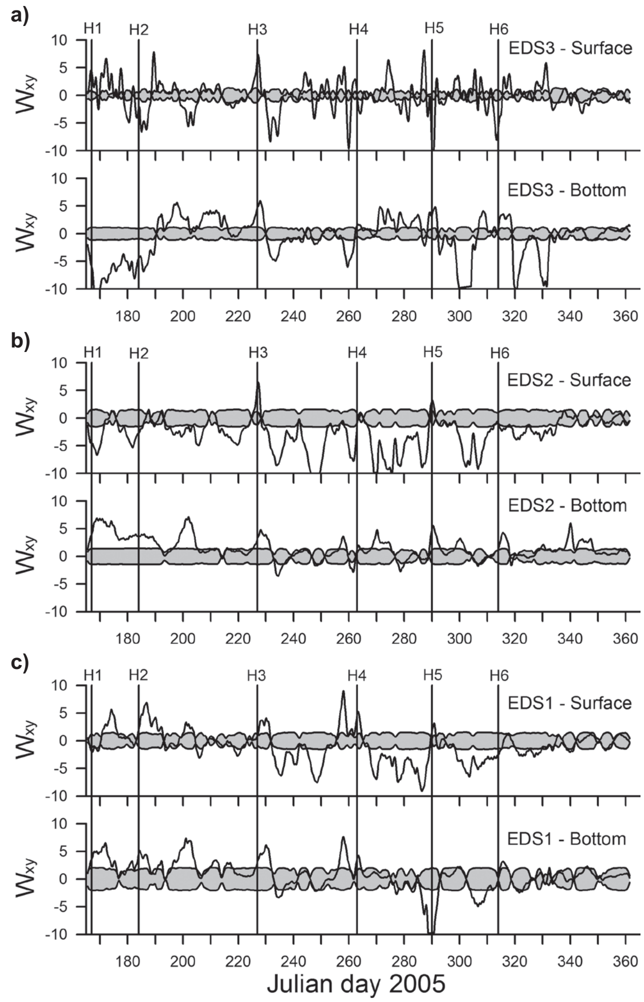

Figure 5. Cross-wavelet power (W_{xy}) at 0.5-day frequency domain between tides and dissolved oxygen (DO) in the surface and bottom layers at the head of estuary (EDS3), mid-estuary (EDS2), and the mouth of estuary (EDS1). Shaded areas indicate the significance of W_{xy} <95%; negative W_{xy} indicate ebb tides associated with high DO; positive W_{xy} indicate ebb tides associated with low DO. Vertical lines indicate the beginning of six hypoxia events starting on Julian days 167 (H1); 184 (H2); 227 (H3); 263 (H4); 290 (H5); and 314 (H6).

phase of tidal cycle in the UNB. High and low W_{xy} occurred at fortnightly intervals and were associated with new-moon or full-moon periods of high tidal range; near-zero W_{xy} occurring between the new moon and full moon were associated with neap tides.

An example of positive W_{xy} (i.e., low DO associated with strong ebb tides at night and in the early morning) was observed in the bottom layer at all three stations in mid-June (around Julian day 200; Figure 5), when strong ebb tides were observed between midnight and 06:00. Negative W_{xy} indicated high DO associated with ebb tides occurring during the day, when macroalgal photosynthesis enriched water with oxygen and tidal flow transported this oxygen-rich water down-estuary. This type of event was most evident in the mid-estuary (EDS2) surface layer from August to October (Figure 5); each event coincided with an afternoon ebb tide.

During all hypoxic events, oxygen-poor waters were transported down-estuary over several tidal cycles as a result of ebb flows. However, not all ebb tides during hypoxic events were associated with oxygen-poor waters because hypoxic bottom waters and oxygen-rich surface waters from the head of estuary mixed at downstream sites. An illustrative example is the development of hypoxia resulting from freshwater discharge on September 20 (Figure 6). Dissolved oxygen concentration at EDS3 surface was significantly higher than down-estuary, while DO in the bottom layer gradually decreased. Both ebb tides on September 20 transported oxygen-rich water from the surface layer down-estuary, resulting in an increase in DO at EDS2 surface during ebb tides compared to flood tide periods. However, the next ebb tide (morning, September 21) transported hypoxic waters from the bottom layer to EDS1 and EDS2; consequently, surface layer DO was as low as zero at the seaward end of the estuary. The next ebb tide (afternoon, September 21) transported oxygen-rich surface water to EDS2 surface and hypoxic water to EDS2 bottom and EDS1 surface and bottom. The next ebb tide on the morning of September 22 transported hypoxic water to EDS1 and EDS2 surface, but not to the bottom layer, where DO didn't change. Over the next several days, DO in the surface waters of EDS1 and EDS2 increased (~4 - 7 mg L^{-1}), while hypoxia continued in the bottom layer at all three observed locations.

Discussion

The combination of high macroalgal biomass and vertical stratification significantly contributed to hypoxia in the UNB. This was most evident at the head of the estuary where both macroalgal biomass and haline vertical stratification were highest. High DO in surface layers resulted from macroalgal photosynthesis; low DO in bottom waters was caused by respiration and decomposition of organic matter produced by macroalgae. A net oxygen sink resulting in low DO was observed when macroalgae consumed more oxygen than they produced; this occurred at night or during the day when thick algal mats shaded themselves (e.g., D'Avanzo and Kremer 1994). Macroalgae also release dissolved organic matter and slough off senescent tissue. Decomposition of this material by aerobic benthic microbes was the likely cause of increased biological oxygen demand (e.g., Valiela *et al*. 1997).

The effects of these processes were compounded by the vertical stratification that reduced mixing, and therefore ventilation, of bottom waters. Vertical

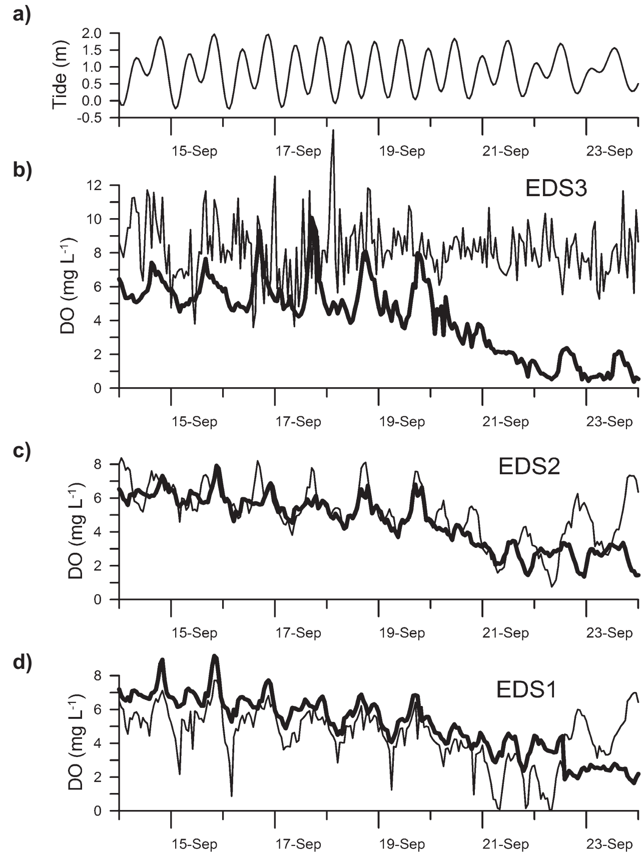

Figure 6. Tides (a) and DO concentrations (b - d) in surface (thin line) and bottom (thick line) layers during the development of the September 20-24 hypoxic event at the head of estuary (EDS3), mid-estuary (EDS2) and the mouth of estuary (EDS1).

mixing by winds and tides (Webb and D'Elia 1980, D'Avanzo and Kremer 1994) can be severely limited by vertical stratification, resulting in insufficient ventilation and bottom water hypoxia (Turner *et al*. 1987, Welsh and Eller 1991, Stanley and Nixon 1992, D'Avanzo and Kremer 1994, Melrose *et al*. 2007). In the UNB, stratification was predominantly haline rather than thermal; similar patterns of haline stratification have also been observed in many other estuaries (e.g., Gale *et al*. 2006, Park *et al*. 2007).

Solar radiation was also an important factor in the occurrence of hypoxia because light availability directly impacts photosynthesis rates and the balance between oxygen production and consumption via respiration. Most hypoxic events in the UNB followed cloudy days when photosynthesis was lower than normal, similar to the findings of D'Avanzo and Kremer (1994). In these cases, it is likely that photosynthetic oxygen production cannot keep pace with cellular respiration and hypoxia results.

In addition to setting up haline vertical stratification, freshwater discharge was crucial in stimulating heterotrophic conditions and hypoxia in the UNB. Similar relationships have been documented in other estuaries, especially in the upper reaches most influenced by freshwater discharge (Stanley and Nixon 1992, Caffrey 2004), which contributes terrigenous organic matter for oxygen consumption (Russell *et al*. 2006). In the UNB, the most severe hypoxic event that began on September 20, 2005: the same day that the San Joaquin Marsh, an 18-ha, 6-pond water treatment wetland located adjacent to SDC just above its confluence with the UNB, was taken off-line for sediment removal. Taking the treatment wetland off-line could have resulted in increased input of organic matter that settled in the UNB and was oxidized, resulting in hypoxia.

Tides were a principal source of ventilation of near-bottom water in the UNB. Spring tides eroded vertical stratification; during neap tides, the residence time of near-bottom waters increased, hindering oxygen flux to bottom layer and increasing the chance of hypoxia. This pattern is typical of small estuaries with intensive tidal mixing (e.g., Melrose *et al*. 2007, Park *et al*. 2007). However, the influence of tides on stratification was not consistent: tidal range was inversely correlated with stratification at the seaward end and mid-estuary, but not at the head of estuary where stratification was consistently high and independent of tides due to sustained freshwater discharge. Also, stratification in the UNB increased during periods of elevated mean tidal level when horizontal tidal flows transported ocean water to the bottom layer enhancing haline stratification.

The influence of wind on stratification and DO dynamics in the UNB was low. There are three possible explanations for this. First, wind speed and direction play an important role in the estuaries where tidal range is small (Geyer 1997, Borsuk *et al*. 2001); in the UNB, the tidal range was high and tidal mixing significantly exceeded the influence of wind. Second, the UNB is long, narrow, and sheltered from wind by surrounding topography. Third, the influence of wind on oxygen balance is nonlinear. Strong winds can induce sediment resuspension and turbidity in the water column resulting in low DO (Reyes and Merino 1991, Lawson *et al*. 2007). Resuspended organic matter consumes dissolved oxygen while turbidity can limit photosynthetic oxygen production, particularly in deep areas. At the same time, strong winds can initiate mixing (Geyer 1997), thus replenishing oxygen in the bottom waters.

This study did not determine the precise role of phytoplankton in contributing to hypoxia in the UNB, but several facts indicate that the impact from phytoplankton was not significant compared to that of macroalgae. The UNB is very turbid, which is not conducive to phytoplankton blooms. Additionally, in estuaries with short water residence time, such as the UNB, phytoplankton cannot reach high biomass because the cells lack sufficient time to grow within the estuaries (Valiela *et al*. 1997, Murrell *et al*. 2007). Lastly, a study of the UNB from 2004 shows relatively low levels of chlorophyll *a* present during a variety of sampling events in both wet and dry seasons (mean ±sd: 2.8 ±1.9 μg L^{-1}; range: 1.7 - 3.66 μg L^{-1}; Sutula *et al*. 2006).

Hypoxia in the UNB was relatively limited compared to large systems with chronic, deep-water hypoxia, such as Long Island Sound and Chesapeake Bay. Only six percent of all the DO measurements were <3 mg L^{-1}, and these mostly occurred in the bottom layers. At the head of the estuary, 18% of bottom layer measurements were <3 mg L^{-1}. In the UNB, hypoxic periods rarely lasted more than two weeks and often occurred only at night with relief during the day. This was partly due to large tidal range (up to 2 m) and relatively shallow average depth (<1 m). Intensive tidal mixing resulted in short water residence time (<two days on average); even during neap tides residence time never exceeded six days. Eyre and Twigg (1997) compiled flush-

ing times for 17 small estuaries around the world, which ranged from <1 day to 196 days; in this context, the UNB was well-mixed.

In the UNB, spatial heterogeneity of DO production and consumption in combination with interaction between horizontal and vertical tidal mixing resulted in complicated patterns of DO distribution in space and time that were not well predicted by simple linear models. Most, but not all, hypoxic events started at the head of estuary, where bottom waters were oxygen-poor and surface waters were oxygen-rich. Ebb tidal flows transported waters that were sometimes oxygen-rich (daytime and afternoon) and sometimes oxygen-poor (nighttime and morning) down-estuary. Similar processes have been observed in other estuarine systems where high photosynthetic and respiratory activity in macroalgae concentrated in intertidal marshes during high tide left a signal that was funneled back to the estuary during ebb tide (e.g., Cai *et al*. 1999, Sanderson and Taylor 2003).

The UNB does not fit the simple scheme of tide-oxygen dynamics expected for small homogeneous well-mixed estuaries in which photosynthetic and respiratory activity of a macroalgal canopy results in DO increasing by afternoon and decreasing by dawn (D'Avanzo and Kremer 1994, D'Avanzo *et al*. 1996). This diurnal DO rhythm is typically most evident in the bottom waters, which are oxic during sunny days and hypoxic at night (Valiela *et al*. 1997). In contrast, diurnal DO variability in the UNB is primarily modulated by tides: high tides cover intertidal zones where macroalgae enrich water with oxygen during the day and decreases DO concentration at night (*c.f.* Cai *et al*. 1999, Edwards *et al*. 2004, Gardner *et al*. 2006). These processes differ from those observed in well-mixed homogeneous estuaries where DO can be predicted from the temporal relationship between tides and daylight (Lucas *et al*. 2006), the trophic status can be assessed from diurnal DO variations (Odum 1956, Odum and Hoskins 1958), and the flux of freshwater and pollutants can be calculated by a tidal prism model (e.g., Luketina 1998). These methods did not work in the UNB because DO distribution was extremely heterogeneous and several physical factors interacted to affect DO levels.

The methodology of data collection and analysis used in this study provides an example of an approach that could be adapted for monitoring and analysis of hypoxic events in small tidally-mixed heterogeneous estuaries with small freshwater inflow. First, dissolved oxygen monitoring in estuaries like the UNB should be based on measurements of high temporal resolution (hourly or better), because most DO processes in these estuaries include significant diurnal and semi-diurnal frequency fluctuations. Measuring DO and other water quality parameters at time resolution too coarse to resolve dominating frequencies could provide misleading or incorrect information (Lucas *et al*. 2006). This is especially true for processes regulated by tides, the phase of which gradually changes with each day. Also, water quality monitoring should be performed at multiple locations because in systems like UNB hypoxia at a given location may result from eutrophic processes in another part of the estuary and subsequent tidally driven transport of low DO waters down-estuary.

Second, simple statistical calculations such as those used in this study can be used in estuaries like the UNB to estimate water residence time based on the time-series of freshwater inflow and salinity. This approach, although not as accurate as other methods, does not require sophisticated computer modeling and detailed knowledge of estuarine hydrodynamics.

Third, the modification of cross-wavelet transform used in this study can be applied to the analysis of many temporally variable environmental processes, such as DO dynamics. Most ecological systems undergo complex, time variable processes. Understanding the factors that control (or influence) these processes aids researchers and managers make more informed decisions. This study demonstrates that modified cross-wavelet analysis can be a tool to help discern complex temporal patterns and the factors that influence them.

As investigators explore the mechanisms of hypoxia in the shallow tide-dominated estuaries typical of southern California, it is important to understand whether the DO heterogeneity observed in the UNB is typical of most estuaries of similar size and tidal mixing or the result of features unique to the UNB. Heterogeneity should be analyzed among the basic factors influencing eutrophication, such as nutrient load, dilution and flushing rates, and the symptoms of eutrophication, including phytoplankton biomass (chlorophyll), macroalgal coverage and DO concentration (see Bricker *et al.* 2007). Comparative analysis of these parameters in several estuarine systems in California and other regions nationwide and worldwide should help environmental scientists and decision-makers in organizing estuarine monitoring, research and management.

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