

Tidal and Watershed Forcing of Nutrients and Dissolved Oxygen Stress within Four Pacific Coast Estuaries: Analysis of Time-Series Data collected by the National Estuarine Research Reserve System-Wide Monitoring Program (2000-2006) within Padilla Bay (WA), South Slough (OR), Elkhorn Slough (CA) and the Tijuana River estuary (CA)

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1. Executive Summary and Key Findings

This report summarizes and compares data from the National Estuarine Research Reserves System-Wide Monitoring Program in four estuaries on the Pacific coast. Data from 2000-2005 from Padilla Bay (WA), South Slough (OR), Elkhorn Slough (CA) and the Tijuana River estuary (CA) are examined. In total over 10 million water quality, nutrient and meteorological data were collected at sixteen sites, four in each of the four estuaries. The data from each estuary were all processed in the same manner in order to facilitate intercomparison. Data from all four sites within each estuary were examined to elucidate the overall functioning of each estuary in terms of nutrient dynamics. The similarities and differences between estuaries were addressed in terms of nutrient concentrations, ratios and dynamics, anthropogenic nutrient impacts and the temporal forcing of seasonal and interannual patterns.

While the estuaries are distributed over a wide latitudinal range (Padilla Bay bordering Canada to the north and the Tijuana estuary bordering Mexico in the South) common climatic and oceanographic forcing factors are present throughout the Pacific coast of the U.S. including seasonal upwelling, distinct wet and dry seasons and longer term phenomena such as ENSO and PDO cycles. The goal of this study was to compare common functioning of the estuaries within their broader geographical, oceanographic and climatological context.

Physical conditions within the estuaries varied widely and the dominant temperature and salinity characteristics depended both on the geographical location of the sites as well as the morphologies of the different estuaries. Estuaries to the south were warmer, and sporadic rainfall led to pulsed freshwater events. The warm climates at these estuaries led to the prevalence of evaporation over freshwater inputs in summer and to hypersalinity in Elkhorn Slough and the Tijuana Estuary. Freshwater inputs in the more northerly estuaries were less pulsed than in the southerly estuaries, and some sites in South Slough were freshwater dominated throughout the year. Padilla Bay experienced less rainfall than South Slough and lower freshwater inputs both due to lower rainfall and its status as an orphan estuary with no major freshwater inputs. Of all the estuaries Padilla Bay showed the most constant salinity pattern which reflected the tidal advection of Puget Sound waters in and out of the estuary on a daily basis. Elkhorn Slough was generally dominated by marine waters and the Tijuana estuary was extremely variable in salinity characteristics exhibiting hypersalinity in summer and almost complete freshwater dominance during extreme freshwater flow events of the rainy season.

Concentrations of nutrients in the estuaries reflected freshwater flow and the land uses of the surrounding catchment areas. The dominant land uses in Padilla Bay and Elkhorn Slough are agriculture and this was apparent in elevated nitrogen concentrations evident in both estuaries. The Tijuana estuary is surrounded by urban land and inputs from sewage resulted in highly elevated nutrient concentrations in this estuary. Of all four estuaries South Slough showed least evidence of anthropogenic disturbance in terms of nutrient concentrations

The molar ratios of the two principal macronutrients, nitrogen and phosphorus showed similar relations with salinity in each estuary. Fresher waters typically had N:P ratios above the Redfield ratio while more marine waters had N:P ratios below the Redfield ratio indicating nitrogen limitation. The spatial extent of the freshwater influence varied with season and estuary. In Padilla Bay with its low freshwater inputs, elevated N:P ratios were limited to the one site where significant freshwater inputs were apparent. In South Slough, each site experienced a wide range of N:P ratios, but during the summer growth season P was generally limiting in the upper estuary and N was limiting at the marine end. Elkhorn Slough which was dominated by marine water typically showed N limitation throughout except during the pulsed high freshwater flow events when P was potentially limiting. As in Elkhorn Slough the Tijuana estuary generally showed potential limitation by nitrogen except during the pulsed high freshwater flow events.

Linear regressions of nitrogen with salinity indicated a common seasonal pattern was in DIN sources throughout the estuaries. The linear regression showed that freshwater nitrogen sources dominated in winter but that in summer marine nitrogen source were of increasing importance. This pattern was caused by the prevalence of high freshwater flows in winter and the availability of nutrients at the marine end in summer caused by upwelling. The pattern in regressions was most apparent in South Slough and was due to the high spatial variability in salinity at this estuary. Regression of salinity with N also indicates a significant sink of nitrogen in South Slough which was associated with eelgrass beds in the central part of the estuary.

A seasonal pattern in P sources was less pronounced. In Padilla Bay, Elkhorn Slough and the Tijuana estuary marine P sources were prevalent in summer. Regressions of P with salinity in South Slough were somewhat anomalous, the regressions indicated a wintertime marine P source and a freshwater P source in summer, and this was the opposite of the pattern in DIN. The freshwater end member of the P regression in South Slough was greatly elevated above measured freshwater P concentrations in the upper Estuary and indicated a localized anthropogenic P source. This anomalous pattern was most likely the result of anthropogenic P from the urban settlement at Charleston, the signal was probably diluted in winter by the high freshwater flow and became apparent in summer because these flow were low. Though no data were available indicating the magnitude of the water flux associated with the high concentrations of P it is likely that the large tidal prism in South Slough is still the major source of P to the upper estuary in summer.

Chlorophyll concentration in the estuaries, like nutrient concentrations, showed great spatial and temporal variability. While elevated concentrations of chlorophyll were found at some sites in Elkhorn Slough and one site in Padilla Bay, the more eutrophied Tijuana River estuary showed no evidence of elevated chlorophyll concentrations. Linear regression of nutrient with chlorophyll indicated significant relationships with DIN at all stations in Padilla Bay and South Slough but in Elkhorn Slough only one weak relationship was found and there was no relationship between DIN and chlorophyll at any station in the Tijuana Estuary. Similar relationships between chlorophyll and PO_4

occurred at 3 of four sites in Padilla Bay and the WI site in South Slough showed a positive relationship between chlorophyll and PO_4 .

Distinct patterns in oxygen concentrations were apparent in all estuaries. And each estuary experienced differing degrees of anoxia, hypoxia and oxygen stress. Photosynthesis and respiration drove the daily pattern in oxygen concentrations, maxima were observed in the afternoon and evening, after a full day of photosynthesis minima were observed in the dark hours indicating the prevalence of respiration over photosynthesis in the absence of light. The magnitude of the variability in daily oxygen concentration was greater in the southern estuaries which also had highest nutrient concentrations. Annual cycles in oxygen depletion were also apparent at some sites, the site which were most affected by nutrient stress did not show any clear annual pattern because oxygen stress rarely eased over the entire year. A general relationship was found between mean number of hours of oxygen stress at each station and the mean annual temperature at each station. In South Slough the duration of oxygen stress at the Sengstacken site in the upper estuary was positively correlated with the upwelling index, the correlation improved when a lag period was included. This relationship indicates the sensitivity of this P limited site to nutrients supplied from a marine source.

Trend analysis was conducted on the water quality data to elucidate any long term patterns in variables. This trend analysis involved the removal of cyclical component of data on timescales less than 1 year so that the long term pattern could be observed. Seven of 10 sites analyzed showed long term temperature trends that were correlated with the Pacific Decadal Oscillation. Of these 7 sites a further four showed negative relationship between the oxygen concentrations and measured at the sites and the Pacific Decadal Oscillation. These findings indicate the same long term climatological trends were affecting the underlying temperature and oxygen characteristics in all the estuaries. However these relationships with PDO were not found at all sites within all estuaries and the variability in responses to the PDO may be as a result of localized events without regular periodicity on timescales of less than one year.

Overall the data indicated that differing mechanisms of functioning in terms of physical structure, the varying anthropogenic stressors apparent at each estuary. Similarities in temporal patterns were found due to freshwater flow and annual patterns of upwelling and the long term patterns in climate influenced each of these estuaries on the Pacific Coast.

The approach taken for this study has proved useful in terms of understanding the local functioning of each estuary and identifying sites that are locally sensitive to nutrient inputs. The methods have identified an emerging phenomenon of anthropogenic impact in South Slough as well as reconfirming previously identified patterns of eutrophication in Padilla Bay, Elkhorn Slough and the Tijuana Estuary. The links between water quality and long term climatic cycles are of importance in themselves shedding light on the long term natural variability in estuarine water parameters and they are a useful step towards understanding the possible effects of warming climate on the waters of estuarine ecosystems.

2. Project Development

a. Abstract

This report summarizes and compares data from the National Estuarine Research Reserves System-Wide Monitoring Program in four estuaries on the Pacific coast. Data from 2000-2005 from Padilla Bay (WA), South Slough (OR), Elkhorn Slough (CA) and the Tijuana River estuary (CA) are examined. The goal of the investigation was to compare common functioning of the estuaries within their broader geographical, oceanographic and climatological context. Over 10 million measurements of water quality parameters, nutrient concentrations, and meteorological variables were collected at sixteen long-term monitoring sites, four in each of the four estuaries. The time-series database from each estuary was processed in the same manner in order to facilitate intercomparisons among the NERR sites. Data from all four sites within each estuary were examined to elucidate the overall functioning of each estuary in terms of nutrient dynamics. The similarities and differences between estuaries were addressed in terms of nutrient concentrations, ratios and dynamics, anthropogenic nutrient impacts and the temporal forcing of seasonal and interannual patterns. While the estuaries are distributed over a wide latitudinal range (Padilla Bay bordering Canada to the north and the Tijuana River estuary bordering Mexico in the south), common climatic and oceanographic forcing factors are present throughout the Pacific coast of the U.S. including seasonal upwelling, distinct wet and dry seasons, and longer-term phenomena such as recurrent El Niño / Southern Oscillation events and the cyclic warming and cooling of the Pacific Decadal Oscillation.

b. Introduction

Estuaries located along the Pacific coast of North America exhibit substantial diversity in geomorphology, and they also differ considerably in the spatial and temporal extent of influence by riverine inputs versus oceanic forcing (Emmett *et al.*, 2000). Many estuaries in the U.S. are known to receive an influx of nutrients primarily from terrestrial sources, and the water column conditions in estuaries are frequently susceptible to nutrient loading from the combination of natural riverine inputs and agricultural drainages, domestic runoff, and other anthropogenic sources (Boyer *et al.*, 2002; Bricker *et al.*, 2007). It is important, however, to gain an increased understanding of the extent to which estuarine nutrient dynamics are also influenced by the input of nitrogen, phosphorus, and other nutrients from the nearshore waters at the mouth of the estuary. Ocean delivery of nutrients is particularly important for the Pacific coast estuaries during the summer season of low riverine discharge when wind-driven upwelling events can periodically bring pulses of nitrogen to the shallow nearshore waters where they are advected by tidal flooding into the estuaries and coastal embayments (Colbert and McManus, 2003; Sigleo and Frick, 2007; Frick *et al.*, 2007). Moreover, seasonal measurements of nutrient concentrations inside and outside estuaries indicate that the shallow nearshore coastal waters along the Pacific coast can also be influenced directly and indirectly by tidal

outflow from nearby estuaries (Emmett *et al.*, 2000; Sigleo *et al.*, 2005; Hickey and Banas, 2003; Rumrill, 2006).

With the exception of San Francisco Bay, the Columbia River mouth, and Puget Sound, estuaries of the Pacific coast of North America are relatively small and shallow, and they experience large tidal prisms, short residence times, and extensive flushing through their open connections with the waters of the nearshore Pacific Ocean (Emmett *et al.*, 2000; Fry *et al.*, 2003; Hickey and Banas, 2003). The small outer coast estuaries of Washington, Oregon, and California are also generally bounded by topographically distinct watersheds that convey riverine inputs rapidly through the tidal channels and out of the estuarine systems (Zedler *et al.*, 1992; Zimmerman and Caffrey, 2002; Sigleo *et al.*, 2005; Rumrill, 2006). Tidal exchanges between the Pacific coast estuaries and the nearshore ocean are also embedded within the seasonal and regional context of larger-scale climatic events and variability within the California Current Large Marine Ecosystem (LME) (Greenland, 1998), and the estuaries are known to receive substantial natural inputs of nitrogen from seasonally upwelled nearshore waters (Fry *et al.*, 2003; Sigleo *et al.*, 2005). Consequently, the dynamics of nutrient fluxes through the Pacific coast estuaries strongly reflect seasonal changes in the extent of climatic forcing, tidal exchanges, and watershed inputs (Roegner and Shanks, 2001; Colbert and McManus, 2003).

In contrast to the small estuaries located along the outer coasts of Washington, Oregon, and California, the estuaries that empty into Puget Sound are complex and vary considerably in geomorphology, tidal characteristics, and watersheds. For example, Padilla Bay (WA) is a broad, shallow, orphaned estuary that persists as a deltaic feature at the mouth of the re-directed Skagit River. Padilla Bay receives freshwater inputs from agricultural drainage systems, seasonal rainfall, and episodic advection of riverine waters discharged into Puget Sound by the Fraiser River. In contrast, Hood Canal (WA) is a deep elongated fjord system that is characterized by low freshwater inputs, minimal tidal exchange, long retention times, and frequent hypoxic conditions. Although the differences in the geomorphology of the estuaries are important, the dynamics of nutrient fluxes through the Puget Sound and its sub-basins and estuaries also reflect seasonal changes in the extent of climatic forcing, tidal exchanges, and watershed inputs (Newton *et al.*, 1997).

Despite widespread recognition that the processes of material transfer and nutrient exchange differ substantially between the Pacific coast estuaries and those of the Atlantic coast (Boyer *et al.*, 2002; Hickey and Banas, 2003), it is not clear how nutrient exchanges, dissolved oxygen concentrations, and other water quality conditions respond to seasonal and spatial differences in tidal and riverine forcing within the estuaries. In addition, it is also not clear the extent to which nutrient dynamics and estuarine water parameters can be influenced by regional El Niño/La Niña events and larger-scale changes in the nearshore ocean associated with the Pacific Decadal Oscillation (Greenland, 1998; Chavez *et al.*, 2002).

c. Principal Question, Goal, and Objectives:

The principal question addressed by the synthesis of Pacific coast NERR SWMP datasets is “*to what extent are estuarine water parameters influenced by larger-scale processes and changes in the nearshore ocean and climatic forcing through coastal watersheds?*” We hypothesize that the extent of oceanic versus watershed forcing of estuarine water parameters varies among the Pacific NERR sites due to large scalar differences in the geomorphology and flushing of the estuarine basins. In the particular case of the four NERR sites encompassed by this synthesis, we anticipate that the extent of ocean forcing and watershed inputs will also vary directly with latitude (*i.e.* high oceanic / sound influence in Padilla Bay, WA – mix of oceanic and riverine influence in South Slough, OR and Elkhorn Slough, CA - high riverine influence in Tijuana River, CA). By this we do not mean to imply any intrinsic relationship between marine/oceanic forcing and latitude in estuaries, but rather to document the specific latitudinal pattern that likely results from the chance selection of NERR sites along the Pacific coast.

The goal of this Pacific coast regional comparison is to *illustrate the scale of variability in the extent to which changes in estuarine nutrient concentrations, phytoplankton blooms, and hypoxic events are driven by watershed inputs and flushing rates versus tidally-driven forcing and upwelling from the nearshore Pacific Ocean.* In addition, we seek to determine the regional and local influence of large-scale ocean events (*i.e.* El Niño / Southern Oscillation and Pacific Decadal Oscillation) on oceanic forcing, upwelling, climate conditions, rainfall, and ambient water quality conditions in several representative estuaries. These issues are important to Pacific coastal resource managers, but identification of changes in the status and condition of the estuaries is limited by a scarcity of relevant time-series data (Bricker *et al.*, 1999; Bricker *et al.*, 2007). Recent assessments indicate that water quality conditions are relatively unchanged over the past decade throughout the Pacific region, and that 5% of the estuaries exhibit highly persistent eutrophic conditions, 80% experience moderately eutrophic conditions, and only 15% of the Pacific coast estuaries exhibit low or minimal levels of eutrophication (Whitney and Welch, 2002; Bricker *et al.*, 2007).

Our specific objectives are to: (A) conduct time-series analyses of short-term variability and interannual changes in the estuarine water parameters collected by the NERR System-Wide Monitoring Program over the period from 2000 to 2006; (B) compile the findings into a region-wide analysis that provides a comparison of estuarine water conditions, status, and trends among the four NERR sites from the perspective of the Pacific coast; and (C) produce a condensed summary and synthesis report for the coastal management community. These objectives apply directly to CICEET goal #2 (apply innovative methods to coastal resource management through synthesis, integration, training, and tool development); and goal #3 (facilitate advances to the NERRS capacity to understand and manage estuarine ecosystems).

Analysis of time-series trends of estuarine water parameters (collected in a consistent manner by the NERR System-Wide Monitoring Program / SWMP) for multiple NERR sites will improve our understanding of short-term variability and longer-term changes in tidal channels and embayments over a large geographic region. In particular, analysis of

the Pacific coast NERR SWMP datasets will add significantly to our appreciation of marine/oceanic and riverine forcing as fundamental processes that establishes distinct biogeochemical signatures for individual estuaries. Understanding of these forcing mechanisms is an important next step toward improvement in national and regional assessments of estuarine water quality conditions (Bricker *et al.*, 1999; USEPA, 2004). Improved understanding of physical forcing in the Pacific coast estuaries is also essential because suspended and dissolved substances are transported through estuarine tidal basins from sources in the upland watershed and/or the nearshore ocean, and they are frequently used to gauge the extent of anthropogenic stress.

d. Methods:

d.1. Pacific Coast Estuaries:

The four Pacific coast estuaries included in this project span nearly 16 deg of latitude and about 2,500 km of coastline from Puget Sound, WA to the boundary between California and Mexico. This vast section of the Pacific coast is highly heterogeneous and encompasses three Large Marine Ecosystems (Puget Sound, California Current, Southern California Bight), at least 5 distinct coastal biogeographic regions, and over 10 biogeographic provinces. This study will draw together a time-series synthesis of variability in estuarine water datasets over the period from 2000 to 2006 collected by the NERR System-Wide Monitoring Program at four NERR sites that are representative of this large section of the temperate Pacific coast (Tables 1 and 2). These estuaries range from a large shallow deltaic embayment fed primarily by co-mingled waters from the Fraser River and Puget Sound (Padilla Bay, WA), to several smaller shallow drowned river-mouth tidal sloughs and inlets located at the interface of coastal watersheds and the Pacific Ocean (South Slough, OR; Elkhorn Slough, CA; Tijuana River, CA).

Padilla Bay (Puget Sound, Washington; 48° 31' N / 122° 28' W): Padilla Bay is a large and expansive, shallow, deltaic embayment formed at the mouth of the Skagit River. Freshwater from the Skagit River has been redirected southward by a water diversion channel, and the tidal waters of Padilla Bay are currently flushed by the co-mingled waters from the Fraser River and Puget Sound. Long-term monitoring stations (Gong, Bay View, Poleg Channel) are located within tidal channels in the marine-dominated / polyhaline waters of the bay. Padilla Bay also receives minor freshwater inputs from a small oligohaline tidal inlet (Joe Leary Slough) and other agricultural drainage systems.

South Slough (southern Oregon; 43° 19' N / 124° 19' W): The South Slough estuary is an ebb-dominated, well-mixed, drowned river-mouth tidal basin that receives primary inputs from greater Coos Bay, the nearshore Pacific Ocean, and from a series of small streams and creeks that drain the adjacent coastal watershed. The South Slough estuarine tidal basin encompasses the full hydrographic gradient from the marine-dominated waters at the mouth (Boathouse and Charleston), to polyhaline waters in the mid region (Valino Island), and mesohaline/oligohaline waters in the riverine region (Winchester Creek and Sengstacken Arm).

Elkhorn Slough (central California; 36° 50' N / 121° 45' W): Elkhorn Slough is a relatively small, tidally-flushed estuary that receives freshwater input primarily from two intermittent creeks (Carneros and Watsonville Creeks) that deliver substantial flows in winter but are virtually dry in the summer. Additional freshwater inputs drain into the slough from extensive agricultural fields in the surrounding hills, and the mouth of Elkhorn Slough may also receive freshwater that is advected into the tidal inlet through the Moss Landing Harbor. Although the Elkhorn Slough tidal basin encompasses the full estuarine hydrographic gradient, the long-term SWMP stations (Vierra Mouth, North Marsh, South Marsh, Azevedo Pond) are located in marine-dominated / euhaline waters that are strongly influenced by the Pacific Ocean.

Tijuana River (southern California; 32° 33' N / 117° 7' W): The Tijuana River estuary is a relatively small, intermittent estuary that receives substantial seasonal inputs of freshwater and sediments from the Tijuana River. The estuary is subject to highly variable inputs of fresh and marine waters, and extended periods of drought can leave parts of the estuary dry during some periods. Minor amounts of freshwater drain into the slough from the adjacent salt marshes and urban areas. The Tijuana River tidal basin encompasses the full estuarine hydrographic gradient, and several of the long-term SWMP stations (Oneata Slough, Model Marsh, Tidal Linkage) are located in marine-dominated / euhaline waters, and the River Channel station is located in the mesohaline region.

d.2. Time-Series Data from the NERR System-Wide Monitoring Program:

The National Estuarine Research Reserve System has operated the NERR System-Wide Monitoring Program (SWMP) since 1995 to collect long-term time-series data to describe ambient conditions within estuaries that are representative of the different biogeographic regions of the United States (Owen and White, 2005). The NERR SWMP time-series database (Table 1) includes a series of estuarine water parameters measured every 30 minutes by deployment of Yellow Springs Instruments Model 6600 dataloggers (water level, temperature, conductivity, salinity, pH, dissolved oxygen, turbidity), a series of local meteorological parameters recorded by Campbell CR-10/CR-1000 weather stations (air temperature, barometric pressure, wind speed, wind direction, precipitation, photosynthetically active radiation), and a suite of nutrient variables measured from grab samples collected on a near-monthly basis from the estuarine water column (Dissolved Inorganic Nitrogen (DIN), Phosphate, Chlorophyll-a, Phaeopigments). Each of the NERR sites located along the Pacific coast is a full participant in the NERR SWMP, and the SWMP time-series datasets are readily available from the NERR Centralized Data Management Office (<http://cdmo.baruch.sc.edu>) for the 2000-06 period of the investigation (Figure 1).

d.3. Numerical Time-Series Analysis:

Analysis of long term trends in the NERR SWMP water quality data was carried out using the “Trends” module for the SPSS 15.0 statistical package. Periodic components of the numerical time-series data were identified using spectral analysis of the daily

averaged measurements of water parameters for each monitoring station. The dominant 100 signals with a periodicity of 1 year or less were removed from the database using the SPSS 15.0 / Trends Seasonal Decomposition procedure. Data requirements for these time series analysis techniques include an unbroken data series and at least four repetitions of the largest seasonal pattern to be removed. Local mean values were used to replace missing data. The availability and completeness of the NERR SWMP water quality database is illustrated for each NERR site (Figure 1). Time-series analyses to detect long term trends were carried in all cases where at least four years of data were available. Statistical testing for differences between water quality parameters and other variables were carried out using t-tests embedded within SPSS 15.0 Trends.

Numerical indices to describe the extent of ocean upwelling (upwelling index) were provided by the Pacific Fisheries Environmental Laboratory (<http://www.pfel.noaa.gov/>). Time-series data to describe the Pacific Decadal Oscillation were compiled from the Joint Institute for the Study of Atmosphere and Ocean (<http://jisao.washington.edu/pdo/PDO>). Upwelling winds for the South Slough were calculated as the cosine of the northerly component of the daily averaged wind speed measured at the South Slough NERR SWMP meteorological station (located at the mouth of the South Slough estuary).

Minimum nutrient concentrations were estimated as half the Method Detection Limits (MDL) for each nutrient. MDLs for each nutrient parameter were obtained from metadata provided by the NERR Centralized Data Management Office (<http://cdmo.baruch.sc.edu>). Illustrations of the spatial variation of parameters within the estuaries are based on annual data from the year where greatest temporal coverage was available.

e. Results and Discussion

e.1. Local Meteorological Conditions:

The four estuaries in this study are distributed over a wide latitudinal range and each experiences different weather conditions. Figure 2 illustrates the variation in mean monthly air temperature and rainfall at each site for the study period. A southward increase in air temperature was observed, however Padilla Bay showed higher average air temperatures than South Slough from April to September and high average air temperatures from June July and August than Elkhorn Slough despite its more northerly latitude. The steeper curve in air temperature apparent at Padilla Bay may be attributed to a continental influence, since the bay is located some 160km inshore of the open waters of the Pacific Ocean. The lower rainfall experienced in Padilla Bay by comparison to South Slough may also be attributed to its distance from the open ocean. On the basis of temperature and rainfall two distinct seasons may be assigned to the estuaries, the rainy season (winter) lasts from October to March and the dry season (summer) occurred between April and September.

e.2 Temperature and Salinity Cycles:

Figure 2 summarizes the spatial and temporal patterns in water temperature at each estuary. The mean annual temperature in the estuaries increased southwards, being 11.4°C in Padilla Bay and 18.6°C in the Tijuana estuary (Figure 2 a). Within estuaries there was considerable variability in temperature, there was a negative correlation between mean depth and mean temperature with shallower sites showing warmer temperatures ($r^2 = 0.572$, $p < 0.01$). In the two northerly estuaries the variability in temperature was negatively correlated with mean salinity ($r^2 = 0.63$, $p = 0.05$). Those stations with lowest salinities (Joe Leary Slough in Padilla Bay, and Winchester and Sengestacken in South Slough) showed higher variability in temperatures reflecting the differential heating and cooling of land and sea. In the two southerly estuaries the maximum salinities observed (>40 psu) indicated the summertime prevalence of evaporation over freshwater input and there was no apparent relationship between salinity and variability in temperature.

Each estuary showed a very different spatial pattern in salinity reflecting their different morphologies and hydrographic conditions as well as the location of the datasondes (Figure 4a). In Padilla Bay, the three sites located in the open bay (BV, GS, and PO) exhibited polyhaline conditions with typical salinities around 29 psu (Figure 3), a daily range of about 1 psu and an annual range for the three sites of 8-10 psu. The salinity characteristics of these sites were dictated by the advection of Puget Sound water in and out of the bay. Greatest variability occurred in winter when salinity could drop by about 9 psu within a single day; these sporadic reductions in salinity were typically short-lived and probably associated with high flows from the Fraser River or the nearby Skagit River (Bulthuis, 1995). By contrast the JLS site in Padilla Bay was oligohaline with a mean salinity of 3.7 psu and an annual range of 28.5 psu. Mean daily ranges at this site were 6 psu with a maximum daily range of 26.6 psu. The fluctuations in salinity at the JLS SWMP station reflect the site's location in an agricultural drainage channel experiencing occasional tidal inundation.

Strong horizontal salinity gradients and the great seasonal variability in salinity conditions were observed at South Slough and reflected the relatively large freshwater inputs to this estuary (Figure 3 a). The two upper estuary sites, SE and WI were generally mesohaline in character with monthly averaged salinities in winter occasionally dropping below 5 psu into the oligohaline category. Maximum summer salinities at these sites were 33.6 psu. (SE) and 35.3 psu (WI) indicating a strong seasonal marine influence and the importance of tidal inundation. The two lower estuary sites in South Slough were polyhaline in winter and euhaline in summer. The polyhaline conditions persisted in the rainy season when strong freshwater influences were present; summer salinities at these sites indicate only minor influences from freshwater (Figure 4c).

Salinities at Elkhorn Slough were largely dominated by marine inputs and evaporation. All sites were euhaline and there was a pattern of decreasing variability in salinity towards the mouth of the slough associated with the decreasing influence of freshwater inputs and of evaporation. Temporal patterns in salinity were similar at all sites within Elkhorn Slough and monthly average salinities were positively correlated between all sites ($p < 0.01$). Hypersalinity (*i.e.* salinities higher than the surrounding seawater)

occurred on an annual basis due to the prevalence of evaporation over freshwater inputs (Figure 2c) and was most pronounced in the upper estuary AP and NM sites.

The Tijuana estuary was characterized by high variability in salinity, all sites had a range in salinity >30 psu. This great range in salinity was caused by a combination of the prevalence of evaporation in summer and extreme freshwater flow events. Three of the sites OS, MM and TL were euhaline while one site RC was mesohaline. Each of the euhaline sites experienced hypersalinity in summer and hypersalinity was the dominant mode at MM (mean salinity 36.5 psu). Typical daily ranges in salinity at the three euhaline sites were between 2 and 10 psu but during sporadic short duration high flow events salinities dropped by 34 psu or more in single day. The effect of these high flow events on mean monthly salinity, and the irregularity of their timing, are illustrated in Figure 4e. Distinct reductions in monthly average salinity were apparent every year except 2002. Mean daily variability was higher at the RC site, which was influenced daily by both tides and freshwater. During high flow events salinities at this site approached pure freshwater concentration <1 psu with low daily variability.

The dominant salinity and temperature regimes in these estuaries indicate systems with very different modes of functioning. Padilla Bay is an orphan estuary with no major direct freshwater inputs. Temperature and salinity signatures in this estuary are largely dictated by advection of the surrounding Puget Sound waters in and out of the bay on a semi-diurnal basis and the salinities of these advected waters are further driver by flow from the Fraser and Skagit rivers (Bulthuis, 1995). There appears to be little influence on the physical properties of the sites in the open bay by the freshwater inputs from JLS or other minor freshwater sources. By contrast South Slough has strong local freshwater inputs which affect the salinity characteristics of all sites in the estuary particularly during the rainy season. These freshwater inputs also have characteristic more variable temperature signatures due to differential heating of land and sea. While Elkhorn Slough has geomorphologic similarities to South Slough (both are small narrow drowned river valley with direct opening to the open ocean) the hydrographic regimes in these two estuaries are very different. The low freshwater inputs in Elkhorn Slough and resultant high residence times ~ 50 days (Largier *et al.*, 1997) result in an environment where during the summer months evaporation dominates over freshwater input and hypersalinity occurs. The Tijuana estuary shares elements of the functioning of both South Slough and Elkhorn Slough and these similarities are caused by the sporadic nature of the water sources in this estuary. During times of low or no flow there may be no connection with the open ocean, and residence times are unpredictable, lasting until the next flood event (Zedler *et al.* 1992) hypersalinity was widely observed at these times however when high flow conditions do arrive freshwater volumes are such that the entire estuary may become freshwater dominated within a day.

e.3 Concentrations of Dissolved Inorganic Nutrients:

Similar to the temporal and spatial pattern observed for variability in salinities, the concentrations of dissolved inorganic nutrients also showed considerable variation within estuaries, between estuaries, and over time (Figure 5). Mean Dissolved Inorganic

Nitrogen (DIN) concentrations at most sites fell within the “medium” ($>0.1\text{mg.l}^{-1}$) range of nitrogen concentrations (as defined by Bricker *et al.*, 1999). The Padilla Bay NERR SWMP station JLS and Tijuana River NERR SWMP station RC each had mean DIN concentrations considered “high” ($>1\text{mg.l}^{-1}$) (Figure 5a). It is important to note that each of these SWMP stations also exhibited the lowest average salinities in their respective estuaries. Within both Padilla Bay and South Slough the maximum DIN concentrations did not exceed the “medium” limit (except at JLS), while in Elkhorn Slough and in the Tijuana River estuary maximum DIN concentrations at all sites exceeded the “high” boundary. Figure 5 (b-e) illustrates the seasonal cycles in DIN from representative sites in each estuary. Seasonal cycles in DIN concentrations were most pronounced in Padilla Bay’s main channel sites (PO, GS and BV) and in the South Slough, but such patterns were less pronounced at Elkhorn Slough and the Tijuana River estuary. Significant differences ($p<0.01$) in DIN concentrations were observed between summer (April to September) and winter (November to March) seasons within Padilla Bay, South Slough and Elkhorn Slough. However, distinctly different seasonal concentrations of DIN did not occur within the Tijuana River estuary. The greatest difference between summer and winter mean DIN concentration occurred in Padilla Bay (0.52mg.l^{-1}), and the lowest significant difference in DIN concentrations occurred in Elkhorn Slough (0.15mg.l^{-1}). The Padilla Bay sites exhibited a more gradual increase to sustained high DIN concentrations in winter than at South Slough and Elkhorn Slough where nutrient peaks were steeper and less regularly timed (Figure 5). Winter peaks in DIN also occurred in the Tijuana River estuary, but the patterns in summer depletion were not as pronounced. The seasonal pattern in the ratio of NH_4 to DIN was similar in all estuaries, highest proportions of NH_4 occurred during summer months exceeding 80% in all estuaries and NH_4 minima occurred in winter (Figure 4 b-e). The minimum concentration of NH_4 varied between estuaries, in the Tijuana River estuary NH_4 rarely made up less than 40% of DIN while in Padilla Bay the proportion of NH_4 regularly fell to $< 1\%$ of DIN in winter.

Mean annual PO_4 concentrations (Figure 6) at the majority of NERR SWMP sites were in the “medium” ($>0.1\text{mg.l}^{-1}$) category of Bricker *et al.* (1999). Exceptions to this generalization occurred in the Tijuana River estuary where all of the water quality monitoring stations exhibited mean concentrations in the “high” category ($>0.1\text{mg.l}^{-1}$), and in the South Slough (SWMP station WI) where mean PO_4 concentrations were “low” ($<0.01\text{mg.l}^{-1}$) (Figure 6a). Significant differences ($p<0.01$) between rainy and dry season PO_4 concentrations occurred in Padilla Bay and Elkhorn Slough with winter maxima and summer minima. In South Slough and the Tijuana River estuary there were no significant differences between rainy and dry season PO_4 concentrations when the estuaries were considered as a whole. However, significant seasonal differences ($p<0.05$) did occur at the Tijuana River TL site and at the South Slough VA site (Figure 6 c,e). At both the VA and WI sites in South Slough, dry season PO_4 concentrations were higher than rainy season PO_4 concentrations but at the WI site PO_4 concentrations were consistently low throughout the study period. These low concentrations of PO_4 may account for the lack of a statistically significant difference between wet and dry seasons. The dry season PO_4 maxima observed at South Slough may be attributed to two factors: the strong freshwater signal at South Slough in winter which dilutes the more PO_4 rich

marine waters and the prevalence of wind-driven upwelling of ocean waters during summer. A similar temporal pattern was observed in Elkhorn Slough (Figure 6d). In contrast, the seasonal pattern of PO₄ concentrations at Padilla Bay likely reflects the seasonal cycle in biological uptake of phosphorus (Figure 6 b,c). The lack of significant statistical differences between summer and winter PO₄ concentrations at most sites in the Tijuana River estuary may reflect the high error in mean concentrations resulting from the very high maxima and the minima which were below detection limits

e.4. Analyses of Nutrient Ratios:

Greatest variability in N:P ratios was observed in sites with the greatest freshwater influence (JLS, WI and RC) (Figure 7a). In Padilla bay N:P ratios at JLS exceeded the Redfield ratio for most of the study period. In contrast, the other sites within Padilla Bay consistently had nutrient ratios under the Redfield ratio (Redfield, 1958) indicating potential nitrogen limitation. In South Slough the annual variability in salinity produced great variability in the N:P ratios at each site, with all sites demonstrating ratios of N:P both above and below the Redfield ratio at different times of year. Mean nutrient ratios for VA, CH and BH combined indicated N limitation during summer months with potential P limitation in winter. These elevated winter N:P ratios were most likely attributable to oversupply of N during times of high river flow. With the single exception of June 2002 N:P ratios at the WI site were persistently above the Redfield ratio indicating almost permanent P limitation. In Elkhorn Slough N:P ratios exceeded the Redfield ratio each year in January, as with South Slough the elevated N:P ratios at this time corresponded with times of reduced salinities suggesting high freshwater flow and were most likely the cause of the oversupply of N. At all other times nutrient ratios lay below the Redfield ratio illustrating the strong marine influence and suggesting potential N limitation throughout. Though nutrient data were collected less frequently for the Tijuana River estuary, N:P ratios were consistently below the Redfield ratio except on 2 occasions where elevated ratios were (as in the other estuaries) associated with high freshwater input.

Though the salinity regimes were very different in each estuary, and the land uses in the watersheds also varied, the estuaries all showed a similar horizontal distribution of macronutrient ratios and potential limitation. The molar ratios of N:P indicated that N was typically the potentially limiting nutrient in lower estuary sites in all estuaries (and throughout Elkhorn Slough) and P was potentially limiting at sites where freshwater dominated (WI, SE, JLS and RC). A temporal pattern in potential nutrient limitation was also common to South Slough, Elkhorn Slough and the Tijuana Estuary estuaries with potential P limitation occurring in winter at times of highest freshwater inputs, however during winter low light conditions and high freshwater flows which reduced residence times of the estuaries probably combined to prevent any actual nutrient limitation from occurring.

Maximum nutrient concentrations, the ratio of NH₄ to DIN and N:P ratios suggest that anthropogenic nutrient sources were apparent in all estuaries and though the horizontal distribution of macronutrient ratios followed a similar pattern the concentrations of DIN

and PO₄ observed in each estuary strongly reflected the differing conditions of the surrounding watersheds. The Tijuana Estuary and Elkhorn Slough and the JLS site in Padilla Bay had highest levels of nutrients. In the Tijuana estuary the greatly enhanced nutrient concentrations reflected the large inputs of sewage to this system (Zedler *et al.*, 1992), PO₄ concentrations in particular showed greater elevation than in other estuaries. Maximum PO₄ concentrations in much of Elkhorn Slough also exceeded the “high” limit but the elevation of PO₄ was not as pronounced as in Tijuana. In Elkhorn Slough and at the JLS site in Padilla Bay the high nutrient concentrations may be attributed to agricultural fertilizer sources (Muller-Parker & Peele, 1998; McLaughlin *et al.*, 2006, Caffrey *et al.*, 2007) but in the JLS site in Padilla Bay N alone was elevated. Overall South Slough showed least evidence of altered nutrient concentrations and ratios.

e.5. Relationships between Nutrients and Other Water Parameters:

Linear regressions of nutrients with salinity were carried out at each site where nutrient time series were conducted (BV, CH, SM and OS). Table 3 (a,b) summarizes the results of the nutrient regressions in each estuary and Figure 6 illustrates the monthly mean strength (r^2) and direction (sign of slope) of DIN regressions with salinity. Full details of nutrient regressions with salinity are provided in Appendix I. For DIN a general pattern of strongly negative regressions in winter was apparent with a progression to positive or more weakly negative values in summer time and there was a statistically significant difference ($p < 0.01$) in the strength and direction (r^2 with sign of slope) between winter and summer. Regressions in winter had mean negative slope and r^2 of 0.313 and summer regressions had mean positive slope and weaker r^2 of 0.052. More than half of the regressions conducted for DIN with salinity at each estuary were statistically significant. In Padilla Bay 19 regressions showed increasing DIN concentrations with increasing salinity indicating that Puget Sound water was the chief source of DIN to Padilla Bay. Of 40 regressions in total only 3 showed statistically significant negative relationships between DIN and salinity. Though significant, these regressions typically explained less than half of the variability in concentrations of DIN suggesting that discreet freshwater inputs around Padilla Bay were not the main factor influencing nutrient concentrations within the open bay.

Regressions of DIN with salinity in South Slough showed strongest correlation coefficients of any of the estuaries and regression in either direction explained more than half of the observed variability (Table 3). Salinity was negatively correlated with DIN in 24 of 32 statistically significant regressions indicating a predominant freshwater DIN source. Eight regressions of DIN with salinity showed positive slope, indicating a marine DIN source. Generally the correlation coefficient of the regression with negative slope was stronger than those with positive slope. Positive correlations were most common in the dry season with negative correlations being strongest and more common in the rainy season. In summer, statistically significant regressions of DIN with salinity having positive slope, predicted DIN concentrations to fall to zero at an average salinity of 31.6 psu. Synoptic measurements of DIN from the upper estuary sites on these dates had measurable quantities of DIN. The discrepancy between the DIN concentrations predicted by the regressions and the larger concentrations measured in fresher waters

indicates a significant sink of nitrogen within the estuary and the predicted salinity where DIN falls to $0\text{mg}\cdot\text{l}^{-1}$ corresponds to typical salinities around the VA site where eelgrass beds are abundant (Everett *et al.* 1995; Rumrill, 2006).

Regression of DIN with salinity in Elkhorn Slough generally showed weaker correlation than in South Slough or Padilla Bay. Of 28 regressions, DIN was negatively correlated with salinity in 17 cases. Correlation coefficients for these regressions typically explained less than half of the variation in DIN. A further 3 regressions showed a positive relationship between salinity and DIN but these regressions were weaker again than the negative ones typically explaining less than 40% of the observed DIN variability.

Fewer data were available for regressions in the Tijuana estuary. Of 8 significant regressions for DIN with salinity, four were positive and four negative. Negative regressions showed stronger mean correlation coefficients, on average explaining less than 50% of variability.

The results of the nutrient regressions indicate a common seasonal pattern in DIN supply to the estuaries; with freshwater sources being prevalent in winter months and marine sources of increased importance in summer months. For Padilla Bay this pattern was less pronounced, here marine nitrogen sources predominated except in the months of November, December and January indicating the minor freshwater inputs to this site. The effects of high rainfall events and consequent elevation of nutrient DIN concentrations was apparent in South Slough, Elkhorn Slough and the Tijuana Estuary. Many studies of Pacific coast estuaries have demonstrated the importance of upwelling as a summer source of both nutrients and chlorophyll to estuaries (Colbert & McManus, 2003; Hickey & Banas, 2003; Sigleo *et al.*, 2005). A similar pattern is apparent in this data with positive relationships being observed between nutrients and salinity in summer months. This temporal pattern in the significance and direction of DIN regressions with salinity suggest that on the large scale, summer DIN supply to estuaries from upwelled marine sources is a widespread phenomenon on the Pacific coast.

Figure 9 illustrates the monthly mean strength (r^2) and direction (sign of slope) of PO_4 regressions with salinity. For regressions of PO_4 with salinity there was no statistical difference in the strength and direction of relationships (r^2 and sign of slope) between seasons. In Padilla Bay, and the Tijuana Estuary half or fewer of PO_4 regressions with salinity were statistically significant. For Padilla Bay significant regressions of PO_4 with salinity typically explained less than half of the variability in observed nutrient concentration. In South Slough and the Tijuana Estuary significant regressions either positive or negative in direction typically accounted for greater than 60% of the variability in nutrients. In South Slough almost 70% of regressions were significant, negative correlations of PO_4 with salinity (indicating a freshwater PO_4 source) were more common than positive correlations. The temporal pattern in the direction of PO_4 correlations with salinity at South Slough showed a consistently marine source during winter months with freshwater sources being prevalent in summer months. This is the opposite of the pattern showed for DIN and the opposite of the pattern in PO_4 concentrations. This pattern was counter-intuitive given that if freshwaters were the

major PO₄ source, elevated concentrations would be expected during winter when freshwater inputs were at their highest. In Elkhorn Slough just over half of regressions were significant and positive regressions of PO₄ with salinity were more common than negative ones and positive regressions typically explained more of the variability than negative ones suggesting that marine waters were an important source of PO₄.

There was less similarity between estuaries in the seasonal patterns of PO₄ supply than there was for DIN, with South Slough having a different pattern than the other estuaries. The regressions of PO₄ in Padilla Bay, the Tijuana Estuary and Elkhorn Slough followed a similar temporal pattern to that of DIN though a lower proportion of total regressions were statistically significant

Figure 10 illustrates the mean values predicted for DIN and PO₄ in freshwater from statistically significant regressions with negative slope in each estuary. Freshwater DIN and PO₄ concentrations were significantly higher in the two southerly estuaries ($p < 0.01$). Fresh waters entering the Tijuana Estuary had concentrations of DIN six times those of Padilla Bay, eight times higher than South Slough and twice as high as Elkhorn Slough. PO₄ concentrations showed a similar pattern being 8 times higher than those in Padilla Bay, six times higher than South Slough and 5 times higher than Elkhorn Slough. In South Slough the mean predicted freshwater concentrations of PO₄ from statistically significant linear regression with negative slope at the CH (0.34 mg.l⁻¹) site was 11 times higher than the mean measured PO₄ concentrations in the at VA (0.05 mg.l⁻¹) and 42 that of the WI site (0.015 mg.l⁻¹). This difference in predicted and observed nutrient concentrations was statistically significant ($p < 0.05$) and indicates a significant source of PO₄ located between the CH and VA sampling stations. This localized P source is probably attributable to the small scale urbanization around the Charleston area at the mouth of South Slough. This elevated source of PO₄ helps to explain the unexpected temporal pattern in PO₄ regressions. Large freshwater flows with low P concentrations in winter probably serve to dilute the localized anthropogenic PO₄ signal resulting in the positive slopes of regression of PO₄ in winter. By contrast in summer low freshwater flows do not dilute the anthropogenic source and summer regressions indicate a freshwater P source. However while the regressions indicate the concentrations of PO₄ in this freshwater source, there are not data to indicate the magnitude of the water flux associated with these high concentrations. Due to the volumes involved in tidal advection marine waters still most likely represent the major source of P to upper estuary sites.

e.6. Variability in Estuarine Chlorophyll Concentrations:

Chlorophyll concentrations showed great spatial variability between sites and temporal variability within sites. Mean concentrations at all sites except JLS in Padilla Bay and NM in Elkhorn Slough lay in the “low” (<5 mg m⁻³) chlorophyll categories of Bricker *et al.* (1999). These two exceptions (JLS and NM) had mean chlorophyll concentration in the “medium” category (>5 mg m⁻³) and maximum chlorophyll concentrations at these two sites exceeded the hypereutrophic category (>60 mg.m⁻³) of Bricker *et al.* (1999). In addition, “high” (>20 mg m⁻³) maximum chlorophyll concentrations were observed in Padilla Bay (GS), South Slough (VA) and Elkhorn Slough (SM). In the Tijuana estuary

maximum chlorophyll concentrations of $14.6 \text{ mg} \cdot \text{m}^{-3}$ and $14.7 \text{ mg} \cdot \text{m}^{-3}$ were observed at the MM and OS sites respectively falling within the “medium” category.

In Padilla Bay, South Slough and Elkhorn Slough there were significant differences between mean wet and dry season chlorophyll concentrations. Dry season chlorophyll concentrations ($6.2 \text{ mg} \cdot \text{m}^{-3}$) were four times those of the rainy season in Padilla Bay and in South Slough dry season chlorophyll concentrations ($3.6 \text{ mg} \cdot \text{m}^{-3}$) were almost twice those of the rainy season. In Elkhorn Slough this seasonal difference was less significant ($p < 0.05$) but dry season chlorophyll concentrations ($4.4 \text{ mg} \cdot \text{m}^{-3}$) were again twice those of the rainy season. There was no statistically significant difference between rainy and dry season chlorophyll concentrations in the Tijuana Estuary. There was great variability in the timing of maximum chlorophyll concentrations in each estuary. No consistent timing for a spring bloom in chlorophyll was found at any site nor was there a consistent relationship between chlorophyll and upwelling.

Linear regressions of ln transformed DIN and chlorophyll data in the two northerly estuaries all showed statistically significant negative relationships (Table 4). Chlorophyll concentrations were highest when DIN concentrations were lowest at all sites. In Padilla Bay the relationships were stronger in the open part of the bay than in JLS. In South Slough stronger relationships were observed in the upper estuary sites (WI, VA) and weaker relationships occurred at the BH and CH sites. In Elkhorn Slough a weak but significant relationship between ln transformed chlorophyll and DIN was observed at the NM station. At all other stations in Elkhorn Slough and the Tijuana estuary there was no significant relationship between chlorophyll and DIN concentration.

Linear regressions of ln transformed PO_4 data with chlorophyll in Padilla Bay showed significant negative relationships at all sites except JLS. There was a significant positive relationship between ln Chlorophyll and ln PO_4 at the WI site in South Slough and at the AP site in Elkhorn Slough, a very weak but significant relationship was observed. A very weak but significant negative correlation was found between ln PO_4 and ln chlorophyll at the CH site in South Slough. No significant relationships were found between PO_4 and ln chlorophyll in the Tijuana Estuary.

To a lesser extent than nutrient concentrations, the chlorophyll concentrations measured at each site reflected the pattern in degree of anthropogenic disturbance. The chlorophyll response of estuarine systems to excessive nutrient loading is highly variable (Cloern, 2001) and can be affected by light availability; mixing depth; residence time or grazing by zooplankton or macrofauna. In this study, JLS and NM had chlorophyll concentrations in the hypereutrophic category showing direct response to nutrient loading, at both these sites significant linear relationships between chlorophyll concentration and DIN concentrations were also observed. However at all other sites in Elkhorn Slough, and in the Tijuana estuary, the lack of significant relations between DIN and chlorophyll indicated decoupling of nutrient supply and chlorophyll concentrations. In the Tijuana estuary chlorophyll concentrations never exceeded the “medium” category despite the fact that this estuary showed by far the highest nutrient concentrations. In the case of the Tijuana Estuary, which displays elevated nutrient sources but lacks similar

response in elevated chlorophyll concentrations some other factor must limit chlorophyll concentrations. Dry season residence times in this estuary are long (Zedler *et al.*, 1992), and therefore unlikely to be a limiting factor. Though water depths were low, high turbidity may have resulted in light limitation of phytoplankton. High turbidity may also play a role in the decoupling of nutrient and chlorophyll concentrations in Elkhorn Slough (Zimmerman & Caffrey, 2002). Elkhorn Slough is a known sink for nitrogen (Chapin *et al.*, 2004) and biological elements other than the phytoplankton, in particular green algae which are abundant in the estuary (Caffrey *et al.*, 2007) may demonstrate more of a response to nutrient loading than the phytoplankton, this may be particularly true in the better flushed lower estuary, where residence times can be limiting to phytoplankton growth.

In the two northerly estuaries nutrient sources sinks and dynamics were more readily apparent. The consistent significance of the linear regressions between chlorophyll and the DIN in the two northerly (less eutrophic) estuaries illustrates tight coupling between the chemical and biological elements of the system. Significant linear relationships between $\ln\text{PO}_4$ and \ln Chlorophyll were also found in the main channel sites at Padilla Bay. Since N limitation of both phytoplankton and seagrasses is known to occur in Padilla Bay (Bernhard & Peele, 1997; Muller-Parker & Peele, 1998 Bulthuis & Marjerum, 2005) these relationships may simply reflect the coincidence of maximum seasonal drawdown of P with maximum summer chlorophyll concentrations. A positive relationship between PO_4 concentration and chlorophyll occurred at the WI site in South Slough. N:P ratios at this site suggest P limitation, and this significant linear suggests that increased P supply increases productivity at this site.

e.7. Variability in Oxygen Concentrations and Temperature:

Figure 12 illustrates the spatial variability in the mean duration of oxygen stress events at each site. In each estuary, sites with more marine influence; the main channel sites in Padilla Bay (GS, BV and PO); VA and CH in South Slough; SM and VM in Elkhorn Slough and OS and MM in the Tijuana Estuary had less stress than the sites in each estuary with higher freshwater influence. Distinct cycles in oxygen concentration were apparent in each estuary on different timescales. The typical daily pattern for summer oxygen concentrations for each estuary is presented in Figure 12b. On a daily basis oxygen concentrations declined from midnight and in the early part of the day. The duration of these declining oxygen periods increased with decreasing latitude. In Padilla Bay, this early morning period lasted approximately 3 hours, while in the Tijuana Estuary the period lasted approximately seven hours with oxygen concentrations declining from stressed to hypoxic conditions over that time. After the morning decline, oxygen concentrations began to increase reaching maxima at 13:00h in Padilla Bay, 15:00h in South Slough and Elkhorn Slough and peaking in the Tijuana Estuary at around 17:00h. Following these peaks oxygen concentrations again began to decline to their early morning levels. The magnitude of the variation in daily oxygen concentrations was greater in the more southerly estuaries and least in the northerly estuaries.

Oxygen stress ($<5\text{mg.l}^{-1}$) occurred in all the estuaries. The amount of time spent under oxygen stress varied from site to site. In Padilla Bay the three sites in the main channel (BV, PO and GS) experienced oxygen stress for less than 3% of the study period while the JLS site experienced oxygen stress or hypoxia for 33% of the time. In South Slough no oxygen stress occurred at the CH site but there were minor occurrences at the WI and VA sites ($<5\%$ of the study period). The SE site experienced oxygen stress or hypoxia for 17% of the study period. In the two southerly estuaries depleted oxygen concentrations were more prevalent. In Elkhorn Slough the AP and NM sites had 46% and 47% combined hypoxia and oxygen stress respectively while the SM and VM sites had 15% and 2% respectively. In the Tijuana estuary oxygen stress and hypoxia existed 71% of the time in the RC site and 66% of the time at TL. Figure 12 c, d, e, f, illustrates the relative proportions of the study period spent under oxygen stress, hypoxia and anoxia at each of the most effected sites in each estuary. Figure 13 illustrates the seasonal cycle in the timing of oxygen stress events at representative sites from each estuary. In the worst effected sites, seasonal cycles were not as pronounced, due to the continual occurrence of oxygen stress. In Padilla Bay oxygen stress was generally short lived on a daily basis and was most pronounced from June to September. At SE in South Slough oxygen stress events though generally occurring less than 10 hours per day recurred throughout most of the year being, absent mainly in the months of January and February. The duration of oxygen stress events at the SE site in South Slough was positively correlated with mean monthly upwelling index ($r^2=0.71$ $p<0.01$) and this correlation improved when a lag period was included ($r^2=0.74$ $p<0.01$; Figure 14). At the SM site in Elkhorn Slough, oxygen stress events generally occurred from June to December and could occur for most of a day however between January and June this site experienced little in the way of oxygen stress. The timing and occurrence of anoxic events in the AP site in Elkhorn Slough has been shown to be linked to differences in flushing rates due to changes in tidal inundation over the spring neap cycle (Beck & Bruland, 2000), these authors identified periods of “hyperventilation” at this site. Data from this study show that this hyperventilation is a continuing phenomenon.

Figure 13 shows a linear relationship between mean number of hours of oxygen stress per day for each year and the mean annual temperature at each site. The number of hours of oxygen stress per day increased linearly with temperature, consequently maximum durations of stress occurred in the more southerly estuaries.

Oxygen concentrations in the estuaries reflected both the supply of nutrients to the estuaries and the seasonal variations in water temperatures and the degree of influence from marine waters. Variability of oxygen concentrations was observed over several different timescales. On a daily basis the availability of light drove the photosynthesis/respiration cycle in each estuary. The estuaries and sites within estuaries more heavily impacted by nutrient inputs showed larger daily ranges in oxygen concentrations and the regular daily cycles in oxygen led to the occurrence of hypoxia on a daily basis in the Tijuana estuary and daily occurrence of oxygen stress in Elkhorn Slough and South Slough. In Padilla Bay, which has shown to be net autotrophic (Sanger *et al.*, 2002) oxygen concentrations showed less pronounced daily fluctuations except at the JLS site. The relationship between upwelling and oxygen stress at the South Slough SE site

indicates the sensitivity of this relatively undisturbed system to the influx of upwelled marine nutrients. Nutrient ratios and the significant positive relationship between chlorophyll and PO_4 at the WI site (which experiences a similar salinity regime) suggest that stimulation of productivity by P is responsible for the oxygen stress, while the lag between the upwelling and the oxygen stress at the SE site is due to the increased respiration following increased productivity. The significant relationship between duration of oxygen stress and mean annual temperature indicates that geographic location is generally an important factor in determining the predominant oxygen conditions that occur within the Pacific coast estuaries. Notable outliers in this relationship were JLS in Padilla Bay and the RC site in the Tijuana estuary, which were also the sites with the highest mean DIN concentrations; when these sites were omitted from the plot the r^2 value for the relationship rose to 0.86 ($p < 0.01$). Estuary water temperature and nutrient supply are the two most important factors controlling the occurrence of oxygen stress. Overall this relationship indicates that the role of nutrient loading in estuarine eutrophication is secondary to that of temperature.

e.8. Long-Term Trends in Estuary Water Parameters:

Long term trends in temperature at BV in Padilla Bay, WI, SE and VA in South Slough and AP, NM and SM in Elkhorn Slough showed positive correlations with the Pacific Decadal Oscillation (Table 5). At these sites the temperature trends showed a decline in temperature from the years 2000 to 2002 and an increase from early 2002 to early 2005 when they again began to decline (Figure 15). The mean range in monthly averaged baseline temperature over the 6 year period was 2.1°C (s.d.=1.3). The greatest ranges in baseline temperatures were observed at AP in Elkhorn Slough (2.4°C) and WI in South Slough (4.6°C). At three of the sites (WI, VA and SM) where temperature was correlated with PDO, long term trends in oxygen concentrations showed negative correlation with the PDO (Figure 16). A significant negative relationship between oxygen trend and PDO was also apparent at the Tijuana Estuary MM site. The mean range in monthly averaged DO baseline concentrations for these sites was 2.1°C (s.d.=1.6). While salinities at some sites (JLS, BV, WI and NM) showed significant correlations with PDO, the sign of these correlations was not consistent. At JLS and NM salinity was negatively correlated with PDO, at BV and WI salinity trend was positively correlated with PDO (Figure 17).

The response of different sites in the estuaries to long term climate conditions varied, with some sites showing strong signals in temperature and oxygen conditions and some sites apparently not responding at all to PDO in terms of temperature or oxygen. It is notable that the NM site in Elkhorn Slough and the VA site in South Slough which of all sites subjected to long term trend analysis experienced the most marine influence and each had correlation of both temperature and oxygen to the PDO. The reasons why some sites showed correlations in temperature and not oxygen or no relationship in any variable to the PDO could be attributed to phenomena within the estuaries on timescales less than 1 year but without regular periodicity. For instance at the BV site in Padilla Bay temperature and salinity reflect the PDO but there was no similar pattern in oxygen. It is possible that variations in the dynamics of the eelgrass ecology produced non-periodic

components in the data on timescales less than 1 year and that these variations effected produced long term variability at this site without a regularly period. Similarly the relationship which was observed between upwelling and oxygen stress at the SE site in South Slough may interfere with the signal caused by PDO, since upwelling events occur without definite periodicity and the statistical process used to remove seasonal effects was based on the removal of phenomena with periodic occurrences. Of all the estuaries the Tijuana River estuary showed least response to the effects of the PDO, the intermittent connection of some of the Tijuana River estuary sites with the open ocean may explain why PDO signals were not observed at these sites.

The positive correlation at some sites between long-term patterns in estuary water temperature and the PDO illustrate that water quality parameters in these estuaries were sensitive to long-term climate fluctuations. The corresponding negative correlations with dissolved oxygen illustrate that the prevailing climate conditions effect the baseline environments upon which anthropogenic effects are superimposed. However, while the relationship between the PDO and the long-term trends in oxygen and temperature was consistent at all sites where it was observed, long-term salinity trends by contrast varied in their relation to the PDO with negative correlations apparent at some sites and positive correlations apparent at other even within the same estuary. The differing direction of these relationships may be the consequence of the unique physical dynamics and subtleties of local physical oceanographic forcing factors.

f. Conclusions:

Previous studies have pointed out the geographical similarities of estuaries on the U.S. west coast (Emmett *et al.*, 2000) and many studies point to the impacts of the seasonal upwelling events and freshwater inputs on nutrient dynamics of west coast estuaries. (Roegner & Shanks 2001; Colbert & McManus, 2003; Hickey & Banas, 2003; Sigleo *et al.*, 2005). A previous comparison of the four estuaries in this study indicated differing degrees of anthropogenic nitrogen impacts in the estuaries with Tijuana Estuary and Elkhorn Slough being heavily impacted and South Slough and Padilla Bay less so (Fry *et al.*, 2003). This synthesis of SWMP monitoring data sought to identify climatic and oceanographic forcing of water quality and nutrient patterns on annual and interannual timescales to identify whether these four ecosystems shared similar reactions to these large scale forcing processes. An additional goal was to compare the degrees of anthropogenic stress between estuaries and examine the extent to which anthropogenic nutrient inputs may influence these four distinct Pacific coast estuaries.

Ambient weather conditions in Padilla Bay differ from those of the other three estuaries in this study in that the seasonal pattern in temperature was more pronounced than at the other estuaries, this was probably due to a continental influence because of its location considerably inland of the open ocean. Padilla Bay is a large tidal orphan estuary with extensive seagrasses, a broad connection to Puget Sound waters and low freshwater inputs. The physical characteristics of the main body of the estuary are determined by tidal exchange with the surrounding waters. Nutrient sources to the bay are chiefly from Puget Sound waters. The bay undergoes pronounced seasonal cycles in the concentrations

of nitrogen and phosphorus and experiences seasonal nitrogen limitation. Nutrient ratios suggest nitrogen is the limiting macronutrient within Padilla Bay. Summer concentrations of nutrient within the bay are determined both by the conditions in Puget Sound waters and by nutrient uptake in the seagrass meadows and from phytoplankton. Despite the high nutrient concentrations observed in the freshwater inputs caused by intensive local agriculture, the bay experiences little in the way of oxygen stress or hypoxia. Though extreme maximum chlorophyll concentrations were observed in the JLS site, and occasional elevated concentrations were observed in the open part of the bay, disturbance to the site seems to be limited by the rapid tidal exchange; the presence of the eelgrass beds and the relatively minor size of the eutrophied freshwater inputs. Long term trends in temperature at the BV site were correlated with the PDO but such correlation was not apparent in oxygen concentrations this may be due to the influence of the extensive eelgrass beds.

South Slough in Oregon is also relatively undisturbed estuary. Unlike Padilla Bay, South Slough experiences large seasonal freshwater inputs and freshwater dominates the upper estuary even during the summer months. There was a gradient of nutrient limitation from P limitation in fresher waters to N limitation in waters with more marine influence. Nutrient sources to the estuary underwent a pronounced seasonal cycle with freshwaters providing nitrogen during the rainy season and marine waters acting as a supplemental nutrient source in summer. In summer upwelled nutrient rich marine waters provided a source of P to the upper estuary Sengstacken site, which showed a biological response in terms of enhanced respiration and an increasing amount of oxygen stress. A strong signal of anthropogenic P was apparent during the dry season around the mouth of the estuary which is probably related to the local urbanization. In the middle part of the estuary nutrient regressions indicate a sink of nitrogen which corresponds in its salinity range to the location of eelgrass beds. Long term trends in temperature showed positive relationships at the WI and VA sites and corresponding negative trends in oxygen concentrations were observed. Though the same trend in temperature was apparent at the SE site, a similar trend in oxygen was not detected, this may be due to the control of oxygen concentrations at the SE by production stimulated by upwelled nutrients, the irregular timing of upwelling events may have caused interference to any underlying trends caused by the PDO.

In Elkhorn Slough the physical characteristics of the water were dominated by marine inputs and in summer evaporation results in the prevalence of hypersalinity in the upper estuary sites. Potential nitrogen limitation dominated throughout and seasonal pulses of freshwater resulted in elevated N concentrations and intensive local agriculture results in a eutrophied system. The seasonal cycle in nutrient supply to this estuary was not as pronounced as in South Slough and both nitrogen and phosphorus only showed weak relationships with salinity. There was some evidence, however, for summer supply of nutrients from the marine end, a phenomenon which has been observed in this estuary in previous studies (Chapin *et al.*, 2004). While the response of chlorophyll concentrations to elevated nutrient concentrations was not marked in much of the estuary, being sporadically high at SM and NM sites, oxygen conditions within the water column and the prevalence of NH_4 over DIN indicated that decomposition of organic matter played a

dominant role in the geochemical cycling and indicated the severity of eutrophication. Long-term trends in temperature and oxygen consistent with the patterns found at the VA and WI sites in South Slough also occurred at the SM site in Elkhorn Slough. At the AP site and the NM site similar trends in temperature but not oxygen were detected. The absence of a consistent trend in oxygen may again be related to non periodic components in the oxygen time series caused by the dynamics of growth and decay of autotrophs at these locations.

The Tijuana River estuary is characterized by variability in prevailing conditions. Like South Slough and Elkhorn Slough freshwater inputs to the Tijuana estuary were highly seasonal. Nutrient concentrations within this estuary were greatly elevated due to inputs of sewage, and though chlorophyll concentrations were not greatly elevated oxygen conditions in the water column underwent prolonged periods of anoxia and hypoxia. As in Elkhorn Slough the Summer DIN pool was dominated by NH_4 indicating that organic matter decomposition was also a dominant process in this Estuary. Of the two sites with sufficient data for examination of long term trends in the Tijuana estuary neither showed a relationship between temperature trend and the PDO, though a negative relationship between oxygen and the PDO was observed at the MM site.

A common pattern in the seasonal supply of DIN to the four estuaries was apparent with freshwater supplies dominating in winter and upwelled marine waters acting as a source of DIN in the summer. This pattern, elucidated through nutrient regressions was strongest at South Slough and weakest in Padilla Bay. The seasonal pattern in P supply was similar in all estuaries except South Slough, where a localized anthropogenic P source dominated the regression patterns in summer, however supply of P to the upper estuary in South Slough probably has a chiefly marine source as in the other estuaries due to its large tidal prism.

The lack of strong temporal patterns in chlorophyll concentrations (apart from the general increase during the dry season and reduction in the rainy season) may reflect the relative infrequency of chlorophyll measurements and aliasing of phytoplankton growth phenomena.

There was a general relationship between the duration of oxygen stress and the mean annual temperature at each site. This relationship suggests that latitude plays an important role in the dominance of autotrophy over heterotrophy in these estuarine environments and that estuaries experiencing warmer water temperatures are more susceptible to the occurrence of hypoxia and anoxia and consequently more vulnerable to anthropogenic stress. Long term variations in baseline temperatures (when the effects of seasonal cycles were removed) showed correlation with the Pacific Decadal Oscillation, and in turn some baseline oxygen concentrations at some of these sites reflected the long term temperature trends. These results suggest that climate fluctuations can impact the ambient concentrations of oxygen in estuaries and that warming trends could increase the degree of oxygen stress and hypoxia experienced within these estuaries. However not all sites at all estuaries showed the influence of the PDO and some examples existed where the variability in temperature with PDO was not reflected

in the trends in oxygen or vice versa. Thus while it is apparent that long term climate fluctuations have a measurable effect on estuarine water quality parameters, these effects varied from site to site, depending on the degree of marine influence at each site within an estuary as well as local dynamics including biological and short timescale phenomena such as upwelling events.

The four estuaries in this study differ in latitudes, morphologies and degree of anthropogenic disturbance but similarities exist in their physical structure in that they are all shallow and generally vertically well-mixed. The combined action of shared seasonal influences and different physical, chemical and biological dynamics experienced at each estuary results in the unique combinations of nutrient and chlorophyll concentrations and oxygen stress events in each estuary.

3. Utilization

a. End User Application

Tidal waters that flow into and out of the relatively small Pacific coast estuaries support a diversity of living resources, including waterfowl, shorebirds, fish, shellfish, invertebrate communities, zooplankton, phytoplankton, and submerged vegetation (Emmett *et al.*, 2000). The ebb and flow of tidal waters also serves several essential human uses, including conveyance of stormwaters and floods from riverine sources to the ocean, transport and flushing of waterborne nutrients and wastes, redistribution of suspended and bedload sediments, and provision of a convenient corridor for recreational boating, shipping, and maritime commerce. Despite widespread recognition that tidal waters provide these essential ecological and social services, the short-term variability and longer-term spatial and temporal changes in estuarine water parameters are still poorly understood for estuaries located along the Pacific coast of the United States (Bricker *et al.*, 1999; Emmett *et al.*, 2000; Colbert and McManus, 2003; Benoit *et al.*, 2004).

The information generated by this investigation provides a better understanding of the scope of variability in the seasonal differences between oceanic forcing versus watershed inputs for four representative Pacific coast estuaries. End-users of the information should be able to compare and contrast the seasonal and longer-term dynamics of the estuaries into their understanding of the regional similarities and differences that occur along the Pacific coast, and incorporate the improved understanding into more accurate and realistic assessments of the ecological condition of the Pacific coast estuaries.

b. Knowledge Exchange

Information generated by this project will be shared with all of the project participants and with the coastal modelers and oceanographers who are active in development of the Pacific coast Regional Associations (RAs) of the US Integrated Ocean Observing System (IOOS). The results and findings from this regional data synthesis will also be shared freely with the local and state-wide coastal management communities in California, Oregon, and Washington to ensure that the data analysis and interpretations are available

to meet their requests for more recent case-history characterizations for the different types of estuaries that occur along the Pacific coast of the United States.

c. Partnerships and Intellectual Property

Information generated by this investigation is freely available to the community of NERRS staff members, coastal resource managers, academic scientists, private-sector investigators, and any others who may wish to use the analyses and/or interpretations of the NERR SWMP time-series datasets.

4. Next Steps to Application

The overall goal of this investigation is to compare and contrast the dynamics of riverine inputs and oceanic forcing across the different estuarine systems that span the Pacific coast of the continental United States. Our analyses of the NERR SWMP time-series measurements should provide a baseline understanding that can be applied directly to future national and regional assessments of the ecological status and condition of coastal and estuarine ecosystems. In particular, the analyses and interpretations contained in this report should be taken into consideration with regard to the findings of the most recent USEPA/NOAA National Coastal Condition Report III (2007) and the NOAA National Eutrophication Report (2007). Information to characterize the timing and extent of oceanic and watershed influences within the Pacific coast estuaries should also be incorporated into future editions of these important national and regional assessments.

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