DISSOLVED NITRATE AND PHOSPHATE CONCENTRATIONS IN SAN FRANCISCO ESTUARY SURFACE WATERS: SPATIAL DISTRIBUTION (2002-2009) AND TEMPORAL TRENDS (1993-2009)

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Introduction

Historically, the San Francisco Estuary has been considered a low primary productivity estuary, despite having relatively high concentrations of nutrients. The low primary production has been attributed to the Estuary being light-limited due to high suspended sediment concentrations and the high energy of wind-wave action. However, recent changes in phytoplankton community structure and Bay ecology, decreases in dissolved oxygen, and a decrease in suspended sediment concentrations have raised concerns about the Estuary's ability to continue to be resilient to the impacts of continuing nutrient loads.

Objective

The Regional Monitoring Program for Water Quality in the San Francisco Estuary (RMP) has monitored nutrients using a targeted sampling design since 1993, and beginning in 2002, a probabilistic sampling design employing the US EPA's Generalized Random Tessellation Stratified (GRTS) sample design. Dissolved nitrate and phosphate concentrations from samples collected at the probabilistic stations (2002-2009) were investigated for spatial distributions, while concentrations from samples collected at five fixed historic stations (1993-2009) were examined for temporal trends (Figure 1).

Figure 1.
RMP water sampling map showing fixed historical stations (1993-2009), and Generalized Random Tessellation Stratified (GRTS) random stations (2002-2009).

Bathymetry data from the CaDFG, 2002
Map datum and projection:
NAD 1983 California Teale Albers.
Map: Created by Marcus Klatt, SFEI in September of 2011.

Methods

SPATIAL COMPARISONS

GRTS sites are allocated into five hydrographic regions of the Estuary: Suisun Bay, San Pablo Bay, Central Bay, South Bay, and Lower South Bay. Regional means, standard deviations, and cumulative distribution functions (CDFs) were calculated using the R statistical software environment (http://www.r-project.org/), and version 2.2 of the spsurvey statistical library (http://www.epa.gov/nheerl/arm/analysispages/software.htm) which was designed by the US EPA specifically for the statistical analysis of GRTS spatial survey designs.

Differences between estimated CDFs were evaluated using the F distribution version of the Wald statistic, with nondetects replaced with one-half the method detection limit. Substitution, however, can produce an invasive pattern alien to the concentrations actually in the samples, resulting in generally poor estimates and incorrect statistical tests (Helsel, 2005; Helsel 2009). Therefore, differences between the dissolved nitrogen cumulative distribution functions were also investigated using a Generalized Wilcoxon (Score) Test for censored data followed by multiple pairwise comparisons (Helsel, 2005). Comparisons were considered significant at a Bonferroni corrected alpha of 0.005.

TEMPORAL TRENDS

At each station without nondetects trends were examined by ordinary least squares (OLS) linear regression analysis using untransformed concentrations as the dependent variable, and sampling date as the independent variable. Normality of the residuals was considered using the Anderson-Darling test, and when sufficient evidence was observed to reject the null hypothesis of normality (p<0.10), attempts were made to normalize by transforming the data. If data transformation was unsuccessful, then a robust regression analysis was conducted using an M-estimation robust regression technique called iteratively reweighted least squares (Chatterjee and Machler, 1997). The presence of first-order autocorrelation was examined using the Durbin-Watson test, but no conclusive evidence of first-order autocorrelation was found in the data.

Trends at each station with nondetects were evaluated by the Akritas-Thiel-Sen method for censored data (Helsel, 2005) using untransformed concentrations as the dependent variable, and sampling date as the independent variable. Unusual observation, observations with standardized residuals >2 or <-2, were identified in the majority of the regressions, but lacking a reason for exclusion were considered extreme, but valid measurements (US EPA, 1992). A significant positive slope (p<0.05) was assumed to indicate an increase at the station over time. Similarly, a significant negative slope assumes a decrease over time, while a lack of significance indicates no change in water concentration over time.

Table 1.
Results of multiple pairwise comparisons between regional cumulative distribution functions (CDFs).

Pairwise Comparison	Wald_F	df1	df2	p	Bonferroni p	Significant
Nitrate						
Central Bay vs. Lower South Bay	6.84	2	66	**0.002**	0.005	Yes
Central Bay vs. South Bay	4.71	2	80	0.012	0.005	No
Central Bay vs. San Pablo Bay	3.76	2	54	0.030	0.005	No
Central Bay vs. Suisun Bay	4.15	2	53	0.021	0.005	No
Lower South Bay vs. South Bay	9.53	2	93	**0.000**	0.005	Yes
Lower South Bay vs. San Pablo Bay	0.70	2	67	0.498	0.005	No
Lower South Bay vs. Suisun Bay	2.86	2	66	0.064	0.005	No
South Bay vs. San Pablo Bay	9.02	2	81	**0.000**	0.005	Yes
South Bay vs. Suisun Bay	14.39	2	80	**0.000**	0.005	Yes
San Pablo Bay vs. Suisun Bay	0.74	2	54	0.484	0.005	No
Generalized Wilcoxon (Score) Test	Chi-Square	df		p		
	30.5923	4		**0.000**		
Pairwise Comparison						
Central Bay vs. Lower South Bay	1.60	1		0.206	0.005	No
Central Bay vs. South Bay	8.31	1		**0.004**	0.005	Yes
Central Bay vs. San Pablo Bay	2.84	1		0.092	0.005	No
Central Bay vs. Suisun Bay	6.95	1		0.008	0.005	No
Lower South Bay vs. South Bay	12.81	1		**0.000**	0.005	Yes
Lower South Bay vs. San Pablo Bay	0.06	1		0.812	0.005	No
Lower South Bay vs. Suisun Bay	0.75	1		0.386	0.005	No
South Bay vs. San Pablo Bay	19.36	1		**0.000**	0.005	Yes
South Bay vs. Suisun Bay	27.70	1		**0.000**	0.005	Yes
San Pablo Bay vs. Suisun Bay	0.54	1		0.461	0.005	No
Phosphate						
Central Bay vs. Lower South Bay	211.02	2	66	**0.000**	0.005	Yes
Central Bay vs. South Bay	49.92	2	80	**0.000**	0.005	Yes
Central Bay vs. San Pablo Bay	0.32	2	54	0.730	0.005	No
Central Bay vs. Suisun Bay	4.32	2	53	0.020	0.005	No
Lower South Bay vs. South Bay	52.81	2	93	**0.000**	0.005	Yes
Lower South Bay vs. San Pablo Bay	85.70	2	67	**0.000**	0.005	Yes
Lower South Bay vs. Suisun Bay	277.17	2	66	**0.000**	0.005	Yes
South Bay vs. San Pablo Bay	18.66	2	81	**0.000**	0.005	Yes
South Bay vs. Suisun Bay	108.80	2	80	**0.000**	0.005	Yes
San Pablo Bay vs. Suisun Bay	4.70	2	54	0.010	0.005	No

Results

SPATIAL COMPARISONS

Considerable variation was observed in the concentrations of dissolved and phosphate concentrations among the five estuary regions (Figure 2 and Figure 3). Mean dissolved nitrate concentrations in water were spatially distributed as Suisun Bay (0.324, sd = 0.131 mg/l), Lower South Bay (0.311, sd = 0.254 mg/l), San Pablo Bay (0.296, sd = 0.147 mg/l), Central Bay (0.235, sd = 0.101 mg/l), and South Bay (0.158, sd = 0.126 mg/l), and dissolved phosphate concentrations as Lower South Bay (0.348, sd = 0.102 mg/l), South Bay (0.185, sd = 0.053 mg/l), San Pablo Bay (0.126, sd = 0.070 mg/l), Central Bay (0.116, sd = 0.061 mg/l), and Suisun Bay (0.097, sd = 0.038 mg/l).

Significant differences were found between estimated regional CDFs for both dissolved nitrate and phosphate (Table 1). Dissolved nitrate concentrations were significantly lower in the South Bay compared to all regions except the Central Bay, while Lower South Bay concentrations were significantly higher than the Central Bay (Table 1, Figure 4). Pairwise comparisons after a significant Generalized Wilcoxon (Score) Test for censored data found significantly lower concentrations in the South Bay compared to all the other regions (Table 1). The difference in results due to the treatment of nondetects measured in several Central Bay, South Bay, and Lower South Bay water samples. Dissolved phosphate concentrations were significantly greater in the Lower South Bay compared to all the other regions, while concentrations in the South Bay were significantly greater than in San Pablo Bay, Central Bay, and Suisun Bay (Table 1, Figure 5).

TEMPORAL TRENDS

Analysis of temporal trends showed a significant decrease in dissolved nitrate concentrations at the Dumbarton Bridge (BA30: South Bay), and Golden Gate (BC20: Reference Site) stations (Table 2). No significant trends were found in dissolved phosphate concentrations.

Figure 2.
Spatial distribution of dissolved nitrate in the San Francisco Estuary generated by ordinary kriging of concentrations measured at Generalized Random Tessellation Stratified (GRTS) random stations (2002-2009).

Dissolved Nitrate (mg/L)
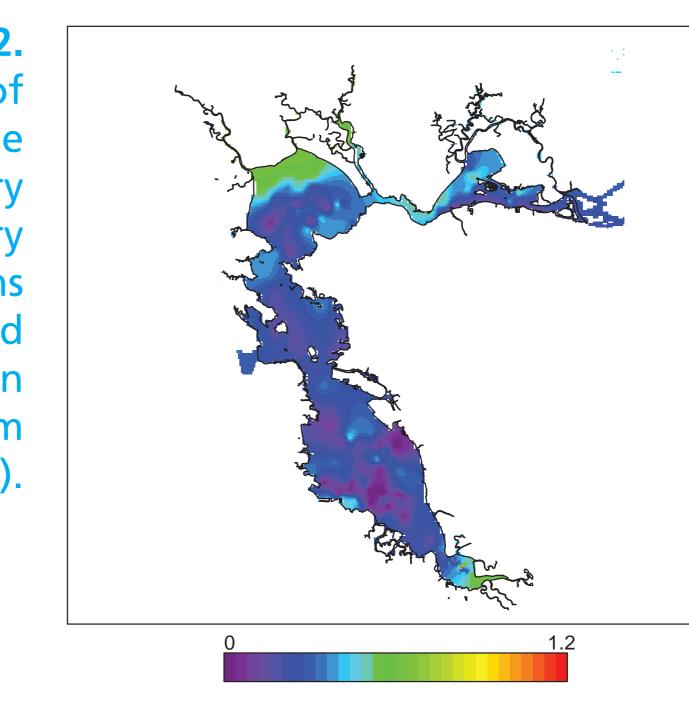
Figure 3.
Spatial distribution of dissolved phosphate in the San Francisco Estuary generated by ordinary kriging of concentrations measured at Generalized Random Tessellation Stratified (GRTS) random stations (2002-2009).

Dissolved Phosphate (mg/L)

Figure 4.
Estimated cumulative distribution function (CDF) plots for dissolved nitrate in the San Francisco Estuary, CA (2002-2009).

Figure 5.
Estimated cumulative distribution function (CDF) plots for dissolved phosphate in the San Francisco Estuary, CA (2002-2009).

Table 2.
Temporal trends in dissolved nitrate and phosphate concentrations at fixed historic San Francisco Estuary, CA Regional Monitoring Program stations, 1993–2009.

OLS = ordinary least squares, A-T-S = Akritas-Thiel-Sen, Robust = Iteratively Reweighted Least Squares (Chatterjee and Machler, 1997), na = not available.

Region	StationCode	StationName	Nondetects	Regression Type	Transformation	Slope	Intercept	n	p	adj-r²	Anderson-Darling (p value)	Durbin-Watson d	Interpretation	Unusual Observations
Nitrate														
Rivers	BG20	Sacramento River	No	OLS	None	-0.000001	0.300	34	0.876	0.0%	0.514	1.8828	Accept null	Yes
Rivers	BG30	San Joaquin River	Yes (1)	A-T-S	None	-0.000014	0.779	33	0.394	na	na	na	na	na
Central Bay	BC10	Yerba Buena Island	No	OLS	None	-0.000004	0.379	32	0.700	0.0%	0.581	2.2421	Accept null	Yes
South Bay	BA30	Dumbarton Bridge	No	OLS	ln(x)	-0.000059	2.56	33	**0.003***	22.7%	0.143	2.4269	Accept null	Yes
Reference Site	BC20	Golden Gate	No	OLS	None	-0.000018	0.789	28	**0.041***	11.8%	0.882	2.0132	Accept null	Yes
Phosphate														
Rivers	BG20	Sacramento River	No	Robust	None	0.000003	-0.050	34	0.090	5.9%	na	1.6911	Accept null	Yes
Rivers	BG30	San Joaquin River	No	Robust	None	-0.000002	0.157	33	0.282	0.6%	na	2.2490	Accept null	Yes
Central Bay	BC10	Yerba Buena Island	No	Robust	None	-0.000002	0.165	33	0.224	1.7%	na	2.2605	Accept null	Yes
South Bay	BA30	Dumbarton Bridge	No	Robust	None	-0.000011	0.657	33	0.131	4.2%	na	2.3932	Accept null	Yes
Reference Site	BC20	Golden Gate	No	Robust	None	-0.000002	0.127	28	0.187	3.0%	na	2.1555	Accept null	Yes

*Significant decrease in dissolved nitrate concentrations.

Discussion

The bimodal spatial distribution of dissolved nitrate and dissolved phosphate concentrations is consistent with the observations that the northern part of the estuary is strongly influenced by agricultural inputs from the Sacramento and San Joaquin rivers (Cloern et al., 2007), while the southern region, being situated in a densely populated urban watershed, receives 98% of its nitrogen input from municipal wastewater treatment plants (Smith and Hollibaugh, 2006).

The significant decline in dissolved nitrate at the Dumbarton Bridge (BA30: South Bay) station is in agreement with the large declines in dissolved inorganic nitrogen and dissolved reactive phosphorus reported by Cloern et al. (2007) in South San Francisco Bay for the period from January 1990 through December 2005. The nutrient declines are consistent with progressive improvements in municipal wastewater treatment leading to decreasing nitrogen and phosphorous input from the urban watershed (Cloern et al., 2007).

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