Assessing linkages between watershed nutrient loading and water quality in a subtropical estuary with semiparametric models.

Michael Schramm[1*]

[1*]Texas Water Resources Institute, Texas A&M AgriLife Research, College Station, United States, 77840, TX, 1001 Holleman Dr. E..

Corresponding author(s). E-mail(s): michael.schramm@ag.tamu.edu;

Abstract

Lavaca Bay is a secondary embayment on the Texas coast displaying early signals of water quality degradation. This study applied a semiparametric approach to assess both watershed nutrient loads and responses in estuary water quality to nutrient loading and streamflow. Cross-validation indicated that, despite data constraints, semiparametric models performed well at nutrient load prediction. Based on these models, delivered annual nutrient loads varied substantially from year to year. In contrast, minimal changes in flow-normalized loads indicate that nutrient loadings were driven by natural variation in precipitation and runoff as opposed to changes in management of nonpoint sources. Models indicated there was no evidence of long-term changes in dissolved oxygen or chlorophyll-*a* within Lavaca Bay. However, site specific long-term increases in both organic and inorganic nitrogen are concerning. Further analysis found freshwater inflow was a strong driver of nutrient and chlorophyll-*a* concentrations within Lavaca Bay but there was no evidence that changes in watershed nutrient loading explained variation in dissolved oxygen or chlorophyll-*a* concentrations. In addition to providing a baseline assessment of watershed nutrient loading and water quality responses in the Lavaca Bay watershed, this study provides methodological support for the use of semiparametric methods in load regression models and estuary assessments.

Keywords: key, dictionary, word

Remaining Items

- keywords
- discussion
- formalize language (reduce first person active?)
- final language review
- springer doesn't want figures in subdirectory, need to knit to same directory as tex file.

1 Introduction

Similar to many coastal areas globally, the coastal watersheds along the Texas Gulf coast are facing pressures from increasing population, increases in point source and non-point source pollution and alterations to freshwater flows that degrade water quality in downstream estuaries (Bricker et al, 2008; Kennicutt, 2017; Bugica et al, 2020). Despite these escalating pressures, national scale assessments have classified coastal estuaries in Texas as moderate or low risk for eutrophic conditions (Bricker et al, 2008). However, a suite of recent studies indicates that estuary water quality dynamics in both agriculturally dominated and urban watersheds within Texas are expressing conditions that are increasingly conducive to algal blooms and eutrophication (Wetz et al, 2016, 2017; Bugica et al, 2020; Chin et al, 2022). With identification of several localized areas of estuary water quality concern along the Texas coast (Bugica et al, 2020), localized studies are being prioritized to better inform management actions.

This project aims to provide an assessment of watershed nutrient loading and resulting water quality responses in Lavaca Bay, Texas. Lavaca Bay is a secondary bay in the larger Matagorda Bay system located roughly halfway between Houston, Texas and Corpus Christi, Texas. Lavaca Bay faces substantial challenges associated with legacy contamination but general water quality parameters such as dissolved oxygen

(DO), nutrients, and biological parameters have been well within state water quality standards. Despite largely meeting statewide water quality standards, there have been concerning recently identified declines in abundance, biomass, and diversity of benthic fauna in Lavaca Bay (Beseres Pollack et al, 2011). These declines are partially attributed to reductions in freshwater inflow and changes in estuary salinity and are indicative of an already stressed system (Beseres Pollack et al, 2011; Palmer and Montagna, 2015; Montagna et al, 2020). More recently, significant linear increases in total phosphorus (TP), orthophosphate, total Kjeldahl nitrogen (TKN), and chlorophyll-a concentrations were identified at monitoring sites within Lavaca Bay (Bugica et al, 2020). Although long-term changes in DO concentrations have not been identified, the trends in nutrient concentrations are concerning due to the role of nitrogen as a limiting factor for primary production in many Texas estuaries (Gardner et al, 2006; Hou et al, 2012; Dorado et al, 2015; Paudel et al, 2019; Wetz et al, 2017) and the ramifications that changes in nitrogen loadings could have for productivity and eutrophication in Lavaca Bay.

There are ongoing efforts between local, state, and federal agencies to address water quality impairments in the freshwater portions of the Lavaca Bay watershed (Jain and Schramm, 2021; Schramm et al, 2018; Berthold et al, 2021). However, at a statewide scale, these approaches have shown limited success and emphasize a need for improved efforts at assessing and linking management actions with downstream water quality to identify and replicate effective management actions across the state (Schramm et al, 2022). The identification and communication of changes and trends in water quality is complicated by the fact that trends are often non-linear and confounded by precipitation and runoff that hinder traditional analysis (Wazniak et al, 2007; Lloyd et al, 2014). The development and application of flexible statistical methods such as Weighted Regressions on Time, Discharge and Season (WRTDS, Hirsch et al, 2010) and Generalized Additive Models (GAMs, Wood, 2011) have provided effective tools for researchers to quantify and communicate non-linear changes in river and estuary pollutant loadings.

WRTDS calculates a time series of in-stream concentrations or loads (daily, monthly, or annually) and flow-normalized estimates of concentrations and loads using locally weighted regresssion for unique combinations of time, discharge, and season. WRTDS has been widely used to assess and identify trends in riverine nutrients (Oelsner and Stets, 2019; Stackpoole et al, 2021), chlorides (Stets et al, 2018), and other pollutants of concern (Shoda et al, 2019). WRTDS has also been succesfully adapted to assess trends in estuarine water quality concentrations (Beck et al, 2018).

While WRTDS is a statistical approach developed specifically for water quality applications, GAMs are a broadly applicable statistical method. GAMs are a semiparametric extension of generalized linear models where the linear predictor is represented as the sum of multiple unknown smooth functions and parametric linear predictors (Wood, 2011). Although the underlying parameter estimation procedure of GAMs is substantially different than WRTDS, both the functional form and results have been demonstrated to be similar when assessing nutrient concentration trends (Beck and Murphy, 2017). Water quality applications of GAMs have included include river and catchment nutrient concentration and load estimation (Wang et al, 2011; Kroon et al, 2012; Kuhnert et al, 2012; Robson and Dourdet, 2015; Hagemann et al, 2016; McDowell et al, 2021; Biagi et al, 2022), assessment of temporal trends of nutrients (Beck and Murphy, 2017; Murphy et al, 2019), phytoplankton (Bergbusch et al, 2021), and cyanobacteria (Hayes et al, 2020). Recently GAMs have also been used to link water quality responses in receiving water bodies to changes in nonpoint source nutrient inputs (Murphy et al, 2022). Beck and Murphy (2017) provides a substantial discussion on the differences (and similarities) between GAMs and WRTDS for water quality applications.

To provide actionable information for resource managers in Lavaca Bay, water quality conditions must be evaluated relative to changes in natural environmental drivers to better understand and manage potential human impacts. This study utilizes GAMs to develop estimates of delivered and flow-normalized nutrient loads and assess changes in loads delivered to Lavaca Bay. GAMs were chosen over other regression-based approached for use in this study due to; (1) the ability to easily explore and incorporate different model terms; (2) the incorporation of non-liner smooth functions that do not require explicit a priori knowledge of the expected shape; and (3) inclusion of a link function that related the expected value of the response to linear predictors thus avoiding unneeded data transformations and bias corrections. The exploratory study also assesses the response of water quality parameters in Lavaca Bay over time and in response to freshwater inflow controlled for seasonality and to watershed nutrient loads that are controlled for environmentally driven variation.

2 Methods

2.1 Location and Data

Lavaca Bay is 190 km^2 with the majority of freshwater inflow provided by the Lavaca and Navidad River systems (Figure 1). The Garcitas-Arenosa, Placedo Creek, and Cox Bay watersheds provide additional freshwater inflows. The entire watershed land area is 8,149 km^2 and primarily rural. Watershed land cover and land use is 50% grazed pasture and rangeland, 20% cultivated cropland (primarily rows crops such as corn, cotton, and sorghum), and 5% suburban/urban. Pasture and rangeland is concentrated in the Lavaca River watershed, while cultivated crops are generally located along the eastern tributaries of the Navidad river. The Lavaca and Navidad River watersheds are a combined 5,966 km^2, or approximately 73% of the entire Lavaca Bay watershed area. Discharge from the Navidad River is regulated by Lake Texana which has been in operation since 1980. Lake Texana provides 0.210 km^3 of water storage and discharges into the tidal section of the Navidad River which ultimately joins the tidal section of the Lavaca River 15 km upstream of the confluence with the Lavaca Bay.

Daily discharges for the Lavaca River (USGS-08164000, Figure 1) were obtained from the United States Geologic Survey (USGS) National Water Information System using the *dataRetrieval* R package (De Cicco et al, 2022). Gaged daily discharges from the outlet of Lake Texana on the Navidad River (USGS-0816425) were provided by the Texas Water Development Board (TWDB) (April 21, 2022 email from R. Neupane, TWDB).

Water quality sample data for the two freshwater and three estuary locations were obtained from the Texas Commission on Environmental Quality (TCEQ) Surface Water Quality Monitoring Information System. Data submitted through the system are required to be collected under Quality Assurance Project Plans and lab method procedures outlined by the TCEQ's procedures manual to ensure consistent collection and laboratory methods are applied between samples collected by different entities and under different projects. All sites had varying lengths of and availability of data. For freshwater locations, TP from January 2000 through December 2020 and nitrate-nitrogen (NO_3) data from January 2005 through December 2020 were downloaded (Table 1). Less than 5-years of total nitrogen and TKN concentration data were available at the freshwater sites and deemed insufficient to develop load estimation models (Horowitz, 2003; Snelder et al, 2017). The three estuary sites included an upper Lavaca Bay site near the outlet of the Lavaca River system (TCEQ-13563), a mid-Lavaca Bay site (TCEQ-13383), and the lower Lavaca Bay site near the mouth of the Bay (TCEQ-13384). For estuary locations, we obtained data for TP, Nitrite+Nitrate (NO_x), TKN, chlorophyll-*a*, and DO concentrations from January 2005 through December 2020 (Table 2).

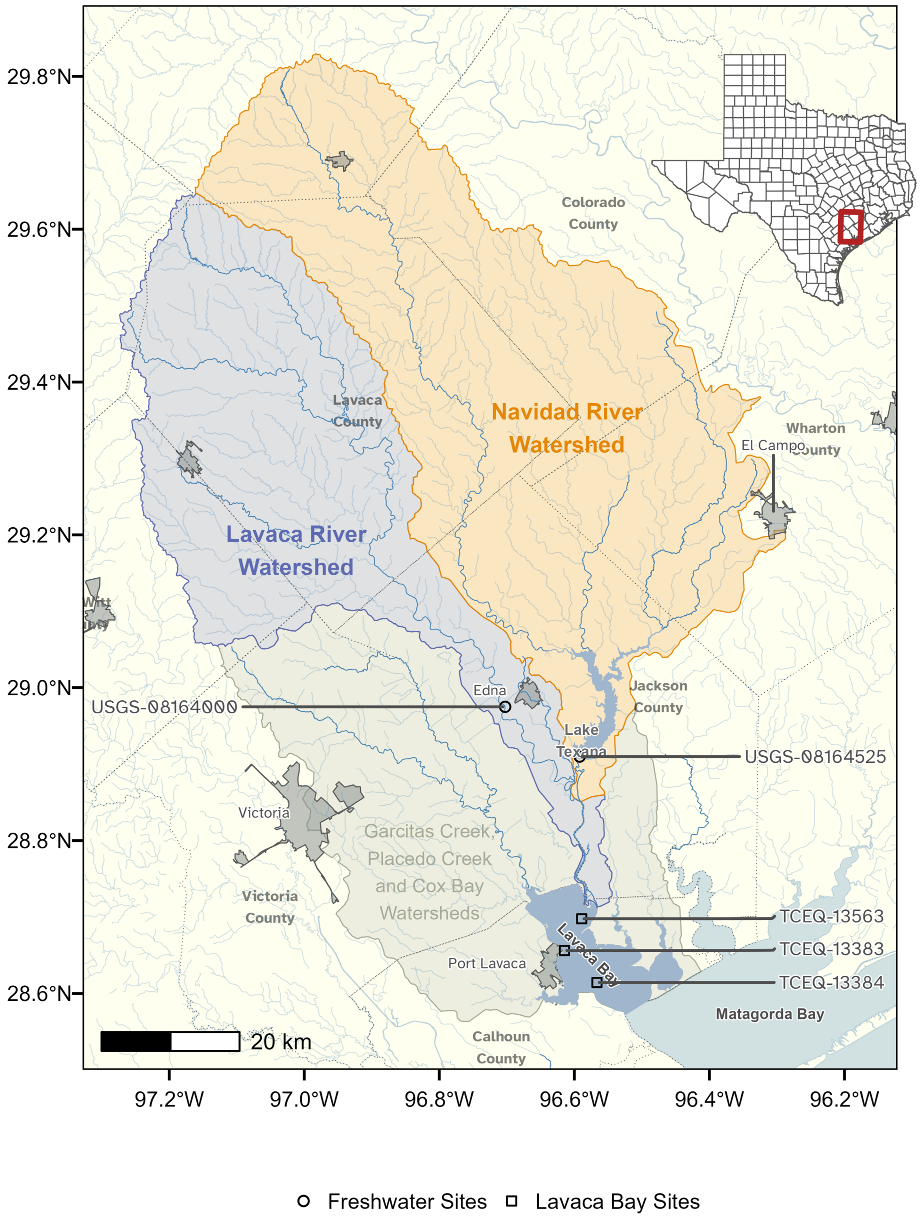

Fig. 1 Map of Lavaca Bay and the contribution watershed. The freshwater sites are the most downstream freshwater stream locations with water quality and streamflow data used for nutrient load models. Water quality concentration data at the three Lavaca Bay sites were used to assess relationships between freshwater flows, loads and estuary water quality.

Table 1 Summary of gauged streamflow and freshwater water quality samples between January 1, 2000 and December 31, 2020.

Station ID	Parameter	Mean	SD	N
USGS-08164000	TP (mg/L)	0.21	0.09	80
	NO_3 (mg/L)	0.18	0.24	74
	Mean Daily Streamflow (cfs)	332.78	1667.47	7671
USGS-08164525	TP (mg/L)	0.20	0.08	81
	NO_3 (mg/L)	0.29	0.26	62
	Mean Daily Streamflow (cfs)	666.14	2957.79	7671

Table 2 Summary of estuary water quality samples collected between January 1, 2005 and December 31, 2020.

Station ID	Parameter	Mean	SD	N
TCEQ-13383	TP (mg/L)	0.11	0.05	47
	NO_x (mg/L)	0.07	0.15	51
	TKN (mg/L)	0.94	0.49	45
	Chlorophyll-*a* (ug/L)	9.43	5.31	47
	DO (mg/L)	7.22	1.35	55
TCEQ-13384	TP (mg/L)	0.08	0.03	51
	NO_x (mg/L)	0.06	0.08	52
	TKN (mg/L)	0.76	0.40	48
	Chlorophyll-*a* (ug/L)	8.22	6.44	46
	DO (mg/L)	7.51	1.32	54
TCEQ-13563	TP (mg/L)	0.13	0.06	50
	NO_x (mg/L)	0.09	0.13	53
	TKN (mg/L)	0.94	0.37	49
	Chlorophyll-*a* (ug/L)	9.67	5.33	49
	DO (mg/L)	7.91	1.34	56

2.2 Estimating Watershed Based Nutrient Loads

Estimates of NO_3 and TP loads at the Lavaca River (USGS-08164000) and the outlet of Lake Texana on the Navidad River (USGS-08164525) were developed using GAMs relating nutrient concentration to river discharge, season, and time. Separate models were fit at each station for each parameter and used to predict nutrient concentrations for each day in the study period. GAMs were fit using the *mgcv* package in R which makes available multiple types of smooth functions with automatic smoothness selection (Wood, 2011). The general form of the model related NO_3 or TP concentration to a long term tend, season, streamflow, and two different antecedent discharge terms, shown in Eq. 1:

$$
\begin{aligned}
&g(\mu) = \alpha + f_1(ddate) + f_2(yday) + f_3(log1p(Q)) + f_4(ma) + f_5(fa), \\
&y \sim \mathcal{N}(\mu, \sigma^2)
\end{aligned}
\tag{1}
$$

where μ is the conditional expected NO_3 or TP concentration, $g()$ is the log-link, α is the intercept, $f_n()$ are smoothing functions. y is the response variable (NO_3 or TP concentration) modeled as normally distributed with mean μ and standard deviation σ. *ddate* is the date converted to decimal notation, *yday* is numeric day of year (1-366), and *log1p(Q)* is the natural log of mean daily streamflow plus 1.

Moving average (ma) is an exponentially smoothed moving average that attempts to incorporate the influence of prior streamflow events on concentration at the current time period (Wang et al, 2011; Kuhnert et al, 2012; Zhang and Ball, 2017), using Eq. 2:

$$
\begin{aligned}
ma(\delta) &= d\kappa_{i-1} + (1-\delta)\hat{q}_{i-1}, \\
\kappa_i &= \sum_{m=1}^{i} \hat{Q}_m
\end{aligned}
\tag{2}
$$

where δ is the discount factor (here, set equal to 0.95), κ_i is the cumulative flow (Q) up to the ith day.

Flow anomaly (*fa*) is a unitless term that represents how wet or dry the current time period is from a previous time period (Vecchia et al, 2009; Zhang and Ball, 2017). Long-term flow anomaly (*ltfa*) is the streamflow over the previous year relative to the entire period (Zhang and Ball, 2017) and calculated using Eq. 3:

$$ltfa(t) = \bar{x}_{1\,year}(t) - \bar{x}_{entire\,period} \tag{3}$$

and the short-term flow anomaly (*stfa*) calculated as the current day flow compared to the preceding 1-month streamflow using 4:

$$stfa(t) = x_{current\,day}(t) - \bar{x}_{1\,month}(t) \tag{4}$$

where x are the averages of log-transformed streamflow over the antecedent period (*1-year*, *1-month*, etc.) for time t. We used *ltfa* in NO_3 models and *stfa* in TP models based on previous work demonstrating major improvements in NO_x regression models that incorporated *ltfa* and moderate improvements in TP regression models that incorporated *stfa* (Zhang and Ball, 2017). Moving averages and flow anomalies were calculated with the *adc* R package (Schramm, 2023).

The calculation of model terms for the Lake Texana site were modified because daily loads are not a function of natural stream flow processes alone, but of dam releases and nutrient concentrations at the discharge point of the lake. *Q*, *ma*, and *fa* terms were calculated based on total gaged inflow from the 4 major tributaries to the lake. Thin-plate regression splines were used for *ddate*, *log1p(Q)*, *fa*, and *ma*. A cyclic cubic regression spline was used for *yday* to ensure the ends of the spline match (day 1 and day 366 are expected to match). First order penalties were applied to the smooths of flow-based variables which penalize departures from a flat function to help constrain extrapolations for high flow measurements.

Left-censored data were not uncommon in this dataset. Several methods are available to account for censored data. We transformed left-censored nutrient concentrations to one-half the detection limit. Although this simple approach can introduce bias (Hornung and Reed, 1990), we considered it acceptable because high concentrations and loadings are associated with high-flow events and low-flow/low-concentration events will account for a small proportion of total loadings (McDowell et al, 2021).

Daily loads were estimated as the predicted concentration multiplied by the daily streamflow. For the Navidad River (USGS-08164525) site, daily loads at the dam were calculated from the discrete daily concentration at the discharge point of the lake and corresponding reported daily discharge from the dam. Flow-normalized loads were estimated similar to WRTDS by setting flow-based covariates on each day of the year equal to each of the historical values for that day of the year over the study period (Hirsch et al, 2010). The flow-normalized estimate was calculated as the mean of all the predictions for each day considering all possible flow values. Standard deviations and 90% credible intervals were obtained by drawing samples from the multivariate normal posterior distribution of the fitted GAM (Wood, 2006; Marra and Wood, 2012; McDowell et al, 2021). GAM performance was evaluated using repeated 5-fold cross validation (Burman, 1989) and average Nash-Sutcliffe Efficiency (NSE), Pearson sample correlation (r) and percent bias (PBIAS) metrics across folds were calculated for each model.

2.3 Linking Estuary Water Quality to Hydrology and Nutrient Loads

To test if changes in freshwater inflow and nutrient loading had explanatory effect on changes in estuary water quality a series of GAM models were fit at each site relating parameter concentration to temporal trends (Eq. 5), temporal trends and inflow (Eq. 6), and temporal trends, inflow, and nutrient loads (Eq. 7):

$$g(\mu) = \alpha + f_1(ddate) + f_2(yday), \tag{5}$$

$$g(\mu) = \alpha + f_1(ddate) + f_2(yday) + f_3(Q), \tag{6}$$

$$g(\mu) = \alpha + f_1(ddate) + f_2(yday) + f_3(Q) + f_4(Load) \tag{7}$$

Table 3 Set of GAM models specified for each water quality parameter response.

Parameter	Model	Model Terms
TP	Temporal	s(ddate) + s(yday)
	Flow	s(ddate) + s(yday) + s(Q)
	Flow+Load	s(ddate) + s(yday) + s(Q) + s(TP Load)
NO_x	Temporal	s(ddate) + s(yday)
	Flow	s(ddate) + s(yday) + s(Q)
	Flow+Load	s(ddate) + s(yday) + s(Q) + s(NO_3 Load)
Chlorophyll-a	Temporal	s(ddate) + s(yday)
	Flow	s(ddate) + s(yday) + s(Q)
	Flow+Load	s(ddate) + s(yday) + s(Q) + s(TP Load) + s(NO_3 Load)
Dissolved Oxygen	Temporal	s(ddate) + s(yday)
	Flow	s(ddate) + s(yday) + s(Q)
	Flow+Load	s(ddate) + s(yday) + s(Q) + s(TP Load) + s(NO_3 Load)
TKN	Temporal	s(ddate) + s(yday)
	Flow	s(ddate) + s(yday) + s(Q)

where μ is the conditional expected response (nutrient concentration), $g()$ is the log link, and response variable was modeled as Gamma distributed with mean μ and scale λ. $f_1(ddate)$ is decimal date smoothed with a thin-plate regression spline, $f_2(yday)$ is the numeric day of year smoothed with a cyclic cubic regression spline, $f_3(Q)$ is mean daily inflow (the combined measurements from Lavaca River and Navidad River) and $f_4(Load)$ is the total NO_3 or TP watershed load. The set of models specified for each water quality response are in Table 3.

Because streamflow and nutrient loads are tightly correlated, freshwater inflow can mask signals from nutrient loads alone. Following the methodology implemented by Murphy et al (2022), both freshwater inflow and nutrient loads were prepossessed to account for season and streamflow respectively. Raw freshwater inflow values were replaced by seasonally adjusted log transformed inflow obtained from the residuals of a GAM model fit between season(day of year) and log transformed daily freshwater inflow. Raw nutrient loads were replaced with flow-adjusted values obtained from the residuals of a GAM model relating log transformed NO_3 or TP loads to log transformed daily inflow. Response residuals from the respective GAM models were used as Q and *Load* in Eq. 6 and Eq. 7.

This study used an information theoretic approach to evaluate evidence of model covariate effects on Lavaca Bay water quality. Model probabilities were calculated and compared using the AIC_c scores between each group of temporal, inflow, and inflow+load models (Burnham et al, 2011). Improvements in model probabilities provide evidence that the terms explain additional variation in the response variable.

3 Results

3.1 Watershed Nutrient Loads

Predictive performance of nutrient loads ranged from "satisfactory" to "very good" based on standardized evaluation metrics of NSE, r, and PBIAS (Moriasi et al, 2015) calculated using 5-fold cross validation. Median goodness-of-fit metrics for NO_3 models in the Lavaca River were 0.34 NSE, 0.70 r, and 2.00 PBIAS. Navidad River NO_3 models appeared to perform slightly better with 0.48 NSE and 0.87 r but with higher bias at 10.90 PBIAS. Generally, TP models performed better than NO_3 models. Median goodness-of-fit metrics for TP in the Lavaca River were 0.81 NSE, 0.93 r, and -7.20 PBIAS. Navidad River TP models has similar performance with 0.91 NSE, 0.99 r, and -3.30 PBIAS. Density plots of metrics show similar distribution of values between sites for the same parameter, with the exception r values for NO_3 loads where Lavaca River had a much larger variance in values compared to the Navidad River (Figure 2). TP GAMS had higher average NSE and r values and lower variance in metric values compared to NO_3.

Annual NO_3 and TP loads show considerable variation, generally following patterns in discharge (Figures 3, 4). Flow-normalized TP loads at both sites and flow-normalized NO_3 loads in the Lavaca River indicated watershed based loads did not change much over time when accounting for variation driven by streamflow (Figure 3). Flow-normalized loads in the Lavaca River showed small variation over time with some decreases in NO_3 loads since 2013.

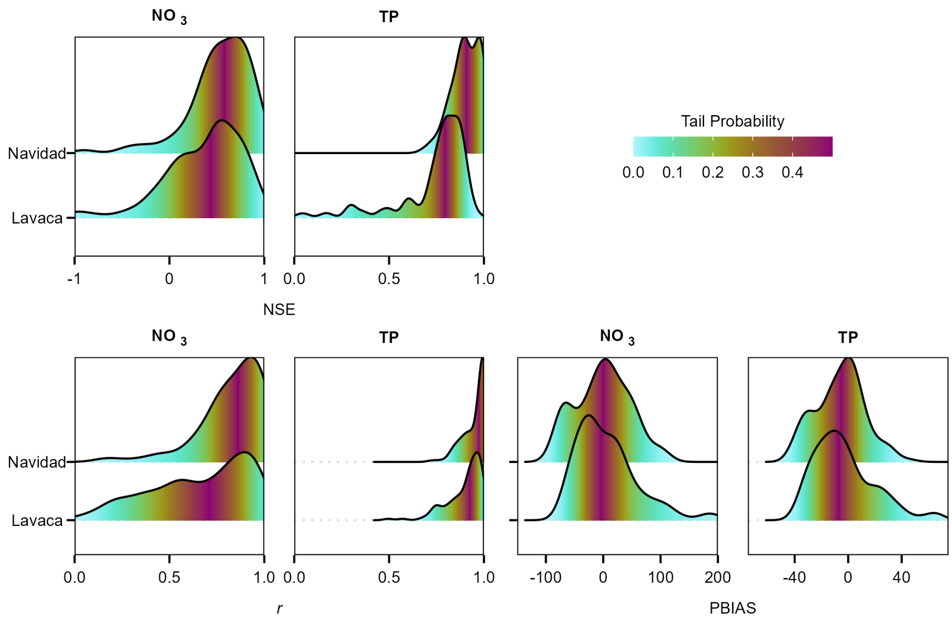

Fig. 2 Density plots of goodness-of-fit metrics (NSE, r, and PBIAS) from repeated 5-fold cross validation between predicted nutrient loads from GAM models and measured nutrient loads. Color indicates the tail probability calculated from the empirical cumulative distribution of the goodness-of-fit metrics.

Aggregated across both sites, the mean annual NO_3 load 2005 through 2020 was 205,405 kg (126,867 kg - 341,569 kg, 90% CI). Annual NO_3 loads ranged from 12,574 kg in 2011 to 794,510 kg in 2007. Total annual TP loads ranged from 7,839 kg in 2011 to 595,075 kg in 2007. Mean annual TP loading from 2005 through 2020 was 182,673 kg (152,227 kg - 219,310 kg, 90% CI). On average, the Navidad River accounted for 68% of NO_3 loads and 59% of TP loads from 2005 through 2020. However, during periods of extreme drought the Lavaca River became the primary source of nutrient loading in the watershed with the Navidad River only accounting for 15% and 25% of NO_3 and TP loads in 2011 (Figure 4).

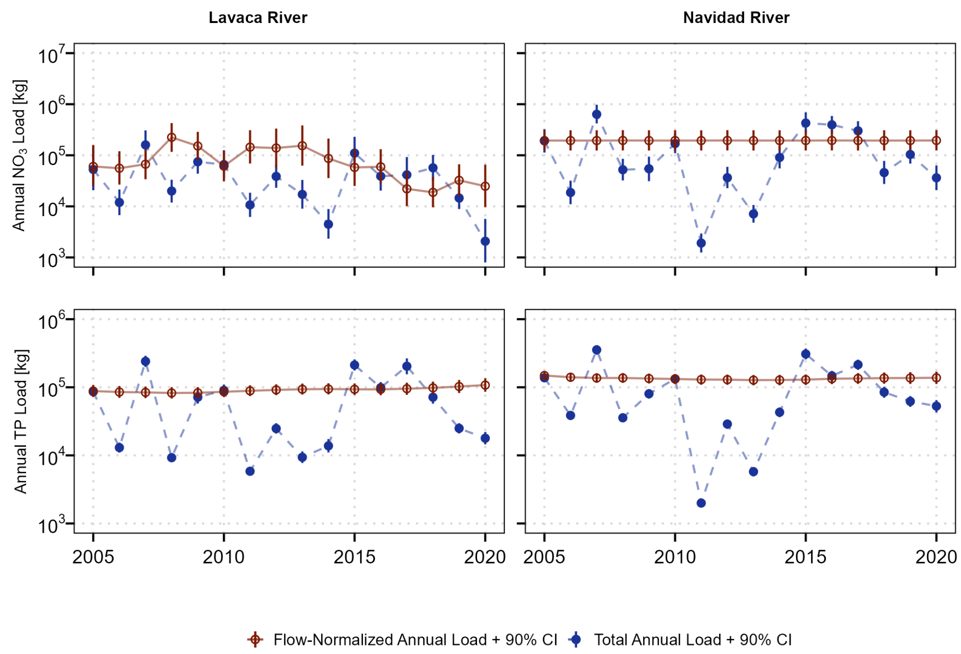

Fig. 3 Aggregated estimated annual and flow-normalized annual NO_3 and TP loads for USGS-08164000 and USGS-08164525.

3.2 Linkages Between Water Quality and Watershed Flows and Loads

There is no evidence of long-term changes in TP or DO concentrations at any Lavaca Bay site (Figure 5). The upper-bay site, TCEQ-13563, shows evidence of a long-term linear increase in NO_x while chlorophyll-a decreased from 2005 through 2014 (Figure 5). NO_x concentration at the mid-bay site, TCEQ-13383, displayed an unusual periodic pattern that is indicative of a strong influence from inflow or precipitation. The temporal GAMs did not provide evidence of long-term trends in any of the water quality constituents at the lower-bay TCEQ-13384 site.

Freshwater inflow provided additional explanation for changes in TP and NO_x concentration at all of the Lavaca Bay sites according to AIC_c and model probability values (Table 4). TCEQ-13563, the site closest to the river outlet, was the only

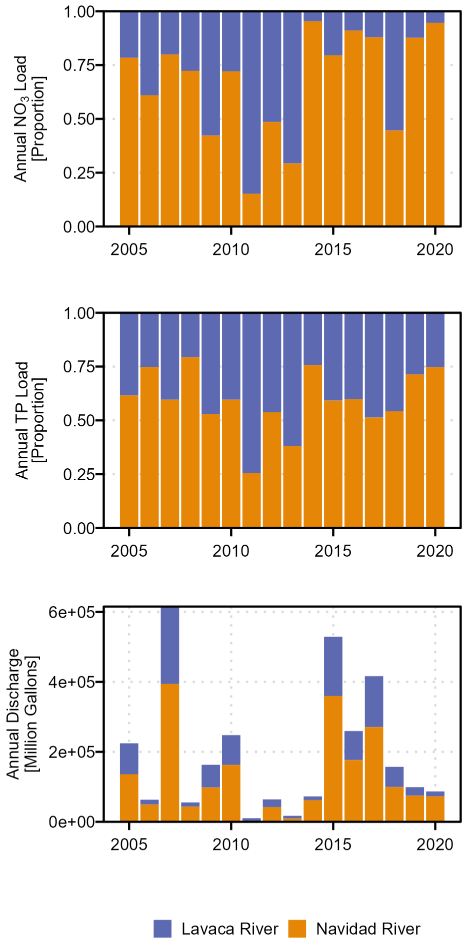

Fig. 4 Comparison of delivered annual loads and annual discharge at the Lavaca (USGS-08164000) and Navidad (USGS-08164525) Rivers.

site that had improvements in the explanations of DO and TKN concentration with the inclusion of inflow. Both TCEQ-13563 and TCEQ-13383, the mid-bay site, saw improvements in explanations for variations in chlorophyll-a with the inclusion of freshwater inflow. The addition of nutrient loads (both TP and NO_3) terms did not provide additional explanation for changes in chlorophyll-a or DO concentrations. Inclusion of TP loads provided additional explanation of TP concentrations at the upper- and mid-bay sites, TCEQ-13563 and TCEQ-13383. Inclusion of NO_3 loads

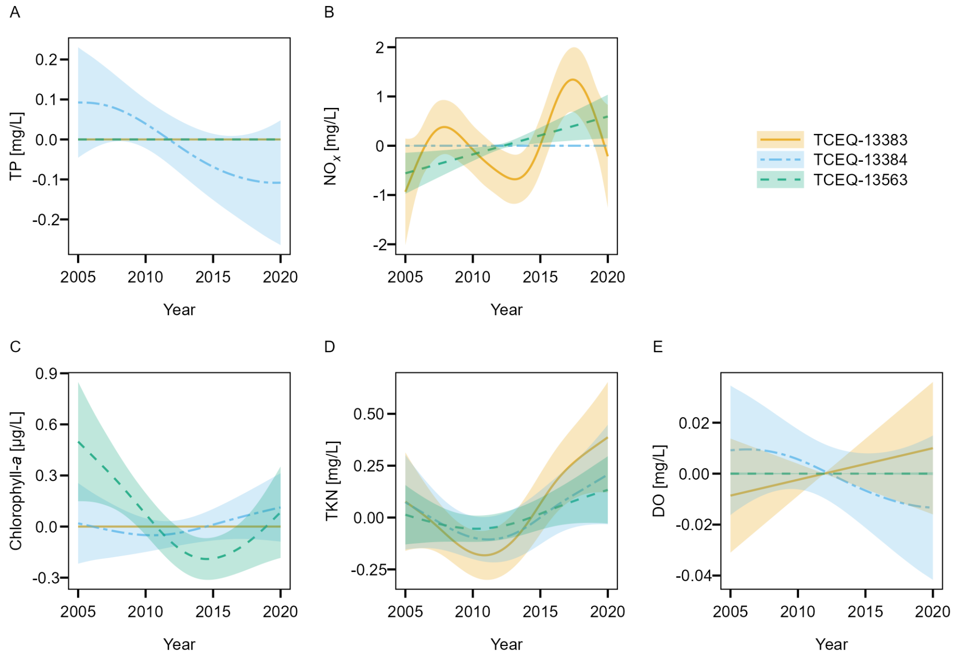

Fig. 5 Fitted splines (shaded regions indicate 90% confidence intervals) from the temporal estuary GAM display the marginal smoothed effect of date on TP (A), NO_x (B), chlorophyll-a (C), TKN (D), and DO (E) concentrations at each site in Lavaca Bay.

only provided marginal improvements in the explanation of NO_X concentration at the lower-bay TCEQ-13384 site.

GAMs showed that increases in freshwater inflow resulted in nearly linear increases in TP and NO_x concentration at all three sites (Figure 6). At the upper-bay TCEQ-13563 site, GAMs showed that increases in freshwater inflow initially increased chlorophyll-a and DO concentration but concentrations leveled and potentially decreased at higher flows. The mid-bay TCEQ-13383 site showed a nearly linear increased in chlorophyll-a concentration in response to increases freshwater inflow. Freshwater flow did not have significant effects on chlorophyll-a, TKN, or DO at the lower-bay TCEQ-13384 site.

Increased TP loads resulted in nearly linear increases of TP concentration at the upper- and mid-bay sites, TCEQ-13563 and TCEQ-13383 respectively (Figure 7).

Table 4 Estuary GAM AIC$_c$ values and associated model probabilities (in parenthesis). Models with the highest probability for each site and water quality parameter combination are bolded and italicized for emphasis.

Parameter	Site	Temporal	Inflow	Inflow + Load
TP	TCEQ-13383	-152.1 (0.03)	-156.1 (0.24)	***-158.2 (0.72)***
	TCEQ-13384	-194.4 (0.03)	***-200.2 (0.49)***	-200.2 (0.49)
	TCEQ-13563	-145.3 (0)	-156.6 (0.41)	***-157.3 (0.59)***
NO_x	TCEQ-13383	-218.9 (0)	***-244.8 (0.5)***	-244.8 (0.5)
	TCEQ-13384	-263.4 (0)	-311.7 (0.48)	***-311.9 (0.52)***
	TCEQ-13563	-175.1 (0)	***-190.2 (0.5)***	-190.2 (0.5)
Chlorophyll-a	TCEQ-13383	279.7 (0.18)	***278.1 (0.41)***	278.1 (0.41)
	TCEQ-13384	***268.2 (0.33)***	268.2 (0.33)	268.2 (0.33)
	TCEQ-13563	289.5 (0.08)	***286.1 (0.46)***	286.1 (0.46)
TKN	TCEQ-13383	***42.2 (0.66)***	43.5 (0.34)	-
	TCEQ-13384	***34.3 (0.57)***	34.8 (0.43)	-
	TCEQ-13563	31.1 (0.22)	***28.7 (0.78)***	-
DO	TCEQ-13383	***146.4 (0.34)***	146.4 (0.34)	146.5 (0.32)
	TCEQ-13384	***135.9 (0.47)***	137 (0.27)	137 (0.27)
	TCEQ-13563	138.3 (0.25)	***137.2 (0.43)***	137.8 (0.32)

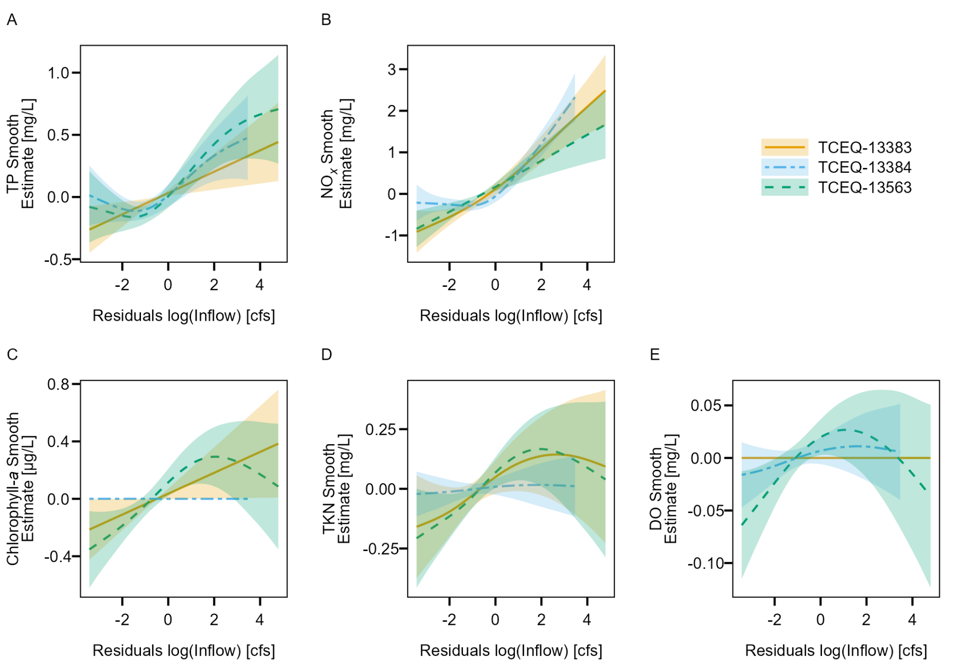

Fig. 6 Fitted splines from estuary GAMs display the marginal smoothed effect of freshwater inflow (controlled for season) on TP (A), NO_x (B), chlorophyll-a (C), TKN (D), and DO (E) concentrations at each site in Lavaca Bay.

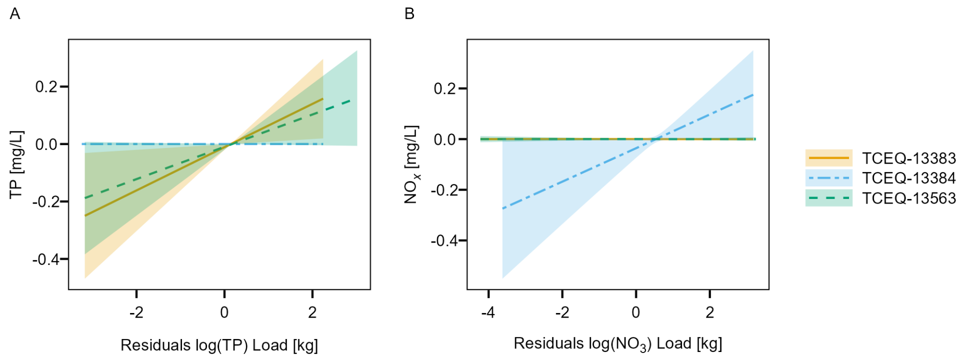

Fig. 7 Fitted splines from the nutrient loading GAMs display the marginal smoothed effect of TP and NO_3 loads on TP (A) and NO_x (B) concentrations at each site in Lavaca Bay.

The relative effect size appeared to much smaller than the effect of freshwater inflow alone. Increased NO_3 loads only showed an effect at the lower-bay TCEQ-13384 site. The effect was quite small compared to streamflow and provided only small improvements to the model (Table 4). As noted above, nutrient loadings did not provide any explanation in changes in the remaining assessed water quality parameters.

4 Discussion

resume here

4.1 Watershed Nutrient Loads

TP and NO_3 loadings from the Lavaca Bay watershed showed high inter-annual variability tied closely with changes in discharge. There is little evidence for changes in flow-normalized TP loads in either river. There is some evidence of recent decreases in flow-normalized NO_3 loads in the Lavaca River. Although there is no work directly correlating water quality planning and implementation efforts in the watershed to water quality outcomes, efforts to increase agricultural producer participation in the watershed have been ongoing since 2016 (Schramm et al, 2018; Berthold et al, 2021).

Table 5 Comparisons of previously published estimates of mean annual TP yield at the Lavaca River site.

Reported Yield (kg·km^2·year^{-1})	Approach	Time Period	Reference
35.2 (28.8, 43.3)[a]	GAM	2005-2020	This work
45.2	SPARROW	2000-2014	Wise et al (2019)
42	SWAT	1977-2005	Omani et al (2014)
20.81-91.58[b]	SPARROW	1980-2002	Rebich et al (2011)
28.9	LOADEST	1972-1993	Dunn (1996)

[a] Mean of the annual point estimates and the lower and upper 95% credible intervals.

[b] Represents a binned value range from a choropleth map.

The decrease in flow-normalized NO_3 loads could be a reflection of those collective efforts but further data collection and research is required to support that statement.

Converted to average annual yield, the estimates of annual TP loads for the Lavaca River are within the ranges in previous published studies (Table 5, Dunn, 1996; Rebich et al, 2011; Omani et al, 2014; Wise et al, 2019). It isn't obvious why TP estimates in Dunn (1996) were notably lower. Given that none of the studies identify substantially sized trends in TP, it is is possible that the period used in Dunn (1996) was drier on average than the other studies. The SPARROW models used in Rebich et al (2011) and Wise et al (2019) utilize a version of LOADEST in the underlying load estimation procedure, so a difference due to methodology alone is unlikely.

Cross-validation of the GAM loading models indicated that GAMs performed well on average at predicting daily nutrient loading values. The variance in scores was very high indicating subsets of values were problematic at characterizing functional relationships between nutrients and predictors. Because all of the water quality data for these two locations in the TCEQ databases were ambient water quality data, collected to be representative of typical flow conditions, there were few data at the highest portions of the flow-duration curve. It was beyond the scope of the current study to evaluate the subsets of cross-validation data and scores. However, the cross-validation procedure is indicative that more robust sampling would be beneficial for reducing prediction variance. Supplementary flow-biased monitoring targeting storm- or high-flow conditions is recommended here to improve the precision of GAM predictions (Horowitz, 2003; Snelder et al, 2017).

4.2 Estuary Water Quality Responses

The non-linear temporal water quality trends identified using GAMs differed slightly from previously identified trends (Bugica et al, 2020). This is not unexpected due to the different time periods, different methodology, and generally small slopes identified for most of the significant water quality parameters in prior work. The trend in DO and cholorophyll-a concentrations are stable in comparison to other Texas estuaries that are facing larger demands for freshwater diversions, higher population growth, and more intense agricultural production (Wetz et al, 2016; Bugica et al, 2020). The trend of increasing NO_x concentration at the upper-bay TCEQ-13563 site and recent increases in TKN concentration at the mid-bay TCEQ-13383 site are concerning due to the nitrogen limitation identified in many Texas estuaries (Gardner et al, 2006; Hou et al, 2012; Dorado et al, 2015; Paudel et al, 2019; Wetz et al, 2017) and the relatively low ambient concentrations observed in Lavaca Bay.

The strong positive effect of freshwater inflow on NO_x, TKN, and TP are suggestive of nonpoint watershed sources, consistent with watershed uses and with other studies relating freshwater inflow with nutrient concentrations in Lavaca Bay and other estuaries (Russell et al, 2006; Caffrey et al, 2007; Peierls et al, 2012; Palmer and Montagna, 2015; Cira et al, 2021). Inflow had a non-linear relationship with TKN at the two upstream sites, with TKN increasing as freshwater inflow transitioned from low to moderate levels. At higher freshwater inflows, the effect was attenuated, possibly indicating a flushing effect at higher freshwater inflow. No relationship between TKN and freshwater inflow were observed at TCEQ-13384 located in the lower reach of Lavaca Bay. Tidal flushing from Matagorda Bay could be responsible for diluting

TKN and acting as a control on the effects of freshwater inflow in lower reaches of Lavaca Bay. Previous work suggests the processing of organic loads in the upper portions of Lavaca Bay might reduce the transport of nutrients into the lower reaches of the Bay (Russell et al, 2006).

Freshwater inflow had a strong positive effect on chlorophyll-a at the upper- and mid-bay sites. The upper-bay site, TCEQ-13563, showed decreases in chlorophyll-a at the highest freshwater inflow volumes. Freshwater flushing or increases in turbidity are associated with decreases in chlorophyll-a in other estuaries (Peierls et al, 2012; Cloern et al, 2014). No relationships between inorganic nitrogen or TP loadings with chlorophyll-a were observed. Due to the lack of TKN loading information, no assessment between organic nitrogen loads and chlorophyll-a were possible.

Although other studies have identified complex relationships between estuary nutrient concentrations, nutrient loading and chlorophyll-a concentrations in Texas estuaries (Örnólfsdóttir et al, 2004; Dorado et al, 2015; Cira et al, 2021; Tominack and Wetz, 2022), this study specifically used flow-adjusted freshwater derived nutrient loads to parse out contributions from changes in nutrient loadings while accounting for variations in load due to flow. Loading GAMs indicated no evidence of changes in flow-normalized TP loads in either river, and no changes in flow-normalized NO_3 loads in the Navidad River. The small changes in flow-normalized NO_3 loads in the Lavaca River are probably masked under most conditions by discharge from the Navidad River. Given the relatively small variation in flow-normalized loads, it can be expected that they would contribute little to the variance in downstream water quality.

GAMs did not identify responses in DO concentration to inflows or nutrient loads. The seasonality term in the temporal GAM models explained a substantial amount of DO variation at all of the sites. Responses of estuary metabolic processes and resulting DO concentrations can be quite complicated and often locally specific (Caffrey, 2004). While the lack of total nitrogen or TKN loading data hinders interpretation, the large seasonal effect on DO suggests physical factors play an important role and should be included in future models. Prior work suggests that Lavaca Bay may not be limited by nutrients alone, with high turbidity or nutrient processing in upper portions of the Bay or intertidal river limiting production (Russell et al, 2006). Finally, it is reasonable to assume that fluctuations in DO may not occur immediately in response to nutrient pulses or freshwater inflow. Work has has shown that various water quality parameters may have lagged effects lasting days or even months following storms and large discharge events (Mooney and McClelland, 2012; Wetz and Yoskowitz, 2013; Bukaveckas et al, 2020; Walker et al, 2021). However, our work only evaluates responses to loading and inflows occuring the day of water quality observations.

5 Conclusion

GAM models appear to provide reliable estimates of nutrient loads in the Lavaca Bay watershed. However, additional flow-biased data collection efforts would decrease the prediction variance and improve accuracy at critical high flow events. Ongoing projects will fill data gaps for total nitrogen and TKN loading. This study, consistent with others along the Texas coast, found strong effects of freshwater flow on nutrient and chlorophyll-a concentrations. DO concentrations, dominated by seasonal effects, did not show strong direct responses to freshwater flow. Small variance in flow-adjusted nutrient loads indicates that (1) there have been limited changes in non-point sources of nutrients and (2) that there isn't strong evidence that those small changes have had effects on chlorophyll-a or dissolved oxygen in Lavaca Bay. Although the study did not identify strong responses to changes in nutrient loading, this does provide a baseline assessment for future water quality management activities in the watershed.

Acknowledgments. The author extends thanks to Dr. Mike Wetz (Harte Research Institute, Texas A&M Corpus Christi), Chad Kinsfather and Partick Brzozowski

(Lavaca-Navidad River Authority), Brian Koch (Texas State Soil and Water Conservation Board), Bill Balboa (Matagorda Bay Foundation), Jason Pinchbeck (Texas General Land Office) and the Lavaca Bay Foundation for supporting development of this project and providing valuable feedback.

Declarations

Funding. This project was funded in part by a Texas Coastal Management Program grant approved by the Texas Land Commissioner, providing financial assistance under the Coastal Zone Management Act of 1972, as amended, awarded by the National Oceanic and Atmospheric Administration (NOAA), Office for Coastal Management, pursuant to NOAA Award No. NA21NOS4190136. The views expressed herein are those of the author(s) and do not necessarily reflect the views of NOAA, the U.S. Department of Commerce, or any of their subagencies.

Data Availability. Reproducible code and datasets generated during this study are available in the Zenodo repository, https://doi.org/10.5281/zenodo.733075.

References

Beck MW, Murphy RR (2017) Numerical and qualitative contrasts of two statistical models for water quality change in tidal waters. JAWRA Journal of the American Water Resources Association 53(1):197–219. https://doi.org/10.1111/1752-1688.12489

Beck MW, Jabusch TW, Trowbridge PR, et al (2018) Four decades of water quality change in the upper San Francisco Estuary. Estuarine, Coastal and Shelf Science 212:11–22. https://doi.org/10.1016/j.ecss.2018.06.021

Bergbusch NT, Hayes NM, Simpson GL, et al (2021) Unexpected shift from phytoplankton to periphyton in eutrophic streams due to wastewater influx. Limnology and Oceanography 66(7):2745–2761. https://doi.org/10.1002/lno.11786

Berthold TA, Olsovsky T, Schramm MP (2021) Direct mailing education campaign impacts on the adoption of grazing management practices. Journal of Contemporary Water Research & Education 174:45–60. https://doi.org/10.1111/j.1936-704X.2021.3360.x

Beseres Pollack J, Palmer T, Montagna P (2011) Long-term trends in the response of benthic macrofauna to climate variability in the Lavaca-Colorado Estuary, Texas. Marine Ecology Progress Series 436:67–80. https://doi.org/10.3354/meps09267

Biagi K, Ross C, Oswald C, et al (2022) Novel predictors related to hysteresis and baseflow improve predictions of watershed nutrient loads: An example from Ontario's lower Great Lakes basin. Science of The Total Environment 826:154023. https://doi.org/10.1016/j.scitotenv.2022.154023

Bricker S, Longstaff B, Dennison W, et al (2008) Effects of nutrient enrichment in the nation's estuaries: A decade of change. Harmful Algae 8(1):21–32. https://doi.org/10.1016/j.hal.2008.08.028

Bugica K, Sterba-Boatwright B, Wetz MS (2020) Water quality trends in Texas estuaries. Marine Pollution Bulletin 152:110903. https://doi.org/10.1016/j.marpolbul.2020.110903

Bukaveckas PA, Tassone S, Lee W, et al (2020) The influence of storm events on metabolism and water quality of riverine and estuarine segments of the James, Mattaponi, and Pamunkey Rivers. Estuaries and Coasts 43(7):1585–1602. https://doi.org/10.1007/s12237-020-00819-9

Burman P (1989) A comparative study of ordinary cross-validation, v-fold cross-validation and the repeated learning-testing methods. Biometrika 76(3):503–514.

https://doi.org/10.1093/biomet/76.3.503

Burnham KP, Anderson DR, Huyvaert KP (2011) AIC model selection and multimodel inference in behavioral ecology: Some background, observations, and comparisons. Behavioral Ecology and Sociobiology 65(1):23–35. https://doi.org/10.1007/s00265-010-1029-6

Caffrey JM (2004) Factors controlling net ecosystem metabolism in U.S. estuaries. Estuaries 27(1):90–101. https://doi.org/10.1007/BF02803563

Caffrey JM, Chapin TP, Jannasch HW, et al (2007) High nutrient pulses, tidal mixing and biological response in a small California estuary: Variability in nutrient concentrations from decadal to hourly time scales. Estuarine, Coastal and Shelf Science 71(3-4):368–380. https://doi.org/10.1016/j.ecss.2006.08.015

Chin T, Beecraft L, Wetz MS (2022) Phytoplankton biomass and community composition in three Texas estuaries differing in freshwater inflow regime. Estuarine, Coastal and Shelf Science 277:108059. https://doi.org/10.1016/j.ecss.2022.108059

Cira EK, Palmer TA, Wetz MS (2021) Phytoplankton dynamics in a low-inflow estuary (Baffin Bay, TX) during drought and high-rainfall conditions associated with an El Niño event. Estuaries and Coasts 44(7):1752–1764. https://doi.org/10.1007/s12237-021-00904-7

Cloern JE, Foster SQ, Kleckner AE (2014) Phytoplankton primary production in the world's estuarine-coastal ecosystems. Biogeosciences 11(9):2477–2501. https://doi.org/10.5194/bg-11-2477-2014

De Cicco LA, Hirsch RM, Lorenz DL, et al (2022) dataRetrieval: R packages for discovering and retrieving water data available from Federal hydrologic web services. U.S. Geological Survey, https://doi.org/10.5066/P9X4L3GE

Dorado S, Booe T, Steichen J, et al (2015) Towards an understanding of the interactions between freshwater inflows and phytoplankton communities in a subtropical estuary in the Gulf of Mexico. PLOS ONE 10(7):e0130931. https://doi.org/10.1371/journal.pone.0130931

Dunn D (1996) Trends in Nutrient Inflows to the Gulf of Mexico from Streams Draining the Conterminous United States, 1972-93. Water-Resources Investigations Report 96-4113, USGS, Austin, Texas, https://doi.org/10.3133/wri964113

Gardner WS, McCarthy MJ, An S, et al (2006) Nitrogen fixation and dissimilatory nitrate reduction to ammonium (DNRA) support nitrogen dynamics in Texas estuaries. Limnology and Oceanography 51(1part2):558–568. https://doi.org/10.4319/lo.2006.51.1_part_2.0558

Hagemann M, Asce SM, Kim D, et al (2016) Estimating Nutrient and Organic Carbon Loads to Water-Supply Reservoir Using Semiparametric Models. J Environ Eng p 9. https://doi.org/10.1061/(ASCE)EE.1943-7870.0001077

Hayes NM, Haig HA, Simpson GL, et al (2020) Effects of lake warming on the seasonal risk of toxic cyanobacteria exposure. Limnology and Oceanography Letters 5(6):393–402. https://doi.org/10.1002/lol2.10164

Hirsch RM, Moyer DL, Archfield SA (2010) Weighted Regressions on Time, Discharge, and Season (WRTDS), with an application to Chesapeake Bay River inputs. JAWRA Journal of the American Water Resources Association 46(5):857–880. https://doi.org/10.1111/j.1752-1688.2010.00482.x

Hornung RW, Reed LD (1990) Estimation of average concentration in the presence of nondetectable values. Applied Occupational and Environmental Hygiene 5(1):46–51. https://doi.org/10.1080/1047322X.1990.10389587

Horowitz AJ (2003) An evaluation of sediment rating curves for estimating suspended sediment concentrations for subsequent flux calculations. Hydrological Processes 17(17):3387–3409. https://doi.org/10.1002/hyp.1299

Hou L, Liu M, Carini SA, et al (2012) Transformation and fate of nitrate near the sediment–water interface of Copano Bay. Continental Shelf Research 35:86–94. https://doi.org/10.1016/j.csr.2012.01.004

Jain S, Schramm MP (2021) Technical Support Document for One Total Maximum Daily Load for Indicator Bacteria in Lavaca River Above Tidal. Technical Report AS-221, Texas Commission on Environmental Quality, Austin, Texas, URL https://www.tceq.texas.gov/downloads/water-quality/tmdl/lavaca-river-above-tidal-rocky-creek-recreational-108/108-lavaca-river-addendum-tsd-2021-october-as-221.pdf

Kennicutt MC (2017) Water Quality of the Gulf of Mexico. In: Ward CH (ed) Habitats and Biota of the Gulf of Mexico: Before the Deepwater Horizon Oil Spill. Springer New York, New York, NY, p 55–164, https://doi.org/10.1007/978-1-4939-3447-8_2

Kroon FJ, Kuhnert PM, Henderson BL, et al (2012) River loads of suspended solids, nitrogen, phosphorus and herbicides delivered to the Great Barrier Reef lagoon. Marine Pollution Bulletin 65(4-9):167–181. https://doi.org/10.1016/j.marpolbul.2011.10.018

Kuhnert PM, Henderson BL, Lewis SE, et al (2012) Quantifying total suspended sediment export from the Burdekin River catchment using the loads regression estimator tool. Water Resources Research 48(4). https://doi.org/10.1029/2011WR011080

Lloyd C, Freer J, Collins A, et al (2014) Methods for detecting change in hydrochemical time series in response to targeted pollutant mitigation in river catchments. Journal of Hydrology 514:297–312. https://doi.org/10.1016/j.jhydrol.2014.04.036

Marra G, Wood SN (2012) Coverage properties of confidence intervals for Generalized Additive Model components: Coverage properties of GAM intervals. Scandinavian Journal of Statistics 39(1):53–74. https://doi.org/10.1111/j.1467-9469.2011.00760.x

McDowell RW, Simpson ZP, Ausseil AG, et al (2021) The implications of lag times between nitrate leaching losses and riverine loads for water quality policy. Scientific Reports 11(1):16450. https://doi.org/10.1038/s41598-021-95302-1

Montagna PA, Cockett PM, Kurr EM, et al (2020) Assessment of the Relationship Between Freshwater Inflow and Biological Indicators in Lavaca Bay. Tech. Rep. Contract # 1800012268, Harte Research Institute, Texas A&M University-Corpus Christi, Corpus Christi, Texas

Mooney RF, McClelland JW (2012) Watershed export events and ecosystem responses in the Mission–Aransas National Estuarine Research Reserve, South Texas. Estuaries and Coasts 35(6):1468–1485. https://doi.org/10.1007/s12237-012-9537-4

Moriasi DN, Gitau MW, Pai N, et al (2015) Hydrologic and Water Quality Models: Performance Measures and Evaluation Criteria. Transactions of the ASABE 58(6):1763–1785. https://doi.org/10.13031/trans.58.10715

Murphy RR, Perry E, Harcum J, et al (2019) A Generalized Additive Model approach to evaluating water quality: Chesapeake Bay case study. Environmental Modelling & Software 118:1–13. https://doi.org/10.1016/j.envsoft.2019.03.027

Murphy RR, Keisman J, Harcum J, et al (2022) Nutrient improvements in Chesapeake Bay: Direct effect of load reductions and implications for coastal management. Environmental Science & Technology 56(1):260–270. https://doi.org/10.1021/acs.est.1c05388

Oelsner GP, Stets EG (2019) Recent trends in nutrient and sediment loading to coastal areas of the conterminous U.S.: Insights and global context. Science of The Total Environment 654:1225–1240. https://doi.org/10.1016/j.scitotenv.2018.10.437

Omani N, Srinivasan R, Lee T (2014) Estimation of sediment and nutrient loads to bays from gauged and ungauged watersheds. Applied Engineering in Agriculture pp 869–887. https://doi.org/10.13031/aea.30.10162

Örnólfsdóttir EB, Lumsden S, Pinckney JL (2004) Nutrient pulsing as a regulator of phytoplankton abundance and community composition in Galveston Bay, Texas. Journal of Experimental Marine Biology and Ecology 303(2):197–220. https://doi.org/10.1016/j.jembe.2003.11.016

Palmer TA, Montagna PA (2015) Impacts of droughts and low flows on estuarine water quality and benthic fauna. Hydrobiologia 753(1):111–129. https://doi.org/10.1007/s10750-015-2200-x

Paudel B, Montagna PA, Adams L (2019) The relationship between suspended solids and nutrients with variable hydrologic flow regimes. Regional Studies in Marine Science 29:100657. https://doi.org/10.1016/j.rsma.2019.100657

Peierls BL, Hall NS, Paerl HW (2012) Non-monotonic responses of phytoplankton biomass accumulation to hydrologic variability: A comparison of two coastal plain North Carolina estuaries. Estuaries and Coasts 35(6):1376–1392. https://doi.org/10.1007/s12237-012-9547-2

Rebich RA, Houston NA, Mize SV, et al (2011) Sources and delivery of nutrients to the northwestern Gulf of Mexico from streams in the south-central United States. JAWRA Journal of the American Water Resources Association 47(5):1061–1086. https://doi.org/10.1111/j.1752-1688.2011.00583.x

Robson BJ, Dourdet V (2015) Prediction of sediment, particulate nutrient and dissolved nutrient concentrations in a dry tropical river to provide input to a mechanistic coastal water quality model. Environmental Modelling & Software 63:97–108. https://doi.org/10.1016/j.envsoft.2014.08.009

Russell MJ, Montagna PA, Kalke RD (2006) The effect of freshwater inflow on net ecosystem metabolism in Lavaca Bay, Texas. Estuarine, Coastal and Shelf Science 68(1-2):231–244. https://doi.org/10.1016/j.ecss.2006.02.005

Schramm M (2023) Adc: Calculate Antecedant Discharge Conditions. URL https://CRAN.R-project.org/package=adc

Schramm M, Berthold A, Entwistle C, et al (2018) Lavaca River Watershed Protection Plan. Technical Report TR-507, Texas Water Resources Institute, College Station, Texas, URL https://twri.tamu.edu/publications/technical-reports/2018-technical-reports/tr-507/

Schramm M, Gitter A, Gregory L (2022) Total Maximum Daily Loads and *Escherichia coli* trends in Texas freshwater streams. Journal of Contemporary Water Research & Education 176:36–49. https://doi.org/10.1111/j.1936-704X.2022.3374.x

Shoda ME, Sprague LA, Murphy JC, et al (2019) Water-quality trends in U.S. rivers, 2002 to 2012: Relations to levels of concern. Science of The Total Environment 650:2314–2324. https://doi.org/10.1016/j.scitotenv.2018.09.377

Snelder T, McDowell R, Fraser C (2017) Estimation of catchment nutrient loads in New Zealand using monthly water quality monitoring data. JAWRA Journal of the American Water Resources Association 53(1):158–178. https://doi.org/10.1111/1752-1688.12492

Stackpoole S, Sabo R, Falcone J, et al (2021) Long-term Mississippi River trends expose shifts in the river load response to watershed nutrient balances between 1975 and 2017. Water Resources Research 57(11). https://doi.org/10.1029/2021WR030318

Stets E, Lee C, Lytle D, et al (2018) Increasing chloride in rivers of the conterminous U.S. and linkages to potential corrosivity and lead action level exceedances in drinking water. Science of The Total Environment 613–614:1498–1509. https://doi.org/10.1016/j.scitotenv.2017.07.119

Tominack SA, Wetz MS (2022) Variability in phytoplankton biomass and community composition in Corpus Christi Bay, Texas. Estuaries and Coasts https://doi.org/10.1007/s12237-022-01137-y

Vecchia AV, Gilliom RJ, Sullivan DJ, et al (2009) Trends in concentrations and use of agricultural herbicides for Corn Belt Rivers, 1996-2006. Environmental Science & Technology 43(24):9096–9102. https://doi.org/10.1021/es902122j

Walker LM, Montagna PA, Hu X, et al (2021) Timescales and magnitude of water quality change in three Texas estuaries induced by passage of Hurricane Harvey. Estuaries and Coasts 44(4):960–971. https://doi.org/10.1007/s12237-020-00846-6

Wang YG, Kuhnert P, Henderson B (2011) Load estimation with uncertainties from opportunistic sampling data – A semiparametric approach. Journal of Hydrology 396(1-2):148–157. https://doi.org/10.1016/j.jhydrol.2010.11.003

Wazniak CE, Hall MR, Carruthers TJB, et al (2007) Linking water quality to living resources in a Mid-Atlantic lagoon system, USA. Ecological Applications 17(sp5):S64–S78. https://doi.org/10.1890/05-1554.1

Wetz MS, Yoskowitz DW (2013) An 'extreme' future for estuaries? Effects of extreme climatic events on estuarine water quality and ecology. Marine Pollution Bulletin 69(1-2):7–18. https://doi.org/10.1016/j.marpolbul.2013.01.020

Wetz MS, Hayes KC, Fisher KV, et al (2016) Water quality dynamics in an urbanizing subtropical estuary(Oso Bay, Texas). Marine Pollution Bulletin 104(1-2):44–53. https://doi.org/10.1016/j.marpolbul.2016.02.013

Wetz MS, Cira EK, Sterba-Boatwright B, et al (2017) Exceptionally high organic nitrogen concentrations in a semi-arid South Texas estuary susceptible to brown tide blooms. Estuarine, Coastal and Shelf Science 188:27–37. https://doi.org/10.1016/j.ecss.2017.02.001

Wise DR, Anning DW, Miller OW (2019) Spatially referenced models of streamflow and nitrogen, phosphorus, and suspended-sediment transport in streams of the southwestern United States. Scientific Investigations Report 2019-5106, U.S. Geological Survey, Reston, Virginia

Wood SN (2006) On confidence intervals for generalized additive models based on penalized regression splines. Australian & New Zealand Journal of Statistics 48(4):445–464. https://doi.org/10.1111/j.1467-842X.2006.00450.x

Wood SN (2011) Fast stable restricted maximum likelihood and marginal likelihood estimation of semiparametric generalized linear models: Estimation of Semiparametric Generalized Linear Models. Journal of the Royal Statistical Society: Series B (Statistical Methodology) 73(1):3–36. https://doi.org/10.1111/j.1467-9868.2010.00749.x

Zhang Q, Ball WP (2017) Improving riverine constituent concentration and flux estimation by accounting for antecedent discharge conditions. Journal of Hydrology

547:387–402. https://doi.org/10.1016/j.jhydrol.2016.12.052