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PHOSPHORUS AND NITROGEN EXPORT ASSOCIATED WITH BIOSOLIDS APPLICATIONS IN TRIBUTARY WATERSHEDS OF THE ST. JOHNS RIVER

by

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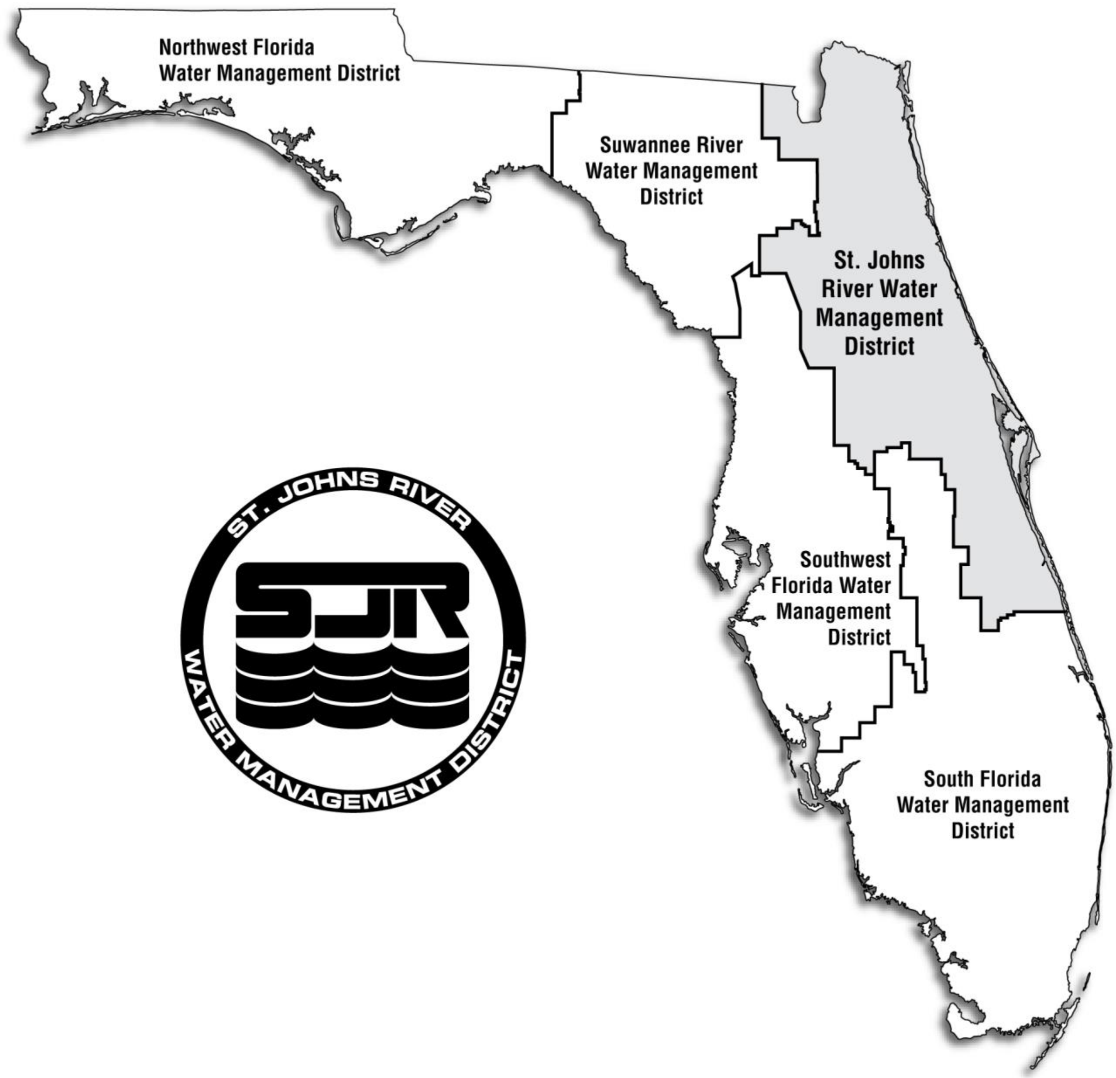

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EXECUTIVE SUMMARY

Biosolids, the solid residuals from the treatment of domestic wastewater, are beneficially used to supplement or replace fertilizer in agricultural production throughout the world. Two classes of biosolids are applied in the United States: 1) Class A biosolids, a highly treated form that are generally applied using fertilizer guidelines, and 2) Class B biosolids, a minimally processed form that may be land-applied on limited crops under federal and state regulations. Approximately two-thirds of the biosolids generated in Florida are Class B, the majority of which are applied to pastureland. The large expanse of cattle ranchland in central Florida (Polk, Osceola, Brevard, Highlands, and Okeechobee counties) historically received the majority of Class B biosolids. However, in 2010, new rules governing Class B biosolids disposal within the Okeechobee, St. Lucie, and Caloosahatchee basins led to a shift in applications outside of these basins. By 2013, when the new Class B regulations went into effect, applications of Class B in the Upper St. Johns River Basin (USJRB) doubled, resulting in the USJRB receiving approximately 66% of all Class B biosolids in the state. Recent water quality trends (2005–2020) in tributaries of the upper St. Johns River have shown significant increases in phosphorus (P) where biosolids applications have increased in the watershed. These watersheds are comprised predominantly of pastureland and have experienced minimal land use change over the last 30 years that could account for observed water quality trends.

The current study examines the relationship between the timing and magnitude of Class B biosolids applications and trends in total P (TP) and total nitrogen (TN) fluxes in seven USJRB tributaries and one Lower St. Johns River Basin (LSJRB) tributary. Annual applications of P and N from Class B biosolids were compiled from Florida Department of Environmental Protection (FDEP) permit records and assigned to watersheds. Weighted Regressions on Time, Discharge, and Season (WRTDS) were used to evaluate long-term (25-year) trends in tributary TP and TN fluxes, and targeted storm-event and high-frequency sampling were performed within one study watershed to confirm correlations between biosolid application intensity and runoff concentrations.

Increases in TP fluxes occurred in seven of the eight study tributaries during periods of intensified Class B biosolids applications. However, TN fluxes were stable across all tributaries over the period of analysis. The WRTDS method also generates flow-normalized fluxes, which are adjusted for interannual hydrologic variability and better represent long-term changes in flux resulting from changes in watershed activities. Flow-normalized TP and TN fluxes were similar to non-normalized fluxes, indicating that trends in TP fluxes were driven primarily by increases in concentrations at high flows and not trends in discharge. Storm-event sampling data showed a positive relationship between Class B biosolids applications and concentrations of both P and N at sampling sites close to pasture land use. Denitrification and assimilation of N in downstream waters and riparian wetlands may explain the lack of trend in downstream TN flux, given that elevated N concentrations were observed near biosolids sites.

Biosolids Application and Water Quality

Following the doubling of biosolids applications in the USJRB beginning in 2013, the estimated total increase in mean annual TP flux for the USJRB tributaries in the present study was estimated to be 36 metric tons (MT). Between 0.4–3.4 % annual loss of land-applied biosolids P would be required to produce to observed trends in flux in each watershed. Previous work to quantify biosolids nutrient loss in surface soils supports this magnitude of loss through immediate runoff and leaching. Longer-term mineralization and transport processes are also likely contributors to legacy P impacts but are not as well understood.

The results of the present study provide strong correlative evidence that Class B biosolids applications have led to export of P into the St. Johns River. Although biosolids applications were within regulatory requirements, two factors that likely led to P export were: 1) application of biosolids based on crop N requirements, leading to excess P application and soil P saturation, and 2) focusing of over two-thirds of the state's Class B biosolids into adjacent watersheds within one basin. New regulations for biosolids have recently been approved that will limit the future excess application of P. However, further investigation into the mechanisms of transport and fate of all forms of P in biosolids is recommended to ensure that receiving waters experience minimal impacts from nutrients in biosolids.

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INTRODUCTION

The use of domestic wastewater solids, or biosolids, for agronomic fertilization and land reclamation is a beneficial use option for material that might otherwise be disposed of through landfilling or incineration. Biosolids contain high concentrations of the essential plant macronutrients nitrogen (N) and phosphorus (P), as well as organic carbon that improves soil physical and biological quality (Brown et al., 2011; Nicholson et al., 2018). Fifty-five percent of the biosolids generated in the 16,583 wastewater treatment facilities in the U.S are applied to soils for agronomic, silvicultural, or land reclamation purposes, with this proportion increasing over time (NEBRA, 2007). Approximately two-thirds of the biosolids generated in Florida are land applied (FDEP, 2014), with the proportions of this roughly evenly split between highly treated class A materials which are marketed as organic fertilizer and soil amendments, and Class B biosolids, which are transported directly from the generating facility to permitted sites by certified hauling firms, after undergoing pathogen and vector attraction reduction sufficient to be safely land applied. Within Florida, Class B biosolids are tracked and quantified with regard to mass, composition, and applied area through a permitting process administered by the state's Department of Environmental Protection (FDEP). The majority of the Class B land application occurs on pasturelands or hay crops (FDEP, 2014). Biosolids fertilization with Class B is a cost-effective practice for ranchers, as in many areas the supply is sufficiently abundant that haulers, contracted by wastewater utilities, provide and apply them at little or no cost.

Original federal guidance described in Title 40 CFR Part 503 on the use of wastewater solids limited application for agronomic purposes to the plant available nitrogen (PAN) requirement (USEPA, 1994). Because of the relatively low N:P mass ratio of class B biosolids, generally in the range of 2:1 or 3:1 (Sommers, 1977; USEPA, 2015), compared to the typical crop requirement for pasture grasses of 9.2:1 (Mayo, 2018), land application at the PAN level supplies P in excess of crop requirements (Kelling et al., 1977; Maguire et al., 2000). This excess P fertilization has led to concerns related to runoff nutrient enrichment and eutrophication (O'Connor et al., 2005; Sharpley et al., 2013), though research related to the fate of this excess biosolids P has provided varied interpretations. Research on pastures and cropland soils with long-term biosolids applications has documented P enrichment to levels of potential environmental concern (Schroder et al., 2008), and which can persist many years after the cessation of applications (Cogger et al., 2013; Lemming et al., 2019), though the implications for off-site surface waters enrichment is often hypothetical. Examinations of soils from fields on which biosolids have been applied, or on biosolids-amended soil boxes subjected to simulated rainfall, confirm high total P (TP) content, though generally indicate low levels of extractable or runoff phosphorus when compared to manure or inorganic P fertilizer applied at equivalent rates (Elliott et al., 2002; O'Connor et al., 2004; Silveira et al., 2019). The presence of calcium, iron or aluminum, introduced at wastewater facilities for effluent treatment or solids processing, has been credited with immobilizing a large portion of the biosolids-applied P (Brandt et al., 2004; Chinault and O'Connor, 2008; Elliott et al., 2002; Maguire et al., 2001; Penn and Sims, 2002; Shober et al., 2006; White et al., 2010). This associated enhancement of soil P storage capacity (SPSC) may be particularly effective in sandy soils with inherently low P binding capability

(Nair et al., 2004; Withers et al., 2001). Limited evaluation on runoff P at the field scale has suggested that long-term biosolids fertilization can result in significantly elevated runoff concentrations (Richards et al., 2004), though stream runoff monitoring following one-time applications of biosolids for mine reclamation or reforestation did not indicate elevated P levels (Grey and Henry, 2002). Studies of the effects of biosolids fertilization at the field and watershed scale are rare and a recognized research need (O'Connor et al., 2005).

The concentrated cattle ranchland region in the center of Florida within Polk, Osceola, Okeechobee, Highlands, Hardee, and Hendry counties historically received the majority of Florida's Class B biosolids land application. This pattern was profoundly reoriented in 2007 with the passage of the Northern Everglades and Estuaries Protection Program. Provisions of this act were directed primarily at the reduction of P loading to Lake Okeechobee, and from there to its downstream estuaries of the St. Lucie and Caloosahatchee Rivers. This act's intent was promulgated in the 2010 revised rules governing biosolids disposal (F.A.C., 2016), which required permittees in the Lake Okeechobee (including the Kissimmee River), St. Lucie River, and Caloosahatchee River watersheds to demonstrate no new watershed P loading. By 2013, the first year of implementation for these revised rules, Class B biosolids applications in watersheds falling under the new restrictions were effectively eliminated, and applications within the adjacent, Upper St. Johns River Basin (USJRB) approximately doubled. Class B biosolid applications in the USJRB have remained at this elevated level to the present.

Within the USJRB, most water quality parameters of concern are stable or declining, however, surface water concentrations of P have recently exhibited significant increases at multiple monitoring sites. The most recent St. Johns River Water Management District (SJRWMD) water quality Status and Trends Assessment (SJRWMD, 2020) identified significantly increasing TP trends for 60% of the long-term ambient water quality sampling sites in the basin, primarily in watersheds on the western side of the USJRB project area where biosolids have been applied. In June 2017, the TP concentration in the St. Johns River at the long-term sampling site near U.S. Highway 192 reached 0.79 mg L^{-1}, doubling the highest value previously measured in the 38-year period of record. These trends in TP may impact the designated use of USJRB waters and the nutrient load reduction targets established for its downstream basins. Most disconcerting, along with sharply rising TP concentrations, the pristine headwaters Blue Cypress Lake, and Lake Washington, the source of a portion of the potable water supply for the City of Melbourne, have exhibited increased frequency of cyanobacteria blooms, in some cases associated with elevated concentrations of the cyanotoxin microcystin.

Given the intensification of applications of Class B biosolids to the USJRB, it is reasonable to investigate the possibility of a relationship between this and the coincident increasing surface water P concentrations in watersheds receiving Class B biosolids applications. In the present study, we investigated the relationship between the timing and application intensity of Class B biosolids and trends in P and N concentrations and export. Datasets from SJRWMD's ambient monitoring programs in seven USJRB watersheds and one Lower St. Johns River Basin (LSJRB) watershed were evaluated against patterns in Class B biosolids application. More recent, synoptic storm-event sampling efforts in the Jane Green Creek watershed within the USJRB were also analyzed to better understand the relationship between Class B biosolids application and stormflow nutrient concentrations.

METHODS

COMPILATION OF CLASS B BIOSOLIDS APPLICATION DATA

Records of Class B land applications were compiled from the Florida Department of Environmental Protection (FDEP) OCULUS permitting website (https://depedms.dep.state.fl.us/Oculus/servlet/login), along with hard copy records stored at FDEP facilities. Application of Class B biosolids occurs primarily on pastureland and hay crops in Florida, and permitted Class B application sites are required to annually report all applications by field in dry tons, as well as total pounds of N and P applied. Acres of application are also provided by field, allowing application rates by field to be calculated (e.g., pounds of N or P per acre).

Digitized field locations were obtained from FDEP or digitized from paper maps and stored in a Geographic Information System (GIS). Maps are provided in nutrient management plans that are prepared as part of the permitting process. Using GIS, every field was assigned to a watershed using the SJRMWD 1:24,000 detailed drainage basin layer (SJRWMD, 2019). Class B biosolid totals in dry tons were calculated annually for major watersheds of the St. Johns River between 2013 and 2019. Total annual land-applied N and P and mean application rates were calculated for the watersheds in the present study between 1995 and 2019 for available data.

STUDY SITES

Ambient monitoring sites

Water chemistry data for long-term (approximately 25 years) analyses of trends in concentration and load were obtained from the District's ambient water quality monitoring network. Ambient monitoring sites are sampled at fixed monthly intervals irrespective of hydrologic conditions. Ambient monitoring sites were selected based on the history of biosolids applications in their respective watersheds and availability of water quality monitoring data starting in 1995 or before. Some candidate sites were eliminated based on prior knowledge of factors that would confound the analysis, for example, reservoirs upstream of the watershed outlet or water quality impacts that were known to be from agricultural practices other than pastureland.

Two study areas with extensive Class B biosolids applications were chosen for analyses (Figure 1). These included the Haw Creek watershed in the LSJRB and seven tributary watersheds on the western side of the USJRB (Figure 2). All ambient water quality sites, except for Blue Cypress Creek, were located at watershed outlets with co-located discharge measurements or modeled discharge. The Blue Cypress Creek site water quality site excluded approximately 7% of the

Blue Cypress Creek watershed as measured from the discharge site, however, no biosolids applications were reported downstream of this water quality site.

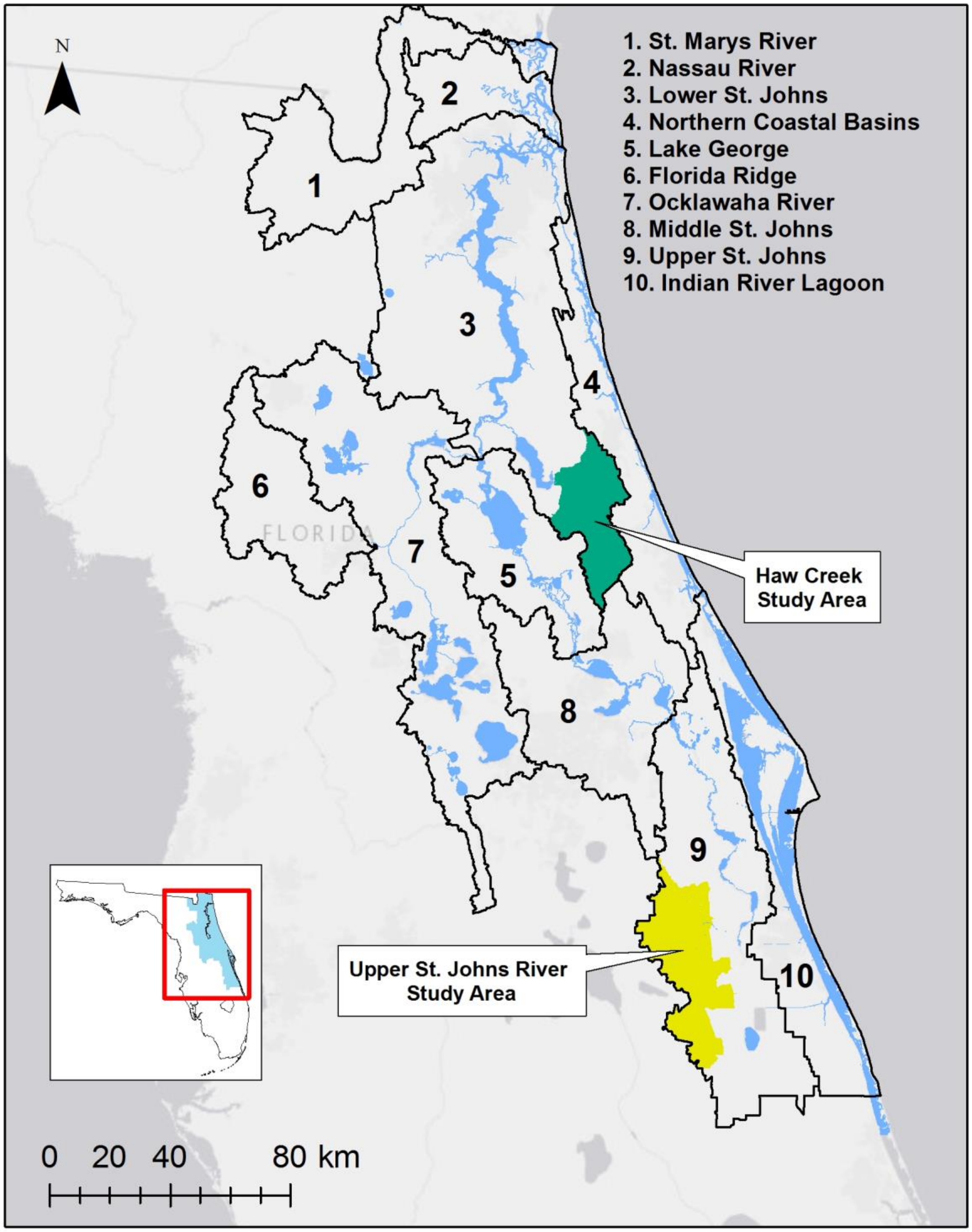

Figure 1. Major basins of the St. Johns River Water Management District in Florida. The Haw Creek and Upper St. Johns study areas are highlighted.

Land Use for the study watersheds is shown for 1994 and 2014 in Table 1 (SJRWMD, 1994; 2014). In Haw Creek, pasture was only 6% and 9% of the total land use in 1994 and 2014, respectively. However, pastures with biosolids applications were located close to the outlet of Haw Creek (approximately 8 km), and the remainder of the watershed was dominated by forested areas, wetlands, and water (80%). For all study watersheds in the USJRB, pastureland was the dominant land use (41–78 %) in both 1994 and 2014 and did not change meaningfully over the 20-year period between land use analysis. Other forms of agriculture and residential/urban development were minor components of land use in these watersheds, and the remainder of area (20–55%) was dominated by natural forested areas, wetlands, and water.

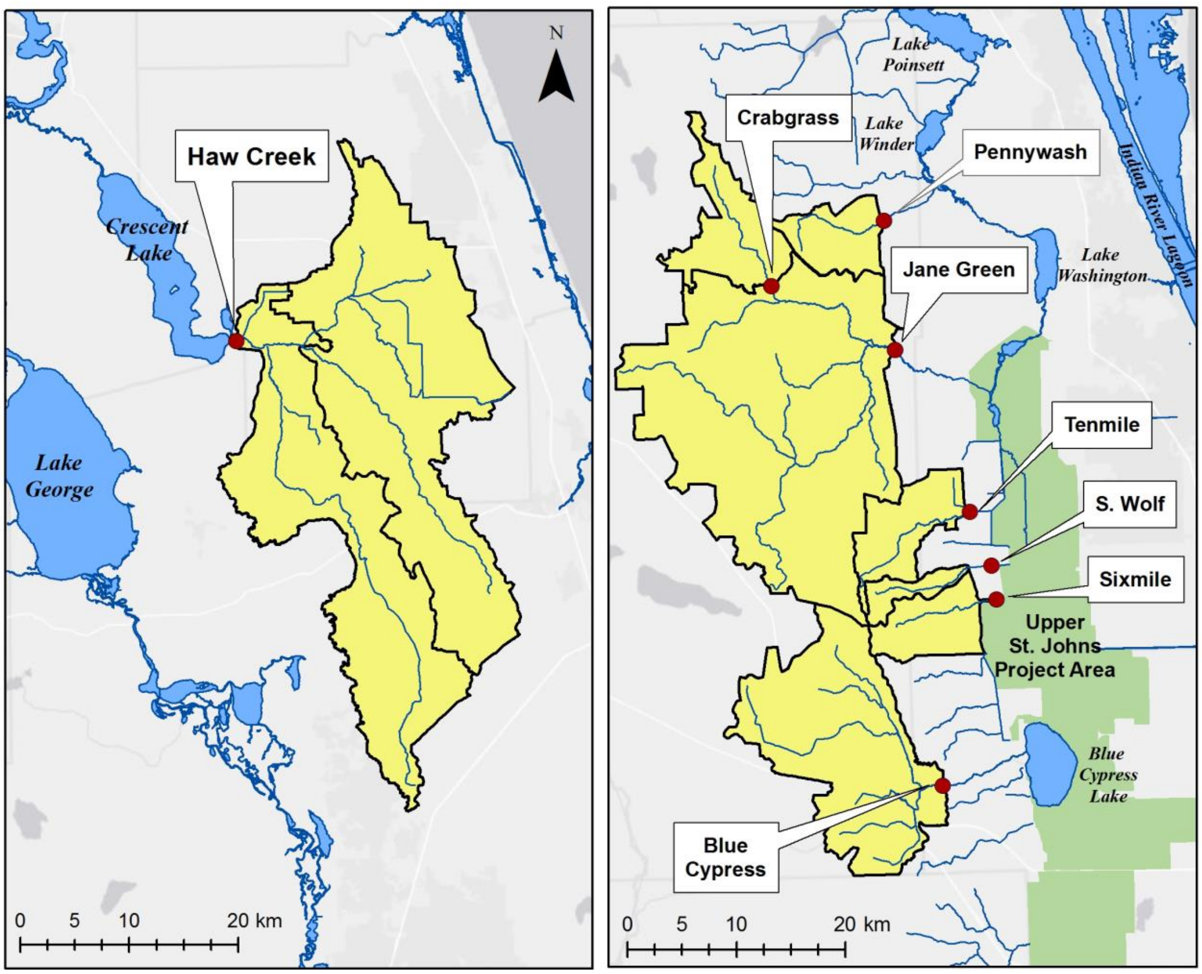

Figure 2. Location of ambient water quality monitoring study sites along creeks. Left panel: Haw Creek watershed and water quality sampling site. Right panel: Upper St. Johns water quality sampling sites and associated watersheds.

Table 1. Land Use for Ambient Site Watersheds in 1994 and 2014.

Year	Watershed	Major Basin	Area (km^2)	% Pasture	% Citrus	% Crops	% Other Agriculture	% Developed	% Natural Areas	% Water / Wetlands
1994	Haw Creek	Lower Basin	817	6	1	3	1	6	48	35
	Jane Green	Upper Basin	625	51	2	2	<0.1	1	18	26
	Blue Cypress	Upper Basin	257	41	1	4	<0.1	2	22	30
	Crabgrass	Upper Basin	80	77	0	0	0	<0.1	2	21
	Tenmile	Upper Basin	66	68	<0.1	0	<0.1	1	13	18
	Sixmile	Upper Basin	55	59	2	4	0	1	18	16
	Pennywash	Upper Basin	50	78	2	0	<0.1	<0.1	2	18
	South Wolf	Upper Basin	21	71	0	0	0	1	7	21
2014	Haw Creek	Lower Basin	817	9	<0.3	2	2	7	45	35
	Jane Green	Upper Basin	625	42	1	<0.1	<0.3	2	29	26
	Blue Cypress	Upper Basin	257	61	1	1	1	2	11	23
	Crabgrass	Upper Basin	80	71	0	1	1	1	3	23
	Tenmile	Upper Basin	66	70	<0.1	0	<0.1	1	12	17
	Sixmile	Upper Basin	55	72	1	0	<0.1	1	12	14
	Pennywash	Upper Basin	50	78	2	1	<0.1	1	1	17
	South Wolf	Upper Basin	21	75	0	0	0	1	6	18

Jane Green Creek storm-event sites

A set of limited duration (2017–present) synoptic grab sampling sites was established to measure stormflow nutrient concentrations within the Jane Green Creek watershed (Figure 3). These sub-watersheds within Jane Green Creek have received varying amounts of Class B biosolids. A Sea-Bird © cycle-P phosphate sampler was installed at the most downstream site in the Jane Green Creek sampling network (JGS, see Figure 3) to measure orthophosphate values every two hours.

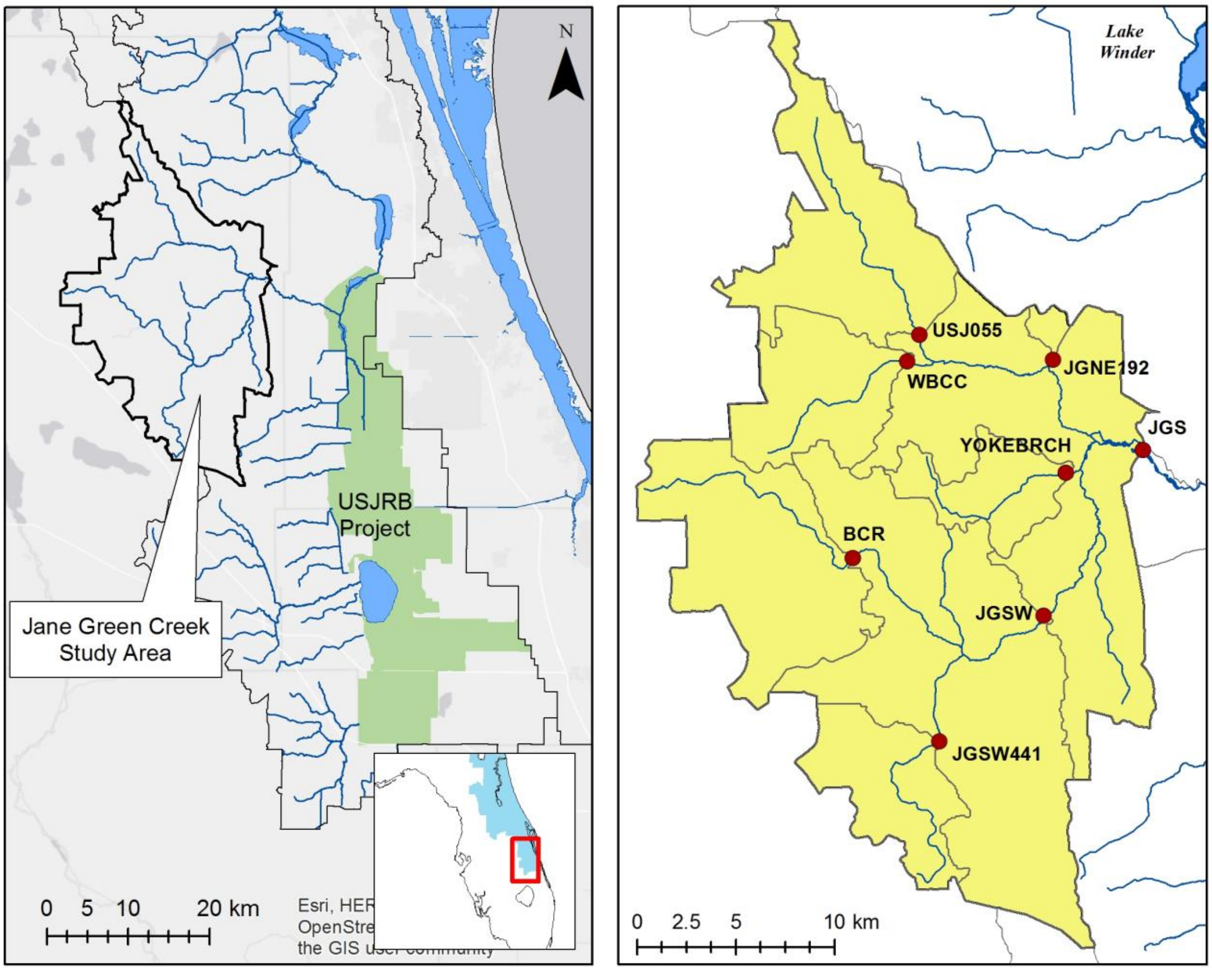

Figure 3. Jane Green Creek storm-event sample sites. Left panel: Site overview showing location of the study watershed and District USJRB project boundary (green). Right panel: Location of sample sites.

Land use for the Jane Green Creek storm-event sample site watersheds is reported in Table 2. Five watersheds (JGS, JGSW, BCR, USJ055, and JGNE192) were dominated by pastureland (42–71%). The remaining three watersheds contained 10 – 14 % pasture and were primarily forested natural areas, water and wetlands (72–89%).

Table 2. Land use in 2014 for Jane Green Creek storm-event sites.

Sub-Watershed	Area (km^2)	% Pasture	% Citrus	% Crops	% Other Agriculture	% Developed	% Natural Areas	% Water Wetlands
JGS	625	42	1	<0.1	<0.3	2	29	26
JGSW	309	51	1	0	<0.3	1	21	26
BCR	91	60	1	<0.1	0	3	15	21
USJ055	80	71	0	1	1	1	3	23
WBCC	49	10	11	<0.3	<0.3	7	50	22
JGSW441	43	14	0	<0.1	<0.3	1	55	30
YOKEBRCH	30	11	<0.1	0	<0.3	<0.3	64	25
JGNE192	4	65	0	0	0	<0.1	6	29

ANALYSIS OF WATER QUALITY PATTERNS

Ambient and storm-event water quality data from the study sites were retrieved from SJRWMD's Environmental Database. Quality codes for each site were examined to ensure poor quality data were not used in the analysis. All data analysis, plots, and statistical tests were executed using R statistical software (R Core Team, 2019). To test for differences between means, the non-parametric Wilcoxon signed-rank test was used.

WEIGHTED REGRESSIONS ON TIME, DISCHARGE, AND SEASON (WRTDS) ANALYSIS

Long-term trends in total N and P flux were analyzed at ambient monitoring sites using the Weighted Regressions on Time, Discharge, and Season (WRTDS) method (Hirsch et al., 2010). The WRTDS method has been recently utilized to evaluate long-term trends in constituent concentration and flux in riverine systems and is a flexible and robust tool for water quality trend analysis (Choquette et al., 2019; Murphy and Sprague, 2019). The method utilizes long-term records of water quality data (>20 years) and daily discharge measurements to estimate daily concentration and flux values. Daily concentration values are modeled as:

$$\ln(c) = \beta_0 + \beta_1 t + \beta_2 \ln(Q) + \beta_3 \sin(2\pi t) + \beta_4 \cos(2\pi t) + \varepsilon$$

where ln is the natural logarithm, c is concentration, Q is daily mean discharge, t is time in decimal years, β_i are fitted coefficients, and ε is unexplained variance. The sin and cos terms introduce seasonal variation into the model. The WRTDS model is fitted using locally weighted regression, that is, local coefficients are fitted with weighted subsets of the full calibration dataset. Weights are assigned based on distance in time, streamflow, and season between the observation and calibration point. The result is a unique set of coefficients for every combination of Q and t. The model can also be conceptualized and displayed as a regression surface, with a time axis, discharge axis, and concentration axis. The model structure provides the flexibility to capture the evolution of the river system over time, including changes in the concentration vs. discharge relationship, changes in seasonal patterns, and long-term linear trends.

WRTDS models were fit for TP and TN at the ambient monitoring sites using the EGRET package (v 3.0.2) in the R software environment (Hirsch and De Cicco, 2015; R Core Team, 2019). Daily discharge datasets were obtained from U. S. Geological Survey (USGS) gauged monitoring sites or previously-calibrated Hydrologic Simulation Program-Fortran (HSPF) models (Jobes et al., 2021). Details of the hydrologic datasets are provided in Table 3. Three gauged discharge datasets were filled with HSPF model values for missing time periods of two years or less, after comparison of overlapping periods. The model parameters that can be adjusted in EGRET WRTDS fitting process are the half-window values for calibration point weights in the time, discharge, and seasonal dimensions. Models were tested with different parameter values, but no significant improvement in model fit was observed as compared to the default values. Model quality was determined by observation of residuals, observed vs. modeled concentration and flux values, and by the flux bias statistic. The flux bias statistic is calculated as:

$$B = (P - O)/P$$

where B is the flux bias statistic, P is the sum of the estimated fluxes on all sampled days, and O is the sum of the measured fluxes on all sampled days. After WRTDS models were fit, annual estimates of mean concentration and flux were calculated from daily estimated values.

Table 3. Discharge datasets used in WRTDS models. The HSPF data source indicates modeled flows from the Hydrologic Simulation Program-Fortran.

Site	USGS Site No.	Data source	Analysis Period	Notes
Haw Creek	02244333	HPSF	1990–2016	USGS discharge dataset not long enough (2010–2020)
Jane Green	02231600	USGS	1995–2020	
Blue Cypress	02231396	USGS	1995–2020	
Crabgrass	02231565	HSPF	1995–2020	Only 2 years of USGS discharge data available
Tenmile	NA	HPSF	1995–2020	
Sixmile	02231454	USGS + HSPF	1995–2020	Filled with HSPF data 9.31.2018 – 12.31.2020
Pennywash	02232155	USGS + HSPF	1995–2020	Filled with HSPF data 6.27.2019 – 11.05.2019
South Wolf	02231458	USGS + HSPF	1995–2020	Filled with HSPF data 9.30.2009 – 12.31.2020

In addition to annual estimates of concentration and flux, the EGRET package provides flow-normalized concentration and flux, which allow for evaluation of trends in concentration and flux after normalizing for interannual hydrologic variability. It should be noted that these values are distinct from the commonly calculated flow-weighted concentrations and fluxes. For

WRTDS models, the flow-normalized concentration or flux on a specific day is the integral of the fitted estimates of concentration or flux as a function of discharge and time multiplied by the probability density function (pdf) of discharge for that day of the year. This can be described for flow-normalized concentration in the following formula (Hirsch and De Cicco, 2015):

$$E[C_{fn}(T)] = \int_{0}^{\infty} w(Q,T) * f_{Ts}(Q)dQ$$

where $E[C_{fn}(T)]$ is flow-normalized concentration at time T (a specific day of a specific year), $w(Q,T)$ is the WRTDS estimate of concentration as a function of discharge and time, and $f_{Ts}(Q)$ is the probability density function of discharge, specific to a particular time of year. For a 20-year dataset, only 20 values would be used to estimate the discharge pdf for each day, however, when aggregated to monthly and annual averages, smooth estimates of flow-normalized concentrations and flux are obtained. To quantify the uncertainty on flow-normalized concentrations and fluxes, a block bootstrap resampling method was developed by Hirsch, et al. (2015). This method was implemented in present study using the EGRETci R package (v 2.0.3) to estimate 95% confidence intervals on annual flow-normalized concentrations and fluxes.

RESULTS

PATTERNS IN CLASS B BIOSOLIDS LAND APPLICATION

Compilation of recent (2013–2019) FDEP permit data for major basins of SRJWMD showed that Class B biosolids applications have been primarily in the USJRB (Table 4). Total applications in the USJRB were between 49,000–73,000 metric tons (by dry weight) annually. The Indian River Lagoon saw the second most application (1,300–3,700 metric tons annually) until 2018, when applications were eliminated by local ordinances. All other basins received annual totals total between 21–1,700 metric tons, with most annual totals falling below 1,000 metric tons. Between 2013–2019, District lands annually received between 56,000 and 75,000 metric tons of Class B biosolids.

Table 4. Application of Class B biosolids (metric tons dry weight) in major basins of the St. Johns River Water Management District.

Year	Upper St. Johns	Middle St. Johns	Lower St. Johns	Ocklawaha	Northern Coastal	Indian River Lagoon	St. Marys River	Total
2013	48,768	653	1,675	596	528	3,693	224	56,137
2014	70,630	106	776	787	284	1,798	440	74,821
2015	62,892	0	398	731	266	1,789	463	66,538
2016	67,585	200	389	419	388	3,557	223	72,761
2017	57,187	142	232	294	194	1,305	233	59,587
2018	58,504	0	21	94	347	0	317	59,283
2019	73,238	0	139	257	0	0	301	73,935

Application records were used to calculate total N and P application beginning in 1995 and 1998 for the for the Haw Creek watershed and Upper St. Johns study watersheds, respectively. Applications prior to these years may have occurred, but records were not available. Biosolids application totals and number of fields applied in the Haw Creek watershed increased in 2007, resulting in annual totals between 47 – 131 metric tons of P and 90 – 211 metric tons of N (Table 5). Applications declined in Haw Creek beginning in 2012 and ended by 2017. Within the study watersheds of the Upper St. Johns, significant applications were documented beginning in 2000, and large increases in land-applied N and P, and number of fields applied, were observed beginning in 2013 (Table 6). Between 2000 – 2012, annual totals were between 36 – 452 metric tons P and 81 – 929 metric tons N. After 2013, annual totals rose to 499 – 918 metric tons P and 1,194 – 2,242 metric tons N.

The average of annual application rates across all fields exhibited different patterns for the two study watersheds. In the Haw Creek watershed, the average N and P application rates (kg ha^{-1}) were not higher during the period when total applications increased (2007 – 2012), but rather, the number of fields applied approximately doubled (Table 5). For the Upper St. Johns watersheds, the average application rate of N doubled, and the application rate of P increased by two-thirds after 2013. The number of fields applied after 2013 increased by a factor of four (Table 6).

Table 5. Total land application of N and P and average application rates by year for the Haw Creek watershed.

Year	Land-applied P (MT)	Land-applied N (MT)	Average P Application Rate (kg ha^{-1})	Average N Application Rate (kg ha^{-1})	Number of Fields Applied
1995	1	1	34	63	2
1996	50	96	109	210	24
1997	19	36	248	466	5
1998	41	73	226	397	6
1999	<1	5	7	68	4
2000	-	-	-	-	-
2001	44	93	196	392	11
2002	31	48	72	137	19
2003	27	43	119	181	14
2004	25	42	94	161	9
2005	39	90	152	331	10
2006	14	44	107	275	5
2007	100	211	145	305	25
2008	131	210	187	301	25
2009	87	206	123	280	27
2010	103	235	122	268	28
2011	47	90	103	205	13
2012	17	45	86	198	3

Table 5. (continued)

Year	Land-applied P (MT)	Land-applied N (MT)	Average P Application Rate (kg ha^{-1})	Average N Application Rate (kg ha^{-1})	Number of Fields Applied
2013	14	40	128	364	4
2014	13	30	117	276	4
2015	9	25	83	242	4
2016	7	23	59	191	4
2017	3	12	26	100	1
2018	0	0	0	0	0
2019	0	0	0	0	0

Table 6. Total land application of N and P and average application rates by year for the Upper St. Johns study watersheds.

Year	Land-applied P (MT)	Land-applied N (MT)	Average P Application Rate (kg ha^{-1})	Average N Application Rate (kg ha^{-1})	Number of Fields Applied
1998	5	14	23	59	6
1999	12	37	22	71	11
2000	49	140	42	104	14
2001	90	264	57	148	11
2002	254	295	99	134	19
2003	141	264	112	201	14
2004	76	132	91	164	13
2005	36	81	85	183	7
2006	110	207	102	245	19
2007	217	388	116	239	35
2008	189	388	128	253	27
2009	237	538	108	232	35
2010	266	420	99	214	35
2011	452	929	202	490	50
2012	209	410	142	283	32
2013	499	1194	180	420	56
2014	918	2164	193	455	90
2015	724	1740	135	331	107
2016	880	2186	149	362	115
2017	671	1730	148	398	97

Table 6. (continued)

Year	Land-applied P (MT)	Land-applied N (MT)	Average P Application Rate (kg ha^{-1})	Average N Application Rate (kg ha^{-1})	Number of Fields Applied
2018	808	2081	144	373	112
2019	828	2242	167	452	94

TRENDS IN PHOSPHORUS AND NITROGEN CONCENTRATION AND FLUX AT AMBIENT MONITORING SITES

Analysis of long-term (25-year) ambient water quality monitoring data revealed increasing trends in P. For the USJRB watersheds, TP annual means and maxima exhibited a clear increase after 2013 in Jane Green, Crabgrass, Tenmile, Sixmile Creeks (Figure 4). Pennywash and South Wolf Creeks did not show a clear increase in mean TP after 2013 but did have intermittent maxima that were much higher than previously observed. In 2019, missing data for summer months at Pennywash Creek may have led to the low annual mean and maxima. Blue Cypress Creek was the exception in the USJRB watersheds and did not show changes in mean or maximum TP. Haw Creek experienced elevated TP (both annual means and maxima) beginning in 2006, and the TP remained elevated through at least 2017, even after biosolids applications declined (Figure 4). Increases in TN were not as widespread as TP at the ambient monitoring sites. In the USJRB, the sites that showed TN increases were Tenmile, Sixmile, and South Wolf Creeks. These sites only had elevated TN in 2017–2018, and TN declined in 2019. In the Haw Creek watershed, TN concentrations were not higher during the intensified application period vs the remainder of the record.

Based on the observations of step changes in biosolids applications, two periods (baseline and impact) were chosen to test means for water quality for each study area. In the Haw Creek watershed, 1990–2006 and 2007–2016 were chosen for the baseline and impact periods, respectively. In the upper St. Johns watersheds, 1995 – 2012 and 2013 – 2020 were chosen for the baseline and impact periods, respectively. Tests for differences in means (Wilcoxon signed-rank test) of P and N species are presented in Table 7. All watersheds except Blue Cypress Creek had significantly different ($p < 0.05$) mean TP during the impact periods. Increases in TP were between 1.3 and 1.6-fold, except for Tenmile Creek, which experienced a 2.6-fold increase in TP. Orthophosphate (PO_4^-) was the primary driver of the TP increase in most of the watersheds. Particulate P (PP) showed significant increases in Tenmile, Pennywash, and South Wolf Creeks, although South Wolf Creek was the only creek where PP was the primary constituent driving increases in TP. Significant decreases in TN were detected at Jane Green and Sixmile Creeks and were likely driven by decreases in Total Kjeldahl Nitrogen (TKN).

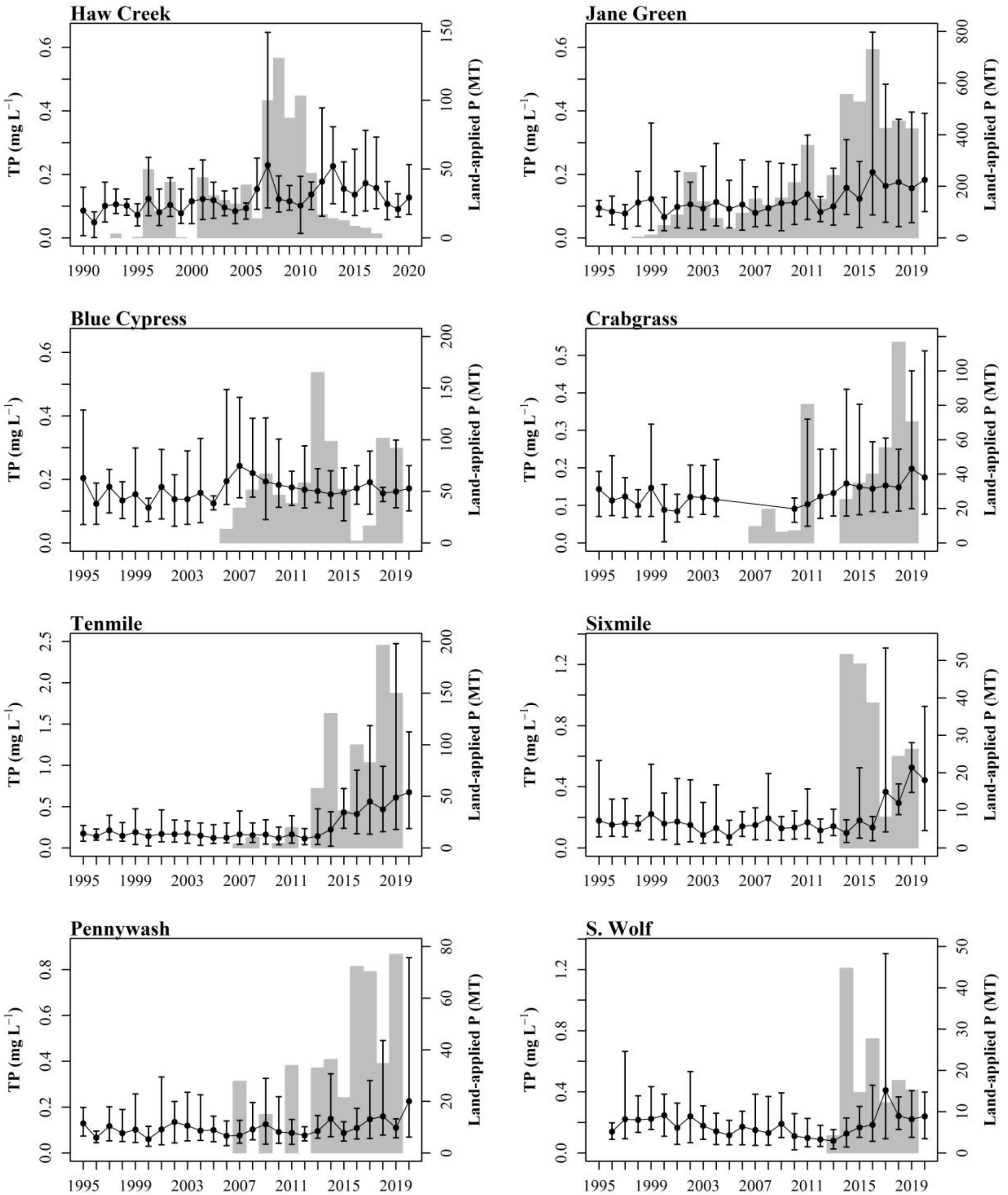

Figure 4. Total P concentrations and biosolids applications. Total P annual mean, minimum, and maximum are indicated by points and error bars. Annual application totals of P (metric tons) from Class B biosolids are shown as bars.

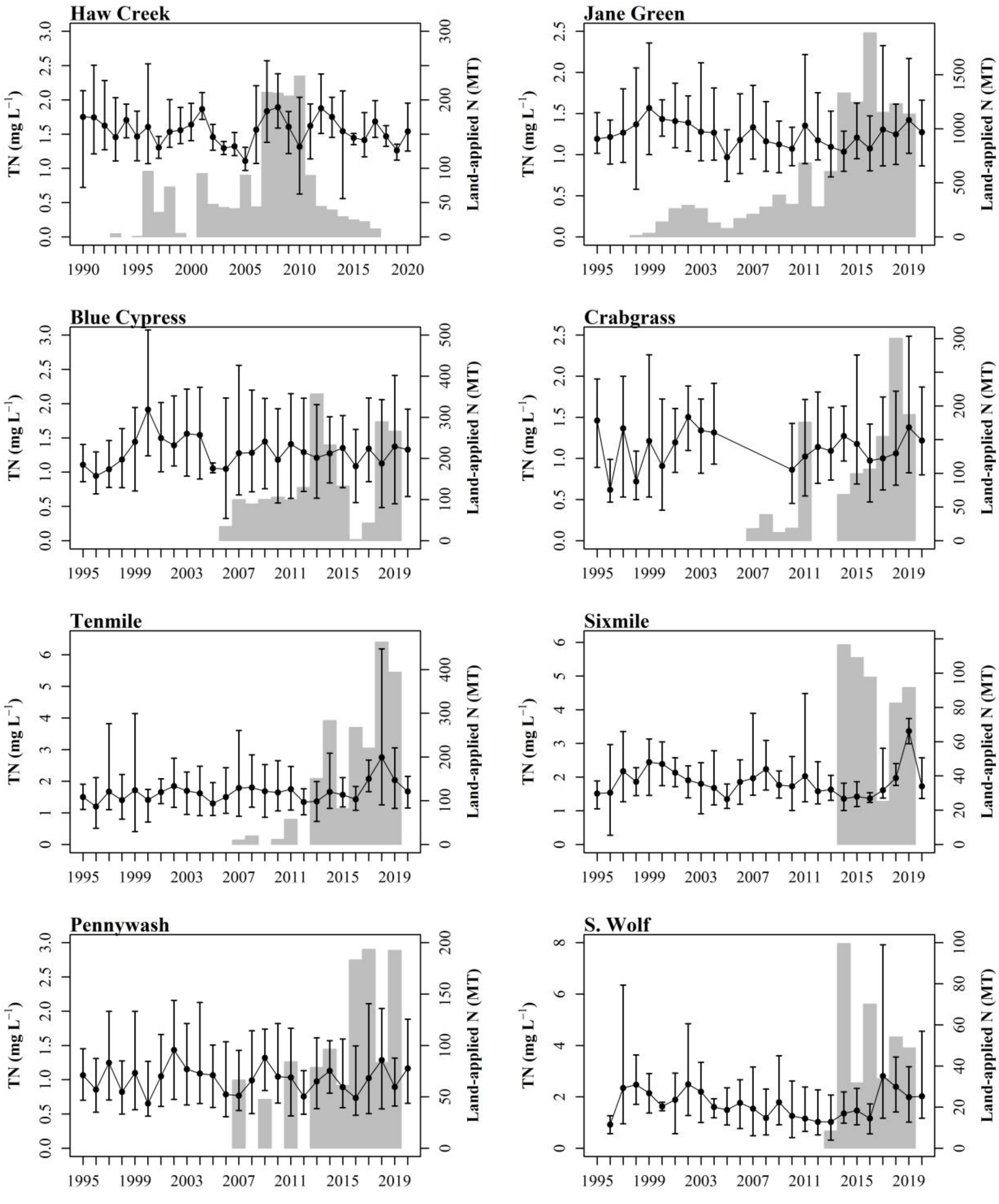

Figure 5. Total N concentrations and biosolids applications. Total N annual mean, minimum, and maximum are indicated by points and error bars. Annual application totals of N (metric tons) from Class B biosolids are shown as bars.

Table 7. Comparison of means of P and N species prior-to and post- intensified biosolids application. Means with significantly different ($p < 0.05$) values are indicated in bold (Wilcoxon signed-rank test). The baseline period was 1990–2006 for Haw Creek and 1995–2012 for all other sites. The impact period was 2007–2016 for Haw Creek and 2013–2020 for all other sites.

	TP		PO_4^-		PP		TN		NO_x		TKN	
Site	Baseline	Impact	Baseline	Impact	Baseline	Impact	Baseline	Impact	Baseline	Impact	Baseline	Impact
Haw Creek	0.098	**0.160**	0.057	0.076	ND	0.060	1.55	1.52	0.08	0.07	1.46	1.45
Jane Green	0.100	**0.159**	0.063	**0.122**	0.011	0.016	1.27	**1.21**	0.02	**0.03**	1.25	**1.18**
Blue Cypress	0.173	0.165	0.134	0.121	0.023	0.019	1.33	1.26	0.04	**0.07**	1.29	1.19
Crabgrass	0.114	**0.150**	0.079	0.106	ND	0.020	1.14	1.12	0.06	**0.10**	1.07	1.02
Tenmile	0.158	**0.413**	0.074	**0.295**	0.038	**0.080**	1.61	1.80	0.03	**0.09**	1.57	1.72
Sixmile	0.152	**0.230**	0.075	**0.162**	0.035	0.038	1.90	**1.61**	0.01	**0.02**	1.88	**1.59**
Pennywash	0.097	**0.133**	0.045	**0.087**	0.016	**0.026**	1.02	0.99	0.09	0.09	0.94	0.90
South Wolf	0.162	**0.205**	0.061	**0.093**	0.031	**0.090**	1.72	1.74	0.02	**0.03**	1.70	1.72

To estimate long-term changes in flux, models were successfully fit using the WRTDS method. Across all models, the flux bias statistic (an indicator of model fit) was between 0.002–0.056 for TP and -0.042–0.044 for TN (Appendix A). A flux bias statistic close to 0 indicates the model is nearly unbiased, and a values between -0.1 and 0.1 indicate less than 10% bias in the long-term mean flux (Hirsch and De Cicco, 2015).

Annual, flow-normalized fluxes of TP and TN are presented in Figures 6–7. Calculation of flow-normalized flux controls for variations in flux driven by interannual hydrologic variability and allows for the analysis of underlying long-term trends in flux. Long-term trends in flow-normalized TP and TN flux were similar to those observed for concentrations. Examination of flow-normalized TP flux against cumulative biosolids application revealed a strong temporal relationship between intensification of biosolids applications and watershed flux (Figure 6). This was most apparent in Jane Green and Tenmile Creeks, where cumulative applications exceeded 80 kg P per hectare of watershed. TN fluxes generally showed little to no response to increases in biosolids applications (Figure 7). Blue Cypress Creek experienced an increase in TN flux between 1997–2004, prior to any application of biosolids. Small increases in TN flux were observed at Tenmile and South Wolf Creeks after 2015.

The average of annual TP and TN fluxes (with and without flow normalization) are compared for baseline and impact periods in Table 8. Haw Creek had minimal increases in TP flux (2 MT) during the impact period, however, the difference between flow-normalized fluxes during the baseline and impact periods was 13 MT, indicating that streamflow was lower than average during the impact period. Haw Creek had lower TN fluxes (flux and flow-normalized flux) during the impact period. In the USJRB watersheds, there was generally less difference between the TP fluxes and flow-normalized fluxes in the baseline and impact periods. For all USJRB study watersheds, the total increase in TP flux was 37 MT during the impact period, and flow-normalized TP flux increased by 36 MT during the impact period. Approximately 30 MT (83%) of the increase in flow-normalized TP flux was accounted for by Jane Green and Tenmile Creeks. Small increases in TN flux were also observed for some USJRB watersheds. The TN flux for the USJRB watersheds increased by 23 MT, whereas the flow-normalized TN flux increased by 18 MT. It is important to note that that increases in TP flux were proportionally much higher (58% increase) than increases in TN flux (4% increase).

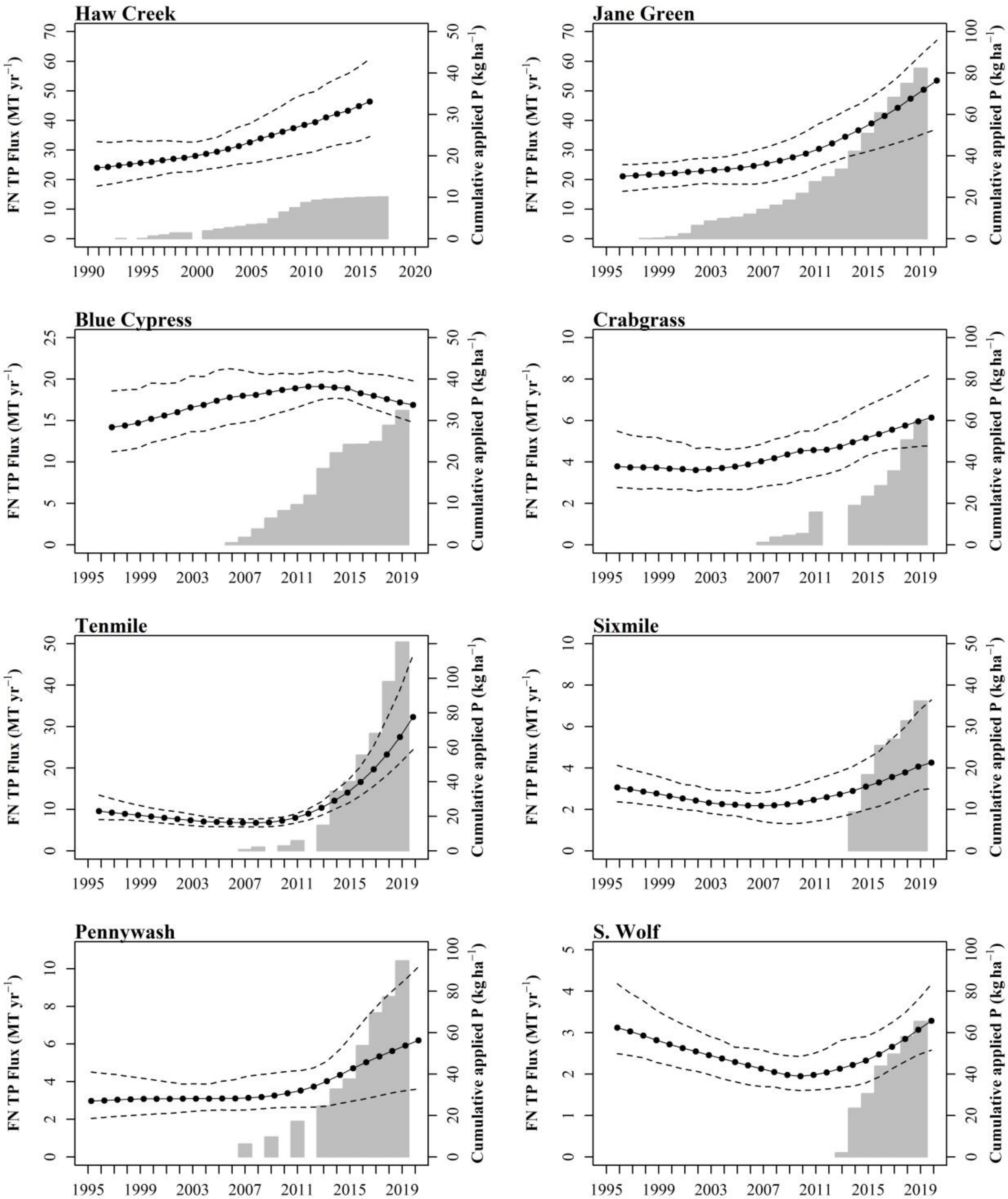

Figure 6. Annual flow-normalized TP flux (points) and cumulative land-applied biosolids P (bars). Dashed lines indicate bootstrapped 95% confidence intervals of WRTDS model estimates. Cumulative biosolids applications have been normalized to watershed area.

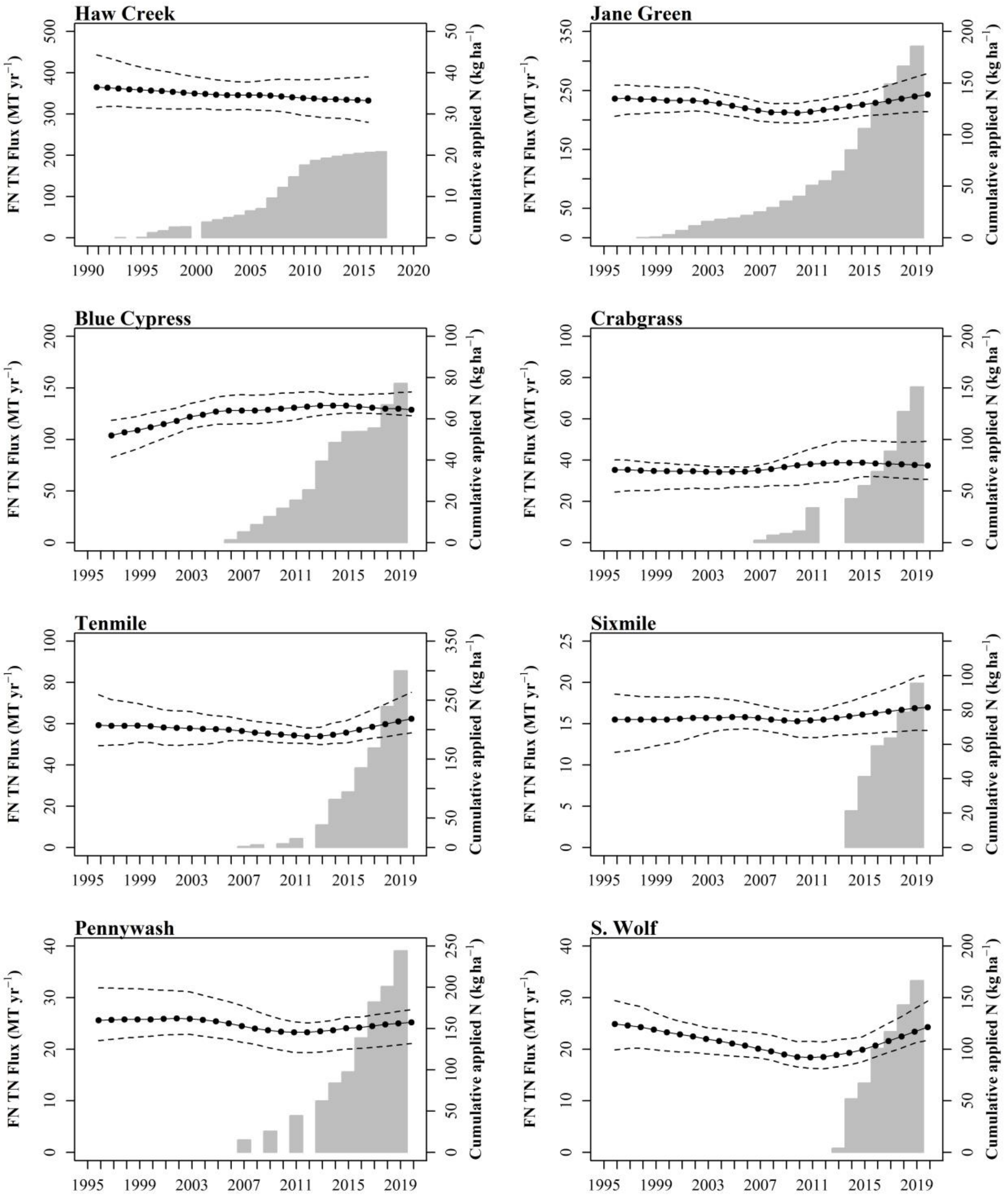

Figure 7. Annual flow-normalized TN flux (points) and cumulative land-applied biosolids N (bars). Dashed lines indicate bootstrapped 95% confidence intervals of WRTDS model estimates. Cumulative biosolids applications have been normalized to watershed area.

Table 8. Comparison of mean annual flux and flow-normalized (FN) flux of TP and TN between the baseline and impact periods. All fluxes are expressed as MT yr^{-1}. The baseline period was 1990–2006 for Haw Creek and 1995–2012 for all other sites. The impact period was 2007–2016 for Haw Creek and 2013–2020 for all other sites.

		TP Flux		FN TP Flux		TN Flux		FN TN Flux	
Basin	**Site**	**Baseline**	**Impact**	**Baseline**	**Impact**	**Baseline**	**Impact**	**Baseline**	**Impact**
LSJRB	Haw Creek	31.8	33.5	28.2	41.0	388.5	287.2	353.2	337.2
USJRB	Jane Green	25.7	40.9	24.7	42.0	229.8	225.8	225.3	229.4
USJRB	Blue Cypress	16.3	19.4	17.1	18.0	116.0	140.9	122.8	131.1
USJRB	Crabgrass	4.3	4.8	4.0	5.6	37.3	33.0	35.7	38.2
USJRB	Tenmile	8.0	21.7	8.0	20.8	57.1	58.3	57.0	58.5
USJRB	Sixmile	2.2	4.6	2.5	3.6	14.0	20.8	15.6	16.5
USJRB	Penny-wash	3.3	4.9	3.2	5.0	24.5	24.6	24.9	24.5
USJRB	South Wolf	2.3	2.4	2.3	2.7	21.0	19.4	21.0	21.7
USJRB total		62.1	98.7	61.8	97.7	499.7	522.8	502.3	519.9

STORM-EVENT PHOSPHORUS AND NITROGEN CONCENTRATIONS

Synoptic grab samples were collected following storm events at eight sites within the Jane Green Creek watershed between 2017–2020. Concentrations of TP, TKN, and total suspended solids (TSS) are provided for each sample date in Appendix C. Runoff concentrations were variable for each site, depending upon discharge and season. Seasonal variation was likely related to antecedent moisture conditions, with the highest concentrations being observed in summer months. Total suspended solids were low (<10 mg L^{-1}) for all sites and sample dates, indicating that erosional processes were negligible in contributing to P and N trends (Appendix C, Table C4).

Storm-event concentrations were pooled by site and plotted against the cumulative application of biosolids in the sampling site watershed (Figure 8). Total P and TKN concentrations showed an increasing trend with higher cumulative biosolids application. A statistical comparison between sites was not performed due to the difference in watershed size and nesting of some watersheds.

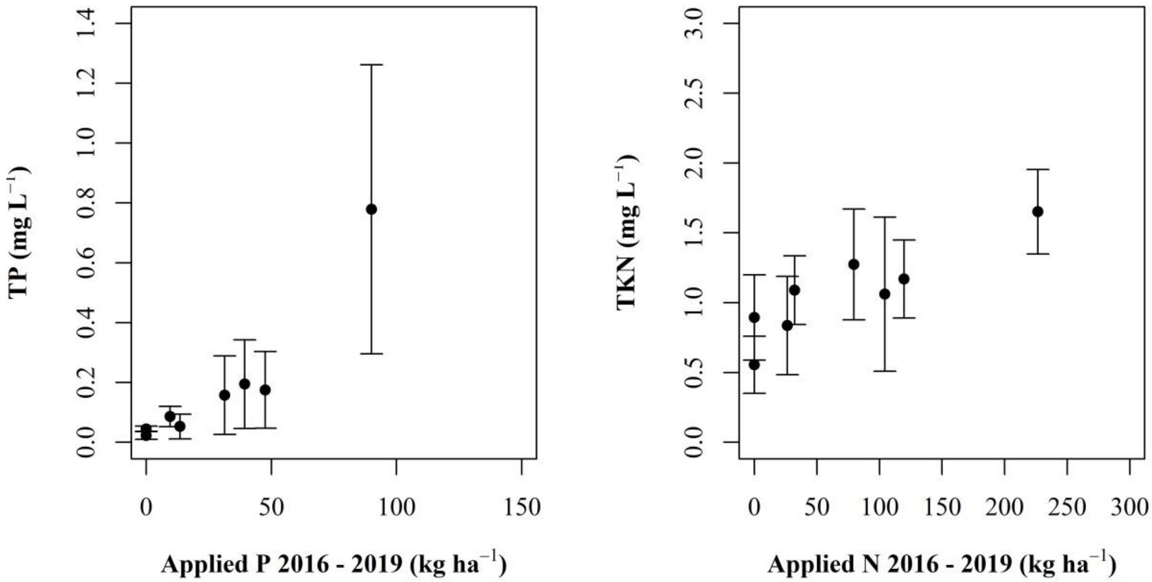

Figure 8. Relationship between biosolids application and nutrient concentrations for Jane Green storm-event sites. The mean (points) and standard deviation (error bars) are given for TP and TKN concentrations. The cumulative applied P (or N) between 2016–2019, normalized to total watershed area, is shown on the x-axis.

Continuous monitoring of orthophosphate at the Jane Green Creek outlet (site JGS) allowed for a higher temporal resolution of concentrations and the ability to compare patterns in daily discharge with daily concentrations (Figure 9). Three wet season periods were captured during the monitoring. Orthophosphate concentrations were mostly below 0.1 mg L^{-1} during the dry season and were elevated to a baseline value of 0.2–0.3 mg L^{-1} during the summer wet season. Additional peaks in orthophosphate concentration above the summer baseline were coincident with large discharge events. A WRTDS model fit using monthly concentrations between 1995–2020 showed good agreement with the independent daily measurements for 2018–2020, providing further support for the utility of WRTDS models to estimate annual TP flux.

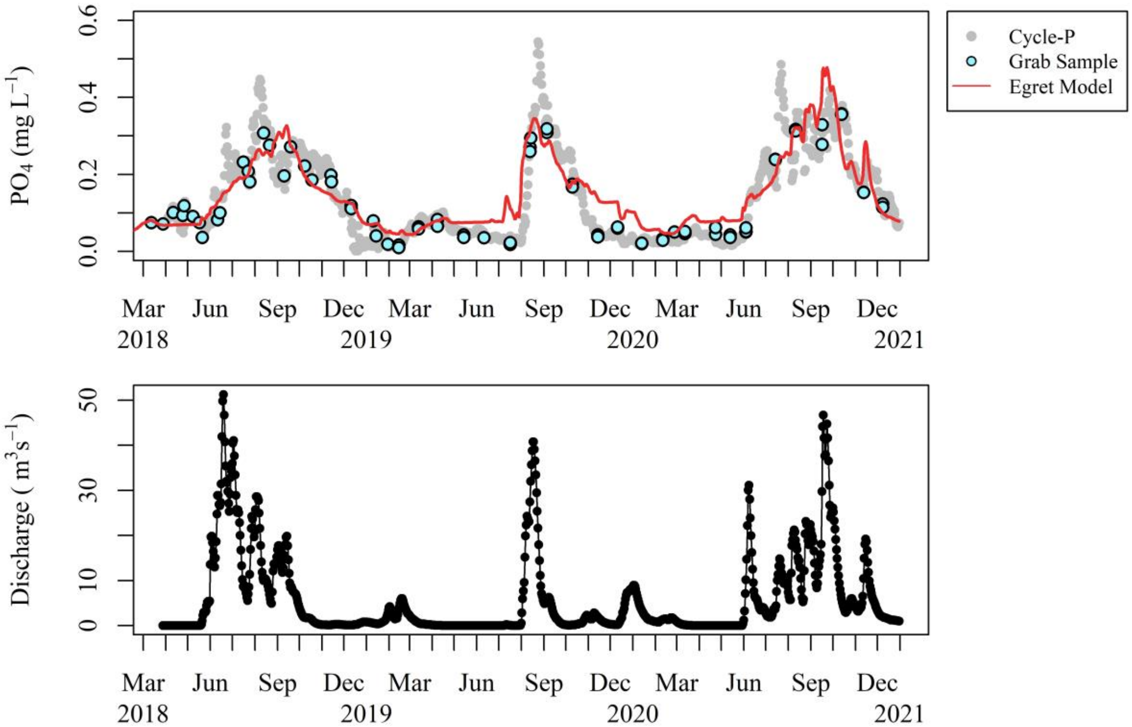

Figure 9. Comparison of high-frequency sampling (Cycle-P), grab samples (ambient and storm - event), and WRTDS model (Egret Model) results for orthophosphate at the Jane Green Creek (JGS) site. Measured discharge at the USGS gauge is shown on the bottom panel.

DISCUSSION

In the present study, significant increases in TP concentrations and fluxes were coincident with intensification of Class B biosolids applications in multiple watersheds of the St. Johns River. Significant increases in TN concentrations and fluxes were not observed. This was likely because biosolids are most often applied at rates based on crop N requirements and because saturated soils (due to high water table conditions) and riparian wetlands promote denitrification of any N exported from the root zone. Land-use change did not likely have an influence on changes in water quality, as the study watersheds were dominated by pasture and natural areas and experienced very little land use change over the 25-year study period. Likewise, changes in cattle density on pastureland were not likely responsible for any changes in export. The two counties (Osceola and Brevard) in which the upper St. Johns study watersheds were located saw a drop in total cattle numbers from 129,000 to 118,000 between 2008 and 2020, and the total number of cattle in Flagler County (Haw Creek) dropped from 5,000 to 3,300 (USDA, 2019).

Class B biosolids are frequently applied based on plant available N requirements, leading to application of P in excess of crop requirements due to the fact that biosolids are an unbalanced fertilizer (N:P ratio approximately 2.5:1). Application based on PAN, even when P applications exceed crop demand, is compliant with current state biosolids rules as of 2020, provided that

National Resources Conservation Service (NRCS) guidelines are followed (USDA-NRCS, 2012). If Florida P Index values are of low or medium risk for movement offsite, then management based on crop N needs is permissible and application of P in excess of crop requirements is permitted. If the P Index is high when a new nutrient management plan is developed for a permit renewal, then P-based application will be required to meet NRCS guidelines. Although it is compliant with regulations, this approach to biosolids management promotes the maximum application of P to fields until a high P Index rating is reached. Recent updates to the biosolids rules in Florida will require the calculation of both N-based and P-based application rates, and will require application based on the use of the most restrictive nutrient (F.A.R., 2020).

Conventionally digested biosolids are approximately 50% as phytoavailable as synthetic fertilizer, although phytoavailability relative to synthetic fertilizer varies between 5% in high iron (Fe) and aluminum (Al) biosolids to greater than 75% in biosolids produced by biological P removal (BPR) (O'Connor and Elliot, 2006; O'Connor et al., 2004). In the present study, applications of total P from biosolids were on average between 100–200 kg ha^{-1} (90–180 lbs $acre^{-1}$) during the most intensive periods of application. Under the assumption that 50% of P was available for plant uptake, phytoavailable P was applied at rates of 50–100 kg ha^{-1}, which is between 3- and 8-fold greater than the recommended fertilization rate of 12–19 kg ha^{-1} for the most common pasture grass, bahiagrass (Mackowiak et al., 2017). Furthermore, P application is only recommended for bahiagrass if soil test values of P are low. Excess phytoavailable P, as well as the less labile P fractions, can accumulate in soils and may be lost to surface waters through both short-term and long-term processes. In Florida soils, short-term leaching and runoff of biosolids P have been shown to be strongly correlated to the water extractable P (WEP) content of biosolids (Alleoni et al., 2008). Biosolids produced using biological P removal (BPR) during treatment have been shown to have higher WEP and are most susceptible to leaching and runoff losses, whereas, biosolids with added iron or aluminum have a high fraction of less labile, mineral-bound P and are more likely to accumulate in soils where they may leach more slowly.

The accumulation and long-term fate of low-P solubility biosolids in Florida soils is less well understood than short-term leaching and runoff potential (Elliott and O'Connor, 2007). Many leaching and runoff studies have been in short-duration lab studies using the upper, A horizon from soils without prior biosolids application (Alleoni et al., 2008; Elliott et al., 2002; Silveira et al., 2019). These studies don’t address the longer-term fate of P through mineralization, migration into deeper soil horizons, and horizontal migration in shallow groundwater. Long-term, in-field studies from other regions of the United States have demonstrated that repeated application of biosolids can significantly increase soil test P (Bray-1, Mehlich-1, or Mehlich-3 P) and water-soluble P in surface (0-15 cm) soils (Cogger et al., 2001; Maguire et al., 2000; Schroder et al., 2008). Soils with high iron and aluminum content may form stable P complexes and prevent immediate leaching, however, many of the sandy soils in Florida quickly become saturated with P. Saturation of P and migration into deeper soil horizons (E, Bh) has been demonstrated under dairy farms in Florida, with solubilization likely occurring over several years (Graetz and Nair, 1995). High water table conditions at these dairy sites also created the potential for lateral transport in the shallow groundwater. Similar soils (Spodosols) with high water tables are predominant in the present study watersheds, and a similar propensity for lateral transport is likely. Recent updates to the biosolids rules in Florida now require application rates to be adjusted based on water-extractable P and Soil Phosphorus Storage Capacity (Nair and Harris, 2004). Additionally, the new rules prohibit application if the seasonal high water is less than 15 cm (6 inches) from the soil surface, unless a water quality monitoring plan is implemented.

In conjunction with application of biosolids P in excess of crop needs, the focusing of Class B biosolids applications into the USJRB after 2013 appears to have exceeded watershed-scale thresholds for storage and assimilation of excess nutrients, primarily P, in multiple watersheds. Permit reports for Class B biosolids applications showed that both application totals and average areal application rates increased in the USJRB following adoption of the biosolids rule (62-640 F.A.C.) in 2010. By 2013, the effective year of the rule, the USJRB was receiving 66% of all land-applied Class B biosolids in Florida (FDEP, 2014), and more recently in 2019, approximately 78% of all statewide applications were in the USJRB (FDEP, *pers. comm.*). Almost all (>90%) of the Class B biosolids applications in the USJRB have occurred in the tributary watersheds on the western side of Upper St. Johns River and USJRB Project area, upstream of Lake Poinsett. Six of the seven watersheds studied in the USJRB showed significant increases (17–160% increase) in TP flux after 2013. The main exception was Blue Cypress Creek, which only experienced a 5% increase in flux. The Blue Cypress Creek watershed received the lowest amount of cumulative biosolids applications when scaled to watershed area, and the application site was approximately 20 km upstream from the monitoring site. It is likely that any mobilized biosolids P was attenuated before reaching the monitoring site.

A comparison of the cumulative biosolids P application within watersheds and increases in TP flux can be made to better understand how much P loss from fields is required to cause the observed increases in watershed TP flux. When the increase in watershed TP flux during the impact periods is expressed as a percentage of the cumulative biosolids P application, between 0.4–0.9% loss of biosolids P would be required to drive the observed TP fluxes in all watersheds except Tenmile Creek. Within Tenmile Creek, an estimated 3.4% loss of biosolids would be required to effect the observed increases in TP flux. This simplified approach does not account for the assimilation of P during travel between fields and the watershed outlet, but it does provide an estimate of the minimum amount of P loss required to produce the observed water quality trends. These loss estimates are reasonable based on previous experimental work. In rainfall simulations with the 6 most prevalent biosolid sources applied in the USJRB, between 1.1–9.2 % of P was lost due to runoff and leaching (Silveira et al., 2019). This suggests that even short-term loss processes could be of high enough magnitude to cause the observed flux increases. Longer-term mobilization processes, including mineralization of more stable P, vertical migration, and lateral transport, are also likely to be contributing to recently observed fluxes and may continue to cause legacy impacts after applications have ceased.

CONCLUSIONS AND RECOMMENDATIONS

The present study provides strong correlational evidence for the export of P from land-applied Class B biosolids. Both long-term (25-year) and storm-event water quality monitoring demonstrated a strong association between the timing and magnitude of intensified application of Class B biosolids application and increases in stream nutrient concentrations and fluxes. Two major factors were identified that are likely contributing to these patterns: 1) Application of biosolids based on plant available (PAN), resulting in excess P application, and 2) Focusing of applications into adjacent watersheds within one basin due to both homogenous land use and regulations limiting applications in other areas of the state. The regulatory framework has recently been revised for Class B biosolids application in Florida, however, the extent to which biosolids application may impact receiving waters requires further understanding of the fate and transport of all forms of P contained within biosolids. Specifically, the following recommendations for further investigation are provided:

1. Expand storm-event water quality sampling to establish the runoff concentration differences between pastureland with and without biosolids.
2. Investigate the extent to which P accumulates and migrates in soils with long-term biosolids applications.
3. Determine the conditions under which lateral transport of P may occur in shallow groundwater.
4. Determine the timescale and magnitude of legacy effects from accumulated P and evaluate remedial actions.
5. Evaluate technologies that may be implemented at wastewater treatment plants that reduce the P content of biosolids so that applications provide both N and P within recommended agronomic rates, while also providing valuable organic carbon.

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APPENDIX A. WRTDS MODEL FIT PLOTS

Appendix A contains model fit plots for the Weighted Regressions on Time, Discharge, and Season (WRTDS) models. All plots have the same results presented in each panel and vary only in the constituent (TP or TN) and site. The Flux Bias Statistic is report above the plots. The panels are as follows:

A. Top Left: Predicted annual mean concentration (dots) and annual flow-normalized mean concentration (blue line) with 95 % confidence intervals (dashed lines).

B. Top Right: Observed vs. predicted instantaneous concentrations.

C. Bottom Left: Predicted annual flux (dots) and annual flow-normalized flux (blue line) with 95 % confidence intervals (dashed lines).

D. Bottom Right: Observed vs. predicted instantaneous flux.

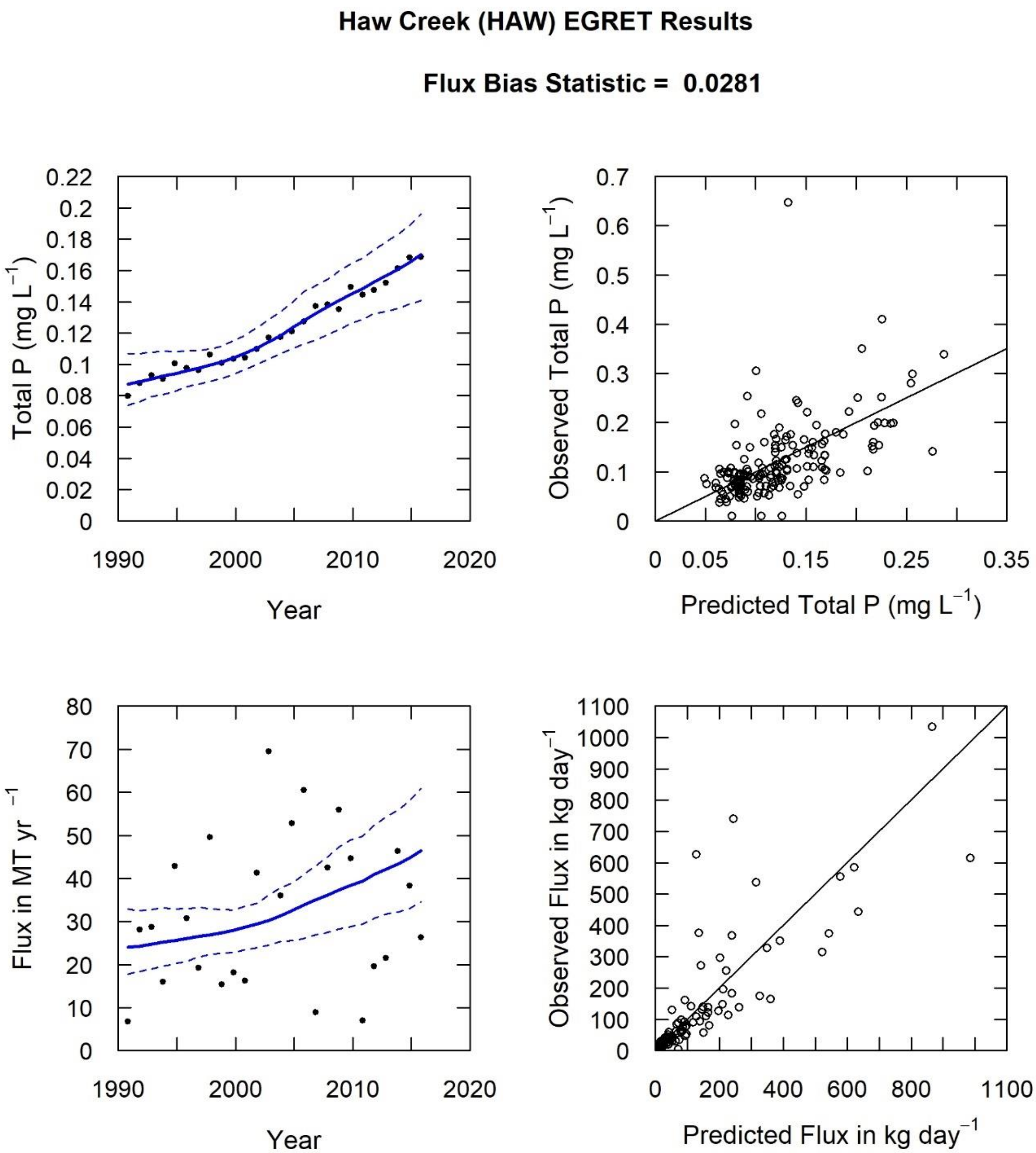

Figure A1. Haw Creek WRTDS model fit for TP. See the beginning of Appendix A for an explanation of each panel.

Haw Creek (HAW) EGRET Results

Flux Bias Statistic = 0.007

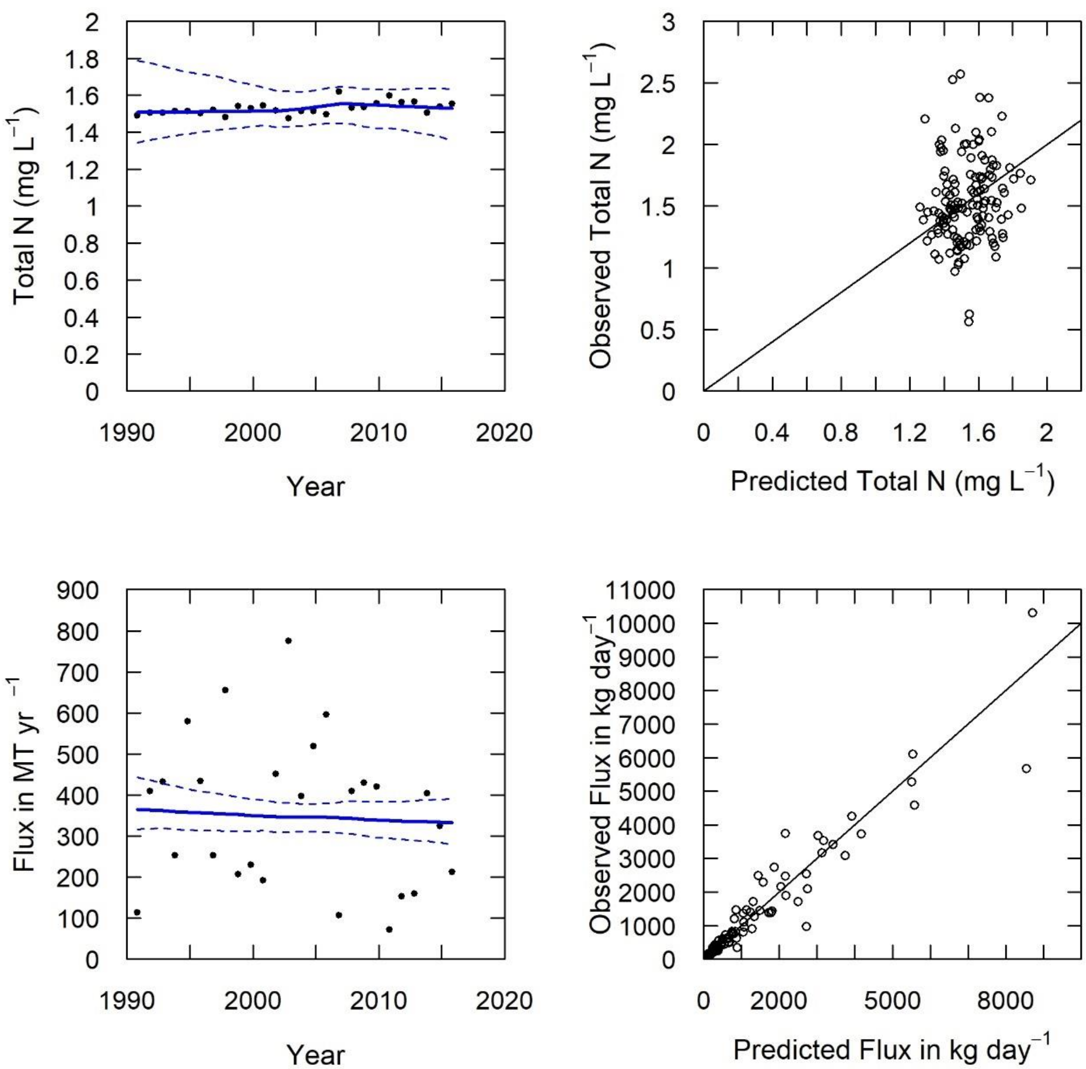

Figure A2. Haw Creek WRTDS model fit for TN. See the beginning of Appendix A for an explanation of each panel.

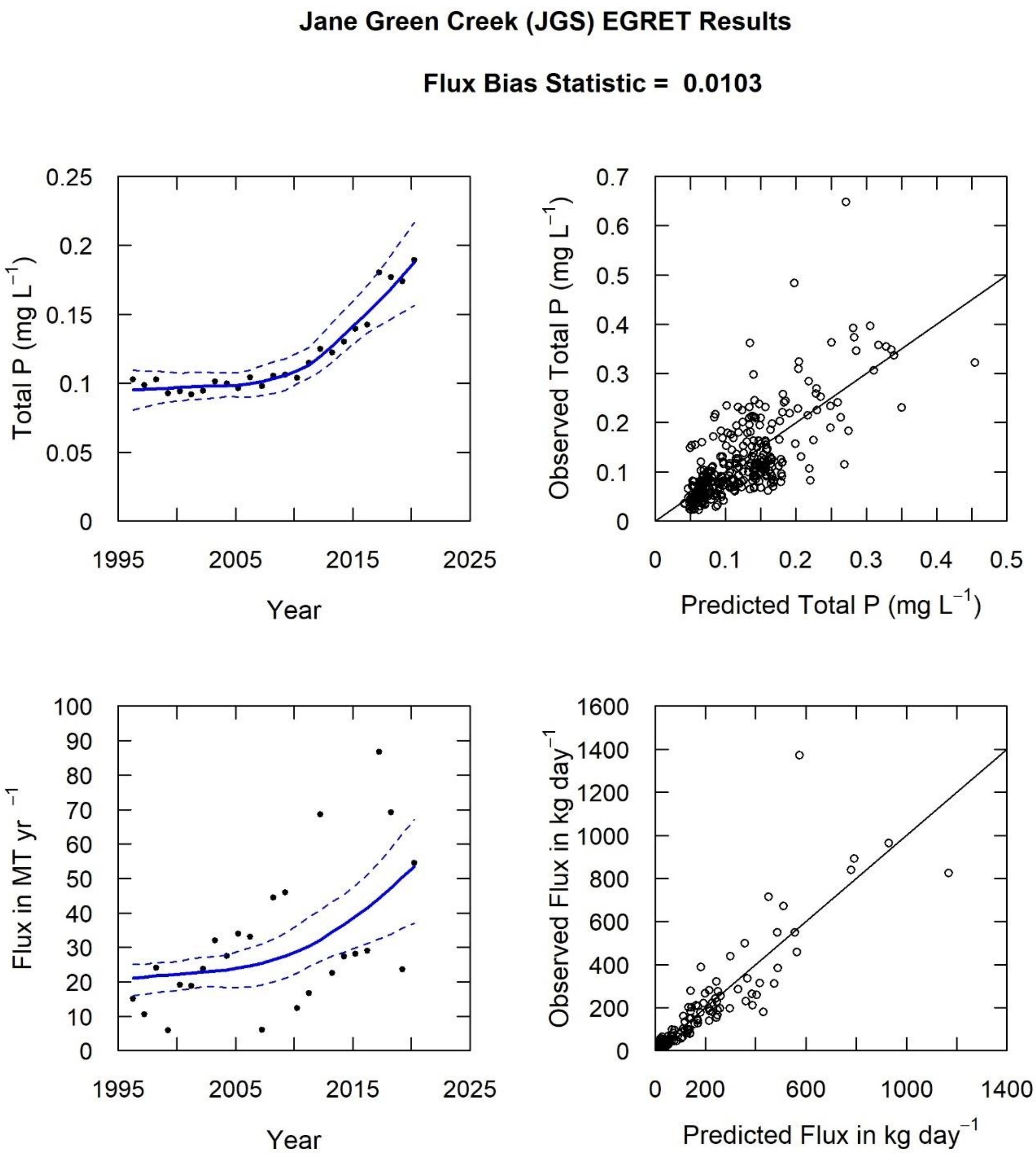

Figure A3. Jane Green Creek WRTDS model fit for TP. See the beginning of Appendix A for an explanation of each panel.

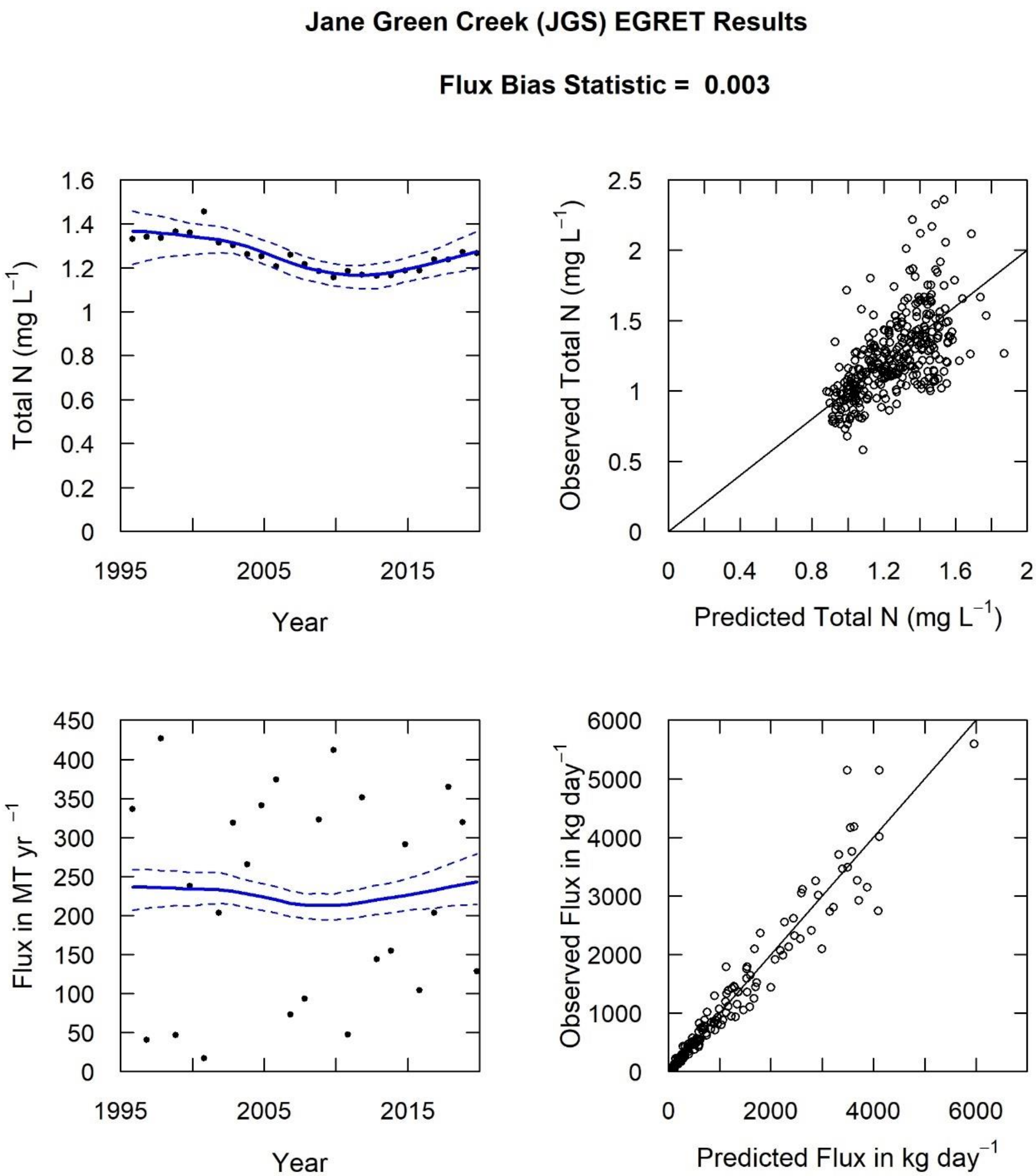

Figure A4. Jane Green Creek WRTDS model fit for TN. See the beginning of Appendix A for an explanation of each panel.

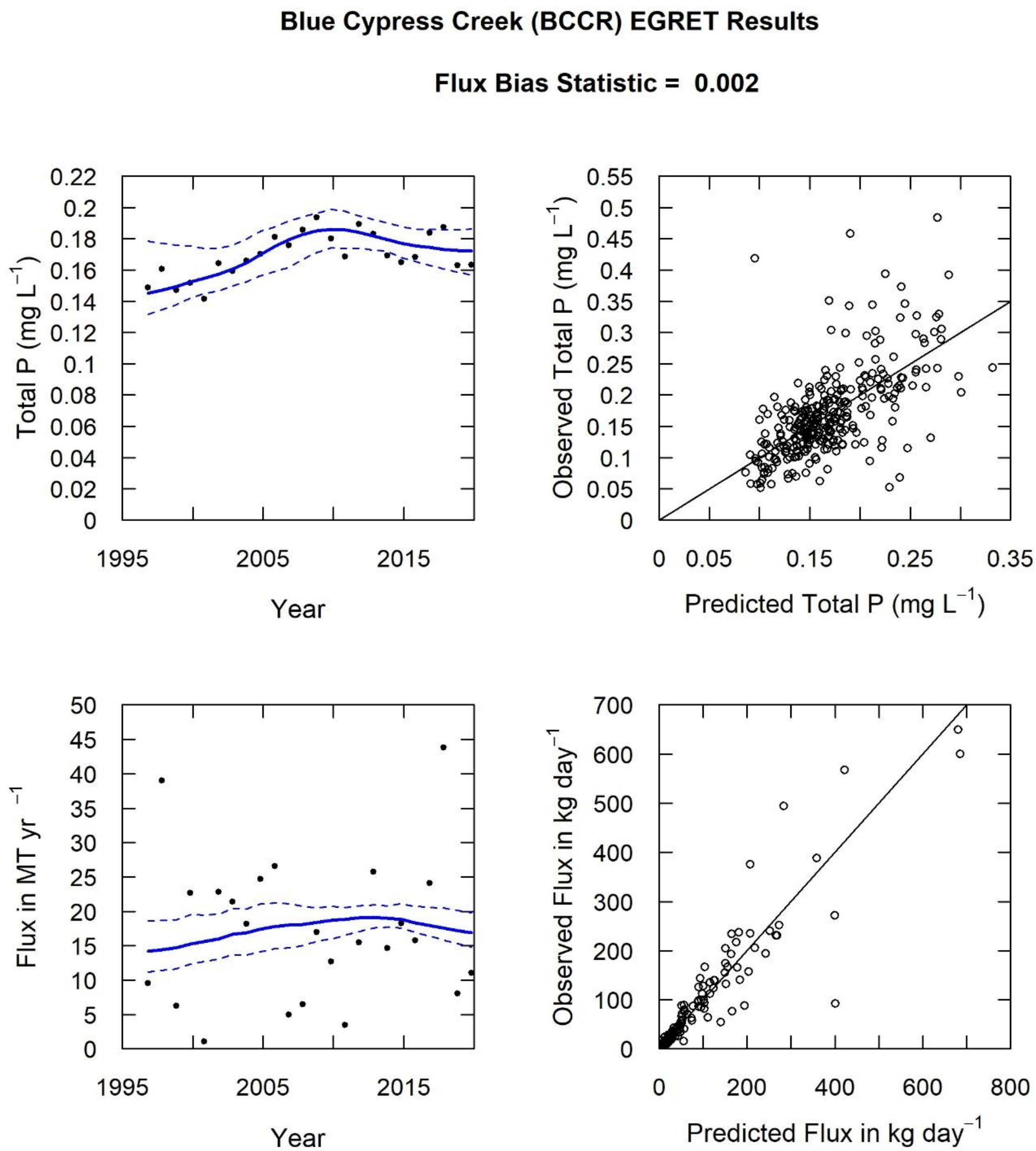

Figure A5. Blue Cypress Creek WRTDS model fit for TP. See the beginning of Appendix A for an explanation of each panel.

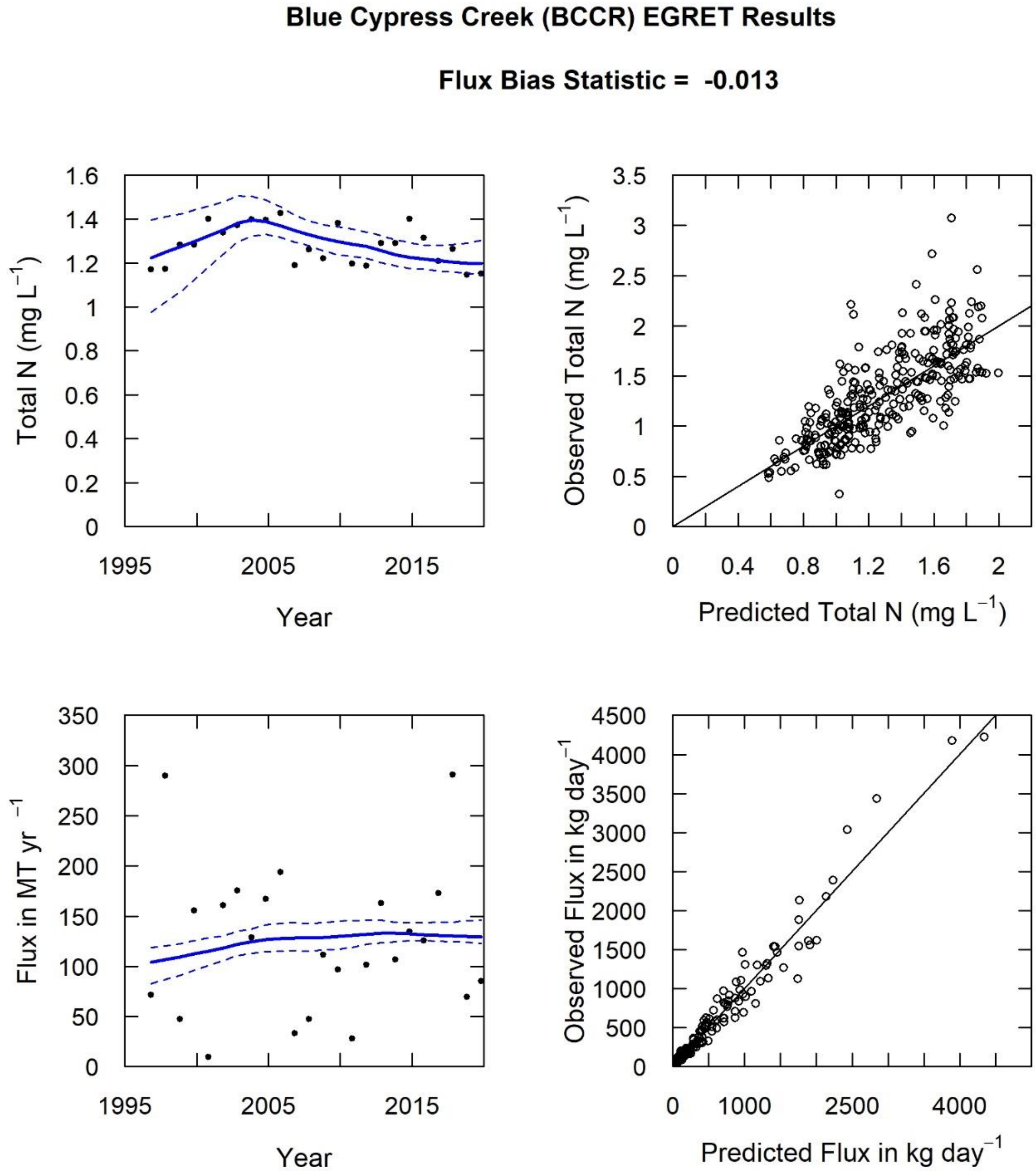

Figure A6. Blue Cypress Creek WRTDS model fit for TN. See the beginning of Appendix A for an explanation of each panel.

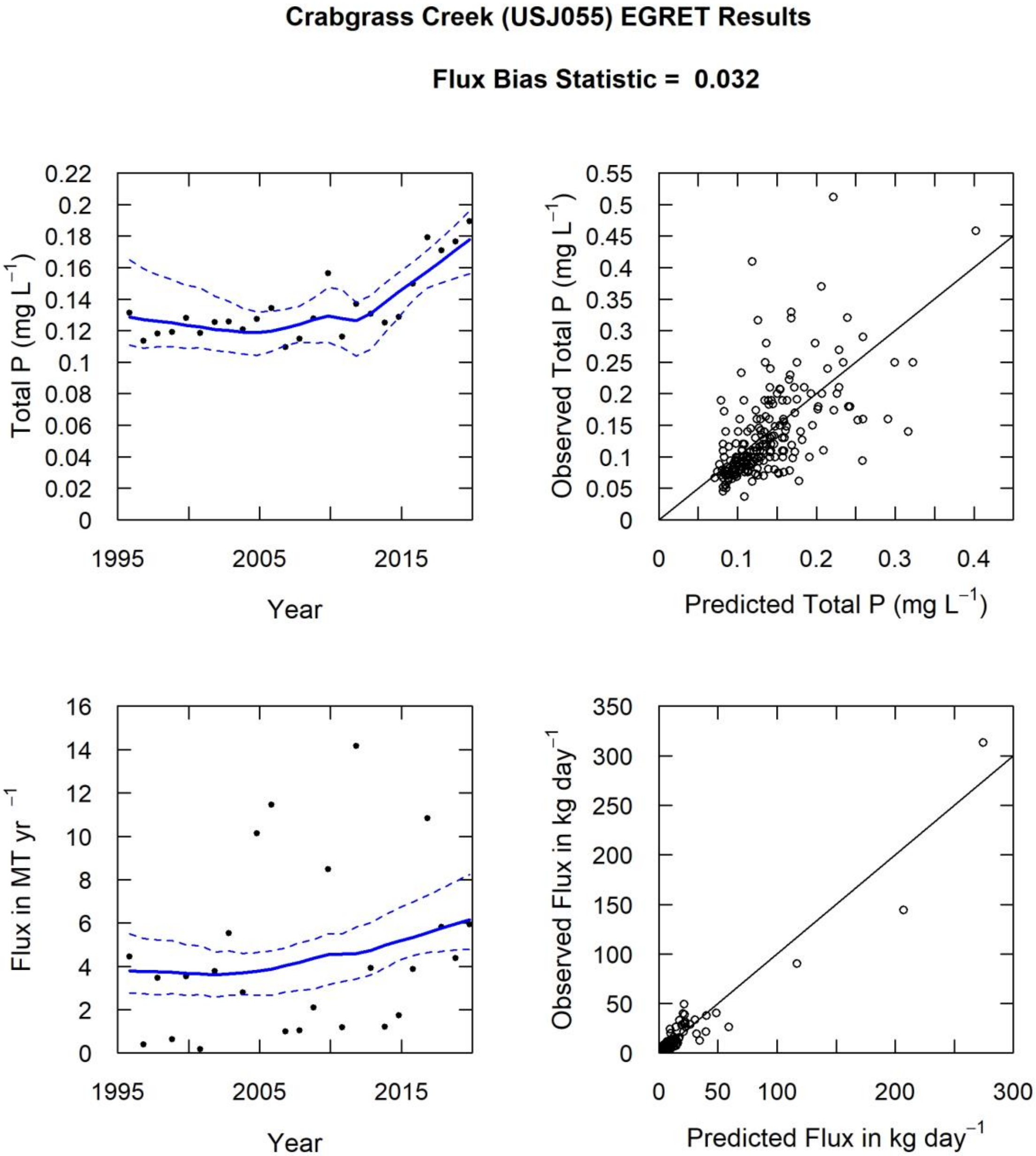

Figure A7. Crabgrass Creek WRTDS model fit for TP. See the beginning of Appendix A for an explanation of each panel.

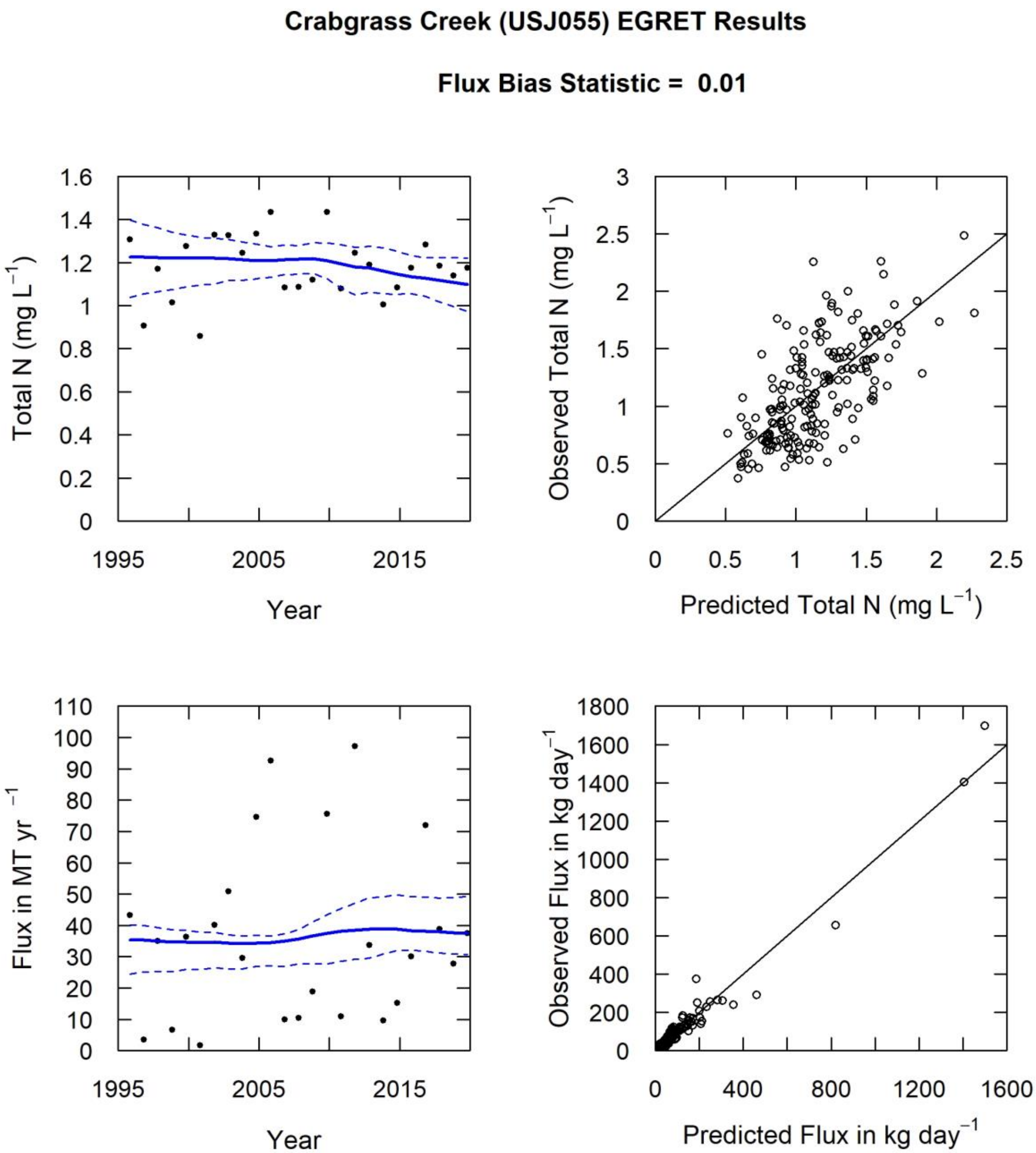

Figure A8. Crabgrass Creek WRTDS model fit for TN. See the beginning of Appendix A for an explanation of each panel.

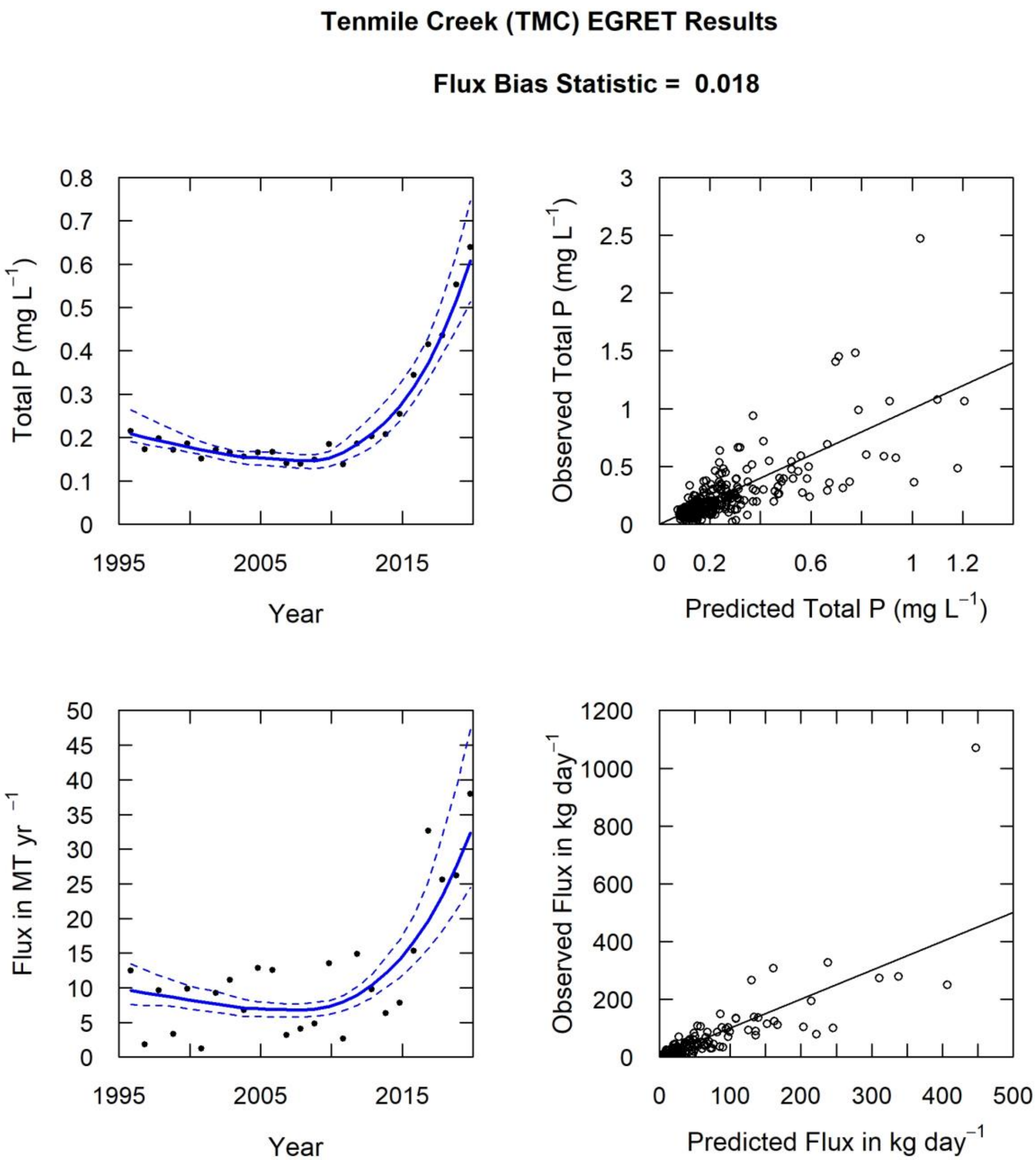

Figure A9. Tenmile Creek WRTDS model fit for TP. See the beginning of Appendix A for an explanation of each panel.

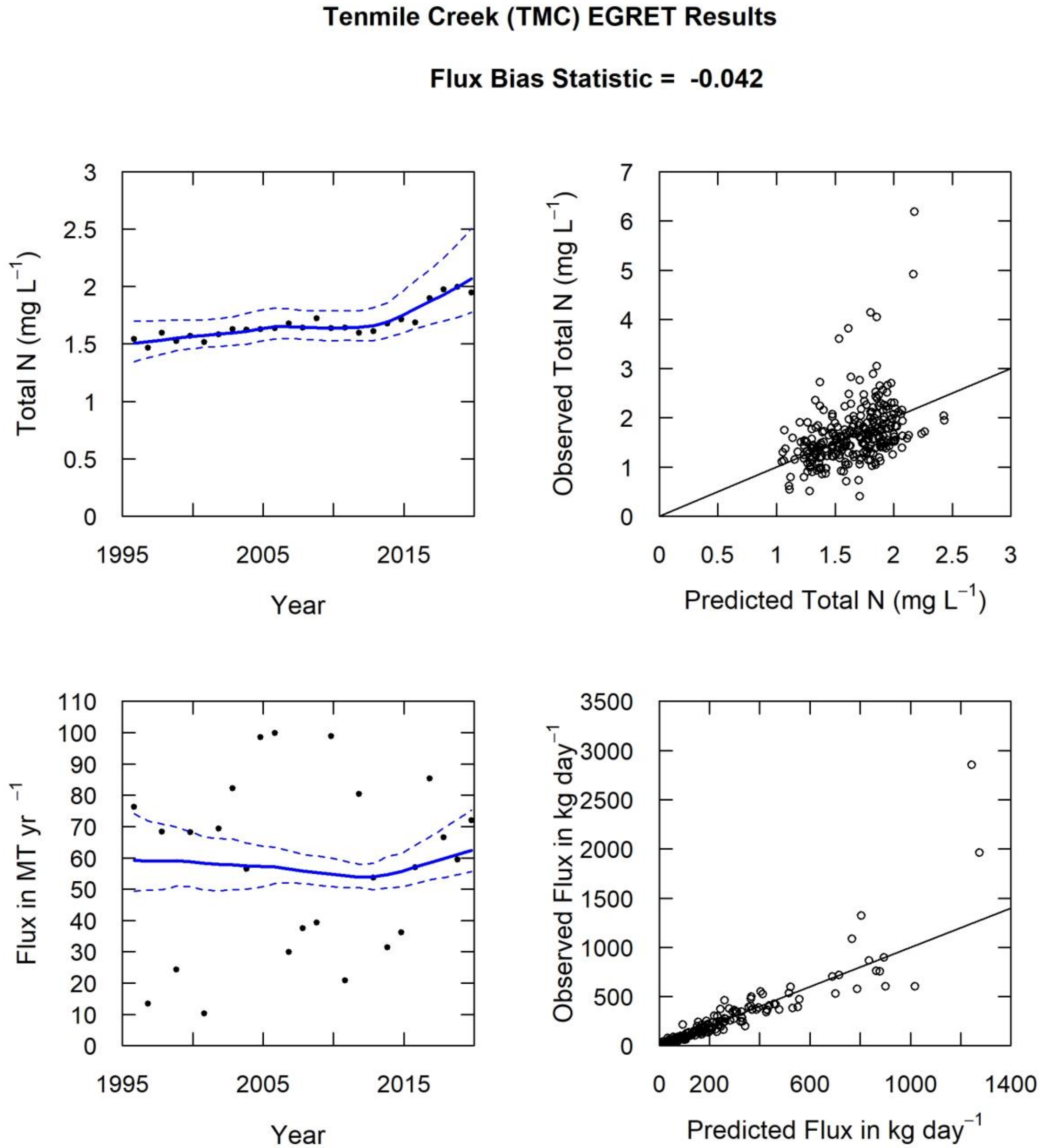

Figure A10. Tenmile Creek WRTDS model fit for TN. See the beginning of Appendix A for an explanation of each panel.

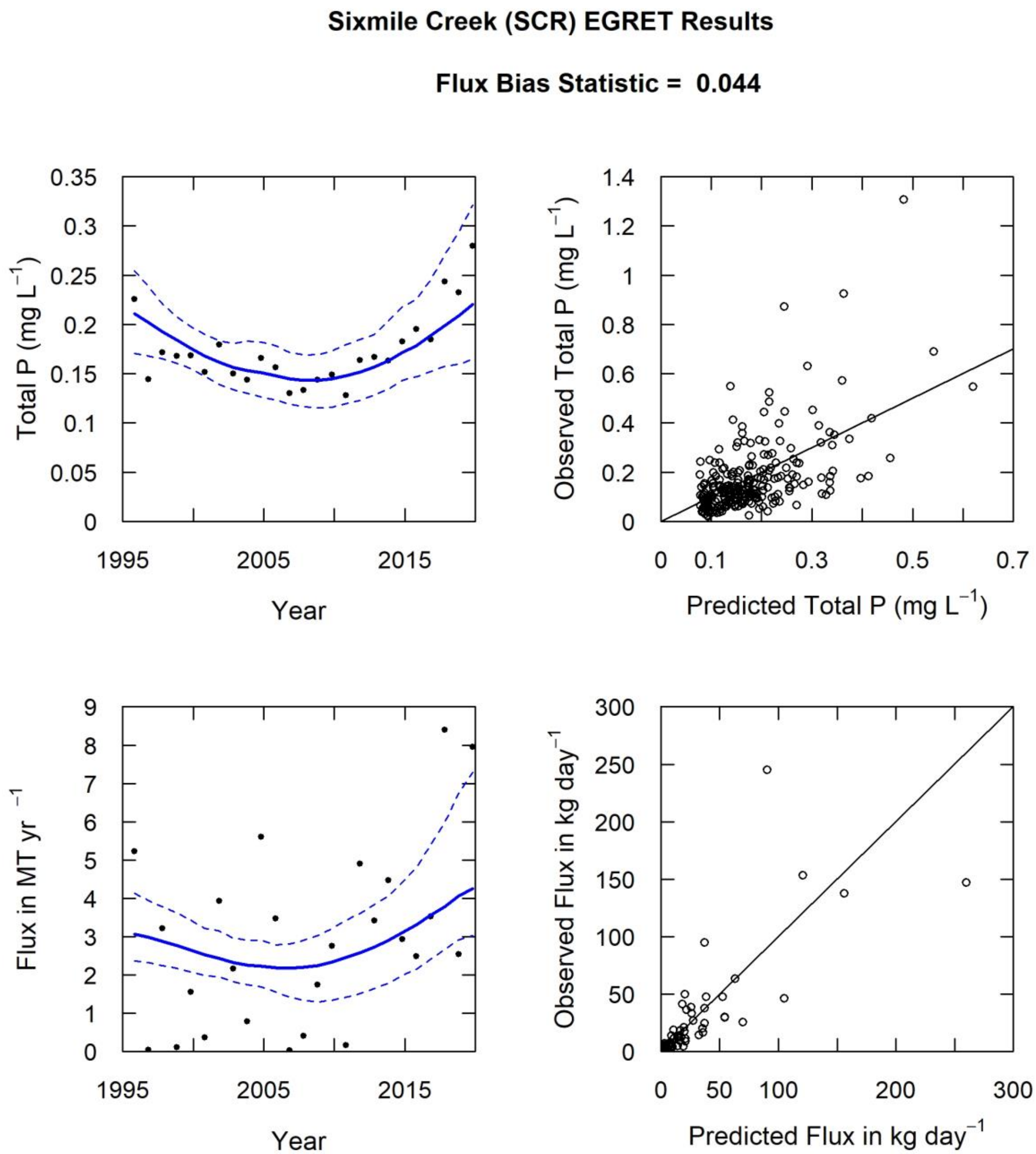

Figure A11. Sixmile Creek WRTDS model fit for TP. See the beginning of Appendix A for an explanation of each panel.

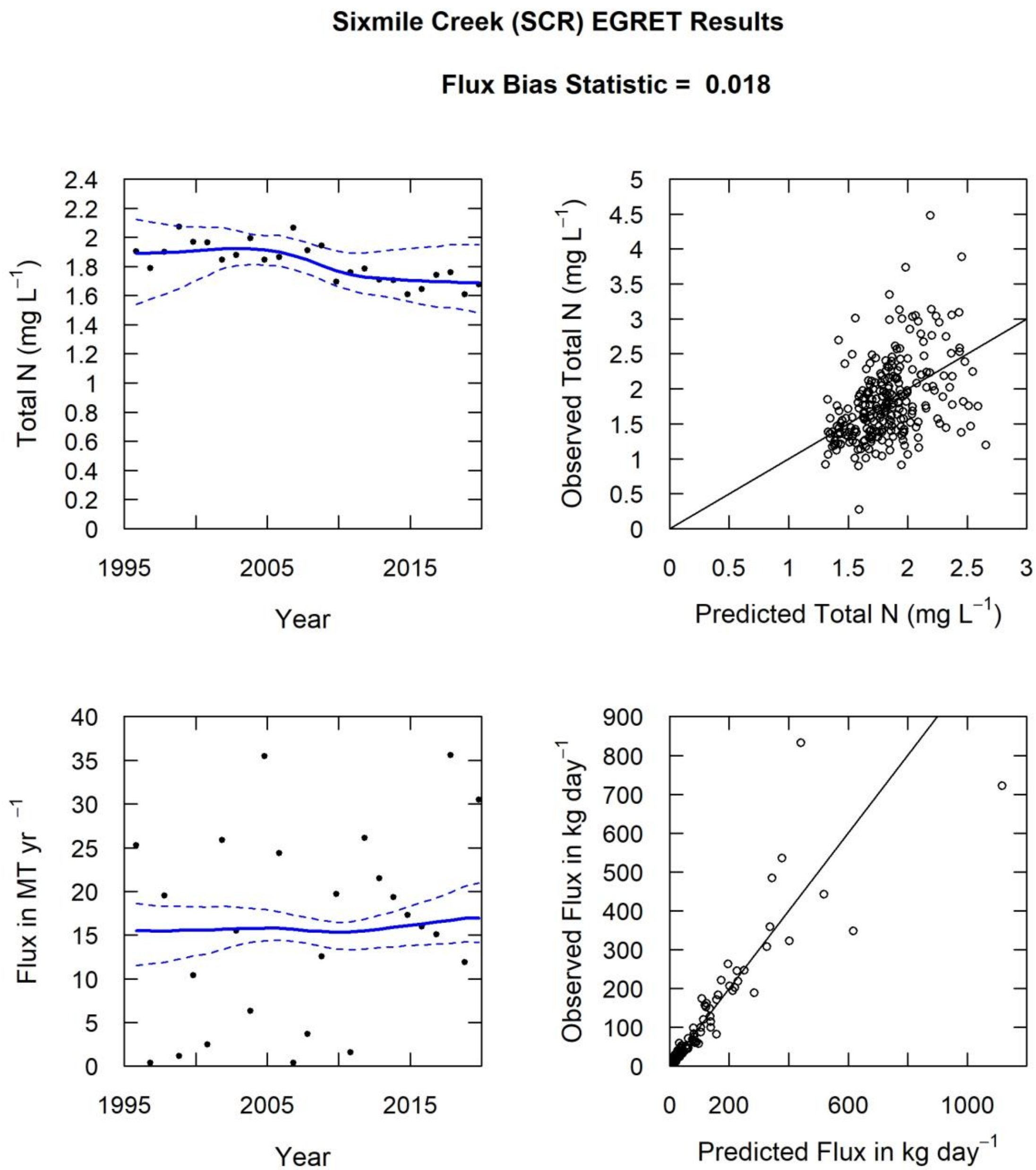

Figure A12. Sixmile Creek WRTDS model fit for TN. See the beginning of Appendix A for an explanation of each panel.

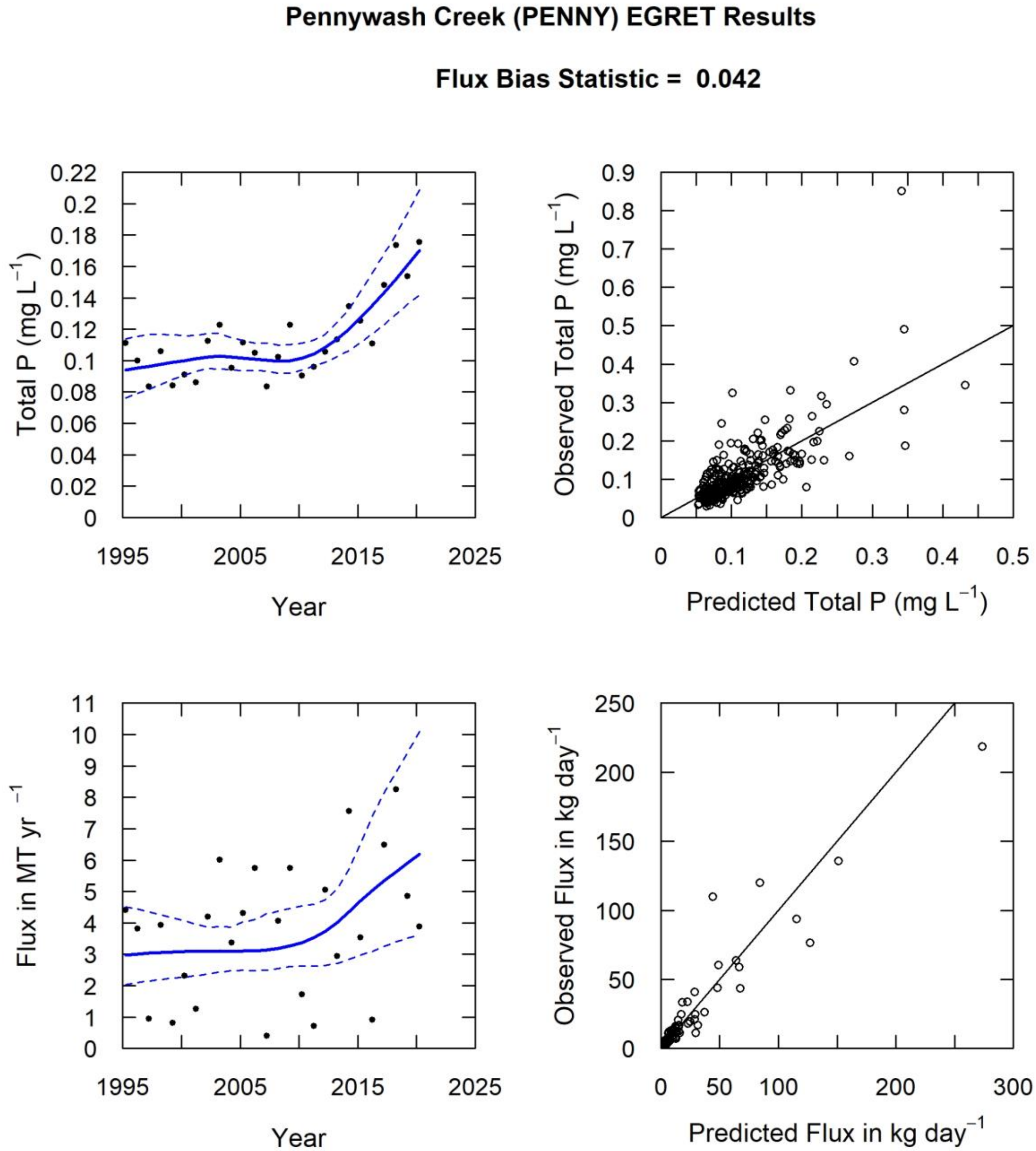

Figure A13. Pennywash Creek WRTDS model fit for TP. See the beginning of Appendix A for an explanation of each panel.

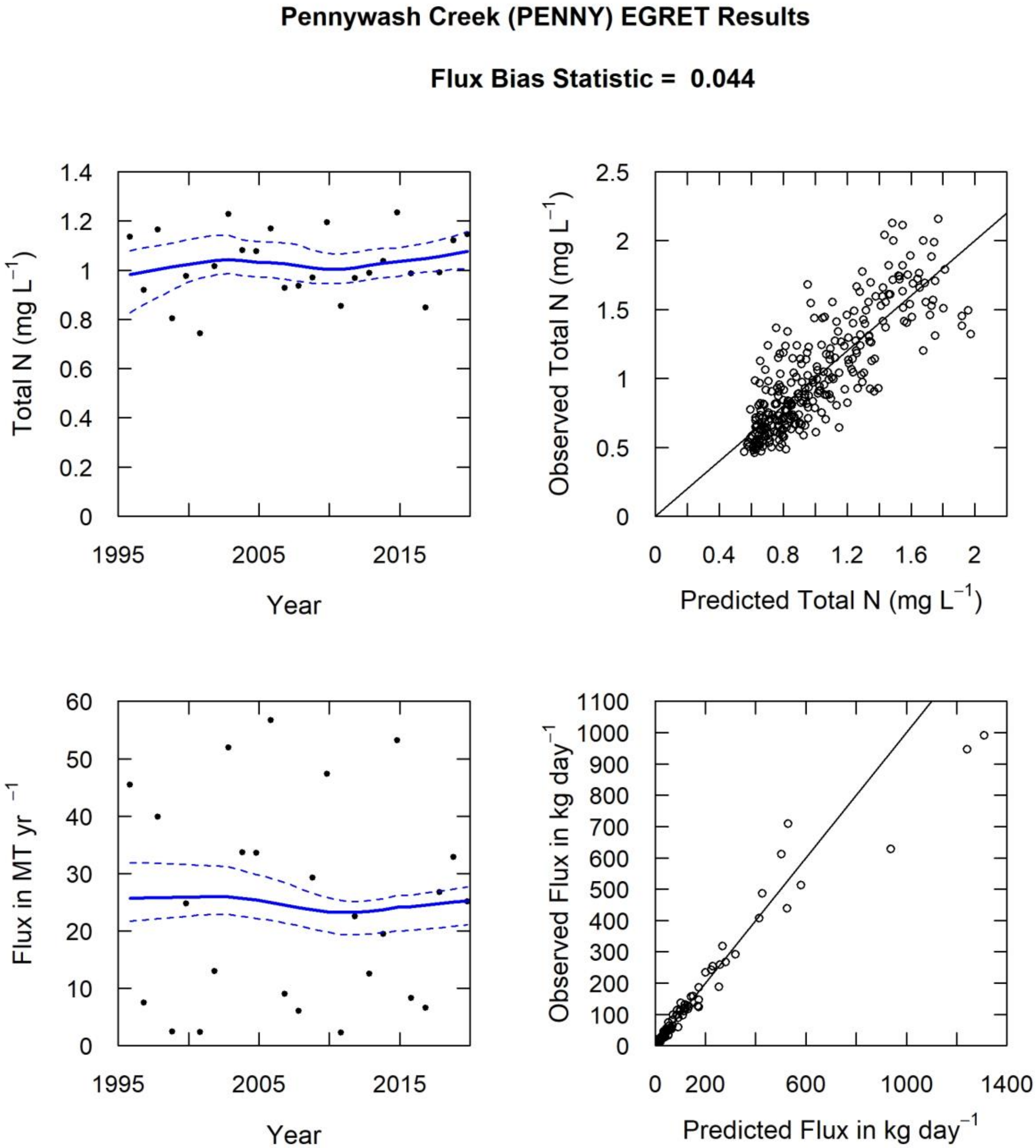

Figure A14. Pennywash Creek WRTDS model fit for TN. See the beginning of Appendix A for an explanation of each panel.

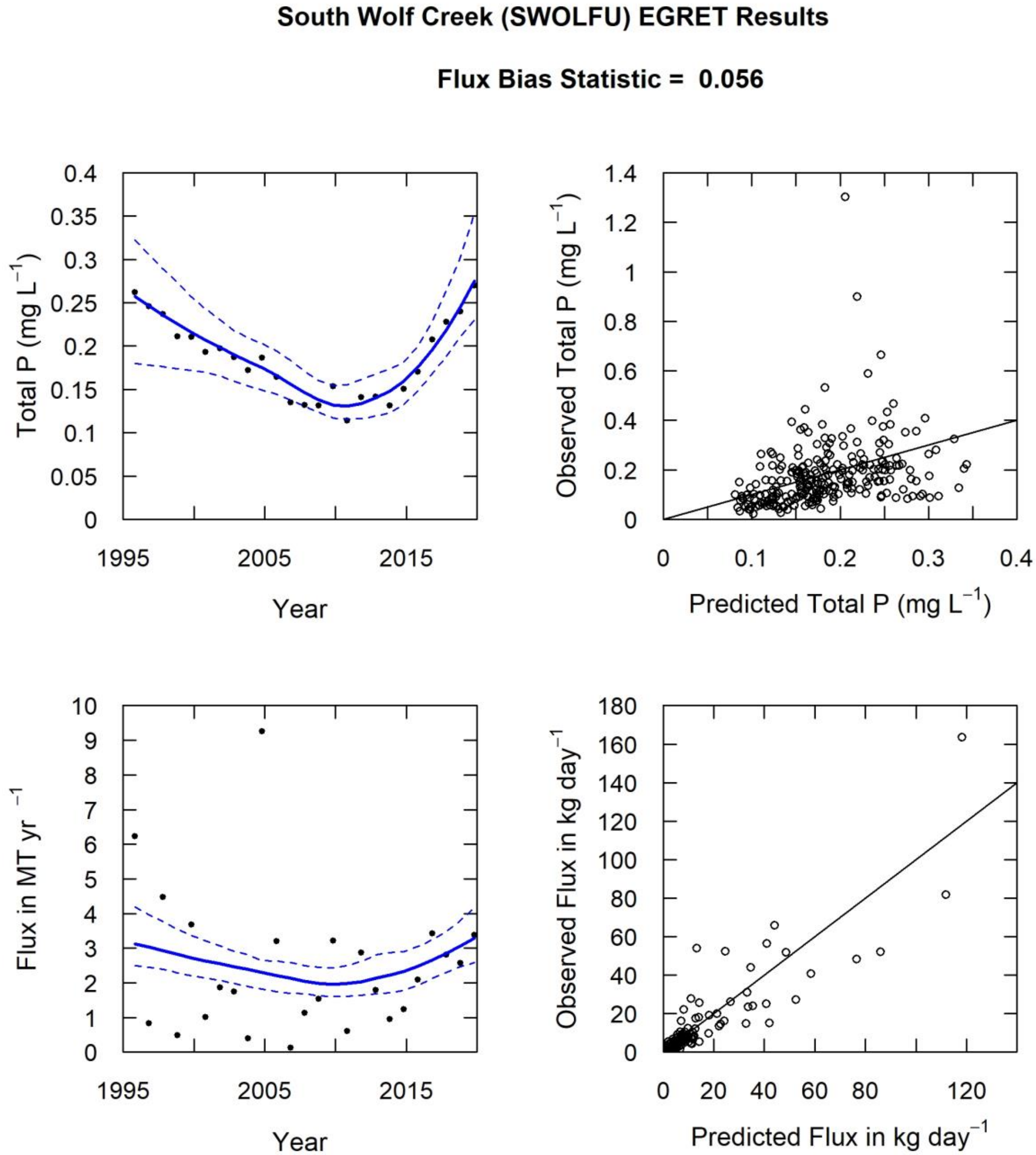

Figure A15. South Wolf Creek WRTDS model fit for TP. See the beginning of Appendix A for an explanation of each panel.

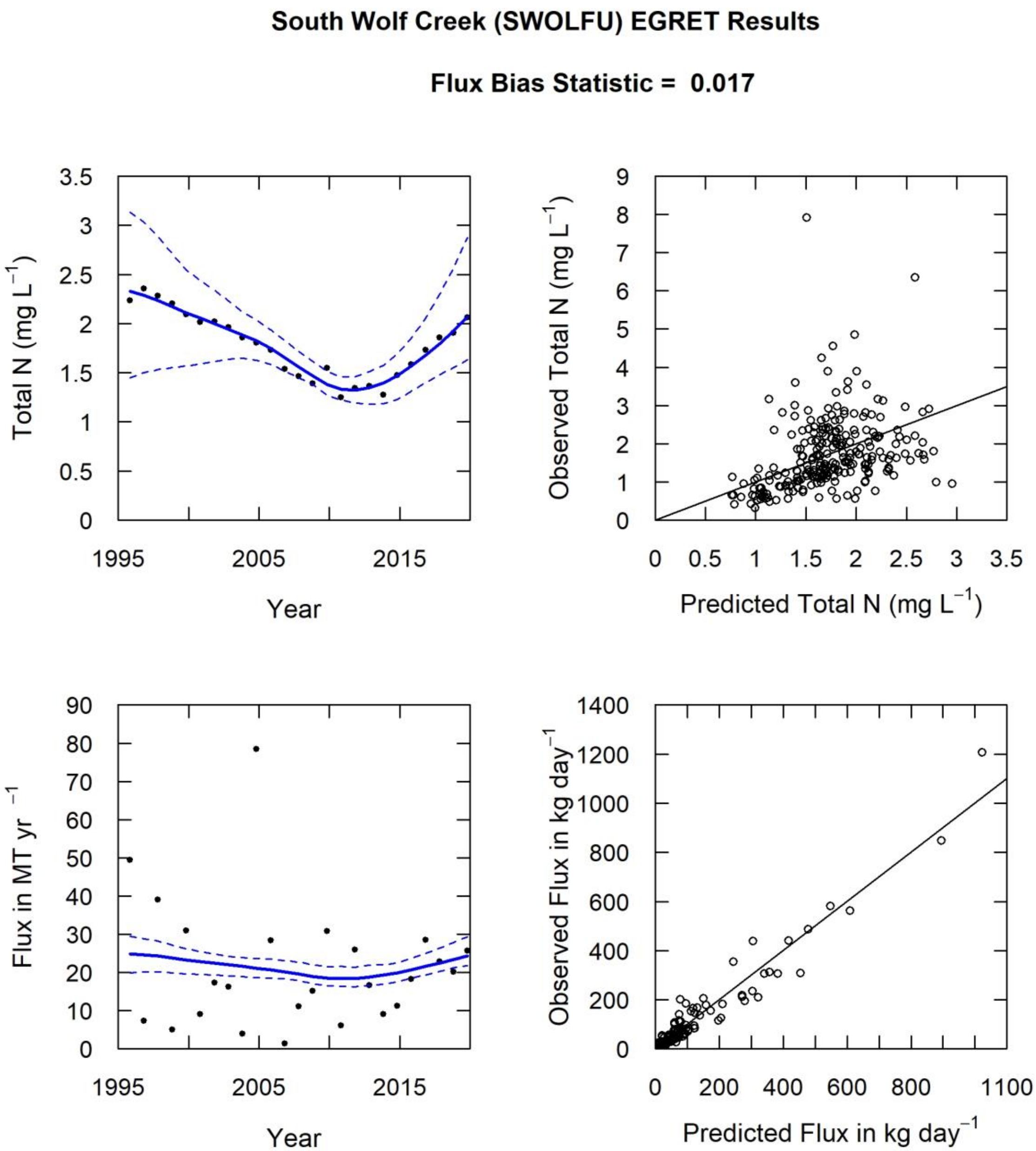

Figure A16. South Wolf Creek WRTDS model fit for TN. See the beginning of Appendix A for an explanation of each panel.

APPENDIX B. EXAMPLE WRTDS MODEL CODE

```
#Load Required Packages
library(EGRET)
library(EGRETci)
library(dplyr)
library(foreach)
library(doParallel)

######################
# 01. Prepare model data
######################

#Read Site Information from USGS National Water Information System
# Site is Jane Green Creek (Site number 02231600)
# Parameter code is Total P (00665)
info <- readNWISInfo('02231600','00665')

#Change water year start month to May
info$paStart = 5

#Read daily discharge data from NWIS
daily <- readNWISDaily('02231600','00060','1994-12-31','2020-12-31')

#Load prepped TP data and filter dates to match discharge POR
Sample <- readUserSample("./data/JGS_EGRETdata/","JGS_PO4.csv")
sample <- sample[sample$Date>as.Date('1994-12-31') &
sample$Date<as.Date('2021-01-01'),]

#Create the eList object required by EGRET with all of the input data
eList <- mergeReport(info,daily,sample)

#Plot Data to check before running model
multiPlotDataOverview(eList,qUnit = 1)
boxConcMonth(eList)
boxQTwice(eList)

#######################
# 02. Fit the Egret model
#######################
eList <- modelEstimation(eList,windowS=1)

#######################
# 03. Evaluate model results
#######################

#Plot Model Fit Diagnostics
fluxBiasMulti(eList)

#Two panel flow normalized conc and flux
par(mfcol = c(2, 1))
plotConcHist(eList, tinyPlot=F,printTitle=T,concMax=.2)
plotFluxHist(eList, tinyPlot=F,printTitle=T,fluxMax=100,fluxUnit = 8)
```

```
#Plot 4 panel Daily Conc
par(mfcol = c(2, 2), oma = c(0, 1.7, 6, 1.7))
plotConcTimeDaily(eList,1995,1997,tinyPlot=TRUE,printTitle=F,cex=1.2)
plotConcTimeDaily(eList,2003,2011,tinyPlot=TRUE,printTitle=F,cex=1.2)
plotConcTimeDaily(eList,1997,2003,tinyPlot=TRUE,printTitle=F,cex=1.2)
plotConcTimeDaily(eList,2011,2020,tinyPlot=TRUE,printTitle=F,cex=1.2)
mtext("JGS TP - Daily Concentration", outer=TRUE, font=2)

#######################
# 04. Bootstrapped confidence intervals
#######################

#May take a long time unless you have > 16 cores
nBoot <- 100
blockLength <- 200
coreOut <- 2 #Number of cores to leave out of processing tasks

widthCI <- 95
ciLower <- (50-(widthCI/2))/100
ciUpper <- (50+(widthCI/2))/100
probs <- c(ciLower,ciUpper)

nCores <- detectCores() - coreOut
cl <- makeCluster(nCores)
registerDoParallel(cl)

repAnnual <- foreach(n = 1:nBoot,.packages=c('EGRETci')) %dopar%
             {annualResults <- bootAnnual(eList,
                                  blockLength,
                                  startSeed = n)}

stopCluster(cl)

#Plot results with confidence intervals
plotConcHistBoot(eList, CIAnnualResults)
plotFluxHistBoot(eList, CIAnnualResults,col.pred='blue',fluxUnit=8)

#######################
# 05. Save final results
#######################

CIAnnualResults <- ciBands(eList, repAnnual, probs)
save(eList,CIAnnualResults,
file="./results/JGS_EGRETresults/JGS_TP_CIAnnualResults.RData")
```

APPENDIX C. JANE GREEN CREEK STORM SAMPLE DATA

Table C1. Annual total P and N applications from biosolids in the watersheds of the Jane Green storm-event sites.

	TP (MT)							
Year	**BCR**	**JGSW**	**JGS**	**USJ055**	**JGSW441**	**WBCC**	**YOKEBRCH**	**JGNE192**
2013	191	223	233	0	0	0	0	0
2014	320	515	552	25	0	0	0	0
2015	328	481	545	35	44	19	0	0
2016	298	523	623	52	21	14	0	0
2017	197	367	491	68	18	12	0	0
2018	145	286	440	117	9	8	0	0
2019	178	293	459	71	9	12	0	0
	TN (MT)							
Year	**BCR**	**JGSW**	**JGS**	**USJ055**	**JGSW441**	**WBCC**	**YOKEBRCH**	**JGNE192**
2013	512	561	585	0	0	0	0	0
2014	799	1,227	1,324	69	0	0	0	0
2015	879	1,138	1,310	100	96	48	0	0
2016	720	1,254	1,515	133	47	34	0	0
2017	468	914	1,245	194	39	32	0	0
2018	359	726	1,121	301	22	27	0	0
2019	508	809	1,222	187	30	36	0	0

Table C2. Storm-event TP concentrations for the Jane Green Creek storm sites. Sites are ordered by decreasing biosolids application per watershed area (highest biosolid application on the left). Mean discharge at the JGS site over seven days prior to the sampling event is also shown. A dash line indicates no sample was collected.

		Total Phosphorus (mg L^{-1})							
Date	Mean Discharge (cms)	BCR	JGSW	JGS	USJ055	JGSW441	WBCC	YOKEBRCH	JGNE192
10/4/2017	24.5	0.93	-	0.36	-	0.05	-	-	0.03
12/11/2017	1.3	0.19	0.16	-	0.08	0.03	0.09	0.04	0.01
1/4/2018	0.5	0.26	0.11	0.08	0.10	0.04	0.08	0.04	0.03
4/11/2018	0.0	0.68	0.25	-	0.18	0.15	0.13	-	-
4/24/2018	0.0	0.75	0.23	0.15	0.14	0.12	0.10	-	-
7/23/2018	7.4	0.90	0.28	0.25	0.17	0.05	0.11	0.05	-
9/17/2018	17.0	0.56	-	-	-	-	-	-	-
1/30/2019	1.5	0.59	0.06	0.04	0.09	0.03	0.05	0.03	-
2/14/2019	2.0	0.76	0.10	0.04	0.13	0.03	0.05	0.05	-
8/14/2019	25.1	1.72	0.48	0.35	0.46	0.07	0.07	0.05	-
2/27/2020	1.6	0.14	0.09	0.06	0.12	0.03	0.07	0.06	-
6/4/2020	3.2	0.57	0.14	0.09	0.16	0.03	0.05	0.05	-
8/6/2020	9.0	1.67	-	-	-	-	-	-	-
9/15/2020	12.9	1.17	0.03	-	0.51	0.02	0.15	0.04	-

Table C3. Storm-event TKN concentrations for the Jane Green Creek storm sites. Sites are ordered by decreasing biosolids application per watershed area (highest biosolid application on the left). Mean discharge at the JGS site over seven days prior to the sampling event is also shown. A dash line indicates no sample was collected.

		Total Kjeldahl Nitrogen (mg L^{-1})							
Date	Mean Discharge (cms)	BCR	JGSW	JGS	USJ055	JGSW441	WBCC	YOKEBRCH	JGNE192
10/4/2017	24.5	1.9	-	1.9	-	-	-	-	0.8
12/11/2017	1.3	1.4	1.2	-	0.8	1.2	0.6	0.8	0.4
1/4/2018	0.5	1.3	0.9	0.9	0.5	0.9	0.4	0.5	0.5
4/11/2018	0.0	1.7	1.2	-	0.6	0.9	0.6	-	-
4/24/2018	0.0	1.7	1.1	1.2	0.6	0.6	0.5	-	-
7/23/2018	7.4	1.8	1.2	1.3	1.3	1.3	1.0	0.9	-
9/17/2018	17.0	1.7	-	-	-	-	-	-	-
1/30/2019	1.5	1.3	0.8	0.9	0.7	0.9	0.7	0.6	-
2/14/2019	2.0	1.6	1.0	0.9	1.1	1.1	1.0	1.0	-
8/14/2019	25.1	2.2	1.8	1.8	2.4	1.5	1.6	1.4	-
2/27/2020	1.6	1.1	1.1	1.0	0.9	1.0	0.6	0.7	-
6/4/2020	3.2	2.1	1.5	1.6	1.1	1.2	1.1	1.3	-
8/6/2020	9.0	1.7	-	-	-	-	-	-	-
9/15/2020	12.9	1.5	1.0	-	1.6	1.1	1.0	1.0	-

Table C4. Storm-event total suspended solids (TSS) concentrations for the Jane Green Creek storm sites. Sites are ordered by decreasing biosolids application per watershed area (highest biosolid application on the left). Mean discharge at the JGS site over seven days prior to the sampling event is also shown. A dash line indicates no sample was collected.

		Total Suspended Solids (mg L^{-1})							
Date	Mean Discharge (cms)	BCR	JGSW	JGS	USJ055	JGSW441	WBCC	YOKEBRCH	JGNE192
10/4/2017	24.5	0.6	-	3.2	-	1.0	-	-	2.0
12/11/2017	1.3	-0.8	1.4	-	0.6	-0.4	1.4	-1.2	-0.4
1/4/2018	0.5	1.4	-0.6	-0.6	1.0	-0.4	0.0	-0.4	-0.2
4/11/2018	0.0	6.6	0.2	-	7.4	3.2	3.0	-	-
4/24/2018	0.0	6.2	-0.2	1.4	3.2	0.4	0.8	-	-
7/23/2018	7.4	0.6	-0.6	-0.8	2.8	-0.6	3.6	0.0	-
9/17/2018	17.0	-	-	-	-	-	-	-	-
1/30/2019	1.5	1.2	0.4	-0.2	0.6	-0.6	0.4	0.8	-
2/14/2019	2.0	1.6	0.0	0.2	0.8	1.0	-0.2	1.4	-
8/14/2019	25.1	0.8	1.2	0.2	0.0	-0.4	0.8	0.0	-
2/27/2020	1.6	1.4	0.4	0.2	-0.8	-0.4	-0.6	-0.6	-
6/4/2020	3.2	0.8	-0.4	0.2	3.2	-0.8	0.6	1.4	-
8/6/2020	9.0	2.4	-	-	-	-	-	-	-
9/15/2020	12.9	1.2	1.2	-	3.8	0.8	1.8	3.0	-