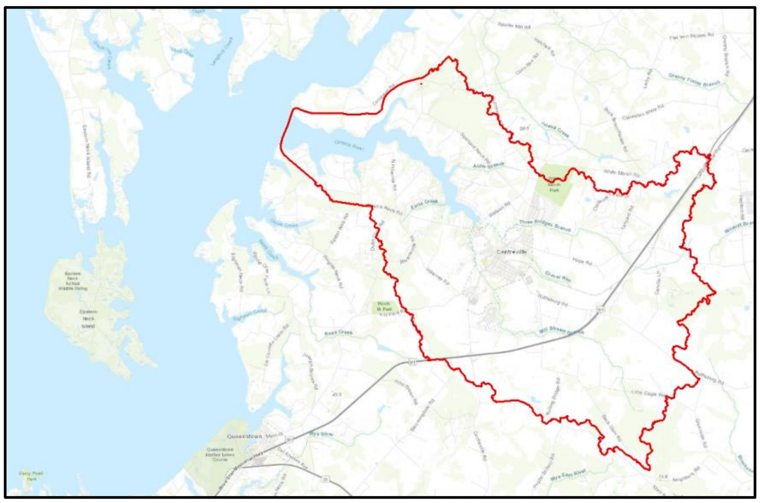
Updating the Statistical Analysis of Non-Tidal Nutrient Monitoring Data in the Corsica River Watershed

FINAL REPORT

June 3, 2019



Prepared by

Carlington W. Wallace
Interstate Commission on the Potomac River Basin
30 West Gude Drive, Suite 450
Rockville, Maryland 20850

for

Maryland Department of the Environment
1800 Washington Blvd
Baltimore, Maryland 21230

ICPRB Technical Report Series No. 19-2

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Executive Summary

Maryland Department of the Environment (MDE), the lead agency for administering Section 319 of the Clean Water Act (CWA) in Maryland, has been sampling in the Corsica River watershed since 2005 on a weekly basis and has generated an important data set comprising of several water quality parameters. MDE established monitoring stations for three major non-tidal tributaries in the Corsica River watershed and one control station in the Jarman Branch watershed. Three types of monitoring are done at the various stations. Flow-weighted composite samples were collected at the 3 tributaries and assessed for total nitrogen and total phosphorus concentrations. Grab samples were also collected at all 4 monitoring stations to define the relationship between dissolved and total nutrient concentrations. Nutrient synoptic surveys were conducted semi-annually (spring and fall) throughout the Corsica River watershed at approximately 40 stations to track watershed nutrient characteristics.

This report provides trend analyses of the nutrient levels in the non-tidal portion of the Corsica River watershed between 2006 and 2017 to determine if the 12 years of comprehensive work within the watershed are resulting in improved water quality.

When the grab samples were used to assess the relationship between dissolved and total nutrient concentrations, results indicate that:

- There is high correlation between NO23 and TN, and between PO_4 and TP, suggesting that soluble nitrogen and soluble phosphorus constitute the bulk of TN and TP concentrations, respectively. TP concentration was also highly correlated with TSS concentration, especially during spring (land preparation and planting of crops) and winter (harvesting of crops).
- Ammonia (NH_4) concentration is highly correlated with soluble phosphorus concentration, and consequently with TP.

Results based on the composite samples that were adjusted for flow show that:

- Both the long-term (2006-2017) and short-term (2012-2018) trends in total nitrogen are significant and downwards for all three non-tidal tributaries to the Corsica River.
- Long-term trends in total phosphorus concentrations are significant and downwards for all three non-tidal tributaries to the Corsica River. However, there is no significant difference in phosphorus concentrations for the short-term except for GVL, which shows a significant downward trend.

Analysis of the synoptic data showed no distinct patterns in nutrients concentrations during the fall and spring seasons. Despite there being a few areas in the watershed where high nutrient concentration continues to persist, the loss of nutrients from the landscape is not concentrated in

a single location within the watershed but tends to vary in concentration both spatially and temporally.

1. Introduction

1.1. Background

Excess nutrients (primarily nitrogen and phosphorus) in water cause prolific growth of algae and other green plants. Algal blooms in the upper tidal reaches of Maryland's Corsica River prompted Maryland Department of the Environment (MDE) in 1996, to add the Corsica River to the state's Clean Water Act (CWA) section 303(d) list of impaired waters for impairment of aquatic life and recreational use. In keeping with the United States Environmental Protection Agency (US EPA) stipulations, MDE developed a Total Maximum Daily Load (TMDL) for nitrogen and phosphorus in 2000 to address the impairment in the Corsica River watershed.

The TMDL established the following water quality goals: (1) chlorophyll A concentrations should remain below 50 µg/L and (2) dissolved oxygen (DO) levels should remain above the state's minimum water quality standard, 5 milligrams per liter (mg/L).[1,2] The major source of nutrient loading in the Corsica River watershed was agricultural runoff, with agriculture accounting for 66 percent of the land use in the watershed. Other sources were forest and urban nonpoint sources and the town of Centreville's wastewater treatment plant (WWTP).

As mandated by the Maryland General Assembly Water Quality Improvement Act of 1998[3], the town of Centreville, along with several key local partners and with support and cooperation from MDE and the Maryland Department of Natural Resources (MDNR), developed the Corsica River Watershed Restoration Action Strategy (WRAS) in 2004. The WRAS outlined implementation strategies needed to protect and restore the watershed. In 2005, the US EPA accepted the Corsica River WRAS, which was highlighted as one of the nation's best watershed plans at the CWA section 319 nonpoint source annual meeting. The governor of Maryland also selected the Corsica River for the state's targeted restoration watershed program.[1]

Beginning in 2005, five major state agencies, MDE, MDNR, Maryland Department of Agriculture (MDA), Maryland Department of Transportation (MDOT), and Maryland

[1] Implementing Best Management Practices Reduces Nitrogen in Two Corsica River Tributaries: https://www.epa.gov/sites/production/files/2015-10/documents/md_corsica.pdf
[2] Total Maximum Daily Loads of Nitrogen and Phosphorus for Corsica River: https://mde.state.md.us/programs/Water/TMDL/ApprovedFinalTMDLs/Documents/www.mde.state.md.us/assets/document/tmdl/corsica/corsica_tmdl_fin.PDF
[3] Maryland Nutrient Management Law: https://mda.maryland.gov/resource_conservation/Documents/NM_Law.pdf

Department of Planning (MDP), collaborated on funding, implementing, and monitoring to restore water quality in the Corsica River watershed and remove it from the 303d list of impaired waters.[4] Queen Anne's County, the town of Centreville, the University of Maryland, and local environmental and citizen groups later joined in the effort. Some of the restoration strategies that were implemented include helping local farmers select and target agricultural best management practices (BMPs); installing urban stormwater infiltration systems; installing stormwater wetland ponds and bio-retention practices; installing stormwater retrofits and rain gardens; and increasing the education and outreach efforts in the watershed.[1,3] Between 2012 and 2018, the following BMPs were installed: 836.6 acres of ag buffers; 5,504 acres of ag cover crops; 35.9 acres of grassed waterways; 31 acres of forest buffers; 191 acres of constructed wetland; and 66.1 acres of wetland enhancement. Additional urban BMPs were also implemented or enhanced.

This report provides trend analyses of the nutrient levels in the non-tidal portion of the Corsica River watershed between 2006 and 2017 to determine if the 12 years of comprehensive work within the watershed are resulting in improved water quality. MDE, the lead agency for administering Section 319, has been sampling in the watershed since 2005 on a weekly basis and has generated a robust data set. MDE is also the lead 319 NPS management agency responsible for coordination of policies, funds, and cooperative agreements with state agencies and local governments. Spooner et al. (2004)[5] conducted trend analyses of the nutrient data collected in the Corsica River's non-tidal subwatersheds between 2006 and 2012 and found that:

- total nitrogen (TN) and total phosphorus (TP) concentrations were decreasing in the Three Bridges Branch (TBB) and Gravel Run (GVL) subwatersheds;
- no trend was detected in TN and TP concentrations for the Old Mill Stream (OMS) subwatershed;
- TN and TP concentrations showed strong seasonal patterns; and
- flow was a weak explanatory variable of nutrient concentrations.

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[4] Corsica River Watershed Section 319 National Monitoring Program Project: https://319monitoring.wordpress.ncsu.edu/files/2016/05/md_corsica_profile.pdf
[5] Analysis of Corsica River Maryland, Water Quality Data: http://www.chesapeake.org/stac/presentations/231_Spooner_Corsica_STAC%202014.pdf

1.2. Watershed

The Corsica River watershed is located entirely in Queen Anne's County on Maryland's Eastern Shore and comprises the town of Centreville, as shown in Figure 1. It is approximately 25,600 acres and drains into the lower portion of the Chester River. The Corsica River is approximately 6.5 miles in length, with the non-tidal portion extending from the headwaters down to its intersection with State Route 213. The land use in the watershed is predominantly agricultural (66%), with approximately 26.3% forestry, 4.5% residential, 3.3% nonresidential urban, and 0.3% wetlands. The landscape can be characterized as gently rolling farm fields with forests along the primary streams. The non-tidal portion of the Corsica River watershed is subdivided into three subwatersheds; namely, Three Bridges Branch (TBB = 6,079 acres), Gravel Run (GVL = 1,229 acres), and the Old Mill Stream (OMS = 9,514 acres) as shown in Figure 1. Annual average rainfall in the watershed is approximately 40 to 42 inches year^{-1}, and average annual temperature is approximately 55°F.

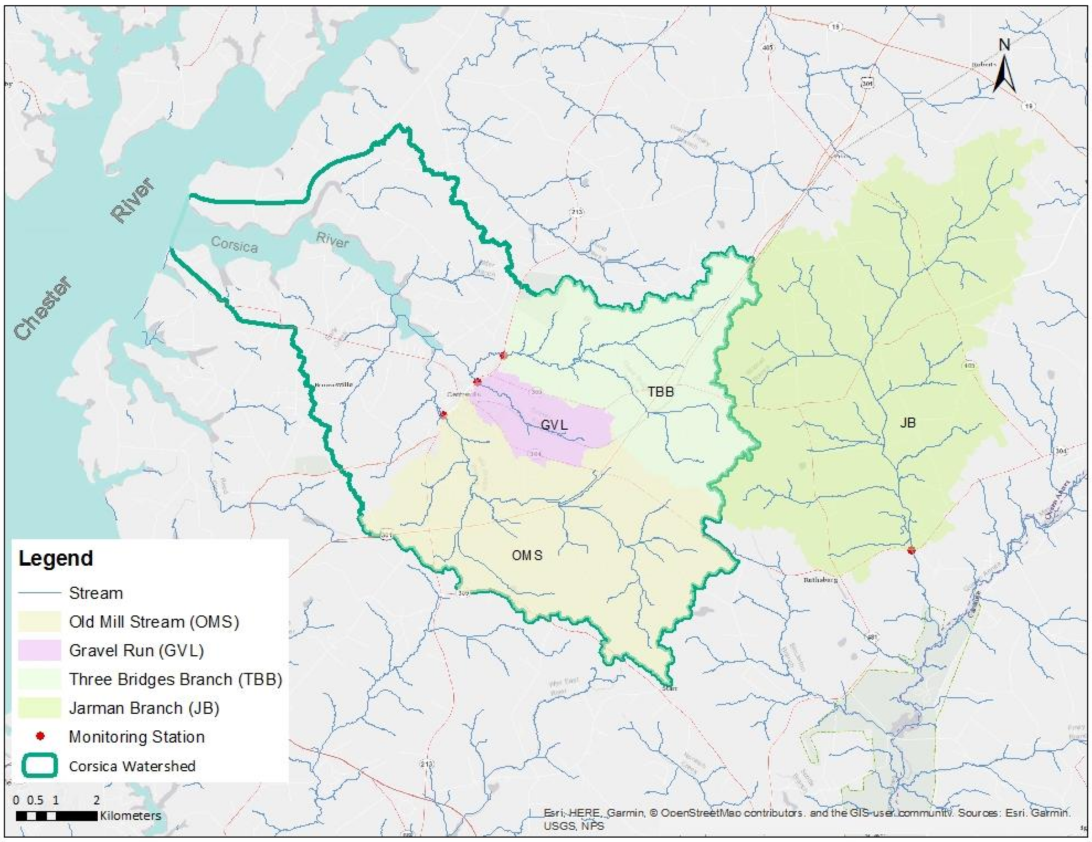

Figure 1. Location of Corsica River watershed and the respective monitoring sites.

1.3. Monitoring

The monitoring program seeks to assess and demonstrate the response of non-tidal and estuarine surface water nutrient loads, and by extension the TMDL endpoints of dissolved oxygen and chlorophyll A levels, as well as watershed management decisions and associated implementation activities. Specific monitoring objectives include documenting tidal and non-tidal surface water nutrient concentrations and loads, and the effectiveness of BMP implementation.

MDE monitors the three major non-tidal tributaries in the Corsica River watershed and one control station in the Jarman Branch watershed (JB = 12,355 acres), located just outside the Corsica River watershed. Base and storm flow water quality samples were collected using ISCO, Inc. automated samplers and flow meters installed on the three main tributaries. Flow-weighted composite samples were collected at these three stations. Weighting criteria were based on a rating curve established for each stream. At a specified flow interval, 10 mL samples were collected, composited, and preserved with sulfuric acid (H_2SO_4). The automated samplers were serviced weekly at baseflow conditions, or as needed during high flow events. At servicing, one 250 mL of the preserved sample was collected and refrigerated. The University of Maryland Center for Environmental Science (UMCES) Horn Point Laboratory (HPL) analyzed the preserved samples for TN and TP. For each sampling period, stream discharge volume and the total sample volume of the carboy were recorded at the time of sample collection. Table 1 (TN) and Table 2 (TP) show the composite samples collected for GVL, OMS and TBB between May 2006 and May 2018. Based on these composite samples, average annual TN in GVL, OMS and TBB were 3.2 mg/L, 4.6 mg/L and 3.2 mg/L, respectively, while average annual TP were 0.5 mg/L, 0.6 mg/L and 0.4 mg/L in GVL, OMS and TBB, respectively.

Additionally, to define the relationship between dissolved and total nutrient concentrations, grab samples (not adjusted for flow) for whole and filtered water were collected weekly and analyzed by UMCES Chesapeake Biological Laboratory (CBL). The whole samples were analyzed for TN and TP while the filtered samples were analyzed for dissolved inorganic nitrogen (NO23 and NH_4) and dissolved inorganic phosphorus PO_4. Table 3 (TN) and Table 4 (TP) show the grab samples collected for GVL, OMS and TBB between July 2005 and February 2018. Based on these grab samples, average annual TN in GVL, OMS, TBB and JB were 2.7 mg/L, 3.7 mg/L, 2.8 mg/L, and 4.5 mg/L, respectively, while average annual TP were 0.1 mg/L, 0.1 mg/L, 0.1 mg/L, and 0.2 mg/L in GVL, OMS, TBB and JB, respectively.

Nutrient synoptic surveys were conducted semi-annually (spring and fall) throughout the Corsica River watershed at approximately 40 stations to track watershed nutrient characteristics. Whole and filtered samples were collected along with stream discharge and in-situ parameters of temperature, pH, dissolved oxygen, and specific conductivity. The samples were stored on ice and frozen on the day of collection. CBL analyzed the whole samples for TN and TP, and the filtered samples for NO23, NH_4, and PO_4.

Table 1. Total nitrogen composite samples (flow-adjusted) collected for Gravel Run, Old Mill Stream, and Three Bridges Branch. The table includes years of sampling, number of samples (n), sample mean for each year (mean) and standard deviation for each year (SD), as well as an overall summary.

	Gravel Run			Old Mill Stream			Three Bridges Branch		
Year	n	mean (mg/L)	SD	n	mean (mg/L)	SD	n	mean (mg/L)	SD
2006	30	4.1	1.5	32	5.3	2.3	32	4.1	1.4
2007	41	4.2	1.1	45	4.9	1.5	47	4.0	0.9
2008	48	4.5	4.0	47	4.9	1.5	48	3.5	1.2
2009	37	3.3	1.5	40	4.6	1.1	41	3.3	1.0
2010	44	3.2	0.8	41	4.9	1.1	44	3.3	0.7
2011	42	3.1	0.8	32	4.7	1.0	36	3.0	0.5
2012	44	2.9	0.8	18	5.2	0.6	42	2.7	0.6
2013	45	2.8	0.8	34	4.4	0.8	43	2.7	0.6
2014	41	3.2	1.1	39	4.7	1.1	42	2.9	0.6
2015	0	-	-	34	4.2	1.0	32	3.1	1.1
2016	32	2.3	0.4	43	4.5	1.4	45	2.9	0.7
2017	48	2.0	0.4	42	3.5	0.7	42	2.6	0.6
2018	15	2.4	0.5	10	3.8	0.4	14	2.9	0.4
Summary	467	3.2	1.0	457	4.6	0.5	508	3.2	0.3

Table 2. Total phosphorus composite samples (flow-adjusted) collected for Gravel Run, Old Mill Stream, and Three Bridges Branch. The table includes years of sampling, number of samples (n), sample mean for each year (mean) and standard deviation for each year (SD), as well as an overall summary.

	Gravel Run			Old Mill Stream			Three Bridges Branch		
Year	n	mean (mg/L)	SD	n	mean (mg/L)	SD	n	mean (mg/L)	SD
2006	30	0.8	0.6	32	1.0	1.0	32	0.6	0.5
2007	41	0.9	0.6	45	1.0	0.9	47	0.5	0.3
2008	48	0.9	1.3	47	0.6	0.5	49	0.6	0.4
2009	37	0.8	0.8	40	0.8	0.5	41	0.5	0.4
2010	44	0.5	0.4	41	0.7	0.5	44	0.3	0.2
2011	42	0.5	0.7	32	0.8	0.5	36	0.3	0.3
2012	44	0.4	0.4	18	0.4	0.3	42	0.3	0.2
2013	45	0.3	0.2	34	0.5	0.3	43	0.2	0.1
2014	41	0.7	0.9	39	0.5	0.3	42	0.3	0.1
2015	0	-	-	34	0.5	0.4	32	0.5	0.3
2016	32	0.1	0.1	43	0.6	0.5	45	0.3	0.2
2017	48	0.2	0.5	42	0.3	0.3	42	0.3	0.2
2018	15	0.2	0.2	10	0.5	0.2	14	0.2	0.1
Summary	467	0.5	0.3	457	0.6	0.2	509	0.4	0.1

Table 3. Total nitrogen grab samples (not adjusted for flow) collected for Gravel Run, Old Mill Stream, Three Bridges Branch, and Jarman Branch. The table includes years of sampling, number of samples (n), sample mean for each year (mean) and standard deviation for each year (SD), as well as an overall summary.

	Gravel Run			Old Mill Stream			Three Bridges Branch			Jarman Branch		
Year	n	mean (mg/L)	SD	n	mean (mg/L)	SD	n	mean (mg/L)	SD	n	mean (mg/L)	SD
2005	22	3.2	0.6	20	4.2	0.9	22	2.9	0.7	10	4.7	0.7
2006	49	3.3	0.7	50	3.9	0.7	51	3.0	0.5	47	5.0	0.8
2007	49	3.2	1.0	50	4.0	0.8	52	3.3	0.8	50	4.7	0.8
2008	54	3.0	0.6	52	3.9	0.8	51	3.3	3.0	52	4.6	0.7
2009	51	2.8	0.6	50	3.6	0.8	51	3.0	2.1	49	4.4	0.1
2010	51	2.8	0.8	50	4.0	0.9	49	3.1	0.8	50	4.6	0.9
2011	51	2.6	0.7	51	3.6	0.8	50	2.7	0.5	51	4.1	0.7
2012	48	2.3	0.7	46	3.9	0.8	49	2.6	0.4	46	4.3	0.8
2013	50	2.5	0.4	50	3.8	0.6	50	2.7	0.6	48	4.5	0.7
2014	50	2.4	0.5	50	3.6	0.8	48	2.7	0.5	50	4.6	1.0
2015	39	2.4	0.7	44	3.6	0.7	43	2.5	0.5	43	4.2	0.7
2016	49	2.5	0.4	47	3.4	0.6	48	2.5	0.4	47	4.2	0.6
2017	51	2.3	0.4	50	3.2	0.6	51	2.5	0.9	38	4.6	1.0
2018	7	2.5	0.2	7	3.3	0.6	7	2.5	0.4	-	-	-
Summary	621	2.7	0.2	617	3.7	0.1	622	2.8	0.8	581	4.5	0.2

Table 4. Total phosphorus (TP) grab samples (not adjusted for flow) collected for Gravel Run, Old Mill Stream, Three Bridges Branch, and Jarman Branch. The table includes years of sampling, number of samples (n), sample mean for each year (mean) and standard deviation for each year (SD), as well as an overall summary.

	Gravel Run			Old Mill Stream			Three Bridges Branch			Jarman Branch		
Year	n	mean (mg/L)	SD	n	mean (mg/L)	SD	n	mean (mg/L)	SD	n	mean (mg/L)	SD
2005	22	0.1	0.1	21	0.1	0.0	22	0.1	0.1	10	0.2	0.2
2006	49	0.1	0.1	51	0.1	0.0	51	0.1	0.1	47	0.1	0.1
2007	49	0.1	0.0	52	0.1	0.1	52	0.1	0.1	50	0.1	0.1
2008	54	0.1	0.2	52	0.1	0.0	51	0.1	0.1	53	0.1	0.1
2009	51	0.1	0.1	50	0.1	0.1	51	0.1	0.1	49	0.2	0.1
2010	51	0.1	0.1	50	0.1	0.0	49	0.1	0.1	50	0.1	0.1
2011	51	0.1	0.1	51	0.1	0.0	50	0.1	0.1	51	0.1	0.1
2012	48	0.1	0.0	46	0.1	0.0	49	0.1	0.1	46	0.2	0.2
2013	50	0.1	0.1	50	0.1	0.1	50	0.1	0.1	48	0.1	0.1
2014	50	0.1	0.1	50	0.1	0.0	48	0.1	0.1	50	0.2	0.1
2015	39	0.2	0.1	44	0.1	0.1	43	0.1	0.1	43	0.2	0.1
2016	49	0.1	0.1	47	0.1	0.1	48	0.1	0.1	47	0.2	0.1
2017	51	0.2	0.1	50	0.1	0.1	51	0.1	0.1	38	0.2	0.1
2018	7	0.1	0.0	7	0.1	0.0	7	0.1	0.0	-	-	-
Summary	621	0.1	0.1	621	0.1	0.1	622	0.1	0.0	582	0.2	0.0

2. Trend Analysis Methods

Methods for statistical trend analysis were based on Helsel's and Hirsh's Statistical Methods in Water Resources.[6] In this study, non-parametric methods of trend analysis were applied for all parameters because, as opposed to parametric tests, non-parametric tests have greater ability (more power) to correctly reject the hypothesis of no trend. Non-parametric tests are also more appropriate for data that are not normally distributed, and it is ill-advised to assume a distribution for the data. Parametric methods such as the two-sample t-test to determine the difference in means between two periods assume the data conform to a specific distribution. In this case, the assumption is that the data are normally distributed. When the distribution of the data are not known, a more robust approach would be to use the non-parametric Wilcoxon rank-sum test (also called the Mann-Whitney test) as an alternative to the two-sample t-test.

Concentrations of certain water quality parameters can be strongly influenced by season and/or streamflow intensity. Trends in these parameters can be clearer if the confounding effects of season and flow are taken into consideration during the analysis. For this study, all trend analyses employed a method to adjust for normal seasonal differences in the parameters. Trend analyses were done on data that were not adjusted for flow (grab samples), as well as data that were flow-adjusted (composite samples). Comparisons of the flow-adjusted and unadjusted analyses can typically identify the influence of extreme or unusual flow events on trend results.

Finally, two trend periods were selected for this study: a long-term period from 2006 to 2017 and a short-term period from 2012 to 2017. This was done to evaluate the cumulative effects of BMP implementation between 2005 and 2012 and to complement the analyses reported in Spooner et al. (2014). The selected periods also provide an opportunity to identify short-term changes that may be masked in the long-term trend results. The following four kinds of trends were evaluated for each combination of station and parameter: 1) long-term trends (2006-2017) on data not adjusted for flow, 2) short-term trends (2012-2017) on data not adjusted for flow, 3) long-term trends (2006-2017) on flow-adjusted data, and 4) short-term trends (2012-2017) on flow-adjusted data.

[6] Statistical Methods in Water Resources (Techniques of Water-Resources Investigations of the United States Geological Survey, Book 4, Hydrologic Analysis and Interpretation Chapter A3) [Policies and Guidance]. Retrieved April 26, 2019, from https://www.epa.gov/quality/statistical-methods-water-resources-techniques-water-resources-investigations-united-states

The goal for all methods is to determine if a trend exists. The existence of a trend is expressed as the p-value of the hypothesis test that there is no trend (null hypothesis). The smaller the p-value, the stronger the evidence that a trend exists, and the larger the argument that the null hypothesis should be rejected. For this analysis, p-values less than 0.05 are considered indicative of real or "significant" trends. If the p-value supports the existence of a trend, the next step is to determine the direction and, if possible the magnitude, of the trend. For a linear trend, the direction and magnitude of the trend is determined by estimating the slope.

2.1 Seasonal Kendall Trend test

The seasonal Kendall test was used to test for long-term and short-term trends for each combination of station and parameter. Because the sampling frequency was consistent (biweekly) over the 12-year timeframe (01/01/2006 to 12/31/2017) of the Corsica River analysis data set, there was no need to perform a culling of the data before applying the seasonal Kendall test. The seasonal Kendall test is a non-parametric test that analyzes data for monotonic trends in seasonal data. In other words, the seasonal Kendall test is primarily a method for testing seasonally adjusted trends on data that are continuous and with few or no censored values. If the period of record was discontinuous, step-trend methods rather than linear trend methods would be more appropriate to use. Step trends divide the data into earlier and later periods on either side of the discontinuity and measure differences in the two periods. Only the composite samples for Gravel Run (GVL) were missing an extensive period of record (2015) due to the removal of the dam at GVL in 2015 by the County. However, when the data set were divided into thirds of equal length, as suggested by Helsel and Hirsch, none of the thirds had less than 20% coverage therefore, a step-trend was not necessary.

In this study, four seasons were defined and the minimum sampling frequency in each season was determined for both the short-term and long-term trend periods. The four seasons are: winter (December, January, February), spring (March, April, May), summer (June, July, August), and autumn (September, October, November). In the seasonal Kendall test, data are only compared to the same season. For example, spring would only be compared with spring and summer would only be compared with summer. The seasonal Kendall test statistic is computed by performing a Mann-Kendall calculation for each season, then combining the results for each season. If a trend is detected, the Theil slope estimator was used to estimate the direction and magnitude of the trend.

2.2 Wilcoxon signed rank test

The Wilcoxon signed rank test (also known as the rank-sum test), used to test for long-term trends in a discontinuous data record with few or no censored values, was used to determine if the distributions or medians of the two periods (2006-2012 and 2012-2017) differed. The

Wilcoxon signed rank test was applied to the grab samples (not adjusted for flow) as well as the composite samples (flow-adjusted).

3. Results and Discussion

Monitoring (grab sampling) for dissolved nitrogen (NO23 and NH_4), dissolved inorganic phosphorus (PO_4), total nitrogen (TN), total phosphorus (TP) and total suspended solids (TSS) began in July 2005 at Corsica River's three non-tidal subwatershed outlets and continues uninterrupted through February 2018 except for GVL where no composite sampling data are available for 2015. Monitoring also began in July 2005 at the Jarman Branch (JB) outlet and continued through 2017. Figures 2-5 show correlation between the different variables, and variation of nutrient concentrations across seasons. As expected, there is high correlation between NO23 and TN, and between PO_4 and TP, suggesting that soluble nitrogen and soluble phosphorus constitute the bulk of TN and TP concentrations, respectively. TP concentration was also highly correlated with TSS concentration, especially during spring (land preparation and planting of crops) and winter (harvesting of crops). What is a bit surprising, and requires further investigation, is that ammonia (NH_4) concentration is highly correlated with soluble phosphorus concentration, and consequently with TP.

MDE conducted nutrient synoptic surveys semi-annually throughout the Corsica watershed at approximately 40 stations to track watershed nutrient characteristics. The samples were analyzed for nitrate-nitrite (NO23), NH_4, TN, PO_4 and TP. The synoptic data provides a snapshot of nutrient concentrations across the Corsica River watershed over time. Synoptic surveys are relatively quick and inexpensive for the level of data provided. They are useful for tracking the impacts of land use/land cover changes, and for targeting potential sites for BMP implementation.

Concentrations of NO23 (Figures A1, A2), TN (Figures A3, A4), PO_4 (Figures A5, A6) and TP (Figures A7, A8) were mapped to show nutrient loss hotspots across the watershed for the period 2012 to 2017 (Appendix), using to the synoptic surveys. The surveys were taken during the fall and spring of each year. Based on the maps shown in the appendix, there are no distinct patterns in nutrients concentrations during the fall and spring seasons. Despite there being a few areas in the watershed where high nutrient concentration continues to persist, nutrient loss from the landscape is not concentrated in a single location within the watershed but tends to vary in concentration both spatially and temporally.

The effects of BMPs on nutrient concentration at the monitoring stations cannot be readily identified in the maps, and though not flow-corrected, the synoptic data allows for quick identification of nutrients hotspots in the watershed to facilitate better targeting of BMP implementation. Effects of combined BMP implementation may be assessed by comparing the nutrient concentrations of the composite samples for the period's pre and post 2012. Between 2012 and 2017, there have been significant BMP implementation efforts.

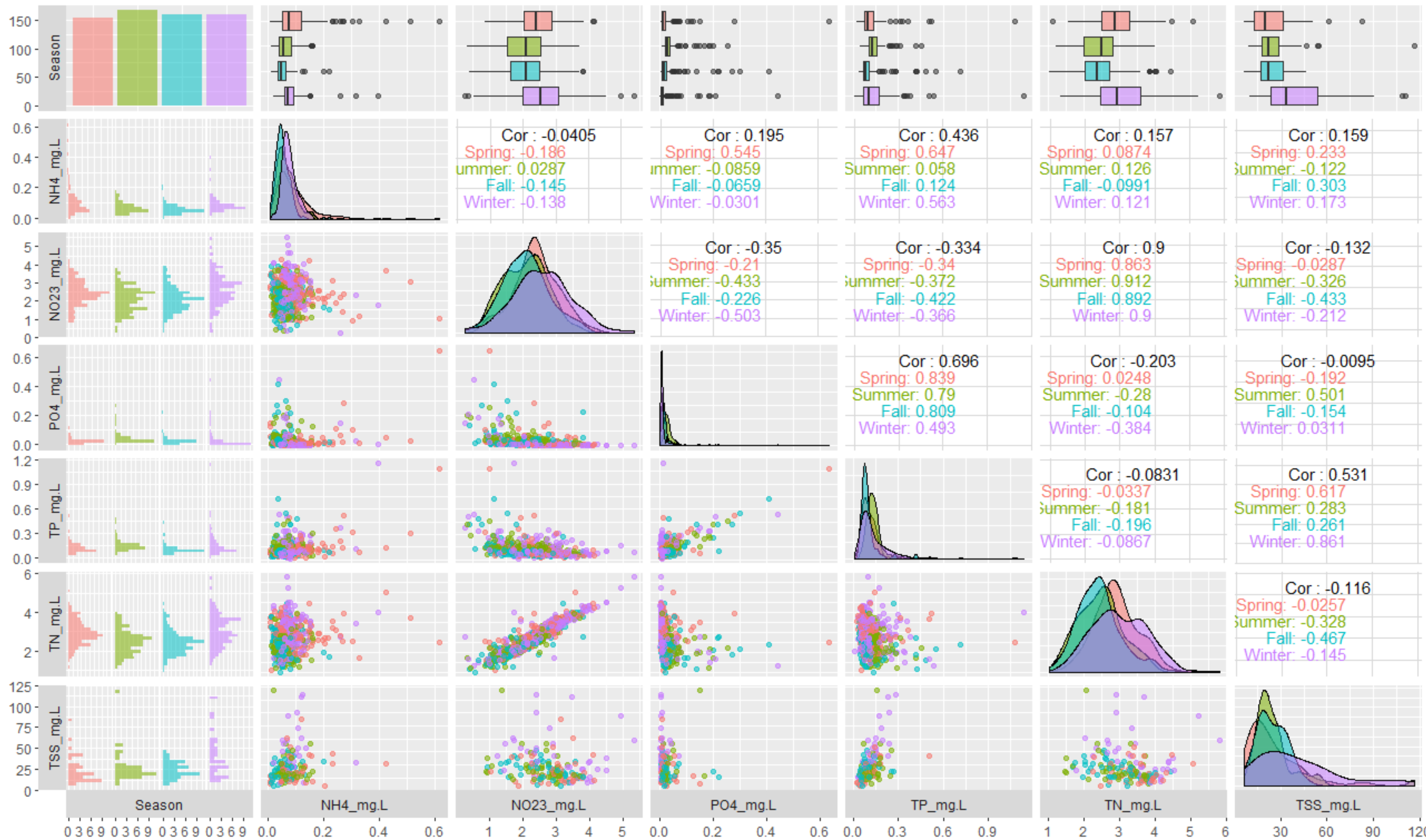

Figure 2. Distribution of nutrients concentration at the Gravel Run (GVL) outlet. The figure shows correlation between the different water quality variables, and variation of nutrient concentrations across the four seasons.

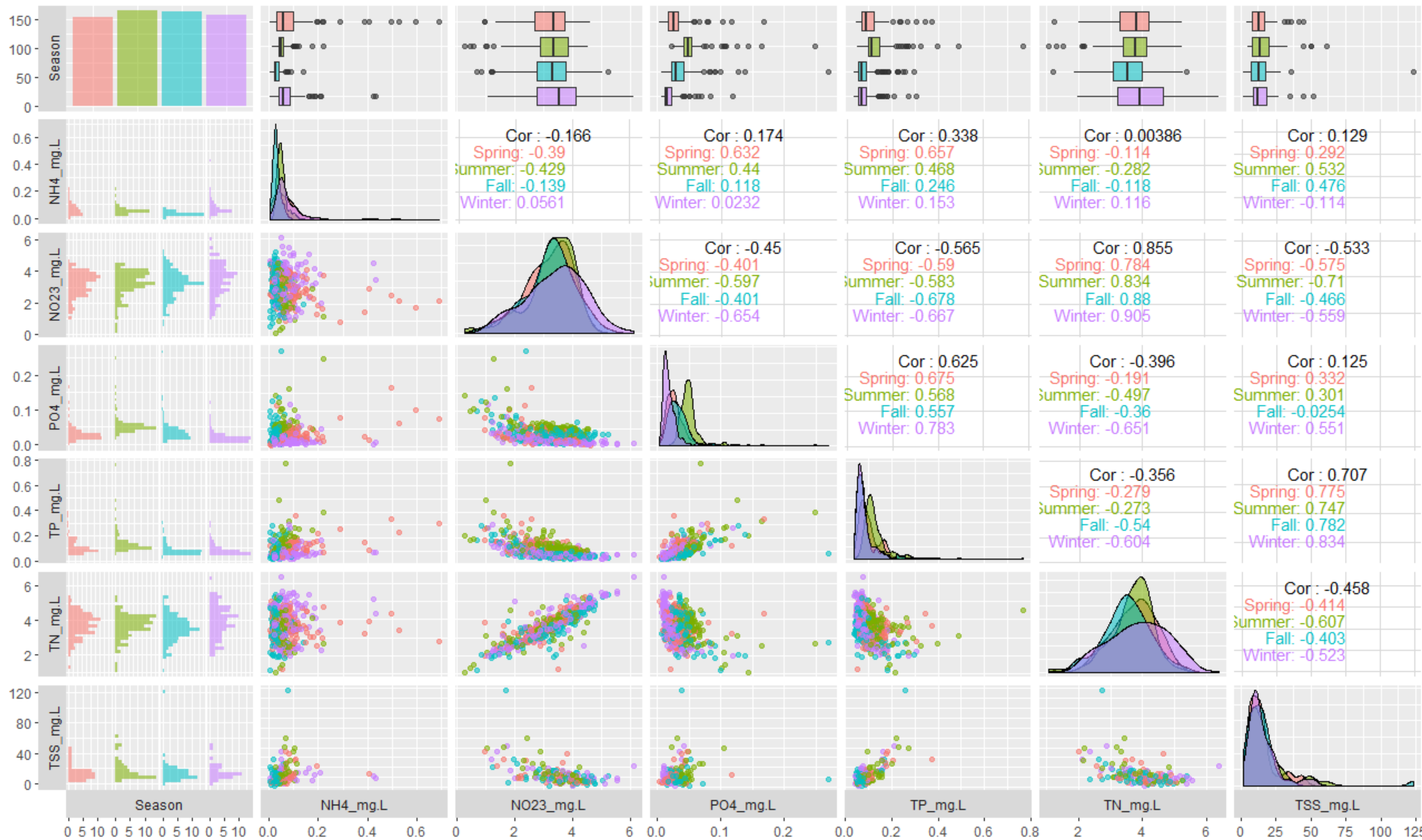

Figure 3. Distribution of nutrients concentration at the Old Mill Stream (OMS) outlet. The figure shows correlation between the different water quality variables, and variation of nutrient concentrations across the four seasons.

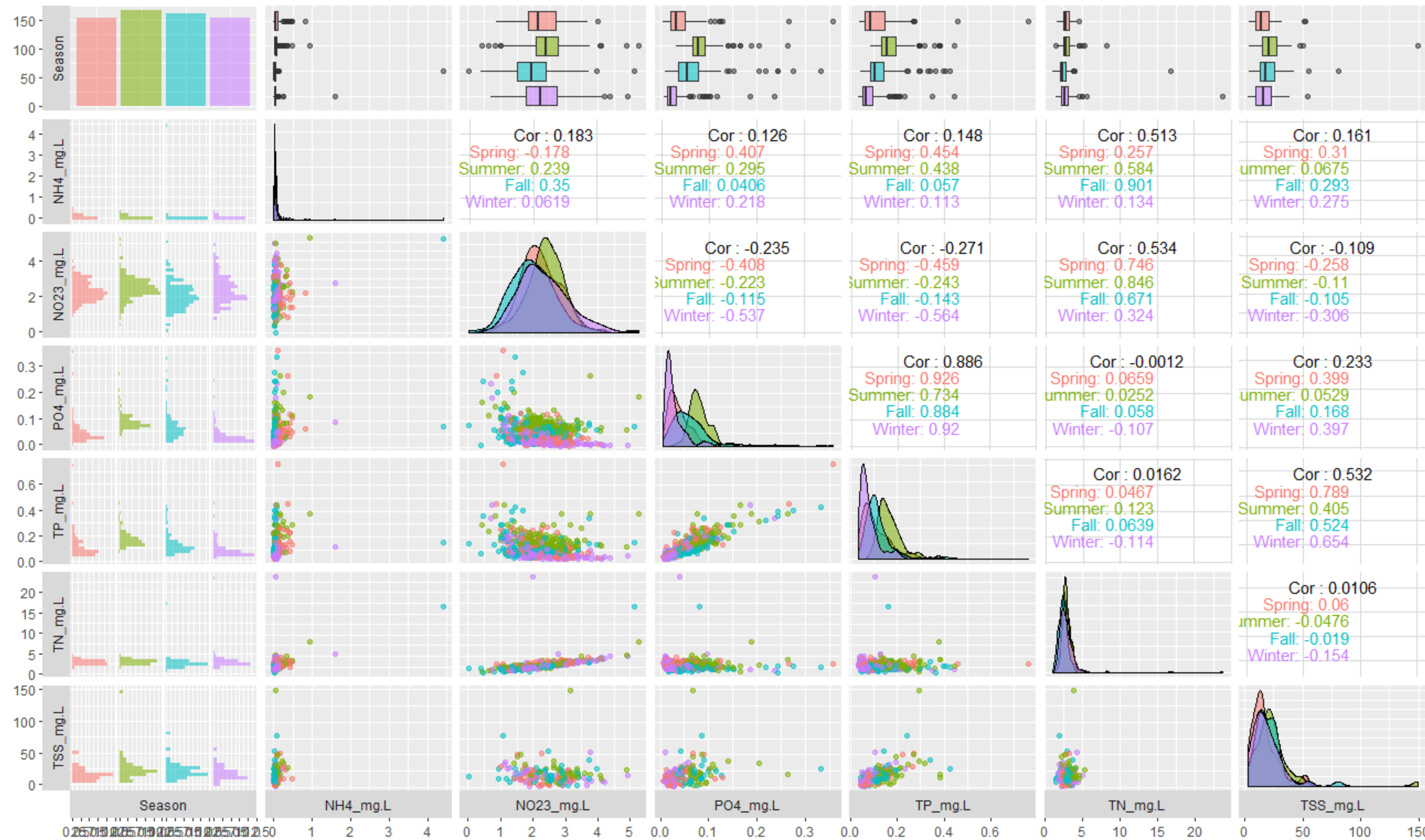

Figure 4. Distribution of nutrients concentration at the Three Bridges Branch (TBB) outlet. The figure shows correlation between the different water quality variables, and variation of nutrient concentrations across the four seasons.

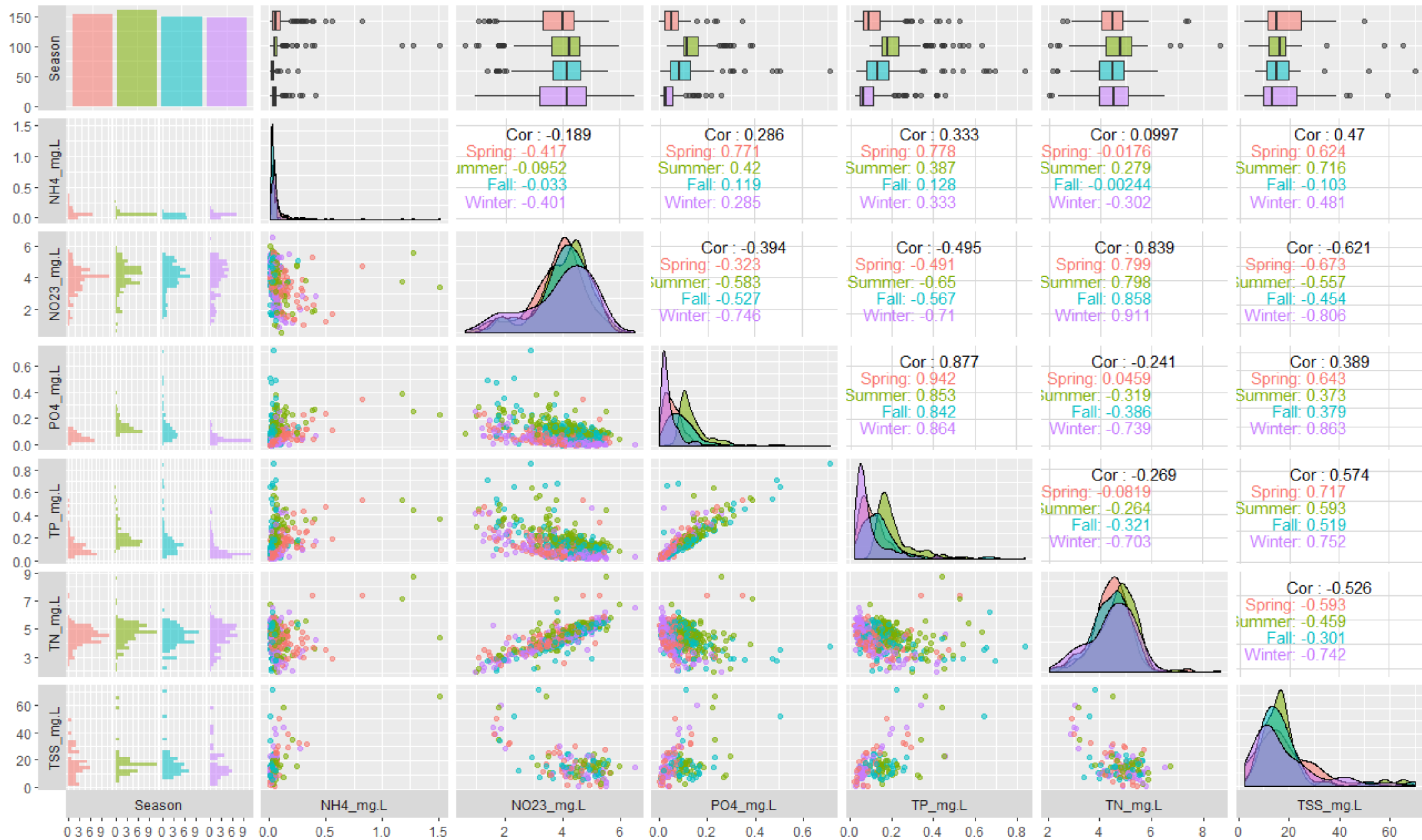

Figure 5. Distribution of nutrients concentration at the JB outlet. The figure shows correlation between the different water quality variables, and variation of nutrient concentrations across the four seasons.

The short-term and long-term trend results for TN and TP are provided below for the grab samples and the composite samples. Additionally, analyses of the synoptic data are also presented in this section. A brief description of each parameter's status in the most recent six-year (2012-2017) period (short-term) is provided to give the reader context. Results for each parameter are summarized by station in Tables 5 and 6. Trends with p-values less than 0.05 (significant trends) are indicated with ↓ (decreasing trend) and ↑ (increasing trend). P-values greater than or equal to 0.05 are considered non-significant (ns). A linear trend slope in the flow unadjusted data is given when the p-value supports the existence of a trend. There were no composite samples available for Jarman Branch (JB); therefore, no flow-adjusted trend was assessed for that station.

Table 5. Total nitrogen (TN) and total phosphorus (TP) trends: long-term (2006 - 2017); short-term (2012 - 2017); slope (mg/liter/year).

Monitoring Station	Data	Total Nitrogen (TN)				Total Phosphorus (TP)			
		Long-term		Short-term		Long-term		Short-term	
		trend	slope	trend	slope	trend	slope	trend	slope
Gravel Run	Not flow adjusted	ns	0.1100	ns	0.0150	↑	0.0066	↑	0.0056
	Flow-adjusted	↓	0.1558	↓	0.1820	↓	0.0357	↓	0.0252
Old Mill Stream	Not flow adjusted	ns	0.0000	↓	0.1350	↑	0.0010	ns	0.0020
	Flow-adjusted	↓	0.0980	↓	0.2555	↓	0.0276	ns	0.0171
Three Bridges Branch	Not flow adjusted	ns	0.0750	↓	0.0433	↑	0.0110	ns	0.0020
	Flow-adjusted	↓	0.1050	↓	0.0182	↓	0.0195	ns	0.0109
Jarman Branch	Not flow adjusted	↓	0.1850	↓	0.0250	ns	0.0070	ns	0.0035
	Flow-adjusted	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a

3.1 Trends in total nitrogen (TN) loss

In addition to the grab samples collected, composite sampling for TN began in May 2006 at all three of Corsica River's non-tidal subwatershed outlets and continues uninterrupted through June 2018. Within each season, there is no trend in the TN observations over time based on the seasonal Kendall test.

Nitrogen (N) *is a critical constituent of proteins and nucleic acids in all living organisms. It is an essential nutrient for growth in aquatic plants and algae. Excess N concentrations in aquatic environments—often from fertilizer runoff and wastewater discharges, but also from atmospheric deposition—can stimulate excess algal growth. Total nitrogen (TN) measures the N from all nitrogen forms. These include elemental nitrogen (N2), nitrite (NO2-), nitrate (NO3-) and the animal waste products ammonium (NH4+), urea, and uric acid. Excess NO3- and NO2- in drinking water can cause serious illness in infants (bluebaby syndrome).*

Maryland has a drinking water source criterion of 10 mg/liter for NO3- and 1.0 mg/liter for NO2

Not flow-adjusted trends: Based on grab sample analysis, long-term trends in TN concentrations are not significant for any of the three non-tidal tributaries to the Corsica River. However, there is a significant and downward trend at the JB monitoring station ($p<0.05$). For the short-term (2012-2017), trend in TN concentrations is significant and downward at all monitoring stations except for GVL where changes in concentration are not significant. Figures 6-9 show plots of TN concentration over time for the three Corsica River non-tidal tributaries. The LOESS curves reveal station differences in the relationship between TN concentration and time and shows the best fitted values within a 95% confidence interval.

Flow-adjusted trends: When measurements of TN concentrations are adjusted for flow (composite samples), both the long-term and short-term trends are significant and downwards for all three non-tidal tributaries to the Corsica River ($p<0.05$). Figures 10-12 show the trend in TN at the different monitoring stations, and the LOESS curves between TN concentrations and time. Shading delineates the 5 and 95 % confidence interval.

The reduction in TN concentrations at the watershed outlets might be directly attributable to increased BMP implementation efforts in the watershed. Nutrient reduction generally varies depending on which BMP is implemented. In the last six to seven years, 18 septic systems were retrofitted, each of which are estimated to reduce nitrogen output by 11 to 15 pounds. Some 742.3 acres of ag buffers were implemented in the short-term with a nitrogen removal efficiency of 16.92 pounds per acre per year for grass buffers and 27.28 pounds per acre per year for forested buffers. Approximately 2,130 acres of cover crops were implemented in the short-term with a nitrogen removal efficiency of 9.48 pounds per acre per year.

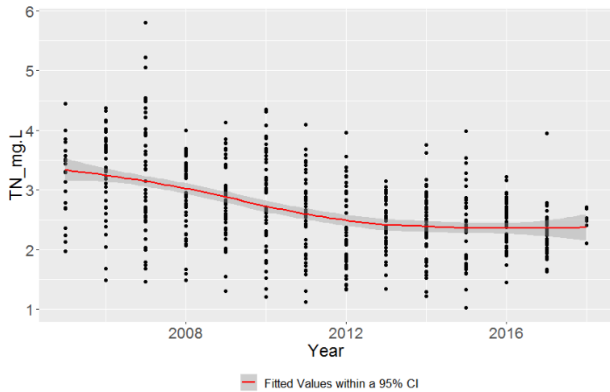

Figure 6. LOESS curve fitted to grab samples of total nitrogen (TN) concentration in Gravel Run (GVL).

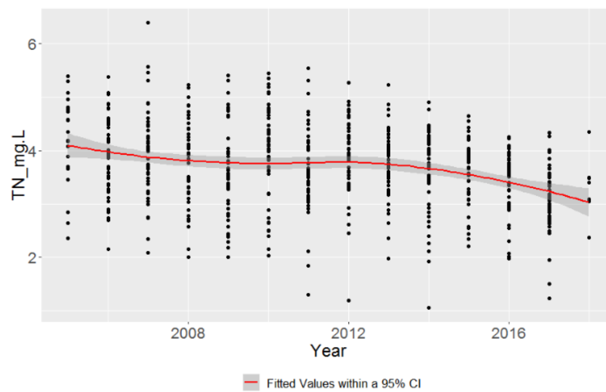

Figure 7. LOESS curve fitted to grab samples of total nitrogen (TN) concentration in Old Mill Stream (OMS).

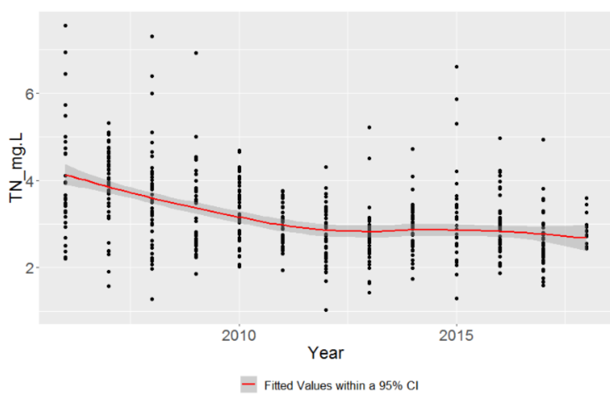

Figure 8. LOESS curve fitted to grab samples of total nitrogen (TN) concentration in Three Bridges Branch (TBB).

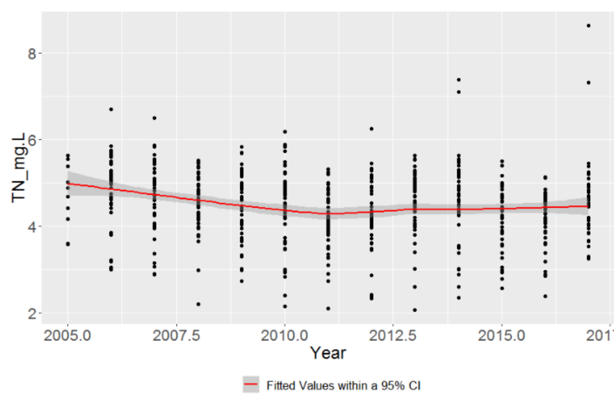

Figure 9. LOESS curve fitted to grab samples of total nitrogen (TN) concentration in Jarman Branch (JB).

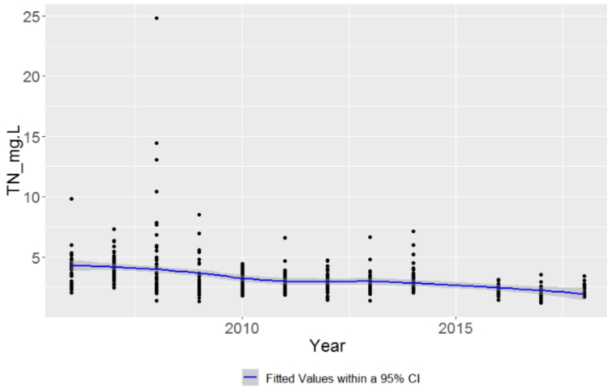

Figure 10. LOESS curve fitted to composite samples of total nitrogen (TN) concentration in Gravel Run (GVL).

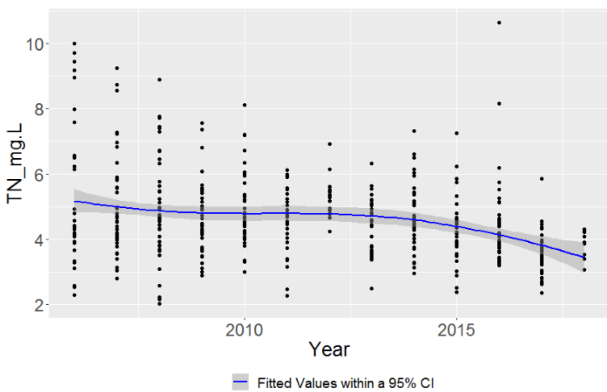

Figure 11. LOESS curve fitted to composite samples of total nitrogen (TN) concentration in Old Mill Stream (OMS).

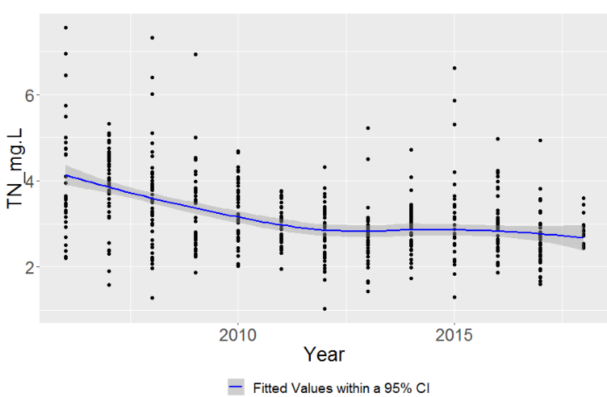

Figure 12. LOESS curve fitted to composite samples of total nitrogen (TN) concentration in Three Bridges Branch (TBB).

3.2. Trends in total phosphorus (TP) loss

In addition to the grab samples collected, composite sampling for total phosphorus (TP) began in May 2006 at all three Corsica River's non-tidal subwatershed outlets and continues uninterrupted through June 2018. TP monitoring (grab samples) also begins in July 2005 at the Jarman Branch (JB) outlet and continued through 2017. Trend results for TP are shown in Table 5.

Phosphorus (P) *is a highly reactive, non-metallic element and an essential nutrient for all living organisms. It is a key component of nucleic acids (DNA, RNA), adenosine triphosphate (ATP), and the phospholipids that form cellular membranes. Phosphate minerals are the most common form of P. Free orthophosphate (PO_4) is the "limiting nutrient" in many aquatic ecosystems because it is often the first nutrient to drop to levels that slow or limit plant growth. Aquatic plants have developed metabolic processes for absorbing and storing P for future use. Wastewater and fertilizers in runoff are the chief source of excess TP to aquatic systems.*

Not flow-adjusted trends: Based on analysis of the grab samples, long-term trends in TP concentrations are significant and upwards for all three non-tidal tributaries to the Corsica River ($p<0.05$). There are slight increases in TP over the short term (recent period) as well, however, only GVL shows significant upwards trend ($p<0.05$). There is no significant change in TP concentration at the JB outlet. Results for the Corsica River tributaries are also shown in Figures 13-16. The LOESS curves reveal station differences in the relationship between total phosphorus concentration and time and shows the best fitted values within a 95% confidence interval.

Flow-adjusted trends. When the data are adjusted for flow (composite samples), long-term trends in TP concentrations are significant and downwards for all three non-tidal tributaries to the Corsica River ($p<0.05$). There is no significant difference in TP concentrations for the short-term period except for GVL, where there is a significant downward trend (as shown in Table 5). Figures 17-19 show the trend in TP at the different monitoring stations, and the LOESS curves between TP concentration and time.

Reduction in TP concentration might be directly attributable to increased BMP implementation efforts in the watershed. While phosphorus reduction generally varies depending on which BMP is implemented, over the last six to seven years, 742.3 acres of agricultural buffers were installed in the watershed. It is estimated the phosphorus removal efficiency for grass buffers and forested buffers is 1.08 and 2.15 pounds per acre per year, respectively. Approximately 2,130 acres of cover crops were implemented in the last six to seven. The phosphorus removal efficiency is estimated to be 0.13 and 0.07 pounds per acre per year for cover crops and small grains, respectively. There was also one mile of stream restoration during the last six years as well.

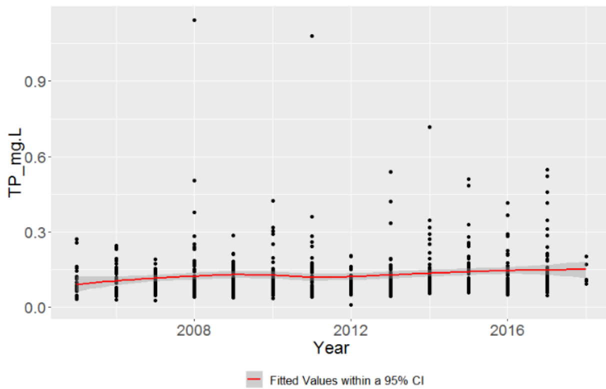

Figure 13. LOESS curve fitted to grab samples of total phosphorus (TP) concentration in Gravel Run (GVL).

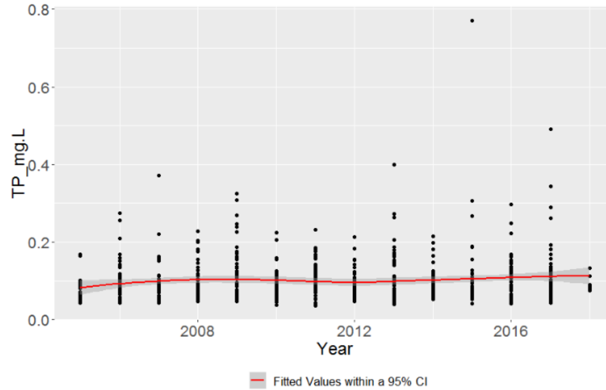

Figure 14. LOESS curve fitted to grab samples of total phosphorus (TP) concentration in Old Mill Stream (OMS).

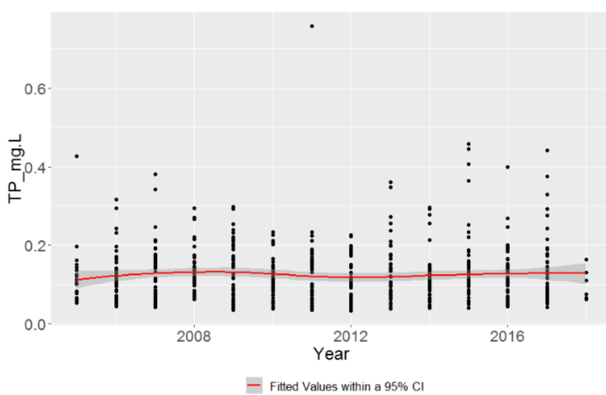

Figure 15. LOESS curve fitted to grab samples of total phosphorus (TP) concentration in Three Bridges Branch (TBB).

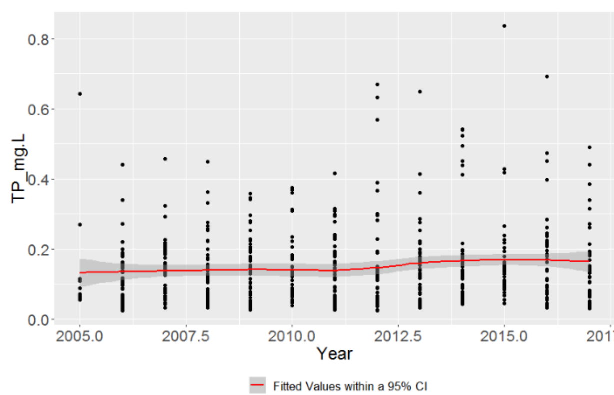

Figure 16. LOESS curve fitted to grab samples of total phosphorus (TP) concentration in Jarman Branch (JB).

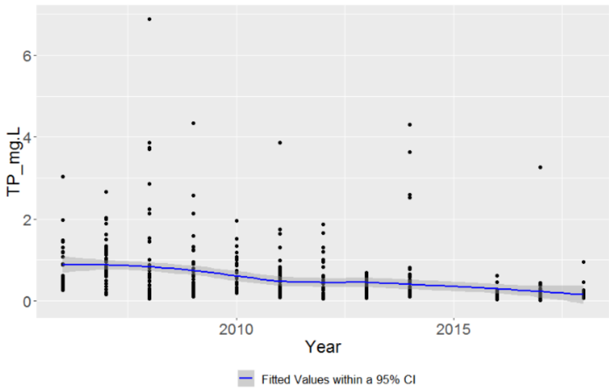

Figure 17. LOESS curve fitted to composite samples of total phosphorus (TP) concentration in Gravel Run (GVL) for the period 2006 to 2018.

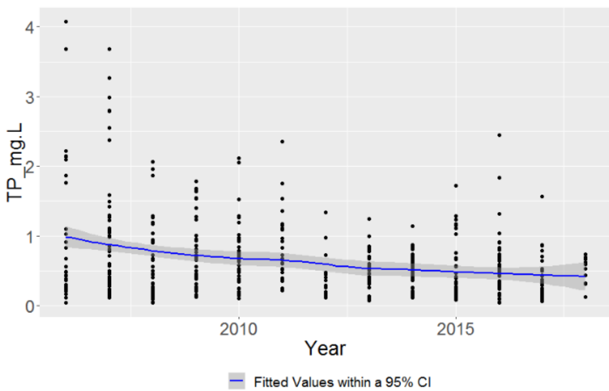

Figure 18. LOESS curve fitted to composite samples of total phosphorus (TP) concentration in Old Mill Stream (OMS) for the period 2006 to 2018.

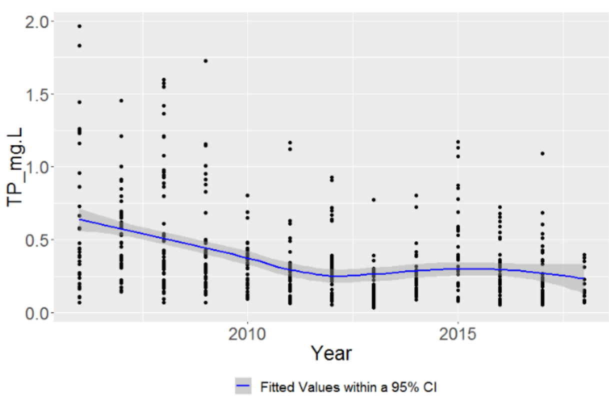

Figure 19. LOESS curve fitted to composite samples of total phosphorus (TP) concentration in Three Bridges Branch (TBB) for the period 2006 to 2018.

4. Conclusions

Monitoring at the three non-tidal stations in the Corsica River watershed is intended to provide information for long-term trend analyses, general water quality assessments, and pollutant loading calculations for the Corsica River. This report analyzed long-term (12-year) and short-term (6-year) trends in key water quality parameters and identified significant trends in those parameters. The short-term trends helped to explain the lack of long-term trends in some instances and confirm the trend directions in other instances. The MDE database has enormous potential to support correlative analysis and integrative assessments over different time periods. This study explored the data for key water quality parameters and examined only two of several possible trend periods.

The grab samples tend to be in general agreement with the composite samples for TN, they seem to diverge when it comes to TP. The values recorded for the composite samples are significantly larger than those of the grab samples for much of the data sets. However, the composite samples show a decreasing trend over time while the grab samples suggest an increase in TP for the three non-tidal tributaries. The synoptic surveys produce results like the grab samples and therefore do not adjust for flow. When data are not adjusted for flow, the time of sampling could significantly affect the recorded nutrient concentrations.

Total nitrogen concentrations in the Corsica River watershed appear to be on a significant downward trend. At two of the three non-tidal stations, there has been greater reduction in TN concentration over the last six years when compared to the long-term trend. Progress in overall TN concentration might be directly attributable to increased BMP implementation efforts in the watershed. Nutrient reduction generally varies depending on which BMP is implemented. For a more accurate representation of the impact of BMPs, the composite samples are acceptable because they account for the impact of flow and sampling time.

Long-term trends in total phosphorus concentrations are tending to decline, although OMS and TBB stations show no significant trends in the short-term (6 years). Short-term trends are non-significant more often than their long-term counterparts, suggesting that changes in TP concentrations are leveling off. Leveling off can be expected in some cases. Flow-adjustment indicates the 12-year trend period was long enough to overcome most of the flow-related variability that can mask short period (6-year) trend results, and the seasonal trend tests applied to the data accounted for seasonal variability. At individual stations, additional efforts to connect water quality trends with historic and recent changes in management actions and nearby land use patterns may help to explain why some of the short-term trends appear to be leveling off.

5. Possible Next Steps

Monitoring at the three non-tidal stations in the Corsica River watershed is intended to provide the MDE database with grab sample data for six water quality parameters (NH_4, NO23, PO_4, TN, TP and TSS). Only TN and TP were investigated in detail for this trend report because composite samples were only available for those two parameters. All parameters could be investigated further to determine their usefulness as potential baselines of past conditions and whether step-trend analyses would be possible if monitoring was reinstated.

Continued bi-weekly monitoring at the non-tidal stations could produce a more robust dataset that could be used to develop and calibrate watershed models. These watershed models could then be used to assess the effectiveness of different levels and types of BMP implementation. By continuing the monitoring program in the Corsica River watershed, MDE would be able to expand the long-term and short-term (recent) trend analysis, which would significantly enhance the monitoring program's capacity to explain the impact of the BMP implementation programs. A review of the station locations should indicate their potential value to the program's current objectives.

Integrative assessments of individual sites are perhaps the most intriguing use of the water quality data. Causal relationships and responses to management action can be investigated using the monitoring data in conjunction with geospatial (GIS) data layers. Additional, site-specific analysis of land and water uses, geology, and soils at sites least affected and most affected by agricultural activities could substantiate that concept and point to effective best management practices.

Appendix: Synoptic Samples

Maps showing the distribution of nitrate-nitrite (NO23), TN, PO_4 and TP concentrations across the Corsica River watershed from 2012 to 2017 (spring and fall for each calendar year).

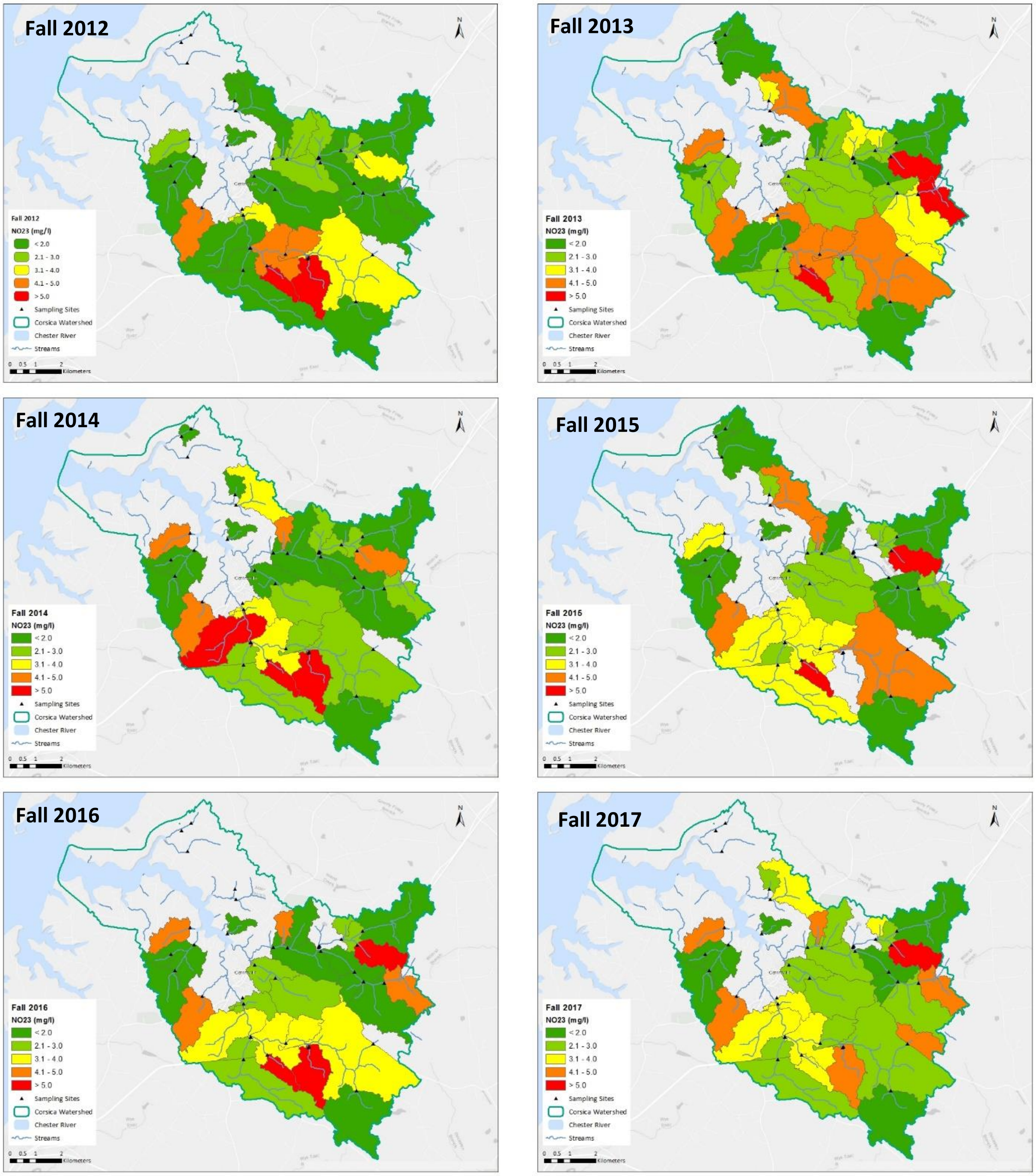

Figure A1. Concentrations of dissolved inorganic nitrogen (NO23) in the Corsica River watershed.

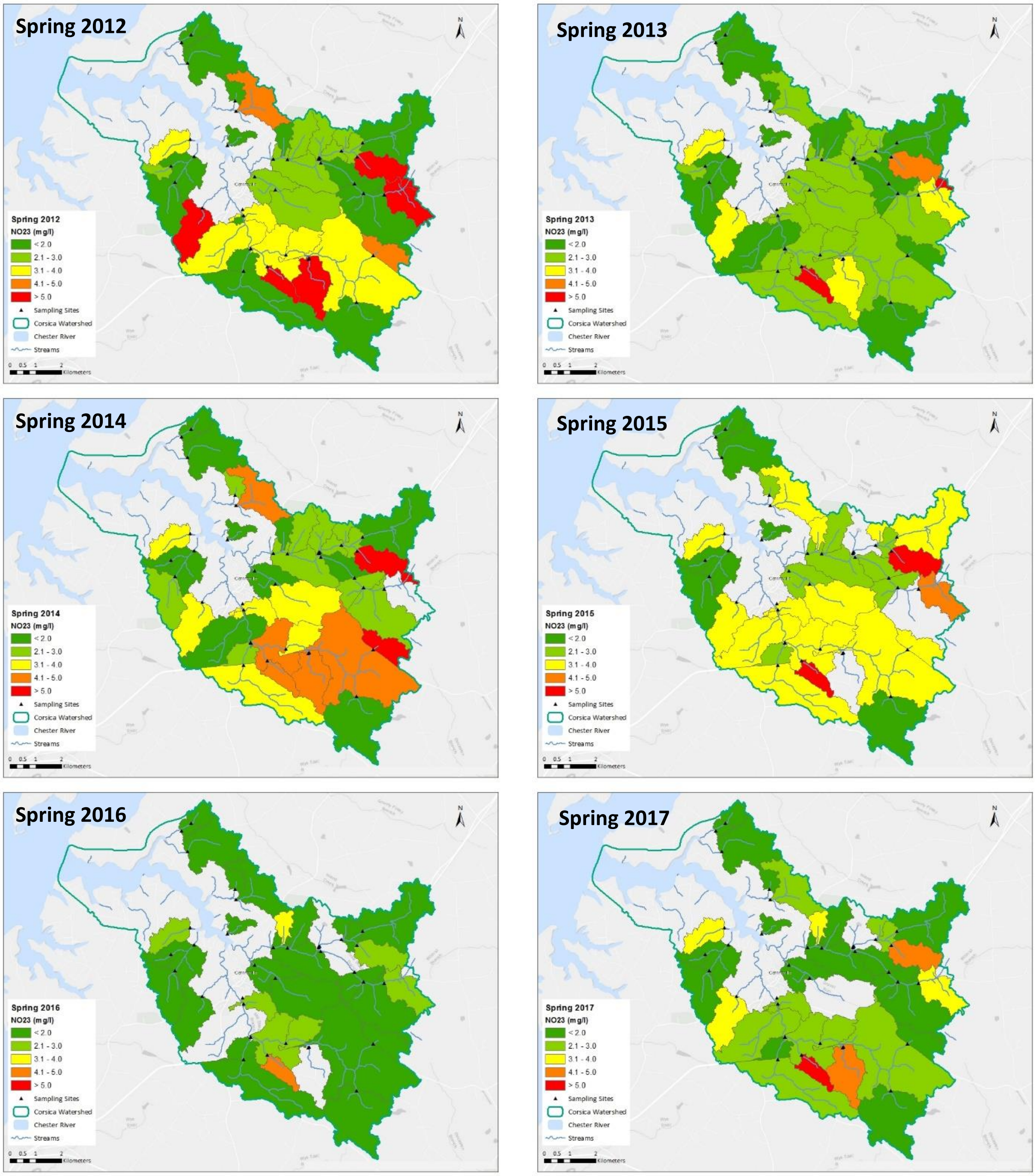

Figure A2. Concentrations of dissolved inorganic nitrogen (NO23) in the Corsica River watershed for spring 2012 to spring 2017.

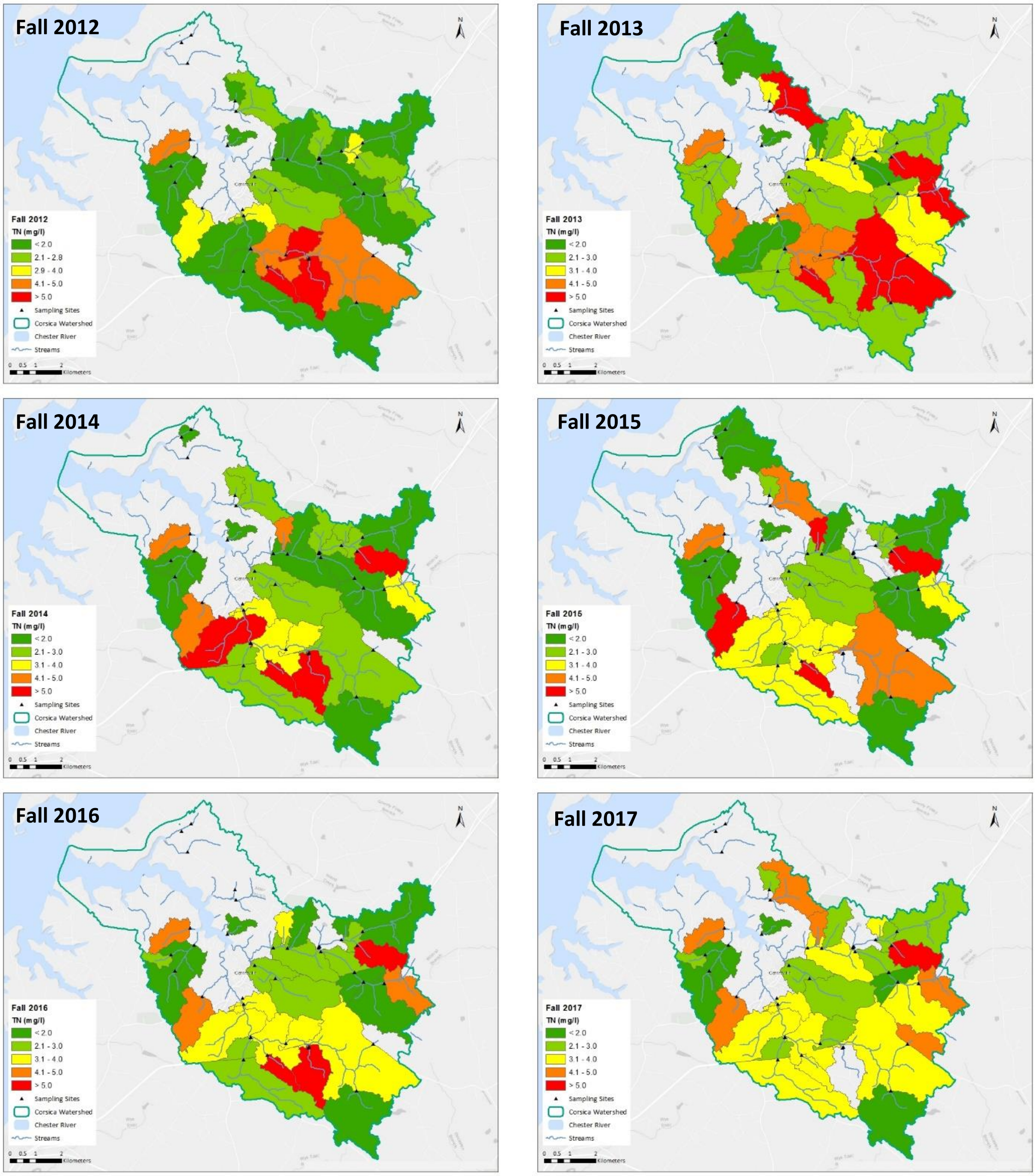

Figure A3. Concentrations of total nitrogen (TN) in the Corsica River watershed for fall 2012 to fall 2017.

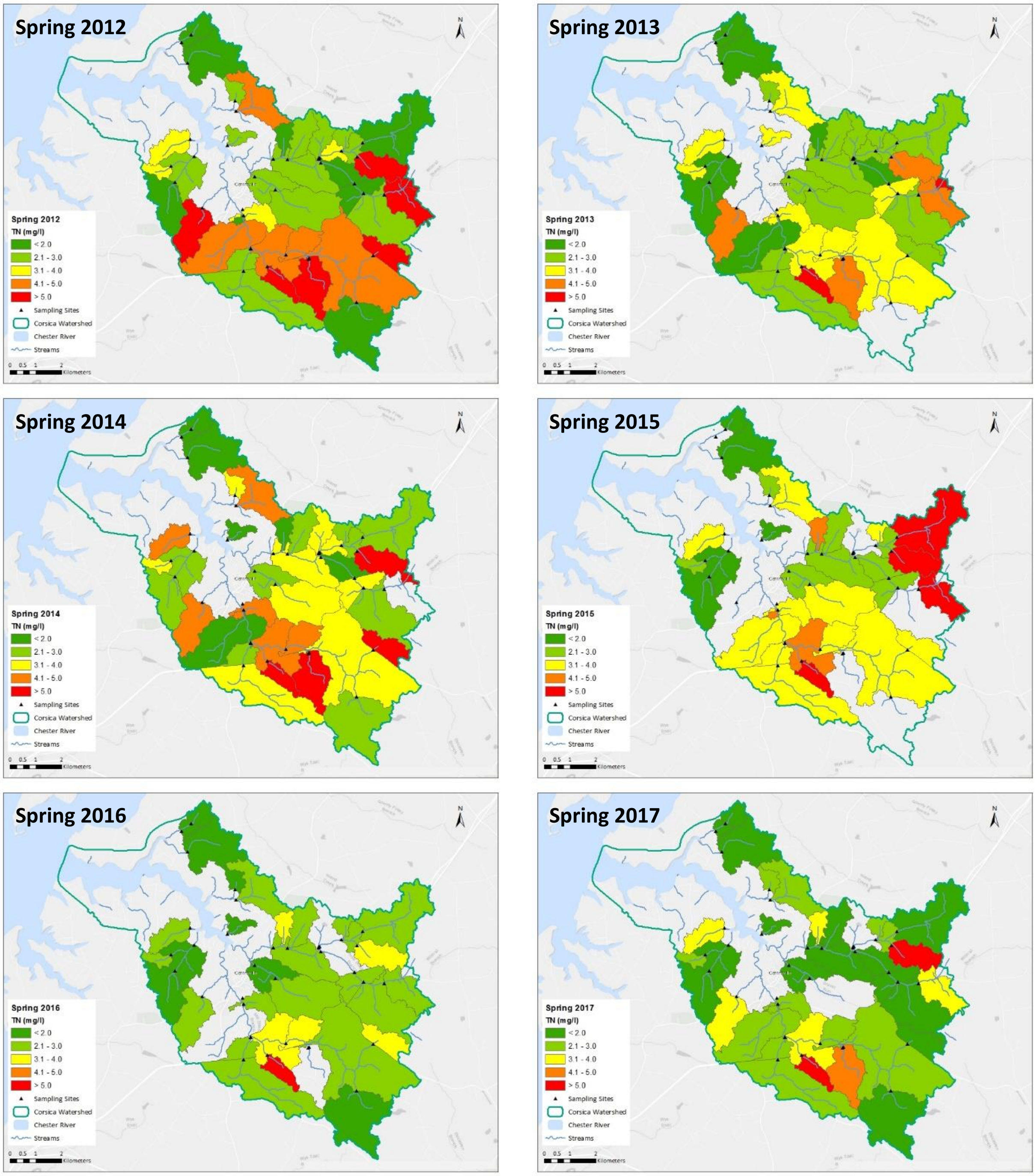

Figure A4. Concentrations of total nitrogen (TN) in the Corsica River watershed for spring 2012 to spring 2017.

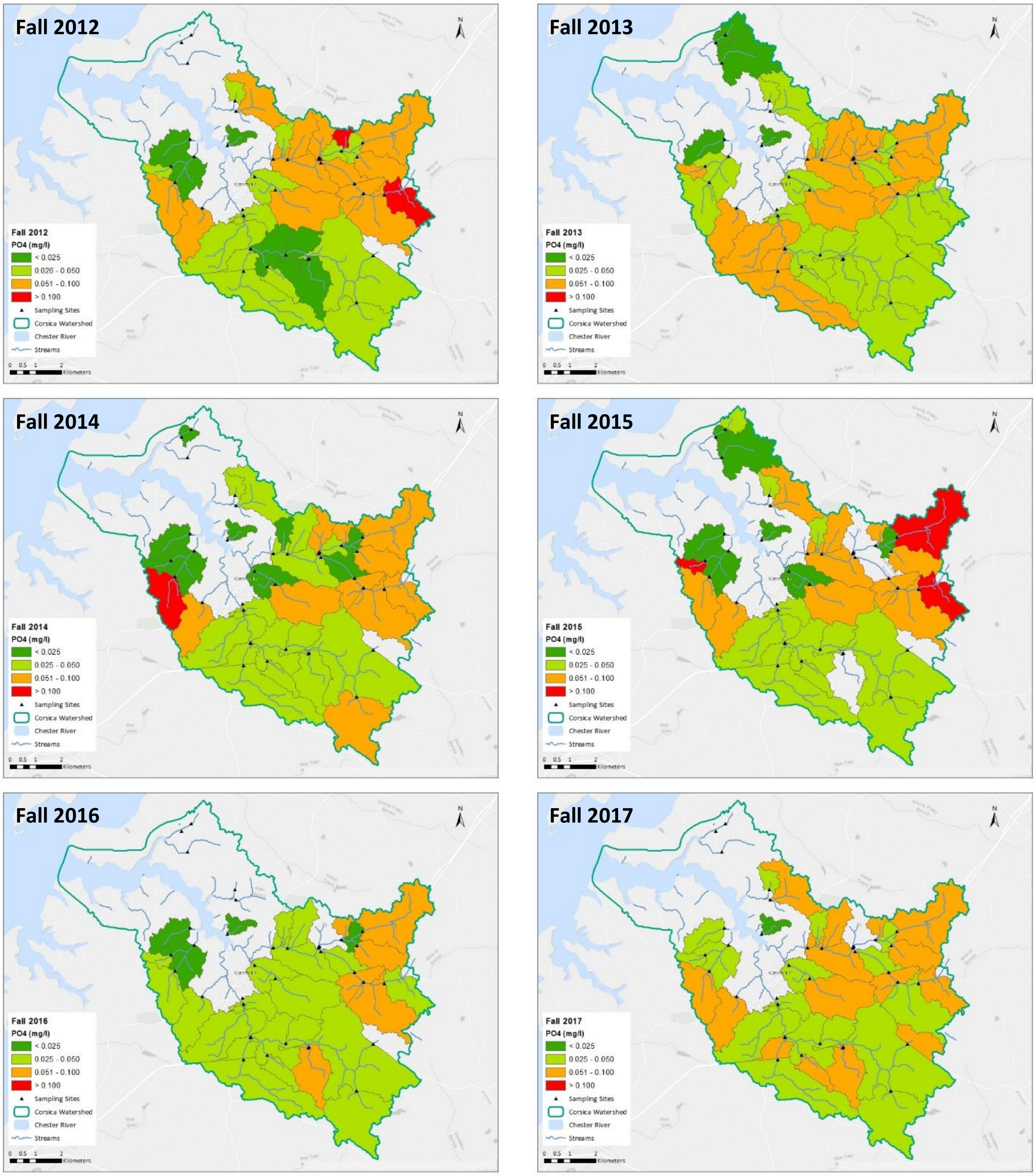

Figure A5. Concentrations of dissolved inorganic phosphorus (PO_4) in the Corsica River watershed for fall 2012 to fall 2017.

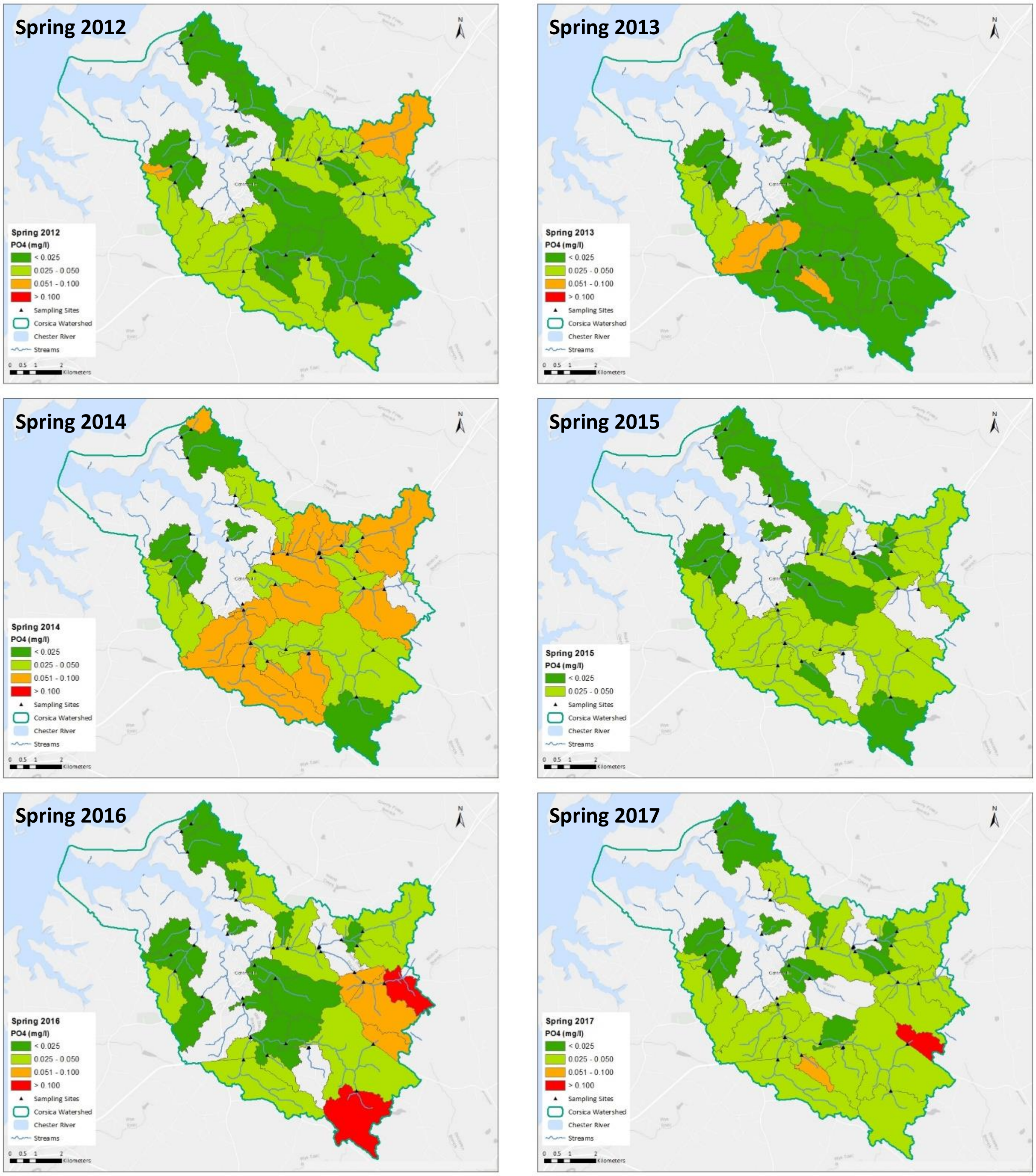

Figure A6. Concentrations of dissolved inorganic phosphorus (PO_4) in the Corsica River watershed for spring2012 to spring 2017.

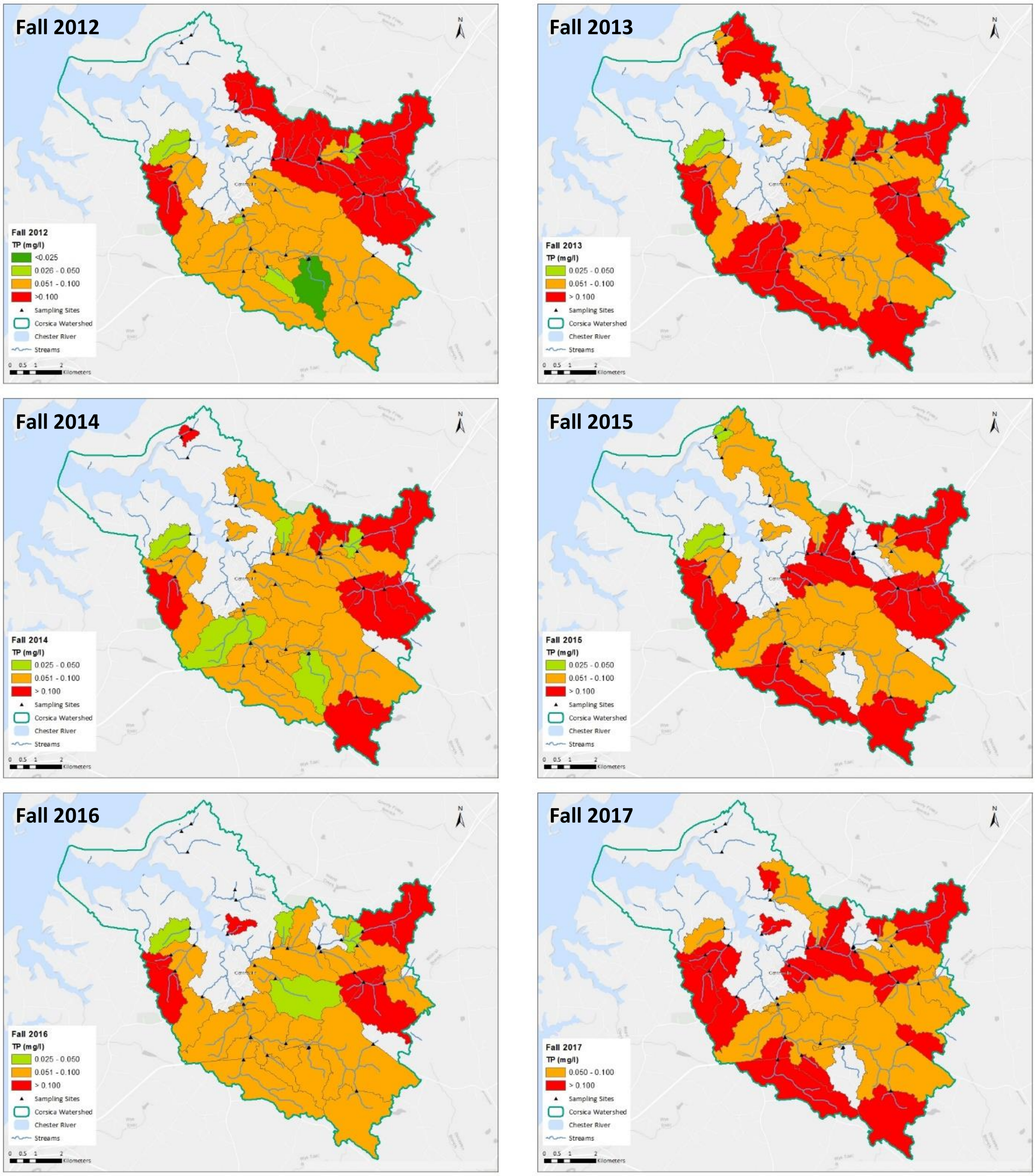

Figure A7. Concentrations of total phosphorus (TP) in the Corsica River watershed for fall 2012 to fall 2017.

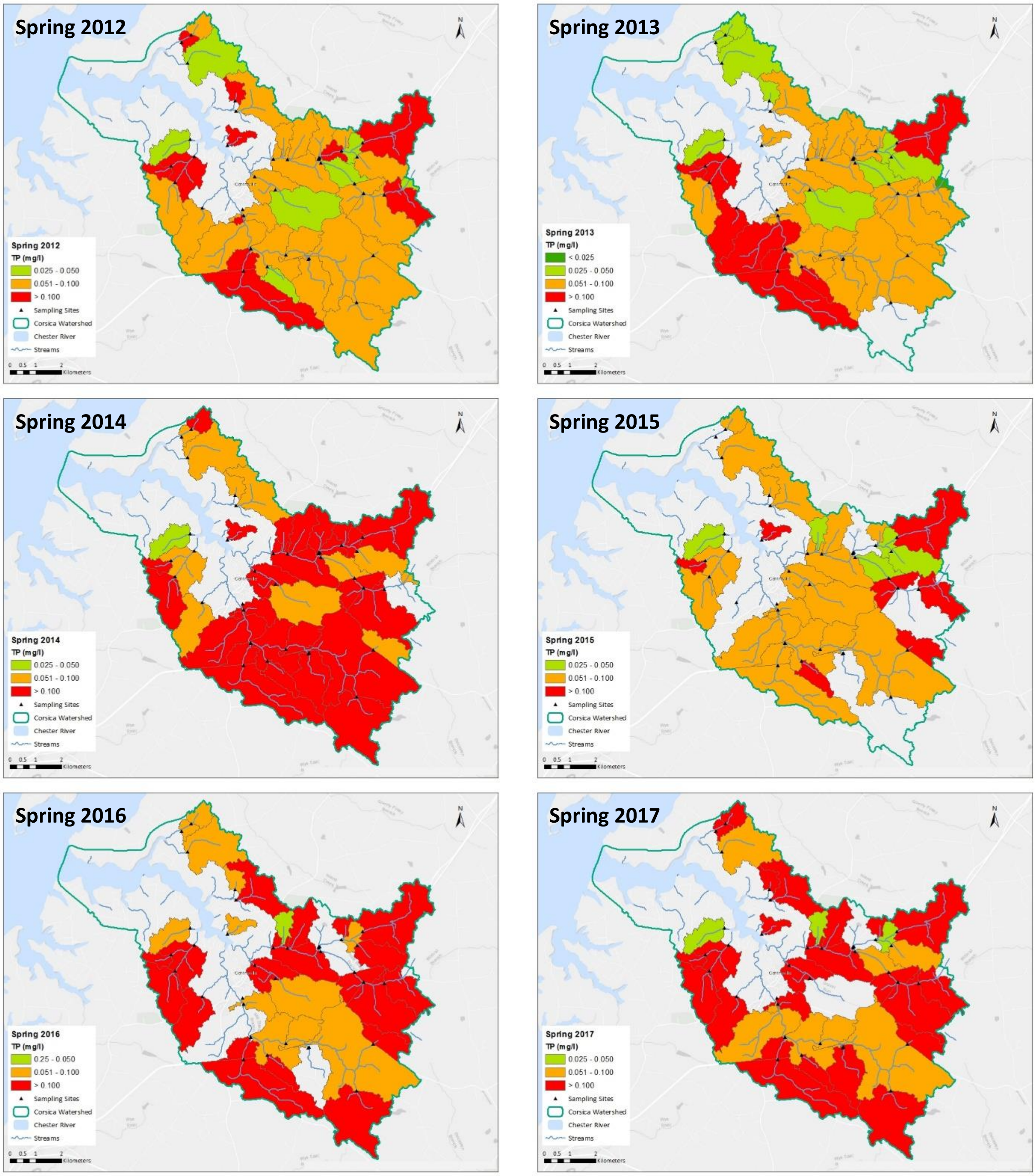

Figure A8. Concentrations of total phosphorus (TP) in the Corsica River watershed for spring 2012 to spring 2017.