Introduction

Water quality is one of the ten Environmental Values defined in the State Water Resource Implementation Rule for consideration when establishing minimum flows. This chapter provides an overview of trends for water quality parameters measured in the Upper Peace River, including exploratory evaluations of water quality and flow relationships. The inclusion of any information pertaining to adopted water quality standards in this chapter is for informational purposes only and not intended to be a determination of impairment by the District.

Minimum Flows and Water Quality Criteria

Water quality is an environmental value affected by flows, water quality criteria in the State of Florida are regulated independently from minimum flows and levels (MFLs). Together, MFLs and water quality regulations address both the quality and quantity of water to ensure sustainable ecosystems and human use. As water quality criteria, Total Maximum Daily Loads (TMDLs) and Numeric Nutrient Criteria (NNC) are designed to control water quality by managing pollutant levels, such as nutrients and sediments, to prevent issues like algal blooms and habitat degradation. On the other hand, Minimum Flows and Levels focus on maintaining the quantity of water in rivers, lakes, and aquifers to ensure that there is enough water to support ecological functions, maintain habitats, and sustain wildlife populations. While TMDLs and NNC aim to reduce pollutant loads through various management actions, MFLs are used in water use permitting and water supply planning to prevent significant harm to water bodies. MFLs, TMDLS, and NNC combine to protect both the quality and quantity of water in Florida's aquatic ecosystems.

Total Maximum Daily Loads and Numeric Nutrient Criteria focus on controlling the quality of water by managing pollutant levels, while Minimum Flows and Levels are concerned with the quantity of water to ensure ecological health. They are distinct in the following ways:

Focus and Purpose

- **TMDLs and NNC** are designed to address water quality issues by setting limits on pollutants such as nutrients, sediments, and other contaminants. These measures aim to reduce pollutant loads to meet water quality standards and prevent issues like algal blooms and habitat degradation.
- **MFLs** are established to protect water bodies from significant harm due to water withdrawals. They ensure that there is enough water to support ecological functions, maintain habitats, and sustain wildlife populations.

Regulatory Framework

- **TMDLs and NNC** are Implemented under section 303(d) of the Clean Water Act and 62-302 and 62-304 Florida Administrative Code (F.A.C.).
- **MFLs** are established under 373.042 F.A.C. and focus on maintaining minimum water levels and flows to prevent ecological damage specifically due to water withdrawals.

Management Actions

- **TMDLs and NNC** lead to actions like upgrading wastewater treatment plants, implementing best management practices in agriculture, and reducing stormwater runoff.
- **MFLs** lead to regulating water withdrawals, managing water use permits, and implementing water conservation measures.

Interconnected but Separate

While TMDLs and NNC focus on improving water quality, MFLs ensure that water quantity is sufficient to support ecological health. Both are crucial for comprehensive water resource management but address different aspects of water sustainability.

Study Area

The waters of the Upper Peace River originate in two tributaries that are its headwaters: Saddle Creek with headwaters at the P-11 structure and Peace Creek (Figure 1).

On Saddle Creek, the P-11 Structure is owned and operated by the District and regulates flows out of Lake Hancock and serves as the location of the P-11 streamflow gage (Figure 2). In addition, the Wetland Outfall is also a District Structure that contributes flows to Saddle Creek from the Lake Hancock Wetland (Figure 1).

On Peace Creek, the Peace Creek Wahneta streamflow gage acts as the upper boundary for this analysis and reports flow data for analysis with water quality parameters. The Peace River Zolfo Springs streamflow gage is the downstream boundary of the study area. These three gages form the upstream and downstream boundaries of the study area. There are ten total United States Geological Survey (USGS) streamflow gages which provide data on the Upper Peace River and its two tributaries included in this study (Figure 1) (Table 1).

Water Body IDs and Impairment

The Florida Department of Environmental Protection (DEP) has designated seven Water Body IDs (WBIDs) overlapping the streams within the study area: 1539, 1623K,1623J, 1623I, 1623H, 1623G, and 1623F (Figure 1) (Table 2). These WBIDs are useful for accessing water quality data from repositories, because those data are typically organized and accessed by WBID. Impairments are listed here as background information (FDEP 2024).

The NNC for total nitrogen (Total Nitrogen) in all WBIDs of the Upper Peace River is an annual geometric mean of 1.65 mg/L. The NNC for total phosphorus (total phosphorus) in all WBIDs of the Upper Peace River is an annual geometric mean of 0.49 mg/L.

Impaired water quality parameters may be one or more lists. The term "303(d) list" is the list of impaired or threatened waters that do not meet state water quality standards. The Clean Water Act Section 303(d) requires states to submit their list for EPA approval every two years (on even numbered years). A waterbody is placed on the Verified List because one or more water quality parameters do not meet applicable water quality criteria, which indicates that the waterbody does not fully support its designated use. A previously Verified Listed waterbody segment may be proposed for removal from the Verified List, which is termed delisted. In general, waterbodies are delisted because they have either been shown to now attain the applicable standard(s) or a restoration plan has been adopted. A parameter by be delisted because it has a restoration plan, including a TMDL, yet still remain on the 303(d) list while it does not meet state water quality standards. A waterbody is placed on the Study List because one or more water quality parameters do not meet applicable water quality criteria, which indicates that the waterbody does not fully support its designated use; however, additional data or information is needed to determine attainment of the designated use.

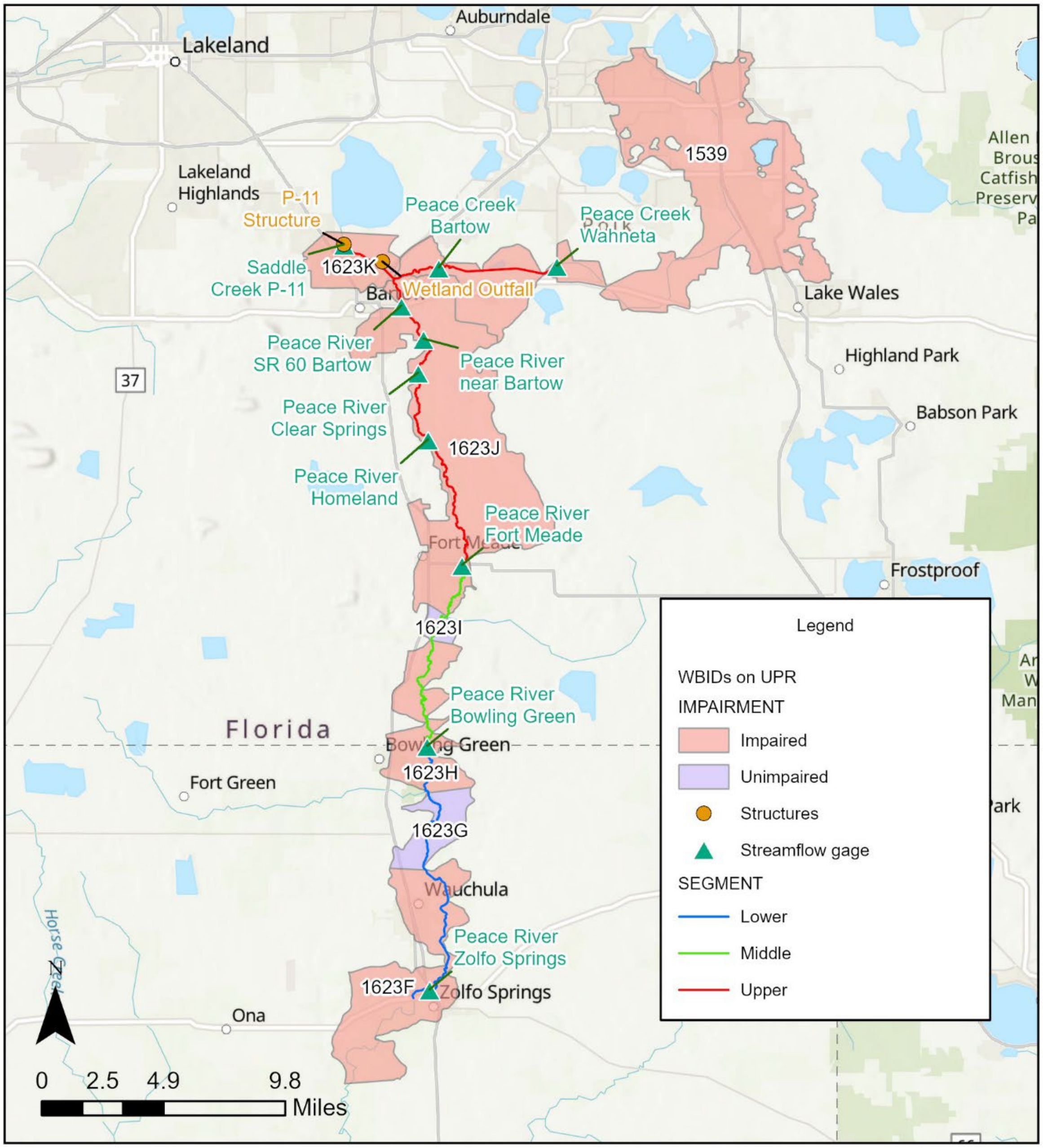

Figure 1. Overview of the Upper Peace River Study Area with USGS streamflow gages, water control structures, and WBIDs.

Figure 2. P-11 structure on Saddle Creek. View from downstream on right bank.

Table 1. Streamflow gages

Number	Long Name	Lat	Lon	Start	End	n
02293987	PEACE CREEK WAHNETA	27.92475	-81.7267	1991-03-01	2022-12-31	11629
02294161	PEACE CREEK BARTOW	27.92444	-81.7956	2005-07-08	2022-12-31	6386
02294491	SADDLE CREEK P-11 (USGS)	27.93788	-81.8507	1963-12-01	2022-12-31	18989
02294650	PEACE RIVER SR 60 BARTOW	27.90225	-81.8173	1939-10-01	2022-12-31	30408
02294655	PEACE RIVER NEAR BARTOW	27.88306	-81.8044	2002-05-15	2022-12-31	7533
02294775	PEACE RIVER CLEAR SPRINGS	27.86333	-81.8075	2002-05-15	2022-12-31	7536
02294781	PEACE RIVER HOMELAND	27.82447	-81.8017	2001-10-01	2022-12-31	7762
02294898	PEACE RIVER FORT MEADE	27.75142	-81.782	1974-06-01	2022-12-31	17746
02295194	PEACE RIVER BOWLING GREEN	27.64614	-81.8023	2010-12-01	2022-12-31	4414
02295637	PEACE RIVER ZOLFO SPRINGS	27.50452	-81.8002	1933-09-01	2022-12-31	32629

Table 2. WBIDs with impaired water quality parameters. Status based on Cycle 6, the 2022–2024 Biennial Assessment (BA).

WBID	Impairment parameter	Status notes
1539	Biology	Failed bioassessments. Study List and the 303(d) List because a causative pollutant has not been identified.
	E. coli	On Verified List and the 303(d) List.
	Fecal Coliform	State Adopted and EPA Approved TMDLs (FDEP 2007a)
1623K	Chlorophyll-a	On 303(d) list and Study List because ongoing restoration activities to address the nutrient impairment documented in the Saddle Creek Pollutant Reduction Plan.
	Total Nitrogen	
	Dissolved Oxygen (Percent Saturation)	Included in the Saddle Creek Pollutant Reduction Plan.
	Fecal Coliform	On 303(d) and Verified List. Impaired based on the previous assessment but is no longer the applicable bacteria parameter for this waterbody classification. Escherichia coli will be included in the FDEP Strategic Monitoring Plan for this waterbody in order to collect the new applicable bacteria parameter.
1623J	Fecal Coliform	State Adopted and EPA Approved TMDLs (FDEP 2007b)
	Total Phosphorus	On Verified List and the 303(d) List.
	Total Nitrogen	On Verified List and the 303(d) List.
	Macrophytes	On Verified List and the 303(d) List.
	Chlorophyll a	This waterbody is impaired for this parameter because the annual geometric means exceed the threshold of 3.2 µg/L but were below 20 µg/L more than once in a three year period and nutrients exceed the threshold. This parameter is being removed from the Verified List, but will added to the Study List and will remain on the 303(d) List.
1623H	Total Phosphorus	On 303(d) list and added to Study List based on insufficient supporting biological data.
	Total Nitrogen	On 303(d) list and added to Study List based on insufficient supporting biological data.
	Chlorophyll a	This waterbody is impaired for this parameter because the annual geometric means exceed the threshold of 3.2 µg/L but were below 20 µg/L more than once in a three year period and nutrients exceed the threshold. This parameter will remain on the Study List and the 303(d) List.
1623F	Total Phosphorus	Study List and the 303(d) List based on insufficient supporting biological data.
	Chlorophyll a	This waterbody is impaired for this parameter because the annual geometric means exceed the threshold of 3.2 µg/L but were below 20 µg/L more than once in a three year period and nutrients exceed the threshold. This parameter is being added to the Study List and the department is requesting EPA add it to the 303(d) List.

Methods of Data Exploration and Analysis

The following steps of exploratory data analysis are described for the National Nonpoint Source Monitoring Program of the EPA and used here as a guide for data analysis (Meals and Dressing 2005):

1. **Data decision** refers to design of a monitoring program. For this analysis, this step includes the process of identifying available data.
2. **Data conception/elaboration** determines data collection procedures.
3. **Data input** procedures ensure accuracy and integrity of a dataset. For this analysis, the import of data from public repositories is considered part of the input process.
4. **Data management** creates and organizes files.
5. **One-dimensional analysis** summarizes data one variable at a time.
6. **Two-dimensional analysis** explores relationships between variables.

The application of exploratory data analysis steps 1-4 is explained in detail below and addresses issues raised for exploring data by Meals and Dressing (2005). One-dimensional and two-dimensional analysis makes up the bulk of the rest of this report, and follows methods described in Helsel and Hirsch (2002).

Data Decision

The analysis presented here makes use of existing data collected as parts of other monitoring programs, as described below

Flow data are collected by the USGS and co-funded in some cases by the District. These data are collected and used for various purposes, and are critical to development of minimum flows.

Likewise, the District Water Quality Monitoring Program (WQMP) performs water quality sampling, data management and analysis, and report writing for several long-term ground and surface water monitoring efforts designed to assess water resource quality. This report makes use of surface water data that was collected as quarterly grab samples as part of this long-term data collection program.

Water quality data was also collected as monthly grab samples by the Peace River Monitoring Program (PRMP) as part of a settlement agreement between Mosaic Fertilizer, LLC (Mosaic), the Sierra Club, Manasota-88, and the People for Protecting the Peace River. The PRMP began in 2012 to ensure that impacts from mining activities at Mosaic's South Fort Meade-Hardee County (SFM-HC) mine are having no significant adverse effects on water quality or biological communities in the Peace River between Fort Meade and Wauchula, FL.

These and other data are imported and stored in publicly accessible repositories. Import and selection of target data from these repositories is described below.

Data Conception/Elaboration

This step typically describes procedures for collecting the data. Data collection procedures were chosen by the individual monitoring programs from which the data comes. The PRMP data sampling and preservation followed FDEP's Standard Operating Procedures (SOPs) for all samples and events (FDEP FS-2000 and FT-1000). The WQMP data collection follows District SOPs (SWFWMD 2020). Data collection procedures for USGS streamflow gages are described for individual gages by USGS at their National Water Information System: Web Interface (USGS 2024).

Data Input/Compilation

The three water quality data repositories surveyed for data are:

1. The Environmental Data Portal (EDP) [https://www.swfwmd.state.fl.us/resources/data-maps/environmental-data-portal]
2. The Watershed Information Network Advanced View & Extraction System (WIN WAVES) [https://prodenv.dep.state.fl.us/DearWin/public/wavesSearchFilter?calledBy=menu]
3. STORET Public Access (SPA) [https://prodenv.dep.state.fl.us/DearSpa/public/searchStoretPI.action]

Water quality parameters are given different names by different collecting agencies at different times, and there is some variation in naming within and among repositories. Parameter names were standardized in this analysis according to Table 3.

Table 3. Parameter names and units used in this analysis

Parameter	Units
Chlorophyll-a	µg/L
Color	PCU
Dissolved Oxygen	mg/L
Fluoride	mg/L
Nitrate + Nitrite	mg/L
Orthophosphate	mg/L
pH	SU
Potassium	mg/L
Specific Conductance	µS/cm
Total Kjeldahl Nitrogen	mg/L
Total Nitrogen	mg/L
Total Phosphorus	mg/L
Total Suspended Solids	mg/L
Turbidity	NTU
Water Temperature	^oC

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Data Management

Water Quality Data Management

The primary data management steps involved in this water quality analysis are data merging and aggregation from other sources. Data from the EDP, WIN, and STORET were combined and filtered. A minimum of 20 data collection events was used as a pre-screening value to narrow down sites with enough data for long-term analysis. There are 17 total site locations where data were collected on at least 20 events (Table 4) (Figure 3). December 31, 2022 was selected as the end date to standardize inclusion of data at all sites in this analysis. Two sites, Peace Rvr10 and Peace Rvr78 were collected by Polk County and have older data stored in STORET and newer data stored in WIN. These were combined prior to analysis. In addition, there are instances where WQMP data is stored in both District EDP, WIN, and STORET. In these cases, WIN and STORET data were prioritized for use.

Of the 17 total sites with at least 20 data collection events, 9 primary sites have the most robust data records and can be apportioned evenly into the three main segments of the Upper Peace River (Table 5). Five WQMP sites have the most data with over 200 sampling dates and over 20 years of data: Peace River at Zolfo Springs (Zolfo Springs), Peace River at Fort Meade WQMP (Ft. Meade), Peace River at Bartow (Bartow), Peace Creek Canal nr Wahneta (Peace Creek), and Saddle Creek at P-11 (Saddle Creek) (Table 5). In addition, four PRMP sites, Peace River at County Line Rd. (Co. Line Rd.), Peace River at Mt. Pisgah Rd. (Mt. Pisgah), Peace River At Heard

Bridge Rd. (Heard Bridge), and Peace River at E. Main Street (E. Main St.) have data from at least 129 dates spanning over 10 years (Cardno 2020) (Table 5). These sites are also evenly divided into three major segments of the river (Figure 4). The analysis presented here will focus on these nine water quality sites.

Table 4. Water quality stations in compiled dataset. Site = unique station identification name or number, Creator = data collecting agency that originally reported the data, Events = number of sampling events, Parameters = number of parameters across all events, Start = First date of data collection, End = last data of data collection. December 31, 2022 was the last date for inclusion of data in this analysis.

Site	Creator	Events	Parameters	Start	End
Peace River at Zolfo Springs	WQMP	310	21	1997-08-04	2022-12-05
Peace River at Fort Meade WQMP	WQMP	290	21	1997-08-04	2022-12-05
Peace River at Bartow	WQMP	290	21	1997-08-04	2022-12-05
Peace Creek Canal nr Wahneta	WQMP	286	21	1997-08-04	2022-12-05
Saddle Creek at P-11	WQMP	211	12	2002-10-01	2022-12-05
Peace River at County Line Rd.	PRMP	154	16	2012-04-16	2022-12-12
Peace River at Heard Bridge Rd.	PRMP	129	16	2012-04-16	2022-12-12
Peace River at E. Main Street	PRMP	129	16	2012-04-16	2022-12-12
Peace River at Mt. Pisgah Rd.	PRMP	129	16	2012-04-16	2022-12-12
Peace River at Fort Meade PRMP	PRMP	123	16	2012-04-16	2022-09-19
Peace Rvr10	Polk Co.	107	16	1993-02-11	2022-11-08
Saddle Crk9	Polk Co.	60	14	1993-02-11	2022-11-03
Peace Rvr78	Polk Co.	52	16	2010-03-24	2022-11-09
Peace Rvr1	Polk Co.	43	14	1994-12-01	2009-08-19
27384668148080	FDEP	36	5	2003-02-12	2013-12-18
25020039	FDEP	28	17	1998-03-10	2008-12-01
Pc Canal8 - 91 Mine	Polk Co.	22	15	2017-07-25	2022-11-08

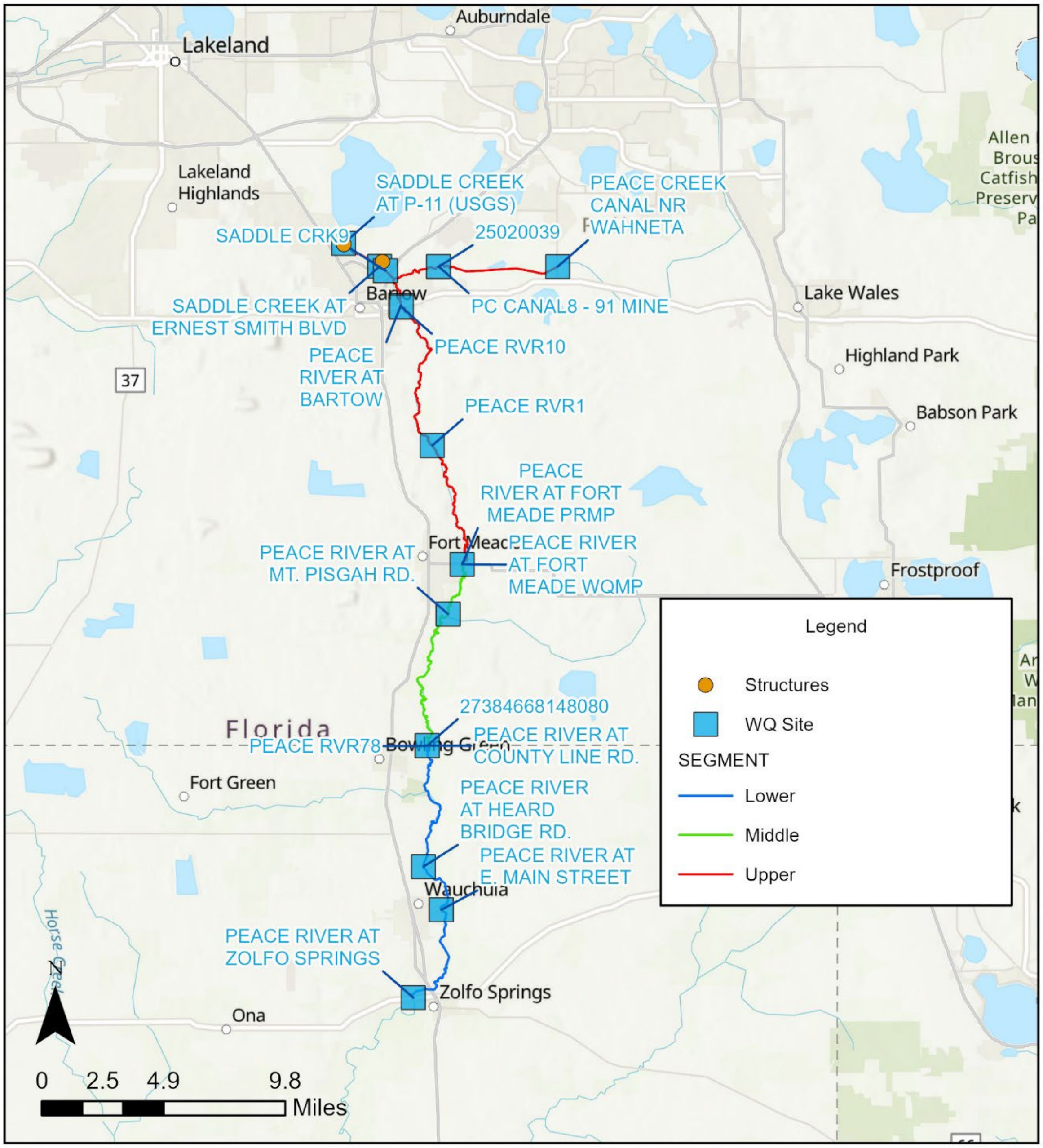

Figure 3. Water quality site locations with at least 20 sampling events.

Table 5. Nine select water quality data sites

Station	Obs	Params	Start	End	Latitude	Longitude	Segment
Saddle Creek	257	20	1997-08-04	2022-12-05	27.9385	-81.8510	Upper
Peace Creek	286	19	1997-08-04	2022-12-05	27.9250	-81.7263	Upper
Bartow	290	19	1997-08-04	2022-12-05	27.9024	-81.8176	Upper
Ft. Meade	290	19	1997-08-04	2022-12-05	27.7517	-81.7819	Middle
Mt. Pisgah	129	16	2012-04-16	2022-12-12	27.7228	-81.7901	Middle
Co. Line Rd.	154	16	2012-04-16	2022-12-12	27.6463	-81.8022	Middle
Heard Bridge	129	16	2012-04-16	2022-12-12	27.5759	-81.8045	Lower
E. Main St.	129	16	2012-04-16	2022-12-12	27.5508	-81.7941	Lower
Zolfo Springs	310	19	1997-08-04	2022-12-05	27.4997	-81.8104	Lower

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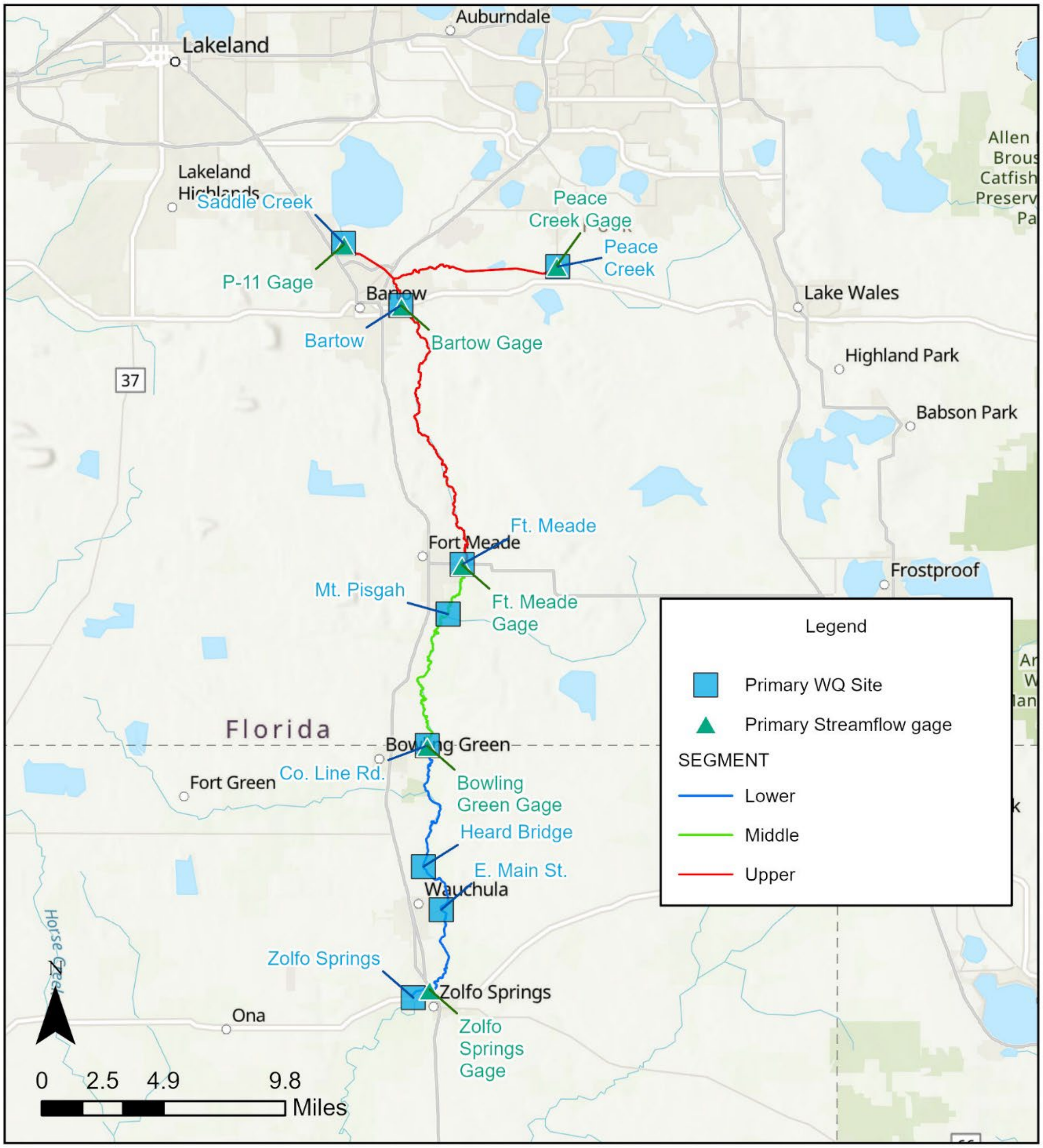


Figure 4. Nine primary water quality sites and seven stream flow gages used in flow analysis.

Flow Data Management

Flow data were compiled from two repositories:

1. USGS National Water Information System (NWIS) [https://waterdata.usgs.gov/nwis]
2. District estimates of discharge at the P-11 structure

There are 10 sites with starting dates between September 1, 1933 and December 1, 2010 (Table 2). All data were truncated at December 31, 2022. Water quality data were paired with flow data at the nearest collocated or upstream streamflow gage (Table 6).

Table 6. Flow and Water Quality site pairings

WQ Station Short Name	Streamflow Gage Long Name	Streamflow Gage Short Name	River Segment
Saddle Creek	Saddle Creek at P-11 (USGS)	P11 Gage	Upper
Peace Creek	Peace Creek Canal nr Wahneta	Peace Creek Gage	Upper
Bartow	Peace River SR 60 Bartow	Bartow Gage	Upper
Ft. Meade	Peace River Fort Meade	Ft. Meade Gage	Middle
Mt. Pisgah	Peace River Fort Meade	Ft. Meade Gage	Middle
Co. Line Rd.	Peace River Bowling Green	Bowling Green Gage	Middle
Heard Bridge	Peace River Bowling Green	Bowling Green Gage	Lower
E. Main St.	Peace River Bowling Green	Bowling Green Gage	Lower
Zolfo Springs	Peace River at Zolfo Springs	Zolfo Springs Gage	Lower

Development of Flow-Based Seasons

The Zolfo Springs gage was chosen as the reference gage for distinction between wet and dry seasons so that seasons could be consistent across all gages and WQ sites. The mean annual flow for each date was calculated. The start of the wet season begins when the mean annual flow rises above the 60^{th} percentile (P60) and the wet season ends when the flow drops below the P60 (Figure 5). These seasons are used to test for effect of season on water quality parameters as a comparison of groups. By adjusting parameter values for flow with Loess regressions, we have accounted for seasonal differences in flow.

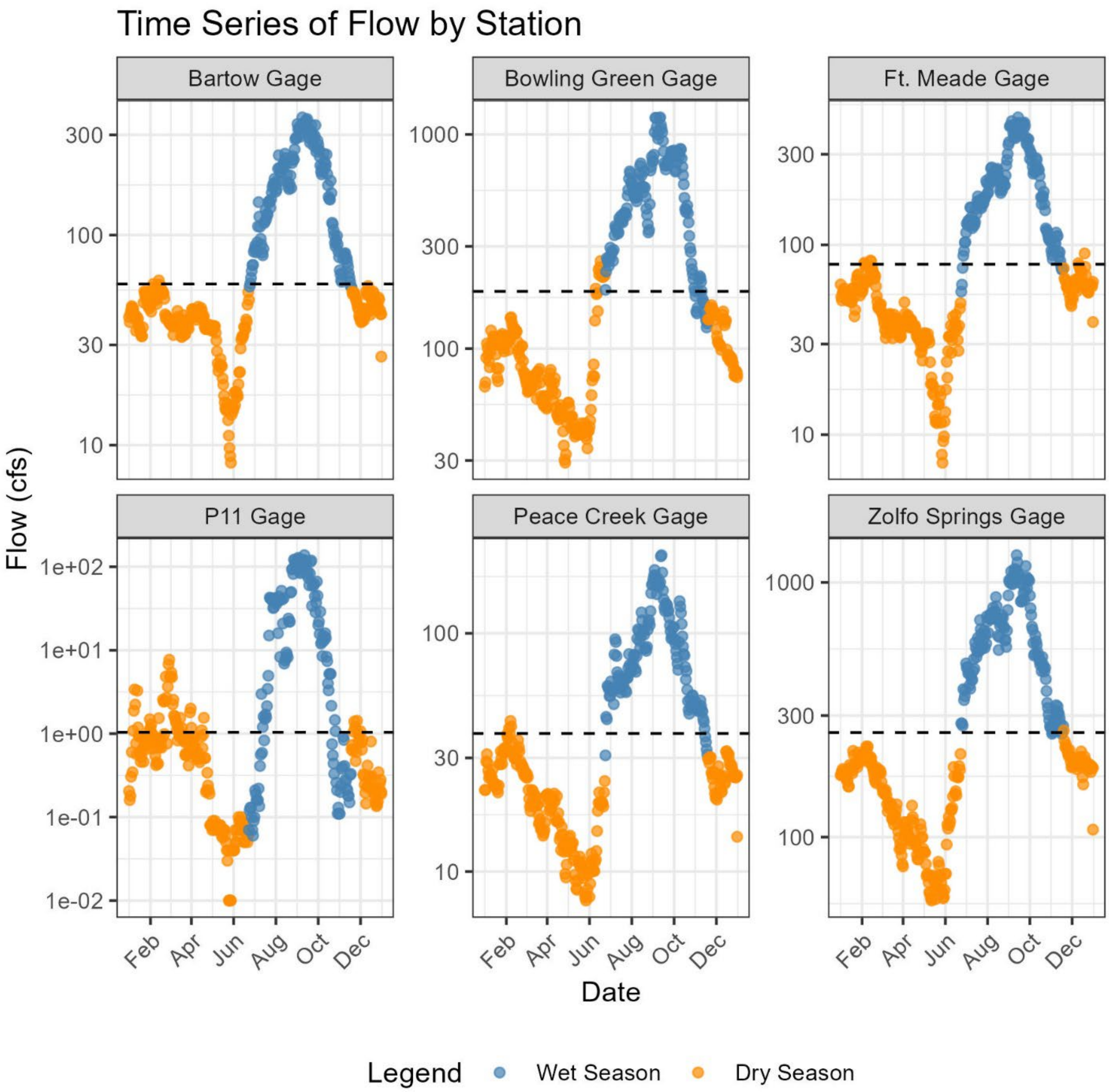


Figure 5. Flow-Based Seasons at six streamflow gaging sites. Dashed line is P60 at each gage, which differs from the P60 at Zolfo Springs Gage.

Water Quality Data Characteristics

Water quality data are typically non-normal, are positively skewed with outliers occurring in the positive direction toward large numbers, and have a lower bound of zero (Helsel and Hirsch 2002). The location, or central tendency of the data can be measured with the mean or median. However, the mean is sensitive to large outliers, where the effect of individual observations on the mean is proportional to the distance from the observation to the mean. On the other hand, the median is insensitive to outliers, and is a better measure of location for these data, as it gives us a better measure of the typical concentration one might expect to see on a random collection event.

The interquartile range (IQR), is a measure of spread or variation in the data that is resistant to outliers because it is the range of the middle 50% of the data. The skewness coefficient (G) is the adjusted third moment divided by the cube of the standard deviation, and is a measure of skewness that is sensitive to outliers (Helsel and Hirsch 2002). The quartile skew coefficient (QS) uses only the middle 50% of the data and quantifies skewness as the difference in distances of the upper and lower quartiles from the median, divided by the IQR for a resistant measure of skewness. Both of these measures quantify a right-skewed distribution with a positive value and a left-skewed distribution with a negative value.

Nutrients: Nitrogen and Phosphorus

Nitrogen and phosphorus are the two primary nutrients required by plants for growth, used in fertilizers, and responsible for eutrophication of natural waters. Both nitrogen and phosphorus are elements, and can be found as constituents of various molecules and as part of both organic and inorganic material in the air, waters, geologic substrate, sediments, and as part of living organisms. Nitrogen is available for uptake by plants, algae, and phytoplankton primarily as nitrate and ammonium. Organic nitrogen is linked to complex carbon-based organic groups and can be changed into ammonium, then into nitrates, by microorganisms. Total nitrogen is the sum of Total Kjeldahl Nitrogen, which consists of organic and reduced nitrogen, plus nitrate, nitrite, and ammonium. Phosphorus is most commonly found as the bioavailable orthophosphate (PO_4^{3-}), condensed phosphates (like pyrophosphate and polyphosphate), and organic phosphorus. Parameters included in this analysis were chosen for their ubiquity in monitoring programs: Total Nitrogen, Nitrate-Nitrite, Orthophosphate, and Total Phosphorus.

Location, spread, and normality

Means and medians across all sites for key nutrient statistics including orthophosphate, nitrate-nitrite, total nitrogen, and total phosphorus are shown in Table 7. Quantile plots illustrate distributions of nutrient data (Figure 6). These are plotted on a log scale due to right skewness and overdispersion. Even after log transformation, orthophosphate and total nitrogen have long nearly horizontal sections near the top of the curves, indicative of values outside a normal distribution. Boxplots (Figure 7) provide visual summaries of 1) the center of the data (the median--the center line of the box), 2) the variation or spread (interquartile range--the box height), 3) the skewness (quartile skew--the relative size of box halves), and 4) presence or absence of unusual values ("outside" – lines, and "far outside" values - circles). The data are displayed on a log scale due to the wide range of concentrations.

Comparing nutrient sampling distributions, we see that total nitrogen is the most skewed with the highest skewness coefficient (G) and quartile skew coefficient (QS) (Table 7). nitrate-nitrite is also positively skewed. total phosphorus and orthophosphate are positively skewed when considering all data indicated by the positive skewness coefficient (G), but negatively skewed within the middle 50% indicated by the negative QS. Histograms provide an alternative method of visualizing differences in shape or symmetry of data, such as whether a data set appears symmetric or skewed (Figure 8) (Helsel and Hirsch 2002).

Total nitrogen is the sum of all nitrogen forms including ammonia and nitrate-nitrite, and also includes organic nitrogen (not included as a standard analyte, but calculated as Total Kjeldahl Nitrogen minus ammonia). Therefore, total nitrogen has larger concentrations than nitrate-nitrite considered alone. Orthophosphate makes up the majority of phosphorus present, such that while total phosphorus values are greater than orthophosphate values, the difference is not as large as the difference between nitrate-nitrite and total nitrogen.

Probability plots of log-transformed data illustrate how well data fit a lognormal distribution (Figure 9). Normal quantiles are the data values expected based on a normal distribution with the same mean and standard deviation as the sample data. The probability plot correlation coefficient (PPCC) tests for normality by computing the linear correlation coefficient between data and their normal quantiles (Helsel and Hirsch 2002). Samples from a normal distribution will have a correlation coefficient very close to 1.0. As data depart from normality, their correlation coefficient will decrease below 1. The critical correlation value corresponds to the value the correlation coefficient must exceed for the data to be considered normally distributed. All parameters are non-normal according to the PPCC as well as Anderson-Darling test for normality after Log10 transformation of data (Table 8).

Table 7. Univariate summary statistics for nutrients at all sites. The interquartile range (IQR) = P75 – P25. The skewness coefficient (G) is the adjusted third moment divided by the cube of the standard deviation, and is a measure of skewness that is sensitive to outliers (Helsel and Hirsch 2002). The quartile skew coefficient (QS) quantifies skewness as the difference in distances of the upper and lower quartiles from the median, divided by the IQR for a resistant measure of skewness.

Parameter	Min	P25	P50	Mean	P75	Max	Obs	G	IQR	QS
Nitrate-Nitrite	0.001	0.122	0.33	0.406	0.604	2.787	1821	1.388	0.482	0.137
Total Nitrogen	0.156	1.301	1.628	2.026	2.093	21.2	1086	4.99	0.792	0.174
Orthophosphate	0.005	0.308	0.627	0.647	0.848	3.92	1597	1.754	0.54	-0.181

Total Phosphorus	0.085	0.386	0.746	0.766	0.986	3.99	1823	1.675	0.6	-0.2

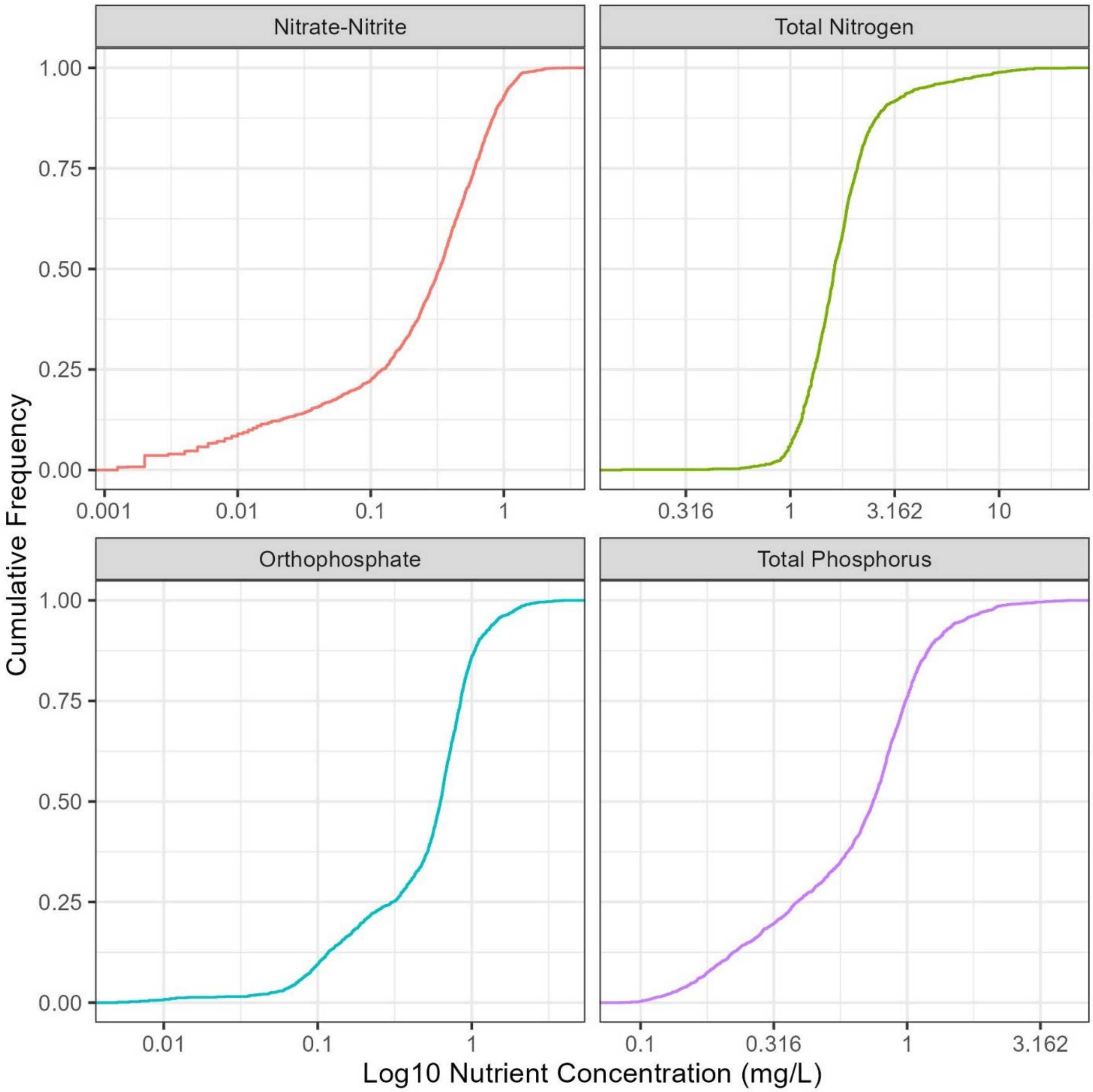


Figure 6. Quantiles of Log10 transformed nutrient concentrations. Quantile plots visually portray the quantiles, or cumulative frequency of observations of nutrient concentrations. Quantiles of importance such as the median are easily discerned (quantile, or cumulative frequency = 0.5) (Helsel and Hirsch 2002).

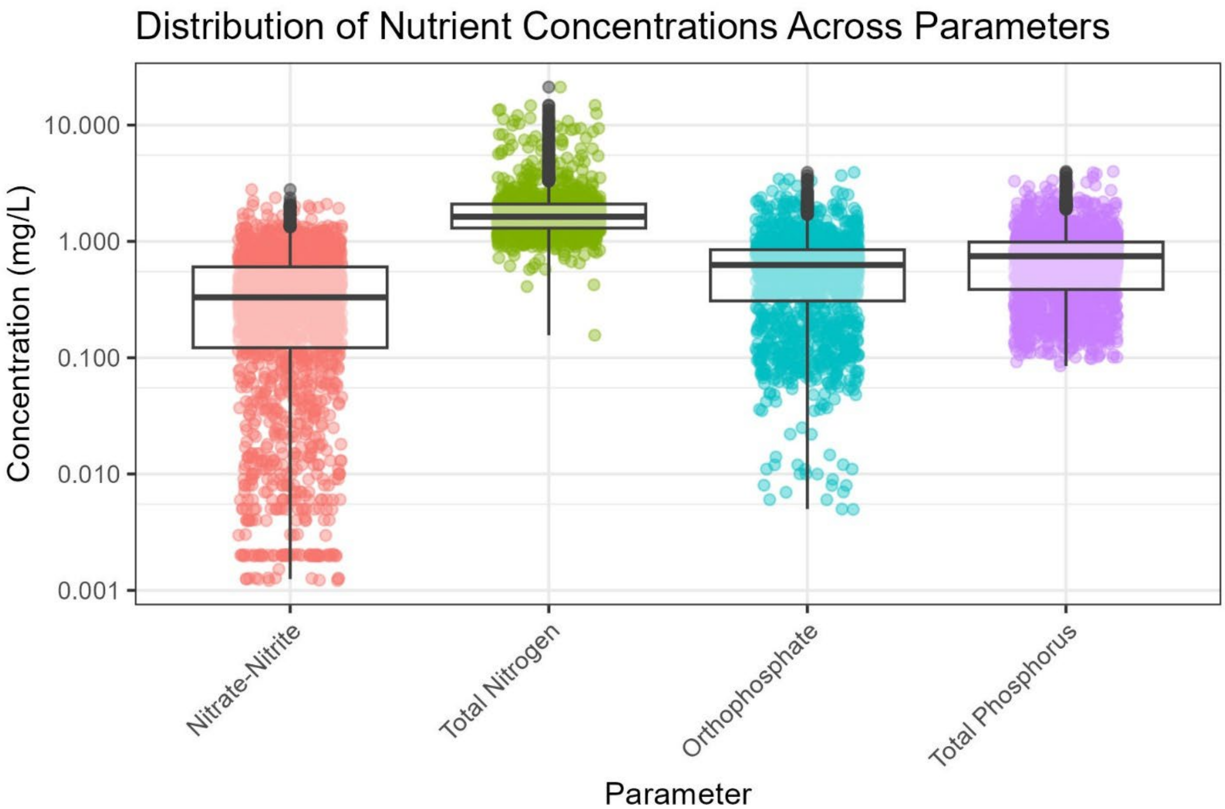


Figure 7. Concentrations of four key nutrients (nitrate-nitrite, total phosphorus, orthophosphate, and total nitrogen) using jittered points to display individual data values and boxplots to summarize the distribution. The y-axis is scaled logarithmically to better visualize the range of concentrations, and boxplot statistics are calculated on non-transformed data.

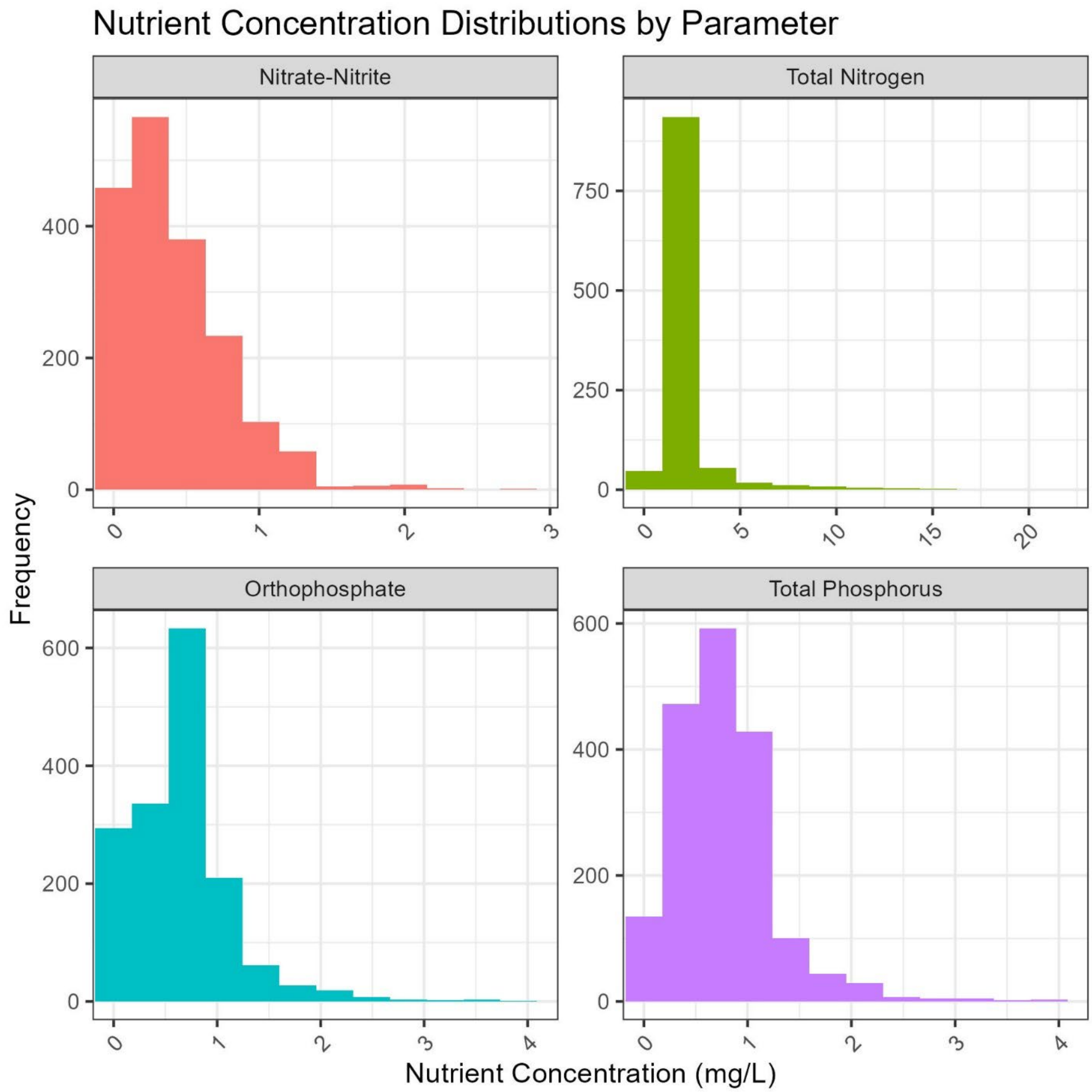


Figure 8. Frequency distributions of nutrient concentrations (nitrate-nitrite, total phosphorus, orthophosphate, and total nitrogen). Each panel represents a specific nutrient, with the x-axis showing concentrations (in mg/L) and the y-axis indicating frequency. The scales are adjusted per nutrient to highlight their unique distribution patterns, and consistent colors are used to differentiate the parameters.

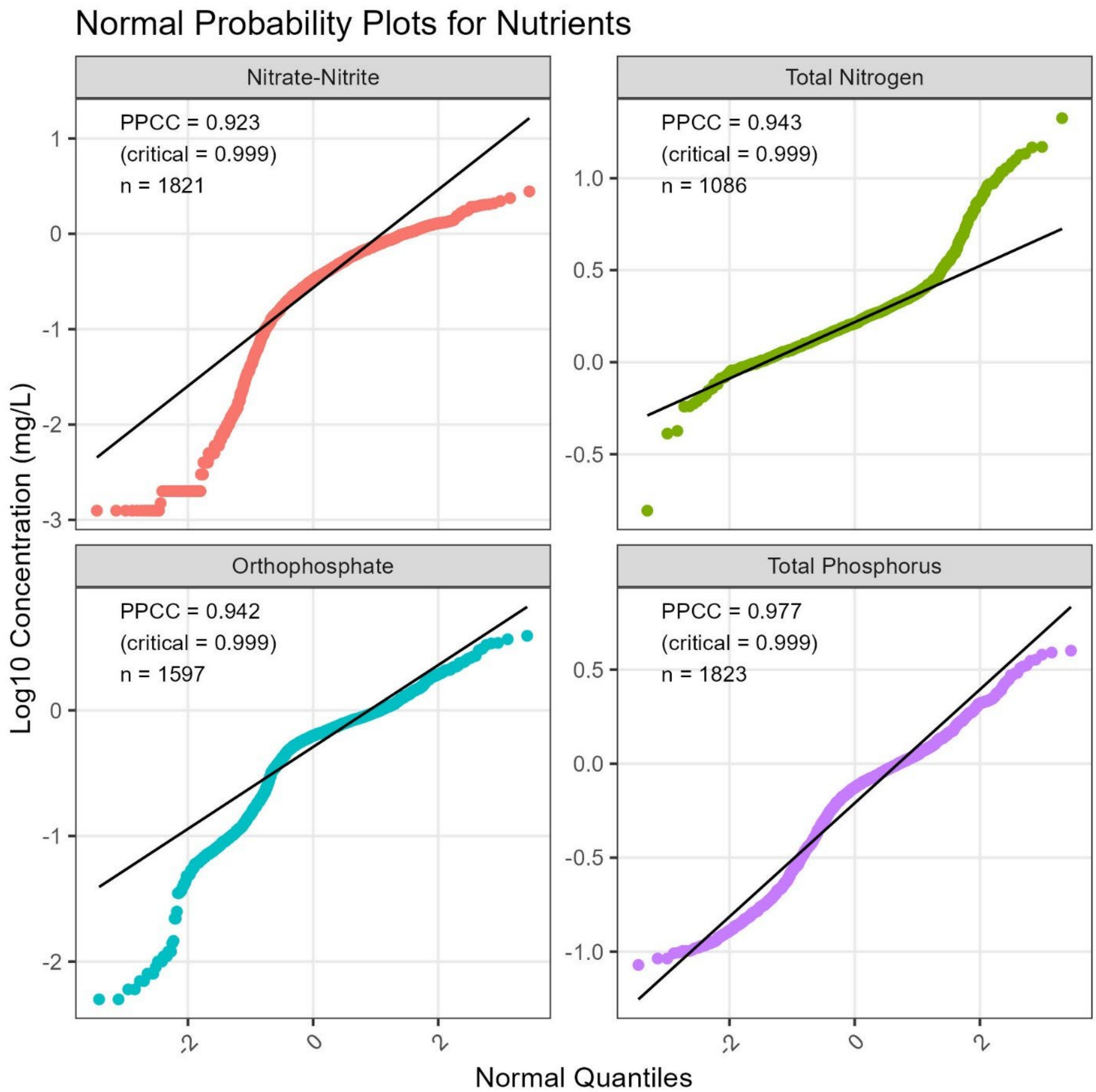


Figure 9. Normal probability plots for nutrient concentrations, comparing theoretical quantiles to sample quantiles. Normal quantiles are values expected from a perfectly normal distribution at specific probabilities, serving as a reference for normality. If the data follow a normal distribution, the points align closely with the diagonal line. Deviations from the line indicate departures from normality. The Probability Plot Correlation Coefficient (PPCC) is the linear correlation coefficient between data and their normal quantiles. PPCC values below the critical value indicate rejection of null hypothesis that data are from a normal distribution. All plots show non-normal distributions.

Table 8. Results of Anderson-Darling test for normality of log10 transformed data. All parameters are non-normal with p values well below 0.001.

Parameter	AD statistic	p
Orthophosphate	63.85704	3.7E-24
Nitrate-Nitrite	92.52499	3.7E-24
Total Nitrogen	27.75935	3.7E-24
Total Phosphorus	37.07674	3.7E-24

Testing for difference between groups

There are significant differences between wet and dry seasons for nitrate-nitrite, but not for total nitrogen, orthophosphate, or total phosphorus (Table 9) (Figure 10). Pairwise Wilcoxson tests reveal differences between nine stations in orthophosphate (Figure 11), nitrate-nitrite (Figure 12), total nitrogen (Figure 13), and total phosphorus (Figure 14). Exploration of these interactions is complicated: there are 9 stations, 2 seasons, and 4 parameters which combine for 72 total interactions between season and station. In addition, pairwise comparisons add a further layer of complication: there are 36 pairwise comparisons of 9 stations for each parameter and 144 total comparisons for 4 parameters. As a result of this complexity, the analysis provided here is intended as a survey general patterns for each parameter, with the caveat that there will always be deeper analysis possible as a follow-up to the analysis presented here.

Table 9. Kruskal-Wallace tests for differences between Stations, Seasons, and Station*Season interactions.

Parameter	Station_chi	Station_p	Season_chi	Season_p	Interaction_chi	Interaction_p
Orthophosphate	622.352	3.7E-130	1.124619	0.288926	630.0484	1.5E-124
Nitrate-Nitrite	836.939	2.24E-175	71.799	2.38E-17	930.783	5.64E-187
Total Nitrogen	172.045	4.81E-33	1.715	1.90E-01	194.393	3.83E-32
Total Phosphorus	847.758	1.04E-177	0.258	6.12E-01	854.197	1.27E-170

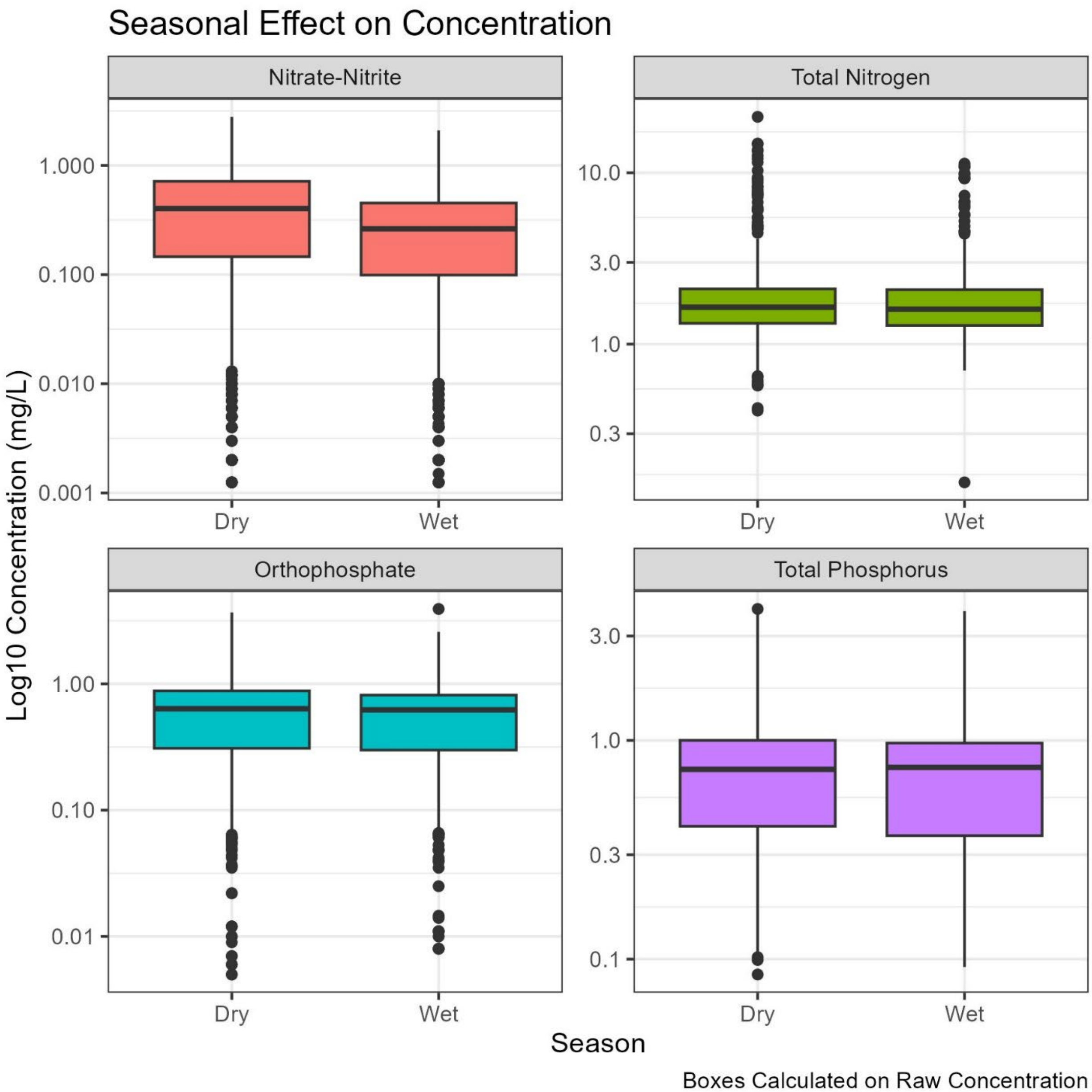


Figure 10. Seasonal differences in nutrient concentrations

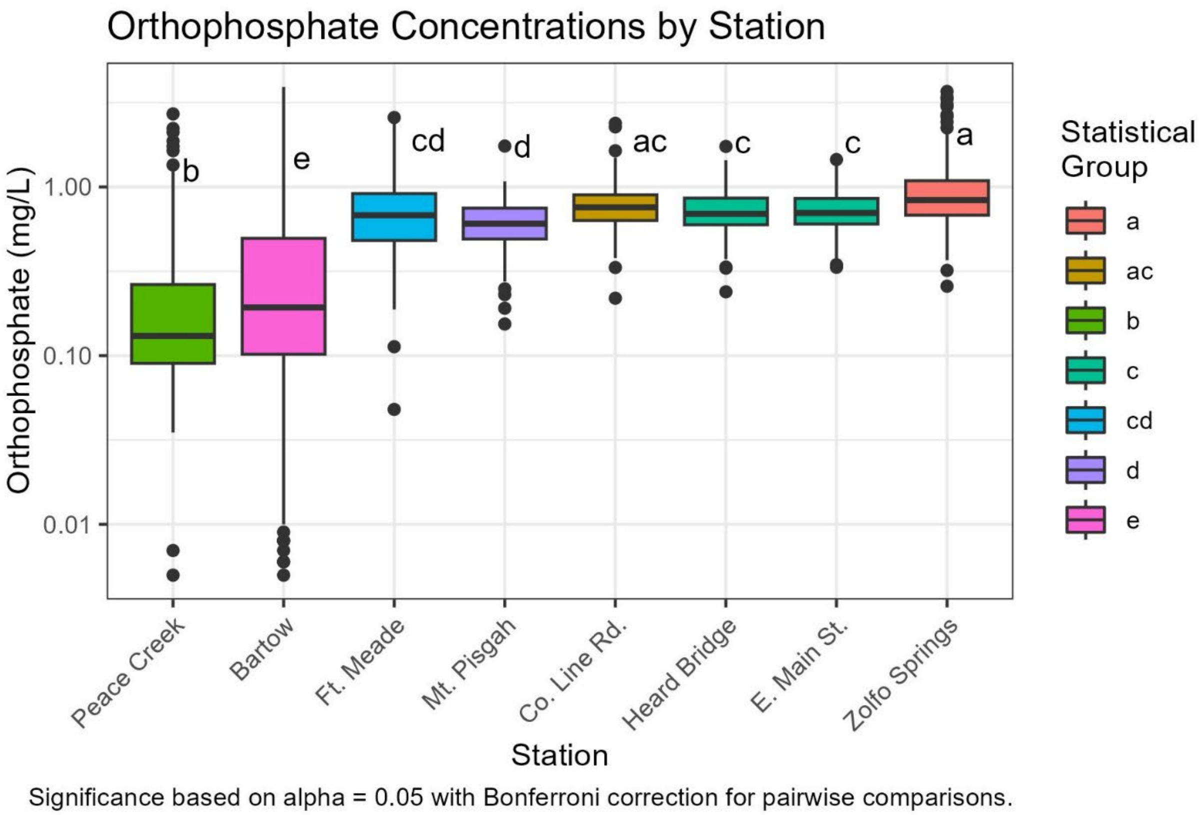


Figure 11. Statistical grouping of orthophosphate by station using pairwise Wilcoxon tests

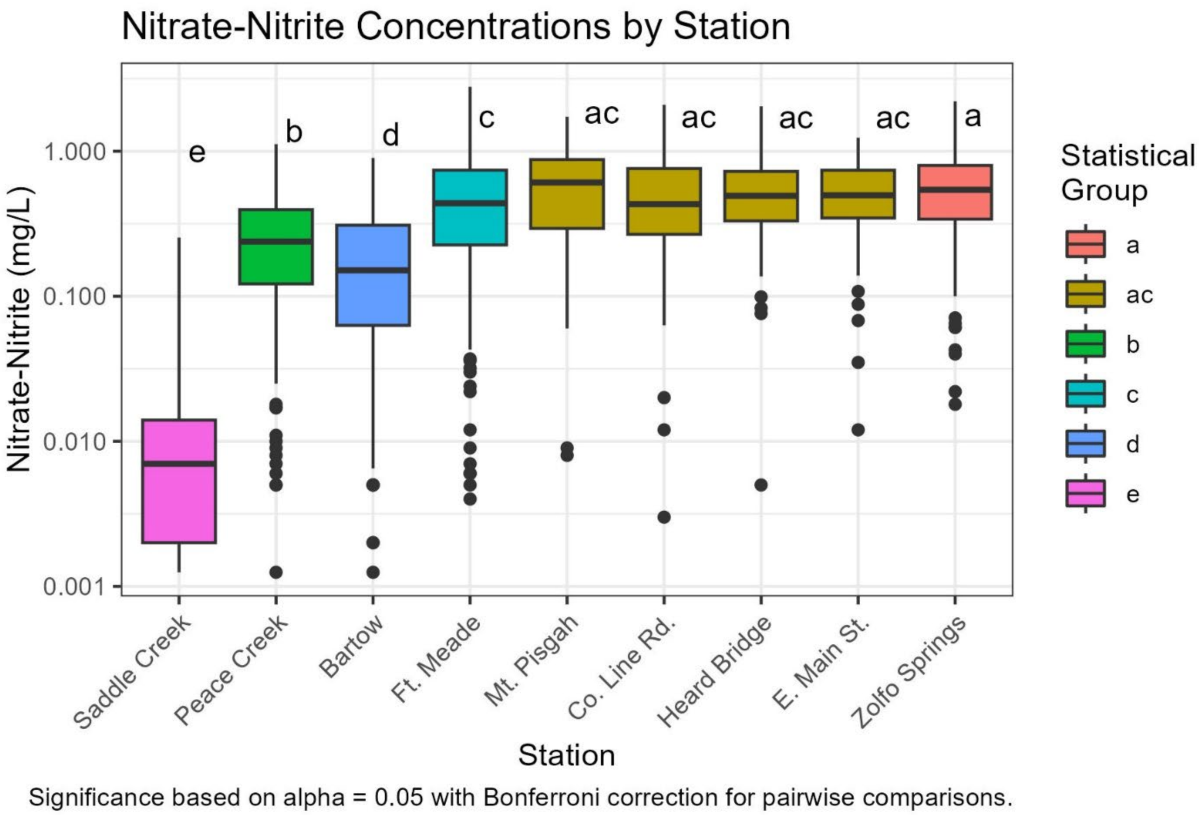


Figure 12. Statistical Grouping of nitrate-nitrite by station using pairwise Wilcoxon tests

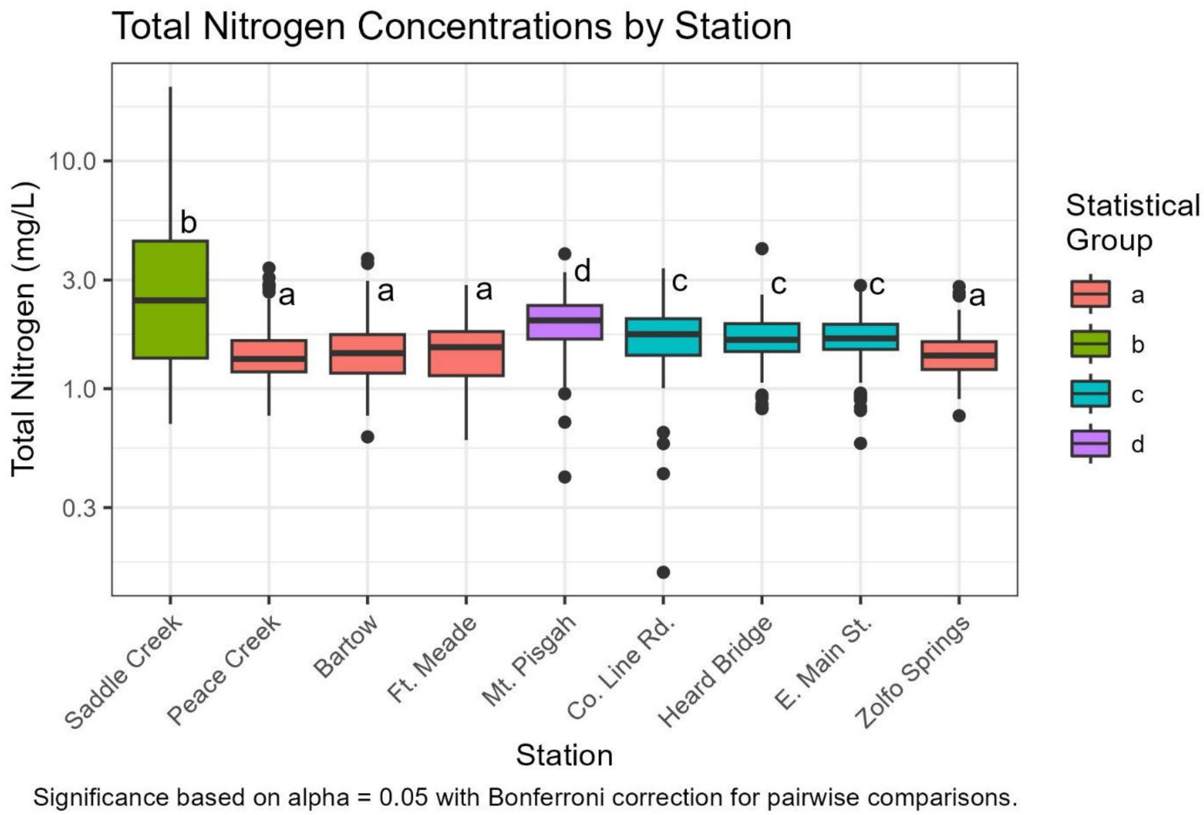


Figure 13. Statistical Grouping of Total Nitrogen by station using pairwise Wilcoxon tests

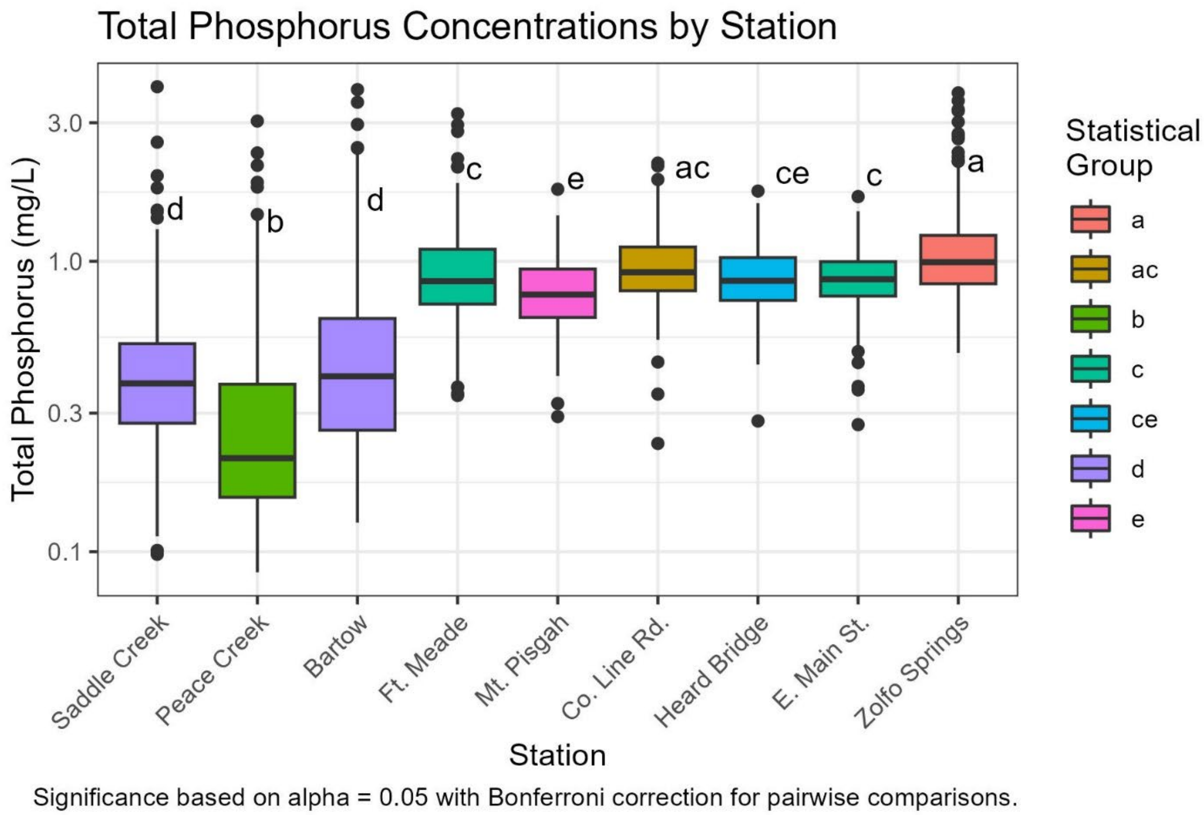


Figure 14. Statistical Grouping of total phosphorus by station using pairwise Wilcoxon tests

Trends

This analysis examines both flow-based and temporal trends in water quality parameters using a two-stage approach following Helsel and Hirsch (2002). We first analyze concentration-date relationships using LOESS smoothing, then use these residuals to examine flow relationships. In a parallel analysis, we examine concentration-flow relationships with LOESS, using those residuals to assess temporal trends. Both approaches employ Kendall's tau with Bonferroni-adjusted p-values (p_adjusted = p_initial * n, where n is the number of stations) and Theil-Sen slopes for trend detection. This dual analysis allows examination of both flow-concentration patterns and temporal trends while controlling for their mutual influences.

The analysis sequence includes:

1. Concentration-date relationships with LOESS smoothing for nitrate-nitrite (Figure 15), total nitrogen (Figure 16), orthophosphate (Figure 17), and total phosphorus (Figure 18). These plots provide a visual representation of nonlinear temporal patterns for each station.

2. Concentration-flow relationships with LOESS smoothing for nitrate-nitrite (Figure 19), total nitrogen (Figure 20), orthophosphate (Figure 21), and total phosphorus (Figure 22) visualize nonlinear patterns in water quality parameters with flow at each station.

3. Residuals from concentration-flow relationships represent flow-adjusted concentrations which can be compared with dates to determine temporal relationships nitrate-nitrite (Figure 23), total nitrogen (Figure 24), with orthophosphate (Figure 25), and total phosphorus (Figure 26). Kendall-Theil lines show increasing, decreasing and not significant relationships depending on the water quality sampling location (Table 10). Statistical significance is based on Bonferroni-corrected p-values adjusted for number of stations.

4. Residuals from date-flow Loess represent date-adjusted concentration which is related to flow for nitrate-nitrite (Figure 27), total nitrogen (Figure 28), orthophosphate (Figure 29), and total phosphorus (Figure 30) with Kendall-Theil lines showing increasing, decreasing and not significant relationships depending on the water quality sampling location (Table 11). Statistical significance is based on Bonferroni-corrected p-values adjusted for number of stations.

The analysis revealed both temporal and flow-dependent trends across stations, suggesting that water quality dynamics are influenced by a combination of temporal and hydrological factors. Trends are also site specific. Most temporal trends were not significant (n = 17) or decreasing through time (n = 17), and only one showed a significant increase (Table 12). The majority of flow trends were decreasing (26), while 8 trends were not significant and 1 was increasing (Table 13).

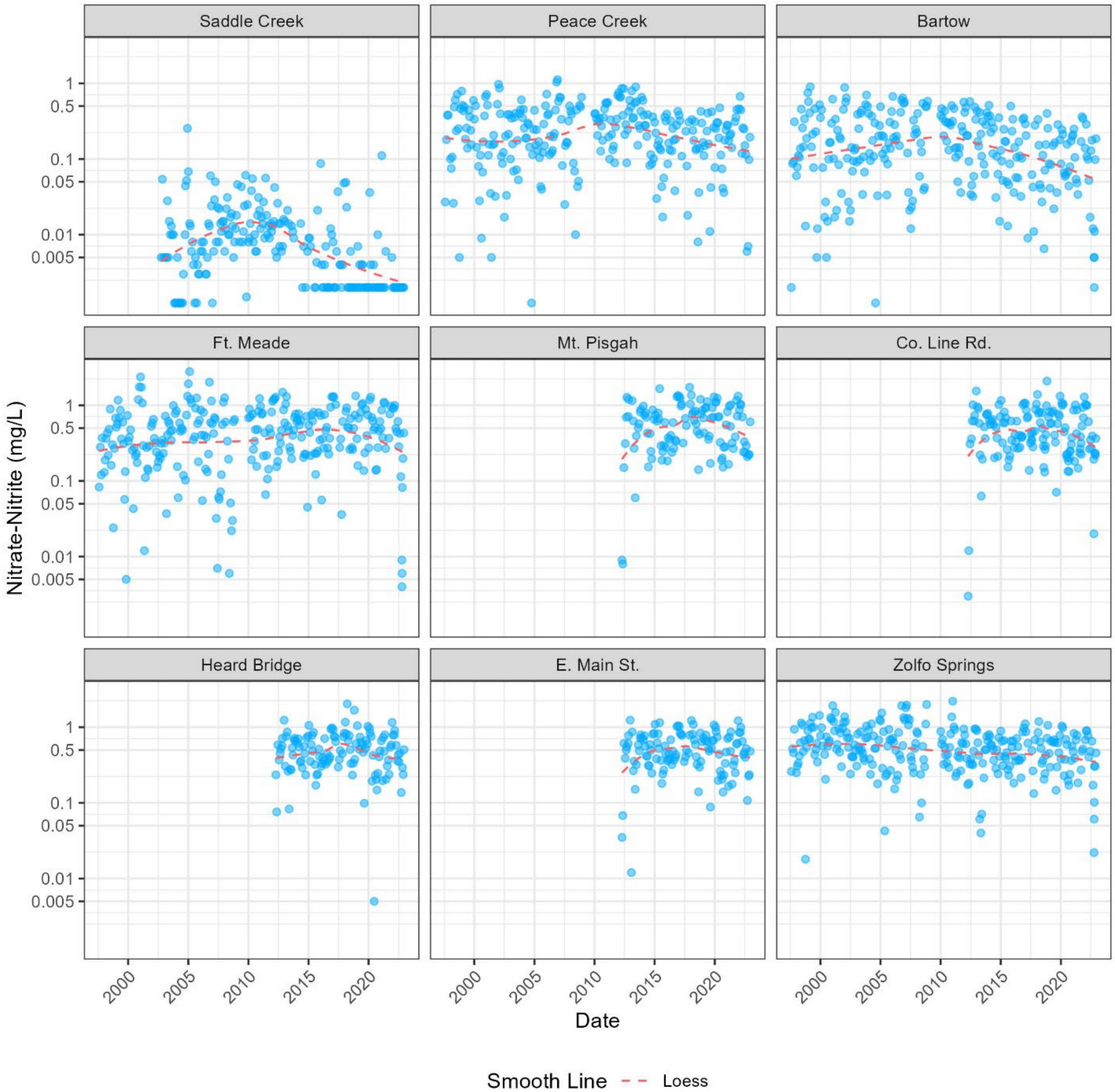


Figure 15. Time series showing observed nitrate-nitrite concentrations (blue points) with LOESS smoothing curves (dashed red lines) across monitoring stations. The LOESS curves capture temporal patterns in the data, with residuals from these fits used for subsequent flow-adjusted trend analysis. Note: Concentrations are displayed on a logarithmic scale.

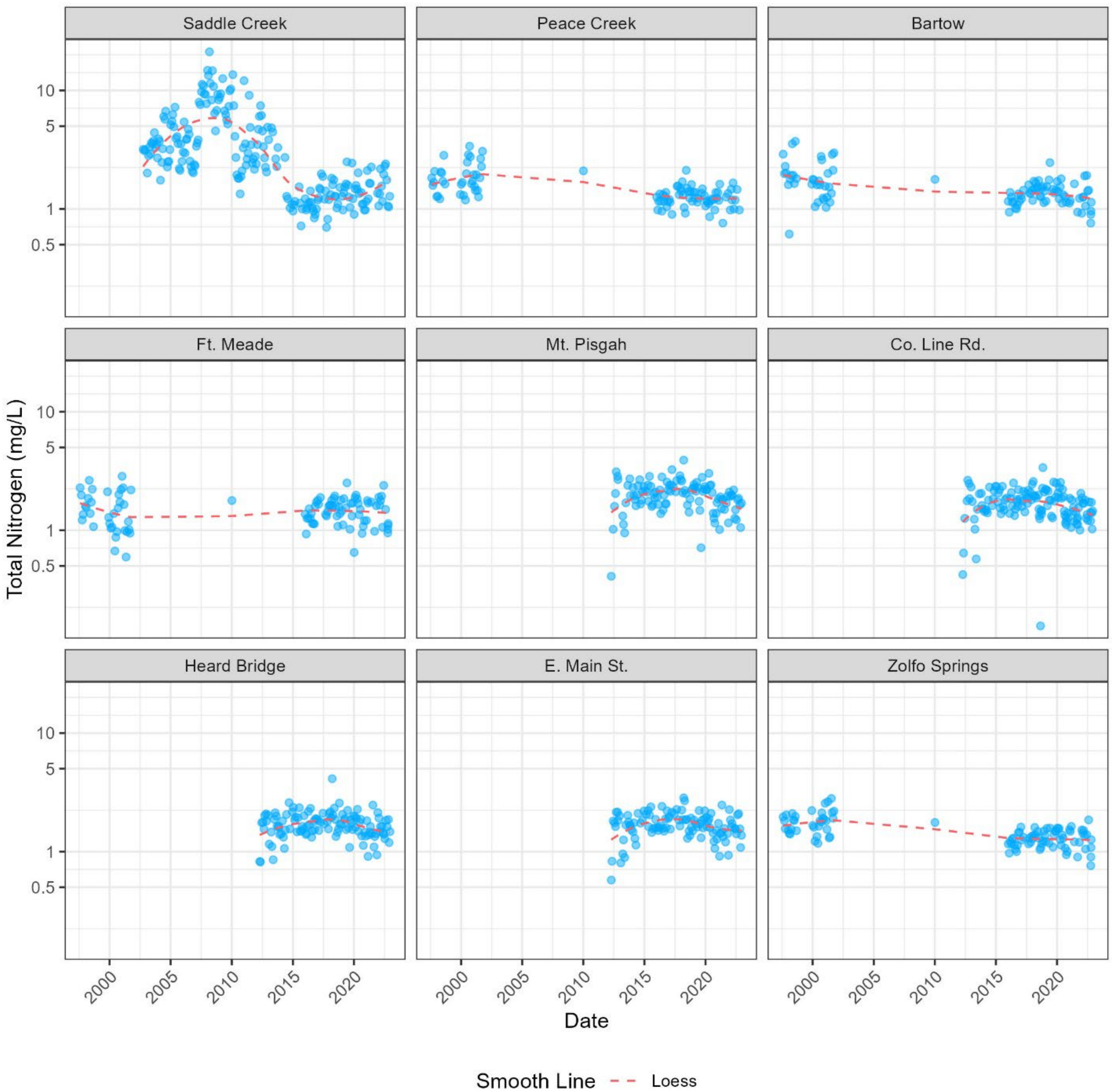


Figure 16. Time series showing observed total nitrogen concentrations (blue points) with LOESS smoothing curves (dashed red lines) across monitoring stations. The LOESS curves capture temporal patterns in the data, with residuals from these fits used for subsequent flow-adjusted trend analysis. Note: Concentrations are displayed on a logarithmic scale.

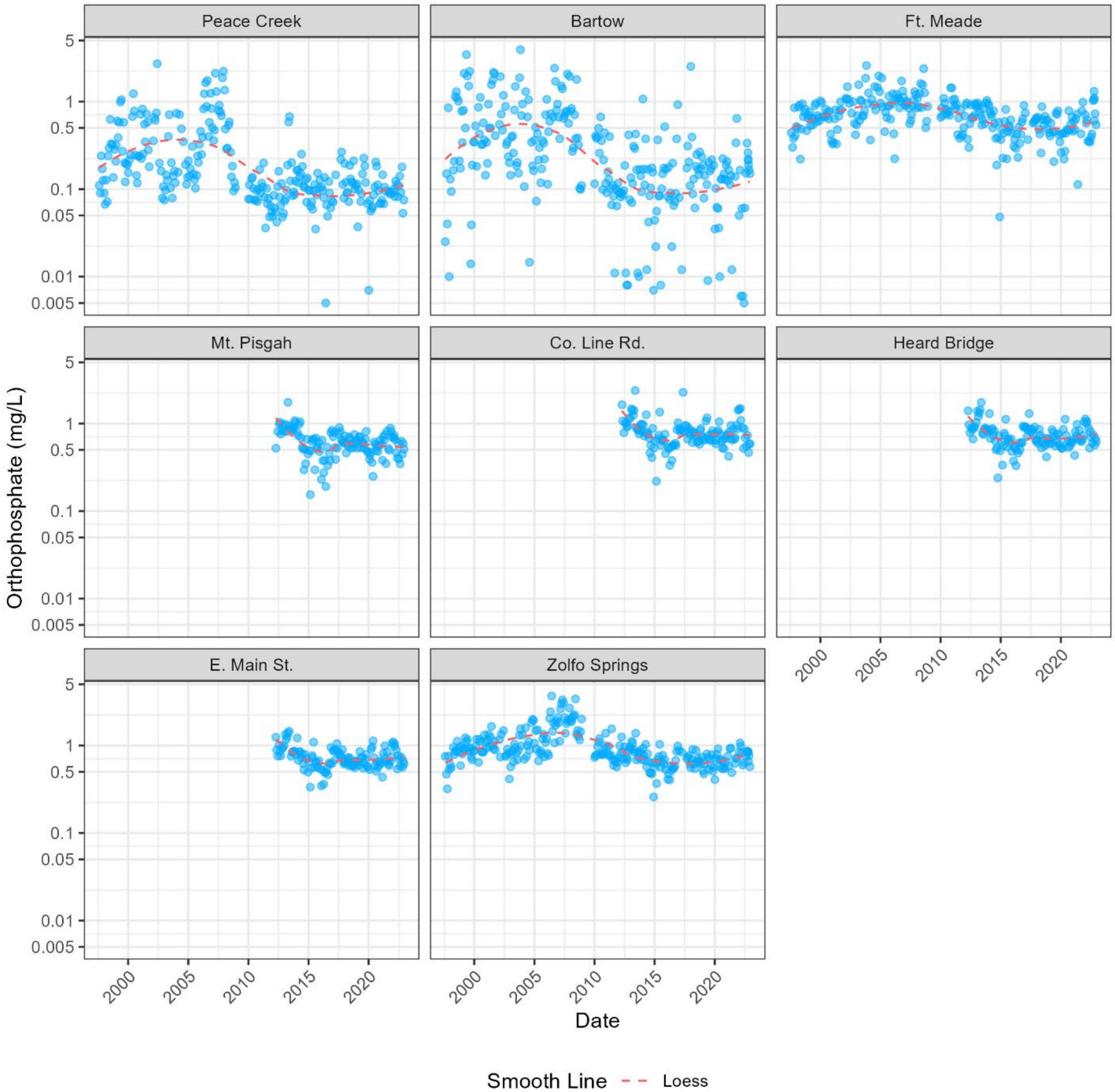


Figure 17. Time series showing observed orthophosphate concentrations (blue points) with LOESS smoothing curves (dashed red lines) across monitoring stations. The LOESS curves capture temporal patterns in the data, with residuals from these fits used for subsequent flow-adjusted trend analysis. Note: Concentrations are displayed on a logarithmic scale.

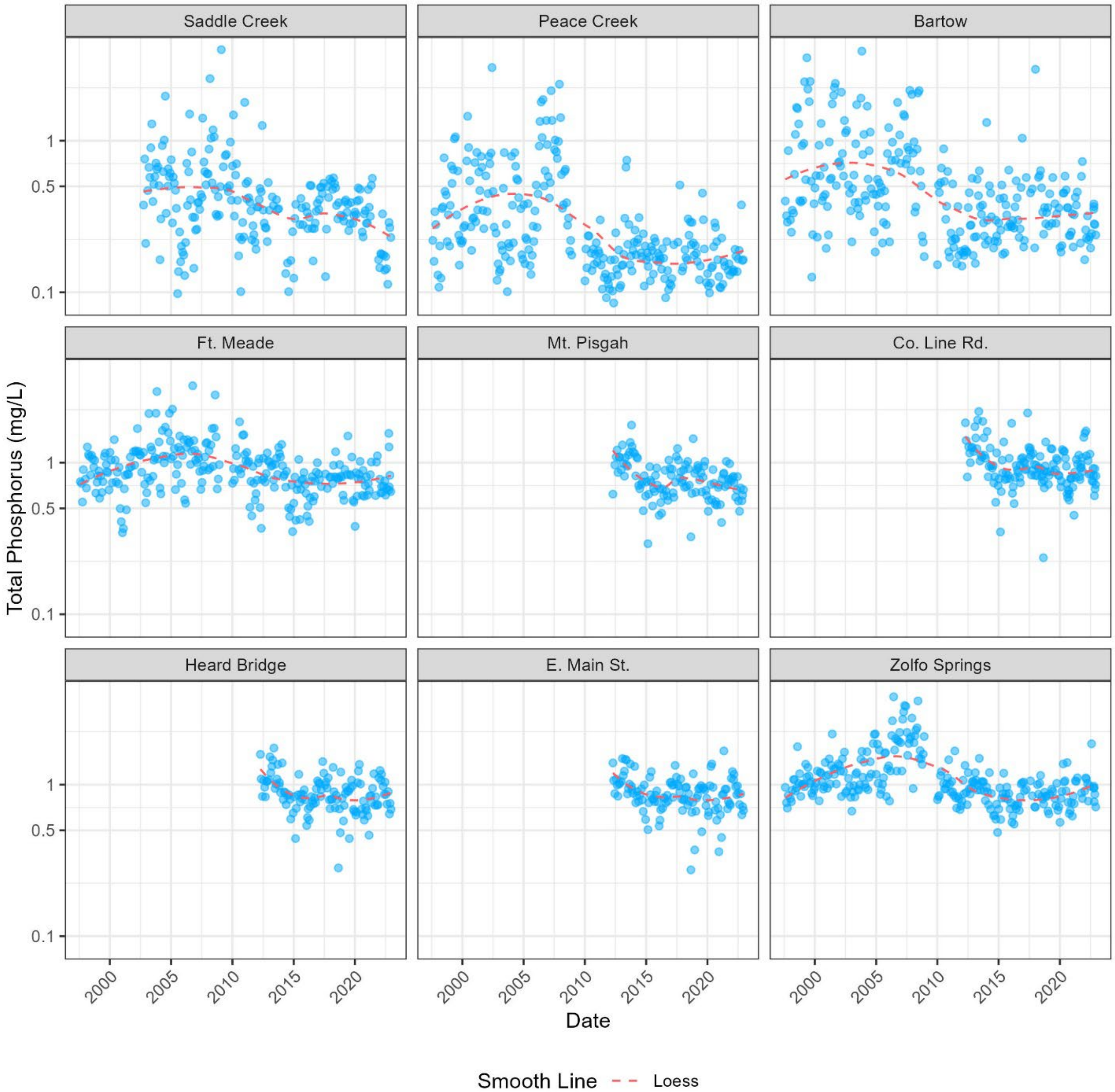


Figure 18. Time series showing observed total phosphorus concentrations (blue points) with LOESS smoothing curves (dashed red lines) across monitoring stations. The LOESS curves capture temporal patterns in the data, with residuals from these fits used for subsequent flow-adjusted trend analysis. Note: Concentrations are displayed on a logarithmic scale.

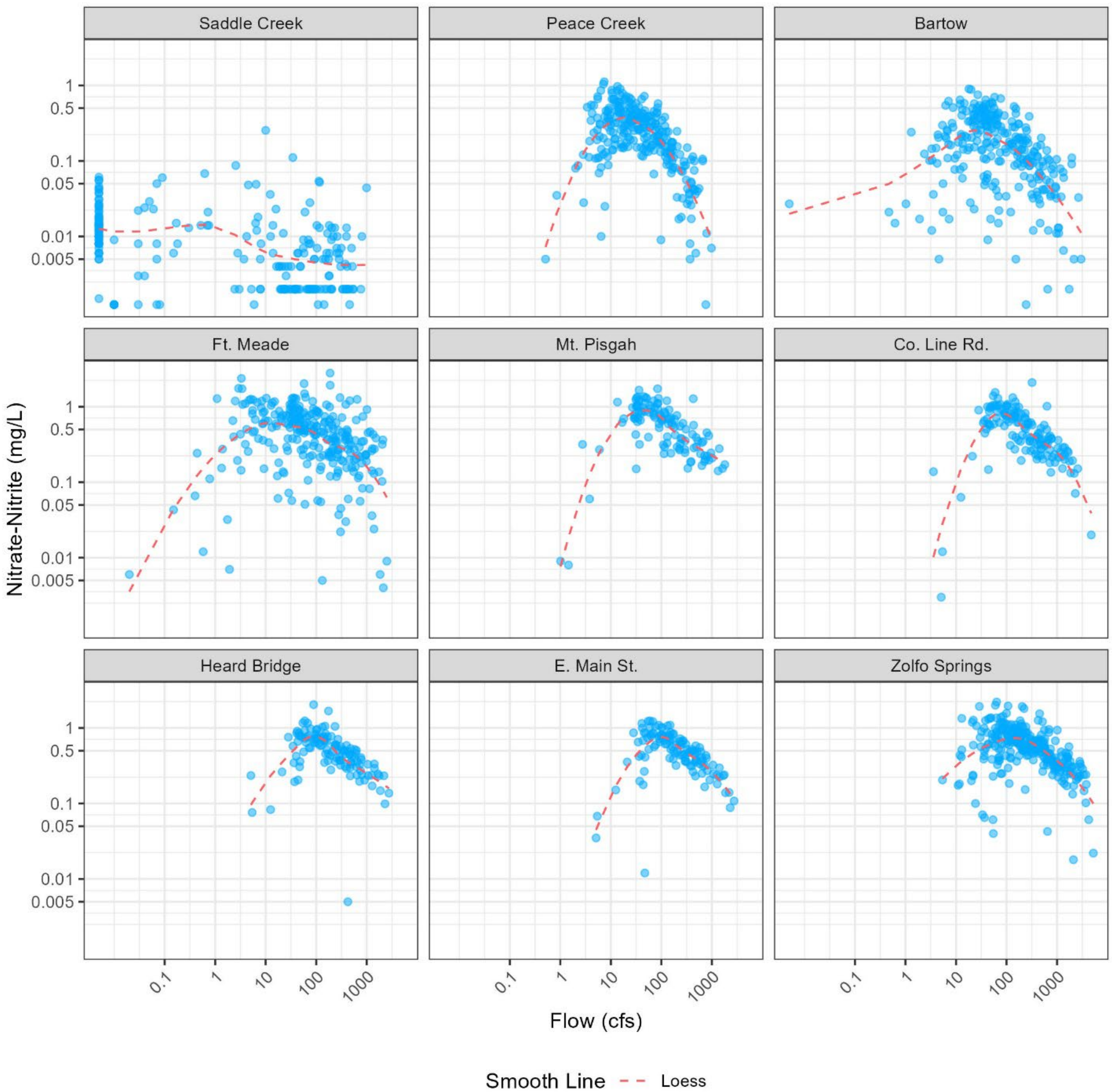


Figure 19. Relationship between streamflow and nitrate-nitrite concentrations (blue points) with LOESS smoothing curves (dashed red lines) across monitoring stations. The LOESS curves capture flow-concentration patterns in the data, with residuals from these fits used for subsequent trend analysis. Note: Both flow and concentration are displayed on logarithmic scales.

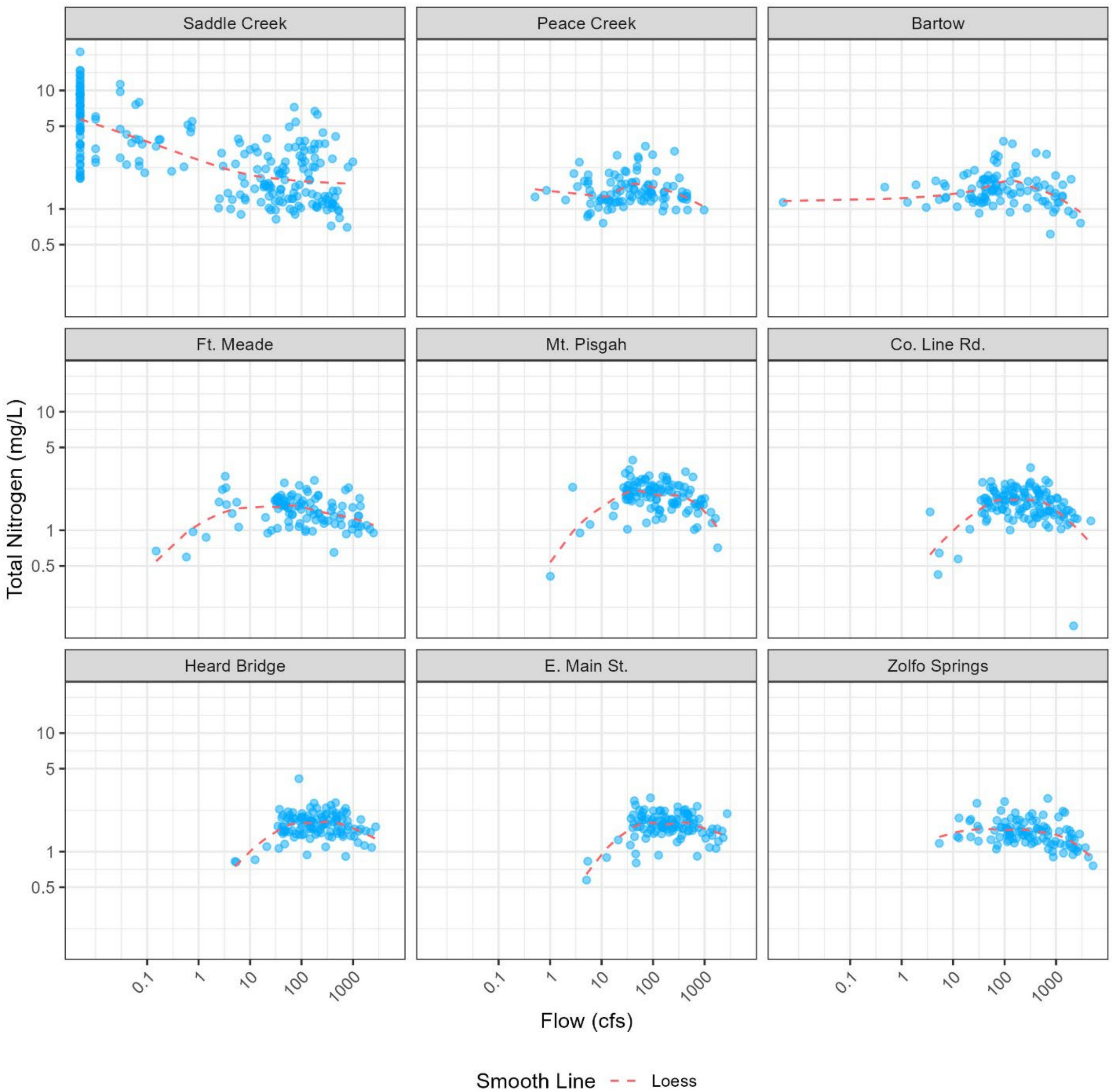


Figure 20. Relationship between streamflow and Total Nitrogen concentrations (blue points) with LOESS smoothing curves (dashed red lines) across monitoring stations. The LOESS curves capture flow-concentration patterns in the data, with residuals from these fits used for subsequent trend analysis. Note: Both flow and concentration are displayed on logarithmic scales.

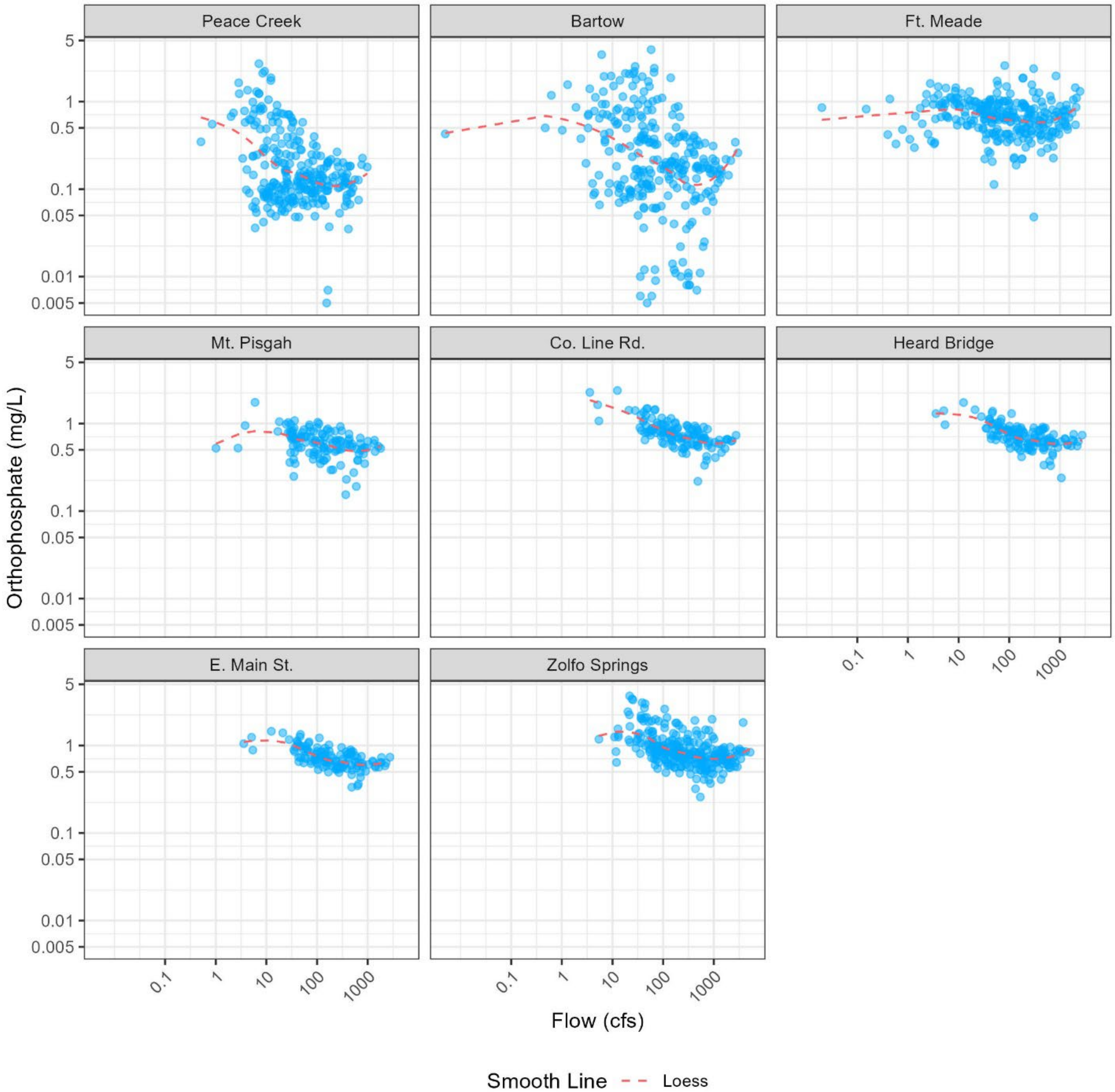


Figure 21. Relationship between streamflow and orthophosphate concentrations (blue points) with LOESS smoothing curves (dashed red lines) across monitoring stations. The LOESS curves capture flow-concentration patterns in the data, with residuals from these fits used for subsequent trend analysis. Note: Both flow and concentration are displayed on logarithmic scales.

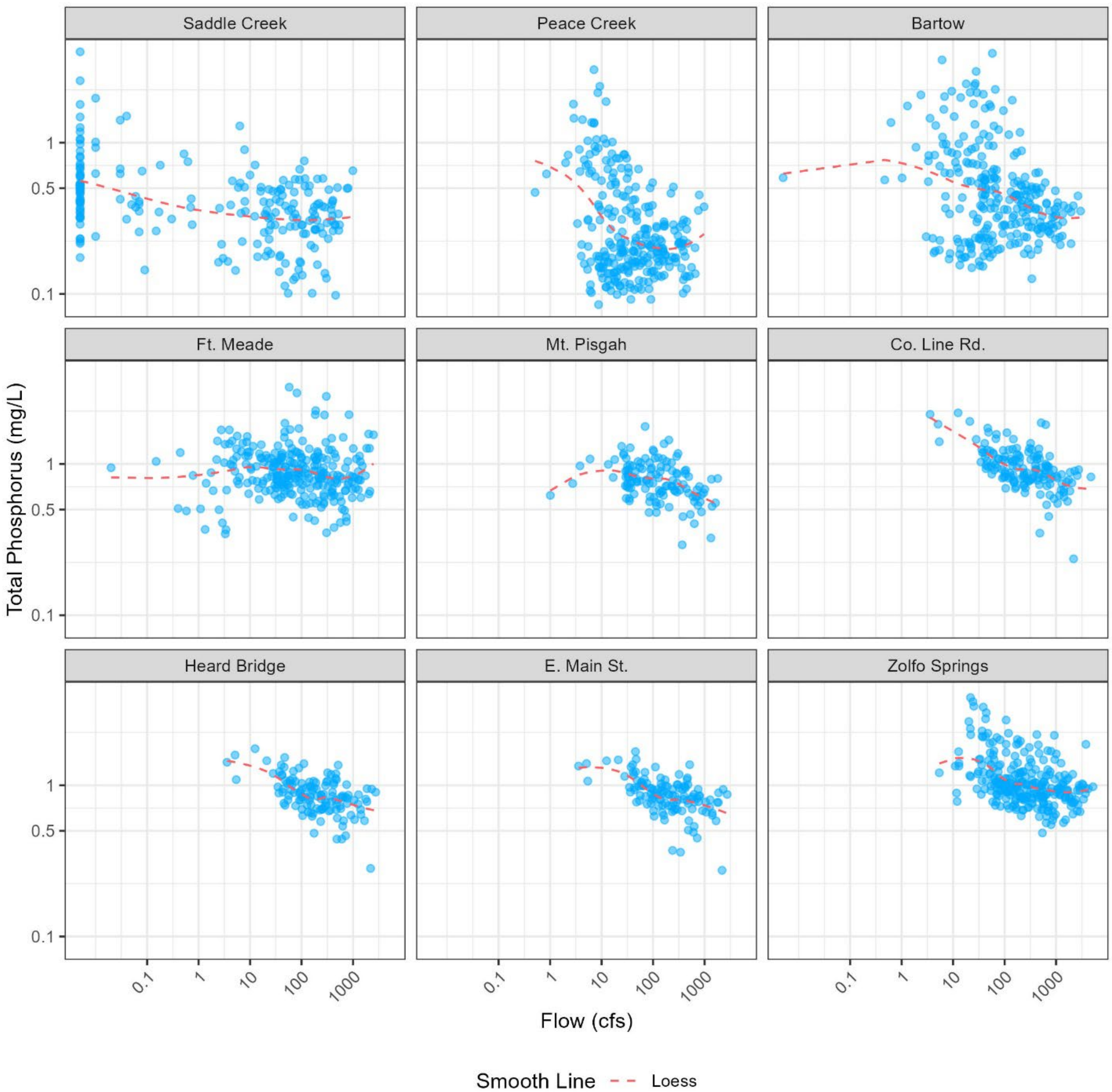


Figure 22. Relationship between streamflow and total phosphorus concentrations (blue points) with LOESS smoothing curves (dashed red lines) across monitoring stations. The LOESS curves capture flow-concentration patterns in the data, with residuals from these fits used for subsequent trend analysis. Note: Both flow and concentration are displayed on logarithmic scales.

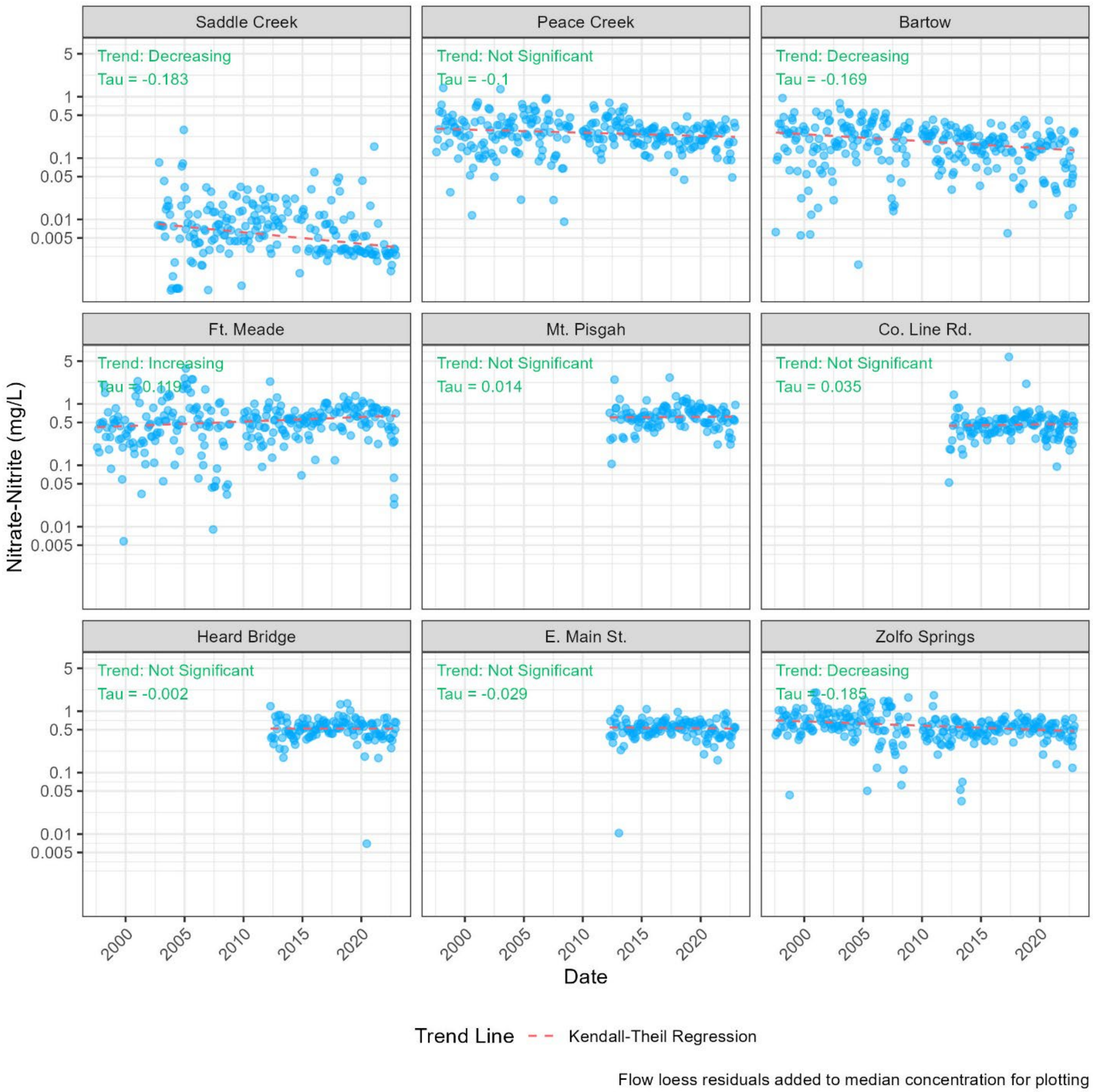


Figure 23. Flow-adjusted trends in nitrate-nitrite concentrations across monitoring stations. Points show LOESS residuals from the flow-concentration relationship (blue points) rescaled to the original concentration units, with Kendall-Theil regression lines (dashed red) indicating long-term trends. Text annotations provide the Sen slope (trend magnitude) and Kendall's tau correlation coefficient for each station. Note: Residuals are centered on the mean concentration for each station to maintain interpretable units.

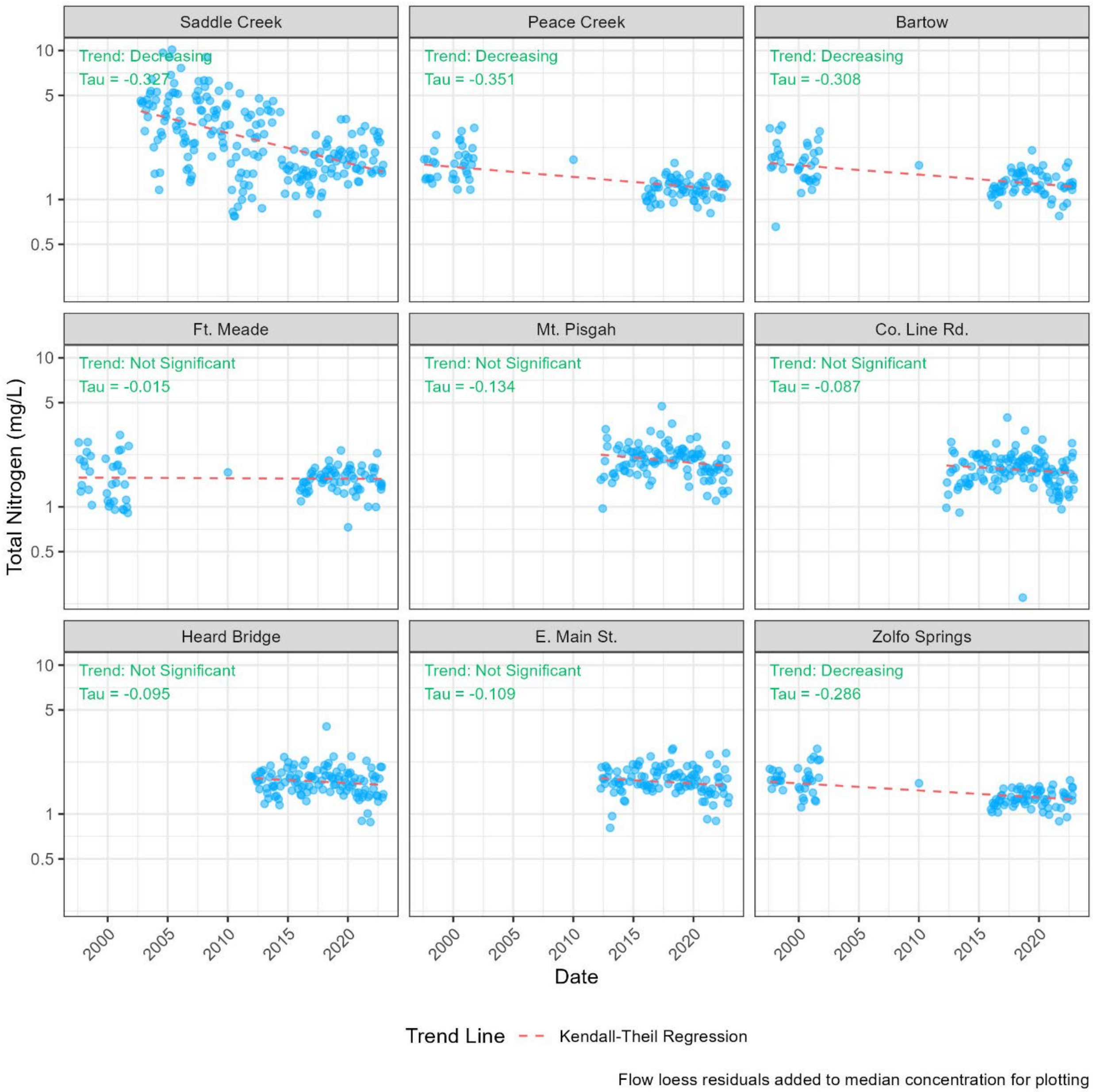


Figure 24. Flow-adjusted trends in total nitrogen concentrations across monitoring stations. Points show LOESS residuals from the flow-concentration relationship (blue points) rescaled to the original concentration units, with Kendall-Theil regression lines (dashed red) indicating long-term trends. Text annotations provide the Sen slope (trend magnitude) and Kendall's tau correlation coefficient for each station. Note: Residuals are centered on the mean concentration for each station to maintain interpretable units.

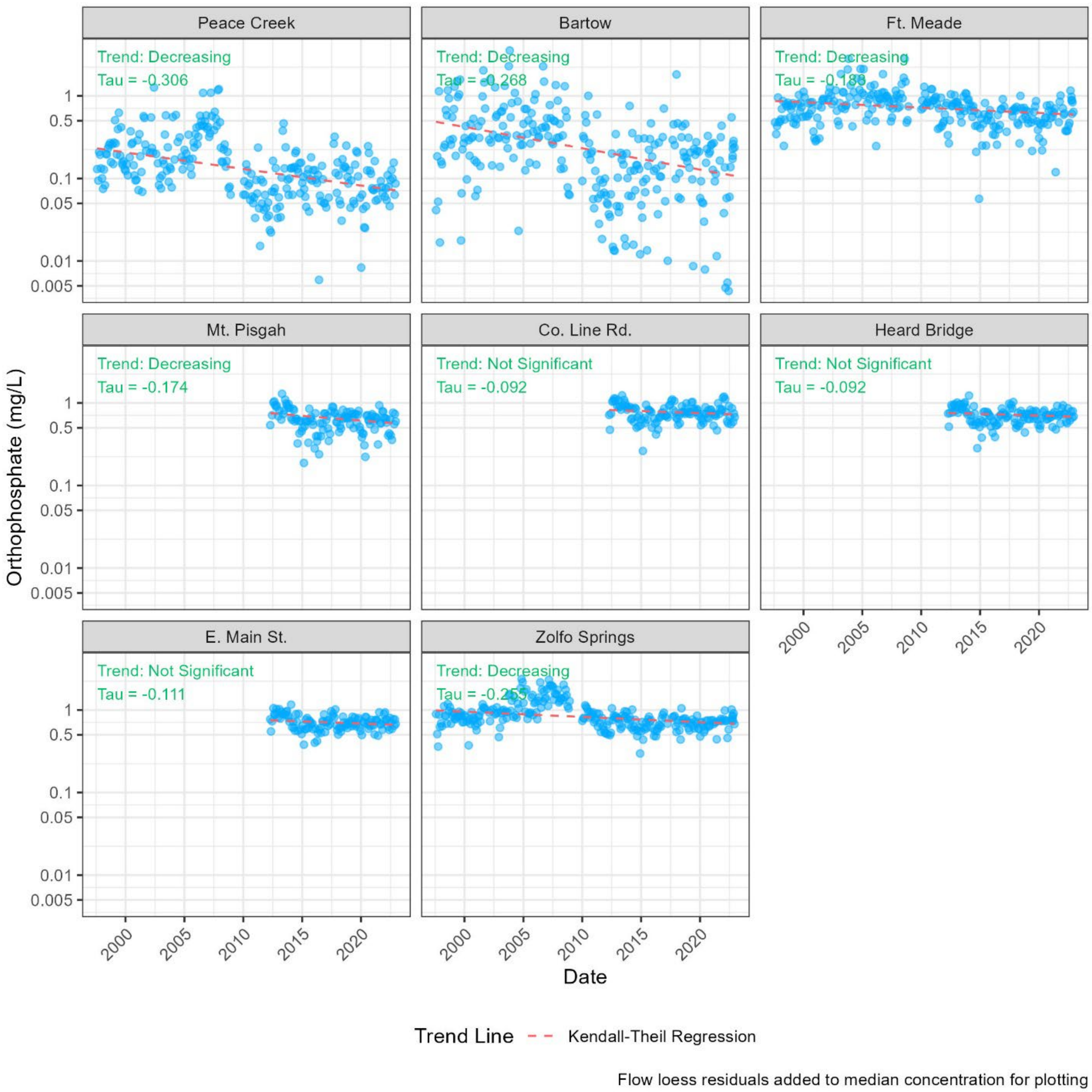


Figure 25. Flow-adjusted trends in orthophosphate concentrations across monitoring stations. Points show LOESS residuals from the flow-concentration relationship (blue points) rescaled to the original concentration units, with Kendall-Theil regression lines (dashed red) indicating long-term trends. Text annotations provide the Sen slope (trend magnitude) and Kendall's tau correlation coefficient for each station. Note: Residuals are centered on the mean concentration for each station to maintain interpretable units.

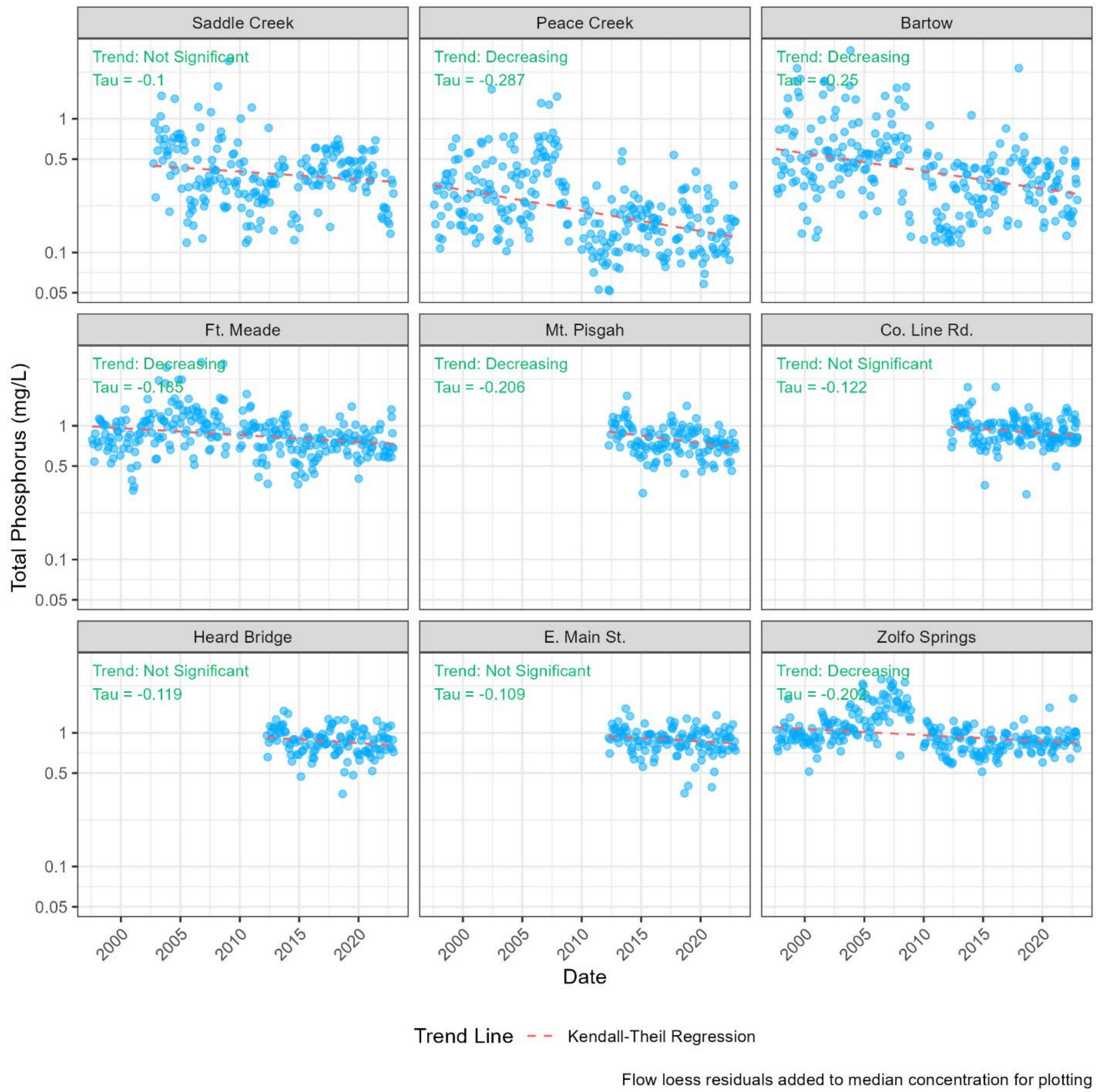


Figure 26. Flow-adjusted trends in total phosphorus concentrations across monitoring stations. Points show LOESS residuals from the flow-concentration relationship (blue points) rescaled to the original concentration units, with Kendall-Theil regression lines (dashed red) indicating long-term trends. Text annotations provide the Sen slope (trend magnitude) and Kendall's tau correlation coefficient for each station. Note: Residuals are centered on the mean concentration for each station to maintain interpretable units.

Table 10. Summary of Kendall-Theil tests for trend with date by station and parameter. Trends are classified as Increasing, Decreasing, or Not Significant, based on Kendall's tau significance (α = 0.05). Raw p values (p_raw) are adjusted using Bonferroni correction for number of stations tested (n_tests) to produce adjusted p values (p_adj).

Parameter	Station	slope	tau	n_tests	p_raw	p_adj	Trend
Nitrate-Nitrite	Saddle Creek	-5.108e-05	-0.183	9	7.78e-05	7.002e-04	Decreasing
Nitrate-Nitrite	Peace Creek	-1.409e-05	-0.1	9	1.35e-02	1.215e-01	Not Significant
Nitrate-Nitrite	Bartow	-3.128e-05	-0.169	9	3.055e-05	2.749e-04	Decreasing
Nitrate-Nitrite	Ft. Meade	2.017e-05	0.119	9	3.283e-03	2.955e-02	Increasing
Nitrate-Nitrite	Mt. Pisgah	3.221e-06	0.014	9	8.215e-01	7.394e+00	Not Significant
Nitrate-Nitrite	Co. Line Rd.	7.585e-06	0.035	9	5.335e-01	4.802e+00	Not Significant
Nitrate-Nitrite	Heard Bridge	-3.907e-07	-0.002	9	9.728e-01	8.755e+00	Not Significant
Nitrate-Nitrite	E. Main St.	-5.132e-06	-0.029	9	6.347e-01	5.712e+00	Not Significant
Nitrate-Nitrite	Zolfo Springs	-1.892e-05	-0.185	9	4.458e-06	4.012e-05	Decreasing
Total Nitrogen	Saddle Creek	-5.517e-05	-0.327	9	1.7e-12	1.53e-11	Decreasing
Total Nitrogen	Peace Creek	-1.838e-05	-0.351	9	2.627e-07	2.364e-06	Decreasing
Total Nitrogen	Bartow	-1.712e-05	-0.308	9	5.504e-06	4.953e-05	Decreasing
Total Nitrogen	Ft. Meade	-9.62e-07	-0.015	9	8.219e-01	7.397e+00	Not Significant
Total Nitrogen	Mt. Pisgah	-1.94e-05	-0.134	9	3.643e-02	3.279e-01	Not Significant
Total Nitrogen	Co. Line Rd.	-1.294e-05	-0.087	9	1.373e-01	1.235e+00	Not Significant
Total Nitrogen	Heard Bridge	-1.134e-05	-0.095	9	1.265e-01	1.138e+00	Not Significant
Total Nitrogen	E. Main St.	-1.23e-05	-0.109	9	9.173e-02	8.256e-01	Not Significant
Total Nitrogen	Zolfo Springs	-1.296e-05	-0.286	9	2.107e-05	1.897e-04	Decreasing
Orthophosphate	Peace Creek	-5.491e-05	-0.306	8	7.312e-14	5.85e-13	Decreasing
Orthophosphate	Bartow	-7.073e-05	-0.268	8	4.264e-11	3.411e-10	Decreasing
Orthophosphate	Ft. Meade	-1.783e-05	-0.183	8	6.08e-06	4.864e-05	Decreasing
Orthophosphate	Mt. Pisgah	-3.178e-05	-0.174	8	3.795e-03	3.036e-02	Decreasing
Orthophosphate	Co. Line Rd.	-1.321e-05	-0.092	8	1.256e-01	1.005e+00	Not Significant
Orthophosphate	Heard Bridge	-1.156e-05	-0.092	8	1.224e-01	9.792e-01	Not Significant
Orthophosphate	E. Main St.	-1.419e-05	-0.111	8	6.647e-02	5.317e-01	Not Significant
Orthophosphate	Zolfo Springs	-1.742e-05	-0.255	8	3.233e-10	2.586e-09	Decreasing
Total Phosphorus	Saddle Creek	-1.639e-05	-0.1	9	2.992e-02	2.693e-01	Not Significant
Total Phosphorus	Peace Creek	-4.202e-05	-0.287	9	1.893e-12	1.703e-11	Decreasing
Total Phosphorus	Bartow	-3.63e-05	-0.25	9	1.069e-09	9.617e-09	Decreasing
Total Phosphorus	Ft. Meade	-1.416e-05	-0.185	9	5.143e-06	4.628e-05	Decreasing
Total Phosphorus	Mt. Pisgah	-3.062e-05	-0.206	9	6.594e-04	5.935e-03	Decreasing
Total Phosphorus	Co. Line Rd.	-1.638e-05	-0.122	9	2.785e-02	2.507e-01	Not Significant
Total Phosphorus	Heard Bridge	-1.568e-05	-0.119	9	4.864e-02	4.378e-01	Not Significant
Total Phosphorus	E. Main St.	-1.333e-05	-0.109	9	7.166e-02	6.449e-01	Not Significant
Total Phosphorus	Zolfo Springs	-1.271e-05	-0.202	9	5.906e-07	5.316e-06	Decreasing

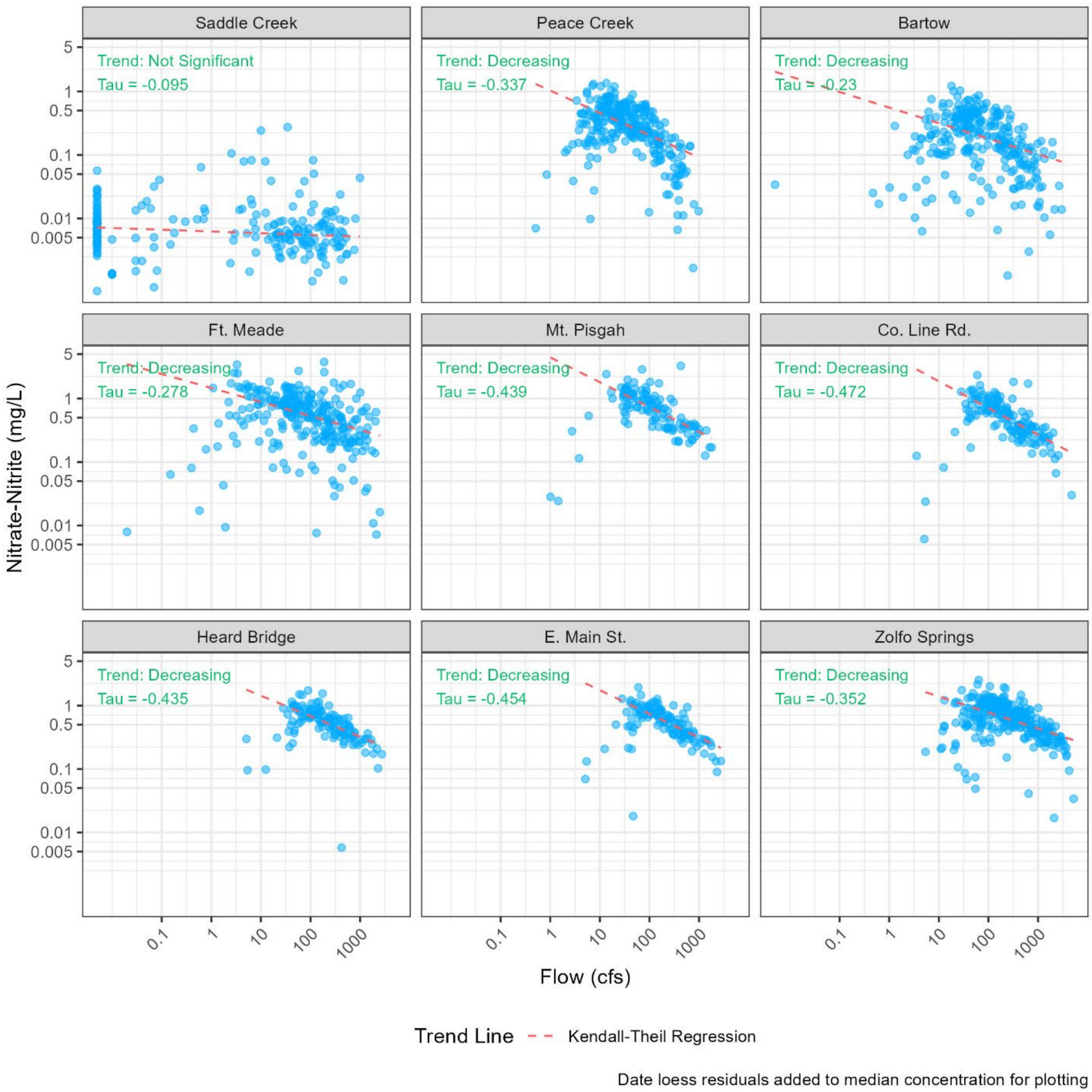


Figure 27. Date-adjusted relationships in nitrate-nitrite concentrations with Flow across monitoring stations. Points show LOESS residuals from the date-concentration relationship (blue points) rescaled to the original concentration units, with Kendall-Theil regression lines (dashed red) indicating long-term trends. Text annotations provide the Sen slope (trend magnitude) and Kendall's tau correlation coefficient for each station. Note: Residuals are centered on the mean concentration for each station to maintain interpretable units.

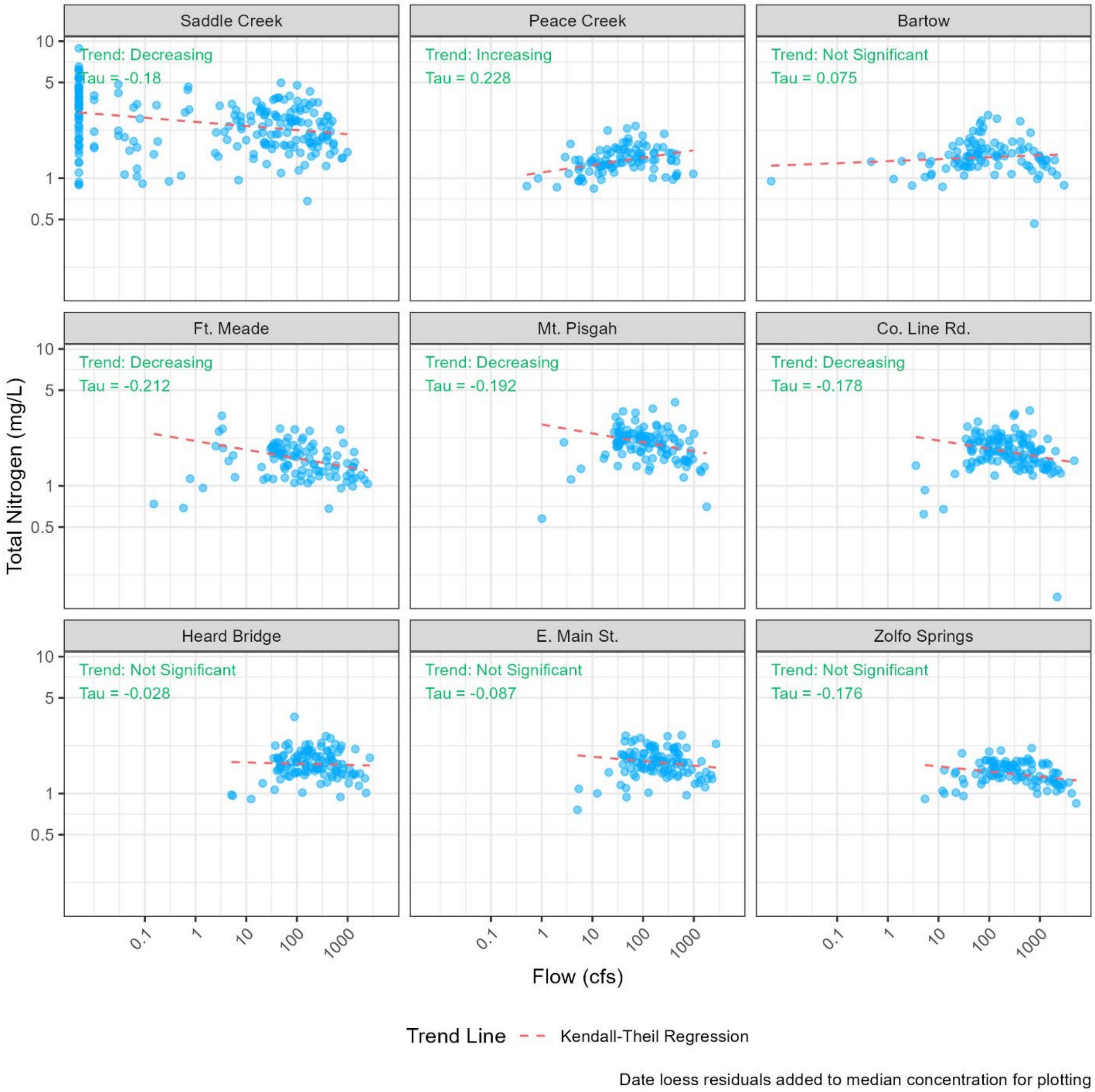


Figure 28. Date-adjusted relationships in total nitrogen concentrations with Flow across monitoring stations. Points show LOESS residuals from the date-concentration relationship (blue points) rescaled to the original concentration units, with Kendall-Theil regression lines (dashed red) indicating long-term trends. Text annotations provide the Sen slope (trend magnitude) and Kendall's tau correlation coefficient for each station. Note: Residuals are centered on the mean concentration for each station to maintain interpretable units.

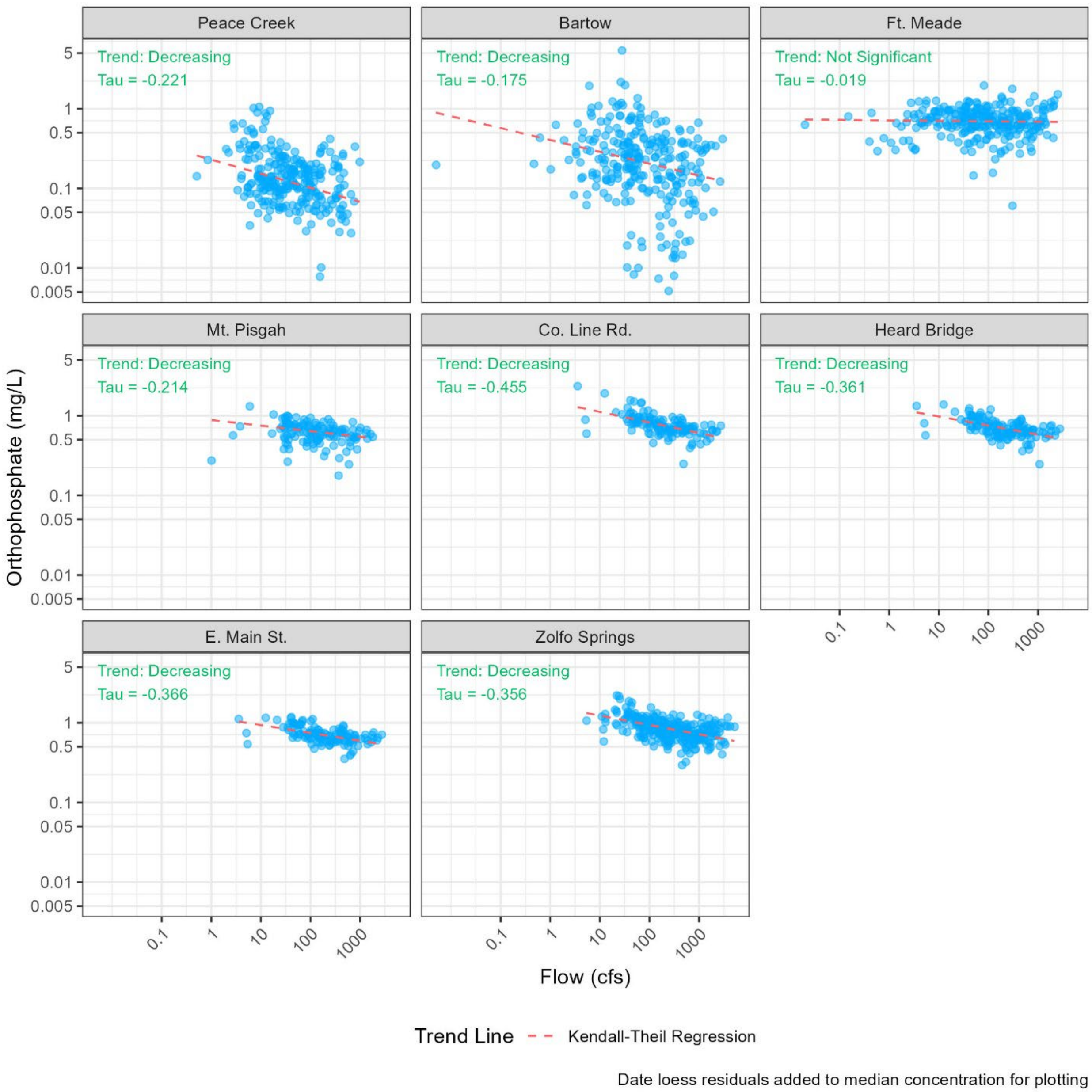


Figure 29. Date-adjusted relationships in Orthophosphate concentrations with Flow across monitoring stations. Points show LOESS residuals from the date-concentration relationship (blue points) rescaled to the original concentration units, with Kendall-Theil regression lines (dashed red) indicating long-term trends. Text annotations provide the Sen slope (trend magnitude) and Kendall's tau correlation coefficient for each station. Note: Residuals are centered on the mean concentration for each station to maintain interpretable units.

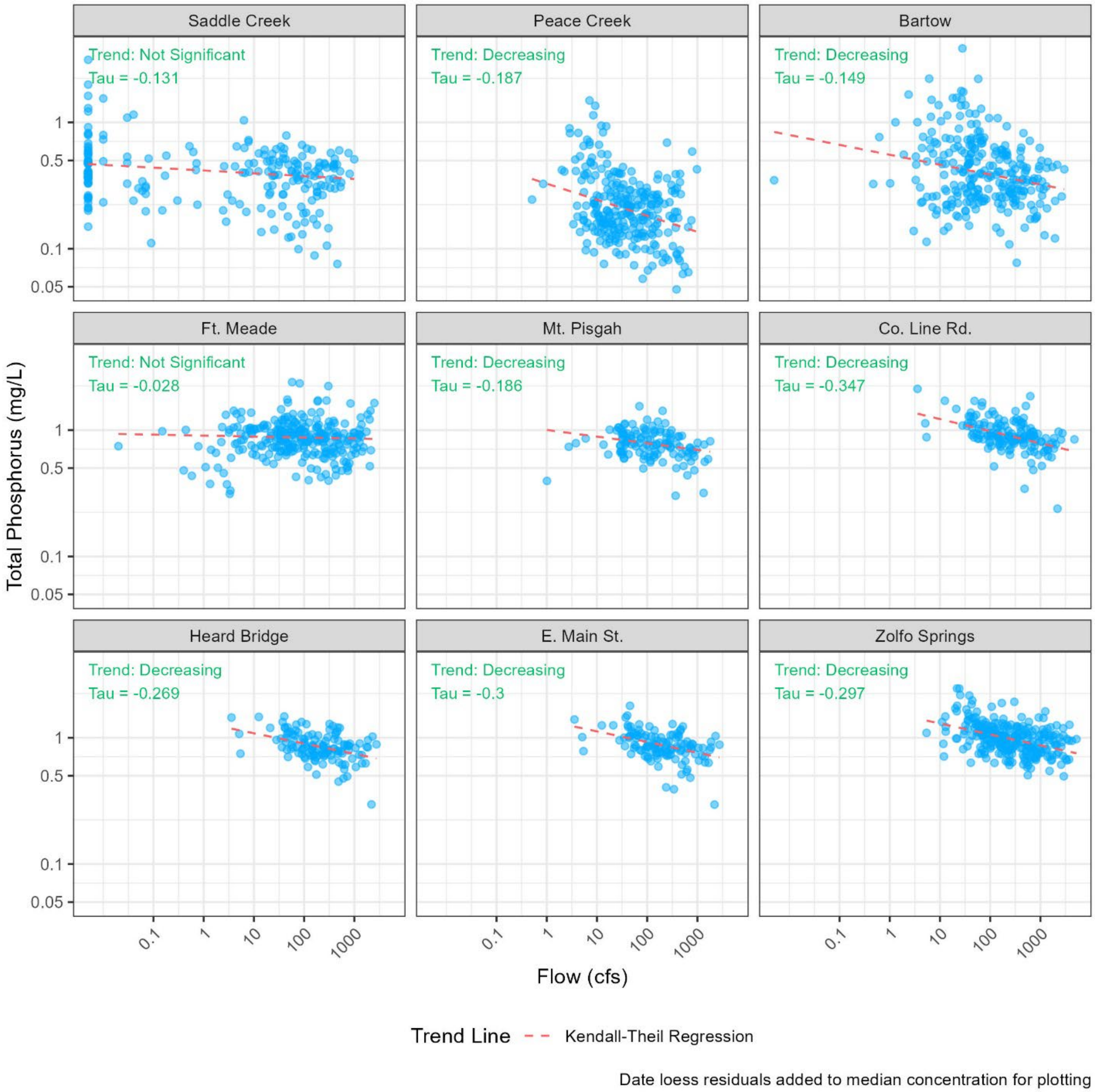


Figure 30. Date-adjusted relationships in total phosphorus concentrations with Flow across monitoring stations. Points show LOESS residuals from the date-concentration relationship (blue points) rescaled to the original concentration units, with Kendall-Theil regression lines (dashed red) indicating long-term trends. Text annotations provide the Sen slope (trend magnitude) and Kendall's tau correlation coefficient for each station. Note: Residuals are centered on the mean concentration for each station to maintain interpretable units.

Table 11. Summary of Kendall-Theil tests for trend with flow by station and parameter. Trends are classified as Increasing, Decreasing, or Not Significant, based on Kendall's tau significance (α = 0.05). Raw p values (p_raw) are adjusted using Bonferroni correction for number of stations tested (n_tests) to produce adjusted p values (p_adj).

Parameter	Station	slope	tau	n_tests	p_raw	p_adj	Trend
Nitrate-Nitrite	Saddle Creek	-2.721e-02	-0.095	9	4.531e-02	4.078e-01	Not Significant
Nitrate-Nitrite	Peace Creek	-3.519e-01	-0.337	9	9.538e-17	8.584e-16	Decreasing
Nitrate-Nitrite	Bartow	-2.454e-01	-0.23	9	1.47e-08	1.323e-07	Decreasing
Nitrate-Nitrite	Ft. Meade	-2.205e-01	-0.278	9	5.441e-12	4.897e-11	Decreasing
Nitrate-Nitrite	Mt. Pisgah	-3.91e-01	-0.439	9	1.76e-12	1.584e-11	Decreasing
Nitrate-Nitrite	Co. Line Rd.	-4.212e-01	-0.472	9	8.192e-17	7.373e-16	Decreasing
Nitrate-Nitrite	Heard Bridge	-3.233e-01	-0.435	9	6.103e-13	5.493e-12	Decreasing
Nitrate-Nitrite	E. Main St.	-3.73e-01	-0.454	9	7.841e-14	7.057e-13	Decreasing
Nitrate-Nitrite	Zolfo Springs	-2.535e-01	-0.352	9	2.031e-18	1.828e-17	Decreasing
Total Nitrogen	Saddle Creek	-3.006e-02	-0.18	9	1.57e-04	1.413e-03	Decreasing
Total Nitrogen	Peace Creek	5.386e-02	0.228	9	8.45e-04	7.605e-03	Increasing
Total Nitrogen	Bartow	1.441e-02	0.075	9	2.666e-01	2.4e+00	Not Significant
Total Nitrogen	Ft. Meade	-6.344e-02	-0.212	9	1.531e-03	1.378e-02	Decreasing
Total Nitrogen	Mt. Pisgah	-6.475e-02	-0.192	9	2.635e-03	2.372e-02	Decreasing
Total Nitrogen	Co. Line Rd.	-5.964e-02	-0.178	9	2.349e-03	2.114e-02	Decreasing
Total Nitrogen	Heard Bridge	-9.072e-03	-0.028	9	6.552e-01	5.897e+00	Not Significant
Total Nitrogen	E. Main St.	-3.238e-02	-0.087	9	1.809e-01	1.628e+00	Not Significant
Total Nitrogen	Zolfo Springs	-3.739e-02	-0.176	9	8.802e-03	7.922e-02	Not Significant
Orthophosphate	Peace Creek	-1.768e-01	-0.221	8	7.036e-08	5.629e-07	Decreasing
Orthophosphate	Bartow	-1.488e-01	-0.175	8	1.784e-05	1.427e-04	Decreasing

Orthophosphate	Ft. Meade	-5.94e-03	-0.019	8	6.306e-01	5.045e+00	Not Significant
Orthophosphate	Mt. Pisgah	-6.987e-02	-0.214	8	3.715e-04	2.972e-03	Decreasing
Orthophosphate	Co. Line Rd.	-1.326e-01	-0.455	8	3.357e-14	2.685e-13	Decreasing
Orthophosphate	Heard Bridge	-1.135e-01	-0.361	8	1.453e-09	1.163e-08	Decreasing
Orthophosphate	E. Main St.	-9.877e-02	-0.366	8	1.41e-09	1.128e-08	Decreasing
Orthophosphate	Zolfo Springs	-1.176e-01	-0.356	8	1.816e-18	1.452e-17	Decreasing
Total Phosphorus	Saddle Creek	-2.216e-02	-0.131	9	5.856e-03	5.27e-02	Not Significant
Total Phosphorus	Peace Creek	-1.271e-01	-0.187	9	4.687e-06	4.218e-05	Decreasing
Total Phosphorus	Bartow	-7.849e-02	-0.149	9	2.777e-04	2.499e-03	Decreasing
Total Phosphorus	Ft. Meade	-7.638e-03	-0.028	9	4.832e-01	4.349e+00	Not Significant
Total Phosphorus	Mt. Pisgah	-5.259e-02	-0.186	9	2.059e-03	1.853e-02	Decreasing
Total Phosphorus	Co. Line Rd.	-9.586e-02	-0.347	9	3.428e-10	3.085e-09	Decreasing
Total Phosphorus	Heard Bridge	-8.152e-02	-0.269	9	7.798e-06	7.019e-05	Decreasing
Total Phosphorus	E. Main St.	-8.43e-02	-0.3	9	8.097e-07	7.287e-06	Decreasing
Total Phosphorus	Zolfo Springs	-8.661e-02	-0.297	9	2.427e-13	2.184e-12	Decreasing

Table 12. Summary of flow-adjusted concentration trends with date showing counts of increasing, decreasing, and not-significant results.

Parameter	n_increasing	n_decreasing	n_not_significant
Nitrate-Nitrite	1	3	5
Total Nitrogen	0	4	5
Orthophosphate	0	5	3
Total Phosphorus	0	5	4
Total	1	17	17

Table 13. Summary of date-adjusted concentration trends with flow showing counts of increasing, decreasing, and not-significant results.

Parameter	n_increasing	n_decreasing	n_not_significant
Nitrate-Nitrite	0	8	1
Total Nitrogen	1	4	4
Orthophosphate	0	7	1
Total Phosphorus	0	7	2
Total	1	26	8

Clarity: Chlorophyll, Turbidity, Total Suspended Solids, and Color

The clarity of water can be affected by numerous factors, the most important of which are chlorophyll, turbidity, total suspended solids, and color. Chlorophyll a is a critical indicator of phytoplankton abundance and overall productivity in aquatic ecosystems, making it a key parameter in water quality assessments. Turbidity and total suspended solids (TSS) are different ways to measure similar water quality characteristics. TSS is the concentration of suspended particles, which include soil particles (clay, silt, organic matter), algae, and microscopic organisms. Turbidity is an optical property of water rather than a chemical or biological measurement. Similarly, color, both apparent and true, is an optical property of water, measured in Platinum Cobalt Units (PCU) based on comparison with a standard platinum-cobalt solution. Apparent color is based on unfiltered samples and includes effects of suspended solids, while true color is based on filtered samples and reflects influence of tannins and other dissolved molecules.

The color parameter reported varies by Station: Saddle Creek has "color", Peace Creek, Bartow, Ft. Meade, and Zolfo Springs have “Color – True”, and Mt. Pisgah, Co. Line Rd. Heard Bridge and E. Main St. have “Color – Apparent”. These will all be referred to simply as “color” from here on. Only corrected Chlorophyll a is analyzed here. TSS is reported as both Total Suspended Solids (Tss) and Residues- Nonfilterable (Tss), both of which are included in this analysis simply as “TSS”.

Location, spread, and normality

These parameters have different units and are associated with different biogeochemical processes in the environment, limiting the utility of comparison of their quantiles, but comparing skewness and frequency distributions is still possible.

Means and medians across all sites for key nutrient statistics including chlorophyll a, color, TSS, and turbidity are shown in Table 14. Quantile plots illustrate distributions of nutrient data (Figure 31). These are plotted on a log scale due to right skewness and overdispersion. Boxplots (Figure 32) provide visual summaries of 1) the center of the data (the median--the center line of the box), 2) the variation or spread (interquartile range--the box height), 3) the skewness (quartile skew--the relative size of box halves), and 4) presence or absence of unusual values ("outside" – lines, and "far outside" values - circles). The data are displayed on a log scale due to the wide range of concentrations.

Histograms are quite useful for depicting large differences in shape or symmetry, such as whether a data set appears symmetric or skewed (Figure 33) (Helsel and Hirsch 2002).

Comparing nutrient sampling distributions, we see that chlorophyll a is the most skewed with the highest skewness coefficient (G) and quartile skew coefficient (QS) (Table 14). Color, TSS, and turbidity are also positively skewed.

Probability plots of log-transformed data illustrate how well data fit a lognormal distribution (Figure 34). Normal quantiles are the data values expected based on a normal distribution with the same mean and standard deviation of the sample data. The probability plot correlation coefficient (PPCC) tests for normality by computing the linear correlation coefficient between data and their normal quantiles. Samples from a normal distribution will have a correlation coefficient very close to 1.0. As data depart from normality, their correlation coefficient will decrease below 1. The critical correlation value corresponds to the value the correlation coefficient must exceed for the data to be considered normally distributed. All parameters are non-normal according to the PPCC as well as Anderson-Darling test for normality after Log10 transformation of data (Table 15).

Table 14. Univariate summary statistics for nutrients at all sites. The interquartile range (IQR) = P75 – P25. The skewness coefficient (G) is the adjusted third moment divided by the cube of the standard deviation, and is a measure of skewness that is sensitive to outliers (Helsel and Hirsch 2002). The quartile skew coefficient (QS) quantifies skewness as the difference in distances of the upper and lower quartiles from the median, divided by the IQR for a resistant measure of skewness.

Parameter	Min	P25	P50	Mean	P75	Max	Obs	G	IQR	QS
Chlorophyll a (µg/L)	0.50	2.10	5.17	42.3	20.6	1628	1610	5.682	18.485	0.668
Color (PCU)	5.00	73.50	130.00	144.7	200.0	600	1811	1	126.5	0.107
TSS (mg/L)	0.25	3.56	6.54	10.0	11.8	151	1516	4.623	8.265	0.28
Turbidity (NTU)	0.07	4.38	7.30	10.6	12.3	103	1851	2.933	7.925	0.262

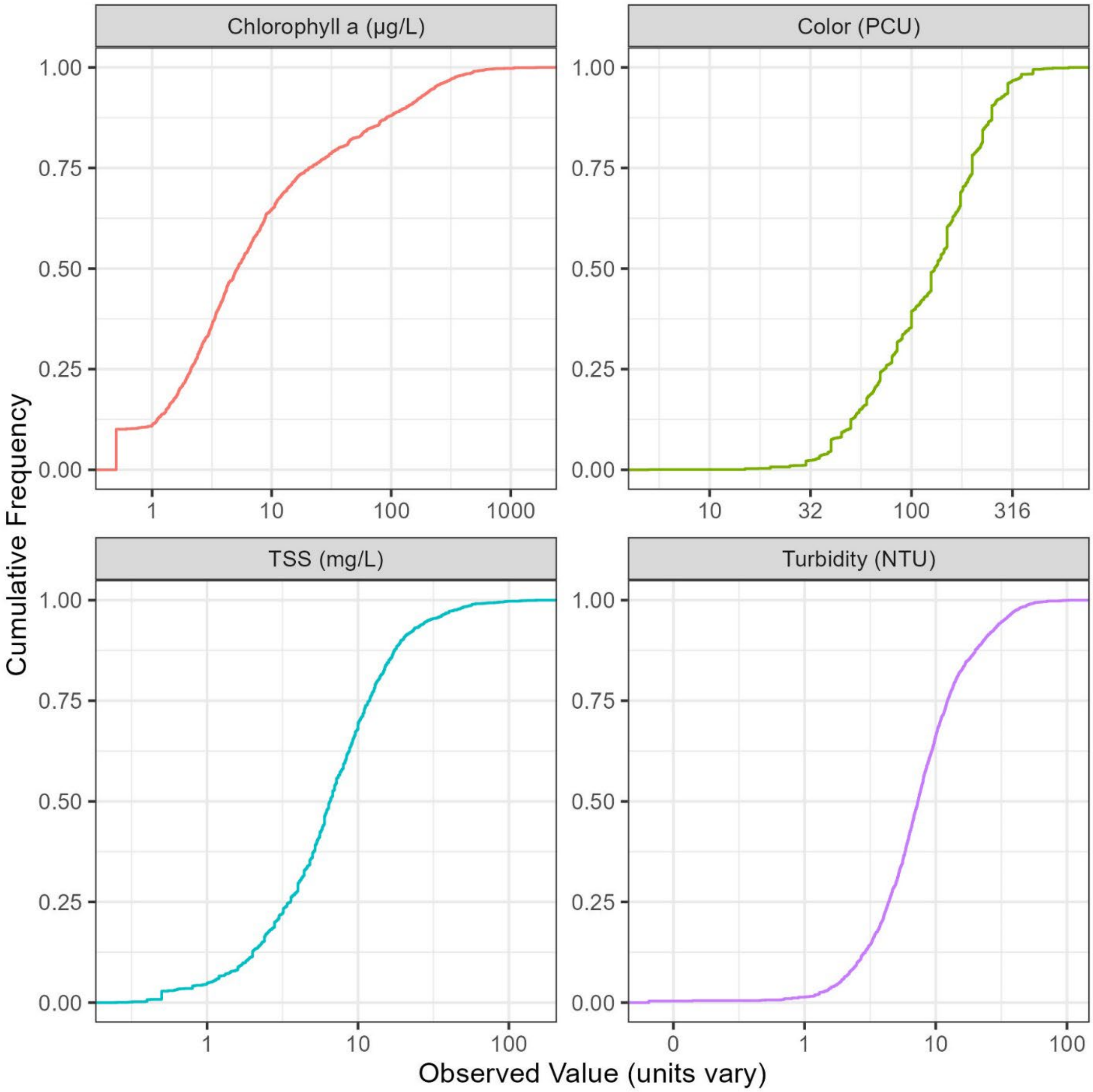


Figure 31. Quantiles of parameter values. Quantile plots visually portray the quantiles, or cumulative frequency of observations of nutrient concentrations. Quantiles of importance such as the median are easily discerned (quantile, or cumulative frequency = 0.5) (Helsel and Hirsch 2002).

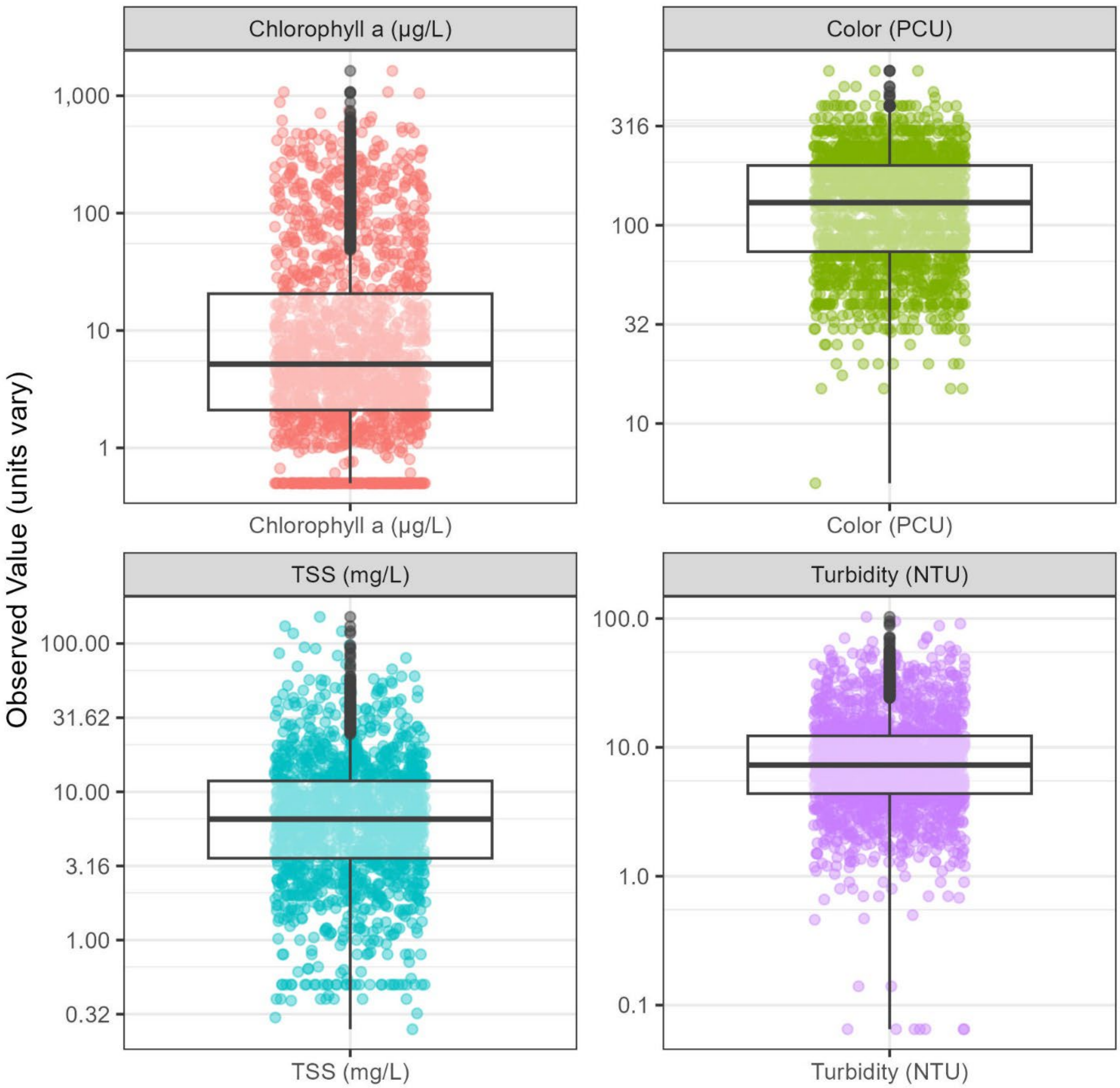


Figure 32. Concentrations of chlorophyll a, color, TSS, and turbidity using jittered points to display individual data values and boxplots to summarize the distribution. The y-axis is scaled logarithmically to better visualize the range of concentrations, and boxplot statistics are calculated on non-transformed data.

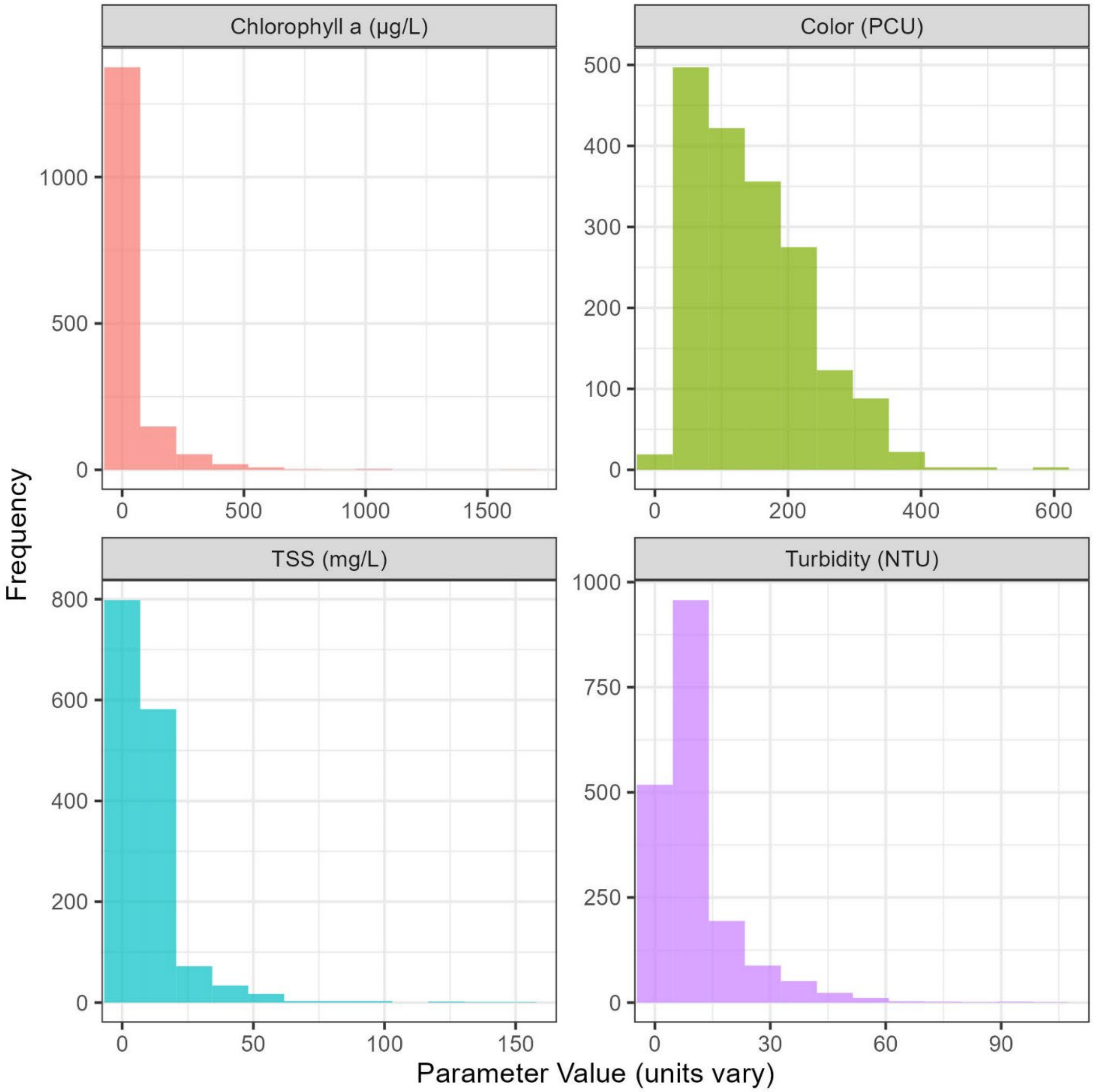


Figure 33. Frequency distributions of chlorophyll a, color, TSS, and turbidity. Each panel represents a specific parameter, with the x-axis showing Chlorophyll a in ug/L, Color in PCU, TSS in mg/L, Turbidity in NTU) and the y-axis indicating frequency. The scales are adjusted per nutrient to highlight their unique distribution patterns, and consistent colors are used to differentiate the parameters.

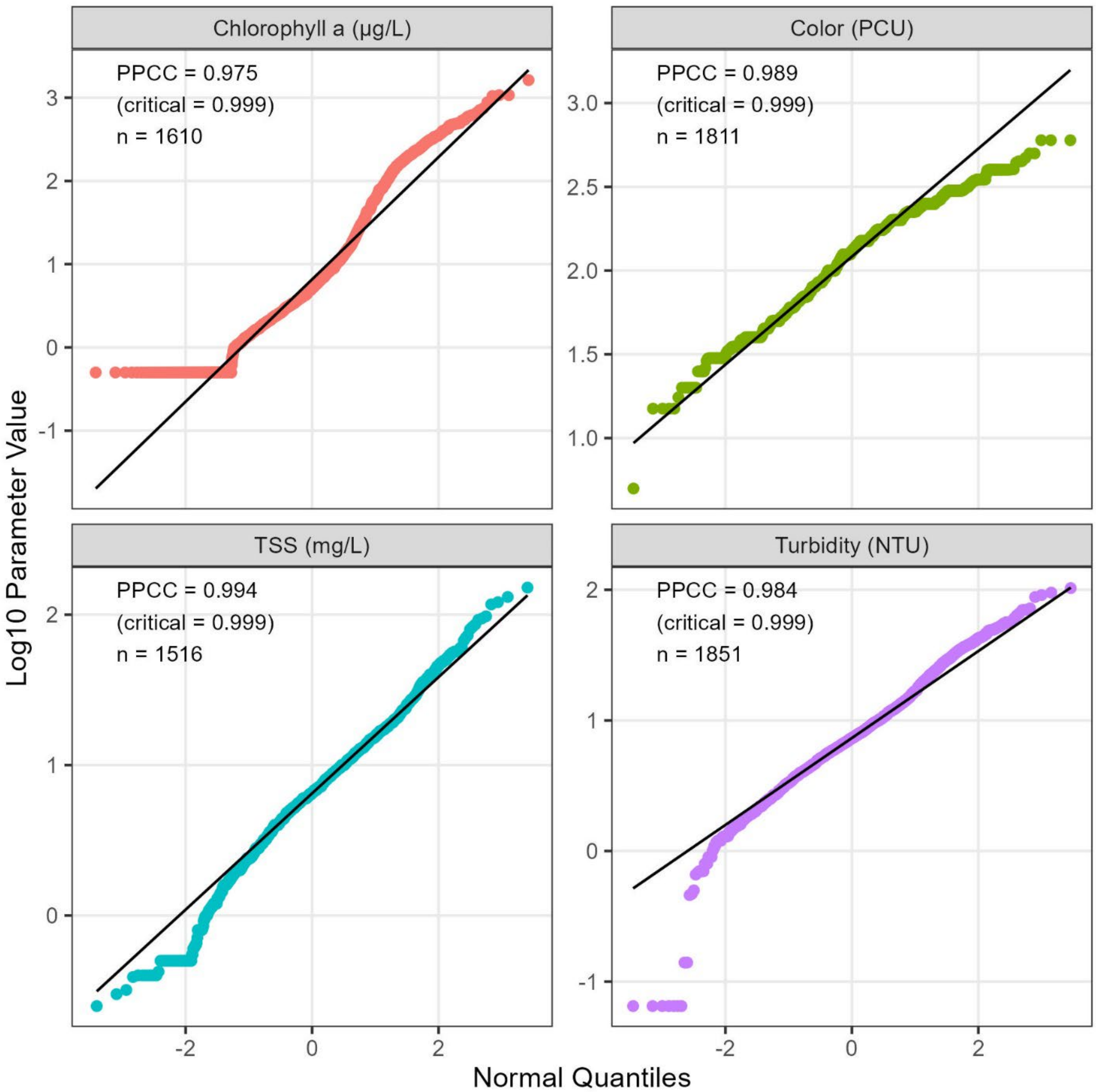


Figure 34. Normal probability plots for parameter concentrations, comparing theoretical quantiles to sample quantiles. Normal quantiles are values expected from a perfectly normal distribution at specific probabilities, serving as a reference for normality. If the data follow a normal distribution, the points align closely with the diagonal line. Deviations from the line indicate departures from normality. The Probability Plot Correlation Coefficient (PPCC) is the linear correlation coefficient between data and their normal quantiles. PPCC values below the critical value indicate rejection of null hypothesis that data are from a normal distribution. All plots show non-normal distributions.

Table 15. Results of Anderson-Darling test for normality of log10 transformed data. All parameters are non-normal with p values well below 0.001.

Parameter	AD_statistic	p_AD
Chlorophyll a (µg/L)	23.36792	3.7E-24
Color (PCU)	13.49858	3.7E-24
TSS (mg/L)	5.333382	3.65E-13
Turbidity (NTU)	5.353717	3.27E-13

Testing for difference between groups

There are significant differences between wet and dry seasons for color, TSS and turbidity but not for chlorophyll a (Table 16) (Figure 35). Pairwise comparisons of stations for each parameter are summarized in Figure 36 through Figure 39, with pairwise Wilcoxon results shown. Pairwise Wilcoxson tests reveal differences between nine stations in chlorophyll a (Figure 36), color (Figure 37), TSS (Figure 38), and turbidity (Figure 39). Chlorophyll is highest at Saddle Creek, which is the outlet for Lake Hancock, and lowest in Peace Creek and at Zolfo Springs (Figure 36). Note that while Mt. Pisgah through E. Main St. report apparent color, while other stations report true color, they do not have higher values of PCU, and the highest values are found at Peace Creek, which reports true (filtered) color (Figure 37).

Table 16. Kruskal-Wallace tests for differences between Stations, Seasons, and Station*Season interactions.

Parameter	Station chi	Station p	Season chi	Season p	Interaction chi	Interaction p
Chlorophyll a (µg/L)	577.8777	1.3E-119	0.971567	0.32429	598.3772	3.1E-116
Color (PCU)	427.7533	2.15E-87	291.1121	2.85E-65	752.5238	5.9E-149
TSS (mg/L)	121.038	4.66E-23	45.22092	1.76E-11	178.1195	5.69E-30
Turbidity (NTU)	589.0032	5.4E-122	7.168528	0.007419	615.3957	7.8E-120

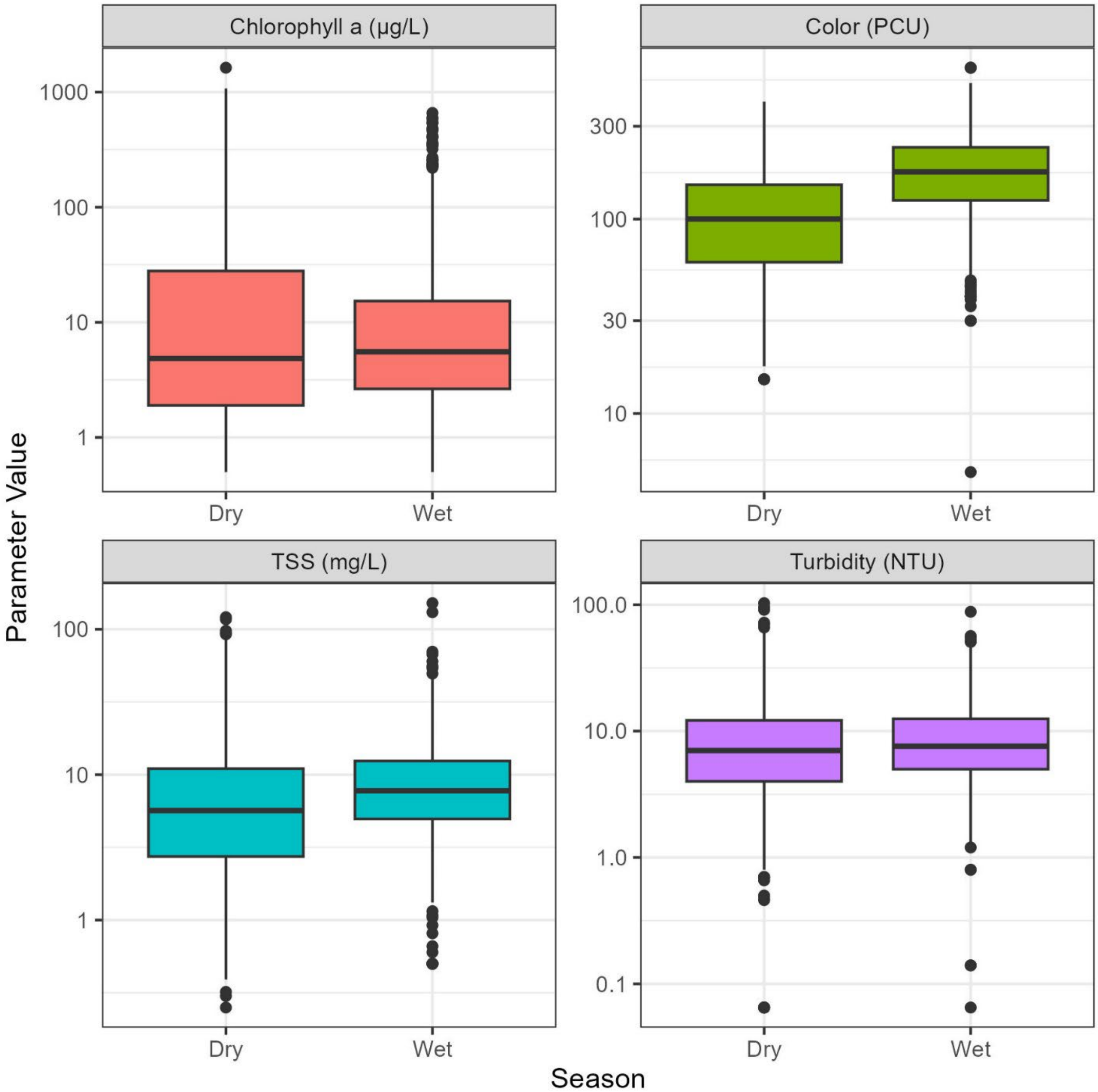


Figure 35. Seasonal differences in nutrient concentrations

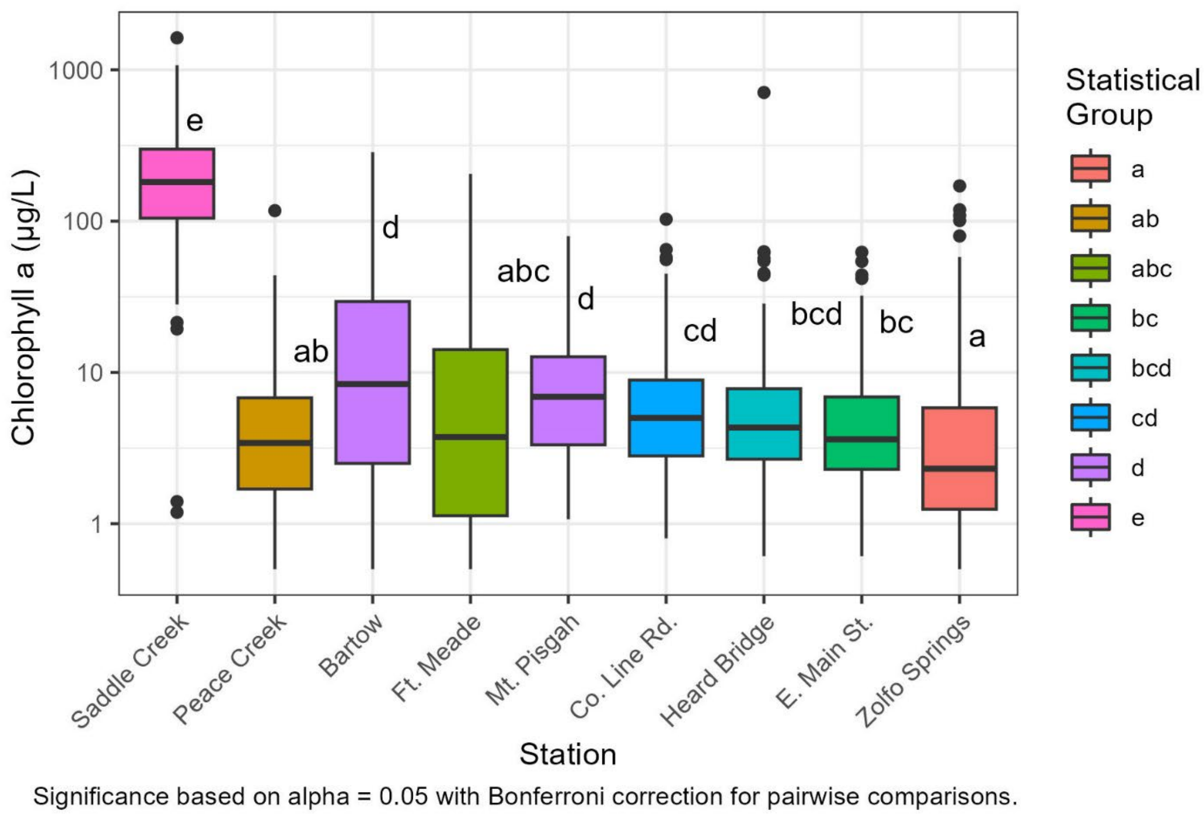


Figure 36. Statistical Grouping of chlorophyll a by Station Using Pairwise Wilcoxon Tests

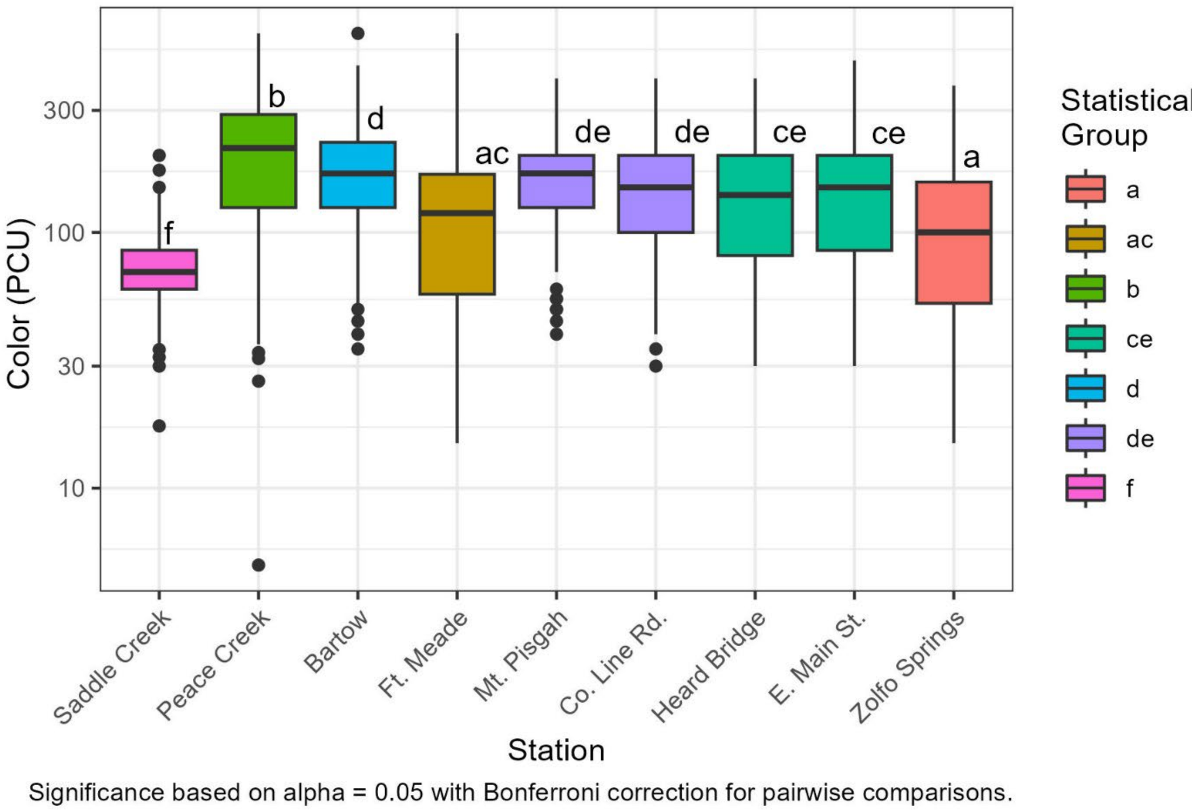


Figure 37. Statistical Grouping of color by Station Using Pairwise Wilcoxon Tests

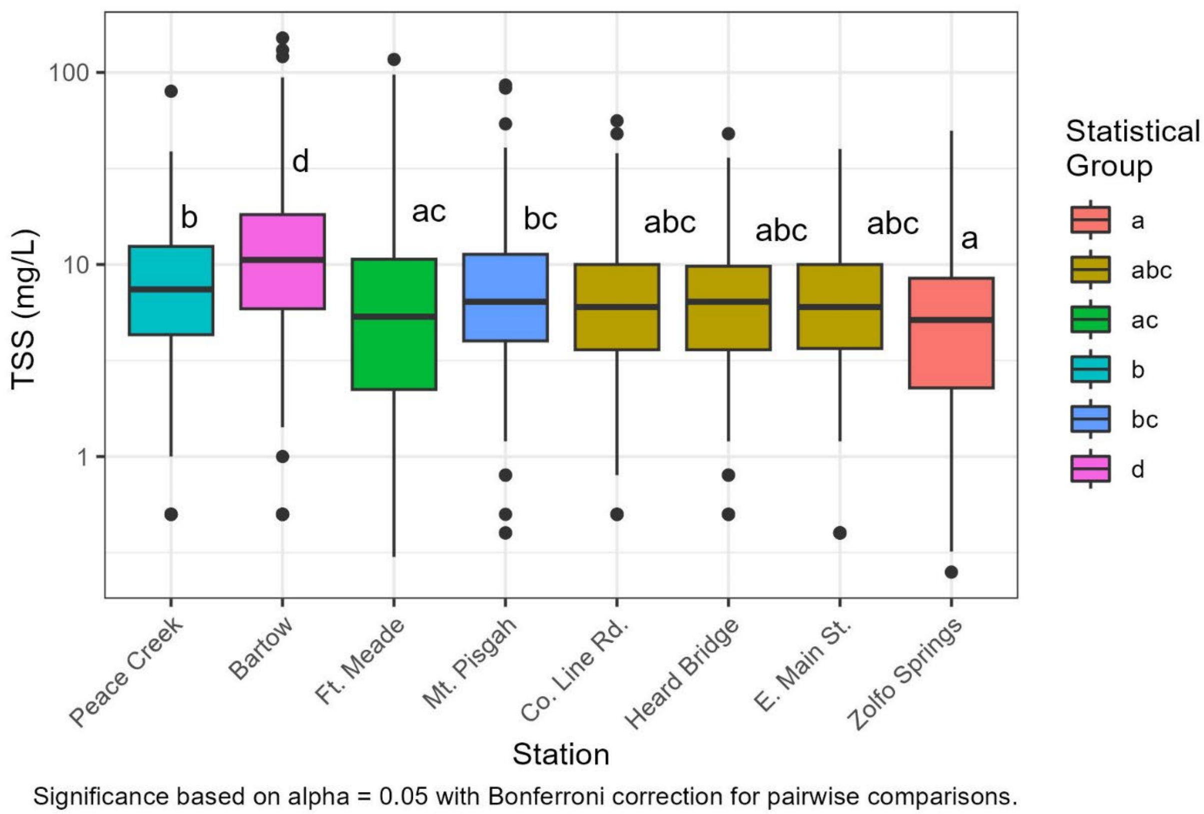


Figure 38. Statistical Grouping of TSS by Station Using Pairwise Wilcoxon Tests

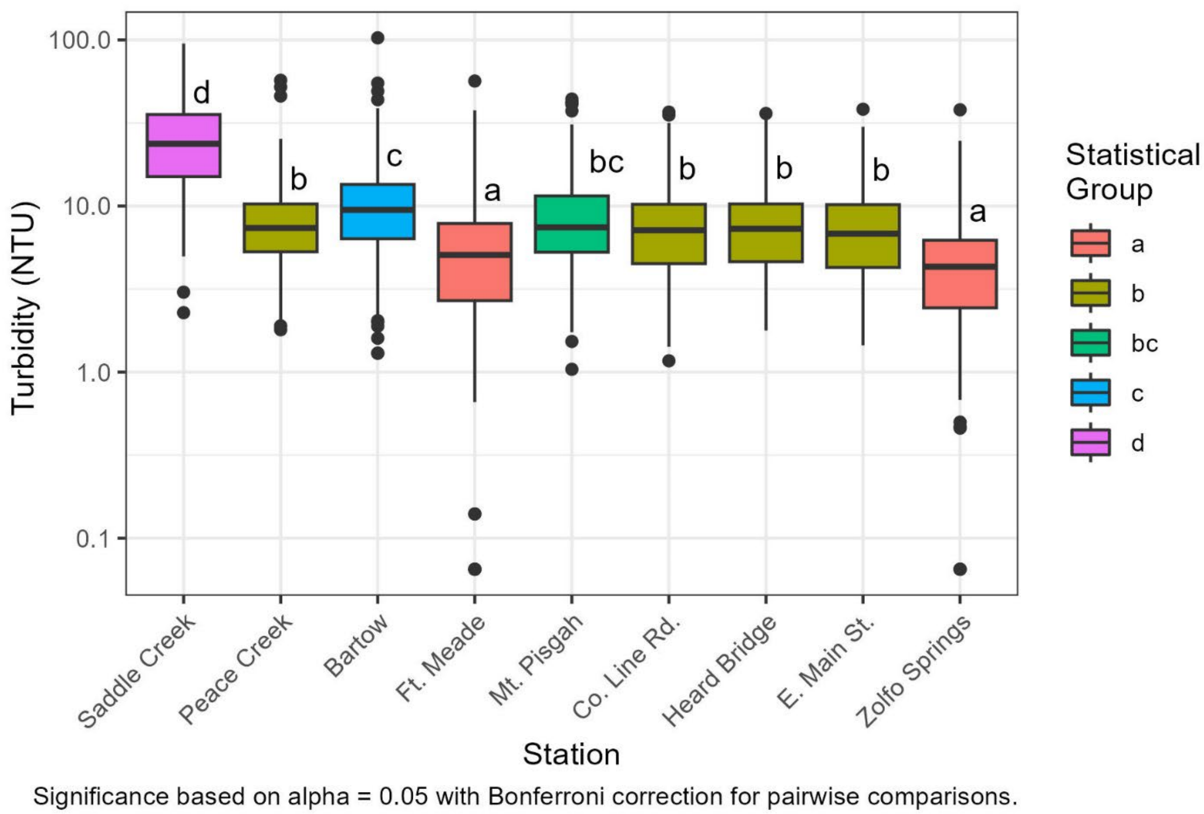


Figure 39. Statistical Grouping of turbidity by Station Using Pairwise Wilcoxon Tests

Trends

This analysis examines both flow-based and temporal trends in water quality parameters using a two-stage approach following Helsel and Hirsch (2002). We first analyze concentration-date relationships using LOESS smoothing, then use these residuals to examine flow relationships. In a parallel analysis, we examine concentration-flow relationships with LOESS, using those residuals to assess temporal trends. Both approaches employ Kendall's tau with Bonferroni-adjusted p-values (p_adjusted = p_initial * n, where n is the number of stations) and Theil-Sen slopes for trend detection. This dual analysis allows examination of both flow-concentration patterns and temporal trends while controlling for their mutual influences.

The analysis sequence includes:

1. Concentration-date relationships with LOESS smoothing for chlorophyll a (Figure 40), color (Figure 41), TSS (Figure 42), and turbidity (Figure 43). These plots provide a visual representation of nonlinear temporal patterns for each station.

2. Concentration-flow relationships with LOESS smoothing for chlorophyll a (Figure 44), color (Figure 45), TSS (Figure 46), and turbidity (Figure 47) visualize nonlinear patterns in water quality parameters with flow at each of the nine stations.

3. Residuals from concentration-flow relationships represent flow-adjusted concentrations which can be compared with dates to determine temporal relationships with chlorophyll a (Figure 48), color (Figure 49), TSS (Figure 50), and turbidity (Figure 51). Kendall-Theil lines show increasing, decreasing and not significant relationships depending on the water quality sampling location (Table 17). Statistical significance is based on Bonferroni-corrected p-values adjusted for 9 stations.

4. Residuals from date-flow Loess represent date-adjusted concentration which is related to flow for chlorophyll a (Figure 52), color (Figure 53), TSS (Figure 54), and turbidity (Figure 55). with Kendall-Theil lines show increasing, decreasing and not significant relationships depending on the water quality sampling location (Table 18). Statistical significance is based on Bonferroni-corrected p-values adjusted for 9 stations.

The analysis revealed both temporal and flow-dependent trends across stations, suggesting that water quality dynamics are influenced by a combination of temporal and hydrological factors. Most temporal trends were not significant (28) while 4 trends were decreasing through time, and 3 showed significant increases (Table 19). The majority of flow trends were decreasing (24), while 11 trends were not significant and 0 were increasing (Table 20).

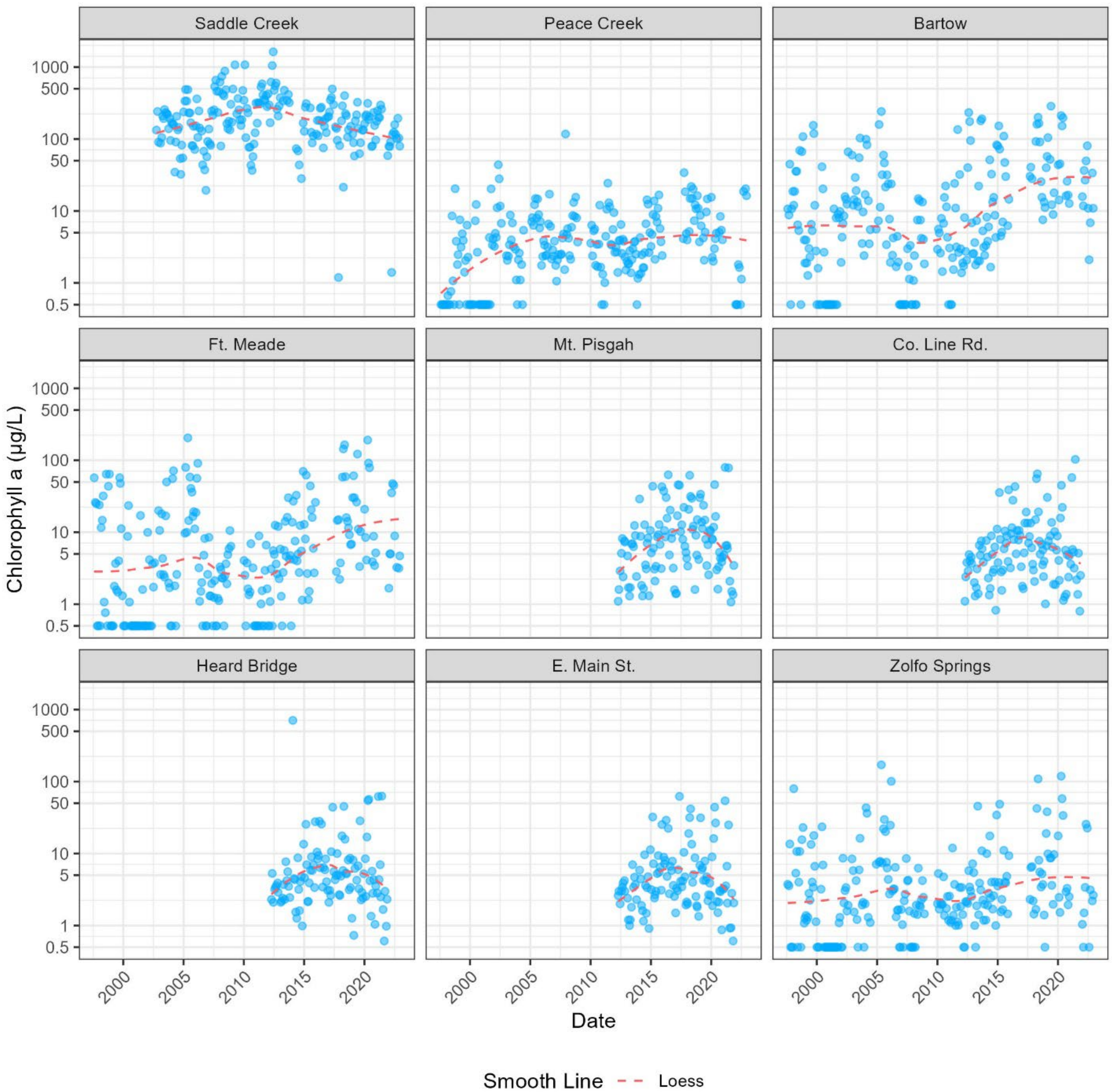


Figure 40. Time series showing observed chlorophyll a (ug/L) concentrations (blue points) with LOESS smoothing curves (dashed red lines) across monitoring stations. The LOESS curves capture temporal patterns in the data, with residuals from these fits used for subsequent flow-adjusted trend analysis. Note: Concentrations are displayed on a logarithmic scale.

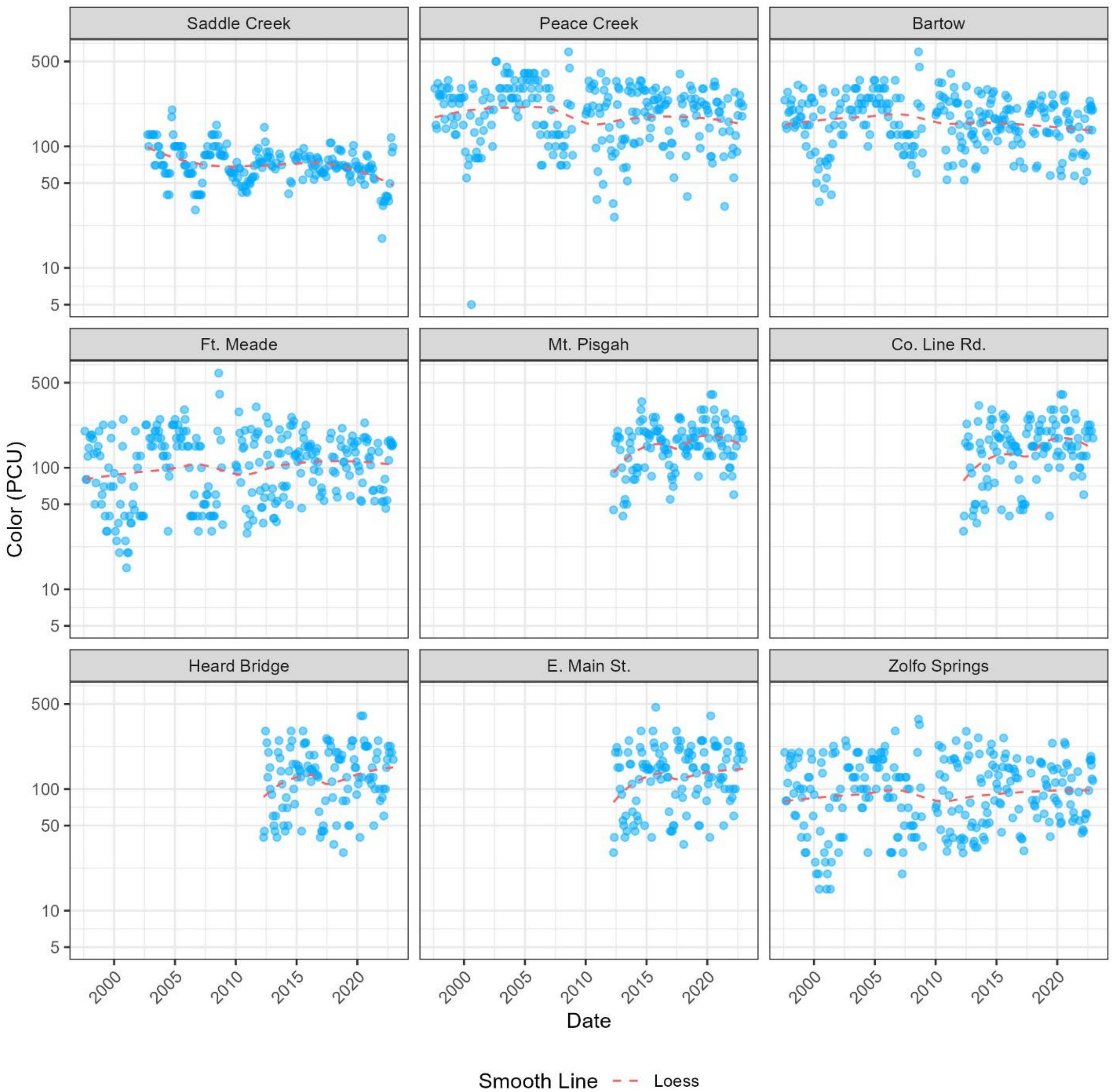


Figure 41. Time series showing observed color (PCU) concentrations (blue points) with LOESS smoothing curves (dashed red lines) across monitoring stations. The LOESS curves capture temporal patterns in the data, with residuals from these fits used for subsequent flow-adjusted trend analysis. Note: Concentrations are displayed on a logarithmic scale.

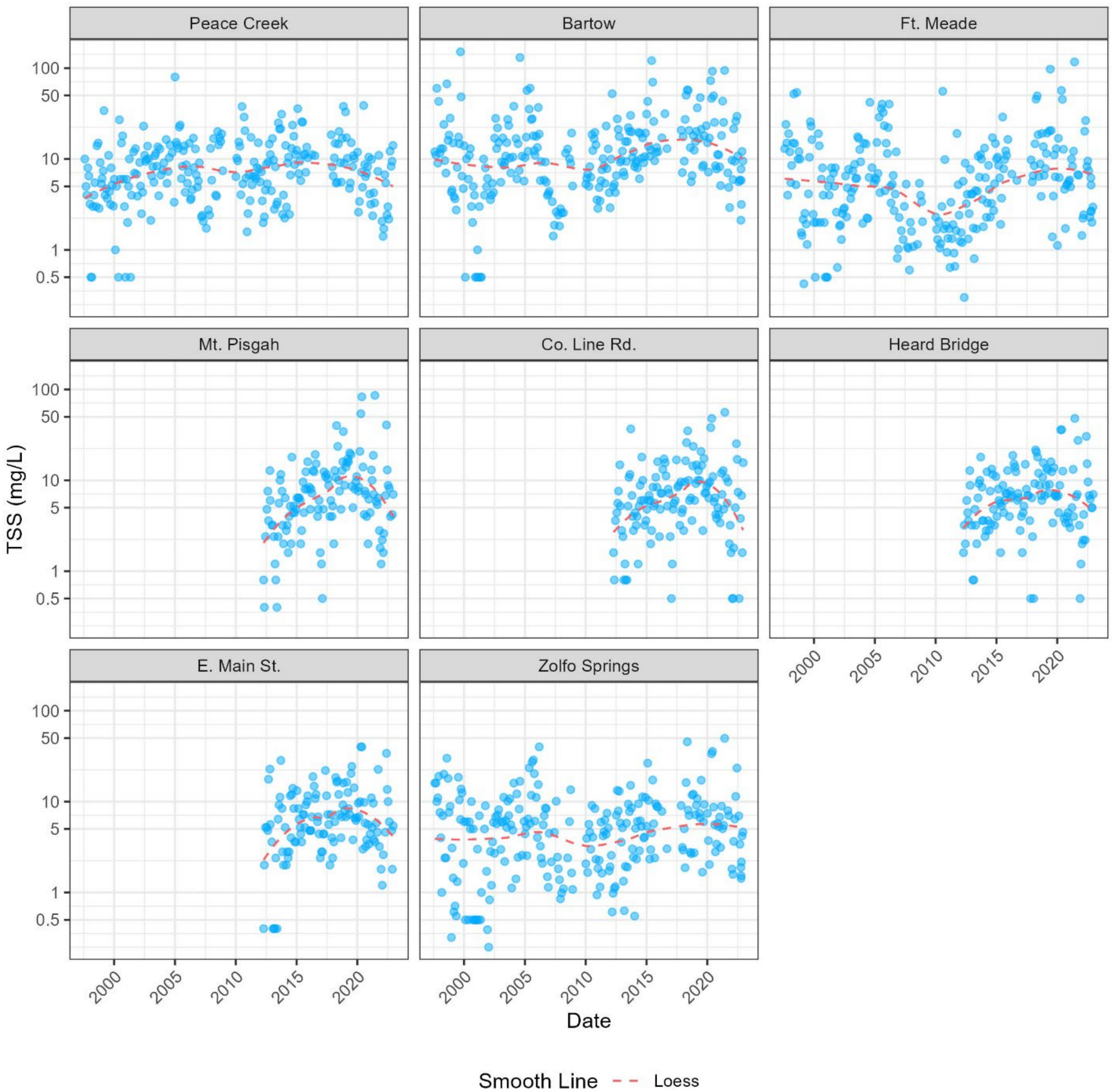


Figure 42. Time series showing observed TSS (mg/L) concentrations (blue points) with LOESS smoothing curves (dashed red lines) across monitoring stations. The LOESS curves capture temporal patterns in the data, with residuals from these fits used for subsequent flow-adjusted trend analysis. Note: Concentrations are displayed on a logarithmic scale.

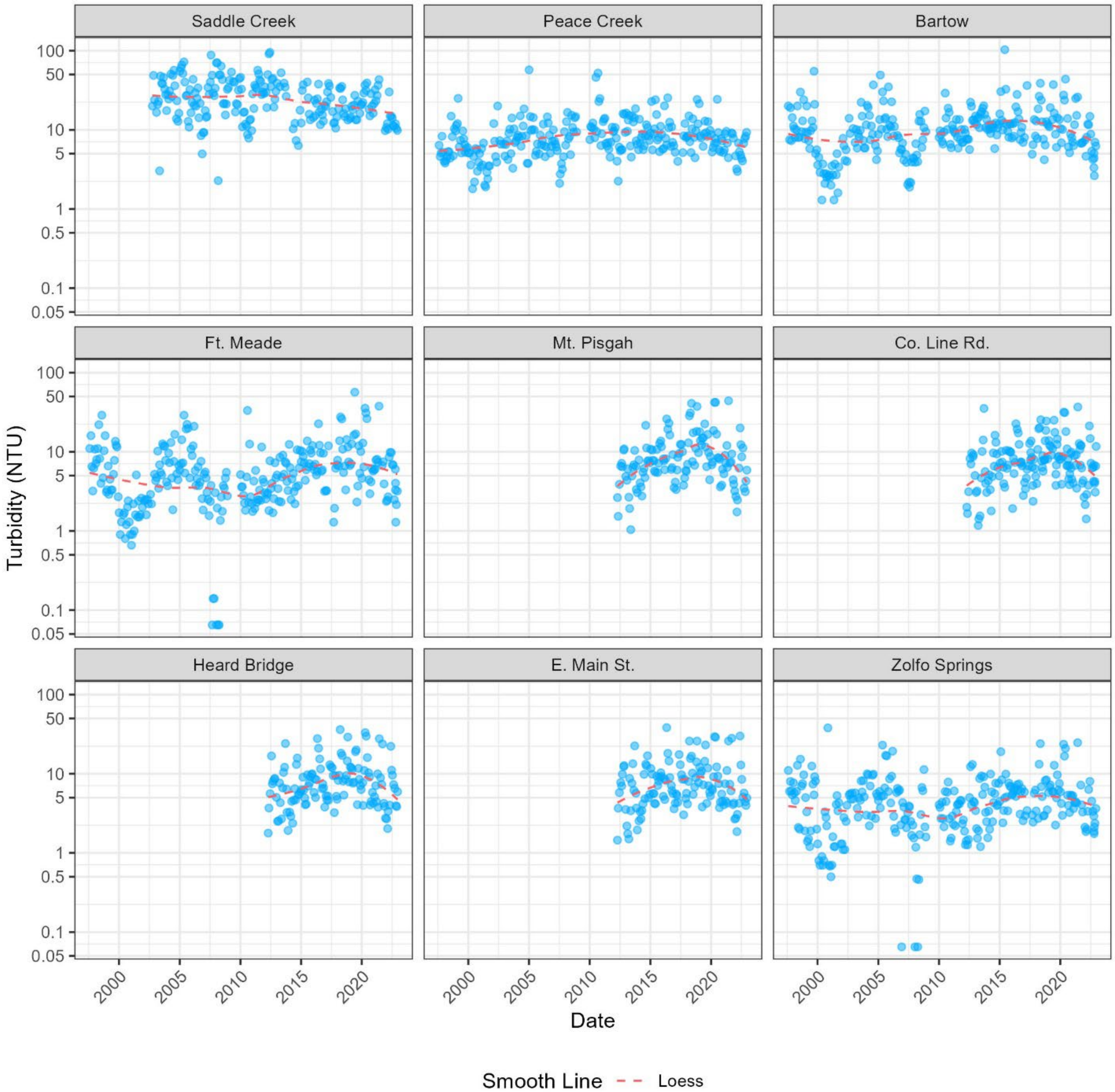


Figure 43. Time series showing observed turbidity (NTU) concentrations (blue points) with LOESS smoothing curves (dashed red lines) across monitoring stations. The LOESS curves capture temporal patterns in the data, with residuals from these fits used for subsequent flow-adjusted trend analysis. Note: Concentrations are displayed on a logarithmic scale.

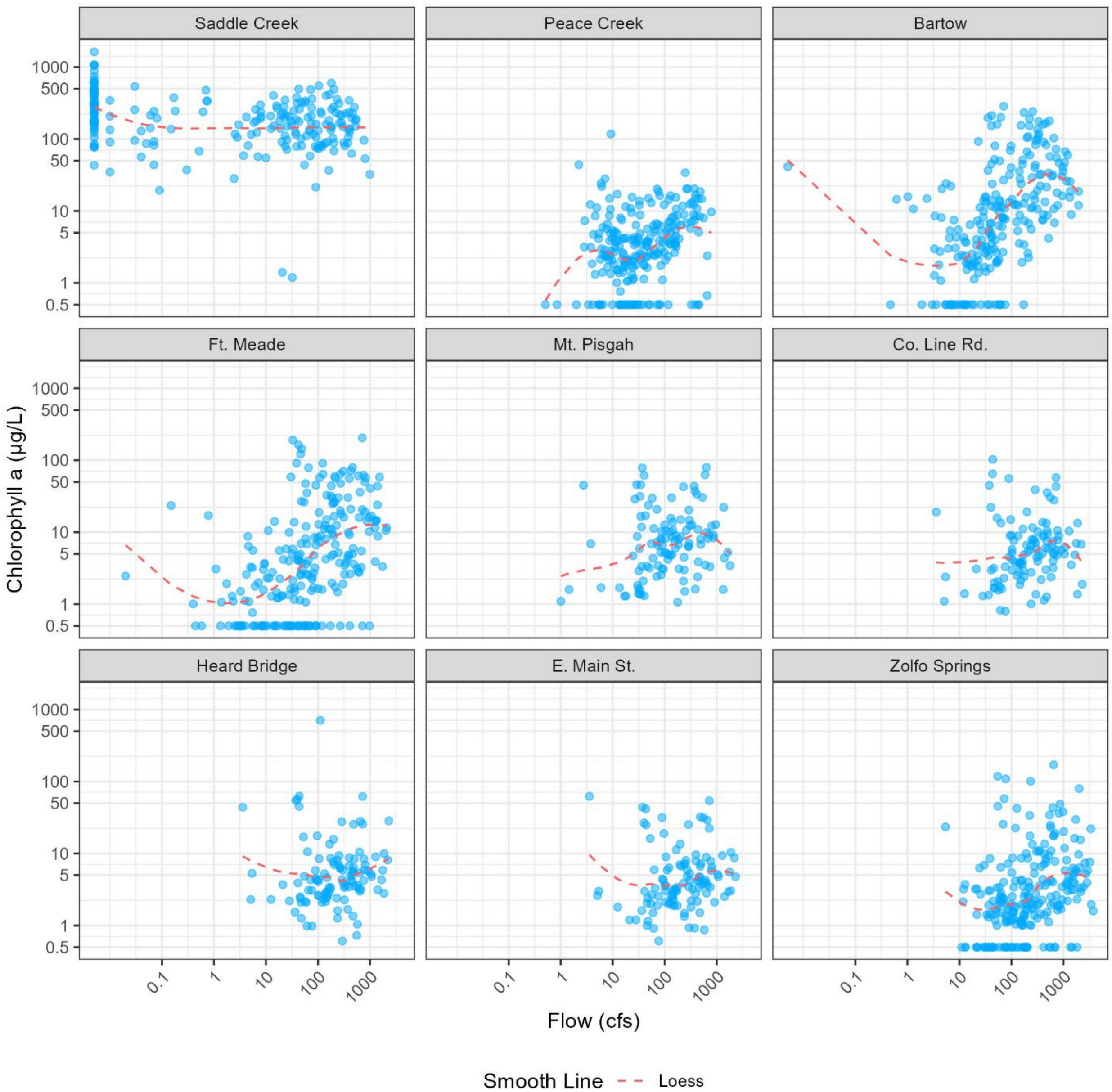


Figure 44. Relationship between streamflow and chlorophyll a (ug/L) concentrations (blue points) with LOESS smoothing curves (dashed red lines) across monitoring stations. The LOESS curves capture flow-concentration patterns in the data, with residuals from these fits used for subsequent trend analysis. Note: Both flow and concentration are displayed on logarithmic scales.

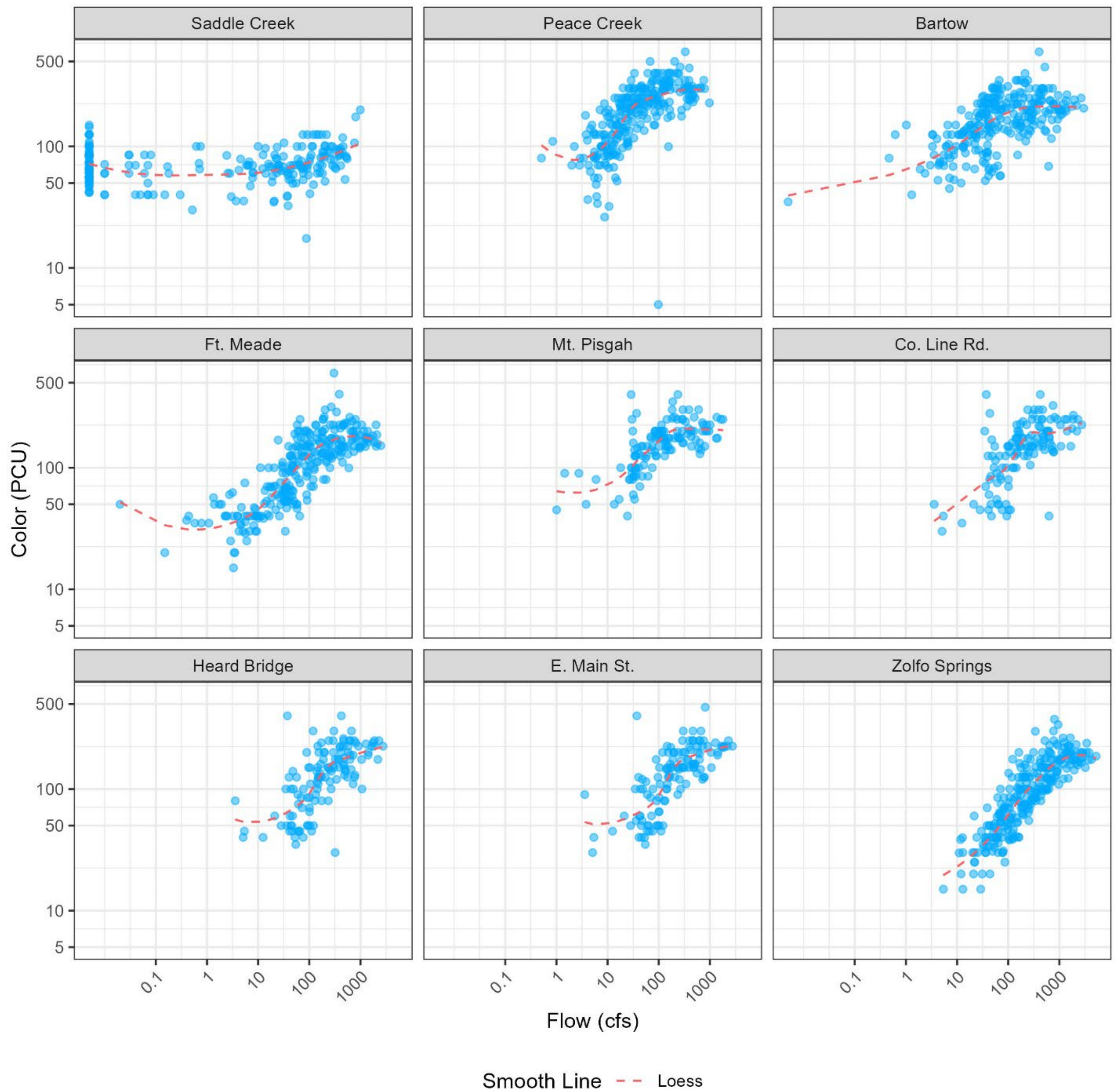


Figure 45. Relationship between streamflow and color (PCU) concentrations (blue points) with LOESS smoothing curves (dashed red lines) across monitoring stations. The LOESS curves capture flow-concentration patterns in the data, with residuals from these fits used for subsequent trend analysis. Note: Both flow and concentration are displayed on logarithmic scales.

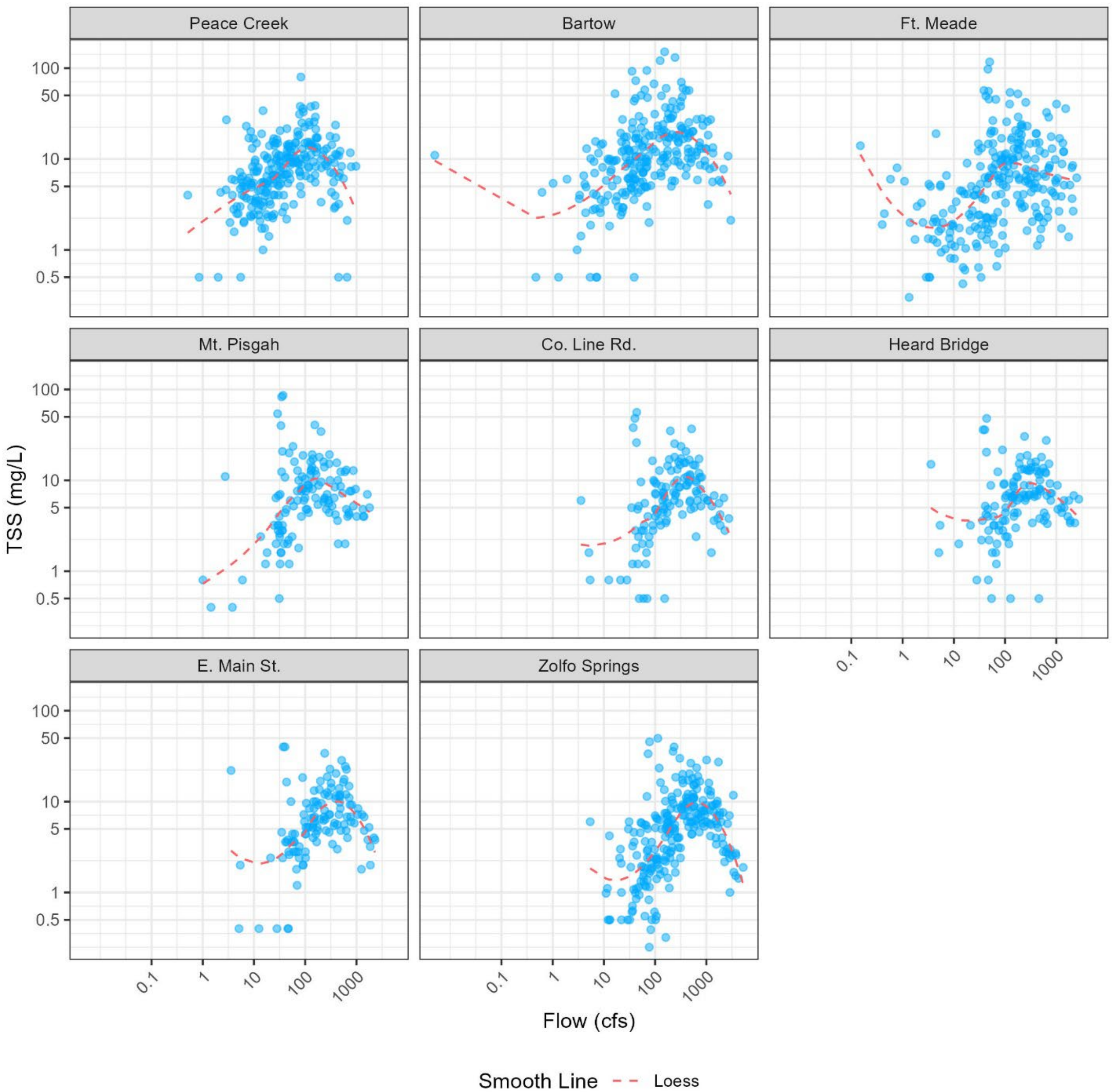


Figure 46. Relationship between streamflow and TSS (mg/L) concentrations (blue points) with LOESS smoothing curves (dashed red lines) across monitoring stations. The LOESS curves capture flow-concentration patterns in the data, with residuals from these fits used for subsequent trend analysis. Note: Both flow and concentration are displayed on logarithmic scales.

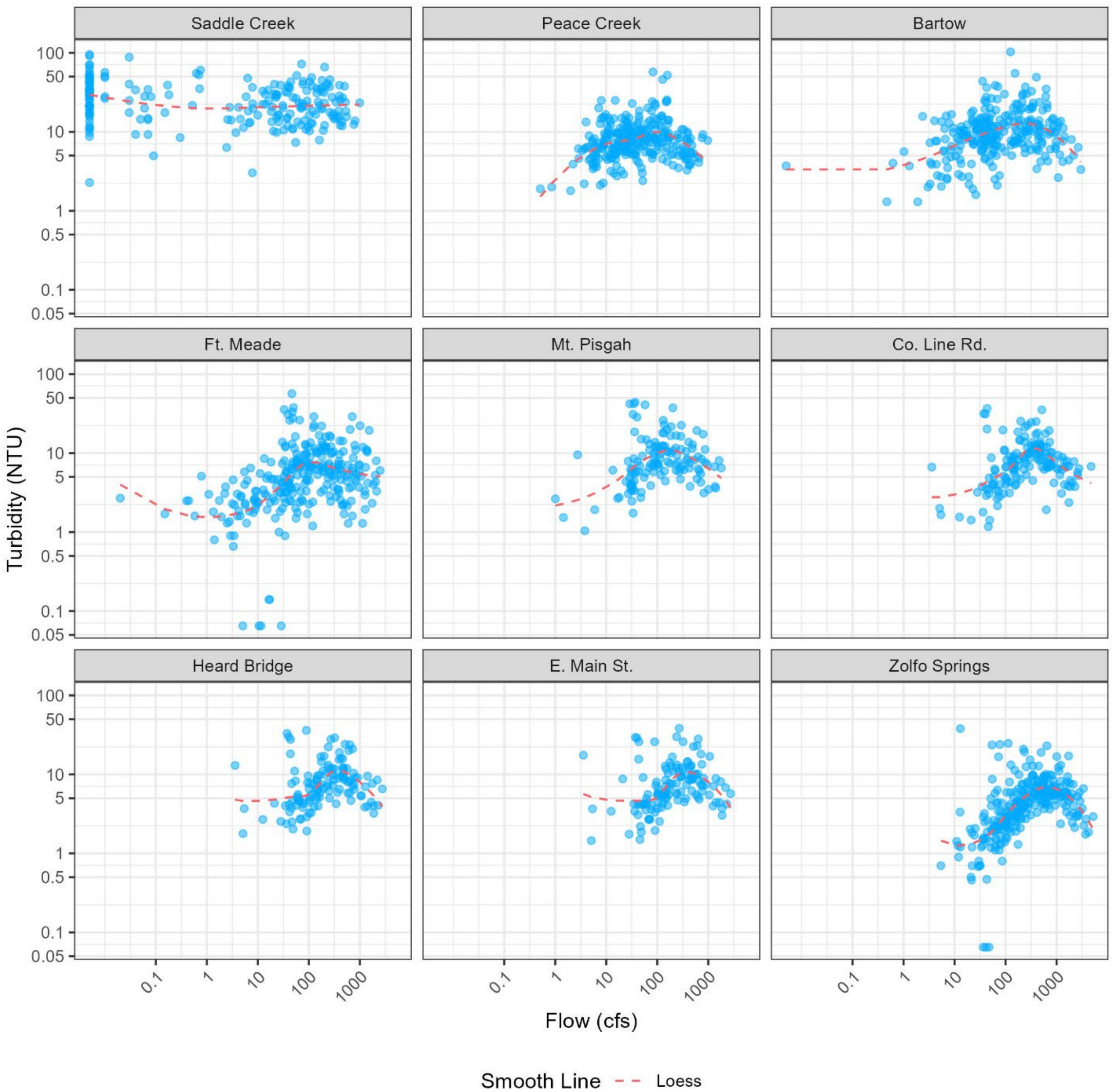


Figure 47. Relationship between streamflow and turbidity (NTU) concentrations (blue points) with LOESS smoothing curves (dashed red lines) across monitoring stations. The LOESS curves capture flow-concentration patterns in the data, with residuals from these fits used for subsequent trend analysis. Note: Both flow and concentration are displayed on logarithmic scales.

Figure 48. Flow-adjusted trends in chlorophyll a (ug/L) concentrations across monitoring stations. Points show LOESS residuals from the flow-concentration relationship (blue points) rescaled to the original concentration units, with Kendall-Theil regression lines (dashed red) indicating long-term trends. Text annotations provide the Sen slope (trend magnitude) and Kendall's tau correlation coefficient for each station. Note: Residuals are centered on the mean concentration for each station to maintain interpretable units.

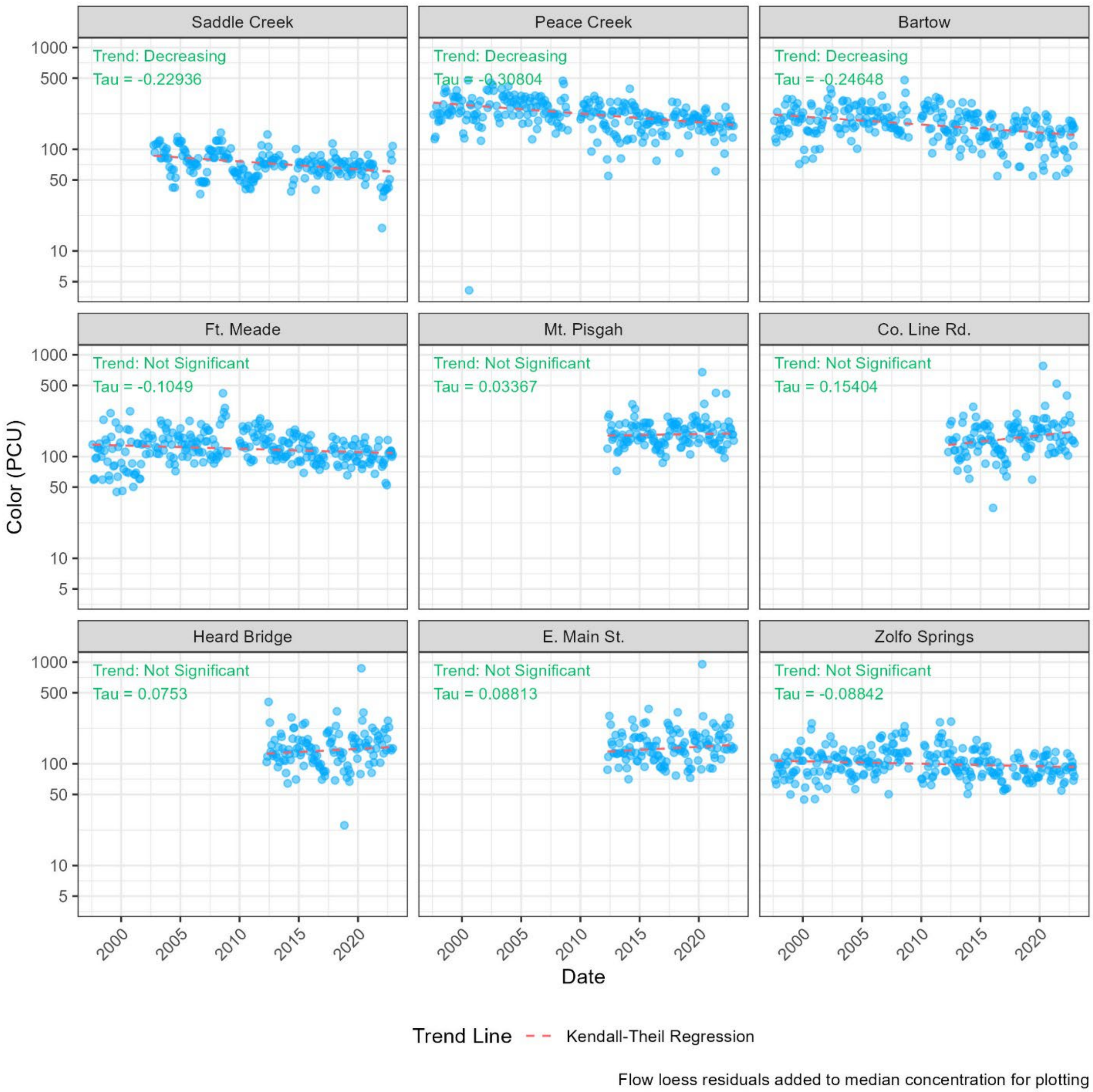


Figure 49. Flow-adjusted trends in color (PCU) concentrations across monitoring stations. Points show LOESS residuals from the flow-concentration relationship (blue points) rescaled to the original concentration units, with Kendall-Theil regression lines (dashed red) indicating long-term trends. Text annotations provide the Sen slope (trend magnitude) and Kendall's tau correlation coefficient for each station. Note: Residuals are centered on the mean concentration for each station to maintain interpretable units.

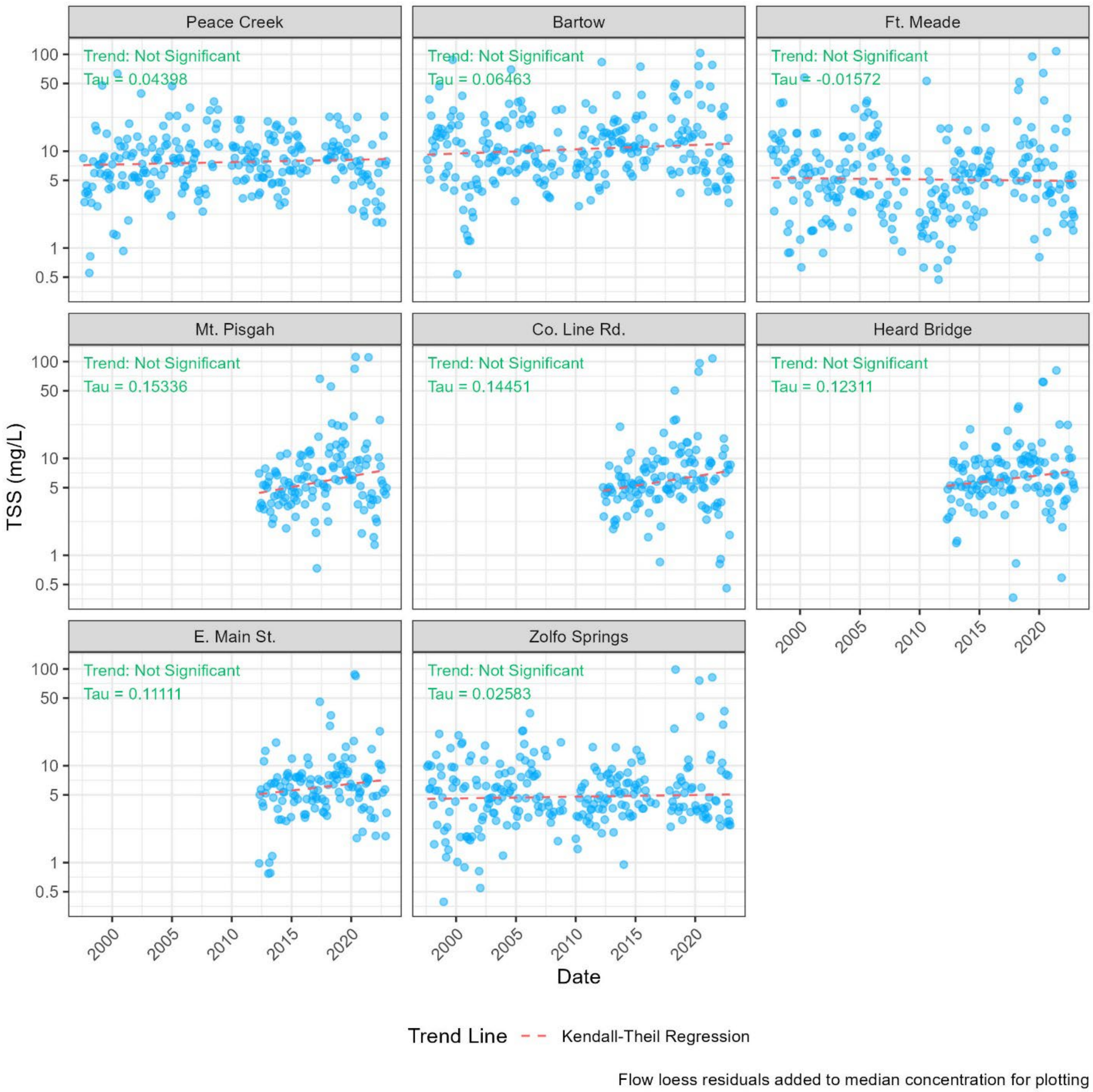


Figure 50. Flow-adjusted trends in TSS (mg/L) concentrations across monitoring stations. Points show LOESS residuals from the flow-concentration relationship (blue points) rescaled to the original concentration units, with Kendall-Theil regression lines (dashed red) indicating long-term trends. Text annotations provide the Sen slope (trend magnitude) and Kendall's tau correlation coefficient for each station. Note: Residuals are centered on the mean concentration for each station to maintain interpretable units.

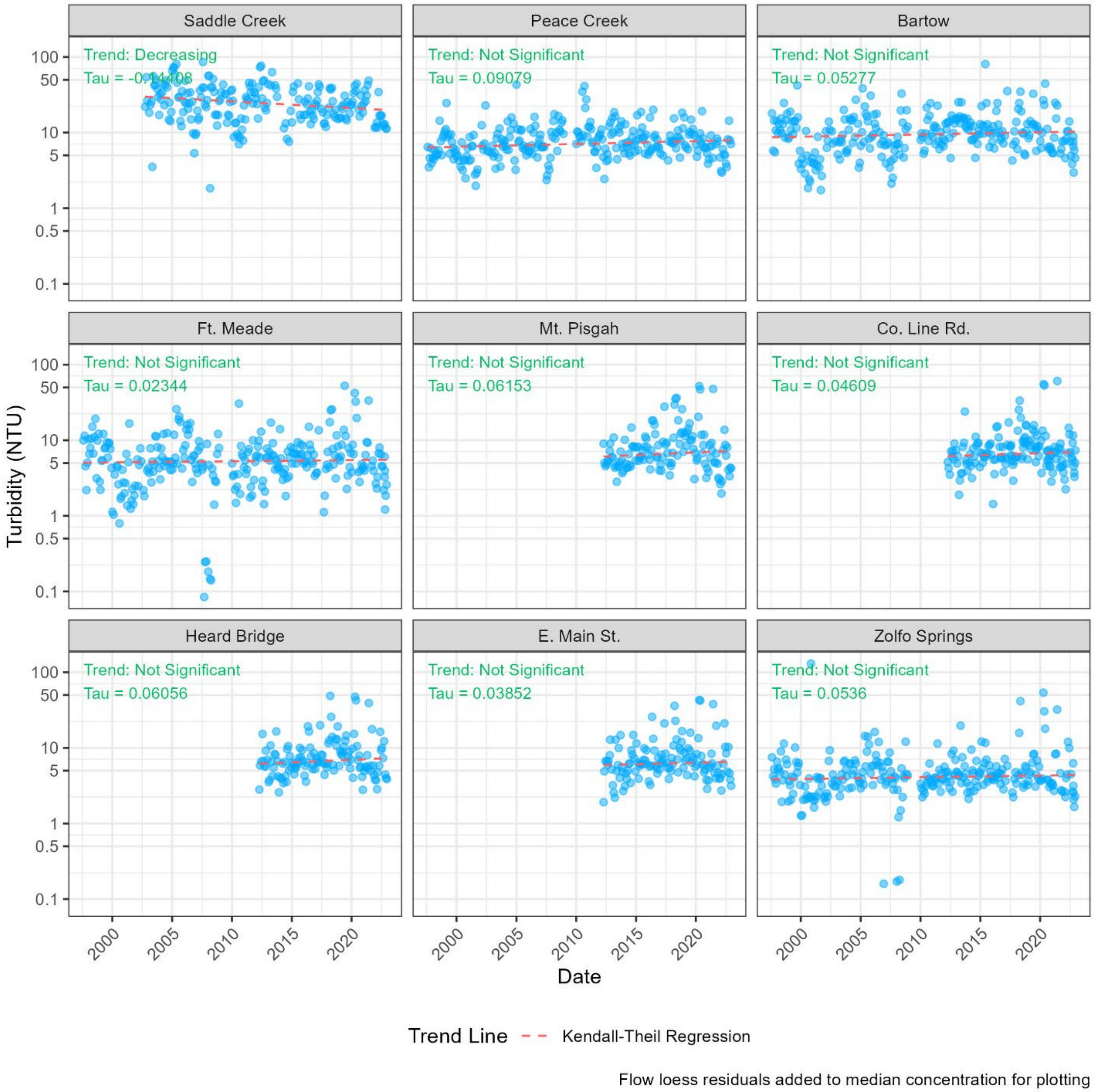


Figure 51. Flow-adjusted trends in turbidity (NTU) concentrations across monitoring stations. Points show LOESS residuals from the flow-concentration relationship (blue points) rescaled to the original concentration units, with Kendall-Theil regression lines (dashed red) indicating long-term trends. Text annotations provide the Sen slope (trend magnitude) and Kendall's tau correlation coefficient for each station. Note: Residuals are centered on the mean concentration for each station to maintain interpretable units.

Table 17. Summary of Kendall-Theil tests for trend with date by station and parameter. Trends are classified as Positive (Pos), Negative (Neg), or Not Significant (NS), based on Kendall's tau significance (α = 0.05). Raw p values (p_raw) are adjusted using Bonferroni correction for number of stations tested (n_t) to produce adjusted p values (p_adj).

Parameter	Station	Slope	Tau	n_t	p_raw	p_adj	Trend
Chlorophyll a	Saddle Creek	1.93e-06	0.009	9	8.39e-01	7.55e+00	Not Significant
Chlorophyll a	Peace Creek	5.29e-05	0.196	9	7.05e-06	6.35e-05	Increasing
Chlorophyll a	Bartow	5.21e-05	0.152	9	5.14e-04	4.62e-03	Increasing
Chlorophyll a	Ft. Meade	5.16e-05	0.138	9	1.47e-03	1.32e-02	Increasing
Chlorophyll a	Mt. Pisgah	3.23e-05	0.047	9	4.63e-01	4.16e+00	Not Significant
Chlorophyll a	Co. Line Rd.	4.05e-05	0.07	9	2.68e-01	2.42e+00	Not Significant
Chlorophyll a	Heard Bridge	2.49e-05	0.036	9	5.70e-01	5.13e+00	Not Significant
Chlorophyll a	E. Main St.	2.52e-05	0.044	9	4.93e-01	4.44e+00	Not Significant
Chlorophyll a	Zolfo Springs	2.96e-05	0.099	9	2.32e-02	2.09e-01	Not Significant
Color	Saddle Creek	-2.14e-05	-0.229	9	7.27e-07	6.54e-06	Decreasing
Color	Peace Creek	-2.36e-05	-0.308	9	4.59e-14	4.13e-13	Decreasing
Color	Bartow	-2.16e-05	-0.246	9	1.58e-09	1.42e-08	Decreasing
Color	Ft. Meade	-8.93e-06	-0.105	9	9.26e-03	8.33e-02	Not Significant
Color	Mt. Pisgah	5.19e-06	0.034	9	5.71e-01	5.14e+00	Not Significant
Color	Co. Line Rd.	3.34e-05	0.154	9	9.92e-03	8.92e-02	Not Significant
Color	Heard Bridge	1.67e-05	0.075	9	2.11e-01	1.90e+00	Not Significant
Color	E. Main St.	1.69e-05	0.088	9	1.45e-01	1.30e+00	Not Significant
Color	Zolfo Springs	-6.67e-06	-0.088	9	2.89e-02	2.60e-01	Not Significant
TSS	Peace Creek	6.75e-06	0.044	8	2.99e-01	2.39e+00	Not Significant
TSS	Bartow	1.22e-05	0.065	8	1.26e-01	1.01e+00	Not Significant
TSS	Ft. Meade	-3.38e-06	-0.016	8	7.09e-01	5.67e+00	Not Significant
TSS	Mt. Pisgah	6.13e-05	0.153	8	1.06e-02	8.44e-02	Not Significant
TSS	Co. Line Rd.	5.32e-05	0.145	8	1.51e-02	1.21e-01	Not Significant
TSS	Heard Bridge	3.84e-05	0.123	8	4.01e-02	3.21e-01	Not Significant
TSS	E. Main St.	3.83e-05	0.111	8	6.50e-02	5.20e-01	Not Significant
TSS	Zolfo Springs	4.83e-06	0.026	8	5.43e-01	4.34e+00	Not Significant
Turbidity	Saddle Creek	-2.42e-05	-0.144	9	1.85e-03	1.66e-02	Decreasing
Turbidity	Peace Creek	1.03e-05	0.091	9	2.56e-02	2.31e-01	Not Significant
Turbidity	Bartow	8.04e-06	0.053	9	1.95e-01	1.75e+00	Not Significant
Turbidity	Ft. Meade	4.19e-06	0.023	9	5.59e-01	5.04e+00	Not Significant
Turbidity	Mt. Pisgah	1.91e-05	0.062	9	3.01e-01	2.71e+00	Not Significant
Turbidity	Co. Line Rd.	1.32e-05	0.046	9	3.96e-01	3.57e+00	Not Significant
Turbidity	Heard Bridge	1.83e-05	0.061	9	3.09e-01	2.78e+00	Not Significant
Turbidity	E. Main St.	1.11e-05	0.039	9	5.17e-01	4.66e+00	Not Significant
Turbidity	Zolfo Springs	6.18e-06	0.054	9	1.84e-01	1.66e+00	Not Significant

Figure 52. Date-adjusted relationships in chlorophyll (ug/L) concentrations with Flow across monitoring stations. Points show LOESS residuals from the date-concentration relationship (blue points) rescaled to the original concentration units, with Kendall-Theil regression lines (dashed red) indicating long-term trends. Text annotations provide the Sen slope (trend magnitude) and Kendall's tau correlation coefficient for each station. Note: Residuals are centered on the mean concentration for each station to maintain interpretable units.

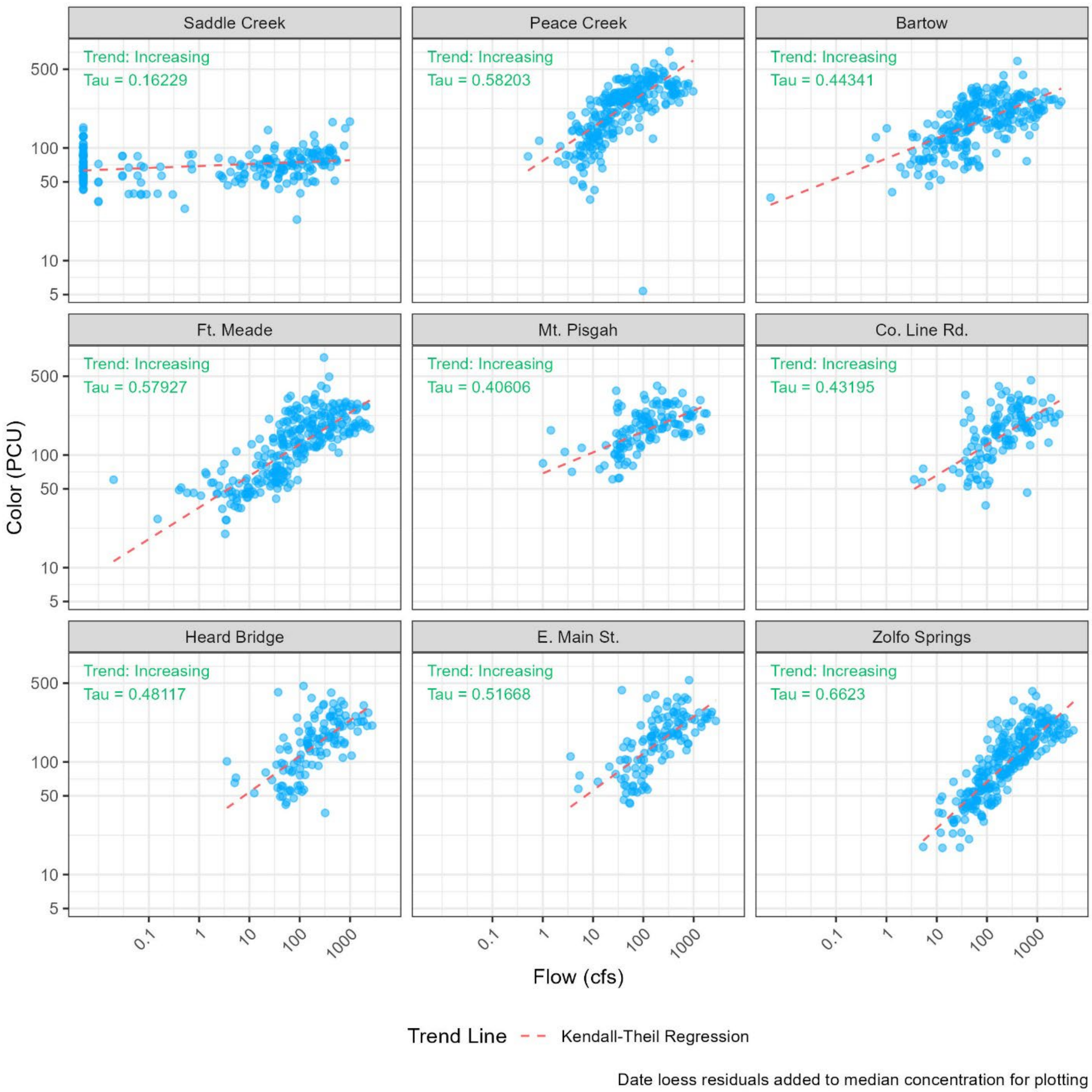


Figure 53. Date-adjusted relationships in color (PCU) concentrations with Flow across monitoring stations. Points show LOESS residuals from the date-concentration relationship (blue points) rescaled to the original concentration units, with Kendall-Theil regression lines (dashed red) indicating long-term trends. Text annotations provide the Sen slope (trend magnitude) and Kendall's tau correlation coefficient for each station. Note: Residuals are centered on the mean concentration for each station to maintain interpretable units.

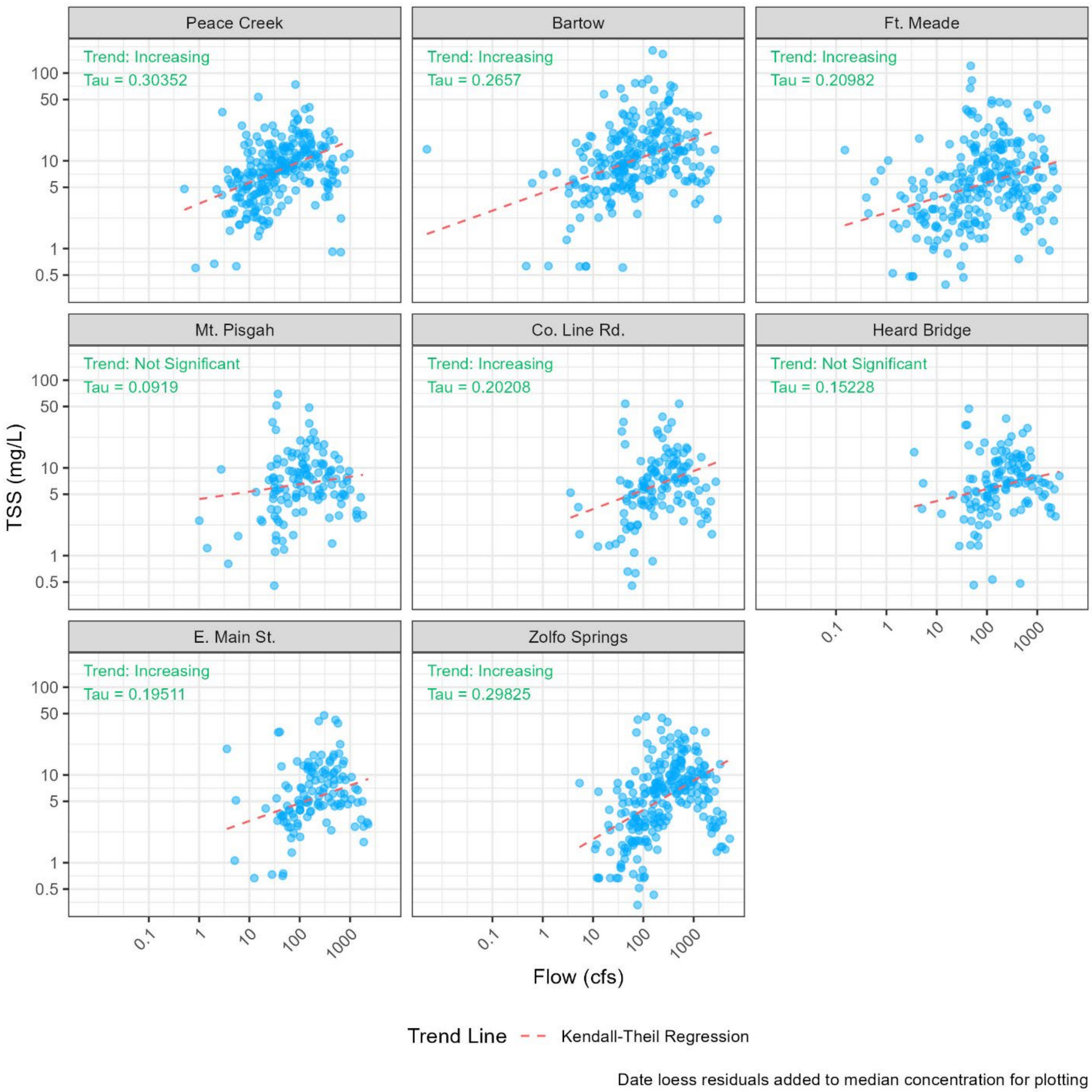


Figure 54. Date-adjusted relationships in TSS (mg/L) concentrations with Flow across monitoring stations. Points show LOESS residuals from the date-concentration relationship (blue points) rescaled to the original concentration units, with Kendall-Theil regression lines (dashed red) indicating long-term trends. Text annotations provide the Sen slope (trend magnitude) and Kendall's tau correlation coefficient for each station. Note: Residuals are centered on the mean concentration for each station to maintain interpretable units.

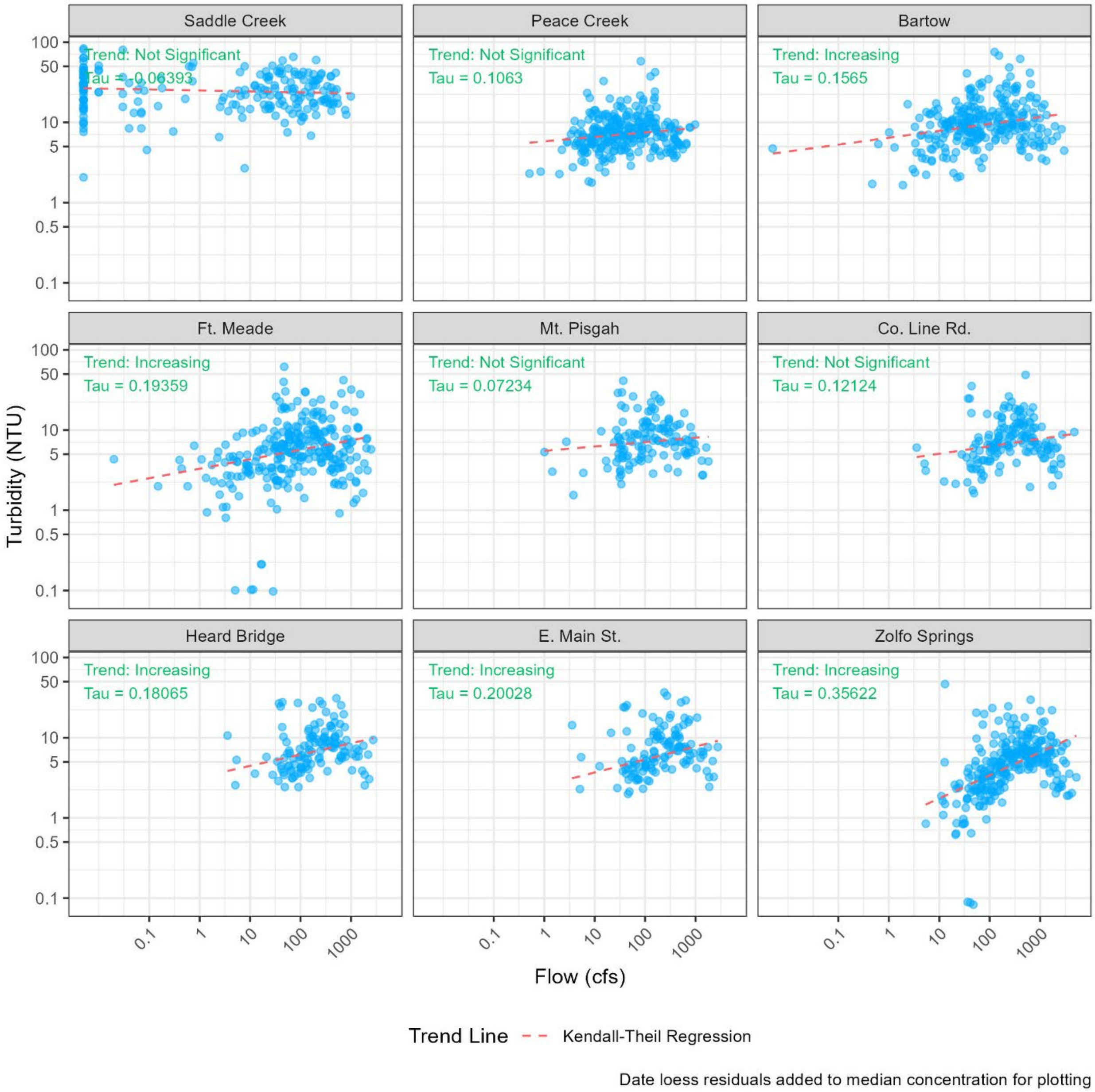


Figure 55. Date-adjusted relationships in turbidity (NTU) concentrations with Flow across monitoring stations. Points show LOESS residuals from the date-concentration relationship (blue points) rescaled to the original concentration units, with Kendall-Theil regression lines (dashed red) indicating long-term trends. Text annotations provide the Sen slope (trend magnitude) and Kendall's tau correlation coefficient for each station. Note: Residuals are centered on the mean concentration for each station to maintain interpretable units.

Table 18. Summary of Kendall-Theil tests for trend with flow by station and parameter. Trends are classified as Positive (Pos), Negative (Neg), or Not Significant (NS),based on Kendall's tau significance (α = 0.05). Raw p values (p_raw) are adjusted using Bonferroni correction for number of stations tested (n_t) to produce adjusted p values (p_adj)

Parameter	Station	Slope	Tau	n_t	p_raw	p_adj	Trend
Chlorophyll a (µg/L)	Saddle Creek	-1.00e-02	-0.042	9	3.77e-01	3.39e+00	NS
Chlorophyll a (µg/L)	Peace Creek	2.41e-01	0.225	9	2.36e-07	2.13e-06	Pos
Chlorophyll a (µg/L)	Bartow	4.83e-01	0.349	9	1.47e-15	1.33e-14	Pos
Chlorophyll a (µg/L)	Ft. Meade	3.49e-01	0.304	9	2.55e-12	2.29e-11	Pos
Chlorophyll a (µg/L)	Mt. Pisgah	7.83e-02	0.067	9	2.95e-01	2.66e+00	NS
Chlorophyll a (µg/L)	Co. Line Rd.	1.09e-01	0.101	9	1.15e-01	1.03e+00	NS
Chlorophyll a (µg/L)	Heard Bridge	9.41e-02	0.095	9	1.37e-01	1.24e+00	NS
Chlorophyll a (µg/L)	E. Main St.	1.10e-01	0.098	9	1.26e-01	1.13e+00	NS
Chlorophyll a (µg/L)	Zolfo Springs	2.65e-01	0.209	9	1.68e-06	1.51e-05	Pos
Color (PCU)	Saddle Creek	1.72e-02	0.162	9	6.29e-04	5.66e-03	Pos
Color (PCU)	Peace Creek	2.98e-01	0.582	9	4.68e-46	4.22e-45	Pos
Color (PCU)	Bartow	1.78e-01	0.443	9	1.89e-27	1.70e-26	Pos
Color (PCU)	Ft. Meade	2.81e-01	0.579	9	8.22e-47	7.40e-46	Pos
Color (PCU)	Mt. Pisgah	1.86e-01	0.406	9	8.95e-12	8.06e-11	Pos
Color (PCU)	Co. Line Rd.	2.71e-01	0.432	9	4.84e-13	4.36e-12	Pos
Color (PCU)	Heard Bridge	3.18e-01	0.481	9	1.37e-15	1.23e-14	Pos
Color (PCU)	E. Main St.	3.27e-01	0.517	9	1.31e-17	1.18e-16	Pos
Color (PCU)	Zolfo Springs	4.13e-01	0.662	9	3.40e-60	3.06e-59	Pos
TSS (mg/L)	Peace Creek	2.39e-01	0.304	8	8.06e-13	6.45e-12	Pos
TSS (mg/L)	Bartow	2.05e-01	0.266	8	3.37e-10	2.69e-09	Pos
TSS (mg/L)	Ft. Meade	1.72e-01	0.21	8	6.35e-07	5.08e-06	Pos
TSS (mg/L)	Mt. Pisgah	8.49e-02	0.092	8	1.26e-01	1.00e+00	NS
TSS (mg/L)	Co. Line Rd.	2.17e-01	0.202	8	6.84e-04	5.47e-03	Pos
TSS (mg/L)	Heard Bridge	1.38e-01	0.152	8	1.11e-02	8.91e-02	NS
TSS (mg/L)	E. Main St.	2.03e-01	0.195	8	1.20e-03	9.59e-03	Pos
TSS (mg/L)	Zolfo Springs	3.34e-01	0.298	8	2.20e-12	1.76e-11	Pos
Turbidity (NTU)	Saddle Creek	-1.20e-02	-0.064	9	1.78e-01	1.60e+00	NS
Turbidity (NTU)	Peace Creek	5.54e-02	0.106	9	9.01e-03	8.11e-02	NS
Turbidity (NTU)	Bartow	8.61e-02	0.156	9	1.20e-04	1.08e-03	Pos
Turbidity (NTU)	Ft. Meade	1.18e-01	0.194	9	1.44e-06	1.30e-05	Pos
Turbidity (NTU)	Mt. Pisgah	5.46e-02	0.072	9	2.24e-01	2.02e+00	NS
Turbidity (NTU)	Co. Line Rd.	9.27e-02	0.121	9	2.57e-02	2.31e-01	NS
Turbidity (NTU)	Heard Bridge	1.41e-01	0.181	9	2.40e-03	2.16e-02	Pos
Turbidity (NTU)	E. Main St.	1.62e-01	0.2	9	7.64e-04	6.88e-03	Pos
Turbidity (NTU)	Zolfo Springs	2.88e-01	0.356	9	1.16e-18	1.05e-17	Pos

Table 19. Summary of flow-adjusted concentration trends with date showing counts of increasing, decreasing, and not-significant results.

Parameter	n_increasing	n_decreasing	n_not_significant
Chlorophyll a (µg/L)	3	0	6
Color (PCU)	0	3	6
TSS (mg/L)	0	0	8
Turbidity (NTU)	0	1	8
Total	3	4	28

Table 20. Summary of date-adjusted concentration trends with flow showing counts of increasing, decreasing, and not-significant results.

Parameter	n_increasing	n_decreasing	n_not_significant
Chlorophyll a (µg/L)	4	0	5
Color (PCU)	9	0	0
TSS (mg/L)	6	0	2
Turbidity (NTU)	5	0	4
Total	24	0	11

Inorganic Ions: Fluoride, pH, Potassium, and Specific Conductance

Inorganic ions grouped in this analysis include fluoride, pH, potassium, and specific conductance. Fluorapatite is a naturally occurring mineral that contains fluoride as a key component of its chemical structure. Phosphate rock mined in Bone Valley is rich in fluorapatite, making it a significant source of fluoride (Cathcart 1952). Fluoride is reported as both "Fluoride" and "Fluoride-dissolved" at Saddle Creek, these are combined to a single parameter here.

pH is a logarithmic measure of the concentration of hydrogen ions (H+), with higher concentrations indicating a lower pH and a more acidic solution, while lower concentrations result in a higher pH and a more alkaline solution. Freshwater systems exhibit natural pH variations influenced by factors like geology and the activity of aquatic organisms. pH significantly impacts the availability of essential nutrients and the toxicity of metals, affecting the health and survival of aquatic organisms.

Potassium is an essential macronutrient for plant growth and plays a crucial role in various biological processes. In aquatic ecosystems, potassium concentrations can vary significantly due to factors such as geology, weathering, and human activities like agriculture and wastewater discharge. Elevated potassium levels can impact aquatic life by altering osmotic balance, influencing plant growth rates, and potentially contributing to eutrophication. Potassium is reported as "Potassium – dissolved" at Saddle Creek and simplified to "potassium" here.

Specific conductance is a measure of the presence of dissolved ions in a solution. For major cations, sodium, potassium, calcium, and magnesium and four major anions bicarbonate, carbonate, sulfate, and chloride are the dominant ions in fresh water (Allan et al. 2021).

Location, spread, and normality

These parameters have different units and are associated with different biogeochemical processes in the environment, limiting the utility of comparison of their quantiles, but comparing skewness and frequency distributions is still possible.

Means and medians across all sites for ion statistics including fluoride, potassium, specific conductance and pH are shown in Table 21. Quantile plots illustrate distributions of nutrient data (Figure 56). Frequencies were calculated on log10 transformed values of fluoride, potassium, and specific conductance. Because pH is already on a log10 scale, it was not transformed for analysis. Boxplots (Figure 57) provide visual summaries of 1) the center of the data (the median--the center line of the box), 2) the variation or spread (interquartile range--the box height), 3) the skewness (quartile skew--the relative size of box halves), and 4) presence or absence of unusual values ("outside" – lines, and "far outside" values - circles). The data are displayed on a log scale due to the wide range of concentrations.

Histograms are useful for depicting large differences in shape or symmetry, such as whether a data set appears symmetric or skewed (Figure 58) (Helsel and Hirsch 2002).

Probability plots of log-transformed data illustrate how well data fit a lognormal distribution (Figure 59). Normal quantiles are the data values expected based on a normal distribution with the same mean and standard deviation of the sample data. The probability plot correlation coefficient (PPCC) tests for normality by computing the linear correlation coefficient between data and their normal quantiles. Samples from a normal distribution will have a correlation coefficient very close to 1.0. As data depart from normality, their correlation coefficient will decrease below 1. The critical correlation value corresponds to the value the correlation coefficient must exceed for the data to be considered normally distributed. All parameters are non-normal according to the PPCC as well as Anderson-Darling test for normality after Log10 transformation of data (Table 22).

Table 21. Univariate summary statistics for nutrients at all sites. The interquartile range (IQR) = P75 – P25. The skewness coefficient (G) is the adjusted third moment divided by the cube of the standard deviation, and is a measure of skewness that is sensitive to outliers (Helsel and Hirsch 2002). The quartile skew coefficient (QS) quantifies skewness as the difference in distances of the upper and lower quartiles from the median, divided by the IQR for a resistant measure of skewness.

Parameter	Min	P25	P50	Mean	P75	Max	Obs	G	IQR	QS
Fluoride (mg/L)	0.01	0.37	0.61	0.70	0.90	5.50	1741	2.226	0.529	0.096
Potassium (mg/L)	0.96	3.91	5.33	7.43	8.36	133	1224	6.897	4.452	0.361
Specific Conductance (µS/cm)	72	237	323	357	439	2115	1585	2.528	202	0.149
pH (SU)	4.34	6.95	7.28	7.27	7.60	9.17	1584	-0.177	0.65	-0.023

"C:\Users\gherrick\OneDrive - Southwest Florida Water Management District\MFL_Rivers\Peace_Upper2025\1_UPR_WQ _GH\data\tab_nuts_river.xlsx" (12/12/2024)

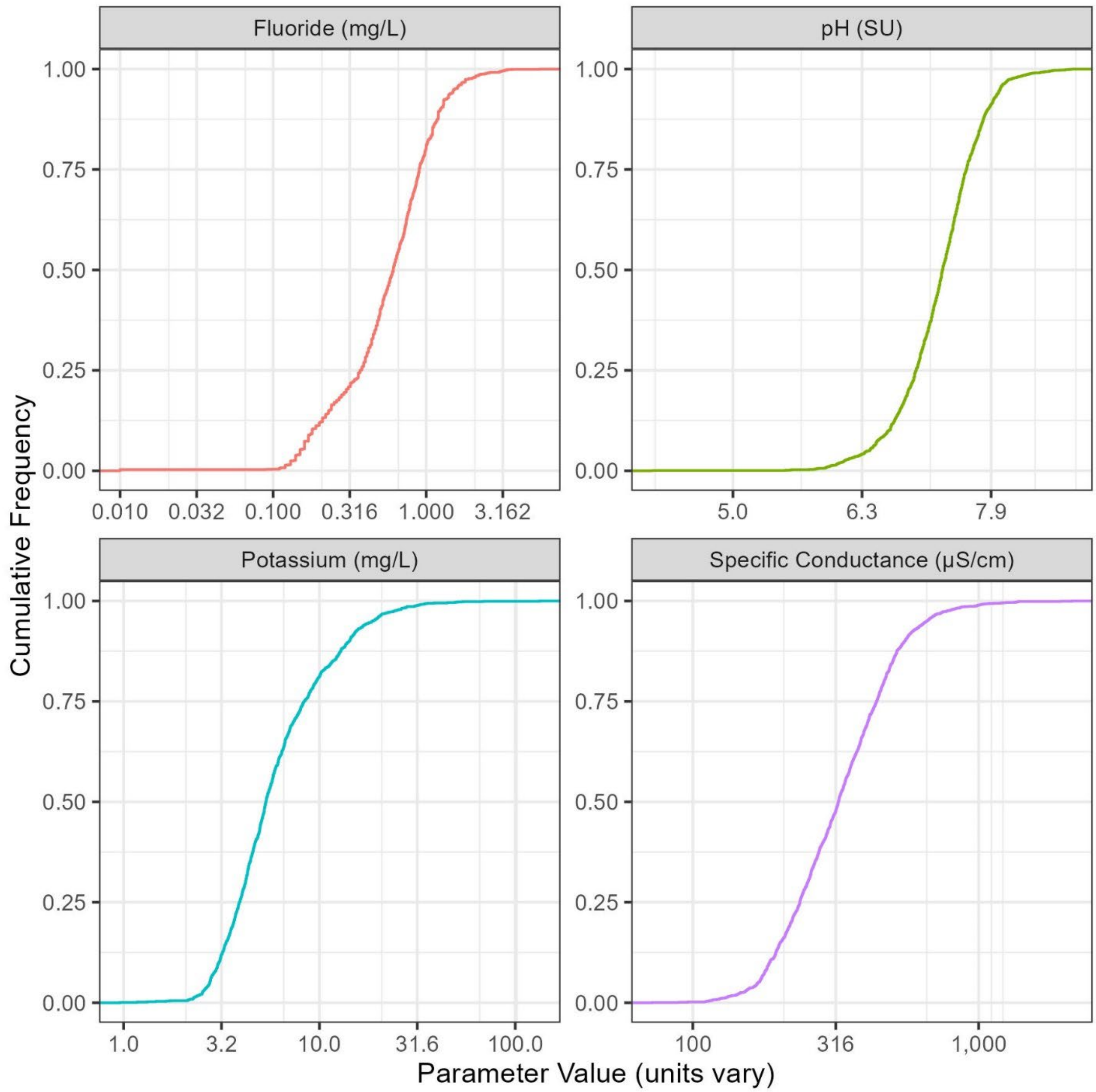


Figure 56. Quantiles of parameter values. Quantile plots visually portray the quantiles, or cumulative frequency of observations of nutrient concentrations. Quantiles of importance such as the median are easily discerned (quantile, or cumulative frequency = 0.5) (Helsel and Hirsch 2002).

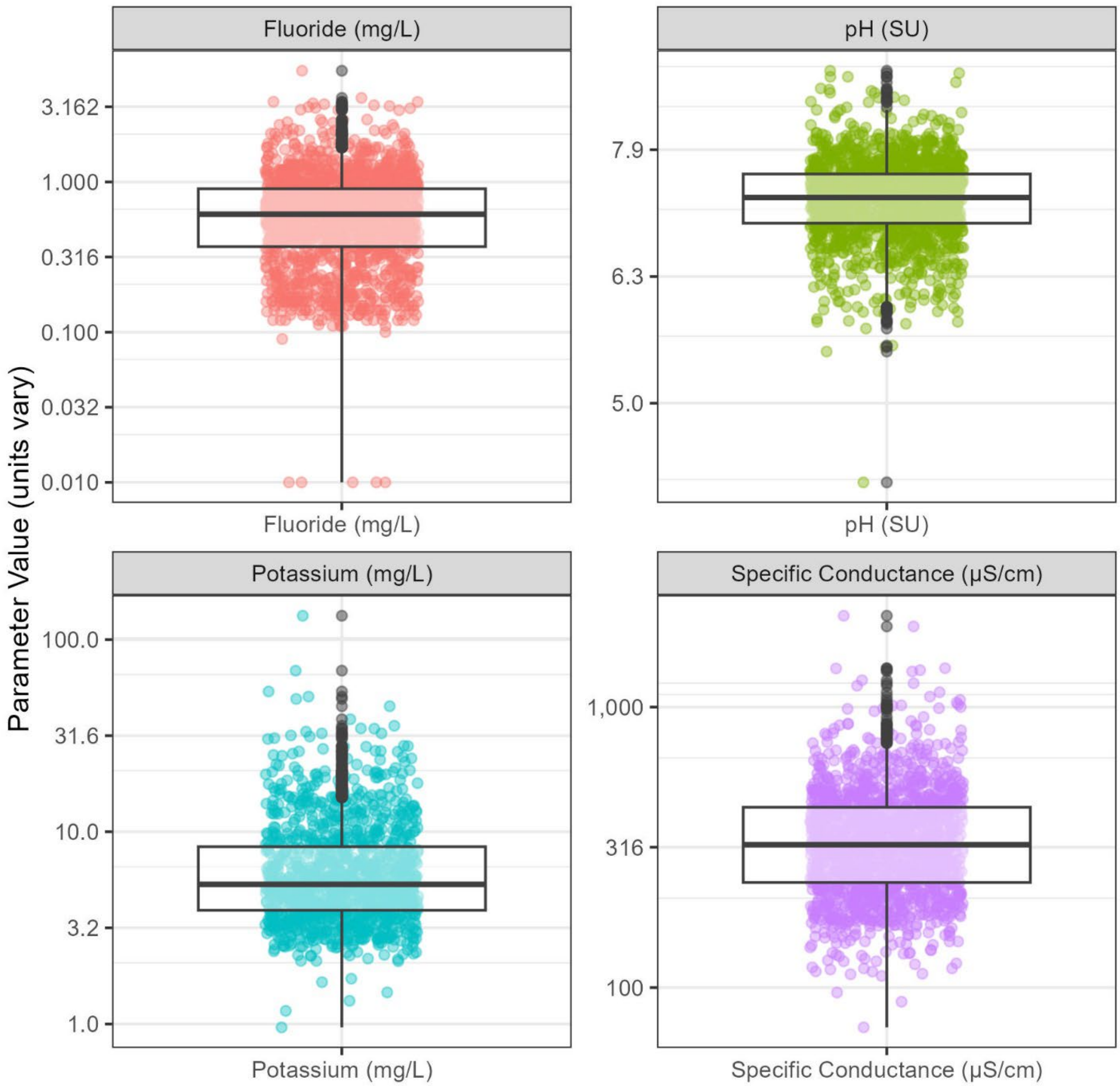


Figure 57. Concentrations of ions using jittered points to display individual data values and boxplots to summarize the distribution. The y-axis is scaled logarithmically to better visualize the range of concentrations, and boxplot statistics are calculated on non-transformed data.

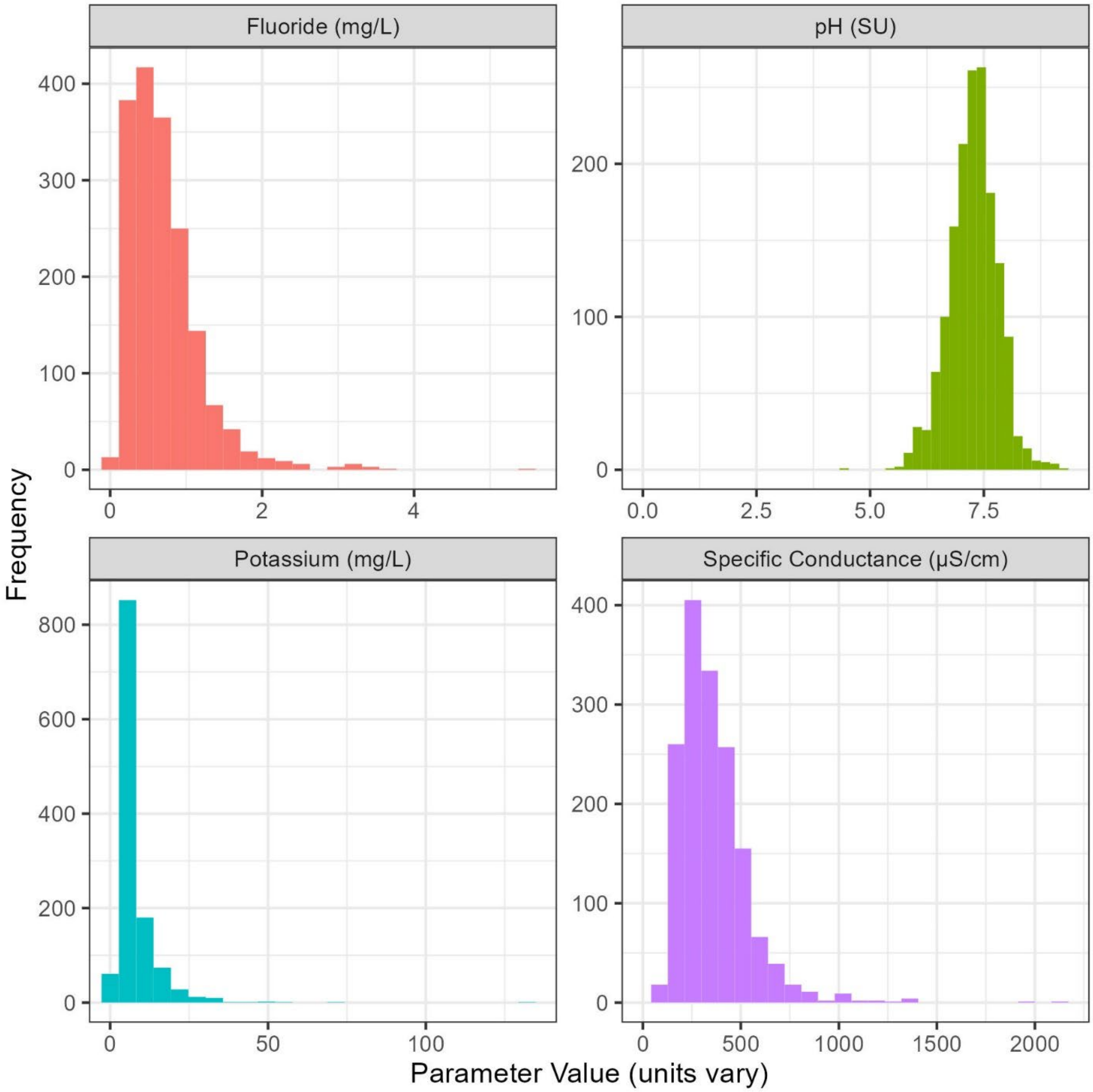


Figure 58. Frequency distributions of ions. The scales are adjusted per nutrient to highlight their unique distribution patterns.

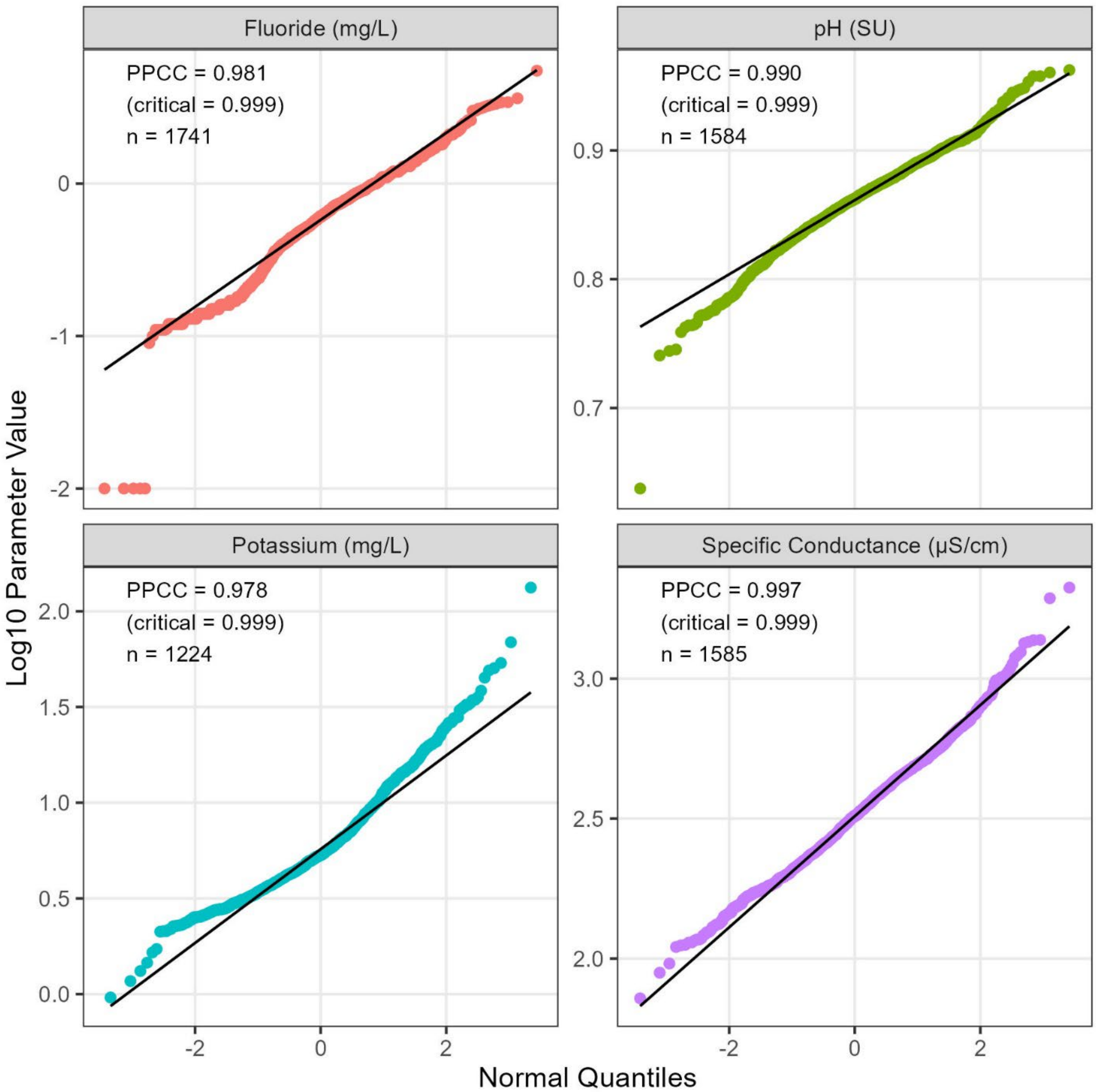


Figure 59. Normal probability plots for parameter concentrations, comparing theoretical quantiles to sample quantiles. Normal quantiles are values expected from a perfectly normal distribution at specific probabilities, serving as a reference for normality. If the data follow a normal distribution, the points align closely with the diagonal line. Deviations from the line indicate departures from normality. The Probability Plot Correlation Coefficient (PPCC) is the linear correlation coefficient between data and their normal quantiles. PPCC values below the critical value indicate rejection of null hypothesis that data are from a normal distribution. All plots show non-normal distributions.

Table 22. Results of Anderson-Darling test for normality of log10 transformed data. All parameters are non-normal with p values below 0.01.

Parameter	AD_statistic	p_AD
Fluoride (mg/L)	13.52593	3.7E-24
Potassium (mg/L)	15.6037	3.7E-24
Specific Conductance (µS/cm)	1.40604	0.00123
pH (SU)	5.424331	2.21E-13

Testing for difference between groups

Exploration of differences between stations and season is complicated: there are 9 stations and 2 seasons for each parameter, which combine for 36 pairwise comparisons between stations and 152 pairwise comparisons between stations and seasons. The results provided here summarize patterns, while deeper analysis is always possible. There are significant differences between wet and dry seasons for color, TSS and turbidity but not for chlorophyll a (Table 23) (Figure 60). Pairwise Wilcoxson tests reveal differences between nine stations in fluoride (Figure 61), potassium (Figure 62), pH (Figure 63), and specific conductance (Figure 64).

Table 23. Kruskal-Wallace tests for differences between Stations, Seasons, and Station*Season interactions.

Parameter	Station chi	Station p	Season chi	Season p	Interaction chi	Interaction p
Fluoride (mg/L)	1098.907	6.6E-232	25.94077	3.52E-07	1138.333	2.2E-231
Potassium (mg/L)	588.5838	4.6E-126	29.60853	5.29E-08	635.119	6E-131
Specific Conductance (µS/cm)	205.7377	6.99E-41	223.2336	1.78E-50	442.8139	6.74E-85
pH (SU)	607.5062	5.9E-127	169.2251	1.09E-38	806.4894	3.5E-162

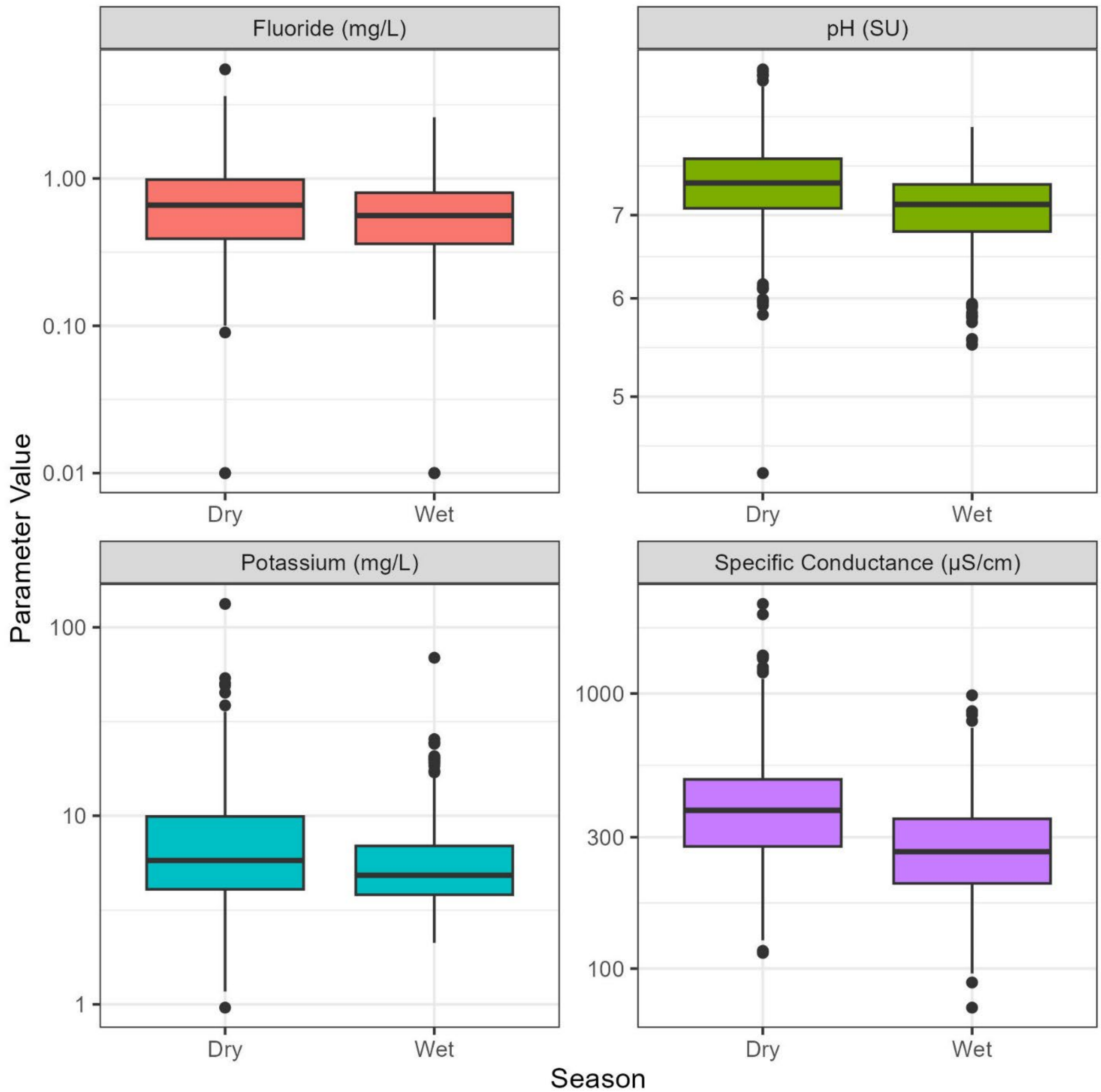


Figure 60. Seasonal differences in parameter concentrations

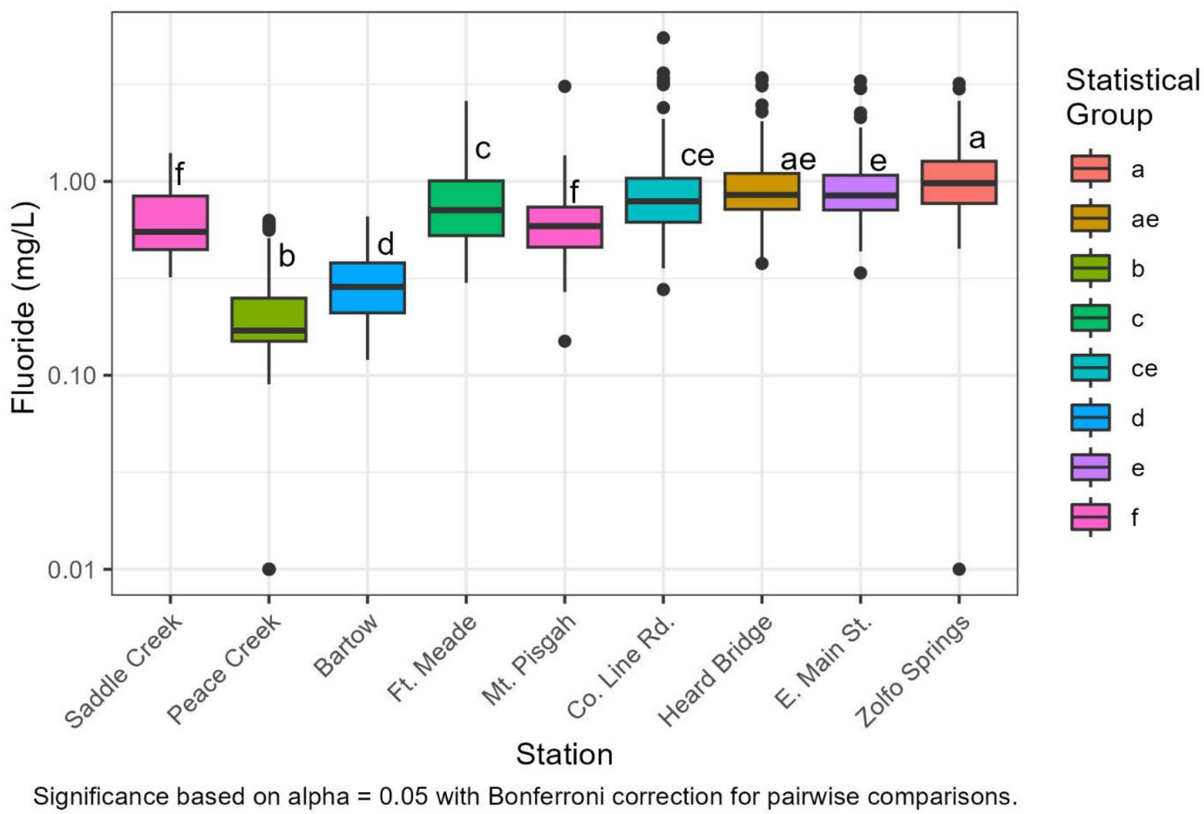


Figure 61. Statistical Grouping of fluoride by Station Using Pairwise Wilcoxon Tests

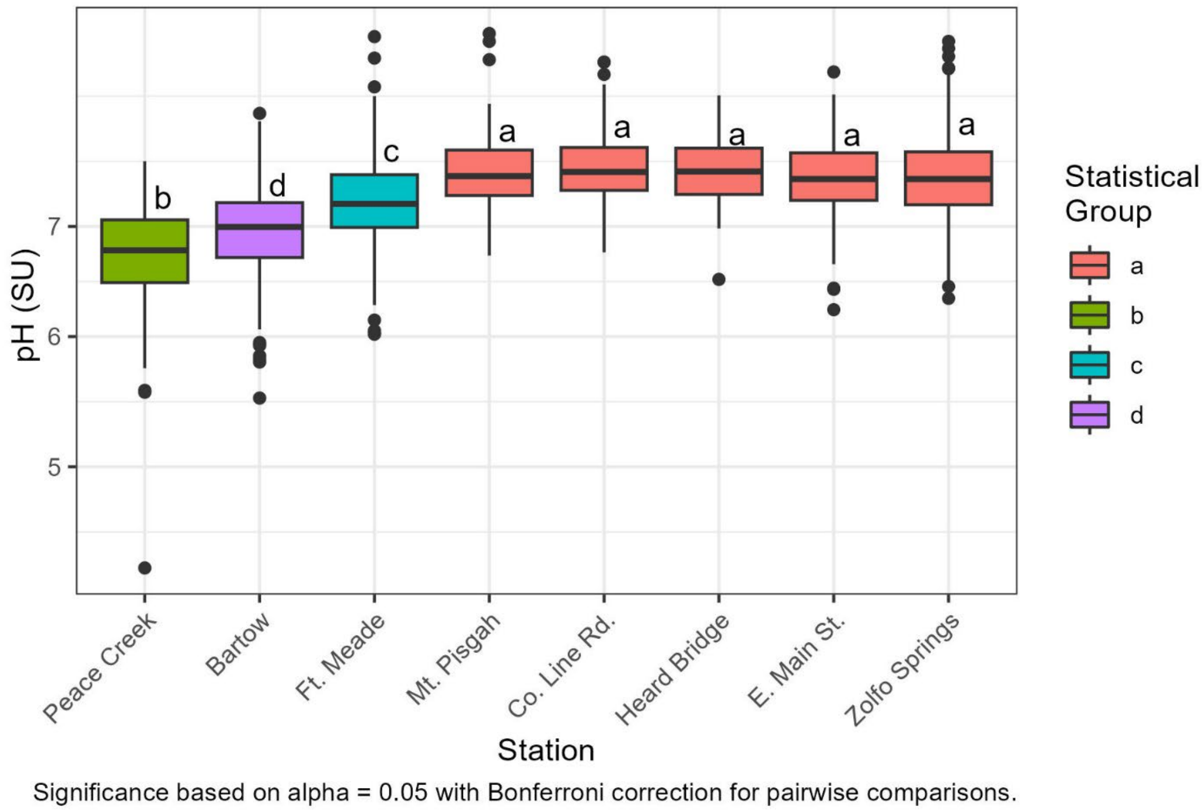


Figure 62. Statistical Grouping of pH by Station Using Pairwise Wilcoxon Tests

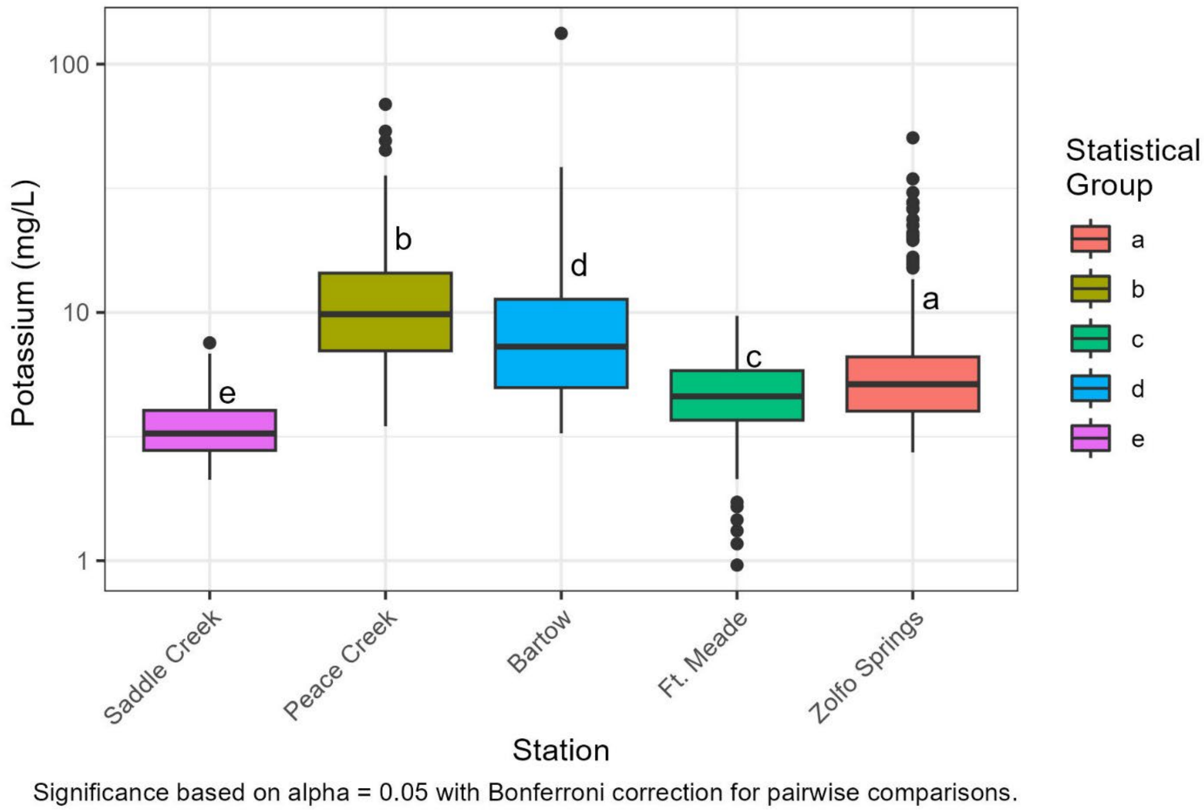


Figure 63. Statistical Grouping of potassiium by Station Using Pairwise Wilcoxon Tests

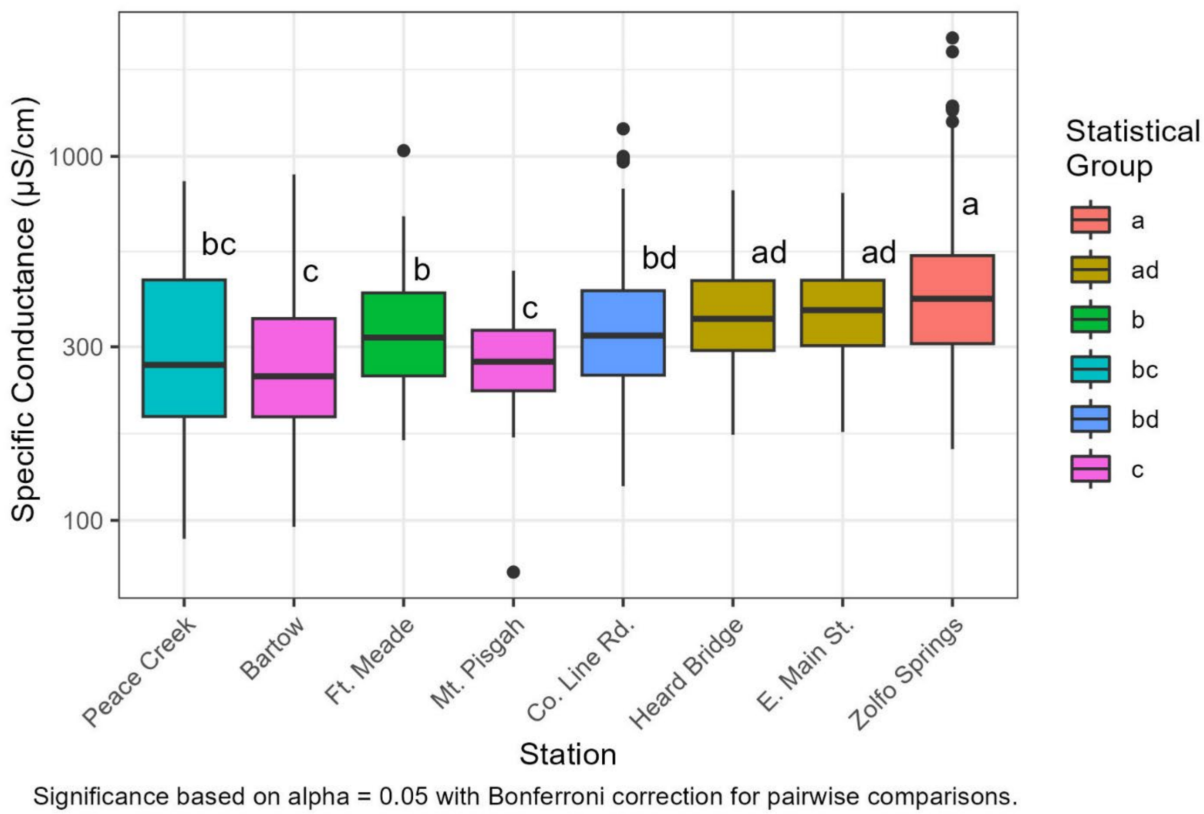


Figure 64. Statistical Grouping of specific conductance by Station Using Pairwise Wilcoxon Tests

Trends

This analysis examines both flow-based and temporal trends in water quality parameters using a two-stage approach following Helsel and Hirsch (2002). We first analyze concentration-date relationships using LOESS smoothing, then use these residuals to examine flow relationships. In a parallel analysis, we examine concentration-flow relationships with LOESS, using those residuals to assess temporal trends. Both approaches employ Kendall's tau with Bonferroni-adjusted p-values (p_adjusted = p_initial * n, where n is the number of stations) and Theil-Sen slopes for trend detection. This dual analysis allows examination of both flow-concentration patterns and temporal trends while controlling for their mutual influences.

The analysis sequence includes:

1. Concentration-date relationships with LOESS smoothing for fluoride (Figure 65), pH(Figure 66), potassium (Figure 67), and specific conductance (Figure 68). These plots provide a visual representation of nonlinear temporal patterns for each station.

2. Concentration-flow relationships with LOESS smoothing for fluoride (Figure 69), pH(Figure 70), potassium (Figure 71), and specific conductance (Figure 72) visualize nonlinear patterns in water quality parameters with flow at each of the nine stations.

3. Residuals from concentration-flow relationships represent flow-adjusted concentrations which can be compared with dates to determine temporal relationships fluoride (Figure 73), pH(Figure 74), potassium (Figure 75), and specific conductance (Figure 76). Kendall-Theil lines show increasing, decreasing and not significant relationships depending on the water quality sampling location (Table 24). Statistical significance is based on Bonferroni-corrected p-values adjusted for number of stations.

4. Residuals from date-flow Loess represent date-adjusted concentration which is related to flow for fluoride (Figure 77), pH(Figure 78), potassium (Figure 79), and specific conductance (Figure 80) with Kendall-Theil lines show increasing, decreasing and not significant relationships depending on the water quality sampling location (

Table 25). Statistical significance is based on Bonferroni-corrected p-values adjusted for 9 stations.

The analysis revealed both temporal and flow-dependent trends across stations, suggesting that water quality dynamics are influenced by a combination of temporal and hydrological factors. Most temporal trends were decreasing (14) while 11 trends were not significant, and five showed significant increases (Table 26). The majority of flow trends were decreasing (28), while 2 trends were not significant and 0 were increasing (Table 27).

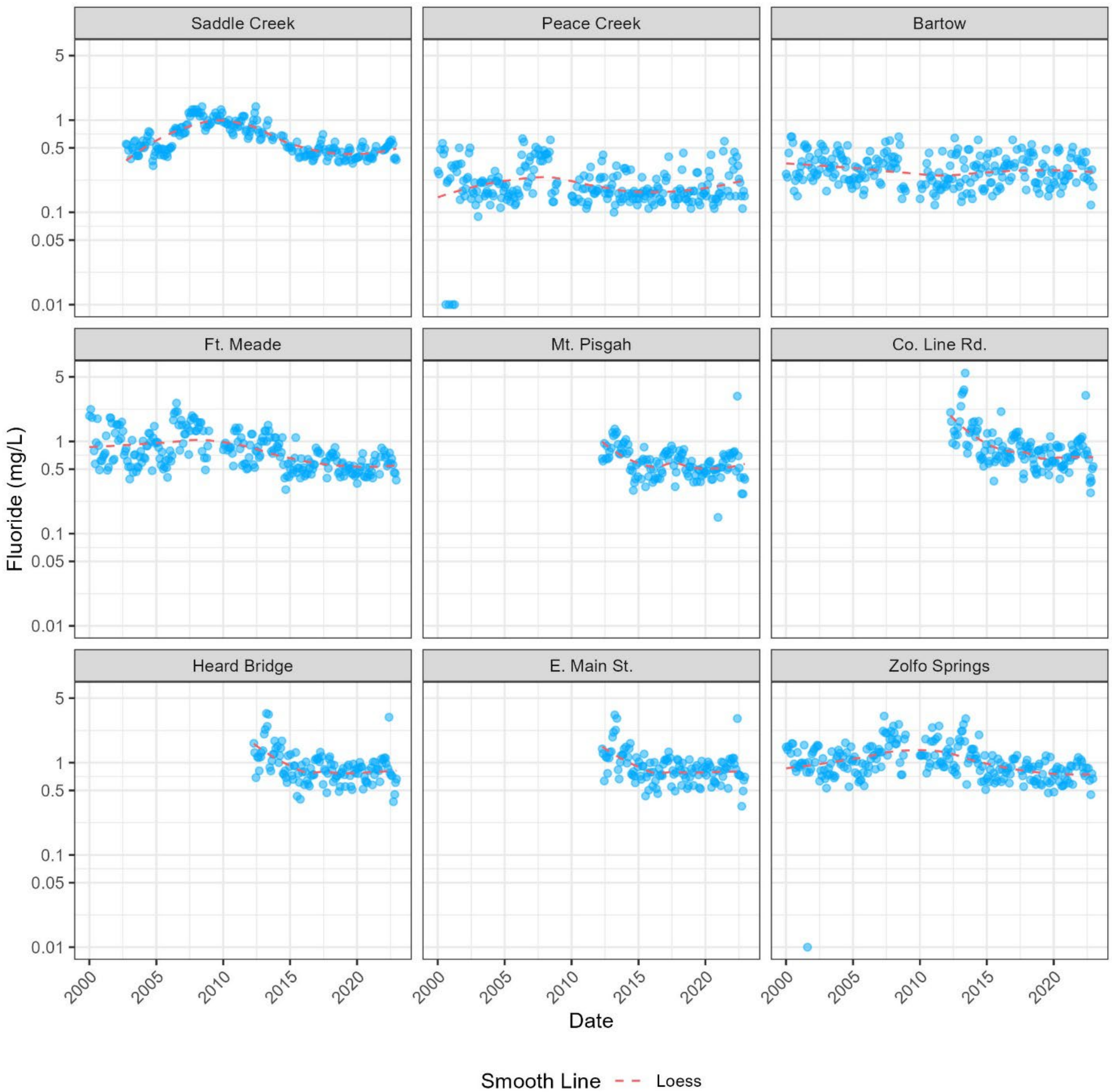


Figure 65. Time series showing observed fluoride (mg/L) concentrations (blue points) with LOESS smoothing curves (dashed red lines) across monitoring stations. The LOESS curves capture temporal patterns in the data, with residuals from these fits used for subsequent flow-adjusted trend analysis. Note: Concentrations are displayed on a logarithmic scale.

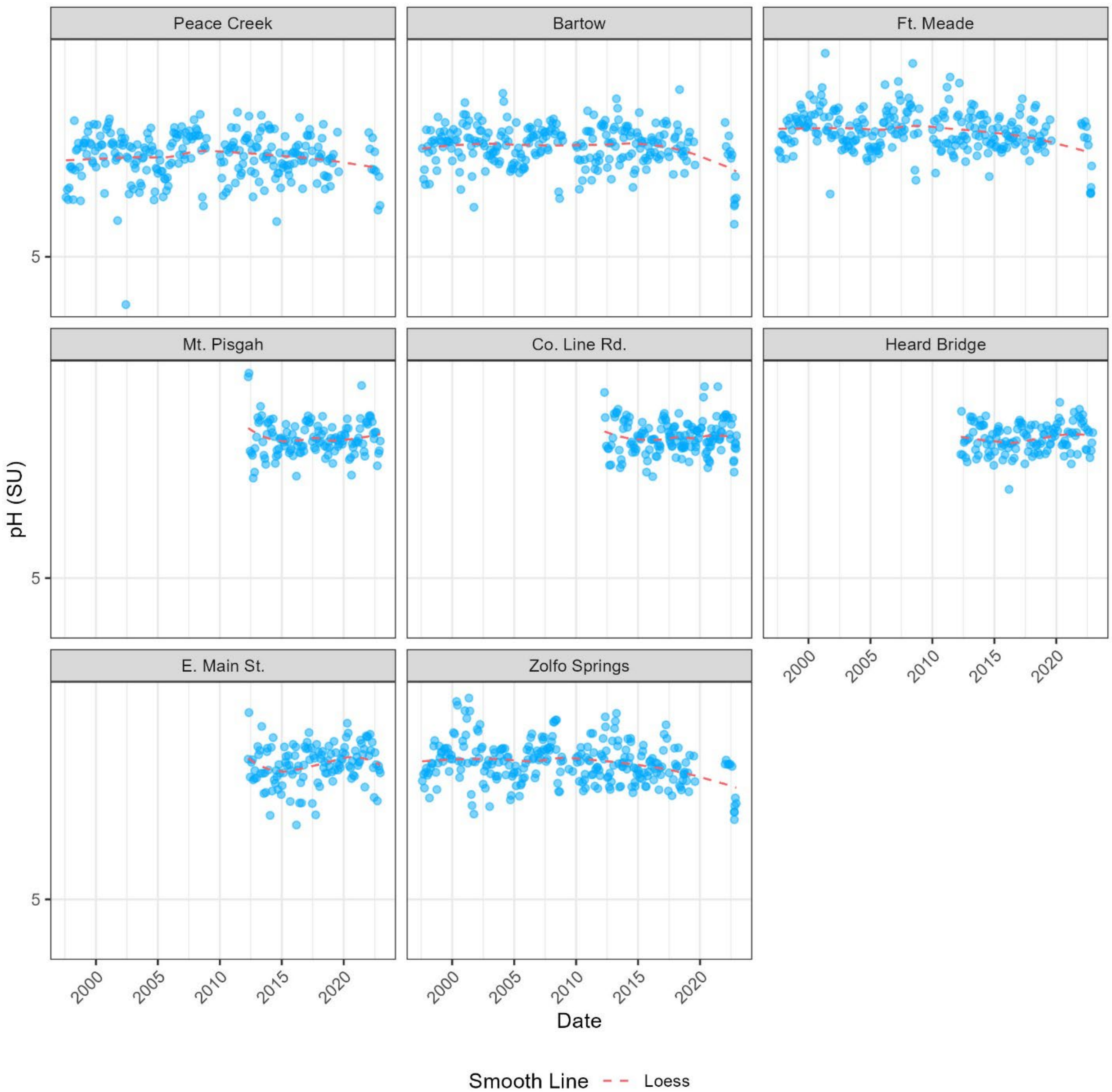


Figure 66. Time series showing observed pH (SU) (blue points) with LOESS smoothing curves (dashed red lines) across monitoring stations. The LOESS curves capture temporal patterns in the data, with residuals from these fits used for subsequent flow-adjusted trend analysis. Note: Concentrations are displayed on a logarithmic scale.

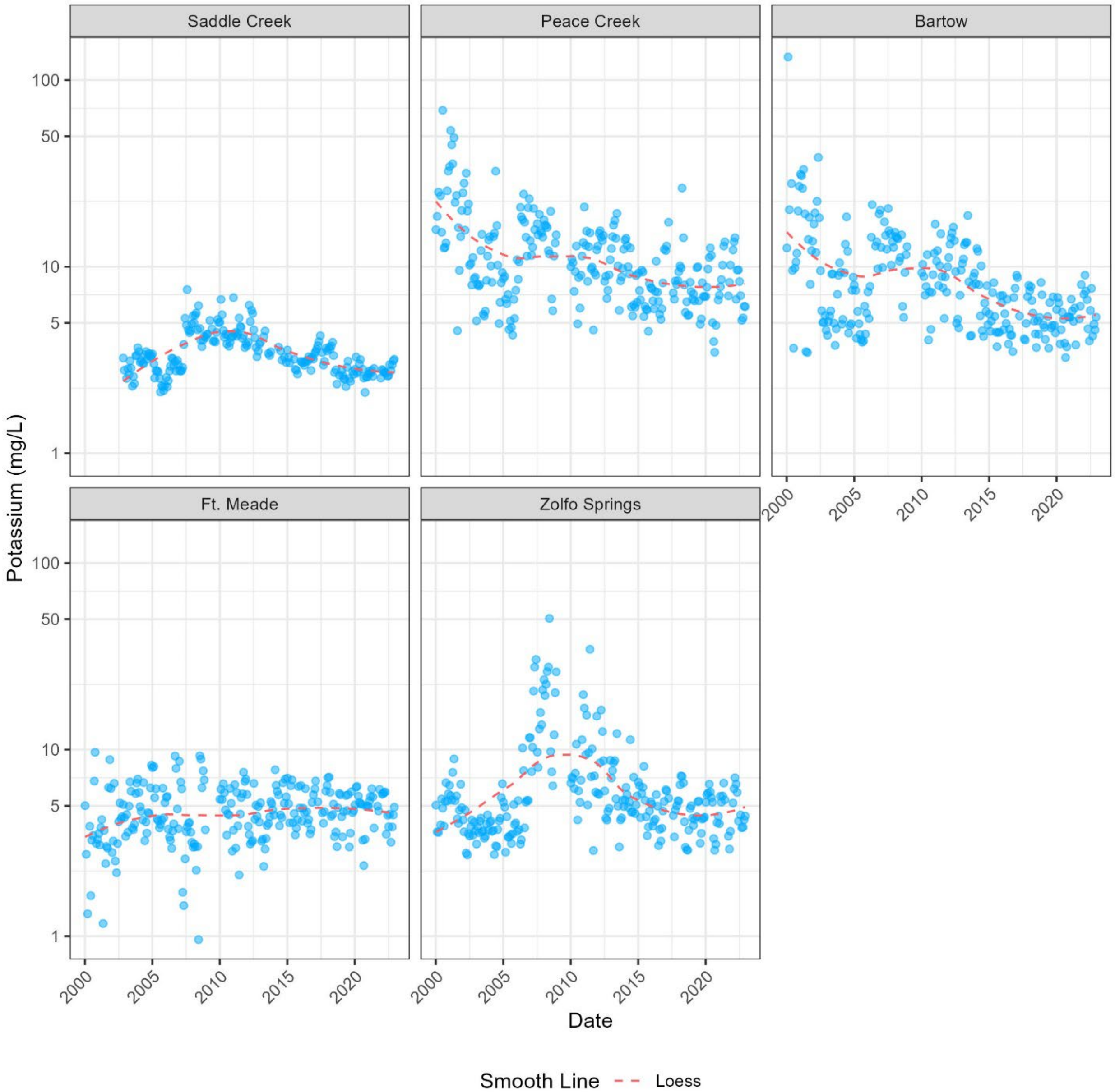


Figure 67. Time series showing observed potassium (mg/L) concentrations (blue points) with LOESS smoothing curves (dashed red lines) across monitoring stations. The LOESS curves capture temporal patterns in the data, with residuals from these fits used for subsequent flow-adjusted trend analysis. Note: Concentrations are displayed on a logarithmic scale.

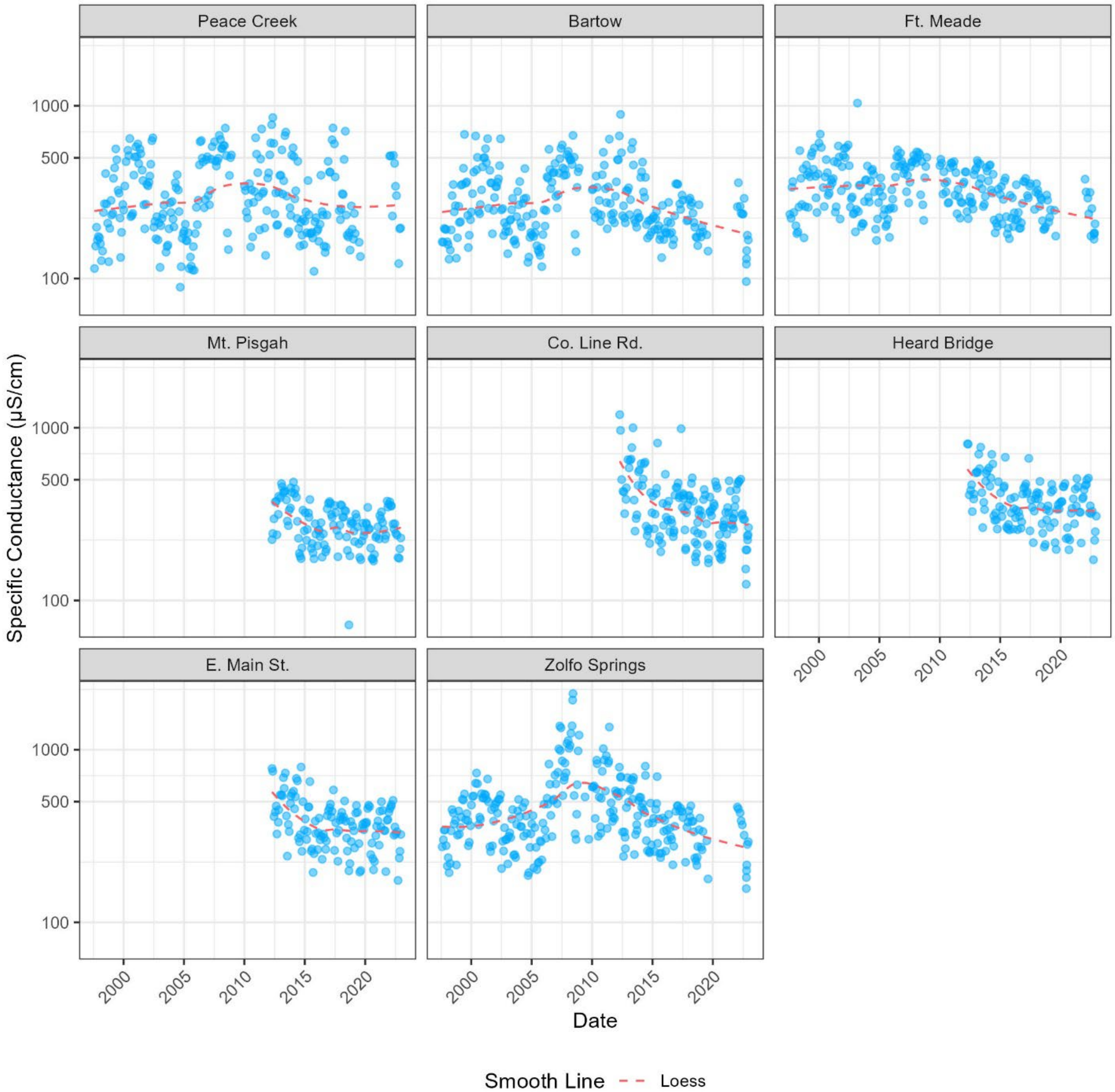


Figure 68. Time series showing observed specific conductance (blue points) with LOESS smoothing curves (dashed red lines) across monitoring stations. The LOESS curves capture temporal patterns in the data, with residuals from these fits used for subsequent flow-adjusted trend analysis. Note: Concentrations are displayed on a logarithmic scale.

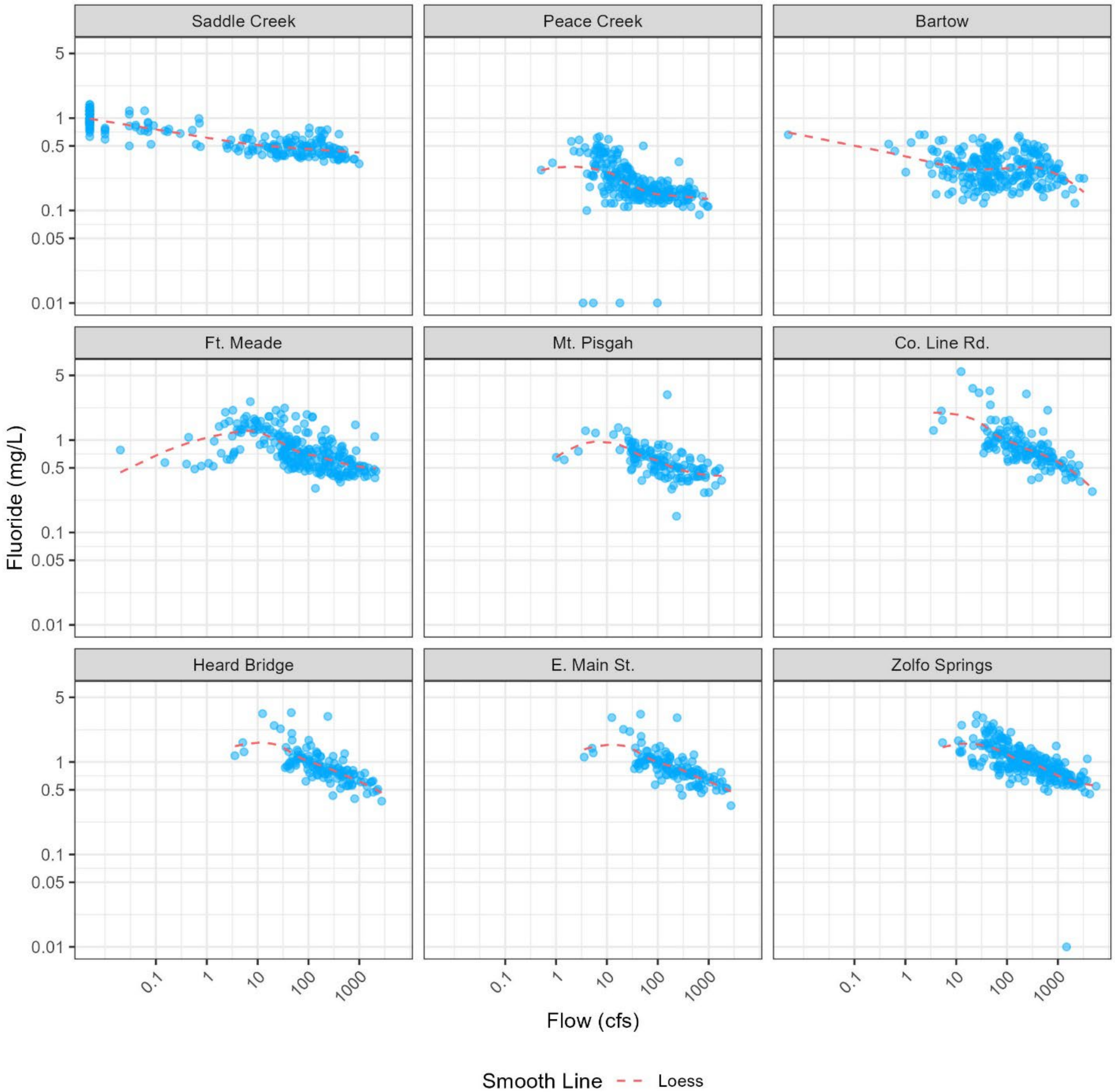


Figure 69. Relationship between streamflow and fluoride (mg/L) concentrations (blue points) with LOESS smoothing curves (dashed red lines) across monitoring stations. The LOESS curves capture flow-concentration patterns in the data, with residuals from these fits used for subsequent trend analysis. Note: Both flow and concentration are displayed on logarithmic scales.

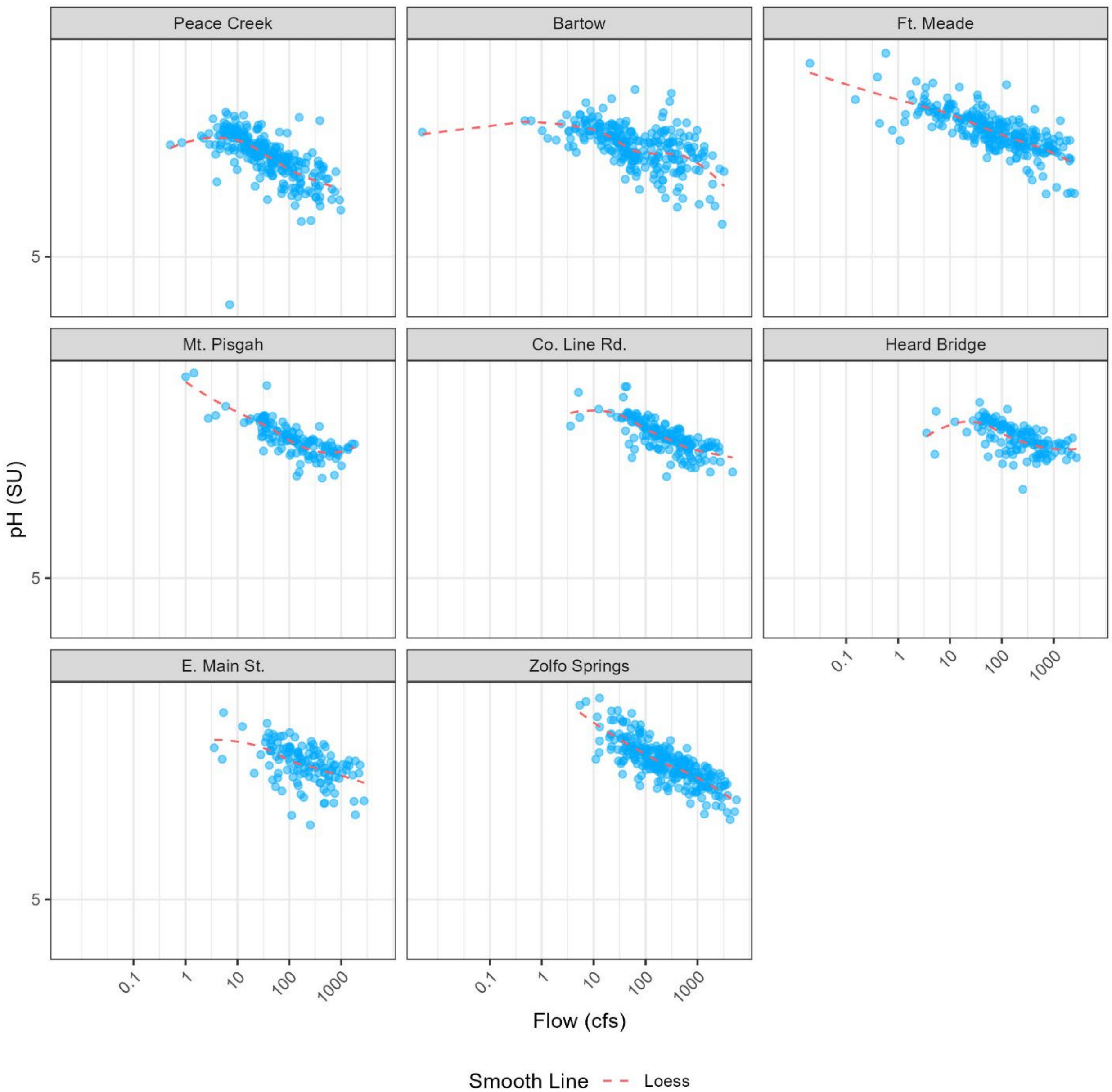


Figure 70. Relationship between streamflow and pH (SU) concentrations (blue points) with LOESS smoothing curves (dashed red lines) across monitoring stations. The LOESS curves capture flow-concentration patterns in the data, with residuals from these fits used for subsequent trend analysis. Note: Both flow and concentration are displayed on logarithmic scales.

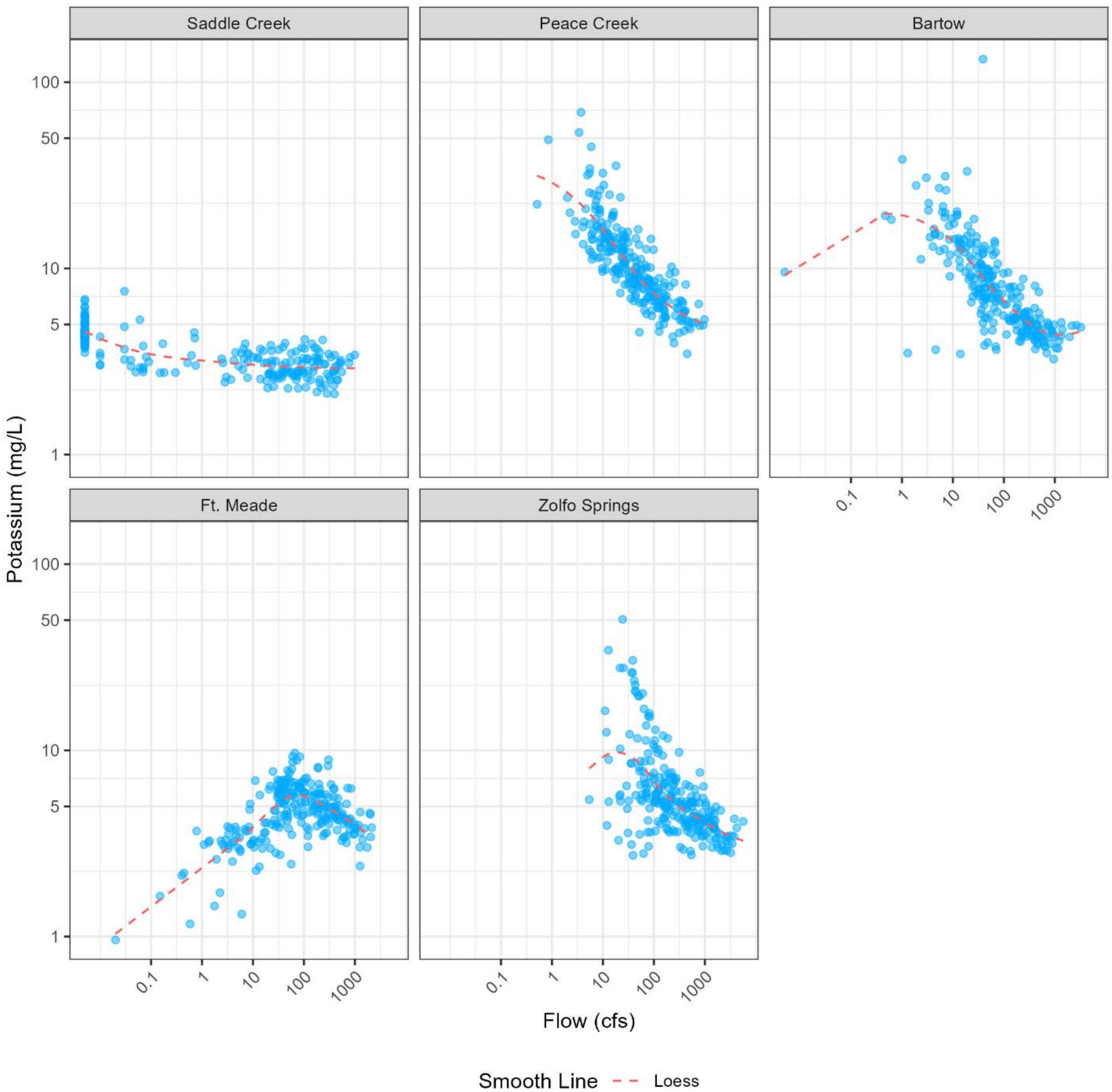


Figure 71. Relationship between streamflow and potassium (mg/L) concentrations (blue points) with LOESS smoothing curves (dashed red lines) across monitoring stations. The LOESS curves capture flow-concentration patterns in the data, with residuals from these fits used for subsequent trend analysis. Note: Both flow and concentration are displayed on logarithmic scales.

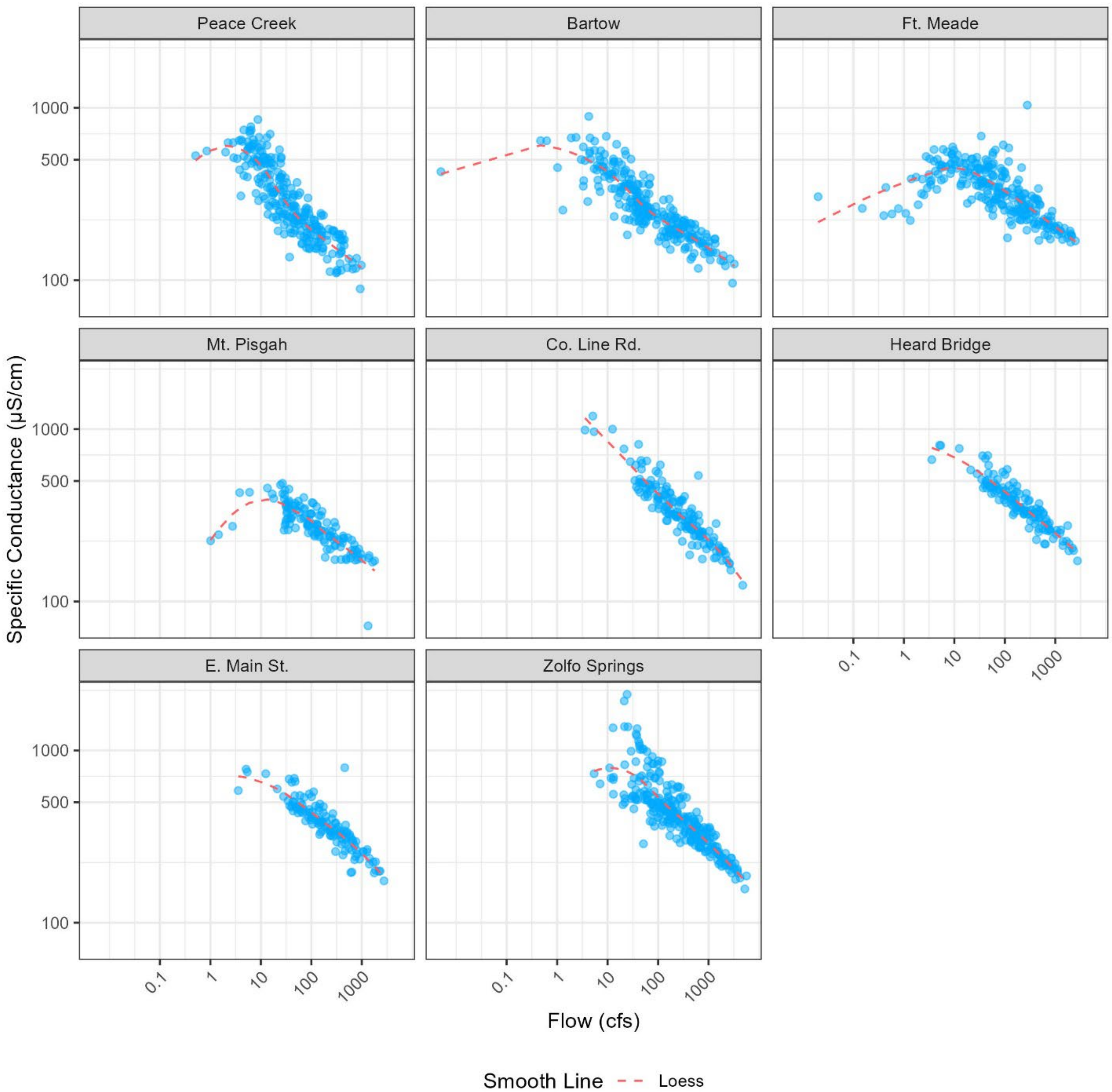


Figure 72. Relationship between streamflow and specific conductance (blue points) with LOESS smoothing curves (dashed red lines) across monitoring stations. The LOESS curves capture flow-concentration patterns in the data, with residuals from these fits used for subsequent trend analysis. Note: Both flow and concentration are displayed on logarithmic scales.

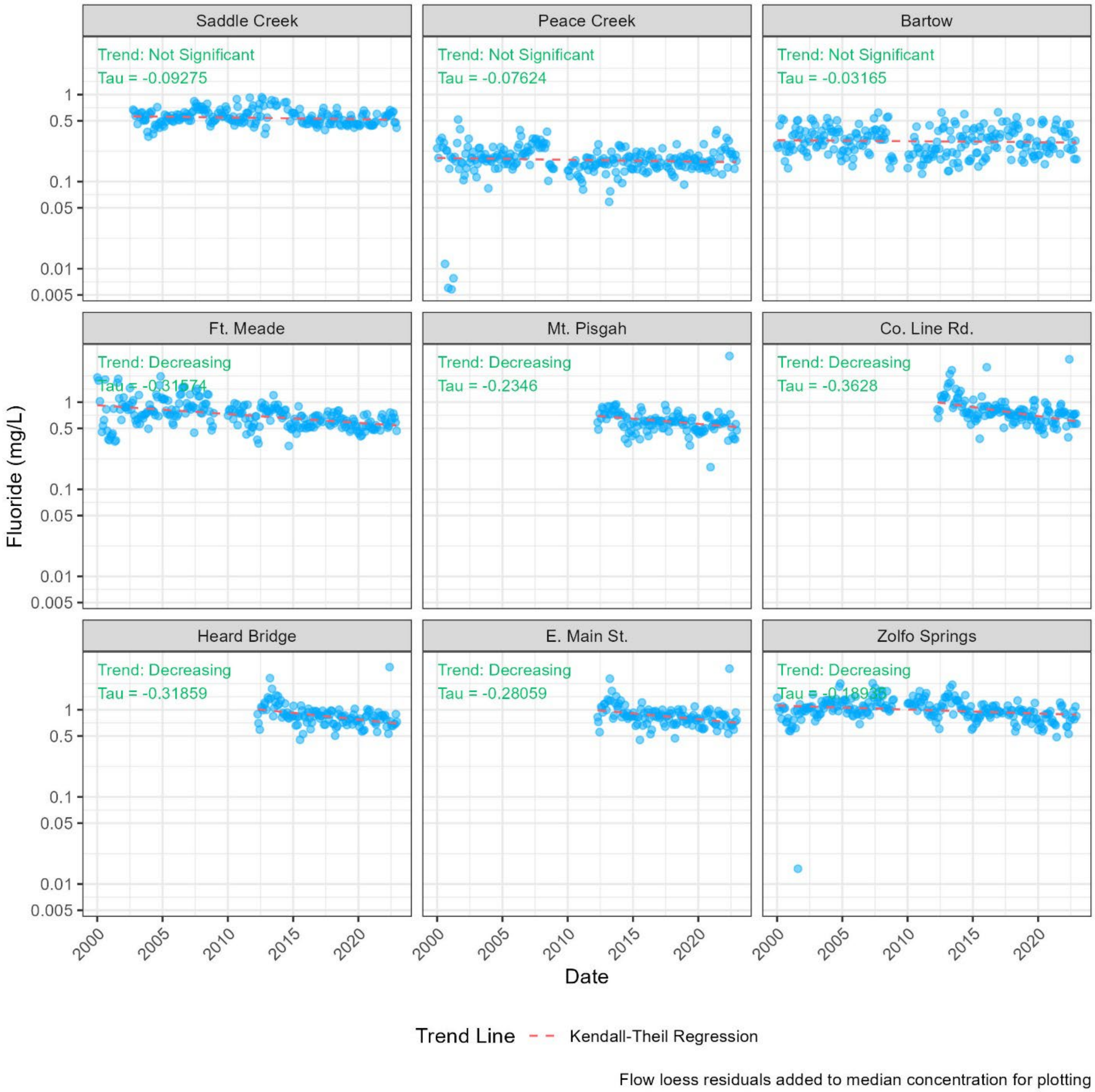


Figure 73. Flow-adjusted trends in fluoride concentrations across monitoring stations. Points show LOESS residuals from the flow-concentration relationship (blue points) rescaled to the original concentration units, with Kendall-Theil regression lines (dashed red) indicating long-term trends. Text annotations provide the Sen slope (trend magnitude) and Kendall's tau correlation coefficient for each station. Note: Residuals are centered on the mean concentration for each station to maintain interpretable units.

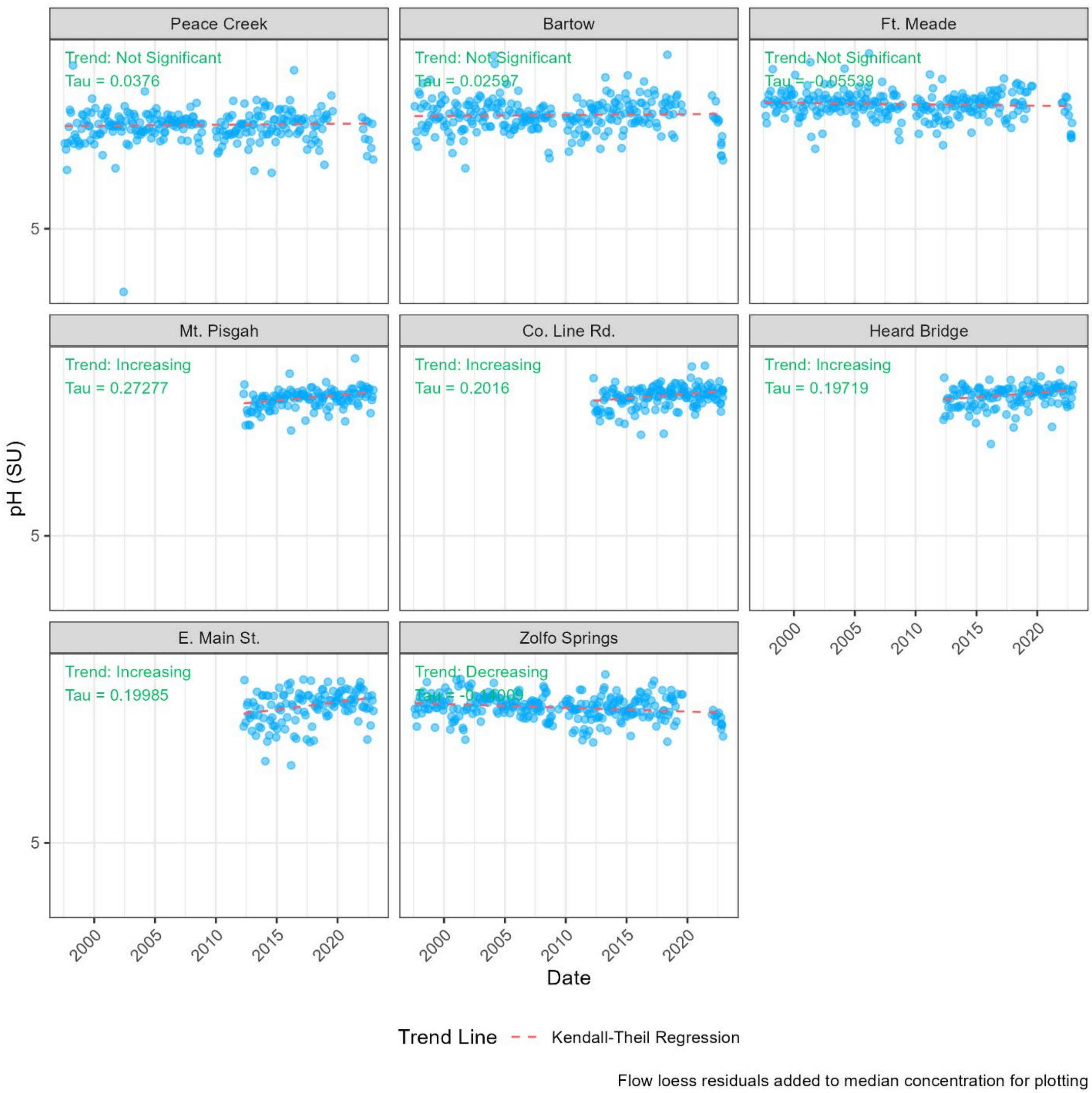


Figure 74. Flow-adjusted trends in pH across monitoring stations. Points show LOESS residuals from the flow-concentration relationship (blue points) rescaled to the original concentration units, with Kendall-Theil regression lines (dashed red) indicating long-term trends. Text annotations provide the Sen slope (trend magnitude) and Kendall's tau correlation coefficient for each station. Note: Residuals are centered on the mean concentration for each station to maintain interpretable units.

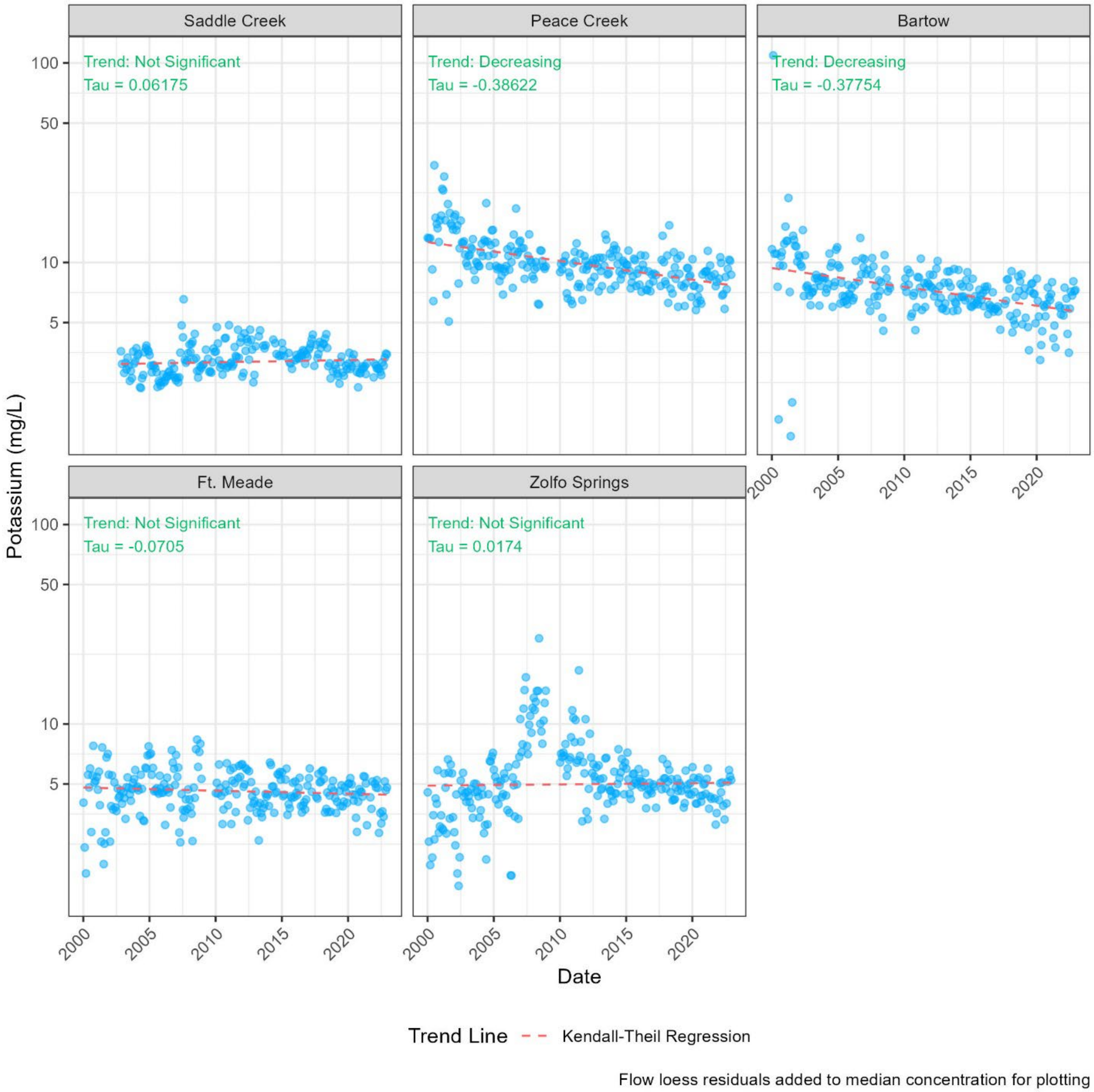


Figure 75. Flow-adjusted trends in potassium concentrations across monitoring stations. Points show LOESS residuals from the flow-concentration relationship (blue points) rescaled to the original concentration units, with Kendall-Theil regression lines (dashed red) indicating long-term trends. Text annotations provide the Sen slope (trend magnitude) and Kendall's tau correlation coefficient for each station. Note: Residuals are centered on the mean concentration for each station to maintain interpretable units.

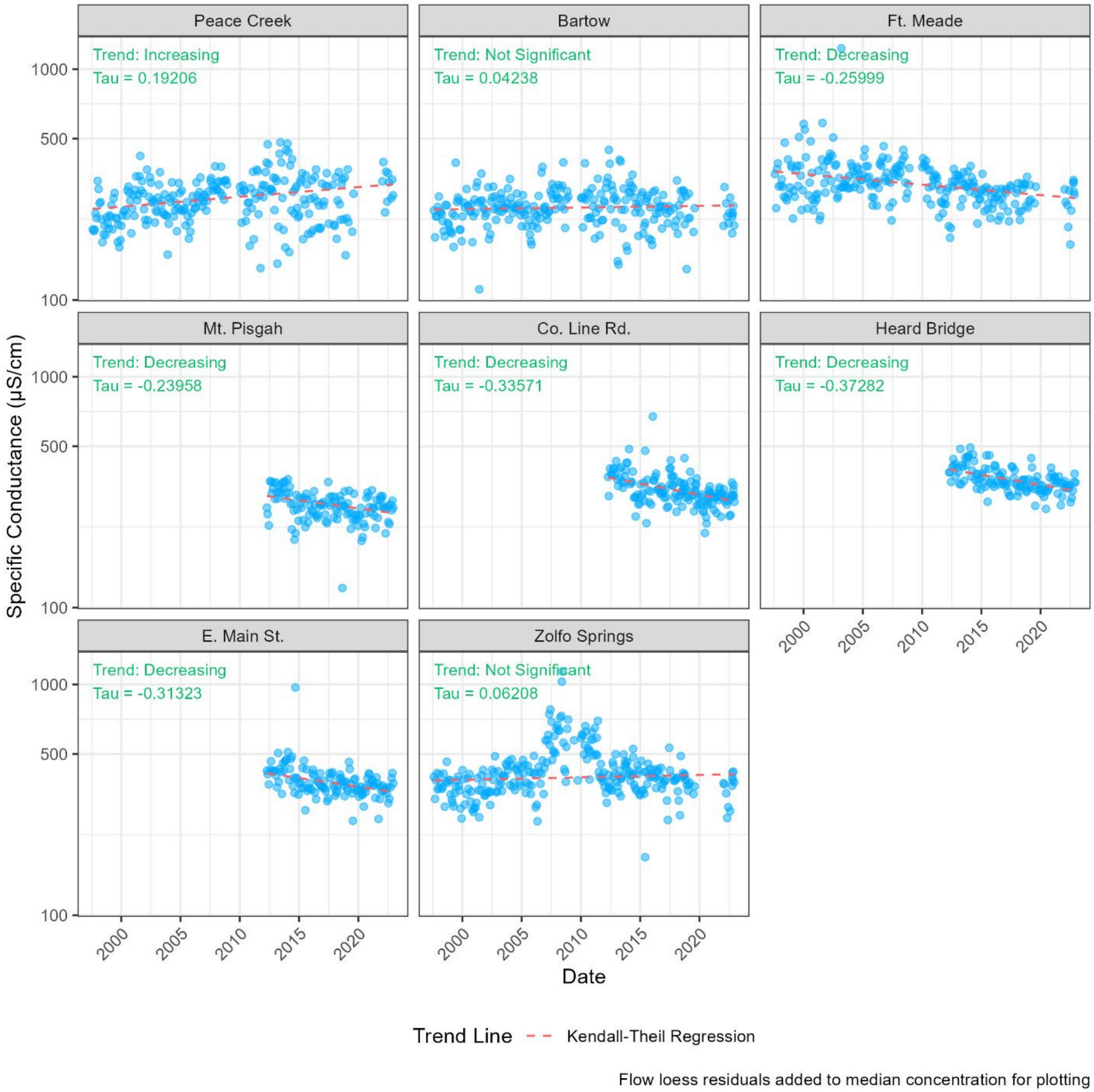


Figure 76. Flow-adjusted trends in specific conductance across monitoring stations. Points show LOESS residuals from the flow-concentration relationship (blue points) rescaled to the original concentration units, with Kendall-Theil regression lines (dashed red) indicating long-term trends. Text annotations provide the Sen slope (trend magnitude) and Kendall's tau correlation coefficient for each station. Note: Residuals are centered on the mean concentration for each station to maintain interpretable units.

Table 24. Summary of Kendall-Theil tests for trend with date by station and parameter. Trends are classified as Positive (Pos), Negative (Neg), or Not Significant (NS), based on Kendall's tau significance (α = 0.05). Raw p values (p_raw) are adjusted using Bonferroni correction for number of stations tested (n_t) to produce adjusted p values (p_adj).

Parameter	Station	Slope	Tau	n_t	p_raw	p_adj	Trend
Fluoride	Saddle Creek	-5.29e-06	-0.093	9	4.54e-02	4.09e-01	Not Significant
Fluoride	Peace Creek	-5.82e-06	-0.076	9	7.14e-02	6.43e-01	Not Significant
Fluoride	Bartow	-3.13e-06	-0.032	9	4.56e-01	4.10e+00	Not Significant
Fluoride	Ft. Meade	-2.76e-05	-0.316	9	6.56e-14	5.90e-13	Decreasing
Fluoride	Mt. Pisgah	-3.27e-05	-0.235	9	9.17e-05	8.25e-04	Decreasing
Fluoride	Co. Line Rd.	-5.61e-05	-0.363	9	2.03e-10	1.82e-09	Decreasing
Fluoride	Heard Bridge	-4.16e-05	-0.319	9	1.08e-07	9.75e-07	Decreasing
Fluoride	E. Main St.	-3.68e-05	-0.281	9	2.89e-06	2.60e-05	Decreasing
Fluoride	Zolfo Springs	-1.25e-05	-0.189	9	7.24e-06	6.51e-05	Decreasing
Potassium	Saddle Creek	3.11e-06	0.062	5	1.83e-01	9.16e-01	Not Significant
Potassium	Peace Creek	-2.58e-05	-0.386	5	5.61e-20	2.81e-19	Decreasing
Potassium	Bartow	-2.58e-05	-0.378	5	4.35e-19	2.17e-18	Decreasing
Potassium	Ft. Meade	-4.27e-06	-0.07	5	9.35e-02	4.68e-01	Not Significant
Potassium	Zolfo Springs	1.65e-06	0.017	5	6.80e-01	3.40e+00	Not Significant
Specific Conductance	Peace Creek	1.16e-05	0.192	8	5.12e-06	4.09e-05	Increasing
Specific Conductance	Bartow	1.92e-06	0.042	8	3.10e-01	2.48e+00	Not Significant
Specific Conductance	Ft. Meade	-1.24e-05	-0.26	8	5.74e-10	4.59e-09	Decreasing
Specific Conductance	Mt. Pisgah	-1.90e-05	-0.24	8	5.65e-05	4.52e-04	Decreasing
Specific Conductance	Co. Line Rd.	-2.61e-05	-0.336	8	6.46e-10	5.17e-09	Decreasing
Specific Conductance	Heard Bridge	-2.38e-05	-0.373	8	3.69e-10	2.95e-09	Decreasing
Specific Conductance	E. Main St.	-2.08e-05	-0.313	8	1.40e-07	1.12e-06	Decreasing
Specific Conductance	Zolfo Springs	2.90e-06	0.062	8	1.24e-01	9.94e-01	Not Significant
pH	Peace Creek	5.43e-06	0.036	8	3.97e-01	3.18e+00	Not Significant
pH	Bartow	4.91e-06	0.025	8	5.57e-01	4.46e+00	Not Significant
pH	Ft. Meade	-8.46e-06	-0.053	8	2.08e-01	1.66e+00	Not Significant
pH	Mt. Pisgah	6.64e-05	0.272	8	4.91e-06	3.93e-05	Increasing
pH	Co. Line Rd.	5.54e-05	0.2	8	2.26e-04	1.80e-03	Increasing
pH	Heard Bridge	5.48e-05	0.197	8	9.32e-04	7.45e-03	Increasing
pH	E. Main St.	9.42e-05	0.199	8	8.29e-04	6.63e-03	Increasing
pH	Zolfo Springs	-2.28e-05	-0.139	8	6.19e-04	4.95e-03	Decreasing

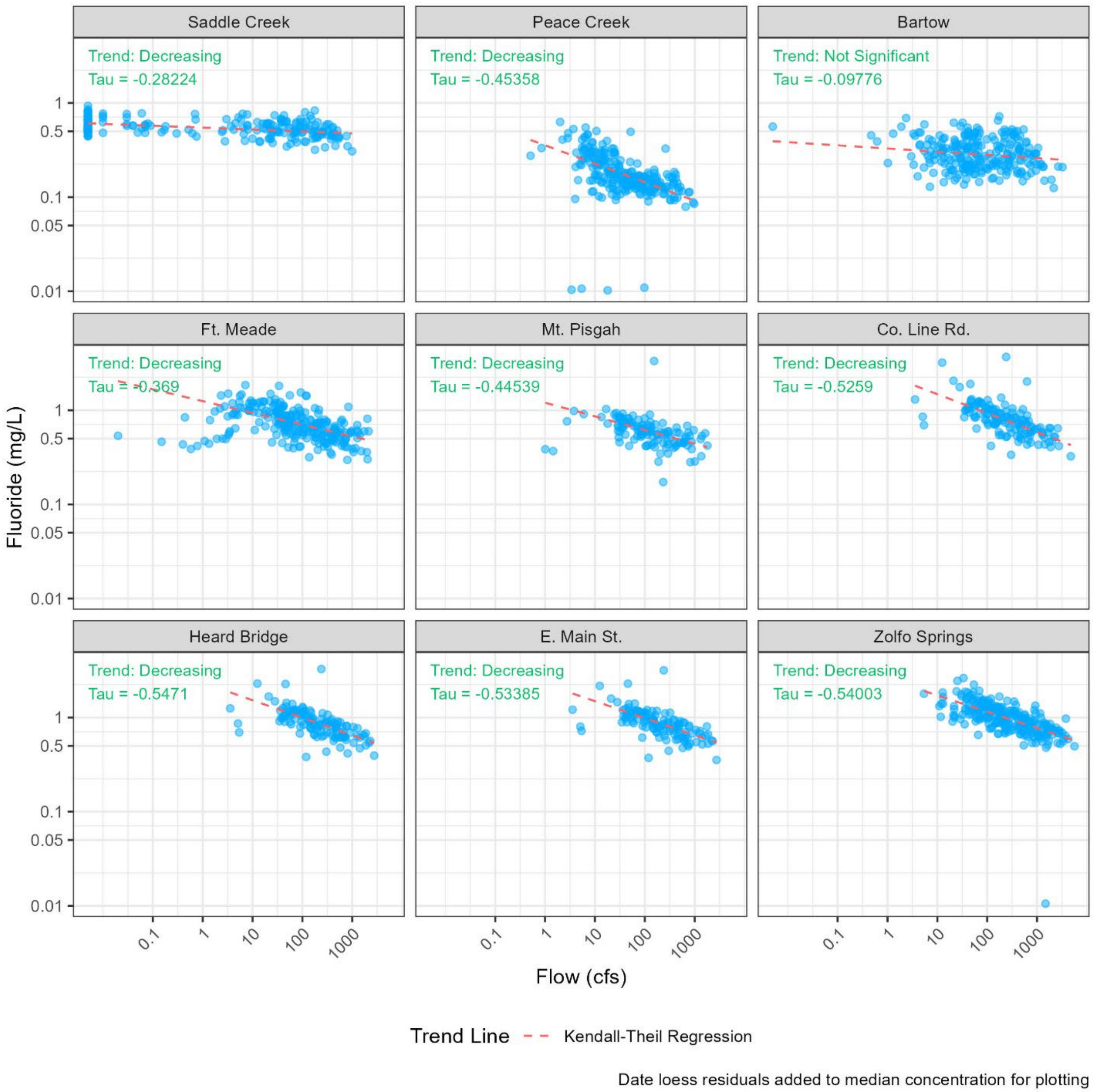


Figure 77. Date-adjusted relationships in fluoride concentrations with Flow across monitoring stations. Points show LOESS residuals from the date-concentration relationship (blue points) rescaled to the original concentration units, with Kendall-Theil regression lines (dashed red) indicating long-term trends. Text annotations provide the Sen slope (trend magnitude) and Kendall's tau correlation coefficient for each station. Note: Residuals are centered on the mean concentration for each station to maintain interpretable units.

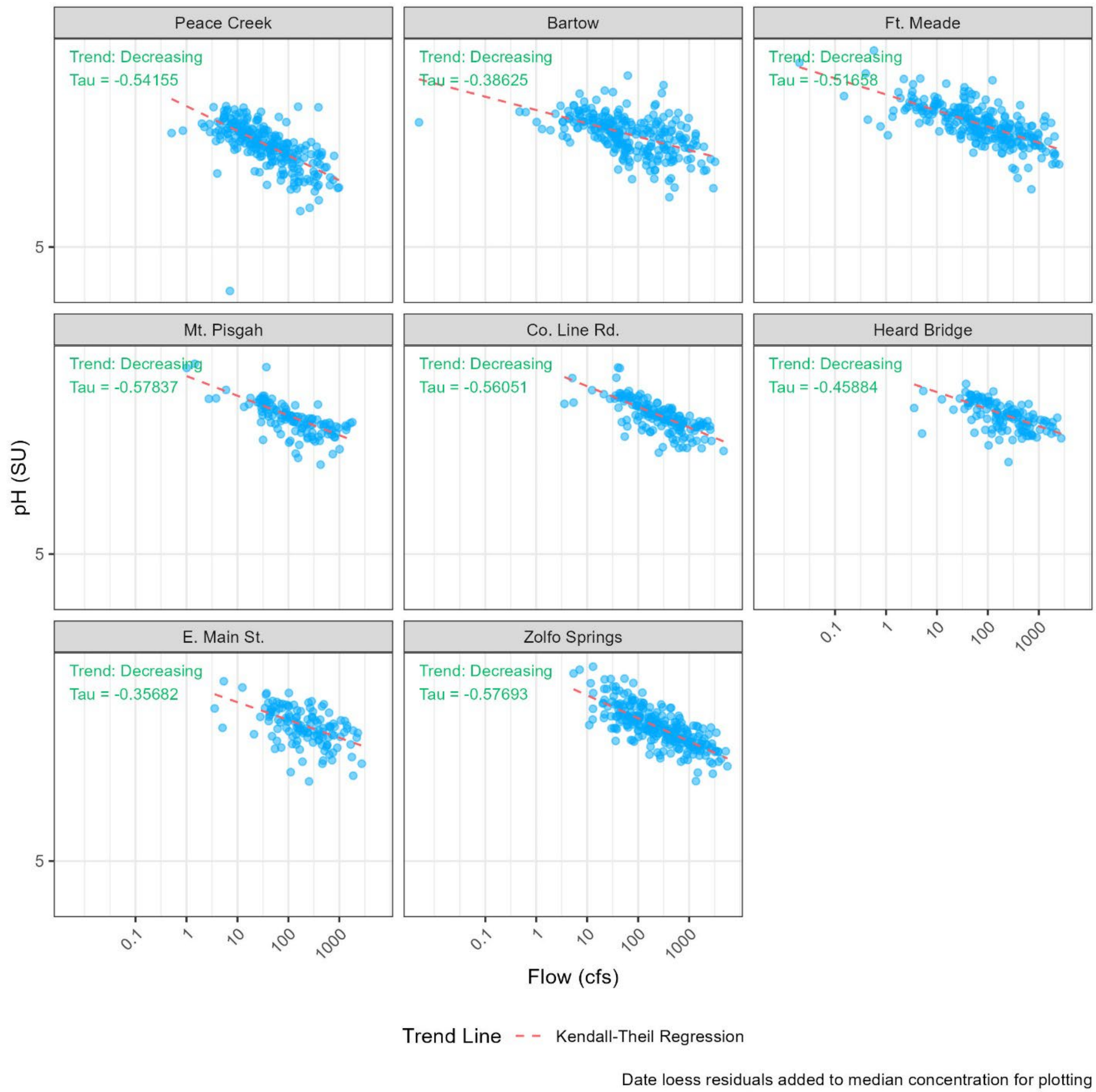


Figure 78. Date-adjusted relationships in pH with Flow across monitoring stations. Points show LOESS residuals from the date-concentration relationship (blue points) rescaled to the original concentration units, with Kendall-Theil regression lines (dashed red) indicating long-term trends. Text annotations provide the Sen slope (trend magnitude) and Kendall's tau correlation coefficient for each station. Note: Residuals are centered on the mean concentration for each station to maintain interpretable units.

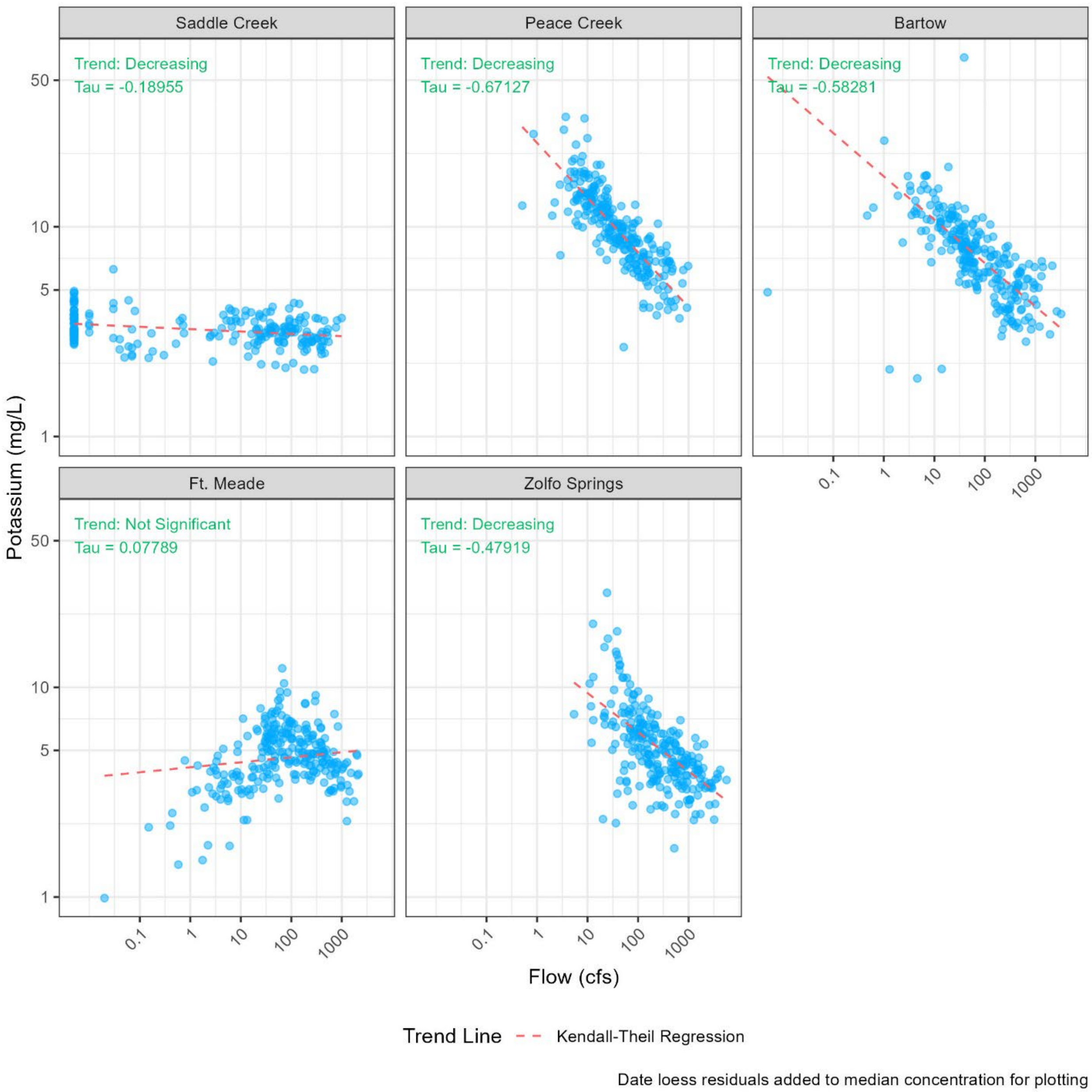


Figure 79. Date-adjusted relationships in potassium concentrations with Flow across monitoring stations. Points show LOESS residuals from the date-concentration relationship (blue points) rescaled to the original concentration units, with Kendall-Theil regression lines (dashed red) indicating long-term trends. Text annotations provide the Sen slope (trend magnitude) and Kendall's tau correlation coefficient for each station. Note: Residuals are centered on the mean concentration for each station to maintain interpretable units.

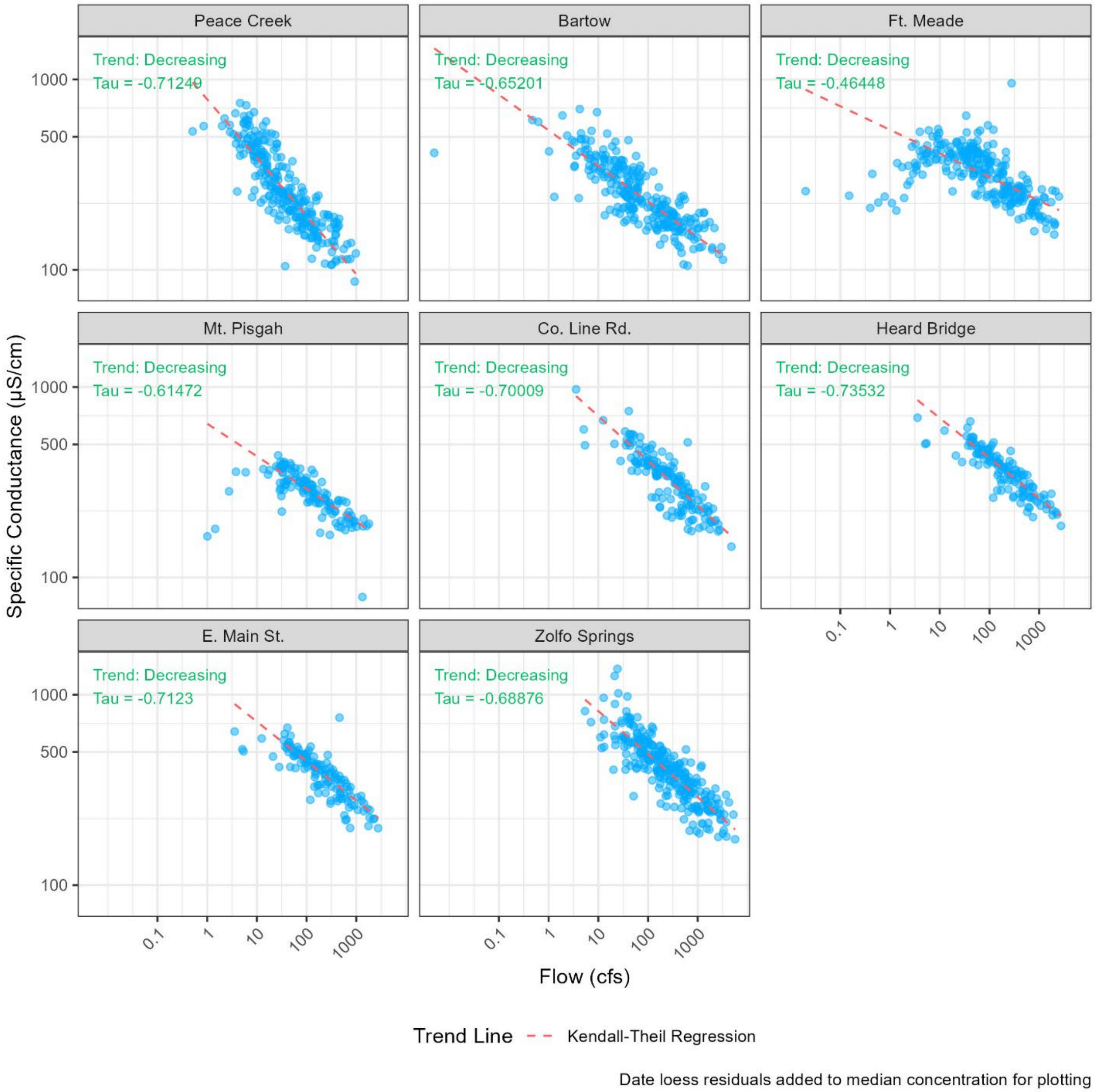


Figure 80. Date-adjusted relationships in specific conductance with Flow across monitoring stations. Points show LOESS residuals from the date-concentration relationship (blue points) rescaled to the original concentration units, with Kendall-Theil regression lines (dashed red) indicating long-term trends. Text annotations provide the Sen slope (trend magnitude) and Kendall's tau correlation coefficient for each station. Note: Residuals are centered on the mean concentration for each station to maintain interpretable units.

Table 25. Summary of Kendall-Theil tests for trend with flow by station and parameter. Trends are classified as Positive (Pos), Negative (Neg), or Not Significant (NS), based on Kendall's tau significance (α = 0.05). Raw p values (p_raw) are adjusted using Bonferroni correction for number of stations tested (n_t) to produce adjusted p values (p_adj).

Parameter	Station	Slope	Tau	n_t	p_raw	p_adj	Trend
Fluoride	Saddle Creek	-2.00e-02	-0.282	9	2.67e-09	2.41e-08	Decreasing
Fluoride	Peace Creek	-1.96e-01	-0.454	9	7.99e-27	7.19e-26	Decreasing
Fluoride	Bartow	-3.40e-02	-0.098	9	2.13e-02	1.92e-01	Not Significant
Fluoride	Ft. Meade	-1.25e-01	-0.369	9	1.97e-18	1.77e-17	Decreasing
Fluoride	Mt. Pisgah	-1.45e-01	-0.445	9	1.14e-13	1.03e-12	Decreasing
Fluoride	Co. Line Rd.	-2.02e-01	-0.526	9	3.06e-20	2.76e-19	Decreasing
Fluoride	Heard Bridge	-1.86e-01	-0.547	9	7.53e-20	6.78e-19	Decreasing
Fluoride	E. Main St.	-1.80e-01	-0.534	9	5.64e-19	5.08e-18	Decreasing
Fluoride	Zolfo Springs	-1.74e-01	-0.54	9	1.83e-37	1.64e-36	Decreasing
Potassium	Saddle Creek	-1.12e-02	-0.19	5	6.81e-05	3.41e-04	Decreasing
Potassium	Peace Creek	-2.61e-01	-0.671	5	6.33e-57	3.16e-56	Decreasing
Potassium	Bartow	-2.07e-01	-0.583	5	3.44e-43	1.72e-42	Decreasing
Potassium	Ft. Meade	2.38e-02	0.078	5	6.39e-02	3.20e-01	Not Significant
Potassium	Zolfo Springs	-1.87e-01	-0.479	5	5.71e-30	2.85e-29	Decreasing
Specific Conductance	Peace Creek	-3.06e-01	-0.712	8	3.91e-64	3.13e-63	Decreasing
Specific Conductance	Bartow	-1.87e-01	-0.652	8	7.47e-55	5.98e-54	Decreasing
Specific Conductance	Ft. Meade	-1.24e-01	-0.464	8	1.76e-28	1.40e-27	Decreasing
Specific Conductance	Mt. Pisgah	-1.71e-01	-0.615	8	5.25e-25	4.20e-24	Decreasing
Specific Conductance	Co. Line Rd.	-2.35e-01	-0.7	8	5.64e-38	4.51e-37	Decreasing
Specific Conductance	Heard Bridge	-2.10e-01	-0.735	8	4.52e-35	3.61e-34	Decreasing
Specific Conductance	E. Main St.	-2.07e-01	-0.712	8	5.15e-33	4.12e-32	Decreasing
Specific Conductance	Zolfo Springs	-2.26e-01	-0.689	8	3.52e-65	2.82e-64	Decreasing
pH	Peace Creek	-5.00e-01	-0.543	8	5.54e-38	4.43e-37	Decreasing
pH	Bartow	-2.79e-01	-0.388	8	1.57e-20	1.26e-19	Decreasing
pH	Ft. Meade	-3.52e-01	-0.516	8	9.77e-35	7.81e-34	Decreasing
pH	Mt. Pisgah	-4.47e-01	-0.572	8	7.73e-22	6.18e-21	Decreasing
pH	Co. Line Rd.	-4.73e-01	-0.558	8	1.06e-24	8.44e-24	Decreasing
pH	Heard Bridge	-3.94e-01	-0.459	8	1.26e-14	1.01e-13	Decreasing
pH	E. Main St.	-4.06e-01	-0.361	8	1.35e-09	1.08e-08	Decreasing
pH	Zolfo Springs	-5.13e-01	-0.578	8	3.03e-46	2.42e-45	Decreasing

Table 26. Summary of flow-adjusted concentration trends with date showing counts of increasing, decreasing, and not-significant results.

Parameter	n_increasing	n_decreasing	n_not_significant
Fluoride (mg/L)	0	6	3
Potassium (mg/L)	0	2	3
Specific Conductance (µS/cm)	1	5	2
pH (SU)	4	1	3
Total	5	14	11

Table 27. Summary of date-adjusted concentration trends with flow showing counts of increasing, decreasing, and not-significant results.

Parameter	n_increasing	n_decreasing	n_not_significant
Fluoride (mg/L)	0	8	1
Potassium (mg/L)	0	4	1
Specific Conductance (µS/cm)	0	8	0
pH (SU)	0	8	0
Total	0	28	2

Dissolved Oxygen and Temperature

Oxygen gas from the atmosphere dissolves into water according to partial pressure and temperature. Oxygen is important for fish habitat and low oxygen can result in fish die-offs. Dissolved oxygen also affects the redox potential, which in turn affects bioavailability of minerals and ions (Allan et al. 2021).

Location, spread, and normality

These parameters have different units and are associated with different biogeochemical processes in the environment, limiting the utility of comparison of their quantiles, but comparing skewness and frequency distributions is still possible.

Means and medians across all sites for ion statistics including fluoride, potassium, specific conductance and pH are shown in Table 28. Quantile plots illustrate distributions of nutrient data (Figure 56). Frequencies were calculated on log10 transformed values of fluoride, potassium, and specific conductance. Because pH is already on a log10 scale, it was not transformed for analysis. Boxplots (Figure 57) provide visual summaries of 1) the center of the data (the median--the center line of the box), 2) the variation or spread (interquartile range--the box height), 3) the skewness (quartile skew--the relative size of box halves), and 4) presence or absence of unusual values ("outside" – lines, and "far outside" values - circles). The data are displayed on a log scale due to the wide range of concentrations.

Histograms are useful for depicting large differences in shape or symmetry, such as whether a data set appears symmetric or skewed (Figure 58) (Helsel and Hirsch 2002).

Probability plots of log-transformed data illustrate how well data fit a lognormal distribution (Figure 59). Normal quantiles are the data values expected based on a normal distribution with the same mean and standard deviation of the sample data. The probability plot correlation coefficient (PPCC) tests for normality by computing the linear correlation coefficient between data and their normal quantiles. Samples from a normal distribution will have a correlation coefficient very close to 1.0. As data depart from normality, their correlation coefficient will decrease below 1. The critical correlation value corresponds to the value the correlation coefficient must exceed for the data to be considered normally distributed. All parameters are non-normal according to the PPCC as well as Anderson-Darling test for normality after Log10 transformation of data (Table 22).

Table 28. Univariate summary statistics for nutrients at all sites. The interquartile range (IQR) = P75 – P25. The skewness coefficient (G) is the adjusted third moment divided by the cube of the standard deviation, and is a measure of skewness that is sensitive to outliers (Helsel and Hirsch 2002). The quartile skew coefficient (QS) quantifies skewness as the difference in distances of the upper and lower quartiles from the median, divided by the IQR for a resistant measure of skewness.

Parameter	Min	P25	P50	Mean	P75	Max	Obs	G	IQR	QS
DO (mg/L)	0.06	4.71	6.14	6.113	7.72	13.94	1309	-0.052	3.01	0.05
DO_sat (%)	24.1	72.9	80.7	79.858	88.1	133	461	-0.332	15.2	-0.026
Temperature (°C)	8.94	20.15	24.4	23.487	27.3	34.64	1585	-0.621	7.15	-0.189

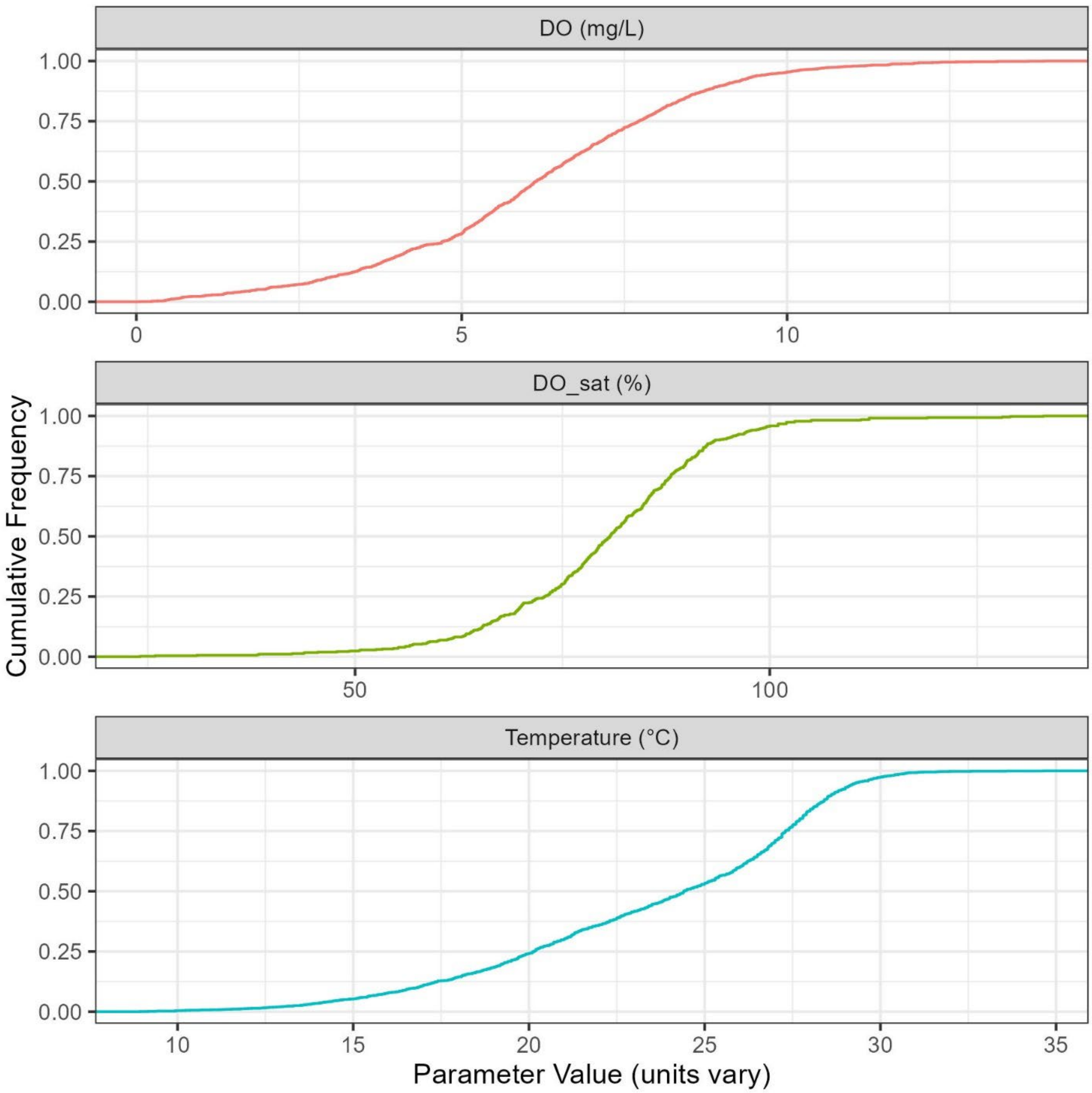


Figure 81. Quantiles of parameter values. Quantile plots visually portray the quantiles, or cumulative frequency of observations of nutrient concentrations. Quantiles of importance such as the median are easily discerned (quantile, or cumulative frequency = 0.5) (Helsel and Hirsch 2002).

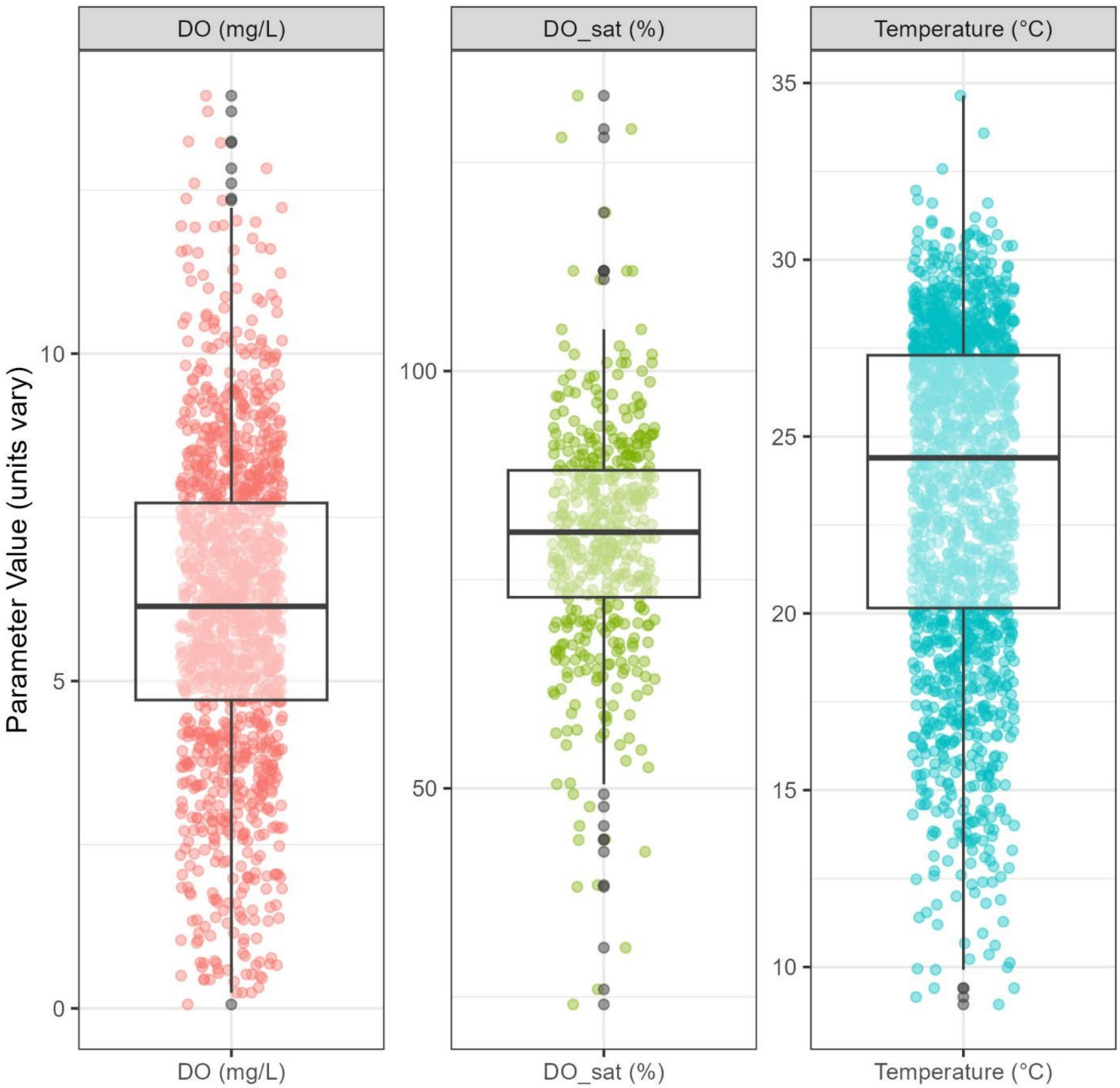


Figure 82. Concentrations using jittered points to display individual data values and boxplots to summarize the distribution. The y-axis is scaled logarithmically to better visualize the range of concentrations, and boxplot statistics are calculated on non-transformed data.

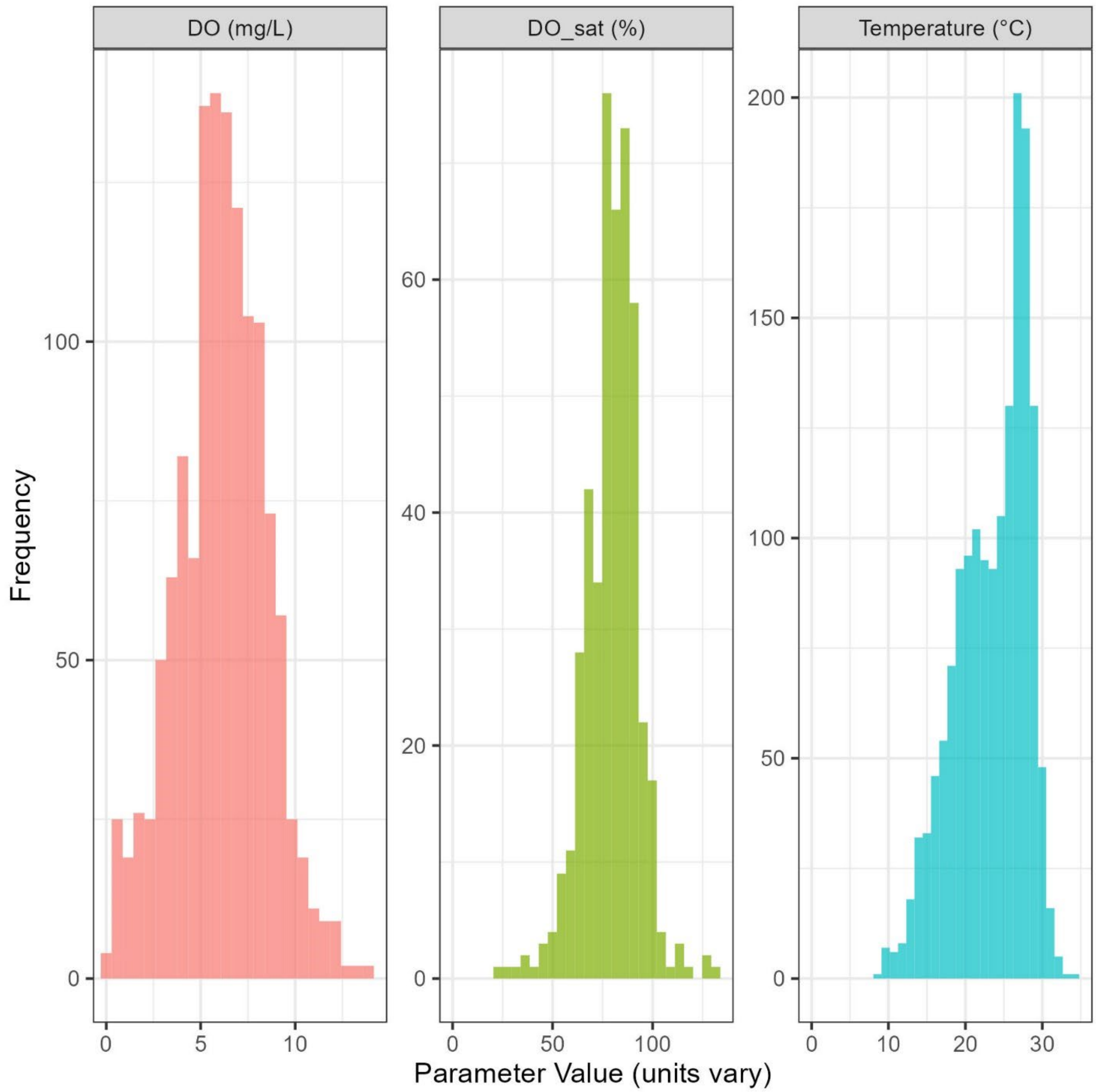


Figure 83. Frequency distributions of parameters. The scales are adjusted per nutrient to highlight their unique distribution patterns.

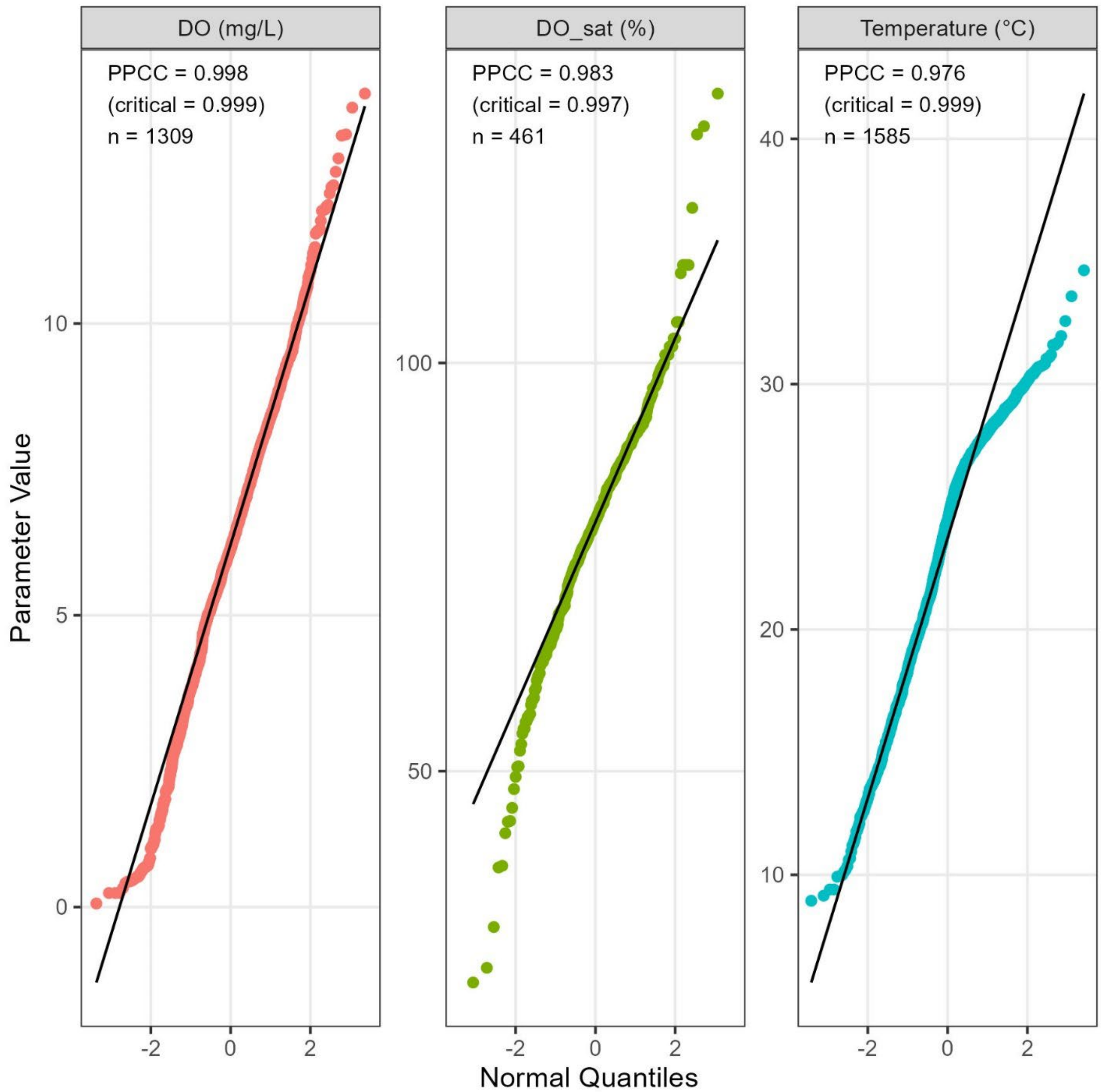


Figure 84. Normal probability plots for parameter concentrations, comparing theoretical quantiles to sample quantiles. Normal quantiles are values expected from a perfectly normal distribution at specific probabilities, serving as a reference for normality. If the data follow a normal distribution, the points align closely with the diagonal line. Deviations from the line indicate departures from normality. The Probability Plot Correlation Coefficient (PPCC) is the linear correlation coefficient between data and their normal quantiles. PPCC values below the critical value indicate rejection of null hypothesis that data are from a normal distribution. All plots show non-normal distributions.

Table 29. Results of Anderson-Darling test for normality of log10 transformed data. All parameters are non-normal with p values below 0.01.

Parameter	AD_statistic	p_AD
DO (mg/L)	1.441676	0.001005
DO_sat (%)	3.044554	1.19E-07
Temperature (°C)	26.20529	3.7E-24

Testing for difference between groups

Exploration of differences between stations and season is complicated: there are 9 stations and 2 seasons for each parameter, which combine for 36 pairwise comparisons between stations and 152 pairwise comparisons between stations and seasons. The results provided here summarize patterns, while deeper analysis is always possible. There are significant differences between wet and dry seasons for DO, DO saturation, and Temperature (Table 30) (Figure 85). Pairwise Wilcoxson tests reveal differences between nine stations in DO (Figure 86), DO saturation (Figure 87), and temperature (Figure 88).

Table 30. Kruskal-Wallace tests for differences between Stations, Seasons, and Station*Season interactions.

Parameter	Station chi	Station p	Season chi	Season p	Interaction chi	Interaction p
DO (mg/L)	237.3122	1.39E-47	305.2564	2.36E-68	560.2521	9.7E-110
DO_sat (%)	2.943248	0.400458	129.5055	5.26E-30	145.1829	4.16E-28
Temperature (°C)	20.63223	0.004354	471.4507	1.5E-104	496.3341	3.37E-96

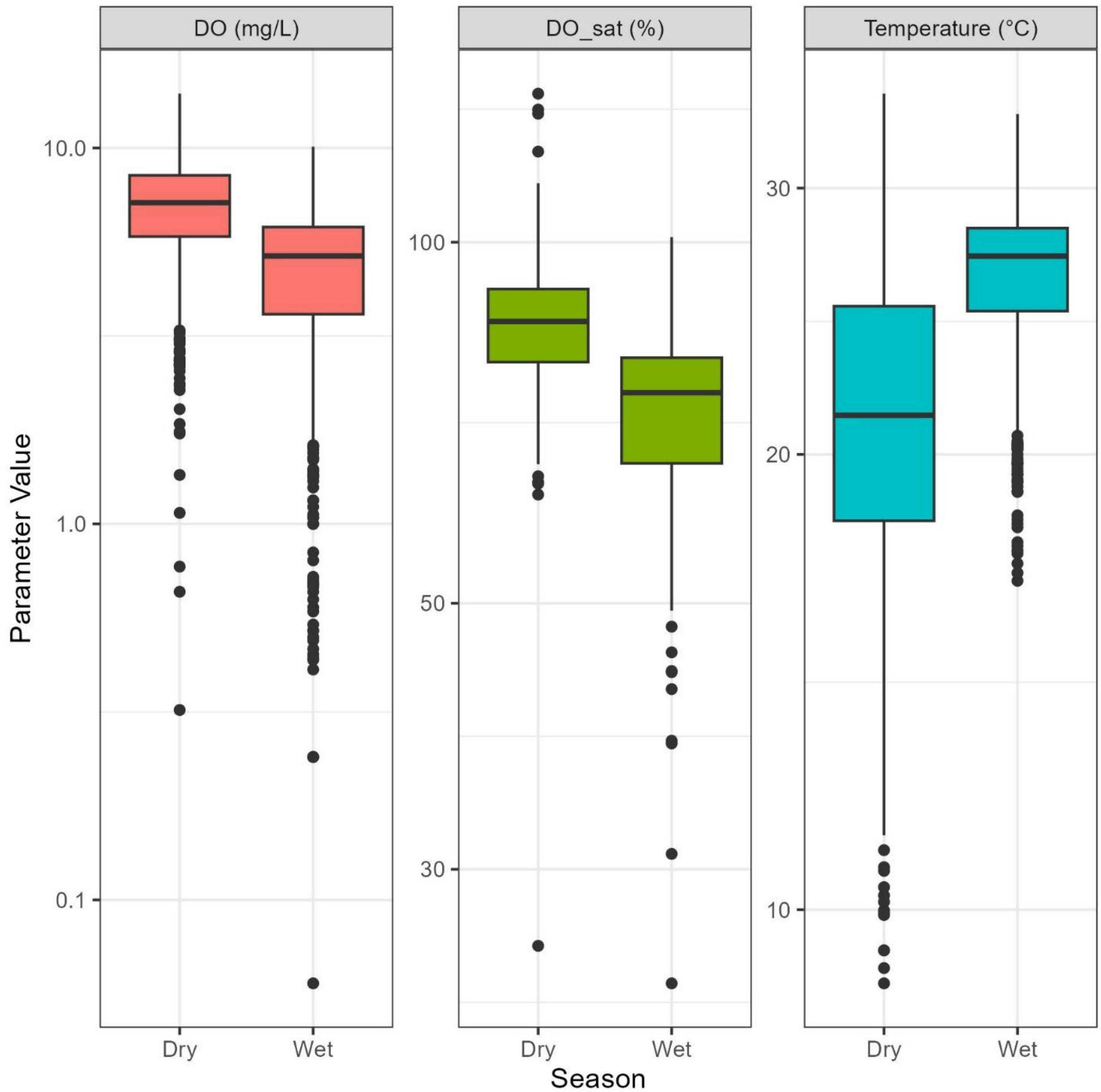
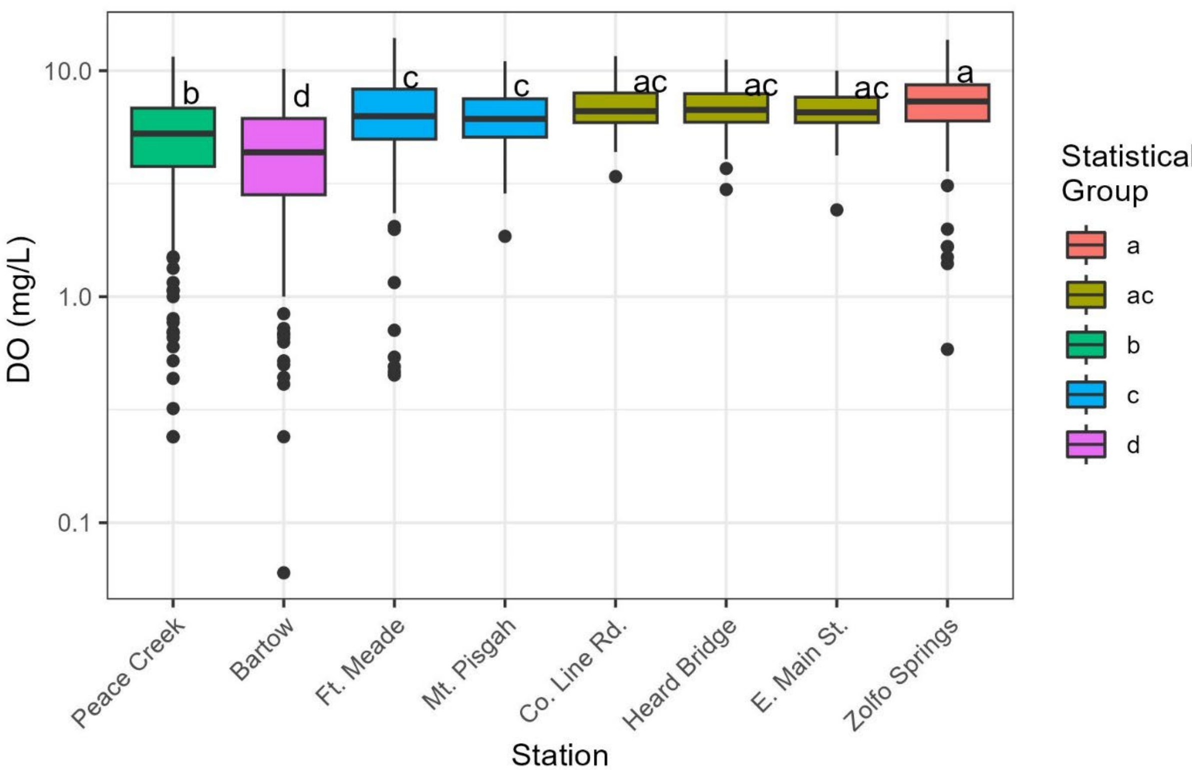


Figure 85. Seasonal differences in parameter concentrations



Significance based on alpha = 0.05 with Bonferroni correction for pairwise comparisons.

Figure 86. Statistical Grouping of DO by Station Using Pairwise Wilcoxon Tests

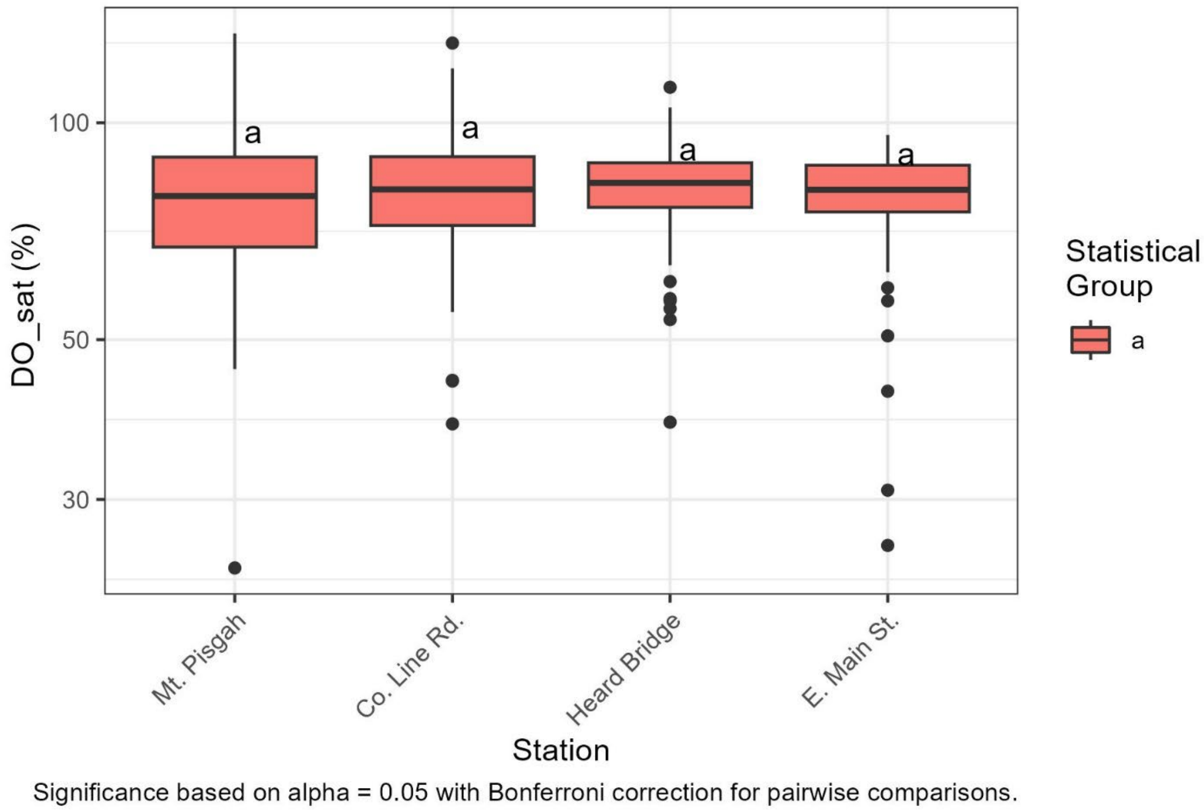


Figure 87. Statistical Grouping of dissolved oxygen saturation by Station Using Pairwise Wilcoxon Tests

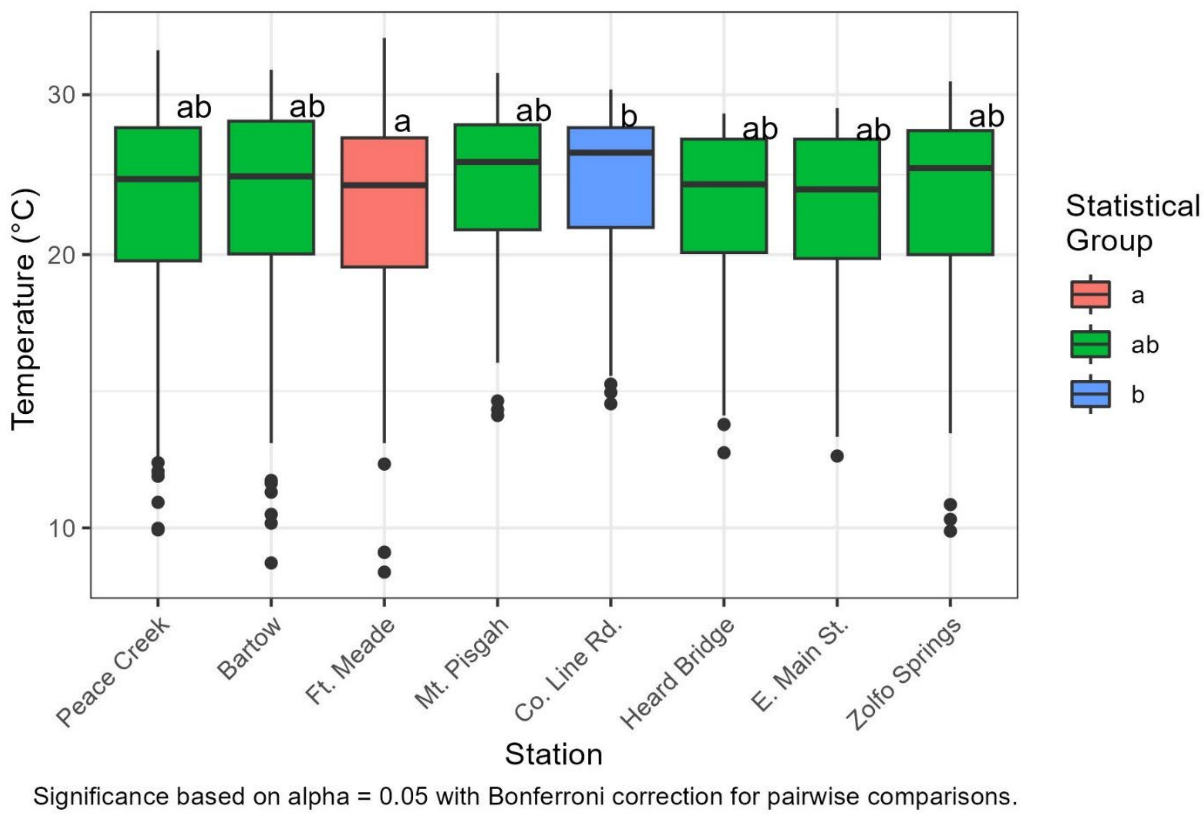


Figure 88. Statistical Grouping of temperature by Station Using Pairwise Wilcoxon Tests

Trends

This analysis examines both flow-based and temporal trends in water quality parameters using a two-stage approach following Helsel and Hirsch (2002). We first analyze concentration-date relationships using LOESS smoothing, then use these residuals to examine flow relationships. In a parallel analysis, we examine concentration-flow relationships with LOESS, using those residuals to assess temporal trends. Both approaches employ Kendall's tau with Bonferroni-adjusted p-values (p_adjusted = p_initial * n, where n is the number of stations) and Theil-Sen slopes for trend detection. This dual analysis allows examination of both flow-concentration patterns and temporal trends while controlling for their mutual influences.

The analysis sequence includes:

1. Concentration-date relationships with LOESS smoothing for DO (Figure 89), DO saturation (Figure 90), and temperature (Figure 91). These plots provide a visual representation of nonlinear temporal patterns for each station.

2. Concentration-flow relationships with LOESS smoothing for DO (Figure 92), DO saturation (Figure 93), and temperature (Figure 94) visualize nonlinear patterns in water quality parameters with flow at each of the nine stations.

3. Residuals from concentration-flow relationships represent flow-adjusted concentrations which can be compared with dates to determine temporal relationships DO (Figure 95), DO saturation (Figure 96), and temperature (Figure 97). Kendall-Theil lines show increasing, decreasing and not significant relationships depending on the water quality sampling location (Table 31). Statistical significance is based on Bonferroni-corrected p-values adjusted for number of stations.

4. Residuals from date-flow Loess represent date-adjusted concentration which is related to flow for DO (Figure 98), DO saturation(Figure 99), and temperature (Figure 100), with Kendall-Theil lines show increasing, decreasing and not significant relationships depending on the water quality sampling location (Table 32). Statistical significance is based on Bonferroni-corrected p-values adjusted for 9 stations.

The analysis revealed both temporal and flow-dependent trends across stations, suggesting that water quality dynamics are influenced by a combination of temporal and hydrological factors. Temporal trends were mostly not significant, and 2 showed significant increases (Table 33). The majority of flow trends were decreasing (12), while 3 trends were not significant and 5 were increasing (Table 34).

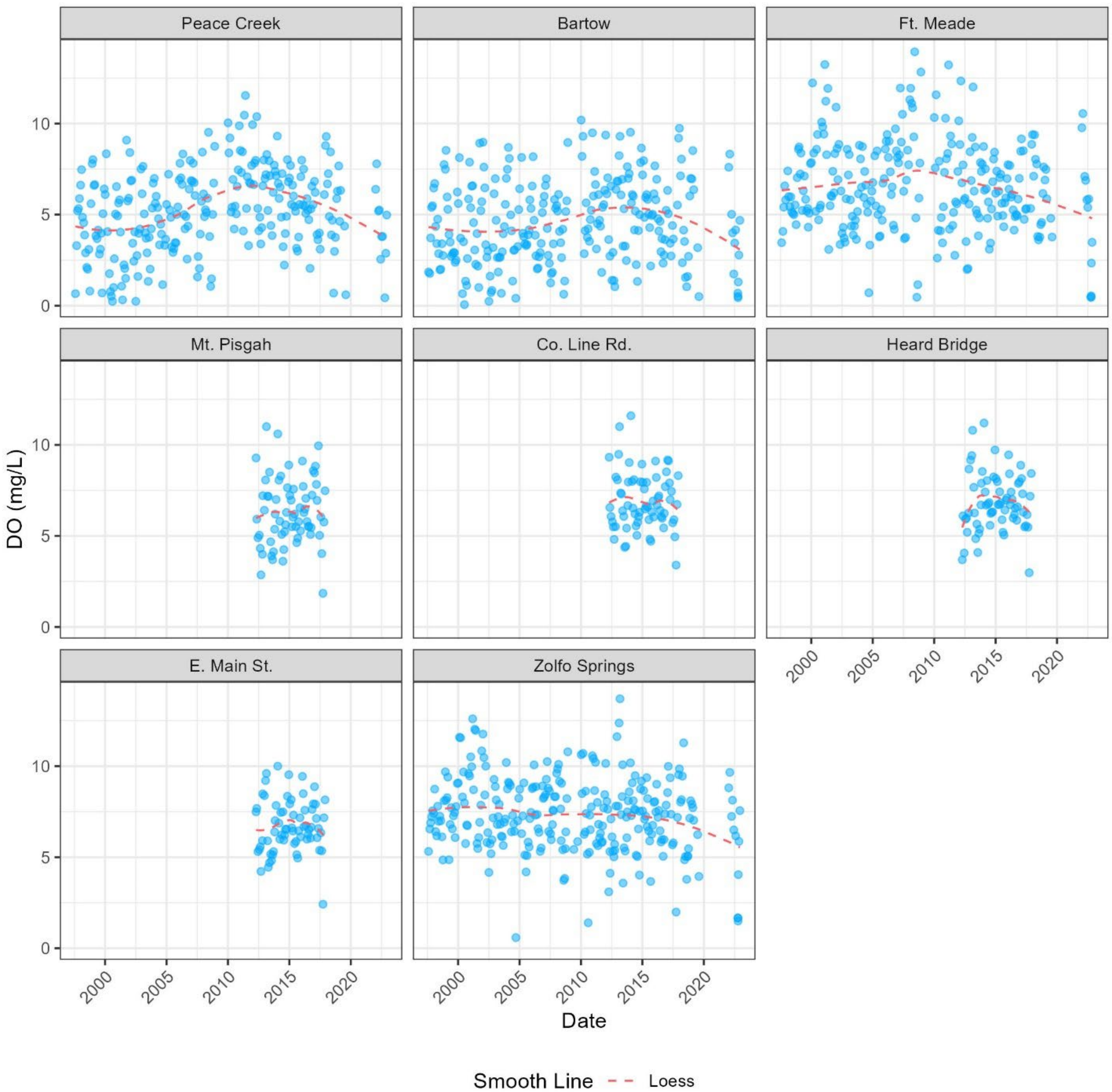


Figure 89. Time series showing observed DO (mg/L) concentrations (blue points) with LOESS smoothing curves (dashed red lines) across monitoring stations. The LOESS curves capture temporal patterns in the data, with residuals from these fits used for subsequent flow-adjusted trend analysis. Note: Concentrations are displayed on a logarithmic scale.

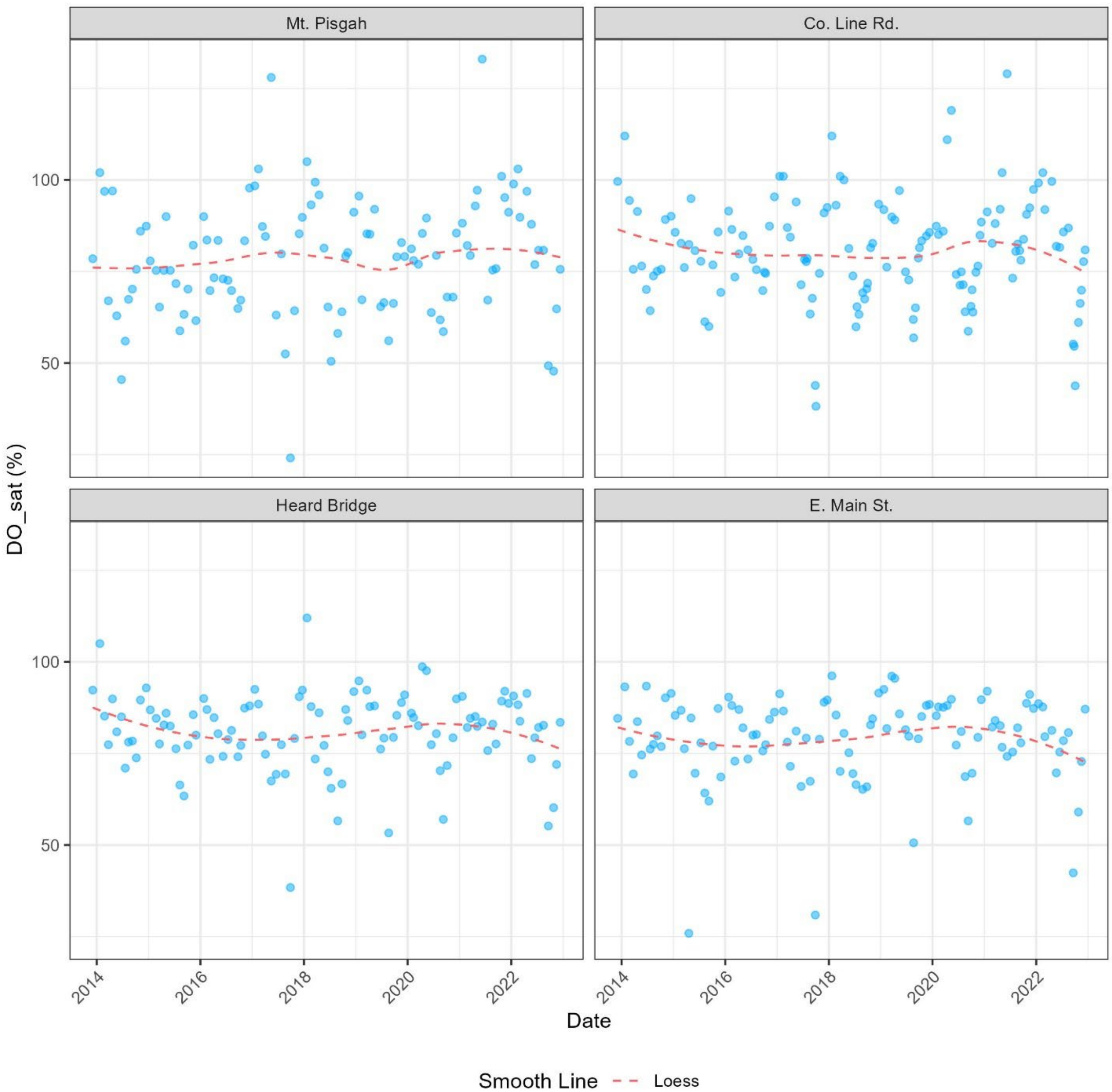


Figure 90. Time series showing observed DO saturation (SU) (blue points) with LOESS smoothing curves (dashed red lines) across monitoring stations. The LOESS curves capture temporal patterns in the data, with residuals from these fits used for subsequent flow-adjusted trend analysis. Note: Concentrations are displayed on a logarithmic scale.

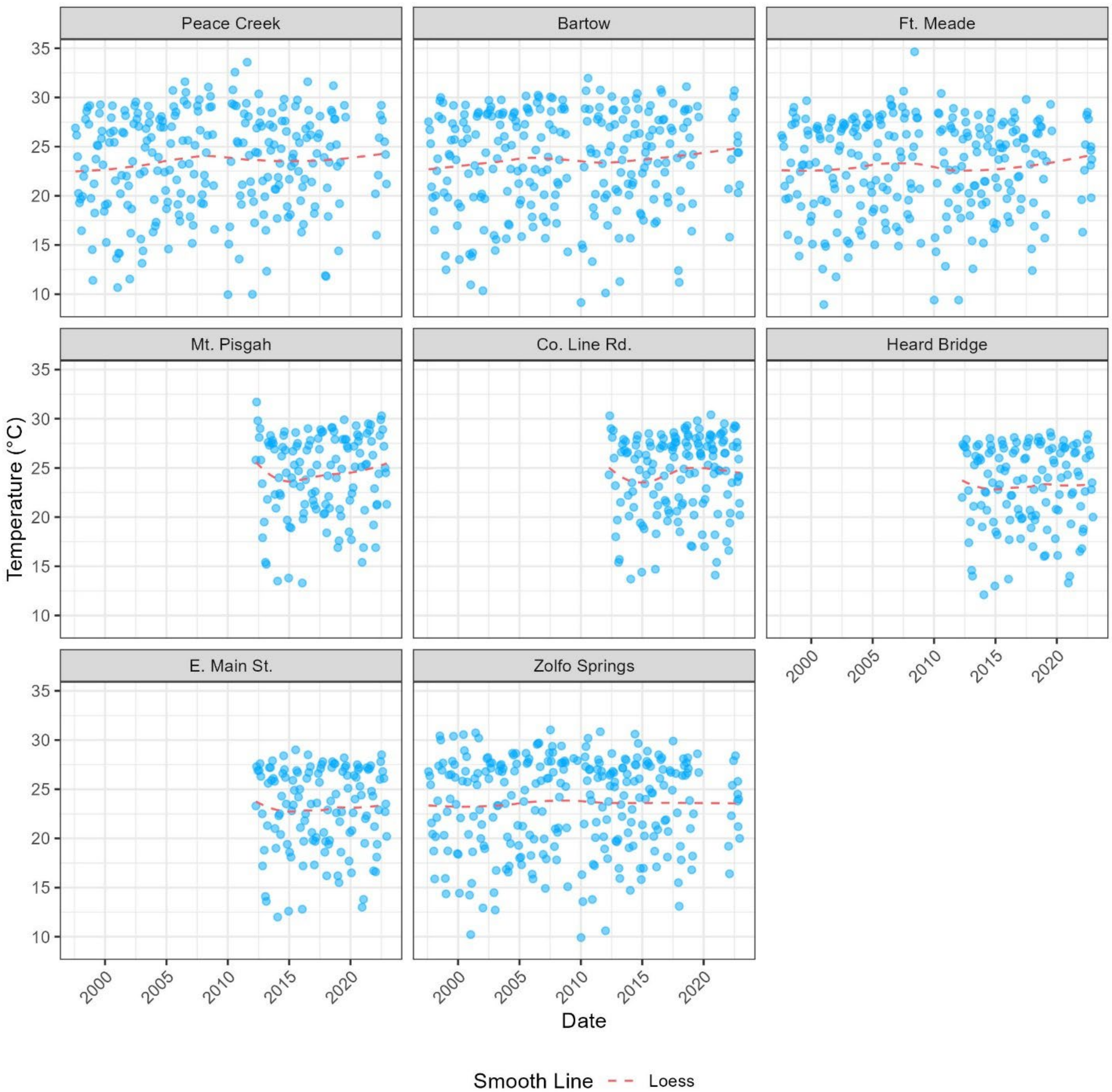


Figure 91. Time series showing observed temperature (mg/L) concentrations (blue points) with LOESS smoothing curves (dashed red lines) across monitoring stations. The LOESS curves capture temporal patterns in the data, with residuals from these fits used for subsequent flow-adjusted trend analysis. Note: Concentrations are displayed on a logarithmic scale.

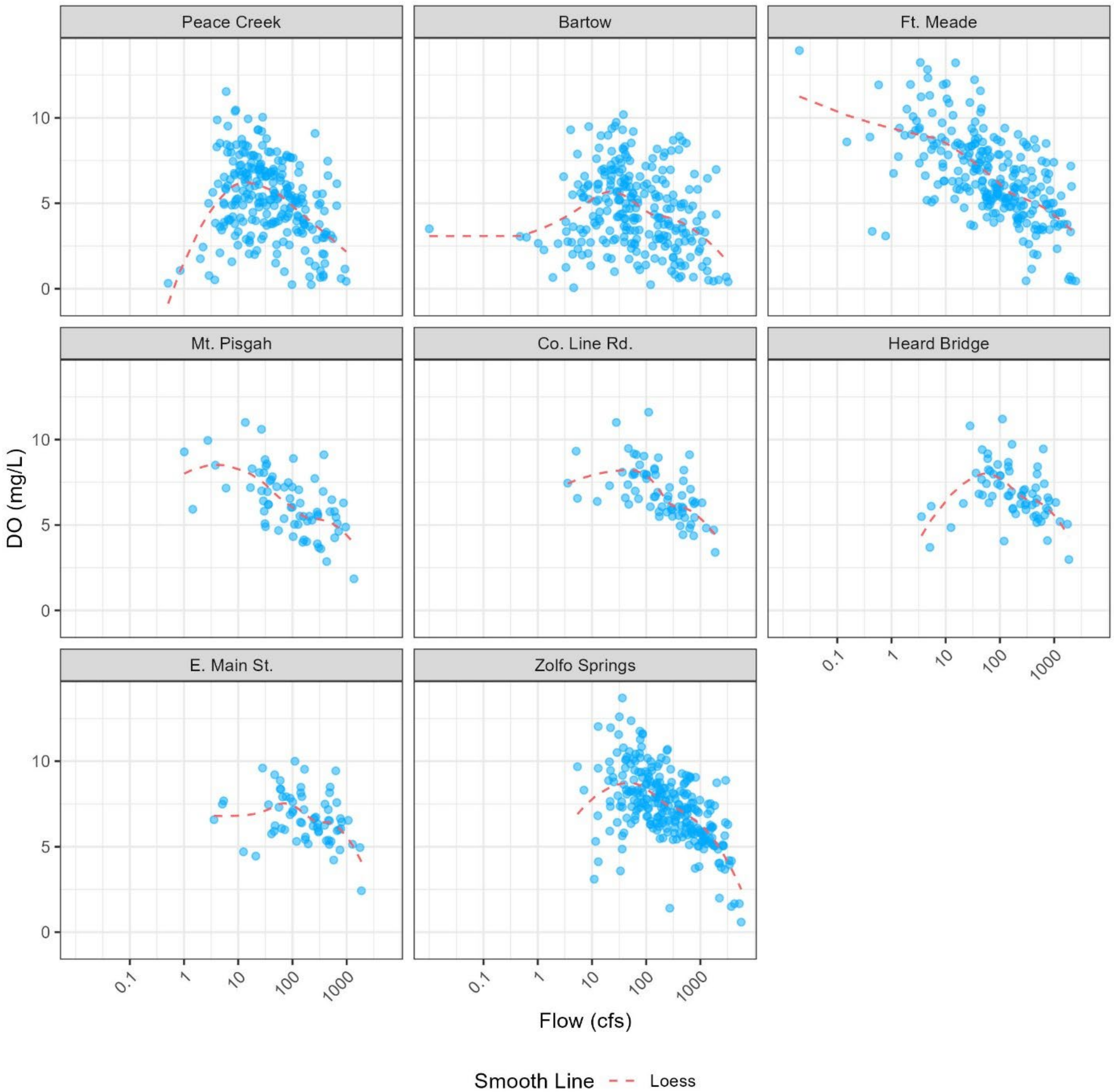


Figure 92. Relationship between streamflow and DO (mg/L) concentrations (blue points) with LOESS smoothing curves (dashed red lines) across monitoring stations. The LOESS curves capture flow-concentration patterns in the data, with residuals from these fits used for subsequent trend analysis. Note: Both flow and concentration are displayed on logarithmic scales.

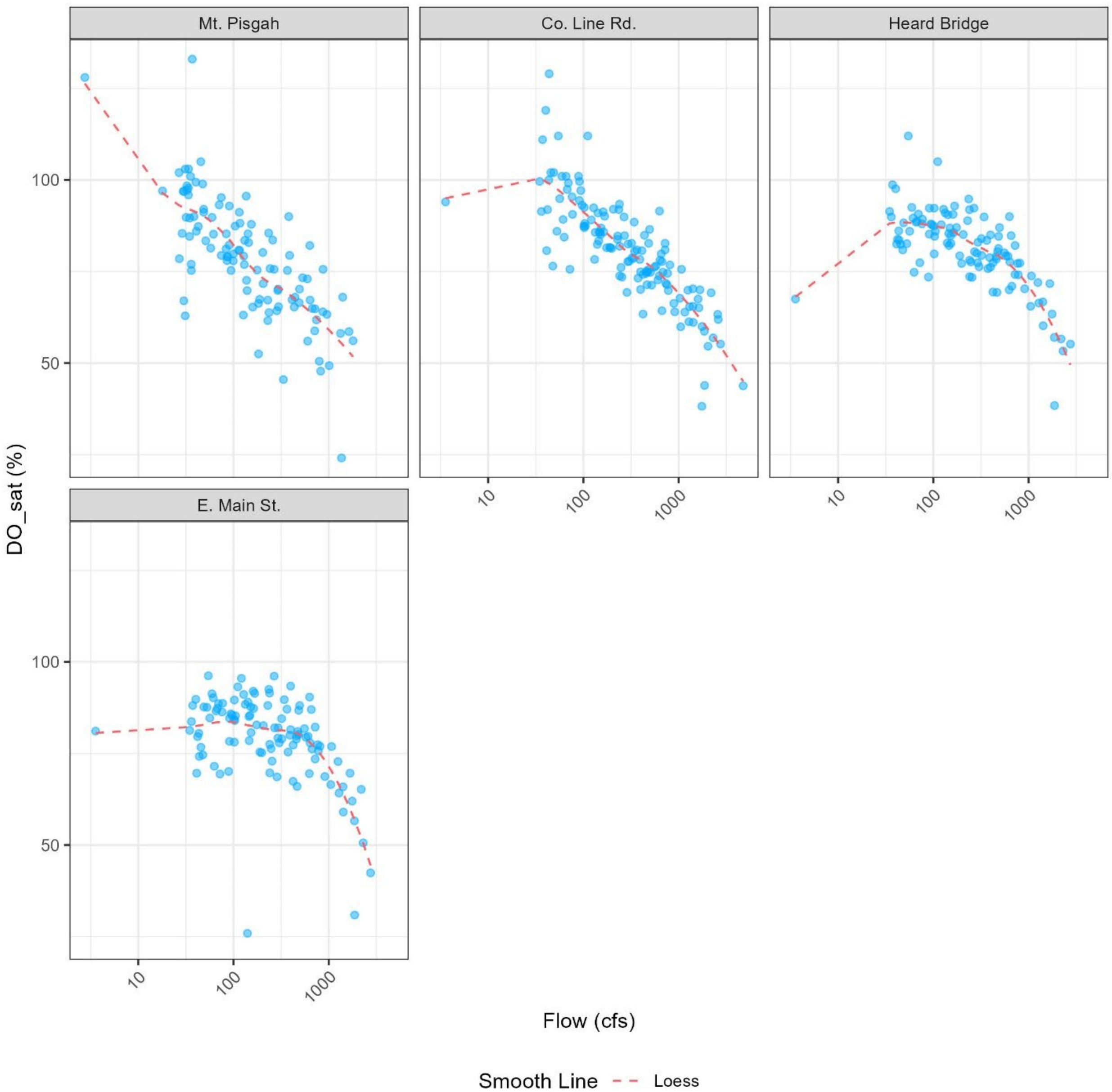


Figure 93. Relationship between streamflow and DO saturation (SU) concentrations (blue points) with LOESS smoothing curves (dashed red lines) across monitoring stations. The LOESS curves capture flow-concentration patterns in the data, with residuals from these fits used for subsequent trend analysis. Note: Both flow and concentration are displayed on logarithmic scales.

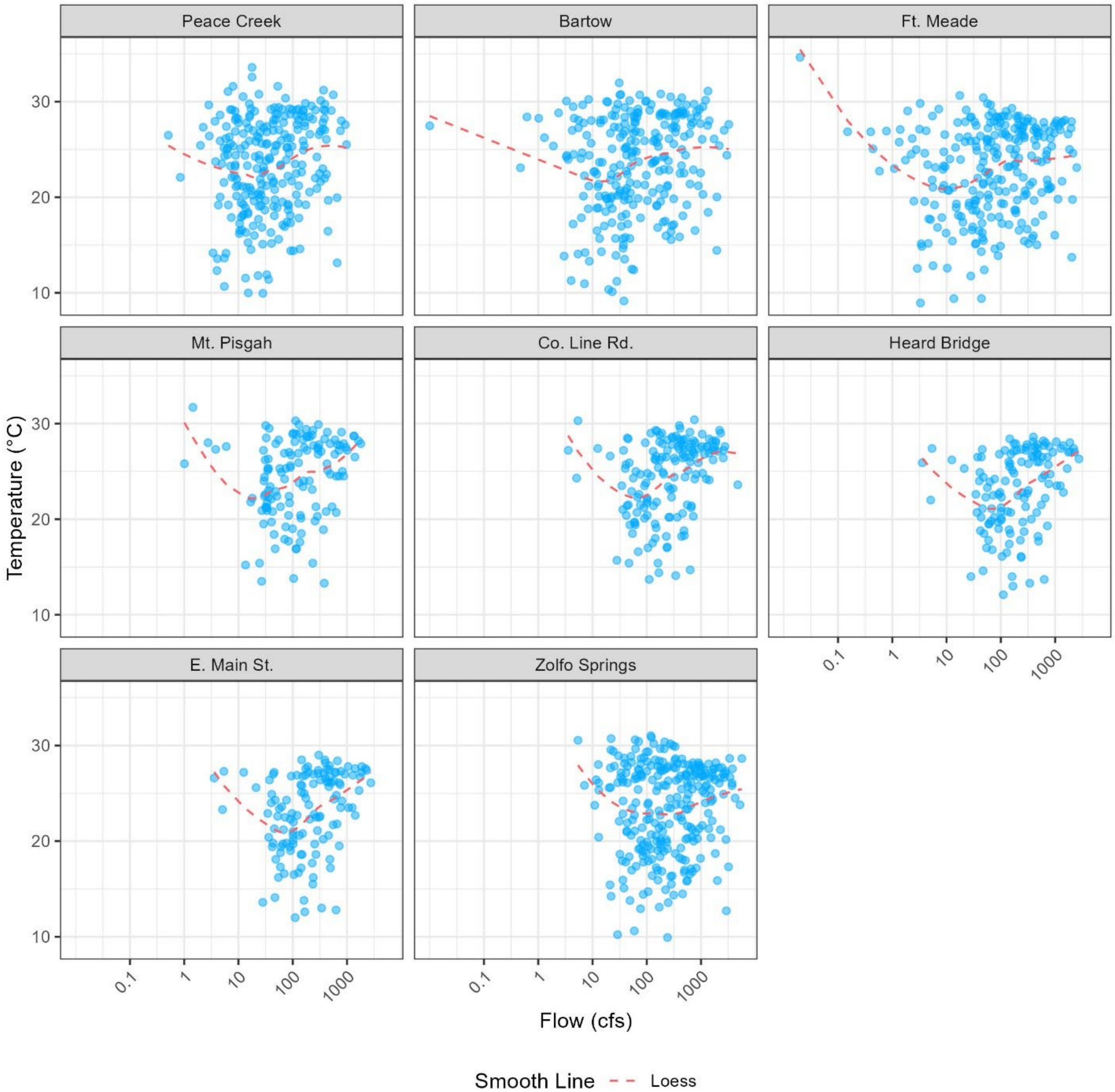


Figure 94. Relationship between streamflow and temperature (mg/L) concentrations (blue points) with LOESS smoothing curves (dashed red lines) across monitoring stations. The LOESS curves capture flow-concentration patterns in the data, with residuals from these fits used for subsequent trend analysis. Note: Both flow and concentration are displayed on logarithmic scales.

Figure 95. Flow-adjusted trends in DO concentrations across monitoring stations. Points show LOESS residuals from the flow-concentration relationship (blue points) rescaled to the original concentration units, with Kendall-Theil regression lines (dashed red) indicating long-term trends. Text annotations provide the Sen slope (trend magnitude) and Kendall's tau correlation coefficient for each station. Note: Residuals are centered on the mean concentration for each station to maintain interpretable units.

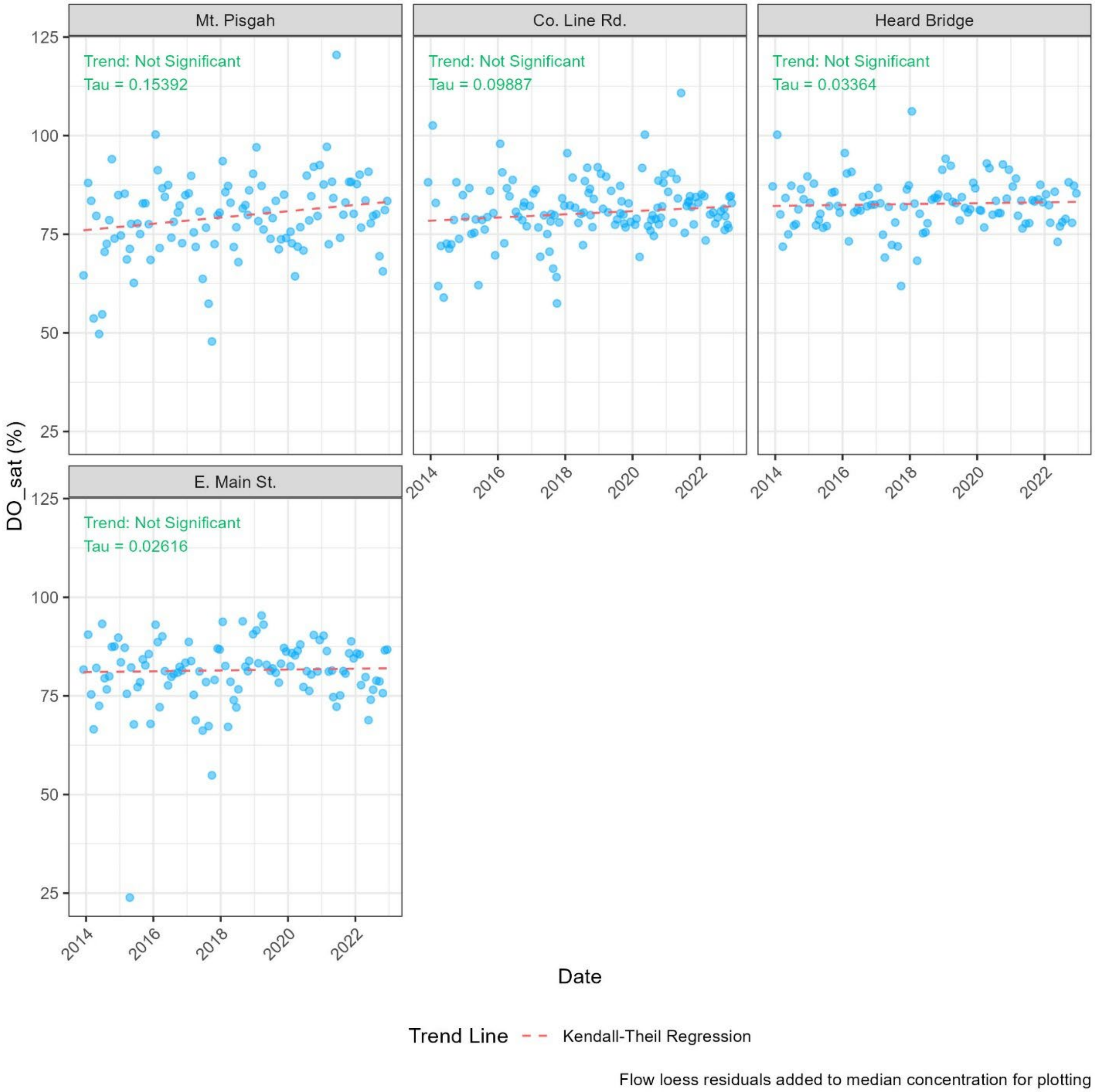


Figure 96. Flow-adjusted trends in DO saturation across monitoring stations. Points show LOESS residuals from the flow-concentration relationship (blue points) rescaled to the original concentration units, with Kendall-Theil regression lines (dashed red) indicating long-term trends. Text annotations provide the Sen slope (trend magnitude) and Kendall's tau correlation coefficient for each station. Note: Residuals are centered on the mean concentration for each station to maintain interpretable units.

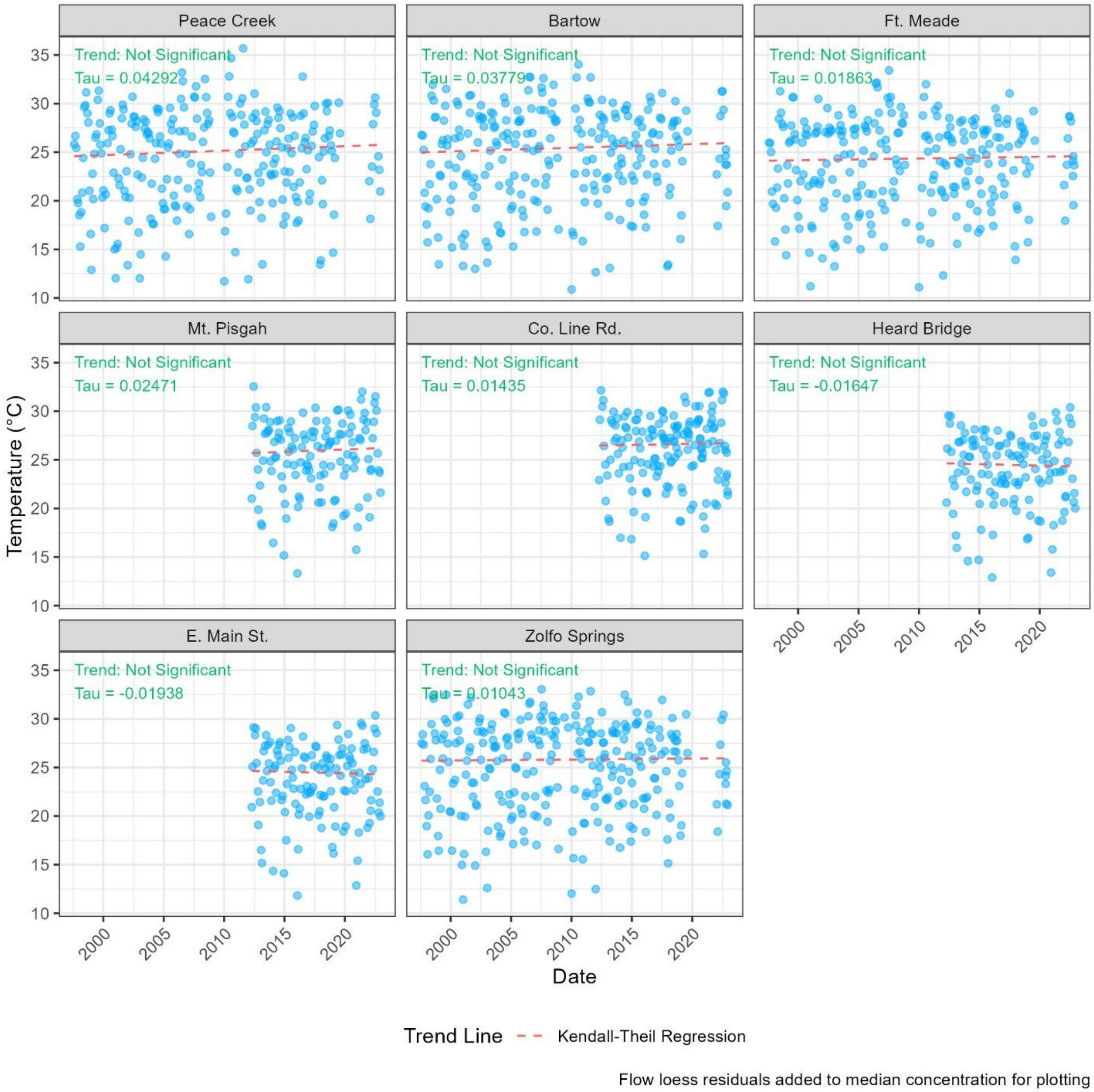


Figure 97. Flow-adjusted trends in temperature concentrations across monitoring stations. Points show LOESS residuals from the flow-concentration relationship (blue points) rescaled to the original concentration units, with Kendall-Theil regression lines (dashed red) indicating long-term trends. Text annotations provide the Sen slope (trend magnitude) and Kendall's tau correlation coefficient for each station. Note: Residuals are centered on the mean concentration for each station to maintain interpretable units.

Table 31. Summary of Kendall-Theil tests for trend with date by station and parameter. Trends are classified as Increasing, Decreasing, or Not Significant based on Kendall's tau significance (α = 0.05). Raw p values (p_raw) are adjusted using Bonferroni correction for number of stations tested (n_t) to produce adjusted p values (p_adj).

Parameter	Station	Slope	Tau	n_t	p_raw	p_adj	Trend
DO	Peace Creek	1.73e-04	0.143	8	7.14e-04	5.71e-03	Increasing
DO	Bartow	9.31e-05	0.075	8	7.38e-02	5.91e-01	Not Significant
DO	Ft. Meade	6.26e-06	0.005	8	9.07e-01	7.26e+00	Not Significant
DO	Mt. Pisgah	1.05e-03	0.284	8	6.27e-04	5.02e-03	Increasing
DO	Co. Line Rd.	5.48e-04	0.187	8	2.41e-02	1.93e-01	Not Significant
DO	Heard Bridge	4.40e-04	0.144	8	8.25e-02	6.60e-01	Not Significant
DO	E. Main St.	4.57e-04	0.13	8	1.17e-01	9.37e-01	Not Significant
DO	Zolfo Springs	-7.84e-05	-0.089	8	2.87e-02	2.29e-01	Not Significant
DO_sat	Mt. Pisgah	2.17e-03	0.154	4	1.77e-02	7.07e-02	Not Significant
DO_sat	Co. Line Rd.	1.10e-03	0.099	4	9.02e-02	3.61e-01	Not Significant
DO_sat	Heard Bridge	3.09e-04	0.034	4	6.04e-01	2.42e+00	Not Significant
DO_sat	E. Main St.	2.96e-04	0.026	4	6.87e-01	2.75e+00	Not Significant
Temperature	Peace Creek	1.25e-04	0.043	8	3.08e-01	2.47e+00	Not Significant
Temperature	Bartow	1.03e-04	0.038	8	3.66e-01	2.93e+00	Not Significant
Temperature	Ft. Meade	4.87e-05	0.019	8	6.57e-01	5.26e+00	Not Significant
Temperature	Mt. Pisgah	1.29e-04	0.025	8	6.78e-01	5.42e+00	Not Significant
Temperature	Co. Line Rd.	6.72e-05	0.014	8	7.92e-01	6.33e+00	Not Significant
Temperature	Heard Bridge	-8.18e-05	-0.016	8	7.82e-01	6.25e+00	Not Significant
Temperature	E. Main St.	-9.05e-05	-0.019	8	7.45e-01	5.96e+00	Not Significant
Temperature	Zolfo Springs	2.62e-05	0.01	8	7.96e-01	6.37e+00	Not Significant

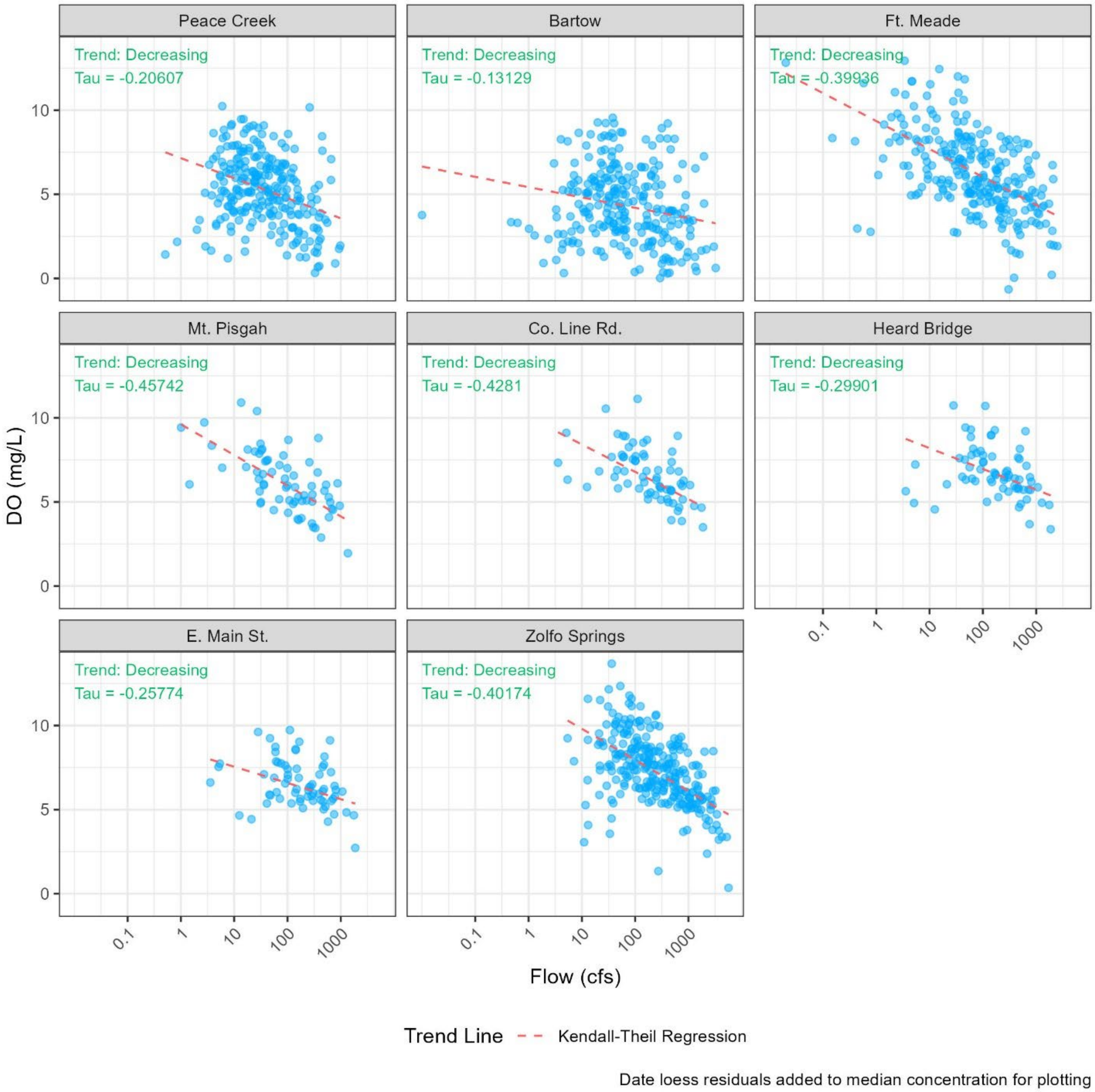


Figure 98. Date-adjusted relationships in DO concentrations with Flow across monitoring stations. Points show LOESS residuals from the date-concentration relationship (blue points) rescaled to the original concentration units, with Kendall-Theil regression lines (dashed red) indicating long-term trends. Text annotations provide the Sen slope (trend magnitude) and Kendall's tau correlation coefficient for each station. Note: Residuals are centered on the mean concentration for each station to maintain interpretable units.

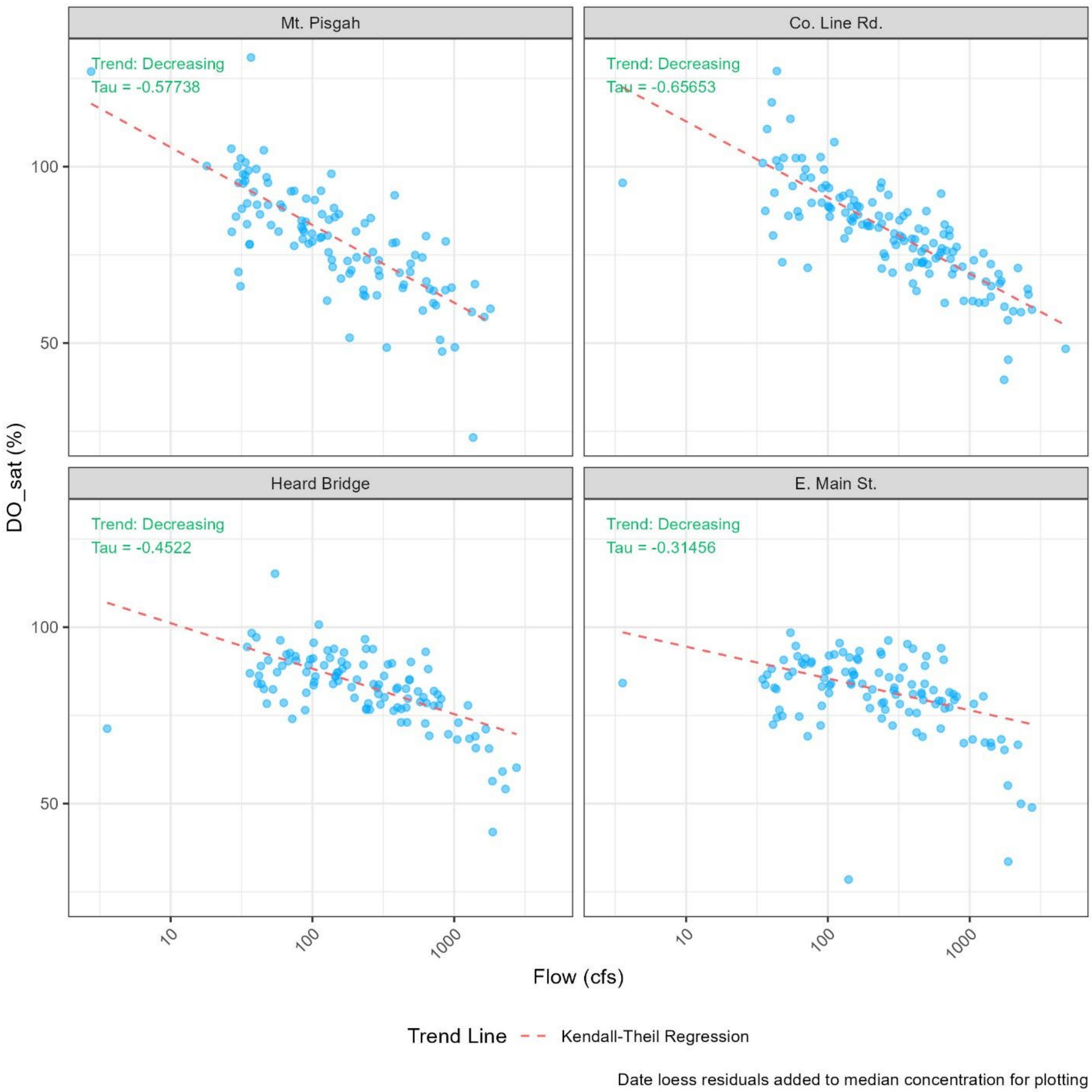


Figure 99. Date-adjusted relationships in DO saturation with Flow across monitoring stations. Points show LOESS residuals from the date-concentration relationship (blue points) rescaled to the original concentration units, with Kendall-Theil regression lines (dashed red) indicating long-term trends. Text annotations provide the Sen slope (trend magnitude) and Kendall's tau correlation coefficient for each station. Note: Residuals are centered on the mean concentration for each station to maintain interpretable units.

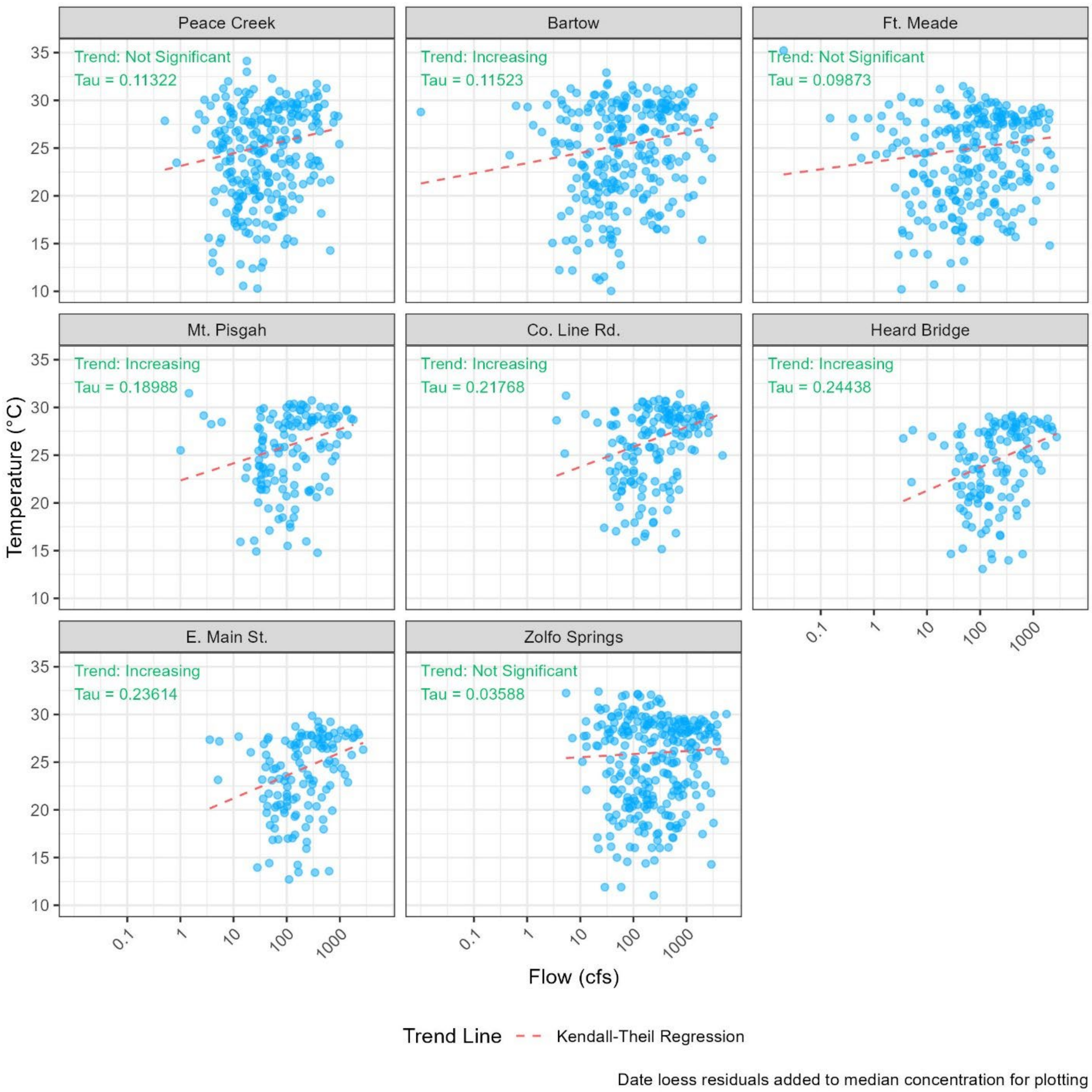


Figure 100. Date-adjusted relationships in temperature concentrations with Flow across monitoring stations. Points show LOESS residuals from the date-concentration relationship (blue points) rescaled to the original concentration units, with Kendall-Theil regression lines (dashed red) indicating long-term trends. Text annotations provide the Sen slope (trend magnitude) and Kendall's tau correlation coefficient for each station. Note: Residuals are centered on the mean concentration for each station to maintain interpretable units.

Table 32. Summary of Kendall-Theil tests for trend with flow by station and parameter. Trends are classified as Increasing, Decreasing, or Not Significant based on Kendall's tau significance (α = 0.05). Raw p values (p_raw) are adjusted using Bonferroni correction for number of stations tested (n_t) to produce adjusted p values (p_adj).

Parameter	Station	Slope	Tau	n_t	p_raw	p_adj	Trend
DO	Peace Creek	-1.19e+00	-0.206	8	1.11e-06	8.90e-06	Decreasing
DO	Bartow	-6.13e-01	-0.131	8	1.76e-03	1.41e-02	Decreasing
DO	Ft. Meade	-1.66e+00	-0.399	8	2.12e-21	1.69e-20	Decreasing
DO	Mt. Pisgah	-1.82e+00	-0.457	8	3.47e-08	2.78e-07	Decreasing
DO	Co. Line Rd.	-1.63e+00	-0.428	8	2.45e-07	1.96e-06	Decreasing
DO	Heard Bridge	-1.24e+00	-0.299	8	3.12e-04	2.50e-03	Decreasing
DO	E. Main St.	-9.65e-01	-0.258	8	1.89e-03	1.51e-02	Decreasing
DO	Zolfo Springs	-1.85e+00	-0.402	8	3.84e-23	3.07e-22	Decreasing
DO_sat	Mt. Pisgah	-2.20e+01	-0.577	4	5.83e-19	2.33e-18	Decreasing
DO_sat	Co. Line Rd.	-2.16e+01	-0.657	4	2.31e-29	9.24e-29	Decreasing
DO_sat	Heard Bridge	-1.29e+01	-0.452	4	3.21e-12	1.29e-11	Decreasing
DO_sat	E. Main St.	-9.02e+00	-0.315	4	1.25e-06	5.01e-06	Decreasing
Temperature	Peace Creek	1.33e+00	0.113	8	7.21e-03	5.77e-02	Not Significant
Temperature	Bartow	1.07e+00	0.115	8	5.84e-03	4.67e-02	Increasing
Temperature	Ft. Meade	7.72e-01	0.099	8	1.86e-02	1.49e-01	Not Significant
Temperature	Mt. Pisgah	1.79e+00	0.19	8	1.42e-03	1.14e-02	Increasing
Temperature	Co. Line Rd.	2.09e+00	0.218	8	6.18e-05	4.95e-04	Increasing
Temperature	Heard Bridge	2.45e+00	0.244	8	4.02e-05	3.21e-04	Increasing
Temperature	E. Main St.	2.38e+00	0.236	8	7.25e-05	5.80e-04	Increasing
Temperature	Zolfo Springs	3.26e-01	0.036	8	3.75e-01	3.00e+00	Not Significant

Table 33. Summary of flow-adjusted concentration trends with date showing counts of increasing, decreasing, and not-significant results.

Parameter	n_increasing	n_decreasing	n_not_significant
DO (mg/L)	2	0	6
DO_sat (%)	0	0	4
Temperature (°C)	0	0	8
Total	2	0	18

Table 34. Summary of date-adjusted concentration trends with flow showing counts of increasing, decreasing, and not-significant results.

Parameter	n_increasing	n_decreasing	n_not_significant
DO (mg/L)	0	8	0
DO_sat (%)	0	4	0
Temperature (°C)	5	0	3
Total	5	12	3

Conclusions

Relationships shown here are correlative, presented with the intent to illustrate status of water quality parameters and trends through the periods of record as well as relationships with flow. Each water quality parameter is unique, and an analysis of causes of how and why levels increase or decrease would require exploration of those unique qualities. For nutrient parameters, the Florida Department of Environmental Protection (DEP) has developed Total Maximum Daily Loads (TMDLs) and Basin Management Action Plans (BMAPS) elsewhere in the state. These BMAPS address causes of nutrient pollution by determining sources of nutrients to the system and developing targets for nutrient reductions within focus areas of the basin by targeting sources of nutrient pollutants.

Trends vary with location and parameter. For example, nitrate – nitrite (nitrate-nitrite) has consistent, negative relationships with flow at all sites but Saddle Creek at P11, which is an outlet for untreated Lake Hancock water. However, Total Nitrogen increases with flow in Peace Creek, is decreasing with flow in the middle three sites (Ft. Meade, Mt. Pisgah, and Co. Line Rd.), and has no significant trends at the lower sites (Heard Bridge, E. Main St., and Zolfo Springs). WBID 1623H, which includes Co. Line Rd. is impaired for Total Nitrogen as well as total phosphorus and chlorophyll a. However, Total Nitrogen has not been increasing at Co. Line Rd. over its period of record, and Total Nitrogen is not impaired at downstream WBIDs. A blanket recommendation to maintain higher flows in the Peace River through this reach based on a correlation between flow and Total Nitrogen at some sites and not others is not a reasonable conclusion based on the regression results. Instead, management of nitrogen should follow the pattern already established by DEP for establishing TMDLs and BMAPs: using an analysis of sources of nitrogen within the watershed and working with local counties, municipalities, and other entities to reduce loads though wastewater treatment and other means.

While a majority of the nutrient trends with flow were negative, showing reduced concentrations with increased flow, temporal trends were also frequently negative, demonstrating decreasing concentrations over the past 10-20 years. In addition, results here show increasing chlorophyll a, and turbidity with increased flow, as well as decreasing DO with higher flows. Therefore, a simple prescription to increase flows as a method of decreasing nutrients based on positive correlations between nutrients and flows would be misguided and would ignore the causes and mechanistic relationships between diverse aspects of water quality and flow. The results presented here describe status and trends as a starting point for inquiry into these various aspects of water quality in this system.

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