Water Quality Trend Analysis at Twenty-Six West Virginia Long-Term Monitoring Sites

FINAL REPORT

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Disclaimer

The opinions expressed in this report are those of the authors and should not be construed as representing the opinions or policies of the United States government, or the signatories or Commissioners to the Interstate Commission on the Potomac River Basin.

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Cover image

Looking upstream from the Shenandoah AWQM station, by Adam N. Griggs.

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Executive Summary

The West Virginia Department of Environmental Protection (WVDEP) recently updated a relational database of water quality data that were routinely collected by the state's monitoring programs, primarily the Ambient Water Quality Monitoring (AWQM) Network. WVDEP approached the Interstate Commission on the Potomac River Basin (ICPRB) about performing trend analysis on selected parameters at 26 fixed monitoring stations. The stations, now sampled bi-monthly, are located at or near the mouths of the state's larger rivers or situated so as to isolate the impacts of major industrial complexes and other potential sources of impairment.

The AWQM program has undergone several modifications since it began in 1946, which led to changes over time in parameter sampling frequency and analytical detection limits. With guidance from WVDEP, ICPRB staff identified the appropriate trend method(s) to apply to each parameter. Two trend periods were examined: a long-term (43-year) period from 1970-2012 and a short-term (17-year) period from 1996-2012. U. S. Geological Survey flow data for gages proximal to the sampling stations were downloaded and used to "flow adjust" both the long- and short-term trends where possible. Initial results were presented to WVDEP in July 2014, a draft final report was delivered in October 2014, WVDEP edits and requests were addressed, and the final report was completed in April 2015.

Trends were determined for 24 water quality parameters, which included several metals and nutrients. Non-parametric tests that account for seasonal differences (e.g., Seasonal Kendall) were performed on actual concentrations and on the residuals produced when concentrations were flow-adjusted. Estimates of the rate of change over time (trend slope) were calculated when the data allowed. In all but a few instances, flow-adjustment did not change trend direction.

Approximately 74% of possible tests for long-term trends and 35% of possible tests for short-term trends were significant ($p<0.05$) or showed strong directional tendencies ($0.05<p<0.10$). At nearly all monitoring stations, long-term trends were increasing for alkalinity and pH, and decreasing for total phosphorus, total suspended solids, and the metals aluminum, iron, manganese, and lead. Short-term trends in these same parameters were often weaker or not significant, indicating rates of change in the parameters may be slowing at many stations. Short-term trends in water hardness and to a lesser extent dissolved oxygen are increasing statewide. Additional efforts to connect the trends with management actions and historic or recent changes in nearby land use patterns may confirm and help explain the trends.

West Virginia streams and rivers appear to be recovering from the acid rain impacts of the 20th century. Trends in pH are upward across the state and fewer stations now experience harmful acidity (pH values below 5 PSU) during daytime. The higher levels of pH, coupled with higher concentrations of water hardness, are probably facilitating the long-term downward trends observed in many metals. Higher alkalinity concentrations statewide are increasing the buffering capacity of West Virginia waterways. Large areas of West Virginia are still impacted by coal mining practices. Increasing trends in total dissolved solids, specific conductivity, hardness, sodium and sulfates are evident in heavily mined areas of the southwestern part of the state. These areas also have unnaturally high and variable concentrations of alkalinity, water hardness, total dissolved solids, specific conductivity, sodium, chlorides, potassium, magnesium, and sulfates, and sometimes iron and aluminum.

Introduction

An important purpose of long-term water quality monitoring programs is to determine trends as environmental conditions change. Management practices are adopted and later modified; environmental regulations are introduced; rural and forested lands are developed for residential and commercial uses; agricultural and industrial activities respond to changing markets and technology. In the face of changing conditions, resource agencies ask whether water quality is degrading or improving.

The West Virginia Department of Environmental Protection (WVDEP) recently assembled a comprehensive database of their monitoring data. The database contains water quality data from currently monitored stations in West Virginia's Ambient Water Quality Monitoring (AWQM) network, but also includes data collected at those same stations for special investigations such as Total Maximum Daily Loads (TMDLs) studies. No targeted storm samples are included in the database. **Table 1** lists the currently active monitoring stations and **Figure 1** shows their locations. Additional station information is

Table 1. Active monitoring stations in West Virginia's Ambient Water Quality Monitoring network. More station information is provided in Appendix A.

Station Code	Stream Name	Period of Record	Ecoregion (Level III)
MC-00001-3.5	Cheat River	1996-2012	Western Allegheny Plateau
KC-00001-11.6	Coal River	1970-2012	Western Allegheny Plateau
ML-00001-20.6	Dunkard Creek	1970-1984, 1996-2012	Western Allegheny Plateau
KE-00001-4.3	Elk River	1973-1974, 1978-2012	Western Allegheny Plateau
OGL-00001-2.8	Guyandotte River (Lower)	1974-2012	Western Allegheny Plateau
LK-00025-1.5	Hughes River	1978-1984, 1996-2012	Western Allegheny Plateau
KL-00001-31.7	Kanawha River (Lower)	1970-1974, 1976-2012	Western Allegheny Plateau
LK-00001-28.9	Little Kanawha River	1970-1978, 1984-2012	Western Allegheny Plateau
OMN-00006-12.3	Middle Island Creek	1970-1984, 1996-2012	Western Allegheny Plateau
MU-00001-99.4	Monongahela River (Upper)	1970-2012	Western Allegheny Plateau
BST-00001-0.15	Tug Fork	1970-2012	Western Allegheny Plateau
OT-00001-8.8	Twelvepole Creek	1996-2012	Western Allegheny Plateau
MT-00001-6.2	Tygart Valley River	1978-2012	Western Allegheny Plateau
MW-00001-12	West Fork River	1970-2012	Western Allegheny Plateau
MC-00001-30	Cheat River	1970-2012	Central Appalachians
KG-00001-8.25	Gauley River	1970-2012	Central Appalachians
KNG-00001-1.6	Greenbrier River	1970-2012	Central Appalachians
OGL-00001-74.1	Guyandotte River (Lower)	1996-2012	Central Appalachians
KU-00001-74.1	Kanawha River (Upper)	1970-2012	Central Appalachians
KNL-00001-1.2	New River (Lower)	1973-2012	Central Appalachians
KNU-00001-67.4	New River (Upper)	1970-1985, 1988-1990, 1996-2012	Central Appalachians
KNU-00001-96.2	New River (Upper)	1970-1984, 1994-1999, 2006-2012	Central Appalachians
PU-00010-6.1	Cacapon River	1976-2012	Ridge & Valley
PL-00014-2.2	Opequon Creek	1970-1984, 1996-2012	Ridge & Valley
PSB-00001-13.4	South Branch Potomac River	1970-2012	Ridge & Valley
PS-00001-0.9	Shenandoah River	1970-2012	Ridge & Valley (Blue Ridge)

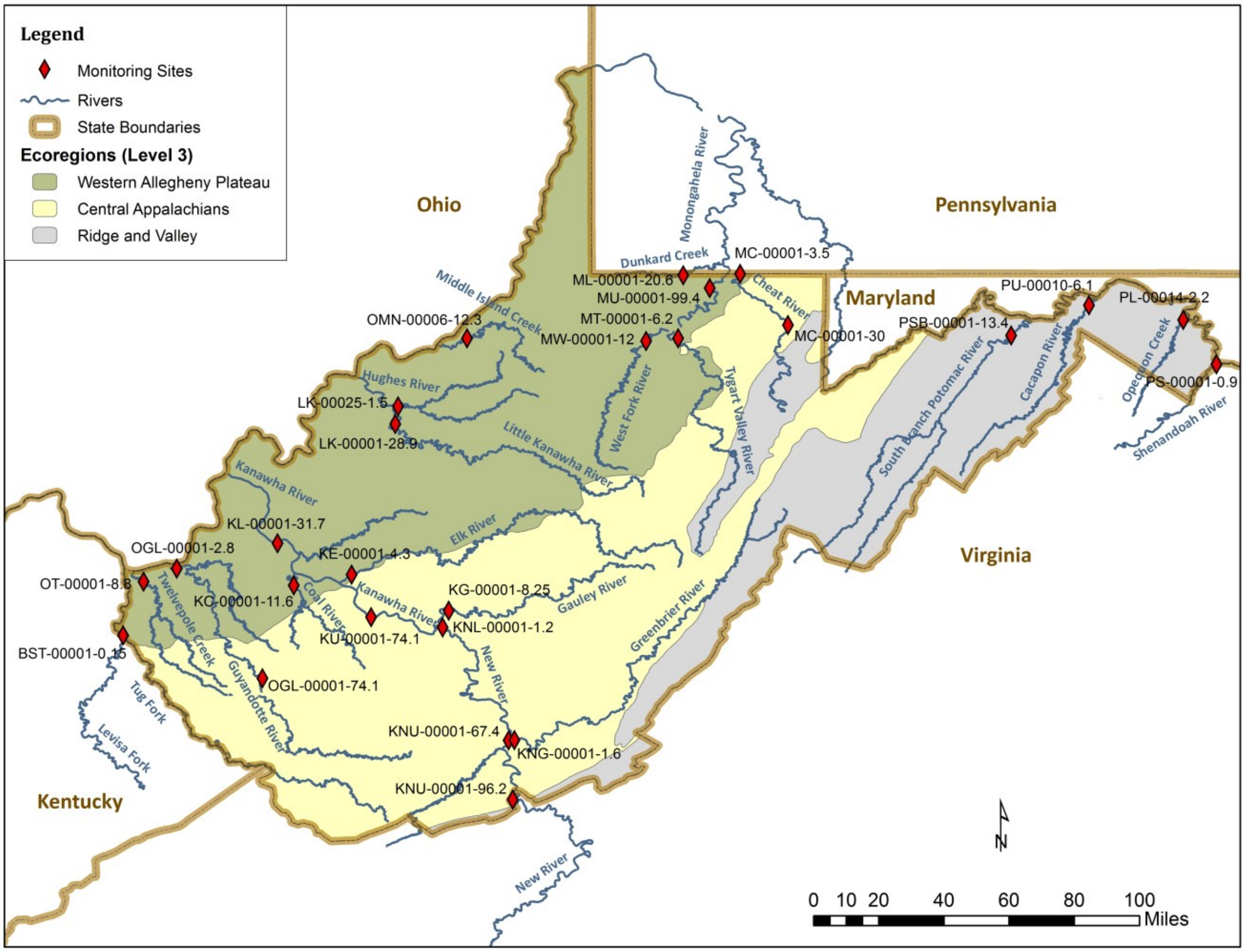

Figure 1. Long-term stations in West Virginia's Ambient Water Quality Monitoring (AWQM) network.

available in **Tables A-1** and **A-2** in Appendix A. Current collection and analytical methods are described in the West Virginia Watershed Assessment Branch 2014 Standard Operating Procedures (WVDEP 2014).

The goal of this analysis is to estimate trends in key water quality parameters at these monitoring stations and provide a broad-brush, statewide perspective of changes in water quality since the 1970's. No attempt will be made in this report to explain trends at each of the individual stations or relate them to changes in local land use, agricultural and industrial practices, or the regulatory environment.

The model for this project was the trend study performed by the Ohio River Valley Water Sanitary Commission (ORSANCO) in 2008 on data from their Ohio River mainstem monitoring network. ORSANCO analyzed trends in data collected 1990-2007, with a look back to two earlier trend studies on data collected 1977-1987, and 1980-1990. Two types of trends were calculated: flow-adjusted trends and non-flow-adjusted trends. Both types were seasonally adjusted. Flow adjustment and seasonal adjustment are often desirable in trend analysis because the concentration of water quality constituents frequently has a significant relation with flow and season, and the effects of flow or season can confound the analysis of trend. Adjustment by flow and season was employed in the trend analysis in this project where possible.

Data

Water Quality

WVDEP has a public website where the state's water quality data can be queried and downloaded: https://apps.dep.wv.gov/dwwm/wqdata/. The database of water quality monitoring data assembled by WVDEP for this project contains data from 7,367 sampling events at 26 stations. Sample results for as many as 307 different parameters are included, although, of course, individual sampling events had far fewer parameters. Some parameters, like dissolved beryllium or dissolved chromium, are represented in the database by a single sampling event at a one station, while parameters measured in the field, like temperature and dissolved oxygen, are measured for almost every sampling event. The database contains 221,850 water quality records, each representing the value of a single parameter.

From the 307 parameters, WVDEP selected 22 parameters to consider for long-term trend analysis (WVDEP, personal communication, 2014). ICPRB added two more parameters to consider because the data were adequate for trend analysis. A final list of the parameters analyzed for long-term and/or short-term trends in this study is shown in **Table A-3** of Appendix A, along with the total number of samples available for each parameter, by station. Recent data for calcium were also examined and used to help explain trends in other parameters.

The water quality database spans 43 years. Several changes in the monitoring program were made over the course of the 43 years. The three most important changes from the point of view of trend analysis are (1) variations in the period of record by station and by parameter; (2) changes in sampling frequency; and (3) changes in laboratory detection limits. Each of these changes is discussed in more detail here.

Period of Record

Table 1 lists the years that each station in the analysis database was sampled at least once. Not all water quality parameters were measured over the entire period of record at a station. In the best case, data for an individual parameter were collected routinely at a station from the 1970's up to the present. Monitoring data at some stations became available only recently. For example, no monitoring data for Lower Guyandotte River at mile 74.1 (OGL-00001-74.1), Twelvepole Creek and Cheat River at mile 3.5 (MC-00001-3.5) are available before 1996. Similarly, a monitoring station may have been sampled in the 1970s and 1980s but analysis of a particular water quality parameter was either very sporadic or did not begin until recently. This is the case for calcium, magnesium and many dissolved metals. Another monitoring pattern that occurs frequently is a gap in the time series of a parameter's measurements. Data gaps were most common between 1985 and 1995. Finally, some parameters were measured in the 1970s and 1980s and then discontinued. These discrepancies in when stations were sampled and what water quality parameters were measured impose limitations on how trends can and should be calculated.

Sampling Frequency

Another source of variability in the analysis database is the frequency of sampling. Over the 43 years, the number of samples taken annually at an individual station ranged from one to 12. **Figure 2** shows the median sampling frequency across all stations in the analysis data set by year. In the early 1970s, the median frequency was seven to eight samples per year. From the mid-1970s to the mid-1990s, the median frequency was ten to 12 samples per year. Then, in the mid-1990s, the median sampling frequency dropped to four samples per year, where it stayed until about 2005, when it increased to

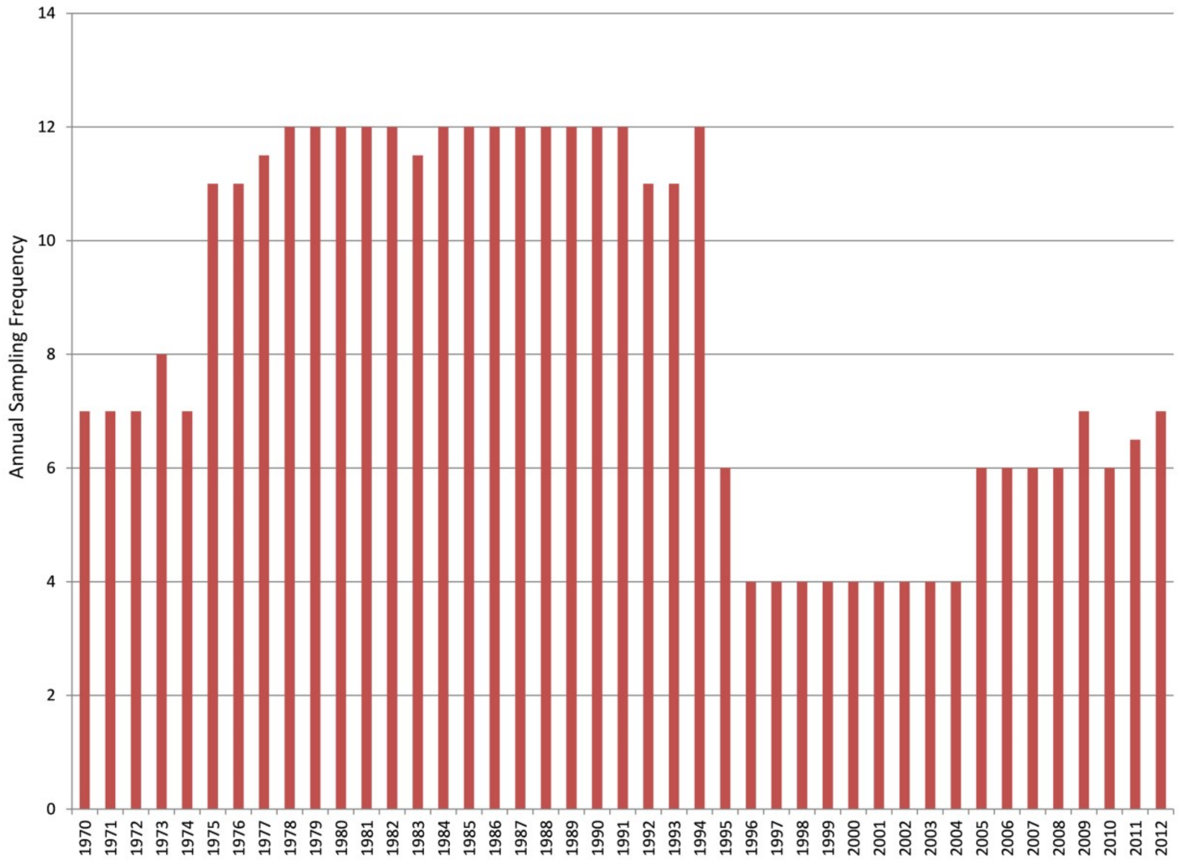

Figure 2. Median sampling frequency across all stations, by year.

about six samples per year. The variation of sampling frequency has implications for making seasonal adjustments in trends.

Detection Limits

By far the most vexing source of variability in the monitoring data is changes that occurred in the minimum detection limits (MDL) of the analytical methods. Reported detection limits for censored data—data that falls below the detection limit—can differ for observations taken within the same year. **Table A-4** of Appendix A shows the percent of observations below the detection limit. Some constituents, like DO or hardness, have little or no censoring, whereas for others, like total lead or hot acidity, the majority of samples are censored. The consequence of the degree of censoring for trend analysis is discussed below.

Flow Data

To facilitate the calculation of flow-adjusted trends, WVDEP (personal communication, 2014) identified USGS gages reporting daily average flows located near 23 of the 26 water quality monitoring stations. The 23 gages are listed in **Table 2**, along with their periods of record. **Figures A-1** through **A-5** in Appendix A show the locations of the stream gages relative to the 23 AWQM stations. In all but one case, the monitoring station is associated with a single, nearby flow gage. Flows for KL-00001-31.7 on the Lower Kanawha River were calculated as the sum of two upstream USGS gages. The period or record for the gage did not always coincide with the period of record for sampling at the monitoring station, shown in **Table 1**, so flow correction was not always possible.

Table 2. USGS streamflow gages associated with West Virginia water quality monitoring stations. Maps showing station and gage locations relative to each other are in Appendix A. *, monitoring stations that are located immediately adjacent to a USGS streamflow gage.

Stream Name	Station Code	USGS Gage	Gage Period of Record
Cacapon River *	PU-00010-6.1	01611500	1970-2012
Cheat River	MC-00001-3.5	NA	
Cheat River *	MC-00001-30	03070260	1996-1997, 2010-2012
Coal River *	KC-00001-11.6	03200500	1970-2012
Dunkard Creek	ML-00001-20.6	03072000	1970-2012
Elk River	KE-00001-4.3	03197000	1970-2012
Gauley River	KG-00001-8.25	03192000	1970-2012
Greenbrier River	KNG-00001-1.6	03184000	1970-2012
Lower Guyandotte River	OGL-00001-2.8	03204000	1970-1995
Lower Guyandotte River	OGL-00001-74.1	03203600	1970-2012
Hughes River	LK-00025-1.5	NA	
Lower Kanawha River	KL-00001-31.7	03198000+03200500	1970-2012
Upper Kanawha River	KU-00001-74.1	03193000	1970-2012
Little Kanawha River *	LK-00001-28.9	03155000	1970-2012
Middle Island Creek	OMN-00006-12.3	03114500	1970-1995, 2009-2012
Upper Monongahela River	MU-00001-99.4	NA	
Lower New River	KNL-00001-1.2	03185400	1981-2012
Upper New River	KNU-00001-67.4	03184500	1970-2003
Upper New River	KNU-00001-96.2	03176500	1970-2012
Opequon Creek	PL-00014-2.2	01616500	1970-2012
Shenandoah River	PS-00001-0.9	01636500	1970-2012
South Branch Potomac River *	PSB-00001-13.4	01608500	1970-2012
Tug Fork	BST-00001-0.15	03214500	1985-2012
Twelvepole Creek	OT-00001-8.8	03207020	1970-1982
Tygart Valley River *	MT-00001-6.2	03057000	1970-1995, 2010-2012
West Fork River *	MW-00001-12	03061000	1970-2012

Ecoregions

The West Virginia analysis data set contains information about the ecoregion in which each monitoring station was located (see **Table 1**). Ecoregions are distinct geographic regions with similar geology, physiography, vegetation, climate, soils, land use, wildlife, and hydrology (Olmernik 1987, 1995). This information was considered when interpreting station results. The intent was to identify the effects, if any, of natural geographic variability on water quality trends. **Figure 1** shows the major Level III ecoregions of West Virginia and **Figure A-6** in Appendix A shows the further subdivided, Level IV ecoregions.

Trend Analysis Methods

Helsel's and Hirsh's *Statistical Methods in Water Resources* (Helsel and Hirsch, 2002) provided guidance on methods for trend analysis. Additional guidance for data sets with censored values was taken from

Helsel's *Statistics for Censored Environmental Data Using Minitab and R* (Helsel, 2012). Several considerations determine which trend analysis approach is best suited for a particular data set.

General Approach

Trend analysis is generally divided into parametric methods and nonparametric methods. Parametric methods assume the data conform to a specific distribution. An example of a parametric procedure for trend analysis is the two-sample t-test to determine the difference in means between two periods. The t-test assumes the data are normally distributed. If that assumption is wrong, the test's ability to reject the hypothesis of no trend (null hypothesis) when there is in fact no trend is diminished. When the data are not normally distributed and it is inappropriate to assume a distribution for the data, nonparametric methods have more power—that is, greater ability to correctly reject the hypothesis of no trend when there is no trend. The nonparametric alternative to the two-sample t-test is the Wilcoxon rank-sum test (also called the Mann-Whitney test). There are also mixed procedures, which usually are performed in two stages. One is parametric while the other is non-parametric. In this study, non-parametric methods were universally applied for all parameters.

Concentrations of certain water quality parameters can be strongly influenced by season and/or streamflow intensity. Trends in these parameters can be clearer if the confounding effects of season and flow are taken into account in the analysis. In this study, all trend analyses employ a method to adjust for normal seasonal differences in the parameters. Trend analyses were always done on data that were not adjusted for flow, and when sufficient flow data were available they were also performed on flow-adjusted data. Comparisons of the flow-adjusted and unadjusted results typically can identify the influence of extreme or unusual flow events on trend results. Finally, two trend periods were selected for study: a long-term period from 1970 to 2012 and a short-term, "recent" period from 1996 to 2012. This was done to accommodate changes in stations and sampling frequencies over the 43-year monitoring history. It also provides an opportunity to identify recent changes that may be masked in the long-term trend results. The ideal was to calculate the following four kinds of trends for each combination of station and parameter, although this was not always possible due to various data limitations (discussed below):

- Long-term trends (1970-2012) on data not adjusted for flow
- Recent trends (1996-2012) on data not adjusted for flow
- Long-term trends (1970-2012) on flow-adjusted data
- Recent trends (1996-2012) on flow-adjusted data

Sampling frequency varied systematically over the 43 year timeframe of the West Virginia analysis data set. When sampling frequency varies like this, Helsel and Hirsch (2002) recommend culling the data to as uniform a frequency as possible across the entire trend period before applying the seasonal Kendall test—the primary method for testing seasonally adjusted trends. In this study, four seasons were defined and the minimum sampling frequency in each season was determined for both the short-term and long-term trend periods. The four seasons are: winter (December, January, February), spring (March, April, May), summer (June, July, August), and autumn (September, October, November). The observation closest to the midpoint of each season was selected as the value to represent that season-year and the other data excluded from the trend analysis. Culling was performed on both flow-adjusted and unadjusted data before testing for trends with the seasonal Kendall test.

The data for each station-parameter combination was classified into a data type in order to identify the most appropriate trend methods. Type classification is based on the period of record and the degree of censoring. If the period of record is discontinuous, step-trend methods rather than linear trend methods are more appropriate to use. Step trends divide the data into earlier and later periods on either side of the discontinuity and measure differences in the two periods. If the degree of censoring is too high to ignore, techniques to handle censored data in trend analyses need to be employed.

The goal of all the methods is to determine if a trend exists. This is usually expressed as the p-value of the hypothesis test that there is no trend (null hypothesis). The smaller the p-value, the stronger the evidence that a trend exists and the null hypothesis should be rejected. For this analysis, p-values less than 0.05 are considered indicative of real or "significant" trends.

Data Type

Characterization of the data for each station-parameter combination is an important prerequisite to selecting the most appropriate trend method to apply. Data coverage is the first factor considered in characterizing data type. Classification is based on the period of record for each station-parameter combination. Helsel and Hirsch (2002) recommend the following procedure to determine whether a gap in the period of record for a given parameter prohibits the calculation of a long-term linear trend:

1. Divide the period of record in thirds of equal length.
2. Determine if any third has less than 20% "coverage," i.e. less than 20% of possible values.
3. If a third contains less than 20% coverage, then a long-term trend including that third is inappropriate.

This procedure was modified for the West Virginia trend study because many of the parameters have an existing data gap between 1985 and 1995. For this reason, the data was divided into three unequal periods: (1) 1970-1984; (2) 1985-1995; and (3) 1996-2012. Station and parameter combinations were classified according to which periods were above the 20% coverage threshold as shown in **Table 3**. Percent coverage was based on the culled data time series determined for each station and parameter combination. Four distinct data types were identified in the data set as suitable for trend testing. Data classified as Type I can be tested for long-term linear trends. Type II data can be tested for long-term trends by dividing the data into a recent period (1996-2012) and an earlier period (1970-1995) and performing a step-trend analysis. The 1996-2012 period in the Types I and II data can also be tested for short-term linear trends. Type III data can only be used for short-term linear trends. For Type IV data, the recent period 1996-2012 has too few data for short-term linear trends but could be used with the early period data to calculate long-term step trends.

The degree of censoring is the second factor used to select the most appropriate trend method. Station-parameter combinations were classified according to the percent of censored data (**Table 4**). For Types I

Table 3. Data type as determined by data coverage. *The recent period of record is not sufficiently long for short-term linear trends but recent data can possibly be used with the earlier data to determine long-term step trends.

Coverage	Greater than 20% Coverage?			Trend types
Type	1970-1984	1985-1995	1996-2012	
I	Yes	Yes	Yes	Long-term and short-term linear
II	Yes	No	Yes	Long-term step-trend, short-term linear
III	No	Not Applicable	Yes	Short-term linear
IV	Yes	Not Applicable	Partial*	Long-term step-trend

and II, the proportion of censored data is determined from the 1970-2012 period data; for Types III and IV, the proportion of censored data is determined from 1996-2012 period data.

The coverage and censoring classifications jointly characterize the data type of a given station-parameter combination and are used to determine which trend method is most appropriate to apply. **Table A-5** in Appendix A lists the assigned data type for each station and parameter combination.

Table 4. Data type as determined by censoring.

Censoring Type	Percent of Data Below Detection Limit
a	<5%
b	5% - 50%
c	>50%

Seasonal Adjustment

Two types of seasonal adjustments were used in the study: the seasonal Kendall test and the median-adjustment method. The seasonal Kendall test is a trend method designed to account for seasonal variability. It assumes that the number of "seasons" per year is constant, with a single value associated with each season, hence the need to cull the data. An alternative method for seasonally-adjusting the data is to subtract the median value for each season from that season's observations. Data modified in this way can be referred to as "median-adjusted" data. The method does not involve culling the data.

Flow Adjustment

Flow adjustments were made only to Type a data (few or no censored values). Data can be flow-adjusted by applying individual log-log regression models for each station and parameter where the log of a parameter's concentration is plotted against the log of the corresponding daily flow rate at the station. If the residuals of a linear regression through the data are normally distributed, trend tests (for example, the seasonal Kendall test) can be directly applied to the residuals to determine flow-adjusted trends. The linear regression assumptions were tested in this study with the Shapiro-Wilk test for normality, the Breusch-Pagan test for homoscedasticity, and Durban-Watson test for serial-correlation. The linear regression assumptions were not met for a majority of station-parameter combinations. Based on these results, the data were flow-adjusted by calculating residuals from the non-linear, Locally Weighted Scatterplot Smooth (LOWESS) curves of log-transformed concentration versus log-transformed flow. LOWESS requires no distributional assumptions for its validity, and the residuals of a LOWESS curve can be used in flow-adjusted trend analyses when the assumptions of linear regression are not met. Default parameters were used to generate the LOWESS curves. The LOWESS plots and regression curves are provided in **Appendix D.**

Trend Methods

The seasonal Kendall test on culled data was used to test for long-term trends in a continuous data record with few or no censored values (Type Ia). Censored observations were set at half the limit of detection before performing the trend analysis. The seasonal Kendall test was applied to both the observed values (not adjusted for flow) and the residuals from the LOWESS curves (flow-adjusted). The rank-sum test, also known as the Wilcoxon signed rank test, was used on median-adjusted data to test for long-term trends in a discontinuous data record with few or no censored values (Type IIa and IVa). Data was divided into a recent period (1996-2012) and earlier period (1970-1995), and the rank sum test determined if the distributions or medians of the two periods differed. The rank sum test was applied to the median-adjusted values of the observed data (not adjusted for flow) and residuals from the LOWESS curves (flow-adjusted).

Short-term trends were calculated on the recent period data from Types Ia, IIa, and IIIa. The season Kendall test on culled data was used to generate these trends. It was applied to both the observed values (not adjusted for flow) and the residuals from the LOWESS curves (flow-adjusted).

Trend methods applicable to censored data were used for data Types b (5%-50% censored values) and c (>50% censored values). The same trend methods were applicable to these two types. The only difference is trend results may be unreliable when the percent of censored is above 50%. The Mann-Kendall test adapted for censored data was performed on the median-adjusted data to test for long-term trends in data Type I and for short-term trends in data Types I, II, and III. Seasonal medians were calculated using regression on order statistics (ROS) as described by Helsel (2012). For some stations the degree of censoring was so high that neither the ROS medians nor the Mann-Kendall test could be calculated. For step-trends on long-term data Types II and IV, the Peto-Peto test (also known as the Peto-Prentice test), was applied to median-adjusted data. It is a version of the rank-sum test adapted for censored data.

Table 5 lists the trend analysis method used for each data type in this study. Since different methods can be used for long-term (1970-2012) and recent (1996-2012) trends, **Table 5** shows the most appropriate method for both long-term and recent trends. If it was possible to flow-adjust the data, the same methods were selected as the primary methods for flow-adjusted trends.

If the trend p-value supports the existence of a trend, the next step was to determine the direction and, if possible the magnitude, of the trend. For a linear trend, the direction and magnitude of the trend is determined by estimating the trend slope. The Theil slope was used to estimate the direction and magnitude of the trend when the seasonal Kendall test was applied. The version of the Theil slope

Table 5. Trend methods applied, by data type, to data not adjusted for flow.

Type	Data Description	Recent (1996-2012)	Long-Term (1970-2012)
Ia	Continuous long-term data record, little or no censoring	Seasonal Kendall Test on Culled Data	Seasonal Kendall Test on Culled Data
IIa	Discontinuous long-term data record, little or no censoring	Seasonal Kendall Test on Culled Data	Rank Sum Test on Median Adjusted Data
IIIa	Only recent data, little or no censoring	Seasonal Kendall Test on Culled Data	Not Applicable
IVa	Data lacking in recent period, little or no censoring	Not Applicable	Rank Sum Test on Median Adjusted Data
Ib, Ic	Continuous long-term data record, moderate (b) to high (c) censoring	Mann-Kendall Test on Median Adjusted Data	Mann-Kendall Test on Median Adjusted Data
IIb, IIc	Discontinuous long-term data record, moderate (b) to high (c) censoring	Mann-Kendall Test on Median Adjusted Data	Peto-Prentice Test on Median Adjusted Data
IIIb, IIIc	Only recent data, moderate (b) to high (c) censoring	Mann-Kendall Test on Median Adjusted Data	Not Applicable
IVb, IVc	Data lacking in recent period, moderate (b) or high (c) censoring	Not Applicable	Peto-Prentice Test on Median Adjusted Data

applied to censored data, the Akritas-Theil-Sen (ATS) slope, was used when the Mann-Kendall test was applied to test for trends on data with moderate or heavy censoring. No slopes were calculated for step trends, but the direction of change was estimated by examining the difference in medians between the earlier and recent periods.

Appendix B explains the trend methods in more detail and provides the R scripts used to calculate long-term and short-term trends for the West Virginia AWQM stations.

Results

Each subsection below provides the short- and long-term trend results for an individual parameter, as well as flow-adjusted short- and long-term trend results if they can be calculated. A brief description of each parameter's status in the most recent four year (2009-2012) period is provided to give the reader context. Sidebars provide general information about the parameter and some relevant water quality criteria obtained from the West Virginia Code (2014), the National Drinking Water Regulations published by the U. S. Environmental Protection Agency (2014), and guideline published by the World Health Organization (2011).

Results for each parameter are summarized by station in a table (**Tables 6 – 28**). Trends with p-values less than 0.01 are indicated with ▽ (decreasing trend) and ▲ (increasing trend). P-values between 0.01 and 0.05 are considered weaker evidence of a trend, but common practice accepts these as significant. They are indicated in the results tables with ▿ and ▴. P-values between 0.05 and 0.1 are not considered significant in this study, but the overall upward (v) or downward (^) tendencies in the data over time are noted. P-values greater than or equal to 0.1 are considered non-significant (ns). A linear trend slope in the flow unadjusted data is given when the p-value supports the existence of a trend. The symbol "-" indicates the available water quality data were insufficient for a particular trend analysis. Either the data coverage was inadequate for that trend period or an appropriate trend method was not available for a particular data type (see above).

Flow adjusted trends were not attempted if a station had insufficient pairs of water quality and daily flow measurements. The Cheat (MC-00001-3.5), Hughes (LK-00025-1.5) and Upper Monongahela (MU-00001-99.4) stations lacked flow data for the entire 43-year period, and six other stations lacked flow data some of the time (**Table 2**). In **Tables 6 - 28**, the symbol *f* under the heading "flow adjusted" indicates more than ten paired measurements of the water quality parameter and its associated daily flow were available at a station in the recent trend period (1996-2012) and in the first portion of the long-term trend period (1970-1995). A blank (i.e., the symbol *f* is not shown) indicates the station had insufficient numbers of paired measurements for the indicated trend period. Flow adjustments can be made only on Type a data (few/no censored values), so the symbol "-" follows *f* for all Type b and c data (some/many censored values) and indicates no trend was calculated for that parameter at that station.

Appendix C contains time series of the data for each parameter-station combination. **Appendix D** contains the parameter concentration *versus* flow scatter plots and LOWESS curves used to flow-adjust the data. **Appendix E** presents the trend results grouped by station rather than by parameter.

Alkalinity, Total

Alkalinity measures the buffering capacity of water, or its ability to neutralize acids. Total alkalinity is the amount of dissociated anions—primarily carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) but also phosphate (PO_4^{3-}), hydroxyl (OH^-), borates, silicates, sulfides, dissolved ammonia, nitrate, and other bases—available to bind with free cations, including H^+. Alkalinity links dynamically to many water quality parameters, so assessing a waterbody's alkalinity is important to understanding the system's health. First order streams with low alkalinity often do not have the mineral content for adequate buffering capacity, making them vulnerable to rapid changes in pH. Landscape disturbances and dissolution of bedrock and cement-based structures by acid rain can increase alkalinity in runoff.

Monitoring data for total alkalinity begins in the 1970s at 17 of the 26 stations and continues uninterrupted through 2012 (Type I). Alkalinity monitoring also begins in 1970 at six other stations but halts for 11 years between 1985 and 1995, resulting in non-continuous data records at these stations (Type II). Alkalinity measurements begin in 1996 in the Cheat at mile 3.5, Lower Guyandotte River at mile 74.1, and Twelvepole Creek (Type III). Sampling intensity varies over the 43 years. Very few samples (7) in the entire data set of 7,082 alkalinity measurements fall below detection limits, so flow-adjusted trends can be estimated for all stations with sufficient flow data. Alkalinity is a very robust parameter to use in trend analyses. Trend results are provided in **Table 6**.

Alkalinity is reported as milligrams per liter of calcium carbonate (mg/liter $CaCO_3$) even though it can be comprised of multiple bases. Median concentrations in 2009-2012 ranged from less than 20 mg/liter (Cheat at mile 3.5, Gauley) to more than 200 mg/liter (Opequon). Minimum and maximum values observed in that time period were 5 mg/liter (Upper New at mile 96.2) and 267 mg/liter (Opequon). Alkalinity concentrations were highly variable at Coal, Dunkard, Lower Guyandotte at miles 2.8 and 74.1, Tug Fork, Opequon, and South Branch Potomac stations, with ranges (maximum minus minimum) of 95 mg/liter or more. The large ranges suggest multiple sources of alkalinity. Ranges were smallest—less than 35 mg/liter—at the Cheat at miles 3.5 and 30, Tygart Valley, Gauley, New at miles 1.2 and 67.4, Elk and Little Kanawha stations. Very high alkalinity levels have associated risks such as increased ammonia toxicity. Alkalinity greater than 30-40 mg/liter in association with relatively low hardness—less than 150 mg/liter—may make streams and rivers more susceptible to the formation of filamentous green algae blooms (Summers 2008).

Long-term trends. All but three of the 23 stations with long-term records (Type I, II) show increasing trends ($p<0.05$). Time series plots in **Appendix C** show the increasing trends can be the result of greater annual variability pulling the median upward (e.g., Coal) or a sudden jump in concentration (e.g., Tygart Valley) as well as steadily increasing concentrations over the long-term (e.g. Middle Island). Of the Type 1a trends, alkalinity in the Coal, Tug Fork, and West Fork rivers are increasing the fastest, with changes of 1 mg/liter/year or more. The South Branch Potomac, Cacapon, and Shenandoah rivers, all of which are in the Potomac River basin, show no long-term trends. These three rivers and Opequon Creek flow through the Ridge and Valley ecoregion which has abundant limestone, dolomite, and other carbonate rocks. These rocks are natural sources of alkalinity, and inputs from natural weathering may be masking human-related trends at this time.

Short-term trends. In contrast to the long-term trends, only six of the 26 stations with recent data (1996 – 2012) show significant or possible trends. Four are increasing, with relatively weak trends ($0.01<p<0.05$); two are possible increasing trends ($0.05<p<0.1$). Examination of the time series at these six stations show they all have comparatively small amounts of annual variability, which could explain why their short-term trends are more readily apparent.

Flow-adjusted trends. The LOWESS curves of alkalinity versus flow are typically linear and increasing flows correlated well with declining alkalinity concentrations at most stations (**Appendix D**). Flow adjustment did not change the upward direction of most short-term and long-term trends.

Table 6. Total alkalinity trends. Recent (1996 - 2012); long-term (1970s - 2012); slope (mg/liter/year as $CaCO_3$); minimum, median, and maximum (mg/liter).

				Not Adjusted for Flow				Flow Adjusted		2009-2012		
				Recent		Long-term		Recent	Long-term			
Ecoreg.	Station	StreamName	Type	trend	slope	trend	slope	trend	trend	min	median	max
Western Allegheny Plateau	MC-00001-3.5	Cheat River	IIIa	▴	1.84E-01	-				8	13	25
	KC-00001-11.6	Coal River	Ia	ns		▲	1.95E+00	*f* ▲	*f* ▲	45	131	262
	ML-00001-20.6	Dunkard Creek	IIa	ns		▲		*f* ▲	*f* ▲	50	116	152
	KE-00001-4.3	Elk River	Ia	ns		▲	3.04E-01	*f* ns	*f* ▲	12	21	42
	OGL-00001-2.8	Guyandotte River (Lower)	Ia	ns		▲	7.79E-01			31	59	137
	LK-00025-1.5	Hughes River	IIa	ns		▲				19	45	64
	KL-00001-31.7	Kanawha River (Lower)	Ia	ns		▲	4.14E-01	*f* ns	*f* ▲	28	47	80
	LK-00001-28.9	Little Kanawha River	Ia	^	3.14E-01	▲	2.73E-01	*f* ns	*f* ▲	18	30	52
	OMN-00006-12.3	Middle Island Creek	IIa	ns		▲		*f* ns	*f* ▲	23	45	70
	MU-00001-99.4	Monongahela River (Upper)	Ia	▴	8.82E-01	▲	7.69E-01			26	45.3	75
	BST-00001-0.15	Tug Fork	Ia	ns		▲	1.31E+00	*f* ▴	*f* ▲	63	143	234
	OT-00001-8.8	Twelvepole Creek	IIIa	▴	5.55E-01	-				8	41.5	80
	MT-00001-6.2	Tygart Valley River	Ia	▴	2.09E-01	▲	3.92E-01	*f* ns	*f* ▴	11	20.5	36
	MW-00001-12	West Fork River	Ia	ns		▲	1.22E+00	*f* ns	*f* ▲	45	82	116
Central Appalachians	MC-00001-30	Cheat River	Ia	^	1.45E-01	▲	2.25E-01	*f* ns		9	16	29
	KG-00001-8.25	Gauley River	Ia	ns		▲	1.67E-01	*f* ns	*f* ▲	10	17	35
	KNG-00001-1.6	Greenbrier River	Ia	ns		▴	1.72E-01	*f* ns	*f* ns	31	46	85
	OGL-00001-74.1	Guyandotte River (Lower)	IIIa	ns		-		*f* ns		43	83	168
	KU-00001-74.1	Kanawha River (Upper)	Ia	ns		▲	2.16E-01	*f* ns	*f* ▲	28	46	79
	KNL-00001-1.2	New River (Lower)	Ia	ns		▴	1.50E-01	*f* ns	*f* ▴	38	53.5	69
	KNU-00001-67.4	New River (Upper)	IIa	ns		▲		*f* v	*f* ns	45	54	73
	KNU-00001-96.2	New River (Upper)	IIa	ns		▲		*f* ns	*f* ▲	5	58	68
Ridge & Valley	PU-00010-6.1	Cacapon River	Ia	ns		ns		*f* ns	*f* ns	32	57.5	89
	PL-00014-2.2	Opequon Creek	IIa	ns		▲		*f* ns	*f* ▲	134	235.5	267
	PSB-00001-13.4	South Branch Potomac River	Ia	ns		ns		*f* ns	*f* ns	10	73.5	105
	PS-00001-0.9	Shenandoah River	Ia	ns		ns		*f* ns	*f* ▿	85	129	153

Aluminum, Total

> ***Aluminum (Al)*** is the most abundant metallic element in the earth's crust. It is used to precipitate phosphorus in waste water treatment plants and is a component of sludge waste. In water, aluminum solubility increases rapidly when pH drops below 4.5, allowing ionic concentrations to rise. Ionic Al is highly reactive and toxic in aquatic environments. It bonds to fish gill membranes, reducing gill permeability and oxygen uptake. Concentrations >1.5 mg/liter are fatal to trout, and lesser concentrations reduce growth rates of other fish. West Virginia's acute aquatic life use criterion for dissolved Al is 0.75 mg/liter. Aluminum is likely mutagenic and carcinogenic to humans. The World Health Organization and USEPA recommend an upper limit of 0.2 mg/liter dissolved Al in drinking water.

Total aluminum measurements begin in the mid-1970s at 23 of the 26 stations. Sixteen stations have continuous or nearly continuous data sets through 2012 with sufficient samples (Type I). Measurements at five stations begin in the 1970s but halt between 1985 and 1995 (Type II). At two stations, samples are sparse in the 1970s and early 1980s (one or two samples per year) and missing between 1985 and 1995 so long-term trends cannot be reliably calculated and the station trends are limited to the recent period (Type III). Measurements at the remaining three stations begin in 1996 and trends there are also limited to the recent period (Type III). The percentage of aluminum measurements below the minimum detection limits (MDL) is between 5% and 12% at half of the stations (Type b), and less than 5% at the other half (Type a). Flow-adjusted trends are not done at stations with more than 5% non-detects (Type b). Trend results are shown in **Table 7**.

Median concentrations of total aluminum in the most recent four years (2009-2012) ranged almost ten-fold, from 0.04 mg/liter (Cacapon, South Branch Potomac) to 0.39 mg/liter (Twelvepole). Minimum and maximum values observed in that time period were 0.01 mg/liter (Cacapon) and 10.5 mg/liter (West Fork), respectively. Concentrations of dissolved aluminum, which were measured by WVDEP between 1999 and 2012, are much lower. Only one measurement exceeded West Virginia's acute aquatic life use criterion for dissolved aluminum of 0.75 mg/liter (Tug Fork).

Long-term trends. Three stations—Middle Island, Greenbrier, and Opequon—show no trends in total aluminum ($p<0.05$). The remaining eighteen stations with long-term records (Type I, II) show significant decreasing trends with the largest declines occurring at the Tug Fork, Cheat (mile 30) and Lower Guyandotte (mile 2.8) stations.

Short-term trends. Significant but slight downward trends occurred at the four Potomac basin rivers: South Branch Potomac, Cacapon, Opequon, and Shenandoah ($p<0.05$). Downward tendencies ($0.05<p<0.01$) occurred at West Fork, Gauley, and Lower Guyandotte River (mile 74.1). A partial explanation for the appearance of significant trends in the Potomac basin may be the small amount of variability in total aluminum values in these four rivers as compared to most other West Virginia rivers, which would make slight trends more discernable.

Flow-adjusted trends. The log-log plots of total aluminum versus flow were usually curvilinear, with weak or no response at low flows and an increasing response at high flows (**Appendix D**). Data censoring and a lack of flow data at some stations limited the computation of some flow-adjusted trends. All flow-adjusted trends confirmed their corresponding flow-unadjusted trends, indicating that variations in concentration due to streamflow were not confounding the trend results.

Table 7. Total aluminum (Al) trends. Recent (1996 - 2012); long-term (1970s - 2012); slope (mg/liter/year); median (mg/liter).

				Not Adjusted for Flow				Flow Adjusted		2009-2012
				Recent		Long-term		Recent	Long-term	
Ecoreg.	Station	StreamName	Type	trend	slope	trend	slope	trend	trend	median
Western Allegheny Plateau	MC-00001-3.5	Cheat River	IIIb	ns		-				0.245
	KC-00001-11.6	Coal River	Ib	ns		▽	-1.93E-05	*f* -	*f* -	0.140
	ML-00001-20.6	Dunkard Creek	IIa	ns		▽		*f* ns	*f* ▿	0.140
	KE-00001-4.3	Elk River	Ib	ns		▽	-1.21E-05	*f* -	*f* -	0.160
	OGL-00001-2.8	Guyandotte River (Lower)	Ia	ns		▽	-1.61E-02			0.380
	LK-00025-1.5	Hughes River	IIIb	ns		-				0.380
	KL-00001-31.7	Kanawha River (Lower)	Ia	ns		▽	-5.00E-03	*f* ns	*f* ▽	0.210
	LK-00001-28.9	Little Kanawha River	Ia	ns		▿	-7.11E-03	*f* ns	*f* ▿	0.350
	OMN-00006-12.3	Middle Island Creek	IIa	ns		ns		*f* ns	*f* ns	0.365
	MU-00001-99.4	Monongahela River (Upper)	Ia	ns		▽	-4.77E-03			0.150
	BST-00001-0.15	Tug Fork	Ia	ns		▽	-1.00E-02	*f* ▿	*f* ▽	0.210
	OT-00001-8.8	Twelvepole Creek	IIIb	ns		-				0.390
	MT-00001-6.2	Tygart Valley River	IIIb	ns		-		*f* -	*f* -	0.100
	MW-00001-12	West Fork River	Ia	v	-1.26E-02	▽	-8.18E-03	*f* ▿	*f* ▽	0.210
Central Appalachians	MC-00001-30	Cheat River	Ia	ns		▽	-1.60E-02	*f* ns		0.350
	KG-00001-8.25	Gauley River	Ib	v	-9.78E-06	▽	-1.02E-05	*f* -	*f* -	0.085
	KNG-00001-1.6	Greenbrier River	Ib	ns		ns		*f* -	*f* -	0.080
	OGL-00001-74.1	Guyandotte River (Lower)	IIIa	v	-1.00E-02	-		*f* ns		0.185
	KU-00001-74.1	Kanawha River (Upper)	Ib	ns		▽	-1.42E-05	*f* -	*f* -	0.135
	KNL-00001-1.2	New River (Lower)	Ib	ns		▽	-7.64E-06	*f* -	*f* -	0.150
	KNU-00001-67.4	New River (Upper)	IIb	ns		▽		*f* -	*f* -	0.130
	KNU-00001-96.2	New River (Upper)	IIb	ns		▽		*f* -	*f* -	0.080
Ridge & Valley	PU-00010-6.1	Cacapon River	Ib	▿	-1.17E-05	▽	-6.23E-06	*f* -	*f* -	0.040
	PL-00014-2.2	Opequon Creek	IIb	▽	-1.97E-05	ns		*f* -	*f* -	0.100
	PSB-00001-13.4	South Branch Potomac River	Ib	▽	-1.23E-05	▽	-9.06E-06	*f* -	*f* -	0.040
	PS-00001-0.9	Shenandoah River	Ib	v	-9.05E-06	▽	-7.67E-06	*f* -	*f* -	0.080

Calcium, Total

Calcium (Ca) measurements appear occasionally in the analysis database before 2001 and sporadically between 2001 and 2008. Routine monitoring of Ca begins in 2009. The 2009-2012 period is too short to determine trends; however, the data can be used as a baseline in future analyses. Ca measurements, in conjunction with magnesium (Mg), provide information on the dominant sources of water hardness (see also "Hardness" and "Magnesium"). None of the 736 Ca measurements made between 2009 and 2012 are below detection limits. Six or seven samples were usually collected yearly at a monitoring station although four stations had higher sampling frequencies (Dunkard Creek, Upper Monongahela River, Tygart Valley River, West Fork River). **Figure 3** shows the distribution of values at each station over the 2009-2012 period and **Table 8** provides the median concentrations.

Calcium (Ca) is an alkaline earth metal abundant in the earth's crust. The element is essential in cellular processes and functions of all living organisms and important in the carbon cycle of aquatic ecosystems. Limestone is composed of several crystalline forms of calcium carbonate ($CaCO_3$). Other Ca-bearing minerals include marble, dolomite, gypsum, and apatite. Ca compounds are generally soluble in water and a major source of Ca in streams and rivers is weathering of Ca-bearing rocks. Industrial processes and fertilizers are other Ca sources. Ca is one of the cations principally responsible for water hardness and $CaCO_3$ is important in buffering streams and rivers against large swings in acidity. West Virginia has no water quality criteria for Ca.

The Ridge & Valley is dominated by carbonate rocks (e.g., limestone, dolomite), and natural weathering of these rocks is a likely cause of the somewhat higher Ca concentrations in that ecoregion. Stations with particularly high Ca concentrations are Opequon in the Ridge & Valley ecoregion and Coal, Dunkard, Tug Fork, and West Fork in the Western Allegheny Plateau ecoregion.

Table 8. Median calcium (Ca) concentrations, 2009-2012 (mg/liter).

	Stream Name	Station	mg/liter
Western Allegheny Plateau	Cheat R.	MC-00001-3.5	13.8
	Coal R.	KC-00001-11.6	48.0
	Dunkard Cr.	ML-00001-20.6	46.2
	Elk River	KE-00001-4.3	16.0
	Hughes River	LK-00025-1.5	17.4
	Little Kanawha R.	LK-00001-28.9	14.2
	Lower Guyandotte R.	OGL-00001-2.8	30.4
	Lower Kanawha R.	KL-00001-31.7	19.2
	Middle Island Cr.	OMN-00006-12.3	18.2
	Tug Fork	BST-00001-0.15	54.1
	Twelvepole Cr.	OT-00001-8.8	23.6
	Tygart Valley R.	MT-00001-6.2	15.9
	Monongahela R. (Upper)	MU-00001-99.4	34.5
	West Fork R.	MW-00001-12	76.8
Central Appalachians	Cheat R.	MC-00001-30	12.0
	Gauley R.	KG-00001-8.25	8.5
	Greenbrier R.	KNG-00001-1.6	22.0
	Guyandotte R. (Lower)	OGL-00001-74.1	33.2
	New R. (Lower)	KNL-00001-1.2	19.8
	Kanawha R. (Upper)	KU-00001-74.1	20.5
	New R. (Upper)	KNU-00001-67.4	19.5
	New R. (Upper)	KNU-00001-96.2	20.4
R. & V.	Cacapon R.	PU-00010-6.1	22.3
	Opequon Cr.	PL-00014-2.2	94.1
	S. Branch Potomac R.	PSB-00001-13.4	37.0
	Shenandoah R.	PS-00001-0.9	42.4

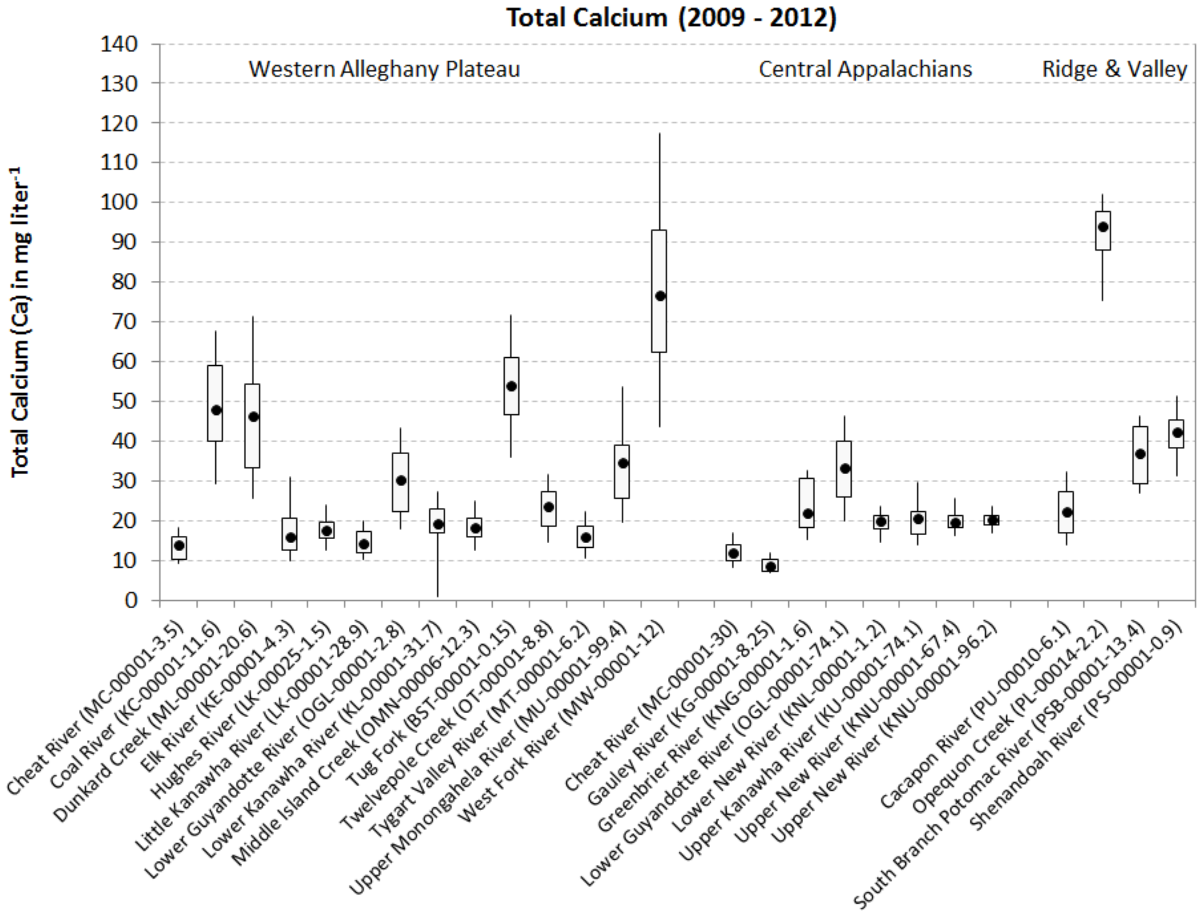

Figure 3. Calcium concentrations, 2009-2012 (mg/liter). Median (•); 25th - 75th %ile (box); 5th - 95th %ile (whiskers).

Chloride, Total

None of the 26 stations has chloride data for the 11 years between 1985 and 1995. Twenty-three of the 26 stations have chloride data before and after this gap. The data have little or no censoring and are sufficient for trend analysis (Type IIa). Three stations have chloride data for the recent period only (1996-2012). These data also have little or no censoring and are sufficient for short-term trend analysis (Type IIIa). Sampling intensity varied over the 43 years. Trend results are shown in **Table 9**.

Chloride refers to the concentration of chlorine anions (Cl^-) in water. Chlorides associate with various cations to form highly soluble salts. The most common chloride salts are sodium, potassium and calcium chlorides. Although many chloride salts are considered essential nutrients, excess amounts can be harmful, particularly in fresh water systems where they impede normal osmoregulation (biological regulation of internal water and salt content). Weathering is a natural source of chlorides in freshwater systems, but excessive chloride concentrations are often attributable to road salt, fertilizer runoff, oil and gas related activities, and other landscape disturbance. West Virginia chloride criteria are 250 mg/liter for recreational contact and drinking water sources and 230 for chronic aquatic life protection. A higher acute criterion for aquatic life use applies to discharges and mixing zones.

Median concentrations in the most recent four years (2009-2012) ranged from 2.0 mg/liter (Gauley, Cheat at mile30) to over 40 mg/liter (Dunkard, Opequon). The minimum observed value of 2 mg/liter was found at many locations over that time period; the maximum observed values exceeded 200 mg/liter and were found at Dunkard Creek. No concentrations greater than West Virginia's chloride criteria of 250 mg/liter (recreational contact) and 230 mg/liter (aquatic life) were observed during these four years.

Long-term trends. Results for the 23 stations with long-term records are mixed. Six stations show increasing trends – Coal, Dunkard, Opequon, Lower New, and both Upper New stations (miles 67.4 and 96.2). Six stations show no trend - Lower Guyandotte (mile 2.8), Monongahela, Tug Fork, West Fork, Upper Kanawha, and Cacapon ($p<0.05$). Tygart Valley shows a possible decreasing trend ($0.05<p<0.1$) and ten other stations show significant decreasing trends – Elk, Hughes, Lower Kanawha, Little Kanawha, Middle Island, Cheat (mile 30), Gauley, Greenbrier, South Branch Potomac, and Shenandoah.

Short-term trends. No decreasing trends are evident in the 17-year period of 1996 - 2012. Trends are not significant (ns) at eleven stations, trending upward ($0.05<p<0.10$) at two stations, and increasing significantly ($p<0.05$) at thirteen stations. Rates of increase are greatest in Opequon Creek (+1.08 mg/liter/year) and Dunkard Creek (+0.97 mg/liter/year). Both of these stations also experienced significant increasing long-term trends.

Flow-adjusted trends. The LOWESS curves reveal station differences in the relationships between total chloride and flow, probably indicating different chloride sources (**Appendix D**). Trends in flow-adjusted concentrations generally verify the trends in flow-unadjusted concentrations. Flow adjustment did change trend results at individual stations. Significant increasing short-term trends appear in the flow-adjusted data at Coal, Dunkard, and Tug Fork, where no trends had been evident in the flow un-adjusted data ($p<0.05$). The opposite result is found in Tygart Valley, Cheat (mile 30) and Upper New (mile 67.4), where significant trends ($p<0.05$) disappear with flow adjustment.

Table 9. Total chloride (Cl) trends. Recent (1996 - 2012); long-term (1970s - 2012); slope (mg/liter/year); median (mg/liter).

				Not Adjusted for Flow				Flow Adjusted		2009-2012
				Recent		Long-term		Recent	Long-term	
Ecoreg.	Station	StreamName	Type	Trend	Slope	Trend	Slope	Trend	Trend	Median
Western Allegheny Plateau	MC-00001-3.5	Cheat River	IIIa	▲	8.75E-02	-				3
	KC-00001-11.6	Coal River	IIa	ns		▲		*f* ▲	*f* ▲	17
	ML-00001-20.6	Dunkard Creek	IIa	^	9.66E-01	▲		*f* ▲	*f* ▲	44
	KE-00001-4.3	Elk River	IIa	^	6.48E-02	▽		*f* ns	*f* ▽	5
	OGL-00001-2.8	Guyandotte River (Lower)	IIa	ns		ns				12
	LK-00025-1.5	Hughes River	IIa	ns		▽				9
	KL-00001-31.7	Kanawha River (Lower)	IIa	ns		▽		*f* ns	*f* ▽	10.5
	LK-00001-28.9	Little Kanawha River	IIa	ns		▽		*f* ns	*f* ▽	6
	OMN-00006-12.3	Middle Island Creek	IIa	ns		▽		*f* ns	*f* ▽	10
	MU-00001-99.4	Monongahela River (Upper)	IIa	▲	4.00E-01	ns				10
	BST-00001-0.15	Tug Fork	IIa	ns		ns		*f* ▲		15.5
	OT-00001-8.8	Twelvepole Creek	IIIa	▴	1.74E-01	-				8
	MT-00001-6.2	Tygart Valley River	IIa	▲	1.57E-01	v		*f* ns	*f* ns	5
	MW-00001-12	West Fork River	IIa	▲	3.84E-01	ns		*f* ▲	*f* ns	16.5
Central Appalachians	MC-00001-30	Cheat River	IIa	▴	4.47E-02	▽		*f* ns		2
	KG-00001-8.25	Gauley River	IIa	ns		▽		*f* -	*f* -	2
	KNG-00001-1.6	Greenbrier River	IIa	ns		▽		*f* ns	*f* ▽	3.5
	OGL-00001-74.1	Guyandotte River (Lower)	IIIa	ns		-		*f* ns		10
	KU-00001-74.1	Kanawha River (Upper)	IIa	▲	2.01E-01	ns		*f* ▴	*f* ns	8
	KNL-00001-1.2	New River (Lower)	IIa	ns		▴		*f* ^	*f* ns	8
	KNU-00001-67.4	New River (Upper)	IIa	▴	7.90E-02	▲		*f* ^	*f* ns	7
	KNU-00001-96.2	New River (Upper)	IIa	▲	1.29E-01	▲		*f* ▲	*f* ▲	8
Ridge & Valley	PU-00010-6.1	Cacapon River	IIa	▴	6.83E-02	ns		*f* ▴	*f* ns	4
	PL-00014-2.2	Opequon Creek	IIa	▲	1.08E+00	▲		*f* ▲	*f* ▲	43
	PSB-00001-13.4	South Branch Potomac River	IIa	▲	1.25E-01	▽		*f* ▴	*f* ▽	5
	PS-00001-0.9	Shenandoah River	IIa	▲	4.08E-01	▽		*f* ▲	*f* ▽	15

Dissolved Solids, Total

Dissolved solids are the sum of all inorganic and organic substances suspended in water in molecular, ionized or colloidal forms that can pass through a filter. Total dissolved solids (TDS) are measured by evaporating a known volume of filtered water and weighing the resulting residue. One use of TDS measurements is to evaluate the aesthetic (taste, odor, color) properties of drinking water. High values indicate the presence of chemical contaminants and potential toxicity to aquatic organisms. TDS is directly correlated to conductivity. West Virginia does not have a TDS criterion; USEPA guidelines recommend less than 500 mg/liter TDS in finished drinking water.

None of the 26 stations has total dissolved solids (TDS) data between 1985 and 2007. Twenty-three of the 26 stations have TDS data before and after this gap. These data have no censoring and are sufficient for trend analysis (Type IIa). Three stations have TDS data for the very recent period only (2008-2012): Cheat (mile 3.5), Twelvepole, and Lower Guyandotte (mile 74.1). These data also have no censoring. Five-year trends were calculated for these data (Type IIIa), but it is not clear if the trends are meaningful due to the abbreviated timeframe. Sampling intensity varied over the 43 years. Trend results are shown in **Table 10**.

Median concentrations in the most recent four years (2009-2012) ranged from 57 mg/liter (Gauley) to over 400 mg/liter (Coal, Dunkard, Tug Fork, West Fork, and Opequon). Individual values less than 40 mg/liter were found at Cheat (mile 30), Gauley, Tygart Valley and Little Kanawha. Numerous individual measurements exceeding 500 mg/liter were found at Coal, Dunkard, Tug Fork, and West Fork. Four Dunkard measurements exceeded 1,000 mg/liter.

Long-term trends. Fifteen stations show significant increasing trends, six show no trends, and two (West Fork, Shenandoah) show significant decreasing trends ($p<0.05$). Significant trends are most likely related to changes over time in anthropogenic sources since the major sources of TDS are agricultural and residential runoff and discharges from point sources.

Short-term trends. Elk and Greenbrier show increasing trends; Dunkard shows a decreasing trend. The remaining stations do not show significant trends ($p<0.05$). Recall that these trends are based on just 6 years of data and not the 17 year Recent period.

Flow adjustment. LOWESS regressions applied to the log-log plots were, for the most part, linear and increasing flows correlated well with declining TDS concentrations at most stations (**Appendix D**). Long-term flow-adjusted station trends generally agree with their corresponding flow-unadjusted trends, indicating that variation due to streamflow had minimal impact on TDS trends over the long-term.

There is a strong, highly significant, linear relationship between specific conductivity and TDS in the West Virginia data ($r^2 = 0.924$, $p<<0.01$). A specific conductivity of 767 µS/cm approximates a TDS concentration of 500 mg/liter. A relationship was derived with all the available, paired data and can be described with the following equation:

$$TDS = (0.6666*\text{Specific Conductance}) – 11.021$$

NOTE: WVDEP began sampling TDS again in 2008 in direct response to the extremely high TDS concentrations being observed downstream in Pennsylvania's Monongahela River during low flows. Short term TDS decreases in Dunkard Creek and Monongahela River at that time (Appendix C pages 578 and 589, respectively) can be explained by change in management practices at mine pool pump discharges located in the Dunkard and Monongahela watershed. Rather than discharge all year, the operators of those pumps now discharge only during higher flows. One significant TDS discharge in the Dunkard watershed has also been relocated.

Table 10. Total dissolved solids (TDS) trends. Recent (2008 - 2012, note the abbreviated timeframe); long-term (1970s – 2012); slope (mg/liter/year); median (mg/liter); exceedance (frequency of samples in the 2009 - 2012 timeframe exceeding 500 mg/liter, as %).

				Not Adjusted for Flow				Flow Adjusted		2009-2012	
				Recent		Long-term		Recent	Long-term		
Ecoreg.	Station	StreamName	Type	trend	slope	trend	slope	trend	trend	median	exceedance
Western Allegheny Plateau	MC-00001-3.5	Cheat River	IIIa	ns		-				73.5	0%
	KC-00001-11.6	Coal River	IIa	ns		▲		ƒ ns	ƒ ▲	479	42%
	ML-00001-20.6	Dunkard Creek	IIa	▿	-1.48E+02	▲		ƒ v	ƒ ▲	457.5	41%
	KE-00001-4.3	Elk River	IIa	▴	9.00E+00	▲		ƒ ns	ƒ ▲	106.5	0%
	OGL-00001-2.8	Guyandotte River (Lower)	IIa	ns		▴				215.5	0%
	LK-00025-1.5	Hughes River	IIa	ns		ns				95.5	0%
	KL-00001-31.7	Kanawha River (Lower)	IIa	ns		▴		ƒ ns	ƒ ▲	136	0%
	LK-00001-28.9	Little Kanawha River	IIa	ns		ns		ƒ ns	ƒ ns	75	0%
	OMN-00006-12.3	Middle Island Creek	IIa	ns		ns		ƒ ns	ƒ ns	98	0%
	MU-00001-99.4	Monongahela River (Upper)	IIa	ns		ns				231.5	3%
	BST-00001-0.15	Tug Fork	IIa	ns		▲		ƒ ns		419	38%
	OT-00001-8.8	Twelvepole Creek	IIIa	^		-				140.5	0%
	MT-00001-6.2	Tygart Valley River	IIa	ns		▲		ƒ ns	ƒ ▲	85	0%
	MW-00001-12	West Fork River	IIa	ns		▽		ƒ v	ƒ ▽	443.5	37%
Central Appalachians	MC-00001-30	Cheat River	IIa	ns		ns		ƒ ns		63.5	0%
	KG-00001-8.25	Gauley River	IIa	ns		▲		ƒ ns	ƒ ▲	57	0%
	KNG-00001-1.6	Greenbrier River	IIa	▲	6.83E+00	▴		ƒ ns	ƒ ns	80	0%
	OGL-00001-74.1	Guyandotte River (Lower)	IIIa	ns		-		ƒ ns		254.5	0%
	KU-00001-74.1	Kanawha River (Upper)	IIa	ns		▲		ƒ ns	ƒ ▲	119.5	0%
	KNL-00001-1.2	New River (Lower)	IIa	^	5.00E+00	▲		ƒ ns	ƒ ▲	99	0%
	KNU-00001-67.4	New River (Upper)	IIa	ns		▲				104	0%
	KNU-00001-96.2	New River (Upper)	IIa	ns		▲		ƒ ns	ƒ ▲	105	0%
Ridge & Valley	PU-00010-6.1	Cacapon River	IIa	ns		ns		ƒ ns	ƒ ns	93.5	0%
	PL-00014-2.2	Opequon Creek	IIa	ns		▲		ƒ ns	ƒ ▲	404	0%
	PSB-00001-13.4	South Branch Potomac River	IIa	ns		▲		ƒ ns	ƒ ▴	134	0%
	PS-00001-0.9	Shenandoah River	IIa	ns		▽		ƒ ns	ƒ ▽	197	0%

Dissolved Oxygen

Seventeen of the 26 stations have dissolved oxygen (DO) measurements from the 1970's through 2012 (Type I). DO monitoring also began in 1970 at six other stations but was halted for 11 years between 1985 and 1995, resulting in non-continuous records for these stations (Type II). Three stations have data records beginning in 1996 (Type III). Sampling intensity varied over the 43 years. Only one measurement is identified as below the detection limit (MU-00001-99.4 Upper Monongahela River 2/8/1995), and its value of 1 mg/liter is suspicious considering the other winter values in the Monongahela River. WVDEP staff concur that this is likely a data entry error and are flagging the value in the database (M. Whitman, pers. comm.) Trend results are shown in **Table 11**.

Dissolved oxygen (DO) is the amount of oxygen dissolved in water. Oxygen is generated in photosynthesis; it is consumed by respiration and decomposition of organic matter. Concentrations in streams and rivers are influenced by temperature, salinity, pressure, and turbulence. Low DO concentrations are generally found in warm waters where nutrient inputs and biological productivity are high. Diel (daily) patterns of daytime highs and nighttime lows are typical. Dissolved oxygen below 5.0 mg/liter stress many types of aquatic life and prolonged periods of DO below 2.0 mg/liter can result in fish kills. West Virginia warm water quality standards call for DO to be greater than or equal to 5.0 mg/liter at all times to protect aquatic life.

Dissolved oxygen concentrations are variable and, in summer, are often highest in the mid- to late-afternoon due to daytime photosynthetic production of oxygen and lowest around dawn due to nighttime respiratory consumption of oxygen. Twenty-three measurements in the analysis data set failed the West Virginia DO criterion of 5 mg/liter, most occurred before the year 2000 at the Lower Kanawha station. After 2000, three stations each failed the criterion once: Upper New (mile 67.4) and Greenbrier in July 2004 and Opequon in April 2012.

Long-term trends. Ten stations exhibited significant long-term increasing trends in DO ($p<0.05$). Dunkard, Lower Kanawha (mile 31.7), Little Kanawha, Tygart Valley, West Fork and Cheat (mile 30) had the strongest trends. The Upper Monongahela showed an upward tendency in DO concentrations ($0.05<p<0.1$), and twelve stations showed no trends. No downward (degrading) trends were found.

Short-term trends. Twenty stations exhibited significant short-term increasing (improving) trends in DO ($p<0.05$). Only four station trends were not significant. No downward trends were found.

Flow-adjusted trends. As expected, relationships between log DO concentration and log flow are highly variable and rather flat, indicating DO is strongly governed by environmental factors other than flow (**Appendix D**). Most of the flow-adjusted trends corroborated the flow un-adjusted trends, both for the short-term and long-term periods.

Too much DO (super-saturation) can also stress fish and other aquatic organisms. DO %saturation is the actual amount of oxygen dissolved in water relative to the total amount of oxygen that water can hold when in equilibrium with the surrounding temperature and atmospheric pressure. High levels of primary production can super-saturate water with oxygen. Turbulence caused by impoundments and hydroelectric dams can super-saturate downstream waters. DO %saturation in excess of 110% begins to stress aquatic life by forming gas bubbles in their circulatory systems (decompression sickness). DO %saturation was measured in the field by WVDEP until December 1998. Between 1970 and 1998, stations with the highest frequencies of super-saturation, or DO %saturation greater than 110%, were

Opequon Creek (15.2%), Shenandoah River (14.7%), and South Branch Potomac River (6.5%). Rough estimates of DO %saturation calculated for the 2009-2012 period indicate wide-spread increases in the frequency of DO super-saturation events may have occurred, with more than half of West Virginia stations experiencing frequencies greater than 20% (**Table 11**).

Table 11. Dissolved oxygen (DO) trends. Recent (1996 - 2012); long-term (1970s - 2012); slope (mg/liter/year); super-saturation (frequency of samples in the 2009-2012 timeframe exceeding 110% DO saturation, as %).

				Not Adjusted for Flow				Flow Adjusted		2009-2012
				Recent		Long-term		Recent	Long-term	Super-
Ecoreg.	Station	StreamName	Type	trend	slope	trend	slope	trend	trend	saturation
Western Allegheny Plateau	MC-00001-3.5	Cheat River	IIIa	ns		-				0%
	KC-00001-11.6	Coal River	Ia	▲	1.29E-01	ns		*f* ▲	*f* ns	22%
	ML-00001-20.6	Dunkard Creek	IIa	▲	1.67E-01	▲		*f* ▲	*f* ▲	25%
	KE-00001-4.3	Elk River	Ia	▲	1.41E-01	ns		*f* ▲	*f* ns	29%
	OGL-00001-2.8	Guyandotte River (Lower)	Ia	▴	8.50E-02	ns				17%
	LK-00025-1.5	Hughes River	IIa	▴	8.80E-02	ns				20%
	KL-00001-31.7	Kanawha River (Lower)	Ia	▲	1.83E-01	▲	2.50E-02	*f* ▲	*f* ▴	37%
	LK-00001-28.9	Little Kanawha River	Ia	▴	7.40E-02	▲	2.72E-02	*f* ▴	*f* ▲	13%
	OMN-00006-12.3	Middle Island Creek	IIa	^	7.56E-02	ns		*f* ns	*f* ^	9%
	MU-00001-99.4	Monongahela River (Upper)	Ia	ns		^	1.50E-02			8%
	BST-00001-0.15	Tug Fork	Ia	ns		▴	1.39E-02	*f* ns	*f* ▴	25%
	OT-00001-8.8	Twelvepole Creek	IIIa	▲	1.21E-01	-				20%
	MT-00001-6.2	Tygart Valley River	Ia	▲	1.06E-01	▲	2.84E-02	*f* ns	*f* ns	27%
	MW-00001-12	West Fork River	Ia	ns		▲	2.50E-02	*f* ns	*f* ▲	17%
Central Appalachians	MC-00001-30	Cheat River	Ia	▴	1.26E-01	▲	2.86E-02	*f* ns		0%
	KG-00001-8.25	Gauley River	Ia	▲	1.16E-01	ns		*f* ▴	*f* ^	11%
	KNG-00001-1.6	Greenbrier River	Ia	▲	1.11E-01	ns		*f* ▲	*f* ▴	30%
	OGL-00001-74.1	Guyandotte River (Lower)	IIIa	▴	9.43E-02	-		*f* ▴		21%
	KU-00001-74.1	Kanawha River (Upper)	Ia	▴	7.67E-02	ns		*f* ns	*f* ns	21%
	KNL-00001-1.2	New River (Lower)	Ia	▲	1.19E-01	▴	1.76E-02	*f* ▲	*f* ▲	26%
	KNU-00001-67.4	New River (Upper)	IIa	▲	8.78E-02	ns		*f* ▴	*f* ns	28%
	KNU-00001-96.2	New River (Upper)	IIa	▲	1.03E-01	ns		*f* ^	*f* ns	22%
Ridge & Valley	PU-00010-6.1	Cacapon River	Ia	▴	8.82E-02	▴	2.22E-02	*f* ▴	*f* ^	17%
	PL-00014-2.2	Opequon Creek	IIa	▴	8.58E-02	ns		*f* ▲	*f* ns	7%
	PSB-00001-13.4	South Branch Potomac River	Ia	▲	2.04E-01	▴	2.55E-02	*f* ▲	*f* ▴	41%
	PS-00001-0.9	Shenandoah River	Ia	ns		ns		*f* ▴	*f* ns	23%

Fecal Coliform

> ***Fecal coliform*** analysis is a rapid test for the mammalian gut bacteria *Escherichia coli* (*E.coli*) and *enterococci.* It is used to indicate potentially harmful bacteria in a body of water. Fecal coliform bacteria in streams are generally attributed to a sewage leak from a waste water treatment plant or local septic field, wild or domestic animal waste, and/or storm run-off. West Virginia water quality standards for human contact allow a fecal coliform count of up to 200 per 100 ml as a monthly geometric mean based on not less than 5 samples per month, and up to 400 per 100 ml in no more than ten percent of all samples taken during the month.

Seventeen of the 26 stations have fecal coliform measurements from the 1970's through 2012 (Type I). Fecal coliform monitoring also began in the 1970's at six other stations but was halted for 11 years between 1985 and 1995, resulting in non-continuous records for these stations (Type II). Three stations have data records beginning in 1996 (Type III). Twenty-two of the 26 stations had 5%-50% of measurements below minimum detection limits (MDL), which ruled out trend analyses on flow-adjusted data at these stations. Sampling intensity varied over the 43 years. Trend results are shown in **Table 12**.

Fecal coliform concentrations are highly variable. Median values for 2009 - 2012 ranged between 12 and 470 counts per 100 ml while maximum values went as high as 25,000 per 100 ml. Almost all stations experienced one or more measurements greater than 400 counts per ml. Median values equaled or exceeded 400 counts per 100 ml at the Lower Guyandotte (mile 2.8) and West Fork stations.

Long-term trends. Twelve stations showed significant downward trends between 1970 and 2012 and eight stations showed no trends ($p<0.05$). Lower Guyandotte (miles 2.8) experienced the largest rate of decline, followed by West Fork and Tug Fork. The Cheat (mile 30), Cacapon and Opequon stations have experienced significant upward trends in fecal coliform over the 43-year period.

Short-term trends. Nine stations showed significant downward trends in the 17-year recent period. Four showed downward tendencies ($0.05<p<0.10$) and thirteen showed no trend. No upward trends were found. Lower Guyandotte (miles 2.8 and 74.1) experienced the greatest rates of decline, followed by Elk and Upper New (mile 96.2).

Flow-adjusted trends. The numerous measurements of fecal coliform below MDL levels preclude calculation of flow-adjusted trends. Log-log plots of fecal coliform counts versus streamflow reflect the influence of the censored values and flow effects as indicated by the LOWESS regressions are inconclusive when the level of censoring is high (**Appendix D**).

Table 12. Fecal coliform trends. Recent (1996 - 2012); long-term (1970s - 2012); slope (count per 100 milliliters per year); median and maximum (count per 100 milliliters).

				Not Adjusted for Flow				Flow Adjusted		2009-2012	
				Recent		Long-term		Recent	Long-term		
Ecoreg.	Station	StreamName	Type	trend	slope	trend	slope	trend	trend	median	max
Western Allegheny Plateau	MC-00001-3.5	Cheat River	IIIb	ns		-				12	740
	KC-00001-11.6	Coal River	Ib	v	-1.35E-02	▽	-1.32E-02	ƒ -	ƒ -	66.5	900
	ML-00001-20.6	Dunkard Creek	IIb	ns		▿		ƒ -	ƒ -	88	5,200
	KE-00001-4.3	Elk River	Ia	▿	-9.33E+00	ns		ƒ ▿	ƒ v	69	6,000
	OGL-00001-2.8	Guyandotte River (Lower)	Ia	▽	-7.50E+01	▽	-2.00E+01			470	4,000
	LK-00025-1.5	Hughes River	IIb	v	-1.29E-02	ns				46	2,400
	KL-00001-31.7	Kanawha River (Lower)	Ib	▽	-2.25E-02	▿	-6.87E-03	ƒ -	ƒ -	47	7,600
	LK-00001-28.9	Little Kanawha River	Ib	▿	-2.71E-02	ns		ƒ -	ƒ -	60	1,200
	OMN-00006-12.3	Middle Island Creek	IIb	ns		▿		ƒ -	ƒ -	75	1,300
	MU-00001-99.4	Monongahela River (Upper)	Ib	ns		▽	-2.18E-02			57.5	12,000
	BST-00001-0.15	Tug Fork	Ib	▿	-4.59E-02	▽	-3.87E-02	ƒ -	ƒ -	75	4,200
	OT-00001-8.8	Twelvepole Creek	IIIa	ns		-				145.5	2,600
	MT-00001-6.2	Tygart Valley River	Ib	ns		ns		ƒ -	ƒ -	40	1,067
	MW-00001-12	West Fork River	Ib	ns		▿	-3.91E-02	ƒ -	ƒ -	400	20,000
Central Appalachians	MC-00001-30	Cheat River	Ib	ns		▲	5.20E-03	ƒ -		50	1,200
	KG-00001-8.25	Gauley River	Ib	▽	-1.01E-02	ns		ƒ -	ƒ -	21	520
	KNG-00001-1.6	Greenbrier River	Ib	ns		▿	-1.42E-03	ƒ -	ƒ -	24.5	6,600
	OGL-00001-74.1	Guyandotte River (Lower)	IIIa	▽	-5.03E+01	-		ƒ ▽		327	4,400
	KU-00001-74.1	Kanawha River (Upper)	Ib	v	-8.58E-03	▽	-1.85E-02	ƒ -	ƒ -	44	2,200
	KNL-00001-1.2	New River (Lower)	Ib	▽	-9.02E-03	▽	-4.15E-03	ƒ -	ƒ -	22	1,100
	KNU-00001-67.4	New River (Upper)	IIb	▿	-2.90E-03	ns		ƒ -	ƒ -	16	3,600
	KNU-00001-96.2	New River (Upper)	IIb	v	-1.00E+00	▽		ƒ -	ƒ -	19	182
Ridge & Valley	PU-00010-6.1	Cacapon River	Ib	ns		▲	1.71E-03	ƒ -	ƒ -	22.5	320
	PL-00014-2.2	Opequon Creek	IIb	ns		▲		ƒ -	ƒ -	300	25,000
	PSB-00001-13.4	South Branch Potomac River	Ib	ns		ns		ƒ -	ƒ -	20	1,400
	PS-00001-0.9	Shenandoah River	Ib	ns		ns		ƒ -	ƒ -	27	2,200

Hardness

Hardness in fresh waters refers to the amount of soluble, divalent, metallic cations, the most common of which are calcium (Ca^{2+}) and magnesium (Mg^{2+}). Water hardness affects aquatic organisms by influencing metal toxicity and nutrient availability. When cation levels are low, usually less than 30 mg/liter ("soft" water), the permeability of tissue membranes (e.g. fish gills) increases and allows for greater metal uptake. High or low hardness is not thought to have direct detrimental effects on humans. However, a water hardness of more than 180 mg/liter ("very hard" waters) requires more soaps and detergents in household laundry and dishwashing, and results in mineral buildup on industrial equipment and breakdowns. Hardness is used to determine the applicable criteria for dissolved cadmium, chromium, copper, lead, nickel, silver and zinc for West Virginia water quality standards.

None of the 26 West Virginia ambient water quality monitoring stations has hardness data for the 11 years between 1985 and 1995. Twenty-three of the 26 stations have hardness data before and after this gap. The data have almost no censoring and are sufficient for trend analysis (Type IIa). Three stations have hardness data for the recent period only (1996-2012). These data also have almost no censoring and are sufficient for short-term trend analysis (Type IIIa). Sampling intensity varied over the 43 years. Trend results are shown in **Table 13.**

Median concentrations in the most recent four years (2009-2012) ranged from less than 60 mg/liter (Cheat at mile 3.5) to more than 180 mg/liter (Coal, Dunkard, Lower Guyandotte at miles 2.8 and 74.1, Upper Monongahela River, Tug Fork, West Fork, Opequon Creek, and Shenandoah). Individual measurements less than 30 mg/liter were found at Cheat (mile 30). Measurements greater than 180 mg/liter were found at 21 of the 26 stations, with maximum values exceeding 600 mg/liter at Coal, Opequon, Tug Fork, and Dunkard. Like alkalinity, the range of hardness concentrations is large at some stations (Coal, Dunkard, West Fork and Opequon), suggesting multiple sources, and small at others (Little Kanawha, Gauley).

Long-term trends. Weak downward trends in hardness occurred at two stations: West Fork and Cheat (mile 30). No significant trends were found at Hughes, Little Kanawha, Middle Island, Upper Monongahela, Cacapon, and Shenandoah. Increasing trends occurred at the remaining 15 stations.

Short-term trends. With the exception of West Fork, all short-term trends in hardness were increasing significantly ($p<0.05$) or trending upward ($0.05<p<0.1$).

Flow-adjusted trends. Log-log plots of hardness versus streamflow show hardness decreasing as flow increases (**Appendix D**). The relationships, however, were not always linear and the steepness of the regression slopes varied. Waters are naturally harder in regions containing Ca- and Mg-bearing minerals such as limestone, chalk and dolomite. The variable log-log plots, however, suggests there may be multiple sources of the metallic cations comprising water hardness. Most of the flow-adjusted trends corroborated the flow un-adjusted trends for the short-term and long-term periods, indicating that variations in concentration due to streamflow were not confounding the trend results.

Note: In the West Virginia database, hardness is a value calculated from total calcium and total magnesium concentrations using the following formula:

Hardness = 2.497*Ca (Total) + 4.118*Mg (Total)

Contributions of other soluble metallic cations such as iron, aluminum, and manganese are not reflected in the value.

Table 13. Hardness trends. Recent (1996 - 2012); long-term (1970s - 2012); slope (mg/liter/year as $CaCO_3$); minimum, median, and maximum (mg/liter as $CaCO_3$).

				Not Adjusted for Flow				Flow Adjusted		2009-2012			
				Recent		Long-term		Recent	Long-term				
Ecoreg.	Station	StreamName	Type	trend	slope	trend	slope	trend	trend	min	median	max	Class
Western Allegheny Plateau	MC-00001-3.5	Cheat River	IIIa	^	5.72E-01	-				30	55	147	soft
	KC-00001-11.6	Coal River	IIa	▲	5.76E+00	▲		*f* ▲	*f* ▲	266	469	800	very hard
	ML-00001-20.6	Dunkard Creek	IIa	▲	2.65E+00	▲		*f* ▲	*f* ▲	86	224	622	very hard
	KE-00001-4.3	Elk River	IIa	▲	2.21E+00	▲		*f* ▲	*f* ▲	69	134	382	hard
	OGL-00001-2.8	Guyandotte River (Lower)	IIa	▲	3.73E+00	▲				158	258	436	very hard
	LK-00025-1.5	Hughes River	IIa	▲	8.60E-01	ns				61	124	188	hard
	KL-00001-31.7	Kanawha River (Lower)	IIa	▲	1.89E+00	▲		*f* ▲	*f* ▲	115	172	280	hard
	LK-00001-28.9	Little Kanawha River	IIa	▲	9.09E-01	ns		*f* ▴	*f* ns	53	90	140	moderate
	OMN-00006-12.3	Middle Island Creek	IIa	▲	1.18E+00	ns		*f* ns	*f* ns	71	129	278	hard
	MU-00001-99.4	Monongahela River (Upper)	IIa	▲	3.51E+00	ns				65	188	504	very hard
	BST-00001-0.15	Tug Fork	IIa	▲	5.69E+00	▲		*f* ▲		284	495	690	very hard
	OT-00001-8.8	Twelvepole Creek	IIIa	▲	2.55E+00	-				94	166	266	hard
	MT-00001-6.2	Tygart Valley River	IIa	▴	1.00E+00	▴		*f* ns	*f* ns	31	75	154	moderate
	MW-00001-12	West Fork River	IIa	ns		▿		*f* ns	*f* ▽	139	369	876	very hard
Central Appalachians	MC-00001-30	Cheat River	IIa	^	4.98E-01	▿		*f* ns		26	45	143	soft
	KG-00001-8.25	Gauley River	IIa	▲	6.71E-01	▲		*f* ▲	*f* ▲	31	67	102	moderate
	KNG-00001-1.6	Greenbrier River	IIa	▴	8.24E-01	▲		*f* ns	*f* ▲	68	116	409	moderate
	OGL-00001-74.1	Guyandotte River (Lower)	IIIa	▲	3.71E+00	-		*f* ▲		175	282	460	very hard
	KU-00001-74.1	Kanawha River (Upper)	IIa	▲	1.76E+00	▲		*f* ▲	*f* ▲	114	167	266	hard
	KNL-00001-1.2	New River (Lower)	IIa	▲	9.02E-01	▲		*f* ▲	*f* ▴	84	148	191	hard
	KNU-00001-67.4	New River (Upper)	IIa	▲	1.42E+00	▲		*f* ^	*f* ns	77	145	228	hard
	KNU-00001-96.2	New River (Upper)	IIa	▴	1.19E+00	▲		*f* ▴	*f* ▲	88	162	210	hard
Ridge & Valley	PU-00010-6.1	Cacapon River	IIa	▲	2.08E+00	ns		*f* ▲	*f* ns	44	103	226	moderate
	PL-00014-2.2	Opequon Creek	IIa	▲	4.60E+00	▲		*f* ▲	*f* ▲	186	337	708	very hard
	PSB-00001-13.4	South Branch Potomac River	IIa	▲	2.73E+00	^		*f* ▲	*f* ▲	82	146	288	hard
	PS-00001-0.9	Shenandoah River	IIa	▲	3.78E+00	ns		*f* ▲	*f* ▿	119	186	380	very hard

Hot Acidity

Hot acidity monitoring was particularly variable over the 43-year sampling period and trend analysis is often prevented by high numbers of values below MDLs. For these reasons, only flow-unadjusted trends were calculated. Long-term trends could be calculated at fourteen stations and short-term trends at six stations (**Table 14**).

Long-term trends. Four stations show significant downward trends ($p<0.05$) and three show downward tendencies ($0.05<p<0.01$). Of these, the fastest decline is occurring at Tygart Valley. Six show no significant trends. One station (Dunkard) shows a significant upward trend.

Short-term trends. No significant trends were found at the six stations where trends could be calculated.

Hot acidity measurements are a function of the pH, alkalinity, and dissolved concentrations of Fe, Mn, and Al in fresh mine drainage. The Standard Method hot peroxide treatment procedure to measure hot acidity removes the buffering influence of carbon (degassing of CO_2) and fully oxidizes the metals. The results are used to evaluate the potential for pH-dependent toxicity, substrate corrosion, and encrustation. Hot acidity can be used with alkalinity measurements to better estimate stream buffering capacity and suggest remediation strategies in mining regions.

Table 14. Flow-unadjusted trends in hot acidity. Recent (1996 - 2012); long-term, (1970s/1980s – 2012); slope (mg/liter/year as $CaCO_3$).

				Not Adjusted for Flow			
				Recent		Long-term	
Ecoreg.	Station	StreamName	Type	trend	slope	trend	slope
Western Allegheny Plateau	MC-00001-3.5	Cheat River	IIIc	ns		-	
	KC-00001-11.6	Coal River	Ic	-		v	-3.69E-03
	ML-00001-20.6	Dunkard Creek	IIc	ns		▲	
	KE-00001-4.3	Elk River	Ic	-		ns	
	OGL-00001-2.8	Guyandotte River (Lower)	Ic	-		ns	
	LK-00025-1.5	Hughes River	IIc	-		-	
	KL-00001-31.7	Kanawha River (Lower)	Ic	-		ns	
	LK-00001-28.9	Little Kanawha River	IIIc	ns		-	
	OMN-00006-12.3	Middle Island Creek	IIc	-		-	
	MU-00001-99.4	Monongahela River (Upper)	Ic	-		▽	-2.96E-03
	BST-00001-0.15	Tug Fork	Ic	-		v	-9.91E-03
	OT-00001-8.8	Twelvepole Creek	IIIc	-		-	
	MT-00001-6.2	Tygart Valley River	Ic	ns		▽	-1.10E-03
	MW-00001-12	West Fork River	Ic	-		▿	-8.56E-03
Central Appalachians	MC-00001-30	Cheat River	Ic	ns		▽	-2.16E-03
	KG-00001-8.25	Gauley River	Ic	-		v	-4.89E-04
	KNG-00001-1.6	Greenbrier River	Ic	-		ns	
	OGL-00001-74.1	Guyandotte River (Lower)	IIIc	-		-	
	KU-00001-74.1	Kanawha River (Upper)	Ic	-		ns	
	KNL-00001-1.2	New River (Lower)	Ic	-		-	
	KNU-00001-67.4	New River (Upper)	IIc	-		-	
	KNU-00001-96.2	New River (Upper)	IIc	-		-	
Ridge & Valley	PU-00010-6.1	Cacapon River	Ic	-		-	
	PL-00014-2.2	Opequon Creek	IIc	-		-	
	PSB-00001-13.4	South Branch Potomac River	Ic	ns		ns	
	PS-00001-0.9	Shenandoah River	Ic	-		-	

Iron, Total

Measurements of total iron (Fe) begin in the early 1970s at 17 of the 26 stations and continue uninterrupted through 2012 (Type I). Fe measurements also begin in 1970 at six other stations but halt for 11 years between 1985 and 1995, resulting in non-continuous data records at these stations (Type II). Measurements at three stations (Cheat at mile 3.5, Lower Guyandotte at mile74.1, and Twelvepole) begin later, in 1996 (Type III). Sampling intensity varies over the 43 years. Only 45 of the 5,936 measurements fall below detection limits. Trend results are shown in **Table 15**.

Median concentrations of total iron ranged over ten-fold in the 2009-2012 timeframe, from 0.07 mg/liter (South Branch Potomac) to 0.86 mg/liter (Twelvepole). Lower Guyandotte (mile 2.8), Little Kanawha, and Twelvepole concentrations exceeded West Virginia's drinking water source criterion of 1.5 mg/liter more than 20% of the time between 2009 and 2012 and eight stations never exceeded the criterion.

Iron (Fe) is by mass the fourth most common element in the earth's crust. It has a wide range of oxidation states, from -2 to +6, and is reactive to oxygen and water. Iron-protein compounds, including hemoglobin, myoglobin, cytochrome P450, and many critical enzymes, facilitate oxygen transport and biochemical reactions in all living organisms. High concentrations of dissolved iron can be toxic to aquatic life in acidic environments. At more neutral pH levels, iron's orange precipitates can impede oxygen uptake in fish gills and coat surfaces. Human contact with the iron precipitates has no detrimental effects. West Virginia has a drinking water source criterion of 1.5 mg/liter and aquatic life chronic criteria of 1.0 and 1.5 mg/liter. USEPA recommends an upper limit of 0.3 mg/liter in finished drinking water to minimize color and taste issues.

Long-term trends. Most trends are significantly downward ($p<0.05$) or trending downward ($0.05<p<0.01$). West Fork is showing the fastest rates of decline (-0.040 mg/liter/year), followed by Lower Guyandotte (mile 2.8) and Cheat (mile 30). Only three stations show no trends: Little Kanawha, Middle Island, and Opequon.

Short-term trends. In contrast to the long-term trends, most of the short-term, 17-year trends are not significant ($p<0.05$). Only West Fork in the Central Appalachians ecoregion and the Cacapon, Opequon, and South Branch Potomac in the Ridge & Valley ecoregion show significant declines.

Flow-adjusted trends. The log-log plots of total iron versus flow were typically curvilinear, with weak or no response at low flows and an increasing response at high flows (**Appendix D**). Most flow-adjusted trends confirmed their corresponding flow-unadjusted trends, indicating the trend periods were long enough that streamflows were not confounding the trend results.

A close association exists between dirt, represented by TSS, and iron suspended in water. A correlation of all coincident measurements of total iron and TSS in the WVDEP database yields a positive, linear relationship with a high regression coefficient ($r^2 = 0.74$).

Table 15. Total iron (Fe) trends. Recent (1996 - 2012); long-term (1970s - 2012); slope (mg/liter/year); median and maximum (mg/liter), exceedance (frequency of samples exceeding 1.5 mg/liter in the 2009-2012 timeframe, as %).

				Not Adjusted for Flow				Flow Adjusted		2009-2012		
				Recent		Long-term		Recent	Long-term			
Ecoreg.	Station	StreamName	Type	trend	slope	trend	slope	trend	trend	median	max	exceed.
Western Allegheny Plateau	MC-00001-3.5	Cheat River	IIIa	ns		-				0.30	9.95	3.6%
	KC-00001-11.6	Coal River	Ia	ns		▽	-1.09E-02	*f* ns	*f* ▽	0.25	6.67	3.8%
	ML-00001-20.6	Dunkard Creek	IIa	ns		▿		*f* ns	*f* v	0.31	13.90	9.3%
	KE-00001-4.3	Elk River	Ia	ns		▿	-5.83E-03	*f* ns	*f* ▽	0.31	4.26	10.7%
	OGL-00001-2.8	Guyandotte River (Lower)	Ia	ns		▽	-2.29E-02			0.72	11.00	30.4%
	LK-00025-1.5	Hughes River	IIa	ns		▽				0.65	3.09	16.0%
	KL-00001-31.7	Kanawha River (Lower)	Ia	ns		▽	-6.62E-03	*f* ns	*f* ▽	0.30	4.99	5.0%
	LK-00001-28.9	Little Kanawha River	Ia	ns		ns		*f* ns	*f* ns	0.64	5.94	21.7%
	OMN-00006-12.3	Middle Island Creek	IIa	ns		ns		*f* ns	*f* ns	0.69	9.32	17.6%
	MU-00001-99.4	Monongahela River (Upper)	Ia	ns		▽	-6.30E-03			0.26	5.52	7.7%
	BST-00001-0.15	Tug Fork	Ia	ns		▿	-1.11E-02	*f* v	*f* ▿	0.45	9.33	12.5%
	OT-00001-8.8	Twelvepole Creek	IIIa	ns		-				0.86	2.22	20.0%
	MT-00001-6.2	Tygart Valley River	Ia	ns		v	-3.51E-03	*f* ns	*f* ▿	0.20	3.05	7.3%
	MW-00001-12	West Fork River	Ia	▽	-3.00E-02	▽	-4.00E-02	*f* ▽	*f* ▽	0.58	24.40	18.9%
Central Appalachians	MC-00001-30	Cheat River	Ia	v	-1.30E-02	▽	-2.17E-02	*f* ns		0.38	1.44	0.0%
	KG-00001-8.25	Gauley River	Ia	ns		▽	-4.60E-03	*f* ns	*f* ▽	0.21	1.44	0.0%
	KNG-00001-1.6	Greenbrier River	Ia	ns		▽	-1.79E-03	*f* ns	*f* ▽	0.16	1.70	3.7%
	OGL-00001-74.1	Guyandotte River (Lower)	IIIa	v	-1.29E-02	-		*f* ns		0.35	3.93	12.5%
	KU-00001-74.1	Kanawha River (Upper)	Ia	ns		▽	-4.49E-03	*f* ns	*f* ▽	0.27	0.86	0.0%
	KNL-00001-1.2	New River (Lower)	Ia	ns		▿	-3.24E-03	*f* ns	*f* ns	0.26	1.27	0.0%
	KNU-00001-67.4	New River (Upper)	IIa	ns		▽		*f* v	*f* ▽	0.27	1.27	0.0%
	KNU-00001-96.2	New River (Upper)	IIa	ns		▽		*f* ns	*f* ▽	0.14	3.25	8.7%
Ridge & Valley	PU-00010-6.1	Cacapon River	Ia	▿	-3.85E-03	▿	-1.30E-03	*f* ns	*f* ▽	0.12	0.74	0.0%
	PL-00014-2.2	Opequon Creek	IIa	▽	-9.43E-03	ns		*f* v	*f* ns	0.15	3.33	6.9%
	PSB-00001-13.4	South Branch Potomac River	Ia	▽	-6.62E-03	▽	-2.50E-03	*f* ▽	*f* ▽	0.07	0.50	0.0%
	PS-00001-0.9	Shenandoah River	Ia	ns		▽	-2.31E-03	*f* ns	*f* ▽	0.16	0.83	0.0%

Lead, Total and Dissolved

Measurements for both total and dissolved lead are reported in the analysis database. Records for total lead (Pb) begin in the 1970s at 23 of the 26 stations but stop for the most part between 1985 and 1995. Routine sampling begins again in 1996, but then stops in 1998. Many measurements fall below MDLs, so the data cannot be tested for flow-adjusted trends. Due to the abbreviated, uneven sampling record and the high number of MDL measurements, total Pb data were classified as Type IVb or IVc (or, in the case of Elk River, Type IIc) and the Peto-Peto step test method was applied. Records for dissolved Pb are sporadic until routine sampling began in 1999. More than 50% of measurements at all the stations are below MDL, causing all the trends to be classified Type IIIc. Trend results are shown in **Table 16.** Particularly high MDLs in 1995, 1996 and 2004 affect medians and quantiles in those years (**Appendix C**).

Lead (Pb) compounds are generally hard to dissolve and often exist as particulates that are either adsorbed into plants and animals or deposited in sediments. Lead is an extremely toxic substance in all its forms. High lead concentrations come primarily from improper wastewater discharge and storage of batteries by manufacturing industries. Lead increased in the atmosphere and waterways when petroleum-based products began to use lead as an additive. Environmental concentrations of lead have diminished with the removal of lead as a gasoline additive. West Virginia's Pb criterion for drinking water sources is 0.05 mg/liter.

Median and maximum concentrations cannot be reliably calculated for total or dissolved Pb because more than half of the measurements at too many stations are below MDL (censoring Type c).

Long-term trends. Most stations show significant downward trends in total Pb ($p<0.05$). The exceptions are Gauley which shows a slight upward trend and Elk and Hughes which show no significant trend.

Short-term trends. All of the trends in dissolved Pb are not significant ($p<0.05$).

Table 16. Flow-unadjusted trends in total and dissolved lead (Pb). Long-term (1970s – 2012); short-term (1999 - 2012).

			Total Pb		Dissolved Pb	
			Long-term		Short-term	
Ecoreg.	Station	StreamName	Type	trend	Type	trend
Western Allegheny Plateau	MC-00001-3.5	Cheat River	IVc	-	IIIc	-
	KC-00001-11.6	Coal River	IVc	-	IIIc	-
	ML-00001-20.6	Dunkard Creek	IVc	▽	IIIc	ns
	KE-00001-4.3	Elk River	IIc	ns	IIIc	ns
	OGL-00001-2.8	Guyandotte River (Lower)	IVb	▽	IIIc	-
	LK-00025-1.5	Hughes River	IVb	ns	IIIc	ns
	KL-00001-31.7	Kanawha River (Lower)	IVc	▽	IIIc	ns
	LK-00001-28.9	Little Kanawha River	IVb	▿	IIIc	ns
	OMN-00006-12.3	Middle Island Creek	IVb	▿	IIIc	ns
	MU-00001-99.4	Monongahela River (Upper)	IVc	▽	IIIc	ns
	BST-00001-0.15	Tug Fork	IVb	▽	IIIc	ns
	OT-00001-8.8	Twelvepole Creek	IVc	-	IIIc	ns
	MT-00001-6.2	Tygart Valley River	IVc	▽	IIIc	ns
	MW-00001-12	West Fork River	IVc	▽	IIIc	ns
Central Appalachians	MC-00001-30	Cheat River	IVb	▽	IIIc	ns
	KG-00001-8.25	Gauley River	IVc	▴	IIIc	ns
	KNG-00001-1.6	Greenbrier River	IVc	▿	IIIc	ns
	OGL-00001-74.1	Guyandotte River (Lower)	IVc	-	IIIc	ns
	KU-00001-74.1	Kanawha River (Upper)	IVc	▽	IIIc	ns
	KNL-00001-1.2	New River (Lower)	IVb	▿	IIIc	ns
	KNU-00001-67.4	New River (Upper)	IVb	▿	IIIc	ns
	KNU-00001-96.2	New River (Upper)	IVc	▽	IIIc	ns
Ridge & Valley	PU-00010-6.1	Cacapon River	IVc	▿	IIIc	ns
	PL-00014-2.2	Opequon Creek	IVc	▽	IIIc	ns
	PSB-00001-13.4	South Branch Potomac River	IVc	▽	IIIc	ns
	PS-00001-0.9	Shenandoah River	IVc	▽	IIIc	ns

Magnesium, Total

Magnesium (Mg) is an abundant, highly soluble, divalent, alkaline earth metal that readily forms metal alloys and magnesium salts. There are numerous natural sources of magnesium, many of which are commercially important. It is an essential element found in many enzymes of living organisms, and it is the ion at the center of chlorophyll's chlorine ring. Natural weathering is an important source of Mg in streams and rivers. Mg^{2+} is one of the cations principally responsible for water hardness. No detrimental effects of Mg in drinking water are known. West Virginia does not have Mg criteria.

Magnesium (Mg) measurements appear occasionally in the analysis database before 2001 and sporadically between 2001 and 2008. Monitoring of Mg begins in earnest in 2009 at all 26 stations. All but two measurements are above MDLs. Although data for the recent time period (1996-2012) are not complete, trend analyses were performed (**Table 17**).

Mg measurements, in conjunction with calcium (Ca), provide information on the dominant sources of water hardness. (See also "Hardness" and "Calcium.") Median concentrations in magnesium ranged more than 10-fold in the 2009-2012 timeframe, from 2.2 mg/liter (Cheat River mile 30) to 28.5 mg/liter (Tug Fork) and 34.2 mg/liter (Coal). Individual measurements ranged from 0.2 mg/liter (Lower New, Tygart Valley) to 53.8 mg/liter (Coal). Many minerals contain Mg and weathering is an important natural source of Mg.

Short-term trends. The abbreviated trends suggest that Mg concentrations are increasing significantly at Elk, Lower Guyandotte at mile 2.8, Twelvepole and Shenandoah but nowhere else ($p<0.05$).

Flow-adjusted trends. The LOWESS curves through the log-log plots of magnesium versus streamflow show magnesium decreasing as flow increases. Despite the brevity of the data records for this element, some station regressions with flow are fairly tight.* The relationships themselves, however, are not always linear and the steepness of the regression slopes varies, suggesting anthropogenic inputs of Mg (**Appendix D**). Most of the flow-adjusted trends corroborated the flow un-adjusted trends, indicating the trend results are not confounded by streamflow.

* This is not surprising since Mg concentrations in undisturbed streams and lakes fluctuate little and are considered a conservative tracer. Mg has been used in mass balance calculations in lakes to determine groundwater inputs (Wetzel 2001).

Table 17. Very short-term trends in magnesium (Mg). Recent (2001-2012, note abbreviated timeframe); slope (mg/liter/year); median (mg/liter).

				Not Adjusted for Flow		Flow Adjusted		2009 - 2012
				Recent		Recent		
Ecoreg.	Station	StreamName	Type	trend	slope		trend	median
Western Allegheny Plateau	MC-00001-3.5	Cheat River	IIIa	ns				2.8
	KC-00001-11.6	Coal River	IIIa	ns		*f*	ns	34.15
	ML-00001-20.6	Dunkard Creek	IIIa	ns		*f*	ns	11.6
	KE-00001-4.3	Elk River	IIIa	▲	5.82E-01	*f*	▲	7.45
	OGL-00001-2.8	Guyandotte River (Lower)	IIIa	▲	7.33E-01			14.85
	LK-00025-1.5	Hughes River	IIIa	ns				4.55
	KL-00001-31.7	Kanawha River (Lower)	IIIa	ns		*f*	ns	8.8
	LK-00001-28.9	Little Kanawha River	IIIa	ns		*f*	ns	3.4
	OMN-00006-12.3	Middle Island Creek	IIIa	ns		*f*	ns	4.8
	MU-00001-99.4	Monongahela River (Upper)	IIIa	ns				8.6
	BST-00001-0.15	Tug Fork	IIIa	ns		*f*	^	28.5
	OT-00001-8.8	Twelvepole Creek	IIIa	▲	3.50E-01			8.5
	MT-00001-6.2	Tygart Valley River	IIIa	ns		*f*	ns	3.41
	MW-00001-12	West Fork River	IIIa	ns		*f*	ns	19.7
Central Appalachians	MC-00001-30	Cheat River	IIIa	ns		*f*	ns	2.2
	KG-00001-8.25	Gauley River	IIIa	ns		*f*	ns	4.1
	KNG-00001-1.6	Greenbrier River	IIIa	ns		*f*	ns	3.55
	OGL-00001-74.1	Guyandotte River (Lower)	IIIa	ns		*f*	▲	16.4
	KU-00001-74.1	Kanawha River (Upper)	IIIa	ns		*f*	ns	7.75
	KNL-00001-1.2	New River (Lower)	IIIa	ns		*f*	ns	6.72
	KNU-00001-67.4	New River (Upper)	IIIa	ns				7.5
	KNU-00001-96.2	New River (Upper)	IIIa	ns		*f*	ns	8.3
Ridge & Valley	PU-00010-6.1	Cacapon River	IIIa	ns		*f*	ns	4.5
	PL-00014-2.2	Opequon Creek	IIIa	ns		*f*	ns	19.5
	PSB-00001-13.4	South Branch Potomac River	IIIa	ns		*f*	ns	5.8
	PS-00001-0.9	Shenandoah River	IIIa	▲	9.50E-01	*f*	ns	14.95

Manganese, Total

Seventeen of the 26 stations have total manganese (Mn) measurements from the 1970's through 2012 (Type I). Mn monitoring also began in the 1970s at six other stations but was halted for 11 years between 1985 and 1995, resulting in non-continuous records for these stations (Type II). Three stations have data records beginning in 1996 (Type III). Sampling intensity varied over the 43 years. Between 0% and 29% of samples are below MDL, so censoring Types were a and b. Trend results are shown in **Table 18**.

Median concentrations of total Mn in the 2009-2012 timeframe were lowest in the South Branch Potomac, Cacapon, and Greenbrier (≤0.015 mg/liter) and highest in Twelvepole and West Fork (>0.10 mg/liter). Maximum levels never exceeded West Virginia's drinking water proximal source criterion of 1.0 mg/liter.

Long-term trends. The Elk and Little Kanawha stations show no trends and the remaining stations show significant downward trends ($p<0.05$).

Manganese (Mn) is an abundant metallic element often alloyed with iron and other metals. High levels darken water clarity and increase turbidity. High concentrations physiologically stress human lung, brain and kidney functions. Mn is one of the few toxic essential nutrients in aquatic environments. Mn deficiencies reduce the ability of plants to break down water into hydrogen and oxygen because of manganese's role as an electron transporter. In animals, Mn deficiencies result in reduced growth and development. Chronic exposure to high Mn concentrations can harm human neurological functioning. West Virginia's Mn criterion for drinking water sources is 1.0 mg/liter. It applies only to the five-mile zone immediately upstream of known public or private water intakes for human consumption. USEPA's Mn guideline for finished drinking water is 0.05 mg/liter.

Short-term trends. Short-term trends were mixed, with seven stations showing significant downward trends, 18 showing no trends, and one station (Upper Kanawha) trending upward ($0.05<p<0.1$).

Flow-adjusted trends. The LOWESS curves reveal station differences in the relationships between total manganese and flow, probably indicating different manganese sources (**Appendix D**). In a few instances, concentrations were highest at low and high flows and lowest at moderate flows. Other relationships were flat, linear and steep, or unresponsive at low flow while increasing at high flows. Flow-adjusted trends in general verified the flow-unadjusted trends, indicating the short- and long-term trend results are not confounded by streamflow.

Table 18. Total manganese (Mn) trends. Recent (1996 - 2012); long-term (1970s - 2012); slope (mg/liter/year); minimum, median, and maximum (mg/liter).

				Not Adjusted for Flow				Flow Adjusted		2009-2012		
				Recent		Long-term		Recent	Long-term			
Ecoreg.	Station	StreamName	Type	Trend	Slope	Trend	Slope	Trend	Trend	Min	Median	Max
Western Allegheny Plateau	MC-00001-3.5	Cheat River	IIIa	ns		-				0.021	0.091	0.299
	KC-00001-11.6	Coal River	Ia	ns		▽	-1.47E-03	*f* ns	*f* ▽	0.028	0.055	0.455
	ML-00001-20.6	Dunkard Creek	IIa	ns		▽		*f* ns	*f* ▽	0.023	0.053	0.521
	KE-00001-4.3	Elk River	Ia	ns		v	-3.67E-04	*f* ns	*f* ns	0.022	0.050	0.123
	OGL-00001-2.8	Guyandotte River (Lower)	Ia	ns		▽	-2.11E-03			0.034	0.068	0.319
	LK-00025-1.5	Hughes River	IIa	ns		▽				0.021	0.046	0.205
	KL-00001-31.7	Kanawha River (Lower)	Ia	ns		▽	-9.66E-04	*f* ▿	*f* ▽	0.029	0.046	0.361
	LK-00001-28.9	Little Kanawha River	Ia	ns		ns		*f* ns	*f* ns	0.021	0.059	0.220
	OMN-00006-12.3	Middle Island Creek	IIa	ns		▽		*f* ns	*f* ▽	0.021	0.036	0.282
	MU-00001-99.4	Monongahela River (Upper)	Ia	▿	-1.86E-03	▽	-6.25E-03			0.030	0.074	0.280
	BST-00001-0.15	Tug Fork	Ia	ns		▽	-1.37E-03	*f* ns	*f* ▽	0.022	0.038	0.225
	OT-00001-8.8	Twelvepole Creek	IIIa	ns		-				0.054	0.113	0.428
	MT-00001-6.2	Tygart Valley River	Ia	▿	-2.65E-03	▽	-3.00E-03	*f* ns	*f* ns	0.003	0.058	0.390
	MW-00001-12	West Fork River	Ia	▽	-7.75E-03	▽	-2.01E-02	*f* ▽	*f* ▽	0.073	0.120	0.822
Central Appalachians	MC-00001-30	Cheat River	Ia	▿	-1.54E-03	▽	-2.91E-03	*f* ns		0.016	0.031	0.134
	KG-00001-8.25	Gauley River	Ib	ns		▽	-2.22E-06	*f* -	*f* -	0.009	0.031	0.152
	KNG-00001-1.6	Greenbrier River	Ib	ns		▿	-3.38E-07	*f* -	*f* -	0.004	0.015	0.088
	OGL-00001-74.1	Guyandotte River (Lower)	IIIa	▽	-2.50E-03	-		*f* ▽		0.023	0.053	0.099
	KU-00001-74.1	Kanawha River (Upper)	Ia	^	6.43E-04	▽	-6.15E-04	*f* ▲	*f* ▽	0.024	0.043	0.186
	KNL-00001-1.2	New River (Lower)	Ia	ns		▽	-4.62E-04	*f* ns	*f* ns	0.008	0.032	0.067
	KNU-00001-67.4	New River (Upper)	IIa	ns		▽		*f* ns	*f* ▽	0.021	0.044	0.227
	KNU-00001-96.2	New River (Upper)	IIb	ns		▽		*f* -	*f* -	0.004	0.020	0.153
Ridge & Valley	PU-00010-6.1	Cacapon River	Ib	ns		▿	-4.59E-07	*f* -	*f* -	0.004	0.013	0.031
	PL-00014-2.2	Opequon Creek	IIb	▿	-1.22E-06	▽		*f* -	*f* -	0.008	0.016	0.106
	PSB-00001-13.4	South Branch Potomac River	Ib	▽	-1.35E-06	▽	-1.35E-06	*f* -	*f* -	0.003	0.010	0.022
	PS-00001-0.9	Shenandoah River	Ib	ns		▽	-1.43E-06	*f* -	*f* -	0.005	0.021	0.037

Nitrate-Nitrite-N

In unpolluted freshwater rivers, nitrate (NO_3^-) is usually the second largest component of total nitrogen after dissolved organic nitrogen, and nitrite (NO_2^-) is one of the smallest components of total nitrogen (Wetzel 2001). In the analysis database, nitrite and nitrate concentrations are combined and expressed as mg/liter nitrogen (NO_2-NO_3-N). Monitoring for NO_2-NO_3-N begins in 1970 at 17 of the 26 stations and continues uninterrupted through 2012 (Type I). NO_2-NO_3-N monitoring also begins in 1970 at six other stations but halts for 11 years between 1985 and 1995, resulting in non-continuous data records at these stations (Type II). NO_2-NO_3-N measurements begin in 1996 in the Cheat at mile3.5, Lower Guyandotte at mile 74.1, and Twelvepole Creek (Type III). Sampling intensity varies over the 43 years. Seventeen stations have less than 5% below MDL (Type a). Nine stations have more than 5% of their measurements below MDL (Type b) and flow-adjusted trends cannot be performed for these stations. NO_2-NO_3-N trends are shown in **Table 19**.

Nitrogen (N) is a critical constituent of proteins and nucleic acids in all living organisms. It is an essential nutrient for growth in aquatic plants and algae. Excess N concentrations in aquatic environments—often from fertilizer runoff and wastewater discharges, but also from atmospheric deposition—can stimulate excess algal growth. Total nitrogen (TN) measures the N from all nitrogen forms. These include elemental nitrogen (N_2), nitrite (NO_2^-), nitrate (NO_3^-) and the animal waste products ammonium (NH_4^+), urea, and uric acid. Excess NO_3^- and NO_2^- in drinking water can cause serious illness in infants (blue-baby syndrome). West Virginia has a drinking water source criterion of 10 mg/liter for NO_3^- and aquatic life use criteria of 1.0 and 0.06 mg/liter for NO_2^- in warm and trout (cold) waters, respectively. Total maximum daily loads (TMDLs) have been established for TN delivered to Chesapeake Bay from West Virginia Potomac watersheds.

For the 2009-2012 timeframe, the highest median concentrations of nitrate-nitrite were found at Opequon (2.07 mg/liter), Coal (1.11 mg/liter), and Shenandoah (1.08 mg/liter). The lowest median concentrations were found at Hughes (0.060 mg/liter) and Middle Island (0.122 mg/liter). Individual values ranged from the MDL concentration which was highly variable (0.001–3.0 mg/liter) to 2.87 mg/liter (Shenandoah, 12/8/2009).

Long-term trends. The results show a mix of NO_2-NO_3-N trends. Concentrations are increasing significantly at Coal, Lower Guyandotte (mile 2.8), Tug Fork, and Upper New (mile 67.4); they are decreasing significantly at Little Kanawha, Middle Island, Tygart Valley, Cheat (mile 30), Gauley, Greenbrier, and Opequon. At the remaining eleven stations, changes are not occurring or are so slight as to be tendencies more than trends ($0.05<p<0.1$).

Short-term trends. Fewer NO_2-NO_3-N trends are occurring in the short-term period. Significant trends are only found at Coal (increasing) and at Hughes, Gauley, Greenbrier, and South Branch Potomac (decreasing).

Flow-adjusted trends. LOWESS regressions applied to the log-log plots of NO_2-NO_3-N versus flow followed no consistent pattern. Relationships varied by station, suggesting multiple sources of NO_2-NO_3-N with different delivery pathways, and regression curves could be positive, negative, flat, linear or curvilinear (**Appendix D**). In most instances, flow-adjusted trends verified the non-adjusted trends indicating the trend analysis was not confounded by stream flow.

Table 19. Nitrite-nitrate (NO_2-NO_3-N) trends. Recent (1996 - 2012); long-term (1970s - 2012); slope (mg/liter/year); minimum, median, and maximum (mg/liter).

				Not Adjusted for Flow				Flow Adjusted		2009-2012		
				Recent		Long-term		Recent	Long-term			
Ecoreg.	Station	StreamName	Type	trend	slope	trend	slope	trend	trend	min	median	max
Western Allegheny Plateau	MC-00001-3.5	Cheat River	IIIa	ns		-				0.161	0.304	2.190
	KC-00001-11.6	Coal River	Ia	▲	4.13E-02	▲	1.73E-02	*f* ▲	*f* ▲	0.702	1.115	1.860
	ML-00001-20.6	Dunkard Creek	IIb	ns		ns		*f* -	*f* -	0.010	0.411	1.720
	KE-00001-4.3	Elk River	Ia	ns		ns		*f* ns	*f* ns	0.060	0.313	0.710
	OGL-00001-2.8	Guyandotte River (Lower)	Ia	ns		▲	5.61E-03			0.326	0.514	0.674
	LK-00025-1.5	Hughes River	IIb	▿	-2.61E-05	-				0.010	0.060	0.329
	KL-00001-31.7	Kanawha River (Lower)	Ia	▴	1.13E-02	ns		*f* ^	*f* ns	0.359	0.615	0.848
	LK-00001-28.9	Little Kanawha River	Ib	ns		▽	-1.29E-05	*f* -	*f* -	0.010	0.206	0.543
	OMN-00006-12.3	Middle Island Creek	IIb	v	-2.05E-05	▽		*f* -	*f* -	0.010	0.122	0.473
	MU-00001-99.4	Monongahela River (Upper)	Ia	ns		ns				0.294	0.482	1.870
	BST-00001-0.15	Tug Fork	Ib	ns		▲	8.73E-06	*f* -	*f* -	0.108	0.425	0.672
	OT-00001-8.8	Twelvepole Creek	IIIb	ns		-				0.100	0.229	0.495
	MT-00001-6.2	Tygart Valley River	Ia	v	-1.00E-02	▽	-4.68E-03	*f* ns	*f* ▽	0.237	0.340	0.801
	MW-00001-12	West Fork River	Ia	ns		ns		*f* ns	*f* ns	0.205	0.575	1.650
Central Appalachians	MC-00001-30	Cheat River	Ia	ns		▽	-5.71E-03	*f* ns		0.035	0.208	0.682
	KG-00001-8.25	Gauley River	Ia	▽	-1.12E-02	▽	-6.35E-03	*f* ▽	*f* ▽	0.155	0.274	0.543
	KNG-00001-1.6	Greenbrier River	Ib	▿	-2.86E-05	▽	-1.09E-05	*f* -	*f* -	0.012	0.378	0.939
	OGL-00001-74.1	Guyandotte River (Lower)	IIIa	^	1.13E-02	-		*f* ^		0.407	0.601	1.350
	KU-00001-74.1	Kanawha River (Upper)	Ia	ns		v	-2.37E-03	*f* ns	*f* v	0.217	0.520	1.720
	KNL-00001-1.2	New River (Lower)	Ia	ns		ns		*f* ns	*f* ns	0.287	0.579	1.460
	KNU-00001-67.4	New River (Upper)	IIa	ns		▲		*f* ns	*f* ns	0.166	0.696	1.630
	KNU-00001-96.2	New River (Upper)	IIa	ns		^		*f* ns	*f* ▴	0.010	0.693	1.470
Ridge & Valley	PU-00010-6.1	Cacapon River	Ib	ns		v	-8.16E-06	*f* -	*f* -	0.010	0.296	0.830
	PL-00014-2.2	Opequon Creek	IIa	ns		▿		*f* ns	*f* ▿	0.999	2.070	2.590
	PSB-00001-13.4	South Branch Potomac River	Ib	▽	-7.46E-05	ns		*f* -	*f* -	0.010	0.288	0.840
	PS-00001-0.9	Shenandoah River	Ia	ns		ns		*f* ▲	*f* ^	0.398	1.083	2.870

Phosphorus, Total

Monitoring for total phosphorus (TP) begins in 1970 at 17 of the 26 stations and continues uninterrupted through 2012 (Type I). TP monitoring also begins in 1970 at six other stations but halts for 11 years between 1985 and 1995, resulting in non-continuous data records at these stations (Type II). TP measurements begin in 1996 in the Cheat at mile 3.5, Lower Guyandotte River at mile 74.1, and Twelvepole Creek (Type III). Sampling intensity varies over the 43 years. Twenty-three of the 26 stations have more than 5% of their TP measurements falling below MDLs and are thus censoring Type b, so flow-adjusted trends were not performed at these stations. Trend results are shown in **Table 20**. **Note**: Suspiciously high concentrations of TP (>1 mg/liter) are recorded for a single date (3/27/2000) at the Upper Monongahela, Dunkard, Cheat, Tygart Valley and West Fork stations. All are from the same analytical laboratory and have been flagged in the WVDEP database.

Phosphorus (P) is a highly reactive, non-metallic element and an essential nutrient for all living organisms. It is a key component of nucleic acids (DNA, RNA), adenosine triphosphate (ATP), and the phospholipids that form cellular membranes. Phosphate minerals are the most common form of P. Free ortho-phosphate (PO_4^{3-}) is the "limiting nutrient" in many aquatic ecosystems because it is often the first nutrient to drop to levels that slow or limit plant growth. Aquatic plants have developed metabolic processes for absorbing and storing P for future use. Wastewater and fertilizers in runoff are the chief source of excess TP to aquatic systems. Total maximum daily loads (TMDLs) have been established for TP delivered to Chesapeake Bay from West Virginia Potomac watersheds.

In the 2009-2012 timeframe, by far the highest median TP concentration occurs at Opequon (0.182 mg/liter). Stations with the lowest median TP concentrations (<0.015 mg/liter) are the two Cheat stations, Tygart Valley and Gauley. Over the four year period, individual values ranged from the MDL concentration which was highly variable (0.001-1.0 mg/liter) to 0.615 mg/liter (Opequon).

Long-term trends. Nineteen of the 23 long-term trends are significant and downward (p<0.05). Two are trending downward (0.05<p<0.1) and one is not changing (South Branch Potomac).

Short-term trends. No clear pattern of short-term trends emerges. Seventeen of the 26 trends show no change. Concentrations are significantly increasing at four stations (Dunkard, South Branch Potomac, Middle Island, West Fork), tending to increase at three stations (Upper Monongahela, both Upper New stations), and significantly decreasing at two stations (Tug Fork, Shenandoah). The differences in the long- and short-term term patterns suggest most of the declines in TP were accomplished before the recent (1996-2012) period.

Flow-adjusted trends. The LOWESS curves reveal station differences in the relationships between total phosphorus and flow, probably indicating different phosphorous sources (**Appendix D**). In a few instances, concentrations were highest at low and high flows and lowest at moderate flows. Other relationships were flat, linear and steep, or unresponsive at low flow while increasing at high flows. Only two flow-adjusted trends could be calculated due to MDL issues. In general, they verified the flow-unadjusted trends.

Table 20. Total phosphorus (P) trends. Recent (1996 - 2012); long-term (1970s - 2012); slope (mg/liter/year); minimum, median, and maximum (mg/liter).

				Not Adjusted for Flow				Flow Adjusted		2009-2012		
				Recent		Long-term		Recent	Long-term			
Ecoreg.	Station	StreamName	Type	trend	slope	trend	slope	trend	trend	min	median	max
Western Allegheny Plateau	MC-00001-3.5	Cheat River	IIIb	ns		-				0.003	0.013	0.062
	KC-00001-11.6	Coal River	Ib	ns		▽	-2.69E-06	*f* -	*f* -	0.003	0.018	0.176
	ML-00001-20.6	Dunkard Creek	IIb	▲	3.57E-06	▽		*f* -	*f* -	0.011	0.037	0.273
	KE-00001-4.3	Elk River	Ib	ns		▽	-1.41E-06	*f* -	*f* -	0.008	0.028	0.216
	OGL-00001-2.8	Guyandotte River (Lower)	Ia	ns		▽	-7.45E-04			0.015	0.048	0.281
	LK-00025-1.5	Hughes River	IIb	ns		▽				0.005	0.034	0.169
	KL-00001-31.7	Kanawha River (Lower)	Ia	ns		▽	-1.00E-03	*f* ▿	*f* ▽	0.017	0.042	0.166
	LK-00001-28.9	Little Kanawha River	Ib	ns		v	-9.01E-07	*f* -	*f* -	0.010	0.050	0.114
	OMN-00006-12.3	Middle Island Creek	IIb	▴	3.02E-06	▽		*f* -	*f* -	0.014	0.036	0.193
	MU-00001-99.4	Monongahela River (Upper)	Ib	^	3.81E-06	▽	-2.35E-06			0.009	0.041	0.224
	BST-00001-0.15	Tug Fork	Ib	▿	-3.39E-06	▽	-3.48E-06	*f* -	*f* -	0.003	0.026	0.131
	OT-00001-8.8	Twelvepole Creek	IIIb	ns		-				0.008	0.029	0.205
	MT-00001-6.2	Tygart Valley River	Ib	ns		▽	-1.13E-06	*f* -	*f* -	0.004	0.014	0.105
	MW-00001-12	West Fork River	Ib	▴	3.23E-06	▽	-3.71E-06	*f* -	*f* -	0.013	0.049	0.376
Central Appalachians	MC-00001-30	Cheat River	Ib	ns		▽	-1.59E-06	*f* -		0.003	0.011	0.047
	KG-00001-8.25	Gauley River	Ib	ns		▽	-2.42E-06	*f* -	*f* -	0.003	0.014	0.059
	KNG-00001-1.6	Greenbrier River	Ib	ns		▽	-2.16E-06	*f* -	*f* -	0.007	0.016	0.107
	OGL-00001-74.1	Guyandotte River (Lower)	IIIb	ns		-		*f* -		0.010	0.023	0.117
	KU-00001-74.1	Kanawha River (Upper)	Ib	ns		▽	-2.54E-06	*f* -	*f* -	0.015	0.034	0.085
	KNL-00001-1.2	New River (Lower)	Ib	ns		▽	-2.97E-06	*f* -	*f* -	0.019	0.037	0.060
	KNU-00001-67.4	New River (Upper)	IIb	^	3.14E-06	-		*f* -	*f* -	0.018	0.049	0.070
	KNU-00001-96.2	New River (Upper)	IIa	^	1.07E-03	▽		*f* ns	*f* ▽	0.024	0.058	0.148
Ridge & Valley	PU-00010-6.1	Cacapon River	Ib	ns		v	-4.68E-07	*f* -	*f* -	0.009	0.016	0.050
	PL-00014-2.2	Opequon Creek	IIb	ns		▿		*f* -	*f* -	0.068	0.182	0.615
	PSB-00001-13.4	South Branch Potomac River	Ib	▲	1.14E-05	ns		*f* -	*f* -	0.009	0.045	0.170
	PS-00001-0.9	Shenandoah River	Ib	▽	-9.88E-06	▽	-7.83E-06	*f* -	*f* -	0.010	0.050	0.408

Potassium, Total

Potassium (K) data were not collected for 24-26 years, between 1985 and the late 2000s, at the 26 stations, which makes trend calculations difficult. Twenty-two of the 26 stations have sufficient potassium data before and after this large gap for Type II or IV trend analyses. Four stations have insufficient data for any trend calculations (Hughes, Cheat mile 3.5, Twelvepole, and Lower Guyandotte mile 74.1). All except the two Cheat stations have little or no censored data. Sampling intensity varied over the 43 years. Type IV trends should be used with caution due to sparse data in the recent period of record. Trend results are shown in **Table 21**.

Potassium (K) is a monovalent, alkali very reactive cation in the same chemical family as sodium (Na) and lithium (Li). It is an essential macronutrient because of its role in cellular ion transport and exchange and nerve function. Fertilizers are used to replenish K lost from soils in heavily agricultural areas. Concentrations in streams and rivers tend to vary according to the drainage basin's lithography, but can be noticeably altered by anthropogenic inputs (runoff, road salting, wastewater).

Median values for the total K data available between 2009 and 2012 are given in **Table 21**. The Coal, Opequon and Tug Fork stations have the highest medians, with concentrations greater than 4.0 mg/liter. Greenbrier, Tygart Valley, Gauley and both Cheat stations have the lowest medians, with concentrations less than 1.0 mg/liter.

Long-term trends. Trends were mostly non-significant (13) or significantly downward (6). The Coal, Tug Fork and Opequon stations trends were significantly increasing ($p<0.05$). These three stations also have the highest 2009-2012 median concentrations.

Short-term trends. The six trends that could be calculated should probably be ignored in preference of the flow-adjusted trends due to the very sparse data avaiable for that period.

Flow-adjusted trends. LOWESS curves of the log-log plots of K concentration and flow generally show K decreasing as flow increases (**Appendix D**). Variability in the curves suggest multiple K inputs occur at some stations. Flow-adjusted trends validate the flow-unadjusted trends with the exception of Tygart Valley, which changed from significantly decreasing ($p<0.01$) to non-significant (ns).

Table 21. Total potassium (K) trends. Recent (late 2000s – 2012, note abbreviated timeframe); long-term (1970s – 2012); slope (mg/liter/year); median (mg/liter).

				Not Adjusted for Flow				Flow Adjusted		2009 -
				Recent		Long-term		Recent	Long-term	2012
Ecoreg.	Station	StreamName	Type	Trend	Slope	Trend	Slope	Trend	Trend	Median
Western Allegheny Plateau	MC-00001-3.5	Cheat River	IVb	-		-				0.60
	KC-00001-11.6	Coal River	IVa	-		▲		*f* -	*f* ▲	4.70
	ML-00001-20.6	Dunkard Creek	IVa	-		ns		*f* -	*f* ns	3.05
	KE-00001-4.3	Elk River	IVa	-		ns		*f* -	*f* ns	1.35
	OGL-00001-2.8	Guyandotte River (Lower)	IVa	-		ns				2.70
	LK-00025-1.5	Hughes River	IVa	-		-				1.60
	KL-00001-31.7	Kanawha River (Lower)	IVa	-		ns		*f* -	*f* ns	1.35
	LK-00001-28.9	Little Kanawha River	IVa	-		▽		*f* -	*f* ▿	1.15
	OMN-00006-12.3	Middle Island Creek	IVa	-		ns		*f* -	*f* ▿	2.00
	MU-00001-99.4	Monongahela River (Upper)	IIa	ns		▿				1.75
	BST-00001-0.15	Tug Fork	IVa	-		▴		*f* -		4.10
	OT-00001-8.8	Twelvepole Creek	IVa	-		-				2.40
	MT-00001-6.2	Tygart Valley River	IVa	-		▽		*f* -	*f* ns	0.90
	MW-00001-12	West Fork River	IIa	ns		ns		*f* ns	*f* ▿	3.40
Central Appalachians	MC-00001-30	Cheat River	IVb	-		▽		*f* -		0.60
	KG-00001-8.25	Gauley River	IVa	-		▽		*f* -	*f* ▽	0.75
	KNG-00001-1.6	Greenbrier River	IVa	-		▿		*f* -	*f* ▽	0.90
	OGL-00001-74.1	Guyandotte River (Lower)	IVa	-		-		*f* -		2.85
	KU-00001-74.1	Kanawha River (Upper)	IVa	-		ns		*f* -	*f* ns	1.20
	KNL-00001-1.2	New River (Lower)	IVa	-		ns		*f* -		1.30
	KNU-00001-67.4	New River (Upper)	IVa	-		ns				1.50
	KNU-00001-96.2	New River (Upper)	IVa	-		ns		*f* -	*f* ns	1.60
Ridge & Valley	PU-00010-6.1	Cacapon River	IIa	ns		ns		*f* ns	*f* ns	1.20
	PL-00014-2.2	Opequon Creek	IIa	ns		▲		*f* ns	*f* ▲	4.15
	PSB-00001-13.4	South Branch Potomac River	IIa	▴	1.00E-01	ns		*f* ns	*f* ns	1.30
	PS-00001-0.9	Shenandoah River	IIa	ns		ns		*f* ns	*f* ns	2.35

pH

> ***pH*** is a measure of water's acidity or basicity. It is one of the most influential properties of water. Technically, pH is the negative log of the concentration of hydronium ions (H^+) in water. H^+ concentrations are strongly moderated by the bicarbonate-carbonate equilibrium system in waters with high alkalinity. However, highly productive nutrient enriched systems can force large diel (daily) swings in pH to occur. As pH levels fall below 6.0 or rise above 9.0, physiological stress occurs in many aquatic organisms. Lower pH levels (increasing acidity) also heighten the toxicity of ammonia and many metals. "Acid rain" caused by industrial air pollution acidified eastern US waterways in the late 20th century. The nation's clean air regulations have substantially reduced the causes of acidification - atmospheric sulfur dioxide (SO_2) and nitrogen oxide (NO_x) gases and particulate sulfates and nitrates. West Virginia §8.24 (requirements governing water quality standards) states that pH should have "no values below 6.0 nor above 9.0. Higher values due to photosynthetic activity may be tolerated."

Acidity as measured by pH is one of the most commonly measured parameters in the analysis database, with a total of 6,415 measurements. Seventeen of the 26 stations have pH measurements from the 1970's through 2012 (Type I). pH monitoring also began in 1970 at six other stations but was halted for 11 years between 1985 and 1995, resulting in non-continuous records for these stations (Type II). Three stations have data records beginning in 1996 (Type III). Sampling intensity varied over the 43 years. No measurements are identified as below the detection limit. Trend results are shown in **Table 22**.

The two Cheat River stations have the lowest median values for the most recent, 2009-2012 period (6.9 and 7.1); the South Branch Potomac and Shenandoah stations have the highest median values, with pH 8.4 and 8.3 respectively. Individual pH values less than 6.0 occurred at the two Cheat stations, Middle Island, Twelvepole, Tygart Valley and Gauley stations. Individual pH values greater than 9.0 occurred at the Greenbrier, Upper New (mile 67.4), South Branch Potomac, and Shenandoah stations.

Long-term trends. All but three stations show significant increasing trends ($p<0.05$), indicating streams and rivers are becoming less acid. Cacapon is trending up ($0.05<p<0.1$) and Opequon and Shenandoah show no trend. This could be expected as the Cacapon, Opequon and Shenandoah are in the Ridge & Valley ecoregion, which has naturally higher levels of bicarbonate minerals (see Alkalinity) and thus a greater buffering capacity. The largest increasing trends are occurring in the Monogahela River basin (West Fork, Tygart Valley, Cheat). The smallest significant increases outside of the Ridge & Valley ecoregion are occurring in the Kanawha River basin (Lower Kanawha, Gauley, Lower New).

Short-term trends. These trends tend to be weaker than their long-term counterparts, with more non-significant changes. However, all significant changes over time are increasing trends.

Flow-adjusted trends. LOWESS curves of the log-log regressions between pH and flow are generally linear and negative, with pH decreasing with increasing flow (**Appendix D**). Some are relatively flat (e.g., Opequon, Tygart Valley) and other show a lot of scatter, possibly indicating multiple sources of acidity (e.g., Upper Kanawha, Lower Kanawha). Overall, the flow-adjusted trends corroborate the unadjusted flows, indicating that variations in pH due to streamflow were not confounding trend results.

Table 22. Trends in pH. Recent (1996 - 2012); long-term (1970s - 2012); slope (standard pH units per year); minimum, median and maximum (standard pH units).

				Not Adjusted for Flow				Flow Adjusted		2009-2012		
				Recent		Long-term		Recent	Long-term			
Ecoreg.	Station	StreamName	Type	Trend	Slope	Trend	Slope	Trend	Trend	Min	Median	Max
Western Allegheny Plateau	MC-00001-3.5	Cheat River	IIIa	ns		-				5.5	6.9	7.8
	KC-00001-11.6	Coal River	Ia	^	1.67E-02	▲	2.50E-02	*f* ▲	*f* ▲	7.0	8.1	8.4
	ML-00001-20.6	Dunkard Creek	IIa	ns		▲		*f* ^	*f* ▲	6.5	8.0	8.9
	KE-00001-4.3	Elk River	Ia	ns		▲	1.53E-02	*f* ns	*f* ▲	6.2	7.4	8.0
	OGL-00001-2.8	Guyandotte River (Lower)	Ia	▲	2.27E-02	▲	1.61E-02			6.2	7.7	8.2
	LK-00025-1.5	Hughes River	IIa	ns		▲				6.8	7.5	8.1
	KL-00001-31.7	Kanawha River (Lower)	Ia	▴	1.71E-02	▲	1.43E-02	*f* ▴	*f* ▲	7.2	7.6	8.2
	LK-00001-28.9	Little Kanawha River	IIIa	▴	2.25E-02	-		*f* ▴	*f* -	6.5	7.5	8.0
	OMN-00006-12.3	Middle Island Creek	IIa	ns		▲		*f* ns	*f* ▲	5.8	7.5	8.1
	MU-00001-99.4	Monongahela River (Upper)	Ia	ns		▲	2.38E-02			6.4	7.4	8.1
	BST-00001-0.15	Tug Fork	Ia	ns		▲	1.80E-02	*f* ^	*f* ▲	6.3	8.0	8.5
	OT-00001-8.8	Twelvepole Creek	IIIa	▲	3.43E-02	-				5.5	7.6	8.0
	MT-00001-6.2	Tygart Valley River	Ia	ns		▲	2.79E-02	*f* ns	*f* ▲	5.3	7.4	8.4
	MW-00001-12	West Fork River	Ia	▴	2.00E-02	▲	3.05E-02	*f* ▴	*f* ▲	7.1	7.7	8.8
Central Appalachians	MC-00001-30	Cheat River	Ia	ns		▲	3.57E-02	*f* ns		5.0	7.1	7.8
	KG-00001-8.25	Gauley River	Ia	ns		▲	1.18E-02	*f* ns	*f* ▲	5.9	7.4	8.1
	KNG-00001-1.6	Greenbrier River	Ia	▲	3.33E-02	▲	2.14E-02	*f* ^	*f* ▲	6.4	8.1	9.0
	OGL-00001-74.1	Guyandotte River (Lower)	IIIa	▴	1.73E-02	-		*f* ▴		6.8	7.9	8.6
	KU-00001-74.1	Kanawha River (Upper)	Ia	▴	2.50E-02	▲	1.63E-02	*f* ▴	*f* ▲	6.3	7.8	8.8
	KNL-00001-1.2	New River (Lower)	Ia	▴	2.00E-02	▲	1.43E-02	*f* ▴	*f* ▲	6.5	8.0	8.3
	KNU-00001-67.4	New River (Upper)	IIa	^	1.92E-02	▲		*f* ns	*f* ▲	6.6	7.9	9.1
	KNU-00001-96.2	New River (Upper)	IIa	▲	3.14E-02	▲		*f* ▴	*f* ▲	6.8	8.1	8.8
Ridge & Valley	PU-00010-6.1	Cacapon River	Ia	▴	3.33E-02	^	8.03E-03	*f* ▴	*f* ^	6.6	7.7	8.7
	PL-00014-2.2	Opequon Creek	IIa	▲	1.59E-02	ns		*f* ▴	*f* ns	7.3	8.1	8.7
	PSB-00001-13.4	South Branch Potomac River	Ia	▲	6.00E-02	▲	1.45E-02	*f* ▲	*f* ▲	6.9	8.4	9.1
	PS-00001-0.9	Shenandoah River	Ia	▴	2.64E-02	ns		*f* ns	*f* ns	7.4	8.3	9.4

Selenium, Total

Selenium (Se) is a trace element found in a variety of minerals. It is a byproduct of metal ore refinement and coal combustion. While toxic in large amounts, selenium is important in the cellular functions of many organisms. West Virginia has an aquatic life acute criterion of 0.02 mg/liter and a chronic criterion of 0.005 mg/liter. It has a drinking water supply criterion of 0.05 mg/liter.

Selenium monitoring begins in the mid-1970s at 23 of the 26 stations but was halted in 1985. Monitoring is picked up again in 2004 and continues through 2012. Long-term trend analyses for these stations can accommodate this 19 year data gap (Type II). Monitoring begins at three additional stations in 2004 and continues through 2012 (Type III). It is worth noting the recent, short-term trends (Type III) for selenium are for a shorter period of record than those of most other parameters. Sampling intensity varied over the 43 years. The trend analysis is confounded by many values below MDLs (censoring Types b and c), so only flow-unadjusted trends can be calculated. Trend results are shown in **Table 23**.

Median values in the most recent, 2009-2012 timeframe were at the MDL at 22 of the 26 stations. Only four station medians exceeded the MDL more than half the time (Coal, Tug Fork, and the two Lower Guyandotte stations). Total selenium concentrations never exceeded the West Virginia drinking water supply criterion of 0.05 mg/liter in the 2009-2012, although they did exceed the aquatic life chronic criterion of 0.005 mg/liter three times at Dunkard and once at Cheat (mile 30).

Long-term trends. Total selenium results are mixed, with seven stations showing significant increases ($p<0.05$), six showing no trends (ns), one showing a decreasing tendency ($0.05<p<0.1$), and two showing significant decreasing trends. Stations with increasing trends in total selenium are Coal, Middle Island, Upper Monongahela, the Upper Kanawha, and the three New River stations.

Short-term trends. Most stations did not show trends in the abbreviated recent period (2004 – 2012). Concentrations are tending to increase in Coal ($0.05<p<0.1$), trending up in the Lower Guyandotte (mile 2.8), and trending down in the Lower New ($p<0.05$). The remaining 19 stations where trends could be calculated show no trends (ns).

Table 23. Total selenium (Se) trends. Recent (2004 – 2012, note abbreviated timeframe); long-term (mid-1970s – 2012); median and maximum (mg/liter, *mdl* indicates no samples exceeded the minimum detection limit, or MDL).

				Not Adjusted for Flow		2009-2012	
				Recent	Long-term		
Ecoreg.	Station	StreamName	Type	trend	trend	median	max
Western Allegheny Plateau	MC-00001-3.5	Cheat River	IIIc	-	-	0.001	*mdl*
	KC-00001-11.6	Coal River	IIb	^	▴	0.0022	0.004
	ML-00001-20.6	Dunkard Creek	IIc	ns	ns	0.001	0.008
	KE-00001-4.3	Elk River	IIc	ns	ns	0.001	0.001
	OGL-00001-2.8	Guyandotte River (Lower)	IIb	▲	v	0.0012	0.002
	LK-00025-1.5	Hughes River	IIIc	-	-	0.001	*mdl*
	KL-00001-31.7	Kanawha River (Lower)	IIc	ns	▽	0.001	0.001
	LK-00001-28.9	Little Kanawha River	IIIc	ns	-	0.001	*mdl*
	OMN-00006-12.3	Middle Island Creek	IIc	ns	▲	0.001	0.001
	MU-00001-99.4	Monongahela River (Upper)	IIc	ns	▴	0.001	*mdl*
	BST-00001-0.15	Tug Fork	IIb	ns	ns	0.002	0.003
	OT-00001-8.8	Twelvepole Creek	IIIc	ns	-	0.001	0.001
	MT-00001-6.2	Tygart Valley River	IIIc	ns	-	0.001	0.001
	MW-00001-12	West Fork River	IIc	ns	ns	0.001	0.001
Central Appalachians	MC-00001-30	Cheat River	IIc	ns	-	0.001	0.010
	KG-00001-8.25	Gauley River	IIc	-	-	0.001	*mdl*
	KNG-00001-1.6	Greenbrier River	IIc	ns	▽	0.001	0.001
	OGL-00001-74.1	Guyandotte River (Lower)	IIIb	ns	-	0.001	0.003
	KU-00001-74.1	Kanawha River (Upper)	IIc	ns	▲	0.001	0.001
	KNL-00001-1.2	New River (Lower)	IIc	▽	▲	0.001	0.002
	KNU-00001-67.4	New River (Upper)	IIc	ns	▲	0.001	*mdl*
	KNU-00001-96.2	New River (Upper)	IIc	ns	▲	0.001	0.002
Ridge & Valley	PU-00010-6.1	Cacapon River	IIc	ns	-	0.001	0.001
	PL-00014-2.2	Opequon Creek	IIc	ns	ns	0.001	0.001
	PSB-00001-13.4	South Branch Potomac River	IIc	-	-	0.001	*mdl*
	PS-00001-0.9	Shenandoah River	IIc	ns	ns	0.001	0.002

Sodium, Total

None of the 26 stations has total sodium (Na) data between 1985 and 2009—a 25 year gap. Twenty-three of the 26 stations have Na data before and after this gap (Type II, IV), however the length of the data records before 1985 is variable. Sodium monitoring begins at three additional stations in 2009 (Type III). Only three measurements fall below MDL levels, so all trend analyses are according to censoring Type a. All of the recent trends are for the abbreviated 2009-2012 period, and it is not clear if these trends are meaningful due to the very short timeframe. Sampling intensity varied over the 43 years. Trend results are shown in **Table 24**.

Sodium (Na) is an abundant, reactive alkali metal and a component of many minerals and salts, including table salt (NaCl). Animals require sodium in their diets to support metabolic, osmotic, and neurological functions. Plants normally contain little sodium but Na requirements of some cyanobacteria can be high. Many sodium salts are highly soluble and the monovalent sodium cation (Na^+) contributes to water's conductivity. In undisturbed streams and rivers, natural sources control Na concentrations and its seasonal variability is small. Industrial and domestic sources and road salting can substantially raise Na concentrations. WVDEP has no Na water quality criteria.

Median concentrations in the very recent 2009-2012 timeframe ranged between 1.8 mg/liter (Cheat mile 30) and 84.1 mg/liter (Dunkard). Individual measurements ranged between 0.5 mg/liter (Hughes, Upper Monongahela, Greenbrier) and 481 mg/liter, or roughly 0.48 ppt salinity (Dunkard).

Long-term trends. Thirteen stations show significant increases in total Na concentrations ($p<0.05$). Seven show no significant trends, and one (South Branch Potomac) shows a significant decreasing trend.

Short-term trends. Almost all stations show no significant trends in total Na concentrations. The exception is Greenbier, which has a significant upward trend ($p<0.05$). The relevance of this trend is questionable due to the very abbreviated 2009-2012 timeframe.

Flow-adjusted trends. The LOWESS curves of log-log plots of Na and flow show Na decreasing as flow increases (**Appendix D**). The relationships are generally tight, but a few show unusal or highly variable regressions (e.g., Cacapon, Cheat mile 30, Lower New). Overall, flow-adjusted trends confirm the unadjusted trends, indicating that variation in Na concentrations due to streamflow were not confounding trend results.

Table 24. Total sodium (Na) trends. Recent (2009 – 2012, note abbreviated timeframe); long-term (1970s – 2012); slope (mg/liter/year); minimum, median, and maximum (mg/liter).

				Not Adjusted for Flow				Flow Adjusted		2009-2012		
				Recent		Long-term		Recent	Long-term			
Ecoreg.	Station	StreamName	Type	trend	slope	trend	slope	trend	trend	min	median	max
Western Allegheny Plateau	MC-00001-3.5	Cheat River	IIIa	ns		-				1.2	2.2	6.6
	KC-00001-11.6	Coal River	IIa	ns		▲		*f* ns	*f* ▲	12.9	54.2	169
	ML-00001-20.6	Dunkard Creek	IIa	ns		▲		*f* ns	*f* ▲	21.3	84.1	481
	KE-00001-4.3	Elk River	IVa	-		▲		*f* -	*f* ▲	2.2	4.5	10.9
	OGL-00001-2.8	Guyandotte River (Lower)	IIa	ns		ns				9.6	23.75	61.6
	LK-00025-1.5	Hughes River	IIIa	ns		-				0.5	6.55	19.7
	KL-00001-31.7	Kanawha River (Lower)	IVa	-		ns		*f* -	*f* ns	5.9	10.7	30.2
	LK-00001-28.9	Little Kanawha River	IIa	ns		ns		*f* ns	*f* ns	1.9	4.85	10.4
	OMN-00006-12.3	Middle Island Creek	IIa	ns		ns		*f* ns	*f* ns	2.5	6.65	14.9
	MU-00001-99.4	Monongahela River (Upper)	IIa	ns		▲				0.5	24.1	74.8
	BST-00001-0.15	Tug Fork	IIa	ns		▲		*f* ns		15.9	48.3	119
	OT-00001-8.8	Twelvepole Creek	IVa	-		-				3.9	7.75	26.2
	MT-00001-6.2	Tygart Valley River	IIIa	ns		-		*f* ns	*f* -	2.6	5.2	10.8
	MW-00001-12	West Fork River	IIa	ns		ns		*f* ns	*f* ns	7.8	32.6	96.8
Central Appalachians	MC-00001-30	Cheat River	IVa	-		ns		*f* -		1	1.8	5.2
	KG-00001-8.25	Gauley River	IIa	ns		▲		*f* ns	*f* ▲	1.5	2.95	10.6
	KNG-00001-1.6	Greenbrier River	IIa	▴	4.00E-01	ns		*f* ns	*f* ▿	0.5	2.2	5.1
	OGL-00001-74.1	Guyandotte River (Lower)	IIIa	ns		-		*f* ns		10.2	28.2	82
	KU-00001-74.1	Kanawha River (Upper)	IIa	ns		▲		*f* ns	*f* ▲	3.1	6.4	21.1
	KNL-00001-1.2	New River (Lower)	IIa	ns		▲		*f* ns		3.3	6.1	9.4
	KNU-00001-67.4	New River (Upper)	IIa	ns		▲				2.8	5	6.6
	KNU-00001-96.2	New River (Upper)	IIa	ns		▲		*f* ns	*f* ▲	3.6	4.6	6.5
Ridge & Valley	PU-00010-6.1	Cacapon River	IIa	ns		▲		*f* ns	*f* ▲	1.9	2.95	4.5
	PL-00014-2.2	Opequon Creek	IIa	ns		▲		*f* ns	*f* ▲	10.1	29.2	51.6
	PSB-00001-13.4	South Branch Potomac River	IIa	ns		▲		*f* ns	*f* ▲	2.2	4.2	8.9
	PS-00001-0.9	Shenandoah River	IIa	ns		▽		*f* ns	*f* ▽	5.4	10.2	13.8

Specific Conductance

Specific conductance measures water's ability to conduct electricity and indicates the amount of salinity. The strength of the electrical conductance depends on the concentrations of all electrolytes, or dissolved ionic substances, in the water. The cations Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+} and the anions HCO_3^{-}, CO_3^{2-}, SO_4^{2-}, and Cl^{-} normally dominate the ionic composition of fresh water. Runoff and discharges to streams and rivers can substantially raise ion concentrations and increase conductivity. Plants and animals physiologically adapted to freshwater are stressed by high conductivity levels. Temperature influences conductivity, so conductance measurements are adjusted to a common temperature (25°C) for comparison purposes.

In the analysis database, field measurements of specific conductance at 17 stations begin sometime in the mid-1970s to 1980, and continue uninterrupted until 2012 (Type 1). Six stations have an 11-year data gap between 1985 and 1995 (Type II). Measurements at three stations begin in 1996 (Type III). Measurements for only two sampling events are below MDL, so all trend analyses are unaffected by censoring (Type a). Sampling intensity varied over the 43 years. Trend results are shown in **Table 25**.

Median levels of specific conductivity in the very recent 2009-2012 timeframe ranged from less than 100 µS/cm (Cheat mile 30, Gauley) to more than 600 µS/cm (Coal, Dunkard, West Fork, Opequon, Tug Fork). The lowest individual value of 56 µS/cm occurred at Cheat (mile 30) on February 23, 2011; the highest individual values occurred at Dunkard (2,558 µS/cm on September 21 and 22, 2009 and 5,000 µS/cm on September 15, 1976).

Long-term trends. Fourteen stations show significant increasing trends in specific conductance ($p<0.05$). Six show no trends. Three show significant decreasing trends ($p<0.05$). They are West Fork, Cheat (mile 30), and Shenandoah.

Short-term trends. Recent trends are either significantly increasing (9), trending upward (1) or not changing (15). There are no decreasing trends.

Flow-adjusted trends. The LOWESS curves of the log of specific conductance versus the log of flow are usually very tight, linear relationships with specific conductance decreasing as flow increases (**Appendix D**). Flow-adjusted trends are very comparable to the unadjusted trends, indicating that variation in concentrations due to streamflow were not confounding trend results.

A strong, highly significant, linear relationship exists between specific conductivity and total dissolved solids in the West Virginia data (see total dissolved solids). Strong relationships also occur between conductivity and sodium, calcium, and magnesium (all $r^2 > 0.6$).

Table 25. Specific conductance trends. Recent (1996 - 2012); long-term (1970s - 2012); slope (µS/cm/year); minimum, median, and maximum (µS/cm).

				Not Adjusted for Flow				Flow Adjusted		2009-2012		
				Recent		Long-term		Recent	Long-term			
Ecoreg.	Station	StreamName	Type	Trend	Slope	Trend	Slope	Trend	Trend	Min	Median	Max
Western Allegheny Plateau	MC-00001-3.5	Cheat River	IIIa	ns		-				70	105.5	166
	KC-00001-11.6	Coal River	Ia	▴	9.20E+00	▲	8.70E+00	*f* ▲	*f* ▲	295	696.5	1230
	ML-00001-20.6	Dunkard Creek	IIa	▲	1.76E+01	▲		*f* ▲	*f* ▲	250	683	2558
	KE-00001-4.3	Elk River	Ia	▲	3.18E+00	▲	2.15E+00	*f* ▲	*f* ▲	90	155	402
	OGL-00001-2.8	Guyandotte River (Lower)	Ia	ns		ns				188	330	633
	LK-00025-1.5	Hughes River	IIa	ns		ns				96	148	281
	KL-00001-31.7	Kanawha River (Lower)	Ia	ns		▴	8.82E-01	*f* ns	*f* ▴	148	226	398
	LK-00001-28.9	Little Kanawha River	Ia	ns		ns		*f* ns	*f* ns	79	114	179
	OMN-00006-12.3	Middle Island Creek	IIa	ns		ns		*f* ns	*f* ns	111	154	263
	MU-00001-99.4	Monongahela River (Upper)	Ia	▴	7.50E+00	▴	1.75E+00			156	366	788
	BST-00001-0.15	Tug Fork	Ia	ns		▲	5.56E+00	*f* ▲	*f* ▲	337	649	1010
	OT-00001-8.8	Twelvepole Creek	IIIa	▲	4.00E+00	-				137	207	326
	MT-00001-6.2	Tygart Valley River	Ia	ns		▴	6.36E-01	*f* ns	*f* ▲	78	133	188
	MW-00001-12	West Fork River	Ia	ns		▽	-5.55E+00	*f* ns	*f* ▽	265	699	1057
Central Appalachians	MC-00001-30	Cheat River	Ia	ns		▿	-5.00E-01	*f* ns		56	86.5	133
	KG-00001-8.25	Gauley River	Ia	ns		▲	5.79E-01	*f* ^	*f* ▲	67	87.5	167
	KNG-00001-1.6	Greenbrier River	Ia	ns		ns		*f* ns	*f* ▿	93	133	230
	OGL-00001-74.1	Guyandotte River (Lower)	IIIa	ns		-		*f* ns		226	397	780
	KU-00001-74.1	Kanawha River (Upper)	Ia	▲	2.56E+00	▲	1.23E+00	*f* ▲	*f* ▲	30	192	257
	KNL-00001-1.2	New River (Lower)	Ia	ns		▴	4.60E-01	*f* ns	*f* ▲	118	166	215
	KNU-00001-67.4	New River (Upper)	IIa	ns		▲		*f* ns	*f* ▲	135	162	240
	KNU-00001-96.2	New River (Upper)	IIa	▴	1.38E+00	▲		*f* ^	*f* ▲	106	170	215
Ridge & Valley	PU-00010-6.1	Cacapon River	Ia	▴	1.85E+00	ns		*f* ▲	*f* ▴	102	153	203
	PL-00014-2.2	Opequon Creek	IIa	▲	6.33E+00	▲		*f* ▲	*f* ▲	368	673.5	790
	PSB-00001-13.4	South Branch Potomac River	Ia	^	1.82E+00	▲	1.00E+00	*f* ns	*f* ▲	158	208.5	301
	PS-00001-0.9	Shenandoah River	Ia	▲	4.92E+00	▿	-1.50E+00	*f* ▴	*f* ▽	235	334	403

Sulfate

> ***Sulfate (SO_4)*** is an anion comprised of one sulfur and four oxygen atoms (SO_4^{2-}). The element sulfur is an essential plant nutrient that forms sulfate in well-oxygenated waters. Sulfuric acid forms when sulfate combines with two H^+ ions. Sulfuric acid is a highly corrosive component of acid rain and forms naturally in mine drainage with the oxidation of sulfide minerals. Sulfate can be a major contaminant in natural waters, and elevated levels indicate anthropogenic inputs from atmospheric deposition, mine drainage, runoff and wastewater discharges. West Virginia does not have a water quality criterion for sulfate. The USEPA guideline for sulfate in drinking water is a concentration less than 250 mg/liter.

Monitoring for sulfate (SO_4) begins in the 1970s at 17 of the 26 stations and continues uninterrupted through 2012 (Type I). Sulfate monitoring also begins in 1970 at six other stations but halts for 11 years between 1985 and 1995, resulting in non-continuous data records at these stations (Type II). Sulfate measurements begin in 1996 in the Cheat at mile 3.5, Lower Guyandotte at mile 74.1, and Twelvepole Creek (Type III). Sampling intensity varies over the 43 years. Only nineteen in the entire data set of 7,018 sulfate measurements fall below detection limits, so flow-adjusted trends can be estimated for all stations. Sulfate is a robust parameter to use in trend analyses. Trend results are shown in **Table 26**.

Median concentrations in the most recent four years (2009-2012) ranged from 9.5 mg/liter (Greenbrier) to 223.5 mg/liter (West Fork). Individual values ranged from 5 mg/liter (Hughes) to 870 mg/liter (Dunkard).

Long-term trends. Sulfate trends were mixed, with eleven stations showing significant declines, five showing no change, and seven showing significant increases ($p<0.05$). Of the 23 stations with long-term trends, Tug Fork and Coal had the fastest rates of increase (+1.68 and +1.59 mg/liter/year, respectively) and West Fork has the fastest rate of decrease (-4.70 mg/liter/year).

Short-term trends. Sulfate trends for the 1996-2012 timeframe were also mixed, but with fewer significant up and down trends. Tug Fork has the fastest rate of increase (+2.3 mg/liter/year) and Hughes, Middle Island, and Cheat (mile 30) the fastest rates of decrease. The Shenandoah's long-term trend contrasted sharply with its short-term trend. The long-term trend is decreasing significantly but the short-term trend is increasing significantly.

Flow-adjusted trends. In most cases, LOWESS curves of log sulfate versus log flow show sulfate concentrations decreasing as flow increases (**Appendix D**). Middle Island was an exception, with sulfate concentrations tending to increase with greater flow. The Shenandoah relationship is particularly unusual with what appears to be two distinctly different groups of data, possibly reflecting an abrupt shift in sulfate inputs (**Figure 4**). Flow adjusted trend corroborate the unadjusted trends for the most part.

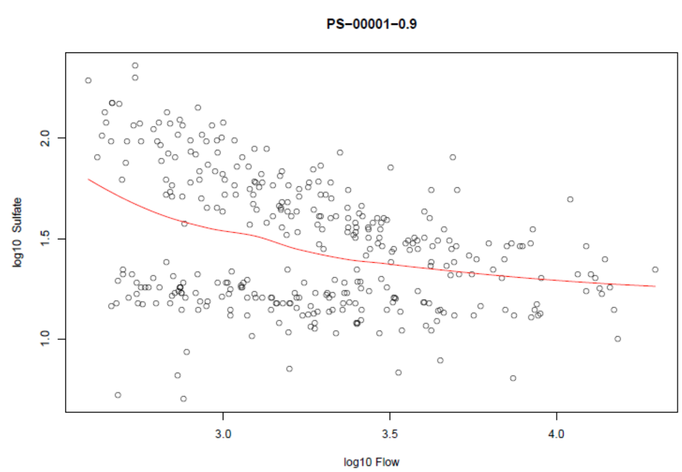

Figure 4. Log-log plot of sulfate vs flow at Shenandoah station. Red line, LOWESS curve through all data. Note the two groups of data with different flow relationships.

Table 26. Sulfate (SO_4) trends. Recent (1996 - 2012); long-term (1970s - 2012); slope (mg/liter/year); minimum, median, and maximum (mg/liter).

				Not Adjusted for Flow				Flow Adjusted		2009-2012		
				Recent		Long-term		Recent	Long-term			
Ecoreg.	Station	StreamName	Type	trend	slope	trend	slope	trend	trend	min	median	max
Western Allegheny Plateau	MC-00001-3.5	Cheat River	IIIa	ns		-				14	24.75	50
	KC-00001-11.6	Coal River	Ia	ns		▲	1.59E+00	*f* ▲	*f* ▲	94	205	335
	ML-00001-20.6	Dunkard Creek	IIa	^	2.60E+00	▲		*f* ▲	*f* ▲	47	146	870
	KE-00001-4.3	Elk River	Ia	▲	1.10E+00	▲	7.33E-01	*f* ▲	*f* ▲	19	41	145
	OGL-00001-2.8	Guyandotte River (Lower)	Ia	ns		ns				40	80	140
	LK-00025-1.5	Hughes River	IIa	▽	-5.38E-01	▿				5	12	17
	KL-00001-31.7	Kanawha River (Lower)	Ia	ns		ns		*f* ns	*f* ns	22	38.5	75
	LK-00001-28.9	Little Kanawha River	Ia	▽	-3.33E-01	▽	-1.76E-01	*f* ▽	*f* ▽	9	14	20
	OMN-00006-12.3	Middle Island Creek	IIa	▽	-5.00E-01	▽		*f* ns	*f* ▽	10.5	15	19
	MU-00001-99.4	Monongahela River (Upper)	Ia	^	2.17E+00	▽	-7.04E-01			37	104	284
	BST-00001-0.15	Tug Fork	Ia	▴	2.35E+00	▲	1.68E+00	*f* ▲	*f* ▲	91	176	273
	OT-00001-8.8	Twelvepole Creek	IIIa	▲	7.00E-01	-				29	45	68
	MT-00001-6.2	Tygart Valley River	Ia	ns		▿	-2.26E-01	*f* ns	*f* ns	14	29	46
	MW-00001-12	West Fork River	Ia	ns		▽	-4.70E+00	*f* v	*f* ▽	61	223.5	408
Central Appalachians	MC-00001-30	Cheat River	Ia	▿	-4.37E-01	▽	-5.00E-01	*f* v		8	17.9	33
	KG-00001-8.25	Gauley River	Ia	ns		▲	1.17E-01	*f* ns	*f* ▲	12	17.5	30
	KNG-00001-1.6	Greenbrier River	Ia	ns		ns		*f* ns	*f* ▽	7	9.5	22
	OGL-00001-74.1	Guyandotte River (Lower)	IIIa	ns		-		*f* ns		54	107.5	195
	KU-00001-74.1	Kanawha River (Upper)	Ia	▴	4.17E-01	▲	1.74E-01	*f* ▴	*f* ▲	12	28	36
	KNL-00001-1.2	New River (Lower)	Ia	ns		▿	-6.45E-02	*f* ▿	*f* ▽	7	13	18
	KNU-00001-67.4	New River (Upper)	IIa	ns		ns		*f* ns	*f* ns	7	12	20
	KNU-00001-96.2	New River (Upper)	IIa	ns		ns		*f* ns	*f* ns	7	13	19
Ridge & Valley	PU-00010-6.1	Cacapon River	Ia	ns		▽	-6.00E-02	*f* ^	*f* ▽	8	11	16
	PL-00014-2.2	Opequon Creek	IIa	▲	8.69E-01	▲		*f* ▲	*f* ▲	28	44	68
	PSB-00001-13.4	South Branch Potomac River	Ia	ns		▽	-1.14E-01	*f* ns	*f* ▽	16	22	38.9
	PS-00001-0.9	Shenandoah River	Ia	▲	3.33E-01	▽	-7.82E-01	*f* ▲	*f* ▽	12	17	24.1

Suspended Solids, Total

> ***Suspended solids*** are the sum of all inorganic and organic substances, including sediments, suspended in water that does not pass through a filter. Total suspended solids (TSS) are measured by drying and weighing the filtrate from a known volume of water. TSS typically correlates with turbidity, or the cloudiness of the water. Many human activities affect TSS concentrations in rivers and streams, including impoundments, irrigation practices, run-off, and discharges. High TSS levels can reduce in-stream photosynthetic productivity and impede respiration in aquatic animals. TSS is also associated with increased bacterial counts because bacteria are often attached to the suspended sediment particles. TSS is listed as a conventional pollutant in the Clean Water Act. Total maximum daily loads (TMDLs) have been established for suspended sediments delivered to Chesapeake Bay from West Virginia Potomac watersheds.

Monitoring for total suspended solids (TSS) begins in the 1970s at 17 of the 26 stations and continues uninterrupted through 2012 (Type I). TSS monitoring also begins in 1970 at six other stations but halts for 11 years between 1985 and 1995, resulting in non-continuous data records at these stations (Type II). TSS measurements begin in 1996 in the Cheat (mile 3.5), Lower Guyandotte (mile 74.1), and Twelvepole Creek (Type III). Twenty-two of the 26 stations have greater than 5% censored data (censoring Types b, c). Sampling intensity varies over the 43 years. Trend results are shown in **Table 27.**

TSS is largely driven by high flow events and the data are heavily skewed at most stations. Median concentrations during the 2009-2012 timeframe ranged from 2 mg/liter, which is the MDL concentration, to 19 mg/liter (Lower Guyandotte at mile 2.8). Maximum concentrations at the 26 stations show large differences, with 12 mg/liter at Cheat (mile 3.5) and 550 mg/liter at West Fork.

Long-term trends. All 26 stations show significant declining trends.

Short-term trends. Twenty stations show no trends. Elk, Tug Fork, Lower Guyandotte (mile 74.1), Opequon, and South Branch Potomac show significant decreasing trends ($p<0.05$) and Little Kanawha is trending downward ($0.05<p<0.1$). No stations are showing increasing trends.

Flow-adjusted trends. LOWESS curves of log-log plots between TSS and flow are curvi-linear (**Appendix D**). TSS shows no relationship to flow at low flow levels but shows a positive relationship with flow at high flow levels. All flow adjust trends are significant and downward, verifying their flow-unadjusted counterparts.

Table 27. Total suspended solids (TSS) trends. Recent (1996 - 2012); long-term (1970s - 2012); slope (mg/liter/year); minimum, median, and maximum (mg/liter).

				Not Adjusted for Flow				Flow Adjusted		2009-2012		
				Recent		Long-term		Recent	Long-term			
Ecoreg.	Station	StreamName	Type	Trend	Slope	Trend	Slope	Trend	Trend	Min	Median	Max
Western Allegheny Plateau	MC-00001-3.5	Cheat River	IIIc	ns		-				2	2.5	12
	KC-00001-11.6	Coal River	Ib	ns		▽	-1.36E-03	*f* -	*f* -	2	4	230
	ML-00001-20.6	Dunkard Creek	IIb	ns		▽		*f* -	*f* -	2	7	344
	KE-00001-4.3	Elk River	Ib	▿	-8.07E-04	▽	-5.28E-04	*f* -	*f* -	2	6	97
	OGL-00001-2.8	Guyandotte River (Lower)	Ia	ns		▽	-4.29E-01			2	19	230
	LK-00025-1.5	Hughes River	IIb	ns		▽				2	7	100
	KL-00001-31.7	Kanawha River (Lower)	Ib	ns		▽	-6.49E-04	*f* -	*f* -	2	7	122
	LK-00001-28.9	Little Kanawha River	Ia	v	-4.44E-01	▿	-1.82E-01	*f* ▿	*f* ▽	2	9	127
	OMN-00006-12.3	Middle Island Creek	IIb	ns		▽		*f* -	*f* -	2	7.25	278
	MU-00001-99.4	Monongahela River (Upper)	Ib	ns		▽	-8.45E-04			2	5	74
	BST-00001-0.15	Tug Fork	Ia	▿	-8.20E-01	▽	-7.00E-01	*f* ▽	*f* ▽	2	12.5	171
	OT-00001-8.8	Twelvepole Creek	IIIb	ns		-				2	14	33
	MT-00001-6.2	Tygart Valley River	Ib	ns		▽	-6.25E-04	*f* -	*f* -	2	2	71
	MW-00001-12	West Fork River	Ia	ns		▽	-6.67E-01	*f* ns	*f* ▽	2	8	550
Central Appalachians	MC-00001-30	Cheat River	Ib	ns		▽	-1.42E-03	*f* -		2	2	35
	KG-00001-8.25	Gauley River	Ib	ns		▽	-5.51E-04	*f* -	*f* -	2	2	35
	KNG-00001-1.6	Greenbrier River	Ib	ns		▽	-4.44E-04	*f* -	*f* -	2	2.75	47
	OGL-00001-74.1	Guyandotte River (Lower)	IIIb	▿	-1.85E-03	-		*f* -		2	6	54
	KU-00001-74.1	Kanawha River (Upper)	Ib	ns		▽	-7.18E-04	*f* -	*f* -	2	4.5	18
	KNL-00001-1.2	New River (Lower)	Ib	ns		▽	-5.79E-04	*f* -	*f* -	2	5	34
	KNU-00001-67.4	New River (Upper)	IIb	ns		▽		*f* -	*f* -	2	5	28
	KNU-00001-96.2	New River (Upper)	IIb	ns		▽		*f* -	*f* -	2	3	103
Ridge & Valley	PU-00010-6.1	Cacapon River	Ib	ns		▽	-4.19E-04	*f* -	*f* -	2	2	15
	PL-00014-2.2	Opequon Creek	IIb	▿	-9.46E-04	▽		*f* -	*f* -	2	6	70
	PSB-00001-13.4	South Branch Potomac River	Ib	▽	-7.53E-04	▽	-6.64E-04	*f* -	*f* -	2	2	13
	PS-00001-0.9	Shenandoah River	Ib	ns		▽	-1.30E-03	*f* -	*f* -	2	5	26

Zinc, Total and Dissolved

Measurements for both total and dissolved zinc are reported in the analysis database. Records for total zinc (Zn) begin in the 1970s at 23 of the 26 stations but stop for the most part between 1985 and 1995. Routine sampling begins again in 1996, but then stops in 1999. Many measurements fall below MDLs (censoring Types b and c), so the data cannot be tested for flow-adjusted trends. Due to the abbreviated, uneven sampling record and the high number of MDL measurements, total Zn data were classified as Type IVb or IVc (or, in the case of Elk River and Tug For, Type IIb) and the Peto-Peto step test method was applied. Records for dissolved Zn are sporadic until routine sampling began in 1999. More than 5% of measurements at all the stations are below MDL, causing all the trends to be classified Types IIIb or IIIc. Trend results are shown in **Table 28.**

Zinc (Zn) is an essential trace element and naturally present in low concentrations in streams and rivers. Higher concentrations are found in agricultural fertilizers, fungicides and insecticides, and in industrial waste water associated with the mining of silver, lead, and other metals as well as coal mining. Elemental zinc itself is not a pollutant, but in compound forms zinc can become toxic in aquatic organisms. The presence of zinc in a water sample will likely represent mining or agricultural inputs into the sampled system. West Virginia has dissolved zinc criteria that are calculated using water hardness.

For the 2009-2012 timeframe, median and even maximum concentrations cannot be reliably calculated for total or dissolved Zn because more than half of the measurements at too many stations are below MDL. The percent of samples with maximum values above the MDL was used to indicate which stations have particularly high concentrations of dissolved Zn. West Fork, Cheat (mile 3.5), and Tygart Valley have the highest percentages of samples exceeding MDLs, with 65.9%, 21.4% and 14.6%, respectively. Thirteen stations did not exceed the MDL in the 2009-2012 timeframe: Elk, Hughes, Lower and Upper Kanawha, Middle Creek, Twelvepole, Gauley, Greenbrier, Lower Guyandotte, Lower New, Upper New (mile 96.2), Cacapon, and Shenandoah.

Long-term trends. Most of the abbreviated long-term trends in total Zn were non-significant. Concentrations in Upper Monongahela, West Fork, and Cheat (mile 30) decreased significantly and concentrations in Upper Kanawha and Upper New (mile 67.4) increased significantly between the 1970s and 1999 ($p<0.05$).

Short-term trends. Most of the short-term trends in dissolved Zn were non-significant. Concentrations at five stations are decreasing signficantly: Upper Monongahela, West Fork, Gauley, Upper Kanawha and Lower New.

Table 28. Total zinc and dissolved zinc (Zn) trends, not adjusted for flow. Recent (1996 - 2012); long-term (1970s - 2012); slope (mg/liter/year); maximum (mg/liter, *mdl* indicates no samples exceeded the minimum detection limit, or MDL); % (percent of samples exceeding the MDL, usually 0.005 mg/liter).

			Total Zn			Dissolved Zn				
				Recent	Long-term		Recent		2009-2012	
Ecoreg.	Station	StreamName	Type	trend	trend	Type	trend	slope	max	%
Western Allegheny Plateau	MC-00001-3.5	Cheat River	IVb	-	-	IIIc	ns		0.015	21.4%
	KC-00001-11.6	Coal River	IVb	-	ns	IIIc	ns		0.005	3.8%
	ML-00001-20.6	Dunkard Creek	IVb	-	ns	IIIc	ns		0.05	4.7%
	KE-00001-4.3	Elk River	IIb	▿	ns	IIIc	ns		*mdl*	0.0%
	OGL-00001-2.8	Guyandotte River (Lower)	IVb	-	ns	IIIc	ns		0.008	4.3%
	LK-00025-1.5	Hughes River	IVc	-	ns	IIIc	ns		*mdl*	0.0%
	KL-00001-31.7	Kanawha River (Lower)	IVb	-	ns	IIIc	ns		*mdl*	0.0%
	LK-00001-28.9	Little Kanawha River	IVc	-	ns	IIIc	ns		0.008	4.3%
	OMN-00006-12.3	Middle Island Creek	IVc	-	ns	IIIc	-		*mdl*	0.0%
	MU-00001-99.4	Monongahela River (Upper)	IVb	-	▽	IIIc	▽	-5.44E-06	0.006	7.7%
	BST-00001-0.15	Tug Fork	IIb	ns	ns	IIIc	ns		0.011	4.2%
	OT-00001-8.8	Twelvepole Creek	IVb	-	-	IIIc	ns		*mdl*	0.0%
	MT-00001-6.2	Tygart Valley River	IVb	-	^	IIIc	ns		0.021	14.6%
	MW-00001-12	West Fork River	IVb	-	▽	IIIb	▽	-1.33E-05	0.034	65.9%
Central Appalachians	MC-00001-30	Cheat River	IVb	-	▿	IIIc	v	-3.42E-06	0.005	3.1%
	KG-00001-8.25	Gauley River	IVb	-	ns	IIIc	▿	-1.59E-05	*mdl*	0.0%
	KNG-00001-1.6	Greenbrier River	IVc	-	ns	IIIc	ns		*mdl*	0.0%
	OGL-00001-74.1	Guyandotte River (Lower)	IVb	-	-	IIIc	ns		*mdl*	0.0%
	KU-00001-74.1	Kanawha River (Upper)	IVb	-	▲	IIIc	▿	-2.88E-05	*mdl*	0.0%
	KNL-00001-1.2	New River (Lower)	IVc	-	ns	IIIc	▿	-2.54E-05	*mdl*	0.0%
	KNU-00001-67.4	New River (Upper)	IVb	-	▴	IIIc	ns		0.055	4.0%
	KNU-00001-96.2	New River (Upper)	IVb	-	ns	IIIc	ns		*mdl*	0.0%
Ridge & Valley	PU-00010-6.1	Cacapon River	IVc	-	▿	IIIc	ns		*mdl*	0.0%
	PL-00014-2.2	Opequon Creek	IVb	-	ns	IIIc	ns		0.007	6.9%
	PSB-00001-13.4	South Branch Potomac River	IVc	-	ns	IIIc	ns		0.009	3.4%
	PS-00001-0.9	Shenandoah River	IVc	-	ns	IIIc	ns		*mdl*	0.0%

Discussion

Flow adjustment

Flow adjustment is done to eliminate flow as a source of variability in concentration and facilitate the detection of trends. Both this study and the ORSANCO (2008) study used the residuals from log-log regressions between daily flow and water quality parameter concentration to flow-adjust data. ORSANCO (2008) used a linear regression through their data to calculate the residuals because the residuals met normality assumptions for linear regressions. These assumptions were not met for a majority of station-parameter combinations in this study, so the data for each station were flow-adjusted by calculating residuals from non-linear, Locally Weighted Scatterplot Smooth (LOWESS) curves. LOWESS requires no distributional assumptions for its validity.

In most cases where flow adjustment was possible, comparisons of flow-adjusted and unadjusted trends showed no overall differences. Trends were conclusively different in only nine long-term and twelve short-term comparisons of the 503 possible paired comparisons. Either the station's flow-adjusted trend in a parameter was significant at $p<0.01$ and its unadjusted trend was non-significant at $p<0.10$, or *vice versa*. At least twelve of these 21 divergent comparisons could be due to incomplete flow records in some rivers, which abbreviated the trend periods of flow-adjusted data at four stations: New River (KNL-00001-1.2, KNU-00001-67.4), Tygart Valley (MT-00001-6.2), and Tug Fork (BST-00001-0.15).

Regional parameter trends

Approximately 74% of possible tests for long-term trends and 35% of possible tests for short-term trends were significant at $p<0.05$ or showing strong directional tendencies ($0.05<p<0.10$). At nearly all monitoring stations, long-term trends were increasing for alkalinity and pH and decreasing for total phosphorus, total suspended solids, and the metals aluminum, iron, manganese, and lead. Short-term trends in these same parameters were often weaker or not significant, suggesting rates of change in the parameters may be slowing down at many stations or variability in the recent period is large enough to mask the underlying trends. Short-term trends in water hardness and to a lesser extent dissolved oxygen are increasing statewide whereas their long-term trends were mixed.

The AWQM network sampling sites can be grouped by shared characteristics, such as ecoregion or river basin, and examined for overall trends within a group. Each water quality parameter's general direction of change within a group can be summarized using the following approach, which mimics the one used by ORSANCO (2008):

$$\frac{\Sigma\,(N\,pos_{p<0.01}*2 + N\,pos_{0.01<p<0.05} + N\,pos_{0.05<p<0.1}*0.5) + (N\,neg_{p<0.01}*-2 + N\,neg_{0.01<p<0.05}*-1 + N\,neg_{0.05<p<0.1}*-0.5)}{N\text{ of possible trends}}$$

The approach sums the number of increasing and decreasing station trends weighted by the significance level of each trend result and divides by the total number of possible trends. Positive trends with significance levels of $p\leq0.01$, $0.01<p\leq0.05$, and $0.05<p\leq0.10$ are weighted by the factors 2, 1 or 0.5, respectively. Negative trends with significance levels of $p\leq0.01$, $0.01<p\leq0.05$, and $0.05<p\leq0.10$ are weighted by the factors -2, -1, and -0.5, respectively. Non-significant results ($p>0.10$) are assigned a value of zero (0).

Grouped by ecoregion Stations were grouped by the three Level III ecoregions in which they were located: the Ridge & Valley, Central Appalachians and Western Allegheny Plateau. The group trend approach was applied to both long-term (**Figure 5**) and short-term or recent (**Figure 6**) flow-unadjusted trends for each water quality parameter. In the long-term, 43-year period between 1970 and 2012, all three ecoregions show substantial declines in the metals aluminum (Al), iron (Fe), manganese (Mn), and lead (Pb) and in total suspended solids (TSS) and total phosphorus (P). All three ecoregions show increases in hardness, pH, dissolved oxygen (DO), alkalinity (TALK), sodium (Na), total dissolved solids (TDS) and specific conductivity. Coliform levels and potassium (K) increased substantially in the Ridge & Valley group and decreased substantially in Central Appalachians and Western Allegheny Plateau groups. Sulfate (SO_4) decreased substantially in Ridge & Valley group but trends were insubstantial in the other two groups. Chloride (Cl), nitrate-nitrite (NO_2-NO_3) and zinc (Zn) trends were insubstantial and mixed in all ecoregion groups.

In the ecoregion-based group trends for the recent 17-year period between 1996 and 2012 (**Figure 6**), increases in hardness, pH, and DO were substantial in all three ecoregions, which echoes the long-term

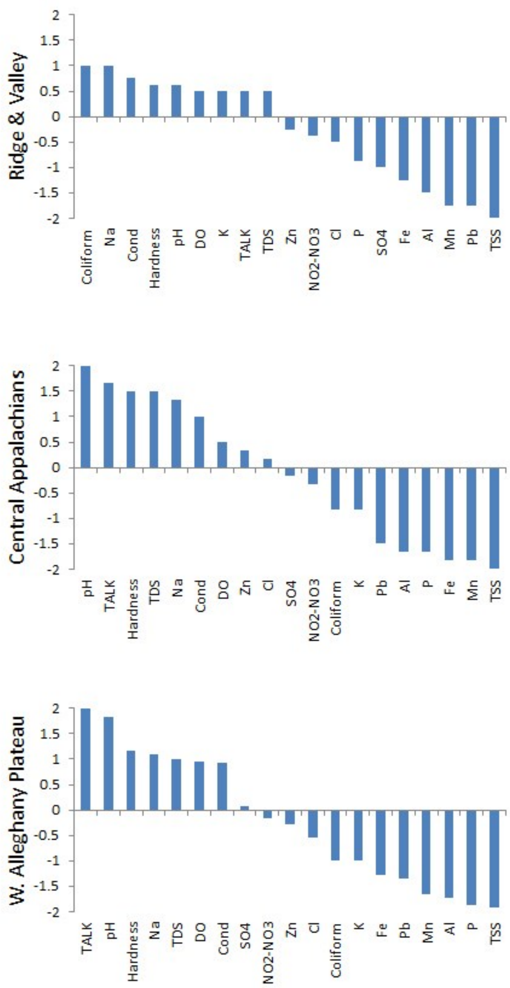

Figure 5. Long-term (1970-2012) trend summary, with stations grouped by ecoregion. See text for parameter abbreviations.

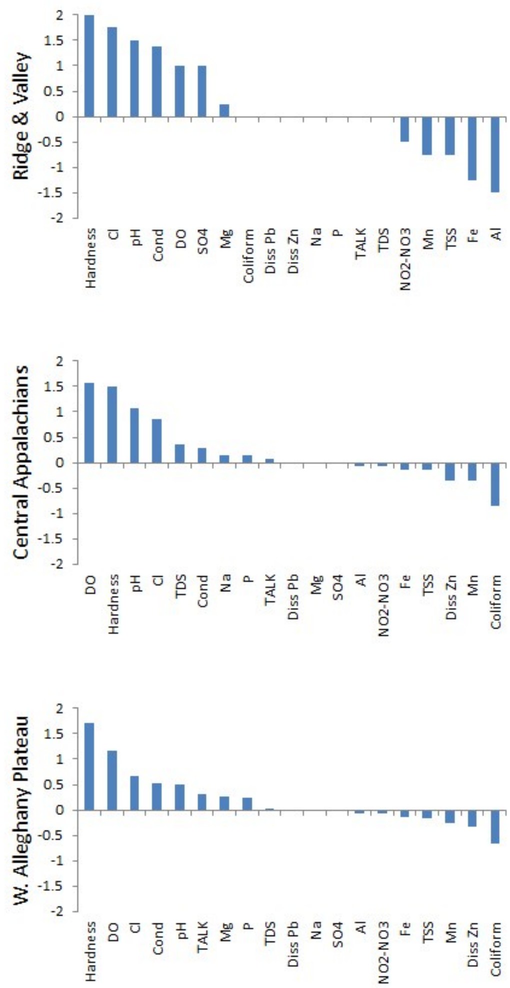

Figure 6. Recent (1996-2012) trend summary, with stations grouped by ecoregion. See text for parameter abbreviations.

trends in these parameters. Short-term trends in the remaining water quality parameters differ to varying degrees from their long-term trends. In all three ecoregions, recent group trends in Cl are increasing strongly, which counters their weak/non-significant long-term trends. Long-term declining group trends in Mn, Fe, Al, TSS and TP are either considerably weaker or not evident over the short-term in one or more ecoregions. Similarly, the increasing group trends in TALK, Na, TDS, and Cond over the long-term are weaker or not evident over the short-term in one or more ecoregions. In the Ridge & Valley ecoregion, the long-term SO_4 group trend reversed direction and has been increasing over the short-term. In some cases, differences between short- and long-term group trend results may be due to inherent variability in the data that can mask short-term trends. In other cases, distinct changes appear to be occurring in the short-term period that eventually could negate the long-term trend (**Appendix C**).

Grouped by river basin Stations were also grouped by river basin and their group trends calculated for this configuration (**Table 29**). Four West Virginia river groups empty to the Ohio River mainstem: the Monongahela River and its tributaries (includes Dunkard, West Fork, Tygart Valley, and Cheat), the Little Kanawha-Middle Creek- Hughes rivers, the Kanawha River and its tributaries (includes Coal, Elk, Gauley, New and Greenbrier), and the Guyandotte-Twelvepole-Tug Fork rivers. A fifth river group empties to the Potomac River mainstem and is synonymous with the Ridge & Valley ecoregion group. Although the comparison is coarse, some parameters showed state-wide similarities. The short-term group trend directions (or lack of direction) in Mg, Cl, NO_2-NO_3 and SO_4 generally agree, suggesting broad, regional changes in these parameters may be occurring. Mixed, and even opposing, short-term group trends are evident in hardness, TP, TSS, Al, Mn, and Fe, suggesting that local watershed sources and activities may have greater influence on the short-term trends of these parameters.

Table 29 provides the group trends for ten parameters in the Ohio mainstem (visually estimated from Figure 13 in the ORSANCO 2008 report). Despite differences in trend period and p-value significance thresholds, group trends for some parameters in the ORSANCO trend report for the Ohio River mainstem (ORSANCO 2008) can be generally compared to the recent (1996 - 2012) group trends at West Virginia AWQM stations. The ORSANCO study period was 1990-2007, and their analysis used a p-value of 0.10 rather than 0.05 to determine the significance of individual station-parameter trends.

Table 29. Short-term group trends in 10 parameters for the Ohio mainstem (estimated from Figure 13 in ORSANCO 2008), the four river groups emptying into the Ohio mainstem, and the Potomac River group. Positive (increasing) group trends are orange; negative (decreasing) group trends are blue. Increasing color intensity signifies stronger trends. See text above for details.

Parameter	Ohio mainstem	Monongahela	Middle-Hughes-Little Kanawha	Kanawha	TugFork-Twelvepole-Guyandotte	Potomac tributaries
Mg	1.7	1.00	2.00	1.78	2.00	0.25
Cl	1.5	0.58	0.17	0.00	0.25	1.75
Hardness	0.95	0.00	-0.50	-1.06	-1.25	2.00
TP	0.8	-0.08	-0.50	0.00	0.13	0.00
SO4	0.75	0.50	0.00	0.56	0.50	1.00
NO3-NO2-N	0.1	0.00	0.00	0.11	0.00	-0.50
TSS	-0.7	-0.17	0.00	0.39	0.13	-0.75
Al	-0.7	0.00	0.00	0.00	0.00	-1.50
Mn	-0.9	0.00	0.00	0.22	0.50	-0.75
Fe	-0.95	0.83	0.83	1.89	1.00	-1.25

Station trends

Four West Virginia AWQM stations stand out as having high parameter concentrations, as well as highly variable concentrations over time and large numbers of significant long-term trends ($p<0.05$) despite the variability: Coal, Dunkard, Tug Fork and West Fork. These stations are experiencing broad changes across many parameters. They are all located along the boundary between the Central Appalachian and Western Allegheny Plateau ecoregions which runs northeast-southwest through the middle of the state (**Figure 1**). The Upper Monongahela, the two Lower Guyandotte River stations and the Opequon show these same characteristics to a slightly lesser degree. Six stations stand out as having comparatively few significant long-term trends ($p<0.05$) and parameter values that tend not to vary a lot: Cacapon, South Branch Potomac, Shenandoah, Greenbrier, Elk, and Middle Island. The first four stations are located in karst-influenced watersheds along the eastern boundary of the state. Aquatic environments at all six stations could be considered relatively stable and predictable, regardless of their status. Trends for all parameters are provided by station in **Appendix E**.

Long-term, significant increasing trends in pH (**Table 22**) have occurred at all AWQM stations in the Western Allegheny Plateau and Central Appalachians. Short-term trends in pH are weaker but still trending upward overall and pH is shifting into the desirable range of 6 - 9 PSU. Some station trends are steep (Cheat mile 30, West Fork) while others are more gradual (Lower New, Lower Kanawha, Gauley). In the karst-influenced Ridge & Valley ecoregion, pH at all four stations dropped precipitously in the 1970s and early 1980s and then rose slowly over time to levels approaching those in the early 1970s (**Appendix C**). Hence, short-term trends are evident in this ecoregion but not long-term trends. All stations currently have minimum pH levels of 5 SU or higher. The statewide increases in pH suggest the trends are due in part to acid rain abatement. Fossil fuel combustion and atmospheric deposition of sulfuric acid (H_2SO_4) and nitric acid (HNO_3), the principal components of acid rain, were responsible for widespread acidification of lakes and streams across eastern U.S. in the late 20th century. The 1990 Clean Air Act and later regulations successfully reduced atmospheric deposition of the acids. The steep trends in pH at stations such as the Cheat (mile 30) and West Fork suggest other factors are responsible for the changing pH levels there. One possibility is the large number of acid mine drainage remediation projects that have been implemented in the past 40 years.

Given the widespread increases in pH coincident with reduced atmospheric deposition of sulfuric and nitric acids, one might expect widespread downward trends in ambient sulfate (**Table 26**) and nitrate-nitrite (**Table 19**) concentrations in West Virginia streams and rivers. This was not the case. Fewer than half of all AWQM stations show long-term or short-term downward trends in either sulfate or nitrate-nitrite, and several stations show significant increases in one or both parameters, even as their pH values rose. Short-term trends are non-significant for the most part, and ambient sulfate concentrations are generally high and highly variable in the mountain top mining areas of the state. Declining ambient concentrations of sulfate and nitrate-nitrite may explain the pH increases at some stations, but they do not explain the widespread rise in pH across the state.

Like pH, long-term increasing trends in alkalinity are occurring at all AWQM stations in the Western Allegheny Plateau and Central Appalachians ecoregions (**Table 6**). Short-term trends are weaker but still trending upward overall. Trends are steep at stations downstream of heavily mined regions (e.g., Coal, Tug Fork, West Fork) and more gradual at other stations (Lower New, Greenbrier, Gauley). In the Ridge & Valley ecoregion, all stations had relatively high alkalinity levels, which would be expected in this karst-influenced region, and only one station exhibited a significant trend over the long-term. Alkalinity is comprised of bases, primarily carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) but also phosphate (PO_4^{3-}), hydroxyl (OH^-), borates, silicates, and other bases. High concentrations of alkalinity increase a waterway's ability to neutralize acids. Biological nitrate uptake and sulfur reduction in streams and rivers can increase alkalinity levels to a certain extent, but bicarbonate inputs from the watershed are considered a major source of the acid neutralizing capacity of waters (Wetzel 2001). It has been known for a while that acid rain can increase the rate of carbonate weathering in watersheds, resulting in higher alkalinity concentrations in runoff (e.g., Kilham 1982). West Virginia's increasing trends in alkalinity are comparable to those calculated by Kaushal et al. (2013) for other eastern U.S. rivers and streams. These authors concluded that the increasing alkalinity trends were largely related to "human-accelerated chemical weathering [acid deposition], in addition to … mining and land use." A dynamic balance in the watershed between H^+ inputs from acid rain and alkalinity (bases) generated from chemical weathering caused by acid rain may be influencing all West Virginia streams and rivers to varying extents. The steep increasing trends at certain stations indicate additional factors are influencing pH and alkalinity trends at these sites.

Calcium and magnesium, the principal components of hardness, contribute to the stability of pH through their associations with the bases CO_3^{2-} and HCO_3^- and the formation of insoluble carbonates at high pH levels. Long-term trends in hardness are somewhat mixed but generally trending up (**Table 13**) while short-term trends are increasing, or tending to increase, at all but one AWQM station ($p<0.10$). Calcium and magnesium are leached from minerals through natural weathering or human-accelerated weathering (mining, acid rain) but also enter streams and rivers through the dissolution of cement-based construction materials, industrial waste, fertilizers, and flocculants in waste treatment plants. High levels of both calcium and magnesium are found in the Ridge & Valley ecoregion, where carbonate rocks can raise concentrations naturally (**Tables 8** and **17**). Very high concentrations and rapidly increasing trends are more likely linked to human activities.

Regardless of why pH, alkalinity, and hardness levels are trending upward in West Virginia streams and rivers, the higher levels appear to have increased the tendencies of certain dissolved metals to precipitate out of the water column. Long-term trends in total aluminum, iron, manganese, and lead concentrations are significantly down at almost all AWQM stations (**Tables 7, 15, 18,** and **16,** respectively). The alkali metals sodium and potassium are not as affected by pH or hardness and their salts are usually very water soluble. Overall, sodium long-term trends are generally increasing (**Table 24**) and potassium trends are relatively unchanging although some stations are trending downward (**Table 21**).

The primary components of hardness and alkalinity are included in measurements of total dissolved solids, which is the sum of all inorganic and organic substances suspended in water in molecular, ionized or colloidal forms that can pass through a filter. The cations (Ca^{2+}, Mg^{2+}, Na^+, K^+) and anions (HCO_3^-, CO_3^{2-}, SO_4^{2-}, Cl^-) that normally dominate the ionic composition of fresh water comprise most of the total dissolved solids in unpolluted waters (Wetzel 2001). Runoff and discharges to streams and rivers can substantially raise these and other ion concentrations and change their proportions. Long-term trends indicate an overall increase is occurring in total dissolved solids concentrations (**Table 10**). (Short-term trends in total dissolved solids are suspect due to the abbreviated 2008-2012 trend period.) The long-term

Table 30. Contingency table of long-term trends in total dissolved solids (TDS) and specific conductance. Inc, increase; ns, non-significant; Dec, decrease ($p<0.10$).

		Specific Conductance		
		Inc	ns	Dec
TDS	Inc	13	2	
	ns	1	4	1
	Dec			2

trends in total dissolved solids parallel the long-term trends in specific conductance (**Table 25**). Specific conductance measures water's ability to conduct electricity and the strength of the electrical conductance depends on the concentrations of all electrolytes, or dissolved ionic substances, in the water. A nearly 1:1 relationship is found between total dissolved solids concentration and specific conductance in the West Virginia AWQM data (r^2=0.92), and the station long-term trends correlate closely as well (**Table 30**).

One of the clearest patterns observed in this study is the coincidence between West Virginia areas experiencing coal extraction (**Figure 7**) and upward (degrading) trends and/or high levels of total dissolved solids, alkalinity, conductivity, hardness, and sulfates. Mining occurs primarily in the Central Appalachians and parts of the Western Allegheny Plateau. Many of the 26 AWQM stations are located within or downstream of the mining areas (compare **Figures 1** and **7**). The Coal and Tug Fork stations exhibit the highest concentrations amongst the stations that have increasing trends for these parameters. The Elk, Twelvepole, Gauley, and Upper Kanawha River stations are also trending higher, but at lower concentrations.

Unlike total dissolved solids, long-term trends in total suspended solids are declining statewide (**Table 27**). The majority of the declines may have taken place before the mid-1990s because recent total suspended solids trends (1996-2012) are for the most part non-significant. Visual examination of station time series for total suspended solids (**Appendix C**) tends to support this inference. Concentrations were

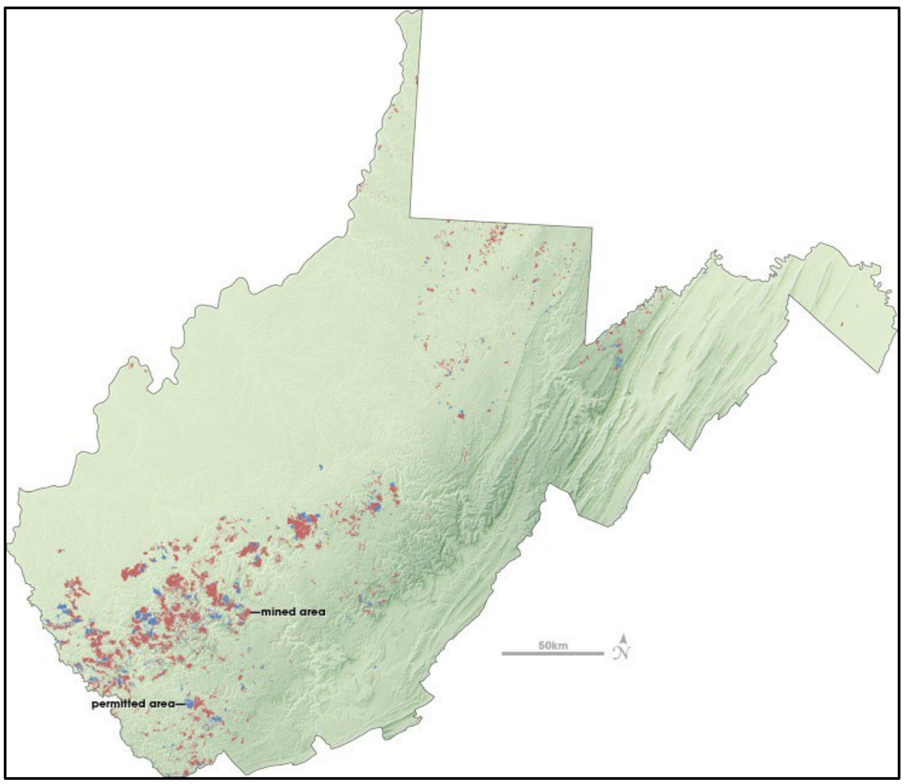

Figure 7. Areas of West Virginia affected by surface mining (light red) and additional areas that have been permitted but not yet mined (blue). [NASA map by Robert Simmon and Jesse Allen, based on topographic data from the Shuttle Radar Topography Mapping (SRTM) mission, and mine permit data from the W.V. Department of Environmental Protection.] Map downloaded from http://earthobservatory.nasa.gov/Features/MountaintopRemoval/ on 10/6/2014.

often more variable and had higher annual maxima in the 1970s – 1990s.

Long-term trends in total phosphorus are also declining statewide (**Table 20**). Total phosphorus is a measure of eutrophication in aquatic systems. Given phosphorus' affinity for particulate matter and the ease with which it precipitates with several cations (Al^{3+}, Fe^{3+}, Ca^{2+}), one could hypothesize that long-term trends in total phosphorus and total suspended solids would be closely related. However, they are not. Correlations between sample concentrations of the two parameters are highly significant ($p<<0.001$) but total suspended solids explains very little of the variability in total phosphorus ($r^2 = 0.046$). Also, median concentrations and trend slopes for the two parameters at the 23 long-term AWQM stations are not significantly correlated ($p<0.05$). The total phosphorus and total suspended solids declines may have been achieved largely independent of each other.

Concentrations of nitrate-nitrite, a large component of total nitrogen, are another indicator of stream eutrophication. As pointed out above, long- and short-term station trends in nitrate-nitrite are mixed (**Table 19**). They likely reflect the influence of multiple, divergent sources and loading rates of nitrogen. Fecal coliform concentrations are an indicator of human and animal organic waste entering streams and rivers. Long-term trends declined overall in the Western Allegheny Plateau and Central Appalachians but increased in the Ridge & Valley ecoregion (**Table 12**), which has four of the six fastest growing counties in West Virginia (http://www.indexmundi.com) and has experienced significant growth in the poultry industry in the past two decades.

Dissolved oxygen is sensitive to nutrient loadings and eutrophication and is considered a good indicator of stream habitat quality. Long-term dissolved oxygen trends are either non-significant or increasing, which suggests statewide efforts to reduce eutrophication and other anthropogenic impacts could be making some headway. The fact that recent, daytime DO concentrations are typically above 5 mg/liter is good; however, the widespread occurrences of super-saturated DO concentrations could be of concern.

Conclusions

The network of twenty-six (26) stations in West Virginia's AWQM program is intended to provide information for long-term trend analyses, general water quality assessments, and pollutant loading calculations for the state's larger rivers (WVDEP 2007). This report analyzed long-term (43-year) and short-term (17-year) trends in key water quality parameters, and identified significant trends in many of those parameters. The short-term trends helped to explain the lack of long-term trends in some instances and indicated that trend directions may be changing in other instances. Large databases such as the West Virginia AWQM network database have enormous potential to support correlative analysis and integrative assessments over different time periods. This study explored the data for just a few of the available parameters and examined only two of several possible trend periods.

West Virginia streams and rivers in areas undisturbed by mining, urbanization and agriculture appear to be recovering from acid rain impacts of the 20th century. Trends in pH are upward and fewer AWQM network stations now experience daytime pH values below 5 SU. Although some progress might be directly attributable to lower sulfur and nitrogen emissions, gradual long-term increases in alkalinity and hardness concentrations that are also occurring at these sites may have helped to improve pH levels. Accelerated weathering of minerals in the watershed by acid rain can increase alkalinity and hardness concentrations in runoff, raising and stabilizing pH levels. Higher pH and hardness levels increase the tendencies of certain dissolved metals to precipitate out of the water, and probably facilitated the long-term downward trends that were observed in aluminum, iron, manganese and lead.

Large areas of West Virginia have been impacted by coal mining practices. Stations in and downstream of the heavily mined areas of the state presently show some of the highest and most variable concentrations of alkalinity, hardness, total dissolved solids, specific conductivity, sodium, magnesium, and sulfates, and sometimes iron and aluminum. The affected stations often show significant long-term degrading (increasing) trends in these parameters as well. Coal, Tug Fork, West Fork, Dunkard, the Upper Monongahela are among the most notably affected sites.

Improving trends are seen in several important indicators of eutrophication. Long-term trends in dissolved oxygen concentrations are tending to increase statewide, and total suspended solids and total phosphorus are declining. Overall, nitrogen (nitrate-nitrite) and fecal coliform (an indicator of human and animal waste) are tending to decline, although a few stations show increasing trends in the short-term.

Recent (17-year) trends are non-significant more often than their long-term counterparts, suggesting that changes in certain parameters are leveling off. Leveling off can be expected in some cases. For example, the increasing trends in alkalinity can be expected to taper off, and may even begin to decrease, as acid deposition rates decline (Kaushal *et al.* 2013). Flow-adjustment indicates the 43-year and 17-year trend periods were long enough to overcome most of the flow-related variability that can mask short period trend results, and the seasonal trend tests applied to the data accounted for seasonal variability. At individual stations, additional efforts to connect water quality trends with historic and recent changes in management actions and nearby land use patterns may help to explain why some of the recent 17-year trends appear to be leveling off.

Some Possible Next Steps

The WVDEP database has data for up to 307 water quality parameters. Only twenty-four (24) water quality parameters were investigated in this trend report. Some of the parameters not analyzed in the study were collected over the course of just 1-2 years and/or only at a few stations (e.g., PAH's, hexavalent-chromium, mercury). Others were collected in just the earlier period (e.g., cyanide, fluoride, BOD5) or latter period (e.g., dissolved copper). All parameters could be investigated further to determine their usefulness as potential baselines of past conditions and whether step-trend analyses would be possible if monitoring was reinstated.

WVDEP started collecting water quality at many sites as early as the mid-1940's. If this older data could be assembled into a useable format, many interesting trend analyses could be conducted over a much longer timeframe than that covered in this report.

Reinstating bi-monthly monitoring at discontinued AWQM stations could produce a substantial number of new long-term, step trends for several parameters. Between 1970 and 1984, the monitoring program had twenty-seven (27) more monitoring stations than the current program, giving that time period much greater spatial coverage. Other stations were sampled for other, shorter time periods (e.g., pre-1970s, 1978-1984, 1975-1978) and then discontinued. If sampling were reinstated at some of these previously sampled stations for five or six years, WVDEP would be able to calculate a much greater number of long-term step trends, which would significantly expand the monitoring program's spatial coverage in the state *and* enhance the potential for correlative analysis and integrative assessments. A review of the station locations should indicate their potential value to the program's current objectives.

Integrative assessments of individual sites are perhaps the most intriguing use of the large AWQM database. Causal relationships and responses to management action can be investigated using the database and its large array of parameters in conjunction with geospatial (GIS) data layers. For example, long-term trends suggest that acid rain abatement is a causal factor in the increasing trends in pH and alkalinity; however, certain mining activities also increase alkalinity concentrations. Additional, site-specific analysis of land and water uses, atmospheric deposition, geology, and soils at sites least affected (e.g., Little Kanawha, Hughes, and Middle Island rivers in the Western Allegheny Plateau ecoregion) and most affected by mining activities could substantiate that concept and point to effective "best management practices."

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