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Effective Management Changes to Reduce Halogens, Sulfate, and TDS in the Monongahela River Basin, 2009–2019

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Abstract: The Monongahela River Basin has an extensive history of fossil fuel development, including coal mining and natural gas extraction. In late summer 2008, total dissolved solids (TDS) concentrations exceeding the United States Environmental Protection Agency′s (EPA) secondary drinking water standards were detected. After determining the source, a voluntary discharge management plan (VDMP) was developed by the West Virginia Water Research Institute (WVWRI) and implemented by the coal industry (2010). Additional remediation actions included Pennsylvania's prohibition of produced wastewater in publicly owned treatment facilities (2011) and construction of a reverse osmosis treatment facility (2013). We used a locally weighted polynomial regression in conjunction with a segmented regression to assess the discharge and concentration trends/changepoints for bromide, chloride, sulfate, and total dissolved solids at various locations relative to the three remedial actions. We detected significant ($\alpha < 0.05$) positive trends for discharge and significant negative trends for bromide, chloride, sulfate, and total dissolved solids. In conjunction, we also detected 1–4 changepoints within each model. Additionally, a linear mixed effects model containing discharge and remedial actions was used to measure the effectiveness of each remediation action in reducing TDS over time. Of the three remedial actions, the VDMP by itself was effective in maintaining river sulfate and TDS levels below the secondary drinking water standards (-0.12, p-value = 0.002). The combination of the VDMP with Pennsylvania's produced water prohibition (-0.16, p-value < 0.001) and the combination of the VDMP with the reverse osmosis treatment facility (-0.19, p-value < 0.001) were also effective. The use of all three remedial actions produced the strongest effect (-0.37, p-value < 0.001) Since the implementation of these changes, primarily the VDMP which encompasses most of the watershed, TDS in the Monongahela has not exceeded the EPA′s secondary drinking water standards. Future management decisions should include efforts to further expand the VDMP and to monitor changes in land use or severe changes in discharge.

Keywords: water quality management; total dissolved solids; discharge management; reverse osmosis; trend analysis; mixed effects model

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1. Introduction

The Monongahela River Basin, a 19,104 square kilometer watershed spanning north-central West Virginia, southwestern Pennsylvania, and western Maryland, has supported a variety of industrial uses throughout its history, most notably historic and present-day coal mining and contemporary oil and gas development. Mine discharges are major sources of sulfate and other salts in the Monongahela River Basin, while oil and gas developments are a major source of halogens such as chloride and bromide. The extent to which these industries have contributed to total dissolved solids (TDS) loading in the Monongahela River is of interest to researchers and water managers. Elevated TDS within the Monongahela River has been shown to impact drinking water during low-flow events [1]. Historically, TDS concentrations in the Monongahela River have exceeded the secondary drinking water standard of 500 mg/L only when flow drops below 2000 cubic feet per second based on

United States Geological Survey (USGS) flow data that were collected near Masontown and Elizabeth, PA. In late 2008, TDS began trending upward in the Monongahela River [2].

Prior to 2008, most of the mine drainage entering the Monongahela River came from deep mine discharges or surface mine seeps at pre-law abandoned mine sites [3,4]. Acid mine drainage (AMD) contains large quantities of TDS, including sulfate, calcium, magnesium, sodium, iron, aluminum, and manganese [5]. Active mines must treat discharged water to remove metals and neutralize acidity. However, treatment processes do not generally remove calcium, sodium, and sulfate ions. In this way, treated mine drainage also contributes to the Monongahela River′s TDS load. Drought conditions that result in low flows often exacerbate the problem by reducing the river′s assimilative capacity when mine discharges are not regulated by seasonal variations in flow [6]. Another potential source of TDS in the Monongahela River Basin is natural gas development which rapidly expanded starting in 2008. Notably, unconventional natural gas development, which utilizes horizontal drilling and hydraulic fracturing to target and extract natural gas from both the Marcellus and Utica Shale formations, has become more prevalent throughout the region right around the same time TDS began trending upwards [2].

In the late fall of 2009, the West Virginia Water Research Institute (WVWRI) sampled the Monongahela River and its major tributaries and determined that active deep coal mines were the most easily managed component of the TDS problem. WVWRI began working with major coal companies in the Upper Monongahela River Basin to implement a voluntary discharge management plan. The model accounted for the pumping capacities of the 14 major mine pumping and treatment plants in the Upper Monongahela River Basin using typical TDS concentrations as well as the flow in the Monongahela on any day [7]. It was designed to ensure the Monongahela River′s mainstem would not exceed the secondary drinking water standards for sulfate or TDS (250 and 500 mg/L, respectively). Operators of mine discharge treatment facilities voluntarily implemented discharge management in January 2010 and continue to this day.

In addition to AMD, a new source of TDS was emerging with the rapid expansion of unconventional oil and gas production in the Monongahela River Basin. From 2009 to 2011 there was sufficient evidence showing that the produced water from unconventional gas extraction was degrading surface waters and elevating TDS in Pennsylvania [2]. The point source for the degradation was identified as centralized publicly owned treatment works not being able to properly treat the produced water and discharging untreated wastewater into surface waters [8,9]. Contained within this produced water is a mixture of brine, toxic metals, and radioactive elements including chloride and bromide ions, which severely damage aquatic ecosystems [1,8,10]. The presence of chloride and bromide in source water can contribute to higher levels of disinfection byproducts such as trihalomethanes (THMs) and haloacetic acids in drinking water [11,12]. In addition, bromide in source waters can lead to a shift toward more carcinogenic brominated THM forms [13].

As a response to the disposal of produced water in publicly owned treatment works, the Pennsylvania state legislature passed a new regulation that went into effect on 1 May 2011, restricting the disposal of produced water into new public treatment facilities to eliminate produced water from making its way into Pennsylvania rivers and lakes [14]. Pennsylvania discharges of inadequately treated produced water ultimately contributed to higher TDS and bromide levels in the Pennsylvanian portion of the Monongahela River Basin before 2011 [15]. Prohibiting the improper disposal of produced water into publicly owned treatment works is likely to have helped alleviate some of the problems, but to what extent is currently unknown.

Another key point took place in the fall of 2009 at Dunkard Creek, a tributary of the Monongahela River, where a combination of low flows and disastrously high TDS concentrations resulted in a devastating fish kill. Improper disposal of produced water within deep mines and exceedingly low flows combined with traditional AMD discharges in Dunkard Creek led to a golden algae (*Prymneisum parvum*) bloom [16]. Nearly 30 miles of Dunkard Creek was impacted leading to the death of many aquatic organisms including 18 species of fish and 14 species of freshwater mussel [17,18].

Following the Dunkard Creek fish kill investigation, a coal mining company, which operates several active coal mines, was ultimately held responsible for the fish kill. The mining company was then tasked with constructing a new reverse osmosis treatment facility as a part of the legal settlement between the company and the PADEP [19]. The established AMD treatment facilities previously discharged their treated wastewater into smaller tributaries of the Monongahela River including Dunkard Creek. These tributaries flowed into the Monongahela River at various points spanning from the confluence of the Monongahela up to the West Virginia-Pennsylvania state border [20] (Figure 1). Construction of the new reverse osmosis treatment facility was completed in May 2013 with a stated objective of treating chloride content in receiving waters. Reverse osmosis treatment facilities are capable of desalinating and purifying waters that have been polluted because of fossil fuel extraction. Unlike passive treatment systems which typically use settling ponds and wetlands to naturally remove contaminants, reverse osmosis plants actively remove contaminants by forcing water through various types of semi-permeable membranes. Reverse osmosis can remove low molecular weight organics, multivalent ions, and monovalent ions which include sulfate, chloride, bromide, and other salts and metals that contribute to TDS [21–23]. TDS levels in the Monongahela River Basin have since decreased from their peak in 2008 and 2009, however to what extent the reverse osmosis facility has contributed to this decline is not currently known.

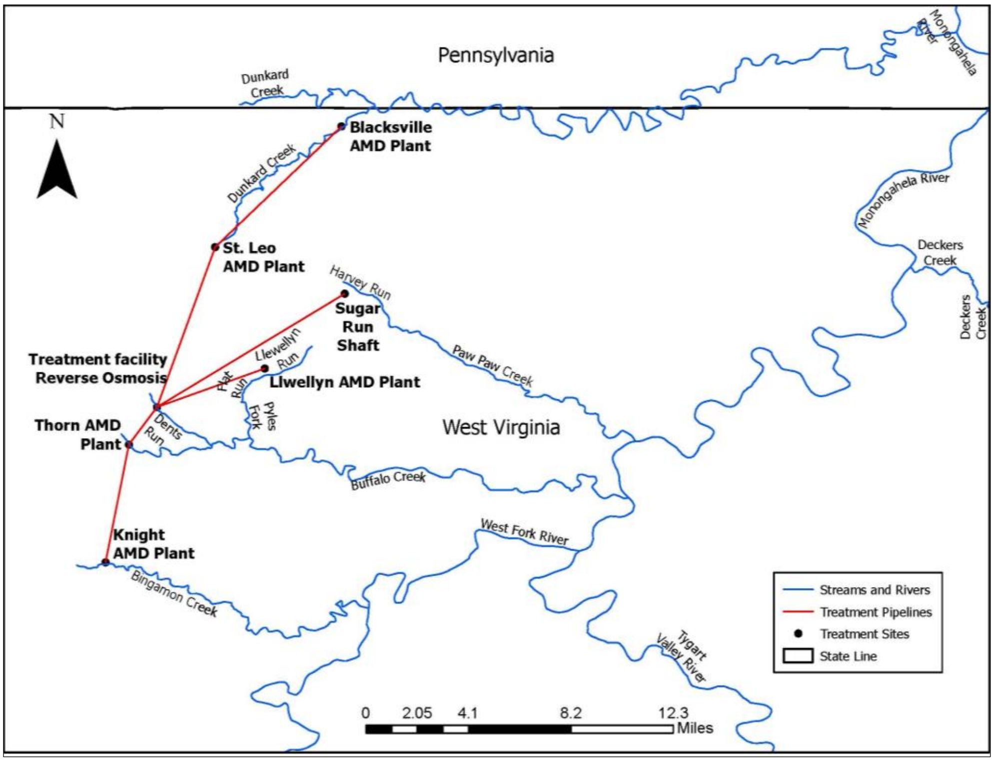

Figure 1. Location of the reverse osmosis plant relative to other AMD treatment facilities. Pipelines on the map are not representative of exact location.

In this study, we seek to evaluate the effectiveness of the voluntary discharge management plan in maintaining compliant TDS and sulfate concentrations in the Monongahela River. We also seek to evaluate the impacts of the Pennsylvania legislature restricting produced water in publicly owned treatment works and the reverse osmosis treatment plant. We attempted to quantify the trends and inflection points caused by the management decisions regarding the concentrations of halogens, bromide, and chloride, as well as the concentration of sulfate and TDS that result from the coal and natural gas industries in the Monongahela River and its tributaries from 2009 to 2019.

2. Materials and Methods

2.1. Study Area

Sampling sites were located throughout the Monongahela River basin which includes a drainage area of 19,104 square kilometers. The Monongahela River forms at the confluence of the West Fork and Tygart Valley rivers in Fairmont, WV, and flows northward 206 km to the confluence with the Allegheny River whereby it flows into the Ohio River in Pittsburgh, PA [24]. Of the 18 sites that are currently sampled within the Three Rivers Quest (3RQ) monitoring program, we selected 12 sites with datasets dating back to the summer of 2009. The reason for this date criterion is based on the voluntary discharge management plan initiation date of January 2010. Out of these 12 sites, 6 are located on the Monongahela River itself or the rivers that form the confluence while the other 6 sites are distributed among key tributaries (Figure 2). The mainstem and the tributaries of the Monongahela River are subject to coal mine AMD, and more recently unconventional gas extraction. Located throughout the Monongahela River basin is a network of private and state-run treatment facilities. The predominant treatment facilities are AMD treatment sites, many of which are enrolled in the voluntary discharge management plan (Figure 3). Other land uses within the Monongahela River basin that have potential impacts include agriculture and general urbanization.

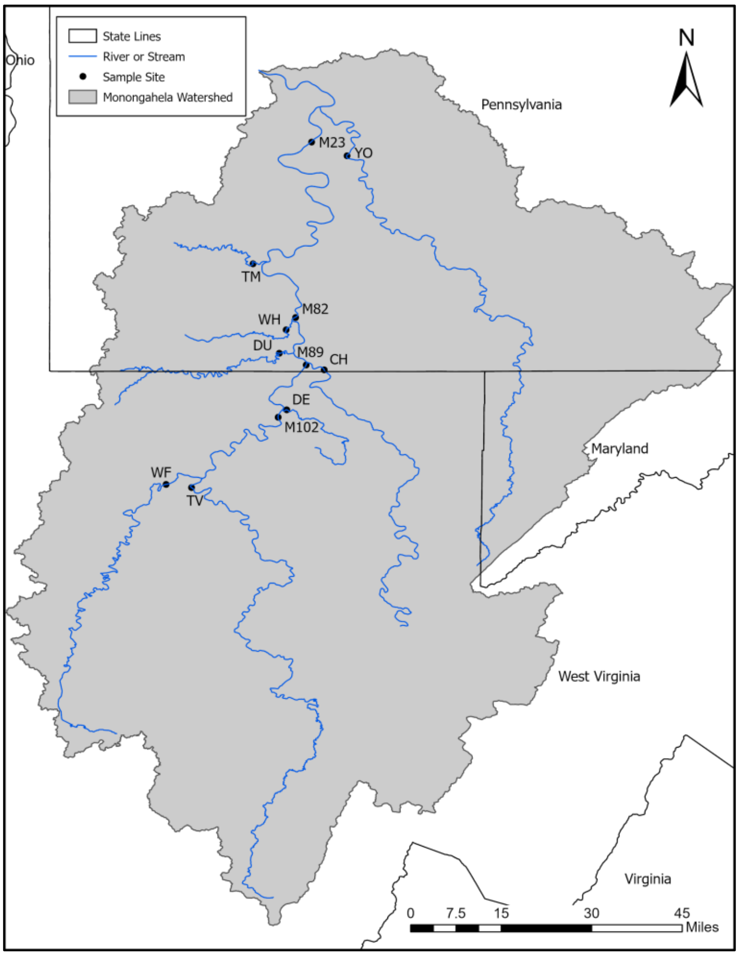

Figure 2. Location of all water quality sampling sites (n = 12) within the Monongahela River Basin.

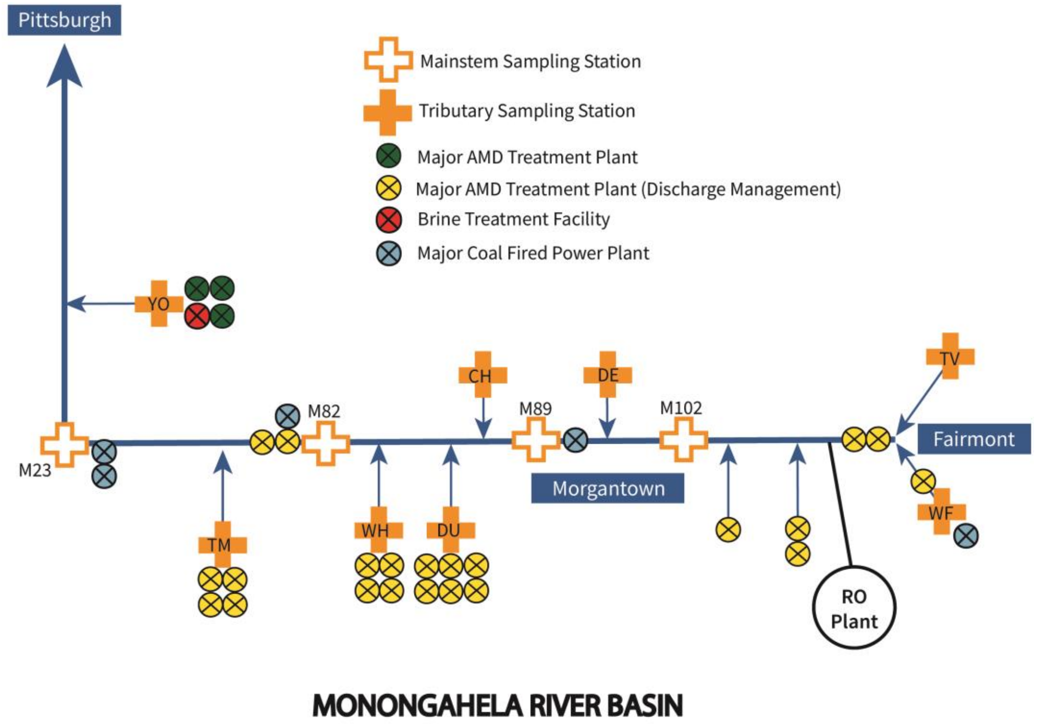

Figure 3. Subway map showing sampling sites relative to known pollution sources and treatment facilities. A key note is the brine treatment facility on the YO handles produced water.

2.2. Data Collection

2.2.1. Water Quality Data

Water samples and water quality parameters were collected and measured twice a month from July 2009 to April 2015. Beginning in May 2015, sample collection was reduced to once a month and took place between the 10th and 20th day of each month. We attempted to consistently collect water samples when the river/stream discharges were near their 30-year median as determined by the USGS.

At each site, 2 water samples were collected, one in a 500 mL unfiltered, unpreserved grab sample and a second 250 mL bottle with ~10 drops of nitric acid as a preservative. Prior to adding the raw water sample to the acidified bottle, the water was filtered using a Nalgene vacuum filtration device (Fisher Scientific) with 47 mm diameter, 0.45 µm pore cellulose filter papers (Millipore). All water samples were placed inside a cooler that was filled with ice and transported to either the laboratory for analysis or placed in a refrigerator until they were ready to be analyzed. Water samples were analyzed for dissolved alkalinity (mg/L $CaCO_3$ equivalents; EPA method SM-2320B); dissolved Al, Ca, Fe, Mn, and Na (mg/L; EPA method 60140B); and dissolved Br, Cl, and SO_4 (mg/L, EPA method 300). Temperature (Celsius), specific conductivity (µS/cm), pH, and calculated total dissolved solids (mg/L) were collected in the field via handheld water probes (YSI 556 and YSI Professional Series).

2.2.2. Hydrologic Data

Discharge (f/s^3) data were obtained from nearby USGS gauges at the time of sample collection. When direct gauge measurements were not available at a site, flow was estimated by averaging flow between an upstream and downstream gauge (Table 1).

Table 1. River and tributary discharge data sources and/or relative formulas used to estimate discharge based on known discharges.

Site	CFS Formula
Youghiogheny River (YO)	USGS Gauge 03083500
Monongahela River Mile 23 (M23)	USGS Gauge 03075071
Tenmile Creek (TM)	USGS Gauge 03073000
Monongahela River Mile 82 (M82)	USGS Gauge 03072655
Whiteley Creek (WH)	DU/2
Dunkard Creek (DU)	USGS Gauge 03072000
Cheat River (CH)	M82/2
Monongahela River Mile 89 (M89)	M82-WH-DU-CH
Deckers Creek (DE)	USGS Gauge 03062500
Monongahela River Mile 102 (M102)	M89-DE
Tygart Valley River (TV)	USGS Gauge 03056250 + USGS Gauge 03056250
West Fork River (WF)	USGS 03061000

2.3. Statistical Analyses

2.3.1. Water Quality Characteristics

Summary statistics, average, and standard deviation, were calculated for flow, bromide, chloride, sulfate, and TDS. Summaries were done on a site-by-site basis to show the variability among the mainstem and tributary sites.

2.3.2. Locally Weighted Polynomial Regression (LWPR)

Trend analyses are often used to determine if the measured water quality parameter is increasing or decreasing over a specified period. The basic linear trend model for a water quality series WQ_i is:

$$WQ_i = \alpha t_i + \beta + \varepsilon_i \tag{1}$$

where t_i is time, α is the regression coefficient indicating the slope of the line, β is the regression constant, and ε_{i} is an irregular noise term. LWPR uses either a local linear polynomial regression or a local nonlinear regression model depending on the circumstances [25]. For this study, a local linear polynomial regression model was used. The LWPR equation for all water quality series WQ_i is:

$$WQ_i = f(t_i) + \varepsilon_i \tag{2}$$

where $f(t_i)$ is a smoothed function and ε_i is an irregular noise term. LWPR was applied to all parameters within the dataset with local polynomial fits being first or second order using weighted least squares. This method gives more weight to points near the point whose response is being estimated and less weight to points that are further away [26]. Traditionally, the weighted function is the tricube weight function, but other functions are suitable if they meet the requirements. Additional information on the LWPR method that was used in this study can be found in Rajagopalan and Lall [27], and Proiettie and Luati [28]. We fitted the LWPR models in R using the “stats” package [29].

2.3.3. Segmented Regression (SegReg)

Segmented regression, also known as piecewise regression or broken-stick regression, is commonly employed with interrupted time series. While often employed in other fields of study such as political science, economics, and healthcare, segmented regression has shown to also be effective at evaluating the effectiveness of environmental pollution control measures [30–32]. Each segment in a segmented regression is separated by breakpoints (i.e., changepoints) with the least squares method being applied separately to each segment and optimized to minimize the sum of squares of the differences (SSD). For a water quality time series WQ_i with m change-points (CPs), a segmented linear regression with $m + 1$ is depicted as:

$$\begin{cases} WQ_i = \alpha_1 t_i + \beta_1 (t_i \leq CP_1) \\ WQ_i = \frac{\alpha_2 t_i + \beta_2 (CP_1 < t_i \leq CP_2)}{\vdots} \\ WQ_i = \alpha_{m+1} t_i + \beta_{m+1} (t_i \leq CP_m) \end{cases}, \tag{3}$$

where t_i represents time, α_m represents the regression coefficient for each line segment, and β_m is the regression constant. A positive α is indicative of an increasing trend while a negative α is indicative of a negative trend. To assess the overall trend, the average annual percent (AAPC) was calculated for each model based on the slopes of each segment and weighted based on the lengths of each segment [33]. Davies statistical test was used to determine the statistical significance of trend for each segmented regression model [34]. The adjusted R-squared value was also used to evaluate the model fit for each regression model. Models were fitted and evaluated in the statistical program R using the "segmented" package [35]. Additional information regarding segmented regression can be found in Mathews and Hamilton [36], Wu and Chang [37], and Muggeo [38].

2.3.4. Linear Mixed Effect Model

In addition to the LWPR-SegReg models, we also used a linear-mixed effect model to quantify the effect of management changes on TDS within the Monongahela River Basin. Discharge and TDS were log[x] transformed to achieve approximate normality. By including a random effect structure, we were able to account for site-specific characteristics that could potentially affect TDS on a site-by-site basis [39]. This was especially crucial given that not all management changes of interest were applied to all sites of interest. Furthermore, this modeling approach enabled us to determine the effectiveness of single management changes against the effect of several management changes. The optimal model was selected by comparing the global model to all possible parameterized models where we retained models with a ΔAIC > 2 [40]. We also assessed model performance by comparing marginal (variance explained by fixed effects) and conditional (variance explained by fixed and random effects) coefficients of determination (R^2). Reported p-values are based on Satterthwatie′s degrees of freedom method [41]. A similar approach has been used for predicting TDS based on discharge [6]. In addition, models that failed to properly converge, were unstable, or displayed singular boundary issues were disregarded. The 'lme4' [41] and 'lmerTest' [40] packages were used to create and extract model statistics. The 'MuMIN' package was used for model selection and for the calculation of R^2 values [42]. All analyses were performed in the Program R [29].

3. Results

3.1. Water Quality Characteristics

There was a high degree of variability in flow and concentration within and among the mainstem sites (Table 2). The mean flow steadily increased downstream with a range of 4003–9192 cfs. The maximum average for flow occurred at M23 (9192 cfs) which is the furthest downstream site among the mainstem sites. The mean bromide concentrations ranged between 0.01 and 1.01 mg/L across all sites. WH, TM, and DU reported the three highest average bromide values of 0.37, 0.35, and 1.01 mg/L, respectively. The mean chloride concentrations varied greatly from site to site (range = 3.5–132.9 mg/L) with the largest mean chloride concentrations occurring at WH, YO, and TM with values of 132.9, 59.5, and 57.3 mg/L, respectively. For sulfates, the mean concentrations throughout all sites ranged from 24.8 to 692.4 mg/L with the highest means recorded on DU (692.4 mg/L), WH (607.8 mg/L), and WF (190.0 mg/L). The mean TDS concentrations also varied greatly between each site with a range of 51.0–966.75. WH and DU displayed the largest mean TDS concentrations compared to all other sites with mean values of 966.8 mg/L and 922.5 mg/L, respectively.

Table 2. Discharge in cubic feet per second (cfs) and concentration (mg/L) averages with confidence intervals for all 12 sample sites. Mainstem sites are identified as 'M' followed by river mile, increasing upstream.

	Discharge	Bromide	Chloride	SO4	TDS
TV	2536 ± 406	0.01 ± 0.004	5.5 ± 0.37	26.5 ± 1.06	62.5 ± 2.13
WF	1061 ± 253	0.05 ± 0.017	14.9 ± 1.16	190.0 ± 11.57	334.0 ± 16.51
M102	4003 ± 650	0.03 ± 0.009	9.6 ± 0.58	89.3 ± 6.27	161.1 ±8.84
M89	4082 ± 649	0.04 ± 0.013	11.3 ± 0.67	95.4 ± 6.84	169.5 ± 9.53
M82	8949 ± 1478	0.04 ± 0.011	11.0 ± 0.73	88.1 ± 6.63	152.3 ± 9.08
M23	9192 ± 1486	0.07 ± 0.016	17.8 ± 1.20	90.6 ± 6.50	172.1 ± 9.58
DE	106 ± 22.4	0.02 ± 0.006	15.2 ± 1.27	102.6 ± 12.29	186.8 ± 16.93
CH	4541 ± 745	0.01 ± 0.003	3.5 ± 0.20	24.8 ± 1.03	51.0 ± 1.65
DU	338 ± 90.3	0.37 ± 0.082	56.2 ± 6.40	692.4 ± 117.5	922.5 ± 136.88
WH	172 ± 46.0	1.01 ± 0.208	132.9 ± 19.70	607.8 ± 73.17	966.8 ± 101.13
TM	169 ±45.2	0.35 ± 0.081	57.3 ± 6.93	157.0 ± 16.44	351.2 ± 25.98
YO	3485 ± 576	0.07 ± 0.020	59.5 ± 6.30	94.5 ± 5.24	242.6 ± 11.30

3.2. LWPR-SegReg Concentration Results

The LWPR-SegReg analysis of the concentration data resulted in the creation of 60 segmented regression models across 12 sites with each site containing a discharge, bromide, chloride, sulfate, and TDS segmented regression model (Appendices A and B). Within every LWPR-SegReg model, at minimum one breakpoint was identified and each segment was assigned a slope value with the overall trend being measured as average annual percent change (AAPC). Each model returned the estimated date(s) of the changepoint(s), the p-value as determined by Davie's test, and the adjusted R-squared value (Tables A1 and A2).

All concentration segmented regression models displayed significant trends with the alpha level being set at 0.05 (p-values ≤ 0.001). Following LWPR smoothing, the segmented models explained between 96 and 99% of variation. The AAPC values for discharge among all the mainstem sites were positive (range = 5.41–56.40) and the AAPC values for the tributary sites were also entirely positive (range = 0.76–27.97). Bromide AAPC among the mainstem sites presented negative values at M102 (−0.0002), M82 (−0.0003), TV (−0.0001), and WF (−0.0002) and positive values at M89 (0.0001) and M23 (0.0001). Additionally, bromide AAPC values for all tributaries were negative (range = −0.014–−0.0001). Chloride AAPC values were negative across all the mainstem and tributary sites (range = −1.47–−0.005). Sulfate AAPC values displayed negative values across all the sample sites (range = −10.761–−0.012) with DU (−10.761) displaying the largest negative AAPC value by far. Finally, TDS AAPC followed the same pattern as sulfate and chloride with negative values at all sites (range = −12.961–−0.012) with DU (−12.961) and WH (−6.281) possessing the largest negative values by far compared to all other sites (Figure 4).

The number of change points for each parameter varied (1 to 4 CPs) with most models possessing two change points (Figure 5). Regarding the discharge models, five out of the six mainstem sites displayed two changepoints with WF being an exception displaying three changepoints (Appendix A). All tributary sites displayed at least two change points within the discharge models (Appendix B). The first changepoints with regards to the discharge models are estimated to have occurred in 2011 while the second changepoint is often estimated to have occurred between late 2013 and the middle of 2014 (Figure 5). The bromide models routinely possessed a greater number of changepoints per model when compared to the other parameters. Dates for bromide changepoints vary between July 2010 and October 2016 with the majority of changepoints occurring between 2012 and 2014 (Figure 5). In comparison, each chloride model identified two changepoints with the first changepoint often occurring in 2012 and the second changepoint occurring in 2014. Sulfate models for the mainstem sites directly on the Monongahela River displayed a single changepoint that ranged between May 2011 and January 2014. However, the sulfate models for the tributaries displayed either one or two changepoints with the first changepoint falling between December 2010 and March 2012. For the sulfate tributary models that contained a second changepoint, it fell between May 2014 and July 2016. There was one exception with YO′s second sulfate changepoint taking place in April 2012. Finally, the TDS models showed two changepoints for four mainstem sites and all the tributary sites with M23′s TDS model detecting a single changepoint. The first changepoints for the mainstem TDS models fell between February 2011 and June 2013 and the second changepoints fell between November 2011 and June 2017 (Figure 5).

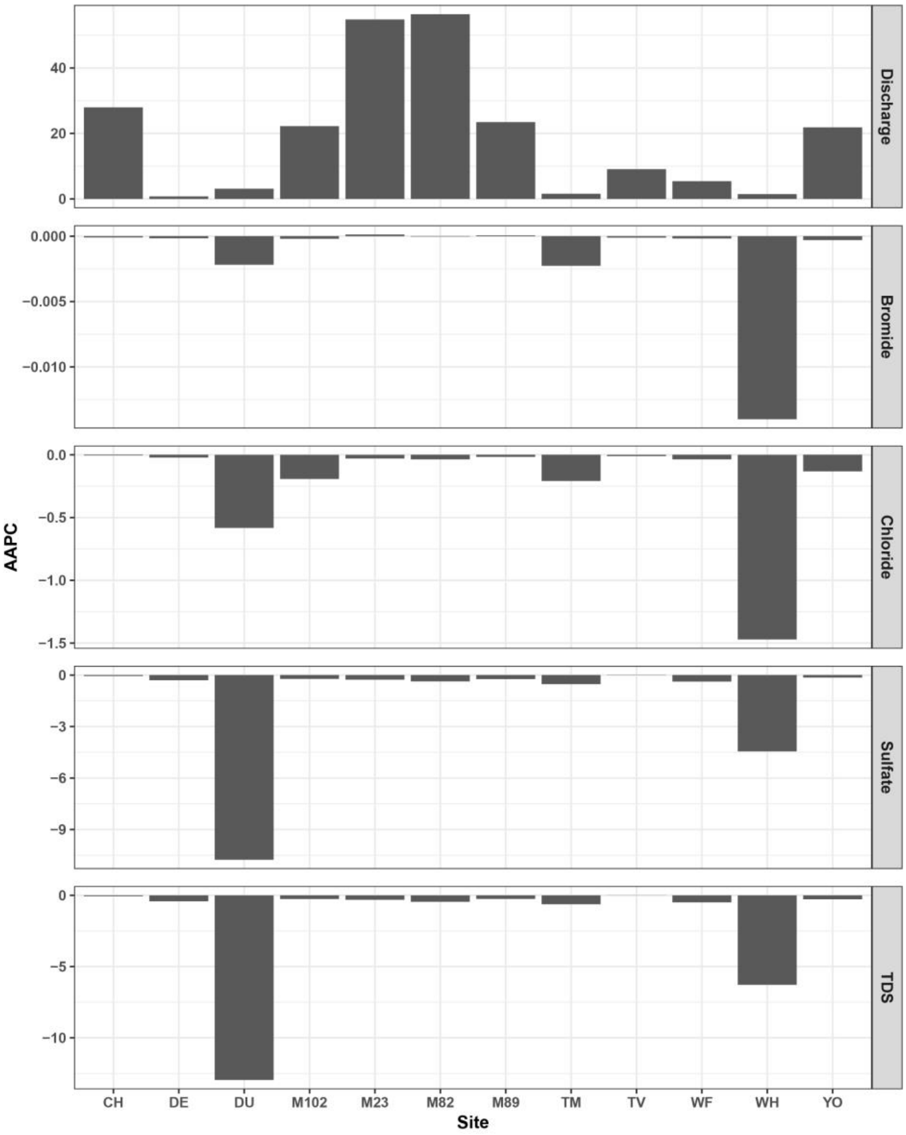

Figure 4. AAPC values across sites and parameters.

3.3. Linear Mixed Effects Model Results

The optimal model for estimating management changes related to TDS concentration included random intercepts and slopes among the sites (Figure 6). Discharge, year, and treatment(s) all had significant negative effects on TDS while the interaction between year and discharge had a significant positive effect (Table 3). All but one treatment type, PA's prohibition on produced water in POTWs (PA_Pro), displayed significant negative effects on TDS concentrations. Combined, the fixed and random effects explained 91% percent of the total variation in TDS (conditional R^2 = 0.91), whereas discharge, year, and treatment type explained 38% of the overall variation (marginal R^2 = 0.38).

Figure 5. Changepoints across all sites in relation to management events.

Table 3. Parameter estimates for the most optimal hierarchical linear mixed effects model predicting log[x] transformed total dissolved solids within the Monongahela River Basin. VDMP (voluntary discharge management plan), PA_Pro (Pennsylvania's prohibition on produced water in POTWs), VDMP_PA (combined treatments of the voluntary discharge management plan and Pennsylvania's prohibition on produced water in POTWs), VDMP_ROP (combined treatments with the voluntary discharge management plan and the reverse osmosis plant), VDMP_PA_ROP (combination of all three treatments).

Parameter	Estimate	SE	*t*-Value	*p*-Value
Fixed Effects				
Intercept	153.14	15.08	10.15	<0.001
Log[cfs]	−19.95	2.17	−9.21	<0.001
Year	−0.07	0.01	−9.68	<0.001
VDMP	−0.12	0.04	−3.10	0.002
PA_Pro	0.05	0.03	1.53	0.126
VDMP_PA	−0.16	0.04	−3.65	<0.001
VDMP_ROP	−0.19	0.05	−4.12	<0.001
VDMP_PA_ROP	−0.37	0.05	−7.93	<0.001
Log[cfs]:Year	0.01	0.00	9.08	<0.001
Random effects				
σ^1 | Site	1.36	–	–	–
σ^1cfs | Site	0.01	–	–	–
$\sigma^{Residual}$	0.09	–	–	–

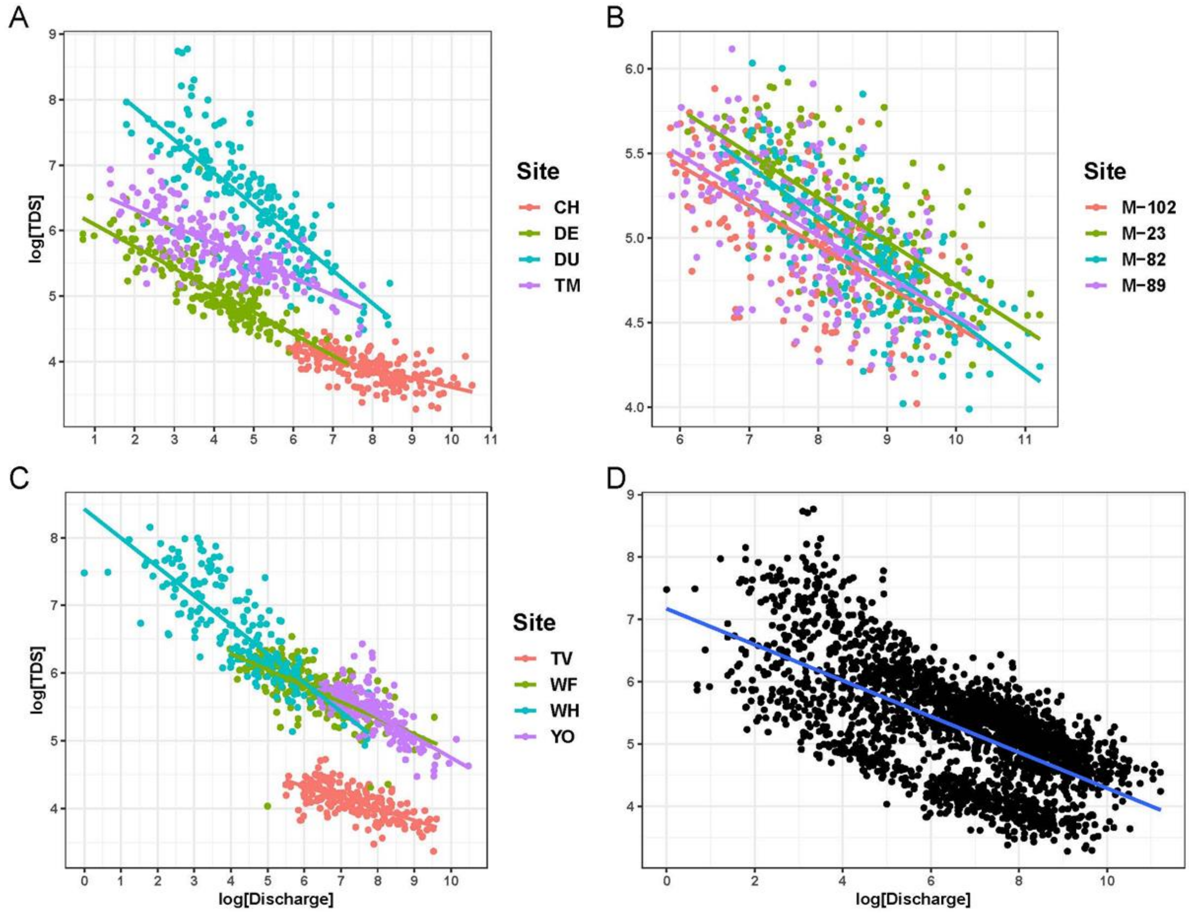

Figure 6. (**A**–**C**) Scatterplots of log-transformed TDS and discharge showing how slopes and intercepts vary based on the site. (**D**) Scatterplot showing the overall slope when all sites are combined into a single group.

4. Discussion

We showed temporal and spatial changes for bromide, chloride, sulfate, and TDS concentrations throughout the Monongahela River Basin, thereby providing valuable understanding of how the overall river basin is changing over time in relation to both discharge and various management decisions. Concentrations for bromide, chloride, sulfate, and TDS showed significant overall downward trends throughout the river basin. Most LWPR-SegReg models identified one or two changepoints over the 10-year time period which often coincided with the changepoints that were identified within each site′s discharge model. Bromide and chloride linear segments exhibited a delayed inverse relationship with their sites′ respective discharge segments. As discharge increased, bromide and chloride concentrations would often decrease and vice versa. By comparison, the sulfate and TDS models for the mainstem sites and some of the tributaries displayed permanent long-term downward shifts regardless of changes within the river or stream discharge following the implementation of the voluntary discharge management plan. After implementing the voluntary discharge management plan, sulfate and TDS concentrations failed to return to their pre-management plan levels. By comparison, bromide, chloride, sulfate, and TDS concentrations showed limited to no change or maintained their trajectories following Pennsylvania′s restriction of produced water into publicly owned treatment works and/or the opening of the reverse osmosis treatment facility.

We followed up the LWPR-SegReg trend analysis with a linear mixed effects model focusing solely on how TDS concentrations responded to changes in discharge over time as well as the various combinations of management decisions that were implemented throughout the Monongahela River Basin. TDS was most significantly affected by discharge, which has been well established by previous works [6,43,44]. However, TDS was also significantly reduced because of the management changes. More specifically, the voluntary discharge management plan was effective in reducing TDS, an effect that was enhanced by other TDS reduction measures. Specifically, Pennsylvania's prohibition of produced water in POTWs did not have a significant effect on TDS concentrations when it was the only management change in place. The reverse osmosis treatment facility was always paired with other management changes but appears to have played some role in further reducing TDS concentrations in the Monongahela River.

The effectiveness of the voluntary discharge management plan is demonstrated by the significant and sustained reduction in sulfate and TDS concentrations after its implementation in January 2010. While discharge varied spatially and temporally on a site-by-site basis, the sulfate and TDS reductions were consistent throughout the Monongahela River basin in streams that were affected by the discharge management plan. Similar management plans have been implemented by state and federal agencies as part of the Clean Water Act (CWA) to reduce various types of pollution and are referred to as total maximum daily loading (TMDL) regulations. The total maximum daily loadings regulations are a common and effective tool for point-source pollution and non-point source pollution that contributes to the impairment of water bodies such as rivers, lakes, and estuaries [45,46]. The voluntary discharge management plan is a non-regulatory TMDL that was developed and deployed by the West Virginia Water Research Institute in partnership with leaders from the coal industry within the Monongahela River basin. This TMDL targets sulfate and TDS originating from treated AMD discharges into surface waters by limiting treated AMD discharges during low flow conditions in the Monongahela River watershed [7]. The discharge management plan went into effect in January 2010 and is still employed as of publishing this study. The voluntary discharge management plan utilizes the large assimilative capacity that is provided by the Monongahela River during high flows to reduce sulfate and TDS concentrations. During low flows, AMD treatment facilities reduce their treated water discharge rates to match the assimilative capacity that is provided by the Monongahela River at these low flows [6,7]. AMD treatment facilities that are involved with the voluntary discharge management plan are distributed among the tributaries and the main stem of the Monongahela River (Figure 3). Our results indicate that the WVWRI voluntary discharge management plan was successful in significantly reducing sulfate and TDS concentrations in the Monongahela River almost immediately upon implementation. The results seen within the Monongahela River basin are just one example of the effectiveness of TMDL plans, both voluntary and regulatory as a tool for implementing the objective of the Federal Clean Water Act. For example, the Chesapeake Bay watershed uses a TMDL in conjunction with other remediation measures to control excessive nutrient loading that has had detrimental effects on the aquatic ecosystem [47]. Other examples include the implementation of TMDLs in the Middle Cuyahoga Valley and the Lynnhaven River to reduce nutrient loads and reduce fecal coliform, respectively [48,49]. In addition to the TMDL, managers and stakeholders in the Monongahela River basin have attempted to use additional remediation actions to further improve water quality.

The second change made to the Monongahela River Basin regarding water quality was Pennsylvania's prohibition of depositing produced water into publicly owned treatment works, effective May 2011. Based on the results from our study, this regulation had a very limited effect on reducing bromide, chloride, sulfate, or TDS concentrations among most sites. It did, however, appear to have reduced bromide concentrations at the TM and WH sites in Pennsylvania. The reduction in bromide concentrations at TM and WH is likely tied to the major publicly owned wastewater treatment facilities that are located along these two streams and their relatively low flows. While this regulation does not appear to have reduced chloride, sulfate, or TDS in a significant way, that is not to say that this regulation has not had a positive impact on water quality or aquatic ecosystems. Benefits of this localized reduction include lowering risks that are associated with excess bromide such as brominated disinfectant byproducts (DBPs) which are a known carcinogen and readily form when bromide concentrations are greater than 0.1 mg/L [8,50]. There is also evidence that produced water from hydraulic fracturing is detrimental to soil quality [51]. Additionally, produced water entering surface waters can impact the gill structures of fish leading to oxidative stress as well as potential liver damage when exposed to larger volumes of produced water [52]. Thus, limiting the volume of produced water entering surface waters does possess positive benefits for the environment.

The final watershed scale change of interest was the impact of opening a new reverse osmosis treatment facility in May 2013, located in Mannington, West Virginia. The results from our study showed limited significant reductions in chloride and TDS concentrations. Dunkard Creek (DU) was the lone site that displayed further downward trends in chloride and TDS concentrations following the opening of the treatment facility. This is to be expected due to the low assimilative capacity of Dunkard Creek based on median discharge and because several AMD plants that were discharging into Dunkard Creek are now sending their wastewater to a reverse osmosis treatment facility. However, when looking at the other sites where concentrations displayed changepoints following the opening of the reverse osmosis treatment facility, it was concluded that the changes more likely coincided with trend changes that were related to discharge. This pattern was observed across many sites, including sites that were not utilizing the reverse osmosis treatment plant which leads us to believe that increased stream or river discharge caused these changes via dilution and not via contaminant removal.

Reverse osmosis treatment facilities differ from TMDL-based waste load reductions and wastewater restrictions by physically removing contaminants from wastewater prior to final discharge and thus do not rely on the assimilative capacity of their receiving waters [21,22]. While a single reverse osmosis facility will have difficulty processing wastewater throughout an entire watershed, TMDLs are capable of being implemented at the watershed scale and are far more cost-effective. Reverse osmosis technology is difficult to implement on a wide scale largely due to the technological complexity and their capital and operating costs [53]. Reverse osmosis is most effective when removing highly soluble salts such as NaCl. However, they suffer from severe scaling when applied to low solubility salts such as $CaSO_4$, typical of AMD. Reverse osmosis facilities are best suited for treating large quantities of wastewater that are discharged to streams that lack the capacity to assimilate salts through natural processes. With real-world implementation, this is not always feasible and, depending on the scale, multiple reverse osmosis facilities may be required to match the effectiveness of other management decisions.

The observed downward trends in concentrations for all four parameters (bromide, chloride, sulfate, and TDS) throughout the Monongahela River Basin are important for improving ecosystem services and drinking water services. Decreasing bromide and chloride concentrations are particularly helpful as both these ions are key components in DBPs such as trihalomethane (THM) formation [8,50,54,55]. THMs are known to be carcinogenic and teratogenic to humans and thus the formation of THMs in drinking water has been linked to serious health risks including birth defects and various types of cancer in humans [56–61]. Chloride reductions are also important as elevated chloride concentrations in surface waters can lead to chronic toxicity impacts to aquatic organisms [62]. Elevated sulfate concentrations within underwater sediments can cause environmental degradation through acidification of significant reductions in dissolved oxygen within aquatic ecosystems [63]. Regarding drinking water, elevated sulfate can lead to a bitter taste, and at exceedingly high levels there is the potential to cause gastrointestinal problems in both humans and animals [64]. Sulfate and chloride ions are notorious for causing infrastructure damage to reinforced concrete as well [65]. Therefore, by reducing the sulfate concentrations in the Monongahela River basin, the risk of degradation to aquatic environments is reduced, the quality of the drinking water has improved, as well as lessening the potential infrastructure damage that is caused through sulfate-related corrosion. Reducing the sulfate concentration throughout the Monongahela River resulted in the river being officially delisted from sulfate impairment by the Pennsylvania Department of Environmental Protection

5 years after the implementation of the voluntary discharge management plant [66]. Finally, reductions in TDS concentrations throughout the Monongahela River basin provide key benefits to drinking water treatment facilities; benefits include better-tasting water, minimal odors, rand educed corrosion and scaling of pipes and boilers. In fact, TDS and sulfate concentrations within the Monongahela River proper, not including the West Fork and Tygart Valley Rivers, have not exceeded the EPA′s secondary drinking water standards since implementation of the Voluntary Discharge Management Program in January 2010. (Figure 7). In addition, reductions in salts that lead to increased surface water salinity are important for preventing harmful algal blooms such as the one that occurred in 2009 at Dunkard Creek [18]. The downward trends of these concentrations provide benefits for the short-term and long-term health of the Monongahela River Basin as well as the communities that rely on the river for various services.

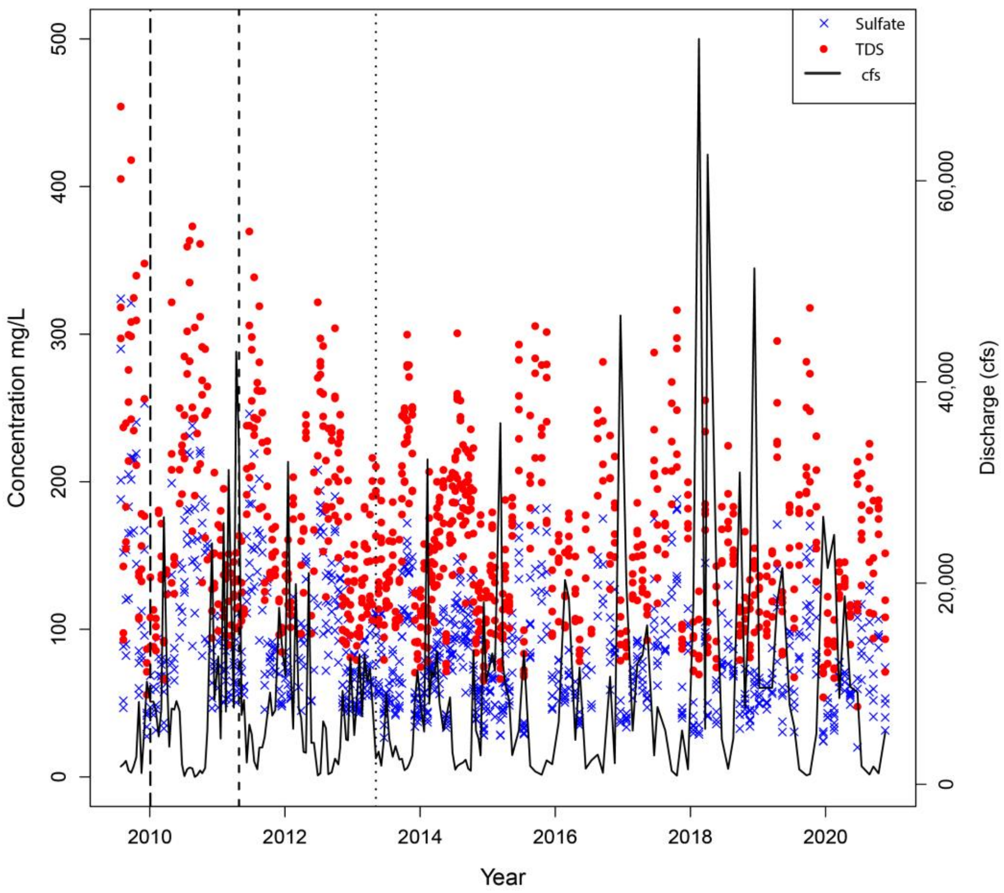

Figure 7. Observed sulfate and TDS concentrations from all four Monongahela River Mainstem (M102, M89, M82, and M23) sites with dashed lines representing the three key management changes.

Large datasets over long periods of time enable researchers and managers alike to conduct better observational studies and it also enables researchers to analyze river systems of interest over both temporal and spatial scales not often found in smaller datasets [67]. For example, trend analyses are often used to investigate temperature or precipitation change over time but the 3RQ dataset allows researchers to analyze a wide array of concentration changes over 10 years at consistent intervals, providing a level of detail that is not found in many water quality datasets. Previous studies have utilized the 3RQ dataset to create models that are of direct use to managers such as how flow impacts TDS concentrations as well as characterizing fossil fuel extraction activities in the Monongahela River Basin [1,5,6]. 3RQ has also enabled researchers to identify potential areas of concern for targeted studies that focus on a specific issue within any of the three watersheds or a specific location in the watersheds (3riversquest.wvu.edu/data/targeted-studies). Going forward, 3RQ provides a plethora of new opportunities for additional research focused on water quality improvement and watershed recovery. Similar analyses can be conducted for the upper Ohio and Allegheny rivers utilizing 3RQ data to better characterize trends in major ions that contribute to elevated TDS concentrations within these basins. Future research should focus on generating detailed, consistent long-term datasets for other major bodies of water and their contributing rivers to enable researchers and managers to better characterize contaminants of concern.

The methodology that was used for this study can be readily applied to other large water quality datasets to determine significant trends and when trend changes occurred relative to key dates or major changes to a system by managers. In addition, using the LWPR-SegReg method on interrupted or non-traditional time series datasets enables greater flexibility compared to traditional time series analysis with environmental datasets. A potential improvement for this methodology includes reducing the number of estimated discharges and instead using direct discharge measurements at as many sites as possible. This study also highlights the advantages of long-term monitoring datasets and the utility that they can provide to researchers and managers alike when investigating various pollutants.

Based on the results of our study, the Monongahela River Basin has seen a significant reduction in sulfate and TDS concentrations from 2009 to 2019. In addition to the sulfate and TDS concentration reduction, bromide and chloride concentrations have also either decreased or remained stable. These concentration reductions coincide with several management decisions, primarily the voluntary discharge management of treated acid mine drainage, followed by state legislation restricting produced water in public treatment facilities, and the construction of a new reverse osmosis wastewater treatment facility. While these management decisions have improved the water quality of the Monongahela River, future threats to the Monongahela River Basin including anthropogenic impacts through land use as well as changes in flow regime through the effects of climate change [6]. Examples of land-use changes include continued urbanization, expansion of unconventional gas extraction, increased acid mine drainage inputs, and reductions in treatment to acid-mine drainage. Climate change-related problems including increasing temperatures and increased probability of drought could leave the Monongahela River Basin vulnerable to low flow events. Continued monitoring of the Monongahela River and key tributaries will allow managers to respond faster to these changes and aid in the creation and implementation of future solutions.

5. Conclusions

The results from this study have demonstrated how bromide, chloride, sulfate, and TDS trend changes coincided with discharge and critical water quality management alterations to the Monongahela River Basin. While individual management decisions may be effective, combining multiple watershed-scale decisions targeting contributing constituents of TDS can lead to greater overall effectiveness. The Monongahela River Basin is a potential example for other watersheds actively managing coal mining and natural gas activities. However, effective management decisions need to first identify the various sources of TDS and its key constituents throughout the entire watershed. It is also important for managers to assess the assimilative capacity of their streams and rivers, especially during low flows, to protect the areas that are currently minimally impacted. Given limited assimilation capacity, the removal or prohibition of pollutants that contribute to TDS may be preferred. Further research will be necessary to determine the appropriate removal methods depending on the source of TDS within a given watershed. Future watershed management scenarios will need to take into consideration several factors, including but not limited to, new emerging pollutants, changes in land use, and climate change.

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Conflicts of Interest: The authors declare no conflict of interest.

Appendix A

The following figures show the results of the LWPR-SegReg models for the mainstem sites of the Monongahela River. Within each site discharge (cfs), bromide (mg/L), chloride (mg/L), sulfate (mg/L), and TDS (mg/L) were modeled and changepoints were estimated based on the segmented regression. Also included within the figures are key dates for each site, which may include the implementation of the voluntary discharge management plan, Pennsylvania's prohibition on depositing produced water into publicly owned treatment works, and the opening of a new reverse osmosis treatment facility.

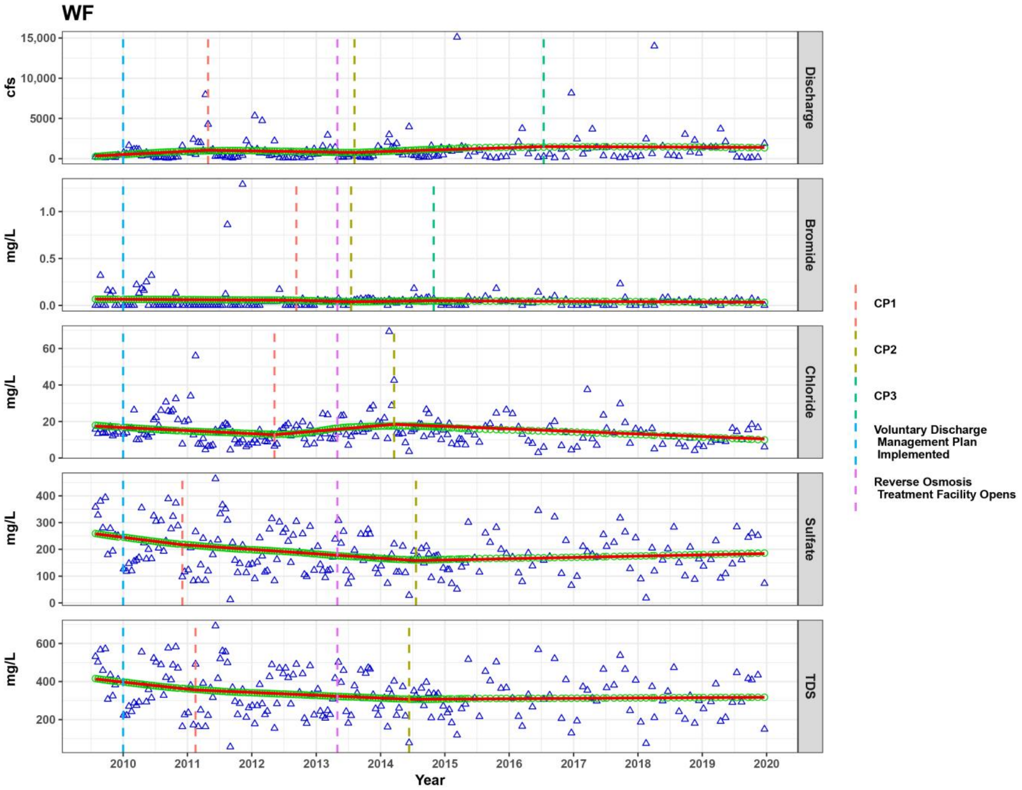

Figure A1. Model output for the West Fork River showing key dates and changepoints. Color coded dashed lines are key dates and changepoints, blue triangles represent the raw data, green circles represent the smoothed data from the locally weighted polynomial regression, and the red lines are the segments from the segmented regression.

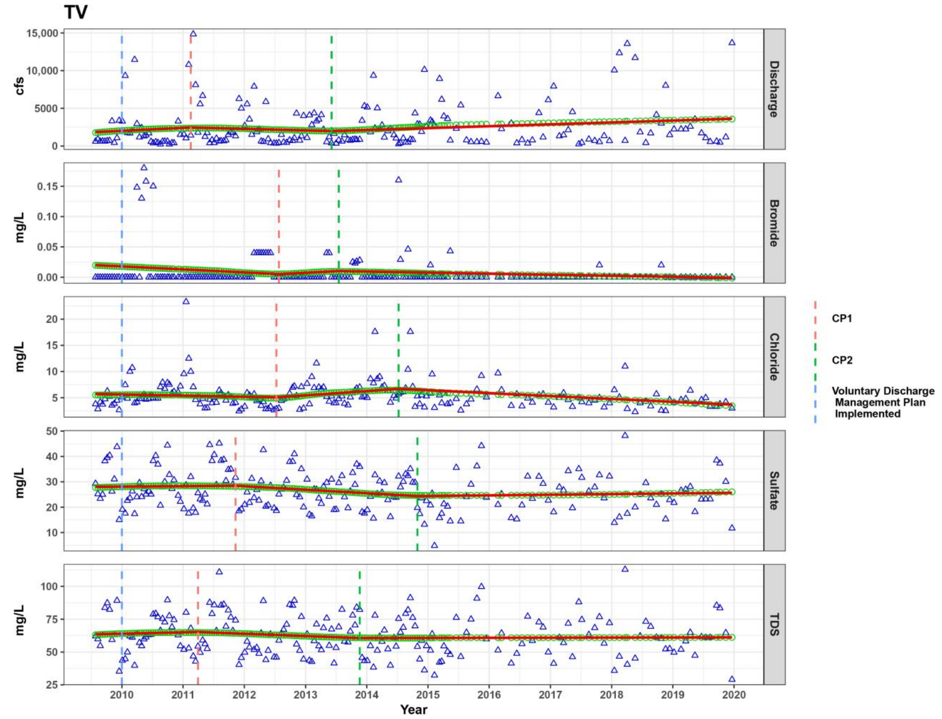

Figure A2. Model output for the Tygart Valley River showing key dates and changepoints. Color coded dashed lines are key dates and changepoints, blue triangles represent the raw data, green circles represent the smoothed data from the locally weighted polynomial regression, and the red lines are the segments from the segmented regression.

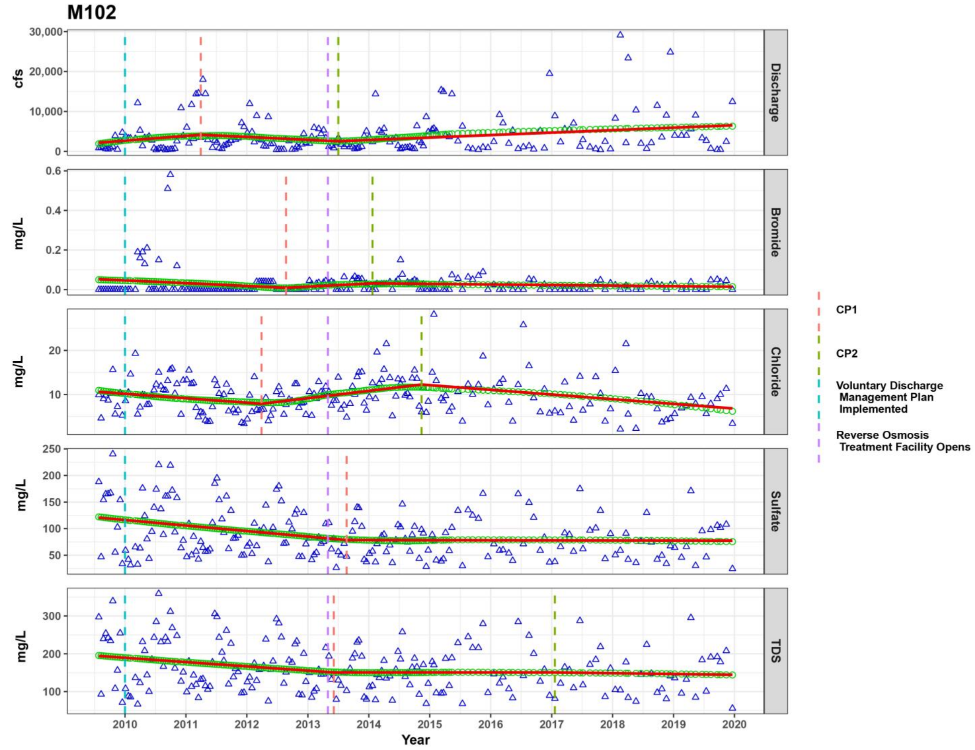

Figure A3. Model output for the Monongahela River at river mile 102 showing key dates and changepoints. Color coded dashed lines are key dates and changepoints, blue triangles represent the raw data, green circles represent the smoothed data from the locally weighted polynomial regression, and the red lines are the segments from the segmented regression.

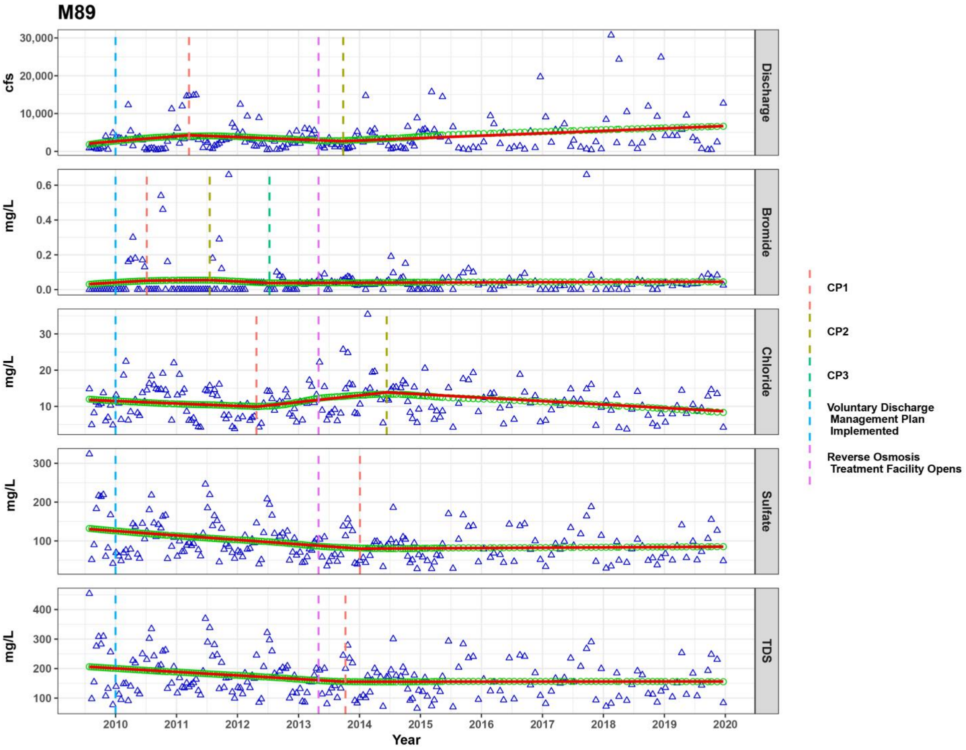

Figure A4. Model output for the Monongahela River at river mile 89 showing key dates and changepoints. Color coded dashed lines are key dates and changepoints, blue triangles represent the raw data, green circles represent the smoothed data from the locally weighted polynomial regression, and the red lines are the segments from the segmented regression.

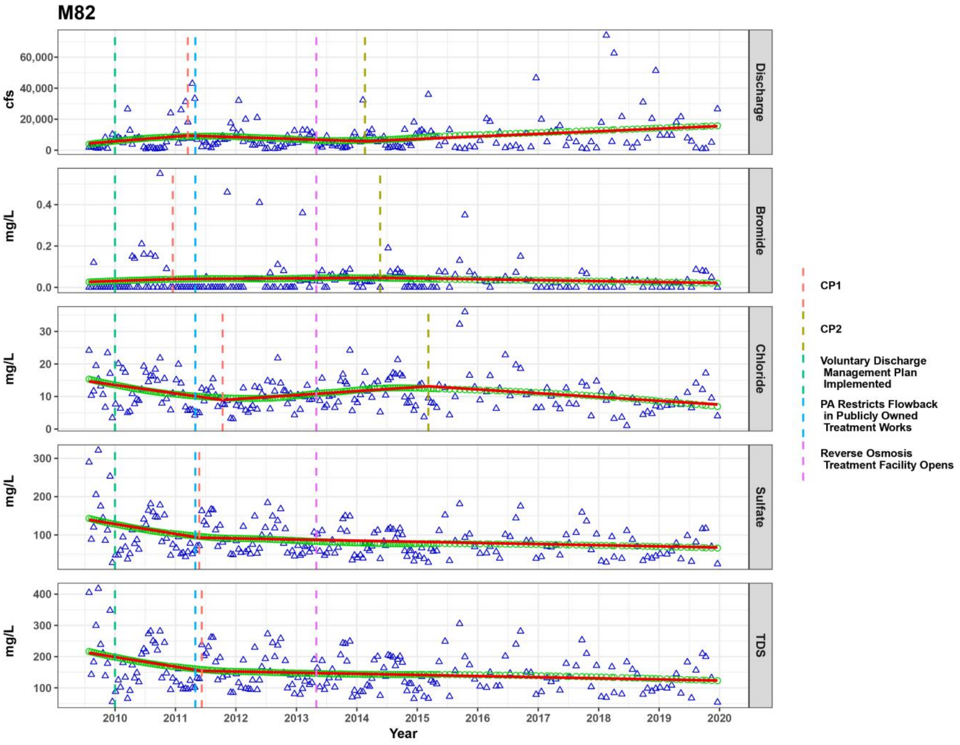

Figure A5. Model output for the Monongahela River at river mile 82 showing key dates and changepoints. Color coded dashed lines are key dates and changepoints, blue triangles represent the raw data, green circles represent the smoothed data from the locally weighted polynomial regression, and the red lines are the segments from the segmented regression.

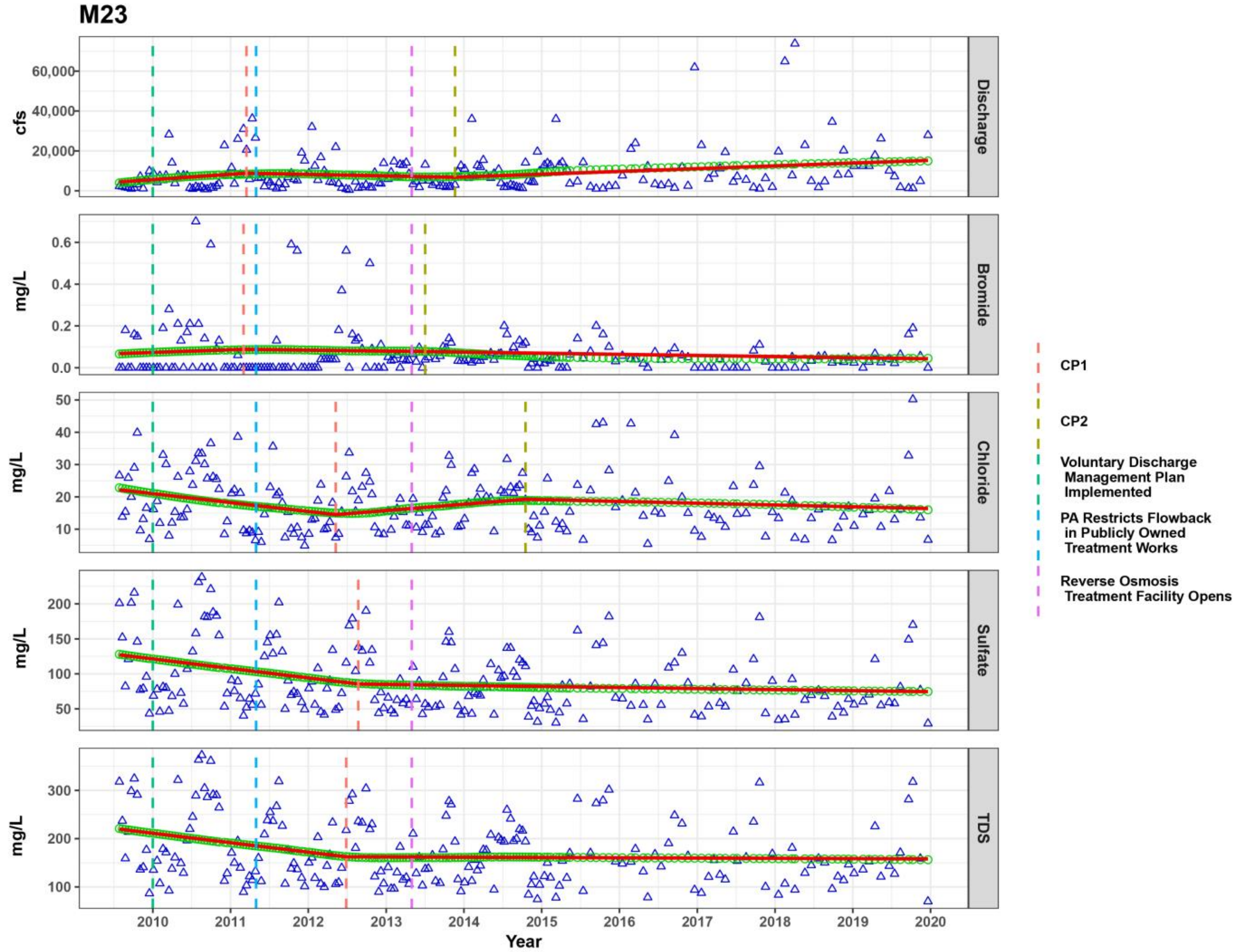

Figure A6. Model output for the Monongahela River at river mile 23 showing key dates and changepoints. Color coded dashed lines are key dates and changepoints, blue triangles represent the raw data, green circles represent the smoothed data from the locally weighted polynomial regression, and the red lines are the segments from the segmented regression.

Table A1. LWPR-SegReg model results for the mainstem sites.

Site	Model	Parameter	Estimate	Std. err	*p*-Value
WF	Discharge	α1	16.406	0.319	<0.001
		α2	−4.999	0.222	
		α3	13.08	0.222	
		α4	−2.554	0.355	
		AAPC	5.411	0.058	
		CP1	2011-04	0.505	
		CP2	2013-08	0.562	
		CP3	2016-07	0.708	
		Adjusted R^2	0.992		
	Bromide	α1	−0.0002	3.56×10^{-6}	<0.001
		α2	−0.0008	2.33×10^{-5}	
		α3	0.0004	1.39×10^{-5}	
		α4	−0.0003	4.38×10^{-6}	
		AAPC	−0.0002	1.17×10^{-6}	
		CP1	2012-08	0.531	
		CP2	2013-07	0.332	
		CP3	2014-10	0.473	
		Adjusted R^2	0.995		
	Chloride	α1	−0.069	0.002	<0.001
		α2	0.126	0.003	
		α3	−0.099	0.001	
		AAPC	−0.036	0.001	
		CP1	2012-05	0.601	
		CP2	2014-03	0.504	
		Adjusted R^2	0.976		
	Sulfate	α1	−1.227	0.015	<0.001
		α2	−0.0663	0.004	
		α3	0.355	0.005	
		AAPC	−0.376	0.002	
		CP1	2010-12	0.633	
		CP2	2014-07	0.274	
		Adjusted R^2	0.999		
	TDS	α1	−1.509	0.013	<0.001
		α2	−0.602	0.004	
		α3	0.141	0.004	
		AAPC	−0.488	0.002	
		CP1	2011-02	0.381	
		CP2	2014-06	0.379	
		Adjusted R^2	0.999		

Site	Model	Parameter	Estimate	Std. err	*p*-Value
TV	Discharge	α1	18.876	0.404	<0.001
		α2	−8.267	0.223	
		α3	16.540	0.010	
		AAPC	9.093	0.054	
		CP1	2011-02	0.488	
		CP2	2013-06	0.377	
		Adjusted R^2	0.996		
	Bromide	α1	−0.0002	1.35×10^{-6}	<0.001
		α2	0.0002	7.00×10^{-6}	
		α3	−0.0001	9.30×10^{-7}	
		AAPC	−0.0001	3.96×10^{-7}	
		CP1	2012-07	0.287	
		CP2	2013-07	0.350	
		Adjusted R^2	0.998		
	Chloride	α1	−0.009	0.0005	<0.001
		α2	0.034	0.0011	
		α3	−0.041	0.0006	
		AAPC	−0.010	0.0002	
		CP1	2012-07	0.880	
		CP2	2014-07	0.500	
		Adjusted R^2	0.977		
	Sulfate	α1	0.008	0.001	<0.001
		α2	−0.057	0.001	
		α3	0.020	0.001	
		AAPC	−0.012	0.0003	
		CP1	2011-11	0.771	
		CP2	2014-10	0.629	
		Adjusted R^2	0.991		
	TDS	α1	0.042	0.002	<0.001
		α2	−0.071	0.001	
		α3	0.006	0.001	
		AAPC	−0.012	0.0002	
		CP1	2011-03	0.421	
		CP2	2013-11	0.511	
		Adjusted R^2	0.995		

Site	Model	Parameter	Estimate	Std. err	*p*-Value
M102	Discharge	α1	48.522	1.274	<0.001
		α2	−29.214	0.828	
		α3	40.486	0.352	
		AAPC	22.234	0.0185	
		CP1	2013-06	0.279	
		CP2	2017-01	0.942	
		Adjusted R^2	0.999		
	Bromide	α1	−0.0006	6.57×10^{-6}	<0.001
		α2	0.0007	4.01×10^{-5}	
		α3	−0.0002	5.37×10^{-6}	
		AAPC	−0.0002	2.00×10^{-6}	
		CP1	2012-08	0.416	
		CP2	2014-01	0.594	
		Adjusted R^2	0.984		
	Chloride	α1	−0.041	0.002	<0.001
		α2	0.069	0.002	
		α3	−0.083	0.002	
		AAPC	−0.192	0.0004	
		CP1	2012-03	0.761	
		CP2	2014-11	0.551	
		Adjusted R^2	0.968		
	Sulfate	α1	−0.422	0.002	<0.001
		α2	−0.012	0.002	
		AAPC	−0.221	0.001	
		CP1	2013-08	0.472	
		Adjusted R^2	0.998		
	TDS	α1	−0.460	0.001	<0.001
		α2	0.004	0.003	
		α3	−0.177	0.007	
		AAPC	−0.254	0.001	
		CP1	2013-06	0.279	
		CP2	2017-01	0.942	
		Adjusted R^2	0.999		

Table A1. *Cont.*

Site	Model	Parameter	Estimate	Std. err	p-Value
M89	Discharge	$\alpha 1$	53.235	1.124	<0.001
		$\alpha 2$	−25.968	0.627	
		$\alpha 3$	43.066	0.341	
		AAPC	23.462	0.165	
		CP1	2011-03	0.446	
		CP2	2013-09	0.419	
		Adjusted R^2	0.994		
	Bromide	$\alpha 1$	0.0008	1.55×10^{-5}	<0.001
		$\alpha 2$	0.0001	1.30×10^{-5}	
		$\alpha 3$	−0.0007	1.55×10^{-5}	
		$\alpha 4$	0.0001	1.35×10^{-6}	
		AAPC	0.0001	1.17×10^{-6}	
		CP1	2010-07	0.410	
		CP2	2011-07	0.354	
		CP3	2012-07	0.300	
		Adjusted R^2	0.990		
	Chloride	$\alpha 1$	−0.028	0.0010	<0.001
		$\alpha 2$	0.079	0.0016	
		$\alpha 3$	−0.068	0.0009	
		AAPC	−0.016	0.0003	
		CP1	2012-04	0.590	
		CP2	2014-06	0.419	
		Adjusted R^2	0.981		
	Sulfate	$\alpha 1$	−0.459	0.002	<0.001
		$\alpha 2$	0.061	0.003	
		AAPC	−0.231	0.001	
		CP1	2014-01	0.497	
		Adjusted R^2	0.998		
	TDS	$\alpha 1$	−0.486	0.002	<0.001
		$\alpha 2$	0.011	0.002	
		AAPC	−0.253	0.001	
		CP1	2013-10	0.298	
		Adjusted R^2	0.999		

Site	Model	Parameter	Estimate	Std. err	p-Value
M82	Discharge	$\alpha 1$	122.150	3.009	<0.001
		$\alpha 2$	−52.374	1.369	
		$\alpha 3$	116.030	1.045	
		AAPC	56.401	0.446	
		CP1	2011-03	0.527	
		CP2	2014-02	0.452	
		Adjusted R^2	0.992		
	Bromide	$\alpha 1$	0.0004	1.33×10^{-5}	<0.001
		$\alpha 2$	0.0008	3.73×10^{-6}	
		$\alpha 3$	−0.0003	4.16×10^{-6}	
		AAPC	-2.70×10^{-5}	1.66×10^{-6}	
		CP1	2010-12	1.095	
		CP2	2014-05	0.650	
		Adjusted R^2	0.970		
	Chloride	$\alpha 1$	−0.103	0.003	<0.001
		$\alpha 2$	0.052	0.001	
		$\alpha 3$	−0.094	0.001	
		AAPC	−0.036	0.001	
		CP1	2011-09	0.687	
		CP2	2015-04	0.712	
		Adjusted R^2	0.964		
	Sulfate	$\alpha 1$	−1.018	0.066	<0.001
		$\alpha 2$	−0.165	0.005	
		AAPC	−0.366	0.003	
		CP1	2011-05	0.651	
		Adjusted R^2	0.992		
	TDS	$\alpha 1$	−1.227	0.016	<0.001
		$\alpha 2$	−0.135	0.004	
		$\alpha 3$	−0.476	0.033	
		AAPC	−0.449	0.004	
		CP1	2011-06	0.495	
		CP2	2017-06	1.898	
		Adjusted R^2	0.994		

Site	Model	Parameter	Estimate	Std. err	p-Value
M23	Discharge	$\alpha 1$	106.760	2.365	<0.001
		$\alpha 2$	−31.677	1.200	
		$\alpha 3$	94.725	0.754	
		AAPC	54.798	0.347	
		CP1	2011-03	0.529	
		CP2	2013-12	0.477	
		Adjusted R^2	0.995		
	Bromide	$\alpha 1$	5.05×10^{-4}	1.30×10^{-5}	<0.001
		$\alpha 2$	-1.82×10^{-4}	7.90×10^{-5}	
		$\alpha 3$	-6.48×10^{-4}	9.07×10^{-6}	
		$\alpha 4$	-2.74×10^{-5}	1.02×10^{-5}	
		AAPC	0.0001	2.08×10^{-6}	
		CP1	2011-03	0.584	
		CP2	2013-07	0.807	
		CP3	2015-12	0.634	
		Adjusted R^2	0.997		
	Chloride	$\alpha 1$	−0.111	0.001	<0.001
		$\alpha 2$	0.082	0.002	
		$\alpha 3$	−0.042	0.001	
		AAPC	−0.029	0.0003	
		CP1	2012-05	0.397	
		CP2	2014-10	0.620	
		Adjusted R^2	0.985		
	Sulfate	$\alpha 1$	−0.543	0.001	<0.001
		$\alpha 2$	−0.091	0.001	
		AAPC	−0.267	0.0003	
		CP1	2012-08	0.146	
		Adjusted R^2	0.999		
	TDS	$\alpha 1$	−0.784	0.005	<0.001
		$\alpha 2$	−0.034	0.002	
		AAPC	−0.313	0.001	
		CP1	2012-06	0.339	
		Adjusted R^2	0.998		

Appendix B

The following figures show the results of the LWPR-SegReg models for the mainstem sites of the Monongahela River. Within each site discharge (cfs), bromide (mg/L), chloride (mg/L), sulfate (mg/L), and TDS (mg/L) were modeled and changepoints were estimated based on the segmented regression. Also included within the figures are key dates for each site, which may include the implementation of the voluntary discharge management plan, Pennsylvania's prohibition on depositing produced water into publicly owned treatment works, and the opening of the new reverse osmosis treatment facility.

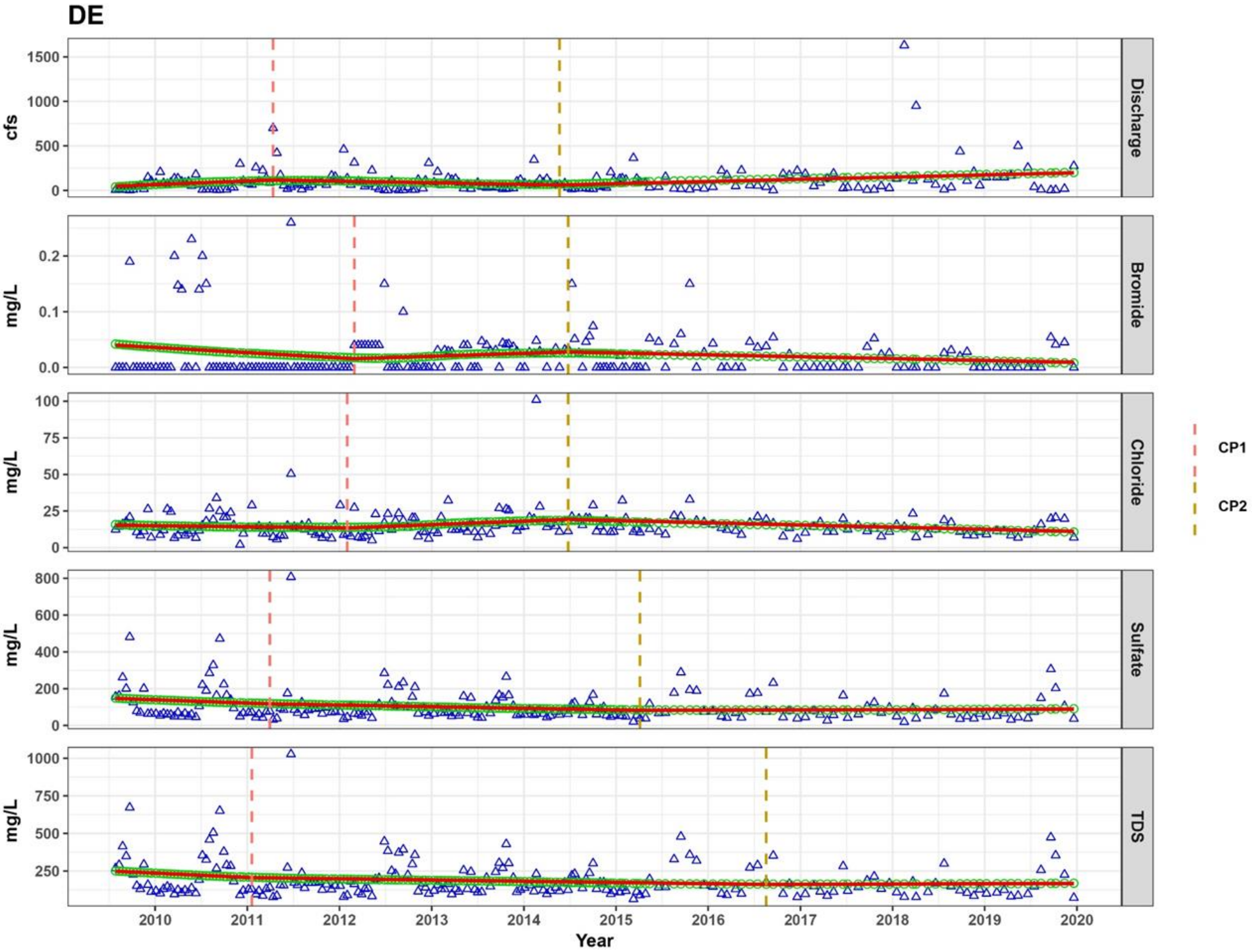

Figure A7. Model output for Deckers Creek showing key dates and changepoints. Color coded dashed lines are key dates and changepoints, blue triangles represent the raw data, green circles represent the smoothed data from the locally weighted polynomial regression, and the red lines are the segments from the segmented regression.

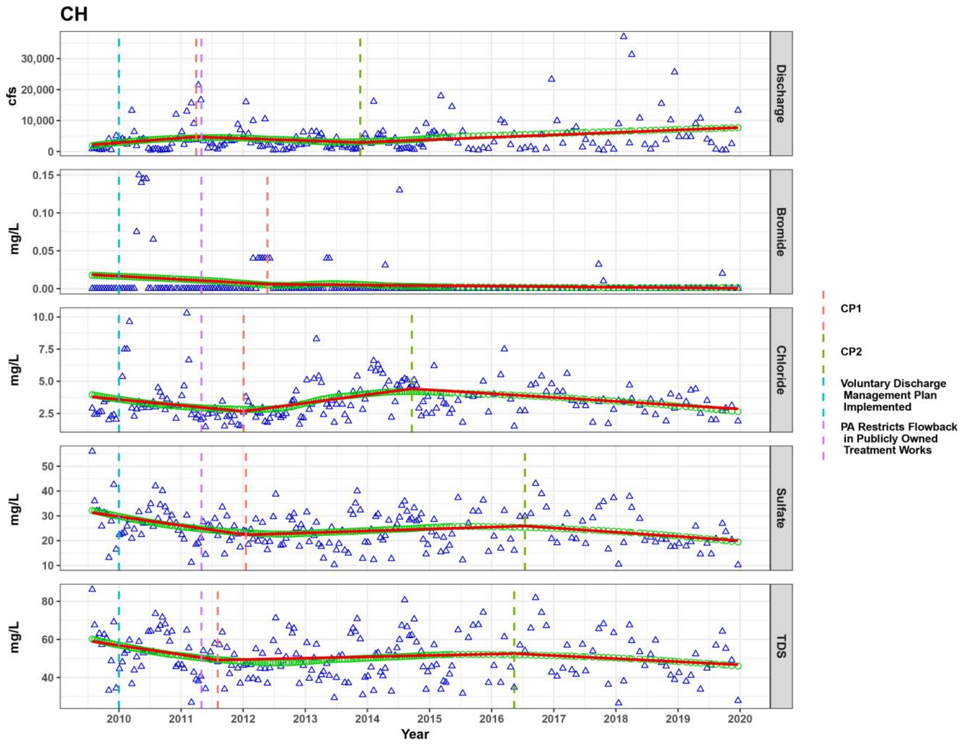

Figure A8. Model output for the Cheat River showing key dates and changepoints. Color coded dashed lines are key dates and changepoints, blue triangles represent the raw data, green circles represent the smoothed data from the locally weighted polynomial regression, and the red lines are the segments from the segmented regression.

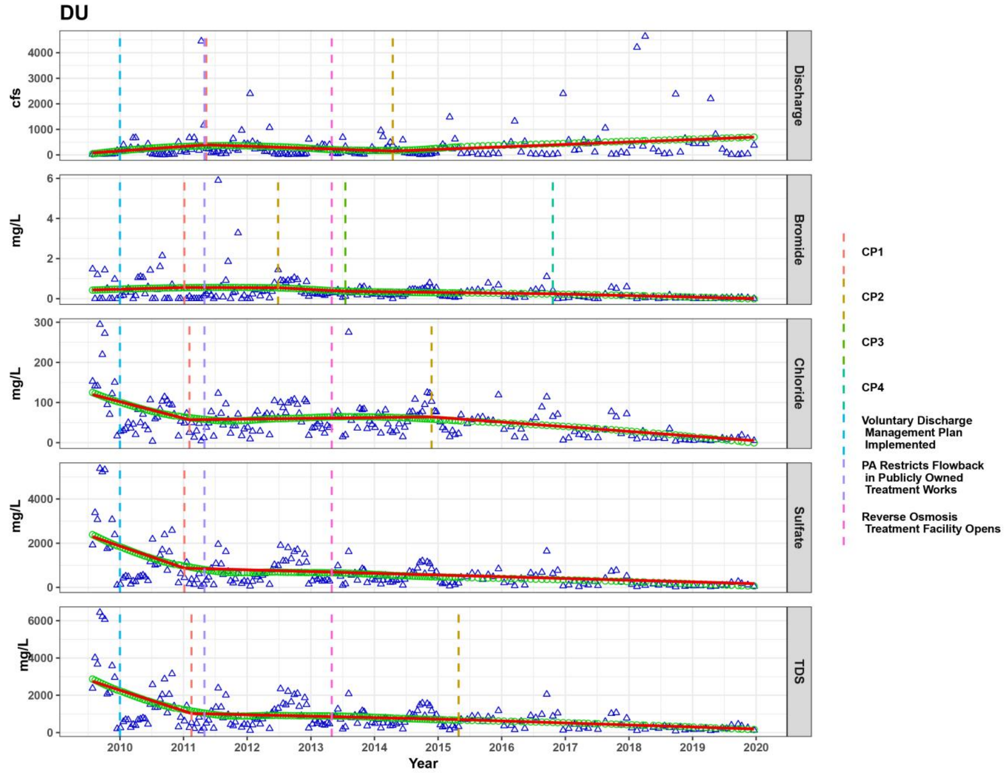

Figure A9. Model output for Dunkard Creek showing key dates and changepoints. Color coded dashed lines are key dates and changepoints, blue triangles represent the raw data, green circles represent the smoothed data from the locally weighted polynomial regression, and the red lines are the segments from the segmented regression.

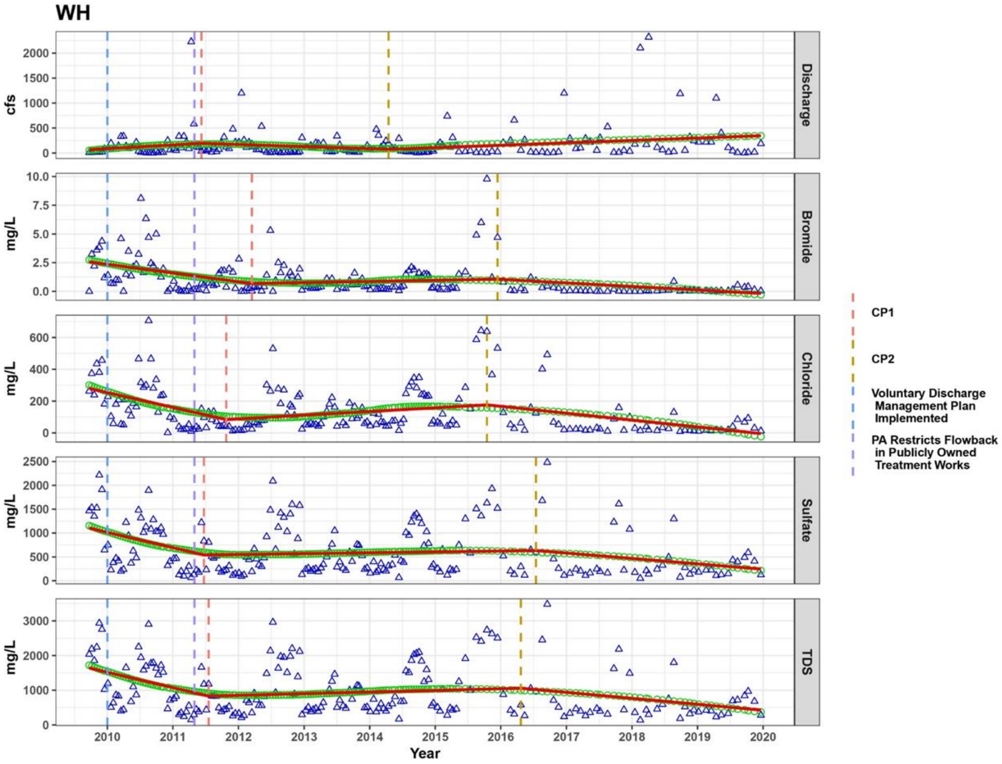

Figure A10. Model output for Whiteley Creek showing key dates and changepoints. Color coded dashed lines are key dates and changepoints, blue triangles represent the raw data, green circles represent the smoothed data from the locally weighted polynomial regression, and the red lines are the segments from the segmented regression.

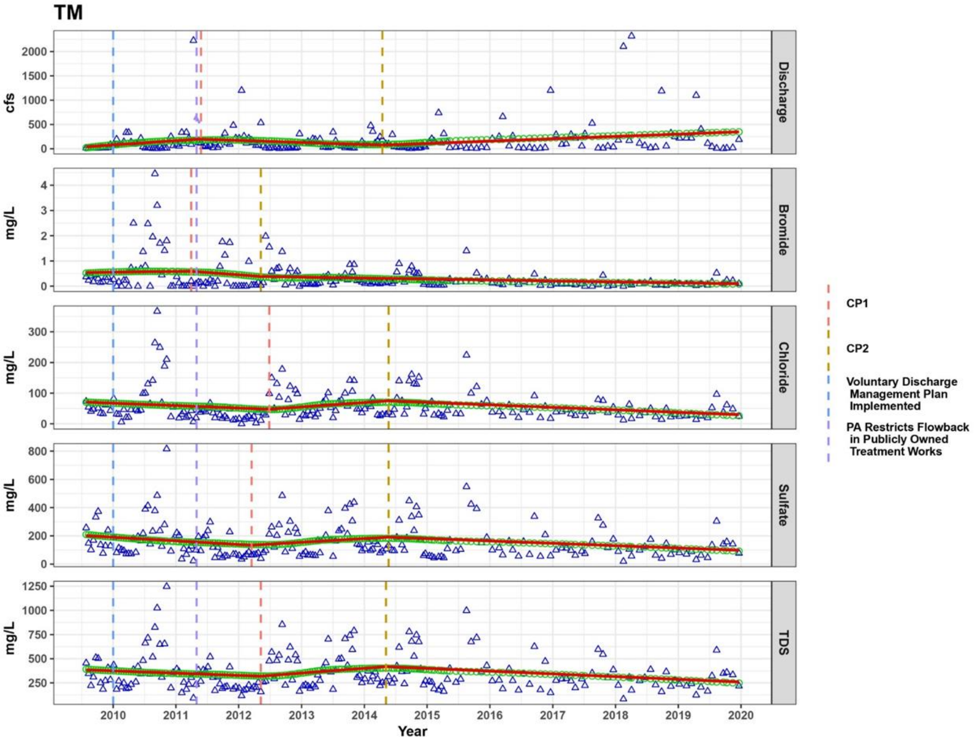

Figure A11. Model output for Tenmile Creek showing key dates and changepoints. Color coded dashed lines are key dates and changepoints, blue triangles represent the raw data, green circles represent the smoothed data from the locally weighted polynomial regression, and the red lines are the segments from the segmented regression.

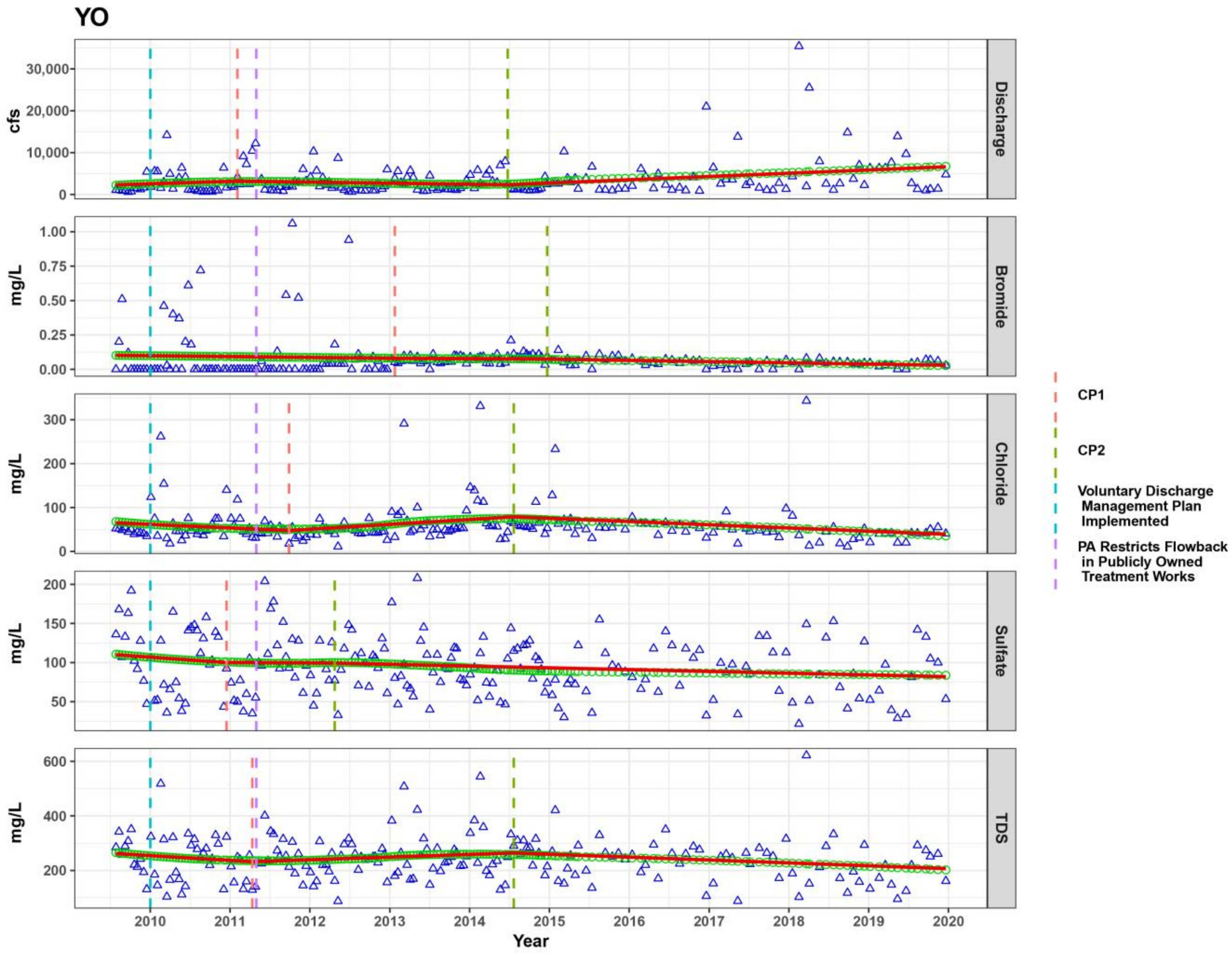

Figure A12. Model output for the Youghiogheny River showing key dates and changepoints. Color coded dashed lines are key dates and changepoints, blue triangles represent the raw data, green circles represent the smoothed data from the locally weighted polynomial regression, and the red lines are the segments from the segmented regression.

Table A2. LWPR-SegReg model results for the tributary sites.

Site	Model	Parameter	Estimate	Std. err	*p*-Value
CH	Discharge	α1	59.917	1.350	<0.001
		α2	−28.258	0.726	
		α3	53.644	0.446	
		AAPC	27.974	0.204	
		CP1	2011-03	0.489	
		CP2	2013-11	0.436	
		Adjusted R^2	0.993		
	Bromide	α1	-2.00×10^{-4}	4.12×10^{-6}	<0.001
		α2	-4.00×10^{-5}	1.72×10^{-6}	
		AAPC	−0.0001	1.06×10^{-6}	
		CP1	2012-05	1.578	
		Adjusted R^2	0.980		
	Chloride	α1	−0.018	0.0007	<0.001
		α2	0.027	0.0006	
		α3	−0.022	0.0006	
		AAPC	−0.005	0.0002	
		CP1	2012-01	0.745	
		CP2	2014-09	0.662	
		Adjusted R^2	0.961		
	Sulfate	α1	−0.144	0.002	<0.001
		α2	0.039	0.001	
		α3	−0.144	0.004	
		AAPC	−0.057	0.001	
		CP1	2012-01	0.583	
		CP2	2016-07	0.675	
		Adjusted R^2	0.981		
	TDS	α1	−0.192	0.003	<0.001
		α2	0.057	0.002	
		α3	−0.135	0.005	
		AAPC	−0.062	0.001	
		CP1	2012-01	0.556	
		CP2	2016-05	0.800	
		Adjusted R^2	0.978		
DE	Discharge	α1	1.613	0.040	<0.001
		α2	−0.757	0.017	
		α3	1.773	0.017	
		AAPC	0.761	0.006	
		CP1	2011-04	0.533	
		CP2	2014-05	0.426	
		Adjusted R^2	0.991		
	Bromide	α1	−0.0004	5.58×10^{-6}	<0.001
		α2	0.0002	7.33×10^{-6}	
		α3	−0.0002	4.42×10^{-6}	
		AAPC	−0.0002	1.45×10^{-6}	
		CP1	2012-02	0.529	
		CP2	2014-06	0.653	
		Adjusted R^2	0.985		
	Chloride	α1	−0.029	0.002	<0.001
		α2	0.101	0.002	
		α3	−0.108	0.001	
		AAPC	−0.022	0.0004	
		CP1	2012-02	0.687	
		CP2	2014-06	0.409	
		Adjusted R^2	0.984		
	Sulfate	α1	−0.706	0.013	<0.001
		α2	−0.358	0.004	
		α3	0.102	0.008	
		AAPC	−0.299	0.002	
		CP1	2011-03	1.078	
		CP2	2015-04	0.741	
		Adjusted R^2	0.997		
	TDS	α1	−1.164	0.013	<0.001
		α2	−0.377	0.002	
		α3	0.152	0.011	
		AAPC	−0.415	0.002	
		CP1	2011-01	0.412	
		CP2	2016-08	0.586	
		Adjusted R^2	0.999		
DU	Discharge	α1	7.002	0.156	<0.001
		α2	−3.511	0.081	
		α3	6.806	0.067	
		AAPC	3.120	0.026	
		CP1	2011-05	0.504	
		CP2	2014-04	0.442	
		Adjusted R^2	0.991		
	Bromide	α1	0.0034	8.10×10^{-5}	<0.001
		α2	−0.0003	8.44×10^{-5}	
		α3	−0.0068	1.30×10^{-4}	
		α4	−0.0021	4.02×10^{-5}	
		α5	−0.0062	7.49×10^{-5}	
		AAPC	−0.0022	1.20×10^{-5}	
		CP1	2011-01	0.671	
		CP2	2012-06	0.410	
		CP3	2013-07	0.512	
		CP4	2016-10	0.523	
		Adjusted R^2	0.999		
	Chloride	α1	−1.651	0.037	<0.001
		α2	0.085	0.010	
		α3	−0.908	0.017	
		AAPC	−0.582	0.005	
		CP1	2011-02	0.573	
		CP2	2014-11	0.847	
		Adjusted R^2	0.988		
	Sulfate	α1	−39.463	0.772	<0.001
		α2	−4.265	0.085	
		AAPC	−10.761	0.091	
		CP1	2011-01	0.517	
		Adjusted R^2	0.990		
	TDS	α1	−44.495	0.602	<0.001
		α2	−3.184	0.142	
		α3	−8.984	0.341	
		AAPC	−12.961	0.088	
		CP1	2011-02	0.388	
		CP2	2015-04	2.408	
		Adjusted R^2	0.994		

Table A2. *Cont.*

Site	Model	Parameter	Estimate	Std. err	p-Value	Site	Model	Parameter	Estimate	Std. err	p-Value	Site	Model	Parameter	Estimate	Std. err	p-Value
TM	Discharge	α1	3.500	0.078	<0.001	WH	Discharge	α1	3.018	0.078	<0.001	YO	Discharge	α1	22.987	0.737	<0.001
		α2	−1.757	0.041				α2	−1.735	0.037				α2	−10.487	0.237	
		α3	3.403	0.033				α3	3.396	0.030				α3	56.820	0.271	
		AAPC	1.559	0.013				AAPC	1.447	0.012				AAPC	21.837	0.102	
		CP1	2011-05	0.504				CP1	2011-06	0.515				CP1	2011-02	0.599	
		CP2	2014-04	0.441				CP2	2014-04	0.402				CP2	2014-06	0.244	
		Adjusted R^2	0.991					Adjusted R^2	0.992					Adjusted R^2	0.998		
	Bromide	α1	0.001	1.85×10^{-4}	<0.001		Bromide	α1	−0.031	0.0005	<0.001		Bromide	α1	−0.0002	3.25×10^{-6}	<0.001
		α2	−0.007	3.40×10^{-4}				α2	0.005	0.0003				α2	−0.0001	8.33×10^{-6}	
		α3	0.002	3.48×10^{-5}				α3	−0.026	0.0008				α3	−0.0007	5.34×10^{-6}	
		AAPC	−0.002	2.59×10^{-5}				AAPC	−0.014	0.0001				AAPC	−0.0003	1.29×10^{-6}	
		CP1	2011-03	0.825				CP1	2012-03	0.714				CP1	2013-01	2.303	
		CP2	2012-05	1.218				CP2	2015-12	0.883				CP2	2014-12	0.505	
		Adjusted R^2	0.992					Adjusted R^2	0.984					Adjusted R^2	0.998		
	Chloride	α1	−0.316	0.009	<0.001		Chloride	α1	−3.730	0.085	<0.001		Chloride	α1	−0.319	0.015	<0.001
		α2	0.592	0.017				α2	1.028	0.038				α2	0.457	0.011	
		α3	−0.582	0.008				α3	−3.646	0.093				α3	−0.542	0.010	
		AAPC	−0.208	0.003				AAPC	−1.471	0.019				AAPC	−0.132	0.003	
		CP1	2012-06	0.647				CP1	2011-10	0.689				CP1	2011-09	0.847	
		CP2	2014-05	0.495				CP2	2015-10	0.715				CP2	2014-07	0.609	
		Adjusted R^2	0.979					Adjusted R^2	0.973					Adjusted R^2	0.966		
	Sulfate	α1	−1.037	0.023	<0.001		Sulfate	α1	−12.888	0.218	<0.001		Sulfate	α1	−0.284	0.014	<0.001
		α2	1.077	0.031				α2	0.851	0.060				α2	−0.017	0.015	
		α3	−1.205	0.018				α3	−9.530	0.243				α3	−0.136	0.002	
		AAPC	−0.525	0.006				AAPC	−4.447	0.041				AAPC	−0.142	0.002	
		CP1	2012-03	0.625				CP1	2011-06	0.479				CP1	2010-12	1.569	
		CP2	2014-05	0.559				CP2	2016-07	0.652				CP2	2012-04	2.835	
		Adjusted R^2	0.979					Adjusted R^2	0.988					Adjusted R^2	0.986		
	TDS	α1	−0.943	0.032	<0.001		TDS	α1	−17.748	0.339	<0.001		TDS	α1	−0.700	0.028	<0.001
		α2	2.060	0.055				α2	2.199	0.100				α2	0.399	0.011	
		α3	−2.025	0.027				α3	−14.405	0.362				α3	−0.778	0.013	
		AAPC	−0.623	0.009				AAPC	−6.281	0.066				AAPC	−0.278	0.004	
		CP1	2012-05	0.675				CP1	2011-06	0.543				CP1	2011-04	0.796	
		CP2	2014-05	0.485				CP2	2016-04	0.664				CP2	2014-07	0.630	
		Adjusted R^2	0.978					Adjusted R^2	0.983					Adjusted R^2	0.973		

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