

**West Virginia Water Research Institute  
Annual Technical Report  
FY 2011**

# Introduction

## West Virginia Water Research Institute

The West Virginia Water Research Institute is dedicated to the preservation and restoration of the natural environment through research and outreach with industry, government agencies, academia and the public.

### Introduction

Water is one of West Virginia's most precious resources. It is essential for life and our economic prosperity, yet so many of the activities that keep our economy alive, and growing, also threaten our water resources. Energy generation, mineral extraction, agricultural production and other industrial activities all impact our water, making it increasingly necessary to find new ways to protect and restore this vital commodity as our economic activity accelerates. For over 40 years, the West Virginia Water Research Institute (WVWRI) has been leading the important work of addressing these issues and is the go-to organization for solving West Virginia's water-related problems.

While much of the work we do is focused on exploring and implementing technologies to improve and protect the quality of our State's water resources, we are also dedicated to expanding the understanding of threats and opportunities related to this critically important resource. We strive to bring together a diverse cross section of stakeholders to participate in water-related research throughout West Virginia. We encourage a constructive and respectful dialog about the future of our lakes, rivers and streams as well as our groundwater supplies.

Today, the WVWRI continues to grow its established programs and develop new initiatives to address emerging problems affecting the State's environmental and economic health. With continued financial support from our State and Federal partners and with the expertise of our staff and collaborating researchers, the WVWRI will continue to work for real improvements to West Virginia's water resources.

### Water Research for West Virginia: A Team Approach

In 1967, under Federal legislation, the United States Geological Survey established the West Virginia Water Research Institute (WVWRI) to conduct research related to water issues in the State. Today, the WVWRI develops state water research priorities with oversight and guidance from the West Virginia Advisory Committee for Water Research, a committee represented by members of Federal and State agencies, academia and industry. Our programs and projects develop strong, multi-disciplinary research teams through collaboration with West Virginia University colleges and divisions, higher education institutions across the country and industry professionals. This team approach offers the best expertise available to address West Virginia's water issues and allows the WVWRI to perform research in a number of areas at any given time. More information on WVWRI programs, research, projects, initiatives and publications can be found at [www.wvwri.org](http://www.wvwri.org).

### West Virginia Advisory Committee for Water Research

Our research program is guided by the West Virginia Advisory Committee for Water Research. It includes representatives from the following:

West Virginia Department of Natural Resources West Virginia Bureau for Public Health West Virginia Coal Association West Virginia Department of Environmental Protection West Virginia Oil and Natural Gas Association GenPower Services, LLC U.S. Federal Bureau of Investigation U.S. Geological Survey U.S. Environmental Protection Agency Region III U.S. Department of Energy - National Energy Technology

Laboratory U.S. Army Corps of Engineers - Huntington, WV District West Virginia University Extension and Public Service

The Advisory Committee develops the Institute's research priority list, reviews its progress and selects startup projects at its annual meeting. With this direction, the Institute recruits new researchers to study emerging water research issues. Because the Advisory Committee understands future regulatory and economic driving factors, these issues tend to grow in importance and have often led to follow-on funding from their agencies.

### Funding Strategy

The Institute received a grant of \$92,335 through the U.S. Geological Survey Clean Water Act section 104b program. We use this funding to develop research capabilities in priority areas and to provide service to State agencies, industry and citizen groups. Our strategy relies on using the USGS section 104b funding to develop competitive capabilities that, in turn, translate into successful proposals funded by a broad spectrum of Federal and State agencies. As of May 2012, the WVWRI has 34 active projects with a total project value of \$4M.

Our strategy also relies on maintaining a broad cadre of researchers within WVU and other institutions within the state. We also work with faculty from institutions across the country to form competitive research partnerships. As West Virginia University is the State's flagship research institution, its researchers have played the dominant role. Our funding strategy relies on successful competition for Federal dollars while teaming with State agency and industry partners. The later provide test sites, in-kind support and invaluable background data. The institute has 15 full time staff and is in the process of hiring 2 new full time staff this year. The institute also supports numerous students (4 within the WVWRI) and more through other departmental projects. All but two positions are supported entirely on grant funds. Roughly two-thirds of the Institute staff is directly engaged in research projects; the remaining is engaged in community economic redevelopment, outreach, and administration.

### Research Priorities

The following is a list of state research priorities identified by the WV Advisory Committee for Water Research for 2011-2012.

Shale Gas: energy production impacts on water resources (oil and gas drilling; hydroelectric; biofuels; etc.); water quality/quantity concerns for gas well hydrofracturing (basin/county/state methods and estimates; need for standard for total dissolved gas);

Coal Mining: valley fills (decay curves/leaching rates; viability of fill areas for community uses; protect as a water source; how to handle sewage; hydraulic properties and geochemistry; water budget impacts); uses for mine water discharge (drinking water potential for underground mine pools, irrigation, industrial heating/cooling);

Aquatic Ecosystem: flooding; aquatic ecosystem integrity (anti-degradation, water quality criteria, nutrient/pathogen impacts, headwater stream valuation/mitigation); water metrics (methods for measuring physical, chemical, biological components, in situ monitoring, PPCP's, pathogens in drinking water); water quality (understanding consumptive uses, altered hydrology with basins, sustainability of stream gages and hydrologic data, climate variability and change, basin-wide regulatory authority of water uses, ecological flow consideration) environmental/In-stream flows (flow requirements for aquatic ecosystems) web content management system (upgrade and make available to the public; include USGS stream stats for WV)

Urban development: industrial processes and urban sprawl (water budgets, contaminants, flooding, ground-water recharge, storm water applications); land use modification (urban impervious surfaces and transfer of land from agriculture/non-developed to urban); inadequate infrastructure (non-existent, failing, or aging water management infrastructure including straight pipes, septic/sewer systems, dams, levees).

Agriculture: agricultural impacts (consumption and runoff; nutrients, pesticides, herbicides);

#### Outreach

The WVVRI performs outreach through meetings, workshops, conferences, site visits, web site, newsletters, and publications. In 2011, the WVVRI co-sponsored a symposium, *Coal and Water in Central Appalachia: The Challenge to Balance*, with water resource research institutes of Virginia and Kentucky. The symposium was held at Virginia Tech in Blacksburg, Virginia with 120 in attendance. Details on this event can be found in the Information Technology Transfer section of this report.

The Institute's web site contains information on all the WVVRI programs and projects. This site is updated on an on-going basis as new information becomes available. This year, the WVVRI purchased the following url addresses for the Institute web site:

[www.wvri.org](http://www.wvri.org) [www.wvri.net](http://www.wvri.net) [www.wvri.com](http://www.wvri.com)

# Research Program Introduction

## Research

USGS 104b funds supported three research projects: 1) Stable Isotope Fingerprinting of Gas Well Drilling Waters, 2) Potential Chemical and Biological Impacts to White Day Creek Due to Gas Well Drilling; and 3) Monongahela River Water Quality Study.

# Stable isotope fingerprinting of waters in area of accelerating Marcellus shale gas development

## Basic Information

<b>Title:</b>	Stable isotope fingerprinting of waters in area of accelerating Marcellus shale gas development
<b>Project Number:</b>	2011WV158B
<b>Start Date:</b>	3/1/2011
<b>End Date:</b>	2/29/2012
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	1
<b>Research Category:</b>	Water Quality
<b>Focus Category:</b>	Geochemical Processes, Groundwater, Surface Water
<b>Descriptors:</b>	None
<b>Principal Investigators:</b>	Shikha Sharma, Shikha Sharma

## Publications

1. Sharma et. al., (in prep) Isotopic fingerprinting dissolved methane in area of accelerating shale gas development in the Appalachians. Environmental Science and Technology.
2. Mulder M. and Sharma S. (in prep) Baseline monitoring of groundwaters in an area of accelerating shale gas development in north central West Virginia. Journal of Environmental Monitoring.
3. The State Journal, October 4, 2011: WVU Researcher to Map Methane Sources in Monongahela-Area Drinking Water
4. Marcellus Drilling News Oct.10, 2011: WVU Researcher to Map Methane Sources in Monongahela-Area Drinking Water
5. The Intelligencer / Wheeling News-Register, October 13,2011: Methane Research at WVU
6. The Daily Journal , Dec 14, 2011: WVU studying impact of hydraulic fracturing on well water
7. Washington Examiner , Charleston Gazette, State Journal, Dec 15, 2011: WVU team to study methane sources in groundwater.
8. Mulder, Michon L., 2012. M.S. Thesis: Ambient geochemical and isotopic variations in groundwaters across an area of accelerating shale gas development. Department of Geology, West Virginia University, Morgantown, WV.

Report title: Stable isotope fingerprinting of waters in an area of accelerating Marcellus shale gas development

Type of report: Annual

Reporting period: February 2011-March 2012

## Summary

The main concern associated with Marcellus shale gas development is that water quality of surface waters and fresh water aquifers can be compromised during gas well drilling, stimulation and improper disposal practices. Under natural conditions the highly saline groundwater occurring within Marcellus shale and other deep formations does not mix with shallow fresh water aquifers due to the barrier provided by several thousand feet of impermeable rocks present between the two end-members. However, during well drilling casing or grouting failures, existing subsurface fractures, and fractures created during hydraulic fracking can generate or augment hydraulic pathways between previously isolated formations. These pathways can allow frack water, deep saline water or methane to contaminate shallow fresh water sources. In addition, improper management and disposal of frack flowback water can deteriorate the water quality of surface water bodies and shallow groundwater aquifers in the area. In order to effectively assess the effect of Marcellus shale development on water quality there is a need to establish the background or ambient geochemical signatures of different water sources. In addition, there is need to develop a suite of natural geochemical tracers that can track the flowback waters and dissolved methane in the groundwaters or surface waters of the area.

The aim of this project is to test the applicability of isotopic composition of water ( $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ ,  $\delta\text{D}_{\text{H}_2\text{O}}$ ) dissolved inorganic carbon ( $\delta^{13}\text{C}_{\text{DIC}}$ ), dissolved sulfate ( $\delta^{34}\text{S}_{\text{SO}_4}$ ,  $\delta^{18}\text{O}_{\text{SO}_4}$ ) and dissolved methane ( $\delta\text{D}_{\text{CH}_4}$  and  $\delta^{13}\text{C}_{\text{CH}_4}$ ) as natural tracers to identify any potential water quality deterioration associated with Marcellus Shale drilling in North Central West Virginia. The main tasks undertaken in collaboration with WV Water Science Center during the first year of this grant were:

- 1) Characterization of baseline O,H,C, and S isotope composition of groundwaters in 11 geological formations (sampled by 41 groundwater wells) overlying the Marcellus shale in north central West Virginia
- 2) Evaluation of ambient concentrations and isotopic composition of dissolved methane in different groundwater formations.
- 3) In collaboration and funding from Department of Energy samples were also collected from natural springs, coalmine drainages, natural gas wells drilled in shallow Devonian sands and Marcellus Shale in PA and WV.

Preliminary data indicates that stable isotope compositions of water and its dissolved constituents can be used to distinguish different water sources indicating the promise of this approach to identify potential contamination ensuing from shale gas drilling activities in future.

## Experimental Methods

Water samples were collected from 41 groundwater wells of both private and public supply, accessed through permissions of the USGS WV Water Science Center (Figure 1). Each well was purged following the EPA Code 540/S-95/504 through a hose line. Water samples were collected after 2-3 casing volumes were removed using Teflon sampling line connected to the well plumbing at a rate of less than 1 L/min.

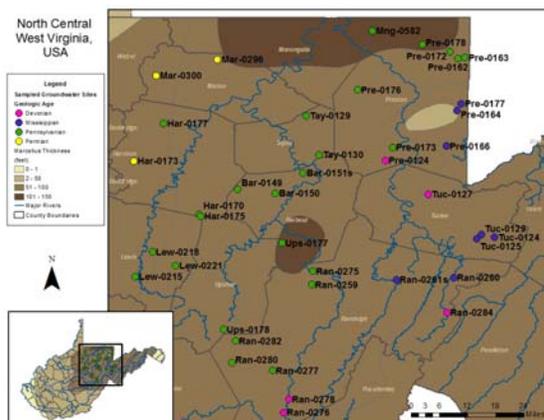


Figure 1: Location of 41 groundwater wells in North central West Virginia

Samples were collected after field parameters i.e. temperature, conductivity, pH, dissolved oxygen were stabilized to  $\pm 10\%$  using a 650MDS YSI meter (Appendix A, Table 1). Isotope samples personally collected at each groundwater well site included one sample for  $\delta^{13}\text{C}_{\text{DIC}}$ , duplicate samples for  $\delta^2\text{H}_{\text{H}_2\text{O}}$  and  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ , one sample for  $\delta^{13}\text{C}_{\text{CH}_4}$  and  $\delta^2\text{H}_{\text{CH}_4}$  at selected sites, and one for  $\delta^{34}\text{S}_{\text{SO}_4}$  and  $\delta^{18}\text{O}_{\text{SO}_4}$ . The USGS scientists sampled each well for major cations and anions, trace elements, dissolved gases, and radiochemistry. All samples were collected wearing nitrile gloves and were

refrigerated until analysis was completed or shipped to the appropriate laboratory. The  $\delta^{13}\text{C}_{\text{DIC}}$  samples were collected through a 60 mL syringe (pre-rinsed 3 times with sample water) with a Luer-Lok tip. The water was filtered through a Cameo 0.45  $\mu\text{m}$  nylon pre-filter into a 10 mL Wheaton serum vial with no headspace. 2-3 drops of benzalkonium chloride (17% w/w) were added to the vial as an astringent. A 20 mm Teflon septa was placed on the top and sealed with Al caps using a crimper. Samples were refrigerated and stored for analysis. Duplicate samples for  $\delta^2\text{H}_{\text{H}_2\text{O}}$  and  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  were taken by filling a pre-rinsed 8 mL glass threaded vial, with no headspace. Parafilm was wrapped around the lid of the vial and refrigerated until analysis. Sulfate samples were collected in a pre-rinsed 1 L polyethylene bottle with no headspace. Each sample was filtered back into the rinsed bottle through a 45 mm diameter, 0.4  $\mu\text{m}$  PCM filter. During the filtering process, a glass petri dish was used to cover the filtering sample to prevent the oxidation of sulfide to sulfate. Further sample preparation at Isotech Laboratory includes precipitating  $\text{BaSO}_4$  powder for the isotopic analysis of sulfate. Numerous duplicate samples were taken to ensure quality control. Samples for dissolved methane were collected in a rinsed 5 gallon bucket. The bucket was filled with sample water through Teflon tubing connected to the groundwater sampler so that the water line was above the height of the sample bottle. The sampling tube was inserted into the pre-rinsed methane sample bottle and fully submerged in the filled bucket. After the duration of approximately 3 sample bottle fills, the sample hose was quickly removed underwater and the sample bottle was capped underwater. Extra care was taken not to expose the sample to air, fully underwater, with no air bubbles present after being capped. The O,H and C isotopic composition were analyzed at the newly established Stable Isotope Laboratory at WVU (WVSIL) using a Finnigan Delta Advantage continuous flow isotope ratio mass spectrometer (IRMS) with the ThermoQuest Finnigan GasBench II

device. Each sample is flushed using the PAL autosampler system, equilibrated for 24 hours, and then sampled with PAL system. The headspace is analyzed using a double-needle; while the carrier gas is being injected continuously into the sample vial through one slit, the other removes headspace evacuated by the gas. Duplicate samples of 10.0  $\mu\text{L}$  are taken over the course of 60 seconds with a total 10 replications for each sample. From there, the head space sample is carried through the components of the IRMS via the carrier gas through the GasBench. Internal lab standards are incorporated in triplicates in the beginning, middle (if a high number of samples), and end of each run sequence for QA/QC checks. These internal standards are calibrated against the respective IAEA international standard. Samples for C and H isotope of methane and S isotope of sulfate were shipped to Isotech Laboratories for analysis.

## Results and Discussion

### Water geochemistry and isotopic composition

A basic Piper Plot shows the wide variation in hydrochemistry of the waters across the study area. This variation is present not only overall, but within individual formations. Analyses were grouped by age of formation to include the Devonian, Mississippian, Pennsylvanian, and Permian. Hydrochemistry shows that a form of carbonate dissolution is occurring within each series of ages, and pyrite oxidation or weathering may be the source of iron and sulfate in the waters. However, due to multiple inputs, cation exchange, and mineral precipitation that can affect concentrations of major cations and anions, a multi-proxy isotopic analysis was used to discern the cause of variations.

The composition of hydrogen and isotope isotopes in water show similar signatures to that of precipitation and river water of the area. The higher  $d$ -excess values in the groundwaters are interpreted to be a result of dominant recharge being sourced by recycled moisture in air masses originating above the Great Lakes area. The original air masses are subjected to high rates of evaporation over the water bodies, of which the evaporative vapor is mixed with atmospheric. In conjunction with local processes such as altitude and latitude, the isotopic signatures of  $\delta^2\text{H}_{\text{H}_2\text{O}}$  and  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  plot above the GMWL in the area of an arid vapor mass. Carbon isotopes of DIC show deviation from the range of natural waters. Enriched values of  $\delta^{13}\text{C}_{\text{DIC}}$  are predominantly the result of carbonate and carbonaceous shale weathering, evident through hydrochemical relationships. Dissolved methane is present throughout the groundwaters with the highest concentration of 48.20 mg/L, and isotopically plots amongst the signature of local CBM. The associated isotopic signatures of dissolved methane are distinguishable from natural gases of Silurian, Ordovician, and Devonian age. The isotopic signatures of methane characterize its source as thermogenic with an overprint of biological processes. Sulfur isotope compositions in dissolved sulfate can indicate the source of sulfur, shown to be ranging from coals, shales, and pyrite. The depleted carbon signatures may be indicative of sulfate reduction, but was not confirmed through the isotopic analysis of  $\delta^{34}\text{S}_{\text{SO}_4}$  with  $\delta^{18}\text{O}_{\text{SO}_4}$  or  $\delta^{13}\text{C}_{\text{DIC}}$  due to the origin of the oxygen atom and variations in carbon input in DIC. The depletion seen in  $\delta^{34}\text{S}_{\text{SO}_4}$  is a preliminary indication of sulfide oxidation. Overall variation, both in hydrochemistry and isotopic signatures, differed widely between and within age series. Specifically, samples collected from Pennsylvanian aged aquifers had more variation than between samples of Permian, Mississippian, and Devonian aquifer ages. The variability may be due to a larger sample pool taken from Pennsylvanian aged aquifers

or it may be the result of higher heterogeneity in the Pennsylvanian systems compared to the other age series. More sampling will be necessary in the other systems to confirm the heterogeneity or homogeneity in the aquifer age systems.

The ambient hydrochemical and isotopic variations in the area groundwaters in this study provide the basis for prospective studies regarding the water quality of north-central West Virginia as shale gas exploration is expanding. Flowback water originates from a different lithological source in extreme depths; it will have undergone different water rock interactions than what is being seen in these shallow groundwater aquifers. If these aquifers are exposed to significant contributions of flowback/produced water from natural gas drilling, the established baseline isotopic signatures will dramatically change. This occurrence will distinctly shift the ambient signatures and hence serve as a natural fingerprint to determine if aquifers are receiving significant contribution from flowback waters. Accordingly, this study provides the foundation for geochemical assessment of water quality issues related to Marcellus Formation gas development in the study area.

### Dissolved Methane

Dissolved methane concentrations were determined for 42 groundwater samples collected in the study area. The dissolved methane concentrations range from 0 to 49mg/L. Thirteen samples were analyzed for the carbon and hydrogen isotopic composition of dissolved methane. The  $\delta^{13}\text{C}_{\text{CH}_4}$  and  $\delta^2\text{H}_{\text{CH}_4}$  values range from -42 to -69 ‰ V-PDB and -99 to -244‰ V-SMOW respectively. For most the dissolved gas samples the higher hydrocarbon concentrations (i.e. C2, C3 and C4 percentages) were below detection limits. Seven samples had some higher hydrocarbons and their C2% ranges from .01 to 4%.

Several of the groundwater wells show high concentrations of methane although there is no Marcellus Shale development within several miles of the well sites. Hence the high methane concentrations cannot be attributed to hydrofracking associated with Marcellus shale drilling. There are several sources of methane leaks into the groundwater aquifers i.e. shallow gas bearing strata, coalbeds, storage gas fields, and abandoned unplugged oil and gas and coalbed methane wells. Methane could also be produced biologically by methanogens in shallow aquifers underlying sewage plants, landfills and coalbeds where right pH, temperature and redox conditions are available. Therefore, the knowledge of the genetic origin of methane gas is important for the correlation of stray gas release with potential sources, and also for understanding the gas migration pathways.

The  $\delta^{13}\text{C}_{\text{CH}_4}$  and  $\delta^2\text{H}_{\text{CH}_4}$  of methane have been widely used in several studies to distinguish different sources of methane i.e. biogenic vs thermogenic. The  $\delta^{13}\text{C}_{\text{CH}_4}$  and  $\delta^2\text{H}_{\text{CH}_4}$  isotopic signatures of the dissolved methane from 21 groundwater wells is distinct from the gas produced from Marcellus and the shallower sands in the area demonstrating the potential of stable isotopes to distinguish sources of methane leaks in the ground waters of the region. The methane in the groundwaters also does not seem to be related to abandoned oil and gas and/or CBM wells near the sampled location. Currently Dr. Sharma is working on finalizing a research paper summarizing the analysis and interpretation of the isotopic data obtained from this study.

## **Conclusions**

The preliminary data indicates stable isotopes of O,H and C can be used to distinguish different sources of waters in areas of accelerating shale gas development in Appalachians. In addition, the study also indicates that dissolved methane concentrations in groundwaters can be naturally high in some areas hence highlights the importance of baseline concentration and isotope monitoring dissolved gases before shale gas drilling.

# WRI-119 Phase 2 Year 1: Mon River Water Quality Study

## Basic Information

<b>Title:</b>	WRI-119 Phase 2 Year 1: Mon River Water Quality Study
<b>Project Number:</b>	2011WV165B
<b>Start Date:</b>	3/11/2010
<b>End Date:</b>	2/12/2012
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	WV 1st
<b>Research Category:</b>	Water Quality
<b>Focus Category:</b>	Water Quality, Surface Water, Non Point Pollution
<b>Descriptors:</b>	None
<b>Principal Investigators:</b>	Paul Ziemkiewicz, Ben Mack, Melissa J. O'Neal, Dave Saville, Tamara Vandivort

## Publication

1. O'Neal, Melissa, David W. Saville, and Paul Ziemkiewicz. 2011. A Collaborative Approach to Managing Total Dissolved Solid Levels in the Upper Monongahela River Basin. Center for Watershed Protection: Environmental Science Bulletin.

# MON RIVER QUEST TOTAL DISSOLVED SOLIDS MONITORING IN THE MONONGAHELA RIVER WATERSHED

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WRI-119

USGS AWARD NUMBER: 2011WV165B

FINAL REPORT

REPORTING PERIOD: MARCH 1, 2011 - FEBRUARY 29, 2012

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MAY 31, 2012

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## ABSTRACT

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The Monongahela River has historically been impacted by acid mine drainage from flooded underground coal mines. More recently, gas exploration and extraction from the region's Marcellus and Utica Shales, has been another cause for concern with episodes of high total dissolved solids (TDS). Previous studies at the West Virginia Water Research Institute (WVWRI) have included the establishment of a watershed-based monitoring program for the Monongahela River Basin (MRB), which has served as the basis for this project which has continued and expanded TDS Monitoring of the MRB. Building upon the existing model has allowed WVWRI to seamlessly continue monitoring of the Monongahela and several of its tributaries.

The foundation had also been laid for a dynamic and user friendly Graphical Information System (GIS) mapping and data visualization system. An established website ([www.MonRiverQUEST.org](http://www.MonRiverQUEST.org)) has been enhanced upon by providing users with the ability to create on the fly graphs of all of the analytical and field parameters. The website includes a description of water quality parameters that are being analyzed, basic information on the Monongahela River Watershed, links to relevant websites, and a list of project participants.

For consistency, and to provide more comprehensive long-term data, the previously established sixteen sites (four mainstem Monongahela and at the mouth's of twelve major tributaries) have remained in the sampling regime. Monitoring the water chemistry and flow rates of the tributaries to the mainstem Monongahela has provided useful information regarding not only the health of those tributaries, but their contribution to the overall water quality in the Monongahela River. The bi-weekly sampling regime has continued with samples collected at each site for analytical laboratory analysis for: alkalinity, sulfate, calcium, chloride, sodium, and magnesium. Field parameters (pH, conductivity, temperature, and dissolved oxygen) have also be recorded at each site.

This project has the support of the West Virginia Advisory Committee for Water Research and stakeholders including the U.S. Geological Survey, U.S. Army Corps of Engineers, WV Department of Environmental Protection, WV Department of Natural Resources, WV Division of Health & Human Resources, West Virginia University Extension Service, Colcom Foundation, industry, citizen organizations and others.

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## EXECUTIVE SUMMARY

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Continuing and expanding upon the previous USGS-funded project to establish a water quality monitoring protocol for the Monongahela River Basin (MRB), this project systematically collects water quality information for the MRB and makes it readily accessible to the public in a user-friendly manner via the internet. The project has also been built upon to include water quality information collected by other agencies and organizations from an expanded area, including the headwater streams, within the MRB.

Current water quality information can be useful to many users of the Monongahela River. Water conditions are also important to industries while upsets in the quality of the water is important information for regulatory agencies. Policy makers need accurate information to develop sound policies to protect our water resources. Nearly one million people get their drinking water from the Monongahela River. This program fulfills a vital need to gather and present current water quality information in a form that is accessible to the public.

## INTRODUCTION

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This project continues and expands upon a USGS funded water quality monitoring program for the Monongahela River Basin (MRB) begun in 2009. The resultant data has strengthened the data set and enabled a more accurate determination of the health of the watershed to be developed. The platform to publicly display the data has been upgraded and regularly updated, now using an ARC GIS Explorer online mapping program.

Expanding on the original monitoring protocol, the program has been enhanced by the incorporation of additional monitoring locations through a project funded by the Colcom Foundation. Begun in May 2011, the Mon River QUEST program works with watershed organizations within the MRB to monitor water quality at many additional locations including headwater streams. The volunteer collected data is then incorporated in the same online database as the data from the analysis of the WVVRI collected samples. The Mon River QUEST program assists watershed organizations with monitoring equipment and training and also provides a common database and online tool for data entry. The success of this project was recognized by the National Institutes of Water Research (NIWR) through a Regional IMPACT Award in February of 2012.

Having this monitoring program in place has also provided the information necessary for a TDS Working Group to help manage TDS levels in the River. This innovative endeavor is a non-regulatory, volunteer, effort coordinated by the WVVRI in collaboration with the major coal companies operating in the MRB. A managed discharge system for draining active coal mines has been implemented which has successfully kept the TDS levels in the River within acceptable EPA standards.

## STATEMENT OF REGIONAL OR STATE WATER PROBLEM

Monitoring of TDS throughout the Monongahela River basin is critical. This project has identified tributaries that may have potentially “high” TDS concentrations and also calculated the total loading (tons per fortnight (tpf) i.e. bi-weekly) of TDS of those tributaries and of the mainstem Monongahela. Building upon the platform of previous work, this study has provided additional detailed information on the contributions of the components of TDS, and how the loadings from tributary sites impact the mainstem Monongahela River.

The project website ([www.MonWQ.net](http://www.MonWQ.net) or [MonRiverQUEST.net](http://MonRiverQUEST.net)) graphically shows users the concentrations (mg/L) and loadings (tpf) of various parameters during each of the bi-weekly samplings. Furthermore, this study has provided the information necessary to allow industry to track trends and monitor TDS concentrations in tributaries, resulting in a successful effort to regulate their discharges. The need for a TDS monitoring program became even more apparent when a fish kill in the fall of 2009 on Dunkard Creek, a tributary of the Monongahela River, gained media attention.

The platform of this study was developed by the WVVRI and originally funded by the USGS. Various partners support the project and include: the WV Department of Environmental Protection, US Environmental Protection Agency Region 3, the TDS Working Group, and US Army Corps of Engineers.

This project gathers and presents current water quality information in a form that is accessible to the public. This information can be used to:

- Assess the quality of the fishery and other recreational opportunities
- Identify upsets in water quality
- Evaluate historic trends
- Provide a framework for other data sources
- Aid in the development of policy and regulations

## STATEMENT OF RESULTS OR BENEFITS

The platform for a successful working water quality monitoring model has been developed and focuses on the needs of recreational, agency, public, and industry users. Online GIS maps utilizing colored and sized markers, allow users to see a snapshot view of TDS concentrations during the bi-weekly sampling events. This study has provided the opportunity to further enhance the website and public dissemination of the data by utilizing ArcGIS mapping tools.

The chemistry data that results from this project helps to identify sources of contamination and assists industry and agencies in regulating nonpoint sources and in developing policy to address such contamination. The public aspect of depicting the data on a website also helps to increase awareness of the water quality of the Monongahela River and its tributaries.

## EXPERIMENTAL METHODS

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Baseline sampling of the Monongahela River and its tributaries began on July 29, 2009. The success of this initial USGS funded project provided the foundation for further monitoring. Samples are being collected by WWRI staff at 16 different locations bi-weekly at four locations on the Monongahela River and twelve locations near the mouths of major tributaries that enter the Monongahela (Table 1, Figure 1).

**Table 1. Sample location descriptions (sites with asterisks were added to the sampling plan during the summer of 2010).**

Site ID	Waterbody	lat	long
WF	West Fork River	39.4460	-80.2464
TV	Tygart Valley River	39.4432	-80.1874
IN*	Indian Creek	39.5697	-80.0833
WD*	Whiteday Creek	39.5472	-80.0439
FM*	Flaggy Meadow Run	39.5836	-80.0375
M102	Monongahela R. mile 102	39.6121	-79.9685
DE	Decker's Creek	39.6288	-79.9685
RO*	Robinson Run	39.6787	-79.9792
M89	Monongahela R. mile 89	39.7382	-79.9014
CH	Cheat River	39.7204	-79.8603
DU	Dunkard Creek	39.7656	-79.9673
WH	Whiteley Creek	39.8227	-79.9495
M82	Monongahela R. mile 82	39.8501	-79.9245
TE	Tenmile Creek	39.9809	-80.0352
M23	Monongahela R. mile 23	40.2760	-79.8888
YO	Youghiogheny River	40.2367	-79.8067

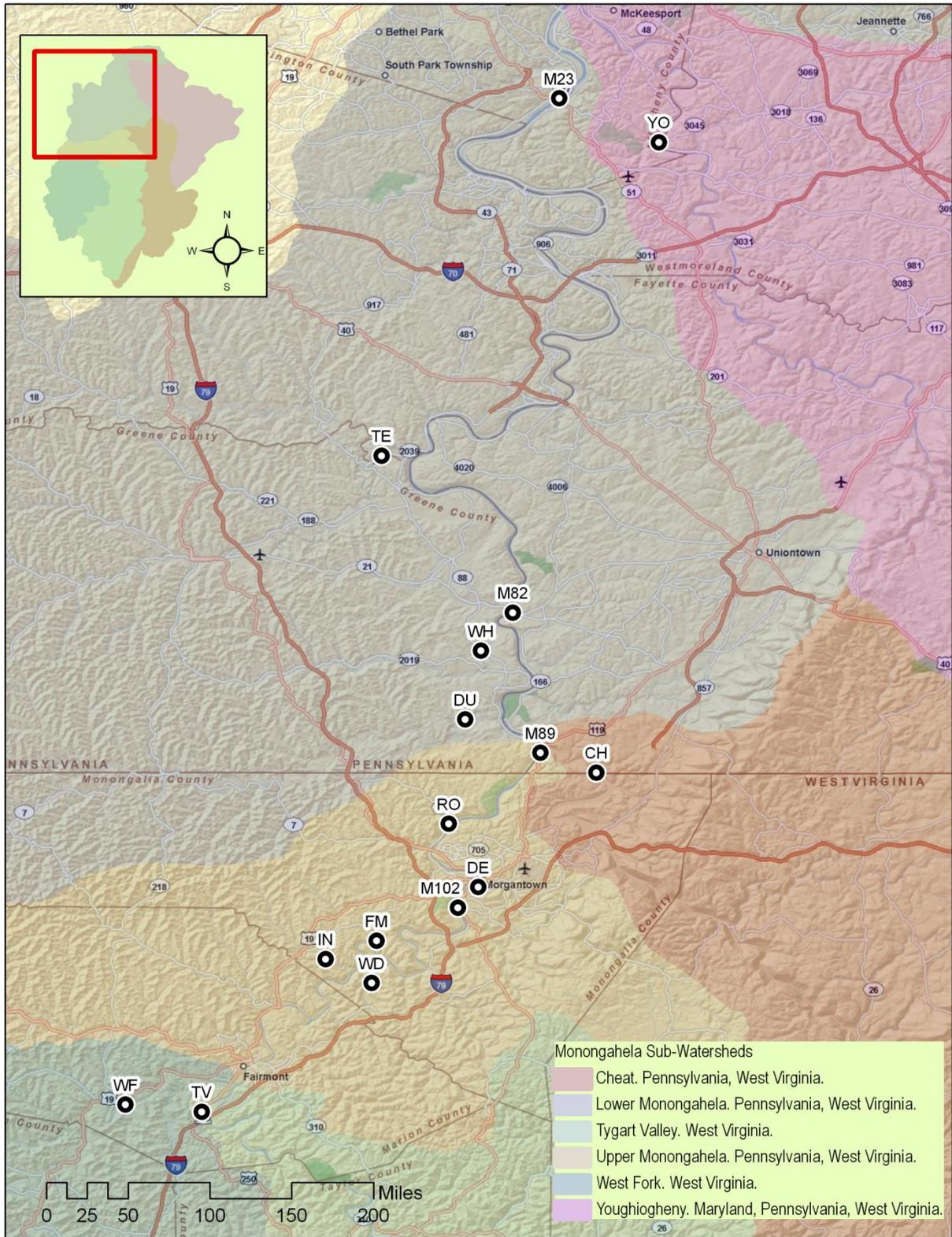


Figure 1. Topographic map of sample locations and sub-watersheds within the study area.

## *FIELD PARAMETERS*

A suite of parameters to incorporate into the monitoring program was determined during early meetings with the project Advisory Committee. Parameters analyzed in the field include: electrical conductivity, pH, and temperature. Flow is determined for some of the sampling points using the nearest USGS gages. Transducers were installed at five sites and flow rating curves were developed and utilized to determine discharge. For those sites that are located on ungaged streams in West Virginia, flow is estimated based on Watershed Characterization Modeling System (WCMS). Appendix 1 contains descriptions of the analytical parameters.

## *SAMPLING METHODOLOGY*

Two water samples are collected at each sample point: (I) a 1 L unfiltered sample was taken for general water chemistry (pH, conductivity, TDS, TSS, total acidity and alkalinity by titration, bromide, chloride, and sulfate), and (II) a 125 mL sample filtered with a 0.45 micrometer Nalgene syringe filter was acidified to pH of <2 with 0.5 ml concentrated nitric acid and used to determine all metal concentrations.

## *ANALYSIS*

Water quality samples have been collected from each of the sixteen sites bi-weekly throughout the reporting period. All samples were analyzed according to EPA procedures and methods (Appendix 1).

# *RESULTS AND DISCUSSION*

---

## *RESULTS*

### *WATER QUALITY*

Healthy, clean, cold tributaries are vital not only in headwaters, but for the overall health and substance of entire watersheds. While this study focuses on the water quality of the Monongahela River, it also provides valuable monitoring of smaller tributaries that ultimately contribute to the health of the Monongahela River Watershed. A sub-watershed within the Upper Monongahela River Basin that has received much attention since the fall of 2009 is Dunkard Creek.

### *DUNKARD CREEK*

Shortly after this monitoring program was implemented in 2009, a devastating fish kill occurred on Dunkard Creek, a major tributary of the Monongahela River flowing along the Pennsylvania/West Virginia border. Sampling for this study had occurred the week prior and week following the initial fish kill. In looking at the Total Dissolved loadings in tons per fortnight (tpf), which is calculated based off of flow discharge (cubic feet per second) and concentration of TDS (mg/L), it is evident that a low flow situation and an increase in high concentrations of TDS existed which helped to create the extremely poor water quality conditions that ultimately led to the fish kill (Figure 2). Between the 25 August 09 and 8

September 09 sampling dates, the TDS concentrations jumped from 3,813 (mg/L) to 8,103 (mg/L) while discharge remained around 20 cubic feet per second.

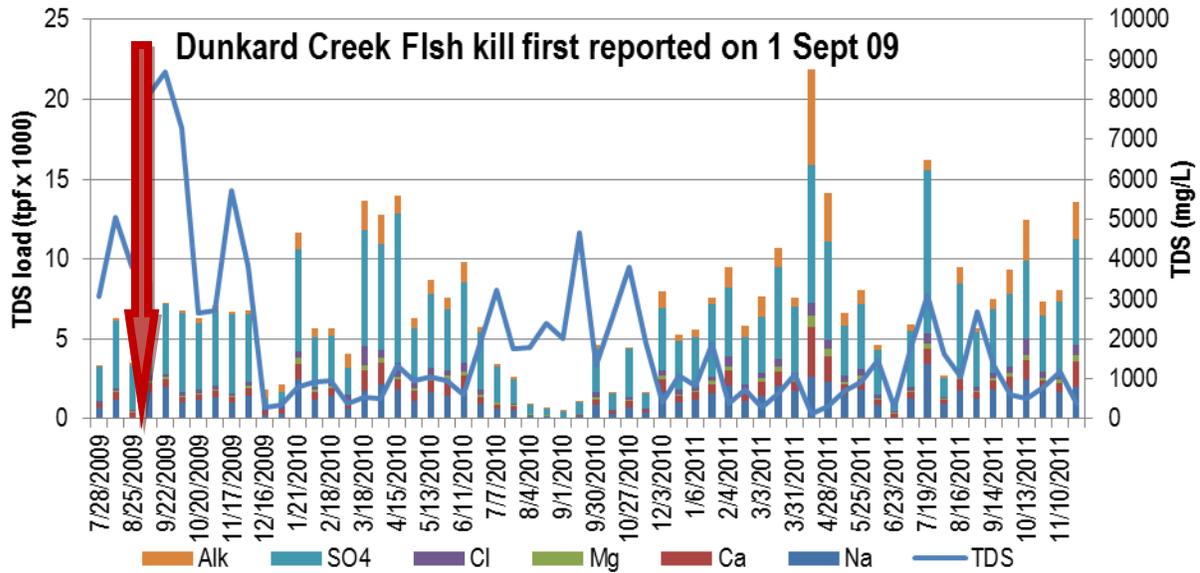


Figure 2. TDS loading on Dunkard Creek between July 2009 and December 2011

### TDS LOADINGS

TDS loadings are quite useful in realizing the contribution of tributaries to the mainstem of the Monongahela (Mon) River. Figure 3 depicts TDS loadings at river miles 23, 82, 89, and 102 between July 2009 and February 2012.

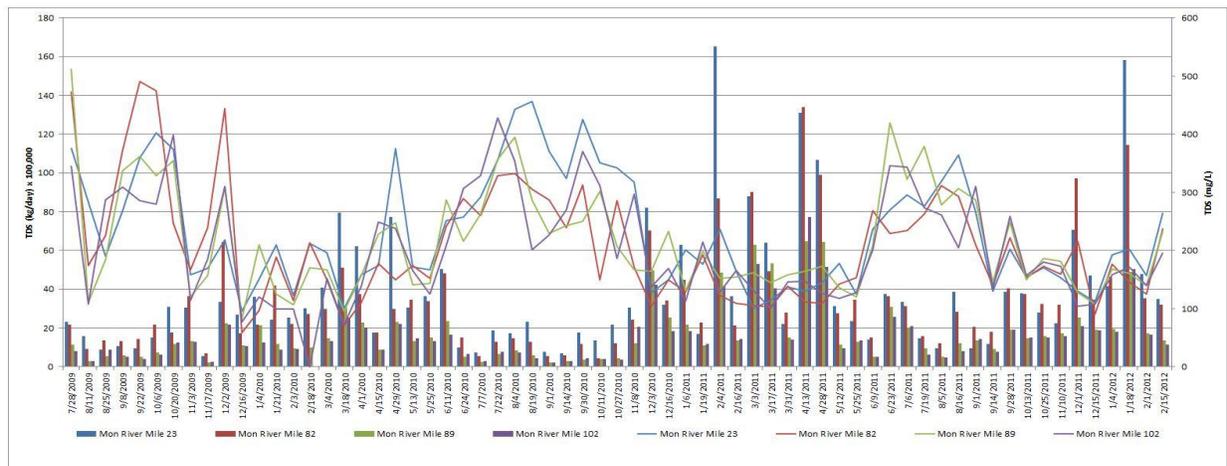
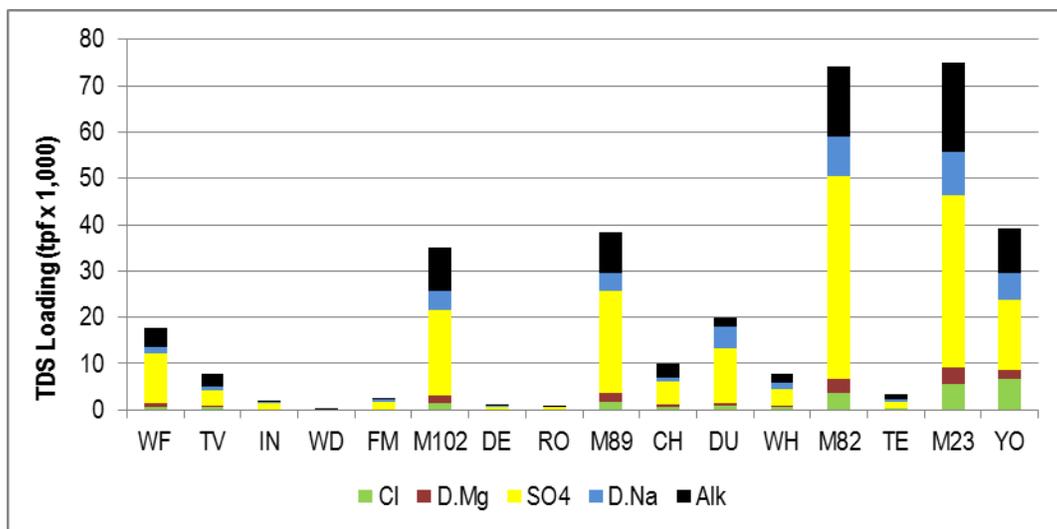


Figure 3. TDS loadings (kg/day) on the Monongahela at river mile 23, 82, 89, and 102 between July 2009 and February 2012.

During our study period, Dunkard Creek (DE) which has a drainage area of 229 square miles, was the highest contributor of TDS among the watersheds in our study with a basin area between 200 - 1500 square miles. In watersheds less than 200 square miles, Flaggy Meadows had the highest TDS loading (Table 2, Figure 4).

**Table 2. Mean TDS loadings during the March 2011 - February 2012 at project sampling locations.**

Site	Q	D.Na	D.Mg	SO <sub>4</sub>	D.Ca	Cl	Alk	TDS
	cfs	tons per fortnight (tpf)						
WF	1398	1389	965	10797	3581	552	4061	21344
TV	3058	655	379	3353	1813	539	2887	9625
IN	43	408	66	1269	196	45	251	2236
WD	77	15	9	69	39	15	73	220
FM	10	504	68	1580	153	38	56	2400
M102	5347	4335	1693	18297	6897	1501	9190	41912
DE	143	114	43	577	198	71	200	1204
RO	16	50	36	588	166	5	36	881
M89	5351	3883	1838	22111	6898	1854	8598	45182
CH	5982	636	533	5115	2720	551	3220	12775
DU	590	4644	545	11739	1646	1024	2007	21606
WH	295	1477	280	3678	757	558	1778	8529
M82	11963	8580	3138	43625	12288	3637	15138	86407
TE	295	543	117	1189	582	310	1325	4066
M23	11039	9516	3491	37181	12297	5630	19266	87380
YO	4016	5662	1889	15185	6423	6800	9763	45721



**Figure 4. TDS loading (tpf) averages at sampling locations between March 2011- February 2012.**

TDS loadings were determined for each sampling period and provide a snapshot of water quality conditions during that day (Figures 5-8).

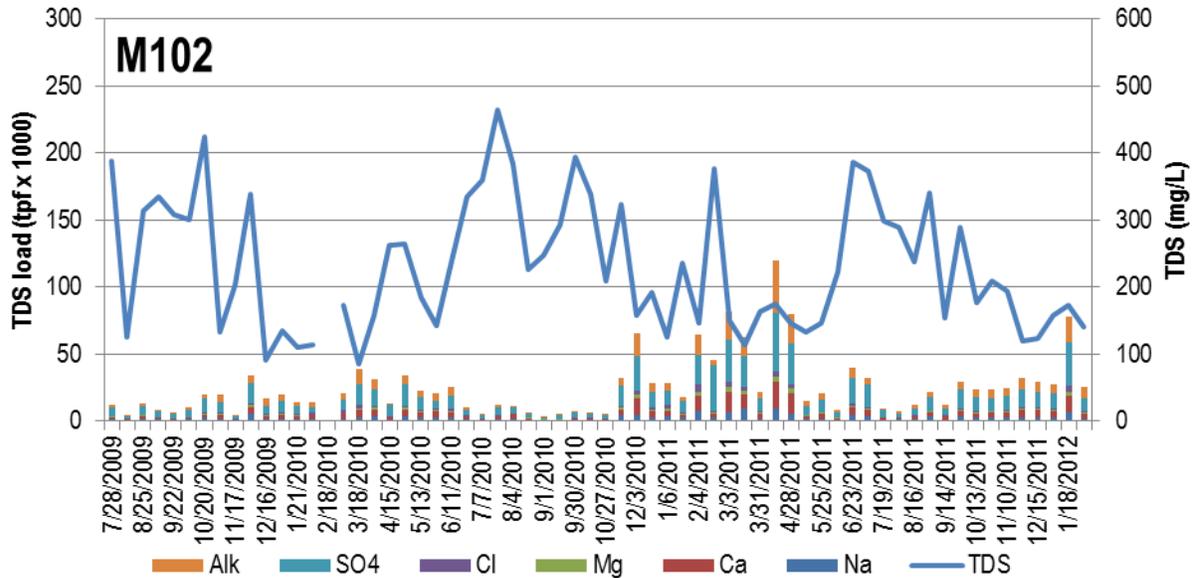


Figure 5. TDS loadings and concentrations at the Monongahela river mile 102 sampling location.

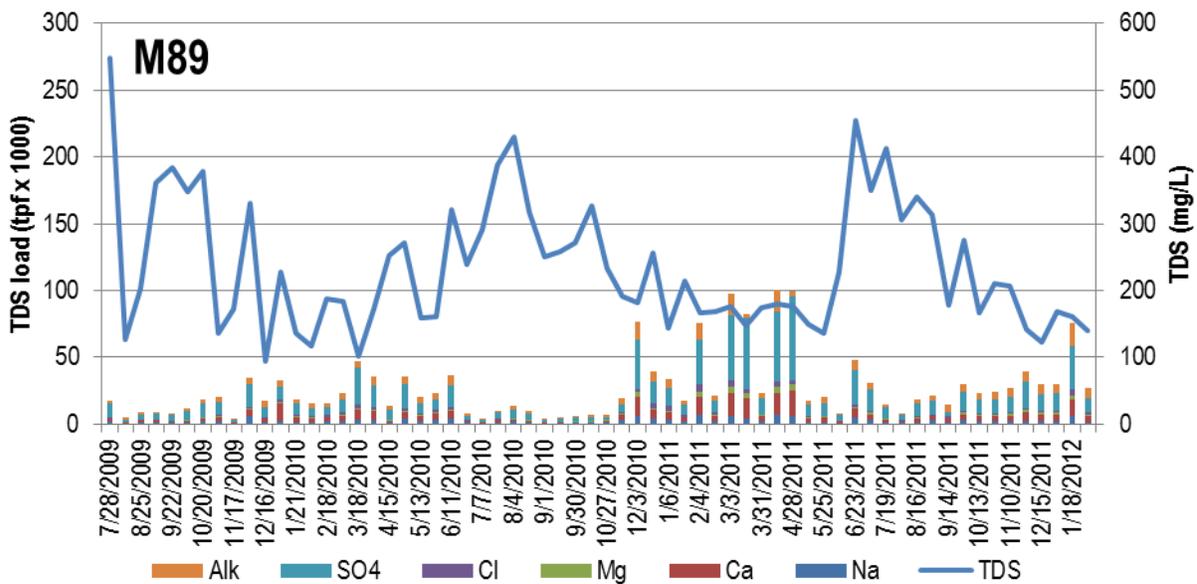


Figure 6. TDS loadings and concentrations at the Monongahela river mile 89 sampling location.

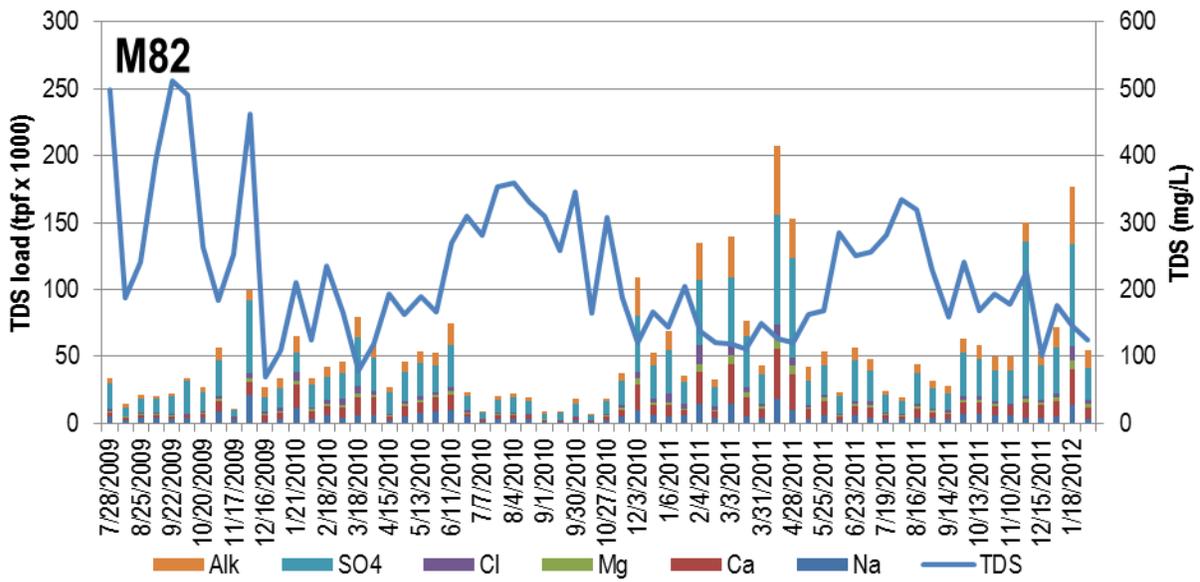


Figure 7. TDS loadings and concentrations at the Monongahela river mile 82 sampling location.

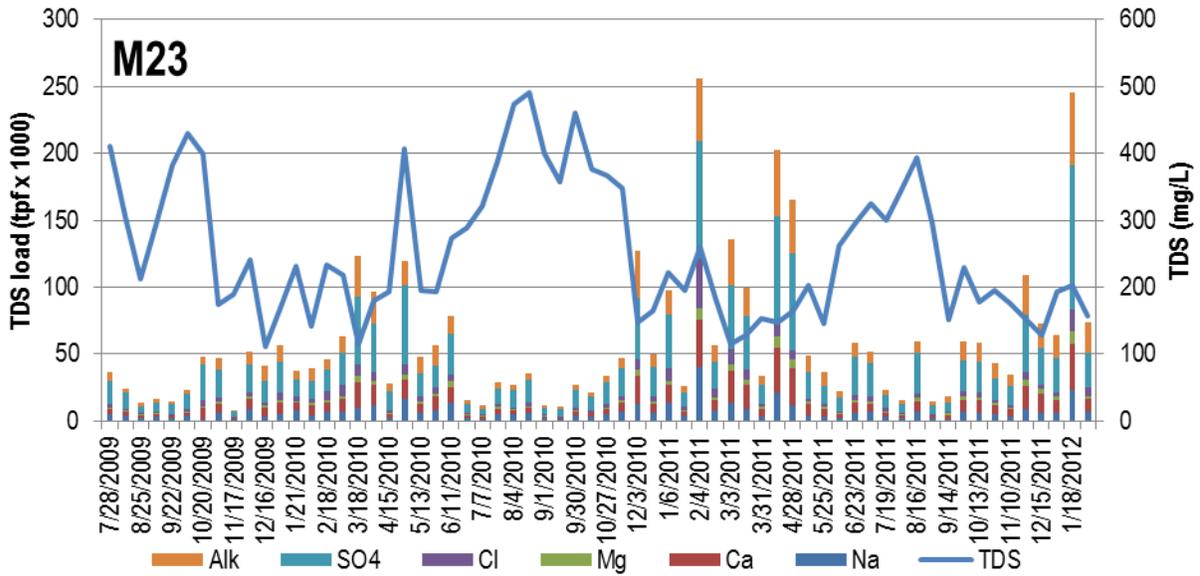


Figure 8. TDS loadings and concentrations at the Monongahela river mile 23 sampling location.

The TDS loadings (tpf) and TDS concentrations (mg/L) of individual streams provides an in-depth look at the conditions on each tributary over time. The concentrations (mg/L) of TDS and loadings of TDS (tpf) vary dependent on flow conditions (as loading is calculated by  $Q \times \text{mg/L}$ ).

As discharges increases, the TDS concentrations (mg/L) are lower. Figures 9-20 depict the TDS concentration and loadings during the 2011-2012 sampling period.

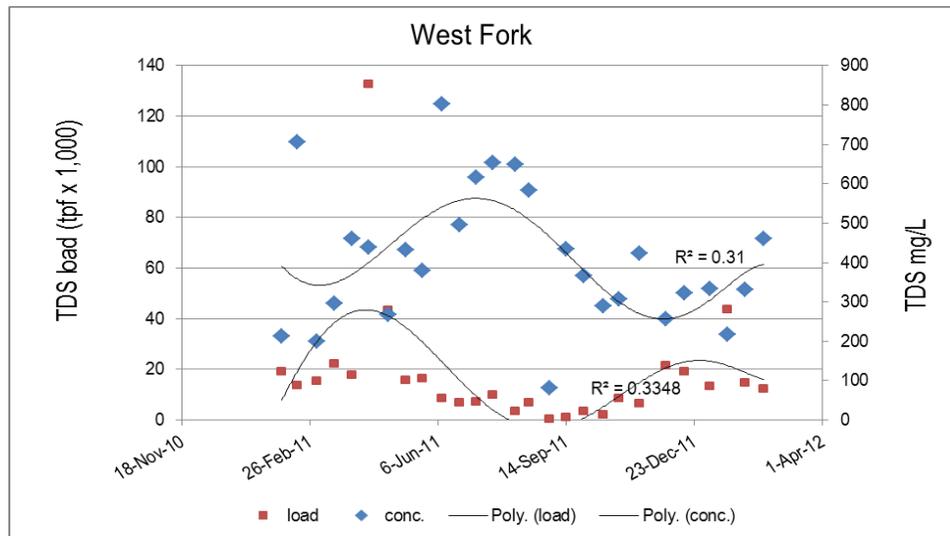


Figure 9. West Fork River (WF) TDS loadings (tpf) and concentrations (mg/L).

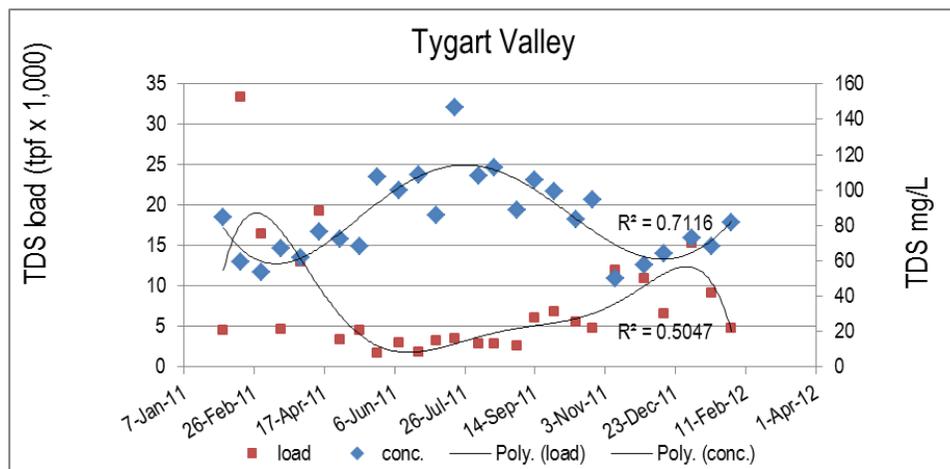


Figure 10. Tygart Valley River (TV) TDS loadings (tpf) and concentrations (mg/L).

Tributaries with lower flows, such as Indian Creek showed a TDS concentrations above 500 mg/L during much of the sampling period (Figure 11). Whiteday Creek, is our most un-impacted waterway in the study and TDS concentrations were below 100 mg/L, with the exception of one recording of 527 mg/L in September 2011 (Figure 12).

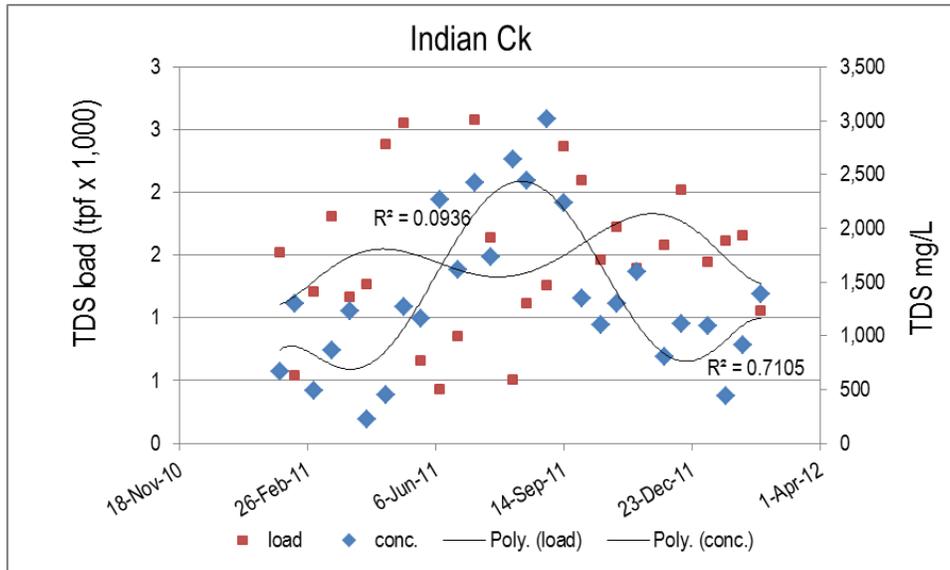


Figure 11. Indian Creek (IN) TDS loadings (tpf) and concentrations (mg/L).

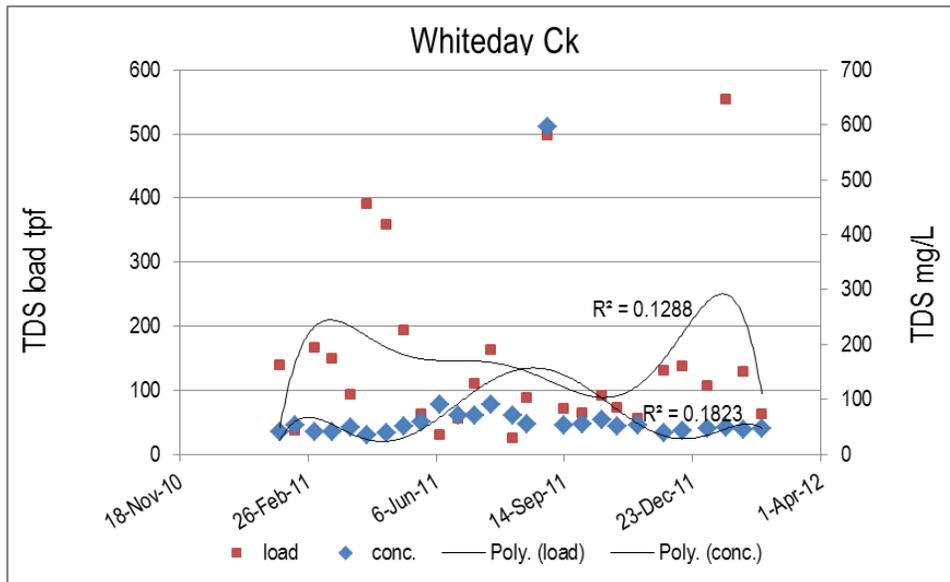
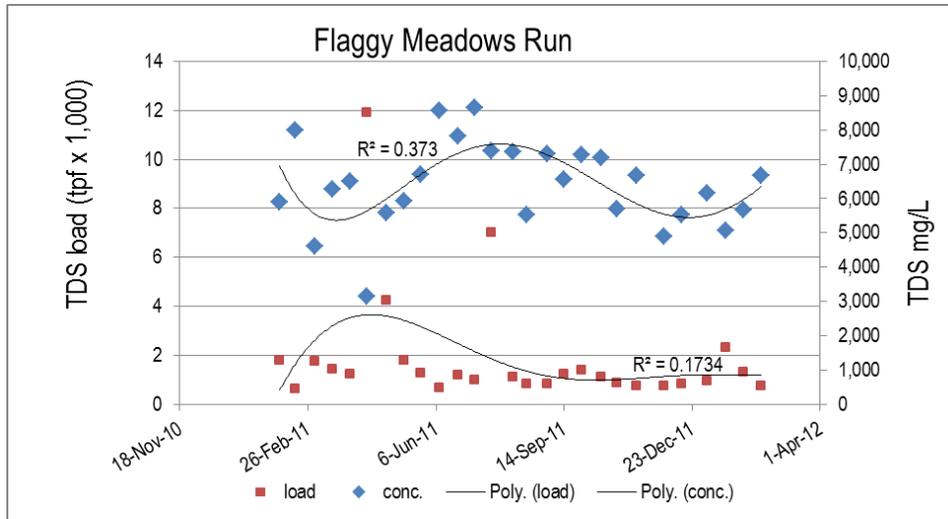


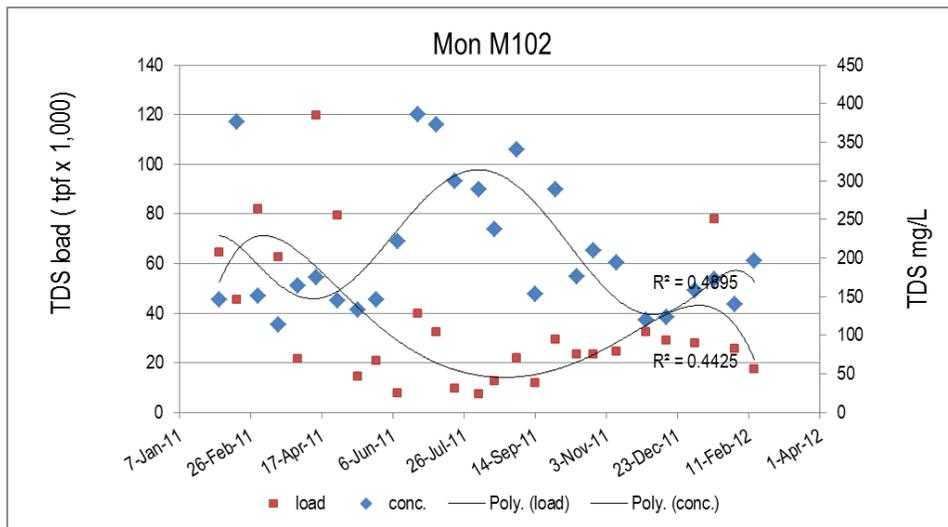
Figure 12. Whiteday Creek (WD) TDS loadings (tpf) and concentrations (mg/L).

The sample site at Flaggy Meadows Run is downstream of an Acid Mine Drainage Treatment system, and impacts from AMD can be noted in the high TDS (mg/L) values, ranging from 3,144 mg/L to 8,668 mg/L (Figure 13).



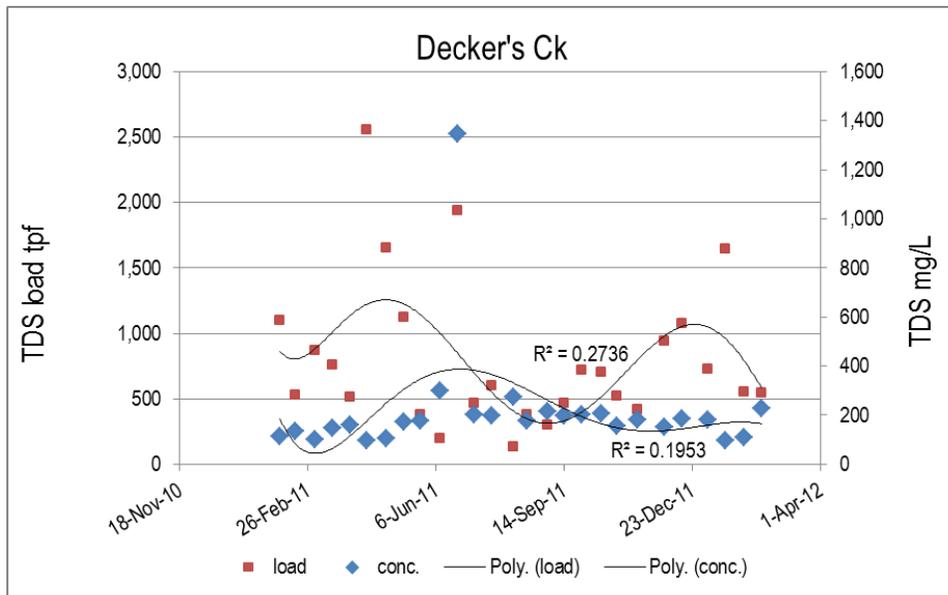
**Figure 13. Flaggy Meadows Run (FM) TDS loadings (tpf) and concentrations (mg/L).**

The sample site on the Monongahela at Morgantown shows the dilution effect of a larger waterbody, as more discharge is input from tributaries during higher flow periods, higher loadings are transported downstream. During low flow situations, TDS concentrations remain somewhat steady and remain below 386 mg/L (Figure 14).



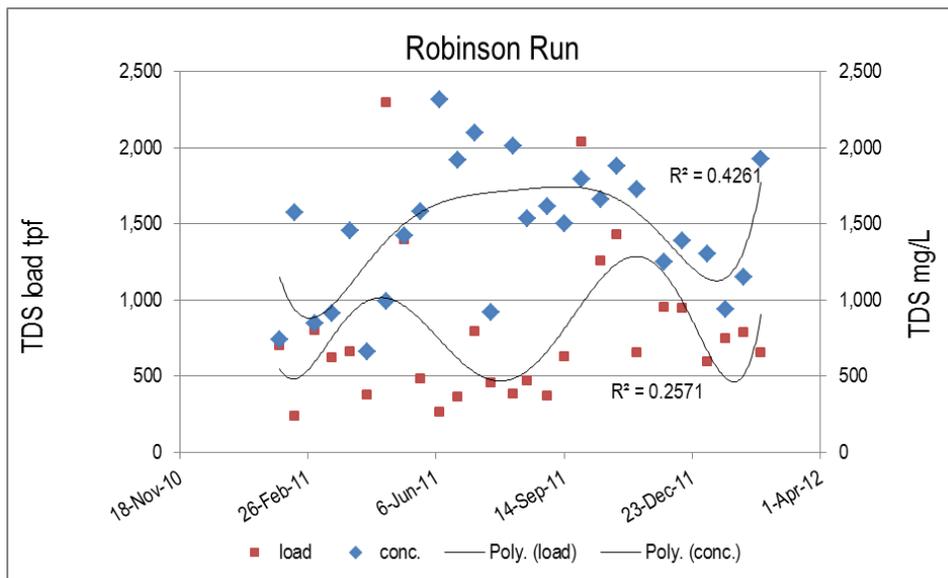
**Figure 14. Monongahela River at Morgantown (M102) loadings (tpf) and concentrations (mg/L).**

Deckers Creek concentrations of TDS (mg/L) ranged from 96 mg/L to 1348 mg/L and loadings from 130 tpf to 2,554 tpf (Figure 15) during the 2011-2012 study period.



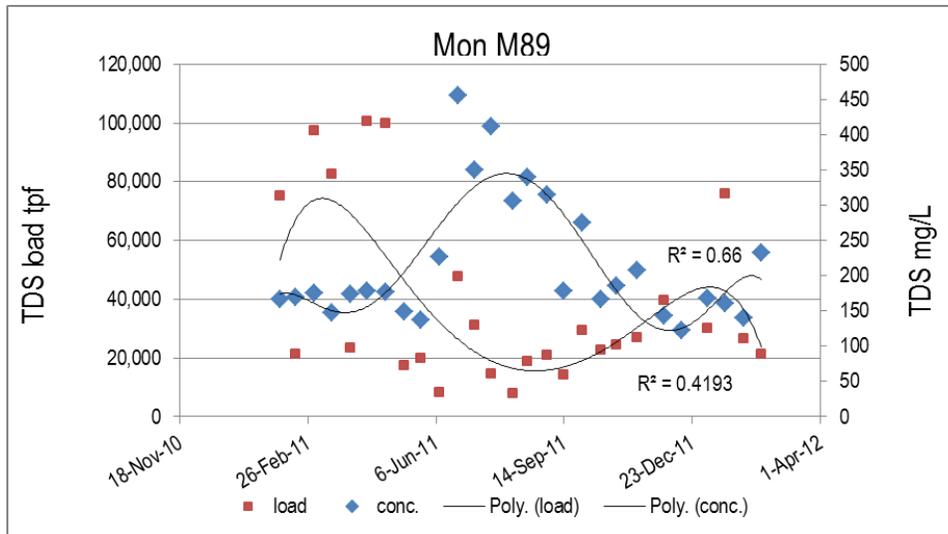
**Figure 15. Decker's Creek (DE) TDS loading (tpf) and concentrations (mg/L).**

Robinson Run is another tributary in the study that is impacted by AMD, the TDS concentrations (mg/L) ranged from 659 mg/L to 2,315 mg/L and loadings (tpf) correlated with concentrations, ranging from 239 tpf to 2,298 tpf (Figure 16).



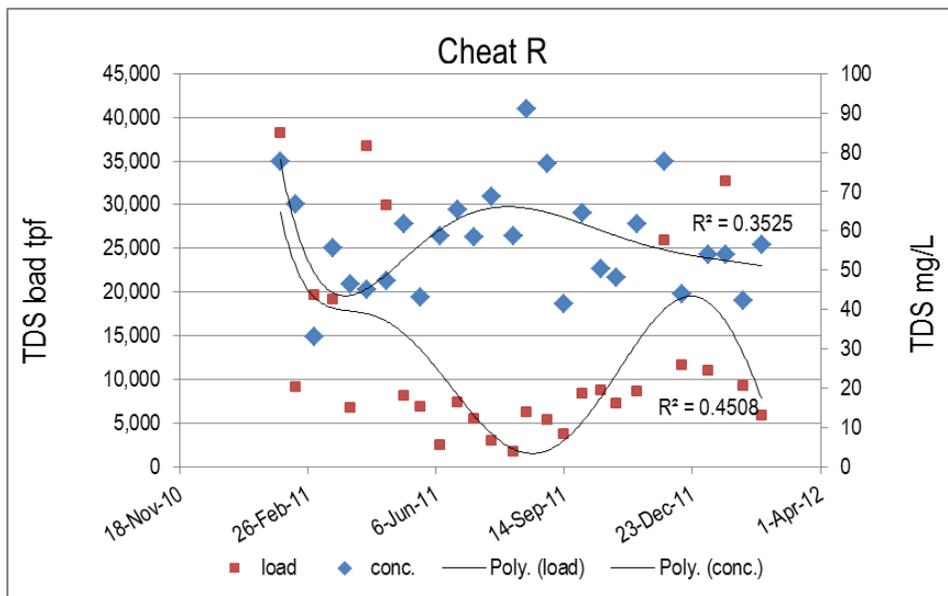
**Figure 16. Robinson Run (RO) TDS loading (tpf) and concentrations (mg/L).**

The Monongahela at Point Marion showed similar trends as the upstream site in Morgantown with slightly lower loadings, with the maximum loading at 100,447 tpf. Concentrations ranged from 122 mg/L to 455 mg/L (Figure 17).



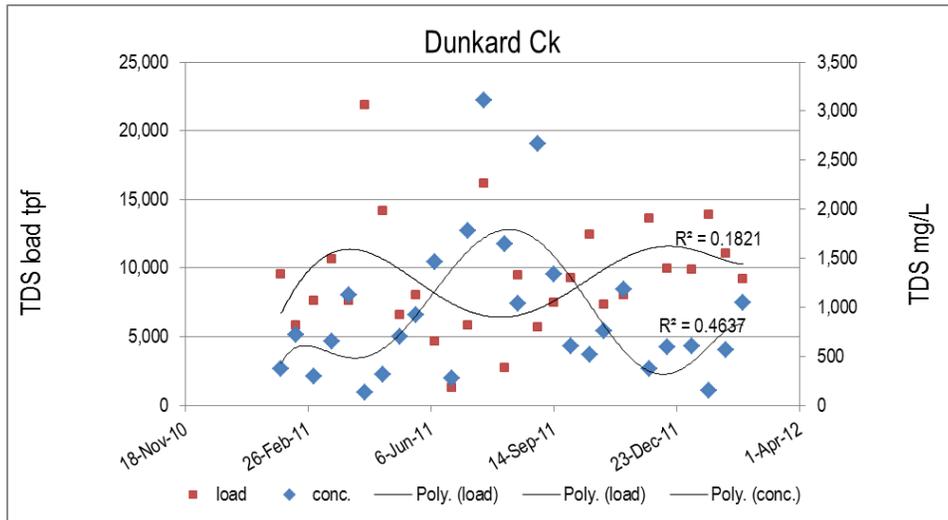
**Figure 17. Monongahela River at Point Marion (M89) TDS loadings (tpf) and concentrations (mg/L).**

The Cheat River TDS concentrations remained somewhat constant throughout the study year, ranging from 33 to 91 mg/L and loadings ranged from 1,662 to 38,252 tpf (Figure 18).



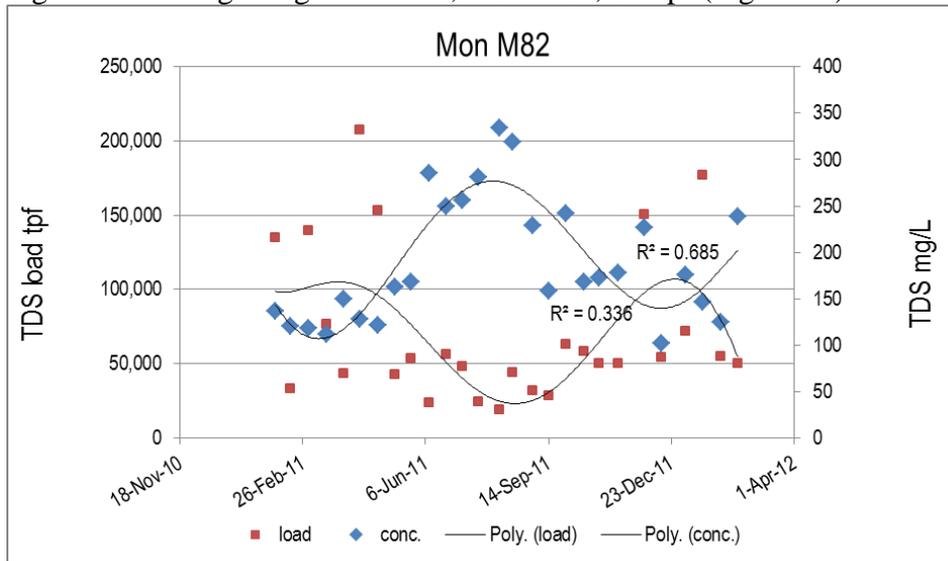
**Figure 18. Cheat River (CH) TDS loadings (tpf) and concentrations (mg/L).**

Concentrations of TDS on Dunkard Creek ranged from 130 to 3,106 mg/L and loadings ranged from 273 to 21,884 tpf (Figure 19).



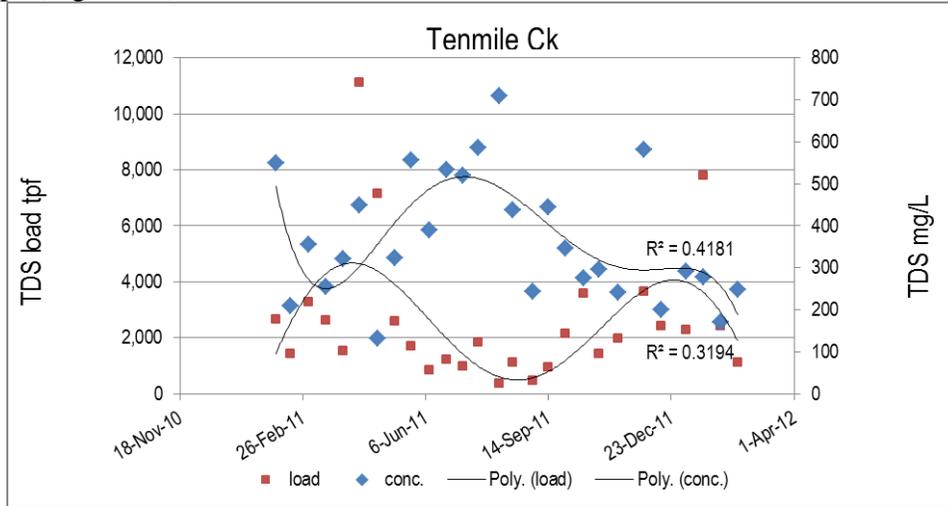
**Figure 19. Dunkard Creek (DU) TDS loadings (tpf) and concentrations (mg/L).**

The Monongahela River site in Masontown, PA showed concentrations of TDS ranging from 101 to 334 mg/L and loadings ranged from 18,906 to 207,494 tpf (Figure 20).



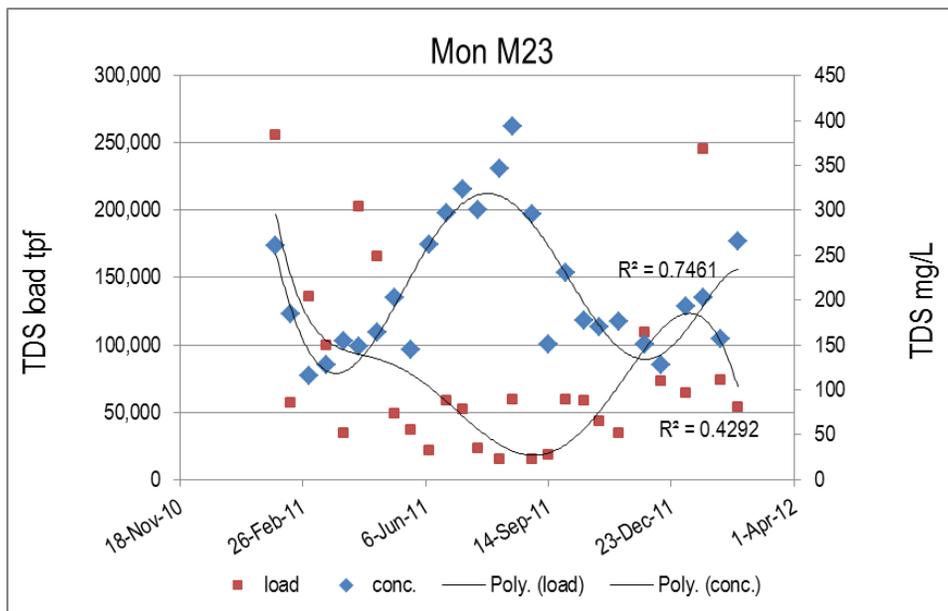
**Figure 20. Monongahela River at Masontown, PA (M82) TDS loadings (tpf) and concentrations (mg/L).**

Tenmile Creek TDS concentrations ranged from 103 to 708 mg/L and loading ranged from 367 to 11,396 tpf (Figure 21).



**Figure 21. Tenmile Creek (TE) TDS loadings (tpf) and concentrations (mg/L).**

Monongahela River at Elizabeth TDS concentrations ranged from 116 to 393 mg/L and loadings ranged from 14,911 to 255,957 tpf (Figure 22).



**Figure 22. Monongahela River at Elizabeth, PA (M23) TDS loadings (tpf) and concentrations (mg/L).**

The Youghiogheny River site TDS ranged from 176 to 497 mg/L and loadings from 12,968 to 83,752 tpf (Figure 23).

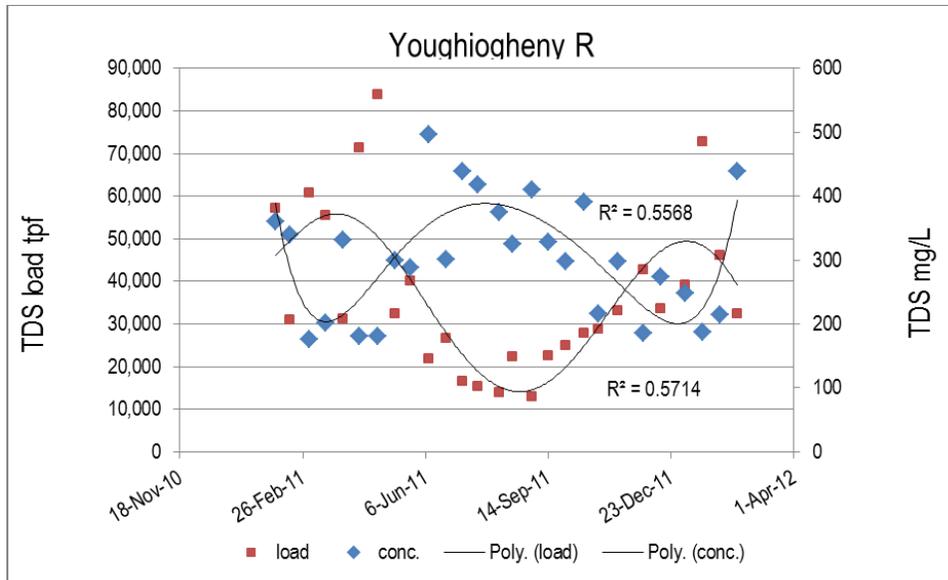


Figure 23. Youghiogheny River (YO) TDS loadings (tpf) and concentrations (mg/L).

### BROMIDE

Bromide concentrations in freshwater are very small, mostly below detection limits. Bromide facilitates the formation of brominated trihalomethanes (THMs) when it comes into contact with chemicals at drinking water treatment facilities. These THMs are volatile organic compounds, and are carcinogenic. Also, bromide is not present in acid mine drainage and is in high concentration in frac flowback water. Bromide is not readily consumed by Sulfates and is likely to remain in the freshwater system for a longer period of time (Flury, 1993). Mostly, bromide results were non-detect in laboratory analysis. However, there were several sampling periods when levels spiked high above the “norm” for that particular site. Whiteley Creek has encountered 25 instances of bromide levels above 1 mg/L between July 09 and February 2012, this highest being 16 mg/L. Several other sites were also frequented by bromide levels greater than 1 mg/L (Figure 24).

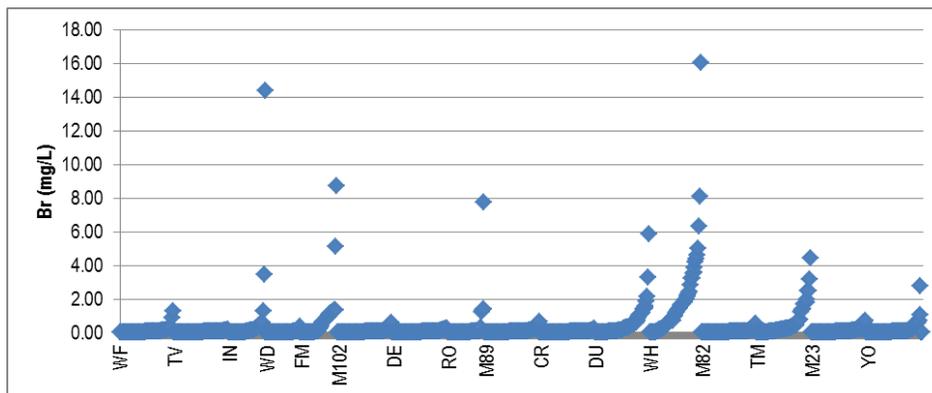
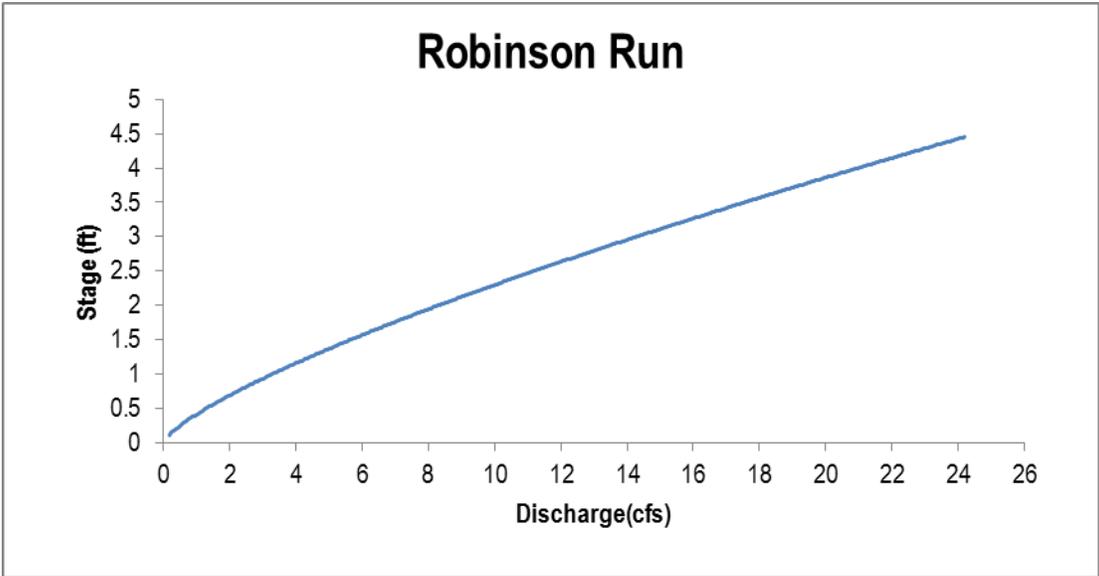


Figure 24. Bromide (mg/L) results at sampling locations.

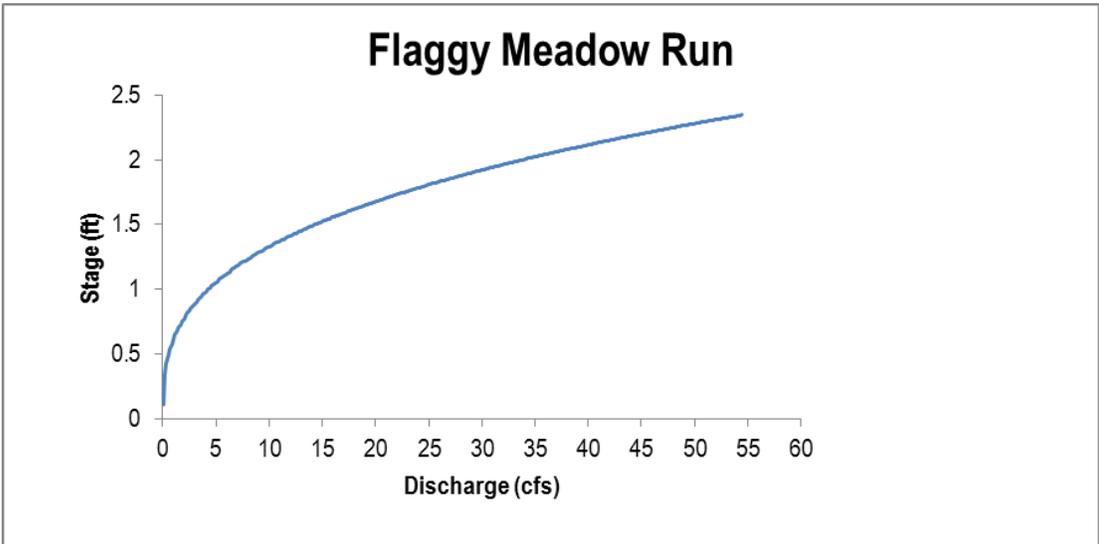
*FLOW DETERMINATIONS*

FLOW RATING CURVES VIA TRANSDUCER

Discharge for some of the smaller tributaries (i.e. Robinson Run) was determined by developing flow rating curves based on transducer readings (Figures 25-29).



**Figure 25. Flow rating curve from Robinson Run transducer.**



**Figure 26. Flow rating curve from Flaggy Meadow Run transducer.**

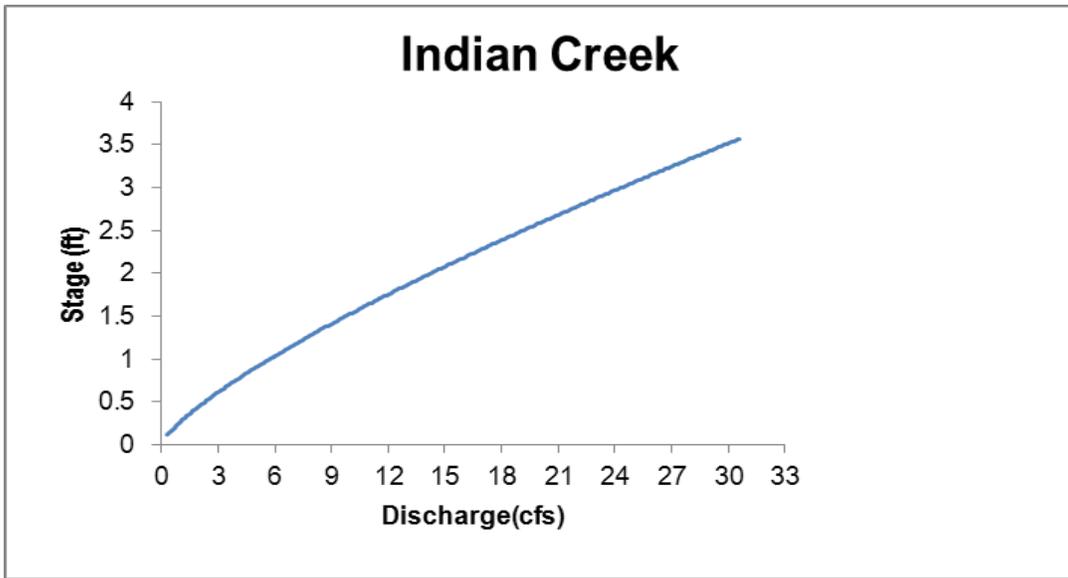


Figure 27. Flow rating curve from Indian Creek transducer.

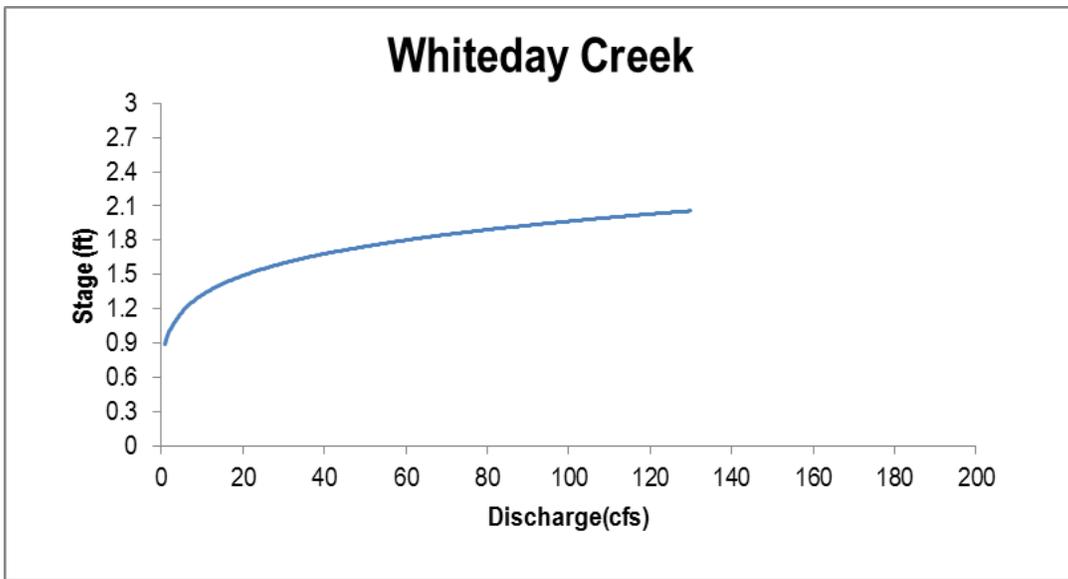


Figure 28. Flow rating curve from Whiteday Creek transducer.

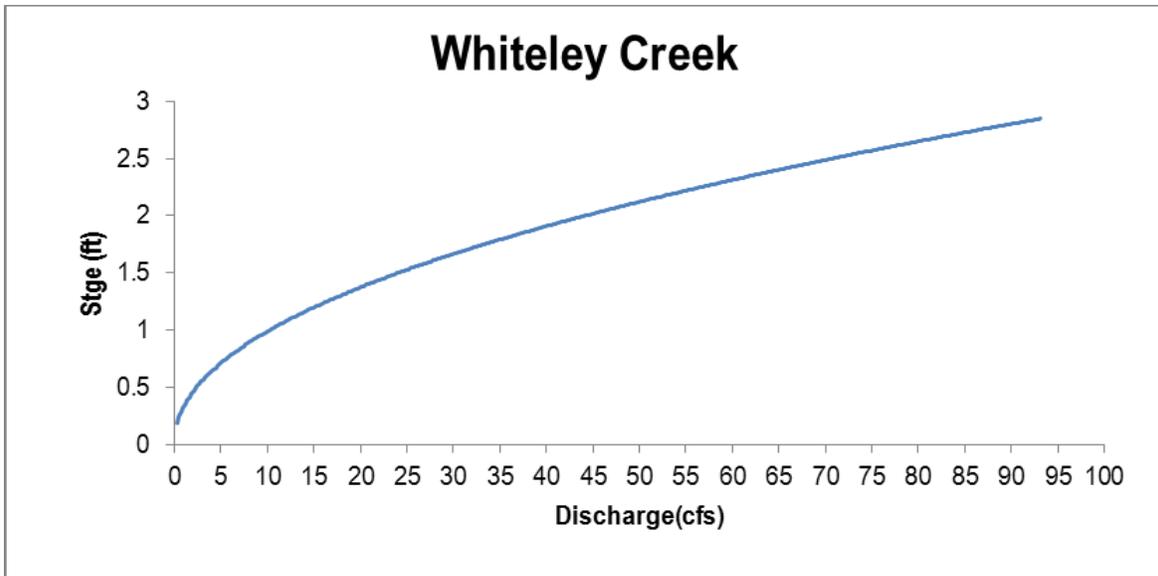


Figure 29. Flow rating curve from Whiteley Creek transducer.

### WATERSHED CHARACTERIZATION MODELING SYSTEM

The Watershed Characterization Modeling System (WCMS) is an extension tool developed for ArcGIS. The WCMS extension tool was utilized to determine the 30 year average flows at all West Virginia sampling sites (WCMS is limited to the state of WV). Flow rating graphs were created for the sites. Discharge on sites that did not have gages, were determined by reviewing the graph for sites with known discharge and relating those current conditions to ungaged sites. For example, when the known discharge of the West Fork is 2000 cfs, the assumed discharge on the Monongahela River at Morgantown (M102) is 7000 cfs (Figure 30).

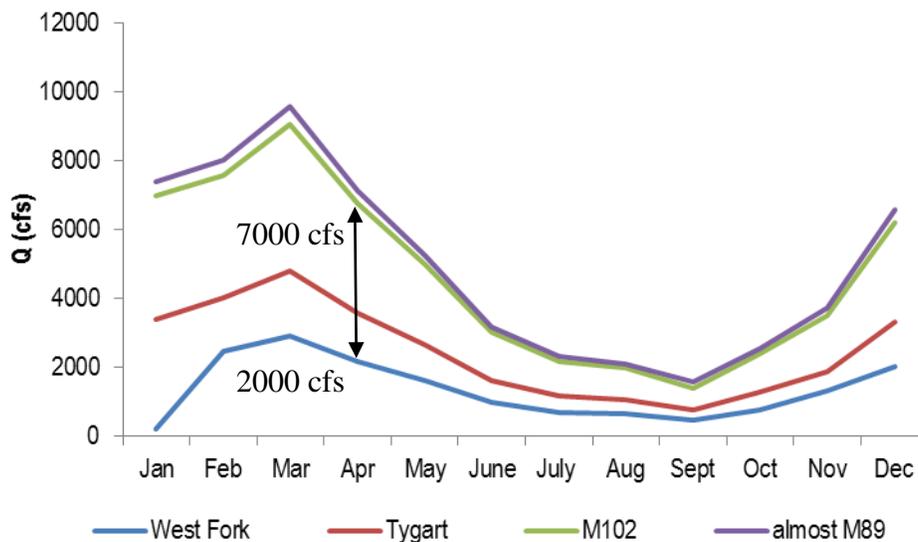


Figure 30. WCMS 30 year average flow ratings for sites with discharges above 1000cfs.

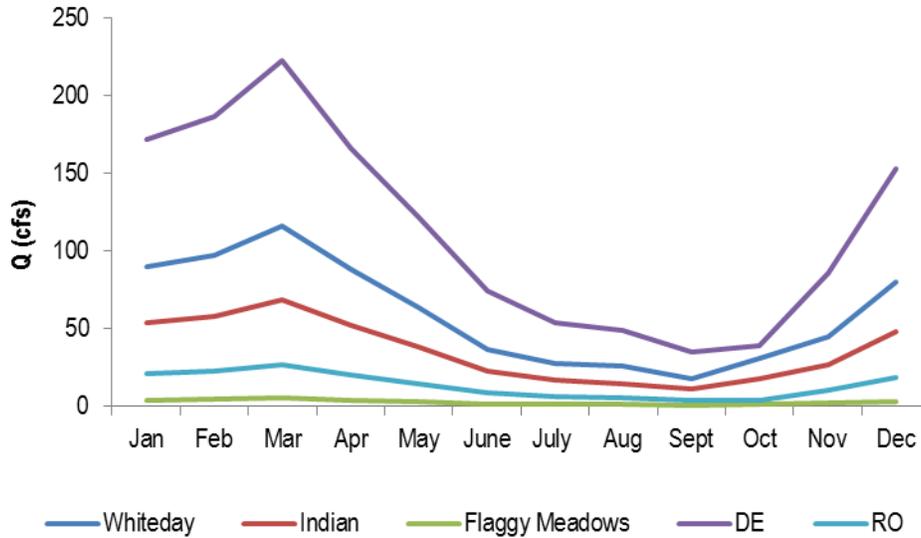


Figure 31. WCMS 30 year average flow ratings for sites with discharges below 1000cfs.

**TRIBUTARY SITES**

Good water quality of headwater streams and major tributaries is vital to maintain a healthy watershed ecosystems and fisheries. Equally as important is the ability of these tributaries to supply the Mononaghela with quality drinking water.

In addition to tributary sampling on the West Fork River, Tygart Valley River, Deckers Creek, Cheat River, Whiteley Creek, Dunkard Creek, Tenmile Creek, and the Youghiogheny River, sample locations were selected and collection initiated in May 2010 for Robinson Run, Flaggy Meadows Run, and Indian Creek. Whiteday Creek was added to the sampling regime in July 2010. Tributary loading data (tpf) were calculated to view the sampling regime prior and post addition of the new sites. Data reveals that the Youghiogheny River is the highest contributor of flow as well as TDS (Figures 32 to 39). Figures were calculated as post-May 11 to signify the closure Pennsylvania waste water treatment facilities for processing return frac water.

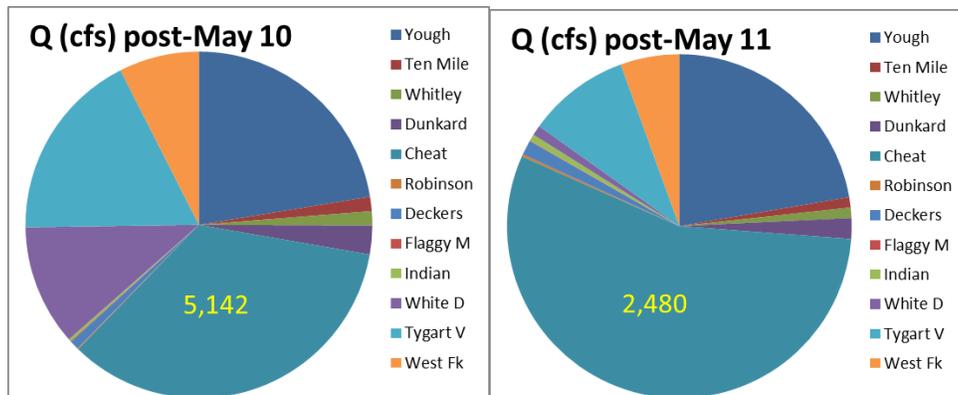


Figure 32. Q (cfs) for tributary sites pre (A) and post (B) addition of Robinson Run, Flaggy Meadows Run, Indian Creek, and Whiteday Creek.

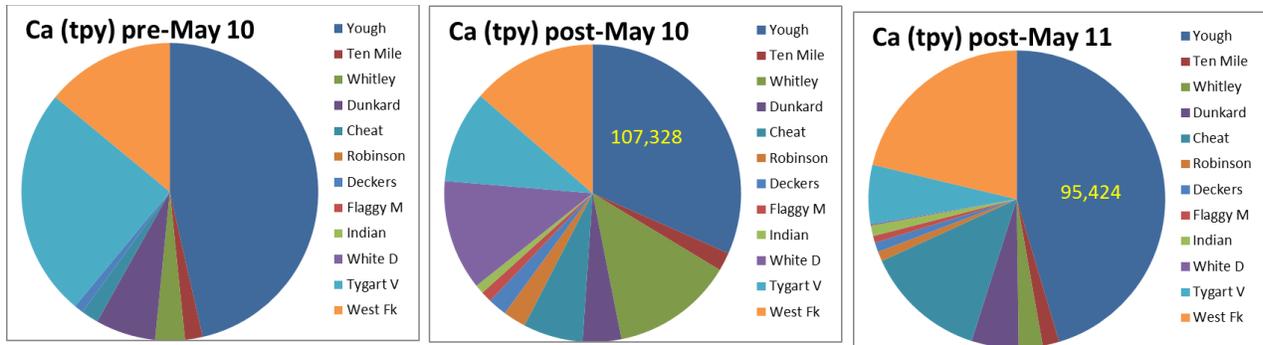


Figure 33. Calcium (tpf) for tributary sites pre (A) and post (B) addition of Robinson Run, Flaggy Meadows Run, Indian Creek, and Whiteday Creek.

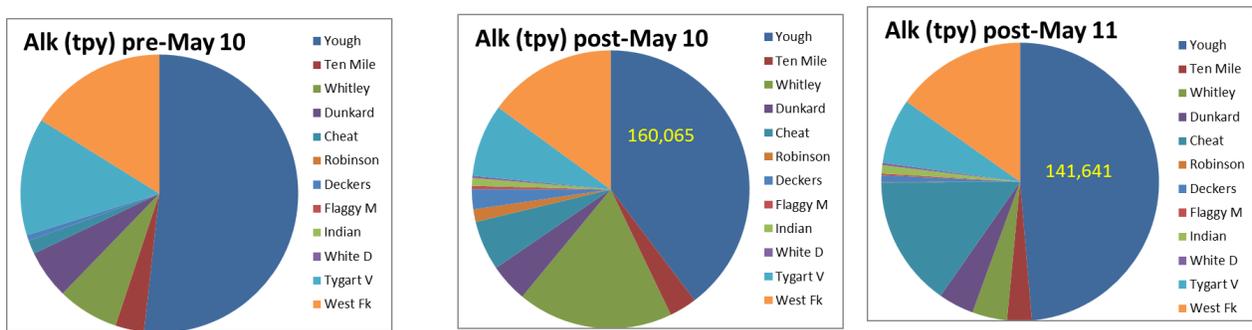


Figure 34. Alkalinity (tpf) for tributary sites pre (A) and post (B) addition of Robinson Run, Flaggy Meadows Run, Indian Creek, and Whiteday Creek.

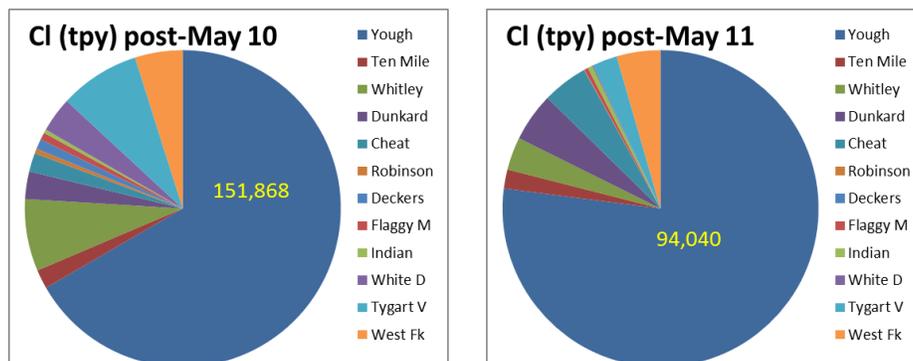


Figure 35. Chloride (tpf) for tributary sites pre (A) and post (B) addition of Robinson Run, Flaggy Meadows Run, Indian Creek, and White day Creek.

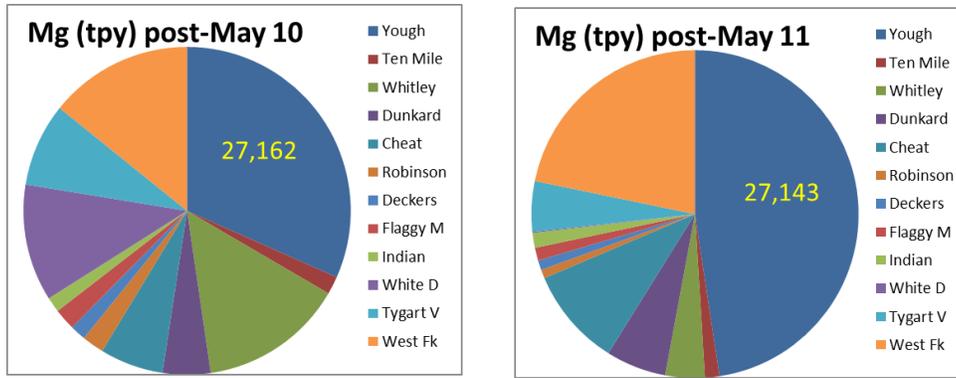


Figure 36. Magnesium (tpf) for tributary sites pre (A) and post (B) addition of Robinson Run, Flaggy Meadows Run, Indian Creek, and White Day Creek.

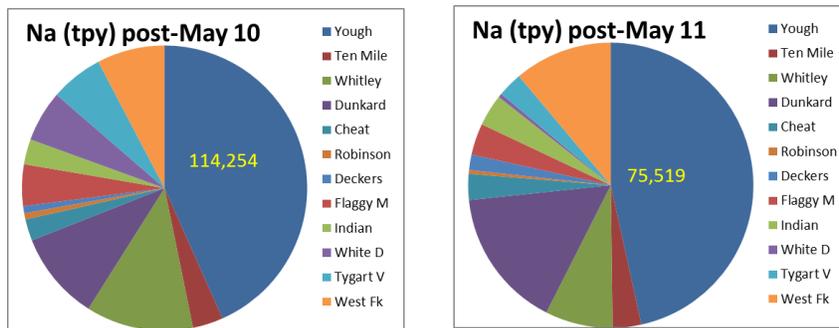


Figure 37. Sodium (tpf) for tributary sites pre (A) and post (B) addition of Robinson Run, Flaggy Meadows Run, Indian Creek, and Whiteday Creek.

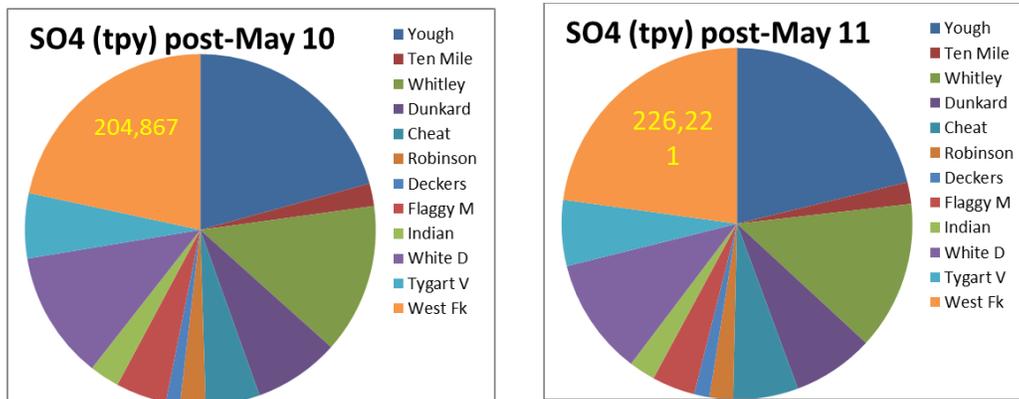
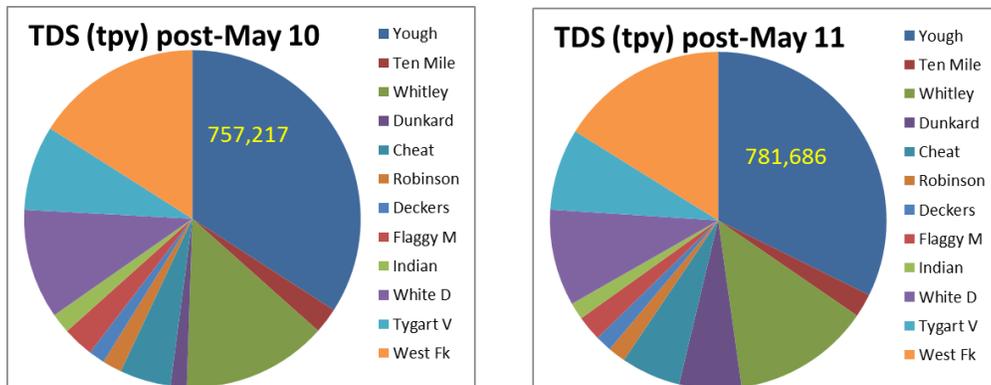


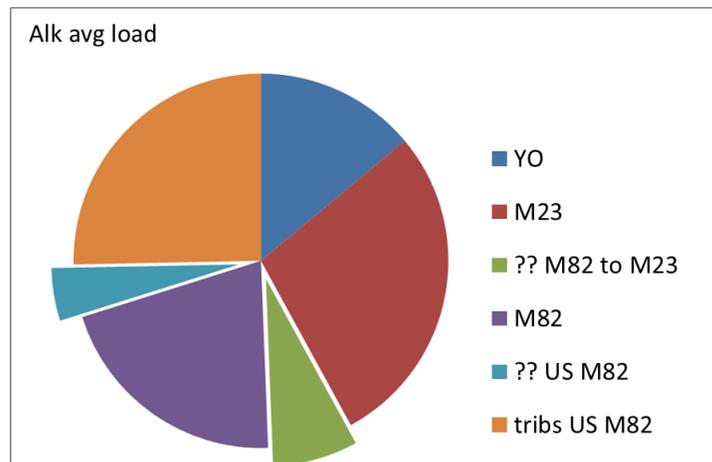
Figure 38. Sulfate (tpf) for tributary sites pre (A) and post (B) addition of Robinson Run, Flaggy Meadows Run, Indian Creek, and Whiteday Creek.



**Figure 39. Total Dissolved Solids (tpf) for tributary sites pre (A) and post (B) addition of Robinson Run, Flaggy Meadows Run, Indian Creek, and Whiteday Creek.**

*LOADINGS AT ELIZABETH PA*

The final downstream site in our study is at river mile 23 on the Monongahela, near Elizabeth PA. For the validity of the study, we determined loadings (tpf) on the Monongahela and the Youghiogheny and combined other tributaries for each of our parameters. The output pie charts show they we capturing the majority of high loading tributary contributions to the Monongahela (Figures 40-47). The “???” are for unaccountable loadings that are contributed by tributaries not included in our study.



**Figure 40. Alkalinity average loading (tpf) at sample locations.**

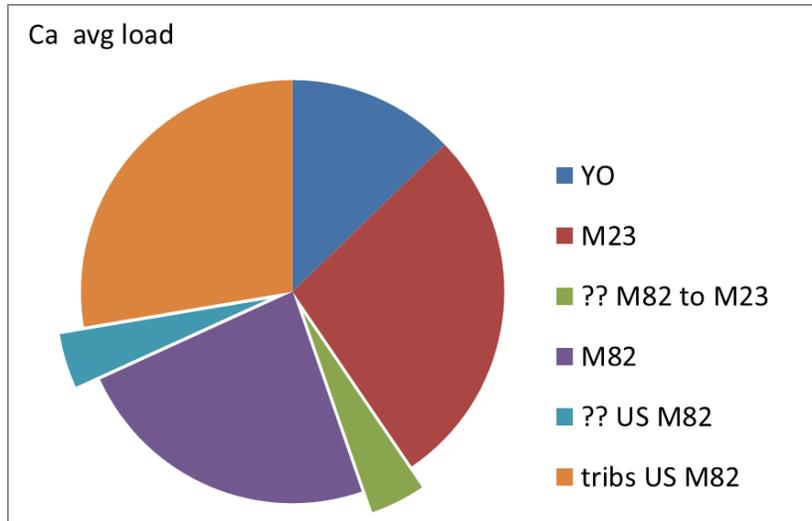


Figure 41. Calcium average loading (tpf) at sample locations.

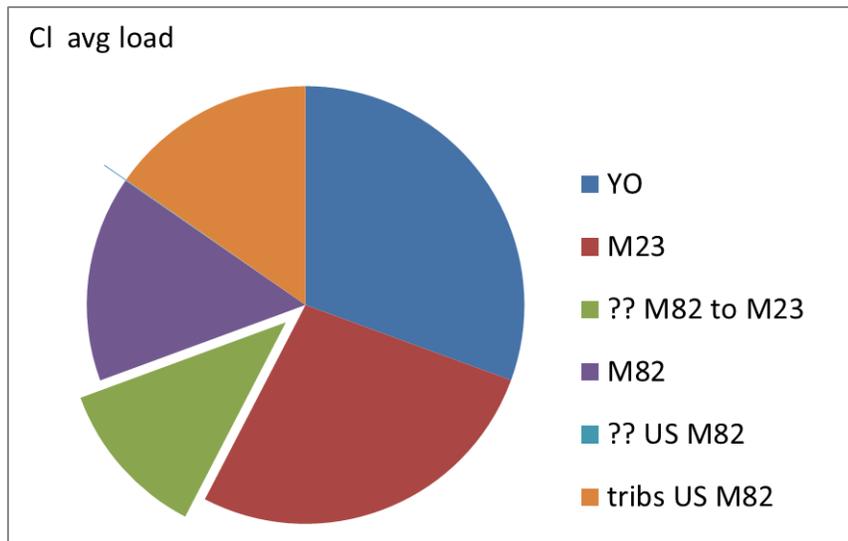


Figure 42. Chloride average loading (tpf) at sample locations.

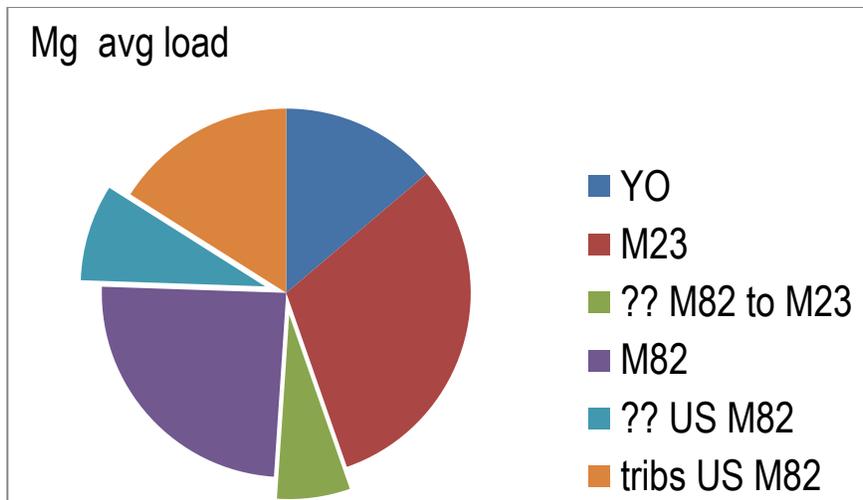


Figure 43. Magnesium average loading (tpf) at sample locations.

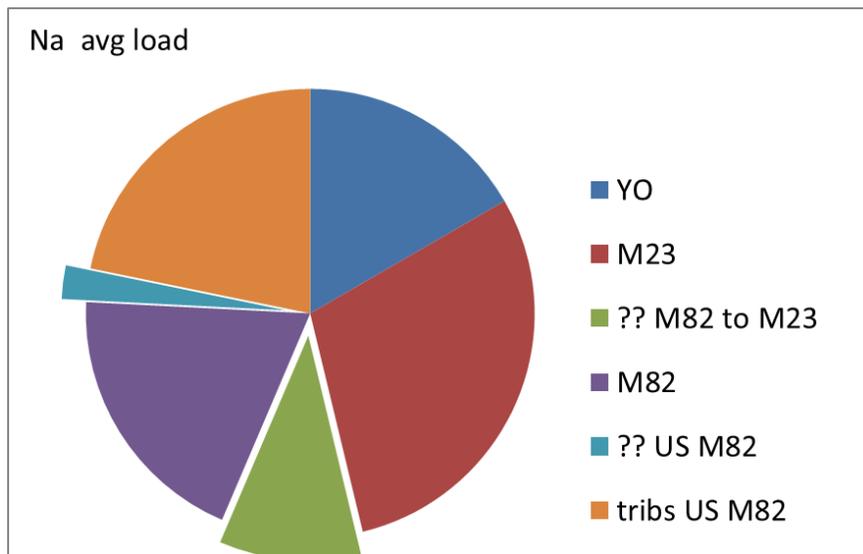


Figure 44. Sodium average loading (tpf) at sample locations.

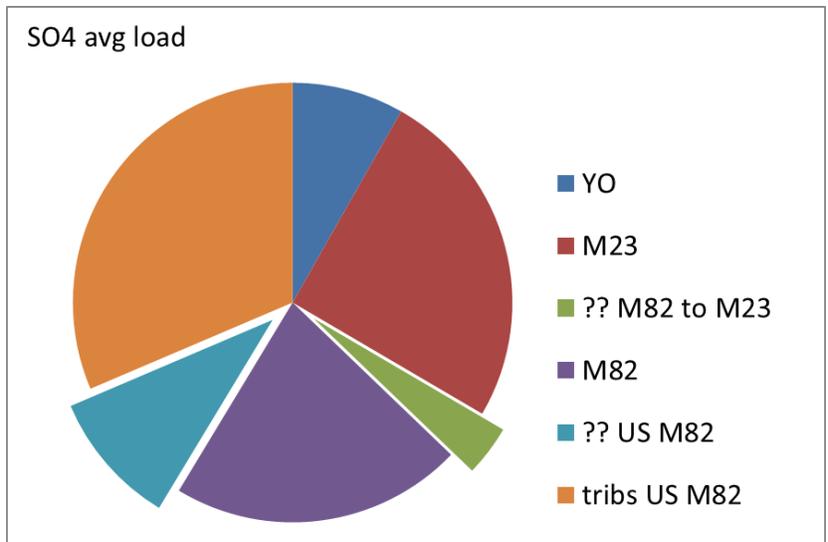


Figure 45. Sulfate average loading (tpf) at sample locations.

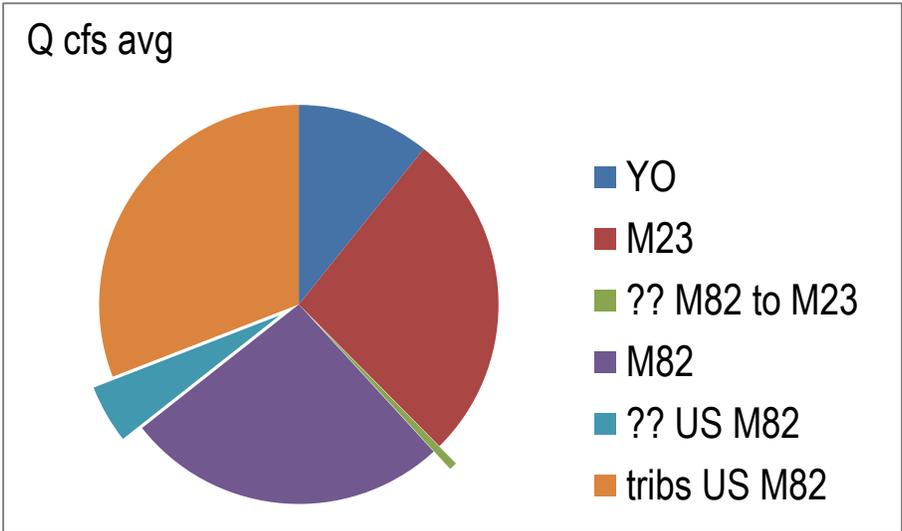


Figure 46. Q (cfs) average at sample locations.

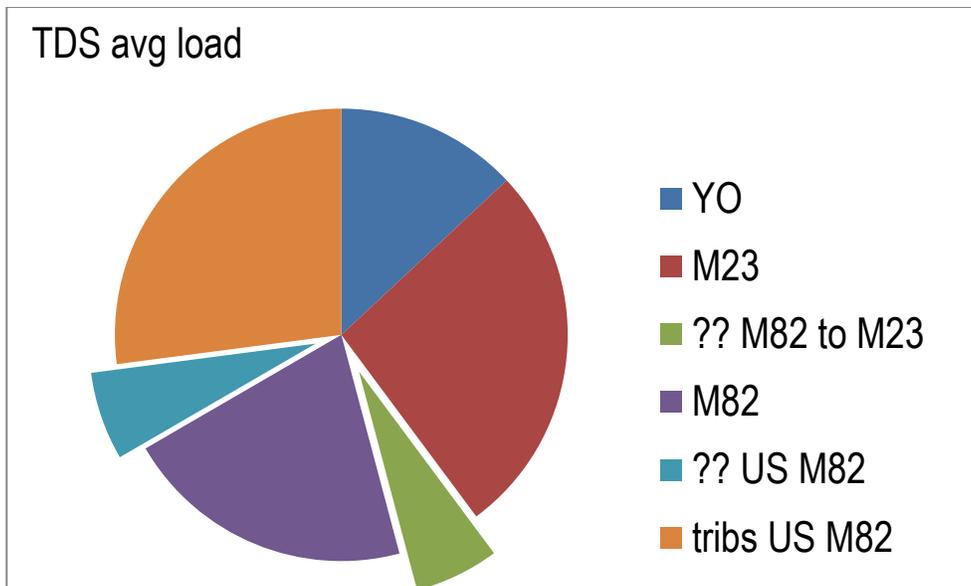


Figure 47. Total Dissolved Solids average loading (tpf) on mainstem Monongahela and Youghiogheny River Sites.

### CHEMICAL SIGNATURES

Calculating the mmol/L for each site revealed unique chemical signatures for the tributaries and mainstem Monongahela. Tributaries that are influenced by acid mine drainage, such as Flaggy Meadows Run, has a high ratio of sodium and sulfates. Whereas waters influenced by brine inputs such as the Youghiogheny River have a chemical signature of sodium chloride (Figure 48).

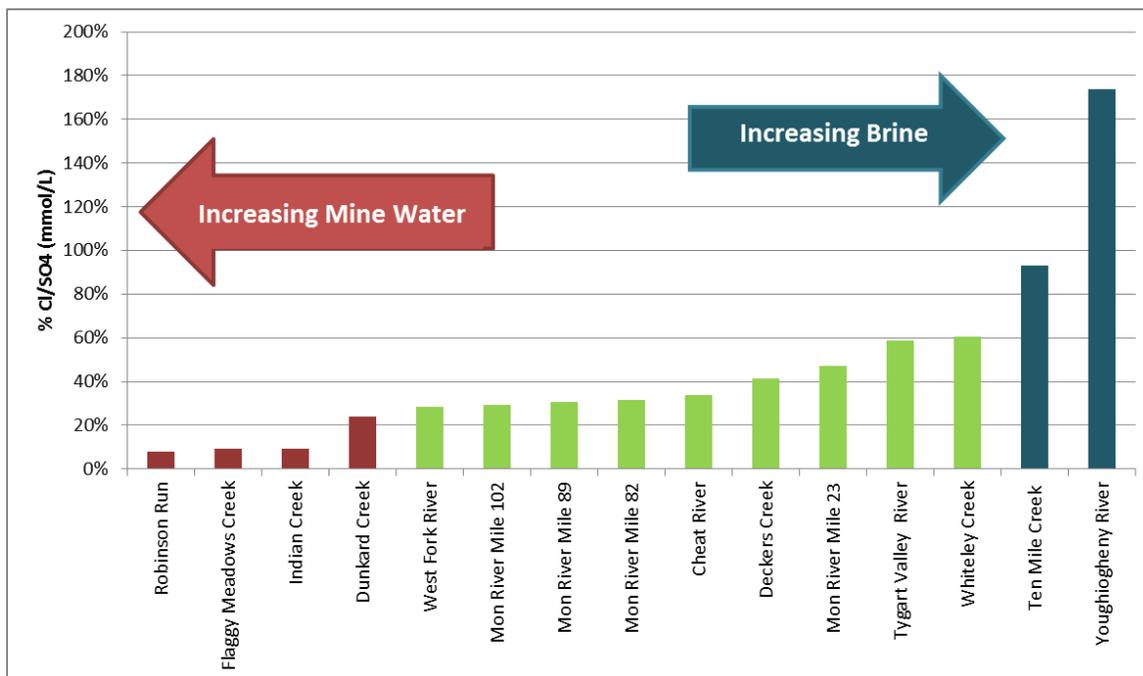


Figure 48. Chemical signatures of AMD and brine water.

## PROJECT WEBSITE

### HOME PAGE

Because the internet is an extremely effective way to disseminate the project results to the most people in the timeliest fashion, a website has been developed as the primary tool for information transfer. A domain name, [www.MonWQ.net](http://www.MonWQ.net), was selected. Short and descriptive, it was decided upon for its simplicity and is easy to remember. The site's home page briefly describes the Monongahela River and the project. It includes hot button links to the other pages on the site including a page detailing the study, a project map, graphically depicted resultant data, measured parameter descriptions, project participants, printable fact sheet, links and contact information. A rolling slide show of pictures representing the sampling locations is also a component of the website's home page. Usage has steadily increased since the site went online (Figure 49).

**MonRiver QUEST**  
— A West Virginia Water Research Institute Project

Home About Volunteers Data News Calendar Resources Contact

Water Quality Map: Detailed information displayed in easy to read charts.

**Welcome to Mon River QUEST**

The Mon QUEST is the West Virginia Water Research Institute's (WVWRI) water quality monitoring program for the entire Monongahela River Basin (MRB).

This site serves as a platform to display resultant data collected by both WVWRI technical staff and participating watershed groups. Valuable information about the current water quality is provided and will give researchers, recreationists, policy makers, regulating agencies and industry a better overall picture of the health of the Mon River Basin.

**News and Announcements**

- 05.11.2012 - DOMINION POST**  
River's dams are showing their age  
We were told we could get a good view of the explosion if we waited along the B&O Railroad tracks. We drove to Jefferson and parked our car. We walked across the railroad bridge...  
[Read More](#)
- 02.06.2012 - WVU TODAY**  
West Virginia Water Research Institute wins regional award, nominated for national  
Mon River Quest, a comprehensive water quality monitoring program established by the West Virginia Water Research Institute at West Virginia University, has been recognized...  
[Read More](#)
- 02.01.2012 - DAILY ATHENAEUM**  
Mon River QUEST monitors local water safety  
Mon River QUEST, a study supported by West Virginia University, aims to monitor water safety in the Monongahela River. The project, which started in 2010 and is funded by the Colcom Foundation, asks volunteers to take water samples...  
[Read More](#)
- 1.19.2012 - HICKESPORT DAILY NEWS**  
River researchers help assess Monongahela water's 'health'  
It's a cold January morning. Ben Mack, a research associate from West Virginia University's West Virginia Water Research Institute, leaves a fresh set of boot prints in the snow as he...  
[Read More](#)

**Upcoming Events and Meetings**

Check out the calendar for the latest information on watershed group meetings and events from throughout the Mon River Basin.

**Tuesday May 29**

- Monday June 4**  
6:30pm Ten Mile Creek Watershe
- Monday June 11**  
8:30pm Peters Creek Watershe
- Monday June 18**  
7:00pm Save The Tygart Month
- Wednesday June 20**  
WVU - Harry Enstrom Chapter Mtg

[Google Calendar](#)

**Volunteer Log-In**

If you are a volunteer and have data to record, log in here.

**Data Map**

See the differences in water quality at different locations at a glance and view changes over time.  
Start exploring the map right now!

**Volunteer**

If you would like to receive more information on how you can get involved with the program, please send your contact information (name, email, phone number) to Glenn Robinson or reach him at (304) 293-7088.

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Web Site hosted at West Virginia University's National Research Center for Coal & Energy

[Find us on Facebook](#)

Figure 49. Project website home page.

## MAP PAGE

Utilizing the ArcGIS program, this interactive and user friendly map serves as the foundation to share the sample locations with website visitors. A “zoom” feature allows site visitors to see the sampling locations as well as anyplace in the watershed at a detailed level. Maps can be displayed showing streets and highways, topographic features, or high resolution aerial imagery. Watershed boundaries for the Monongahela River and the monitored tributaries are outlined. Monitoring site data is graphically displayed on the map by sampling date. A color coded “dot” display indicated levels of TDS by color and size of the dot located at the monitoring site (Figure 50).

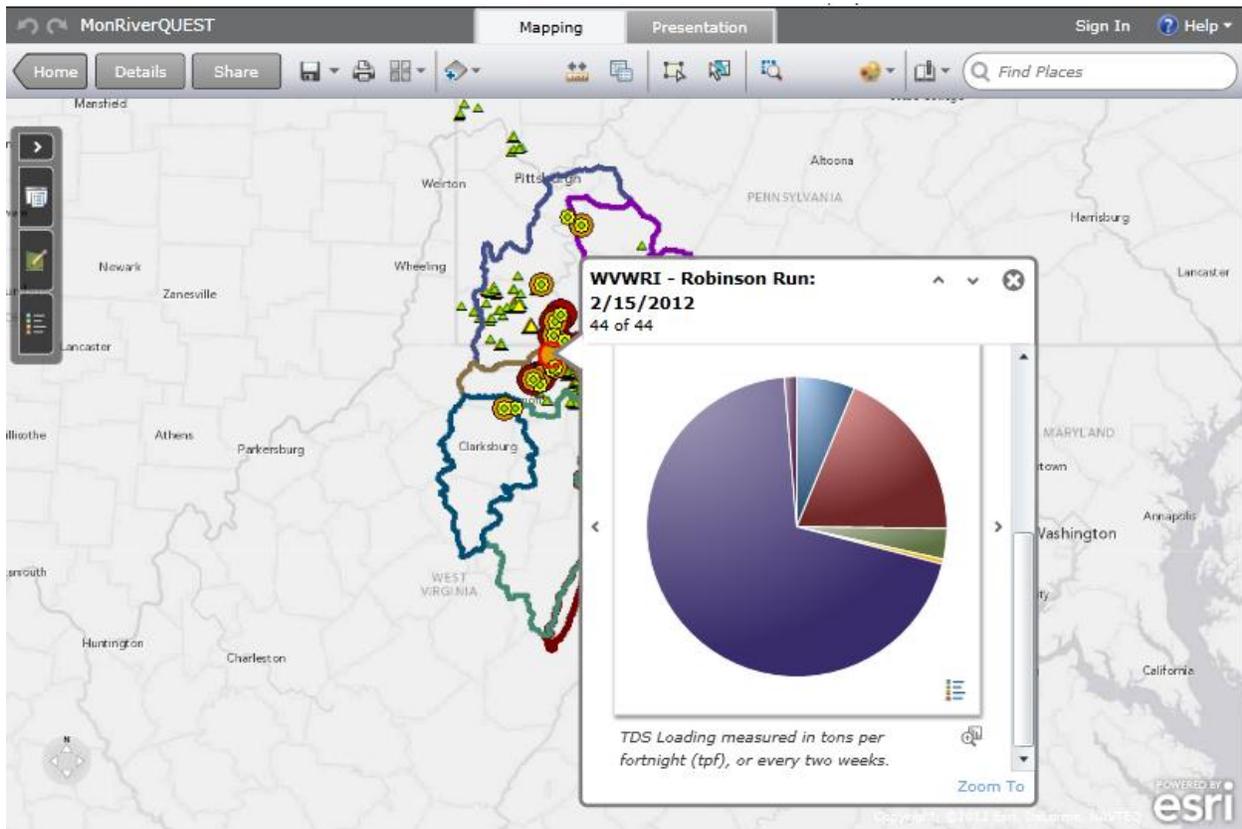


Figure 50. Website screen image of interactive ArcGIS map.

## WEBSITE TRAFFIC

The website has received more than 5,500 unique visitors and approximately 117,368 hits between March 2011 and March 2012 (Figure 51).

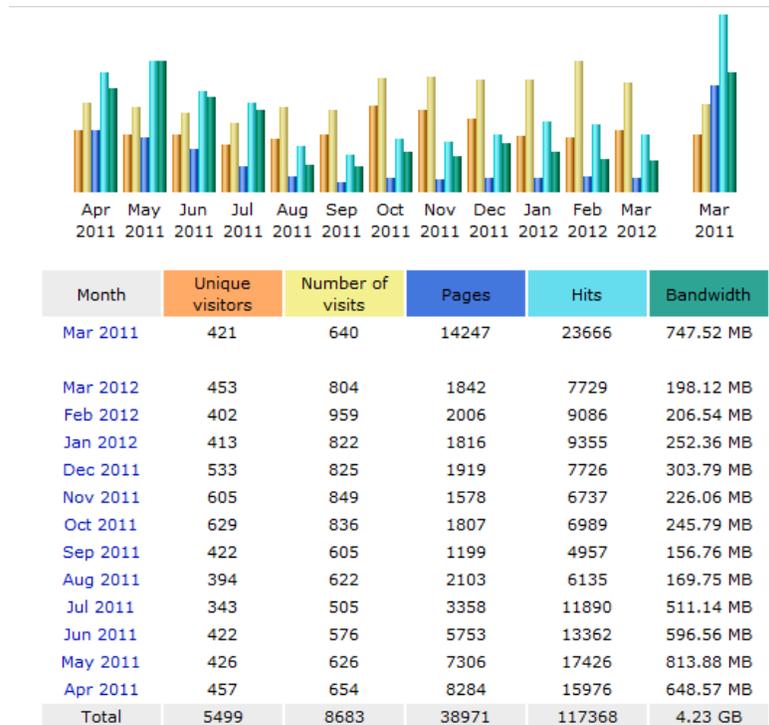


Figure 51. Monthly user statistics from the project website.

## DISCUSSION

As the local population grows and as industrial users of the river increase, the importance of the Monongahela River as a clean source of water, which helps to drive the regional economy and quality of life of the Basin's residents, has become increasingly clear. Good information gleaned from a reliable water quality monitoring program is critical to managing the long-term health of the River.

Legacy water impacts from historic coal mining, mine drainage from active coal mines and the emergence of a booming natural gas industry within the Monongahela River Basin are all putting pressure on the quality of the water in the Monongahela River while at the same time making increasing demands on the river to provide a clean and reliable source of water to drive these economic engines. Elevated levels of Total Dissolved Solids, or TDS, are a troubling result of some of these activities. To effectively manage the levels of these pollutants requires quality information about where, when and how much of these pollutants are entering the River. Since

July of 2009, this project has generated an unprecedented amount of data for a large river system such as the Monongahela.

The results of this monitoring program have allowed or resulted in three important outcomes. 1.) It has been recognized as important by additional funding agencies and received funds to keep extend and expand the program; 2.) Its success has captured the attention of other water researchers in the region who have awarded it with the Regional IMPACT Award through the National Institutes of Water Research; and 3.) the data generated in this program have enabled mining companies active in the basin to institute a “Managed Discharge” system to control TDS levels in the River.

Originally funded by the United States Geological Survey’s (USGS) 104B program, the project has received additional support from other entities. In May 2011, the Colcom Foundation from Pittsburgh, PA provided additional funding to extend and expand the program. This funding made it possible to continue with the original monitoring program and also expand it to include volunteer collected data from Watershed organizations within the MRB. This program, called the Mon River QUEST, has provided training, equipment and data management and display functions for local watershed organizations. The data they are collecting is often in the headwater streams within the basin which has expanded the monitoring reach of the program and allowed a greater awareness of the River’s health to the residents and users within the basin. In May 2012, the Colcom foundation announced a major new funding initiative for the program to extend the protocol developed for the Monongahela River Basin to include the Allegheny River and upper Ohio River in the program. This newly expanded program is being launched as the 3 Rivers Quest.

In February 2012, WVVRI was awarded a Regional IMPACT Award for the project by the National Institutes for Water Resources (NIWR). The award recognizes the best research, education, and outreach projects in the nation. WVVRI Director, Dr. Paul Ziemkiewicz was invited, along with the 6 other Regional Award winners, to speak at the annual NIWR meeting in Washington, D.C. on February 14<sup>th</sup>, 2012. Dr. Ziemkiewicz also noted that it was a “great honor” to be recognized by peers in the water research community.

The NIWR plays a major role in providing a national platform for research, training and collaboration needed to manage our water resources. Housed in the country’s top land-grant universities in all 50 states, three U.S. territories and the District of Columbia, member institutes are positioned to assist state and federal governments in advancing the state of water knowledge and management to protect and preserve our water supply for generation to come.

In the late summer of 2008 the Monongahela River experienced a rise in levels of TDS that caused the river to exceed the US EPA’s secondary drinking water standards for taste and smell (Pittsburgh Post-Gazette 2009). There was a heightened concern because the increasing TDS concentrations in the Monongahela River were affecting drinking water supplies as well as residential and industrial users. Because there was no regular monitoring program in place, it was unclear exactly where the salts were coming from, whether the situation was getting worse, or whether this was a seasonal phenomenon.

The data generated from the study suggested a way to manage TDS in the Monongahela River. The most easily managed component of the TDS picture was the active deep coal mines. Water, often high in concentrations of dissolved solids, from these mines must be pumped to allow continued coal production. Using concentration and flow monitoring data, a strategy was developed to reduce pumping of the deep mines during the dry period, store the water in worked-out parts of the mines, and then pump during the wet season when the river's assimilative capacity was high. One of the challenges, however, was to organize the industry and provide the management tools that would allow them to determine how much they can pump in order to keep the TDS below the secondary drinking water standard of 500 mg/L in the Monongahela River.

In the late fall of 2009, armed with the data from this monitoring program, WVWRI began working with major coal companies in the MRB to form the *TDS Working Group* which designed and implemented a "managed discharge" system. This system accounted for the pumping capacities of the fourteen major mine pumping and treatment plants as well as the discharge's typical TDS concentrations. It then ties the total salt output to the flow in the River on any particular day. The model is set not to exceed 500 mg/L with a safety factor of 2. This voluntary, non-regulatory, process for controlling TDS from mine discharges is effective, low cost and efficient. Since the initiation of the managed discharge program in January 2010, none of the four sites on the main-stem of the Monongahela River that are monitored as part of the WVWRI monitoring program, have exceeded 500 mg TDS/L or 250 mg SO<sub>4</sub>/L.

## CONCLUSIONS

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The successful foundation created by this USGS funded study has provided the leverage for securing additional funding to expand and continue water quality monitoring in the Monongahela River Basin.

Data processing revealed clear chemical signatures of typical mine influenced water versus brine waters (Figure 48). TDS concentrations in the mainstem of the Monongahela remain below 500 mg/L during the study period (Figures 5-8). The majority of tributary contributions upstream of the Monongahela River at Elizabeth, PA are captured during this study, with only 4% of discharge unaccounted for (Figure 46). The Youghiogheny River is a major contributor of flow to the Monongahela and has shown a shift in sodium chloride ratios during higher flow periods (Figures 35 and 37). High concentrations of bromide appeared sporadically throughout the study, most frequently in the West Fork River and Tenmile Creek.

By utilizing the platform provided by this USGS grant opportunity, the Mon River QUEST launched to include the data collected by volunteers throughout the Mon River Basin.

Because of the interest level in this project now, and the completely operational nature of the project website, we have been working closely with the media, local watershed organizations, industries and regulatory agencies to help raise awareness of the program and the public's ability to access the information via the internet.

## REFERENCES

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American Public Health Association, American Water Works, and Water Environment Federation. 1998. *Standard Methods for the Examination of Water and Wastewater*. Edited by Arnold E. Greenberg, Andrew D. Eaton, and Lenore S. Clesceri. 1,220 p.

Andrews, J., Brimblecombe, P, Jickells, T, Liss, P., and Reid, B. 2004. *An Introduction to Environmental Chemistry*. Blackwell Science Ltd. 296 p.

Flury, M., A. Papritz. 1993. Bromide in the Natural Environment. *Journal of Environmental Quality*. Vol .22, no. 4.

Jernejcic, F. and Wellman, D. 2009. Dunkard Creek Fish Kill Assessment. 12<sup>th</sup> Water Quality Forum, December 3, 2009. Mount Morris, PA.

Kentucky Water Watch. 2010a. Conductivity and Water Quality. <http://www.kywater.org/ww/ramp/rmcond.htm>. Accessed 5/21/2010.

Kentucky Water Watch. 2010b. pH and Water Quality. <http://www.kywater.org/ww/ramp/rmph.htm>. Accessed 5/21/2010.

Kentucky Water Watch. 2010c. Aluminum and Water Quality. <http://www.kywater.org/ww/ramp/rmal.htm>. Accessed 5/21/2010.

Kentucky Water Watch. 2010d. Calcium and Water Quality. <http://www.kywater.org/ww/ramp/rmcalc.htm>. Accessed 5/21/2010.

Kentucky Water Watch. 2010e. Sodium and Water Quality. <http://www.kywater.org/ww/ramp/rmna.htm>. Accessed 5/21/2010.

Kentucky Water Watch. 2010f. Sulfate and Water Quality. <http://www.kywater.org/ww/ramp/rmso4.htm>. Accessed 5/21/2010.

Sollars, C., Peters, C, and Perry, R. 1982. Effects of Waste Disposal on Groundwater and Surface Water (Proceedings of the Exeter Symposium, July 1982). IAHS Publ. no. 139.

US Environmental Protection Agency. 1986. *Quality Criteria for Water 1986*. EPA 440/5-86-001. 477 p.

Wilkes University Center for Environmental Quality, Environmental Engineering and Earth Sciences. 2010a. Hard Water, Water Hardness. <http://www.water-research.net/hardness.htm>. Accessed 5/21/2010.

Wilkes University Center for Environmental Quality, Environmental Engineering and Earth Sciences. 2010b. Sulfates and Hydrogen Sulfide. <http://www.water-research.net/sulfate.htm>. Accessed 5/21/2010.

# APPENDIX 1

## *FIELD PARAMETERS*

### **Electrical Conductivity**

Electrical conductivity is an indicator of dissolved metals. Some common metals that may be found in surface water include: iron, aluminum, calcium, magnesium, and others. High conductivity levels may be due to several different factors, including: untreated wastewater infiltration, mining, and agricultural runoff. High conductivity concentrations can be damaging to aquatic life because of increased salinity in the stream and possible smothering of the stream bottom (Kentucky Water Watch, 2010a). A notable example of increased conductivity causing water quality problems is the Dunkard Creek fish kill that occurred in September 2009 (Jernejcic and Wellman, 2009).

For the purposes of this study, the graphical range for conductivity is 0-10,000  $\mu\text{s}/\text{cm}$ . Detection limits for conductivity are as low as 0  $\mu\text{s}/\text{cm}$ , with an upper value of 9,999  $\mu\text{s}/\text{cm}$ . Conductivity is measured in the lab using SM 2510 B (American Public Health Association et al., 1998) and in the field with an YSI model 556 multiprobe or a YSI Professional Series multiprobe.

### **pH**

Values of pH in surface water outside acceptable ranges can indicate human impacts such as agricultural runoff, mining, or infiltration of untreated wastewater. Low pH is acidic and can cause corrosion of pipes, as well as increased dissolved metals concentrations in surface water. High pH is alkaline and can cause scale buildup in fixtures, bad taste, and reduce the effectiveness of chlorine disinfection, as well as increased metal concentrations in stream sediments (Kentucky Water Watch, 2010b).

For the purposes of this study, the graphical range for pH is 4-10 standard units. Detection limits for pH are between 0 and 14 standard units. pH is measured in the field using a portable YSI multiprobe instrument.

### **Temperature**

Temperature has a large impact on the biological activity of aquatic organisms. All aquatic organisms have a preferred temperature range. If the water temperature gets too far above or below this range, then the biological community becomes stressed and may have difficulty maintaining a stable population (USEPA, 1986)

Temperature is also important because of its influence on water chemistry. The rate of chemical reactions generally increases at higher temperature, which in turn affects biological activity. Another important example of the effects of temperature on water chemistry is its impact on oxygen. Warm water holds less oxygen than cool water, so it may be saturated with oxygen but still not contain enough for survival of aquatic invertebrates or certain fish (USEPA, 1986).

For the purposes of this study, the graphical range for temperature is -30 to 100 degrees Centigrade. There are no upper or lower detection limits for water temperature. Water temperature was measured in the field with YSI multiprobe instrumentation.

## LABORATORY PARAMETERS

Parameters analyzed in the laboratory include: aluminum (Al), acidity (acid), alkalinity (alk), bromide (Br), calcium (Ca), chloride (Cl), electrical conductivity (EC), iron (Fe), magnesium (Mg), manganese (Mn), pH, sodium (Na), sulfate (SO<sub>4</sub><sup>2-</sup>), Total Dissolved Solids (TDS), and Total Suspended Solids (TSS)

### **Aluminum (Al)**

Aluminum is the third most common element on Earth. In most forms, aluminum is not very soluble in water. However, low pH waters, such as those associated with mine drainage, may contain large amounts of dissolved aluminum due to dissolution of aluminum-containing minerals within the local geology. When aluminum precipitates within the water column, it is in the form of an aluminum hydroxide. Aluminum hydroxide may be very harmful to aquatic life due to smothering of the stream bed of the water body. Aluminum may also clog the gills of aquatic organisms if the concentration is high enough (Kentucky Water Watch, 2010c).

For the purposes of this study, the graphical range for both dissolved and total aluminum is 0-20 mg/L. The lower detection limit for aluminum is 0.021 mg/L and there is no upper detection limit. Both total and dissolved aluminum is measured in the lab using EPA method 200.7. (American Public Health Association et al., 1998)

### **Acidity**

Low pH values indicate that surface water is acidic. High acidity values in surface water may come from several sources including mining and acid precipitation. Acid precipitation may cause the dissolution of aluminum in soils with poor buffering capacity, which in turn causes acidity to increase in surface water when the soil enters the stream as runoff. As acidity increases, dissolved metal concentrations increase, which in turn may cause problems for aquatic life in streams and rivers (Kentucky Water Watch, 2010b).

For the purposes of this study, the graphical range for acidity is 0-1,000 mg/L as CaCO<sub>3</sub>. Detection limits for acidity are as low as 2 mg/L, with no upper value. Acidity was measured in the lab using SM 2310 B (American Public Health Association et al., 1998).

### **Alkalinity**

High pH values indicate that surface water is alkaline in nature and that the water has a greater neutralization capacity. Alkalinity is made up of the constituents of the water that elevate pH above 4.5 (USEPA, 1986). Typically, a small to moderate amount of alkalinity in water is also important to have for the well-being of the organisms that live in the water body. However, too much alkalinity can be toxic to wildlife. High alkalinity can also have other impacts including scale buildup in fixtures, bad taste in drinking water, and a reduction in the effectiveness of chlorine disinfection. Alkaline water may also impact irrigation if the alkalinity of the water is greater than the alkalinity of the surrounding soil.

For the purposes of this study, the graphical range for alkalinity is 0-1,000 mg/L as CaCO<sub>3</sub>. Detection limits for alkalinity are as low as 2 mg/L, with no upper value. Alkalinity was measured in the lab using SM 2320 B (American Public Health Association et al., 1998).

**Bromide (Br)**

Bromide is an ion of bromine, which is a chemical element found in the halogen group. At room temperature, it is a reddish-brown liquid that is slightly soluble in water. Dissolved bromide comes from several sources, including surrounding geology, fluids used in gas well drilling, seawater infiltration, and industrial waste (Sollars et al., 1982). Elevated levels of dissolved bromide may interfere with water treatment as well as pose an increased cancer risk to humans and wildlife.

For the purposes of this study, the graphical range for dissolved bromide is 0-5 mg/L. The lower detection limit for bromide is 0.13 mg/L and there is no upper detection limit. Bromide is measured in the lab using EPA method 300.0 (American Public Health Association et al., 1998).

**Calcium (Ca)**

Calcium is an element that is found naturally in water due to its abundance in the Earth's crust. Large bodies of surface water, such as rivers, typically contain 1-2 mg/L of calcium. High levels of calcium in surface water mean that the water is “hard,” which helps aquatic life by buffering the pH of the water and protecting those organisms with gills from direct metal uptake. However, if calcium and hardness are too high, hardening of pipes and staining may occur (Kentucky Water Watch, 2010d).

For the purposes of this study, the graphical range for dissolved calcium is 0-20 mg/L. The lower detection limit for calcium is 0.007 mg/L and there is no upper detection limit. Dissolved calcium is measured in the lab using EPA method 200.7 (American Public Health Association et al., 1998).

**Chloride (Cl)**

Chloride is an ion of chlorine. It occurs naturally as a green gas. It appears in many different compounds. The most important chloride compound for many forms of life is NaCl, or salt. Chloride (as the Cl<sup>-</sup> ion) is the most abundant dissolved ion in salt water, and is also found in freshwater in much smaller concentrations. Freshwater chloride is usually derived from chlorine mineral dissolution. Other sources of chloride in freshwater may include wastewater runoff and breakdown of chlorinated compounds. High amounts of dissolved chlorine can be very harmful to wildlife due to the oxidative properties of chloride (USEPA, 1986). When chloride concentrations reach a certain level within the organism, it combines with the water and oxygen to create hydrochloric acid, which destroys animal tissues.

For the purposes of this study, the graphical range for dissolved chloride is 0-20 mg/L. The lower detection limit for chloride is 0.10 mg/L and there is no upper detection limit. Dissolved chlorine is measured in the lab using EPA method 300.0 (American Public Health Association et al., 1998).

**Iron (Fe)**

Iron is the most abundant metal in the Earth's core. It is found in a large range of compounds in either a +2 or +3 oxidation state. It is also very important to humans and other organisms, as it is partially responsible for transporting oxygen through the bloodstream (USEPA, 1986). Iron is

easily dissolved in water and can be found naturally occurring in water bodies. High levels of precipitated iron oxides may cause smothering of stream bottoms and plugging of organism's gills.

For the purposes of this study, the graphical range for both dissolved and total iron is 0-20 mg/L. The lower detection limit for iron is 0.013 mg/L and there is no upper detection limit. Both total and dissolved iron is measured in the lab using EPA method 200.7 (American Public Health Association et al., 1998).

### **Magnesium (Mg)**

Magnesium is found in large concentrations in both the Earth's crust and the human body. It is highly soluble in water, and is the third most abundant element in sea water. Concentrations of magnesium in freshwater vary according to surrounding geology. Along with calcium, magnesium concentrations are used to determine water hardness. High concentrations of magnesium cause similar problems to high concentrations of calcium, including staining and hardening of pipes and fixtures (Wilkes University Center for Environmental Quality, Environmental Engineering and Earth Sciences, 2010a).

For the purposes of this study, the graphical range for both dissolved and total magnesium is 0-20 mg/L. The lower detection limit for magnesium is 0.003 mg/L and there is no upper detection limit. Both total and dissolved magnesium is measured in the lab using EPA method 200.7 (American Public Health Association et al., 1998).

### **Manganese (Mn)**

Manganese is commonly found in soil in its oxide form (pyrolusite) (USEPA, 1986). It is used in the steel making process, and is also an essential nutrient for most living organisms. High concentrations of manganese in humans can cause many different health problems, including Parkinson's disease and bronchitis. Manganese is also soluble in water, with large concentrations causing health problems in aquatic life. Manganese can also bioaccumulate through the food chain, causing top predators to have unhealthy levels of manganese in their bodies.

For the purposes of this study, the graphical range for both dissolved and total manganese is 0-20 mg/L. The lower detection limit for manganese is 0.017 mg/L and there is no upper detection limit. Both total and dissolved manganese is measured in the lab using EPA method 200.7 (American Public Health Association et al., 1998).

### **Sodium (Na)**

Sodium is a very common element found in rocks and soils. It is needed for all life forms to aid in the transmission of nerve impulses. It is also highly soluble in water and will react violently with water to form lye and hydrogen gas. Sodium is found naturally in freshwater bodies. Concentrations of sodium vary greatly, and are dependent on the surrounding soil and geology (Kentucky Water Watch, 2010e). Too much sodium can raise the pH level of a water body to the point where it is too high for certain species of aquatic life to survive.

For the purposes of this study, the graphical range for both dissolved and total sodium is 0-5 mg/L. The lower detection limit for sodium is 0.012 mg/L and there is no upper detection limit.

Both total and dissolved sodium is measured in the lab using EPA method 200.7 (American Public Health Association et al., 1998).

### **Sulfate (SO<sub>4</sub> -2)**

Sulfate is a salt consisting of one sulfur atom and four oxygen atoms with an oxidation number of -2. Sulfate is naturally occurring in almost all water bodies. It usually comes from oxidation of sulfite ores, dissolution of sulfate minerals, shale, and industrial wastes. High concentrations of dissolved sulfate may give water an unpleasant taste and may be corrosive to plumbing. It may also have health effects including nausea and diarrhea (Kentucky Water Watch, 2010f).

For the purposes of this study, the graphical range for both dissolved and total sulfate is 0-200 mg/L. The lower detection limit for sulfate is 0.15 mg/L, and there is no upper detection limit. Both total and dissolved sulfate is measured in the lab using EPA method 300.0 (American Public Health Association et al., 1998).

### **Sulfur (S)**

Sulfur is a non-metal that is a yellow solid at room temperature. Sulfur is found in many different minerals and is extracted by melting the surrounding rock and collecting the molten sulfur. It may also be produced from hydrogen sulfide. It is a required nutrient for life on Earth and it is an essential building block of cells. It is insoluble in water. However, high concentrations of sulfur-containing compounds, such as sulfate, may be found in water due to human activities, such as mining. High concentrations of sulfur may cause corrosion of pipes and fixtures, as well as reducing the effectiveness of water used for laundry (Wilkes University Center for Environmental Quality, Environmental Engineering and Earth Sciences, 2010b).

For the purposes of this study, the graphical range for both dissolved and total sulfur is 0-20 mg/L. The lower detection limit for sulfur is 0.05 mg/L, and there is no upper detection limit. Both total and dissolved sulfur is measured in the lab using EPA method 200.7 (American Public Health Association et al., 1998).

### **Total Suspended Solids (TSS)**

TSS, or turbidity, is the measure of the suspended particles in the water column. High levels of turbidity can come from many sources, such as urban runoff, soil erosion, wastewater discharges, agriculture, and removal of riparian zones. Increased levels of turbidity may cause water to darken, which in turn leaves less light for aquatic plants to perform photosynthesis. This in turn decreases the amount of dissolved oxygen being added to the water, which can affect aquatic organisms that are higher on the food chain (USEPA, 1986). Extreme levels of TSS can also clog fish gills.

For the purposes of this study, the graphical range for TSS is 0-250 mg/L. The lower detection limit for TSS is 2.4 mg/L and there is no upper detection limit. TSS was measured in the lab using Standard Method SM2540D (American Public Health Association et al., 1998).

### **Total Dissolved Solids (TDS)**

TDS is measured in the lab as part of this research using gravimetric methods. The gravimetric method is considered more accurate, particularly for solutions where most of the TDS is composed of inorganic salts (American Public Health Association et al., 1998).

The lower detection limit for TDS is 3.36 mg/L and there is no upper detection limit. Standard Method SM2540 C was used by the laboratory to determine TDS concentrations (American Public Health Association et al., 1998).

## WRI-143 Potential Chemical and Biological Impacts to White Day Creek Due to Gas Well Drilling

### Basic Information

<b>Title:</b>	WRI-143 Potential Chemical and Biological Impacts to White Day Creek Due to Gas Well Drilling
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<b>Principal Investigators:</b>	Paul Ziemkiewicz, Ben Mack

### Publications

There are no publications.

# Potential Chemical and Biological Impacts to Whiteday Creek Due to Gas Well Drilling

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**WRI-143**  
**USGS award number: 11HQPA0002**

FINAL REPORT

REPORTING PERIOD: MARCH 1, 2011 - FEBRUARY 29, 2012

PRINCIPAL INVESTIGATORS:

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MAY 2012

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## Abstract

Whiteday Creek has not been severely impacted by resource extraction throughout its history. However, shale gas exploration has recently become a potential source of water quality impairment. The West Virginia Water Research Institute developed and implemented a monitoring program to determine what effects, if any, gas drilling had on water quality and quantity. One sampling site was selected near the confluence of Whiteday Creek with the Monongahela River. Field parameters and flow were recorded, and water samples were collected every two weeks. Benthic macroinvertebrates were also collected twice per year.

The analytical chemistry program included a suite of parameters associated with mine drainage (acidity, alkalinity, pH, specific conductivity, sulfate, iron, manganese, aluminum, calcium, magnesium), as well as dissolved constituents (aluminum, iron, manganese, calcium, sodium, chloride, bromide, and total suspended solids). The resultant data was compiled into a database for later analysis.

Flow values and contaminant loads were compared to determine the effects of shale gas drilling /water withdrawals on water quantity. Four parameters (TDS, Br, Cl, and Na) were used as a gauge of drilling activity within the watershed. Loads of all four parameters increased during the sampling period. A final determination could not be made if these increases were due to natural fluctuations or if shale gas drilling was affecting water quantity.

Concentrations of the same four parameters were graphed over time to determine potential impacts of shale gas drilling on water chemistry. Concentrations of all four parameters decreased over time. Parameter concentrations decreased more slowly after drilling began than before.

This project has the support of the West Virginia Advisory Committee for Water Research and stakeholders including the WV Department of Environmental Protection, the Whiteday Creek Watershed Association, WVUCEE, and others.

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## Executive Summary

This project was designed to collect water quality information for the Whiteday Creek watershed and use it to determine if shale gas drilling caused water quantity and/or quality effects.

Unlike most large, direct tributaries to the Upper Monongahela River, Whiteday Creek has almost no history of coal mining or gas production. Data gathered during this research will provide a “baseline” for comparison of present and past water quality. It may also be used as a framework for future data collection by other entities and aid in the development of policy and regulations.

## Introduction

### Background

Since 2008, shale gas development using horizontal drilling and hydraulic fracturing (fracking) has expanded rapidly in north central West Virginia. Water resources may be affected by this industry. Total Dissolved Solids (TDS) is a possible contaminant of concern from shale gas drilling. Water quality data taken before drilling begins is of great importance in order to determine potential effects on TDS concentrations from gas extraction. Whiteday Creek, a tributary of the Monongahela River in northern West Virginia, provided an ideal area for this type of research, as no drilling had yet occurred at the onset of this project. Pre-drilling water quality values served as a baseline to be compared against post-drilling water quality values.

Another potential effect on water resources from shale gas drilling includes water withdrawals. Shale gas drilling needs large amounts of water, especially during the hydraulic fracturing process. A shale gas well requires 1-4 million gallons of water to complete hydraulic fracturing (Andrews et al., 2009). Large withdrawals of water can change water chemistry and negatively affect aquatic life. This project determined how shale gas drilling activities, such as water withdrawals, affected both the chemical and biological health of the stream during these low-flow periods.

### Project Implementation

A monitoring program for Whiteday Creek was developed and implemented in July, 2010. The program included water quality monitoring and sampling on a bi-weekly basis. The monitoring location used was 1.4 miles from the confluence of Whiteday Creek with the Monongahela River. Since there is no stream gauge to measure flow on Whiteday Creek, flow measurements were taken at the same time as water samples with a portable flow meter. Benthic macroinvertebrate collection and identification was also performed two times during the project period.

The monitoring program tested the water for six field parameters: electrical conductivity, oxidation reduction potential, pH, temperature, total dissolved solids, and dissolved oxygen. Water samples were collected and analyzed in the laboratory at the National Research Center for

Coal and Energy at West Virginia University for aluminum, acidity, alkalinity, bromine, calcium, chlorine, iron, magnesium, manganese, sodium, sulfate, sulfur and total suspended solids.

## Public Outreach

An important part of this research is the transfer of research data to the general public. To disseminate the information as widely as possible, the data will be shared on a website, [www.monriverquest.org](http://www.monriverquest.org). This website uses a GIS database and map to easily display the data. The map is used to view the monitoring location and the “zoom-in” feature allows website users to see other details about the Whiteday Creek watershed. Map view options include highways, topographic features, and aerial imagery.

Website users are able to view data generated by the monitoring program by entering a query for the name of the monitoring site. Graphs are then generated for each of the monitored parameters. Lab analyzed data for the various parameters are compiled and depicted in “stacked bar graphs.” A color-coded map displays parameter concentrations at the Whiteday Creek monitoring location. These are depicted by different color and size “dots” at the sample site.

The project website also includes basic information about the Monongahela River and its tributaries, as well as project details including participants, news items, and links to related websites. Detailed descriptions of the measured parameters are also included.

## Project Importance

Marcellus Shale drilling has been occurring in West Virginia for the last 3-5 years. This type of drilling has the potential to significantly affect nearby water resources, both through changes in water quality and quantity. Baseline water quality data needed to be gathered to determine the effects, if any, of shale gas drilling on Whiteday Creek. Comparison of pre-drilling data vs. post-drilling data will allow any effects to be quantified.

Whiteday Creek was selected as the site for this research because of its unique history. Although the watershed is located near areas of historic coal mining activities, little to no coal mining has occurred within the watershed. Other resource extraction, including timbering and traditional vertical gas well drilling, has been limited in scope.

The water quality of Whiteday Creek is a topic of much concern as shale gas drilling begins in the watershed. Increases in the demand for water by both the gas industry and the public have further intensified the debate. Whiteday Creek is currently used as a warm water fishery by private citizens. More information is needed to determine the effects of changes in water chemistry and quantity on this fishery.

Increases in water usage, recreational usage, and industrial effects to the creek have caused considerable debate about the adequacy of existing water quality regulations. Data generated by this study have provided crucial information to inform many of these concerns. It has provided

the accurate and current water quality information necessary to inform the public and to aid regulatory personnel in making future policy decisions.

### **Project Continuance**

Future project plans include continued monitoring of the current sampling site. Flow values will be taken every two weeks and benthic macroinvertebrates will be sampled every 6 months (April and October). The project website will be updated regularly and improvements in data depiction and usefulness will be incorporated.

### **Experimental Methods**

Whiteday Creek enters the Monongahela River 0.5 km upstream of the Opekiska Lock and Dam. The sampling site is located approximately 2,400 m upstream of the mouth of Whiteday Creek. The site is above the maximum elevation of the Opekiska pool on the Monongahela River. Sampling of Whiteday Creek began July 2010 and is currently ongoing. Samples have been collected by WVVRI staff at one location every other week. (Table 1, Figure 1).

**Table1. Sample location description.**

Site ID	Site Name	Site Description	Lat	Long
WD	Whiteday Creek	Upstream of the second creek crossing on Opekiska Road from Rt. 73	39 32 58	80 02 32



**Figure 1. Topographic map of sample location.**

## Analysis

Water quality samples have been collected from the sampling site bi-weekly throughout the reporting period and have been submitted to the National Research Center for Coal and Energy (NRCCE) laboratory same day of sampling. Parameters analyzed in the field included: electrical conductivity (EC), pH, temperature, and TDS. Parameters analyzed in the laboratory included: aluminum (Al), acidity, alkalinity, bromine (Br), calcium (Ca), chlorine (Cl), electrical conductivity, iron (Fe), magnesium (Mg), manganese (Mn), pH, sodium (Na), sulfate (SO<sub>4</sub>-2), and Total Suspended Solids (TSS). Methods used for determination of field and lab values can be found at [www.monriverquest.org/parameters.cfm](http://www.monriverquest.org/parameters.cfm).

Flow was also measured using a Marsh-McBirney Flo-Mate 2000 flow meter. Flow values were used to create a flow rating curve in conjunction with data from a pressure transducer.

## Field parameters

### Electrical Conductivity

Electrical conductivity is an indicator of dissolved constituents. EC components vary depending on their source. For example, sulfate is an excellent indicator of mining activity in Tennessee and Kentucky (Rikard and Kunkle, 1990), while brine constituents, such as bromine, chloride, and sodium, are found in streams affected by gas drilling (Virginia Department of Mines, Minerals, and Energy, 2006).

### pH

pH is the measure of the activity of hydrogen ions in a solution (Bellingham, 2009). Within the Monongahela River basin, pH between 3 and 5 is an indicator of mining activity, while shale gas brine water has a “typical” pH of 6.0 (Keister, 2010).

## **Temperature**

Temperature affects both the biological activity of aquatic organisms and water chemistry. The biological community becomes stressed and may have difficulty maintaining a stable population if the water temperature gets too far out of range (USEPA, 1986).

Temperature is also important because of its influence on water chemistry. The rate of chemical reactions generally increases at higher temperature. Temperature also affects oxygen concentrations in the water. Warm water holds less oxygen than cool water, so it may be saturated with oxygen but still not contain enough for survival of aquatic invertebrates or certain fish (USEPA, 1986).

## **Total Dissolved Solids (TDS)**

TDS is a measure of inorganic and organic materials dissolved in water. High levels of TDS in the Monongahela River basin are often indicative of mining and/or gas drilling. “Typical” TDS concentrations in Marcellus shale brines have 195,000 mg/L (Keister, 2010).

## **Laboratory parameters**

### **Aluminum (Al)**

Aluminum is often used as an indicator of coal mining activity because aluminum-containing minerals are dissolved in acidic environments. Aluminum precipitates in the form of aluminum hydroxide, which will clog the gills of aquatic organisms at high concentrations (Hoehn and Sizemore, 1977).

### **Acidity**

High acidity values are often an indication of coal mining in the Monongahela River basin. Sulfur-containing minerals dissolve to form sulfuric acid, which increases acidity concentrations (USEPA, 1994). Acidity also increases concentrations of dissolved metals in water bodies.

### **Alkalinity**

High pH values indicate that surface water is alkaline in nature and that the water has a greater neutralization capacity. Alkalinity is made up of the constituents of the water that elevate pH above 4.5 (USEPA, 1986). A small to moderate amount of alkalinity is also important to have for the well-being of the organisms that live in the water body.

### **Bromine (Br)**

Dissolved bromine comes from several sources, including surrounding geology and fluids used in gas well drilling (Sollars et al., 1982). Elevated levels of dissolved bromine may indicate shale gas drilling activities.

### **Calcium (Ca)**

Calcium enters the water column through the dissolution of calcite or other calcium minerals (Watzlaf et al., 2004). Coal mining hastens this process by fracturing surrounding geology and exposing it to water. Calcium is also found in high concentrations in shale gas brines (Keister, 2010).

**Chlorine (Cl)**

Chlorine minerals are typically not plentiful in the geology of the Monongahela River basin. For this reason, chlorine is not a good indicator of mining activity. However, chlorine is found in high concentrations in shale gas drilling fluids (Keister, 2010).

**Iron (Fe)**

Iron is found naturally occurring in many water bodies. Extremely high concentrations of iron in the Monongahela River basin are often due to oxidation of iron-rich minerals during and after coal mining. Iron is used as an indicator of coal mining for this reason.

**Magnesium (Mg)**

Magnesium may be an indicator of drilling and/or mining activity. Shale gas drilling wastewater contains approximately 1,300 mg/L in a “typical” sample (Keister, 2010). Coal mining creates high magnesium concentrations when clay minerals are dissolved in an acidic environment (Watzlaf et al., 2004)

**Manganese (Mn)**

Manganese is a better indicator of mining activity than shale gas drilling. Manganese concentrations are typically low in shale gas brines (Keister, 2010). However, it is released from carbonate minerals during coal mining and may reach significant concentrations (Watzlaf et al., 2004).

**Sodium (Na)**

Sodium is a reliable indicator of natural gas drilling. It is found in extremely high concentrations in flowback water (Keister, 2010). Sodium concentrations far above mean levels could denote failure of water treatment/containment practices on a drill site.

**Sulfate (SO<sub>4</sub> -2)**

Sulfate comes from oxidation of sulfite ores and/or dissolution of sulfate minerals. An average sulfate concentration of 1,750 mg/L was observed in 156 coal mines in Pennsylvania (Watzlaf et al., 2004). Sulfate concentrations that large are only found in mining-affected areas in the Monongahela River basin.

**Total Suspended Solids (TSS)**

TSS, or turbidity, is the measure of the suspended particles in the water column. Mining or drilling activities can cause high turbidity levels. Increased TSS can be caused by improper sediment and erosion controls on mining and drilling sites.

**Sampling Methodology**

Two water samples were taken at each sample point: (I) a 500 mL unfiltered sample was taken for general water chemistry (pH, conductivity, total acidity and alkalinity by titration, and sulfate) and (II) a 125 mL sample filtered with a 0.45 micrometer Nalgene syringe filter was acidified to pH of <2 with 0.5 ml concentrated nitric acid and used to determine all metal concentrations.

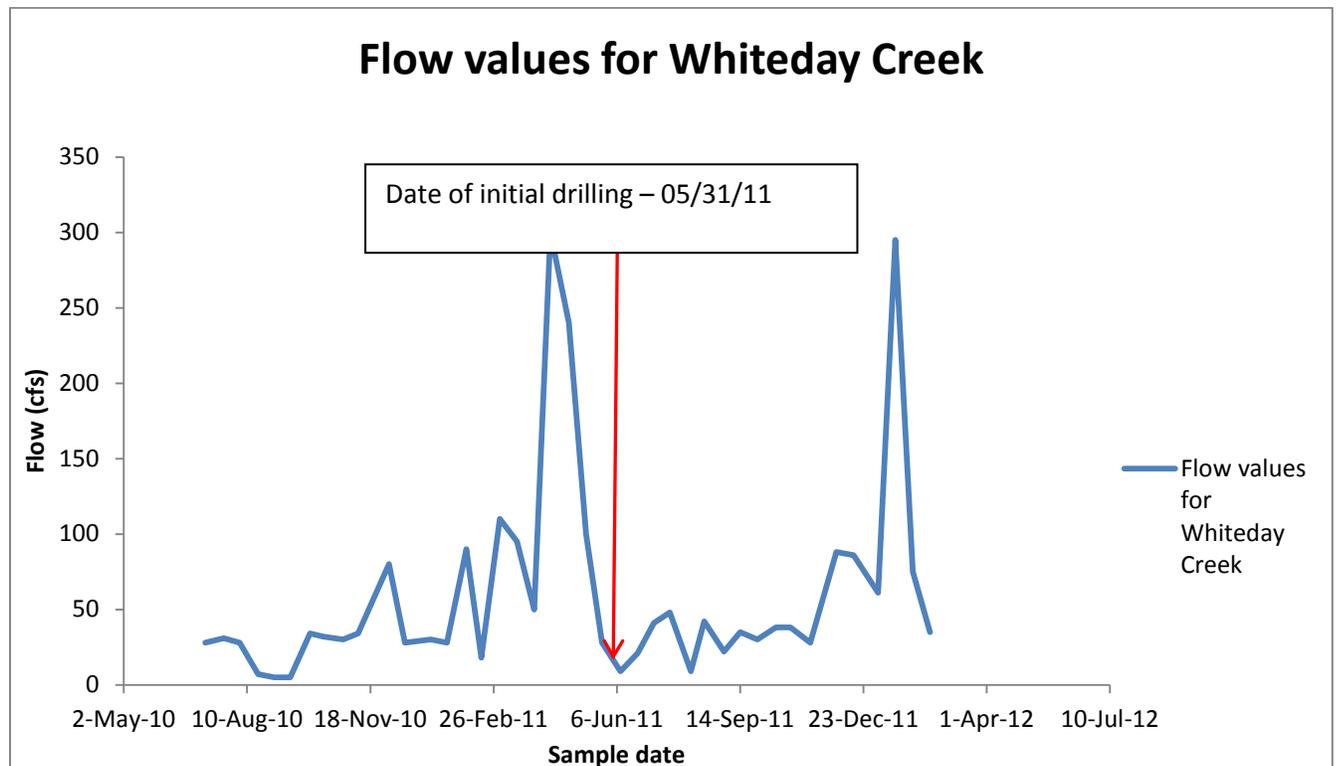
## Results and Discussion

### Creation of a water quality database for Whiteday Creek

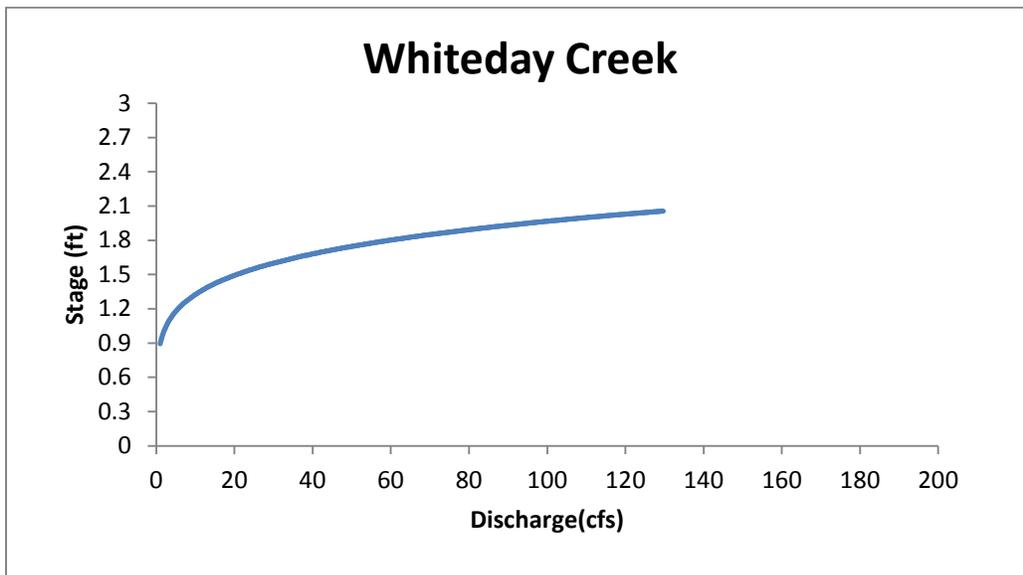
A water quality database was constructed to facilitate data storage and retrieval. The database consisted of water quality results from July 7, 2010 to February 29, 2012. Mean water quality values are shown in Table 2. Flow values were also taken with a flow meter at the same time as water samples. The raw flow data taken with the flow meter can be seen in Figure 2. Flow values were used in conjunction with water pressure readings from a transducer to create a flow rating curve (Figure 3).

**Table 2. Mean water quality parameters collected by WVVRI. Flow (Q) is expressed in cubic feet per second (CFS), specific conductance (EC) in  $\mu\text{s}/\text{cm}$ , and all other concentration measurements are expressed in mg/L.**

Q	Temp	EC	pH	Alk	Acid	Br	D. Al	D. Fe	D. Mn	D. S	Cl	D. Ca	D. Na	D. Mg	SO4
cfs	$^{\circ}\text{C}$	$\mu\text{s}/\text{cm}$		mg/L	mg/L	(mg/L)									
59.32	14.43	125.40	7.90	32.24	1.95	0.05	0.06	0.13	0.04	7.53	7.26	14.29	7.42	3.15	20.10
TSS		TDS													
(mg/L)		mg/L													
10.61		84.45													



**Figure 2. Raw flow values taken with a portable flow meter.**



**Figure 3. Flow rating curve for Whiteday Creek.**

Benthic macroinvertebrates were also sampled two times during the grant period (November 2011 and April 2012). They were collected according to WVDEP guidelines. Each collection was scored using the West Virginia Stream Condition Index (WVSCI) (WVDEP, 2011). The WVSCI rates stream health on a scale of 0-100 within four categories: Poor, Marginal, Suboptimal, and Optimal. Whiteday Creek scored in the top of the Marginal category in November 2011 and in the Suboptimal category in April 2012. The score likely increased in the spring because the sampling time coincided with the hatch of numerous aquatic organisms. Table 3 gives the WVSCI scores for the two benthic collections.

**Table 3. WVSCI scores on Whiteday Creek.**

Site	November 2011 WVSCI	April 2012 WVSCI
Whiteday Creek near mouth	60 (Marginal)	73.3 (Suboptimal)

## Determination of effects of shale gas drilling on water quantity

There are currently five well sites permitted in the Whiteday Creek watershed. One hundred days was chosen as an average time from well permitting to well drilling. Table 4 details permit names, permit issuance date, and estimated beginning drilling date. For the purposes of this study, drilling began in the watershed on 5/31/11.

**Table 4. Gas well permit information for five well sites in Whiteday Creek.**

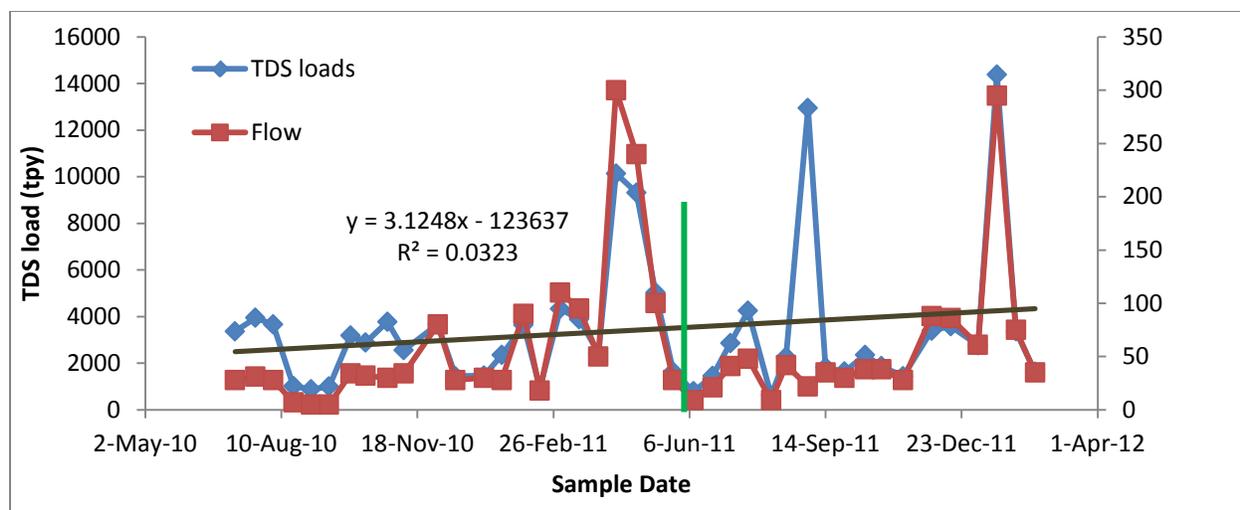
<b>Permit name</b>	<b>API #</b>	<b>Permit issuance date</b>	<b>Estimated drilling date</b>
Bunner	049-02141	2/10/11	5/31/11
Neel	049-02144, 049-02143	3/10/11, 4/8/11	6/19/11, 7/17/11
Morris	049-02173, 049-02190	9/30/11, 11/17/11	1/8/12, 2/25/12
Langley	049-02189	11/5/11	2/13/12
Orthodox Educational Society	091-01264	4/5/12	7/14/12

Flow data are shown in Figure 2. There is a definite seasonal component to these data, as the two highest flow values were seen in April 2011 and January 2012. It is likely that increased precipitation and/or snowmelt caused these large spikes in flow. Inversely, the lowest flow values were seen in the summer months. It was expected that there would be a greater effect on water quality during the months of June – August. Three wells were also drilled from May-July 2011. Flows were lower during this time period than in 2010. It is possible that water was being withdrawn in preparation for fracturing these wells.

In order to determine the effects of water quantity on water chemistry, the research team selected four water quality parameters that may be indicative of shale gas drilling: TDS, Br, Cl, and Na.

### **TDS**

TDS is a general measurement of the concentration of salts in water. Higher TDS loads are often an indicator of resource extraction activities, including gas drilling. Whiteday Creek had a TDS load of roughly 11 tons per year (tpy) at the beginning of the sampling period (Figure 4). TDS loads increased throughout 2010 and into 2011. During April 2011, multiple large rain events caused the TDS loads to spike due to an increase in flow. Loads then dropped down to roughly 7 tpy by the start of drilling. TDS loads remained low for the rest of summer 2011. TDS loadings and flow coincided with each other for the rest of the sampling period except for the September 14 sampling date. In this case, TDS loads spiked to nearly 300 tpy while flow remained low (Figure 4). Gas drilling or some other large source of sediment likely explains this phenomenon. Unfortunately, the exact reason is not known for this spike.



**Figure 4. TDS loads in Whiteday Creek. The green line is the estimated drilling start date.**

TDS loads increased over the sampling period (Figure 4). It is possible that TDS loads within the watershed are being affected by shale gas drilling. Continued sampling will determine if this trend will continue.

### **Bromine (Br)**

Bromine is found in flowback water from shale gas drilling operations (States et al., 2011). If high concentrations of Br are found in groundwater or surface water, the source could be a gas drilling operation. Because of this, it is a good indicator of drilling activity.

Bromine loads were compared against flow during the sampling period (Figure 5). Br was heavily influenced by flow, with the exception of the August 2010 and September 2011 sampling dates. The large spike in Br loads from August 2010 was before drilling began in the watershed, which means drilling could not have influenced the Br load. The difference between Br load and flow in September 2011 may have been influenced by drilling activities, but it is more likely that this was due to a natural variation in Br because the difference between the two values is very small.

A slight increasing trend in bromine loads was observed (Figure 5). This trend was even less significant than TDS. The large spike in Br loads at the end of the sampling period was the greatest contribution to the observed trend.

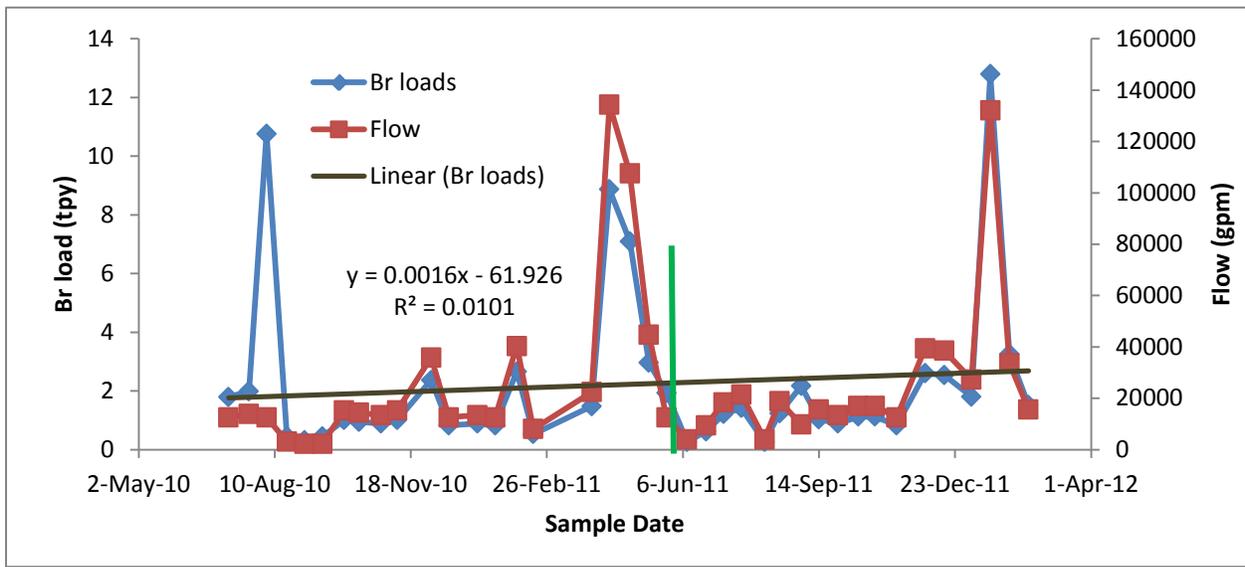


Figure 5. Br loads in Whiteday Creek. The green line is the estimated drilling start date.

### Chloride (Cl<sup>-</sup>)

Chloride is found in flowback water during shale gas drilling. As the shale is fractured, the chloride stored within the shale layer is released (Baker, 2009). High concentrations of Cl<sup>-</sup> in groundwater could mean leakage of Cl<sup>-</sup> from an improperly cased well, while high concentrations in surface water could be from a breach of a flowback pit.

Cl<sup>-</sup> loads were compared against flow to determine effects of water quantity changes on loads (Figure 6). Cl<sup>-</sup> loads were less influenced by flow than either TDS or Br loads. Pre-drilling Cl<sup>-</sup> loads were consistently higher than flow with the exception of the April 2011 sample date. Post-drilling loads showed a less distinct trend, with Cl<sup>-</sup> loads both higher and lower than flow values. A slight upward trend was observed in Cl<sup>-</sup> loadings during the sampling period (Figure 6). However, the R<sup>2</sup> value of the line is not large enough to confirm a scientifically valid trend.

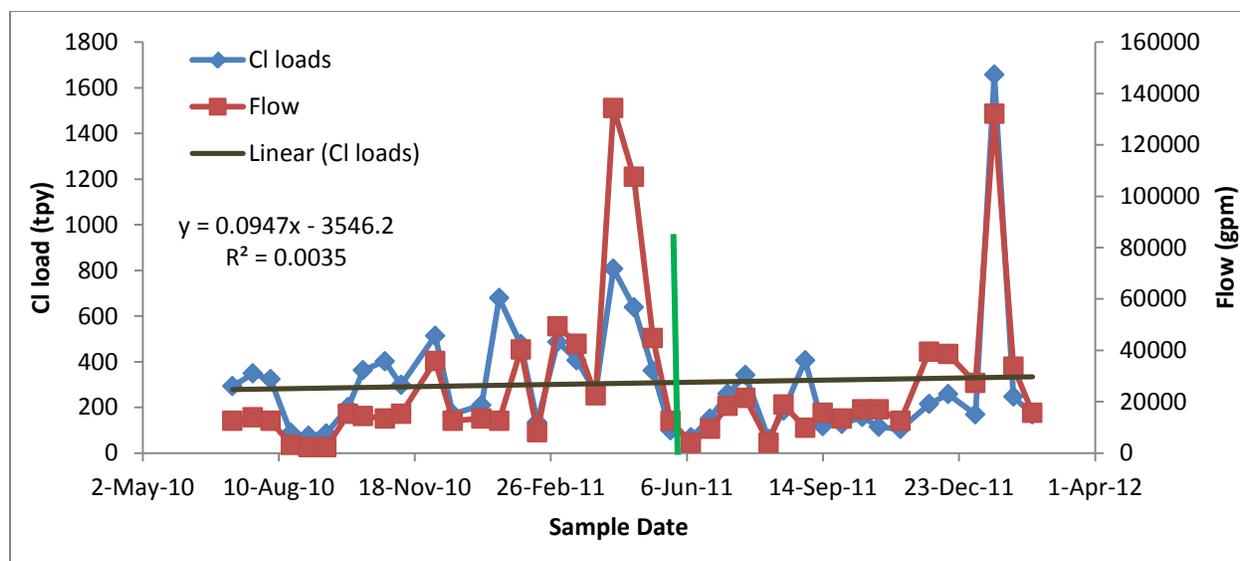
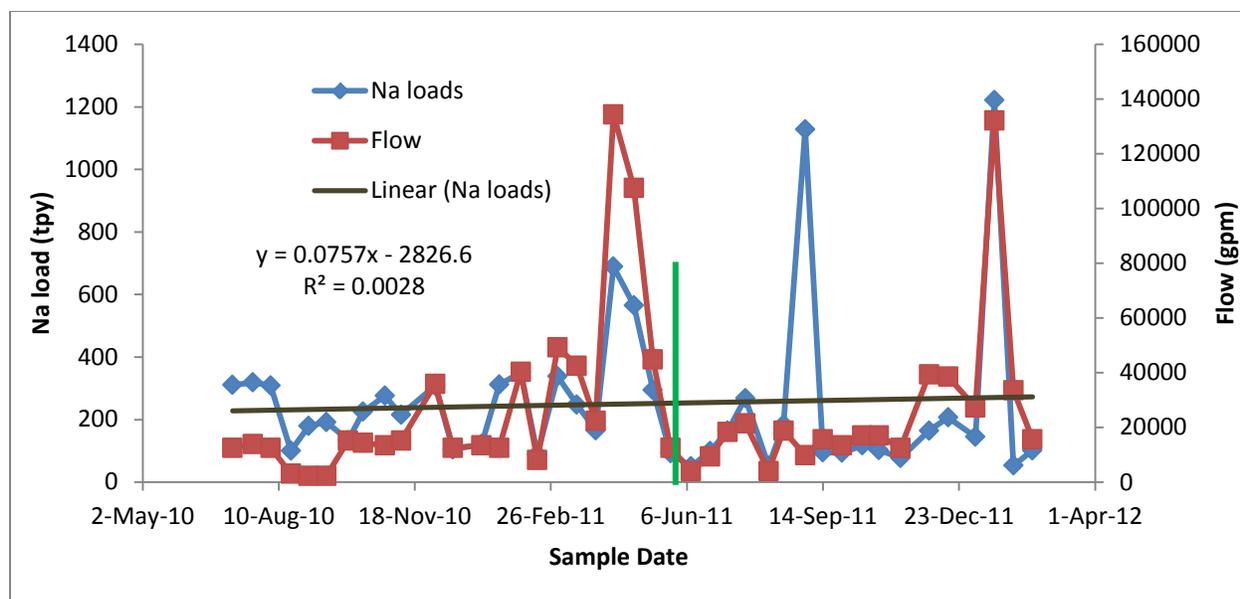


Figure 6. Cl loads in Whiteday Creek. The green line is the estimated drilling start date.

## Sodium (Na)

Sodium is often found in high concentrations in flowback water (Titler and Curry, 2009). High concentrations in water bodies could be indicative of improper well casing or a spill from a flowback water pit.

Comparison of Na loads to flow yielded similar results to Cl loads (Figure 7). Both pre- and post-drilling Na loads fluctuated less with changes in flow. Pre-drilling Na loads were consistently higher than flow with the exception of the April 2011 sampling date. Post-drilling loads showed the opposite trend, with Na loads roughly equal to or lower than flow values. A spike in Na loads on September 1, 2011 was the exception to this trend. However, there is no way of knowing the source of this increase. A slight upward trend was observed in Na loadings during the sampling period (Figure 7). The trend line showed the least amount of correlation between Na loads and time of all four parameters.



**Figure 7. Na loads in Whiteday Creek. The green line is the estimated drilling start date.**

### Determination of effects of shale gas drilling on water quantity

Shale gas drilling may also affect the surrounding environment through changes in water quality. Drilling can affect water quality both through the addition of chemicals into the environment during the drilling process and through chemicals released from the shale layer when it is fractured. Substances found in discharges from treated brine water include: barium, strontium, benzene, 2-butoxyethanol, ethylbenzene, toluene, xylenes, chlorides, and sodium, among others (Volz et al., 2011). This study will use four chemical parameters to assess the effects of shale gas drilling on water quality. These parameters include TDS, Br, Cl, and Na. Benthic macroinvertebrate sampling results will also be discussed.

### TDS

TDS concentrations are a very useful indicator of drilling activity. Drilling adds TDS to surface water in many ways. For example, clearing and grubbing of new well pads can add extra sediment to streams if proper Erosion and Sedimentation (E&S) plans are not implemented. The largest potential source of TDS is from flowback water. Flowback water is the water that comes back up the well bore as the well is being drilled. This water contains high TDS concentrations due to the substances in the drilling fluid mixing with the metal salts that are freed from the drilled geology. The average TDS concentration is 106,000 mg/L in flowback water from PA shale gas wells. Major ions found in flowback water include Cl, Na, Ca, Br, and Mg (McSurdy, 2011).

TDS concentrations before and after drilling were compared in order to ascertain possible water quality effects. TDS concentrations steadily decreased over time both before and after drilling

began, indicating that changes in TDS are driven by factors not related to gas drilling (Figure 8). Time and TDS concentrations were fairly correlated ( $R^2=0.42$ ). Further sampling is needed to determine if the trend was due to natural variations (e.g. seasonal) in TDS concentrations or if other factors influenced changes in TDS.

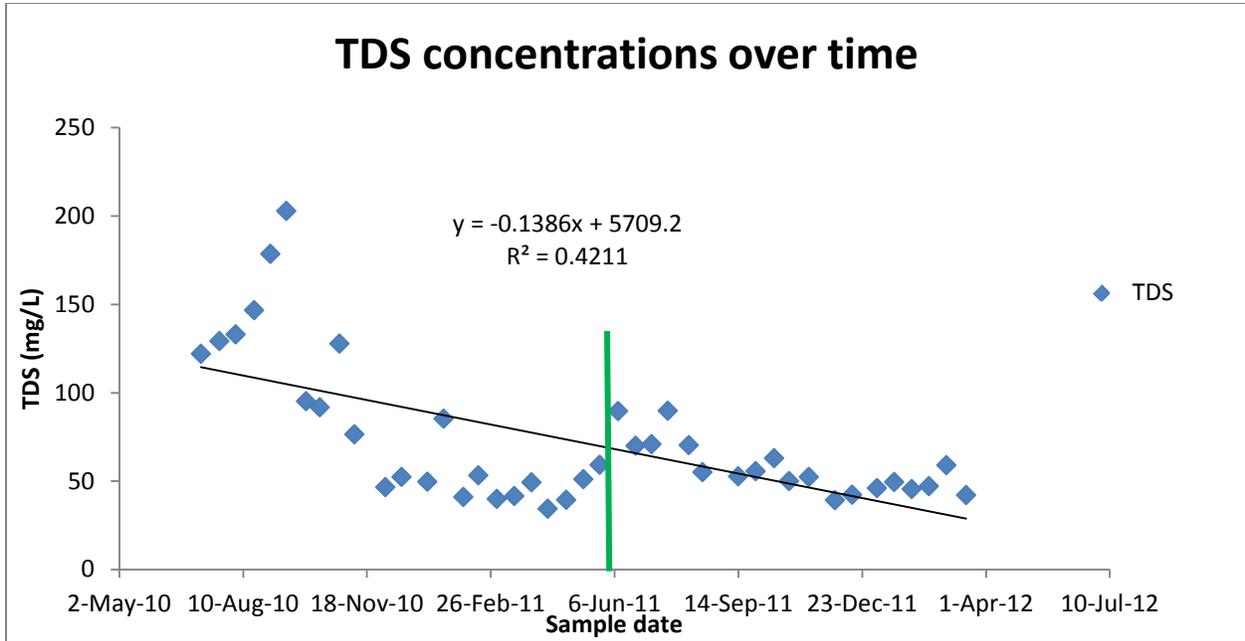


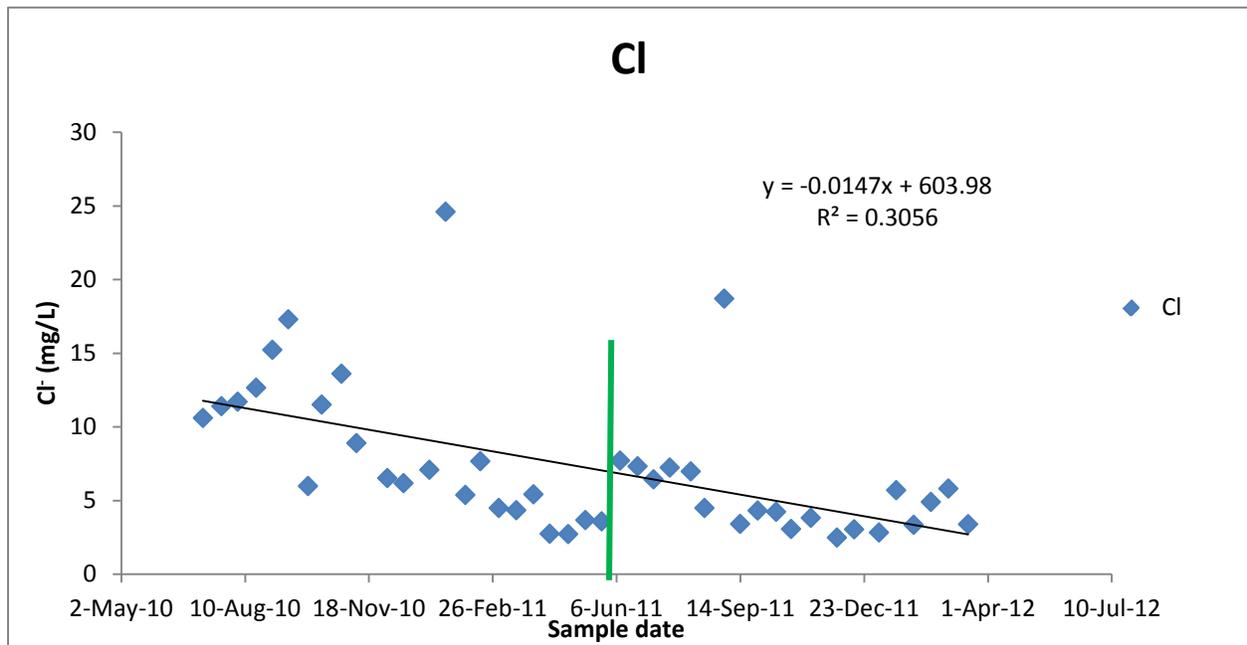
Figure 8. TDS concentrations over time. The green line is the estimated drilling start date.

## Br

Br concentrations remained mostly steady over the sampling period (Figure 9). Concentrations fluctuated between 0.03 mg/L and 0.10 mg/L. One outlying point (0.39 mg/L) was observed on the August 4, 2010 sampling date. This high concentration cannot be explained by drilling activity because this value was observed before drilling began. The cause of this high concentration is unknown.

The data showed a slight decreasing trend over time. However, the  $R^2$  value of 0.09 is too small to draw any correlation between Br concentrations and time (Figure 9). It is possible that the trend may become more significant as more sampling data is acquired.





**Figure 10. Cl<sup>-</sup> concentrations in Whiteday Creek. The green line is the estimated drilling start date.**

## Na

Na concentrations fluctuated between roughly 1 and 14 mg/L over time (Figure 11). However, three Na concentrations of 36 mg/L on September 1, 2010, 39 mg/L on September 14, 2010, and 52 mg/L on September 10, 2011 were also observed. The high concentrations from September 1 and 10, 2010 were observed before drilling began. Figure 7 also shows that the two samples taken during September 2010 were taken during low flow periods. These higher concentrations could be due to a lack of dilution within the watershed.

The highest Na concentration was seen after drilling began. Similar to the high Cl<sup>-</sup> concentration, Na concentrations rapidly declined after this date. It is unlikely that drilling was the cause of the high Na concentration observed on September 1, 2011 for this reason. The decreasing trend of the data after drilling also illustrates a lack of effect on Na concentrations from drilling (Figure 11).



## Conclusions

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Three objectives were accomplished during this research. A monitoring program was designed and implemented. Data was gathered through stream and benthic sampling and establishment of flow values. A database was constructed consisting of water quality data from July 2010 to March 2012. Data was compiled and prepared for future analysis.

Flow values and contaminant loads were compared to determine the effects of shale gas drilling /water withdrawals on water quantity. Four parameters (TDS, Br, Cl, and Na) were used as a gauge of drilling activity within the watershed. Loads of all four parameters increased during the sampling period. However, these increases were very slight with  $R^2$  values ranging from 0.03 to 0.003. Such small changes give no indication if these increases are due to natural fluctuations in flow or if shale gas drilling is affecting water quantity.

Concentrations of the same four parameters were graphed over time to determine potential effects of shale gas drilling on water chemistry. Concentrations of all four parameters decreased over time. TDS and Cl<sup>-</sup> had the highest correlation between time and concentrations (0.42 and 0.31, respectively). Concentrations decreased more slowly after drilling began than before drilling began for all parameters. There was no way to determine if this trend would continue because only 18 months of data were available.

Benthic macroinvertebrates were also sampled twice during the project period. Unfortunately, both samples were taken after drilling began. A biological comparison could not be made before and after drilling for this reason. A higher WVSCI score was observed during the second benthic sampling, which was likely due to increased macroinvertebrate population during the spring. There are currently only two wells within the watershed that have been drilled and fracked. Further benthic data collection before more wells are drilled will aid in the determination of any long-term effects from shale gas drilling.

Stream sampling will continue beyond the time period of this funding. Sampling continuation will give a higher degree of certainty to future analyses.

## References

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- American Public Health Association, American Water Works, and Water Environment Federation. 1998. Standard Methods for the Examination of Water and Wastewater. Edited by Arnold E. Greenberg, Andrew D. Eaton, and Lenore S. Clesceri. 1,220 p.
- Andrews, A., Folger, P., Humphries, M., Copeland, C., Tiemann, M., Meltz, R., and Brougher, C. 2009. Unconventional Gas Shales: Development, Technology, and Policy Issues. Congressional Research Service. Document # R40894.
- Baker, L. 2009. Source Water Protection and the Marcellus Shale. West Virginia Department of Environmental Protection. 4 p.
- Bellingham, K. 2009. Physiochemical Parameters of Natural Waters. <http://www.stevenswater.com/articles/waterparameters.aspx>. Accessed 05/2012.
- Hoehn, R.C. and D.R. Sizemore, 1977. Acid mine drainage (AMD) and its impact on a small Virginia stream. Water Res. Bull. v. 13, pp. 153-160.
- Keister, T. 2010. Marcellus Hydrofracture Flowback and Production Wastewater Treatment, Recycle, and Disposal Technologies. The Science of Marcellus Shale. Williamsport, PA. January 29, 2010.
- McSurdy, S. 2011. Utilizing Acid Mine Drainage for Marcellus Shale Drilling Activities in Pennsylvania. Pennsylvania Statewide Conference on Abandoned Mine Reclamation. August 4-6, 2011. Hazelton, PA.
- Rikard, M. and Kunkle, S. 1990. Sulfate and Conductivity as Field Indicators for Detecting Coal Mining Pollution. Environmental Monitoring and Assessment 15: 49-58.
- Sollars, C., Peters, C, and Perry, R. 1982. Effects of Waste Disposal on Groundwater and Surface Water (Proceedings of the Exeter Symposium, July 1982). IAHS Publ. no. 139.
- States, S., Cyprych, G., Stoner, M., Wydra, F., Casson, L., and Monnell, J. 2011. Bromide in the Allegheny River and THMS in Pittsburgh Drinking Water: a Link with Marcellus Shale Drilling. American Water Works Association-Water Quality Technology Conference. Nov. 13-17, 2011. Phoenix, AZ.
- Titler, R. and Curry, P. 2009. Chemical Analysis of Major Constituents and Trace Contaminants of Rock Salt. Pennsylvania Department of Environmental Protection, Bureau of Water Standards and Facility Regulation. 28 p.
- USEPA. 1994. Acid Mine Drainage Prediction. EPA 530-R-94-036. 52 p.
- USEPA. 1986. Quality Criteria for Water 1986. EPA 440/5-86-001. 477 p.

Virginia Department of Mines, Minerals, and Energy. 2006. Hydraulic Fracturing in Virginia and the Marcellus Shale Formation.

<http://www.dmme.virginia.gov/DGO/documents/HydraulicFracturing.shtml>. Accessed 05/2012.

Volz, C., Ferrar, K., Michanowicz, D., Christen, C., Kearney, S., Kelso, M., and Malone, S. 2011. Contaminant Characterization of Effluent from Pennsylvania Brine Treatment Inc., Josephine Facility: Implications for Disposal of Oil and Gas Flowback Fluids from Brine Treatment Plants *In* EPA Hydraulic Fracturing Study Technical Workshop 3, Fate and Transport. March 28-29, 2011.

Watzlaf, G., Schroeder, K., Kleinmann, R, Kairies, C., and Nairn, R. 2004. The Passive Treatment of Coal Mine Drainage. DOE/NETL-2004/1202.

WVDEP. 2011. West Virginia Save Our Streams Program Level-One Standard Operating Procedures Manual. <http://www.dep.wv.gov/WWE/getinvolved/sos/Pages/SOPintro.aspx>. Accessed 05/2012.

## Information Transfer Program Introduction

2011 Water Research Symposium Coal & Water in Central Appalachia: The Challenge to Balance

The West Virginia Water Research Institute partnered with the Institutes for Water Resources Research in Virginia and Kentucky to sponsor the 2011 Water Research Symposium; Coal & Water in Central Appalachia: The Challenge to Balance.

This one-day symposium focused on the challenges of balancing the management of coal and water in central Appalachia. Invited experts from the region provided contemporary insights into the policies and scientific information associated with water resources and coal mining in the central Appalachians. Representatives of federal and state agencies provided perspectives on water-protection policies that affect mining operations. Technical presentations by university scientists addressed the influences of coal mining practices on total dissolved solids, selenium, aquatic biota, and hydrology of rivers and streams in the region. Symposium participants had the opportunity to ask questions and participate in lively group discussions.

A capacity crowd of over 120 people attended the event which was held on the Campus of Virginia Tech. The Event Program as well as Speaker Presentations and Biographies are available on the event website at; [www.wvwaterconference.org](http://www.wvwaterconference.org)

Symposium Presentations: Historical Perspectives on Coal Mining, Water Quality, and Prediction of Impacts Perspectives on Surface Coal Mining and Water in Central Appalachia Coal and Water: Virginia's Challenge to Balance Division of Mining and Reclamation Adapting to a Radically Different "Balance" Adapting to Meet Emerging Challenges Achieving the Hydrologic Balance During Mining and Reclamation Total Dissolved Solids from Coal Mining in Central Appalachia Natural Rate of Selenium Attenuation at Southern West Virginia Surface Mines Informed Environmental Decision Making in Mined Appalachian Watersheds

Symposium Speakers: John (Randy) Pomponio, Director, Mid-Atlantic Environmental Assessment & Innovation Division, U.S. Environmental Protection Agency - Region 3 Richard Davis, Abandoned Mine Land Projects Coordinator, Division of Mined Land Reclamation, Virginia Department of Mines, Minerals and Energy Tom Clarke, Director, Division of Mining and Reclamation, West Virginia Department of Environmental Protection John Jones, Director of Environmental Regulatory and External Affairs, Alpha Natural Resources W. Lee Daniels, Professor, Crop & Environmental Sciences, Virginia Tech Richard Warner, Extension Professor, Biosystems and Agricultural Engineering, University of Kentucky Paul Ziemkiewicz, Director, West Virginia Water Research Institute Carl Zipper, Associate Professor, Crop & Environmental Sciences, Virginia Tech Todd Petty, Associate Professor, Forestry and Fisheries Resources, West Virginia University

Project 2011WV165B Mon River Monitoring Project

Information Transfer

Raising the awareness of the general public to Monongahela River water quality issues and making the project results readily accessible to the public are principal components of this project. A project website, [www.MonWQ.net](http://www.MonWQ.net), was created to disseminate as much pertinent information generated by this project in the timeliest fashion possible. Presentations of the data generated have been presented at numerous public forums. A project fact sheet was produced and disseminated at various meetings and also available in a printable format on the project website. Project findings were presented at the 2010 state water conference, an information transfer project funded through the USGS 104b program.

## Information Transfer Program Introduction

### Conferences/Events/Meetings

Because the data generated by this project is extremely pertinent to the public dialog currently being undertaken regarding the water quality of the Monongahela River, its presentation has been of interest.

Maryland Stream Symposium, August 10-12, 2011 Table display set up to engage potential volunteer groups.

Dunkard Fish Restoration Meeting, WV Division of Natural Resources, August 25, 2011 WVDNR's proposed Fish and Mussel Restoration Plan open to the public to provide input, comments and suggestions to WVDNR officials.

Marcellus Drilling Symposium, Oct. 28, 2011 Forums and presentations from people across the country that looked at how shale drilling is regulated outside of West Virginia and to discuss the challenges to drilling on the Marcellus in the state. Display was set up for this event.

Maryland Streams Symposium, August 11, 2011 Presentation: Monongahela River QUEST: A Collaborative Approach to Monitoring Water Quality in the Mon River BGasin

Marcellus Shale Coalition's Research Collaborative in Cannonsburg, PA, March 14, 2012 oWVWRI Director, Paul Ziemkiewicz, attended the second meeting of the Marcellus Shale Coalition's Research Collaborative. He has been tasked with developing a screening process for vendors of water treatment technology in advance of the MSC's September 2012 meeting in Philadelphia. Selected Vendors will have an opportunity to present their technologies to the MSC's producer community. The screening procedure will develop a standardized set of criteria and metrics to help the producers evaluate technologies that will meet the needs of their operations.

West Virginia Workshop for WV Department of Environmental Protection, Division of Natural Resources, US Geological Survey and US Environmental Protection Agency March 29th 2012 Todd Petty, Associate Professor of Forestry, Paul Ziemkiewicz, Director, WVWRI along with Graduate Assistant Allison Anderson organized and participated in a workshop to introduce and receive feedback on a legislatively-mandated project to develop criteria for quantifying fish habitat quality. The results of this project will help develop metrics for aquatic habitat quality to assist in regulatory determinations and improvement of degraded habitat through mitigation programs. EPA Knowledge Transfer Session April 11th, 2012 WVWRI Director, Dr. Paul Ziemkiewicz gave a presentation to US EPA Region III in Philadelphia, PA about Total Dissolved Solids in the Monongahela River. His presentation also described and discussed the data generated by the Mon River QUEST project.

Meeting with US Geological Survey and PA Department of Environmental Protection April 10th 2012 WVWRI Director, Paul Ziemkiewicz, gave presented data from the bromide portion of this monitoring research. Bromide is an emerging public health issue and the Monongahela River QUEST Monitoring Program has a unique data base that allows analysis of sources and trends in Bromide and other pollutants in Northern WV and SW PA.

H2O Know Awareness Advocacy Event April 12th, 2012 Public forum hosted by The Izzak Walton League (Harry Enstrom Chapter) and the Waynesburg University EcoStewards Club. Invited speakers included WVWRI Director, Dr. Paul Ziemkiewicz, who spoke about managing Total Dissolved Solids in the Monongahela River as well as the Mon River QUEST project, the data generated and its implications. A Mon River QUEST table display was also set up and staffed by Mon River QUEST's Volunteer Coordinator, Glenn Waldron, to engage potential volunteer groups and to discuss the project with interested individuals

Marcellus Shale Coalition's Research Collaboration, Cannonsburg, PA April 16th 2012 Dr. Ziemkiewicz submitted a procedure for evaluating water technologies for the Shale Gas Industry which will be distributed

## Information Transfer Program Introduction

to the Coalition members for comment. When completed it will be used to develop a treatment technology database indicating technology components, performance and cost data.

Meeting with US Army Corps of Engineers and Officials from Greene County in Waynesburg PA April 17th 2012 Dr. Ziemkiewicz participated in a Water Assessment and Management Program for the Monongahela River Basin.

US State Department, Washington, DC April 18th 2012 Dr. Ziemkiewicz made a presentation on Shale Gas water issues to a sponsored delegation from Poland.

National Water Monitoring Conference (Portland Oregon) April 30th May 4th, 2012 WVVRI Outreach Coordinator Dave Saville and Environmental Specialist, Melissa O'Neal, presented at the 8th annual National Water Monitoring Conference Water: One Resource Shared Effort Common Future, in Portland, OR. The Conference is a national forum that provides exceptional opportunities for federal, state, local, agency, volunteer, academic and other stakeholders to exchange information and technology related to water monitoring, assessment, research, protection, restoration, and management. Dave and Melissa's abstract, Monongahela River QUEST: A collaborative approach to monitoring water quality in the Monongahela River Basin was selected to be presented at the event in the Monitoring Impacts of Hydraulic Fracturing Session. The event was attended by over 1,100 people.

USEPA's Wheeling Office May 10th, 2012 WVVRI Director, Dr. Paul Ziemkiewicz, with WVU Geology Professor, Joe Donovan, met with scientists at USEPA's Wheeling Office to discuss statistical methods used in their studies linking stream water quality with various impairment indices.

US Department of Energy/National Energy Technology Laboratory Office of Research and Development, Geological and Environmental Sciences May 9th & 10th, 2012 Dr. Ziemkiewicz served on this Focus Area Review Panel for the, EPAct Subtitle J, Section 999, Complementary Research Program Merit Review, Fiscal Year 2012.

### Media and News Exposure

February 6, 2012, WVU Today, West Virginia Water Research Institute wins regional award, nominated for national

<http://wvutoday.wvu.edu/n/2012/02/06/west-virginia-water-research-institute-wins-regional-award-nominated-for-national>

February 13, 2012 The Daily Athenaeum, Front Page, Mon River QUEST wins regional IMPACT Award for water research

<http://www.thedaonline.com/news/mon-river-quest-wins-regional-impact-award-for-water-research-1.2776970#.Tzkc7>

February 1, 2012 Daily Athenaeum, Mon River QUEST monitors local water safety

<http://www.thedaonline.com/news/mon-river-quest-monitors-local-water-safety-1.2761837#.T6w6SVKrSwH>

January 19, 2012, McKeesport Daily News River researchers help assess Monongahela water's 'health'

January 10, 2012 The State Journal Mon River QUEST Harnesses Volunteers as Early Warning System

<http://www.statejournal.com/story/16487343/mon-river-quest-harnesses-volunteers-as-early-warning-system>

December 28, 2011, WVU Today WVU Institute partners with volunteers on "QUEST" for Mon River Water Quality info

<http://wvutoday.wvu.edu/n/2011/12/28/wvu-institute-partners-with-volunteers-on-quest-for-mon-river-water-quality-info>

## Information Transfer Program Introduction

### 2011WV158B Isotopic Fingerprinting

#### Presentations

Mulder M., Sharma S., Bevans H., Chambers D., White J., and Paybins K. 2011. Ambient geochemical and isotopic variations in waters of an area of accelerating shale gas development. GSA National Annual Meeting 9-12 October, Minneapolis, MN. Sharma S., Mulder M., Edenborn H., and Hammack R., 2011. Stable isotope fingerprinting of co-produced waters associated with Marcellus Shale natural gas extraction. GSA National Annual Meeting 9-12 October, Minneapolis, MN. Mulder M., and Sharma S., 2011. Geochemical and isotopic variations in waters of an area of accelerating shale gas development. AAPG Eastern Section Meeting, Washington DC.

#### Media/News Channel Reports

WVU Today, Dec 21, 2011: WVU geochemist works to uncover the origins of methane gas in areas of Marcellus shale drilling WVNS Channel 59 News, Oct 4, 2011: WVU Researcher to Map Methane Sources in Monongahela-Area Drinking Water. WD TV and NPR News, Dec 18 2011: WVU to Study Impact of Fracking on Well Water

# USGS Summer Intern Program

None.

<b>Student Support</b>					
<b>Category</b>	<b>Section 104 Base Grant</b>	<b>Section 104 NCGP Award</b>	<b>NIWR-USGS Internship</b>	<b>Supplemental Awards</b>	<b>Total</b>
<b>Undergraduate</b>	1	0	0	1	2
<b>Masters</b>	5	0	0	5	10
<b>Ph.D.</b>	0	0	0	0	0
<b>Post-Doc.</b>	0	0	0	0	0
<b>Total</b>	6	0	0	6	12

## Notable Awards and Achievements

Research Project: Stable isotope fingerprinting of waters in an area of accelerating Marcellus shale gas development

1 MS student working on this project graduated 2 research papers will be submitted by end of summer 2012 Results presented in national AAPG and GSA meetings Research highlighted in several regional newspapers and news channels

Research Projects: Monongahela River Water Quality Study and Potential Chemical and Biological Impacts to Whiteday Creek Due to Gas Well Drilling

Coal industry cooperation and support: Coal industry support is allowing researchers to continue the work of these two projects. The coal industry is using TDS concentration data provided by project researchers to manage mine discharges to the Monongahela River. By coordinating mine discharges with TDS concentrations in the river, TDS limits are kept at acceptable limits.

Project 2011WV165B: Mon River Monitoring Project

In February 2012, WVWRI was awarded a Regional IMPACT Award for the project by the National Institutes for Water Resources (NIWR). The award recognizes the best research, education, and outreach projects in the nation. WVWRI Director, Dr. Paul Ziemkiewicz was invited, along with the 6 other Regional Award winners, to speak at the annual NIWR meeting in Washington, D.C. on February 14th, 2012. Dr. Ziemkiewicz also noted that it was a great honor to be recognized by peers in the water research community.