

Investigation of Total Dissolved Solids Regulation in the Appalachian Plateau Physiographic Province: A Case Study from Pennsylvania and Recommendations for the Future

by
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ABSTRACT

WOZNIAK, MARK. Investigation of Total Dissolved Solids Regulation in the Appalachian Plateau Physiographic Province: A Case Study from Pennsylvania and Recommendations for the Future. (Under the direction of Linda Taylor and Dr. Chris Hofelt).

Total dissolved solids (TDS) are a natural constituent of surface water throughout the world. The World Health Organization, U.S. Environmental Protection Agency, and most states regulate TDS as a secondary drinking water criteria, affecting taste and odor, limiting discharges to 500 mg/L. This method of regulation fails to account for the conservative nature of TDS, with in-stream concentrations increasing with each addition, as well as impacts to aquatic life. New sources of TDS are further stressing historically contaminated waterways throughout the Appalachian Plateau, leaving them unable to assimilate additional TDS. With these new sources only projected to increase, it is necessary, now more than ever, for the states to develop total maximum daily loads for the affected waterways. This is the most effective method for regulating TDS to ensure the sustained health of the regional aquatic communities and human health.

BIOGRAPHY

Mark Wozniak has lived in western Pennsylvania all his life, where he attained an interest in all aspects of the natural environment at an early age. He traveled not far from his home near Pittsburgh, PA to study environmental science and geology at Edinboro University of Pennsylvania, near Lake Erie, where he obtained his Bachelor of Science in both. Mark began his career at North Carolina State University in the Soil Science Department. When the Environmental Assessment program was launched in the fall of 2010, he switched departments to finish his Masters.

Mark has worked for the U.S. Army Corps of Engineers in Pittsburgh, PA since 2008. He has worked on a variety of projects, including developing a human health risk assessment focused on private wells adjacent to a site contaminated by radionuclides. His area of interest is focused on soil, groundwater, and surface water contamination, and the human and ecological effects. He is currently serving a temporary assignment to the Pittsburgh District, Water Quality Section.

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TABLE OF CONTENTS

BIOGRAPHY	iii
ACKNOWLEDGMENTS	v
CHAPTER 1 - INTRODUCTION.....	1
CHAPTER 2 - PROBLEMS AND OPPORTUNITIES	4
CHAPTER 3 - RECOMMENDATIONS	13
CHAPTER 4 - CONCLUSIONS	Error! Bookmark not defined.
REFERENCES	17

LIST OF TABLES AND FIGURES

Table 1. Constituents of Marcellus Shale wastewater (Reilly, 2011).....	5
Figure 1. Graph of trend in chloride concentrations in the Monongahela River, Pennsylvania (Reilly, 2011).	6
Figure 2. Monongahela River watershed (Reilly, 2011).....	7
Figure 3. Flow and specific conductivity for Dunkard Creek, West Virginia (Reilly, 2011). ..	9

CHAPTER 1 - INTRODUCTION

Total dissolved solids (TDS) are a natural component of surface waters throughout the world. Mainly comprised of inorganic salts, organic material, and various other dissolved materials, the minerals and organic molecules in TDS can benefit the stream health by contributing valuable nutrients. However toxic heavy metals and organic pollutants may also be present that can have negative impacts to both humans and aquatic organisms (Commonwealth of Pennsylvania, 2010). The potential and actual impacts of elevated levels of TDS in surface water have become an increasingly contentious issue throughout much of the Appalachian Plateau. The streams in this region have been historically affected by mine drainage, which is a significant source of TDS, with road de-icing, wastewater effluent, and other legacy sources also contributing to the total. The recent emergence of large quantities of flowback fluid and brine produced from the hydraulic fracturing of deep shale-gas formations in the region has provided a new source of concern due to their high levels of TDS. Increasing amounts of this high TDS wastewater are being conveyed to treatment systems that are unable to effectively eliminate it, leading to increased TDS concentrations in treatment plant outflows. Also, more low TDS water is being withdrawn from headwater streams, leaving these streams with less assimilative capacity. The legacy sources of TDS have left streams with little or no capacity for dilution, and this increased water withdrawal is only acting to exacerbate the problem. Much of the water resources in this region are controlled or managed by the Federal Government through a system of dams and reservoirs, leading most of the concerned parties to turn to them for increased releases for dilution, which is most often not possible due to strict operation guidelines. In the case of U.S. Army

Corps of Engineers, Pittsburgh District, 8,000 lineal miles of stream in the upper Ohio River watershed are controlled by their reservoirs and 1,032.5 miles of 21 different major streams are directly influenced by their reservoir releases.

Total dissolved solids are addressed by regulating the concentration in discharges, also known as “end-of-pipe” regulation. The levels can be approximated by measuring the specific conductivity and can be measured easily with a field meter. The conductivity of sample is determined by measuring the electrical resistance of the sample between two electrodes and comparing it to a standard solution of potassium chloride at 25 degrees Celsius. The conductivity is the reciprocal of resistance. A value for TDS can be calculated by the equation; $TDS = 0.584 \times \text{conductivity} + 22.1$. Total dissolved solid concentration is most often expressed in the units of milligrams per liter (mg/L) (U.S. Department of the Interior, 1998). Measurements of TDS do not take into account the different ions that comprise it.

The Pennsylvania Environmental Quality Board has concluded that many streams throughout Pennsylvania are impaired or are at risk of becoming impaired due to elevated levels of total dissolved solids. The increasingly elevated levels could have significant consequences to both human and the ecological health of the receiving waters. The World Health Organization recommends TDS levels based on taste and palatability, with less than 300 mg/L considered to be excellent (World Health Organization, 2003). The Safe Drinking Water Act, as amended (42 U.S.C. 300f et seq.), lists TDS as a secondary contaminant, that primarily affects the aesthetic quality of drinking water. A secondary maximum contaminant

level (SMCL) of 500 mg/L is provided by the U.S. Environmental Protection Agency (EPA) to limit TDS in wastewater discharges. The regulation and enforcement of TDS in Pennsylvania has been delegated to the Pennsylvania Department of Environmental Protection (PADEP), which utilizes the EPA's suggested SMCL for their drinking water standard (Commonwealth of Pennsylvania, 2010). The concern cited by all three of the agencies mentioned above is that when concentrations of TDS go above 500 mg/L, excessive scaling in water pipes, water heaters, boilers and household appliances may occur. The current regulation scheme is problematic for two reasons; (1) TDS is a conservative parameter that does not degrade downstream, and therefore increases the in-stream concentration with every addition, and (2) the ecological health of surface waters are not taken in to account. Many studies have provided evidence that TDS can cause severe disruption to aquatic communities and some components can have human health impacts. In this paper I will investigate whether there is significant evidence for TDS to be regulated for aquatic life as well, and whether this could provide the basis for establishing a total maximum daily load for affected waterways.

CHAPTER 2 - PROBLEMS AND OPPORTUNITIES

Several factors have led to the increasing awareness and concern of TDS regulation in western Pennsylvania waters. Most apparent, TDS cannot be removed by the current treatment systems operating throughout western Pennsylvania. Some of the metal components can be removed, but the salts and other constituents are simply treated by dilution. Gas production from the Marcellus Shale presents another concern. These wells need large quantities of freshwater, often up to 5 million gallons per well, and produce highly contaminated wastewater (Soeder & Kappel, 2009). Table 1 shows the constituents of Marcellus Shale wastewater from a survey of four sites. In a study conducted on effluent from a Pennsylvania Brine Treatment Inc. facility that accepts only wastewater from the oil and gas industry, Volz et al. (2011) measured concentrations of TDS of 186,625 mg/L. This is 373 times the level set by PADEP and the EPA. In a statement made by the Pennsylvania Environmental Quality Board, it is declared that “dilution is insufficient to protect water quality...[and] designated uses such as drinking water” (Warren, 2010). A Department of Energy study (2010) conducted on water usage in the Marcellus Shale industry found that, as of July 2010, all of the companies surveyed relied on traditional wastewater treatment facilities to handle their flowback and produced water.

Constituent	Units	Flowback water				Production water
		Sample 1	Sample 2	Sample 3	Sample 4	
acidity						
aluminum						
barium	mg/l	3,310	2,300	8	4,300	690
bromide						
calcium	mg/l	14,100	5,140	683	31,300	23,200
chemical oxygen demand	mg/l	600	567	1,814	2,272	2,332
chloride						100,000
chromium						
conductivity	mmhos/cm				500,000	366,600
copper						
dissolved solids	mg/l	175,268	69,640	6,220	400,000	224,300
fluoride						
hydrocarbons						
iron	mg/l	53	11	211	134	160
lead						
magnesium	mg/l	938	438	32	1,630	2,240
manganese	mg/l	5	2	16	7	10
nitrogen compounds						
Oil & grease	mg/l					9
pH	pH units					5
strontium	mg/l	6,830	1,390	5	2,000	732
surfactants	mg/l					106
suspended solids	mg/l	416	48	490	330	33
uranium						
zinc						

Table 1. Constituents of Marcellus Shale wastewater (Reilly, 2011).

Increasing Trends

To assure optimum operation of projects for authorized purposes, the U.S. Army Corps of Engineers, Pittsburgh District, (Corps) has been monitoring water quality, both time-series and grab samples, since the mid 1970's. After about four decades of improving water quality, the data began to show negative trends for TDS, chlorides, sodium, and strontium, thought to be related to exploitation of the Marcellus Shale, in 2008. Figure 1, shows the data for grab samples of chlorides in the Monongahela River in Pennsylvania.

These data also show that the assimilative capacity for total TDS during low flow periods has already been reached in the lower Monongahela, Casselman, Youghiogheny, and West Fork Rivers. Figure 2 shows a map of the Monongahela River watershed with the major streams and navigation dams. The Corps' also maintains that their ability to realize authorized water quality benefits could be further impacted by excessive withdrawals from reservoir inflows or their downstream regulated reaches, or with permitted or unpermitted discharge of high TDS wastewater into surface waters. In addition, Corps reservoirs have little or no capacity to release enough water to dilute the Monongahela River TDS load during low flow periods. Because of the trends throughout their district, the Corps supports implementation of a sustainable watershed-based approach for water withdrawals and management of the growing TDS load in the entire upper Ohio River watershed (Reilly, 2011).

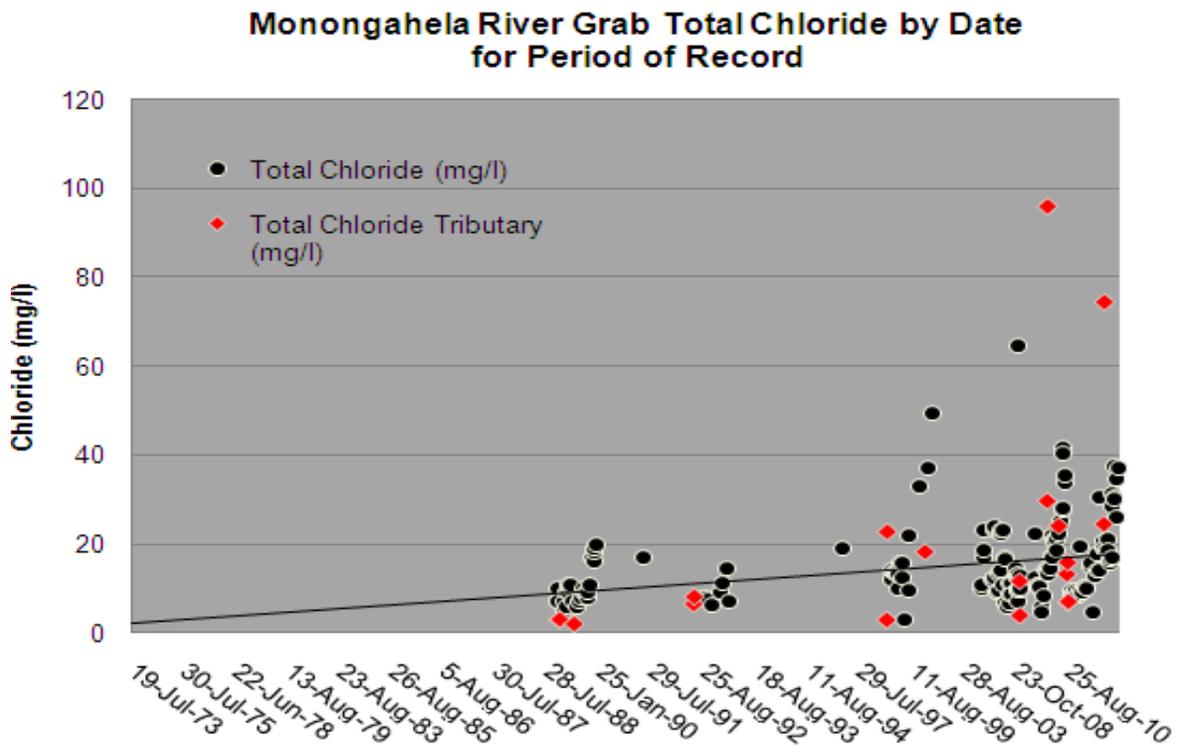


Figure 1. Graph of trend in chloride concentrations in the Monongahela River, Pennsylvania (Reilly, 2011).

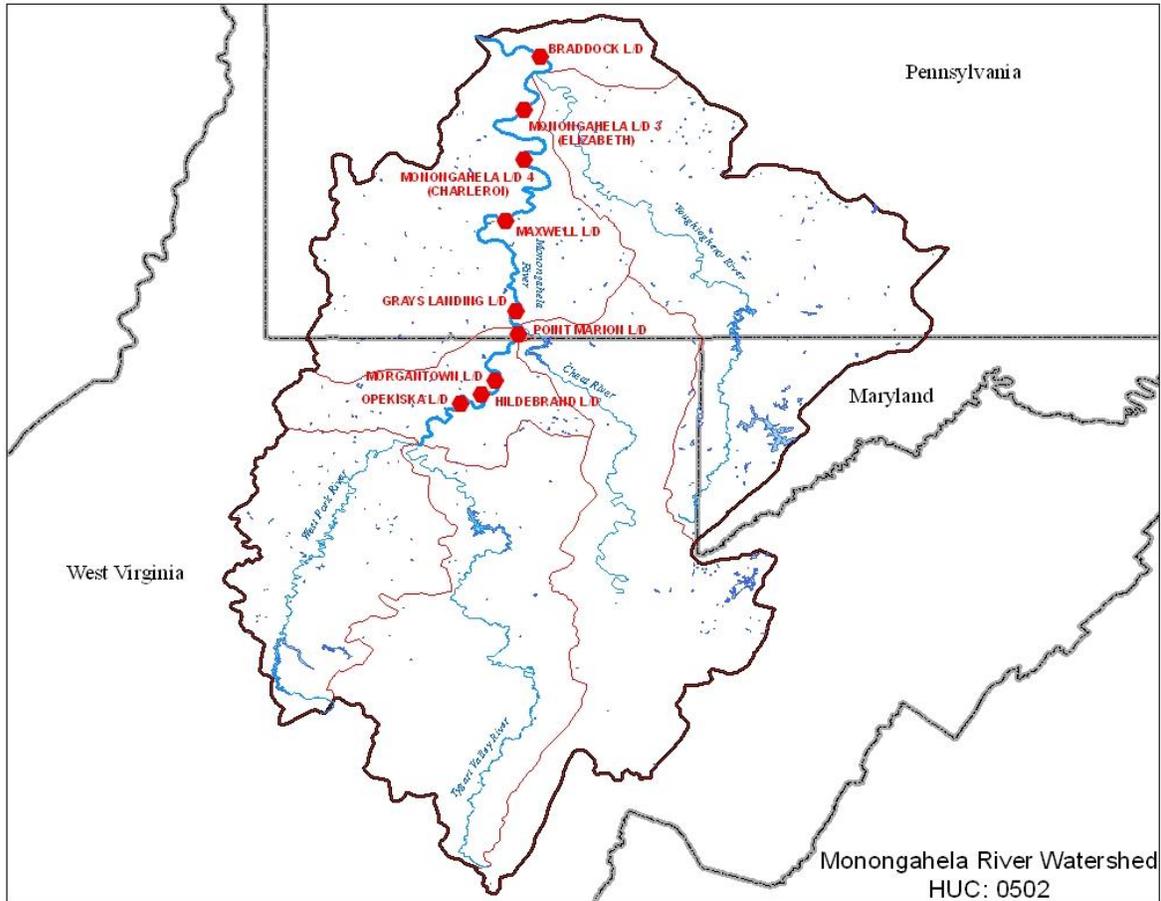


Figure 2. Monongahela River watershed (Reilly, 2011).

The Commonwealth of Pennsylvania has also conducted numerous studies on the major watersheds throughout the region that have reinforced the limited assimilative capacity the streams and rivers have for TDS, sulfates, and chlorides. Most often cited is the November and December 2008, low-flow event, where concentrations of TDS and sulfates exceeded historic high values at all 17 of the potable water supply intakes along the Monongahela River in Pennsylvania. On South Fork Tenmile Creek, a major tributary to the Monongahela River, increased concentrations of chlorides and bromides were also observed during this event. The EPA, PADEP, and the Allegheny County Health Department

conducted several studies on the Monongahela River during this period to examine any effects of the TDS, sulfate and chloride discharges. In one of these studies, bromide was found to be a significant concern as well, due to the formation of brominated disinfection by-products (DBPs), specifically trihalomethane (THM), at all 17 of the potable water supply intakes along the Monongahela River (Commonwealth of Pennsylvania, 2011). When a disinfectant, usually chlorine or monochloramine, reacts with organic matter and bromide in source water, these compounds can occur. The EPA established maximum contaminant level goals for brominated species of THMs, which dominate DBPs when excess bromide is present in source water, of zero and are listed as probable human carcinogens (Handke, 2009). The EPA studied the 2008 event and although they did not determine a specific source for elevated TDS levels, other than loss of dilution from low-flow, they did establish a strong correlation between the formation of trihalomethane (THM) at public water supplies and increased bromides “caused by TDS and sulfate in surface water” (Warren, 2010).

Another recent event occurred in September 2009, when much of the aquatic life in Dunkard Creek was destroyed by the combination of a bloom of golden algae (*Prymnesium parvum*) and extensive osmotic pressure within the stream. In a matter of days, at least 18 species of fish and 14 species of freshwater mussels were wiped out by the toxins produced by the bloom. This particular species is native to east Texas coastal environments and was most likely transported north by some type of drilling equipment used in the Barnett Shale of east Texas that is now being utilized on Appalachia's Marcellus Shale. As shown in figure 3, before the bloom, TDS concentrations reached as high as 6,000 mg/L in the stream. This

stream has been monitored for over ten years in order to provide information on abandoned mine discharges. Director of the Water Research Institute at West Virginia University, Dr. Paul Ziemkiewicz, calculated that the existing discharges could not account for the extreme levels of TDS present during the bloom. The current hypothesis revolves around unregulated discharges of high TDS wastewater from the hydraulic fracturing process (Renner, 2009).

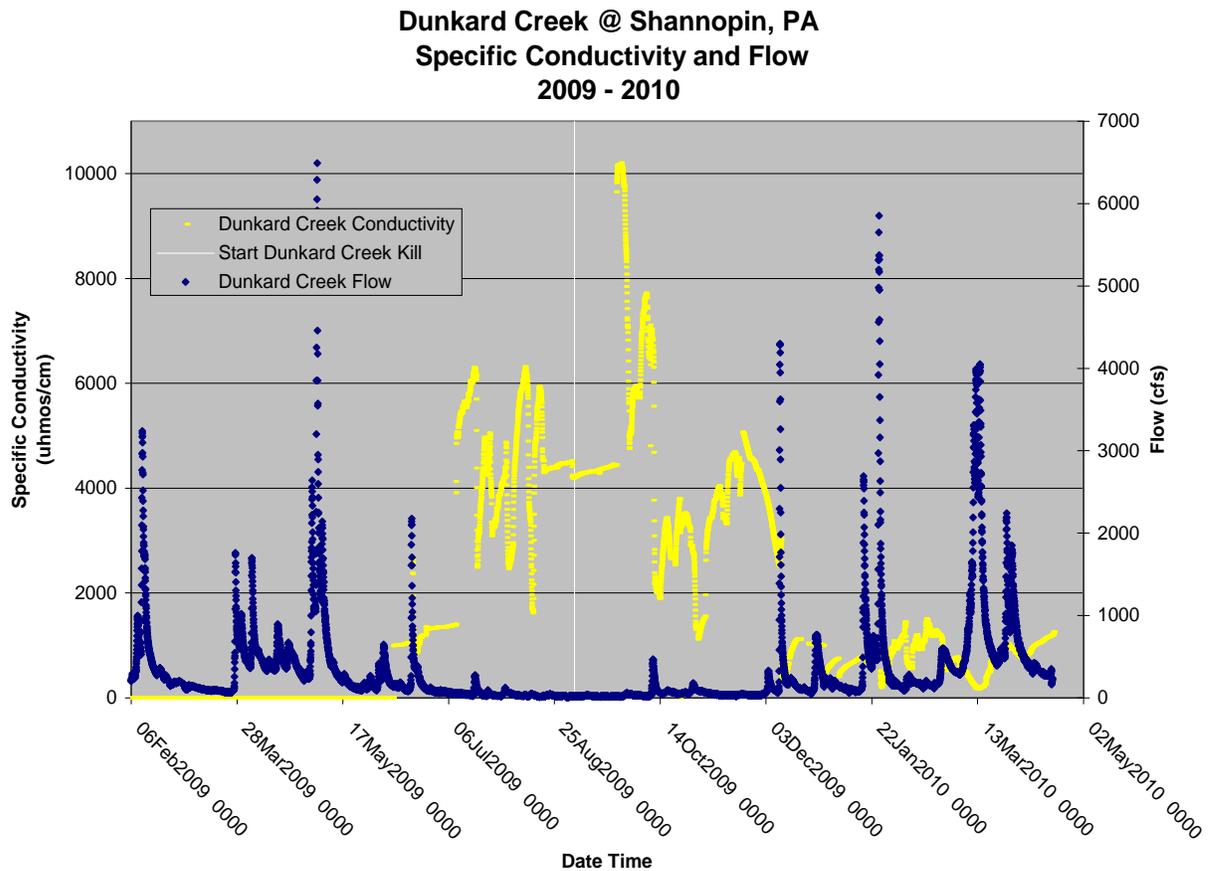


Figure 3. Flow and specific conductivity for Dunkard Creek, West Virginia (Reilly, 2011).

Human Health Concerns

The rivers of western Pennsylvania have been exhibiting elevated levels of bromide in the past few years as well. The treatment process used for high TDS wastewater generated

by the natural gas industry removes suspended solids and biodegradable material, but does not remove TDS or bromide. During the disinfection process at water treatment facilities, bromide can lead to the formation of trihalomethane (THM). The American Water Works Association (2011), concluded that bromide concentrations, in the Allegheny River in Pennsylvania, increased downstream of industrial wastewater treatment facilities that regularly accepted wastewater generated from Marcellus Shale sites but, did not increase downstream of publicly owned treatment works. In fact, the Pennsylvania Department of Environmental Protection Secretary, Michael Krancer, has stated that if disposal of wastewater from the hydraulic fracturing process at wastewater treatment facilities was curtailed, bromides would “quickly and significantly decrease” in surface waters (Gresh, 2011). Increased bromide concentrations in incoming water of treatment plants is directly correlated with elevated levels of total THM, as well as the percentage of which are brominated. As a constituent of TDS, bromide is a conservative parameter, and has been found to increase downstream and is considerably affected by the volume of water transporting it (Roberson, 2011).

Aquatic Ecological Impacts

Elevated TDS levels in the aquatic environment can result in shifts in the biotic community of a stream, as well as limit biodiversity, exclude less tolerant species, and cause both chronic and acute toxicity to aquatic organisms at definite life stages. Total dissolved solids cause toxicity to aquatic organisms in three main ways; increasing the salinity of the natural environment, changing the ionic composition of the natural water, and by toxicity of

individual ions, such as bromide. Mount et al., conducted toxicity tests on fathead minnows with 30 different combinations of ions. They found that the vast majority has 96-hr LC50 less than 510 mg/L (Weber-Scannell and Duffy, 2007). This value is just slightly higher than the allowable discharge limit for TDS at 500 mg/L in Pennsylvania. Elevated levels of TDS can also increase the toxicity of other parameters, as shown by Erickson et al. Erickson et al. reported that adding a potassium chloride solution to a simulated aquatic environment dramatically increased the copper toxicity. Timpano et al. (2010) strategically selected sites to isolate the effects of TDS from other parameters often present in the field, such as pH and sedimentation. Timpano et al. had results that were in agreement with other studies that did not isolate TDS, concluding that sites with elevated TDS showed a significant negative correlation with several parameters in the aquatic communities.

In a study conducted by EPA Region 3 focusing on the central Appalachian region, the report stated that most streams in the region have natural TDS concentrations of 50 mg/L or below. This means that the organisms present in the streams have adapted to those concentrations. The EPA suggests that due to the use of cultured organisms, that are more tolerant of TDS, in toxicological studies, the results are often not adequate to protect the region's organisms (Pond & Passmore, 2007). The EPA report cites additional studies which document the impact of elevated levels of TDS. High levels of TDS can also interfere with osmoregulation of aquatic organisms.

One study conducted in streams throughout the eastern Kentucky Coalfields region, found that the percentage of Ephemeroptera, an ecological indicator of good water quality, in

the macroinvertebrate community dropped virtually to zero when the conductivity of the water reached 500 microSiemens per centimeter ($\mu\text{S}/\text{cm}$) (~ 315 mg/L TDS) (Pond & Passmore). A similar study, conducted by the West Virginia Department of Environmental Protection in the Mountain Bioregion, concluded that the aquatic community became impaired when conductivity reached 600 $\mu\text{S}/\text{cm}$ or 375 mg/L TDS. Empirical data from similar studies are currently being used as the basis for developing water quality criteria for sediment and nutrient pollution, and could serve a similar purpose for TDS (Pond & Passmore, 2007).

CHAPTER 3 – RECOMMENDATIONS AND CONCLUSIONS

Total dissolved solids (TDS) have been shown to affect more than the aesthetic qualities of drinking water, and should be regulated as such. Additional regulation is needed to protect other aspects of surface waters, as well as to ensure the stability of aquatic communities. The U.S. Army Corps of Engineers, Pittsburgh District (Corps), has suggested regulating TDS for an aquatic life standard as opposed to the current secondary drinking water standard. This action would require a limit to be set for TDS based on the anticipated impacts to aquatic life statewide. Although a Federal agency, the Corps has no authority to impose such standards and can only make their opinion known to the agencies with this power. In Pennsylvania, the Commonwealth of Pennsylvania (Pennsylvania) could take this step but it would be an unfavorable move in a political sense and would also be highly variable. Due to the variations in aquatic communities, a sufficient exposure level would also be difficult to determine for a large scale. Pennsylvania could, however, list certain streams or rivers as “impaired” on their yearly report to the U.S. Environmental Protection Agency (EPA).

A body of water can be placed on the list of impaired waterways, pursuant to section 303d of the Clean Water Act, submitted each year to the EPA if data gathered by the state indicates impairment to a designated use, by a specific constituent. In Pennsylvania, the designated uses of waterways include; agriculture and wildlife, public water supply, trout waters, warm water fisheries, water contact recreation, water supply for industrial, transportation, cooling, or power, fish consumption, and aquatic life. Once a waterway is

listed, the EPA will evaluate the data to determine if they concur. If concurrence is found, the state can then begin the process of formulating a total maximum daily load (TMDL) of the constituent for the waterway. This seems to be the best option for TDS regulation throughout the Appalachian Plateau. As TDS is a conservative parameter, a waterway should be regulated as a whole, rather than as independent point sources. By laying out the data gathered regarding impairment, as well as the methods using in determining the TMDL, this will serve as an important step for regulating TDS in the Appalachian Plateau states.

For this reason, it is increasingly important that the state regulatory agencies take notice of degradation within their jurisdiction and strengthen the case against elevated TDS in their waterways. By sharing data and documenting and investigating events such as the Dunkard Creek fish kill, the Appalachian Plateau states can regulate TDS properly, and once again show improving water quality and healthy aquatic communities.

Water quality has long been a concern throughout the Appalachian Plateau due to the various sources of contamination, including a long history of coal mining and associated discharges. The increased awareness of this fact, beginning in the 1970s, led to the implementation of regulations and eventually a steady increase in the overall surface water quality. Recently, however, elevated levels of total dissolved solids (TDS) have been seen in many areas with the negative effects becoming more apparent. Incidents such as the Dunkard Creek fish kill, which occurred in late 2009 along the Pennsylvania-West Virginia border, served to illustrate how new sources of TDS are bringing levels to unsafe concentrations in waterways. The legacy sources of TDS, such as mine drainage, treated and

untreated sewage, and road de-icing runoff, are not able to account for these elevated levels. Many scientists and regulators point to the increasing amount of high TDS wastewater generated by the shale gas drilling industry that is occurring throughout the region. This wastewater typically contains TDS levels between 6,000 and 225,000 mg/L and is regularly taken to plants unable to remove it.

Whatever the source, data from the U.S. Army Corps of Engineers, Pittsburgh District, show that in-stream concentrations of TDS have been increasing since about 2008, particularly in the Monongahela River watershed. The Pennsylvania Department of Environmental Protection has concluded that the Monongahela River is at or very near its capacity to assimilate TDS, yet TDS is still regulated only as a secondary drinking water standard. In Pennsylvania, contributions of TDS are regulated as independent, end-of-pipe, sources, not to exceed 500 mg/L. Since TDS is a conservative parameter that increases the overall concentration with each contribution, it is important to regulate it likewise.

Many studies have indicated that increased TDS loads in waterways negatively affect aquatic communities in various ways, and should be regulated as such. However, establishing an aquatic life standard would be difficult due to the variability in aquatic environments within states, as well as political pressure from the main sources, namely the coal and natural gas industries. The establishment of total maximum daily loads would be the most effective method of regulating TDS. This method, however, relies heavily on the states and requires sufficient data to prove impairment of a specific waterway, which is both costly and time intensive. The legacy sources of TDS show no signs of disappearing anytime

soon, while the emerging source from unconventional natural gas production is only projected to expand. The current method of regulating TDS throughout the Appalachian Plateau does not provide adequate protection for aquatic communities, making some type of action necessary. Only time will tell whether the states within this region will take notice of and acknowledge their responsibility to effectively regulate TDS in their waterways.

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