Assessment of Filamentous Algae in the Greenbrier River and Other West Virginia Streams

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During the summer of 2007, WVDEP received numerous complaints regarding the amount of algae in the Greenbrier River. Most of the complaints centered on the Caldwell to Alderson section of the river; and at least one complaint was received about the level of algae further upstream in the Denmar area. Several employees of WVDEP were familiar with the problem and indicated that the algae bloom had been occurring at various intensities for decades; some asserted that the algae had been getting worse, and perhaps starting earlier, than it had historically.

In September 2007, a meeting within the WVDEP Division of Water and Waste Management was held to discuss the problem. Results of water quality samples from the Watershed Assessment Branch sample database (WAB-Base) were summarized at the meeting. The WAB-Base results showed elevated levels of phosphorus in Howard Creek. Howard Creek flows into the Greenbrier River at Caldwell where the algae problem was reported to begin. WAB-Base results also showed that phosphorus levels in Howard Creek were significantly higher below the White Sulphur Springs sewage treatment plant (WSS STP) than above the plant.

The WSS STP had a history of solids "washout" which resulted in sludge beds in Howard Creek. Seven golf courses and a fish hatchery are located on Howard Creek, upstream of the WSS STP. Additionally, significant cattle pasturing occurs in the Greenbrier basin upstream of Howard Creek, and the gradient of the river lessens somewhat near Caldwell. It was suggested that the soil particles from the upstream pastures that are high in phosphorus were settling out in this lower gradient section on the river, allowing some of the phosphorus bound to the soil to be released into the water column. Perhaps all these factors were combining to fuel a "perfect storm" of algae. There was no consensus in the September meeting on what the primary source of the algae problem was.

A TMDL effort for the Greenbrier river basin was already underway. All the field work for this TMDL had been completed, making available a large amount of recent water quality, biological, and pollutant source tracking data. During the 12 months of monitoring at 130 stations, the only violation of water quality standards was for fecal coliform bacteria. Nutrient samples were taken at several locations; there were no violations listed for nitrate, and currently there is no water quality standard for phosphorus in WV streams. Therefore, TMDLs were not required for nutrients. Pollutant source tracking efforts focused only on the fecal coliform impairments, not on nutrient sources. One outcome of the September meeting was to perform additional source tracking on Howard Creek and the Greenbrier River to better quantify the nutrient sources that could be contributing to the algae problem.

Nutrient Source Tracking

Observations of the location and intensity of the algae, both on the Greenbrier River and Howard Creek, were made; the accumulation and impact of sediment was evaluated in the "lower gradient" section of the Greenbrier River near Caldwell; historical river flow and rainfall data was assessed; a review of WAB-Base nutrient data was made; additional sampling included a storm event sampling on Howard Creek, a low flow "snap shot" of nutrient levels in Howard Creek, and a winter sampling event coordinated with DEP Environmental Enforcement inspection staff which included concurrent stream sampling and Compliance Sampling Inspections of the WSS STP and fish hatchery.

Photo 1. Greenbrier River at Hillsboro STP discharge where algae begins *(9-12-08).*

Photo 2. Greenbrier River 200-300 feet below the Hillsboro STP discharge *(10-17-07).*

Photo 3. Greenbrier River at mouth of Howard Creek *(9-25-07).*

Photo 4. Greenbrier River at above Fort Spring -between Ronceverte and Alderson *(8-29-08).*

Photo 5A. Different species of algae growing in cold water of Davis Spring *(8-25-08).*

Photo 5B. Vigorous periphyton growth on a rock taken from Tuscarora Creek near Martinsburg *(11-11-08).*

Photo 6. South Fork of South Branch Potomac River at Moorefield bridge *(8-17-08).*

Photo 7. Tygart Valley River near Elkins, above quarry *(9-25-08)*.

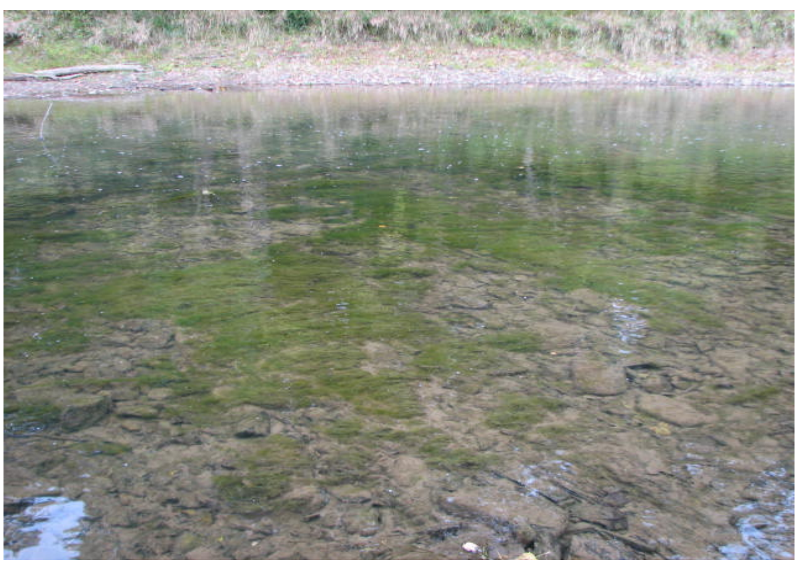


Photo 8. Cacapon River near Yellow Spring- below Wardensville *(9-25-08).*

Photo 9. *Hydrilla* beds on New River with some filamentous algae development. Near Glade Creek campground *(9-17-08).*

Photo 10. Filamentous algae along edge of New River just above Gauley Bridge *(9-17-08)*.

Photo 11. *Hydrilla* beds in the Caldwell pool of the Greenbrier River above Howard Creek *(9-25-07).*

River Flow and Rainfall

Archives from the USGS gaging station at Alderson and the National Weather Service were reviewed. While the summer precipitation and river flow have been below average for three of the last four years, the river flow was not exceptionally low - from an historical perspective (see Attachment 4).

Sediment Impact and Rooted Aquatic Vegetation

Sediment accumulates in the Greenbrier River in the long pool at Caldwell. This is one of the few places on the river where the typical rocky substrate of Greenbrier is completely coated with sediment. Moving from the top of the pool down, it was noted that as the sediment increased the amount of rooted aquatic vegetation (not algae) increased dramatically and eventually covered the entire river bottom (Photo 11). This type of rooted vegetation, genus *Hydrilla*, grows in large beds in several other rivers where sediment accumulated, most notably the New River. See Photo 9.

As a rule, wherever sediment accumulated in the Greenbrier River, the rooted vegetation thrived. This nutrient rich sediment most likely results from agricultural activities in the Greenbrier watershed. No biological impairments occurred in the Greenbrier basin during the pre-TMDL monitoring, indicating the gradient is high enough to move the sediment downstream with only minimal accumulation in the Greenbrier.

Algae Distribution

In the upstream section of the Greenbrier River in the Denmar area, there is a very clear starting point for the algae – immediately below the sewage treatment plant discharge for the town of Hillsboro (Photo 1 and 2). Hillsboro's discharge is about 20 times smaller than that from WSS STP or Ronceverte STP, so the algae bloom is relatively short lived. It begins waning just before the sewage discharge from the Denmar Correctional Center enters the river; there the algae bloom increases and continues down the river, again for only a relatively short distance, until it is gone.

Filamentous algae does not show up significantly in the Caldwell pool until Howard Creek, which drains the White Sulphur Springs area, enters the Greenbrier River. At this point filamentous algae clogs the *Hydrilla* beds and fills the water column (Photo 3). The algae gradually disperses across the river over the next half mile of riffles. Once the river reaches Ronceverte the algae is well dispersed. When the discharge from the Ronceverte sewage treatment plant enters the river, the algae again fills the water column along the side of the river into which the plant effluent is discharged.

Below Ronceverte the level of algal development continues to be significant through Fort Spring and Alderson (Photo 4). A slight temporary increase is found below the Alderson sewage treatment plant discharge, but the algae level is already high enough that the smaller discharge from Alderson doesn't have the dramatic increase that is seen below Howard Creek (White Sulphur Springs) and Ronceverte. Significant levels of algae continue through Pence Springs and begin tapering off by Talcott. A few sporadic small algae blooms were noted on down the river to its mouth (Attachment 1).

There is no algae bloom below the Durbin sewage treatment plant discharge to the Greenbrier River. An algae bloom was noted below Marlinton in mid-summer 2008, but disappeared by September. This is probably due to a varying calcium level in the river at this point. (The critical role of calcium will be explained later in this report.)

Away from the Greenbrier mainstem, the amount of filamentous algae found on Howard Creek itself was surprisingly low compared to the Greenbrier River. Rooted aquatic vegetation dominates the creek where sediment accumulates and periphyton thrives on the rocky substrate in other places. Even though there was less filamentous algae than originally expected (found later to be due to the calcium/hardness level) there were areas where filamentous algae accumulated in Howard Creek, and particularly of note were the areas upstream of the WSS STP discharge. Seven golf courses, a trout hatchery, and some minimal pasturing are located on Howard Creek upstream of the WSS STP.

Source Characterization

Fertilizer information was gathered from six of the seven golf courses. Nutrient content, application rates and dates, soil and water sample results, management practices, and other information was compiled and evaluated by WVDEP. (The seventh course is the farthest upstream and located on a section of Howard Creek where no filamentous algae was noted; fertilizer application rates from the other courses were used to estimate the loading from this course.) Research conducted jointly by Ohio State University and the USDA studied nutrient loss rates from golf courses; the phosphorus loss rate was 6.2% of the total applied, or 0.51 kg/ha/year (King *et al*, 2004). These USDA values were used to calculate the combined annual phosphorus loading contribution from the golf courses on Howard Creek. The combined phosphorus loss from the golf courses totaled 200-300 lbs/year, or about 3% of the total phosphorus loading in Howard Creek at its mouth.

During the pre-TMDL monitoring, WVDEP had taken monthly samples for one year on Howard Creek near its mouth, just below the WSS STP, just above the WSS STP, and upstream of six of the golf courses. This intensive sampling helped to segregate the WSS STP loading from other categories of sources (*Figure 1).* Grab samples of the stream taken during the low flow conditions of early fall of 2007 and a series of stream samples taken during a storm event both showed similar results (*Attachment 3*).

Figure 1. **Phosphorus Loading at Various Locations Along Howard Creek.** Stream loadings (lbs/day) are based on pre-TMDL sample results taken May through October 2004. The loading from the White Sulphur Springs STP was calculated from effluent sample results.

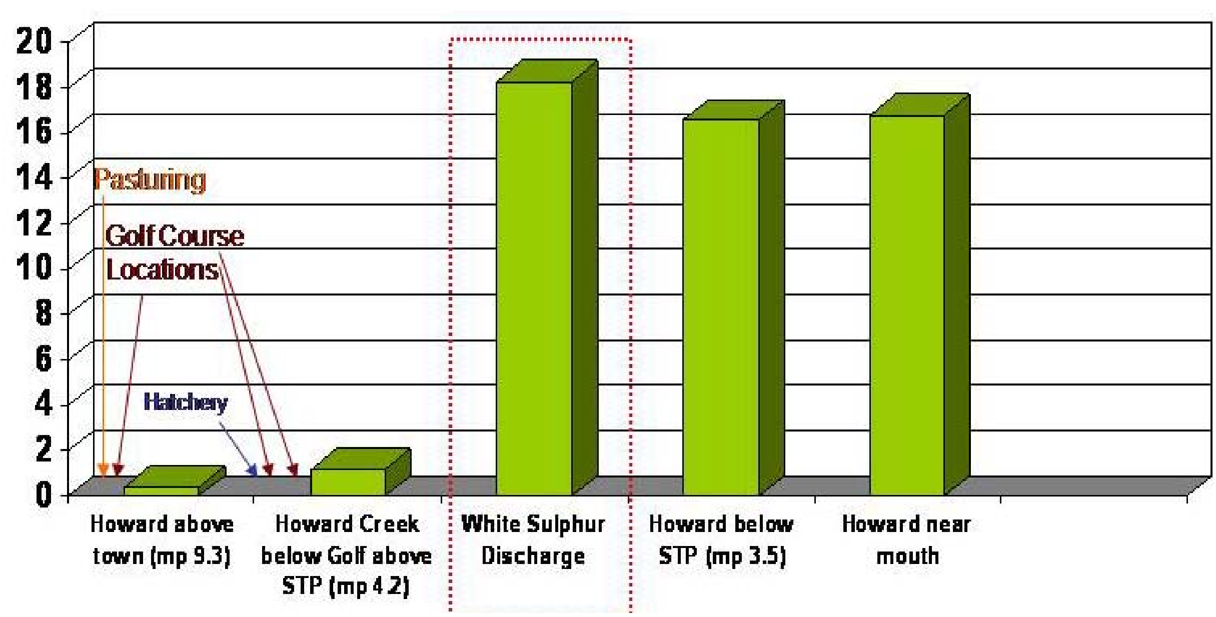
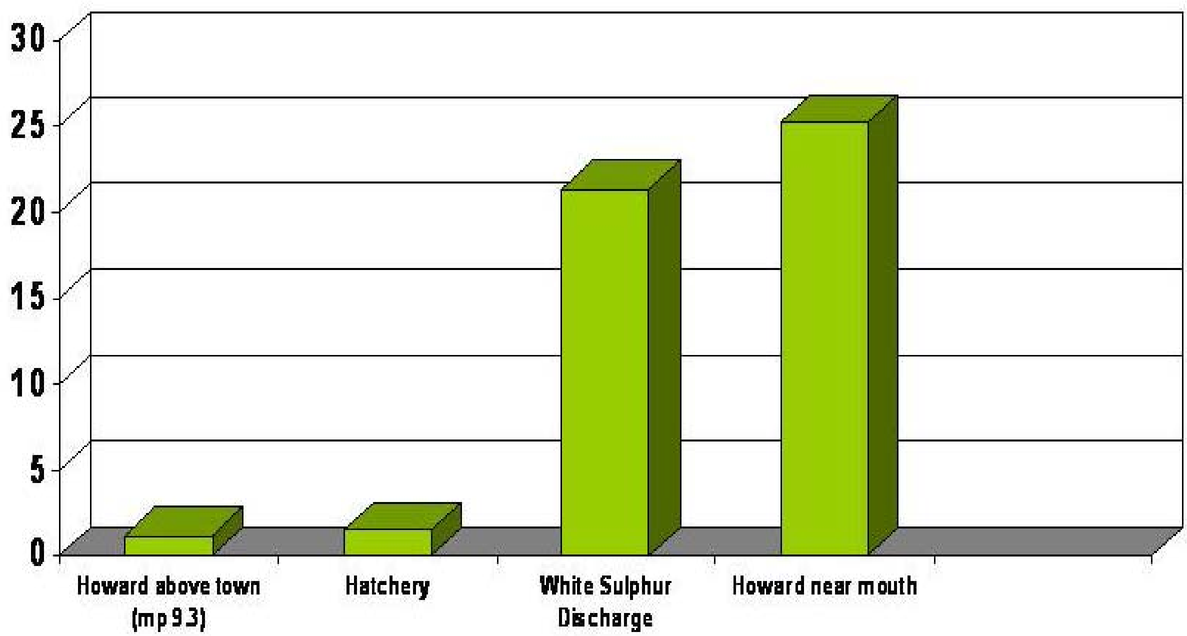


Figure 2. **Phosphorus Loading (lbs/day) During Compliance Sampling Inspections.**



Compliance Sampling Inspections were conducted concurrently at the WSS STP and the national fish hatchery; Howard Creek was sampled during the same time as the composite effluent samples were taken from the hatchery and WSS STTP. Again, the WSS STP accounted for most of the phosphorus loading in Howard Creek (*Figure 2).* Generally, the WSS STP accounted for 80-90% of the total phosphorus loading in Howard Creek throughout the year.

The conclusion drawn from the nutrient source tracking was that the algae in the Greenbrier River results primarily from the dissolved phosphorus in municipal sewage treatment plant effluent combining with nitrogen from a host of sources (agriculture, municipal discharges, and failing septic systems).

Keys to Algae Development

After the initial pollutant source tracking was performed, one question was obvious and had to be answered: If the algae bloom is driven by sewage treatment discharges, why is the algae bloom so severe on some portions of the Greenbrier River and not present on many other rivers in the state. A query of WAB-Base, which contains over 30,000 samples from across the state, turned up a clear difference in two important parameters – alkalinity and hardness. These two parameters, along with pH, serve as controlling variables and strongly influence the behavior of other constituents present in water (Weiner, pp 53).

Both alkalinity and hardness are indirect measures of multiple constituents, and are usually expressed as an equivalent concentration of $CaCO_3$. Hardness is a property of cations (Ca^{+2} and Mg^{+2}) while alkalinity is a property of anions (HCO_3^{-1} , CO_3^{-2} , PO_4^{-3}, and OH^{-1}).

Threshold Alkalinity

Significantly, no algae blooms were noted on streams where the alkalinity was less than 30 mg/l. Low alkalinity (less than 25 mg/l) keeps phosphorus from being available as a nutrient (Wurts, 1992) and could even limit algae growth due to low mineralized carbon levels. An alkalinity of greater than 50 mg/l is recommended for productive aquaculture ponds (Brunson, 1999). In West Virginia, low alkalinity rivers with municipal sewage treatment plant discharges include the Elk River, Cherry River, Little Kanawha River, and the upper Greenbrier River (Durbin area). Algae blooms have not been documented on these rivers.

Hardness Ceiling

Further, no significant algae blooms were present on several other rivers even though ample phosphorus, nitrogen, and alkalinity were present. When reviewing the WAB-Base data, it was noted that the hardness level on these streams tended higher than on the Greenbrier River (see *Table 4,* p 14). Hardness on the Greenbrier did not exceed 100 mg/l. The hardness on the West Fork River below the Weston STP discharge was 250-400 mg/l. Since hardness is a measure of Ca^{+2} and Mg^{+2} cations (sometimes iron and aluminum can mildly influence total hardness), a literature search was conducted to determine if there was any research on the role of calcium and magnesium in the development of algae in nutrient rich waters. There is a body of research on the topic, and it concludes that calcium and magnesium are key factors in algae development. Details are given in the "*Literature Review.*"

Nutrients

A stoichiometric formula for algae has been estimated as $C_{106}H_{181}O_{45}N_{16}P$ (Craggs, 2005). One pound of phosphorous can then produce around 78 pounds of algae. (Some sources have reported this as 350 pounds, but this is incorrectly based on the molar ratios in algae, not the mass ratios). Nitrogen and phosphorus are incorporated into the algae cell structure at approximately a 16:1 nitrogen to phosphorus molar ratio (Redfield, 1958). But because nitrates leach from the soil more readily than phosphorus, nitrogen is generally much more available than phosphorous to aquatic vegetation. Consequently, algae growth in most surface waters will be limited by phosphorous (Weiner pp 98). Removing phosphorus is, chemically, the most efficient way to limit algae growth (Kennedy, 2004).

Under ideal summer growing conditions, algae blooms can occur with inorganic phosphorus concentrations as low as 0.005-0.01 mg/l (Weiner, pp 101; Kawaga, 1989). Weiner also notes that when phosphorous levels increase and cause algae growth to be limited by either carbon or nitrogen, long term mechanisms (CO_2 diffusion from atmosphere and changes in biological growth mechanisms) act to compensate for these deficiencies and algal growth once more becomes proportional to the phosphorous concentration (Weiner, pp 100).

In the Greenbrier River, algae blooms were occurring with P concentrations as low as 0.01-.014 mg/l. The amount of algae formation increased with an increase in P concentrations found below the discharges of the sewage treatment plants. (See graph in *Attachment 1*.)

This is not to say that phosphorus is more important than nitrogen in the growth of algae, only that growth tends to be limited by phosphorus in most cases. Nitrates are very soluble and come from a number of sources including pasturing, crop and lawn fertilizers, failing septic systems, and treated sewage discharges. Consequently, nitrates are rather ubiquitous in river systems. In the Greenbrier River, summer nitrate-nitrite concentrations run about half their winter level, despite the much higher winter time river flow which dilutes the phosphorus concentration. The summer N:P mass ratio in the Greenbrier River above Howard Creek is about 23:1. There is essentially enough nitrate loading in the Greenbrier at Ronceverte, 220 lbs/day, to fuel the algae growth for the combined phosphorus loading from both WSS STP and Ronceverte STP, even if the entire nitrate load from these sewage treatment plant discharges was removed. *Phosphorus seems to be the key to not only understanding the algae problem, but to alleviating it as well.*

Other Factors (Turbidity & Temperature)

Several other streams had a chemistry (alkalinity, hardness, phosphorus, and nitrogen concentrations) that seemed favorable for algae development, but no algae bloom had been reported. When these rivers were visited, many had significant algae development. These streams include portions of the Cacapon River, Bluestone River, New River, and Tygart Valley River. The North Fork of the Hughes River had some low to moderate algae development, but was somewhat suppressed given its chemistry; however, water turbidity was clearly a factor in limiting the algae development on the North Fork of Hughes. Other streams with favorable chemistry which did not have significant levels of filamentous algae had obvious limiting factors for algal growth, most often turbidity (Kanawha River and Brush Fork of Bluestone) or temperature (Piney Creek).

Given these observations, it seems likely that alkalinity and hardness, along with the known factors of nitrogen, phosphorus, and turbidity, play a key role in filamentous algae development in West Virginia's streams. It is reasoned that a minimum alkalinity is needed to make the phosphorous available for plant uptake, and that at higher hardness levels Ca/Mg precipitation with phosphorous occurs, making the phosphorus much less available for algae development.

Literature Review

Understanding the relationship between algae and phosphorus is complicated by the fact that an algae cell's ability to use specific forms of phosphorus is strongly influenced by several factors, including pH, hardness, the amount of dissolved oxygen, and temperature (Florida, 2000). Other environmental factors such as shading, grazing, turbidity, and substrate condition can maintain low algal biomass despite abundant nutrients (Dodds and Welch, 2000). Further, algae in streams and rivers occur in multiple forms, such as sestonic cells which are suspend in the water column, periphyton which grows on the substrate, and filamentous mats; these various forms may differ in their response to nutrient enrichment and the degree to which they are affected by other environmental factors (Royer, 2008).

The environmental behavior of phosphorous is largely governed by the generally low solubility of most of its inorganic compounds, and its strong adsorption to soil particles (Weiner, pp 97). Einsele and Mortimer demonstrated in the late 1930s and early 1940s that sediments retain phosphorous by fixation to iron. These results created a widespread opinion that phosphorous sedimentology was completely linked to iron chemistry, although it was known that calcareous sediments behaved differently (Bostrom *et al* , 1988). It has become evident in more recent research that phosphorus exchange between sediment and water is a highly complex phenomenon and includes many interrelated chemical, biological, and physical processes (Bostrom *et al* , 1988).

Orthophosphate, the mineralized form of phosphorus which is used by the algae, associates with particles by several types of bonding, from physical adsorption, to co-precipitation, to chemical bonds of different strengths (complex, covalent, and ionic bonds) (Bostrom *et al,* 1988). Supersaturation and/or undersaturation of phosphate salts may also occur, further complicating the study of the chemical processes which govern phosphorus availability (Diaz, 1994).

The role of calcium in phosphorus water chemistry has received far less attention than iron-phosphorus interactions (Bostrom *et al,* 1988). However, several researchers have investigated the connection of calcium to phosphorus uptake in algae. Magnesium ions, with the same plus two charge as calcium, behave similarly to calcium and are sometimes considered together with calcium in their combined impact on algae growth.

Bedore *et al* found that in the upper Illinois River, pH combined with Ca and Mg activity are the dominant chemical controls on phosphorus chemistry (2008). Vasata reported that the optimal concentrations of Ca and Mg for the productivity of algae decreased with increasing P concentration, and Kawaga *et al* found a regulating effect of dissolved Ca and Mg on the P-nutrition of algae, i.e. their Ca-Mg index could predict both the amount of suspended phytoplankton and the amount of phosphorus contained in the sestonic algae (1989). Masayoshi found a Ca/Mg ratio less than 4 had a negative effect on algal growth, and a Ca/Mg ratio greater than 5 enhanced growth (2000).

The effect of calcium and magnesium on phosphorus precipitation is variable depending on the chemical and physical conditions of the water system. Bedore found highly variable associations of phosphorus in sediment in streams impacted by municipal sewage treatment plant effluents. In five different sample locations, 20-70% of P was Fe-associated, 20-50% of P was bound in organic compounds, and 5-35% of P was associated with calcium minerals (2008). Bedore also noted that naturally hard water streams and rivers regularly experience high ionic strength, greatly complicating in-stream chemistry. Plant *et al* (2002) established that phosphorus co-precipitates with calcite in highly alkaline aquatic environments, although this may be inhibited as dissolved phosphorus levels approach 0.6 mg/l due to the cessation of calcite growth. Other reports have also suggested that phosphorus co-precipitates on calcite in hard water rivers (Avimelech 1980; Salinger 1993). Hartley suggested that Ca-P precipitation is a natural mechanism to control eutrophication in hard water lakes (1997). Long term P-accumulation in the Everglades was linearly correlated with Ca^{+2} accumulation (Reddy *et al* 1993).

That calcium and magnesium concentrations are strongly linked with algae growth is well established by research and observation. Generally, the Ca-Mg ions act to control the availability of phosphorus for algae uptake by the formation of relatively insoluble phosphate precipitates. The specifics of the phosphate precipitation are complex and can vary with the individual chemistry of each river system. Although the complexities of the mechanisms of Ca-P precipitation is not fully understood, the consensus is that the chemistry of the aqueous phase from which precipitation takes place is of paramount importance (Koutsoukos, 2000).

Phosphate Precipitation

Phosphorus based anions occur in several forms and are most often associated with calcium, magnesium, sodium, iron, and aluminum cations. All of the compounds have different solubilities, most of which vary significantly with pH, and formation of some P compounds will always be favored over others depending on the general chemical environment (alkalinity, hardness, conductivity, pH, redox potential, iron availability, etc.) in which formation occurs. *Table 1* shows the negative log of the solubility product constants (K_{sp}) for several simple phosphate compounds; while all (except sodium) are fairly insoluble, calcium phosphate is the *most* insoluble and is closely followed by magnesium phosphate.

Table 1. ***Solubility of Selected Phosphate Salts***

Compound	Formula	-log (Ksp) @25°C
Aluminium phosphate	$AlPO_4$	20
Calcium phosphate	$Ca_3(PO_4)_2$	27
Iron(III) phosphate dihydrate	$FePO_4 \cdot 2H_2O$	15
Magnesium phosphate	$Mg_3(PO_4)_2$	24
Sodium Phosphate	Na_3PO_4	Highly soluble

Table 2. ***Solubility of Calcium-Phosphate Minerals:*** From *Octacalcium Phosphate (Chow, 2001)*

Compound	Abbreviation	Formula	-log (K*sp*) @25°C
Monocalcium phosphate monohydrate	MCPM	$Ca(H_2PO4)_2 \cdot H_20$	Highly soluble
Monocalcium phosphate anhydrous	MCPA	$Ca(H_2PO4)_2$	Highly soluble
Dicalcium phosphate anhydrous	DCPA	CaHPO4	6.9
Dicalcium phosphate dihydrate	DCPD	$CaHPO4 \cdot 2H_20$	6.6
Calcite with co-precipitated P	CCP	$CaCO_3 \cdot PO_4$	8.47
alpha-Tricalcium phosphate	α-TCP	$Ca_3(PO4)_2$	25.5
beta-Tricalcium phosphate	β-TCP	$Ca_3(PO4)_2$	28.9
Tetra Calcium phosphate	TTCP	$Ca_4(PO4)_2O$	38
Octacalcium Phosphate	OCP	$Ca_8 H_2(PO4)_6 \cdot 5H_20$	46.9
Hydroxyapatite	HAP	$Ca_5OH(PO4)_3$	58.3
Fluorapatite	FAP	$Ca_5F(PO4)_3$	60.5

The Ca-P family of compounds may take on several different chemical forms (*Table 2*). Solubility product constants are experimentally determined, and there is some disagreement in scientific research and publication over the reported Ksp values for some of the Ca-P compounds. Perhaps the most important cause for inconsistent reporting is the metastability of some Ca-P salts in relation to other more stable forms (Moreno *et al*, 1966). (Metastable salts form an apparent equilibrium in solution, but change quickly to a more stable form with only a slight change of conditions. This further complicates the understanding of the specific chemical mechanisms of Ca-P precipitation.) There is, however, a generally accepted order of relative solubility.

$$MCP \gg DCP > TTCP > \alpha\text{-}TCP > \beta\text{-}TCP \gg OCP > HAP$$

Role of Magnesium

Hydroxyapatite (HAP) can account for up to 80% of phosphate precipitation, but the formation of HAP can be inhibited by the presence of magnesium ions (Cragg, 2005). Inhibition of HAP formation results in the formation of other Ca-P precipitates, mainly OCP and TCP (Diaz, 1994). Mg-P precipitates can also be produced. Magnesium forms similar chemical compositions as calcium with the phosphate ion: magnesium phosphate monobasic ($Mg(H_2PO_4)_2$) , dibasic ($MgHPO_4$), and tribasic ($Mg_3(PO_4)_2$). The solubility of magnesium salts is generally only slightly higher than that of calcium salts. All these compounds have low solubility products.

Diaz found the Ca-P equilibrium of stream water with various hardness levels could be controlled by OCP, β-TCP, HAP, or possibly a Ca-Mg-Fe-P complex. Which Ca-P mineral controlled the equilibrium depended on pH and Ca-Mg concentrations. It was suggested higher magnesium concentrations in harder water may be responsible for the formation of these less soluble Ca-P forms whenever dolomite (not calcite) is the thermodynamically dominant phase of carbonate. It has been reported that a Mg^{+2}/Ca^{+2} ratio greater than 0.6 indicates that dolomite is the thermodynamically stable phase, and calcite the dominant phase of waters where ratios are less than 0.6 (Hsu, 1963).

Literature Summary

1. Phosphorus is commonly the limiting factor for algae growth.
2. Ca and Mg play a key role in controlling instream phosphorus chemistry by forming numerous phosphate precipitates.
3. When phosphorous is in solid form, it is unavailable for algae to use.
4. Dolomitic streams are higher in magnesium content, and insoluble Mg-P precipitates can form in these waters.
5. Ca-Mg-P chemistry is very complex, and precipitate formation is dependent on stream-specific chemistry.

Application in West Virginia

Most streams in West Virginia can easily be classified as being dominated by either the calcite or dolomite by determining the Mg^{+2}/Ca^{+2} ratio during low flow summer conditions. Dolomitic streams include the Tug Fork, Coal, Guyandotte, and Mud rivers. Steams near equilibrium include the lower Elk, Birch, upper Kanawha, lower Gauley, Shenandoah, and New rivers. Strongly calcite streams include the Greenbrier, upper Gauley, upper Elk, Little Kanawha, Hughes, West Fork, Tygart, Cheat, Monongahela, South Branch Potomac, and Cacapon rivers. These lists show that streams from the southern coalfields region of the state are dolomitic streams. Magnesium is expected to play a dominant role in the phosphorus chemistry in these streams.

The Ca-Mg Index proposed by Kawaga was based on data for sestonic algae in lakes, but it also yields interesting results when applied to West Virginia rivers. Their index is proposed as the

$$\log[Ca^{+2}/Mg^{+2}] - 0.5 \log[Ca^{+2} + Mg^{+2}],$$

where Ca and Mg are expressed in molar concentrations, not mg/l.

Table 3 ranks the Ca-Mg Index for several WV rivers; those rivers with alkalinity below the threshold value for algae development (average 30 mg/l) are not shown in the table. The table shows an excellent correlation between the Ca-Mg Index and the level of algae development. It must be noted that the only factor removed from consideration here is low alkalinity; other factors, such as nutrient content and turbidity, also impact algae development and largely explain variations in the level of algae development in *Table 3*.

Table 3. **Ca-Mg Index for West Virginia Rivers**

River	Ca-Mg Index	Algae Development
Greenbrier River	2.15	Severe
Tygart Valley River	2.10	High
South Branch Potomac River	2.08	Low-Moderate
North Fork Hughes River	2.05	Low
South Fork/South Branch Potomac River	2.01	Moderate
Cacapon River	1.92	High
Bluestone River	1.81	Moderate-High
West Fork River	1.80	None
Monongahela River	1.77	None
New River	1.74	Moderate
North Branch Potomac River	1.71	None
Kanawha River	1.68	None
Guyandotte River	1.65	None
Shenandoah River	1.54	None
Tug Fork	1.50	None
Birch River	1.50	None
Coal River	1.25	None

Table 4. **Modified Ca-Mg Index for West Virginia Rivers**

River	Modified Ca-Mg Index	Avg. Hardness (mg/l)	Algae Development
Greenbrier River	3.26	65	Severe
North Fork Hughes River	3.24	63	Low ^{T}
Tygart Valley River	3.18	70	High
New River	3.1	79	Moderate ^{D}
Kanawha River	3.08	85	None ^{T}
Cacapon River	3.10	96	High
South Fork/South Branch Potomac River	2.95	112	Moderate
Bluestone River	2.94	121	Moderate-High
South Branch Potomac River	2.88	130	Low-Moderate
Guyandotte River	2.86	145	None
West Fork River	2.85	190	None
Monongahela River	2.84	149	None
Tug Fork	2.79	178	None
North Branch Potomac River	2.78	214	None
Shenandoah River	2.76	174	None
Birch River	2.74	221	None
Coal River	2.51	284	None
Mud River	2.49	373	None

T= Algae level reduced by turbidity. D= Algae level probably reduced by depth of pools in river.

For the sample results from WAB-Base used to calculate the Ca-Mg Index, the first half of the equation (*log*$[Ca^{+2}/Mg^{+2}]$)accounted for an average of 10.2% of the total Index score. The largest percentage impact was on streams with the lowest overall Ca-Mg concentrations, i.e. the Greenbrier and Tygart where it accounted for 15-20% of the Index score. A Modified Index, *-log*$[Ca^{+2} + Mg^{+2}]$, was calculated and shown in *Table 4*. The results show a similar ranking of the rivers, and a good (perhaps even better) correlation between the modified index and the amount of filamentous algae development.

This Modified Index is a simple function of the Ca^{+2} and Mg^{+2} molar concentrations; *so is hardness*. It seems hardness could indeed be used as a basic indicator of a West Virginia stream's propensity to grow filamentous algae. A hardness level of less than 100 mg/l appears ideal for algae development. Suppression of algal growth seems to occur around 120-150 mg/l. And very little filamentous algal growth is seen when the hardness level is above 150 mg/l (except in AMD impacted streams where the low pH drives P-availability more than Ca and Mg do). Interestingly, this is a similar range to the hardness scale used for predicting soap performance, mineral deposits, and metals toxicity.

Table 5. **Hardness Scale** (Weiner, pp 77)

Degrees of Hardness	***mg CaCO3/L***	***Effects***
Soft	<75	No scale desposits Efficient use of soap Increase dissolution of metals.toxicity
Moderately Hard	75-120	Above 100 mg/l, significant scale deposits may form Requires more soap for cleaning Not objectionable for most purposes
Hard	120-200	Scale buildup and staining occurs Needs softened at ~180 mg/l
Very Hard	>200	Requires softening for household and commercial use

Hardness was originally used as a measure of the ability of water to precipitate soap and interfere with lathering. The interference occurs as a result of calcium ion replacing sodium ions in the soap molecules; the sodium carboxylates (like sodium phosphates) are very soluble, but the calcium carboxylates (like calcium and magnesium phosphates) are relatively insoluble when they form. This interferes with the surface tension created by the soap, reducing the lather. It is noteworthy that the negative log of Ksp values for the calcium carboxylates used in soap range from 7-19 (Bulatovic 2007); this is a similar, but slightly lower, range to the Ksp values of the expected and observed Ca/Mg-P precipitates which occur in hard water – indicating that the Ca/Mg-P precipitates would begin to form at somewhat lower concentrations. This is exactly what observations of algae development indicate.

This concept also lines up well with Diaz *et al*, who found that phosphorus solubility at calcium concentrations less than 50 mg/l (equating to 125 mg/l hardness) was not affected by pH in the range of pH 6-9. But where there was high calcium levels (>100mg/l) appreciable amounts of phosphate precipitated as the pH was raised from 6 to 9. Diaz points out that other researchers have found that P precipitation is minimal at Ca concentrations <50 mg/l and water pH <8.0 (Ferguson *et al* 1970, 1973; Jenkins *et al*, 1971; Otsuki and Wetzel, 1972; and Feenstra and de Bryun, 1979). Ferguson *et al* reported that a Ca concentration of 80 mg/l and a water pH >8, were needed to precipitate 80% of the P in municipal wastewater (1970, 1973). And Strang and Wareham (2006) reported significant P-removal through HAP precipitation in a sewage stabilization pond with a hardness of 190 mg/l and Ca of 60 mg/l.

Based on the observations, evidence, and research it seems that a sound explanation for the lack of algae in the many West Virginia streams with naturally hard water is the precipitation of calcium and/or magnesium phosphates, which makes the phosphate unavailable in the water column for uptake by filamentous algae. This is especially true of the dolomitic streams in the southern coalfields.

Other Factors

Turbidity/Substrate

Lower gradient streams with sediment laden substrate consistently have higher levels of turbidity, even during periods of low flow, due to recurring suspension of fine sediments (Royer, 2008). Such streams do not support algae growth since light penetration is drastically reduced by the turbidity. *Cladophora,* which is the dominant type of filamentous algae in the problematic areas in West Virginia, generally begins its growth attached to a rocky substrate or other hard surface (Harris, 2005). Parts of the North Fork of Hughes River, Little Kanawha River, Kanawha River, Brush Creek, Dunkard Creek, and others would fall into this category of streams with a turbid water column and silty substrate.

Secchi tube readings from the Hughes River show variation of the water clarity at different points along the stream. Clarity varied with bottom conditions in the river, and showed no longitudinal pattern. One thing was clear, though – filamentous algae grew in the least turbid areas of the river.

Table 6. **Role of Turbidity in Algae Development West Virginia Rivers**

River	Location	Secchi Tube Depth	Algae Development
North Fork of Hughes	North Bend	114	High
North Fork of Hughes	Cairo	84	Low
North Fork of Hughes	Below Cairo	76	None
North Fork of Hughes	Near Mouth	104	Low
South Fork Hughes	Smithville	103	None
Little Kanawha	Gilmer Station	114	None
Little Kanawha	Below Glenville	96	None
Kanawha	Charleston	108 (very good day)	None
Elk	Gassaway & Mink Shoals	>120	None
South Branch Potomac	Old Fields	>120	Low-moderate
Tygart Valley River	Above Norton	>120	High
Greenbrier	Ronceverte	>>120	High

Temperature

The temperature range for *Cladophora* growth is between 15-25^oC (Harris, 2005). No significant amounts of filamentous algae were found growing in any cold water streams (maximum temperature of 20^oC) in West Virginia, although another species of filamentous algae was growing in the Davis Spring (at Fort Spring) and Trout Run (near Franklin). It was noted that as the average temperature of the Greenbrier River at Alderson slipped below 20^oC this fall, algae began dying, and the diurnal pH and DO swings lessened – even as the flow in the river continued to decrease. See graphs in Attachment 2.

Table 7. **Average Summer Temperature for Selected Streams**

Stream	Average Temperature (°C) (May –October)	Maximum Temperature (°C)
Piney Creek (mp 0)	18.6	21.2
Indian Creek (mp 26.2)	18.6	20.1
Second Creek (mp 0)	18.5	23.3
Knapps Creek (mp 0)	18.3	21.6
Opequon Creek (mp 0)	18.0	21.9
Davis Spring	13.4	14.3
Greenbrier River	21.4	26.7

Temperature and/or shade are suspected to be the key suppression factors in Piney Creek, and a secondary factor in upper Indian Creek of New River and Second Creek of Greenbrier River. (Hardness was still the primary factor in Indian and Seconds creeks.)

Non-filamentous Algae

Other forms of algae may thrive in the nutrient rich waters of streams which have suppressed filamentous algae development. Tuscarora Creek, for example, is a tributary of Opequon Creek and receives flow from the Martinsburg STP. The average hardness of Tuscarora Creek is over 300 mg/l. With no filamentous algae development in this stream, it is expected that the phosphate is precipitating out of the water onto the bottom. Excessive periphyton development noted on the rocky substrate of Tuscarora Creek (see Photo 5B) seems to support of this conclusion. Similar colonies were noted in the mainstem of Opequon Creek and less vigorous development was observed in the Coal River. The interface of the rock, phosphate salts, and water would provide the most likely site for phosphorus release/exchange during equilibrium shifts. The periphyton development has not resulted in public outcry, and was not part of the scope of this investigation of filamentous algae development. No judgment is being made in this report as to whether the periphyton colonies constitute or contribute to any water quality problem.

Measuring Filamentous Algae

Schaller (2004) and Morgan (2006) employed similar methods for measuring filamentous algae in streams during their research. At a given stream transect, a tape is stretched across the stream; wetted width and portions of the stream covered by algae are recorded. At one location along the transect where the bottom is completely covered, all algae and plant material is collected in a 314 cm^2 area. The material collected is rinsed, dried, and weighed in a laboratory, and then expressed as mass per unit area. These researchers used that value to estimate mean biomass for the stream reach.

This method was used as a basis for algae measurement in West Virginia in the fall 2008. Measurements were made on several locations on the Greenbrier River, the North Fork of Hughes River, and at one location on the South Branch of Potomac River. The measurements were done as a trial to determine the feasibility of the method; no lab work was done determine a dry weight. An additional measurement was made of the algae depth across the transect, so that amount of water column impact, not just stream bottom, could be calculated. Results are summarized in *Table 8* and shown graphically in *Attachment 1*.

Table 8. **Algae accumulation at Selected Sites.**

River and Location	Bottom Cover (%)	Water Column Fill (%)
South Branch @ Old Fields	53	3.7
North Fork Hughes at North Bend	54	60
North Fork Hughes at Cairo	23	4
Greenbrier-Hillsboro 1	40	18
Greenbrier-Hillsboro 2	53	28
Greenbrier- Caldwell	53	32
Greenbrier –Coffman Hill Rd.	80	27
Greenbrier - near Rt 62 bridge 1	41	16
Greenbrier - near Rt 62 bridge 2	85	7
Greenbrier-Ronceverte	74	50
Greenbrier- US Alderson	64	23
Greenbrier- 1 mile below Alderson	39	10
Greenbrier-Lowell	46	9

WVDEP will continue work in the summer of 2009 to develop a measurement index which might be useful to define an acceptable level of algal development that still maintains unhindered recreational uses of the stream, including fishing, swimming, and aesthetic enjoyment.

Summary of Conclusions

1. Dissolved phosphorus discharged from sewage treatment facilities along the Greenbrier River is able to combine with nitrates in the river from a variety of sources and cause objectionable algae blooms.
2. Similar, but less severe, blooms are also occurring on the Bluestone, New, Cacapon, Tygart Valley, South Fork of the South Branch of the Potomac, and North Fork of Hughes River.
3. Lack of alkalinity keeps the algae blooms from occurring on several rivers: Elk, Cherry, Little Kanawha, and upper Greenbrier. A minimum alkalinity of 30-40 mg/l is needed for filamentous algae blooms to occur.
4. Hardness, in the form of calcium and magnesium, prevents algae blooms from occurring on several other rivers: West Fork, Tug, Shenandoah, Guyandotte, Mud, and Coal Rivers. The mechanism for suppressing the algae is the precipitation of Ca-P and Mg-P salts which makes the phosphorus unavailable for uptake by the filamentous algae.
5. Hardness levels exceeding 150 mg/l appear to inhibit algae growth. Some suppression of growth may begin occurring when hardness exceeds 100 mg/l. The South Branch of Potomac River appears to have suppressed filamentous algae development.
6. Hard water rivers with elevated phosphorus tend to have enhanced periphyton development on the substrate, probably due to its ability to utilize precipitated phosphorus at the substrate interface.
7. Algae blooms on some rivers, including the Kanawha River, are inhibited by turbidity.
8. Enhanced phosphorus removal at sewage treatment facilities along the Greenbrier River should substantially reduce the algae bloom occurring in that river.

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USGS Gaging Station 03183500, Greenbrier River at Alderson, WV. Archives Website: http://waterdata.usgs.gov/nwis/monthly?referred_module=sw&site_no=03183500&por_03183500_1=1547792,00060,1,1895-08,2007-

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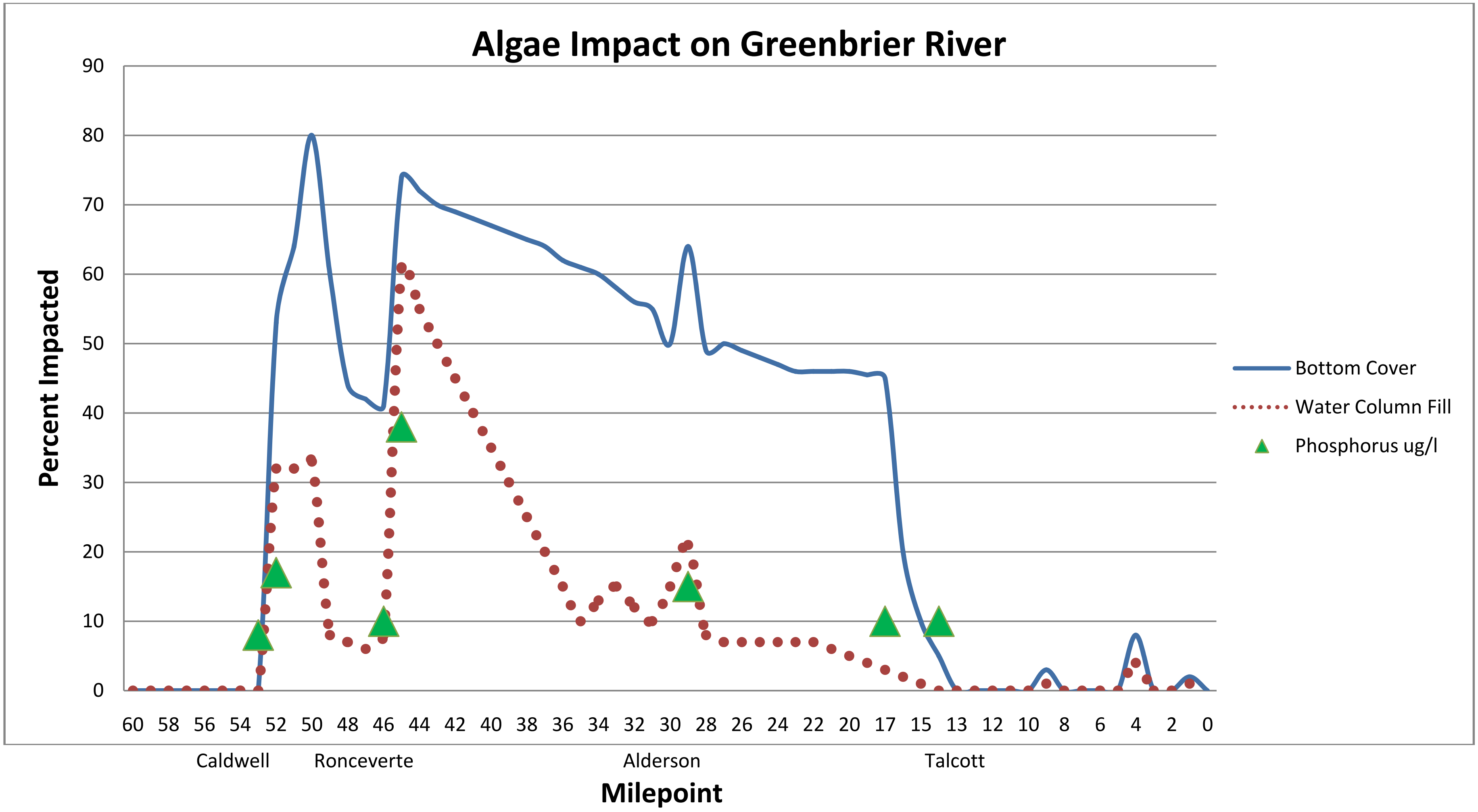
Attachment 1



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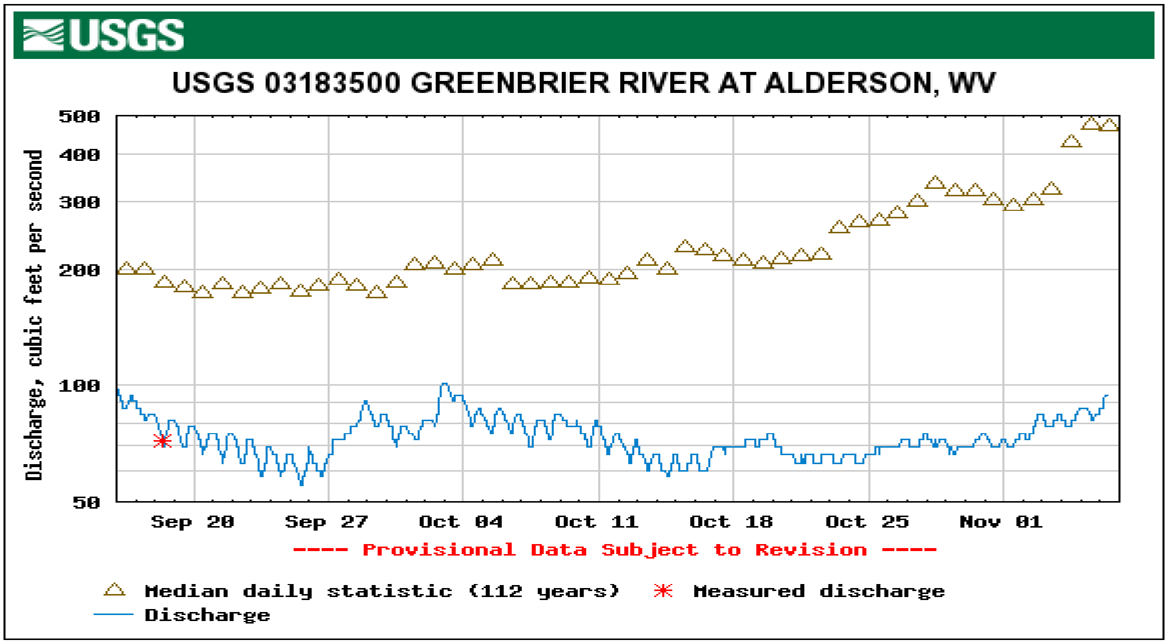

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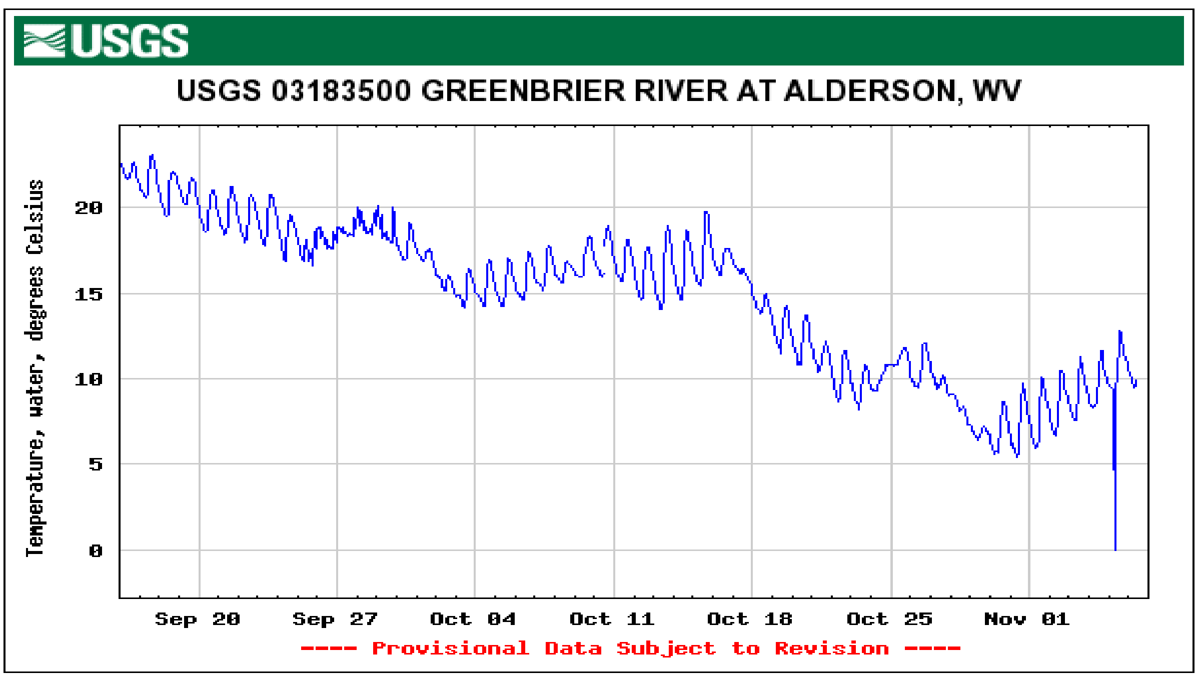

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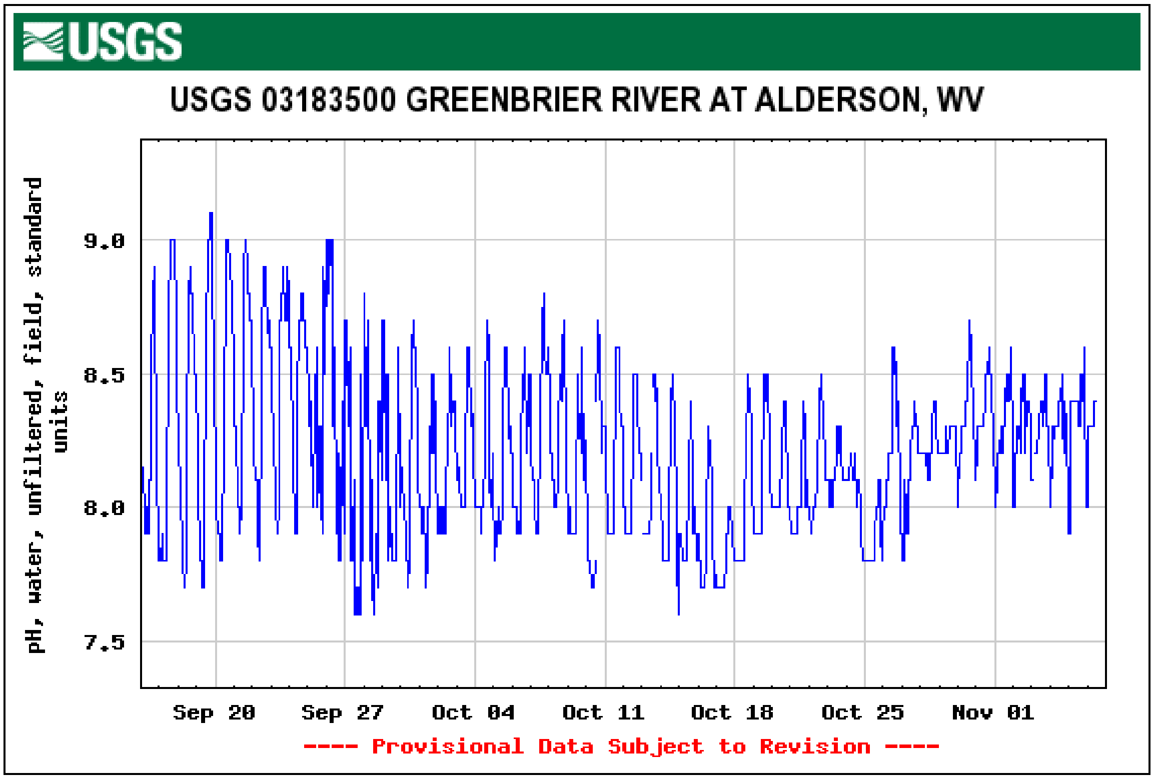

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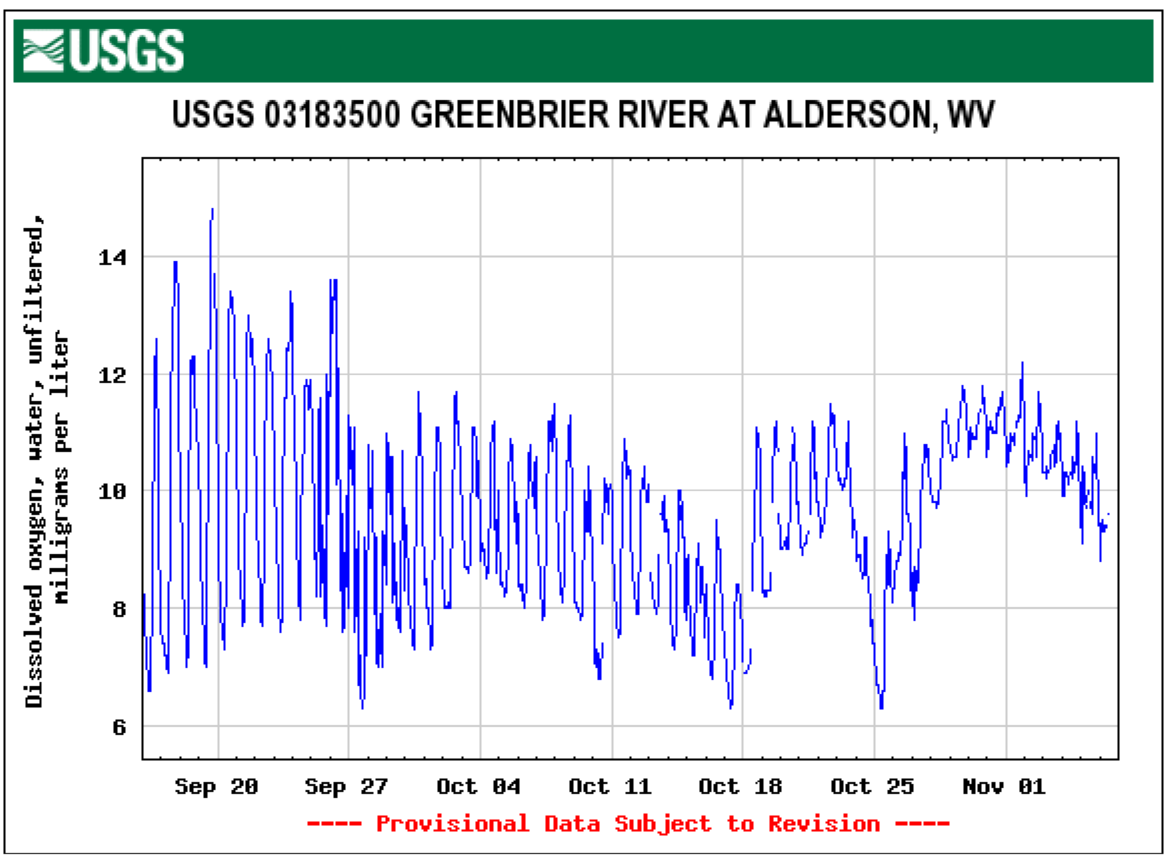
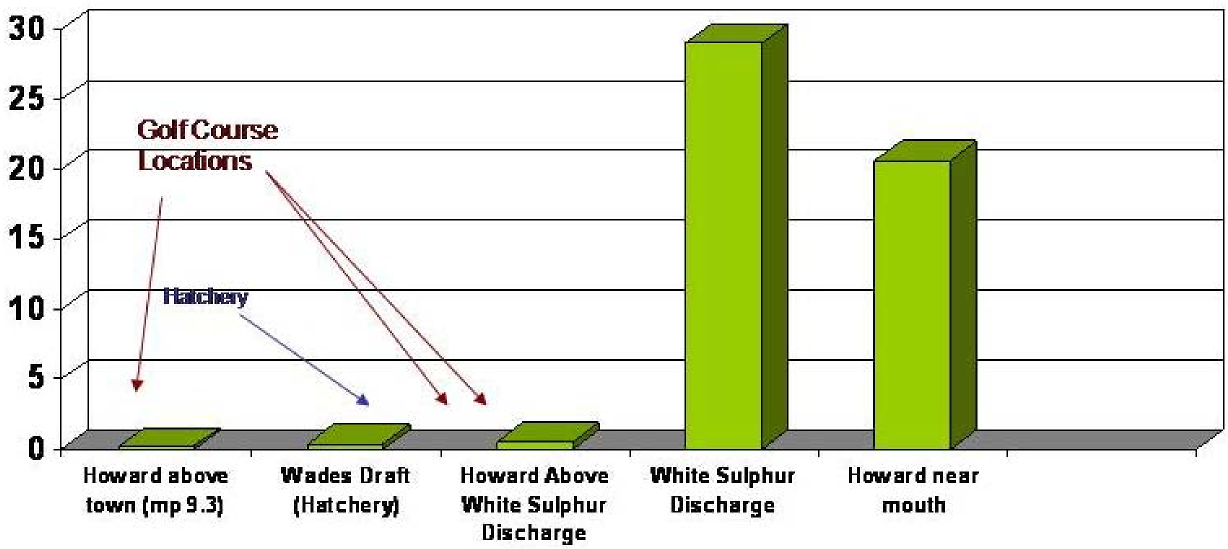


2008 Data

Attachment 3

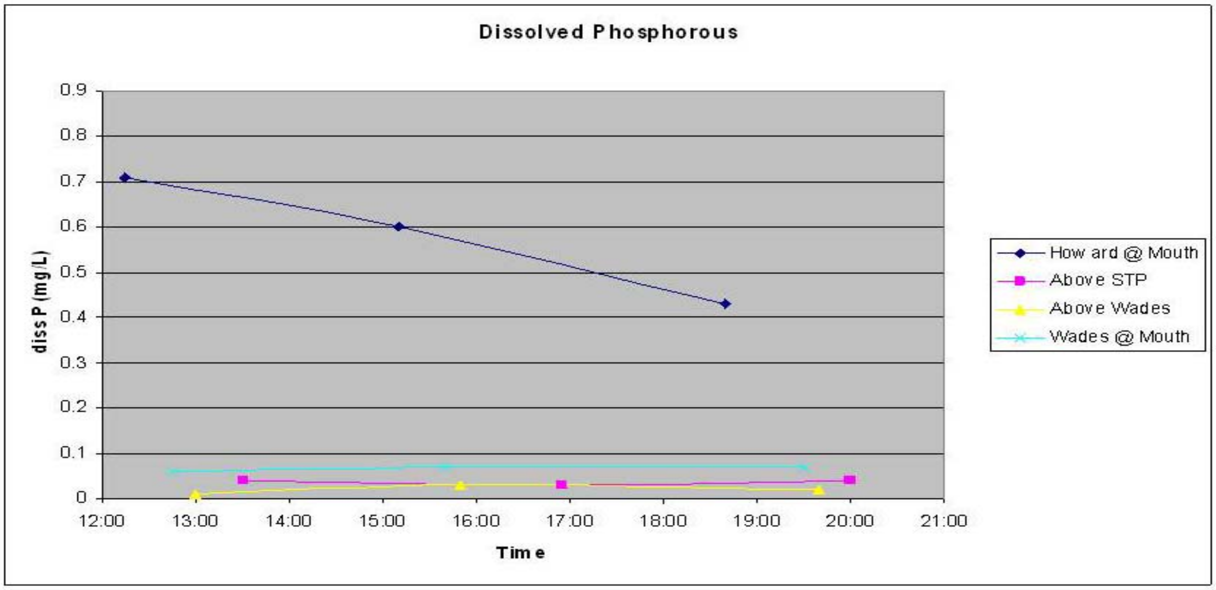
Dry Conditions Snapshot

Total Phosphorus Loading (lbs/day)



Storm Event

Phosphorus Concentrations (mg/l)
during a 2" rainfall event

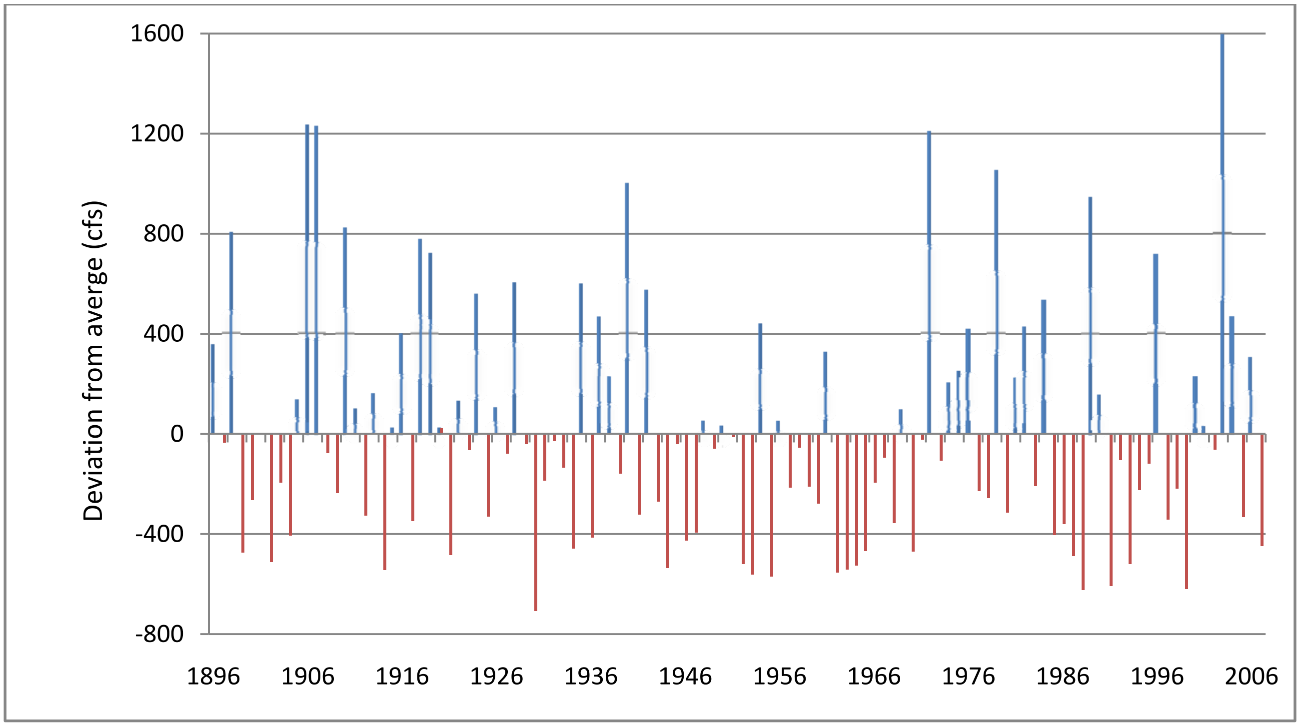


Attachment 4

Greenbrier River at Alderson

Deviation from the average summer flow, June through October, 1896-2007

(The average summer flow was 807 cfs)


1600
1200
800
400
0
-400
-800
Deviation from averge (cfs)
1896
1906
1916
1926
1936
1946
1956
1966
1976
1986
1996
2006

SDG