Determination of Water Quantity and Quality in Surface Waters of the Karst System of Jefferson County, West Virginia

Submitted by Peter Vila, Dan DiLella, and Kristen Trevey

Shepherd University, Department of Environmental Studies, Shepherdstown, WV 25443-3210

pvila@shepherd.edu

<u>Summary</u>

- 1) The purpose of this study was to assess: 1) Water quality, by measuring nutrients and other ions, and bacterial contamination, and 2) Water quantity, by measuring discharge at springs and mainstem sites in the county.
- 2) Six streams in six watersheds in the carbonate karst valley area of Jefferson County were sampled. Each stream was sampled at the mainstem prior to it flowing into the Potomac or Shenandoah Rivers and at an upstream spring site that flowed into the stream. In addition, six streams in the metamorphic Mountain area were sampled.
- 3) Seasonal means for mainstem nitrate ranged from 5 to 32mg NO₃/L and did not exceed the 10 mg/L NO₃-N water quality standard. There was little seasonal variation in nitrate concentrations within streams but there were significant differences in nitrate concentrations between sites.
- 4) Seasonal means for spring nitrate ranged from 6 to 32mg NO₃/L and did not exceed the 10 mg/l NO₃-N water quality standard. There were little seasonal differences in concentrations within each spring but there were significant differences between springs.
- 5) There was little difference between valley springs and valley mainstem concentrations. Valley spring ion levels appear to dominate mainstem baseflow concentration.
- 6) Mountain concentrations for ions were one-quarter to one-half valley ion concentrations.
- 7) Chloride valley mainstem concentrations were 15-68 mg Cl/L and higher than valley spring concentrations of 9-39 mg Cl/L indicating enrichment along the mainstem.
- 8) Load as NO₃-N for valley streams totaled 196 tons. Mountain stream load was much lower at 2 tons. 83% of the county load was from the Bullskin and Evitts Run.
- 9) Jefferson County load at baseflow was 975,502 lbs NO₃-N/yr. Jefferson County nitrogen load is approximately 43% of the total allotted estimated-on-site (EOS) from the Chesapeake Bay Model Phase I WIP. The Charlestown WWTP on Evitts Run nitrogen load is 1.4% of the total allotted EOS for the county.
- 10) Load can be significantly underestimated if stormflow is not measured. It is recommended that nutrient load be determined in wet and dry years and to sample during stormflow and baseflow conditions. In addition Total Nitogen (TN) and Total Posphorus (TP) should be analyzed.
- 11) Springs had low bacterial contamination indicating clean groundwater. However, valley mainstem sites exceeded the EPA 409 CFU/100ml 29-57% of the sampling dates. Mountain sites exceeded 4-21% of the sampling dates. A source determination study to determine the source of the bacterial contamination is recommended.
- 12) Values for physical parameters, temperature, oxygen, pH, and specific conductivity were typical for these streams and indicated a healthy system.
- 13) Turbidity ranged up to 55 NTU and measurements serves as background data for baseflow conditions. Nitrate concentrations for Evitts and Bullskin springs decreased significantly with higher discharge. It may be that nitrate concentrations are variable at low groundwater discharge due to variable mixing with surface or shallow subsurface waters. However, baseflow sampling after a significant discharge flushed any nitrate compounds and concentrations equal background groundwater nitrate levels (15-20 mg NO₃/L) at high discharge.

Introduction

The current and long term status of water quality and water quantity in Jefferson County directly impacts the 16,000 families in the county using wells and the 23 community water systems in Jefferson County that utilize groundwater. From 200 to 2010 the population of the county increased by 26.8% to 53,498; this increase with the concomitant required development will put further demands on the counties water and natural resources.

On a regional scale, the impact of increased population in the Chesapeake Bay Watershed has had significant impacts on the Chesapeake Bay. As a result, a TMDL on the Bay has resulted in the assignment of significant reductions of nutrients each state, and therefore, Jefferson County, can send to the Bay via the connecting waters. These nutrient caps (WV Phase II Draft Plan 2012) could have significant impacts on how we conduct business in the county; these impacts include changing practices on how we deal with septic system permits and upkeep, Waste Water Treatment Plants, agricultural practices, stormwater regulation, industrial facilities, and application of turf fertilizer.

The water resources in our county provide us with recreation, tourism, fishing, drinking water supplies, and wildlife habitat and thus are an invaluable asset to the county.

Due to the porous nature of the Karst geology found in much of Jefferson County, surface water can potentially connect directly to the groundwater system. Moreover, due to channels and fractures groundwater can move rapidly between wells and springs in the county, and water quality problems in one area of the county could rapidly spread and impact other areas.

The purpose of this study was to assess the water quality, by measuring nutrients and other ions, bacterial contamination, and quantity, by measuring discharge at springs and mainstem sites in the county.

<u>Methods</u>

The county was divided into two main areas based on geology: the karst valley area with six streams and six watersheds: Town Run, Rattlesnake, Elks Run, Evitts, Bullskin and Opequon, and the mountain area with six streams and three watersheds: Double Run, Forge Run, Mountain 5, Dry Lake Run, Furnace Run, and Hog Run (Fig. 1). Three watersheds were sampled in the mountain area: Hog (Hog Run site), Furnace (Dry Lake, Furnace Run, and Mountain 5 sites), Forge (Forge Run and Double Run sites). The geology in the karst area is underlain with folded and faulted carbonate rocks and the mountain area underlain with folded shale and metamorphic rocks (Kozar et al. 1991).

Each stream in the karst area was sampled at an upstream spring site and at a downstream mainstem site prior to flowing into the Potomac or Shennandoah Rivers. Streams in the mountain area were sampled in the mainstem prior to flowing into the Shenandoah River. Streams were sampled from February 2010 to April 2011.



Figure 1. Locations of the six karst (valley) watersheds and three mountain watersheds. Circles indicate locations of sampling sites. Dry Lake and Furnace Run are situated close to each other and not differentiated at this scale.

Water Quality

Chemical parameters

Two water samples were taken at each site with the final concentration reported as the average of the two concentrations. In the laboratory, samples were filtered through a 0.45um syringe filter and concentrations of nitrate, nitrite, sulfate, phosphate, fluoride and chloride were determined with ion chromatography (Dionex).

Physical parameters

Turbidity, pH, specific conductivity, dissolved oxygen (mg/l and percent saturation) and temperature were determined using a Eureka multiparameter probe. Discharge was calculated from field velocity measurements utilizing a Marsh McBirney velocity probe and field determination of stream cross section area. Discharge for the Bullskin was determined from the USGS gauge.

Discharge

Discharge was calculated every time water samples for chemical analysis were taken. Velocity was determined with a Marsh McBirney velocity meter. Stream cross-section measurements for area calculations were taken at time of velocity measurement. Evitts Spring flowed into a wide, shallow, low velocity and braided wetland that prevented determination of water velocity directly downstream of the Spring. In this case, Evitts Spring discharge was determined by subtracting the discharge of the mainstem above the inflow of Evitts Spring from the discharge of mainstem Evitts Run determined downstream of the Spring.

Bacterial sampling

Escherichia coli (E. coli) samples were taken in the water colum below the surface. Quantitative concentrations in CFU/100ml were determined utilizing the Idexx EPA approved methodology.

Frequency of sampling

Chemical and physical samples were taken monthly at all sites. Discharge was determined at the time of chemical sampling. Bacterial samples were taken monthly at the valley sites and weekly at the mountain sites.

SigmaPlot 11 was used for statistical analysis. Prior to tests or significance an equal variance test was applied. The Shapiro-Wilk test was used for test of normality. A t-test comparing means or an ANOVA utilizing Pairwise Multiple Comparison Procedures (Holm-Sidak method) was used if data were normal, or, if the equal variance test was not accepted, or, if the test for normality was not accepted, a Kruskal-Wallis One Way Analysis of Variance on Ranks (Dunn's method), or a Mann-Whitney Rank Sum Test was used to test for significance. Linear regression was used to detect significance between ion concentration and discharge.

Results and Discussion

Chemistry

Nitrite, phosphate, and fluoride concentrations were extremely low or at nondetectable levels over the sampling period and thus not discussed in this report.

Valley Mainstem Sites

Seasonal means for nitrate ranged from 5 to 32mg NO₃/l (Fig. 2, top) and did not exceed the 10 mg/l NO₃-N water quality standard (WVDEP). There was a large variation of sulfate mean values of 14-67 mg SO4/l (Fig 2. mid). West Virginia has no water quality standards for sulfate; a secondary maximum contamination level of 250 mg/L is established for taste and odor (EPA); however, high levels can cause diarrhea in some people. Chloride (Fig. 2, bot) ranged widely from 12 to 101 mg Cl/l but did not exceed the chronic West Virginia water quality standard of 230 mg Cl/l (WVDEP). Sample concentrations were similar to those found by Kozar et al. (1991).

Except for the Bullskin, there were no seasonal differences in nitrate concentrations. The Bullskin had significantly higher levels of nitrate in the winter than summer (mean of 32 and 26 mg/l, respectively). This would be expected as biological utilization of nitrate would be decreased in winter due to reduced photosynthesis and bacterial uptake at lower temperatures.



Figure 2. Seasonal means of valley mainstem chloride (Bot), sulfate (Mid), and nitrate (Top) concentrations. Mean ± standard deviation. Spring = Feb, Mar, Apr; Summer = May, Jun, Jul; Fall = Aug, Sep, Oct; Winter = Nov, Dec, Jan.

There were significant differences in the nitrate concentrations between streams (Fig. 3) and streams can be grouped into three main groups based on nitrate concentrations. Group one consists of Bullskin Run whose nitrate levels were significantly higher than all streams sampled (mean of 28.4 mg NO₃/l); group two consists of Elks Run, Evitts, and Town Run (mean of 16.7 mg NO₃/l); and group three consists of Rattlesnake Run and Opequon Creek (mean of 10.7 mg NO₃/l).



Figure 3. Mean annual mainstem nitrate concentrations for the six sampled streams. Bars with the same letters do not have significantly different nitrate concentrations. The Bullskin nitrate concentration was significantly different from all other stream nitrate concentrations. Elks, Evitts, and Town Run nitrate levels were significantly higher than Opequon nitrate levels; and Evitts was significantly higher than Rattlesnake Run. Mean ± standard deviation.

Valley Spring Sites

Nitrate concentrations found in springs were similar to those in the mainstem; they ranged from 6 to 32mg NO₃/l (Fig. 4 Top) and did not exceed the 10 mg/l NO₃-N water quality standard (WVDEP) (approximately 44 mg NO₃/L). These values were significantly higher than the highest value of 11.5 mg/L (Nitrate + nitrite) found in the groundwater of Morgan County, WV (Boughton 2006) but similar to those found by Kozar et al. (1991). However, sulfate spring levels were approximately one half concentrations in the mainstem and ranged from 2-27 mg SO4/l (Fig 4 Mid). Chloride concentrations (Fig. 4 Bot) were also approximately one half the mainstem chloride concentrations and ranged from 7 to 52 mg Cl/l. Mainstem sites have potential ion input along their length from differing land use and thus would be expected to have higher concentrations of ions than groundwater.

Evitts Run spring was the only spring that had small but significant seasonal variation in nitrate concentration; nitrate concentration in winter (mean 19.7 mg NO₃/l) was higher

than summer (mean 15.2 mg NO_3/l) and spring (mean 16.2 mg NO_3/l). The difference is not likely due to temperature differences driving biological uptake as the yearly temperature varied by only 1.1 °C, but may be due to the complexities of groundwater flow in karst systems mixing shallow subsurface waters, perched water tables, or surface runoff.



Figure 4. Seasonal means of valley spring chloride (Bot), sulfate (Mid), and nitrate (Top) concentrations. Mean ± standard deviation. Spring = Feb, Mar, Apr; Summer = May, Jun, Jul; Fall = Aug, Sep, Oct; Winter = Nov, Dec, Jan.

There were significant differences in the nitrate concentrations between springs (Fig. 5) and springs were grouped by nitrate levels. Group one consisted of the Bullskin and

Elks springs with the highest nitrate concentrations (23.2 and 28.7 mg NO₃/l); group two consisted of the Evitts, Rattlesnake, and Town Run springs with intermediate nitrate concentrations of 14-18 mg NO₃/l; The Opequon spring made up the third group with the lowest spring nitrate concentrations (mean of 7.7 mg NO₃/l). Opequon spring nitrate levels were significantly lower than other sampled springs that suggests a separate groundwater source.



Figure 5. Mean annual spring nitrate concentrations. Bars with the same letters do not have significantly different nitrate concentrations. Mean ± standard deviation.

Mountain Mainstem Sites

Mountain site nitrate concentrations were approximately one quarter valley mainstem values and means ranged from 0.1 to 8 mg NO₃/l (Fig. 6, top). With no development above the study site, Hog Run was used as a reference stream; nitrate concentrations were extremely low and ranged from 0.04-0.4 mg NO₃/l. Other streams with development in the watershed had higher and variable levels ranging to 8 mg NO₃/l (Fig. 6, top). There were significant seasonal nitrate differences in Hog run with summer concentration (mean 0.4 mg NO₃/l) higher than other seasons (0.04-0.1 mg NO₃/l). A closed canopy

during summer may inhibit photosynthetic activity and nutrient uptake relative to other months. Sulfate means ranged from 5 to 15 mg SO₄/l (Fig. 6, mid) and were approximately one quarter valley mainstem concentrations. Mean concentrations for chloride ranged from 1.5 to 39 mg Cl/l (Fig. 6, bot) and were approximately one half valley mainstem means.



Figure 6. Seasonal means of mountain stream chloride (Bot), sulfate (Mid), and nitrate (Top) concentrations.
Mean ± standard deviation. Spring = Feb, Mar, Apr; Summer = May, Jun, Jul; Fall = Aug, Sep, Oct; Winter = Nov, Dec, Jan

Comparison between Spring and Mainstem Nitrate Concentrations

While there are significant differences in nitrate concentrations between streams (Fig. 5), spring and mainstem nitrate concentrations were essentially identical (Fig. 7 and 8). Spring waters and the receiving mainstem concentrations were expected to be similar as 80-90% of mainstem streamflow is due to groundwater discharge (Hobba 1981). The only significant seasonal differences between spring and mainstem nitrate values were during the Elks Run summer and Town Run spring seasons. This provides a strong indication that nitrate values are dominated by spring input; not unexpected as streams were sampled during baseflow in which primarily groundwater inputs sustain discharge. Only two streams, Elks Run and Rattlesnake Run, have significantly different higher nitrate utilization (*e.g.*, higher primary productivity) in the mainstem of these streams. Given the essentially non-detectable concentrations of orthophosphate, it is likely that phosphorus is colimiting in valley streams. Phosphorus inputs could be higher in Elks Run and Rattlesnake Run, reducing nitrate until phosphorus levels become limiting.



Figure 7. Comparisons of seasonal nitrate levels between mainstem and springs. Mean ± standard deviation. Spring = Feb, Mar, Apr; Summer = May, Jun, Jul; Fall = Aug, Sep, Oct; Winter = Nov, Dec, Jan.



Figure 8. Comparisons of yearly average nitrate levels between mainstem and spring sites. A star indicates significantly different means. Mean ± standard deviation.

Chloride

While chloride is an essential solute, it is commonly found in concentrations that exceed biological need and is treated as a conservative element (Triska et al. 1989). Downstream increase indicates additional inputs along the stream channel rather than differential biological uptake, storage, and release as seen for biologically active nutrients such as nitrate and phosphorus that are important for primary productivity.

Mainstem chloride concentrations ranged from 15 to 68 mg Cl/L (Figs. 9, 10), and were, in general, higher than the range of chloride concentrations in springs (9-39 mg Cl/L) (Figs. 9, 11). The highest levels occurred during fall and winter (Fig. 9) most likely due to input of road salt. Other inputs of chloride are septic and agricultural from organic applications (Hobba 1991). There were significant differences in chloride concentrations between mainstem sites and between spring sites, but the pattern was different. In the mainstem sites, Opequon, Elks and Evitts chloride levels were similar to each other and were significantly higher than chloride levels in other streams (Fig. 10). In the spring sites, Elks and Town Run were similar and significantly higher than other streams; the spring Elks and Town Run spring chloride levels were also significantly higher than chloride levels found in their respective mainstem (Fig. 12), thus, other springs feeding these streams are likely lower in chloride diluting concentrations in the mainstem. Source groundwater for these streams may be different or higher chloride shallow subsurface waters (due to surface activities or septic input) may be mixing with the groundwater prior to surfacing. Streams with waste water treatment plants (WWTP), Evitts Run and Opequon Creek, had significantly higher chloride levels in the mainstem sites (Fig. 12). Bullskin mainstem chloride levels were also significantly higher than spring levels indicating surface input.



Figure 9. Seasonal means for valley mainstem and spring chloride concentrations. Mean ± standard deviation. Note larger axis scale for Fall and Winter. Spring = Feb, Mar, Apr; Summer = May, Jun, Jul; Fall = Aug, Sep, Oct; Winter = Nov, Dec, Jan.



Figure 10. Mean annual mainstem chloride concentrations. Bars with the same letters do not have significantly different nitrate concentrations. Mean \pm standard deviation.



Figure 11. Mean annual spring chloride concentrations. Bars with the same letters do not have significantly different nitrate concentrations. Mean \pm standard deviation.



Figure 12. Year mean chloride levels between mainstem and spring sites. A star indicates significantly different means. Mean ± standard deviation.

Nitrogen Load Estimates

Monthly load, or the quantity of material (*e.g.*, lbs) carried in the stream per month, was calculated by applying the discharge and concentration values determined at each monthly sampling to the entire month. This will underestimate load as does not account for stormflow events (see below).

Total yearly nitrate (NO₃-N) load for the five valley streams was 196 tons (Fig. 13 Top) (Opequon Creek was not included in load calculations as it does not flow inside Jefferson County). Two streams, Bullskin and Evitts dominated the load (83%) with 66 and 97 NO₃-N tons/year, respectively; the other three streams had much lower values ranging from 6 to 15 NO₃-N tons/yr.

Total nitrate load for streams in the mountain area was much lower at 2 NO₃-N tons/yr (Fig. 13 Bot). The reference stream Hog Run load was very low at 0.08 NO₃-N tons/yr, approximately four times lower than other Mountain streams that had loads ranging from 0.3 to 0.5 NO₃-N tons/yr.



Figure 13. Individual and total nitrogen load for valley (Top) and mountain (Bot) streams.

The 14 tons of nitrogen contributed by the Charlestown WWTP is approximately 21% of the 66 tons contributed at baseflow by Evitts Run (Fig. 14) and approximately seven percent of the load in the five streams sampled. The total nitrogen reported by the

Charlestown WWTP includes organic nitrogen, ammonium, nitrate, and nitrite; in this study total nitrogen reported was determined from nitrate levels, thus, this study may have underestimated total nitrogen. However, nitrate is the dominant form of nitrogen in natural waters not impacted by sewage outflow.

While TN values from the Charlestown WWTP were low, monthly load exceeded Evitts Run total nitrogen load, especially during winter months when biological activity at the WWTP was low (Fig. 15). Changes in monthly TN load at the Charlestown WWTP were due to changes in concentration (Fig. 16) as discharge remained relatively constant at 0.9 to 1.5 Mgal/day (million gallons per day). Evitts Run maintained a relatively constant nitrate concentration, but varied widely in discharge (Fig. 17). Thus, the seasonal discharge curve (Fig. 17) is similar to the monthly TN load (Fig. 15).



Figure 14. Total load for Mountain and Valley streams relative to load for Evitts Run and the Waste Water Treatment Plant on Evitts Run. WWTP load is expressed in TN as reported to the EPA; all other loads expressed as NO₃-N. Numbers above each bar indicate the total nitrogen load in tons.



Figure 15. Evitts Run and Charlestown WWTP monthly total nitrogen values.



Figure 16. Charlestown WWTP monthly TN concentration. Dashed line marks the yearly average concentration.



Figure 17. Evitts Run discharge over the sampling period. The two parallel straight lines below the plot of Evitts Run discharge indicate the limits of the WWTP variable discharge of 0.9 to 1.5 Mgal/day (approximately 1.4 to 2.3 CFS).

Total load for the county was determined by applying the average load per acre for the sampled valley watersheds (8.2 NO₃-N lbs/acre) and sampled mountain watersheds (0.3 NO₃-N lbs/acre) to their respective non-sampled areas and summing the total. Load for the karst valley area was estimated to be 970,688 lbs NO₃-N/yr and 4,814 lbs NO₃-N/yr for the mountain area, totaling 975,502 lbs NO₃-N/yr (Fig. 18). This results in an annual load of 7.2 lbs/acre per year for Jefferson County.

Jefferson County nitrogen load is approximately 43% of the total allotted estimatedon-site (EOS) from the Chesapeake Bay Model Phase I WIP (WVCA). Even though reducing the Charleston WWTP nitrogen concentrations to Chesapeake Bay target total nitrogen concentrations for WWTP's of 5 mg/l (average during this study was approximately 12 mg TN/l), reducing to these levels or even removing all nitrogen from the WWTP outflow would do little to reduce the Jefferson County nitrogen load as it comprises only 1.4% of the total allotted EOS for the county. Reductions of nutrient loads at WWTP's are only part of the solution to reduce total load. The mean annual yield for the valley watersheds ranged from approximately 3-14 NO₃-N lbs/yr/acre (Fig. 17a); yields of Evitts Run and Bullskin Run watersheds were approximately 2-3 times greater than those of other watersheds.



Figure 17a. Mean annual yield (mean annual load/watershed area) of NO₃-N for valley watersheds.



Jefferson

Figure 18. Total nitrogen load determined for Jefferson County. Also plotted is the Charlestown WWTP nitrogen load and the estimated-on-site (EOS) allotted to Jefferson County from the Phase I implementation WIP (Watershed Improvement Plan).

Stormflow

Stormflow is the water that enters a stream after a precipitation event that results in a relatively fast rise of the water in the stream channel. Overland flow, or the water that exceeds the infiltration rate at a site, is a major component to stormflow and is important to nutrient and other contaminant load as it entrains any material on the land surface and carries it directly into the stream channel. Shallow subsurface stormflow or saturation overland flow also contributes to the stormflow. Baseflow is the water in the stream channel that results from groundwater or from shallow subsurface flow that slowly moves to the stream channel; it is also called dry weather flow as it is the water that enters the stream channel during dry weather periods.

This study determined discharge and sampled nutrient concentrations during baseflow conditions and did not sample stormflow conditions. Specialized equipment that triggers on rising water in the channel and subsequently retrieves samples during the rise and fall of the hydrograph are needed for this type of work. However, load can be significantly underestimated if nutrients carried at stormflow are not evaluated. Much of the load carried by a stream is carried during periods of the rise of water in the channel, or during stormflow. For example, the percent of total baseflow yield to total flow nitrate yield for streams in the Chesapeake Basin can be as low as 14% (Bachman et al. 1998) (the range is up to approximately 80%) indicating that nitrate loads can be underestimated by up to 86%. Stormflow can also be important in forested catchments where 73% of the total nitrogen was carried by surface runoff during stormflow events (Bhat et al. 2006). Even a single or a few large storm events may account for substantial proportions of annual loads load and can deliver up to 73% of annual load (McHale and Phillips 2002; Longabucco and Rafferty 1998).

Modeling approaches to estimate load (Bachman et. al. 1998; Langland et al. 2004; Hirsch et al. 2010) may not produce accurate estimates for small scale watersheds such as those in Jefferson County. Local practices may have a dramatic impact on nutrient and sediment concentrations and these concentrations levels need to be determined not estimated. Moreover, it is determination at local levels that will serve as input to models and serve to refine model parameters. The assessment of whether a BMP (Best Management Practice) is having an affect in reducing loads can only be determined by actual assessment. This study provides background levels in order to set targets for reduction. Load determination evaluates the quantity and while it may provide an indication, it does not provide the definitive answer for the specific sources and transport mechanisms to the stream. Moreover, BMP's and assessments to reduce load from watersheds may take years before results are observed as there may be lag periods in system response.

Bacteria

E. coli is a microorganism that lives in the gastrointestinal tract of almost all warmblooded animals. *E. coli* can be found in all human waste and makes up about 90 to 100% of the coliform organisms in human and animal feces. Principal sources of *E. coli* (and other fecal coliform bacteria as well as pathogens) are wastewaters from sewage plants, septic systems, runoff from agricultural feedlots and fields, food processing plants, and stormwater runoff, which carries animal and bird (domestic and wildlife) fecal material.

The EPA standard for the maximum *E. coli* concentration in a single sample for a designated bathing beach is 235 cfu/100ml; 298 cfu/100ml for moderately used waters with full body contact; 409 cfu/100ml for lightly used waters with full body contact; and 575 cfu/100ml for infrequently used waters with full body contact. 409 cfu/100 ml was used as the criteria for this study.

Valley springs had very low bacterial contamination; the 409 CFU/100ml criteria was exceeded only once each in two springs (Fig. 19) over the sampling period. The sporadic contamination was likely due to mice or other rodents in the vicinity at the time of sampling.



Figure 19. *E. coli* levels at Valley spring sites over the 14 sampling dates. The dashed line marks the EPA 409 CFU/100ml criteria for lightly used waters with full body contact. The upper dashed line marks the 2419 limit for the method; *E. coli* levels were likely to be higher but were not determined. Note the break in the axis.

Valley mainstem sites had much higher bacterial levels with 29-57% of the sampling dates exceeding the EPA 409 CFU/100ml (Fig. 20). This indicates widespread *E. coli* bacterial contamination of surface waters of Jefferson County. Since groundwater have relatively low bacterial contamination, it appears that surface water bacterial levels are due to input from shallow subsurface and overland flow. Other surface constituents would also be carried into the mainstem through this pathway and may be correlated with sources for bacterial contamination.



Figure 20. *E. coli* levels at Valley mainstem sites over the 14 sampling dates. The dashed line marks the EPA 409 CFU/100ml criteria for lightly used waters with full body contact. Numbers below the site name indicate the percentage of samples that exceeded the 409 CFU/100 ml criteria. The upper dashed line marks the 2419 limit for the method; *E. coli* levels were likely to be higher but were not determined. Note the break in the axis.

Bacterial levels at the mountain sites were lower than those at the Valley mainstem sites with only 4-21% of the 52 dates sampling exceeding the EPA 409 CFU/100 ml criteria (Fig. 21).



Figure 21. *E. coli* levels at mountain sites. The dashed line marks the EPA 409 CFU/100ml criteria for lightly used waters with full body contact. Numbers below the site name indicate the percentage of samples that exceeded the 409 CFU/100 ml criteria. The upper dashed line marks the 2419 limit for the method; *E. coli* levels were likely to be higher but were not determined. Note the break in the axis.

Three main sources for bacterial contamination are septic, agricultural runoff, and concentrated populations of wildlife. A source determination study is needed in order to determine the origin of the bacterial contamination. In a first step towards restoring Jefferson County surface water quality, we suggest to monitor bacterial contamination and to identify potential sources for bacterial contamination in two highly contaminated streams in Jefferson County: Bullskin Run and Evitt's Run. The Bullskin is a largely rural stream and Evitt's Run is a more urban stream that passes through the Charles Town municipality. Effective management of non-point source inputs requires a better understanding of the sources in order to make effective recommendations. Once non-point sources of contamination are determined we would be able to communicate and recommend specific reduction BMP's (Best Management Practices); for example, riparian fencing for agricultural inputs and septic pumping or upgrades for human bacterial sources.

Physical Parameters

Temperature

Temperature (Fig. 22) for all streams ranged from approximately 0-27 °C. There was little variation (approximately 3 °C) between streams in mountain streams with a higher variation (approximately 6 °C) between valley mainstem streams. Temperature in springs over the sampling period (Fig. 22 Mid) varied a maximum of 3.5 °C in Elks Run and a minimum of 0.1 °C and 0.6 °C in the Bullskin and Opequon; other springs varied 1.3-2.2 °C.



Figure 22. Temperature for valley streams (Bot) valley springs (Mid) and Mountain streams (Top).

Oxygen

Oxygen levels in all streams and springs (Fig. 23) were sufficient for aquatic life. Oxygen concentrations in mountain streams ranged from 3.5-14.7 mg/L and appeared to be controlled more by physical factors than biological photosynthetic input. Mountain oxygen levels are inversely correlated with temperature (Fig. 22 Top). Temperature and gas solubility are inversely related; colder water can hold higher concentrations of a gas than warmer water. Mountain streams have low discharge (see Fig. 28), thus, low thermal inertia, and flow will respond faster to hot summer ambient air temperature fluctuations. Valley mainstem streams with higher discharge and thermal inertia do not respond as quickly to and lag behind ambient air temperature. Moreover, the valley mainstem streams have an open canopy in many areas and the increased sunlight results in increased photosynthetic output and high oxygen levels (approximately 6-18 mg/L).

Spring oxygen levels (Fig. 23 Mid) are much lower and range from 4-9 mg/L. Springs typically have low oxygen concentrations due to groundwater bacterial respiration.

Percent oxygen saturation is the percent of oxygen in the water compared to the maximum that could be dissolved in the water at that temperature. Values for valley mainstem sites and Mountain sites range from approximately 45-150 percent saturation (Fig. 24 Bot and Top) with most values 90-100. Supersaturation, or values above 100%, usually indicates photosynthetic activity. Spring sites are lower at 36-95 percent saturation, and reflect the reduced levels of oxygen due to respiration.



Figure 23. Oxygen levels in valley mainstem streams (Bot), valley springs (Mid) and Mountain streams (Top).



Figure 24. Percent oxygen saturation in valley mainstem streams (Bot), valley springs (Mid) and Mountain streams (Top).

Specific Conductivity

Specific conductance measures the ability of the water to conduct electricity and is related to the concentration of ions; the higher the concentration of dissolved substances in the water, the higher the specific conductance. Karst streams are typically dominated by bicarbonate ions due to the underlying calcium carbonate bedrock. Specific conductivity can decrease after dilution from rain typically very low in ionic concentration or it can increase by concentrating ions from evaporation, or an input from surface runoff, such as road salt.

Specific conductance values for valley mainstem sites (Fig. 25 Bot) were approximately equal to those at spring sites (Fig. 25 Mid). Within the valley mainstem streams, specific conductance was approximately equal for all sites (approximately 500 μ S) at the start of sampling, increased to approximately 650 uS by December as discharge decreased, most likely due to concentration by evaporation at low flow drought conditions and high temperature, and remained at that level as discharge increased in January. Levels at the Opequon site were higher, most likely due to input from the upstream Martinsburg WWTP. Evitts mainstem specific conductivity was also higher and variable than other streams, most likely due to input from the upstream Charlestown WWTP.

Although there was some variability, each spring site maintained a slight but distinct trajectory over the sampling period. This could indicate a different water groundwater source.

Mountain stream specific conductance was approximately one half those at valley sites (Fig. 25 Top). Values for reference Hog Run are every low and range from 6 to 90 μ S. This is typical given the metamorphosed rocks underlying the area (McCoy et al. 2005). Other sites maintain relatively distinct but higher trajectories (up to 360 μ S) over the sampling period. Nitrate, sulfate, and chloride concentrations increase in all these developed watersheds (Fig. 6) indicating a likely shallow subsurface input from anthropogenic sources.



Figure 25. Specific conductivity for valley mainstem streams (Bot), valley springs (Mid), and Mountain streams (Top).

pH for valley and Mountain streams (Fig. 26 Top and Bot) ranged from 7.5-8 and were typical of values in streams underlying carbonate bedrock (for valley streams). pH for Hog Run is lower and reflects the low buffering capacity as indicated by the low specific conductance values. Spring pH values (Fig. 26 Mid) are slightly lower and typically circumneutral and reflect the decrease from respiration in groundwater.



Figure 26. pH at valley mainstem (Top), valley springs (Mid) and Mountain streams.

Turbidity

Turbidity is the amount of suspended particles in water and is measured in Nephelometric Turbidity Units (NTU). Typical standards for drinking water are 0-5 NTU (EPA National Primary Drinking Water Standards); water around 10 NTU is slightly cloudy and waters with approximately 40 NTU are noticeably cloudy. In West Virginia the standard stipulates that activities cannot increase the background NTU by 10 NTU's when the background is 50 NTU or less, or, if the background is more than 50 NTU, increase turbidity by more than 10% (plus 10 NTU minimum).

Values for turbidity determined in this study serve as background level turbidity levels for surface streams at baseflow conditions. While not measured in this study, observations at high waters due to overland flow result in high amounts of suspended material and should be measured. Turbidity in valley streams Fig. 27 Bot) was variable and ranged to 55 NTU. Turbidity in valley springs (Fig. 27 Mid) ranged up to 25 NTU; those high values are likely due to localized disturbance as low NTU values in springs indicate very clear waters. Likewise, streams in the Mountain at baseflow conditions are clear with NTU values ranging up to 35 NTU (Fig. 27 Top). Low NTU values for Hog Run (0-4 NTU) indicate the importance of a riparian zone to reduce sediment and other materials from entering the stream.



Figure 27. Turbidity at valley mainstem (Top), valley springs (Mid) and Mountain streams.

Discharge

The study period included a dry period in which discharge for streams decreased from initial high flows at the start of the study in Feb 2010 to low flows during Jul to Feb with an increase after February. In Valley streams (Fig. 28 Bot), discharge for all streams decreased from 10-50 CFS to 0.2-9 CFS during the low flow period and then increased to 6-22 by early 2011. Discharge at Mountain streams (Fig. 28 Top) also followed this pattern (although with much lower discharge overall) with initial levels of 0.5-6 CFS at the start of the study, decreasing to 0.1-0.5 CFS during the low flow period, with an increase to 3.5-25 CFS at the end of the study. The relatively April high flow at Hog run is likely due to a localized rainfall; this rainfall exceeded the capacity of the culvert and water flooded the road. Groundwater discharge also declined during the low flow period at the valley springs (Fig. 28 Mid).



Figure. 28. Discharge for sampled streams over the sampling period; Mountain streams (top), Valley springs (mid), and Valley mainstem streams.

Discharge and Ion Concentration

A correlation between chloride concentrations in valley springs and discharge separated sites into two main groups (Fig. 29). The first group of Town Run and Elks Run had large differences in chloride concentrations with little change in discharge. Since either low or high discharge could contain high chloride concentrations, it is likely that groundwater from these springs mixed with chloride input from variable subsurface or surface overland waters. The second group of Evitts, Rattlesnake, Bullskin, and Opequon, had very little difference in chloride concentration over the range of discharge sampled. This indicates that groundwater discharge was in equilibrium with the subsurface lithology and soils and that there were no additional local and variable chloride inputs as the groundwater surfaced. A similar pattern and grouping exists for valley mainstem chloride concentrations (Fig. 30) over a much larger range of discharge. However, Town Run, which varied little over the range of discharge in the spring site, had background chloride levels of approximately 17 mg/L chloride at 50 CFS (Fig. 30). It is likely that sampling took place after significant surface chloride deposition or higher content subsurface waters had been removed and flushed downstream.



Figure 29. Relationship between valley spring chloride concentrations to discharge.



Figure 30. Relationship between valley mainstem chloride concentrations to discharge.

There was a significant decrease of specific conductivity as discharge increased for valley spring sites (Fig. 31) and for valley mainstem sites (Fig. 32). This indicates a dilution of ions at higher flows and was probably due to sampling at baseflow conditions after flushing of compounds from surface and subsurface features.

There were no correlations of nitrate with discharge for all valley spring samples (Fig. 33) or for all valley mainstem samples (Fig. 34). However, nitrate concentrations for Evitts (Fig. 35) and Bullskin (Fig. 36) springs decreased significantly with higher discharge. It may be that nitrate concentrations are variable at low groundwater discharge due to variable mixing with surface or shallow subsurface waters. However, baseflow sampling after a significant discharge flushed any nitrate compounds and concentrations equal background groundwater nitrate levels (15-20 mg NO₃/L) at high discharge.

In contrast to Evitts and Bullskin springs, nitrate concentrations for valley mainstem Evitts and mainstem Bullskin did not vary with discharge; this is most likely due to the stream constantly receiving nitrate input from different sources along its length and thus increasing the probability of variable nitrate input at high and at low discharge.



Figure 31. Relationship between specific conductivity and discharge for valley spring sites.



Figure 32. Relationship between specific conductivity and discharge for valley mainstem sites.



Figure 33. Relationship between nitrate and discharge for valley spring sites. The relationship was not significant.



Figure 34. Relationship between nitrate and discharge for valley mainstem sites. The relationship was not significant.



Figure 35. Relationship between nitrate and discharge for valley Evitts spring site.



Figure 36. Relationship between nitrate and discharge for valley Bullskin spring site.

Monitoring

Monitoring the surface and groundwater provides the data necessary to make rational decisions for our present and future water needs. The Chesapeake Bay TMDL has set caps on nutrient export. Monitoring provides us with important information and benefits.

- It provides knowledge of the baseline data for water quantity, nutrient concentrations and load. Given the large extent of the Bay watershed, models were used to allocate target loads. The county should know actual not predicted loads and any decision on how to reduce loads should be based on actual, not modeled data.
- 2) Monitoring provides the means to evaluate and assess any implemented BMP to reduce local nutrient load. Faced with potentially costly nutrient allocation, we should implement only those BMP's that are effective. The prescription to solving problems at a small watershed scale will be site specific, locally implemented and locally assessed.
- Data collected on a small watershed scale can be used to refine general model predictions.
- 4) Participation in a regional effort to reduce nutrient loads acknowledges our shared commitment with other communities, especially those near the Bay and those who depend upon the Bay economically. This acknowledges the economic catastrophe that a polluted bay causes for Chesapeake Bay local communities and that we have a role in the solution. Jefferson County desires clean and healthy aquatic systems precisely for the same reasons. Clean water is an attraction for development and business in addition to providing for recreation, tourism, fishing, drinking water supplies, and wildlife habitat.
- 5) By monitoring we provide opportunities to bring in grant resources and cooperation and advisement with other entities state, federal, or private.
- 6) Monitoring provides us with the local knowledge to create solutions, innovations and business opportunities for nutrient reduction and resource management. These include application of waste processing techniques that reduce impact of septic systems or septic pumping.

Acknowledgments

We gratefully acknowledge funding from the West Virginia Department of Human and Health services that funded the chemical and bacterial analysis for Valley streams and Valley springs and for two Mountain streams. This grant was awarded to Jefferson County by the West Virginia Human and Health Services as a result of the efforts of the Jefferson County Watershed Advisory Committee.

We gratefully acknowledge the Jefferson County Commission for funding of weekly bacterial sampling in the Mountain streams at four stream sites.

We also gratefully acknowledge the volunteer services of Dr. Peter Vila and Dr. Dan DiLella for their time and effort in planning the study, collecting samples, analyzing laboratory data, presenting results, and writing the report. In addition, the authors provided additional field work and chemical sampling for four streams in the Mountain region; this was an unfunded volunteer contribution.

We thank the School of Natural Sciences and Mathematics at Shepherd University for providing laboratory space and support.

We gratefully acknowledge the assistance of many field hands, in particular, Kyle Crapster, Cara Schildtknecht, and Joe Freeman. These hard working individuals labored through hot and cold conditions with a cheery disposition and keen interest in environmental stewardship.

References

- Bachman, L. J., B. Lindsey, J. Brakebill, and D. S. Powars. 1998. Ground-Water Discharge and Base-Flow Nitrate Loads of Nontidal Streams, and Their Relation to a Hydrogeomorphic Classification of the Chesapeake Bay Watershed, Middle Atlantic Coast. Water-Resources Investigations Report 98-4059.
- Bhat, S. K. Hatfield, J. M. Jacobs, R. Lowrance and R. Williams. 2007. Surface runoff contribution of nitrogen during storm events in a forested watershed. Biogeochemistry 85:253-262.
- Boughton, C.J., and McCoy, K.J., 2006, Hydrogeology, aquifer geochemistry, and ground-water quality in Morgan County, West Virginia: U.S. Geological Survey Scientific Investigations Report 2006–5198, 56 p.
- Charles J. Patton and Jennifer R. Kryskalla. 2003. Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Evaluation of Alkaline Persulfate Digestion as an Alternative to Kjeldahl Digestion for Determination of Total and Dissolved Nitrogen and Phosphorus in Water. U.S. Geological Survey Water-Resources Investigations Report 03–4174.
- EPA. National Drinking Water Standards. http://water.epa.gov/drink/contaminants/index.cfm
- EPA. National Secondary Drinking Water Regulations. http://water.epa.gov/drink/contaminants/index.cfm#SecondaryList.
- Hirsch, Robert M., Douglas L. Moyer, and Stacey A. Archfield, 2010. Weighted Regressions on Time, Discharge, and Season (WRTDS), With an Application to Chesapeake Bay River Inputs. *Journal of the American Water Resources Association* (JAWRA) 46(5):857-880.
- Hobba, W.A., Jr., 1981, Ground-water hydrology of Jefferson County, West Virginia: West Virginia Geological Survey Environmental Geology Bulletin 16, 21 p.
- Langland, M.J., Phillips, S.W., Raffensperger, J.P., and Moyer, D.L., 2004, Changes in streamflow and water quality in selected nontidal sites in the Chesapeake Bay Basin, 1985-2003: U.S. Geological Survey Scientific Investigations Report 2004-5259, 50 p.
- Longabucco, Patricia and Rafferty, M.R., 1998, Analysis of material loading to Cannonsville Reservoir—advantages of event-based sampling: Journal of Lake and Reservoir Management, v. 14, p.197-212.

- McCoy, J.K., M.H. Podwysocki, E.A. Crider, and D.J. Weary. 2005. Fracture Trace Map and Single-Well Aquifer Test Results in a Carbonate Aquifer in Jefferson County, West Virginia. U.S. Geological Survey Open-File Report 2005-1407. Online Only - Version 1.0.
- McHale, M. R. and Patrick J. Phillips. 2002. Stream-Water Chemistry, Nutrients, and Pesticides in Town Brook, a Headwater Stream of the Cannonsville Reservoir Watershed, Delaware County, New York, 1999. U.S. Geological Survey Water-Resources Investigations Report 01-4050
- Kozar, M. D. W. A. Hobba, Jr. and J. A. Macy. 1991. Geohydrogeology, water availability, and water quality of Jefferson County, with emphasis on the carbonate area. U.S. Geological Survey Water-Resources Investigations Report 90-4118
- Schill, W.B. and M.V. Mathes. 2008. Real-time PCR detection and quantification of nine potential sources of fecal contamination by analysis of mitochondrial cytochrome b targets. Environ. Sci. Technol. 42:5229-5234
- Triska, F.J., V.C Kennedy, R.J. Avanzino, G.W. Zellweger, and K.E. Bencala. 1989. Retention and transport of nutrients in a third-order stream in northwestern California: Hyporheic processes. Ecology 70:1893-1905.
- WV Phase II Draft Plan. 2012. <u>http://www.wvca.us/bay/files/bay_tmdl_documents/67_WV_WIP_Draft_Phase_II_for_Public_Comment_01172012.pdf</u>)
- WVCA. 2012. http://www.wvca.us/bay/index.cfm.