Monitoring the water chemistry of the Upper Susquehanna River in Otsego County, New York, June - October 2009

Zsuzsanna Balogh-Brunstad

INTRODUCTION

The Susquehanna River is a significant contributor to the water budget and the water quality of the Chesapeake Bay Estuary. The river flows from Otsego Lake in Cooperstown, NY to the Chesapeake Bay and travels 444 miles through three different states, New York, Pennsylvania, and Maryland (Zurmuhlen 2006). It provides water for agriculture, industry, municipality consumption, recreation and it is a vital part of the surrounding ecosystems. These various applications of the river system could potentially introduce contamination that would affect both human and the ecosystem. Surface runoff from surrounding farms and urban areas, leaky septic systems, and wastewater treatment plant discharges could contribute to increased metal, nutrient and emerging contaminant (such as pesticides, herbicides, pharmaceuticals) concentrations (Focazio et al. 2008, Goodale et al., 2009). Most common pollutants are nitrogen and phosphorus compounds in the Susquehanna River (Reed 2008). It is important to continue a monitoring effort of the water quality in the Upper Susquehanna watershed to be able to detect changes due to human activity, such as land use changes caused by farming, industry, or recreation. In addition, the EPA has specified total maximum annual loads for nitrogen, phosphorous and land-based sediment measured at the New York/Pennsylvania boarder which New York State must comply with by 2011 in order to improve the water quality of the Chesapeake Bay. The goal of our study was to monitor the water chemistry of a 60 km stretch of the Susquehanna River between Cooperstown and Unadilla, NY. We selected 14 sites (Figure 1), 11 of them are sites that were monitored during 2008 summer by Reed (2008) to continue building a long term data base. Field and laboratory based approaches were applied to measure and analyze for various parameters that can determine water quality and locate any problems, allowing for the development of more effective management strategies.

METHODS

Ten sites out of 14 along the Susquehanna River were sampled between 8 June and 3 August 2009 every other week (5 times) and four additional sites were added at end of August. All 14 sites were sampled three times, at end of August, September and October. Sampling efforts will continue through the winter and spring months to evaluate seasonal variations. The site locations and descriptions are found in Table 1 and illustrated on Figure 1. The sites were selected based on the work of Reed (2008) and SR1, SR2 and SR12 were added for better coverage of the river basin, but only the main river water was sampled due to financial and time constrains. Many sites are located just below the confluences with the tributary streams (Figure 1 & Table 1). At every site temperature, pH, dissolved oxygen, electrical conductivity, and turbidity were measured by various field probes and portable instrumentation (see Table 2).

1 Assistant Professor of Chemistry and Geological and Environmental Sciences, Hartwick College, Oneonta, NY.
Each of the probes and instruments were calibrated every time at the beginning of the sampling day and check standards were measured along the samples at each site to ensure quality control.

Water was collected in one liter size acid washed Nalgene bottles from the fastest flowing part of the river if that was accessible via three methods. In the shallower section of the river (SR1 to SR4), samples were obtained via wading in to the main stream of the river, then from SR5 to SR14 samples were collected by a Nalgene bottle tied to a rope and tossed in about 5 meters from bank with the exception of SR7 and SR9 that were collected by lowering the Nalgene bottles from a bridge. The bottles were rinsed with the river water three times at each site before they were filled for collection. The samples were kept on ice in a cooler until the arrival to Hartwick College’s geochemistry laboratory.

Each sample was well shaken after transport and divided in to two aliquots for cation and nutrient analytical work. The aliquots for cation analysis were filtered with a 0.45 µm nylon membrane filter and acidified below a pH of 2 with concentrated nitric acid to keep metals/cations in solution. The aliquots for nutrient analysis were preserved with 0.8 ml of 5.76 M sulfuric acid per 125 ml of sample. All preserved samples were kept in the refrigerator at 4°C at Hartwick College until further processing.

Cation concentrations were determined via an Inductively Coupled Plasma Atomic Emission Spectrophotometer (ICP-AES) at the Chemistry department of SUNY Oneonta, and recorded in mg/L following standard analytical methods for standards, calibration and quality control (Martin et al. 1994). Total nitrogen, total phosphorus, nitrates, and ammonia were measured in mg/L through the use of a Lachat QuickChem FIA + Water Analyzer® following methods summarized by Meehan (2005) at the Biological Field Station of SUNY Oneonta.
Figure 1. Sample location map of the Upper Susquehanna River study sites between Cooperstown and Oneonta, in Otsego County, NY showing 13 sites. Site - SR14 is at Unadilla, NY, 20 miles SW from Oneonta. (Map from USGS.gov; scale 1:24,000).
Table 1. Description and coordinates of sites sampled on the Susquehanna River, 2009.

<table>
<thead>
<tr>
<th>Sites</th>
<th>Description</th>
<th>GPS Coordinates</th>
</tr>
</thead>
<tbody>
<tr>
<td>SR1</td>
<td>Otsego Lake Outflow - Just above the Main Street Bridge in Cooperstown, sample collected by wading in to the river</td>
<td>N 42°41.983'; W 74°55.213’ ±24ft</td>
</tr>
<tr>
<td>SR2</td>
<td>Under the Susquehanna Ave. Bridge in Cooperstown, sample collected by wading in to the river</td>
<td>N 42°41.544'; W 74°55.648’ ±48ft</td>
</tr>
<tr>
<td>SR3</td>
<td>Under an unused bridge in Phoenix Mills on Phoenix Road, sample collected by wading in to the river</td>
<td>N 42°40.021'; W 74°56.713’ ±22ft</td>
</tr>
<tr>
<td>SR4</td>
<td>Downstream from the convergence with Oaks Creek on Hyde Park Road, surrounded by railroad tracks, bridge, and fields, sample collected by wading in to the river</td>
<td>N 42°39.683’; W 74°57.012’ ±20ft</td>
</tr>
<tr>
<td>SR5</td>
<td>Clintonville – under an old bridge location, dead end street, slow moving water, collected by a Nalgene bottle tied to a rope and tossed in about 5 m from bank</td>
<td>N 42°36.953’; W 74°57.242’ ±44ft</td>
</tr>
<tr>
<td>SR6</td>
<td>Downstream from the convergence with Cherry Valley Creek, surrounded by fields, slow moving water collected by a Nalgene bottle tied to a rope and tossed in about 5 m from bank</td>
<td>N 42°35.392’; W 74°55.949’ ±22ft</td>
</tr>
<tr>
<td>SR7</td>
<td>Portlandville - above Goodyear Lake, in residential area, collected by lowering a Nalgene bottle from a bridge</td>
<td>N 42°31.749’; W 74°58.092’ ±36ft</td>
</tr>
<tr>
<td>SR8</td>
<td>Just before the intake of Colliersville dam on Goodyear lake, zebra mussels, collected by a Nalgene bottle tied to a rope and tossed in about 5 m from bank</td>
<td>N 42°30.220’; W 74°59.108’ ±24ft</td>
</tr>
<tr>
<td>SR9</td>
<td>Downstream from the convergence with Schenevus Creek, in Colliersville, on County Road 58, collected by lowering a Nalgene bottle from a bridge</td>
<td>N 42°29.133’; W 74°59.346’ ±37ft</td>
</tr>
<tr>
<td>SR10</td>
<td>Just upstream from the Mill Race Dam, across from South Side Mall, collected by a Nalgene bottle tied to a rope and tossed in about 5 m from bank</td>
<td>N 42°26.956’; W 75°02.682’ ±22ft</td>
</tr>
<tr>
<td>SR11</td>
<td>Upstream from Oneonta’s Waste Water Treatment Plant, fishing access, collected by a Nalgene bottle tied to a rope and tossed in about 5 m from bank</td>
<td>N 42°26.483’; W 75°05.980’ ±22ft</td>
</tr>
<tr>
<td>SR12</td>
<td>At the effluent pipe of Oneonta’s Waste Water Treatment Plant, dark colored plume entering the river, no mixing with river for several 100s of meters</td>
<td>N 42°26.301’; W 74°06.051’ ±22ft</td>
</tr>
<tr>
<td>SR13</td>
<td>Downstream from Oneonta’s Waste Water Treatment Plant, about 500 meters, collected by a Nalgene bottle tied to a rope and tossed in about 5 m from bank</td>
<td>N 42°26.147’; W 75°06.100’ ±22ft</td>
</tr>
<tr>
<td>SR14</td>
<td>Unadilla, NY, at the USGS gauging station, on Bridge Street, collected by a Nalgene bottle tied to a rope and tossed in about 5 m from bank</td>
<td>N 42°19.301’; W 75°18.977’ ±26ft</td>
</tr>
</tbody>
</table>
Table 2. Instruments that were used to measure field parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Temperature</th>
<th>Dissolved Oxygen</th>
<th>pH</th>
<th>Electrical Conductivity</th>
<th>Turbidity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Instrument</td>
<td>YSI 55</td>
<td>Dissolved Oxygen</td>
<td>HACH</td>
<td>HACH CO150 2100P</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Portable</td>
<td>and Temperature</td>
<td>HQ40d</td>
<td>Conductivity Meter</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Portable</td>
<td>Portable robe</td>
<td>Multi M</td>
<td>Meter</td>
<td>Turbidimeter</td>
</tr>
</tbody>
</table>

RESULTS AND DISCUSSION

Temperature

The measurements were taken about 5 cm below the water surface at every location. The summer mean temperatures follow a typical pattern of previous years (Matus 2008), averaging around 20°C with the coolest temperatures right above the Mill Race Dam (Figure 2a). Fall temperatures have not been recorded in previous reports and they show about a 10 degree drop by end of October. Notice the warming effect of Oneonta’s waste water treatment plant effluent pipe, which is 4-5 degrees warmer than the rest of the river in October. However, this warming effect disseminate quickly as the effluent mixes with the river water by about 500 meter below the pipe at SR13 (Figure 2b).

a)

![Graph showing seasonal mean temperatures with error bars representing standard deviation](image)

b)

![Graph showing temperature variations by sampling times](image)

Figure 2. Temperature profile of the Susquehanna River that shows a) seasonal mean temperatures with error bars representing standard deviation; b) temperature variations by sampling times.
pH

Acids and bases play an important role in environmental and geochemical processes. Acids are substances that produce hydrogen ions in aqueous solutions and they increase the effective concentration (activity) of the hydrogen ion (Ritz and Collins 2008). Acidity is indicated by a pH value below 7. Bases are substances that produce hydroxide ions in aqueous solutions and they decrease the effective concentration (activity) of the hydrogen ion (Ritz and Collins 2008). Basic solutions have a pH value above 7. If the activities of hydrogen and hydroxide ions are the same the solution has a pH of 7. Overall, the pH of the Susquehanna River is slightly basic, normally between 7.5 and 8.5, which is seen on Figure 3a. A decreasing pH trend can be observed through the course of the river with Oneonta’s waste water treatment effluent being the lowest, close to neutral (Figure 3b). There are no significant differences found among the sampling times at most of the locations, but SR4 site had the largest variation which might be due to the incoming Oaks creek (Figure 3b).

![Figure 3a: pH profile of the Susquehanna River showing mean pH values with error bars representing standard deviation.](image1)

![Figure 3b: Variations by sampling times.](image2)

Figure 3. The pH profile of the Susquehanna River that shows a) mean pH values with error bars representing standard deviation; b) variations by sampling times.

**Electrical Conductivity**

This is a measure of the capacity of water (or other media) to conduct electrical current (Radtke et al. 2005). It is a function of the types and quantities of dissolved substances in water, but there is no universal linear relationship between total dissolved solids and electrical conductivity. However, electrical conductivity is a good approximation for total dissolved solids; it is temperature dependent. The average measurement is about 220 $\mu$S/cm with a decreasing trend from Cooperstown to Unadilla (Figure 4a). Again, Oneonta’s waste water treatment plant releases a high concentration of dissolved solids (Figure 4a & b), but the river still...
has a capacity to dilute the effluent to background concentrations within 500 m. The 20 July and 3 August data are missing from Figure 4b because of instrument failure.

![Graph A](image1)

![Graph B](image2)

Figure 4. The electrical conductivity profile of the Susquehanna River a) mean EC values with error bars representing standard deviation; b) variations by sampling times.

**Turbidity**

Turbidity is an expression of the optical properties of a liquid that causes light to be scattered and absorbed rather than transmitted in straight lines through a sample (Anderson 2005). All small suspended matter contributes to turbidity including clays, silt, plankton and other microorganisms and generally caused by waste discharge, runoff, algae, humic acids and high iron concentration. It is an indicator of the environmental health of water bodies because high turbidity water can transmit disease causing pathogens, heavy metals and pesticides by encasing these materials. High turbidity could also increase the temperature of water, which can be lethal for certain organisms, lower photosynthetic rate and settling to the bottom will fill lakes over time and could suffocate organisms at the bottom. It is measured in NTU (Nephelometric Turbidity Unit) which is equal to 0.6 to 1 mg/L total suspended solid depending on the particle size and scattering properties, so it is a cheap and easy estimation of total suspended solids (Anderson 2005).

Turbidity was one of the most variable parameter through the studied period because it was greatly influenced by rain events that provided a substantial sediment load to the river and
2009 had a wet summer. The averages (Figure 5a) were high and increased from source; however differences were not significant by distance due to the high variability in measurements (Figure 5b).

**Figure 5.** The turbidity profile of the Susquehanna River **a)** mean turbidity values with error bars representing standard deviation; **b)** variations by sampling times.

**Dissolved oxygen**

Dissolved oxygen is an indicator of the health of the aquatic environment and used in determination of water quality (Lewis 2006). For example, it can indicate discharge of organic matter to water from waste water, manure etc sources; thermal pollution from industrial cooling towers; and excess nutrient release (accelerated eutrophication). When dissolved oxygen levels fall below 5 mg/L concentration, the water cannot support the majority of fish or other aquatic animal populations. New York State Department of Environmental Conservation requires all waste water treatment plants to maintain a minimum of 5 mg/L dissolved oxygen concentration below the effluent introduction (Polus 2003). Dissolved oxygen levels mainly fluctuated due to the conditions at the sampling sites such as slow versus fast flowing water (see descriptions in Table 1; Figure 6a) and they also varied by season, weather and temperature (Figure 6b). Overall, dissolved oxygen levels were the highest in October when the water temperatures were the lowest, so the water was able to hold larger amount of dissolved gases. The SR5 and SR6 sites had slowly flowing water with low concentration of dissolved oxygen and Oneonta’s waste water treatment plant released consistently lower dissolved oxygen concentrations than the background levels. However, the river conditions always provided above 5 mg/L dissolved oxygen levels (Figure 6b).
Figure 6. The dissolved oxygen profile of the Susquehanna River a) mean DO values with error bars representing standard deviation; b) variations by sampling times.

**Total Phosphorus**

This measurement contains both inorganic and organic forms of phosphorus in the river water. The phosphorus is either dissolved in water or in a form of small particulates that are digested through preservation and preparation of the water samples following an established analytical method (Ebina 1983). The summer average total phosphorus concentrations are shown on Figure 7a and without SR12 on Figure 7b. Unfortunately, the summer samples were filtered before analyzing for nutrients, so they are not directly comparable to last year’s results and averaged around 12 µg/L (Figure 7a&b). The SR13 site (Reed’s SR19 site, 2008) exhibited a high concentration of 72 µg/L on summer average due to the municipal sewage effluent of the City of Oneonta after 500 m of mixing with river water (Figure 7b). The SR12 site which is directly at the effluent pipe of Oneonta’s waste water treatment plant contributed water to the river having 1550 µg/L phosphorus, on summer average (Figure 7a). The fall samples that were prepared unfiltered (same method as Reed 2008) showed higher concentration of total phosphorus than the summer samples for most of the sites, between 20 and 70 µg/L (Figure 7c). Oneonta’s waste water treatment plant (SR12) released a large amount of phosphorus in September, so after 500 m river mixing (SR13) the concentrations were still around 300 µg/L (Figure 7c). According to current regulations the waste water treatment plants are not mandated to remove phosphorus from the effluent and there are no regulations on the maximum
contamination levels for phosphorus (EPA 2009). According to EPA recommendations in our region total phosphorus levels above 80 µg/L could trigger eutrophication of surface water (EPA 2000).

![Graph a) Total P vs Distance from Otsego Lake](image1)

![Graph b) Total P vs Distance from Otsego Lake](image2)

![Graph c) Total P vs Site](image3)

Figure 7. Total phosphorus concentrations along the Susquehanna River with error bars representing standard deviation; a) mean values for all sites summer 2009; b) mean values without SR12 summer 2009; c) fall measurements, SR12 values added without scale.

**Ammonia**

Results for ammonia testing followed similar trends than the total phosphorus (Figure 8a & b). Overall, concentrations were low and many samples were below the laboratory detection limit (0.02 mg/L). For graphing purposes all below detection limit samples were considered as 0 mg/L. The only summer samples that were above detection limit were SR12 and SR13, at and below Oneonta’s waste water treatment plant (Figure 8a). Ammonia is a volatile compound, so filtration must have released most the ammonia from the samples. Half of the fall samples were below detection limit as well and all site had a concentration below 0.07 mg/L ammonia with the exception of SR12 (6 to 18 mg/L) and SR13 (0.2 to 1.4 mg/L), which represent the effect of Oneonta’s waste water treatment plant (Figure 8b). The results are consistent with findings of Reed (2008); however Oneonta’s waste water treatment plant released a significantly higher concentration of ammonia in summer 2009 (3.2 mg/L) than in summer 2008 (0.18 mg/L) comparing the average values at the site 500 m downstream from the effluent pipe.
Figure 8. Ammonia concentrations along the Susquehanna River with error bars representing standard deviation; a) mean values for all sites summer 2009; b) fall measurements.

Nitrate and Nitrite

The major sources of nitrate and nitrite are acid deposition, runoff from animal feed lots and fertilizers used on agricultural fields, golf courses and other sport fields in the Upper Susquehanna Basin. The concentrations were mostly below 0.35 mg/L at every site throughout the sampling period (Figure 9a&b), which is well below the EPA secondary maximum contaminant level for nitrate (EPA 2009). Most of the results are comparable to Reed (2008) and lower than the concentrations in Otsego Lake (Albright 2008). Oneonta’s waste water treatment plant complies with the EPA regulations by releasing less than 10 mg/L nitrate at the pipe (Figure 9b).
Figure 9. Nitrate and nitrite concentrations along the Susquehanna River with error bars representing standard deviation; **a)** mean values for all sites summer 2009; **b)** fall measurements.

**Total Nitrogen**

This measures both inorganic and organic sources of nitrogen in the water, which are either dissolved or particulate matter in unfiltered samples. The patterns are similar to total phosphorus values (Figure 7 & 10). The highest concentrations are released at Oneonta’s waste water treatment plant, but disseminate quickly due to the large volume of the river. During the summer total nitrogen concentrations were 6.8 mg/L and in the fall 19 to 20 mg/L at site SR12. These values are higher than the EPA recommendations for our region, which is maximum 1.88 mg/L to avoid eutrophication of aquatic ecosystems (EPA 2000). Most of the sites exhibited concentrations below 0.7 mg/L similarly to the results of 2008 summer (Figure 10a). Summer and fall values had a little or no difference (Figure 10a & b), indicating that nitrogen sources are dissolved nitrogen species or particulates that are smaller than 0.45 μm because the summer samples were filtered and the fall samples were not.
Figure 10. Total nitrogen concentrations along the Susquehanna River with error bars representing standard deviation; a) mean values for all sites summer 2009; b) fall measurements.

**Base Cations**

The base cation chemistry of the Susquehanna River mainly reflects the local geology of shale and limestone in the basin. The calcium levels are high, 40-45 mg/L at the origin, and then gradually decrease to Oneonta, NY. The decrease could be caused by dilution effect of tributary stream with lower calcium concentrations. Other base cations, magnesium, potassium and sodium are naturally low, below about 5 mg/L and these concentrations do not change significantly through the river path that was studied. Oneonta’s waste water treatment plant introduces high concentrations (60 mg/L on average) of sodium and elevates both potassium and magnesium concentrations. However, these higher concentrations are diluted quickly due to the large volume of the river water compared to the effluent volume.
Metals

The samples were analyzed for eleven metals and most of them were below instrumental detections limit (20 µg/L) and those data are not shown. Iron, aluminum, zinc and manganese were the only metals that were found in low detectable amounts, in the low µg/L range (Figure 12). These findings also agree with the high pH values (Figure 2) because most of the metals precipitate out of solution above pH of 4. The EPA only regulates maximum contaminant levels for few metals for drinking water and those were not found in detectable amounts in the river. However, secondary standards recommended for several elements and compounds for drinking water, 300 µg/L for iron, between 50 and 200 µg/L for aluminum, 50 µg/L for manganese, and 5 mg/L for Zinc (EPA 2009). Overall, all metal concentrations are below the EPA recommendations for drinking water standards (Figure 12). Criteria have not been developed for ecosystem maximum contaminations levels, there are a few for aquatic life, but no regulations and enforcement are in place. The graphs below show that Oneonta’s waste water treatment plant releases some dissolved metals in to the river which is consistent with the higher electrical conductivity (Figure 4). These higher than background concentrations are not a concern at normal operation, but might cause a problem at overflow stage.
SUMMARY AND CONCLUSIONS

Among the sites sampled only Oneonta’s waste water treatment plant caused elevated ion concentrations, both nutrients and metals, but the high concentrations were diluted by 500 m downstream from the effluent pipe due to mixing with large volume of river water. No evidence was found that dairy farming, agricultural runoff and tourism of the baseball fields had a significant contribution to the nutrient budget. The waste water treatment plant is important to clean Oneonta’s waste water, but it is over 30 years old and it has a hard time to keep up with the demand. It has compiled with the federal and EPA regulations during normal operation and all of our samples were collected during normal operation. This plant processes both sewage and surface runoff from the City of Oneonta, so during rain storm events it is close to or over its capacity. When over capacity situation occurs the waste water is only minimally (physically) treated and potentially more contaminants enter the river. It could be important to study such events to better understand the impact of the plant on the river. Further monitoring of the water quality of the Upper Susquehanna River is needed to ensure a clean ecosystem.

ACKNOWLEDGMENTS

I thank Matt Albright and Holly Waterfield at the Biological Field Station of SUNY Oneonta, NY for analyzing the samples for nutrients, John Schumloffel at the Department of Chemistry of SUNY Oneonta for helping with cation/metal analytical work, Kyle Armstrong, Brian Terbush and Andrew Parisi Hartwick College, Oneonta, NY for sampling and preparation of samples throughout the summer months, Keith Brunstad for driving the students to the sampling sites during July and August, Devin Castendyk for introducing me to this research project and helping to build connections. Thanks to The Otsego County Conservation
Association and Hartwick College Faculty Research Grant and Milne Family Fund Award for sponsoring this research.

REFERENCES


