

Preliminary Evaluation of Dissolved Metals in Water Samples from Seven Locations Across the Upper Main Stem of the Susquehanna River near Sunbury, PA

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Abstract

River water samples from seven locations across the upper main stem of the Susquehanna River near Sunbury, PA were analyzed for the presence of dissolved metals. A Perkin Elmer AAnalyst 800 Atomic Absorption Spectrometer was used to analyze the filtered water for presence of the following metals: copper (Cu), mercury (Hg), manganese (Mn), selenium (Se), nickel (Ni), lead (Pb), iron (Fe), zinc (Zn), arsenic (As), magnesium (Mg), calcium (Ca), and strontium (Sr). Spiked control samples were also analyzed to determine if the metals may adsorb onto the sediment found in several of the sample locations. The concentrations of metals varied from below detection limits using flame atomization to 78 µg/mL. Those metals which could not be detected will be re-evaluated using the more sensitive graphite furnace method for lower concentrations. The results are considered preliminary because all samples were filtered so results indicate dissolved metals only. Digestion of the samples before analysis for total metals will be performed next. Analysis of organic components in the water will also be performed.

Introduction

The upper main stem of the Susquehanna River is formed by the confluence of the West and North Branches, each of which is chemically and physically distinctive. The upper main stem retains the signatures of the two branches due to weak lateral mixing, and they are referred to as the North Branch plume (NBP) and West Branch plume (WBP). Samples were collected from the sites located at a transect that straddles Byers Island near Shamokin Dam, PA and below the Adam T. Bower inflatable dam at Sunbury, PA. To gain an understanding of each site location, a map with site # locations is shown in Figure 1. It is interesting to note the distance of each site from the Sunbury Generation Light and Power Plant.

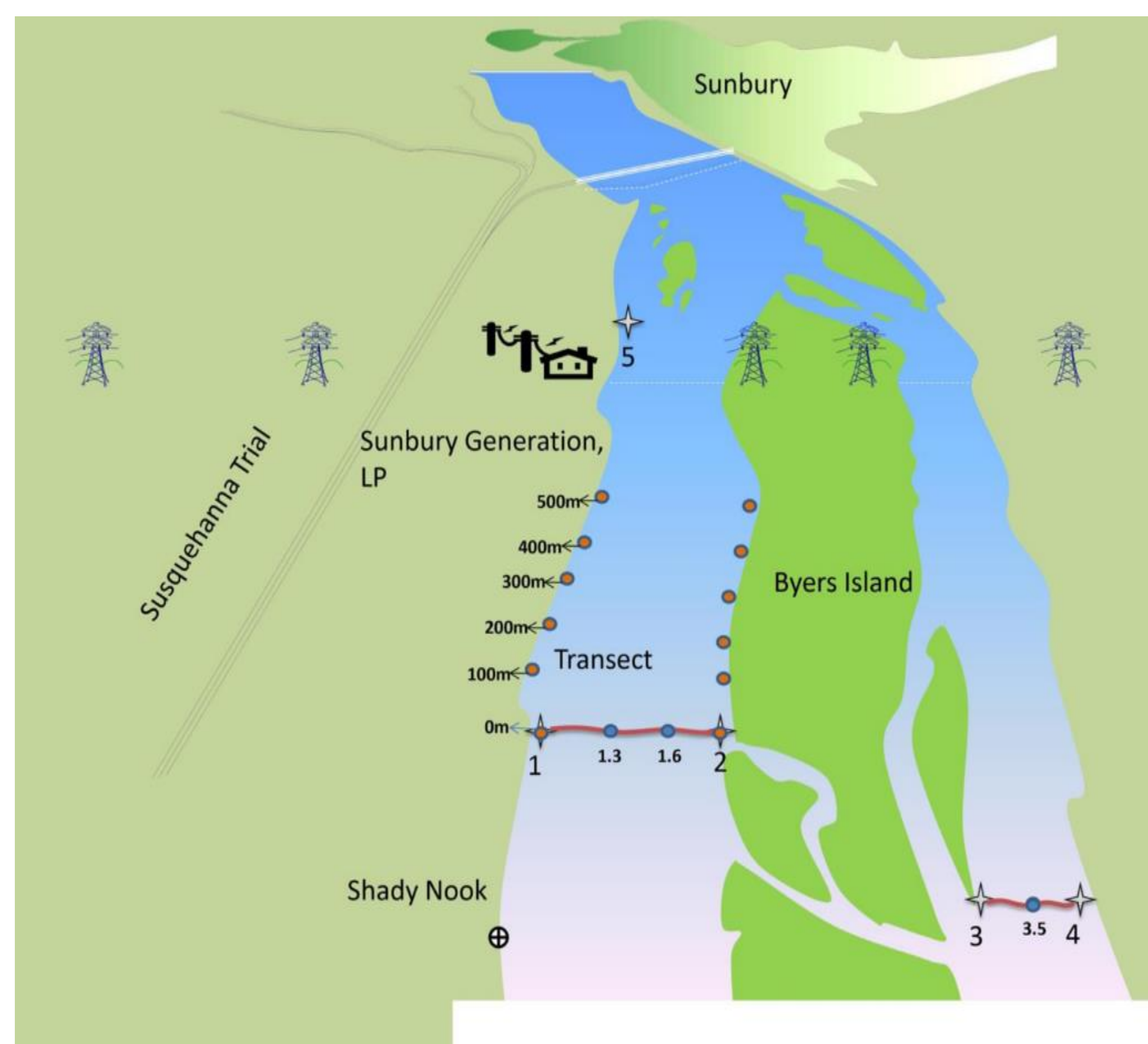


Figure 1. A map demonstrating the location of each site from which the seven water samples were collected.

The goal of this research is to determine what metals (dissolved and total) are found in the Susquehanna River, the sediment, and eventually several different organisms. Information regarding which metals are present and at what concentration will help to understand whether metal concentrations in different locations along the river have different influences on the environment.

Samples were analyzed using a flame atomic absorption spectroscopy (AA). AA is used for determining the concentration of metals in samples. AA can be used to determine over 70 different elements in solution or directly in solid samples used in pharmacology, biophysics, toxicology, and other research.¹ For the current study, the AA was used to determine the concentration of twelve different metals in river water using external standard calibration. Additional metals will also be analyzed as the study continues.

Experimental

Standard Preparation:

To prepare standard curves, five standards were prepared for each metal corresponding to recommended concentration ranges for the instrumental method (Table 1). Starting with 1000 µg/mL stock standards, serial dilutions of five standards were made in 1 % nitric acid.

Table 1. The standard concentration range and the wavelength of analysis used for each metal.

Metal	Concentration (µg/mL or ppm)	Wavelength (nm)
Cu	0.2-10	324.8
Hg	0.1-50	253.7
Mn	0.1-10	279.5
Se	0.1-10	313.3
Ni	0.3-10	232.0
Pb	1.0-20	283.3
Fe	0.3-10	248.3
Zn	0.1-100	213.9
As	0.1-10	193.7
Mg	0.1-10	285.2
Ca	0.1-20	422.7
Sr	0.1-10	460.7

Filtered Sample Preparation:

To remove any particles or sediment from the river water samples, filtration of the samples was performed. Using a disposable syringe with a syringe filter, 6 mL of river water was added to the syringe, and the water was filtered into a 10 mL volumetric flask, which was filled to volume with 1% nitric acid. All results were multiplied by 1.67 to account for the dilution. The samples were transferred into falcon tubes for analysis.

Spiked Sample Preparation:

To determine if metals may adsorb onto any particles which were removed by filtration in the river water samples, three samples were spiked with 1 µg/mL of each metal to determine if this amount could be recovered. For each spiked sample, 5.0 mL of the sample was pipetted into a 10.0 mL volumetric flask. A volume of 0.1 mL of the 100 µg/mL standard was added to the flask, which was then diluted to volume with 1% nitric acid. These spiked samples were then filtered and analyzed. Because all sample results were multiplied by 2 to account for the 2x dilution with nitric acid, the amount of metal in these samples should result in a 2 µg/mL increase in concentration.

Atomic Absorption Analysis:

To determine the concentration of each sample, blanks, the five standards, filtered samples, and spiked samples were added to the autosampler of the Perkin Elmer AAnalyst 800 Atomic Absorption Spectrometer (Figure 2). Each metal required the use of a lamp and wavelength specific to that metal.



Figure 2. Flame atomization using the Perkin Elmer AAnalyst 800 Atomic Absorption Spectrometer for a sample of magnesium, which yielded an orange flame.

Results and Discussion

The AA instrument aspirated and analyzed each sample three times and the final concentration was calculated from the average of these three readings. The analyses, including linear calibration curves for each metal, were only used if the correlation coefficient was at least 0.99. Results are shown in Table 2.

Table 2. The concentration of each metal in all samples and spiked samples. Cells with an * indicate that none was detected so concentration is less than the lowest standard (see Table 1 for standard concentration ranges).

Site #	Metals (all units are µg/mL or ppm)											
	Cu	Hg	Mn	Se	Ni	Pb	Fe	Zn	As	Mg	Ca	Sr
1	1.3	*	0.17	*	*	3.2	*	*	*	12.2	29.6	0.17
1.3	1.3	*	0.17	*	*	3.3	*	*	*	11.5	27.1	0.17
1.6	*	*	0.17	*	*	3.3	*	*	*	13.2	30.6	0.17
2	0.8	*	0.17	*	*	3.3	*	*	*	12.9	29.7	0.17
2 spiked	*	2.4	4.8	*	3.8	6.4	77.8	47.8	*	16.0	32.6	2.2
3	*	*	0.17	*	*	3.2	*	*	*	12.7	29.9	0.17
3 spiked	0.2	*	4.8	*	3.6	6.6	41.2	*	*	16.4	31.6	2.2
3.5	*	*	0.17	*	*	3.3	*	*	*	8.2	30.6	0.17
4	*	*	0.17	*	*	3.2	*	12.4	*	7.8	30.9	0.17
4 spiked	8.8	*	5.0	*	4.4	6.0	40.6	55.6	*	16.4	34.0	2.2

Many of the results in Table 2 indicate concentrations that are too low to be detected by flame AA. For future work, the samples will be analyzed using the more sensitive graphite furnace method. It can also be noted that some of the spiked samples that should show the additional 2 µg/mL increase in concentration, showed an acceptable increase of ~2 µg/mL compared with the corresponding unspiked sample. However, the spike could not be detected in some spiked samples, indicating that the metal might be adsorbed by particulates in the river water which were filtered out before analysis. Other results showed an exaggerated increase in concentration due to the spike, indicating a problem with the sample or method. These results will be investigated and the methods evaluated for improvement. River water samples will also be analyzed for several metals not yet evaluated.

The metals that did demonstrate detectable concentrations in some samples consisted of copper, manganese, nickel, lead, iron, zinc, magnesium, calcium and strontium. Iron has the highest concentration of the metals, but was only found in some samples. Calcium is the next highest concentration and is found in every sample, which is not surprising.

Conclusions

Much of the data collected demonstrate concentrations too low to be detected with flame AA. These sample sites will be re-evaluated using the more sensitive graphite furnace method of AA. Spiked samples which showed excessively low or high spike recoveries will be evaluated further. Results shown so far are dissolved metals. Total metals evaluated after sample digestion of river water samples will also be analyzed. Analysis of organic compounds found in the river water will also be performed in future studies.

References

1. Kantowski, B.; Buttel, O.; Jena, A. "Atomic Absorption Spectroscopy (AAS) through the Ages." *Chemical Industry Digest*. 28 Feb. 2013.

Acknowledgements

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