Evaluation of Dissolved and Total Metals, and Volatile Organic Compounds, in Water Samples from Seven Locations Across the Upper Main Stem of the Susquehanna River near Sunbury, PA

Kristen M. Benitez, Amir Y. Awali, and Lou Ann Tom, Ph.D.
Department of Chemistry and Biochemistry, Susquehanna University, Selinsgrove, PA 17870

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 and total metals and volatile organics. This portion of the river is unique in that it retains the signatures of the two branches for many miles after they combine due to weak lateral mixing. Atomic absorption spectrometry was used to analyze water samples for the presence of 13 metals. Spiked control samples for each metal were also analyzed to determine if metals may absorb onto any sediment in some samples. The concentrations of individual metals varied from below detection limits to about 10 µg/mL using flame atomization. For metals which could not be detected, samples will be re-evaluated using a more sensitive graphite furnace method. Initial analysis of organic components in the water using solid phase microextraction (SPME) and gas chromatography/mass spectrometry (GC/MS) determined that butylated hydroxytoluene is present in each sample.

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 and West Branch plume. 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. A map with site # locations is shown in Figure 1.
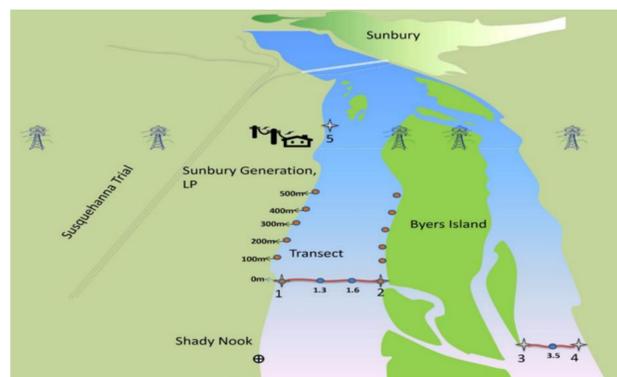

Figure 1. Map showing the location of each site from which the seven water samples were collected.

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 different locations along the river have different influences on the environment. Samples were analyzed using flame atomic absorption spectroscopy (AA) to determine the concentration of each metal (the analyte) in the sample. AA can be used to determine the concentration of many metals in solution or solid samples used in environmental, pharmacology, biophysics, toxicology, and other research.[1] For the current study, AA was used to determine the concentration of metals in river water using external standard calibration. Additional metals will also be analyzed as the study continues. SPME is a fairly new technique used with GC/MS for identification of trace components. In this technique, the volatiles from the water are first absorbed onto the SPME fiber, and then desorbed and analyzed on the GC/MS.[2,3]

Experimental

Sample Preparation and Analysis for Filtered (Dissolved) Metals

Samples were prepared by filtering 6 mL by syringe filter into a 10 mL volumetric flask, followed by dilution with 1 % nitric acid. Samples were analyzed on a Perkin Elmer AAnalyst 800 Atomic Absorption Spectrometer with autosampler. Wavelengths for each metal are shown in Table 1.

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

Metals	Concentration Range (ppm)	Wavelengths (nm)
Cu	0.2-10	324.8
Hg	0.1-50	253.7
Mn	0.1-10	279.5
Ni	0.3-10	232.0
Pb	1.0-20	283.3
Fe	0.3-10	248.3
Zn	0.1-10	213.9
As	0.1-10	193.7
Mg	0.1-10	285.2
Se	0.1-10	313.3
Ca	0.1-20	422.7
Sb	1.0-100	217.6
Sr	0.1-10	460.7

Spiked Sample Preparation for Filtered (Dissolved) Metals

All river water samples were filtered before analysis by AA. To determine if metals may absorb into any particles which are removed by filtration of the samples, three samples with the most sediment were spiked with 1 µg/mL of each metal to determine if this amount was recovered or removed with the sediment. For each spiked sample, 5.0 mL of the sample was pipetted into a 10.0 mL volumetric flask. To this, 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.

Sample Preparation for Digested (Total) Samples

250 mL of each sample was added to a 1000 mL beaker with 10 mL of concentrated AA-grade nitric acid. A watch glass was placed on top of each beaker, and the water evaporated until 20-40 mL remained. The walls of the beaker as well as the watch glass were rinsed with Milli-Q-grade water. Samples were filtered using vacuum filtration with a 0.45 µm membrane filter prewashed with 1% nitric acid, followed with 5 mL rinses of Milli-Q-grade water. All collected samples were transferred into a 250 mL volumetric flask and diluted with Milli-Q water, filtered and then analyzed using flame AA. Blank filters were also rinsed with 1% nitric acid which were also analyzed to determine in the acid would remove any metal residue from clean filters (see acid rinse row in Table 3). For Ca and Mg analysis, 1.0 mL of 5000 µg/mL lanthanum solution was added as a releasing agent to 10.0 mL of digested sample and standards and blanks resulting in a final lanthanum concentration of 500 ppm.

Spiked Sample Preparation for Digested (Total) Metals

One spiked sample was prepared for each metal. To 50 mL of each digested sample preparation, 2.5 mL of concentrated nitric acid was added as well as 0.5 mL of the 1000 ppm standard. The amount of metal in these samples should result in a 10 µg/mL increase in concentration.

Standard Preparation

For each metal, an external standard curve was created using five standards prepared by serial dilution in in 1% nitric acid starting with 1000 µg/mL stock standards according to recommended concentration ranges for the instrumental method (Table 1).

Gas Chromatography/ Mass Spectroscopy Analysis

To determine volatile organic compounds in each sample, a SPME fiber (75 µm carboxen/polydimethylsiloxane) was suspended for 24 hours above each water sample heated in an 80 ° C sand bath. Blanks using heated Milli-Q water were also run. The fiber was then injected into a Thermo Scientific Trace 1300 GC with an ISQ Mass Spectrometer, on a TG-5mS 30 m x 0.25 mm x 0.25 µm column with a 250 ° C injection port. The oven program was 40 ° C for 3 min, followed by a 3 ° C/min ramp to 300 ° C for 10 min. Samples had been sitting refrigerated for several months before analysis of volatiles was performed, so this study will be repeated on fresh samples.

Results and Discussion

The dissolved metal results are shown in Table 2. Each result is an average of three readings of the samples. Linear calibration curves for each metal all had correlation coefficients of at least 0.99.

Table 2. The concentration of dissolved metals (µg/mL) in filtered samples and spiked samples. (* indicates less than the lowest standard. See Table 1 for standard concentration ranges).

	Cu	Hg	Mn	Se	Ni	Pb	Fe	Zn	As	Mg	Ca	Sr
1	*	*	0.1	*	*	2.0	*	*	*	4.9	18.3	0.1
5	*	*	0.1	*	*	1.9	*	7.4	*	4.7	18.5	0.1
Spiked 5	4.4	*	2.5	*	2.2	3.0	20.3	27.8	*	8.2	17.0	1.1
9	*	*	0.1	*	*	1.9	*	*	*	7.6	17.9	0.1
Spiked 9	0.1	*	2.4	*	1.8	3.3	20.6	*	*	8.2	15.8	1.1
21	0.8	*	0.1	*	*	1.9	*	*	*	7.3	17.7	0.1
22	0.8	*	0.1	*	*	2.0	*	*	*	6.9	16.2	0.1
23	*	*	0.1	*	*	2.0	*	*	*	7.9	18.3	0.1
24	0.5	*	0.1	*	*	2.0	*	*	*	7.7	17.8	0.1
Spiked 24	*	1.2	2.4	*	1.9	3.2	38.9	23.9	*	8.0	16.3	1.1

Many results show levels below the detection limit by flame analysis so will be repeated using the more sensitive furnace method. Some spiked samples show an inconsistent increase in metal concentrations, so all samples were prepared using digestion for total metal analysis (Table 3) to determine if this improves the accuracy of metal recovery from spiked samples, and therefore acceptable sample preparation. Results are shown in Table 3.

Table 3. Concentration of total metals (µg/mL) in digested samples and spiked samples.

	Cu	Hg	Mn	Ni	Pb	Fe	Zn	Mg	Ca	Sr	Sb
Site Number											
1	0.19	*	0.14	0.006	*	*	*	3.4	15.0	0.19	1.5
5	0.22	*	0.16	0.03	*	*	*	3.5	15.0	0.22	2.6
9	0.06	*	0.22	0.03	*	2.1	*	3.3	15.0	0.25	2.9
21	0.04	*	0.12	0.006	*	*	*	3.8	14.0	0.25	2.5
22	0.04	*	0.12	0.006	*	*	*	3.6	14.0	0.37	1.7
23	0.22	1.8	0.12	0.03	*	*	*	3.4	14.0	0.22	1.2
24	0.02	*	0.24	0.006	*	3.3	*	2.7	11.0	0.19	2.9
Filtered Acid Rinse	0.02	*	0.78	0.15	*	*	*	1.4	1.8	0.12	3.1
Spiked (Site #)	9.4 (1)	7.9 (1)	9.6 (5)	8.9 (24)	10.0 (9)	16.0 (9)	8.6 (21)	3.9 (21)	30.0 (22)	9.9 (22)	11.0 (23)

Results demonstrate that the highest concentration of any metal was 15.0 µg/mL (calcium) and most were below the detection limit. Most spiked samples showed the expected increase in concentration (10 µg/mL) demonstrating that the digestion method is accurate. Ca and Mg were prepared with a lanthanum releasing agent and show concentrations greater than the other metals, so preparation of some of the other metals will be repeated with the addition of a releasing agent to confirm results. The acid rinse of the filter also showed trace amounts of several metals, indicating the need to rinse all filter paper with acid prior to use for river water filtering.

The data collected from the GC/MS showed the presence of several different organic compounds not present in the blank (Figure 2). One peak, butylated hydroxytoluene, is a compound that could potentially be a river water contaminant, and is used in chemical food preservatives in addition to aid in the treatment of genital herpes. SPME and GC/MS analysis of fresh river water samples will be repeated.
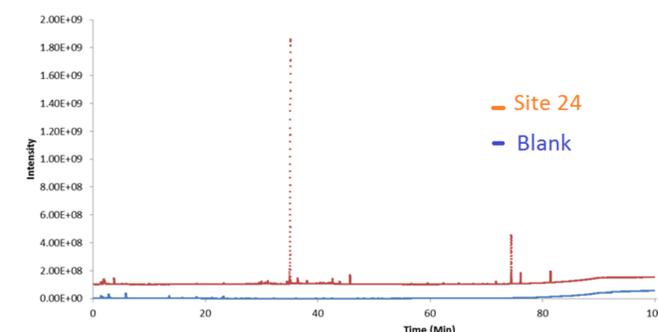

Figure 2. Chromatograms of SPME of site 24 sample and a Milli-Q blank.

Conclusions and Future Work

Data collected during the AA flame analysis for the digested samples demonstrated that most metals had concentrations ranging from below detection limit to 15 ug/mL. Much of the data collected demonstrate concentrations too low to be detected with flame AA. Samples analyzed by SPME and GC/MS determined the presence of butylated hydroxytoluene, but will be repeated on fresh samples. For future work, lanthanum releasing agent will be added to other metals to ensure accurate results, and the more sensitive graphite furnace method will be used for metals that could not be detected by flame AA. Additional metals will be also be analyzed.

References

1. Skoog, D. A.; Holler, F. J.; Crouch, S. R; Principles of Instrumental Analysis, 6th ed.; Thomson Brooks/Cole, Belmont, CA, 2007.
2. Penalver, A.; Pocurull, E.; Borrull, F.; Marce, R.M.; Trends in Anal Chem. 1999, 18 (8), 557-568.
3. Prosen, H.; Zupancic-Kralj, L.; Trends in Anal Chem. 1999, 18 (4), 272-282.

Acknowledgements