

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

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## Abstract

River water samples from four 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 12 metals. 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 the 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) found the possible presence of several trace organics, including methyl 2-methyl-3-oxobutylidithiocarbamate or 2-amino-2-carboxyethylhomocysteine, but neither has been confirmed.

## 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 the 4 locations is shown in Figure 1.

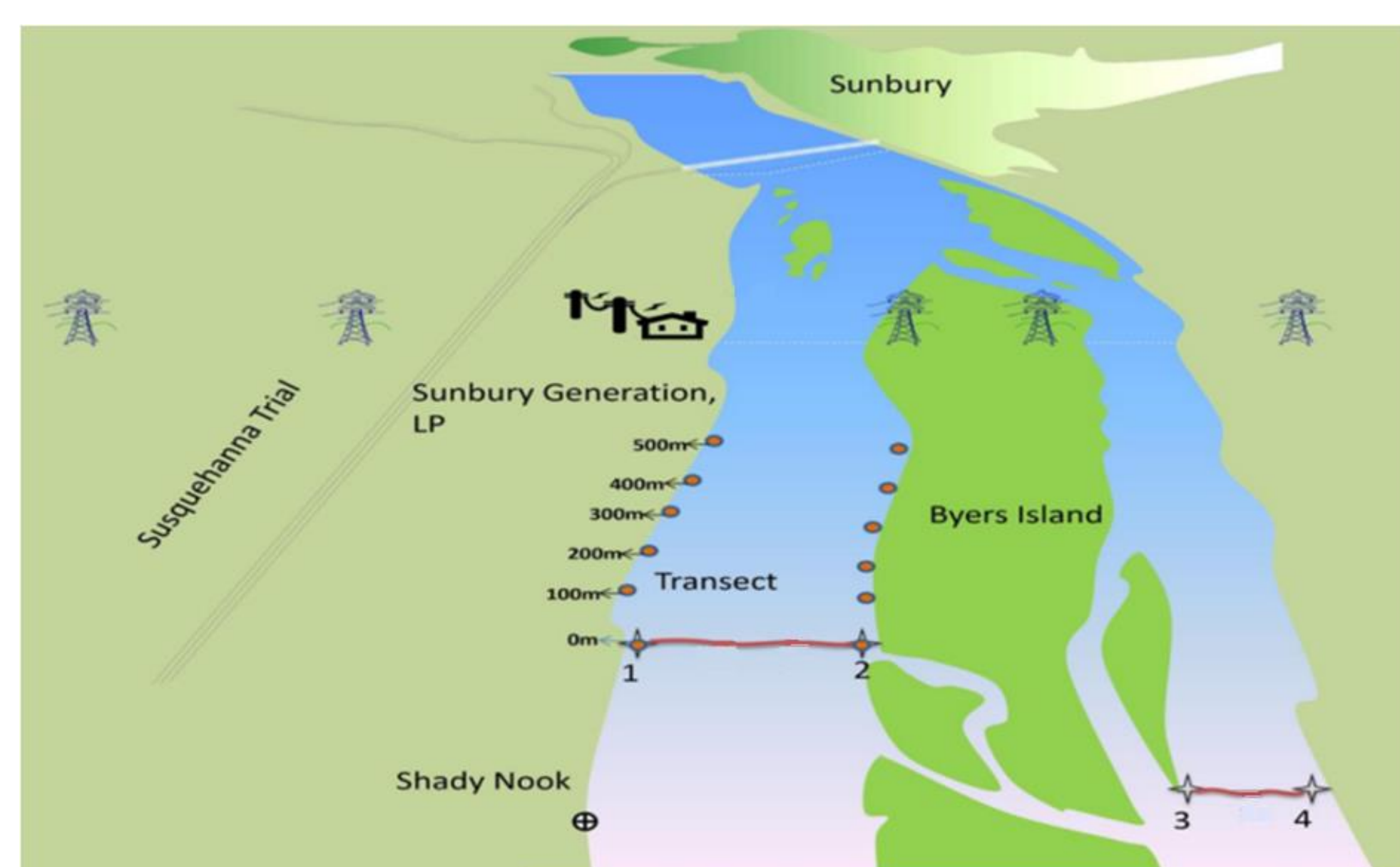


Figure 1. Map showing the location of each site from which the four water samples were collected.

The goal of this research was to determine what metals are detectable in the Susquehanna River. Information regarding which metals are present and at what concentration give a snapshot into the health of the river. Samples were analyzed using flame atomic absorption spectroscopy (AA) to determine the concentration of 12 metals. AA is a powerful tool in determining the concentration of metals in samples from environmental, pharmacology, biophysics, and toxicology research.<sup>1</sup> For the current study, AA was used to determine the concentration of metals in river water using external standard calibration. Additional metals and lower concentrations will also be analyzed using more sensitive graphite furnace mode. Also, SPME was used with GC/MS for identification of trace organic compounds. In this technique, the volatiles from the water were absorbed onto the SPME fiber, and then desorbed and analyzed on the GC/MS.<sup>2,3</sup>

## Experimental

### 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 2% nitric acid, followed with 5 mL rinses of Milli-Q water. Each digested sample was transferred into a 250-mL volumetric flask and diluted with Milli-Q water, filtered and then analyzed using flame AA.

Table 1. Standard concentration ranges for each metal analyzed. Each standard was diluted in 2% nitric acid.

Metal	Range (ppm)	Metal	Range (ppm)
Barium (Ba)	1.0-20	Lithium (Li)	0.05-2.0
Cobalt (Co)	0.1-10	Nickel (Ni)	0.2-10
Copper (Cu)	0.2-10	Lead (Pb)	1.0-20
Iron (Fe)	0.1-10	Antimony (Sb)	0.2-50
Potassium (K)	0.05-2.0	Selenium (Se)	0.1-10
Lithium (Li)	0.05-2.0	Strontium (Sr)	0.1-10
Nickel (Ni)	0.2-10	Zinc (Zn)	0.05-2.0

### Sample Preparation and Analysis for Filtered (Dissolved) Metals

Samples were prepared by filtering 300 mL into a filter flask and adding AA-grade nitric acid. Samples were analyzed on a Perkin Elmer Analyst 800 Atomic Absorption Spectrometer with autosampler at the appropriate wavelength for each metal.

### Standard Preparation

For each metal, an external standard curve was created using five standards prepared by serial dilution in 2% nitric acid starting with 1000 µg/mL stock standards to create standards within the ranges of 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. A blank using heated Milli-Q water was also analyzed. 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.

## Results and Discussion

The dissolved metal results are shown in Table 2. Each result is an average of three readings. Linear calibration curves for each metal all had correlation coefficients of at least 0.999.

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

Trial Information		Concentration (ppm)			
Metal	Sample Type	Site 1	Site 2	Site 3	Site 4
Ba	6/12/15 Filtered	6.50	6.50	6.50	9.83
	6/15/15 Filtered	*	*	3.17	3.17
	7/20/15 Filtered	*	*	*	*
Co	6/12/15 Filtered	*	*	*	*
	6/15/15 Filtered	*	*	*	*
	7/20/15 Filtered	*	*	*	*
Cu	6/12/15 Filtered	*	*	*	*
	6/15/15 Filtered	*	*	*	*
	7/20/15 Filtered	*	*	*	*
Fe	6/12/15 Filtered	*	*	*	*
	6/15/15 Filtered	*	0.13	*	*
	7/20/15 Filtered	*	0.17	0.17	0.34
K	6/12/15 Filtered	1.44	1.98	1.99	2.04
	6/15/15 Filtered	1.42	1.84	1.85	2.08
	7/20/15 Filtered	1.25	1.67	1.84	1.95
Li	6/12/15 Filtered	*	*	*	*
	6/15/15 Filtered	*	*	*	*
	7/20/15 Filtered	*	*	*	*
Ni	6/12/15 Filtered	*	*	*	*
	6/15/15 Filtered	*	*	*	*
	7/20/15 Filtered	*	*	*	*
Pb	6/12/15 Filtered	*	*	*	*
	6/15/15 Filtered	*	*	*	*
	7/20/15 Filtered	*	*	*	*
Sb	6/12/15 Filtered	4.61	4.61	4.61	4.45
	6/15/15 Filtered	3.50	3.81	4.13	4.13
	7/20/15 Filtered	2.86	3.18	3.34	3.66
Se	6/12/15 Filtered	*	*	*	*
	6/15/15 Filtered	*	*	*	*
	7/20/15 Filtered	*	*	*	*
Sr	6/12/15 Filtered	0.11	0.11	0.11	0.11
	6/15/15 Filtered	*	*	*	*
	7/20/15 Filtered	*	*	*	*
Zn	6/12/15 Filtered	*	*	*	*
	6/15/15 Filtered	*	*	*	*
	7/20/15 Filtered	*	*	*	*

Most of the metals were below the detection limit. Most of the metals that were within the detection limit were low, with the exception of barium which was 9.83 ppm. Many of the metals in the digested metals (see Table 3) were also below the detection limit; however, the concentrations of some metals increased in digested samples, as expected. It is interesting to note that zinc was highest at site 4, and upstream of site 4 was an old zinc mine. Further testing of river samples using furnace AA mode will lower detection levels to the ppb concentration range for many of the metals.

SPME GC/MS results did not detect any compounds of interest in large concentration that were not seen in the Milli-Q water blank (Figure 2). However, site 4 collected on 7/20/15 did contain a small peak at 13.27 min corresponding to a compound of 191 g/mol, which was identified by the MS library as a 31% possibility of being 2-amino-2-carboxyethylhomocysteine, or 33% possibility of S-methyl-N-(2-methyl-3-oxobutyl)-dithiocarbamate, which has known anti-cancer properties.<sup>4</sup>

Table 3. Concentration of total metals (µg/mL) in digested samples. (\* indicates less than the lowest standard. See Table 1 for standard concentration ranges).

Trial Information		Concentration (ppm)			
Metal	Sample Type	Site 1	Site 2	Site 3	Site 4
Ba	6/15/15 Digested	3.17	3.17	6.50	6.50
	7/20/15 Digested	*	*	*	*
Co	6/15/15 Digested	*	*	*	*
	7/20/15 Digested	*	*	*	*
Cu	6/15/15 Digested	*	*	*	*
	7/20/15 Digested	*	0.02	*	*
Fe	6/15/15 Digested	*	0.17	0.17	0.34
	7/20/15 Digested	0.23	0.77	1.36	1.77
K	6/15/15 Digested	1.52	1.89	1.87	2.15
	7/20/15 Digested	1.33	1.87	2.18	2.31
Li	6/15/15 Digested	*	*	*	*
	7/20/15 Digested	*	*	*	*
Ni	6/15/15 Digested	*	*	*	*
	7/20/15 Digested	*	*	*	*
Pb	6/15/15 Digested	*	*	*	*
	7/20/15 Digested	*	*	*	*
Sb	6/15/15 Digested	4.61	4.61	4.77	4.77
	7/20/15 Digested	1.75	1.91	2.23	2.54
Se	6/15/15 Digested	0.38	0.18	*	*
	7/20/15 Digested	*	*	*	*
Zn	6/15/15 Digested	*	*	*	*
	7/20/15 Digested	0.05	*	*	0.48

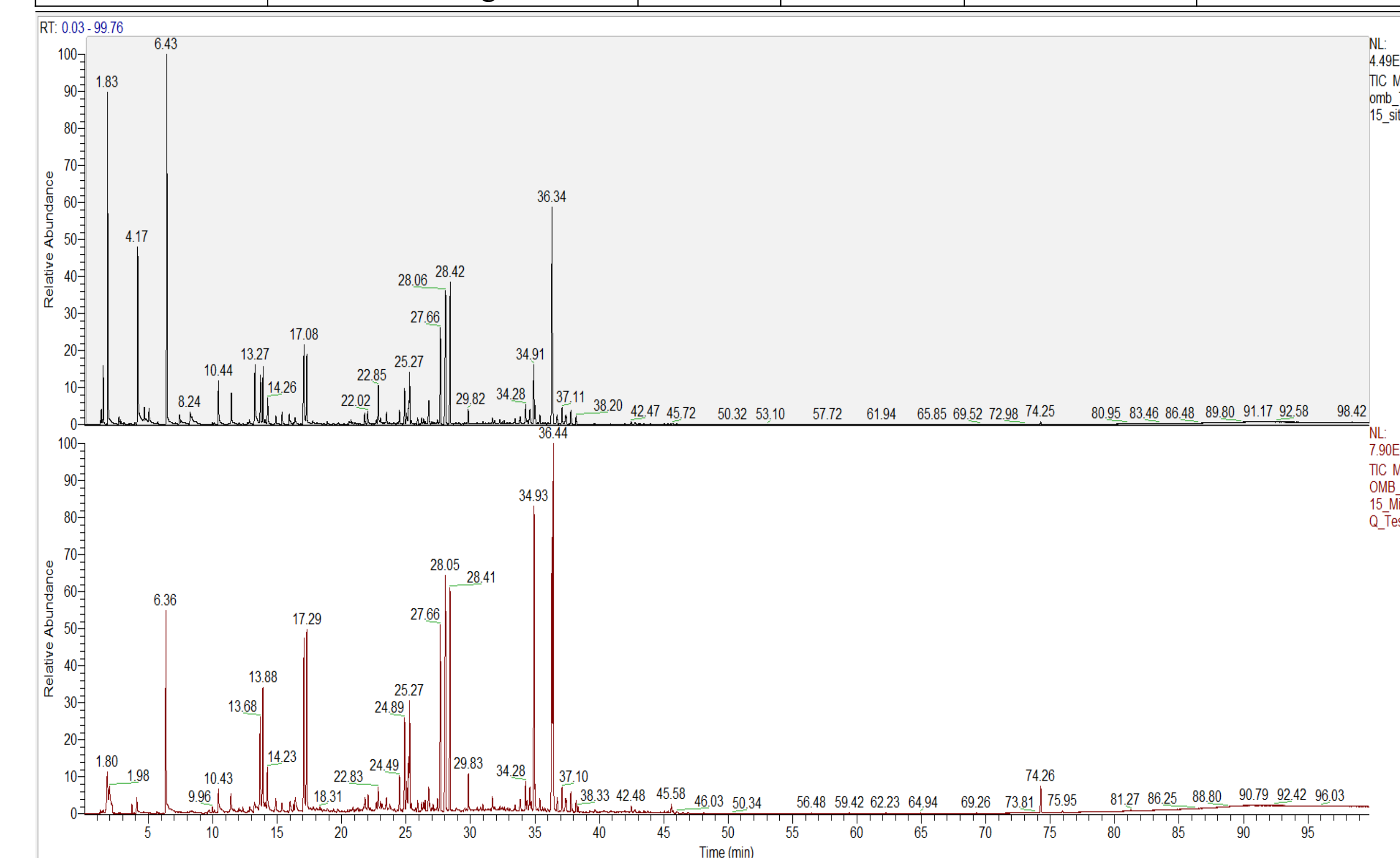


Figure 2: GC/MS spectra of site 4 collected 7/20/15 (top) and Milli-Q blank (bottom)

## 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 <10 µg/mL. Much of the data collected demonstrate concentrations too low to be detected with flame AA, so future samples will be collected and analyzed by AA in graphite furnace mode for ppb (µg/L) detection limits. Alternate extraction methods will be used to reduce the interferences from the Milli-Q water blank for SPME with GC/MS analysis.

## References

- Skoog, D. A.; Holler, F. J.; Crouch, S. R.; Principles of Instrumental Analysis, 6<sup>th</sup> ed.; Thomson Brooks/Cole, Belmont, CA, 2007.
- Penalver, A.; Pocurull, E.; Borrull, F.; Marce, R.M.; Trends in Anal Chem. 1999, 18 (8), 557-568.
- Prosen, H.; Zupancic-Kralj, L.; Trends in Anal Chem. 1999, 18 (4), 272-282.
- Al-Marzoqi, A.; Hameed, I.; Idan, S.; African J. of Biotech. 14 (40), 2015, 2812-2830.

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