Characterization of the organic matter found in the suspended solids of the Musconetcong River, NJ, using Pyrolysis – GC/MS

AN EXPANDED VERSION of the presentation made at the 2018 Delaware Watershed Research Conference
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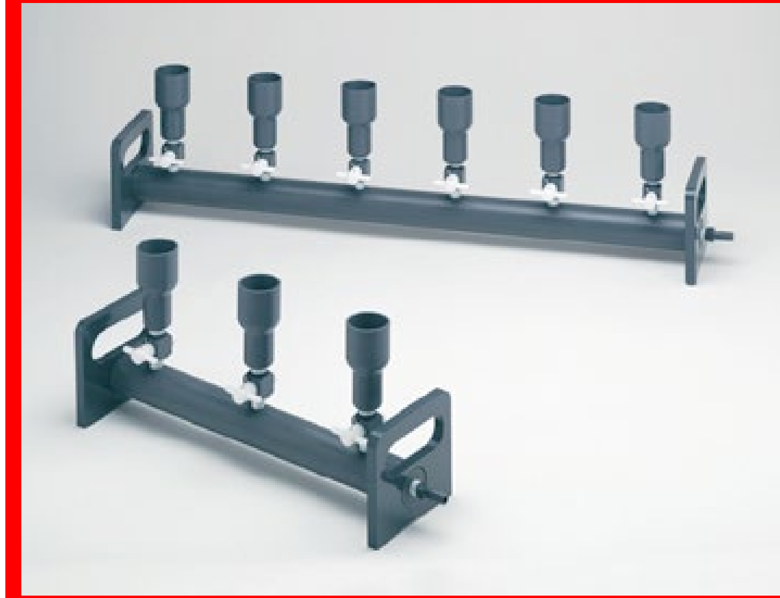
Or….TSS-Py-GC/MS

Combining Total Suspended Solids (TSS) by Standard Methods 2540D-11 with Pyrolysis-GC/MS as used in sediment geochemistry



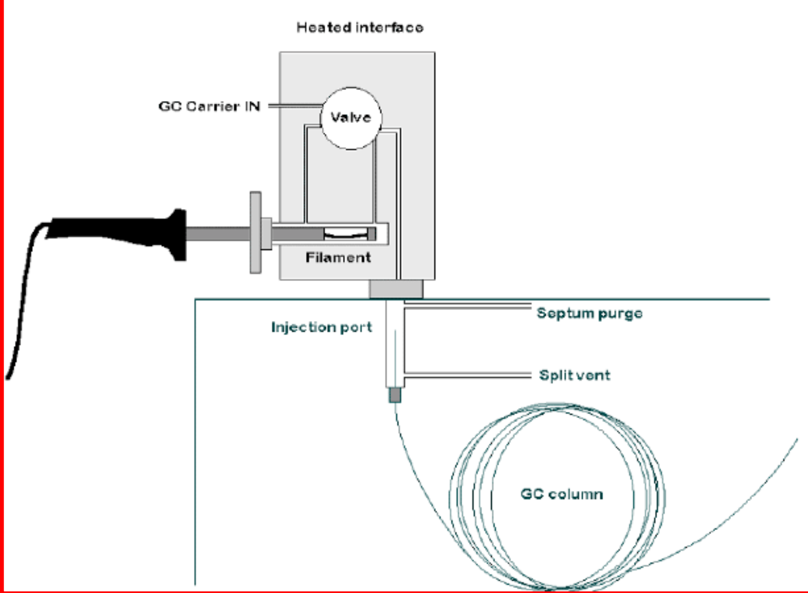


Diagram provided by Gaojin Lyu

Objectives

The specific goal of this project is to combine two well-established analytical techniques and see what insights they might provide into the ecology of our study area. As part of 6-month Musconetcong River monitoring project, we were already running TSS samples.

Our pyrolysis-GC/MS system was already being used to study sediment geochemistry and we had a large data set from freshwater lakes, estuaries, and soils.

What is Analytical Pyrolysis and how was it used in this project?

Pyrolysis usually describes rapid heating in the absence of oxygen.

We packed strips torn from the TSS filter into small quartz tubes (next slide, right) and heated them to 610c in an inert atmosphere. Our CDC model 5150 is shown on the left of the next slide.

In geochemical applications pyrolysis can reveal two types of organic matter.

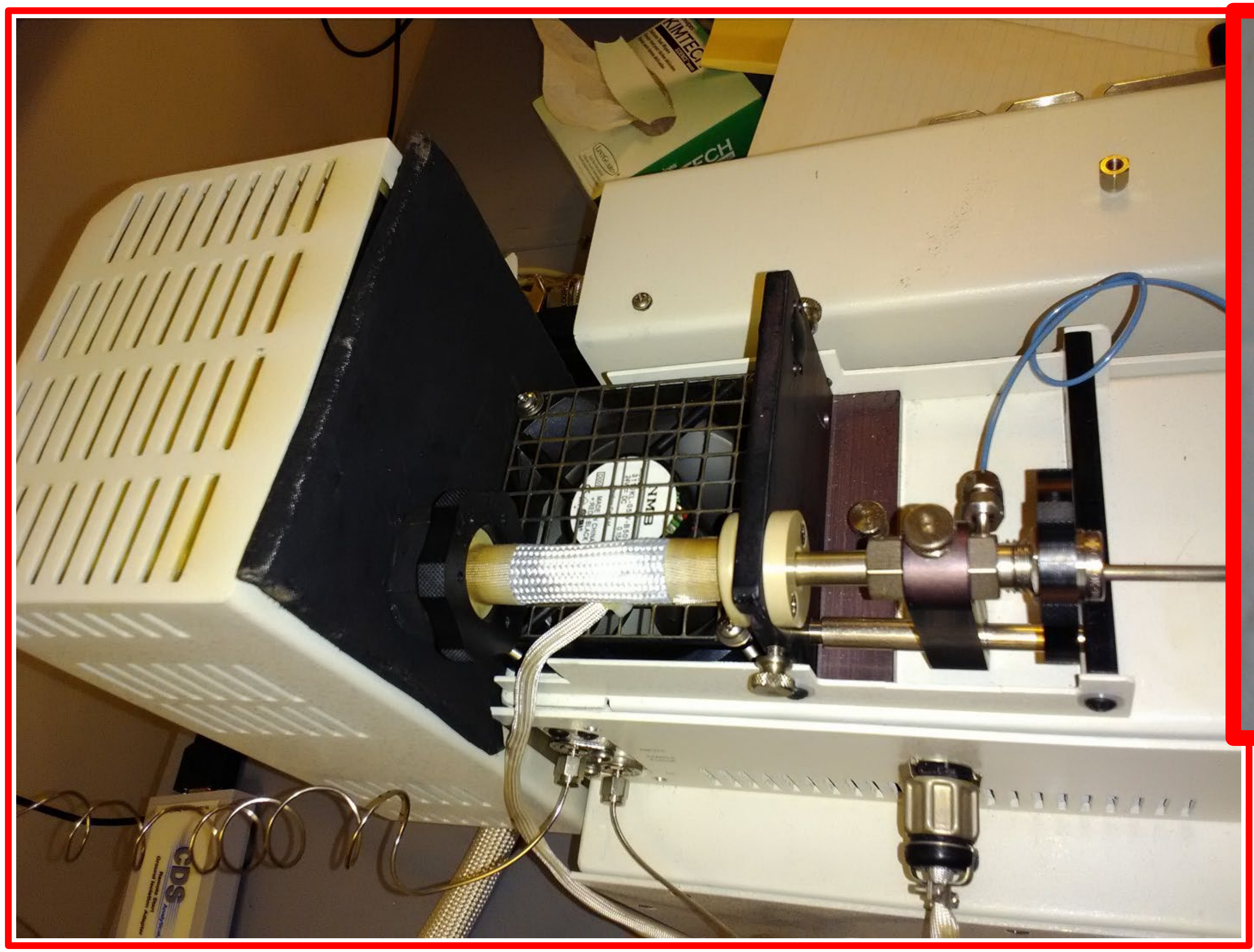
The first are intact molecules that are desorbed from sediment particles (or in this case, the glass-fiber TSS filter) simply by heating.

A second category of materials recovered in pyrolysis include the thermal breakdown products of larger organic molecules including lignins, biopolymers, proteins, and polysaccharides.

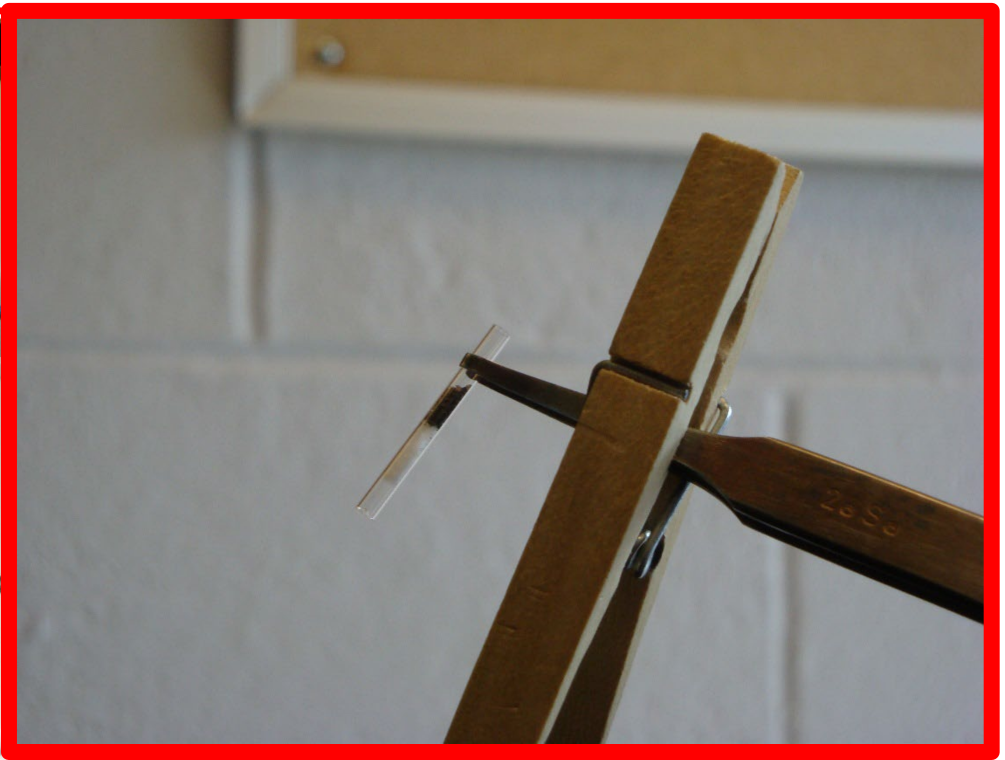
These smaller breakdown products are often more suited to GC/MS analysis than the original molecules.

For the sake of simplicity, both categories of material will simply be grouped together as “pyrolysis products.”

Pyrolysis



The protective cover was removed from the CDS pyrolyzer to show the oven.



Pyrolysis tube loaded with a sediment sample

TSS-Py-GC/MS obviously can only detect a subset of all the organic matter in the river (see next slide).

Any volatile, or unstable organic matter trapped on the filter is going to be lost or destroyed during the TSS procedure.

Because the sample size is so small, only the most abundant materials will be detected.

Fortunately the materials most useful for diagnostic purposes are both recalcitrant and abundant.

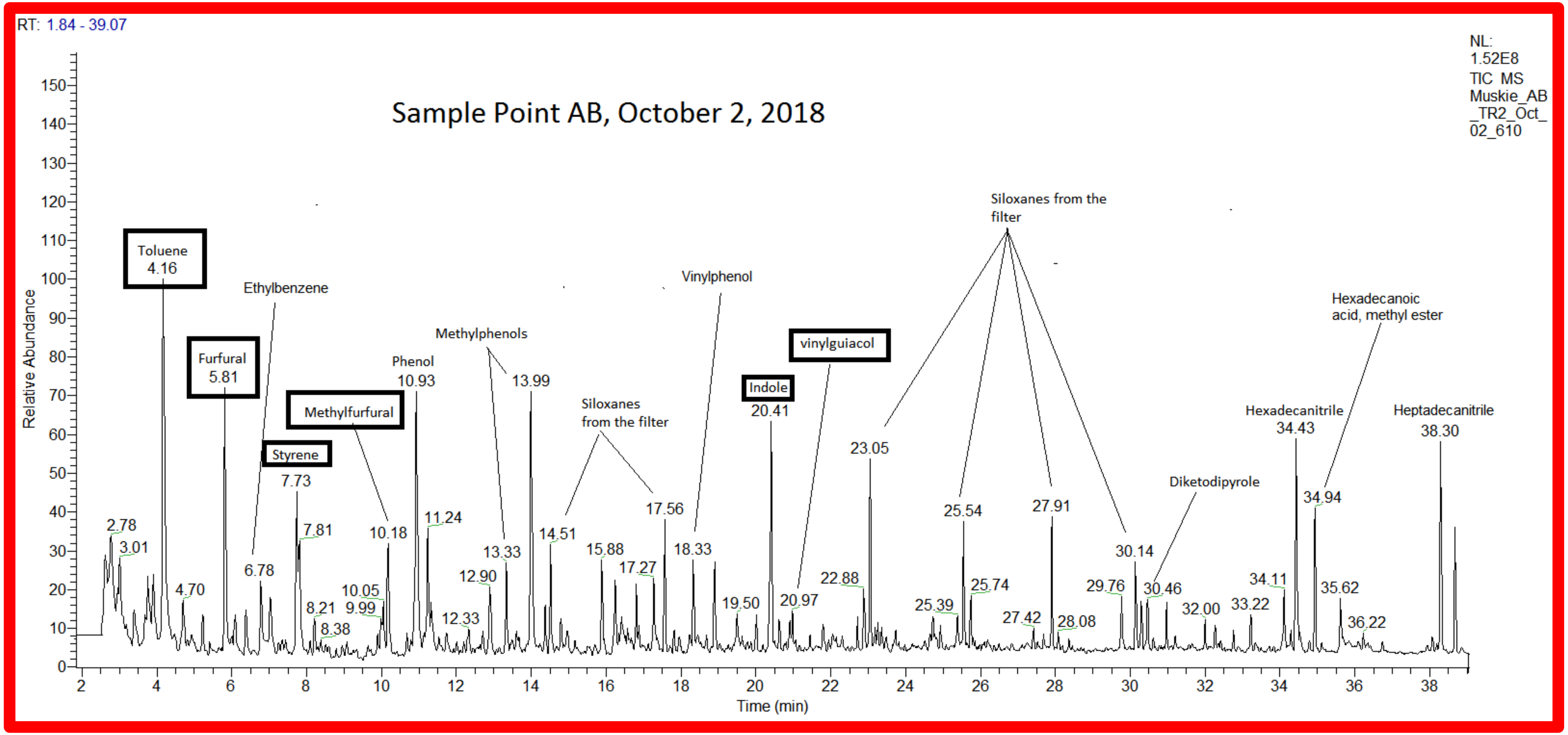
ALL ORGANIC MATTER

Dissolved Organic Matter

Volatile particulate Organic Matter.
Particulate organic matter too small to be trapped on the filter.

Sedimentary Organic Matter (unless re-suspended)

Particulate organic matter big enough to be trapped on the TSS filter…and….
Organic matter bound to suspended particles



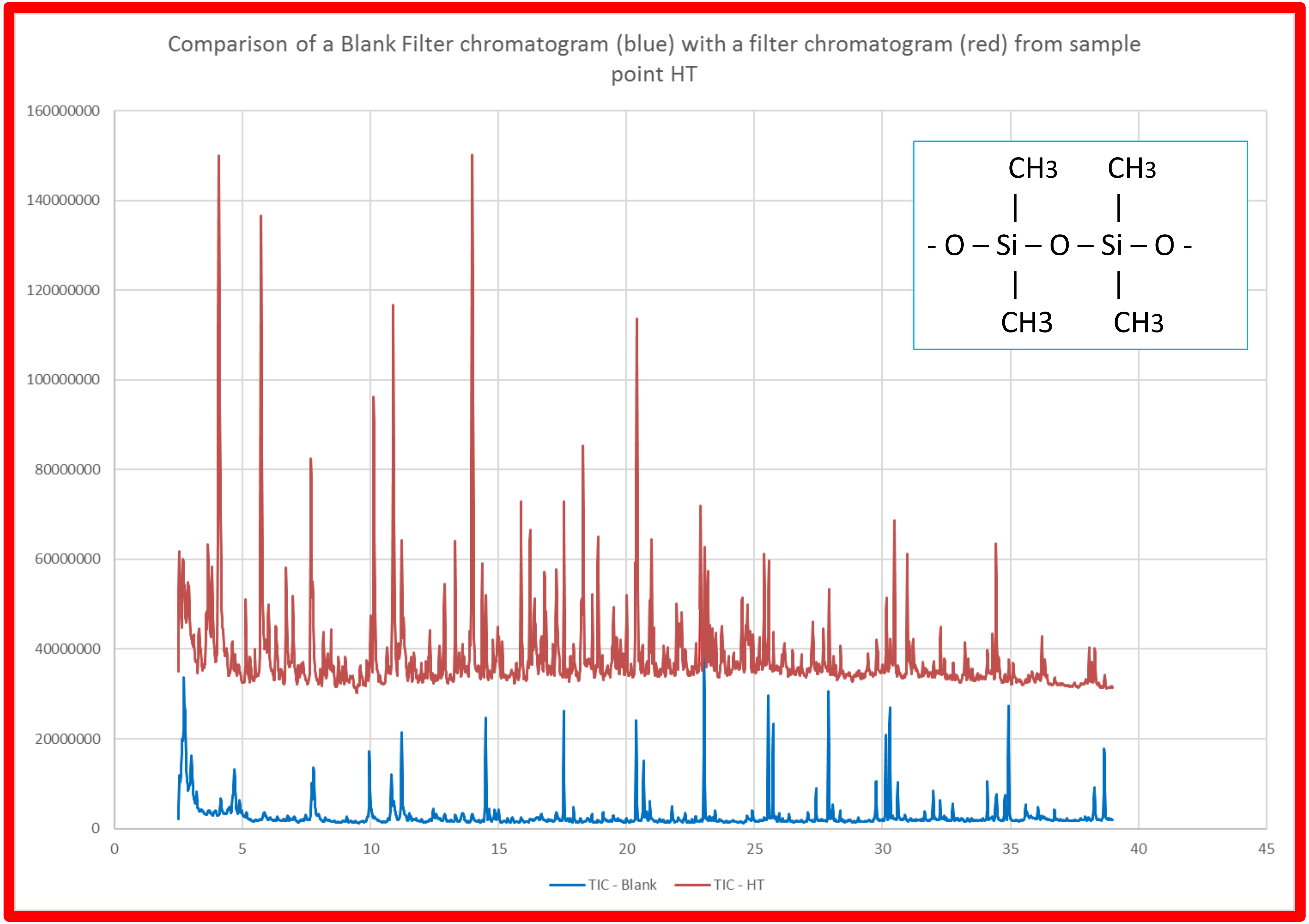
Here is a sample chromatogram from one of the tributary streams.

The compounds marked with a box around their name are all examples of compounds that are both abundant pyrolysis products and particularly significant biomarkers. These however, are not the only ones discussed in the text.

If you are familiar with GC/MS, you will know that siloxanes are a polymer consisting of repeating silicon-oxygen groups which can be released from the fused silica tube that supports the column's stationary phase.

The filters used for TSS are made from glass fibers and will release siloxanes (blue chromatogram).

The red trace shows the chromatogram with the pyrolysis products



Quantifying the Pyrolysis Products

Sample point and date sampled

Compound	BP 7/2/2018
Toluene	5389381.133
Furfural	30676028.93
Styrene	2593325.711
Benzaldehyde	22964955.48
Methylfurfural	85024027.63
Phenol	22964955.48
2-methylphenol	6770989.902
3- & 4-methylphenol	34805620.69
Benzeneactonitrile	15689938.53
Methylindene isomer	5453046.028
Methylindene isomer	199223.593
Naphthalene	34508103.94
Vinylphenol	58065029.38
Indole	34962716.9
vinylguiacol	96501981.95
Diketodipyrole	19255853.18
Total area counts	475825178.4

The peak areas for all of the major pyrolysis products were obtained by integration.

The total peak area was the sum of all of the individual peak areas.

Toluene	0.0113
Furfural	0.0645
Styrene	0.0055
Benzaldehyde	0.0483
Methylfurfural	0.1787
Phenol	0.0483
2-methylphenol	0.0142
3- & 4-methylphenol	0.0731
Benzeneactonitrile	0.0330
Methylindene isomer	0.0115
Methylindene isomer	0.0004
Naphthalene	0.0725
Vinylphenol	0.1220
Indole	0.0735
vinylguaiacol	0.2028
Diketodipyrole	0.0405

One limitation of TSS-Py-GC/MS is that the sample is embedded in the filter's fibers and the amount of material subjected to pyrolysis is difficult to quantify.

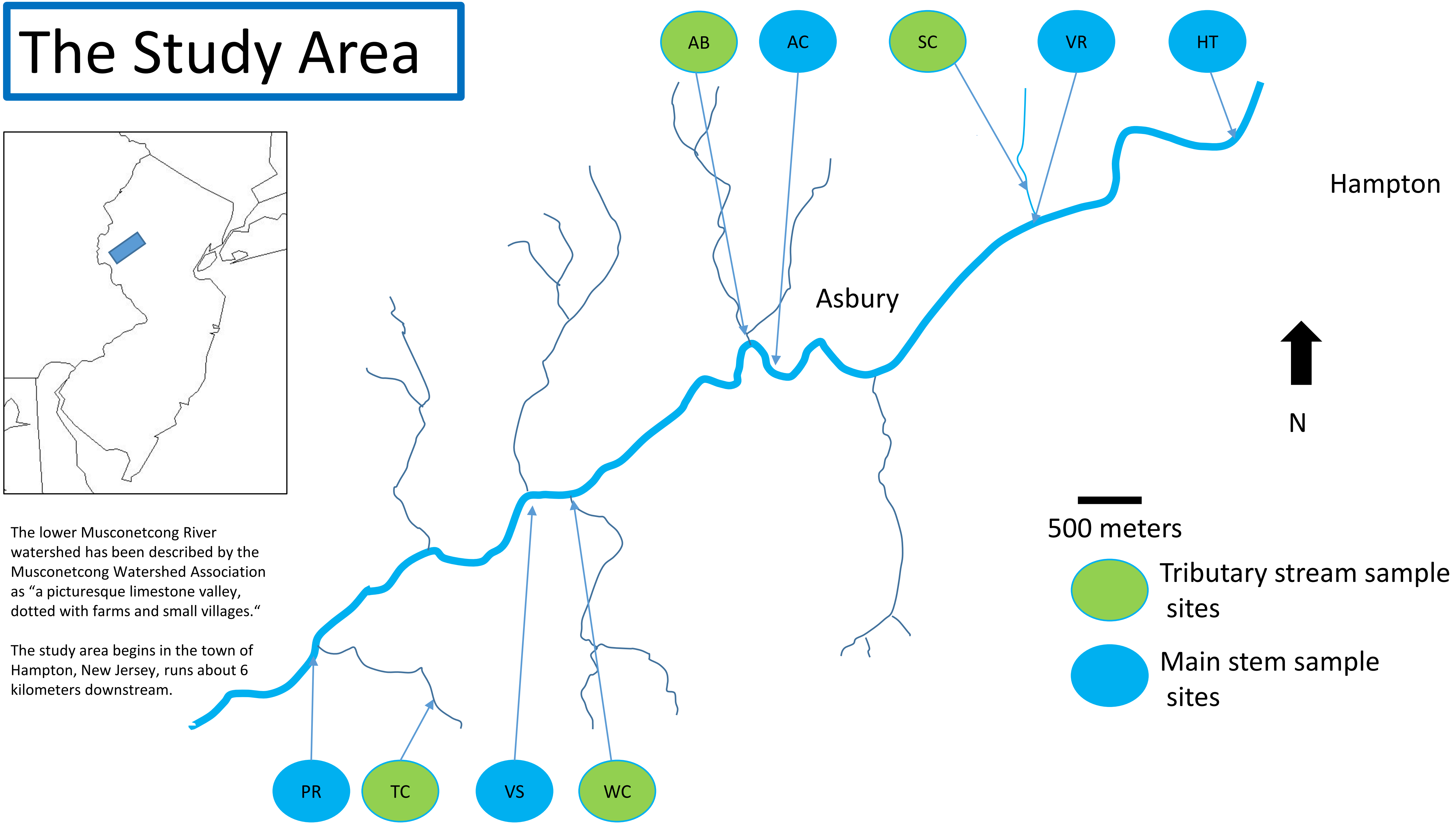
The amount of each pyrolysis product is presented as a proportion of the total peak area. For example, the toluene peak had an area of 5,389,281.133

Divided by the sum of all the peak areas gives:

5,389,281.133 / 475825178.4 = 0.0113 or 1.13%

The most abundant pyrolysis product was vinylguaiacol, 0.2028 or 20.28% of the total peak area.

The Study Area



The lower Musconetcong River watershed has been described by the Musconetcong Watershed Association as “a picturesque limestone valley, dotted with farms and small villages.“

The study area begins in the town of Hampton, New Jersey, runs about 6 kilometers downstream.

The Study Area

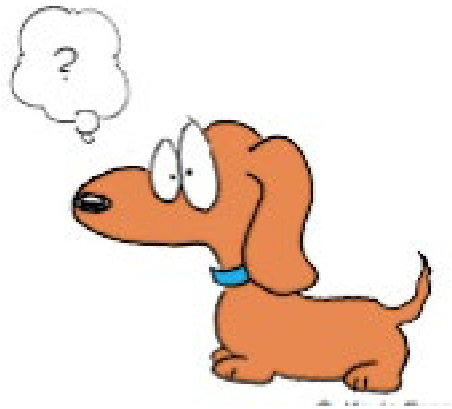
These photographs were taken by our field crew and show a corn field and an equestrian center. The well maintained fences and pastures are typical of the horse farms in the study area.

Musconetcong Valley near the village of Asbury
which is visible to the left. (Courtesy MWA)

Agricultural runoff has been problematic in the tributary streams (Courtesy MWA)

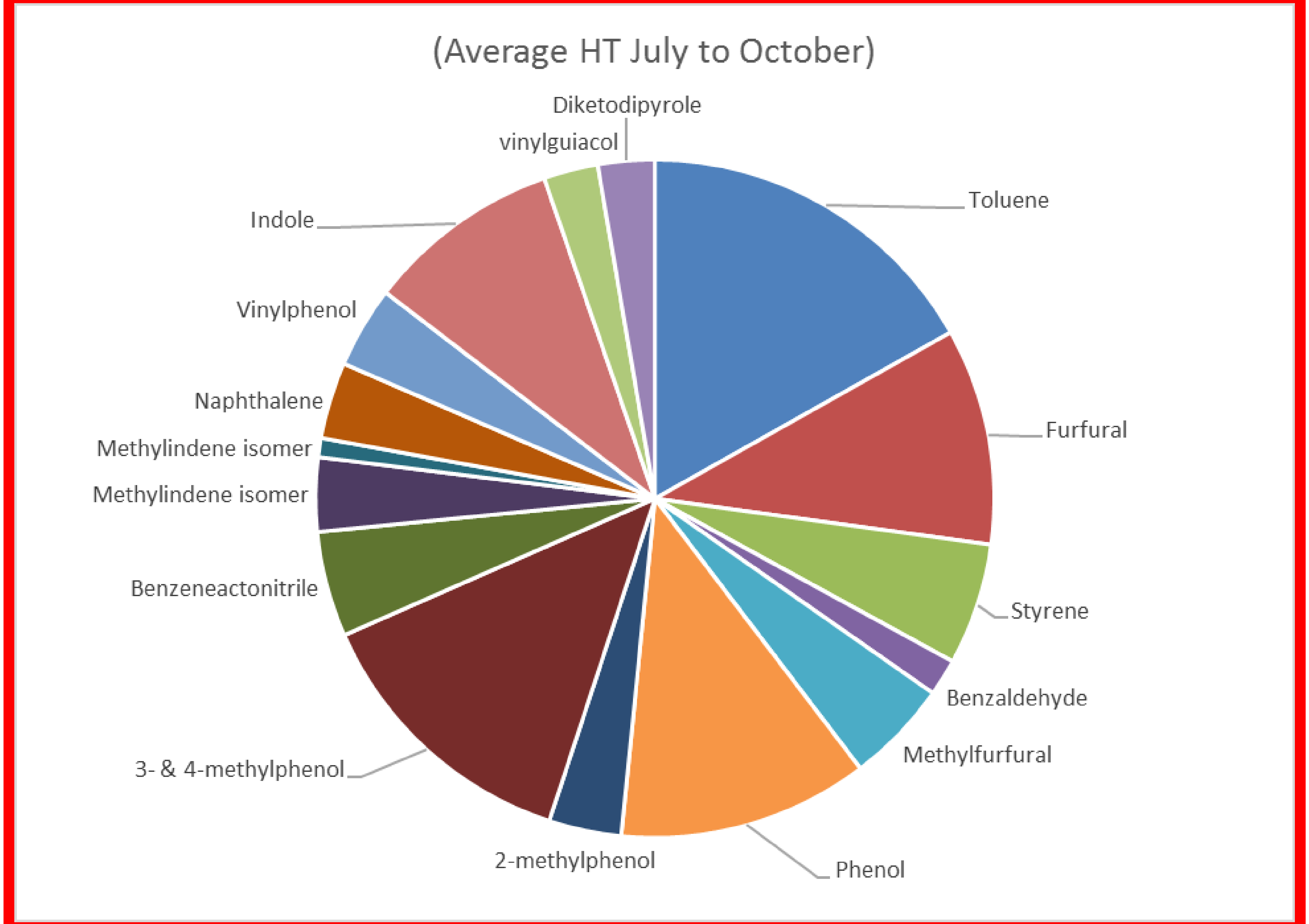
Very quaint and charming but still a source of agricultural runoff in one of the tributary streams (Courtesy MWA)

The first question is whether the organic matter entering the study area undergoes any changes before leaving the study area.

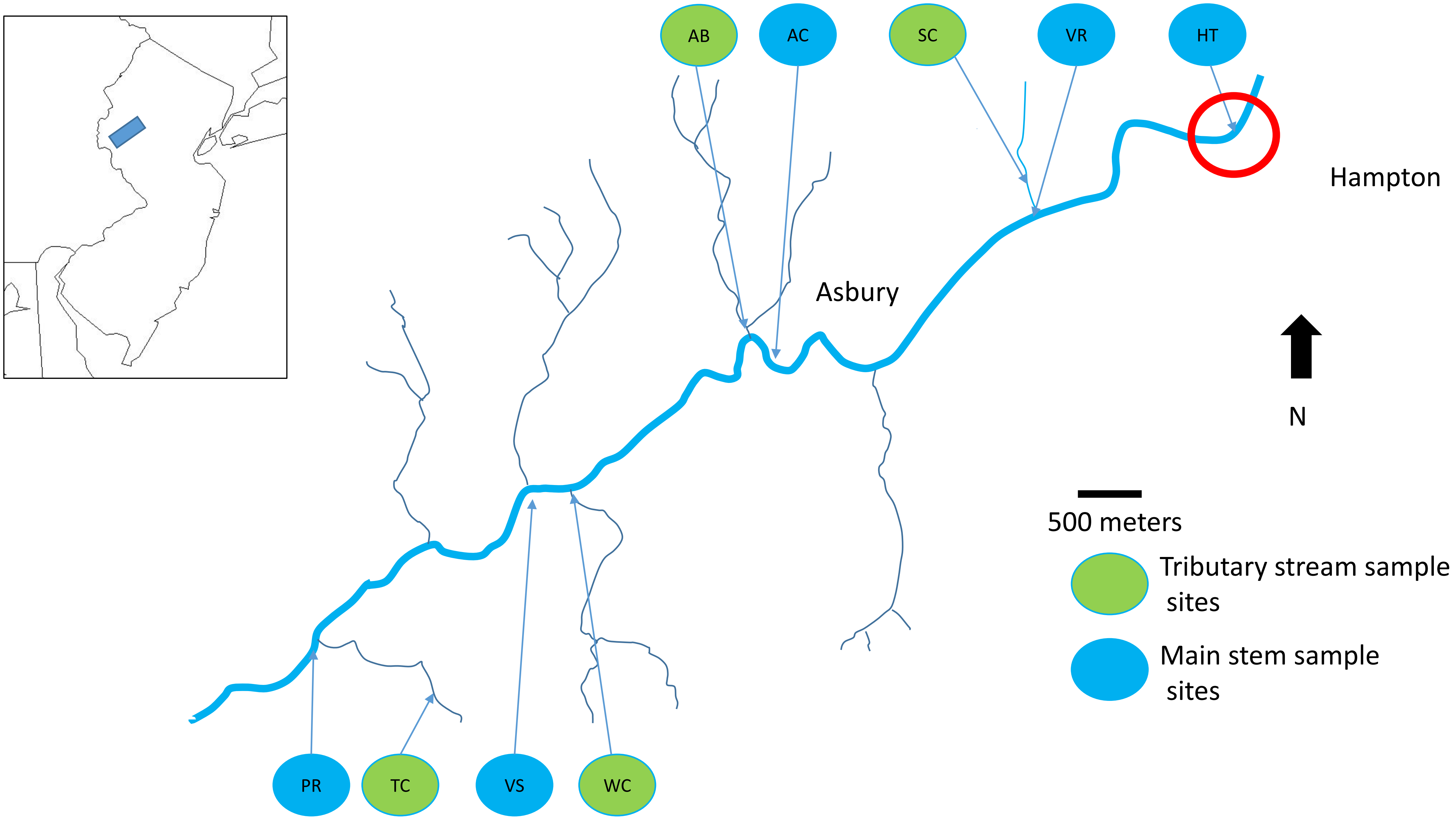


Water comes into the study area at sample point HT.

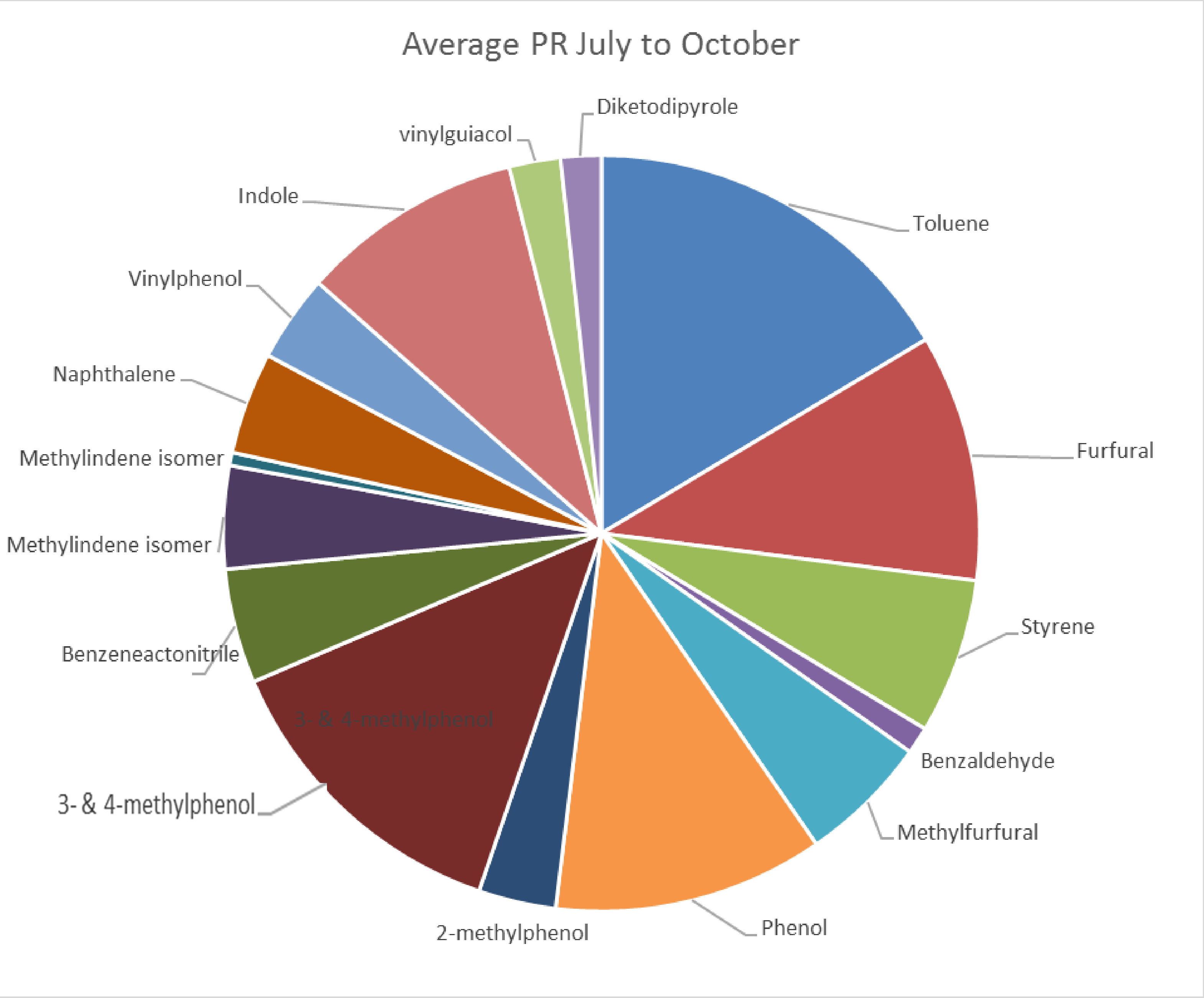
These graphs will show the average proportions for the major pyrolysis products measured between July and October.



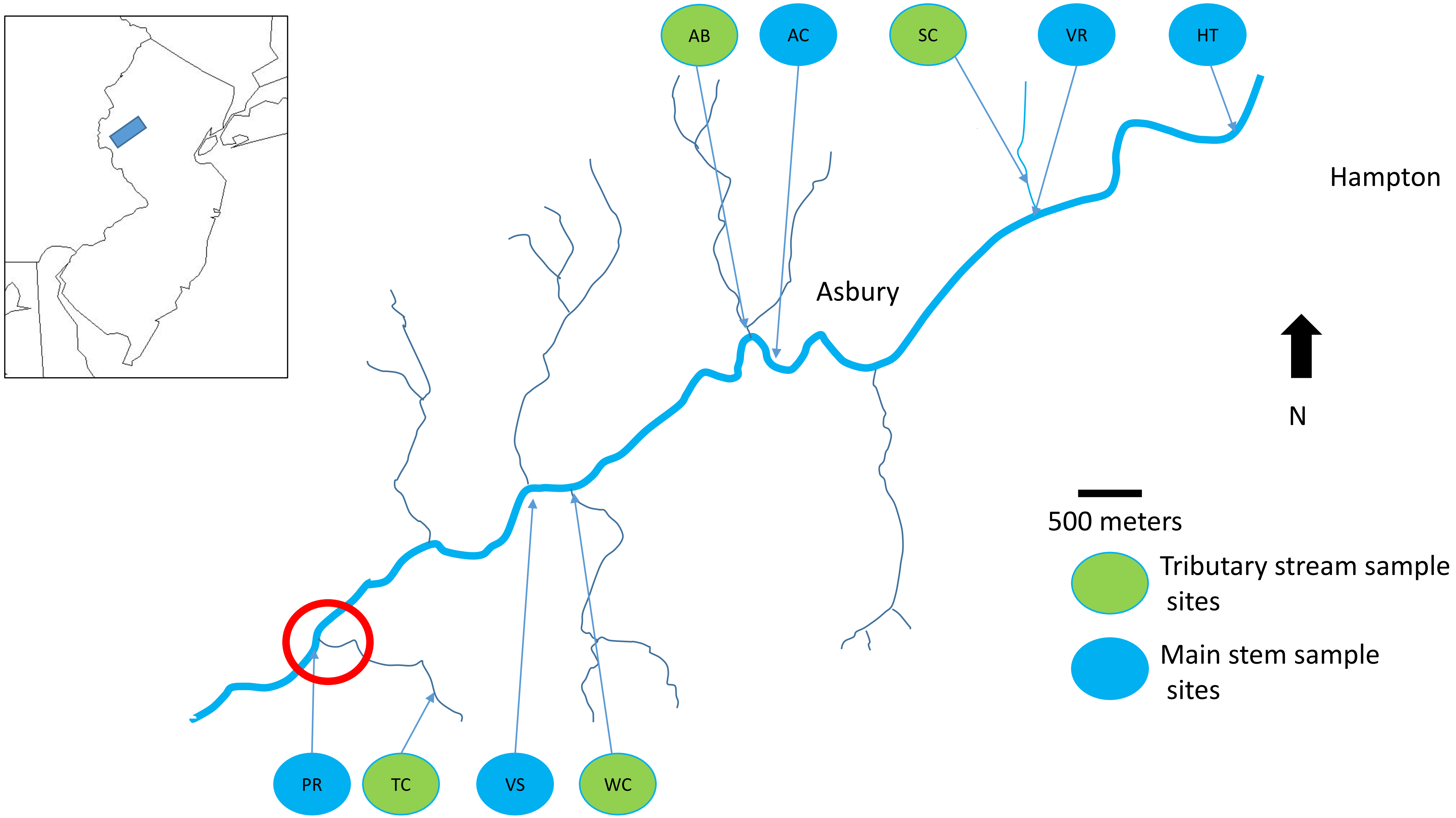
Sample Point HT is just downstream of the Route 31 bridge west of the town center at the borough park.


AB
AC
SC
VR
HT
Hampton
Asbury
N
500 meters
Tributary stream sample sites
Main stem sample sites
PR
TC
VS
WC

Water leaves the study area at sample Point PR it is located north of I-78 in Bloomsbury, New Jersey.



Sample Point PR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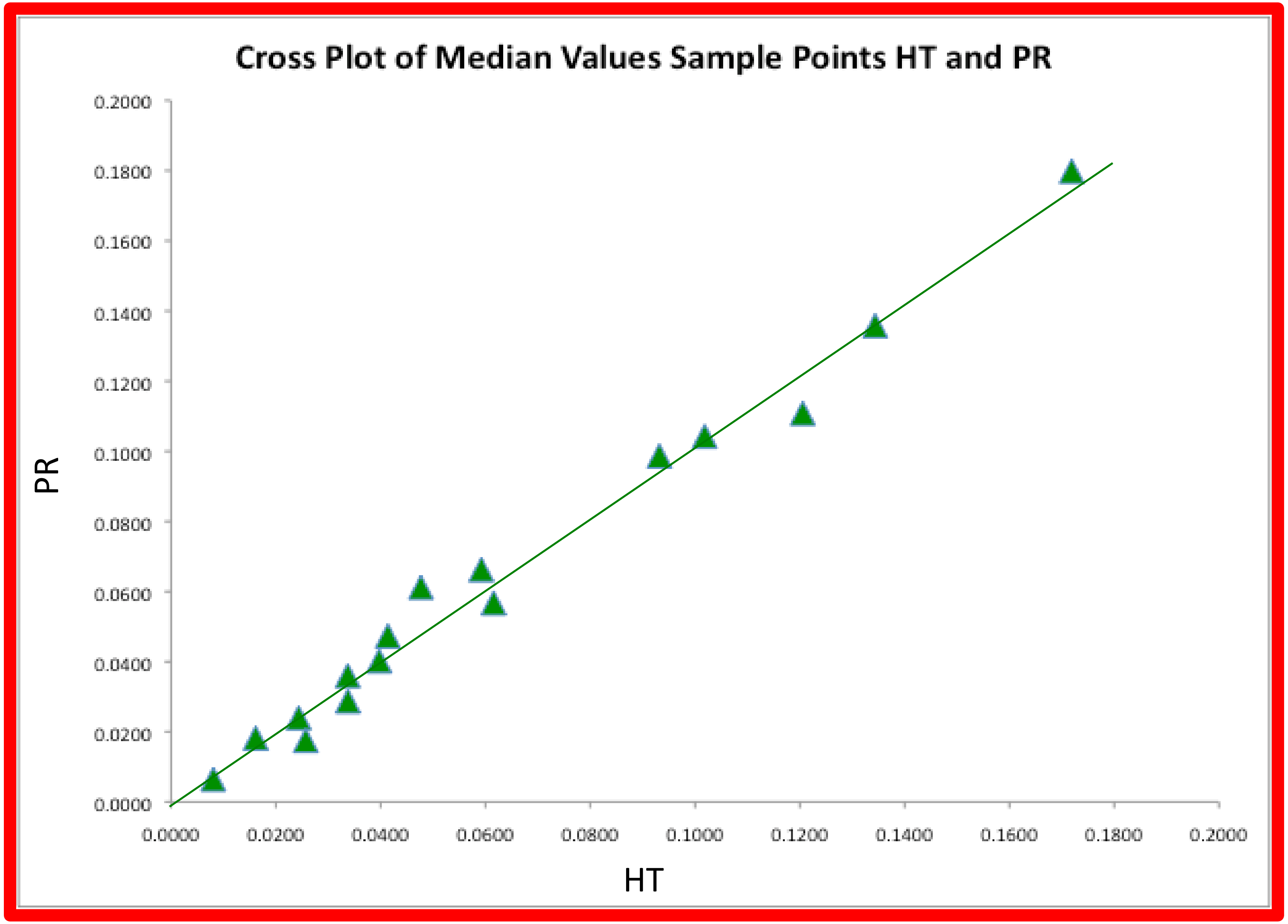


In this plot, the median values for of all major pyrolysis products were calculated. The calculation spanned the time from July to October.

The values for each pyrolysis products from point HT are on the X axis and the corresponding values for point PR, are on the Y axis.

The resulting trend line is straight (r = 0.996) and this suggests that the distribution of the pyrolysis products are essentially the same at both sample points throughout the study period.

Compound	PR/HT
Diketodipyrole	0.6810
Methylindene isomer	0.7991
Naphthalene	0.8507
Phenol	0.9193
Methylfurfural	0.9212
vinylguiacol	0.9848
3- & 4-methylphenol	1.0106
Vinylphenol	1.0125
Furfural	1.0237
Toluene	1.0462
Indole	1.0586
2-methylphenol	1.0680
Styrene	1.1186
Benzaldehyde	1.1273
Methylindene isomer	1.1437
Benzeneactonitrile	1.2827

More abundant at sample point HT:

- Diketodipyrole which is an algal pyrolysis product
- Methylindene which is a nitrogen compound
- Lignin and vascular plant biomarkers
- Possible microbial biomarkers

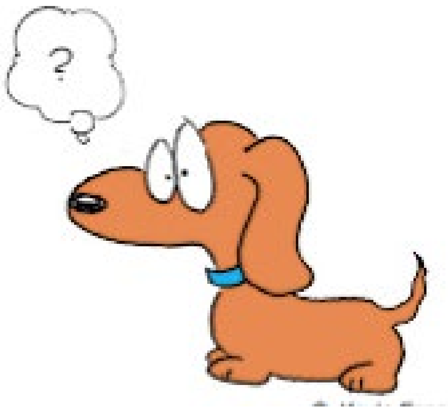
More abundant at sample point PR:

- Indole which is an algal pyrolysis product
- Methylindene and Benzeneacetonitrile which are nitrogen compounds
- Lignin and vascular plant biomarkers
- Possible microbial biomarkers

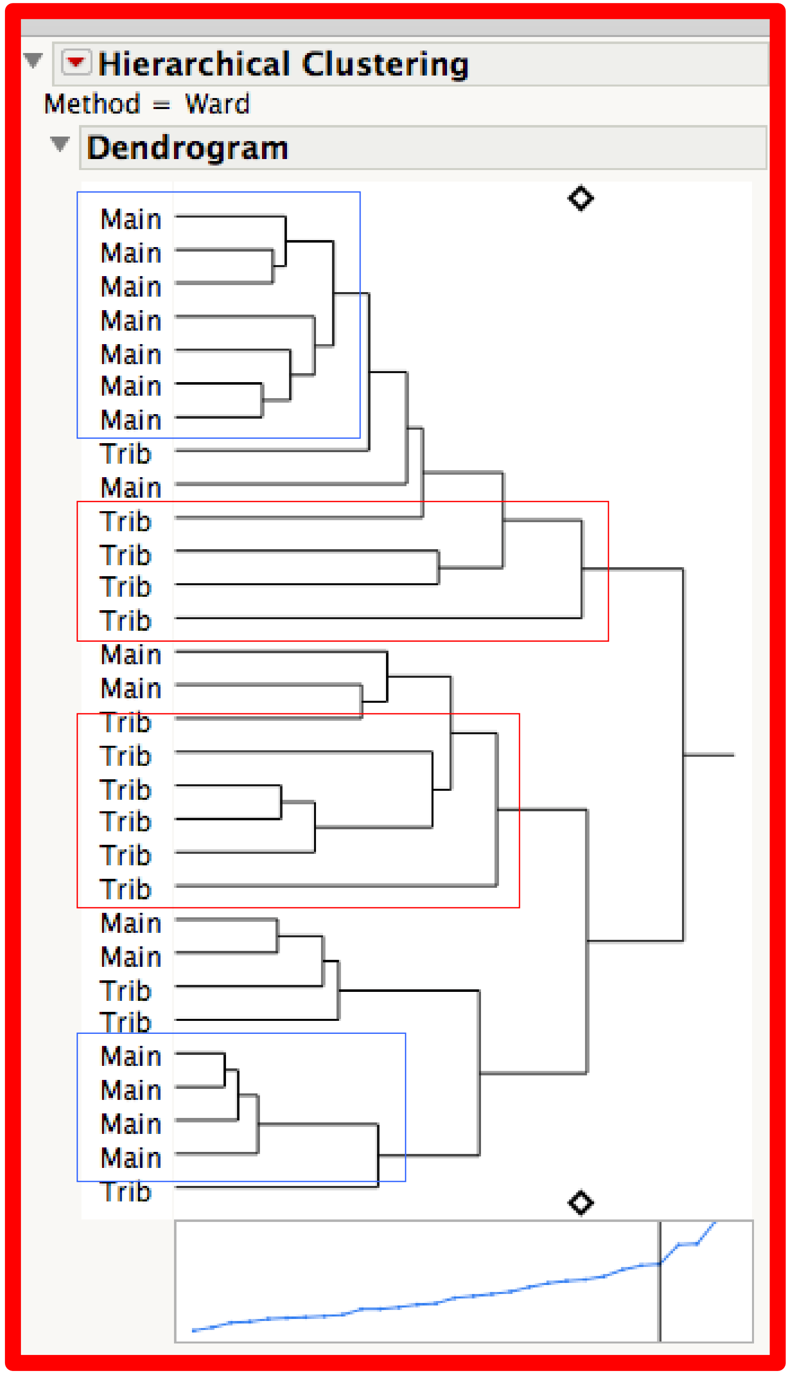
In other words, it is very hard to distinguish pyrolysis product distribution between one site to the other

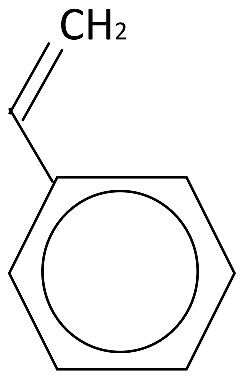
The organic matter suspended in the water entering the study area and the water leaving the study area are very similar.

We should ask if there are substantial differences between the main stem and the tributaries?



When we subject all data, including water quality information, to an Hierarchical Clustering analysis in JMP, we see distinct groupings.

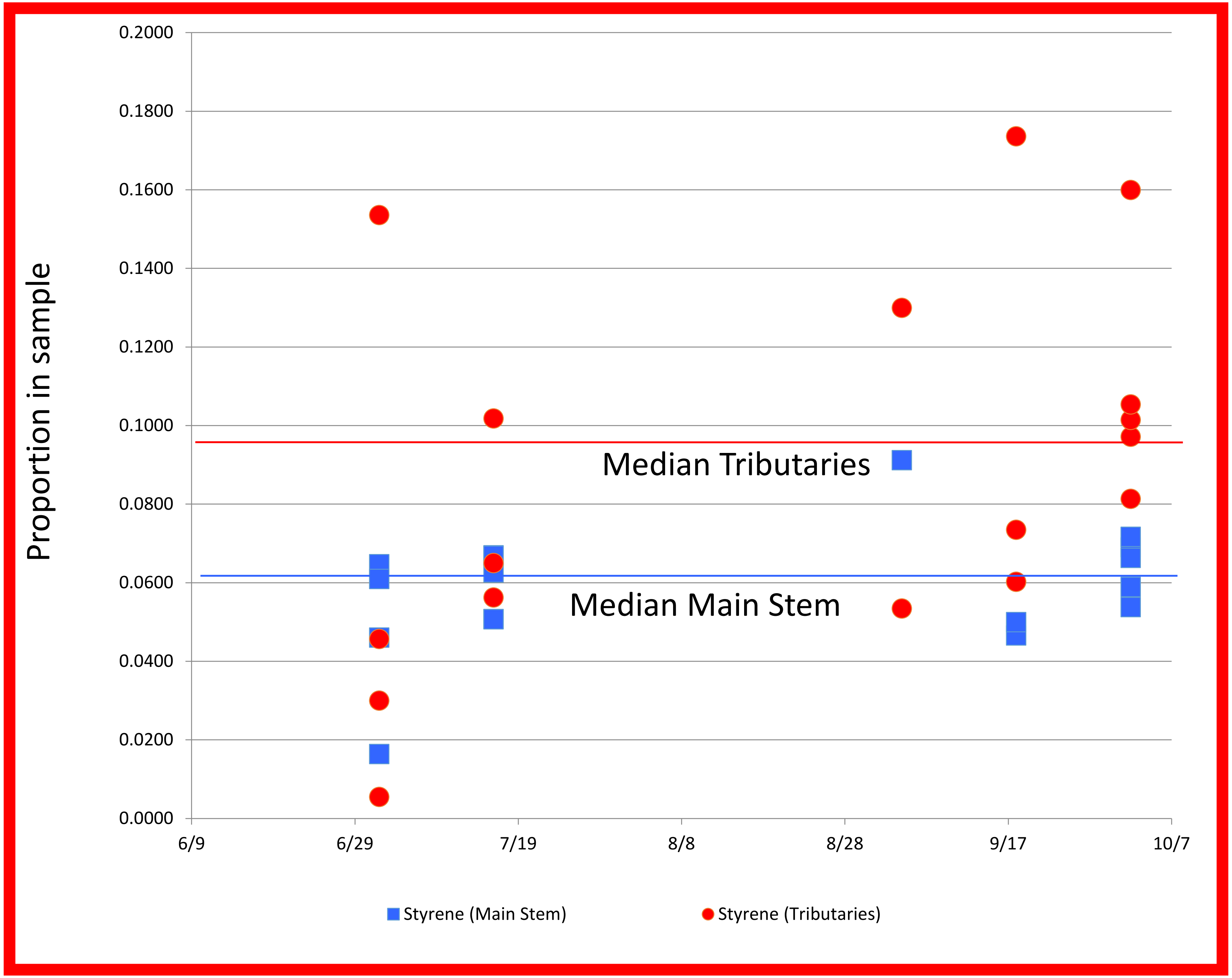


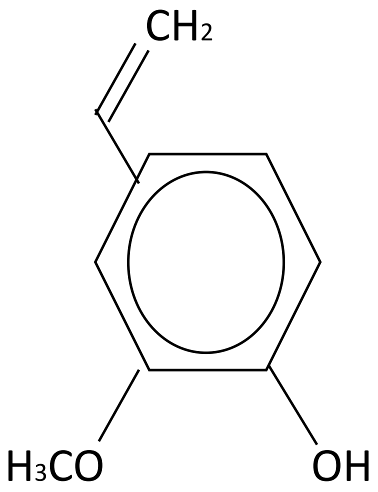


Styrene is a known pyrolysis product of humic acids.

However, is not the only product of humic acids and there are other potential sources.

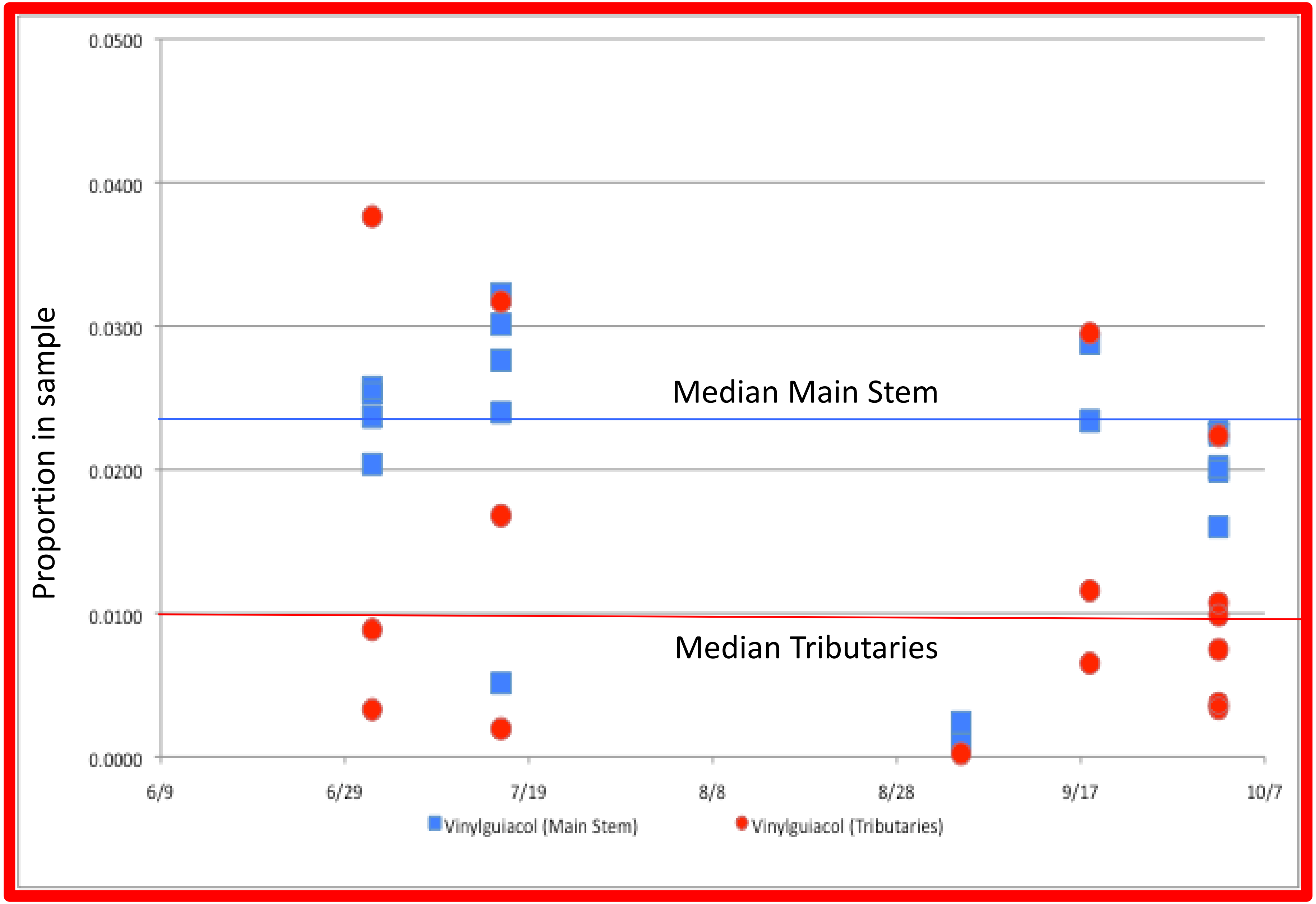
It is more of a strong suggestion about the origins of the TSS-Py-GC/MS organic matter than a definitive marker.





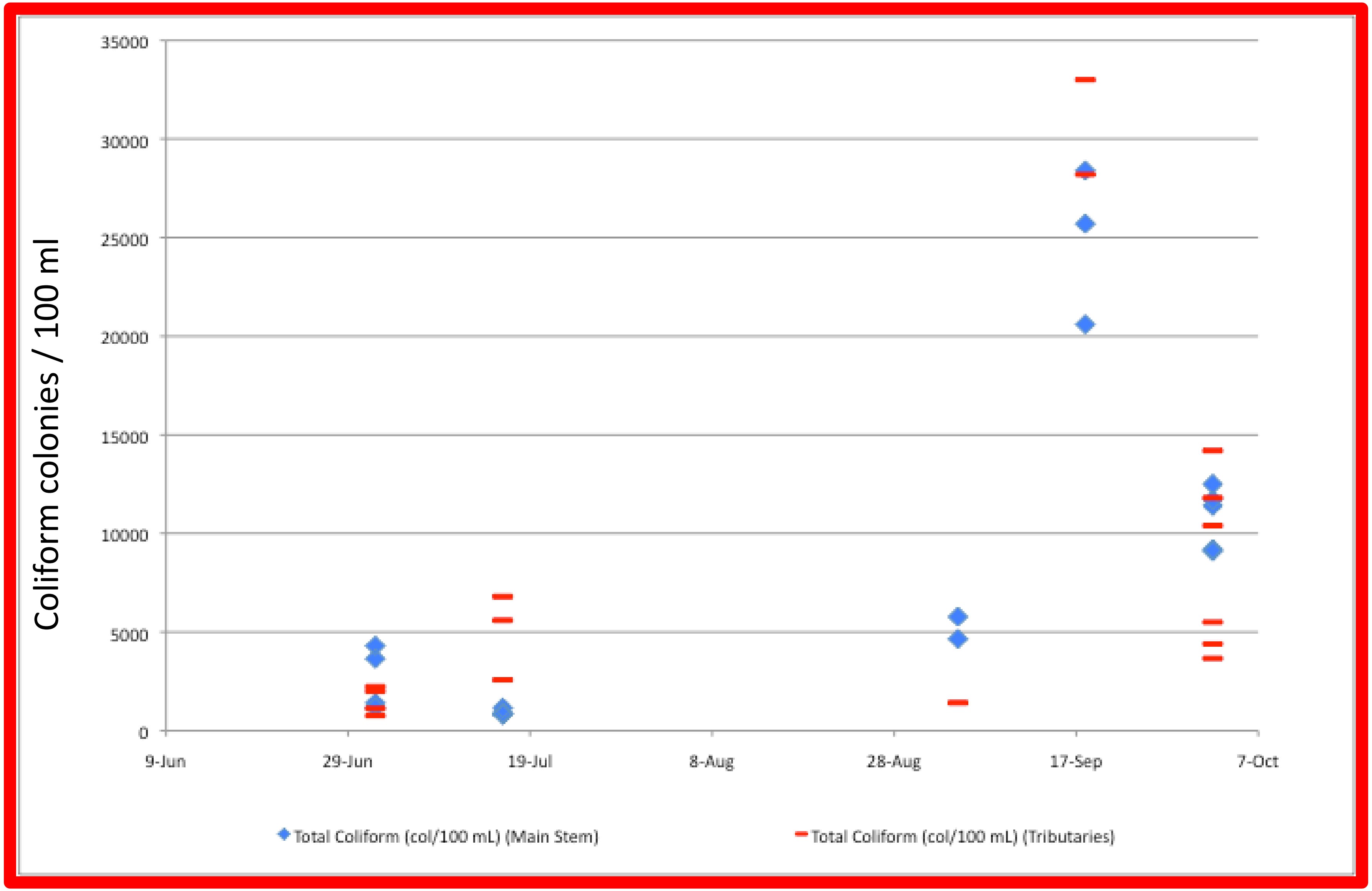
Vinylguaiacol is a known pyrolysis product of vascular plant lignins.

Note that it is more abundant in the main stem samples.

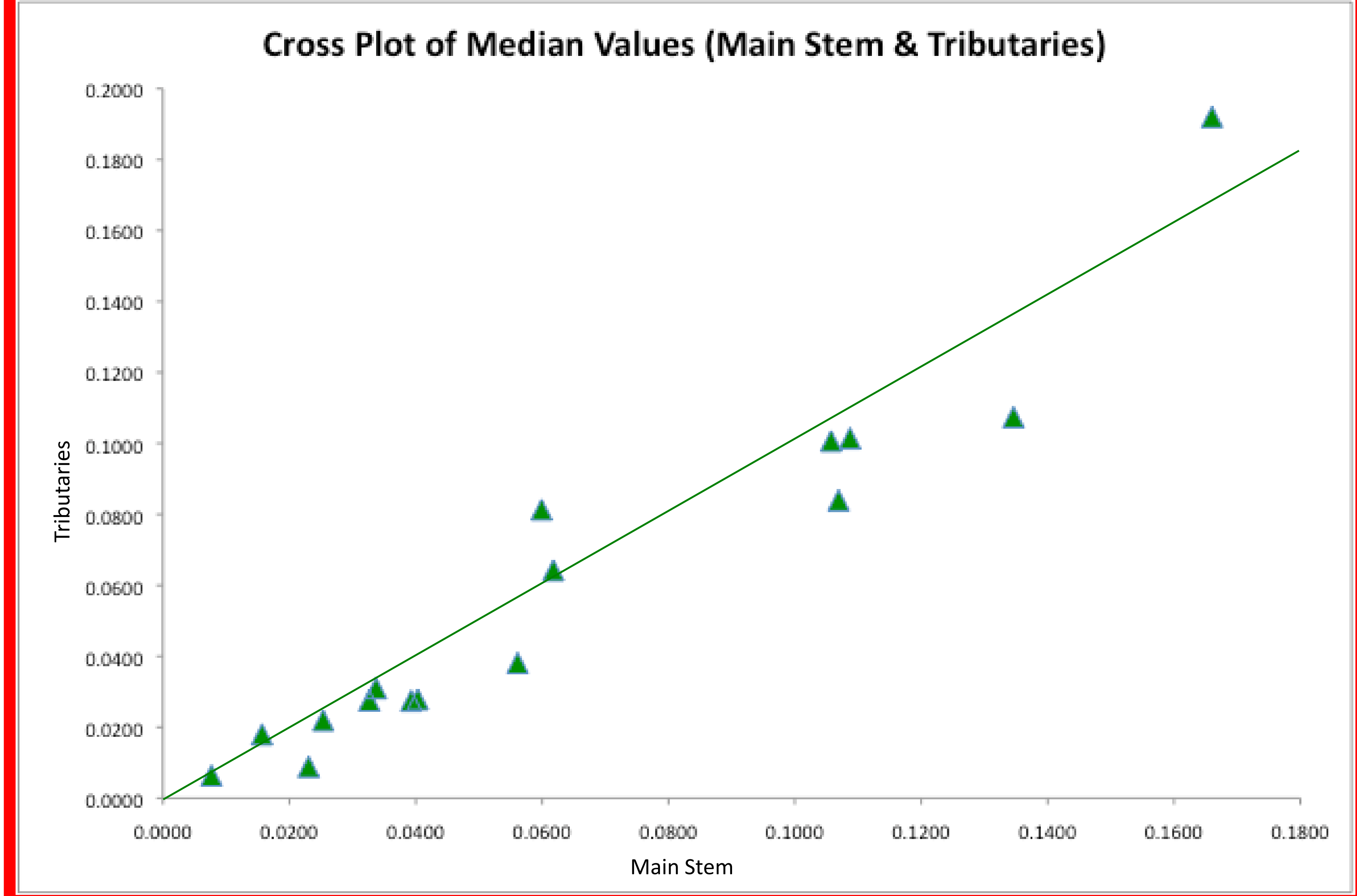


The bacterial sample counts are provided for the interested reader.

There appears to be little difference in bacteria levels in the main stem and the tributaries.



	Total Coliform (col/100 mL) (Main Stem)	Total Coliform (col/100 mL) (Tributaries)
Median	4650	4950
Mean	8113	8354


Cross Plot of Median Values (Main Stem & Tributaries)
0.2000
0.1800
0.1600
0.1400
0.1200
0.1000
0.0800
0.0600
0.0400
0.0200
0.0000
Tributaries
0.0000
0.0200
0.0400
0.0600
0.0800
0.1000
0.1200
0.1400
0.1600
0.1800
Main Stem

Compound	Main / Tributary
Styrene	0.7369
Toluene	0.8646
Benzaldehyde	0.8731
Methylfurfural	0.9618
Furfural	1.0505
Phenol	1.0720
Naphthalene	1.0902
Diketodipyrole	1.1576
2-Methylphenol	1.1873
Methylindene isomer	1.2061
3- & 4-methylphenol	1.2532
Indole	1.2736
Vinylphenol	1.4317
Methylindene isomer	1.4492
Benzeneactonitrile	1.4726
Vinylguiacol	2.6005

<u>More abundant in tributaries:</u>

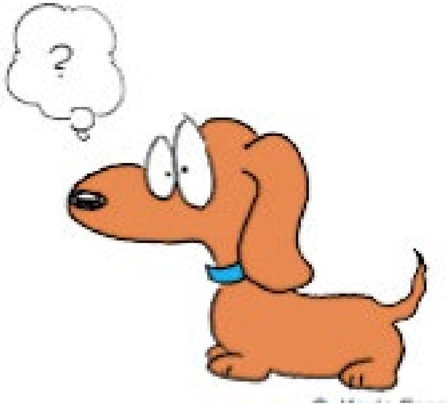
- Humic acid pyrolysis products.
- Very slight excess of methylfurfural which can be a bacterial pyrolysis product.

<u>More abundant in main stem:</u>

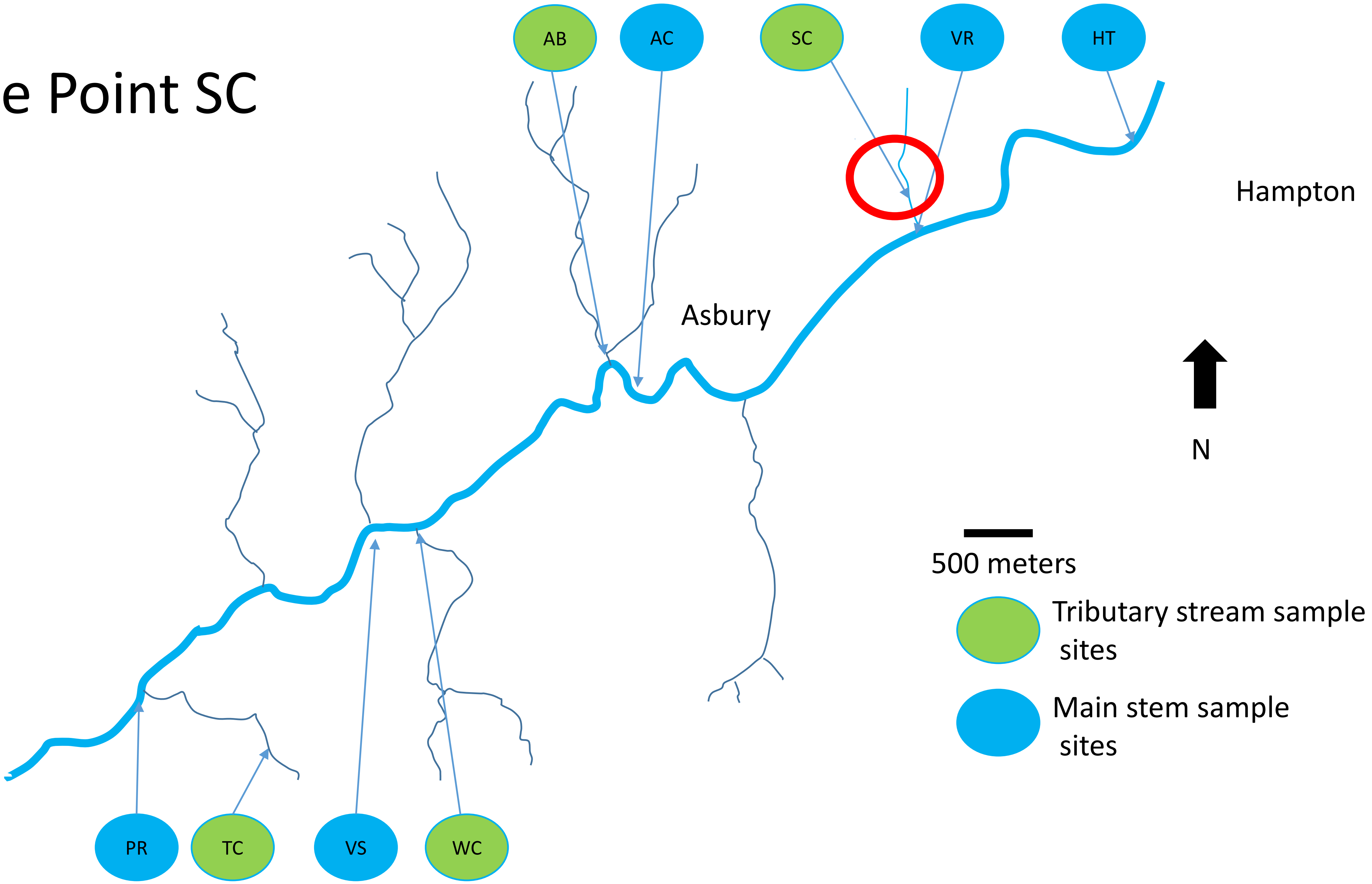
- Lignin and other vascular plant pyrolysis products.
- Nitrogen containing compounds including algal pyrolysis products.

What can TSS-Py-GC/MS show us about specific sample points?

Let’s look at one point as an example.

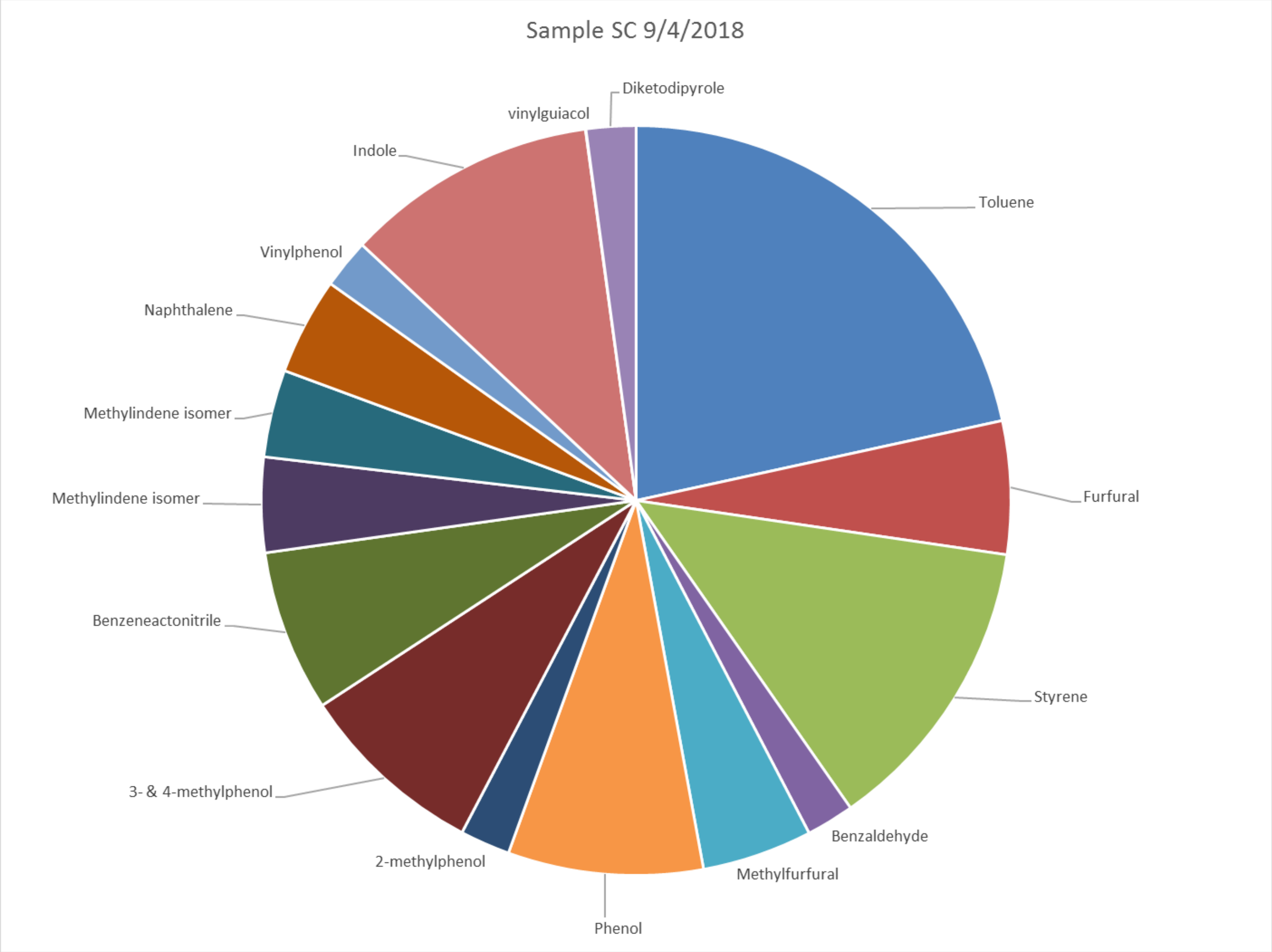


Sample Point SC



SC

The proportions of the pyrolysis products in the beginning of September looks fairly typical for the project area.



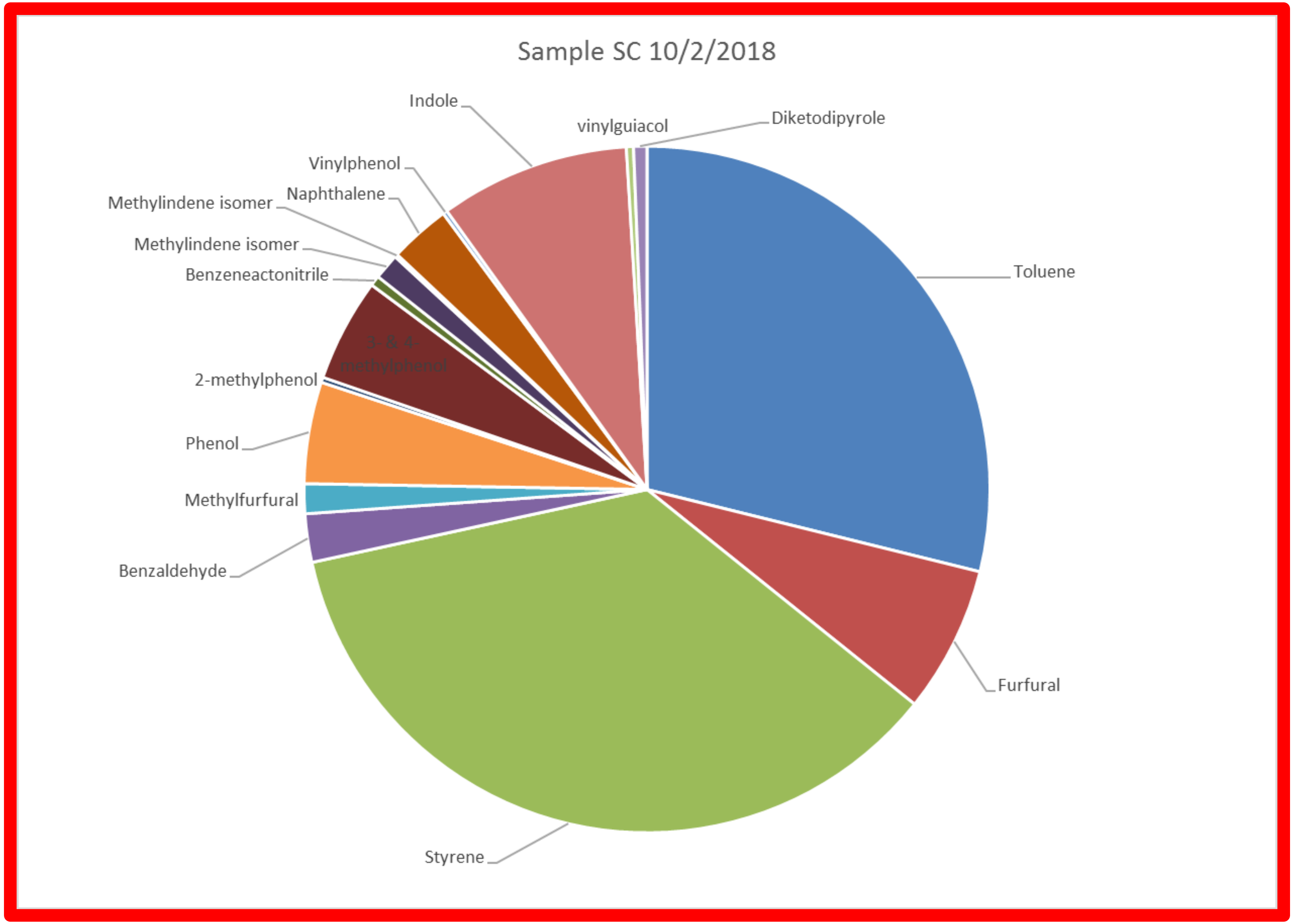
Sample point SC is a tributary that drains an agricultural area

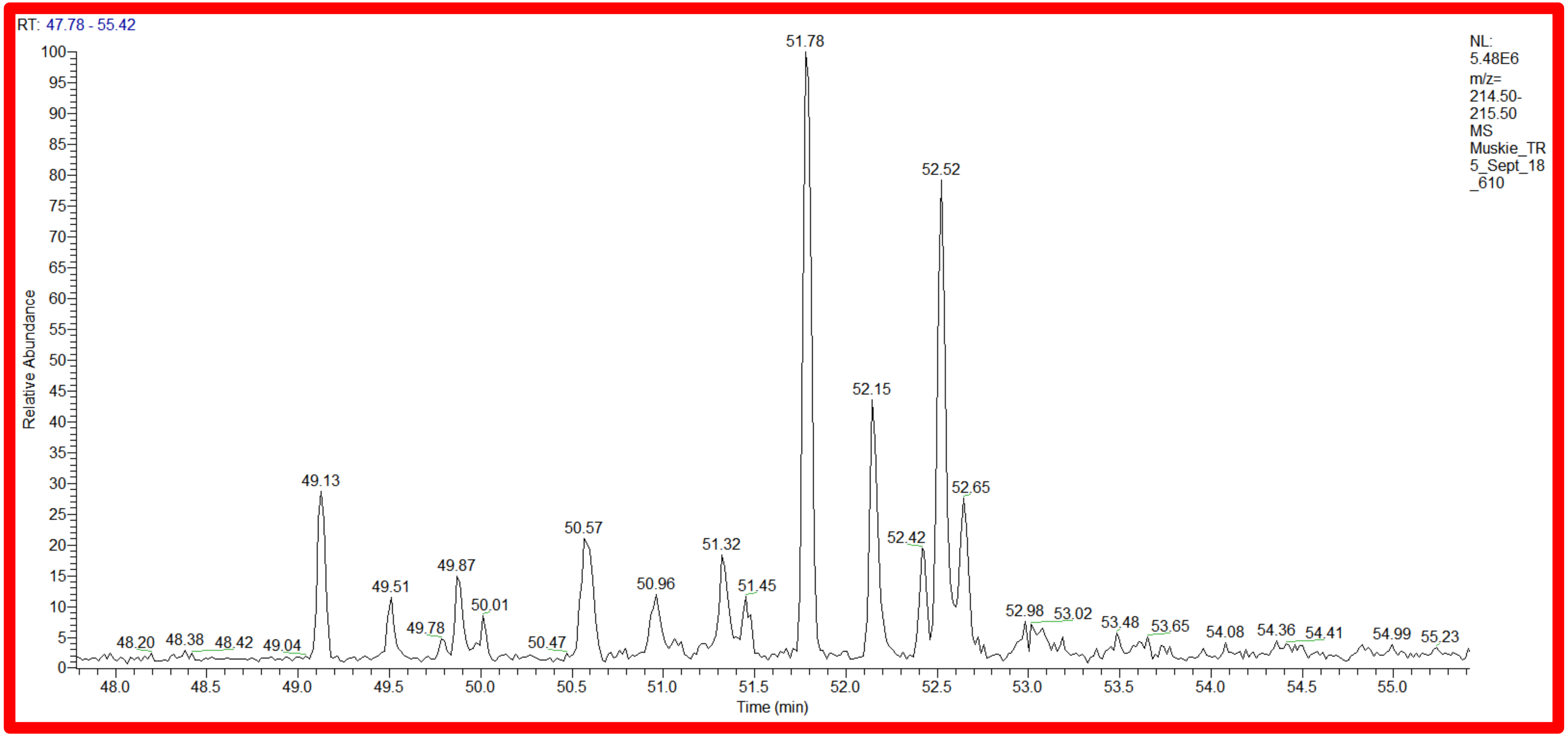
SC

About a month later, the proportions of styrene and toluene increased dramatically.

Why might this happen?

1. Total coliforms (colonies/100 ml) more than doubled, from 1409 in September to 3667 in October. (More bacteria producing more humic acids?)
2. TSS Declined from 6.6 to 1.2 ppm (Has the nature of the TSS organic matter changed?)
3. Nitrates, bio-available phosphorus, and total phosphorus were all comparable.
4. Discharge went from 2.902 to 3.242 cubic feet/second

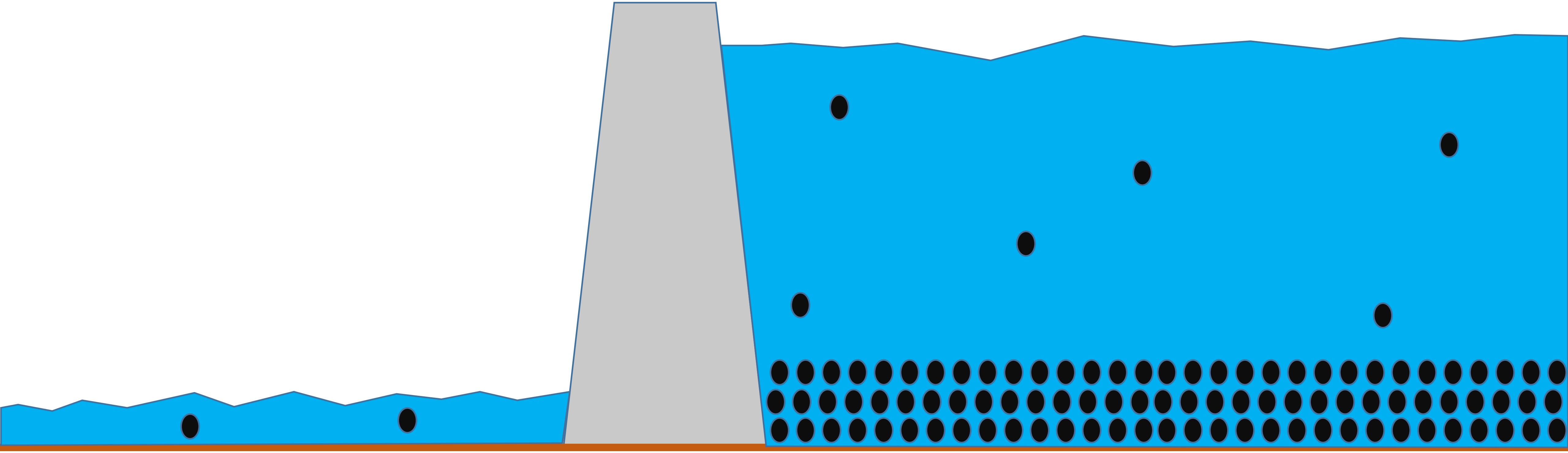




Cholestenes found in sample point SC TSS for Sept 18.

In the September 18th sample, there were abundant cholestenes. These compounds are part of a group of 4-cyclic molecules derived from steroids or sterols. They usually indicate fecal contamination in sediments. The identity of individual peaks has not been determined at this time.

What does it mean for the Sediment Shed?



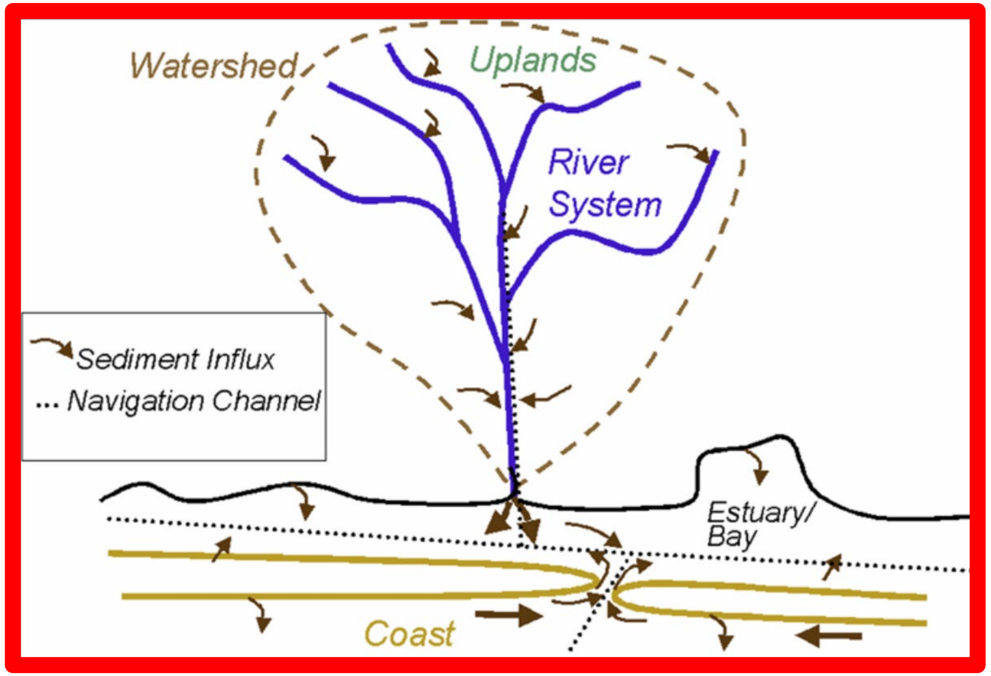
Throughout the world, the ability of many coastal regions to provide ecosystem services is compromised by a shortage of sediments.

There are an estimated 45,000 large dams in the world storing approximately 7000 cubic kilometers of water and trapping an estimated 25% of global sediment load.

These sediments and the nutrients they contain never reach the coasts. Shrinking deltas, marsh loss, and beach erosion are well known problems that result from a shortage of sand and fine particles.

We also have to ask how trapping the organic matter behind dams is also affecting coastal ecosystems?

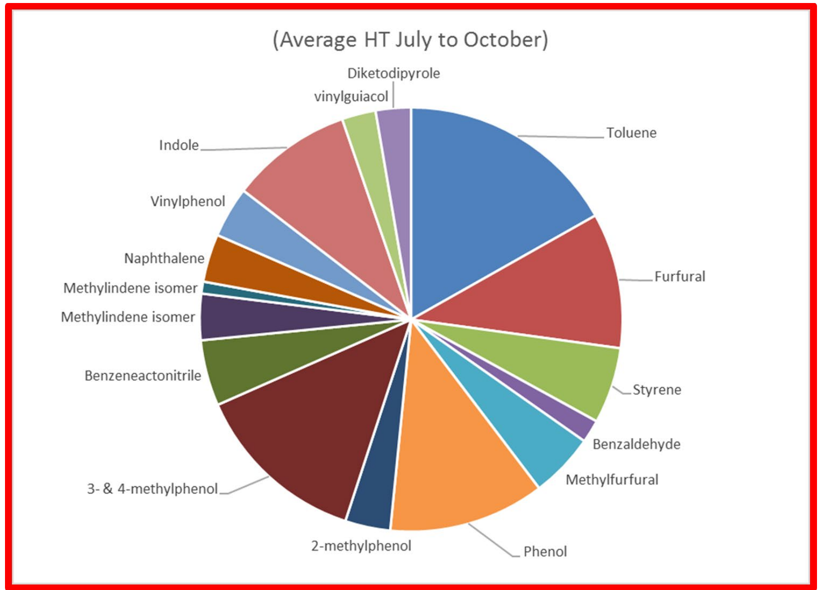
Hopefully TSS-Py-GC/MS will help answer this question.

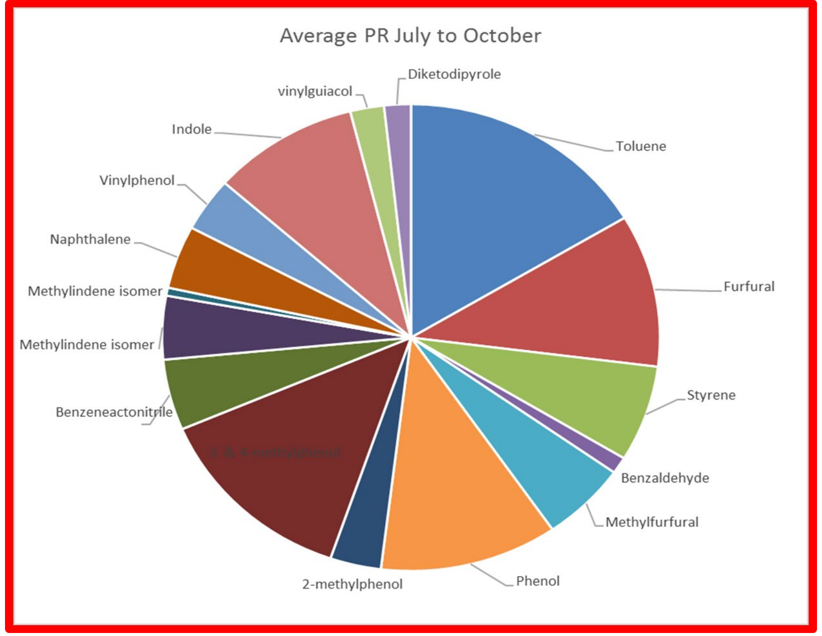


Coastal Sediment Transport, USACE

Conclusions - 1

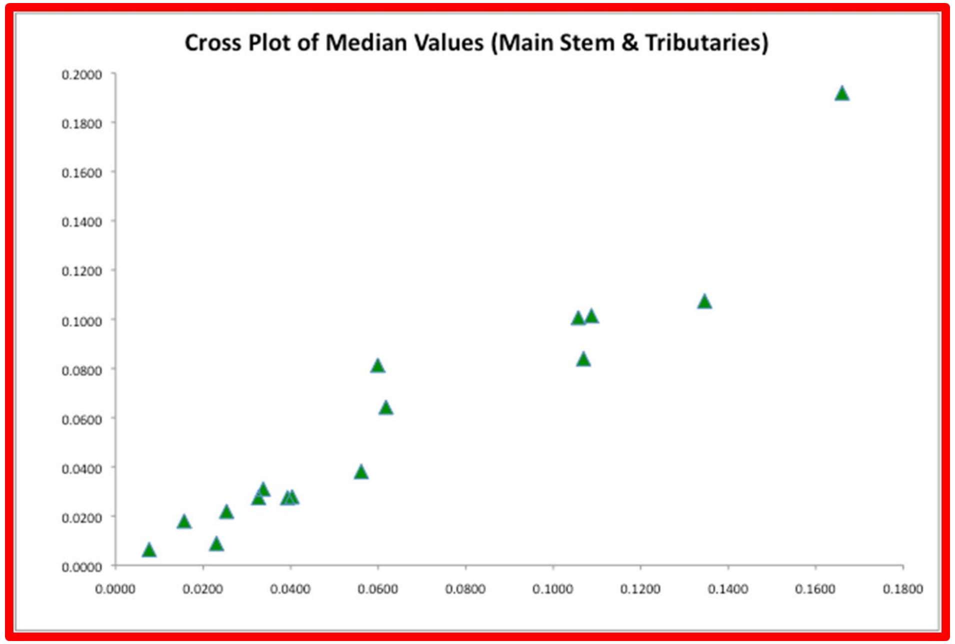
- The Musconetcong River water leaving the study area has essentially the same TSS-Py-GC/MS profile as water entering the study area, though there does seem to be a small dilution of the algal pyrolysis products.





Conclusions - 2

- The TSS-Py-GC/MS profiles of the tributary streams differ from the main stem of the river. There is a very strong suggestion that the tributaries were enriched in humic acids. Much of the main stream organic matter appears to originate with lignins and vascular plants. The main stem is also richer in nitrogenous organic matter.



Conclusions - 3

- The TSS-Py-GC/MS can provide insight into conditions at individual sample sites.

Thank you to the field work crew who did all of the hard work, while I sat in the air conditioned lab

David Hsu

Alessandra Rossi, Eddie Wong, Kevin W. Zerbe (Kevin did all of the TSS samples, thank you!)

THANK YOU

Musconetcong River and valley, NY / NJ Trail Conference