# UPDATE AND PHASE 2 RESULTS TONAWANDA COKE SOIL STUDY

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November 21, 2019

# Overview

- Background on the Tonawanda Coke Soil Study
  - History
  - Study Goals
- Latest Results for the Public
  - Sampling report for Phase 2
  - Maps generated
  - What this means for residents
- Current efforts
  - Source apportionment

# US vs. Tonawanda Coke Corporation

- Decided in March, 2013: Appeal Denied Jan 2016
- Found TCC guilty of violations of US Clean Air Act
- Fined $12.5M
- Additionally, directed $12.1 M toward follow-up community studies
  - 10 year epidemiology and health (Tonawanda/Grand Island Health Study)
  - TCC went into Bankruptcy and failed to pay the final $2M payment for the Health Study
  - (Tonawanda Coke Soil Study) A study of neighborhood soil contamination from deposition of air pollution ***originating from Tonawanda Coke Corp.***
  - **Both projects were awarded to UB; UB waived all overhead (ca. $4M) but agreed to provide all services normally funded by overhead**

# TONAWANDA COKE SOIL STUDY **TIMELINE**

## 2016

### PLANNING

Soil study was initiated, with project staff hired.

## 2017

### PHASE 1

Scientists from the U.S. Environmental Protection Agency (EPA) and New York State Department of Environmental Conservation (DEC) reviewed and provided feedback on the study's standard operating procedures.

Community meetings were held, and a community advisory committee established.

About 160 soil samples were taken in Grand Island, the City of Tonawanda, the Town of Tonawanda and North Buffalo. Sampling was done, where possible, in an evenly distributed grid, with the goal of screening for pollutants.

## 2018

### PHASE 2 BEGINS

EPA and DEC scientists reviewed and provided feedback on Phase 1 findings.

About 130 new samples were taken, focusing on regions of interest identified through Phase 1 sampling, and on schools and churches. The regions of interest are regions where a number of soil samples contained higher levels of selected pollutants than the directly surrounding area.

## 2019

### PHASE 2 CONTINUES

EPA and DEC scientists reviewed and provided feedback on Phase 2 findings.

Scientists at UB and SUNY Fredonia use advanced analytical and statistical techniques (source apportionment) to study whether pollutants found in soil may have originated from the Tonawanda Coke plant.

Community meetings are held in January and November, respectively, to share Phase 1 and Phase 2 findings.

## 2020

### STUDY CONCLUDES (ANTICIPATED)

The study is expected to conclude in 2020, with scientists completing the source apportionment research.

Findings will be sent to EPA and DEC scientists for review, and a community meeting will be planned to share the study's conclusions with the public.

# Completed Sampling and Testing components of Soil Study previously reported in January 2019

- Phase 1 survey study using geographic grid design
  - Learn where regions of interest are located
  - Learn geographic extent of pollutant deposition
  - Learn what pollutants are distributed in the community
  - Public meeting January 16, 2019, released Phase 1 maps and ROI Map
- 182 samples taken, evaluated public data from 65 superfund sites in the test grid area
  - Testing for 169 chemicals at ALS Laboratories, Rochester, NY (NYS DOH Certified)
  - Heavy metals, VOCs, SVOCs, PCBs, Pesticides, PAHs

# Definitions

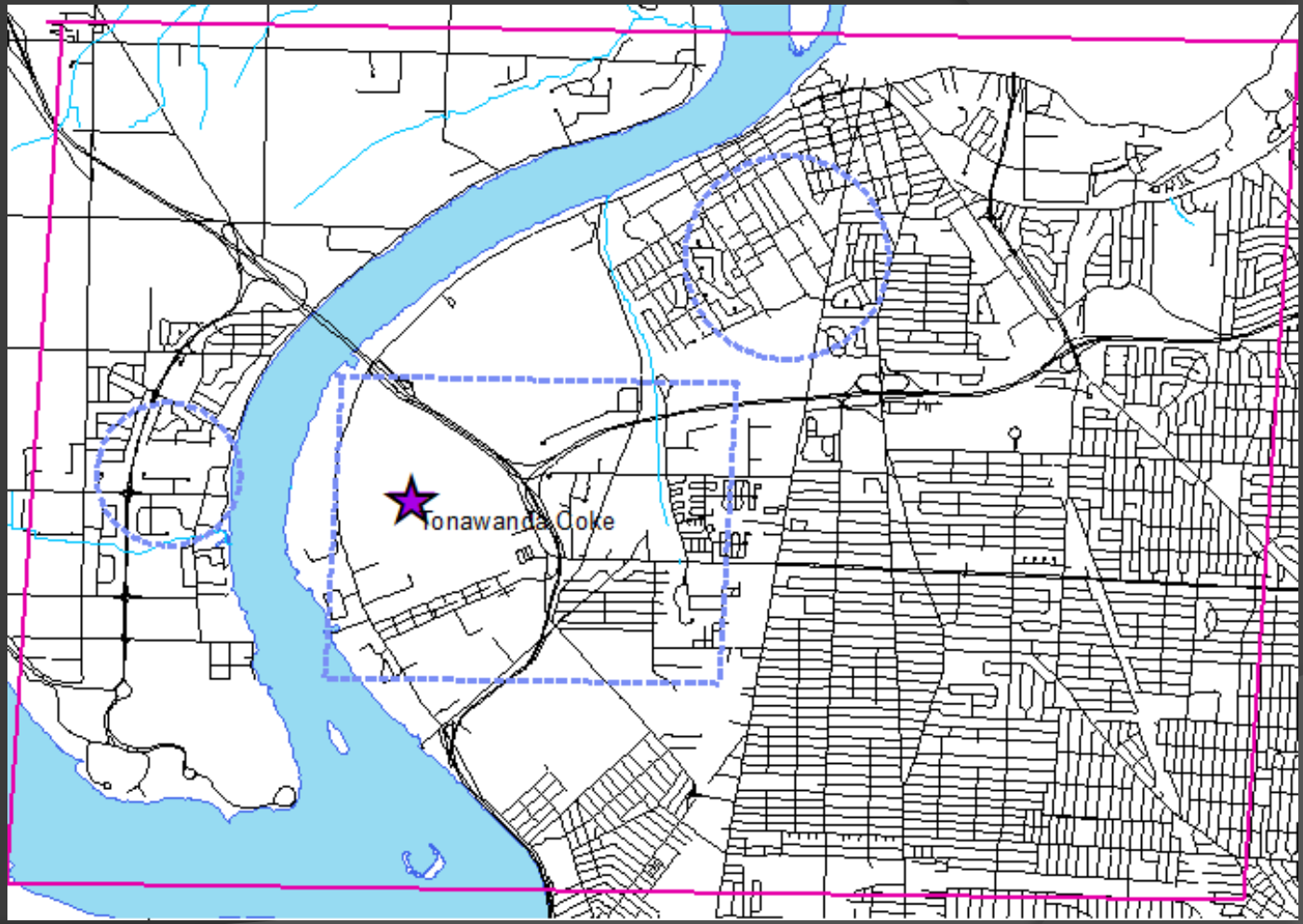
- Contaminant
  - Any physical, chemical, biological, or radioactive substance that can adversely affect air, water or soil.
- Region of Interest (ROI)
  - A region or area known to have high concentrations of a contaminant
- Soil Cleanup Objective (SCO)
  - the concentration of a given contaminant for a specific site that must be achieved under a remedial program for soil.

EPA Terminology Service:
https://iaspub.epa.gov/sor_internet/registry/termreg/searchandretrieve/termsandacrony

NYS-DEC CP-51 / Soil Cleanup Guidance

# Regions of Interest

- Solid pink outline: Study Boundary
- Purple Star: Tonawanda Coke Plant
- Dashed blue lines: Regions of Interest




Credit: Tammy Milillo / Tonawanda Coke Soil

# Current Phase 2 of Soil Study

- Phase 2: study the ROIs identified in phase 1 (COMPLETED)
- Establish boundaries of any potential contamination (COMPLETED)
- Soil and air sampling at Tonawanda Coke for Source Apportionment (COMPLETED)
- Air Sampling of residences in area (now for background data) (Analysis under way)

- Innovative methods to identify source(s) of pollutants in soil (including air sample and soil samples from TCC) (UB and Fredonia) (Analysis under way)

- Community participation and education

- Reporting to community

# Community engagement

**The community has played a major role in the study since it began:**

- Hundreds of local residents, as well as school districts and churches, have participated by having soil sampled from their properties. Some residents and community members have volunteered to contribute to  sample collection.
- The TCC Soil Study Community Advisory Committee met about monthly during the sampling phase of the study, and members continue to be consulted as the study nears its conclusion.
- The minutes of these meetings are posted on the UB Chemistry TCC Soil Study Website: http://arts-sciences.buffalo.edu/chemistry/tonawanda-coke-soil-study.html
- About 300 soil samples from homes, schools and churches have been tested through the study, providing homeowners and other property owners with information on what chemicals are in their soil. Property owners receive a copy of lab results for their property.

# Reporting to the Public

- With consultative planning from the community advisory committee, held multiple public meetings to update the community on the study's progress, share findings, get feedback and answer questions.
- Facebook, Twitter and Instagram accounts provide information through social media
- A TCC Soil Study email account gives direct communication to Dr. Gardella
- Presented on soil sampling results at public school board meetings in districts that had soil sampled.
- Held numerous “Talks with Tammy” events, during which participants and other community members had the chance to meet with Tammy Millilo, PhD, one of the study’s core researchers, to ask questions and learn about the research.
- Distributed about 25,000 flyers door-to-door in neighborhoods involved, informing residents about the study.
- Contacted and met with elected officials on multiple occasions to discuss the study and share findings.
- Reports to the Probation Office every six months as per Judge’s order: These reports (through March 2019) are available on TCC Soil Study Website http://arts-sciences.buffalo.edu/chemistry/tonawanda-coke-soil-study.html
- New report will be uploaded as soon as it is approved by US Dept. of Justice

# Completed Sampling and Testing components of Soil Study

- Phase 2 study on three regions of interest
- Additional samples at GI Central Schools and COT Schools
- Additional Samples on north east portion of grid
- 129 samples taken in regions of interest, 87 Residential properties, 40 school properties and 2 church properties
  - Testing for ca: 100 chemicals at ALS Laboratories, Rochester, NY (NYS DOH Certified)
  - Heavy metals, SVOCs, PCBs, PAHs

# Polycyclic Aromatic Hydrocarbons (PAHs) are interpreted differently by NYS DEC and EPA

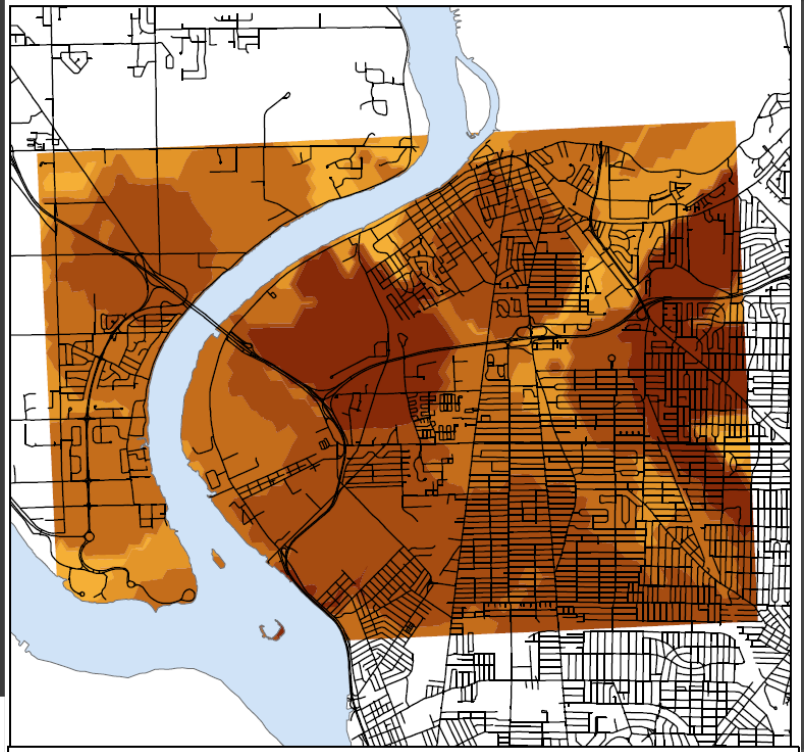
- EPA uses a method to combine all data into a single parameter to evaluate
- This is the Benzo a Pyrene (BAP) Equivalents.
- Makes chemical sense because all these PAH compounds are generated together, not separately.
- EPA SCO is 1 ppm of the combined values

- NYS DEC evaluates each result for separate PAHs
- Examines a number of PAHs with high toxicity
- An example of the distribution of one PAH is also included in Map Packet for Phase 2

# Benzo(a)Pyrene Equivalents

## Polycyclic Aromatic Hydrocarbons (PAHs)

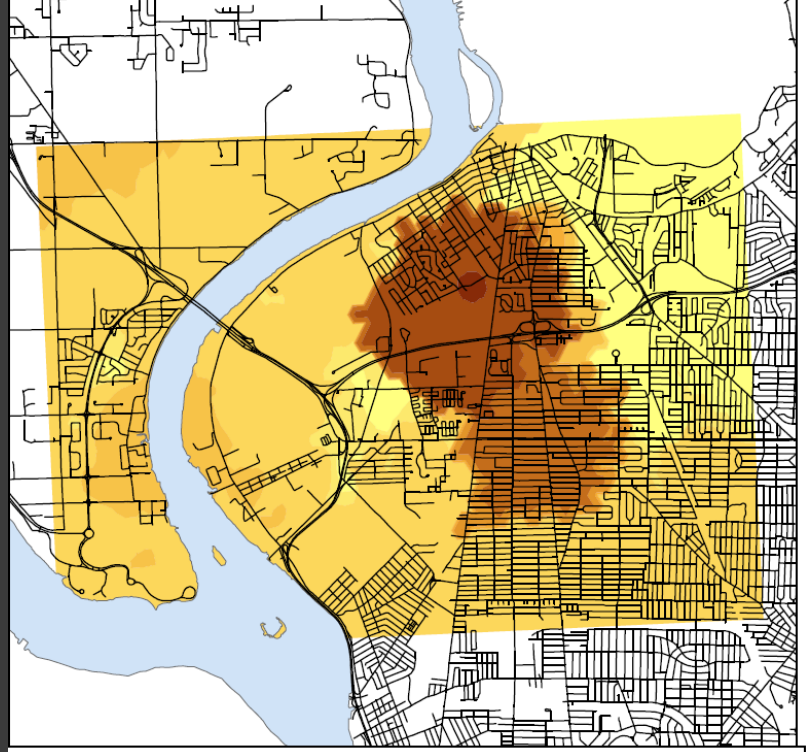
### Without Tonawanda Coke Data




Map of Benzo[a]pyrene (BAP) equivalents in mg/kg. The map shows the modeled surface, as the color darkens, the predicted concentration of BAP equivalents increases. Samples taken on properties owned by the Town of Tonawanda and the City of Tonawanda are excluded, due to lack of permission from elected officials. BAP equivalents are a measure used by the EPA to evaluate polycyclic aromatic hydrocarbon (PAH) concentrations. The TCC soil study used an SCO of 1 mg/kg for BAP equivalents. Intervals below the SCO are of no immediate concern to residents. Intervals which contain values above the SCO do not directly correlate to risk. Credit: Dr. Tammy Milillo/Tonawanda Coke Soil Study

# Aroclor 1016

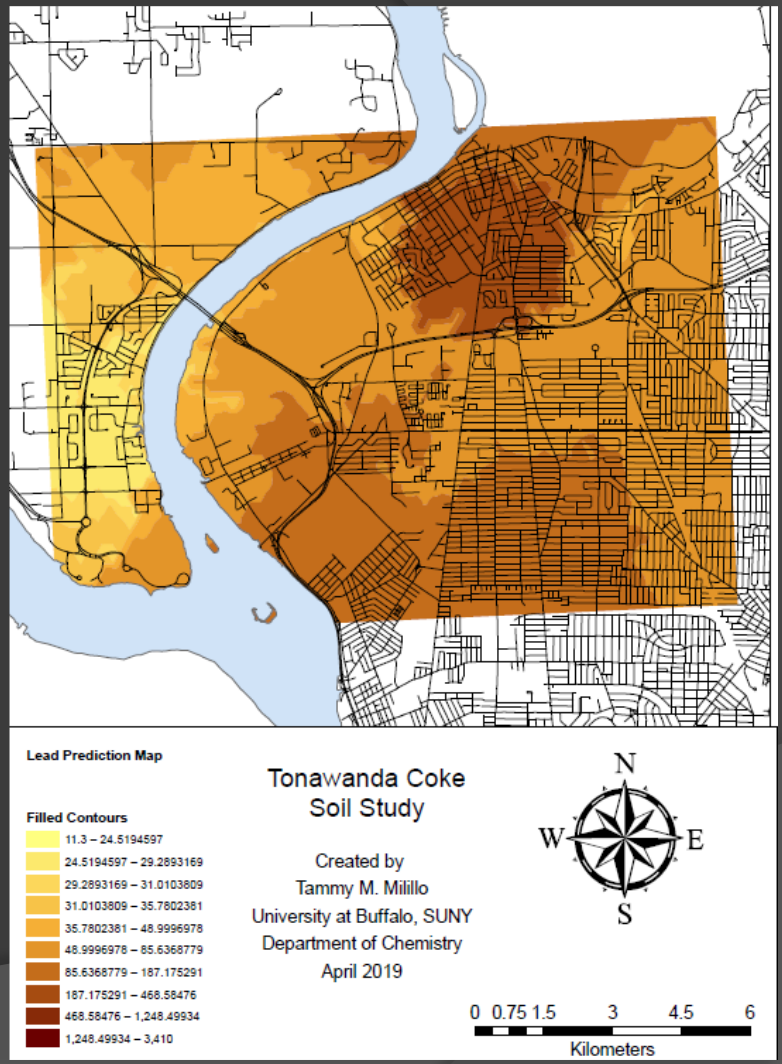
- Polychlorinated Biphenyl (PCB)
- Estimated concentration increases as color darkens
- Localized concentrations were found above SCO
- DEC Followup showed no sites at 2” with elevated levels of PCBs




Map of Arochlor 1016 in µg/kg. The map shows the modeled surface, as the color darkens, the predicted concentration of Arochlor 1016 increases. The TCC soil study used an SCO of 9000 µg/kg for Arochlor 1016. Intervals below the SCO are of no immediate concern to residents. Intervals which contain values above the SCO do not directly correlate to risk. Credit: Dr. Tammy Milillo/Tonawanda Coke Soil Study

# Lead

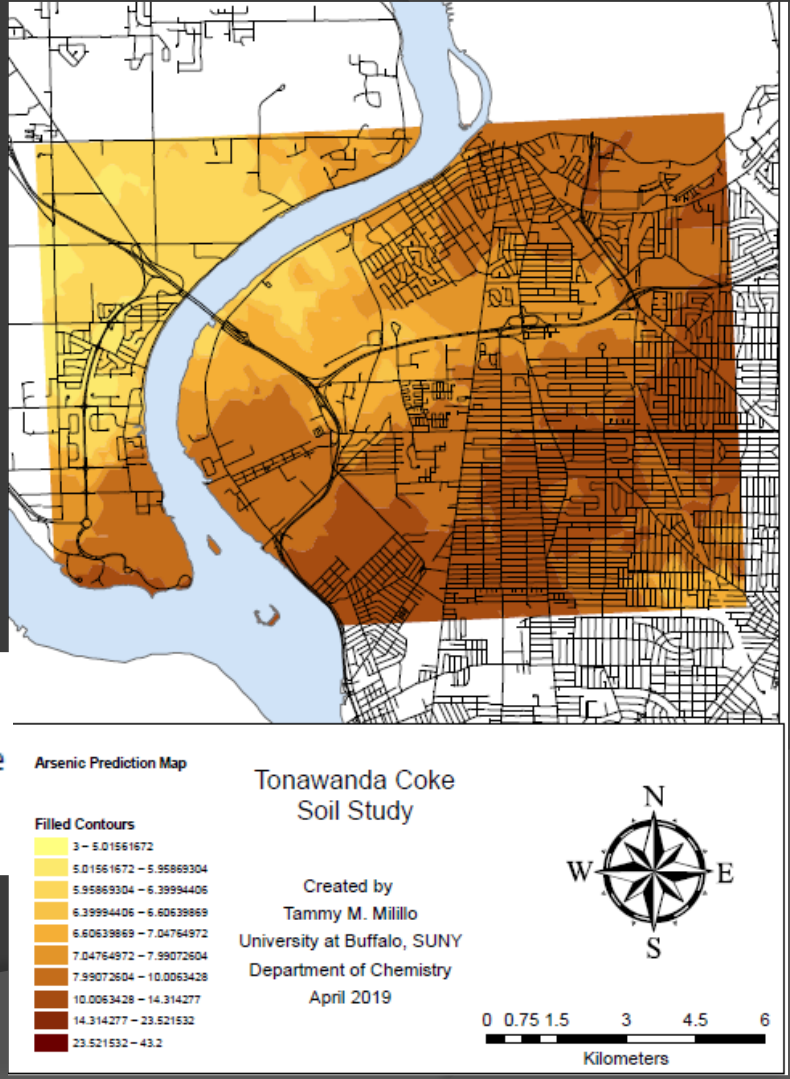
- Estimated concentration increases as color darkens
- Not every sample in the ROI exceeded the SCO level




Map of lead in mg/kg. The map shows the modeled surface, as the color darkens, the predicted concentration of lead increases. The TCC soil study used an SCO of 200 mg/kg for lead. Intervals below the SCO are of no immediate concern to residents. Intervals which contain values above the SCO do not directly correlate to risk. Credit: Dr. Tammy Milillo/Tonawanda Coke Soil Study

# Arsenic

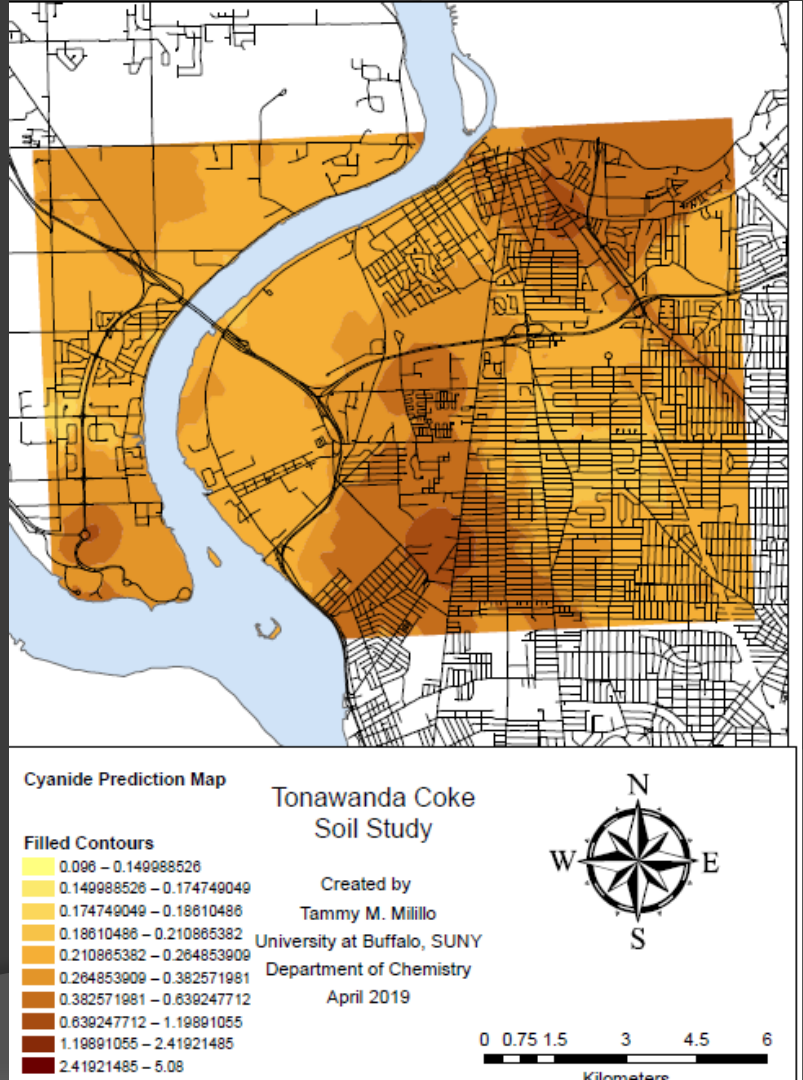
- More study by source apportionment methods needed to determine origins of arsenic




Map of arsenic in mg/kg. The map shows the modeled surface, as the color darkens, the predicted concentration of arsenic increases. The TCC soil study used an SCO of 8 mg/kg for arsenic. Intervals below the SCO are of no immediate concern to residents. Intervals which contain values above the SCO do not directly correlate to risk. Credit: Dr. Tammy Milillo/Tonawanda Coke Soil Study

# Cyanide

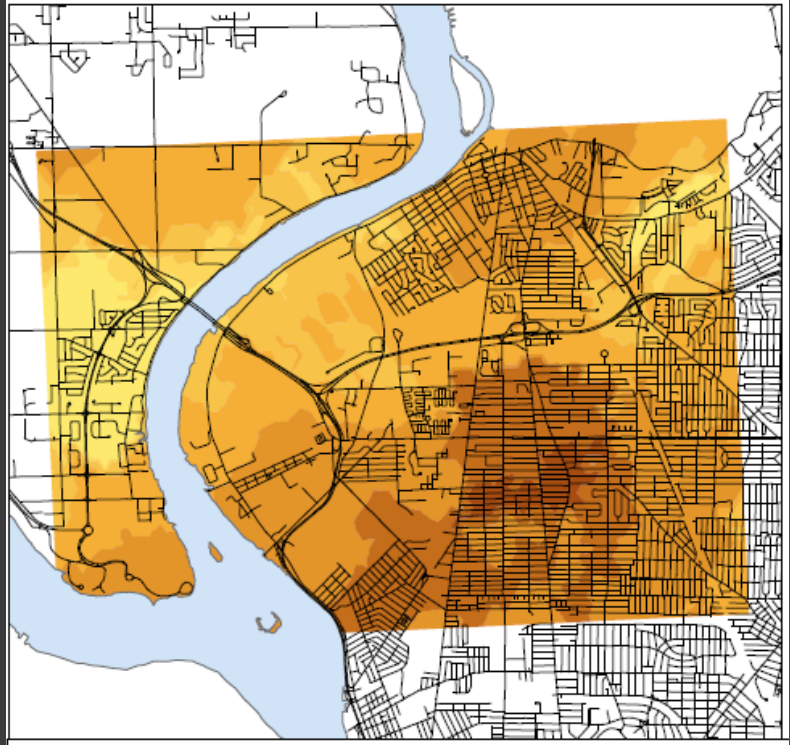
- Chemical of concern based on contamination found on TCC site
- Shows elevated levels not above DEC's SCO
- Important for source apportionment analysis




Map of cyanide in mg/kg. The map shows the modeled surface, as the color darkens, the predicted concentration of cyanide increases. The TCC soil study used an SCO of 27 mg/kg for cyanide. Intervals below the SCO are of no immediate concern to residents. Intervals which contain values above the SCO do not directly correlate to risk. Cyanide is not a suspected contaminant from Tonawanda Coke, but it may provide necessary information for distinguishing Tonawanda Coke Corporation impact compared to other industries in the area. Credit: Dr. Tammy Milillo/Tonawanda Coke Soil Study

# Mercury

- Not a known TCC contaminant
  - Known contaminant from the Huntley plant
- Court Order included determining historic impact of TCC only
  - Source apportionment




Map of mercury in mg/kg. The map shows the modeled surface, as the color darkens, the predicted concentration of mercury increases. The TCC soil study used an SCO of 0.1 mg/kg for mercury. Intervals below the SCO are of no immediate concern to residents. Intervals which contain values above the SCO do not directly correlate to risk. Credit: Dr. Tammy Milillo/Tonawanda Coke Soil Study

# City of Tonawanda Schools

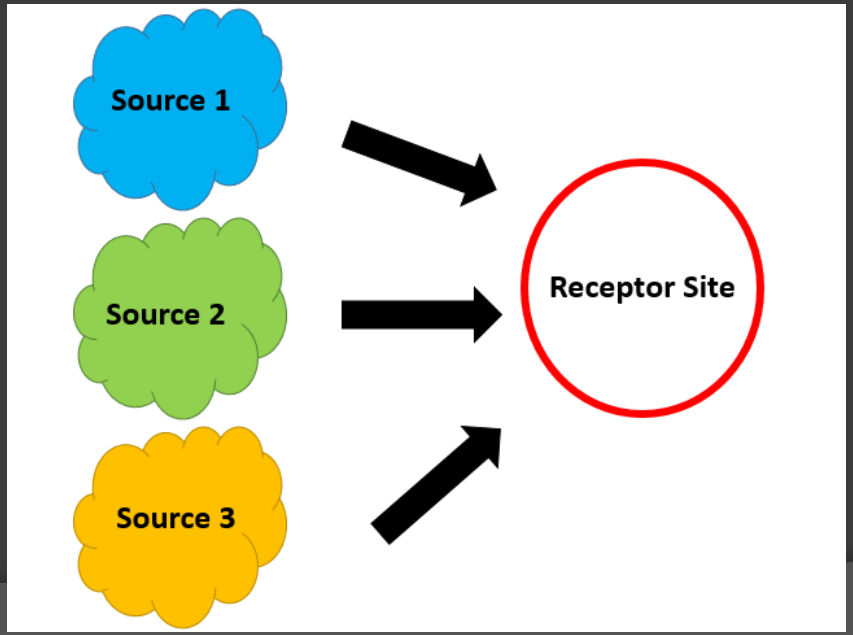
- TCC Soil Study staff collected samples at sites at all district schools with guidance of Director of School Facilities and Operations Jeffrey Hatten
- Location of City Schools near former Spaulding Fibre site and in ROI from Phase 1
- All testing results were below SCOs for all chemicals tested
- Reported results to COT School Board

# ROI on Grand Island (directly west of TCC)

- Only ROI ***without*** samples above SCO values
  - Some sites elevated above surrounding samples
  - Inclusive of William Kaegebein Elementary school
- Phase 2 results: Arsenic and PAHs detected at two individual sites at Grand Island Central Schools (William Kaegebein Elementary and Charlotte Sidway Elementary)
- Sources were likely due to railroad ties (As) and school buses (PAH emissions)
- Cleanup underway by Grand Island Central Schools

# Source Apportionment

How much does a source contribute to the pollutant concentration at a receptor site?

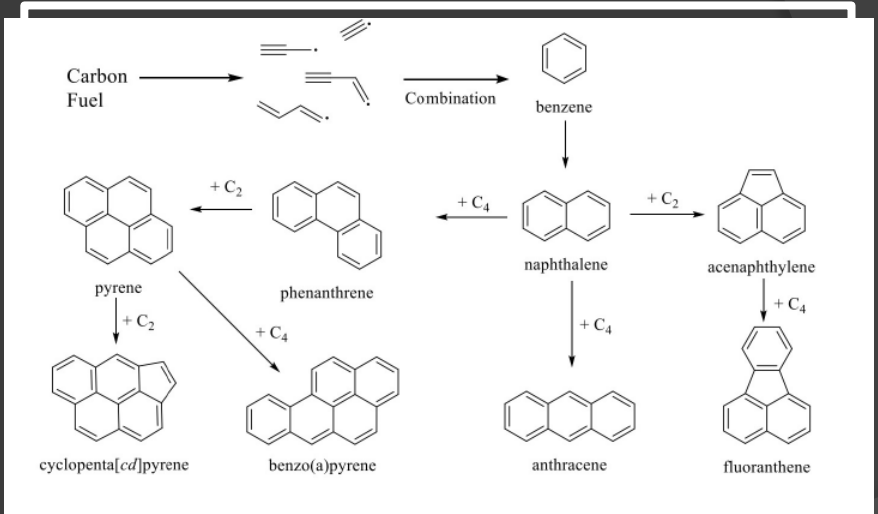



Vast Field

- Methods
  - Qualitative
  - Quantitative
- Pollutants Measured
- Analytical Techniques
  - Chromatography
  - Surface Analysis

# Polycyclic Aromatic Hydrocarbons (PAHs)

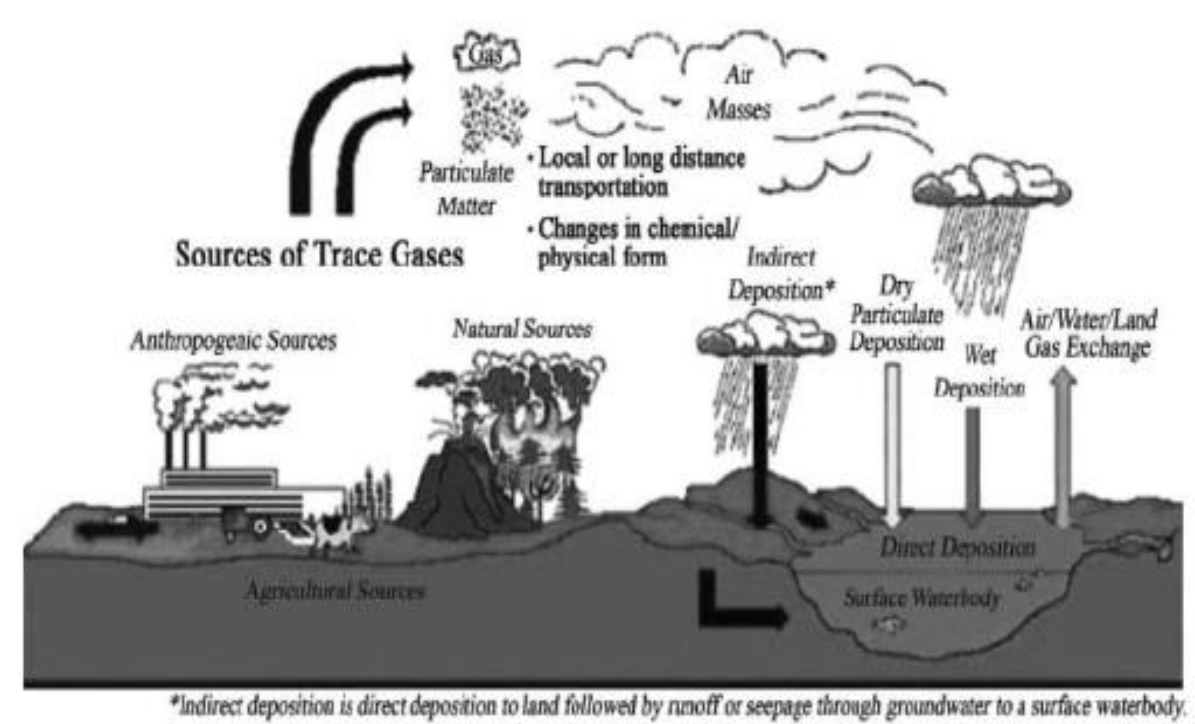
- Hydrocarbons composed of series of fused rings
- Formed during combustion processes
- Dependent on:
  - Combustion Temp
  - Residence Time
  - Fuel Source




Generic PAH formation scheme


Wallace, J. S. Modernizing environmental analysis. Dissertation, University at Buffalo, SUNY, **2016**.
Richter, H.; Howard, J. B., Progress in Energy and Combustion Science **2000**.

# Exposure Pathways

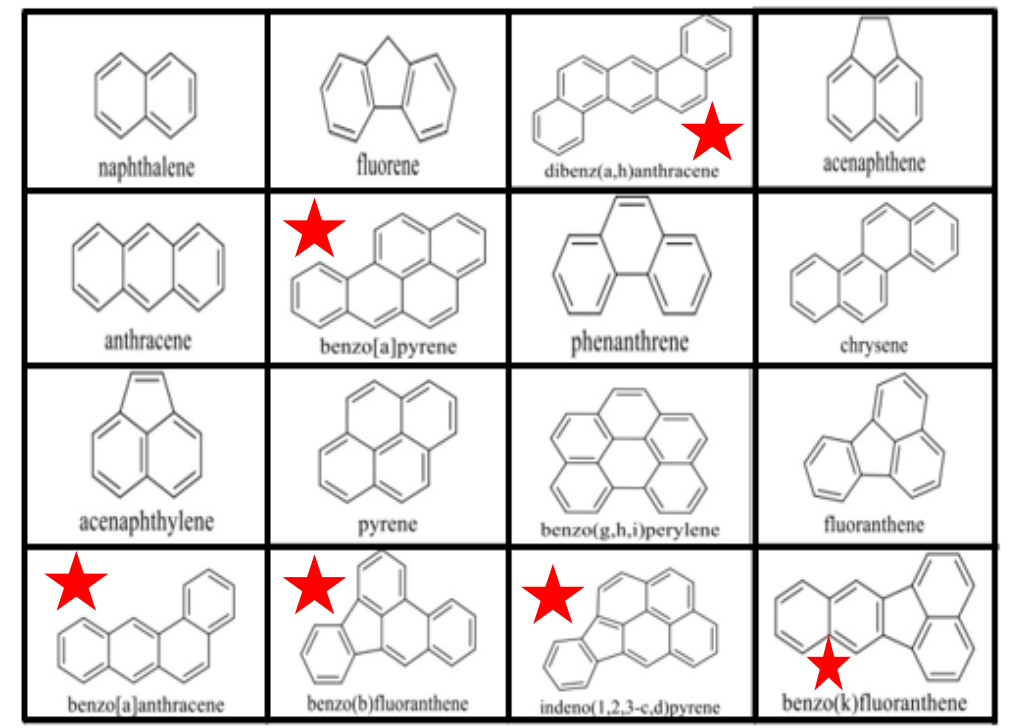



- Aromaticity→ Resistant to degradation
- Undergo local and long range deposition
- Wide range of vapor pressures→ Partitioning between vapor and particulate phases
- Ubiquitous distribution

U.S. EPA. Office of Air Quality Planning and Standards. EPA-453/R-00-0005; **2000**.

# Health Impacts of PAHs

- 15 PAHs listed as probable human carcinogens
- DNA alteration
- Lipophilic Nature
  - log $K_{ow}$ ~3.3-6.95




List of EPA's 16 priority PAHs


Wallace, J. S. Modernizing environmental analysis. Dissertation, University at Buffalo, SUNY, **2016**.
Sahu, S. K.; Pandit, G. G., *Journal of Liquid Chromatography & Related Technologies* **2003**..
EPA, U. S., Priority Pollutant List United States Environmental Protective Agency **2014**.
NTP, Report on Carcinogens, 14th Ed. U.S. HHS. **2016**.

# Source Apportionment Methods

## Traditional Methods

- GC/LC-MS
  - Limited Mass Range <300Da

- Focus only on priority PAHs
  - 2-5 rings → Less source specific

- Allows for separation of isomers

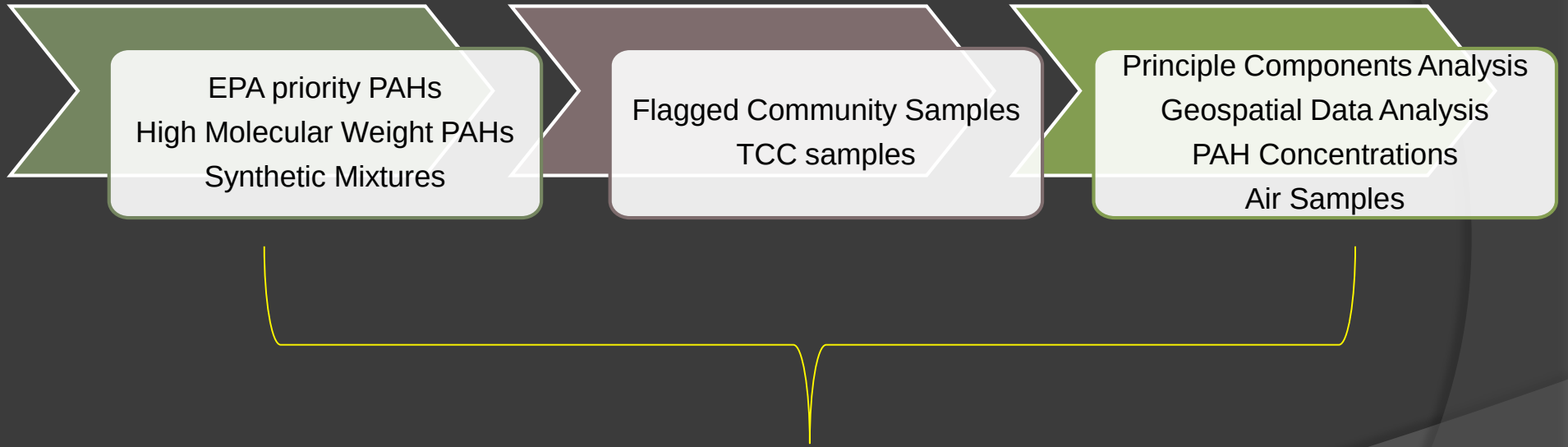
## Proposed Method

- ToF-SIMS

- Focus on high mass PAHs
  - 300-500Da

- No separation component

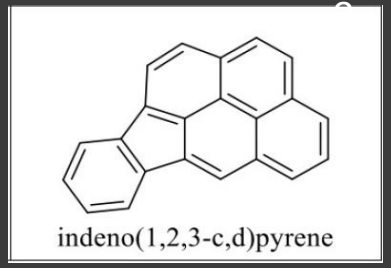
# Source Apportionment Work Flow

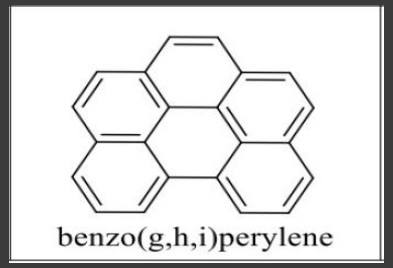



**How much did TCC contribute to the PAH concentration found in the community soil samples?**

# ToF-SIMS Results: PAH Standards

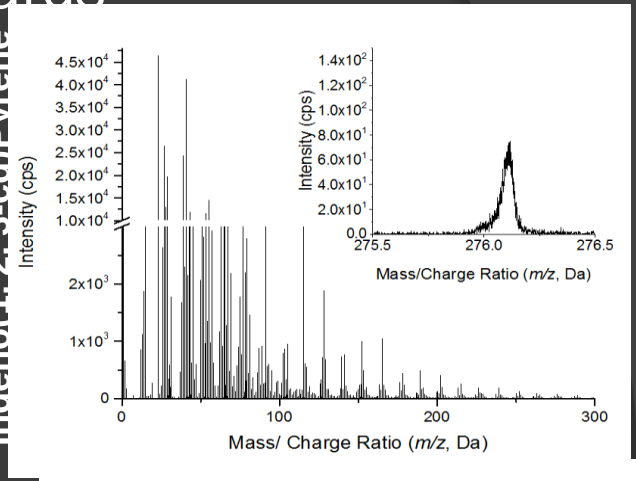
$C_{22}H_{1}$



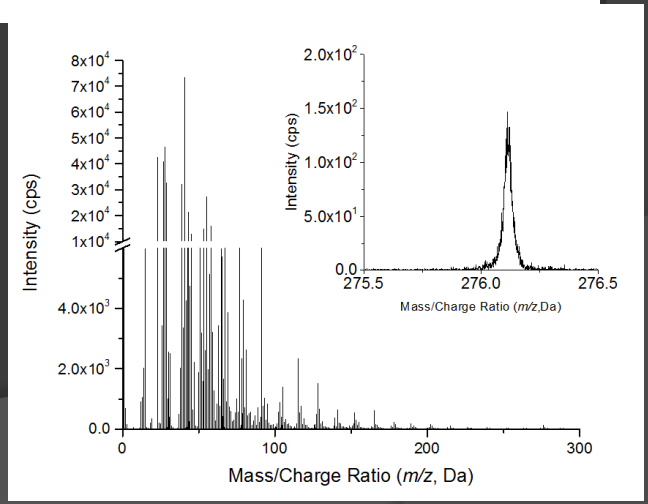




- Molecular ions of PAHs detected
- Cannot distinguish between isomers

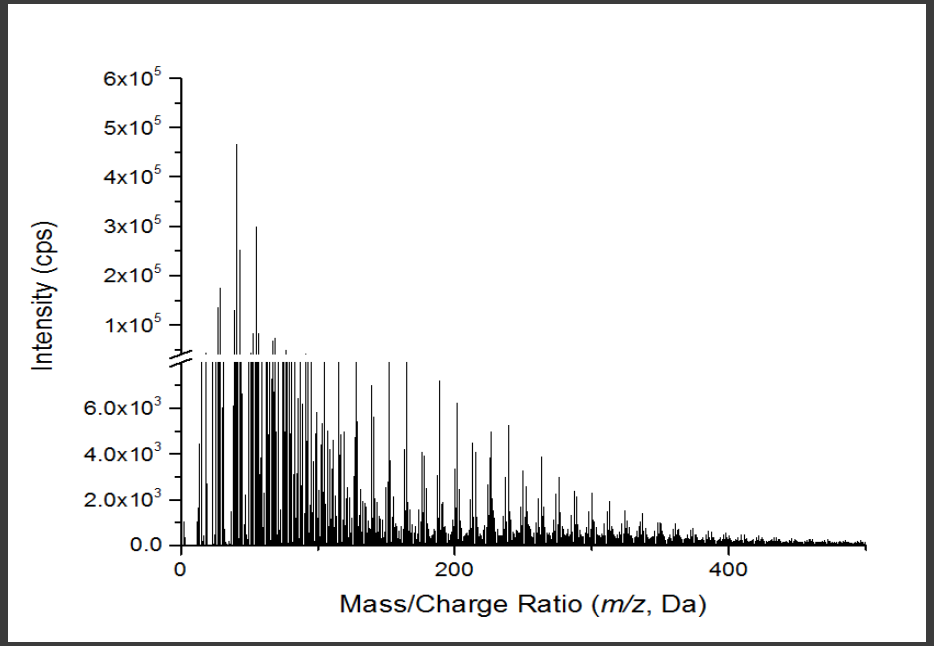
Indeno(1,2,3-cd)Pyrene

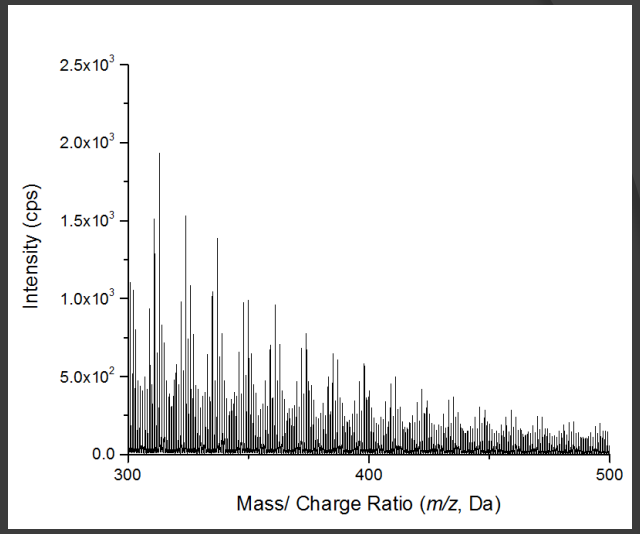



Benzo(g,h,i)perylene



# ToF-SIMS Results- TCC Site #1

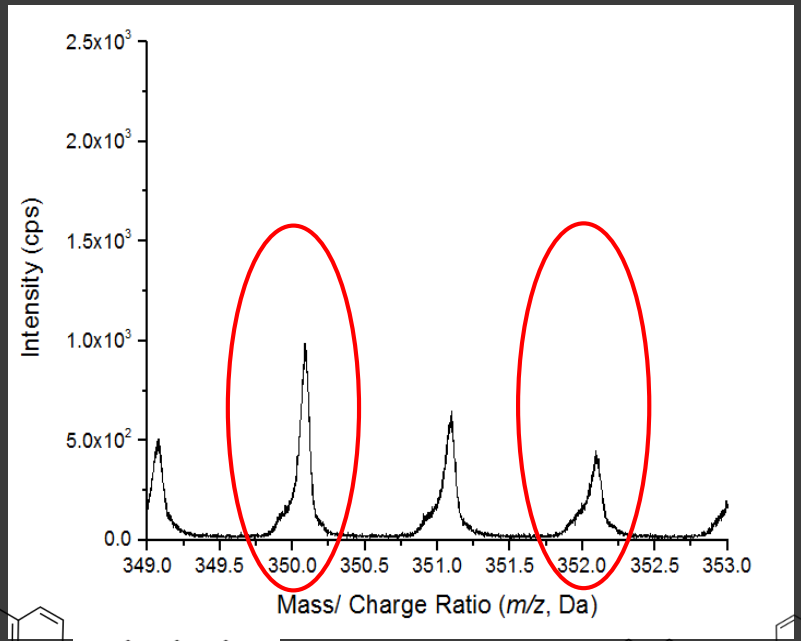


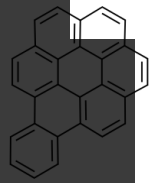



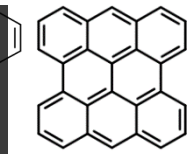

High Mass Region >300Da

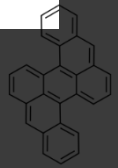
High MW PAHs are detected

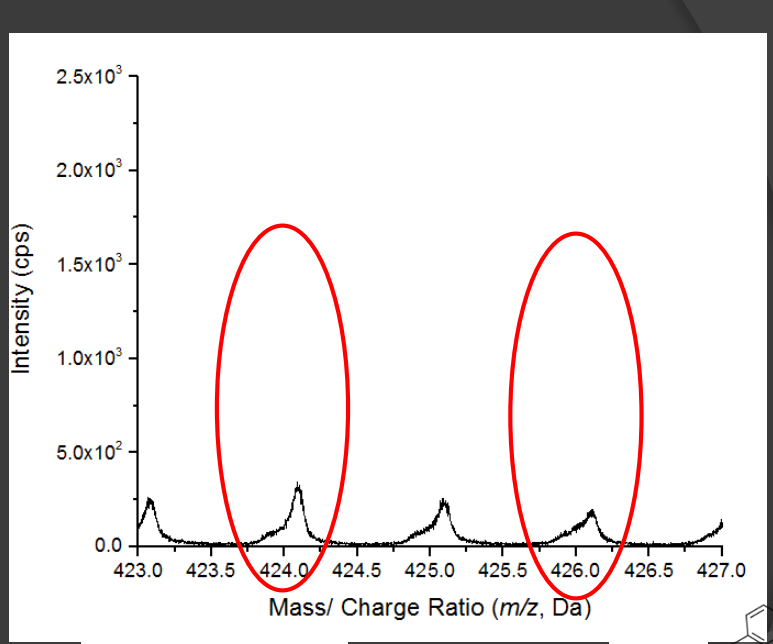
# ToF-SIMS Results- High MW PAHs

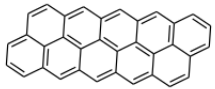








# Future Work

EPA priority PAHs
High Molecular Weight PAHs
Synthetic Mixtures

- Analyze commercially available PAHs
- Synthetic Mixtures
- Hydrocarbon without aromatic rings
- Determine unique fragments for isomers

Flagged Community Samples
TCC samples

- Continue analysis
- Determine unique fragments for isomers
- Determine ratios and compare to quantitative results

Principle Components Analysis
PAH Concentrations
Air Samples

- Create peak lists
- Data pretreatment method
- Combine ToF-SIMS, Air sampling and quantitative results

**How much did TCC contribute to the PAH concentration found in the community soil samples?**

# Take Home Messages

- Large parts of the study area are free from contamination above SCO values
- There are some regions where individual samples had elevated levels of PAHs at the six inch depth, but not broad systematic elevated levels in an entire area.
- Source apportionment analysis, ordered by Judge, begins now.

# Findings from the Tonawanda Coke Soil Study will benefit local communities.

- Results will provide communities with information on:
  - What chemicals are in their soil
  - How widespread any pollution may be
  - Whether pollutants may have originated at the Tonawanda Coke plant
  - Areas with no concern for elevated levels of pollutants
- This knowledge is the first step in understanding whether a clean-up is needed, and where.

# Next Steps: Community Involvement

- Community members are encouraged to:
  - ***Contact local elected officials and encourage them to give permission to use data collected on public sites***
  - Reach out to members of the soil study team with questions regarding study findings

# Contact Us

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# THANK YOU