

UPDATE AND PHASE 2 RESULTS

TONAWANDA COKE SOIL STUDY

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Department of Chemistry, SUNY Fredonia

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
- ⦿ Response to Concerns

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 180 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
- ◎ 181 samples mapped, 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

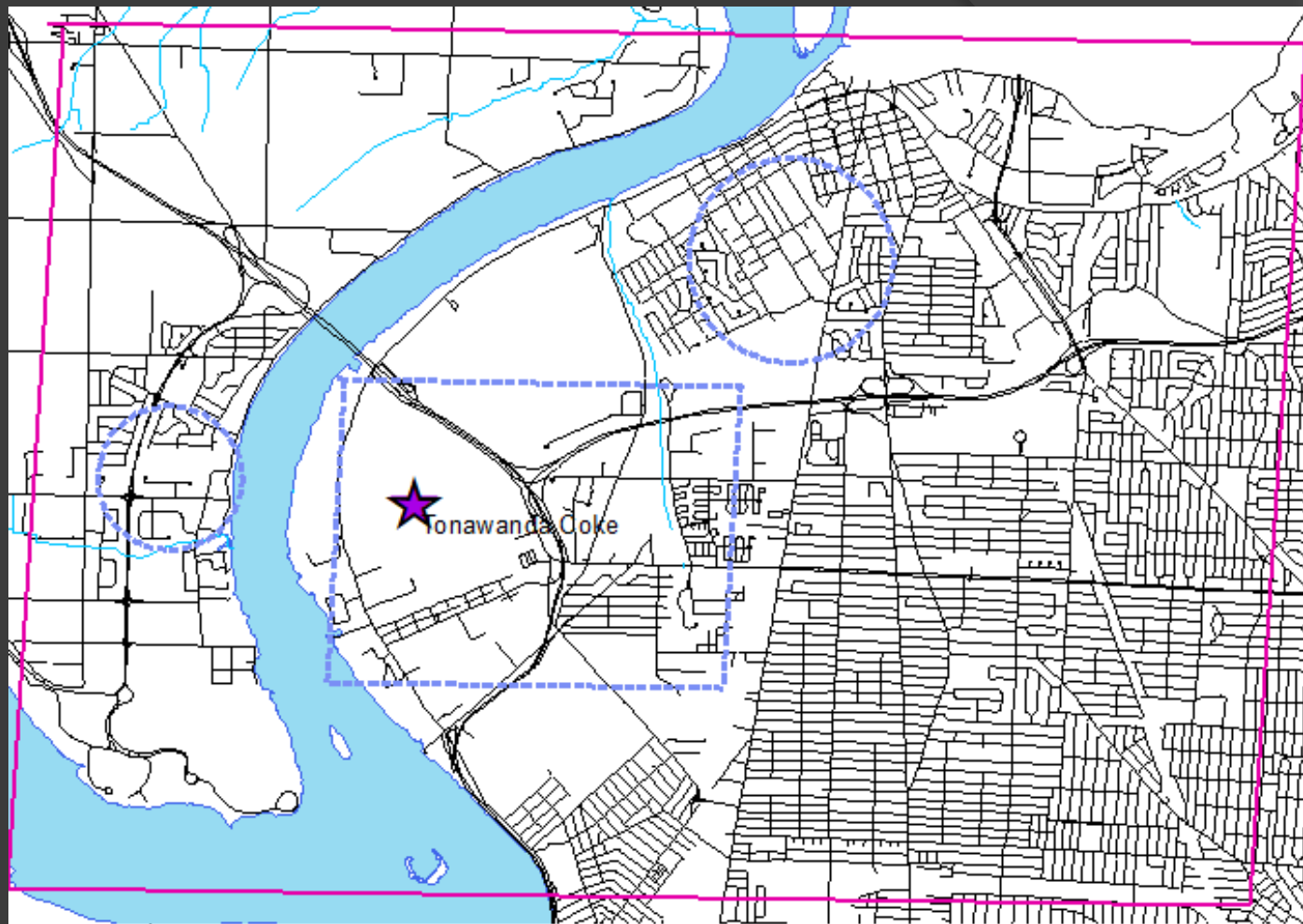
⦿ Soil Cleanup Objective (SCO)

- 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

Regions of Interest

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



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
- 131 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

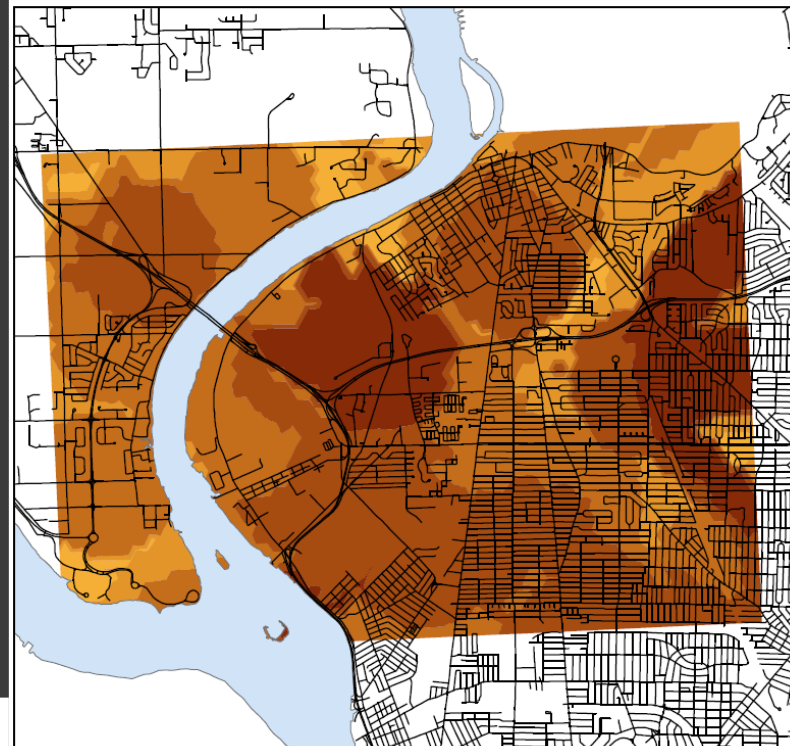
Polycyclic Aromatic Hydrocarbons (PAHs) are interpreted differently by NYS DEC and EPA

- 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



BAP Equivalent Prediction Map

Tonawanda Coke
Soil Study

Created by
Tammy M. Milillo
University at Buffalo, SUNY
Department of Chemistry
April 2019



Filled Contours

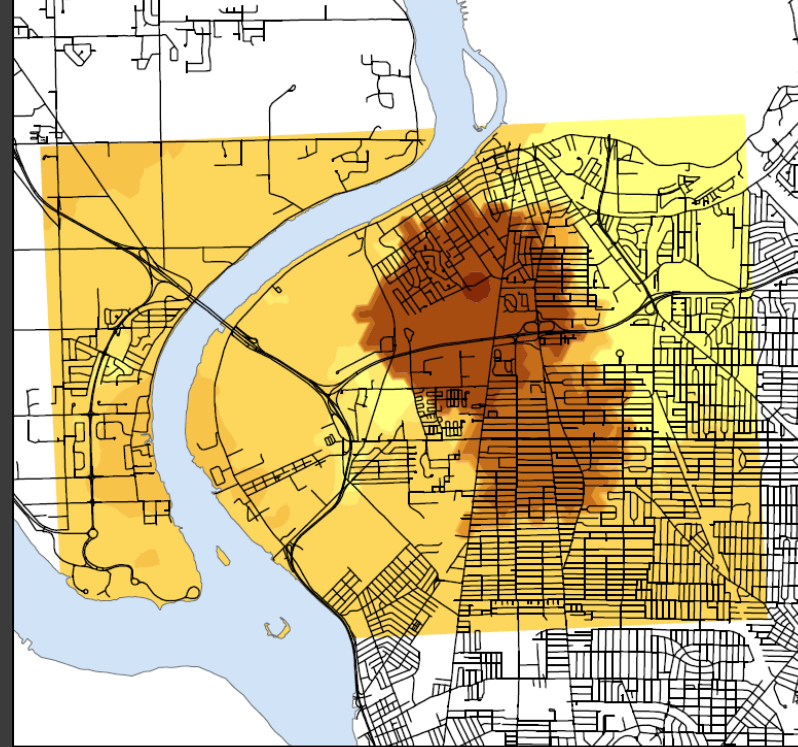
0.07296 – 0.08849112
0.08849112 – 0.092899995
0.092899995 – 0.094151559
0.094151559 – 0.098560433
0.098560433 – 0.114091554
0.114091554 – 0.168802948
0.168802948 – 0.361534485
0.361534485 – 1.04046884
1.04046884 – 3.43214725
3.43214725 – 11.8573

0 0.75 1.5 3 4.5 6

Kilometers

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



This is a map of Arochlor 1016 (a polychlorinated biphenyl (PCB) in $\mu\text{g}/\text{kg}$. 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 900 $\mu\text{g}/\text{kg}$ 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

Arochlor 1016 Prediction Map

Tonawanda Coke
Soil Study

Created by
Tammy M. Milillo
University at Buffalo, SUNY
Department of Chemistry
April 2019

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36 – 39.1519045
39.1519045 – 40.1019398
40.1019398 – 43.2538443
43.2538443 – 53.7108269
53.7108269 – 88.4036561
88.4036561 – 203.503054
203.503054 – 585.365004
585.365004 – 1,852.25737
1,852.25737 – 6,055.38959
6,055.38959 – 20,000

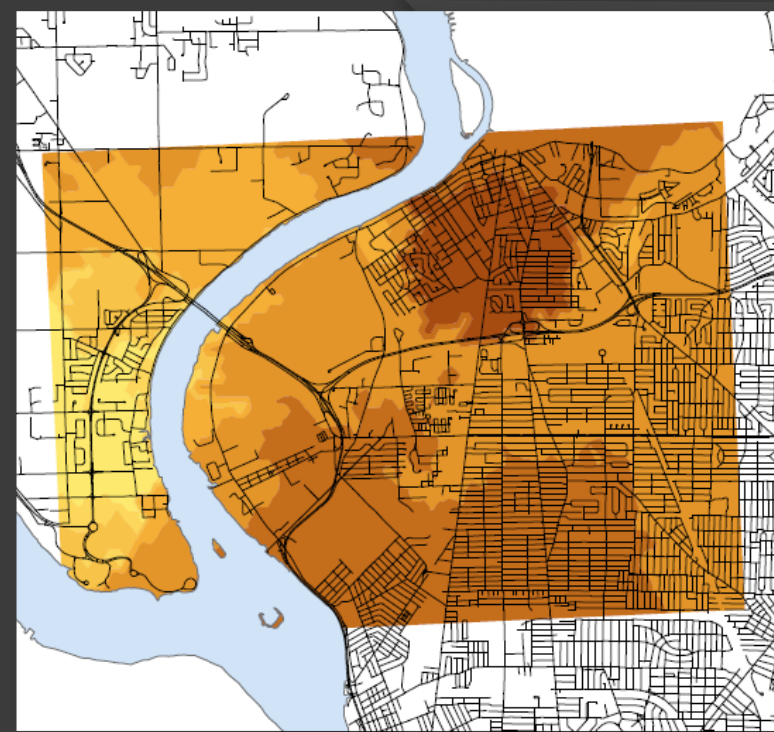


0 0.75 1.5 3 4.5 6

Kilometers

Lead

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



Lead Prediction Map

Filled Contours

11.3 – 24.5194597
24.5194597 – 29.2893169
29.2893169 – 31.0103809
31.0103809 – 35.7802381
35.7802381 – 48.9996978
48.9996978 – 85.6368779
85.6368779 – 187.175291
187.175291 – 468.58476
468.58476 – 1,248.49934
1,248.49934 – 3,410

Tonawanda Coke
Soil Study

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April 2019

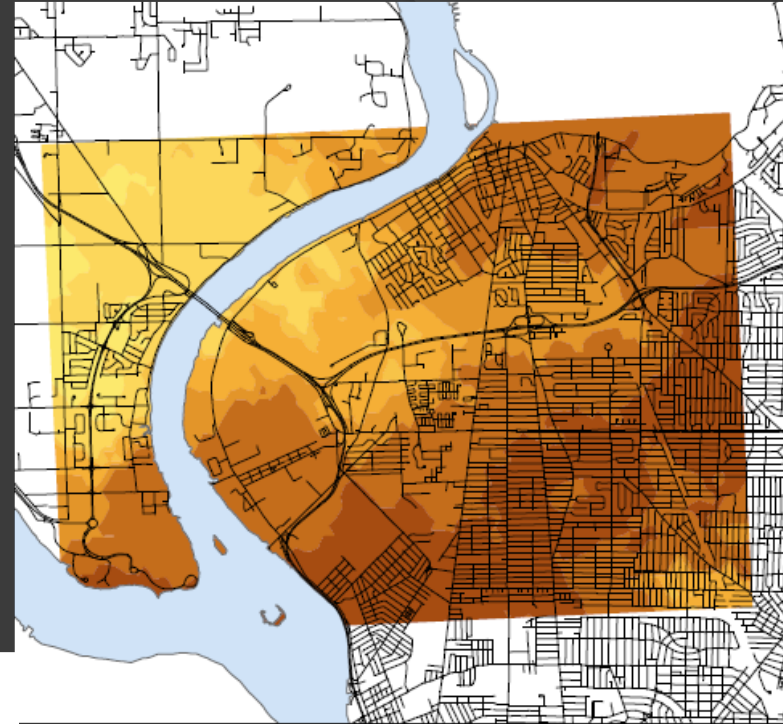


0 0.75 1.5 3 4.5 6
Kilometers

Arsenic

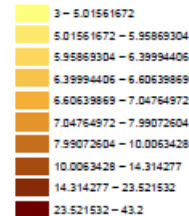
- More study by source apportionment methods needed to determine origins of arsenic

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



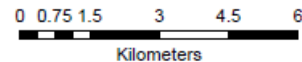
Arsenic Prediction Map

Filled Contours



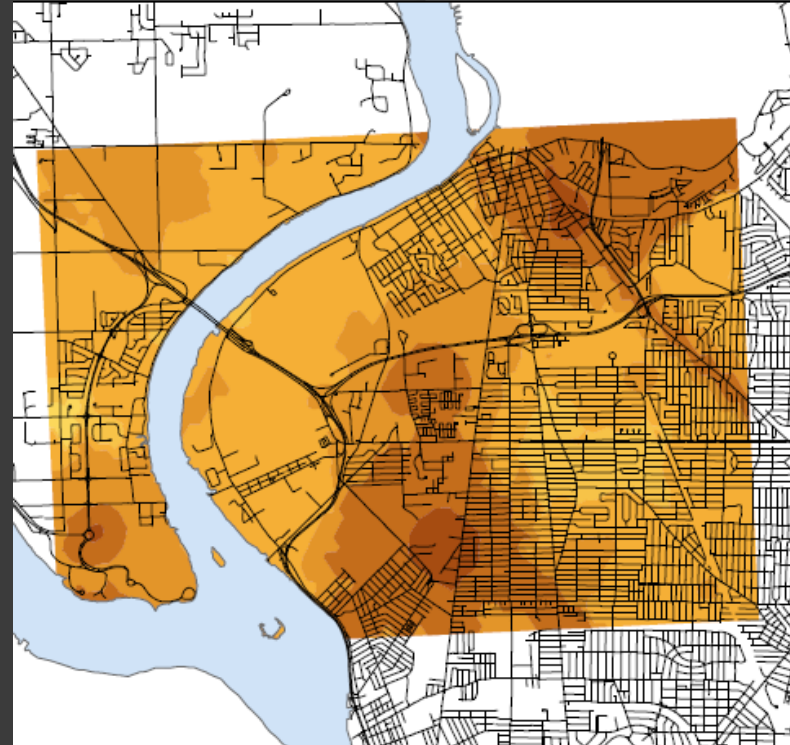
Tonawanda Coke
Soil Study

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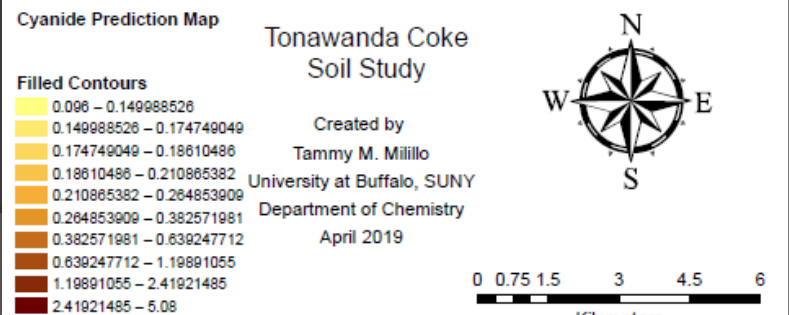


Cyanide

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

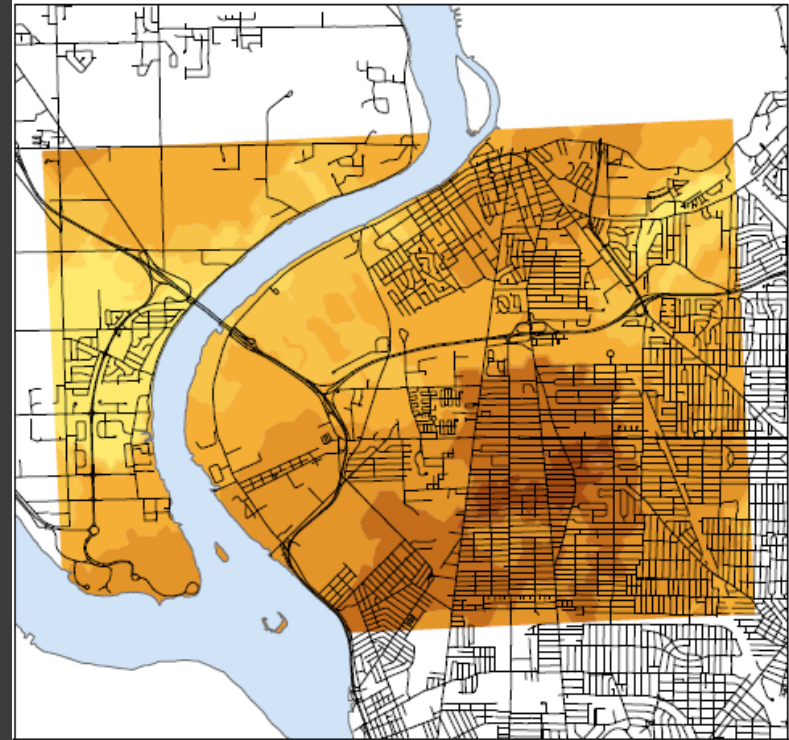


Map of cyanide in mg/kg. The map shows the modeled surface, as the color darkens, the predicted concentration of cyanide increases. The TCC soil study used an SCO of 27 mg/kg for cyanide. Intervals below the SCO are of no immediate concern to residents. Intervals which contain values above the SCO do 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

Mercury Prediction Map

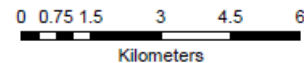
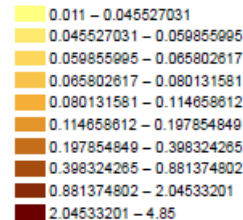
Tonawanda Coke
Soil Study

Created by
Tammy M. Milillo

University at Buffalo, SUNY
Department of Chemistry
April 2019



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City of Tonawanda Schools

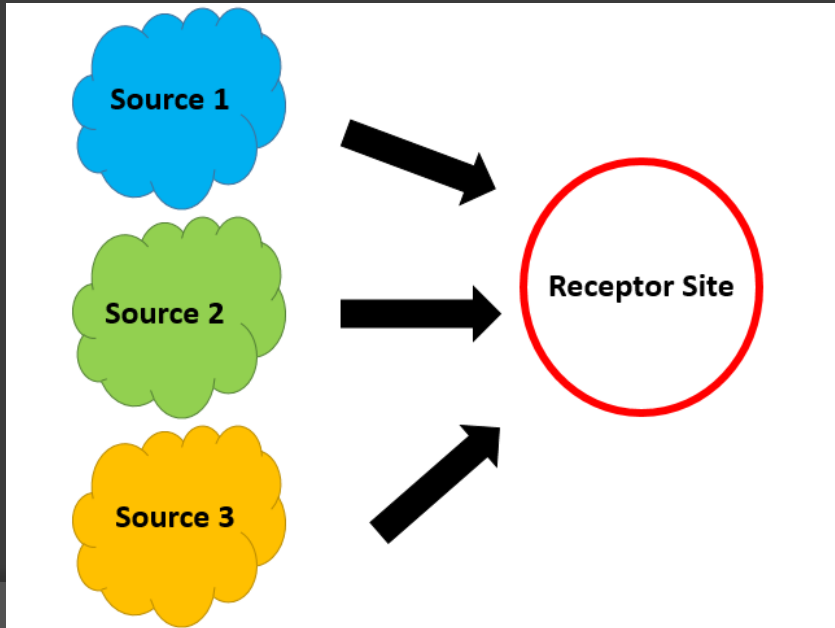
- TCC Soil Study staff collected samples at sites at all district schools with guidance of Director of School Facilities and Operations Jeffrey Hatten
- Location of City Schools near former Spaulding Fibre site and in ROI from Phase 1
- All testing results were below SCOs for all chemicals tested
- Reported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

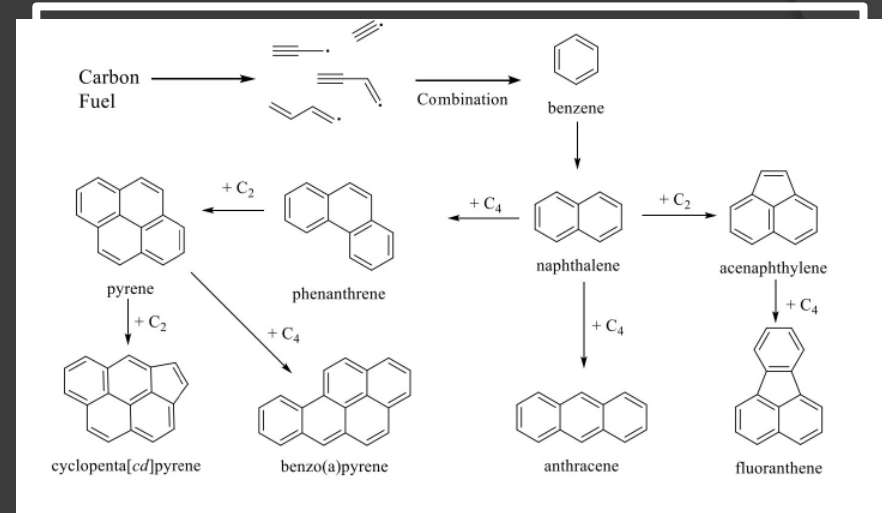
Pollutants Measured

Analytical Techniques

- Chromatography
- Surface Analysis

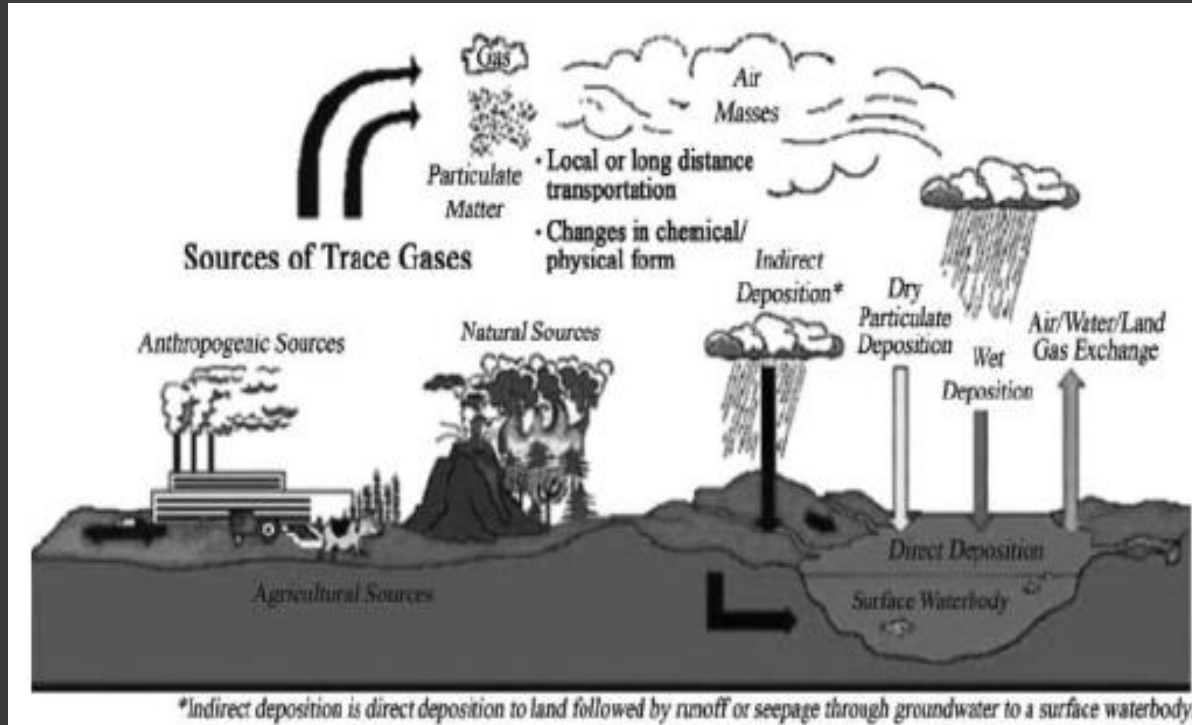
Polycyclic Aromatic Hydrocarbons (PAHs)

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



Generic PAH formation scheme

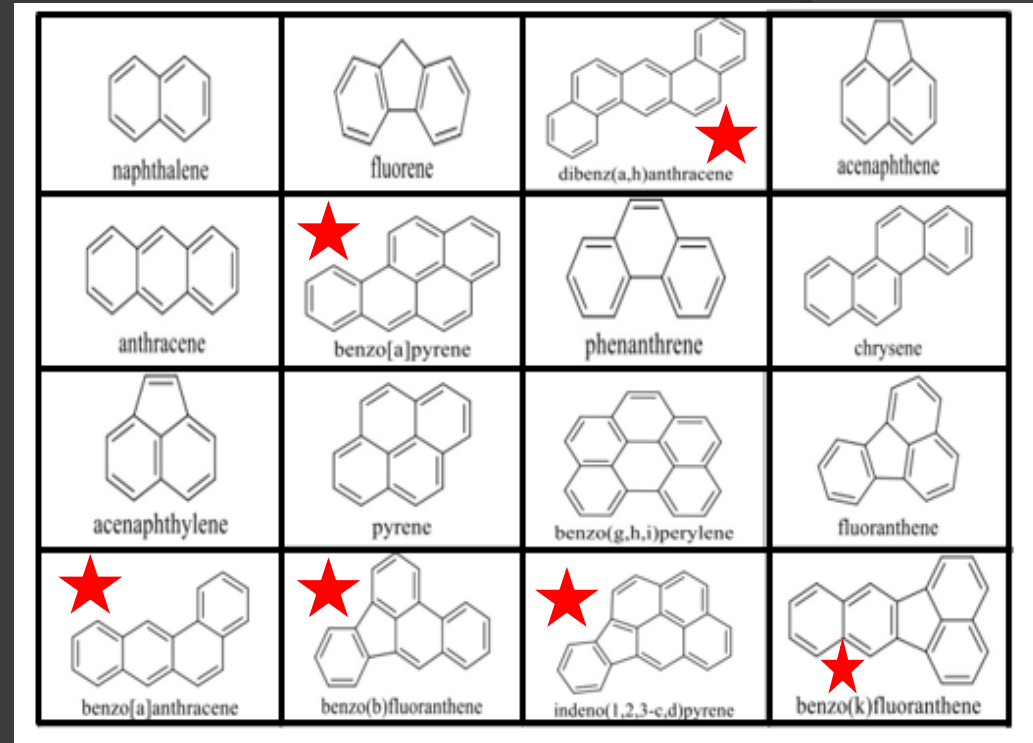
Exposure Pathways



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

Health Impacts of PAHs

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



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

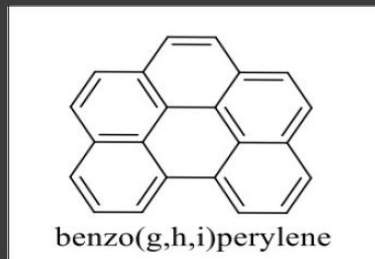
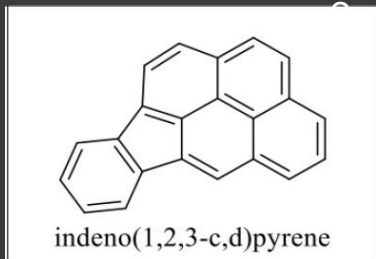
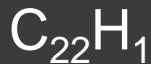
EPA priority PAHs
High Molecular Weight PAHs
Synthetic Mixtures

Flagged Community Samples
TCC samples

Principle Components Analysis
Geospatial Data Analysis
PAH Concentrations
Air Samples

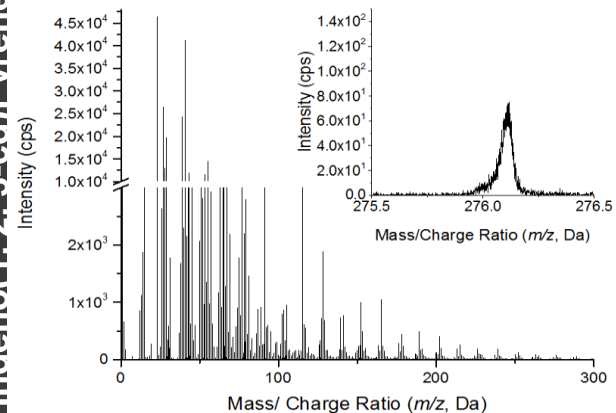
How much did TCC contribute to the PAH concentration found in the community soil samples?

ToF-SIMS Results: PAH Standards

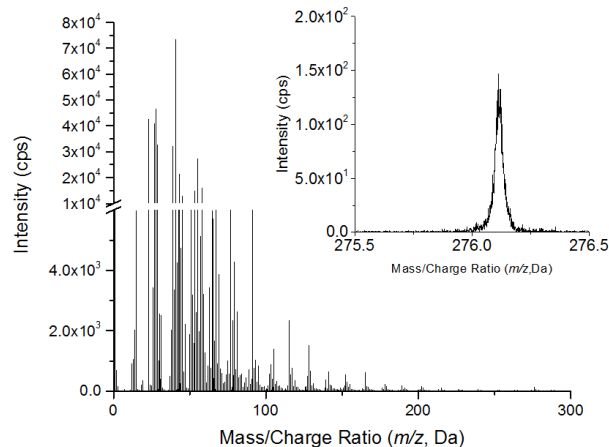


- Molecular ions of PAHs detected
- Cannot distinguish between isomers

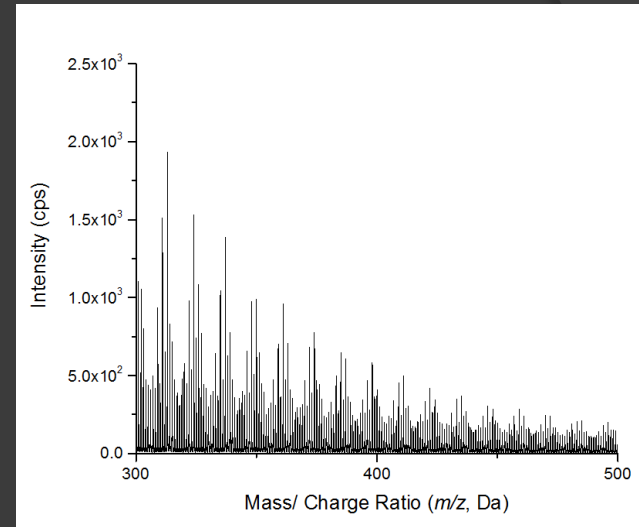
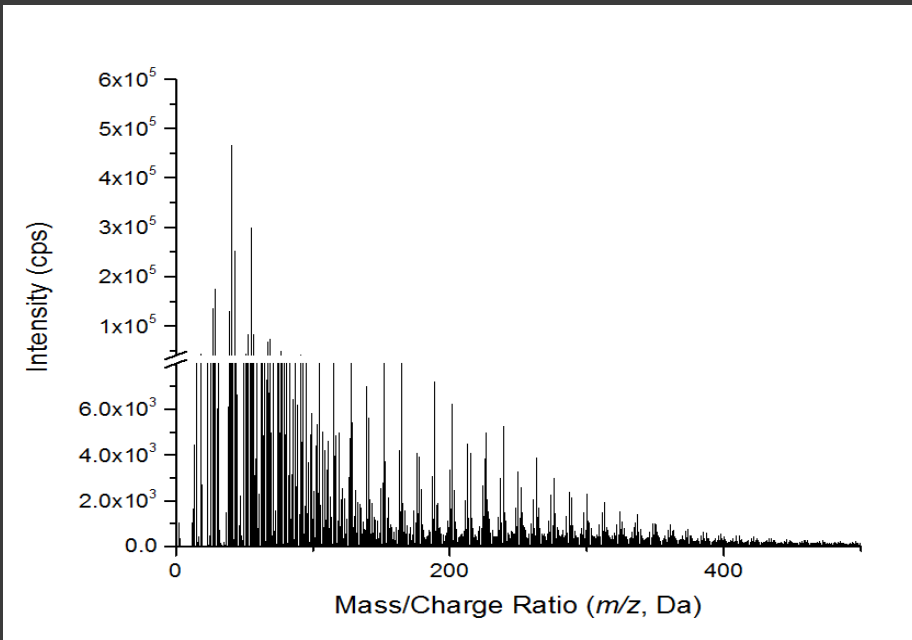
Indeno(1,2,3-c,d)pyrene



Benzo(g,h,i)perylene



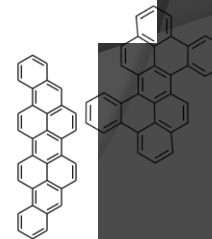
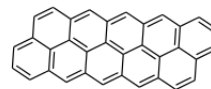
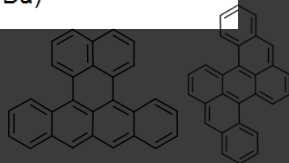
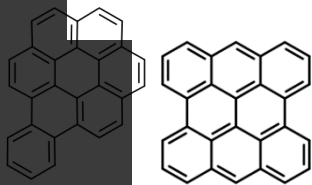
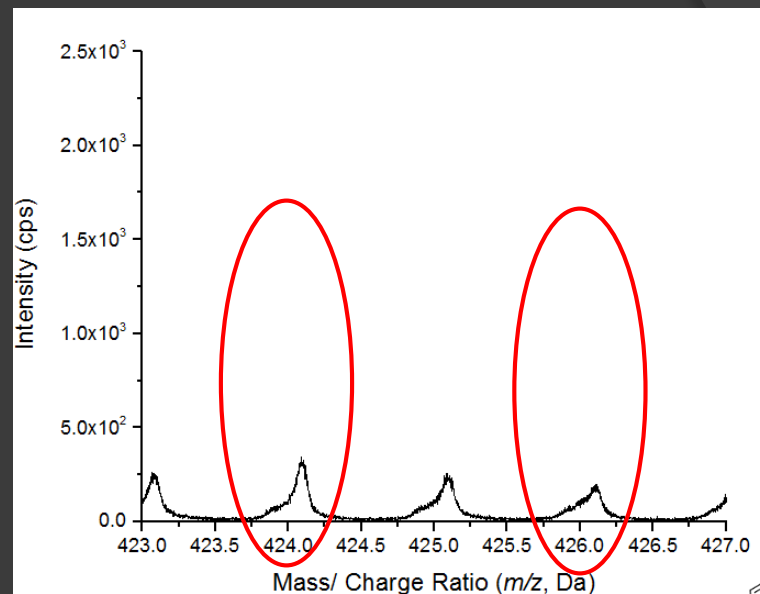
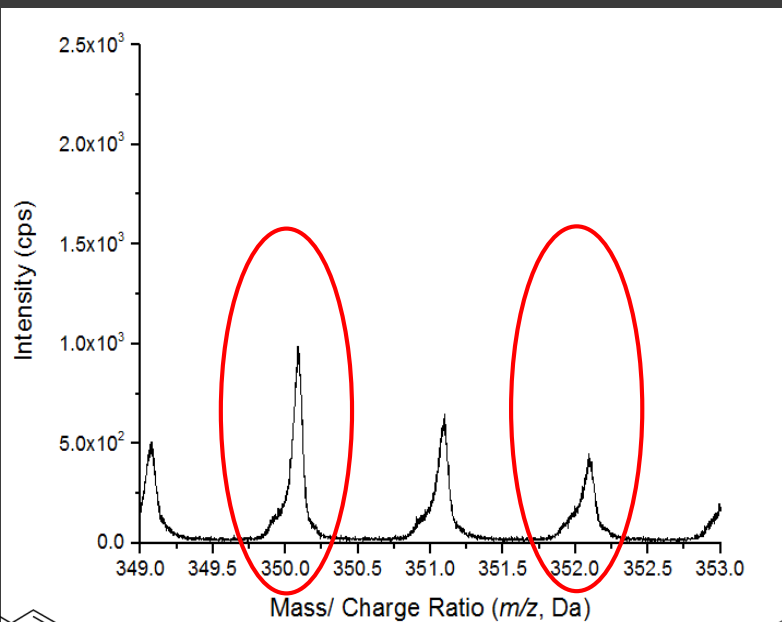
ToF-SIMS Results- TCC Site #1



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

Flagged Community Samples
TCC samples

Principle Components Analysis
PAH Concentrations
Air Samples

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

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

- 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, is underway with promising results

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 Joseph Emminger and Rick Davis and encourage them to give permission to use data collected on public sites and RELEASE this information to the public***
 - Reach out to members of the soil study team with questions regarding study findings

Why did we plan this meeting?

- We have detected pollutants that are likely due to Tonawanda Coke and provided maps of the results
- As Judge ordered, we are working on the testing to separate the emissions from TCC from other emissions
- There are areas of elevated levels of PAHs detected above EPA's SCO

Response to Concerns about this Study

- ◎ **The Judge's order requires the study to determine the historic impact of TCC (only).**
- ◎ **Why 6" samples? Decades of Residential use (aerial photos from 1927 and 1955)**
 - We also sampled at 2" (approx. 60 samples) and saw smaller amounts of pollutants as expected.
 - We detected pesticides at 6" depth which gave us a time stamp for at least a 30 year time
- ◎ **We did a pilot study to test this hypothesis before using it in Phase 1 and 2**

Response to Concerns about this Study

- Jackie James-Creedon was part of the planning team that design the approach in this study. She never raised an objection until long after the study was underway.
- Judge Skretny issued an order (Docket #463) in March 2019 indicating that the Probation Office reported that it had “received all documents and information necessary to confirm to its satisfaction that the scope and financial expenditures associated with the Soil Study [were] consistent with the study as approved.”

Contact Us

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716-673-3500

michael.milligan@fredonia.edu

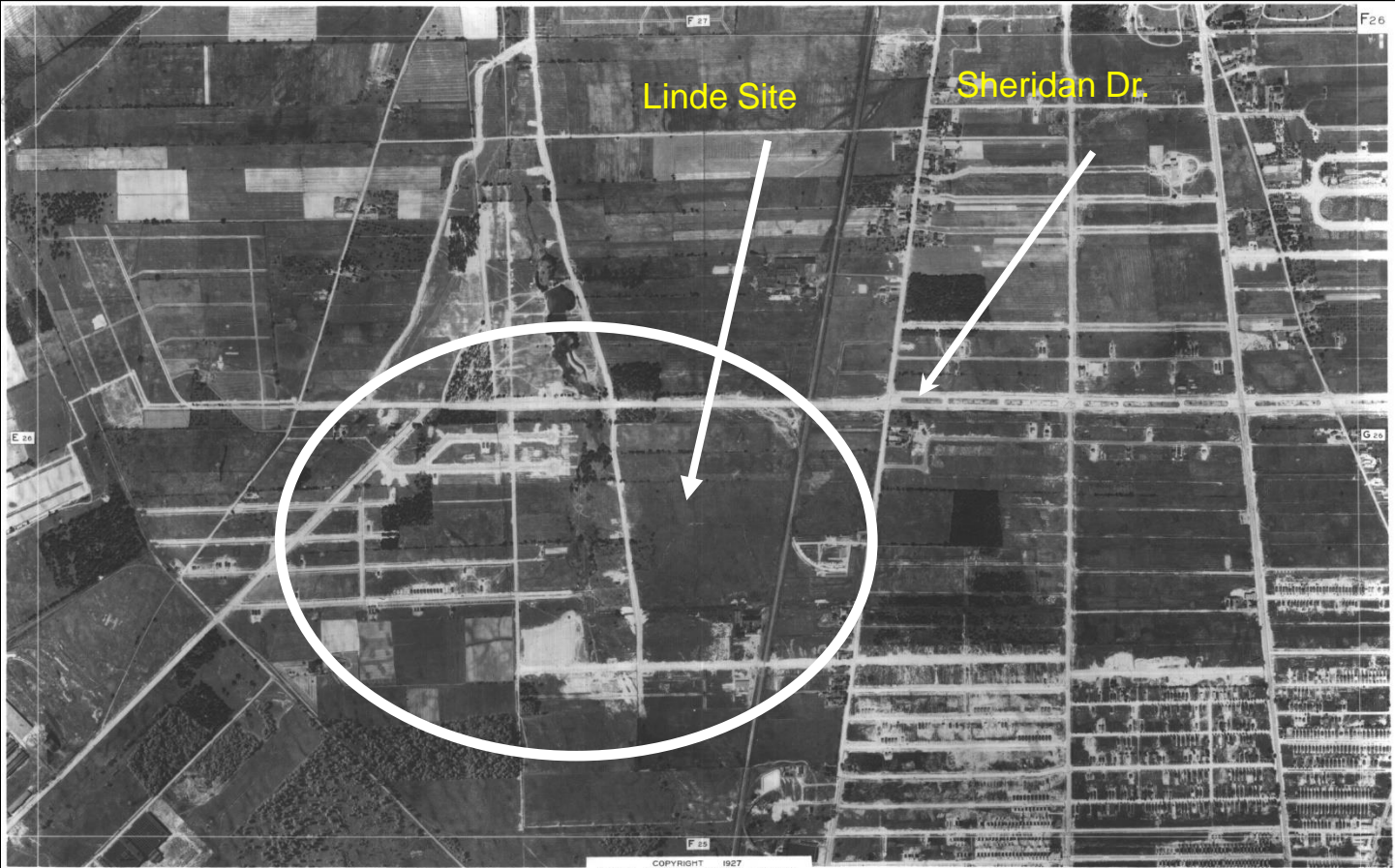
Dr. Tammy Milillo
465 Natural Sciences Complex
Buffalo, NY 14228
716-645-4168

milillo@buffalo.edu

THANK YOU







Linde Site

Sheridan Dr

AERIAL WORK BY ADWINE & WASHBURN BUFFALO NEW YORK
ENGINEERING & MAP BY FAIRCHILD AERIAL SURVEYS INC NEW YORK

COPYRIGHT 1927
GEORGE C. DIEHL, COUNTY ENGINEER

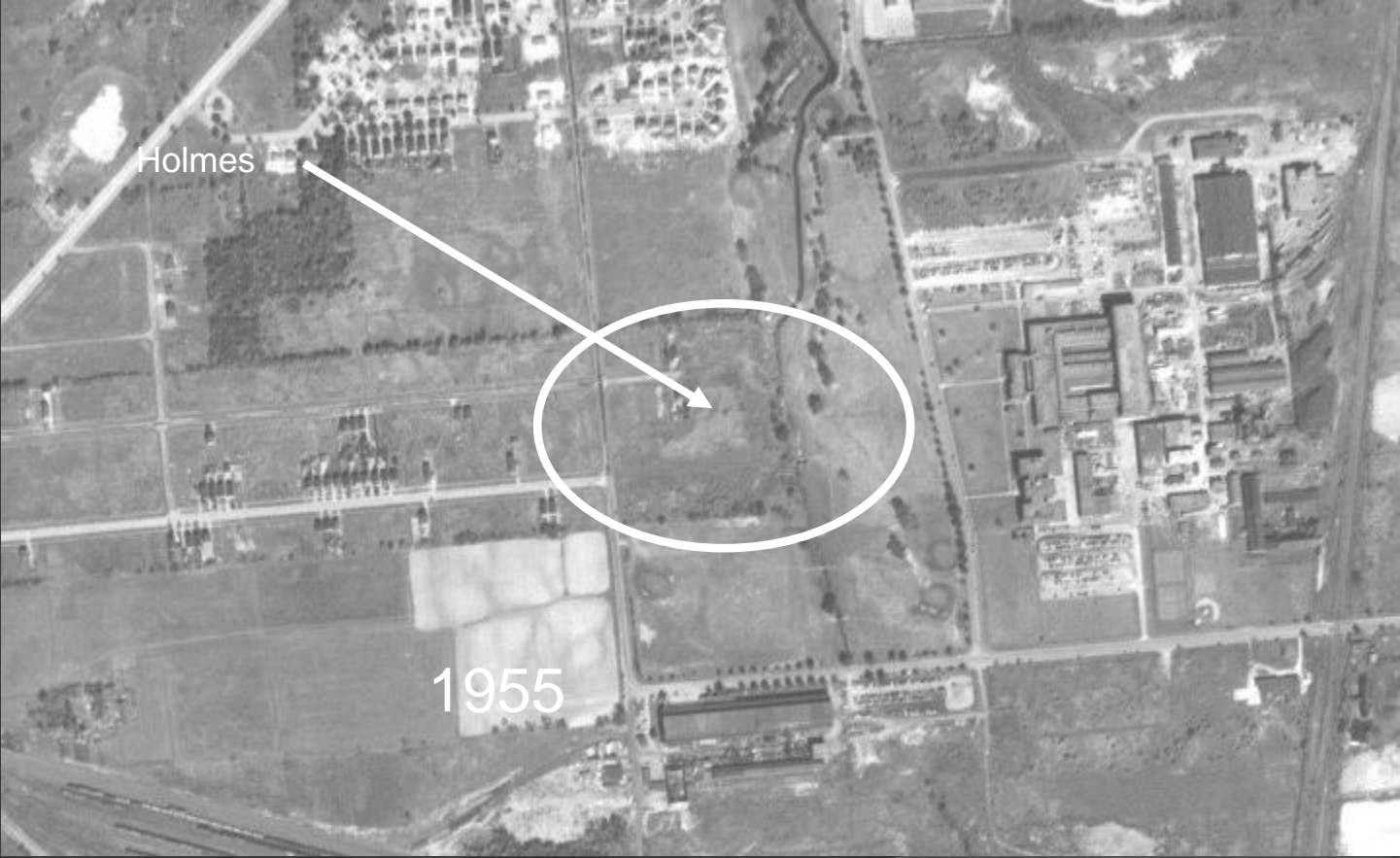
ERIE COUNTY NEW YORK
OFFICE OF THE COUNTY ENGINEER
GREATER MOTORWAY SYSTEM
JUNE 1ST 1927

SCALE



Holmes/Linde Area

1955



Holmes

1955



Ken-Ton Holmes School

Legend

-  Erie_st
-  parcels_sp

