Characterization of Benzene and Other Air Toxics in Akwesasne

Cassie David
St. Regis Mohawk Tribe, Akwesasne

Dr. Alan Rossner
Clarkson University, Potsdam NY.
**Introduction: Research team**

<table>
<thead>
<tr>
<th>Name</th>
<th>Title</th>
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<tr>
<td>Angela Benedict-Dunn</td>
<td>PI</td>
</tr>
<tr>
<td></td>
<td>Air Program Manager SRMT Environment</td>
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<tr>
<td>Les Benedict</td>
<td>QAO &amp; Assistant Director of SRMT Environment</td>
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<tr>
<td>Cassie David</td>
<td>Air Toxics Technician SRMT Environment</td>
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<tr>
<td>Waylon Cook</td>
<td>Air Tech/Student Intern SRMT Environment</td>
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<tr>
<td>Dr. Philip K. Hopke</td>
<td>CARES Director and Professor for Clarkson University</td>
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<tr>
<td>Dr. Alan Rossner</td>
<td>Assistant Professor and Director of Environmental Health Sciences</td>
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<td>Environmental Science and Policy Program Clarkson University</td>
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<tr>
<td>Sheila Kalenge</td>
<td>Clarkson University Environmental Science and Engineering Graduate Student</td>
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<tr>
<td>Rui Li</td>
<td>Clarkson University Chemical Engineering Graduate Student</td>
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Outline

1. Problem description & background
2. Project purpose, objectives & activities
3. Project rationale
4. Context for this project
   - Previous monitoring
   - Modeling
   - Data analysis
5. Approach (sampling and analytical)
6. Preliminary results and findings
7. Data validation techniques
8. Conclusions
9. Future work
Problem description & background
Problem description: Industrial emissions

Aluminum smelter and Automotive Plant are both within close proximity to Akwesasne
Aluminum smelter 2006
Paper Mill
Cornwall Ontario, Canada

The now closed Paper Mill’s lasting effects may be around for generations to come.
Other benzene sources
multiple gas stations in Akwesasne
Rationale for the project

- Sources of benzene
  - 29,140 lbs per year of benzene released per TRI
  - Motor vehicles
  - 15 gas stations, gasoline contains (BTEX)
- Other Possible Sources
  - Stored gasoline in homes for small engine operations
  - Tobacco and cigarette smoke
- Short term exposure (50-150 ppm)
- Long term exposure
  - Human carcinogen
Objectives

- Estimate BTEX Concentrations
- Characterize Sources
- Create Model – Predict Trends
- Source Apportionment
- Provide Information to Akwesasne Community
Initial Project Activities

- Identify sampling locations, recruit volunteers
- Develop a QAPP and associated SOPs
- Perform preliminary data analyses: ambient air, personal and source
- Identify sources of benzene
- Estimate ambient benzene concentrations from emission inventories using dispersion modeling
Design and Implementation of the Project

- Approach
- Community notification
- Identify sampling sites
- Landowner consent
- Stands for canisters
- Frequency & duration
Approach: Sampling & analytical methodology

- Ambient sampling
- Personal sampling
- Source sampling
  - Head space
  - Tail pipe
- Analytical methods
- Modeling
- Quality Assurance
- Detection limits
Akwesasne community involvement in the project

Public Service Announcements aired informing the community of the project.
Identifying sites

How sites were chosen
Consent from landowners

Once the community learned of the project many were willing to participate by volunteering their land
Designing sampling stands

The sampling stands were designed to:

- Withstand four seasons outside
- Allow air flow
- Secure the sampling canisters
Installing the stands
Ambient sampling

- 6-L passivated silonite stainless steel Summa canisters
- Sampling at 9 locations for ~24 hours every 6th day
  - 9 ambient air samples, 1 field blank and 1 collocated sample (duplicate)
- Determine concentration of BTEX
- Analyze air toxic profiles
Preferred pic canister on the stand

zdm, 9/25/2007
Personal sampling

- 300 ml stainless steel canister (~565g) (Capillary flow controlled (~0.1ml/min)
- Collects BTEX (and other VOCs) in breathing zone,
- 3-4 days every 3 months
- Estimate human exposure
- IRB approved in the spring of 2007

Rossner and Farant, 2004; Rossner et al., 2002; 2004, Rossner and Wick, 2006)
Source sampling

- Head space analysis
  - collection from all gasoline stations in the reservation (~1 gallon)
  - provide for seasonal changes in formulation of BTEX profiles compared with headspace samples from different stations

- Tailpipe emission analysis
  - 10 cars sampled each season from volunteers
  - 3 samples collected from each vehicle
  - analyzed with GC/FID (HP 5890 series II)
  - Assess the emission of BTEX from vehicles
Modeling

- AERMOD air dispersion modeling software
- Steady state plume model
- Designed for short range dispersion
- Uses meteorological hourly data (wind direction, velocity, sky condition e.g. cloudy or clear, temperature), behavior of the air plume and topological features (terrain type)
Analysis Performed at Clarkson University – CARES Lab

- GC/FID (Thermo) interfaced with Preconcentrator (Entech 7100 A)
- GC/MS
- US EPA TO-15 and TO-14a procedures to analyze BTEX
- Obtain Detection Limit < 0.1ppb. For each compound
Quality Assurance (QAPP)

- Field blanks
- Laboratory blanks
- Leak checks
- Calibration standards (external)
- Dynamic dilution system
- Precision checks, collocated data
- Laboratory audits (NYS DEC Air resources lab)
- SOPs
- Chain of custody forms
**Data Validation : Access sampling field notes**

![Microsoft Access - Ambient Air Sampling Field Note](image)

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Chain of custody forms

St. Regis Mohawk Tribe Environment Division
412 State Route 37
Akwasasne, NY 13655

SRMT ENV AIR TOXICS PROGRAM

BENZENE PROJECT

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Laboratory: ____________________________  Carrier: ____________________________

Instructions: ____________________________  Notes: ____________________________

COC Signature List:
1. Reinquish By: ____________________________  Date: ____________________________  Time: ____________________________
2. Reinquish By: ____________________________  Reinquish By: ____________________________  Date: ____________________________  Time: ____________________________
3. Reinquish By: ____________________________  Reinquish By: ____________________________  Date: ____________________________  Time: ____________________________
4. Reinquish By: ____________________________  Reinquish By: ____________________________  Date: ____________________________  Time: ____________________________
Sampling Information Validation
# Data Quality Objectives

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<th>Sensitivity</th>
<th>Completeness</th>
<th>Accuracy</th>
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<tr>
<td>BTEX</td>
<td>+/- 10%</td>
<td>Compound specific</td>
<td>&gt;80%</td>
<td>+/- 25%</td>
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<tr>
<td></td>
<td></td>
<td>0.1 ppbv</td>
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Calibration

- Instrument calibration
- Routine calibration, before each analysis
- BTEX standard, volumetrically generated in 6-L canister
- 5 point calibration curve $r^2 \geq 0.95$
- Range of interest 0.1-25ppbv
BTEX calibration curve 071707

\[ y = 2020663.823x - 36977.000 \quad R^2 = 1.000 \]

\[ y = 1815348.139x - 34231.000 \quad R^2 = 1.000 \]

\[ y = 1697377.451x - 20957.000 \quad R^2 = 1.000 \]

\[ y = 1220799.871x - 17662.500 \quad R^2 = 1.000 \]
Preliminary results

Benzene concentrations

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<th>1A</th>
<th>1B</th>
<th>1C</th>
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Preliminary results: toluene concentrations
Ethyl benzene concentrations

Xylene concentrations

Xylene concentrations

Locations

1A 1B 1C 2A 2B 2C 3A 3B 3C

ug/m³


5/7/2007

11/7/2007

17/7/2007

23/7/2007

30/7/2007

5/8/2007

11/8/2007

Locations

1A 1B 1C 2A 2B 2C 3A 3B 3C
# Benzene concentrations (ug/m³)

<table>
<thead>
<tr>
<th>Locations</th>
<th>1A</th>
<th>1B</th>
<th>1C</th>
<th>2A</th>
<th>2B</th>
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-999 - below the detection limit
## Toluene concentrations (ug/m³)

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<th>1A</th>
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<th>1C</th>
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Conclusions and Future Work

- Excellent community Involvement
- Preliminary data has shown variation both temporal and spatially
- Sampling and analytical instrumentation is providing the detection limits necessary to develop exposure profiles
- Personal sampling will begin this fall
Questions