Characterization of Benzene and Other

Air Toxics in Akwesasne

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Introduction: Research team

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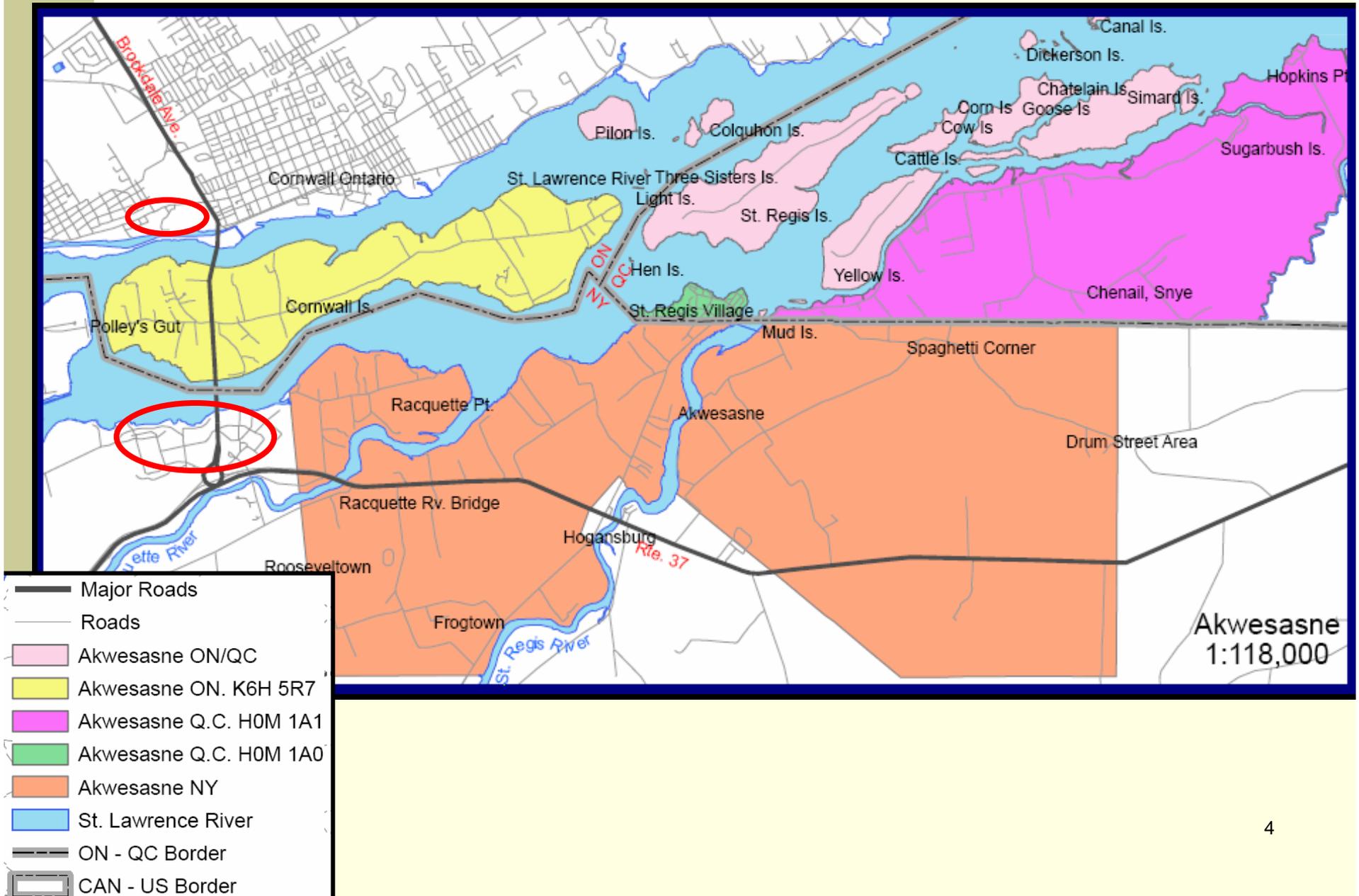
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Outline

- Problem description & background
- Project purpose, objectives & activities
- Project rationale
- Context for this project
  - Previous monitoring
  - Modeling
  - Data analysis
- Approach (sampling and analytical)
- Preliminary results and findings
- Data validation techniques
- Conclusions
- Future work

Problem description & background

Legend:
- Major Roads
- Roads
- Akwesasne ON/QC
- Akwesasne ON. K6H 5R7
- Akwesasne Q.C. H0M 1A1
- Akwesasne Q.C. H0M 1A0
- Akwesasne NY
- St. Lawrence River
- ON - QC Border
- CAN - US Border

Akwesasne
1:118,000

Problem description: Industrial emissions

Aluminum smelter and Automotive Plant are both within close proximity to Akwesasne

Aluminum smelter 1996

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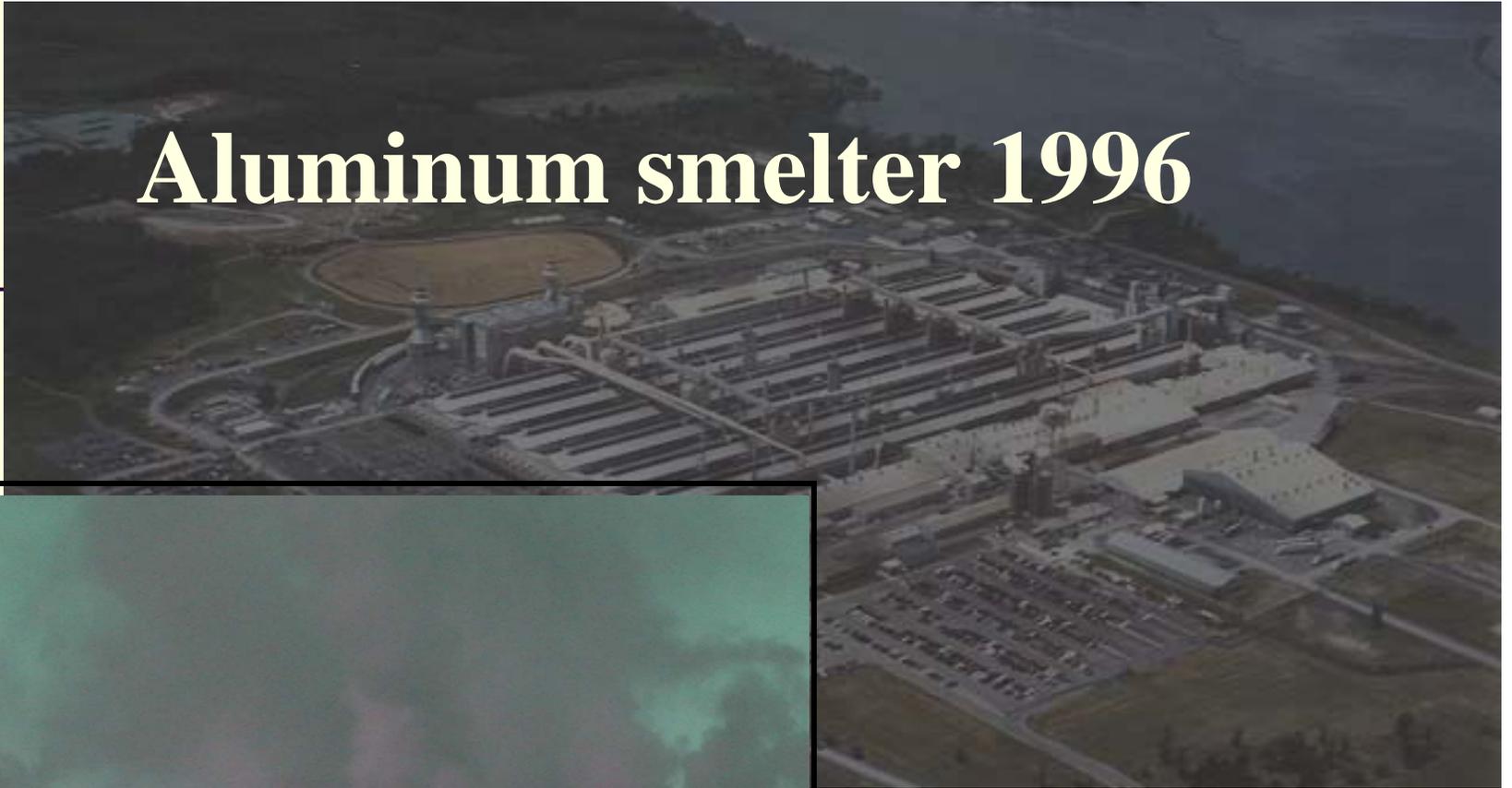
Aluminum smelter 2006

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
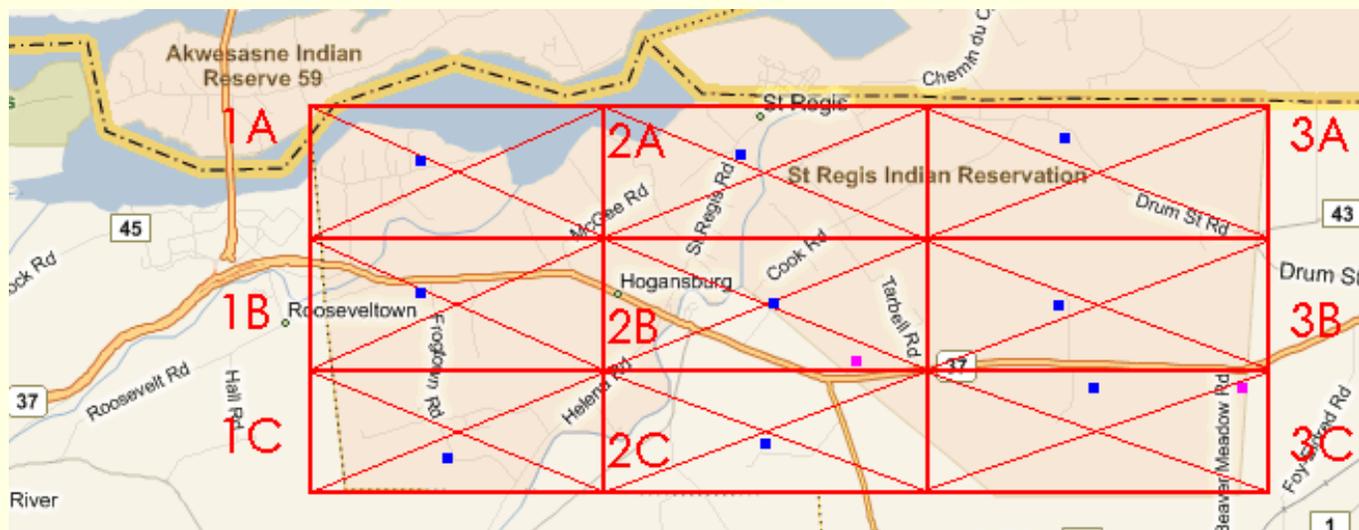- Quality Assurance
- Detection limits

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

St. Regis Mohawk Tribe - Environment Division – Air Toxics Program

Land Owner Consent Form

I _____, verify that I am the legal owner of land plot number _____
    NAME   PLOT NUMBER
located at _____
                 PHYSICAL ADDRESS

consent to the St. Regis Mohawk Tribe - Environment Division – Air Toxics Benzene Program Air Technicians to place the necessary equipment as described to me on my property to assist the St. Regis Mohawk Tribe - Environment Division - Air Toxics Benzene Program to conduct sampling. I have read and understood the information provided about the procedures of the testing and realize that my property and the air surrounding it will not be introduced to air toxics as the result of the testing being conducted by the St. Regis Mohawk Tribe - Environment Division, it is only being tested for benzene that is already in the air. I understand that I will remain anonymous. I understand that photographs may be taken for the SRMT Environment records.

_____
Signature

_____
Mailing Address if different from above (optional if you want results mailed to you)
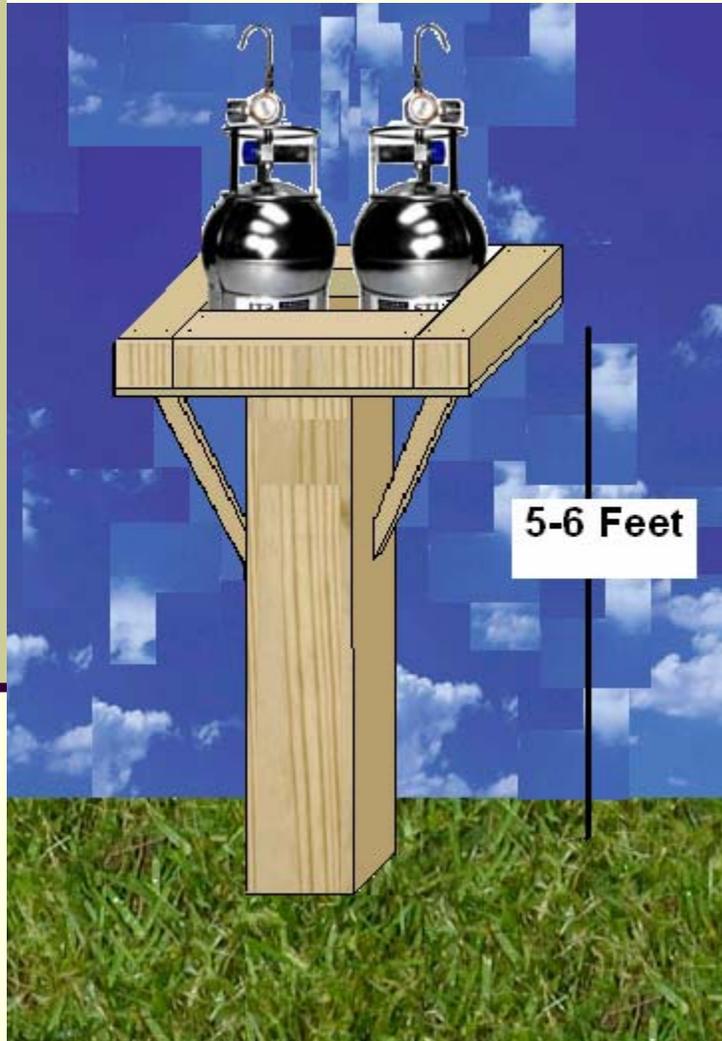
_____
Contact Information

If there is more than one owner please enclose the name below and contact information.

_____
Co-Owner Name

_____
Contact Information

Date Received By Technicians: _____ / _____ / _____

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

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Designing sampling stands

5-6 Feet

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

z1   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(~1gallon)

  -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

Chain of custody forms

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

Chain of Custody

SRMT ENV AIR TOXICS PROGRAM

BENZENE PROJECT

	Canister Number	Flow Control Number	LOCATION	Canister Pressure START/STOP	Flow Control Pressure START/STOP	DATE	TIME START	TIME STOP	SAMPLER Name
1				/	/				
2				/	/				
3				/	/				
4				/	/				
5				/	/				
6				/	/				
7				/	/				
8				/	/				
9				/	/				
10				/	/				
11				/	/				
12				/	/				

Laboratory: _____ Carrier: _____

Instructions: _____

Notes: _____

COC Signature List: Name   Date   Time
1 Relinquished By: _____   Received By: _____
2 Relinquished By: _____   Received By: _____
3 Relinquished By: _____   Received By: _____
4 Relinquished By: _____   Received By: _____

If you have any questions please contact SRMT Environmental:
Phone: 518-358-5937 Fax: 518-358-6252   Email: angela_benedict_dunn@srmtenv.org   Page

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Sampling Information Validation

Data Quality Objectives

|	Precision	Sensitivity	Completeness	Accuracy
BTEX	+/- 10%	Compound specific 0.1 ppbv	>80%	+/- 25%

Calibration

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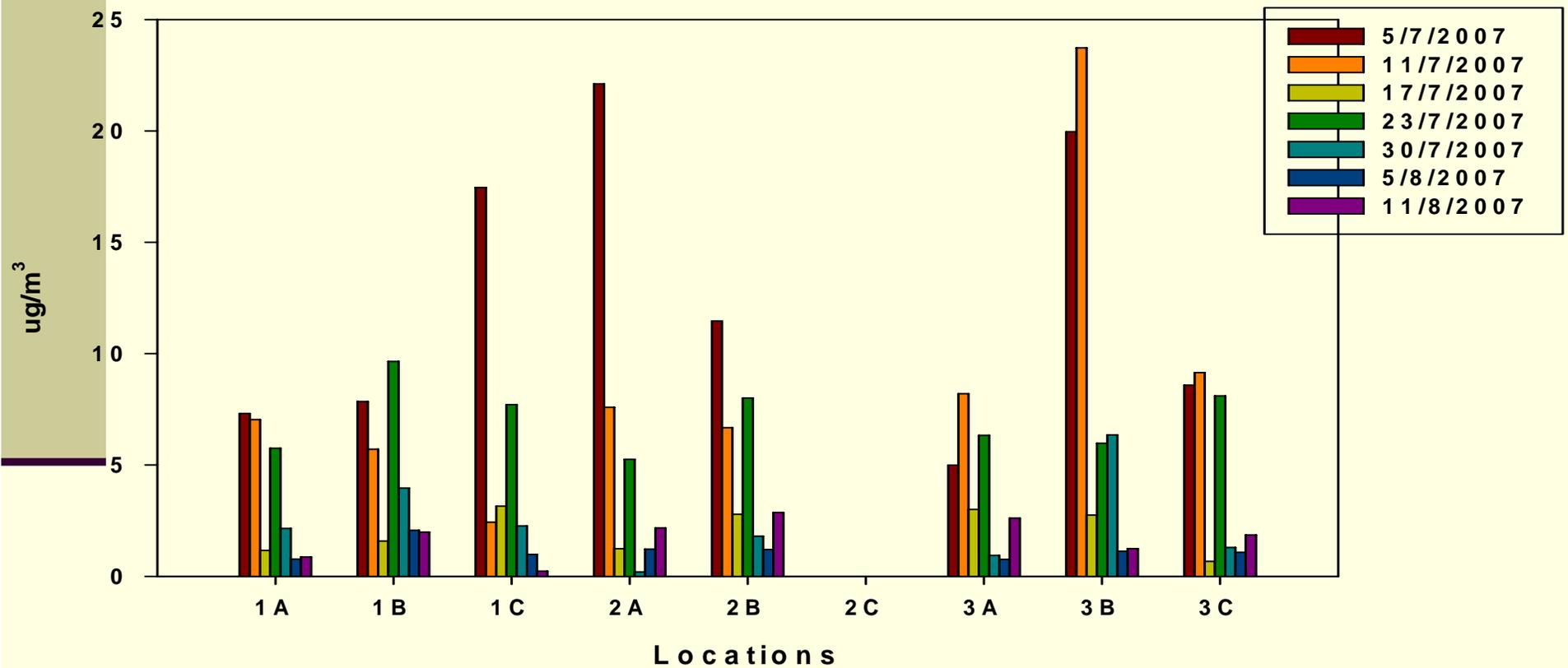- Range of interest 0.1-25ppbv

Btex calibration curve 071707
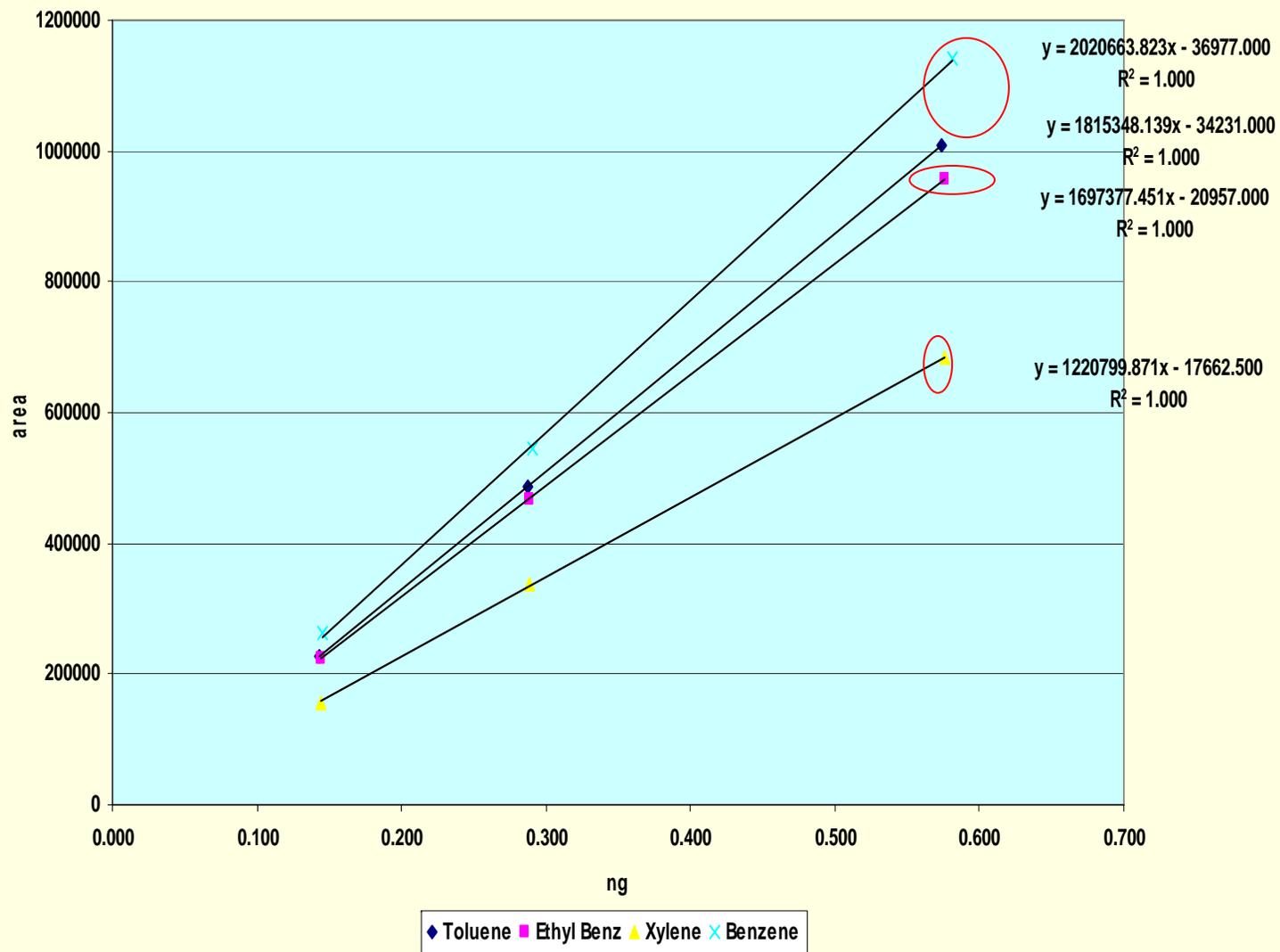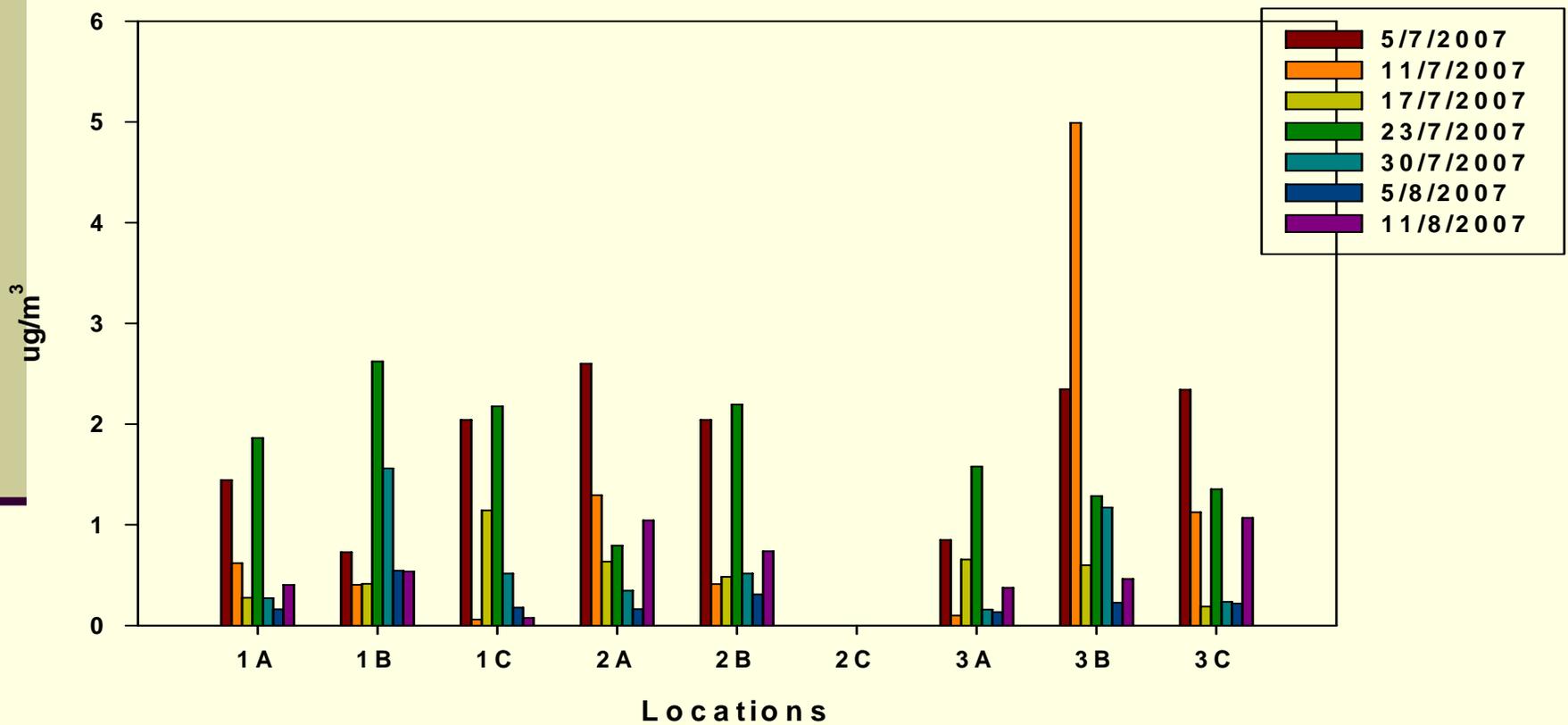
Preliminary results

Benzene concentrations
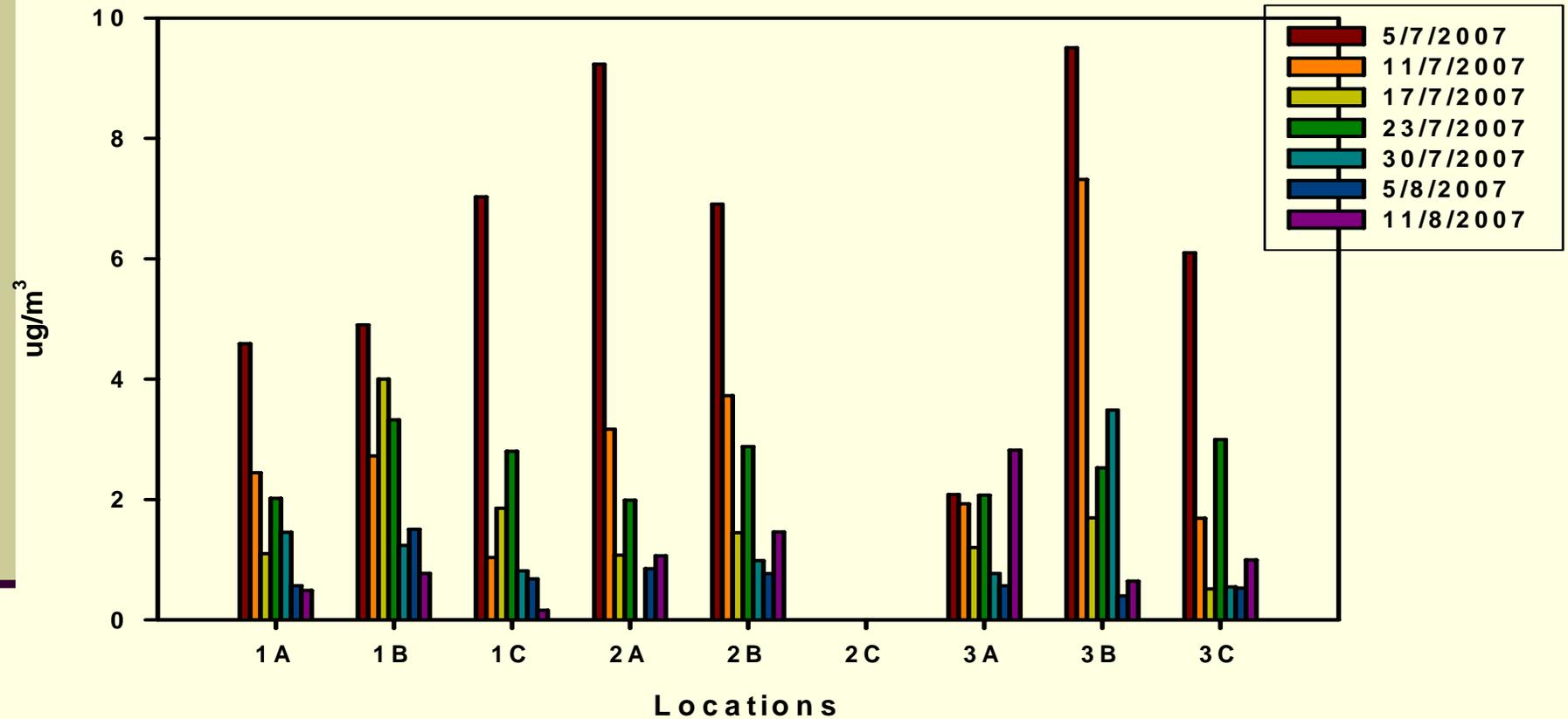
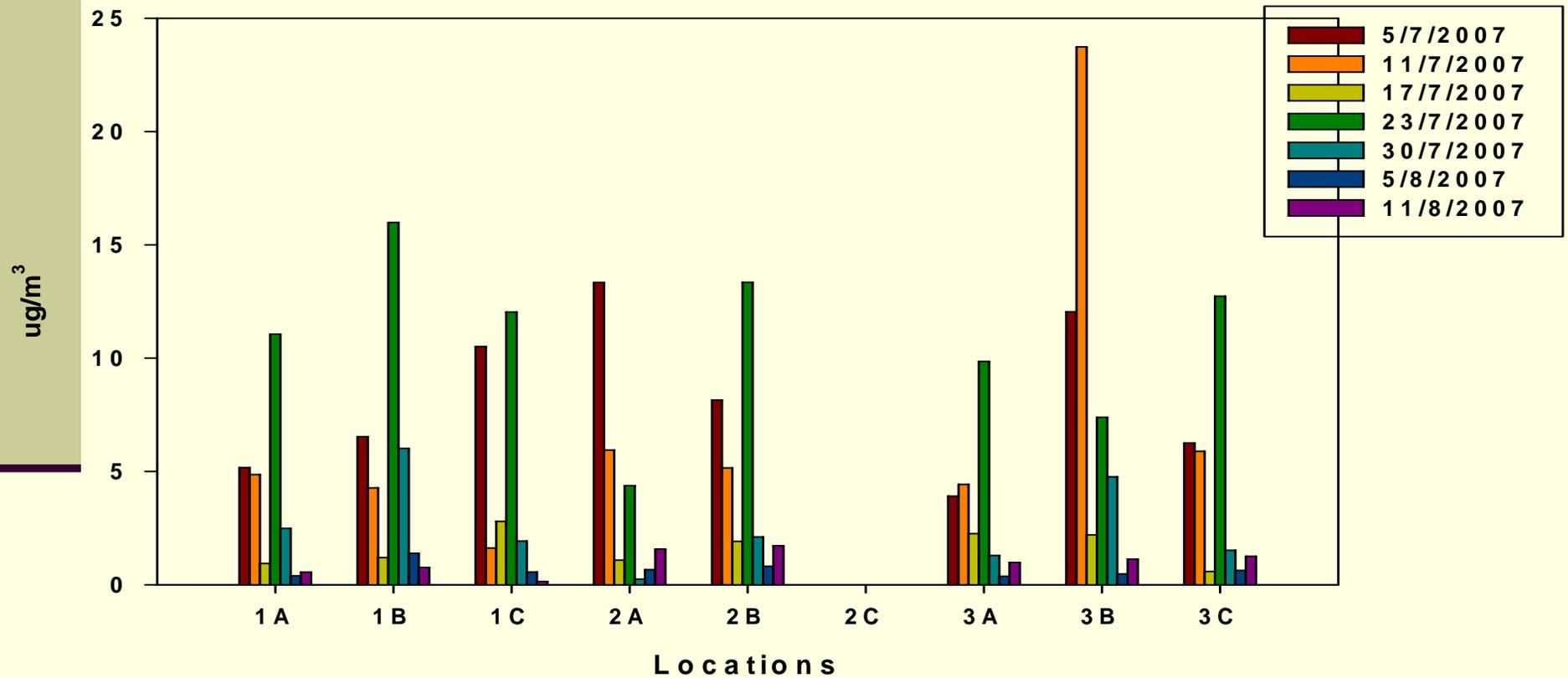# Preliminary results: toluene concentrations

T o l u e n e   c o n c e n t r a t i o n s

Ethyl benzene concentrations

Ethyl benzene concentrations

Xylene concentrations

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Benzene concentrations (ug/m^3)

Locations	1A	1B	1C	2A	2B	3A	3B	3C
7/5/2007	4.59	4.90	7.03	9.23	6.91	2.08	9.50	6.10
7/11/2007	2.45	2.72	1.04	3.17	3.73	1.93	7.32	1.69
7/17/2007	1.10	4.00	1.86	1.08	1.45	1.20	1.69	0.51
7/23/2007	2.02	3.32	2.80	1.99	2.88	2.07	2.53	3.00
7/30/2007	1.45	1.24	0.81	-999	0.98	0.77	3.49	0.55
8/5/2007	0.57	1.51	0.68	0.85	0.77	0.57	0.40	0.53
8/11/2007	0.49	0.78	0.16	1.07	1.46	2.82	0.65	0.99
8/17/2007	0.11	0.48	0.15	0.85	2.63	1.41	-999	0.23

-999 - below the detection limit

Toluene concentrations (ug/m^3)

Locations	1A	1B	1C	2A	2B	3A	3B	3C
7/5/2007	7.31	7.85	17.46	22.11	11.46	4.99	19.96	8.58
7/11/2007	7.04	5.70	2.43	7.59	6.67	8.20	23.73	9.15
7/17/2007	1.16	1.58	3.15	1.24	2.78	3.00	2.75	0.68
7/23/2007	5.75	9.65	7.71	5.25	8.00	6.33	5.97	8.10
7/30/2007	2.15	3.96	2.26	0.19	1.80	0.94	6.35	1.29
8/5/2007	0.77	2.06	0.98	1.22	1.20	0.76	1.12	1.07
8/11/2007	0.86	1.98	0.23	2.17	2.87	2.61	1.24	1.86
8/17/2007	0.35	0.72	0.73	0.95	6.42	7.55	0.16	0.32

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