



SOURCE APPORTIONMENT OF PAHs AT ONTARIO SITES BY RECEPTOR MODELING

3 June 2008

**Deniz Karman
Angelos Anastassopoulos
Civil & Environmental Engineering**



Carleton
UNIVERSITY

Outline

1. Introduction

- research objectives

2. Background

- sources
- NAPS monitoring

3. Project scoping

4. NAPS data trends

5. Data screening for receptor modeling

- candidate receptor models
- preliminary assessment
- challenges & recommended model



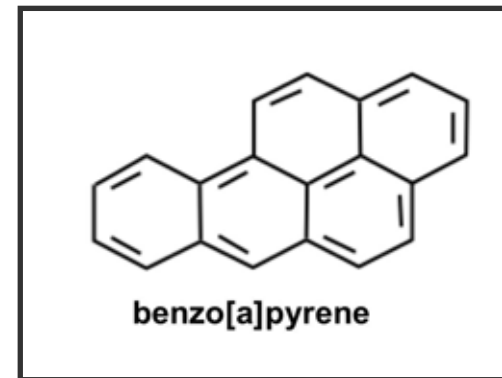
1. Introduction: Research Objectives

- For scoped urban and rural Ontario sites
 - seasonal, long-term trends in ambient PAH concentrations for scoped urban/rural sites
 - identify major PAH sources
 - quantify relative contribution of major PAH sources
 - focus on BaP

- Inform and link to
 - emission inventory estimates
 - regulatory/control initiatives

2. Background: Sources

- Manufacture of some commercial products (e.g., coal tar, creosote, road asphalts, plastics)
- Largely from incomplete combustion of organic matter
 - Biogenic
 - forest fires
 - Anthropogenic
 - industrial processes - Aluminum
 - heating
 - open air fires/agricultural burning
 - waste incineration
 - transportation



2. Background:

NAPS Monitoring of PAHs

- PAH monitoring at 13 Ontario sites
 - urban (industrial, commercial, residential)
 - rural (agricultural, undeveloped, forest)
- Single central monitoring station at most sites
- 24-hr integrated sample, typically 6-day sampling schedule
- Two-filter active sampling for particle/vapour phases
 - glass-fiber filter (particle phase)
 - PUF filter (vapour phase)
 - samplers co-extracted for GC-MSD; total species concentrations analysed without particle/vapour phase distinction
- Sampler analysis at Environmental Technology Centre (River Road, Ottawa)



2. Background: NAPS Monitoring of PAHs

- 29 species analysed via GC-MSD

Acenaphthene

Acenaphthylene

Anthanthrene

Anthracene

Benz(a)Anthracene

Benzo(a)Fluorene

Benzo(a)Pyrene

Benzo(b)Fluoranthene

Benzo(k)Fluoranthene

Benzo(b)Chrysene

Benzo(b)Fluorene

Benzo(e)Pyrene

Benzo(g,h,i)Fluoranthene

Benzo(g,h,i)Perylene

Chrysene

Dibenz(a,c)&(a,h)Anthracene

Fluoranthene

Fluorene

Indeno(1,2,3-cd)Fluoranthene

Indeno(1,2,3-cd)Pyrene

Perylene

Phenanthrene

Pyrene

Retene

Triphenylene

1-Me-Pyrene

2-Me-Fluorene

3-Me-Cholanthrene

7-Me-Benz(a)Anthracene





3. PROJECT SCOPING



Carleton
UNIVERSITY

3. Project Scoping

- Seven communities selected for study
 - Urban: Toronto, Hamilton, Windsor
 - Rural: Pt. Petre, Egbert, Simcoe, Walpole Island
- Urban communities selected for study of
 - high local traffic source (e.g., Toronto)
 - local industrial / manufacturing sources (e.g., Hamilton, Windsor)
 - transboundary sources (e.g., Windsor)
 - intra-urban spatial differences (i.e., Toronto has multiple NAPS sites measuring PAHs; land use type “Residential”, “Commercial”, “Industrial”)
- Rural communities selected for diversity of land use type
 - “agricultural”, “undeveloped”
- First Nations community (i.e., Walpole Island FN reserve)
- Use recent years of PAH data as model permits



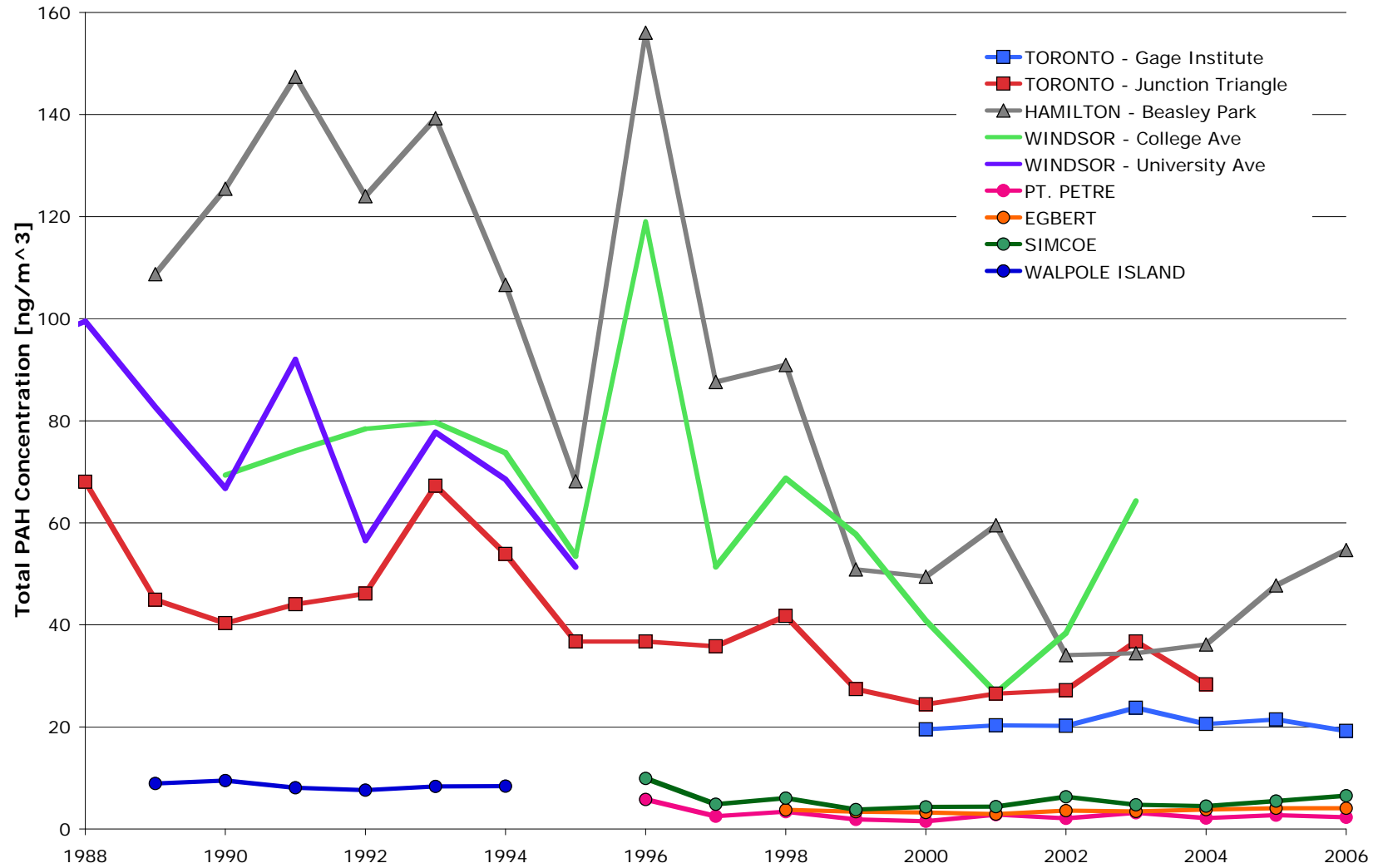


4. PAH TRENDS FROM NAPS DATA

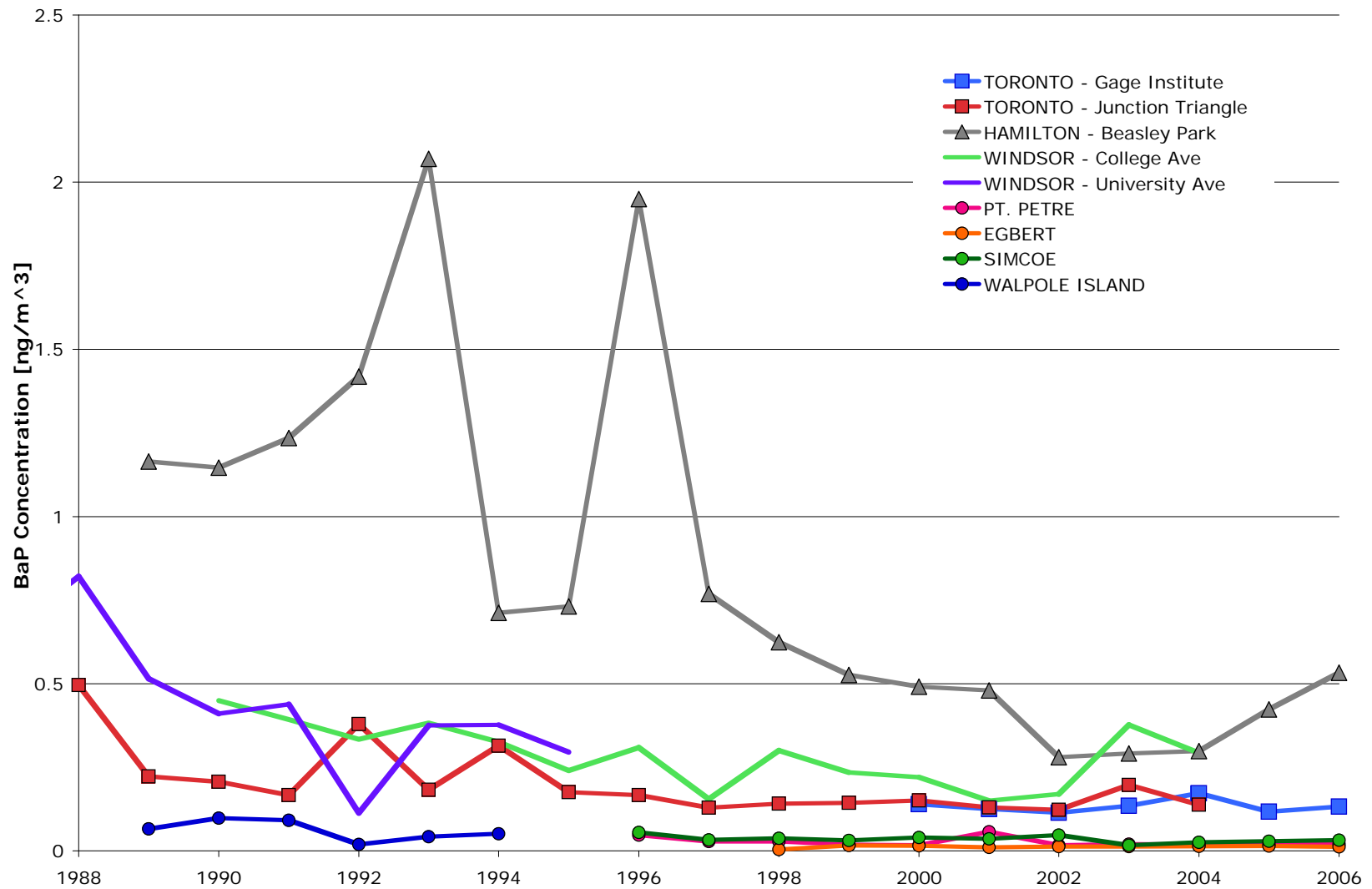
4. PAH Trends: Annual NAPS Levels

- Reviewed urban sites have monitored ambient levels of Total Named PAH and BaP several times higher than reviewed rural sites
- Highest urban PAH concentrations were seen at Hamilton, followed by Windsor and then Toronto.
- Generally, a decreasing trend in concentrations was noted at the urban sites over the entire available time period 1989-2006
- Differences between levels at rural sites were small and a decreasing trend was not noted over the more recent time period of 1998-2006

4. PAH Trends: Annual NAPS Levels Total Named PAH v. Year (all sites)



4. PAH Trends: Annual NAPS Levels BaP v. Year (all sites)



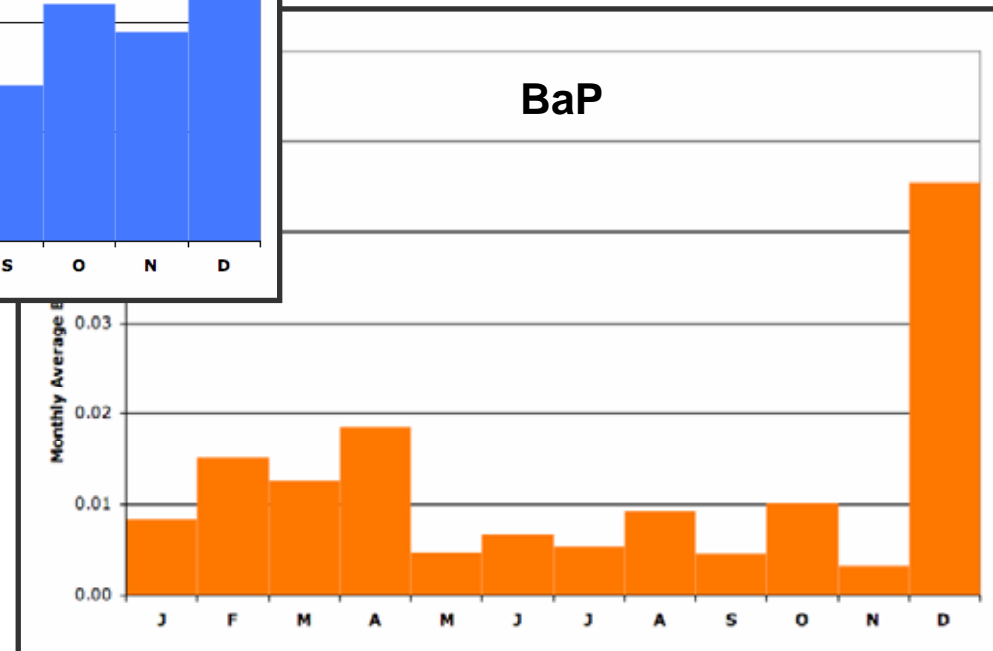
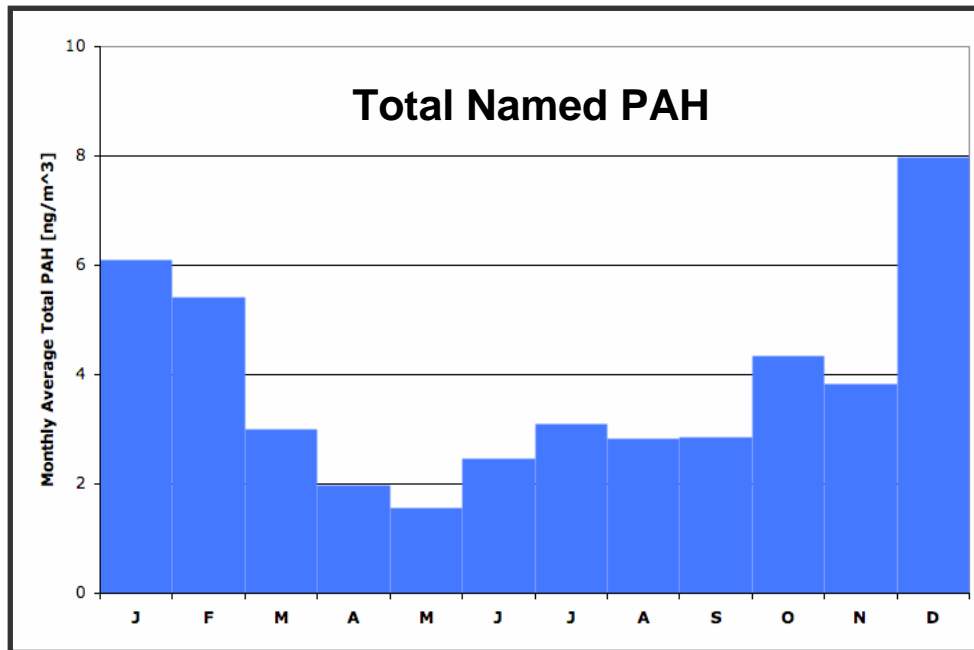
4. PAH Trends:

Seasonal NAPS Levels

- Seasonal trend analysis indicated peak levels (Total Named PAH, BaP) occurring most frequently in fall and winter months
 - months of prevalent combustion-based heating (i.e., October through March)
- Toronto Gage Institute site an exception
 - Total Named PAH peaks occur more often in spring and summer months (April - September)
 - BaP followed typical pattern, peak in fall/winter

4. PAH Trends: Seasonal NAPS Levels

Monthly Average Total Named PAH, BaP (Egbert, 2003)



4. PAH Trends: Species Abundance

- Urban sites, 8 dominant species make up >85% of Total Named PAH:
 - Acenaphthene
 - Acenaphthylene
 - Anthracene
 - Fluoranthene
 - Fluorene
 - Phenanthrene
 - Pyrene
 - 2-Me-Fluorene

*(alphabetical order,
not rank order)*
- Rural sites, similar suite; however, some species observed as abundant only at rural sites:
 - Benzo(b)Fluoranthene (Point Petre, Simcoe)
 - Chrysene (Point Petre)
 - Retene (Simcoe)

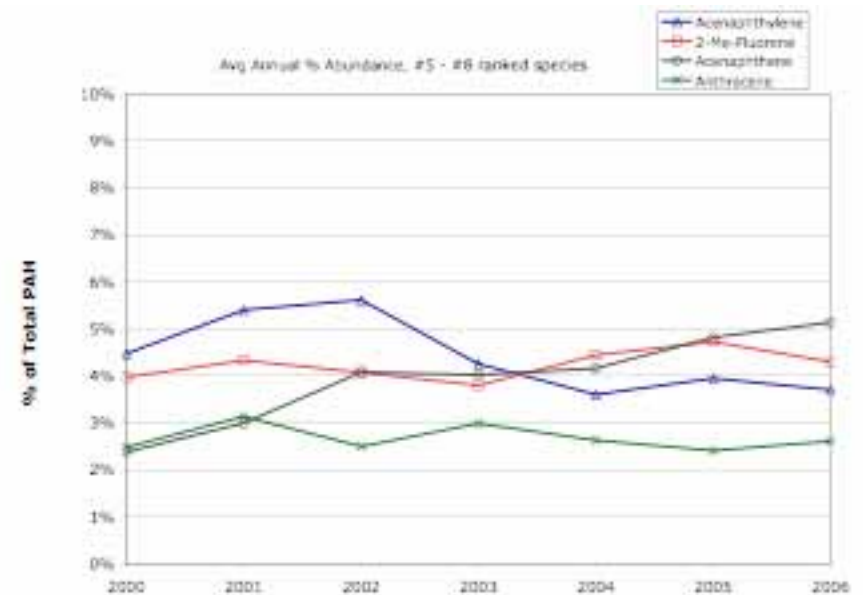
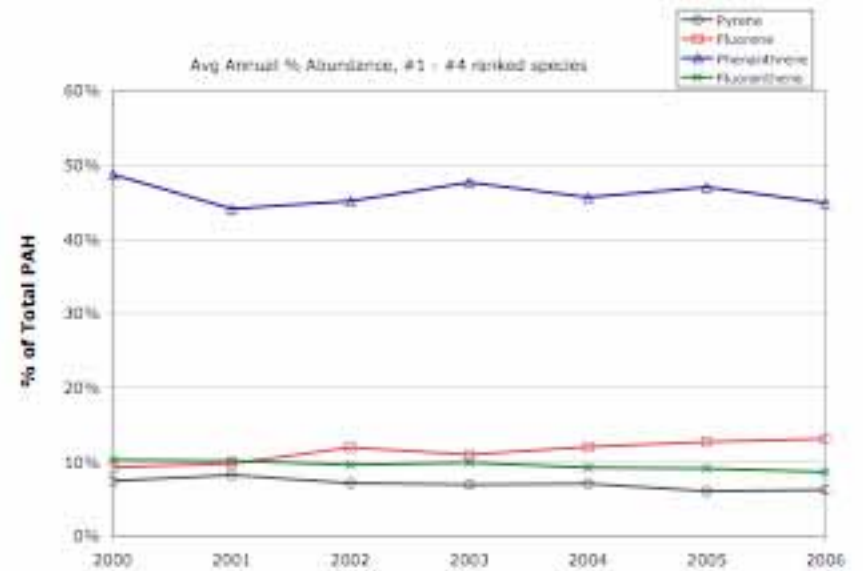
4. PAH Trends: Species Abundance

- Dominant species at most sites and time-series
 - relatively constant annual average abundance ratios over monitoring period
 - centred around a mean species abundance ratio
- Suggests no significant change in source mix over the monitoring period (particularly recent years) for most sites



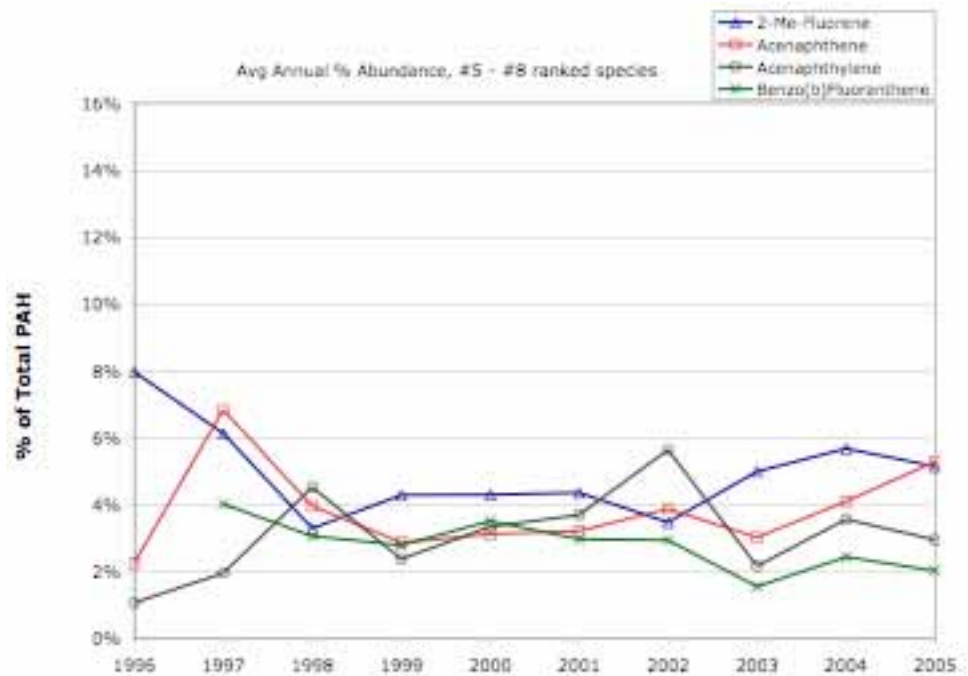
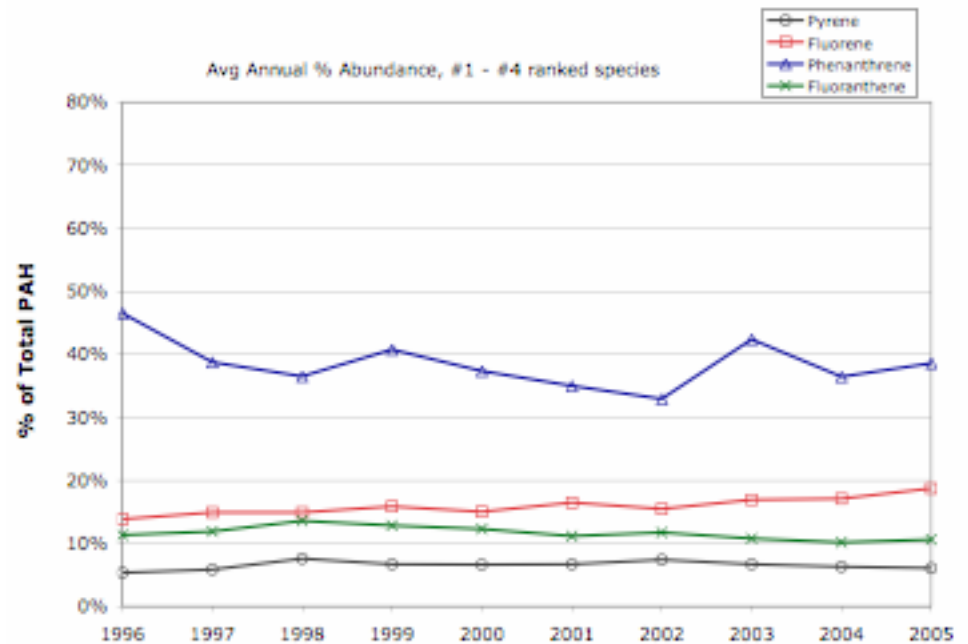
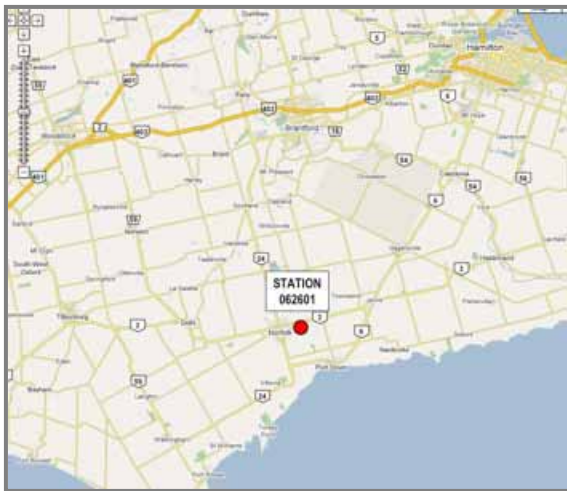
4. PAH Trends: Species Abundance

% of Total Named PAH for top eight-ranked species v. Year
(Toronto @ Gage)



4. PAH Trends: Species Abundance

% of Total Named PAH for top eight-ranked species v. Year (Simcoe)





5. PAH DATA SCREENING FOR RECEPTOR MODELING



Carleton
UNIVERSITY

5. Data Screening: Candidate Receptor Models

- Chemical Mass Balance (CMB)
 - apportion relative contribution of sources from PAH measurements at receptor and knowledge of relevant source profiles
 - PAH source profiles from variety of studies / locations / analysis methods
 - poor compatibility between source and receptor measurements
 - limited to sources input a priori, no identification of unknown sources

- Positive Matrix Factorization (PMF)
 - apportion relative contribution of sources from long time-series PAH measurements at receptor
 - statistical method with some 'art' required for interpretation of model results

5. Data Screening: Preliminary Assessment

- Generally, the scoped site PAH data is amenable to receptor modeling, with sufficient
 - number of species
 - data density
 - data completeness (i.e., low % BDL)
- Collaboration initiated with Dr. Phil Hopke (Clarkson U) for PMF
 - Hamilton dataset reviewed
 - found amenable to US EPA PMF2

5. Data Screening: Previous Studies

- Reference studies on PMF of PM_{2.5}
 - typically using PM_{2.5}-associated metals
- PMF has been applied to speciated VOCs
 - recent study on NAPS, Curren et al (Environment Canada, 2007)
 - similar challenges to PAH modeling (e.g., differential reactivity)
- Interest in PAH sources more recent
 - Larsen et al, 2003 (Baltimore, MD)
 - Harrison et al, 1996 (Birmingham, UK)
 - Otson et al, 1989 (Toronto, Whitehorse)
- Have reference PAH source profiles to assist interpretation of PMF “factors”
 - gasoline, diesel fuel vehicle (mobile sources)
 - coal, oil, natural gas, wood stove combustion (heating)
 - biomass combustion (biogenic sources)
 - asphalt operations
 - food preparation, cigarettes (indoor sources)



5. Data Screening: Challenges to Receptor Modeling

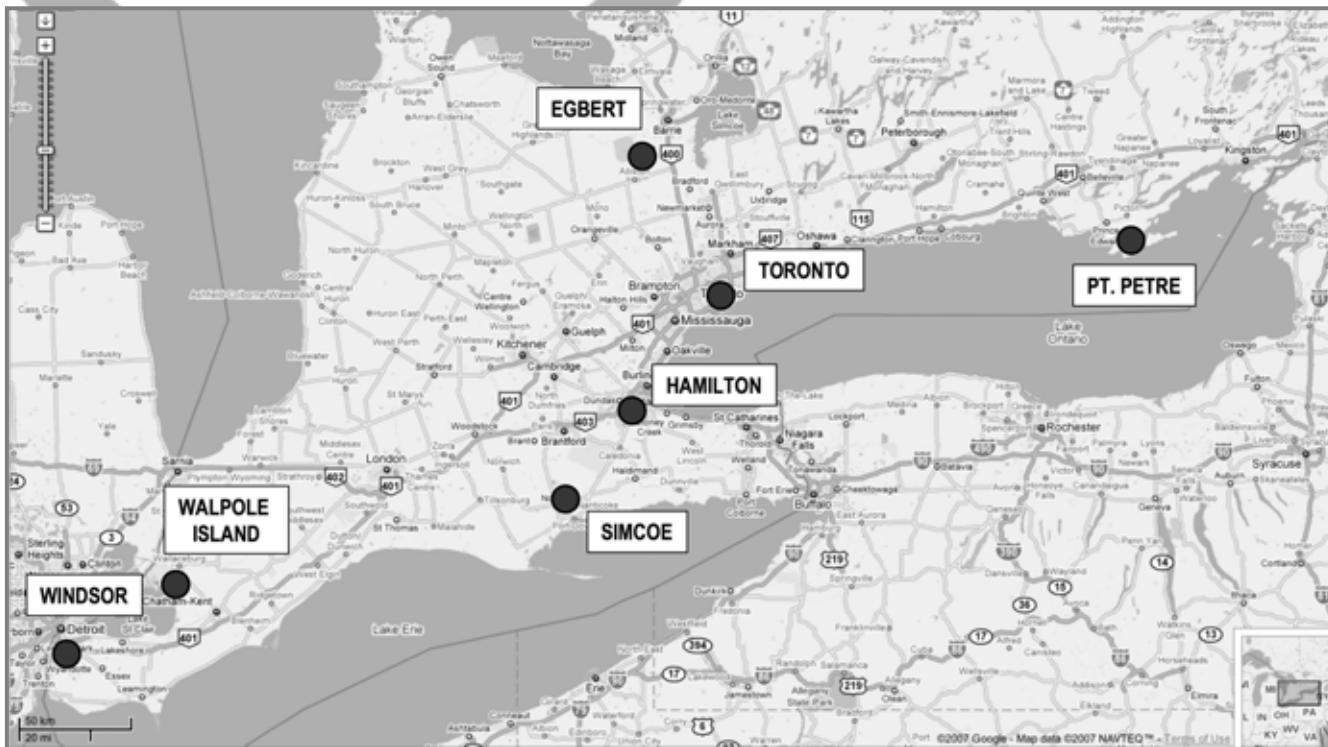
- Differential reactivity of PAH species
 - apportioning to particle / vapour phase
 - *model scenarios with / without reactive species*
 - *model scenarios with varying time between source and receptor*
- Similarity among factors / sources
 - *use source marker species, reference source profiles*
- Care needed interpreting results from PMF
 - *build a 'body of evidence' to validate source findings*
 - a priori known sources (emissions inventory by Galarneau et al, 2007)
 - other pollutant trends / source apportionment (e.g., PM_{2.5} - metals, VOC - speciated)
 - wind rose analysis for identified local sources
 - backward trajectory analysis (HYSPLIT) for identified transboundary sources

5. Data Screening: Recommended Receptor Model

- PMF (US EPA PMF2)
- Rationale
 - data amenable to PMF (long time series, dense, complete, multi-species)
 - most sites show stable source mix over most years
 - collaborative support from Dr. Hopke, Clarkson U
 - available tools for interpreting results
 - source markers / profiles for major source types
 - emissions inventory
 - wind rose / backward trajectory analysis
 - can identify sources otherwise missed and 'minor' (by % contribution) but possibly important for human health effects / available interventions

Thank you!

Questions?



Carleton
UNIVERSITY



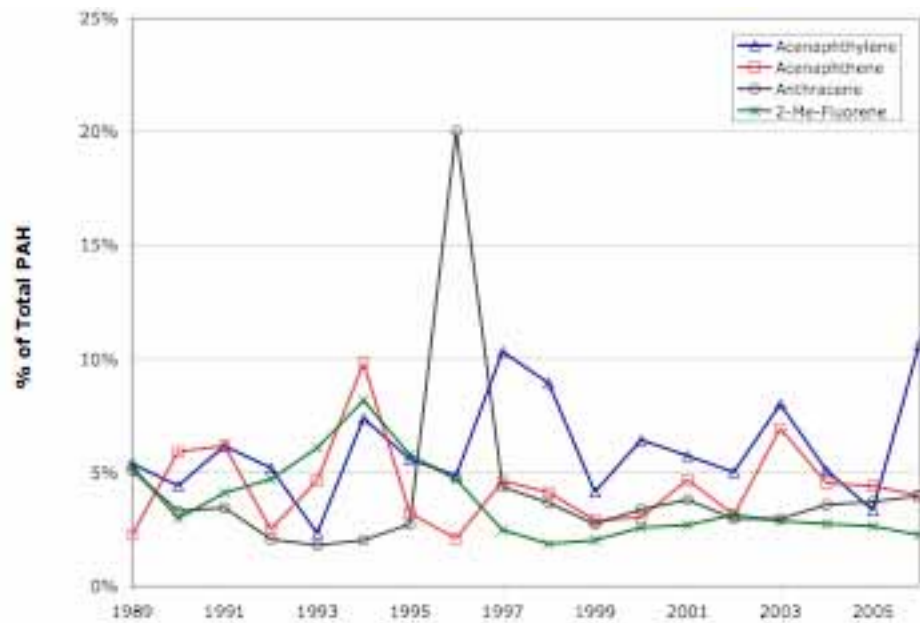
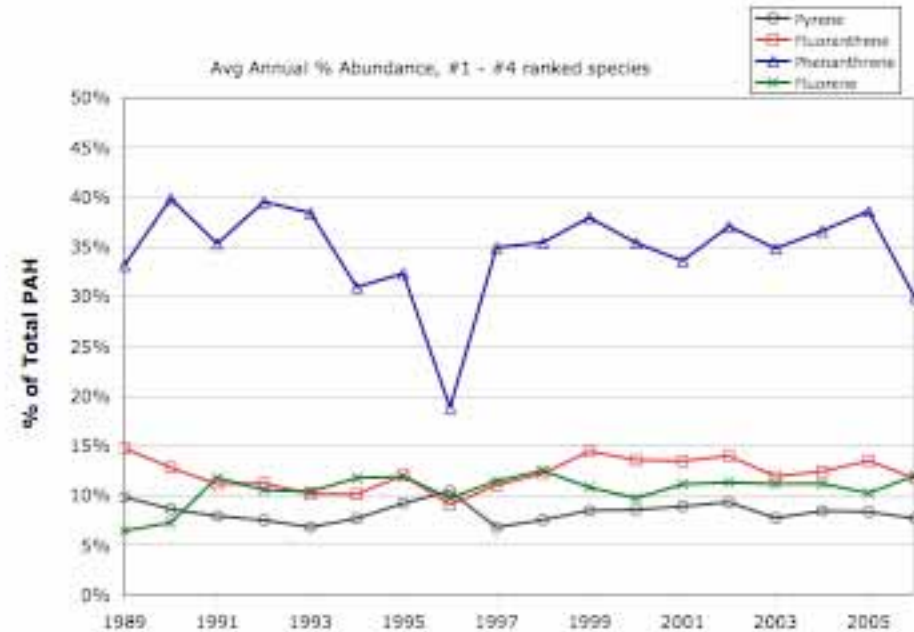
GRAPHICS & EXTRA MATERIAL



Carleton
UNIVERSITY

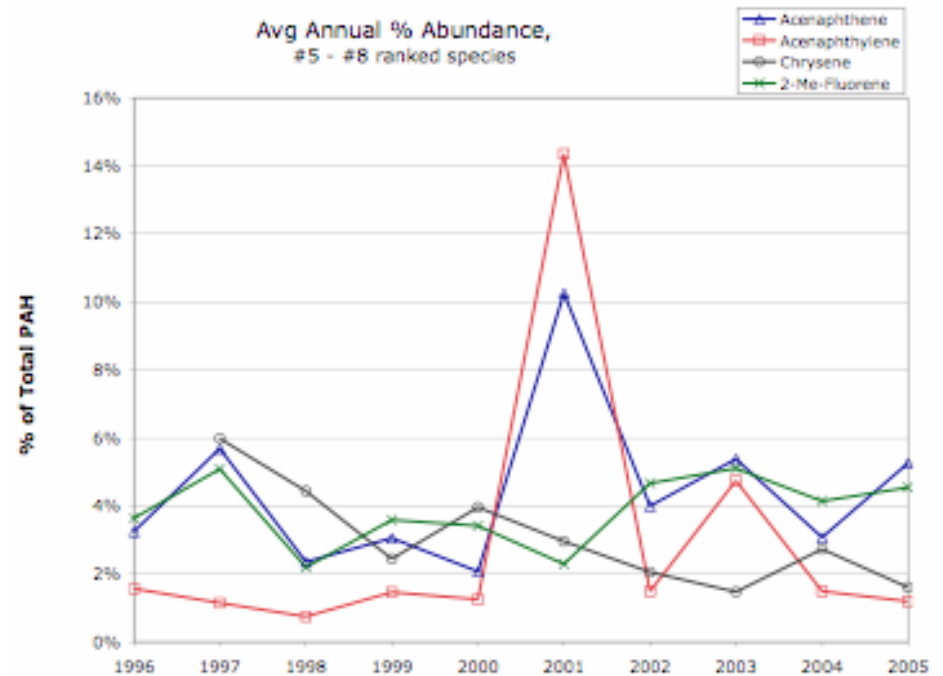
4. PAH Trends: Species Abundance

% of Total Named PAH for top eight-ranked species v. Year (Hamilton)



4. PAH Trends: Species Abundance

% of Total Named PAH for top eight-ranked species v. Year
(Pt. Petre)



2. Background: Mobile Sources

- Karman D, Shen J (2006). “MOBILE6C Modelling and Emissions of Selected Toxic Substances from On-Road Motor Vehicles in Ontario”
 - submitted to Toxics Prevention Division, Environmental Protection Branch-Ontario Region, Environment Canada
 - 14 PAH emissions estimated using PAH/PM₁₀ or PAH/VOC ratios from available emission measurements and MOBILE estimates of PM₁₀ and VOC emissions in 1988-2020 period
 - contribution to emission inventories show a decline over the years despite the increase in VKTs, because of the decrease in PM or VOC emission factors as calculated by MOBILE6C
- Recommended investigation of receptor modelling as validation of results

