SOURCE APPORTIONMENT OF PAHs AT ONTARIO SITES BY RECEPTOR MODELING

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Outline

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2. Background
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   - NAPS monitoring
3. Project scoping
4. NAPS data trends
5. Data screening for receptor modeling
   - candidate receptor models
   - preliminary assessment
   - challenges & recommended model

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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

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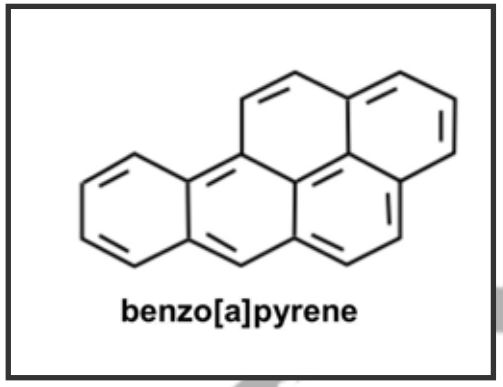
2. Background:
Sources

- 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



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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)

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2. Background:
NAPS Monitoring of PAHs

- 29 species analysed via GC-MSD

Acenaphthene	Benzo(b)Fluorene	Perylene
Acenaphthylene	Benzo(e)Pyrene	Phenanthrene
Anthanthrene	Benzo(g,h,i)Fluoranthene	Pyrene
Anthracene	Benzo(g,h,i)Perylene	Retene
Benz(a)Anthracene	Chrysene	Triphenylene
Benzo(a)Fluorene	Dibenz(a,c)&(a,h)Anthracene	1-Me-Pyrene
Benzo(a)Pyrene	Fluoranthene	2-Me-Fluorene
Benzo(b)Fluoranthene	Fluorene	3-Me-Cholanthrene
Benzo(k)Fluoranthene	Indeno(1,2,3-cd)Fluoranthene	7-Me-Benz(a)Anthracene
Benzo(b)Chrysene	Indeno(1,2,3-cd)Pyrene	

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3. PROJECT SCOPING

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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

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EGBERT
TORONTO
PT. PETRE
HAMILTON
WALPOLE ISLAND
SIMCOE
WINDSOR
Lake Ontario
Lake Erie
Street View
Traffic
Map
Satellite
Terrain
50 km
20 mi
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4. PAH TRENDS FROM NAPS DATA

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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

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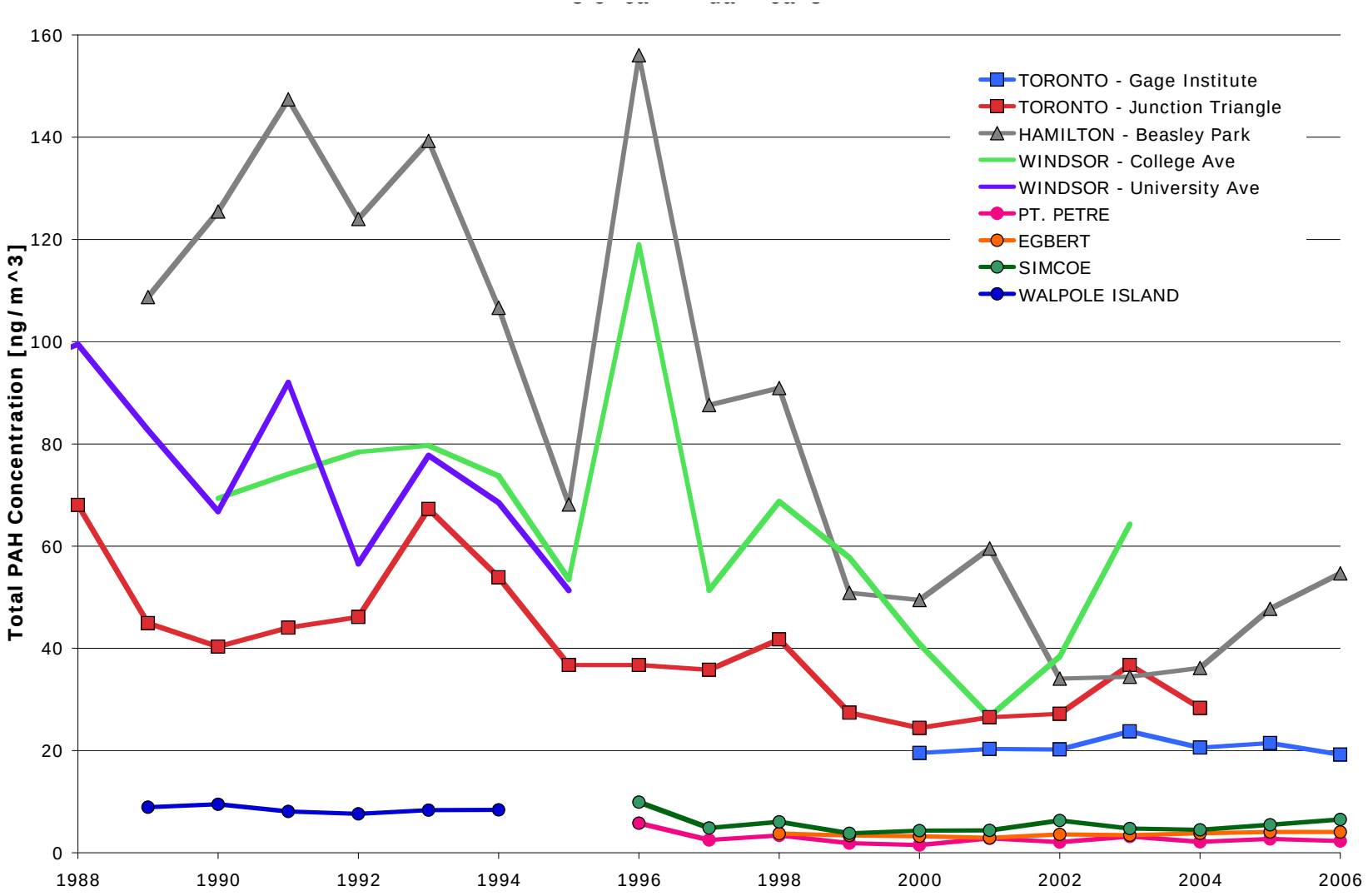
4. PAH Trends:

Annual NAPS Levels

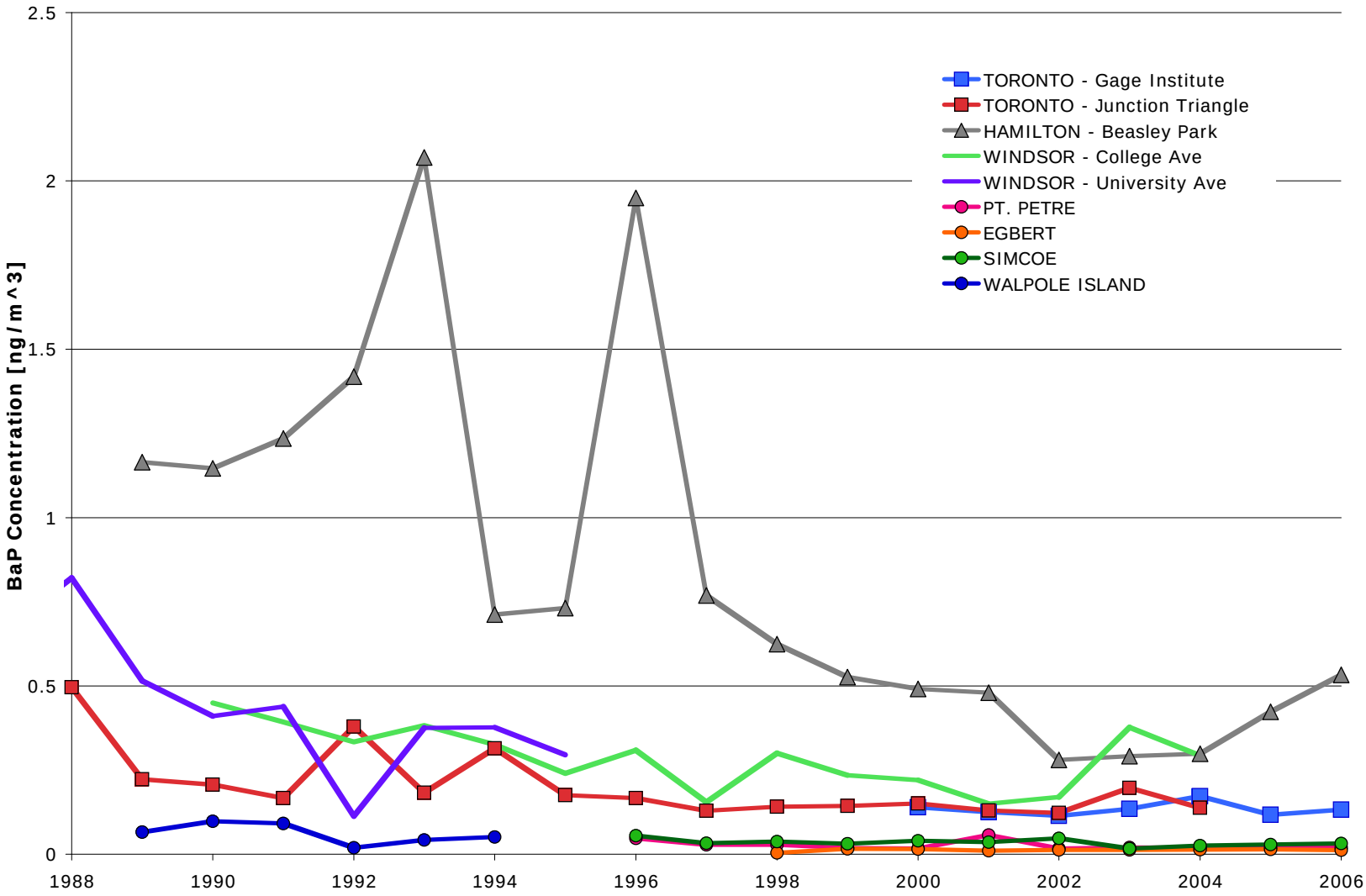
Total Named PAH v. Year (all sites)



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

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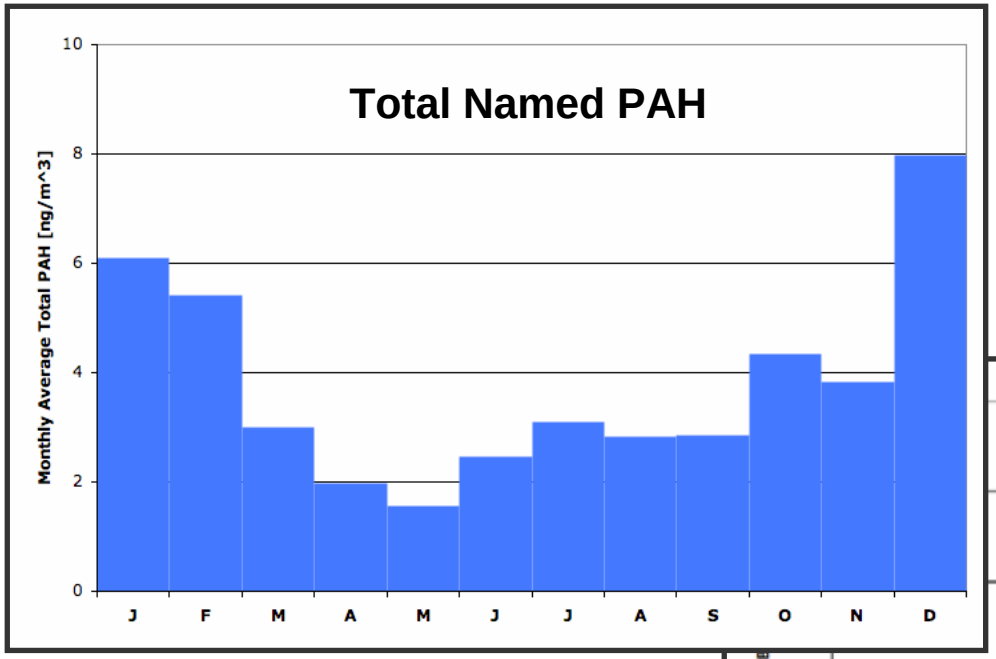
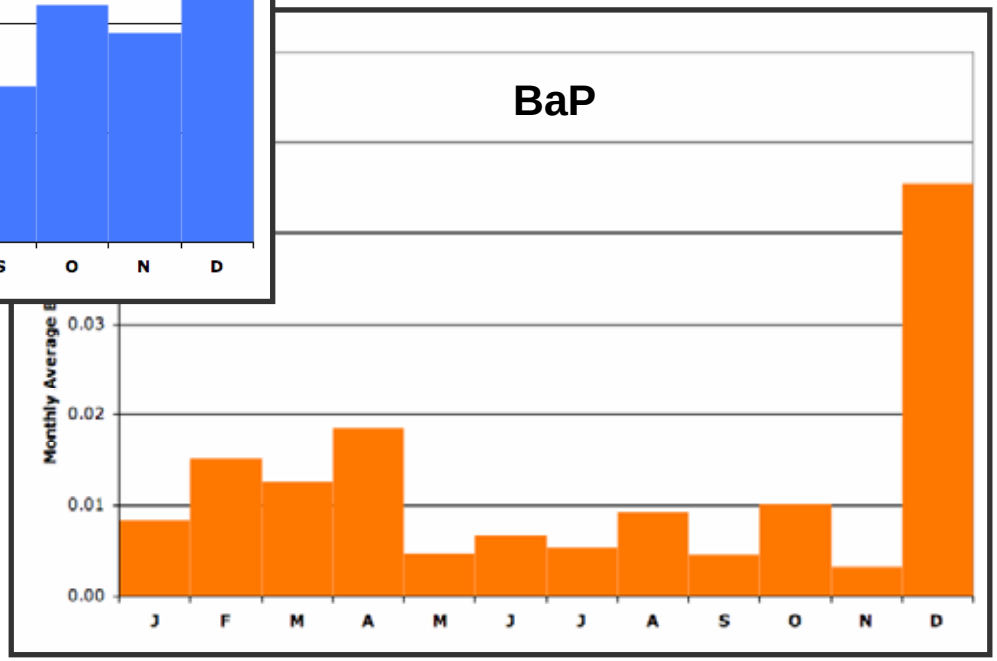
4. PAH Trends:

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)

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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

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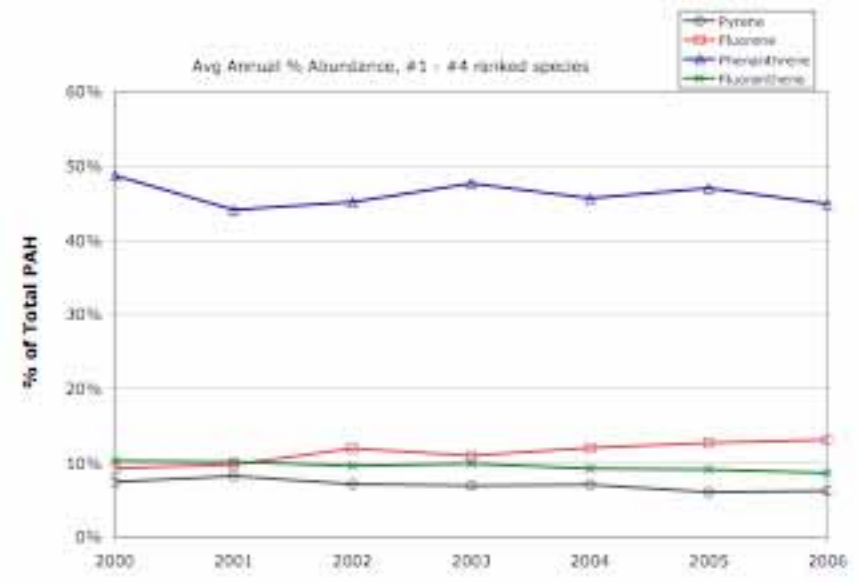
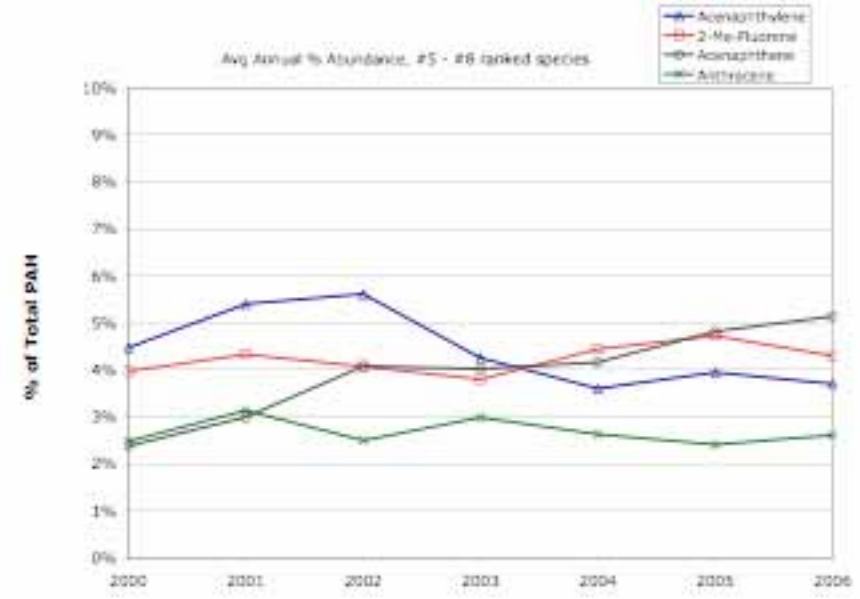
4. PAH Trends:

Species Abundance

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

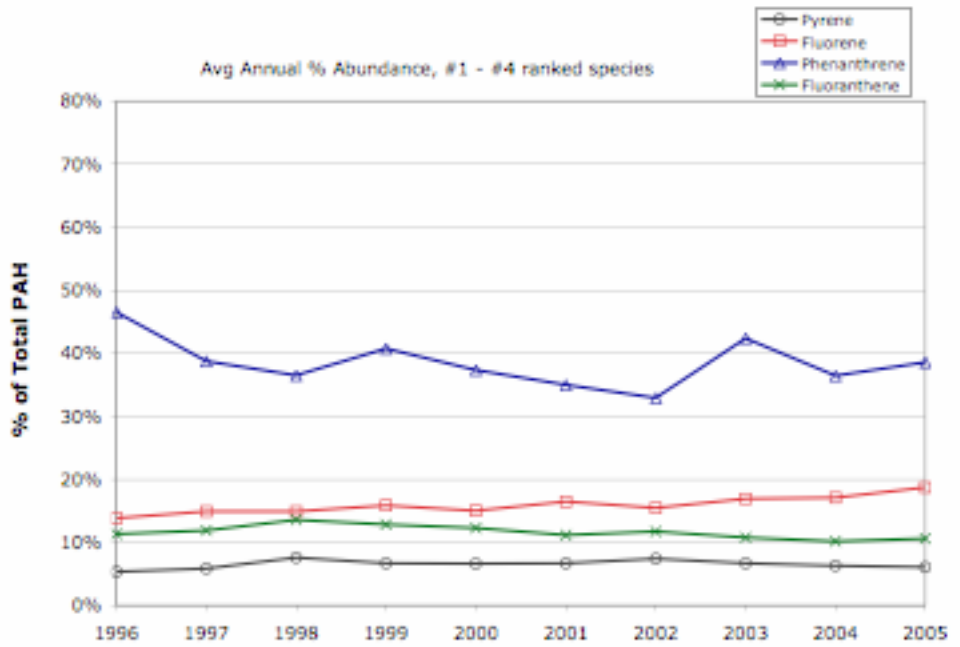


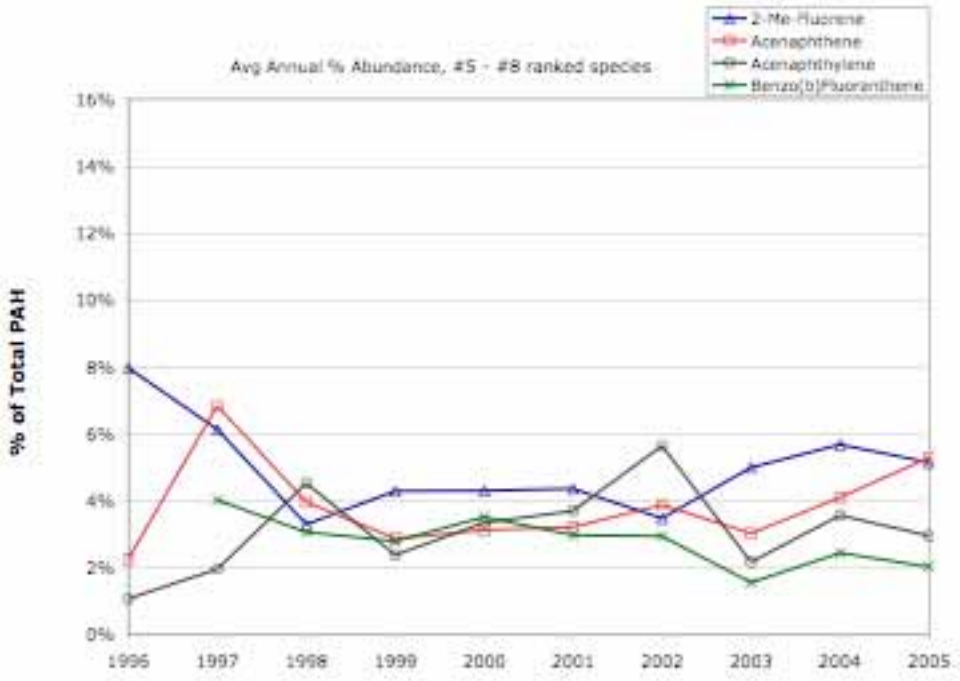


4. PAH Trends:

Species Abundance

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





5. PAH DATA SCREENING FOR RECEPTOR MODELING

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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

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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

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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)

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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 apportionnment (e.g., $PM_{2.5}$ - metals, VOC - speciated)
    - wind rose analysis for identified local sources
    - backward trajectory analysis (HYSPLIT) for identified transboundary sources

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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

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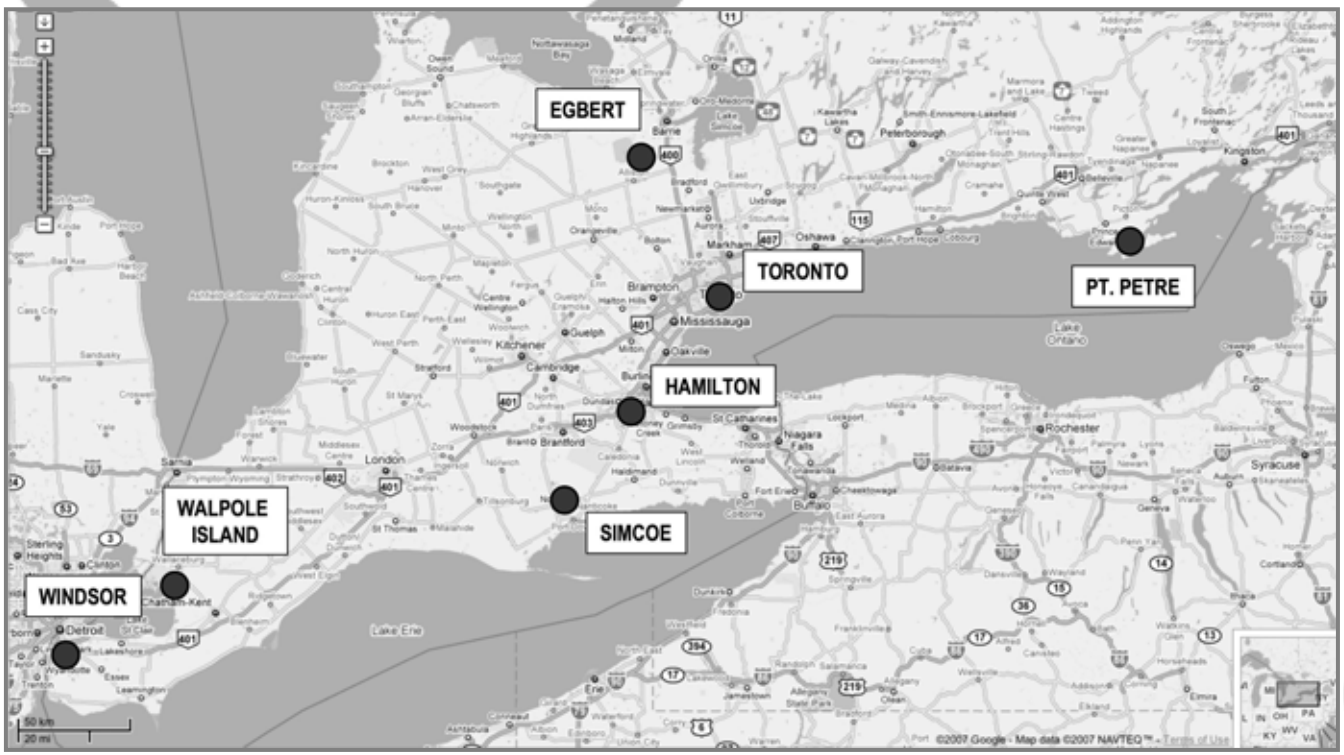
Thank you!

Questions?



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GRAPHICS & EXTRA MATERIAL

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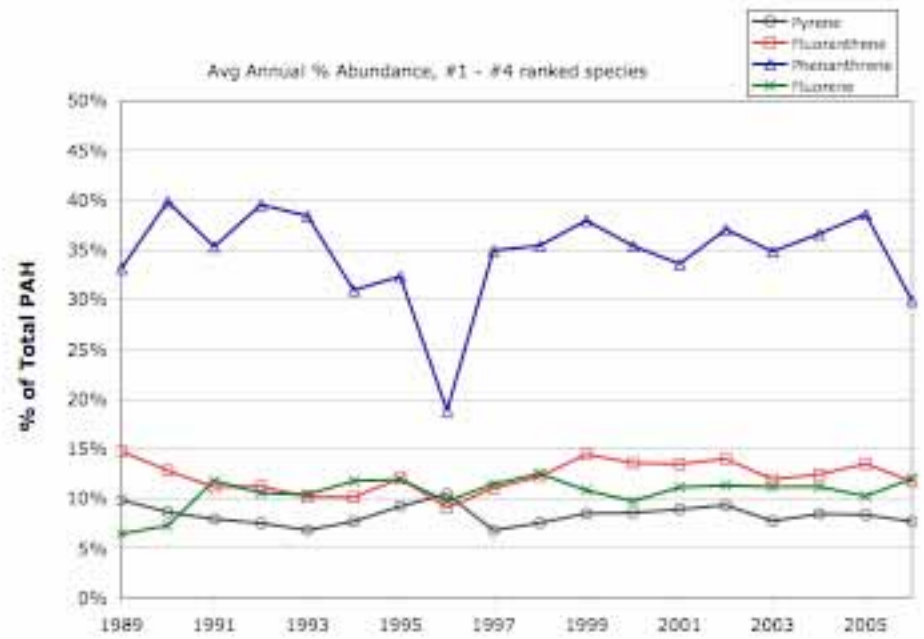
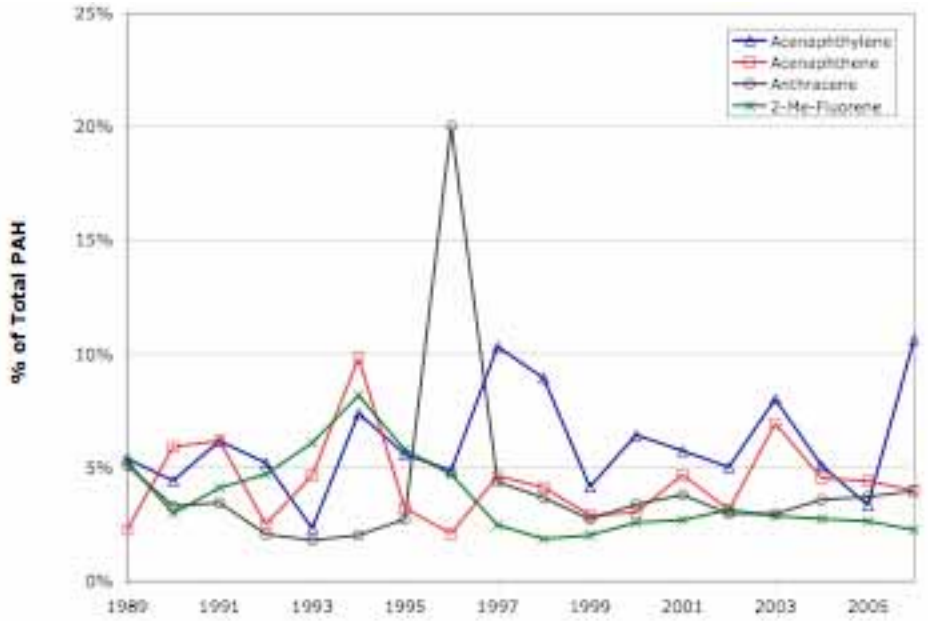
4. PAH Trends:

Species Abundance

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

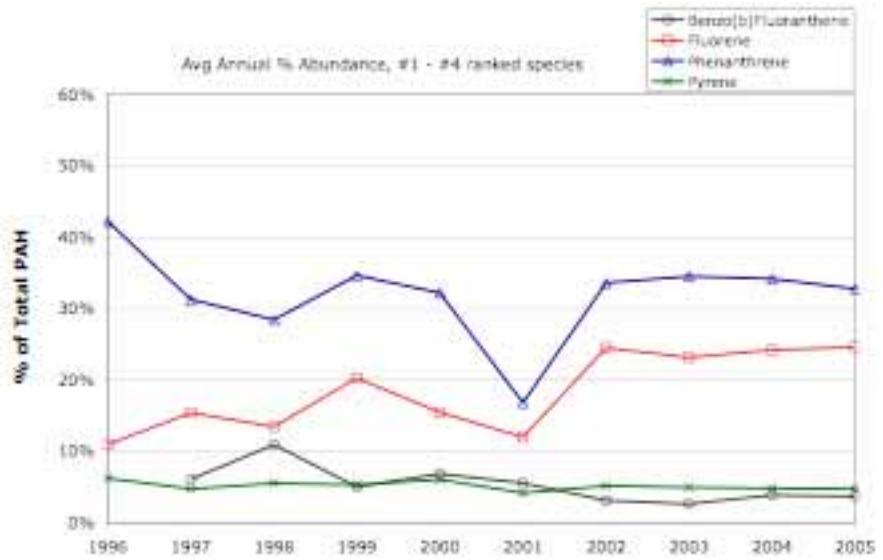


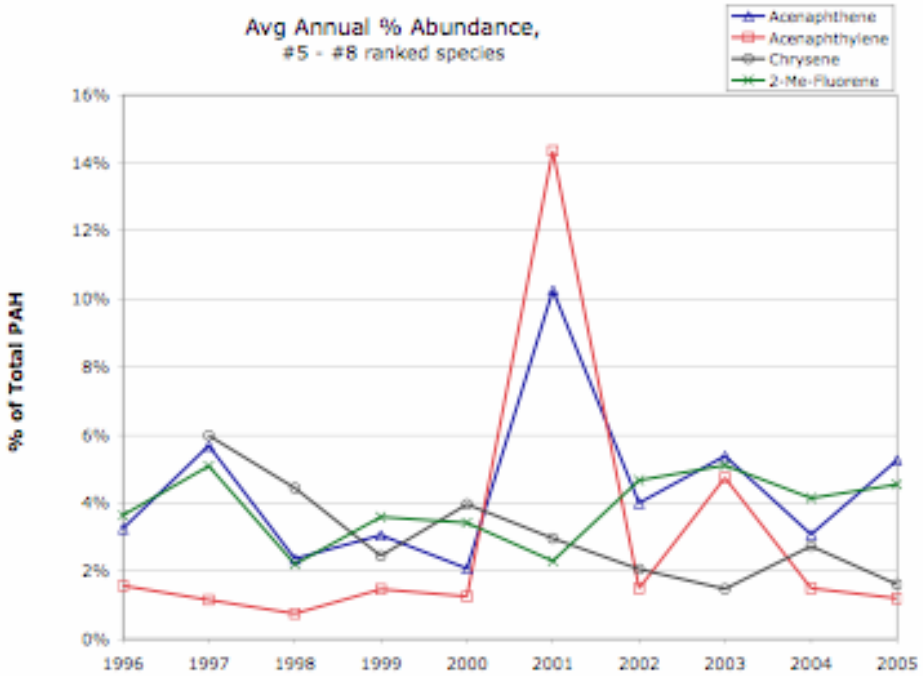


4. PAH Trends:

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/PM_{10} or PAH/VOC ratios from available emission measurements and MOBILE estimates of PM_{10} 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

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