# VOC Source Apportionment in Windsor Ontario

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## Outline

- Project Background
- Design and Methodology
- Model Results
- Spatial Patterns
- Conclusions
- Collocated study in 2007
- Recommendations

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## Windsor Ontario Exposure Assessment Study (WOEAS)

- Personal/Indoor/Outdoor study
  - 46-48 locations in the Windsor, Ontario area in winter and summer of 2005 and 2006
  - Monitoring of PM, $NO_2$, $SO_2$, $O_3$ and VOCs for 5 days per season per site
  - Sampling of indoor, outdoor and personal air quality in the homes of local residents

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## Objective and Scope- source apportionment

- Focus:  VOC outdoor 2005 data
- Source apportionment using the Chemical Mass Balance (CMB) model
  - Identify significant sources and estimate relative contributions
- Investigate spatial patterns of contributions
- Identify seasonal variability

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## Receptor Locations

- 2004: Survey sent to all elementary school children in Windsor to assess respiratory health
- 2005: 46 respondents were chosen for study based on selection criteria
- Included National Air Pollution Surveillance (NAPS) network data
  - Windsor-West site
  - Data only available for winter season

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## Data Collection

- Eight weeks in winter and again in summer
  - Five 24-hour samples per week per site
- VOCs monitored by 6 L Summa Canisters
- Shipped to Environment Canada labs, analyzed for VOC concentrations by GC
- 188 VOC species
  - Used only NMHC species (112) since majority of VOC source profiles only include NMHC

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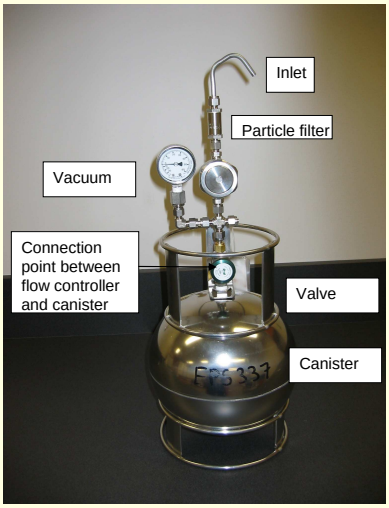


Summa Canister

Outdoor Sample Set-up

## Chemical Mass Balance (CMB) Model

- Input: - Receptor data with uncertainties
  - Profiles of probable sources with uncertainties
  - Choice of fitting species
- Model creates and solves linear mass balance equations
- Output: - Source contribution estimates with uncertainties
  - Performance measures

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## CMB Performance Measures

**$R^2$** – Variance in ambient species conc explained by the calculated species conc [Target 0.8 – 1]

**%Mass** – The sum of source contribution estimates divided by the total mass concentration [Target 100% ± 20%]

**Standard Error** – The uncertainty of the source contribution estimate [Target small, associated with uncertainty of conc data]

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## Source Profile Compilation

- Reviewed local emission inventories
- Chose the most published and reviewed profiles
- Where possible, profiles developed in nearby or similar areas to Windsor were chosen

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## Fitting Species

- Fitting species are the species chosen to be used in the calculation of source contribution estimates
- Should be
  - Major or unique components of the source types influencing the receptor concentrations
  - Long atmospheric lifetime
- Ex: Fitting species for vehicle exhaust – ethene, acetylene, propene, benzene, nonane, decane and undecane

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## Source Profile Evaluation

- Used method developed by Fujita and Lu (1998)
- CMB performance measures examined and source profiles with best results chosen

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## Sources found to contribute emissions

- Vehicle Emissions
  - Diesel and gasoline exhaust
  - Gasoline vapour
  - Liquid gasoline
- Commercial Natural Gas (CNG)
- Liquefied Petroleum Gas (LPG)
- Industrial refineries
- Coke ovens
- Solvents
- Biogenic emissions

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## Data Processing

- Of the 480 planned samples for the outdoor measurements 467 VOC canisters were deployed (>97%), of those, 41 samples were considered invalid (<9%) leaving a total sample size of 426.
- Averaged ambient results for 5-day sampling week
- Ambient data assigned 15% uncertainty
- Fitting species chosen: 32 total

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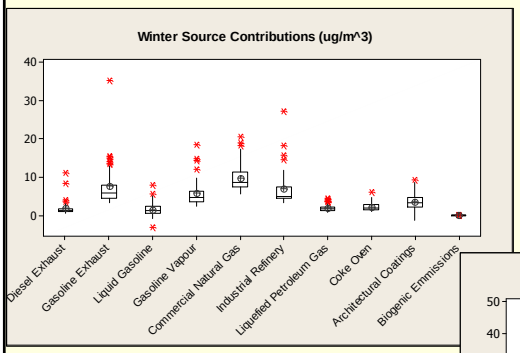
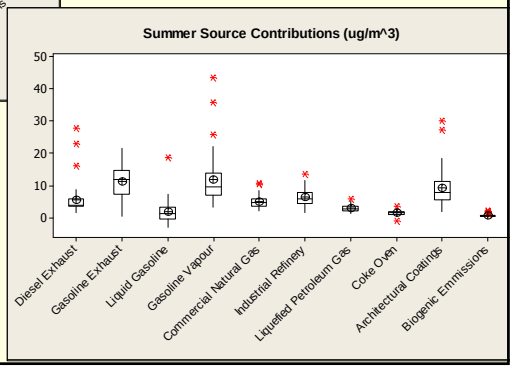
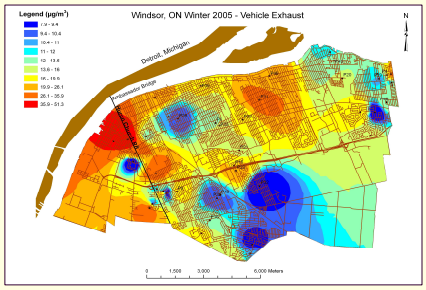
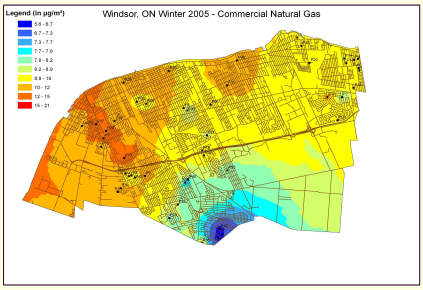
# Results: Source Contributions

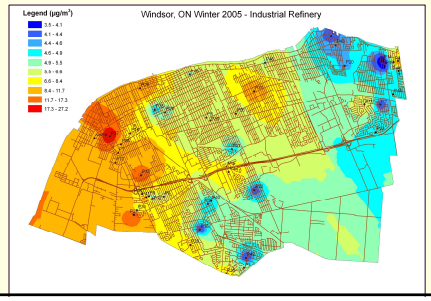


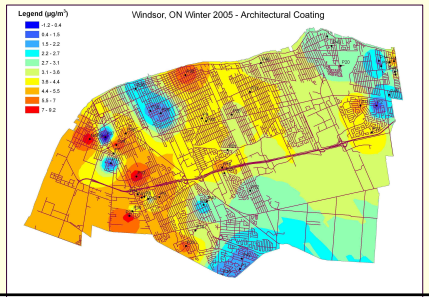




# Results: Source Contributions (Winter)



## Model Output - Highlights

- Results agreed reasonably well with the values for the other CMB studies in Southeast Michigan and Northeast US (Kenski *et al*., 1995; Scheff *et al*., 1993; Fujita and Lu, 1998)
- Higher gasoline vapour contribution for both seasons (13% for winter and 20% for summer), could be due to backyard sampling .

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## Model Output - Highlights

- Spatial variability
  - High in both seasons
  - Spatial patterns were more apparent for the Winter, possibly due to weaker atmospheric mixing and slower chemical reactions
  - There were small contributions, and small variability, between sites for Liquefied Petroleum Gas, Coke Oven and Biogenic Emissions.
  - NAPS results differ from backyards

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## Model Output - Highlights

- Seasonal variability
  - Ambient concentrations and therefore source contribution estimates (μg/m$^3$) higher in summer than in winter
  - Ranking of sources changed

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## Conclusions-CMB modeling

- Vehicle emissions consistently the greatest source
  - 40% of winter and 54% of summer emissions
- General trend of higher vehicle emissions along major traffic routes
- The Commercial Natural Gas impact was possibly coming from USA.
- Large spatial and seasonal variability in source contribution estimates were observed, this demonstrates the usefulness of the two sampling sessions at ~ 48 sites.
- Backyard samples may be unduly influenced by residential sources (e.g.. parked cars, lawn mowers).

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## Recommendations- CMB modeling

- Future studies
  - Second year of data
  - Extend to Detroit
  - ***Collocated samples:*** uncertainty estimates for the data and, in turn, provide more accurate source contribution estimates
  - Use dispersion and/or second receptor model

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## Collocated Sampling

- Objective: to estimate the uncertainties of VOC by 6 L Canister
- Study site: Windsor West NAPS Station, to allow further source appointment and comparison with the CMB results of 2005 data

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## Sampling Procedure

- 6 L Summa Canisters, as in 2005 WOEAS
  - Sampling duration 24 hrs, a daily midnight change out, June 24 to July 8, 2007
  - Two canisters placed side by side
  - Sampling protocols developed and followed carefully to ensure high quality
- Samples analyzed for VOC concentrations in EC lab, as in 2005 WOEAS
  - Total of 12 valid pairs (24 samples)

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## Data Analysis

- Lab reported VOC conc. used to estimate uncertainties of collocated samples
  - Excluded: species having conc. of 0 in all 24 samples
  - Excluded: species having 7 or more pairs of at least one 0
  - Rest: conc. <MDL replaced with 0.5 MDL
  - Excluded: overall conc. by species < MDL
  - Remaining (133): analysis
- For each species, Relative Difference was calculated for each pair
  - Relative Difference (%) = 2*[(a - b) / (a + b)] *100 %

  a, b = concentration of collocated sample #1 and #2, respectively
- General statistics, mean and median of Relative Diff (N=12) for each species
- Focus on 32 fitting species

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## General Statistics- Relative Diff

- By species: mean > median, in general
- Median of relative differences considered as the measure of uncertainties, since it is less sensitive to extreme values
- Low conc, high Relative Diff

| Median of Relative Diff (%) N=133 | Species |
|---|---|
| >50 | 4 % |
| 25-50 | 11% |
| 15-25 | 13% |
| <15 | 72% |

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## General Statistics: 32 fitting species

| Median of Relative Diff (%) | Species |
|---|---|
| >15 | 6% |
| 10-15 | 6% |
| 5-10 | 22% |
| <5 | 66% |

- Coefficient of variation
  - 0.35 (propane) to 0.84 (acetylene)
  - In acceptable zone

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# 32 Fitting Species: trends

| **Trend** | Species |
|---|---|
| Relative difference increase with increasing concentration | Acetylene |
| Relative difference decrease with increasing concentration | 16 |
| No trend | 15 |

- No association of trend and conc. observed

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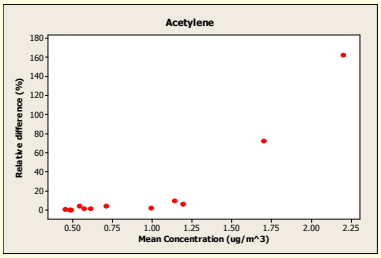
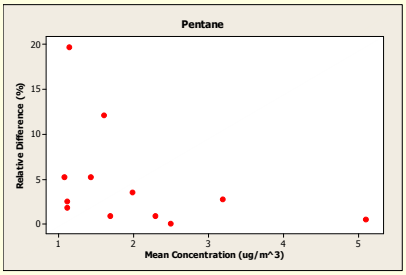
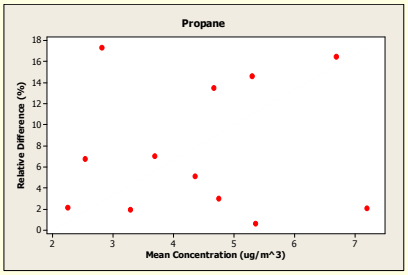
# 32 Fitting Species: trends



# Conclusion and Recommendations

## -collected sampling

- Variation in collocated concentrations is in an acceptable range for all 32 CMB fitting species
  - All <18%
  - Majority <15%
  - Over half <5%
- Uncertainties found in this study could be used to rerun the CMB model for the Windsor outdoor VOC source apportionment study (using 2005 data).
- Source apportionment study using 2006 data.
- Use VOC concentrations and corresponding uncertainties in the CMB model to determine the source apportionment at the NAPS location in summer 2007. Hence, the obtained results can be compared with that of the 2005 study to determine the validity of the previous study.

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# Acknowledgements


- Study participants
- University of Windsor students: sample collection
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