Receptor Modeling Applied to $PM_{2.5}$ and Air Toxics Monitoring Sites in the Midwest

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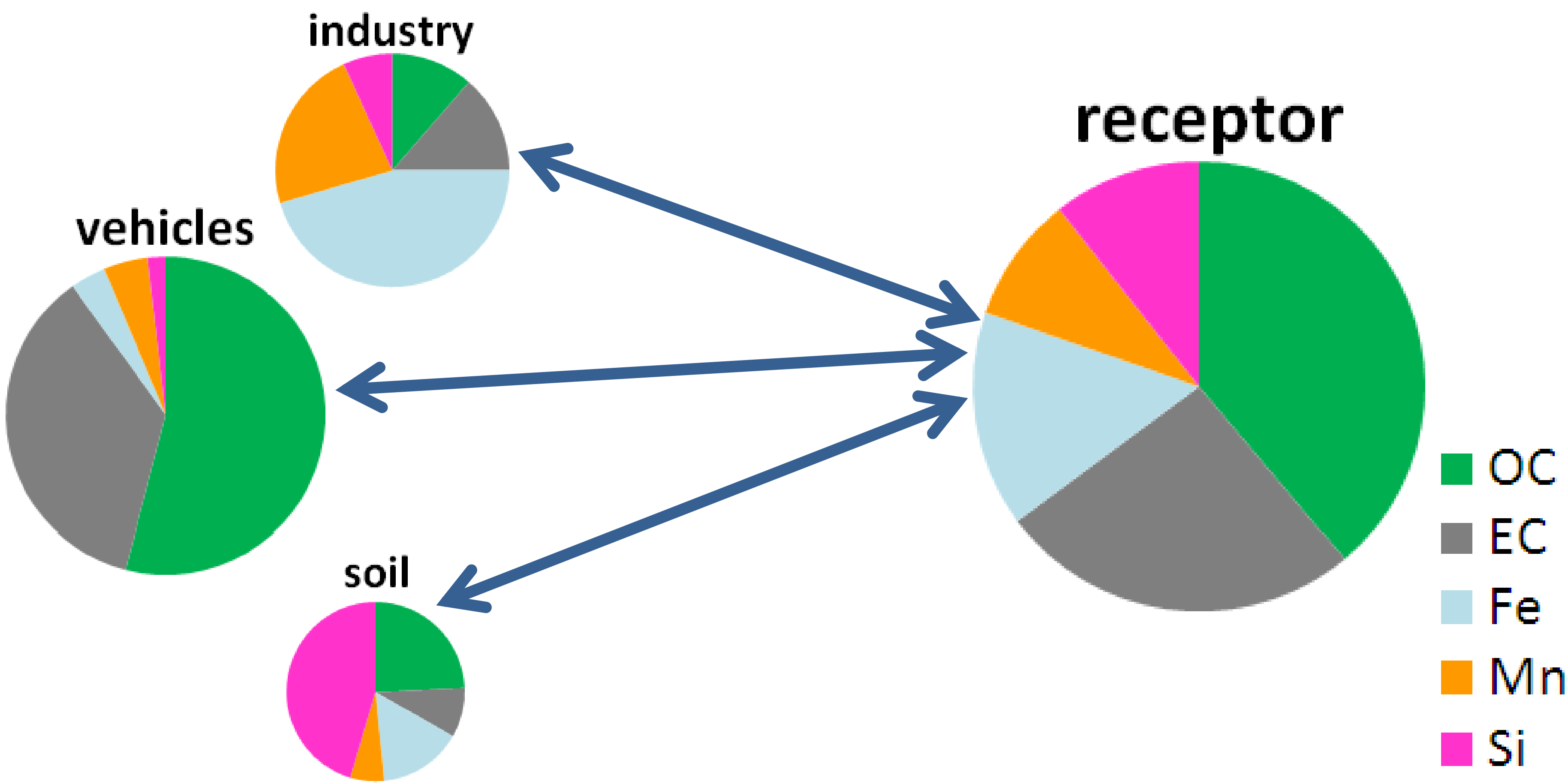
Previous Receptor Modeling Work

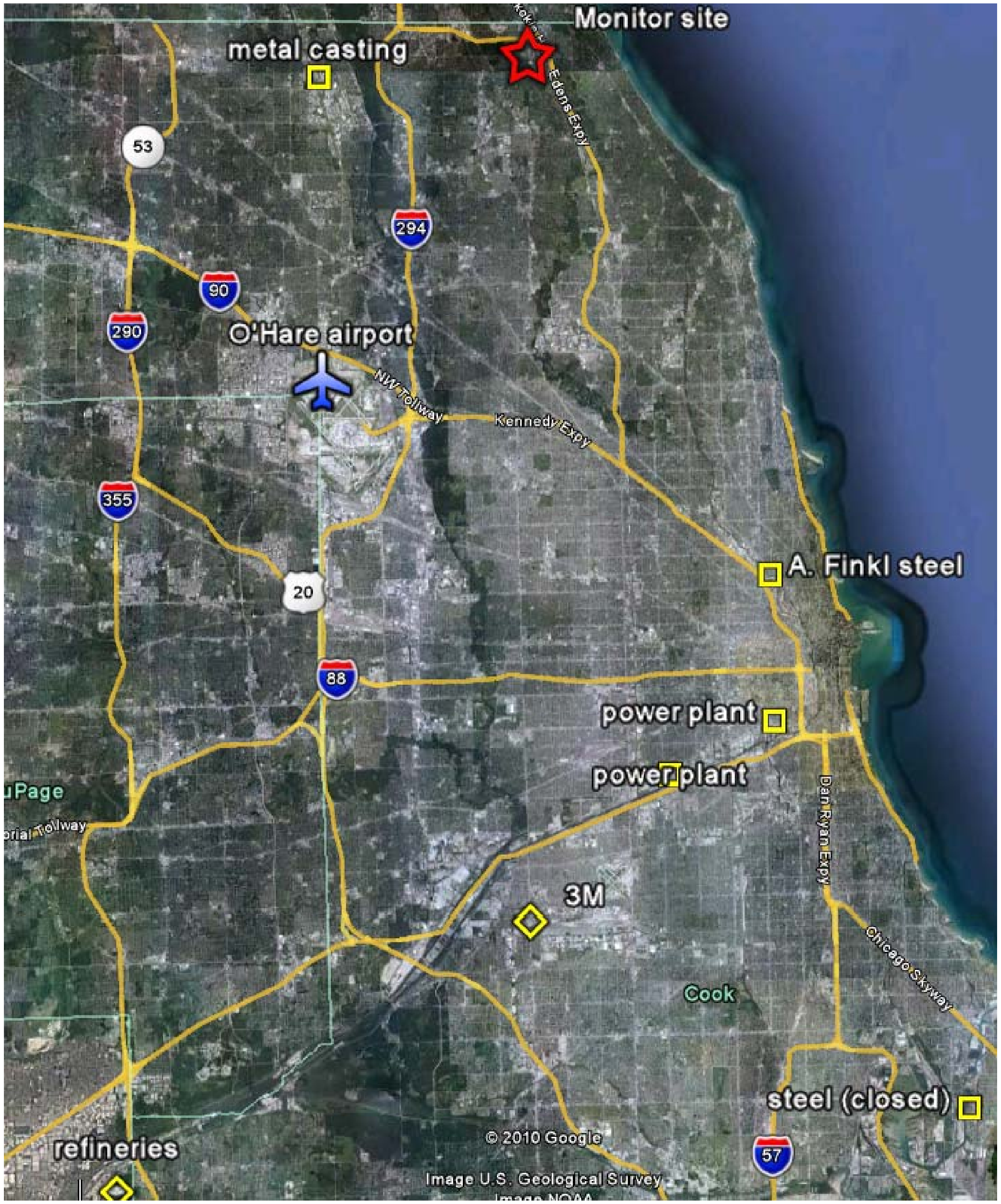
- 1990's, Chemical Mass Balance (CMB) applied to VOCs as precursors to Ozone
- 2000's, Positive Matrix Factorization (PMF), UNMIX, other newer models used for $PM_{2.5}$
- 2000's, some PMF/UNMIX modeling of VOCs
- Late 2000's, PMF for $PM_{2.5}$ molecular markers
  - OC no longer just "gasoline combustion"
  - secondary organic aerosols (SOA)
- Minimal study of $PM_{2.5}$ + VOCs datasets

Receptor Models Do the Opposite of Dispersion Models



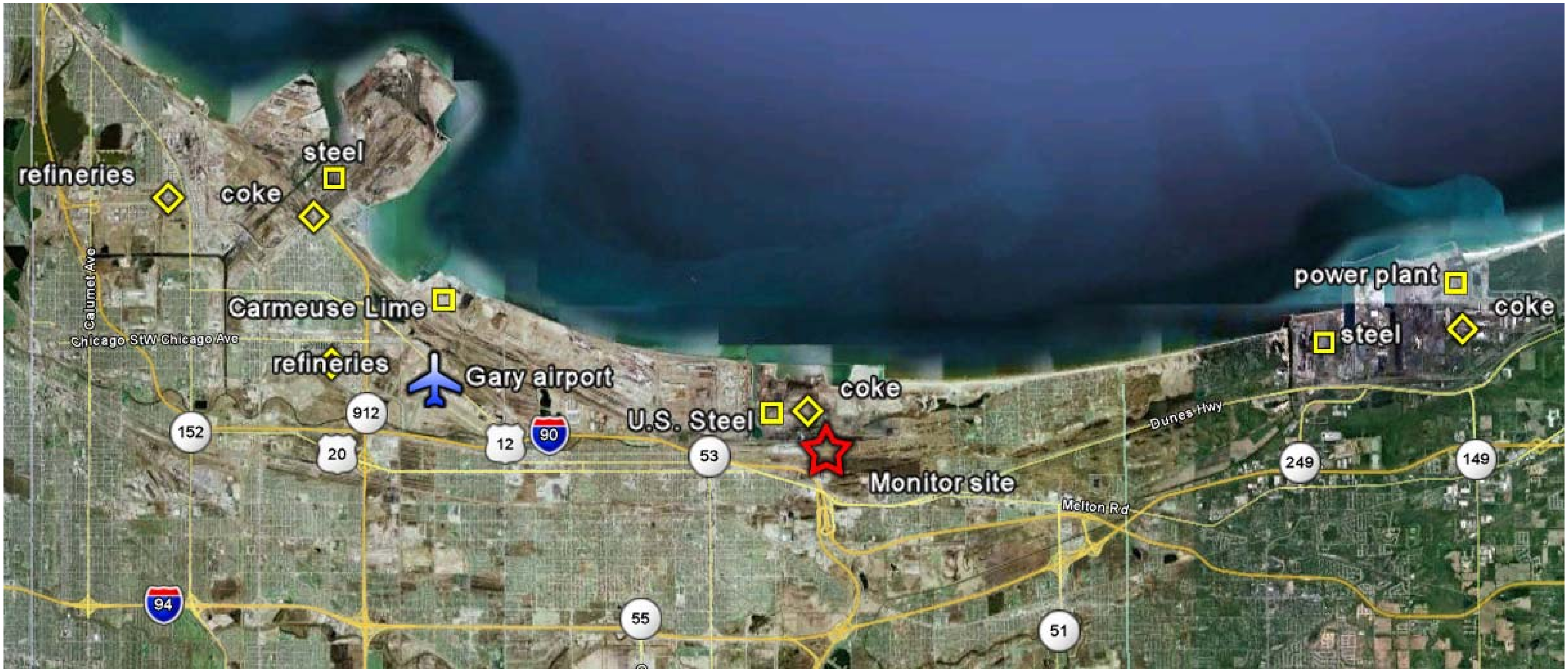
Study Plan

1. Find sites with n>150, $PM_{2.5}$ & VOC; 2003-07
2. Apply PMF model to $PM_{2.5}$ at each site
3. Apply PMF model to VOCs at each site
4. PMF validation – pollution roses, time trends
5. Correlate $PM_{2.5}$ vs. VOC factors at each site
6. Apply PMF to case study of combined PM & VOC dataset



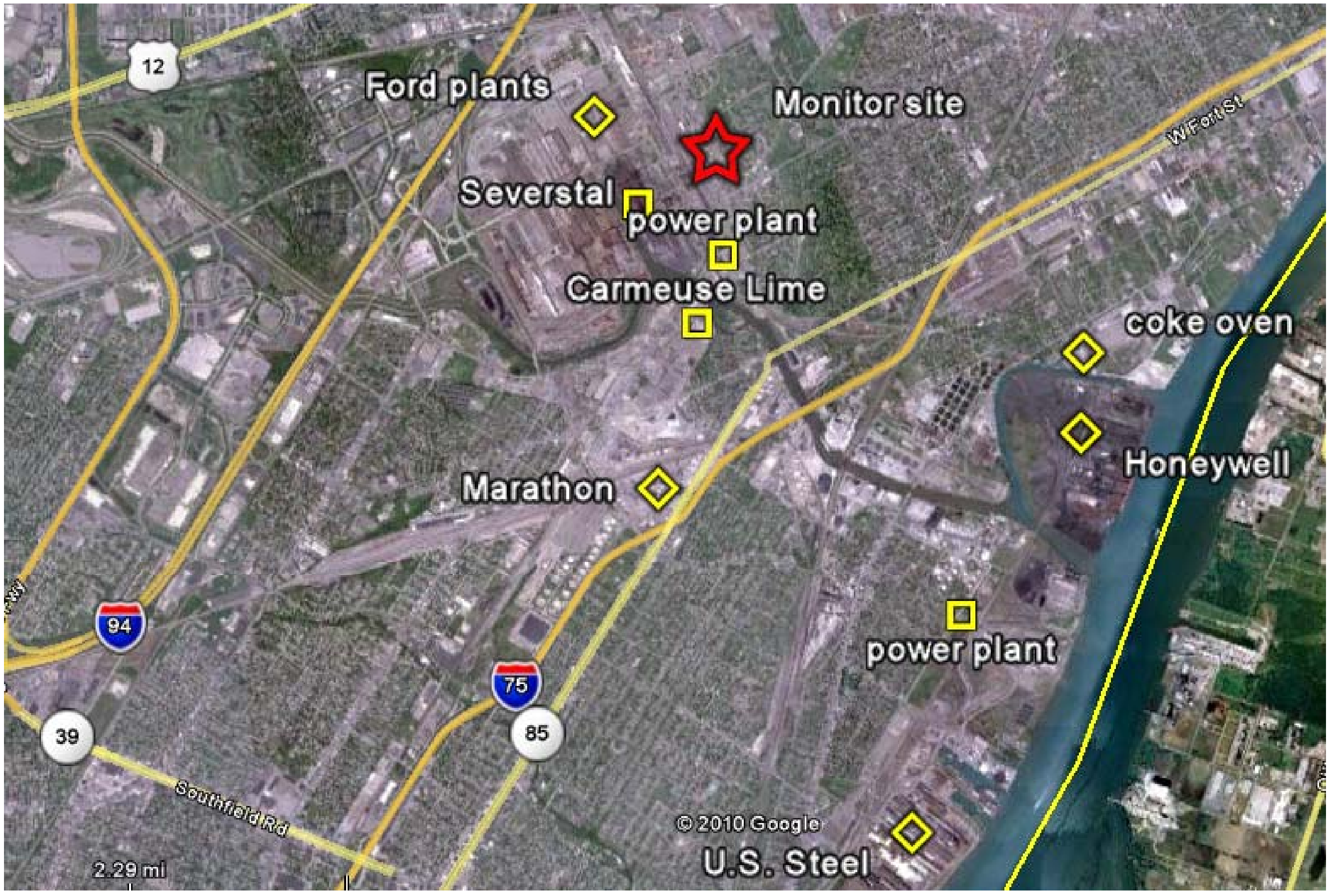
Northbrook, IL

- NATTS, PAMS, etc.
- 20 mi. NW of downtown Chicago
- 10 mi. NE of O'Hare
- Far from major point sources



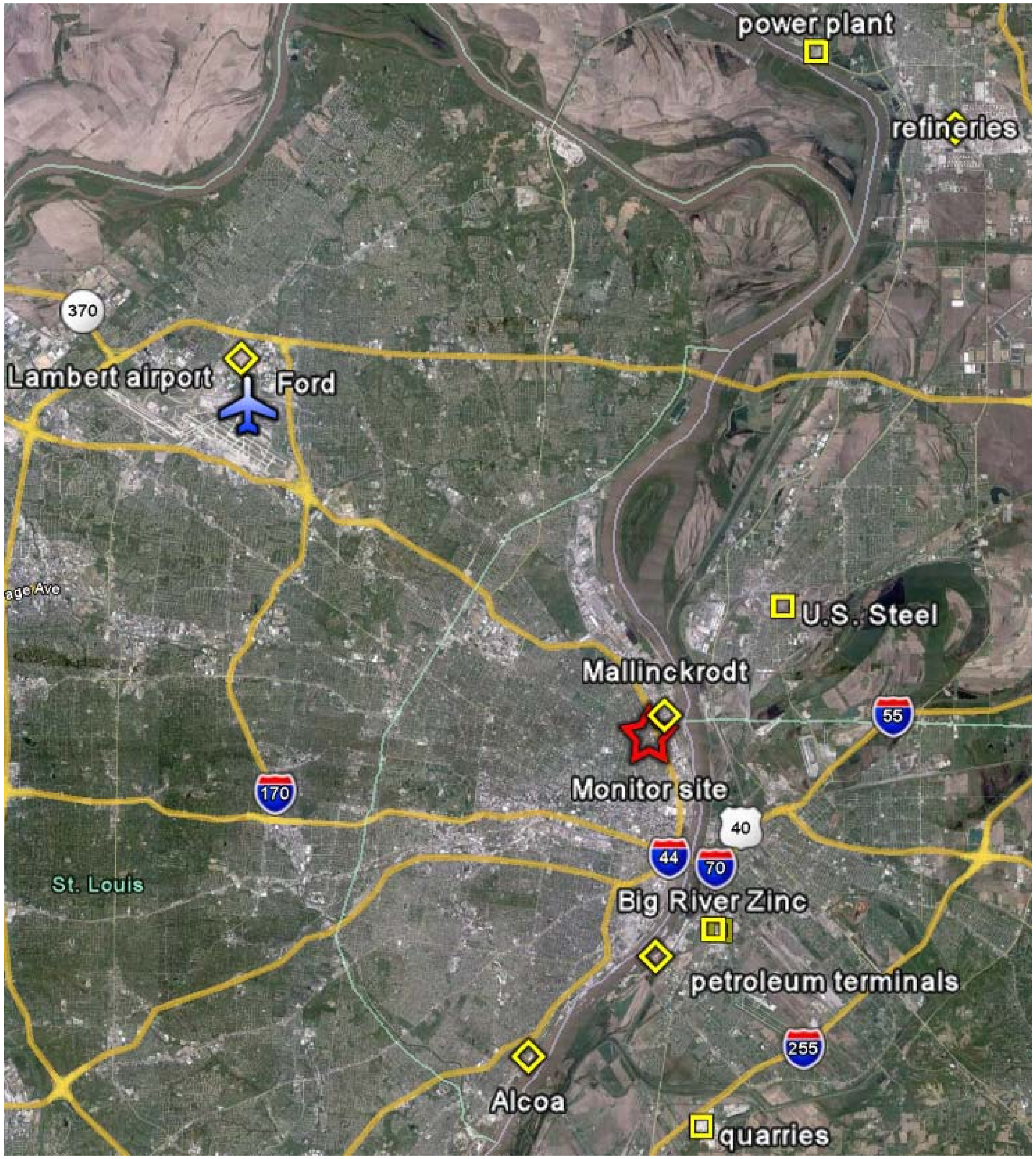
Gary, IN

- Adjacent to US Steel Gary Works
- 7 mi. W of Burns Harbor coke/steel
- 8 mi. E of East Chicago coke/steel
- ½-mi. N of I-90/94/65



Dearborn, MI

- Adjacent to steel, auto, power, lime plants
- 2-4 mi. N of Marathon, Detroit Coke, U.S. Steel, petrochemical, coal power



St. Louis, MO

- Blair St., 2 mi. N of downtown
- ½-mi. W of Mississippi River
- 4 mi. W of US Steel, refineries, zinc, and lime facilities

$PM_{2.5}$ PMF Results, ug/m^3

Sources	Northbrook	Gary	Dearborn	St. Louis
sulfate	4.2	3.5	5.1	4.2
OC	3.1	4.8	3.2	3.3
nitrate	3.0	3.5	4.2	3.0
EC	1.0	2.5	1.5	0.61
soil	0.58	0.27	1.2	0.91
steel	0.55	0.63	1.1	0.49
salt		0.92	0.75	
burning	0.37			0.58
zinc			0.57	0.34
copper				0.72
lime				0.44
TOTAL	**12.8**	**16.2**	**17.6**	**14.6**

$PM_{2.5}$ Notes

- Results comparable to previous studies
- What is OC? Gasoline vehicle emissions?
  - Northbrook and St. Louis high in summer, SOA?
  - Gary and Dearborn results suggest most contribution from local industry and roads
- What is EC? Diesel vehicle emissions?
  - All sites indicate a mix of mobile and industrial sources. Higher weekday contributions.

VOC receptor modeling

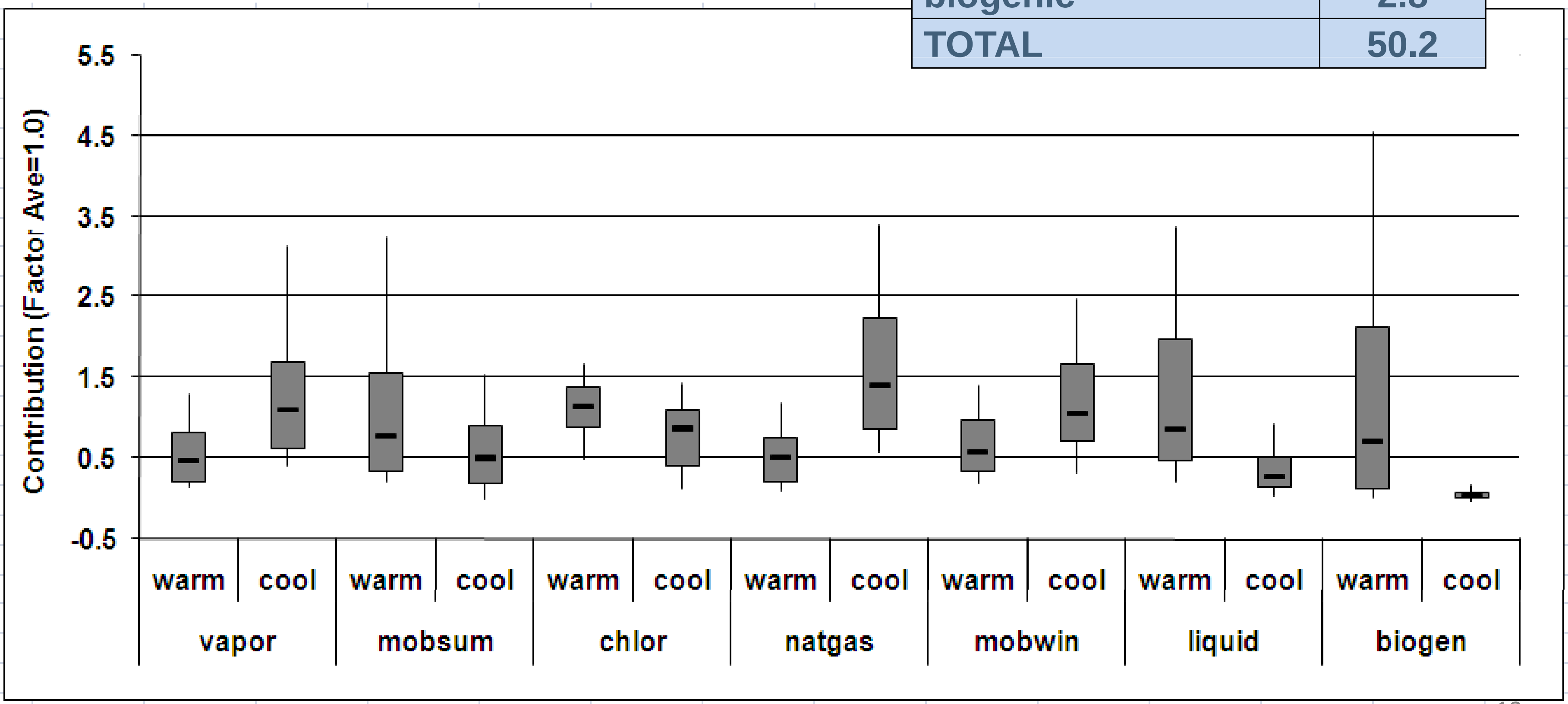
- Datasets not consistent –
  between 28-78 VOCs reported per site
- Resolution of source factors depends on presence of specific indicator compounds:
  - Isoprene, biogenic
  - Ethane, natural gas
  - Gasoline-related factors
    - Acetylene & ethylene, fuel combustion
    - C5 "-pentane" compounds, liquid gasoline
    - C3-C6, e.g. butane & propane, vaporized fuel

VOC Interpretation is Complex

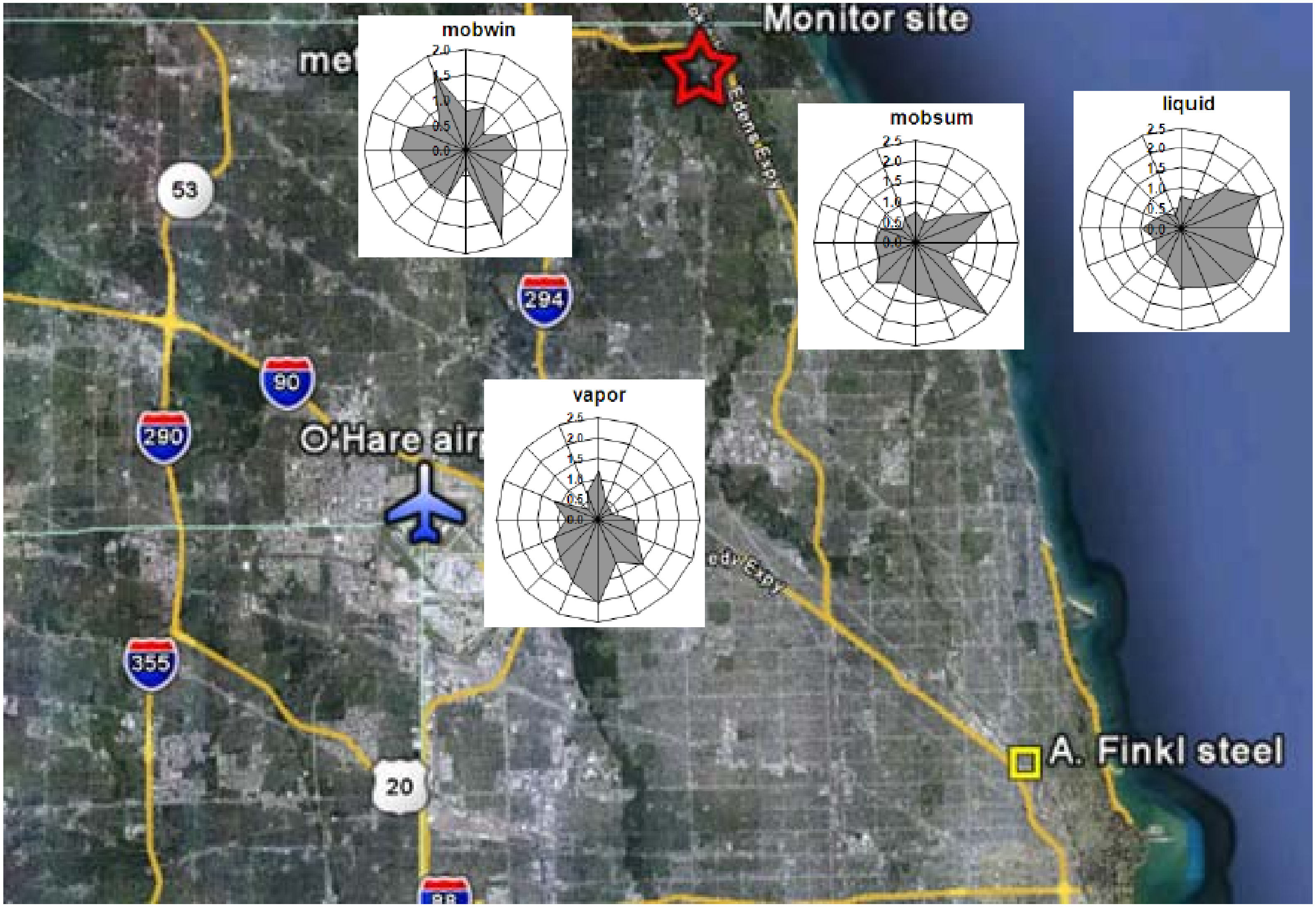
- Midwest sites have great seasonal extremes
  - Source factors can dominate in warm/cool season
  - Individual VOCs may volatilize more in summer or persist longer in winter, allowing the same source factor to have two different versions depending on season
- VOCs have varied atmospheric half-lives
  - Butane/propane long-lived; Pentanes shorter half-lives
  - Must consider how far monitor is from potential source and what happened to the source factor over time
  - Consider seasonal temperature impact on VOC half-life

Northbrook, IL
VOC Results

VOC PMF results, ug/m^3	
fuel vapor; aged air	11.8
mobile, summer	9.2
chlorinated VOCs	8.6
natural gas	8.5
mobile, winter	5.0
liquid fuel	4.4
biogenic	2.8
TOTAL	50.2

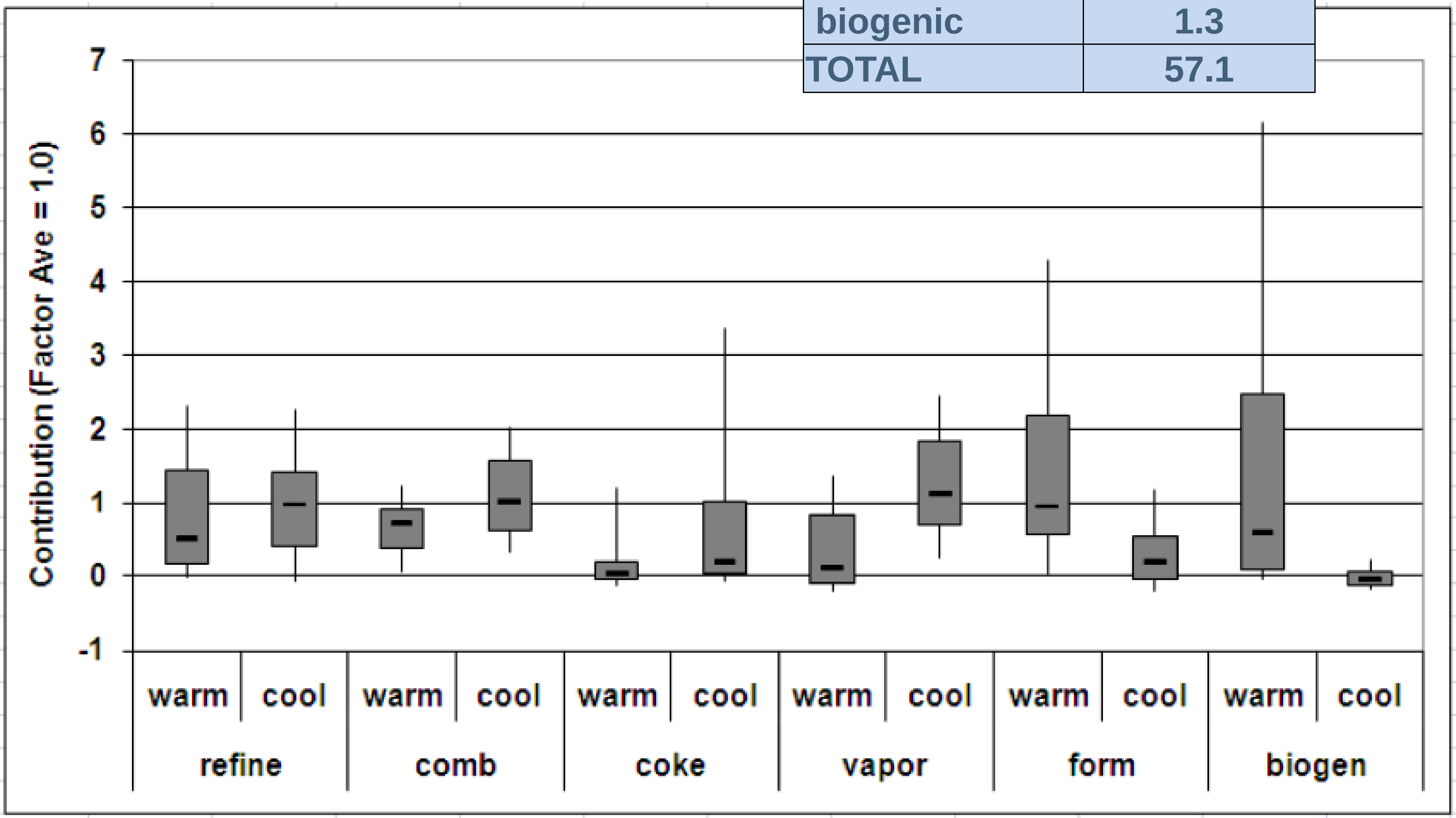


Northbrook, VOC factor pollution roses

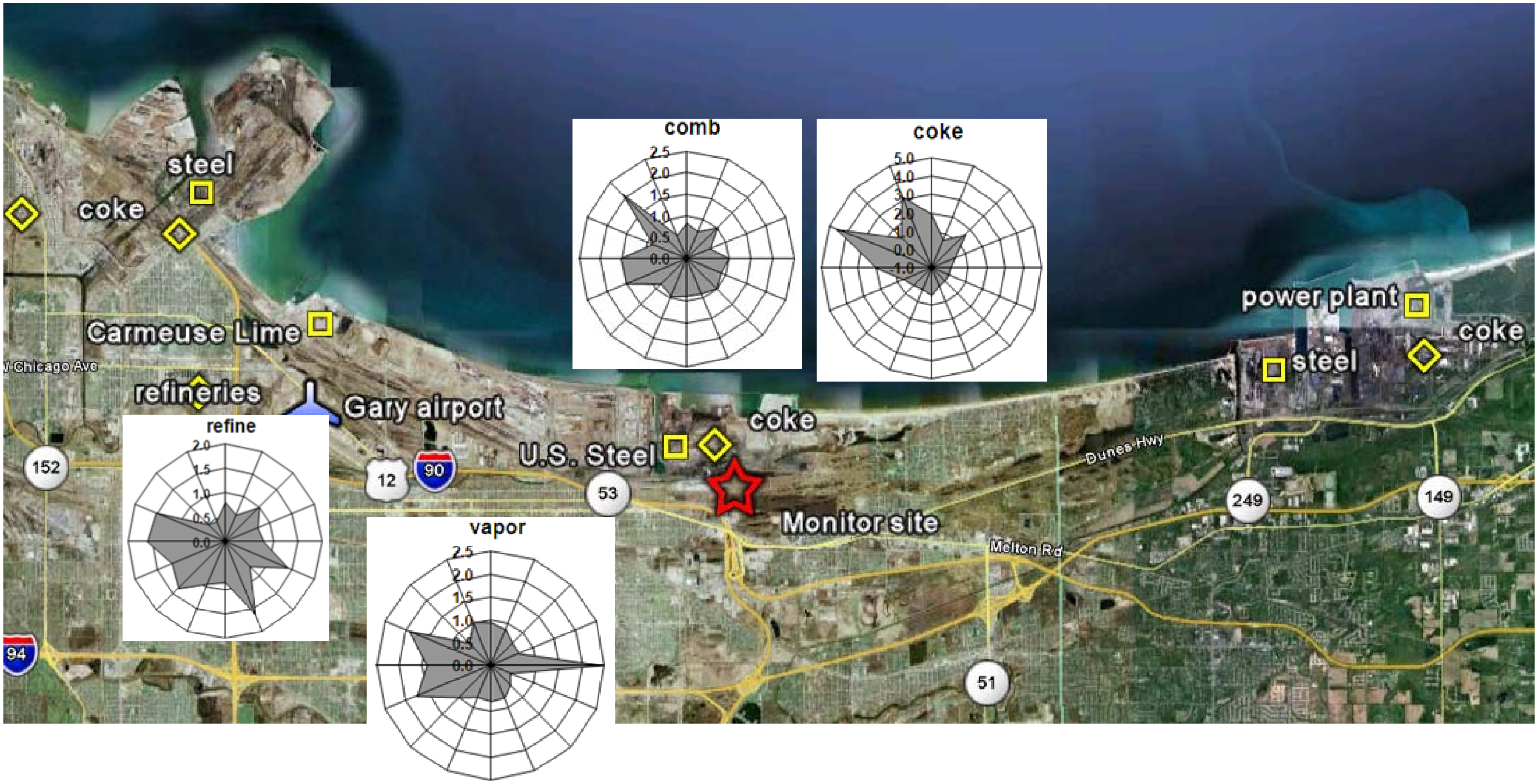


Gary, IN
VOC Results

VOC PMF results, ug/m³	
refinery	21.1
fuel combust.	18.1
coke oven	6.9
fuel vapor	5.0
formaldehyde	4.6
biogenic	1.3
TOTAL	57.1

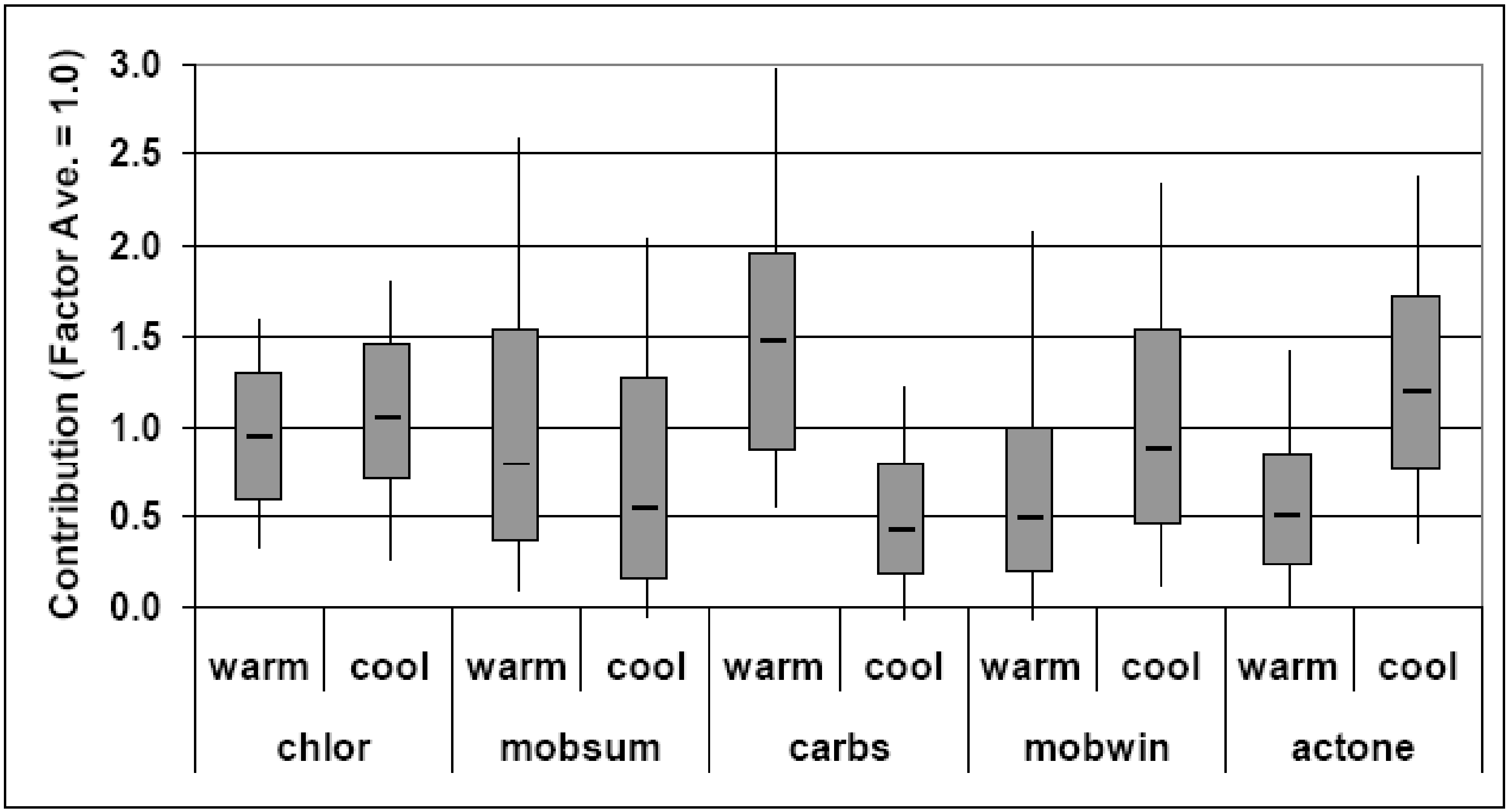


Gary, VOC factor pollution roses



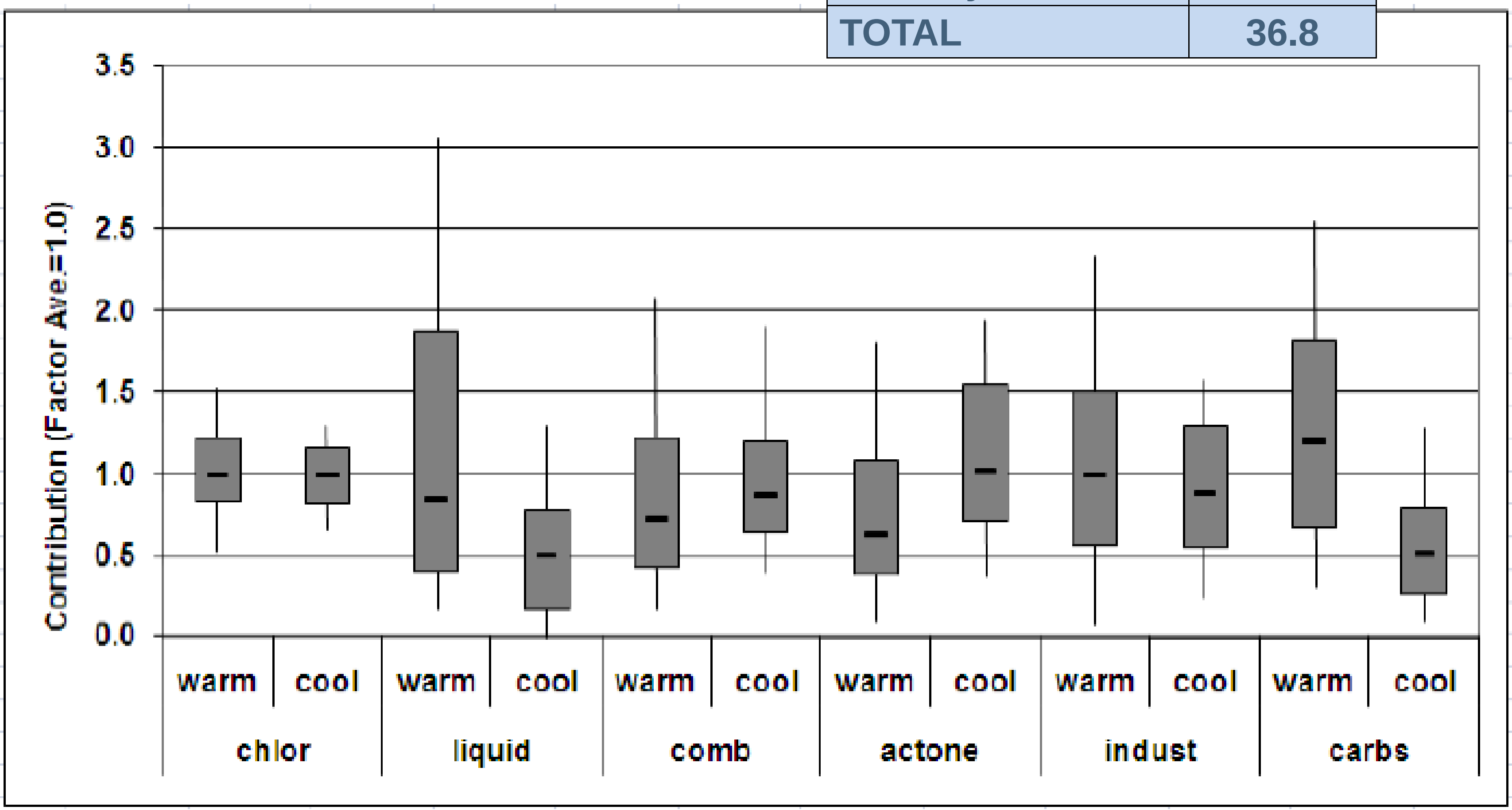
St. Louis, MO VOC Results

VOC results, ug/m^3	
chlorinated	6.8
mobile, summer	5.9
carbonyls	4.3
mobile, winter	3.8
acetone	2.7
TOTAL	23.5



Dearborn, MI
VOC Results

VOC results, ug/m^3	
chlorinated	9.3
liquid fuel	8.7
combustion	5.7
acetone	5.0
industrial	4.6
carbonyls	3.5
TOTAL	36.8



$PM_{2.5}$ & VOCs comparison?

- If OC and EC factors in $PM_{2.5}$ solution represent mobile sources, then we should see correlation with certain VOC factors
- But OC may be mostly representative of wood burning, cooking meat, and SOA
- EC may be largely contributed by industry

Northbrook Factor Correlation (R^2)

		VOC source factors						
		vapor	mobsum	chlor	natgas	mobwin	liquid	biogen
$PM_{2.5}$ source factors	sulfate	**0.48**	0.18	**-0.36**	0.25	0.23	0.11	0.07
	OC	0.16	**0.36**	-0.10	-0.16	0.02	**0.51**	**0.49**
	nitrate	**0.57**	-0.11	**-0.42**	**0.61**	**0.43**	-0.24	**-0.53**
	EC	**0.42**	**0.47**	**-0.44**	0.15	**0.32**	**0.44**	0.14
	soil	0.13	0.26	0	-0.07	0.03	0.17	0.12
	steel	0.09	**0.51**	-0.09	-0.03	0.13	**0.51**	0.24
	burning	0.13	0.25	-0.13	0.02	0.11	**0.37**	0.17

- Strongest correlation: nitrates vs. natural gas (0.61)
- Mobile-source related:
  - OC vs. liquid gas (0.51) and summer fuel combustion (0.36)
  - EC vs. summer combustion (0.47), liquid gasoline (0.44), and fuel vapor (0.42)

Apportionment of HAP risk

- Manganese
  - contributed by steel industry; 52% at Northbrook, 69-84% at others
  - But this is $PM_{2.5}$; underestimate of risk
- Benzene
  - Gary, 89% to coke oven factor
  - Dearborn, Northbrook & St. Louis, mobile sources

❖ VOC datasets that include butane, ethylene, etc., can better help determine origin of benzene risk

Conclusions

- Findings support $PM_{2.5}$ molecular marker studies that show complexity of OC & EC, i.e. not simply gasoline and diesel vehicles
- Future VOC modeling at Midwest sites useful for ozone precursor and HAP risk attribution
- Correlation of $PM_{2.5}$ and VOC factors can shed light on nature of OC and EC sources, support multi-pollutant control strategies