The Twin Cities VOC/$PM_{2.5}$ Personal Exposure Study

Funding Sources: EPA STAR Grants
GR825241-01-0 and R827928-010

Gregory C. Pratt, Don Bock, Chun Yi Wu
Minnesota Pollution Control Agency, St. Paul
Ken Sexton*, John Adgate, Gurumurthy Ramachandran
University of Minnesota, Minneapolis
Thomas Stock, Maria Morandi
University of Texas, Houston

***now at University of Texas, Brownsville**

$PM_{2.5}$: 116 24-hour periods
VOCs: 58 48-hour periods

Personal

$PM_{2.5}$

OVM

N=70 subjects

6-12/person

Indoor

$PM_{2.5}$

OVM

Outdoor

$PM_{2.5}$

OVM

Neighborhood

$PM_{2.5}$ (FRM)

OVM

VOC Canister

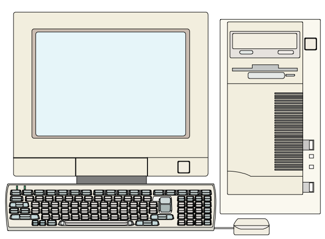
N=3

Central Site

$PM_{2.5}$ (FRM)

VOC Canister

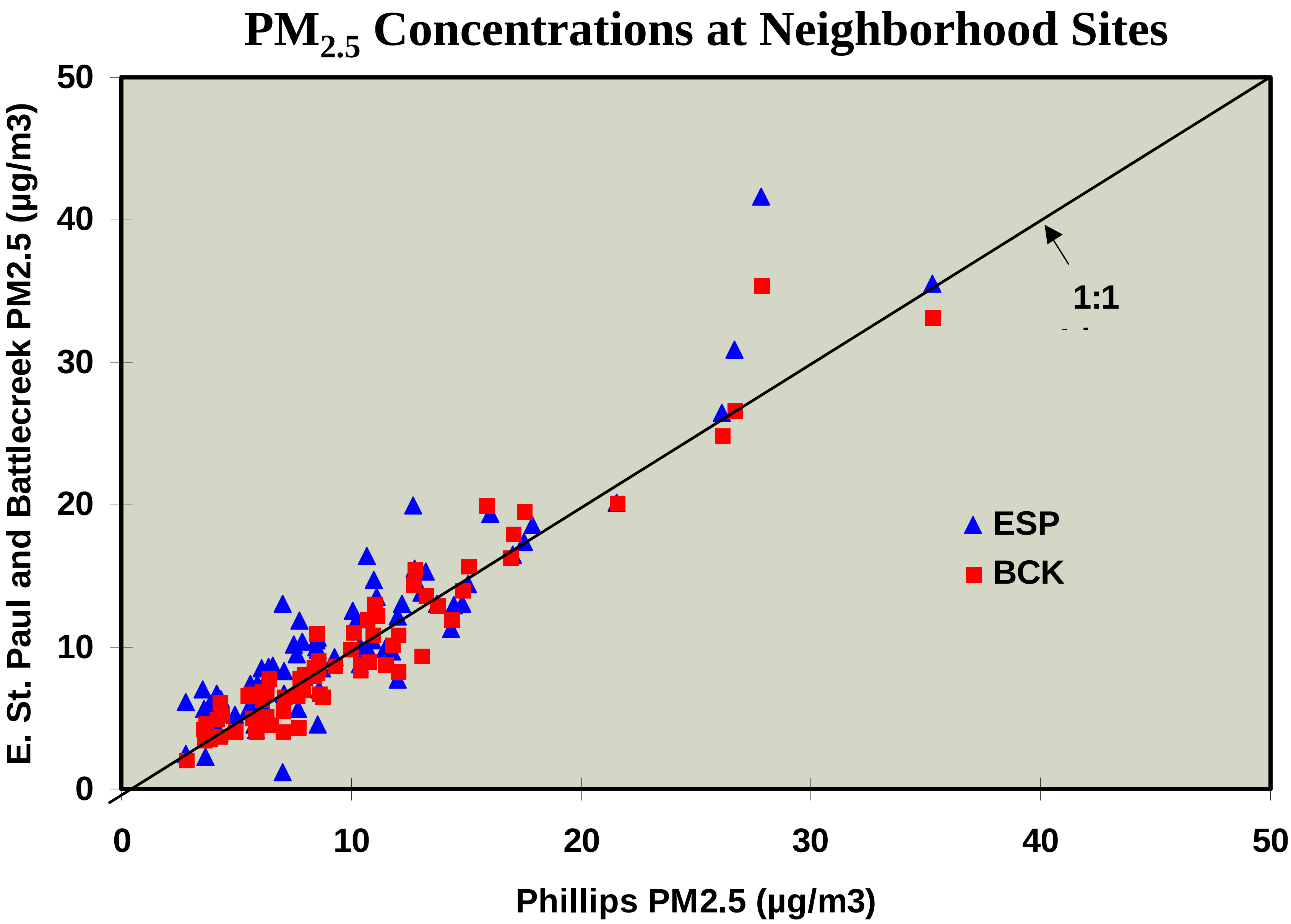
N=2



Modeling

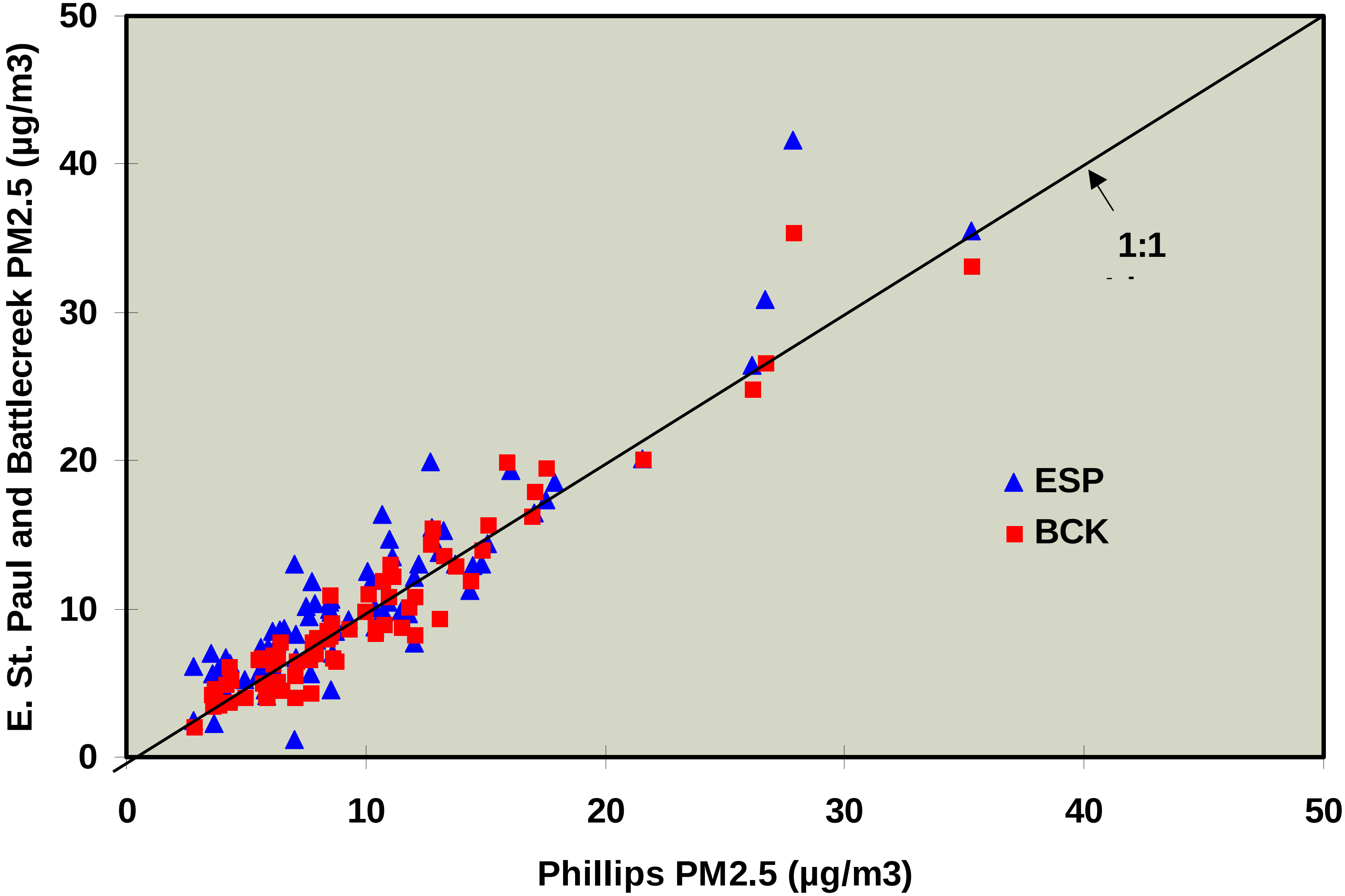
VOCs

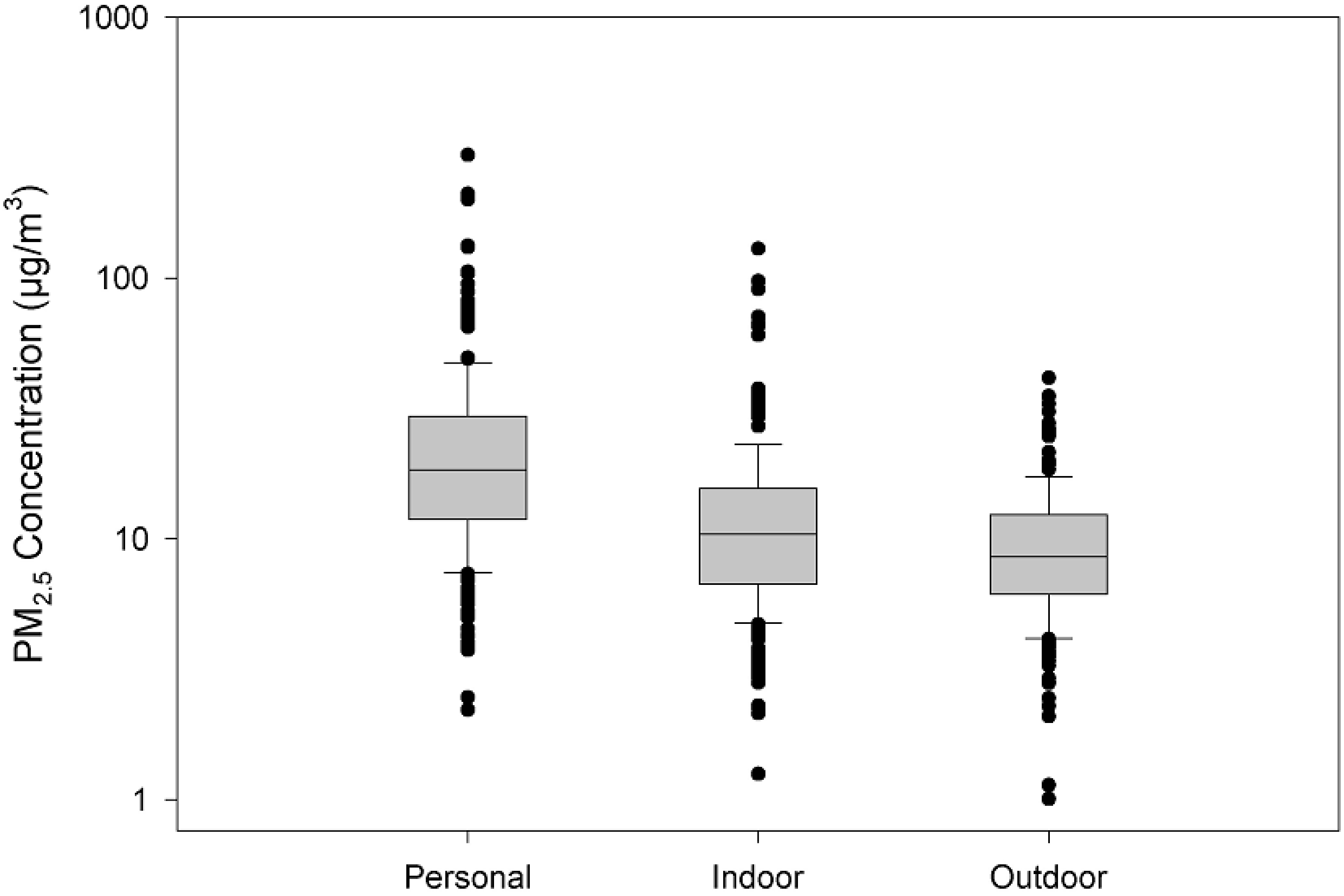
Personal $PM_{2.5}$ Monitor

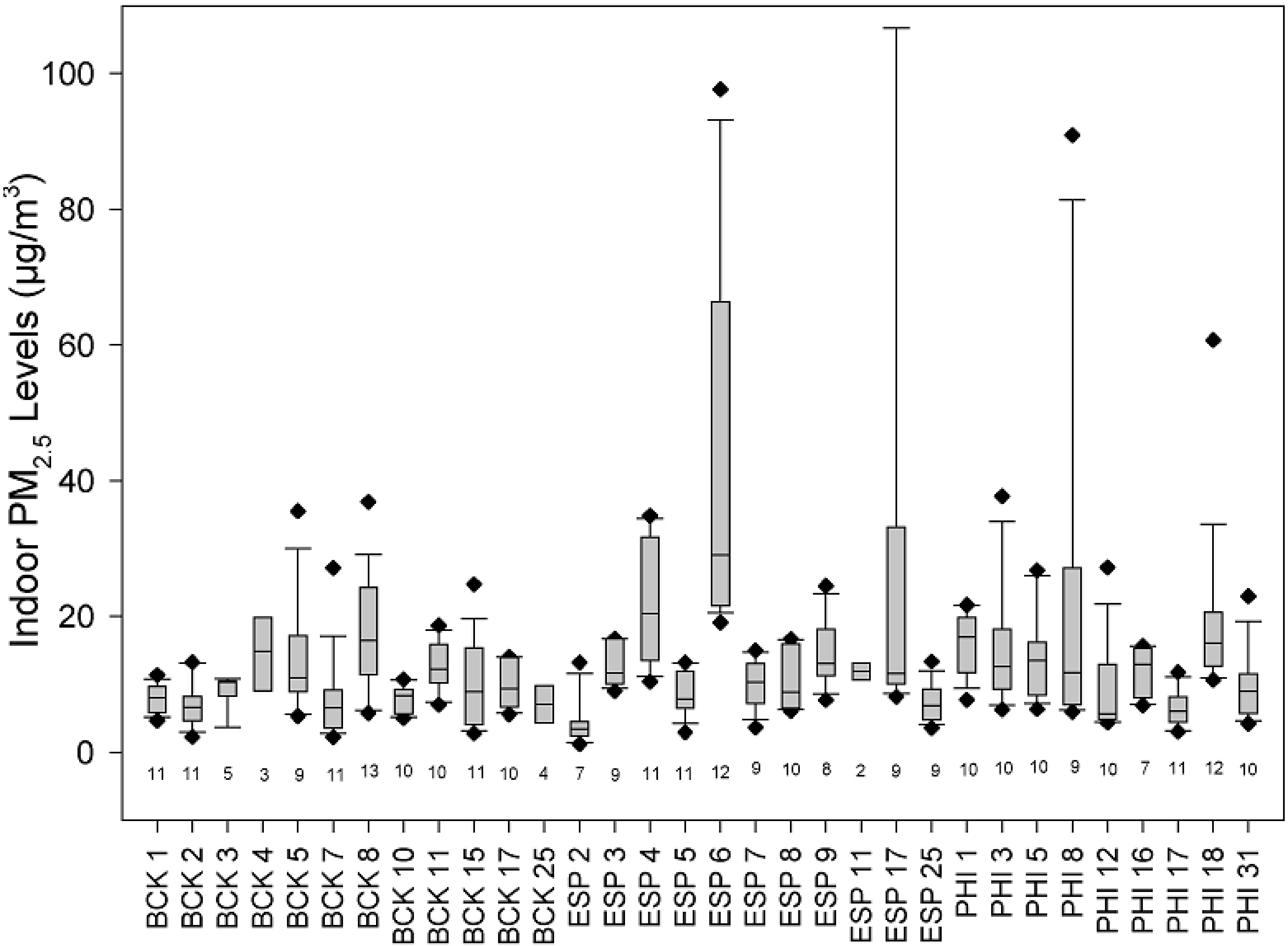


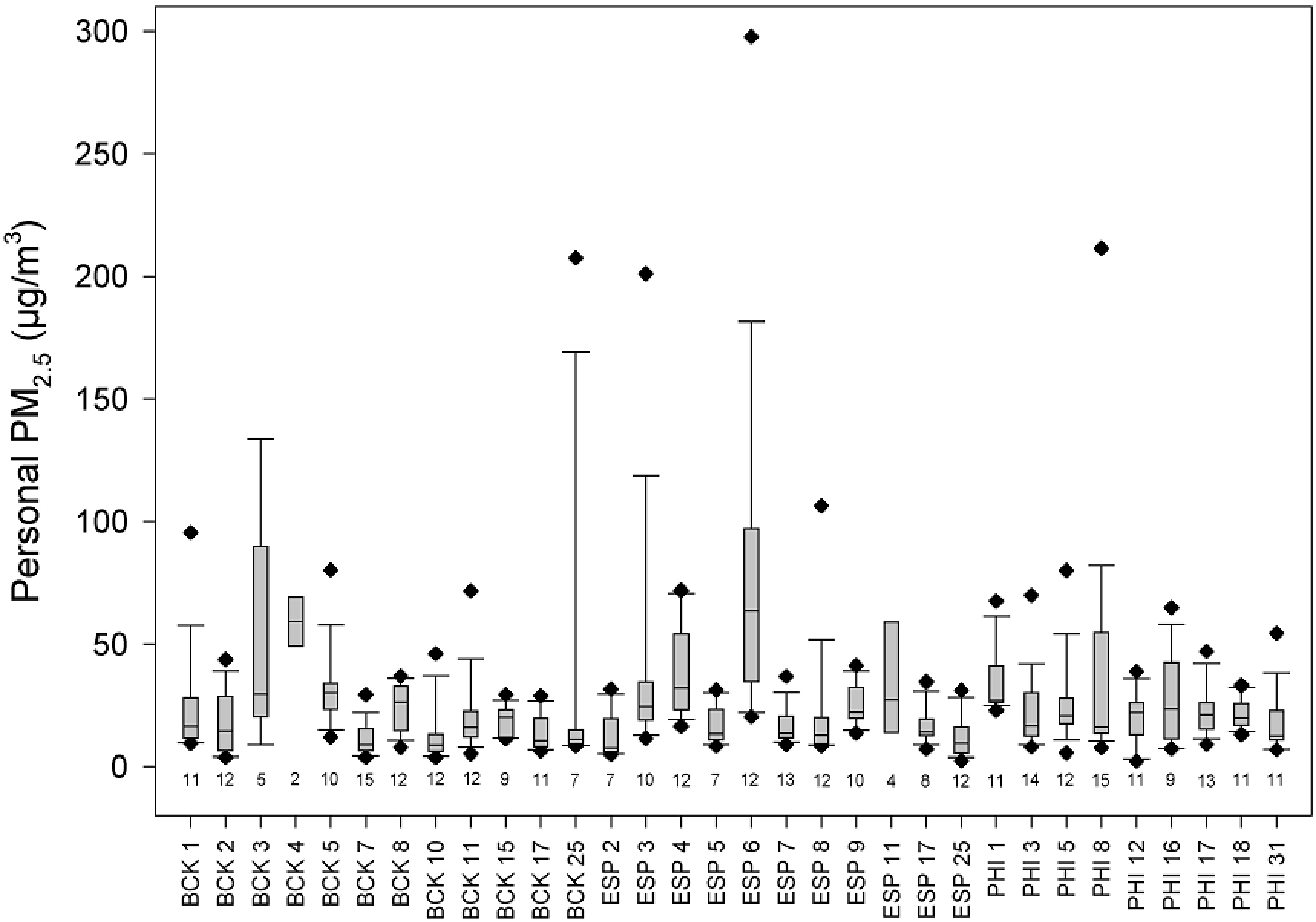
PM2.5 Concentrations at Neighborhood Sites
E. St. Paul and Battlecreek PM2.5 (µg/m3)
Phillips PM2.5 (µg/m3)
0
10
20
30
40
50
0
10
20
30
40
50
1:1
ESP
BCK

$PM_{2.5}$ Concentrations at Neighborhood Sites

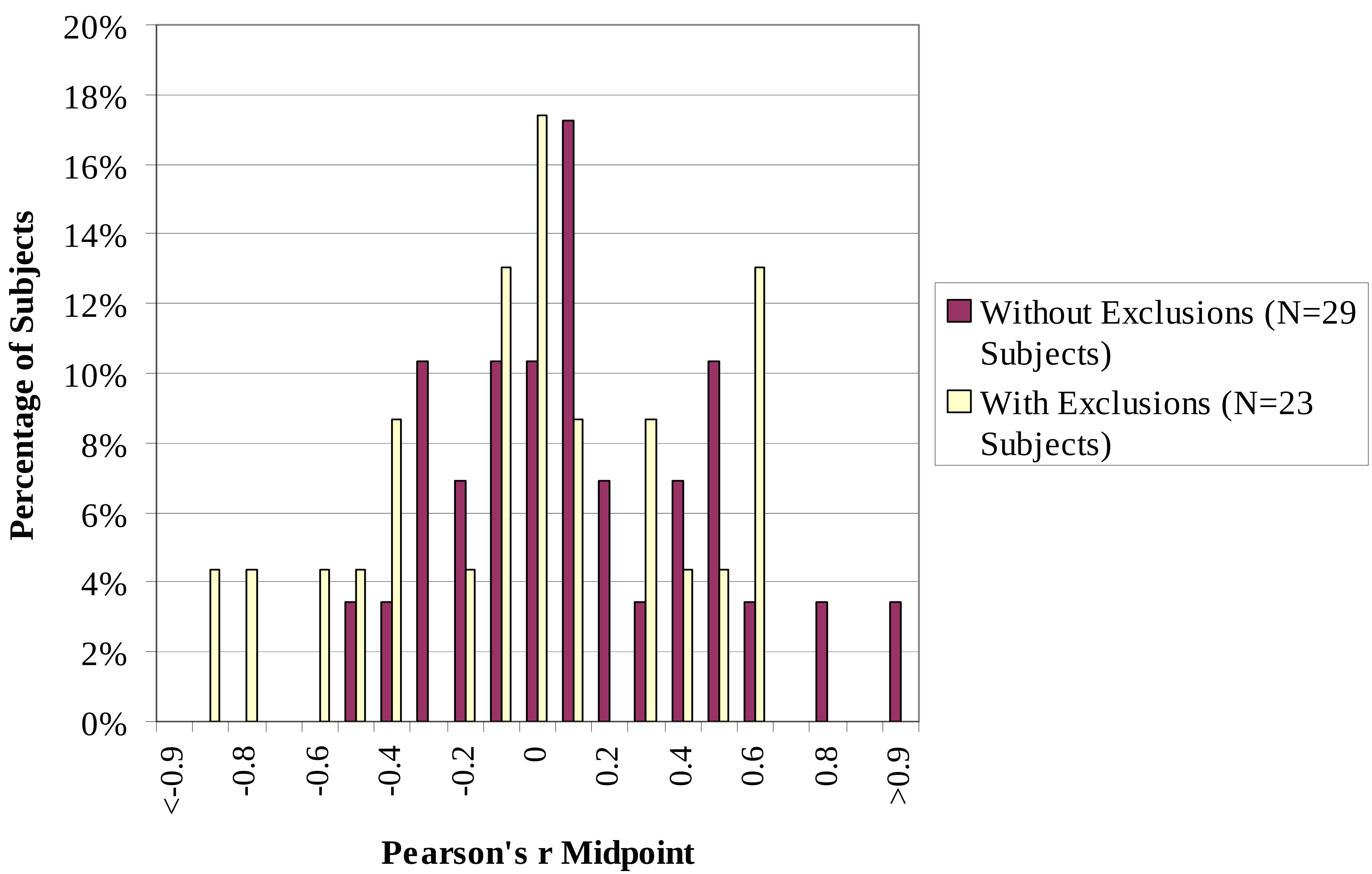



1000
100
10
1
PM2.5 Concentration (µg/m3)
Personal
Indoor
Outdoor

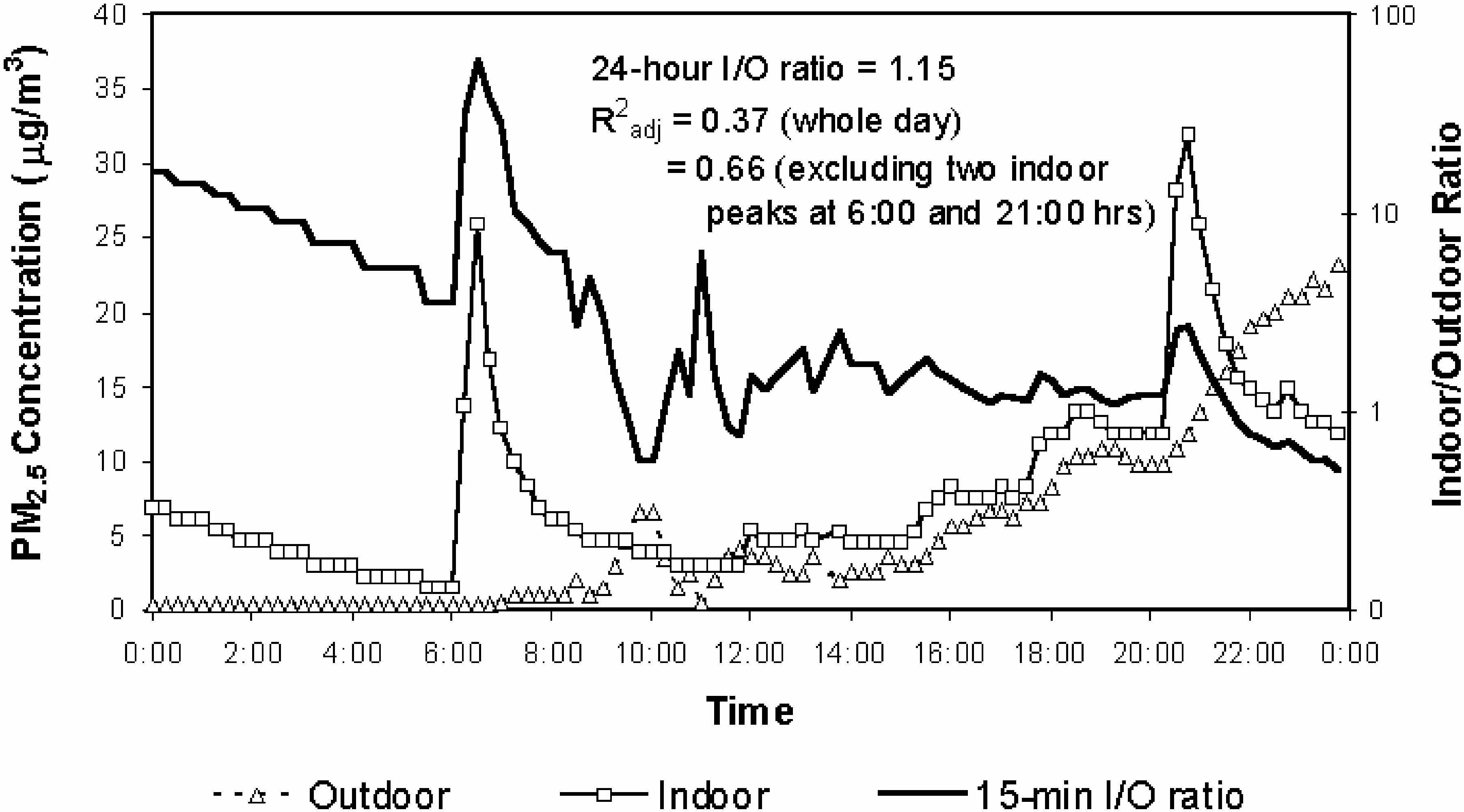

Indoor PM2.5 Levels (µg/m3)
100
80
60
40
20
0
11 11 5 3 9 11 13 10 10 11 10 4 7 9 11 11 12 9 10 8 2 9 9 10 10 10 9 10 7 11 12 10
BCK 1
BCK 2
BCK 3
BCK 4
BCK 5
BCK 7
BCK 8
BCK 10
BCK 11
BCK 15
BCK 17
BCK 25
ESP 2
ESP 3
ESP 4
ESP 5
ESP 6
ESP 7
ESP 8
ESP 9
ESP 11
ESP 17
ESP 25
PHI 1
PHI 3
PHI 5
PHI 8
PHI 12
PHI 16
PHI 17
PHI 18
PHI 31


Personal PM2.5 (µg/m3)
300
250
200
150
100
50
0
11
12
5
2
10
15
12
12
12
9
11
7
7
10
12
7
12
13
12
10
4
8
12
11
14
12
15
11
9
13
11
11
BCK 1
BCK 2
BCK 3
BCK 4
BCK 5
BCK 7
BCK 8
BCK 10
BCK 11
BCK 15
BCK 17
BCK 25
ESP 2
ESP 3
ESP 4
ESP 5
ESP 6
ESP 7
ESP 8
ESP 9
ESP 11
ESP 17
ESP 25
PHI 1
PHI 3
PHI 5
PHI 8
PHI 12
PHI 16
PHI 17
PHI 18
PHI 31

Longitudinal $PM_{2.5}$ Correlations



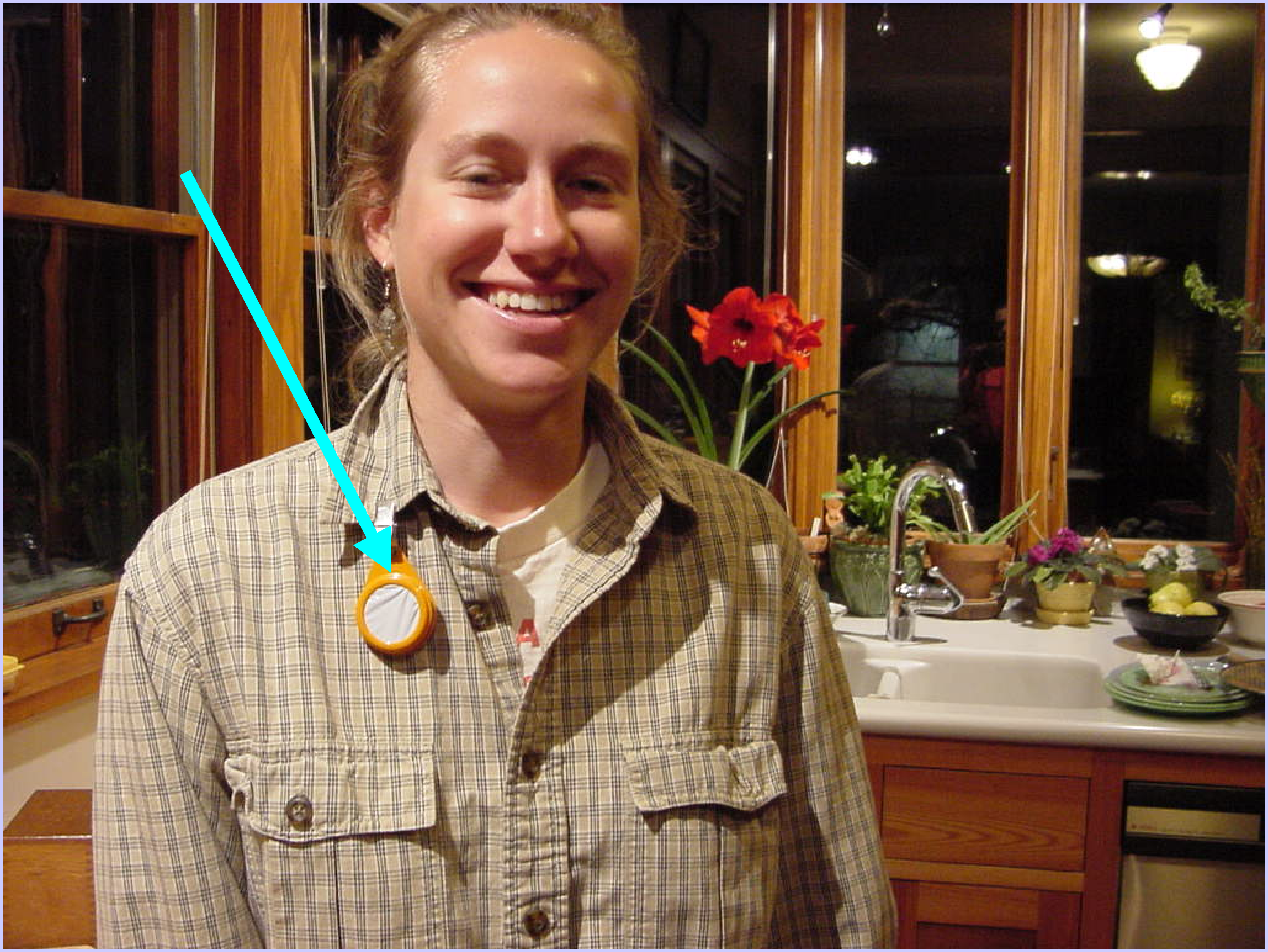
Real-Time $PM_{2.5}$ Measurements

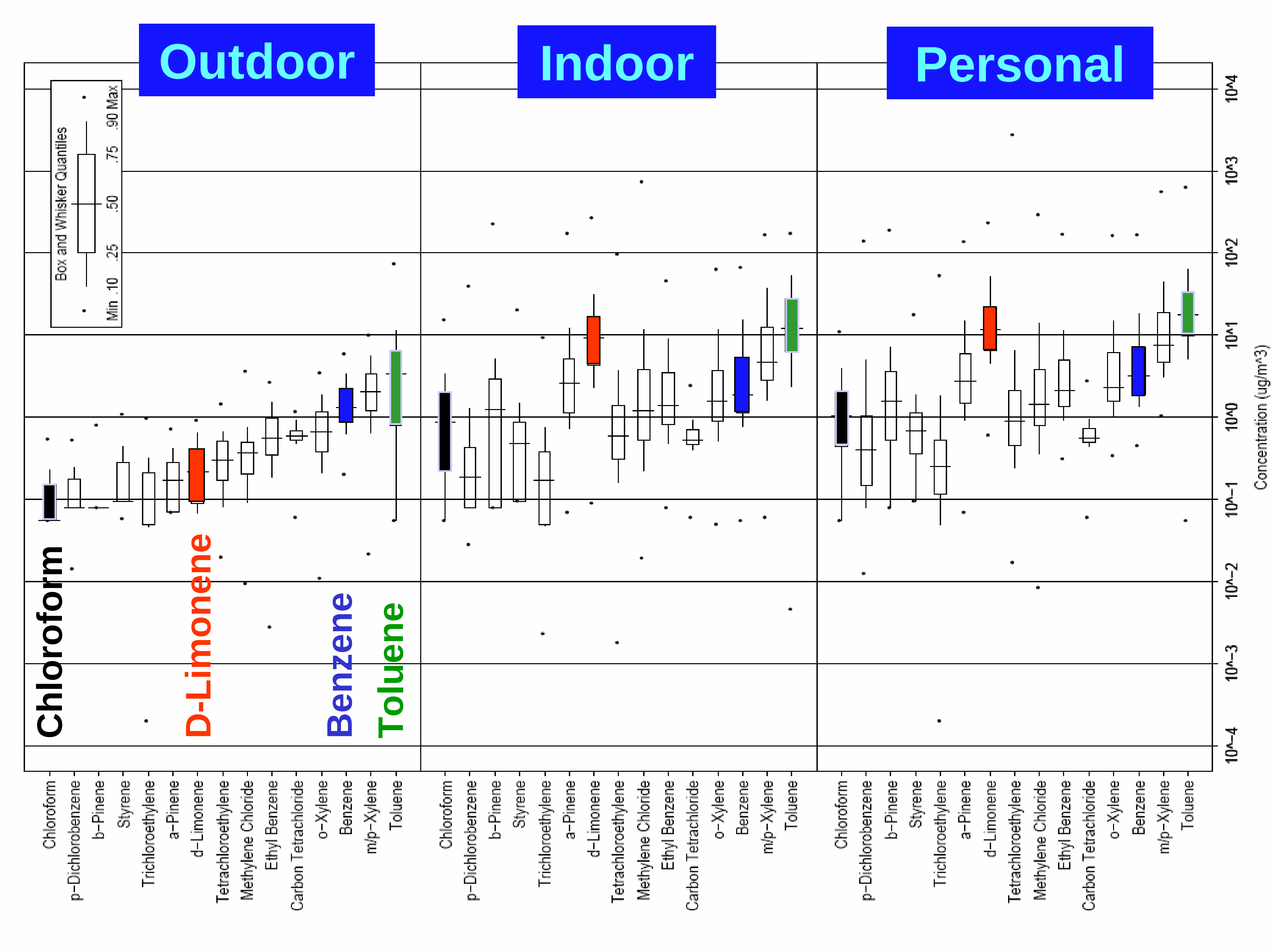


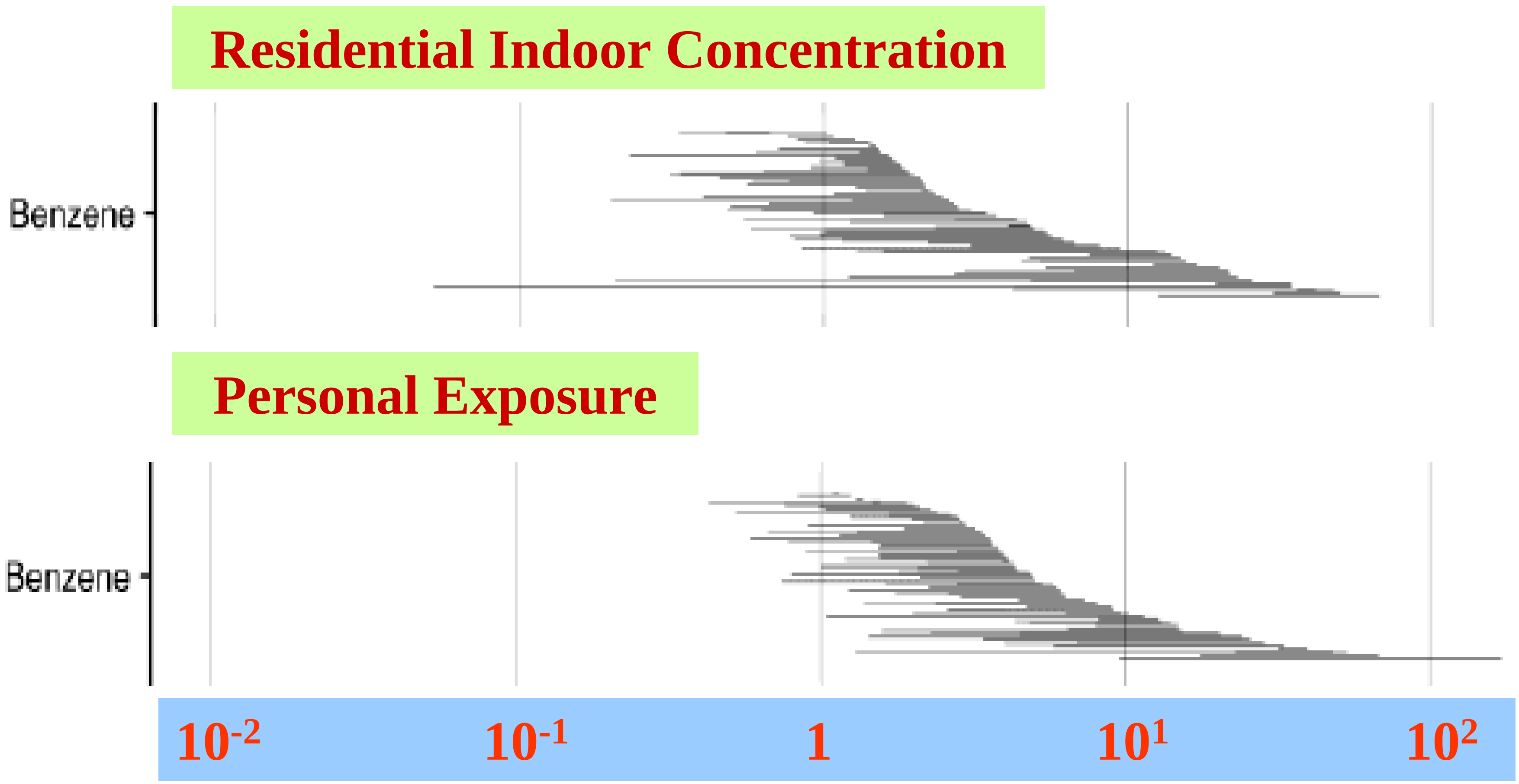
PIO $PM_{2.5}$ Results

- O similar across communities
- P > I > O for most subjects
- O not correlated with P, and weakly correlated with I (r = 0.27)
- I moderate predictor of P (r = 0.51)
- Longitudinal correlation low
- Outdoor central monitoring sites underestimate $PM_{2.5}$ exposures

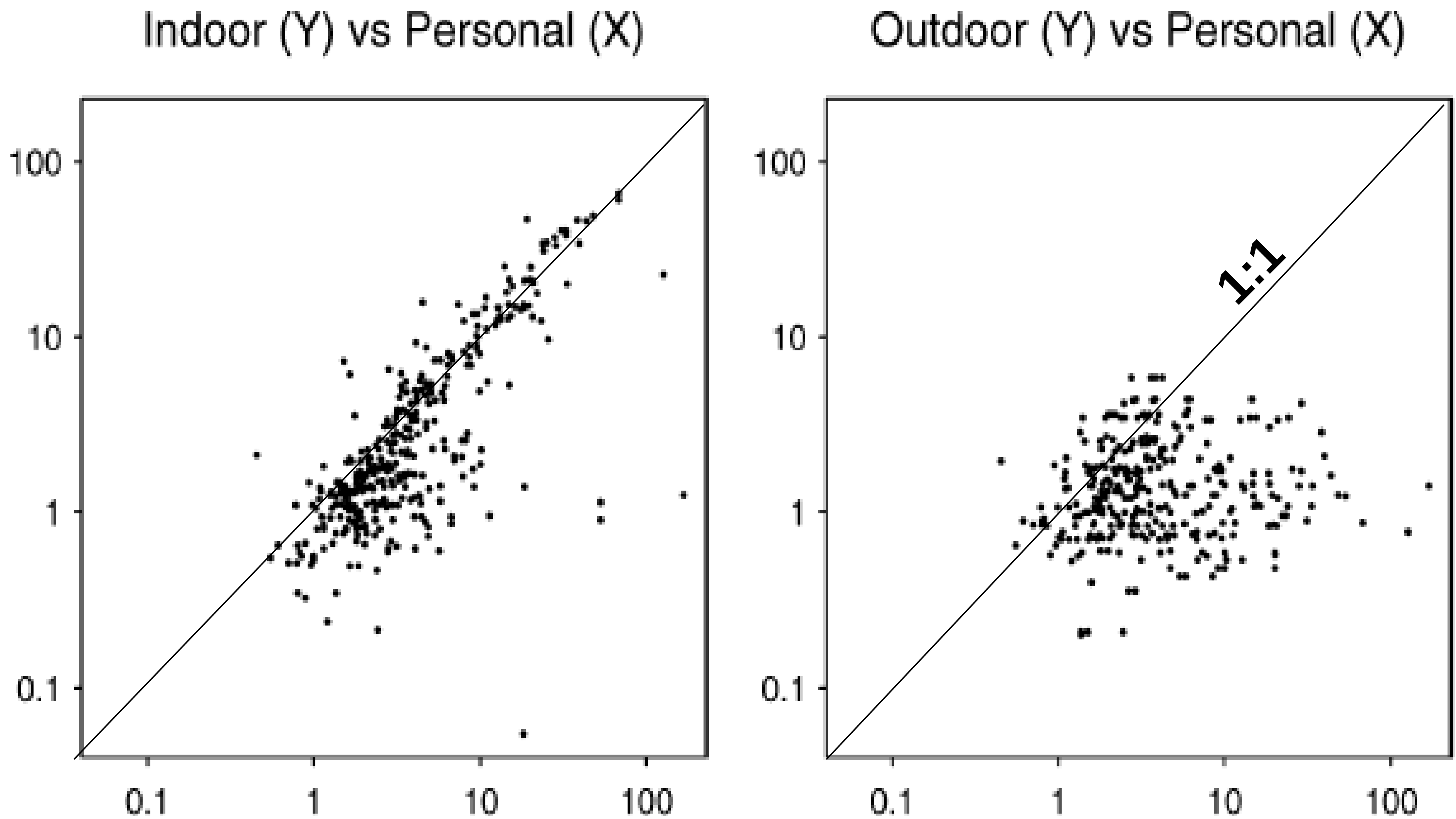
3M Personal Organic Vapor Monitor (OVM)




Outdoor
Indoor
Personal
Box and Whisker Quantiles
Min .10 .25 .50 .75 .90 Max
Chloroform
D-Limonene
Benzene
Toluene
Concentration (ug/m^3)
10^4
10^3
10^2
10^1
10^0
10^-1
10^-2
10^-3
10^-4
Chloroform
p-Dichlorobenzene
b-Pinene
Styrene
Trichloroethylene
a-Pinene
d-Limonene
Tetrachloroethylene
Methylene Chloride
Ethyl Benzene
Carbon Tetrachloride
o-Xylene
Benzene
m/p-Xylene
Toluene


Residential Indoor Concentration
Benzene
Personal Exposure
Benzene
10-2
10-1
1
101
102

Benzene


Indoor (Y) vs Personal (X)
Outdoor (Y) vs Personal (X)
100
10
1
0.1
0.1
1
10
100
1:1

VOC	Cancer bench-mark	Personal		Indoor		Outdoor	
		Median	90%	Median	90%	Median	90%
benzene	1.3	3.2	18.3	1.9	15.3	1.3	3.3
carbon tetrachloride	0.7	0.6	0.9	0.5	0.9	0.6	0.9
chloroform	0.4	1.0	3.9	0.9	3.4	0.1	0.2
p-dichloro-benzene	0.9	0.4	5.1	0.2	1.5	0.1	0.2
methylene chloride	20	1.4	12.1	1.1	11.5	0.4	0.8
Trichloro-ethylene	5	0.2	1.4	0.2	0.8	0.1	0.3

VOC Results

- P > I > O
- P and I within person variability ≈ 1 order of magnitude
- P and I between person variability ≈ 2 orders of magnitude or more
- O not correlated with P and weakly correlated with I
- I moderate predictor of P
- Outdoor central monitoring sites underestimate VOC exposures

$$Personal\ Exposure = \frac{\sum (conc_i \times time_i)}{total\ time}$$

- **Why is P not correlated with O and only weakly with I?**
- **70% of time indoors at home**
- **Microenvironments of high concentration (commuting, gas station, dry cleaner, etc.)**

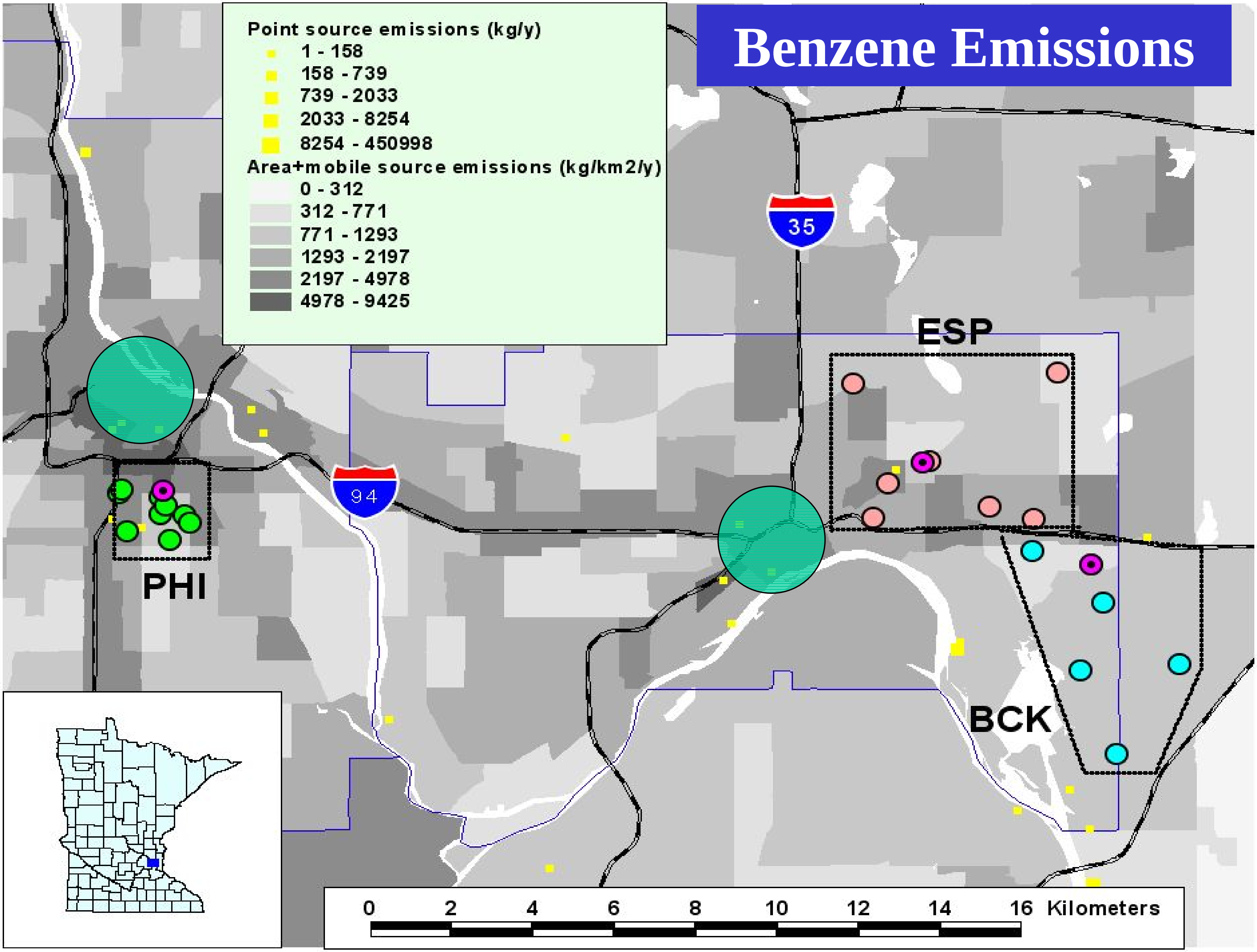
Air Dispersion Modeling of VOCs

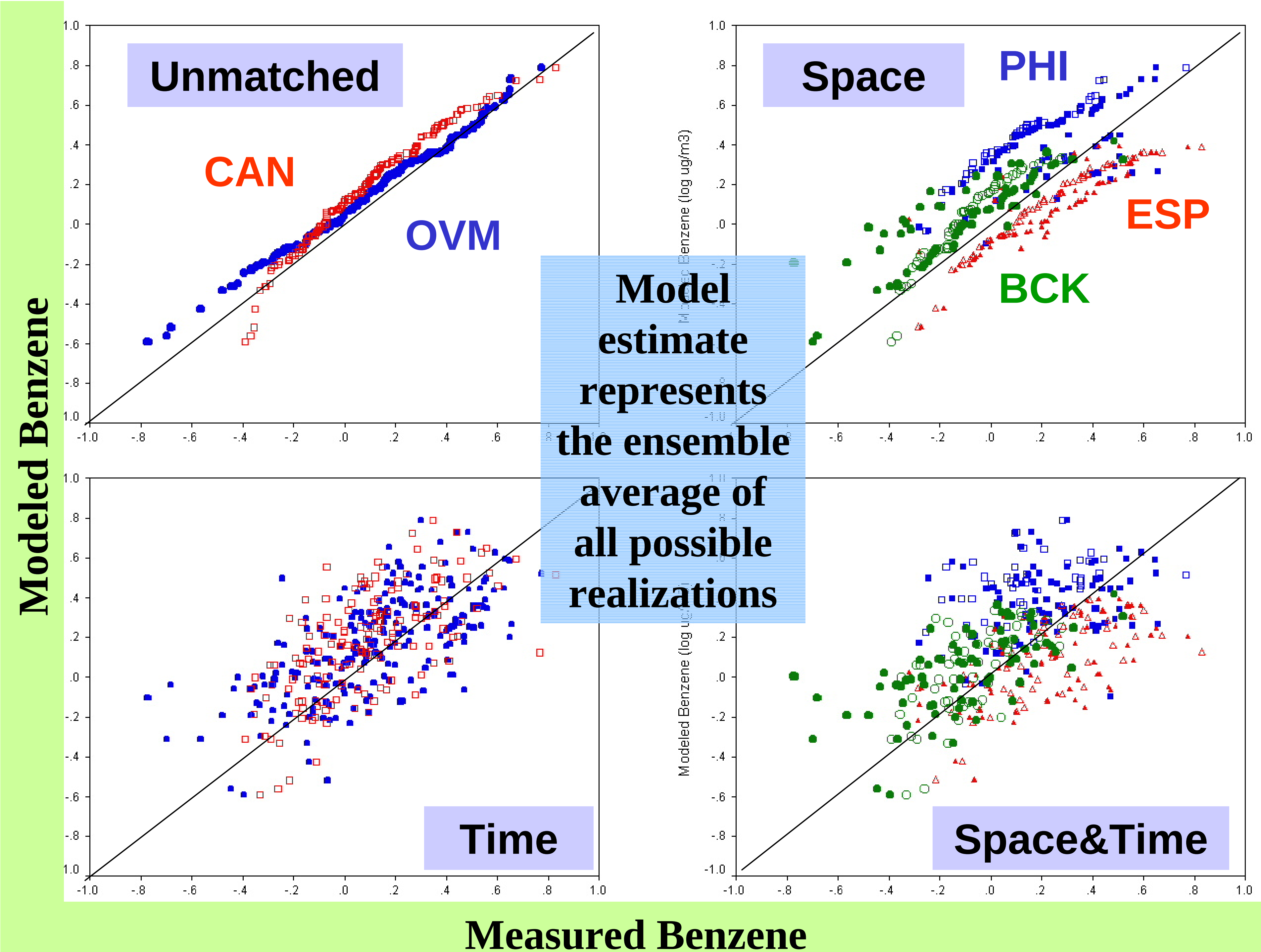
- Model = ISCST3 version 01001 (EPA regulatory model)
- Met data = 1999 MSP airport
- Modeled times = 58 48-hour periods corresponding to measurement periods
- Receptors = community monitoring sites (OVMs and canisters) and outside participant homes (OVMs)

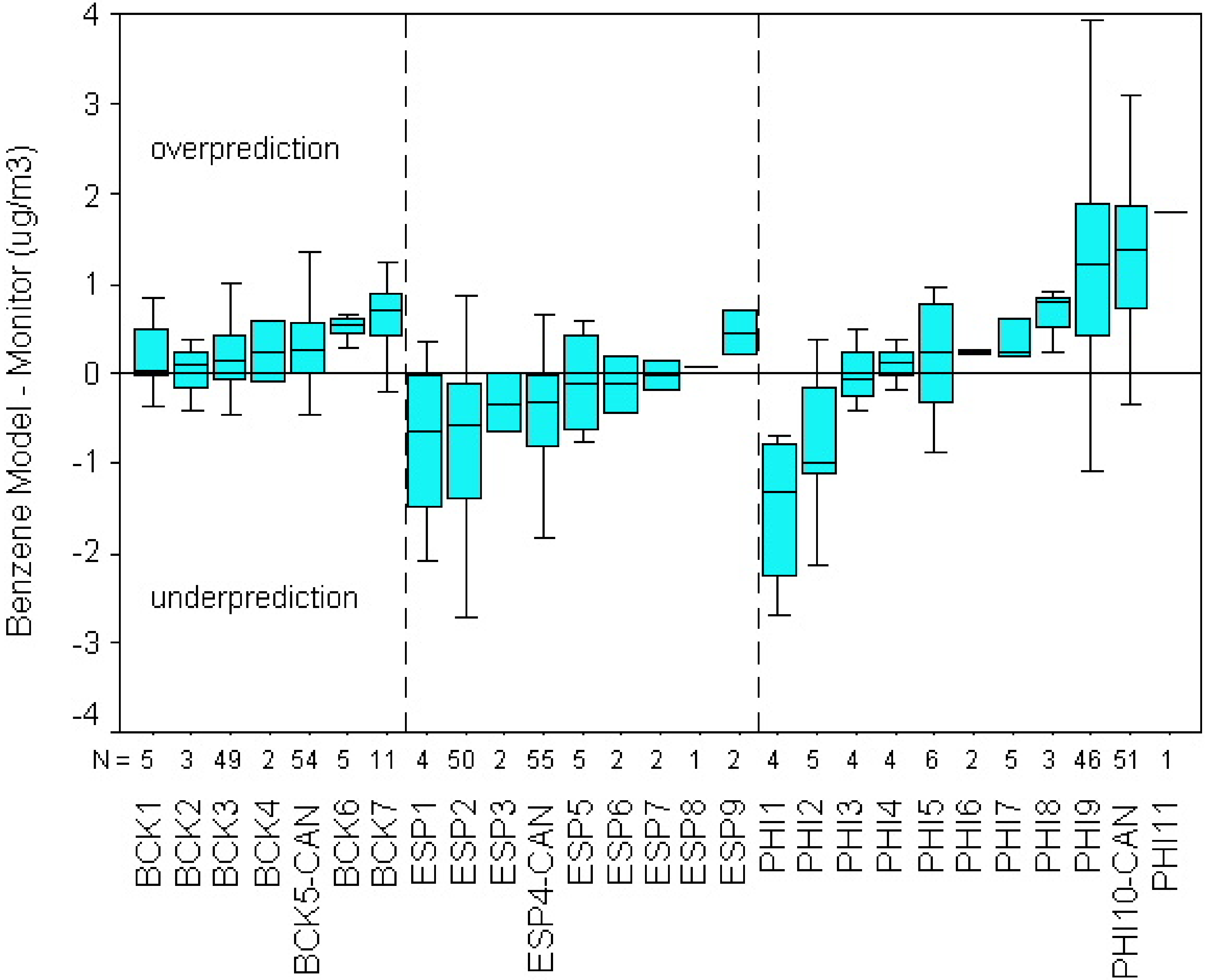
Sources

- **Point Sources - large stationary sources inventoried individually (424 in metro)**
- **Mobile Sources - cars, trucks, planes, trains, boats, construction equipment, farm equipment, off-road vehicles, lawn and garden equipment, etc. (apportioned to census tracts)**
- **Area Sources - smaller stationary sources inventoried collectively (22 categories apportioned to census tracts)**

Benzene Emissions

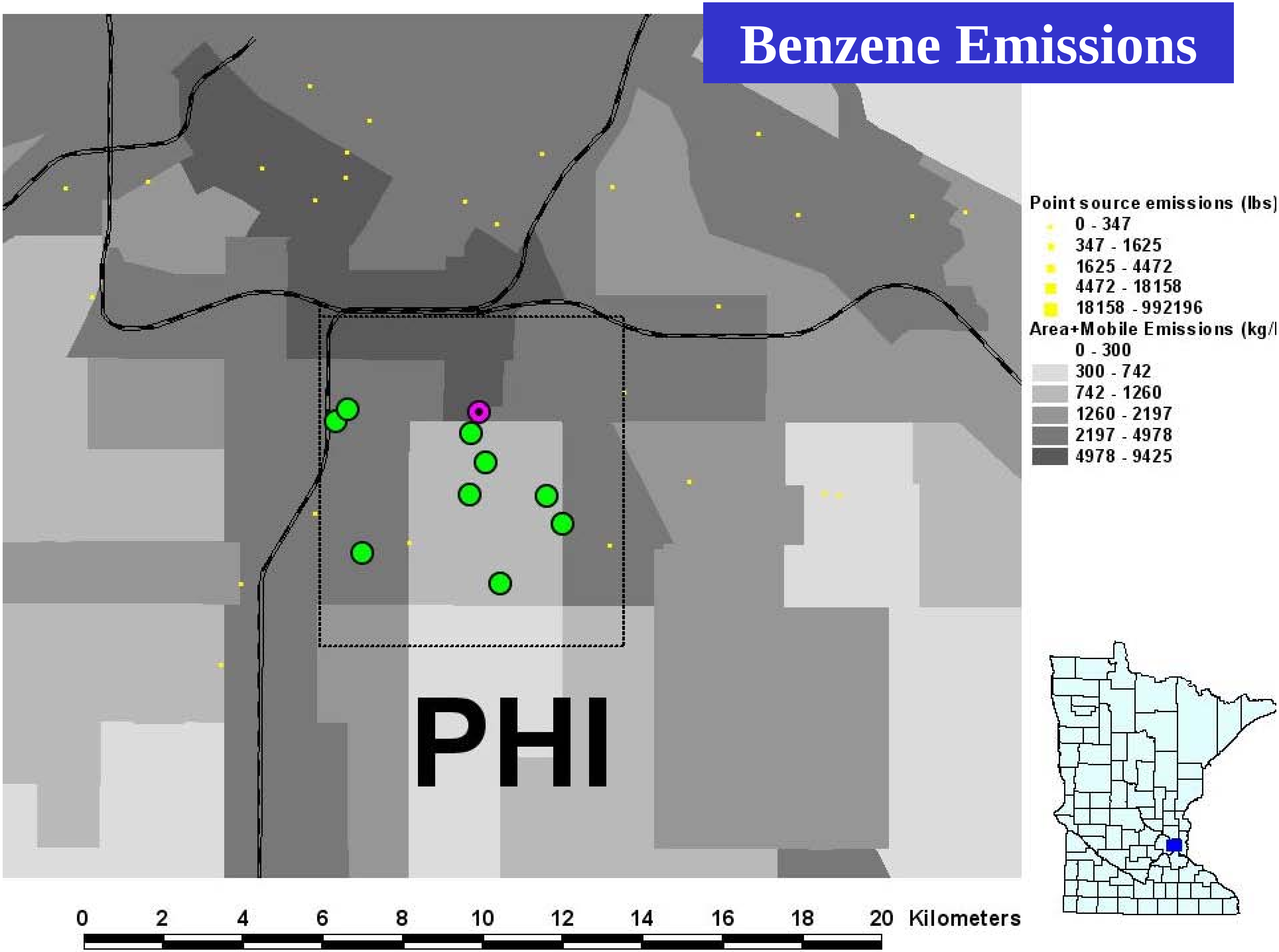



Unmatched
CAN
OVM
Space
PHI
ESP
BCK
Time
Space&Time
Model estimate represents the ensemble average of all possible realizations
Modeled Benzene
Measured Benzene
Modeled Benzene (log ug/m3)



Benzene Model - Monitor (ug/m3)
overprediction
underprediction
4
3
2
1
0
-1
-2
-3
-4
N = 5 3 49 2 54 5 11 4 50 2 55 5 2 2 1 2 4 5 4 4 6 2 5 3 46 51 1
BCK1
BCK2
BCK3
BCK4
BCK5-CAN
BCK6
BCK7
ESP1
ESP2
ESP3
ESP4-CAN
ESP5
ESP6
ESP7
ESP8
ESP9
PHI1
PHI2
PHI3
PHI4
PHI5
PHI6
PHI7
PHI8
PHI9
PHI10-CAN
PHI11

Benzene Emissions



Conclusions

- Generally for measured $PM_{2.5}$ & VOCs:
  Personal > Indoor > Outdoor
- High cross-sectional and longitudinal variability
- Outdoor not a good predictor of personal —indoor better, but not great >> implies microenvironments are important

Conclusions

- ISCST model predictions (matched in time and space) average within factor of 2 of measured outdoor for most VOCs (better unmatched)
- Modeled (as with monitored) O concentration not good predictor of P
- OVMs compared well with canisters for most VOCs in this study – poorly for some VOCs

Extra Slides

Point Sources

- **Emissions of 82 pollutants using RAPIDS**
- **Company review of emission estimates**
- **Source locations by GIS address-matching + GPS**
- **Stack parameters averaged over all sources at a facility from (by priority):**
    1. **DELTA (state permitting system)**
    2. **Default OTAG values by SCC code**
    3. **Average OTAG values**

Mobile Sources - On-Road and Non-Road

- Miles of each road category in each census tract calculated using GIS
- MnDOT traffic count data obtained (counts by county and road category)
- Used GIS to calculate VMT in census tract
- Emission Factors (per VMT) from RAPIDS (based on Mobile 5 model)
- Emissions assigned to census tract and modeled as an area source

Mobile Sources - Rail and Air

- **RAPIDS rail emission were apportioned to census tracts based on the length of rail line in the tract**
- **Airport-related emissions from each airport in RAPIDS were apportioned to the census tract containing the airport**

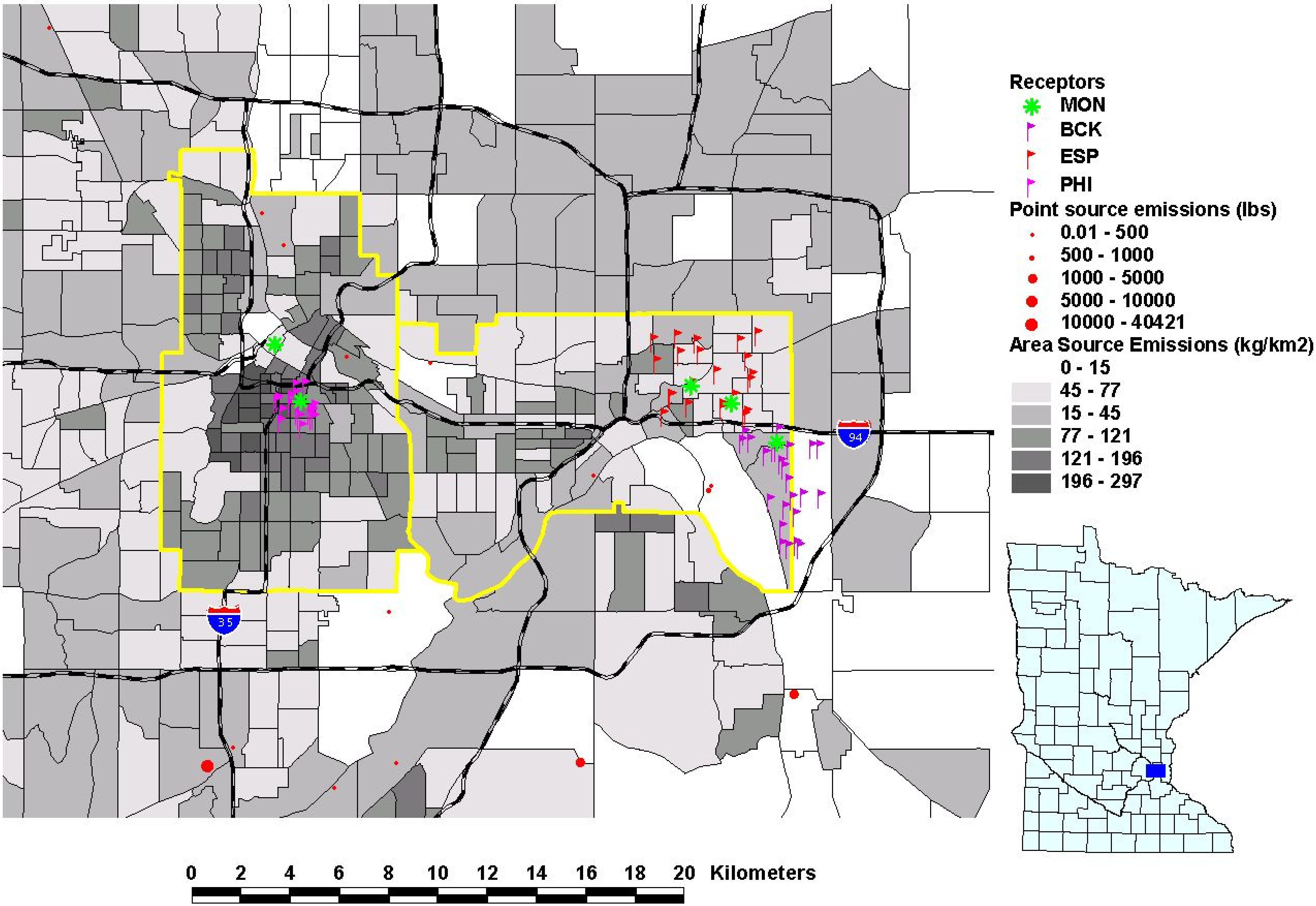
Area Source Categories - 1

Agricultural Pesticide Application	Not Done (no VOCs from study)
Architectural Surface Coatings	Population parsing
Asphalt Paving	Not Done (no VOCs from study)
Auto Body Refinishing	Population parsing
Chromium Electroplating	Not Done (no VOCs from study)
Consumer and Commercial Solvent Use	Population parsing
Dry Cleaning	Population parsing
Gasoline Marketing	Population parsing
Graphic Arts	Population parsing
Hospital Sterilizers	Population parsing
Human Cremation	Not Done (no VOCs from study)

Area Source Categories - 2

Industrial Surface Coating	Population parsing
Landfills	Assign to Census Tract
Marine Vessel Loading etc.	Not Done (only Duluth)
Prescribed Burning	Not Done (data not available)
Public Owned Treatment Works	Done as Point Sources
Residential Fuel Combustion	Population parsing
Residential Wood Combustion	Population parsing
Solvent Cleaning	Population parsing
Structure Fires	Population parsing
Traffic Markings	Lane Miles
Wild Fires	Area

Tetrachloroethylene Emissions



Regressions between modeled and monitored concentrations

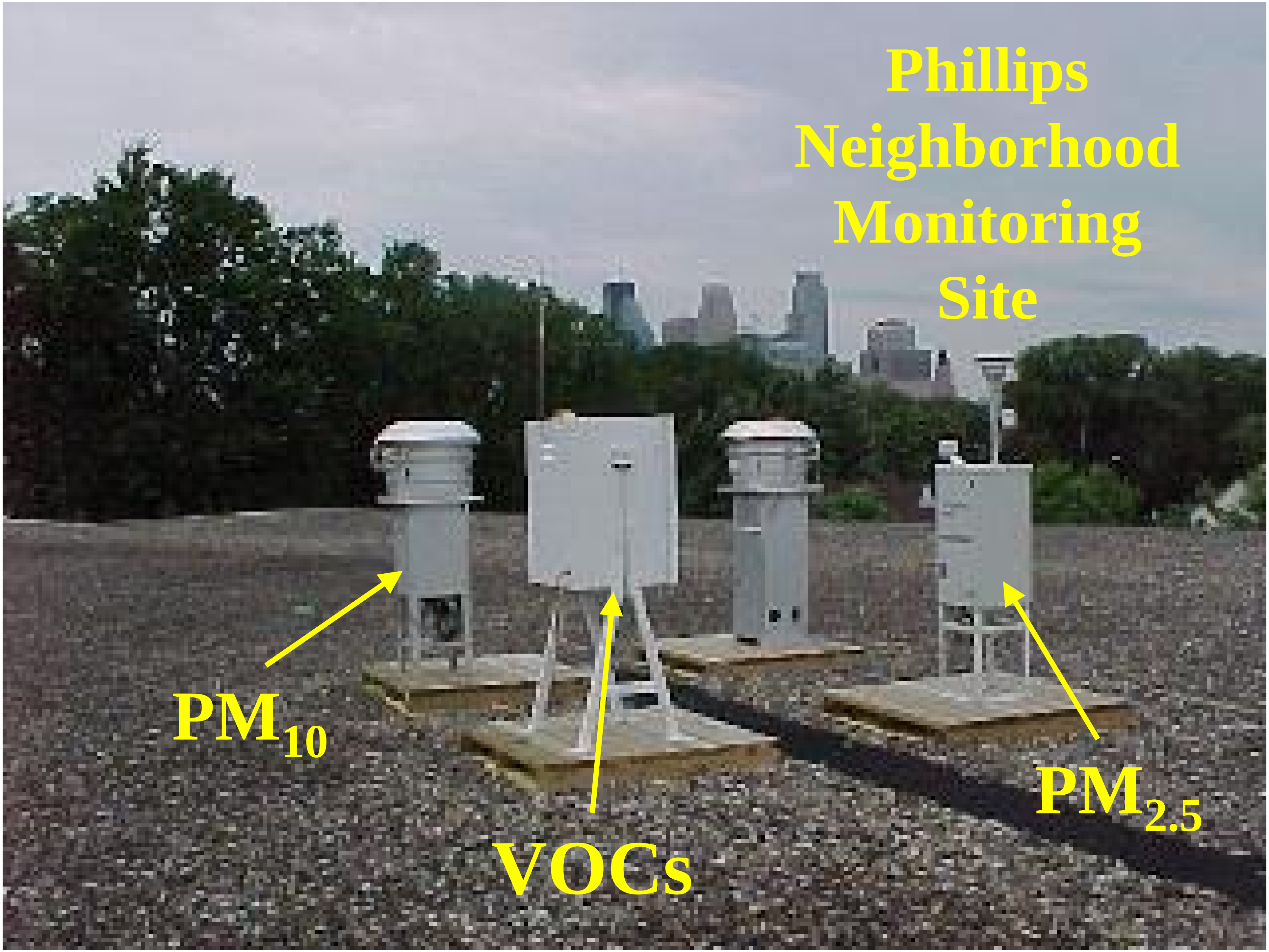
Pollutant	Canisters			Outdoor OVMs		
	BCK	ESP	PHI	BCK	ESP	PHI
Benzene	0.38	0.43	0.16	0.44	0.37	0.08
Carbon Tetrachloride	-0.02	-0.01	-0.01	0.01	-0.01	-0.01
Chloroform	-0.03	0.02	0.36	-0.03	-0.01	-0.02
Ethylbenzene	0.32	0.40	0.17	0.42	0.32	0.04
Methylene Chloride	-0.02	0.03	0.19	-0.01	-0.02	0.04
Styrene	-0.02	0.13	0.12	0.01	0.12	-0.02
Tetrachloroethylene	n/a	n/a	n/a	-0.01	0.14	0.01
Toluene	0.50	0.46	0.19	-0.02	0.08	-0.01
Trichloroethylene	-0.02	-0.02	0.00	0.08	0.00	0.00
Xylenes	0.36	0.39	0.19	0.51	0.34	0.09

Green: $p \leq 0.05$ and $R2 > 0.1$

Yellow: $p \leq 0.001$ and $R2 > 0.2$

Pollutant	Source Category	Emissions (%)	Modeled Concentrations (%)		
			BCK	ESP	PHI
Tetrachoroethylene	Point	14	5	3	3
	Area	86	95	97	97
	Mobile	0	0	0	0
Toluene	Point	5	5	16	2
	Area	37	39	37	41
	Mobile	58	55	46	57
Trichloroethylene	Point	66	56	71	90
	Area	34	44	29	10
	Mobile	0	0	0	0
Xylenes	Point	7	6	5	5
	Area	34	40	44	44
	Mobile	59	54	51	51

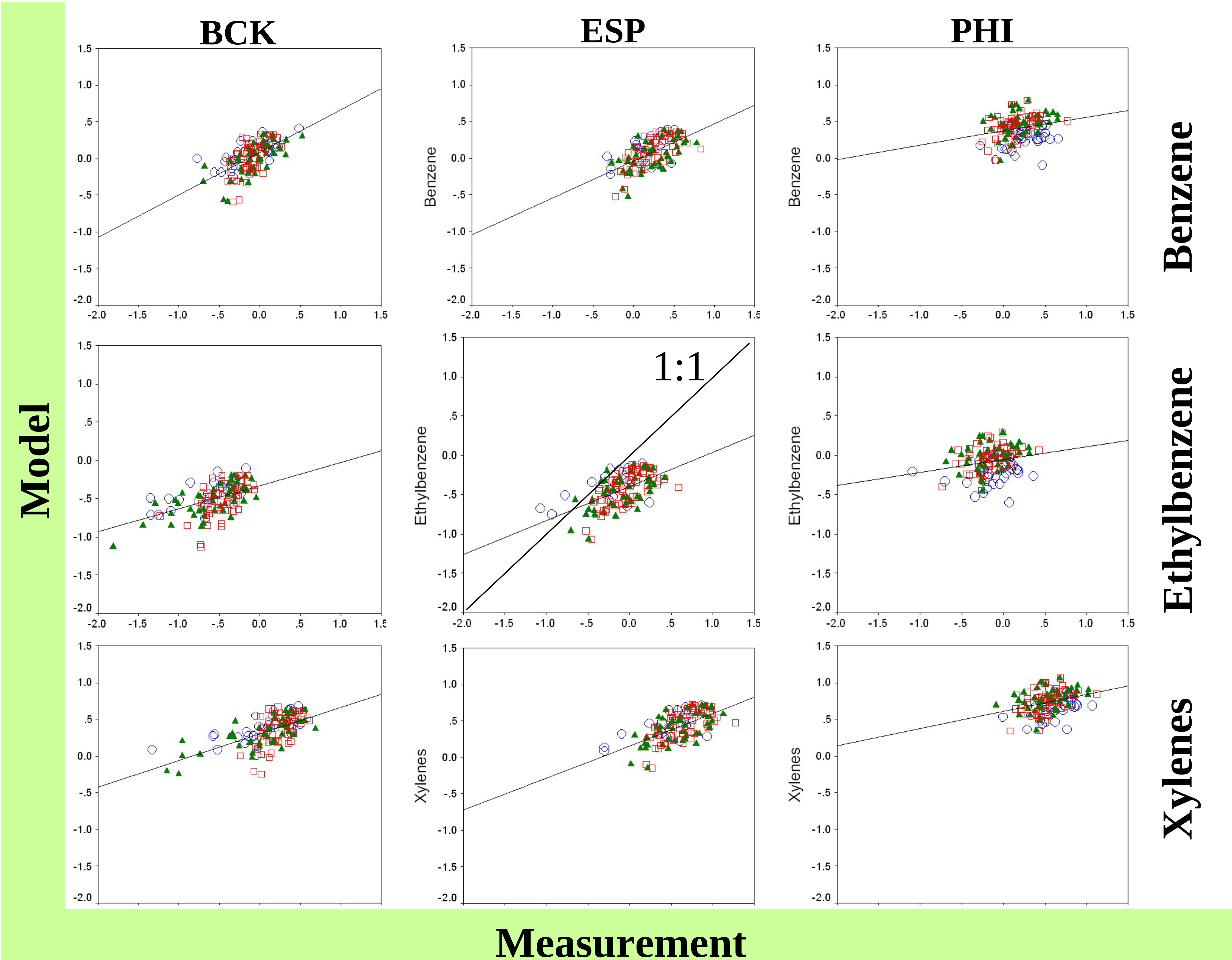
Pollutant	Source Category	Emissions (%)	Modeled Concentrations (%)		
			BCK	ESP	PHI
Benzene	Point	1	1	0	0
	Area	26	12	13	9
	Mobile	73	87	86	91
Chloroform	Point	26	6	6	4
	Area	74	94	94	96
	Mobile	0	0	0	0
Ethylbenzene	Point	5	4	4	6
	Area	10	4	5	2
	Mobile	85	92	91	92
Dichloromethane	Point	21	38	39	39
	Area	79	62	61	61
	Mobile	0	0	0	0
Styrene	Point	55	10	10	9
	Area	1	1	1	0
	Mobile	44	89	89	91


Phillips Neighborhood Monitoring Site
PM_{10}
VOCs
$PM_{2.5}$


Canister
VOC Monitor

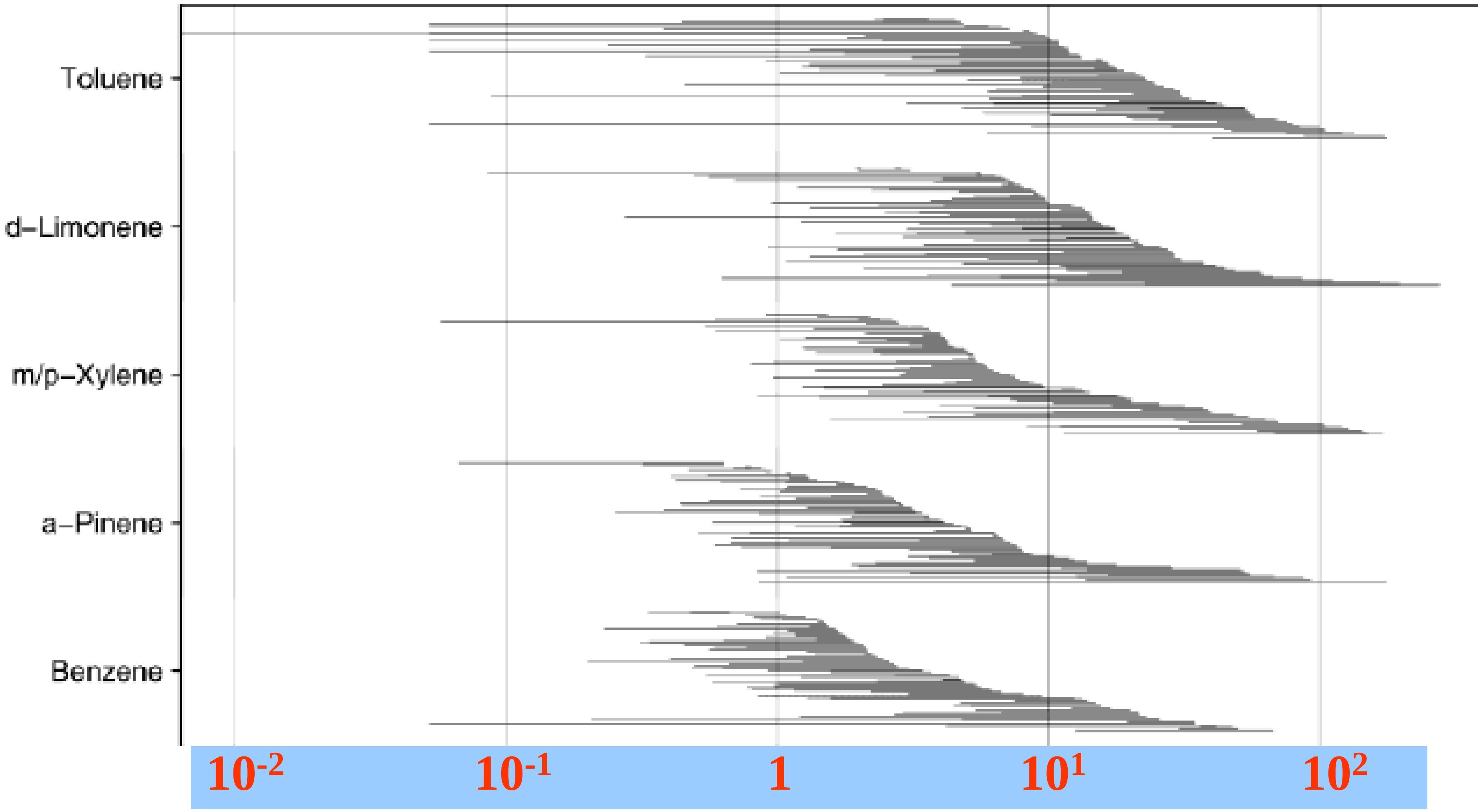
Pollutant	Source Category	Emissions (%)	Modeled Concentrations (%)		
			BCK	ESP	PHI
Benzene	Point	1	1	0	0
	Area	26	12	13	9
	Mobile	73	87	86	91
Chloroform	Point	26	6	6	4
	Area	74	94	94	96
	Mobile	0	0	0	0
Ethylbenzene	Point	5	4	4	6
	Area	10	4	5	2
	Mobile	85	92	91	92
Dichloromethane	Point	21	38	39	39
	Area	79	62	61	61
	Mobile	0	0	0	0
Styrene	Point	55	10	10	9
	Area	1	1	1	0

Model-Monitor Comparisons		Monitor Site Canisters		
		BCK (n=54)	ESP (n=55)	PHI (n=51)
Benzene	Mon. mean mean diff. RMSE Fx-Bias	0.9 0.3 0.5 -0.3	1.9 -0.6 1.1 0.4	1.5 1.4 1.8 -0.6
Ethylbenzene	Mon. mean mean diff. RMSE Fx-Bias	0.4 -0.0 0.2 0.1	1.1 -0.6 0.9 0.9	0.8 0.2 0.5 -0.3
Styrene	Mon. mean mean diff. RMSE Fx-Bias	0.3 -0.2 0.2 0.6	0.4 -0.2 0.3 0.7	0.4 0.1 0.3 -0.2
Toluene	Mon. mean mean diff. RMSE Fx-Bias	2.0 1.7 2.1 -0.6	8.4 -2.3 7.1 0.3	3.9 4.0 5.0 -0.7
Trichloroethylene	Mon. mean mean diff. RMSE Fx-Bias	0.3 -0.1 0.3 0.7	0.4 -0.3 0.4 0.9	0.6 -0.4 0.5 1.0
Xylenes	Mon. mean mean diff. RMSE Fx-Bias	1.8 0.8 1.2 -0.4	5.1 -1.9 3.3 0.5	3.7 2.4 3.3 -0.5

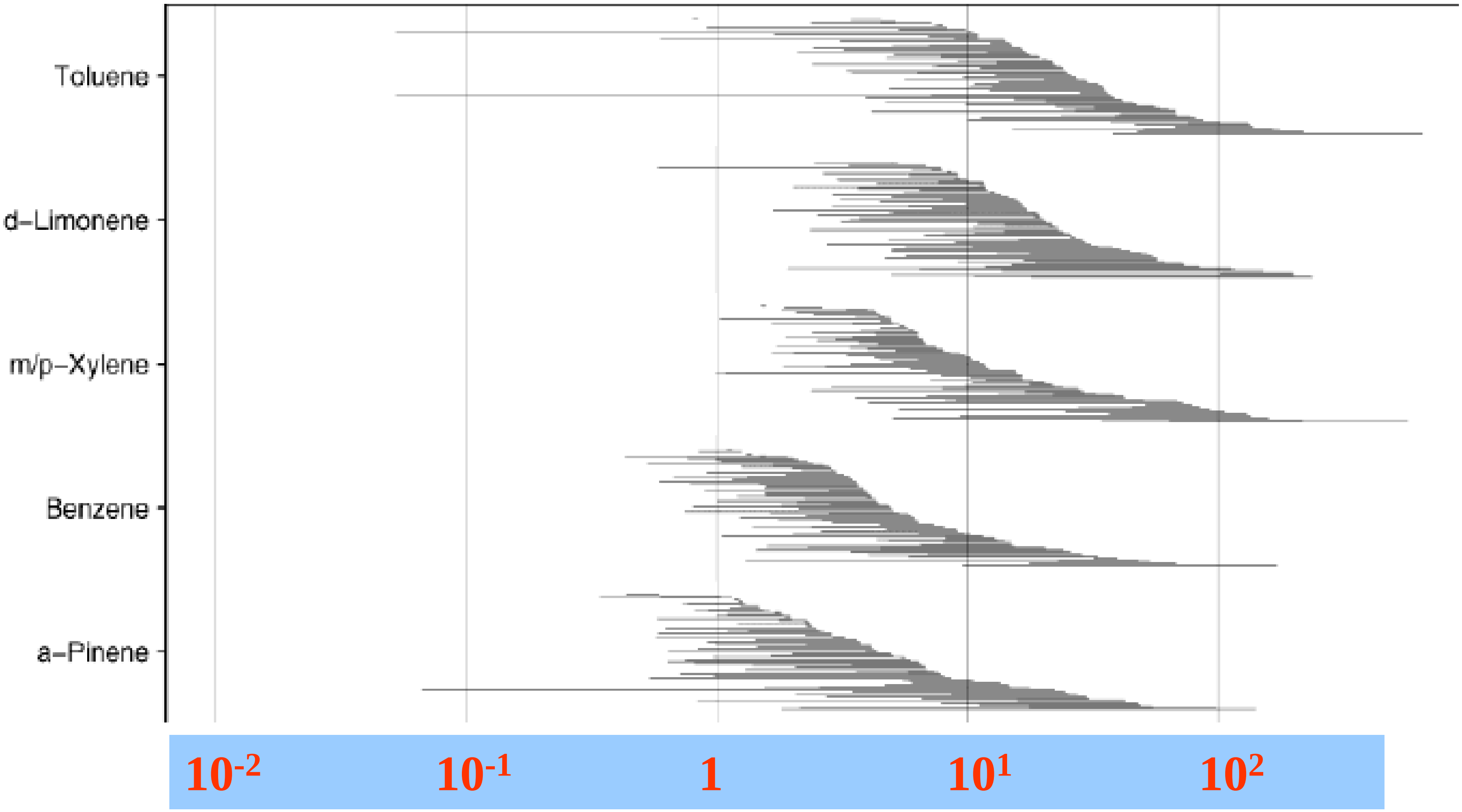


BCK
ESP
PHI
Benzene
Ethylbenzene
Xylenes
Model
Measurement
1:1

Residential Indoor Concentration



Personal Exposure



Summary/Conclusions:

- **Generally for measured VOCs/PM2.5:**
  P > I > O
- **Relatively high P-O/P-I longitudinal correlation coefficients mean that in healthy adults the variability in VOC exposures can be reasonably predicted within individuals over time.**
- **This was not true for $PM_{2.5}$, probably because of low outdoor variability and activity patterns of the working adult population**
- **Risk assessments based on outdoor VOC measures appear to seriously underestimate lifetime cancer risks from these compounds**

VOCs Measured

VOCs Measured with OVM Badges (and FRM)	
Benzene	**a-Pinene**
Carbon tetrachloride	**b-Pinene**
Chloroform	**Styrene**
p-Dichlorobenzene	**Tetrachloroethylene (PERC)**
Ethylbenzene	**Toluene**
d-Limonene	**Trichloroethylene**
Methylene Chloride	**m,p-Xylene**
	o-Xylene

PM2.5 Measurements

- Central sites: FRM
- Personal and Indoor at home: MSP impactors, pumps, time dairies
- Flow rates O>I>P
- Detection Limits: P>I>O
- Pretty good (but not perfect) temporal match

Number of People/Samples

(Non-Smoking Adults)

VOCs: 71 Subjects

- 2-18 samples per subject
- 58 48-hr sampling periods
  - P = 288
  - I = 292
  - O = 132

PM2.5: 29 Subjects

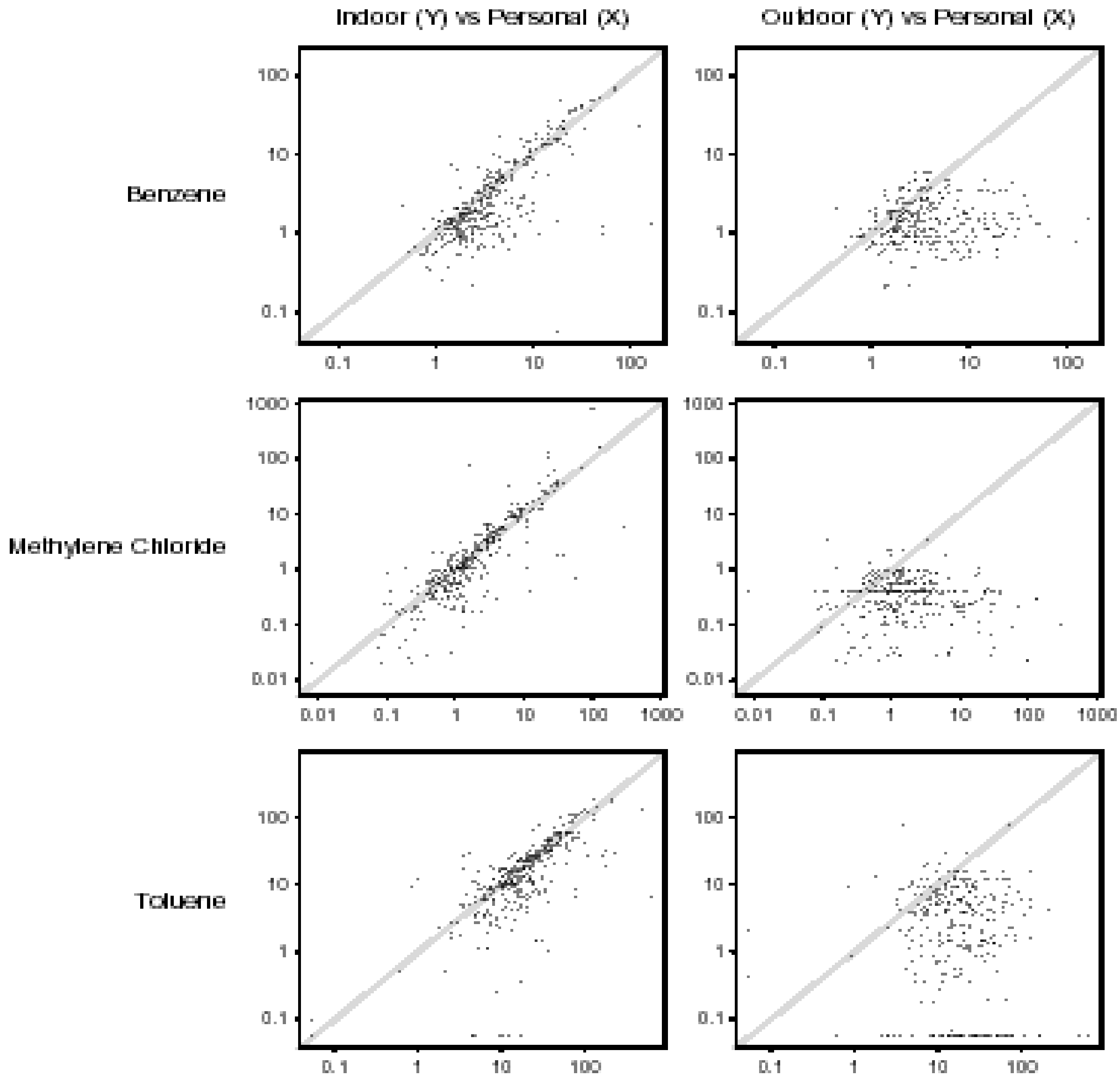
- 7-15 samples per subject
- 112 24-hr sampling periods
  - P= 332
  - I = 294
  - O= 270

Primary VOC Sources Indoors

(source: Wallace 1991*)

Pollutant	Sources
Chloroform	**Chlorinated water, especially when heated as in showering, dishwashing, etc.**
p-Dichlorobenzene	**Mothballs, toilet block deodorizers, other consumer products (check labels), chemical manufacturing industry**
α- and β-Pinene	**Cleaning products, room fresheners**
d-Limonene	**Cleaning products, room fresheners**

*Chapter 11 in: Indoor Air Pollution: A Health Perspective. Eds. Samet, J.M. and Spengler, J.D. The Johns Hopkins University Press, Baltimore, MD, p.253-27.



Indoor (Y) vs Personal (X)
Outdoor (Y) vs Personal (X)
Benzene
Methylene Chloride
Toluene
0.01
0.1
1
10
100
1000

VOC Results: PIO

- Consistent P>I>O observed for 13 of 15 chemicals
  - Exceptions: Carbon Tetrachloride, Chloroform
- I does better than O
- Underestimation is greater at the upper end of the exposure distribution
- Central sites under estimate actual exposures for urban residents even when measured in their own community

Longitudinal VOC Results

- How well do O levels predict I and P within people over time?
- Mixed model approach:
  - Adjust for season and community effects
  - Address issue of within person and within monitoring period autocorrelation

Longitudinal VOC Results

- Benzene:
  - P-O median r=0.59 (range -0.85-0.99)
  - P-I median r=0.86 (range -0.26-0.99)

- p-Dichlorobenzene
  - P-O median r=0.00 (range -0.72-0.98)
  - P-I median r=0.57 (range -0.54-0.99)

- People pass through microenvironments of high concentration (commuting, gas station, dry cleaner, etc.)

- Higher income homes may
  - use more consumer products
  - have air conditioning
  - have attached garage
  - have tighter construction
  - spend more time commuting