EERC Technology… Putting Research into Practice

Identifying the Source of Benzene in Indoor Air Using Different Compound Classes from TO-15 Data

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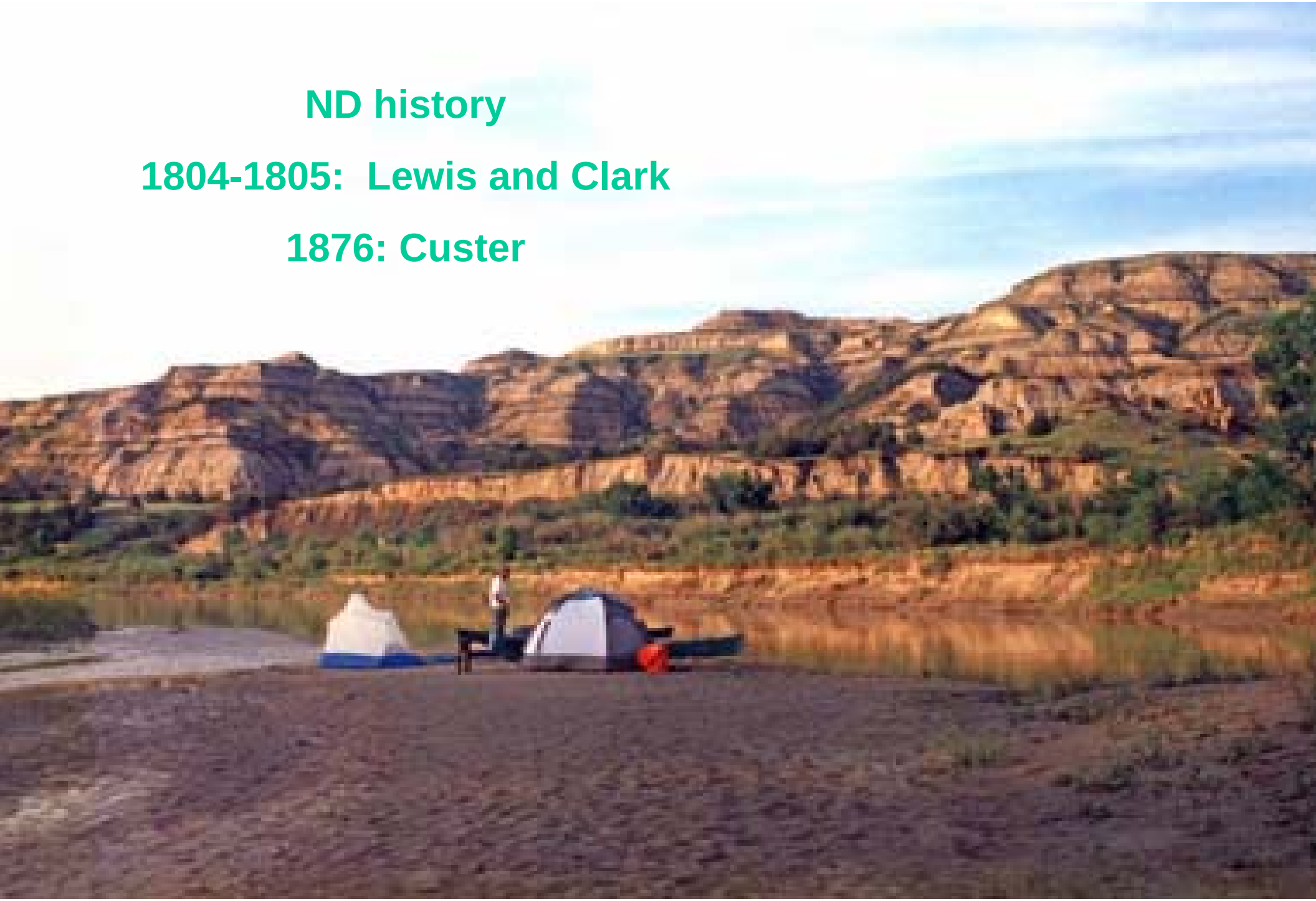
Supported by:
American Petroleum Institute
United States Department of Energy

ND history

1804-1805: Lewis and Clark

1876: Custer



Apparent bias in indoor air studies:

If soil is contaminated, then benzene in indoor air must be from soil (perhaps because of the radon story?)

BUT, the average commercial and residential buildings are designed to exchange air about once per hour (ASHRAE Handbook, 1981). Therefore, outdoor air must be considered as a source of indoor air organics.

Background

Benzene is in every air sample everywhere.

Urban background (outdoor and indoor) concentrations are often of regulatory concern, and are often similar.

9 out of 17 state screening levels are <2 ug/m^3 (CA is 0.084) for indoor benzene. (Eklund et al.)

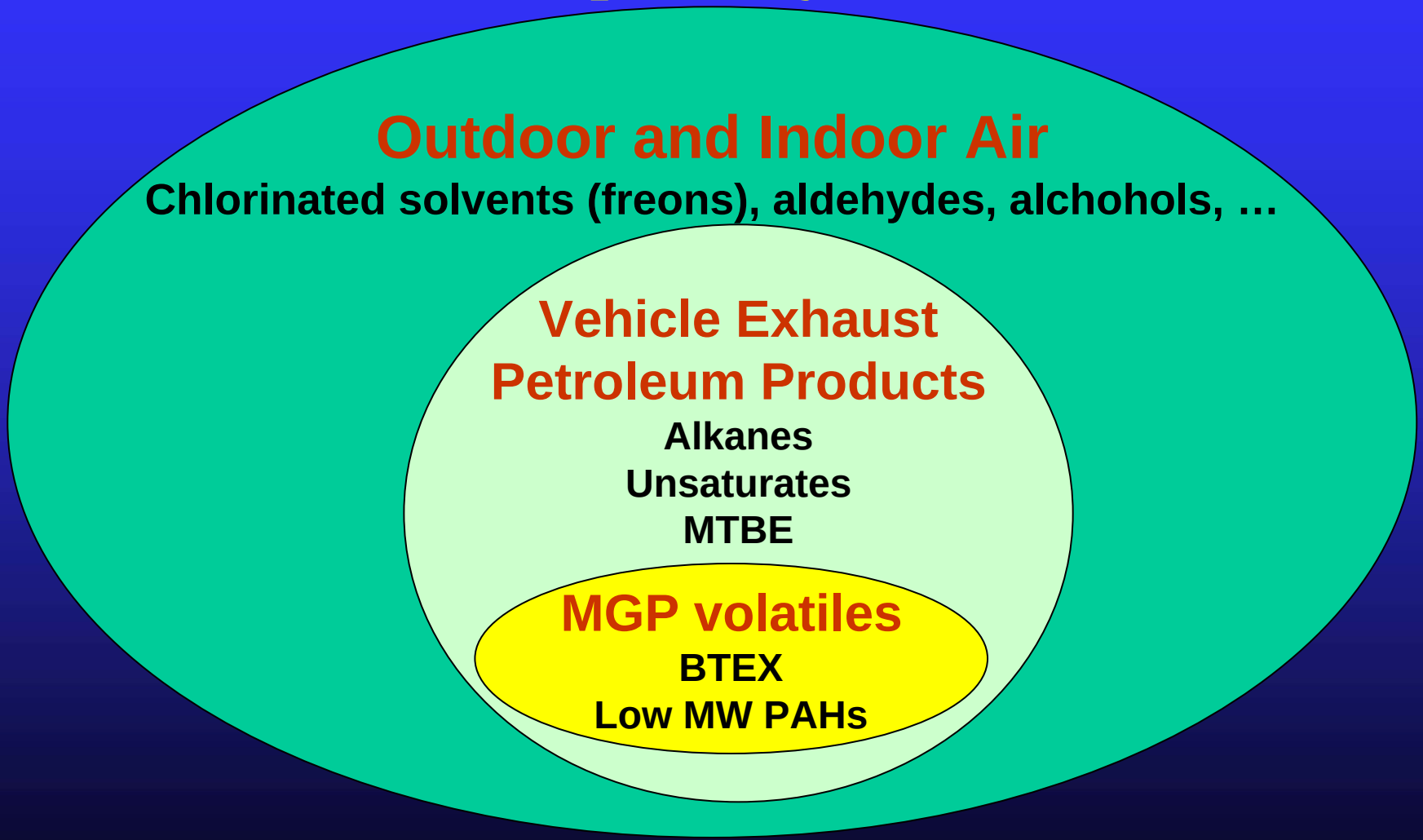
Benzene comes from different sources (pyrogenic and petrogenic).

Indoor air comes from outdoor air.

Soil breathes.

Urban air has many organics indicative of different sources, but benzene is not one of them.

Hypothesis: benzene can be ratioed to other indicators to determine primary source to indoor air.



1,2,4-trimethylbenzene
1,3,5-trimethylbenzene
2,3-Dimethylpentane
2-Hexanone
2-Methylpentane
4-Ethyltoluene
4-Methyl-2-pentanone
benzene
carbon disulfide
Cyclohexane
ethylbenzene
heptane
hexane
2,2,4-trimethylpentane
Indan
Indene
Isopentane
naphthalene
styrene
Thiophene
toluene
m/p-xylenes
o-xylene

1,1,1-trichloroethane
1,1,2,2-tetrachloroethane
1,1,2-trichloroethane
1,1-dichloroethane
1,1-dichloroethene
1,2,4-trichlorobenzene
1,2-dibromoethane (EDB)
1,2-dichlorobenzene
1,2-dichloroethane
1,2-dichloropropane
1,3-Butadiene
1.3-dichlorobenzene
1,4-dichlorobenzene
1,4-Dioxane
2-butanone (MEK)
acetone
benzyl chloride (a-chlorotoluene)
bromodichloromethane
bromoform
bromomethane
carbon tetrachloride
chlorobenzene
chloroethane

chloroform
chloromethane
cis-1,2-dichloroethene
cis-1,3-dichloropropene
dibromochloromethane
Ethanol
trichlorofluoromethane (Freon 11)
1,1,2-trichlorotrifluoroethane (Freon 113)
1,2-dichlorotetrafluoroethane
dichlorodifluoromethane (Freon 12)
hexachlorobutadiene (C-46)
Methyl tert-Butyl Ether
methylene chloride (dichloromethane)
2-Propanol
Propene
tetrachloroethene
Tetrahydrofuran
trans-1,2-dichloroethene
trans-1,3-dichloropropene
trichloroethene
Vinyl Acetate
vinyl chloride

Classes of Organics in Urban Air (from TO-15)

Examples	mixed source	"pure" source
Benzene	MGP, petroleum, exhaust	none
Toluene,xylenes, etc.	MGP, petroleum, exhaust	solvents (paint, adhesives)
Alkanes	petroleum, exhaust	some solvents
Halogenated (chlorinated, Freons)		refrigerants, propellants solvents
Oxygenates MTBE	petroleum	
Ethanol, isopropanol, acetone		baking, rubbing alcohol, nail polish remover

Goal:

Use widely available "cheap" data (EPA TO-15) to determine major source of benzene in indoor air.

Approach:

1) ***Statistical (principal component analysis and canonical discriminate analysis).***
2) ***Comparison of "tracer" organics with benzene based on the sources' organic composition and air chemistry.***

Air sampling sites (all thought to be impacted by former MGP activities)

2 Schools

Strip mall (bar/grill, bakery, appliance dealer, beautician, etc.)

Mixed residential/small business neighborhood

Apartment complex

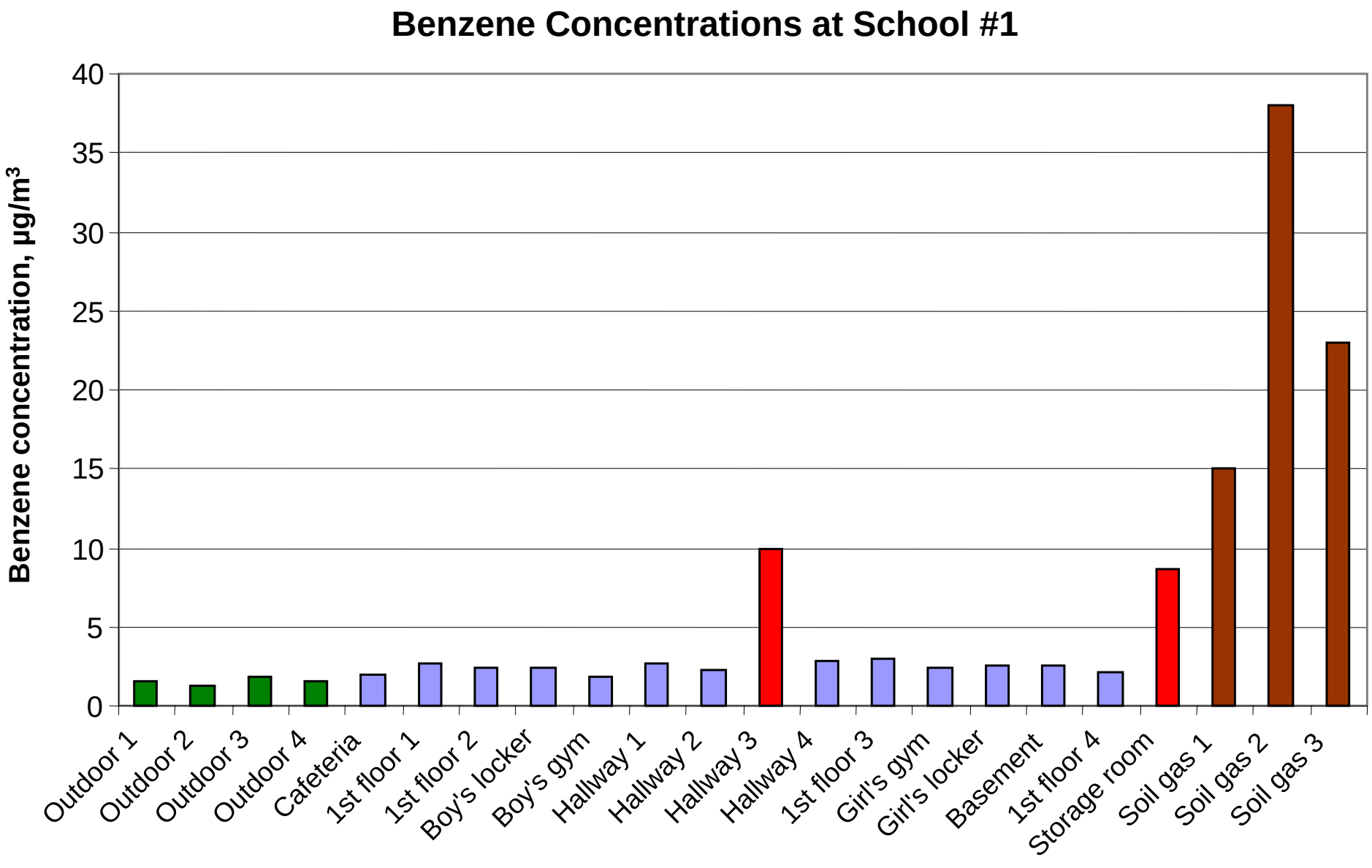
No petroleum-impacted site data sets could be found with parallel outdoor air samples.

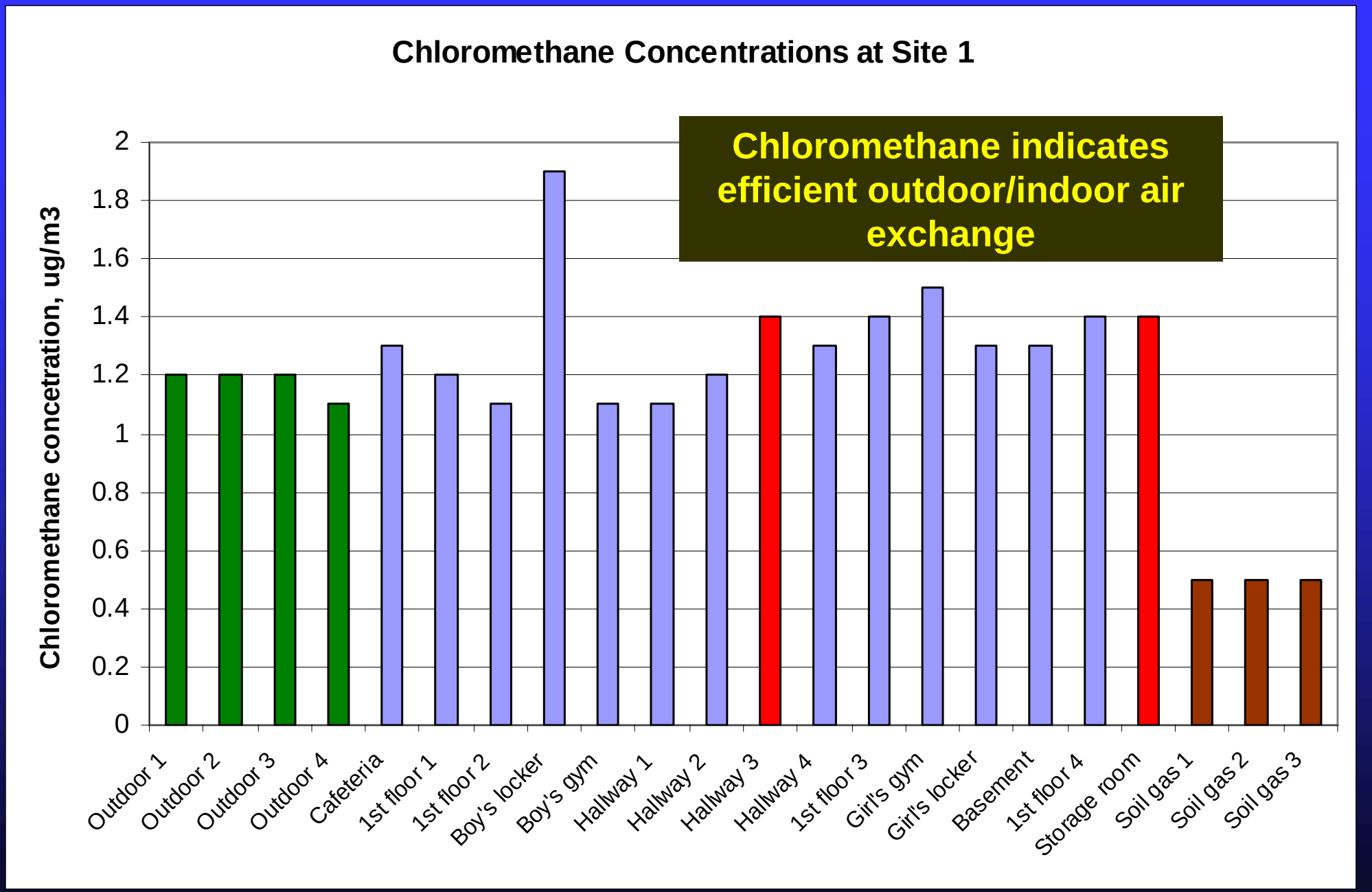
Case 1: School located over an MGP site.

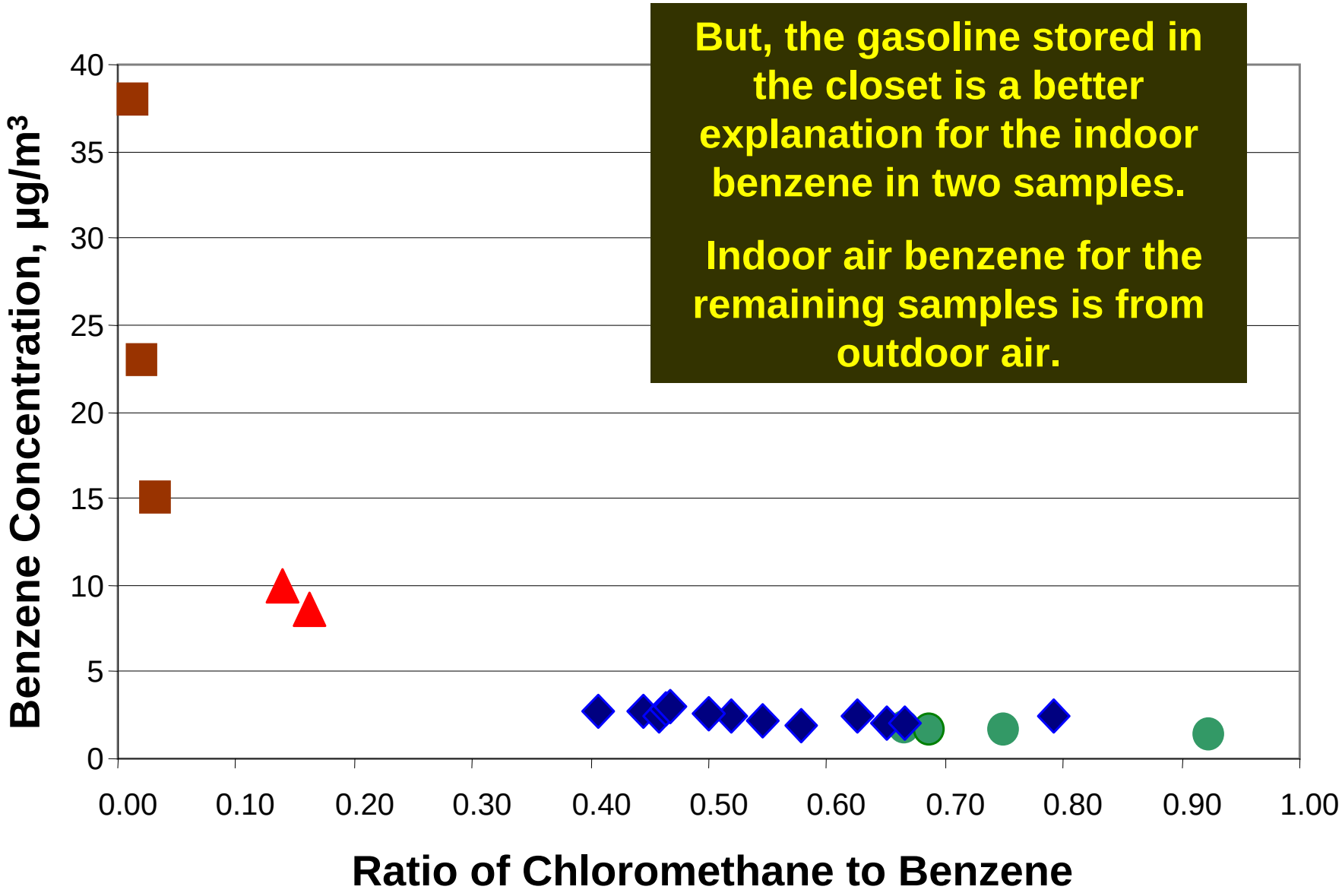
15 indoor air samples

4 outdoor (ambient) air samples

3 soil gas samples


Benzene Concentrations at School #1
Benzene concentration, µg/m³
40
35
30
25
20
15
10
5
0
Outdoor 1
Outdoor 2
Outdoor 3
Outdoor 4
Cafeteria
1st floor 1
1st floor 2
Boy's locker
Boy's gym
Hallway 1
Hallway 2
Hallway 3
Hallway 4
1st floor 3
Girl's gym
Girl's locker
Basement
1st floor 4
Storage room
Soil gas 1
Soil gas 2
Soil gas 3


Chloromethane Concentrations at Site 1
Chloromethane indicates efficient outdoor/indoor air exchange
Chloromethane concetration, ug/m3
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
Outdoor 1
Outdoor 2
Outdoor 3
Outdoor 4
Cafeteria
1st floor 1
1st floor 2
Boy's locker
Boy's gym
Hallway 1
Hallway 2
Hallway 3
Hallway 4
1st floor 3
Girl's gym
Girl's locker
Basement
1st floor 4
Storage room
Soil gas 1
Soil gas 2
Soil gas 3


But, the gasoline stored in the closet is a better explanation for the indoor benzene in two samples.
Indoor air benzene for the remaining samples is from outdoor air.
Benzene Concentration, µg/m³
40
35
30
25
20
15
10
5
0
0.00
0.10
0.20
0.30
0.40
0.50
0.60
0.70
0.80
0.90
1.00
Ratio of Chloromethane to Benzene

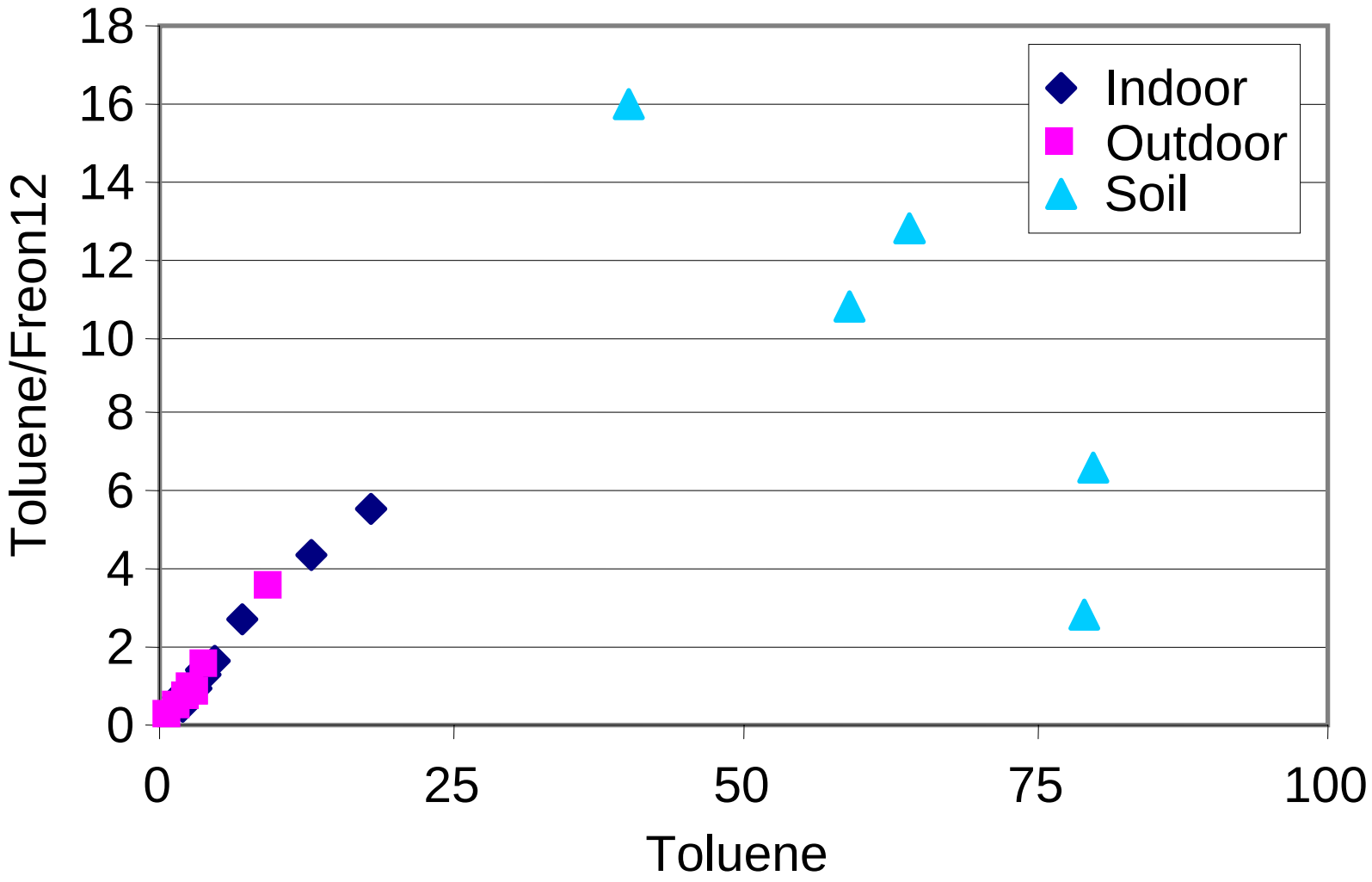
School #1: Compound Ratio Results

1. ***Outdoor air is the major source of indoor benzene, even though soil gas benzene concentrations are higher.***
2. ***Unique sources (gas can) must be considered.***
3. ***Excavation of MGP materials will not lower indoor benzene concentrations.***

School #2

1. *Too many NDs for chloromethane to be useful, but Freon 12 was detected.*
2. *Volume of soil gas was too small (detection limits were less than detected values in indoor and outdoor air)—so toluene was used as a model for benzene.*

School #2


Toluene/Freon12
18
16
14
12
10
8
6
4
2
0
0
25
50
75
100
Toluene
Indoor
Outdoor
Soil

Strip Mall over MGP site.

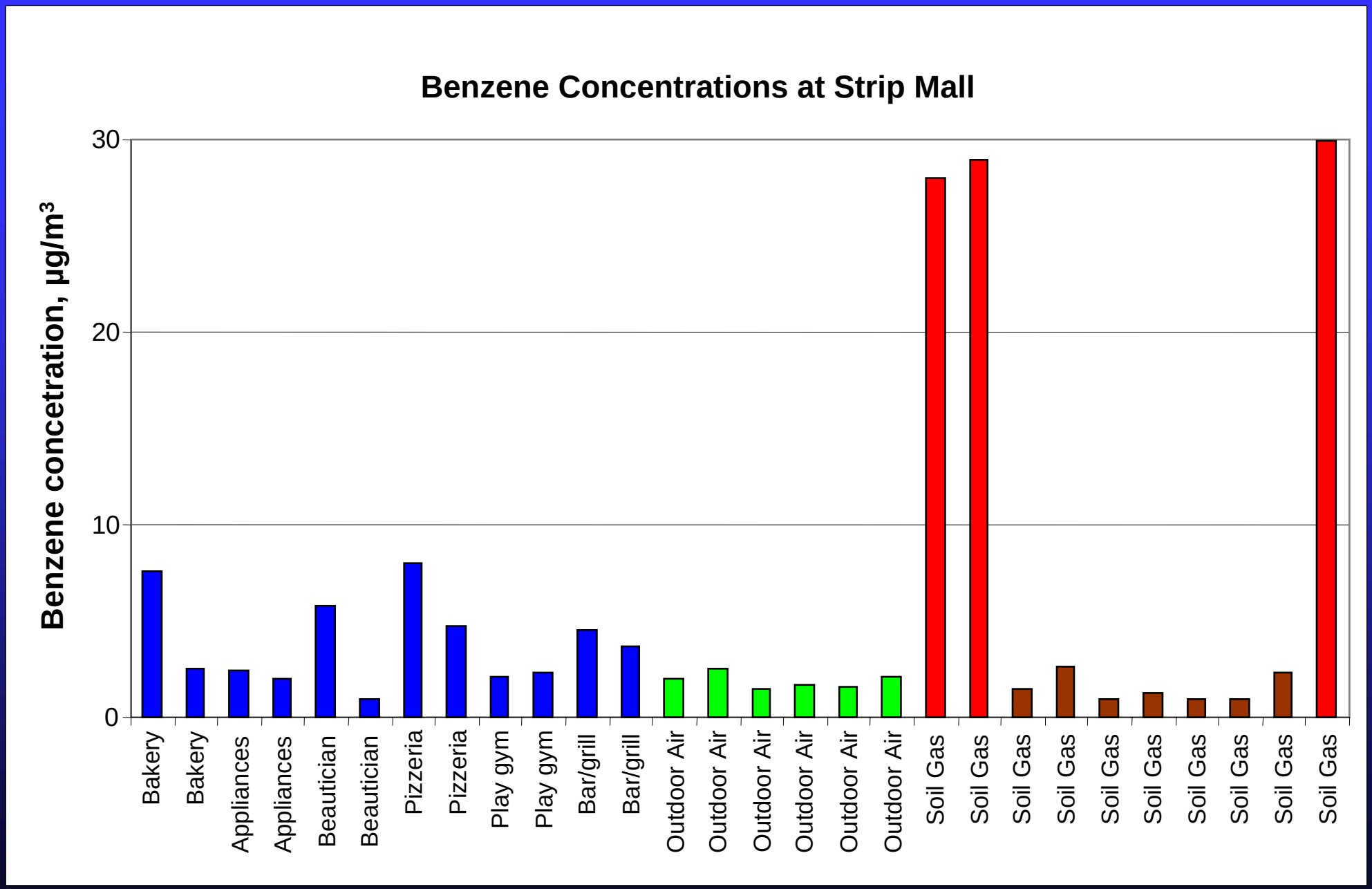
12 indoor air samples

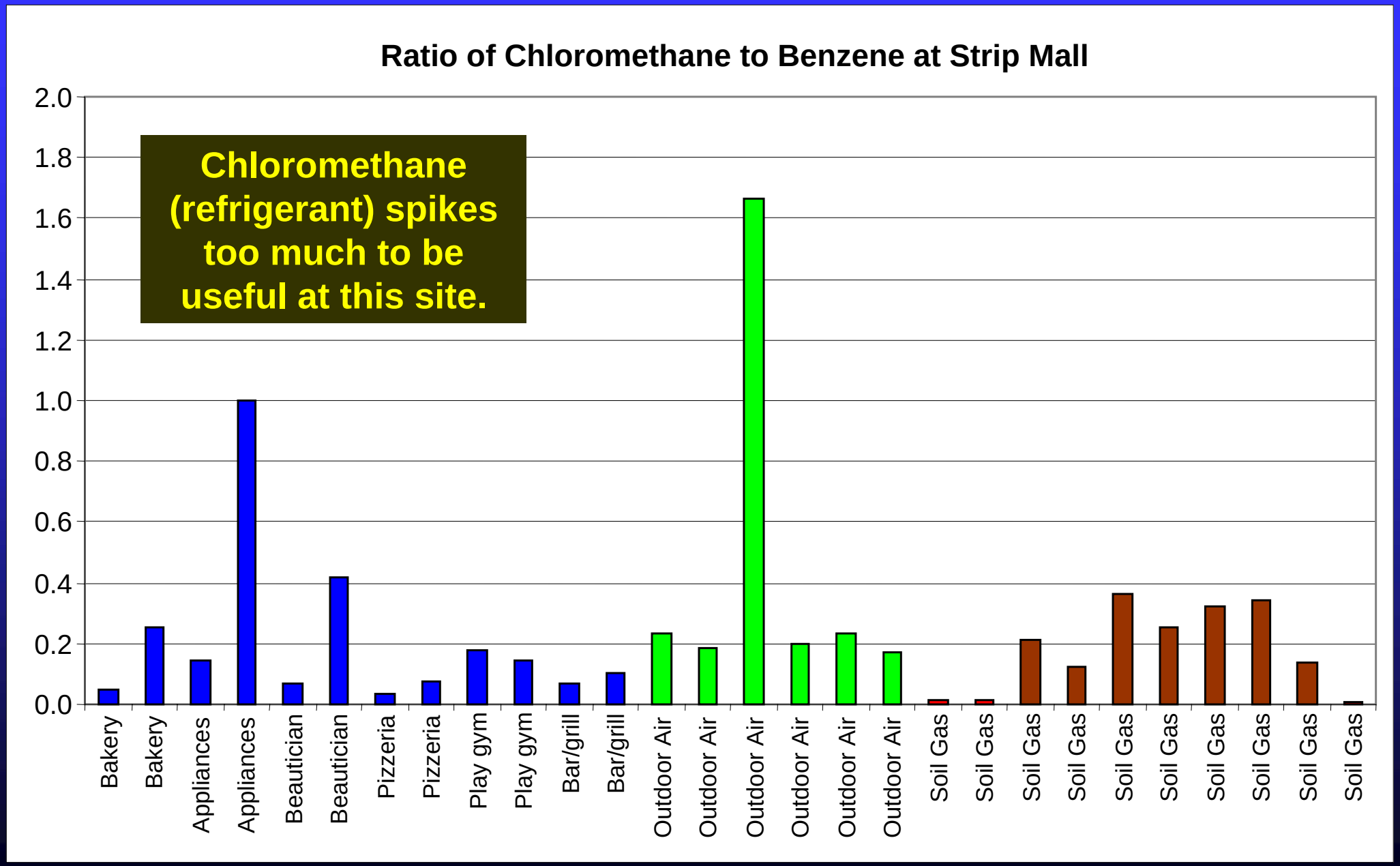
6 outdoor (ambient) air samples

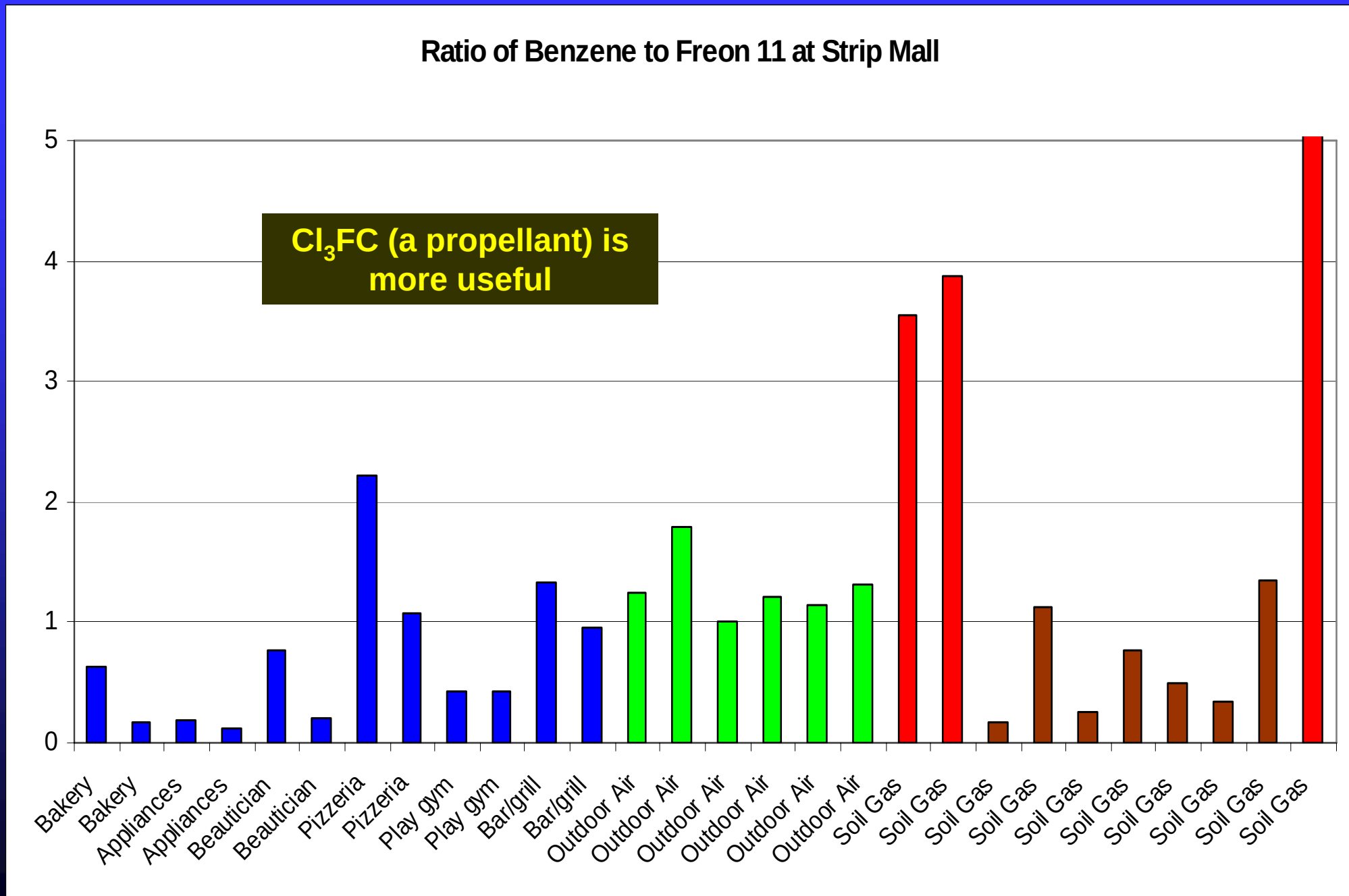
10 soil gas samples

Problem: Chemical "soup" is more complicated (Bakery, bar/grill, appliances, beautician, etc.)

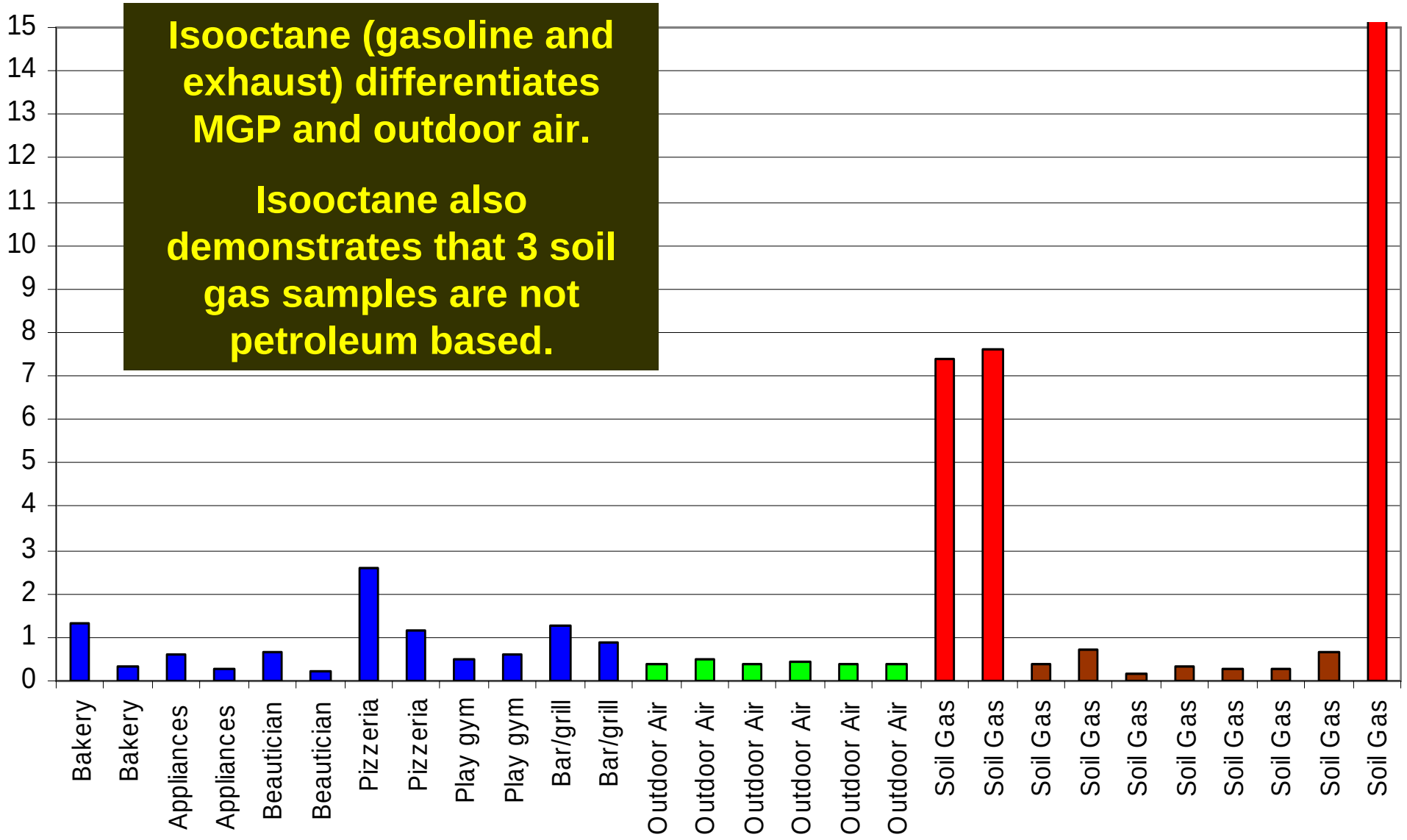
Advantage: Locations of MGP sources are known

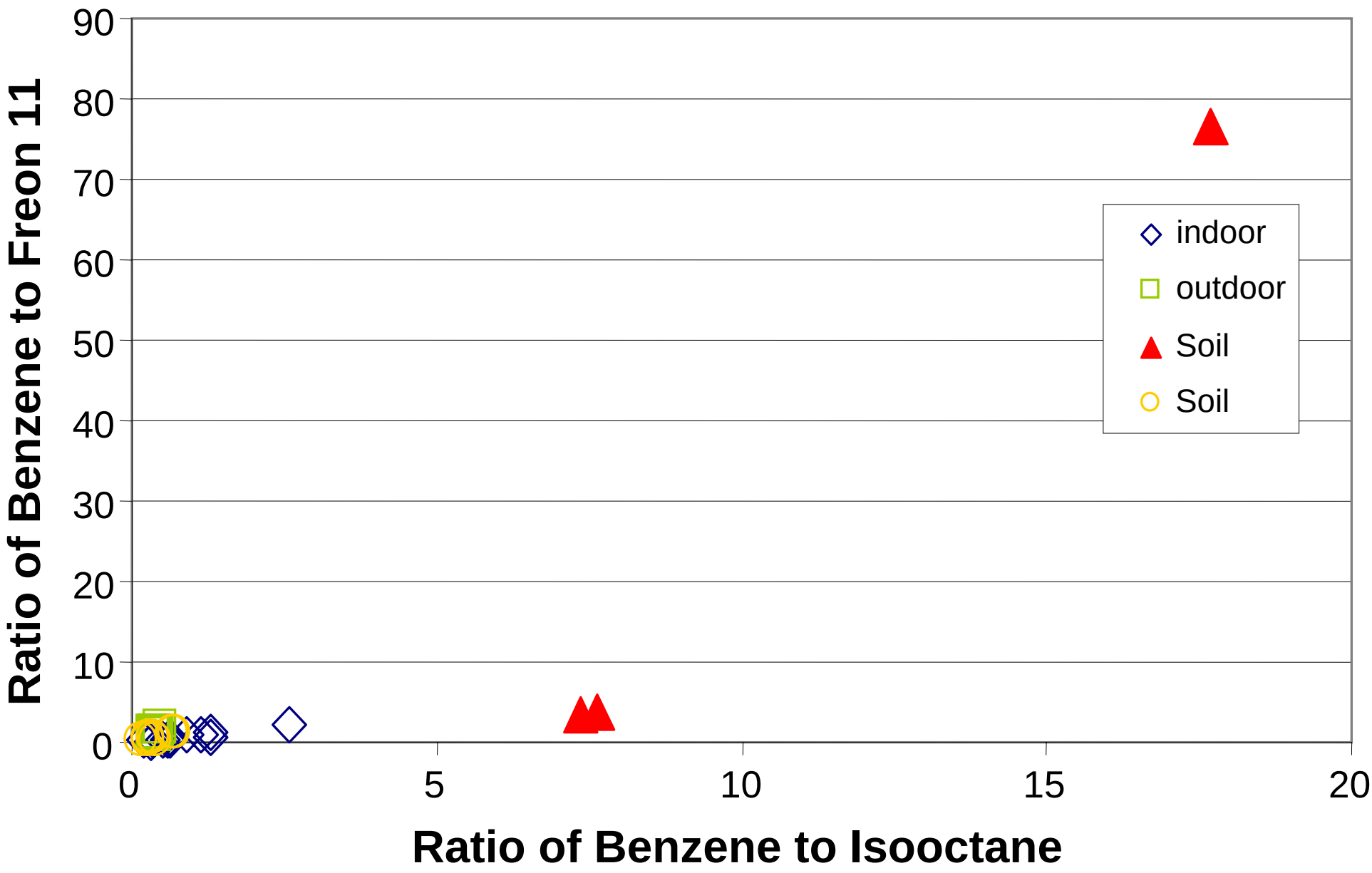

Benzene Concentrations at Strip Mall
Benzene concetration, µg/m³
30
20
10
0
Bakery
Bakery
Appliances
Appliances
Beautician
Beautician
Pizzeria
Pizzeria
Play gym
Play gym
Bar/grill
Bar/grill
Outdoor Air
Outdoor Air
Outdoor Air
Outdoor Air
Outdoor Air
Outdoor Air
Soil Gas
Soil Gas
Soil Gas
Soil Gas
Soil Gas
Soil Gas
Soil Gas
Soil Gas
Soil Gas
Soil Gas

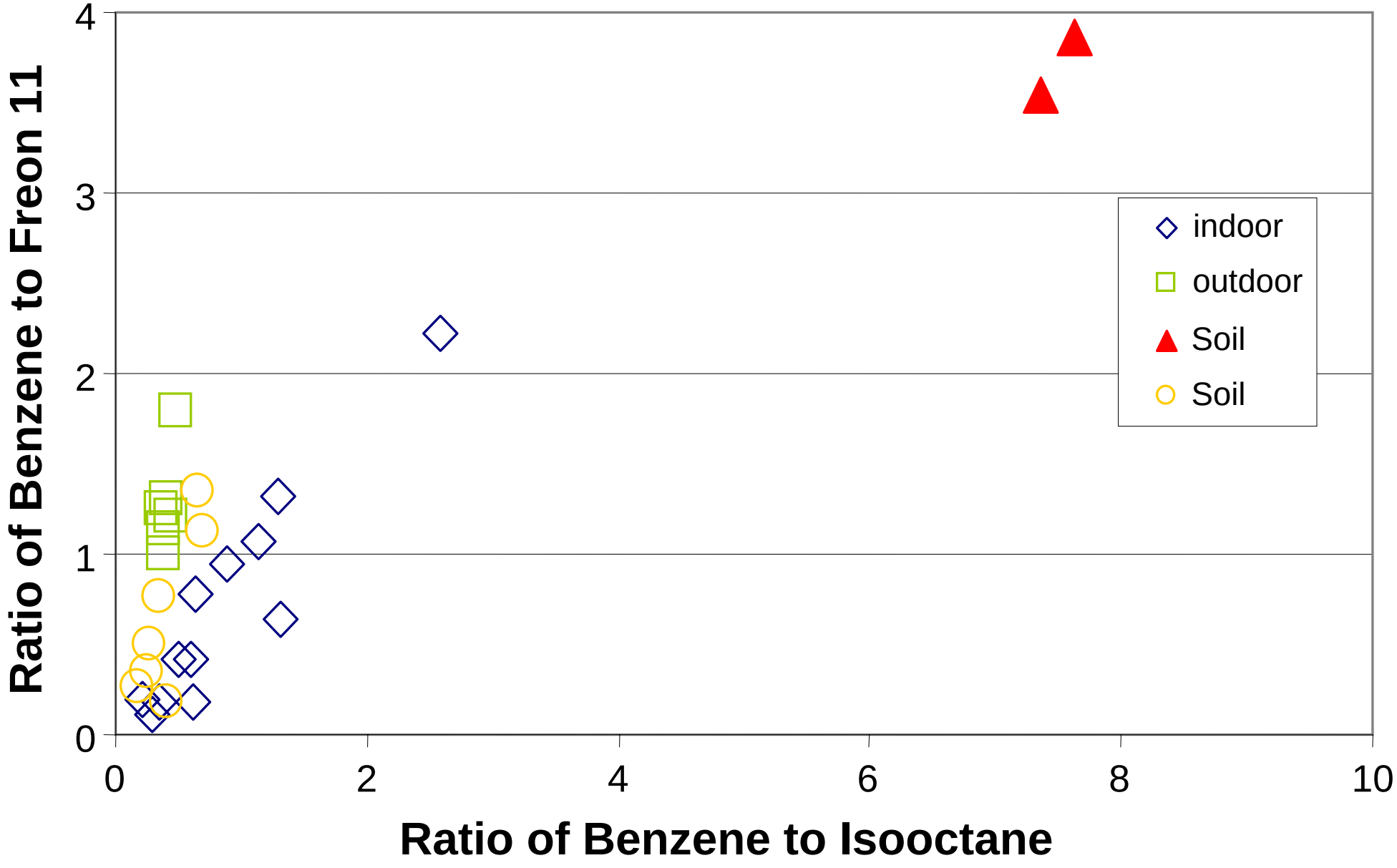

Ratio of Chloromethane to Benzene at Strip Mall
Chloromethane (refrigerant) spikes too much to be useful at this site.
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
Bakery
Bakery
Appliances
Appliances
Beautician
Beautician
Pizzeria
Pizzeria
Play gym
Play gym
Bar/grill
Bar/grill
Outdoor Air
Outdoor Air
Outdoor Air
Outdoor Air
Outdoor Air
Outdoor Air
Soil Gas
Soil Gas
Soil Gas
Soil Gas
Soil Gas
Soil Gas
Soil Gas
Soil Gas
Soil Gas
Soil Gas

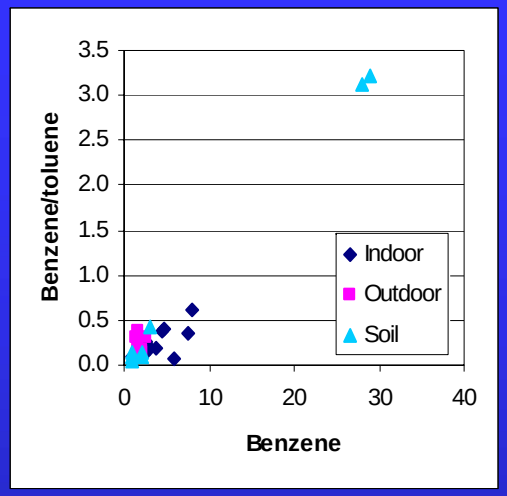

Ratio of Benzene to Freon 11 at Strip Mall
Cl_3FC (a propellant) is more useful
5
4
3
2
1
0
Bakery
Bakery
Appliances
Appliances
Beautician
Beautician
Pizzeria
Pizzeria
Play gym
Play gym
Bar/grill
Bar/grill
Outdoor Air
Outdoor Air
Outdoor Air
Outdoor Air
Outdoor Air
Outdoor Air
Soil Gas
Soil Gas
Soil Gas
Soil Gas
Soil Gas
Soil Gas
Soil Gas
Soil Gas
Soil Gas
Soil Gas

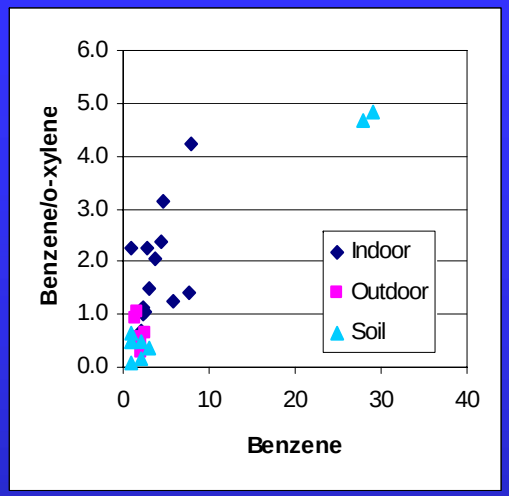
Ratio of Benzene to Isooctane at Strip Mall

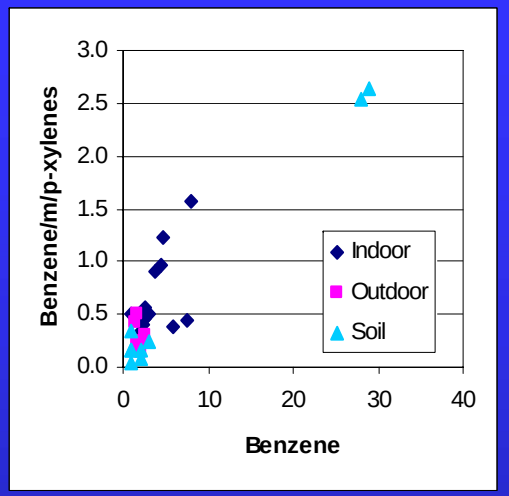


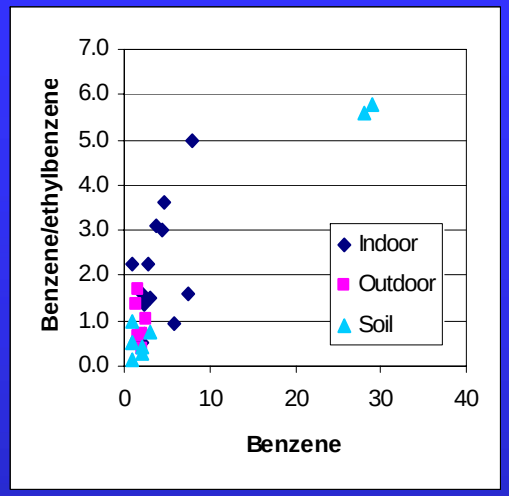

Ratio of Benzene to Freon 11
90
80
70
60
50
40
30
20
10
0
0
5
10
15
20
Ratio of Benzene to Isooctane
indoor
outdoor
Soil
Soil

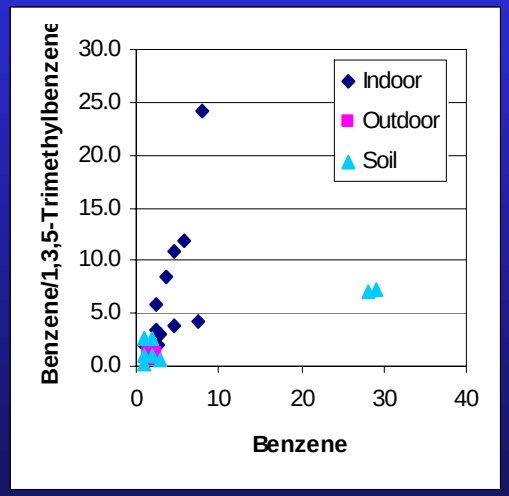

Ratio of Benzene to Freon 11
Ratio of Benzene to Isooctane
0
1
2
3
4
0
2
4
6
8
10
indoor
outdoor
Soil
Soil

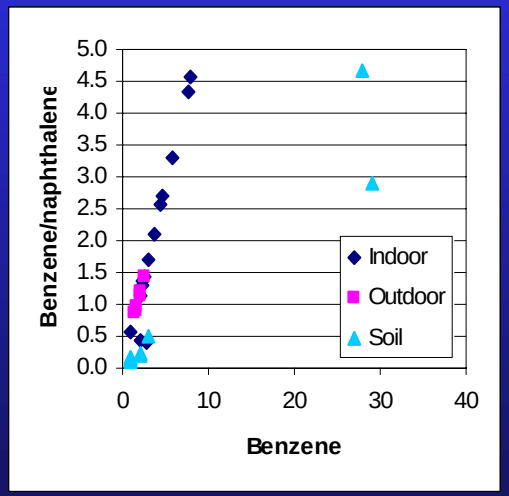


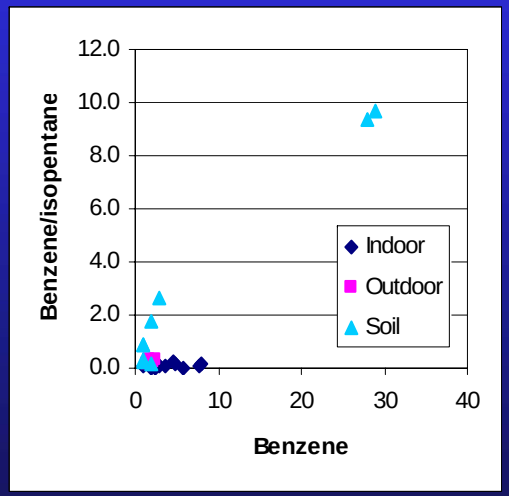


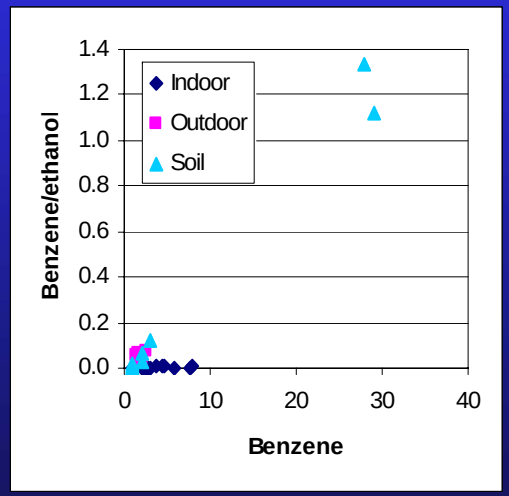




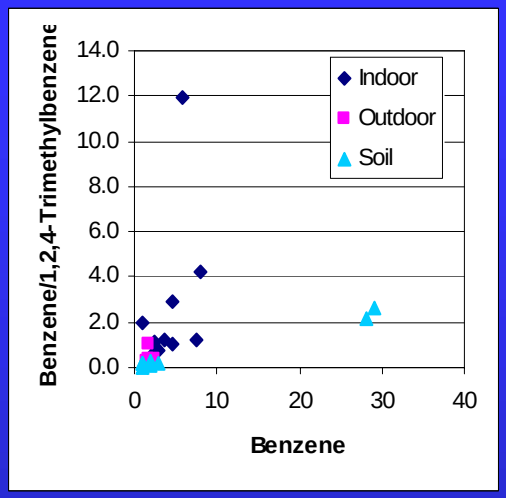


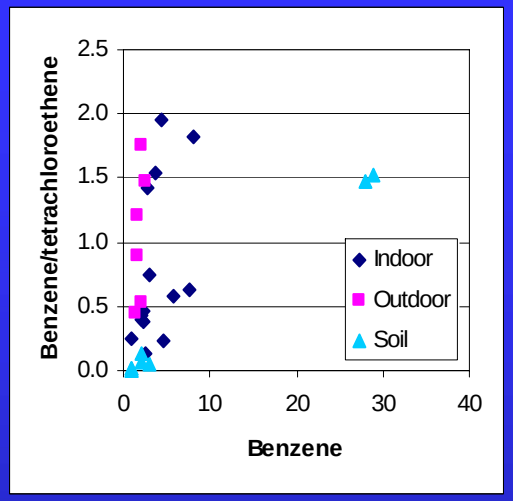


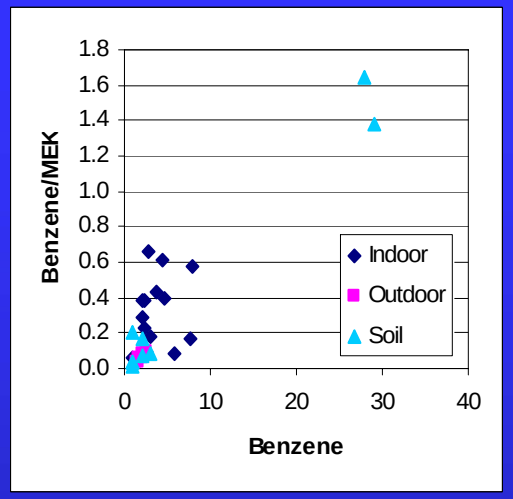


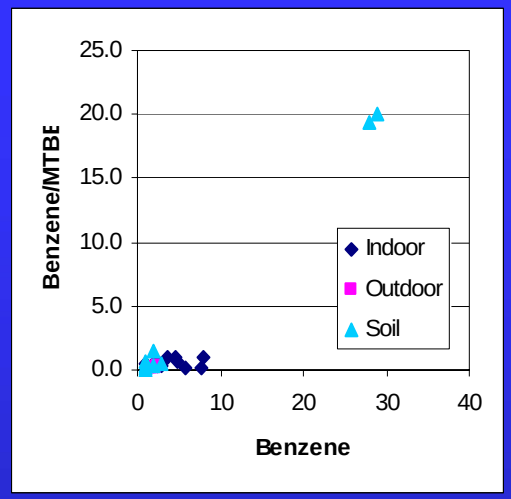


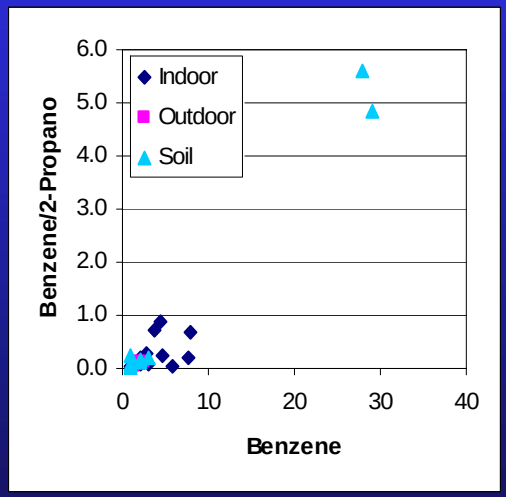
Several compounds appear capable of distinguishing sources (Strip Mall site) when detection limits are low enough (Page 1).

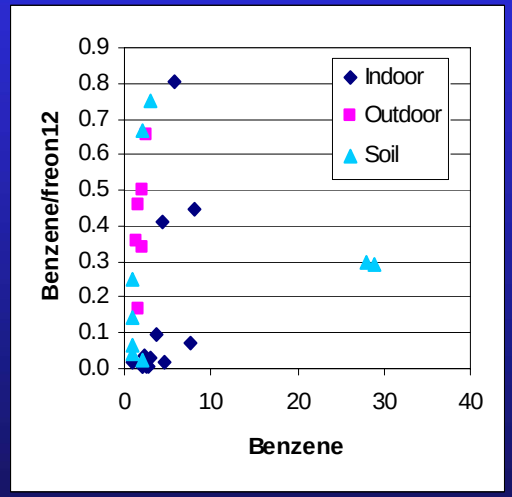


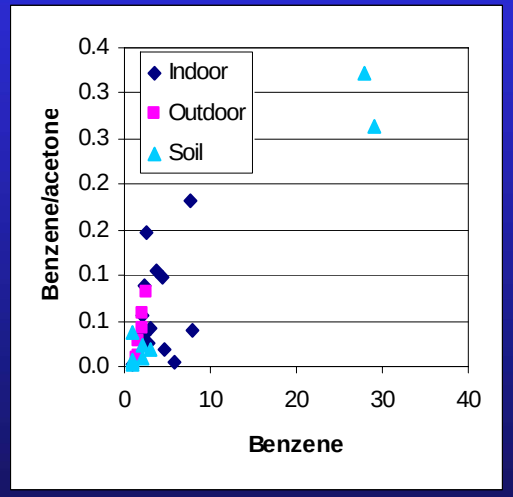


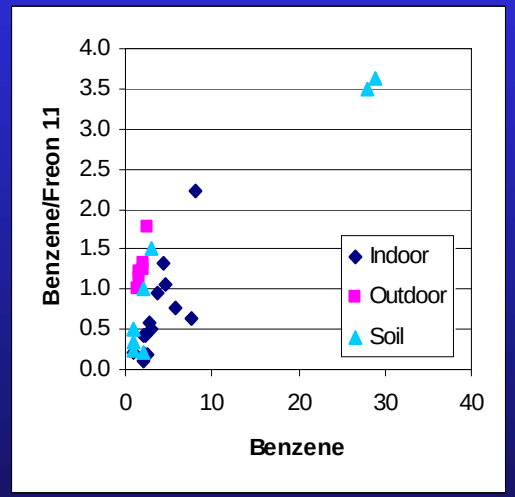










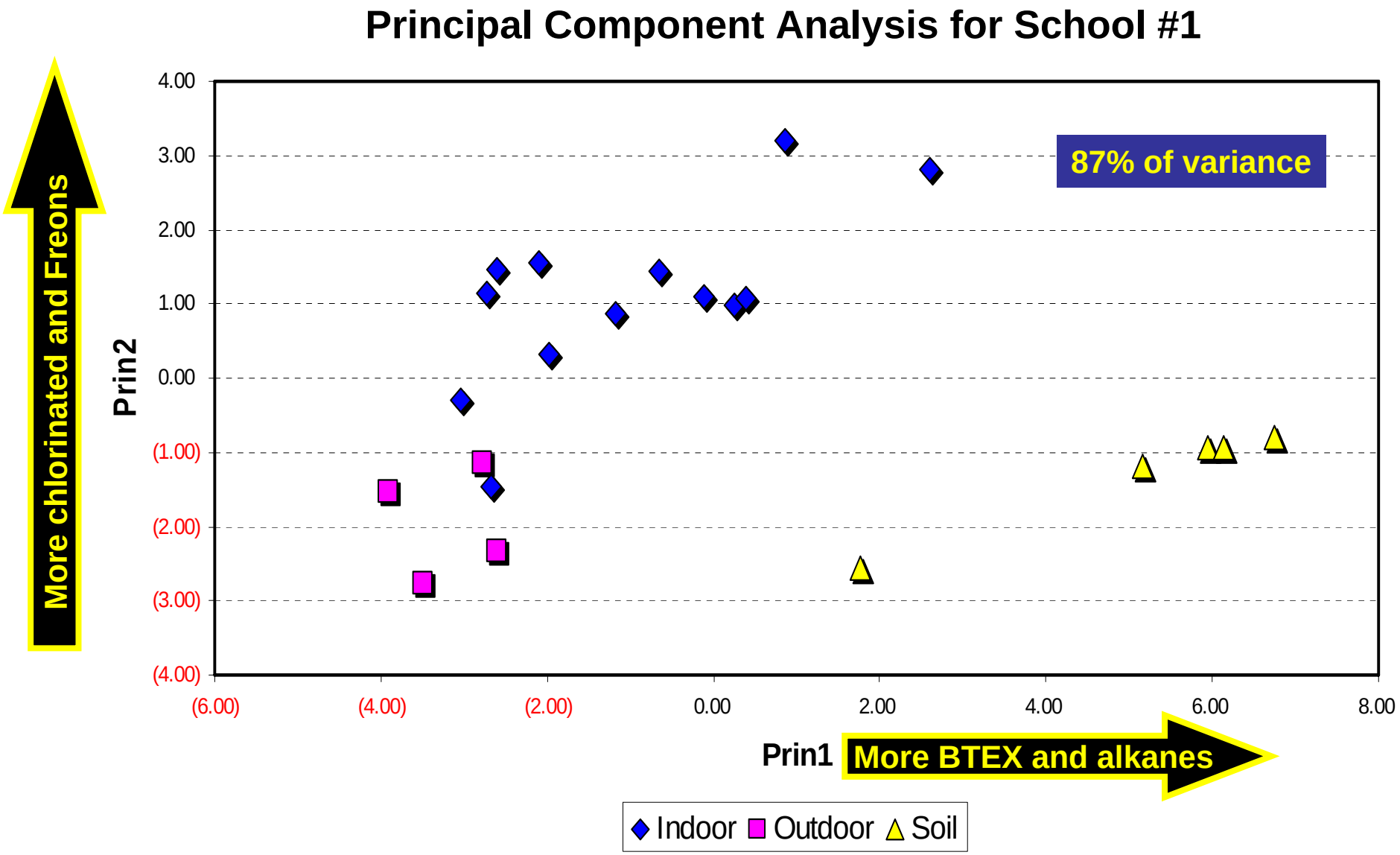


Several compounds appear capable of distinguishing sources (Strip Mall site) when detection limits are low enough (Page 2).

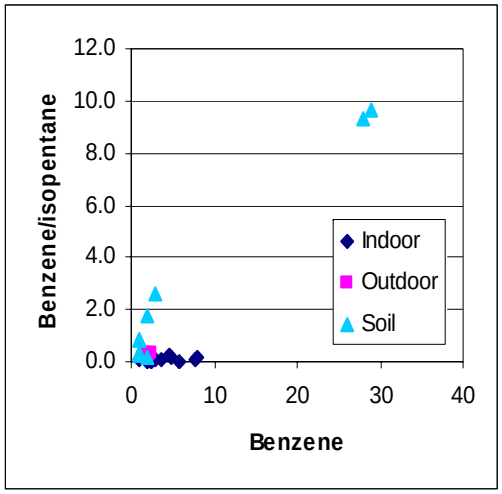
- Principal components analysis (PCA):
  - Makes no assumptions about sample classification
  - Explains the total variation in the variables for all air samples
  - Finds linear combinations of all variables to produce each principal component
    - Prin1 = (0.39*Toluene) + (0.43*o-Xylene) + … + (0.14*Freon12)

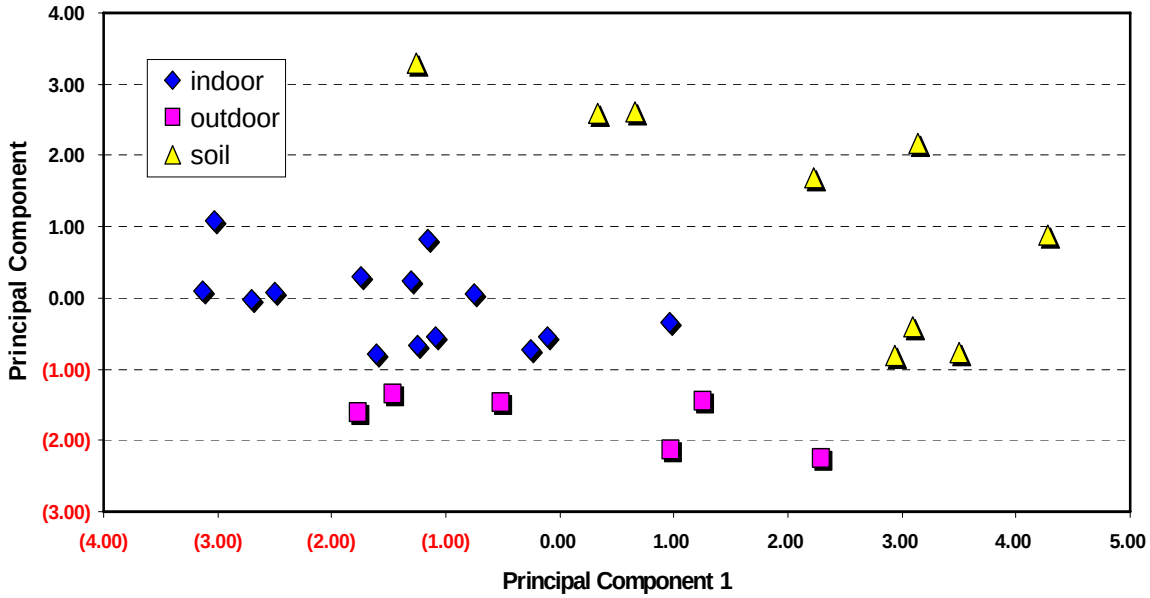
- Canonical discriminant analysis (CanDisc):
  - Classifies sample groups as indoor, outdoor or soil gas
  - Finds linear combinations of all variables to maximize separation between groups
  - Provides quantitative measures of which “shotgun patterns” are most closely related.
    - Can1 = (0.84*Toluene) + (0.92*o-Xylene) + … + (0.29*Freon12)

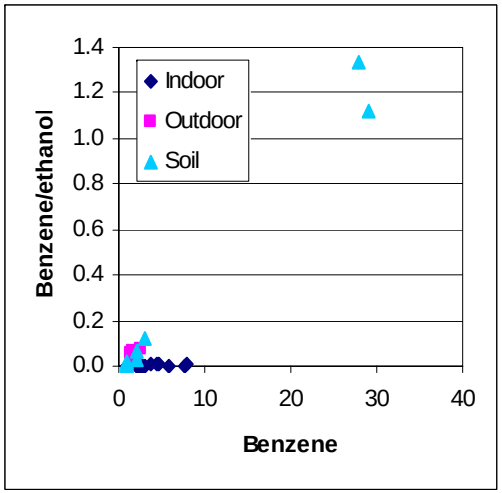
- Principal components analysis (PCA):
  - PCA tries to group sites (regardless of source) based on similarities in chemistry compound distribution
- Canonical discriminant analysis (CanDisc):
  - Tries to separate the “shotgun blasts” from indoor air, outdoor air, and soil gas using combinations of the chemistry data.

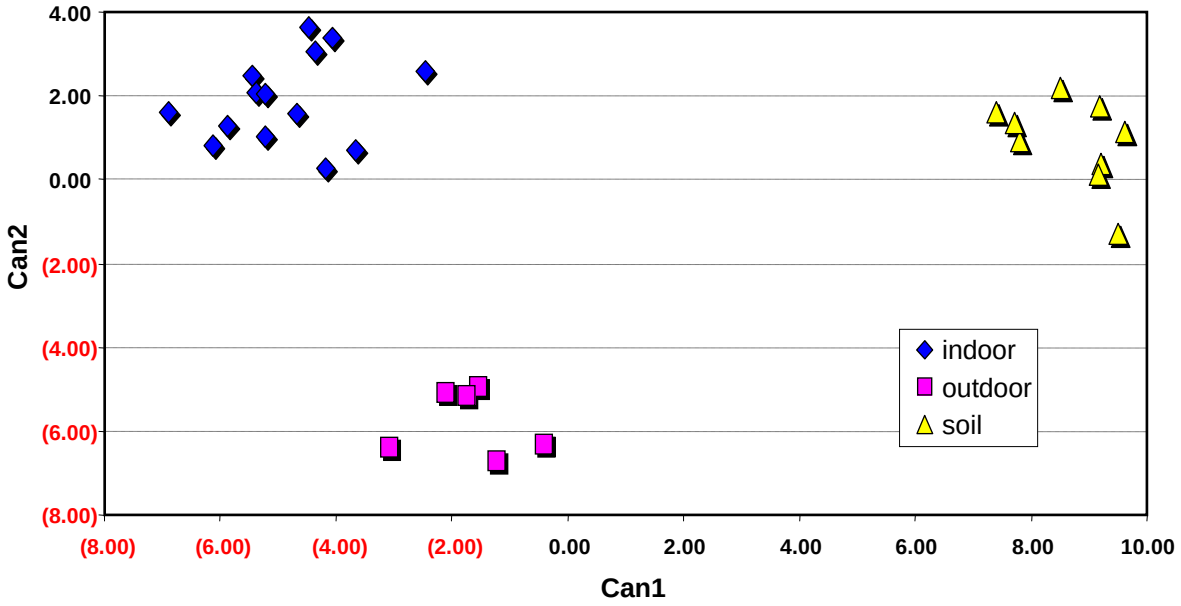

Principal Component Analysis for School #1
More chlorinated and Freons
Prin2
4.00
3.00
2.00
1.00
0.00
(1.00)
(2.00)
(3.00)
(4.00)
87% of variance
(6.00)
(4.00)
(2.00)
0.00
2.00
4.00
6.00
8.00
Prin1
More BTEX and alkanes
Indoor
Outdoor
Soil

Strip Mall

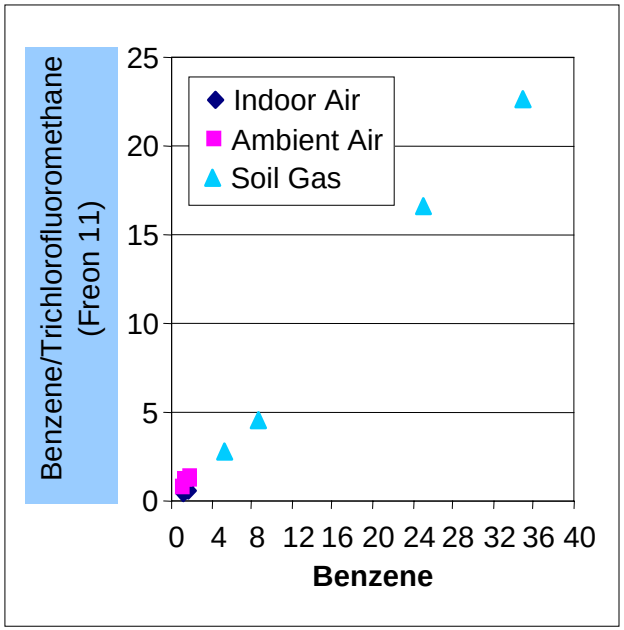

Benzene/isopentane
12.0
10.0
8.0
6.0
4.0
2.0
0.0
0
10
20
30
40
Benzene
Indoor
Outdoor
Soil

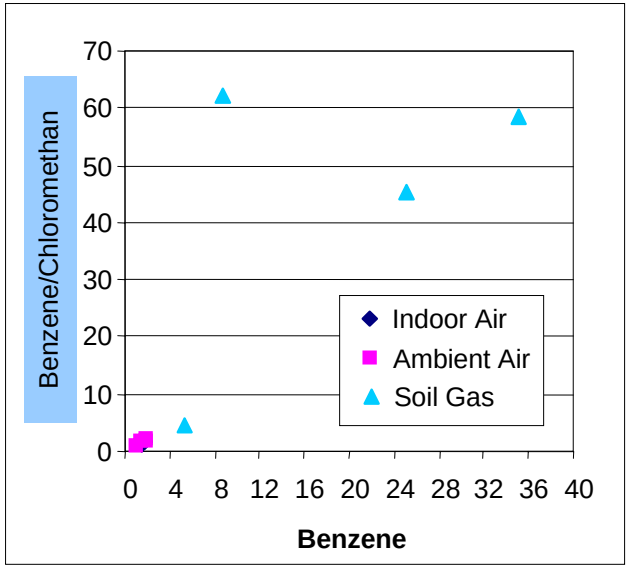

Principal Component
4.00
3.00
2.00
1.00
0.00
(1.00)
(2.00)
(3.00)
(4.00)
(3.00)
(2.00)
(1.00)
0.00
1.00
2.00
3.00
4.00
5.00
Principal Component 1
indoor
outdoor
soil

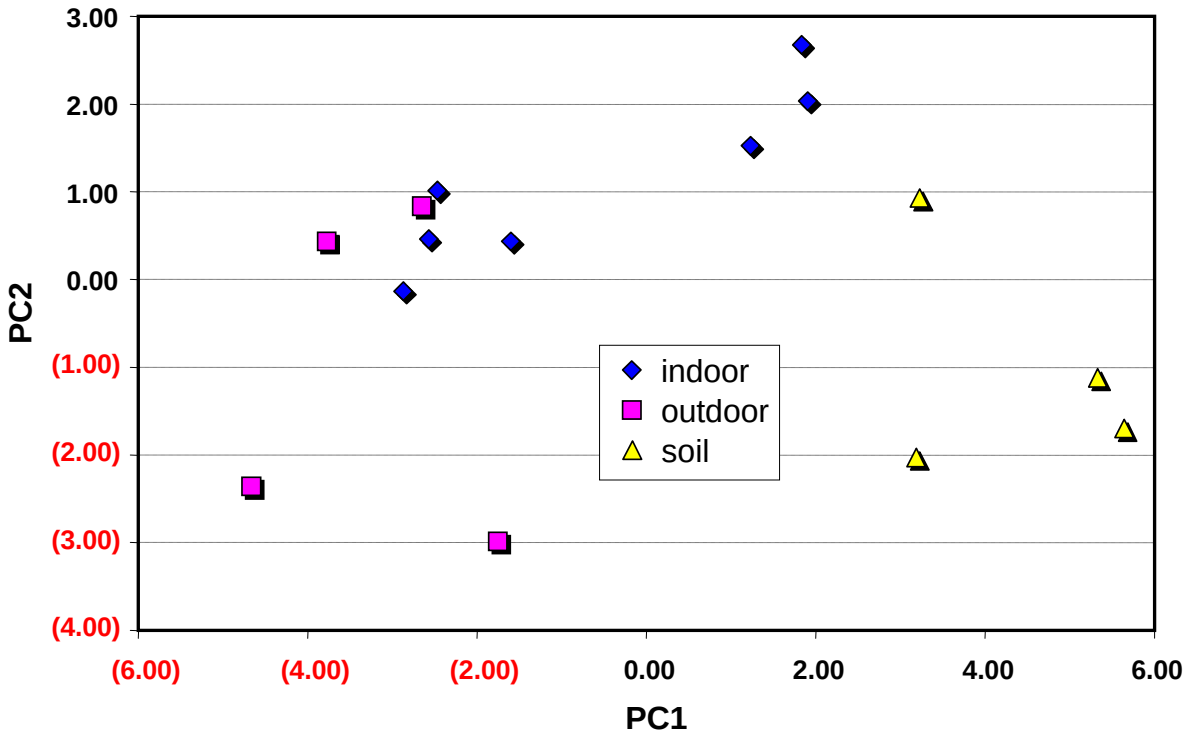

Benzene/ethanol
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
10
20
30
40
Benzene
Indoor
Outdoor
Soil


Can2
4.00
2.00
0.00
(2.00)
(4.00)
(6.00)
(8.00)
(8.00)
(6.00)
(4.00)
(2.00)
0.00
2.00
4.00
6.00
8.00
10.00
Can1
indoor
outdoor
soil

Residential/business street

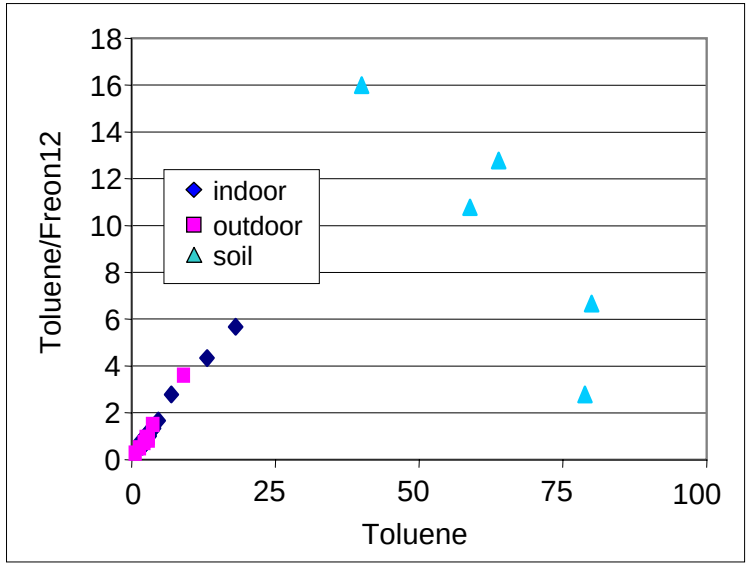


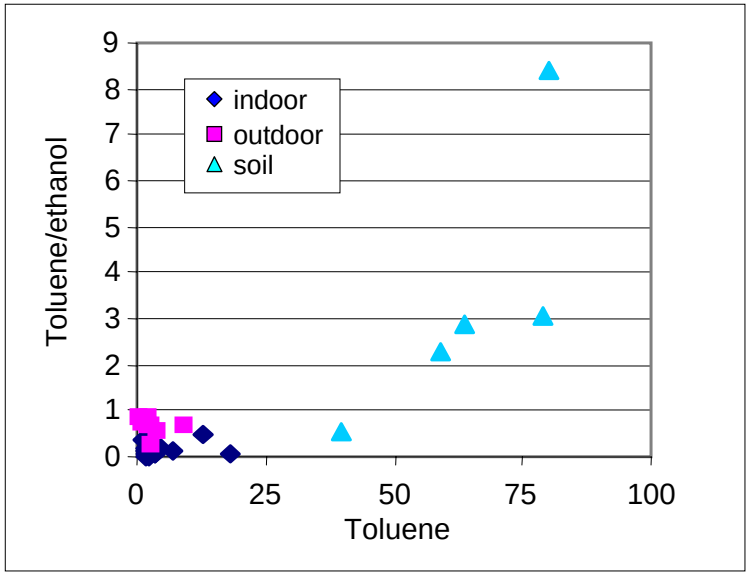


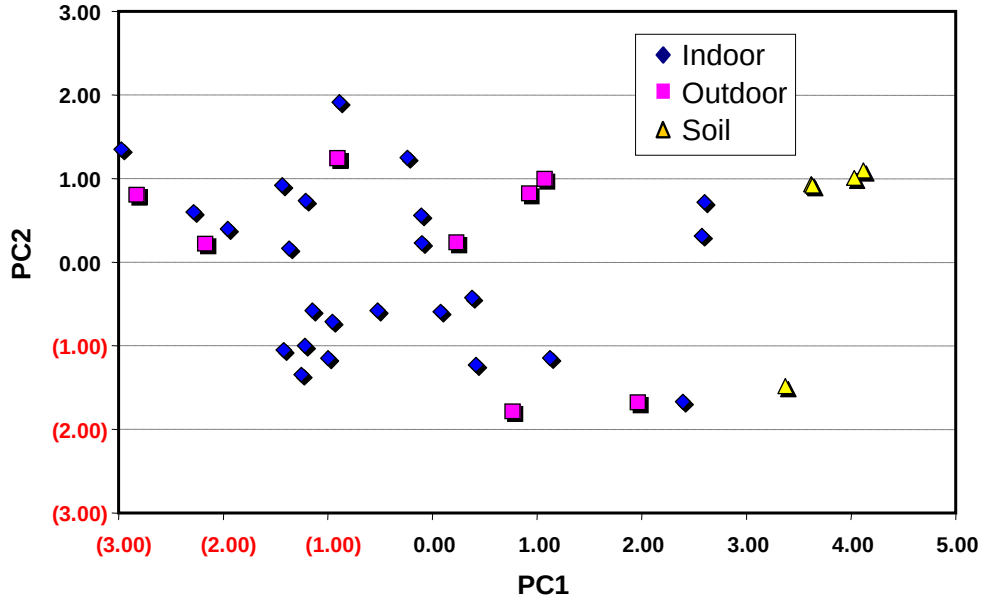


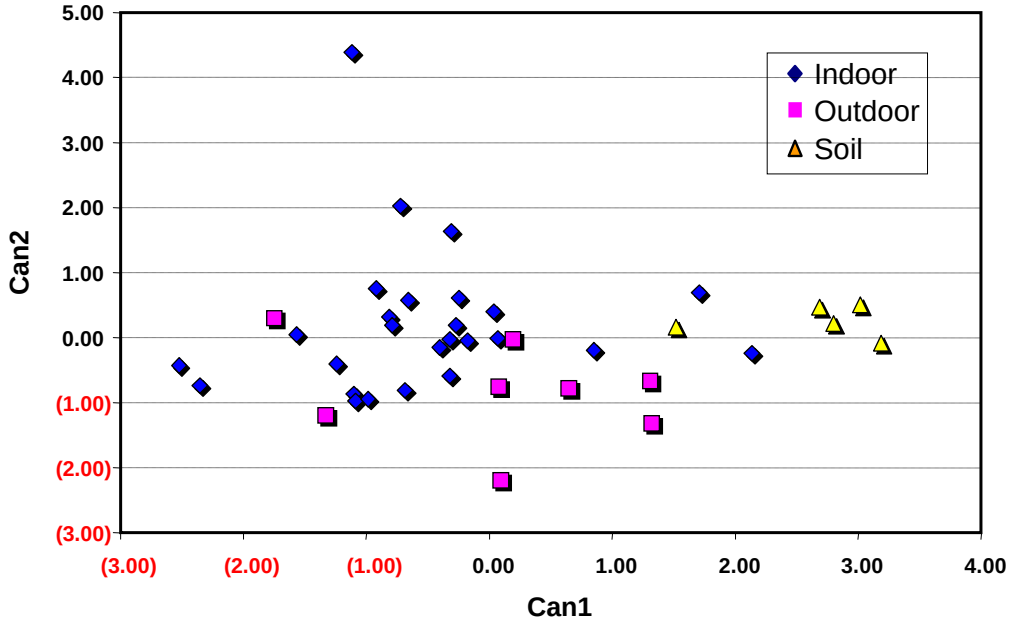
Candisc analysis failed—possibly because of spurious very high toluene and xylenes in the post office and two auto paint shops.

School #2


Toluene/Freon12
Toluene
indoor
outdoor
soil
0
2
4
6
8
10
12
14
16
18
0
25
50
75
100

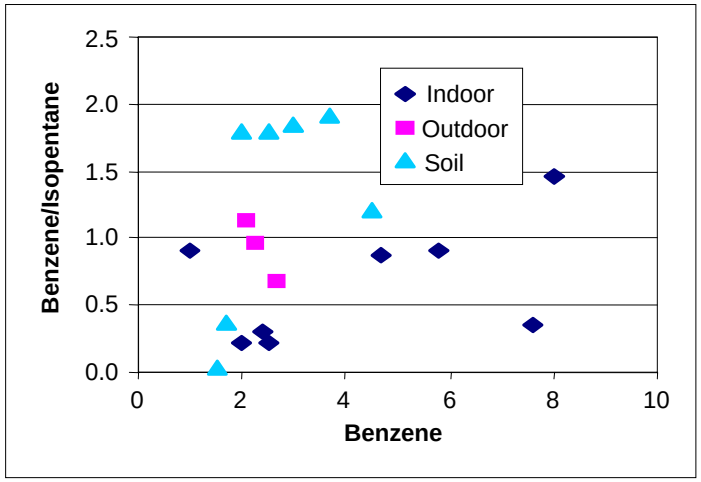

Toluene/ethanol
Toluene
indoor
outdoor
soil
0
1
2
3
4
5
6
7
8
9
0
25
50
75
100

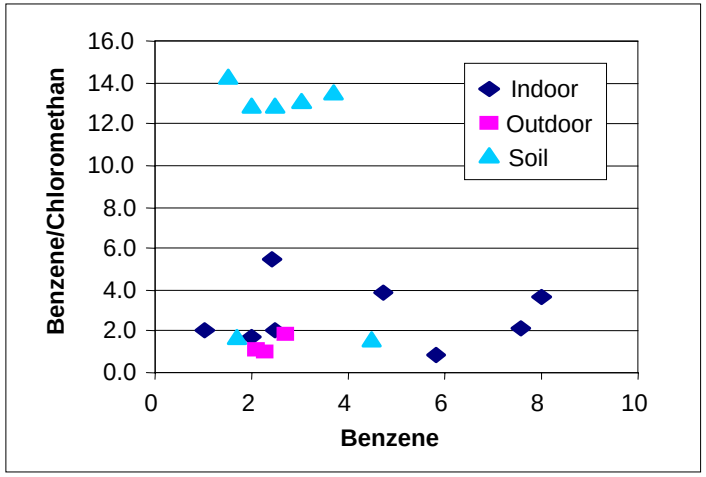

PC2
PC1
Indoor
Outdoor
Soil
3.00
2.00
1.00
0.00
(1.00)
(2.00)
(3.00)
(3.00)
(2.00)
(1.00)
0.00
1.00
2.00
3.00
4.00
5.00

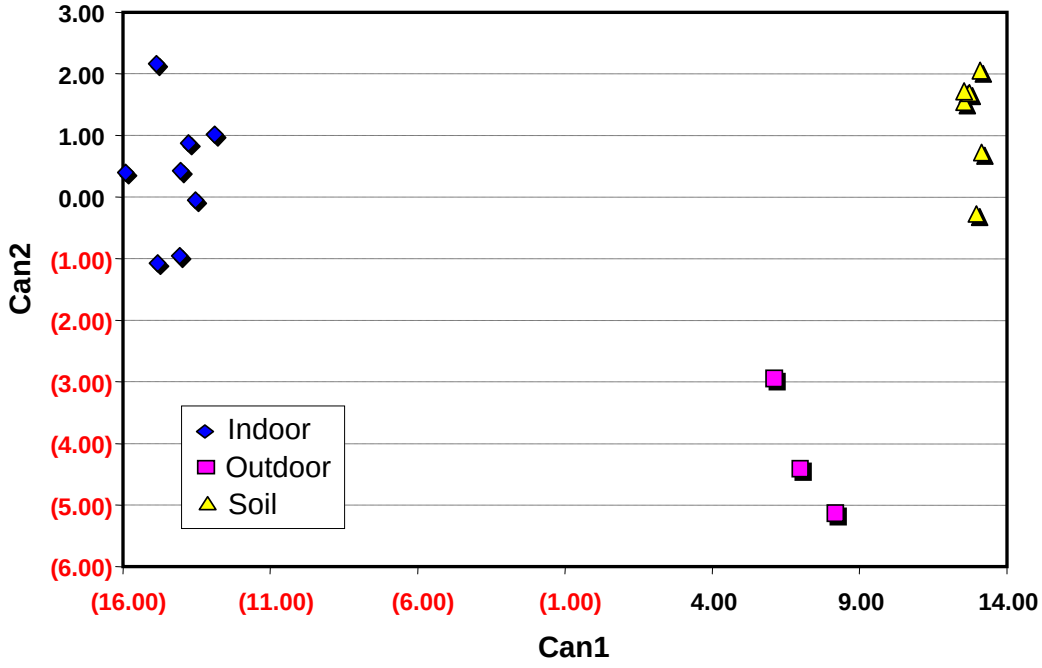

Can2
Can1
Indoor
Outdoor
Soil
5.00
4.00
3.00
2.00
1.00
0.00
(1.00)
(2.00)
(3.00)
(3.00)
(2.00)
(1.00)
0.00
1.00
2.00
3.00
4.00

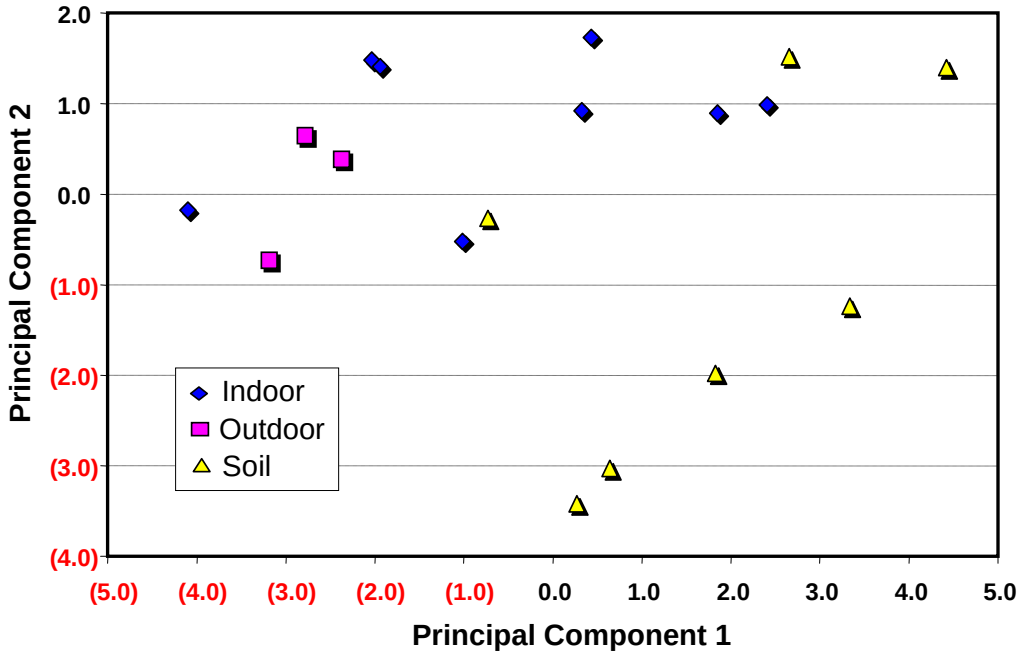
Apartment Complex

(note: some elevated indoor air benzene, but not in soil gas)

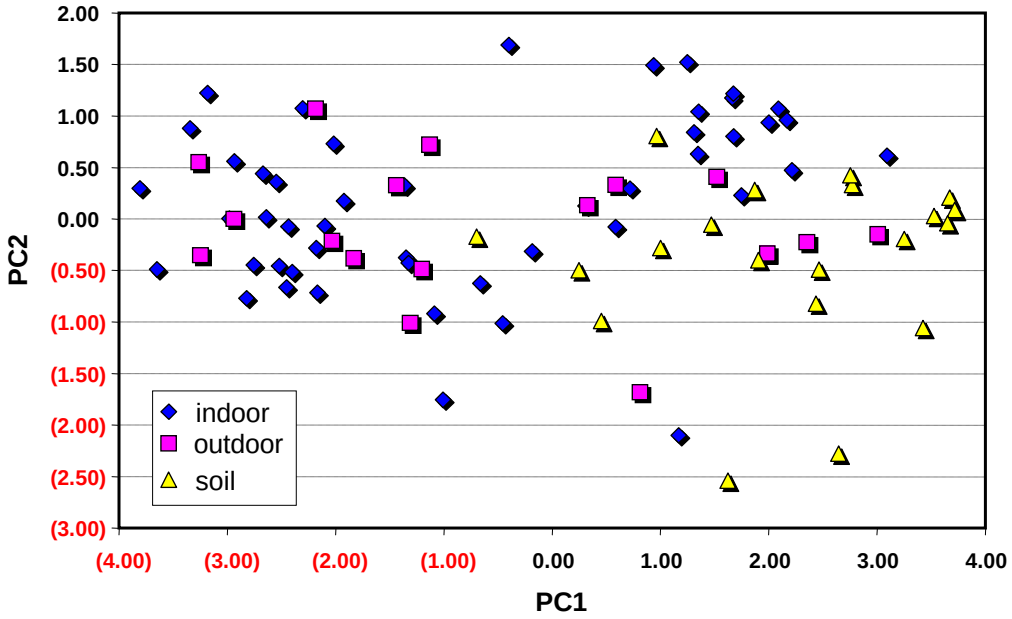


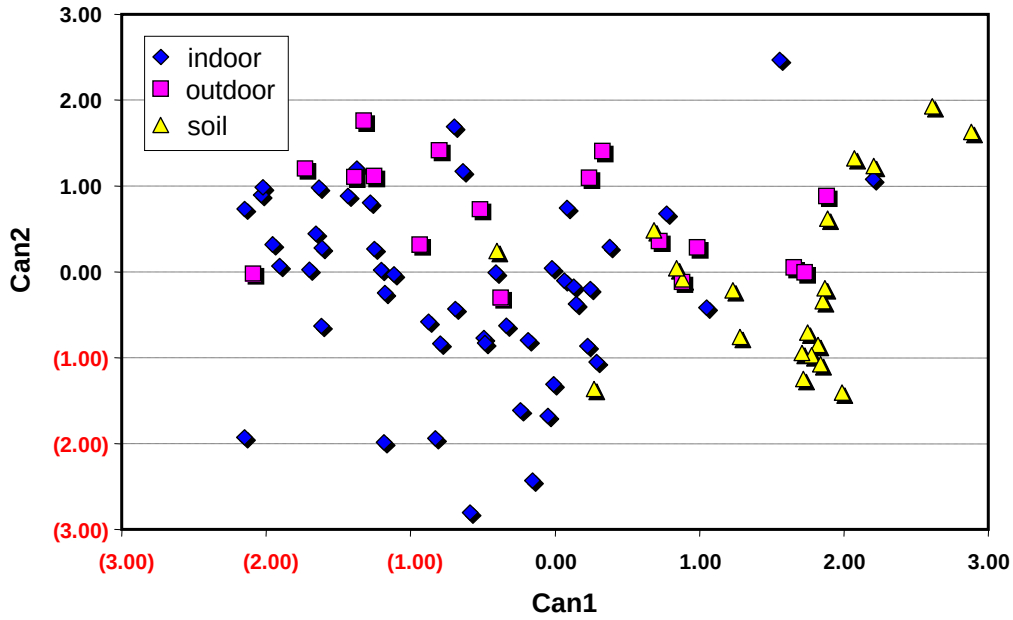






Preliminary data analyses of combined data sets may show potential for a generalized approach for multiple sites.





Tentative Conclusions for 5 sites

(not all data analyses are completed)

Ambient air is the major contributor to indoor air benzene, even when soil is contaminated with benzene. ***Both general chemical knowledge (ratio plots) and "blind" statistical approaches (principal component, and CanDisc analyses) support this conclusion.***

"Universal" pollutants (Cl-organics, Freons, etc.) can be ratioed to benzene to indicate sources of benzene in indoor air.

Shallow (0.5 ft) soil gas generally reflects ambient air.

Removal of MGP materials is unlikely to reduce indoor benzene levels (for these five sites).

Problems/Challenges

Non-detects limit the use of many possible tracers (especially when the soil gas samples are much smaller than air samples).

Many potential tracers have spurious sources (e.g., chloromethane was good at several sites, but not at the strip mall). Thus, different sites may require different tracers.

Recommendations

Always collect outdoor air along with indoor air and soil gas.

Try to keep all sample volumes large (for low detection limits) and the *same* for all sites.