VOC Measurement Considerations in Developing Exposure Databases

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UMDNJ University of Medicine & Dentistry of New Jersey

Why & Where Have VOCs been Measured in the Air

- Industrial settings to protect workers
- Ambient air
  - Evaluate HAPs
  - Meet state requirements
  - PAMs network ozone reduction
- Indoor & Personal Air
  - Research projects
  - Evaluate complaints
- Estimate cancer and non-cancer risk

Consideration in Study Design

- Decision criteria
  - Sample duration
    - Continuous/Integrated
  - Sensitivity needed
  - Target compounds
  - Size and power requirements
  - Numbers of samples and Cost
- Data set use
  - Representative
  - Population based or convenience sample

Selection of Methods Compound Considerations

- Single compound
  - Continuous Monitor
  - Portable Sensor
  - Spectrometric Techniques
  - Integrated Sample
- Multiple compounds
  - Collection Media (integrated sample)
    - Compatibility Across Compound Group
  - Analysis Methodology
  - Continuous or “Real Time” Instruments

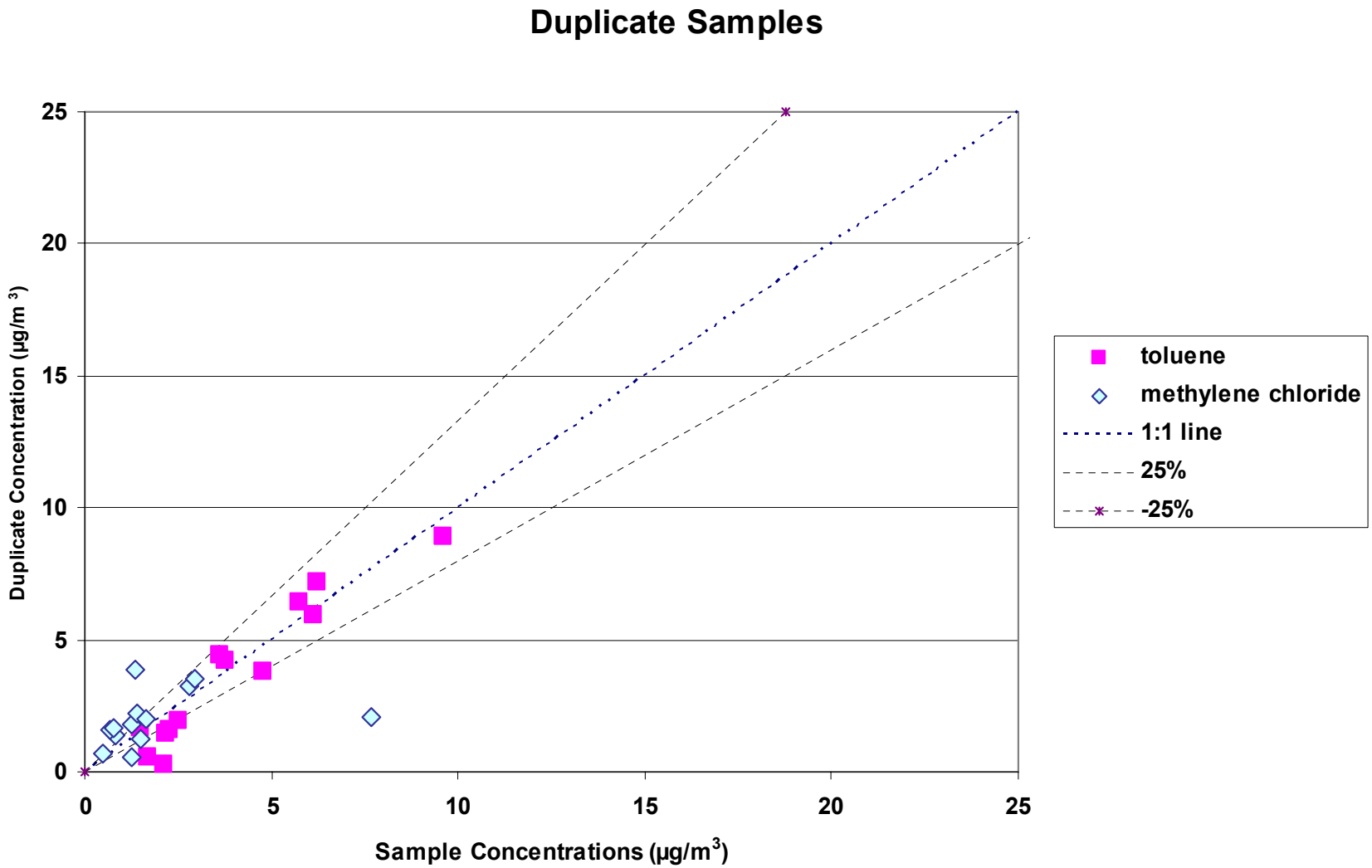
Current Data Approaches

- **Multi-compound Studies**
  - **12/24/48hr integrated samples**
  - **Non-polar VOC**
  - **Polar VOC (carbonyls)**
  - **Canisters – possible wide range of cmpds**
  - **Subsequent analyses by gas chromatography or liquid chromatography**
- **Semi-automated Gas Chromatogram**
  - **1 hr grab or integrated sample**

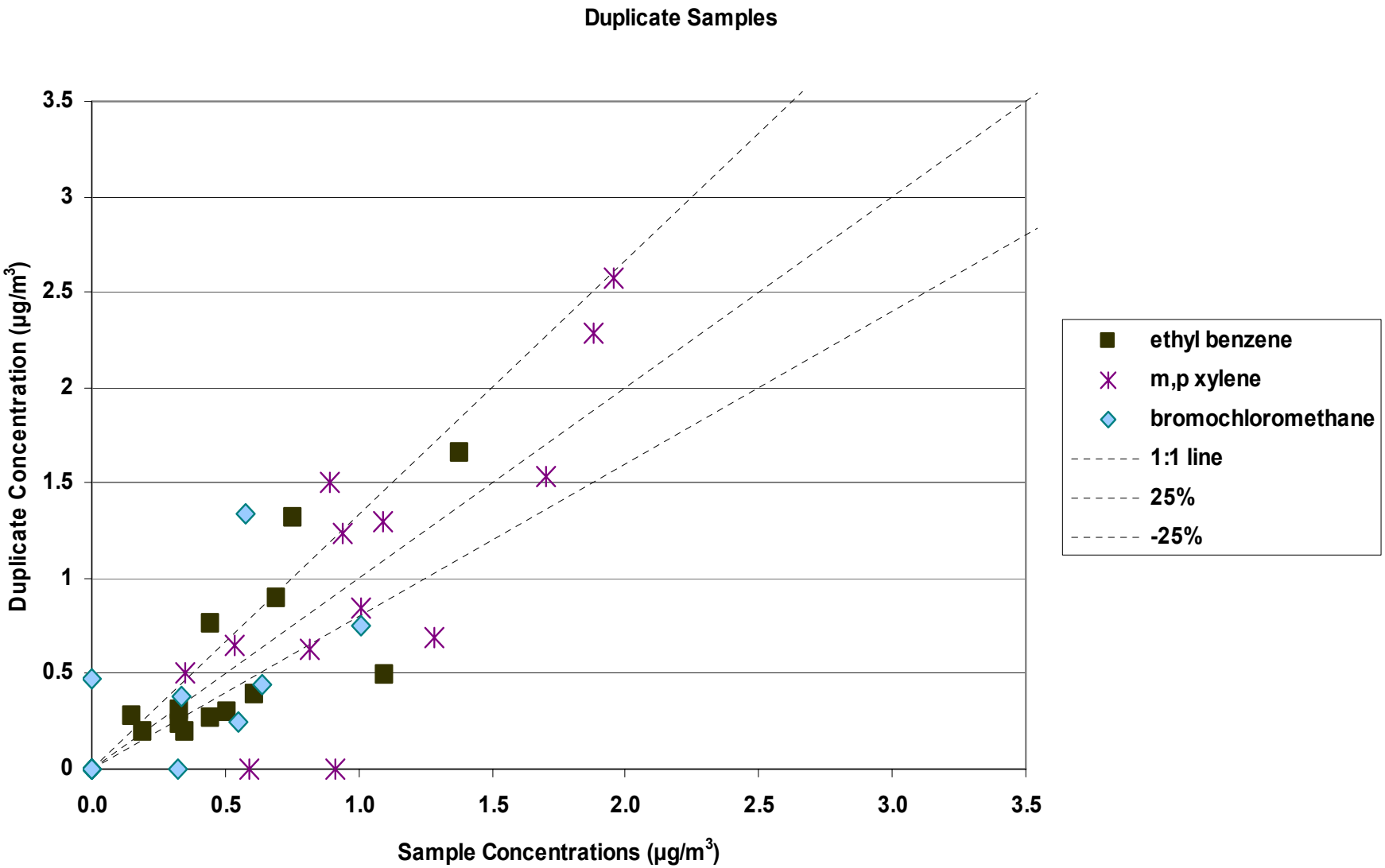
Uncertainty in Measurements

- **Two components**
  - **Estimate of air volume**
    - **±5 to 10% for accuracy, precision better**
  - **Analytical measurement**
    - **±5 to 20% for precision**
    - **±10 to 30% for accuracy**
    - **These are dependent upon concentration, higher near MDL**
- **Therefore: a better comparison exists between microenvironments within single study than across studies**

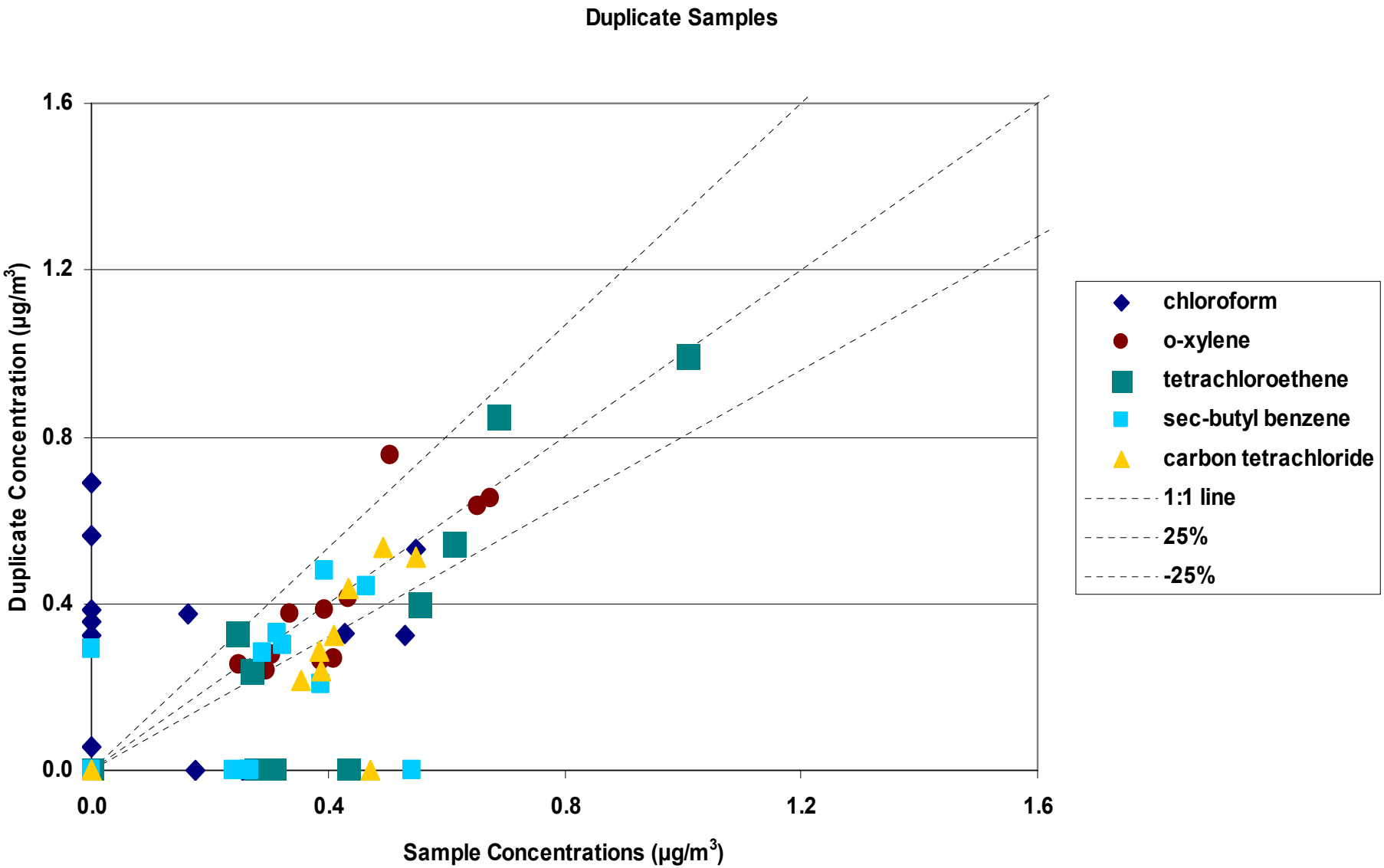
DUPLICATES – HIGH CONC



DUPLICATES – MEDIUM CONC



DUPLICATES – LOW CONC



RIOPA STUDY HYPOTHESES

At residences immediately adjacent to outdoor sources a measurable & significant portion of the average air toxic exposures will be attributable to ambient sources

HYPOTHESES (cont.)

Residential air exchange rates and ambient air measurements can predict the contribution from ambient sources to indoor air & personal exposure

PREMISE

- **A large percentage of time is spent indoors, but ambient emissions penetrate indoor & can exceed indoor sources. To quantify the ambient influence on exposure, homes in proximity to ambient sources need to be oversampled.**

STUDY DESIGN

- **Sample 100 homes twice, 3 months apart in each of three urban centers: Elizabeth, NJ; Houston, TX; Los Angeles, CA**
- **Target air toxics: VOCs, Aldehydes, $PM_{2.5}$ for mass, metals & PAHs**
- **Personal, Indoor & Outdoor Air Sample Collected over 48 hours**

STUDY DESIGN (continued)

- Personal Samples from:
  - Adults who stay primarily at home
  - Children
- Air Exchange Measurements
- In-vehicle samples for aldehydes

- Understand chronic exposures

BASIS FOR SELECTION OF CITIES FOR SAMPLING

Source characteristics considered by site

- **NJ - mixture of point, mobile, area & commercial sources near residences**
- **TX - predominantly industrial point sources**
- **CA -predominantly mobile sources**

The sites have different meteorological & housing stock characteristics

SAMPLING & ANALYSIS PROTOCOLS

- **VOCs - Passive badges solvent extracted with GC/MS analysis**
- **Aldehydes - Active & passive sampling onto DNPH or DNSH cartridges with HPLC/UV/FLOR**
- **Particulate Matter (PM2.5) - Active filters Mass (weighing), Metals (XRF & ICP/MS), PAHs (extraction GC/MS)**
- **Air Exchange using Perfluorocarbon tracer**

TARGET AIR TOXICS

VOCs: benzene, chloroform, ethylbenzene, toluene, *m/p* xylenes, *o* xylene, methylene chloride, carbon tetrachloride, methyl *tert* butyl ether , tetrachloroethylene, 1,4dichlorobenzene, trichloroethylene, 1,3butadiene

Aldehydes: Acetaldehyde, Formaldehyde, Acrolein, Propionaldehyde, Benzaldehyde, Crotonaldehyde, Gloxal, Methylglyoxal

PM2.5: Mass, Organic Carbon, Elemental Carbon, FTIR Characterization, Elements (S, Be, Al, Ti, Cr, Fe, Ni, Zn, As, Rb, Ag, Cd, in, Ba, hg, Tl, Pb, Bi) and PAHs (2 to 5 rings)

QC ASPECTS

- **Duplicate and split samples for VOCs, aldehydes & PAHs by EOHSI and U of T**
- **Blanks/Duplicates (10%), Positive Controls (5%)**
- **Standardized Questionnaires, Sampling Protocols (SOPs), Analysis (SOPs)**

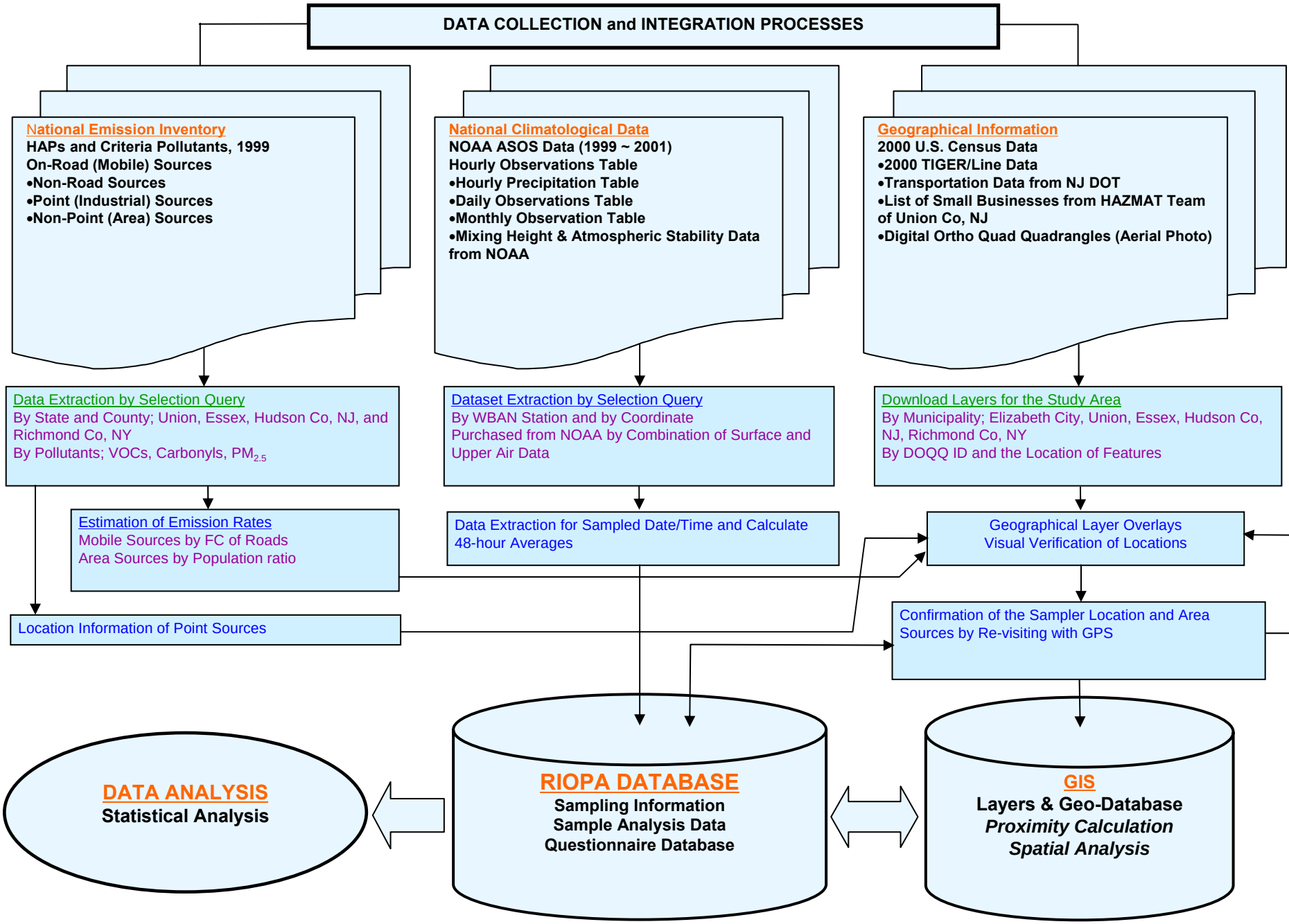
RECRUITMENT EFFORTS

- Emission information from Toxic Release Inventory & traffic density
- Population density & characteristics from Geographic Information Services
- Selection of target homes within several blocks of sources

VISIT PROTOCOLS

Eligibility - non-smokers, at home >14hr/day

- **I - Explain study, obtain consent, characteristics questionnaire, place AER sources**
- **II - Place samples, demonstration of personal sampling & leave activity questionnaires, give instructions**
- **III - Retrieve samples, review activity questionnaires, breath sample**


DATA COLLECTION and INTEGRATION PROCESSES
National Emission Inventory
HAPs and Criteria Pollutants, 1999
On-Road (Mobile) Sources
•Non-Road Sources
•Point (Industrial) Sources
•Non-Point (Area) Sources
National Climatological Data
NOAA ASOS Data (1999 ~ 2001)
Hourly Observations Table
•Hourly Precipitation Table
•Daily Observations Table
•Monthly Observation Table
•Mixing Height & Atmospheric Stability Data from NOAA
Geographical Information
2000 U.S. Census Data
•2000 TIGER/Line Data
•Transportation Data from NJ DOT
•List of Small Businesses from HAZMAT Team of Union Co, NJ
•Digital Ortho Quad Quadrangles (Aerial Photo)
Data Extraction by Selection Query
By State and County; Union, Essex, Hudson Co, NJ, and Richmond Co, NY
By Pollutants; VOCs, Carbonyls, PM2.5
Dataset Extraction by Selection Query
By WBAN Station and by Coordinate
Purchased from NOAA by Combination of Surface and Upper Air Data
Download Layers for the Study Area
By Municipality; Elizabeth City, Union, Essex, Hudson Co, NJ, Richmond Co, NY
By DOQQ ID and the Location of Features
Estimation of Emission Rates
Mobile Sources by FC of Roads
Area Sources by Population ratio
Data Extraction for Sampled Date/Time and Calculate 48-hour Averages
Geographical Layer Overlays
Visual Verification of Locations
Location Information of Point Sources
Confirmation of the Sampler Location and Area Sources by Re-visiting with GPS
DATA ANALYSIS
Statistical Analysis
RIOPA DATABASE
Sampling Information
Sample Analysis Data
Questionnaire Database
GIS
Layers & Geo-Database
Proximity Calculation
Spatial Analysis

VOC Concentration Changes for Shorter Time Scales

- Variations in ambient air
  - Source emission profiles
    - Are industrial emissions constant
    - Mobile emission follow traffic patterns
  - Photochemical changes and diurnal cycles
- How do people activity patterns affect variations in personal exposure
  - Use of cleaning products
  - Showering/bathing
  - Cooking/smoking
- Most activities and exposures have acute peaks

Examples of “Acute” Exposures Measurements

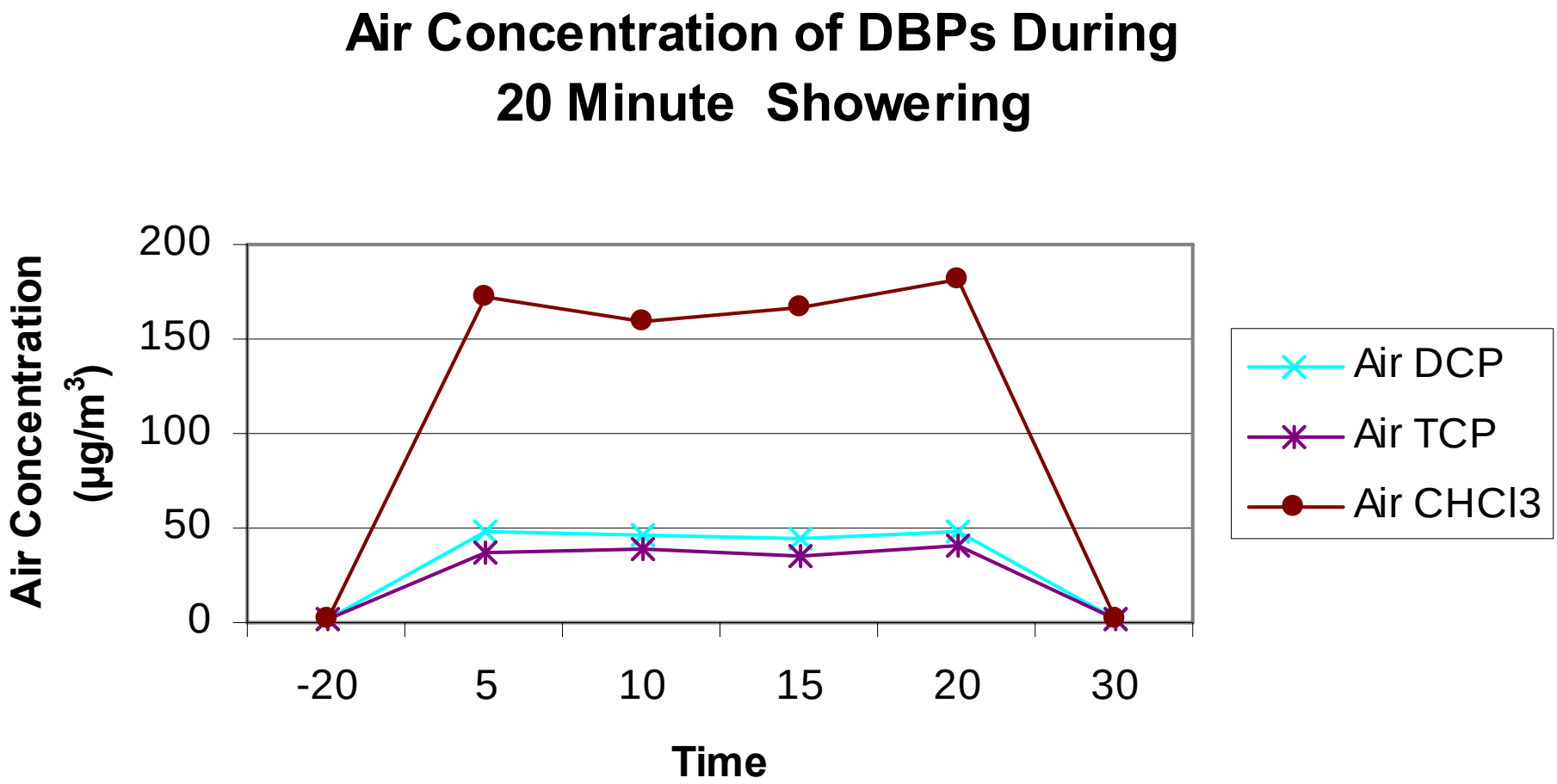
- Real time monitors for VOCs are rare and generally compound specific
- Sensitivity of monitors is an issue
- Approach followed - use shorter term integrated sampler at higher flow rate
- Pump system – limited personal sampling use
- 24 - 1 hour require 24 X the number of analyses that a daily sample needs

Shower Studies

Understanding inhalation exposure to disinfectant by-products and water contaminants

A human activity driven acute exposure

Temporal Variability Near Source



PAMS Network

Use a “continuous”/“automated” Gas Chromatograph to determine hourly VOC levels (hydrocarbons) that are important in ozone formation

Has this data set been used in exposure modeling considerations to its full extent?

PAMS Network: One Hour Continuous Sampling for Ozone Precursors -- Should this approach be applied to exposure measurement studies and model evaluation?

EPA-454/R-96-006
Chapter 1
Revision Number: 0
Date: November 1996
Page: 34

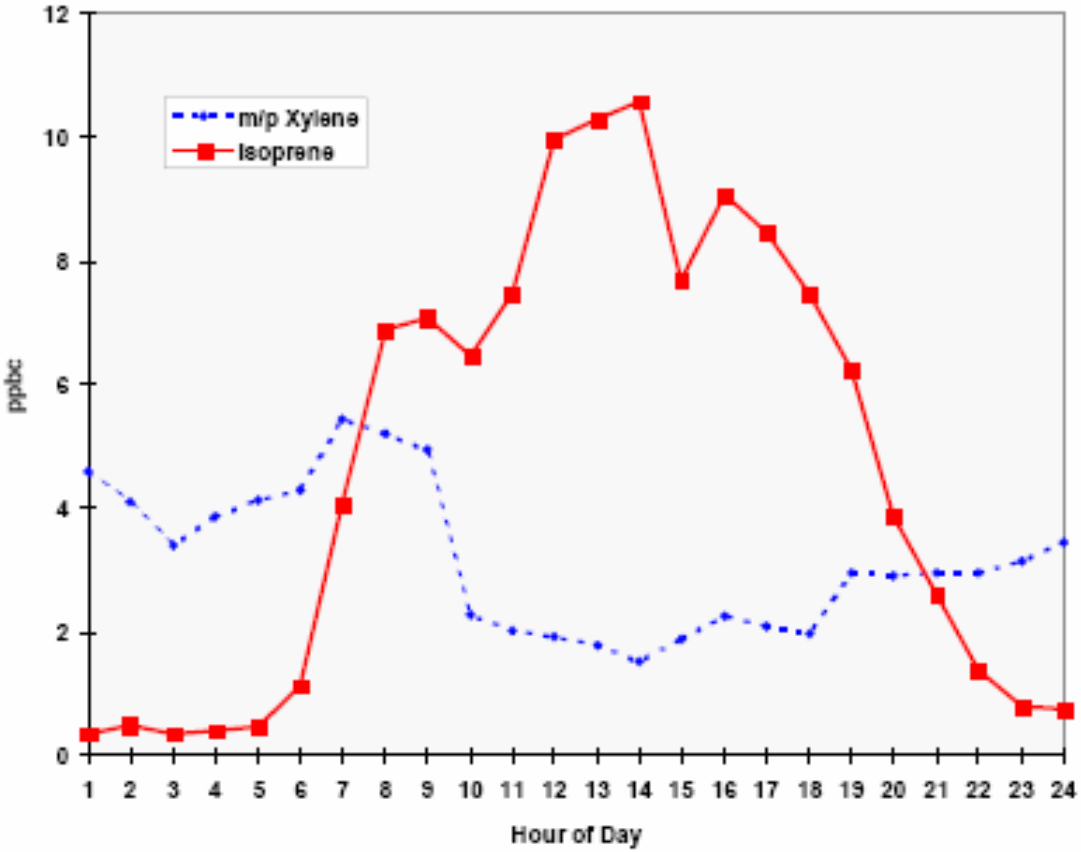
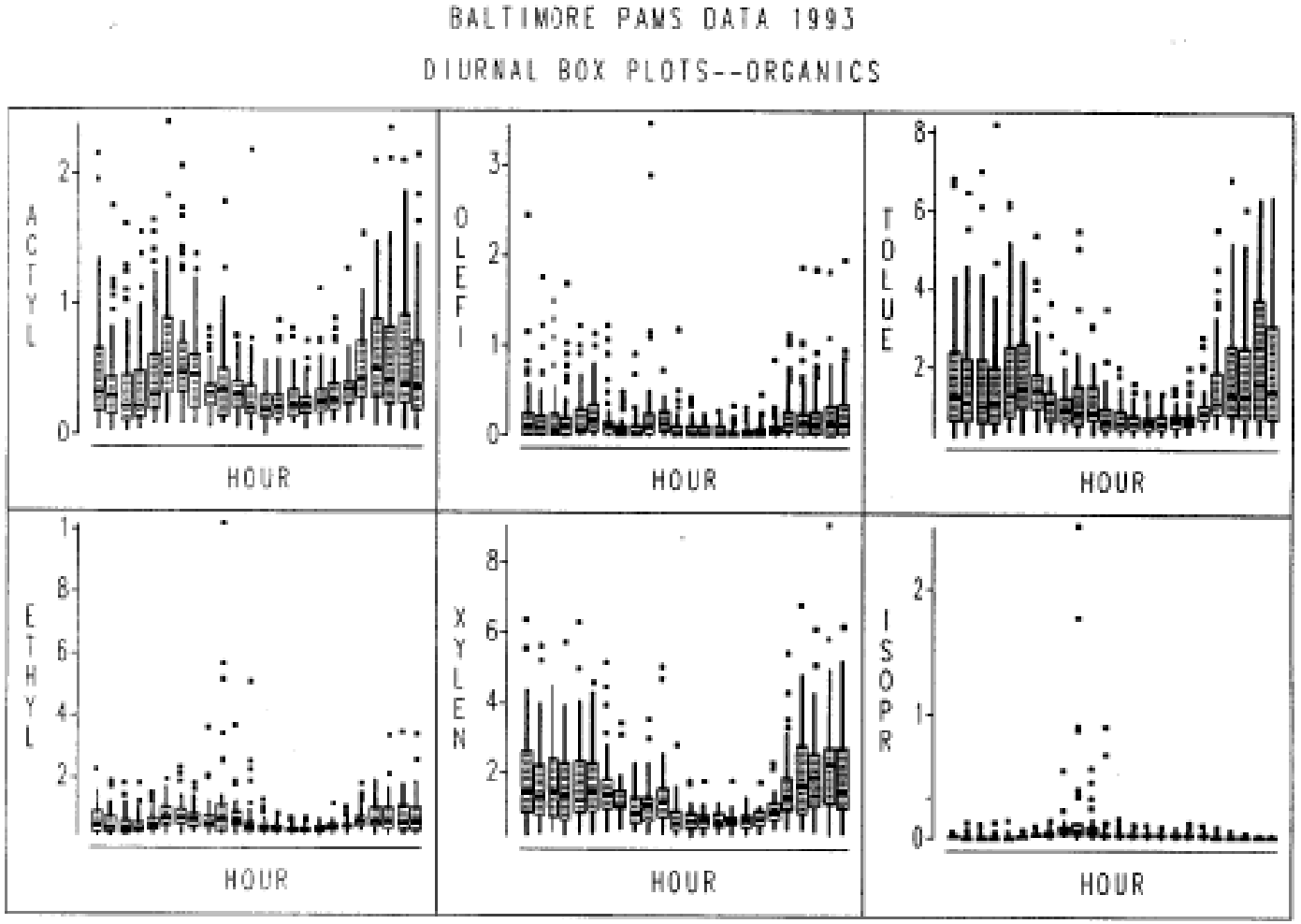


Figure 1-18 Diurnal Isoprene and m/p Xylene (averaged for 6 NESCAUM PAMS Sites for July, 1994 Episodes)

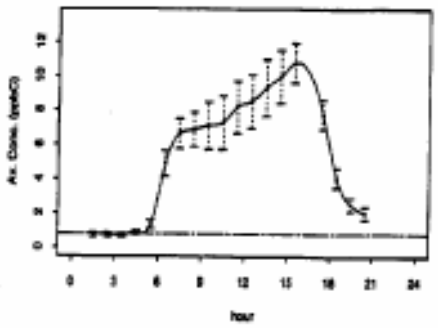
Figure 20-19.


BALTIMORE PAMS DATA 1993
DIURNAL BOX PLOTS--ORGANICS
ACTYL
OLEFI
TOLUE
ETHYL
XYLEN
ISOPR
HOUR

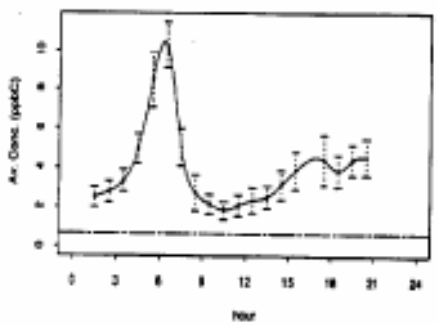
Diurnal Profiles for
HOUSTON - Galleria

Weekday

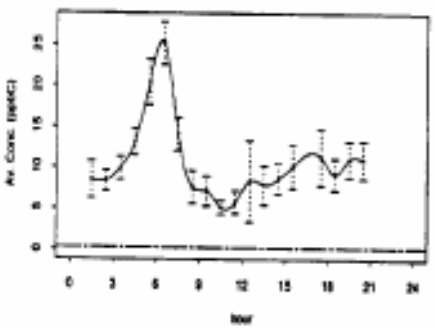
Isoprene



Benzene

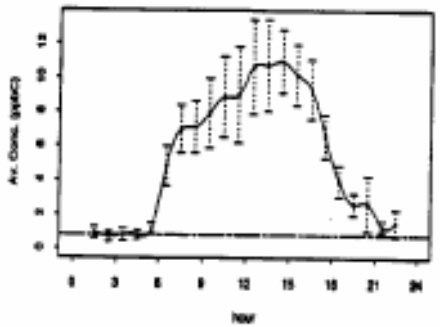


Toluene

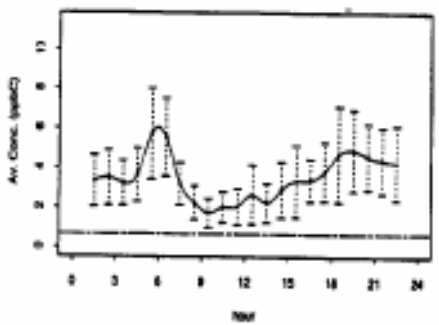


Weekend

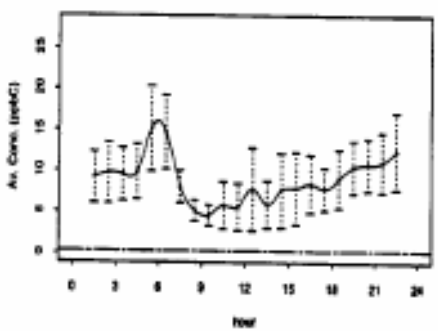
Isoprene



Benzene



Toluene



Extending the PAMS approach

- Can be used for outdoor or indoor microenvironments, not personnel sampling due to power and size considerations
- Use different detectors for other compounds to improve sensitivity (sub $\mu g/m^3$)
  - PID for aromatic compounds (benzene etc.)
  - ECD for halogenated compounds
- Look to fast GC to improve time resolution
- How to handle the amount of data generated

Some Compound Specific Studies

Formaldehyde in Houston

Continuous Reading using Laser Based Sensor

Mobile Sources & In-vehicle Exposures

Traveling or living near roadways result in peak exposures to compounds from exhaust or fuel

e.g. CO, BTEX and Carbonyls

Future Consideration

- A few large data bases from studies designed for exposure evaluation and smaller target exposure studies exist – based on integrated sampling
- Monitoring of ambient air, evaluating indoor air quality or specific activities may provide additional data for model evaluation
- If exposure modeling needs greater temporal or spatial resolution for evaluation -- measurements are possible & techniques are improving, but cost and efforts are higher than for previous studies for similar numbers of people and locations

Designing a RIOPA-VOC Study for MENTOR/DORIAN Model Evaluation

- What VOCs to evaluate
- Define time resolution
- What temporal/spatial range
- Range of exposure distribution of interest
- Define population activity
- Biomarker measurement
- Genetic variability
- & --- get the users together for other issues