Emissions From PCB Transformers- Preliminary Data

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UIC University of Illinois at Chicago

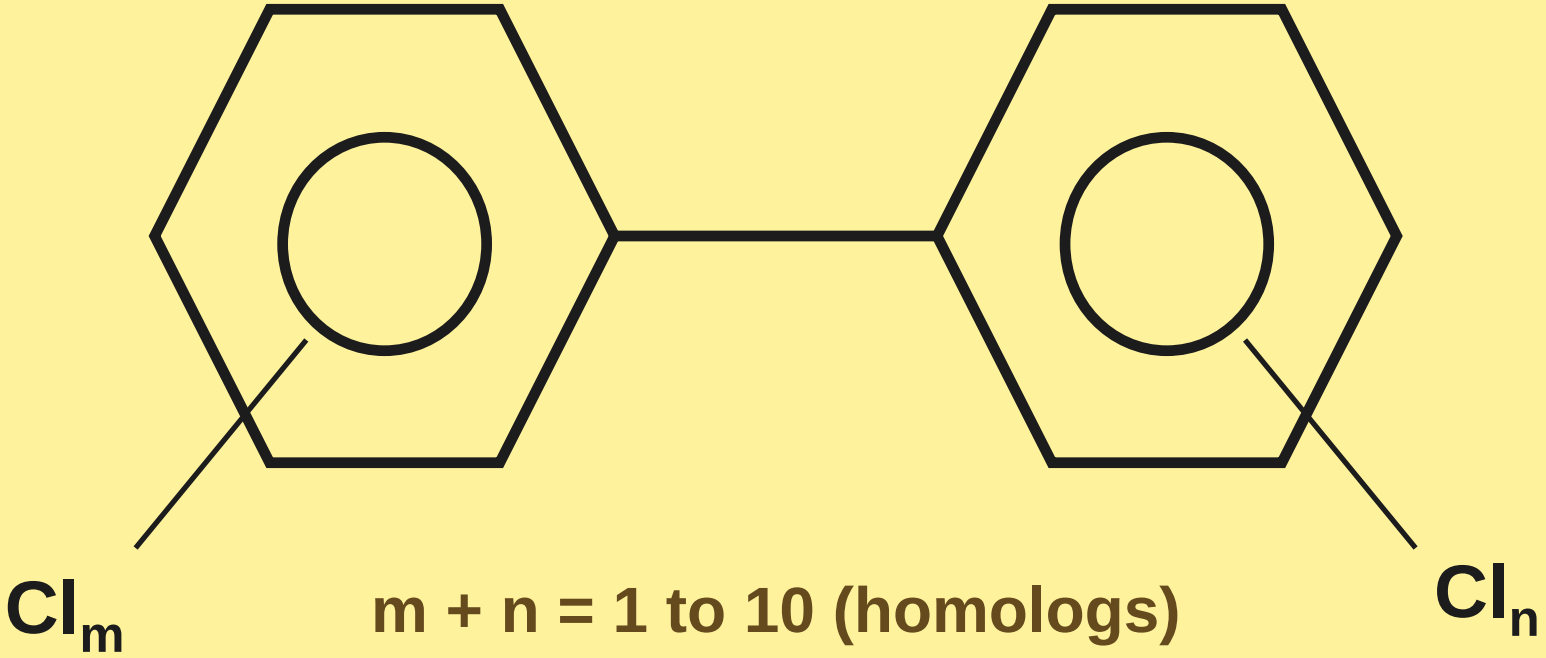
BNS Meeting
Nov. 30/04

Outline

- Background
- Introduction
- Methodology
- Improvements
- Some Results
- Discussion
- Conclusions
- Future Work

Transformer Storage Yard – Ying-Kuang Hsu

PCB:
polychlorinated biphenyls



m + n = 1 to 10 (homologs)
209 possible congeners

"Typical" PCB Air Concentrations

Type of Site	PCBTOT Air Concentration (ng/m^3)
Remote •Canadian Arctic •IADN-Eagle Harbor	 •0.002-0.100 •0.05-0.300
Rural	0.3-1.0
Urban	1.0-5
Locally Influenced	5-100
Contaminated Indoor Air	>500

Some Regulatory Limits

Agency	Air Concentration (ng/m^3)
Ontario MOE	•450 (1/2 hr ave) •150 (24 hr ave.)
OSHA PEL (8 hr, TWA,5 day)	•1,000,000 (1242) •500,000 (1254)
NIOSH REL (10 hr, 5 day)	•1,000
NIOSH IDLH	•5,000,000
Vapor Pressure (25 ^{o}C)	•7,580,612 (1242) •5206 (1254)

1978 PCB Production Ban

Use of PCBs Still Allowed

-"closed systems"

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In Service PCB Transformers-US

	US	IL	IN
No. of Transformers	21854 21563	511 551	668 675
Weight (kg)	140119776 139969890	814533 951310	1244021 1310013
Weight (tonnes)	140120 139970	814.5 951.3	1244 1310

Oct-01

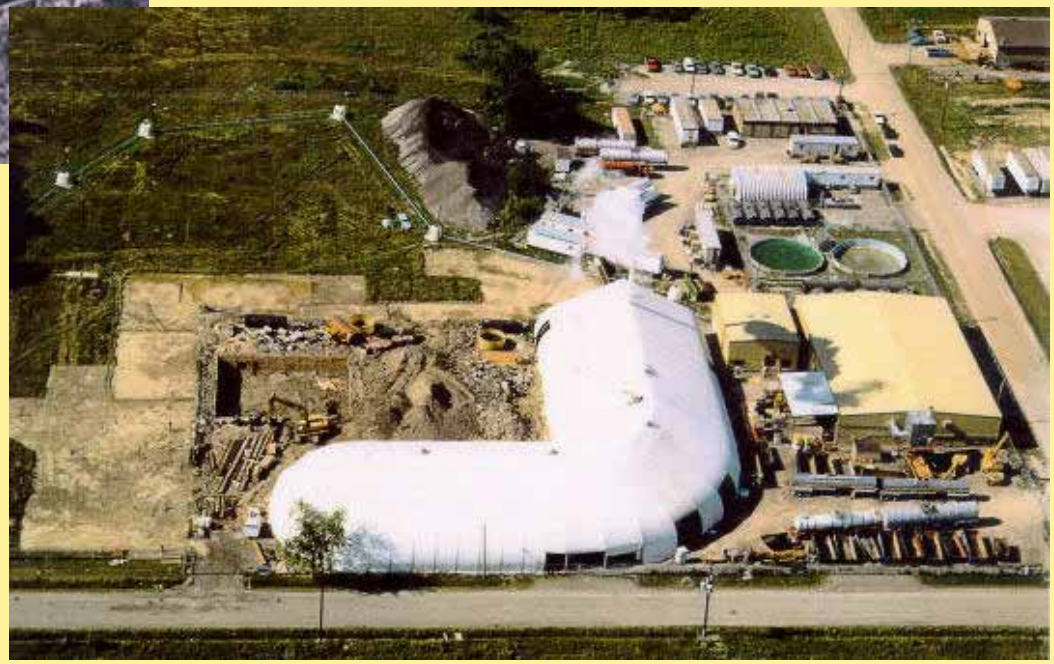
May-03

Source: US EPA Tranformer database

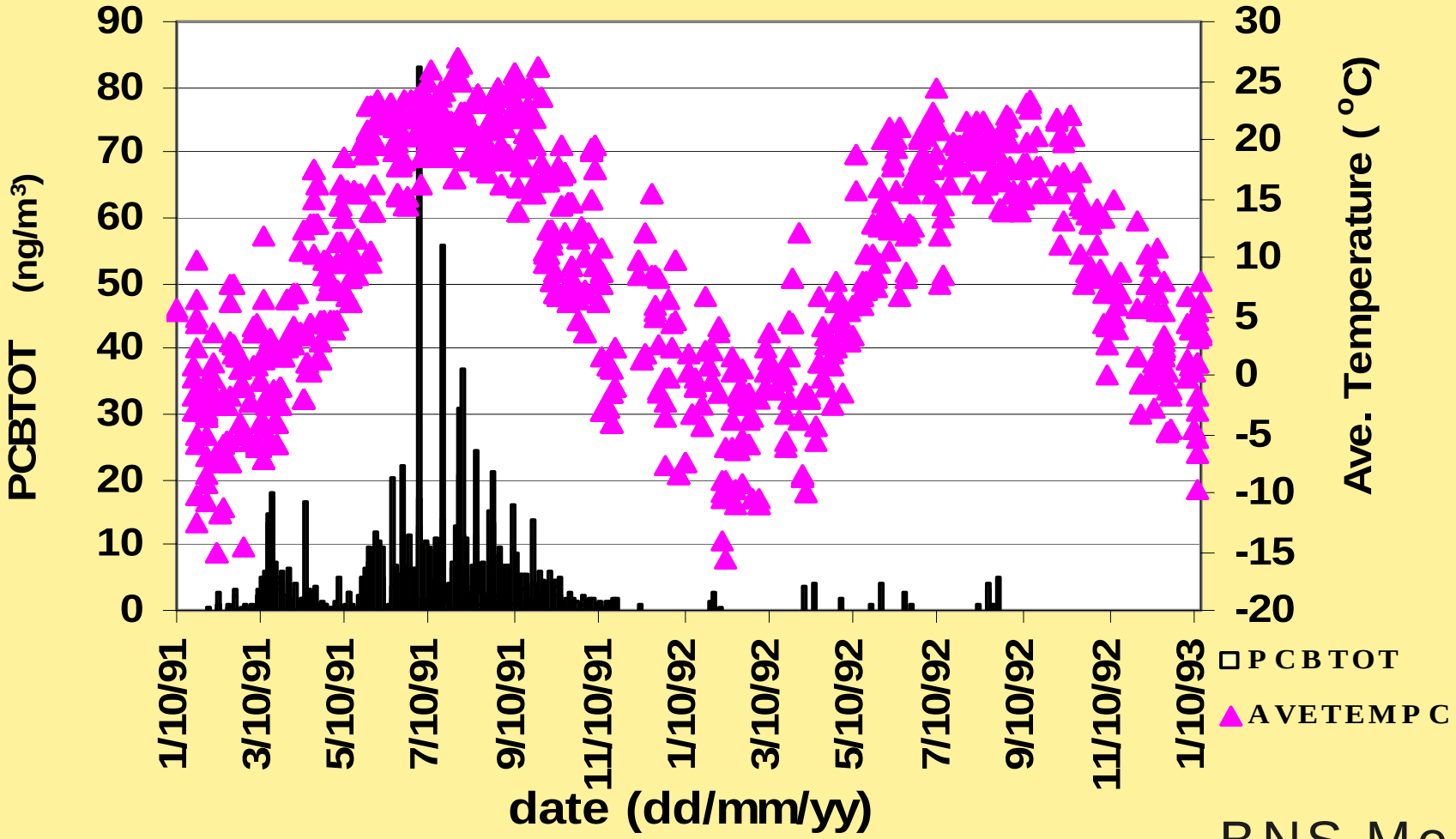
Smitville CWML Site

1985, from N

1991 from S



PCBTOT & Temperature



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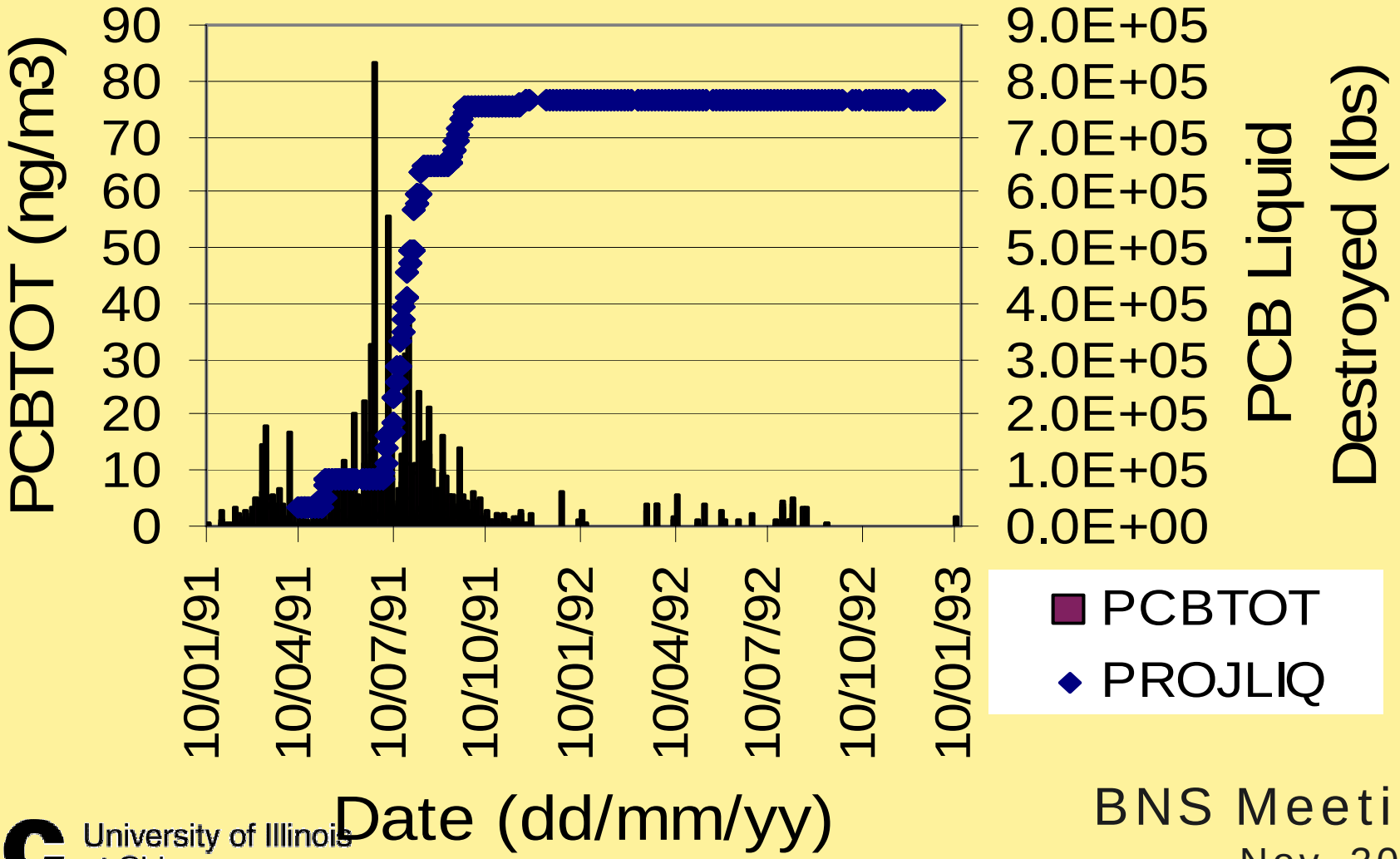
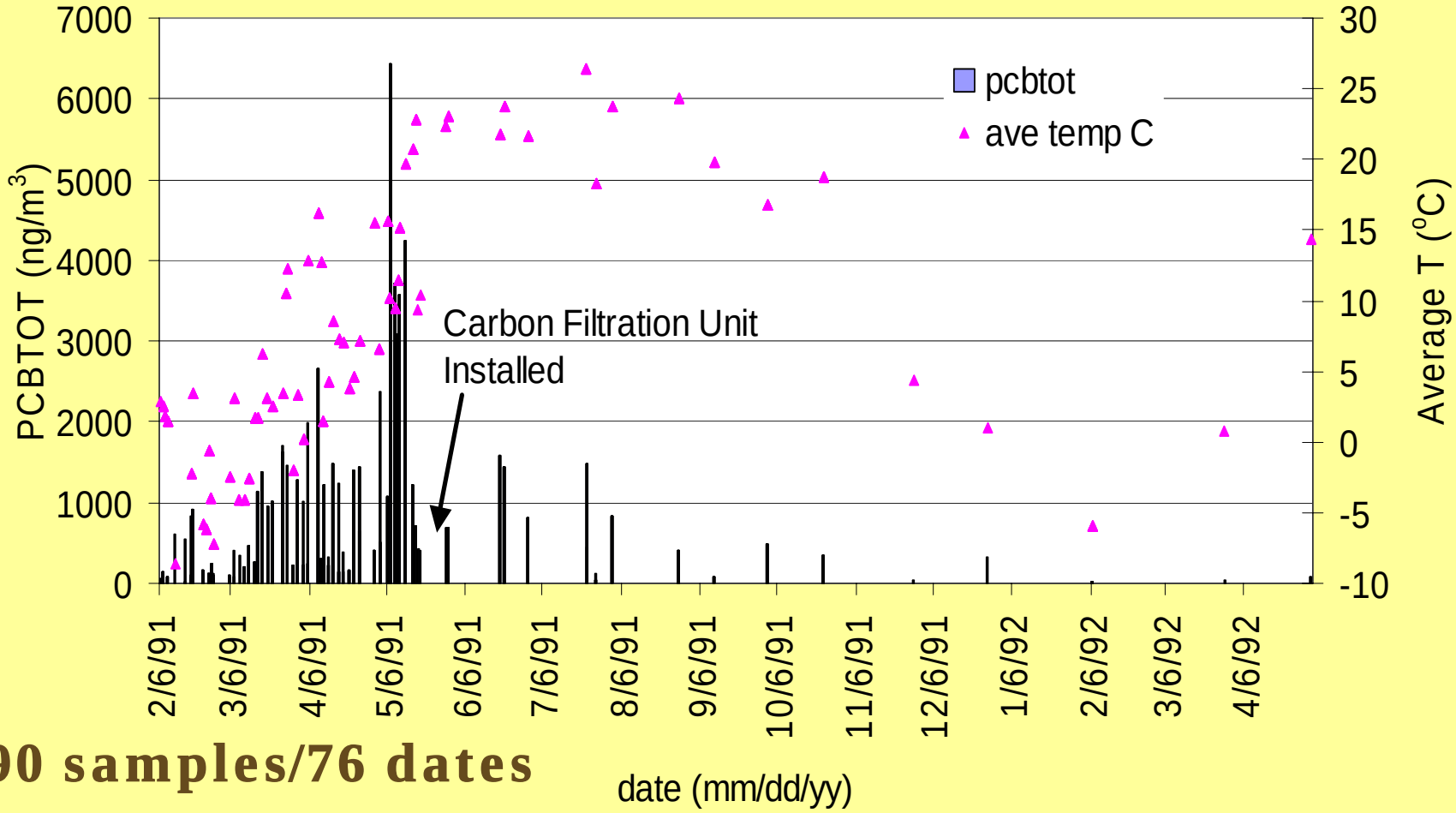
PCB Liquids Are Major Source



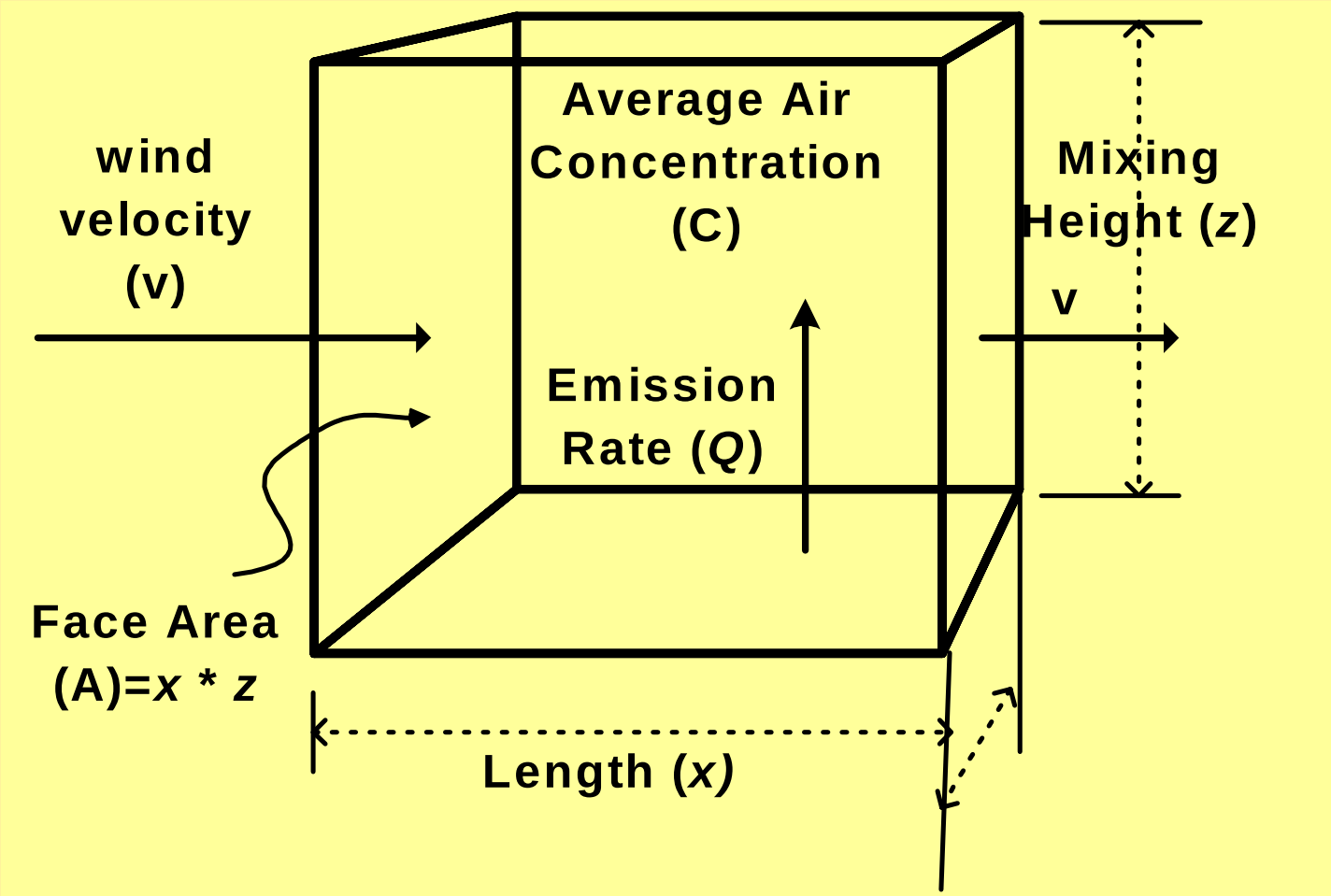
PCB Items
Stored In Containment Bldg

Carbon Filtration Reduces Emissions

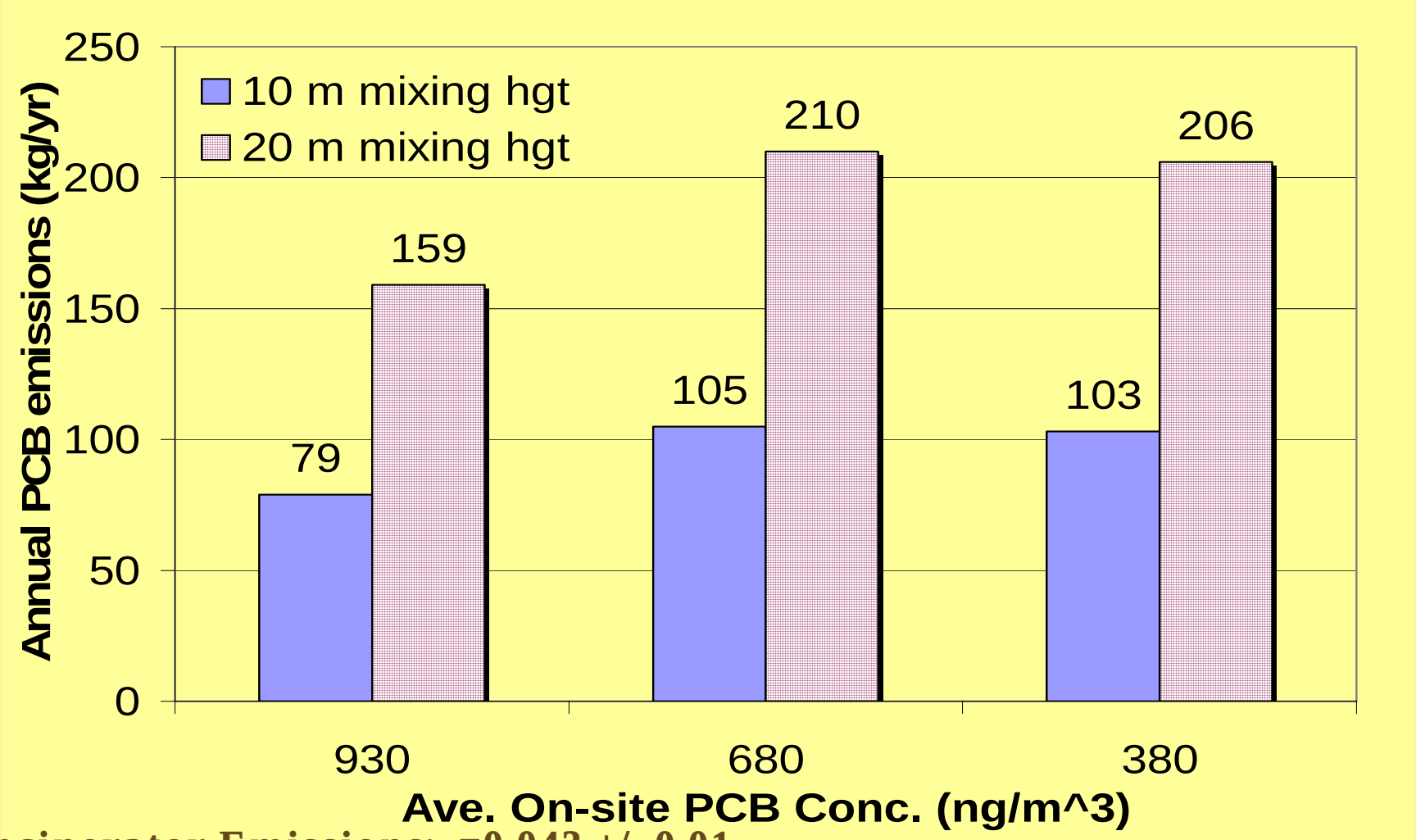


~90 samples/76 dates

Simple Box Model



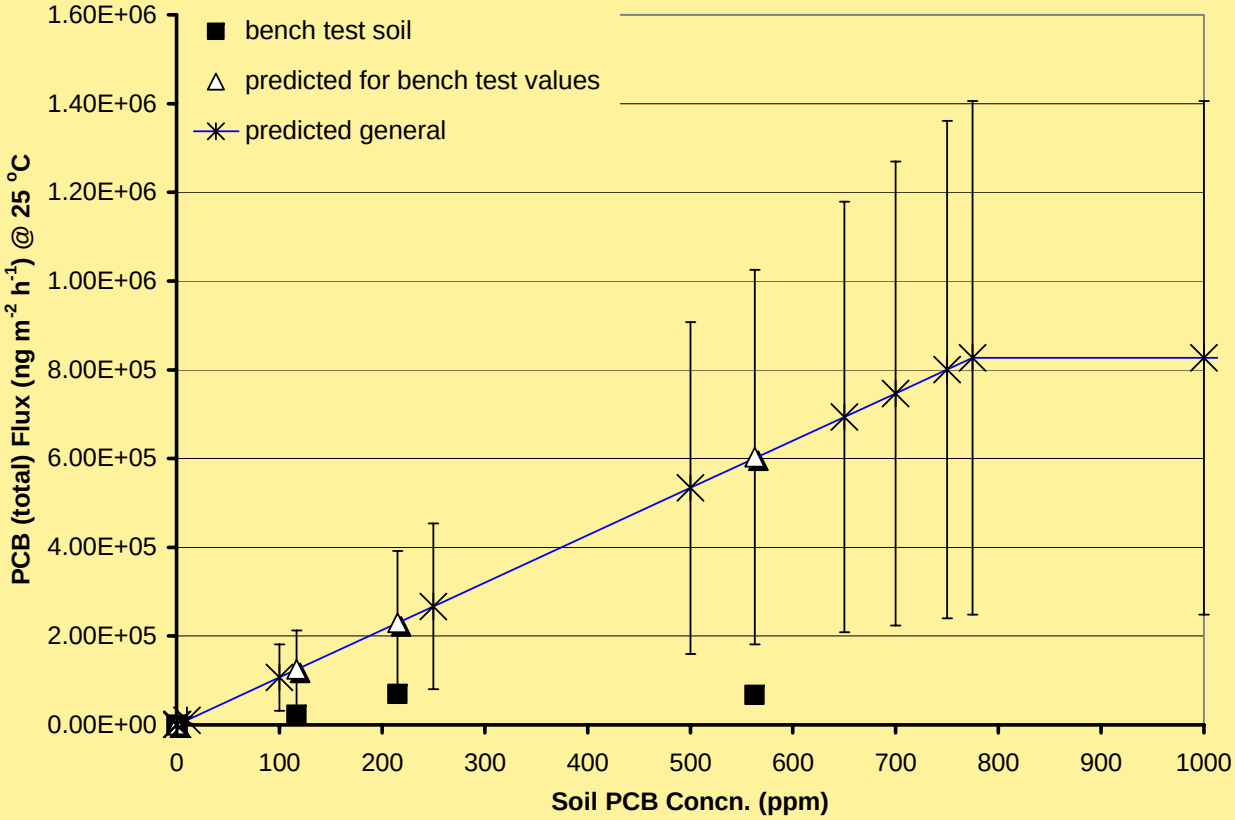
Calculated Annual PCB Emissions (kg/yr)



Incinerator Emissions: =0.043 +/- 0.01

Flux Chamber Testing

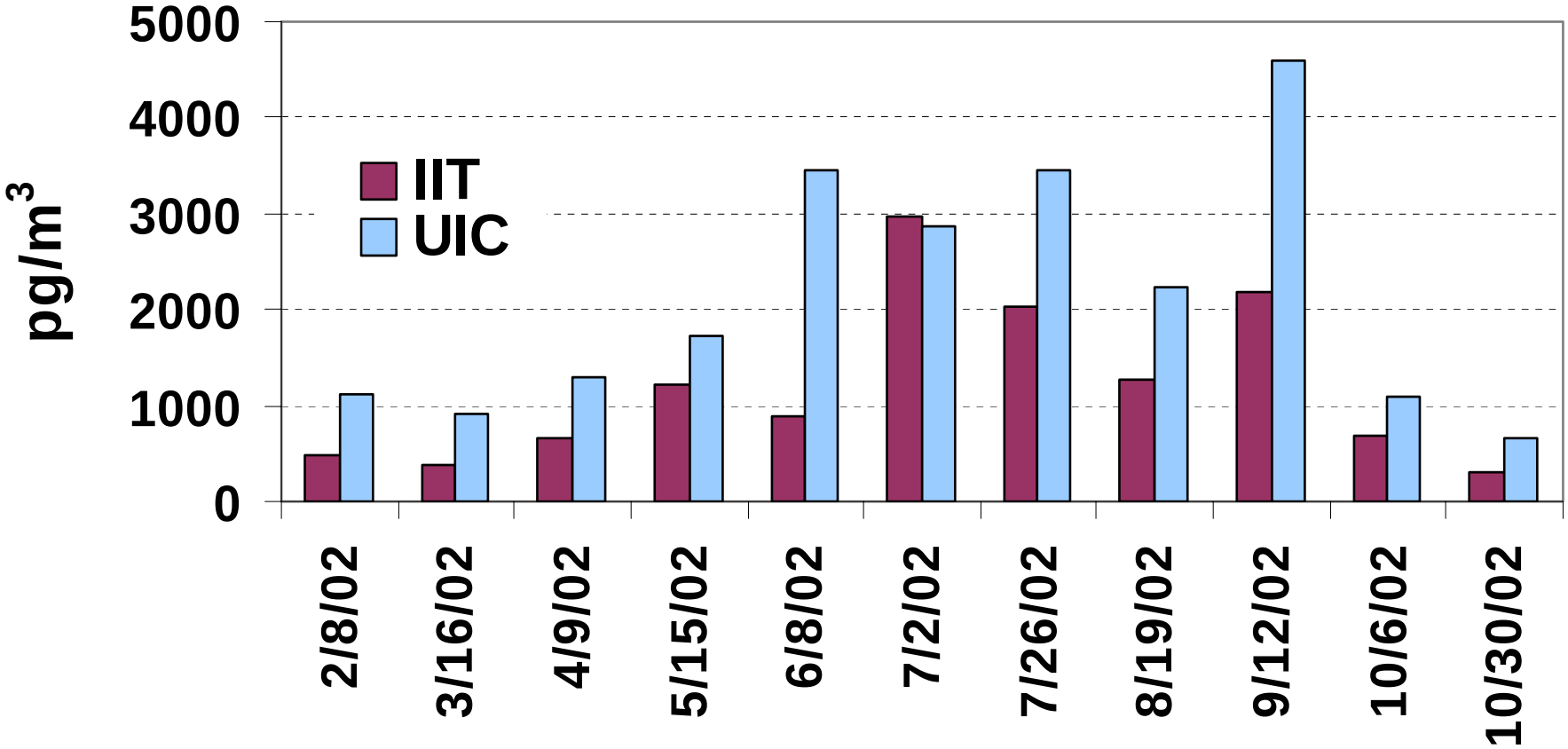
Soil Flux Calculation



Mills et al

Total PCB Concentrations of Chicago Vapor Samples at Two Sites

IIT Average: 1200 pg/m^3 UIC Average: 2200 pg/m^3



Ref. Basu, Hafner, Mills & Hites JGLR, 30(2), 310-315, 2004

Lake Michigan Mass Balance &AEOLOS

- Lake Michigan Mass Balance
  - PCB flux to Lake Michigan estimated to be 3200 kg/yr
  - Chicago urban area ~320 kg/yr
- Hsu et al (2003)
  - Sludge drying beds ~10 kg/yr

Introduction

- PCBs cycling in the environment
  - Volatility
- Atmospheric deposition
  - Major path for some areas
- Emissions Inventories
  - Major discrepancies
- **WHAT ARE THE MAJOR MASS SOURCES?**
- **WHAT ARE THE SOURCE PROFILES** ?

OPPORTUNITIES FOR SOURCE REDUCTION?

Introduction

- Two locations have been targeted:
  1) A location with a number of large (>200 L) in-service PCB Askarel transformers
  2) A commercial PCB transformer storage and decontamination facility

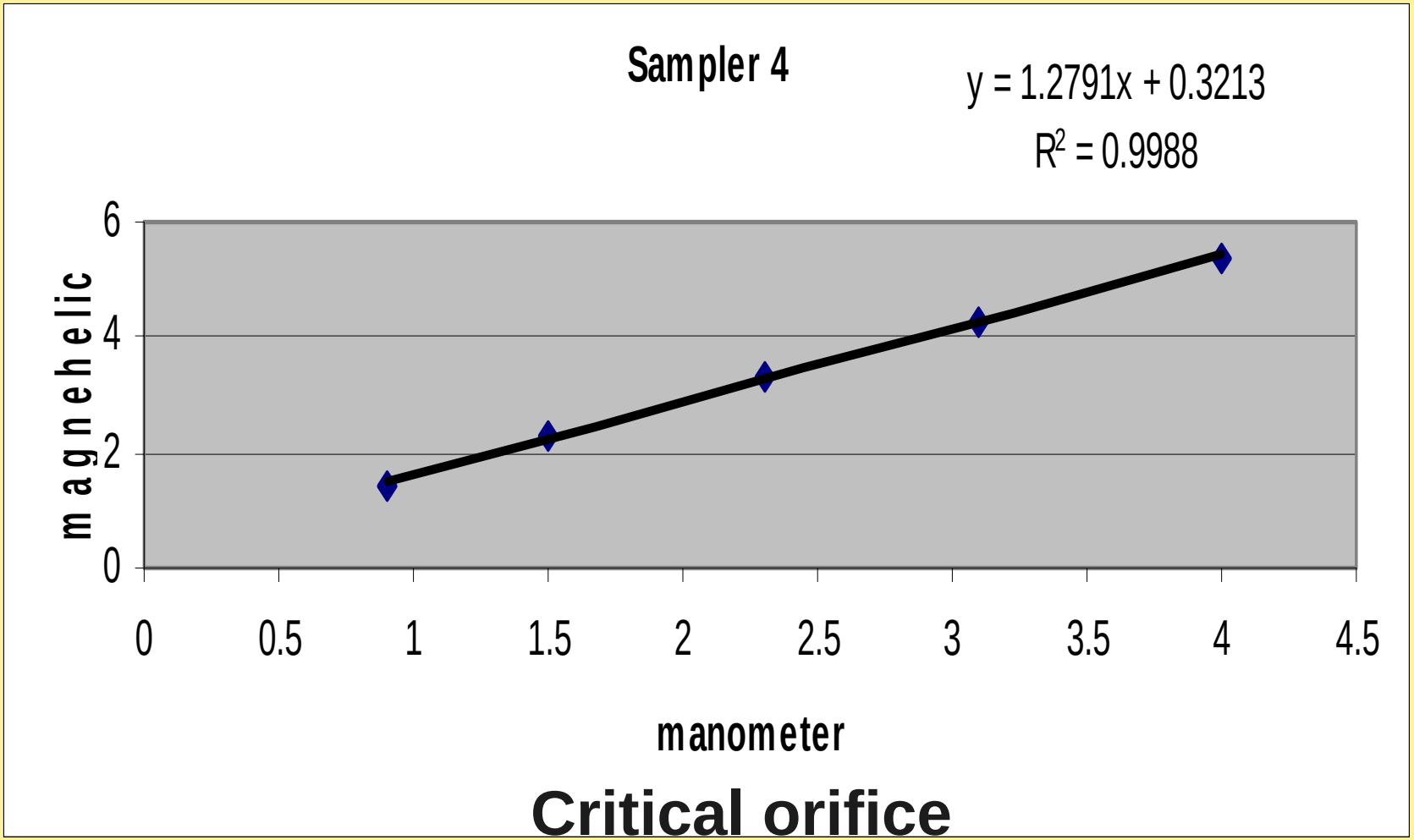
Methodology

- Obtain air samples from Operating Askarel transformers
  - *Maintenance operations ?*
  - *Transformer storage?*
- Analyze samples for concentration and PCB congener profile

Air Sampling

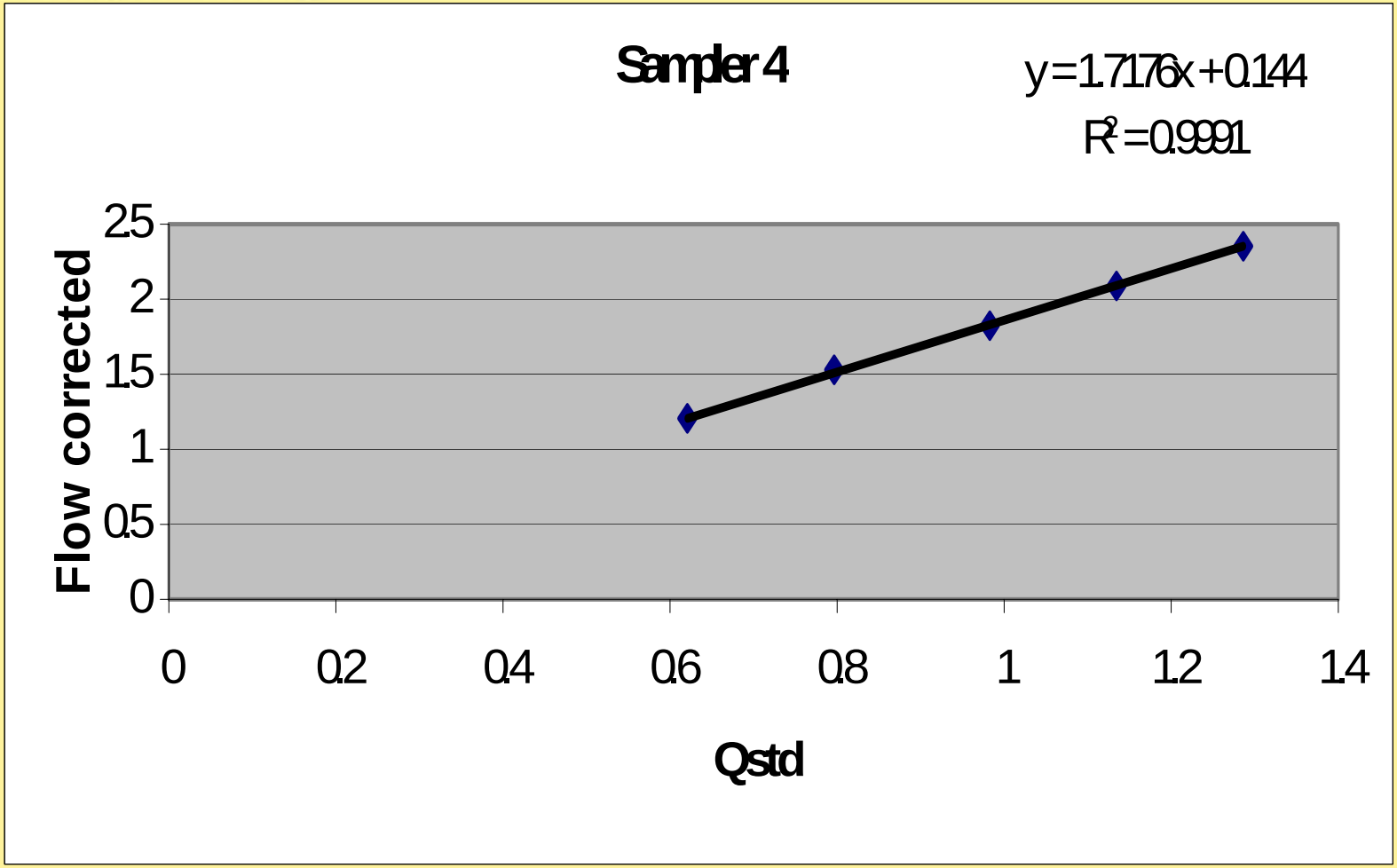
- Tisch high volume air sampler
- Air is drawn through system using flow controlled vacuum motor
  - Particulate matter collected with quartz fiber filter
  - Gas phase collected using Sorbet (pre-cleaned XAD-2 resin)

Air Sampler Calibration



Critical orifice

Air Sampler Volume



Total Volume=elapsed time * flow corrected

Laboratory Sample Extraction

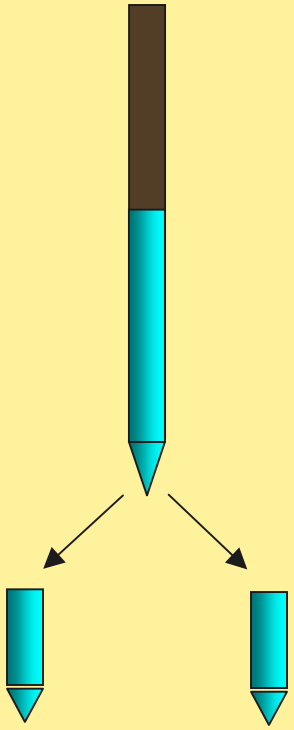
- Soxhlet extraction of Xad-2 and/or filters
  - 50:50 Hex:Acetone
  - 24h extraction

Add extraction Surrogates PCB-14, 65, 166

- The extracts are rotary evaporated before undergoing column cleanup

Cleanup & Analysis Prep

- Silica column cleanup (3.5% deactivated)
  - Elute with hexanes
- Rotary evaporate and transfer to 1 or 2 mL volumetric flask
- Concentrate by N_2 blowdown
- Add internal standards PCB 30 and 204, make up to exact volume



Analysis

- Samples primarily analyzed using Agilent 6890 GC-ECD
  - GC-MS or second column analysis used for confirmation on subset of samples

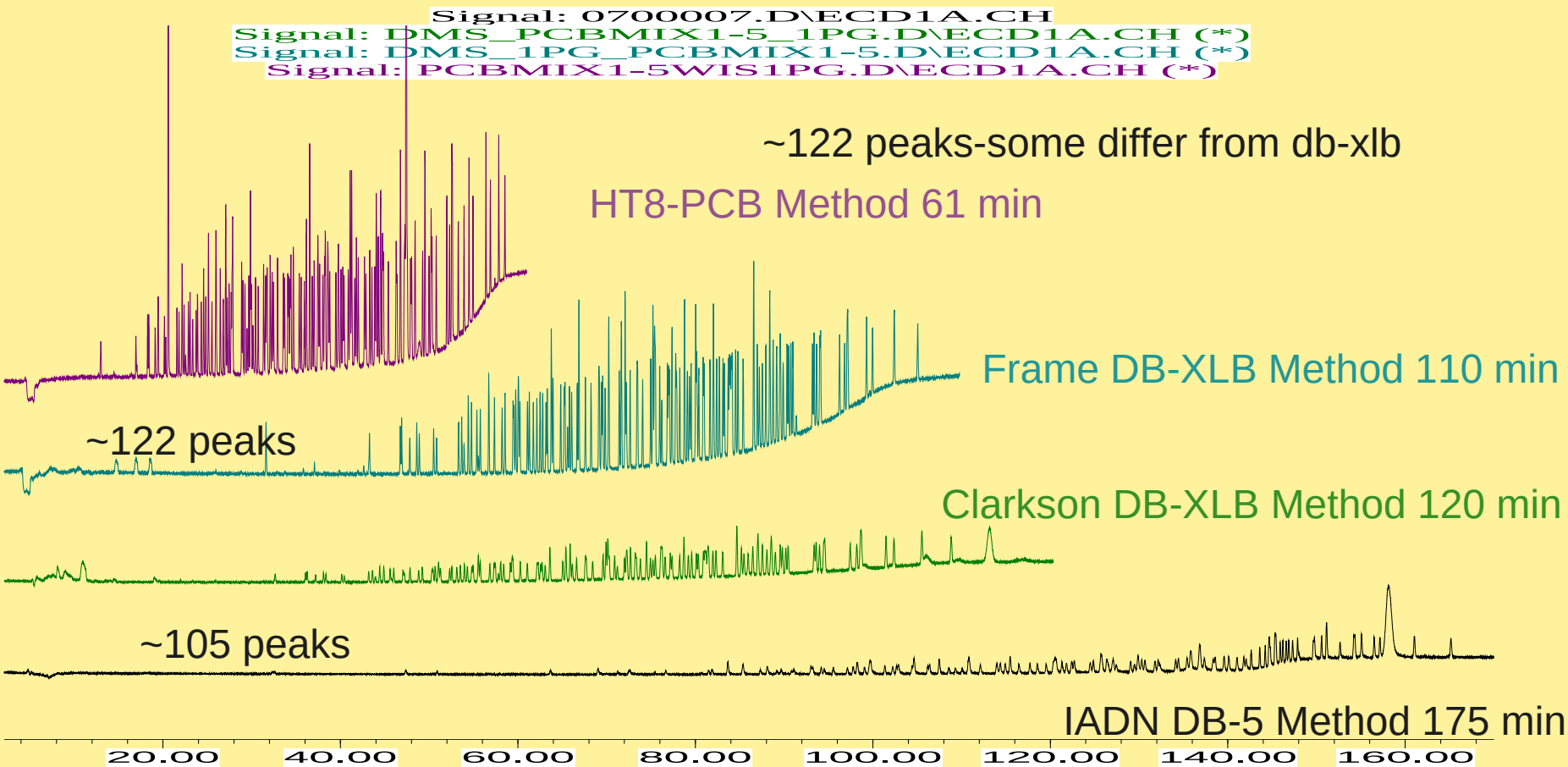
CALIBRATION STDS

- All 209 congeners now available individually
- Accustandard Mix 1-5 contain 144 “Aroclor” congeners
- Accustandard mix -9 contains “non-Aroclor” congeners
  - All congeners at same concentration
    - RRFs can be calculated

GC Column Choices

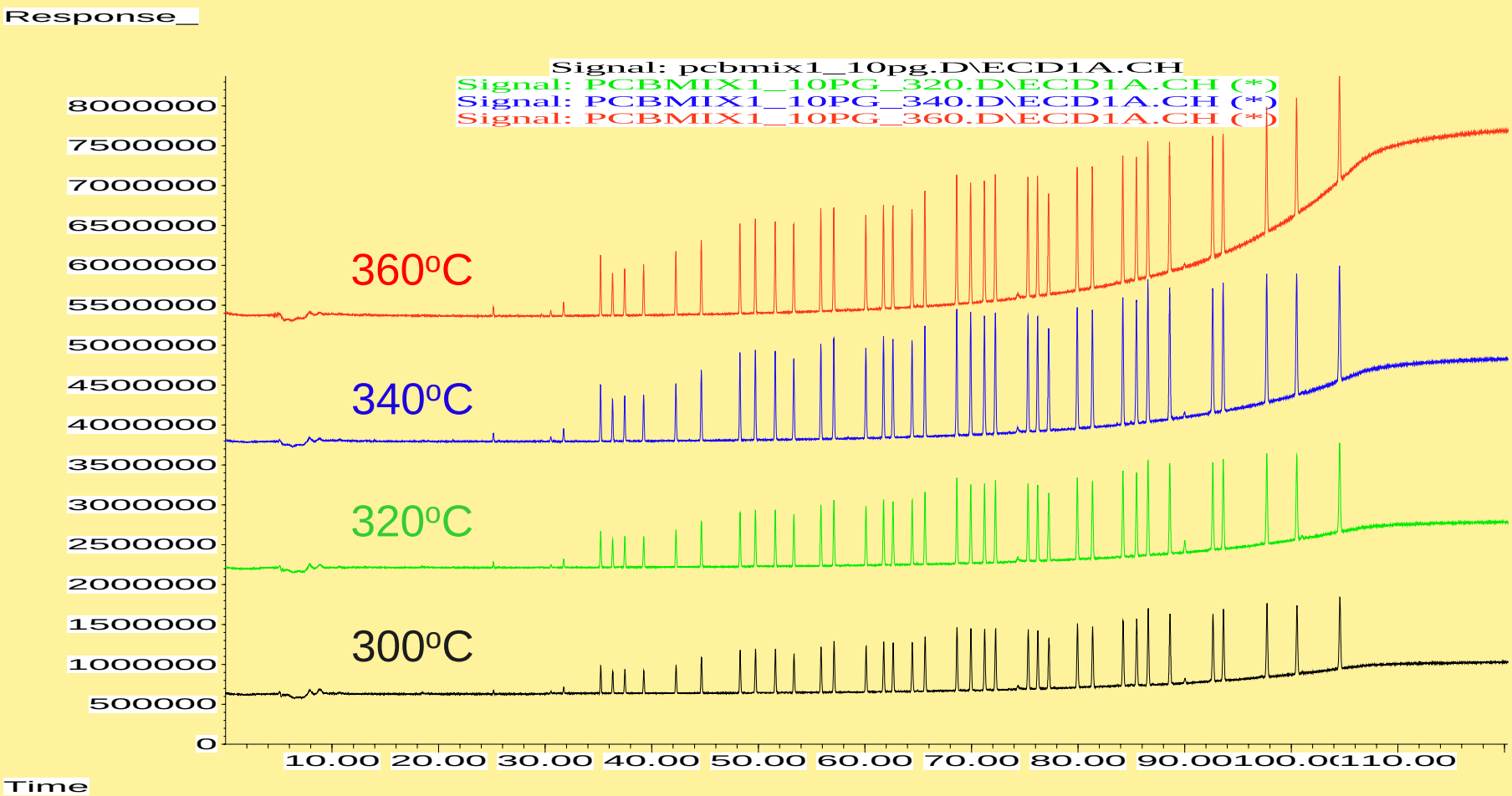
- Initial samples analyzed using 60m DB-5
  - Detector temp: 300°C, ECD Makeup: ArMe
  - Analysis time: 175 minutes with IADN method
- Converted to 60m DB-XLB
  - Detector temp: 340°C, ECD Makeup: N_2
  - Analysis time: 110 minutes with modified Frame method
- Currently using 60m HT8-PCB (SGE)
  - Detector temp: 340°C, ECD Makeup: N_2
  - Analysis time: 61 minutes with modified Matsumura method
  - Resolution: ~122 peaks for 144 congeners
  - Detection limits: <100 fg (10^{-13} g)
  - Quantitation limits: 1 pg (1 uL injection)

GC Method Development

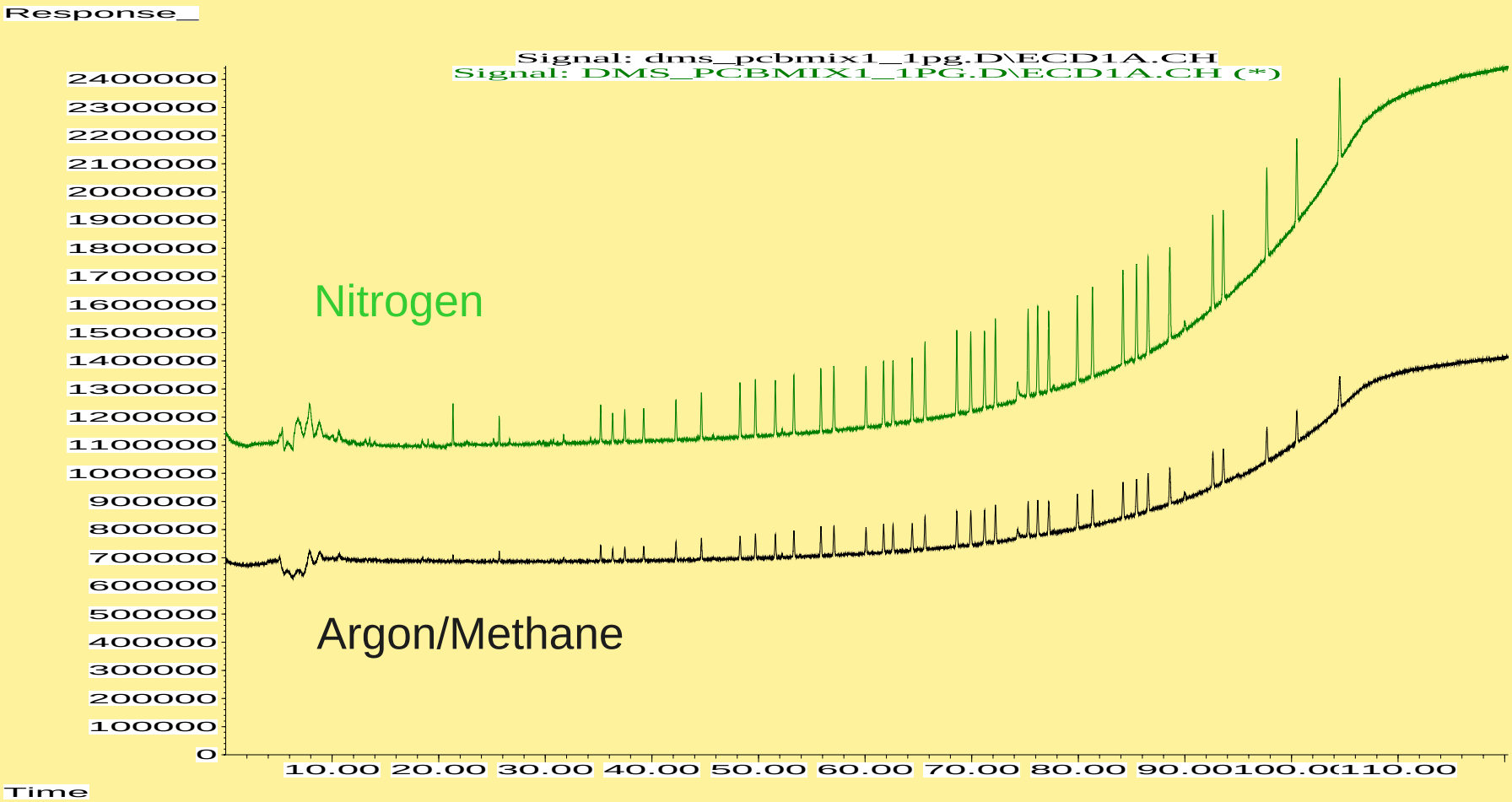


HT-8PCB CONGENER ELUTION ORDER

Detector Temperature

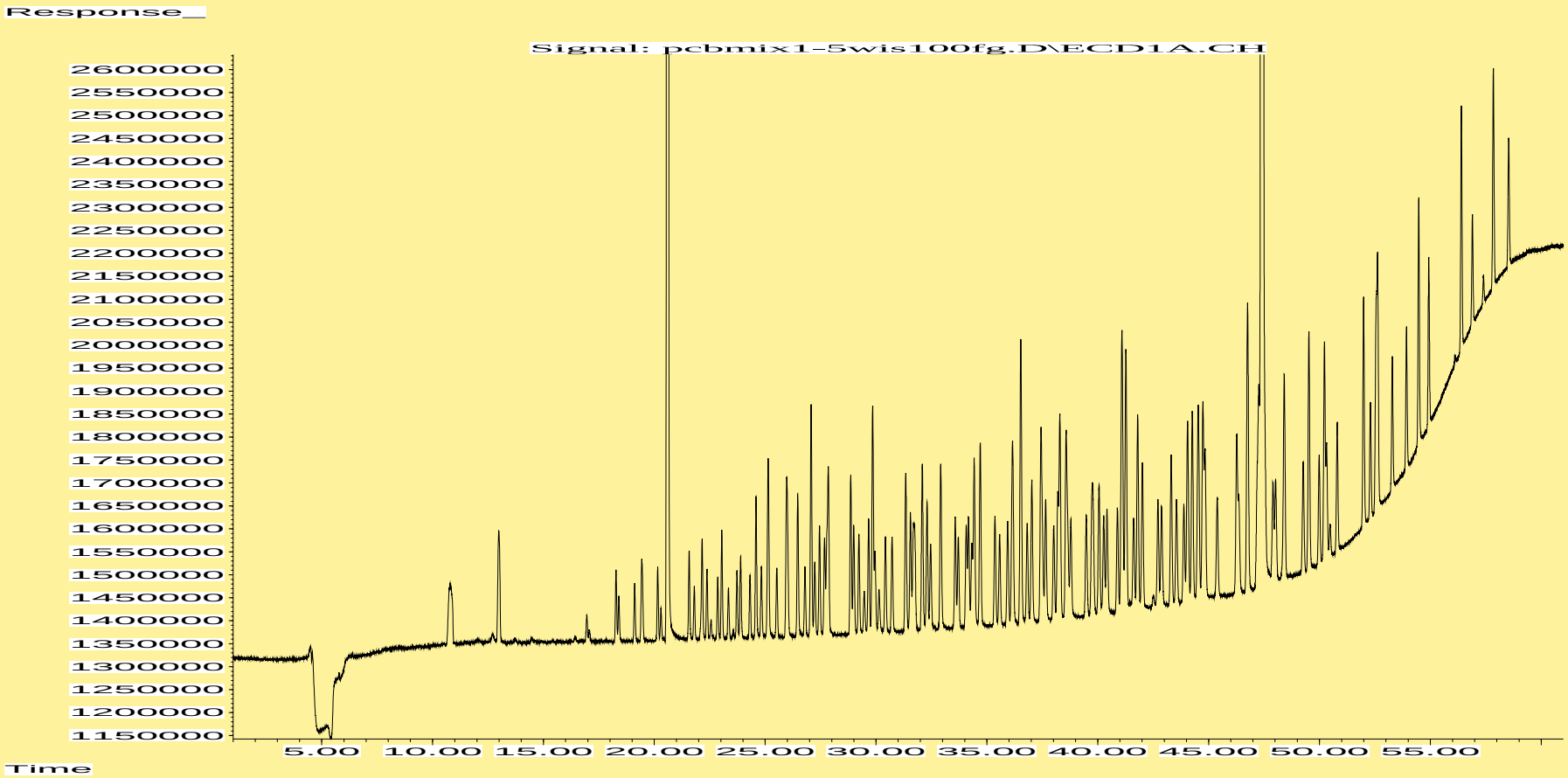


GC-ECD Makeup Gas



6890 GC u-ECD Sensitivity

Accustandard PCB Mixes 1-5 at 100 fg injection



Column Conclusions

- Changing columns from DB-5 to HT8-PCB and modifying existing methods has expedited analysis time from 175 min to 61 min!

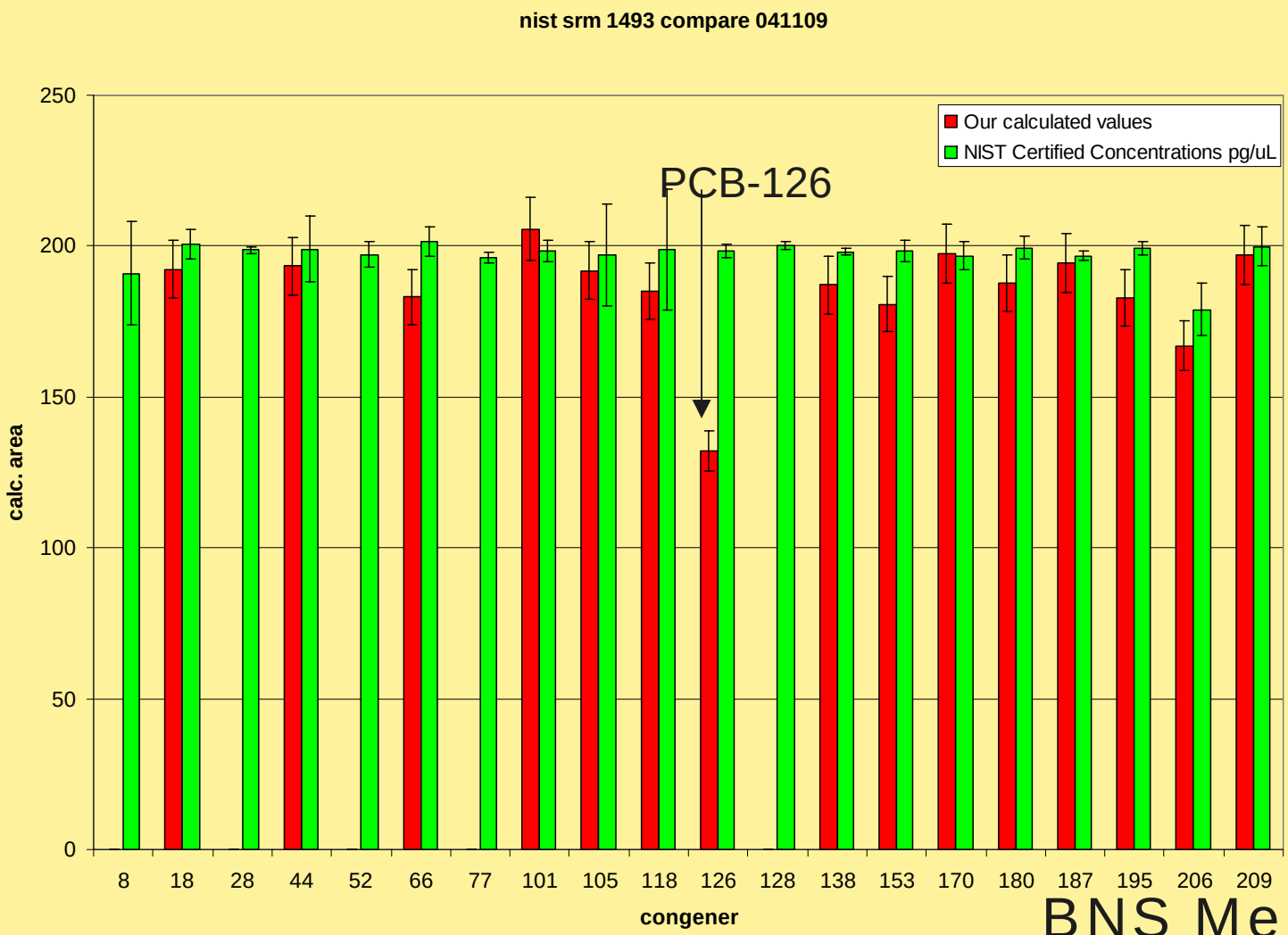
- Resolution increased >10% with switch in column and method
  - 105 peaks seen on DB-5 with IADN method
  - 122 peaks seen on HT8-PCB with Matsumura method
  - 144 peaks possible

- Changing detector temperature from 300°C to 340°C and changing ECD makeup gas from argon/methane to N_2 has lead to 4x increased sensitivity!
  - 2X increase from temperature change
  - 2X increase from change of makeup gas

Project QA/QC

- Laboratory Analysis
  - Accuracy
    - NIST SRMs
      - GC: SRM solution
      - Method: Sediment SRM
    - Internal standard method
    - Recovery surrogates
    - Confirmatory analysis
  - Precision: Inter- and Intra- analyst
  - Laboratory blanks
  - Injection replication

NIST INJECTION SRM



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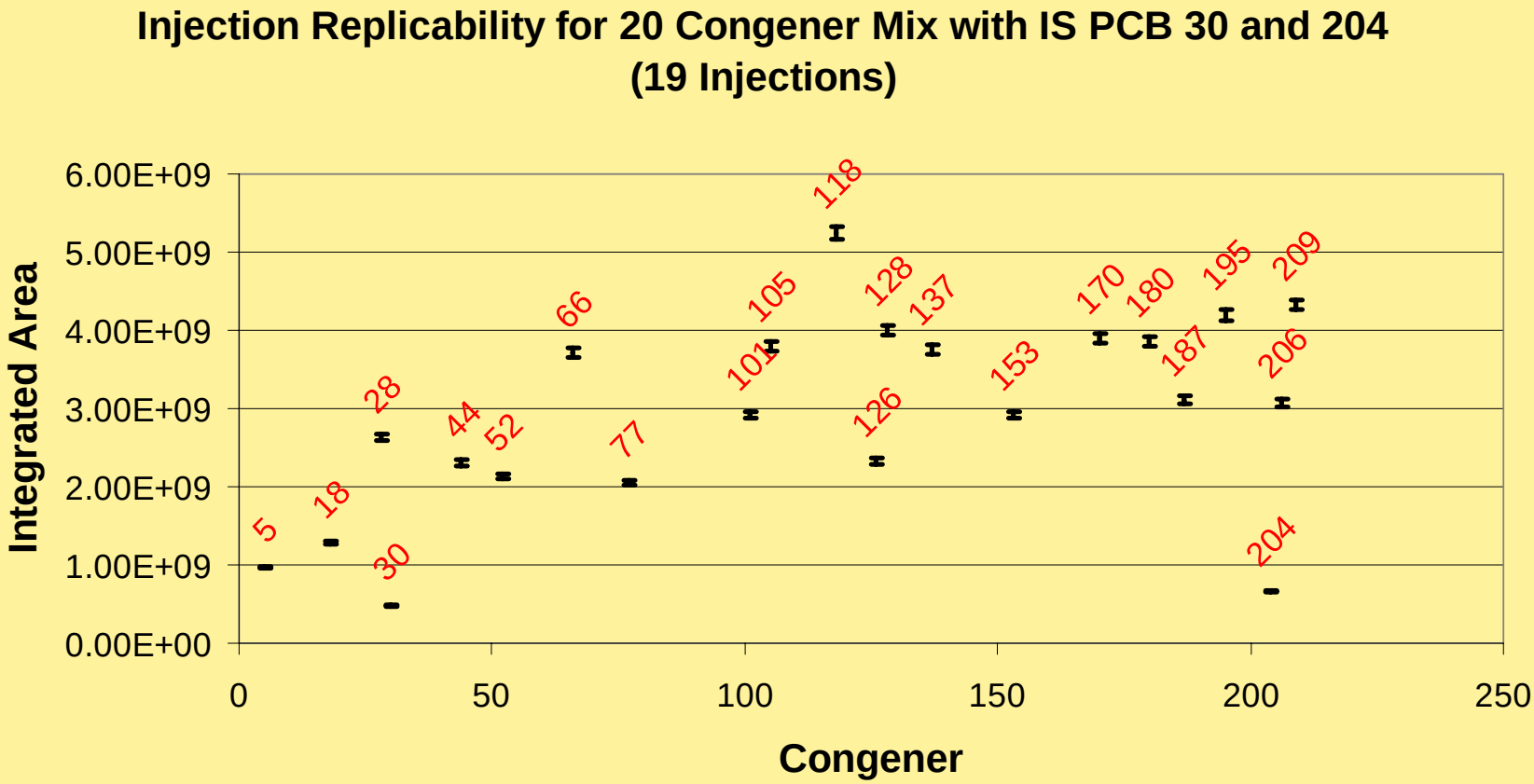
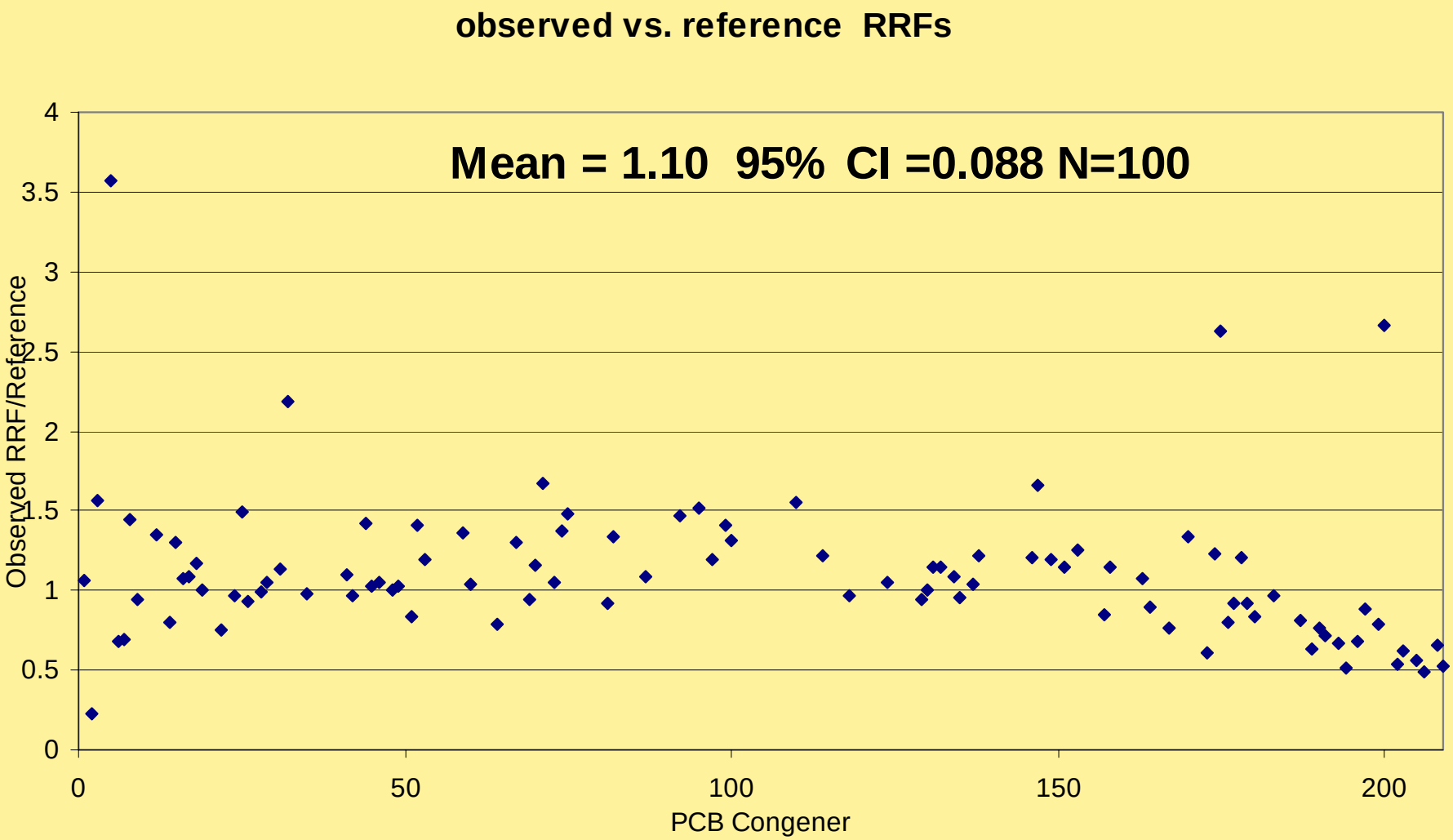
Project QA/QC



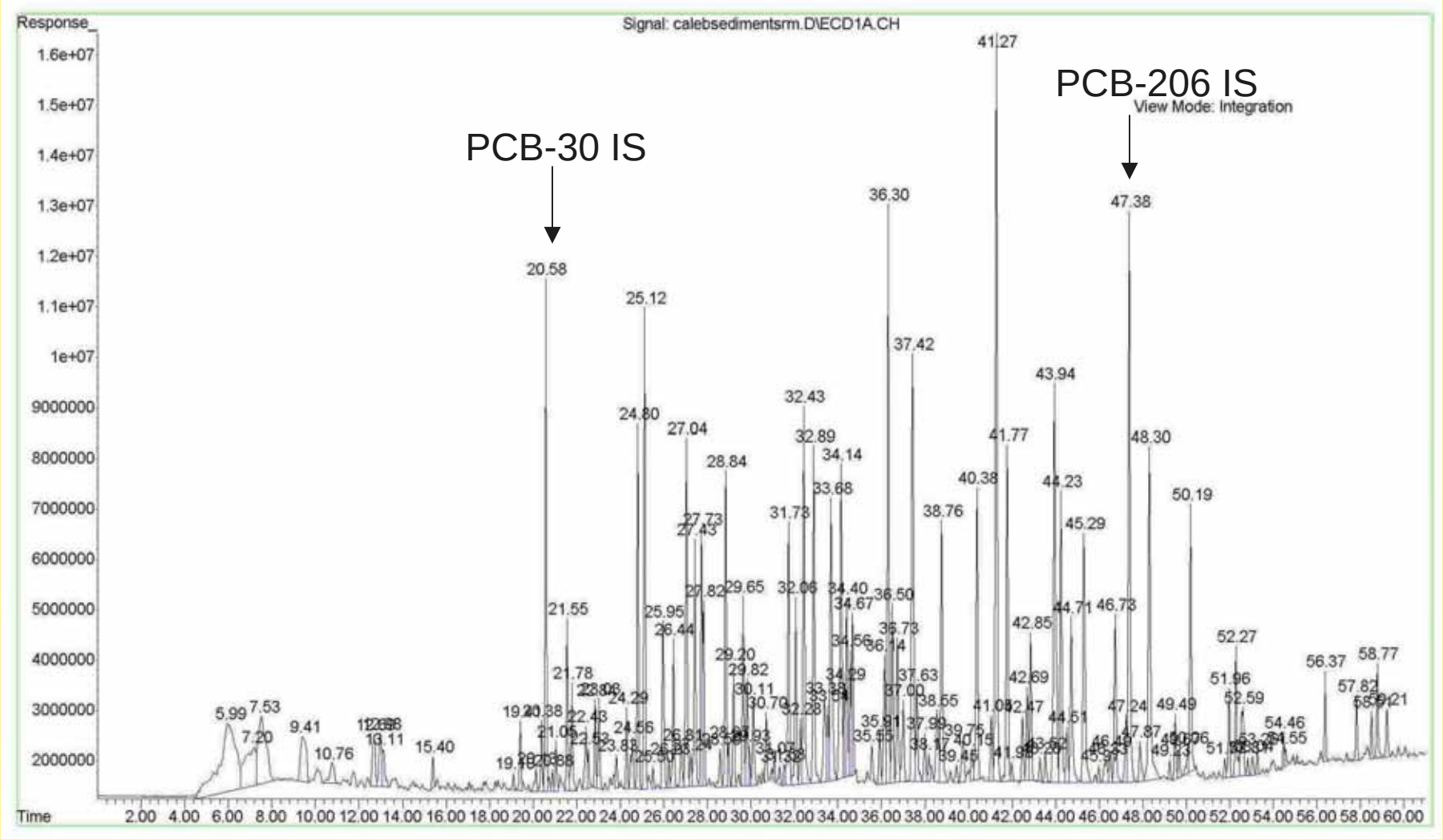
95% CI=1.5% FOR IS

Mean 95% CI: 3.5%

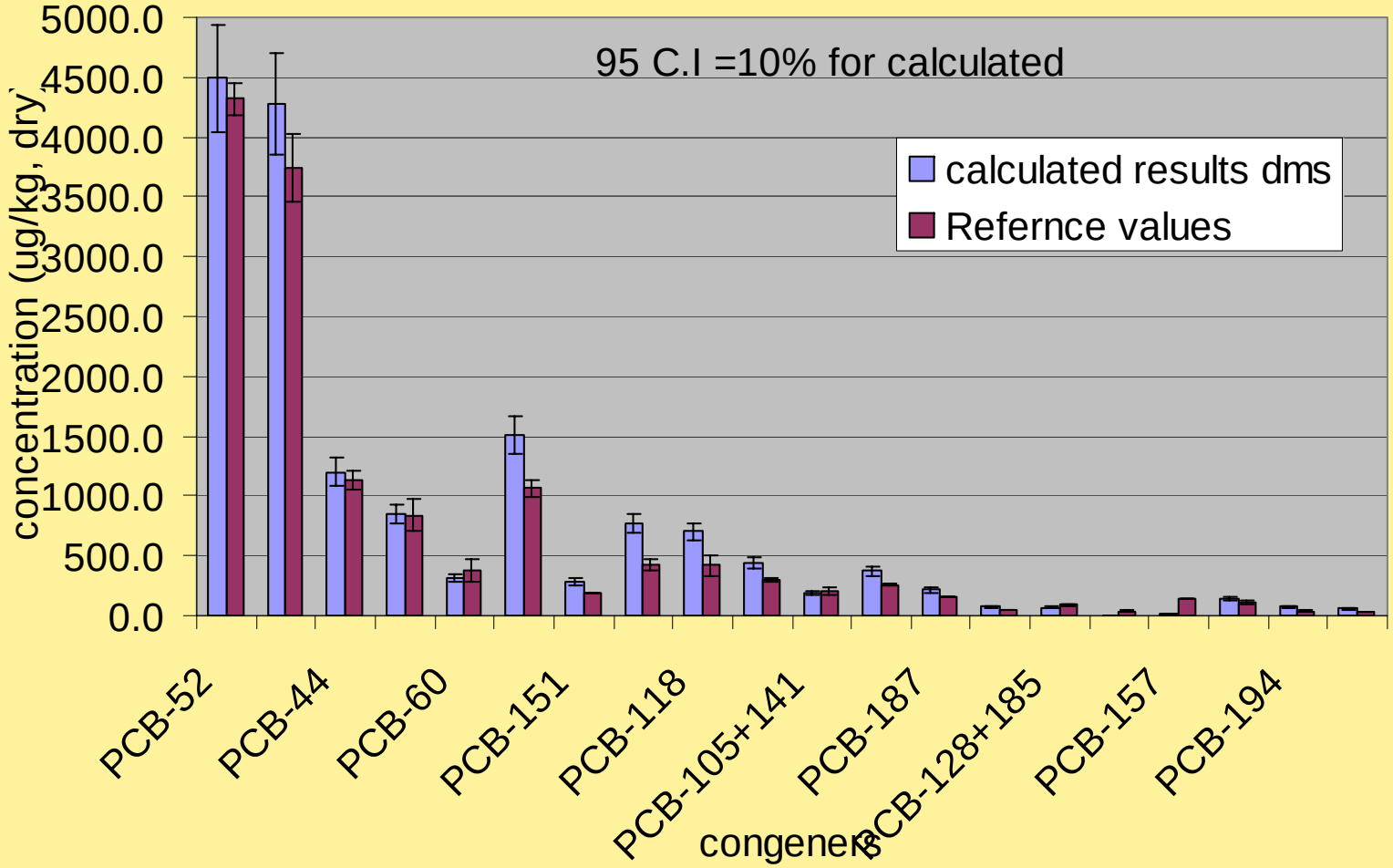
Relative Response Factors



NIST SEDIMENT SRM



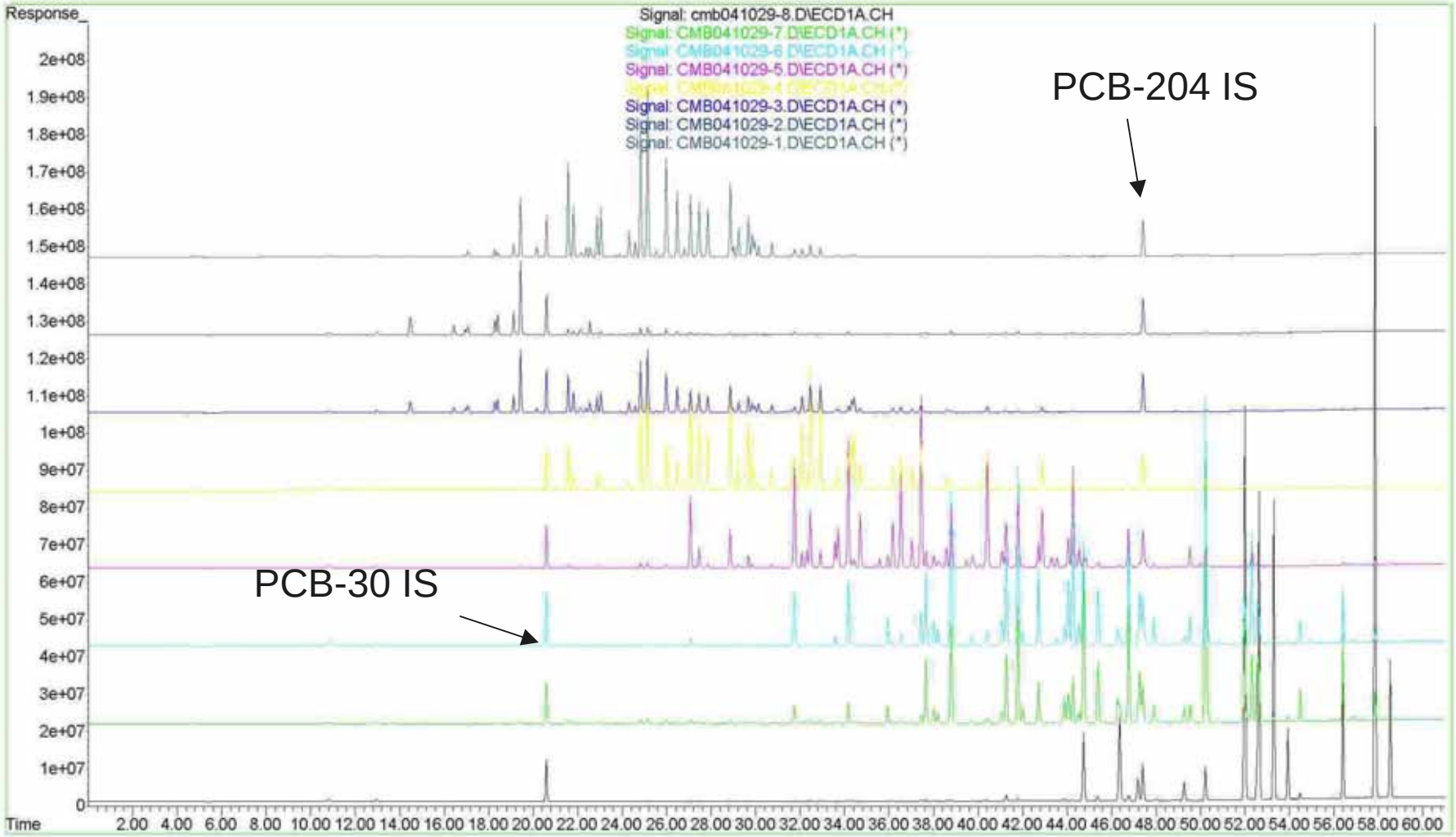
NIST Sediment SRM



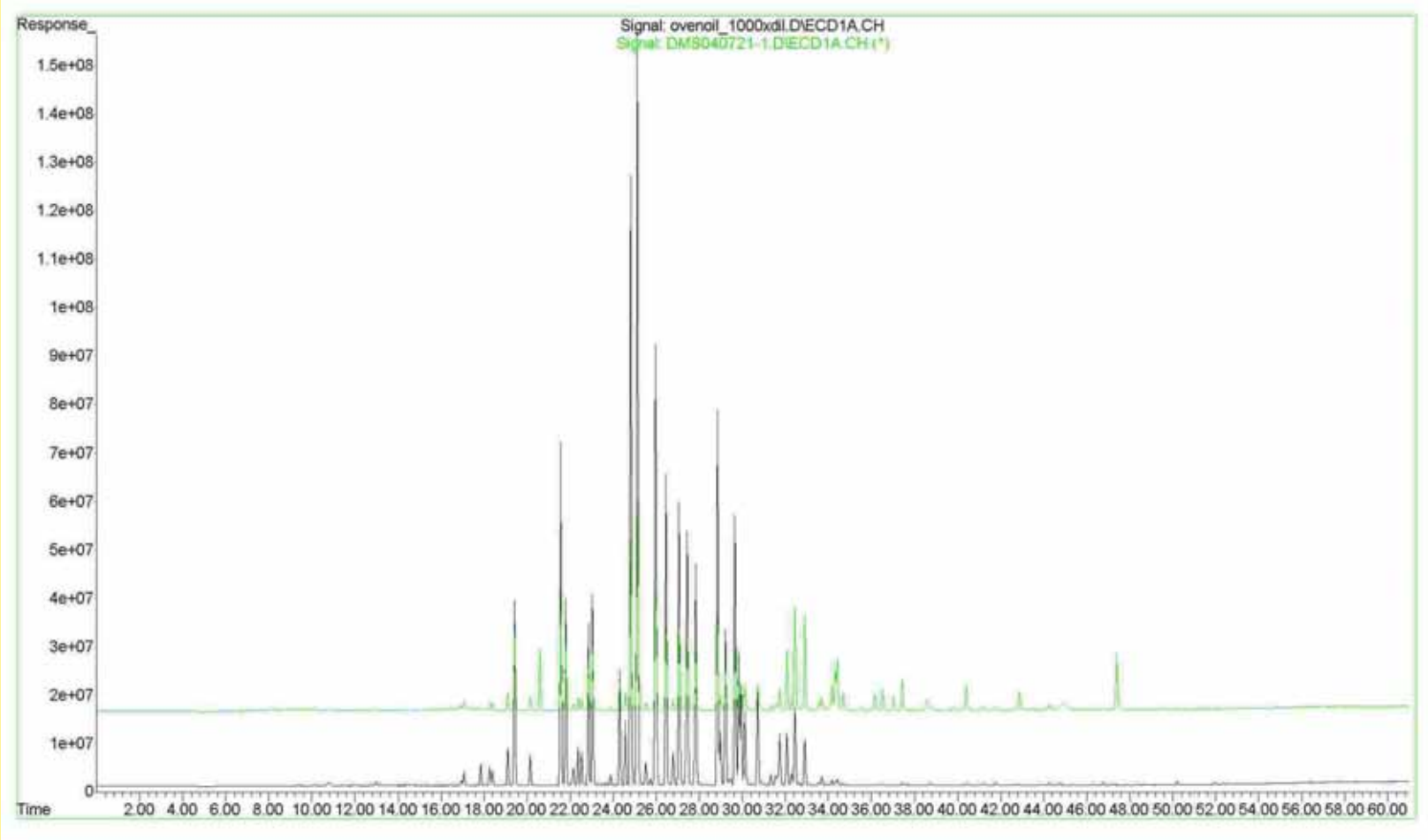
Aroclor vs. Congener Specific

- Aroclor patterns acceptable for fresh or unweathered spills
- Congener specific provides more accurate results in cases where aroclor pattern is altered or for mixtures of aroclors
- Roughly equivalent for unweathered samples but congener specific more versatile

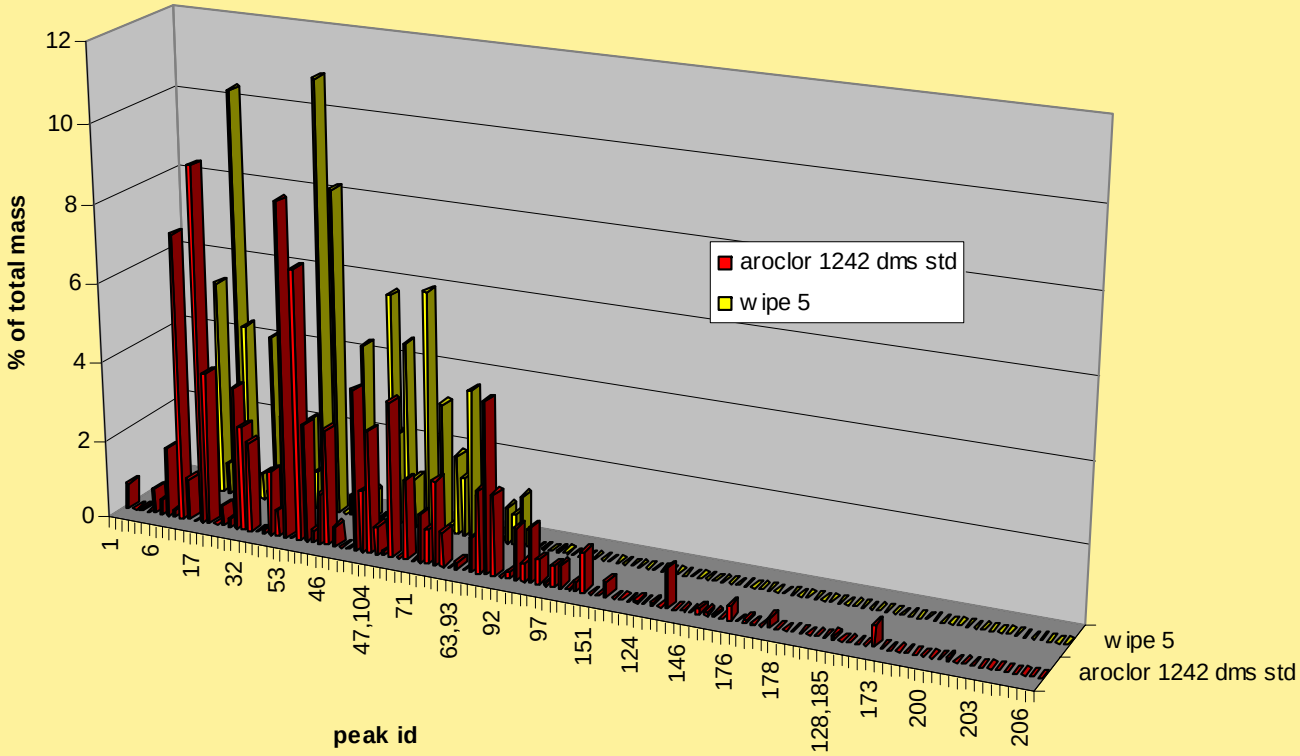
Aroclors on Ht-8PCB



Oil vs. Aroclor 1242



Floor tile Swab vs Aroclor 1242

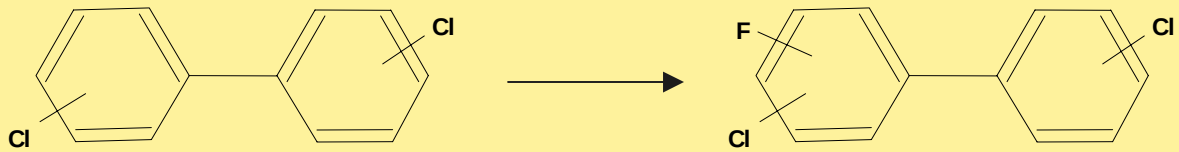


Aroclor vs Congener

- Comparison of aroclor quantitation vs. congener specific
- 1000 pg/uL Aroclor 1242, quantified by external standard =805 pg/uL
  - DB-XLB w coeluting peaks
  - Using PCBCong8 data from PCBID Page
    - No-coeluting peaks
    - Expected 780 pg/ul
    - Calculated 700 (~10% low)

F-PCB for Internal Stds and Surrogates

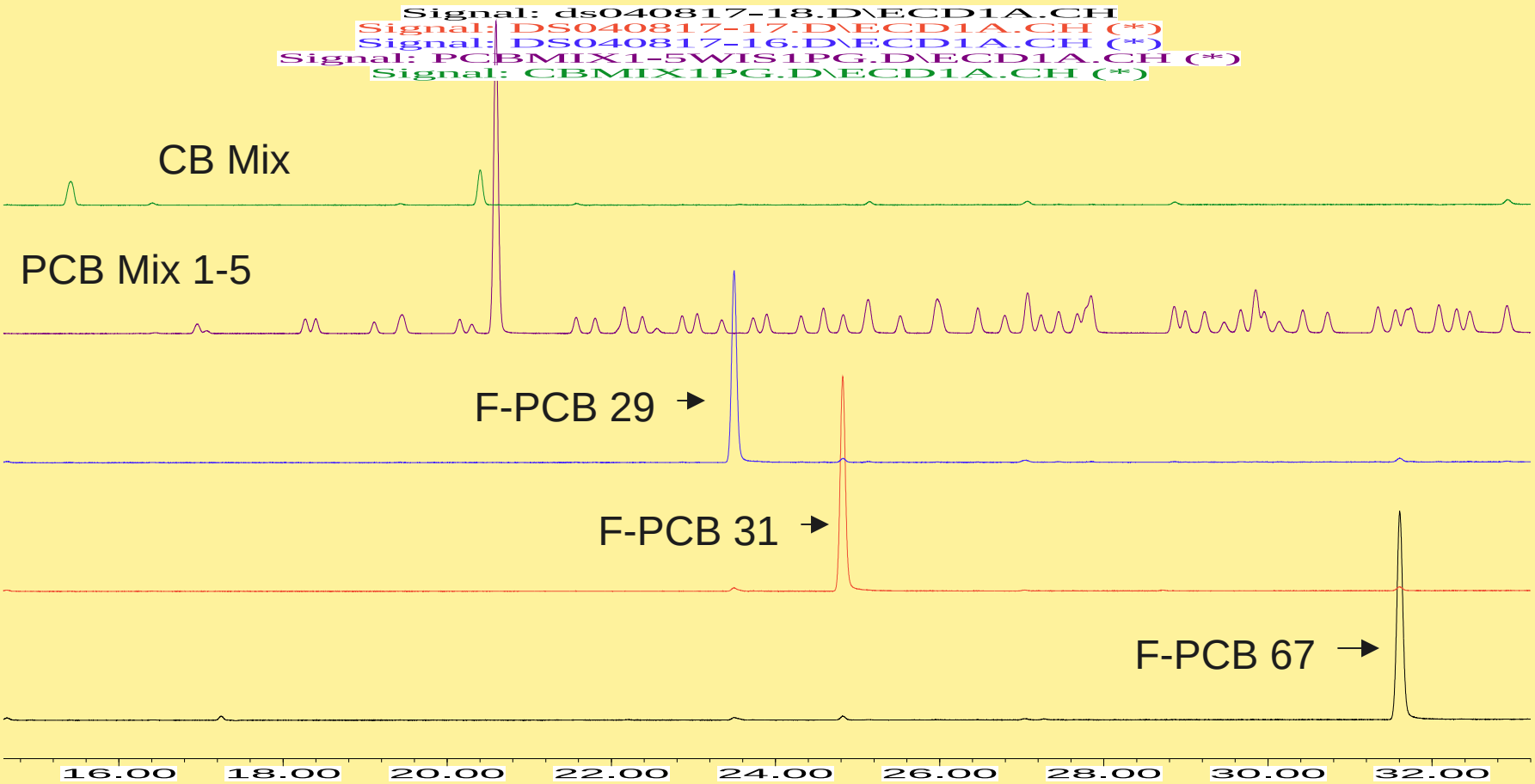
- F-PCBs are fluorine-substituted PCBs
  - i.e.



- F-PCBs
  - Possess similar physical properties
  - Different polarities = different retention times
  - Provide a source of surrogates and IS outside of the traditional “non-aroclor” PCBs
  - Possess different mass = good for GC/MS work
    - Allows GC-ECD and GC-MS analysis on same extract.

F-PCB Studies

HT8-PCB 60m Column



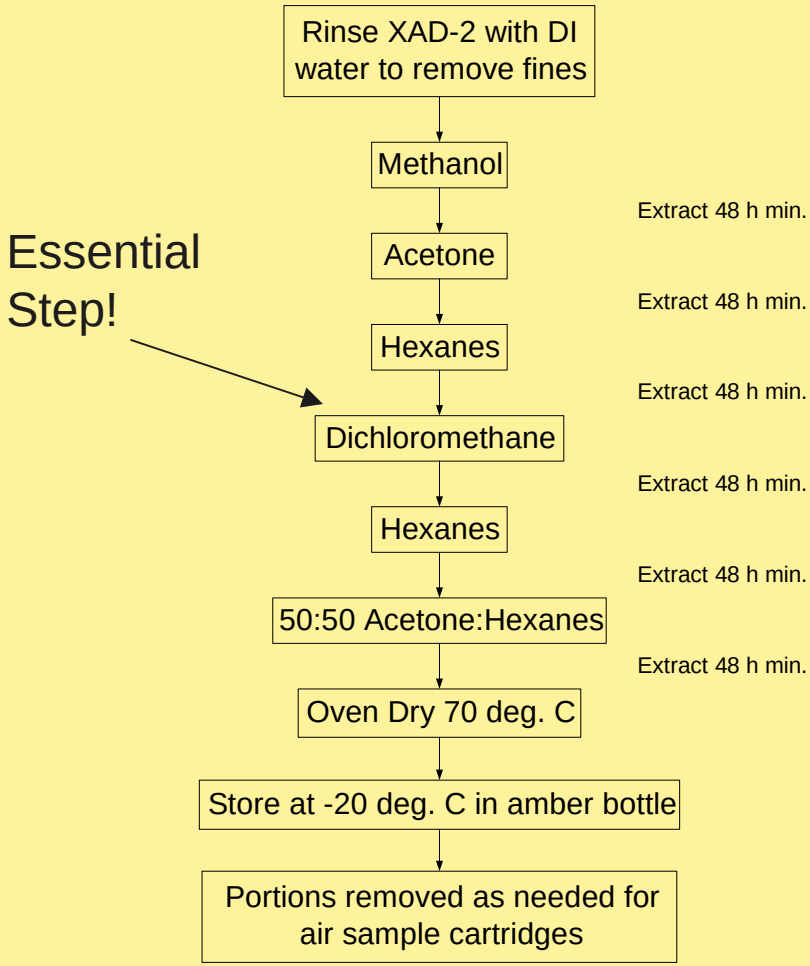
Project QA/QC continued

- Sampling
  - Mass flow controller calibrated using manometer
  - Calibrated timer used
  - Duplicate samples taken
  - Field blanks taken
  - Use of field surrogate compound (TCMX) investigated

Obtaining Samples

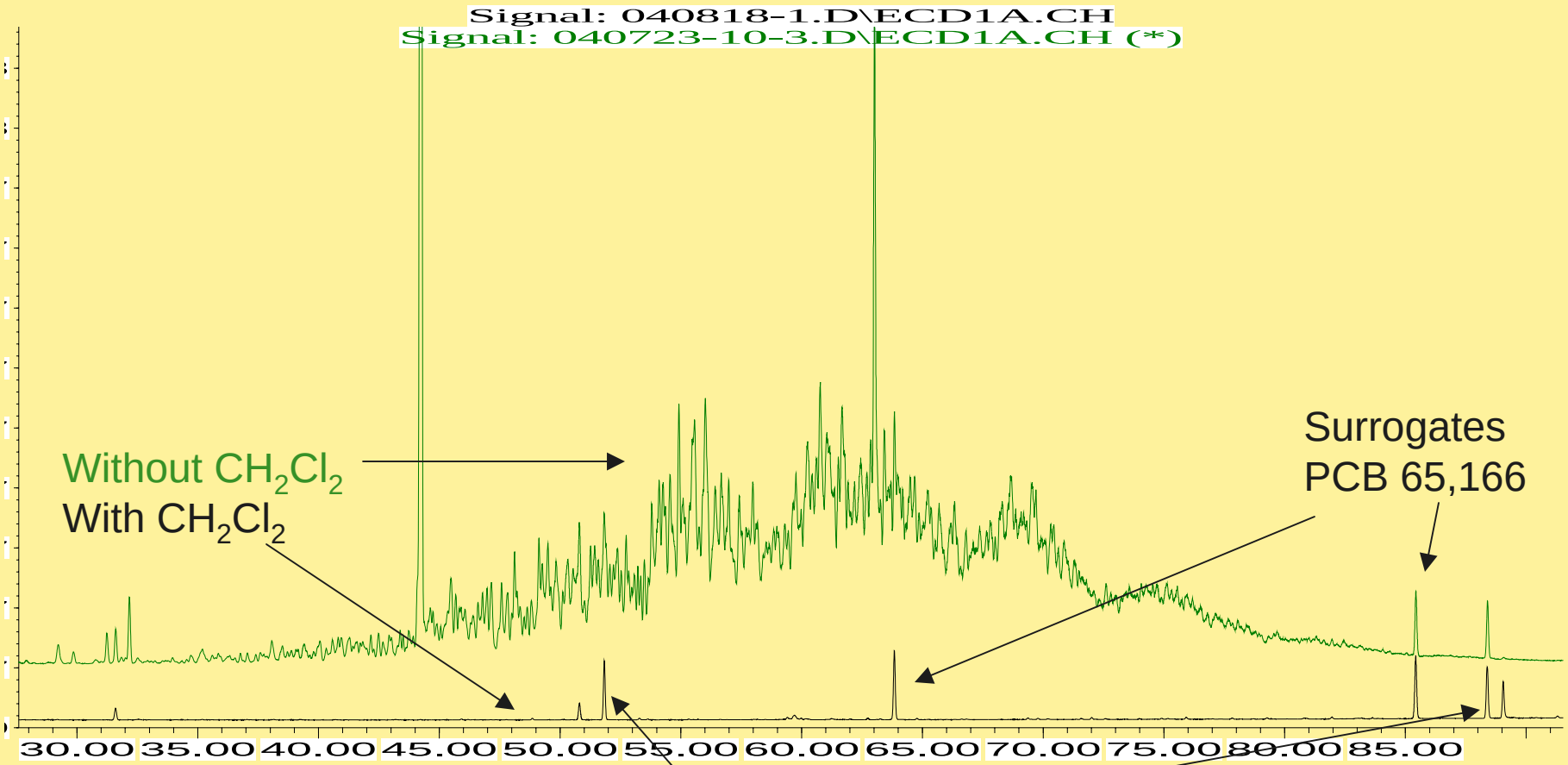
- Gas phase PCBs collected using XAD-2 resin (shown right)
- XAD-2 provides better loading capabilities than PUF plug and other resins
- XAD-2 is economical
- XAD-2 resin must be pre-cleaned prior to use

XAD-2 Pre-cleaning



- XAD-2 pre-cleaning steps listed to left
- Initially attempted cleaning procedure without use of CH_2Cl_2
  - Expensive
  - Toxicity
  - Disposal Costs
- Unfortunately…

XAD-2 Pre-cleaning

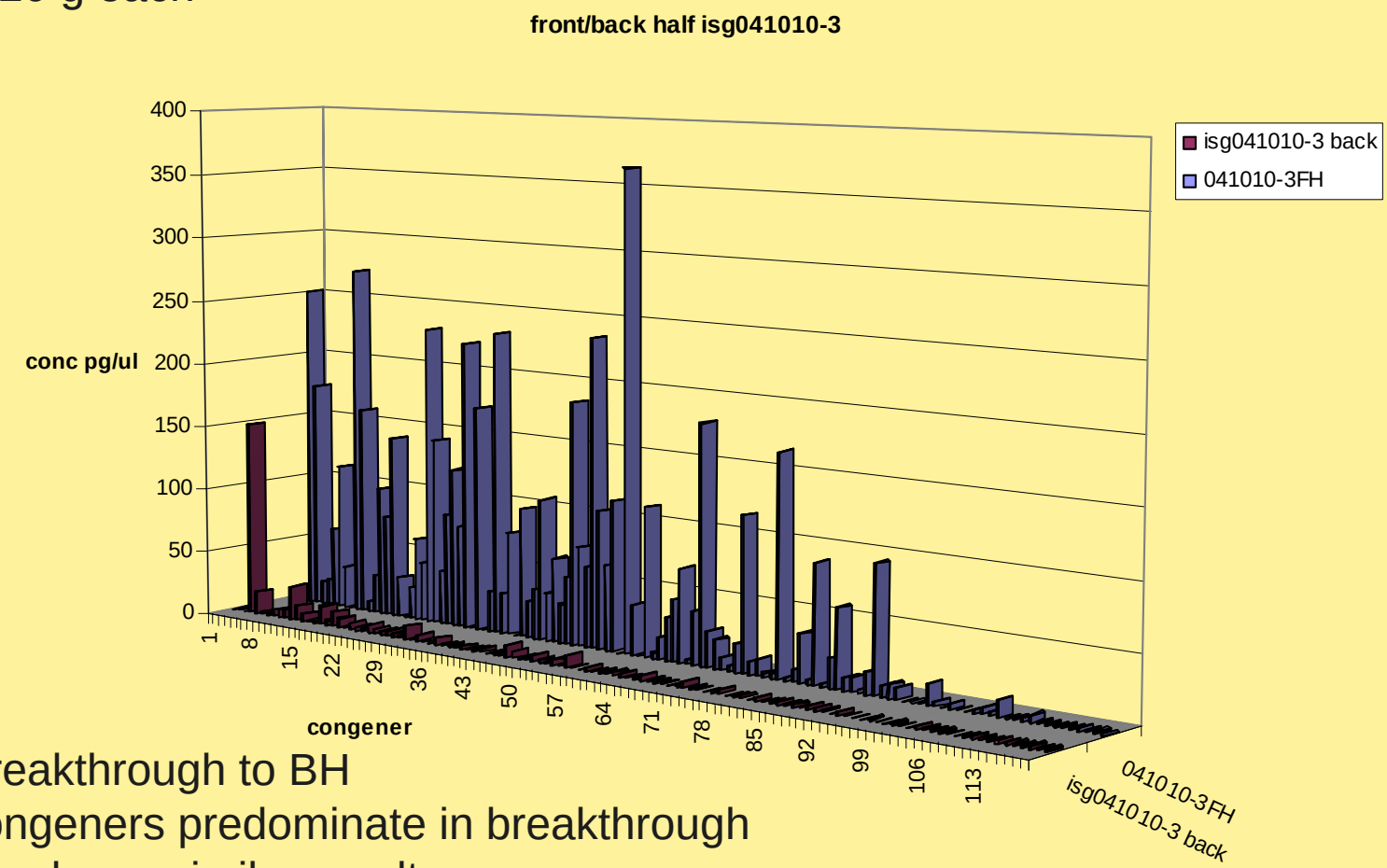


Amount of resin is important !

- Collocated samples outdoors (20g XAD-2)
  - 2.78 and 3.1 ng/m^3
- At PCB transformer
  - Collocated samplers 20g vs 40g
    - 20g < 40 g always
  - Is breakthrough occurring?

XAD-2 FH vs BH

20 g each



~ 10% breakthrough to BH
-lower congeners predominate in breakthrough
-duplicate shows similar result

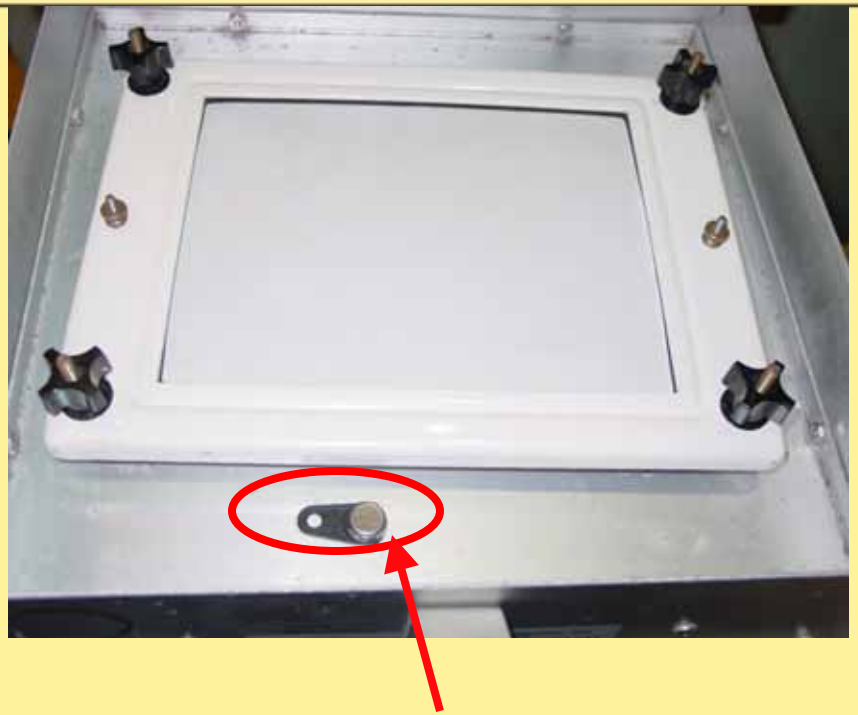
Sampling Results

- Preliminary UIC vs IIT data:
  - UIC average: 2.9 ng/m^3
  - IIT average: 1.9 ng/m^3

- Results consistent with previous studies (Basu, et al.)

Thermochron iButton

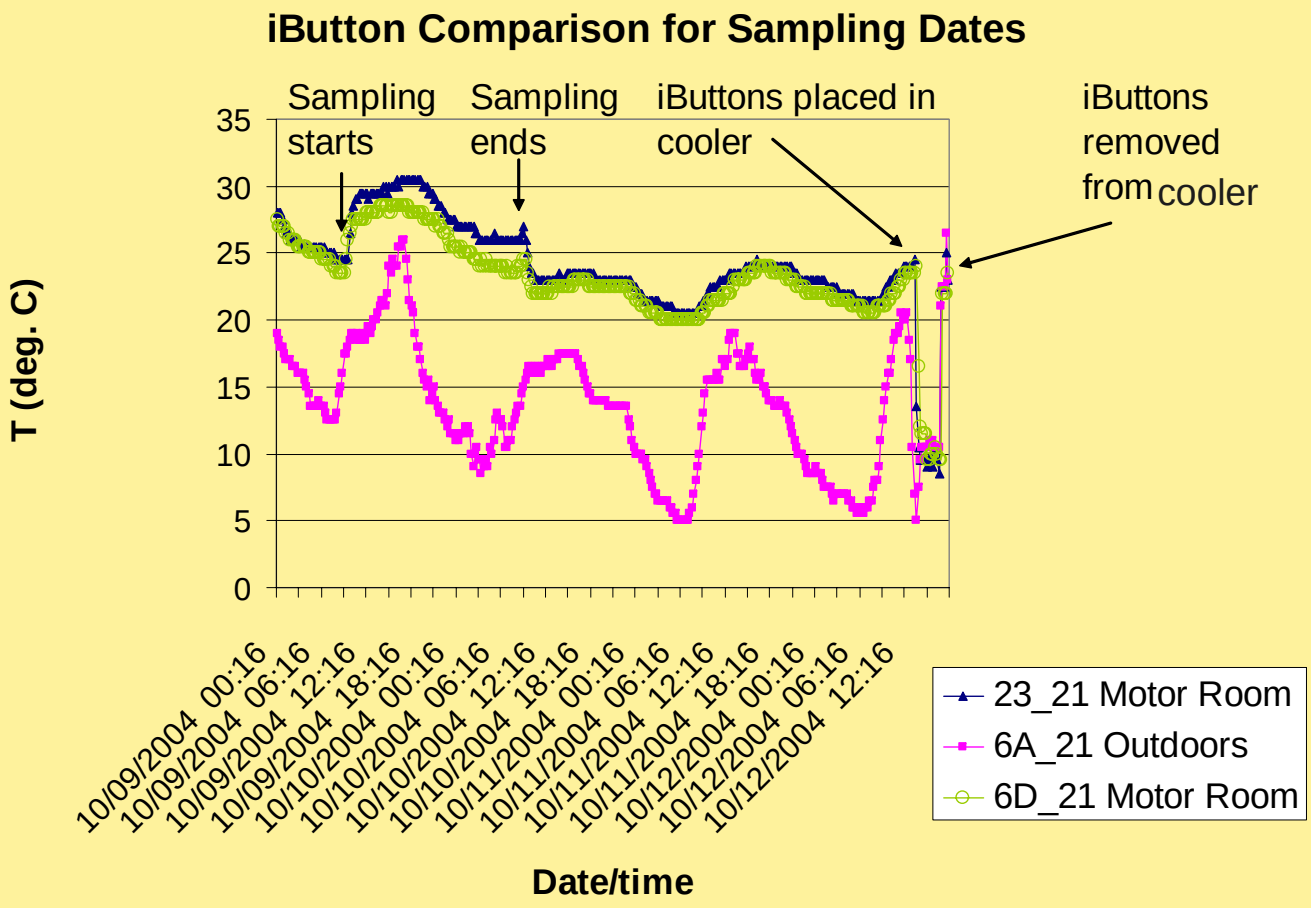
- iButtons acquired from DALLAS SEMICONDUCTOR MAXIM
- iButtons measure and log temperature
- Very sensitive to change in T (±0.5°C)
- Robust
- Low cost
- Small
- Ease of use



Why monitor temperature?

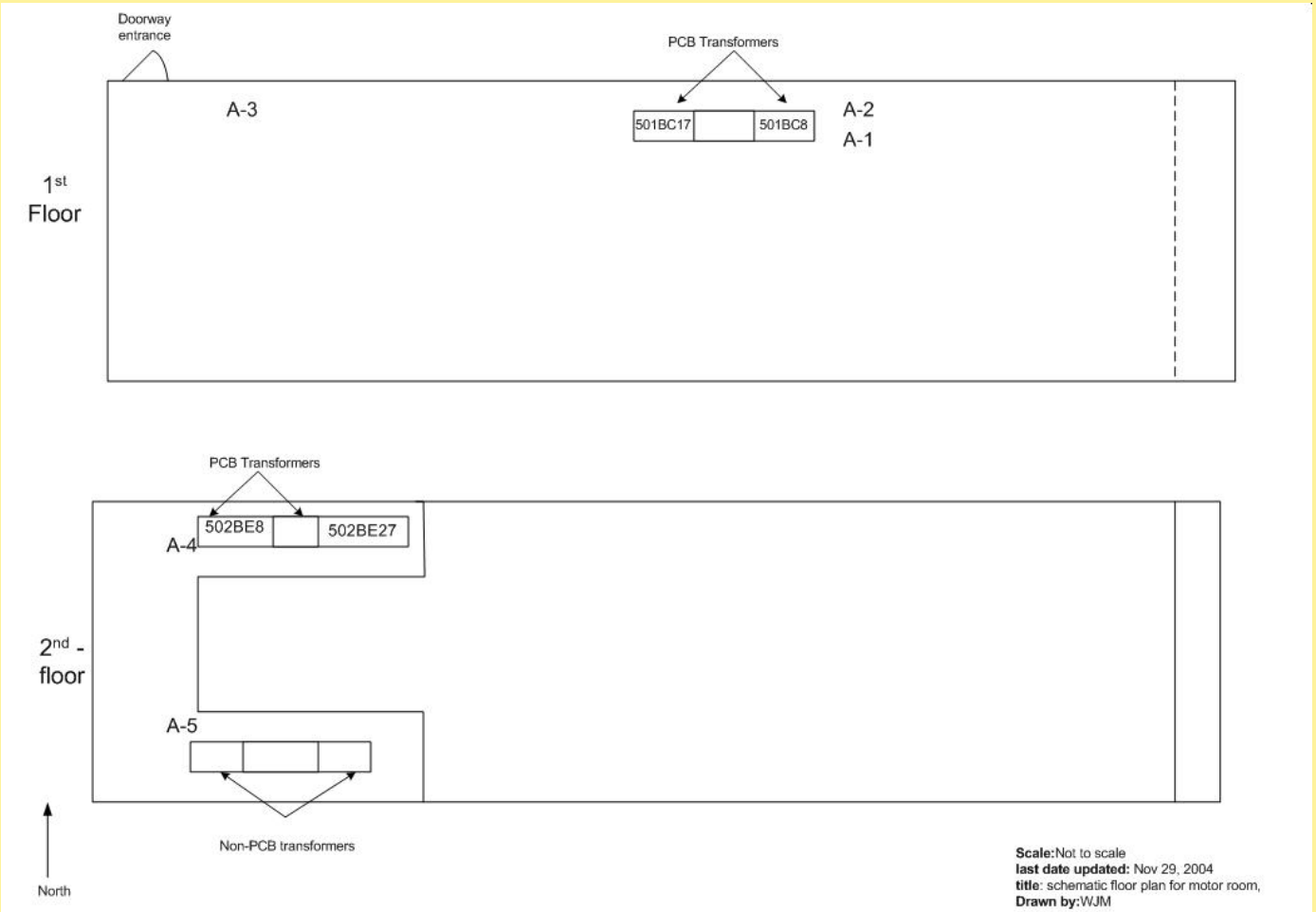
- Total flow calculations
- PCB volatility
- Sampler motor effects?

iButton Comparison



Air Sampling
-Operating PCB Xformers

•Steel mill with 50+ Operating PCB Xformers provided Access
-Sampling Jan., Sept.,Oct. , Nov.



1 additional sampler at env. office

Outdoor Air at Site

Indoors

Large volume (1.59E5 M^3) and air flowrate (2.2E4 m^3/min)

PCB vs Non-PCB Xformer

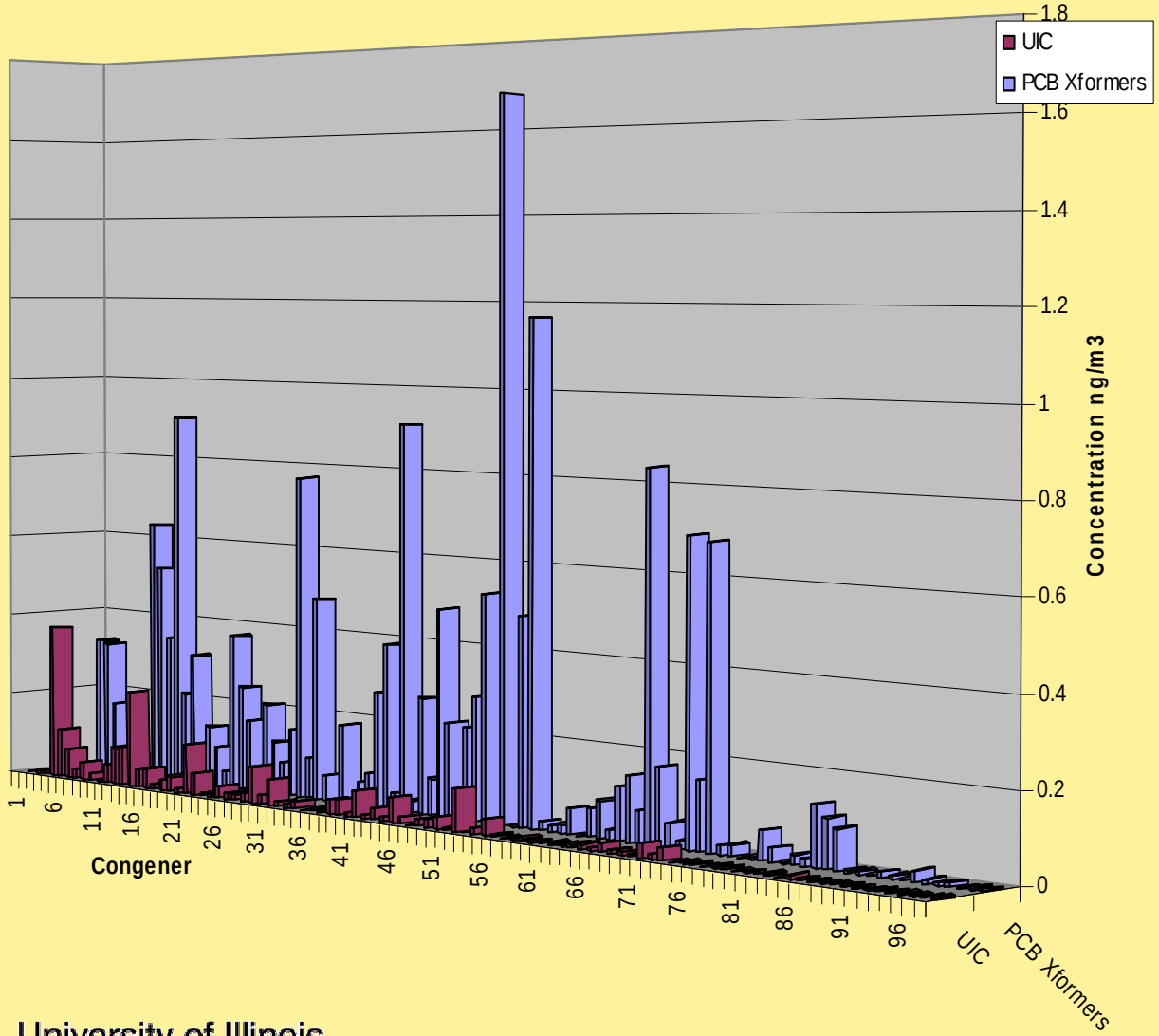
Askarel Xformers Replaced by non-PCB

Note firewalls: not needed with original Askarel xformers

Sampling Results

- Preliminary sampling results
  - Air near PCB Xformers results average 5X higher than UIC outdoor results
  - Initial XAD-2 weight not sufficient for loading ssamples near PCB Xformers (20g v. 40g)
    - Subsequent sampling with 40 g
- > 60 samples obtained to date
- Not all samples extracted
  - Stored in freezer
  - Extraction needed to confirm initial results
  - determine if loading is appreciable
  - determine variables affecting concentrations
- Source profiling still possible!

PCB Concentration Profile



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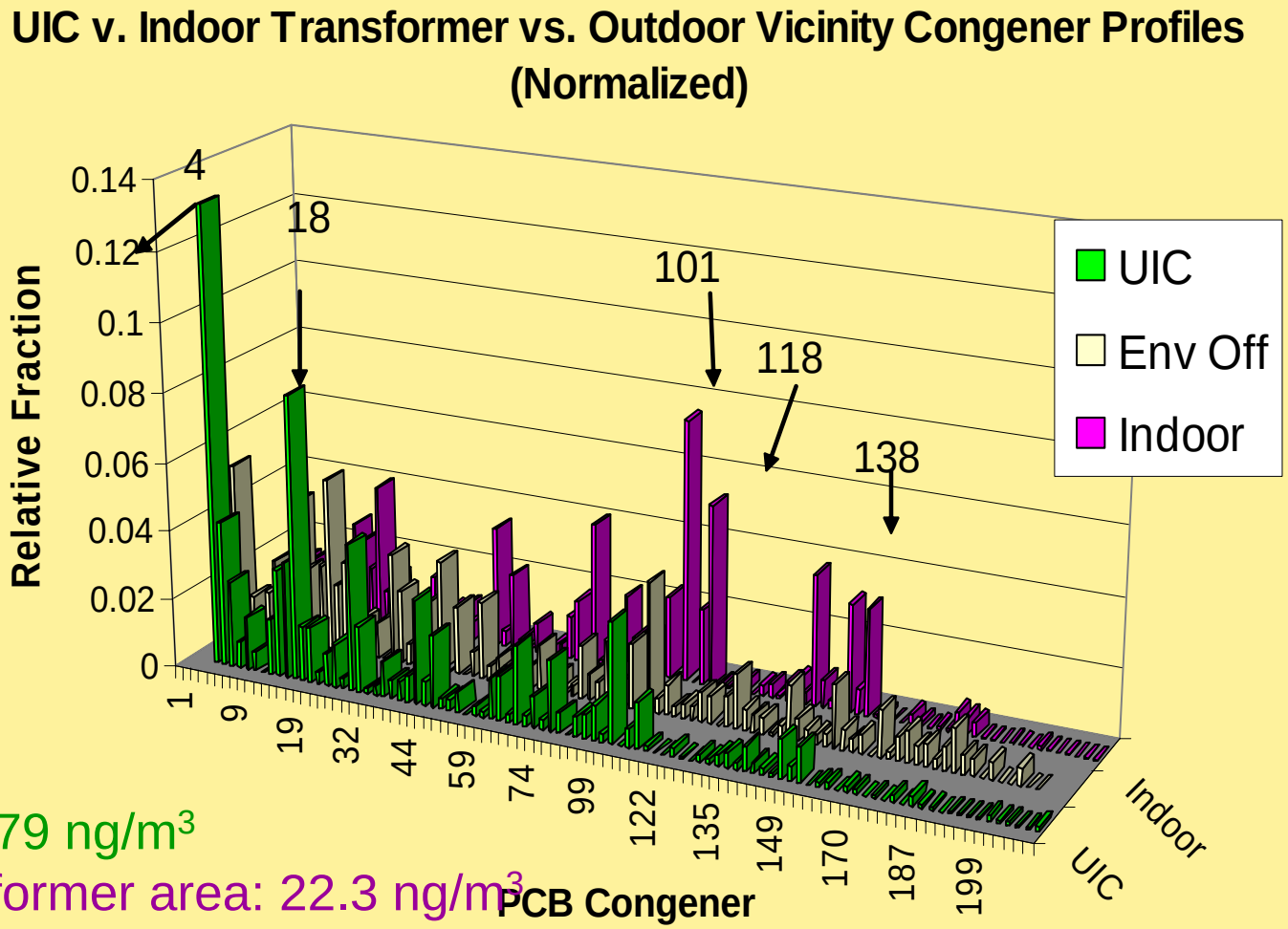
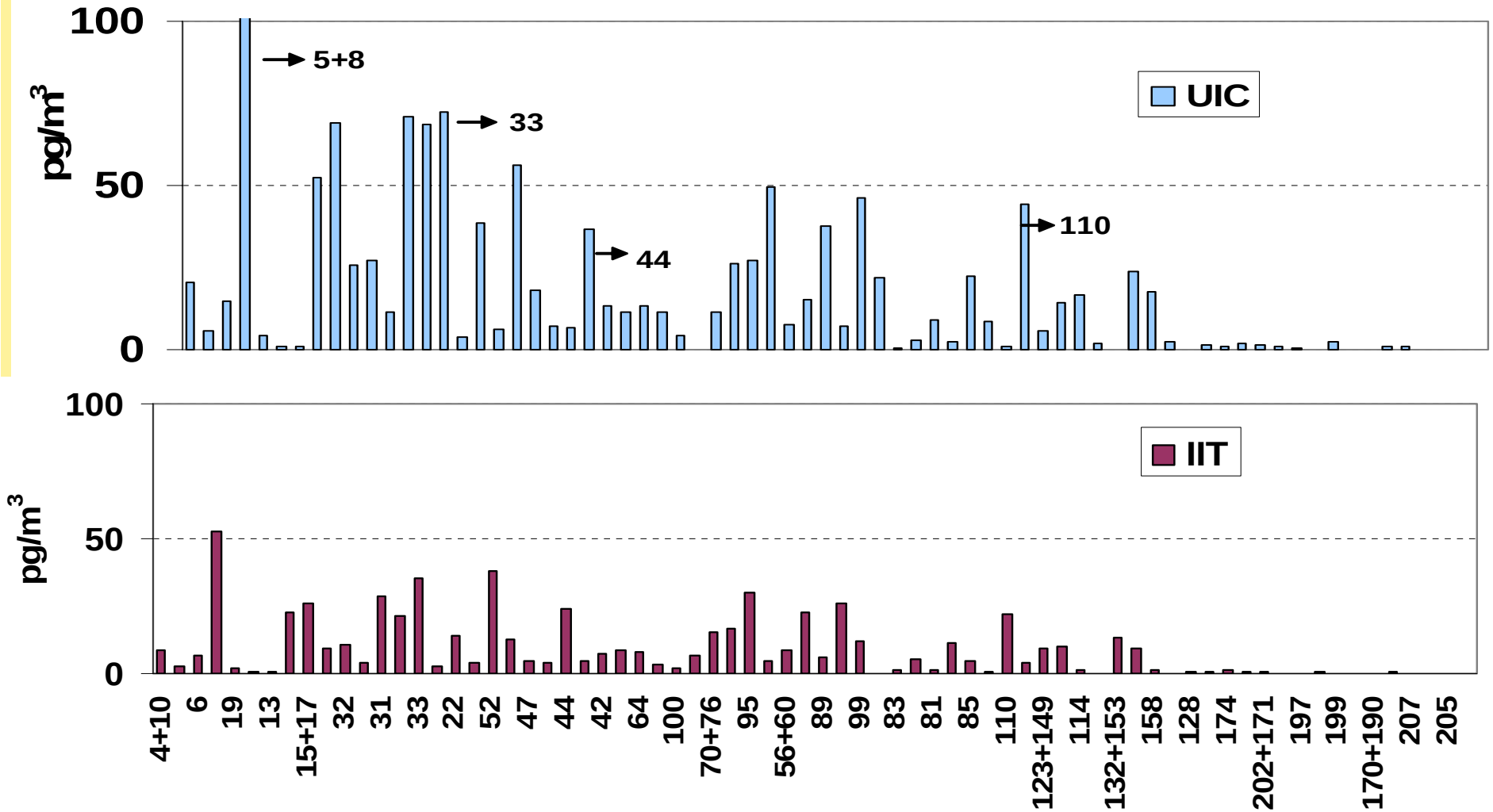
Different Profiles



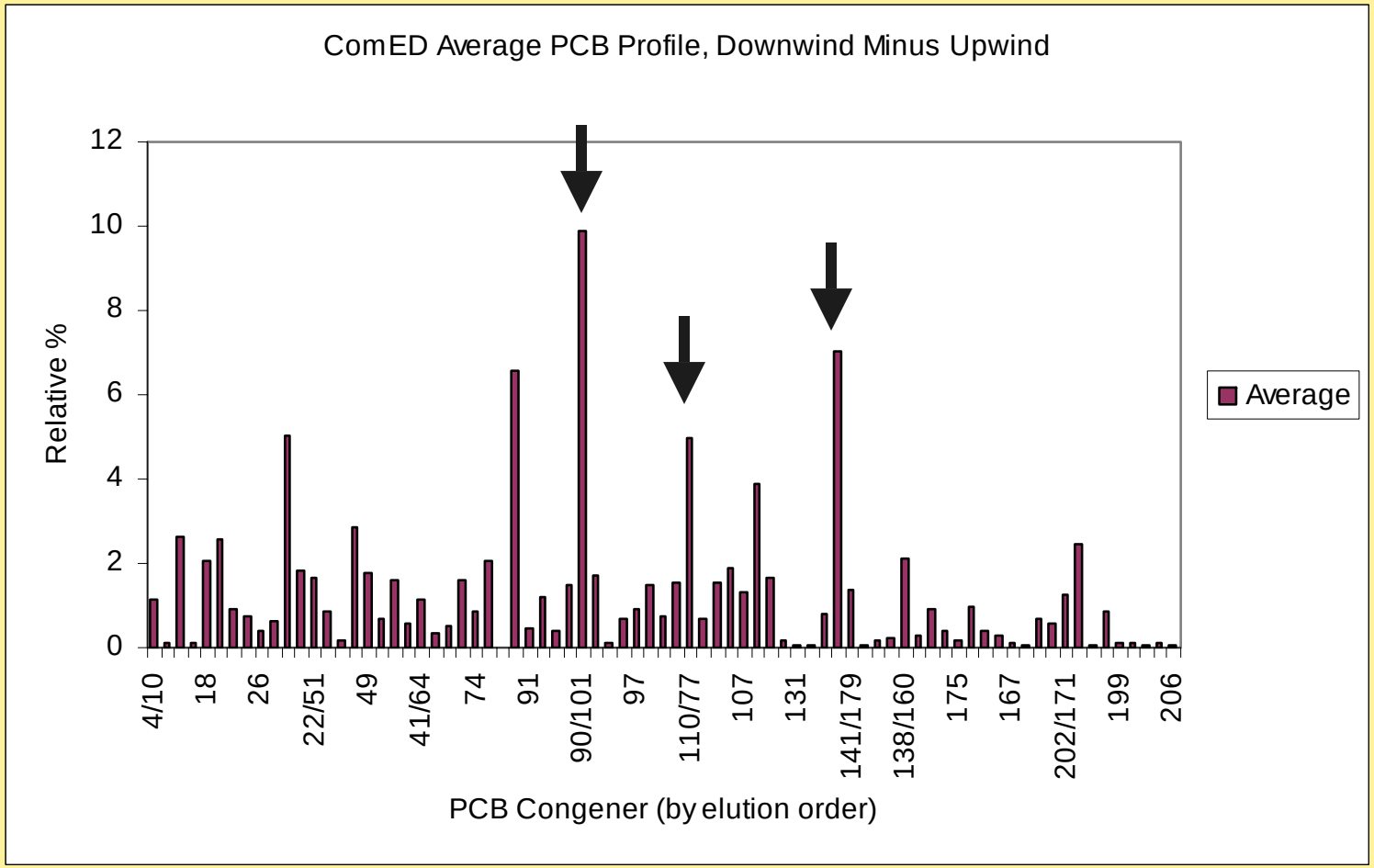
UIC: 2.79 ng/m^3

PCB Xformer area: 22.3 ng/m^3

The PCB Congener Pattern in Air Vapor from Two Sites at Chicago, 4/9/02

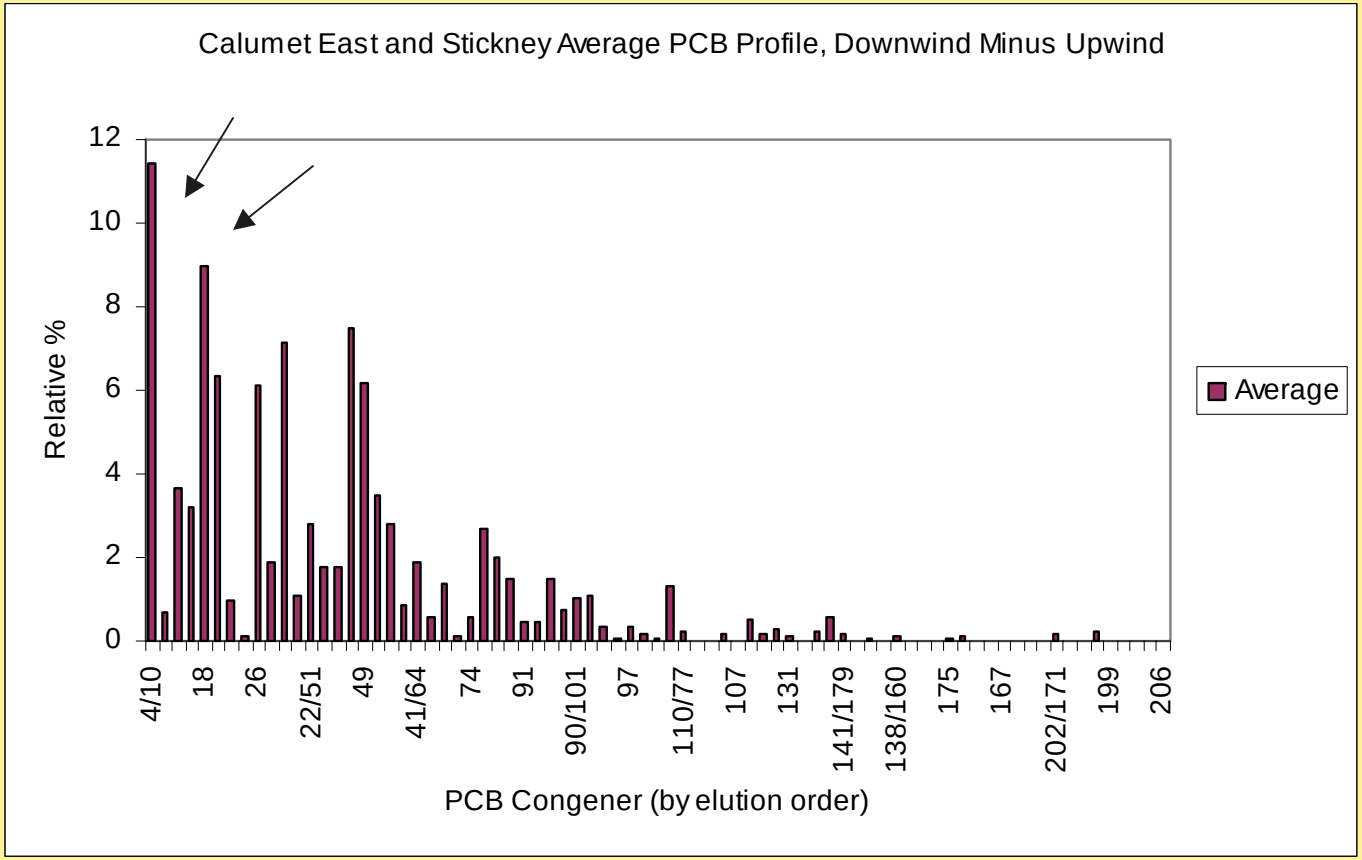


Transformer Storage Yard



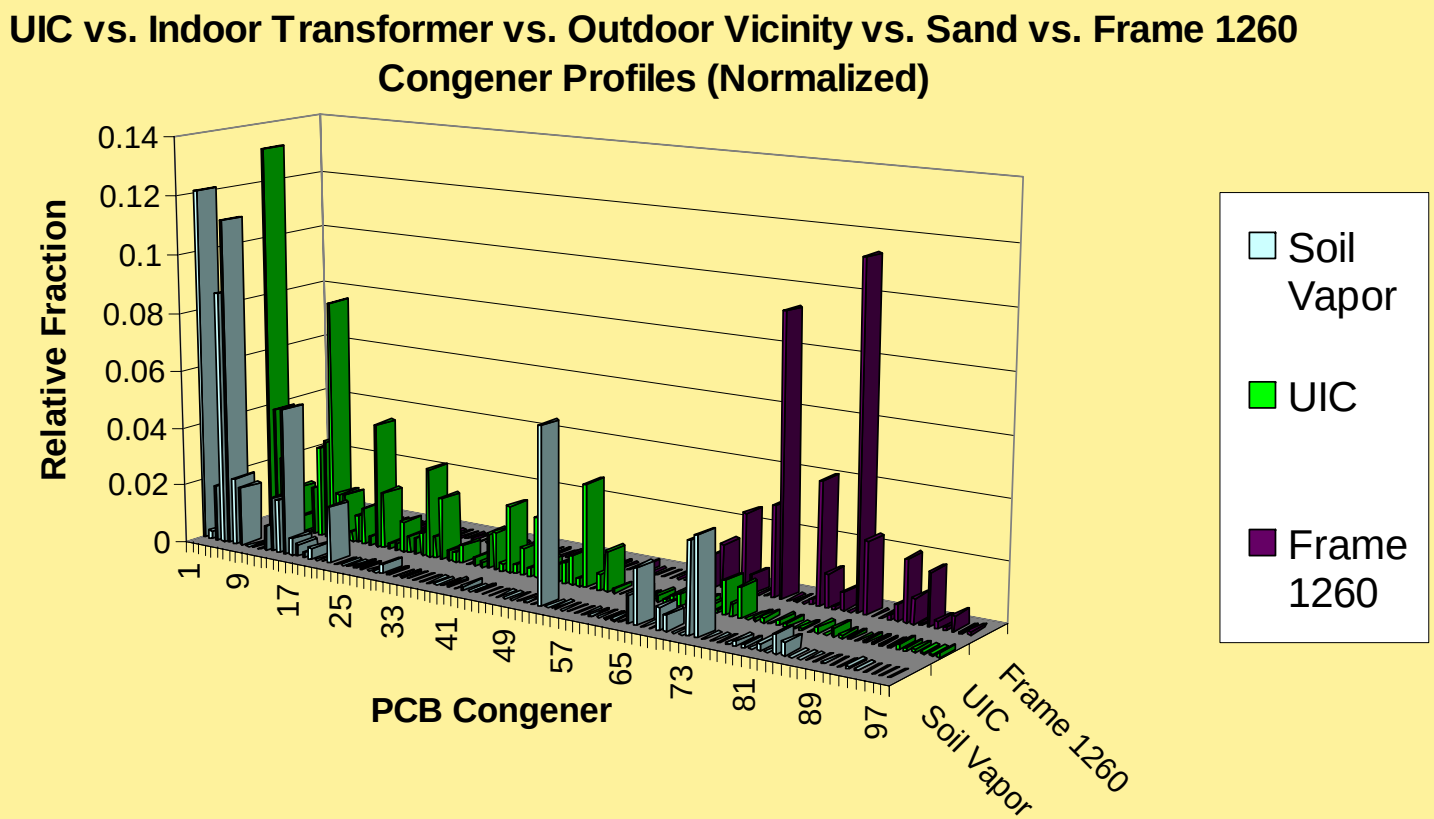
Hsu et.al. Env. Sci. Technol. (2003)

Sludge drying beds



Hsu et.al. Env. Sci. Technol. (2003)

PCB Profiles



Soil vapor from mills et al ET&C Oct. 2004

Conclusions

- Improved PCB analytical methods
  - Speed
  - Resolution
  - sensitivity
  - Accuracy & precision info
- good precision from sampling
- PCB concentrations are elevated

Issues

- PCB concentrations are elevated near operating PCB Xformers
  - What from?
  - repair status
  - Seasonal changes
  - Profiles
  - Mass emissions
  - Controlling factors
  - representativeness

Future Work (2004)

Further exploration of F-PCBs
- Use as internal standards
- Use as field and/or extraction surrogates

- Sample Extraction and analysis
  - Filter vs. XAD-2
  - Setup and use of an ion trap GC-MS
  - Analysis using med-res. MS?
  - Second column confirmation

- Examine activity- emissions relationships

- Passive sampling campaigns
  - Around PCB transformers
  - Transformer decontamination facility

Future Work (2005)

- Additonal sampling at the same and additional locations during warmer periods and the installation of passive samplers so that seasonally integrated samples may be obtained
  - Tranformer decontamination facility
  - Poorly maintained Xformers
  - Xformer storage yard
  - Removl of PCB xformers from service for disposal
- Dioxin-like PCBs
- Estimate air emission estimates (kg/yr) for each of these sources
- Determine the relative importance of these emissions with respect to environmental impact
- Develop source “fingerprints” for use in Multivariate Data Analysis
  - PCA
  - Q-Mode factor analysis
  - receptor modeling

Passive Sampling

Acknowledgements

- Funding Sources
  - USEPA Region V
  - USEPA HQ
  - Illinois EPA
- Unnamed steel mill
  - Facility access
- Tisch Environmental
  - Donation of a HiVol Sampler to project
- Chiron Inc.
  - Donation of F-PCBs
- SGE Inc.
  - Donation of 60m HT8-PCB column, and others

Disclaimer

This presentation has not been reviewed or approved by any of the above groups.

Questions

- Any questions or comments would be greatly appreciated!
- References available upon request