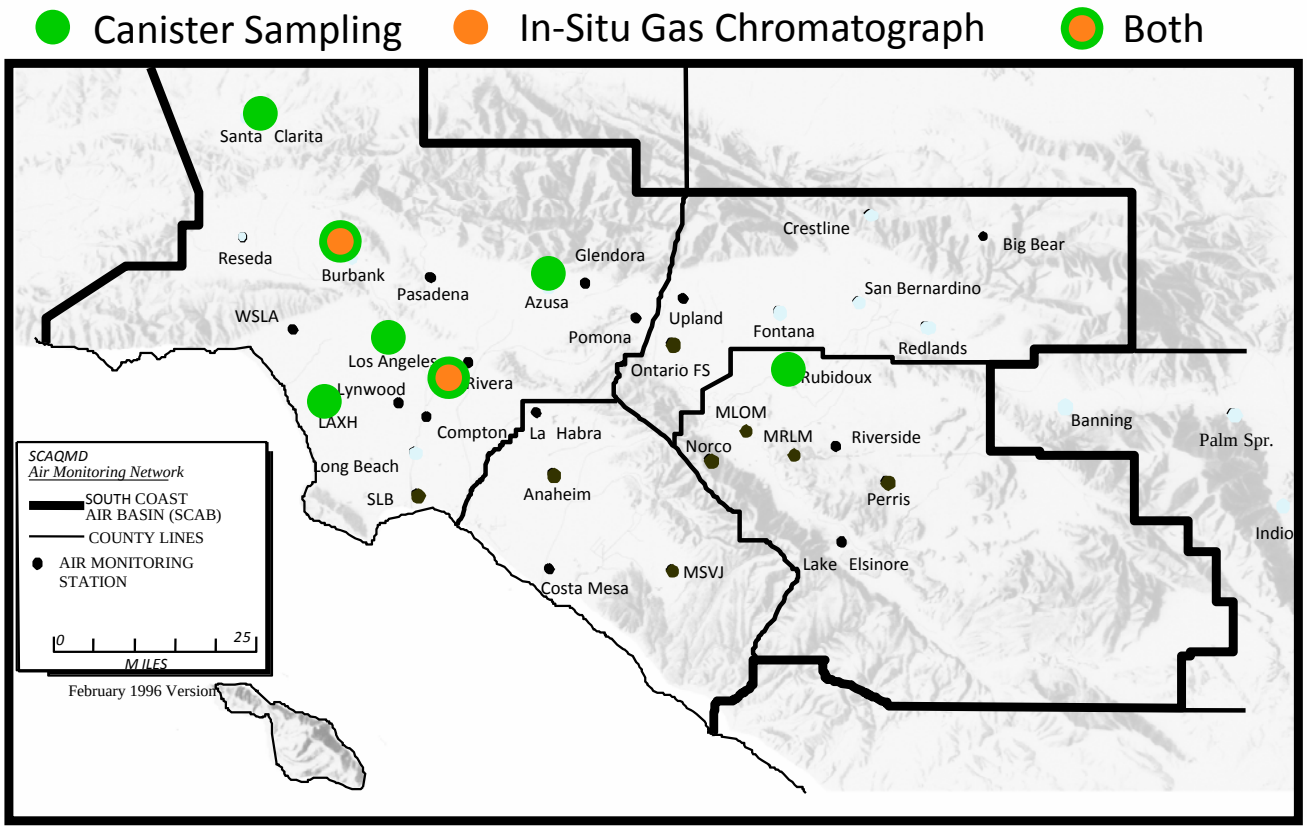
Developing Together: A Local PAMS GC Analysis Method and U.S. EPA Regional Performance Evaluation Program

South Coast Air Quality Management District/U.S. EPA Region 9

National Ambient Air Monitoring Conference

May 16th, 2012

SCAQMD PAMS Sites/ Methods



Region 9

- Jurisdiction

- Several PAMS programs in Region 9

- Initiated Performance Evaluation (PE) Program to compliment Technical Systems Audits and have an assessment of PAMS VOC Analyses of agencies within the Region

- Survey different PAMS analytical methods being implemented

- PAMS PE's not funded individually so Regional funding supported

Arizona, California, Hawaii, Nevada, Pacific Islands & 147 Tribes

Performance Evaluations

- Definition:
  Assessment of quantitative data generated in a measurement system that are obtained independently for evaluation.

- One tool from the QA Toolbox (technical systems audit, lab audits, field audits, data tracking, control chart review, etc.)

- Target analytes & concentrations known to evaluators but unknown to lab

- Effective and inexpensive means of assessing lab performance

Performance Evaluations: Importance

- Assessment of current analytical methods

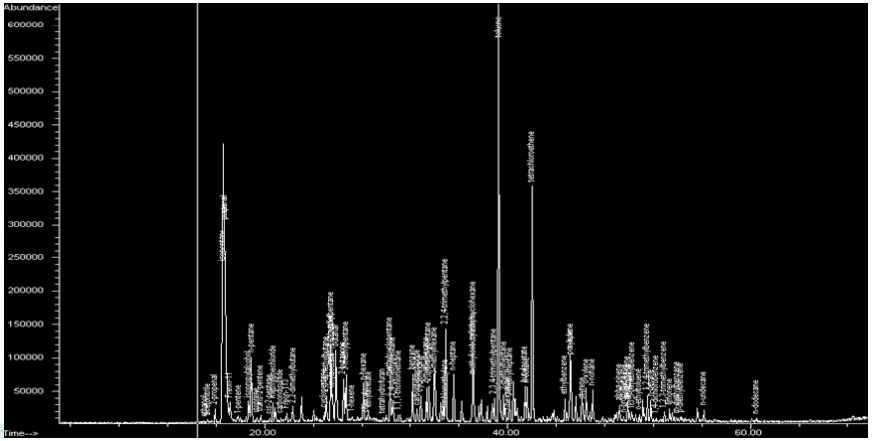
- Establish comparability between agencies
  - Gas standards
  - Instrumentation
  - Analytical Methods

- Findings may give indicators of potential analytical issues
  - Potential to improve methodology and technical guidance

- Trend of performance over time

Performance Evaluation Considerations

- Analyte Selection
  - Calibration Compounds
  - Challenge of the long chain hydrocarbons
  - Lighter, more volatile representative
  - Prevalent pollutant
  - Overlap with BTEX (TO-15) Analysis
- Concentration Levels
- Single or Multiple Samples
- Timing



Initial Performance Evaluation (2009)

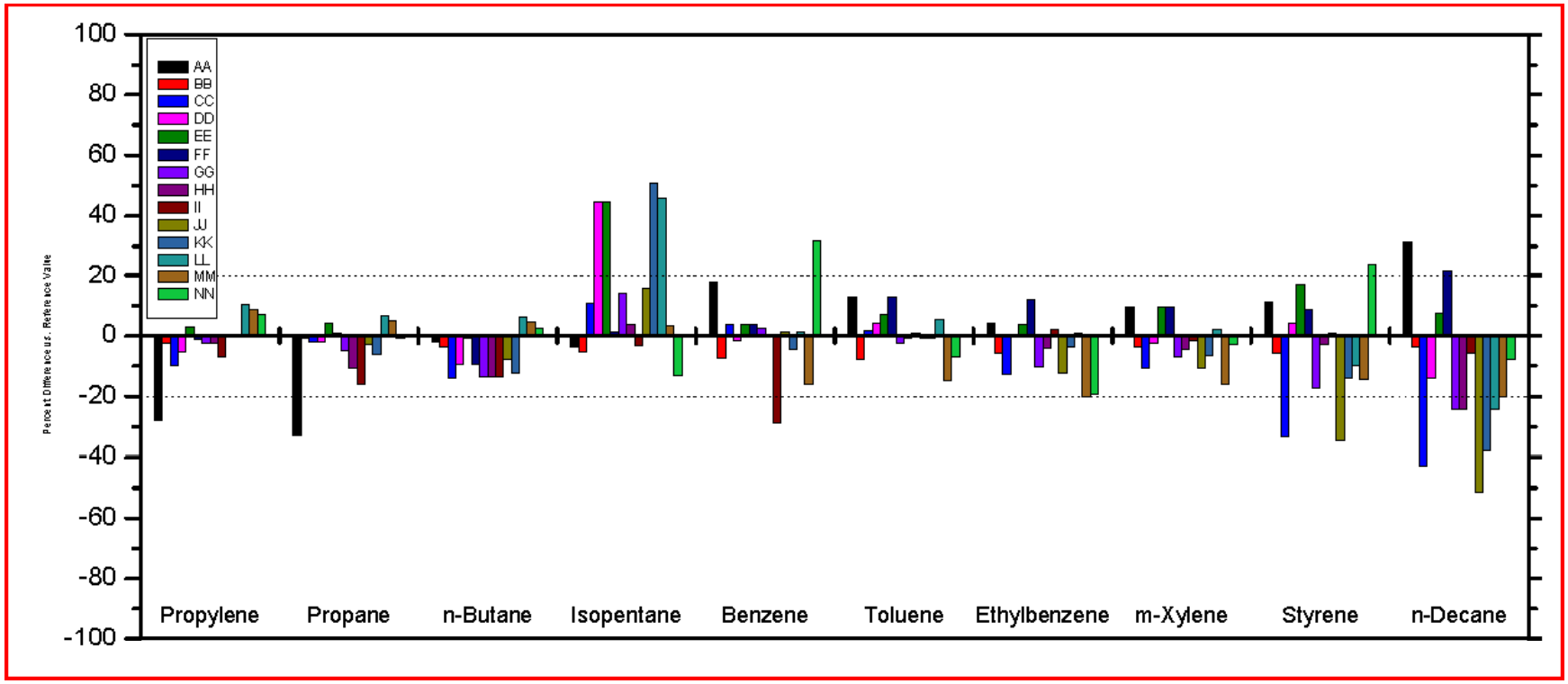
- Analytes Selected

Propylene	Benzene	m-Xylene
Propane	Toluene	Styrene
n-Butane	Ethylbenzene	n-Decane
Isopentane		

- Gravimetric Preparation of Master
  - Raw Materials transferred to inert cylinder
  - Balance: Humidified zero air
  - Transfer manometrically to 6L canisters

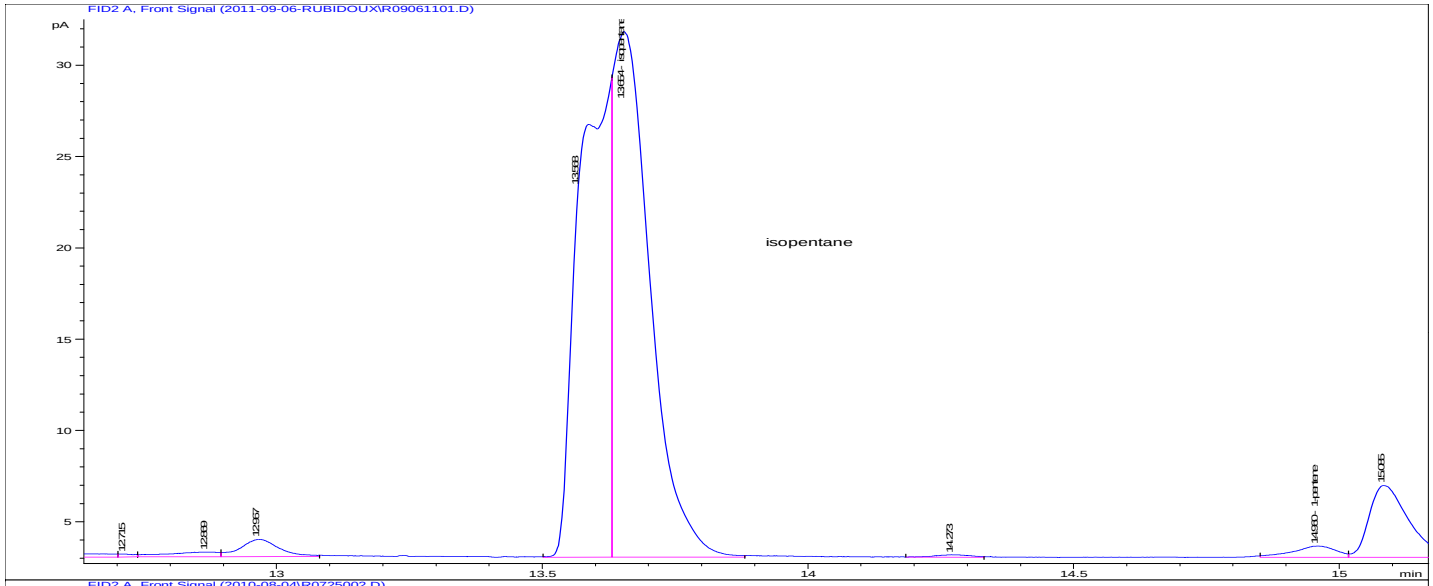
- Analytical Check
  - +/- 5% of Gravimetric

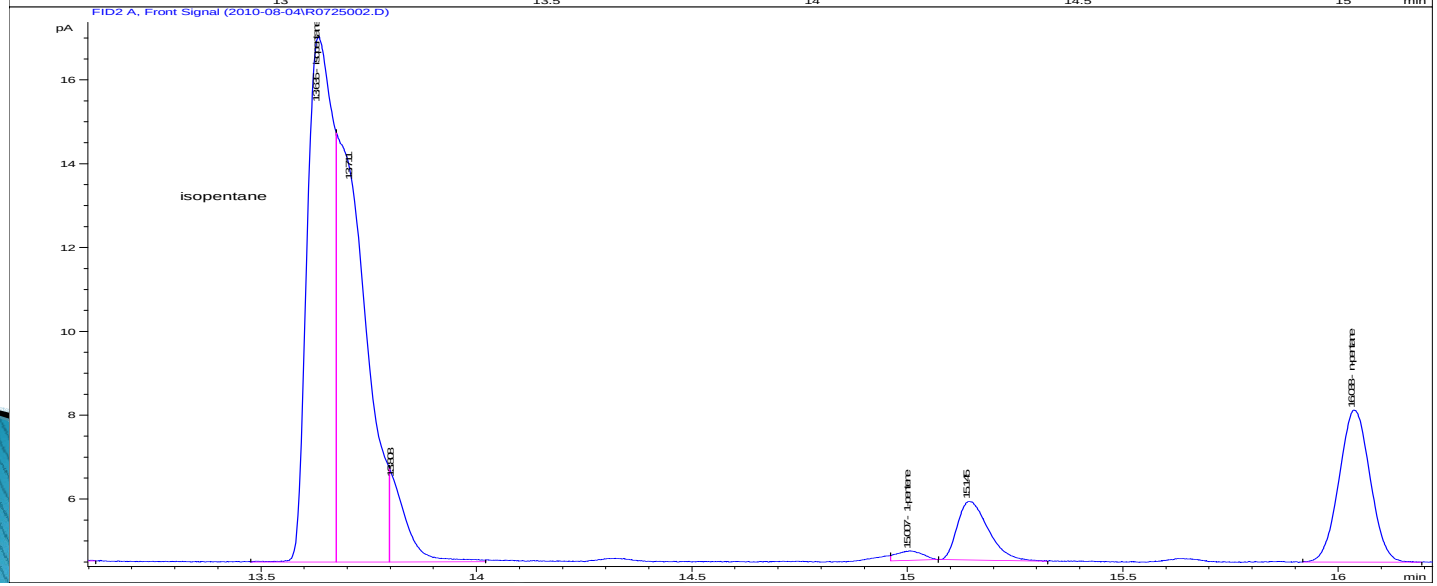
Results: All Participants



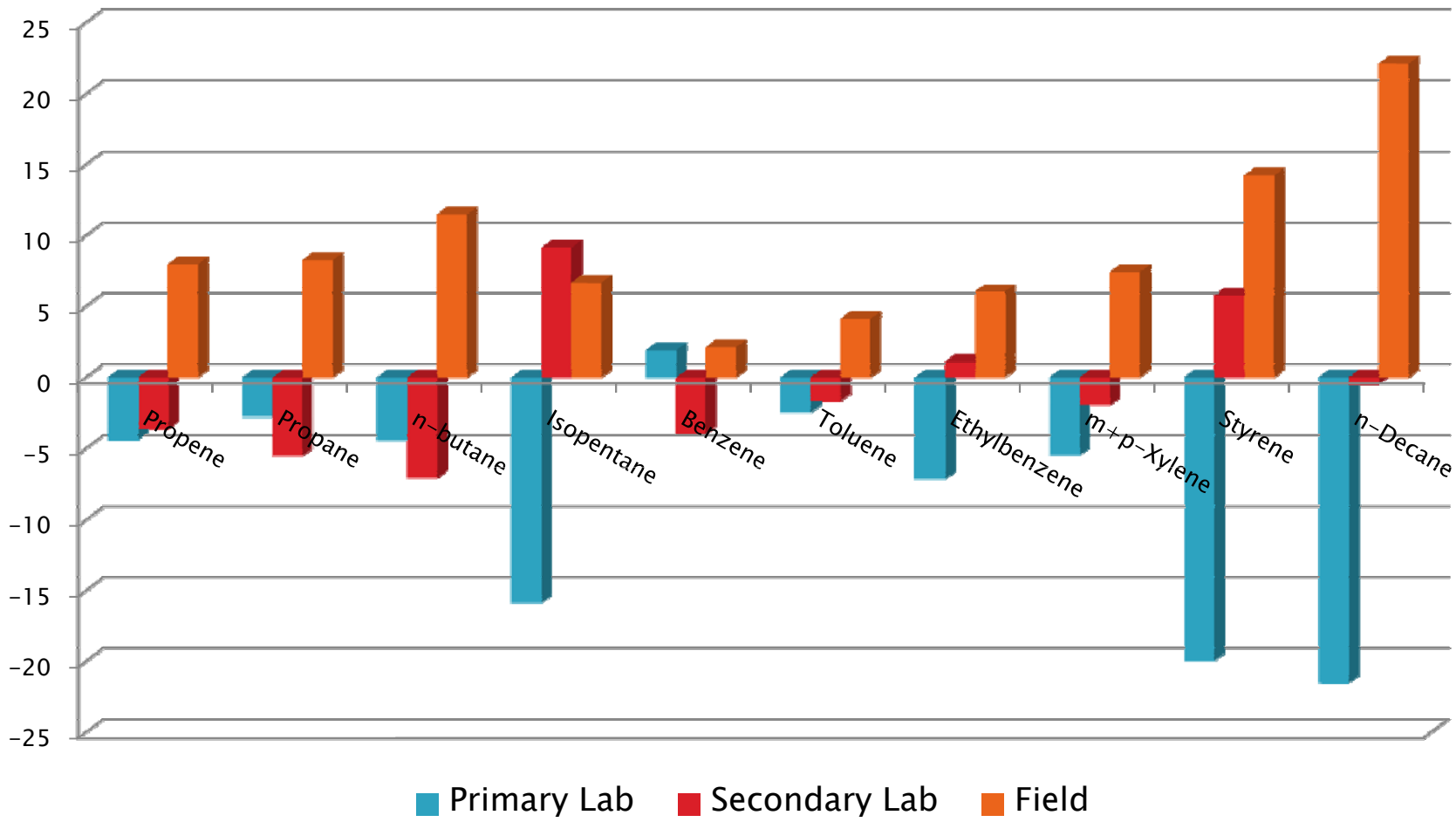
2009

PAMS VOC Analysis: Isopentane

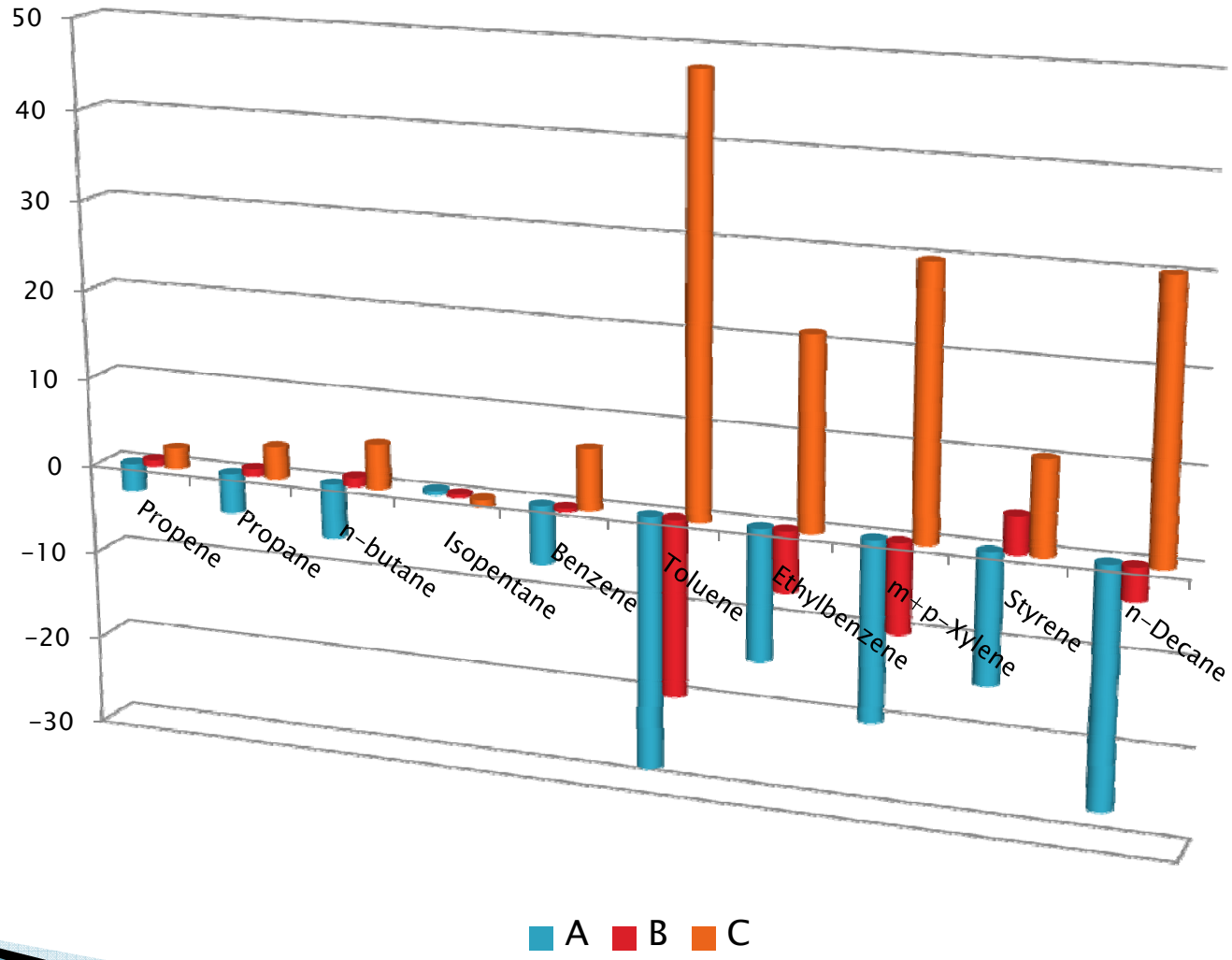




AQMD Results: Precision



Results: Audit Sample Variability



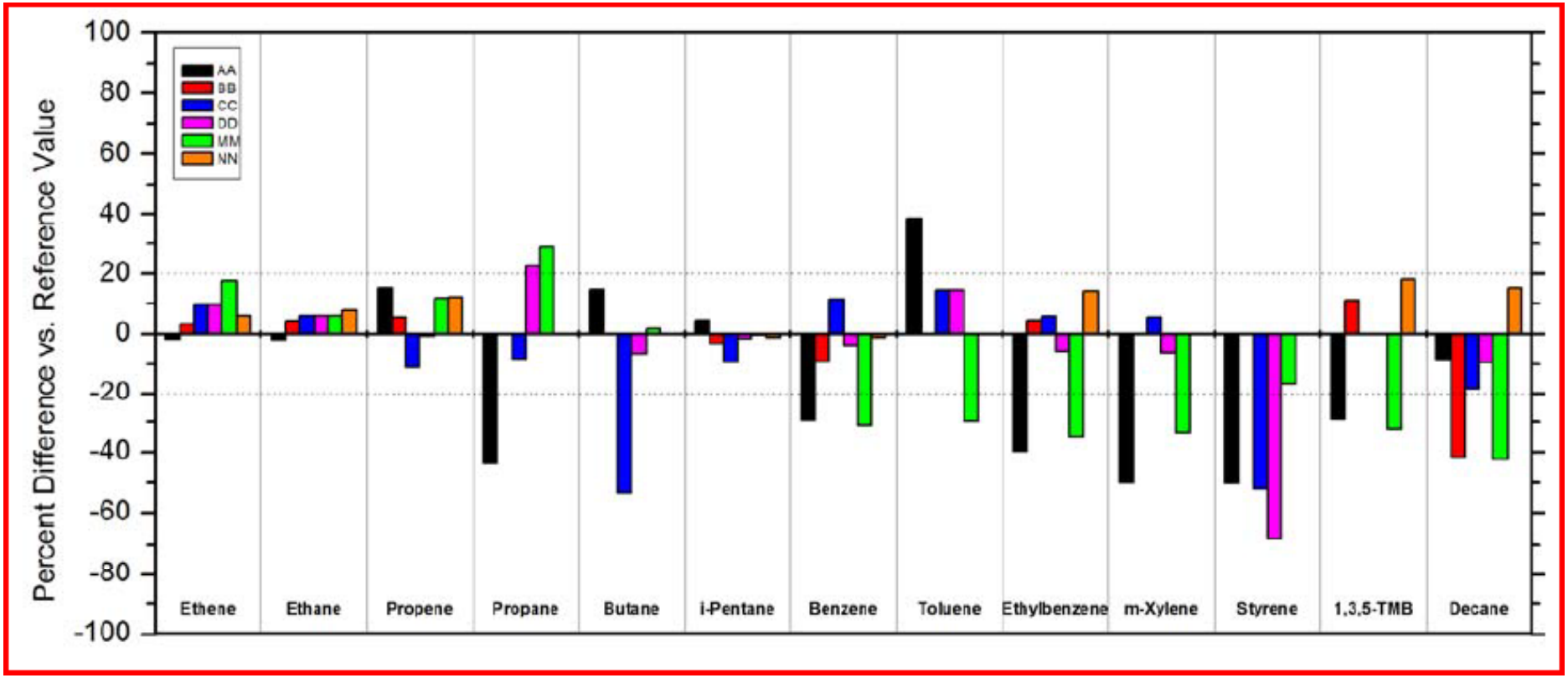
PE Program: Lessons Learned

- Positive feedback from local agencies and worthwhile to continue.
- High confidence in stability of performance samples of C3 through C6 compounds.
- High variability on the heavier compounds (styrene and n-decane) in audit samples.

PE Program: 2010

- Lower Concentrations (0.3 to 3 ppb)
- Addition of lower boiling compounds
  - Ethane
  - Ethene
- Addition of one more aromatic
  - 1,3,5-trimethylbenzene

2010 Results: All Participants



PE Program: 2011

- Two types of samples
  - Diluted VOC mixture as in previous years
  - Amended sample using urban air as the matrix
    - Concentration: ~ 4ppb
    - 72 compound mix

2011 Challenge Sample Variability from Reference Analysis

- NIST/ DOE VOC Mix
  - Most Compounds RSD~4%
  - Ethene (16%)
  - Propene (15%)
  - O-Xylene (28%)

- Amended Urban Sample
  - Most Compounds RSD ~8%
  - Many Compounds >8C Large

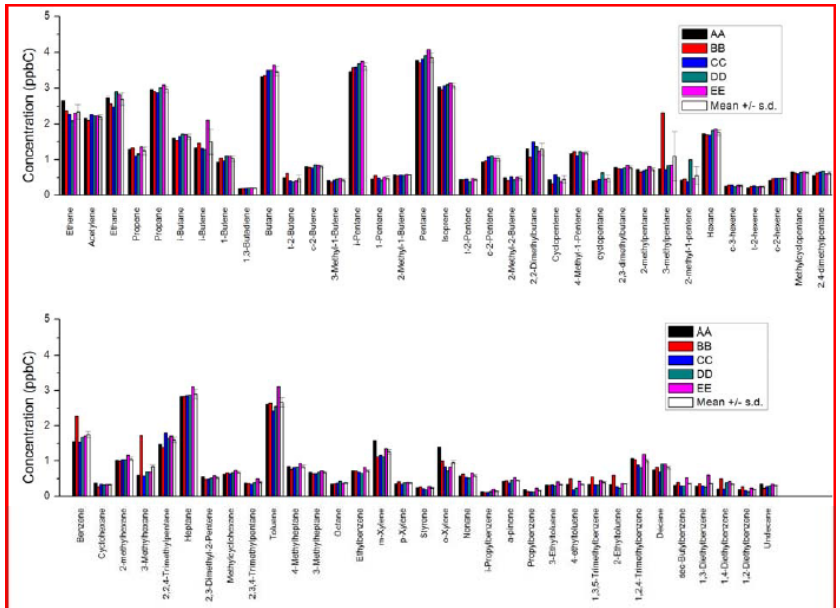


Figure 2. Data showing reference lab measured differences between different canisters filled with the same blend of amended Miami urban air.

2011 Results VOC Mix: All Participants

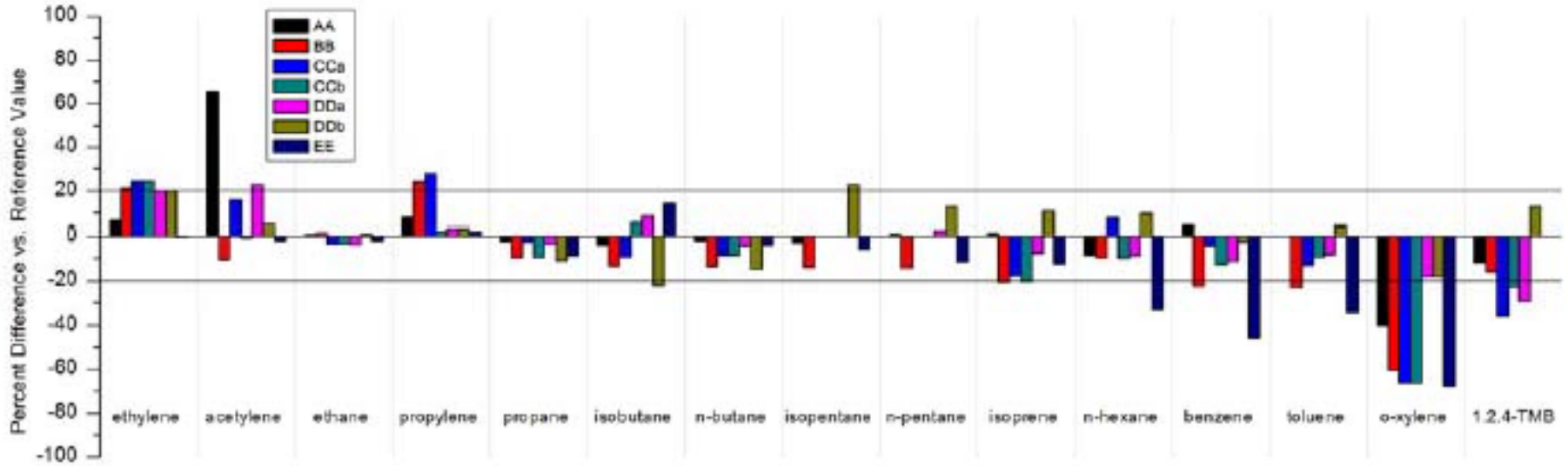


Figure 3. All NIST/DOE sample data shown as percent difference vs. reference value.

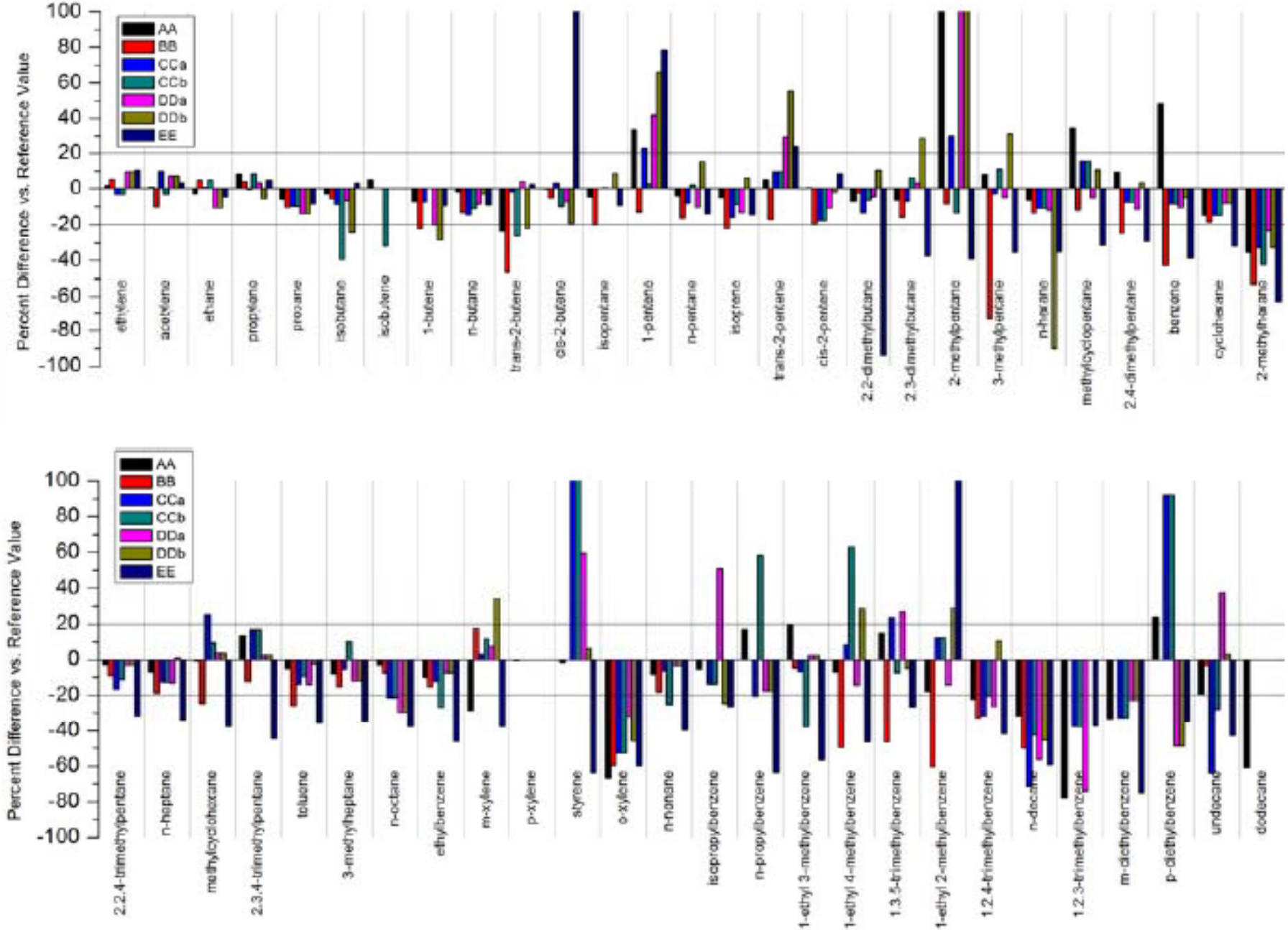


Figure 4. All amended Miami urban air sample data shown as percent difference vs. reference value.

Future Considerations

- Invitation to other Regions/ Local Agencies to Participate
- Improvements to Urban Air PE Design
- Investigate stability of specific compounds in PE samples
- Calibration Gases Comparability
- Canister cleaning procedures (Aging in canisters)