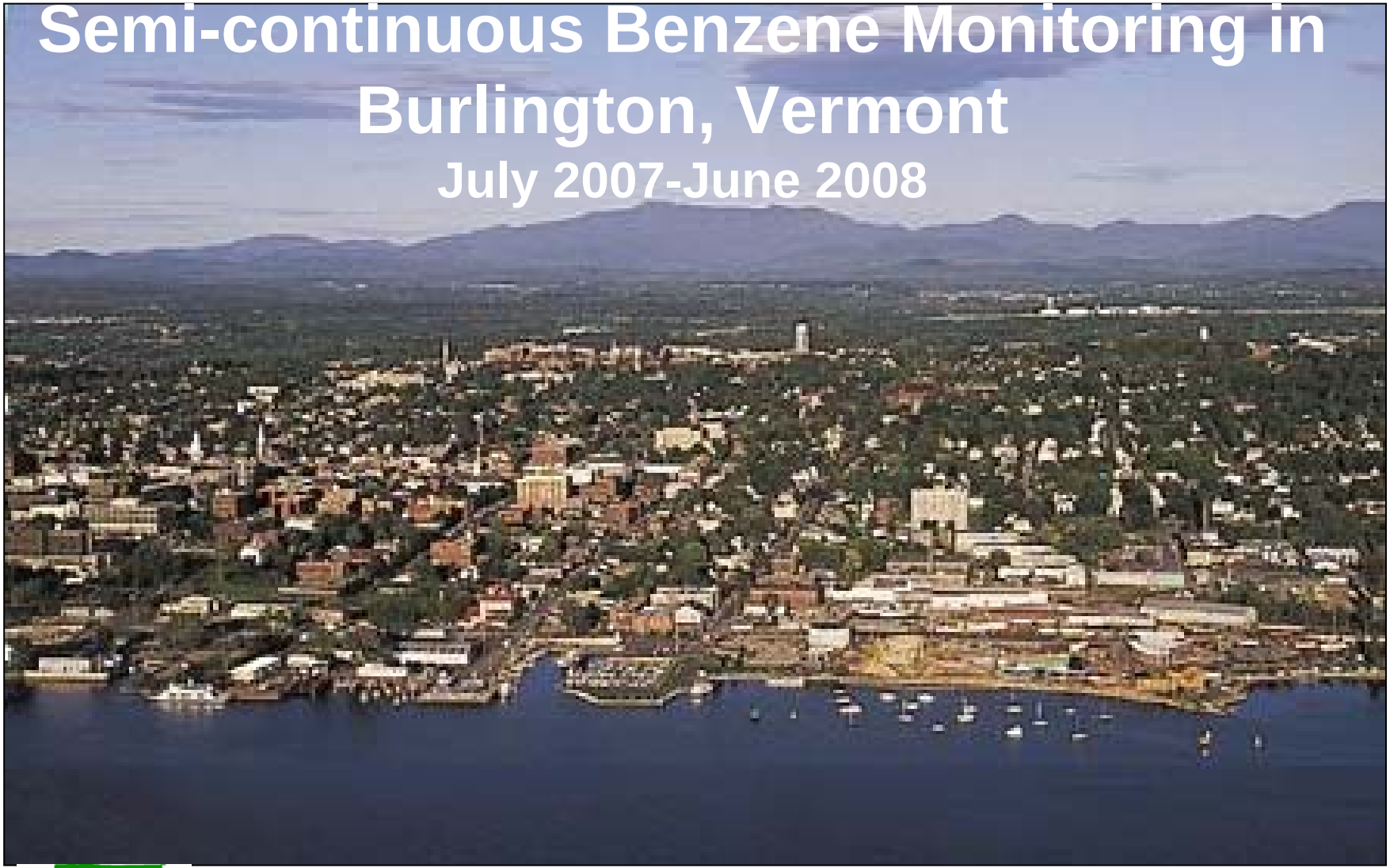
Semi-continuous Benzene Monitoring in Burlington, Vermont

July 2007-June 2008



Robert C. Lacaillade, Vermont APCD

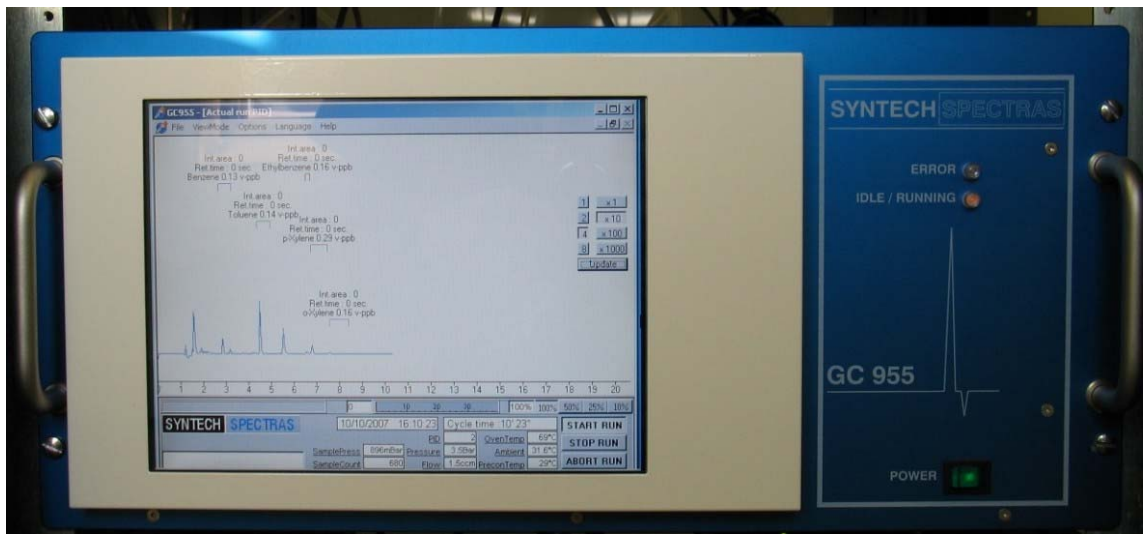
NESCAUM Monitoring Assessment Committee

Putney, VT

11/6/2008

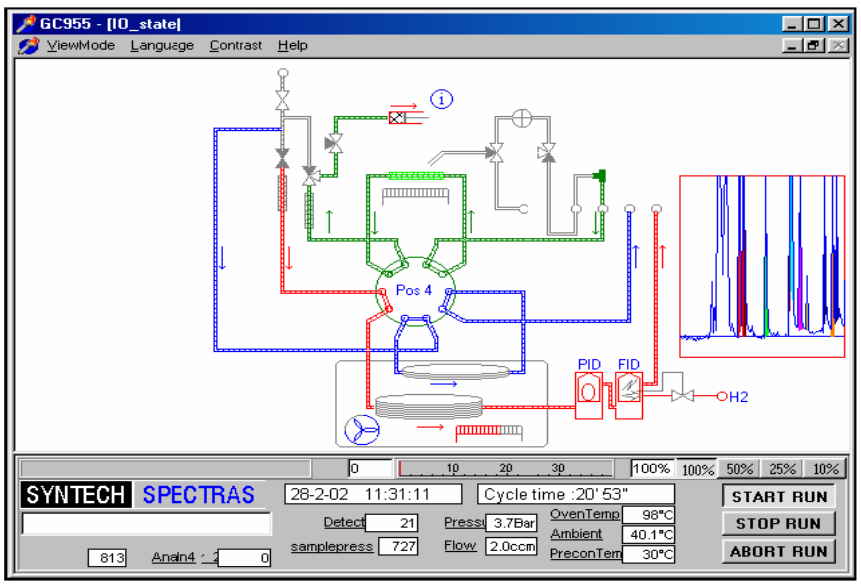
Syntec Spectras GC955 Series 600 BTEX Analyzer

- Manufacturer: *Synspec* (The Netherlands)
  - U.S. Distributor/Customer Support: Wilbur Technical Services, LLC
- Computer controlled-embedded PC running proprietary software
  - *Windows XP,* 40 Gigabyte HD, *PC-Anywhere*
  - 19” Standard Rack Mount
  - 10” integrated monitor, External keyboard & mouse
  - Various communication/data options (USB, modem, ethernet etc..)



Design Specifications

GC955 Inside Top view



- Carrier gas- N_2 (Ultra High Purity)
- Preconcentrator- *Tenax GR*
- GC-Based
  - Column: 15 m x .32mm (ID)
    - 95% dimethylpolysiloxane; 5% diphenylpolysiloxane
    - 2-meter “stripper” column
    - 13-meter “analysis” column
- PID- 10.6 eV, 50 µl measurement cell
- “Semi-continuous”; 15-minute analysis run time per sample
- 2 operating modes:
  - sample Injection
  - sampling/Analysis
- Design keys
  - 10-port valve
  - preconcentrator
  - sampling piston

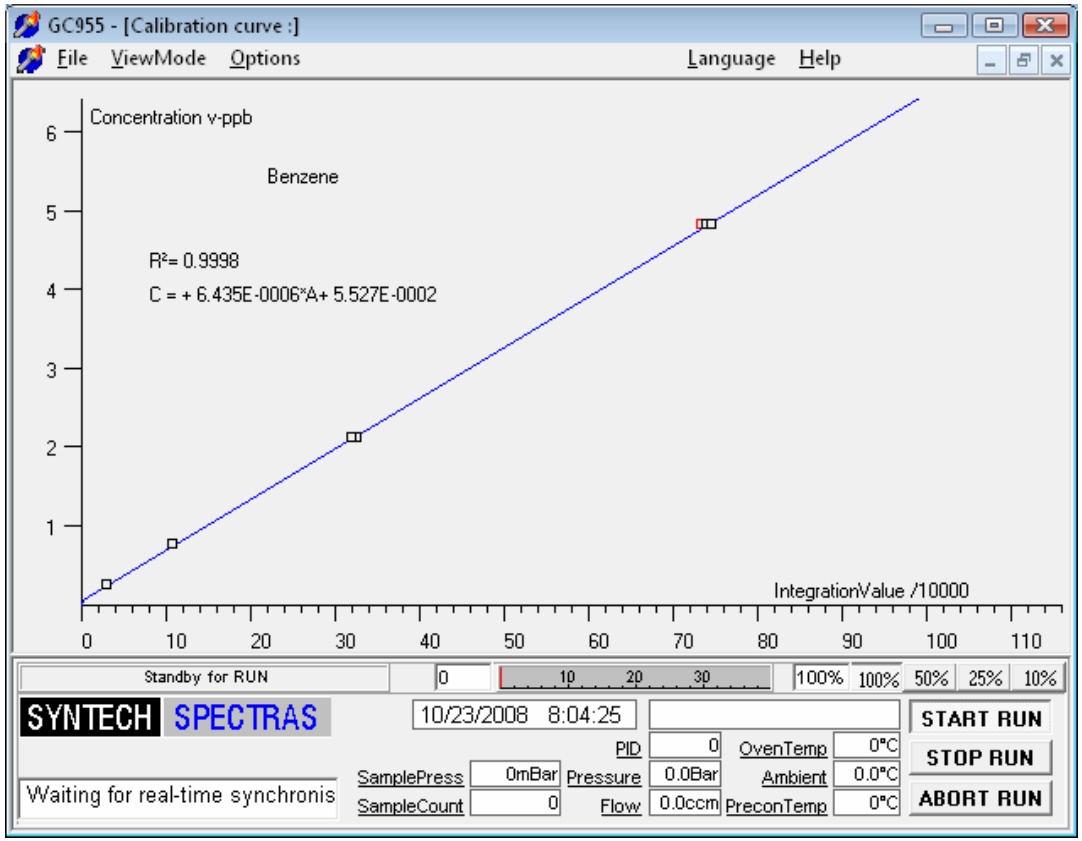
Installation

- Burlington Trailer
  - In City Parking lot on corner of 2 busy streets
  - Near 3 gas stations, fire station, news paper publisher
- Connected to common glass sample manifold
  - 1/8” Silco-coated SS tubing
  - 2µ sintered-SS particulate inlet filter
- Internet connection via dedicated DSL line
  - Allows offsite communication, data review/download
  - Remote control via PC-anywhere
- LAN connection with trailer PC

Calibration

- Calibration gas:
  - *Spectra* or *Scott* Cylinder
    - BTEX compounds at 1 ppmv nominal, Balance Nitrogen
- ZAS: *TEI* Model 111
- Dilution Calibrator:
  - *Environics* Model 6103
    - 0-10 sccm gas MFC
    - 0-20 lpm Air MFC

Benzene Calibration



- 4-point calibration, 0-5 ppbv range
  - ppbv input concentration levels 0.25, 0.75, 2.00, 4.75
- linear regression (not thru 0, auto-linearization not activated)
  - R^2=0.9998
  - y-intercept becomes lowest reportable level (0.06 ppbv)

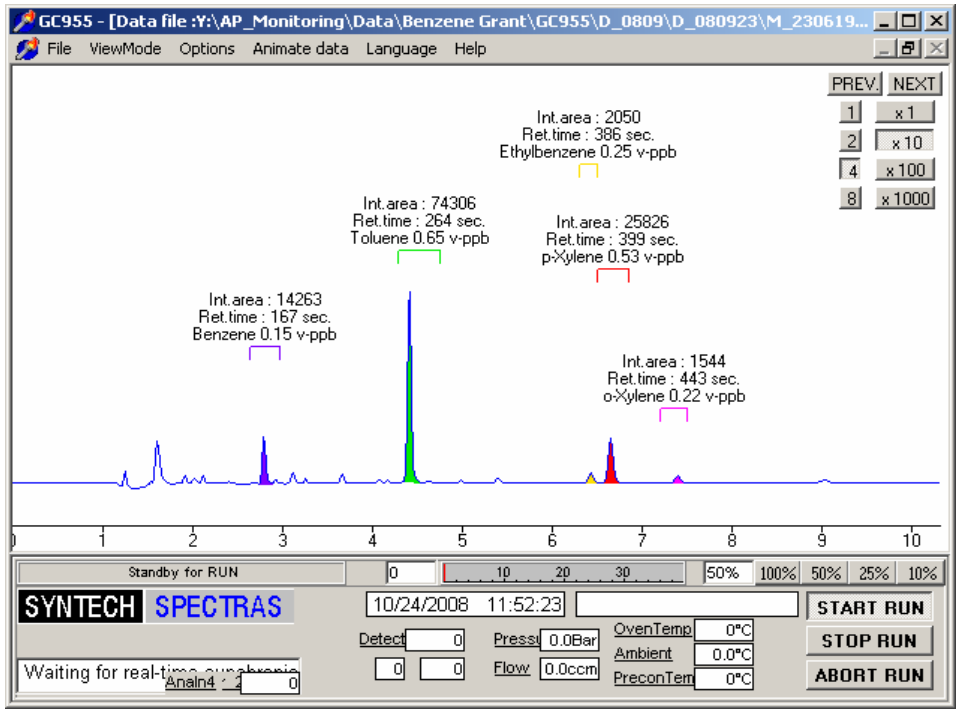
Data Handling

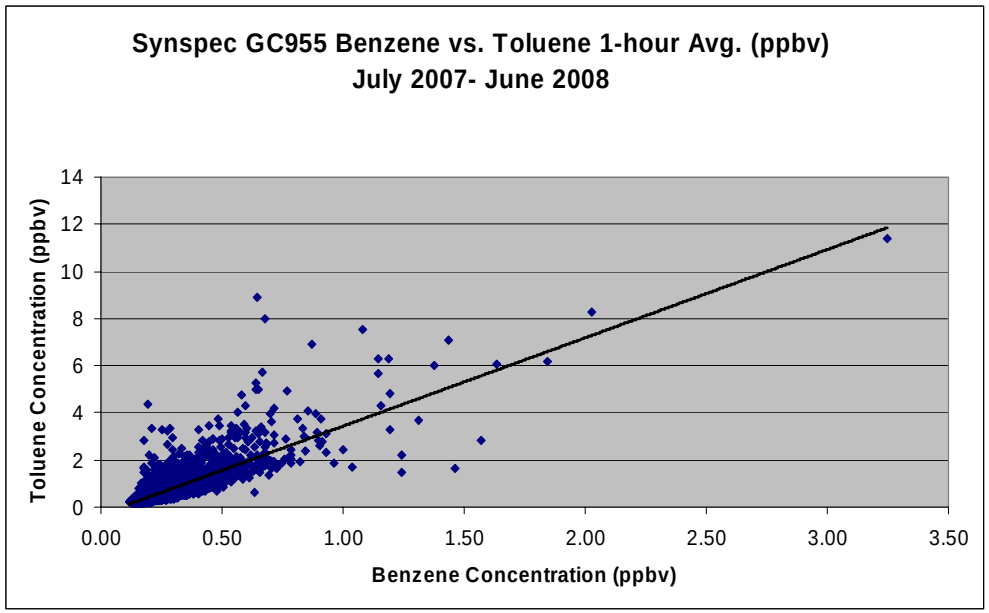
- Chromatogram results from each 15-min sample run saved to unique data file
  - Saved files can be loaded and reviewed in main screen for review and final validation
- ppbv results for each 15-minute sample are written to a text file
  - Each text file contains 1 month of data
  - Text file is retrieved using PC-Anywhere
  - Text file imported to *EXCEL* and *ACCESS* for review, processing, validation etc…..
  - 15-min values used to generate 1-hour averages
    - 75% data averaging rule (min. of 3, 15-min values for 1-hr avg)

Data Validation

- Text file of 15-min results imported to Excel/Access for review:
  - missing, suspect or elevated values, retention time verification
  - Flagging and validation
- Review chromatograms of selected runs
  - Verify retention time, peak area, identification, concentration
- Review results graphically
  - Time series, Fingerprint plots
  - Scatter Plot of benzene/toluene

    ratios for review of suspect values:





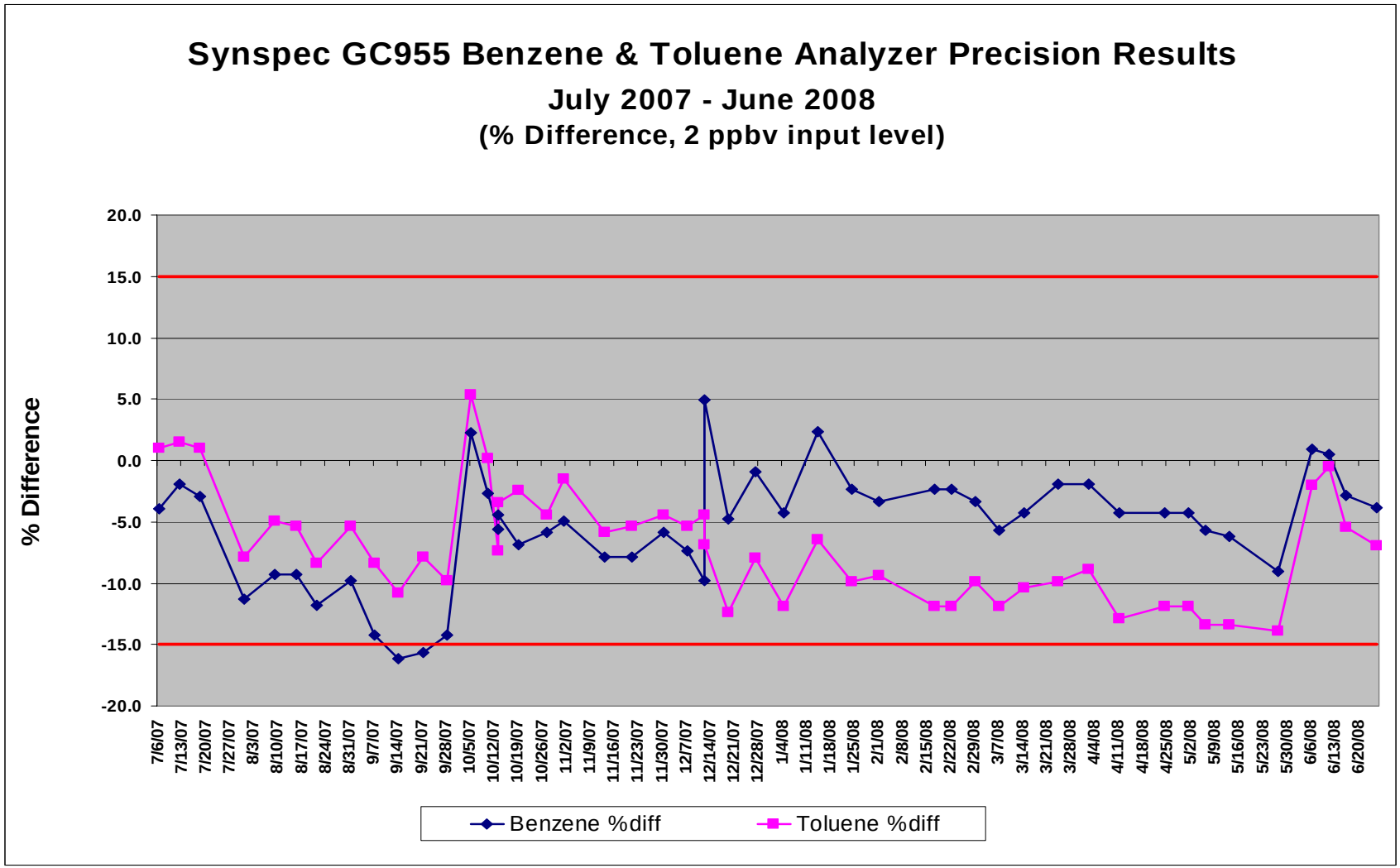
Quality Assurance

- Weekly performance/precision audit
  - 2 ppbv input
  - DQO +/-15% *(85%-115% recovery)*
- Biannual accuracy audit
  - second source standard; mid-range
  - DQO +/-20%
- Data capture
  - Quarterly DQO: 75%

Summary of Weekly Audit of Synspec GC955

(@ 2 ppbv)

July 2007- June 2008



Benzene CV= 5.3% (***40CFRPart58, App.A, 7-1-08 Rev.)*** **Eq. 2)** **Upper/Lower Probability Limits= 3.6%/-14.3%** **(Eq. 6 & 7)**

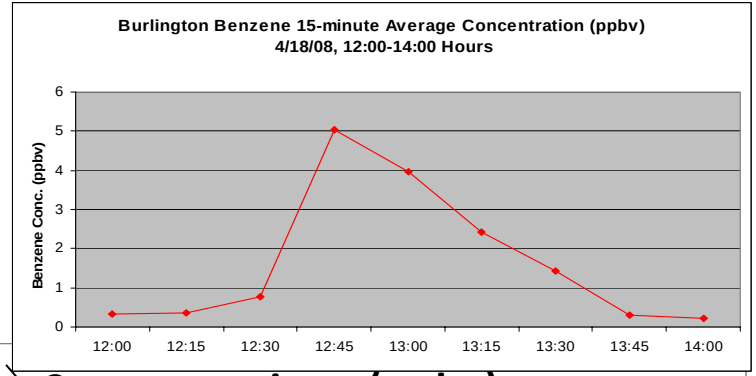
Mean precision error for project period: **Benzene=-5.3%** **Toluene=-6.9%**

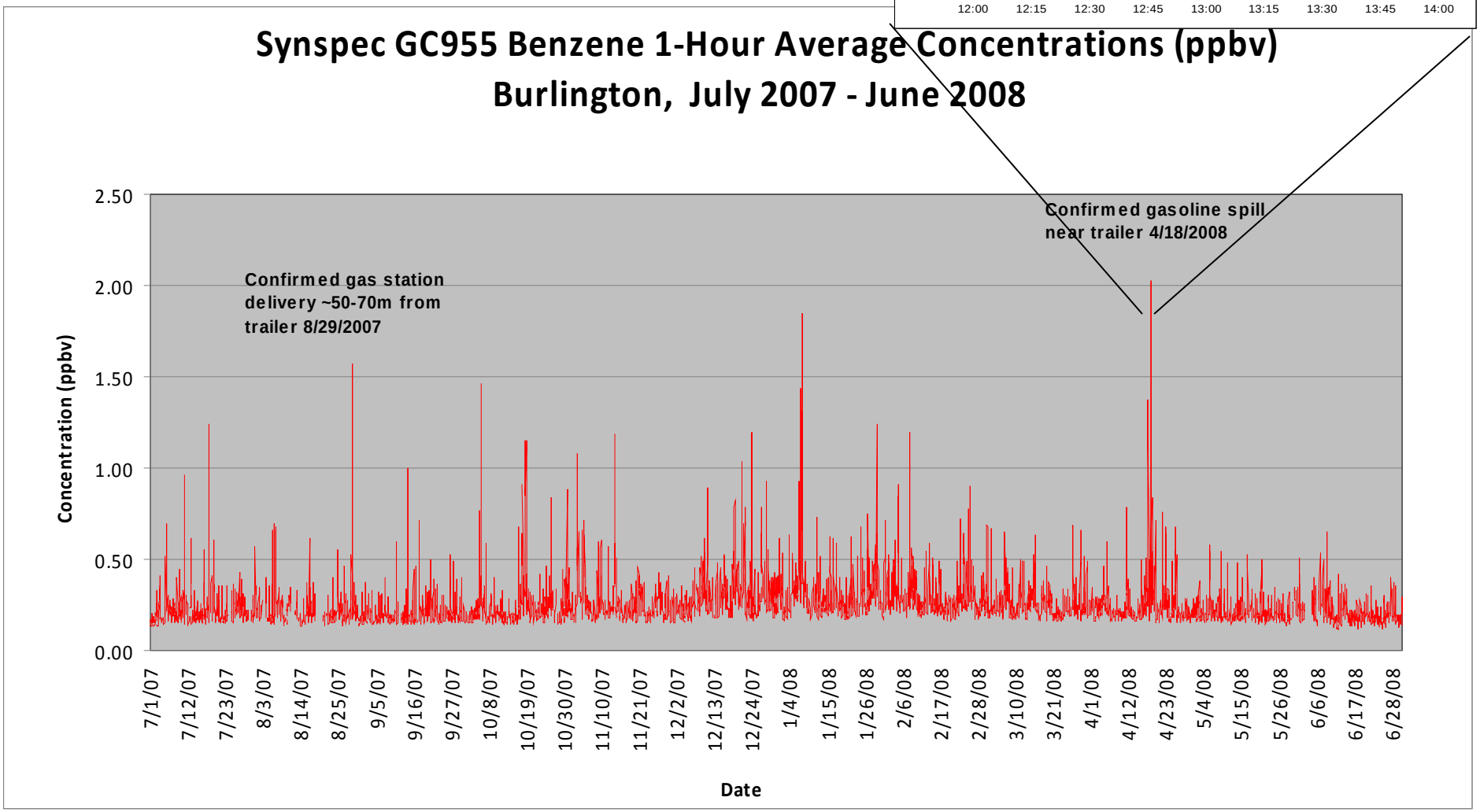
Second Source Benzene Performance Audit Results For Synspec GC955

Audit Date	Input (ppbv)	Response (ppbv)	% Diff.
5/4/07 (Source: Spectra)	1.4	1.1	-21
8/31/07 (Source:ERG)	2.7	3.0	11
4/24/08 (Source:Spectra)	3.0	3.0	0
8/2/08 (Source:Spectra)	2.0	2.0	0

GC955 1-hour Benzene Averages for Project Period

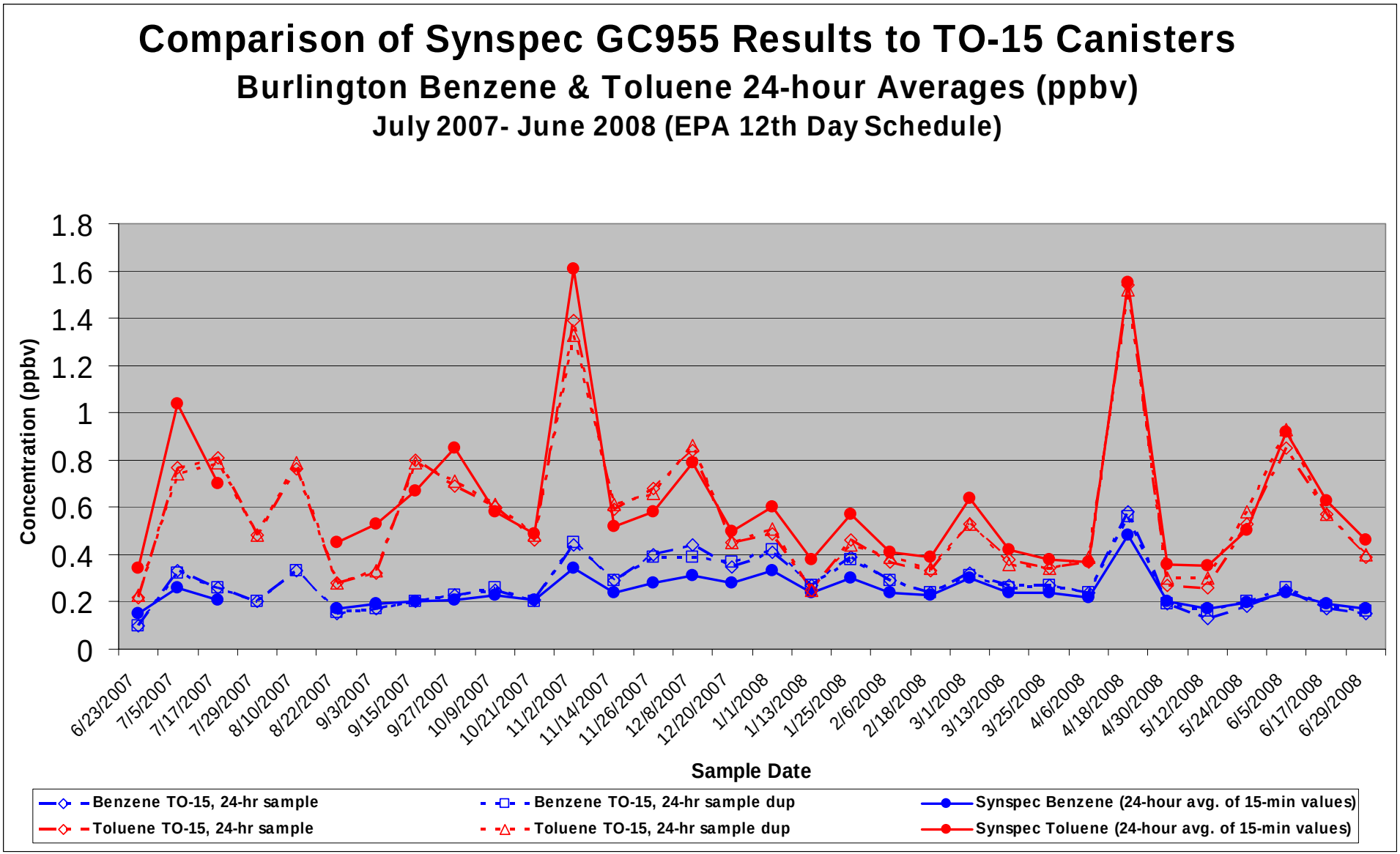
Based on 15-minute values; 94% Data Capture





Semi-Continuous (GC/PID) Compared to Whole Air Sample (GC/MS)

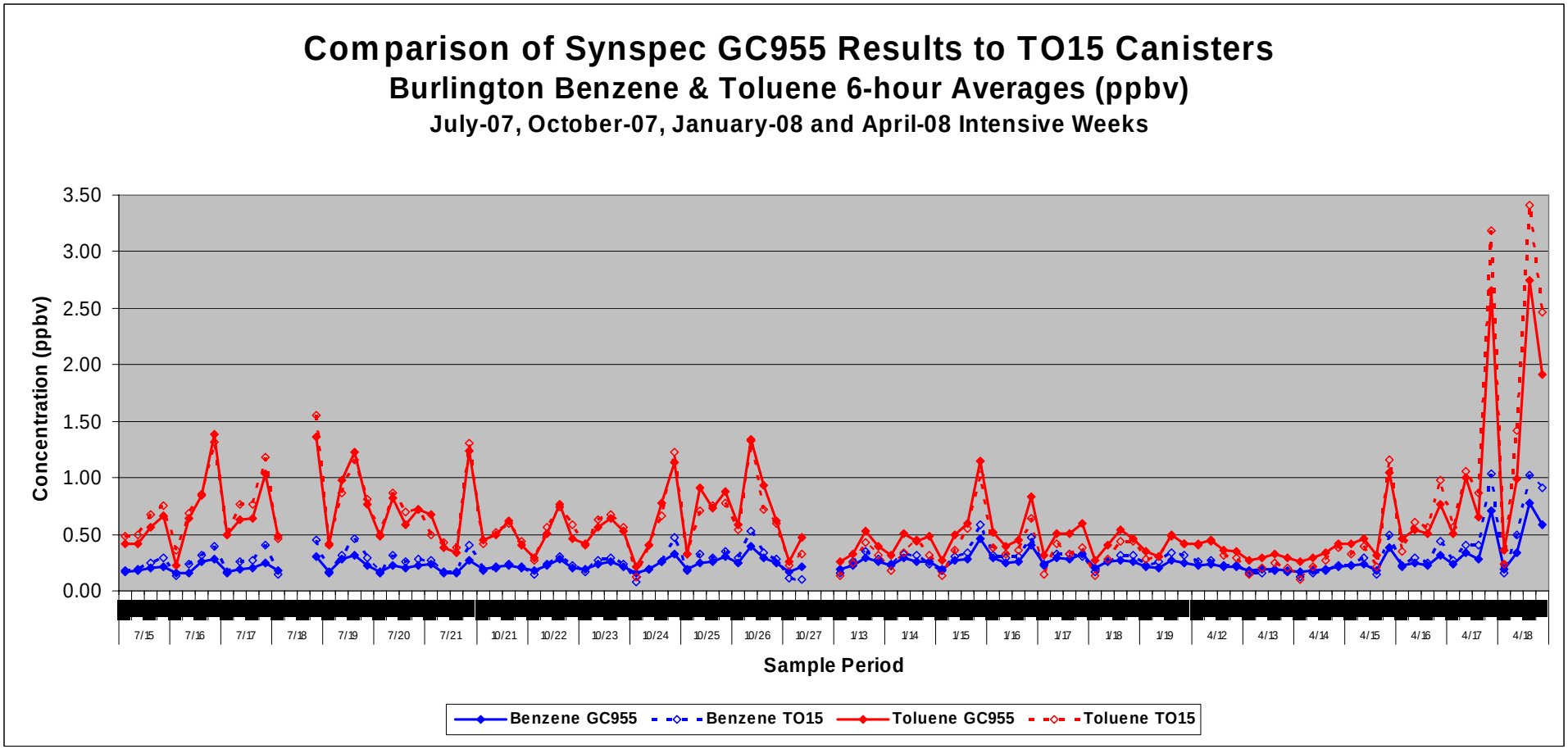
(24-hour Average Concentrations)



Note: Synspec 24-hr averages based on mean of 96 separate 15-minute values for each day; TO-15 results based on individual analysis of 24-hour whole-air canister sample

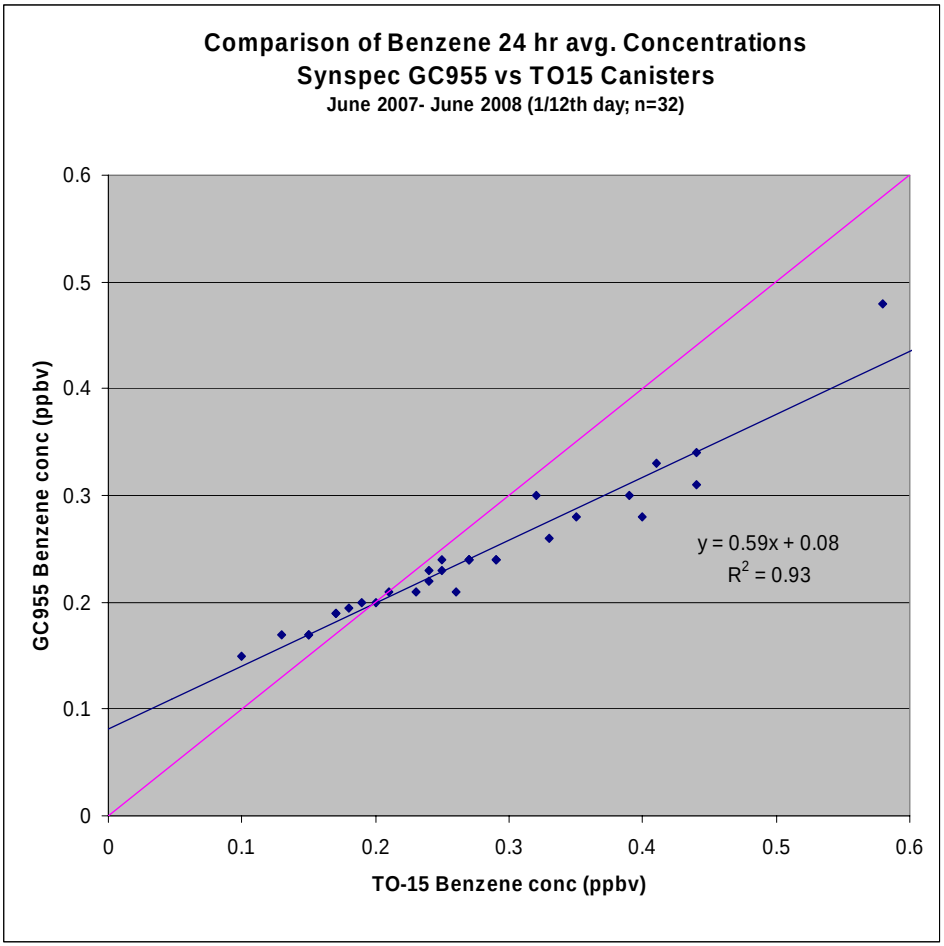
Semi-Continuous (GC/PID) Compared to Whole Air Sample (GC/MS) Continued

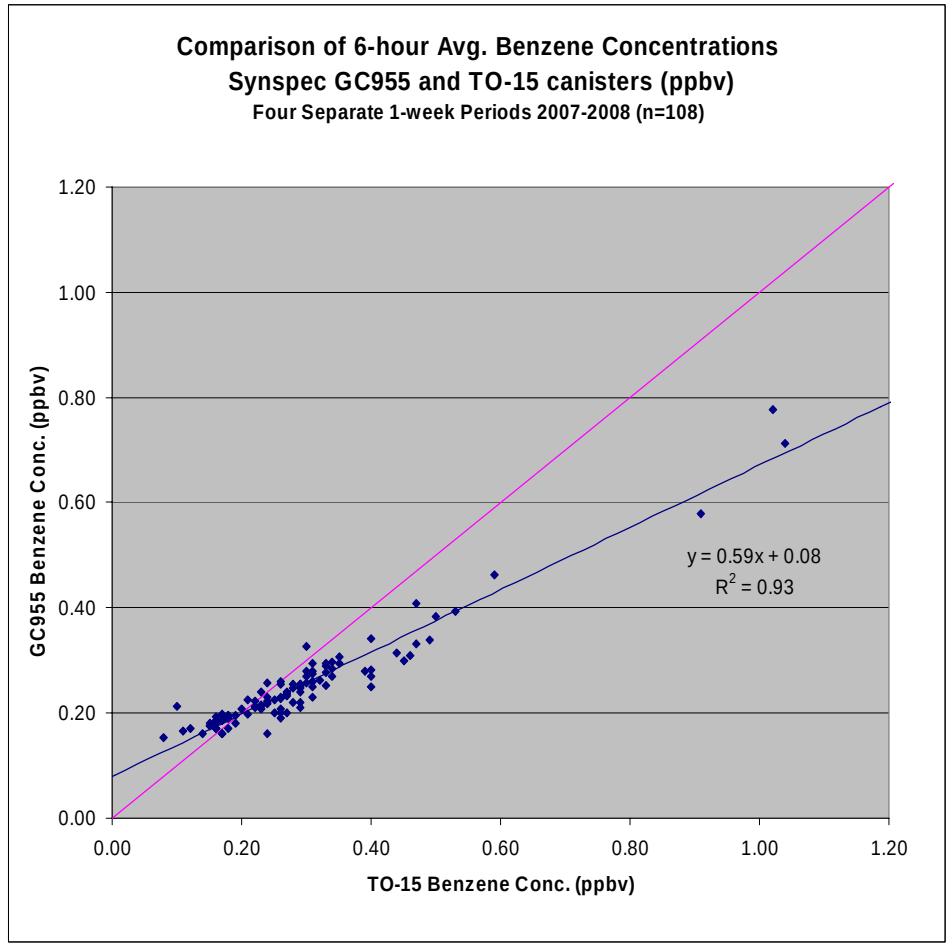
(6-hour Average Concentrations)



Note: Synspec 6-hr averages based on mean of 24 separate 15-minute values for each day; TO-15 results based on individual analysis of 6-hour whole-air canister sample

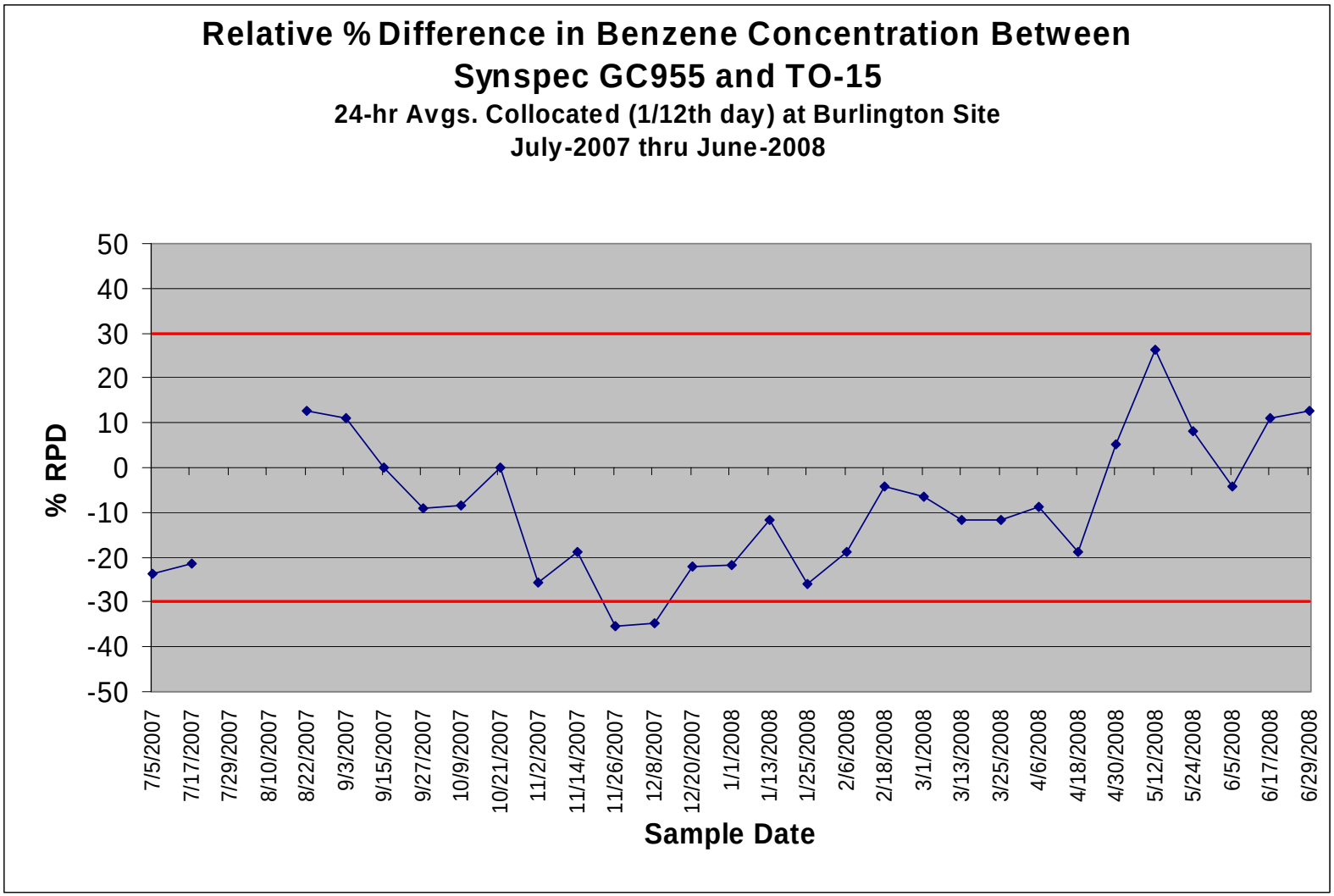
Semi-Continuous (GC/PID) Compared to Whole Air Sample (GC/MS) Continued





Note: Synspec 24-hr and 6-hr averages based on mean of 96 or 24 separate 15-minute values for each sample period, respectively; TO-15 results based on an individual analysis of 24-hour or 6-hour whole-air canister sample

Semi-Continuous (GC/PID) Compared to Whole Air Sample (GC/MS) Continued



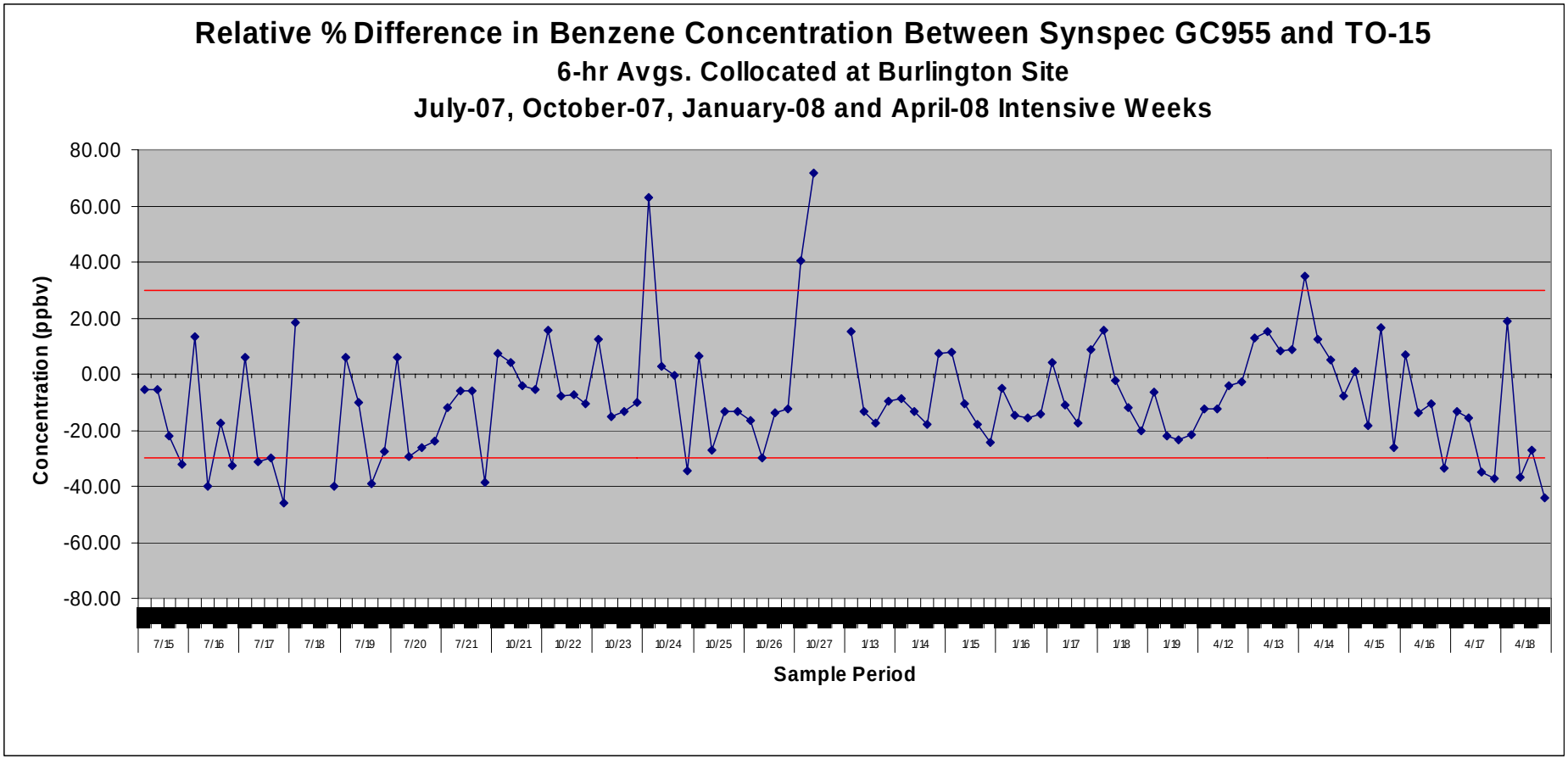
CV=13.2%

(40CFRPart58, AppendixA, 7-1-08 Revision)

Equation 11

$$CV = \sqrt{\frac{n \cdot \sum_{i=1}^{n} d_i^2 - \left(\sum_{i=1}^{n} d_i\right)^2}{2n(n-1)}} \cdot \sqrt{\frac{n-1}{X^2_{0.1,n-1}}}$$

Semi-Continuous (GC/PID) Compared to Whole Air (GC/MS) Continued



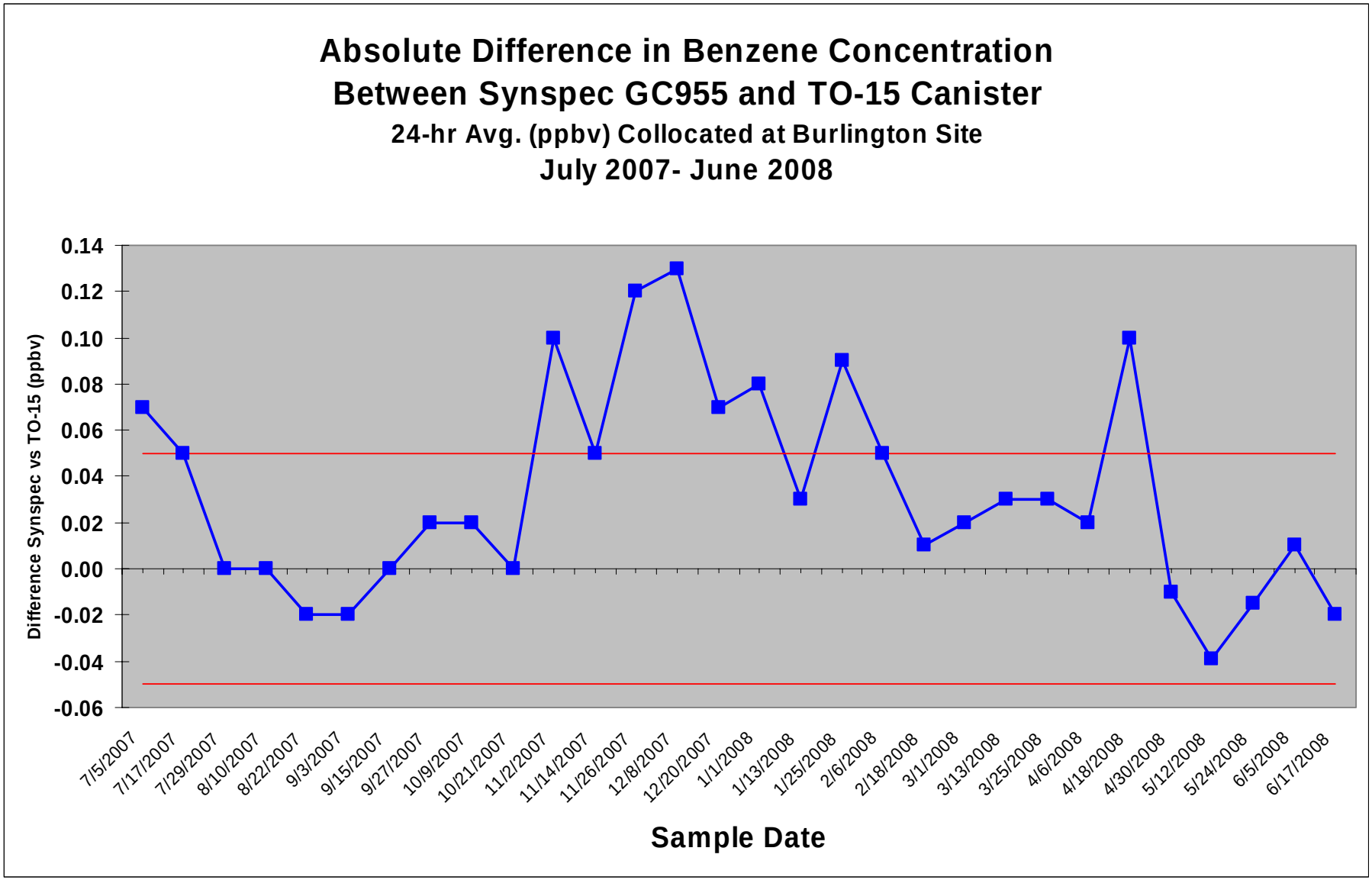
CV = 15.6 %

(40CFRPart58, AppendixA, Eq. 11, 7-1-08 Revision)

Equation 11

$$CV = \sqrt{\frac{n \cdot \sum_{i=1}^{n} d_i^2 - \left(\sum_{i=1}^{n} d_i\right)^2}{2n(n-1)}} \cdot \sqrt{\frac{n-1}{X^2_{0.1,n-1}}}$$

Semi-Continuous (GC/PID) Compared to Whole Air (GC/MS) Continued



Mean Difference= -0.04 ppbv Range= -0.13 to 0.04 ppbv

Conclusions/Observations on GC955 from Burlington Benzene Study

- **Analyzer installation and operation straight forward**
  - Field ready
  - Windows based software
  - Calibration/audit gas available from multiple vendors
  - Ability to use existing station diluter & ZAS
  - Time/experience necessary for familiarity with program and establishing proper integration parameters and proper review/validation of results
    - Vendor training was helpful
- **Consumables and maintenance manageable**
  - Nitrogen consumption: 1 large (size 300 Airgas) cylinder every 6 weeks
  - Particulate filter: quarterly
  - Critical analyzer maintenance able to be performed in-house
    - Sample preconcentrator and carrier gas filters exchanged annually
    - PID cleaned biannually or as-needed
- **Performance enhancements**
  - Trace level blender necessary for calibration & audits
  - Silco-coated ss tubing for sample inlet
  - Linearity achieved without auto-linearization function enabled
- **Acceptable data quality achievable**
  - with regular performance checks and calibrations
  - with thorough data review, management and validation
    - Although it's time intensive and can be complicated

Conclusions/Observations on GC955 from Burlington Benzene Study (Continued)

- **Analyzer is well designed and reliable**
  - For Burlington location, measurement range appropriate for observed short-term benzene concentrations
    - Very few 15-minute measurements recorded > 5 ppbv
  - After startup and imbedded PC issues, GC955 operated with minimal down time during entire project period
    - **94%** Data capture for project period
- **Enhancement to Vermont Air Toxics Monitoring Program**
  - Provides real-time Benzene concentrations that on average correlate well with collocated TO-15 canister analyses but indicate a negative bias mainly +/- 0.05 ppbv (average difference for 24-hr average comparisons over the project= -0.04 ppbv; n=30)
  - Benzene ppbv minimum detection level is comparable to TO-15(<0.2 ppbv)
  - All QAPP DQO's were met for this project
  - Overall, meets applicable EPA performance-based criteria for NATTS and TO methods
- **Continue to optimize calibration, performance and data quality and evaluate relationship to TO-15 results.**

Acknowledgement:

Thanks to

Jenny Berschling

John Simone

****For all of their hard work, diligence and invaluable efforts which significantly contributed to the success of this project!****