COMMUNITY-SCALE CONTINUOUS AIR TOXICS MONITORING IN SOUTH PHILADELPHIA.

AN EVALUATION

Air Management Services, Philadelphia Dept. of Public Health
By Dennis Sosna, 10-21-2015

Community Toxics Monitoring in South Philadelphia - Purpose

- **Assessment** - Assist Air Management Services (AMS) in assessing the degree and extent to which air toxics from a major oil refinery and other activities in the area impact the immediate community of South Philadelphia. The site would operate the first continuous VOC monitor in Philadelphia.
- **New Technology** - Open Path Continuous Monitoring Technologies will be explored to provide real-time measurements of air toxic compounds including Hydrogen Fluoride (HF).
- **Community Involvement** - The community surrounding the oil refinery, will be kept informed and involved on air toxics issues and measurements from the site through the use of:
  - Web-based near real-time data
  - Community outreach through the Philadelphia School System and other partners.

Why South Philadelphia?

- The Community has long been concerned about the health impacts of exposure to air toxics due to the refinery.
- This neighborhood has high poverty rates, lower-than-average education levels, and a large at-risk population.
- The 2005 National Air Toxics Assessment (NATA) indicated high health risks in the City http://www.epa.gov/nata/
  - Philadelphia is ranked 87th out of 3222 counties in the nation for total cancer risk.
  - Various Air Toxic compounds show a excess lifetime cancer risk of greater than one in a million in the City.
  - The refinery is one of approximately 50 that uses Hydrofluoric acid (HF) as a catalyst in the manufacture of gasoline. This highly toxic compound is of great concern to the surrounding community.
- The 2008 and 2011 NATA are under review. Few changes to the 2005 Assessment are expected.

Grant Schedule of Events

Goal	Progress
Community Toxics Grant	Application submitted May 2011. Funds awarded Sept 2011. Period covered: Jan 2012 through June 2014. Extension thru June 2016 was granted on Feb 2014.
Develop QAPP, SOP and support documentation	QAPP submitted 1st quarter 2012. Data Analysis SOP draft completed 05/14, Calibration SOP completed Spring 2015 (currently in peer review.)
Site Selection and Site Agreement	Site surveys conducted during 2012/13. Site Chosen and initial agreement finalized October 2013. Agreement renewed July 1, 2015 - (Modified for ORD, contractors and compressed gases).
Equipment Purchased	Initial Purchase completed March 2013. Gas Cell purchased Spring '2015. Hardware/software upgrade for ORD project (see below) scheduled for Fall'15.
Equipment/Software Training	Staff Initial Training completed 04/13/2013
Community Outreach	Began Ritner site tours with GAMP school students and faculty Spring 2013. U of P (Dr. Pepino) funds allocated Winter 2014/Spring 2015. GAMP teacher and students presented with an Open Path data set in August 2015. Report under development.
Install equipment and begin sampling	Equipment installed and operational at PHA February 2014
Reports - Compare results with TO-15, passive sampling and Ritner (and other) site Toxics data	Progress report presented at Regional Air Director's Meeting May 2014, and during MARAMA Meeting December 2014. Addition report for Toxics Workshop, RTP (October 2015). Final report to EPA due Spring 2016. Regular quarterly reports submitted on schedule.
Integrate real time data into the Agency's AirVision database. Publish data to the web.	Current data sent to AirVision starting 6/30/2015. Data to the web and historical data awaiting integration.
EPA-ORD Project to study MDL's, challenge instruments, and possibly explore other sites.	Scheduled for late Fall '15. Equipment sent for upgrade early October 2015.
Grant deliverables and Project Completion	Summer 2016

Site Selection Criteria

- Select a site in S. Philadelphia in reasonable proximity to the refinery at a distance within ~2 miles from the source. Site is also 2.6 miles from the Ritner Toxics site.
- Site must be downwind of the refinery given the prevailing winds
- The siting of the monitors and retro-reflectors must have a clear unobstructed open path of (at least 125 meters) to support sufficient detection limits in the PPB range, yet not so far as to cause alignment difficulties.
- The site should be relatively free from other emission sources (background)

Chosen Site – PHA Facility 3100 Penrose Ferry Rd, 19145

Which Air Toxic Compounds?

- A combination of the 2005 NATA, the capabilities of the available technology, and the expected detection limits lead to the proposal to monitor the following list of 14 compounds:
  - Acetaldehyde
  - Benzene
  - Butadiene
  - Ethylbenzene
  - Formaldehyde
  - m -Xylene, o -Xylene, and p –Xylene (measured individually)
  - Nitrogen Oxide
  - Styrene
  - Sulfur Dioxide
  - Toluene
  - Trimethylbenzene – (3 isomers measured in the aggregate)
  - Hydrogen Fluoride (Measured by the TDL)

Open Path Monitoring Technology

- Develop and Employ New Technologies
  - Explore the use of Open Path Monitors for the measurement of Air Toxic Compounds
    - Ultra Violet- Differential Optical Absorbance Spectroscopy (UV-DOAS)
      - Offers Method Detection Limits at PPB (Parts per Billion) Levels vs. FTIR (PPM) given the same path length.
      - Good mainly for unsaturated aliphatic and aromatic hydrocarbons such as benzene and BTEX.
      - Deuterium source can detect 1,3-butadiene
    - Tunable Diode Laser (TDL)
      - Suitable for Monitoring Hydrogen Fluoride (HF) only

Open Path Technology - Core Principles

All open path methods operate on the well established principles of light absorption – i.e. the Lambert-Beer Law:

$$A = ebc = -\log(I/I_0)$$

Where:

- A is absorbance (no units)
- e is the molar absorbtivity. This quantity is characteristic of each compound to be measured
- b is the path length of the sample
- c is the concentration of the compound
- I = transmitted light intensity (sample absorbance)
- I_0 = incident light intensity (background absorbance)

Since Absorbance is proportional to path length, in principle, the longer the path length the greater the absorbance (signal) for a given concentration. In practice, the path length is limited by the practical limit of maintaining a stable signal over great distances.

Site Installation

- Container with monitors and roof

- Container with retro-reflectors

PHA - 3100 Penrose Ferry Rd – Our Backyard

UV-DOAS Evaluation
– ask the following questions

1. **Detection Limits** – is the instrument capable of detecting the levels we expect to see in the environment?
2. **Operating Parameters** – is the instrument operating correctly, how do we know?
3. **Correct Identification and Detection** - If a compound is in detection, how do we know that the instrument correctly and accurately identifies it?
4. **Interferences** - Are there any interferences that would lead to incorrect identification or quantification?

UV-DOAS Evaluation –
1. Detection Limits

- Determine the Desired (Optimal)Path Length:
  - Determine the desired levels of each compound to detect. For example, PPB levels of Benzene are expected in the range from 0-5ppb.
  - Obtain the Path Integrated Method Detection Limit from the manufacturer expressed in Parts per Million – Meter (PPM-M). For benzene using the UV-Sentry this value is 0.27 PPM-M (see table). At a distance of 150 meters (300 meter path length), the MDL is:

0.27PPM-M/300 Meters X 1000 PPB per PPM = 0.9 PPB benzene MDL.

  - A detection limit of <1 PPB for benzene should be achievable with a 300M path length. Actual path length is 323M.

Detection Limits PHA Site – Calculated MDLs (Path Integrated MDLs obtained from the manufacturers)

UV-DOAS Deuterium Source	**PHA Path Length (meters):**	323
Compound	**Path Integrated MDL (PPM-m)**	**MDL ppb (323M path)**
Acetaldehyde (C2H4O)	3.00	9.29
1,3 Butadiene (C4H6)	0.20	0.62
Benzene (C6H6)	0.27	0.84
Ethylbenzene (C6H5CH2CH3)	0.30	0.93
Formaldehyde (CH2O)	3.20	9.91
Nitrogen Oxide (NO)	0.29	0.90
Styrene (C8H8)	0.60	1.86
Sulfur Dioxide (SO2)	0.32	0.99
Toluene (C7H8)	0.84	2.60
m-Xylene (C8H10)	0.35	1.08
o-Xylene (C8H10)	3.77	11.67
p-Xylene (C8H10)	0.24	0.74
Trimethylbenzene (3 isomers)	NA*	NA*

NA* Not tested by equipment manufacturer. Instrument dependant.

TDL Spectra-1	**PHA Path Length (meters):**	161.5
Compound	**Path Integrated MDL (PPM-m)**	**MDL ppb (161.5M path)**
Hydrogen Fluoride (HF)	0.40	2.48

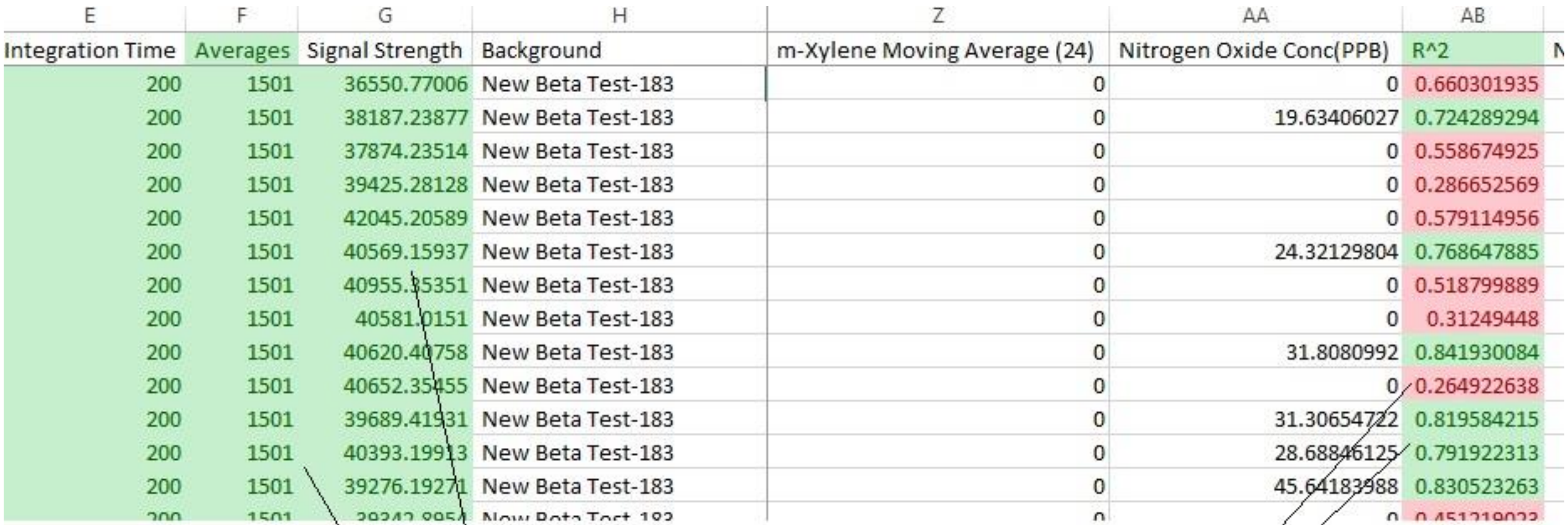
UVDOAS Evaluation –
2. Best Operating Parameters

- **Spectrometer Performance** - The UV-Sentry is a 60,000 count UV Spectrometer. The lamp energy (Deuterium) should be set to a minimum of 75% of full scale or 45,000 counts.
  - The Spectrometer should be set to achieve a minimum of 400 integrations per scan (aka: number of averages) by setting the integration time in msecs and the scan time in minutes.
  - 400 integrations per scan ensures that – through averaging – noise is reduced. Averaging reduces random peaks of detector/electrical noise leaving only the actual signal for processing. The noise level is reduced by the square root of the number of acquisition scans. System noise is reduced by 90% by averaging 100 acquisitions, and 95% by averaging 400 acquisitions.
  - For example: at a 5 minute sampling interval, and a 200ms integration time, you will achieve the following number of integrations:

$$\mathbf{5\,\cancel{min}\text{ interval} \times \frac{60\,\cancel{sec}}{\cancel{min}} \times \frac{1000\,\cancel{ms}}{\cancel{sec}} \times \frac{1\text{ int}}{200\,\cancel{ms}} = 1500\text{ integrations per scan } (>>400\text{ minimum})}$$

2. **Best Operating Parameters** – Can we achieve and sustain them?

YES - Typical Daily Data Summary File Section



E	F	G	H	Z	AA	AB
Integration Time	Averages	Signal Strength	Background	m-Xylene Moving Average (24)	Nitrogen Oxide Conc(PPB)	R^2
200	1501	36550.77006	New Beta Test-183	0	0	0.660301935
200	1501	38187.23877	New Beta Test-183	0	19.63406027	0.724289294
200	1501	37874.23514	New Beta Test-183	0	0	0.558674925
200	1501	39425.28128	New Beta Test-183	0	0	0.286652569
200	1501	42045.20589	New Beta Test-183	0	0	0.579114956
200	1501	40569.15937	New Beta Test-183	0	24.32129804	0.768647885
200	1501	40955.35351	New Beta Test-183	0	0	0.518799889
200	1501	40581.0151	New Beta Test-183	0	0	0.31249448
200	1501	40620.40758	New Beta Test-183	0	31.8080992	0.841930084
200	1501	40652.35455	New Beta Test-183	0	0	0.264922638
200	1501	39689.41931	New Beta Test-183	0	31.30654722	0.819584215
200	1501	40393.19913	New Beta Test-183	0	28.68846125	0.791922313
200	1501	39276.19271	New Beta Test-183	0	45.64183988	0.830523263
200	1501	39342.8954	New Beta Test-183	0	0	0.451219023

Signal Strength near 75% of full scale

Integration time (ms) optimal btw 150 -200

Integrations per Scan (averages) are well above 400

No value reported unless R^2 >= 0.72

UVDOAS Evaluation –
3. Compound Detection, Identification and Quantification

How do we know that the correct compound is detected, identified and quantified?

- The UV-DOAS software uses three types of spectra to detect, quantify and identify target compounds:
  - Background Spectra
  - The Sample (Single Beam) Spectra
  - Reference Spectra

UVDOAS Evaluation –

3. **Compound Detection, Identification and Quantification**

- Background Spectra

- **How do we know that the correct compound is detected?**
  - **Background Spectra –**
    - To arrive at gas concentration values the software requires a background spectrum.
    - This spectrum is a sample spectrum acquired in “clean” air free of target compounds.
    - If target gases are present when the background is recorded, their concentrations will be offset in future measurements by the concentration present in the background.
    - The background spectrum represents the instrument’s numerical zero.

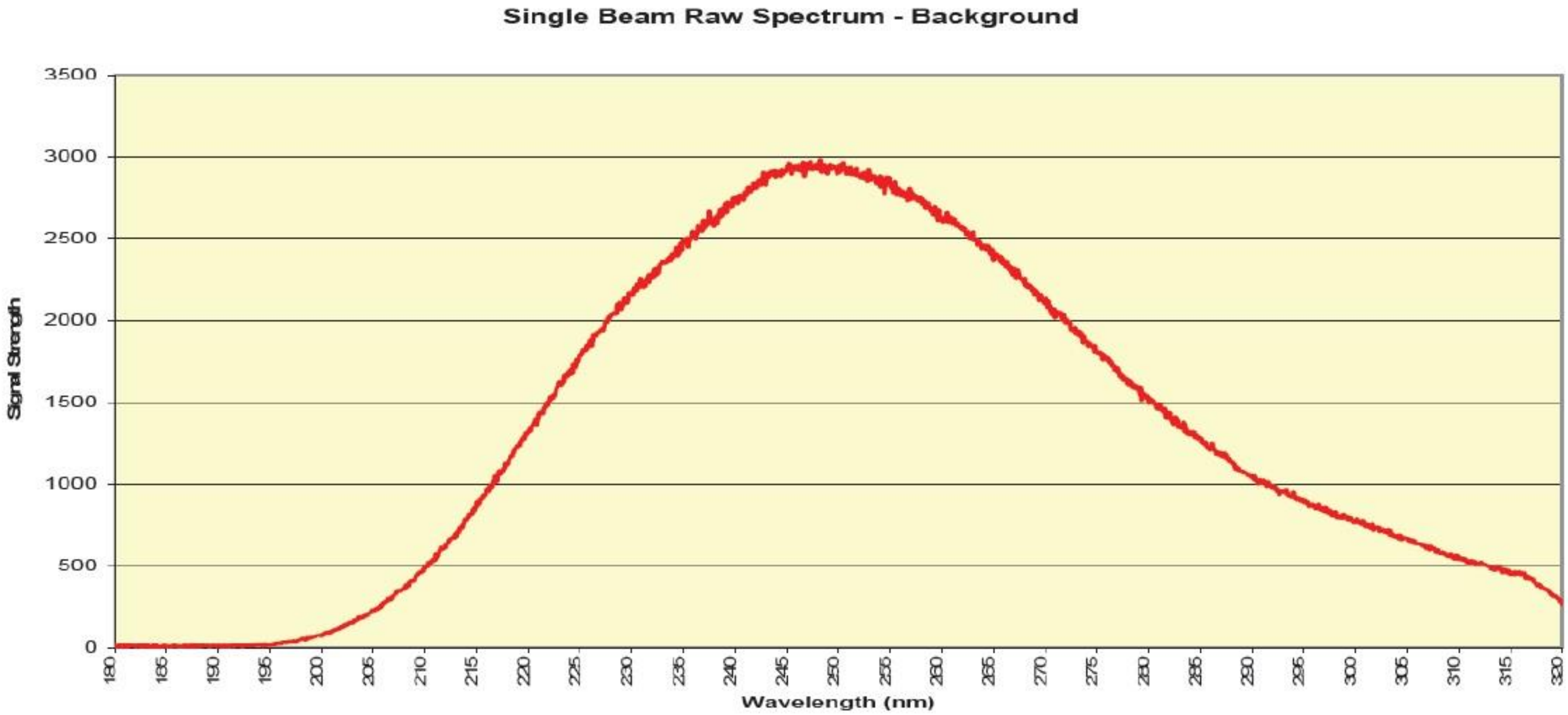
UVDOAS Evaluation –

3. Compound Detection, Identification and Quantification

- Background Spectra

- **Special Exception** – synthetic background
  - In cases where certain compounds are present at all times and the monitor is unable to obtain a "clean" air background, a **synthetic background** may be required.
  - A synthetic background is derived for each acquisition.
  - In the field a synthetic background achieves a lower minimum detection limit for each compound.
  - According to the manufacturer, use of a synthetic background is preferable to a natural background for most installations.

UVDOAS Evaluation –
3. **Compound Detection, Identification and Quantification**
- Clean Background Spectrum (Deuterium Lamp) – I_0


Single Beam Raw Spectrum - Background

UV single beam with no analyte present.

UVDOAS Evaluation –

3. **Compound Detection, Identification and Quantification**

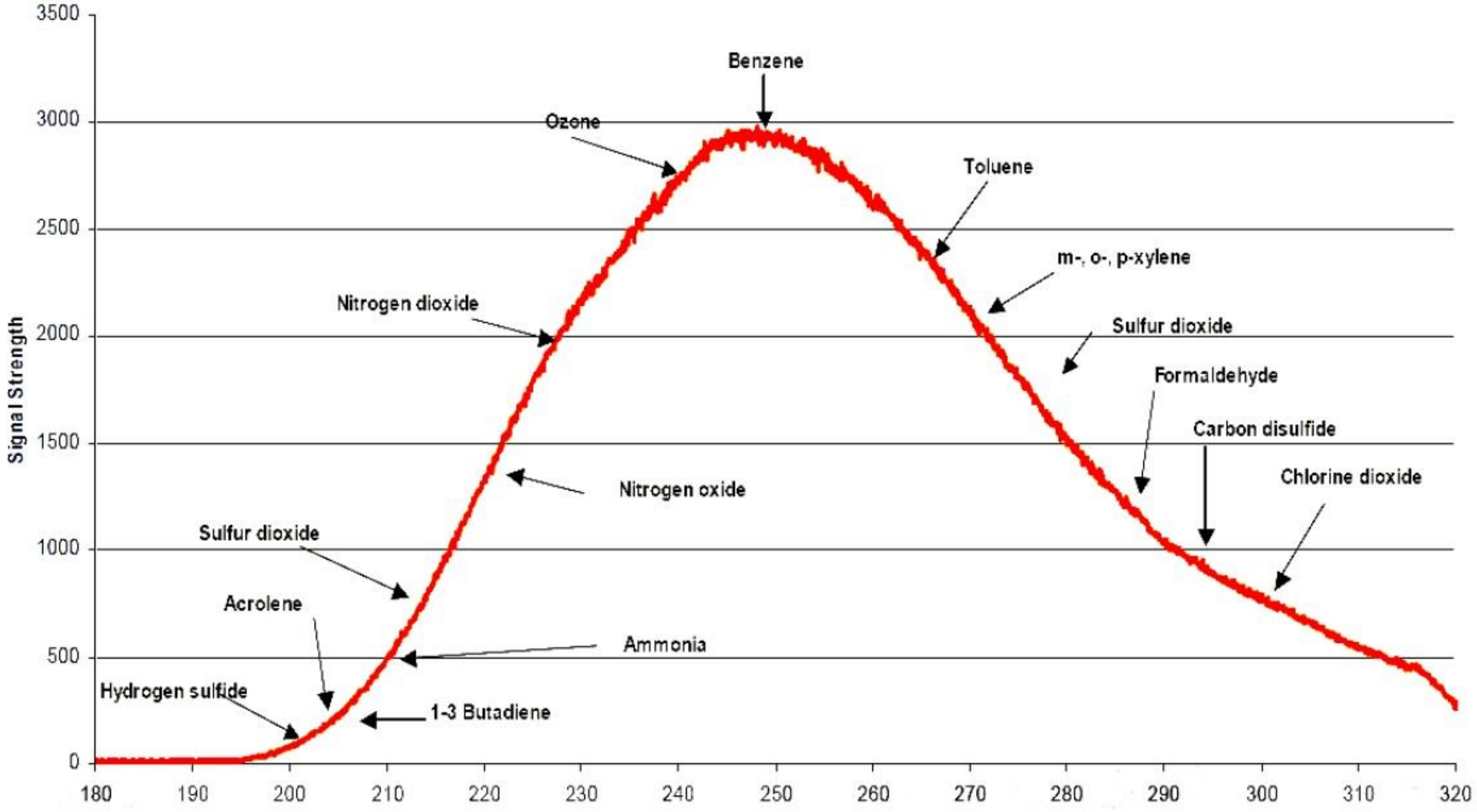
- Sample Spectrum

- **Sample Spectrum –**
  - Every gas has a distinct absorption spectrum, a unique fingerprint characteristic of the gas species.
  - Molecules of gases sensitive to UVDOAS detection in the UV beam path selectively absorb light at specific energies in the spectrum. This absorption changes the intensity curve of the single beam spectrum.
  - The magnitude of each peak in the absorbance spectrum is proportional to the concentration of gas present.
  - Spectra collected by the UV-DOAS are called single beam spectra.

UVDOAS Evaluation –

3. **Compound Detection, Identification and Quantification**

- Sample Spectrum (Deuterium Lamp) – I



UVDOAS Evaluation –

3. **Compound Detection, Identification and Quantification**

- Reference Spectrum

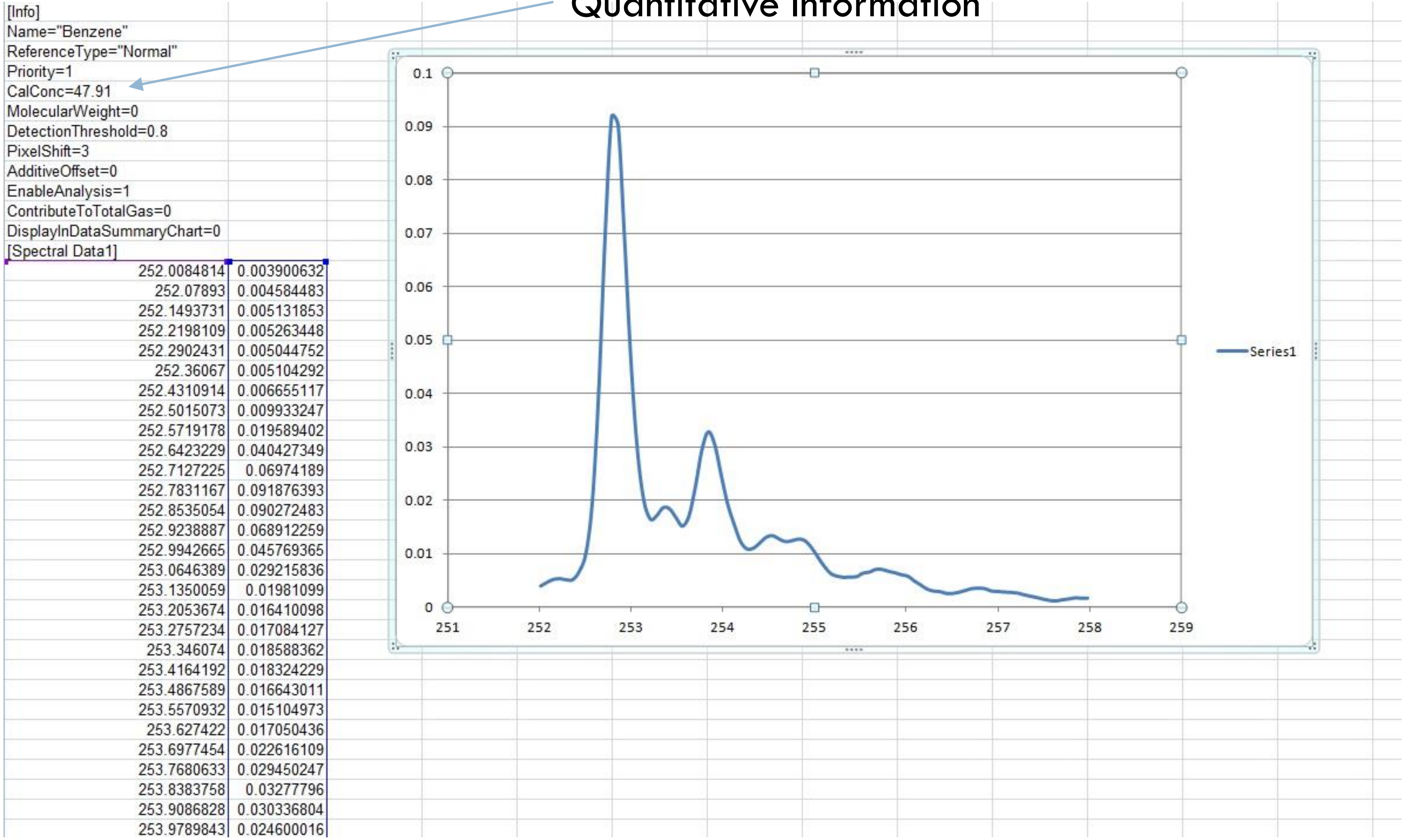
- **How do we know that the correct compound is detected?**
- **Comparison to the Reference – Least Squares, R^2**
  - **Reference Spectra –** a library of reference spectra files - one reference for each monitored compound - are stored on the monitor's computer. These reference files are created under controlled laboratory conditions at the manufacturer. This library contains quantitative information which will be used to both
    - Identify the compound of interest if present, and
    - quantify the compounds of interest by proportion.

UVDOAS Evaluation –

3. **Compound Detection, Identification and Quantification**

A Sample Reference Spectrum for Benzene

Quantitative Information



[Info]
Name="Benzene"
ReferenceType="Normal"
Priority=1
CalConc=47.91
MolecularWeight=0
DetectionThreshold=0.8
PixelShift=3
AdditiveOffset=0
EnableAnalysis=1
ContributeToTotalGas=0
DisplayInDataSummaryChart=0
[Spectral Data1]

252.0084814	0.003900632
252.07893	0.004584483
252.1493731	0.005131853
252.2198109	0.005263448
252.2902431	0.005044752
252.36067	0.005104292
252.4310914	0.006655117
252.5015073	0.009933247
252.5719178	0.019589402
252.6423229	0.040427349
252.7127225	0.06974189
252.7831167	0.091876393
252.8535054	0.090272483
252.9238887	0.068912259
252.9942665	0.045769365
253.0646389	0.029215836
253.1350059	0.01981099
253.2053674	0.016410098
253.2757234	0.017084127
253.346074	0.018588362
253.4164192	0.018324229
253.4867589	0.016643011
253.5570932	0.015104973
253.627422	0.017050436
253.6977454	0.022616109
253.7680633	0.029450247
253.8383758	0.03277796
253.9086828	0.030336804
253.9789843	0.024600016

UVDOAS Evaluation –

3. Compound Detection, Identification and Quantification

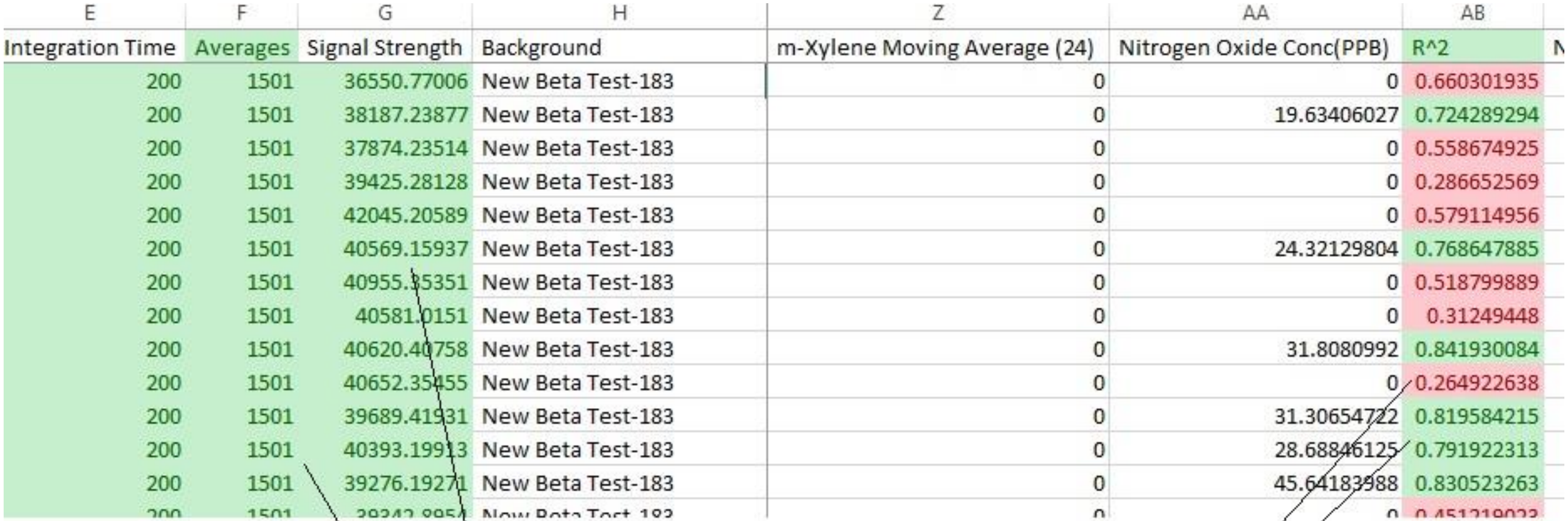
- Reference Spectrum

- **How do we know that the correct compound is detected?**
  - After calculating the sample absorbance spectrum (averaging), a comparison is made between the sample spectrum and the reference spectrum. The comparison is performed using a classical least squares regression analysis per USEPA TO-16 methodology
- **Comparison to the Reference – Least Squares, R^2**
  - The R^2 or R^2 is a measure of the “Goodness of Fit” between the sample and the reference spectra.
  - It is a unit-less value between 0 and 1.
  - Values near zero show poor fit, and values close to “1” demonstrate “good” fit.
  - For the PHA monitors R^2 values >= 0.72 are considered a good fit and positive identification of the compound of interest.

UVDOAS Evaluation –

3. **Compound Detection, Identification and Quantification**

- Daily Data Summary File – showing concentrations and R2 values for NO. Zeros are reported for any measurement with $R^2 < 0.72$



E	F	G	H	Z	AA	AB	
Integration Time	Averages	Signal Strength	Background	m-Xylene Moving Average (24)	Nitrogen Oxide Conc(PPB)	R^2	N
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Signal Strength near 75% of full scale

Integration time (ms) optimal btw 150 -200

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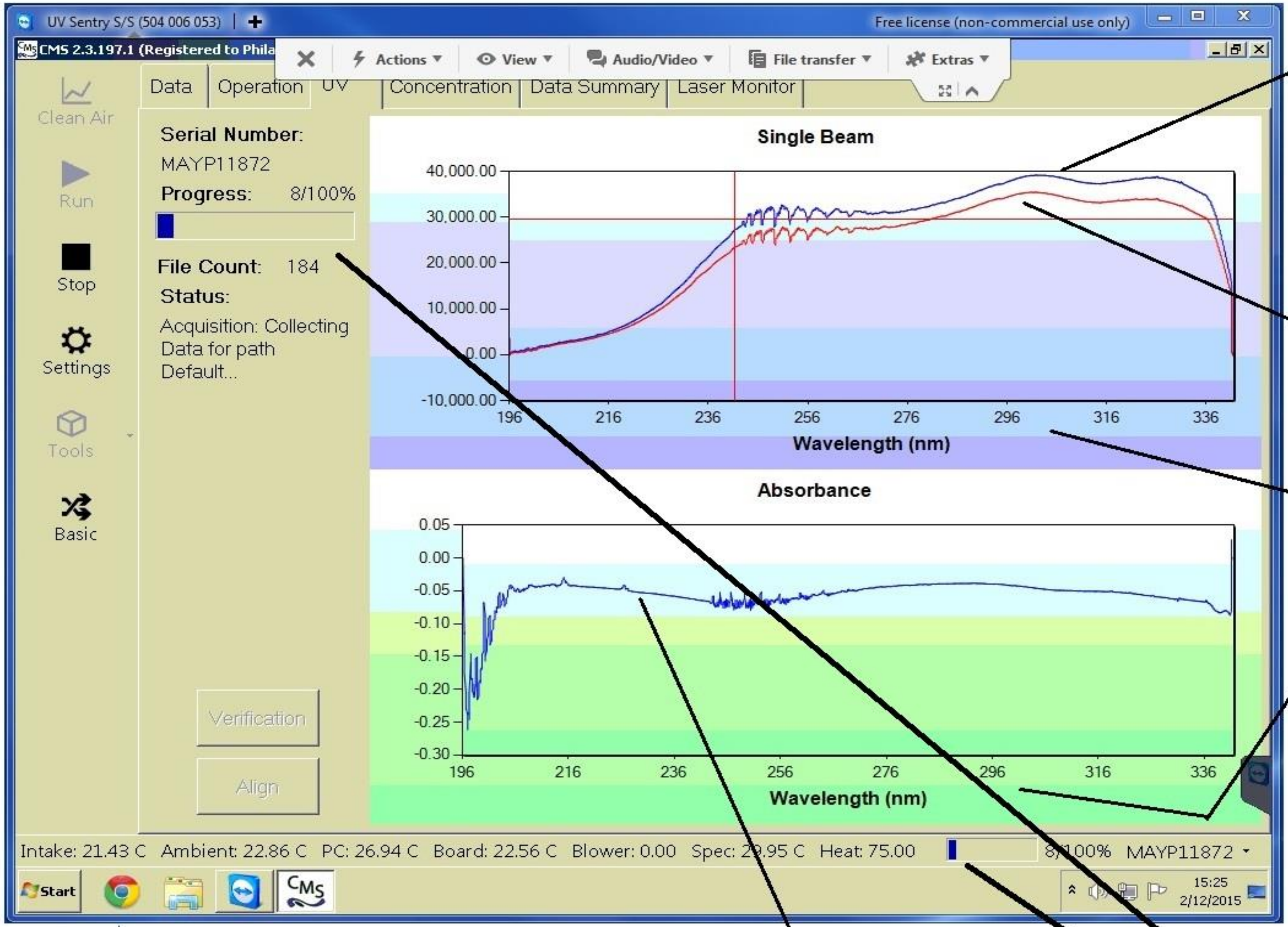
No value reported unless R^2 >= 0.72

UV-DOAS Evaluation
3. CMS Software



Serial Number: MAYP11872

Progress: 8/100%

File Count: 184

Status: Acquisition: Collecting Data for path Default...

Intake: 21.43 C Ambient: 22.86 C PC: 26.94 C Board: 22.56 C Blower: 0.00 Spec: 2[illegible].95 C Heat: 75.00 8/100% MAYP11872

Sample Signal Blue Trace

Background Signal Red Trace

Wavelength range of Deuterium Lamp

Corrected Spectrum showing Absorbance

Scan progress bar

UV-DOAS Evaluation
3. Compound Detection, Identification and Quantification
Example of PHA site data and manufacturer supplied reference libraries

Data from 11/15/2014 13:07:11

Blue: Data from PHA Site

Red: Toluene reference
Yellow: Nitric Oxide reference
Green: Benzene reference

UVDOAS Evaluation –

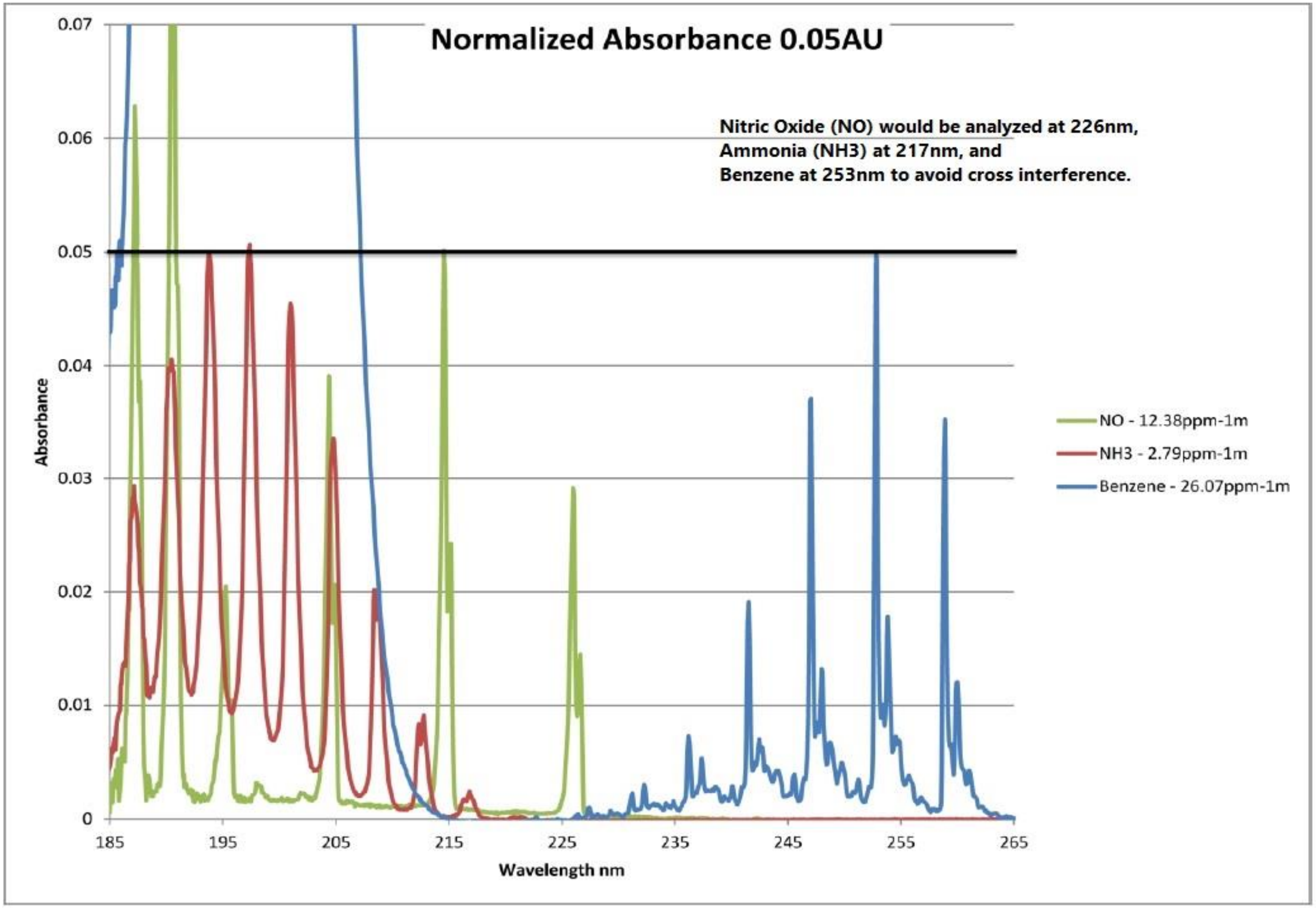
4. Interferences

- **Interferences -** many different compounds absorb UV radiation at the same wavelength – even multiple wavelengths. These absorbances are additive and can lead to compound misidentification and incorrectly quantifying the concentration of a particular compound.
- Interferences are minimized by studying the prospective gases which can be expected to be found in the sample area. Regions of the UV spectrum can be selected which minimize overlap (interference) in the spectrum of the various compounds of interest.

UV-DOAS Evaluation
– Interference Example of Interferences vs Choice of Wavelength

Remember: Absorbances are additive.

The reference file cannot always choose the strongest absorbtion band because other compounds may absorb in the same region.



Nitric Oxide (NO) would be analyzed at 226nm, Ammonia (NH3) at 217nm, and Benzene at 253nm to avoid cross interference.

Hydrogen Fluoride – Why do we wish to monitor HF?

- ❑The Refinery in South Philadelphia is one of approximately 50 that uses Hydrofluoric acid (HF) as a catalyst in the manufacture of gasoline.

- ❑This highly toxic compound is of great concern to the surrounding community.

    - ❑HF is an inhalation, eye, and skin contact hazard.

    - ❑ INHALATION EXPOSURE – Inhalation of hydrofluoric acid vapors may cause severe throat irritation, cough, dyspnea, cyanosis, lung injury and pulmonary edema resulting in death.

Hydrogen Fluoride –
Why do we wish to monitor HF?

Chemical Information Overview:
Hydrofluoric Acid - Chemical Safety Information

Hydrofluoric acid (HF) differs from other acids because the fluoride ion readily penetrates the skin, causing destruction of deep tissue layers, including bone. Pain associated with exposure to solutions of HF (1-50%) may be delayed for 1-24 hours. If HF is not rapidly neutralized and the fluoride ion bound, tissue destruction may continue for days and result in limb loss or death. HF is similar to other acids in that the initial extent of a burn depends on the concentration, the temperature, and the duration of contact with the acid.

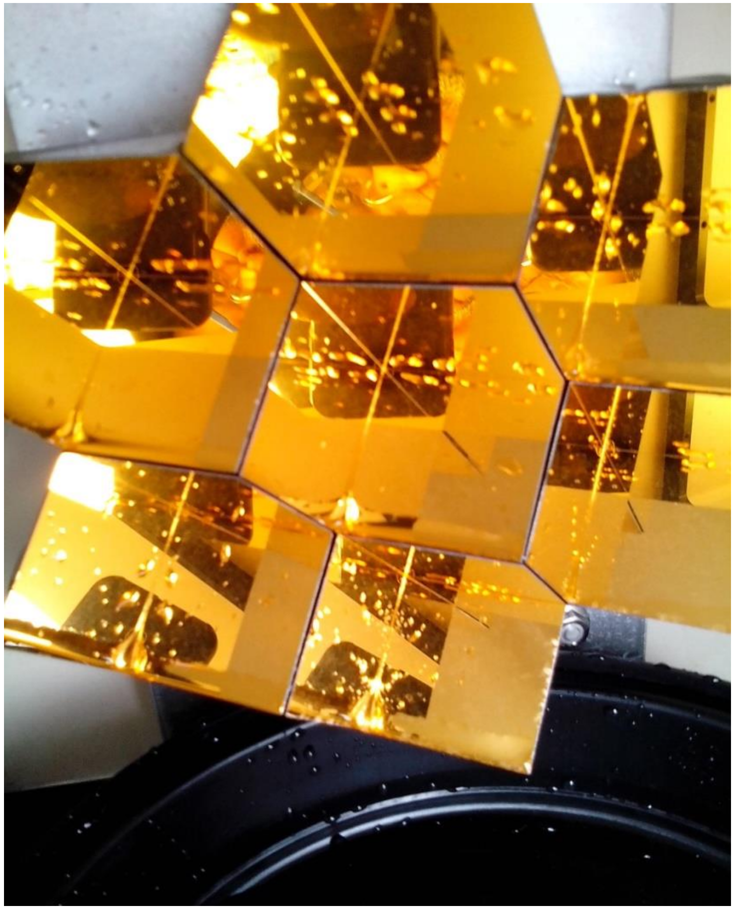
NIOSH Recommended Exposure Limit (REL): (NIOSH, 1996)
- 8-Hour Time Weighted Average (TWA): 3 ppm (2.3 mg/m3)
- Ceiling: 6 ppm (5 mg/m3) (15-minute)
- Skin Notation: Not Listed • Carcinogen: Not Listed
- IDLH VALUE: (Immediately Dangerous To Life and Health): 30 ppm

Source: University of North Carolina – Dept. of Environmental Health and Safety Material Data Sheet
http://ehs.unc.edu/environmental/docs/hydrofluoricacid.pdf

Monitoring for Hydrogen Fluoride (HF) – by Tunable Diode Laser (The "Other" Monitor)

PKL Technologies – Spectra-1

Gold Foil Retro reflector



Monitoring for Hydrogen Fluoride – TDL, Tunable Diode Laser

- **Advantages**
  - Field units are light weight, relatively easy to transport and setup.
  - Unattended measurement collection.
  - Rapid response – typically 1 second.
  - Less expensive than alternative technologies.
  - Wide linear response resulting in measurements from 0.1 to 1,000 ppm for many target compounds.
  - Robust field use with low maintenance, minimal consumables to operate.
  - Lower equipment cost per measurement, ability to multiplex signals.
  - Minimizes interference from other gases resulting in high compound specificity.

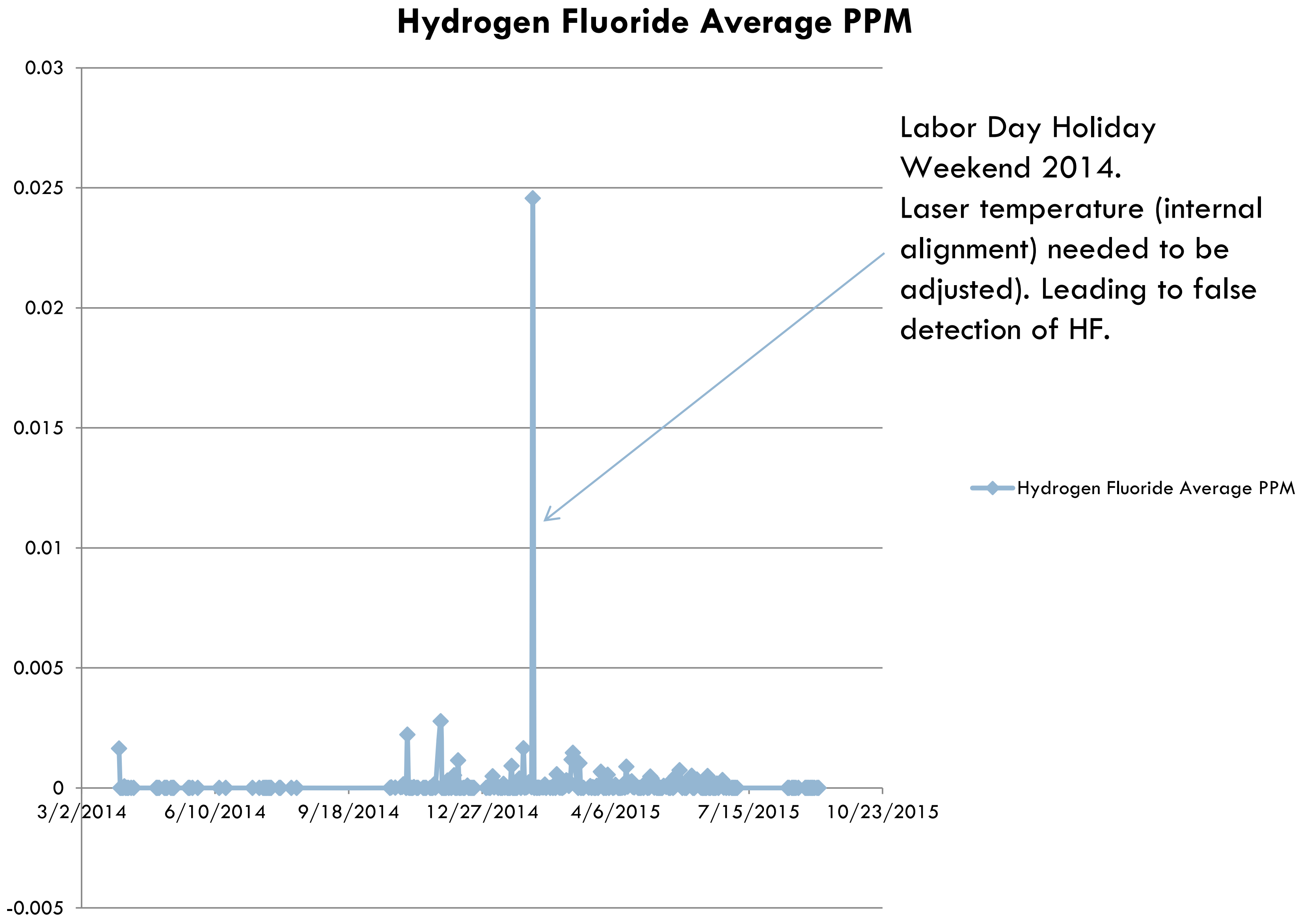
Tunable Diode Laser Characteristics –Disadvantages

- **Disadvantages**
  - Detects only one compound per laser.
  - Fewer measurable compounds and limited sensitivity.
  - Quantitation limited to compounds with overtone absorbencies in the near- and mid-IR range.
  - Need to challenge instrument with known compound to verify detection.

Challenging the Spectra-1 - a dedicated HF Cell

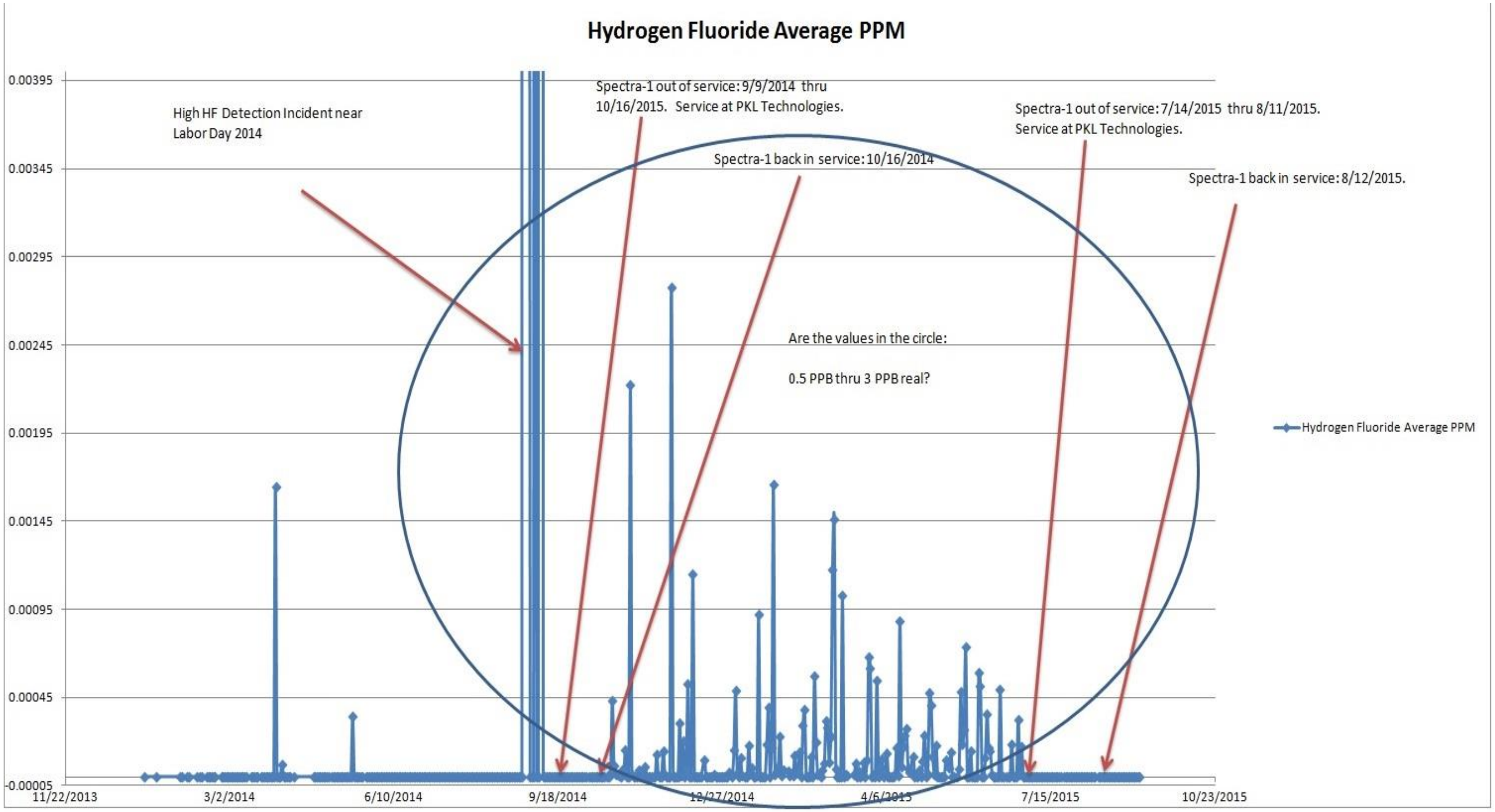
- An HF cell containing a small amount of Hydrogen Fluoride vapor designed to challenge the instrument periodically and verify that HF can be detected.
- This challenge works well but is insufficient to determine if the instrument is in need of internal alignment.

Are We Measuring This Dangerous Compound?



Labor Day Holiday Weekend 2014.
Laser temperature (internal alignment) needed to be adjusted). Leading to false detection of HF.

If you expand the y-axis, HF has been in periodic detection with good R^2 and good signal strength.
Nevertheless, all values below the MDL of 2.5PPB (0.0025 PPM) should be ignored.



High HF Detection Incident near Labor Day 2014

Spectra-1 out of service: 9/9/2014 thru 10/16/2015. Service at PKL Technologies.

Spectra-1 back in service: 10/16/2014

Spectra-1 out of service: 7/14/2015 thru 8/11/2015. Service at PKL Technologies.

Spectra-1 back in service: 8/12/2015.

Are the values in the circle:

0.5 PPB thru 3 PPB real?

Evaluation

- The monitors have been collecting data since February 2014. How are we doing?
  - Technology – Is the technology operating as expected?
  - Community – Have the efforts at outreach been successful?
  - Discuss plans for the future

UV-DOAS Evaluation – Results and Detection Limits

- Given the Detection Limits of the Technology, How did the UV-DOAS Perform?
  - Is there any other data to corroborate our results?
  - Were canister (TO-15) data collected at the site?
  - Were Carbonyl Compounds (TO-11a) Measured at the site (or nearby)?
  - How about any NAAQS gases?
  - Did EPA/ORD Passive Sampling Results Differ? How about the RARE Project?

UV-DOAS Results
– except for Xylenes and Trimethylbenzene

Compound All Values - Average(Range)	**UV-DOAS MDL ppb**	UV-DOAS Daily Avg PPB	TO-15 Canisters at PHA	TO-11 Cartridges at RIT	RIT SO2 Data	CHS NO Data from Nox	UV-DOAS Data Consistent with Other Technologies?
Acetaldehyde (C2H4O)	9.29	0		1.22(0.22/3.82)			YES
1,3 Butadiene (C4H6)	0.62	0(0/0.04)	0.01(0/0.29)				YES
Benzene (C6H6)	0.84	0.00(0/0.73)	0.31(0/2.33)				YES
Ethylbenzene (C6H5CH2CH3)	0.93	0	0.04(0/0.13)				YES
Formaldehyde (CH2O)	9.91	0.00(0/0.42)		2.12(0.03/6.81)			YES
Nitrogen Oxide (NO)	0.90	8.74(0/146.92)				9.67(2.11/98.41)	YES
Styrene (C8H8)	1.86	0.00(0/0.01)	0.02(0/0.35)				YES
Sulfur Dioxide (SO2)	0.99	0.17(0/1.74)			2.55(0/8.42)		NO. Measurements are on the low side.
Toluene (C7H8)	2.60	0	0.32(0/0.7)				YES
Date Range of Data		Mar '14 thru Aug '15	May '14 thru Jun '15	May '14 thru Mar '15	July '14 thru Sep '15	Feb '14 thru July '15	
Source				Site 2.6 Miles Away from PHA	Site 2.6 Miles Away; NAAQS Data in AirVision	Site ~5 Miles Away, Closed July'15, NAAQS Data in AirVision	

UV-DOAS Results

–Xylenes (3 isomers)

Compound All Values - Average(Range)	UV-DOAS MDL ppb	UV-DOAS Daily Avg PPB	TO-15 Canisters at PHA	UV-DOAS Data Consistent with Other Technologies?
m/p-Xylene (C_8H_{10})	*	*	0.16(0/0.55)	YES. Combined UV-DOAS m/p-Xylene values are below DL.
m-Xylene (C_8H_{10})	1.08	0	*	YES
o-Xylene (C_8H_{10})	11.67	Negative Values ?	0.05(0/0.19)	Negative values reported with good R^2 values. Conclusion: Xylene is constantly present even in Bkd file.
p-Xylene (C_8H_{10})	0.74	0.00	*	YES
Date Range of Data		Mar '14 thru Aug '15	May '14 thru Jun '15	
Comments			* TO-15 unable to resolve m/p-Xylene. Reported as a single m/p-Xylene value	

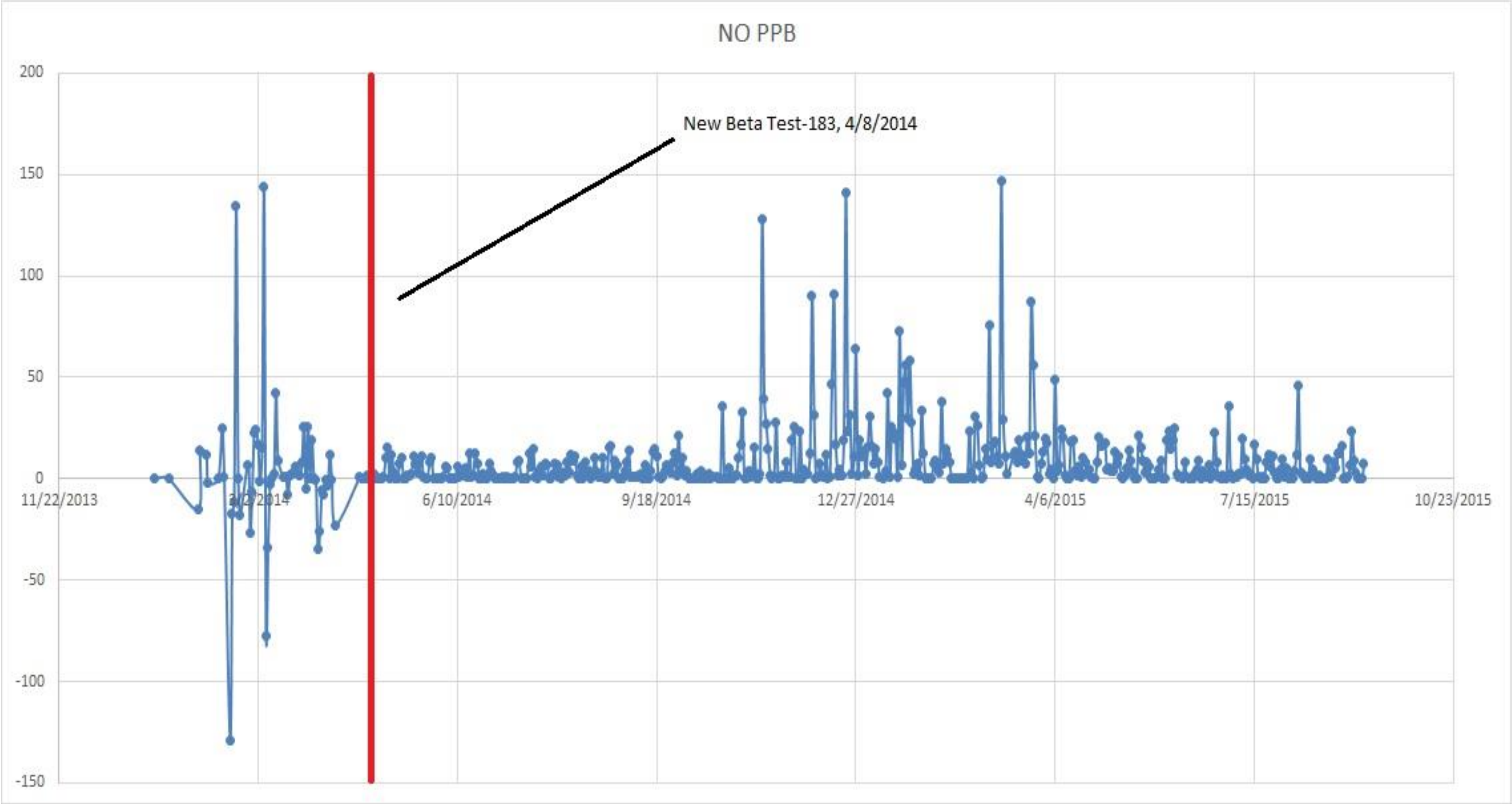
UV-DOAS Results
–Trimethylbenzene (3 isomers)

Compound All Values - Average(Range)	UV-DOAS MDL ppb	UV-DOAS Daily Avg PPB	TO-15 Canisters at PHA	UV-DOAS Data Consistent with Other Technologies?
Trimethylbenzene (C9H12)	NA	1.50(0/15.17)	*	No. Sum of two TMB isomers from TO-15 do NOT give the UV-DOAS value.
1,3,5-Trimethylbenzene (C9H12)	NA	*	0.01(0/0.05)	*
1,2,4-Trimethylbenzene (C9H12)	NA	*	0.04(0/0.12)	*
1,2,3-Trimethylbenzene (C9H12)	NA	*	Not Measured by TO-15 at AMSL	*
Date Range of Data		Mar '14 thru Aug '15	May '14 thru Jun '15	
Comments	*UV-DOAS has no PI-MDL available from Manuf.	*UV-DOAS does not distinguish btw different isomers.	*TO-15 measures 2 out of 3 indiv TMB isomers	

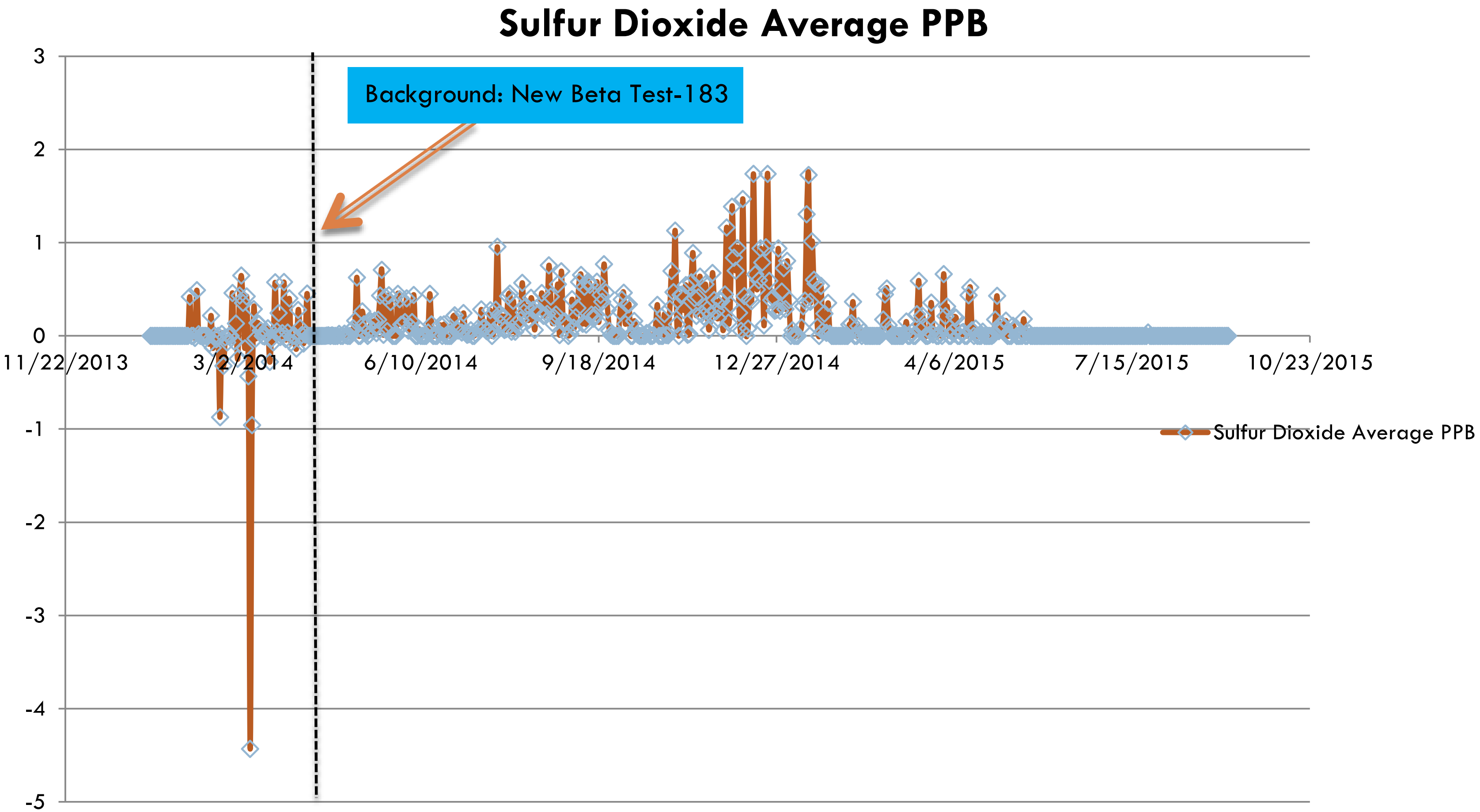
UVDOAS Evaluation –
The Importance of the background file.

- **Background** - Do we have the correct background file?
- After allowing the background file to vary periodically, on 4/8/2014 a single background file was chosen. Was this effective.?

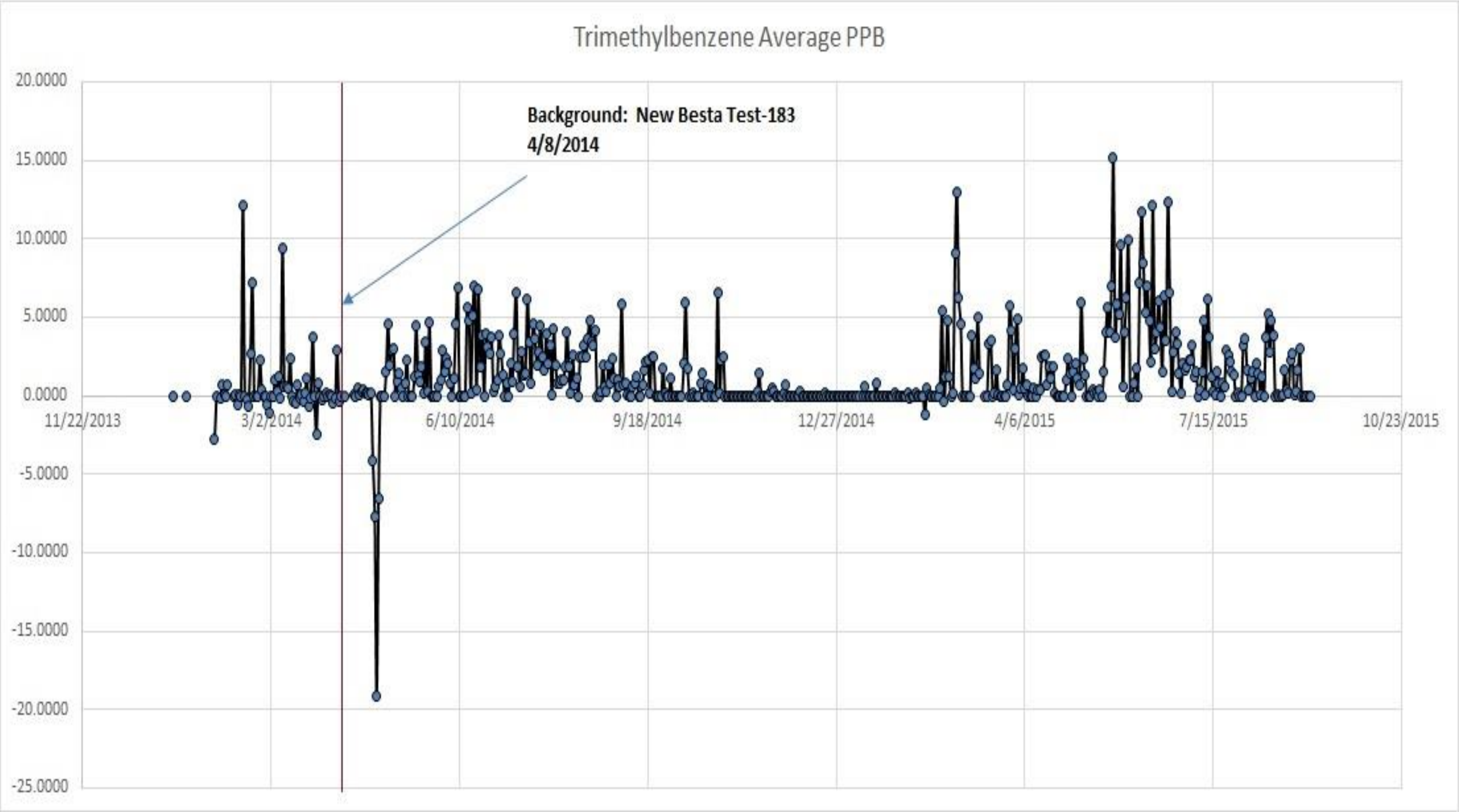
UV-DOAS – Nitrogen Monoxide
The Effect of the Background File – BEFORE & AFTER 4/8/2014



UV-DOAS – Sulfur Dioxide The Effect of the Background File – BEFORE & AFTER 4/8/2014

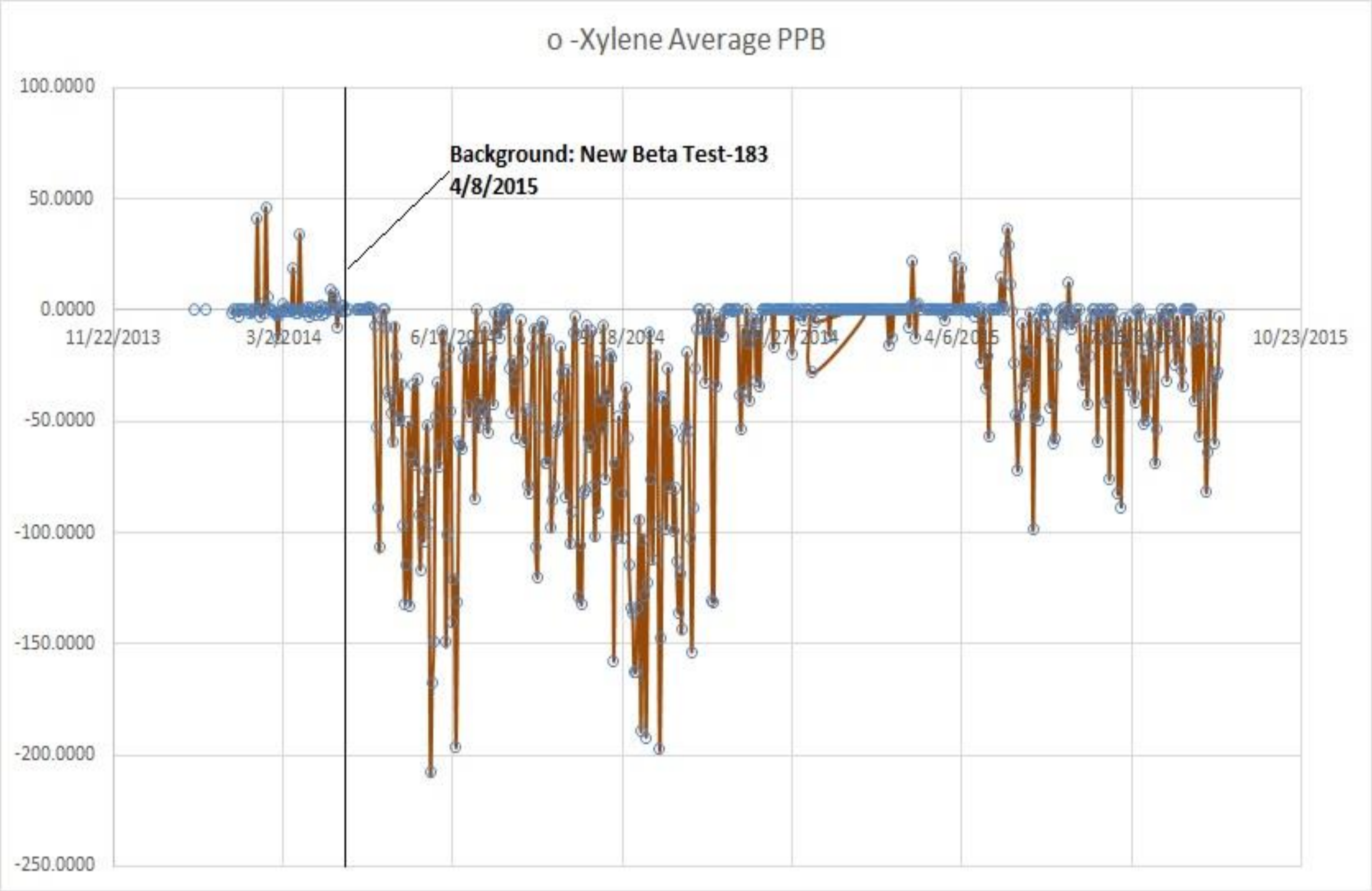


UV-DOAS – Trimethylbenzene
The Effect of the Background File
– BEFORE & AFTER 4/8/2014


Trimethylbenzene Average PPB

Background: New Besta Test-183
4/8/2014

UV-DOAS – o-Xylene
The Effect of the Background File
– BEFORE & AFTER 4/8/2014

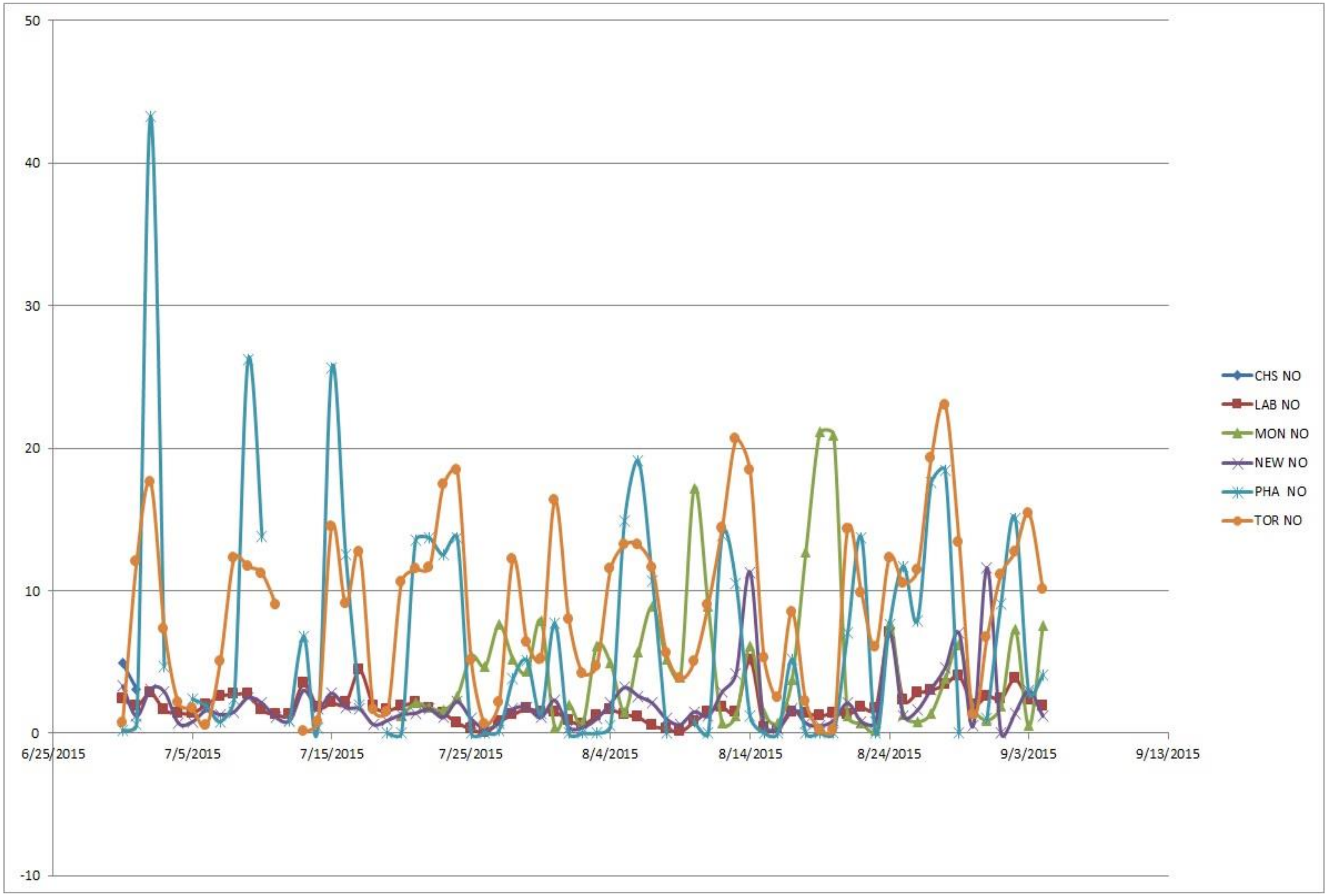


Project Evaluation – Integration into the City's Air Pollutant Database and Data on the Web.

- **AirVision-** The acquisition of a data logger in the Summer of '15 enabled integration of current data into the AirVision database.
- **Archival Data** – has yet to be integrated
- **Data on the Web** – has yet to be accomplished.
- **Nitric Oxide (NO) Data –** seems comparable to the City's other sites.

UV-DOAS – Nitric Oxide Daily Comparison to Other Sites

– AIRVISION DATA the monitoring data has recently (6/30) been incorporated into the AirVision database.



Project Evaluation – Outreach

- Began Ritner site tours with GAMP school students and faculty Spring 2013.
- GAMP School Funds through U of P (Dr. Pepino) were allocated Winter 2014/Spring 2015.
- GAMP teacher and students presented with an Open Path data set in August 2015. Report under development.
- Full Community Involvement will be assisted when the data is available on the web.
- Project is scheduled for completion by Summer of 2016.

Project Evaluation – How are we Doing?
3 Elements: Technology, Location, and Outreach

- **Technology Evaluation** – Have we given the technology a fair shake?
  - **UVDOAS** – Do these systems have detection limits too high for ambient air work?
  - **TDL** – Is the TDL adequate to the job of detecting HF? What are the consequences of putting this data on the web?
- **Site Evaluation** –
  - Are we in the right place?
  - Do we have the correct monitor/reflector orientation-perpendicular to the plume or parallel? Too far away or too close.
- **Citizen Involvement** – are we alarming people or is the sky really falling?

Conclusions

-Technology

- **UV-DOAS**
  - **Operating Parameters** indicate that we have collected good sample spectra. Good sample spectra can be saved and re-processed with a more appropriate background to provide better results.
  - **False positives –** Operators and QA staff must become spectrum analysts. Compare the sample to the reference spectra to determine whether a false positive has been obtained (per slide 28). Did we really detect TMB?
  - **New Software –** UV-DOAS is currently being modified to have better software which will have an innovative way of acquiring a **Synthetic Background.** This should help improve the back problems shown in slides 45, 46, 47, and 48. This should help in the detection of the xylenes by eliminating negative results. The new software calculates MDL in real time based on each acquisition's noise level.
  - **NAAQS Gases - NO** has been detected at levels similar to other sites in our network which monitor this compound. **SO2** has been in regular detection, but does not match well with the values obtained at the nearby RIT site.

Conclusions

-Technology

- **TDL Laser for HF**
  - **Annual Alignment –** Instrument must be sent to manufacturer annually (Canada) for internal alignment resulting in ~ 1 month downtime. Alternatively, staff can be trained by the manufacturer to perform the alignment locally ($$$). Newer models operate a lower laser temperatures requiring less frequent alignment.
  - **False Detection –** This is a turnkey device. Despite the R^2 and HF cell, there is no reliable Data Quality Indicator to determine if the instrument is in **false** detection. Spectral information is not recorded.
  - **Data on the Web –** the MDL at our path length is ~2.5PPB. Values are often measured at this level with good R^2 values. If this data is on the web will we unduly alarm the Public? This reduces the value of this instrument for use as an early warning device.

Next Steps

-from Fall ‘15 till Summer 2016

- **Data**
  - Complete the transfer of data to AirVision database – including data quality indicators (R^2).
  - Allow re-processed data to overwrite real time results.
  - Place VOC data, NO, and SO2 data on the web in real time.
- **Outreach**
  - Check on the reports provided by the GAMP School
- **Final Report and Wrap-up**
  - Due Spring 2016

Next Steps
– from Fall '15 till Summer 2016

- **ORD Project –**
  - Challenge the instrumentation with small gas mixtures of selected compounds (benzene, BTEX) in a gas cell to verify detection and the correctness of the R^2 values.
  - Check MDLs and appropriate detection of the xylenes and BTEX.

Next Steps
– from Fall ‘15 till Summer 2016

- **ORD Project – Site Evaluation -**
  - ORD will employ a newer (Gen-4) spectrometer at RTP vs Gen-2 at Philly. This device will have better signal and noise characteristics in a smaller, lighter device.
  - Device will employ a Xenon UV Source instead of Philly’s Deuterium.
  - Path Length - 880 meter total path driven by the stronger 100 watt source. More path is possible.
  - 4 passes through the sample volume (additional mirror is used)
  - NEW Cerex Advanced CMS software as installed at Philly.
  - The new system has a touchscreen interface for easier setup and alignment.
  - 646m effective path length if deployed at Philly with an extra mirror.

References:

- EPA Handbook: Optical Remote Sensing for Measurement and Monitoring of Emissions Flux http://www3.epa.gov/ttnemc01/guidlnd/gd-052.pdf
- Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air 2nd Edn, Compendium Method TO-16 Long-Path Open-Path Fourier Transform Infrared Monitoring Of Atmospheric Gases http://www3.epa.gov/ttnamti1/files/ambient/airtox/to-16r.pdf
- Hydrofluoric Acid - Chemical Safety Information, University of North Carolina – Dept. of Environmental Health and Safety Material Data Sheet, http://ehs.unc.edu/environmental/docs/hydrofluoricacid.pdf
- SPECTRA-1 User Manual Rev.d. Update 2, PKL Technologies, Inc
- UV Sentry Multi-Gas Air Analyzer End-User Hardware Manual Version 20121203-Rev.6 and various training notes supplied by Cerex Monitoring Solutions, LLC

- Cerex Monitoring Solutions, LLC has kindly provided some slides and graphics for this presentation.