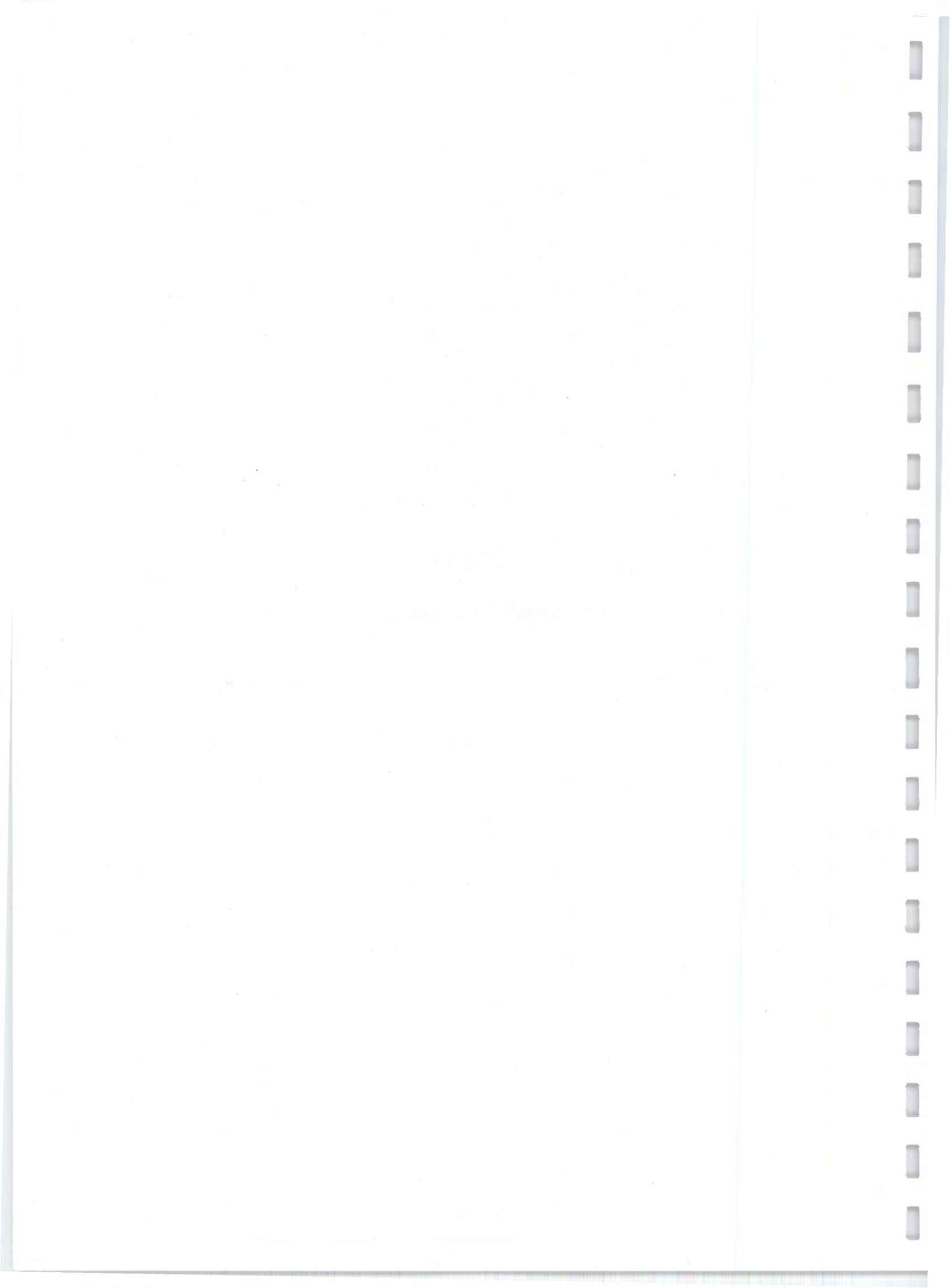


US EPA ARCHIVE DOCUMENT

APPENDIX C

ENVIRON OP-FTIR REPORT



September 3, 2010

Mr. Rick W. Kennedy  
Hodgson Russ LLP  
The Guaranty Building  
140 Pearl Street, Suite 100  
Buffalo, New York 14202

**Re: Benzene Measurements by OP-FTIR for the Tonawanda Coke Facility during the NPL DIAL Study**

Dear Mr. Kennedy:

As outlined in the project test plan, ENVIRON International Corporation (ENVIRON) has conducted field measurements of benzene concentrations at the Tonawanda Coke Corporation ("Tonawanda") facility in Tonawanda, New York, using Open Path Fourier Transform Infrared Spectroscopy ("OP-FTIR") as a mean of verification of the National Physical Laboratory ("NPL") Differential Absorption Lidar ("DIAL") benzene emissions results. This letter discusses the results of that study as well as compares the results to those obtained using DIAL measurements by NPL.

#### **OP-FTIR Measurement Approach**

ENVIRON's benzene measurement approach entailed using an OP-FTIR and a retro-reflector set up to coincide with the NPL DIAL measurement line of sight. OP-FTIR measurements were taken using an Industrial Monitor and Control Corporation ("IMACC") instrument in the monostatic mode in which a single telescope is used at one end of the path aimed at a retro reflecting mirror placed on the other end of the desired configuration path. Once aligned with the mirror, OP-FTIR path-average benzene concentrations were collected every one minute. Measurements were taken on May 25, 26, 27 and 28, 2010. The location of the OP-FTIR and retro reflecting mirror are shown in Figures 1 – 4 which are included at the end of this letter report.

The OP-FTIR data was collected, analyzed and quality assured according to Compendium Method TO-16.<sup>1</sup> Because of data quality concerns at the beginning of the campaign associated with OP-FTIR hardware problems, only validated results obtained on May 27 and 28 are discussed within this summary.

The OP-FTIR was set up to track NPL's DIAL measurement line of sight (LOS) #1 and #2 from Location 5 for May 27<sup>th</sup> and LOS #1 from location 6 for May 28<sup>th</sup>. The OP-FTIR set-up parameters for May 27<sup>th</sup> and 28<sup>th</sup> are listed in Table 1.

<sup>1</sup> U.S. Environmental Protection Agency, *Compendium of Methods for Determination of Toxic Organic Compounds, in Ambient Air, Second Edition, Compendium Method TO-16, Long-Path Open-Path Fourier Transform Infrared Monitoring of Atmospheric Gases*, January 1999.

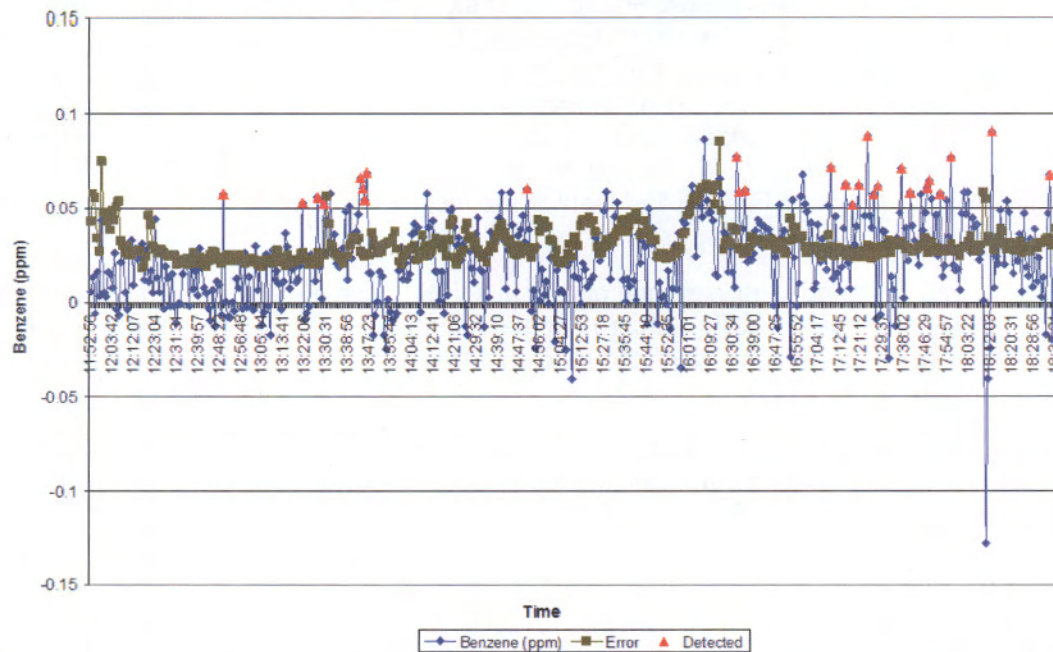
Table 1. OP-FTIR measurement system set-up parameters for May 27<sup>th</sup> and 28<sup>th</sup>

Device	May 27th			
	Latitude	Longitude	Distance Between Units (m)	Angle from North
OP-FTIR	42°59'1.23"N	78°55'27.45"W	186	290
Scissor	42°59'3.29"N	78°55'35.07"W		
Device	May 28th			
	Latitude	Longitude	Distance Between Units (m)	Angle from North
OP-FTIR	42°59'2.71"N	78°55'35.54"W	230	271
Scissor	42°59'2.84"N	78°55'45.69"W		

**OP-FTIR Measurement Results**

Two series of data were obtained on May 27<sup>th</sup> due to alignment drift that occurred between 16:09 and 16:25. Figure 5 displays the benzene concentrations (ppm) versus time for samples taken on May 27<sup>th</sup>.

Figure 5. Benzene measurements from May 27<sup>th</sup>, 2010



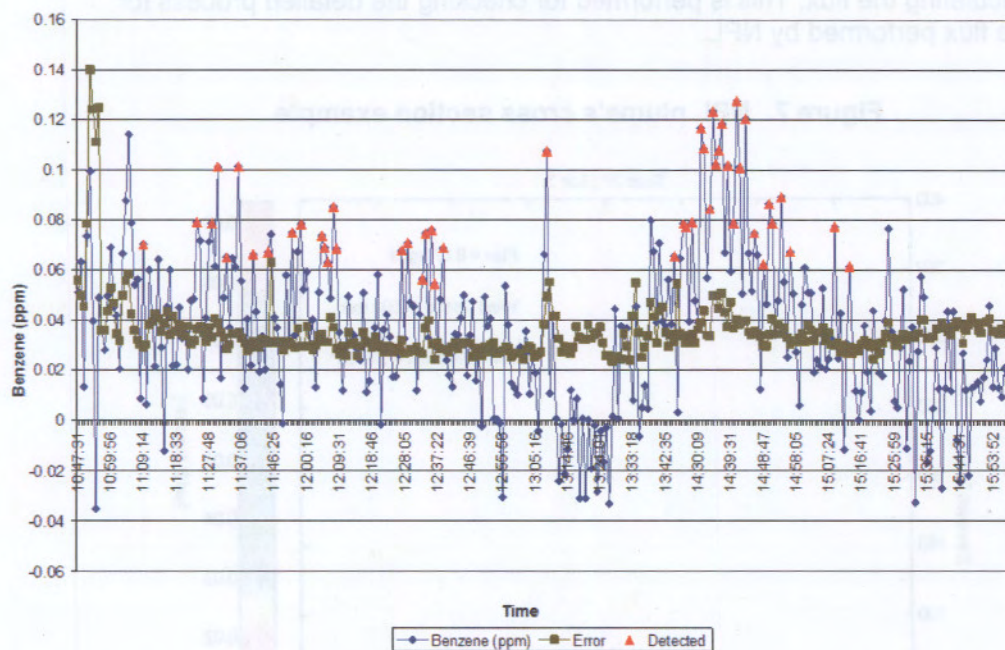
The data points represented by red triangles are above 4 standard deviations ( $4\sigma$ ) which is defined for the IMACC system as the minimum detection limit ("MDL"). The error in the graph is the  $2\sigma$  value and is determined for each concentration data point. Occasions with elevated error values indicate that the beam was obscured by steam or particle plumes. Data points with an error of more than 50% of the daily minimum are considered invalid for averaging purposes. The deep negative concentration value around 18:12 is an invalid determination associated with

a significant increase in error level. The average of all valid values as defined above (including concentrations below  $4\text{-}\sigma$ ) for each series of May 27<sup>th</sup> is given in Table 2: 24 and 34 ppb benzene, respectively.

Since many of the averaged values are below the corresponding MDL, it is expected that these average determinations are slightly positively biased. Therefore, all of the corresponding valid spectra for each series are averaged together and one concentration determination is retrieved using the same daily background. The results of this determination for each series spectral average with its corresponding error value are also given in Table 2. As the error value is much lower than the concentration for each of these spectral averaged concentrations, we report these results as actual average concentration values for the respective time interval. On May 27<sup>th</sup> generally the concentrations were low and very close to the OP-FTIR MDL, and therefore the average of the valid concentrations was positively biased up to 25% above the value of the spectral average concentration.

Figure 6 displays the time series of benzene measurements obtained on May 28<sup>th</sup>. On this day the benzene levels were slightly higher, probably due to the fact that the beam path was in the corridor between the process area and the coke oven. The spectral average concentration (reported as 36 ppb in Table 2) is almost identical to the average of all valid benzene determinations. This means that each of these one-minute values is accurate with the uncertainty of  $\pm$ error.

Figure 6. Benzene measurements from May 28<sup>th</sup>, 2010



The results of the two averaging techniques described above are shown in Table 2.

**Table 2. Daily benzene concentration results for May 27th and 28th**

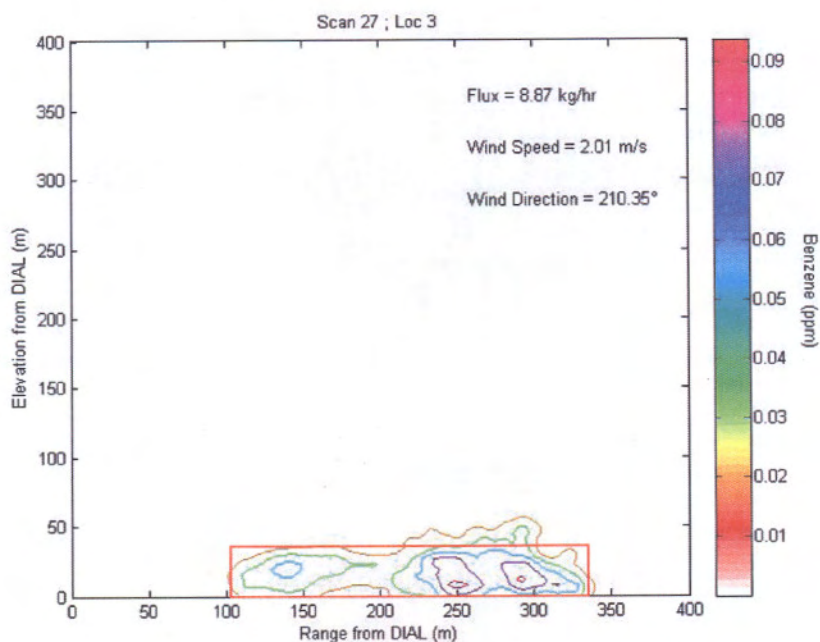
Date	Series	Number of valid values	Spectral Averaging		Average of valid values (ppm)	Difference
			Benzene (ppm)	Error		
5/27/2010	1	177	0.019	0.003	0.024	+26%
5/27/2010	2	134	0.027	0.004	0.034	+26%
5/28/2010	1	299	0.036	0.010	0.036	0%

**Review of NPL DIAL Results**

The first step of the assessment of DIAL results is to compare the benzene concentrations measured by the OP-FTIR and the DIAL at ground level. For the several events that we have measurements above detection limits we do not have matching DIAL data at the same time interval or along a similar path. However, the OP-FTIR long period average concentrations of 19 ppb on the 27<sup>th</sup> and 36 ppb on the 28<sup>th</sup> agree very well with the overall DIAL concentrations at ground level on these two days.

The second step is to evaluate whether plume map concentrations and corresponding wind data accurately report the flux. Figure 7 (Figure 2.3a1 in the NPL report) demonstrates the actual process of calculating the flux. This is performed for checking the detailed process for calculating the flux performed by NPL.

**Figure 7. NPL plume's cross section example**



The equation for flux estimation as a function of Benzene Plane Average concentration ("PAC") is:

$$F \text{ [g/s]} = \text{PAC [ppm]} \times \text{MW [g/mol]} \times (10^{-6}/0.0245) \times Y \text{ [m]} \times Z \text{ [m]} \times \text{WS [m/s]} \times 3.6$$

Where:

- MW is the gas molecular weight (78.1 g/mole for Benzene)
- $(10^{-6}/0.0245)$  is the conversion factor from ppm to  $\text{g/m}^3$
- Y is the length of the plane
- Z is the height of the plane
- 3.6 is the conversion factor from g/s to kg/hr

WS is the wind speed and RWD is the rotated wind direction with respect to the normal to the plane. Substituting  $Y=40$  m,  $Z=230$  m (see overlaid box in Figure 7),  $\text{PAC}=0.04$  ppm (about middle of the color scale to the right in Figure 7),  $\text{WS}=2$  m/s, benzene  $\text{MW}=78.1$  g/mol, yields a flux of 8.4 kg/hr. Comparing with the NPL output flux calculation of 8.9 our estimate is -6% which within the allowed  $\pm 30\%$  in the EPA facility manual for such evaluation.

The overall review of the NPL DIAL results shows a consistent range of 5 – 15 kg/hr of total benzene emissions from the site.


### Conclusions

The use of a monostatic OP-FTIR configuration was found to result in benzene concentrations generally consistent with those determined using DIAL by NPL (and USEPA DOAS system).

Please feel free to contact Dr. Ram Hashmonay at +1 919.967.9104 or by email at [rhashmonay@environcorp.com](mailto:rhashmonay@environcorp.com) if you have questions or comments regarding the findings presented herein.

Regards,

ENVIRON

  
Steven H. Ramsey, PE, BCEE  
Principal Consultant

cc: T. Ferrara, CRA  
G. Reusing, CRA



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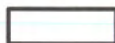
LEGEND



RETROREFLECTOR



OP-FTIR



COKE OVEN BATTERY

0 200  
SCALE IN FEET

**ENVIRON**

www.environcorp.com

**OP-FTIR AND RETROREFLECTOR LOCATION ON MAY 25TH**

TONAWANDA COKE CORPORATION  
NEW YORK

FIGURE

1

PROJECT




DRAFTED BY: BJK

DATE: 9/3/2010

BKLEIN\_9/3/10 [0224681A\_B01]



LEGEND

-  RETROREFLECTOR
-  OP-FTIR
-  COKE OVEN BATTERY

0 200  
SCALE IN FEET

**ENVIRON**

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**OP-FTIR AND RETROREFLECTOR LOCATION ON MAY 26TH**

TONAWANDA COKE CORPORATION  
NEW YORK

FIGURE

2




PROJECT

DRAFTED BY: BJK

DATE: 9/3/2010



LEGEND

-  RETROREFLECTOR
-  OP-FTIR
-  COKE OVEN BATTERY

0 200  
SCALE IN FEET

**ENVIRON**

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**OP-FTIR AND RETROREFLECTOR LOCATION ON MAY 27TH**

TONAWANDA COKE CORPORATION  
NEW YORK

**FIGURE  
3**

PROJECT

DRAFTED BY: BJK

DATE: 9/3/2010

BKLEN 9/3/10 [0224681A\_B01]



LEGEND

■ RETROREFLECTOR

● OP-FHIR

☐ COKE OVEN BATTERY

0 200  
SCALE IN FEET

**ENVIRON**

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**OP-FHIR AND RETROREFLECTOR LOCATION ON MAY 28TH**

TONAWANDA COKE CORPORATION  
NEW YORK

FIGURE

4

PROJECT

DRAFTED BY: BJK

DATE: 9/3/2010

BKLEIN 9/3/10 [0224681A\_B01]

