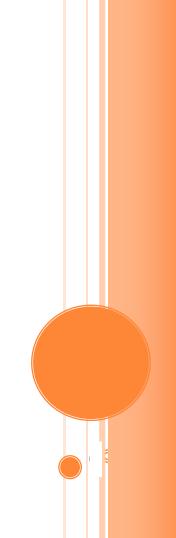


# BRIDGETOWN AMBIENT AIR QUALITY PASSIVE MONITORING PROJECT

June 2012-May 2013 Final Report





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> Barbados Government Electrical Engineering Department Barbados Investment Development Corporation (BIDC) Barbados Supreme Court Combermere School Ministry of Public Works and Transport

#### EXECUTIVE SUMMARY

The Bridgetown Ambient Air Quality Passive Monitoring Study (BAAQPMS) was designed to characterize the levels of sulphur dioxide (SO<sub>2</sub>), nitrogen dioxide (NO<sub>2</sub>), Ozone (O<sub>3</sub>) and Volatile Organic Compounds (VOCs) generated by the combustion of fossil fuels and other industrial activities in and around the Bridgetown area.

Exposure to primary and secondary pollutants may result in impacts on human health and the environment. In terms of human health, impacts may include respiratory problems and allergic reactions in sensitive individuals triggered by exposure to  $SO_2$ ,  $NO_2$ ,  $O_3$  and VOCs. Environmental damage can take the form of property damage and crop damage due to acid rain and sulphurous deposits; ground level ozone damage to electrical equipment; and ground water pollution.

In order to establish the baseline levels of primary and secondary pollutants in the Bridgetown area, sampling was conducted at seven locations for  $30 (\pm 5 \text{ days})$  days over a twelve month period. The locations were selected based on the different types of activities i.e. commercial, industrial or residential along with combinations such as residential/industrial or residential/commercial activities common to the areas. An additional round of 8-hour interval sampling was conducted to determine exposure levels.

The results obtained through passive monitoring revealed that the highest levels for both  $SO_2$  and  $NO_2$  were recorded at Broad Street while the highest levels of  $O_3$  were detected at Harbour View #2. The lowest value for  $SO_2$ ,  $NO_2$  and  $O_3$  were detected on Cypress Street, Waterford and the Elsie Payne Complex respectively. The 8-hour sampling results were inconclusive because the levels were below the detectable limits of the sampling media.

In the case of VOCs detected, no top 5 VOCs were consistently present at each site from month to month. As a result, various aromatics, alkanes, alcohols, aldehydes and ketones were represented in the different samples.

At the conclusion of the study, the data collected could be used to establish initial baseline levels for NO<sub>2</sub>, SO<sub>2</sub>, O<sub>3</sub> and a range of top 5 VOCs, within Bridgetown. Additionally, it was recommended that in order to identify any trends and to determine real time exposure comparable to international standards for the Bridgetown area, the study should be repeated using passive samplers supplemented with continuous air monitoring equipment and traffic volume monitoring equipment. However, at present the development of a continuous air monitoring programme falls outside of the EPD's financial capabilities.

# GLOSSARY OF TERMS AND ABBREVIATIONS

Aldehydes	Simple compounds which contain a carbonyl group - a
and Ketones	carbon-oxygen double bond. They are simple in the sense
	that they don't have other reactive groups like -OH or -Cl
	attached directly to the carbon atom in the carbonyl group
Alcohols	An organic compound in which the hydroxyl functional group
	is bound to a carbon atom. In particular, this carbon center
	should be saturated, having single bonds to three other atoms.
Alkanes	Comprised of only carbon and hydrogen atoms, it is the
	simplest and least reactive hydrocarbon species due to the
	saturation of the carbon atoms.
Aromatics	A hydrocarbon with alternating double and single bonds
	between carbon atoms forming rings; these hydrocarbons
	have a sweet pleasant odour
BAAQPM	Bridgetown Ambient Air Quality Passive Monitoring
Baseline	A minimum or starting point used for future data
	comparisons
CZMU	Coastal Zone Management Unit
Detectable	Detection Limit for Purposes of Reporting (DLR); this is the
limits	lowest quantity/concentration of a substance detectable by
	analysis. It is not laboratory specific and it is independent of
	the analytical method used.
Duplicate	Two samples taken from and representative of the same
Dupileute	population and carried through all steps of the sampling and
	analytical procedures in an identical manner. Duplicate
	samples are used to assess variance of the total method
	including sampling and analysis.
EPD	Environmental Protection Department
Flexible	Flexible scopes of accreditation can allow a laboratory to
0	undertake certain tests/calibrations, and to report the results as
scope of	accredited, even though they may not be explicitly stated on their
accreditation	accreditation schedule.
MTW	Ministry of Transport and Works
Nitrogen	A toxic reddish brown gas that is a strong oxidizing agent, is
Dioxide	produced by combustion (as of fossil fuels), and is an
(NO <sub>2</sub> )	atmospheric pollutant (as in smog)
·/	1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1

Ozone (O3)	Ground level ozone is not emitted directly into the air, but is created by chemical reactions between oxides of nitrogen (NOx) and volatile organic compounds (VOC) in the presence of sunlight. Emissions from industrial facilities and electric utilities, motor vehicle exhaust, gasoline vapours, and chemical solvents are some of the major sources of NOx and VOC.	
ppb	Parts per billion	
ppm	Parts per million	
Primary	An air pollutant emitted directly from a source	
Pollutant		
Secondary	An air pollutant that is not directly emitted, but forms when	
pollutant	primary pollutants react in the atmosphere	
Sorbent	A material used to absorb or adsorb liquids or gases	
Sulphur	A colourless, toxic gas with a strong odour. It	
Dioxide (SO <sub>2</sub> )	is formed naturally by volcanic activity, and by the	
	combustion of fossil fuels and several industrial processes.	
	It is also a hazardous air	
	pollutant and a major contributor to acid rain.	
Trip Blanks	Unopened passive samplers that are transported to and from	
	the field with exposed and unexposed samplers. They are	
	used to identify any contaminants introduced into the	
	samples during transit to and from the laboratory.	
USEPA	United States Environmental Protection Agency	
UKAS	United Kingdom Accreditation Service	
Volatile	Compounds of carbon, excluding carbon monoxide, carbon	
Organic	anic dioxide, carbonic acid, metallic carbides or carbonates, and	
Compounds	ammonium carbonate, which participate in atmospheric	
(VOCs)	photochemical reactions. Excludes carbon compounds	
	designated by EPA as having negligible photochemical	
	reactivity.	
WHO	World Health Organisation	

# BRIDGETOWN AMBIENT AIR QUALITY PASSIVE MONITORING PROJECT

June 2012-May 2013 Final Report

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### 1.0 INTRODUCTION

The Environmental Protection Department made representation in the draft Ambient Air Quality Policy Paper for continuous monitoring of the quality of the ambient air in Barbados. Continuous monitoring will act as a tool to determine peak pollutant concentrations, which will allow the EPD to characterize the state of the ambient air and provide sound scientific information to direct the focus of policy development and strategic planning.

However, due to the current economic situation and the high cost of procuring the required equipment, the continuous monitoring option is not a viable option at this time; passive sampling was determined to be a feasible alternative.

Given the limitations in human and financial resources at the EPD, rather than conducting a full-scale national ambient air quality assessment, the Department is seeking to conduct assessments in key areas on a project basis. This report documents the first assessment, which was conducted in Bridgetown.

#### 1.1 Bridgetown Study Area

Bridgetown was chosen as the study area for several reasons but primarily because it is the economic centre of the Barbadian economy and is characterised by densely situated mixed-use activity (commercial, industrial and residential).

Additionally, Bridgetown was designated a United Nations Educational, Scientific and Cultural Organization (UNESCO) World Heritage site in 2011. As a result of that designation, the Barbados World Heritage Committee was formed comprising of several governmental, non-governmental organisation and private stakeholders responsible for the preservation, management and development of Bridgetown. In order to capitalize on the UNESCO World Heritage designation the Bridgetown Redevelopment Project has been undertaken to preserve, enhance and manage the Bridgetown area. Upgrades to the area include the redevelopment of the Constitution River through the creation of new embankments, landscaping and the dredging of the river; as well as the nearby Church Village Green Park and Amphitheatre. Additional projects earmarked for the area include the Sugar Point Cruise Terminal and the Pier Head Marina Project. These projects, in addition to the existing infrastructure within Bridgetown may be negatively impacted by poor ambient air quality. Therefore, this study will be instrumental in creating a baseline for ambient air quality parameters within Bridgetown and consequently allow for the management and preservation of the status of Bridgetown as a UNESCO World Heritage site.

### 2.0 PROJECT OBJECTIVE

The objective of the Bridgetown Ambient Air Quality Assessment (BAAQA) was to characterize the air quality in and around different areas of Bridgetown and to determine any trends in primary and secondary pollutant levels. The study was undertaken at seven locations across Bridgetown over the course of twelve (12) months.

To assist with the analysis, weather data was collected from various sources such as the Coastal Zone Management Unit and web sources. Traffic data was collected by the Ministry of Transport and Works (MTW) for two weeks at each location during different months.

#### 2.1 Passive Sampling vs. Real-Time Continuous Monitoring

As noted during the introduction the project will utilize passive sampling to determine the average, primary and secondary pollutant levels. All primary and secondary pollutant standards used world-wide are based on continuous monitoring which provides real time concentrations on an incremental basis, which allows one to identify peak concentrations whereas passive monitoring provides an average concentration over the period monitored. In addition to the differences in the average and peak concentrations detected by passive and continuous monitoring, there are several other differences such as:

- Real time continuous monitoring methodologies are utilized by the United States Environmental Protection Agency (USEPA) and the World Health Organisation (WHO) to formulate their standards for both primary and secondary pollutants such as; nitrogen dioxide and its derivatives (NO<sub>2</sub>), sulphur dioxide (SO<sub>2</sub>) and its derivatives and ozone (O<sub>3</sub>), due to the accuracy of the equipment and the rigid sampling methodologies. No standards have been derived from passive sampling methodologies.
- Passive sampling methodologies do not require complicated set up and access to power to conduct sampling as they only require passive airflow over sample media. The concentrations are then calculated based on the levels detected on the sample media and the estimated exposure times providing an average concentration over time. Conversely, real time continuous monitoring utilizes pumps to draw a specific volume of air into a chamber; the air is then analyzed by specialized equipment, providing a more accurate real time concentration.

Despite the differences, if one were to observe a comparison of data collected over a similar timeframe, data collected by passive monitors will show similar trends and patterns as continuous monitors. However, it must be noted that the actual concentrations registered by passive samplers are generally lower than those collected through continuous monitoring.

#### 2.2 Primary and Secondary Pollutants

The draft Ambient Air Quality Policy Paper submitted by the EPD has identified the World Health Organization (WHO) Ambient Air quality standards as the primary reference standard. Therefore, the pollutants of focus in the study are those highlighted by the WHO guidelines as primary and secondary pollutants. These primary pollutants include sulphur dioxide (SO<sub>2</sub>), nitrogen dioxide (NO<sub>2</sub>) and Volatile Organic Compounds (VOCs). Ozone (O<sub>3</sub>) is considered a secondary pollutant, as it is formed by photochemical reactions between nitrogen oxides and VOCs. It should be noted that  $SO_2$  and  $NO_2$  are utilized as indicators of the presence of sulphur oxides ( $SO_X$ ) and nitrogen oxides ( $NO_X$ ). The selected pollutants and their impacts are highlighted in Table 1.

Primary pollutants may consist of air pollutants that may result in smog, acid rain and other health and infrastructural hazards, if present in sufficient quantities. In addition, primary pollutants are generally emitted from various stationary sources such as industry, transportation, mining, agriculture and electricity generation. In Bridgetown, the most prominent sources of pollutants and VOCs would be industrial activities and the combustion of fossil fuels.

PRIMARY POLLUTANT	DESCRIPTION
Sulphur Dioxide (SO <sub>2</sub> )	By far the main source of sulphur dioxide is the combustion of fossil fuels such as diesel and fuel oil. According to the USEPA, short- term (5 minutes to 24 hours) exposures to SO <sub>2</sub> , may result in several adverse respiratory problems including the constriction of bronchial tubes and increased asthma symptoms in children and the elderly. It is also a component of acid rain formation, which can cause property and environmental damage.
Nitrogen Dioxide (NO2)	The main source of NO <sub>2</sub> would be high temperature combustion of fossil fuels and therefore, electricity generation and road traffic are the primary sources of NO <sub>2</sub> . According to the USEPA, short-term (30 minutes to 24 hours) NO <sub>2</sub> exposure may trigger respiratory problems inclusive of airway inflammation in healthy people and increased respiratory symptoms in people with asthma. Emissions that lead to the formation of NO <sub>2</sub> generally also lead to the formation of other nitrogen oxides and tropospheric ozone (O <sub>3</sub> ).
Volatile Organic Compounds (VOCs)	<ul> <li>VOCs are comprised of a very wide range of hydrocarbons, oxygenates, halogenates and other carbon compounds existing in the atmosphere in the vapour phase.</li> <li>The predominant source of VOCs is typically through leakage from pressurized systems (e.g. natural gas, methane) or evaporation of a liquid fuel such as benzene from vehicle fuel tanks However, the incomplete combustion of fossil fuels and other incineration processes may also give rise to fragments that are emitted in the form of VOCs.</li> </ul>
SECONDARY POLLUTANT	DESCRIPTION

# Table 1: List of Primary and Secondary Pollutants measured during theBridgetown Ambient Air Quality Passive Monitoring Survey

Ozone (O <sub>3</sub> )	Ground level ozone is the main component of smog and is created by the
	chemical interactions between NO <sub>2</sub> ,VOCs and sunlight. The
	concentration generated is dependent on atmospheric convection, the
	thermal inversion layer and an optimal VOC/nitrogen oxides ratio
	ranging from 4:1 to $10:1^{1}$ . At high concentrations, O <sub>3</sub> may irritate
	airways and cause breathing difficulties and damage lungs. It can also
	trigger asthma attacks, especially in children, the ill and the elderly and
	can damage vegetation and reduce crop yields.

## 4.0 STUDY AREA AND METHODOLOGY

#### 4.1 Study Area

The sampling programme consisted of seven sites, six of which were located in the area of Bridgetown and one background site located north-east of the Bridgetown sites (Waterford, St. Michael) as shown in Figure 1.

The background site was selected due to its upwind location outside of the study area. Site selection was initially accomplished through the differentiation between activities occurring in the area and assigning the following classifications;

- Commercial activities
- Residential activity
- Industrial activity
- Mixed use activities (a combination of any of the first three activities)

In addition to the activity type, the sample locations were also classified based on the recommendations provided by the passive sampler manufacturer and the proximity to the nearest heavily trafficked roadway. Table 2 outlines the criteria associated with each site location.

<sup>&</sup>lt;sup>1</sup> World Health Organization, Europe. (2005). *Air Quality Guidelines 2005*. Available: http://www.euro.who.int/\_\_data/assets/pdf\_file/0005/78638/E90038.pdf. Last accessed January 15, 2014.



Figure 1: Map of sampling locations

Site Location	Location Type	Distance From Major Roadway	Other Selection Criteria
Waterford, St. Michael	Background	>50 m	Located NE of all other sites outside of Bridgetown
Broad Street, Bridgetown	Near road	~1-5 m	Commercial area
Harbour View #2, Prescod Blvd, St. Michael	Intermediate	20-30 m	Industrial area
Pickwick Gap, St. Michael	Intermediate	20-30 m	Residential
Supreme Court Complex Whitepark Road, St. Michael	Near road	1-5 m	Residential/Commercial/Industrial
Elsie Payne Complex, Constitution Road, St. Michael	Urban Background	>50 m	Residential/Commercial
Cypress Street	Intermediate	20-30 m	Residential

#### Table 2: Site location and selection criteria

#### 4.2 Tube Deployment

The air quality at seven (7) locations was assessed utilizing passive monitors designed to allow passive air flow over treated sampling media, which was then analysed by gas chromatography and other proprietary methodologies by the manufacturer Enviro Technology Services PLC UK (ET), within their flexible scope of accreditation. The passive samplers were removed, packaged and shipped to ET monthly for analysis.

The passive samplers were deployed at each of the sample sites in the following manner.

- Three types of passive samplers were utilized in the study: one that measured top five VOCs, another for  $SO_2/NO_2$  and a third for  $O_3$ .
- One of each type of passive sample tube was placed at each of 6 locations
- In addition, a single duplicate tube was placed at various locations, resulting in four (4) tubes per site per month<sup>2</sup>, as shown in Table 3.
- No duplicates were used at the background site. Therefore three (3) samplers (VOC, SO<sub>2</sub>/NO<sub>2</sub>, and O<sub>3</sub>) were deployed on a monthly basis at this site.
- Three trip blanks, one each for Top Five VOC, SO<sub>2</sub>/NO<sub>2</sub>, and O<sub>3</sub> were transported with the other samples for analysis.
- Tubes were placed at a height between two (2) and four (4) metres from the ground and secured by zip ties and double sided tape. See (Appendix I for photos)

### 4.3 Additional Data

<sup>&</sup>lt;sup>2</sup> A monthly sample is considered to be valid if the exposure period is within +/- 5 days of the 30 day period (calendar month); it is also desirable to have the 'on' and 'off' dates as close as possible to the start and end of a calendar month in order to minimize uncertainty in the determination of the exposure month. - <u>Operations Manual for Air Quality Monitoring in Ontario Ministry of the Environment Operations Division Technical Support Section</u>

In addition to passive monitoring sampling, the following supplementary data was collected;

- Ministry of Transport traffic counters were utilized to conduct traffic counts along the main roads closest to the sampling site for a period of seven (7) days, to account for both weekday and weekend traffic.
- Meteorological data was provided by the Coastal Zone Management Unit (CZMU) weather stations closest to the sampling sites.
- Sampling was conducted monthly at each location for twelve months. However, an additional round of sampling was conducted between July 21<sup>st</sup> and July 24th 2013 at Harbour View #2. During this supplementary sampling, the tubes were exposed over 8 hour intervals, in an effort to determine diurnal levels of the primary and secondary pollutants.

Table 3: Shows the diffusion tube allocation from June 2012 to May 2013. Values represented by "2" indicate that a duplicate is placed on site.

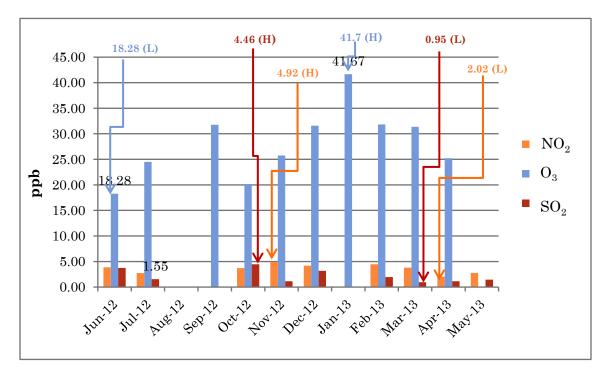
		Ŧ			a		N	P	Ŧ		X		X
Site ID#	Parameters	Jun- 12	Jul- 12	Aug- 12	Sep- 12	Oct- 12	Nov- 12	Dec- 12	Jan- 13	Feb- 13	Mar- 13	Apr- 13	May- 13
	voc	1	1	1	1	1	1	1	1	1	1	1	1
	<b>SO</b> <sub>2</sub> / <b>NO</b> <sub>2</sub>	1	1	1	1	1	1	1	1	1	1	1	1
Waterford, St. Michael	(03)	1	1	1	1	1	1	1	1	1	1	1	1
	(03)				1	1	1	1				1	
	voc	2	1	1	2	1	1	2	1	1	2	1	1
	$SO_2/NO_2$	1	2	1	1	2	1	1	2	1	1	2	1
Broad Street, Bridgetown	<b>(O</b> <sub>3</sub> )	1	1	2	1	1	2	1	1	2	1	1	2
	VOC	1		0	1	0		1			1	0	
	VOC SO <sub>2</sub> /NO <sub>2</sub>	1	2	2	1	2	2	1	2	2	1	2	2
Harbour View #2, Prescod Blvd, St.	(03)	1	1	1	1	1	1	1	1	1	1	1	1
Michael	(03)	L	L	T	1				Ŧ	L		1	
	voc	1	1	1	1	1	1	1	1	1	1	1	1
	$SO_2/NO_2$	1	1	2	1	1	2	1	1	2	1	1	2
Pickwick Gap, St. Michael	<b>(O</b> 3 <b>)</b>	2	2	1	2	2	1	2	2	1	2	2	1
	VOC SO <sub>2</sub> /NO <sub>2</sub>	2 1	1	2	2	1 2	2	2	1	2	2	1 2	2
Supreme Court Complex Whitepark	(O <sub>3</sub> )	1	1	1	1	1	1	1	1	1	1	1	1
Elsie Payne Complex , Constitution Road, St. Michael	VOC	1	1	1	1	1	1	1	1	1	1	1	1
	SO <sub>2</sub> /NO <sub>2</sub> (O <sub>3</sub> )	2	1	2	2	1	2	2	1	2	2	1	2
	VOC	1	2	1	1	2	1	1	2	1	1	2	1
	SO <sub>2</sub> /NO <sub>2</sub>	1	1	1	1	1	1	1	1	1	1	1	1
Cypress Street, St. Michael	<b>(O</b> <sub>3</sub> <b>)</b>	2	1	2	2	1	2	2	1	2	2	1	2

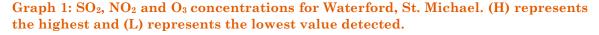
#### 5.0 RESULTS

#### 5.1 Waterford, St. Michael Background Site

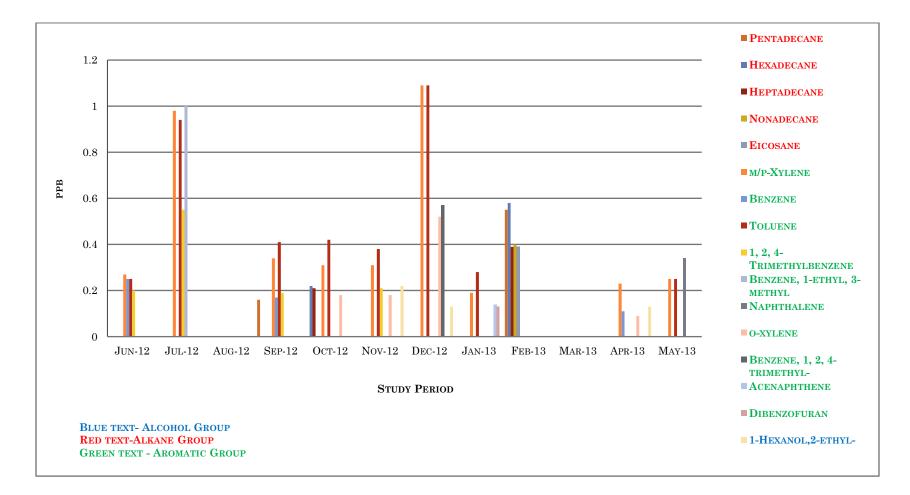
Sampling conducted at the Combermere School, located at Waterford, St. Michael, upwind and to the north-east of the other sampling sites was conducted between June 2012 and May 2013. During the months of August 2012 and May 2013, O<sub>3</sub> samplers were removed without authorization. In August and September 2012 and January 2013, SO<sub>2</sub>/NO<sub>2</sub> samplers were removed. In August 2012, February and March 2013, VOC passive samplers were removed without authorization, resulting in no data for those months.

According to Graph 1, SO<sub>2</sub> concentrations at Waterford were highest (4.92 ppb) in October 2012 and lowest (0.95 ppb) in March 2013. Additionally, the NO<sub>2</sub> concentrations at Waterford peaked at 4.92 ppb in November 2012 and O<sub>3</sub> levels peaked at 41.7 ppb in January 2013.





The top five VOCs consisted of compounds from the alkane groups, aromatic compounds such as benzene and toluene, as well as alcohols and glycols compounds as shown below in Graph 2. The most frequently detected compounds were from the aromatic groups. The highest concentrations were approximately 1.09 ppb for both toluene and heptadecane with the lowest concentration detected recorded for  $\sigma$ -xylene with a value of approximately 0.09 ppb.



Graph 2: Top Five VOC at the Waterford sample site for the period June 2012 to May 2013. The compounds shown represent only those compounds covered in the laboratory accredited flexible scope and are not blank corrected.

As shown in Graph 2 the compounds detected were those included in the laboratory's United Kingdom Accreditation Service (UKAS) accredited scope (i.e. the values can be considered accurate and verifiable). However, several compounds were detected during the analysis that fell outside of the laboratory flexible scope. These are provided in Table 4 below.

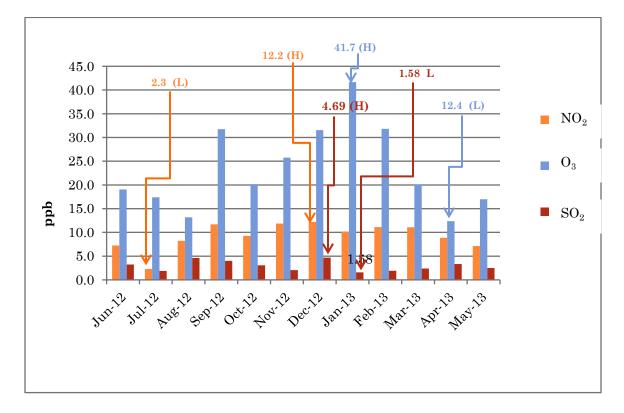
	CONCENTRATION IN PARTS PER BILLION (PPB)		
Hydrocarbons	Jun-12	<b>DEC-12</b>	<b>M</b> AY 13
HEPTANE, 2, 2, 4, 5, 5-PENTAMETHYL-+	0.34		
CYCLOHEXADECANE +			0.43
CYCLOHEXANE, ISOTCYANATO-		0.62	
ALCOHOLS & GLYCOLS			
ISOPROPYL MYRISTATE			0.30

# Table 4: VOC Compounds outside of the laboratory accredited flexible scope for the Waterford sampling location.

## 5.2 Broad Street, Bridgetown, St. Michael

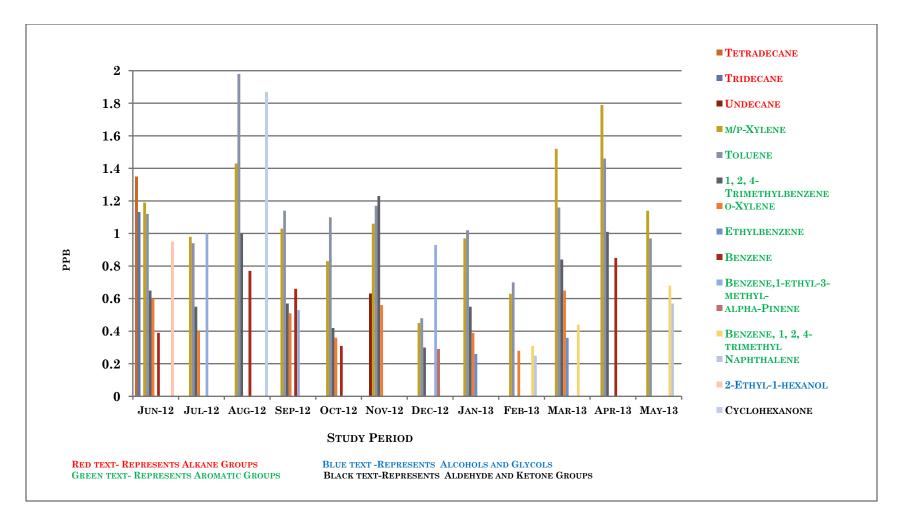
Broad Street can be considered one of the busiest locations in Bridgetown for both human and vehicular traffic. Samplers were mounted on a light pole outside of the Bank of Nova Scotia for the period June 2012 to May 2013.

Results showed that  $SO_2$  levels peaked (4.69 ppb) in December 2012, with the lowest levels (1.58 ppb) detected in January 2013. In the case of NO<sub>2</sub>, the highest level (12.2 ppb) was detected in November 2012, with the lowest level (2.30 ppb) detected in July 2012. Ozone levels peaked (41.7 ppb) in January 2013 and the lowest (12.4 ppb) in April 2013.





With respect to the top five VOC compounds, alkanes, aldehydes and ketones, alcohols and glycols and aromatic compounds were detected at various times throughout the sampling period and can be observed in the following graphs. As shown in Graph 4, the most frequently detected compounds were from the aromatics group.



Graph 4: VOC compounds detected at the Broad Street sampling location during the study period June 2012 to May 2013. The compounds shown represent only those compounds covered in the laboratory accredited flexible scope and are not blank corrected.

As shown in Graph 4 the compounds detected were those included in the laboratory's UKAS accreditation. Only one compound, 2, 2, 4, 5, 5 Pentamethyl- heptane, fell outside of the laboratory flexible scope was detected during the analysis. The concentrations detected are indicated in Table 5.

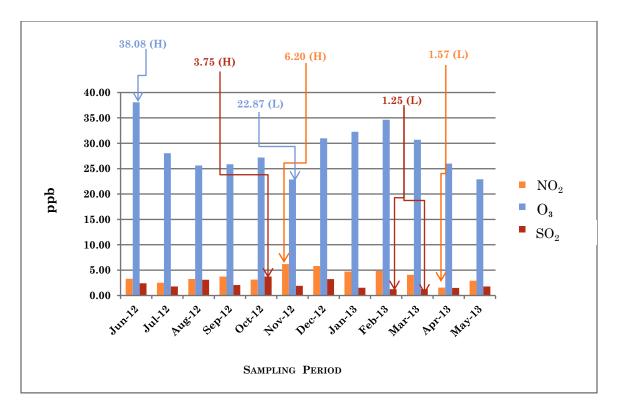
	CONCENTRATION IN PART	'S PER BILLION (PPB)
Hydrocarbons	JUN-12	DEC-12
HEPTANE, 2, 2, 4, 5, 5-PENTAMETHYL-	1.73	0.32

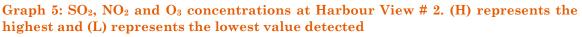
# Table 5: VOC Compounds outside of the laboratory accredited flexible scope forthe Waterford sampling location.

#### 5.3 Harbour View #2

Samplers were placed near the entrance to the Barbados Deep Water Harbour along Harbour View #2 located NW of Broad Street as shown in Figure 1. The results of the monthly samples have been represented graphically in Graph 5.

The highest  $SO_2$  concentration of 3.75 ppb was detected in October 2012. Equally low concentrations of 1.25 ppb were detected in February and March 2013. In the case of NO<sub>2</sub>, the highest concentration (5 ppb) was detected in November 2012 with the lowest concentration (1.57) detected in April 2013. The highest recorded ozone level (38.08 ppb) was detected in June 2012, whereas the lowest (22.87 ppb) was detected in November 2012.





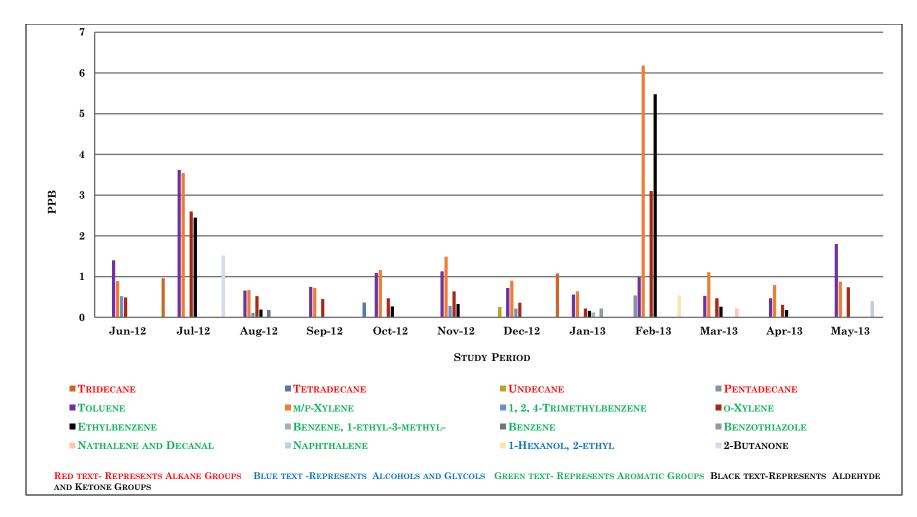
As shown in Graph 6, aromatic compounds accounted for the most frequent top five VOCs detected during the sampling period with a total of nine (9) compounds detected belonging to that group. The most frequently detected compounds were m-p-xylene and  $\sigma$ -xylene. The highest concentrations of m-p xylene (6.18 ppb) and  $\sigma$ -xylene (3.1 ppb) were detected in February 2013.

The highest concentration of any compound detected was 6.18 ppb of m/p-xylene, the lowest concentration of m/p-xylene (0.64 ppb) was detected in January 2013. The second highest concentration detected was that of 5.48 ppb of Ethylbenzene, in February 2013.

As shown in Graph 6, the compounds detected were those included in the laboratory's UKAS accreditation. Several compounds were detected during the analysis that fell outside of the laboratory flexible scope. The recorded compound concentrations detected are indicated in Table 6 below.

Table 6: The table below highlights the compounds detected but not covered by the flexible scope in addition to compounds(\*\*) that may be due to the reaction of ozone and the Tenax sorbent.

	CONCENTRATION IN PARTS PER BILLION (PPB)					
HYDROCARBONS	JUN-12	JULY-12	Sept-	Apr-13	MAY-13	
HEPTANE, 2, 2, 4, 5, 5-PENTAMETHYL-	0.52					
CYCLOHEXANE, ISOTHIOCYANATO-			0.60			
CYCLOHEXANE, ISOCYANATO-			0.29			
AROMATICS						
BUTYLATED HYDROXYTOLUENE		1.95				
ACIDS						
PHENYLMALEIC ANHYDRIDE				0.32		
ALDEHYDES & KETONES						
CO-LOCATED BENZEALDEHYDE**					0.50	
BENZEALDEHYDE**					0.45	

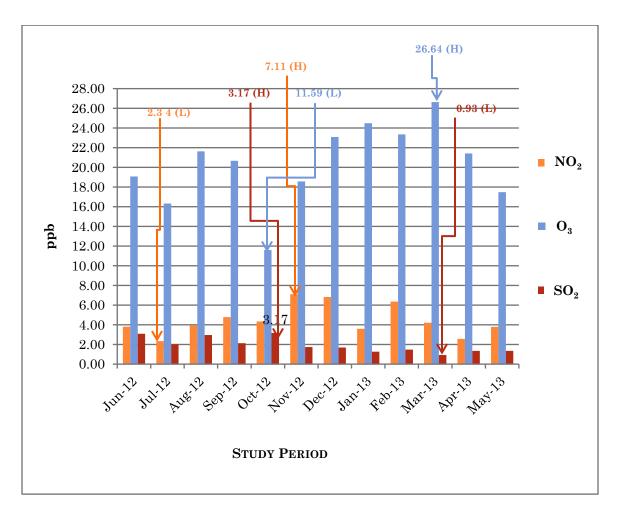


Graph 6: VOC compounds detected at the Harbour View #2 sampling location during the study period June 2012 to May 2013. The compounds shown represent only those compounds covered in the laboratory accredited flexible scope and are not blank corrected.

#### 5.4 Pickwick Gap, St. Michael

Passive samplers were placed in the Pickwick Gap area which represented an intermediate distance from the main roadway in a residential area. The results of the sampling are shown in Graph 7.

 $SO_2$  levels peaked (3.17 ppb) in October 2012 and the lowest concentration of 0.93 ppb was detected in March 2013. The highest  $NO_2$ concentration (7.11 ppb) was detected in November 2012 with the lowest concentration (2.34 ppb) detected in July 2012. Ozone levels peaked (26.64 ppb) in March 2013 and the lowest (11.59 ppb) was detected in July 2012.



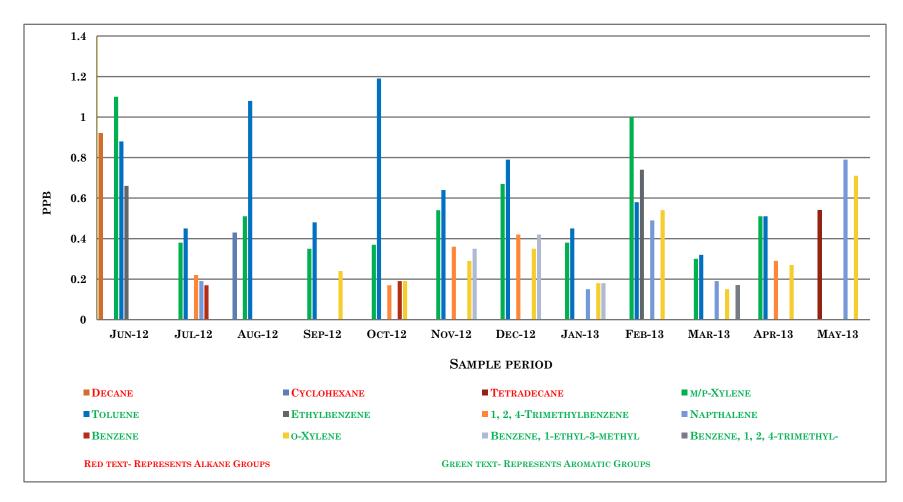
Graph 7: SO<sub>2</sub>, NO<sub>2</sub> and O<sub>3</sub> concentrations detected at Pickwick Gap, St. Michael. (H) represents the highest and (L) represents the lowest value detected.

Based on Graph 8, m-p-xylene was the most commonly detected (11 times) VOC during the sampling period. Aromatics accounted for the majority of the compounds detected. The highest concentration of any compound detected was that of toluene with a concentration of 1.19 ppb, followed by m-p-xylene with a concentration of 1.10 ppb.

As shown in Graph 8 the compounds detected were those included in the laboratory's UKAS accreditation. Several compounds were detected during the analysis that fell outside of the laboratory flexible scope. The recorded concentrations detected have been highlighted in Table 7.

Table 7: The table below highlights the compounds detected but not covered by the flexible scope in addition to compounds(\*\*) that may be due to the reaction of ozone and the Tenax sorbent.

Hydrocarbons	CONCENTRATION IN PARTS PER BILLION (PPB)						
	Jun-12	Aug-12	Sep-12	Apr-13	May-13		
Pentane, 2-methyl-		0.40					
Cylohexanone		0.74					
Cyclohexane, isocyanato-			0.53				
Cyclohexane, isthiocyanato-			0.39	0.36	0.80		
Cyclohexadecane					0.53		
ALKENES	CONCENTRATION IN PARTS PER BILLION (PPB)						
2, 4-Dimethyl-1-heptene	0.68						
ALDEHYDES AND KETONES	Conc	ENTRATION	IN PARTS PI	ER BILLION	I (PPB)		
Nonanal**					0.57		

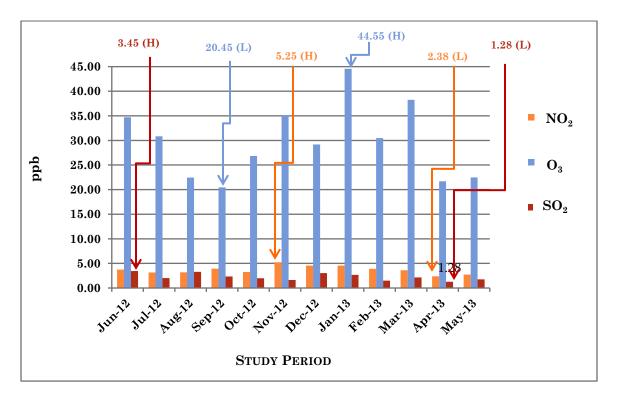


Graph 8: VOC compounds detected at the Pickwick Gap sampling location during the study period June 2012 to May 2013. The compounds shown represent only those compounds covered in the laboratory accredited flexible scope and are not blank corrected.

#### 5.5 Supreme Court Complex, Whitepark Road, St. Michael

This location was considered a near road sampling location in a combination, residential/commercial/industrial zone due to the presence of several businesses, residences and industrial operations. The results of the sampling are highlighted in the graphs below.

Based on Graph 9, SO<sub>2</sub> levels peaked (3.45 ppb) in June 2012 and the lowest SO<sub>2</sub> concentration (1.28 ppb) was detected in April 2013. The highest NO<sub>2</sub> concentration (5.25 ppb) was detected in November 2012, whereas the lowest concentration (2.38 ppb) was detected in April 2013. The highest ozone level (44.55 ppb) was detected in January 2013 and the lowest (20.45 ppb) in September 2012.

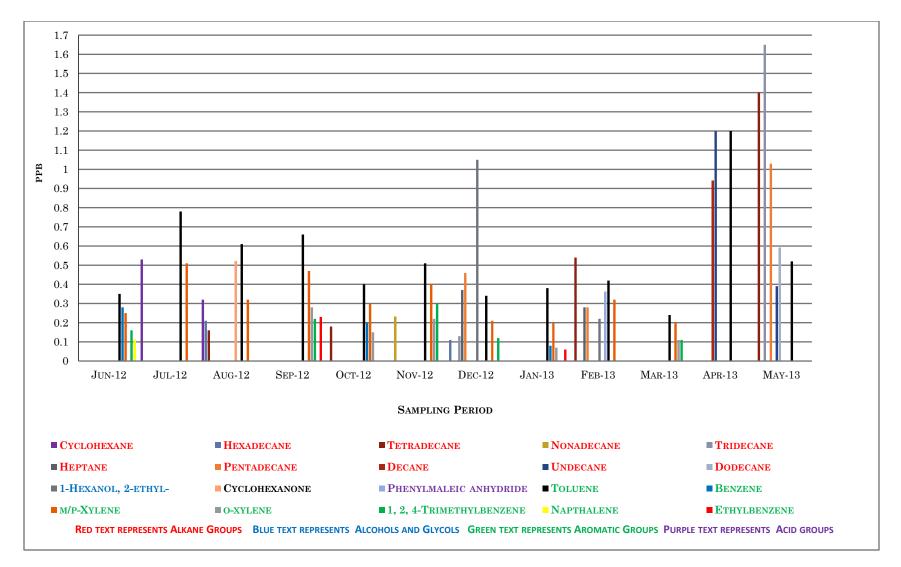




During the sampling period the most frequently detected compounds were alkanes accounting for 50% of the compounds detected as shown in Graph 10. For each group detected the highest concentrations were as follows; Tridecane (alkane) 1.65 ppb, Toluene (aromatic) 1.20 ppb, 1-hexanol,2-ethyl (alcohol) 1.05 ppb and phenylmalic anhydride (acid) 0.36 ppb. The following table highlights the compounds detected which were outside of the flexible scope of the laboratory but have been detected within the samples.

# Table 8: The table below highlights the compounds detected but not covered by the flexible scope.

	CONCENTRATION IN PARTS PER BILLION (PPB)						
Hydrocarbons	Jun-12	Jul-12	AUG-12	Nov-12	MAR-13	Apr-13	<b>MAY-13</b>
Hexane,3-methyl-	0.18						
Pentane, 2-methyl-		1.61	0.44				
Cyclohexane, isothiocyanato-				0.42		0.42	
Decane, 4-methyl-						0.55	
Cyclohexadecane							0.68
ALCOHOLS & GLYCOLS	CONCENTRATION IN PARTS PER BILLION (PPB)						
isopropyl Myristate							0.77
1-Pentene, 2-methyl-		1.28					
AROMATICS	CONCENTRATION IN PARTS PER BILLION (PPB)						
Napthalene and Decanal					0.48		

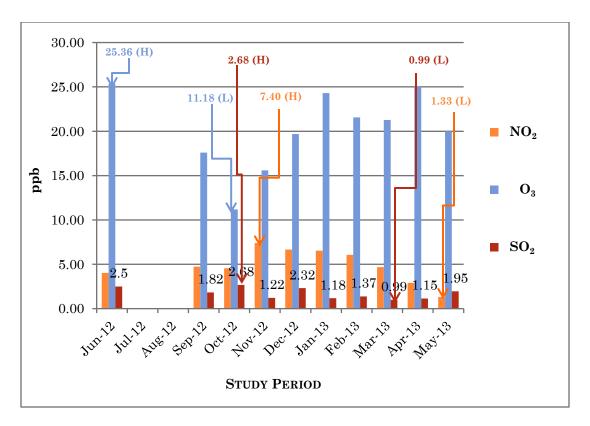


Graph 10: VOC compounds detected at the Supreme Court, Whitepark Rd. sampling location during the study period June 2012 to May 2013. The compounds shown represent only those compounds covered in the laboratory accredited flexible scope and are not blank corrected.

#### 5.6 Elsie Payne Complex /Queens Park

Samplers were originally deployed at Queens Park, Constitution Road, St, Michael. However, due to the unauthorized removal of samplers during the month of July 2012, alternative arrangements were sought but were not secured until August 2012. From September 2012 until May 2013, samplers were deployed at the Elsie Payne Complex, Constitution Road, St. Michael which was across the street from Queens Park. The results of the sampling are highlighted below in Graph 11.

The highest level (2.68 ppb) of  $SO_2$  was detected in October 2012 at the Elsie Payne Complex. The lowest level detected (0.99 ppb) was observed during the month of March 2013.





The highest NO<sub>2</sub> concentration (7.40 ppb) was detected in November 2012, with the lowest level (1.33 ppb) detected in May 2013. The highest ozone concentration (25.36 ppb) was detected in June 2012 and the lowest (11.18 ppb) in October 2012.

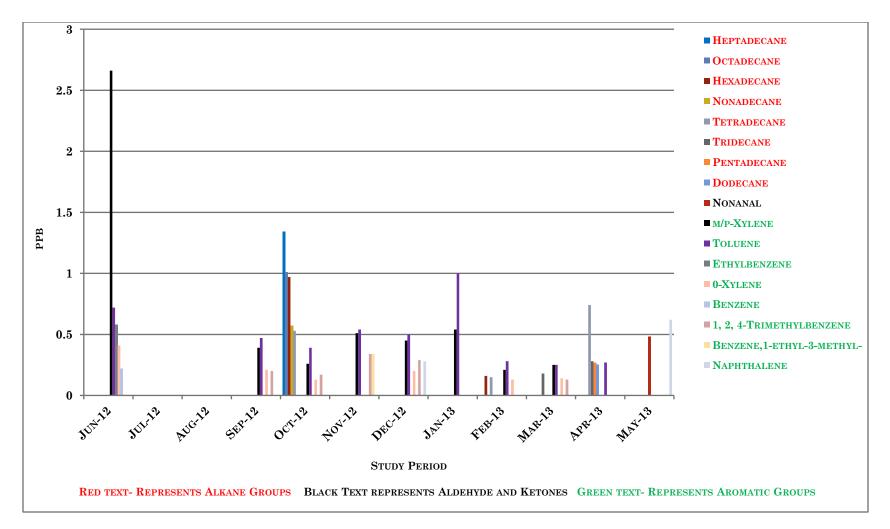
Alkanes (hydrocarbons), alkenes, aldehydes and ketones, halogens and aromatic compounds were detected at various times throughout the sampling period and can be observed in the following graphs.

As shown in Graph 12, the aromatics and alkanes were detected in equal amounts. However the highest VOC concentration detected among the top five for each month was 2.66 ppb of m/p-xylene in June 2012 followed by 1.34 ppb of heptadecane in October 2012 and 1 ppb of toluene in January 2013.

Table 9 outlines the compounds detected which were outside of the flexible scope of the laboratory but have been detected within the samples.

Table 9: The table below highlights the VOC compounds detected at The Elsie Payne Complex but not covered by the flexible scope.

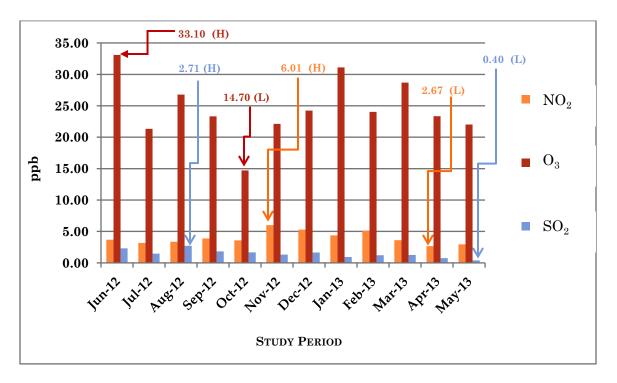
	CONCENTRATION IN PARTS PER BILLION (PPB)			
Hydrocarbons	Sept-12	Nov-12	JAN-12	<b>M</b> AY-13
Cyclohexane,isocyanato-	0.25		0.48	
Cyclohexane, isothiocyanato-			1.08	0.62
Cyclohexanone			0.52	0.67
AROMATICS				
Benzothiazole		0.43		0.57



Graph 12: VOC compounds detected at the Supreme Court, Whitepark Rd. sampling location during the study period June 2012 to May 2013. The compounds shown represent only those compounds covered in the laboratory accredited flexible scope and are not blank corrected.

## 5.7 Cypress Street, Bridgetown

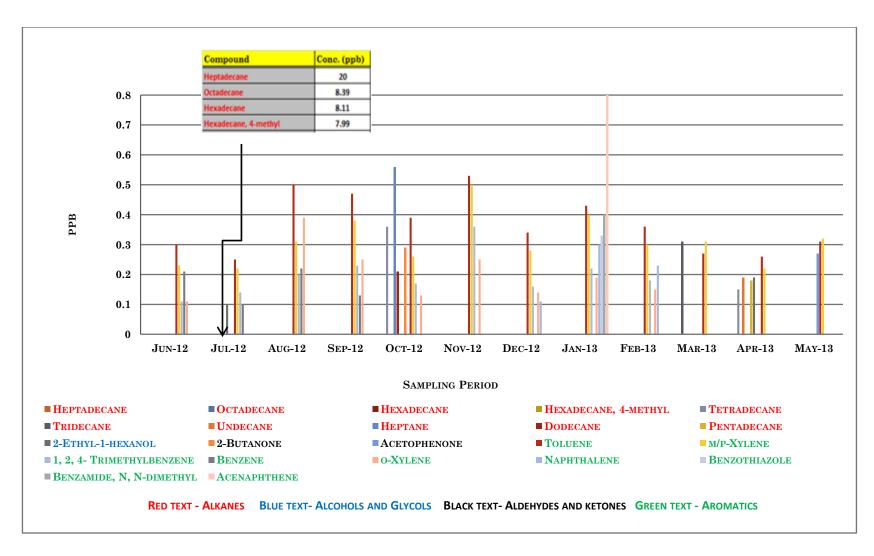
Cypress Street is the second city location to be sampled. The area where the sampler was deployed may be considered residential within an intermediate distance (20-30m) to the nearest busy main road. The results for Cypress Street are highlighted in Graph 13.





 $SO_2$  concentrations of 2.71 ppb peaked in August 2012, the lowest detected concentration of 0.4 ppb of  $SO_2$  was observed in May 2013. Based on Graph 13, the highest  $NO_2$  level of 6.01 ppb was detected in June 2012 and the lowest of 2.67 ppb in October 2012. The highest ozone concentration of 33.10 ppb was observed during the month of June 2012 and the lowest of 14.70 ppb in October 2012.

Alkanes (hydrocarbons), alcohols and glycols, acid and acetate, aldehydes and ketones, halogens and aromatic compounds were detected at various times throughout the sampling period and can be observed in the following graph. Ten (10) aromatic and (9) alkane compounds were detected. As shown in Graph 14 the aromatic compounds were detected with greater frequency. It must be noted that in July 2012, several alkanes were detected at concentrations, which made graphical representation difficult when compared to the majority of the other VOCs detected. As a result, those compounds were represented in the tabular insert within Graph 14. The values highlighted in Graph 14 represent the highest VOC concentration detected in the corresponding month.



Graph 14: VOC compounds detected at Cypress Street during the study period June 2012 to May 2013. The compounds shown represent only those compounds covered in the laboratory accredited flexible scope and are not blank corrected.

## 5.8 Eight Hour Sampling Harbour View # 2

On July  $21^{st}$  2013 samplers were deployed at Harbour View # 2 and were changed approximately every 8 hours for a period of 72 hours.

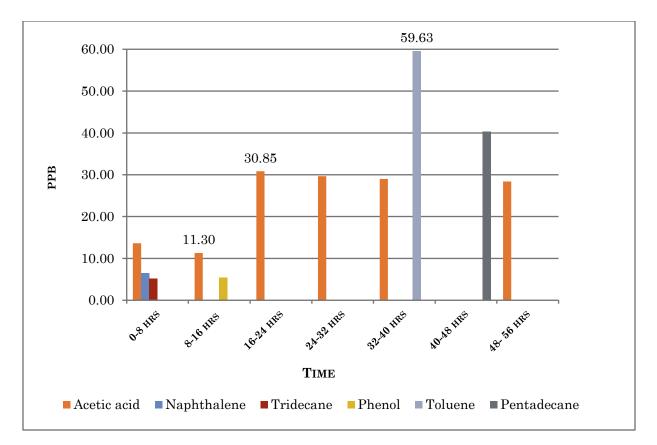
As shown in the table below, the results for  $NO_2$  and  $O_3$  over the 8-hour intervals were below the detection limits of the tubes. Similar results for  $SO_2$  were observed with the exception of the final sample which showed a value of 11.20 ppb after 7  $\frac{3}{4}$  hours of exposure.

Table 10: The detected values of SO<sub>2</sub>, NO<sub>2</sub>, and O<sub>3</sub> at Harbour View #2 over 8 hour intervals from June 2ist 2013 to June 24<sup>th</sup> 2013. "<L.O.D" indicates that the values were below the detectable limits for each tube.

SAMPLE		Sample Number							
Түре (ррв)	Detectable Limit	1	2	3	4	5	6	7	8
NO <sub>2</sub>	0.05µg NO2	< L.O.D	< L.O.D	< L.O.D	<l.o.d< td=""><td>&lt; L.O.D</td><td>&lt; L.O.D</td><td>&lt; L.O.D</td><td>&lt; L.O.D</td></l.o.d<>	< L.O.D	< L.O.D	< L.O.D	< L.O.D
$\mathbf{SO}_2$	0.03 μg S	< L.O.D	< L.O.D	< L.O.D	<l.o.d< th=""><th>&lt; L.O.D</th><th><l.o.d< th=""><th>&lt; L.O.D</th><th>11.2</th></l.o.d<></th></l.o.d<>	< L.O.D	<l.o.d< th=""><th>&lt; L.O.D</th><th>11.2</th></l.o.d<>	< L.O.D	11.2
<b>O</b> <sub>3</sub>	0.13µg/ml	<l.o.d< td=""><td><l.o.d< td=""><td><l.o.d< td=""><td><l.o.d< td=""><td><l.o.d< td=""><td><l.o.d< td=""><td><l.o.d< td=""><td><l.o.d< td=""></l.o.d<></td></l.o.d<></td></l.o.d<></td></l.o.d<></td></l.o.d<></td></l.o.d<></td></l.o.d<></td></l.o.d<>	<l.o.d< td=""><td><l.o.d< td=""><td><l.o.d< td=""><td><l.o.d< td=""><td><l.o.d< td=""><td><l.o.d< td=""><td><l.o.d< td=""></l.o.d<></td></l.o.d<></td></l.o.d<></td></l.o.d<></td></l.o.d<></td></l.o.d<></td></l.o.d<>	<l.o.d< td=""><td><l.o.d< td=""><td><l.o.d< td=""><td><l.o.d< td=""><td><l.o.d< td=""><td><l.o.d< td=""></l.o.d<></td></l.o.d<></td></l.o.d<></td></l.o.d<></td></l.o.d<></td></l.o.d<>	<l.o.d< td=""><td><l.o.d< td=""><td><l.o.d< td=""><td><l.o.d< td=""><td><l.o.d< td=""></l.o.d<></td></l.o.d<></td></l.o.d<></td></l.o.d<></td></l.o.d<>	<l.o.d< td=""><td><l.o.d< td=""><td><l.o.d< td=""><td><l.o.d< td=""></l.o.d<></td></l.o.d<></td></l.o.d<></td></l.o.d<>	<l.o.d< td=""><td><l.o.d< td=""><td><l.o.d< td=""></l.o.d<></td></l.o.d<></td></l.o.d<>	<l.o.d< td=""><td><l.o.d< td=""></l.o.d<></td></l.o.d<>	<l.o.d< td=""></l.o.d<>

With respect to the top five VOC, Graph 15 highlights the VOC compounds detected within the flexible scope and those compounds that were not the result of the reaction of ozone with the Tenax TA sorbent. The most commonly detected compound was acetic acid with the highest concentration of 30.85 ppb and a low of 11.30 ppb. The highest concentration of any compound detected was 59.63 ppb of toluene during the 32-40 hr period of monitoring.

#### 1/9/2015

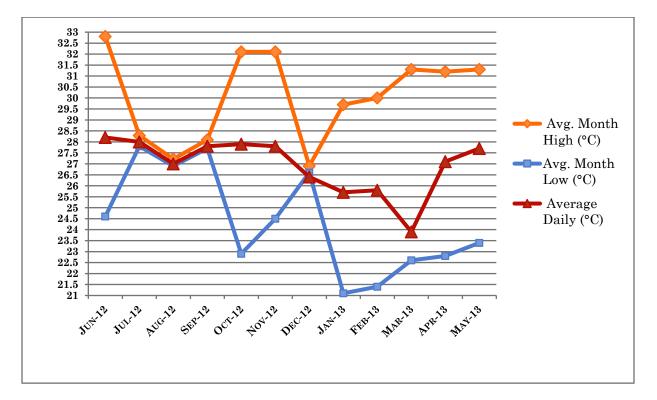


Graph 15: Highlights those compounds detected at Harbour View #2 within the flexible scope and not those compounds which may be a result of the reaction of the Tenax sorbent with Ozone and are not blank corrected.

#### 5.9 Weather Data

Weather data was collected from weather stations located in Bridgetown and operated by the Coastal Zone Management Unit (CZMU) for the period of the study. Some data was supplied directly though the CZMU and other data were collected from <u>www.weatherunderground.com</u>, which cited the CZMU weather stations as a source. The weather data was incomplete in some areas resulting in gaps for some months in the graphs below.

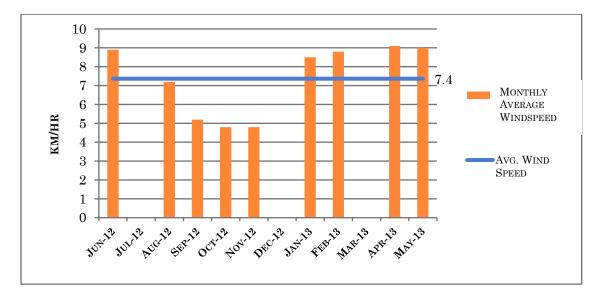
Graph 16 below, displays the highest and lowest temperatures, in addition to the average monthly temperatures recorded. A study conducted by E Stathopoulou *et al*<sup>3</sup> in Athens during 2008, established that temperature was a predominant driving force in the formation of ground level ozone a correlation between temperature and ozone formation.



# Graph 16: Monthly Highs, Lows and Average Temperatures recorded during the period June 2012 to May 2013.

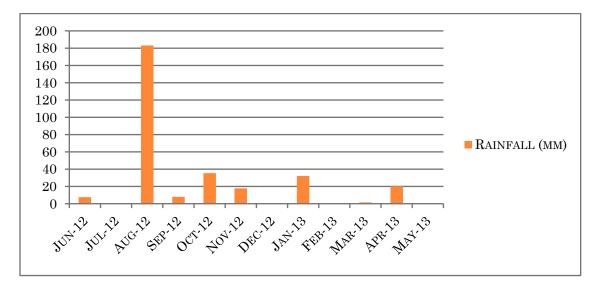
<sup>&</sup>lt;sup>3</sup> E Stathopoulou , G Mihalakakou , M Santamouris and H S Bagiorgas, (June 2008). On the impact of temperature on tropospheric ozone concentration levels in urban environments. *Journal of Earth System Science*. 117 (Issue 3), 227–236.

Graph 17 highlights the average wind speed and the monthly wind speeds for the study period. According to the graph, the highest wind speed was recorded in April 2013. Additionally, the average wind speed for the year was approximately 7.4km/h.





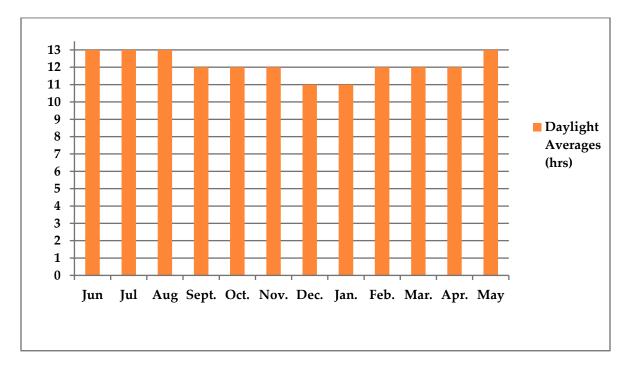
Graph 18 shows the average rainfall per month during the study period. The observable gaps indicate that no data was available during the period. Based on the data, it appears that the highest rainfall occurred during the month of August 2012.



Graph 18: Average monthly rainfall data collected during the period June 2012 to May 2013 as provided by CZMU weather stations.

## 5.10 Daylight Hours

In addition to temperature, sunlight acts as catalyst for the generation of ozone along with the interactions of  $NO_2$  and VOCs. Graph 19 below shows the average monthly daylight received by Barbados<sup>4</sup> throughout the year during the study period. The months with the lowest averages of daylight were December and January at 11 hours. A maximum of 13 hours was observed from May to August.

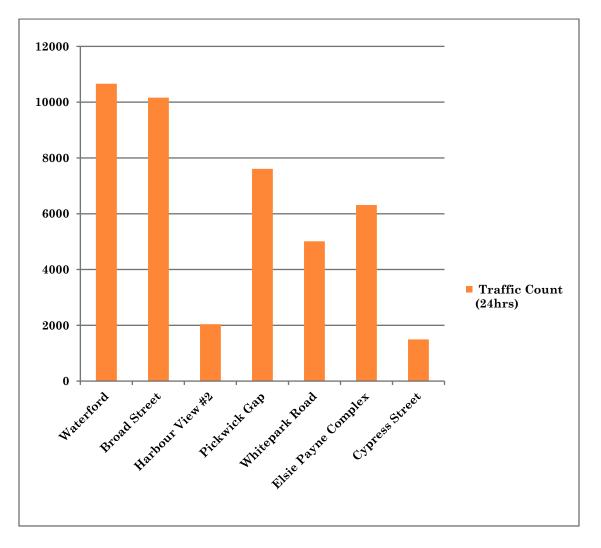


Graph 19: Daylight averages for Barbados

<sup>&</sup>lt;sup>4</sup> http://www.barbados.climatemps.com/

## 5.11 Ministry of Transport and Works Traffic Data

Using traffic data provided through the use of traffic counters by the Ministry of Transport and Works, a 24 hour average<sup>5</sup> of the number of vehicles utilizing the nearest busy road (in both directions) to the sampling points was calculated and the results are shown below in Graph 20. Based on the data it appears that Waterford was the busiest roadway with greater than 10,622 vehicles per 24 hrs, followed by Broad Street which had 10,161 vehicles per 24 hrs. The least travelled roadway per 24 hours was Cypress Street with 1,496 vehicles per 24 hrs.



Graph 20: Traffic volume per 24 hours. Peak traffic was observed at both Waterford main road and along Broad Street

<sup>&</sup>lt;sup>5</sup> Measurements were taken over 14 day periods during the months of January, February and March 2013

## 6.0 DISCUSSION

The adopted WHO guidelines were developed using real time continuous sampling methodologies which differ from passive monitoring. The results of the passive monitoring therefore cannot be compared to the WHO guidelines. However, passive studies trend lower but retain similar fluctuations over time compared to real time continuous monitoring studies. This enables a useful characterization of existing levels and changes based on activities within Bridgetown.

Based on information from the Electoral and Boundaries Commission there are approximately 7,000<sup>6</sup> persons over the age of 18 residing within Bridgetown. These numbers do not take into account persons commuting to and from Bridgetown daily, outlying areas and persons under the age of 18. Therefore, the number of persons impacted at varying levels by both primary and secondary pollutants may be in excess of 10,000 daily. The impacts of exposure to the primary and secondary pollutants may vary according to an individual's health, tolerances and the pollutant levels to which they are exposed.

Sections 6.1 and 6.2 will address possible reasons for variations in pollutant concentrations at the various sampling locations. The potential impacts persons living or working in these areas may be exposed to on a daily basis, based on the international guidelines, will also be addressed.

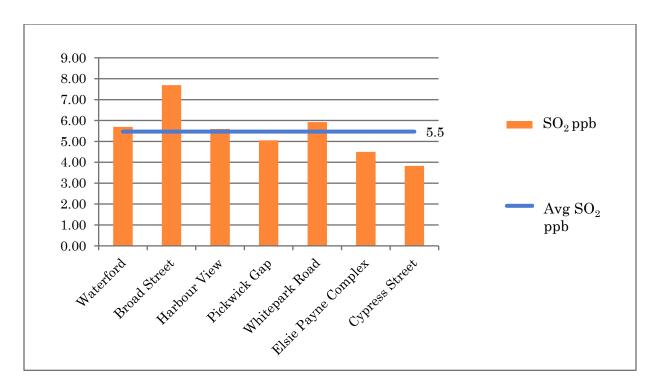
## 6.1 Sulphur Oxides (SO<sub>2</sub>) Concentrations

#### 6.1.1 Highs and Lows

As shown in Graph 21, the highest recorded  $SO_2$  level of 2.94 ppb was detected on Broad Street in December 2012. The lowest levels were detected at the Cypress Street Sampling location with a value of 1.93 ppb in May 2013 as shown in Graph 21 below. The average level of  $SO_2$  for all the sample locations across Bridgetown was 2.10 ppb.

<sup>&</sup>lt;sup>6</sup> Electoral and Boundaries Commission, City of Bridgetown

http://www.electoral.barbados.gov.bb/constituencies/cobconstituency.php. Last Accessed May 7th, 2014



#### Graph 21: Average SO<sub>2</sub> levels per location in µg/m<sup>3</sup>.

6.1.2 Analysis of the Potential impacts on SO<sub>2</sub> Concentration

Although Waterford received higher traffic counts per 24 hours than Broad Street (Graph 20), the higher  $SO_2$  levels may be due to the differences in the geographical layout of Broad Street versus Waterford. Broad Street is characterized by a narrow strip with several buildings on either side ranging from 10-30m in height at various points.

The possible resultant effect is that emissions may become trapped or take longer to disperse as opposed to the open space in Waterford which may allow for easy dispersal and dilution by wind action. Broad Street is a hotbed of commercial activity including several restaurants where cooking may result in increased  $SO_2$ emissions from the petroleum based fuels used. There are also several side streets upwind of Broad Street and vehicular emissions from incomplete combustion may travel downwind and impact upon Broad Street.

Additionally, distance between the road and the samplers, the traffic speed as well as engine ignition and idling also contribute to the concentration of  $SO_2$ 

detected. This was evident as Broad Street, Harbour View#2<sup>7</sup> and Whitepark Road were designated as near road sites (Table 2) and were prone to large volumes of idling or slow-moving vehicular traffic and therefore saw higher levels of SO<sub>2</sub>.

With respect to Whitepark Road, St. Michael, the third highest average  $SO_2$ levels were recorded despite having less vehicular traffic. In addition to vehicular traffic the surrounding area supports several industrial operations which may also act as stationary sources of  $SO_2$  emissions.

The residence time for  $SO_2$  in the atmosphere is approximately 1-5 days and concentrations may be affected by precipitation which may remove  $SO_2$  from the atmosphere.  $SO_2$  may also be removed from the atmosphere through the deposition of solid particulates on vegetation, soil and buildings as evident by black sooty deposits on buildings within Bridgetown as seen in Photos 2 and 6 in Appendix 2. High wind-speed can also disperse  $SO_2$  over a greater distance and reduce concentrations.

Another potential source of sulphates may be the trans-boundary movement of sulphates attached to sea salts. Due to wind action sulphates may be transported onshore from sources outside of Barbados

Barbados is approximately 34 km x 23 km at its widest points and the average wind-speed for the period was approximately 7.4 km/h (Graph 17) in a north easterly direction. It may therefore be possible for contaminants to be transported from other locations or out to sea within a matter of hours if sufficiently high wind-speeds were maintained. However, it is not known if the average wind-speed persisted at the sample locations.

6.1.3 Comparison to Other Passive Sampling Studies

According to research<sup>8</sup> conducted by the World Meteorological Organization Global Atmosphere Watch, 1997 (WMO GAW) global annual SO<sub>2</sub> values are similar to the levels detected in several locations such as South Korea, Thailand

<sup>&</sup>lt;sup>7</sup> Although Harbour View #2 was designated an intermediate site in Table 2, observations revealed that large numbers of taxis were parked/idling in the general vicinity of the sampler awaiting tourists exiting the cruise ship terminal several days during the week.

<sup>&</sup>lt;sup>8</sup> World Meteorological Organization -Global Atmospheric Watch. (1997). Report on passive samplers for atmospheric chemistry measurements and their role in GAW. -. WMO TD No. 829, (122), 16.

and Malaysia where local values and values sampled by the GAW did not exceed 10  $\mu$ g/m<sup>3</sup> (3.6 ppb).

Based on WHO documentation<sup>9</sup>, the annual mean concentrations in urban areas were in the range of  $20-60 \mu g/m^3$  or (7.09–21.3 ppb) while daily means seldom exceeded  $125\mu g/m^3$  (44.3 ppb). It appears that the data for the sites sampled in Barbados is below that average. However, it must be noted that WHO data was collected using real time continuous sampling methodologies and not passive sampling techniques.

#### 6.1.4 Impacts of SO<sub>2</sub> exposure based on International Standards

In the case of  $SO_{2}$ , standards are represented in terms of 24-hour exposures and 10-minute means in the case of the World Health Organization (WHO) and 1hour primary and 3-hour secondary standards by the US EPA National Ambient Air Quality Standards (NAAQS). The standards are outlined in Table 12 below.

PRIMARY/SECONDARY	CONCENTRATION	TIME	Agency
Primary	20 µg/m (7.63 ppb)	24-hour mean	WHO
	500 μg/m (190.84 ppb)	10 minute mean	WHO
Primary	75 ppb (196.5 μg/m <sup>3</sup> )	1- hour	US EPA
Secondary	500 ppb ( 1310 μg/m <sup>3</sup> )	3- hour	US EPA

Table 11: Exposure limits for  $SO_2$  based on WHO and US EPA Guidelines

The WHO standard indicates that the  $SO_2$  concentration of  $500\mu$ g/m<sup>3</sup> should not be exceeded for greater than 10 minutes. According to the WHO, studies have revealed that a proportion of asthmatics experience changes in pulmonary function and respiratory symptoms after periods of exposure to  $SO_2$  in less than 10 minutes.

The 24-hour guideline for  $SO_{2}$  has been revised downwards from 125 µg/m (47.7 ppb) to 20µg/m (7.63 ppb) based on the belief that although the causality of

<sup>&</sup>lt;sup>9</sup> World Health Organization. (2000). Air Quality Guidelines Chapter 2<sup>nd</sup> Ed. 7.4 Sulphur dioxide. Available:

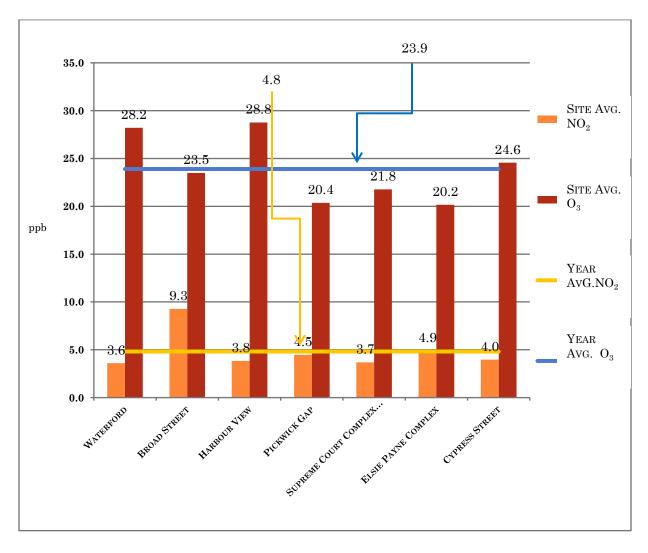
http://www.euro.who.int/\_\_data/assets/pdf\_file/0020/123086/AQG2ndEd\_7\_4Sulfurdioxide.pdf. Last accessed December 5, 2013.

the effects of low concentrations of  $SO_2$  is still uncertain, a reduction in  $SO_2$  was likely to decrease exposure to co-pollutants.

## 6.2. Nitrogen Dioxide (NO<sub>2</sub>) and Ozone (O<sub>3</sub>) Concentrations

#### 6.2.1 Highs and Lows

As shown in Graph 22, the higher than average  $O_3$  levels were recorded for Cypress Street, Waterford and Harbour View #2.



Graph 22: The average NO<sub>2</sub> and O<sub>3</sub> concentrations per location.

With respect to NO<sub>2</sub>, the highest average for the year (9.3 ppb) for all locations was detected at the Broad Street sampling location. The lowest average NO<sub>2</sub> concentration (3.6 ppb) was detected at Waterford. This may be due to the differences in the geography at both locations as alluded to in the previous section.

In the case of  $O_3$ , the highest average ozone concentrations were detected at Harbour View # 2 (28.8 ppb) followed by Waterford (28.2 ppb). The lowest concentration (20.2 ppb) was detected at the Elsie Payne Complex. The average  $O_3$ concentration for all locations was approximately 23.9 ppb. This may be due to several factors such as temperature variations at each location, available sunlight and vehicular traffic all of which can impact upon ground level ozone production.

Although, Cypress Street showed the lowest traffic count (Graph 20), the ozone levels were slightly higher than those at Elsie Payne Complex. This could possibly be because the sampling point at Elsie Payne Complex was further setback from the busy road and parking lot, whereas the sampling location at Cypress Street was located close to the parking lot and entrance to a school, indicating that the source of ozone may be due to mobile sources. However, further investigation may be required into other factors such as sunlight, temperature and NO<sub>2</sub> concentrations, which will be discussed in section 6.3.

All 8-hour samples for ozone at the Harbour View #2 were returned with a value below the detection limit, because the eight-hour exposure period was insufficient for the sample media to absorb enough ozone to be detected by analysis.

#### 6.2.2 Impacts of NO<sub>2</sub> and O<sub>3</sub> based on International Standards

The following table provides the WHO and US EPA standards for  $NO_2$  for both annual and one hour rates.

PRIMARY/SECONDARY	CONCENTRATION	TIME	AGENCY
Primary	40 μg/m³ (21.3 ppb)	Annual	WHO
	200 μg/m <sup>3</sup> (106.4 ppb)	1 hr	WHO
Primary & Secondary	53 ppb	Annual	US EPA
Primary	100 ppb	1 hour	US EPA

In the case of the WHO standards the current air quality guidelines for  $NO_2$  have been set at the level for the following reasons

- 1. Epidemiological studies have shown that symptoms of bronchitis in asthmatic children increase in association with long-term exposure to  $NO_2$
- 2. Reduced lung function growth is also linked to  $NO_2$  at concentrations currently measured (or observed) in cities of Europe and North America.
- 3. Short term exposure to concentrations exceeding 200µg/m<sup>3</sup>, may trigger significant inflammation of the airways.
- 4.  $NO_2$  is the main source of nitrate aerosols, which form an important fraction of  $PM_{2.5}$ . In the presence of ultraviolet light,  $NO_2$  is the main source of ozone.

With respect to ozone, the results of the 8-hour sampling appeared to be below the detection limit<sup>10</sup> and therefore are below the 8-hour standard of 75 ppb and 100  $\mu$ g/m<sup>3/</sup> or 50 ppb for the US EPA NAAQS and the WHO Standard respectively. According to the WHO, excessive ozone exposure in the air can have a marked effect on human health. It can trigger breathing problems, asthma attacks, reduce lung function and exacerbate pre-existing lung and heart diseases. In Europe, it is listed as a pollutant of prime concern. Several European studies have reported that per 10  $\mu$ g/m<sup>3</sup> increase in ozone exposure, the daily mortality rises by 0.3% for the average person and by 0.4% for those with pre-existing heart disease.

# 6.3 Relationship between Nitrogen Oxides (NO<sub>X</sub>), VOCs, Weather and Ozone

#### 6.3.1 Mechanics of Ozone Formation

Ozone at ground level is formed through a series of complex photochemical reactions between  $NO_X$  and volatile organic compounds (VOCs) in the presence of heat and sunlight. Major sources of ground level ozone are the result of photochemical processes and the movement of stratospheric ozone into the lower atmosphere.

 $<sup>^{10}</sup>$  0.13  $\mu\text{g/ml}\,$  is the detection limit for the  $O_3$  passive sampler tubes

The formation of ground level ozone is dependent on the intensity of solar radiation, the presence of NO<sub>X</sub> and VOCs, and the sensitive ratio of VOCs and NO<sub>X</sub> usually in the range of 4: 1 to 10:1. Ozone is a photochemical pollutant and forms roughly 2-3 hours after initial NO<sub>X</sub> and VOCs emissions. Ozone is only formed during daylight hours when sunlight is intense and air temperature is warm, but is destroyed at night due to the NO<sub>X</sub> and ozone combining to form nitrogen monoxide (NO) and oxygen. This conversion process continues until either the NO or ozone is consumed in the process.

The formation of ozone in rural sites or areas with reduced sources of  $NO_X$  is governed by the following;

- the decreasing intensity of the regional ozone pollution episodes, tending to reduce the ozone metric  $^{11}$
- the decreasing depletion of ozone by traffic generated  $\ensuremath{\text{NO}_X}\xspace$  emissions, which increases the metric

Therefore, rural concentrations may be a combination of background ozone and that produced by more local activities (probably up to the regional scale). When precursor emissions such as NOx and VOC are diminished, there is a decrease in rural ozone, though not necessarily in proportion to the decrease in precursors.

In urban areas or areas with a number of  $NO_X$  and VOC sources, either point or mobile sources, ozone levels are expected to be lower than in rural areas due to depletion of any ozone formed by its reaction with NO which is produced from  $NO_X$ sources. Therefore, it is expected that a reduction in VOC and  $NO_X$  emissions may result in an initial ozone increase. However, provided there was a drastic reduction in VOCs and  $NO_X$  levels, ozone concentrations should diminish.

The relative balance of VOCs and  $NO_X$  at a particular location may determine whether the  $NO_X$  behaves as a net ozone generator or a net ozone inhibitor. When the VOC/NO<sub>x</sub> ratio in the ambient air is low,  $NO_x$  concentrations are higher relative to VOC concentrations. As a result  $NO_x$  tends to inhibit ozone formation and the resultant ozone formation is called "VOC limited". When the VOC/  $NO_x$  ratio is high,

<sup>&</sup>lt;sup>11</sup> The metric is a measure of the number of 'good' air quality days (as defined by EPA's Air Quality Index - AQI) in a quarter. The AQI is calculated by EPA as a measure of local air quality and its effect on human health. The higher the AQI value the greater the level of air pollution and the greater the health concern. 'Good' air quality corresponds to an AQI of 50 or less (on a scale of 0-500) and poses little or no risk of adverse health effects. An ozone target of 75% 'Good' days in a quarter was selected to evaluate local air quality conditions.

the VOC concentration is higher relative to the NO<sub>x</sub> concentration and NO<sub>x</sub> tends to generate ozone. In this instance, ozone formation is considered as "NO<sub>x</sub> limited".

The VOC/NO<sub>x</sub> ratio can differ substantially by location and time-of-day between location specific microclimates. Furthermore, the VOC/ NO<sub>x</sub> ratio measured near the ground might not represent the ratio that prevails in the air above the breathing zone, where most of the tropospheric ozone is generated.

Sunlight/ UV radiation may not be a limiting factor year round in the formation of ozone as the yearly daylight hours range between 11 and 13 hours of sunlight daily. Temperatures over 26.7°C<sup>12</sup> may enhance the rate of the reactions associated with ozone formation and increase the rate of evaporative emissions of VOCs. However, the amount of cloud cover present may reduce ozone production. When cloud cover is high it will prevent the penetration of excessive UV radiation reducing the potential of photochemical reactions occurring and generating ozone.

Additionally, low wind speeds allow for the accumulation of precursors of ozone formation (VOCs and  $NO_x$ ) and the subsequent formation of ozone. Higher wind speeds tend to dilute or disperse emissions. However, they can still transport ozone from other locations.

Dry weather is generally favourable to ozone generation as low precipitation allows ozone to remain in the air. Additionally, the occurrence of scattered showers may not produce enough precipitation to completely eliminate ozone, but heavier prolonged rainfall may be adequate in cleansing ozone from the atmosphere. The presence of other weather phenomenon such as weather fronts and tropical waves may impact upon ozone production due to their potential to affect cloud cover, precipitation, air mass variations and temperature.

#### 6.3.2 Observed NO<sub>X</sub>, VOC and O<sub>3</sub> interactions

The data collected included  $NO_2$ ,  $O_3$  and Top five VOCs. Unfortunately, no total VOC data was collected and as a result it was difficult to determine the exact relationship between VOC levels and  $NO_2$ .

Based on traffic patterns, Cypress Street and Harbour View showed the lowest volumes of traffic per 24 hours. When compared to their respective  $NO_2$  and

<sup>&</sup>lt;sup>12</sup> West Michigan Clean Air Coalition. (2009). *Factors that Contribute to the Formation of Ozone and Particulate Matter*. Available: http://www.wmcac.org/airquality/factors.html. Last accessed September 5, 2013

ozone levels, as seen in Graph 22, these sites showed some of the highest ozone levels as discussed (in the previous section) for areas with a smaller number of  $NO_X$  sources.

Broad Street was the only location with above average  $NO_2$  levels and showed a lower ozone level than other locations such as Waterford and Harbour View #2 which had lower  $NO_2$  levels but higher ozone levels. Therefore, it may be possible that the higher  $NO_X$  levels on Broad Street were inhibiting the formation of ozone.

Based on the available meteorological data obtained from the CZMU station in Bridgetown, the average temperature for the year was approximately 27.3°C, which was above the optimal temperature of 26°C for ozone generation. No data for the individual sites was available and therefore localized variations may have occurred. Additionally, the monthly averages and the year average (7.4km/hr) for wind speed were all under the 16 km/h maximum allowable wind speed for ozone propagation as shown in Graph 17.

Real time monitoring in conjunction with simultaneous traffic counts and real time weather data would be beneficial in determining whether the pollutant levels fluctuate with traffic and weather patterns. If the pollutant levels remain relatively stable with no significant variations, despite fluctuation, it may indicate that the source of the pollutant is a stationary source rather than a mobile source. However if pollutant levels fluctuate with changes in temperature and traffic it may indicate that the main source may be mobile in nature. Once the nature of the source has been determined it would be useful in formulating the appropriate policy and planning decisions for Bridgetown and Barbados in general.

## 7.0 Study Limitations

The use of Waterford as a background site was problematic due to the loss of several tubes. In addition, the location was the most heavily trafficked area and levels for SO<sub>2</sub>, NO<sub>2</sub> and ozone were high and not indicative of a control site, an area with minimal impacts, to which a comparison could be made.

Additionally, the methodology did not allow for any real time correlation between activities and weather occurring at the sample sites. As a result, it was difficult to accurately conclude the nature of the relationships observed between  $SO_2$ ,  $NO_2$  and ozone levels and other factors which such as weather, mobile and stationary sources.

Site to site comparisons as shown in Appendix 1 Graphs 23-24 showed that certain sites such as Broad Street had consistently higher emissions. However, amongst the other locations it was difficult to establish a trend as there was no on site real time information with respect to meteorological parameters, real time traffic counts and an inventory of all industrial operations and their emissions in proximity to the sampling locations.

Traffic pattern data was limited as it only provided a snapshot of the true traffic patterns at each location. This could be bolstered in various ways including; conducting origin/destination surveys, estimating vehicle emissions by class and by conducting continuous traffic volume analysis along with real time pollutant monitoring. This will assist in determining whether pollutant sources are mobile or stationary in nature and to more effectively determine the causes of observed pollutant concentrations.

## 8.0 CONCLUSION

The objective of the assessment was to characterize the air quality and to determine any possible trends in primary and secondary pollutant levels in and around different areas of Bridgetown. This objective was achieved as the passive sampling methodology utilized allowed for the determination of the average concentrations of primary and secondary pollutants as well as VOCs in Bridgetown. The release of the various organic and inorganic compounds may be the result of the emissions from restaurants, hair and nail salons, industrial activities and transportation.

As previously mentioned, the methodology utilized in the passive sampling albeit less costly than real time sampling is not comparable to the adopted WHO methodologies and the associated standards. Considering the results generated, the economic activities conducted in Bridgetown, the designation of Bridgetown as a UNESCO World Heritage site and the introduction of low sulphur diesel to Barbadian consumers, further assessment should be conducted using continuous sampling, to allow comparison to the WHO standards for the primary and secondary pollutants. Additionally, passive monitoring should be repeated once the baseline has been established in lieu of continuous monitoring to determine if there are any ongoing fluctuations in levels and to assess the effectiveness of policy initiatives over time.

In the case of the other urban centres such as Oistins, Christ Church, Speightstown, St. Peter and Holetown, St. James, both passive and real time continuous sampling would be useful in establishing baselines and peak concentrations for future studies in those locations.

## 9.0 **Recommendations**

#### 9.1 Background Site Selection

The background site selected should be relatively free from human impact and be upwind of all future sites. This will allow for a better comparison of pollutant levels between areas with heavy activity and areas which have not been severely impacted by human activity.

#### 9.2 Real-Time/Continuous Monitoring

The use of real time continuous monitoring of primary and secondary pollutants would be beneficial as the existing ambient air quality could be compared to an established standard such as the WHO Air Quality Guidelines. It would also allow for the assessment of how the results obtained from passive monitoring compared to the real time sampling.

Additionally, real time data (pollutant, traffic and meteorological) will allow for the recognition of spikes in levels, instead of an average which provides an incomplete view of the accumulation/dispersion and interaction of pollutants and the changes throughout the course of the day. Continuous monitoring of traffic and meteorological data can be achieved through the use real time continuous monitors specific to those parameters. Unfortunately, at this time the EPD does not have access to the required equipment.

Also of importance real time data allows for the determination of whether pollution was emanating from mobile (vehicle or trans-boundary transport) or stationary sources. It will also assist in the determination of appropriate emission limits when comparing to established standards, setting attainment or nonattainment goals for urban centres and determining the impact of future development on the human health and environment.

#### 9.3 Total VOCs

The analysis of the VOC samples taken was represented as the top five VOCs. This would have provided insight as to which VOCs were most popular and most concentrated at each sampling location. Throughout the analysis it was observed that the type of VOCs along with their concentrations varied from month to month at each site and therefore no distinct pattern could be detected. VOC trends in future monitoring plans would be better displayed as Total VOCs (TVOCs) and it would allow for an investigation into the relationship between  $NO_2$  and TVOCs in ozone formation.

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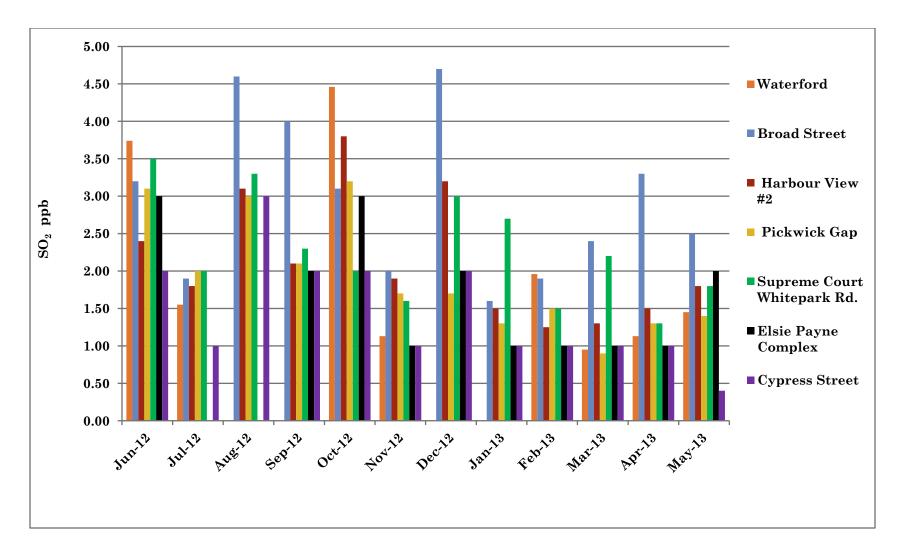
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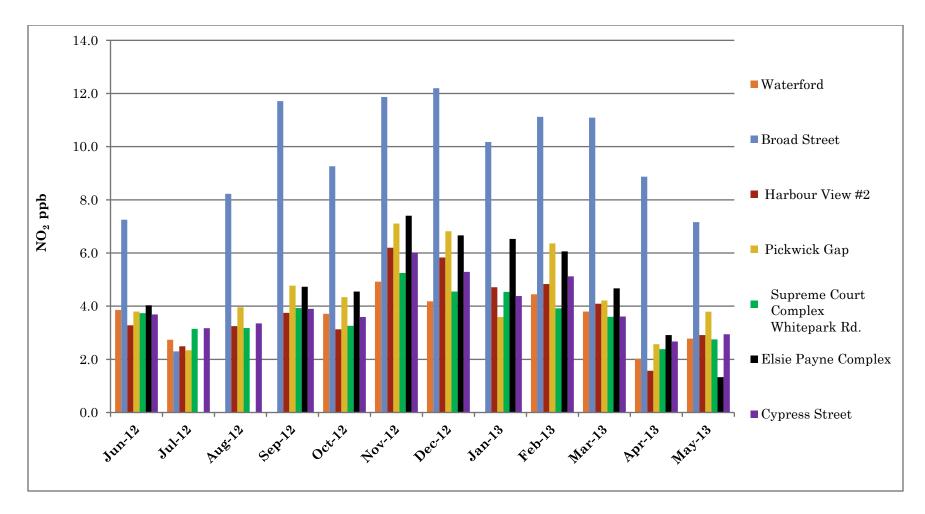
#### 1/9/2015

# APPENDIX I



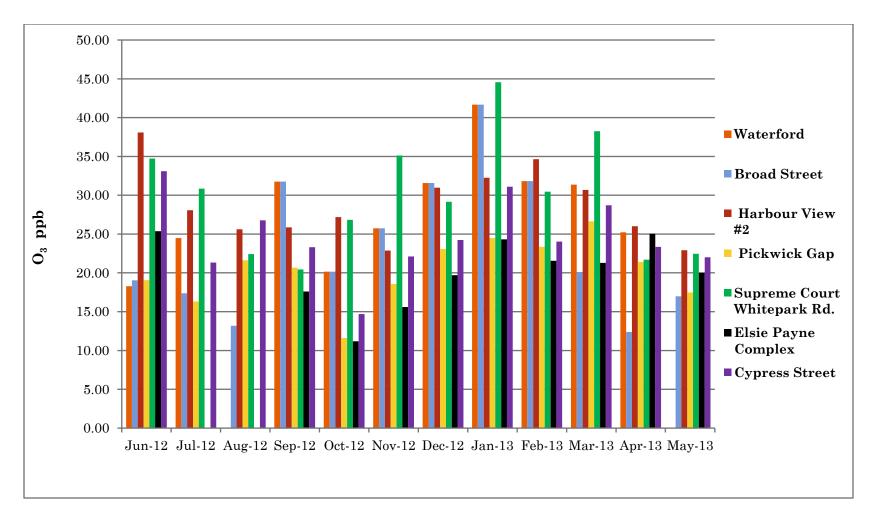


#### 1/9/2015



Graph 24: Average NO<sub>2</sub> concentrations for the study period for all sample locations.

1/9/2015



Graph 25: The average O<sub>3</sub> concentration across all sampling locations for the study period

## APPENDIX II- PHOTOS



Photo 1: Broad Street sampling location June 4th 2013

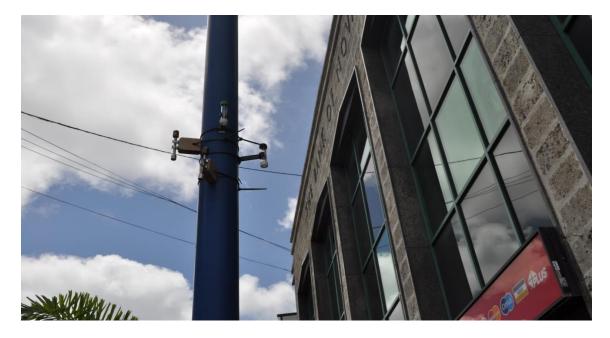


Photo 2: Close up of passive samplers located on Broad Street, Bridgetown.



Photo 3: Harbour View # 2, St Michael



Photo 4: Passive samplers mounted at Pickwick Gap, St. Michael

## 1/9/2015



Photo 5: Passive samplers located at Waterford St. Michael

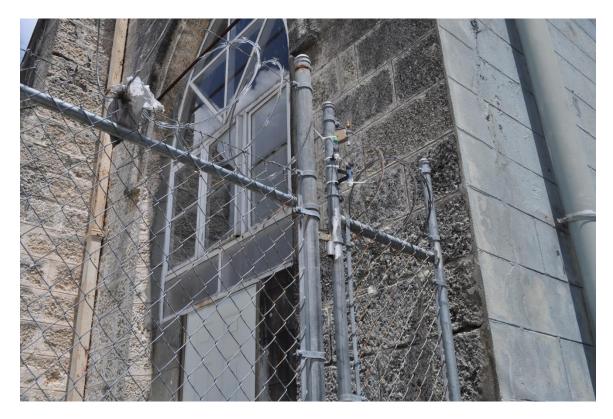


Photo 6: Passive samplers mounted at Cypress Street, St Michael



Photo 7: Samplers mounted in Queens Park, Constitution Road, St, Michael. The sampling location was moved across the street to the Elsie Payne Complex after an unauthorized tube removal.

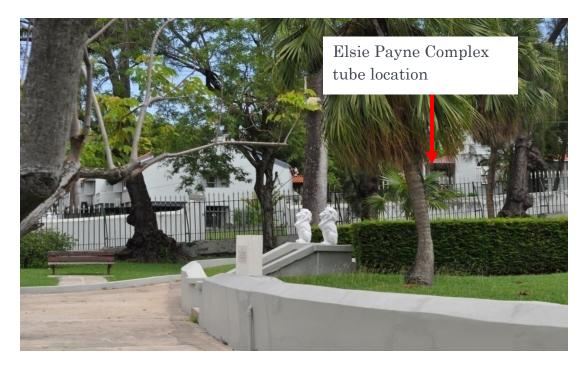


Photo 8: the revised sampling location from the perspective from the initial sampling location in Queens Park, St. Michael



Photo 9: Passive samplers located at the Supreme Court Complex, Whitepark Road, St. Michael.



Photo 10: Passive samplers located on a pole at the Supreme Court Complex, Whitepark Road, St, Michael