

# OISTINS AND SPEIGHTSTOWN Ambient Air Quality Passive Monitoring Project

AUGUST 2013-JULY 2014

FINAL REPORT



ENVIRONMENTAL PROTECTION DEPARTMENT

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## EXECUTIVE SUMMARY

The Oistins and Speightstown Ambient Air Quality Passive Monitoring Study (OSAAQPMS) 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 occurring in the smaller city centres of Oistins and Speightstown.

Exposure to primary and secondary pollutants may impact 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 and around the Oistins and Speightstown areas, 30 day/monthly samples were taken at seven (7) locations over the period of a year (i.e. 12 samples from each location). 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.

The highest recorded  $SO_2$  level of 4.85 ppb was detected at a private residence (VTTH) in January 2013; conversely in October 2013 the level of  $SO_2$  for all locations was below the detectable limit of the laboratory analysis. The average  $SO_2$  level for Oistins and Speightstown combined was approximately one quarter of the average Bridgetown  $SO_2$  concentration.

With respect to NO<sub>2</sub>, the highest average concentration (5.78 ppb) was detected at First Caribbean CIBC Bank Speightstown (FCCIBC). The lowest average NO<sub>2</sub> concentration was below the detectable limit (<  $0.05\mu$ g NO<sub>2</sub>) and was detected at the background location at Ragged Point (RP), St. Philip. When compared to the Bridgetown study; both Speightstown and Oistins displayed lower average concentrations of NO<sub>2</sub>. Although Oistins had a greater traffic volume than Speightstown, Oistins showed lower NO<sub>2</sub> and O<sub>3</sub> concentrations when compared to Speightstown. The highest O<sub>3</sub> concentrations were detected at Oistins Police Station (OPS) and the lowest were detected at the Speightstown Police Station (SPS). The top five VOC concentrations included fifty-three (53) individual compounds; consisting of various aldehydes, aromatic, ketone, alkene and alcohol groups with no particular pattern emerging. It must be noted that in March 2014 the concentrations of VOCs were approximately 100 times higher than those recorded in other monitoring periods. The reason for this reading could not be determined.

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 Oistins and Speightstown. Additionally, it was recommended that in order to establish a trend and to determine real time exposure comparable to international standards for the Oistins and Speightstown area, the study should be repeated using passive samplers co-located with continuous air monitoring equipment.

GLOSSARY OF TERMS AND ABBREVIATIONS

Aldehydes and	Simple compounds which contain a carbonyl group - a
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.
	The simplest and least reactive hydrogenhan energies due to
Aikanes	The simplest and least reactive hydrocarbon species due to
	the saturation of the carbon atoms containing only carbons
Anomatica	A hydrogen.
Aromatics	A hydrocarbon with alternating double and single bonds
	between carbon atoms forming rings.
Baseline	A minimum or starting point used for future data
	comparisons
Co-located/	Two samples taken from and representative of the same
Duplicate	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.
Detectable limits	Method detection limits are statistically determined values that
	define how easily measurements of a substance by a specific
	analytical protocol can be distinguished from measurements of
	a blank (background noise). Method detection limits are matrix,
	instrument and analyst specific and require a well defined
	analytical method. Method detection limits provide a useful
	mechanism for comparing different laboratories' capabilities
	with identical methods as well as different analytical methods
	within the same laboratory. In this report the detectable limits
	within the same faboratory. In this report the detectable limits are as follows for $SO_2$ the DRL is $< 0.03 \text{ µg S}$
FPD	Finite as follows for 502 the Ditt is < 0.05 µg 5
Flovible scope of	Flovible scenes of accreditation can allow a laboratory to
accreditation	undertake certain tests/calibrations and to report the results
accieuitation	as accredited even though they may not be explicitly stated
	on their accreditation schedule
Guideline	A plan or explanation to guide one in setting standards or
	determining a course of action
MTW	Ministry of Transport and Works
Nitrogen Dioxide	A toxic reddish brown gas $NO_2$ that is a strong oxidizing
(NO <sub>2</sub> )	agent, is produced by combustion (as of fossil fuels), and is an
	atmospheric pollutant (as in smog).
OSAAQPM	Oistins and Speightstown Ambient Air Quality Passive
(0)	Converse level evens is not emitted directly into the side of the
Uzone (U <sub>3</sub> )	Ground level ozone is not emitted directly into the air, but is
	(NOw) and valatile amonia company de (NOC) in the set
	of suplight Emissions from industrial facilities and electric
	utilities motor vehicle exhaust geseline veneurs and
	chemical solvents are some of the major sources of NOV and
	inclinear solventes are some of the major sources of NOX allu

	VOC.			
ppb	Parts per billion			
Primary Pollutant	An air pollutant emitted directly from a source			
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 Dioxide	A colourless, toxic gas with a strong odour. It			
(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 component of			
	acid rain.			
Standard	A level of quality or attainment which can be used for			
Stallualu	A level of quality of attainment which can be used for			
	comparative evaluations.			
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.			
UKAS	United Kingdom Accreditation Service			
USEPA	United States Environmental Protection Agency			
Volatile Organic	Compounds of carbon, excluding carbon monoxide, carbon			
Compounds (VOCs)	dioxide, carbonic acid, metallic carbides or carbonates, and			
	ammonium carbonate, which participate in atmospheric			
	photochemical reactions. Excludes carbon compounds			
	designated by EPA as having negligible photochemical			
	reactivity.			
WHO	World Health Organisation			

# OISTINS AND SPEIGHTSTOWN AMBIENT AIR QUALITY PASSIVE MONITORING PROJECT

August 2013-July 2014 Final Report

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## 1.0 INTRODUCTION

The Environmental Protection Department has 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 in an effort to systematically achieve the goals set out in the Strategic Plan through focussed planning and development processes. The study presented in this report is a continuation of the Bridgetown Ambient Air Quality Passive Sampling project conducted during the period 2012-2013, which utilized passive samplers to collect data on average concentrations of SO<sub>2</sub>, NO<sub>2</sub>, O<sub>3</sub> and top five VOCs at seven locations throughout Bridgetown.

The focus of this phase of the project was to determine the average concentrations of primary and secondary pollutants in the urban centres of Oistins, Christ Church and Speightstown, St. Peter. It is anticipated that data collected in this study, the previous Bridgetown study and future studies will be compiled to determine baseline levels of both primary and secondary pollutants in Barbados.

#### 1.1 Speightstown and Oistins Study Area

Oistins was chosen as a study area due to the mix of residential, commercial and industrial activities such as fisheries, entertainment, and manufacturing occurring within the southern part of the island. In contrast Speightstown is located in the North of the island; but exhibits similar land use characteristics, albeit at a reduced level compared to Oistins. This may change in the future due to a renewed push for the revitalization of the Speightstown area by various private and public sector entities.

The Oistins study area was located in the southernmost parish of Christ Church. It was bounded to the west by the Cane Vale Seventh Day Adventist Church, with the Oistins Police Station in the centre and a residence located in Thornbury Hill to the east as shown in Figure 2.

Whereas, the geographic orientation of the Oistins study area ran west to east, the Speightstown study area ran in a north to south orientation and was situated in St. Peter, in the northwest part of the island. The study area as shown in Figure 3; was bounded to the north by the Sand Street sampling location, with the Speightstown Police Station (SPS) in the centre and the most southern of the sampling points at First Caribbean CIBC Bank (FCCIBC).

## 2.0 PROJECT OBJECTIVE

The objectives of the Oistins and Speightstown Ambient Air Quality Passive Monitoring Assessment (OSAAQPMA) were to:

- 1. characterize the air quality in and around different areas of Speightstown, and Oistins; and
- 2. determine any trends in primary and secondary pollutant levels at seven locations across Oistins and Speightstown over the course of twelve (12) months.

To assist with the analysis, weather data was collected from various sources and traffic data was collected by the Ministry of Transport and Works (MTW) at each location for eight (8) days during different months.

#### Primary and Secondary Pollutants

The draft Ambient Air Quality Policy Paper prepared by the EPD has identified the World Health Organization (WHO) Ambient Air Quality Guidelines 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, because it is formed by photochemical reactions between nitrogen oxides and VOCs. It should be noted that SO<sub>2</sub> and NO<sub>2</sub> are utilized as indicators of the presence of sulphur oxides (SO<sub>X</sub>) and nitrogen oxides (NO<sub>X</sub>). Additionally, it must be noted that the laboratory detection limit is based on the amount of sulphur (S) and nitrogen (N) present with detectable limits of  $0.03\mu$ g for sulphur and  $0.05\mu$ g for nitrogen dioxide. The selected pollutants and their impacts are highlighted in Table 1.

Primary pollutants 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 industrial activities, transportation, personal care (e.g. salons), agricultural activities and electricity generation. In Oistins and Speightstown, the most prominent sources of pollutants and VOCs would be industrial and commercial activities and the combustion of fossil fuels.

PRIMARY	DESCRIPTION						
POLLUTANT							
Sulphur	By far the main source of sulphur dioxide is the combustion of fossil fuels						
Dioxide (SO <sub>2</sub> )	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	The main source of $NO_2$ would be high temperature combustion of fossil						
Dioxide (NO <sub>2</sub> )	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	VOCs comprise a very wide range of hydrocarbons, xygenates,						
Organic	halogenates and other carbon compounds existing in the atmosphere in						

 Table 1: List of Primary and Secondary Pollutants measured during the Oistins and

 Speightstown Ambient Air Quality Passive Monitoring Survey

Compounds	the vapour phase.				
(vocs)	The predominant source of VOCs is typically through leakage from pressurized systems (e.g. natural gas, methane) or evaporation of a liquid fuel compounds such as benzene from fuel tanks of vehicles. 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.				
SECONDARY	DESCRIPTION				
POLLUTANT					
Ozone (O3)	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. Additional impacts include damaged vegetation and reduced crop yields.				

## 3.0 Study Area and Methodology

#### 3.1 Study Area

The sampling programme consisted of seven sites as shown in Figures 1-3. Three (3) of the sites were located in the vicinity of Oistins, Christ Church, three (3) in Speightstown, St. Peter and one at Ragged Point, St. Philip, which served as a background site.

The background site was selected because it was an upwind location outside of the study area. Furthermore, this site was situated at the easternmost part of the island and consequently should not be affected by any land based activities that may generate high levels of VOC, SO<sub>2</sub> or NO<sub>2</sub>. Site selection was initially accomplished through the differentiation between activities occurring in the area and assigning the following classifications;

• Commercial activities

<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.

- Residential activity
- Industrial activity
- Mixed use activities (a combination of any of the 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.



Figure 1: Map of urban areas sampled in relation to the background sampling location.



Figure 2: Locations of the selected sampling sites in Oistins: CVSDA (Cane Vale 7<sup>th</sup> Day Adventist Church); VTTH (Residence in Thornbury Hill) and OPS (Oistins Police Station)



Figure 3 Locations of sampling sites located in Speightstown: SPS (Speightstown Police Station); FCCIBC (First Caribbean CIBC Bank) and SS (Sand Street)

Site Location	Location Type	Distance From Major	Other Selection Criteria
		Roadway	
Ragged Point, St.	Background	>50 m	Located NE of Oistins and SE of
Philip (RP)			Speightstown.
Residence,	Residential	>50 m	Residential/Industrial
Thornbury Hill,	Background		
Oistins, Christ			
Church (VTTH)			
Oistins Police	Intermediate	20-30 m	Commercial/Residential
Station, Oistins,			
Christ Church (OPS)			
Cane Vale Seven	Background	> 50 m	Residential
Day Adventist			
Church, Cane Vale,			
Ch. Ch. (CVSDA)			
First Caribbean	Near road	1-5 m	Commercial
Commercial Bank,			
Speightstown, St.			
Peter (FCCIBC)			
Speightstown Police	Urban	>50 m	Residential/Commercial
Station,	Background		
Speightstown St.			
Peter (SPS)			
Sand Street, St.	Background	>50 m	Residential
Peter (SS)			

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

## 3.2 Tube Deployment and Recovery

The air quality at seven (7) locations was assessed utilizing passive monitors designed to allow passive air flow over treated sampling media (TenaxTA Sorbent in the case of the VOC tubes), which was then analysed by gas chromatography and other proprietary methodologies by the manufacturer Enviro Technology Services PLC UK, within their flexible scope of accreditation.

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 7 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 (Top Five VOCs,  $SO_2/NO_2$ , and  $O_3$ ) were deployed on a monthly basis at this site.
- Three trip blanks, one each for Top Five VOCs,  $SO_2/NO_2$ , and  $O_3$  were utilized during the deployment and returned 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.

### 3.3 Supplemental Data for Oistins and Speightstown

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 sites for a period of eight (8) days, to account for both weekday and weekend traffic. No data was collected for VTTH as the location was outside of the defined boundary of Oistins as defined in the physical development plan. Therefore, any traffic recorded in this area cannot be considered as part of the overall Oistins traffic volume.
- Meteorological data was collected utilizing weather data from <u>www.wunderground.com</u> whose data was sourced from the weather station at the Grantley Adams International Airport, Christ Church which was the closest weather station to Oistins.

<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</u> of the Environment Operations Division Technical Support Section

0 ID#		4	G=== 10	0 == 10	Nov 10	D== 10	Tread (		M 14			Jame 10	
Ragged Point	PARAMETERS	AUG-13	SEPT-13	1 UCT-13	NOV-13	1 DEC-13	JAN-14	1 FEB-14	MAR-14	APR-14	MAY-14	JUN-13	JUL-14
(RP)	SO: /NO:	1	1	1	1	1	1	1	1	1	1	1	1
	(0)	1	1	1	1	1	1	1	1	1	1	1	1
	(03)	T	1	1	1	1	1	1	1	1	1	1	1
Residence,	VOC		1	1		1	1		1	1		1	1
Thornbury		1	1	9	1	1	9	1	1	1	1	1	1 2
11111 (V 1 111)	$(\Omega_2)$	1	2	1	1	2	1	1	2	1	1	2	1
	(03)	Ŧ	-	-	1		-	-	~	1	1	~	1
Oistins Police	VOC	1	2	1	1	2	1	1	2	1	1	2	1
Station (OPS)	SO <sub>2</sub> /NO <sub>2</sub>	2	1	1	2	1	1	2	1	1	2	1	1
	(O <sub>3</sub> )	1	1	2	1	1	2	1	1	1	1	1	2
										• 	•	•	
Cane Vale 7 <sup>th</sup>	VOC	1	1	2	1	1	2	1	1	1	1	1	2
Day Adventist Church	SO <sub>2</sub> /NO <sub>2</sub>	1	2	1	1	2	1	1	2	1	1	2	1
(CVSDA)	(O <sub>3</sub> )	2	1	1	2	1	1	2	1	1	2	1	1
									-				
First	VOC		1	1		1	1		1	1		1	1
International	100		1	1	4	1	1	4	1			1	
Bank Speightstown	SO <sub>2</sub> /NO <sub>2</sub>	1	1	2	1	1	2	1	1	2	1	1	2
(FCCIBC)	(O <sub>3</sub> )	1	2	1	1	2	1	1	2	2	1	2	1
Speightstown Police Station (SPS)	VOC	1	2	1	1	2	1	1	1	1	1	2	1
	SO <sub>2</sub> /NO <sub>2</sub>	2	1	1	2	1	1	2	1	1	2	1	1
	(O <sub>3</sub> )	1	1	2	1	1	2	1	1	1	1	1	2
Sand Street	VOC	1	1	2	1	1	2	1	1	2	1	1	2
Point (SS)	SO <sub>2</sub> /NO <sub>2</sub>	1	2	1	1	2	1	1	1	1	1	2	1
	(O <sub>3</sub> )	2	1	1	2	1	1	2	1	1	2	1	1

Table 3: The diffusion tube allocation from August 2013 to July 2014. The value "2" indicates that a duplicate is placed on site.

### 4.0 Results

#### 4.1 Ragged Point (RP), St. Philip Background Site

Sampling was conducted at Ragged Point, St. Philip which is the easternmost point of Barbados, located north east of Oistins and south east of Speightstown.

As depicted in Graph 1, the SO<sub>2</sub> concentrations observed at Ragged Point were highest (1.25 ppb) in January 2014 and lowest in October 2013 and July 2014 where the values were below the detectable limit for SO<sub>2</sub><sup>3</sup>.



Graph 1: SO<sub>2</sub> levels detected at Ragged Point, St. Philip for the period August 2013 to July 2014.

In the case of NO<sub>2</sub>, the highest level detected (3.11 ppb) was observed in February 2014. It must be noted that the lowest levels were observed during August 2013, September 2013, October 2013 and July 2014, where the laboratory analysis indicated that the concentrations were below the detectable limit for  $NO_2^4$ .

 $<sup>^3</sup>$  0.03µg is the laboratory detectable limit for S0\_2.

<sup>&</sup>lt;sup>4</sup> 0.05µg is the laboratory detectable limit for NO<sub>2</sub>.

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Graph 2: NO<sub>2</sub> and O<sub>3</sub> concentrations observed at Ragged Point, St. Philip for the period August 2013 to July 2014.

With respect to  $O_3$ , the highest value of 41 ppb was detected in November 2013; no data was collected in December 2013 as samplers at this site where not present when officers went to retrieve them. The lowest value of approximately 20.03 ppb was detected in June 2014. Both the high and low concentrations are shown in Graph 2.

In the case of the top five VOCs, Graph 3 highlights only those compounds detected that were within the UKAS accredited scope (i.e. the values can be considered accurate and verifiable) and those that were not formed as a result of interactions with  $O_3$  and the sample media. During the months of January, March, April and May 2014, all of the top five VOCs were outside the flexible scope and were possibly the result of an artefact reaction with  $O_3$ , and as a result were not shown in Graph 3.

Additionally, no data was collected in December 2013 due to lost tubes. The highest concentration of any top five VOC detected was 1.37 ppb of 2-Ethyl-1-hexanol in July 2014. For the full list of compounds detected please refer to Appendix 1.



Graph 3: Top Five VOCs at detected at Ragged Point, St. Philip for the period August 2013 to July 2014. The compounds shown represent only those compounds covered in the laboratory accredited flexible scope and are not blank corrected and do not include compounds that may be the result of reactions between O<sub>3</sub> and the Tenax TA sorbent.

#### 4.2 Private Residence, Thornbury Hill, Christ Church (VTTH)

This location, represented a residential background location, greater than 50 m from the busiest roadway; it was also in close proximity less than 30 m away from an industrial park located north of the property.

Results showed, that  $SO_2$  concentrations peaked (4.85 ppb) in January 2013. The lowest levels observed were those below the detectable limit in September and October 2013.



Graph 4: SO<sub>2</sub>, levels at VTTH, Thornbury Hill, Christ Church during the period August 2013 to July 2014.

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With respect to NO<sub>2</sub>, the highest level (1.45 ppb) was detected in August 2013. The lowest level (0.65 ppb) was detected in April 2014. The highest level (42.73 ppb) of O<sub>3</sub> was detected in May 2014 and the lowest (15.95 ppb) in September 2013.



Graph 5: O<sub>3</sub> and NO<sub>2</sub> concentrations detected at a private residence in Thornbury Hill, Christ Church for the period August 2013 to July 2014.

With respect to the top five VOCs, the highest levels were detected in March 2014 with Acetic acid concentrations (47.75 ppb) being the highest, the lowest concentrations (< 0.15 ppb) in general were detected in August 2013, as shown in Graph 6. Additionally, the majority of the top five VOCs did not exceed 2.5 ppb.



Graph 6: Top five VOC compounds detected at a private residence, located at Thornbury Hill Christ Church. The compounds shown represent only those which are covered in the laboratory accredited flexible scope, are not blank corrected and do not include those compounds that may be the result of reactions between O<sub>3</sub> and the TenaxTA sorbent.

As shown in Graph 6 the compounds detected were those included in the laboratory's UKAS accreditation and those compounds that were not formed as a result of the sample media sorbent interacting with  $O_3$ . For the full list of compounds please refer to Appendix 1.

#### 4.3 Oistins Police Station (OPS)

Samplers were placed near the entrance to Oistins Magistrates Court and Police Station. The results of the monthly samples have been presented below in Graphs 7-9.

The highest  $SO_2$  concentration of 0.79 ppb was detected in November 2013. Lows were detected in September and October 2013 when those concentrations were observed to be below the laboratory detectable limit as seen below in Graph 7.





In the case of NO<sub>2</sub>, the highest concentration (4.12 ppb) was detected in November 2013 with the lowest concentration (0.22 ppb) detected in July 2014. The highest recorded ozone level (73.66 ppb) was detected in October 2013, whereas the lowest (14.83 ppb) was detected in August 2013.

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Graph 8: NO<sub>2</sub> and O<sub>3</sub> concentrations detected at OPS for the period August 2013 to July 2014.

As shown in Graph 9, the highest concentrations of top five VOCs were detected in March 2014. The highest value detected was 72.63 ppb of 2, 5-Cyclohexadiene- 1, 4 Dione, 2, 5 diphenyl and the lowest value (0.11 ppb) of  $\sigma$ -xylene was detected in October 2013. Additionally, in November 2013 there was a spike of Nonanal which had an average concentration of 35 ppb.

As represented in Graph 9, 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. Please refer to Appendix 1 for the full list of compounds detected.



Graph 9: Top Five VOC compounds detected at the OPS sampling location during the study period August 2013 to July 2014. The compounds shown represent only those covered in the laboratory accredited flexible scope, are not blank corrected and do not include those reactions that may be the result of reactions between  $O_3$  and the TenaxTA sorbent.

# 4.4 Cane Vale Seventh Day Adventist Church (CVSDA), Cane Vale, Oistins Christ Church

Passive samplers were placed on the exterior of the CVSDA which was classified as a residential area. The results of the sampling are shown in Graphs 10-12.

 $SO_2$  levels peaked (0.71 ppb) in November 2013 and the lowest concentrations, which were below the detection limit, were recorded in October 2013.



Graph 10: SO<sub>2</sub> concentrations detected at CVSDA during the period August 2013 to July 2014.

As shown in Graph 11; the highest  $NO_2$  concentration (3.53 ppb) was detected in August 2013 and the lowest concentration (0.19 ppb) detected in July 2014. Ozone levels peaked (39.0 ppb) in December 2013 and the lowest (13.95 ppb) was detected in August 2013.



Graph 11:  $NO_2$  and  $O_3$  concentrations detected at CVSDA, for the period August 2013 to July 2014.

Based on Graph 12 below, the highest concentrations of top 5 VOCs were detected in March 2014. The highest concentration of any VOC detected was 76.41 ppb of Diethyl phthalate, the lowest concentration of any top 5 VOCs was 0.17 ppb of 1,2,4 trimethyl-benzene which was observed in August 2013.

As shown in Graph 12, 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. Please refer to Appendix 1 for the full list of compounds detected.



Graph 12: Top five VOC compounds detected at the CVSDA sampling location during the study period August 2013 to July 2014. The compounds shown represent only those covered in the laboratory accredited flexible scope, are not blank corrected and do not include tho reactions that may be the result of reactions between O<sub>3</sub> and the TenaxTA sorbent.

## 4.5 First Caribbean CIBC Speightstown (FCCIBC)

This location was considered as a near road sampling location in a commercial area zone due to the presence of several businesses. The results of the sampling are shown in the graphs 13-15 below.

Graph 13 shows that  $SO_2$  levels peaked (0.76 ppb) in November 2013 and the lowest  $SO_2$  concentration was below the detectable limit in October 2013.





The highest NO<sub>2</sub> concentration (5.78 ppb) was detected in December 2013 and the lowest detected (0.36 ppb) in July 2014. With the exception of September 2013 and July 2014, all other NO<sub>2</sub> concentrations were between 4.78 and 5.78 ppb. The highest ozone level (31.24 ppb) was detected in December 2013 and the lowest (9.96 ppb) in October 2013.

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Graph 14: NO<sub>2</sub> and O<sub>3</sub> concentrations detected at FCCIBC, for the period August 2013 to July 2014.

As shown in Graph 15, during the sampling period the majority of the VOCs detected were below 2.50 ppb, except in March 2014 where a high of 48.87 ppb of m-p-xylene was detected. The lowest concentration of any top five VOC detected was 0.17 ppb of 1, 2, 4 trimethyl benzene in May 2014. Several compounds were detected during the analysis that fell outside of the laboratory flexible scope. Please refer to Appendix 1 for the full list of compounds detected.



Graph 15: Top five VOC compounds detected at FCCIBC, Speightstown, St. Peter sampling location, during the study period August 2013 to July 2014. The compounds shown represent only those covered in the laboratory accredited flexible scope, are not blank corrected and do not include those reactions that may be the result of reactions between O<sub>3</sub> and the TenaxTA sorbent.

#### 4.6 District E Police Station (SPS), Speightstown St. Peter

Passive samplers were deployed in the parking lot of the District E, Speightstown Police Station, St. Peter. The results of the sampling are provided below in Graphs 16-18.

The highest level (1.50 ppb) of  $SO_2$  was detected in May 2014. The lowest level detected was below the detectable limit and was recorded in October 2013.



Graph 16: SO<sub>2</sub> concentrations for the District E Police Station (SPS), Speightstown, St. Peter.

As observed in Graph 17, the highest  $NO_2$  concentration (3.97 ppb) was detected in November 2013, and the lowest concentration (0.37ppb) was detected in July 2014. The highest ozone concentration detected was 45.67 ppb in March 2014. The lowest  $O_3$  concentration detected was 15.86 ppb in September 2013.

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Graph 17:  $NO_2$  and  $O_3$  concentrations detected at SPS, for the period August 2013 to July 2014.

As demonstrated in Graph 18 below, the majority of the VOCs detected were below 1.50 ppb. However the levels in March 2014 were significantly higher, the highest of which was 2, 5-Cyclohexadiene-1,4-dione, 2-5 diphenyl with a concentration of 168.70 ppb. The lowest concentration of any top five VOC detected was 0.10 ppb of  $\sigma$ -xylene which was detected in December 2013. Several compounds were detected during the analysis that fell outside of the laboratory flexible scope. Please refer to Appendix 1 for the full list of compounds detected.



Graph 18: Top five VOC compounds detected at SPS, Speightstown, St. Peter sampling location during the study period August 2013 to July 2014. The compounds shown represent only those compounds covered in the laboratory accredited flexible scope, are not blank corrected and do not include those reactions that may be the result of reactions between  $O_3$  and the TenaxTA sorbent.

### 4.7 Sand Street, Speightstown (SS)

Sand Street, Speightstown was the northern most location sampled and was classified as a background residential sampling location. The results for SS are highlighted in Graph 19-21.



Graph 19: SO<sub>2</sub> concentrations at SS during the period August 2013 to July 2014.

 $SO_2$  concentrations (0.73 ppb) peaked in August 2013; the lowest detected concentrations were detected in September 2013 and October 2013 which were below the laboratory detectable limit of  $0.03\mu g$  for S. No data was collected in January 2014 as the tubes were not present when officers went to retrieve them.

As observed in Graph 20, the highest  $NO_2$  level of 2.87 ppb was detected in August 2013 and the lowest of 0.14 ppb in July 2014. The highest ozone concentration of 43.85 was observed during the month of December 2013 and the lowest of 17.71 ppb in October 2013.

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Graph 20:  $NO_2$  and  $O_3$  concentrations detected at SPS, for the period August 2013 to July 2014.

As shown in graph 20, during the sampling period the majority of the VOCs detected ranged between 1.46 ppb and 0.17 ppb, however, the concentrations being detected in March 2014 were significantly higher, the highest of which was Napthalene with a concentration of 12.80 ppb. The lowest concentration of any top five VOC detected was that of 0.17 ppb of Tridecane in December 2013. Several compounds were detected during the analysis that fell outside of the laboratory flexible scope. Please refer to Appendix 1 for the full list of compounds detected.



Graph 21: Top five VOC compounds detected at SS, Speightstown, St. Peter sampling location, during the study period August 2013 to July 2014. The compounds shown represent only those compounds covered in the laboratory accredited flexible scope, are not blank corrected and do not include those reactions that may be the result of reactions between  $O_3$  and the TenaxTA sorbent.

#### 4.8 Weather Data

Weather data was collected via Weather Underground<sup>5</sup> which cited the Coastal Zone Management Unit and independent weather stations as a source.

Graph 22 below, displays the average highest and average lowest temperatures, in addition to the average temperatures recorded during the monitoring period. Studies have demonstrated a link between temperature and ozone formation where temperatures above 26.7°C have been shown to increase ozone generation reactions.



Graph 22: Monthly Highs, Lows and Average Temperatures recorded during the period August 2013 to July 2014.

Graph 23, represents the average monthly wind speed recorded during the sampling period. According to the graph, the highest wind speed was recorded in June 2014.

<sup>&</sup>lt;sup>5</sup> Various. Weather History at Grantley Adams International Airport. Available:

http://www.wunderground.com/history/airport/TBPB/2013/8/1/CustomHistory.html?dayend=31& monthend=7&yearend=2014&req\_city=&req\_state=&req\_statename=&reqdb.zip=&reqdb.magic=&reqdb.wmo=. Last accessed Feb 20, 2015.





Graph 24, shows the average rainfall per month during the study period. According to the data, the highest levels of rainfall were recorded in October 2013 and the lowest in May 2014. Graph 25 shows the monthly average of the relative humidity during the study period.



Graph 24: Average monthly rainfall data collected during the period August 2013 to July 2014.



Graph 25: The average humidity recorded during the monitoring period of August 2013 to July 2014.

#### 4.9 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 26 below shows the average monthly daylight received by Barbados<sup>6</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 are generally observed from May to August.

<sup>&</sup>lt;sup>6</sup> http://www.barbados.climatemps.com/



#### Graph 26: Daylight averages for Barbados

## 4.10 Ministry of Transport and Works Traffic Data

Using traffic data provided by the Ministry of Transport and Works through the use of traffic counters, an estimated 30 day average<sup>7</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 Graphs 27 and 28.

Based on the data it appears that in the case of Oistins, the nearest busy roadway was in the vicinity of OPS. When compared to CVSDA, the number of vehicles estimated per 30 days was less than 10% of the volume of OPS. No data

<sup>&</sup>lt;sup>7</sup> Measurements were taken over 8 day periods. From this a single day estimate was calculated then multiplied by 30 to generate a 30 day average for each location.



was collected for VTTH as the location was located in a residential cul-de-sac.

## Graph 27: Estimated number of vehicles per 30 days utilizing the busy roadway adjacent to the sampling points in Oistins, Christ Church.

As demonstrated in Graph 28 it appears that in the case of Speightstown, the nearest busy roadway was in the vicinity of FCCIBC. The traffic volume at SS and SPS were approximately 50% and 43% of the volume at FCCIBC respectively.



Graph 28: Estimated number of vehicles per 30 days utilizing the busy roadway adjacent to the sampling points in Speightstown, St. Peter.

## 5.0 DISCUSSION

The adopted WHO Ambient Air Quality Guidelines 2005 were developed using real time continuous sampling methodologies which are then used to formulate standards for both primary and secondary pollutants such as nitrogen dioxide (NO<sub>2</sub>) and its derivatives, 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. Consequently, the results obtained in this study cannot be compared to existing standards. However, it must be noted that 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 Oistins and Speightstown. Additionally, passive sampling results also represent chronic exposure to pollutants under investigation as they are composite samples and hence average concentrations over time.

Using information from the Barbados Statistical Service<sup>8</sup> there are approximately 1,203 residents in Oistins while 2,604 persons reside in Speightstown. These numbers do not take into account persons commuting to and from Oistins and Speightstown daily and persons living in the outlying areas. The impacts of exposure to the primary and secondary pollutants may vary according to an individual's health, tolerances and level of exposure. Sections 5.1 and 5.2 which follow, will address the areas with high and low concentrations, in addition to the potential impacts these persons may be exposed to on a daily basis based on the international guidelines.

#### 5.1 Sulphur Oxides (SO<sub>2</sub>)

#### 5.1.1 Highs, Lows and Averages

The highest recorded  $SO_2$  level was 4.86 ppb, detected at VTTH in January 2013. This may be due to activity occurring at a nearby industrial park or activities occurring on the property, since the remainder of the readings were below 1ppb for the other monthis of the year.

During October 2013, the level of  $SO_2$  for all locations was below the detectable limit of the laboratory analysis. The highest rainfall levels were

<sup>&</sup>lt;sup>8</sup> Barbados Statistical Service, <u>http://www.barstats.gov.bb/census/redatam-1/</u> Last accessed January 30<sup>th</sup> 2015.

recorded during this period of the study, which may have an impact upon  $SO_2$  concentrations. However, it must be noted that other months recorded only slightly lower rainfall levels without the  $SO_2$  levels dropping below detectable limits. Therefore, the low in October may be due to a combination of anthropogenic and natural factors.

Graph 29 below shows the average  $SO_2$  levels at each location as well as the overall averages for the Bridgetown 2012 study and the overall averages for Oistins and Speightstown.



Graph 29: Average SO<sub>2</sub> levels for all locations, in addition to the average SO<sub>2</sub> levels for Bridgetown and total average for Oistins and Speightstown (OS)

When compared to the average  $SO_2$  levels for the Bridgetown study (2.10 ppb), the average  $SO_2$  combined average for both Oistins and Speightstown was approximately 0.5 ppb or 25% of the average Bridgetown  $SO_2$  concentration.

6.1.2 Impacts on SO<sub>2</sub> Levels

SO<sub>2</sub> levels in Oistins and Speightstown may be impacted by several factors such as the introduction of low sulphur diesel to consumers in 2013, the different classes (buses, trucks, cars and motorcycles), different types and volume of activities such as kitchens and industrial processes and the noticeably different traffic volumes for Oistins and Speightstown in comparison to Bridgetown. Graph 30 below highlights the difference in traffic volume over a 30 day period between the different urban centres.



Graph 30: Estimated number of vehicles traversing Bridgetown, Oistins and Speightstown over a 30 day period.

As depicted in Graph 30, traffic in Bridgetown over a 30 day period was thirty (30) times higher compared to that in Speightstown during a 30 day period. In the case of Oistins, traffic volumes were ten (10%) percent of the volume experienced by Bridgetown over a 30 day period. It must be noted that the dates of traffic monitoring conducted for the Oistins and Speightstown study were dissimilar, when compared to the Bridgetown study.

The land use characteristics of Oistins and Speightstown (with the exception of FCCIBC) differed from Bridgetown; as the sampling locations in Oistins and Speightstown were not populated by as many tall buildings in close proximity to each other. As a result dilution via wind action was far more likely to occur. In the case of VTTH, where the highest  $SO_2$  level was recorded in January 2014; the levels in the remaining months of the study were less than 1 ppb. However, if this outlying value were removed, the average  $SO_2$  value would be similar to the average value calculated for Ragged Point (RP).

The residence time for  $SO_2$  in the atmosphere can vary over several days depending on atmospheric conditions. For example  $SO_2$  levels may be affected by precipitation and deposition of solid particulates on vegetation, soil and buildings. Additionally, 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 between 18 and 32 km/h (Graph 23) 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 was unknown if the average wind-speed persisted at the sample locations.

## 5.1.3 Comparison to Other Passive Sampling Studies and Continuous Monitoring Studies

According to research<sup>9</sup> conducted by the World Meteorological Organization Global Atmosphere Watch, 1997 (WMO GAW) global annual averaged  $SO_2$  values utilizing passive sampling methodologies in South Korea, Thailand and Malaysia did not exceed 3 ppb; which was higher than the averages for either; Bridgetown, Oistins or Speightstown.

Based on WHO documentation<sup>10</sup>, the annual mean concentrations in urban areas were in the range of 7–21 ppb while daily means seldom exceeded 47.7 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. As was mentioned earlier, these results follow the trend of passive samplers' results trending lower than values obtained via continuous monitoring.

## 5.1.4 Impacts of $SO_2$ Exposure based on International Guidelines and Standards

In the case of SO<sub>2</sub>, the World Health Organization (WHO) guidelines are represented in terms of 24 hour exposures and 10 minute means. The USEPA National Ambient Air Quality Standards (NAAQS) are represented by 1 hour primary and 3 hour secondary standards. Table 12 below highlights the respective guideline and standards used by the WHO and the USEPA

<sup>&</sup>lt;sup>9</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.

<sup>&</sup>lt;sup>10</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.

PRIMARY/SECONDARY	CONCENTRATION	TIME	AGENCY
Dreim over	20 μg/m³ (7.63 ppb)	24-hour mean	WHO
Primary	500 μg/m <sup>3</sup> (190.84 ppb)	10 minute mean	WHO
Primary	75 ppb (196.5 μg/m³)	1 hour	USEPA
Secondary	500 ppb ( 1310 μg/m <sup>3</sup> )	3 hour	USEPA

The WHO guideline indicates that the  $SO_2$  concentration of  $500\mu g/m^3$  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<sup>3</sup> (47.71 ppb) to 20µg/m<sup>3</sup> (7.63 ppb) based on the belief that although the causality of the effects of low concentrations of  $SO_2$  is still uncertain, a reduction in  $SO_2$  was likely to decrease exposure to co-pollutants.

#### 5.2. Nitrogen Dioxide (NO<sub>2</sub>) and Ozone ( $O_3$ )

#### 5.2.1 Highs and Lows

As shown in Graph 31, the highest average  $O_3$  levels were observed at both police station locations OPS and SPS. Additionally, the lowest  $O_3$ concentration was detected at FCCIBC which incidentally registered the highest NO<sub>2</sub> concentration.

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#### Graph 31: The average NO<sub>2</sub> and O<sub>3</sub> concentrations per location.

With respect to  $NO_2$ , the highest average detected was 4.72 ppb at FCCIBC. The lowest average  $NO_2$  concentration (0.69 ppb) was detected at the background location Ragged Point (RP). This may be due to the differences in the vehicular traffic volumes, where FCCIBC registered higher traffic volumes in comparison to RP which based on observations was not a frequently visited location and therefore should have a much smaller traffic volume.



Graph 32: Comparison of Urban Centre Average NO<sub>2</sub> and O<sub>3</sub> concentrations from Bridgetown in 2012-2013 and for Oistins and Speightstown 2013-2014

Based on the results in Graph 32, Bridgetown displayed a higher average concentration of NO<sub>2</sub> than both Speightstown and Oistins due to the higher traffic volume. Surprisingly, despite Oistins exhibiting greater traffic volume than Speightstown, Oistins showed lower concentrations for both NO<sub>2</sub> and O<sub>3</sub> when compared to Speightstown. This may be due to the Oistins locations being more open and therefore being more influenced by the sea breezes which may have resulted in the dilution and dispersion of pollutants via wind action.

In the case of Speightstown, higher pollutant concentrations may be due to the following factors; the high traffic volume at FCCIBC coupled with the presence of a narrow roadway and tall buildings on either side of the sample site at FCCIBC. Additionally the close proximity of the Speightstown Bus Terminal to the SPS location could potentially impact upon NO<sub>2</sub> and O<sub>3</sub> levels due to increased numbers of diesel vehicles located upwind of the sampling site.

Despite Bridgetown having higher traffic volumes, higher  $O_3$  levels were detected in both Oistins and Speightstown, with the highest level detected in Speightstown. Therefore, the traffic volume may not be a major factor influencing  $O_3$  concentration. A combination of NO<sub>2</sub>, VOC concentrations and weather conditions may have a greater impact on  $O_3$  concentration.

#### 5.2.2 VOC Trends

The vast majority of the top 5 VOCs detected exhibited concentrations below 1 ppb. However, there were several instances where individual VOC compounds exhibited concentrations between 1 and 2.1 ppb. In March 2014, the VOC levels for each location ranged between a minimum of 12.6 ppb at Sand Street to a maximum of 168.70 ppb at SPS. No explanation for the dramatic increase in VOC levels across all sampling locations during March 2014 could be determined as it may have been the result of changes in weather or it may have been a problem with the sample media or an error during analysis.

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

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

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

#### Table 5: Primary and secondary NO<sub>2</sub> guidelines and standard for the WHO and USPEA

In the case of the WHO guidelines<sup>11</sup> 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 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.

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

#### 5.3.1 Mechanics of Ozone Formation

Ozone at ground level is formed through a series of complex photochemical reactions among NO<sub>X</sub> 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>&</sup>lt;sup>11</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

The formation of ground level ozone is dependent on the intensity of solar radiation and the sensitive ratio of NO<sub>X</sub> to VOCs 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  $^{12}$
- the decreasing depletion of ozone by traffic generated  $NO_{X}\,emissions,$  which increases the metric

Therefore, rural concentrations may be a combination of background ozone and that produced by more national activities (probably up to the regional scale). When precursor emissions such as NOx and VOCs 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 either point or mobile  $NO_X$  and VOC 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<sub>x</sub> concentrations are higher relative to VOC concentrations. As a result NO<sub>x</sub> tends to inhibit ozone formation and the resultant ozone formation is called "VOC limited". When the VOC/ NO<sub>x</sub> ratio is high, the VOC concentration is higher relative to the NO<sub>x</sub>

<sup>&</sup>lt;sup>12</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.

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.

UV radiation derived from sunlight exposure 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>13</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 phenomena 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.

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

The data collected included  $NO_2$ ,  $O_3$  and Top 5 VOCs. Unfortunately, no total VOC data was collected and as a result it was difficult to determine the exact relationship between VOC levels and  $NO_2$ .

Although areas with higher traffic volumes showed higher  $NO_2$  concentrations, the reverse trend was observed when compared to  $O_3$ . For instance in Graph 28, FCCIBC registered the highest traffic volume per 30 days,

<sup>&</sup>lt;sup>13</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

but when  $O_3$  concentrations were compared to those at SPS and SS which showed lower traffic volumes, the  $O_3$  levels were lower at FCCIBC, indicating that  $O_3$  production may be limited by  $NO_2$  concentration. However, without total VOC concentrations available, it may be difficult to establish a more comprehensive relationship between  $NO_2$  and VOC concentrations.

Based on the available meteorological data, the average temperature for the year was approximately 27.2°C, compared to 27.3 in 2012-2013. Both average temperatures were 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 (27.3km/hr) for wind speed exceeded the 16 km/h maximum allowable wind speed for ozone propagation. Wind speeds above 16 km/hr do not allow for the necessary accumulation of precursors of ozone formation (VOCs and NOx) and as a result dilute or disperse the subsequent formation of ozone conversely;  $O_3$  may be transported from their formation points to other locations.

## 6.0 STUDY LIMITATIONS

The study suffered from similar limitations of the Bridgetown 2012-2013 study as the methodology did not allow for any real time correlation 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, ongoing activities and weather conditions specific to the sample sites. As a result, it was difficult to accurately assess the relationships observed between SO<sub>2</sub>, NO<sub>2</sub>, ozone and VOC levels and other factors such as weather conditions, mobile and stationary sources.

There were some challenges associated with the use of Top Five VOC as an analytical tool in that it did not provide a total of all VOCs detected and instead reflected the top five VOCs. As a result, no relationship could be established between VOCs and NO<sub>2</sub> and the resultant O<sub>3</sub> concentrations. Additionally, the Top Five (5) VOCs varied considerably between the sampling locations in terms of concentrations and the individual VOCs detected.

## 7.0 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 Oistins and Speightstown was achieved. The passive sampling methodology utilized allowed for the determination of the average concentrations of primary and secondary pollutants as well as VOCs in Oistins and Speightstown. 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, although the methodology utilized in the passive sampling is less costly than real time sampling, it is not comparable to the adopted WHO methodologies and the associated standards. The results observed may be the result of existing economic activities, along with the introduction of low sulphur diesel to Barbadian consumers.

In light of the fact that there may be changes in terms of economic activity and general human activities over time, further assessment should be conducted using continuous sampling, which would allow comparison to the WHO standards for the primary and secondary pollutants.

### 8.0 **Recommendations**

#### 8.1 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 guideline such as the WHO Air Quality Guidelines 2005. This would allow for the assessment of the accuracy of the passive samplers in comparison to the real time samplers.

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 effects throughout the course of the day.

In totality, it will allow for the determination of whether pollution was emanating from mobile (vehicle or trans-boundary transport) or stationary sources, setting emission limits when comparing to establish standards, setting attainment or non attainment goals for urban centres and determining the impact of future development on the human health and environment.

#### 8.2 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<sub>2</sub> and TVOCs in ozone formation.

## 9.0 **REFERENCES**

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## 11/10/2016

APPENDIX I

TOP 5 VOCS

## LABORATORY ANALYSIS REPORT

**REPORT NUMBER** 

CUSTOMER GRADKO LAB REFERENCE DATE SAMPLES RECEIVED DESPATCH REF.NUMBER JOB NUMBER BOOKING IN REF. Y2862R Ministry of Environment, Water Resources Management & Drainage PE6H1528-1537 02.10.13 SOR012668 9892 Y2862

#### IDENTIFICATION AND ESTIMATION (SEMI-QUANTITATIVE ANALYSIS) FOR TOP 5 VOC ON TENAX DIFFUSION TUBES BY GC/MS Analysis has been carried out in accordance with in-house method GLM 13

Tube Number	GRA 04847	
Sample Location	Ragged Point	
Exposure Time (mins)	38821	
TOP 5 VOC	ng on tube	ppb
Styrene	39.08	0.50
1-Hexanol, 2-ethyl-	18.22	0.23
Tridecane	16.42	0.21
Benzaldehyde** <sup>+</sup>	16.14	0.21
Acetophenone** <sup>+</sup>	12.70	0.16



## Air Pollation Solutions

Tube Number Sample Location Exposure Time (mins)	GRA 11704 Thornbury Hill 38812		
TOP 5 VOC		ng on tube	ppb in
Cylcohexanone <sup>+</sup>		14.27	0.18
Cyclohexane, isothiocyanato <sup>+</sup>		11.85	0.15
Toluene		11.63	0.15
Cyclohexane, isocyanato <sup>+</sup>		11.38	0.15
Tridecane		11.16	0.14
Tube Number Sample Location Exposure Time (mins)	GRA 11993 Thornbury Hill 38812		
TOP 5 VOC		ng on tube	ppb in
Tridecane		11.85	0.15
Toluene		9.27	0.12
1-Hexanol, 2-ethyl-		8.38	0.11
Benzene		6.25	0.08
Decane		6.21	0.08
Tube Number	GRA 09731		
Sample Location	<b>Oistins Police</b>		
Exposure Time (mins)	38806		
TOP 5 VOC		ng on tube	ppb in
Toluene		30.35	0.39
m/p-Xylene		30.16	0.39
Benzene		12.82	0.17
Benzene, 1,2,4-trimethyl-		12.81	0.17
o-Xylene		12.42	0.16

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## Air Pollation Solutions

Tube Number Sample Location Exposure Time (mins)	GRA 09619 Cane Vale S.D.A. Church 38806		
<b>TOP 5 VOC</b> Toluene m/p-Xylene Decanal <sup>** *</sup> Pentadecane Benzene, 1,2,4-trimethyl-		ng on tube 26.46 26.36 20.83 13.97 13.15	<b>ppb in</b> 0.34 0.34 0.27 0.18 0.17
Tube Number Sample Location Exposure Time (mins)	GRA 04578 CIBC Speightstown 38919		
TOP 5 VOC Toluene m/p-Xylene Tetradecane Pentadecane o-Xylene		na on tube 63.25 59.76 25.62 23.71 23.47	0.81 0.77 0.33 0.30 0.30
Tube Number Sample Location Exposure Time (mins)	GRA 09650 CIBC Speightstown 38919		
TOP 5 VOC m/p-Xylene Toluene Nonanal** <sup>+</sup> Tridecane o-Xylene		ng on tube 75.38 73.55 57.97 32.65 30.30	<b>ppb in</b> 0.97 0.94 0.74 0.42 0.39

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## Air Pollation Solations

Tube Number Sample Location Exposure Time (mins)	GRA 09468 Speightstown Police 38903		
TOP 5 VOC		ng on tube	ppb in air*
Cyclohexane, isothiocyanato $^{\scriptscriptstyle +}$		40.38	0.52
Tridecane		25.21	0.32
Nonanal** <sup>+</sup>		20.88	0.27
m/p-Xylene		18.71	0.24
loluene		18.39	0.24
Tube Number	GRA 03040		
Sample Location	Geed		
Exposure Time (mins)	38905		
TOP 5 VOC		ng on tube	ppb in air*
Cyclohexane, isocyanato <sup>+</sup>		33.57	0.43
Nonanal** <sup>+</sup>		28.36	0.36
Tridecane		22.74	0.29
Cyclohexane, isothiocyanato <sup>+</sup>		19.19	0.25
Toluene		16.17	0.21
Tube Number	GRA 11928		
Sample Location	Blank		
TOP 5 VOC		ng on tube	
Tetradecane		<5	
Benzene		<5	
Pentadecane		<5	
Hexadecane		<5	
Heptane, 2,2,4,6,6-pentamethyl <sup>+</sup>		<5	

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Comments:

Results are not blank

<sup>+</sup> These compounds are not covered by our UKAS accredited flexible scope.

\*\*Compounds may be an artifact due to reaction of ozone with the Tenax Identification and estimation results for ng on tube are calculated using toluene standards.

Tubes are outside the recommended shelf-life.

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		Date of Analysis	14.10.13
Analysts Name	G. Aikman	Date of Report	15.10.13

The Diffusion Tubes have been tested within the scope of the supplier's Lab Quality Procedures. Calculations and assessments involving the exposure procedures and periods provided by the client are not within the scope of the suppliers UKAS Accreditation. Those results obtained using exposure data shall be indicated by an asterisk. Expressions of Opinions and Interpretations are not included in UKAS accreditation schedule. Any queries concerning the data in this report should be directed to Enviro Technology Services.

## LABORATORY ANALYSIS REPORT

**REPORT NUMBER** 

CUSTOMER GRADKO LAB REFERENCE DESPATCH NOTE No. JOB REFERENCE DATE SAMPLES RECEIVED BOOKING IN REF. Y3036R Ministry of Environment, Water Resources Management & Drainage GMSH1625-1635 SOR012668 9832 24.10.13 Y3036

#### IDENTIFICATION AND ESTIMATION (SEMI-QUANTITATIVE ANALYSIS) OF TOP 5 VOC ON TENAX DIFFUSION TUBES BY GC/MS Analysis has been carried out in accordance with in-house method GLM 13

Tube Number Exposure Time(mins) Sample ID	GRA 08820 43176 Ragged Point		
Top 5 VOC		ng on tube	ppb in air*
Tridecane		31.51	0.36
Cyclohexane, isothiocyanato- +		20.22	0.23
Nonanal** +		19.13	0.22
Naphthalene		17.52	0.20
Dodecane		16.49	0.19
Tube Number	GRA 09328		
Exposure Time(mins)	43170		
Sample ID	Velda Thomas		
Top 5 VOC		ng on tube	ppb in air*

	ing on tabo	pps man
Diethyl Phthalate +	116.34	1.35
Acetone +	70.91	0.82
Pentadecane	53.09	0.61
Tridecane	47.97	0.56
Heptadecane	34.57	0.40

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Tube Number Exposure Time(mins)	GRA 09337		
Sample ID	Oistins Police		
Top 5 VOC		ng on tube	ppb in air*
Diethyl Phthalate +		69.77	0.81
Tube Number		40.86	0.47
Toluene		38.55	0.45
Naphthalene		37.11	0.43
Tridecane		34.25	0.40









Air Pollation Solutions

Tube Number Exposure Time(mins) Sample ID	GRA 02049 43092 Speightstown Police		
<b>Top 5 VOC</b>		ng on tube	ppb in air*
Tridecane		53.45	0.62
Nonanal** <b>+</b>		29.91	0.35
m/p-Xylene		28.93	0.34
Benzaldehyde**		26.19	0.30
Toluene		23.20	0.27
Tube Number Exposure Time(mins) Sample ID	GRA 07935 43080 Geed Sand Street		
<b>Top 5 VOC</b>	liisooctyl ester +	ng on tube	ppb in air*
1,2-Benzenedicarboxylic acid, o		325.08	3.77
Diethyl Phthalate +		85.18	0.99
Tridecane		73.59	0.85
Nonanal** +		52.01	0.60
Naphthalene		35.38	0.41
Tube Number Sample ID	GRA 06200 BLANK		
Top 5 VOC Diethyl Phthalate + Decanal** + Nonanal** + Isopropyl Myristate + Benzaldehyde**		ng on tube 61.44 28.38 20.69 13.89 13.19	
Tube Number	GRA 06926	6	
Sample ID	Unlabelled	I	
<b>Top 5 VOC</b>	diisooctyl ester +	ng c	on tube
1,2-Benzenedicarboxylic acid, o		58	37.50
Nonanal** +		11	31.84
Decanal** +		12	22.35
Isopropyl Myristate +		4	5.93
Benzaldehyde**		3	2.49

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Comment: Results are not Blank corrected.

Tubes are outside the recommended shelf-life.

\*\*Compounds may be an artifact due to reaction of ozone with the Tenax sorbent. Identification and estimation results for ng on tube are calculated by reference to toluene and toluene-d8 Internal standard.

<sup>+</sup> These compounds are not covered by our UKAS accredited flexible scope. Two extra tubes received, but have not been analysed.Tube numbers GRA 09992 and GRA 07936

		Date of Analysis	31.10.13
Analysts Name	Mariella Angelova	Date of Report	11.11.13

The Diffusion Tubes have been tested within the scope of the supplier's Lab Quality Procedures. Calculations and assessments involving the exposure procedures and periods provided by the client are not within the scope of the suppliers UKAS Accreditation. Those results obtained using exposure data shall be indicated by an asterisk. Expressions of Opinions and Interpretations are not included in UKAS accreditation schedule. Any queries concerning the data in this report should be directed to Enviro Technology Services.