2020

Holetown and Two Rural Areas Ambient Air Quality Passive Monitoring Assessment

FEBRUARY 2015-JANUARY 2016 FINAL REPORT

ENVIRONMENTAL PROTECTION DEPARTMENT

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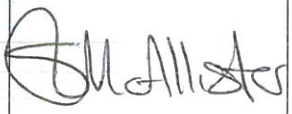
REVIEWED BY	S. McAllister BEng Chemical Engineering; P. Eng; PG Cert. Project Management; Master of Business Administration		09th January, 2020
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EXECUTIVE SUMMARY

The Holetown and Two Rural Areas Ambient Air Quality Passive Monitoring Assessment (H2RAAAPMA) was designed to characterize the levels of sulphur dioxide (SO_2), nitrogen dioxide (NO_2), ozone (O_3) and volatile organic compounds (VOCs) generated by the combustion of fossil fuels and other industrial activities occurring in the Holetown area and two rural areas which have been identified as Farley Hill National Park, St. Peter and Gun Hill Signal Station located in St. George.

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 and crop damage due to acid rain and sulphurous deposits; damage of electrical equipment by ground level ozone; and ground water pollution.

In order to establish the baseline levels of primary and secondary pollutants in and around Holetown, Gun Hill and Farley Hill, 30 day/monthly samples were taken at seven (7) locations, five (5) in Holetown and one (1) each at Farley Hill and Gun Hill over the period of a year. 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.

For the duration of the February 2015 to January 2016 study, the following observations were made;

- The average temperature was approximately 28° C. An average wind speed of 28 km/hr and an average monthly rainfall of 0.3 mm for the period were observed. Additionally, the number of sunlit hours ranged from 11 to 13 hours during the study period.

- The most heavily trafficked location was at the Holetown Police Station with an estimated 13,382 vehicles daily. The least trafficked location was Gun Hill Signal Station with 131 vehicles daily.
- The highest recorded SO_2 level was 3.91 ppb, detected at Ragged Point in January 2016. This may be due to the decomposition of a large influx of sargassum seaweed offshore and on the rocks below resulting in hydrogen sulphide (H_2S) emissions. SO_2 concentrations were below the detectable limit for all months at Divi Heritage Resort and the Crossing Lights Jus' Grillin' sampling sites.
- The highest mean NO_2 and TVOC levels were observed at Holetown Police Station, whereas the highest O_3 levels were detected at St. James Cemetery. Since O_3 is not formed immediately, the higher O_3 levels at St. James Cemetery may be due to O_3 being formed upwind and drifting downwards towards the St. James Cemetery. The lowest NO_2 concentration was detected at Ragged Point. The lowest mean TVOC concentration was detected at Crossing Lights Jus' Grillin' and the lowest mean O_3 level was detected at Divi Heritage Resort.

HOLETOWN AND TWO RURAL AREAS AMBIENT AIR QUALITY PASSIVE MONITORING ASSESSMENT

February 2015-January 2016 Final Report

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1.0 INTRODUCTION

The Environmental Protection Department has made representation in the 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 to provide strategic direction with regards to regulatory action.

This project was a continuation of the national monitoring programme, which entailed the Bridgetown Ambient Air Quality Passive Sampling project conducted during the period of 2012-2013 and the Oistins and Speightstown Ambient Air Quality Passive Monitoring project conducted in 2013-2014. Those two previous projects utilized passive samplers to collect data on average concentrations of SO_2, NO_2, O_3 and top five VOCs at locations throughout Bridgetown, Oistins and Speightstown.

During this project, the focus was on determining the average concentrations of primary and secondary pollutants in the urban centre of Holetown St. James and the rural locations of Gun Hill, St. George and Farley Hill National Park, St. Peter. It is hoped that data collected in this study and previously collected data will be utilized to determine baseline levels of both primary and secondary pollutants in Barbados.

1.1 Location Rationale for Holetown and Two Rural Areas

The previous studies monitored pollutant levels in other urban centres such as Bridgetown, Oistins and Speightstown. Holetown was chosen as it was the remaining similarly designated town in Barbados and it contained a mix of residential, commercial and industrial activities such as hotels, restaurants, bars, gas stations and malls within the area.

Farley Hill National Park was chosen as it was located in a rural area on the border of St. Peter and St. Andrew. The area was utilized mainly as a recreational area/ tourist attraction and was characterised by a small number of residents in the immediate area and low vehicular traffic. Similarly, Gun Hill Signal Station was located in a rural residential area in St. George. The area was characterized by lower vehicular traffic compared to Holetown. Both Farley Hill and Gun Hill were tourist attractions and recreational space used for picnicking, with the former being used for the hosting of several large concerts throughout the year.

2.0 PROJECT OBJECTIVE

The objective of the Holetown and Two Rural Areas Ambient Air Quality Passive Monitoring Assessment (H2RAAAPMA) was to characterize the air quality around different areas of Holetown and two rural locations over the course of twelve (12) months, in order to determine any possible trends in primary and secondary pollutant levels at the selected sample sites. To assist with the analysis, weather data was collected from the Caribbean Institute of Meteorology and Hydrology (CIMH) and traffic data was collected by the Ministry of Transport and Works (MTW) for 15-18 days at each location during different months.

2.1 Primary and Secondary Pollutants

The 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_2), nitrogen dioxide (NO_2) and volatile organic compounds (VOCs). Ozone (O_3) is considered a secondary pollutant, due to it being 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). Additionally, it must be noted that the laboratory detection limit is based on the amount of sulphur (S) or nitrogen (N) present in the media. The selected pollutants and their impacts are highlighted in Table 1.

Primary pollutants may cause smog, acid rain and other health and infrastructural hazards if present in sufficient quantities. Primary pollutants are generally emitted from various stationary sources such as industrial activities, transportation, personal care facilities (e.g. salons), agricultural activities and electricity generation. In Holetown and in the rural areas, the most prominent

sources of pollutants and VOCs would be industrial and commercial activities and the combustion of fossil fuels.

Table 1: List of Primary and Secondary Pollutants measured during the Holetown and two Rural Areas Ambient Air Quality Passive Monitoring Survey

PRIMARY POLLUTANT	SOURCES
SULPHUR DIOXIDE (SO_2)	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_2, 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 (NO_2)	The main source of NO_2 would be high temperature combustion of fossil fuels and therefore, electricity generation and road traffic are the primary sources of NO_2. According to the USEPA, short-term (30 minutes to 24 hours) NO_2 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_2 generally also lead to the formation of other nitrogen oxides and tropospheric ozone (O_3).
VOLATILE ORGANIC COMPOUNDS (VOCS)	VOCs comprise a very wide range of hydrocarbons, oxygenates, halogenates and other carbon compounds existing in the atmosphere in the vapour phase.

	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 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 POLLUTANT	**SOURCES**
OZONE (O_3)	Ground level ozone is the main component of smog and is created by the chemical interactions between NO_2, 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 (WHO, 2000). At high concentrations, O_3 may irritate airways, 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, including four (4) located in Holetown, one (1) within Farley Hill National Park, St. Peter and one (1) within Gun Hill Signal Station, St. George. One sample site was located at the eastern-most part of the island, Ragged Point St. Philip which served as a background site. The sampling locations are shown in Figures 1-4.

The background site was selected because it was an upwind location outside of the study area. Furthermore, this site was situated at the eastern-most part of the island and given the prevailing wind direction, should not be affected by any land based activities that may generate high levels of VOCs, SO_2 or NO_2. 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 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.

Holetown Farley Hill National Park Gun Hill Signal Station Ragged Point

Figure 1: Map showing the sampling locations in relation to each other. (Not to Scale)

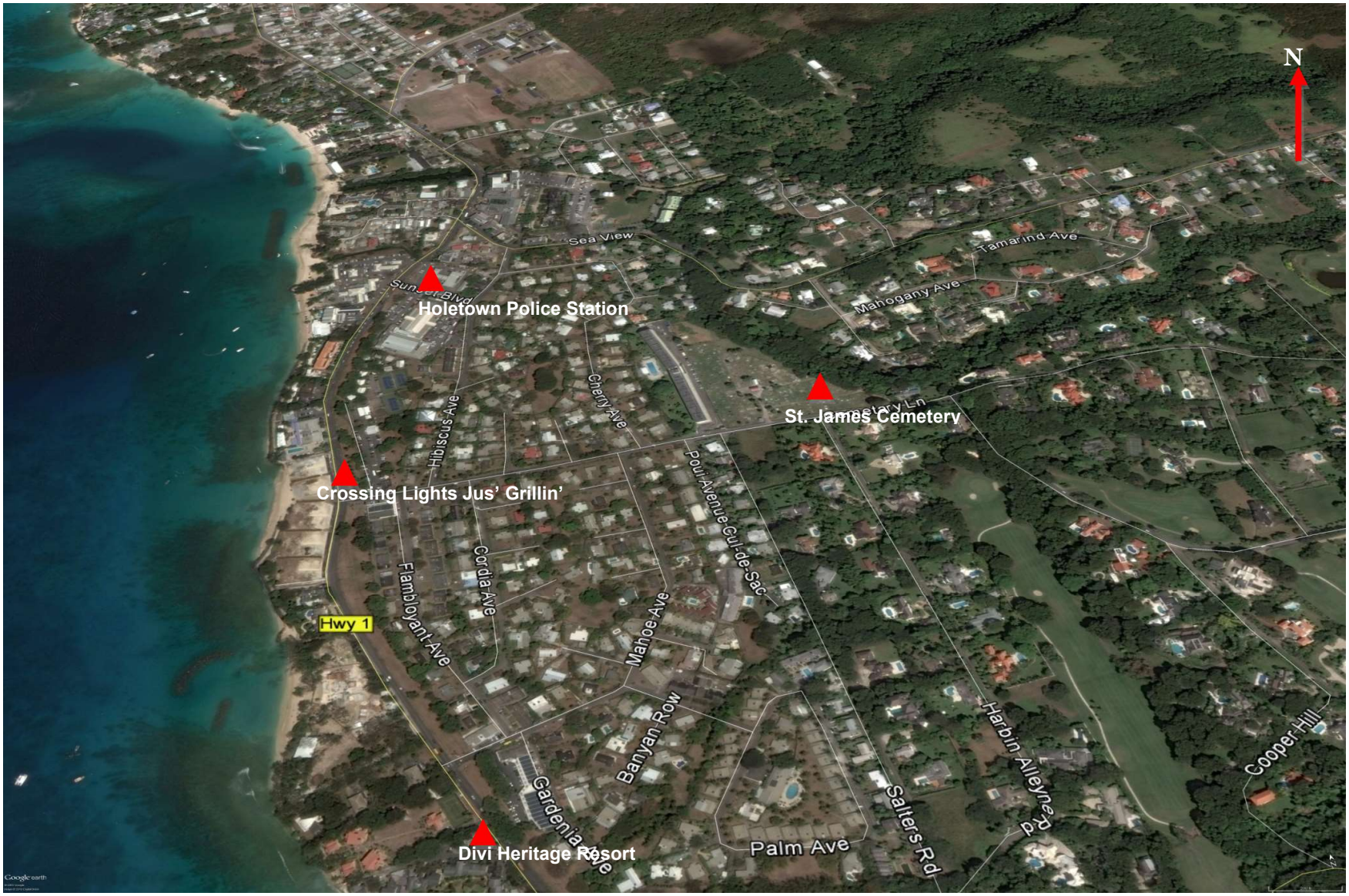

Figure 2: Sample locations in Holetown (Not to scale)

Figure 3: Gun Hill Signal Station in relation to the residential areas to the north and north east. (Not to scale)

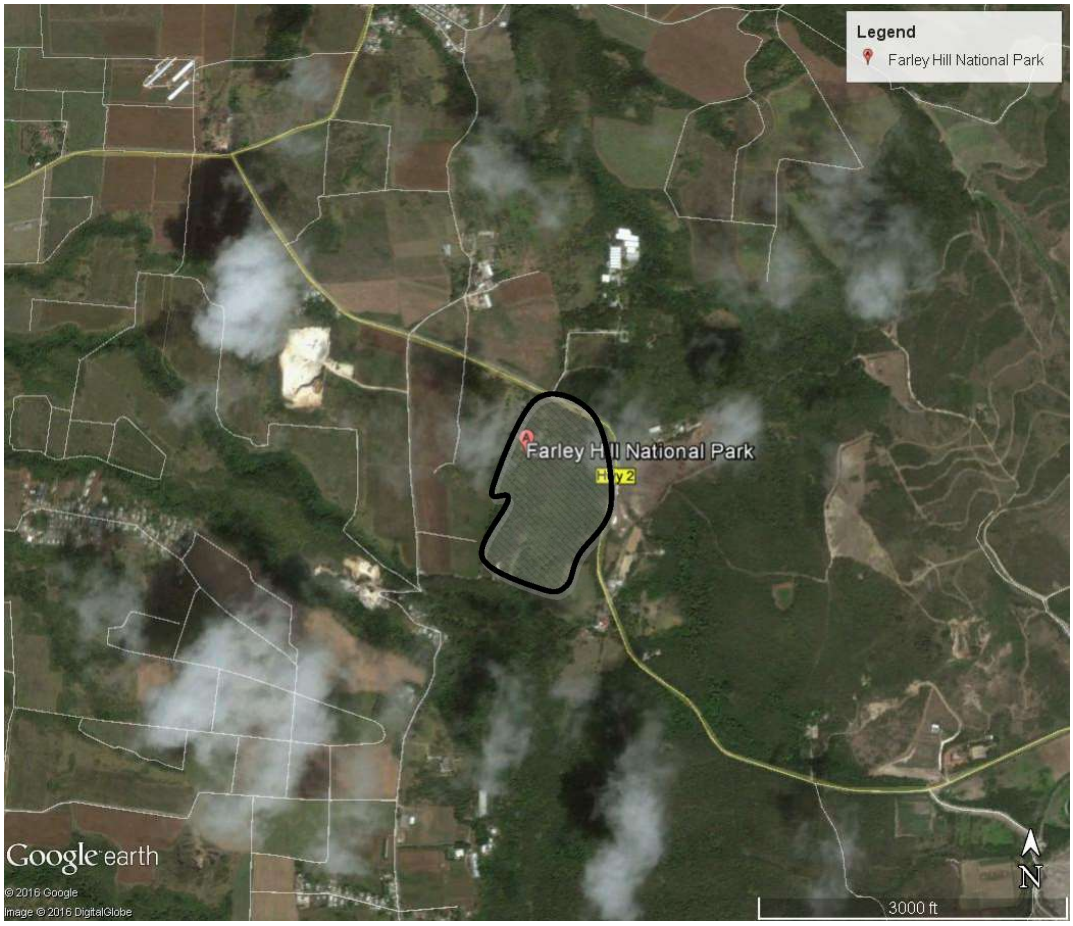

Figure 4: Farley Hill National Park (For illustrative purposes only. Not to Scale)

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Table 2: Site location and selection criteria

SITE LOCATION	LOCATION TYPE	DISTANCE FROM MAJOR ROADWAY	OTHER SELECTION CRITERIA
Ragged Point, St. Philip (RP)	Background	>50 m	Located SE of all locations
Gun Hill Signal Station, St. George (GH)	Rural	20-30m	Residential/Commercial
Farley Hill National Park, St. Peter (FH)	Rural	>50 m	Residential/Commercial
Divi Heritage Resorts, Holetown St. James (DH)	Near road	20 m	Residential/Commercial
Crossing Lights Opposite Jus Grillin Holetown, St. James (CLJG)	Near road	1 m	Commercial
Holetown Police Station, Holetown St. James (HPS)	Urban	1 m	Industrial/Commercial
St. James Cemetery, Holetown, St. James (SJC)	Residential	>50 m	Residential/Commercial

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, which was then analysed by gas chromatography and other proprietary methodologies by the manufacturer EnviroTechnology 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 Total 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[1], as shown in Table 3.
- No duplicates were used at the background site. Therefore, three (3) samplers (Total VOCs, SO_2/NO_2, and O_3) were deployed on a monthly basis at this site.
- Three Field Blanks, one each for Total 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.

[1] 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. - **Operations Manual for Air Quality Monitoring in Ontario Ministry of the Environment Operations Division Technical Support Section**

3.3 Additional Data

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

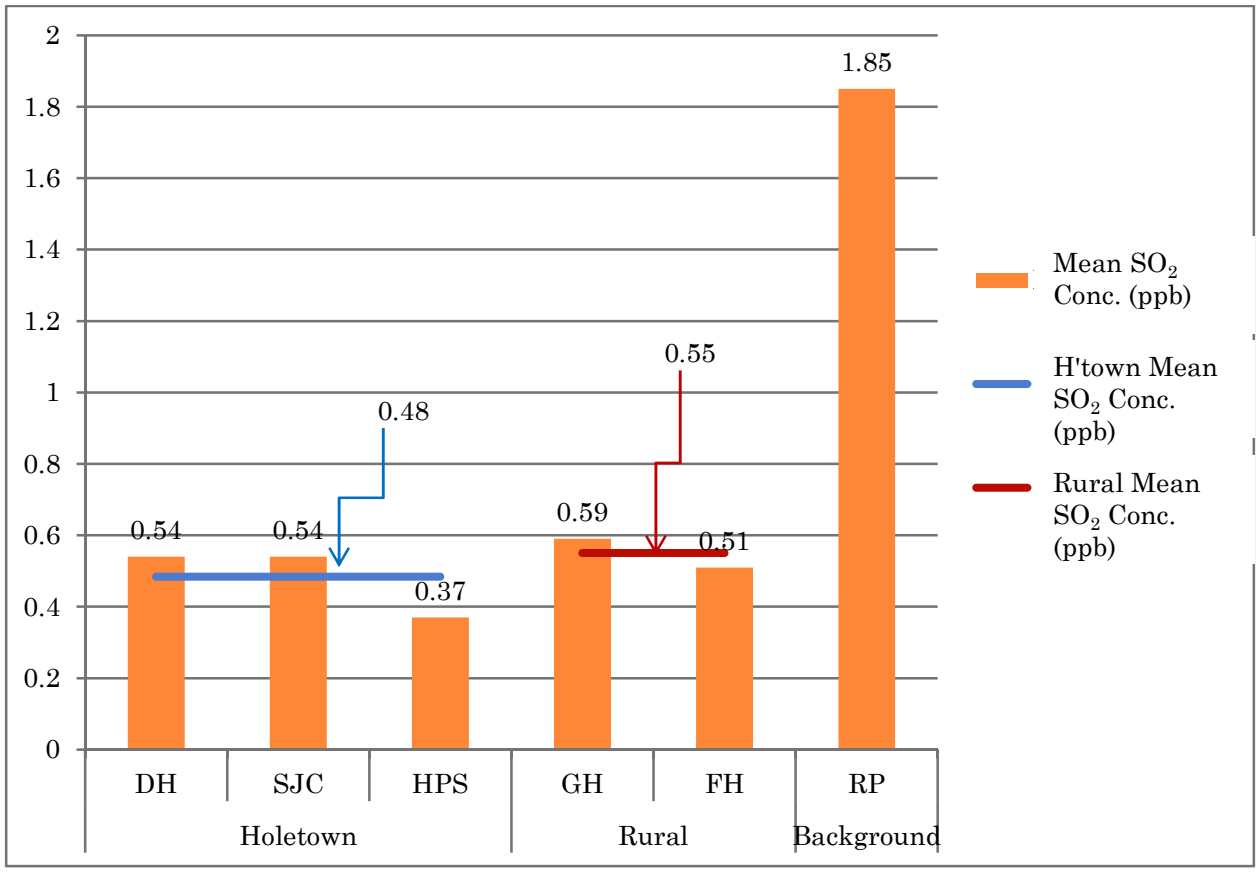
- Ministry of Transport traffic counters were utilized to conduct traffic counts along the main roads closest to the sampling site for a period of fifteen to eighteen (15-18) days, to account for both weekday and weekend traffic. The average daily traffic count was then provided, based upon the data collected.
- Meteorological data was collected utilizing weather data from the Caribbean Institute for Meteorology and Hydrology (CIMH) which was sourced from weather stations in close proximity to the sampling locations.
- Sampling was conducted monthly at each location for twelve months.

Table 3: The diffusion tube allocation from February 2015 to Jan 2016. The value "2" indicates that a duplicate was placed on site.

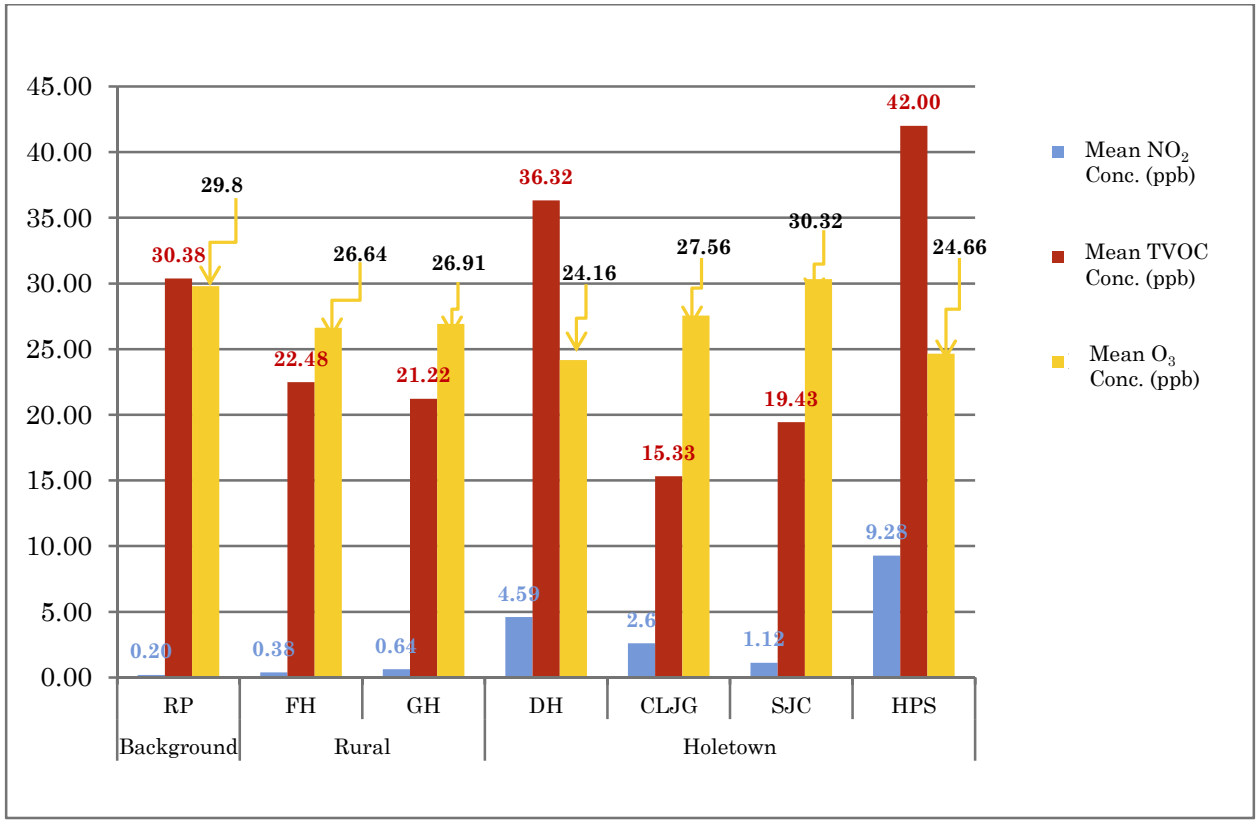
Location	Parameter	Feb 2015	Mar 2015	Apr 2015	May 2015	Jun 2015	Jul 2015	Aug 2015	Sept 2015	Oct 2015	Nov 2015	Dec 2015	Jan 2016	Total
Ragged Point	TVOC	1	1	1	1	1	1	1	1	1	1	1	1	12
	SO_2/NO_2	1	1	1	1	1	1	1	1	1	1	1	1	12
	O_3	1	1	1	1	1	1	1	1	1	1	1	1	12
Ragged Point Total														36
Farley Hill	TVOC	1	2	1	1	2	1	1	2	1	1	2	1	16
	SO_2/NO_2	2	1	1	2	1	1	2	1	1	2	1	1	16
	O_3	1	1	2	1	1	2	1	1	2	1	1	2	16
Farley Hill Total														48
Gun Hill	TVOC	1	1	2	1	1	2	1	1	2	1	1	2	16
	SO_2/NO_2	1	2	1	1	2	1	1	2	1	1	2	1	16
	O_3	2	1	1	2	1	1	2	1	1	2	1	1	16
Gun Hill Total														48
Divi Heritage Resort	TVOC	2	1	1	2	1	1	2	1	1	2	1	1	16
	SO_2/NO_2	1	1	2	1	2	2	1	2	1	1	2	1	17
	O_3	1	2	1	1	1	1	1	1	2	1	1	2	15
Divi Heritage Resort Total														48
Crossing Lights Jus' Grillin'	TVOC	1	2	1	1	2	1	1	2	1	1	2	1	16
	SO_2/NO_2	2	1	1	2	1	1	2	1	1	2	1	1	16
	O_3	1	1	2	1	1	2	1	1	2	1	1	2	16
Crossing Lights Jus' Grillin' Total														48
St. James Cemetery	TVOC	1	1	2	1	1	2	1	1	2	1	1	2	16
	SO_2/NO_2	1	2	1	1	2	1	1	2	1	1	2	1	16
	O_3	2	1	1	2	1	1	2	1	1	2	1	1	16
St. James Cemetery Total														48
Holetown Police Station	TVOC	2	1	1	2	1	1	2	1	1	2	1	1	16
	SO_2/NO_2	1	1	2	1	2	2	1	2	1	1	2	1	17
	O_3	1	2	1	1	1	1	1	1	2	1	1	2	15
Holetown Police Station Total														48

4.0 RESULTS

Graphs 1 and 2 below, show the overall mean concentrations for SO_2, NO_2, O_3 and TVOC in parts per billion for the duration of the study.



Graph 1: Overall mean SO_2 concentration and the area designated means for all locations monitored during the Holetown and Two Rural Areas study



Graph 2 Overall mean NO_2, O3 and TVOC concentrations for all locations monitored during the Holetown and Two Rural Areas study

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

Sampling was conducted at Ragged Point, St. Philip which is the eastern-most part of Barbados, located east south east of Holetown, east of Gun Hill and south east of Farley Hill.

4.1.1 Ragged Point SO_2 Results

As shown in Graph 1, the mean SO_2 concentration observed at Ragged Point was approximately 1.85 ppb. According to Table 4, a maximum concentration of 3.91 ppb was observed. Several samples were observed to have concentrations below the detectable limits for SO_2.

Additionally, several samples collected during the monitoring period were not used in this analysis as they were compromised by high chloride content. This may have been due to the high salt content on the sample substrate which may have been derived from sea spray on the substrate.

Table 4: SO_2 data for the monitoring period for Ragged Point, St. Philip

Month	Feb-15	Mar-15	Apr-15	May-15	Jun-15	Jul-15	Aug-15	Sep-15	Oct-15	Nov-15	Dec-15	Jan-16
SO_2 (ppb)	<0.53	7.78	234.84	<0.35	0.85	7.3	0.71	<0.23	<0.38	1.52	3.9	3.91

Values in red are those samples which were determined to be below detectable limits, in the case of SO2 it is represented as 0.03 µg of S. Therefore the values observed are only estimates and cannot be verified.

Values in blue are those samples which may have been compromised by the presence of a high chloride content.

4.1.2 Ragged Point NO_2, O_3 and TVOC Results

Based upon the data displayed in Graph 2 and Table 5 the following observations were made with respect to NO_2, O_3 and TVOC concentrations at Ragged Point.

- According to Graph 2; the mean NO_2 concentration observed for Ragged Point was approximately 0.20 ppb.
- It must be noted that all other results were below the detectable limit for NO_2.
- With respect to O_3, the mean concentration was 29.8 ppb.
- O_3 concentrations ranged between 19.79 ppb and 41.44 ppb, as shown in Table 5.
- The mean TVOC concentration was approximately 30.38 ppb as shown in Graph 2.
- TVOC levels ranged from a low of 0.45 ppb to a high of 53.56 ppb as shown in Table 5.
- TVOC data in February 2015 was not utilized due to a lab analysis error.

Additionally, the lab indicated that the extremely high result measured in August 2015 may have been because the sample was compromised due to the age of the analyte in the passive sampling tube. Whether the error was a manufacturing defect or the result of a delay in deployment by EPD could not be determined. There were no other replications of this particular error.

Table 5: NO_2, O_3 and TVOC for the period February 2015 to January 2016 for Ragged Point, St. Philip.

Month	Feb-15	Mar-15	Apr-15	May-15	Jun-15	Jul-15	Aug-15	Sep-15	Oct-15	Nov-15	Dec-15	Jan-16
NO_2 (PPB)	<0.13	0.26	<0.17	<0.09	<0.18	<0.13	<0.29	<0.26	<0.16	<0.21	<0.16	<0.15
O_3 (PPB)	35.85	39.71	41.44	36.81	23.45	19.79	22.28	33.46	29.30	31.50	24.88	19.11
TVOC (PPB)	IA	20.00	9.30	13.05	25.70	0.45	137.22	53.56	23.07	10.63	16.66	24.59

Values in red are those samples which were determined to be below detectable limits in the case of NO2 it is represented as 0.05 µg of NO2. Therefore, the values observed are only estimates and cannot be verified.

Values in blue are those samples which may have been compromised by the presence of a high chloride content.

IA - No data collected. An incorrect analysis (IA) was performed Top 5 VOC analysis conducted instead of TVOC analysis

4.2 Farley Hill National Park, St. Peter

This location was a rural location, greater than 50 m from the busiest roadway. Additionally the area was utilized as a recreational area hosting picnics, parties and occasional concerts. Figure 5 shows the sampling location.

Figure 5: Tubes placed on disused flagpole adjacent to the Great House ruins at Farley Hill National Park

4.2.1 Farley Hill SO_2 Results

As shown in Graph 1 the mean SO_2 concentration was approximately 0.51 ppb. There were several instances where concentrations detected were below the verifiable limits. No data was collected in March 2016 due to the unsanctioned removal of the sample tube. The results have been highlighted in Table 6.

Table 6: SO_2 levels detected during the period February 2015 to January 2016 at Farley Hill National Park, St. Peter.

Month	Feb-15	Mar-15	Apr-15	May-15	Jun-15	Jul-15	Aug-15	Sep-15	Oct-15	Nov-15	Dec-15	Jan-16
SO_2 (PPB)	<0.54	ND	<1.43	<0.35	2.6	0.59	<0.29	0.4	<0.38	<0.24	<0.33	<0.53

Values in red are those samples which were determined to be below detectable limits, in the case of SO2 it is represented as 0.03 µg of S. Therefore, the values observed are only estimates and cannot be verified.
ND- No data collected due to missing passive sampling tubes

4.2.2 Farley Hill NO_2, O_3 and TVOC Results

Based upon the data displayed in Graph 2 and Table 7 the following observations were made with respect to NO_2, O_3 and TVOC concentrations at Farley Hill.

- With respect to NO_2, the mean concentration detected as shown in Graph 2 was 0.38 ppb.
- As shown in Table 7, NO_2 concentrations ranged between 0.22 ppb and 0.88 ppb with several months registering concentrations that were below detectable limits.
- No NO_2 data was collected in March 2016 or any O_3 data for April, due to the unauthorised removal of the sample tubes.
- The mean O_3 concentration was approximately 26.64 ppb, as shown in Graph 2. The range of values was between 17.06 ppb and 34.70 ppb as shown in Table 7.
- The mean TVOC concentration as shown in Graph 2 was approximately 22.48 ppb.
- TVOC values ranged between 3.71 ppb and 124.53 ppb.

The maximum TVOC concentration appeared to be anomalous, as it was five (5) times higher than the next closest result. This may be the result of an unknown in-field event or a problem with the sampling tube itself.

Table 7: Data for NO_2, O_3 and TVOC for the period February 2015 to January 2016 at Farley Hill National Park

Month	Feb-15	Mar-15	Apr-15	May-15	Jun-15	Jul-15	Aug-15	Sep-15	Oct-15	Nov-15	Dec-15	Jan-16
NO_2 (PPB)	<0.23	ND	0.88	0.22	0.41	0.50	0.29	<0.23	<0.16	0.31	<0.16	0.27
O_3 (PPB)	34.70	27.35	ND	30.35	31.37	17.23	17.06	27.92	28.97	25.19	30.34	31.34
TVOC (PPB)	IA	6.75	6.75	13.33	18.12	24.66	21.19	124.53	3.71	8.13	11.68	8.45

Values in red are those samples which were determined to be below detectable limits in the case of NO_2 it is represented as 0.05 µg of NO_2. Therefore, the values observed are only estimates and cannot be verified.

IA- No data collected. An incorrect analysis (IA) was performed Top 5 VOC analysis conducted instead of TVOC analysis
ND- No data collected due to missing passive sampling tubes

4.3 Gun Hill Signal Station (GH), St. George

The second rural location, Gun Hill Signal Station was situated in the centre of the island south east of Holetown, south of Farley Hill and North West of Ragged Point, as shown in Figure 1. Passive samplers were placed at various locations around the lookout to reduce the intrusiveness of the samplers in the environment. The sample locations are shown in Figures 6 and 7. The location was characterized as primarily residential as there was no observable industrial or commercial activity in the immediate vicinity.

Figure 6: TENAX TA VOC Sampler at Gun Hill Signal Station

Figure 7: SO_2/NO_2 and Ozone Samplers on light pole at Gun Hill Signal Station

4.3.1 Gun Hill Signal Station SO_2 Results

Table 8 shows that the majority of the SO_2 samples taken at the Gun Hill Signal station were below the detectable limit. The only verifiable concentration was detected in December 2015 at a value of 0.64 ppb.

Table 8: SO_2 concentrations detected at Gun Hill Signal Station during the period February 2015 to January 2016.

MONTH	FEB-15	MAR-15	APR-15	MAY-15	JUN-15	JUL-15	AUG-15	SEP-15	OCT-15	NOV-15	DEC-15	JAN-16
SO_2 (ppb)	<0.54	<0.43	<0.46	<0.35	<0.46	<0.34	<0.36	<0.23	<0.38	<0.24	0.64	<0.53

Values in red are those samples which were determined to be below detectable limits in the case of SO_2 it is represented as 0.03 µg of S. Therefore the values observed are only estimates and cannot be verified.

4.3.2 Gun Hill Signal Station NO_2, O_3 and TVOC Results

Based upon the data displayed in Graph 2 and Table 9 the following observations were made with respect to NO_2, O_3 and TVOC concentrations at Gun Hill.

- NO_2 levels ranged between 0.37 ppb and 0.89 ppb; the mean concentration detected was 0.64 ppb.
- O_3 levels ranged between 10.24 ppb and 37.35 ppb.
- Mean O_3 levels were approximately 26.91 ppb.
- No data for O_3 was collected in December due to a missing passive sampler tube.
- In the case of TVOC concentrations; the mean concentration was approximately 21.22 ppb with values ranging from 5.24 ppb to 81.62 ppb.

Table 9: Range of data collected at the Gun Hill Signal Station for NO_2, O_3 and TVOC for the period February 2015-January 2016.

MONTH	FEB-15	MAR-15	APR-15	MAY-15	JUN-15	JUL-15	AUG-15	SEP-15	OCT-15	NOV-15	DEC-15	JAN-16
NO_2 (PPB)	0.37	0.65	0.70	0.38	0.48	0.63	0.84	0.89	0.86	0.70	0.87	0.37
O_3 (PPB)	37.35	36.24	28.63	32.88	25.10	25.75	10.24	14.86	22.48	29.22	ND	33.25
TVOC (PPB)	IA	9.69	7.59	25.83	5.93	18.26	81.62	44.77	10.48	11.95	12.04	5.24

IA- No data collected. An incorrect analysis was performed Top 5 VOC analysis conducted instead of TVOC analysis
ND- No data collected due to missing passive sampling tubes

4.4 Divi Heritage Resort (DH), Holetown, St. James

The Divi Heritage Resort was the southernmost site located in the Holetown area and it was characterised as a near road site. Samplers were placed approximately 20 metres from the roadside in this residential commercial area; this is shown in Figure 8.

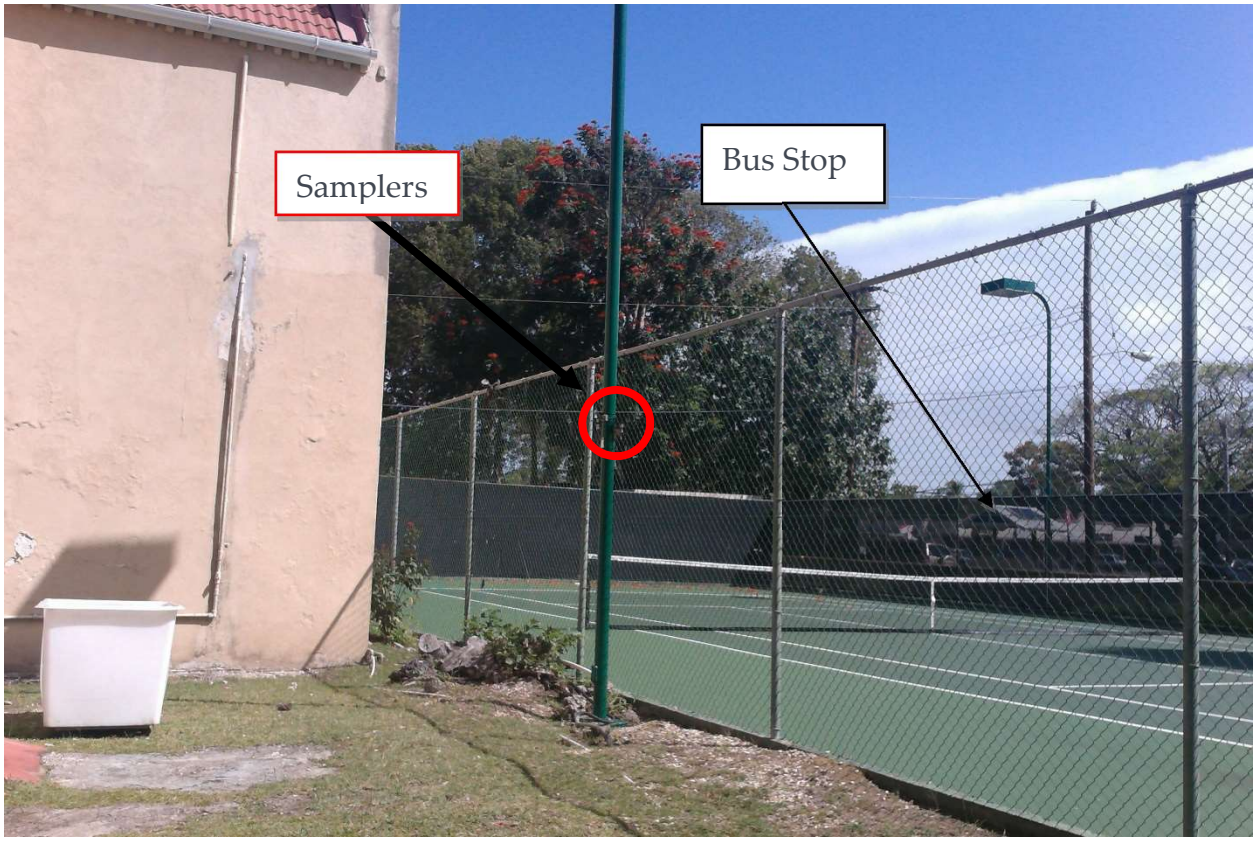


Figure 8: Passive samplers placed at the Divi Heritage Resort located approximately 20 m from Highway 1

4.4.1 Divi Heritage Resort SO_2 Results

As shown in Table 10, all of the SO_2 samples taken at the Divi Heritage Resort were below the detectable limit.

Table 10: SO_2 concentrations detected at the Divi Heritage Resort in Holetown at a near road site during the period February 2015 to January 2016.

Month	Feb-15	Mar-15	Apr-15	May-15	Jun-15	Jul-15	Aug-15	Sep-15	Oct-15	Nov-15	Dec-15	Jan-16
SO_2 (ppb)	<0.54	<0.43	<0.46	<0.35	<0.46	<0.34	<0.36	<0.23	<0.38	<0.33	<0.33	<0.53

Values in red are those samples which were determined to be below detectable limits in the case of SO_2 it is represented as 0.03 µg of S. Therefore the values observed are only estimates and cannot be verified.

4.4.2 Divi Heritage Resort NO_2, O_3 and TVOC Results

Based upon the results presented in Graph 2 and in Table 11 below, the following observations were made with respect to NO_2, O_3 and TVOC concentrations at the Divi Heritage resort.

- NO_2 levels ranged between 3.31 ppb and 5.98 ppb; with a mean concentration of 4.59 ppb shown in Graph 2.
- O_3 levels ranged between 13.70 ppb and 33.71 ppb, the mean concentration detected was 24.16 ppb.
- Graph 2 showed a mean concentration of 36.32 ppb.
- According to Table 11, TVOC values ranged from a low of 2.32 ppb to a high of 93.89 ppb.

Table 11: NO_2, O_3 and TVOC concentrations recorded at the Divi Heritage Resort near road site during the period February 2015 to January 2016

Month	Feb-15	Mar-15	Apr-15	May-15	Jun-15	Jul-15	Aug-15	Sep-15	Oct-15	Nov-15	Dec-15	Jan-16
NO_2 (PPB)	4.25	4.78	4.86	3.52	3.31	3.34	3.79	4.63	5.39	5.39	5.83	5.98
O_3 (PPB)	28.46	26.04	33.71	25.33	25.80	22.62	13.70	18.42	19.18	25.61	26.22	24.79
TVOC (PPB)	IA	2.32	8.26	17.40	78.27	2.18	10.94	93.89	66.13	54.90	25.65	39.60

IA- No data collected. An incorrect analysis was performed Top 5 VOC analysis conducted instead of TVOC analysis

4.5 Crossing Lights opposite Jus' Grillin (CLJG), Holetown, St. James

Passive samplers were placed at the pedestrian crossing opposite the Jus' Grillin restaurant located in Holetown, St. James. The site was classified as a near road site with the samplers approximately 1 m from Highway 1. Figure 9 below shows the location of the samplers in relation to Highway 1.

Figure 9: Passive samplers located at pedestrian crossing approximately 1m from Highway 1 close to Jus' Grillin' in Holetown St. James for the period February 2015 to January 2016

4.5.1 Crossing Lights Jus' Grillin' SO_2 Results

The analysis showed that all of the SO_2 samples taken at the Crossing Lights Jus' Grillin' were below the detectable limit; the results can be seen in Table 12.

Table 12: SO_2 concentrations detected at the Crossing Lights Jus' Grillin' in Holetown at a near road site during the period February 2015 to January 2016

Month	Feb-15	Mar-15	Apr-15	May-15	Jun-15	Jul-15	Aug-15	Sep-15	Oct-15	Nov-15	Dec-15	Jan-16
SO_2 (ppb)	<0.54	<0.43	<0.46	<0.35	<0.46	<0.34	<0.36	<0.23	<0.38	<0.33	<0.33	<0.53

Values in red are those samples which were determined to be below detectable limits in the case of SO_2 it is represented as 0.03 µg of S. Therefore the values observed are only estimates and cannot be verified.

4.5.2 Crossing Lights Jus' Grillin' NO_2, O_3 and TVOC Results

Based upon the observations in Graph 2 and in Table 13 below the following observations were made with respect to NO_2, O_3 and TVOC concentrations at Crossing Lights Jus' Grillin'.

- NO_2 levels ranged between 1.54 ppb and 3.93 ppb; the mean NO_2 concentration was approximately 2.60 ppb.
- In the case of O_3; the mean concentration was 27.56 as shown in Graph 2, the values ranged between 14.76 ppb and 39.71 ppb.
- In the case of TVOC concentrations based upon data from Graph 2 and Table 13; the mean concentration was approximately 15.33 ppb with a range of concentrations between 2.92 ppb and 33.21.

Table 13: NO_2, O_3 and TVOC concentrations recorded at the Crossing Lights Jus' Grillin' < 1 m from Highway 1 during the period February 2015 to January 2016.

Month	Feb-15	Mar-15	Apr-15	May-15	Jun-15	Jul-15	Aug-15	Sep-15	Oct-15	Nov-15	Dec-15	Jan-16
NO_2 (PPB)	2.27	2.34	2.56	1.97	1.76	1.54	2.27	3.93	3.13	2.44	3.19	3.75
O_3 (PPB)	38.40	39.71	27.86	21.18	28.37	20.20	21.02	14.76	25.07	32.29	33.24	28.66
TVOC (PPB)	IA	7.89	15.86	6.08	33.21	2.92	23.54	10.51	27.38	14.14	13.69	13.39

IA- No data collected. An incorrect analysis (IA) was performed Top 5 VOC analysis conducted instead of TVOC analysis

4.6 St. James Cemetery (SJC), Holetown, St. James

Passive samplers were placed in the St. James Cemetery, located > 50 m away from Highway 1 and Molyneux Road in a residential area. Figure 10 shows the placement of the samplers within the cemetery.

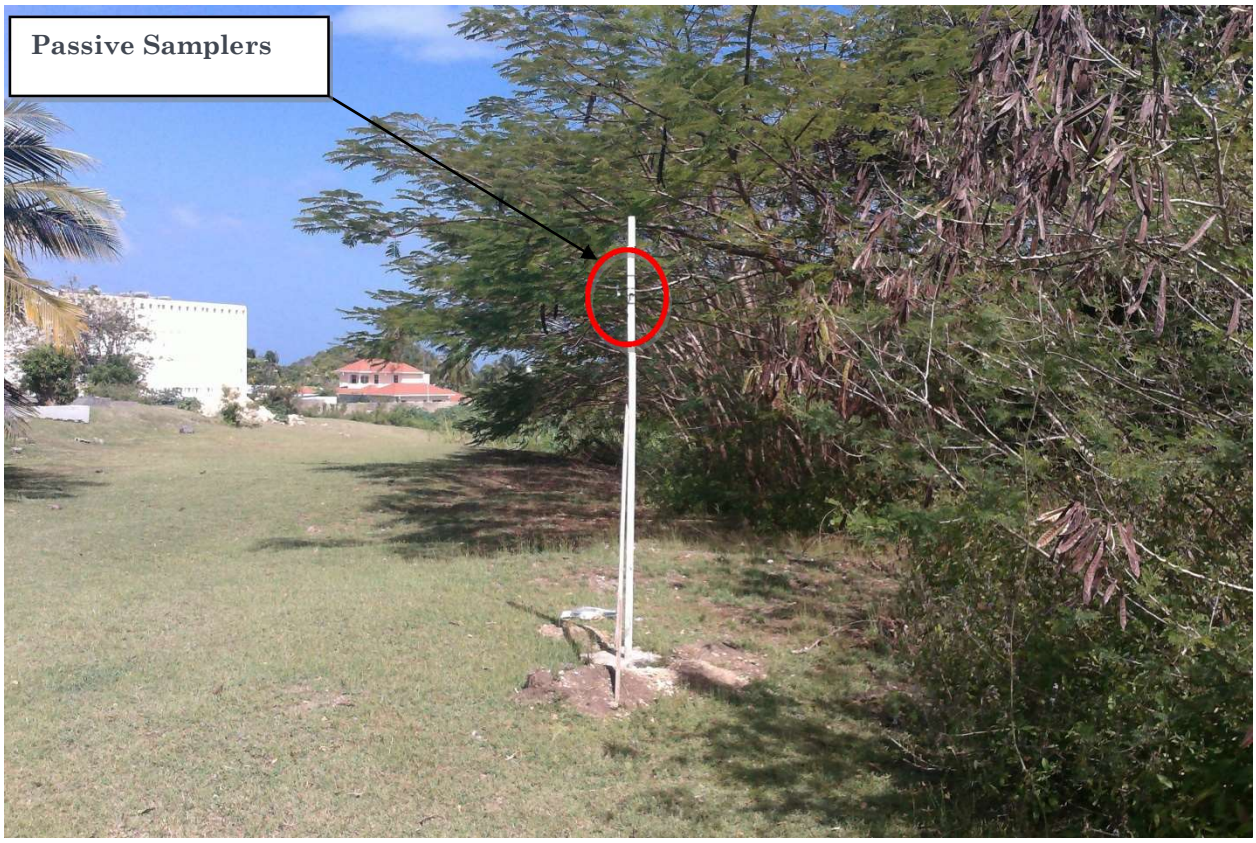


Figure 10: Passive samplers placed on pole within the St. James Cemetery greater than 50 m away from Highway 1 and Molyneux Road, Holetown St. James for the period February 2015 to January 2016

4.6.1 St. James Cemetery SO_2 Results

Graph 1 showed a mean SO2 concentration 0.54 ppb. As shown in Table 14, half the samples collected were below the detectable limit and no data was collected in January 2016 due to missing tubes.

Table 14: SO_2 concentrations detected at the St. James Cemetery in Holetown at a near road site during the period February 2015 to January 2016

MONTH	FEB-15	MAR-15	APR-15	MAY-15	JUN-15	JUL-15	AUG-15	SEP-15	OCT-15	NOV-15	DEC-15	JAN-16
SO_2 (ppb)	<0.54	<0.43	<0.46	<0.35	<0.46	<0.34	0.54	0.23	0.38	0.38	0.33	ND
Values in red are those samples which were determined to be below detectable limits in the case of SO_2 it is represented as 0.03 µg of S. Therefore the values observed are only estimates and cannot be verified.												
ND - No data collected due to missing passive sampling tubes												

4.6.2 St. James Cemetery NO_2, O_3 and TVOC Results

According to Graph 2 and the data presented in Table 15 below; the following observations were made with respect to NO_2, O_3 and TVOC concentrations at St. James Cemetery.

- NO_2 levels ranged between 0.54 ppb and 1.41 ppb; with a mean NO2 concentration of 1.12 ppb. No data was collected in January 2016 due to missing tubes.
- O_3 levels ranged between a low of 17.92 ppb and a high of 41.45 ppb, additionally the mean O_3 concentration was recorded as 30.32 ppb. No data was collected in January 2016 due to missing tubes.
- In the case of TVOC concentrations; values ranged between 2.92 ppb and 33.21 ppb. The mean TVOC concentration as highlighted in Graph 2 was approximately 19.43 ppb.

Table 15: NO_2, O_3 and TVOC concentrations recorded at the St. James Cemetery during the period February 2015 to January 2016

MONTH	FEB-15	MAR-15	APR-15	MAY-15	JUN-15	JUL-15	AUG-15	SEP-15	OCT-15	NOV-15	DEC-15	JAN-16
NO_2 (PPB)	0.89	1.21	1.41	1.20	1.05	0.98	0.54	1.32	1.12	1.46	1.15	ND
O_3 (PPB)	41.45	37.15	39.98	32.42	26.60	28.66	23.80	17.92	24.00	29.20	31.04	ND
TVOC (PPB)	IA	15.00	18.14	49.17	32.42	16.37	17.02	12.91	19.39	7.48	6.44	13.75

IA- No data collected. An incorrect analysis (IA) was performed Top 5 VOC analysis conducted instead of TVOC analysis. ND- No Data collected

4.7 Holetown Police Station (HPS), Holetown, St. James

Passive samplers were placed in the car park of the Holetown Police Station St. James, approximately two (2) m from Highway 1. For the purpose of the exercise, this site was classified as a commercial/ industrial location due to the presence of a gas station and several restaurants and retail businesses in close proximity. Figure 11 shows the placement of the samplers in the parking lot of the police station complex.

Figure 5: Passive samplers placed on pole within the car park adjacent to the Holetown Police Station, Holetown St. James. The location was classified as commercial/industrial for the period February 2015 to January 2016.

4.7.1 Holetown Police Station SO_2 Results

Graph 1 showed that the mean SO_2 concentration detected at the Holetown Police Station was approximately 0.37 ppb. As shown in Table 16, the majority of the samples collected were observed to have concentrations of SO_2 below the detectable limits.

Table 16: Shows the SO_2 concentrations detected at the Holetown Police Station in Holetown at a near road site during the period February 2015 to January 2016

Month	Feb-15	Mar-15	Apr-15	May-15	Jun-15	Jul-15	Aug-15	Sep-15	Oct-15	Nov-15	Dec-15	Jan-16
SO_2 (ppb)	<0.54	<0.43	<0.46	<0.35	<0.46	<0.34	<0.36	0.24	<0.38	<0.24	0.33	<0.53

Values in red are those samples which were determined to be below detectable limits in the case of SO_2 it is represented as 0.03 µg of S. Therefore the values observed are only estimates and cannot be verified.

4.7.2 Holetown Police Station NO_2, O_3 and TVOC Results

Based upon the results in Table 17 below along with information presented in Graph 2, the following observations were made with respect to NO_2, O_3 and TVOC concentrations at the Holetown Police Station.

- NO_2 levels ranged between 6.52 ppb and 12.42 ppb; the mean concentration was approximately 9.23 ppb.
- O_3 levels ranged from 15.79ppb to 34.90 ppb, with a mean concentration of 24.66 ppb.
- In the case of TVOC concentrations; the mean concentration was approximately 42.00 ppb as shown in Graph 2, with values ranging from 18.76 ppb to 57.76 as shown in Table 17.

Table 17: NO_2, O_3 and TVOC concentrations recorded at the Holetown Police Station during the period February 2015 to January 2016

MONTH	FEB-15	MAR-15	APR-15	MAY-15	JUN-15	JUL-15	AUG-15	SEP-15	OCT-15	NOV-15	DEC-15	JAN-16
NO_2 (PPB)	10.92	10.09	10.10	7.82	7.49	6.56	6.52	7.80	9.83	10.42	11.36	12.42
O_3 (PPB)	31.11	34.90	22.75	25.32	26.26	19.82	15.79	20.98	22.35	22.26	27.51	26.93
TVOC (PPB)	IA	30.00	27.95	50.39	18.76	28.05	53.98	57.76	51.45	46.79	52.00	44.89

IA- No data collected. An incorrect analysis (IA) was performed Top 5 VOC analysis conducted instead of TVOC analysis

4.8 Weather Data

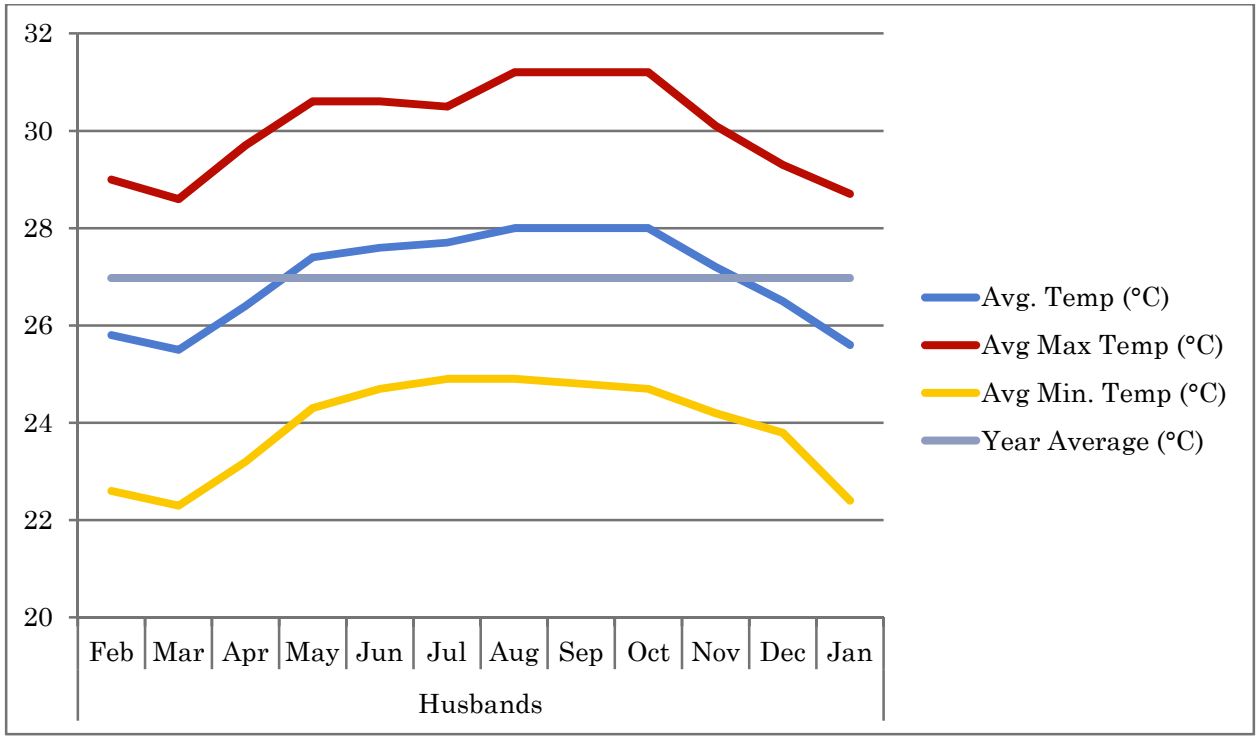
Weather data was collected from various weather stations operated by the Caribbean Institute for Meteorology and Hydrology (CIMH), Husbands, St. James. However, only temperature, rainfall and relative humidity data was available for Husbands, St. James which was close to the Holetown sites. Rainfall data was available for the other locations as shown below in Table 18. Table 18 also shows the location where weather data was collected and the closest location where passive sampling was conducted.

Table 18: Show data collected from the various weather stations operated by CIMH and the closest passive sampling point.

CIMH LOCATION	DATA COLLECTED	CLOSEST PASSIVE SAMPLING LOCATION
Husbands, St. James	Temperature, Relative Humidity and Rainfall	Holetown, St. James
Orange Hill, St. James	Rainfall	Farley Hill, St. Peter
Walkers Terrace, St. George	Rainfall	Gun Hill, St. George
Union, St. Philip	Rainfall	Ragged Point, St. Philip

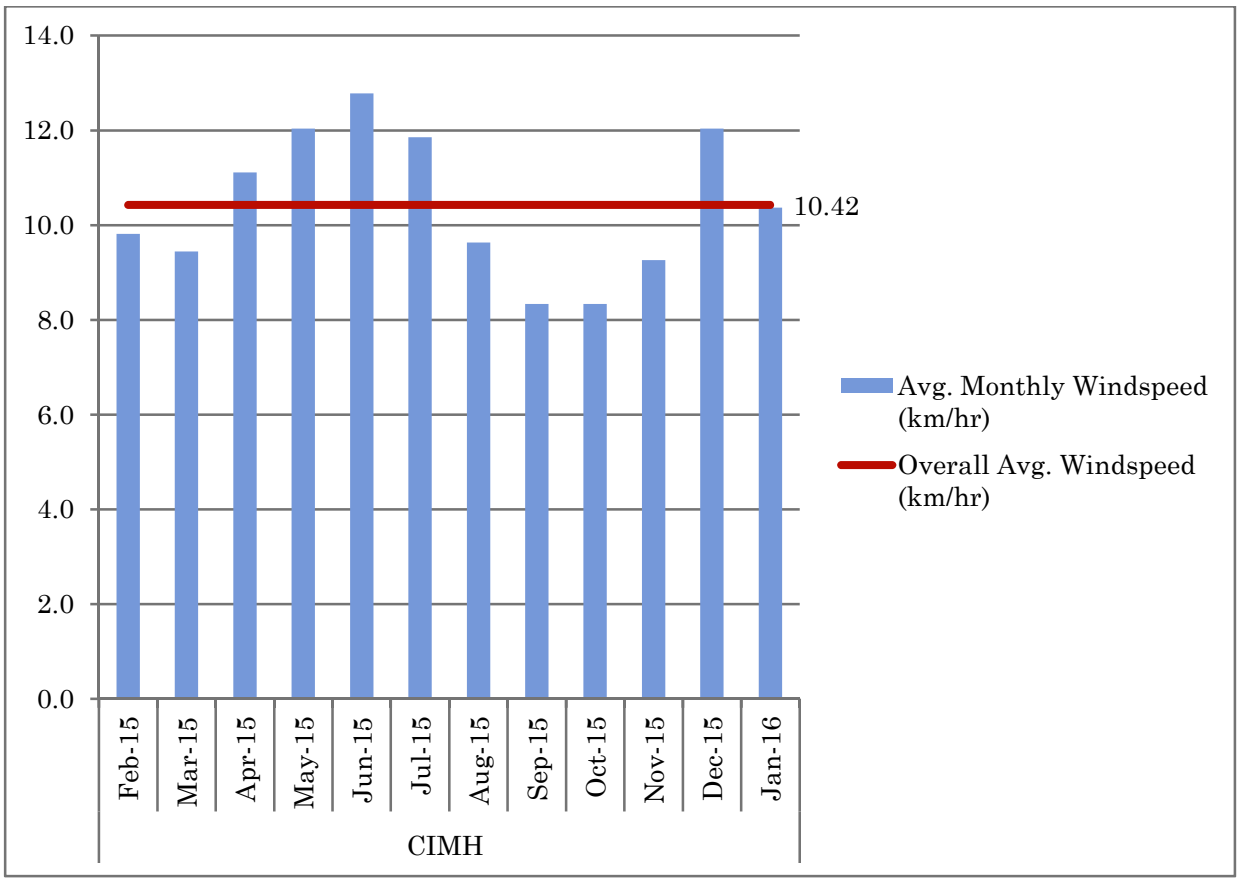
Based on the data collected, the CIMH weather station in Husbands, St. James appears to provide the most complete dataset and would be used for the Holetown passive monitoring sites.

Graph 3 below displays the average highest and average lowest temperatures, in addition to the average temperatures recorded during the monitoring period. Recent studies have demonstrated a link between temperature and ozone formation where temperatures above 26.7°C have been shown to increase ozone generation reactions. Based on the graph, temperatures peaked between May 2015 and October 2015, it then declined steadily in November 2015. The average yearly temperature was 27°C; slightly above the 26.7°C required to increase the level of ozone production.



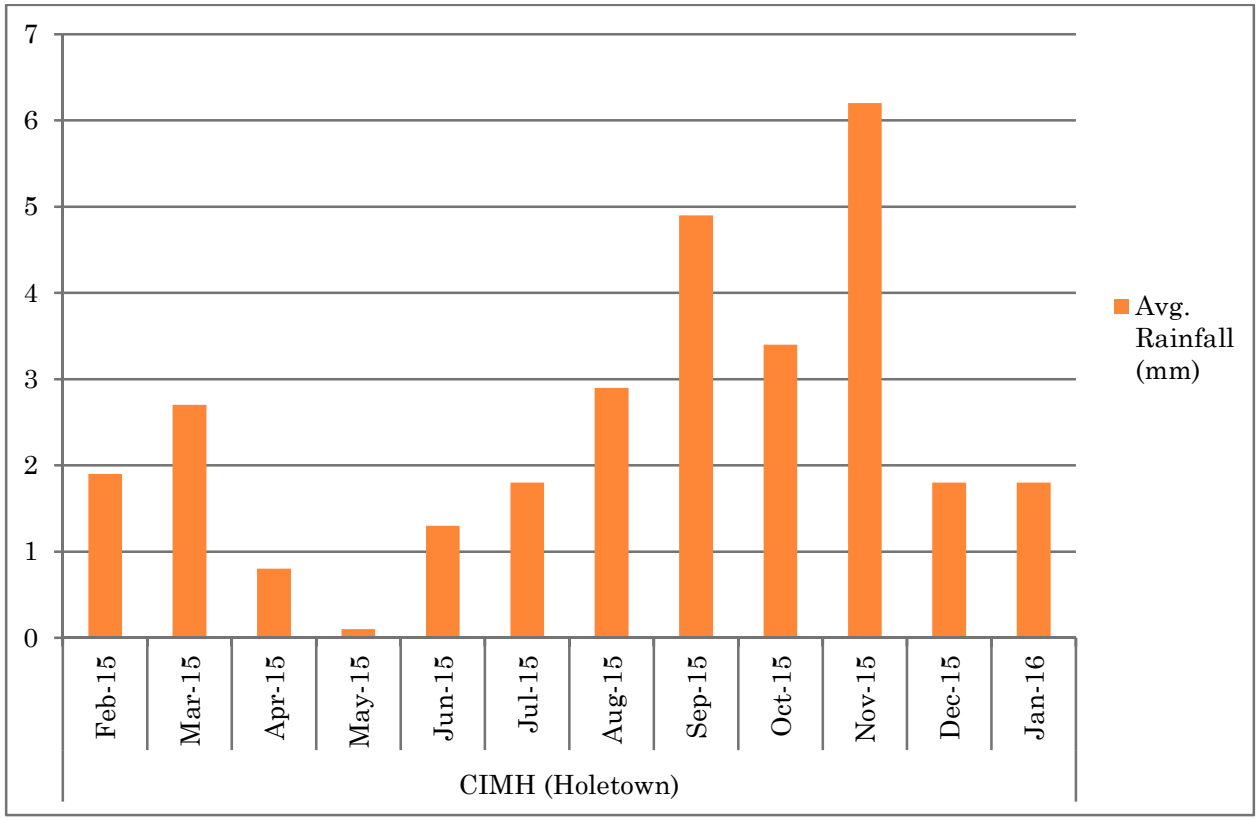
Graph 3: Average Monthly Maximum, Average Minimum and Average Temperature readings and Year Average Temperature recorded during the period February 2015 to January 2016 at CIMH, Husbands, St. James

Graph 4 represents the average monthly and overall wind speed recorded during the sampling period. As shown in the graph, the highest wind speed was recorded in June 2015 (12.8 km/hr) and the overall mean wind speed was 10.42 km/hr.



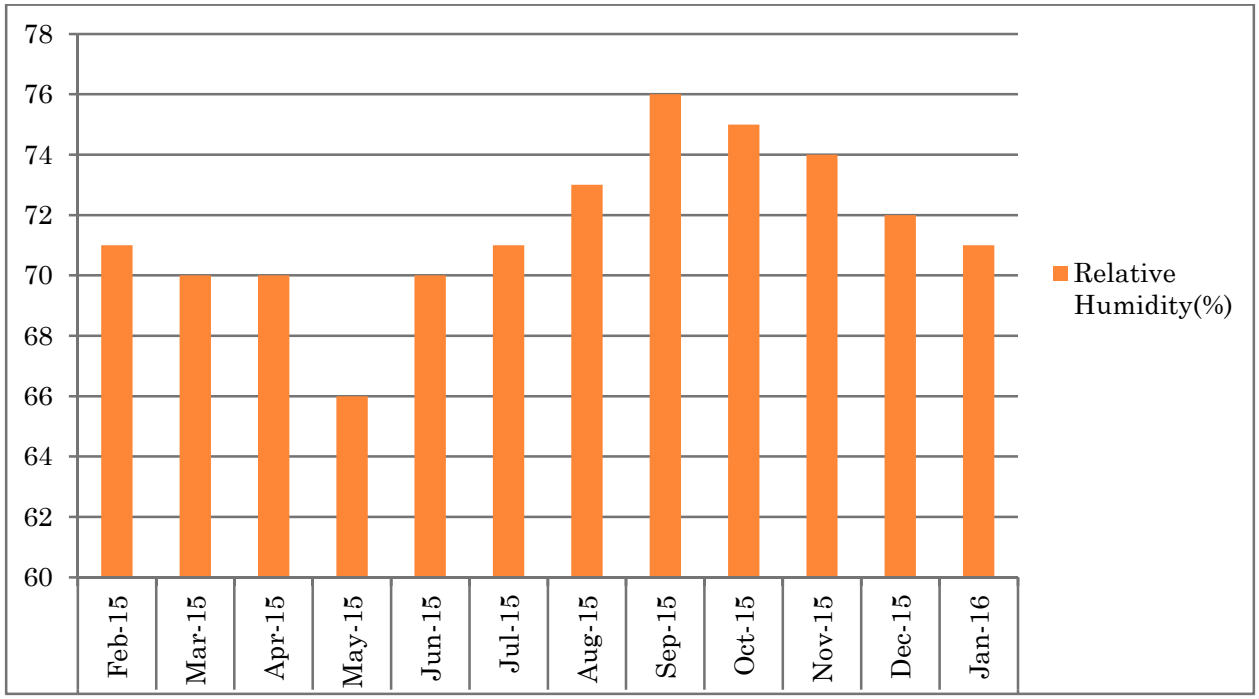
Graph 4: Average monthly wind-speed (km/h) for the period 2015-2016 sampled.

Graph 5 shows the average rainfall per month during the study period. Based on the pattern observed the majority of rainfall occurred during the period of July to January, possibly extending into March the following year.



Graph 5: Rainfall data at CIMH Holetown location and their corresponding passive sampling locations for the period February 2015 to January 2016.

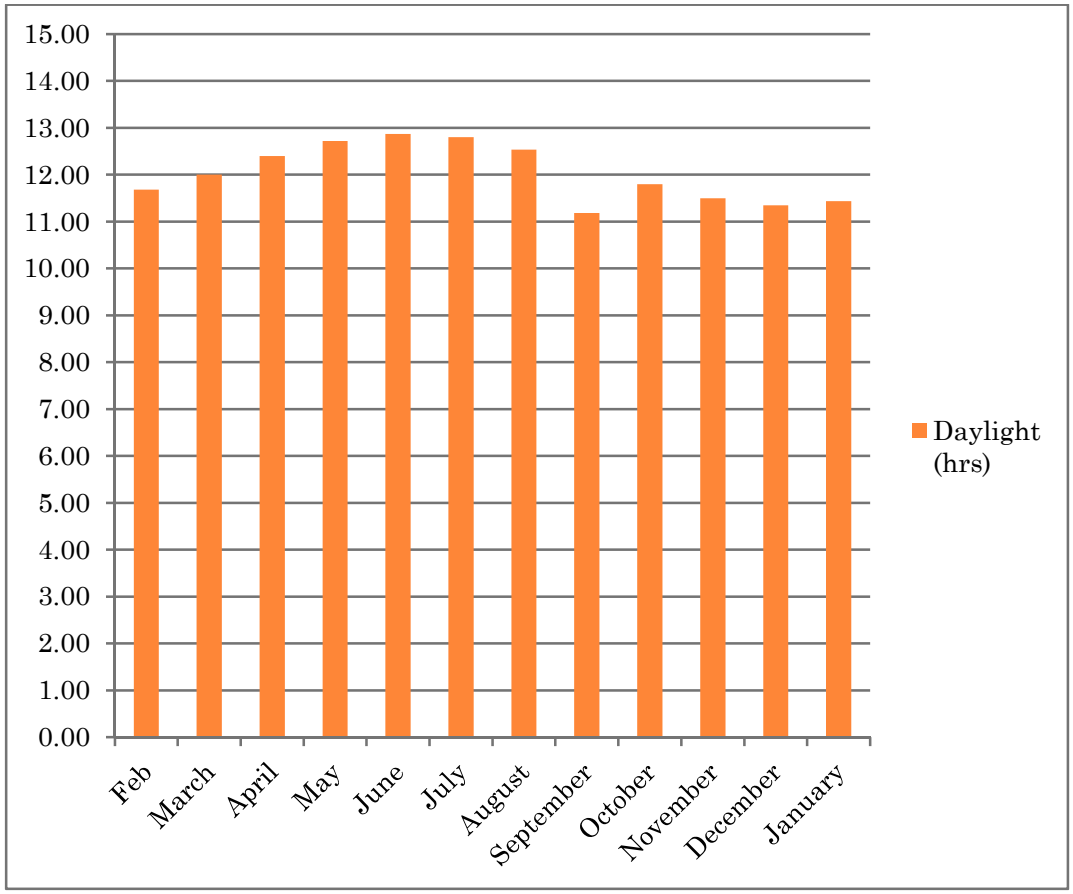
Based on Graph 6, the average relative humidity peaked during the period of July 2015 to January 2016. The average relative humidity ranged from 66% to 76 % during the monitoring period.



Graph 6: Average Relative Humidity recorded during the monitoring period at CIMH.

4.9 Daylight Hours

In addition to temperature, sunlight acts as a catalyst for the generation of ozone along with the interactions of NO_2 and VOCs. Graph 7 below shows the average monthly daylight recorded for Barbados[2] during the study period. The lowest daylight average was recorded in September 2015, while the highest average was recorded in June 2015. In general the average daylight experienced did not dip below 11 hours per day in the study period.

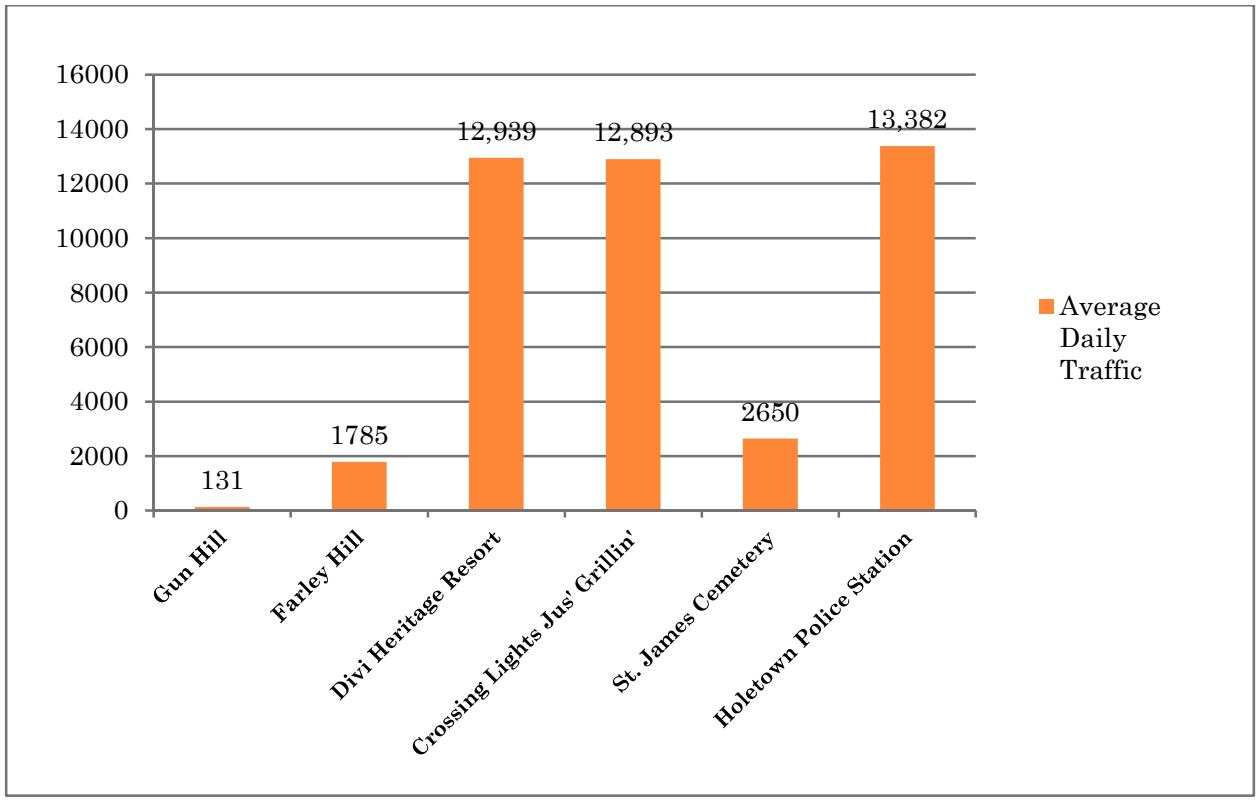


Graph 7: Daylight averages for Barbados

[2] http://www.barbados.climatemps.com/

4.10 Ministry of Transport and Works Traffic Data

Based on traffic data provided through the use of traffic counters on the nearest busy road (in both directions) to the sampling points; the calculated average daily traffic is shown in Graph 8.



Graph 8: Average daily traffic counts (in both directions combined) utilizing the nearest roadway adjacent to the various sampling points.

The data represented in Graph 8, shows that the main road associated with the Gun Hill Signal Station was the least travelled road observed in the study. The Holetown Police Station (HPS) was the busiest intersection with approximately 13,382 vehicles passing daily. Generally, the Holetown area showed heavier traffic patterns than both rural areas as expected.

5.0 DISCUSSION

The adopted WHO guidelines for primary and secondary pollutants were developed using real time continuous 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 can facilitate a useful characterization of existing levels and changes based on activities within Holetown and the two rural areas.

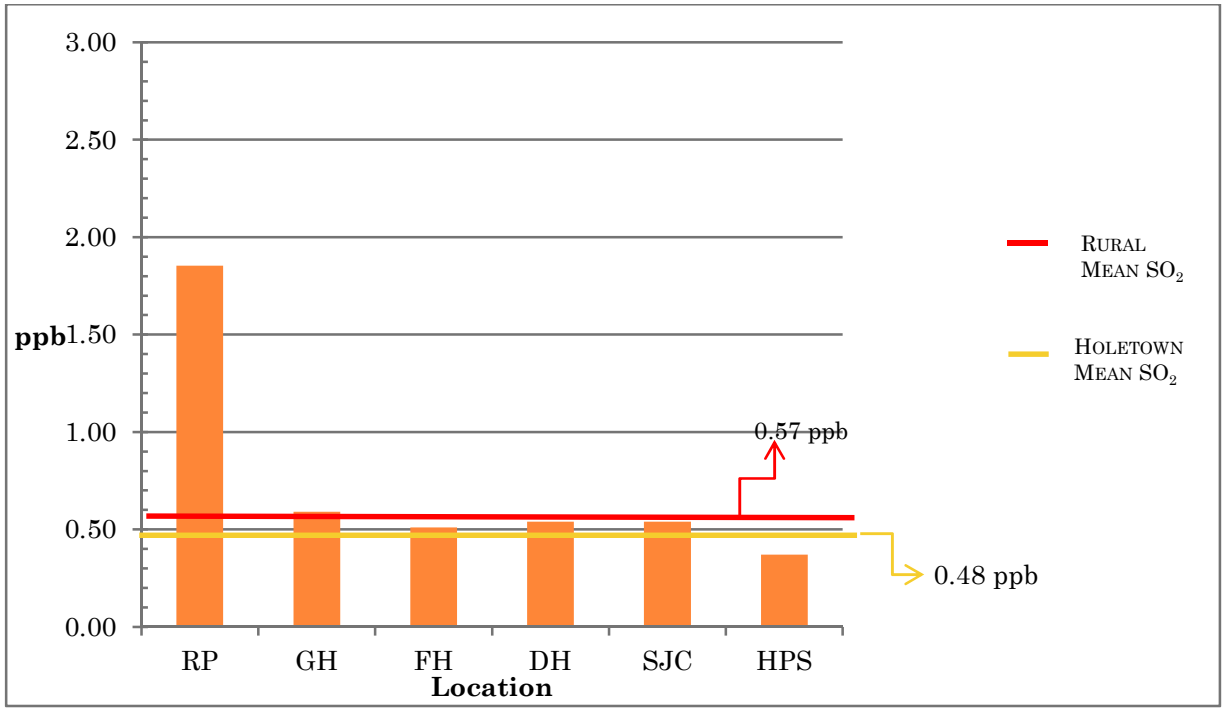
5.1 Sulphur Oxides (SO_2) Data

5.1.1 Highs, Lows and Averages

The highest recorded SO_2 level 3.91 ppb, was detected at Ragged Point (RP) in January 2016 as seen in Table 4 and the highest average SO_2 concentration was also recorded at Ragged Point as seen in Graph 1. This may be due to the decomposition of a large influx of Sargassum seaweed offshore and on the rocks below the sampling site resulting in hydrogen sulphide (H_2S) emissions. The lowest verifiable SO_2 level detected was recorded in September 2015 at Holetown Police Station.

The levels of SO_2 for all locations was noted as being below the detectable limits for the period March 2015 - August 2015 and again in October and November 2015 and in January 2016. The highest rainfall levels were recorded in March 2015 but decreased subsequently, however wind speeds were higher during this period as well, which may have an impact upon SO_2 concentrations.

Therefore, the low SO_2 levels may be due to a combination of anthropogenic and natural factors, which cannot be quantified within the limits of this study.



Graph 9: The mean SO_2 concentrations for all locations and the combined rural and the combined Holetown mean SO_2 concentration.

5.1.2 Impacts on SO_2 Levels

SO_2 levels in Holetown and the two rural areas may be affected by several factors such as the introduction of low sulphur diesel to consumers in 2013, the different classes of vehicles (buses, trucks, cars and motorcycles), different types and volume of activities such as kitchens and industrial processes and the noticeably different traffic volumes for the greater Holetown area and the two rural areas as shown in Graph 8. It must be noted, that despite having one of the lower traffic counts, Gun Hill had the 2nd highest SO_2 mean level exceeding that of the Holetown sites as shown in Graph 9. This does not discount the impacts of vehicle emissions, as SO_x can be generated by other activities and from the road network and subsequently transported by wind action.

Farley Hill recorded one of the lowest estimated traffic counts but with the exception of Ragged Point, showed similar SO_2 concentrations to the other sample sites which had higher daily traffic counts. This may be due to other factors such as

localized weather variations as well as anthropogenic factors such as public events occurring at the particular location and the type of vehicles present in the area. Vehicles such as buses along the route and other heavy vehicles may produce more SO_2 than smaller vehicles.

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 (sulphates) on vegetation, soil and buildings. 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 by 23 km at its widest points and the average wind-speed for the period was between 20 and 34 km/h (Graph 4) 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 conducted by the World Meteorological Organization Global Atmosphere Watch, (World Meteorological Organization Global Atmosphere Watch, 1997) 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 (2.00 ppb), Oistins (0.54 ppb), Speightstown (0.44 ppb), Holetown (0.57 ppb) and the two rural areas (0.48 ppb)

Based on documentation by the (WHO, 2000), 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.

5.2 NO_2, TVOCs and Ozone Data

Because of their interactions, the data for nitrogen dioxide, ozone and total volatile organic compounds will be discussed together.

5.2.1 Observed Relationships between NO_2, TVOCs and Ozone at Sample Locations

5.2.1.1 Holetown Police Station

As shown in Graph 2, the highest mean NO_2 and TVOC levels were observed at Holetown Police Station. This location was adjacent to the Rubis Service Station, two malls (Limegrove Lifestyle Centre and West Coast Mall) in addition to the civic complex. The resultant VOCs and NOx levels may be as a result of increased vehicular traffic at the intersection and emissions from the various activities.

5.2.1.2 Divi Heritage Resort

The next highest average TVOC and NO_x concentrations were detected at the Divi Heritage Resort sampling site. Although the sampling site was not specifically a roadside sample point, a heavily used bus stop was located directly opposite the

sampling location resulting in emissions from large diesel buses as they stopped to pick up and let off passengers.

The frequent stopping and idling of buses may have contributed to increased exhaust which may result in increased VOC levels in close proximity to the passive sampler on a daily basis. Additionally, the lower levels corresponded with school holidays with the exception the Christmas period. Anecdotal observations indicate that commercial and tourist activity increases in Holetown during the Christmas period, as compared to other times of the year.

Additionally, there may be other activities at Divi Heritage Resort such as the use of chemical compounds for cleaning and maintenance which may have impacted on the samplers, resulting in higher TVOC and NO_X concentrations being detected.

The lowest mean O_3 level was detected at Divi Heritage Resort, this may be the result of ozone formed at the sample location being formed and eventually dispersed by wind action. Unfortunately, passive monitoring does not allow for the tracking of any resultant ozone spikes; to determine if ozone was formed at the sample point at high traffic volume times or was transient in nature.

5.2.1.3 St. James Cemetery

In contrast, the highest O_3 levels were detected at St. James Cemetery (SJC). This may be the result of O_3 formed upwind and drifting towards the sample location as there were no observed anthropogenic sources of either NO_2 or VOCs in the immediate vicinity. However, biogenic emissions may contribute to the VOC concentrations and thereby assist in the formation of ozone.

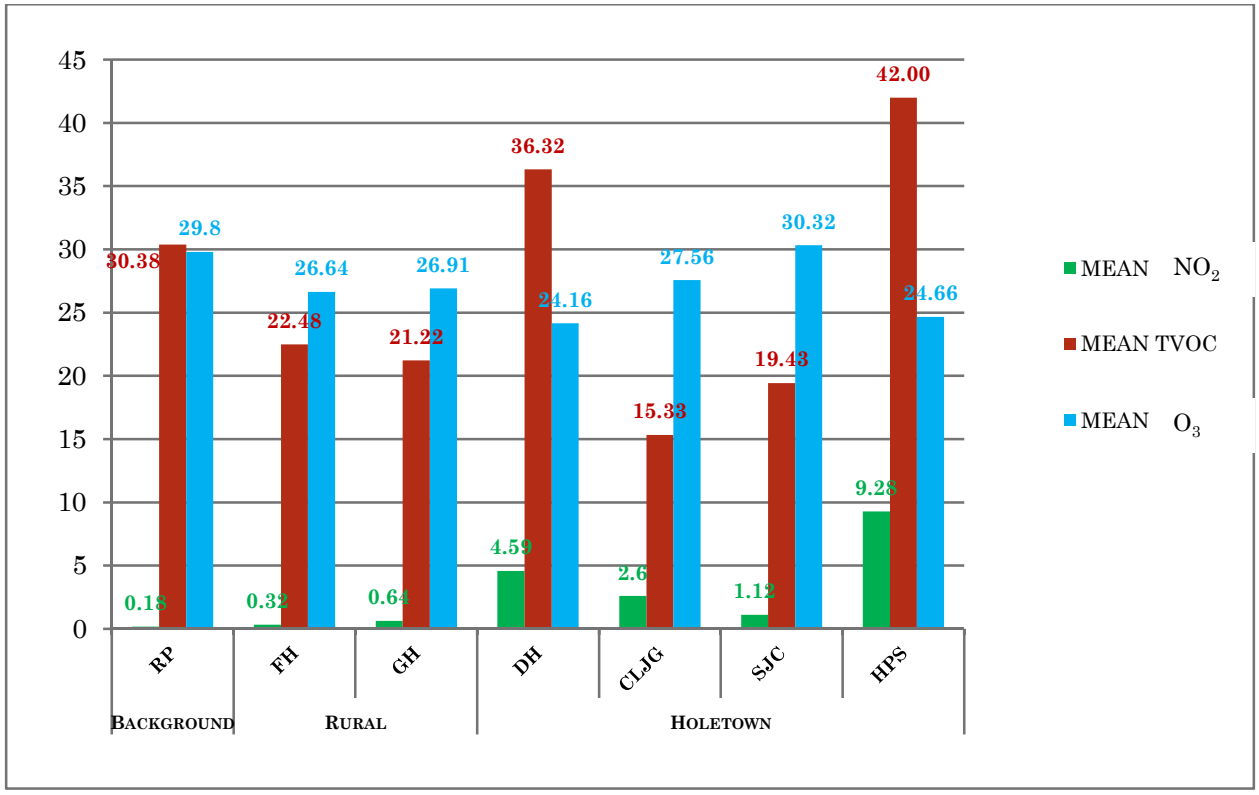
5.2.1.4 Crossing Lights Jus' Grillin

The lowest mean TVOC concentration was detected at Crossing Lights Jus' Grillin' (CLJG) Although, the sampling location at the Crossing Lights Jus' Grillin

was in close proximity to a bus stop, visual observations showed that this bus stop was less frequently utilized than the one closer to Divi Heritage Resort. As a result, there was potentially less idle time for buses, due to less people embarking and disembarking buses at that particular location, possibly resulting in lower NO_2 and TVOC levels. Although visual observations revealed that traffic flows tend to become restricted at this location during peak hours; the low average TVOC concentration cannot be explained unless additional factors are taken into consideration such as wind dispersal and the density of development in the area. Additionally, traffic counters would be unable to provide data on vehicle idle times in either instance.

5.2.1.5 Ragged Point

The lowest mean NO_2 concentration was detected at Ragged Point (RP). This may be the result of NO_x being utilized at a faster rate during the production of ozone. It must be noted that despite having the lowest mean NO_2 concentration, Ragged Point showed the 2nd highest mean ozone concentration.



Graph 10: Average NO_2, TVOC and O_3 concentrations per location.

5.2.1.6 Observed NOx to VOC Ratios

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_x 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, the VOC concentration is higher relative to the NO_X concentration and NO_x tends to generate ozone. In this instance, ozone formation is considered as "NO_x limited".

The VOC/NO_x ratio can differ substantially by location and time-of-day between location specific microclimates. Furthermore, the VOC/NO_x 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.

Based on the ratio of NO_X to VOC calculated; it appears that four (4) of the locations (RP, Gun Hill Signal Station, St. James Cemetery and Farley Hill) were

NOx limited i.e. the concentration of VOCs was higher than NOx concentrations and therefore this prevented excess ozone formation while the remaining three (3) (Holetown Police Station, Divi Heritage Resort and Crossing Lights Jus' Grillin') were between the optimal 1:4 to 1:15 ratio of NOx to VOCs for ozone formation. The results can be seen in Table 19.

Table 19: Calculated NO_x to VOC ratio for the seven sampling locations.

Location	% NOx	% VOC	Ratio
Ragged Point	0.4	99.6	**1:233**
Divi Heritage Resort	12.6	87.4	**1:7**
Crossing Lights Jus' Grillin'	17.0	83.0	**1:5**
St. James Cemetery	5.8	94.2	**1:16**
Holetown Police Station	22.0	78.0	**1:4**
Farley Hill	1.4	98.6	**1:69**
Gun Hill	3.0	97.0	**1:32**
Average	8.89	91.11	**1:10**

5.2.2 Expected Nitrogen Dioxide (NO_2), Total Volatile Organic Compounds (TVOC) and Ozone (O_3) Interactions

One of the biggest challenges associated with urban air pollution, is the relationship between ozone formed as a result of the interactions between NO_X and VOCs along with other components such as; sea salts, other particulates and catalysts for photochemical reactions (sunlight, weather conditions e.g. temperature and rainfall and wind-speed).

In some situations, ozone formation is largely controlled by the presence of NOx and formation is largely independent of VOC. In other situations, ozone production increases with increasing VOC and does not increase (or sometimes even decreases) with increasing NOx. The true difficulty lies in determining whether the observed O_3 levels during the sampling period were due to specific events occurring or were the result of complex NOx-sensitive chemistry or VOC-sensitive chemistry.

5.2.2.1 Mechanics of Ozone Formation

Ozone at ground level is formed through a series of complex photochemical reactions among NO_X and volatile organic compounds (VOCs) in 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.

The formation of ground level ozone is dependent on the intensity of solar radiation and the sensitive ratio of NO_X to VOCs usually in the range of 1: 4 to 1:15. Ozone is a photochemical pollutant and forms roughly 2-3 hours after initial NO_X 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_X 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[3]
- 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, 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

[3] 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.

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.

5.2.2.2 Photochemical Reactions and Weather

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 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, thereby reducing the potential of photochemical reactions occurring and generating ozone (West Michigan Clean Air Coalition, 2009).

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.

Based on the available meteorological data in Graphs 3-7, the average temperature Holetown and Two Rural areas study was approximately 27.0 °C. As a result the average temperature was above the optimal temperature of 26°C for ozone generation. No real time data for the individual sites was available and therefore localized variations may have occurred.

Additionally, the average wind speed during the Holetown and two rural areas study was 10.42 km/hr, did not exceed the 16 km/h maximum allowable wind speed for ozone propagation. This low wind speed may have facilitated O_3 production as it allows the necessary accumulation of precursors of ozone formation (VOCs and NOx). Conversely, O_3 may be transported from their formation points to other locations.

It must be noted that the localized wind speeds at sample locations may vary and since these could not be monitored at the time of the study, the impact of wind speed cannot be accurately judged and would require real time monitoring to complete the assessment.

Additionally, high relative humidity levels (>50%) tend to reduce the formation of ozone and according to the West Michigan Clean Air Coalition[9], *"enhances the formation of nitrate and sulphate aerosol particles. The chemistry for forming aerosols is limited in a restricted moisture environment."*

5.2.2.3 Interactions with Sea Salt

A 2008 study conducted by (Ostroff, 2008) showed that nitryl chloride ($ClNO_2$) was efficiently formed as a result of the interaction of sea salt and NO_X, specifically dinitrogen pentaoxide (N_2O_5) from anthropogenic sources.

The high yield of $ClNO_2$ produced at night was photolyzed after sunrise to produce chlorine atoms, at a time when other oxidants and radicals (for example, OH, NO_3) were scarce, very likely leading to enhanced oxidation of volatile organic compounds (VOCs) and acceleration of photochemical ozone production. Therefore increased concentration of sea salt at Ragged Point could account for the elevated O_3 concentrations shown in Graph 10. The extent to which sea salt impacts Barbados has not been established in this study.

5.2.2.4 Biogenic Emissions

VOC sources may be classified as natural (biogenic) or anthropogenic (man-made) in nature. As previously mentioned, man-made sources of VOCs are primarily as a result of incomplete combustion of fossil fuels and other processes involving the use of hydrocarbons.

All trees and flowering plants emit varying levels of non-methane hydrocarbon, the volume of which is dependent on plant/tree species and other factors such as land coverage, physiological health, light availability and several others. According to the International society of Environmental Botanists (Varshney, 2007); "*Biogenic VOC emission predominantly occurs in tropics (23° S 23° N) with small amounts emitted in the northern mid-latitudes. Almost about 99 per cent of the total biogenic non-methane VOCs (NMVOCs) are emitted from terrestrial sources including forests, grasslands, shrub-lands and croplands. Biogenic NMVOCs comprised of isoprene, monoterpene, alkane, alkene, carbonyls, alcohols, acids, esters, ethers and aromatic hydrocarbons.*"

As shown in Graph 10; the rural areas of Gun Hill and Farley Hill, and to some extent St. James Cemetery, exhibited TVOC levels that were unexpectedly high due to their distance from roadside sources. However, these locations were characterised by open spaces and large amounts of vegetation in the form of trees and flowering plants. As a result there is a possibility that the levels observed may be partially due to biogenic emissions.

Additionally, at Farley Hill, bird droppings were plentiful in the immediate vicinity of the sampling location which may account for increased VOC levels as well.

6.0 IMPACTS OF NO_2 AND O_3 ON HUMAN HEALTH

6.1 NO_2 Impacts

Short term inhalation of raised levels of nitrogen dioxide may inflame the lining of the lungs and it can stymie resistance to respiratory infections, increasing the likelihood of respiratory problems. This can cause problems such as wheezing, coughing, colds, flu and bronchitis.

Increased levels of nitrogen dioxide can have significant impacts on people with asthma, because it can cause more frequent and more intense attacks. Children with asthma and older people with heart disease are most at risk (Australian Government Department of Energy and Environment, 2005).

Additionally the following have been observed in various studies;

- Epidemiological studies have shown that symptoms of bronchitis in asthmatic children increase in association with long-term exposure to NO_2 (Krzyzanowski, 2008).
- Reduced lung function growth is also linked to NO_2 at concentrations currently measured (or observed) in cities of Europe and North America (WHO, 2017).
- 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 (WHO, 2017).

6.2 O_3 Impacts

According to the (USEPA, 2017), exposure to ground level ozone can cause respiratory problems as it causes the muscles in airways to constrict, trapping air in the alveoli leading to wheezing and shortness of breath. Children are particularly susceptible as they tend to breathe more deeply than adults. In persons, suffering from illness, excessive exposure may exacerbate illness and complicate the recovery process. Examples of the impacts of exposure to high levels of ground level ozone are as follows:

- Make it more difficult to breathe deeply and vigorously.
- Cause shortness of breath, and pain when taking a deep breath.
- Cause coughing and sore or scratchy throat.
- Inflame and damage the airways.
- Aggravate lung diseases such as asthma, emphysema, and chronic bronchitis.
- Increase the frequency of asthma attacks.
- Make the lungs more susceptible to infection.
- Continue to damage the lungs even when the symptoms have disappeared.
- Cause chronic obstructive pulmonary disease.

7.0 STUDY LIMITATIONS

The study limitations were similar to those of the Bridgetown 2012-2013 study and the Oistins/Speightstown 2014-2015 study as the methodology did not allow for the following; real time correlation with respect to meteorological parameters, real time traffic counts, 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_2, NO_2, ozone and TVOC levels and other factors which such as weather conditions, mobile and stationary sources.

Ragged Point may have been impacted by factors such as sargassum seaweed which could affect SO_2 levels and sea salt which may impact upon ozone levels. SO_2 levels on average were 3-4 times higher than all other sampling locations and the TVOC levels were on average higher than several inland sites. The use of Ragged Point as a background site for future studies of this nature may therefore need to be reassessed.

The impact of sea-salt on the levels of pollution could not be explored in this study. It would be beneficial in the future to determine the extent of sea salt aerosol dispersion across the island.

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 Holetown and two Rural Areas was achieved.

According to 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. In Holetown and the two rural areas the average for Holetown was 0.57 ppb and the two rural areas was 0.48 ppb, well below the 3 ppb. Despite being below 3 ppb, the SOx levels should be monitored to determine the rate of increase or decrease over time to judge more accurately the impacts of anthropogenic or natural emissions.

Only a partial understanding of the anthropogenic, biogenic and photochemical interactions between ozone, NO_X and VOCs, could be gleaned from the existing dataset. Therefore, further assessment should be considered to focus on peak formation times and real time measurements.

9.0 RECOMMENDATIONS

The results observed may be the result of existing economic activities, and other factors. 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. 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 guidelines for the primary and secondary pollutants and assist in improving policy with respect to ambient air quality management in Barbados.

9.1 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 standard such as the WHO Air Quality Guidelines. 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 time sensitive 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 (vehicular or trans-boundary) 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.

9.2 Additional Monitoring Parameters

Additional monitoring should be conducted in the previously monitored areas to determine the impacts of particulates such as total suspended solids, PM_{10} and sea salt in order to establish their impacts on the propagation of ambient air pollution.

10. GLOSSARY OF TERMS AND ABBREVIATIONS

Baseline	A minimum or starting point used for future data comparisons
Co-located/ Duplicate	Two samples taken from and representative of the same population and carried through all steps of the sampling and analytical procedures in an identical manner. Duplicate samples are used to assess consistency in the methods used including sampling and analysis.
CIMH	Caribbean Institute of Meteorology and Hydrology
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 levels).
EPD	Environmental Protection Department
Flexible scope of accreditation	Flexible scopes of accreditation can allow a laboratory to undertake certain tests/calibrations, and to report the results as accredited, even though they may not be explicitly stated on their accreditation schedule.
Field Blanks	These consist of unexposed sampling media taken into the field and handled as regular samples then returned to the Lab for analysis. This procedure allows the lab to make corrections for any contamination that may arise in the sampling media whether it occurs prior to, during, or after the sampling event.
MTW	Ministry of Transport and Works

H2RAAAPMA	Holetown and Two Rural Areas Ambient Air Quality Passive Monitoring Assessment
ND	No data collected due to missing passive sampling tubes
Nitrogen Dioxide (NO_2)	A toxic reddish brown gas that is a strong oxidizing agent, is produced by combustion (as of fossil fuels), and is an atmospheric pollutant (in smog).
NOx	Oxides of Nitrogen
Ozone (O_3)	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 (VOCs) in the presence of sunlight.
ppb	Parts per billion
Primary Pollutant	An air pollutant emitted directly from a source
Secondary pollutant	An air pollutant that is not directly emitted, but forms when primary pollutants react in the atmosphere
Sorbent	A material used to absorb or adsorb liquids or gases
Sulphur Dioxide (SO_2)	A colourless, toxic gas with a strong odour. It is formed naturally by volcanic activity, by the combustion of fossil fuels and in 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 comparative evaluations.
Total Volatile Organic Compounds (TVOCs)	Compounds of carbon, excluding carbon monoxide, carbon 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.
UKAS	United Kingdom Accreditation Service
USEPA	United States Environmental Protection Agency
WHO	World Health Organisation
WMO-GAW	World Meteorological Organization Global Atmospheric Watch

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