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### Investigation of the Levels, Composition and Reactivity of VOCs in the Marine Boundary Layer of Bermuda

Kelli Deja

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# **Investigation of the Levels, Composition and Reactivity of VOCs in the Marine Boundary Layer of Bermuda**

By

Kelli Deja

A thesis submitted in partial fulfillment  
Of the requirements of the  
University Honors Program  
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Assistant Professor, College of Arts and Sciences

University Honors Program  
University of South Florida  
St. Petersburg, Florida

CERTIFICATE OF APPROVAL

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Honors Thesis

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This is to certify that the Honors Thesis of

**Kelli Deja**

has been approved by the Examining Committee on December 2020  
as satisfying the thesis requirement  
of the University Honors Program

Examining Committee:

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Professor of Political Science

**Acknowledgment**

The completion of my Honors Thesis would not have been possible without my family, whom I would like to thank for all of their love and encouragement throughout my academic career. I would not be the person I am today without their endless support and selflessness.

I would like to extend my sincerest gratitude to my thesis director, Dr. Elshorbany, for giving me the proper guidance throughout this project and always extending a helpful hand whenever needed.

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**Abstract**

Two field measurements were performed to evaluate the oxidation capacity and HONO formation mechanism on sea salt aerosols in the marine boundary layer (MBL) of Bermuda. The Volatile Organic Compounds (VOC's) composition and reactivity has also been investigated during the field measurements. During the summer, the measurement site was impacted by two different air masses, local air masses from the north/northeast and aged marine air masses from the west. Initial VOC measurements reveal varying concentrations based on the origin of the air masses and are composed mainly of aromatics and haloalkanes in addition to minor contributions from alkenes and ketones. Correlations of key VOC's indicate aged air masses, and  $\text{NO}_x$  limited conditions. It seems that westerly winds bring not only haloalkane rich marine air masses but also aged polluted air masses.

## 1 Introduction

The Earth's atmosphere is composed primarily of N<sub>2</sub> and O<sub>2</sub> and several noble gases. The remaining gaseous constituents, the trace gases, comprise less than 1 % of the atmosphere. These trace gases play a crucial role in the earth's radiative balance and in the chemical properties of the atmosphere (Seinfeld and Pandis, 1998). Atmospheric chemistry focuses on the investigation of the atmospheric chemical composition in the region closest to the earth's surface, the troposphere ( $\leq 10-15$  km), but also to the tropopause ( $\sim 10$ ) and the stratosphere ( $\sim 10-50$  km) (Finlayson Pitts and Pitts, 2000). The troposphere is the lowest layer of the atmosphere and can be seen as two different layers, the lower layer, which is in close contact with the Earth's surface, is the planetary boundary layer (PBL) while the one above is the free troposphere (FT). The marine boundary layer (MBL) is the layer in close contact with the ocean or sea surface.

Emissions of both anthropogenic and biogenic volatile organic compounds are being released into the atmosphere. These emissions may be subjected to local and regional transportation and/or subsequent oxidation processes that may result in the formation of other harmful secondary products such as ozone and PAN, which are the main constituents of the summer photochemical smog in many polluted areas around the world. Recent studies also indicated that secondary oxidized VOC (SVOC) may also form on the marine surface microlayer. These OVOCs can either create original aerosol particles or cause pre-existing particles to grow due to the condensation on existing particles. Aerosols have immense effects on the balance of Earth's radiation, which can have negative impacts on the Earth's climate. Small amounts of research have been conducted on these particles in the marine boundary layer (MBL), which has proximal interactions with the ocean. There are various different VOCs that are massively abundant in our atmosphere. Haloalkanes are one of the most commonly found VOCs in the MBL

(Badia et al., 2019; Tadic et al, 2020). The most substantial haloalkane found in the atmosphere is known to be chloromethane having an average background mixing ratio to be about 550 pptv (Keppler, 2005) and they emerged from locations that are oceanic and terrestrial and have an approximate lifetime of one year.

HONO is a major source of OH radical, the main oxidizing species in the atmosphere (Elshorbany et al., 2009a). Recent studies have shown that HONO can be formed from the photolysis of nitrates on sea salt aerosols, which in turn photolyzes to form NO and OH. This process is called re-noxification (Ye et al, 2016) and can have large impacts of OH budget in the marine boundary layer, which makes ~70% of the earth, and can transport NO and aerosols to other areas. In this study, we investigate the VOCs composition and reactivity in the MBL of Bermuda and their impact on the atmospheric oxidation capacity and HONO photochemical formation.

## **2 Methodology**

### **2.1 Field measurements**

The measurements took place in the spring and late summer of 2019 at the Tudor Hill Marine Atmospheric Observatory of Bermuda. The Tudor Hill site is located over a cliff on the west coast of Bermuda (32° 19' N, 64° 45' W) with a sampling tower 23-m above the ground on the cliff and ~53 m above the sea surface. Measurements included HONO, NO<sub>x</sub> (NO+NO<sub>2</sub>), nitric acid, ozone and particulate nitrate (pNO<sub>3</sub>, in addition to VOCs. The initial goal of this study is to determine the VOC levels and distribution and at a later phase, constrain it to an explicit box model to investigate the oxidation capacity and HONO re-noxification mechanism in the MBL.



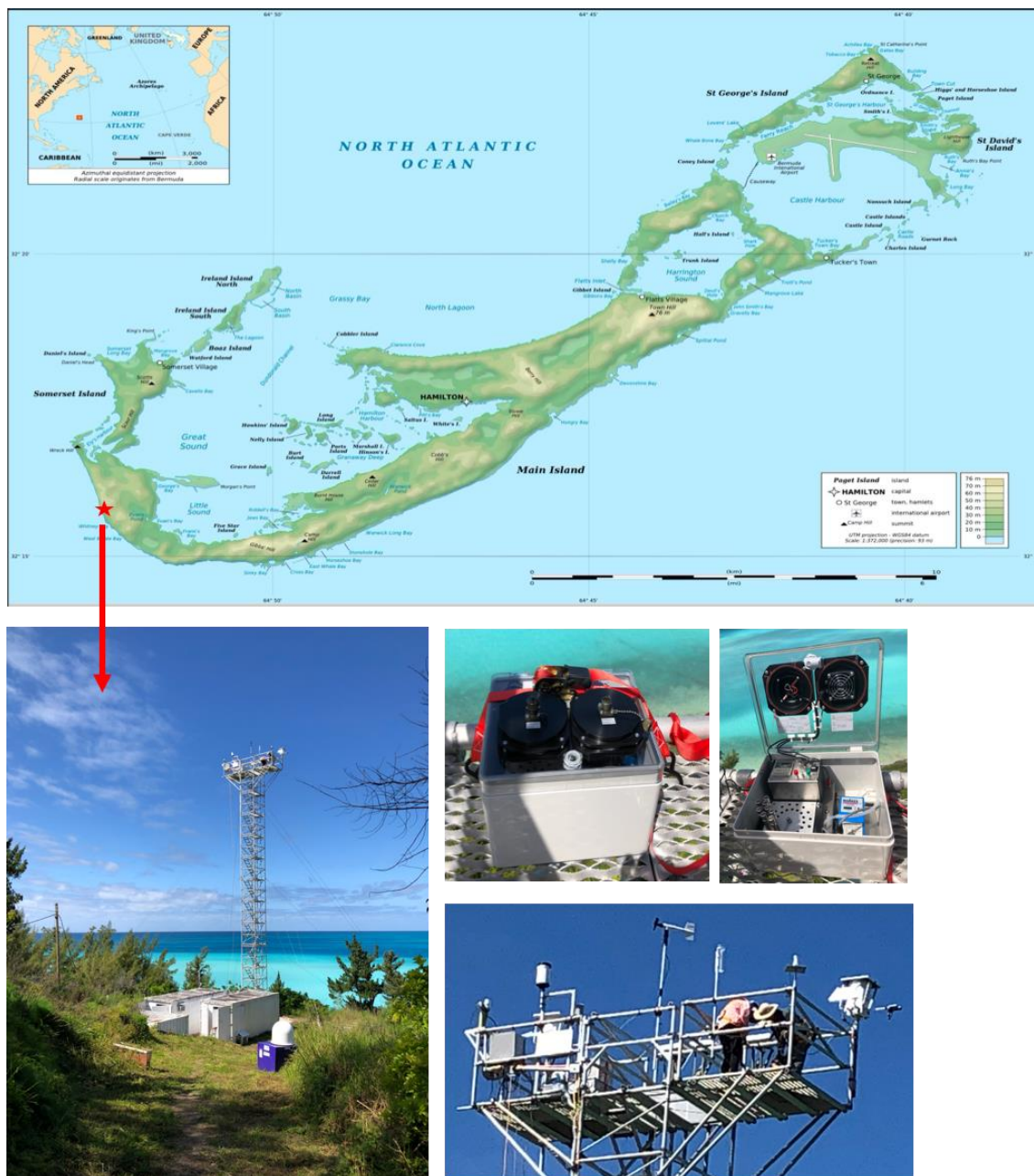


Figure 1: UP: The Tudor Hill Marine Atmospheric Observatory site in Bermuda, indicated by the red star. The geological location of Bermuda in the North Atlantic Ocean is indicated by the red square in the inserted map. Lower: The VOC automatic sampling system was installed on top of the 53 meters high (above sea level) sampling tower. Photos courtesy of Dr. Elshorbany.

The measurements were impacted by two different air masses, east/northeast (from Hamilton), carrying local biogenic and anthropogenic emission, and westerly winds, carrying marine air

masses but possibly also aged air masses from the eastern US. We present initial results from the summer field measurements.

## 2.2 Laboratory Analysis

VOCs were collected in Bermuda every three hours on adsorption tubes at a constant flow rate of  $40 \text{ ml min}^{-1}$  and were analyzed offsite at the USF's Atmospheric Chemistry and Climate laboratory using a cryogen-free thermal desorption and GC/MS system, following the TO-17 EPA method. A dynamic multipoint calibration method using a NIST traceable 65 components TO-15/17 cylinder was used to calibrate the system.

The analysis of the samples was conducted using the thermal desorption (TD) gas chromatography mass spectrometry (GC/MS) technique as shown in Figure 2. Analysis of the sample begins by inserting the tube into the thermal desorption unit where the sample within the tube is vaporized and transferred into the chromatographic column, by the flow of the carrier gas, helium. This column allows the compounds to be isolated from one another because of the difference in their interactions that occur within the column. These separated compounds are then moved into the mass analysis of mass identification.

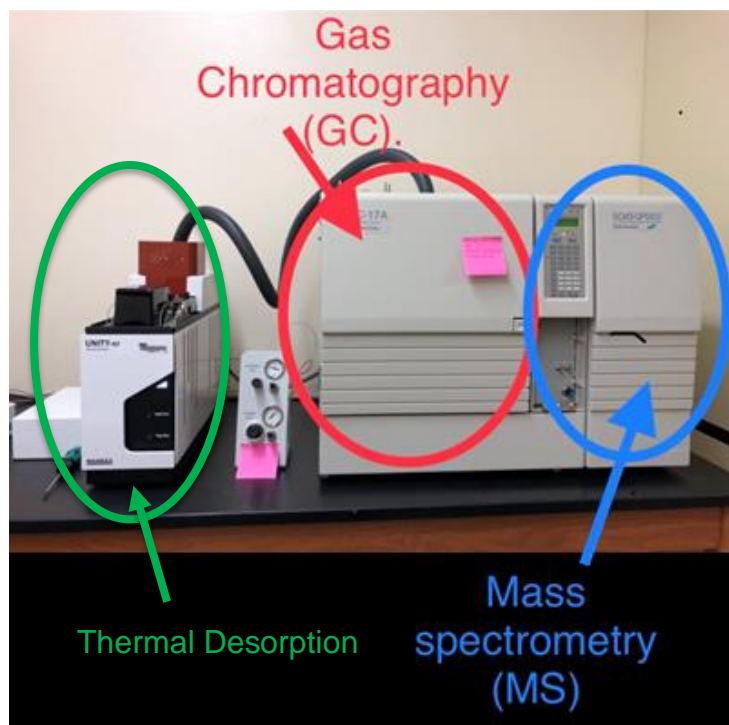


Figure 2: Gas Chromatography Mass Spectrometry technique courtesy of USF St. Petersburg

### 2.3 Data Analysis and QC/QA

A dynamic multipoint calibration method using a NIST traceable 65 components TO-15/17 cylinder was used to calibrate the system (Figure 3).

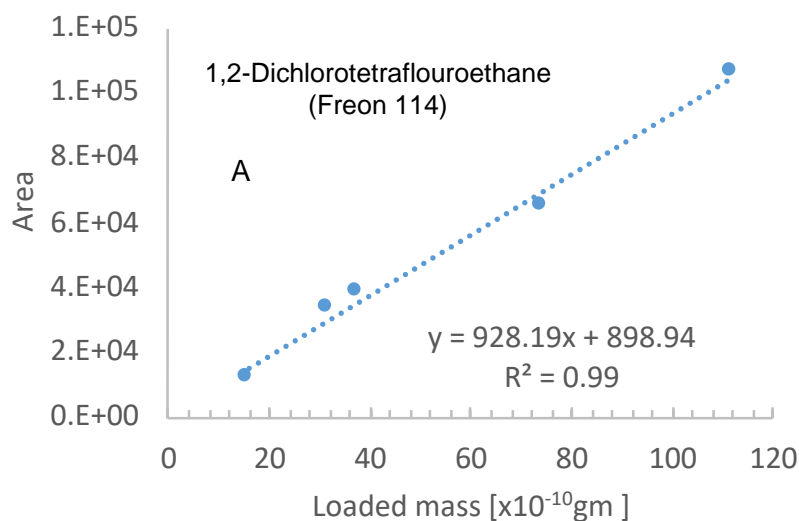
<u>Component</u>	<u>CAS Number</u>	<u>Requested Conc</u>	<u>Certified Conc</u>
Propylene	115-07-1	1.00 ppm	1.10 ppm
Freon-12	75-71-8	1.00 ppm	1.05 ppm
Chloromethane	74-87-3	1.00 ppm	1.08 ppm
Freon-114	76-14-2	1.00 ppm	1.02 ppm
Vinyl Chloride	75-01-4	1.00 ppm	1.04 ppm
1,3-Butadiene	106-99-0	1.00 ppm	1.06 ppm
Bromomethane	74-83-9	1.00 ppm	1.06 ppm
Chloroethane	75-00-3	1.00 ppm	1.04 ppm
Ethanol (Analytical Accuracy $\pm$ 10%)	64-17-5	1.00 ppm	1.10 ppm
Acrolein (Analytical Accuracy $\pm$ 10%)	107-02-8	1.00 ppm	1.10 ppm
Acetone	67-63-0	1.00 ppm	1.10 ppm
Freon-11	75-35-4	1.00 ppm	1.02 ppm
Isopropyl Alcohol	67-63-0	1.00 ppm	1.10 ppm
1,1-Dichloroethene	75-35-4	1.00 ppm	1.10 ppm

Carbon Disulfide (Analytical Accuracy $\pm$ 10%)	75-15-0	1.00 ppm	1.05 ppm
Methylene Chloride	75-09-2	1.00 ppm	1.10 ppm
Freon-113	76-13-1	1.00 ppm	1.10 ppm
Trans-1,2-Dichloroethane	156-60-5	1.00 ppm	1.07 ppm
1,1-Dichloroethane	75-34-3	1.00 ppm	1.07 ppm
Methyl Tert Butyl Ether	1634-04-4	1.00 ppm	1.10 ppm
Vinyl Acetate	108-05-4	1.00 ppm	1.10 ppm
Methyl Ethyl Ketone	78-93-3	1.00 ppm	1.10 ppm
Cis-1,2-Dichloroethene	156-59-2	1.00 ppm	1.10 ppm
Hexane	110-54-3	1.00 ppm	1.10 ppm
Chloroform	67-66-3	1.00 ppm	1.06 ppm
Ethyl Acetate	141-78-6	1.00 ppm	1.06 ppm
Tetrahydrofuran	109-99-9	1.00 ppm	1.05 ppm
1,2-Dichloroethane	107-06-2	1.00 ppm	1.10 ppm
1,1,1-Trichloroethane	71-55-6	1.00 ppm	1.10 ppm
Benzene	71-43-2	1.00 ppm	1.10 ppm
Carbon Tetrachloride	56-23-5	1.00 ppm	1.10 ppm
Cyclohexane	110-82-7	1.00 ppm	1.10 ppm
1,2-Dichloropropane	78-87-5	1.00 ppm	1.10 ppm
Trichloroethylene	79-01-6	1.00 ppm	1.09 ppm
Bromodichloromethane	75-27-4	1.00 ppm	1.09 ppm
1,4-Dioxane	123-91-1	1.00 ppm	1.09 ppm
Methyl Methacrylate	80-62-6	1.00 ppm	1.09 ppm
Heptane	142-82-5	1.00 ppm	1.10 ppm
Cis-1,3-Dichloropropene	10061-01-5	1.00 ppm	1.09 ppm
Methyl Isobutyl Ketone	108-10-1	1.00 ppm	1.10 ppm
Trans-1,3-Dichloropropene	10061-02-6	1.00 ppm	1.06 ppm
1,1,2-Trichloroethane	79-00-5	1.00 ppm	1.10 ppm
Toluene	108-88-3	1.00 ppm	1.10 ppm
Methyl Butyl Ketone	591-78-6	1.00 ppm	1.10 ppm
Dibromochloromethane	124-48-1	1.00 ppm	1.07 ppm
1,2-Dibromoethane	106-93-4	1.00 ppm	1.10 ppm
Tetrachloroethylene	127-18-4	1.00 ppm	1.08 ppm
Chlorobenzene	108-90-7	1.00 ppm	1.10 ppm
Ethylbenzene	100-41-4	1.00 ppm	1.10 ppm
p-xylene	106-42-3	1.00 ppm	1.06 ppm
m-xylene	108-38-3	1.00 ppm	1.06 ppm
Bromoform	75-25-2	1.00 ppm	1.06 ppm
Styrene	100-42-5	1.00 ppm	1.09 ppm
o-xylene	95-47-6	1.00 ppm	1.08 ppm
1,1,2,2-Tetrachloroethane	79-34-5	1.00 ppm	1.08 ppm
4-Ethyltoluene	622-96-8	1.00 ppm	1.06 ppm
1,3,5-Trimethylbenzene	108-67-8	1.00 ppm	1.05 ppm
1,2,4-Trimethylbenzene	95-63-6	1.00 ppm	1.04 ppm
1,3-Dichlorobenzene	541-73-1	1.00 ppm	1.05 ppm
Benzyl Chloride (Analytical Accuracy $\pm$ 10%)	100-44-7	1.00 ppm	1.05 ppm

1,4-Dichlorobenzene	106-46-7	1.00 ppm	1.04 ppm
1,2-Dichlorobenzene	95-50-1	1.00 ppm	1.03 ppm
1,2,4-Trichlorobenzene	120-82-1	1.00 ppm	1.03 ppm
Napthalene (Analytical Accuracy $\pm$ 10%)	91-20-3	1.00 ppm	1.03 ppm
Hexachloro-1,3-Butadiene	87-68-3	1.00 ppm	1.09 ppm

Figure 3: NIST traceable 65 components TO-15/17 cylinder

To simulate the sampling process, we performed dynamic calibration to the NIST standard calibration mixture using synthetic air and sampled the calibration gas on adsorption tubes (similar to that used in the field) and then followed the same analytical procedure to analyze the samples (TD-GC-MS). Below is a calibration diagrams for few VOCs (as examples)



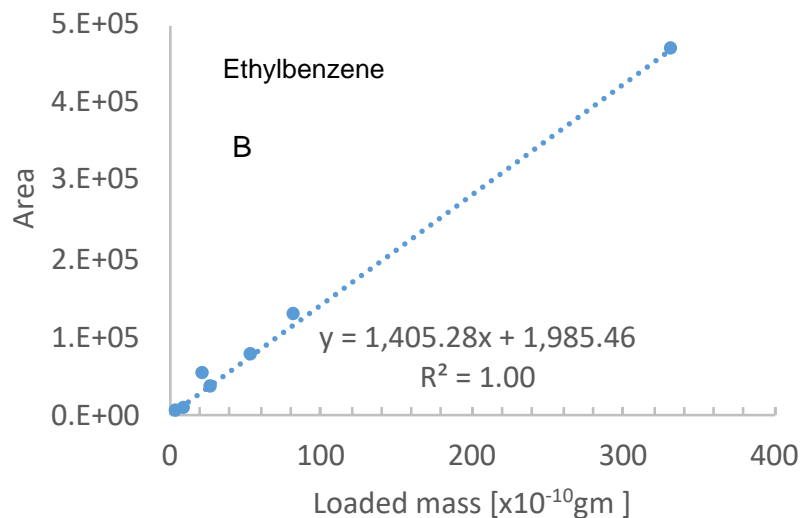


Figure 4: Calibration graphs for Freon 114 (a) and Ethylbenzene (B), using the dynamic dilution of the NIST standard.

We use the calibration parameters of each species, slope, intercept, and their associated uncertainties to calculate the concentration of atmospheric VOCs in the MBL as well as their detection limits.

### 3 Results and discussion

The detection limits and average concentrations during the summer and Spring field campaigns (Table 1). As shown in Table 1, only few compounds were above the detection limits, indicating very low VOC levels.

Table 1: List of the VOCs measured during the summer campaign.

Compound Name	RT	DL (pptv)		Average Mixing Ratios [pptv]			
		Summer	Spring	Summer	SD	Spring	SD
Propene	4.35	62	124	308	194	426	204
1,2-Dichlorotetrafluoroethane (Freon 114)	4.47	28	57	237	132	195	65
chloroethene	5.49	70	141	122	102	<DL	<DL
1,3-Butadiene	5.63	17	33	<DL	<DL	<DL	<DL
Ethyl Chloride	7.15	279	557	<DL	<DL	<DL	<DL
Trichloromonofluoromethane (Freon 11)	8.16	41	82	80	39	33	14
(E)-1,2-dichloroethene,	10.44	188	377	<DL	<DL	<DL	<DL
Acetone	10.78	33	65	67	50	201	131
Carbon disulfide	11.32	123	247	170	161	21	21
Isopropyl Alcohol	11.51	7	14	<DL	<DL	<DL	<DL
dichloromethane	12.67	110	220	<DL	<DL	<DL	<DL
cis-1,2-dichloroethene	13.77	19	37	<DL	<DL	<DL	<DL
n-Hexane	14.88	56	111	<DL	<DL	<DL	<DL
Ethane, 1,1-dichloro-	15.46	175	351	<DL	<DL	<DL	<DL
(E)-Ethene, 1,2-dichloro	17.63	69	137	<DL	<DL	<DL	<DL
2-Butanone (MEK)	17.73	35	70	<DL	<DL	<DL	<DL
Ethylacetate	17.98	38	76	<DL	<DL	<DL	<DL
tetrahydrofuran	18.64	32	63	<DL	<DL	<DL	<DL
Chloroform	18.80	146	291	<DL	<DL	<DL	<DL
1,1,1-trichloroethane	19.37	163	326	<DL	<DL	<DL	<DL
Cyclohexane	19.53	48	97	<DL	<DL	<DL	<DL
Carbon Tetrachloride	19.92	50	101	<DL	<DL	<DL	<DL

Continue: Table 2: List of the VOCs measured during the summer campaign.

Compound Name	RT	DL (pptv)		Average Mixing Ratios [pptv]			
		Summer	Spring	Summer	SD	Spring	SD
Benzene	20.66	32	64	353	242	538	538
1,2-dichloroethane	20.75	72	144	<DL	<DL	<DL	<DL
Heptane	21.53	37	75	<DL	<DL	<DL	<DL
Trichloroethylene	22.79	52	104	<DL	<DL	<DL	<DL
1,2-dichloropropane	23.56	30	59	<DL	<DL	<DL	<DL
1,4-Dioxane	23.91	100	200	<DL	<DL	<DL	<DL
bromodichloromethane	24.44	119	238	<DL	<DL	<DL	<DL
(cis)-1,3-dichloro-1-propene	25.87	44	88	<DL	<DL	<DL	<DL
4-methyl-2-Pentanone, (MIBK, Methylisobutylketone)	26.36	71	142	<DL	<DL	<DL	<DL
Toluene	26.92	62	123	105	69	380	27
(E)-1,3-dichloro-1-Propene	27.63	100	200	<DL	<DL	<DL	<DL
1,1,2-trichloro-ethane	28.23	82	164	<DL	<DL	<DL	<DL
Tetrachloroethylene	28.65	95	190	<DL	<DL	<DL	<DL
2-Hexanone (MBK, Methyl n-Butly ketone)	28.99	45	91	<DL	<DL	<DL	<DL
dibromochloromethane	29.49	67	135	<DL	<DL	<DL	<DL
1,2-dibromoethane	29.88	81	162	<DL	<DL	<DL	<DL
chlorobenzene	31.41	59	117	<DL	<DL	<DL	<DL
Ethylbenzene	31.73	35	69	64	40	<DL	<DL
1,2-dimethylbenzene (m- & p-xylene)	32.10	48	73	42	35	<DL	<DL
Styrene, o-xylene	33.39	66	132	<DL	<DL	<DL	<DL



Continue: Table 3: List of the VOCs measured during the summer campaign.

Compound Name	RT	DL (pptv)		Average Mixing Ratios [pptv]			
		Summer	Spring	Summer	SD	Spring	SD
tribromomethane	34.08	151	302	<DL	<DL	<DL	<DL
1,1,2,2-tetrachloroethane	35.53	133	266	<DL	<DL	<DL	<DL
1,3,5-trimethylbenzene	36.23	71	141	<DL	<DL	<DL	<DL
1,2,4-trimethylbenzene	36.42	70	139	<DL	<DL	<DL	<DL
1-Ethyl-4-Methylbenzene	37.16	147	295	<DL	<DL	<DL	<DL
1,2,3-trimethylbenzene	37.65	139	278	<DL	<DL	<DL	<DL
1,3-dichlorobenzene	38.62	8	16	<DL	<DL	<DL	<DL
1,4-dichlorobenzene	38.92	92	185	<DL	<DL	<DL	<DL
1,2-dichlorobenzene	40.16	187	375	<DL	<DL	<DL	<DL
1,2,4-trichlorobenzene	48.58	79	158	<DL	<DL	<DL	<DL
Hexachlorobutadiene	49.92	85	171	<DL	<DL	<DL	<DL

Total average mixing ratios of VOCs in the marine boundary layer of Bermuda during the summer campaign are  $\sim 5000 \pm 2700$  pptC,  $\sim 200$  times lower than that measured under polluted urban conditions (Elshorbany et al., 2009). A VOC/NO<sub>x</sub> ratio of 17 confirms dominating NO<sub>x</sub> limited conditions.

Aromatics represent  $\sim 38\%$  and are represented by the BTEX compounds (benzene, toluene, ethylbenzene, and xylenes). Haloalkanes represent the second-highest category with 36% followed by alkenes (18%). Carbon disulfide and ketones were also present albeit with low relative mixing ratios. VOCs originating from oceanic sources were also identified in the mass spectra but were not quantified due to the lack of their calibration standards.

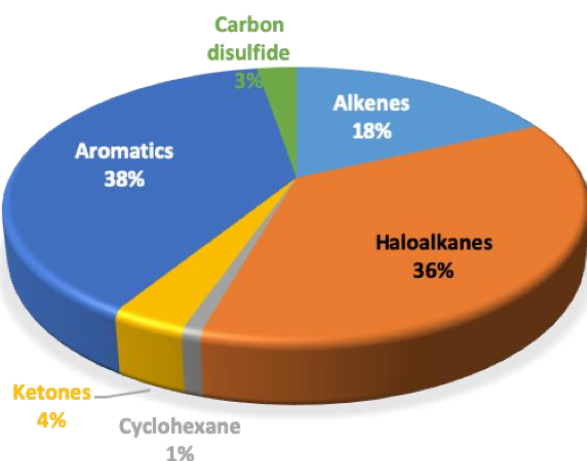


Figure 3: Average campaign relative contributions of different categories of VOCs in the MBL in Bermuda during the summer 2019 field measurements.

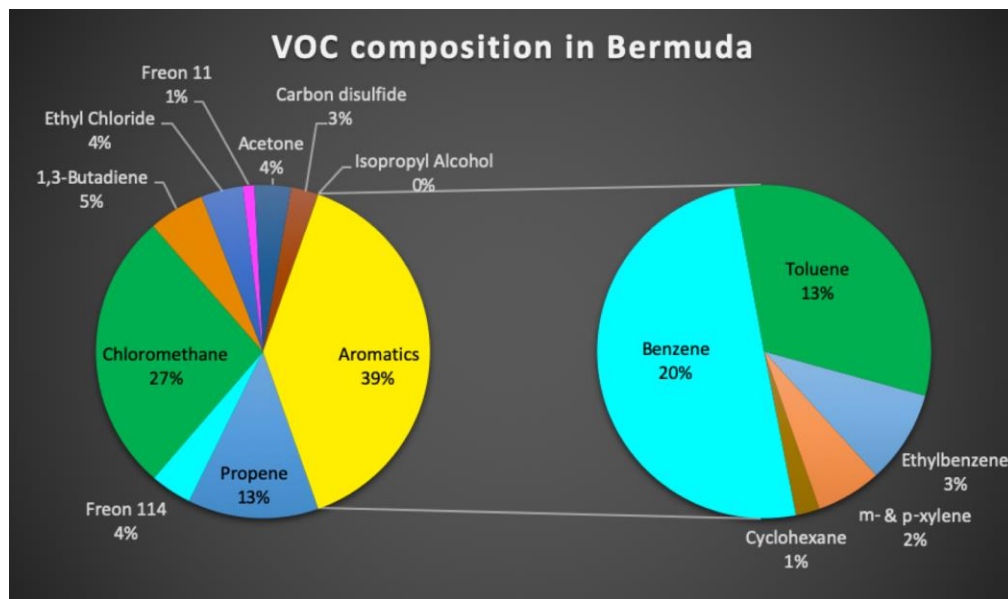


Figure 4: Average campaign relative contributions of speciated VOCs in the MBL in Bermuda during the summer 2019 field measurements. Average total mixing ratios were ~5000 2700 pptC.

### Haloalkanes

Chloromethane is the most abundant haloalkane in the atmosphere with average background mixing ratios of ~550 pptv (e.g., Keppler et al., 2005) and originates from oceanic and terrestrial sources, with an atmospheric lifetime of one year. Measured chloromethane levels (~1500 ±600 pptv) are ~3 times the background levels but similar to chloromethane levels from tropical terrestrial mangrove forests in Brazil (Kolusu et al., 2018). The large variation can be explained by the varying air masses impacted the measurement site (see figure below).

### Aromatics

Aromatics are dominated by BTEX compounds. The small mixing ratios of BTEX compounds and the small toluene/benzene ratio of <1.5x is an indication of long-range transport of vehicular

emissions (e.g., Miller et al., 2011) since the OH oxidation rate of toluene is 5 times that of benzene. That is also indicated by the increased ratio with westerly winds.

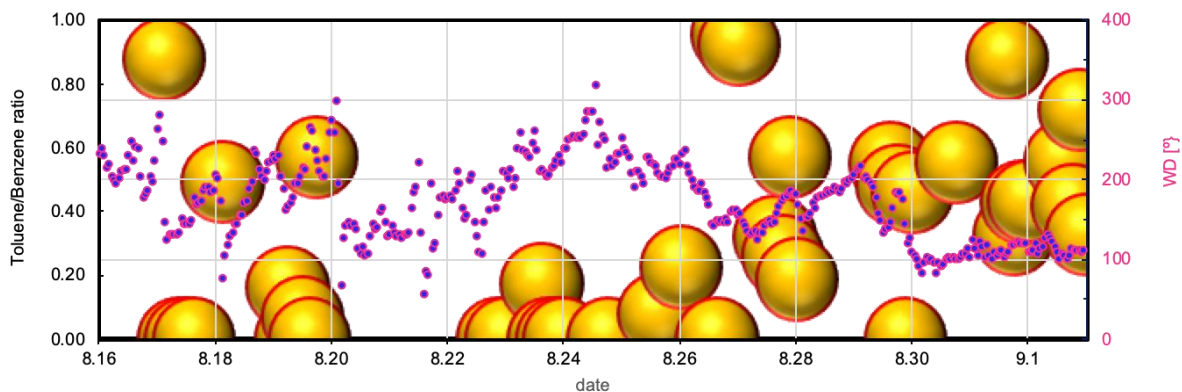


Figure 5: Increased toluene/benzene ratio correlates with westerly winds at the Tudor Hill site

Similarly, ethylbenzene was found to correlate with m-&p-xylene indicating the same source and the very small ratio of  $\sim 0.70$  indicates long-range transport rather than fresh emissions.

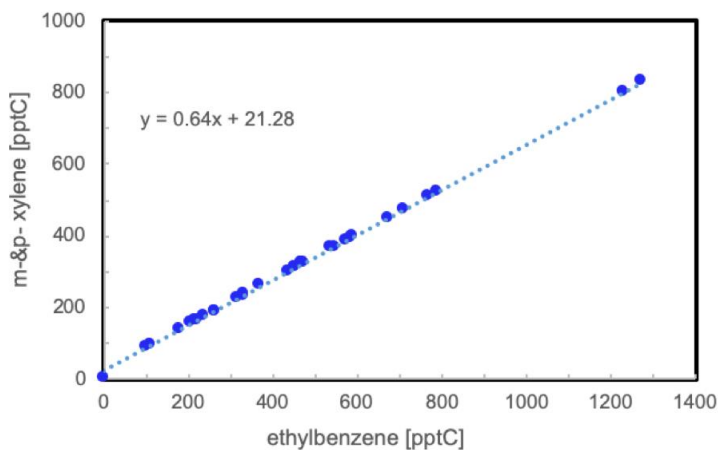


Figure 6: Correlation between m-&p-xylene and ethylbenzene during the summer 2019 field measurements in Bermuda

Aromatics low concentrations and low ratios of toluene/benzene and m-&p-xylene/ethylbenzene indicate that westerly winds bring not only halocarbon rich marine air masses but also polluted aged air masses.

## 1. Summary

Two field measurements were performed to evaluate the oxidation capacity and HONO formation mechanism on sea salt aerosols in the MBL of Bermuda. In the summer of 2019, the measurements site was impacted by two different air masses, local air masses from the north/northeast and aged marine air masses from the west. Initial VOC measurements revealed varying concentrations based on the origin of the air masses and are composed mainly of aromatics and haloalkanes in addition to minor contributions from alkenes and ketones. As expected, air masses are NO<sub>x</sub> limited. Correlations of key VOCs indicate aged air masses. It seems that westerly winds bring not only haloalkane rich marine air masses, but also aged polluted air masses. The results of this study will be further implemented in an explicit box model to investigate the marine boundary layer chemistry and will be then implemented in a 3D model to investigate the climate impacts

#### 4 Bibliography

- Badia, A., Reeves, C. E., Baker, A. R., Saiz-Lopez, A., Volkamer, R., Koenig, T. K., Apel, E. C., Hornbrook, R. S., Carpenter, L. J., Andrews, S. J., Sherwen, T., and von Glasow, R.: Importance of reactive halogens in the tropical marine atmosphere: a regional modelling study using WRF-Chem, *Atmos. Chem. Phys.*, 19, 3161–3189, <https://doi.org/10.5194/acp-19-3161-2019>, 2019.
- Bahlmann, et al.: A high volume sampling system for isotope determination of volatile halocarbons and hydrocarbons, *Atmos. Meas. Tech.*, 4, 2073–2086, <https://doi.org/10.5194/amt-4-2073-2011>, 2011.
- Elshorbany, et al.: Oxidation capacity of the city air of Santiago, Chile, *Atmospheric Chemistry and Physics*, 9, 2257-2273, 2009
- Finlayson-Pitts, B. J. and Pitts, Jr., J. N.: *Chemistry of the Upper and Lower Atmosphere*, Academic Press, 2000.
- Keppler, et al.: New insight into the atmospheric chloromethane budget gained using stable carbon isotope ratios. *ACP, EGU*, 5 (9), 2403-2411, 2005.
- Kolusu et al.: Determination of chloromethane and dichloromethane in a tropical terrestrial mangrove forest in Brazil by measurements and modelling, *Atmospheric Environment* 173 (2018) 185–197, 2018.
- Kolusu et al.: Chloromethane and dichloromethane in the tropical Atlantic Ocean, *Atmospheric Environment* 173 (2018) 185–197, 2017.
- Miller et al., *Spatial Variability and Application of Ratios between BTEX in Two Canadian Cities*, doi:10.1100/2011/167973, 2011.
- Seinfeld, J. H. and Pandis, S. N.: *Atmospheric chemistry and physics: From air pollution to climate change*, A Wiley-Interscience publications, 1998.
- Tadic, I., Crowley, J. N., Dienhart, D., Eger, P., Harder, H., Hottmann, B., Martinez, M., Parchatka, U., Paris, J.-D., Pozzer, A., Rohloff, R., Schuladen, J., Shenolikar, J., Tauer, S., Lelieveld, J., and Fischer, H.: Net ozone production and its relationship to nitrogen oxides and volatile organic compounds in the marine boundary layer around the Arabian Peninsula, *Atmos. Chem. Phys.*, 20, 6769–6787, <https://doi.org/10.5194/acp-20-6769-2020>, 2020.
- Toyota, K., Kanaya, Y., Takahashi, M., and Akimoto, H.: A box model study on photochemical interactions between VOCs and reactive halogen species in the marine boundary layer, *Atmos. Chem. Phys.*, 4, 1961–1987, <https://doi.org/10.5194/acp-4-1961-2004>, 2004.