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Case Study Analysis of Ozone Concentrations in Houston TX During Hurricane Harvey

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Abstract

Ozone and sulfur dioxide are two of the six criteria pollutants monitored by the Clean Air Act, as they pose many human health and environmental risks, which is of particular concern in Houston TX. Due to the several hundred petrochemical plants and the several dozen crude oil refineries in Houston, the city experiences some of the highest concentrations of ozone, sulfur dioxide, and peroxy radicals of any city in the United States. The complex geography, influence of the sea breeze, and the normal synoptic-scale flow makes Houston unique regarding ozone attainment. The landfall of Hurricane Harvey in Houston in August 2017 created an opportunity to assess the city's ozone response. Ozone, wind, and volatile organic compound (VOC) data collected before, during, and after the hurricane are analyzed. Using a network of automated observation sites between the Houston ship channel and the city center, VOC (e.g. Benzene, Ethane, Ethylene, and Sulfur Dioxide) increases were correlated with Non-Typical Ozone Changes (NTOCs). As a result of the flooding, winds, and shutdown of petrochemical plants, several tons of VOCs were released, contributing to the highest 8-hour ozone average in 2017 for the entire state of Texas. Additionally, from September 1 to September 5 average wind speeds were $\leq$ 5 mph, and wind directions were primarily from the East, allowing ozone and VOCs to advect to and build up in the Houston downtown area.

1. Introduction

Background concentrations of ozone decreased from 2000 to 2014 in Houston, TX since the Environmental Protection Agency's (EPA) implementation of an ozone attainment strategy set up by the Texas Commission on Environmental Quality[1,2,3]. This reduction of ozone is in large part a result of a reduction of volatile organic compound (VOC) emission sources from the many petrochemical plants and oil refineries in the Houston ship channel and surrounding area. However, there are also other chemical and meteorological factors that have led to the reduction of non-attainment events in the Houston area. Several studies have found that given relatively constant VOC and nitrous oxide (NOx) emissions, shifts in the wind direction and intensity can create large concentrated plumes of ozone that are in excess of the 70 parts per billion by volume (ppbv) threshold set by the EPA[2,4,5].

Little consideration has been given to the secondary effects of extreme weather events occurring in metropolitan and industrial areas. Ozone data collected from 5 Continuous Ambient Monitoring Stations (CAMSs) in Houston, TX show an extreme nonattainment event (i.e. ozone $\geq$ 70 ppbv) occurring just after hurricane Harvey made landfall. Data for this event are limited as many of the CAMS were either shut down prior to Harvey making landfall, or damaged during the event. However, existing data show Houston TX experienced the highest 8-hour ozone concentration average in 2017 for the entire state of TX[1]. Many meteorological, chemical and photochemical factors contribute to the genesis of ozone; this research is an attempt to lay a simple groundwork for an understanding of the local meteorological and chemical factors in Houston TX that lead to the extreme nonattainment event following Hurricane Harvey.

Understanding the role of ozone in the post-Hurricane Harvey Houston area requires an understanding of the local atmospheric patterns that lead to increased ozone concentrations. Darby[4] found that peaks in ozone (≥ 120 ppbv) generally occurred after a shift from an offshore breeze to an onshore breeze with a period of ~1 hour of stagnant wind in between. Also, on days when the sea-breeze was not significant it was found that after a shift in wind direction greater than 45°, ozone concentrations peaked. These findings are corroborated by other studies[2,5]. Additionally, Couzo[6] found that that non-typical ozone changes (NTOCs) occurred mainly when winds were less than 6.5 km h^{-1} for a period of 3 hours. Many NTOCs occur when there is a large petrochemical leak of VOCs. However, Banta[2] constructed a 15-yr climatology of wind patterns and ozone concentrations in Houston and found that many ozone concentration peaks were not correlated with emission increases.

The chemical and photochemical processes of ozone production are well understood, but many of the meteorological factors that lead to exacerbated ozone events are not[7]. Darby[4] and Liu[8] have attempted to isolate the meteorological factors that contribute to the unique ozone problem in Houston, but Darby concludes that in order to gain a complete understanding of the issue the chemical, photochemical, and meteorological factors must be considered. A better understanding of the meteorological factors that influence ozone concentrations can serve as a preventative measure for many NTOCs, and a better understanding of meteorological events can be gleaned from a better understanding of ozone concentrations. This idea is illustrated in a study[9] that used ozone measurements collected using ozonesondes to get a better understanding of the wind patterns in the eyes of two Atlantic basin hurricanes. However, this study focused on the wind patterns implied by the ozone measurements; it did not address the risks that ozone posed to humans and the environment as a result of the hurricane damage. Carsey[9] et. al. took ozone measurements in and around the eyewall of a hurricane by dropping ozonesondes to get a better understanding of stratospheric intrusion into the eye of a hurricane. The study suggests that there is a limited amount of stratospheric intrusion into the eye of a hurricane. Carsey's findings are corroborated by a previous study conducted by Penn[10] that found weak ozone and temperature gradients above hurricane cloud tops. Compared to surface-level ozone measurements, the concentration of ozone found by Penn was not close to the threshold set by the EPA. However, Penn conducted this study on two hurricanes in the Atlantic Ocean where there are much lower concentrations of both VOCs and NOx emissions which are precursors to ozone. Understanding how a hurricane will affect ozone concentrations in coastal regions, especially in port cities that are crucial for commerce, could help to avoid potential risks of ozone to human health, agriculture, and the environment[11].

In understanding Houston's ozone problem, it is important to consider the vulnerability of emissions sources of ozone precursors to natural disaster. The EPA has stated that the "production and processing sectors are responsible for over half of the natural gas industry emissions," and most of these VOC emissions are gas leaks from valves and connectors, which are susceptible to damage via natural disaster[12]. Considering these VOC sources is important when considering ozone concentrations during hurricane events in Houston, TX., such as the landfall of Hurricane Harvey on 25 August 2017 as a category 3 hurricane. Harvey wind speeds were ≥ 100 mph, and it brought ≥ 50" of rainfall to the Houston area causing extreme flooding. This study will investigate the post-Harvey atmospheric conditions and chemical constituents that contributed to an increase in ozone in Houston TX in early September 2017.

The next section of this paper will discuss the data and methods used in the case study analysis of the landfall of Hurricane Harvey and its effects on ozone in Houston TX. Then, the subsequent section will include results and discussion on the significance of the ozone measurements relative to typical ozone concentrations in Houston. The main conclusions will be summarized in the final section, which also includes suggestions for future work.

2. Data and Methods

Hourly ozone, benzene, sulfur dioxide, ethane, ethylene, wind speed, and wind direction data were collected from 1 August 2017 to 30 September 2017 using the TCEQ's Automated Gas Chromatograph (AutoGC) sites at Wallisville Rd, Channelview, HRM3, and Clinton. The four AutoGC sites were chosen based on their locations between downtown Houston and the Houston ship channel ~10 miles east of downtown Houston. Additionally, monthly average, maximum, and standard deviation ozone data were collected from January 2012 to October 2017 at five CAMS locations (CAMS: 558, 553, 26, 53, 695). Figure 1 shows the locations of the four observation sites where benzene and ozone data were collected, in addition to the five CAMS locations.

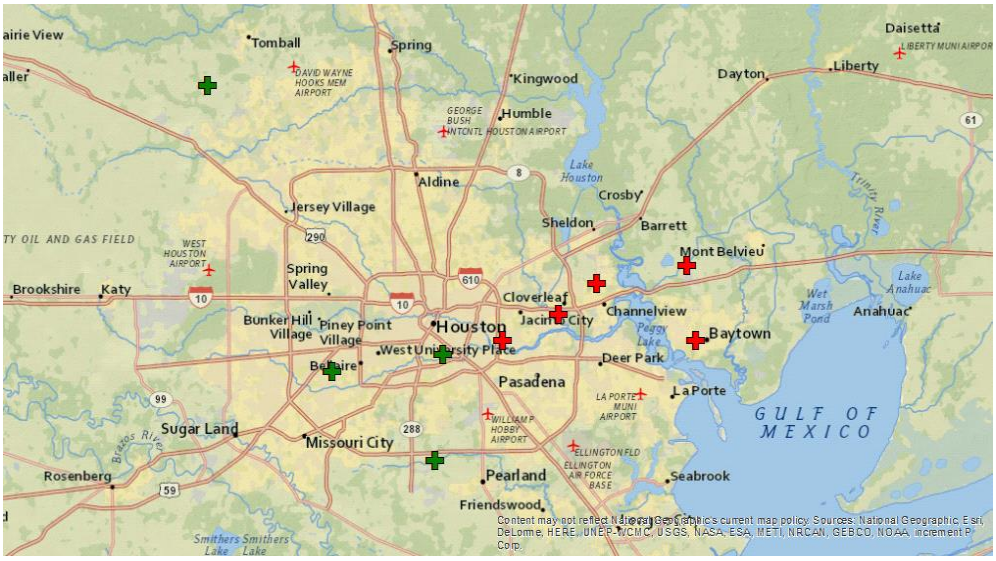


Figure 1. AutoGC sites (red cross) and CAMS sites (green cross) in Houston TX.

Wind data were analyzed from 1 August through 30 September. Wind data from 00:00 CST September 1 to 23:00 CST September 6 were scrutinized as they constitute the primary post Hurricane Harvey study period. Additionally, NOAA's Air Resources Laboratory HYSPLIT model was run using HRRR meteorological data for parcel trajectories staring at 10 m in the Houston ship channel to understand the trajectories of VOC and ozone advection in the planetary boundary layer[13]. The average wind direction was calculated at the four AutoGC sites to determine how to analyze the advection and genesis of ozone and VOC emissions between the sites. Winds were primarily easterly ($\mu = 103.6°$) from 1 September to 6 September; therefore, the Pearson Product Moment correlation coefficient was calculated between benzene data from Wallisville Rd. AutoGC (i.e. East) and ozone data from Channelview AutoGC (i.e. West). The correlation coefficients were calculated at lag 0 to 9 hours, since VOC increases tend to precede ozone increases by several hours. The same correlation coefficients were calculated for the subsequent AutoGC stations in Figure 1, and for several other species of VOCs with respect to ozone. For Clinton, which is the most westward AutoGC site and the site closest to downtown Houston, the correlation coefficients were calculated using benzene and ozone data from only the Clinton AutoGC location. Missing data were excluded from the statistical analysis.

Finally, maximum ozone measurements from 0000 CST September 1 to 2300 CST September 6 at five CAMSs were compared with the January 2012 to October 2017 monthly average and maximum ozone measurements using a one tailed t-test to check for significance. The significance of the ozone values measured from 1 September to 6 September were most likely inflated relative to monthly average values since ozone approaches 0 ppbv at night. The next section summarizes the Z-scores and cumulative probabilities of the maximum ozone measurements at the 5 CAMS locations during the study period compared to January 2012 through October 2017 maximum monthly concentrations.

3. Results

It should be noted that most of the AutoGC and CAMS sites are missing data from approximately 24 to 31 of August; therefore, most of the statistical analysis is taken from September. Additionally, from ozone data and solar radiation data collected in August, it can be seen that ozone concentrations were depressed as a result of the increased cloud cover and winds associated with Hurricane Harvey. Clouds reduce incoming solar radiation which is a necessary component for photochemical synthesis of ozone, and high winds tend to disperse ozone and its precursors. Figure 2 shows ozone concentrations from 1 August 2017 to 30 September 2017, and a marked depression can be seen in late August associated with Hurricane Harvey.

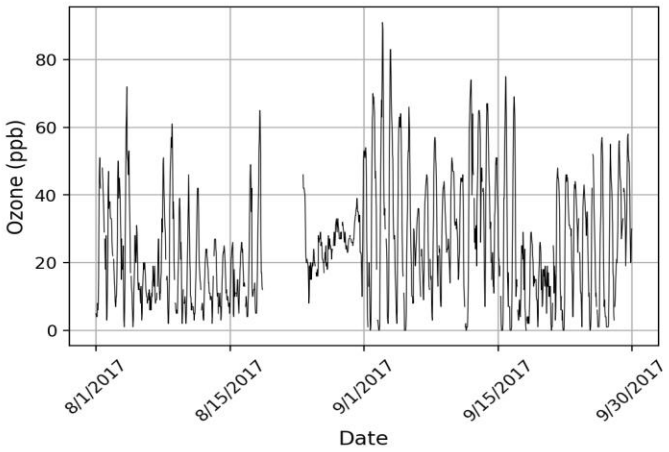
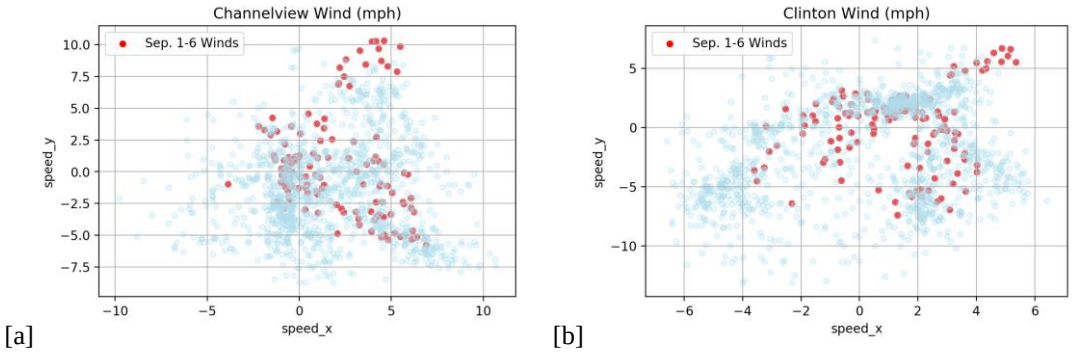
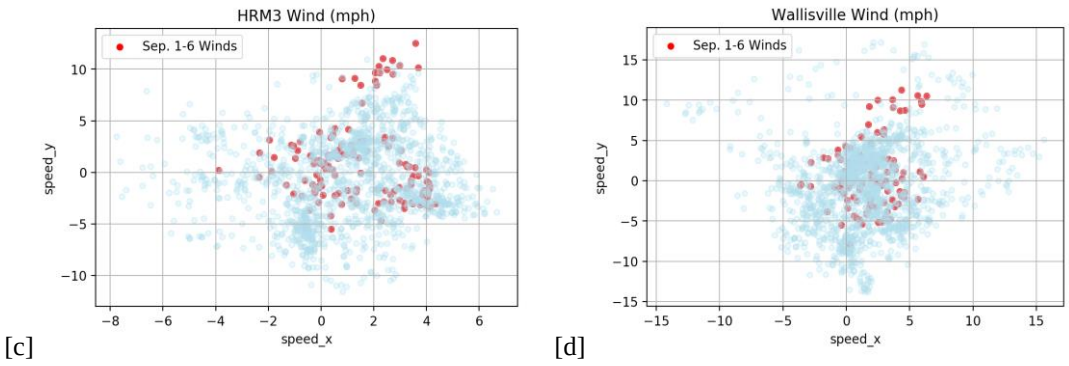


Figure 2. Ozone concentrations (ppb) at HRM3 AutoGC site from 1 August 2017 to 30 September 2017.

Maximum wind speeds from 1 September 2017 to 5 September 2017 at the Clinton, HRM3, and Wallisville Rd. AutoGC sites did not exceed 8.0 mph, while maximum wind speeds at the Channelview AutoGC did not exceed 10.0 mph. Additionally, the average wind directions during the same period at the Clinton, HRM3, Wallisville Rd, and Channelview AutoGCs were 104.8°, 100.8°, 92.4°, and 116.4° respectively. Figure 3 summarizes the winds at the four AutoGC sites, with winds from 0000 CST 1 September to 2300 CST 6 September highlighted as the primary post Harvey study period. Additionally, Figure 4 shows the 120-hour HYSPLIT model parcel trajectories initiated at 14:00 UTC 1 September, and it can be seen that there is strong model agreement initially where most parcel trajectories are towards the west. Westward parcel trajectories is a favorable condition for the advection of VOCs and ozone from the Houston ship channel towards downtown Houston. Figure 4 also shows the planetary boundary layer mixed layer depth, which is extremely shallow during nighttime hours and extends only to 2 km during the day. The relatively shallow mixed layer depth indicates stagnant conditions due to upper level subsidence which is favorable for rapid ozone production.



[a] [b]



[c] [d]

Figure 3. Wind speed and direction at [a] Channelview, [b] Clinton, [c] HRM3, and [d] Wallisville Rd. AutoGC sites.

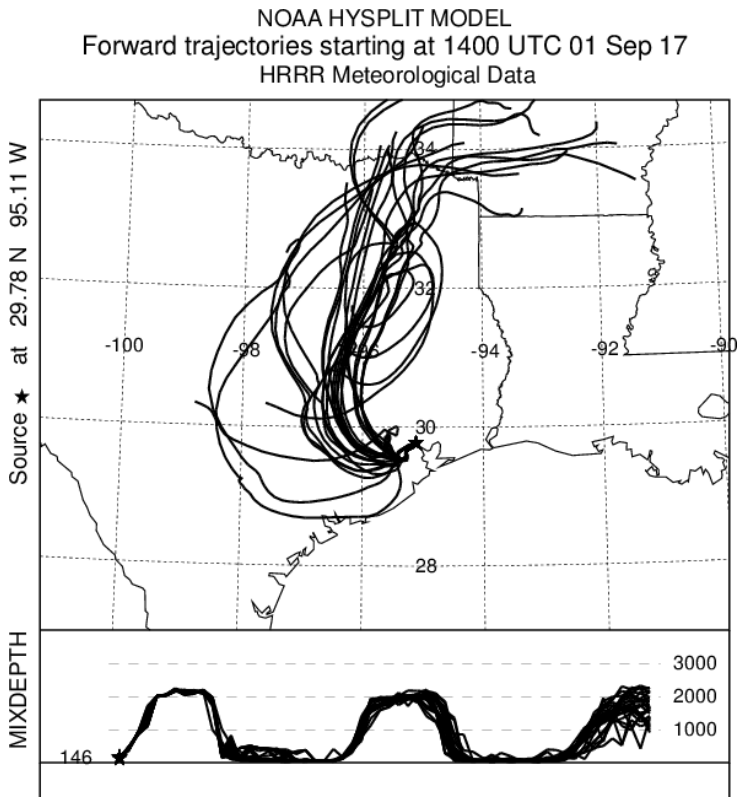


Figure 4. 120-hour NOAA Air Resource Laboratory HYSPLIT model parcel trajectories for 24 trajectories starting at 10 m on 14:00 UTC 1 September 2017, and mixed layer depth (m).

The lag-0 Pearson Product correlation between wind speed and ozone at the Channelview AutoGC for September 2017 was positive (+0.518057), which contradicts the standard understanding of wind speeds in relation to ozone concentrations. However, it should be noted that wind speeds increase significantly during the day as a result of the sea breeze in Houston, so the positive correlation coefficient between ozone and wind speed for September 2017 can be attributed to the influence of mesoscale wind patterns during the day coinciding with the general daily ozone pattern.

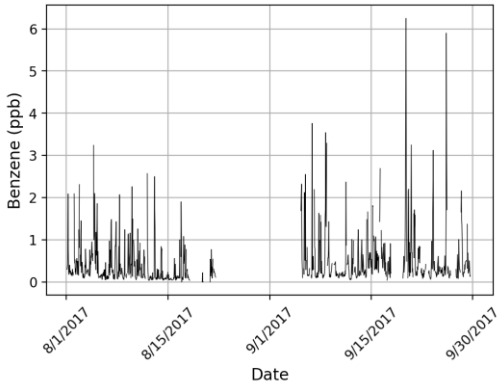
The coefficients for ozone data correlated with benzene, ethane, and ethylene data for September 2017 were all negative or zero with 0-hour lag at all four AutoCG sites. The correlation coefficients generally increased as the lag time increased to a maximum of 9 hours. The 0 hour lag correlation coefficient for the Wallisville Rd. AutoGC benzene correlated with the Channelview AutoGC ozone is $r = -0.325407$, but the 9 hour lag coefficient for the same sites

is $r = +0.450185$. Other AutoGC sites show similar correlation patterns, and overall increased benzene, ethane, and ethylene concentrations correlate with later ozone increases at AutoGC sites to the West. Table 1 summarizes the correlation coefficients calculated using benzene and ozone data between the four AutoGC locations. It should be noted that the correlation coefficients were calculated between two datasets influenced by many independent forcings, but the positive trend suggests a relatively strong relationship considering the spatial orientation of the AutoGC sites and the large time step for observations.

Table 1. r values calculated between AutoGC stations with lag time from 1 to 9 h.

AutoGC Sites	Wallisville Benzene - Channelview O3	Channelview Benzene - HRM3 O3	HRM3 Benzene - Clinton O3
r (Lag-0)	-0.325407	-0.29949	-0.1787
r (Lag-1)	-0.244885	-0.254262	-0.076655
r (Lag-2)	-0.1149	-0.196207	-0.072927
r (Lag-3)	0.011995	-0.140675	-0.040302
r (Lag-4)	0.133449	-0.101287	-0.045656
r (Lag-5)	0.222592	-0.031829	-0.038034
r (Lag-6)	0.305644	0.018627	-0.026314
r (Lag-7)	0.370574	0.071198	-0.010882
r (Lag-8)	0.425468	0.126257	0.010017
r (Lag-9)	0.450185	.167540	0.079096

Benzene, ethane, and ethylene concentrations were markedly higher from 1 September to 5 September, which is when most routine observations began after the majority of observation stations had been either shut down or damaged during Hurricane Harvey. Benzene concentrations are illustrated in Figure 4 for 1 August 2017 through 30 September 2017 at the four AutoGC sites. Ethane and ethylene concentrations mirrored those of benzene in early September, as did concentrations of sulfur dioxide. Sulfur dioxide is not a precursor to ozone like benzene, ethane, and ethylene are, but Couzo[6] found that sulfur dioxide emission increases tend to precede ozone increases due to the association of sulfur dioxide emissions with certain VOC emissions. There are some small disparities among the different AutoGCs owing to the site specific orographic features, but overall there is a significant increase in various VOC compounds followed by a significant increase in ozone concentrations several hours later.



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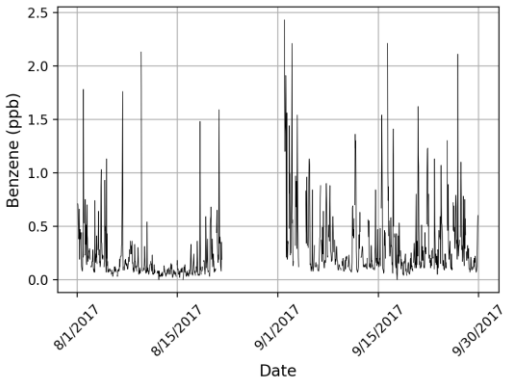

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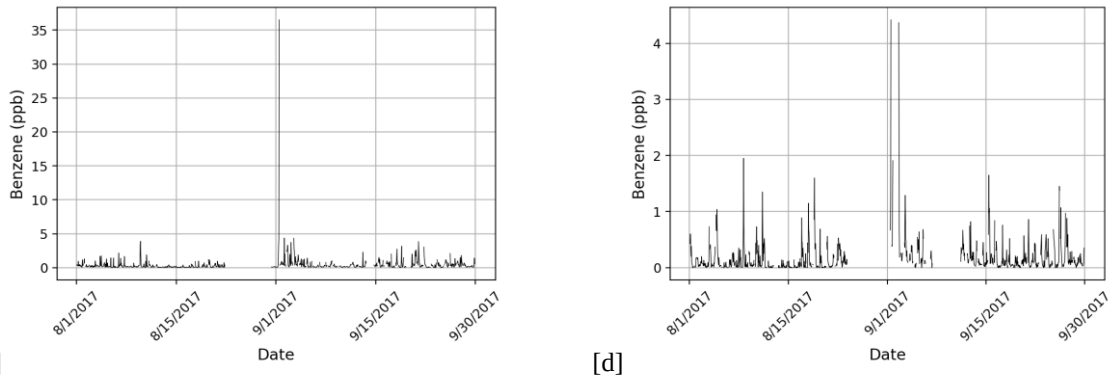

Figure 5. Benzene concentrations (ppb) at Channelview [a], Clinton [b], HRM3 [c], and Wallisville Rd. [d] AutoGC sites from 1 August 2017 to 30 September 2017.

When compared to the 2012 to 2017 monthly average ozone concentrations, ozone data collected during the 1 September to 6 September period display extreme significance with a Z-score maximum from CAMS 53 of -5.93617. This Z-score is not included in most probability tables as the cumulative probability is assumed to be essentially 1.0 (100%). However, this analysis of significance is not useful in understanding the significance of the ozone values measured, as monthly average ozone concentrations are influenced heavily by low concentrations of ozone (~0 ppbv) at night. The Z-scores of the data when tested against the 2012 to 2017 monthly maximum values again displays statistical significance, but within a reasonable degree. The different Z-scores and associated cumulative probabilities are included in Table 2, but it should be noted that the highest cumulative probability was $p = 0.9929$ at the 5% level from an ozone measurement of 115 ppbv at CAMS 53 at 12:00 CST 1 September. Other CAMS observed ozone concentrations with cumulative probability ranging from $p = 0.8023$ to $p = .9265$ at the 5% level.

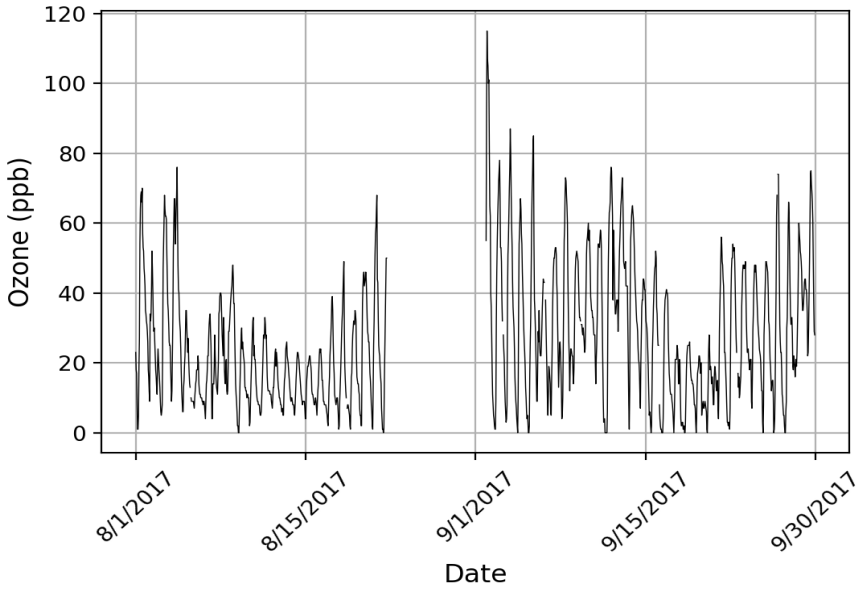

Figure 6. Ozone concentrations (ppb) at CAMS 53 from 1 August 2017 to 30 September 2017.

Table 2. Summary of Z-scores and cumulative probabilities based on CAMS location.

CAMS	558	552	53	26	695
ppbv	82	66	115	84	92
Z-Score	-1.17	-0.82	-2.39	-1.40	-1.43
p	.959	.802	.992	.927	.927

4. Conclusions

After Hurricane Harvey, average winds speeds were relatively low (≤ 2 mph), and wind direction was primarily easterly (~100°). Low wind speeds allow for the buildup of VOCs, and those VOCs were subsequently advected westward toward downtown Houston, which is a nitrous oxide (NOx) rich environment. The advection of VOCs from the Houston ship channel to the downtown area allowed for the rapid genesis of ozone due to the mixing of large amounts of ozone precursors in the relatively shallow and stable planetary boundary layer.

Considering the winds were primarily easterly, benzene data at a relative eastern AutoGC were correlated with ozone data at a relative western AutoGC. This was done for the four AutoGC sites by calculating the Pearson Product Moment correlation coefficient with a lag time of up to 9 hours. The Clinton AutoGC was the west-most AutoGC; therefore, benzene data collected at that site was correlated with ozone data collected at the same site. The correlation between the Wallisville Rd. benzene data and Channelview ozone data displayed the most significant r-values, however all of the r-values increased with increasing lag time for all of the sites. Ozone and benzene data are provided hourly; therefore, there are large amounts of "noise" associated with calculating the correlation coefficient between the two monthly datasets. The large fluctuations in hourly benzene as a result of leaks and routine offgassing, in addition to the fluctuations of ozone, make the subsequent r values small. Additionally, there are 66 other VOC emissions measured at the AutoGC sites such as ethane and ethylene which are ozone precursors, which again dampen the r-values as they increase ozone relative to benzene. The primary implication is the lag time of an increase in ozone after an increase in Benzene. Figure 6 shows the lag time of ozone emissions relative to benzene emissions at the Deer Park 2 AutoGC on 4 September 2017.

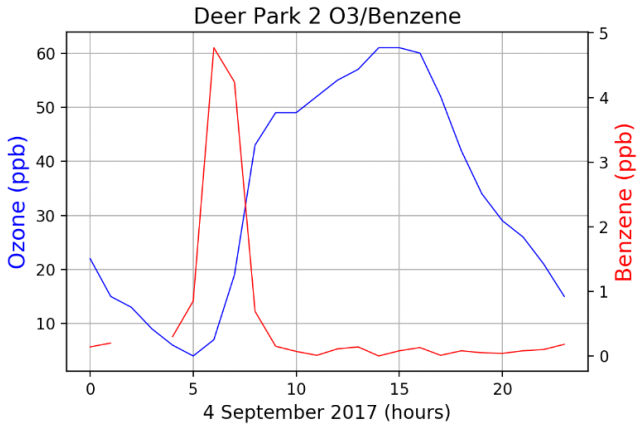

Figure 7. Benzene and ozone concentrations from 0000 CST 4 September to 2400 CST 4 September.

In addition to analyzing the relationship between ozone and ozone precursors, the significance of the maximum ozone values measured from 1 September to 6 September was analyzed by comparing the measured values to the January 2012 to October 2017 monthly maximum values. It was found that all CAMS measured ozone concentrations exhibiting statistical significance ($p > 0.75$) at the 5% level, and several CAMS measured ozone concentrations with

$p > 0.9$ at the 5% level. Three of the five CAMS measured ozone concentrations in excess of the 70 ppbv set by the EPA, which indicates significant human health risks in the several days superseding Hurricane Harvey making landfall. The data show relatively low ozone concentrations before Harvey made landfall (20 August to 26 August). After Harvey moved northeast, ozone concentrations increased rapidly as a result of the increased VOC emissions. The direct sources of the VOC emissions cannot be located without definitive data from oil refineries and petrochemical plants. However, considering the wind direction and species of VOCs, it can be inferred that the primary source of the increased emissions was the several hundred petrochemical and oil refineries in and around the Houston ship channel. This ozone event is similar to other events that are correlated with large petrochemical leaks. It should be noted that this study did not investigate the dynamics between floodwater and VOC liberation, and this study did not investigate the influence scavenging and deposition of VOC/ozone by the rainfall associated with Hurricane Harvey.

Further studies should investigate the following: the exact sources of the increased VOC and/or NOx emissions, the floodwater, petrochemical, and atmospheric interconnectivity, and finally the direct impacts of the increased ozone on human and environmental health. Understanding these issues will allow for better preparedness and mitigation during future extreme weather events in urban and industrial areas.

5. Acknowledgments

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6. References

1. TCEQ, 2018: Texas State Implementation Plan. Available online at [https://www.tceq.texas.gov/airquality/sip]

2. Banta, R.M., C. J. Senff, J. Nielsen-Gammon, L. S. Darby, T. B. Ryerson, R. J. Alvarez, S. P. Sandberg, E. J. Williams, and M. Trainer, 2005: A bad air day in Houston, *Bull. Amer. Meteor. Soc.*, **86**, pp. 657–669.

3. Vizuete, W., H.E. Jeffries, T.W. Tesche, E.P. Olaguer, and E. Couzo, 2011: Issues with ozone attainment methodology for Houston, TX., *J. Air Waste Manag. Assoc.*, **61**, pp. 238–253.

4. Darby, L.S., 2005: Cluster analysis of surface winds in Houston, Texas, and the impact of wind patterns on ozone, *J. Appl. Meteor.*, **44**, pp. 1788–1806.

5. Souri, A.H., Y. Choi, X. Li, A. Kotsakis, and X. Jiang, 2016: A 15-year climatology of wind pattern impacts on surface ozone in Houston, Texas, *Atmos. Research*, **174-175**, pp. 124–134.

6. Couzo, E., H. E. Jeffries, and W. Vizuete, 2013: Houston's rapid ozone increase: preconditions and geographic origins, *Environmental chemistry (Collingwood, Vic)*, **10**, pp. 260–268.

7. Jacobson, M. Z., 2012: *Air Pollution and Global Warming: History, Science and Solutions*.Cambridge UniversityPress, 375 pp.

8. Liu, L., R. Talbot, and X. Lan, 2015: Influence of climate change and meteorological factors on houston's air pollution: ozone a case study. *Atmosphere*, **6**, pp. 623–640.

9. Carsey, T.P., and H. E. Willoughby, 2005: Ozone measurements from eyewall transects of two Atlantic tropical cyclones, *Mon. Wea. Rev.*, **133**, pp. 166–174.

10. Penn, S., 1964: Ozone and temperature structure in a hurricane, *J. Appl. Meteor.*, **4**, pp. 212–216.

11. WHO, 2016: Ambient (outdoor) air quality and health. Available online at [http://www.who.int/mediacentre/fact sheets/fs313/en/]

12. EPA, 2006: Direct inspection and maintenance and IR leak detection, producers and processors technology transfer workshop. Available online at [https://www.epa.gov/sites/production/files/201708/documents/dim_and_leak_detect_rock_2006.pdf]

13. Stein, A.F., Draxler, R.R, Rolph, G.D., Stunder, B.J.B., Cohen, M.D., and Ngan, F., (2015). NOAA's HYSPLIT atmospheric transport and dispersion modeling system, Bull. Amer. Meteor. Soc., **96**, 2059 2077, Available online at [http://dx.doi.org/10.1175/BAMS-D-14 00110.1]