Characterizing Overwater High Ozone Events in the Houston–Galveston–Brazoria Region during the 2021 GO3 and TRACER-AQ Campaigns

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ABSTRACT: Photochemical modeling outputs showing high ozone concentrations over the Gulf of Mexico and Galveston Bay during ozone episodes in the Houston–Galveston–Brazoria (HGB) region have not been previously verified using in situ observations. Such data were collected systematically, for the first time, from July to October 2021 from three boats deployed for the Galveston Offshore Ozone Observations (GO3) and Tracking Aerosol Convection Interactions Experiment—Air Quality (TRACER-AQ) field campaigns. A pontoon boat and a commercial vessel operated in Galveston Bay, while another commercial vessel operated in the Gulf of Mexico offshore of Galveston. All three boats had continuously operating sampling systems that included ozone analyzers and weather stations, and the two boats operating in Galveston Bay had a ceilometer. The sampling systems operated autonomously on the two commercial boats as they traveled their daily routes. Thirty-seven ozonesondes were launched over water on forecast high ozone days in Galveston Bay and the Gulf of Mexico. During the campaigns, multiple periods of ozone exceeding 100 ppbv were observed over water in Galveston Bay and the Gulf of Mexico. These events included previously identified conditions for high ozone events in the HGB region, such as the bay/sea-breeze recirculation and postfrontal environments, as well as a localized coastal high ozone event after the passing of a tropical system (Hurricane Nicholas) that was not well forecast.

SIGNIFICANCE STATEMENT: This work aims to address the observational gap of overwater air quality monitoring in the Houston–Galveston–Brazoria region by instrumenting multiple vessels with different operating profiles to collect overwater observations, which will improve air quality forecasting and the direct understanding of ozone formation and transport over water.
1. Introduction

Surface ozone is a regulated criterion pollutant by the U.S. Environmental Protection Agency (EPA) through the National Ambient Air Quality Standards (NAAQS) because of its harmful effects on human health, agriculture, and ecosystems (Gong et al. 1998; Avnery et al. 2011). Currently classified as moderate nonattainment for the 2015 maximum daily 8-h (MDA8) ozone standard (EPA 2022), the Houston–Galveston–Brazoria (HGB) region has historically struggled with compliance with the NAAQS standard for surface ozone.

Coastal regions, such as within the HGB area, have inherent long-term air quality monitoring challenges where the infrastructure is less developed and often more remote. The environment is harsh and prone to unique hazards such as persistent moisture, heat, and oxidation, with frequent, at times severe, storms. These limitations often equate to sparse coastal monitoring. Rigorous monitoring is less frequent overwater if not entirely lacking (Sullivan et al. 2019; Rasp 2021). Despite these challenges, air quality monitoring in coastal areas is critical, given that approximately 127 million people live in coastal counties in the United States (Oceanservice.noaa.gov; EPA).

Due to coastal and offshore monitoring challenges, agencies responsible for these areas often use photochemical air quality models to represent the large unmonitored sections near the shore and over the water. Air quality in the densely populated HGB region is affected by land–water interactions with the expansive unmonitored areas over Galveston Bay (>1600 km²) and the Gulf of Mexico offshore of Galveston. Multiple field campaigns were conducted in the HGB region in 2021 and 2022 to address this observational deficiency. The Galveston Offshore Ozone Observations (GO3) during July and August 2021 focused on collecting offshore air quality data related to coastal ozone processes. The Tracking Aerosol Convection Interactions Experiment (TRACER) was active from 2021 to 2022 and aimed to investigate aerosol impacts on convective cloud dynamics (Jensen 2019; Jensen et al. 2022). A campaign with an air quality focus (TRACER-AQ) was also conducted in the HGB region in September 2021 (Judd et al. 2021). The extensive HGB air monitoring network complemented the field campaigns.

While photochemical models can be powerful tools, they depend on observations to parameterize the mesoscale meteorology and chemical processes occurring over water. Previous studies comparing modeled and observed ozone identified biases in model outputs between inland and coastal locations (Goldberg et al. 2014; Caicedo et al. 2019; Dunker et al. 2019). These differences have been attributed primarily to discrepancies between modeled and observed local-scale meteorological development. Overwater data collected during the 2021 field campaigns using the novel boat sampling systems have begun to address these discrepancies. Li et al. (2023) compared the Weather Research and Forecasting (WRF) Model coupled with the Comprehensive Air Quality Model with extensions (WRF-CAMx) performance against in situ overwater observations. The study found that the model captured ozone spatiotemporal variability during the daytime but overestimated ozone during clean periods and underestimated ozone during high ozone periods. Liu et al. (2023) used the WRF model coupled with GEOS-Chem (WRF-GC) to evaluate model results of boundary layer
heights and vertical profiles of ozone with measurements. The research found differences in land–water planetary boundary layer (PBL) estimates due to shallow PBL heights over water and underestimates of PBL heights over land. Findings from these studies highlight the importance of capturing local meteorological conditions, particularly the winds and PBL development, to modeling near-surface ozone accurately. Additionally, changes in the background levels of nitrogen oxides (NOx) and volatile organic compounds (VOCs) significantly impacted ozone formation in the HGB area during ozone episodes in September 2021 (Soleimanian et al. 2023).

Meteorological conditions at land–water interfaces have an integral role in ozone chemistry, influencing PBL development, photolysis rates from cloud development, and the rate of dry deposition (Goldberg et al. 2014; Caicedo et al. 2019). Land–sea-breeze cycles significantly impact surface air quality in coastal regions (Simpson 1994; Banta et al. 2005; Rappenglück et al. 2008; Caicedo et al. 2019; Stauffer and Thompson 2015; and others). Though episodic, the land–bay breeze circulation typically occurs under weak synoptic-scale forcing with sufficient sunshine to drive temperature differences between land and water surfaces, conditions favorable for the photochemical production of ozone. In the HGB region, bay breeze events bring light onshore winds from Galveston Bay through petrochemical production facilities and into the urban core of Houston. Overwater observations are thus crucial for understanding the underlying chemical and meteorological processes that drive high ozone events.

2. Methods
Two automated sampling systems were developed and installed on commercial boats. An enhanced monitoring instrument package was installed on a pontoon boat owned and operated by the University of Houston (UH). A commercial shrimp boat and the UH Pontoon Boat (UHPB) operated throughout Galveston Bay, while a second commercial boat, the Red Eagle, primarily operated offshore of Galveston Island in the Gulf of Mexico. Free-release balloon-borne ozonesondes were launched from the UHPB within Galveston Bay and, on select occasions, the Red Eagle in the Gulf of Mexico.

a. Autonomous instrument packages. The automated instrument packages on the commercial boats included a 2B Technologies model 205 ozone analyzer, a global positioning system (GPS), and a ruggedized industrial computer. A compact, all-in-one weather station was installed to measure temperature, relative humidity, pressure, and wind speed and direction. An internal digital compass with GPS data corrected the winds for the boat’s motion. This equipment was installed into a light-colored (yellow) weatherproof enclosure to protect the instrumentation and reduce heat. Additional insulation and a radiant barrier reduced solar heating. A thermodiagnostic heat exchanger attached to the enclosure further reduced heat and maintained a stable environment for the instrumentation. Desiccant bags helped control internal relative humidity. This enclosure was secured to the boat exterior on top of the cabin. A Teflon sample line was run from the ozone monitor to an elevated location on each boat for the sample inlet. A Teflon rain shroud prevented water from entering the 90-mm Teflon particle filter before being sampled. The relatively large area of the filter required less frequent access to the commercial boats and equipment for filter changes.

b. Boat platforms. The three boats with instrument packages are shown in Fig. 1. A commercial shrimp boat (Fig. 1a) had an autonomous mobile sampling package and a ceilometer installed onto the roof of the pilothouse. The Vaisala CL-51 ceilometer uses aerosol gradients to derive a vertical profile of boundary layers. The ceilometer on UHPB stopped operating on 30 August 2021, at which point the shrimp boat ceilometer was moved to the UHPB.
A dedicated high-output marine alternator and battery were installed for additional power to operate the science equipment while underway. The dock of the shrimp boat was at Smith Point (29.546, −94.782) on the east side of Galveston Bay. The shrimp boat operated in Galveston Bay on 22 occasions, averaging six outings per month.

The Red Eagle (Fig. 1b) is a 30-m-long crew/utility vessel with two 40-kW three-phase power generators. The typical operating profile for the Red Eagle was to depart the Galveston docks to service larger vessels in the Galveston Anchorage and Lightering areas up to 90 km offshore in the Gulf of Mexico. Over 50 tankers and cargo ships routinely wait to enter the Houston Shipping Channel at the anchorage locations offshore of Galveston. The more distant lightering area is designated for cargo (e.g., oil) transfer between ships. Occasionally, the Red Eagle conducted operations as far as 200 km to the southwest or traveled north into Galveston Bay and through the ship channel to the port of Houston. The Red Eagle operated any hour of the day and in nearly all weather conditions.

The UHPB, a 6-m pontoon boat (Fig. 1c), was outfitted with an instrument package and deployed on selected days in July–October 2021 throughout Galveston Bay. The onboard instruments included Thermo Scientific 49c ozone and 49i O₃ (O₃ + NO₂; added 17 September) analyzers, a Vaisala CL-51 ceilometer, and an Airmar 220wx all-in-one GPS and meteorological sensor. The Airmar and the inlet for the trace gas analyzers were mounted to a pole 1 m above the canopy of the UHPB along the side of the boat to sample marine air unaffected by the boat and its onboard generator. The UHPB had a sampling bias toward areas closer to the marina (west Galveston Bay), with operational times typically between 0800 and 1600 central daylight time (CDT) on account of fuel limitations, personnel constraints, and water conditions.

During the campaigns, 37 ozonesondes were launched from the UHPB (30) in Galveston Bay and the Red Eagle (7) in the Gulf of Mexico offshore of Galveston Island to determine the vertical distribution of ozone and the marine boundary layer height. In combination, the three boat platforms extensively sampled Galveston Bay and the offshore waters of the Gulf of Mexico. When the boat platforms were not mobile, they were connected to shore power, which allowed for continuous data collection.

<table>
<thead>
<tr>
<th>Episode No.</th>
<th>High O₃ episodes (2021)</th>
<th>Peak 1-h O₃ (ppbv)</th>
<th>MDA8 [O₃] (ppbv)</th>
<th>Wind conditions</th>
</tr>
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<td></td>
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<td>Onshore</td>
<td>Offshore</td>
<td>Onshore</td>
</tr>
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<td>130</td>
<td>98</td>
<td>97</td>
</tr>
<tr>
<td>2</td>
<td>25–26 Aug</td>
<td>109</td>
<td>67</td>
<td>78</td>
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<tr>
<td>3</td>
<td>6–11 Sep</td>
<td>105</td>
<td>92</td>
<td>89</td>
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<td>17–19 Sep</td>
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<tr>
<td>6</td>
<td>6–9 Oct</td>
<td>130</td>
<td>112</td>
<td>92</td>
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3. Results

a. High offshore ozone. The boat instrument packages operated continuously from July to October 2021, during which 609 mobile hours were accumulated between the three boats over Galveston Bay and the Gulf of Mexico, constituting 134 unique trips. Six high ozone episodes occurred where either a boat or an HGB region monitor exceeded the current NAAQS ozone standard (MDA8 [O₃] > 70 ppbv). The prevailing wind conditions, peak 1-h ozone, and MDA8 ozone for each episode are shown in Table 1.

Fig. 2. Ozone mixing ratios along the tracks of the three instrumented boats for six high ozone events during the GO3 and TRACER-AQ 2021 field campaigns.
The 1-h ozone mixing ratios reached above 70 ppbv on five of the six episodes, potentially contributing to exceedances of the 8-h ozone standard at monitors in the HGB region. During four episodes (all but episodes 1 and 2), ozone mixing ratios above 70 ppbv were observed over Galveston Bay and the Gulf of Mexico. Episode 1 was an example of a high ozone episode driven by light synoptic forcing and bay breeze recirculation that led to high ozone over Galveston Bay that likely did not extend to the Gulf of Mexico (see the online supplemental material).

Episodes 3–6 had high ozone over the Gulf of Mexico and Galveston Bay (Fig. 2) driven by synoptic-scale frontal and tropical system passages. Episode 4 was a unique case where light winds on the lee side of the tropical system, Hurricane Nicholas, produced a high ozone episode in the HGB region that air quality models did not forecast. This event may have been driven by light northerly winds resulting from cutting off the westward extension of the high pressure center of the Bermuda high. Episode 4 was a localized coastal event, with all monitoring stations exceeding the 8-h ozone standard <10 km from Galveston Bay or the Gulf of Mexico.

**b. Wind/ozone roses.** Flow reversals associated with mesoscale circulations (i.e., gulf and bay breezes) driven by differential heating of the land and water is a common mechanism for nearshore monitoring locations in the HGB region (Banta et al. 2005) and elsewhere (Stauffer et al. 2015; Sullivan et al. 2019) exceeding the 8-h ozone standard. Observations from the 2021 field campaigns supported this paradigm, with the highest 5-min averaged ozone concentrations at all three boats correlated with wind directions from overwater (Fig. 3).

Periods of ozone exceeding 70 ppbv at the UHPB while docked generally had winds from the east/southeast (E/SE) in the early to midafternoon. The UHPB dock location on the west-northwest (WNW) side of Galveston Bay puts the water in the upwind direction for these observations, and the timing coincides with a typical bay breeze flow reversal from offshore to onshore winds. The shrimp boat docked at Smith Point on the east side of Galveston Bay. It recorded the majority of >70-ppbv ozone observations coming from the northwest (NW) direction, which suggests contributions from the HGB region that were transported over Galveston Bay. The *Red Eagle* observed a distinctly bimodal distribution...
of >70-ppbv ozone in the 5-min data when docked on the north side of Galveston Island. High ozone values detected at the Red Eagle came from the north/northeast (N/NE) and Galveston Bay in the late morning and afternoon and from the south/southwest (S/SW) and the Gulf of Mexico in the late afternoon and early evening, the latter associated with late-developing gulf breezes.

c. Case days. For three high ozone episodes, we performed a detailed analysis of the observations from the sampling boats, due to their air quality relevance.

1) 9 September 2021. Amid six continuous MDA8 ozone exceedance days in the HGB region, air quality forecasts for 9 September 2021 predicted high ozone offshore of Galveston Island in the Gulf of Mexico and in Galveston Bay. The Red Eagle was chartered to assess the levels of ozone encountered in the Gulf of Mexico while deploying to the Galveston Anchorage and Lightering areas, approximately 16 and 42 km offshore, respectively.

The UHPB observed a relatively homogenous spatial distribution of ozone mixing ratios > 60 ppbv over the western half of Galveston Bay from approximately 1000–1630 CDT. In the Gulf of Mexico, the Red Eagle traveled 42 km offshore toward the ship lightering area and observed 1-min ozone mixing ratios as high as 110 ppbv (Fig. 4). An ozonesonde was launched from the deck, and >100 ppbv of ozone well-mixed within a shallow (370 m) marine boundary layer was observed.

Eight stationary monitoring sites in the HGB region exceeded the MDA8 [O₃] standard on 9 September 2021; the highest among them was the coastal Texas Commission on Environmental Quality (TCEQ) C1607 Oyster Creek site, which had an MDA8 [O₃] of 81 ppbv. The 24-h wind run at the C1607 Oyster Creek site (Fig. 5) shows a rotation of the
winds from northwesterly in the morning, associated with a land breeze and lower ozone values, to easterly in the afternoon, associated with a sea breeze, which brought higher ozone values to the site. Distinctive recirculation patterns in coastal areas can often be observed in hourly wind run patterns on days exceeding the ozone standard (Levy et al. 2008; Li et al. 2020). In the Gulf offshore of Galveston Island, the high ozone plume confined within the shallow marine layer likely had contributions from urban ozone and precursor emissions being transported throughout the morning. With the midday shift to easterly winds, this ozone-rich plume over the Gulf was then likely transported to the coastal monitors that exceeded the ozone standard (C1607 Oyster Creek, C620 Texas City, C1034 Galveston, and C1016 Lake Jackson). However, a different mechanism influenced inland sites with ozone exceedances, which were affected by long-range transport of VOC-rich air masses, where midday convection allowed for the mixing of the nocturnal residual layer into the boundary layer (Liu et al. 2023; Soleimanian et al. 2023; Sullivan et al. 2023). The inland exceeding monitors did not observe the same increase due to the shift to easterly winds, given the lower ozone concentrations over Galveston Bay compared to offshore of Galveston in the Gulf of Mexico. While subsidence may have played a role in the shallow depth of the marine boundary layer over the Gulf, there is no sign that downward transport and convective mixing of residual layer air into the boundary layer played the same role in the exceedances at the coastal monitors as it did for the inland monitors. Further details about the measurements made on 9 September 2021 are provided in the supplemental material.

2) 17 September 2021. Following the passage of Hurricane Nicholas 3 days prior, a high ozone episode began on 17 September 2021 that was not well forecast by air quality models such as GOES-CF. Ozone mixing ratios > 90 ppbv (1-min average) were observed over wide areas of Galveston Bay. On the same day in the Gulf of Mexico, the Red Eagle observed ozone < 40 ppbv offshore while headed to service a commercial vessel at ~1200 CDT. Approximately 5 h later, while heading back to the dock in Galveston, ozone offshore had increased to over 70 ppbv.

A unique feature of this episode was that the locations that exceeded the MDA8 [O₃] standard were all coastal monitors. On 17 September, the UHPB observed the highest 1-h ozone average in the HGB region, recorded at 92 ppbv over Galveston Bay, as seen in Fig. 6. The high ozone over the bay likely resulted from light northerly winds in the HGB region due to being on the lee side of Hurricane Nicholas, which advected ozone precursor emissions over water.

Figure 7 shows the ozone mixing ratios at the three boat platforms and four TCEQ monitoring sites for 17 September. The coastal Texas City (C620) monitor exceeded the MDA8 [O₃] standard.
standard, while the three inland monitors are characteristic of the lower ozone observed inland. The differences in the diurnal patterns illustrate the strong gradients of ozone concentrations observed inland compared to along the coast and overwater during this ozone episode.

3) 7 October 2021. The state monitoring agency TCEQ designated 7 October 2021 as an Ozone Action Day, a day forecast to have conditions favorable for ozone production. The HGB region was in a postfrontal environment with light offshore winds and abundant sunshine. The UHPB recorded the highest overwater ozone values (>130 ppbv) during the campaign in the W/NW area of Galveston Bay on the afternoon of 7 October. The approximate heights of the retrieved boundary layers from the ceilometer on the UHPB show the diurnal evolution of the boundary layer over and around Galveston Bay on 7 October 2021. The overnight period to approximately 2 h after sunrise (∼0000–1400 UTC) shows a stratification with the nocturnal boundary layer measuring between 500 and 1000 m and the residual layer between 1500 and 2000 m. Just after sunrise, a shallow marine boundary layer developed, measuring as low as 80 m to begin the day, and appeared to trap surface emissions. This layer developed as the convective boundary layer with surface heating, growing to ∼1700 m,
approximately 500 m taller than a typical October day in 2021. Just before sunset, the convective boundary layer was cut off from the surface with the redevelopment of the nocturnal boundary layer (Fig. 8).

High NO₂ values were observed over Galveston Bay on this day (Fig. 9), in both broad and discrete plumes. The initial 8-km transect across the western portion of Galveston Bay, denoted with a black arrow in Fig. 9, showed area-wide elevated levels of NO₂ that coincided with the minimum values of observed ozone and boundary layer height during the deployment.

The time series of ozone, NO₂, and O₃ in Fig. 10 from the UHPB deployment on 7 October 2021 shows the relationship between the trace gases. Initially, the NO₂ was elevated over a broad area of Galveston Bay, possibly resulting from morning rush hour and ship emissions being trapped by a low marine boundary layer while ozone was suppressed. During this initial transect, the O₃ values did not show as much spatial variability as ozone or NO₂. During the midmorning to afternoon, NO₂ mixing ratios generally decreased while photolysis rates and ozone mixing ratios increased.

Occasionally, NO₂-rich exhaust plumes were encountered, often while nearby or crossing the shipping channels, coinciding with a precipitous drop in ozone due to titration. Figure 10 shows two instances that occurred during the 1400–1500 CDT hour, while the UHPB was transiting back to dock. During the first event, as much as 25 ppbv of ozone was titrated while crossing the Houston Shipping Channel. A second ozone titration event occurred while traveling near a large recreational vessel and generated a similar response in ozone, titrating approximately 22 ppbv. Notably, there is little response to the emissions when examining the O₃ concentrations during these events. These observations illustrate the value of considering the total reservoir of O₃ (O₃ + NO₂), as titration and photolysis cause an exchange between species over the water.

4. Conclusions

The installation of air quality instruments onto three boats for measurements spanning from July to October 2021 resulted in a robust dataset of ozone, O₃ (from which NO₂ was calculated), boundary layer, and meteorological parameters. Collectively, the boats made
134 trips logging >600 mobile hours, including 37 ozonesonde launches. Six high ozone episodes are reported here, and detailed analyses are described for three of them. Ozone varied spatially across Galveston Bay and the Gulf of Mexico with considerable heterogeneity. Surface ozone mixing ratios routinely above 70 ppbv and at times greater than 100 ppbv were observed over the Gulf of Mexico and Galveston Bay. A poorly forecast coastal high ozone event following the passage of a tropical system was observed over Galveston Bay and the Gulf of Mexico. During the periods when the UHPB had \( O_3 \) and ozone measurements, an estimate of \( NO_2 \) frequently showed both isolated and expansive plumes in Galveston Bay. As a result of the partitioning between ozone and \( NO_2 \), apparent spatial gradients in ozone were less pronounced when examining \( O_3 \) than ozone alone. This emphasizes the importance of

![Ceilometer backscatter data plotted vs altitude on 7 Oct 2021 showing a low mixing layer trapping emissions in the afternoon.](image)

![Fig. 9. (left) Ozone, (middle) \( NO_2 \), and (right) \( O_3 \) mixing ratios along the path of the UHPB on Galveston Bay for 7 Oct 2021. The black arrows highlight the initial 8-km transect across Galveston Bay with broadly elevated \( NO_2 \).](image)
characterizing the atmospheric processes and emissions sources involving ozone and NO$_2$
in a marine environment near a large urban and industrialized region such as the Houston
metroplex, where a variety of emission sources can be influential, and ozone titration plays
a prominent role at times.

Historically, air quality data have not been routinely collected over the water. However,
observations are critical to evaluate and constrain photochemical models used for forecast-
ing air quality, especially in densely populated coastal regions such as the HGB area. The
overwater data collected during the 2021 field campaigns has already begun to be used
to evaluate model accuracies and identify improvements (Li et al. 2023; Liu et al. 2023;
Soleimanian et al. 2023). Additionally, current and future satellite missions focusing on
tropospheric air quality can be aided by the wide-ranging dataset provided by this over-
water campaign.

Acknowledgments. The State of Texas Air Quality Research Program (AQRP; Project 20-004) and the
Texas Commission for Environmental Quality (TCEQ; Grants 582-21-22179-015 and 582-22-31913-020)
provided funding for this project. The findings, opinions, and conclusions are the work of the authors
and do not necessarily represent findings, opinions, or conclusions of the AQRP or the TCEQ. We are
grateful for our supportive partnership with Ryan Marine. We also thank the Department of Energy
(DOE) Atmospheric Radiation Measurement (ARM) TRACER and NASA TRACER-AQ teams, who
provided forecasts during September 2021 and whose campaigns helped make this work possible.

Data availability statement. Ozone sonde data for this project are available on the NASA TRACER-AQ
data archive (https://www-air.larc.nasa.gov/missions/tracer-aq/). Other data for this project are available
upon request from the authors.
References


