Mobile Laboratory Measurements of High Surface Ozone Levels and Spatial Heterogeneity During LISTOS 2018: Evidence for Sea Breeze Influence

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Abstract The Long Island Sound Tropospheric Ozone Study (LISTOS) was organized to investigate ozone formation and transport in the New York City metropolitan area and locations downwind. During LISTOS, the University at Albany Atmospheric Sciences Research Center (ASRC) mobile laboratory was used for measuring surface O₃, NO₂, and aerosol number and mass concentration. Sharp O₃ concentration gradients, with ΔO₃ Δy⁻¹ over 15 ppb km⁻¹, were measured both at and near the land-water interface and on the highway on days characterized by high regional O₃ concentrations. These large O₃ gradients at or near the land-water interface, and in air masses relatively low in NO₂, are shown to be influenced in part by the transport of highly oxidized air masses via sea breeze circulation and convergence with gradient flow. On the highway under regionally high O₃ concentrations, strong anticorrelation (R² = 0.78, p < 0.05) between O₃ and NO₂ and an absolute slope less than 1 suggested that O₃ concentrations (O₃ + NO₂) increased with increasing NO₂. Overall, the on-road measurements made during LISTOS help to better characterize the interaction between the emitted pollution and the meteorological conditions on Long Island, thereby having potential policy implications.

Plain Language Summary Ozone pollution is a significant problem for the New York City (NYC) Metropolitan Area, which has been classified by the U.S. Environmental Protection Agency as being in noncompliance with the National Ambient Air Quality Standard for ozone. The southern coast of Connecticut is the most severely affected by ozone pollution, which is produced in the atmosphere as it travels downwind from emission sources of precursor gases like oxides of nitrogen and volatile organic compounds. The impact of ozone on a given location involves a complex interplay of emissions, meteorology, and chemistry. Our study explored aspects of this interplay on several polluted days in summer 2018 using a Dodge Sprinter van mobile laboratory equipped with instrumentation to measure ozone, one of the critical oxides of nitrogen, and other parameters. Some of the analysis days yielded significant and rapid changes in ozone concentration near the south or north shore of Long Island. Our results suggest that sea breeze winds can greatly influence ozone concentrations near the coast in some cases. Understanding when and how the sea breeze affects air quality in regions downwind of NYC and other coastal metropolitan areas will help efforts to improve air quality in these locations.

1. Introduction

Ground-level ozone (O₃) is a regional pollutant with an 8-hr standard of 70 parts per billion (ppb), as mandated by the U.S. Environmental Protection Agency (US EPA, 2017). O₃ is mainly formed due to photochemical reactions involving nitrogen oxides (NOₓ) and volatile organic compounds (VOCs; National Research Council, 1991; Gaudel et al., 2018; Ninneman et al., 2019). High ground-level O₃ concentrations contribute to photochemical smog and negative human health and ecosystem impacts (Karnosky et al., 2007; Martins et al., 2012). Regional surface O₃ is related to (1) precursor emissions and mixing ratios, (2) photochemistry, and (3) meteorological conditions, including temperature, wind speed, and planetary boundary layer (PBL) height (Bloomer et al., 2009; Banta et al., 2011; Martins et al., 2012). Factors influencing local surface O₃ concentrations are more complex for coastal areas affected by local-scale phenomena such as sea, bay, or lake breezes (hereafter sea breeze; Banta et al., 2005; Tucker et al., 2010; Martins et al., 2012).
Sea breezes are formed due to a pressure difference between warm, continental air and cool, marine air (Meir et al., 2013; Sills et al., 2011; Wentworth et al., 2015). Previous studies have indicated that sea breezes contribute to poor air quality (Loughner et al., 2014) and often lead to dramatic variations in O₃ levels over short time periods (Hastie et al., 1999; Lennartson & Schwartz, 2002; Loughner et al., 2014; Stauffer et al., 2015; Wentworth et al., 2015; Blaylock et al., 2017; Mazzuca et al., 2019). The main characteristics that cause sea breeze circulation contributions to poor air quality are (1) sunny conditions, (2) relatively low synoptic wind speeds, (3) a capping inversion over the water, and (4) a period of precursor pollutant transport occurring from the land to the sea, where O₃ is photochemically produced and undergoes less depositional loss (Hauglustaine et al., 1994; Martins et al., 2012), followed by transport back to the land by the developing or fully developed sea breeze (Mazzuca et al., 2019; Wentworth et al., 2015). The influence of the sea breeze on O₃ concentrations depends on the timing of the initiation and propagation of the sea breeze front (Martins et al., 2012). Sea breeze fronts are generally formed in late morning or during the afternoon, which allows time for the accumulation of precursors and photochemical production of O₃ in the shallow marine boundary layer (Martins et al., 2012; Oh et al., 2006). Previous studies assessing the impact of the sea breeze circulation on inland O₃ concentrations have been conducted at several coastal areas throughout the United States, including the Chesapeake Bay (Loughner et al., 2014; Mazzuca et al., 2019; Stauffer et al., 2015), the Great Lakes region (Hastie et al., 1999; Lennartson & Schwartz, 2002; Wentworth et al., 2015), the Salt Lake Valley (Blaylock et al., 2017), and the Houston area (Banta et al., 2005). In addition, the sea and shore breeze circulations affecting the coast of Long Island (LI) Sound, the New York City (NYC) Harbor area, and Brooklyn and Queens on LI, New York (NY), are well characterized (Colle & Novak, 2010; Meir et al., 2013; Thompson et al., 2007). However, to the best of our knowledge, the influence of these sea and shore breeze circulations on LI O₃ levels in low to moderate NOₓ conditions has not been examined by previous studies.

The NYC metropolitan area has abundant NOₓ and VOC emissions (Civerolo et al., 2017; McDonald et al., 2018). Consequently, summertime O₃ concentrations exceeding the 70 ppb National Ambient Air Quality Standard (NAAQS) can frequently occur in the NYC metropolitan area and locations downwind (Connecticut, Rhode Island, Massachusetts, eastern LI, etc.; Zhang et al., 1998; Zhao et al., 2019). In these areas, NOₓ and VOC emissions interact with sea/shore breeze circulations to yield a complex ozone problem requiring further investigation. Therefore, the Long Island Sound Tropospheric Ozone Study (LISTOS) was organized by Northeast States for Coordinated Air Use Management (NESCAUM, http://www.nescaum.org/documents/listos) to examine ozone formation and transport in the NYC metropolitan area and locations downwind. Several institutions and agencies participated in LISTOS, including NASA, EPA, NOAA, local state agencies, and numerous other research institutions and air quality management agencies (https://wwwair.larc.nasa.gov/missions/listos/index.html). As one of the LISTOS participants, the University at Albany Atmospheric Sciences Research Center (ASRC) deployed its mobile laboratory to (1) measure the surface NO₂, O₃, and aerosol number and mass concentration during high-O₃ events and (2) study the transport of pollutant plumes.

2. Methodology

2.1. Study Area

The measurements were made on LI and the northern suburbs of NYC from 24 June 2018 to 16 August 2018. LI is located east of the borough of Manhattan, and the two most-populated of the five boroughs of NYC (Brooklyn and Queens) are located on the western end of the island (Figure S1 in the supporting information). On-road measurements were made on 6 days when version 5.2 of the Community Multiscale Air Quality (CMAQ) model predicted an O₃ exceedance somewhere on LI (30 June, 1 July, 2 July, 10 July, 16 July, and 6 August), and the mobile laboratory was driven to those locations. Several on-road measurements were also made on O₃ nonexceedance days to determine typical summertime air pollutant concentrations on LI (24 June, 11 July, 15 July, and 5 August). For the remaining days, the mobile laboratory was parked at Flax Pond Marine Laboratory for continuous measurements. In this study, on-road measurements from four of the six O₃ exceedance days are analyzed in detail. Specifically, the days of interest were (1) 30 June and 1 July, which were characterized by significant O₃ spatial gradients influenced or possibly influenced by the sea breeze circulation, and (2) 10 July and 16 July, which were characterized by more typical O₃ spatial...
gradients attributable to variability in NO$_2$. The 2 July on-road measurements were excluded due to their similarity to 10 July, while the 6 August on-road measurements were excluded due to the combined influence of the sea breeze and complicated regional O$_3$ exceedance conditions.

### 2.2. Mobile Laboratory Instruments and Other Data Sources

The ASRC mobile laboratory is a modified 2007 Dodge Sprinter van containing (1) an Aerodyne high-resolution time of flight aerosol mass spectrometer (HR-ToF-AMS), used for measuring the nonrefractory submicron aerosol mass concentration (DeCarlo et al., 2006; Drewnick et al., 2005); (2) a TSI water Condensation Particle Counter (CPC Model 3785), used for measuring the aerosol number concentration; (3) one Thermo Scientific MIE pDR-1500, which was used to (a) provide an estimate of aerosol mass concentration in the sample line that fed the HR-ToF-AMS and (b) draw a larger flow from the mobile laboratory aerosol sample system, which served to reduce the sample line residence time for the HR-ToF-AMS; (4) two O$_3$ sensors (Teledyne API Model 430 and 2B Model 205); (5) one NO$_2$ sensor (Teledyne API Model 500U), which utilized a patented Cavity Attenuated Phase Shift (CAPS) technique and was thus unlikely subject to interferences from organic nitrates, HNO$_3$, and among others, (http://www.teledyne-api.com/products/nitrogen-compound-instruments/1500u); (6) VOC canister samplers; (7) an eight-battery power supply system with 13.25 kWh of power and a lifetime of approximately 7 hr for this set of instruments; and (8) a GPS. The mobile laboratory had one inlet for gases and one inlet for aerosols mounted over the driver's seat to sample the slipstream as the vehicle was in motion. A URG PM cyclone (URG-200-30EC) followed the aerosol sample inlet to remove large aerosol particles and liquid drops (>2 μm) at a flow rate of 56 LPM. After the cyclone, a silica gel dryer was used to dry the aerosol (RH < 40%) before going to the aerosol instruments' inlets (Zhang Lance, Freedman, et al., 2019). The uncertainty (1σ) of the submicron aerosol mass concentrations measured by HR-ToF-AMS is roughly 25% (Aiken et al., 2008; Bahreini et al., 2009; Canagaratna et al., 2007; Canagaratna et al., 2015; Corbin et al., 2015). The uncertainties (2σ) of the gas monitors—the TAPI model 430 O$_3$ sensor, the 2B Model 205 O$_3$ sensor, and the TAPI Model 500 U NO$_2$ sensor—are roughly 15%, 10%, and 20%, respectively, based on the comparison with the New York State Department of Environmental Conservation (DEC) instruments at Flax Pond when the mobile laboratory was parked at Flax Pond Marine Laboratory (Figure S2). More details regarding the ASRC mobile laboratory can be found elsewhere (Zhang Lance, Brandt, et al., 2019). The gas sensors report mixing ratios in units of ppb. In this study, mixing ratios were described as concentrations, consistent with EPA terminology (https://www3.epa.gov/region1/airquality/avg8hr.html).

During the on-road measurements, the HR-ToF-AMS was only operated in “V” mode with a time resolution of 30 s. The averaging times for the CPC, gas sensors, and VOC canister samples were set to 30 s, 1 min, and about 1 hr, respectively. For consistency, the final average time resolution reported and analyzed for all continuous instruments was set to 1 min, yielding a spatial resolution of at least 1–1.7 km for on-road deployments at normal speeds. The HR-ToF-AMS data were analyzed using SQUIRREL v1.59D and PIKA v1.19 (Allan et al., 2003; Canagaratna et al., 2007). In this software, the default relative ionization efficiency (RIE) values were used (4 for ammonium, 1.1 for nitrates, 1.2 for sulfate, 1.3 for chloride, and 1.4 for organic aerosol compounds, hereafter organics; Zhang et al., 2005), with a collection efficiency (CE) of 0.5 for all aerosol chemical compounds (Sun et al., 2011). Ionization efficiency (IE) calibrations of HR-ToF-AMS were done before and after the field measurements using 300 nm ammonium nitrate particles (Canagaratna et al., 2007). These two IE values were very similar, and the average IE value was used for analyzing the measurement periods. The weekly O$_3$ and NO$_2$ data were rescaled based on comparison with the DEC instruments, also reported with a time resolution of 1 min. Figure S2 shows an example of the comparison between the ASRC monitors with the DEC ones during the second week of July (9 July 2018 to 15 July 2018). In general, high correlation coefficients ($R^2 > 0.80$) were obtained between ASRC monitors and DEC ones with slopes near to 1. The DEC instruments were regularly calibrated using known concentrations of O$_3$ and NO$_2$.

To complete the analysis, this study also used (1) New York State Mesonet data for the lidar wind vertical profiles (Yang & Min, 2018, www.nysmesonet.org/data/), (2) New York State DEC air quality data for O$_3$ concentration and PM$_{2.5}$ mass concentration (http://www.nyairnow.net/), and (3) TROPOMI satellite data for the tropospheric NO$_2$ column concentration (Van Geffen et al., 2019, http://www.temis.nl/airpollution/no2.html). The locations of Mesonet sites and DEC O$_3$ sites are shown in Figure S1.
2.3. Sea and Shore Breeze Analysis

Part of the methodology presented by Sills et al. (2011) and Wentworth et al. (2015) for identifying lake-breeze circulations in the Great Lakes region was used to identify sea and shore breeze circulations off the LI coast. This was done to assess whether sea and shore breeze circulations may have contributed in part to the sharp spatial gradients in LI O₃ levels observed during selected on-road measurement days.

The approach taken to identify sea and shore breeze circulations consisted of three steps. First, consistent with Sills et al. (2011) and Wentworth et al. (2015), the daily visible satellite imagery from the National Aeronautics and Space Administration Earth Observing System Data and Information System (NASA EOSDIS) Worldview (https://worldview.earthdata.nasa.gov/) was used to help manually detect sea and shore breeze circulations. Then, two other items were used for identifying a sea or shore breeze circulation that were not employed by Sills et al. (2011) and Wentworth et al. (2015). These included (1) 24-hr back trajectories from the NOAA Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model (https://ready.arl.noaa.gov/HYSPLIT.php) and (2) daily lidar vertical profiles with wind barbs included (www.nysmesonet.org/data/). However, it is noteworthy that HYSPLIT back trajectories may have limitations in their ability to accurately represent the sea breeze circulation (https://ready.arl.noaa.gov/hypub/limitations.html). This was why the other data sets indicated above were also used to identify the formation of sea or shore breeze circulations. Since multiple sea and shore breeze circulations can develop off the coast of LI (e.g., Meir et al., 2013; Thompson et al., 2007), back trajectories were constructed for six different locations on LI using 3-km resolution meteorological data from the High-Resolution Rapid Refresh (HRRR) model. The six locations were (1) southwestern LI (40.59°N, 73.97°W), (2) south-central LI (40.74°N, 73.10°W), (3) southeastern LI (40.89°N, 72.37°W), (4) northeastern LI (41.08°N, 72.44°W), (5) north-central LI (40.94°N, 73.13°W), and (6) northwestern LI (41.08°N, 73.68°W) (Figure S1). The lidar vertical profiles were generated using data from the six profiler sites on or near LI that are maintained by the New York State Mesonet (NYSM). The six LI profiler sites are located in Staten Island, Bronx, Queens, Wantagh, Stony Brook, and East Hampton (Figure S1). Finally, the images from the steps outlined above were visually inspected to identify clear evidence of a sea or shore breeze circulation, and only the images that support the formation of a sea and/or shore breeze circulation are presented and discussed here. Ultimately, it was concluded that a sea and/or shore breeze circulation formed if there was (1) an abrupt shift in the wind direction from offshore to onshore and/or (2) a line of cumulus clouds virtually parallel to the LI shoreline that did not form due to a synoptic frontal passage or a gust front (e.g., Sills et al., 2011; Wentworth et al., 2015).

3. Results

The observed 8-hr average O₃ concentration on LI and the NYC metro area during the measurement period (24 June 2018 to 16 August 2018) is shown in Figure 1a. During this period, there were 6 days where the O₃ concentration exceeded the 70 ppb NAAQS - 30 June to 2 July, 10 July, 16 July, and 6 August (Figure 1a).
On-road measurements were conducted for all of these O₃ exceedance days (30 June, 1 July, 2 July, 10 July, 16 July, and 6 August), and the results from four representative deployments (30 June, 1 July, 10 July, and 16 July) are analyzed and discussed below.

Figure 1b shows the average diel variation of O₃ at Queens College on LI for the O₃ exceedance days (30 June, 1 July, 2 July, 10 July, 16 July, and 6 August) and the remaining O₃ non-exceedance days. The average diel cycle of O₃ on the non-exceedance days is typical of an urban/suburban site in O₃ attainment (Martins et al., 2012). Specifically, O₃ concentrations increased during the morning due to photochemistry at a rate of 4.0 ppb hr⁻¹ (Figure 1b). In contrast, the average diel cycle of O₃ on the exceedance days shows a higher growth rate of 8.0 ppb hr⁻¹, with the concentration peak occurring at approximately 15:00 Eastern Daylight Time (EDT; Figure 1b).

3.1. Ozone Spatial Heterogeneity Influenced by Sea Breeze

Sharp O₃ spatial gradients were observed through on-road measurements near LI coastlines on 30 June and 1 July, when maximum O₃ concentrations exceeded 100 ppb (Figures 2a–2b). The O₃ gradient (ΔO₃ Δy⁻¹) was found to be (1) 18 ppb km⁻¹ at Robert Moses State Park (RMSP) on the south shore of LI on 06/30...

Figure 2. The spatial distribution of the on-road O₃ concentration on (a) 30 June (15:20–16:20, depart from Flax Pond at 15:20 EDT, encountered O₃ gradient at around 16:15, and arrived at RMSP at 16:20) and (b) 1 July (15:10–16:30, depart from Flax Pond at 15:10 EDT, encountered O₃ gradient at around 16:35, and arrived at Sands Point at 16:50) (the arrows indicate the locations mentioned in the text. Port W = Port Washington; RMSP = Robert Moses State Park; SP = Sands Point. The blue boxes indicate the location of the O₃ gradients. The blue text indicates the timing and magnitude of the O₃ gradient).
These large \( O_3 \) spatial gradients were missed in the hourly \( O_3 \) forecasts made by Version 5.2 of the Community Multiscale Air Quality (CMAQ) model (Figure S3; Appel et al., 2017), which was run at a relatively coarse 15-km resolution. Model simulations with a finer spatial resolution of about 1–2 km would be required to potentially capture such a large spatial gradient. In addition, consistently low to moderate \( NO_2 \) concentrations were measured on 30 June and 1 July at the times when there were large \( O_3 \) and \( Ox \) spatial gradients (Figures S4, 3, and 4). This suggests that the dramatic \( O_3 \) spatial variation on those days was influenced by factors other than \( NO-NO_2-O_3 \) cycling kinetics, which are discussed in section 3.2. Meteorological data presented below suggest that an important factor influencing the large \( O_3 \) spatial variability in these cases is the sea breeze circulation, a local-scale process. Due to the sharpest \( O_3 \) gradients occurring at different locations on LI (south shore on 30 June, and north shore on 1 July), the influence of the sea and sea/shore breeze for
the south and north shore, respectively, will be discussed using the 30 June and 1 July on-road measurements as case studies.

3.1.1. Case Study A—South Coast (30 June)

Figure 3a shows the time series of O₃, NO₂, and the HR-ToF-AMS measured concentrations of organics, NO₅, SO₄, and NH₄ during the on-road measurement period on 30 June. As shown in Figures 2a and 3a, the O₃ concentration dramatically increased from 76 to 112 ppb in about 2 km before arriving at RMSP on the LI south shore, yielding the aforementioned ΔO₃ Δy⁻¹ value of 18 ppb km⁻¹. Additionally, enhanced gradients for organics, SO₄, NO₂, and NH₄ of 0.6, 0.4, 0.1, and 0.2 μg m⁻³ km⁻¹, respectively, were simultaneously found just before arrival at RMSP (Figure 3a). The enhanced O₃ concentrations persisted during the stationary 1-hr sampling time period at RMSP (about 110 ppb) and decreased to approximately 60 ppb when the van departed from RMSP and began driving back to Flax Pond (Figure 3a). Similar trends were observed for the aerosol compounds (Figure 3a). Due to the combination of (1) the low NO₂ concentrations at the time of the dramatic increase in O₃, (2) the NYSM lidar signals (Figure S5), and (3) HYSPLIT back trajectories (Figure S6), the enhanced O₃ and aerosol concentrations at RMSP, and in particular the rapid increase in concentrations over a relatively short distance on 06/30, are likely attributable in part to the development of a sea breeze circulation.

Figure S5 shows the lidar vertical profiles for Staten Island (Figure S5a), Wantagh (Figure S5b), East Hampton (Figure S5c), Bronx (Figure S5d), Queens (Figure S5e), and Stony Brook (Figure S5f), which demonstrate that a sea breeze circulation developed on LI at different times on the afternoon of 30 June. For example, at approximately 12:00 EDT on 30 June, the wind direction shifted from offshore to onshore and persisted for several hours at Wantagh (approximately 22 km west northwest of RMSP), consistent with the formation of a sea breeze circulation (Figure S5b). The influence of the sea breeze circulation was also supported by the enhanced sea salt aerosol signal (NaCl and I) detected by the HR-ToF-AMS (Figure 3b). This was determined by taking the difference of the signals in the “open” and the “closed” (or “background”) mass spectrum modes of the HR-ToF-AMS. However, due to the semirefractory nature of NaCl and I (Drewnick et al., 2015), it was difficult to get their RIE to quantify their mass concentrations accurately. Additional evidence for the sea breeze formation comes from the 24-hr HYSPLIT back trajectories for northwestern (Figure S6a), north-central (Figure S6b), northeastern (Figure S6c), southwestern (Figure S6d), south-central (Figure S6e), and southeastern (Figure S6f) LI ending at 14 UTC (10:00 EDT) on 30 June and for the same locations ending at 20 UTC (16:00 EDT, Figure S7). In particular, the back trajectory for south-central LI (Figure S6e) indicates that inland emissions were transported out over the Atlantic Ocean earlier in the day. Over water, pollutants were largely contained in the shallow marine boundary layer, where O₃ production and aerosol concentration enhancement likely occurred through rapid photochemistry. These highly oxidized species were then transported near the surface by the sea breeze circulation back inland (e.g., Figure S7e), thereby contributing to the enhanced O₃ and aerosol concentrations measured at RMSP. Due to the relatively long lifetime of aerosol compounds, the measured enhanced aerosol concentration was also undoubtedly due in part to transport from the mainland (Figures S6e and S7e). It is worth noting that the stationary 1-hr sampling time period with O₃ concentrations over 110 ppb was from 16:30 to 17:30 (Figure 3a), which was when the sea breeze front appeared to have passed Stony Brook on the north shore of LI (Figure S5f). Overall, three meteorological phenomena led to the formation of a measurable sea breeze circulation and to the occurrence of high O₃ concentrations at RMSP, namely, (1) the shallow marine boundary layer height in the marine environment and near the coast; (2) the accumulation of precursors, followed by the development and persistence of the pollution plume in the shallow marine boundary layer; and/or (3) rather weak flow conditions that kept the high ozone and other secondary pollution from readily ventilating out of the vicinity.

In contrast to the O₃ trend during the sampling period at RMSP (16:20–17:20 EDT), some aerosol compounds (organics, SO₄, NH₄, and I) increased again at approximately 17:00 EDT (Figures 3a and 3b). The second increase in aerosol concentrations without significant variation in O₃ suggested that the HR-ToF-AMS measured another plume containing higher concentrations of organics, SO₄, NH₄, and iodine but little to no ozone precursors. In addition, the aerosol mass spectra during the period of high O₃ concentration at RMSP shows higher signals at m/z 28 (f₂₈, CO⁺) and m/z 44 (f₄₄, CO₂⁺), and lower signals at m/z 43 (f₄₃, C₂H₂O⁺) and hydrocarbon-like ions (CₓHᵧ family) compared to the aerosol mass spectra under low O₃.
Aerosol measured during this sea breeze-influenced period had a higher oxidation state in this aged air mass containing high ozone. Other evidence for the presence of marine-influenced air comes from the greater imbalance in inorganic ions during this period. Specifically, the predicted NH$_4$ found by assuming full neutralization of NO$_3$ and SO$_4$ was about 16% higher (on average) than the measured NH$_4$ by HR-ToF-AMS. This is attributed in part to the presence of organic sulfate, as suggested by the enhanced signal of CH$_3$SO$_2$ (a tracer for methanesulfonic acid; Huang et al., 2017; Figure 3b).

3.1.2. Case Study B—North Coast (1 July)

The 1 July measurements showed large O$_3$ spatial variation near Port Washington on the north shore of LI during late afternoon (blue box in Figure 2b and gray box in Figure 4). On average, the measured NO$_2$ concentrations were below 10 ppb for this deployment. Shortly before 16:30 on 1 July, the O$_3$ concentration rapidly increased from 50 to 100 ppb with a $\Delta O_3 / \Delta y$ of 15 ppb km$^{-1}$ when the van drove east, and it remained at 100 ppb for about 6 km (Figure 4). Then, the O$_3$ concentration rapidly decreased back to below 60 ppb by 16:40 with a similar rate ($\Delta O_3 / \Delta y$ of 15 ppb km$^{-1}$) when the van began to drive north (Figure 4). This dramatic O$_3$ variation was not observed again when driving the van back to Flax Pond, suggesting that the plume did not persist into the late afternoon.

Several of the 24-hr HYSPLIT back trajectories on 1 July indicate that the wind direction shifted from northwesterly in the morning (10:00 EDT, Figure S9) to south-southwesterly in the late afternoon (15:00 EDT, Figure S10). The late afternoon south-southwesterly winds were most likely due to the development of the sea breeze circulation that occurred throughout LI at different times on the afternoon of 1 July, as shown by the NYSM lidar vertical profiles (Figure S11) and back trajectories (Figure S10). The delayed onset of the sea breeze front at the northern sites indicates the movement of the sea breeze pattern from south to north across LI (Figure S11). For example, the wind direction measured by lidars deployed at the Queens and Stony Brook Mesonet sites in central and northern LI, respectively, illustrates the wind transport patterns on 1 July from south to north (Figure S11). Figure S11e shows that the offshore wind noticeably weakened at Queens at approximately 11:00 EDT and calm conditions persisted for the next 3 hr. Then, the wind direction abruptly shifted from offshore to onshore at approximately 14:00 EDT (Figure S11e), which further suggests that a sea breeze circulation developed on 1 July and passed central LI at that time. Meanwhile, weak northerly winds were present near the surface at the Stony Brook site at approximately 11:00 EDT (Figure S11f) and persisted for several hours until about 17:00 EDT, when the wind direction shifted to southwesterly, consistent with the presence of the sea breeze. Therefore, it is hypothesized that the convergence of the northward transport of O$_3$ and its precursors by the sea breeze circulation and the weak northerly winds at northern LI played a critical role in forming the observed O$_3$ gradient measured on 1 July (Figures 2b and 4).

It is noteworthy that the aerosol number concentrations at Port Washington during the O$_3$ exceedance period were much higher than immediately before or after (such as Sands Point), with number concentrations of 17,000 # cm$^{-3}$ at Port Washington versus 3,000 # cm$^{-3}$ at Sands Point. At the same time, any low O$_3$ concentrations measured on 1 July were likely not due to rapid NO titration chemistry, since NO$_2$ concentration at RMSP (Figure S8). Aerosol measured during this sea breeze-influenced period had a higher oxidation state in this aged air mass containing high ozone. Other evidence for the presence of marine-influenced air comes from the greater imbalance in inorganic ions during this period. Specifically, the predicted NH$_4$ found by assuming full neutralization of NO$_3$ and SO$_4$ was about 16% higher (on average) than the measured NH$_4$ by HR-ToF-AMS. This is attributed in part to the presence of organic sulfate, as suggested by the enhanced signal of CH$_3$SO$_2$ (a tracer for methanesulfonic acid; Huang et al., 2017; Figure 3b).
concentrations on 1 July were typically less than 10 ppb (Figure 4). In sum, as previously discussed, the measured O₃ concentration gradient on 1 July appears to have been influenced by the interaction of the southerly sea breeze and the northerly wind.

### 3.2. Ozone Spatial Heterogeneity Influenced by Traffic Emissions

In contrast to 30 June and 1 July, two measurement days—10 July and 16 July—were characterized by sharp spatial variability of both O₃ and NO₂ on the highway, indicative of more polluted conditions in terms of the important NOₓ precursors. This is also supported by the generally high aerosol number concentration when NO₂ and O₃ concentrations were high and low, respectively (Figure 5). The detailed on-road measurement routes and O₃ spatial distribution map are shown in Figure S12. Specifically, the highest measured O₃ concentrations were approximately 100 ppb in LI on 10 July and in White Plains on 16 July (Figure S12). Such high O₃ concentrations were consistent with (1) the high NO₂ column concentration measured by TROPOMI over the NYC metropolitan area (Figures 6a and 6b), (2) the 24-hr HYSPLIT back trajectories for central LI on 10 July (Figure S13a), and (3) the Layer 1 ozone contours and wind vectors from a CMAQ forecast run for 16 July (Figure S13b). The back trajectories for the locations where high O₃ was measured suggest that southwesterly winds were prevalent on 10 July (Figure S13a). Together, Figures 6a, S12a, and S13a are consistent with the urban emissions being advected eastward from the most densely populated parts of NYC and producing high levels of ozone over LI, while Figures 6b, S12b, and S13b are consistent with the higher observed ozone north of NYC.

For the on-road measurements in these two cases on days favorable to high O₃ conditions, the NO emitted by the highway traffic quickly reacted with O₃ to form NO₂. This contributed to strong anticorrelation between O₃ and NO₂ on 10 July and 16 July (Figure 7; $R^2 = 0.78$, $p < 0.05$). Figure 7 shows that the slope of O₃ versus NO₂ was $-0.56$ (larger than $-1$), which indicates that O₃ concentrations ($O₃ + NO₂$) increased with increasing NO₂. The NO₂ may have either formed due to the reactions of NO and VOCs from fresh traffic emissions (Yao et al., 2005) or originated from primary NO₂ emissions from diesel traffic (Anttila et al., 2011; Grice et al., 2009).

### 4. Summary and Conclusions

Several LISTOS on-road measurements were made from 24 June 2018 to 16 August 2018. Four of the mobile laboratory deployment days—30 June to 1 July, 10 July, and 16 July—were analyzed and discussed. The 30 June and 1 July on-road measurements yielded (1) sharp O₃ concentration gradients ($\Delta O₃ \Delta y^{-1}$) of over 15 ppb km⁻¹ at some locations (Figure 2) and (2) maximum O₃ concentrations of 100 ppb or greater (Figures 2–4) at some coastline locations in environments with relatively low NOₓ abundances. The large O₃ gradients were measured on the south

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**Figure 6.** (a) The TROPOMI NO₂ column concentration for 10 July. (b) The TROPOMI NO₂ column concentration for 16 July.

**Figure 7.** The relationship between O₃ and NO₂ on 10 July and 16 July.
shore of LI on 30 June and on the north shore of LI on 1 July. A number of co-occurring factors created such sharp spatial heterogeneity in ozone in low-NOx conditions. First are high temperatures and weak offshore flows, which allow emissions from highways and urban areas to accumulate in shallow marine boundary layers. These relatively concentrated emissions and near-stagnant flow conditions allow rapid and efficient photochemical processing. The formation of a sea breeze circulation that is in nearly direct opposition to the weak gradient flow transports this processed and highly oxidized air back onto land. The front where the sea breeze and land breeze (in extreme cases the LI Sound breeze) meet was shown to be a consistent explanation of the observed ozone spatial gradients.

Although the 10 July and 16 July measurements also yielded maximum O3 levels well above the 70 ppb NAAQS (approximately 100 ppb; Figure 5), the processes driving the high O3 variations differed from 30 June and 1 July. In these cases, the abundant O3 precursors (NOx and VOC) that are characteristic of the NYC metropolitan area on both days (Figures 6a and 6b) were transported downwind, where photochemical processing of these precursors produced the high O3 measured on the highway. Then, widespread NO titration due at least in part to the highway traffic contributed to the strong anticorrelation between O3 and NO2 on 10 July and 16 July (Figure 7; \( R^2 = 0.78, p < 0.05 \), and \( O_3 + NO_2 \) increased with increasing NO2.

Overall, the on-road measurements presented in this study provide evidence to support the hypothesis that the sea breeze circulation can redistribute ozone produced in shallow marine boundary layers and under special conditions transport air masses with enhanced O3 back to land, thereby contributing to O3 exceedances and enhanced aerosol levels on LI. Even though the findings presented in this study begin to elucidate the interaction between the emitted pollution and the meteorological conditions on LI, additional on-road, and even airborne measurements over multiple summers are needed to better inform future air-quality policy.

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