Use of Tethersonde and Aircraft Profiles to Study the Impact of Mesoscale and Microscale Meteorology on Air Quality

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Abstract

Highly-resolved vertical profiles of ozone and reactive nitrogen in the lower troposphere were obtained using Millersville University's tethered balloon system and NASA's P-3B aircraft from the July 2011 Baltimore, MD/Washington DC and the September 2013 Houston, TX deployments of the NASA DISCOVER-AQ mission. Identified here are two case studies where the P-3B, tethersonde, and surface measurements captured localized pollution peaks in the lower boundary layer enhanced by bay and gulf breezes in two different coastal regions on the United States known to have ozone mixing ratios exceeding the air quality standard. In both cases, the highest ozone concentrations observed at the surface was the result of polluted air moving out to the respective body of water with the mean flow where precursor and ozone concentrations are able to increase for a variety of reasons, and then travel back over land due to the bay or gulf breeze. Surface and lower boundary layer pollutant concentrations were found to have a large dependence on the vertical and horizontal extent of the bay and gulf breezes at the two sites analyzed. Edgewood, MD, a site of historically high ozone concentrations, was shown to be afflicted with thin, but highly polluted layers advected landward off the Chesapeake Bay in several, separate recirculation events throughout the day. The Houston Metro case demonstrates that for sites including Smith Point, TX located downwind of industrial chemical sources, gulf and bay breezes are important for high surface concentrations observed initially due to transport and again later in the day due to recirculation.

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NASA – National Aeronautics and Space Administration
DISCOVER-AQ- Deriving Information on Surface conditions from Column and Vertically Resolved Observations Relevant to Air Quality
AGL- above ground level
O_3- ozone
NO_2, NO, NOx- nitrogen dioxide, nitrogen oxide, NO_2 + NO
NOy- NOx + other reactive nitrogen species
CO – carbon monoxide
VOCS- volatile organic compounds
EPA- Environmental Protection Agency
NAAQS- National Ambient Air Quality Standard
ppbv- parts per billion by volume
ppmv- parts per million by volume
TCEQ- Texas Commission on Environmental Quality
NCAR- National Center for Atmospheric Research
CH_2O- Formaldehyde
DFGAS- Difference Frequency Generation Absorption Spectrometer
NAA- Non-Attainment Area
MARAF- Millersville Atmospheric Research and Aerostat Facility
APG- Aberdeen Proving Ground
MPL- MicroPulse Lidar
SODAR- SOnic Detection And Ranging
RASS- Radio Acoustic Sounding System
NATIVE- Nittany Atmospheric Trailer and Integrated Validation Experiment
MDE- Maryland Department of the Environment
KNMI- Royal Netherlands Meteorological Institute
NCEP- National Centers for Environmental Prediction
EDT- Eastern Daylight Time (UTC-4)
HYSPLIT- Hybrid Single-Particle Lagrangian Integrated Trajectory
CDT- Central daylight time (UTC-5)
WRF- Weather Research and Forecasting
CMAQ- Community Multi-scale Air Quality

1. Introduction

1.1 Boundary Layer Trace Gases

Boundary layer ozone is a secondary photochemical pollutant formed through a reaction mechanism involving nitrogen oxides ($NO_x = NO + NO_2$), volatile organic compounds (VOCs), carbon monoxide (CO), and sunlight. Since ozone harmfully affects human respiratory systems as well as photosynthesis for vegetation, the United States Environmental Protection Agency (EPA) implemented air quality standards for ozone as a criteria pollutant (Krupa and Manning 1988; Burnett et al., 1997). Surface ozone is regulated according to the current primary National Ambient Air Quality Standard (NAAQS) of 70 parts per billion by volume (ppbv), calculated as the daily maximum of an 8-hour running mean.

While major efforts are put forth by the EPA and state and local agencies to regulate emissions of ozone precursors, the concentration of ozone at or near the surface is also contingent upon meteorological conditions such as the synoptic-scale circulation, boundary layer height and turbulence, advection, incoming solar radiation, temperature, and humidity (Seaman and Michelson, 2000; Hegarty et al., 2007). Areas most commonly affected by high ozone concentrations are downwind of metropolitan centers. Additionally, coastal regions are frequently subject to poor air quality due to a bay or sea breeze that acts to recirculate pollution in the lower boundary layer (Banta et al., 2005; Loughner et al., 2011; 2014).

1.2 Impact of Sea, Bay, and Gulf Breezes on air quality

The same meteorological conditions that lead to ozone events also lead to sea, bay, and gulf breezes: weak winds, warm temperatures, intense solar radiation, and subsidence inversions. These conditions allow pollutants to accumulate and ozone to form as well as allow the breezes

to compete with synoptic forcing. With pressure gradients in place, air near the surface moves from water to land during the day due to differential heating. The reversal of this occurs at night when the land cools much more quickly than water and causes a pressure gradient force in the opposite direction. This sequence forces early morning emissions over land to be transported over the adjacent body of water, and then re-circulated back to the land in the afternoon (Wang et al., 2001).

Several studies have shown that sea, bay, and gulf breezes can contribute to poor air quality (Banta et al., 2005; Evtyugina et al., 2006; Darby et al., 2007; Loughner et al., 2011). The 2011 DISCOVER-AQ (Deriving Information on Surface conditions from Column and Vertically Resolved Observations Relevant to Air Quality) campaign yielded data demonstrating the influence of the Chesapeake Bay breeze as it enhanced pollution inland of the coastline (Stauffer et al., 2012; 2013; Loughner et al., 2014). During the July 2011 DISCOVER-AQ campaign, the 2008 8-hour ozone standard of 75 ppbv was violated at Edgewood, MD on ten days, and a bay breeze was also measured on eight of these days (Stauffer et al., 2012). Studies during the 2011 DISCOVER-AQ campaign showed that concentrations of surface ozone tended to be higher over the Chesapeake Bay than upwind land areas due to a shallower boundary layer, ship emissions, lower deposition rates, higher photolysis rates, and decreased boundary layer venting due to a decrease in cloud cover compared to the nearby land (Goldberg et al., 2014).

Concentrations of background ozone in eastern Texas tend to be higher in late summer and early fall due to the synoptic circulations of northerly and easterly flow transporting continental high ozone air to the area. Higher background concentrations could contribute to the frequency and magnitude of ozone episodes (Langford et al., 2009). The Texas Commission on Environmental Quality (TCEQ) uses the background ozone concentration to estimate the local

contribution of ozone as the difference between the 8-hr maximum background ozone and the 8-hr maximum measured ozone (Nielson-Gammon et al., 2005). While there is generally good agreement between the background and maximum ozone concentration using this method, discrepancies between background and maximum ozone concentration are observed due to the gulf and bay breeze (Langford et al., 2009). High ozone in the Houston area is often a result of small-scale circulations with advection of pollutants from the Houston Ship Channel to the southwestern part of the Houston Metro area (Ngan and Byun, 2011) and in many cases is the result of wind shifts in a postfrontal environment (Rappengluck et al, 2008). When a gulf or Galveston bay breeze sets up after these pollutants are advected over the water behind the front, the Houston Metro area can experience a second dose of pollution.

Studies performed in Houston, TX, showed that ozone episodes begin when the synoptic-scale winds transport pollutants from the land to Galveston Bay or the Gulf of Mexico before a bay or gulf breeze sets up (Darby, 2005). As the bay or gulf breeze develops, pollutants are recirculated over the adjacent land adding to the pollution generated locally in these areas. Additionally, Banta et al. (2005) discusses an ozone event during the Texas Air Quality Study 2000 field campaign where a particular set of meteorological conditions, including the gulf / bay breeze, led to surface hourly ozone concentrations of 200 ppbv.

Similarly in this paper, we focus on the effects of bay and gulf breezes and local meteorology on air quality in Edgewood, MD and Smith Point, TX, as measured during DISCOVER-AQ during the summer and late summer months, respectively.

2. The DISCOVER-AQ Field Project

It remains a challenge to accurately detect and resolve near-surface pollution with Earth observations from space (Liu et al., 2005; Fishman et al., 2008; Martin 2008; Chatfield and Esswein 2012). DISCOVER-AQ, a five-year NASA Earth Venture campaign, was designed to advance satellite observation capabilities by investigating the relationship between column-integrated trace gas quantities and pollution in the near-surface environment (http://discover-aq.larc.nasa.gov). Goals of DISCOVER-AQ include assessing uncertainties in column, surface trace gas, and aerosol observation correlations, characterizing the diurnal variation of the column and surface observations, and to investigate how much horizontal variability can be captured in satellite retrievals and model calculations. DISCOVER-AQ had four deployment locations: Baltimore/Washington D.C. (July 2011), San Joaquin Valley, CA (January - February 2013), Houston, TX (September 2013), and Denver, CO (July - August 2014). Its deployment strategy consisted of multiple aircraft (NASA P-3B with in-situ measurements and NASA King Air with remote sensing instruments) as well as a plethora of instrumented ground sites. The P-3B aircraft provided profiling of meteorological, trace gas, and aerosol variables centered over several surface air quality monitoring sites per deployment domain.

The ability to understand and predict air pollution events has been limited in part by the lack of vertical meteorological and chemical profile observations with which to evaluate air quality models and analyze case studies with in-situ observations. With this unprecedented DISCOVER-AQ data set in terms of horizontal, vertical and temporal coverage, the spatial-temporal variability of air pollution can be better addressed.

2.1 P-3B Aircraft Measurements

NASA's P-3B aircraft was deployed throughout the DISCOVER-AQ campaign to capture vertical profiles of meteorological and air quality measurements over ground sites. Existing surface air quality monitoring stations were typically used for the spiral locations. The P-3B spiraled over each ground site three to four times within an operational day. The P-3B spiral vertical extent was approximately 300 m AGL to 3 to 5 km. Therefore, the aircraft did not measure the vertical structure of air pollutants near the surface. However in some DISCOVER-AQ deployments, missed approaches were used to fill this gap between 300 m and the surface at some sites. In the Maryland deployment, tethered balloons were used at Beltsville and Edgewood, MD however; only Millersville University's tethered balloon at Edgewood is used in this study as described in the following section. In the Houston deployment, the Millersville University tethered balloon was used at Smith Point. Onboard the P-3B there was continuous ozone, NO, NO_2, and NO_y measurements made using the National Center for Atmospheric Research (NCAR) 4-Channel Chemiluminescence Instrument with one second averages with 5% uncertainty for ozone and NO, 10% for NO_2, and 20% for NO_y. CH_2O measurements were made on the P-3B using the Difference Frequency Generation Absorption Spectrometer (DFGAS) with 30 second averaging and 13% uncertainty (Weibring et al., 2007).

2.2 Ground sites for Tethersonde Deployment

Edgewood, Maryland

The Baltimore/Washington metropolitan area is vulnerable to exceeding the 70 ppbv; 2015 (75 ppbv; 2008) EPA ozone standard due to the abundance of precursor emissions along with meteorological conditions that are favorable for ozone production during summer months

(He et al., 2013). The ozone design value is defined as the 3-year average of the fourth highest annual 8-hr maximum ozone-mixing ratio. This value determines compliance with the EPA NAAQS. The highest ozone design value in the Baltimore Non-Attainment Area (NAA) has been consistently measured at the air-monitoring site in Edgewood operated by the Maryland Department of the Environment (MDE). This site experienced the highest ozone measured on the U. S. east coast region for 2011 and was many times the only monitoring station within the NAA that exceeded the ozone standard of 75 ppbv standard at that time. This may be due in part to its location in a bay breeze convergence zone. For these reasons, Edgewood was selected as one of the spiral sites for the P-3B during DISCOVER-AQ.

Smith Point, Texas

Houston, TX has large emissions of ozone precursors coupled with meteorological conditions favorable for ozone production, typically during late summer. The Houston area emits significant amounts of ozone precursors from power plants, refineries, and petrochemical industrial plants. Emissions are particularly large along the Ship Channel and western shore of Galveston Bay (Banta et al., 2005). Aircraft observations from Kleinman et al. (2005a) found that NO_x and light olefins emitted from petrochemical facilities in the Houston area led to the highest ozone production observed in the study. Smith Point is a peninsula extending into Galveston bay from the eastern shore. Due to its coastal bay location and close proximity to the Gulf of Mexico (approximately 14.5 km), Smith Point is susceptible to both bay and gulf breeze pollution recirculation. The combination of high emissions and gulf and bay breeze circulations lead to ozone exceedances in areas such as Smith Point that are downwind of industrial sources.

2.3 Methods

Table 1 provides a summary of measurements used for the Edgewood, MD and Smith Point, TX studies

2.3.1 Edgewood Measurements

Millersville University deployed its mobile lab including a suite of instruments and equipment in support of boundary layer and atmospheric chemistry research (Millersville Atmospheric Research and Aerostat Facility (MARAF; see http://www.millersville.edu/esci/maraf). One hundred-sixty seven tethered balloon soundings captured the temporal and vertical evolution of ozone on P-3B flight days and some non-flight days throughout the campaign. The continuous profiles provide a useful data set to characterize profile shapes and how they vary as a result of meteorological conditions such as bay breezes, the amount of boundary layer turbulence, and influences of local plumes versus longer-range transport. MARAF was deployed at Eagle Point on the Edgewood side of the Aberdeen Proving Ground (APG; lat: 39.4°, lon:-76.3°) for the first DISCOVER-AQ deployment in July 2011 (Figure S1). APG, a U.S. Army facility, is often influenced by transport of ozone precursors from the Baltimore-Washington Metro area. MARAF includes a 4-meter flux tower, a Sigma Space MicroPulse Lidar (MPL), an acoustic SOnic Detection And Ranging (SODAR) with Radio Acoustic Sounding System (RASS) extension, surface trace gases (O_3, NOx, SO_2, and CO), and a 3-wavelength Nephelometer. The surface instruments integrate with the measurements obtained by the tethered balloon. The tethered balloon system consists of a Vaisala TTS111 system that measures temperature, pressure, relative humidity, wind speed, and wind direction along with a 2B-Technologies Inc. trace gas analyzer for ozone. Semi-continuous

profile measurements were taken in blocks of approximately 1.5 to 2.5 hours depending on available platform battery power, where typically four vertical profiles were measured per charge. The soundings coincided in time with the P-3B spirals to fill the gap from the lowest P-3B spiral to the surface. Profiles were also conducted between spirals to capture the temporal evolution of vertical variability throughout the day.

The MARAF site was set up 2.7 km SE of the Edgewood Maryland Department of the Environment monitoring site (MDE) as well as the Nittany Atmospheric Trailer and Integrated Validation Experiment (NATIVE; Martins et al., 2012) for optimal boundary layer sampling immediately on the coast of the bay (Figure S2). MDE and NATIVE were collocated platforms for air quality and ground-based in-situ measurements. Chemical measurements included O_3, NO, NO_y, SO_2, and CO for NATIVE and O_3 for MDE.

2.3.2 Smith Point Measurements

MARAF was deployed at Smith Point, TX (lat: 29.5°, lon:-94.8°) for the third deployment of DISCOVER-AQ in September 2013 (Figure S3) alongside the NATIVE trailer. The tethered balloon operation was similar to the Edgewood deployment, but the 2B-Technologies Inc. NOx analyzer and an NO_2 sonde developed by the Royal Netherlands Meteorological Institute (KNMI) were added for this deployment. The KNMI NO2-sonde uses the NO_2 chemiluminescent reaction in a nearly specific to NO_2 aqueous luminol solution (Sluis et al., 2010). Similar surface instruments to the Maryland deployment were used such as the MPL, SODAR, Nephelometer, and trace gas suite; however, the flux tower experienced technical issues and was not used for this study. A Coastal Environmental WeatherPak 2000 was used in this deployment, which measured surface meteorological constituents such as: pressure,

temperature, humidity, wind speed, and wind direction. Again for this campaign, the NATIVE mobile platform for air quality and ground-based in-situ measurements were used which included surface chemical measurements of O_3, NO, NO_y, SO_2, and CO.

3. Bay and Gulf Breeze Case Studies

3.1 Bay Breeze Edgewood, MD 29 July 2011

During the Baltimore/Washington DISCOVER-AQ campaign, there were five days that exhibited a bay breeze and four additional days that displayed evidence of bay breeze initiation but were unable to persist due to a thunderstorm or gust front. During this deployment there were ten days with ozone exceedances of the EPA 8-hour 2011 ozone standard of 75 ppbv at Edgewood, and eight of these exceedances were associated with a bay breeze or "interrupted" bay breeze (Stauffer et al., 2012). On 29 July 2011, three bay breeze fronts were observed at the Edgewood MARAF site, which were indicated by surface and tethersonde observations. The morning of the 29th featured weak synoptic forcing with a surface high pressure and an upper-level ridge in place over the Mid-Atlantic region, which is typically conducive for both ozone events and bay breezes. By 12 UTC (08:00 EDT; UTC-4), the synoptic wind pattern over the site was northwesterly (NW) at 850mb (Figure S4; *NCEP* Reanalysis data provided by the NOAA/OAR/ESRL PSD, Boulder, Colorado, USA, from their website at http://www.esrl.noaa.gov/psd/).

The earliest bay breeze passage of the day was around 13:30 EDT and was noted by both the surface observations and a tethersonde profile to be a shallow and brief, but intense boundary between the land environment and the high ozone air over the bay. Measurements made at the NATIVE trailer only 2.7 km NW of MARAF did not exhibit any effects of the first bay breeze

event (Stauffer et al., 2012). A second bay breeze front passed through the site around 16:15 EDT affecting surface concentrations for about an hour until a wind direction shift brought cleaner air to the research site. By 18:00 EDT, a third bay breeze passage was measured which was sustained until 20:00 EDT when a gust front pushed the ozone rich marine air off the coast bringing in cleaner continental air from the thunderstorm outflow. The tethersonde captured much of the variability observed during this day during its continuous profiling. The NATIVE trailer was also affected by the second and third bay breeze passages with slightly smaller magnitude fluctuations (Stauffer et al., 2012).

July 29, 2011 was part of a multi-day ramp up of summertime air pollution as a consequence of the synoptic meteorological conditions. Around 08:30 EDT, a combination of stored ozone from the (nocturnal) residual layer mixing down to the surface during the growth of the mixed layer and photochemical production led to a rapid increase in surface ozone from 25 ppbv to 75 ppbv within two hours (Figure 1). This corresponds to negative vertical eddy momentum flux (downward transport) as measured by the flux tower, as well an end to directional wind shear and development of vertical speed shear (Figure 2). Tethered balloon soundings between 08:20 and 09:07 EDT (Figure 3) show enhanced ozone concentrations relative to the surface between 150-340 m. The ascending profile (08:20-08:42 EDT) from the surface to 340 m shows increasing ozone concentration with altitude between 150 – 330 m. The descending profile (08:42 – 09:07 EDT) shows the downward transport of higher ozone concentrations from aloft to the layer below 200 m. The descending profile indicates a layer (260 – 340 m) of lower water vapor mixing ratio along with higher potential temperature and higher wind speeds than the ascent sounding. From 260 m to the surface, the descending profile shows fairly well-mixed, enhanced water vapor mixing ratio, higher potential temperature, and higher

wind speeds than the ascending profile. Back trajectory analysis calculated for the period six hours prior to these profiles from the Air Resources Laboratory's Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (Draxler and Hess, 2004) shows transport from central Pennsylvania at 1000 m and western Pennsylvania at 100 m. Back trajectories from the period one hour before are from eastern Maryland at 1000 m and between Edgewood and Baltimore intersecting I-83 at 100 m. This suggests that some of the enhanced ozone concentration found in these profiles was due to transport from Pennsylvania cities and Baltimore, MD during early to mid morning, before there were effects from the bay breeze.

Ozone concentration at the surface fluctuated from 75 to 80 ppbv from 11:00 EDT until the first bay breeze passage, which initiated around 13:30 EDT. This bay breeze swept through the site briefly in a very shallow wedge (<100 m) bringing with it spikes in ozone concentration, specific humidity, and a drop in surface temperature. The combined P-3B and tethersonde profile (Figure 4) for the first spiral of the day demonstrates the very shallow but intense bay breeze that was too shallow for P-3B measurement due to altitude limitations. At the surface, specific humidity increased from 15.6 to 18.5 g/kg, temperature decreased from 37.8 to 35.8 degrees C, and ozone concentration increased from 77 to 113 ppbv between 13:20 to 13:30 EDT (Figure 5). The bay breeze also transported other trace gases during this passage: NO_x increased from 6.5 to 8.8 ppbv, SO_2 increased from 2.7 to 3.6 ppbv, and CO increased from 0.71 to 0.76 ppmv. (Figure 1). This bay breeze was too brief for the 30 minute averaged SODAR wind measurements, however, the tethersonde anemometer measured wind direction in the bay breeze layer to be between 90 and 190 degrees, but fluctuating between 80 and 280 degrees near the surface (Figure S5; wind direction light pink sounding). At 13:50 EDT, trace gas concentrations, specific humidity, and temperature returned to previous levels throughout the vertical profile (Figure S5;

green sounding) and at the surface (Figure 5). The brevity of this intense yet shallow bay breeze demonstrates the steep, localized gradients at the bay breeze front and the significant impact on surface concentration.

A second bay breeze frontal passage occurred later in the day around 16:15 EDT when specific humidity increased from 13.6 to 16.5 g/kg, temperature decreased from 38.5 to 37.5 degrees C, and ozone increased from 84.3 to 90.8 ppbv at the surface between 16:00 and 16:15 EDT (Figure 5). This was associated with a wind shift from NW to SSW with air coming from the Baltimore area and passing over the bay. By 17:25 EDT the wind shifted direction again from SSW to SSE along with a change in surface concentrations. Although this air temporarily passed over the bay, specific humidity decreased to 14.6 g/kg, temperature increased to 38.2 degrees C, and ozone decreased to 85.3 ppbv (Figure 5). A combined P-3B and tethersonde profile was captured during this transition period between wind directional shifts. The tethersonde profile from 16:48 to 16:57 EDT captured the ozone and water vapor rich air mass from the bay breeze, whereas the P-3B spiraled down 25 minutes later (from 17:24 to 17:36 EDT) over the site measuring the air from the SSE with the previously detailed lower ozone and specific humidity concentrations along with slightly warmer temperatures (Figure 6).

By 18:00 EDT, the bay breeze returned and affected the site for a much longer duration than the previous two events. Specific humidity increased from 15.0 to 18.0 g/kg, temperature decreased from 37.6 to 36.3 degrees C, and ozone concentration increased from 87 to 107 ppbv at the surface from between 18:00 and 19:20 EDT (Figure 5). Around 20:00 EDT, the bay breeze was terminated by NW flow from a gust front heading southeastward from southern Pennsylvania / northern Maryland as shown by the Sterling, VA radar (KLWX) in Figure S6. With the passage of the gust front, specific humidity decreased from 18.4 to 13.4 g/kg,

temperature decreased from 36.4 to 35.6 degrees C, and ozone concentration dropped from 88 to 67 ppbv from 20:00 to 20:35 EDT (Figure 5).

3.2 Bay- Gulf- Breeze, Smith Point, TX 25 September 2013

The effects of local meteorology on this day resulted in the highest instantaneous measured ozone during all of the DISCOVER-AQ deployments. Leading up to 25 September 2013, and for most of the DISCOVER-AQ Houston deployment, onshore flow dominated at Smith Point. The 25th was not part of a ramp up pollution episode or heat wave common to high pollution case study events, but instead, the result of postfrontal and local wind shifts carrying polluted air masses. On this day, the local winds behind the front were northerly and pollution observed at Smith Point was largely, a function of the flow from Houston industrial area and chemical plants. The localized Houston pollution that accumulated over the bay and gulf was recirculated back over the research site at Smith Point by the gulf and bay breeze around 17:30 CDT (UTC-5) with concentrations of 175 ppbv of ozone observed at the surface at Smith Point.

3.2.1. Synoptic Conditions, Local Winds, and Air Quality Observation Overview

In the early hours of 25 September 2013, a weak cold front stemming from a low over NW Arkansas moved SE over the Gulf of Mexico. High pressure filled in behind this front and a ridge was in place over much of the south-central United States by 12 UTC (07:00 CDT) featuring subsidence over southeast Texas (Figure S7). At 10:00 CDT, SODAR (Figure 7; colored background) detected a near-surface wind shift from WSW to N bringing higher concentrations of NO_y to Smith Point. Refineries and chemical plants in Baytown and Deer Park lie to the NW and NNW of Smith Point. While ozone was increasing since 7:00 CDT, an abrupt

jump in ozone concentration was observed at the surface around 11:00 CDT, most likely due to mixing down of higher concentrations of ozone and precursors. From 12:00 to 15:00 CDT, surface winds were NNE while winds at 130 m to 200 m were NNW and NW. The NNW and NW winds were associated with the transport of ozone and ozone precursors to Smith Point as shown by the tethered balloon profiles in Figure S8. These profiles, which started at 13:14 CDT, exhibit peaks in ozone concentration of 220 ppbv and 200 ppbv with NO_y concentration of 18 ppbv between 100 and 200 m with low NO_2 concentration.

Ozone continued to increase at the surface under northwesterly winds until easterly winds at 16:00 CDT brought a brief respite until 17:00 CDT. At this time, gulf and bay breezes brought the poorest air quality of the campaign – ozone concentrations at the surface soared from 70 ppbv to 175 ppbv. By 20:00 CDT, ozone concentrations retreated between 60 and 70 ppbv (Figure 7).

3.2.2 Transport to Smith Point from Major Sources

During the first P-3B circuit of the day, the aircraft flew over the largest petrochemical facility in the U.S. near Baytown (29.741, -95.010) between 09:47 to 09:49 CDT. At the time of the overpass, primary formaldehyde (CH_2O) concentrations rose dramatically (Fried et al. AQRP report, 2016) between 18 – 20 ppbv. CO concentrations were between 500 – 600 ppbv and NO_y concentrations were between 45 - 50 ppbv during the overpass (Figure 8; concentrations near the white square).

As the P-3B made its closest approach near Deer Park (29.703, - 95.131) during the first circuit around 11:21 CDT, CH_2O concentrations were between 8-12 ppbv. Measured during this

time, the CO concentrations were between 480 – 520 ppbv and the NO_y concentrations were between 55-60 ppbv (Figure 8; concentrations near the black square).

During the second circuit, the non steady state air parcel of high precursor concentrations from Baytown and Deer Park area were observed over the Galveston Bay and at Smith Point as resultant transport downwind between 12:15 – 12:28 CDT. During this pass over the Galveston Bay and spiral over Smith Point, primary CH_2O concentrations were observed between 20-23 ppbv, CO concentrations were 300-400 ppbv, NO_y was between 0-5 ppbv, and ozone was 110-145 ppbv (Figure 9). The combined P-3B and tethersonde profile during this spiral shows an elevated layer of ozone concentration between 400 m to the surface from both the precursor reactions and transport from upwind. Due to small differences in time and space between the P-3B and the tethersonde, the P-3B measured a NO_y plume at 100 m with an associated decrease in ozone where the balloon did not. This is likely due to NO titration from a local emission source (Figure 10). The tethered balloon continued to profile between the second and third P-3B overpasses. In the next set of tethersonde balloon profiles from 12:56 to 13:59 CDT, the highest concentration of ozone was observed within the first 500 m at Smith Point due to photochemistry from significantly elevated precursors emitted upwind (Figure 11). Six-hour backward trajectories from a 1 km horizontal resolution by the Weather Research and Forecasting (WRF; Skamarock et al., 2008) were run at six different initialization altitudes relevant to the tethersonde at Smith Point (namely 2 m, 100 m, 200 m, 300 m, 400 m, 500 m). The trajectory and wind directions agree with measured surface wind direction with variations in near-surface vertical wind shear observed by SODAR. The back trajectory from the first profile, which started at 12:56 CDT (Figure 12a), shows that air passed over the Deer Park plants between 200 and 300 m altitude. This corresponds to the layer of highest ozone concentration from the first sounding

in Figure 11 (red) in the layer between 125 m and 275 m. At 13:14 CDT, the sounding in Figure 11 (green) shows ozone concentrations of 220 ppbv between 100 and 200 m altitude, which correspond to air coming from the Baytown facilities at 100 m and air from the Deep Park Plants at 200 m according to the WRF back trajectory (Figure 12b). The sounding at 13:31 CDT Figure 11 (dark blue) showed that ozone concentration retreated to mostly below 150 ppbv from 150 m to 500 m and increased to 180 ppbv in a shallow layer between 25 m and 75 m. By 13:49 CDT, the entire tethersonde profile retreated to ozone concentrations below 150 ppbv from the surface to 500 m (Figure 11; purple sounding).

3.2.3. Recirculation from Bay and Gulf Breeze

The synoptic and local northwesterly winds observed throughout the day led to transport of pollutants offshore over the Galveston Bay and the Gulf of Mexico where the pollutants mixed and formed secondary pollutants.

An intense, ozone-rich, shallow layer only 200 m deep was observed in the vertical balloon soundings between 14:31 – 15:42 CDT due to the static stability of the air over the relatively cool surface of the bay. In this series of balloon soundings, the shallow marine boundary layer was diluted and warmed by mixing with free tropospheric air from aloft (Figure 13a). Around 15:00 CDT, a negatively buoyant thermal that overshot its neutral level fell down back into the mixed layer bringing with it drier free tropospheric air. This was also associated with a wind directional change from NNE to NNW at the surface. A combination of this warmer, drier air that entrained into the boundary layer as well as the easterly wind shift observed around 16:00 CDT diluted the amount of ozone and water vapor observed within the first 200 m above the surface (Figure 13b).

By 17:30 CDT, the gulf and bay breezes made their way over Smith Point (Figure 14). At the surface, ozone concentration rose from 80 ppbv to 175 ppbv during the bay breeze passage (Figure 7). Water vapor mixing ratio increased from 9 g/kg to 18 g/kg, temperature decreased from 36 to 32 degrees C, and wind direction shifted from E to SW during the passage of the bay breeze between 17:28 to 18:00 CDT (Figure 15). This stagnant, ozone-rich air at the edge of the gulf breeze and bay breeze front acted as a convergence zone for ascent of air with ozone concentrations of 120 ppbv from the surface to 100 m and up to 150 ppbv at 100 m – 320 m by 17:49 as observed by the tethersonde soundings. By 18:25 CDT, ozone concentrations of 120 ppbv were observed within the layer between 200 to 360 m while the surface concentration retreated to 90 ppbv (Figure 13c).

4.0 Discussion

Microscale and mesoscale meteorological processes are essential to understanding and forecasting the dispersion of background and local pollution through growing boundary layer/frontal mixing and bay/gulf breezes. Shown here are case studies where high ozone events were directly influenced by boundary layer dynamics and recirculation of the bay and gulf breezes. While the theme for coastal pollution recirculation is the same for each case – pollutants are transported out to the adjacent body of water where concentrations increase and are transported back over the land when the bay or gulf breeze forms, specific and important differences remain between these two cases.

The case study in Edgewood, MD (29 July 2011) demonstrates both vertical mixing and bay breeze phenomena. Rapid subsidence shortly after sunrise led to an increase in surface ozone from around 15 ppbv to 75 ppbv within two hours. Analyzed back trajectories show that this

ozone aloft originated over western and central Pennsylvania six hours earlier and from near Baltimore one hour before the rapid increase in surface ozone concentration before effects from the bay breeze. Later on that day, the bay breeze reached the Edgewood site first as a shallow, short-lived (10 min) burst of ozone above 100 ppbv, reformed several hours later as a smaller in magnitude bay breeze, and then reformed once again as a larger-scale incursion lasting roughly two hours. Ozone concentration remained above 85 ppbv for 4 hours after from the second and third bay breezes. In all bay breeze events, the air showed meteorological characteristics of having been over the Chesapeake Bay – lower temperatures and higher humidity. These air parcels also showed chemical signatures characteristic of reduced venting, that is, higher concentrations of primary pollutants CO and NO_x as well as higher concentrations of ozone, where the latter could be the result of these precursors or from faster photochemistry over the cloud-free bay.

The nature of this case having three separate events (two shorter duration, one long duration) of recirculation significantly affected (the amount of) pollution at the surface. The frequent wind shifts to and from the bay at Edgewood, allowed pollutants to accumulate and be transported over the bay from the Baltimore/Washington Metro area. Here, conditions were favorable for accelerated formation of pollutants along with recirculation from the bay breeze that transported these high concentrations back over the land. As the wind transitioned to NW winds, urban pollution was again advected over the bay where even higher concentrations of pollutants formed and were transported back over land via bay breeze recirculation. These bay breezes were frequent, but not strong enough to penetrate inland to areas not directly on the coast. Edgewood's coastal location, at a convergence zone with specific mesoscale dynamics, is a key factor for unique pollution episodes not seen at other MDE monitoring stations.

The case study at Smith Point, TX demonstrated a broad mid-to-late day event with ozone in excess of 80 ppbv for 5 hours when NW winds aloft brought pollution from the Port of Houston area including petrochemical plants that mixed to the surface at Smith Point. Around 17:30 CDT, the winds shifted dramatically to the south / southwest bringing air from over the gulf and the Galveston Bay to the MARAF and NATIVE site with concentrations that exceeded 125 ppbv at the surface for over an hour.

For this case, light to calm winds throughout most of the afternoon allowed the pollution to stagnate and build up over Houston, Galveston Bay and the gulf where active photochemistry occurred for an extended period of time, but with possible effects of halogen reactions with ozone. Concentrations observed at Smith Point were mostly due to the transport of high pollution from the chemical plants and the Houston Metro area. A major shift in wind as the bay and gulf breeze developed in the early evening, resulted in one large event with a huge impact on pollution at the surface and affecting a broad horizontal extent. This set of conditions, as opposed to the Edgewood case study with a smaller horizontal extent but more frequent smaller bay breezes, resulted in one large dramatic event.

In both cases, the marine boundary layer was extremely shallow, resulting in the buildup of ozone concentrations confined to the shallow wedge close to the surface as it passed over land. Edgewood experienced an extremely shallow bay breeze < 100 m deep with ozone surface concentrations of 113 ppbv and 75 ppbv around 100 m. Conditions measured at Smith Point were also representative of a shallow marine boundary layer, however, this was not part of the bay breeze passage that occurred later in the day. Due to the location of Smith Point on a small peninsula in Galveston Bay, it is susceptible to marine-like conditions without much forcing from specific bay breezes. The profiles that captured the conditions of the marine boundary layer

over Smith Point measured a shallow layer < 200 m deep with ozone surface concentrations 132 ppbv and 70 ppbv around 200 m. This further demonstrates the buildup of ozone concentration over the bay due to factors such as slower deposition rates, higher photolysis rates, and trapping of emissions over the bay as discussed in [Goldberg et al., 2013].

It is important to consider the differences between Edgewood and Smith Point in terms of the site locations relative to large bodies of water, types of emissions from urban centers, and regional buildup of background concentrations over several days vs. local, quick burst emissions. Each of these factors had a significant influence on the severity of the events. Detailed case studies as described here are important for determining under what meteorological conditions, and on which relevant scales (i.e., synoptic, mesoscale, and microscale), high-pollution episodes can occur. This knowledge can lead to better air quality prediction. Most regional atmospheric chemistry models such as CMAQ in regulatory or forecasting operational mode are run at 12-km resolution for computational ease and as such have difficulty resolving some of the drivers of the largest pollution episodes. It is difficult for models such as CMAQ to accurately resolve vertical transport and horizontal gradients near coastal sites. High resolution (< 4 km) is required to resolve bay/gulf breezes (Loughner et al., 2011). However, CMAQ run at 1 km for both Edgewood and Smith Point were unable to capture the high ozone transport due to the multiple bay breeze circulations from the Chesapeake Bay at Edgewood and the single, strong bay breeze from the Galveston Bay at Smith Point. Despite the inability to capture the effects of the bay breeze at Smith Point, largely due to the low emissions bias upwind of this location, the CMAQ model was able to capture the gulf breeze over the immediate Houston area during this day's event. This could be due to the much larger spatial extent along and across the gulf breeze frontal boundary. Thus, accurate representation of these phenomena can sometimes be difficult even at

fine spatial resolution (1 km) depending on frequency, duration, biases in upwind emissions, and horizontal/vertical extent of the bay breeze event.

5.0 Conclusions

The tethersonde is a powerful tool for studying composition and circulation in the lowest few hundred meters of the atmosphere where air can be quickly mixed vertically and where pollutants have the greatest impact on human health. Without this information the origins of ozone and other pollutants cannot be reliably discerned. The tethered balloon soundings and the dense network of surface observations during DISCOVER-AQ allowed observations of the depth and extent of chemical constituents along with meteorological variables during bay and gulf breezes in areas subject to poor air quality. Profiling before, during, and after the bay and gulf breezes by the tethersonde provided a rich data set.

Both case studies presented here are valuable examples to the air quality monitoring and modeling community of the importance of mesoscale and microscale meteorological processes for air quality. Large concentration gradients can exist both vertically and horizontally due to small-scale meteorological features that are difficult to accurately predict. A detailed model characterization of the flow at high resolution, in the absence of unbiased emissions, may be the only way to successfully resolve high pollution events at individual locations near bodies of water. In each case, the driving mechanism for such significant pollution episodes is the coupling of chemistry and small-scale meteorological features. These processes include: mixing down of polluted air from the residual layer air, a shallow marine boundary layer trapping emissions, localized wind shifts, and recirculation of pollution from the meso-high set up over the bay/gulf and meso-low set up over the adjacent land. Because many of the world's large cities are located

near major bodies of water, these results from Baltimore/Washington Metro and Houston Metro areas may be generalized to help understand the origins of pollution in other areas.

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Figures:

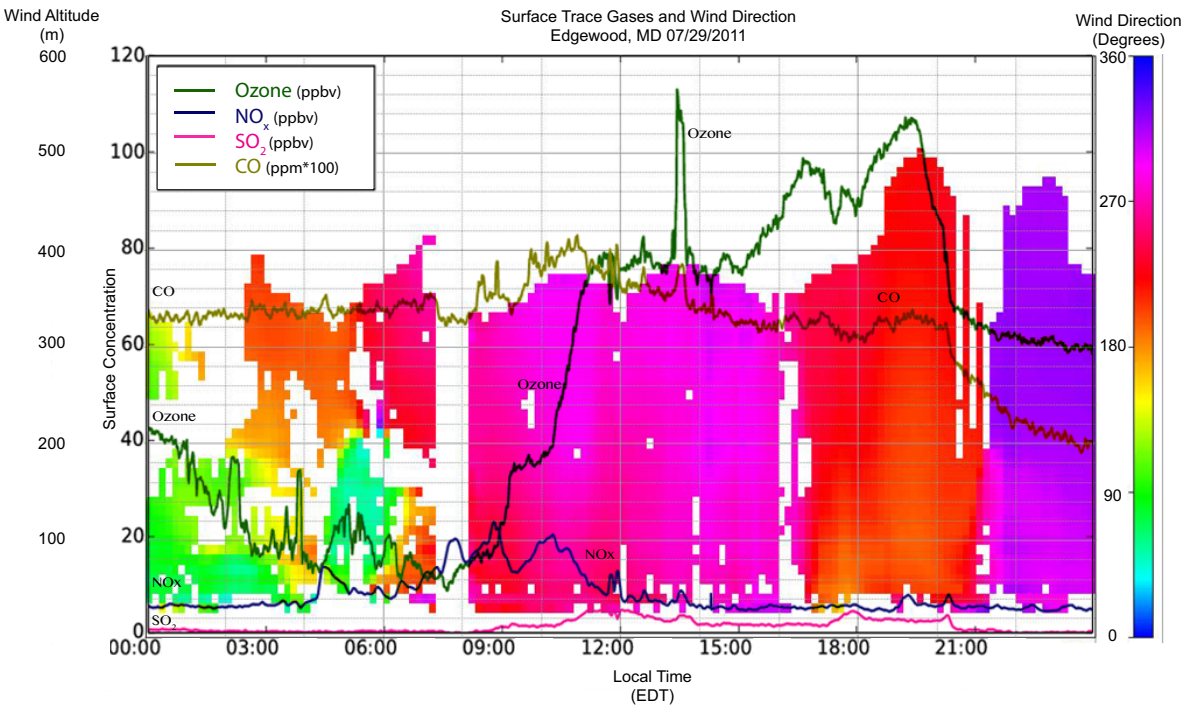


Figure 1. 07/29/2011 Edgewood MARAF site wind direction with height derived from SODAR wind profiler (colors) and labeled surface trace gases: ozone (dark green), NOx (blue), SO_2 (pink), and CO (olive green). Note WSW winds starting at 8:30 EDT as the nocturnal PBL broke up and concentrations of primary pollutants CO and NO_x increased. This is followed by inflow of more ozone rich air from over the Chesapeake Bay in a shallow (~100m; see also Figures 2 and 3) layer, shifting to generally SSW winds with sustained high O_3 concentrations by 16:30 EDT.

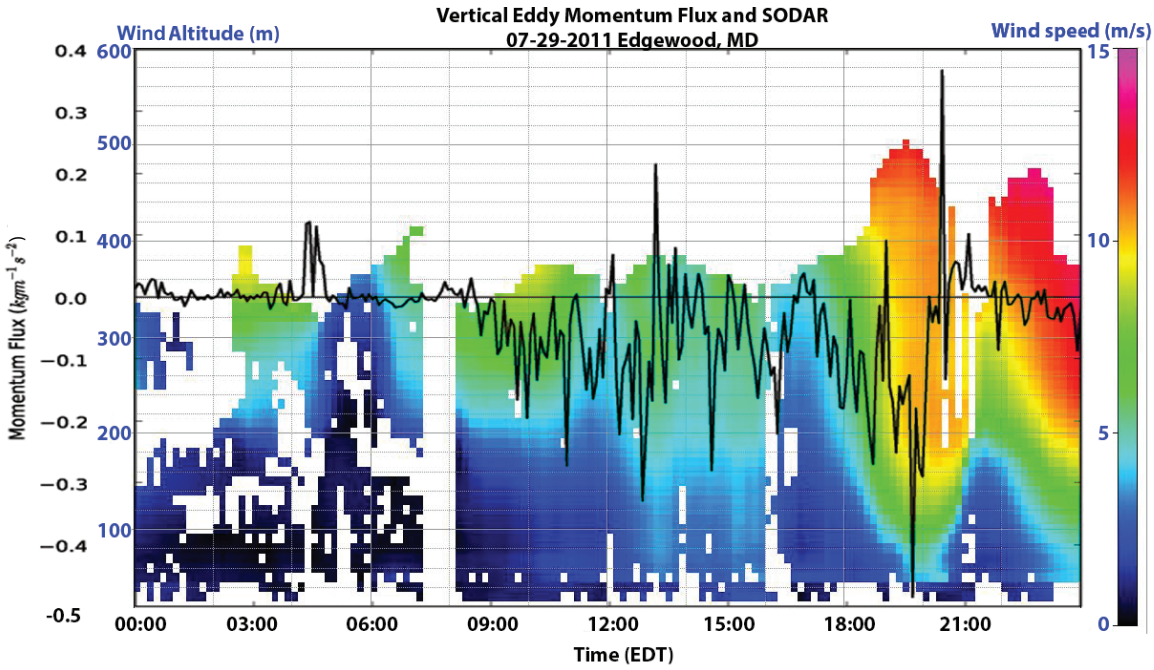


Figure 2. 07/29/2011 Edgewood MARAF site wind speed with height derived from SODAR (colors) and 4-meter vertical eddy momentum flux (black line).

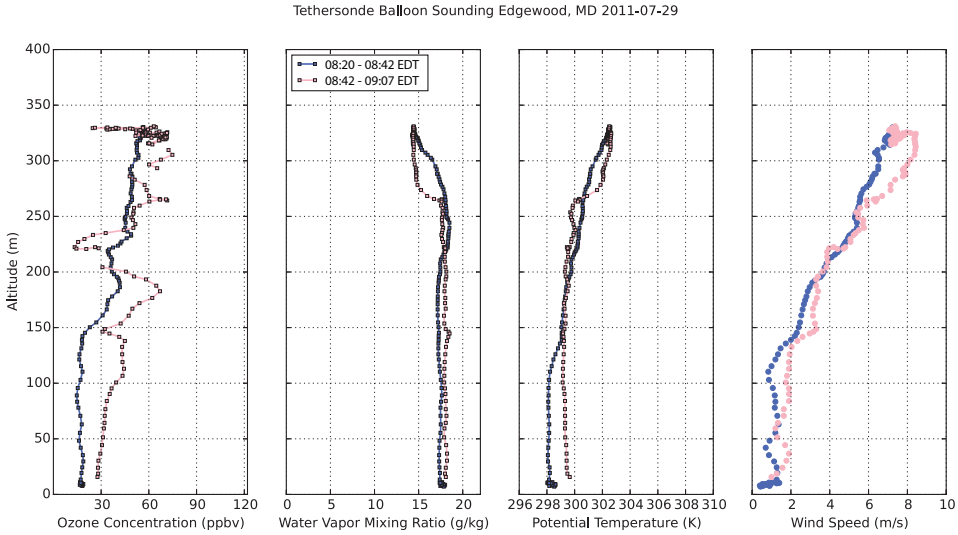


Figure 3. 07/29/2011 Millersville tethersonde profiles of ozone concentration, water vapor mixing ratio, potential temperature, and wind speed from the surface to ~340 m. The first sounding (blue) is from the surface to maximum altitude (08:20 – 08:42 EDT) and the second sounding (pink) is down from maximum altitude (08:42 – 09:07 EDT). Profiles indicate higher ozone concentration and water vapor mixing ratio layer aloft during first sounding and mixing down (weaker vertical gradient) by the second sounding.

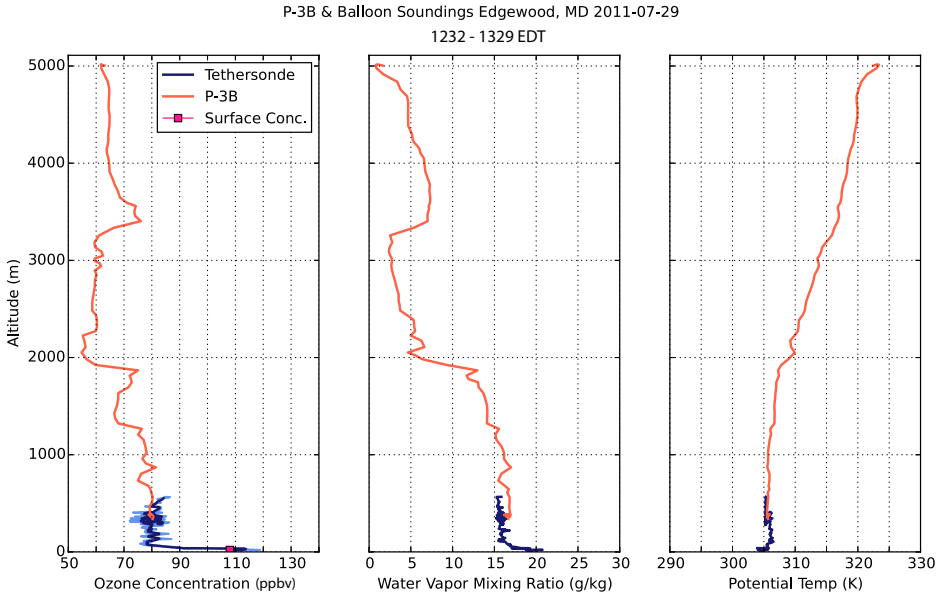


Figure 4. 07/29/2011 Midday blended profile of the first circuit P-3B spiral over Edgewood (orange) and the corresponding Millersville tethersonde sounding (blue) of ozone concentration, water vapor mixing ratio, and potential temperature from the surface to ~5000 m; surface ozone concentration (pink dot; at maximum surface ozone concentration). The shallow bay breeze passage is observed in the tethersonde profile and the surface, but not by the P-3B due its extremely shallow depth.

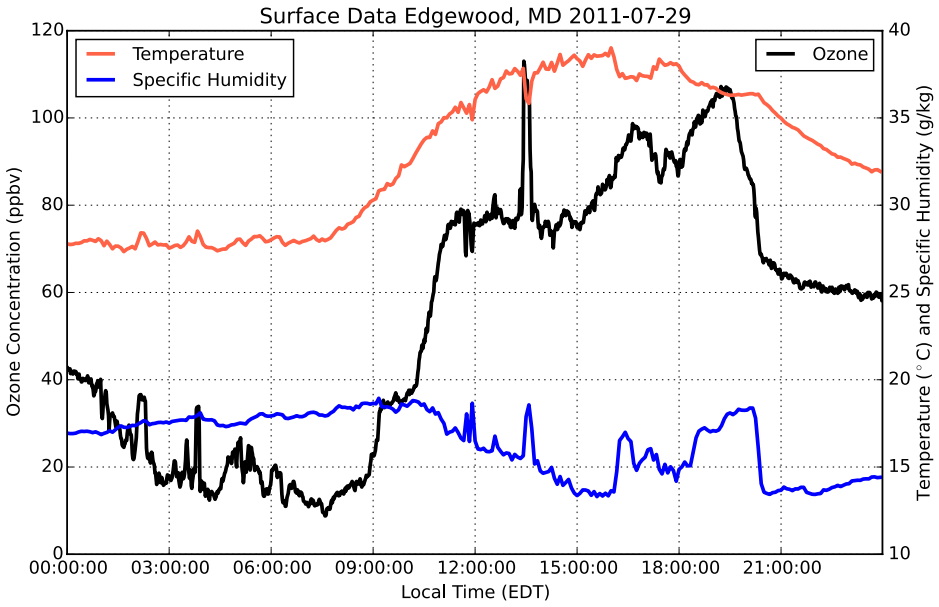


Figure 5. 07/29/2011 MARAF surface ozone concentration (black line), 4-m temperature (orange line) and 4-m flux tower specific humidity (blue line). Spikes that positively correlate between ozone concentration and specific humidity and negatively correlate to temperature observed (13:30, 16:15, 18:00 EDT) indicate two small-scale bay breeze passages and then a larger scale passage from 16:00 to 19:00 EDT.

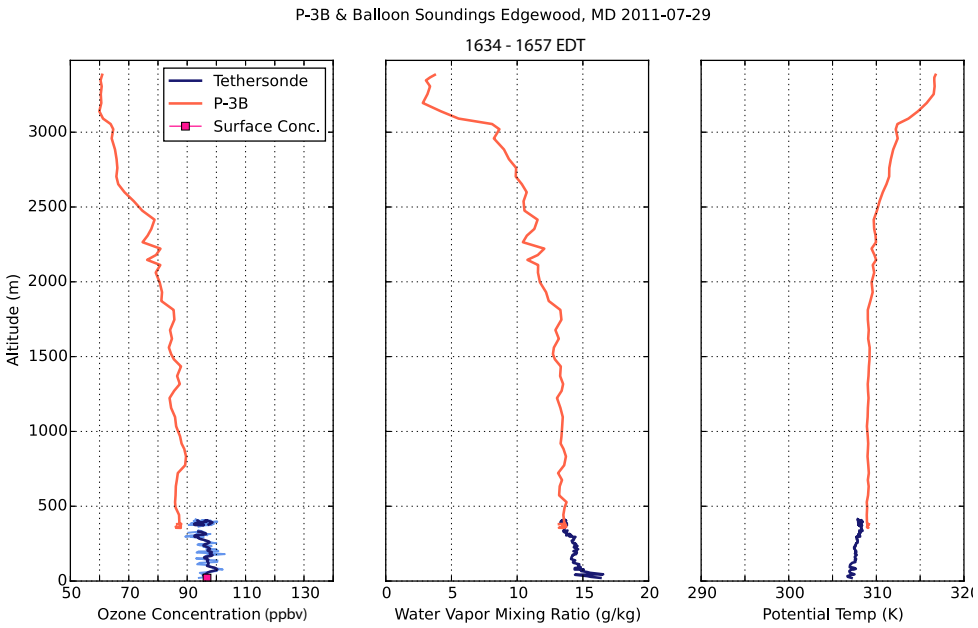


Figure 6. 07/29/2011 Late afternoon blended profile of the third circuit P-3B spiral over Edgewood (orange) and the corresponding Millersville tethersonde sounding (blue) of ozone concentration, water vapor mixing ratio, and potential temperature from the surface to ~4000 m; surface ozone concentration (pink dot). The tethersonde profile was taken ~25 minutes before the P-3B spiral, resulting in somewhat greater disparity between platforms.

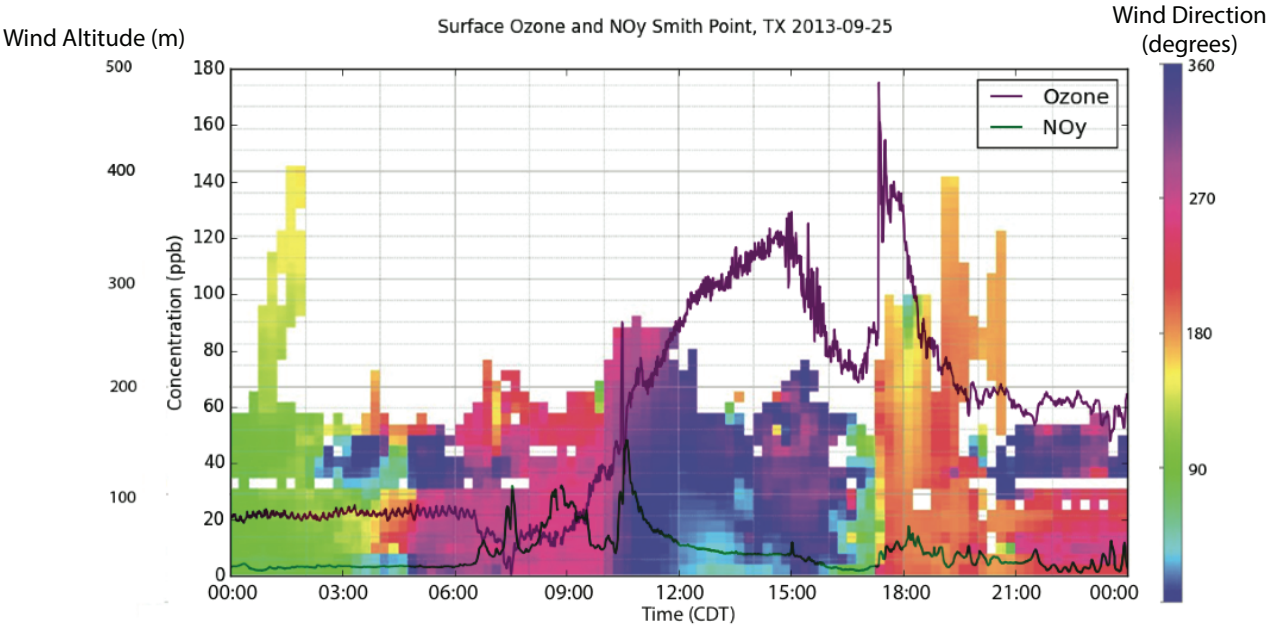
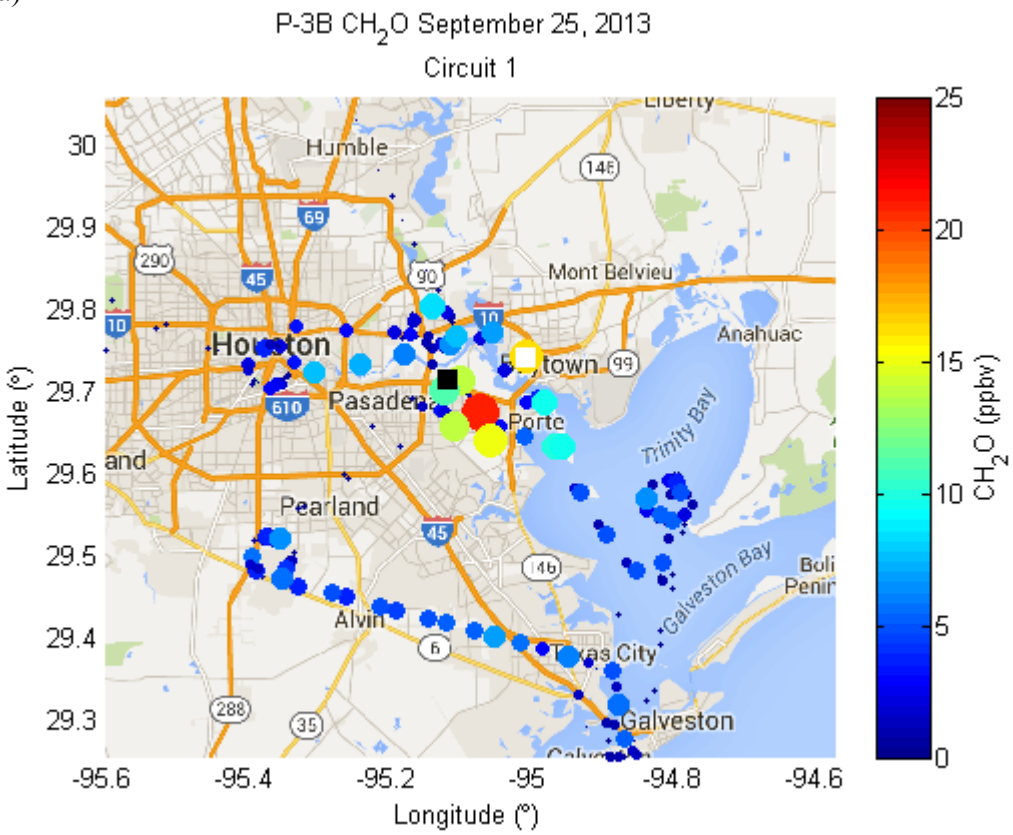
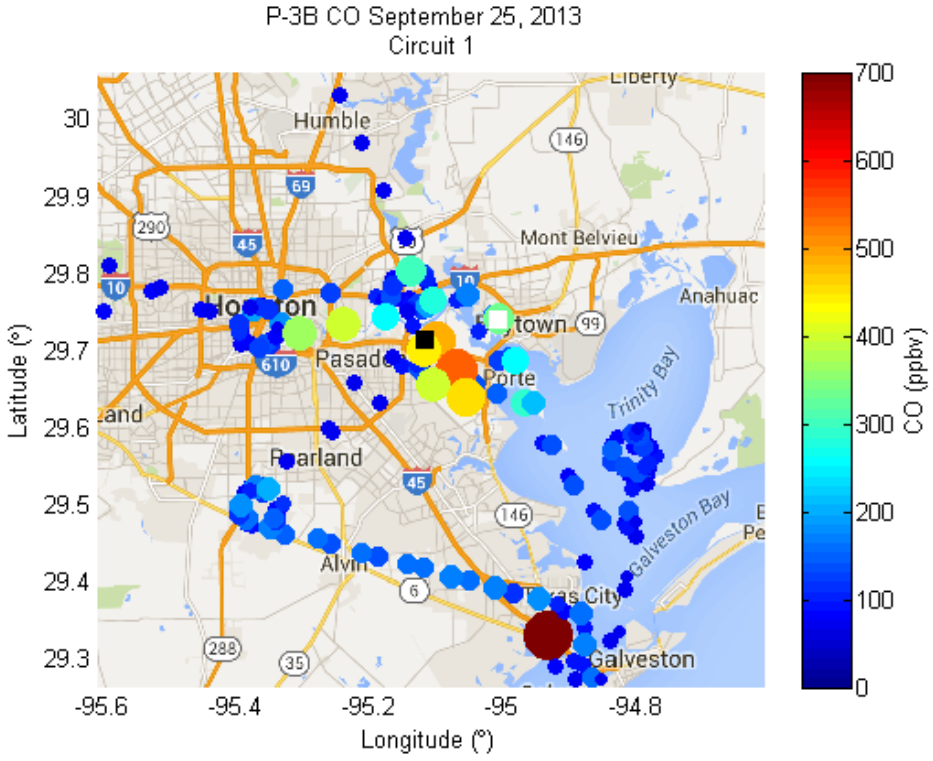


Figure 7. 09/25/2013 Smith Point, TX MARAF site wind direction with height derived from SODAR (colors) and NATIVE surface trace gases: ozone (purple) and NO_y (green). Note: consistent buildup of ozone under NW winds was followed by a spike as winds shifted to SW around 17:00 EDT, which brought photochemically aged smog to the site.

a)


P-3B CH2O September 25, 2013
Circuit 1
Humble
Mont Belvieu
Anahuac
Houston
Pasadena
Porte
Pearland
Alvin
Galveston
Trinity Bay
Galveston Bay
Latitude (°)
Longitude (°)
CH2O (ppbv)
30
29.9
29.8
29.7
29.6
29.5
29.4
29.3
-95.6
-95.4
-95.2
-95
-94.8
-94.6
25
20
15
10
5
0

b)


P-3B CO September 25, 2013
Circuit 1
Humble
Mont Belvieu
Anahuac
Pearland
Alvin
Galveston
Trinity Bay
Galveston Bay
Latitude (°)
Longitude (°)
CO (ppbv)
30
29.9
29.8
29.7
29.6
29.5
29.4
29.3
-95.6
-95.4
-95.2
-95
-94.8
700
600
500
400
300
200
100
0

c)

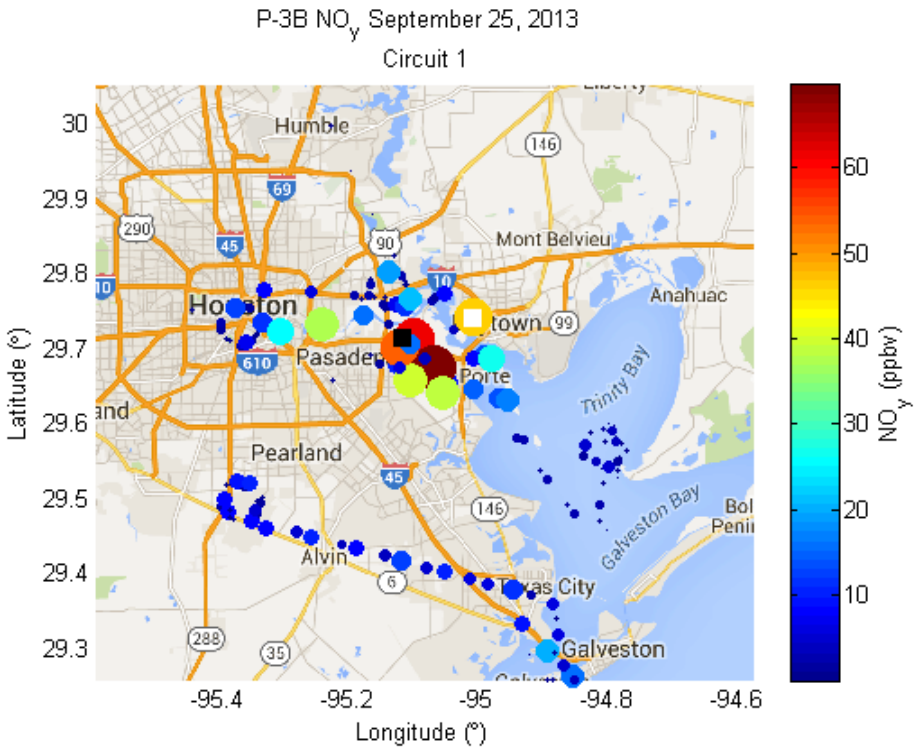
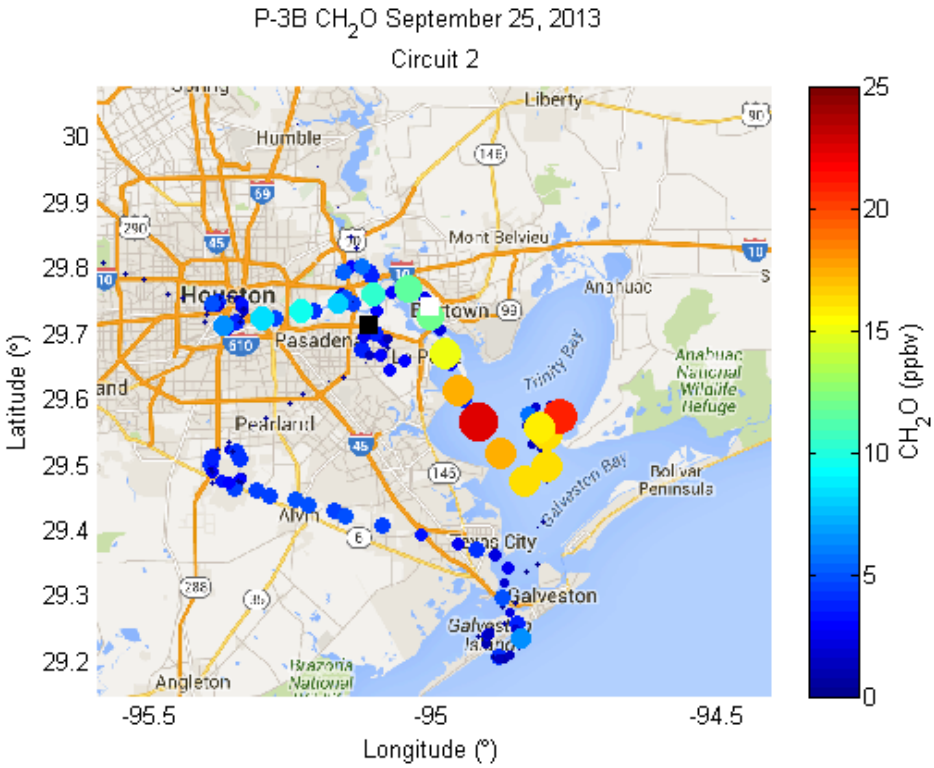
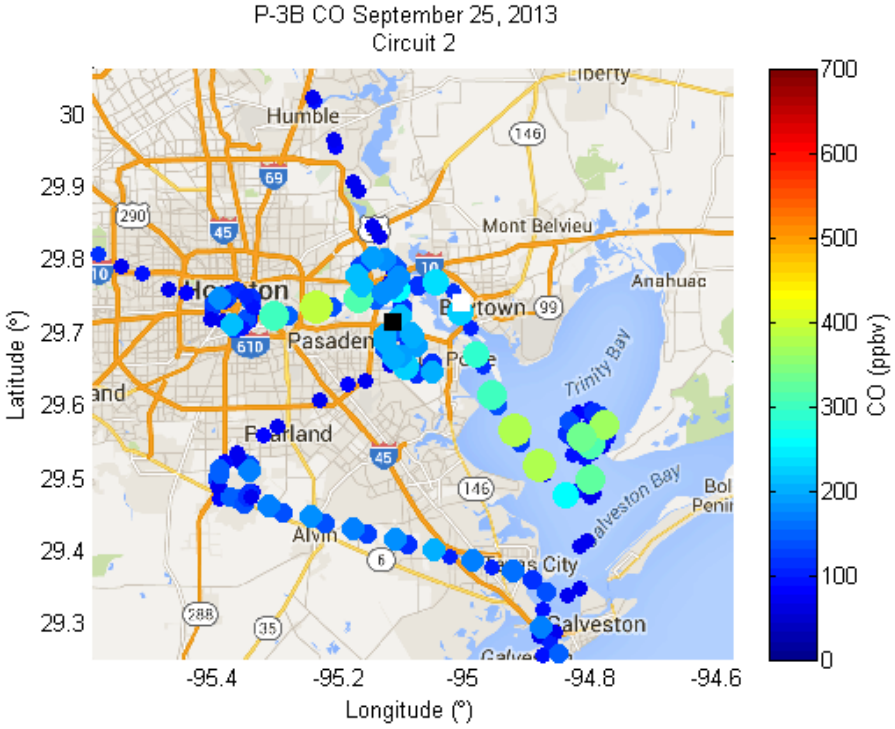


Figure 8. 09/25/2013 (a) CH_2O, (b) CO, and (c) NOy concentrations measured on the P-3B flight track during the first circuit. Black square is location of Deer Park and white square is location of Facilities at Baytown.

a)


P-3B CH2O September 25, 2013
Circuit 2
Latitude (°)
Longitude (°)
CH2O (ppbv)
Humble
Liberty
Mont Belvieu
Houston
Pasadena
Pearland
Alvin
Galveston
Anahuac
Trinity Bay
Galveston Bay
Bolivar Peninsula
Anahuac National Wildlife Refuge
Angleton
30
29.9
29.8
29.7
29.6
29.5
29.4
29.3
29.2
-95.5
-95
-94.5
25
20
15
10
5
0

b)


P-3B CO September 25, 2013
Circuit 2
Latitude (°)
Longitude (°)
CO (ppbv)
Humble
Mont Belvieu
Anahuac
Pasadena
Pearland
Alvin
Galveston
Trinity Bay
30
29.9
29.8
29.7
29.6
29.5
29.4
29.3
-95.4
-95.2
-95
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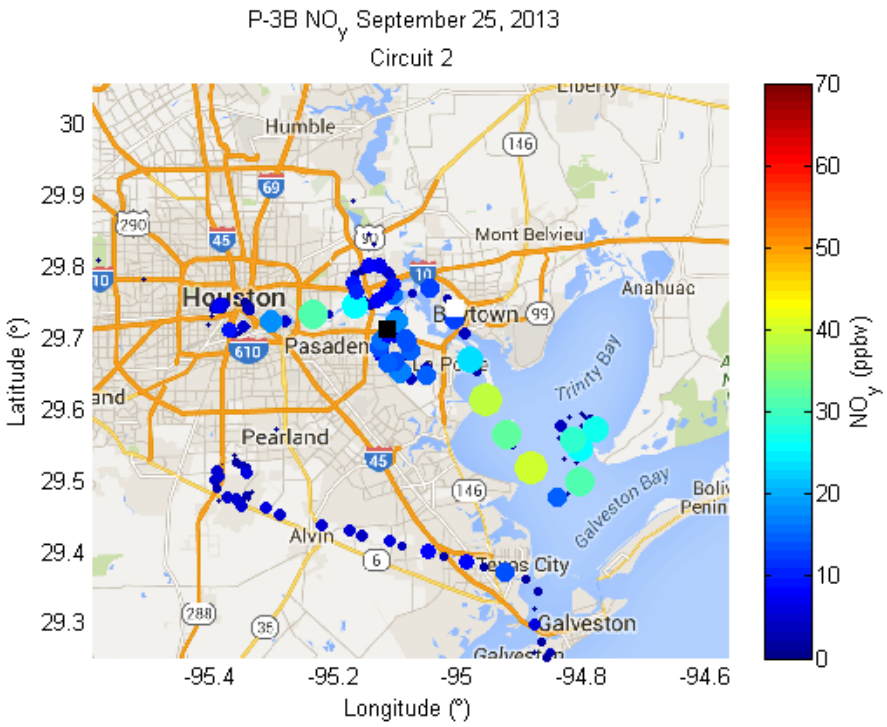
-94.6
700
600
500
400
300
200
100
0



c)

Figure 9. 09/25/2013 (a) CH_2O, (b) CO, and (c) NOy concentrations measured on the P-3B flight track during the second circuit

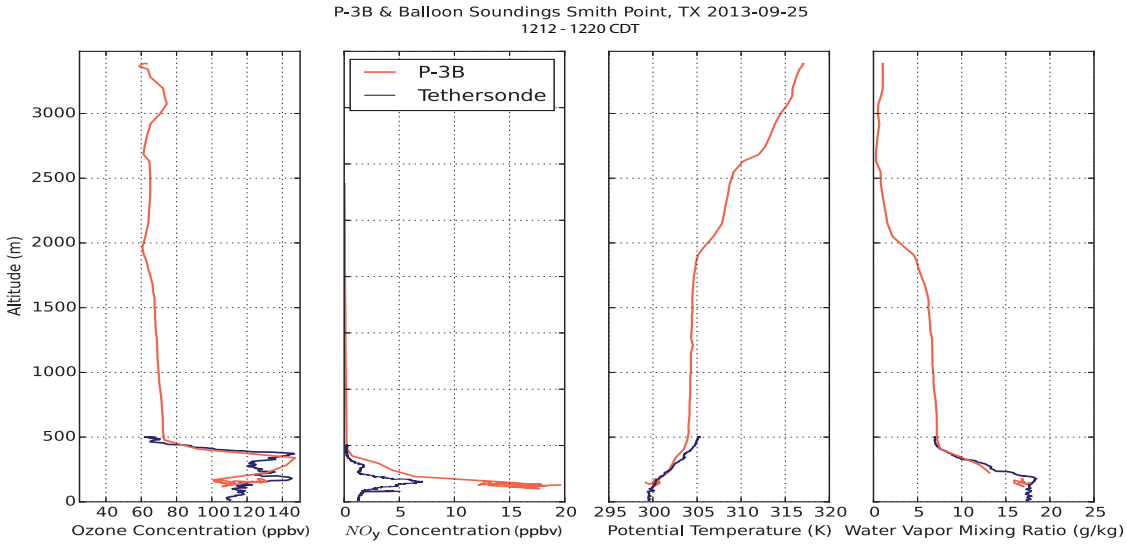


Figure 10. 09/25/2013 Blended profile of the second circuit P-3B spiral over Smith Point (orange) and the corresponding Millersville tethersonde sounding (blue) of ozone concentration, NO_y concentration (NO_x with interferences from other reactive nitrogen species on tethersonde), water vapor mixing ratio, and potential temperature from the surface to ~4000 m. The P-3B measured a NOy plume at ~100 m that the tethersonde did not due to temporal and spatial differences between the soundings.

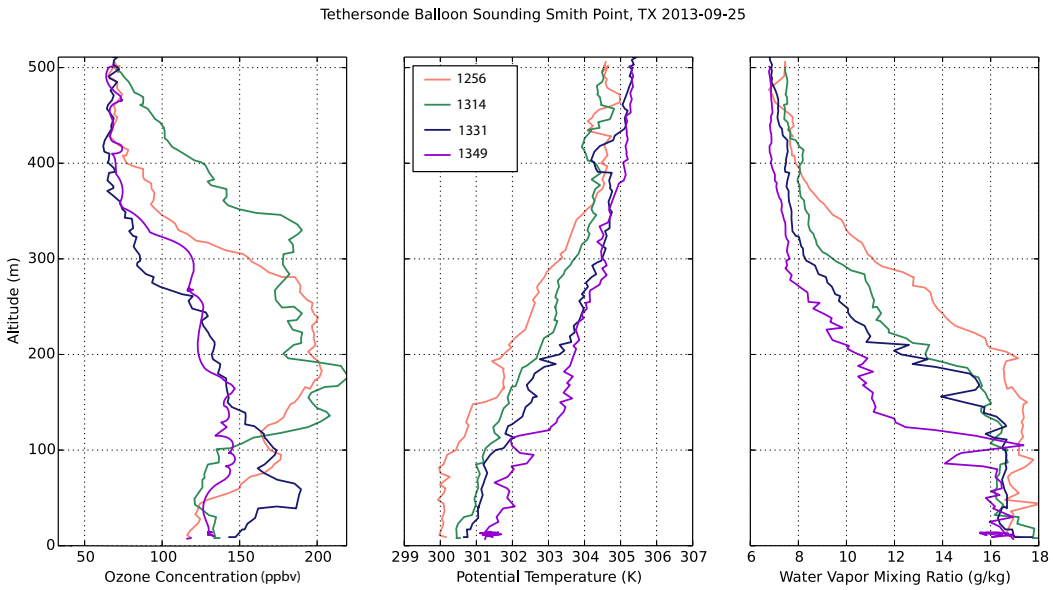
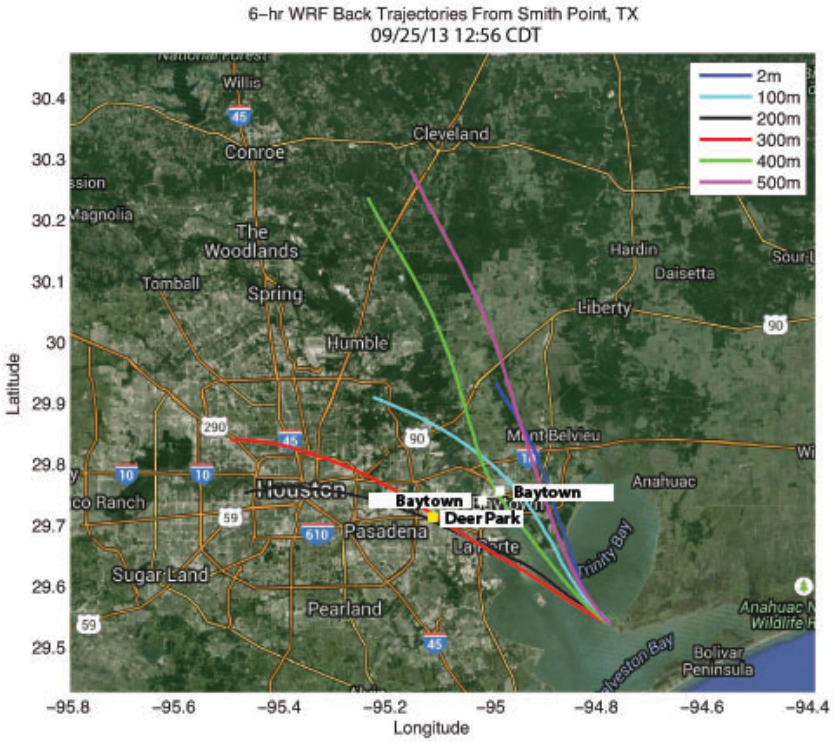
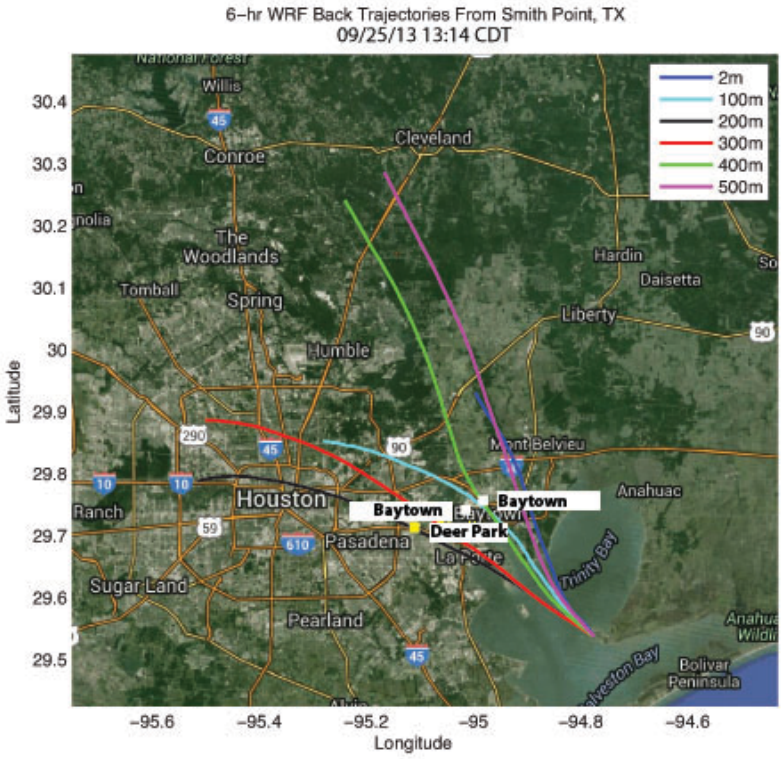


Figure 11. 09/25/2013 Tethersonde soundings of ozone concentration, potential temperature, and water vapor mixing ratio at Smith Point from 12:56 – 13:49 CDT from the surface to 500 m.

a)

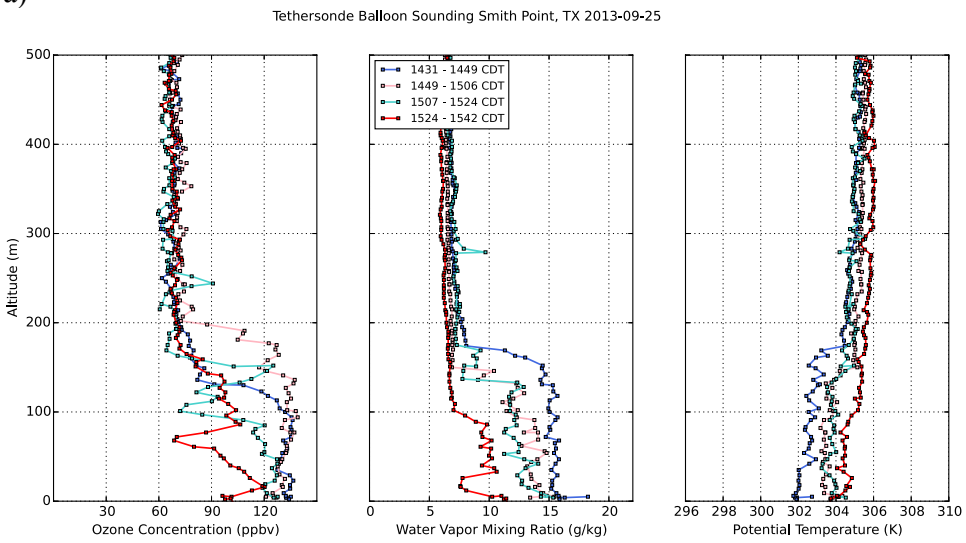




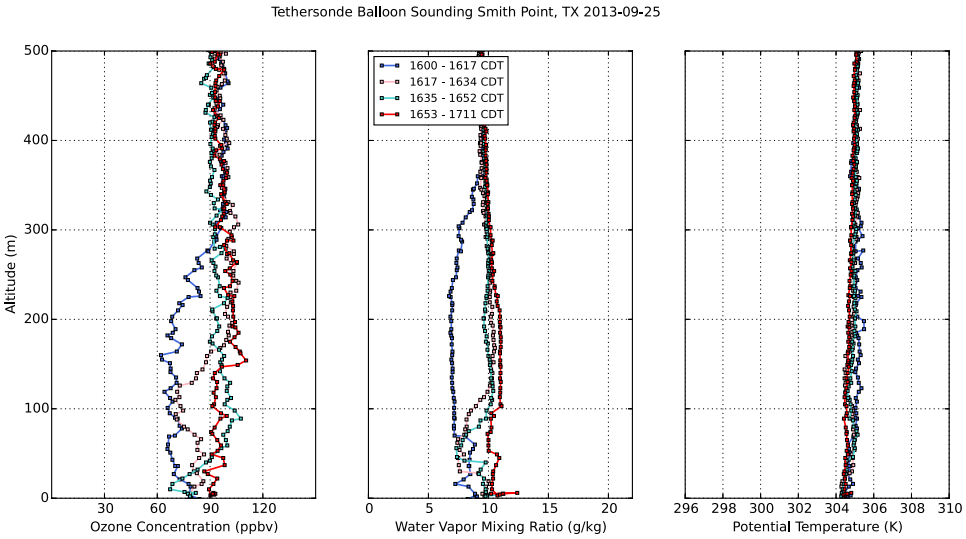
b)

Figure 12. Six-hour WRF back trajectories at six initialization altitudes (2 m, 100 m, 200 m, 300 m, 400 m, 500 m) from the location of the tethersonde at Smith Point. (a) Initialized at 12:56 CDT (b) Initialized at 13:14 CDT

a)



b)



c)

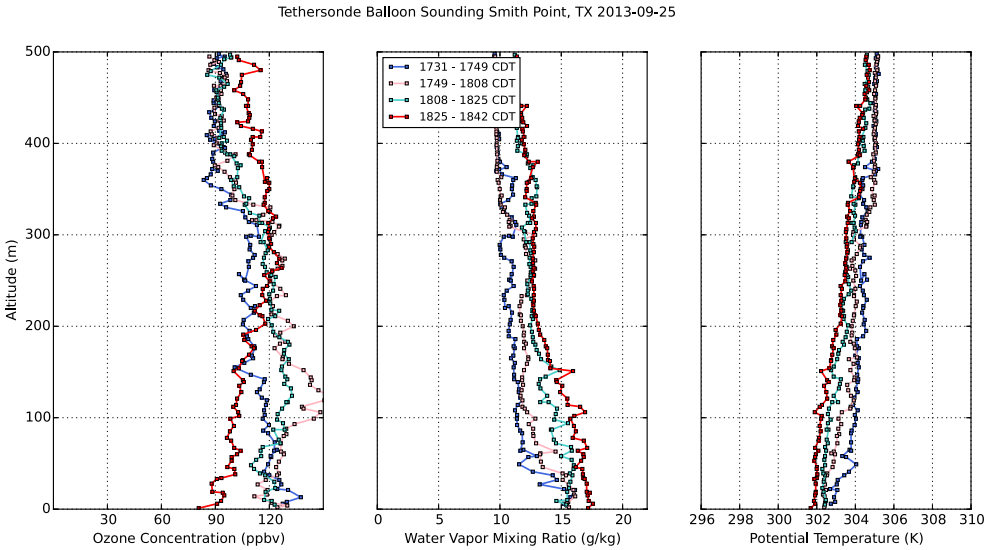


Figure 13. 09/25/2013 Tethersonde soundings of ozone concentration, water vapor mixing ratio, and potential temperature at Smith Point from (a) 14:31 – 15:42 CDT, (b) 16:00 – 17:11 CDT, (c) 17:31- 18:42 CDT from the surface to 500 m

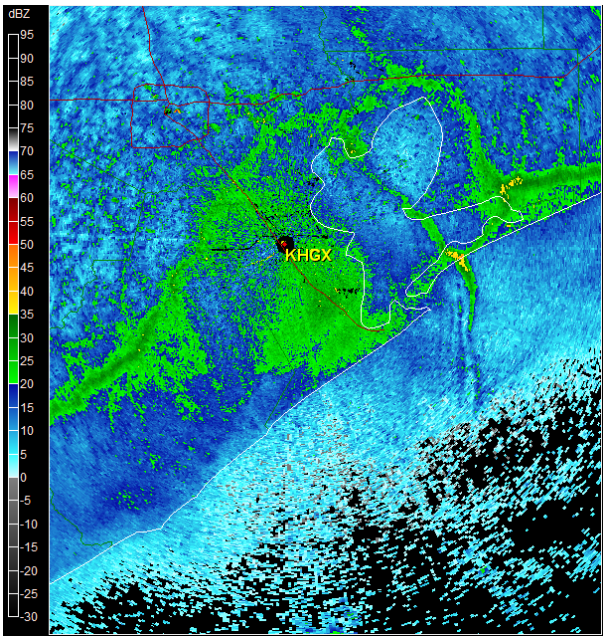


Figure 14. 09/25/2013 Houston/Galveston, TX (KHGX) radar reflectivity in dBZ of the bay and Gulf breezes at 22:30 UTC (17:30 CDT) passing over Smith Point.

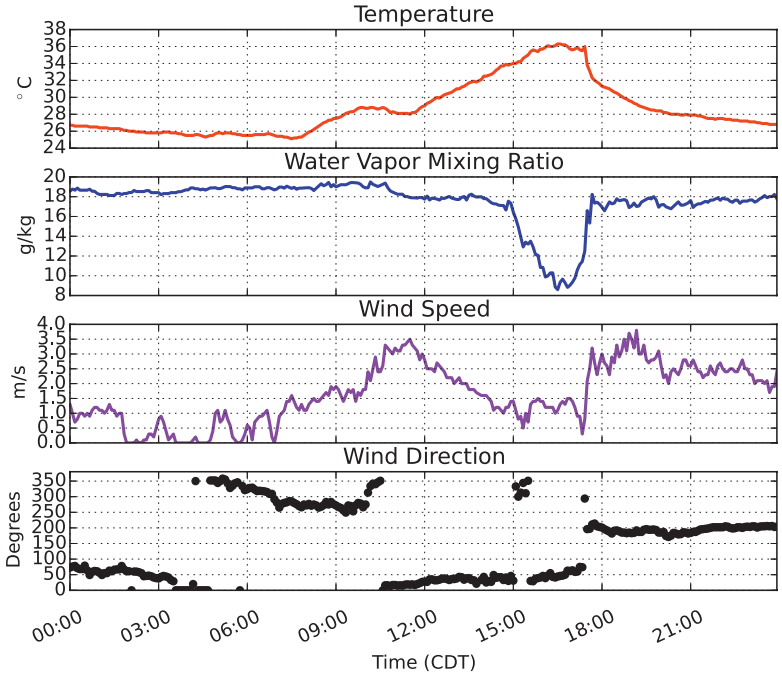


Figure 15. 09/25/2013 surface WeatherPak observations of temperature, water vapor mixing ratio, wind speed, and wind direction from MARAF platform at Smith Point.

Supplemental Figures:

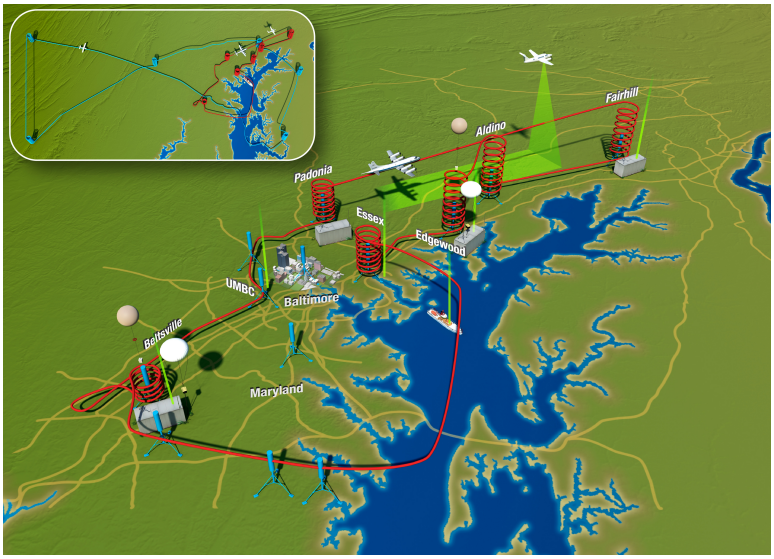


Figure S1. DISCOVER-AQ ground and spiral sites during the July 2011 Baltimore/Washington campaign. Edgewood is where the Millersville Tethersonde/MARAF and NATIVE were located (http://discover-aq.larc.nasa.gov).

Figure S2. Relative locations of MDE/NATIVE, and MARAF sites, both in Edgewood, MD northeast of Baltimore and surrounded by the Chesapeake Bay and its estuaries.

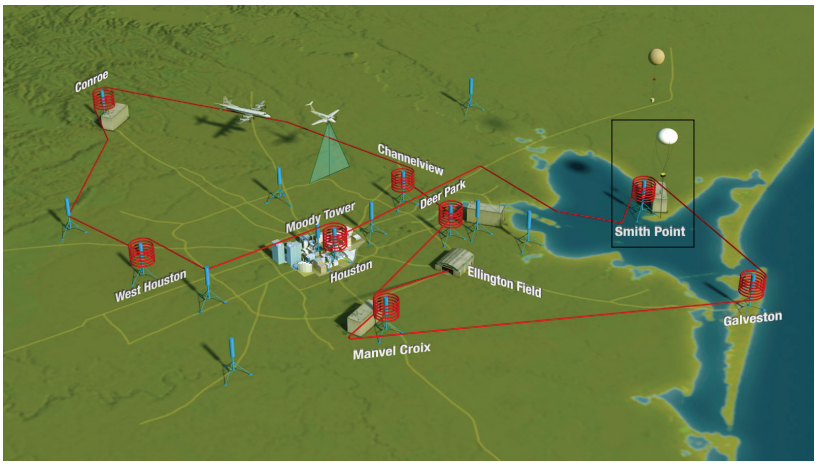


Figure S3. DISCOVER-AQ ground and spiral sites during the September 2013 Houston campaign. Smith Point is where the Millersville Tethersonde/MARAF and NATIVE were co-located (http://discover-aq.larc.nasa.gov).

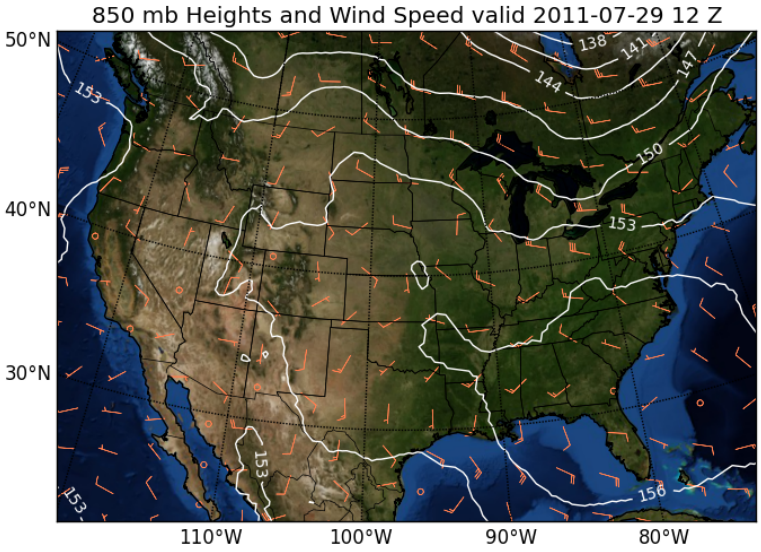


Figure S4. NCEP North American Regional Reanalysis (NARR) 850 mb geopotential heights (white lines) and wind barbs (orange barbs) on 07/29/2011 at 12 UTC (08:00 EDT) over the U.S.

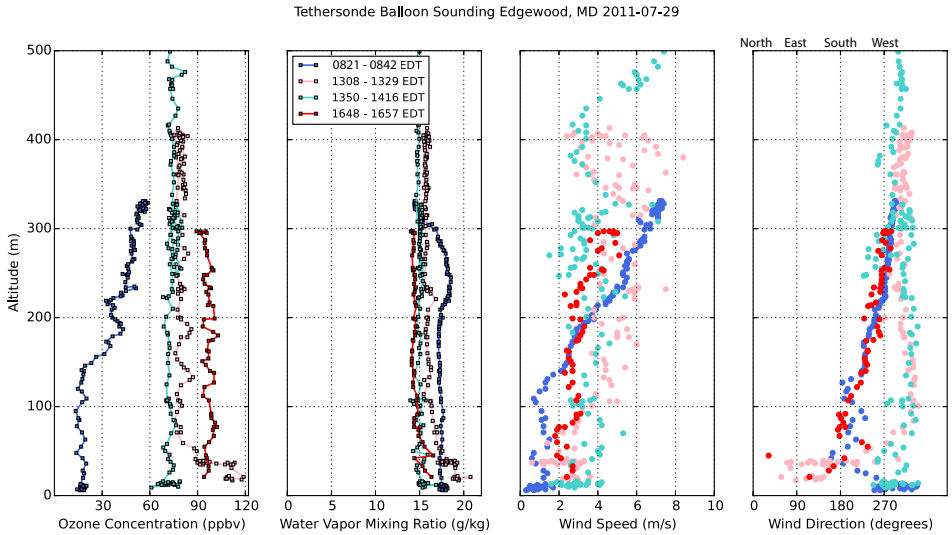


Figure S5. 07/29/2011 Millersville tethered balloon soundings throughout the day capturing temporal variations in concentrations and meteorological parameters at Edgewood. Blue: morning sounding before mixing (08:21-08:42 EDT), light pink: sounding during the first bay breeze (13:30 – 13:29 EDT), green: sounding showing retreated levels of ozone concentration and water vapor mixing ratio before second bay breeze (13:50 – 14:16 EDT), red: sounding ~30 minutes after second bay breeze passage (16:48- 16:57 EDT).

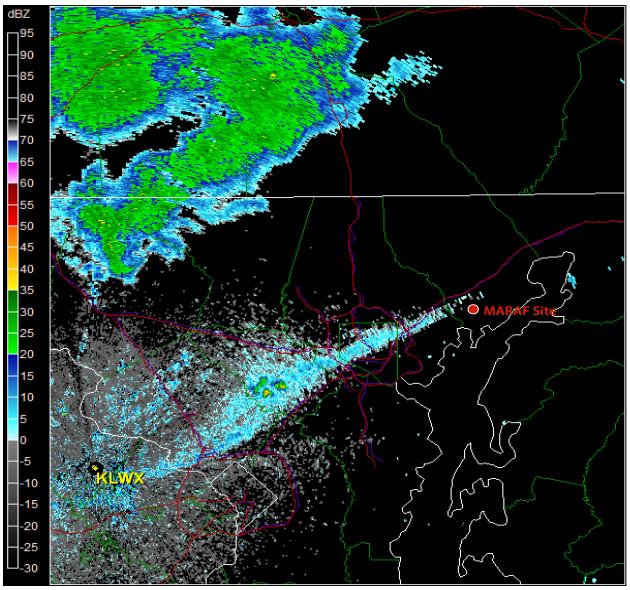


Figure S6. 07/29/2011 Sterling, VA (KLWX) radar reflectivity in dBZ of gust front passage over the MARAF site at 00:03 UTC (20:03 EDT).

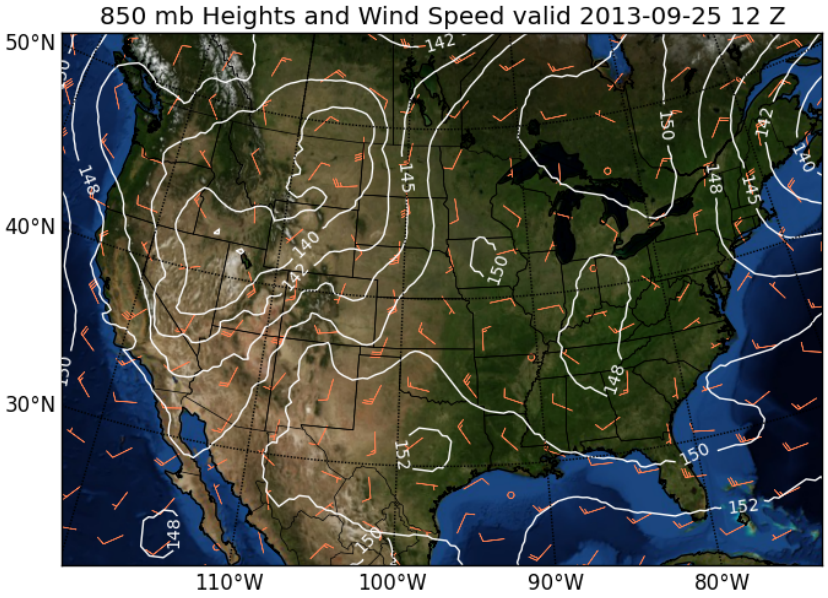


Figure S7. NCEP North American Regional Reanalysis (NARR) 850 mb geopotential heights (white lines) and wind barbs (orange barbs) on 09/25/2013 at 12 UTC (07:00 CDT) over the U.S.

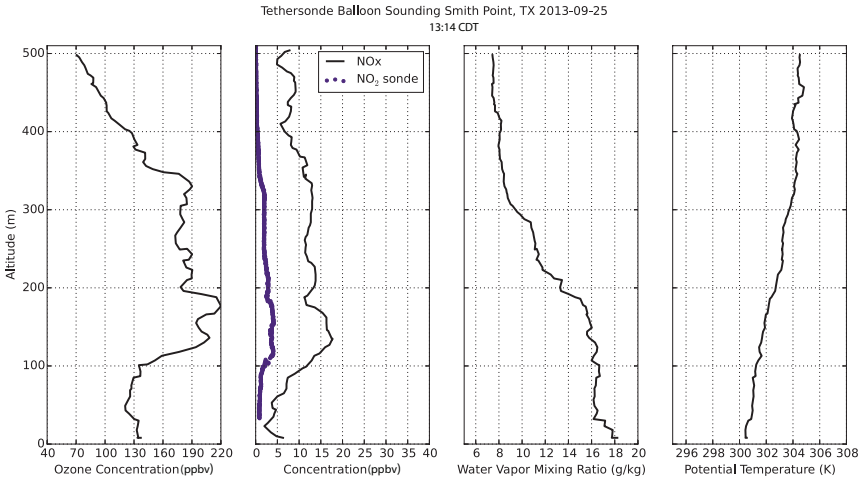


Figure S8. 09/25/2013 Millersville University tethersonde sounding of ozone, NOx, NO_2 sonde, water vapor mixing ratio concentration and potential temperature from the surface to 500 m at Smith Point.

Tables:

Table 1 Measurements with uncertainties/ accuracies and deployment platform for Edgewood and Smith Point

Instrument & Model	Measurement	Platform	Uncertainty/Accuracy
Vaisala, TTS111	Temperature, RH, Pressure	Tethered Balloon	±0.5 °C, ±5 %, ±1.5 hPa
2B Technologies, 205	Ozone	Tethered Balloon	±2 %
2B Technologies, 401/410	NO/NO_2	Tethered Balloon	±2%
KNMI NO2-sonde	NO_2	Tethered Balloon	N/A (TBD)
ScinTec, MFAS SODAR & RAE1 RASS	Vertically Resolved Wind Speed & Direction	MARAF	0.3-0.5 m/s, ± 3° (<2.0 m/s)
Flux Tower Instruments (denoted by *)	Near-surface Fluxes	MARAF	
CSI 3-D Sonic Anemometer, CSAT3*	u,v,w; Tv	MARAF	Ux,Uy: ±8 cm/s Uz: 4 cm/s Direction: ±0.7° at 1 m/s Tv: N/A
LI-COR H_2O/CO_2 Gas Analyzer, LI-7500*	H_2O/CO_2 concentration	MARAF	CO_2 ±1% H_2O ±2%
Vaisala Pressure Sensor, PTB220B*	Pressure (hPa)	MARAF	±0.25 hPa
Micromet Systems Net Radiometer, Q*7*	Net Radiation (Wm^{-2})	MARAF	-6% @ 7m/s for positive fluxes, -1% at 7 m/s for negative fluxes
Surface WeatherPak 2000	WxPak Pressure	MARAF	±1 hPa at 22°C
	WxPak Compass	MARAF	< ±30 °
	WxPak Wind Speed	MARAF	±0.3 m/s
	WxPak Wind Dir.	MARAF	± 3 °
	WxPak Humidity and Temperature	MARAF	± 0.8% / ±0.1 K at 23°C
TECO Inc., 29C	Surface O_3	NATIVE	±2 %
TECO Inc., 42C-Y	Surface NO/ NO_y	NATIVE	±3 %
NCAR 4 Channel Chemiluminescence	Ozone	P-3B	±5 %
NCAR 4 Channel Chemiluminescence	$NO/NO_2/NO_y$	P-3B	10-15 %
General Eastern, 1011B	Temperature	P-3B	±0.2 °C
Rosemount, MADT 2014	Pressure	P-3B	±0.25 hPa