PHYS 650: Atmospheric Measurement
Dr. Ruben Delgado

Chemistry and Dynamics of May 2022 Ozone Exceedance

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Abstract
A large effort has been made to establish ozone lidars across the mid-Atlantic region of the United States. By 2023 there will be 4 Tropospheric Ozone Lidar Network (TOLNet) sites across the mid-Atlantic region: Hampton, VA with Hampton University and NASA Langley Research Center (LMOL); Greenbelt, MD with NASA Goddard Space Flight Center (TROPOZ); and Manhattan, NY will have one at the City College of New York (CCNY). This novel venture will bring much-needed profiling of ozone to key areas in the region, however, its networked coverage will be sparse with sites being ≤ 200 miles apart. To extend the utility of both the TOLNet and Pandora networks, we have begun using their observational products to interpret boundary layer abundances to extract new science and understanding of pollution dynamics. We present a case study of this effort from a NAAQS ozone exceedance episode from May 19 - 21, 2021. High-resolution observations from active and passive remote sensors capture the evolution of this event. The ozone episode evolved from entrainment of a transported polluted air-mass followed by recirculation in the region leading to a quick lofting by down-slope winds (as noted by ceilometer backscatter and vertically resolved wind profiles) which situated the plume for next-day entrainment. Collocated wind, aerosols, and ozone profiles in the Beltsville - Greenbelt, MD area indicated an air-mass change occurring near 14 LT May 20, 2021, marking the arrival of a well-mixed layer of ozone from the north. For this case, the Pandora total column ozone enhancement showed good agreement both temporally and quantitatively with TROPOZ 0 - 2 km integrated column (a TEMPO-like proxy). This shows the potential for future synergy in air quality event identification and characterization, especially in those that are driven by meteorological enhancement and transport. A bi-product of this work is an analysis of the seasonal variability of ozone in the mid-Atlantic domain using TOLNet, Pandora, sondes, and surface trace-gas monitors. This work aims to aid in the resolution of NASA decadal surface questions, support the upcoming

TEMPO mission, and serves to demonstrate the usefulness of multi-instrument perspectives in the analysis of air quality event evolution and spatio-temporal variability. Further work will focus on the comparison of these datasets with NASA GEOS-CF and current satellite products.

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1 Introduction

The coasts are where 40% of the nation's population lives, where 55.8 million people are employed, and where $8.3 trillion in goods and services are traded yearly (National Coastal Population Report, 2013). Unfortunately, air quality in these communities is known to be highly variable. Within the first three kilometers of the atmosphere (i.e., the atmospheric boundary layer, ABL) resides most of the natural and anthropogenic trace-gases pollutants that affect human health, agriculture, and ecosystems. Previous studies of coastal air quality have not fully characterized the spatial and temporal variability of atmospheric dynamics, chemistry, or their coupling. Accurately forecasting weather and air quality in coastal environments depends largely on detailed process level understanding of ABL dynamics and chemical budgets in a four-dimensional (4D) observational framework. The ABL has a wide variety of weather and climate attributes that directly impact this nation's prosperity, and thus understanding these processes is critical for our ability to mitigate (through observation and prediction) the effects of adverse coastal phenomena.

1.1 Primary Emission and Photochemical Production

There are two categories of air pollutants, those that are emitted directly from either natural or anthropogenic sources (i.e., primary pollutants), and those that are formed in the atmosphere from chemical reactions and/or collisions while suspended in the atmosphere (i.e., secondary pollutants) (Cooper, 2011). Nitrogen dioxide (NO_2) is a key primary pollutant trace-gas that contributes to the formation of secondary pollutants, most notably the critical oxidant trace gas known as ozone (O_3). About 90% of the atmosphere's ozone resides in the stratosphere shielding the Earth's surface from harmful Ultra-Violet (UV) radiation. However, ozone at the surface level is responsible for respiratory illnesses, degradation of land & marine ecosystems, and oxidation of agricultural resulting in loss of yields. Ozone is a photochemical biproduct of many reactions that take place within the atmosphere, largely beginning with nitrogen oxides (NO_x, NO, & NO_2) and volatile

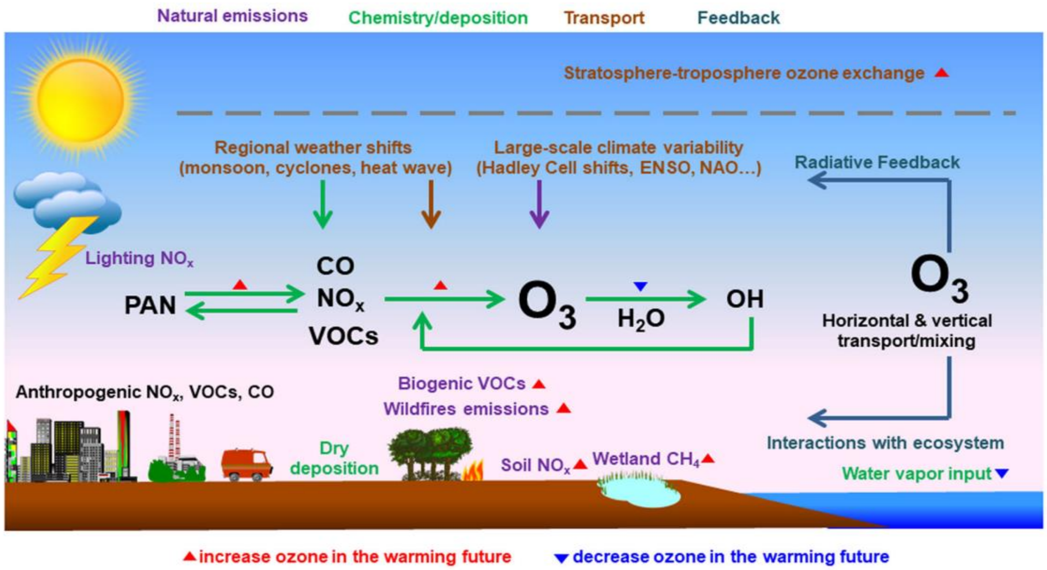

Figure 1: Tropospheric ozone (O_3) sources and sinks. Primary photochemical sources are outlined: nitrogen oxides (NO_2) and volatile organic compounds (VOC) (Lu et al., 2019).

organic compounds (VOCs). A diagram of tropospheric ozone production and dynamics is provided in Figure 1. Nitrogen oxides photolyze in the presence of near UV-radiation and while VOCs volatize with high surface temperatures, together they create a series of reactions that produce ozone.

1.2 Meteorological Drivers of Air Quality

Atmospheric dynamics plays an important role in boundary layer ozone as it dictates the chemical budget for production by horizontal and vertical transport/mixing of precursors from emitted from the surface, or downmixing of ozone from the upper-troposphere and stratosphere. Stagnation of the boundary layer, like weak vertical mixing and low wind speeds can create conditions that favor photochemical production, leading to haze (i.e., smog) and in turn decreasing breathability and visibility at the surface and/or aloft.

Bad air quality is not only dominated by chemistry but by atmospheric dynamics as well. The chemistry that produces bad air quality is enhanced or inhibited by the altering of chemical budgets by vertical mixing and advection. Distributions of pollutants with coastal boundary layers are largely dictated by the meteorological drivers. Within the Washington, DC – Baltimore, MD corridor (WBC) the heterogenous topography, being the Appalachian Mountains to the West, and the Chesapeake Bay to the East, create three inherent mesoscale features in wind patterns that are strong drivers of air quality in the region. Those being Nocturnal Low-Level Jets (NLLJ), Downslope Winds (DSW), and Bay-Breeze (BB), all of which contribute advection and/or vertical mixing and thus effecting air quality and its distribution in space and time (Delgado et al., 2013, Rabenhorst et al., 2014, Sullivan et al., 2017, and Dreessen et al., 2016; Loughner et al., 2014 and Caicedo et al., 2021).

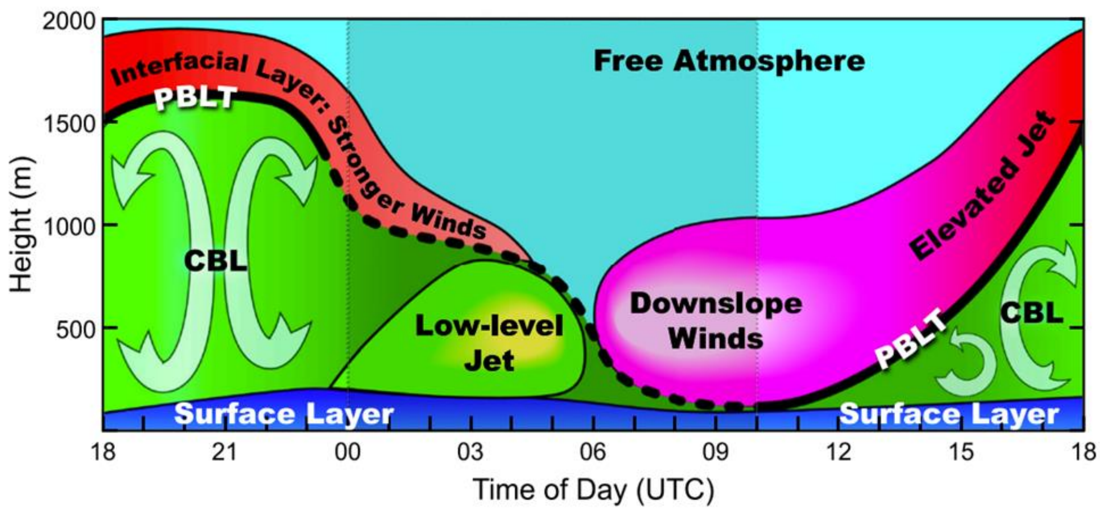

Figure 2: Schematic of 3-Stage Mid-Atlantic Atmospheric Boundary Layer Evolution as modeled by Rabenhorst et al (2014) and adapted from the classic Stull (1988) model. Note the addition of the low-level jet and downslope winds.

The Mid-Atlantic NLLJ is described as a shallow layer of fast-moving air of at least 2 m s^{-1} greater than winds at the levels above and below the maximum, or "nose," flowing parallel to the Appalachian Mountains (perpendicular to the sloping terrain) (Delgado et al., 2013 and Zhang et al., 2006). Its key mechanism for development is believed to be the diurnal heating and cooling of the surface across the sloped terrain (Zhang et al., 2006). Mid-Atlantic NLLJ have been observed between 00:00 and 08:00 Eastern-Time (ET) and can transport pollutants over mesoscale distances in a single night (Delgado et al., 2013, Rabenhorst et al., 2014, Sullivan et al., 2017). The vertical shear produced by NLLJ presence is responsible for the nocturnal increases in surface concentrations of pollutants causes by turbulent downburst that can mix pollutants from the residual layer into the stable nocturnal boundary layer and then the surface layer. Nocturnal increase in photochemically produced pollutants like ozone can indicate the presence of the NLLJ. In the Mid-Atlantic region, the presence of the Appalachian Mountains allows for the formation DSW which originate from the mountain's orographic effect on wind and thus flows perpendicular to the mountains (parallel to the sloped terrain). The Mid-Atlantic DSW is also a key dynamic phenomenon that can redistribute pollution over large distances. Use Figure 2 as a schematic for the combination of these two drivers into a 3-stage boundary layer evolution for the Mid-Atlantic.

1.3 May 2021 Ozone Exceedance

Presented here is an analysis of a recent air ozone episode (May 19 - 21, 2021) that impacted the mid-Atlantic region with multiple exceedances of the National Ambient Air Quality Standards (NAAQS) for surface ozone concentrations. Interesting features of this episode include deviation from recent exceedance trends, the arrival of the well-mixed polluted air mass, and nocturnal ozone increases. The analysis incorporates multiple datasets of in-situ and remote sensing measurements.

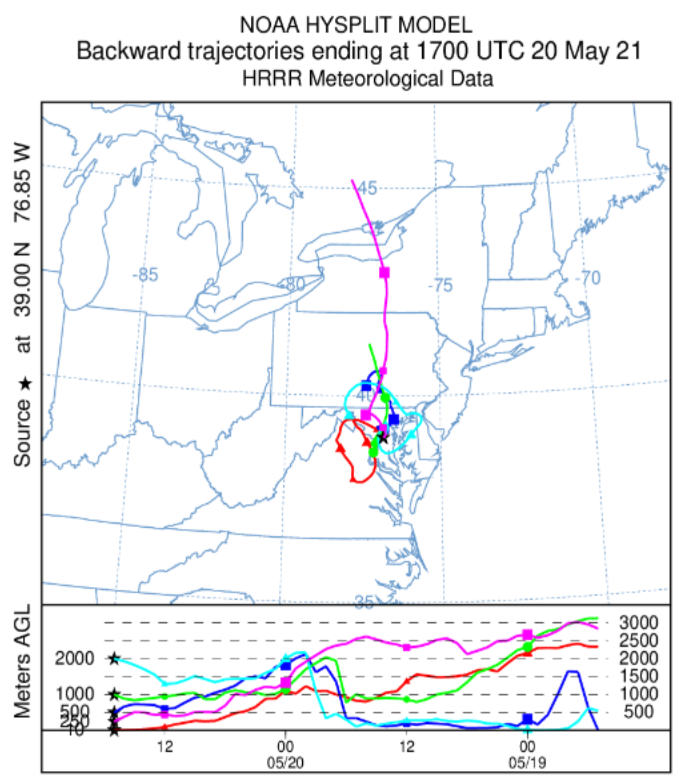

Figure 3: HYSPLIT backtrajectory with mixing layer heigh inset initialized from NASA GSFC at 17 UTC. Shows recirculation and long-range transport.

Observations of ozone were taken in column abundance from Pandora spectrometers, with vertically resolved profiles from balloon-borne ozone-sondes and in high-temporal resolution from the NASA GSFC Tropospheric Ozone (TROPOZ) lidar, part of TOLNet. Profiles of aerosols and winds were taken by ceilometers (Unified Ceilometer Network, UCN) and MDE radar wind profilers (RWP), respectively. In addition to ground-based instruments, satellite products from OMI and TROPOMI, and HYSPLIT were used in the analysis. The focus of this work is on the Beltsville, MD - Greenbelt, MD area of which TROPOZ, RWP, Ceilometer, Pandora, Sonde, and MDE surface samplers are of near-colocation.

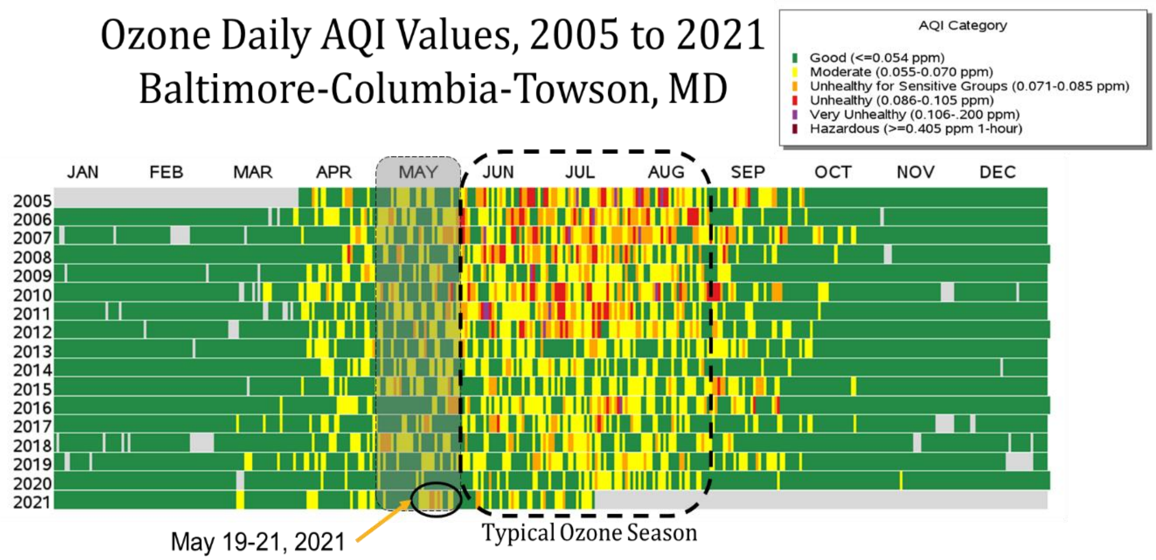

Figure 4: Tile plot of ozone exceedances by year. Note that this May 2021 case is a deviation from the previous 5 years (2015 - 2022). Taken from EPA AirData.

2 Data & Methods

Surface ozone concentrations were observed in excess of 70 ppb for 4 days (May 18-22, 2021). Seven of the twenty Maryland surface monitoring sites recorded exceedances of the 8-hr NAAQS Ozone standard. Strong nocturnal increases in surface ozone were observed on the night of May 20th, influenced by NLLJ turbulent downmixing [4]. HYSPLIT back-trajectory initialized from May 20th 17 UTC shows recirculation of air in the Maryland-Virginia region accumulating from days prior. On May 20th the TROPOZ system, Ceilometer, Sonde profiles observed a well-mixed

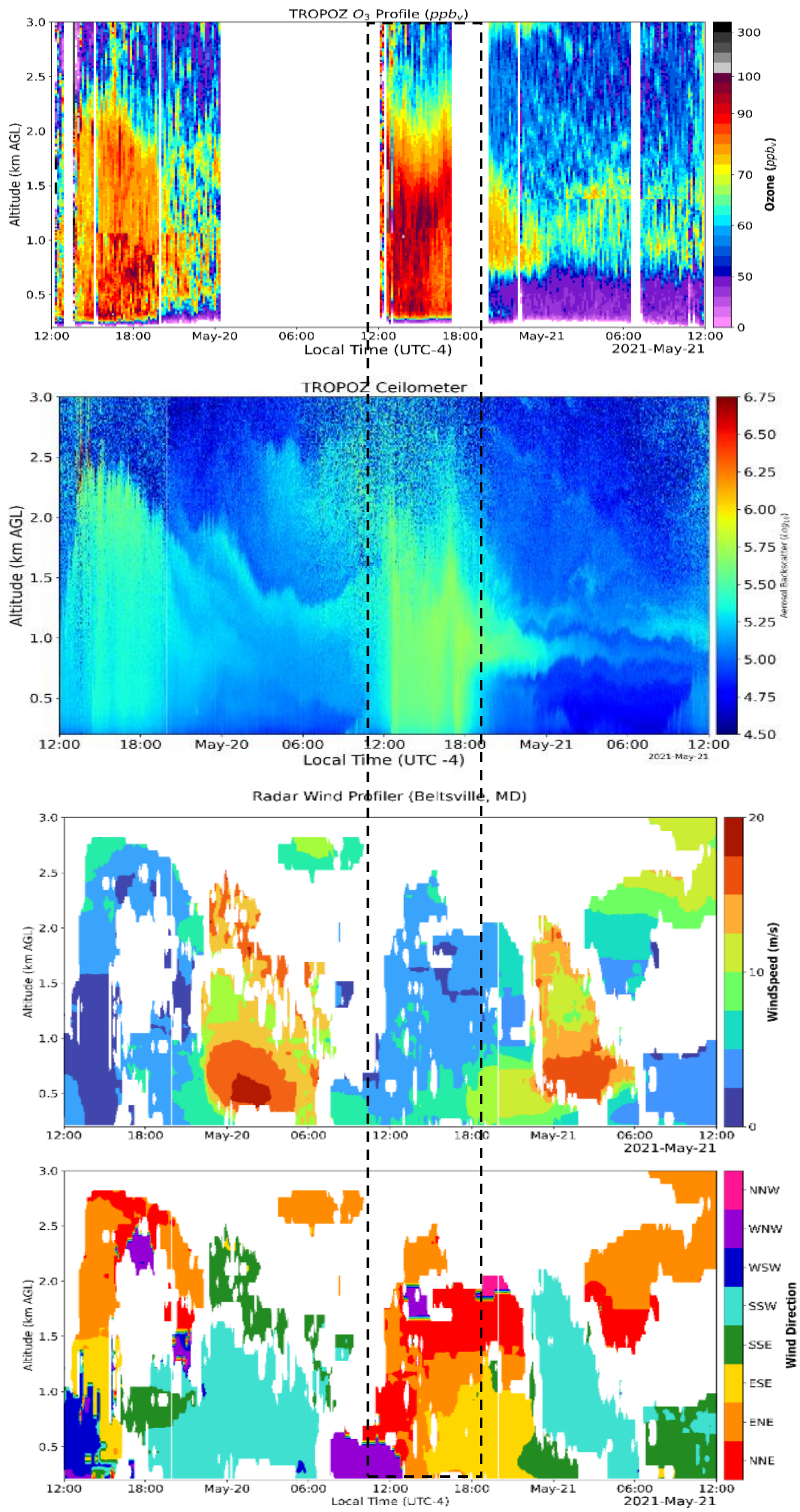

Figure 3: 19-21 May 2021 profiles during a polluted episode in MD (a) TOLNet observed ozone, (b) ceilometer aerosols backscatter, (c) and radar wind speed and direction.

polluted boundary layer marked by the arrival of northeasterly winds observed at 12 UTC by RWP at Beltsville, MD (see Figure 2).

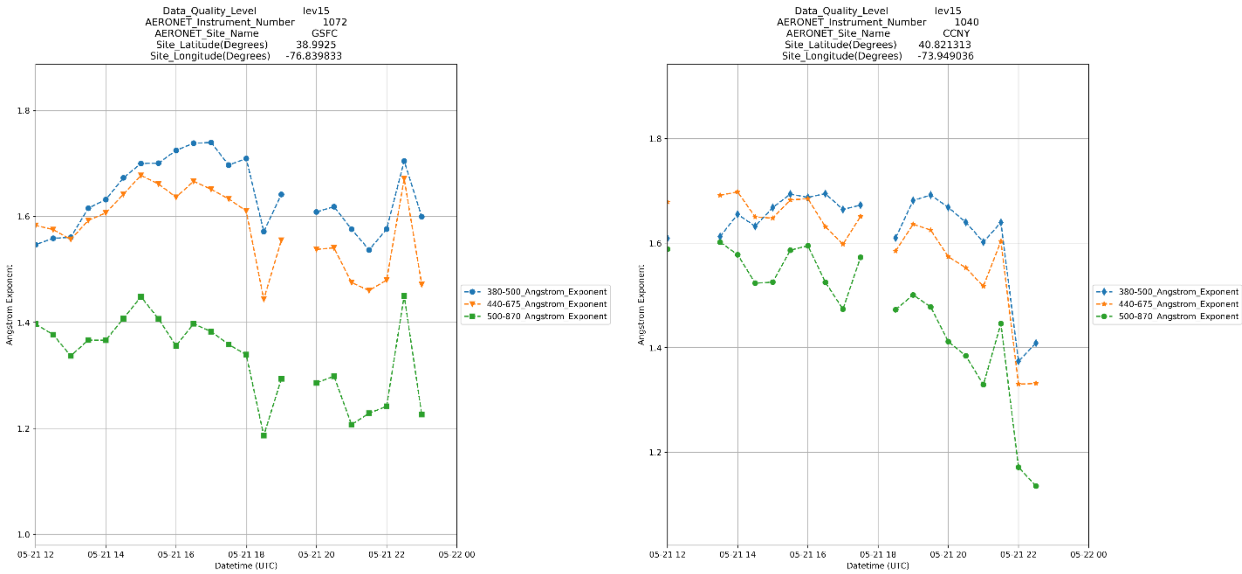

Figure 4: AERONET angstrom exponent from (left) NASA GSFC and (right) CCNY.

Note that the temporal evolution is led by CCNY and followed by GSFC indicating that the influx of aerosols see by the TROPOZ ceilometer (see Figure 3) is originating from the North and transported to South. Using Russell et al. (2010) schemes for aerosol classification by absorption angstrom exponent (AAE) we see that the aerosols are of biomass burning origin (1 > AAE < 2). Biomass burning smoke typically carries with it a large amount of NO_2 able to be photolyzed into Ozone.

The Pandora spectrometer has been validated to retrieve total column O_3 and NO_2 in agreement with satellite retrievals from the Ozone Monitoring Instrument (OMI). The Pandora delivers these column abundances at 5-minute temporal resolution diurnally. TOLNet has been validated to deliver accurate vertical profiles of ozone at high vertical and temporal resolution (≤20 meters @ ≤10 minutes). By the fourth quarter of 2022 (Q4 2022) there will be 4 TOLNet sites across the Mid-Atlantic: Hampton, VA will have one at Hampton University, and another at NASA Langley Research Center; Greenbelt, MD will have the NASA Goddard Space Flight Center

(GSFC) Tropospheric Ozone Lidar (TROPOZ); and Manhattan, New York will have one at the City University of New York (CUNY), each ≤ 200 miles apart.

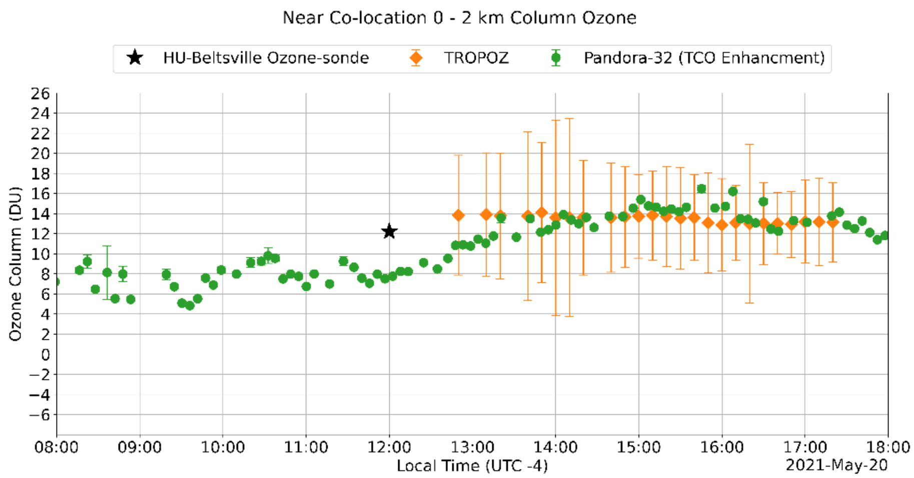

Figure 5: Figure 3: Evolution of Ozone May 20 ozone episode from TOLNet lidar (TROPOZ), Pandora, and sonde. TCO enhancement derived from removal of multi-year (2017 - 2021) mean, and sonde 0 -2 km nocturnal column (not shown).

To extend the utility of both TOLNet and Pandora networked observations, an effort has been created to convert the available TOLNet and Pandora observations into column abundances of ozone into a boundary layer product (as demonstrated in Figure 5). The boundary layer ozone abundance is derived from removal of multi-year (2017 - 2021) mean and 0 – 2 km nocturnal sonde profile, and the residual in Pandora TCO is taken as boundary layer contribution in the absence of aloft layers.

3 Results & Summary

Ozone episode May is out of the norm for this location. The episode evolved from entrainment of a transported polluted air-mass then recirculation in the mid-Atlantic on May 19 & 20, 2021 followed by quick lofting by DSW (as shown by ceilometer and wind) resulting in next-day entrainment. The evolution of the PBL height from May 19 - 21 shows a clear relation to the 3-Stage Diurnal Boundary Model (Rabinhorst et al., 2014). High resolution observations from active and passive remote sensors captured the evolution of the ozone episode. Turbulent downburst from NLLJ is identified as causes of the nocturnal surface ozone increases. The Pandora total column ozone (TCO) data plotted in Figure 3 from May 20th, 2021, show agreement with a subset of lidar derived ozone (integrated from 0 – 2 km only) – a proxy for a TEMPO ozone product – thus encouraging potential for further usage in air quality episode characterization. A more in-depth analysis is required to identify what fraction of the Pandora TCO is background ozone, boundary layer ozone, and due to small scale variability. This venture can be used to extract new science and understanding surrounding pollution transport throughout the troposphere. This work also serves to demonstrate the usefulness of multi-instrument perspectives in air quality event analysis and study of spatio-temporal variability.

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