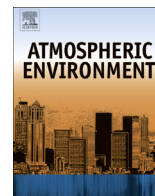




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An elevated reservoir of air pollutants over the Mid-Atlantic States during the 2011 DISCOVER-AQ campaign: Airborne measurements and numerical simulations



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HIGHLIGHTS

- An elevated reservoir was observed over Baltimore and its downwind area.
- Trajectory analyses revealed its origins and impacts on downwind air quality.
- The Chesapeake Bay Breeze played an important role in the formation of the reservoir.
- High resolution is needed to resolve the bay breeze for air quality prediction.

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ABSTRACT

During a classic heat wave with record high temperatures and poor air quality from July 18 to 23, 2011, an elevated reservoir of air pollutants was observed over and downwind of Baltimore, MD, with relatively clean conditions near the surface. Aircraft and ozonesonde measurements detected ~120 ppbv ozone at 800 m altitude, but ~80 ppbv ozone near the surface. High concentrations of other pollutants were also observed around the ozone peak: ~300 ppbv CO at 1200 m, ~2 ppbv NO₂ at 800 m, ~5 ppbv SO₂ at 600 m, and strong aerosol optical scattering ($2 \times 10^{-4} \text{ m}^{-1}$) at 600 m. These results suggest that the elevated reservoir is a mixture of automobile exhaust (high concentrations of O₃, CO, and NO₂) and power plant emissions (high SO₂ and aerosols). Back trajectory calculations show a local stagnation event before the formation of this elevated reservoir. Forward trajectories suggest an influence on downwind air quality, supported by surface ozone observations on the next day over the downwind PA, NJ and NY area. Meteorological observations from aircraft and ozonesondes show a dramatic veering of wind direction from south to north within the lowest 5000 m, implying that the development of the elevated reservoir was caused in part by the Chesapeake Bay breeze. Based on *in situ* observations, CMAQ forecast simulations with 12 km resolution overestimated surface ozone concentrations and failed to predict this elevated reservoir; however, CMAQ research simulations with 4 km and 1.33 km resolution more

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successfully reproduced this event. These results show that high resolution is essential for resolving coastal effects and predicting air quality for cities near major bodies of water such as Baltimore on the Chesapeake Bay and downwind areas in the Northeast.

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1. Introduction

High concentrations of ambient ozone (O_3) have been known to threaten human health and the environment after the discovery of the Los Angeles Photochemical Smog (Haagensmit, 1952; Crutzen, 1971; Adams et al., 1999; WHO, 2003; Anderson, 2009). Ozone in the lower troposphere is mainly produced through photochemical reactions with precursors: carbon monoxide (CO), volatile organic compounds (VOCs), and nitrogen oxides (NO_x) (National Research Council, 1991; Jacob, 2000; EPA, 2006). The accumulation of air pollutants under specific meteorological conditions leads to poor air quality episodes (e.g., Seaman and Michelson, 2000; Taubman et al., 2004; Hegarty et al., 2007). Previous studies suggest that high ozone episodes are usually associated with summertime anticyclones and heat waves under stagnation (e.g., Logan, 1989; Vautard et al., 2005; Eremenko et al., 2008; Ordonez et al., 2010; Vieno et al., 2010). Sea or bay breezes are also found to play an important role in some areas (e.g., Lyons et al., 1995; Mao and Talbot, 2004; Papanastasiou and Melas, 2009; Loughner et al., 2011; Martins et al., 2012; Stauffer et al., 2013; Loughner et al., 2013).

A classic heat wave hit the Baltimore/Washington area during July 18 to 23, 2011, leading to record high temperature and poor air quality. On July 22, the metropolitan Baltimore region reached a high temperature of 41.7 °C and poor air quality with daily maximum 8-h average (MDA8) ozone of ~97.0 part per billion by volume (ppbv). This episode was thoroughly studied in the first segment of the National Aeronautics and Space Administration (NASA) Deriving Information on Surface Conditions from Column and Vertically Resolved Observations Relevant to Air Quality (DISCOVER-AQ) campaign in July 2011 (NASA, 2012a). The objective of the DISCOVER-AQ campaign was to improve the ability of monitoring near-surface pollution based on Earth observations from space, using trace gas and aerosol measurements from airborne and ground observations. The first segment of the DISCOVER-AQ campaign in 2011 focused on air quality over the Baltimore/Washington metropolitan area. One NASA aircraft (P-3B airborne laboratory) was deployed to measure the vertical and horizontal distribution of air pollutants. Surface measurements were collected by the Maryland Department of the Environment (MDE) air monitoring network, NASA Aerosol Robotic Network (AERONET) sunphotometers, Pandora UV/Vis spectrometers, Pennsylvania State University (PSU) and Howard University (HU) ozonesondes, Millersville University tethered balloons, and lidar instruments (NASA, 2012b). The University of Maryland (UMD) Regional Atmospheric Measurement Modeling and Prediction Program (RAMMPP, 2012) deployed a Cessna aircraft to conduct airborne measurements upwind and downwind of the Baltimore/Washington area during the DISCOVER-AQ campaign (Brent et al., 2013; Loughner et al., 2013; Martins et al., 2013; Oyola et al., 2013; Stauffer et al., 2013).

This study describes an elevated reservoir of ozone and other air pollutants observed on July 21, 2011, through aircraft measurements, ozonesonde data, and numerical simulations. Section 2 describes datasets from aircraft and ozonesondes, and the model set-up. In section 3, characteristics of this elevated reservoir and the influence of bay breeze circulation on its formation are described. Section 4 evaluates the performance of air quality models, both low

resolution (12 km) forecast simulations and high resolution (4 km and 1.33 km) research simulations. Finally, the importance of the elevated reservoir and the influence on regional air quality, crucial for future policy decision, interstate transport, and air quality regulations, is discussed.

2. Data and method

2.1. Aircraft, ozonesonde and surface measurements

Archived DISCOVER-AQ data are available from the NASA Langley Research Center (LaRC) Airborne Science Data for Atmospheric Composition website (NASA, 2012c). Data used in this study include airborne measurements of ozone, nitrogen dioxide (NO_2), CO, sulfur dioxides (SO_2), aerosol particle counts and scattering from the NASA P-3B and UMD aircraft; ground-level ozone measurements from the MDE network; ozone and wind observations from the PSU ozonesondes. All the techniques are described in previous studies so only a brief summary is provided here.

On the UMD aircraft, observations of ozone were conducted using a commercially available analyzer (Model 49C, Thermo Environmental Instruments, TEI, Franklin, Massachusetts) (Taubman et al., 2006). CO was measured using a modified commercially available nondispersive infrared gas filter correlation analyzer (TEI Model 48) (Dickerson and Delany, 1988). Ambient SO_2 was monitored by a modified commercially available trace level pulsed fluorescence analyzer (TEI Model 43C) (Luke, 1997; He et al., 2012). NO_2 was measured using a modified commercially available cavity ring-down spectroscopy (CRDS) detector (Castellanos et al., 2009; Brent et al., 2013). Aerosol scattering was measured using an integrating nephelometer (Trust Science Innovation, TSI Model 3563) at 450, 550, and 700 nm (Anderson et al., 1996; Taubman et al., 2006). The count of particles with optical diameters between 0.01 and 1.0 μm was provided using a condensation particle counter (CPC, TSI Model 3007). All the instruments were routinely serviced and calibrated (see details in Taubman et al., 2004, 2006; Brent et al., 2013).

On the NASA P-3B aircraft, ambient ozone was measured using the National Center for Atmospheric Research (NCAR) 4-channel chemiluminescence instrument (Weinheimer et al., 1993, 1994). These two ozone detectors on the Cessna and P-3B agreed well with each other except for occasional excursions when relative humidity (RH) changed suddenly (Arkinson et al., 2013). NO_2 was monitored by both NCAR 4-channel chemiluminescence instrument (Weinheimer et al., 1993, 1994) and the UC Berkeley thermal-dissociation laser-induced fluorescence (TD-LIF) analyzer (Thornton et al., 2000; Day et al., 2002). CO was monitored by a tunable diode laser spectrometer (Sachse et al., 1987; Fried et al., 2008). Aerosol scattering was measured using the TSI Model 3563 nephelometer (Thornhill et al., 2008). The P-3B aircraft also provided measurements of meteorological variables, such as pressure, temperature, relative humidity, wind speed, and wind direction.

The PSU ozonesondes measured the vertical distribution of ozone using coupled ElectroChemical Concentration cells with Droplet Measurement Technology (ECC, DMT type) and standard radiosondes (International Met System, Grand Rapids, MI) to measure pressure, wind speed and wind direction (Thompson et al., 2003, 2007). For these ozonesondes, a 1% potassium iodide (KI)

sensing solution was employed. A correction to the ozone mixing ratios from the ozonesondes was made to account for a known bias of using a 1% KI solution (Martins et al., 2013). Previous studies have shown that ECC sensors using a 1% KI solution are biased 5–10% high, most likely due to side reactions of the solution buffer producing an iodine artifact (Saltzman and Gilbert, 1959; Johnson et al., 2002). A total of 39 ozonesondes were launched from Edgewood (Fig. 1) during July 2011, approximately daily. Ozone measurements were collected at 1–2 Hz with an effective vertical resolution of 50 m. The ozonesonde data extended from the surface to an average of 30 km. Hourly surface observations of ozone pollution in other Mid-Atlantic States (Fig. S1) were obtained from the Environmental Protection Agency (EPA) Air Quality database (EPA, 2012).

2.2. Numerical simulations of air quality

Air quality forecasting was provided by the National Oceanic and Atmospheric Administration (NOAA) Air Resource Laboratory (ARL) Community Air Quality Multi-scale Model (CMAQ) experimental forecast, based on its National Air Quality Forecasting Capability (NAQFC) system from the National Weather Service (NWS) (NOAA, 2012a). Details of the NOAA forecasting model system are summarized in Garner et al. (2013) and Section S1.1 of the auxiliary material.

The NASA high resolution research CMAQ simulations were conducted using CMAQ version 5.0 (Byun and Schere, 2006), driven by the WRF version 3.3 (Skamarock et al., 2008). The WRF-CMAQ system was run at 36, 12, 4, and 1.33 km horizontal resolution (Fig. S2 in the auxiliary material) with 34 vertical levels. The 1.33 km simulations (named ‘high-res’ simulations hereafter) covered the Baltimore/Washington metropolitan area and the Chesapeake Bay. Details on the high resolution WRF-CMAQ simulations are summarized in Loughner et al. (2013) and Section 1.2 of the auxiliary material.

3. Results

3.1. Airborne measurements of ozone and other air pollutants

Fig. 1 shows the flight routes of the UMD Cessna and NASA P-3B aircraft on July 21, 2011. In the morning, the Cessna airplane visited upwind regions of northwestern MD: Cumberland at 10:10 (Eastern Daylight Time, ‘EDT’, hereafter all times are EDT), Luray at 10:50, and Frederick at 11:50. The afternoon flight covered eastern MD: Aldino at 14:50, Massey at 15:20, and Easton at 15:50. At each airport, a spiral from the surface to 3000 m (morning) or 2500 m (afternoon) was conducted to measure the vertical distribution of air pollutants. Ozone altitude profiles (Fig. 2) show that in the early morning low ozone concentrations (~ 60 ppbv) near the surface and relatively high levels (~ 80 ppbv) between 1000 and 2500 m above mean sea level (MSL, hereafter for all altitudes) over Cumberland and Luray. Ozone near the surface is removed by dry deposition and reactions with other chemical species such as NO_x during the night, but ozone in the free troposphere (FT, above ~ 1000 m altitude during these spirals) has a longer lifetime (Law, 2010). Therefore, a substantial amount of ozone already existed in the FT ~ 200 km upwind of Baltimore on July 21, 2011, i.e., in a nocturnal residual layer (Yorks et al., 2009). With the rise of planetary boundary layer (PBL), air pollutants in the nocturnal residual layer were entrained and mixed into the PBL. When the Cessna reached Frederick around noon, ozone concentrations near the surface had increased to ~ 80 ppbv, while the value aloft (1000–2000 m) decreased to ~ 65 ppbv; part of the nocturnal residual layer still existed (~ 80 ppbv ozone above 2000 m). We employed the NOAA ARL Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (NOAA, 2012b) driven by the North American Mesoscale (NAM, 12 km resolution) meteorology to calculate the back trajectories (Fig. S3 in the auxiliary material). The back trajectory calculations show that air masses in the nocturnal

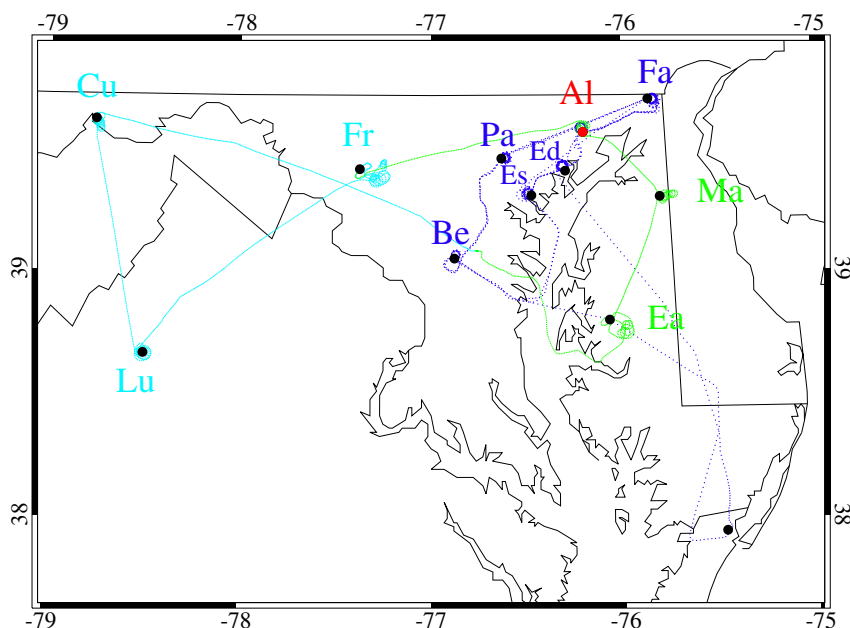


Fig. 1. Flight route of the UMD Cessna and the NASA P-3B aircraft on July 21, 2011. Black/red dots show locations of airports where spirals were conducted; Cyan/Green lines show the route of morning/afternoon flight of Cessna; Blue line shows the route of P-3B. Six airports covered by Cessna (from the lower left, clockwise): Luray, VA (38.67° N, 78.50° W, ‘Lu’), Cumberland, MD (39.62° N, 78.76° W, ‘Cu’), Frederick, MD (39.42° N, 77.37° W, ‘Fr’), Aldino, MD (39.57° N, 76.20° W, ‘Al’), Massey, MD (39.30° N, 75.80° W, ‘Ma’), and Easton, MD (38.80° N, 76.07° W, ‘Ea’). Six airports covered by P-3B (from the lower left, clockwise) are: Beltsville, MD (39.05° N, 76.88° W, ‘Be’), Padonia, MD (39.46° N, 76.63° W, ‘Pa’), Fairhill, MD (39.70° N, 75.86° W, ‘Fa’), Aldino, MD, Edgewood, MD (39.41° N, 76.30° W, ‘Ed’), and Essex, MD (39.31° N, 76.47° W, ‘Es’). The Aldino site (highlighted in red) was covered by both aircraft. PSU ozonesondes were launched at the Edgewood site. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

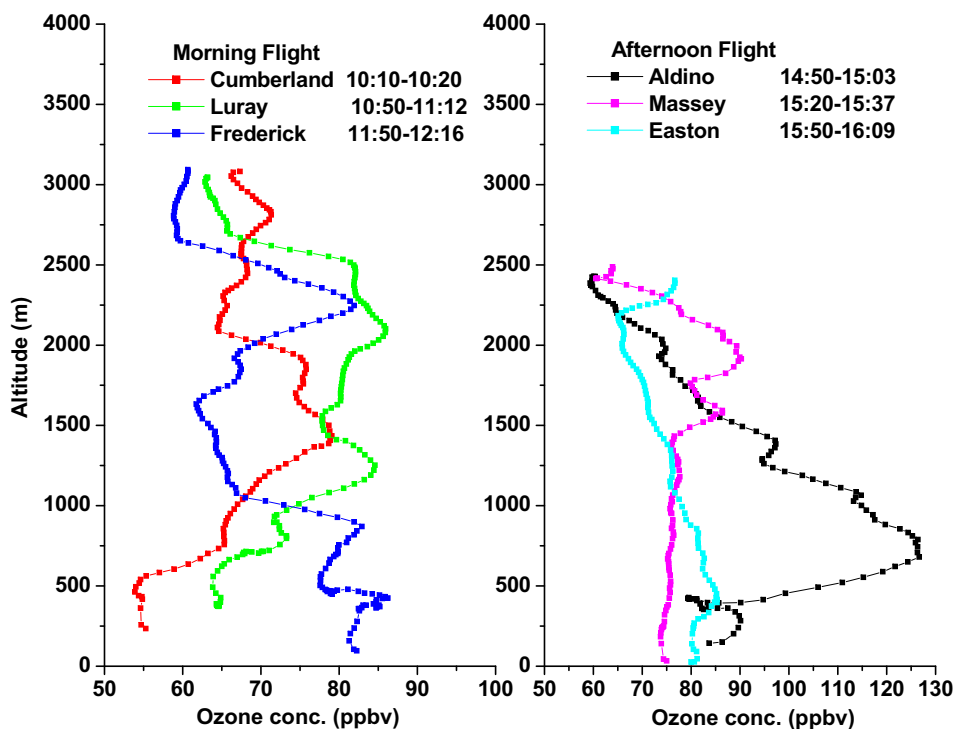


Fig. 2. Ozone profiles observed by the UMD Cessna aircraft on July 21, 2011. All times are EDT.

residual layer over Cumberland, Luray, and Frederick originated from the same source, the Ohio River Valley. These results show high ozone concentrations in the nocturnal residual layer upwind of Baltimore, which can mix down to ground-level as the boundary layer increases impacting surface air quality before noon.

During the afternoon flight of the Cessna airplane (Fig. 2), due to the fully developed PBL, we observed well-mixed ozone (70–

80 ppbv) over Massey and Easton. However, the ozone profile over Aldino shows a different distribution: moderate ozone near the surface (~80 ppbv below 500 m) and high ozone aloft (90–120 ppbv between 500 m and 1500 m) with a maximum ~120 ppbv at 800 m. Surface observations at Aldino show that hourly mean ozone concentrations reached ~100 ppbv at noon (Fig. 3). The surface ozone concentration was ~75 ppbv at 14:30

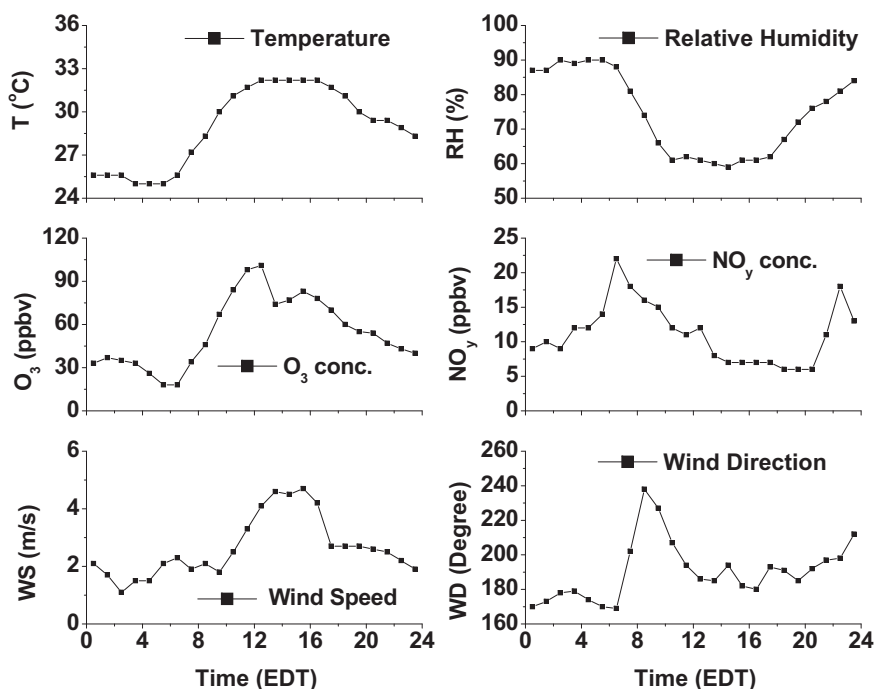


Fig. 3. Surface observations of trace gas concentrations and meteorological conditions at Aldino on July 21, 2011. Hourly average values are presented.

EDT when the spiral was conducted, suggesting that the ground-level air quality was relatively good but a substantial amount of ozone remained aloft. An air mass with high level of air pollutants aloft can act as a ‘reservoir’ that affects downwind air quality; details on this elevated reservoir are discussed in the following sections.

During the DISCOVER-AQ campaign, the NASA P-3B aircraft performed spirals over all the DISCOVER-AQ ground sites, leading to multiple profiles over each site within one day. The P-3B aircraft could only fly as low as ~ 300 m for safety, so vertical structure of air pollutants close to the surface is not well sampled in P-3B measurements. Fig. 4 presents ozone altitude profiles measured at different times over Padonia (3 profiles), Fairhill (4 profiles), Aldino (3 profiles), and Edgewood (4 profiles) on July 21, 2011. The airborne measurements started around noon, so the dissipation of the nocturnal residual layer in the morning was not detected. However, a part of the residual layer might be still observed, with secondary maximum ~ 80 ppbv ozone at 2500 m (red line in each panel of Fig. 4). These results are consistent with Cessna observations in the morning over the upwind region. With photochemical production of tropospheric ozone, the frequent samplings by P-3B tracked the development of ozone pollution in the lower troposphere, where ozone reached its maximum value in the late afternoon (blue line in

each panel of Fig. 4). After 14:00 EDT, an elevated reservoir with ~ 100 ppbv ozone was observed over Fairhill, Aldino, and Edgewood at ~ 1000 m, but not detected over Padonia. The time, location and high ozone levels observed by the P-3B were consistent with the Cessna measurements over Aldino (Fig. 2). Given the elevated reservoir was not observed over Padonia, Massey, and Easton, P-3B observations suggest that the size of the elevated reservoir is at least 50 km in length (distance from Edgewood to Fairhill) along the Interstate 95 highway.

Now we investigate other trace gases and aerosols within the elevated reservoir, observed by the Cessna, the P-3B and PSU ozonesondes, as well as ozone. The PSU ozonesondes were launched over Edgewood, ~ 20 km southwest of Aldino, so we can assume the same air mass was observed. Fig. 5 shows the altitude profiles of O_3 , NO_2 , CO , SO_2 , particle counts, and scattering (measured at 450 nm) observed during the afternoon of July 21, 2011. Ozone measurements from the Cessna agree well with P-3B observations, showing the high ozone between 500 m and 1500 m with a maximum higher than 100 ppbv at 800 m. PSU ozonesonde measurements before/after (12:31/16:50 EDT) aircraft observations show the similar structure of elevated reservoir peaking at altitude slightly lower/higher than 800 m. These results imply that the high ozone layer is lifted during the development of this reservoir. NO_2

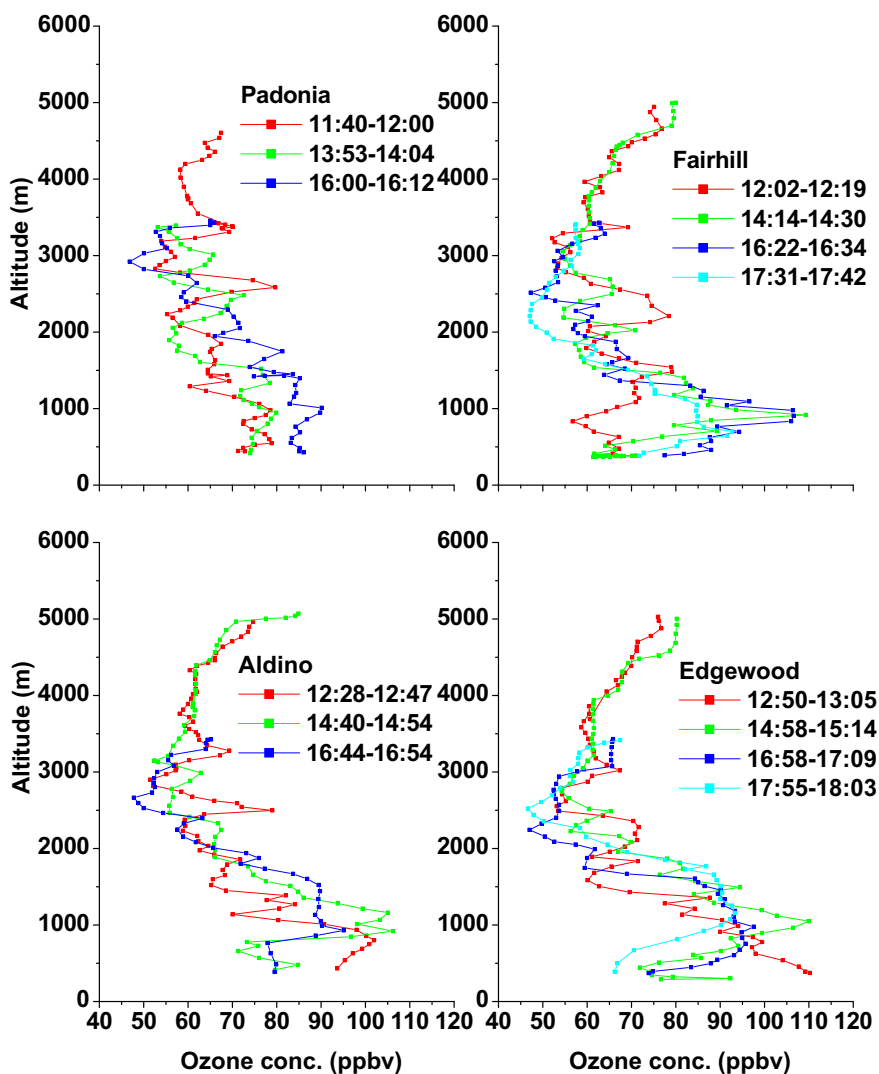


Fig. 4. Ozone altitude profiles observed by the NASA P-3B airplane over four Maryland monitoring sites (Padonia, Fairhill, Aldino, and Edgewood) on July 21, 2011.

measurements from three different instruments agree well with each other (Brent et al., 2013), with ~2.0 ppbv at 800 m (Thompson et al., 2013). CO altitude profiles observed from both Cessna and P-3B have a broad peak with CO higher than 200 ppbv between 500 and 2000 m and a maximum ~300 ppbv at 1000 m. CO and NO₂ (as proxy of NO_x) are important precursors of tropospheric O₃. The altitude profiles of SO₂ (an important precursor of sulfate aerosol) and aerosol properties (particle counts and scattering) also show co-located peaks of ~5 ppbv SO₂, ~13,000 particles cm⁻³, and 2–3 m⁻¹ as scattering, all at 600 m.

3.2. Structure of the elevated reservoir and trajectory analysis

In the Mid-Atlantic States, major sources of anthropogenic emissions of CO and NO₂ are automobiles, while SO₂ is mainly released from power plants. A layer of high O₃, CO, and NO₂ at 800 m and a layer of high SO₂, particle counts, and aerosol scattering at 600 m imply that this elevated reservoir reflects two sources, automobile emissions (at 800 m) and power plant emissions (at 600 m). We calculated back and forward trajectories from the 4 km NASA WRF meteorology (Fig. 6). The back trajectory suggests stagnation in the Mid-Atlantic States, with an air mass moving slowly within a 300 km radius in 36 h, making two passes over areas with high anthropogenic emissions. The slow moving air

mass favors the accumulation of air pollutants and their precursors, which explains the mixture of automobile emissions and power plant emissions in the elevated reservoir. The high CO and NO₂ concentrations can be attributed to the local vehicle emissions. Since the lifetime of SO₂ in summer over the Mid-Atlantic State is less than one day (Hains et al., 2008), the high level of SO₂ at 600 m suggests fresh emissions from local power plants.

Air pollutants, especially ozone in the elevated reservoir, are relatively stable and can be transported throughout the night then mixed downward when the new PBL develops the next day. Forward trajectories show transport of the elevated reservoir to Pennsylvania (PA), New Jersey (NJ) and New York City (NYC) in New York (NY) in the next 12 h. To investigate the influence of regional transport, we analyzed surface ozone observations from selected EPA AQS monitoring sites (Fig. S1 in the auxiliary material) on the transport pathway. Fig. 7 compares the monthly mean diel cycle of surface ozone in July 2011 and ozone observations on the next day, July 22, 2011. The monthly mean diel cycle shows that ozone gradually reached the maximum value around 14:00 EDT, the same as observed in MD on July 22, 2011. However, surface ozone in PA, NJ, and NYC had a rapid increase in the early morning (10:00 to 12:00 EDT), before the photochemical production of ozone reached the maximum rate at noon. Especially in NYC, surface ozone was already higher than 80 ppbv at 10:00 EDT, well before peak

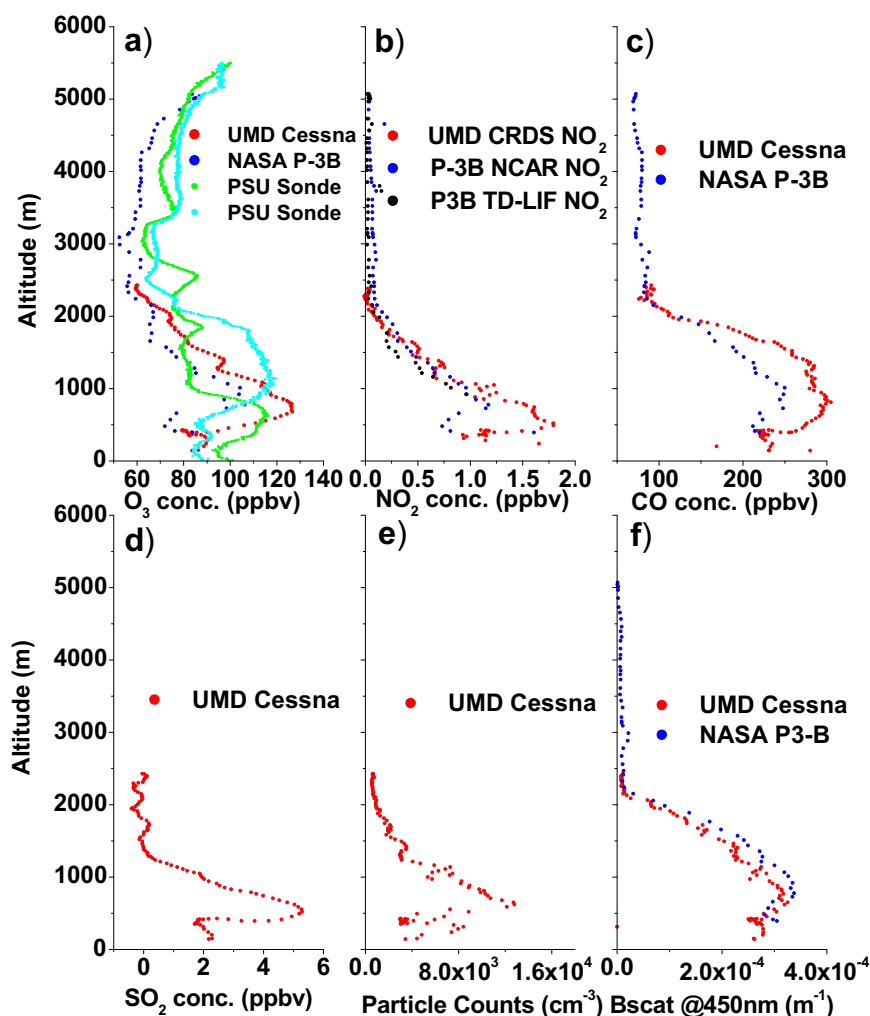


Fig. 5. Profiles of air pollutants within the elevated reservoir observed over Aldino (UMD Cessna and NASA P-3B observations) and Edgewood (PSU ozonesondes): a) O₃, b) NO₂, c) CO, d) SO₂, e) Particle counts, f) Scattering UMD Cessna spiraled over Aldino during 14:45–15:03; NASA P-3B spiraled over during 14:40–14:54; PSU ozonesondes were launched over Edgewood during 12:31–14:12 and 16:50–17:08.

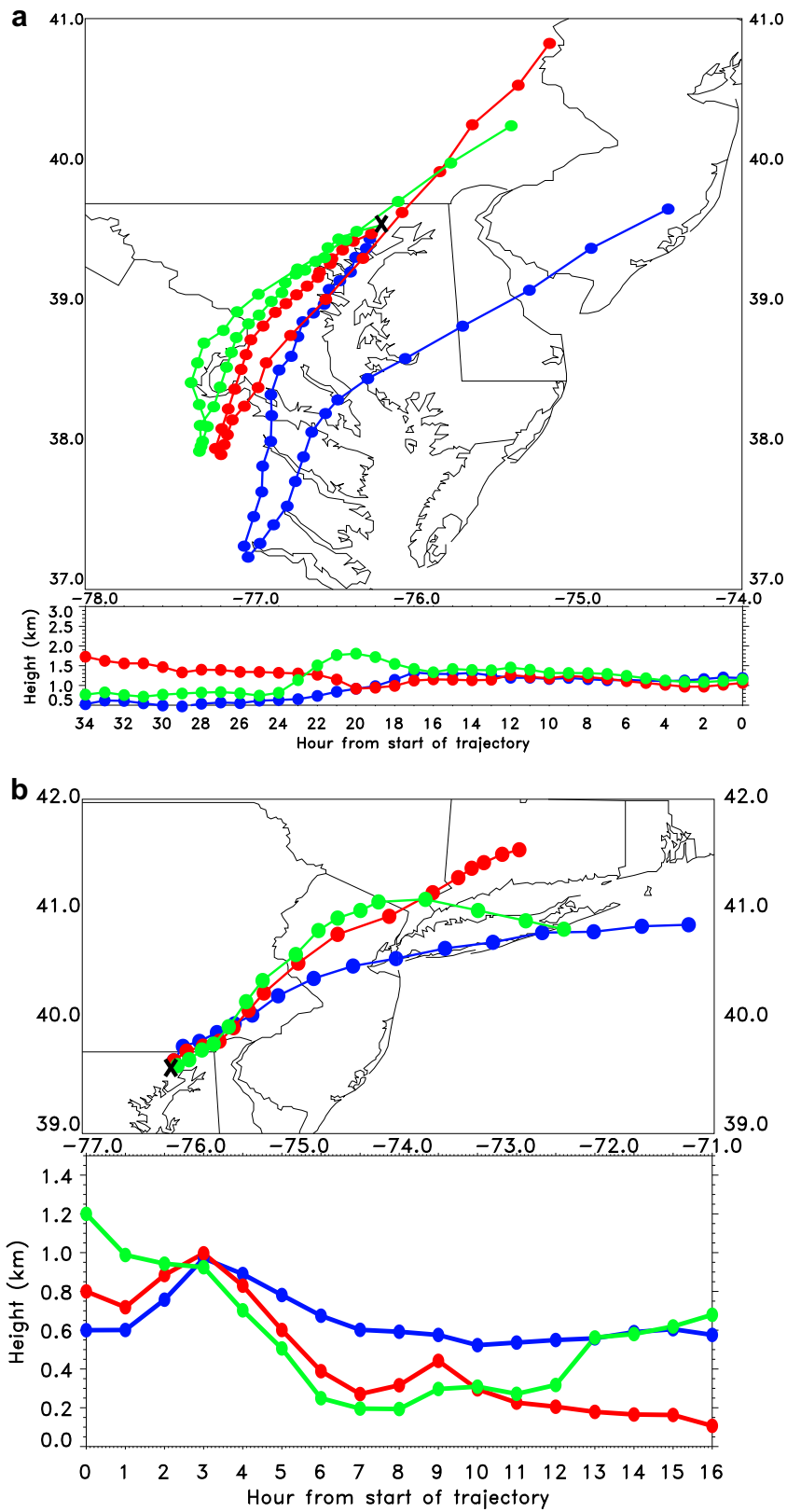


Fig. 6. Back (34 h) and forward (16 h) trajectories for the elevated reservoir. The trajectories were initiated over Aldino at heights of 600 m, 800 m, and 1200 m and at 1900 UTC (3 PM EDT) driven by the 4 km WRF simulations: a) back trajectories; b) forward trajectories. Black X shows the location of Aldino, MD.

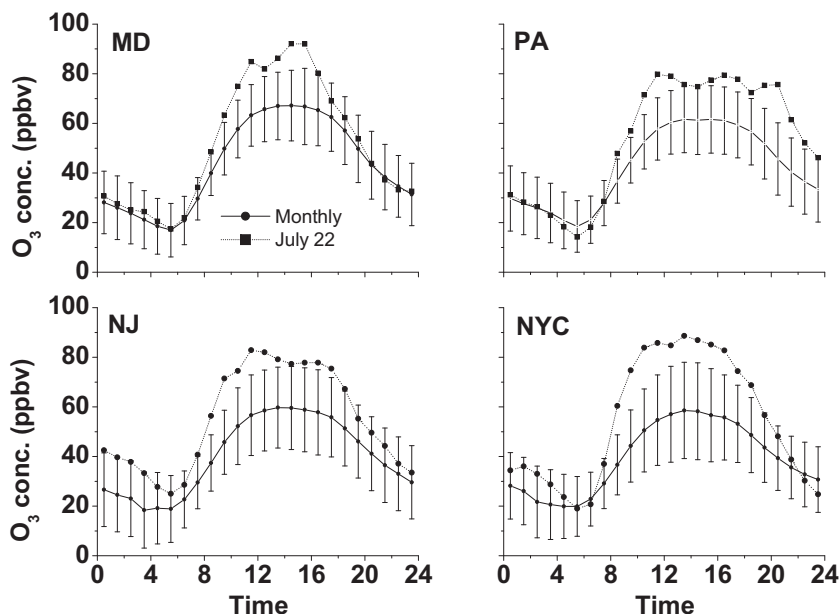


Fig. 7. Comparison of monthly mean (solid) and July 22, 2011 diel cycle (dotted) of surface ozone concentrations and ozone observations in MD, PA, NJ, and NYC. Error bars show the ± 1 standard. Notice NYC ozone peaked early (essentially by 11 AM EDT on July 22, 2011) due downward mixing from the residual layer.

photochemical production of ozone is expected. These results suggest that air pollutants in the elevated reservoir can significantly affect surface air quality a day later in regions downwind of the Baltimore/Washington area.

3.3. Effects of bay breeze on the formation of the elevated reservoir

Previous studies demonstrate that the Chesapeake Bay breeze can substantially influence air quality of the Baltimore area (Loughner et al., 2011; Stauffer et al., 2013; Stauffer and Thompson, 2013, Loughner et al., 2013). When the bay breeze is formed, the air pollutants cannot be transported toward the Chesapeake Bay but are concentrated in the bay breeze convergence zone and lifted

aloft (Loughner et al., 2011). A case study of a bay breeze event on July 11, 2011 during the DISCOVER-AQ campaign reveals the existence of a convergence zone west of Aldino and Edgewood with relatively high ozone at ~ 1300 m (see details in Loughner et al., 2013). Here, we analyzed the meteorological measurements from MDE surface sites, aircraft, and ozonesondes to investigate effects of the bay breeze on the elevated reservoir.

Surface observations (Fig. 3) show high temperatures (as high as ~ 32 °C between 12:00 and 18:00 EDT), moderate wind speeds ($2\text{--}5$ m s $^{-1}$) and consistent south-southwesterly surface wind ($190\text{--}210^\circ$). The NASA P-3B aircraft and PSU ozonesondes both provide vertical profiles of meteorological parameters, such as wind speed, wind direction, temperature, and relative humidity. Ambient

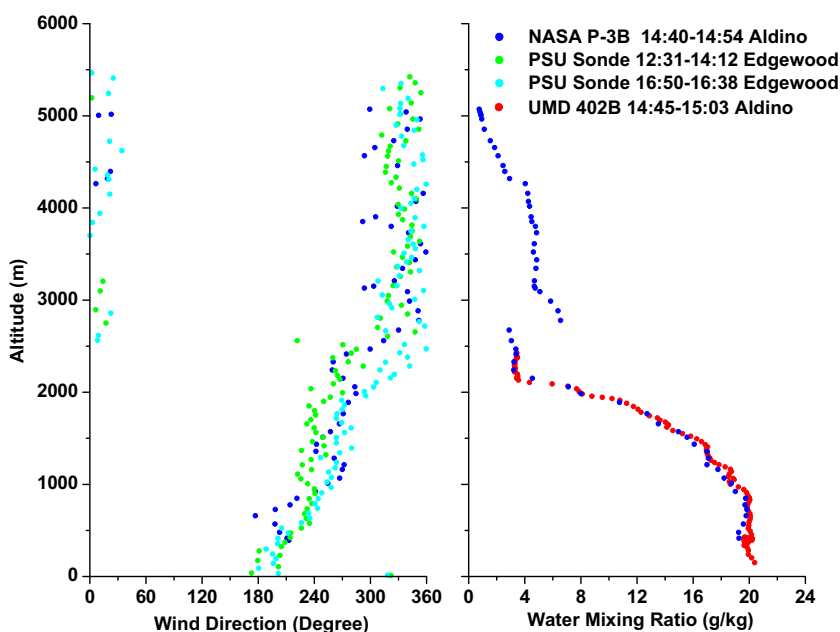


Fig. 8. Wind direction and water vapor mixing ratio altitude profiles observed over Aldino and Edgewood on July 21, 2011.

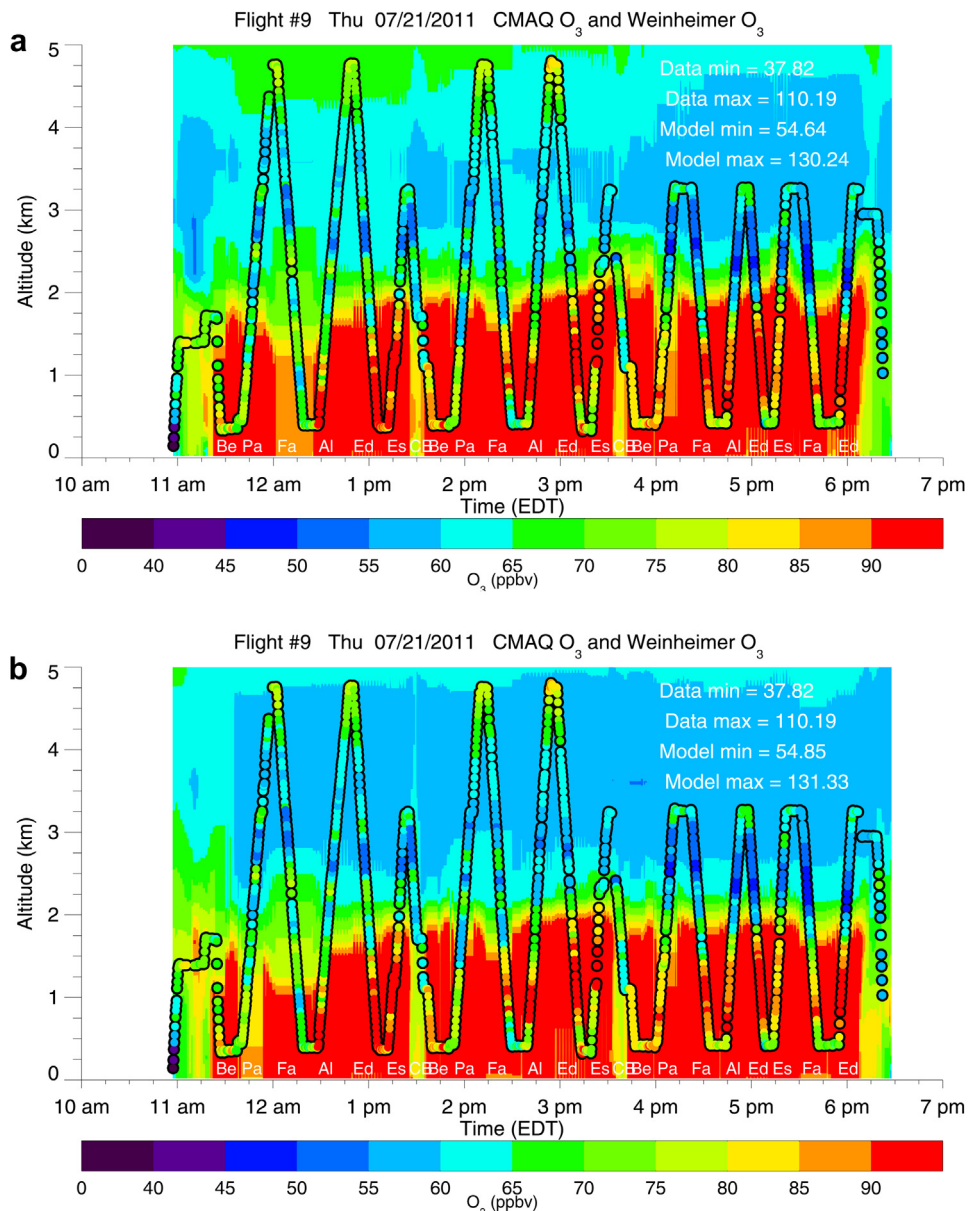


Fig. 9. NOAA forecast CMAQ simulations (12 km) and P-3B ozone measurements along the flight track on July 21, 2011. Background: CMAQ simulations; Overlay: P-3B observations. The white letters at the bottom, 'Be', 'Pa', 'Fa', 'Al', 'Ed', 'Es', and 'Cb', stand for the spiral sites Beltsville, Padonia, Fairhill, Aldino, Edgewood, Essex, and Chesapeake Bay, respectively. a), 07/20 forecast, b) 07/21 forecast.

temperature profiles show an inversion at ~ 2000 m, where the relative humidity profiles have a dramatic decrease; the wind speed is $5\text{--}10\text{ m s}^{-1}$ (Fig. S4 in the auxiliary material). We calculated the water vapor mixing ratio, shown with wind direction in Fig. 8. The wind direction, observed by the P-3B aircraft and PSU ozonesondes, changes gradually from southerly (from the Chesapeake Bay) near the surface to westerly (from Baltimore/Washington metropolitan area) at 2000 m, and further to northerly (from inland) above 2500 m. The water vapor mixing ratio profiles show a humid air mass ($\sim 20\text{ g kg}^{-1}$) near the surface and a dry air mass ($\sim 5\text{ g kg}^{-1}$) above 2000 m.

The boundary between a polluted air mass and a relatively clean air mass is at ~ 2000 m demonstrated in Fig. 5. These results imply that the polluted air mass with high humidity observed near the surface was generated by transport of air pollutants from the Baltimore/Washington metropolitan area into a bay breeze

convergence zone and then lifted upward (Loughner et al., 2011, 2013). The southerly to southwesterly winds below 2000 m blew air pollutants to the north and northeast. Thus, the elevated reservoir was observed by the P-3B and Cessna aircraft over Fairhill (northeast of Aldino), but not found over Padonia (west of Aldino), Massey and Easton (southeast of Aldino).

4. Evaluation of numerical simulations

The NOAA CMAQ experimental forecast system provided a 48-h forecast every day, so we have two forecasts for July 21, 2011, one issued on July 20, 2011 (named '07/20 forecast' hereafter) and the other one issued on July 21, 2011 (named '07/21 forecast' hereafter). Fig. 9 shows that the high ozone levels over Aldino, Edgewood, Essex, and Fairhill were suggested by both '07/20 forecast' and '07/21 forecast', but ozone concentrations over Padonia and Beltsville

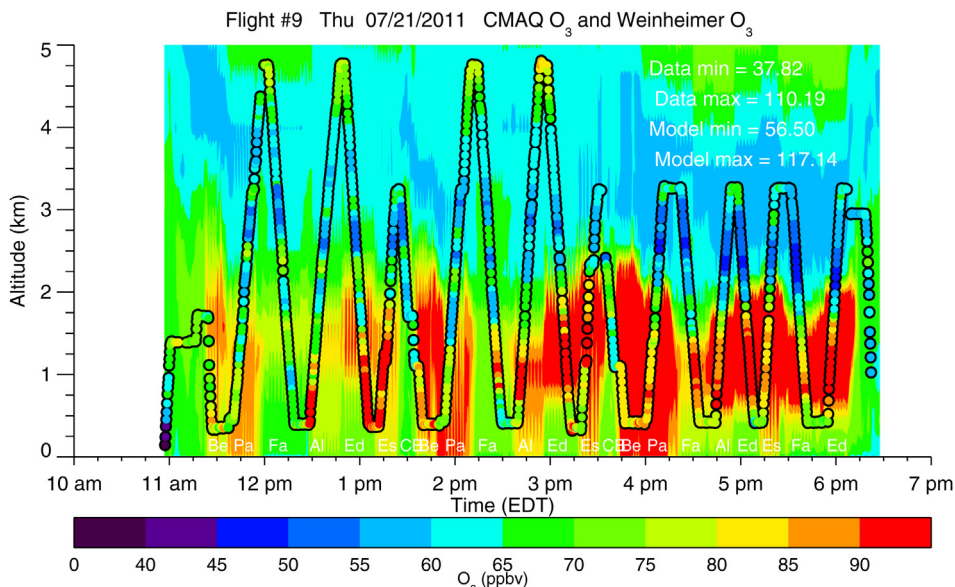


Fig. 10. Same as Fig. 9, but data from NASA high-res (1.33 km) CMAQ simulations.

were substantially overestimated (more than 15 ppbv). On the vertical distribution, the NOAA forecasts significantly overestimated the ozone levels from the surface to 400 m by more than 15 ppbv. Even though the NOAA forecasts successfully predicted the high ozone event on July 21, 2011, relatively low ozone concentrations near the surface were not predicted. The reason could be that the NOAA forecasts are conducted with a horizontal resolution of 12 km, which is insufficient for resolving the Chesapeake Bay breeze (Loughner et al., 2011). For the air quality community, summertime air pollution is mainly determined by the surface MDA8 ozone. On July 21, 2011, even though the high ozone event was successfully forecasted, the failure of resolving the Chesapeake Bay breeze and its effects in the afternoon would lead to a failed forecast of surface ozone for Baltimore and its downwind regions.

We followed the approach by Loughner et al. (2013) to analyze the NASA high-resolution (1.33 km) CMAQ simulations. The ‘high-res’ simulations showed better results compared with P-3B

observations (Fig. 10). The high ozone levels in the elevated reservoir (500 m to 1500 m) were reproduced over Aldino, Edgewood, Essex, and Fairhill especially after 3 pm. Lower ozone near the surface (below 500 m) was also suggested by the ‘high-res’ simulations. The 4 km simulations showed similar results (Fig. S5 in the auxiliary material). Fig. 11 compares the MDA8 ozone from the ‘high-res’ simulations and surface observations, showing the highest ozone concentrations near the bay breeze convergence, which penetrated inland west of Baltimore. Fig. 12 demonstrates the evolution of the reservoir. The surface maps show the bay breeze convergence zone with high ozone levels to the west of Baltimore, inland of the Chesapeake Bay. At 4 pm on July 21, 2011, the surface ozone concentrations reached the daily maximum (higher than 100 ppbv) near the bay breeze convergence zone. This area of peak surface ozone decreased to less than 90 ppbv at 6 pm. At ~1300 m, the elevated reservoir started to form by 12 pm with a widespread area of ozone over 120 ppbv at 6

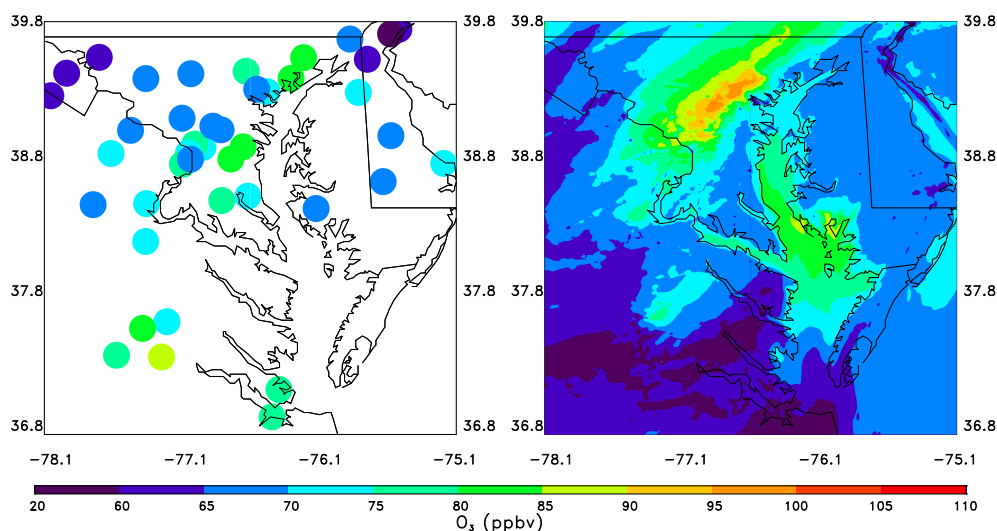


Fig. 11. Surface MDA8 ozone observed by the MDE and EPA AQS monitoring sites and predicted by the NASA ‘high_res’ CMAQ simulations on July 21, 2011. Left: MDE observations; Right: CMAQ simulations.

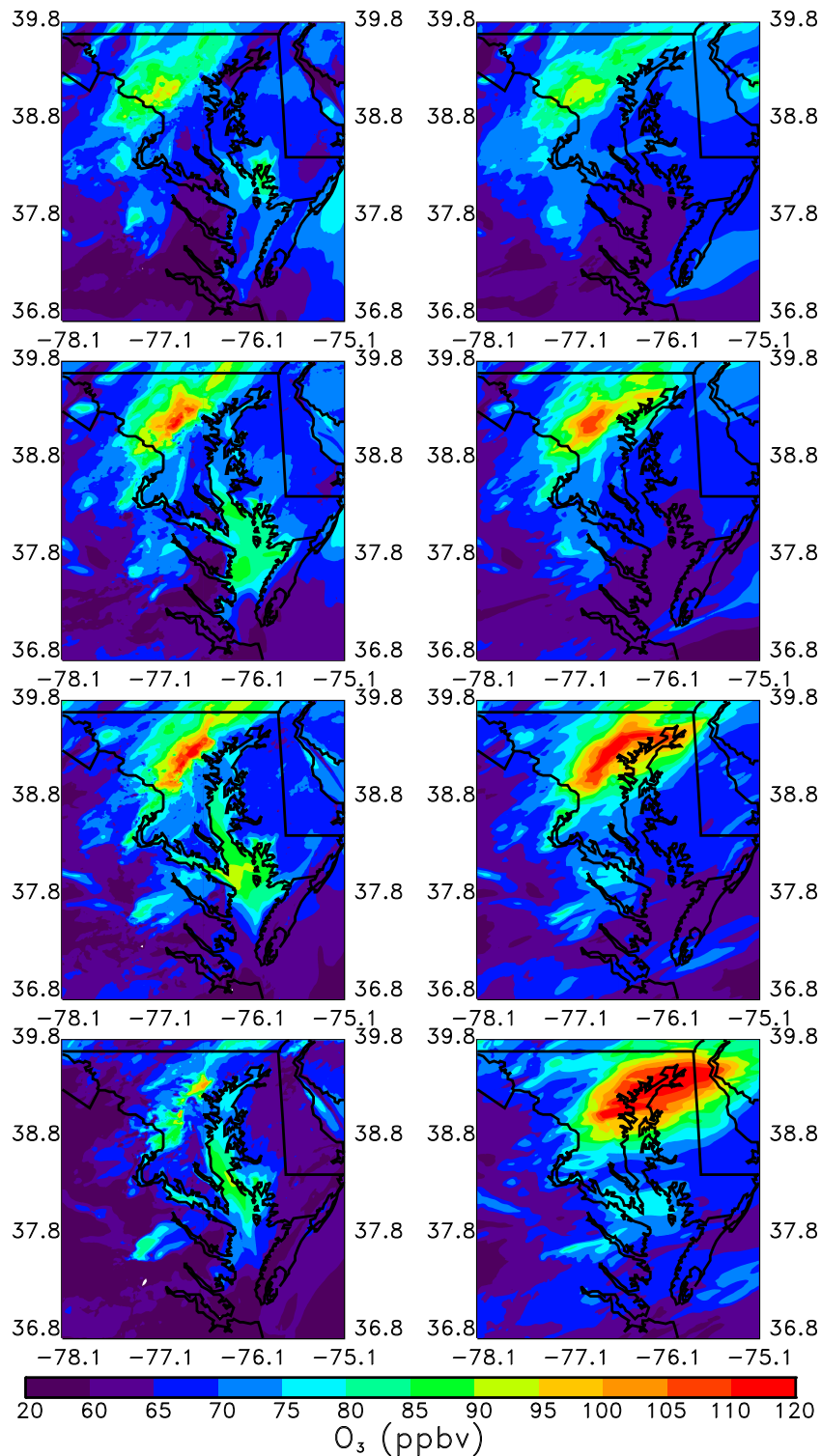


Fig. 12. NASA 'high-res' CMAQ simulated ozone concentrations at the surface (left) and at about 1300 m (right) on July 21, 2011 at 12 pm (top row), 2 pm (second row), 4 pm (third row), and 6 pm EDT (bottom row).

pm. The elevated reservoir extended from the bay breeze convergence zone near Baltimore into Delaware, southern Pennsylvania, and southern New Jersey. The evolution process of the elevated reservoir is similar to the case on July 11, 2011 described in Loughner et al. (2013), but with higher concentrations and a larger area covered.

5. Discussion and conclusions

The regional transport of pollutants is controlled by a combination of photochemistry and meteorology. In July 2011, an interesting episode was observed where the Bay breeze and winds veering with altitude generated an elevated pollution reservoir that

carried ozone and other trace gases and aerosols northeastward to heavily populated areas in the Mid-Atlantic States. Observations on July 21, 2011 showed that this elevated reservoir had ~ 120 ppbv O_3 , ~ 300 ppbv CO, ~ 2 ppbv NO_2 , ~ 5 ppbv SO_2 , and high aerosol concentrations at altitudes from 500 m to 1500 m, spanning a horizontal extent of at least 50 km (from Edgewood to Fairhill, MD). The maximum hourly mean ozone level observed on the ground however was less than 90 ppbv. The morning aircraft flight in the upwind areas (western MD) revealed the existence of a nocturnal residual layer containing ~ 80 ppbv ozone. Back trajectory analyses suggested that the nocturnal residual layer moving toward the Washington–Baltimore metropolitan region originated from the Ohio River Valley upwind. As this residual layer was transported eastward and the boundary layer height increased throughout the morning, air pollution aloft was mixed down to the surface. The frequent sampling by the NASA P-3B airplane over all DISCOVER-AQ monitoring sites and ozonesondes over Edgewood described the evolution of an elevated reservoir originating from a bay breeze circulation. The elevated reservoir consisted of automobile emissions (high O_3 , CO, and NO_2) at 800 m and power plant emissions (high SO_2 and aerosol concentrations) at 600 m. Meteorological analyses showed locally weak winds for much of the day. Backward trajectories showed recirculation over the Baltimore/Washington area. Forward trajectories and surface ozone monitoring suggested an adverse impact on air quality in downwind areas, PA, NJ, and NY.

Meteorological conditions observed from aircraft and ozonesondes indicate that the wind direction veered from southerly near the surface to northerly at 2500 m. Water vapor mixing ratios decreased with altitude even within the PBL, but a temperature inversion at ~ 2000 m separated polluted, humid air from cleaner dry air. The cleaner air aloft arose from rural areas to the west and north, while the polluted air originated from the transport of effluents from the Baltimore/Washington metropolitan area. The bay breeze convergence zone west of Baltimore helped concentrate and lift these air pollutants.

Two CMAQ simulations, NOAA forecast and NASA 'high-res' run, were evaluated. The NOAA forecast successfully predicted the high ozone event over downwind areas of Baltimore. However both forecasts on July 20 and July 21 failed to simulate the vertical structure of the elevated reservoir, predicting much higher ozone levels near the surface. Air quality violations are determined by the surface concentrations, thus the NOAA CMAQ 12-km experimental forecast system failed when it overestimated surface ozone. The NOAA CMAQ simulations apparently lacked sufficient spatial resolution to resolve the Chesapeake Bay breeze. The NASA 'high-res' and 4-km CMAQ simulations show better results compared to the P-3B ozone observations. In particular, the local minimum ozone concentrations near the surface (below 500 m) were successfully simulated, leading to a better prediction of surface ozone. We conclude that high-resolution (4 km or better) is necessary to predict accurately surface ozone for the Baltimore metropolitan area, and probably for other urban coastal areas where a bay breeze or sea breeze plays an important role in circulation and local air quality.

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Appendix A. Supplementary material

Supplementary material related to this article can be found at <http://dx.doi.org/10.1016/j.atmosenv.2013.11.039>.

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