



Smart balloon observations over the North Atlantic: O₃ data analysis and modeling

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[1] The temporal and spatial variations of ozone (O₃) in polluted continental outflow over the North Atlantic were investigated during the International Consortium for Atmospheric Research on Transport and Transformation (ICARTT) field campaign in July–August 2004. Our analysis utilized measurements of O₃ from three smart balloons traveling at 0.5–3 km altitude in combination with simulations using the MM5/SMOKE/CMAQ air quality modeling system. Model results for over and within 300 km off North America were corroborated by comparison to a suite of measurements from ground stations, ozonesondes, and the NOAA ship *Ronald H. Brown* cruising in the Gulf of Maine. A prominent feature of the O₃ distribution was the high mixing ratios over the North Atlantic, reaching a peak value of 171 ppbv, compared to the northeastern United States (<~100 ppbv). The enhanced O₃ levels over ocean, mostly observed at night, appeared to be the result of four factors: (1) a supply of precursors in prevailing flow off the polluted U.S. east coast, (2) significant daytime in situ chemical production, (3) minimal depositional loss to the ocean at the balloon altitudes, and (4) small nighttime chemical loss. An important implication is that quantification of O₃ export from the United States must include estimation of downwind chemical processing in polluted air masses. Balloons 3 and 4 were launched within 18 hours of each other, and their tracks allowed examination of horizontal gradients in O₃ across distances varying from 200 to 400 km. In air masses influenced by recent outflow (<2 days) the O₃ gradient was -0.2 to 0.2 ppbv km⁻¹, while by distant source regions (>2 days) it exhibited only -0.05 – 0.05 ppbv km⁻¹. These same two balloons encountered Hurricane Alex at different times, but both measured O₃ mixing ratios >100 ppbv. Our model results show clearly that polluted air from the mid-Atlantic states was channeled directly into Alex's inflow region. Overall, variations in O₃ on timescales of tens of minutes to hours are attributed to its highly heterogeneous distribution in urban plumes, with variations over hours to days caused by changing source regions related to cyclonic activity.

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1. Introduction

[2] Ozone (O₃) is produced in the lower troposphere by photochemical processes involving carbon monoxide (CO) and hydrocarbons in the presence of nitrogen oxides (NO_x). The lifetime of O₃ ranges from about a week in summer to several months in winter, which permits O₃ together with

other pollutants to be transported over long distances. As a result, remote atmospheric regions such as over the North Atlantic and North Pacific Oceans episodically receive polluted air masses with enhanced levels of O₃ from continental outflow [Talbot *et al.*, 1996, 1997; Merrill and Moody, 1996; Berkowitz *et al.*, 1996; Dickerson *et al.*, 1995].

[3] To identify the role of anthropogenic emissions in shaping atmospheric chemistry, considerable attention has been paid to quantifying surface-level background O₃ concentrations and associated trends, as they serve to define a lower boundary of the tropospheric oxidative capacity. Background O₃ is generally defined as the fraction of O₃ present in a given area that is not attributed to anthropogenic sources of local origin [Vingarzan, 2004]. For the European continent, O₃ mixing ratios are commonly considered to be at the background level if the air masses originate from over the North Atlantic Ocean [Monks, 2000]. Changes in the O₃

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mixing ratio over the North Atlantic will then directly alter the background level of O₃ in Europe. Therefore it is critical to understand the input of O₃ to the North Atlantic from North America.

[4] However, accurate estimation of the background level of O₃ is hampered by the paucity of O₃ measurements over space and time in remote atmospheric regions, and in particular over oceanic areas. Few studies have reported the O₃ distribution over the Atlantic Ocean during the past two decades. On the basis of the measurements conducted on the *Polarstern* Cruise in spring 1987, Smit *et al.* [1989] constructed a latitude-height cross section of O₃ mixing ratios over the Atlantic Ocean between 30°S and 52°N. They showed that a large latitudinal gradient existed for O₃ in the northern hemisphere with mixing ratios ranging from <30 ppbv in the tropics to >50 ppbv at 25°N and relatively less variable levels of around 50 ppbv at midlatitudes. Weller *et al.* [1996] reported a mean value of surface-level O₃ of around 40 ppbv in the northern hemisphere from two meridional transects over the Atlantic in 1993, whose composite vertical profiles were also observed by Thompson *et al.* [2000] during a trans-Atlantic cruise lasting from 17 January to 6 February 1999. Averaged values from daily ozonesonde profiles at five sites over the North Atlantic in August 1993, found O₃ mixing ratios of 25 ppbv at the surface and ~37 ppbv at 1 km [Oltmans *et al.*, 1996].

[5] A number of tropospheric chemistry field missions (e.g., WATOX, NARE I and II, and ITCT2002) have been dedicated to understanding the chemical composition of North American continental outflow. One of the major findings has been that O₃ over the North Atlantic during summertime is dominated by transport from North America, particularly from the northeastern United States. For instance, surface measurements show that O₃ pollution from North America is easily detectable as far as 3,000 km downwind in the central North Atlantic [Parrish *et al.*, 1993, 1998; Berkowitz *et al.*, 1996]. Studies suggested that the transport of polluted air from North America is potentially responsible for enhanced O₃ mixing ratios over the Atlantic Ocean [Li *et al.*, 2002] and the significant positive trend in O₃ of 0.49 ± 0.19 ppbv yr⁻¹ at Mace Head, on the west coast of Ireland from 1987 to 2003 [Simmonds *et al.*, 2003].

[6] A recent study by Honrath *et al.* [2004] suggests that the hemispheric impact of O₃ export from North America may be substantially greater than current estimates based on measurements from a mountaintop site in the Azores. This echoes the results from the Global Chemical Transport Model study by Li *et al.* [2002] where they showed that more than half of the ultimate O₃ impact of continental emissions occurs from O₃ production over the continent and downwind over the North Atlantic. At present, this hypothesis cannot be verified because of the scarcity of measurements in the near-field oceanic region adjacent to North America.

[7] The application of a unique mobile platform, the National Oceanic and Atmospheric Administration (NOAA) smart balloon, and a newly developed miniature O₃ sensor during the International Consortium for Atmospheric Research on Transport and Transformation (ICARTT) campaign in summer 2004 provided an opportunity for us to address the aforementioned issues. Four smart balloons

were successfully released into the New York City urban plume from Long Island. As the first flight took place over land and also served as a test flight, we focus here on smart balloon flights 2, 3, and 4 which occurred over the remote North Atlantic Ocean. In this study, we examined the measured spatial distribution and temporal evolution of O₃ levels in urban plumes over the North Atlantic and attempted to understand the observed variability on timescales ranging from minutes to days using a regional air quality model.

2. Measurements and Models

2.1. Ozone Observations

[8] The details of the smart balloon platform equipped with the University of New Hampshire's custom-fabricated miniature O₃ sensor are provided in the companion paper by Talbot *et al.* (R. Talbot *et al.*, Smart balloon observations over the North Atlantic: 1. MiniO₃ sensor sampling of urban plumes, submitted to *Journal of Geophysical Research*, hereinafter referred to as Talbot *et al.*, submitted manuscript, 2006). Briefly, version 4.1 of the smart balloon was employed for the ICARTT flight series [Businger *et al.*, 2006]. The ~3 m diameter superpressure balloon was constructed with a very high strength and extremely durable outer shell material of Spectra[®] fabric and two inner bladders, one filled with pressurized ambient air and the other helium. The Spectra shell provided the strength necessary to withstand the internal pressure that allows the balloon to compensate for precipitation rates of up to 7.6 cm h⁻¹. Balloon altitude was controlled using a pump to move air in/out of the pressurized air bladder to effectively increase/decrease its buoyancy. The ability to both remotely and autonomously control the ascent/descent timing and rate makes the balloon "smart."

[9] The UNH miniature O₃ sensor was developed specifically for the smart balloon autonomous platform. The dimensions of the sensor were 22.9(L) × 7.6(W) × 7.6(D) cm. It weighed ~200 grams and used 2.5 watts of electrical power (±15 and 5 VDC). This sensor was only a fraction of the size and weight of previous small instruments designed for similar applications [e.g., Bognar and Birks, 1996]. The measurement applied the established method of absorption of ultraviolet light at 253.7 nm using a mercury lamp source and quartz lens coupled with charge integration through an optically filtered photodiode. The flow rate through the sensor was ~700 cm³ min⁻¹ with a sample chamber volume of 8.5 cm³, which gave a residence time of 0.7 s. Temperature and pressure were monitored continuously in the detector cell. The sensor was interfaced with the smart balloon system using RS232 serial communication.

[10] During summer 2004 the smart balloon was released from Orient, Long Island situated on the northern tip of the island. These flights were a component of ICARTT field campaign focused on studying intercontinental transport of pollutants from North America across the Atlantic Ocean. We successfully released four balloons which traveled distances ranging from 600 to 7000 km, with flight times of 1 to 12.5 days. The balloons flew at altitudes of 0.5–3.5 km. The balloon operator was in constant communication with the balloon system during all flights using Iridium satellite communications. Critical operating parameters of the sensors and balloon, including latitude,

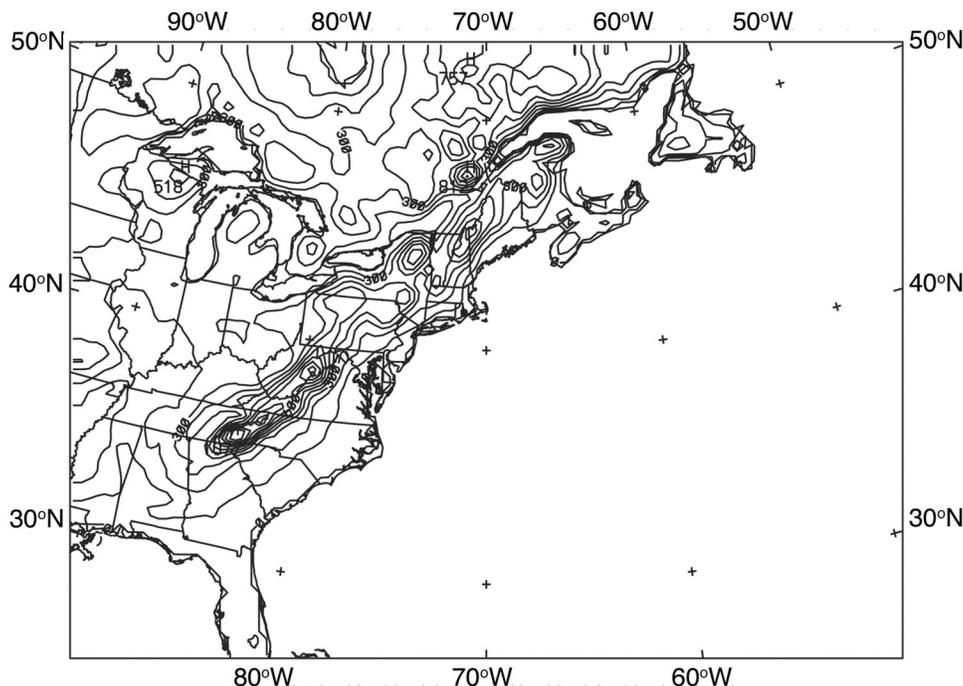


Figure 1. Domain for the MM5 and CMAQ simulations with terrain height (m) in contour increments of 100 m.

longitude, and altitude monitored with a miniature Global Positioning System (GPS), were transmitted every 10 s to our Long Island operation center. Post processing of the data provided merged data files on various timescales ranging from 15-min to 1-hour averages.

2.2. Validation of O₃ Measurements

[11] The O₃ data quality was verified during the ICARTT campaign and with laboratory and ground-based intercomparisons. More details are given by Talbot et al. (submitted manuscript, 2006). The miniature O₃ sensors were rigorously calibrated and tested to ensure proper operation using a NIST/EPA certified primary O₃ standard diluted with zero air to generate multiple mixing ratios over the range of zero to 200 ppbv. Intercomparisons were conducted at our local field site measuring ambient levels of O₃ with the miniature O₃ sensor and a Thermo Environmental Instruments model 49C-PS [Mao and Talbot, 2004]. Excellent agreement was observed between the two ($r^2 = 0.994$) (Talbot et al., submitted manuscript, 2006) using the actual sensors flown on the ICARTT smart balloon flights.

[12] Data obtained on flight 2 were examined for artifacts related to the sampled air potentially touching the Spectra[®] outer shell and causing decreases or enhancements of O₃ mixing ratios. Plots of the cumulative distribution of frequency (CDF) changes in O₃ for balloon ascent rates of <0.5, 0.5–1.0, 1.0–1.5 and >1.5 m s⁻¹ were distributed smoothly and nearly identical to each other. This strongly indicates a coherence in the measurements during the worst case scenarios of the balloon in the ascending mode.

[13] To further confirm the reliability of the O₃ distributions measured with the miniature O₃ sensor over the North Atlantic, we compared data collected on balloon flight 2 with coincident nearby O₃ measurements performed on the

NOAA WP-3D (P3) aircraft. For these time periods the average measured O₃ difference between the two platforms was 5 ppbv (Talbot et al., submitted manuscript, 2006). These comparisons provide further evidence for the reliability of the general trends in O₃ observed from the smart balloon platform.

2.3. Model Simulations

[14] Mesoscale meteorological, emission, and photochemical models were employed to help interpret the balloon-based observations. The Penn State/NCAR Mesoscale Meteorological Model Generation 5 (MM5) version 3.6 was used to simulate meteorology for the periods of 0000 UT on 19 July to 2300 UT on 25 July and 0000 UT on 3 August to 2300 UT on 8 August, 2004. The model configuration was very similar to that used by Mao and Talbot [2004], except that nesting was not used and the domain area and resolution were different. Since our study was focused on continental outflow and the longest balloon flight crossed the Atlantic Ocean, the domain was centered at 70°W and 40°N, spanning from ~90°W to 50°W and ~25°N to 60°N with more than half of the domain covering the North Atlantic (Figure 1). There were 119 × 81 cells in the domain at a spatial resolution of 36 km and 30 vertical σ -levels with 13 in the convective layer (<~1.5 km). The lowest layer was located at 10 m height and the top at 100 hPa.

[15] The Grell cumulus [Grell et al., 1991], simple ice [Dudhia, 1989], cloud radiation [Stephens, 1984], and Medium Range Forecasting planetary boundary layer scheme [Hong and Pan, 1996], and the Oregon State University land surface module were applied. We also used the four-dimensional data assimilation (FDDA) technique [Stauffer and Seaman, 1990, 1994] to force the simulations

closer to reality using the National Center of Environmental Prediction $1^\circ \times 1^\circ$ reanalysis data and NCAR surface and upper air observations. In this study, FDDA nudged horizontal winds, temperature, and specific humidity. FDDA was applied above the mixed layer or above 1.5 km whichever was higher.

[16] We used the National Emission Inventory 1999 (NEI-1999) and the recently updated version of SMOKE that includes Mobile 6 and Biogenic Emission Inventory System 3 (BEIS3). CMAQ [Byun and Ching, 1999] was employed to simulate two pollution episodes that occurred around our 20 July and 3 August balloon release dates. The first two simulation days were used for model spin-up. The 36 km horizontal grid structure in CMAQ follows that of MM5 with 96×68 cells. There were 21 vertical layers, with the lowest 13th identical to those in MM5 to maintain high resolution in the PBL. The CB-IV chemical mechanism was employed because of its common applicability in photochemical modeling and efficient computational schemes.

3. Model Evaluation

[17] The MM5 and CMAQ results provided three-dimensional distributions of key pollutants including O_3 over the North Atlantic during the smart balloon flight periods. Model output was evaluated carefully using observed meteorological and chemical data from the (1) UNH AIRMAP air quality monitoring network (<http://www.airmap.unh.edu>), (2) smart balloon flights (<http://tws.unh.edu/TWS-DEV/TWS/balloondata.htm>), (3) surface observations from the NOAA ship *Ronald H. Brown* (<http://www.al.noaa.gov/ICARTT/fieldoperations/fomp.shtml>), (4) Environmental Protection Agency AIRNOW sites in the northeastern United States (<http://airnow.gov/>), and (5) ozone soundings from the INTEX Ozone Network Study (IONS (A. M. Thompson et al., IONS-04 (INTEX Ozone Network Study, 2004): New perspective on summertime UT/LS (upper troposphere/lower stratosphere) ozone over northeastern North America, submitted to *Journal of Geophysical Research*, 2006)). In this section we show that the models utilized in this study did a reasonable job of simulating the meteorological and chemical environments over the northeastern United States and the adjacent Gulf of Maine during the time period of the three balloon flights.

[18] Modeled and observed surface air temperatures at the AIRMAP sites, with elevations ranging from sea level to 406 m, are presented in Figures 2a and 2b for time periods of 17–25 July (flight 2) and 1–8 August 2004 (flights 3 and 4). AIRMAP observations at Thompson Farm show that daily maximum temperature remained relatively constant near 28°C from 17 to 23 July except for a brief dip on 19 July, and then it dropped to 20°C on 24 July because of a frontal passage across New England (Figure 2a). Despite varying site elevation, the model reasonably simulated the temporal trend and spatial gradient in surface temperature at all sites. During the August period, the observations displayed a decreasing trend in daily maximum temperature with a more distinct spatial gradient between Castle Springs (406 m) and Appledore Island (10 m). The model captured the temporal trend at all sites, although it did not well reproduce the large temperature difference of $\sim 10^\circ\text{C}$ between Castle Springs and Appledore Island.

[19] Modeled wind speed and direction over the North Atlantic were evaluated using data derived from the balloon time-dependent GPS locations. For flight 2, the model simulated wind speed reasonably well and it performed even better in reproducing wind direction (Figures 3a and 3b). One exception was in the near-coastal region where high spatial resolution is needed to simulate the large variability in wind speed traversing from land to ocean as demonstrated by Mao and Talbot [2004]. Toward the end of flight 2 the model even captured the complex wind currents that the balloon was subjected to over Nova Scotia, although there was a 3 hour time lag compared to observations (marked by arrows 1 and 2 in Figure 3b). At this time wind direction was variable because of the influence of a migratory high-pressure system. Winds were weak at $\sim 2 \text{ m s}^{-1}$ causing the balloon to circle slowly as shown by both GPS location and modeled wind direction.

[20] During flights 3 and 4 the balloons flew at largely varying speeds and bearings, particularly on 5 and 6 August when they encountered Hurricane Alex (marked by arrows 3 and 4 in Figure 3b). The two balloons were released sequentially ~ 18 hours apart on 3 August. The travel speed and bearing of balloon 3 were more variable than balloon 4 since it encountered several small cyclones in addition to Alex that correlated with our simulated sea level pressure maps (not shown). Regardless of the complicated meteorological conditions, the model reasonably reproduced the observed large variability in wind speed and direction during the two flights. In particular, it accurately captured their directional veering on 5 and 6 August because of encounters with Hurricane Alex.

[21] Measurements of atmospheric species from the ship *Ronald H. Brown* in summer 2004 had extensive spatial and temporal coverage over the Gulf of Maine. Hence comparison of these observations (data courtesy of E. Williams, NOAA Aeronomy Laboratory) with our model results provides a rigorous evaluation. The *Ronald H. Brown* cruise tracks during the balloon flight periods spanned the Gulf of Maine near the coast extending from Cape Cod in the south to Nova Scotia in the north, and eastward to 67°W . The modeled results well replicated the overall trends in observed temperature, specific humidity, and winds during nearly all flight time intervals (Figure 4).

[22] To evaluate the performance of CMAQ, we first compared the simulated spatial patterns of daily O_3 maximum values with those obtained at EPA AIRNOW network sites in the Northeast and the UNH AIRMAP Castle Springs (43.75°N , 71.35°W , elevation 396 m), Thompson Farm (TF) (43.11°N , 70.95°W , elevation 23 m), and Appledore Island (AI) (42.97°N , 70.62°W , sea level) near the New Hampshire sea coast. The observations during the July episode showed an elongated area of enhanced O_3 mixing ratios along the U.S. east coast reaching from the mid-Atlantic states to New Hampshire (NH) (Figure 5a). In early August the higher values of O_3 were shifted to southeastern New York State and into southern New England. These same spatial patterns and daily O_3 maximum values were largely captured by the model simulations (Figure 5b).

[23] Our simulated surface O_3 distributions were also compared with measurements conducted aboard the NOAA ship *Ronald H. Brown* in the near-coastal region off of New England. It is evident from Figure 6 that the modeled O_3

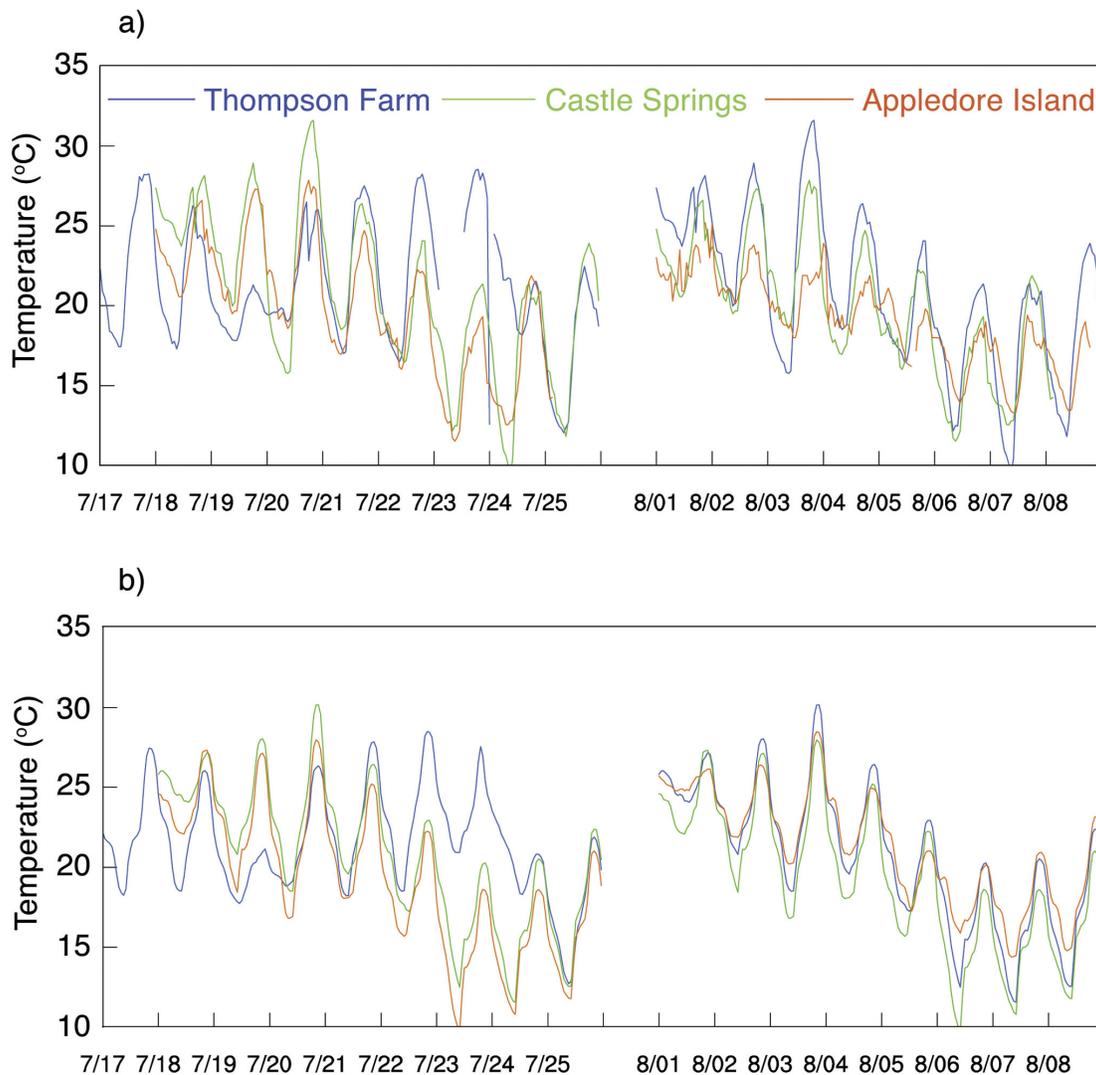


Figure 2. (a) Observed and (b) modeled surface temperature ($^{\circ}\text{C}$) at the UNH AIRMAP sites, Thompson Farm (blue), Castle Springs (green), and Appledore Island (red) during the time periods of 17–25 July and 1–8 August 2004.

mixing ratios along the *Ronald H. Brown* cruise tracks during the two episodes agreed very well with shipboard measurements of surface O_3 (>70 ppbv), especially along the near-coastal areas northeast of the Greater Boston metropolitan area and in southern Maine. The lowest O_3 mixing ratios (<30 ppbv) occurred in the near-coastal area east of Boston, and slightly higher levels of 40–50 ppbv ~ 50 km farther out over the ocean. A scatterplot (Figure S1 in auxiliary material¹) of modeled versus observed values showed a 1-to-1 correlation with an $r^2 = 0.85$, indicating that the model captured both the phase and magnitude of the measured O_3 mixing ratio near the coast.

[24] In addition to ground-level comparisons, we examined model performance in simulating upper air O_3 mixing ratios using ozonesonde data obtained at three ICARTT-IONS locations in Narragansett, Rhode Island, the ship *Ronald H. Brown*, and Sable Island, Nova Scotia. The

model-observational agreement varied between locations and on a daily basis. Overall, the model profiles agreed best in both magnitude and trend with the ozonesonde launches from the *Ronald H. Brown* during the August episode (Figures 7a–7f). On average, the model results were in agreement with observations within ± 5 ppbv below 250 m, differed by 15 ppbv at altitudes of 250–550 m and 2200–8000 m which increased to ~ 20 ppbv between 550 and 2200 m (Figure 7g). This model typically does a good job of simulating daily maximum O_3 mixing ratios at the surface, but is prone to difficulties at higher altitudes which are still not reconcilable. However, delving into the causal mechanisms of this problem is beyond the scope of our present study.

4. Synoptic Conditions

[25] The meteorological conditions over the eastern United States during summer 2004 were atypical. Most notable was the few number of high-pressure systems that

¹Auxiliary materials are available in the HTML. doi:10.1029/2005JD006507.

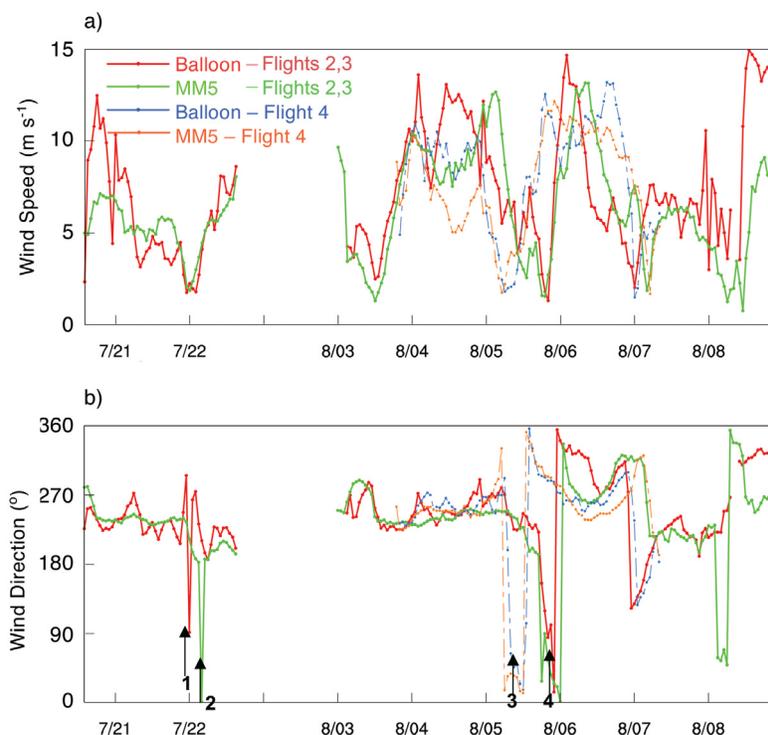


Figure 3. Balloon GPS position derived (red) and modeled (green) (a) wind speed (m s^{-1}) and (b) direction ($^{\circ}$) during flight 2 (20–22 July) and flights 3 (3–9 August) and 4 (3–7 August). Dashed lines are for flight 4 with blue for balloon derived wind and orange for MM5 simulated wind. Arrows 1 and 2 in Figure 3b mark the observed (0000 UT) and modeled (0300 UT) balloon circling over PEI, while arrows 3 and 4 mark the observed/modeled encounters with Hurricane Alex during flights 3 and 4, respectively.

stagnated near the mid-Atlantic coastal region and together with a Canadian low formed the primary synoptic transport route of polluted air masses into New England [Mao and Talbot, 2004]. Instead in 2004, a trough, appearing to be the southward extension of the Canadian low, was frequently situated off the eastern U.S. coastline, and in concert with high-pressure systems formed strong southwesterly to westerly flow over the Atlantic near the continent. It was this flow regime that we released the smart balloons into from our Long Island launch site.

[26] During the second balloon flight on 20 July a sea level trough axis was oriented parallel to the northeast U.S. coast causing weak wind conditions over New England (Figure 8a). In contrast, an offshore migratory high-pressure system located south of Nova Scotia generated strong southerly winds over the Gulf of Maine. Two days later on 22 July weak wind conditions prevailed over the Gulf of Maine and Nova Scotia under the influence of the surface and subtropical highs at the 925 hPa level (Figure 8b). Under these two synoptic conditions balloon 2 first traveled straight from Long Island to Nova Scotia in the strong southwesterly flow, and then slowed and circled once it encountered weak winds over Prince Edward Island (PEI). This latter pattern is evident in the looping feature of the balloon bearing near 0300 UT on 22 July (Figure 3).

[27] Balloons 3 and 4 followed variable tracks during their long traverse of the North Atlantic. Smoothing of their tracks showed that they were reasonably close to that

expected from the climatological flow route from North America to Europe [Eckhardt *et al.*, 2004], which confirms that the balloons were Lagrangian horizontally, drifting in the prevailing flow regime. Synoptic weather maps for these balloon flight periods showed complex interplay of high- and low-pressure centers including Hurricane Alex in determining the overall path of the balloons (Figures 8b and 8d).

5. Balloon O_3 Observations

5.1. Flight 2: 20–22 July

[28] Balloon 2 was released from Long Island at 1430 UT on 20 July 2004 and it traveled northeasterly across the Gulf of Maine to Nova Scotia and finally PEI before descending and dropping into the North Atlantic. This flight provided an opportunity to study the characteristics of the New York urban plume over the ocean after its departure from the continent. The total flight duration was 49 hours, and it coincided with an O_3 episode over the northeastern United States.

[29] The balloon traveled toward Nova Scotia with a fairly constant bearing of 50° , except during 0100–0200 UT on 22 July when it was caught in wind currents of an anticyclone located over Nova Scotia (Figure 9a). The horizontal velocity was $5\text{--}13 \text{ m s}^{-1}$ during the first 17 hours of the flight and then decreased to $<5 \text{ m s}^{-1}$ under the influence of the anticyclone.

[30] Large variability in the 15-min averaged O_3 mixing ratios was observed, fluctuating by as much as 84 ppbv

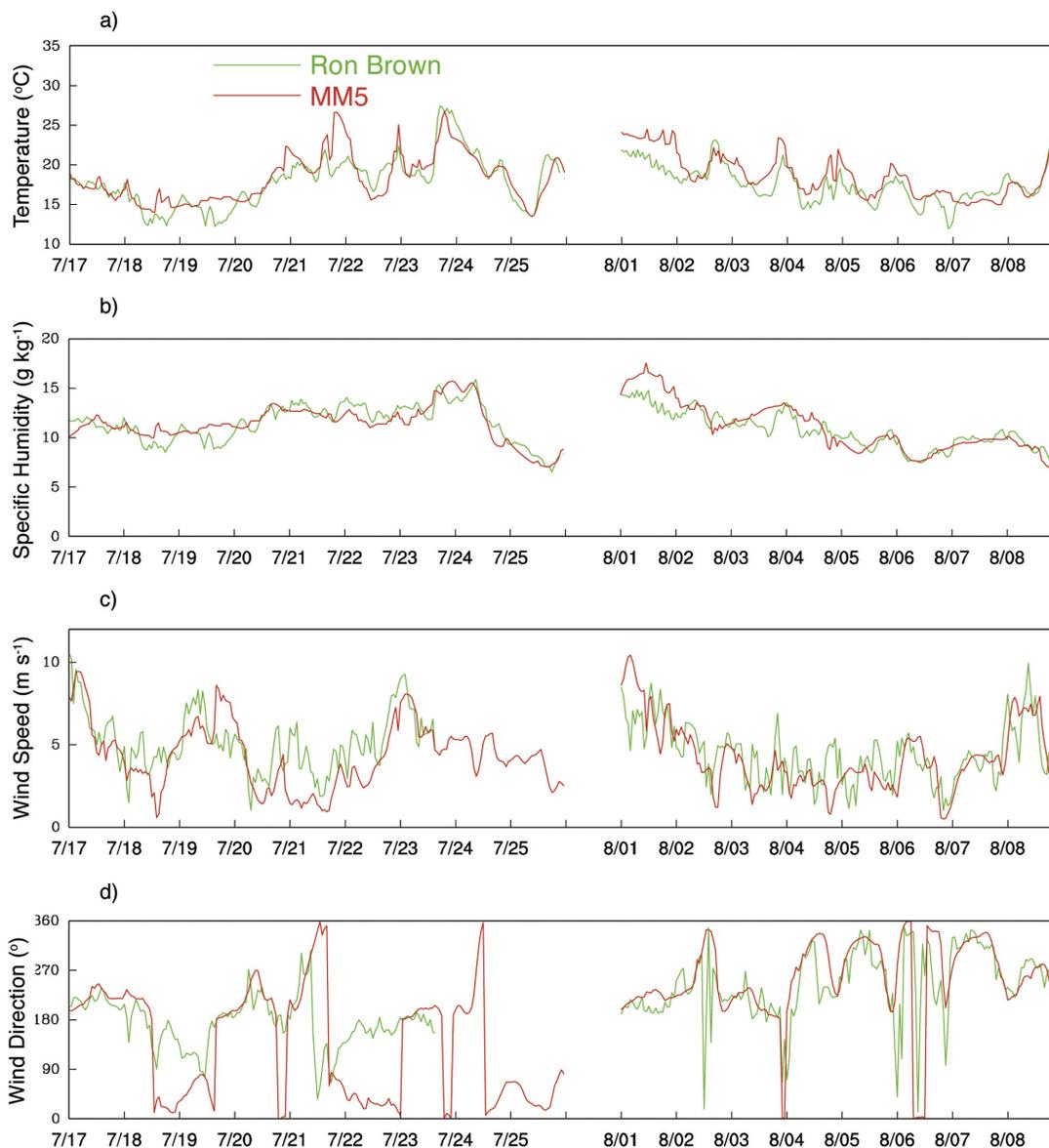


Figure 4. (a) Surface temperature (°C), (b) specific humidity (g kg⁻¹), (c) wind speed (m s⁻¹), and (d) wind direction (°) from the *Ronald H. Brown* measurements (green) and model simulations (red) during the time periods of 17–25 July and 1–8 August 2004.

within a horizontal distance <10 km (Figure 9b). For the entire flight, the mean mixing ratio of O₃ was 78 ppbv with a standard deviation of 31 ppbv. The maximum mixing ratio of O₃ was encountered about 200 km offshore over the Gulf of Maine where it reached 171 ppbv at 0000 UT on 21 July. After 10 hours O₃ dropped to <80 ppbv and then decreased to 60 ppbv for the next 2 hours coincident with a brief excursion of the balloon from 500 m to 700 m altitude. At around 1430 UT on 22 July, the balloon reached Nova Scotia and then continued its journey to PEI where O₃ mixing ratios continued to drop to ~50 ppbv.

[31] During this flight, the balloon traveled at an altitude of ~500 m with a few ascending and descending motions over a vertical distance <200 m (Figure 9b). These vertical motions were due to natural rising or subsiding air masses and were not induced by our control of balloon altitude. The

associated variability in O₃ mixing ratios can be attributed to many factors such as vertical mixing, the balloon drifting in and out of the urban plume, and heterogeneity in air mass composition within the urban plume. Changes in O₃ mixing ratios, especially the larger ones, appeared to coincide with fluctuations in balloon altitude, specific humidity, or wind speed. For instance, the first large increase in O₃ occurred at ~0100 UT on 21 July, where it increased from 67 ppbv to 150 ppbv within 30 min, and over a horizontal distance of ~9 km. This abrupt increase corresponded to a rapid increase in wind speed from 5 to 13 m s⁻¹, but with little change in balloon bearing, altitude, and specific humidity. The geopotential height and wind fields at the 925 hPa level (~700 m) showed that the trough axis was located over the ocean 100–200 km away from the NH coastline with a large horizontal gradient in wind speed (not shown). The

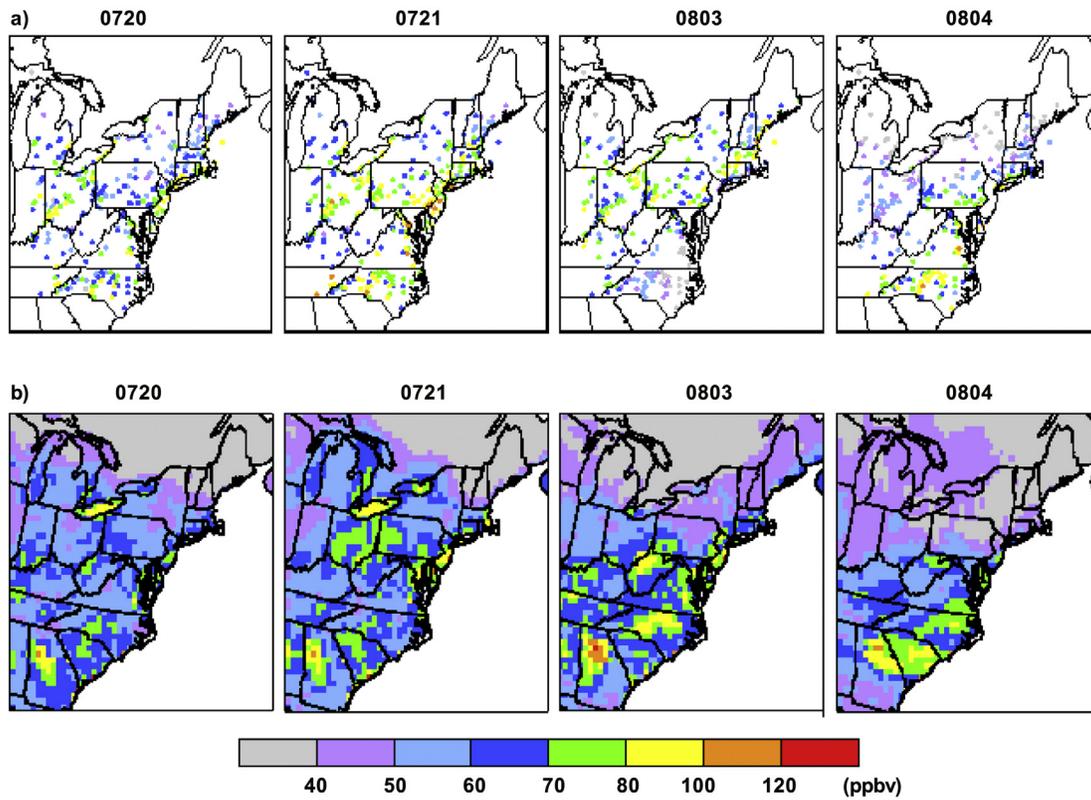


Figure 5. (a) Observed (discrete) and (b) modeled (continuous) daily maximum O_3 mixing ratios (ppbv) near the surface for 20–21 July and 3–4 August.

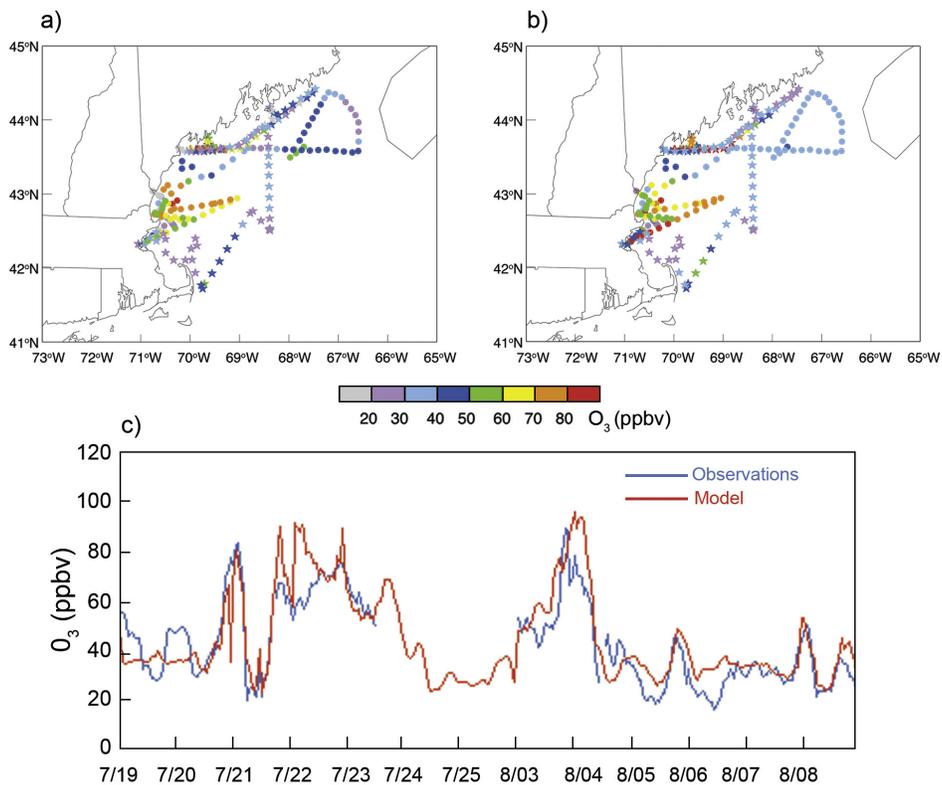


Figure 6. Geographic distribution of surface O_3 during 19–25 July (dots) and 3–8 August (asterisks) from the (a) *Ronald H. Brown* measurements, (b) CMAQ model simulations, and (c) as a time series comparison.

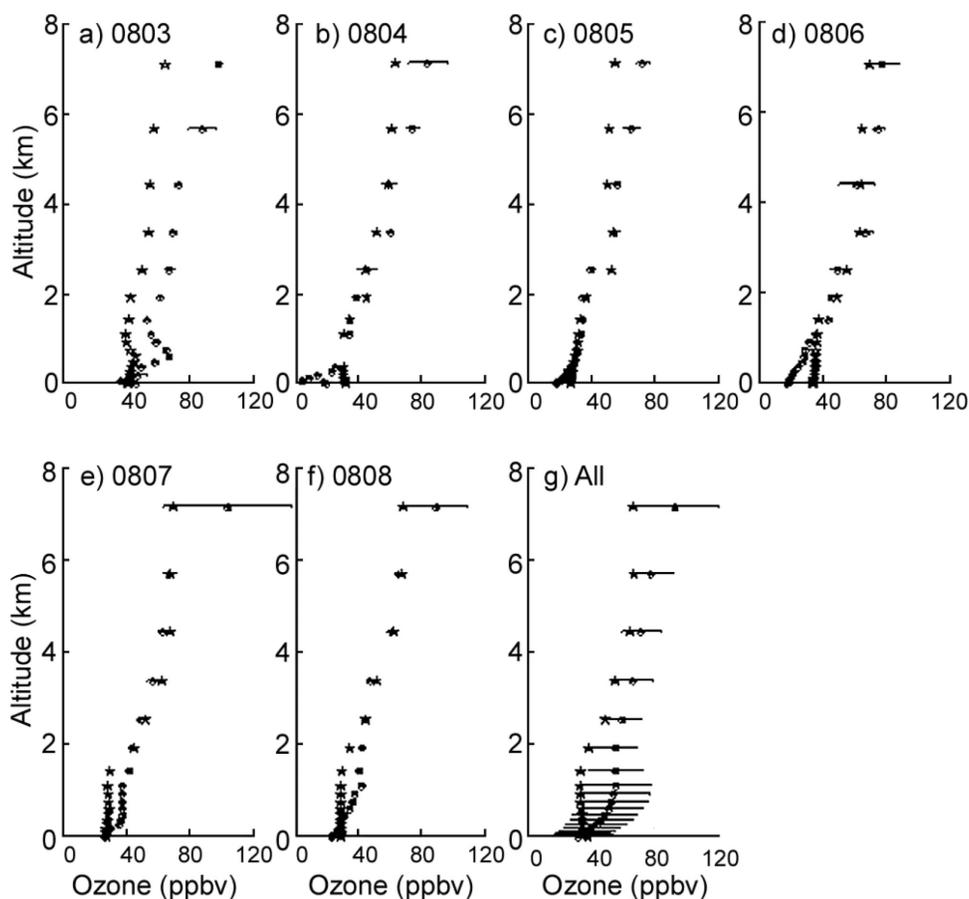


Figure 7. Model-ozonesonde comparison of O_3 mixing ratios from the surface to 8 km altitude. (a–f) Data from sonde launches from the *Ronald H. Brown* during 3–8 August. (g) Sonde data from launches at Narragansett, Rhode Island, the *Ronald H. Brown*, and Sable Island over the periods of 19–25 July and 3–8 August. Circles represent ozonesonde observations, and asterisks represent CMAQ results.

balloon and urban plume containing high O_3 possibly traveled over this region transitioning within 15 min from a calm zone to a windy one with attendant changes in O_3 . These data document the highly heterogeneous distribution of O_3 within an urban plume over a horizontal distance of <10 km. The details of these high-resolution measurements are presented in the companion paper by Talbot et al. (submitted manuscript, 2006).

[32] It should be noted that during this 2-day flight, none of the observations made by the AIRMAP network or EPA AIRNOW stations across the Northeast reported O_3 levels exceeding 120 ppbv. In contrast, the 15-min average balloon measurements over the Atlantic during the 49 hour flight had a cumulative 345 min exceeding that level, and on half of the flight O_3 mixing ratios were >80 ppbv.

5.2. Flight 3: 3–15 August

[33] Balloon 3 was launched at 0153 UT on 3 August 2004, and traveled 295 hours (12.3 days) covering a distance of 6,780 km. The balloon first rose to 500 m altitude and remained there for the next 124 hours. During this time the net velocity of the balloon varied from 5 to 15 m s^{-1} while it tracked on an $\sim 90^\circ$ bearing (Figure 10a). At 0800 UT on 8 August ($\sim 41.5^\circ\text{W}$) the balloon was brought up to 3.3 km altitude to charge the batteries, with power subse-

quently lasting another 157 hours (Figure 10b). Over this altitude change of ~ 3 km specific humidity decreased from $\sim 12 \text{ g kg}^{-1}$ to 5 g kg^{-1} , but O_3 mixing ratios did not vary much except for a couple of peaks exceeding 100 ppbv. At 3.3 km altitude the balloon tracked on a 120° bearing, and headed southeastward under cyclonic influence. During this leg the balloon flew through two distinct air masses characterized by specific humidities of 5 g kg^{-1} and 2.5 g kg^{-1} , but the corresponding small changes in O_3 did not appear to be equally indicative of varying air mass composition.

[34] Throughout flight 3 O_3 levels were highly variable, ranging from 7 to 171 ppbv (15 min averaged), with a mean of $52 \text{ ppbv} \pm 25 \text{ ppbv}$. In the eastern North Atlantic region (10–14 August) spikes in O_3 mostly stayed below 100 ppbv, with the exception of a sharp rise to nearly 150 ppbv near the North African coast (15 August). Surprisingly, these high values also appear to be related to U.S. urban outflow as discussed in more detail by Talbot et al. (submitted manuscript, 2006).

[35] Overall, a small horizontal spatial trend in O_3 mixing ratios of $-1.3 \text{ ppbv } \text{O}_3 \text{ per } 10^\circ$ in longitude was observed with the slightly higher mixing ratios occurring early in the flight near North America. Farther out over the Atlantic, photochemically aged marine air masses should be predom-

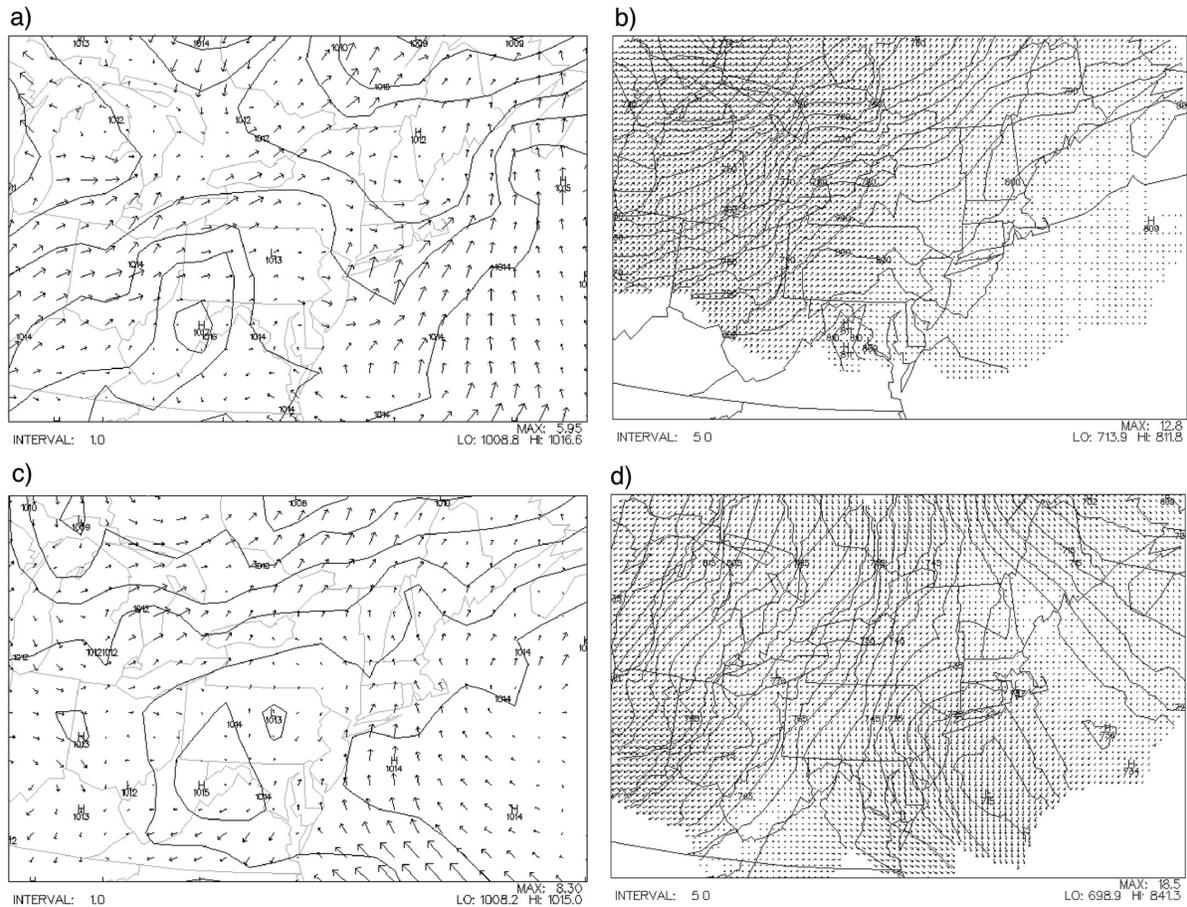


Figure 8. (a) Wind vectors (m s^{-1}) superimposed on sea level pressure (hPa) at 1500 UT on 20 July and (b) geopotential height (m) for the 925 hPa level at 0000 UT on 22 July, (c) wind vectors (m s^{-1}) superimposed on sea level pressure (hPa) at 0000 UT on 3 August and (d) geopotential height (m) for the 925 hPa level at 1200 UT on 5 August.

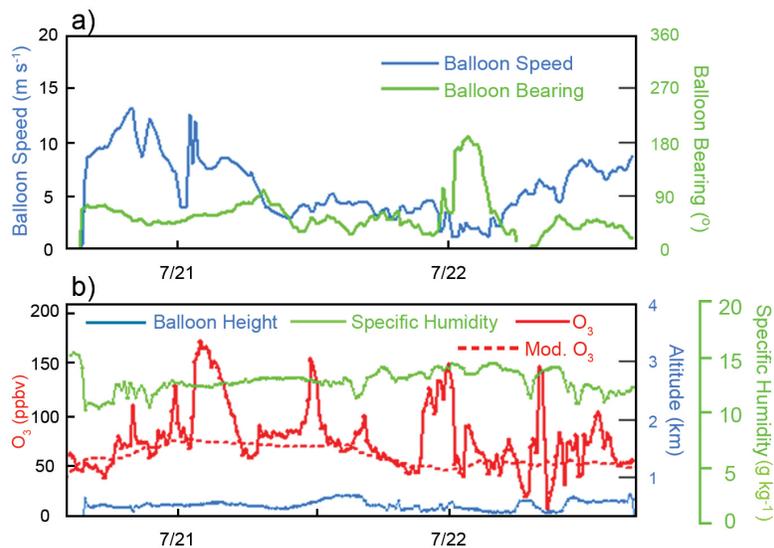


Figure 9. Flight 2 time series of 15 min averaged (a) balloon speed and bearing and (b) O_3 mixing ratios, balloon altitude, and specific humidity. The red dashed line in Figure 9b represents the modeled O_3 level along the balloon track.

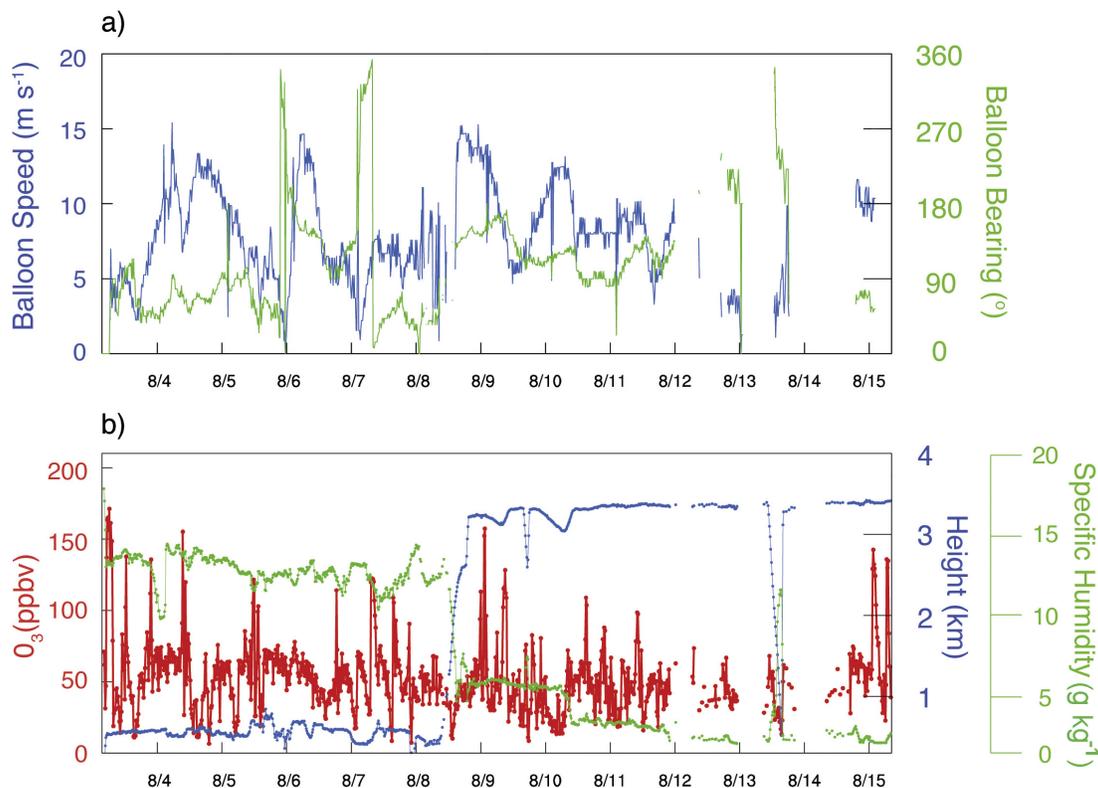


Figure 10. Flight 3 time series of 15 min averaged (a) balloon speed and bearing and (b) O₃ mixing ratios, balloon altitude, and specific humidity.

inant with embedded layers of urban plumes indicated by enhanced O₃ (Talbot et al., submitted manuscript, 2006).

5.3. Flight 4: 3–7 August

[36] To examine the horizontal distribution of O₃ and its evolution in urban plumes, balloon 4 was released at 1959 UT on 3 August, 18 hours after balloon 3 took off from the same location. The flight lasted 85 hours and the balloon traveled 2,530 km. The mean level of O₃ during this flight was 59 ppbv with a standard deviation of 28 ppbv. These values are very similar to those from flight 3, even though balloon 4 only traveled 37% of the distance covered by balloon 3. A great deal of the flight 4 was influenced both dynamically and chemically by multiple encounters with Hurricane Alex in the central North Atlantic (<http://www.osei.noaa.gov/Events/Tropical/Atlantic/2004/>). Balloon 3 also encountered Alex, but to avoid duplication our discussion is focused on balloon 4.

[37] More than 50% of the flight occurred at 500 m altitude with a bearing of 78° and at a remarkably constant speed of 10 m s⁻¹ (Figure 11a). During the first 6 hours of the flight, before 0200 UT on 4 August, the balloon measured O₃ in an air mass freshly transported off the continent with levels near 90 ppbv. The air mass sampled during this portion of the flight was denoted as phase I (Figure 11b). This was followed by a period with O₃ levels <50 ppbv during the next 26 hours (0200 UT on 4 August to 0600 UT on 5 August) that we defined as phase II of the flight.

[38] The balloon altitude was then adjusted to 1.8 km to charge the batteries, and it remained there until 2200 UT on

6 August (Figure 11b). As the balloon began its ascent, O₃ mixing ratios peaked at 155 ppbv near 1.3 km altitude, a period which we defined as phase III of the flight. This was followed by phase IV where a decrease to ~80 ppbv occurred from 2100 UT on 5 August to 0300 UT on 6 August. During the next portion of the flight O₃ mixing ratios dropped to ~25 ppbv and remained there during ensuing 9 hours of the flight (phase V). As the balloon descended to the sea surface in phase VI it encountered an air mass similar to the one in phase II. These changes in air mass characteristics during different phases of the flight are corroborated by corresponding variations in specific humidity (Figure 11b), which indicates that the pollution was dispersed in stratified layers over the North Atlantic (Talbot et al., submitted manuscript, 2006). The clearest example is phase III and initial stage of phase VI when the balloon was at 1.3 km altitude and was seemingly flying in the New York urban plume.

5.4. Encounter With Hurricane Alex: 5 August

[39] During 3–4 August, Hurricane Alex was moving northeastward along the U.S. eastern coast with its western periphery passing over the heavily polluted urban area extending from Georgia to the northeast corridor. Our model results illustrate a possible scenario as shown in Figure 12. Here we present a “snap-shot image” from a 3-D visualization of the MM5 flow vectors, CMAQ O₃ mixing ratios, and the GPS/O₃ real-time data from the balloon, all superimposed to provide a simulation of the conditions over the Atlantic. This simulation shows the widespread outflow of air from the U.S. east coast as Alex veered northeastward

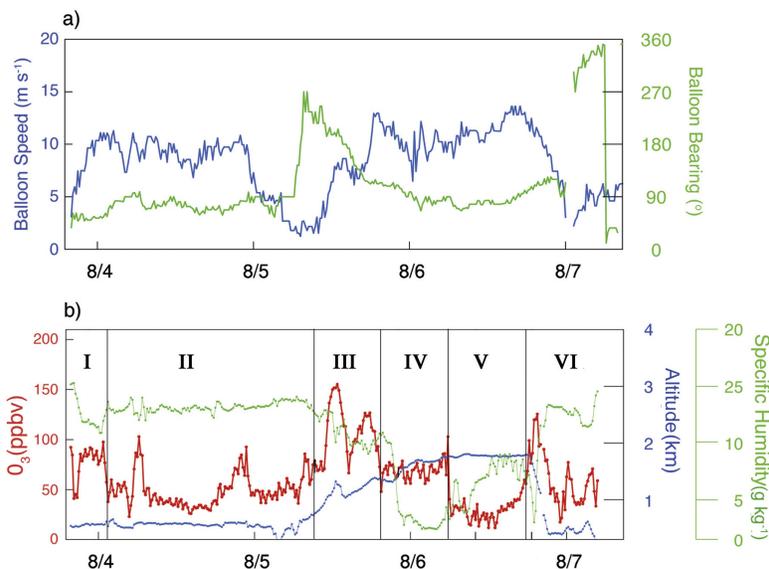


Figure 11. Flight 4 time series of 15 min averaged (a) balloon speed and bearing and (b) O₃ mixing ratios, balloon altitude, and specific humidity. The “six phases” of the flight balloon 4 experienced are indicated with the Roman numerals I–VI (see text for description).

across the Atlantic. It is highly likely that pollutants were entrained in Alex’s anticyclonic flow regime and transported eastward as the hurricane traveled across the North Atlantic.

[40] The presumably entrained pollution was sampled by the balloon on 5 August between 0600–1800 UT (phase III, Figure 11b) when it was on the southwestern periphery of Hurricane Alex. The O₃ mixing ratios were <50 ppbv before the balloon encountered Alex, but they rose to >150 ppbv at

1600 UT when balloon 4 drifted to within a few hundreds km of Alex. In a study of Super Typhoon Murielle in the North Pacific, *Newell et al.* [1996] suggested a similar scenario for over the Pacific where there was substantial entrainment of boundary layer air from the equatorial and Asian continental regions into the eye wall region with subsequent transport of pollutant-rich air across the remote ocean.

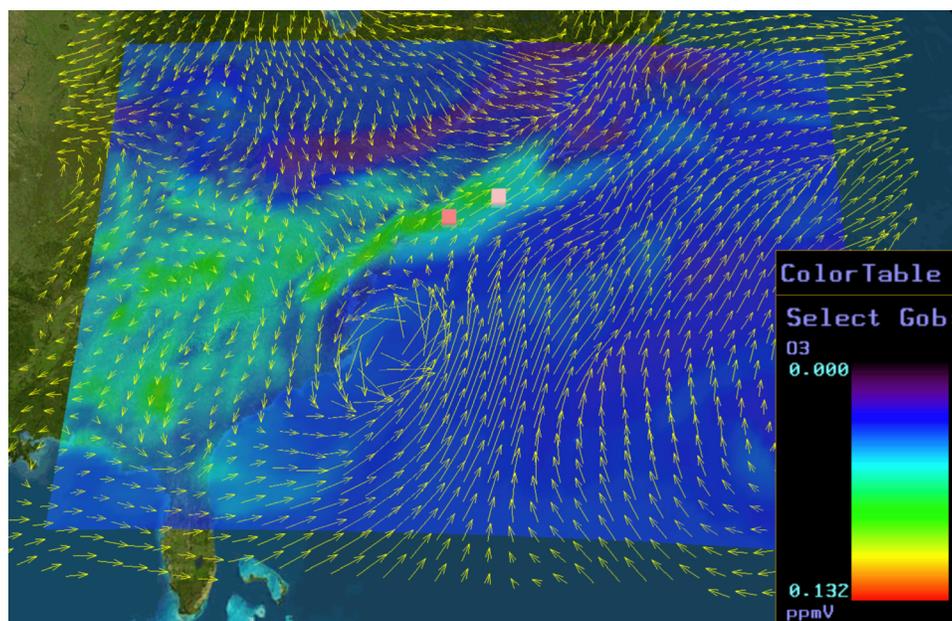


Figure 12. “Snap-shot image” of northeastern U.S. urban outflow for 0000 UT on 4 August with balloons 3 (top right) and 4 drifting in the center of the plume as simulated using MM5 and CMAQ combined with the real-time GPS/O₃ data from the balloons (indicated by the balloon color). The O₃ mixing ratios from CMAQ and the balloons are on same color scale. Hurricane Alex is seen moving northward along the U.S. east coast.

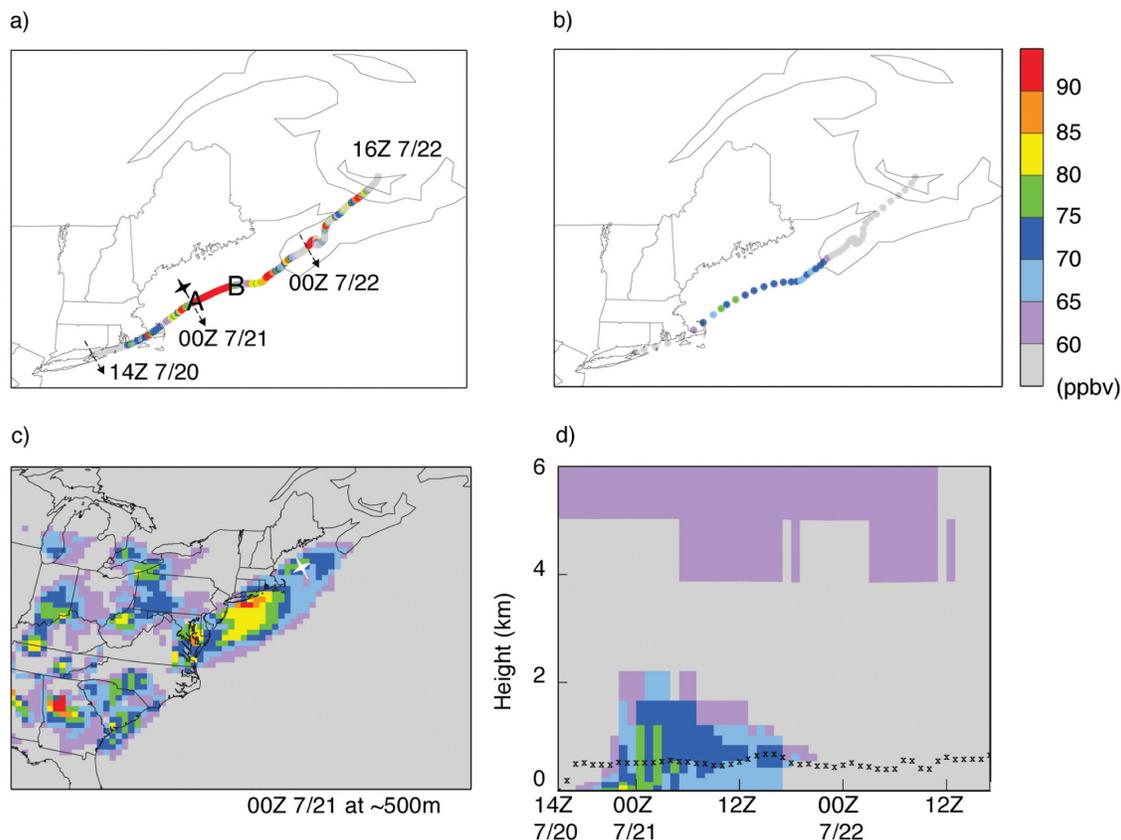


Figure 13. O_3 mixing ratios (a) measured on balloon 2 and (b) as modeled using CMAQ along the flight track. (c) Modeled horizontal distribution of O_3 at 0000 UT on 21 July at the balloon altitude of ~ 500 m and (d) the altitude-time cross section of O_3 from CMAQ where the black asterisks designate the balloon flight path. In Figure 13a the arrows correspond to the marked times, the arrow with the black star is the time for Figure 13c, and the portion of the track A-B includes the period of continuous high O_3 levels that was the focus of the discussion in section 6.

[41] As the balloon traveled at 1.8 km altitude, an extended region of low O_3 (<30 ppbv) was encountered that covered a large area from 47°W to 53°W , as represented by phase IV in Figure 11b. We suspect that these low mixing ratios of O_3 may represent clean (aged) air masses lofted from the remote marine boundary layer by updrafts associated with Alex and other cyclonic features in the same area. This speculation is supported by GOES images (not shown) which show extensive cloudiness in the vicinity of the balloon indicative of convective conditions. The low mixing ratios of O_3 observed at 1.8 km are identical to those sampled by balloon 4 in the marine boundary layer during phase II and at other locations over the North Atlantic by *Banic et al.* [1996] and *Oltmans et al.* [1996].

6. An Urban Plume Over the Gulf of Maine

[42] We demonstrated in section 3 that the model underestimated O_3 mixing ratios over the Atlantic by 20–30 ppbv. It also missed variations in O_3 that lasted 1–3 hours, which covered 18–54 km in horizontal distance given an average balloon speed of 5 m s^{-1} . This was most likely caused by limitations imposed by the model spatial resolution of 36 km, which smoothed features that existed on finer

spatial/temporal scales. However, the model did capture the overall spatial distribution in observed O_3 (Figure 9b).

[43] Here we show a typical example using the urban plume sampled on flight 2. Ozone measurements on board balloon 2 on 21 July from 0115 to 0130 UT showed that O_3 mixing ratios increased from 97 to 152 ppbv over a horizontal distance of only 5 km. This was followed by 12 hours of sustained levels of $\text{O}_3 >80$ ppbv over a horizontal distance of 255 km (Figures 9b and 13a). This flight segment is marked as points A and B in Figure 13a (hereinafter referred to as track A-B). The model results showed that the O_3 mixing ratio increased from 63 ppbv near 0000 UT on 20 July to 77 ppbv at 0100 UT on 21 July, and then remained near that level throughout the morning of 21 July (Figures 9b and 13b). Thus the model missed the short-lived peaks in O_3 and predicted changes in O_3 slightly in advance of what was observed, but nonetheless it got the overall O_3 distribution remarkably correct.

[44] Our simulations showed that on 21 July there was a large area of enhanced O_3 oriented toward the northeast that extended from off the mid-Atlantic states to Nova Scotia. Embedded in this large plume were two centers of high O_3 , one over Long Island and the other ~ 120 km off the NH and Maine coastlines (Figure 13c). At 0000 UT balloon 2 was positioned inside the latter center, as indicated by the white

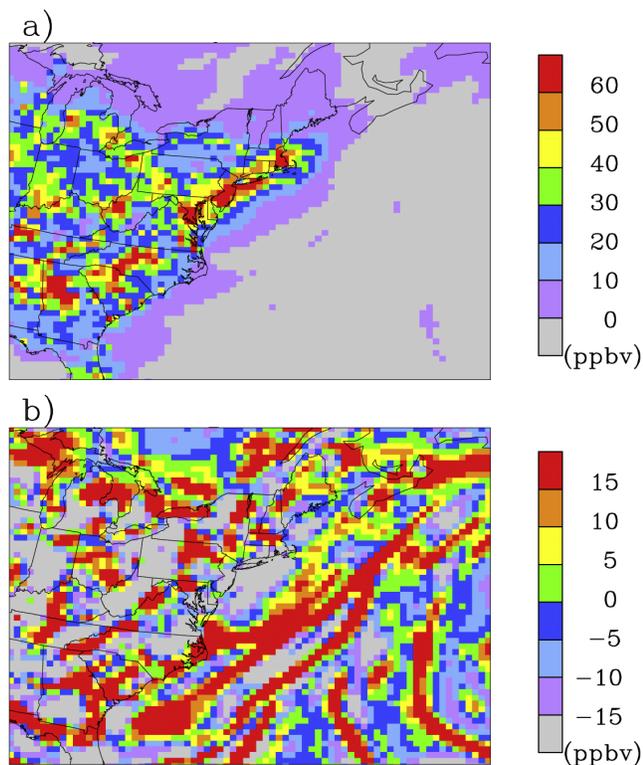


Figure 14. (a) Net O_3 production (ppbv) at the balloon altitude of ~ 500 m integrated over the daytime period of 1200–2300 UT on 20 July and (b) the transport component integrated over the nighttime period of 2200 UT on 20 July to 0900 UT on 21 July.

asterisk on Figure 13c. Our MM5 results revealed a divergence gradient in horizontal winds over the Gulf of Maine, with convergence in the regions near the New England coast and Nova Scotia (not shown). We speculate that the steep increases/decreases in O_3 on 21 July, on the timescale of minutes, can be attributed to a heterogeneous O_3 distribution inside the plume associated with a varying horizontal wind distribution over the greater Gulf of Maine region.

[45] The temporal evolution of the urban plume was examined using the modeled cross section of O_3 along the balloon track (Figure 13d). The model predicted O_3 levels of 40–50 ppbv confined to a 200 m thick surface layer during the first two hours of the flight. The balloon was flying above this layer at 500 m and recorded O_3 mixing ratios of 55–60 ppbv. Modeled O_3 in the shallow surface layer increased to 60–70 ppbv over the next four hours. During hours 7–8, the area of enhanced O_3 (>70 ppbv) gradually expanded upward reaching 2 km altitude. The layer of maximum values (70–80 ppbv) was predicted to be at ~ 500 m, the altitude at which the balloon was traveling. The balloon O_3 measurements showed values >90 ppbv, which strongly suggests that it was flying in the mainstream of the urban plume. It is noteworthy that the highest values of O_3 in the plume were encountered in the middle of the night.

7. Higher O_3 Over the Ocean Than the Continent

[46] We utilized our model simulations to investigate the mechanisms that caused higher levels of O_3 over the remote ocean than across the northeastern United States. The cross

section of simulated net O_3 chemical production rate was calculated along the balloon 2 flight track at all altitudes (not shown). The rate peaked at 6 ppbv hr^{-1} within the thin surface layer as the plume departed from the continent. Net O_3 production decreased to $<1 \text{ ppbv hr}^{-1}$ by around 0000 UT on 21 July, accompanied by a sharp increase in O_3 mixing ratios a few hundred kilometers from the coast (Figure 13a). We examined the amount of O_3 that potentially could be chemically produced upwind of track A-B. To do so, the rate of net O_3 production at ~ 500 m height was integrated over the daytime hours on 20–21 July (Figure 14a). During the daytime on 20 July high net O_3 production ($>60 \text{ ppbv}$) occurred along the urban corridor with a significant amount (10–60 ppbv) continuing out over the Gulf of Maine toward Nova Scotia. On the basis of the magnitude of the measured O_3 mixing ratios it is likely that net O_3 production was actually much greater than what we estimated using CMAQ. Together our measurement and model results demonstrate significant net production of O_3 downwind from the North America continent.

[47] As described in section 4, the flow regime on 20–21 July was conducive to transport of pollutant-rich air masses from the northeastern urban corridor to the North Atlantic. The model results show a contribution of up to 15 ppbv due to nighttime transport of O_3 at the balloon

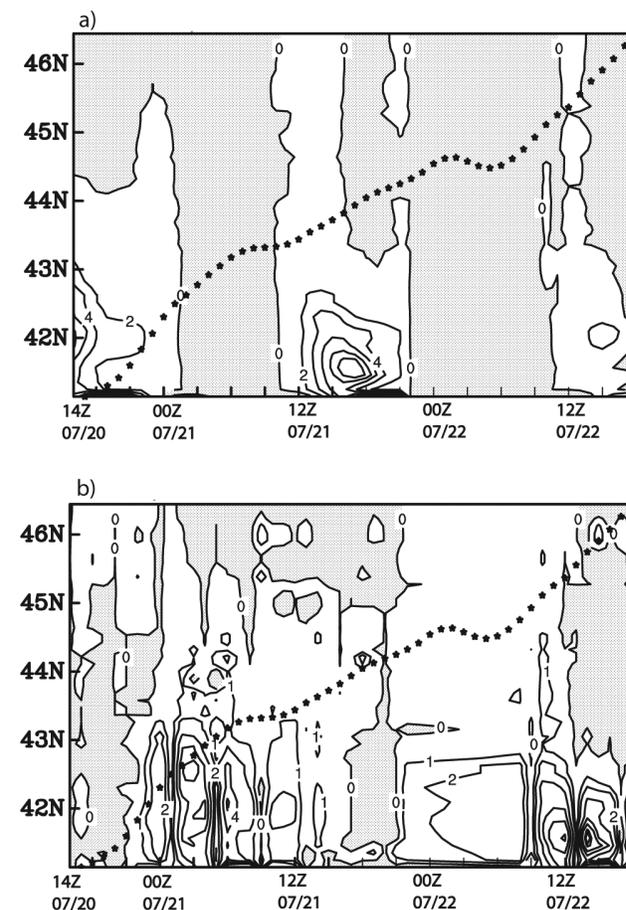


Figure 15. Temporal variation in (a) net O_3 production and (b) transport (ppbv hr^{-1}) along the balloon flight track (15-min averaged data).

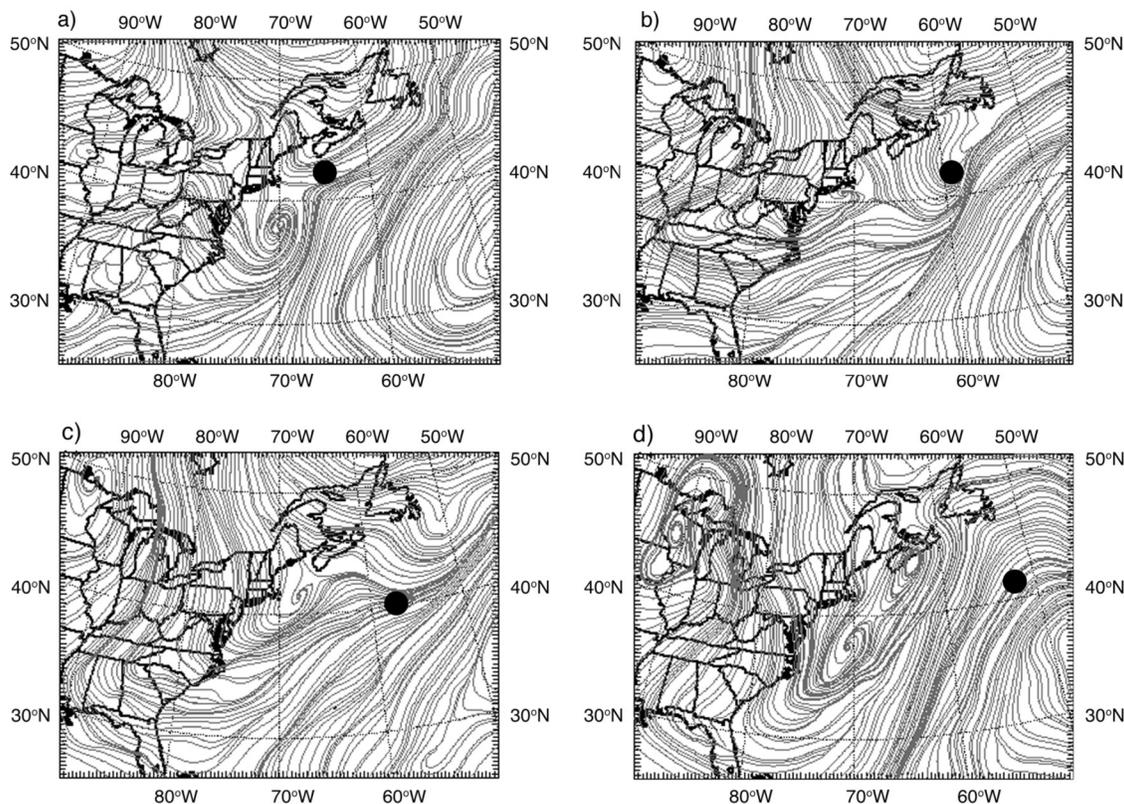


Figure 16. MM5 simulated streamlines at the balloon 4 altitude for (a) 1200 UT on 4 August (phase II), (b) 1200 UT on 5 August (phase III), (c) 0000 UT on 6 August (phase IV), and (d) 1800 UT on 6 August (phase V). The solid circle represents the balloon position.

altitude of ~ 500 m (Figure 14b). Thus the diurnal cycle in the individual contributions from photochemistry and transport to elevated O_3 mixing ratios along track A-B over the Gulf of Maine are opposite in phase (Figure 15). Our model results showed that the largest contribution of in situ net O_3 production to the simulated O_3 mixing ratio over water was up to 10 ppbv hr^{-1} prior to 2100 UT on 20 July, while the transport contribution reached as large as 8 ppbv hr^{-1} during the following night. These two factors, in addition to a sustained continental influence and the divergence gradient in horizontal winds, are conducive to causing patchiness and pockets of high O_3 over the Gulf. In addition, the small deposition of O_3 to the ocean surface and minimal oxidation at night can reduce O_3 loss significantly during the nighttime period. The combined effect of all these mechanisms can cause much higher levels of O_3 over the North Atlantic than over land.

8. O_3 Variability Over the North Atlantic

[48] One of the most pronounced features of the smart balloon O_3 data was its variability on the timescale of days, as demonstrated with the six distinct air mass phases defined by balloon 4 measurements (Figure 11). To explain these, the large-scale circulation patterns were examined using streamlines generated by our MM5 simulations with four selected example snapshots shown in Figure 16, which displays the apparent changeable flow patterns balloon 4

sampled. These streamlines were extracted from the model layer that includes the instantaneous balloon height.

[49] Phase II saw the balloon flying over south of Nova Scotia which was dominated by air masses originating from northern Maine and Canada (Figure 16a), and the balloon was sampling clean marine air during phase V that had originated from lower latitudes over the tropical Atlantic (Figure 16d). The encounter with Hurricane Alex where the balloon drifted along the southwestern periphery of the storm measuring high levels of O_3 for an entire day was not captured in the examples shown in Figure 17. However, the modeled streamlines suggested that in phases III and IV the air mass was derived from the mid-Atlantic and southern states which was rapidly transported off the continent and entrained into Alex (Figures 16b and 16c). To better illustrate this point, we selected another “snap-shot image” at 2100 UT on 5 August from our 3-D movie visualization (Figure 18). In this representation both balloons 3 and 4 are shown, with their color corresponding to the measured O_3 . The relatively higher O_3 plume in the rear of Alex was likely from the entrainment of the outflow off the U.S. east coast toward the inflow area of the hurricane. Our model results seem to have accurately simulated the position of the relatively high O_3 mixing ratios (Figure 18), but considerably underestimated the absolute values of the channeled pollution. It appears that CMAQ has an inherent problem in underpredicting O_3 levels in continental outflow.

[50] In addition, the evolution of O_3 distribution in the urban plume was investigated using the horizontal gradient

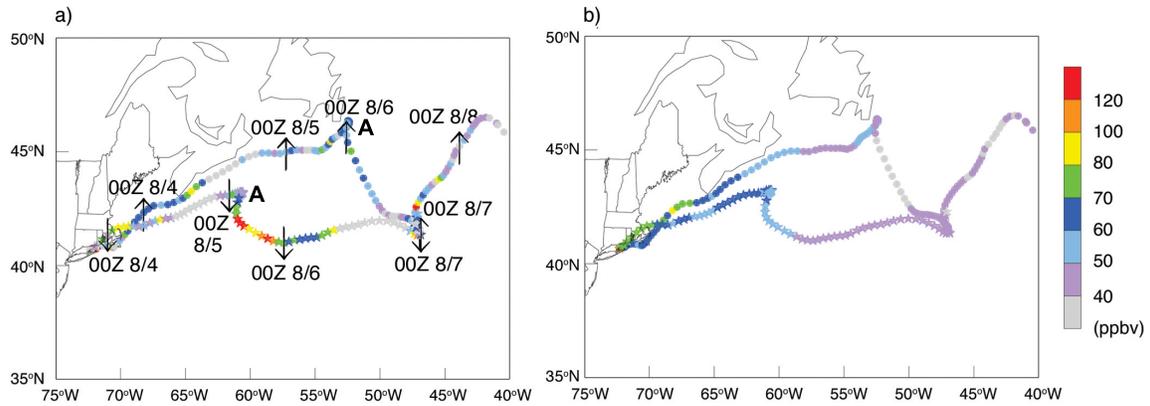


Figure 17. (a) O₃ measurements during flights 3 (dots) and 4 (asterisks) and (b) the corresponding CMAQ modeled values. The letter “A” in Figure 17a indicates the balloon encounter points with Hurricane Alex.

calculated from measurements made by the two balloons. We examined two time periods when balloons 3 and 4 were within 200–400 km of each other on 4 August. Inspection of the streamlines suggested that the two balloons should be measuring air masses of the same origin identified in Figure 16a. The first window was 0000–1200 UT when the O₃ levels on balloon 3 were in the range of 70–100 ppbv. This range is higher than the balloon 4 measurements by 20–30 ppbv during the first 5 hours, but O₃ decreased to lower levels over the rest of the day. These measurements yielded horizontal O₃ gradients ranging from -0.2 to 0.2 ppbv km⁻¹ spanning a distance of 250–277 km in what appears to be the same polluted air mass. During the

second time window 1400–2000 UT, when the balloons drifted slightly farther apart, they both measured O₃ mixing ratios <40 ppbv in an air mass the streamlines suggest originated from northern Maine and Canada (Figure 16b). Compared to the first time window, these air masses exhibited much more uniform O₃ levels, showing horizontal gradients of one order of magnitude smaller, mostly in the range of -0.05 – 0.05 ppbv km⁻¹ spanning a horizontal distance of 300–400 km. These estimates suggest that over a time period of less than a day (~20 hours) the urban plume expanded horizontally by at least ~100 km with subsequent dilution of pollutant concentrations inside the plume and resulting in an air

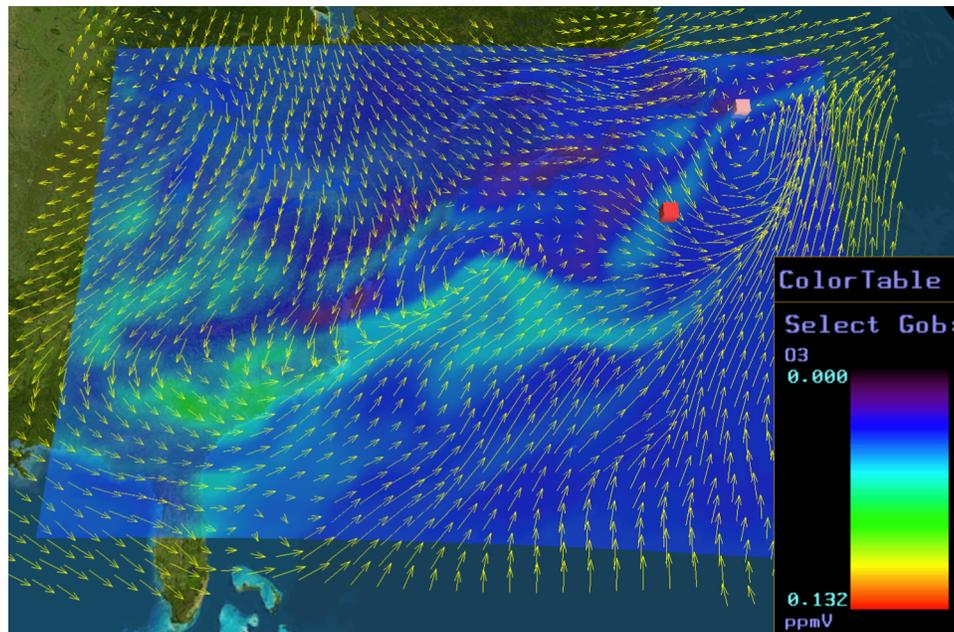


Figure 18. “Snap-shot image” of the MM5 instantaneous wind vectors at ~500 m altitude with CMAQ O₃ mixing ratios and balloon GPS/O₃ superimposed on the domain field for 2100 UT on 5 August. The O₃ mixing ratios from CMAQ and the balloons are on same color scale. Balloon 3 leads the way in the top right corner of the domain.

mass that became more homogeneous as evidenced by the measured O₃ distribution. This unique analysis demonstrates the importance of applying small mobile platforms in future field measurements.

9. Summary

[51] This study examined the evolution of northeastern urban plumes in North American continental outflow using smart balloon measurements during the ICARTT campaign over the periods of 20–22 July and 3–15 August 2004. An extensive data analysis was conducted to document the spatial and temporal variation in O₃ at altitudes of 500 m to 3.5 km over the North Atlantic. Distributions of O₃ were simulated using the MM5/SMOKE/CMAQ air quality modeling system to help interpret our observational data. The models were extensively evaluated using the meteorological and chemical measurements from ground, ozonesonde and mobile platforms employed in the ICARTT campaign. The model simulations captured the general temporal and spatial variations in O₃ and meteorological variables, especially the New York urban plume as evidenced by simulated distribution of O₃ over the Gulf of Maine.

[52] Two most prominent features were observed in the balloon O₃ measurements. First, O₃ mixing ratios over the North Atlantic far exceeded the highest mixing ratios from inland sites in New England which were reported to be <100 ppbv. During the flight on 20–22 July, the balloon remained at altitudes of 400–600 m, with a peak value of 171 ppbv recorded on the night of 20–21 July. We speculate that a significant amount of the observed high O₃ levels at night over the near-coastal region was a result of factors including (1) in situ chemical production inside the urban plume during daytime, (2) conducive synoptic transport of O₃, in particular at night, (3) minimal dry depositional loss of O₃ at the balloon altitudes, and (4) little loss of O₃ by oxidation processes at night.

[53] Second, the observed O₃ levels exhibited large variation in North American outflow over the timescale ranging from minutes to days. Our model results suggest that the measured variation in O₃ levels within minutes to hours likely reflects the evolution of air masses in the plume. Large O₃ variability on the timescale of days over the remote North Atlantic was observed during flights 3 and 4 with levels frequently exceeding 100 ppbv. These two flights, one lasting from 3 to 7 August and the other crossing the Atlantic to near North Africa (3–15 August), encountered Hurricane Alex and survived with continuous high-quality measurements. Changes in specific humidity and O₃ mixing ratios showed that balloon 4 experienced distinctly different air mass types. Our model results suggest that the complex interplay of the hurricane, cyclones, and the migratory/subtropical high over the Atlantic led to air masses of diverse sources reaching the North Atlantic that contributed to the observed large O₃ variability.

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