WOE CHAPTER 4

Analysis of the Details of CMAQ 4.5 Chemistry

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Abstract

In order to accurately predict changes in ozone resulting from changes in emissions, CMAQ must accurately represent the chemistry of the lower atmosphere in both urban and rural locations and during both daytime and nighttime conditions. Several studies suggest that CMAQ underestimates the benefit from reduced emissions of NOx from elevated sources. Comparison of aircraft profiles to CMAQ-generated ozone profiles show that the model calculates too much ozone in the lowest few hundred meters and too little between 600 and 2500 m altitude. This analysis addresses the questions:

- Does CMAQ capture all the relevant reactions that sequester or remove NOx in urban plumes?
- Would consideration of the impact of aerosols on the rate of photolysis of NO_2 change the column content and shape of the ozone profile calculated by CMAQ?

The take away message from this study is that the CB4 mechanism and photochemical processor used in the version of CMAQ run for this SIP are simplified and missing reactions that were thought to be inconsequential, but are now known or in some instances suspected to play a major role. All higher aldehydes are treated as acetaldehyde (C_2), but other higher aldehydes (such as C_3 and C_4) are certainly formed and they react faster with NO_3 radicals to form HNO_3 at night representing an irreversible removal of NOx. CB4 also neglects the small fraction of alkanes that react directly with NO_3 radicals to form HNO_3 at night as well as a fraction of higher alkanes that rearrange to form alkyl nitrates in daytime reactions with OH and NO. Altogether these reactions probably sequester at least 1.5 ppb NOx, and unless there are compensating errors, CMAQ may be overestimating the mixing ratio of ozone formed in the Baltimore urban plume by about 6 ppb at the surface. Scattering of radiation by aerosols can accelerate ozone formation in the lower free troposphere and inhibit it closer to the Earth's surface. Model simulations of the impact of aerosols on jNO_2 indicates that CMAQ should calculate 1-18 ppb less ozone in the lowest few hundred meters and 1-3 ppb more ozone above - this moves the model closer to aircraft observations, but not into agreement. Indirect evidence suggests that MM5/CMAQ is underestimating low level cloud cover, and this could contribute substantially to the disagreement between measurement and model.

Maryland’s attainment demonstration model runs may well overestimate the rate of formation and concentration of ozone especially in VOC-rich urban plumes. The overall chemistry may be more NOx-limited than CMAQ would suggest. In comparison to aircraft observations, the base-case model run underestimates the rate of photochemical smog production above about 500 m and overestimates it below this altitude. Comparison of the details of the chemical processes simulated in CMAQ to observations shows that the model may still underestimate the importance of photochemistry in large-scale, multi-day processes involving transport and processing at higher altitudes, thus the simulations may underestimate the benefit of decreasing NOx emissions especially from elevated emissions sources such as power plants.

4.1 Introduction

UMD has investigated the chemical module of CMAQ to see if it accurately represents observed chemistry of smog events in the Northeast, with an emphasis on reasons that the model might overestimate ozone production and under-represented the benefit of reduced NOx emissions from elevated non-urban sources such as power plants. These studies also help quantify the uncertainty in CMAQ calculations of ozone. Observed concentrations of ozone in the eastern United States have fallen substantially in the past few years during a time when the major change in emissions was the SIP-Call for diminished NOx emissions from power plants e.g., (Gégo et al. 2007). This section deals with the CB4 chemical mechanism of CMAQ and where it might miss details of NOx and volatile organic compound (VOC) photochemistry that enhance the efficacy of emissions reductions.

4.2 NO_3-VOC Reactions

Recent measurements of ozone formation during the 2003 electrical blackout and investigations of nighttime boundary layer chemistry suggest that some of the NOx from urban areas may be lost or sequestered. This reduces the rate of ozone formation in areas of high concentrations of VOC’s and implies lesser ozone formation potential for urban plumes (Brown et al. 2006a; Brown et al. 2006b; EPA 2006; Marufu et al. 2004).

NO_2 can react with ozone to for highly reactive nitrate radicals, NO_3. During daylight hours the nitrate radical NO_3 is easily returned to NOx by photolysis or reaction with NO, but at night NO_3 concentrations can build up and these radicals attack some VOC’s, shown schematically in Figure 4.1. Organo-nitrates sequester NOx for several days, and HNO_3 is basically inactive in smog photochemistry. If NO_3 reacts with VOC’s to form HNO_3 quickly at night, it could make NOx in urban plumes relatively less important for O_3 formation than NOx in power plants plumes where VOC concentrations are lower.

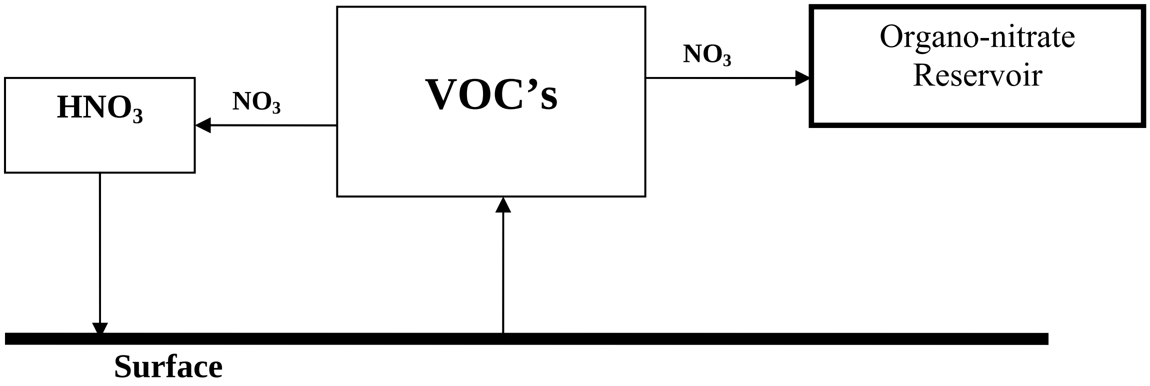

Figure 4.1 Schematic diagram of nighttime VOC/NO$_3$ chemistry in the urban boundary layer. VOC's can react with NO3 radicals to form organo nitrates such as alkyl nitrates that sequester NOx or to form nitric acid which is lost permanently form the system.

CMAQ, as configured for the SIP, employs an abridged set of NO_3 reactions. Different treatments of VOC reactions are known to lead to substantial differences in calculated ozone (Kuhn et al. 1998). This version of CMAQ uses CB-4 which explicitly includes formaldehyde, cresols (CRES) and reaction products of isoprene (ISPD).

$$H_2CO + NO_3 \rightarrow HNO_3 + HCO\cdot$$

$$CRES + NO_3 \rightarrow HNO_3 + CRO$$

$$ISPD + NO_3 \rightarrow HNO_3 + PROD \text{ (7.5\% yield)}$$

CB4 also contains a variable called XO2N which is an alkene adduct species.

$$OLE + NO_3 \rightarrow ... \rightarrow RO_2 + 0.09*XO2N + \text{products}$$

Although this reaction does not make HNO_3 it sequesters NOx; CB4 uses a rate constant of $7.7x10^{-15}$ cm^3 s^{-1} appropriate for propene, but butenes react about 50 times faster. The Regional Acid Deposition Model (RADM2), no longer an option for CMAQ, has more NO_3 + ORG reactions including GLY, (glyoxal) MGLY (methyl glyoxal; $H_3CC(O)C(O)H$), DCB (unsaturated dicarbonyl), CSL (cresol), and MACR (methacrolein).

In CB4, higher aldehydes are grouped as ALD2 and assumed composed entirely of acetaldehyde for reaction with the nitrate radical; this proceeds with a rate constant of $2.5x10^{-15}$ cm^3 s^{-1}.

$$ALD2 + NO_3 \rightarrow HNO_3 + C_2O_3$$

The rate constants for reactions of higher aldehydes with NO_3 radicals are faster; $6x10^{-15}$ cm^3 s^{-1} for propanal and $11.0x10^{-15}$ for butanal, so the lifetime of these carbonyls in the polluted nighttime environment is hours (Bossmeyer et al. 2006); see also http://www.iupac-kinetic.ch.cam.ac.uk/.

CMAQ estimated the concentration of ALD2 as about 3 ppb at Essex during high ozone days of 2002. Because the rate constant used is appropriate for acetaldehyde, the rate of reaction of higher aldehydes with NO_3 radicals is underestimated. Table 4.1 shows that carbonyl concentrations can be substantial even at remote sites in the Northeast, but measurements of aldehydes longer than formaldehyde are rare, and there are no well-accepted detection and calibration techniques. The concentration of higher aldehydes can be estimated from the concentration of alkenes. For reactions with OH, simple alkenes (methy-substituted ethenes, and 1-alkenes) form the aldehydes (two per alkene) with high yield, essentially 100% for butenes and decreasing for the larger 1-alkenes to about 50-30% for the 1-hexene through 1-octene. The O_3 reactions form roughly 50% carbonyls per alkene reacted. The aldehydes are less reactive than the larger alkenes and have longer lifetimes in the atmosphere. Table 4.2 gives the mean concentrations of higher alkenes (up to C_5) measured at Essex, MD during high ozone days in 2002. The total of measured C_3 to C_5 alkenes is about 1 ppb with little diurnal variation, and the lifetimes can be short (e.g., a few hours for trans-2-butene in the presence of 20 ppb ozone) indicating that these unsaturated hydrocarbons are roughly in steady state.

For a concentration of $5\text{x}10^9$ cm^{-3} (200 ppt) NO_3, the lifetime of propanal is 9 hr and the lifetime of butanal is 5 hr. The steady state total of higher aldehydes (greater than or equal to C_2) is thus at least 1 ppb. Over the course of a night, reactions of aldehydes C_3 and greater, not included in CB4, generate a mixing ratio of HNO_3 of at least 1 ppb.

A small fraction (about 2%) of alkanes reacts directly with NO_3 radicals at night, and this leads to alkyl radicals and HNO_3 production.

$$RH + NO_3 \rightarrow HNO_3 + R\cdot$$

Table 4.3 shows the nighttime mean alkane concentrations, relative rate constants, and the amount of HNO_3 formed The total for all alkanes is about 0.2 ppb NOx converted to HNO_3 by this process every night. Together these mechanisms account for in excess of 1.2 ppb conversion of NO_3 to HNO_3 each night and one can reasonably expect that CMAQ missed the irreversible loss of at least 1.2 ppb NOx.

Table 4.1 Carbonyl measurements[1]

	Minimum	Maximum	Mean	Median	σ	N
PSP[2]						
HCHO	45	6215	2038	2027	1079	1791
CH_2OHCHO	5	966	301	323	187	673
$CH_2OHCOCH_3$	30	1650	372	332	256	1740
WFM[3]						
HCHO	30	6170	1340	1260	821	3178

All units pptv (parts per trillion by volume).

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[2] Pinnacle State Park in Addison, NY, from June 26 to July 14, 1998

[3] Summit of Whiteface Mountain, from June 14 to July 20, 1999

Table 4.2 Mean alkene concentrations for high ozone days in 2002 at Essex, MD.

VOC	Mean ppbC	Cn*	Mean (ppb)
Propene	1.443	3	0.481
1-butene	0.374	4	0.093
trans-2-butene	0.451	4	0.113
cis-2-butene	0.314	4	0.078
1-pentene	0.413	5	0.083
trans-2-pentene	0.637	5	0.127
cis-2-pentene	0.336	5	0.067
Total			**1.043**

*Carbon number.
Notes: VOC concentrations as measured at Essex, MD on high ozone for days in 2002. Concentration units are ppb or parts per billion substance derived from ppbC. The total of 1.043 ppb represents the lower limit of mixing ratio of unsaturated VOC's that could form carbonyls in reactions not appropriately represented in the CB4 ozone formation mechanism.

Table 4.3 Alkane reactions to produce HNO_3 for high ozone days, 2002 Essex, MD.

VOC	Mean (ppb)	$(k_{OH}/k_{NO3})*10^3$	HNO_3 formed (ppb)
Propane	2.82	0.015	0.043
n-butane	1.44	0.027	0.038
Isobutane	0.87	0.033	0.028
n-pentane	1.70	0.020	0.034
n-hexane	0.48	0.019	0.009
Cyclohexane	0.11	0.018	0.002
2-me-pentane	0.62	0.018	0.011
3-me-hexane	0.23	0.020	0.005
2-me-hexane	0.18	0.020	0.004
n-heptane	0.21	0.019	0.004
n-octane	0.08	0.021	0.002
2-me-heptane	0.05	0.023	0.001
3-me-heptane	0.07	0.036	0.002
n-nonane	0.07	0.024	0.002
n-decane	0.08	0.023	0.002
n-undecane	0.07	0.002	0.000
Total			**0.187**

Notes: VOC concentrations measured between 0:00 to 05:00 EST as measured at Essex, MD on high ozone for days in 2002 and calculated formation of nitric acid. Concentration units are ppb or parts per billion substance not ppbC. The fraction reacting with the nitrate radical is computed with the ratio of rate constants for reaction with OH to that with NO_3, and assuming 1000 times more NO_3 than OH. The total of 0.0.187 ppb represents the mixing ratio of NOx that would be irreversibly removed from the possibility of ozone formation. The reactions considered here are not part of the CB4 mechanism.

4.3 Alkyl Nitrates

Most alkanes react with OH radicals in the daylight hours to form alkyl radicals that quickly form alkyl peroxy radicals:

$$RH + OH\ (+O_2) \rightarrow H_2O + RO_2\cdot$$

The reaction of alkyl peroxy radicals with NO usually leads to NO_2 and rapid ozone formation.

$$RO_2\cdot + NO \rightarrow RO\cdot + NO_2$$

Some fraction of the alkyl peroxy radicals however rearranges to form not NO_2, but alkyl nitrates.

$$RO_2\cdot + NO + M \rightarrow RONO_2 + M$$

The reactions producing alkyl nitrates are not included in the CB-4 mechanism of the CMAQ runs performed. For the alkyl nitrates that have been investigated, the lifetime with respect to photolysis or OH attack is several days or longer; alkyl nitrates thus sequester NOx to slow the rate of formation of ozone ((JPL 2006; Luke et al. 1989), R. Atkinson personal communication, 2007). In the mid Atlantic region, the residence time of an air mass is typically only a few days, so formation of alkyl nitrates may effectively delay the formation of ozone until air parcels have been advected over the Atlantic Ocean.

Alkane concentrations measured at Essex, MD on high ozone days in 2002 are listed on Table 4.4; this list is not exhaustive. The mixing ratio of alkyl nitrate formed in OH attack is the product of the mean alkane mixing ratio, the fraction reacting, and the yield. The fraction reacting is computed with the rate constant for reaction with OH times the assumed mean OH concentration of 5×10^6 cm^{-3} for an eight hour period. The yield is the rate of formation of all alkyl nitrates divided by the total product yield (Arey et al. 2001) R. Atkinson personal communication 2007]. The total of 0.24 ppb represents the mixing ratio of NOx that would be sequestered against ozone formation for a period of several days. This is a few percent of the total NOx of 5-10 ppb; the reactions considered here are not part of the CB4 mechanism although are included in other mechanisms.

Table 4.4 Alkyl nitrate formation for high ozone days at Essex, MD.

VOC	Mean (ppbC)	Fraction Reacting	Yield	C_n*	Alkyl Nitrate formed (ppb)
propane	3.567	0.17	0.036	3	0.007
n-butane	2.918	0.36	0.077	4	0.020
isobutane	1.543	0.36	0.077	4	0.011
n-pentane	2.501	0.6	0.105	5	0.032
n-hexane	1.210	0.8	0.141	6	0.023
cyclohexane	0.261	0.8	0.17	6	0.006
2-me-pentane	1.644	1	0.14	6	0.038
3-me hexane	0.873	1	0.178	7	0.022
2-me-hexane	0.627	1	0.178	7	0.016
n-heptane	0.809	1	0.178	7	0.021
n-octane	0.318	1	0.226	8	0.009
2-me-heptane	0.211	1	0.226	8	0.006
3-me-heptane	0.226	1	0.226	8	0.006
n-nonane	0.322	1	0.25	9	0.009
n-decane	0.412	1	0.25	10	0.010
n-undecane	0.364	1	0.25	11	0.008
Total					**0.244**

* Carbon Number

Notes: VOC concentrations are means for 8:00 to 16:00 EST as measured at Essex, MD on high ozone days in 2002. Concentration units are ppbC or parts per billion of the substance divided by the number of carbon atoms in the molecule, Cn. The fraction reacting is computed with the rate constant for reaction with OH times the assumed mean OH concentration of 5×10^5 cm^{-3} for an eight hour period. The yield is the rate of formation of all alkyl nitrates divided by the total product yield (Arey et al. 2001; R. Atkinson personal communication 2007). The total alkyl nitrate formed is the product of the mean alkane mixing ratio (ppbC/Cn), the fraction reacting, and the yield. The total of 0.244 ppb represents the mixing ratio of NOx that would be removed sequestered against ozone formation for a period of several days. This is a few percent of the total NOx of 5-10 ppb, and the reactions considered here are not part of the CB4 mechanism. If each ppb NOx produces 4 ppb ozone, then formation of alkyl nitrates accounts for about 1 ppb O_3.

4.5 NOx/VOC Chemistry Conclusions

High concentrations of VOC's can sequester or remove NOx from the atmosphere, and many of these processes are missing from the CB4 mechanism employed in CMAQ as used for these studies; CB5 attempts to correct some of these shortcomings (Luecken; Sarwar 2006). NOx removal due to reactions with higher aldehydes can be expected to exceed 1 ppb; about 2% of alkanes are removed by direct attack by NO_3 radicals for about 0.2 ppb NOx loss; OH attack on alkanes will produce about 0.24 ppb alkyl nitrates. The total is thus about 1.5 ppb NOx – a fair fraction of the mean 5-15 ppb NOx present. CMAQ showed a high bias for NOx of 1.3 ppb (G. Sistla, personal communication 2006). CB4 may however have compensating errors; early versions of CB5 calculate a few ppb more ozone (Luecken; Sarwar 2006). For the typical ozone production efficiency of 4 ppb O_3 per ppb NOx this represents about 6 ppb of ozone loss unaccounted for in CMAQ. The 6 ppb estimated is a lower limit for model uncertainty. The loss of NOx in urban plumes may also explain the apparent greater efficiency of ozone production in plumes from elevated NO sources and help to explain why ozone in the mid-Atlantic has decreased substantially in response to power plant NOx emissions reductions.

4.6 Photolysis Rates

We have identified the impact of aerosols on photolysis rates as process occurring in the atmosphere and not represented in the SIP runs of CMAQ. CMAQ generates ozone mixing ratios similar to or slightly greater than observations near the earth's surface, but underestimates ozone aloft. The impact of highly scattering aerosols on the rate of NO_2 photolysis is to inhibit ozone formation near the Earth's surface and to accelerate ozone formation aloft with an overall impact of more ozone (Dickerson et al. 1997). Hains (2007) used an improved profile of photolysis rates to bring CMAQ output into closer agreement with aircraft observations.

4.6a Recalculated NO_2 photolysis rate coefficients

Figure 4 of Chapter 2 shows the median aircraft measured and CMAQ ozone profiles for 2002. The aircraft ozone is on average 10% (6 ppb) larger than in the CMAQ profiles between 600 and 2600 m while about 6 ppb smaller than CMAQ below 500 m in the PBL. CMAQ under-predicts ozone in the lower free troposphere and over-predicts ozone near the surface, with the model integrated ozone column content is 4% smaller than observed.

Reasons for measurement/model differences may include problems with emissions inventories, advection, vertical mixing, cloud cover, or chemistry. The NO_2 photolysis rates that CMAQ uses impact how much ozone is produced by the model. The rate coefficient for the photolysis of NO_2 (hereafter referred to as jNO_2 value) used by the default version of CMAQ assumes no aerosol loading. Earlier UMD work (Dickerson et al. 1997; Park 2001; Park et al. 2001) show that an increase of aerosols from an optical depth of 0 to 2 increases the jNO_2 values by 30% above the boundary layer and increases the total mass of ozone formed. Park et al. [2001] performed a sensitivity test of CMAQ using jNO_2 values associated with CMAQ aerosols. UMD (Hains 2007) performed a sensitivity study using jNO_2 values associated with typical aerosols measured in the Mid-Atlantic from July 15-18, 2002 using the (Park 2001) program. The optical properties of the aerosols must be specified in the model. These include the Angstrom exponent (also called Angstrom slope) and intercept related to the size of the particles (slope of 2.0, intercept of 0.1 were used); the single scattering albedo that gives the probability that a photon will be scattered rather than absorbed (0.96); and the asymmetry parameter that indicated the fraction scattered in the forward direction (0.8). Based on aircraft measurements, aerosols were assumed to be confined to the lowest 1.5 km of the atmosphere. The observed mean aerosol optical depth was 0.3 at 550 nm, which corresponds to 0.6 at 380 nm, the wavelength most relevant for NO_2 photolysis. Results (Figure 4.2) show diminution in jNO_2 near the Earth's surface but substantial increase aloft and at all times of the day.

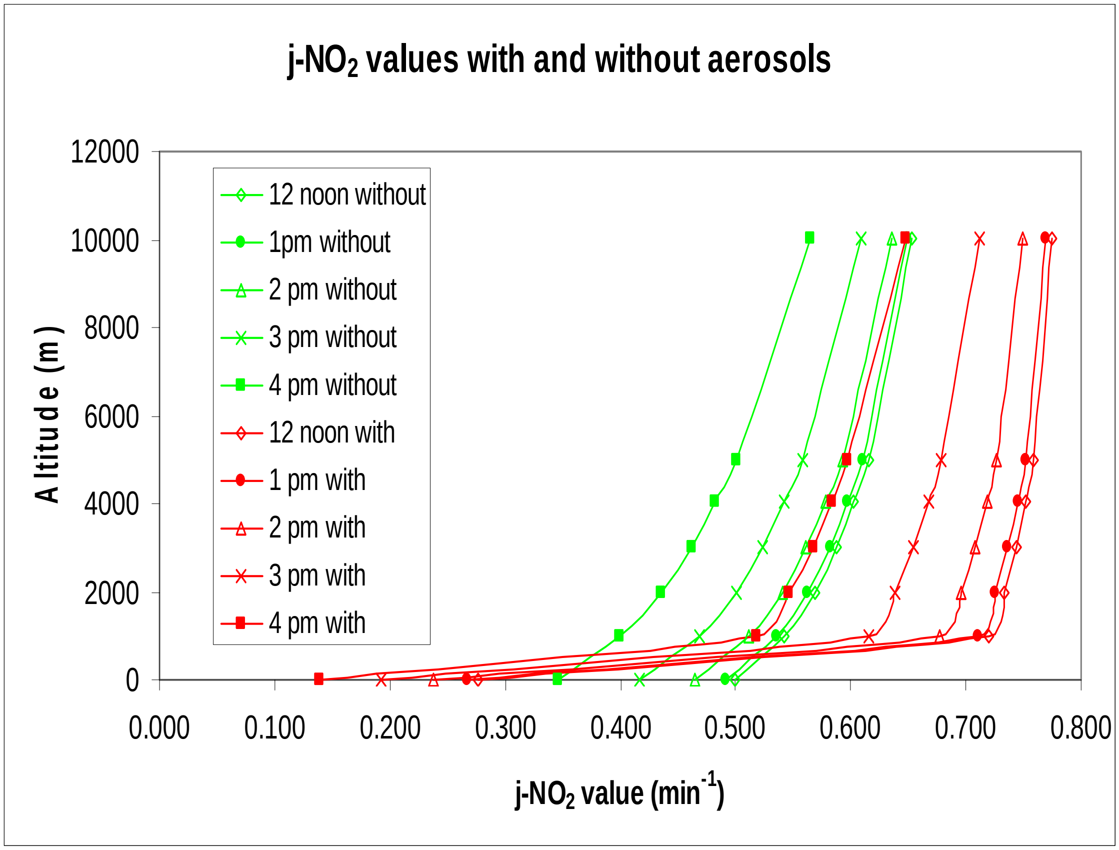

Figure 4.2 Standard (without aerosols, green) and revised (with aerosols, red) jNO_2 values used in CMAQ for several daylight hours. Aerosols reduce photolysis rate coefficients in the first few hundred meters of the PBL, but increase them aloft. Altitude is in m-AGL.

4.6b CMAQ runs with revised photolysis rates

UMD ran CMAQ from July 15-18, 2002 with the standard jNO_2 values (assuming no aerosol) and revised jNO_2 values, using aerosol concentrations and properties typical for the episode. The same aerosol values were used throughout the domain. The aircraft flies over rural and suburban areas, but also downwind of urban areas with large optical depths, so using the average optical depth from all of the flights should be a reasonable approximation of the Mid-Atlantic average optical depth.

Two emissions scenarios were used; one with 2002 emissions and one with substantially lower emissions for 2018. This resulted in four model runs for comparison:

- 2002 emissions with standard jNO_2 values (2002, j-values no aerosols)
- 2002 emissions with revised jNO_2 values (2002, j-values with aerosols)
- 2018 emissions with standard jNO_2 values (2018, j-values no aerosols)
- 2018 emissions with revised jNO_2 values (2018, j-values with aerosols).

Figures 4.3 – 4.7 show ozone generated by CMAQ using the standard jNO_2 values, ozone generated using the modified jNO_2 values, and ozone measured from the aircraft; note Universal Time (UT) is 5 hr ahead of Eastern Standard Time (EST) which is close to local solar time (LST). When the jNO_2 values were changed, ozone at altitudes above ~1000 m increased by about 1-2 ppb, and below this altitude decreased by a few ppb on average, but by as much as 15 ppb near the Earth's surface. Using improved photolysis rates did not eliminate measurement/model differences, but brought the CMAQ output closer to observations. Aircraft observations for the 2002 season are compared to CMAQ output for the same time and in the grid box. The spatial resolution of the observations is greater than that of the CMAQ (12 km) and sometimes the aircraft flew out of one model box into another and this can result in a discontinuity of 5-10 ppb ozone.

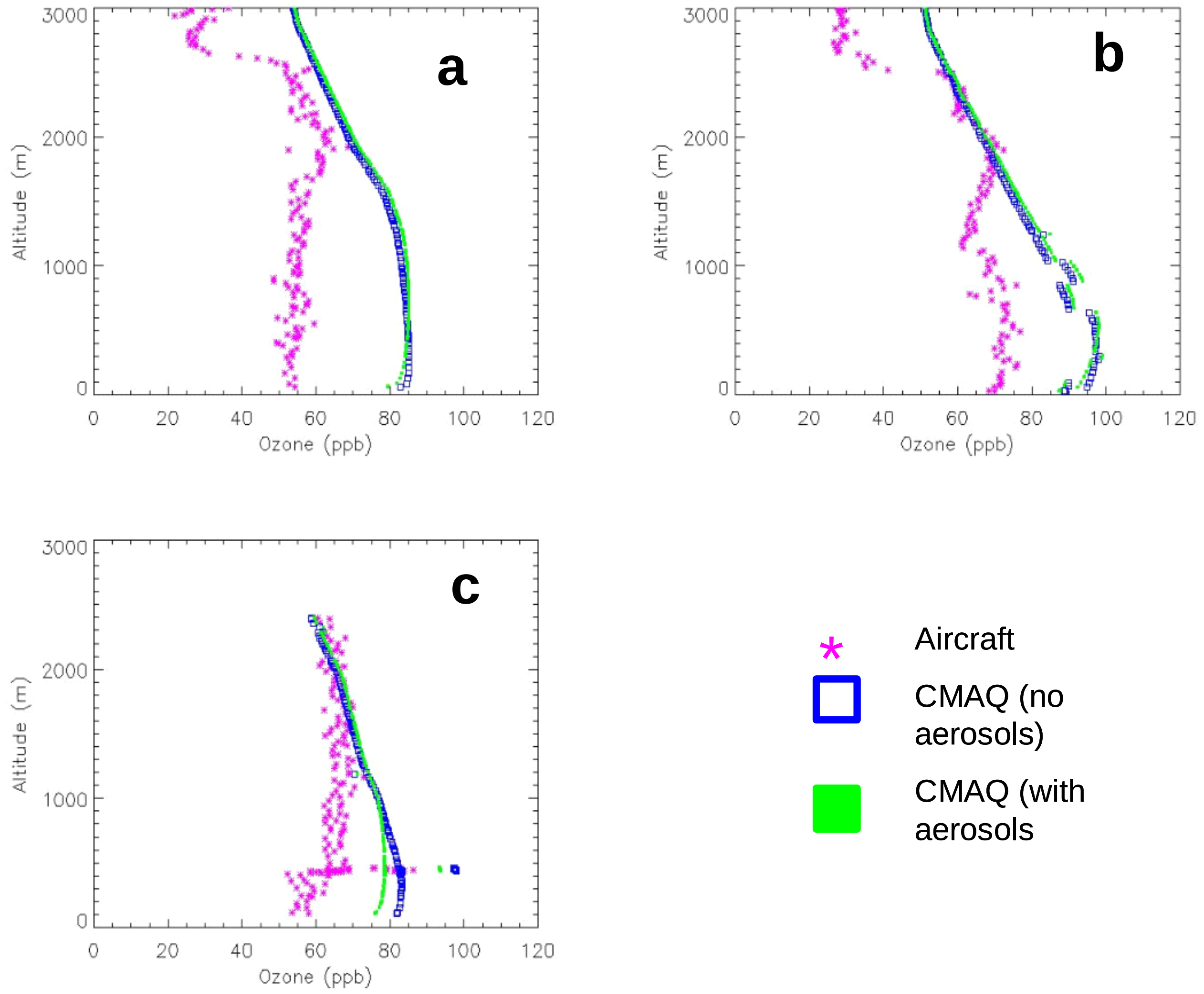

Figure 4.3 Ozone profiles from the aircraft (pink stars), CMAQ using standard jNO_2 values (without aerosols, shown in blue open squares), and CMAQ using revised jNO_2 values (with aerosols, shown in green closed squares) for July 15, 2002 at a) Fort Meade, MD 1400 EST, b) Easton, MD 1600 EST, c) Churchville, MD 1500 EST. Above 1000 m the revised CMAQ profiles (with revised jNO_2 values, shown in green) are about 1 ppb larger than the standard CMAQ profiles shown in blue. Below 1000 m the standard CMAQ profiles are up to 5 ppb larger than the revised CMAQ profiles. Note the discontinuity in observed ozone at 500 m altitude over Churchville, MD – the model also shows a strong gradient there.

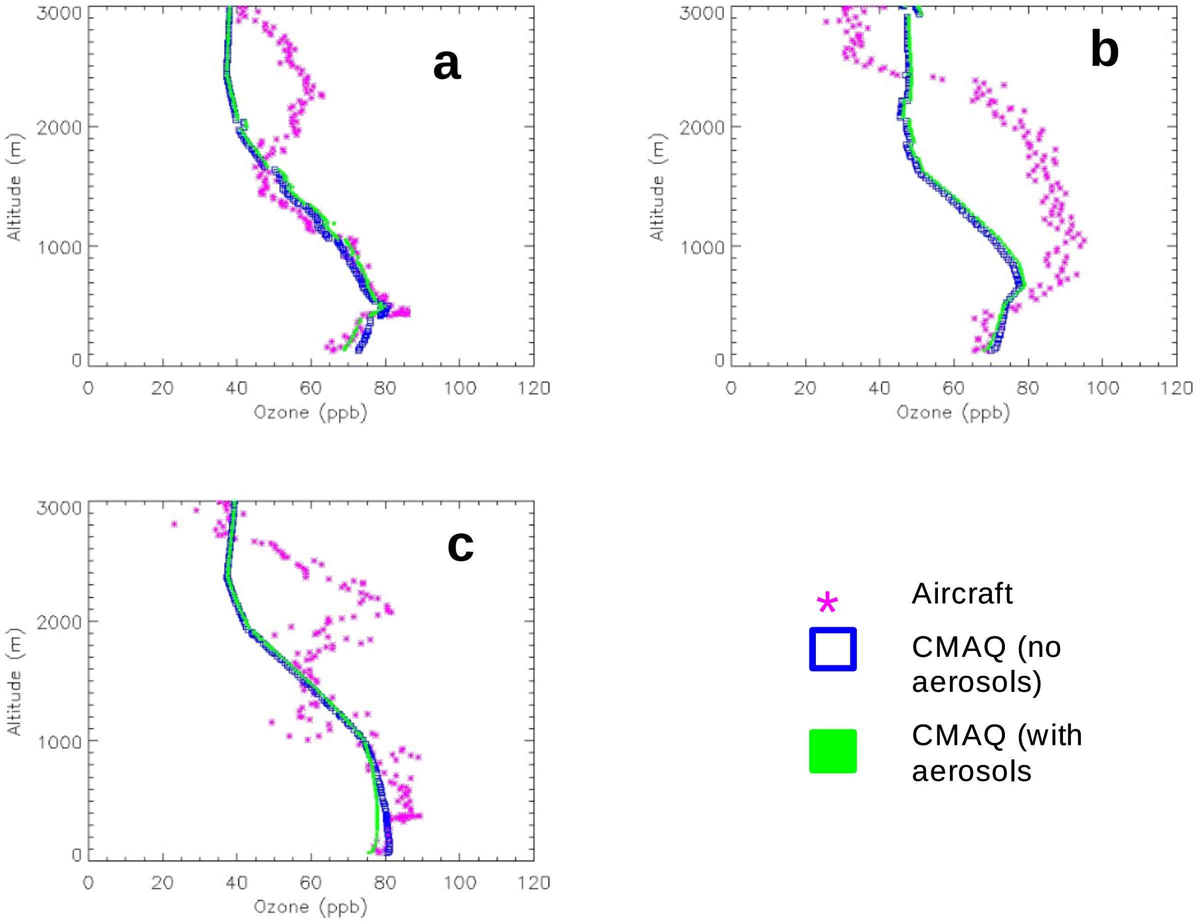

Figure 4.4 Ozone profiles from the aircraft (pink stars), CMAQ using standard jNO_2 values (without aerosols, and shown in blue open squares), and CMAQ using revised jNO_2 values (with aerosols, shown in green closed squares) for the morning of July 16, 2002 at a) Louisa, VA 0900 EST, b) Crewe, VA 1000 EST, and c) Richmond, VA 1000 EST. Above 1000 m the revised CMAQ profiles (with revised jNO_2 values, shown in green) are about 1 ppb larger than the standard CMAQ profiles shown in blue. Below 1000 m the standard CMAQ profiles are 1-10 ppb larger than the revised CMAQ profiles.

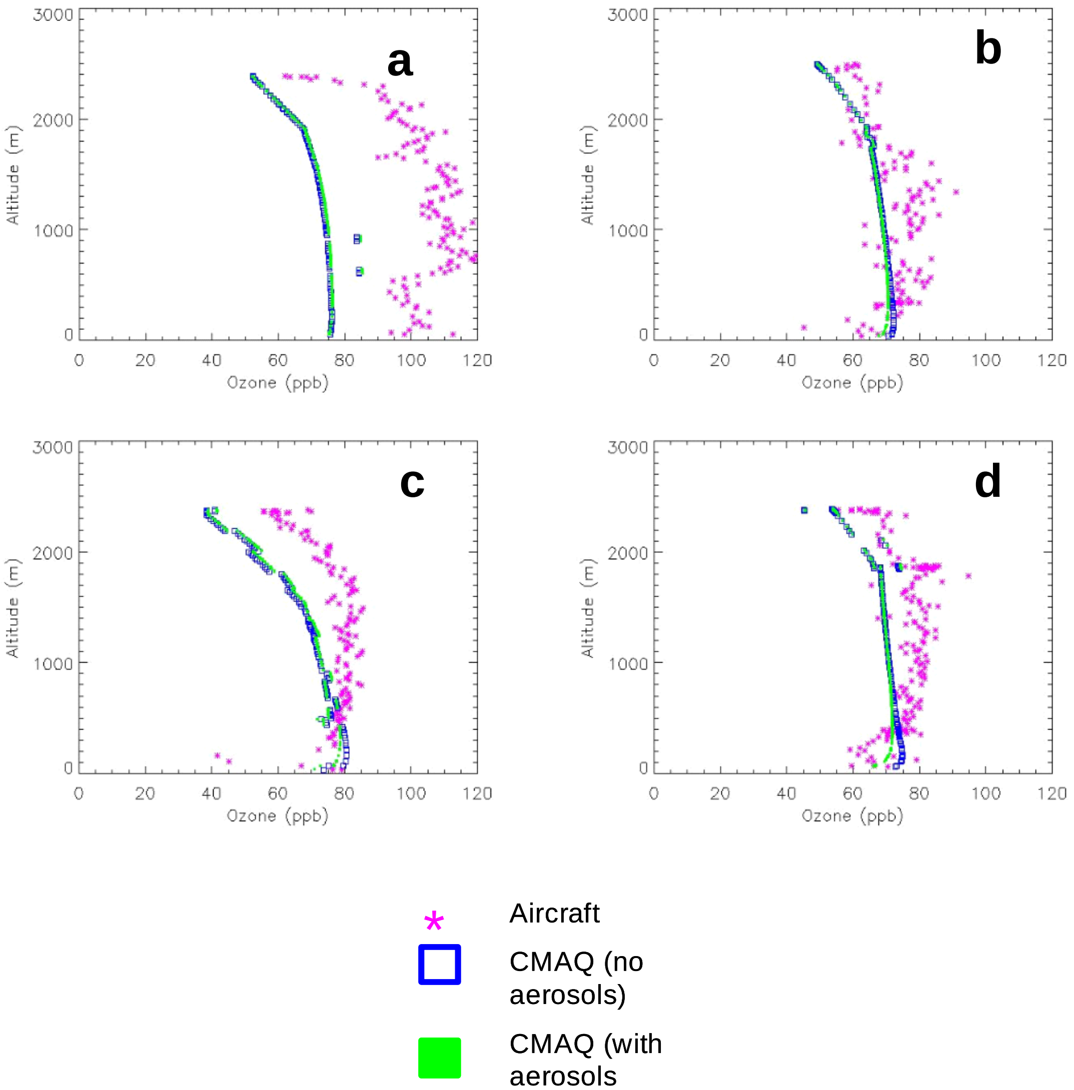

Figure 4.5 Ozone profiles from the aircraft (pink stars), CMAQ using standard jNO_2 values (without aerosols, and shown in blue open squares), and CMAQ using revised jNO_2 values (with aerosols, shown in green closed squares) for the afternoon of July 16, 2002 at a) Wakefield, VA 1300 EST, b) Quinton, VA 1400 EST, c) Tappahannock, VA 1500 EST, d) Richmond, VA 20 UT. Above 1000 m the revised CMAQ profiles (with revised jNO_2 values, shown in green) are about 1 ppb larger than the standard CMAQ profiles shown in blue. Below 1000 m the standard CMAQ profiles are about 1 ppb larger than the revised CMAQ profiles.

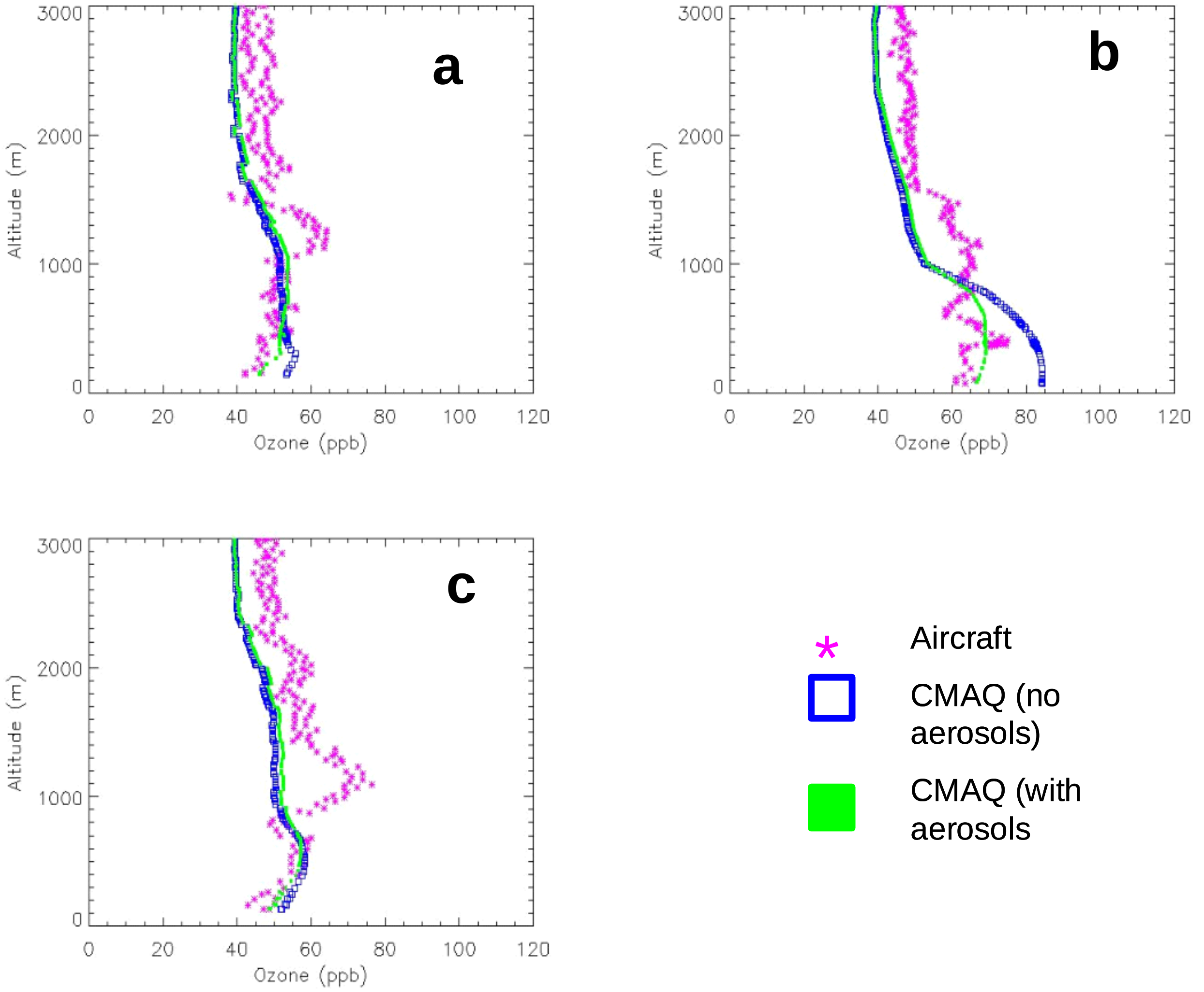

Figure 4.6 Ozone profiles from the aircraft (pink stars), CMAQ using standard jNO_2 values (without aerosols, and shown in blue open squares), and CMAQ using revised jNO_2 values (with aerosols, shown in green closed squares) for July 17, 2002 at a) Louisa, VA 0800 EST, b) Richmond, VA 1000 EST, and c) Crewe, VA 0900 EST. Above 1000 m the revised CMAQ profiles (with revised jNO_2 values, shown in green) are about 1 ppb larger than the standard CMAQ profiles shown in blue. Below 1000 m the standard CMAQ profiles are as much as 18 ppb larger than the revised CMAQ profiles.

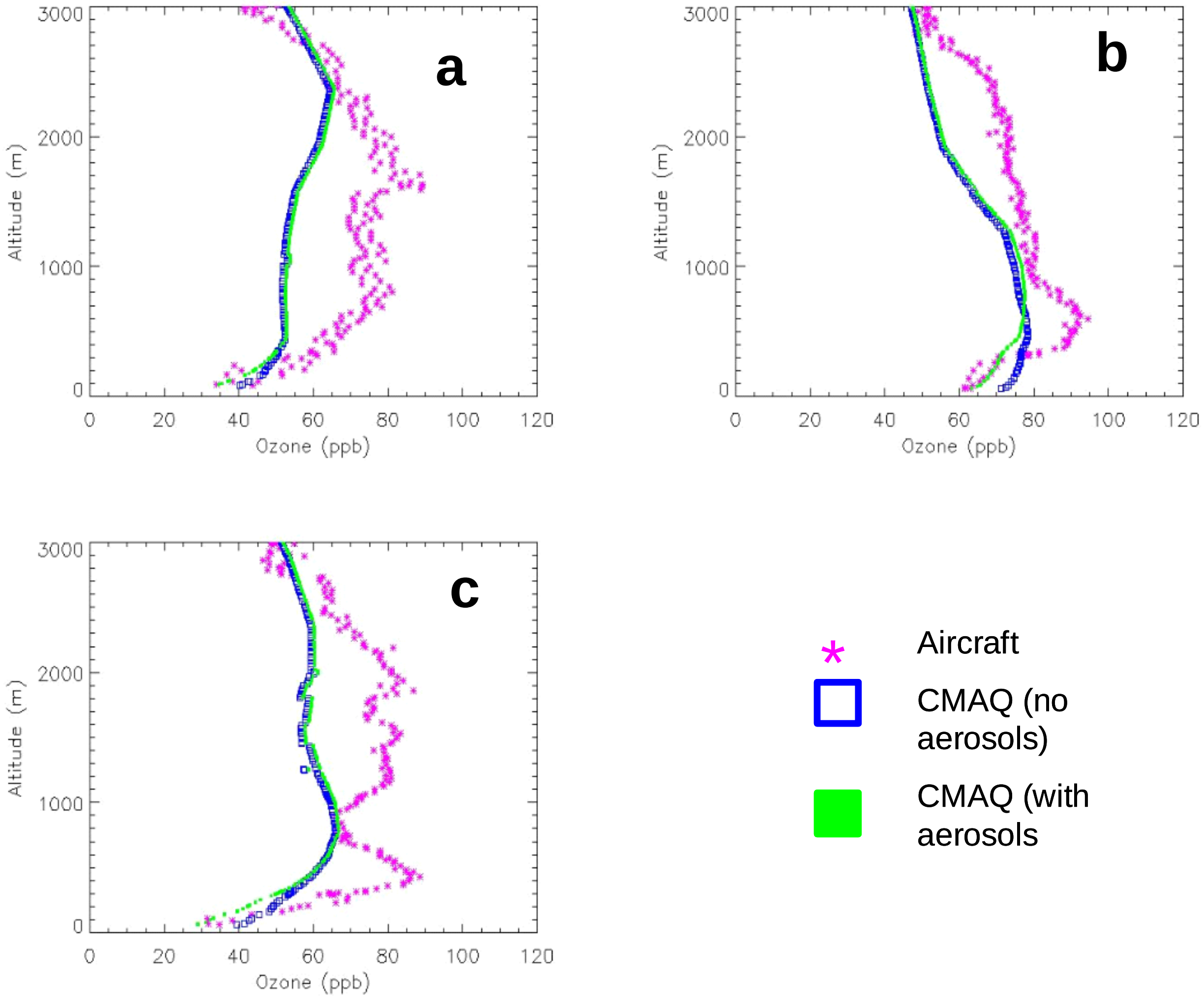

Figure 4.7 Ozone profiles from the aircraft (pink stars), CMAQ using standard jNO_2 values (without aerosols, and shown in blue open squares), and CMAQ using revised jNO_2 values (with aerosols, shown in green closed squares) for July 18 2002 at a) Richmond, VA 0700 EST, b) Fort Meade, MD 0900 EST, and c) Ashland, VA 0800 EST. Above 1000 m the revised CMAQ profiles (with revised jNO_2 values, shown in green) are about 1 ppb larger than the standard CMAQ profiles shown in blue. Below 1000 m the standard CMAQ profiles are larger than the revised CMAQ profiles.

Differences in CMAQ runs with and without revised photolysis rate coefficients are seen in Figure 4.8 for model levels 1, 8, and 16 (approximately at the surface, 500, and 2000 m altitude) at 0900 EST (14 UT) when the largest differences occurred. Values from the revised run are subtracted from the standard run such that negative numbers mean the standard CMAQ overestimated ozone (generally at low altitudes) and positive numbers mean that the standard CMAQ underestimated ozone (generally in the free troposphere). There are positive changes of 10 ppb or more near the surface and small negative changes (mean of 1 ppb) above 500 m.

A curtain plot (Figures 4.9 and 4.10) was used to examine the diurnal variation in the first 2000 m of CMAQ showing the differences in ozone generated from:

2002, j-no aerosols − 2002, j-with aerosols

Positive numbers (green, yellow, orange, red) indicate that standard CMAQ overestimates ozone; negative numbers (gray, blue, dark blue, indigo) indicate that CMAQ underestimates ozone. The x-axis represents a one grid cell swath at 77º W longitude running north-south through the Washington/Baltimore urban area and extending from 31º to 47º N over the eastern United States. The y-axis represents the first 16 layers of CMAQ reaching from the surface to about 2000 m altitude. Six time periods of 2100, 0200, 0600, 1000, 1400, 1800 EST (3, 7, 11, 15, 19 and 23 UT) are shown for July 17, 2002. In the early morning, there are negative changes (where the standard version of CMAQ underestimates ozone) above 500 m that are mixed down to the surface. At 10:00 to 17:00 EST (15 and 23 UT) there is a positive change (where the standard version of CMAQ overestimates ozone) near the surface.

The altitude dependence of the changes in ozone due to changes in photolysis rates is summarized in Figure 4.11. The median change is a little more than 2 ppb near the surface and about 1 ppb aloft with the standard version of the model overestimating ozone at lower altitudes and underestimating at higher altitudes.

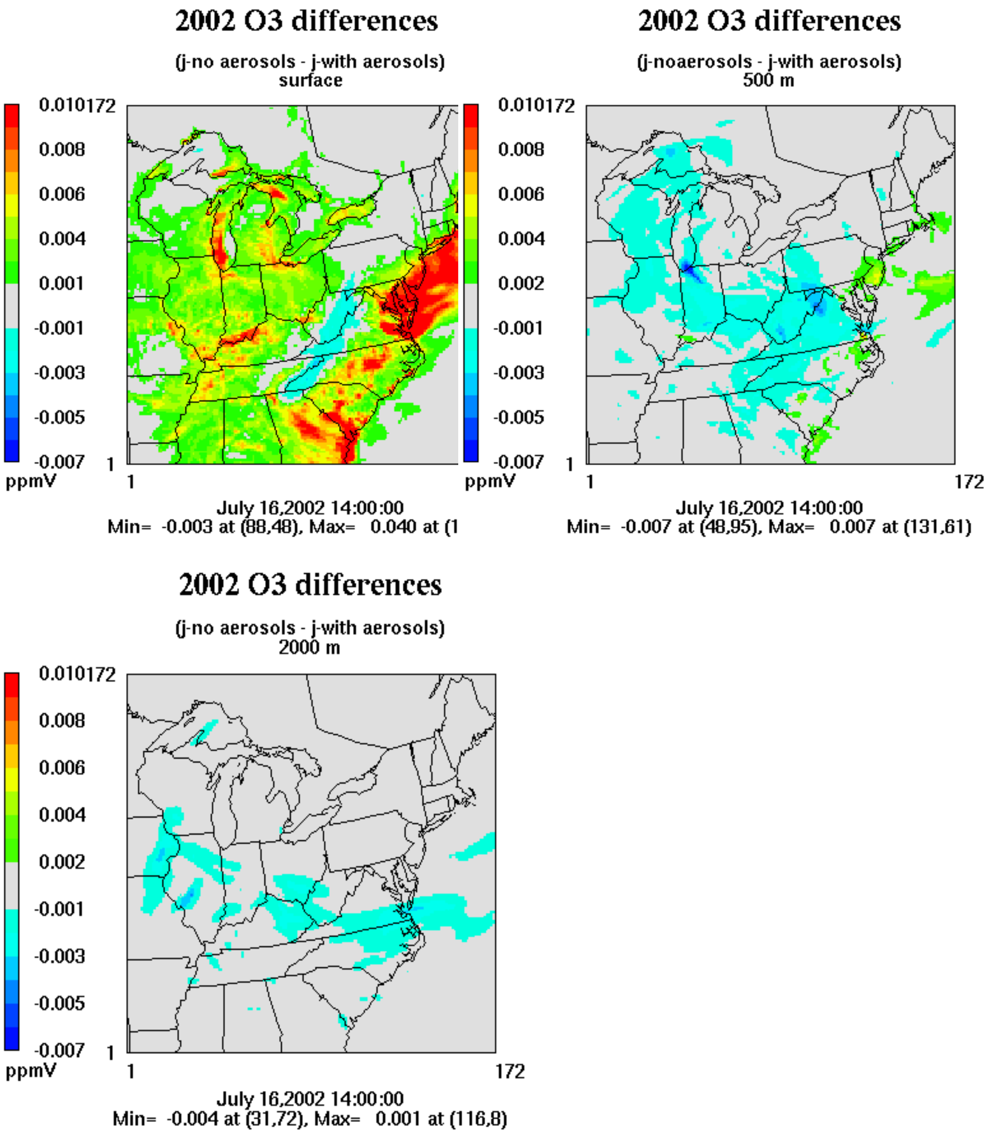

Figure 4.8 Differences between standard and revised CMAQ ozone (standard – revised). The standard CMAQ used jNO_2 values that did not account for aerosols, while the revised CMAQ used jNO_2 values that did account for aerosols measured for a July 2002 smog and haze episode. These plots are for 0900 EST. The differences are positive at the surface meaning that the standard CMAQ overestimated ozone there. Above 500 m the differences are negative and the revised CMAQ run produces more ozone than the standard CMAQ, generally in better agreement with observations.

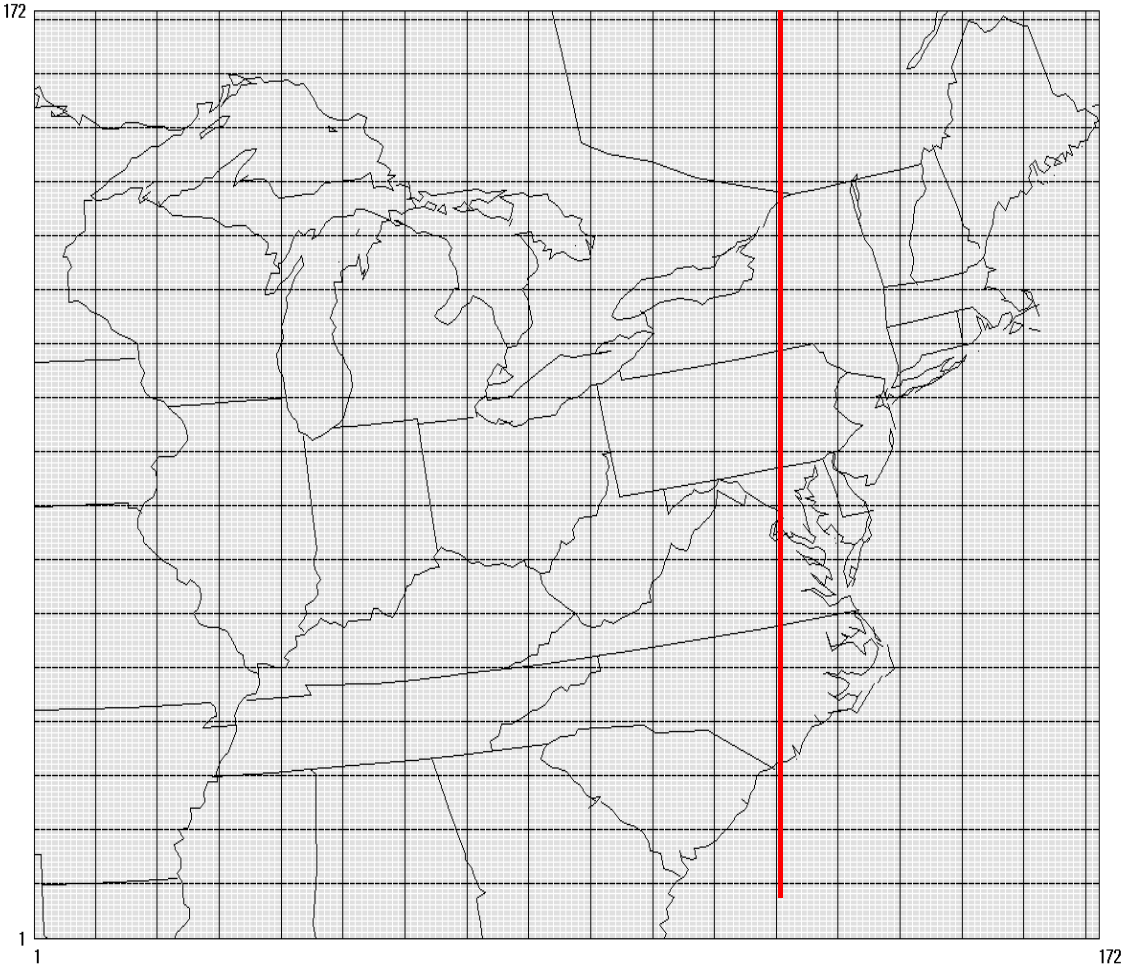

Figure 4.9. Map of eastern United States with swath used for curtain plot (Figure 4.10) shown as a thick, red through the Washington/Baltimore area at 77° W longitude.

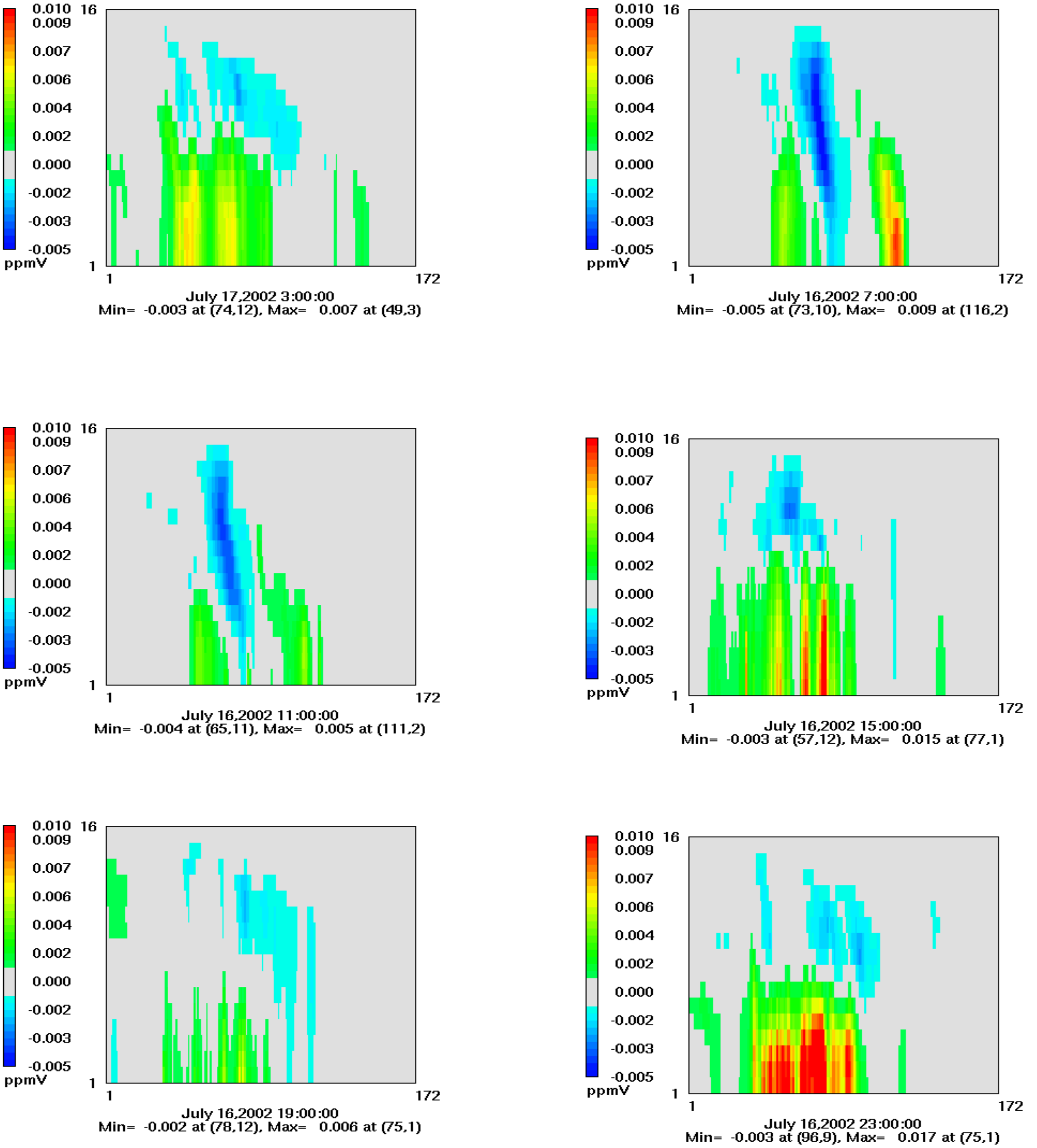

Figure 4.10. Ozone differences (standard – revised) for a single swath in the CMAQ grid. The y-axis represents the 16 altitude layers used in CMAQ. The 16th altitude layer is around 2000 m and the 8th altitude layer is around 500 m. The x-axis represents the grid cells examined, where 1 is the southernmost grid cell and 172 is the northernmost grid cell. Here positive differences mean that the standard CMAQ run generates more ozone than the revised CMAQ run and these are seen closer to the surface.

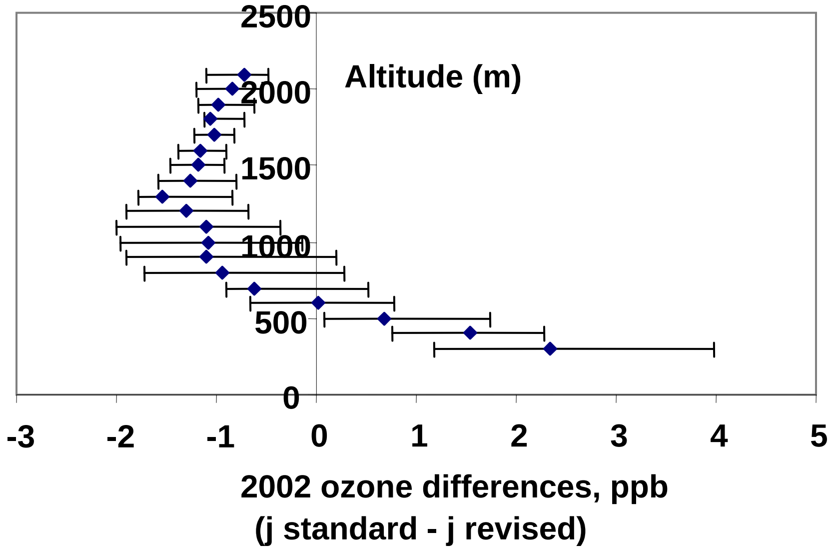

Figure 4.11 Differences in ozone mixing ratios generated with CMAQ with standard photolysis rates minus – that calculated with revised photolysis rates) for 16 profiles generated between July 15-18, 2002. Diamonds represent medians; error bars represent the 25th and 75th percentiles. Near the surface the standard CMAQ run generates more ozone than the revised CMAQ run and above 500 m the standard CMAQ run generates less ozone than the revised CMAQ run.

4.6c Photolysis rate conclusions

Compared to aircraft measurements of ozone, CMAQ under-predicts ozone by 10% between 600 and 2600 m-AGL and over-predicts by ~15% at lower altitudes, with the CMAQ ozone column content 4% smaller than the aircraft ozone column content. UMD improved the simulation of photochemistry in CMAQ to account changes in the UV flux due to aerosol scattering. The photolysis rate coefficient for NO_2 increased aloft and decreased near the Earth's surface. Ozone mixing ratios increased aloft (above 500 m) by 1-2 ppb and decreased below 500 m with a median change of ~2 ppb and a range of 1-16 ppb. Maximum differences were observed in late afternoon. The impact of including aerosol radiative effects was not sufficient to bring model output into agreement, but it did improve the situation and show that the standard CMAQ runs underestimate the role of ozone production aloft. This may contribute to the simulations' underestimating the benefit from reduced emissions of NOx from tall stacks.

4.7 Future work.

To more rigorously quantify the impact of simplifications in the CB4 mechanism UMD recommends comparing existing CMAQ runs to CMAQ runs with alternative chemical mechanisms that explicitly include reactions involving longer VOC's. It would also be illustrative to compare CB4 to model with detailed chemistry such as the Master Mechanism for a reduced domain such as Essex, MD where a variety of direct observations are available. Direct measurements of NOx, NOy, and nitric acid formation at night, as well as VOC's and, if possible, higher aldehydes are called for. Further comparisons to observations of surface and high altitude trace gases must be made. Night flights in the Baltimore or Washington urban plumes would help determine the role of NOx removal in the efficiency of ozone formation.

The impact of changes in photolysis rates was tested for only one episode, and a more thorough study is called for. The entire summer should be run with well characterized aerosol loading. This will entail compiling data from the aircraft, MODIS (Levy 2007) and GASP (Knapp et al. 2005), satellite instruments as well as AERONET sun photometer observations. CMAQ appears to underestimate substantially aerosol optical depth, so self-generated aerosols would not be appropriate (Levy 2007). Low level clouds, such as the fair weather cumulus common on hot summer days in the Mid-Atlantic region, have an effect on UV flux similar to that of aerosols. They may also affect mixing. CMAQ CO fields should be improved so that they can be used to evaluate mixing. Clouds accelerate NO_2 photolysis above and retard it below. CMAQ does account for radiative properties of clouds as generated by MM5. Several lines of reasoning, however, suggest that MM5 may underestimate the cloud cover. In prior investigations of simulated clouds (Mueller et al. 2006) a serious bias was discovered in MM5/CMAQ – the model consistently under-estimated spatially averaged clouds below 3.7 km altitude. Over the Mid-Atlantic region, CMAQ overestimates SO_2 concentrations (Hains 2007) and underestimates aerosol loading, dominated by sulfate (Levy 2007). Insufficient low-level cloud cover would explain both of these observations. Clouds in MM5 and CMAQ should be evaluated for the summer of 2002 against National Weather Service surface observations as well as satellite observations. The models should be modified to better match cloud observations and then evaluated for agreement with SO_2, sulfate, and aerosol optical depth measurements.

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