Atmospheric Environment 50 (2012) 255–266

Contents lists available at SciVerse ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Winter ozone formation and VOC incremental reactivities in the Upper Green River Basin of Wyoming

William P.L. Carter[a,b,1], John H. Seinfeld[c,d,*]

[a] Statewide Air Pollution Research Center, University of California, Riverside, CA 92521, United States
[b] CE-CERT, University of California, Riverside, CA 92521, United States
[c] Department of Chemical Engineering, California Institute of Technology, 1200 E. California Boulevard, Mail Code 210-41, Pasadena, CA 91125, United States
[d] Department of Environmental Science and Engineering, California Institute of Technology, 1200 E. California Boulevard, Mail Code 210-41, Pasadena, CA 91125, United States

ARTICLE INFO

Article history:
Received 23 September 2011
Received in revised form
9 December 2011
Accepted 9 December 2011

Keywords:
Winter ozone
Natural gas production
Incremental VOC reactivity
Upper Green River Basin
SAPRC-07 mechanism

ABSTRACT

The Upper Green River Basin (UGRB) in Wyoming experiences ozone episodes in the winter when the air is relatively stagnant and the ground is covered by snow. A modeling study was carried out to assess relative contributions of oxides of nitrogen (NO_x) and individual volatile organic compounds (VOCs), and nitrous acid (HONO) in winter ozone formation episodes in this region. The conditions of two ozone episodes, one in February 2008 and one in March 2011, were represented using a simplified box model with all pollutants present initially, but with the detailed SAPRC-07 chemical mechanism adapted for the temperature and radiation conditions arising from the high surface albedo of the snow that was present. Sensitivity calculations were conducted to assess effects of varying HONO inputs, ambient VOC speciation, and changing treatments of temperature and lighting conditions. The locations modeled were found to be quite different in VOC speciation and sensitivities to VOC and NO_x emissions, with one site modeled for the 2008 episode being highly NO_x-sensitive and insensitive to VOCs and HONO, and the other 2008 site and both 2011 sites being very sensitive to changes in VOC and HONO inputs. Incremental reactivity scales calculated for VOC-sensitive conditions in the UGRB predict far lower relative contributions of alkanes to ozone formation than in the traditional urban-based MIR scale and that the major contributors to ozone formation were the alkenes and the aromatics, despite their relatively small mass contributions. The reactivity scales are affected by the variable ambient VOC speciation and uncertainties in ambient HONO levels. These box model calculations are useful for indicating general sensitivities and reactivity characteristics of these winter UGRB episodes, but fully three-dimensional models will be required to assess ozone abatement strategies in the UGRB.

1. Introduction

The Upper Green River Basin (UGRB) in Wyoming (Fig. 1) is one of the fastest growing and largest areas of natural gas production in the United States. The area consists of three fields: the Jonah Field, the Big Piney–LaBarge complex, and the Pinedale Anticline. Total production in 2008 was approximately 843 million cubic feet of gas and 7 million barrels of condensate, making the UGRB the second largest natural gas-producing region in the U.S. Owing to the location of the fields within a basin surrounded by mountain ranges on the west, north, and east sides, the UGRB can experience periods of remarkably high ozone levels in the winter when the air is relatively stagnant and the ground is covered with snow. The occurrence of these wintertime ozone episodes, unusual relative to customary summertime ozone formation, is a result of emissions of volatile organic compounds (VOCs) and oxides of nitrogen (NO_x) from the gas production operations, combined with occasional low inversions, stagnant conditions, and enhanced ultraviolet intensity due to the high albedo of the snow-covered surface (Schnell et al., 2009). The conditions leading to wintertime ozone episodes, while first identified in the UGRB, are characteristic of those in similar gas production areas in the intermountain U.S. West, such as The Uintah Basin, Utah (Utah Department of Environmental Quality, 2011).

The fundamental ozone abatement problem is to determine the response of ozone to reduction of either VOC or NO_x and to design control strategies accordingly. In order to understand the effect of VOC and NO_x emission control strategies in the UGRB on ground-level ozone, it is necessary to determine whether ozone formation is NO_x-limited, and thus most responsive to NO_x controls, or whether

---

* Corresponding author. Department of Chemical Engineering, California Institute of Technology, 1200 E. California Boulevard, Mail Code 210-41, Pasadena, CA 91125, United States. Tel.: +1 626 395 4635; fax: +1 626 796 2591.

E-mail addresses: carter@cert.ucr.edu (W.P.L. Carter), seinfeld@caltech.edu (J.H. Seinfeld).

[1] Tel.: +1 951 788 8425; fax: +1 951 781 5790.

1352-2310/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.atmosenv.2011.12.025

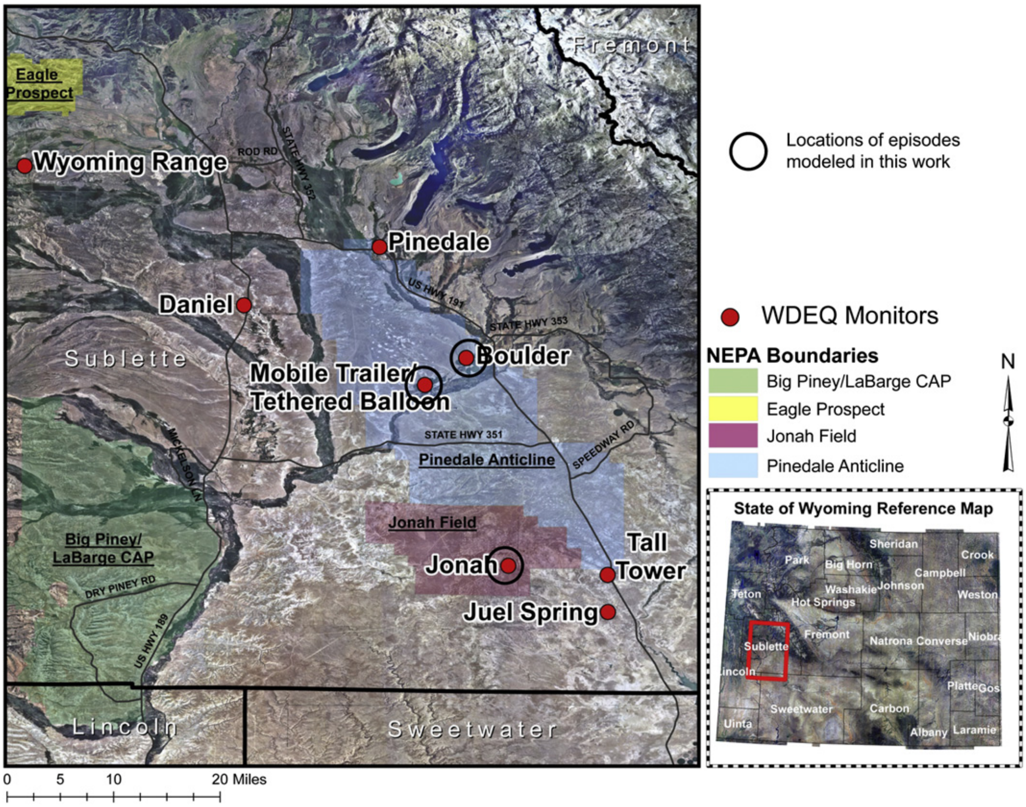

Fig. 1. Map of Upper Green River Valley in Wyoming, showing the locations of the episodes that are modeled in this work.

it is VOC-sensitive and therefore most responsive to reducing VOC emissions. If the latter, it is useful to know which VOCs are the most influential in ozone formation. The effect of a VOC on ozone formation can be measured by its *incremental ozone reactivity*, which is defined as the change in peak ozone concentration caused by adding a small amount of the VOC to the emissions, divided by the amount added (Carter, 1994). The response of peak ozone to changes of VOC and NO_x is unique for each city or region, depending on the mix of pollutants, including the individual species that make up the total VOC, the local meteorology, the surface albedo that affects light intensity, and the locations and magnitudes of the source emissions. Individual VOCs have markedly different contributions to ozone formation depending on how fast they react in the atmosphere and how reactive their products are in promoting the chain reactions that eventually lead to ozone formation.

This work presents a detailed analysis of several winter ozone episodes in the Upper Green River Basin. We describe here the results of a modeling study carried out to simulate ozone formation in two episodes in the UGRB, to assess the effects of VOC and NO_x reductions on ozone levels, and to calculate the ozone reactivities of the individual VOC compounds present. Both of these episodes had snow cover and therefore high surface albedos and UV light intensity. The first episode we consider occurred on February 20–21, 2008, for which monitoring data are available at the Jonah site (February 20) and the Boulder, Wyoming site (February 21) (see Fig. 1). The second episode considered occurred on March 1–2, 2011, for which monitoring data are available at the Boulder site and at a mobile trailer/tethered balloon (denoted “Mobile Trailer”) located at the Pinedale Federal 13-2A well location about 5 km southwest of the Boulder site (see Fig. 1).

Ideally, a numerical model of the three-dimensional atmosphere with emissions, airflow, mixing, and chemistry is used to simulate air quality over a region. However, at present there are insufficient data for these episodes to support use of such models. In view of this, a useful starting point in assessing the factors that affect ozone formation is a so-called “box model” in which the air over the region of interest is assumed to be contained in a well-mixed box. Thus, any complex wind flows are neglected, as is the geographical distribution of emission sources. However, the overall goal of the modeling effort carried out here is to assess whether it is possible to roughly duplicate the ozone levels attained in the episodes studied and if it is possible to assess the extent to which ozone formation in these episodes is in the VOC-sensitive or NO_x-sensitive regime. We consider the box modeling approach to be sufficient to address this objective. The box model simulations do have a representation of the changes of the mixing depth during the day, and the resulting dilution of the pollutants at the ground level with less polluted (but not entirely clean) air from aloft, and also the variation of light intensity, temperature, and humidity throughout the day. Furthermore, calculations of VOC reactivity require use of chemical mechanisms that are much more detailed than those currently implemented in 3-D models, and a box model is ideally suited for such calculations.

The incremental ozone reactivity of a VOC depends on the conditions of the episode as well as the chemistry of the VOC, with the relative availability of NO_x in the episode being particularly important (Carter, 1994). Since incremental reactivities are highest when NO_x is abundant, and O_3 formation is the most sensitive to changes in VOC emissions under those conditions, Carter (1994) developed the Maximum Incremental Reactivity (MIR) scale to represent those conditions. This is derived from a set of box model scenarios representing various urban areas with NO_x inputs adjusted to yield maximum sensitivities of ozone to changes in VOC levels, and has been widely used as a general reactivity scale (RRWG, 1999a,b; CARB, 1993, 2000, 2010). The current version of the MIR scale was calculated using the SAPRC-07 chemical mechanism documented by Carter (2010).

The MIR scale was developed to represent summer urban conditions, so it may not be appropriate for the conditions of the winter ozone episodes in the UGRB. In addition to the much lower temperature and much higher surface albedos and UV intensities, the distribution of pollutants emitted by the oil and gas operations in the UGRB tend to be very different from those in the urban scenarios used to calculate the MIR scale. We present here a reactivity scale developed to represent the conditions of the UGRB, based on data obtained during high ozone episodes in 2008 and 2011. The initial modeling work of one 2008 episode by Environ (2011) provided a very useful starting point, with this work examining more locations and episodes and using a more chemically detailed mechanism needed for reactivity scale calculation and with the mechanism modified for low temperature conditions. This work involved (1) deriving a box model to approximately represent the conditions of these episodes, using the Environ (2011) work as the starting point; (2) adapting the current SAPRC-07 chemical mechanism for calculating VOC reactivities for the low temperatures of the UGRB episodes; (3) calculating the incremental reactivities (change of ozone caused by changing emissions) of the individual VOC compounds measured during the episodes; and (4) conducting sensitivity studies to determine the effects of uncertainties on the ozone and incremental reactivity results. Incremental reactivity is calculated for each of the types of VOCs measured at the sites plus several additional representative VOCs, which consists of 106 VOCs in total. This is a subset of the ~1200 types of VOCs whose reactivities can be calculated using the SAPRC-07 mechanism (Carter, 2010).

2. Chemical mechanism

2.1. Baseline low temperature mechanism

The chemical mechanism employed is based on the SAPRC-07 mechanism that is used to derive the current version of the MIR and other reactivity scales based on the SAPRC mechanisms (Carter, 2010). This mechanism consists of two major components: the "base" mechanism that is used to represent the full set of VOC emissions from all sources, and the specific mechanisms for the individual VOCs whose ozone impacts are being assessed. In the calculation of incremental reactivity, the individual VOCs whose incremental reactivity are calculated are represented explicitly, while most of the other VOCs that are present are represented using lumped model species in the base mechanism. See Carter (2010) for a more complete discussion of how the SAPRC-07 is used to represent the various VOCs in reactivity assessment calculations.

Several modifications were made to the SAPRC-07 mechanism for the low temperature conditions of the UGRB. The mechanism already has temperature-dependent rate constants for essentially all of the inorganic and explicitly represented organic product gas-phase reactions that are believed to be temperature dependent, as well as for the initial reactions for the emitted VOCs and the lumped model species whose mechanisms were derived from them. Therefore, no modifications to the mechanism are required to represent these temperature effects. However, temperature changes will also affect the distribution of products and radicals formed when the individual VOCs react, but the current version of the mechanism represents these by lumped overall processes in which the product and radical distributions are treated as if they are temperature independent. The mechanisms for most non-aromatic VOCs are derived using the SAPRC mechanism estimation and generation system that is discussed in detail by Carter (2000), with updates for SAPRC-07 (Carter, 2010). That system can calculate product yield parameters for any temperature, though for some VOCs the branching ratios for some competing processes are adjusted to fit chamber data at a single temperature, and the system treats these as temperature independent. For the standard SAPRC-07 mechanism these parameters are calculated at 300 K, which is appropriate for modeling ozone formation under summertime conditions.

For the purpose of this study, the mechanisms for the non-aromatic compounds were re-derived using the mechanism generation system with the temperature changed from 300 K to 265 K, the average temperature measured during the Jonah 2008 episode. The resulting mechanisms for the individual compounds whose reactivities were calculated for this work are given in Table A-1 in the Supplementary Material. In terms of reactivity predictions, the most important effect of this change is the overall nitrate yield, which is a radical termination process that tends to increase with decreasing temperature, and the total number of NO to NO_2 conversions, the process responsible for O_3 formation, which is reduced as the temperature is reduced because of decreasing rates of alkoxy radical decompositions. The effects of this temperature change on these parameters for the OH radical reactions of the individual compounds are shown on Figure A-1 of the Supplementary Materials. Overall, the lower temperature causes the average number of NO to NO_2 conversions to decrease by an average of 27% for alkanes and 8% for alkenes, alcohols and ethers, respectively, and caused the overall nitrate yields to increase by factors of 41%, 52%, and 31% for alkenes, alkenes, and alcohols and ethers, respectively.

At present there is no information available to estimate how aromatic mechanisms may change at lower temperature, since uncertain portions of the mechanism have to be adjusted to fit chamber data (Carter, 2010), and there are insufficient data available to derive mechanisms for lower temperatures. Therefore, the individual or lumped mechanisms for the aromatics were not modified except for a few sensitivity calculations that are discussed below.

Although the reactivity calculation uses an explicit representation of the individual compound whose reactivity is being calculated, it uses lumped model species to represent the reactions of the mixture of VOCs in the base case simulation, i.e., in the simulation of the episode without the test VOCs added to the simulated ambient mixture. The reactivity calculation depends not only on the mechanisms for the individual compounds, but also on the mechanisms used for the distribution of compounds in the ambient mixture being taken as representative. This representative ambient mixture is referred to as the "base ROG" (reactive organic gas) mixture in the subsequent discussion. Most of the compounds in this mixture are represented using *lumped model species* used to represent groups of compounds assumed to have similar reaction rates and mechanisms. The mechanisms for these lumped model species are derived from mechanisms of the distribution of individual compounds they are designed to represent. For example, the mechanistic parameters (rate constants and product yields) of the OLE1 model species, used to represent primarily terminal alkenes other than ethene, is derived by weighted averages of the parameters for the various non-ethene terminal alkenes in the base ROG mixture, with the weighting factors being the mole fractions of the individual compounds divided by the total mole fractions of all terminal alkenes in the mixture.

For the standard SAPRC mechanisms (Carter, 2000, 2010), the base ROG mixture used to derive the mechanisms of the lumped model species was based on VOC measurements made in various cities around the U.S. in the 1980's (Lonneman, 1986; Jeffries et al., 1989), with modifications as discussed by Carter (1994). This mixture is also used to represent total VOC emissions in the MIR and other Carter (1994, 2000, 2010) reactivity scales, and is referred to as the "urban base ROG" mixture in the subsequent discussion. As discussed below, this mixture is quite different from the mixture of VOCs measured in at the time of the UGRB episodes considered here. Therefore, for the baseline SAPRC-07 Jonah and Boulder simulations, the mechanisms for the lumped model species were re-derived using the distribution of compounds in the mixtures of VOCs measured at Jonah and Boulder in 2008. For the simulations of the 2011 episodes, the mechanisms for the lumped model species derived for the Jonah 2008 episodes were used because the compositions of the mixtures were similar. The compositions of the mixtures used are given in Table A-2 in the Supplementary Materials and are discussed in Section 3.

Since the 2008 Jonah and Boulder base ROG mixtures are quite different, separate lumped mechanisms for the baseline simulations of these two episodes are used. The lumped model species mechanisms for UGRB simulations also differ from standard SAPRC-07 in that for the non-aromatic species the mechanisms were derived for the lower temperature (265 K) associated with these scenarios, rather than the 300 K used for standard SAPRC-07. The modified lumped species mechanisms derived for the Jonah and Boulder mixtures at 265 K are given in Table A-3 of the Supplementary Material.

2.2. Photolysis reactions

Photolysis rates for the episodes modeled were calculated from actinic fluxes as a function of zenith angle calculated using the TUV model version 5.0 (TUV, 2010), using inputs specified in Table A-4 in the Supplementary Materials. The most important difference compared to the light model used to calculate the photolysis rates for the MIR and other Carter (2010) reactivity scale calculations was the surface albedo, where a high value of 75% was used to reflect the effect of snow cover. The same actinic fluxes as a function of zenith angle were used for both the Jonah and Boulder 2008 simulations. As discussed in the Supplementary Materials, this change in the light model used to calculate the photolysis rates for wintertime conditions results in an increase in SAPRC-07 photolysis rates by factors of 1.3–2.4 (average of 2.1 ± 0.3) for midday in wintertime in the UGRB, though the increase is much less (factors ranging from 0.7 to 1.3, with average of 1.2 ± 0.2) when comparing midday summertime with midday wintertime, and depends on the time of day as well as the photolysis reaction and time of year.

SAPRC-07 photolysis rates calculated for the zenith angle of solar noon for the Jonah 2008 episode using this wintertime light model are shown on Table A-5 in the Supplementary Materials, where they are compared with photolysis rates calculated used in the reactivity scale calculations of Carter (2010) both for the same zenith angle (i.e., for midday Feb 22) and for midday zenith angle during the summer solstice. The wintertime midday photolysis rates calculated for this work are a factor of 1.3–2.4 (average of 2.1 ± 0.3) times higher than those used by Carter (2010) for the same zenith angle (54°), but are only a factor of 0.7–1.4 (average of 1.2 ± 2) than those calculated for midday in summertime (20 vs. 54°). The smaller change for winter vs. summer is because the lower zenith angles in summer counteract the effects of the higher surface albedos in winter. Nevertheless, for most photolysis reactions the midday photolysis rates are still higher in winter than in summer, though this is not true for all reactions and all times of day (see Figure A-2 in the Supplementary Materials for a comparison of selected wintertime and summertime photolysis rates as a function of time).

2.3. Modified mechanisms for sensitivity calculations

2.3.1. Low reactivity aromatics mechanism

Some sensitivity simulations of the Jonah scenario were conducted using "low reactivity" mechanisms for the lumped SAPRC-07 aromatic species ARO1 and ARO2 to assess how the predicted ozone might change if the aromatics are significantly less reactive at low temperatures. It is not known whether this will actually be the case, but lower temperatures may cause lower rates of decomposition reactions that may give rise to reactive products. The model species used to represent photoreactive products such as glyoxal, methyl glyoxal, and photoreactive unsaturated dicarbonyls such as 2-butene-1,4-dial were replaced by non-photoreactive products. This can be considered a reasonable lower limit reactivity assumption for sensitivity calculation purposes. The "low reactivity" aromatics lumped aromatic mechanisms used for these sensitivity calculations are included in Table A-2 in the Supplementary Material.

2.3.2. Lumped species based on the urban base ROG mixture

In order to determine the effects of modifying the mixture used to derive the lumped model species in the base case calculations, test calculations were conducted using lumped species derived for the standard urban base ROG mixture used in the previous reactivity scale calculations (Carter, 1994, 2000, 2010), though for the lower temperature (265 K) of the UGRB scenarios. Note that this is not the same as the calculations using the standard urban mixture used to represent the base case VOCs present, which involves changes to the scenario conditions as well as the lumped mechanisms. In this case, the only change involves the mechanisms of the individual non-aromatic lumped species, not the amounts of these species that were emitted.

2.3.3. Room temperature mechanism

These calculations use the standard SAPRC-07 mechanism, with the rate constants for the inorganic and initial VOC reactions appropriate for the lower temperature but with the product yields for the lumped VOC reactions being those derived for 300 K. This differs from the baseline mechanism both in the temperature used to derive the mechanisms and in the ambient mixture used to derive the mechanistic parameters for the lumped species. A comparison of the calculations using this mechanism with those using the lumped species based on the standard ambient mixture, discussed above, reveals the effects of changing only the temperature.

2.4. Modified mechanism for HONO formation

Nitrous acid (HONO) is a reactive component of the HO_x/NO_x system, the rapid daytime photolysis of which serves as an OH radical source. Its major formation process in current gas-phase mechanisms is the reaction of OH with NO, which does not have a significant effect overall because it is reversed by the rapid HONO photolysis. HONO measurements made in 2010 and 2011 in the UGRB (Rappenglük, 2010, DEQ, 2011) show, however, much higher HONO levels than predicted by known gas-phase reactions. They tend to peak during the day despite expected rapid loss due to photolysis, and tend to correlate with measured NO_2 levels, with $HONO/NO_2$ ratios ranging from about 1.5% to 4%, as shown on Fig. 2. Such a large ratio could be the result of a light-induced conversion of NO_2 to HONO on surfaces, perhaps on the snow (e.g., see Grannas et al., 2007 and references therein).

In order to assess the extent to which this possible heterogeneous formation of HONO may affect predictions of O_3 formation and VOC reactivity in the UGRB, we performed a series of calculations in which the mechanism included light-induced HONO formation from NO_2 at various rates. This was represented in the box model by the following pseudo-gas-phase process:

$$\mathrm{NO_2} + h\nu \rightarrow \mathrm{HONO} \quad k = k\left(\mathrm{NO_2} + h\nu \rightarrow \mathrm{O^3P} + \mathrm{NO}\right) \times \alpha$$

The parameter α is adjusted to yield a specified calculated NO_2/HONO ratio. The values of α used in the calculations were 0 (baseline), 0.001, 0.0022, 0.0035, and 0.005, to yield approximate average

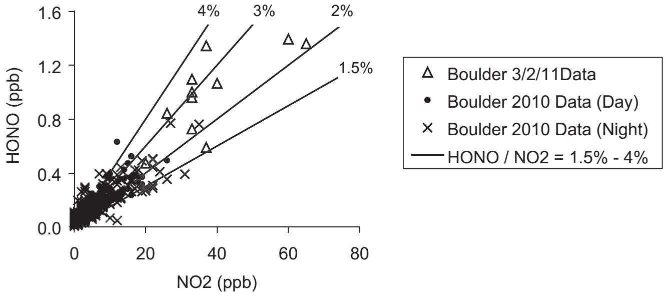

Fig. 2. Measured HONO/NO_2 ratios measured in Boulder in during the 2010 Winter measurement campaign and during the 3/2/2011 episode. For the purpose of this figure "Day" is defined as between the hours of 6 AM and 5 PM, and "Night" is any other time.

HONO/NO_2 ratios of 0.2–0.3% (baseline), 1%, 2%, 3%, and 4%, respectively. The initial HONO in the scenario inputs was also increased to yield 1%–4% initial HONO/NO_2 ratios in the added HONO simulations. The reaction above is almost certainly a simplification of heterogeneous HONO formation processes that may actually be occurring, but is useful for an initial sensitivity analysis of the extent to which additional HONO formation may affect predictions of O_3 and VOC reactivity.

3. UGRB ozone episodes

Fig. 3 shows the measured O_3, NO, NO_2, and NMHC data for the four UGRB winter high ambient ozone episodes that were modeled in this study. The peak hourly O_3 in these episodes ranged from 88 to 143 ppb, which is very unusual for winter conditions. Results of model simulations, discussed below, are also shown. All four of these episodes were simulated using a highly simplified box model where all the pollutants were assumed to be present initially, and no subsequent emissions of pollutants were assumed. This is the same as the model formulation used by Environ (2010) in their previous modeling study of the 2008 Jonah episode.

Although use of continuous pollutant emissions throughout the day may be more realistic, assuming all pollutants present initially should be sufficient for the purpose of this study. The calculations are begun essentially at sunrise, using the measured VOC and NO_x as initial conditions. In reality, it is expected that throughout the day, air parcels will be advected to the monitoring sites carrying additional VOC and NO_x. During each of the episodes, however, conditions were close to stagnant, and the extent of advective inflow is unknown. Moreover, unlike an urban area, the emission sources in the UGRB are solely a result of the gas production operations, for which no diurnal cycle of emissions is expected. It is reasonable to assume, therefore, that the VOC composition and the VOC-to-NO_x ratio of air impacting the monitoring sites will not have varied substantially from those at the site in the early morning. It is unlikely that a simulation that includes a continuous influx of emissions of essentially the same composition as that at sunrise would lead to different conclusions concerning the ozone level attained and the extent to which the ozone formation is in the VOC-sensitive or NO_x-sensitive regime.

For the 2008 episodes the mixing height was assumed to increase throughout the day, as used in the Environ (2010) simulations, resulting in dilution of the initial pollutants and entrainment of low levels of pollutants assumed to be aloft. The mixing height data provided by the Wyoming Department of Environmental Quality (DEQ) (DEQ, 2011) suggested that the mixing height can be assumed to be constant in the simulations of the 2011 episodes, so no dilution and entrainment was assumed to occur in the model for those episodes. Fig. 3 shows the initial pollutant concentrations used in the model simulations, along with selected results of model simulations that are discussed later in this paper. The lines on the NMHC plots on Fig. 3 show the initial NMHC used in the simulations, and the relative amount of dilution assumed to occur throughout the simulated day. The hours shown on the figure indicate the start and end of the simulated days. More detailed information about the model inputs, and the derivations of the values used are given in Table A-6 and Table A-7 of the Supplementary Materials. The episodes are discussed further below.

3.1. Jonah, February 20, 2008 episode

This episode, which had a peak hourly O_3 of 88 ppb, has been modeled previously by Environ (2010), and is used as the primary basis for the reactivity scale calculation discussed in this work. As indicated in Table A-6, the mixing height schedule and aloft pollutant levels were taken from the Environ (2010) study without modification. The pollutant inputs and ambient VOC speciation were modified somewhat based on our independent analysis of the air quality data provided by DEQ (DEQ, 2010) as indicated on Table A-6, but most of the changes were relatively minor. The main differences between our study and that of Environ (2010) is the chemical mechanism used, with the Environ study using Carbon Bond 05 (Yarwood et al., 2005), while this study used modified versions of SAPRC-07 as discussed above.

The composition of the ambient NMHCs used in the simulations of this scenario is given in Table A-2, and its overall composition and reactivity characteristics are shown and compared with the other ambient NMHC mixtures on Fig. 4. This composition was derived from speciated VOC data measured at Jonah on 2/20/08 (DEQ, 2010). The data give averages for hours 0400–0700, 0900–1200, and 1400–1700, but show no significant differences or trends over time. For this reason, we averaged the data for these three time periods to obtain the composition for the scenario inputs, rather than using only the 0400–0700 values. A few outliers were excluded when computing the averages.

Fig. 4 shows that the VOC mixture measured at the 2008 Jonah site is quite different from that used in the MIR and other reactivity scale calculations of Carter (1994, 2000, 2010), with much higher levels of ethane and propane which have relatively low O_3 reactivities, and much lower levels of alkenes, which have high reactivities, making the ozone reactivity of the mixture a factor of 2.5 lower in the MIR scale. This is undoubtedly a result of the different types of sources present near or upwind from the Jonah site as compared to the mixture of VOCs emitted in urban areas, which tend to be dominated by vehicle emissions (at least in the mid-1980's, the period when the current urban mixture profile was derived (Lonneman, 1986; Jeffries et al., 1989)).

3.2. Boulder, February 21, 2008 episode

This episode had a peak hourly O_3 of 143 ppb. The initial NO_x and total VOC inputs are based on air quality data provided by the DEQ (2010). Despite the higher O_3, this episode had lower NO_x and NMHC levels than the 2008 Jonah episode by factors of ~7.5 and ~4.5 respectively, but had a significantly higher initial NMHC/NO_x ratio, and also had a higher reactivity of the NMHC mixture, as discussed below. Because of the lack of available information, the other inputs used in the model simulation were the same as those used for the simulation 2008 Jonah inputs, as discussed above and indicated in Table A-6 and Table A-7.

The composition of the non-methane ambient VOCs used for the Boulder scenario is based on averages of the hours 0400–0700, 0900–1200, and 1400–1700 speciated data provided by DEQ (2010) for the Boulder site on February 21, 2008. As with the Jonah

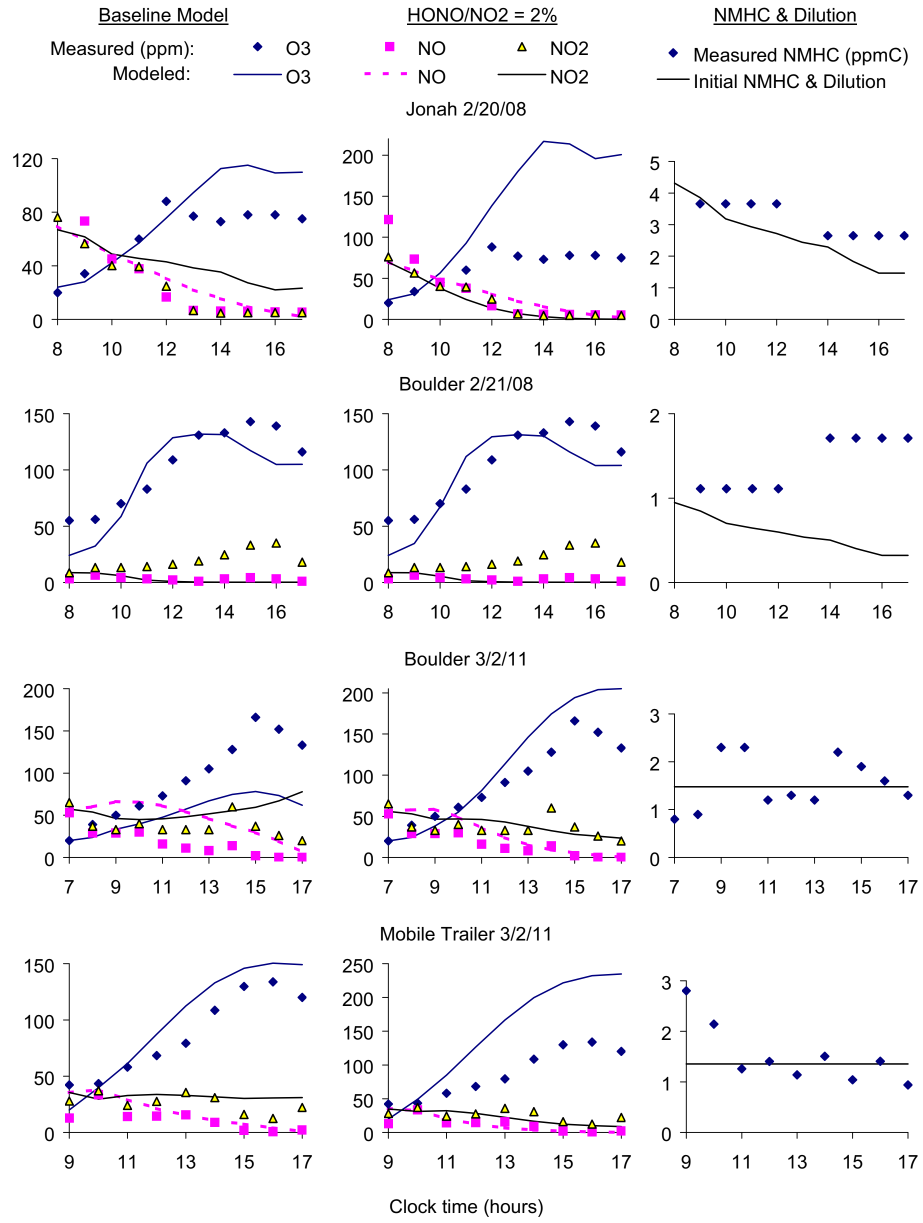

Fig. 3. Measured and calculated ozone, NO, NO_2, NMHC in the UGRB scenarios modeled in this work.

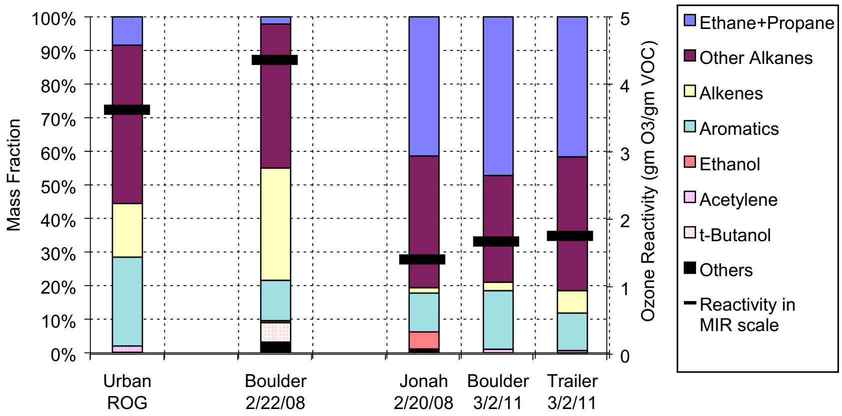

Fig. 4. Mass fractions of various types of VOCs and incremental reactivities in the MIR scale for the ambient mixtures used in the UGRB simulations described in this work. The urban ROG mixture used in the MIR and other Carter (2000, 2010) reactivity scale is shown for comparison. The mixtures are grouped by similarity.

speciated VOC data, there is no apparent trend in composition with time at the Boulder site on this day, so use of averages should be appropriate, with a few outliers excluded. The resulting composition is given in Table A-2, and is summarized and compared with the other VOC mixtures in Fig. 4.

Fig. 4 shows that the VOC mixture for this February 21, 2008 Boulder episode is quite different from that for the 2008 Jonah episode, having very low levels of ethane and propane, very high alkene levels, and an ozone reactivity a factor of 3 times higher than the Jonah mixture in the MIR scale, and even higher than the urban ROG mixture. This is also very different from the VOC speciation derived for the March 2011 UGRB episodes modeled for this study, which are more like that derived for the Jonah episode discussed above. The reason for the significantly different VOC speciation for this 2008 Boulder episode needs to be investigated, but is beyond the scope of the present paper.

3.3. *March 1–2, 2011 episodes*

The 2011 winter season resulted in additional high O_3 episodes for the UGRB, and two sites near Boulder were modeled as part of this study, for comparison with our modeling of the 2008 episodes discussed above. High O_3 levels occurred on both March 1 and 2, but only March 2 was modeled because ambient data provided by DEQ (2011) suggest that the conditions on March 2 are better approximated by the box model formulation used in this study. The maximum O_3 concentration achieved on March 2, 2011 at the Boulder monitoring site was 166 ppb, and at a mobile trailer/tethered balloon site located at the Pinedale Federal 13-2A well location, about 5 km southwest of the Boulder site (Fig. 1), a peak O_3 concentration of 134 ppb was measured. These are referred to as the 2011 Boulder 3/2/11 and 2011 Mobile Trailer episodes in the subsequent discussion. The pollutant and other scenario inputs used for these episodes were based on data provided by DEQ (2011), as shown on Fig. 3 and given in Table A-6 and Table A-7 in the Supplementary Materials. The mixing height data provided by DEQ (2011) did not indicate any clear change of mixing height in Boulder with time, so constant mixing heights were assumed for both episodes.

The two locations were modeled separately primarily because of problems with speciated VOC data at the Boulder site. VOC data at Boulder on March 1–2 consisted only of selected VOCs for toxic assessment and were not sufficiently complete for ozone reactivity modeling. A week-long canister survey, conducted by Dr. Robert Field of the U. of Wyoming over Feb 22–Mar 1, 2011 at the Boulder site and 9 other locations using the University of Wyoming mobile laboratory (Field et al., 2011), provide data sufficiently complete for reactivity modeling. (Some minor alkane species were not reported that may be non-negligible as a group, but corrections were made for this based on ratios of alkanes in the 2008 Jonah mixture when deriving the compositions used for modeling. The exclusion of these from the initial study design was based on the fact that these species are not present in significant amounts in natural gas.) Because of the uncertainty of using a week-long sample for modeling a single day episode, we also modeled the mobile trailer/tethered balloon site, where two samples of detailed VOC speciation data were taken on March 2 at ground level as well as a sample at 100 m altitude. The compositions of the two samples were reasonably consistent and were averaged to provide model inputs for the 2011 episode at that location.

The compositions of the two VOC mixtures derived for the two March 2, 2011 episodes are compared with the other mixtures in Fig. 4 and are given in Table A-2 of the Supplementary materials. These mixtures are very similar to each other and to the mixture derived for the 2008 Jonah episode, with very high levels of ethane and propane, very low levels of alkenes, and very low ozone reactivity as measured in the MIR scale. Because of the similarity of both these 2011 mixtures with the mixture used for the 2008 Jonah episode, the modified SAPRC-07 lumped model species parameters derived for modeling the Jonah 2008 episode were also used when modeling these two 2011 episodes.

3.4. *Incremental reactivity calculations*

Incremental ozone reactivities of all the VOCs measured in the UGRB episodes were calculated using the Jonah and Boulder 2008 episodes, with the calculations for the Jonah 2008 episode being conducted with both the baseline mechanism with no added HONO, and with the mechanism derived to simulate approximate HONO/NO_2 ratios of 3%. Reactivity calculations were not conducted for the 2011 episodes. Added HONO simulations were not conducted for the Boulder 2008 episode because as discussed below the calculated O_3 formation in this scenario was found not to be sensitive to changes in HONO inputs.

The incremental reactivity calculation methodology is the same as that employed previously by Carter (1994, 2000, 2010) when calculating the MIR and other reactivity scales. These consisted of base case model simulations using the inputs for the scenarios discussed above, together with simulations with small amounts of the test VOCs added, with the incremental reactivities being derived from the change in mass of O_3 formed divided by the mass of VOC added. The amounts added were derived based on the rates of reactions of the test compound as discussed by Carter (2010). The reactions of the VOC whose reactivity was calculated was represented explicitly, unless it is represented in SAPRC-07 using the “lumped molecule” approach (Carter, 2010), in which case its molar reactivity was taken from that compound(s) representing it.

4. Results and discussion

4.1. *Simulations of ozone*

Fig. 3 shows O_3, NO, and NO_2 simulations for all four episodes modeled in this study. The plots on the left show the results for the baseline model without a heterogeneous HONO source, and those in the middle show the results for the model with HONO inputs adjusted to yield HONO/NO_2 of ~2%. The addition of the HONO caused significantly increased O_3 for all episodes except the 2008 Boulder episode, as discussed further below. The baseline model gave fair simulations of O_3 for all episodes except for the 2011 Boulder episode, where O_3 is substantially underpredicted. The model with added HONO gives much better simulations of O_3 in the 2011 Boulder episode, but overpredicted O_3 in the Jonah 2008 and the mobile trailer 2011 episodes, Both models simulated O_3 reasonably well in the Boulder 2008 episode, but had other inconsistencies with the data as discussed below.

In the Jonah 2008 and the 2011 scenarios, the consumption of NO_x and dilution in NMHC concentrations throughout the day and the onset and rate of O_3 formation are moderately well simulated, but the model does not does not represent well the variation of NO_x and NMHC concentrations throughout the day in the Boulder 2008 scenario. This suggests that the approximation of representing all pollutants as being present initially without being emitted or transported into the air mass throughout the day may not be a good representation of the conditions of the 2008 Boulder scenario, though it may not necessarily be inappropriate for the other three. However, the 2008 Boulder scenario gives a good simulation of the amount of O_3 formed. Importantly, the simulations of all four sites give an indication of the range of variability of conditions in the UGRB during wintertime ozone episodes.

4.2. Effect of varying NO_x and NMHC on peak ozone concentrations

Fig. 5 shows the predicted effect of varying the initial NO_x concentration (upper panels) and the initial NMHC concentration (lower panels) on peak O_3 at the four sites in 2008 and 2011. Observed levels of O_3, NO_x, and NMHC are indicated by the filled circle in each plot. With respect to the variation of NO_x, the episodes at Jonah 2008, Boulder 2011, and Mobile Trailer 2011 each exhibit NO_x-saturated behavior: reduction of NO_x leads to peak O_3 increase towards an O_3 maximum, followed by eventual decrease. The episode at Boulder 2008 lies in the VOC-saturated (NO_x-sensitive) regime, wherein peak O_3 decreases as NO_x decreases. As initial NMHC decreases (bottom panels), the episodes at Jonah 2008, Boulder 2011, and Mobile Trailer 2011 exhibit VOC-sensitive behavior, with peak O_3 decreasing as NMHC is decreased. Peak O_3 at Boulder 2008, which lies in the NO_x-sensitive regime, is insensitive to changes in NMHC. Since Jonah 2008, Boulder 2011, and Mobile Trailer 2011 exhibit NO_x-saturated behavior, the additional OH generated by an increased HONO level ($HONO/NO_2 = 2\%$ case shown in Fig. 5) enhances O_3 formation. Under Boulder 2008 VOC-saturated conditions, OH levels are not limiting and thus the addition of more HONO has no effect on peak O_3.

The Boulder 2008 ozone episode appears to be an outlier with respect to $VOC/NO_x/O_3$ behavior. As indicated on Fig. 4, it is also an outlier with respect to VOC speciation. A key question is whether the effect of NO_x and VOC reductions on ozone levels in the UGRB varies significantly over the region. Further monitoring is needed to establish the overall behavior of the UGRB ozone to reduction in NO_x and VOC emissions.

4.3. Effect of nitrous acid (HONO)

Nitrous acid (HONO) is a highly photoreactive form of NO_x whose relatively rapid photolysis forms OH radicals that can enhance rates of O_3 formation under conditions where O_3 is not NO_x-limited. Ambient HONO data are not available for the 2008 UGRB episodes modeled here, but relatively high levels of HONO were observed in 2010 field studies (Rappenglük, 2010), and also at the Boulder site during the March 2, 2011 episode (DEQ, 2011). As discussed above, this can be attributed to heterogeneous formation of HONO from NO_2 on surfaces, and can be modeled (albeit simplistically) as a light-induced first-order conversion of NO_2 to HONO, with the conversion rate and initial HONO levels adjusted to yield observed $HONO/NO_2$ ratios.

Fig. 6 shows measured and modeled concentration-time data for HONO for the 2011 Boulder episode, with model calculations with no added HONO (baseline) and with HONO inputs (i.e., initial HONO and values of the parameter α in the parameterized HONO formation reaction discussed in Section 2.4) adjusted to yield $HONO/NO_2$ ratios of 2% and 3% also shown. It can be seen that the baseline model significantly underpredicts the observed HONO in this scenario, while the calculations with the $HONO/NO_2$ ratio in the 2–3% range predict HONO levels in approximately the appropriate range. The model tends to overpredict the initial HONO and underpredict the final values, though more episodes need to be modeled to determine if this is a consistent indication of a problem with the simplified HONO formation model used.

As discussed above, Fig. 3 shows the effects of varying the HONO inputs on simulations of O_3 and NO_x in the four episodes modeled. The effects of varying HONO inputs on calculated O_3 levels is also shown on Fig. 7, which plots calculated maximum O_3 against average $HONO/NO_2$ ratios for the baseline and varied HONO calculations for all four of the scenarios. The range of maximum O_3 concentrations in these scenarios and of the $HONO/NO_2$ ratios indicated by the data shown on Fig. 2 is also shown. Note that the baseline simulations with no light-induced NO_2 to HONO formation yield $HONO/NO_2$ ratios of 0.2–0.3%, far lower than the ambient ratio for the UGRB. All locations except Boulder 2008 exhibit large sensitivity of the maximum O_3 concentration to the additional HONO formation, with the predicted maximum O_3 increasing to levels that are higher than observed for most episodes when the HONO is increased to levels consistent with the data on Fig. 6.

The effects of additional HONO input on the dependence of O_3 on initial NO_x and NMHC is shown on Fig. 5, where calculations with HONO inputs adjusted to yield $HONO/NO_2$ of 2% are compared with the baseline calculation with no additional HONO input. The addition of HONO does not significantly affect the maximum O_3 when the NO_x levels are below those yielding the maximum O_3 concentrations in the baseline simulations, such as in Boulder 2008, but has the effect of increasing the amount of O_3 formed in simulations where NO_x is increased above these levels, and increases the NO_x level that is most favorable for O_3 formation. This is because O_3 formation under higher NO_x conditions (low VOC/NO_x ratios) tends

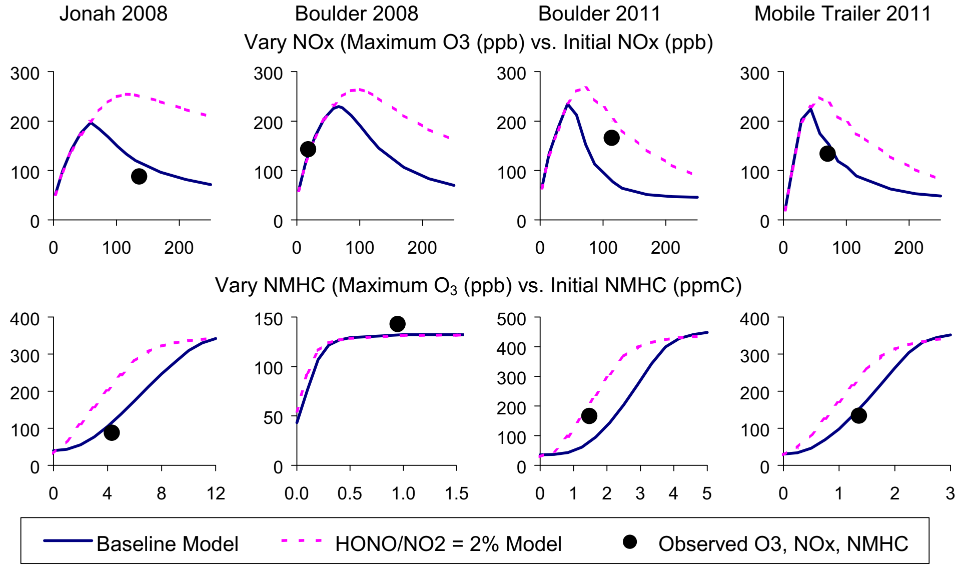

Fig. 5. Observed and calculated maximum O_3 as a function of initial NO_x and NMHC for the UGRB scenarios modeled in this study.

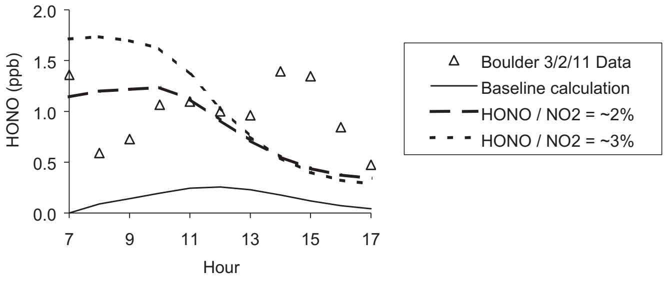

Fig. 6. Experimental and calculated HONO for the Boulder 3/2/2011 episode.

to be very sensitive to overall radical levels that affect rates of reactions, which are enhanced by the OH radicals formed from the photolysis of HONO. In addition, the higher NO_x levels cause increased HONO input if HONO is assumed to be formed from NO_2, as is the case in our added HONO calculations.

4.4. Incremental reactivities

Fig. 8 compares incremental reactivities calculated for the baseline Jonah 2008 and Boulder 2008 scenarios against those calculated using the standard MIR scale (Carter, 2010). These incremental reactivities are also tabulated in Table A-2 in the Supplementary Materials. In the case of Jonah, the reactivities calculated for the episode generally correspond to those in the MIR scale. We would not expect the magnitudes of the reactivities to be the same because of the differences in the scenarios, but the orderings of reactivities are in most cases preserved, though there are differences. Notable is that most of the lower reactivity compounds, especially alkanes, have much lower reactivities in the Jonah scenario than in the MIR scale, even if the 65% difference in the overall magnitude of the reactivities indicated by the best fit line is taken into account. Many of the higher alkanes with positive MIR values are calculated to have negative ozone impacts in the Jonah scale. This may be due at least in part to a greater sensitivity in the Jonah scenario to the negative effects on reactivity of radical sinks in the alkane mechanism due to organic nitrate formation from peroxy + NO reactions.

In the case of the Boulder 2008 scenario, Fig. 8 shows that there is essentially no correlation between the incremental reactivities calculated for Boulder 2008 and the MIR scale. In fact the correlation is slightly negative, due to the fact that the VOCs tend to reduce O_3 more when they react faster, because more of them react. This lack of correlation is a result of the highly NO_x-limited nature of the Boulder 2008 scenario, where O_3 responds primarily to changes in NO_x levels, and is relatively insensitive to VOCs. Negative VOC reactivities can occur because VOCs whose reactions deplete NO_x by forming NO_x-containing products such as organic nitrates or PANs, tend to have negative O_3 impacts under highly NO_x-limited conditions. Clearly, for the conditions of the Boulder 2008 scenario the concept of VOC reactivity is essentially irrelevant because O_3 formation under these highly NO_x-limited conditions is insensitive to VOC.

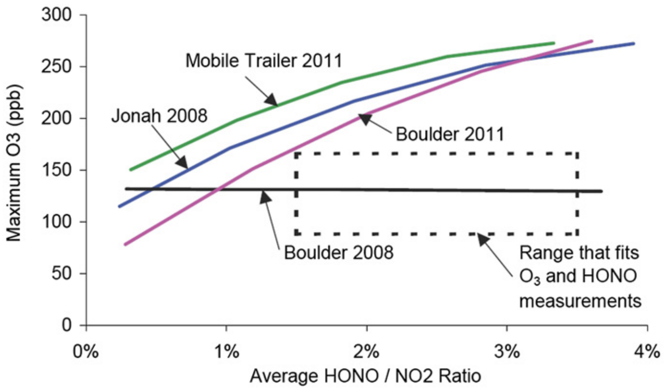

Fig. 7. Simulated maximum O_3 levels against average $HONO/NO_2$ ratios in the model simulations of the UGRB scenarios with HONO inputs varied. The lowest ratios shown are those calculated using the baseline calculations with HONO formed only from the gas-phase reactions in the SAPRC-07 mechanism.

Fig. 9 shows the incremental reactivities calculated for the standard urban ROG mixture, which is a measure of the sensitivity of O_3 formation to changes in VOC levels, as a function of initial NO_x for the baseline and 3% added HONO simulations of the Jonah 2008 and Boulder 2008 scenarios. The incremental reactivities of most individual VOCs tend to show the same type of NO_x dependence as the urban ROG mixture, though the magnitude of the incremental reactivities may differ. As observed in simulations of urban scenarios (Carter, 1994), the NO_x levels giving the highest incremental reactivities (the MIR levels) are higher than the NO_x level yielding maximum ozone, and the incremental reactivities approach zero or become negative if NO_x levels are sufficiently low. Fig. 9 also shows that added HONO causes the incremental reactivity of the urban ROG mixture to be lower under most conditions, and it tends to cause the incremental reactivities to become relatively insensitive to NO_x inputs when NO_x levels are sufficiently high, unlike the case for the baseline simulations.

The largest difference between the Jonah 2008 and the Boulder 2008 scenarios in terms of reactivity affects is not necessarily the composition of the ambient VOC mixture, but the NO_x levels relative to those yielding maximum O_3 concentrations. The base case Boulder scenario is very much in the NO_x-limited regime, while the base case Jonah scenario is very much in the VOC-sensitive regime, with NO_x levels even higher than those yielding MIR conditions. The relative NO_x levels in the base case Boulder simulation are so low that the incremental reactivities of the ambient mixture (and also of the Jonah ROG mixture, as discussed below) are negative, i.e., VOC control is predicted to be counterproductive to reducing O_3 in this scenario. The only effective ozone control strategy for the Boulder 2008 scenario is predicted to be NO_x control. On the other hand, O_3 formation is predicted to be very sensitive to changes in VOC emissions in the base case Jonah 2008 scenario, and reductions in NO_x levels will cause O_3 formation initially to increase. Thus these two scenarios are on opposite extremes with respect to their reactivity characteristics and relative effectives of VOC and NO_x control.

The effects of additional HONO input on incremental reactivities under the conditions of the Jonah 2008 scenario are shown on Fig. 10, where the reactivities calculated using the model with $HONO/NO_2$ at ~3% are plotted against those calculated using the baseline model with no added HONO input. The incremental reactivities for this added HONO scenario are also given in Table A-2 of the Supplementary Materials. For most compounds, the effects of the additional HONO input on incremental reactivities, both in an absolute and relative sense, are relatively minor. However, the addition of HONO causes the relative reactivities of the internal alkenes and the aldehydes to be significantly lower than is the case with the baseline model. The low reactivity alkanes whose reactivities are negative in the Jonah 2008 baseline scale also tend to have somewhat higher, in some cases positive, reactivities in the added HONO calculations. The reasons why these particular compounds would be more affected by the addition of HONO than most of the other compounds need to be investigated. It is not known whether the incremental reactivity results would be different if a different model for HONO input were adopted, but we suspect the results would mainly be sensitive to the amount of HONO input, not exactly how it is formed.

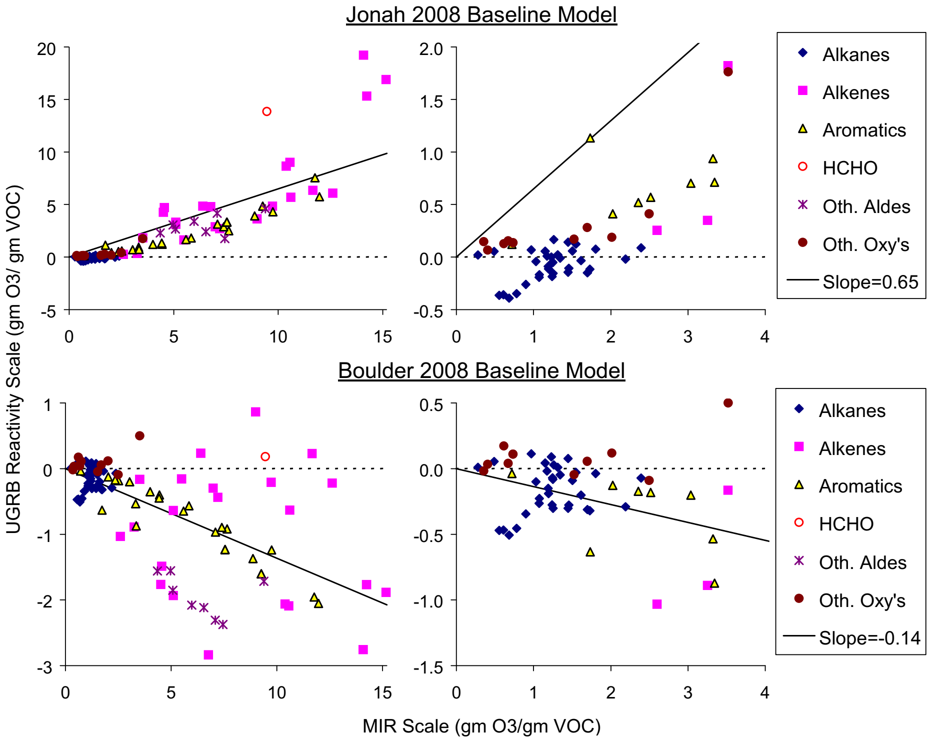

Fig. 8. Comparisons of incremental reactivities calculated for the Jonah and Boulder scenarios against incremental reactivities in the standard MIR scale.

4.5. *Effects of surface albedo*

As shown in Table A-5 in the Supplementary Materials the photolysis rates used for the conditions of these snow-covered UGRB scenarios are about a factor of 2 higher than those used in the urban scenario simulations of Carter (1994, 2000) for a given solar zenith angle, though if the effect of the season on the zenith angle is taken into account then the photolysis rates are only ~20% higher than for a summer simulation. The relatively high winter photolysis rates are due to the high surface albedo caused by the snow cover. To assess the effects of this high albedo, the 2008 Jonah and Boulder scenarios were simulated using the urban actinic fluxes used by Carter (1994, 2000), with all other scenario inputs, including temperature and date, the same. The maximum O_3 in the Jonah 2008 simulation decreased from 115 to 58 ppb, while the maximum O_3 in the highly NO_x-limited scenario decreased from 132 to 110 ppb, only a 17% change. This is consistent with our expectations because O_3 formation in highly VOC-sensitive scenarios such as Jonah 2008 is highly sensitive to overall radical levels, which are driven primarily by the photolysis reactions, while peak O_3 levels in NO_x-limited scenarios are determined primarily by the availability of NO_x.

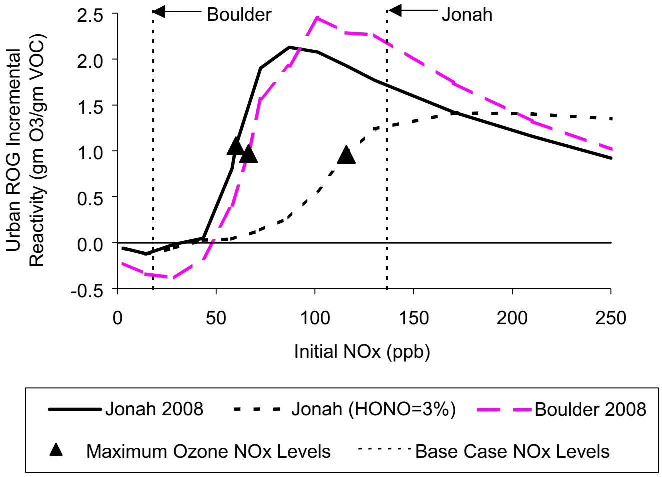

Fig. 9. Effects of varying NO_x inputs on maximum ozone and the incremental reactivity of the urban ROG mixture calculated for selected scenarios.

4.6. *Other sensitivity studies*

The Supplementary Materials discuss various other sensitivity calculations that were carried out on effects of changing the various aspects of the mechanisms or scenario inputs on maximum ozone levels for the 2008 Jonah and Boulder scenarios. The results indicate that VOC-sensitive Jonah scenario is much more sensitive to most model inputs than the NO_x-sensitive 2008 Boulder scenario, and that the temperature and the composition of the ambient ROG are important in affecting the results. The O_3 calculated for summer temperature and lighting conditions are calculated to be considerably higher than for the winter scenarios despite the lower photolysis rates caused by the lower summer albedos. The CB05 mechanism used in the Environ (2010) studies predicted ~16% lower O_3 levels in the Jonah simulation than the SAPRC-07 mechanism, even after the latter is adjusted for low temperature conditions.

4.7. *Contribution of VOCs to total ambient ROG reactivity*

Fig. 11 shows the relative contributions of the various types of VOCs measured in the Jonah and Boulder 2008 episodes to the overall mass or reactivity of the mixture, using various reactivity scales. These include the standard MIR scale, the baseline Jonah 2008 scale, and the Jonah 2008 scale calculated for HONO input yielding a HONO/NO_2 ratio of 3%. The contributions of the Boulder 2008 scale are not shown because relative VOC reactivity is not a useful concept for such a NO_x-limited scenario, and the overall reactivities of these mixtures

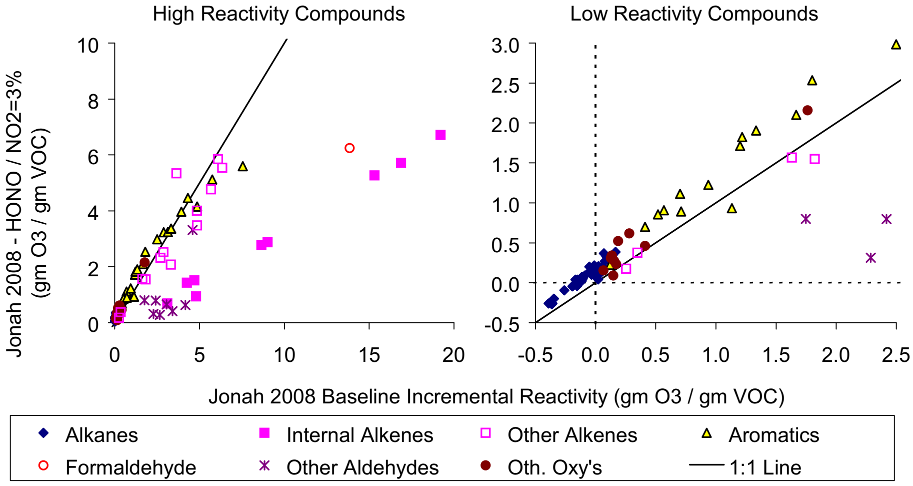

Fig. 10. Incremental reactivities calculated for the Jonah 2008 scenario with the model with HONO inputs adjusted to yield HONO/NO_2 = 3% against those calculated for the same scenario with no additional HONO input.

in this scale are near zero or negative. It can be seen that reactivity weighting decreases the relative contributions of ethane and propane and in most cases the higher alkanes, and increases the contributions of alkenes, aromatics, and aldehydes, relative to the mass contributions. The relative contributions of the alkanes depends significantly on the scale used, with the Jonah 2008 baseline scale showing almost no contribution of the alkanes to the reactivities of either mixture, while the Jonah scale for the scenario with additional HONO showing higher alkane contributions, though still less than calculated using the MIR scale. For the Jonah 2008 mixture, the Jonah 2008 scales give larger contributions of the alkenes and aromatics relative to MIR, with the alkene contribution being somewhat less for the scale with additional HONO. For the Boulder 2008 mixture, the two Jonah scales give similar contributions of the various types of compounds to the mixture reactivity, and except for the lower alkane contribution (which is relatively small in any case) the contributions are similar to those calculated for the MIR scale. It is interesting to note that the addition of HONO makes the reactivity contributions for both mixtures using the Jonah scale more like those calculated using the standard MIR scale.

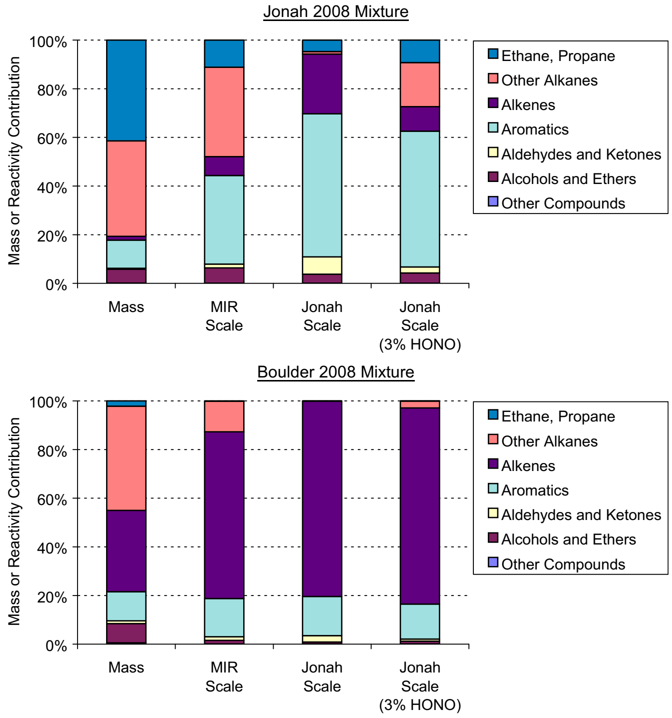

Fig. 11. Relative mass and reactivity contributions of various types of VOCs for the 2008 Jonah and Boulder ambient mixtures.

5. Summary and conclusions

This study provides insights concerning potential factors affecting ozone formation in the winter ozone episodes in the Upper Green River Basin of Wyoming. The modeling analysis employed a number of simplifying assumptions that may not appropriately represent the actual conditions of the 2008 and 2011 episodes being modeled, and additional data are needed concerning the variability of pollutant levels with time and space, pollutant transport, the role of HONO formation, and the chemistry of aromatics and other VOCs at the very low temperatures of the winter ozone episodes.

The overriding finding is that conditions in the UGRB appear to be highly variable with respect to pollution levels, VOC/NO_x ratios, reactivity characteristics with respect to sensitivity to VOC and NO_x controls, and VOC speciation. For example, the February 2008 Jonah March 2011 Boulder/mobile trailer episodes appear to be highly VOC-sensitive, for which VOC reactivity scales may be useful for determining VOC control strategies. The February 2008 Boulder episode appears to be highly NO_x-sensitive, for which VOC controls would be ineffective and reactivity scales are not useful. However, more data are needed to assess whether the 2008 Boulder episode, which also has a significantly different VOC composition than the other episodes modeled here, is an anomaly. These results suggest that determination of emission controls for the UGRB will require careful attention to the geographical distribution of both VOC and NO_x emissions and the local meteorology. Moreover, the sources of and role of HONO in the atmospheric chemistry of this region need to be clarified.

The relative contributions of the different types of VOCs to the overall ozone impacts are different for the Boulder 2008 ambient ROG mixtures than for the other three scenarios that were modeled in this study. For the Jonah 2008 and the 2011 scenario mixtures, the MIR scale predicts that the alkanes and the aromatics make about equal contributions to ozone and are the most important. However, the Jonah 2008 scale with no additional HONO predicts that the alkane contribution is small, the aromatics make the major contribution, and the alkene contribution becomes more significant. For the Jonah 2008 scale with additional HONO, the alkanes are calculated to have a somewhat larger contribution (though much less than the MIR scale), at the expense of the alkene and aromatic contributions. For the Boulder 2008 mixture, the MIR and the low and additional HONO Jonah scales all predict that the alkenes make the major contributions to the reactivity of this mixture, with the aromatics contributing about 15–20%. The MIR scale predicts some contribution to alkanes but the Jonah scales predict the alkanes make an insignificant contribution to the reactivity of this mixture.

The findings reported in this paper have important implications for designing and implementing future monitoring strategies for the UGRB. It will be important in future winters to simultaneously acquire information at multiple sites on concentrations of NO_x (NO, NO_2), HONO, Non-methane Hydrocarbons (ppm C), and VOC speciation along with measurements of surface albedo and standard meteorological measurements. This information is essential to applying the box modeling approach at multiple locations and times and for the fuller 3-D modeling of ambient ozone across the UGRB that is ultimately required. The results obtained to date using robust data sets for a few locations emphasize that spatial and temporal heterogeneity in the multiple parameters that determine ambient ozone concentrations suggest less robust data sets will not be adequate for the fuller 3-D modeling of ozone that is needed to plan and implement control strategies.

Acknowledgments

This work was funded by Shell Exploration and Production Company. We wish to thank Cara Keslar of the Wyoming Department of Environmental Quality (DEQ) for providing air quality data and for helpful discussions, Dr. Robert Field of the University of Wyoming for making his VOC speciation data available prior to publication, Greg Yarwood and Uarporn Nopmongcol of Environ Corporation for valuable assistance with the scenario inputs, and Roger McClellan and Jim Sewell for helpful discussions. The contents of this report reflect only the opinions and conclusions of the authors, and not necessarily those of Shell Exploration and Production Company, the Wyoming DEQ, or any other individuals or organizations mentioned herein.

Appendix. Supplementary material

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.atmosenv.2011.12.025.

References

CARB, 1993. Proposed Regulations for Low-Emission Vehicles and Clean Fuels – Staff Report and Technical Support Document. California Air Resources Board, Sacramento, CA. August 13, 1990. See also Appendix VIII of "California Exhaust Emission Standards and Test Procedures for 1988 and Subsequent Model Passenger Cars, Light Duty Trucks and Medium Duty Vehicles," as last amended September 22, 1993. Incorporated by reference in Section 1960.

CARB, 2000 May 5. Initial Statement of Reasons for the Proposed Amendments to the Regulation for Reducing Volatile Organic Compound Emissions from Aerosol Coating Products and Proposed Tables of Maximum Incremental Reactivity (MIR) Values, and Proposed Amendments to Method 310, 'Determination of Volatile Organic Compounds in Consumer Products'. California Air Resources Board, Sacramento, CA.

CARB, 2010 July. Final Statement of Reasons for Rulemaking: Public Hearing to Consider Proposed Amendments to the Tables of Maximum Incremental Reactivity (MIR) Values. California Air Resources Board, Sacramento, California. Available at: http://www.arb.ca.gov/regact/2009/mir2009/mir2009.htm.

Carter, W.P.L., 1994. Development of ozone reactivity scales for volatile organic compounds. J. Air & Waste Manage. Assoc. 44, 881–899.

Carter, W. P. L., 2000. Documentation of the SAPRC-99 Chemical Mechanism for VOC Reactivity Assessment, Report to the California Air Resources Board, Contracts 92-329 and 95-308, May 8. Available at: http://www.cert.ucr.edu/~carter/absts.htm#saprc99 and http://www.cert.ucr.edu/~carter/reactdat.htm.

Carter, W.P.L., 2010. Development of the SAPRC-07 chemical mechanism. Atmospheric Environment 44, 5324–5335. See also Carter, W.P.L., 2010. "Development of the SAPRC-07 Chemical Mechanism and Updated Ozone Reactivity Scales," Final report to the California Air Resources Board Contract No. 03-318. January 27. Available at: www.cert.ucr.edu/~carter/SAPRC.

DEQ, 2010. Data provided by Cara Keslar of the Wyoming Department of Environmental Quality to John Seinfeld on October 21, 2010. Data in Excel file named "DEQ Reactivity Inputs.xls". Except as indicated otherwise, data from the sheet titled "Jonah AQ and Met". Ambient VOC data taken from the sheet titled "Jonah VOC and aldehyde".

DEQ, 2011. Upper Green Winter Ozone Study. Web page at. http://deq.state.wy.us/aqd/Upper Green Winter Ozone Study.asp.

Environ, 2010. Final Technical Report, 2008 Winter Box Model Study. Prepared by U. Nopmongcol, G. Yarwood, and T. Stoeckenius. Environ International Corporation, Novato, CA. Available at: http://deq.state.wy.us/aqd/Ozone/Appendix%20A_BoxModel_WY_RevFinal.pdf.

Environ, 2011. Input files used in the Environ simulations provided by Uarporn Nopmongcol of Environ on January 11, 2011.

Field, R.A., Soltis, J., Emergy, B.R., Pearce, A.M., Montague, D.C., 2011. Pinedale Anticline Spatial Air Quality Assessment (PASQUA) Spatial Distribution Surveys 2010–2011. Univ. of Wyoming, Laramie, WY. Available at: http://www-das.uwyo.edu/ozone/index.html.

Grannas, A.H., et al., 2007. An overview of snow photochemistry: evidence, mechanisms and impacts. Atmos. Chem. Phys. 7, 4329–4373.

Jeffries, H.E., Sexton, K.G., Arnold, J.R., Kale, T.L., 1989. Validation Testing of New Mechanisms with Outdoor Chamber Data. In: Analysis of VOC Data for the CB4 and CAL Photochemical Mechanisms, vol. 2 Final Report, EPA-600/3-89-010b.

Lonneman, W.A., 1986. Comparison of 0600–0900 AM hydrocarbon compositions obtained from 29 cities. In: Proceedings APCA/U.S. EPA Symposium on Measurements of Toxic Air Pollutants, Raleigh, NC.

Rappenglük, B., 2010. WDEQ UGWOS 2010 HONO Measurements. Report to Meteorological Solutions Inc, Salt Lake City, UT, May, 2010.

RRWG, 1999a. VOC Reactivity Policy White Paper Prepared by the Reactivity Research Work Group Policy Team, October 1. Available at: http://www.narsto.org/voc_reactivity.

RRWG, 1999b. VOC Reactivity Science Assessment: Executive Summary Prepared by the Reactivity Research Working Group Science Team, May 5, Available at: http://www.narsto.org/voc_reactivity.

Schnell, R.C., Oltmans, S.J., Neely, R.R., Endres, M.S., Molenar, I.V., White, A.B., 2009. Rapid photochemical production of ozone at high concentrations in a rural site during winter. Nat. Geosci. 2, 120–123.

TUV, 2010. TUV 3.0 model version 3, November 2010. Downloaded from http://cprm.acd.ucar.edu/Models/TUV/. Madronich, S. and Flocke, S., Theoretical estimation of biologically effective UV radiation at the Earth's surface, in Solar Ultraviolet Radiation – Modeling, Measurements and Effects (Zerefos, C., Ed.). NATO ASI Series vol. I52, Springer-Verlag, Berlin, 1997.

Utah Department of Environmental Quality, 2011. Air Quality and Energy Development in the Uintah Basin. Web page at. http://www.deq.utah.gov/issue/uintah_basin/index.htm (accessed 03.11.11.).

Yarwood, G., Rao, S., Yocke, M., Whitten, G., 2005. Updates to the Carbon Bond Chemical Mechanism: CB05 Final report to the U.S. EPA, RT-0400675. Available at: www.camx.com.