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LaBarge Analysis Memorandum

To	Josh Nall (WDEQ)
From	Marco Rodriguez and Courtney Taylor (AECOM), Steve Reid (STI)
Subject	Summary of Additional Analysis for the LaBarge Monitoring Site
Date	November 17, 2014

The following memorandum presents an assessment of the ozone model performance at the LaBarge monitoring site compared to other monitoring sites in the Upper Green River Basin (UGRB).

Ozone formation during winter in the UGRB was modeled by AECOM Technical Services, Inc. (AECOM) and Sonoma Technology, Inc. (STI) for the Wyoming Department of Environmental Quality (WDEQ). The analysis of modeling results showed that both the CMAQ and CAMx models were generally not able to replicate episodes of elevated ozone concentrations observed at various monitoring sites within the UGRB during February and March 2008 (Rodriguez et al., 2014). However, both models were consistently able to predict both the timing and magnitude of observed ozone concentrations at the LaBarge monitoring site during all Intensive Operation Periods (IOP) as illustrated for IOP 1 in **Figure 1**.

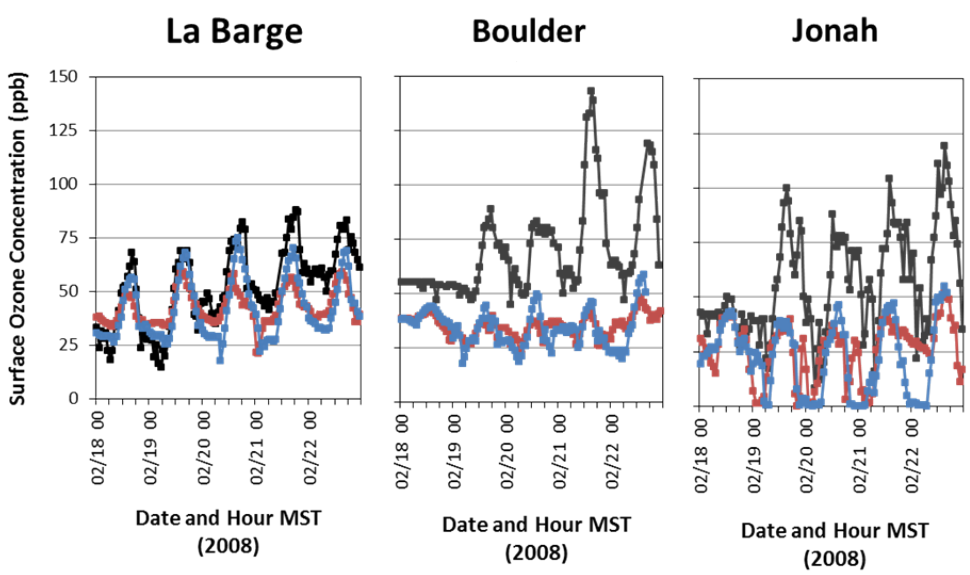

Figure 1 Time series of Observed (black), CAMx (red) and CMAQ (blue) ozone concentrations at LaBarge, Boulder, and Jonah during the first IOP

In order to understand the spatial differences in ozone model performance, several analyses were performed focusing on ozone precursors, namely volatile organic compounds (VOC)[1] and nitrogen oxides (NO_x). The analyses tend to focus on four monitoring sites – Boulder, Daniel, Jonah, and LaBarge – and the three IOPs. First, the gridded emissions inputs used for CMAQ and CAMx modeling were examined to compare VOC and NO_x emission levels in the vicinity of LaBarge to emissions of these pollutants at other sites in the UGRB. These comparisons included analysis of VOC-to-NO_x ratios. In addition, the modeled oil and gas VOC speciation profile was compared with other estimates of speciated VOCs.

Next, modeled VOC and NO_x concentrations in the vicinity of LaBarge were compared to modeled concentrations of these pollutants at other sites in the UGRB. These comparisons included timeseries plots isolating: different VOC species; NO_x; VOC-to-NO_x ratios; and formaldehyde to nitrogen dioxide (HCHO-to-NO_2) ratios. VOC-to-NO_x and HCHO-to-NO_2 ratios can aid in determining regions within the modeling domain that are in a NO_x or VOC limited regime (Duncan et al., 2009) and could be informative during the assessment of model performance. In addition the timeseries analyses, spatial plots of the VOC-to-NO_x and HCHO-to-NO_2 ratios are compared with spatial plots of ozone concentration on select days during IOP events.

In general, it was found that the modeled VOC emission rate is similar in the vicinity of the Boulder, Jonah, and LaBarge monitors, but that the NO_x emission rate at LaBarge is much lower than the other sites. Together this resulted in a VOC-to-NO_x emissions ratio at LaBarge that is much higher than the other sites. This finding is similar to the analysis of modeled VOC-to-NO_x concentrations, whereby the LaBarge site has higher VOC-to-NO_x concentration ratios than other sites.

An unexpected finding is that the modeled formaldehyde concentrations at Boulder and Jonah exhibit period spikes that are significantly higher than measurements. However, it should be noted that primary emissions of formaldehyde in the UGRB are low, which means that formaldehyde concentrations are likely driven by secondary formation. In addition, greater uncertainties are associated with the measurement method for carbonyls such as formaldehyde (TO11) than with the measurement method for other VOC species (TO14).

The remainder of this memorandum describes the analyses conducted and summarizes key findings.

Emissions Analysis

To support the assessment of air quality modeling results, several analyses of the emissions inputs were conducted. First, the emissions spatial distribution was reviewed for individual ozone precursors (VOC and NO_x), as well as emissions-derived VOC-to-NO_x ratios. Second, the VOC speciation data used to characterize oil and gas sources in the UGRB was reviewed by comparing the speciated data from this study to other available speciation profiles for oil and gas sources.

VOC-to-NO_x Ratios

VOC emissions and VOC-to-NO_x emissions ratios were examined using two methods: (1) mass-based analysis; and (2) a molar-based analysis. The molar-based results are presented in terms of moles of

[1] This memorandum includes ethane as part of the VOC analysis, so while the term VOC is used throughout the memorandum it actually represents non-methane hydrocarbons.

carbon (moles-C), making the results more comparable to ambient monitoring data.[2] For both mass-based and molar emissions data, the data was processed so that local emissions around each monitoring site could be extracted and examined.

Mass-Based VOC-to-NO_x Ratios

As a first step, emissions data and calculated mass-based pollutant ratios were summarized: (1) at the county level, and (2) for a "region of influence" around each monitoring site. These regions of influence are based on wind speed data[3] for each site and represent the average distance that emissions could potentially travel over a 3-hour period (roughly a 40-km radius around each site). At the county level, it was found that NO_x levels are much higher in Sublette County than in Lincoln and Sweetwater Counties, largely as a result of active drilling operations during 2008 in Sublette County. These higher NO_x emissions result in a mass-based VOC-to-NO_x ratio of 2.3 in Sublette County, which is much lower than corresponding ratios in Lincoln (20.3) and Sweetwater (10.1) counties (**Figure 2**). A similar pattern was identified for the regions around ambient monitoring sites, also shown in **Figure 2**. Sublette County sites (Boulder, Daniel, and Jonah) have higher NO_x emissions and lower VOC-to-NO_x ratios than the LaBarge site near the Sublette-Lincoln border.

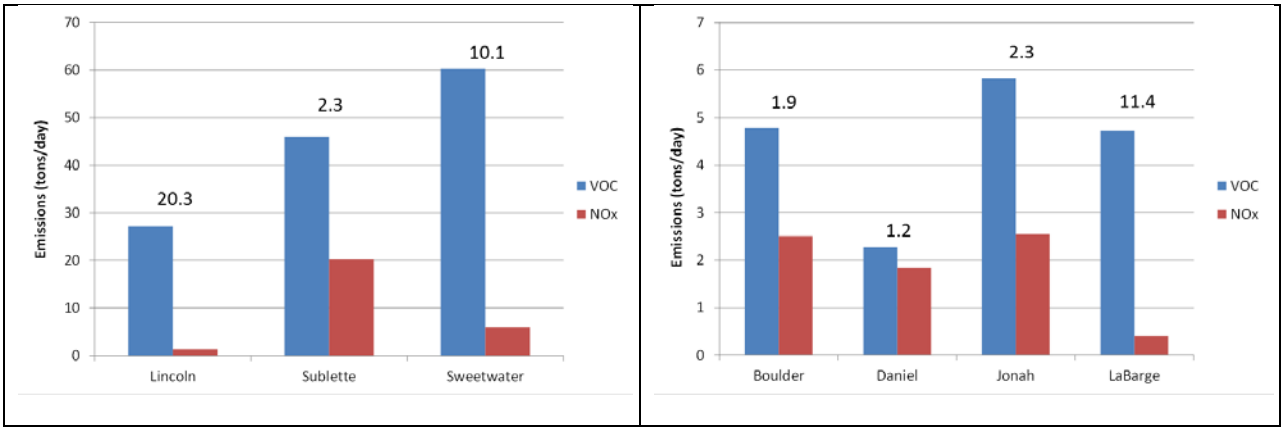

Figure 2 Summary of VOC and NO_x emissions levels by county (left) and by monitoring site (right). Corresponding VOC-to-NO_x ratios are shown above each set of bars

[2] For molar-based VOC-to-NOx ratios, VOC emissions data are defined on the basis of carbon bond types and are used to represent a grouping of organic compounds. These speciated emissions inputs were aggregated to a total VOC value in molar units using the following equation, which was also subsequently applied to CMAQ outputs:

VOC (moles-C) = (2*ALD2 + 3*ALDX + 6*BENZENE + 2*ETH + 2*ETHA + 2*ETOH + FORM + 4*IOLE + 5*ISOP + MEOH + 2*OLE + PAR + 10*SESQ + 10*TERP + 7*TOL + 8*XYL)

Note that the multipliers indicate the assumed number of carbon atoms in a molecule of each lumped species and are used to present the results in terms of moles of carbon (moles-C). This equation is based on the VOC definition provided by the USEPA's AMET tool available for download at https://www.cmascenter.org.

[3] Average wind speed data for the 0400 to 0700 time period during February and March 2008 were used for this analysis. These hours match the first canister sample collection period. Note that early morning average wind speeds for IOP days were also evaluated and found to be very similar to the Feb-Mar averages (wind speeds were slightly lower on IOP days at Boulder and Daniel, and slightly higher on IOP days at Jonah).

Molar-Based VOC-to-NO_x Ratios

In addition to the mass-based pollutant ratios shown above, molar VOC-to-NO_x emissions ratios in moles-C/mole were using the equation in footnote 2. **Figure 3** shows the spatial distribution of the VOC and NO_x emissions data.[4] This figure indicates that VOC emissions levels are similar in the Pinedale/Jonah and LaBarge areas, while NO_x emissions are generally higher in the Pinedale/Jonah than in the LaBarge area. As a result, emissions-based VOC-to-NO_x ratios (shown in **Figure 4**) are highest in the LaBarge area and are generally much lower across the remainder of the domain. (Note that this molar method produces higher VOC-to-NO_x ratios than the mass-based method, so it is important to focus on relative differences across the domain rather than compare the results to **Figure 2**.)

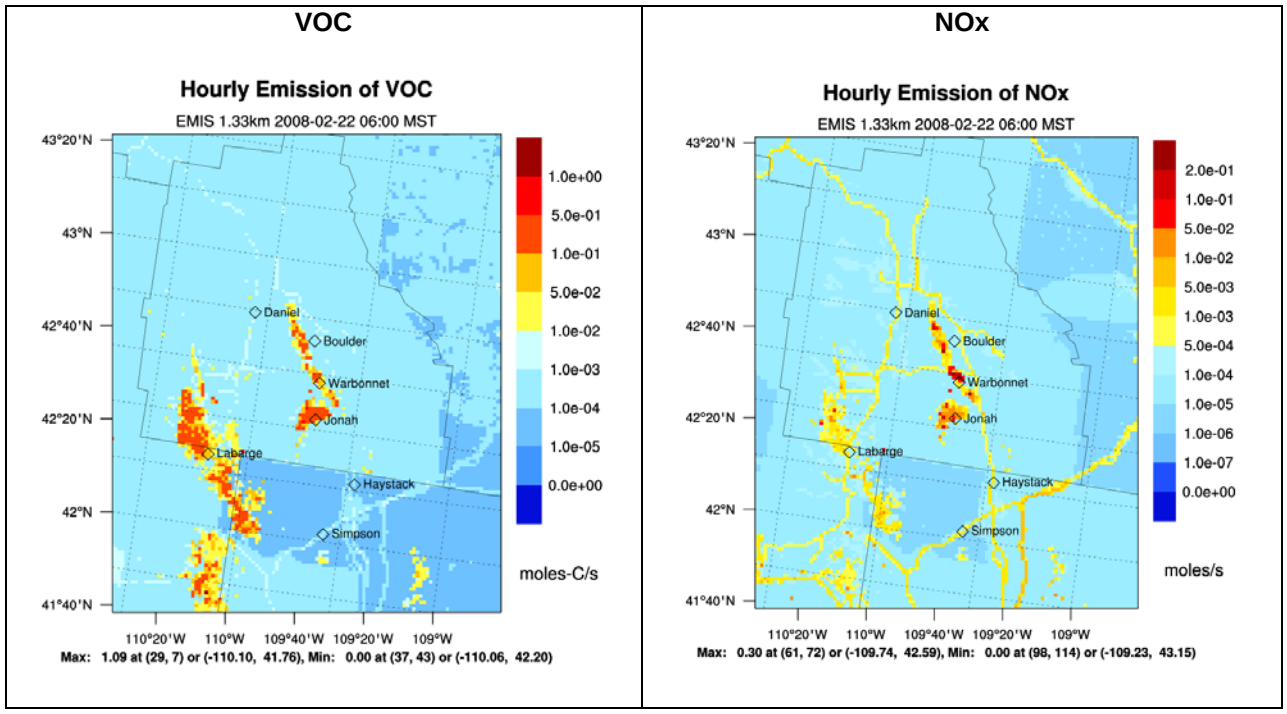

Figure 3 Spatial plots of VOC and NOx emissions, February 22, 2008 at 0600

Where possible, observed VOC-to-NO_x ratios were calculated for early morning hours (0400-0700) on each IOP day and compared with emissions-based pollutant ratios for the same time period.[5,6] Measurement data availability limited these comparisons to the Jonah site and one day at the Daniel site, as shown in **Figure 5**. At the Daniel site, emissions-based VOC-to-NO_x ratios

[4] Figures 3 and 4 show the total emissions within a grid cell regardless of the release height of the emissions.
[5] For comparisons between emissions inventories and ambient measurements, it is best to use data from early morning hours when photochemistry is not active and monitoring sites are most likely to be impacted by local emissions.
[6] For the ambient data, individual hydrocarbon species in the Upper Green River Winter Ozone Study (UGWOS) 2008 database were mapped to the SMOKE/CMAQ lumped species using species assignments in the documentation for the Carbon Bond V (CB05) chemical mechanism (Yarwood et al., 2008). Concentrations for these lumped species were summed to produce a "CMAQ VOC" parameter in ppbC that is comparable to the total VOC values derived from the speciated emissions data and the CMAQ modeling outputs.

were consistently near 20, while the available ambient ratio (during 0400-0700 on February 21, 2008) was 284. At the Jonah site, emissions-based VOC-to-NO_x ratios were around 5, while ambient ratios range from about 20 to 60.

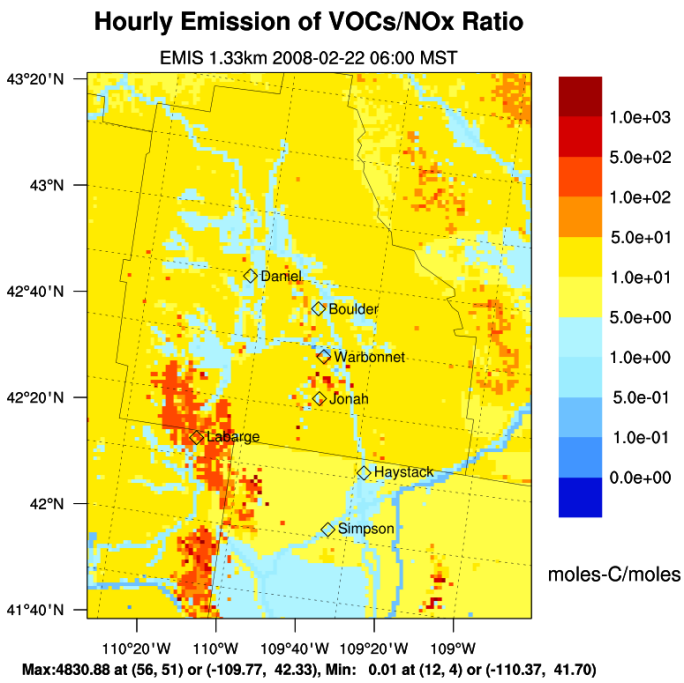

Figure 4 Spatial plot of VOC-to-NO_x emission ratios, February 22, 2008 at 0600

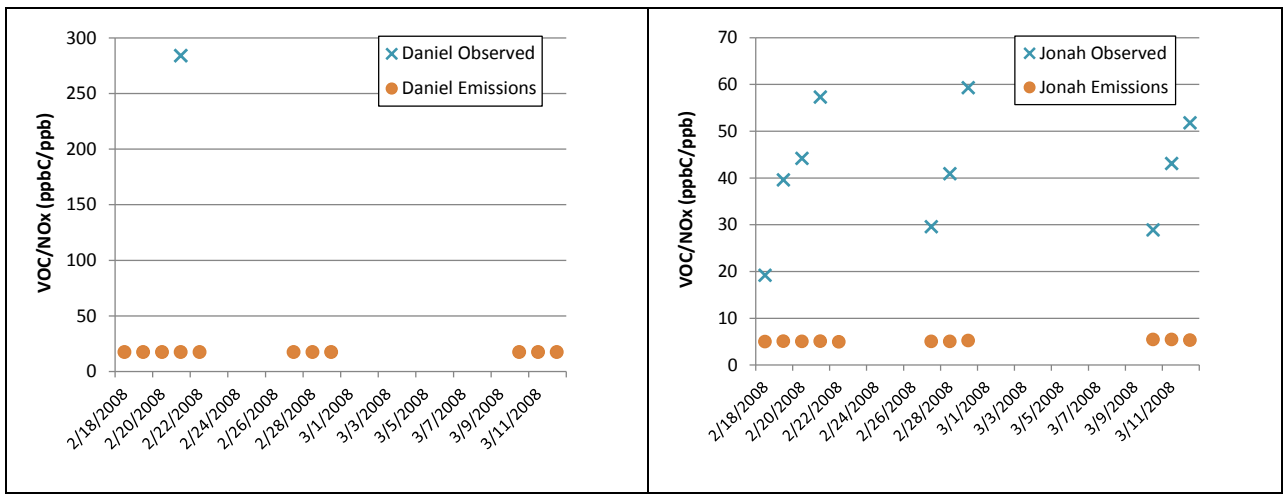

Figure 5 Comparison of emissions-based and observed VOC-to-NO_x ratios at the Daniel (left) and Jonah (right) sites

Speciation Profiles

For oil and gas sources, air quality model-ready emissions inputs were developed using detailed oil and gas emissions inventories for 2008 provided by WDEQ. These inventories included speciated hydrocarbon emissions for Sublette County for several source categories, including tanks and pressurized vessels, glycol dehydration units, and fugitive losses. The speciated hydrocarbon emissions were reported by individual oil and gas operators in Sublette County in response to an emissions inventory data request. Analysis of the data reported by various operators shows that the speciation of hydrocarbon emissions are generally consistent. For example, the operator-specific VOC speciation reported for fugitive losses shows that, while two operators report somewhat lower fractions of methane and somewhat higher fractions of ethane and propane than the other operators, the data for more reactive species are very similar (**Figure 6**).

The only source category for which significant differences in speciation appear is glycol dehydration units (GDUs). For this source, the various operators report methane fractions ranging from 20% to 63%, as shown in **Figure 7**. In cases where lower methane fractions are reported, higher weight fractions are reported for more reactive compounds. For example, BP reports a methane fraction of only 25%, while the hexane and toluene fractions reported by BP are the highest of any operator.

To further evaluate the hydrocarbon speciation data reported by Sublette County operators, the VOC speciation profiles derived from these data were compared to other available speciation profiles for oil and gas sources. Specifically, we used speciation profiles assembled for the WRAP Phase III emissions inventory for this comparison. The WRAP profiles were derived from gas composition analysis data provided by operators in various oil and gas basins in the western U.S. (e.g., Colorado's Denver-Julesburg and Piceance Basins). Like the VOC speciation profiles developed from the Sublette County hydrocarbon data, these WRAP profiles were prepared for the CB05 chemical mechanism.

Speciation profile comparisons showed that, in general, the VOC profiles developed from Sublette County hydrocarbon data were quite similar to speciation profiles developed for other regions. For example, an average speciation profile for fugitive losses was developed using data from all operators in Sublette County, and this average profile is comparable to fugitive speciation profiles from basins in Colorado, as shown in **Figure 8**. However, an average speciation profile for GDUs developed from Sublette County data has higher fractions of paraffins (PAR) and toluene (TOL) than profiles for GDUs developed for basins in Colorado (see **Figure 9**). As described above, these differences are, in part, due to the variability in the data for this source category across various fields and formations, as reported by Sublette County operators.

The speciation profiles in the emissions inventory have an important influence in the model's concentrations. **Figure 10** presents the total VOCs (in ppbC) in the form of bar chart showing the composition profiles from CMAQ hourly model concentrations at monitoring sites in the UGRB for all IOPs. VOC model concentrations are the largest at Jonah with peak concentrations close to 1400 ppbC, while Daniel exhibits the lowest concentrations with peak concentrations of 80 ppbC. Boulder and LaBarge are intermediate with concentrations peak in the 400 to 800 ppbC range. In general at all sites, the bulk of modeled concentrations is due to paraffin and ethane concentrations with smaller contributions from toluene and xylene. The rest of the VOC concentrations are presented in the figure but their contribution to model-predicted concentrations is negligible.

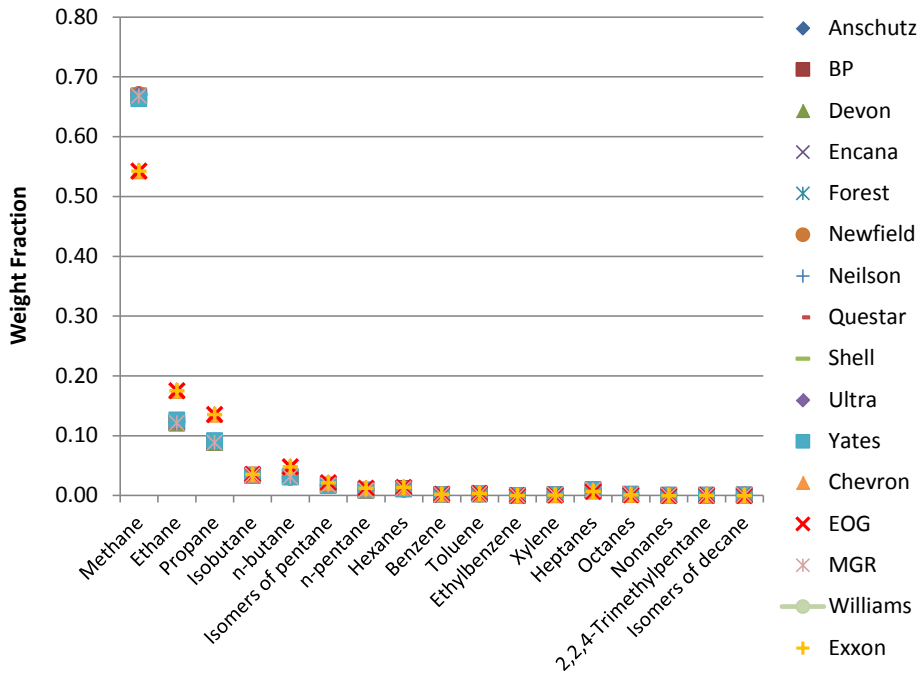

Figure 6 Hydrocarbon speciation for fugitive losses reported by Sublette County oil and gas operators.

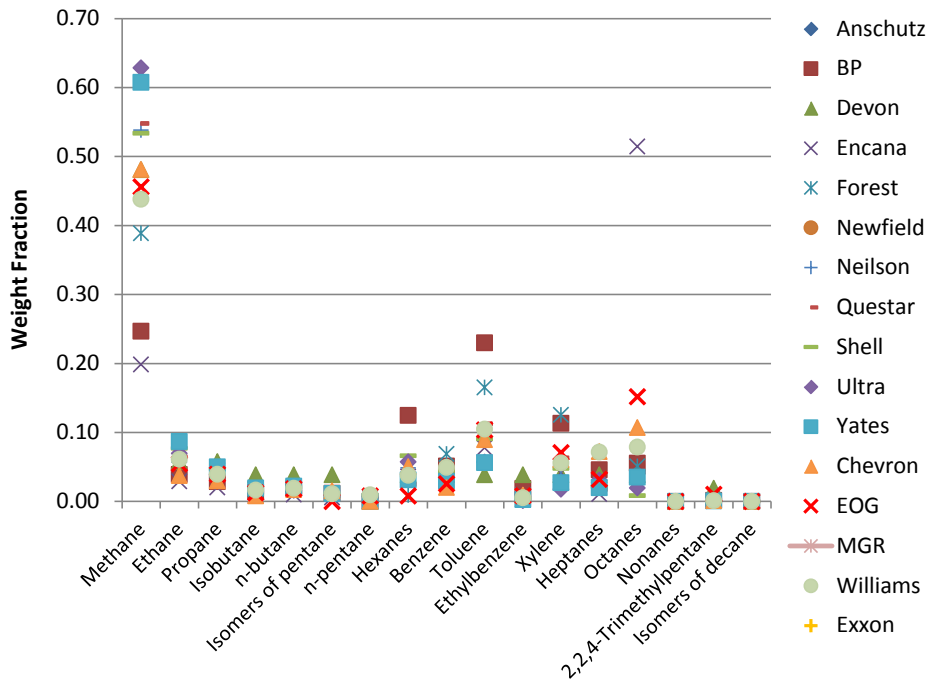

Figure 7 Hydrocarbon speciation for glycol dehydration units (uncontrolled) reported by Sublette County oil and gas operators.

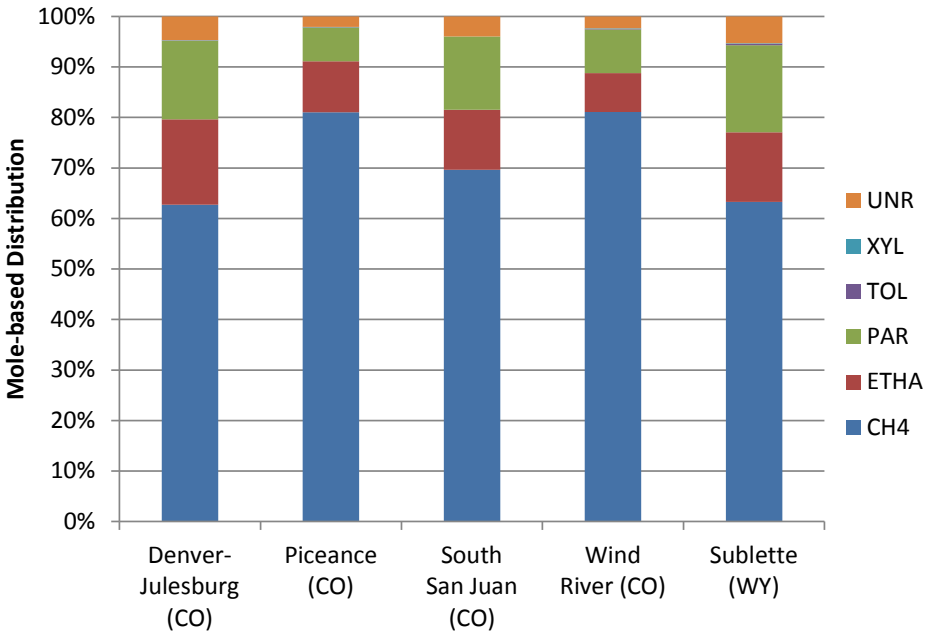

Figure 8 Comparison of VOC speciation profiles for fugitive losses developed from basin-specific data

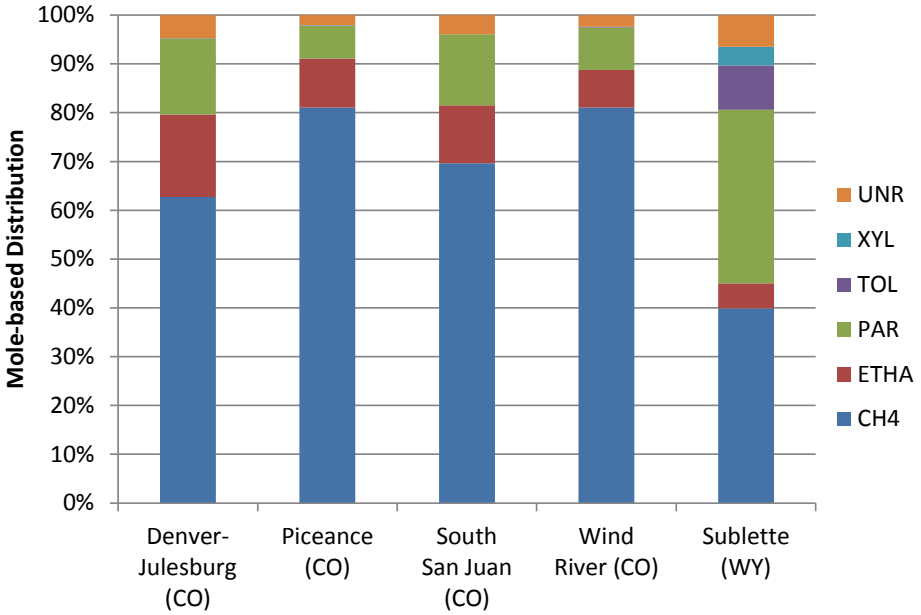

Figure 9 Comparison of VOC speciation profiles for glycol dehydration units (uncontrolled) developed from basin-specific data

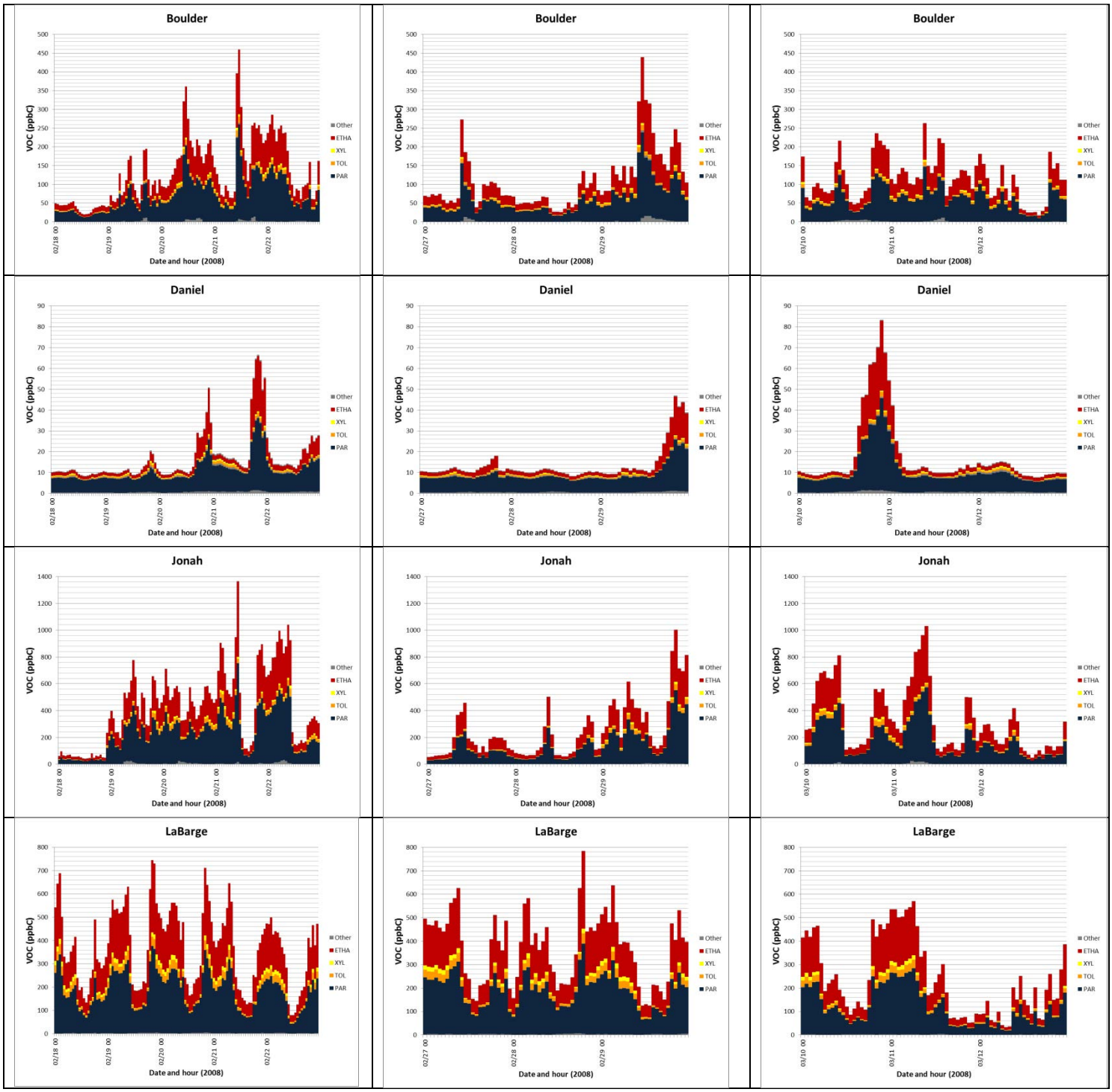

Figure 10 Time Series bar charts of CMAQ total VOC concentrations in ppbC at Boulder, Daniel, Jonah, and LaBarge During the First (left), Second (center) and Third (right) IOPs.

Model Concentrations Analysis

To build on the emissions inventory analyses described above, similar analyses were performed on air quality model outputs and ambient monitoring data. To generate a total VOC estimate from model-predicted concentrations, the same approach described in the emissions analysis section was used as described in footnote 2, with the additional conversion between model units (ppbV) to ppbC. Model results are compared with measurements collected during the 2008 Upper Green River Winter Ozone Study (UGWOS). Several analyses were conducted comparing modeled to measured concentrations. Analyses include timeseries of individual pollutant concentrations, timeseries of pollutant ratios, and spatial plots of pollutant ratios.

Time Series of Individual Pollutants

Time series plots of selected VOC species and NO_x are shown in **Figures 11** through **14**. For the VOC species, the 3-hr canister data is compared to hourly model concentrations. In general, the time series comparison of CMAQ model-predicted concentrations with measured precursor VOC and NO_x yields very similar results to those reported for CAMx in the interim report (Rodriguez et al., 2014).

Paraffin concentrations are compared in **Figure 11**, which shows that both CMAQ and CAMx significantly underpredict concentrations at sites with measurements (Boulder, Daniel, and Jonah), often by an order of magnitude. Although measurements were not available at the LaBarge site, model-predicted paraffin concentrations at LaBarge are significantly higher than other areas. This finding is similar for xylene, a more reactive VOC species. For xylene, both models show consistent and substantial underpredictions relative to measurements (**Figure 12**).

For formaldehyde, results are more ambiguous. Primary emissions of formaldehyde in the UGRB are low, which means that modeled and measured concentrations are likely to be driven by secondary formation. Formaldehyde is formed in the atmosphere through the photochemical oxidation of VOCs, and removal mechanisms include photolysis and reaction with the hydroxyl radical (OH). In addition, it should be noted that greater uncertainties are associated with the measurement method for carbonyls such as formaldehyde (TO11) than with the measurement method for other VOC species (TO14). **Figure 13** shows model-predicted and measured formaldehyde concentrations which are generally comparable, although CMAQ produces periodic spikes in formaldehyde concentrations not observed in the CAMx results nor in the available 3-hr average observations.

During the IOP periods hourly NO_x observations are available only at the Daniel and Jonah sites. As shown in **Figure 14**, both models underpredict NO_x concentrations at Daniel, which is not in the vicinity of any large NO_x sources. At Jonah, the models somewhat underpredict NO_x concentrations and do not to capture peak concentrations exceeding 100 ppb. It should also be noted that, similar to the spatial analysis of the NO_x emissions, modeled NO_x concentrations at LaBarge are much lower than model-predicted concentrations at Boulder and Jonah but higher than Daniel (**Figure 14**).

Figure 11 Time Series of Observed (red), CMAQ (blue), and CAMx (green) paraffin concentrations at Boulder, Daniel, Jonah, and LaBarge During the first (left), second (center), and third (right) IOPs

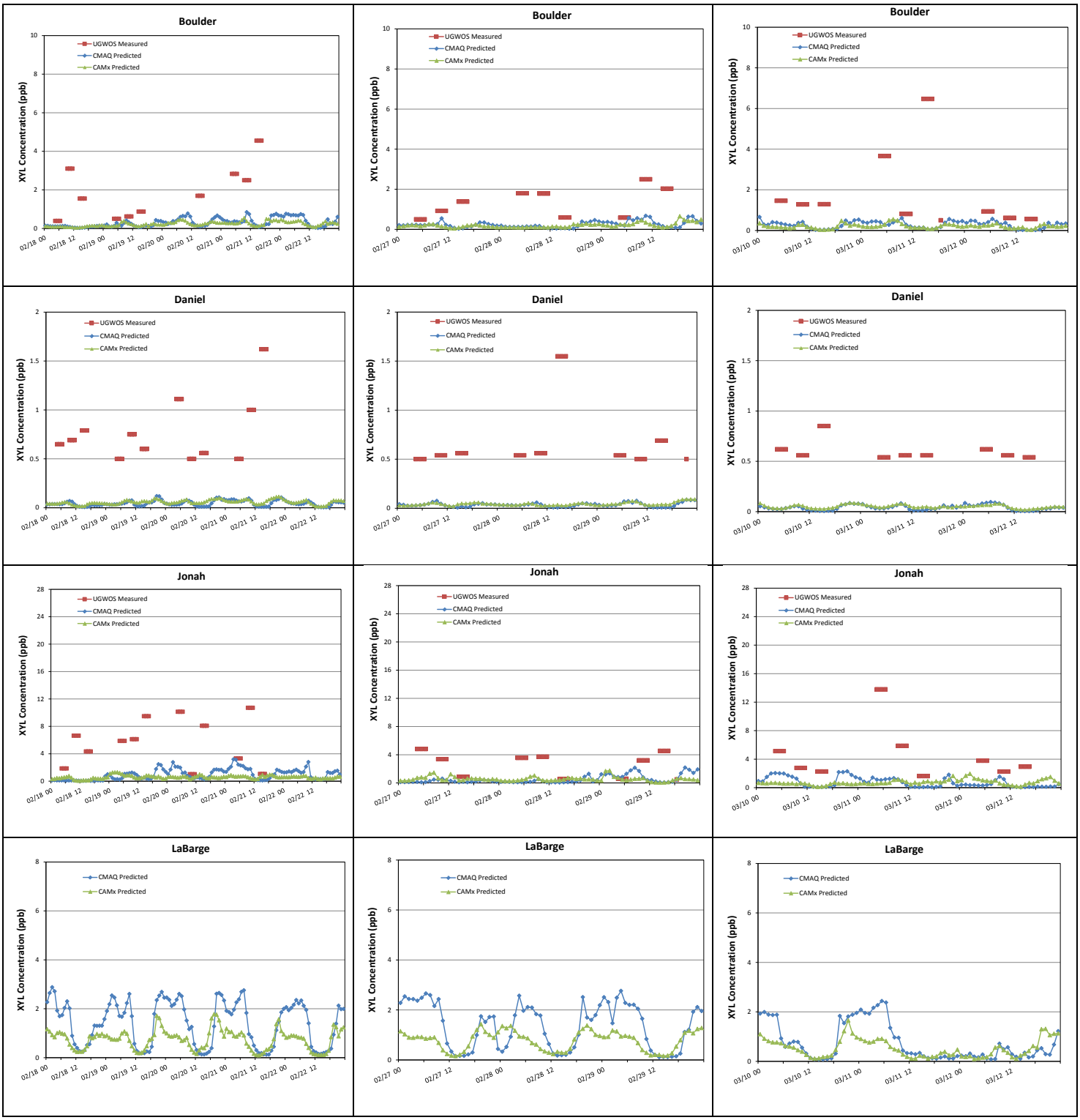

Figure 12 Time Series of Observed (red), CMAQ (blue), and CAMx (green) xylene concentrations at Boulder, Daniel, Jonah, and LaBarge during the first (left), second (center), and third (right) IOPs

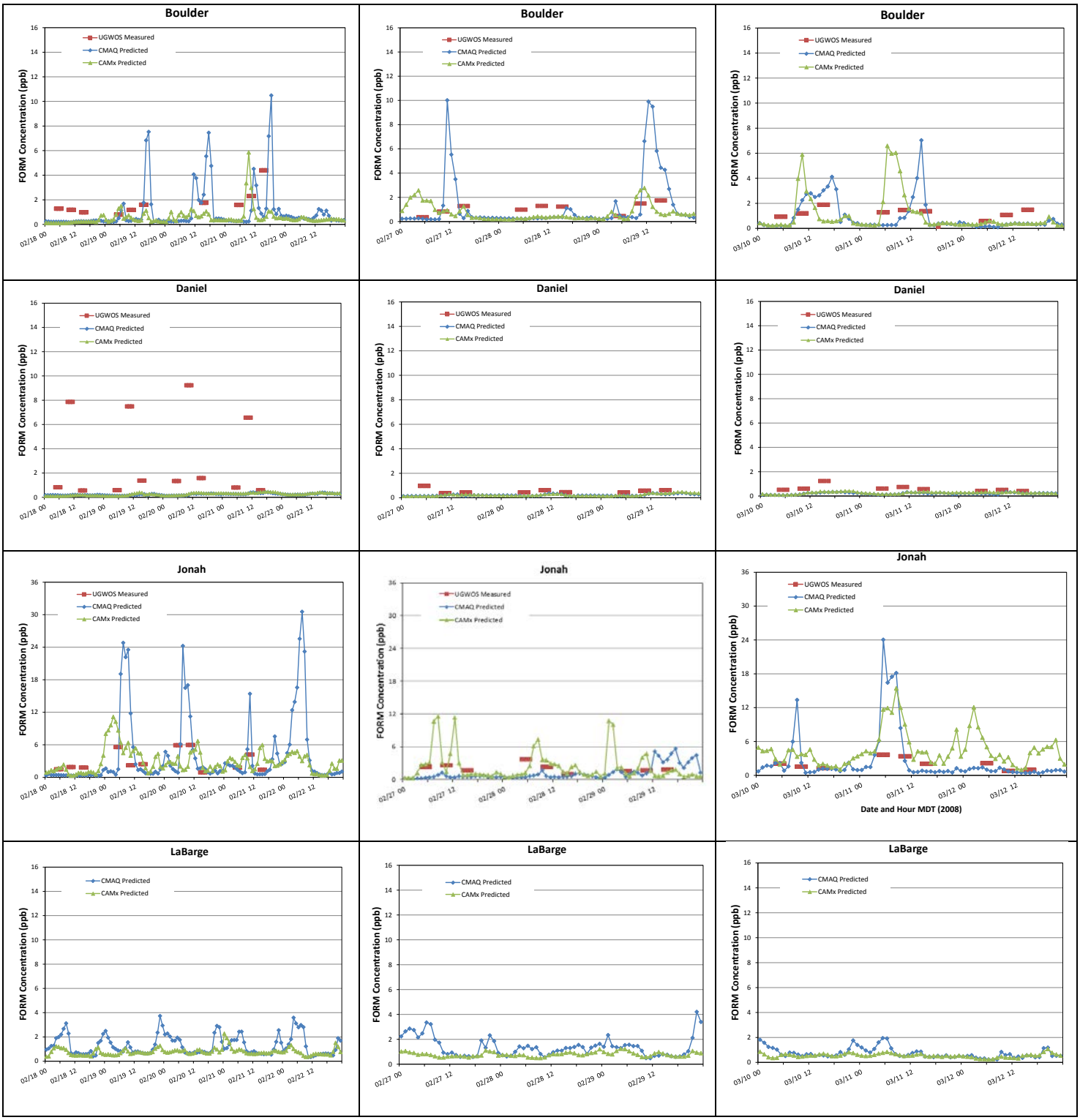

Figure 13 Time Series of Observed (red), CMAQ (blue), and CAMx (green) formaldehyde concentrations at Boulder, Daniel, Jonah, and LaBarge during the first (left), second (center), and third (right) IOPs

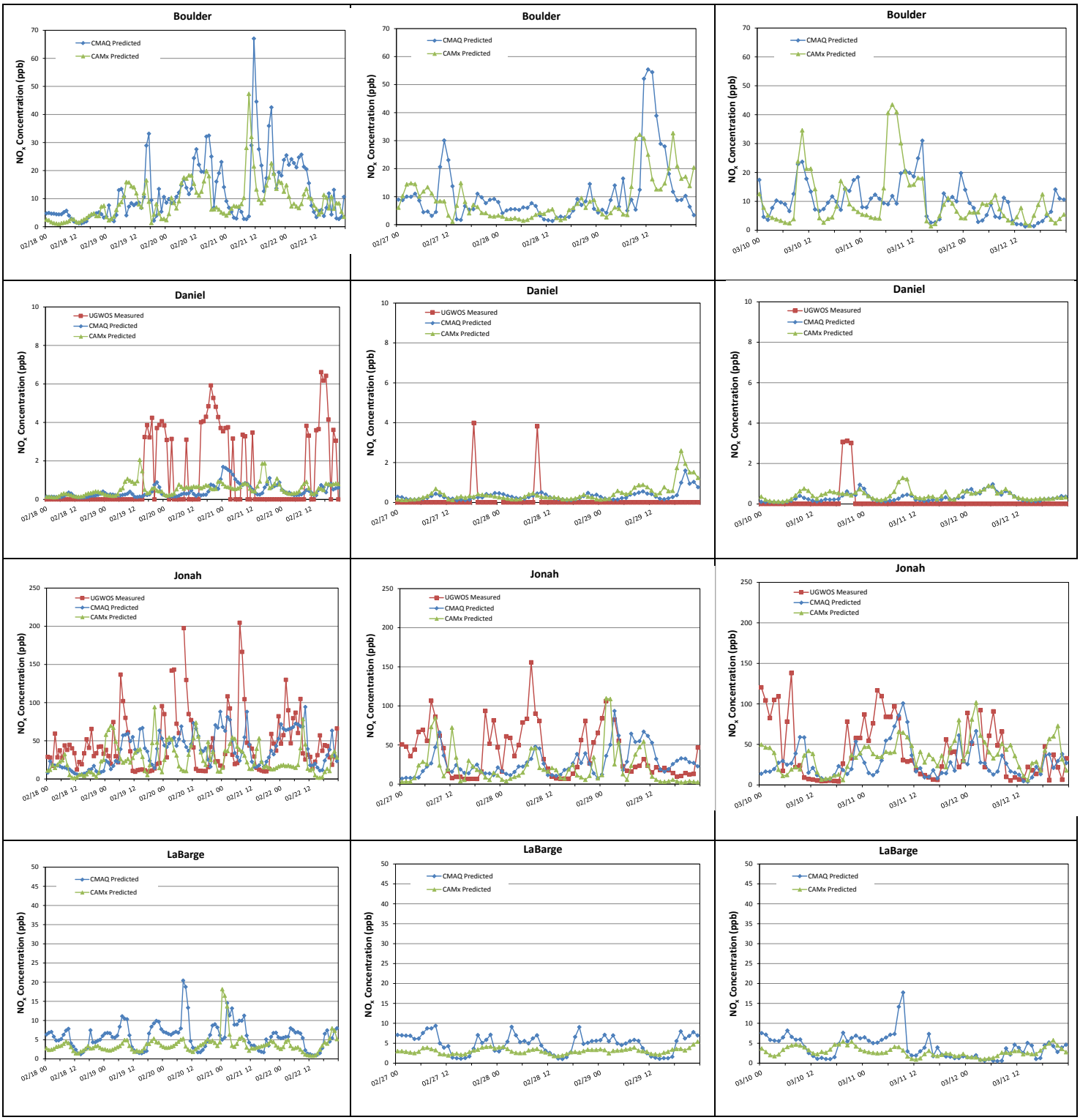

Figure 14 Time Series of Observed (red), CMAQ (blue), and CAMx (green) NOx concentrations at Boulder, Daniel, Jonah, and LaBarge during the first (left), second (center), and third (right) IOPs

Time Series of Pollutant Ratios

Figure 15 shows estimates of VOC-to-NOx concentration ratios based on CMAQ outputs and measurements where available.[7] In general, the VOC-to-NO_x ratios are highest at the LaBarge site, where they range from values of 50 to 200 ppbC/ppb. At the Daniel site, the CMAQ ratios are generally near 50 and are well below ratios calculated from available ambient data. However, it should be noted that VOC-to-NO_x ratios may not be as meaningful for the Daniel site, which is not in the vicinity of any large NO_x sources and where pollutant concentrations are generally low (see **Figure 14**).

The lowest modeled VOC-to-NOx ratios occur at the Boulder and Jonah sites, where ratios are generally below 20. At Jonah, modeled ratios are well below ratios calculated from ambient data that range from 20 to 240. At LaBarge, the high VOC-to-NO_x ratios are driven by VOC concentrations that are comparable to those modeled at other sites, combined with lower NO_x concentrations.

Formaldehyde-to-NO_2 (HCHO-to-NO_2) ratios have been used to diagnose the sensitivity of surface ozone concentrations to NO_x and VOC emissions. Specifically, HCHO-to-NO_2 ratios above one have been identified with NO_x-limited regimes (i.e., ozone concentrations are most sensitive to changes in NO_x emissions); while HCHO-to-NO_2 ratios below one indicate NO_x-saturated conditions (Martin et al., 2004). As previously noted, CMAQ HCHO results showed periodic concentration spikes that were not seen in CAMx results or ambient measurements, which introduces uncertainty into conclusions that can be drawn from modeled HCHO-to-NO_2 ratios alone.

Modeled and measured HCHO-to-NO_2 ratios are shown in **Figure 16.** Modeled HCHO-to-NO_2 ratios were consistently below one at Boulder and Jonah, but had consistent diurnal cycles that peaked well above one at the Daniel site. The scarcity of NO_x emissions sources in the vicinity of Daniel probably contributes to the higher HCHO-to-NO_2 ratios at that site. At the LaBarge site, modeled HCHO-to-NO_2 ratios are consistently higher than those at Boulder and Jonah and generally peak near or above one.

The higher VOC-to-NO_x and HCHO-to-NO_2 pollutant ratios at the LaBarge site indicate that the region around the site is likely NO_x-limited, while the lower *modeled* ratios around the Boulder and Jonah sites indicate that the *modeled* ozone are VOC-limited (i.e., ozone concentrations are most sensitive to changes in VOC emissions). It is important to emphasize that findings based on model data are only as accurate as the model performance for that area. While the low modeled pollutant ratios near Boulder and Jonah indicate that the *modeled* ozone formation is more sensitive to VOC concentrations this is not necessarily indicative of the actual ozone concentrations given the poor model performance near Boulder and Jonah.

Spatial Plots of Pollutant Ratios

Further examination of the CMAQ modeled VOC-to-NO_x ratios, the HCHO-to-NO_2 ratios, and ozone concentrations are shown in **Figure 17** at 1400 MST for the same days selected from each IOP in the interim report (February 22, February 28, and March 11). In general, **Figure 17** shows that both ratio indicators have significant similarities (good spatial correlation).[8] It also shows that the southwestern part of the domain (near and around the LaBarge monitoring site) has pollutant ratios indicative of a NO_x-limited regime, consistent with the findings from the timeseries analyses. This region is where ozone formation and higher concentrations were consistently observed in the analysis of the base case results.

[7] Note that only CMAQ results are presented in **Figure 15** since CAMx model outputs were only available for a subset of VOC species.
[8] Note that high pollutant ratios in the northeastern part of the domain occur in mountainous areas with few emission sources and therefore the ratios are less meaningful there.

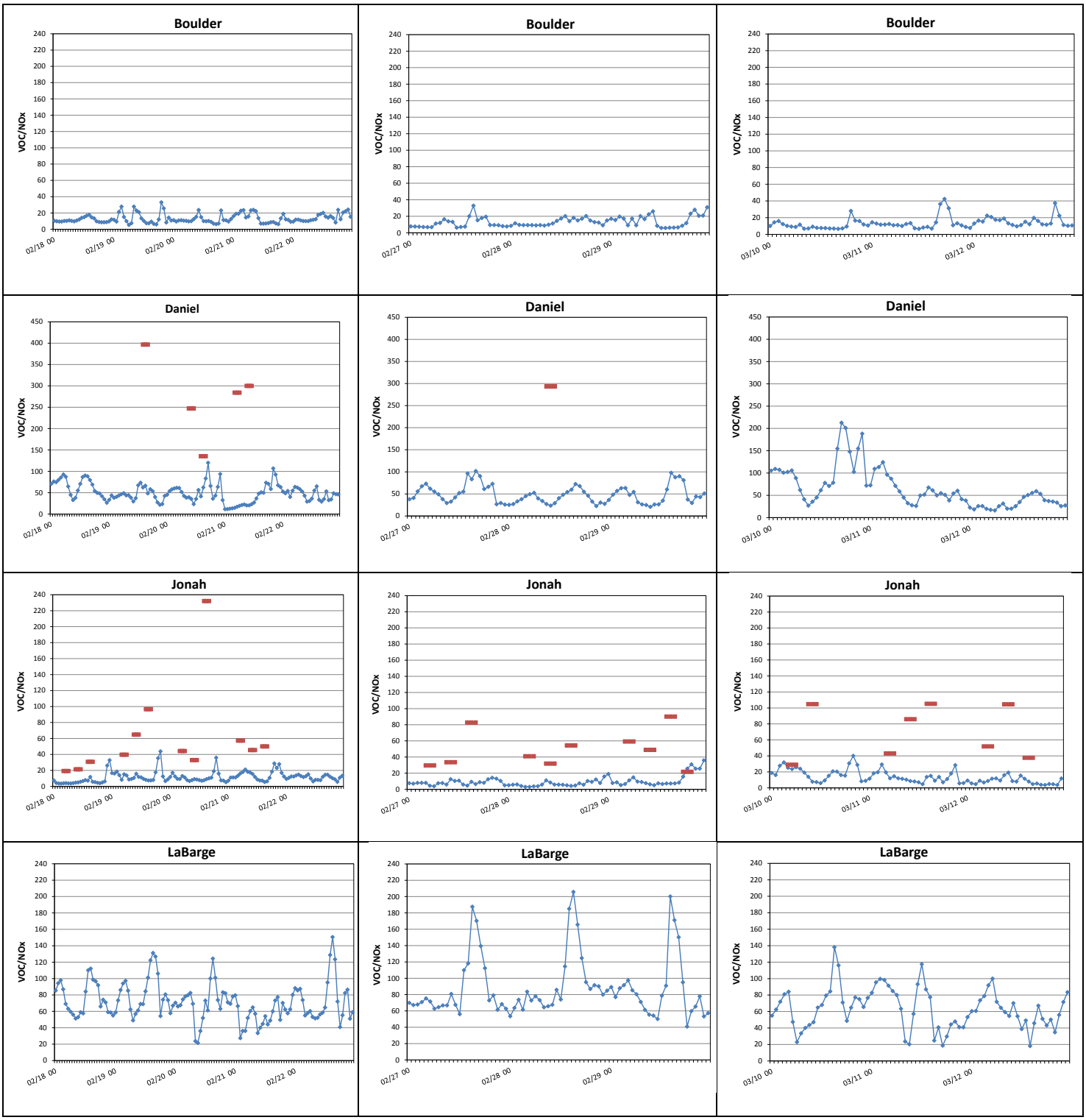

Figure 15 Time Series of CMAQ (blue) and observed (red) VOC-to-NOx ratios at Boulder, Daniel, Jonah, and LaBarge during the first (left), second (center), and third (right) IOPs

Figure 16 Time Series of CMAQ (blue), CAMx (green) and observed (red) HCHO-to-NO_2 Ratios at Boulder, Daniel, Jonah, and LaBarge during the first (left), second (center), and third (right) IOPs

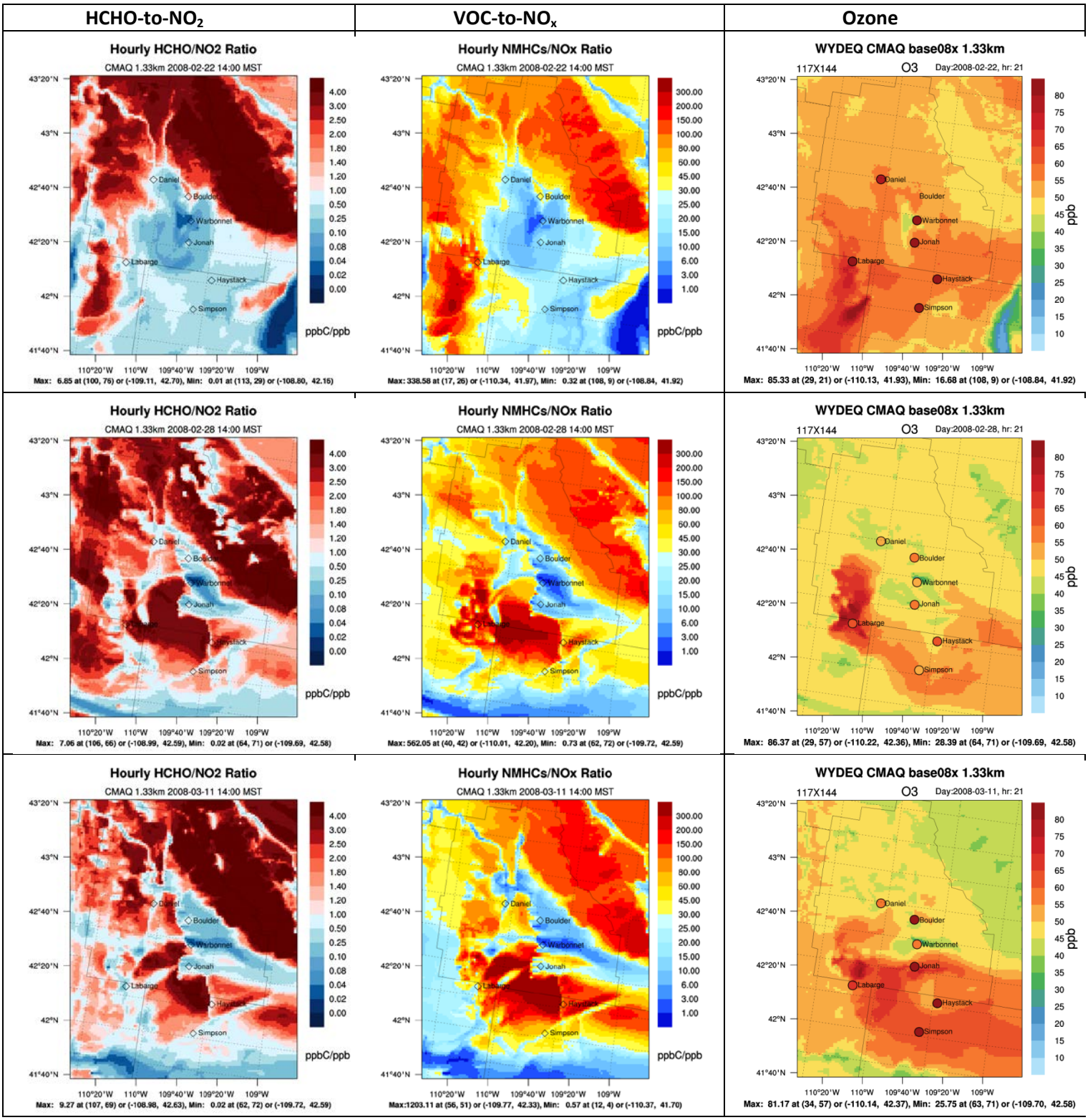

Figure 17 HCHO-to-NO_2 ratios, VOC-to-NO_x ratios, and surface ozone concentrations (left to right) at 1400 MT on February 22, February 28, and March 11, 2008 (top to bottom).

Although **Figure 17** shows values at a specific hour (when ozone concentrations were higher in the model), it was verified that the high values in the ratio indicators in the southwestern region of the domain were fairly persistent throughout the day. **Figure 17** also shows that in general the region around the Boulder and Jonah monitoring sites exhibit the lowest values for the ratio indicators, with the HCHO-to-NO_2 generally below one (VOC-limited).

Conclusions

The analyses described above were performed to understand differences in ozone model performance at the LaBarge site compared to other monitors in the UGRB. As previously noted, it is important to emphasize that findings based on model data are only as accurate as the model performance for a given area. In summary, key findings from these analyses include:

- Both CMAQ and CAMx show substantial underpredictions of VOC species paraffin and xylene, while CMAQ formaldehyde concentrations at Boulder and Jonah are often higher than measurements.
- The models underpredict NO_x levels to a lesser degree, failing to capture peak (>100 ppb) NO_x concentrations. Consistent with the emissions inventory, modeled NO_x concentrations at LaBarge are generally lower than NO_x concentrations at Boulder and Jonah.
- Due to the lower NO_x emissions around LaBarge, modeled pollutant ratios (VOC-to-NO_x ratios and HCHO-to-NO_2) are higher at LaBarge than at Jonah and Boulder. Both spatial and temporal analyses of pollutant ratio patterns appear to correlate well with modeled ozone concentrations.
- Both emissions-based and concentration-based pollutant ratios are also substantially higher in the region around the LaBarge site than in the regions around the Jonah and Boulder sites.
- Modeled pollutant ratios indicate that the area around LaBarge is NO_x-limited, while the areas around Boulder and Jonah are predicted by the model to be VOC-limited with respect to ozone formation.
- The speciated hydrocarbon data collected from Sublette County operators shows that speciated data reported for various VOC-emitting processes are generally consistent across the various operators. In addition, the VOC speciation profiles derived from Sublette County data are generally comparable to speciation profiles developed for other oil and gas production areas in the western region.

These findings indicate that the higher modeled ozone concentrations observed around the LaBarge site are driven by higher VOC-to-NO_x ratios in that region, which are more favorable for ozone formation. Lower VOC-to-NO_x ratios around the Boulder and Jonah sites could indicate an overestimate of NO_x emissions, an underestimate of VOC emissions, or both. For the upstream oil and gas industry, NO_x emissions estimates are generally based on higher quality emission factors and are generally considered to be more accurate than VOC emissions, which include fugitive sources and assumed control efficiencies. Coupled with better model performance for NO_x than for VOC species, this may indicate that VOC emissions might be under-represented in the Sublette County inventory. A potential exception to this trend is formaldehyde, for which modeled concentrations show periodic spikes that are significantly higher than measured concentrations. However, primary emissions of formaldehyde in the UGRB are low, and the measurement method for carbonyls such as formaldehyde (TO11) has greater uncertainties than the measurement method for other VOC species (TO14). VOC emissions could also be under-represented in the LaBarge area as well, but since that area is NO_x-limited, changes in VOC emissions will have less effect on modeled ozone concentrations.

As previously noted in the interim modeling report for this project (Rodriguez et al., 2014), several “off-the-shelf” modeling options were explored during this study, including sensitivity analyses such as an additional HONO emissions source to account for snow pack chemistry. The models’ poor performance for ozone and precursor concentrations at the observation sites of Boulder, Jonah, and Daniel may indicate that future steps for improving model peformance should evaluate model and/or chemical mechanism development, which are options beyond the scope of this project.

References

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