

Logan Maintenance
State Implementation Plan

Photochemical Model Performance
Evaluation

Utah Division of Air Quality

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Photochemical Model Performance Evaluation

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1. Introduction

To assess how accurately the photochemical model predicts observed concentrations and to demonstrate that the model can reliably predict the change in pollution levels in response to changes in emissions, a model performance evaluation was conducted. This model performance evaluation also provides support for the model modifications that were implemented (ammonia injection, ammonia surface resistance, ozone deposition velocity, snow albedo, vertical diffusion modifications and paved road dust emissions adjustment) to more accurately reproduce winter-time inversion episodes. A detailed explanation of these model modifications was provided earlier.

Various statistical metrics and graphical displays were considered for evaluating the model with the objective to determine whether modeled variables are comparable to observations. These included:

- Time series plots of modeled and observed 24-hr PM2.5 concentrations.
- Scatter plots of modeled and observed 24-hr PM2.5 concentrations.
- Coefficient of determination, R^2 , which shows the degree to which modeled and observed 24-hr PM2.5 concentrations are linearly related.
- Pie charts showing modeled and observed PM2.5 chemical species
- Soccer plots with purpose to visualize model performance of both bias and error on a single plot.
- Mean bias, which is a metric that averages the model/observation residual paired in time and space.
- Normalized mean bias, which is a statistic of normalized mean bias to the average observed value.
- Normalized mean error, which is determined by normalizing the mean error by average observation.
- Mean fractional bias, which is determined by normalizing the mean bias by the average of observed and modeled concentrations.
- Mean fractional error, which is determined by normalizing the mean error by the average of observed and modeled concentrations.
- Mean error, which is a performance statistic that averages the absolute value of the model/observation residual paired in time and space.

Available ambient monitoring data were also used for this photochemical model performance evaluation. Data included ozone (O_3), nitrogen oxides (NO, NO₂ and NO_x where NO_x=NO+NO₂), 24-hr total PM2.5 and 24-hr chemically-speciated PM2.5 measurements collected at Logan monitoring station in the Logan non-attainment area. The chemically-speciated data were collected during a special air quality field study conducted in January 2011. Ammonia measurements collected during a special field study carried out in winter of 2017 were also used for this performance evaluation. These measurements were used since measurements of ammonia were not available during 2011. The evaluation was based on the December 31-January 10 2011 episode and the 2011 emissions inventory was used as input data for the model simulations. The evaluation focused on days with PM2.5 concentration exceeding the 24-hr national

ambient air quality standard ($> 35 \mu\text{g}/\text{m}^3$). Results for December 31, which is a model spin-up day, are excluded from this evaluation.

2. Daily PM2.5 Concentrations

Figure 1 shows 24-hr modeled and observed PM2.5 concentration during January 1-10 2011 at Logan monitoring station in the Logan non-attainment area where 24-hr filter PM2.5 data is available. The model overall captures well the temporal variation in PM2.5. The gradual increase in PM2.5 concentration and its transition back to low levels are generally well reproduced by the model. This overall good temporal agreement is further confirmed by the high correlation between modeled and measured 24-hr PM2.5 over the modeling episode (Figure 2). The coefficient of determination (R^2) between modeled and measured 24-hr PM2.5 at Logan station was 0.72, indicating their high temporal correlation.

It is noteworthy that the overestimation in PM2.5 at the beginning of the modeling episode, mainly on January 1-2, is related to the meteorological model performance on these days. The mixing height was underestimated by about 100 m in the meteorological model on January 1-2, leading to an increasingly stable low-level boundary layer¹, which limited the mixing of pollutants in the photochemical model on these days and resulted in an over-prediction in PM2.5 levels. The underestimation in PM2.5 on January 4-10 2011, particularly on January 4-5, is also related to the meteorological model performance on these days. On January 4-5, a low cloud cover was simulated in the meteorological model while clouds were not observed in reality. This resulted in an increasingly deep sub-cloud mixing layer in the model compared to reality, which led to an underprediction in modeled PM2.5 concentrations.

¹PM2.5 State Implementation Plan Meteorological Modeling, available at <https://documents.deq.utah.gov/air-quality/planning/technical-analysis/research/model-improvements/3-wintertime-episodes/DAQ-2017-014342.pdf>

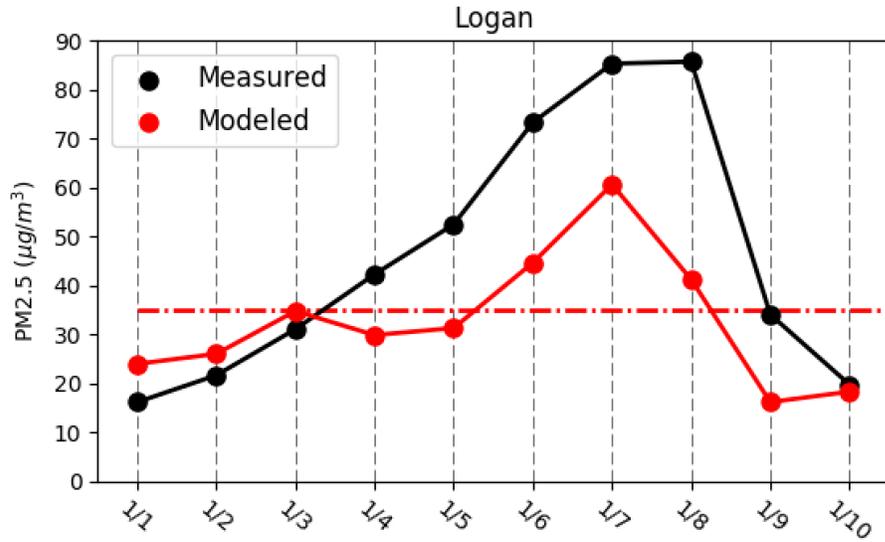


Figure 1. Measured and modeled 24-hr average PM2.5 concentration during January 1-10 2011 (MDT) at Logan monitoring station in Logan non-attainment area. Dashed line represents 24-hr PM2.5 National Ambient Air Quality Standard (NAAQS).

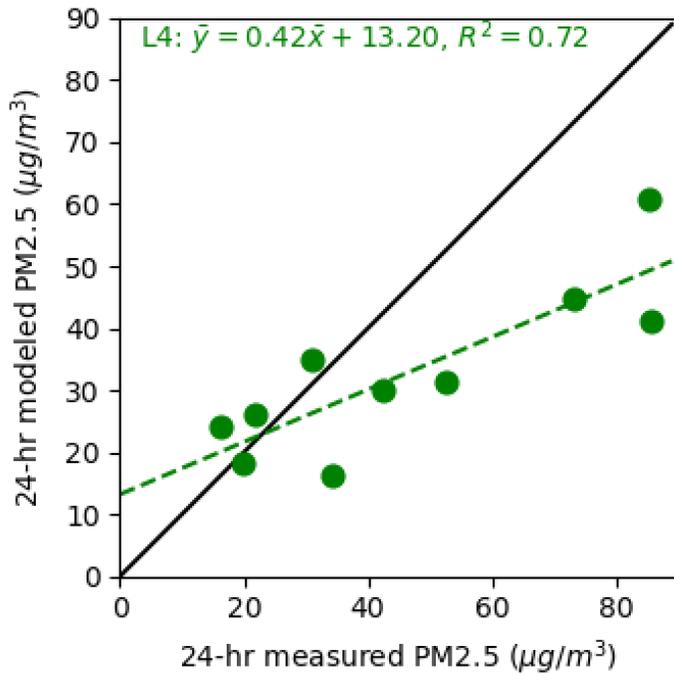


Figure 2. Linear regression between 24-hr average modeled and measured PM2.5 concentrations. Measured concentrations correspond to filter concentration data collected with a Federal Reference Method (FRM) monitor.

3. PM2.5 Chemical Speciation

To further investigate the photochemical model performance, measured and modeled PM2.5 chemical species were compared at the Logan monitoring site, where chemical speciation data was collected during a special air monitoring study conducted in 2011. Figures 3a-b, 4a-b, 5a-b and 6a-b show a comparison of the bulk chemical composition of measured and modeled PM2.5 at Logan on January 3, 5, 7 and 9 2011, which correspond to days when measurement data are available. Chemical species, including nitrate (NO3), sulfate (SO4), ammonium (NH4), organic carbon (OC), elemental carbon (EC), chloride (Cl), sodium (Na), crustal material (CM) and other species (other mass), were considered in this analysis.

On PM2.5 non-exceedance days (January 3 and 9 2011, when PM2.5 measured was below 35 ug/m3, Figures 3a-b and 4a-b), the model underestimated nitrate and ammonium by up to 14.4 and 6.7 ug/m3, respectively. On the other hand, the model performance for sulfate was reasonably good. Measured and modeled concentrations of sulfate were generally comparable, respectively accounting for 1.1 and 1.7 ug/m3 of PM2.5 on January 3 and 1.3 and 1.2 ug/m3 of PM2.5 on January 9. The model also overall overestimated OC, crustal material and EC. The overprediction in these species, even on days when the mixing height was underestimated, suggests that this overestimation in measured concentrations is potentially related to an overestimation in source emissions.

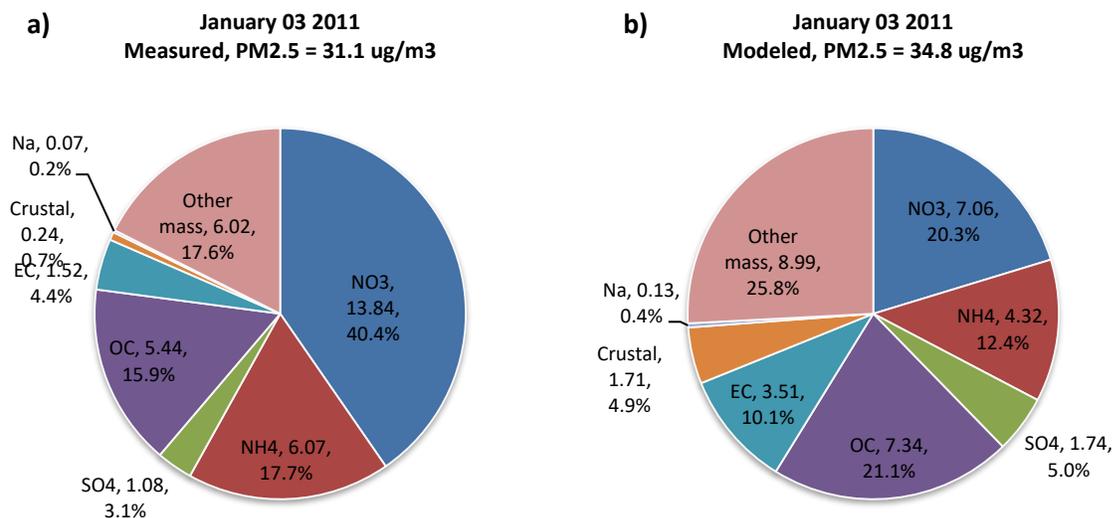


Figure 3a-b. a) Measured and b) modeled chemical composition of 24-hr PM2.5 in ug/m3 and percent of PM2.5 at Logan monitoring station on January 3 2011.

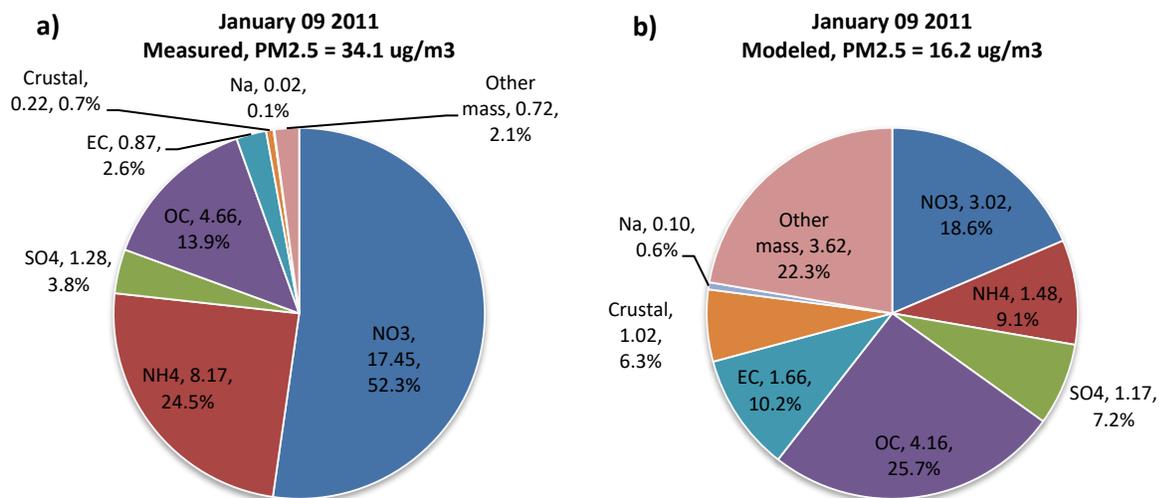


Figure 4a-b. a) Measured and b) modeled chemical composition of 24-hr PM2.5 in ug/m3 and percent of PM2.5 at Logan monitoring station on January 9 2011.

The photochemical model performance on PM2.5 exceedance days (January 5 and 7, Figures 5a-b and 6a-b) was overall similar to that on PM2.5 non-exceedance days. The model performance for sulfate was reasonably good, with measured and modeled sulfate displaying comparable concentrations. The model, on the other hand, underestimated nitrate and ammonium, which is likely related to the meteorological model performance. Temperature was overestimated by 5-15 °C in the meteorological model during January 4-10 2011 and thick low-level clouds were simulated on January 5 while clouds were not observed on this day. This resulted in a weaker temperature inversion in the model compared to reality, which likely led to an underprediction in modeled concentrations relative to measurements².

²<https://documents.deq.utah.gov/air-quality/planning/technical-analysis/research/model-improvements/3-wintertime-episodes/DAQ-2017-014342.pdf>

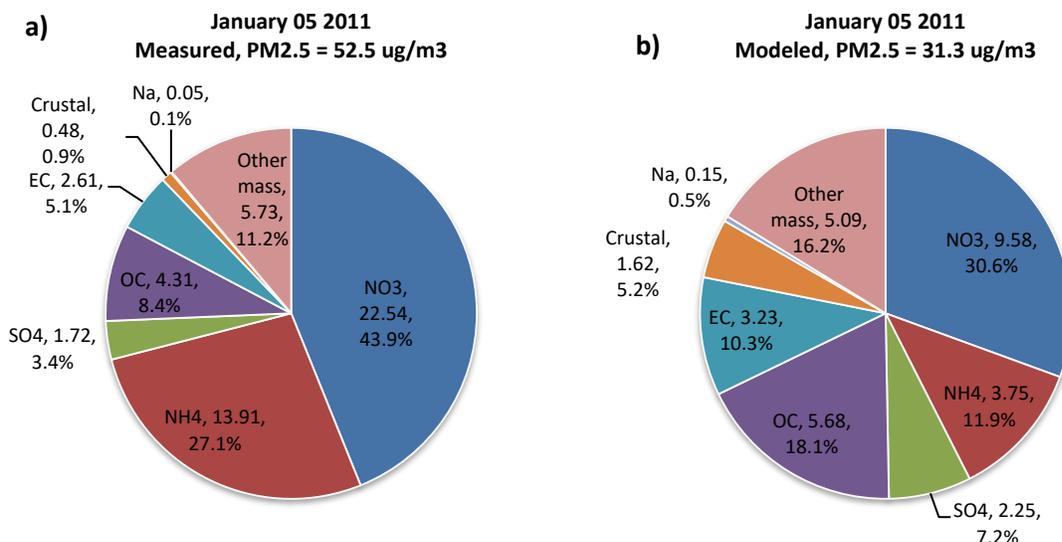


Figure 5a-b. a) Measured and b) modeled chemical composition of 24-hr PM2.5 in ug/m3 and percent of PM2.5 at Logan monitoring station on January 5 2011.

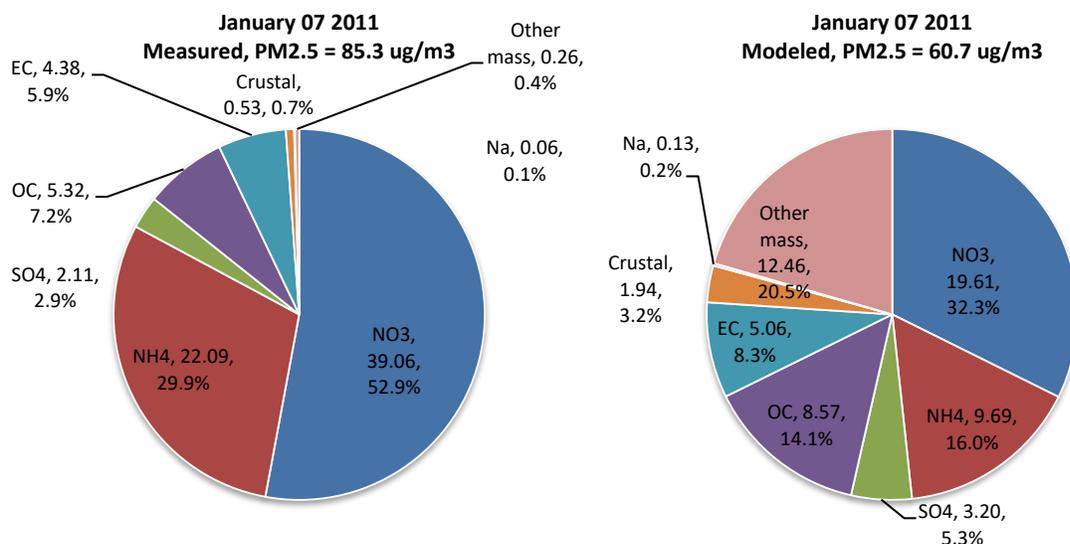


Figure 6a-b. a) Measured and b) modeled chemical composition of 24-hr PM2.5 in ug/m3 and percent of PM2.5 at Logan monitoring station on January 7 2011.

The underestimation in modeled nitrate and ammonium can also be related to an underestimation in modeled hydrochloric acid (HCl) and nitryl chloride (ClNO₂). Modeled ClNO₂ reached a peak concentration of 450 pptv at Logan monitoring station on January 7 (Figure 7), which corresponds to a PM2.5 exceedance day, while values as high as 1200 pptv were observed at Logan station on typical wintertime exceedance days during a special field study (2017 Utah Winter Fine Particulate Study (UWFPS)³, Figure 8). Similarly, modeled HCl was underestimated in the model. Maximum hourly modeled values were below 0.25 ppb in the Logan non-attainment area on January 7 (Figure 9) while values as high

³ <https://www.esrl.noaa.gov/csd/groups/csd7/measurements/2017uwfyps/finalreport.pdf>

as 8 ppb were observed in the Logan area during the 2017 UWFPS (Figure 10). The model also overall overestimated crustal material, EC and OC. The overprediction in these species on days when the simulated atmospheric mixing was particularly strong, suggests that this overestimation is potentially related to an overestimation in source emissions. Lastly, it is noteworthy that despite these biases in modeled PM2.5 species, modeled nitrate and ammonium account for most of the PM2.5 mass, in agreement with measurements.

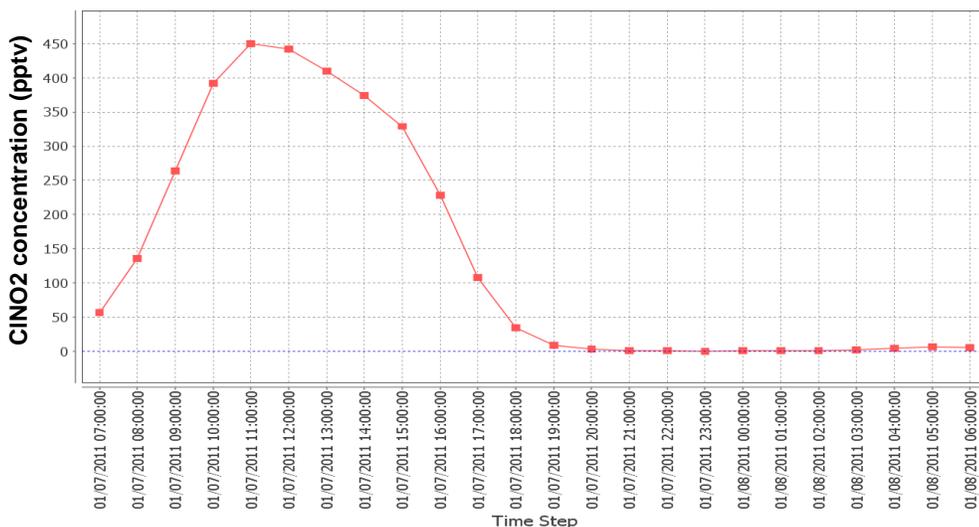


Figure 7. Hourly time series (UTC) of ClNO₂ concentration in pptv at Logan monitoring station on January 7 2011.

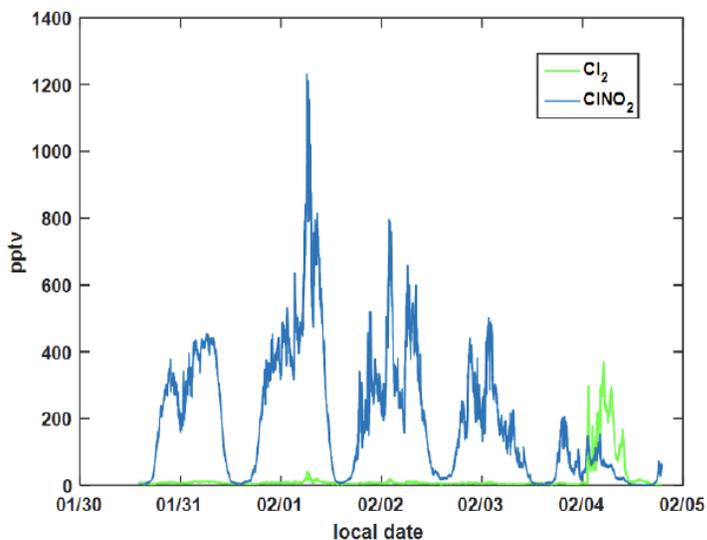


Figure 8. ClNO₂ and Cl₂ measurements observed at the Logan monitoring site during the 2017 Utah Winter Fine Particulate Study. Figure retrieved from the 2017 Utah Winter Fine Particulate Study, final report, Figure 3.51 (<https://www.esrl.noaa.gov/csd/groups/csd7/measurements/2017uwfps/finalreport.pdf>).

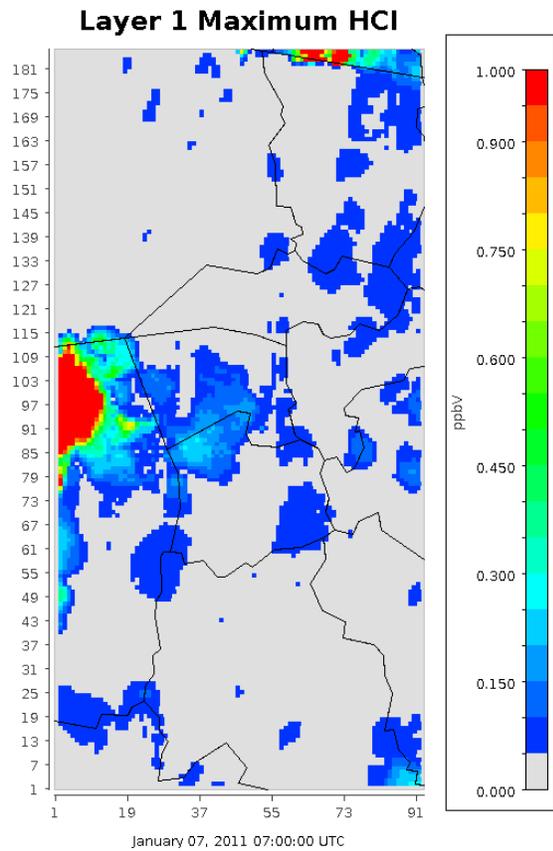


Figure 9. Spatial distribution of maximum hourly HCl concentrations (in ppb) on January 7 2011, which represents a typical 24-hr PM_{2.5} exceedance day.

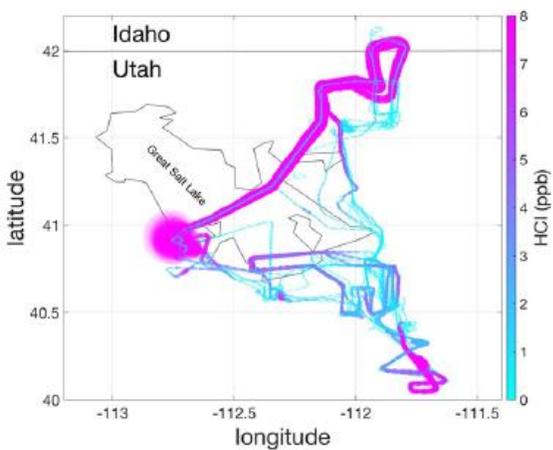


Figure 10. Spatial distribution of HCl during the 2017 Utah Winter Fine Particulate Study. The color scale saturates at 8 ppb, the thickness of the lines is directly proportional to mixing ratio. Figure retrieved from the 2017 Utah Winter Fine Particulate Study, final report, Figure 3.44 (<https://www.esrl.noaa.gov/csd/groups/csd7/measurements/2017uwfps/finalreport.pdf>).

4. Hourly Ambient Gaseous Compounds

The model performance was also evaluated for gaseous compounds, particularly precursor species to PM_{2.5} formation. Gaseous compounds considered in this analysis include nitrogen oxides (NO, NO₂, and NO_x defined as NO+NO₂), ozone (O₃) and ammonia (NH₃).

A comparison of modeled and measured nitrogen oxides (NO, NO₂ and NO_x, Figures 11-13) and ozone (Figure 14) shows that modeled NO, NO₂ and NO_x are overestimated while ozone is underestimated during daytime hours (6 am - 8 pm), particularly during January 3-8 when the atmospheric mixing height was overestimated in the meteorological model. This overestimation in modeled NO, NO₂ and NO_x concentrations on days when atmospheric mixing was greater than observed suggests that the overprediction in these gaseous species is likely due to an overestimation in their source emissions or an underestimation in the conversion of NO_x to other nitrogen species, including nitric acid and ammonium nitrate. The underestimation in ozone is likely a result of increased ozone titration due to an overabundance of NO_x or an underestimation in sources of free radicals, such as ClNO₂. An underprediction in the sources of free radicals would lead to an underestimation in the photochemical production of ozone. On the other hand, modeled NO, NO₂ and NO_x were underestimated and ozone was overestimated during nighttime hours (8 pm – 6 am). The lack of nightly modeled NO_x and the abundance of modeled ozone may be related to overmixing vertically and/or underestimation of nighttime NO_x emissions.

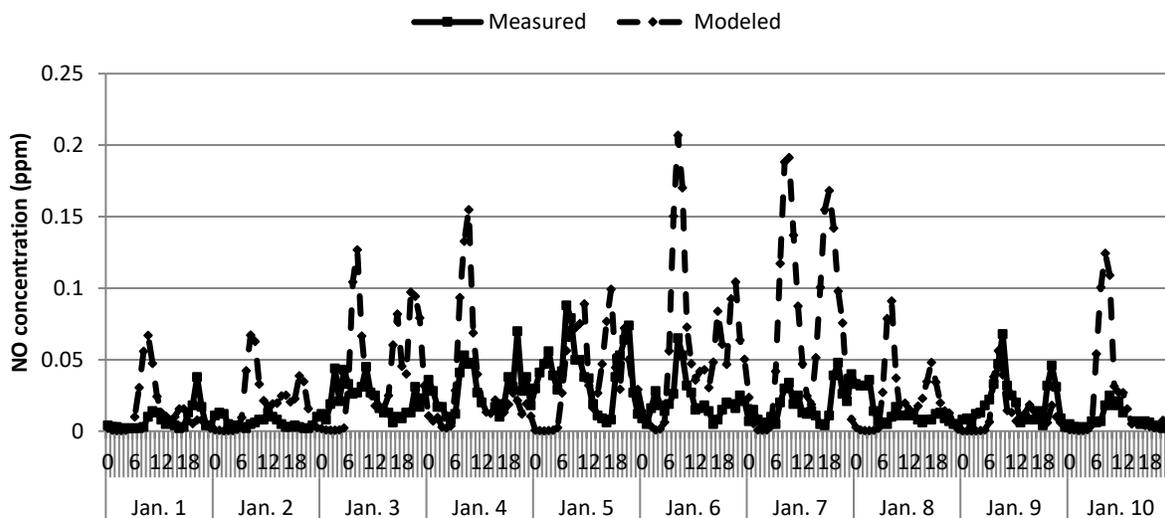


Figure 11. Modeled and measured hourly time series of NO (ppm) at Logan monitoring site during January 1-10 2011.

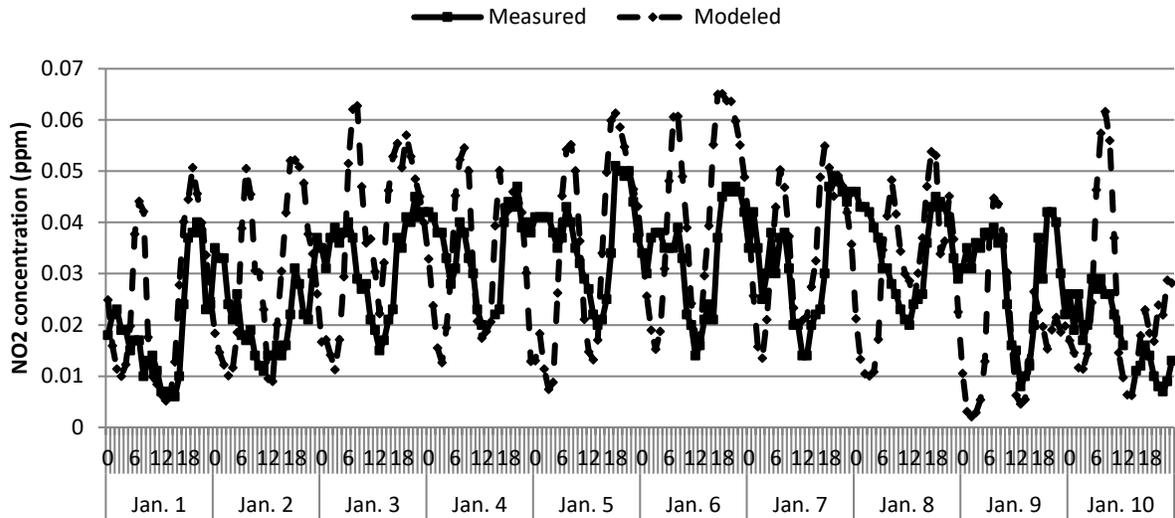


Figure 12. Modeled and measured hourly time series of NO₂ (ppm) at Logan monitoring site during January 1-10 2011.

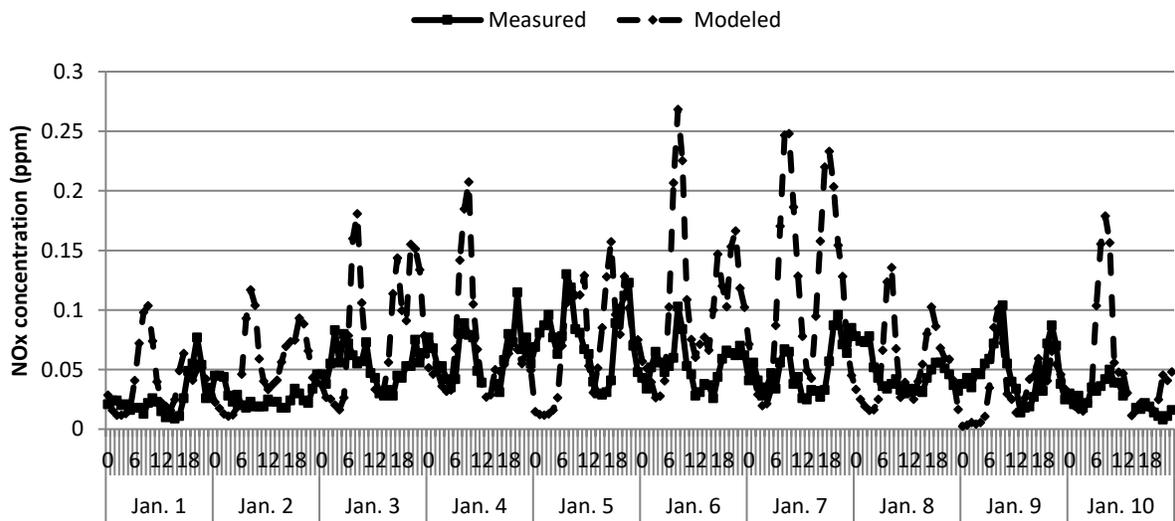


Figure 13. Modeled and measured hourly time series of NO_x (NO+NO₂ in ppm) at Logan monitoring site during January 1-10 2011.

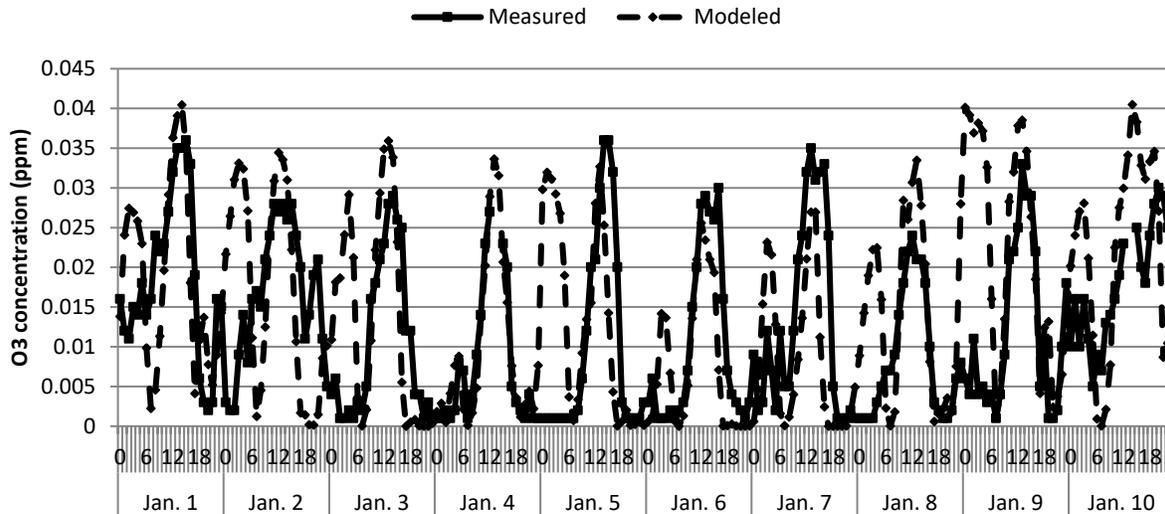


Figure 14. Modeled and measured hourly time series of ozone (ppm) at Logan monitoring site during January 1-10 2011.

The model performance was also evaluated for NH₃, which is an important precursor to the formation of nitrate and ammonium, which account for over 50% of PM_{2.5} mass during wintertime inversion events (Figures 5a and 6a).

Hourly modeled ammonia (Figure 15) was compared to hourly ammonia measurements (Figure 16) conducted at the Logan air monitoring station during a special field study in winter 2017. Measurements from 2017 were considered since measurements of ammonia were not available during 2011. However, while these 2017 field study measurements cannot be directly compared to day-specific 2011 model simulations, the measurements are qualitatively useful to assess if the model predicts similar levels of ammonia during strong inversion conditions. A comparison of measured and modeled ammonia shows that modeled ammonia at the Logan site is well within the range observed in 2017. For example, during the inversion episode from January 28-February 4 2017, Figure 16 shows that measured NH₃ concentrations were mostly in the range of 20 to 80 ppb, which is similar to the modeled NH₃ concentrations during the January 2011 inversion episode shown in Figure 15.

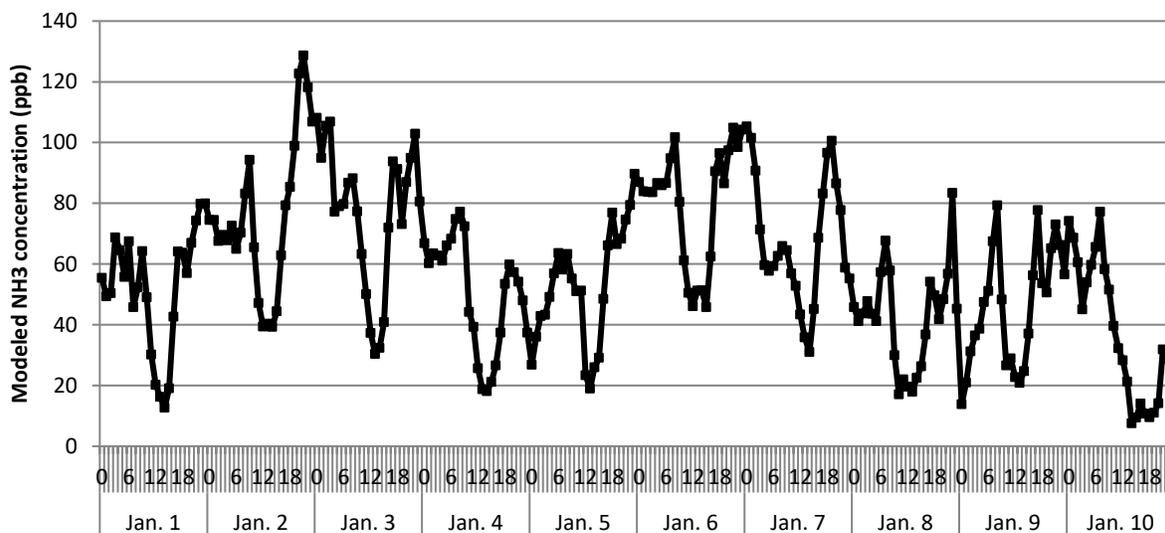


Figure 15. Modeled hourly ammonia concentration (ppb) at Logan monitoring site during January 1-10 2011.

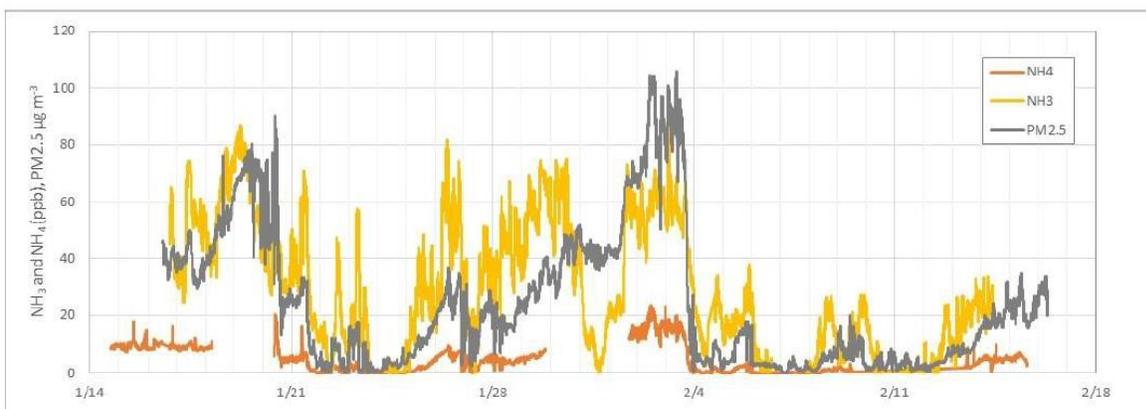


Figure 16. Measured ammonia, ammonium and PM2.5 at Logan monitoring site during the 2017 Utah Winter Fine Particulate Study. Figure retrieved from the 2017 Utah Winter Fine Particulate Study, final report, Figure 3.33 (<https://www.esrl.noaa.gov/csd/groups/csd7/measurements/2017uwfps/finalreport.pdf>).

5. Model Performance Evaluation Metrics

The model performance was further evaluated by examining various bias and error metrics. These were developed according to Boylan et al. 2008⁴ and are discussed in “Guidance on the Use of Models and Other Analyses for Demonstrating Attainment of Air Quality Goals for Ozone, PM2.5, and Regional Haze” (EPA, April 2007). Chemical speciation data collected during a special field study at the Logan monitoring station on January 1, 3, 5, 7 and 9 2011 was considered for this analysis.

⁴ James W. Boylan, Armistead G. Russell (2006) PM and light extinction model performance metrics, goals, and criteria for three-dimensional air quality models, *Atmospheric Environment* 40 (2006) 4946–4959, doi:10.1016/j.atmosenv.2005.09.087

Soccer plots were first considered for the model performance evaluation, where two thresholds of +/- 30% and +/-60% were considered for the normalized mean bias and fractional mean bias evaluation (Figure 17). As can be seen, the model performance for OC, EC and CM was weak while that for secondary inorganic ionic species, including sulfate, nitrate and ammonium which account for over 50% of PM2.5 mass on wintertime inversion days, was better.

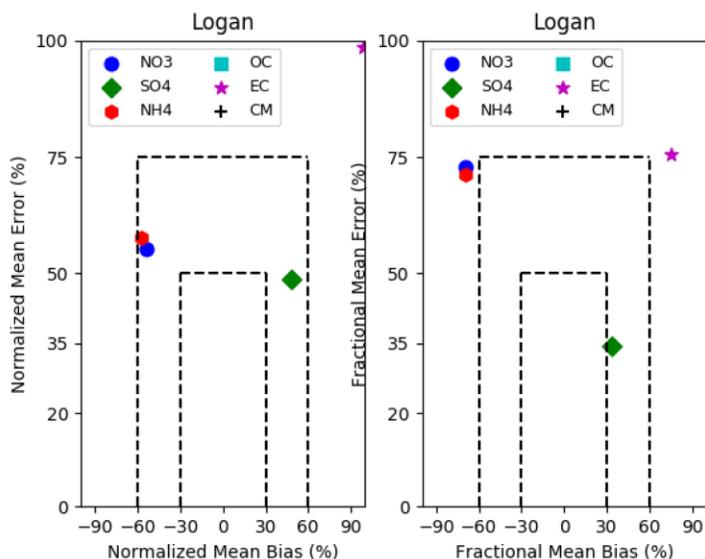


Figure 17. Soccer plot depicting modeled PM2.5 species performance for five days during the modeling episode when speciated PM2.5 filter data was available at Logan monitoring site.

Model performance was further evaluated by examining various model performance metrics for PM2.5 species at the Logan monitoring site during the January 2011 modeling episode (Table 1). As can be seen, the model was biased low for secondary nitrate and ammonium species while it was biased high for primary species, particularly OC.

Table 1. Model performance statistics for five days during the modeling episode when speciated PM2.5 filter data was available at Logan monitoring site.

PM2.5 Species	Mean (obs) ug/m3	Mean (modeled) ug/m3	Mean Bias ug/m3	Mean Error ug/m3	Normalized Mean Bias	Normalized Mean Error	Mean Fractional Bias	Mean Fractional Error
FCRS	0.326	1.686	1.36	1.36	417.047	417.047	137.059	137.059
OC	4.642	16.319	11.677	11.677	251.555	251.555	106.131	106.131
PEC	1.994	3.958	1.964	1.964	98.48	98.48	75.573	75.573
PNH4	10.51	4.495	-6.015	6.065	-57.233	57.707	-69.146	71.245
PNO3	19.722	9.061	-10.661	10.879	-54.056	55.162	-69.088	72.726
PSO4	1.474	2.183	0.709	0.719	48.081	48.797	33.578	34.41

6. Summary of Model Performance

The model performance was overall acceptable. The model captures well the temporal variation in $PM_{2.5}$. The gradual increase in $PM_{2.5}$ concentration and its transition back to low levels are generally well reproduced by the model. Moreover, total modeled $PM_{2.5}$ mass is dominated by nitrate, in agreement with measurements. Simulated concentrations of ammonia, which is an important precursor to $PM_{2.5}$ formation, were also within the range of those observed. However, while $PM_{2.5}$ mass is dominated by nitrate, the model tends to underestimate ammonium nitrate. It also overestimates NO_x and underestimates ozone during daytime hours, which is potentially due to an underestimation in free radical sources, such as $ClNO_2$. An underprediction in free radical sources leads to a decrease in the photochemical production of oxidants, including ozone, which results in an underprediction in the conversion of NO_x to nitric acid and ammonium nitrate. Future research is needed to evaluate how accurately the model simulates free radical sources, including aldehydes and chlorine species, which would help improve the model performance for NO_2 , ozone and ammonium nitrate.