

**Preliminary Draft
Precursor Demonstration**

DRAFT

March 22, 2017

As part of requirements for subpart 4 Non-Attainment Area (NAA) PM_{2.5} State Implementation Plan (SIP), all of the precursor gases that contribute to PM_{2.5} (NO_x, SO₂, NH₃ and VOCs) are addressed for potential controls in addition to the primary PM_{2.5} com.

EXECUTIVE SUMMARY

This document serves as a preliminary optional precursor demonstration for the PM_{2.5} Serious SIP. Precursor gases include (sulfur dioxide, nitrogen oxides, ammonia, and volatile organic compounds) and contribute to the formation of PM_{2.5} in the Fairbanks, Alaska Non-Attainment Area (NAA). The goal of the precursor demonstration is to determine whether controls are not needed on any of the four precursors in order to attain the standard. EPA has provided guidance to produce a precursor demonstration.¹ This analysis has chosen a threshold of 1.3 µg/m³ in assessing the need for controls of a precursor. This is the value suggested by the EPA guidance. This analysis applies to the BACT/BACM and MSM control analysis under development now and which will be included in the Serious Area plan due in December, 2018.

As part of the Serious SIP development the Clean Air Act (Subpart 4 of Part D of Title I, id. 7513-7513b (Subpart 4)) calls upon states to develop an analysis called BACM (Best Available Control Measures) for all source sectors that emit PM_{2.5} and the four major precursor gases. The BACM process treats area and mobile sources differently from major stationary sources. A Best Available Control Technology (BACT) analysis is conducted specifically for the major stationary sources as a part of the BACM process. BACM and BACT are required to be evaluated regardless of the level of contribution by the source to the problem or its impact on the areas ability to attain². If the state seeks an extension of the attainment date of the area then further control measures must also be evaluated. These measures are called Most Stringent Measures (MSM). The PM_{2.5} NAAQS Final SIP Requirements Rule states if the state determines through a precursor demonstration that controls for a precursor gas are not needed for attaining the standard, then the controls identified as BACT/BACM and MSM for the precursor gas are not required to be implemented³.

SO₂: Direct emissions and atmospheric formation of particulate sulfate contribute to measured sulfate concentrations. Most of the sulfate is in the form of ammonium sulfate; in absolute terms sulfate contributes 5.4 µg/m³ in Fairbanks and 4.9 µg/m³ in North Pole on the average of high concentration days. These values are above the 1.3 µg/m³ and SO₂ does not pass a contribution-based analysis. Given the magnitude of these exceedances above the threshold no sensitivity-based precursor demonstration was pursued. As a result SO₂ precursor emissions are considered significant and any controls deemed feasible for the Fairbanks nonattainment area would be implemented.

NO_x: Ammonium nitrate is the main particulate compound formed from NO_x emissions. The underlying chemistry and sensitivity are explained in the following chapter. Concentrations of ammonium nitrate were calculated as 2.4 µg/m³ in Fairbanks, 2.0 µg/m³ in North Pole Fire Station, and 1.0 µg/m³ in North Pole Elementary. The Fairbanks and North Pole Fire Station

¹ 40 CFR 51.1006 – Optional PM_{2.5} precursor demonstrations

² <https://www.gpo.gov/fdsys/pkg/FR-2016-08-24/pdf/2016-18768.pdf>, Clean Air Act 189 (b)(1)(B) and 189 (e) and CFR 51.1010(4)(i) require the implementation of BACT for point sources and precursors emissions and BACM for area sources.

³ Federal Register, Vol. 81, No. 164, August 24, 2016 (FR 81 58010).

sites do not pass a comprehensive contribution-based analysis. ADEC has decided to perform an optional modeling precursor demonstration for NO_x from all sources (comprehensive) and from major stationary sources. For the comprehensive demonstration NO_x passes a 75% sensitivity-based analysis. A separate major stationary source analysis shows that NO_x passes a zero-out sensitivity-based analysis. Both of these demonstrations and supplemental analysis are provided in this document.

NH₃: Emitted ammonia is a precursor to the formation of particulate ammonium nitrate and ammonium sulfate. The major contributors to PM_{2.5} from ammonia (biomass burning, mobile, home heating) in wintertime Fairbanks are drastically different from those commonly found in the contiguous US, where ammonia from agricultural activities typically dominate with smaller contributions from vehicles, and other industrial activities. In the Fairbanks nonattainment area, ammonium nitrate is a minor contributor to the total PM_{2.5} while ammonium sulfate does contribute significantly to ambient concentrations of PM_{2.5}. Contributions of emitted ammonia to PM_{2.5} were calculated as 4.6 µg/m³ and 4.2 µg/m³ at the Fairbanks monitors and 4.4 µg/m³ and 2.1 µg/m³ at the North Pole monitors. These values do not pass the contribution-based analysis. No sensitivity tests were performed for ammonia.

VOCs: Emissions of VOCs contribute to PM_{2.5} by condensing after exiting a high temperature stack and then undergoing further chemical processing in the atmosphere to form secondary organic aerosols (SOA). Given the atmospheric and meteorological conditions in wintertime Fairbanks, VOCs are not expected to be major contributors to PM_{2.5} in the nonattainment area. A contribution-based analysis of ambient data for VOC was not performed. A contribution-based zero-out air quality modeling demonstration shows VOC's contributing well below the threshold of 1.3 µg/m³ at all monitors. For this reason we believe the contribution from VOCs to PM_{2.5} are insignificant and do not plan to implement the BACT/BACM and MSM controls for VOCs.

EPA's *Draft PM_{2.5} Precursor Demonstration Guidance* recommends five analyses that can be performed to demonstrate that a precursor gas is not significant in contributing to concentrations of PM_{2.5}. There are two main steps in the precursor demonstration process first a concentration-based analysis is conducted and failing that a sensitivity based analysis can be conducted. These analyses can be performed in a comprehensive manner meaning that it considers precursor emissions from all sources or they can be performed specifically for major stationary sources. The concentration based analysis is initially conducted using ambient data collected at monitors within the nonattainment area where the precursor gas contributions are measured and assessed against the threshold of 1.3 µg/m³ for 24-hour PM_{2.5}. Air quality modeling can also be used to perform the concentration based analysis by zeroing out the emissions of a precursor and running a photochemical grid model (PGM) to estimate the impact on PM_{2.5}. Should the concentration based analysis show impacts above the threshold a sensitivity based analysis can be performed with an air quality model. There are three recommended tiers in the sensitivity based analysis, 70%, 50%, and 30%. For each tier the PGM is configured to reduce a precursor's emissions by a large percentage, and the impacts on PM_{2.5} concentration are modeled. These impacts are compared to the same threshold as the concentration based analysis. Supplemental analysis may also be included to further support the findings of the precursor demonstration.

A preliminary precursor demonstration has been conducted for NO_x and VOC. Table 1 summarizes the precursor demonstration tests that were passed at all monitor sites. VOCs were shown to be insignificant using a comprehensive air quality modeling zero-out analysis. NO_x was demonstrated to be insignificant from a 75% sensitivity based analysis. A second NO_x demonstration was performed for major stationary sources with a zero-out air quality modeling analysis. This major stationary source demonstration was conducted in the event that EPA does not approve the comprehensive sensitivity based analysis.

Table 1: NO_x and VOC Precursor Demonstrations

Precursor	Source(s)	Test Details	Pass
NO _x	Comprehensive	Sensitivity Based Analysis 75%	Y
NO _x	Major Stationary Source	Concentration Based Analysis - Air Quality Modeling zero-out	Y
VOC	Comprehensive	Concentration Based Analysis - Air Quality Modeling zero-out	Y

FAIRBANKS AMBIENT AIR QUALITY OVERVIEW

Addressing the precursor gases and how they are related to PM_{2.5} requires understanding the Fairbanks and North Pole wintertime characteristics that lead to the formation of PM_{2.5} from both direct and secondary formations. Precursor gases form secondary PM_{2.5} and this component of PM_{2.5} is addressed through reviewing current knowledge of the chemistry involved in the secondary formation in the Fairbanks and North Pole NAA.

State Office Building winter FRM-derived species percentage of high PM 2.5 days from years 2011-2015 and average modeling design value (DV) of 38.9 ug/m3

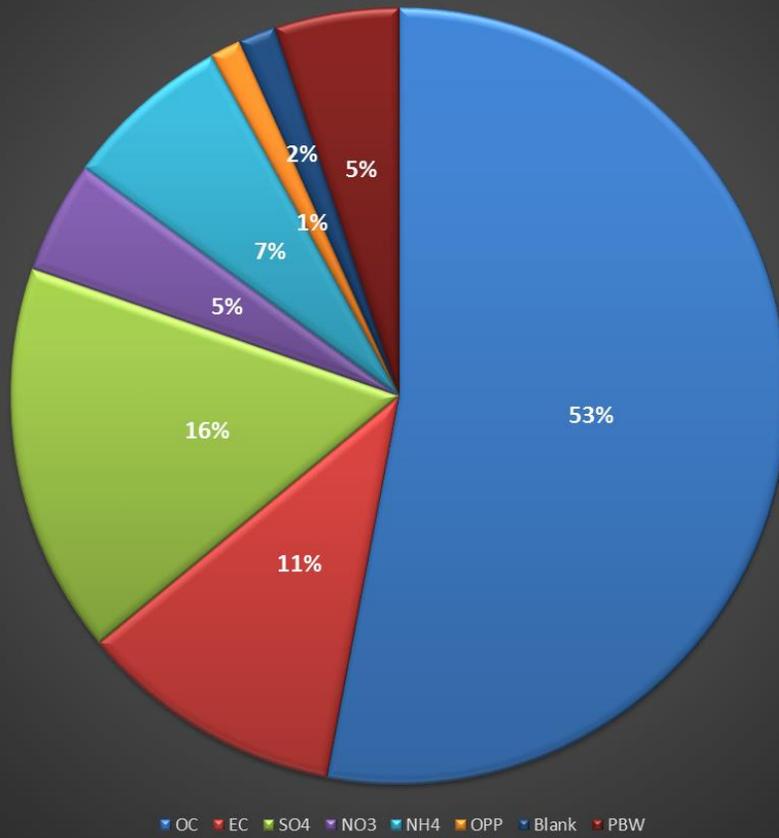


Figure 1: 24-hr average FRM-derived PM_{2.5} speciation concentrations based on the design value (DV) of 131.6 µg/m³ for the high PM_{2.5} winter days at North Pole Fire Station

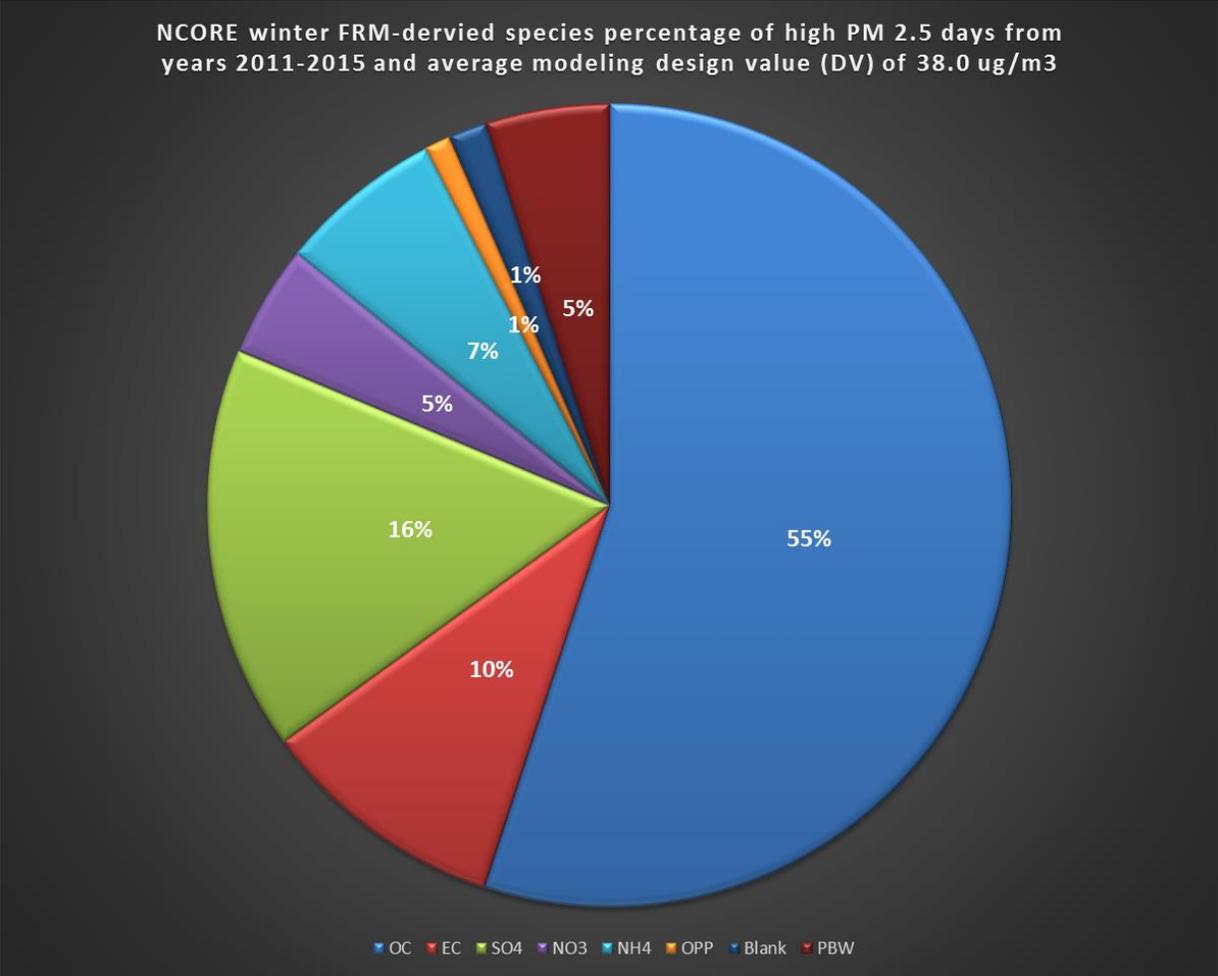


Figure 2: 24-hr average FRM-derived PM_{2.5} speciation concentrations based on the design value (DV) of 38.0 μg/m³ for Fairbanks NCORE Monitor.

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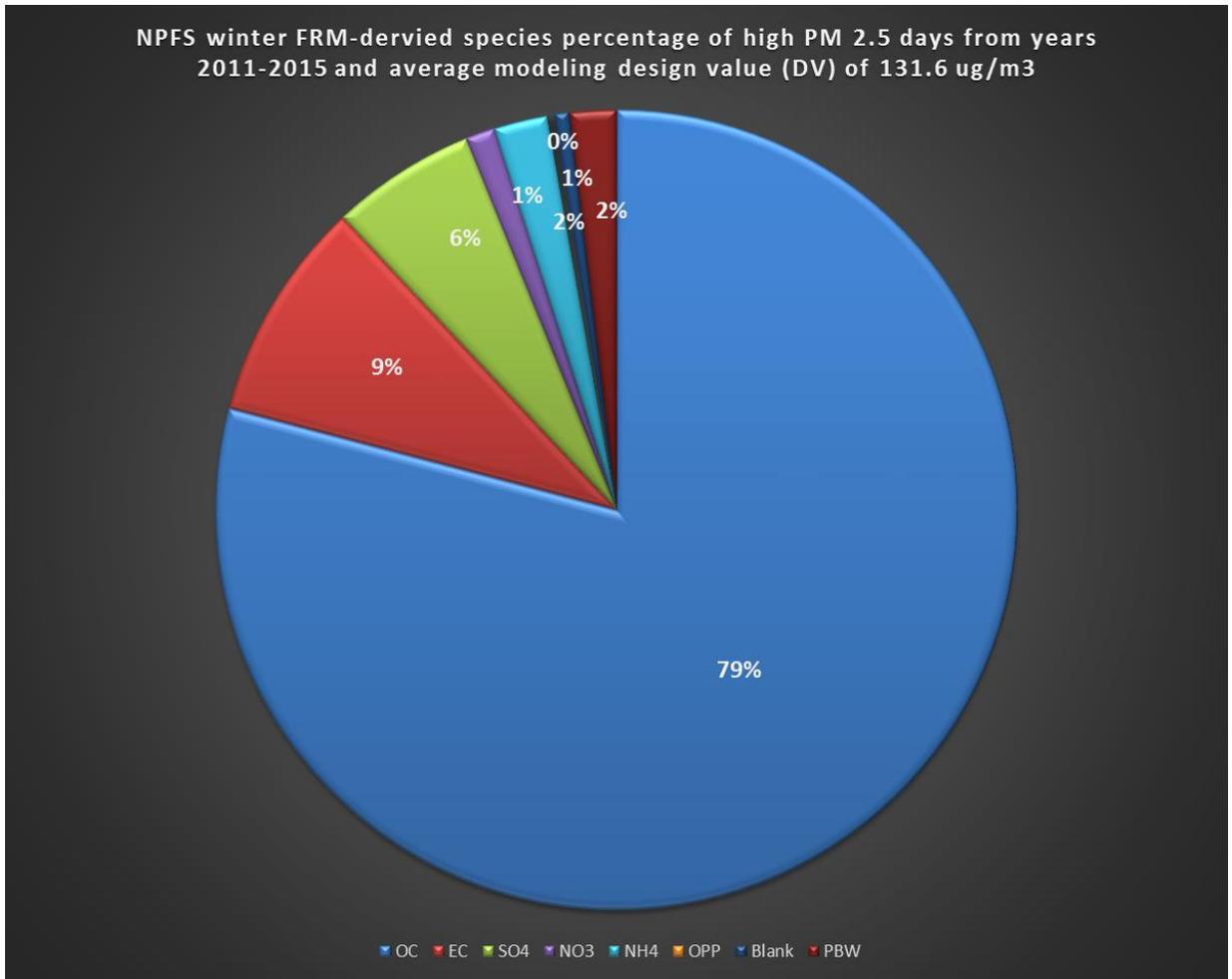


Figure 3: 24-hr average FRM-derived PM_{2.5} speciation concentrations based on the design value (DV) of 38.9 µg/m³ for Fairbanks State Office Building Monitor.

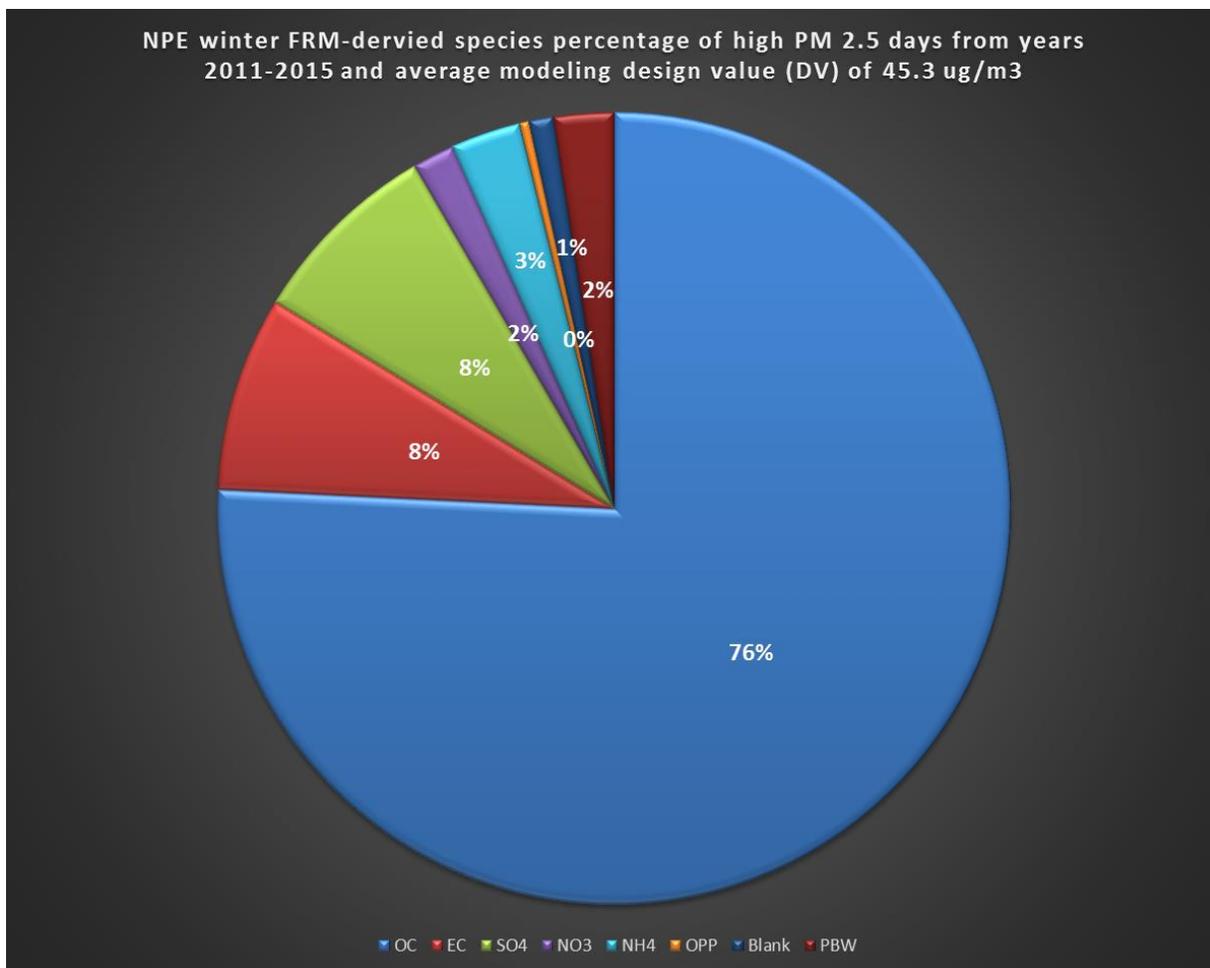


Figure 4: 24-hr average FRM-derived PM_{2.5} speciation concentrations based on the design value (DV) of 45.3 μg/m³ for North Pole Elementary School Monitor.

Particulate Matter (PM_{2.5}) is directly emitted into the atmosphere or formed by secondary chemical reactions from precursor gases. The major components of atmospheric aerosols formed by secondary chemistry are nitrate (NO⁻³), sulfate (SO₂⁻⁴) and ammonium (NH₄⁺). These species are formed primarily from chemical reactions in the atmosphere involving the gas-phase precursors, nitrogen oxides (NO_x), sulfur dioxide (SO₂) and ammonia (NH₃). The major component of Fairbanks PM_{2.5} is organic carbon and is directly emitted as particles, condenses to existing particles, or contributes to the formation of new particles from gaseous molecules.

The NO_x emissions by source category are 62% point sources, 21% mobile, 14% area, 3% non-road and less than 1% for all other sources combined. In the winter, nitrate composes 1% -5% (Figure 1-4) of the total PM_{2.5} in the nonattainment area.

Sulfates are a major component of the PM_{2.5} mass; estimates show that sulfates comprise approximately 6-16% of the total mass of Fairbanks PM_{2.5} (Figures 1-4). Direct emissions and atmospheric formation of particulate sulfate contribute to measured sulfate concentrations. The speciation profiles used for the different emission categories show that primary sulfate is emitted

by point, area (home heating) and mobile sources. Direct emissions of sulfate are not enough to account for the amount of sulfate observed in Fairbanks and North Pole. The CMAQ inventory for point and area sources reveal that point sources are a majority of primary sulfate emissions, but not concentrations at the monitors. Sulfate contribution at the monitors is 6-16% (Figure 1-4) and that equates to 4.9-5.4 $\mu\text{g}/\text{m}^3$.

Speciation data shows that 3-8 % of total PM_{2.5} mass on violation days is ammonium (Figure 1-4). Based on the emissions inventory used in the CMAQ modeling the leading sources of ammonia are automobiles and industrial sources.

Speciation of the Fairbanks winter PM_{2.5} components (Figure 1) are derived from the high PM_{2.5} days from the years 2011-2015. The speciation concentrations that represent the breakdown of the components of PM_{2.5} in the Fairbanks area are measured from the SASS (Speciation Air Sampling System) speciation instrument. The speciation SASS monitor is different from the Federal Reference Monitor (FRM) that measures total PM_{2.5}, we want to compare the components of PM_{2.5} measured by the SASS instrument to the FRM measurements that measure total PM_{2.5} for regulatory purposes, but have different measurement artifacts. The goal is to derive concentrations of chemical components as they would be found on the official Federal Reference Method (FRM) monitor filter, not as they are found through the SASS instrument. To convert the concentrations of each chemical species from the measurement by the SASS to what would have been found on the FRM filter, we use the SANDWICH method⁴. A detailed account of the adjustments made to compare speciation measurements to FRM total PM_{2.5} measurements as well conversion of precursor gases and chemistry are found in Appendix III.D.5.8 of the Moderate Area SIP.

The largest component of PM_{2.5} in the Fairbanks area is organic carbon. Organic carbon is primarily due to direct emission with very little resulting from secondary formation. The direct PM_{2.5} reductions will be addressed as part of BACM, which is evaluating controls for all source sectors for PM_{2.5} and precursor gases except point sources which are evaluated through BACT.

PRECURSOR GAS CHEMISTRY OVERVIEW

Nitrogen oxide precursors and nitrates

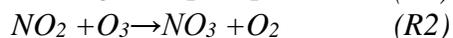
Nitrogen oxides are referred to as the chemical family NO_x (NO₂+NO), NO and NO₂ with primary emissions coming from combustion processes, home heating, vehicles and industry. Typically, during the day, NO_x is oxidized by reacting with ozone and OH radical chemistry and forms nitric acid (HNO₃) and during the night NO_x is oxidized to form N₂O₅ (g), which reacts on aerosol surfaces to form HNO₃ (aq) and deposition to snowpack. Particles containing nitrate are neutralized via reaction with ammonia gas (NH₃) to form ammonium nitrate.

⁴ Frank, N. (2006): Retained nitrate, hydrated sulfates, and carbonaceous mass in Federal Reference Method fine particulate matter for six Eastern U.S. cities. J. Air and Waste Manage. Assoc. 56:500-511.

The photochemistry in Fairbanks and North Pole areas due to the low to no sunlight and cold conditions during the winter, limits the photochemical production of nitric acid from the daytime processes of OH and NO₂. In addition at night, NO titrates the ozone removing the main oxidant to form nitrate (Joyce et. al, 2012). Joyce showed that ammonium nitrate is formed downwind of downtown, adding to the probability that aerosol nitrate from nitric acid is not being formed in downtown Fairbanks. Heterogeneous nighttime chemistry from N₂O₅ is thought to be responsible for 80% of the nitric acid formation at high latitudes⁵, but in polluted areas the fast reaction of excess NO with the nitrate radical, nitric acid formation is hindered at night⁶. Nitric acid formation is further oxidized to form particle nitrate, it is important to understand the production of nitric acid and ammonium nitrate.

Aerosol processes play a dominant role in the formation of nitrate. Most nitrate is formed in the atmosphere from NO_x emissions that transform into ammonium nitrate from secondary processes. The monitored observations show that ammonium nitrate accounts for between 1% and 5% and of the total PM_{2.5}. As mentioned in the Moderate Area Plan, ammonium nitrate production is limited by the dark and cold conditions and by NO emissions hindering the nitrate production. The formation of ammonium nitrate is controlled by day time processes of OH and NO₂, at night NO titrates the ozone removing the main oxidant to form nitrate⁷. During the day the photochemistry is limited by low sunlight and under low wind conditions when PM_{2.5} is high, the NO emissions hinder further formation of nitrate (Figure 11). There are no OH measurements to compare to the model in the Fairbanks area, but there is no high ozone days which would form from reactions with VOCs and sunlight. Figure 11 shows that daytime ozone measurements are near background and photochemistry for ozone is not present and therefore the OH forming from photochemistry and producing nitric acid that creates particle nitrate is also low.

The modeling precursor demonstration for NO_x having the potential to create ammonium nitrate should be representative of the ammonium nitrate that we see on the filters, in that only a few percent of PM_{2.5} even on the highest days is ammonium nitrate. The modeling outputs were examined for NO, O₃, and NO₂. In the modeling outputs, ozone is titrated a majority of the time as can be seen in Figure 8 and 9. When the ozone is not titrated out and NO is low, the presence of wind and/or snow have reduced the PM_{2.5}. The background level ozone present under clean air quality conditions (approximately 40 ppb) on 1/23/2008 until 1/24/2008, is when there is a light wind of 5-10 mph. During these conditions PM_{2.5} is reduced by the wind. Under the conditions when we have high PM_{2.5} (Figure 8 from date 2/3-2/7): low wind, strong inversion in place, a buildup of excess NO and low ozone, further oxidation of NO_x and reactions with ammonia that produce particle nitrate are hindered (R2).



⁵ Dentener, F. J. and Crutzen, P. J.: Reaction of N₂O₅ on tropospheric aerosols: Impact on the global distributions of NO_x, O₃, and OH, J. Geophys. Res., 98, 7149–7163, doi:10.1029/92jd02979, 1993

⁶ Seinfeld and Pandis, Atmospheric Chemistry and Physics, 1998

⁷ Joyce, P.L., Gasow, R.V., Simpson, W.R., The fate of NO_x emissions due to nocturnal oxidation at high latitudes: 1-D simulations and sensitivity experiments, Atoms. Chem. Physics. 14 7601-7616, 2014

At night when there is no excess NO and temperature is cold, the following is the dominant pathway to form nitric acid.⁸



N_2O_5 further reacts on a surface to form nitric acid. Once nitric acid is formed, the remaining reactions depend on the availability of ammonia, temperature and the pH of the aerosol to form ammonium nitrate. Joyce et al found in a modeling study that secondary formation of particulate nitrate downtown Fairbanks does not contribute significantly to the $PM_{2.5}$ concentration, but there is a potential to react with ammonia downwind of the Fairbanks area.

At night, when there is no photolysis controlling the oxidation of NO_x , the reaction of NO and NO_3 is very fast and if there was enough ozone to produce NO_3 , it would quickly be removed by fresh NO emissions (5 seconds)⁹ in an urban polluted environment.



The CMAQ model version 4.7.1 was applied in the precursor demonstrations to estimate $PM_{2.5}$ concentrations. The model has full representations of gas and aerosol phase chemistry. Nitrate formation involves chemical reactions in both gas and aerosol phases. The chemical reactions related to nitrate formation represented in the model is illustrated in Figure 1.

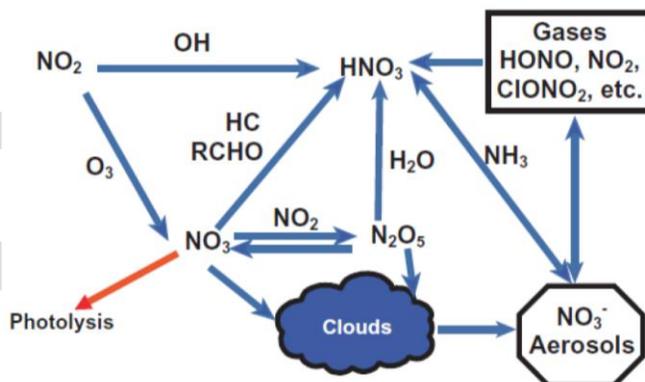


Figure 7. Chemistry processes related to nitrate formation represented in CMAQ¹⁰

Two major pathways of nitrate formation are parameterized in CMAQ 4.7.1:

1. Heterogeneous reaction of N_2O_5 ; and
2. Thermodynamic equilibrium reactions among HNO_3 , NH_3 and aerosols.

N_2O_5 is considered the reservoir for NO_x and it's thermally unstable. Its reaction with water on aerosol surface was found to be a significant source for aerosol nitrate¹¹. Parameterization of heterogeneous reactions of N_2O_5 in CMAQ 4.7.1 is based on the method developed by Davis et

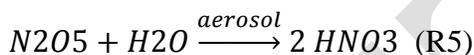
⁸ Dentener, F. J. and Crutzen, P. J.: Reaction of N_2O_5 on tropospheric aerosols: Impact on the global distributions of NO_x , O_3 , and OH, J. Geophys. Res., 98, 7149–7163, doi:10.1029/92jd02979, 1993

⁹ Seinfeld and Pandis, Atmospheric Chemistry and Physics, 1998, pg 283

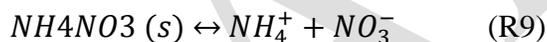
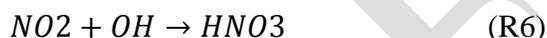
¹⁰ NARSTO 2004. PDF version is available here: <http://www.narsto.org/sites/narsto-dev.ornl.gov/files/Ch3813KB.pdf>

¹¹ https://www.atmos.illinois.edu/~nriemer/papers/riemer_n2o5_2003.pdf

al. (2008)¹², which calculates the N₂O₅ hydrolysis probability as a function of temperature, relative humidity (RH), inorganic aerosol composition, and phase state. The N₂O₅ photolysis probability is defined as the fraction of collisions between N₂O₅ molecules and particle surfaces that lead to the production of HNO₃. The photolysis probability is higher at lower temperature and higher RH, so nitrate formation through this pathway is more active at nighttime when N₂O₅ is accumulated and the temperature is low and RH is high. The N₂O₅ hydrolysis can be simply represented by the reaction below. More detailed reactions can be found in Reactions R1a – R3 of Davis et al. (2008).



Nitrate formation through the second pathway occurs when gas phase HNO₃, NH₃, and aerosols try to reach a thermodynamic equilibrium¹³. The major reactions represented in the model are listed below:



Reaction R6 produces gas phase HNO₃ during daytime. Gas phase HNO₃ and NH₃ react to form NH₄NO₃ particles. Both gas phase HNO₃ and NH₄NO₃ particles hold thermodynamic equilibrium with aerosols, as shown in reactions R8 and R9. The thermodynamic equilibrium is simulated by a thermodynamic model implemented in CMAQ.

Sulfur Dioxide precursor gas and Sulfate

It is very likely that SO₂ is converted into sulfate in the atmosphere after being emitted and thus accounts for the remainder of the observed sulfate. As control strategies are adopted for BACT and BACM, for example, switching from fuel oil has higher SO₂ and primary sulfate emissions to ULSD will reduce the SO₂ and sulfate. Due to the complex nature of the sulfate chemistry a white paper on sulfur chemistry was included in the Moderate Area SIP, the white paper concludes that the lack of oxidants available in the dark and cold conditions would impede production of sulfate by the most common photochemical pathways¹⁴.

Ammonia precursor gas and ammonium

Ammonia gas (NH₃) reacts with acid aerosols containing nitrate (NO₃⁻) and sulfate (SO₄²⁻) to form ammonium nitrate (NH₄NO₃) and ammonium sulfate ((NH₄)₂SO₄). Nitrate is assumed to be

¹² <https://www.atmos-chem-phys.net/8/5295/2008/>

¹³ http://nenes.eas.gatech.edu/Preprints/ISORROPIA_AGPP.pdf

¹⁴ Peltier, R.E. (2011): Aerosol Chemistry in Fairbanks: A Summary of Prevailing Conditions, May 27, 2011.

all ammonium nitrate. Sulfates are partially neutralized to form ammonium sulfate and are associated with a degree of neutralization. As discussed in the moderate area SIP, if sulfate is reduced in Fairbanks, PM_{2.5} is reduced by the weight of the sulfate reduced and also by the weight of the ammonium.

Volatile Organic Compounds

The emissions of Volatile Organic Compounds (VOCs) are precursor gas emissions that contribute to the secondary formation of PM_{2.5} by forming particulate organic carbon through condensing in the cold air after emission and through photochemistry to form secondary organic aerosols (SOA). The VOC emissions for home heating are 15.9 TPD. The condensable fraction of PM from point sources, gases that are emitted and form particles right out of the high temperature stack could be significant from the condensation due to low temperature.

PRELIMINARY PRECURSOR DEMONSTRATION

Methodology

We applied a tiered approach to the precursor demonstration for both NO_x and VOCs in the Fairbanks North Star Borough 24-hour PM_{2.5} Nonattainment Area. This process is in keeping with EPA's *Draft PM_{2.5} Precursor Demonstration Guidance*¹⁵ and 2016 PM_{2.5} Implementation rule¹⁶. The tiered analysis can be broken down into five stages each with a decreasing level of confidence in the demonstration. The various precursor demonstration available are the following:

- Concentration Based Analysis
 - Ambient data
 - Air Quality Modeling (zero-out)
- Sensitivity Based Analysis
 - 70% Reduction
 - 50% Reduction
 - 30% Reduction

These analyses are broken down further in the sections below. EPA recommends a threshold of 1.3 µg/m³ as a starting point for the precursor demonstration for 24-hour PM_{2.5}¹⁷. This analysis has chosen the recommended threshold. A precursor can be identified as not significant when it does not exceed the threshold. Except for the ambient data analysis the precursor demonstration can be conducted in either a comprehensive manner meaning that it applies to all sources or specifically for major stationary sources. The ambient data analysis test can only be conducted on a comprehensive basis. The threshold for significance is the same in both the comprehensive or major stationary source tests.

¹⁵ *Draft PM_{2.5} Precursor Demonstration Guidance*, US EPA Office of Air Quality Planning and Standards, November 17 2016.

¹⁶ Federal Register, Vol. 81, No. 164, August 24, 2016 (FR 81 58010).

¹⁷ IBID.

CONCENTRATION-BASED AMBIENT DATA ANALYSIS

First the concentration-based analysis is performed using ambient data. For this step we assessed the concentration of different precursor contributions for all four monitor sites between 2011 and 2015 on the highest concentration days. The high concentration days are described in the Speciated Modeled Attainment Test (SMAT) portion of the Technical Analysis Protocol (TAP), which is included as an attachment in this review. In short, the top 25% days were analyzed for the N CORE, SOB, and NPE monitors and all days over $35 \mu\text{g}/\text{m}^3$ were used for the NPFS monitor. The speciated $\text{PM}_{2.5}$ data was analyzed using the results of the SANDWICH¹⁸ data processing technique. The ambient dataset is the same that is used in the attainment plan portion of the Serious area plan.

Contributions from SO_2 , NO_x , and NH_4 could be determined from the data available, but the data was not analyzed in such a way that VOC contributions could be determined. Section 3.1.5 of EPA's *Draft $\text{PM}_{2.5}$ Precursor Demonstration Guidance* summarizes the means by which each precursor gas is assigned to a $\text{PM}_{2.5}$ species in the ambient $\text{PM}_{2.5}$ measurements. These assignments are summarized for SO_2 , NO_x , and NH_3 below. Contributions for SO_2 were assessed using the mass of sulfate measured on the filters on the highest concentration days at each monitor site. Contributions for NO_x were assessed as the concentration of nitrate and the portion of the ammonium associated with nitrate. This is calculated as the sum of the nitrate concentration with the molar ratio equivalent amount of ammonium. If the ammonium is assumed to perfectly balance the nitrate then we determine the concentration of ammonium associated with nitrate in $\mu\text{g}/\text{m}^3$ as $18/62$ multiplied by the nitrate concentration in $\mu\text{g}/\text{m}^3$. NH_3 contributions were calculated from the ambient data as the sum total of all ammonium and all nitrate. Any precursor demonstrations using ambient data would be considered comprehensive meaning that controls for that precursor would not be required on any source.

CONCENTRATION-BASED AIR QUALITY MODELING ANALYSIS

An air quality modeling analysis of precursor impacts on $\text{PM}_{2.5}$ utilizes a photochemical grid model (PGM) that can account for the non-linear secondary effects of precursor gases. PGMs account for the atmospheric chemistry, transport, and deposition of pollutants using local emissions and meteorological data. This demonstration used the Community Multiscale Air Quality (CMAQ) model version 4.7.1 as configured for the Moderate and Serious $\text{PM}_{2.5}$ SIPs for Fairbanks¹⁹. Precursor significance for Fairbanks was determined using the zero-out approach. The zero-out approach compares a baseline model run with a model run where a precursor's emissions are set to zero in order to determine the influence of that precursor on $\text{PM}_{2.5}$ formation. The emissions base year was updated to 2013 for this preliminary analysis. The final demonstrations will be updated to use the 2019 projected baseline to better represent the impacts for the attainment year. The CMAQ model was run with the 2013 baseline inventory first without any alterations to generate baseline modeled concentrations for the nonattainment area.

¹⁸ Frank, N. (2006): Retained nitrate, hydrated sulfates, and carbonaceous mass in Federal Reference Method fine particulate matter for six Eastern U.S. cities. *J. Air and Waste Manage. Assoc.* 56:500-511.

¹⁹ Moderate SIP Chapter 5.08.

Separate runs were performed for VOC and NOx where each precursor's emissions were set to zero for all sources while all other emissions were left at baseline 2013 levels. Another separate model run was conducted where NOx emissions from major stationary sources were set to zero.

SENSITIVITY BASED MODELING ANALYSIS

Modeling Performance

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Results

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Table 1: NOx Comprehensive and Major Stationary Precursor Demonstrations

NOx Episode Average Contributions (SMAT $\mu\text{g}/\text{m}^3$)						
Test	SOB	NCORE	NCORE BAM	NPFS	NPE	Max Cell
Comprehensive Ambient	2.4	2.4	2.4	2.0	1.0	N/A
CMAQ 100%	1.5	1.4	1.5	1.3	0.5	1.6
CMAQ 75%	0.7	0.7	0.7	0.8	0.3	0.8
Major Stationary Zero-out	0.3	0.3	0.3	0.4	0.1	0.3

Table 2: VOC Comprehensive Precursor Demonstrations

VOC Episode Average Contributions (SMAT $\mu\text{g}/\text{m}^3$)						
Test	SOB	NCORE	NCORE BAM	NPFS	NPE	Max Cell
Comprehensive Ambient						N/A
Modeled Zero-out	0.1	0.1	0.1	0.1	0.0	0.1

Supporting Analysis

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Table 3: NO_x Comprehensive and Major Stationary Precursor Demonstrations Maximum Daily Impacts

NO _x Highest Daily Contributions (SMAT µg/m ³)						
Test	SOB	NCORE	NCORE BAM	NPFS	NPE	Max Cell
Modeled Zero-out	1.81	1.69	1.84	1.33	0.62	1.85
Modeled 75% Sensitivity	0.81	0.76	0.83	0.72	0.35	0.89
Major Stationary Sources Zero-out	0.38	0.38	0.36	0.39	0.74	0.29

The following figures are the histograms of the daily PM_{2.5} differences at the grid cells where the monitors are located. The differences were calculated based on the raw CMAQ output by subtracting the control case results (i.e., PT0NOX and NOX75OFF) from the baseline for each day of the total 35 episode days.

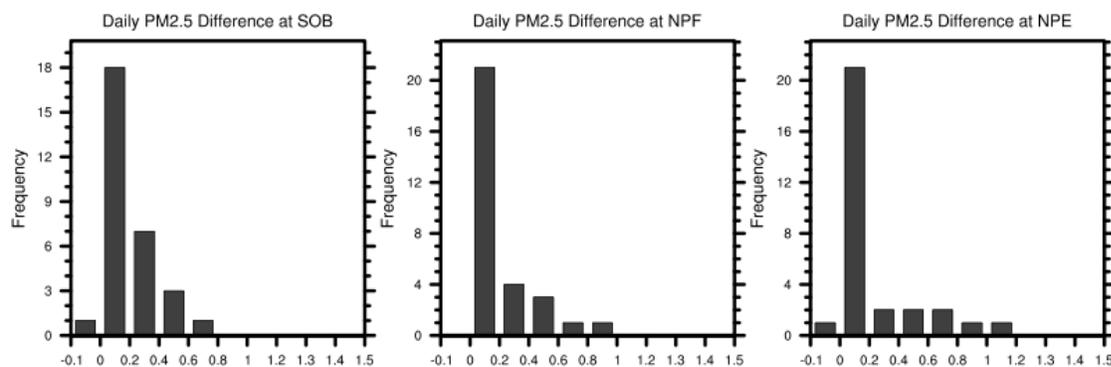


Figure 5. Histograms of the daily PM_{2.5} differences at monitor grid cells for the point source NO_x knock out run (PT0NOX).

For the point stationary source NO_x zero out case, the reductions in daily PM_{2.5} at the three grid cells containing monitored locations are mostly (~20 days) less than 0.2 µg/m³. None of the daily differences exceed the 1.3 µg/m³ threshold. There is one day at the SOB grid cell monitor and another day at the NPE grid cell monitor with a slight increase (less than 0.1 µg/m³) in daily PM_{2.5} when point source NO_x emissions were removed. The nitrate concentration was decreased for both days, but the other PM_{2.5} species were slightly increased due to the removal of point source NO_x emissions. Both days have a relatively low nitrate concentrations, and it could be that the interaction of various PM_{2.5} species on those days is very sensitive to the changes in NO_x emissions.

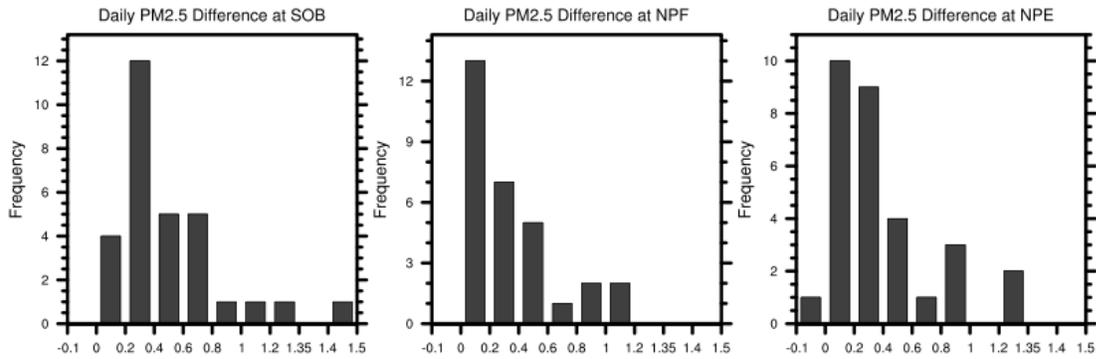


Figure 6. Histograms of the daily PM_{2.5} differences at monitor grid cells for the comprehensive NOx 75% off sensitivity run (NOX75OFF).

For the comprehensive NOx 75% off case, most of the days have a reduction of PM_{2.5} less than 0.6 $\mu\text{g}/\text{m}^3$. There is one day at SOB with a reduction slightly larger than 1.3 $\mu\text{g}/\text{m}^3$. There are two days at NPE that have a reduction above 1.3 $\mu\text{g}/\text{m}^3$, but below 1.35 $\mu\text{g}/\text{m}^3$. When rounded to the nearest tenth of a $\mu\text{g}/\text{m}^3$, these days fall within the threshold value.

<<< Text to be completed >>>

Table 4: Bounding Runs NOx Comprehensive and Major Stationary Precursor Demonstrations

NOx Episode Average Contributions (SMAT $\mu\text{g}/\text{m}^3$)						
Test	SOB	NCORE	NCORE BAM	NPFS	NPE	Max Cell
Comprehensive Ambient	2.4	2.4	2.4	2.0	1.0	N/A
CMAQ Zero-out						
Modeled 75%	0.24	0.23	0.25	0.57	0.24	0.57
Major Stationary Zero-out	0.03	0.03	0.03	0.19	0.09	0.00

Table 5: Bounding Runs NOx Comprehensive and Major Stationary Precursor Demonstrations Maximum Daily Impacts

NOx Highest Daily Contributions (SMAT $\mu\text{g}/\text{m}^3$)						
Test	SOB	NCORE	NCORE BAM	NPFS	NPE	Max Cell

CMAQ Zero-out						
Modeled 75%	0.62	0.58	0.64	0.36	0.22	0.89
Major Stationary Zero-out	0.50	0.47	0.52	0.14	0.12	0.12

Table 6: Sensitivity Runs NOx Comprehensive and Major Stationary Precursor Demonstrations Maximum Daily Impacts

NOx Highest Daily Contributions (Unprocessed Modeled $\mu\text{g}/\text{m}^3$)						
Test	SOB	NCORE	NCORE BAM	NPFS	NPE	Max Cell
CMAQ Zero-out						
Modeled 75%	2.16	2.16	2.16	2.15	2.29	3.13
Major Stationary Zero-out	0.87	0.87	0.87	0.84	1.13	1.13

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NITRATE CHEMISTRY COMPARISON

In addition to the bounding and sensitivity runs we developed a comparison of the modeled and ambient chemistry to provide confidence that the photochemical model was producing a reasonable nitrate response to changes in emitted NO_x.

Modeled Nitrate Chemistry Investigation

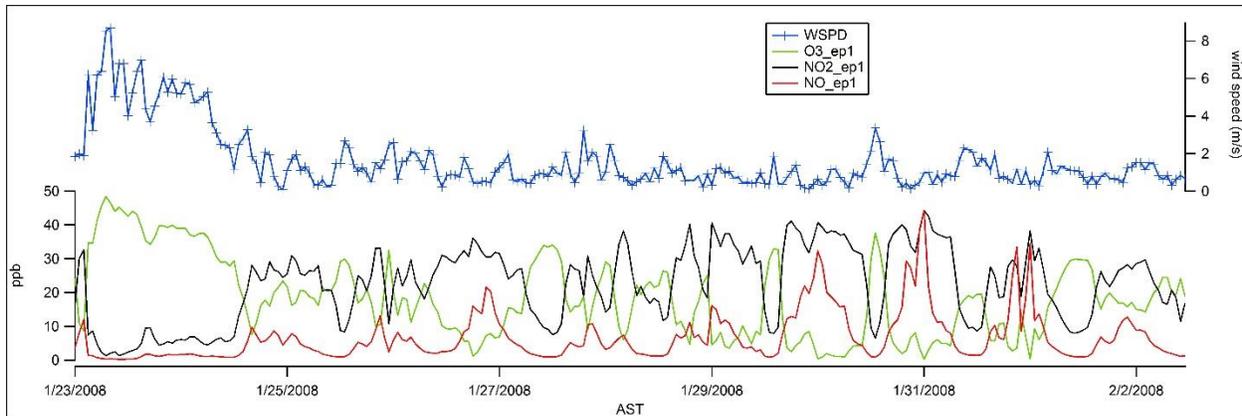


Figure 8 CMAQ modeling output for episode 1 for NO (red), NO₂ (black), O₃ (green) all in ppb and wind speed (blue) in m/s.

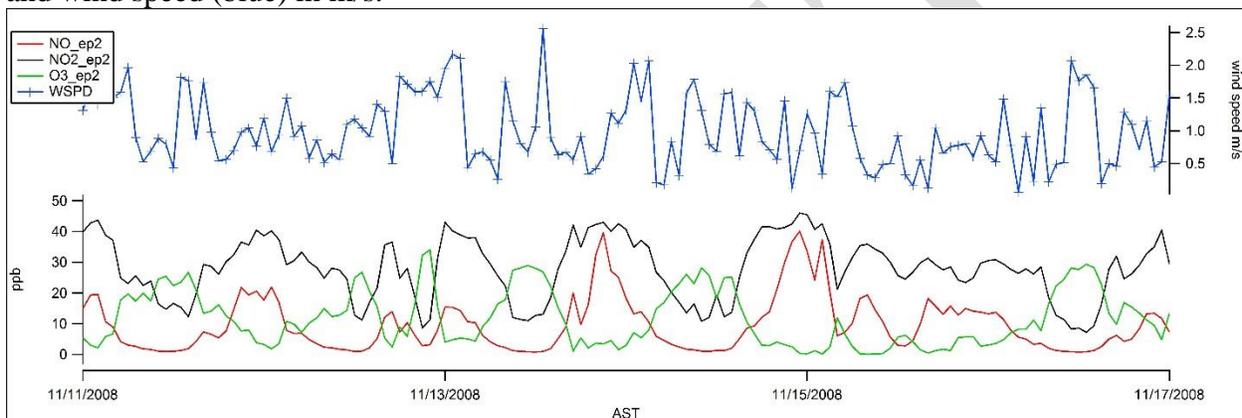


Figure 9 CMAQ modeling output for episode 2 for NO (red), NO₂ (black), O₃ (green) all in ppb and wind speed (blue) in m/s.

The episode average ozone and NO₂ are similar to ambient winter average O₃ and NO₂ measured at the NCORE monitor for episode 1 and 2. The winter averages from 2012 through 2016 at the NCORE site for ozone is 9 ppb, NO₂ is 22 ppb and the NO is 35 ppb. In comparison the modeling average hourly data for the episodes is 13 ppb O₃, 25 ppb of NO₂ and 10 ppb for NO. The NO in the model is lower than ambient NO for the base case model run, this could be due to the grid cell emission rate in the model or the higher advection the model has compared to ambient zero wind conditions. We do not have ambient measurements outside of town, but away from the urban polluted downtown Fairbanks area, we would expect to see clean background concentrations of ozone around 40 ppb and the extracted northeast corner of the modeling domain has ozone levels of 40-45 ppb during both modeling episodes and only a few hours of NO_x at <3 ppb over both episodes.

As mentioned in the precursor demonstration section, the NO emissions were increased by 3.6 times in order to see if the model produces more ammonium nitrate if we add more precursor NO_x emissions. Figure 10 shows the modeled outputs and a large increase in NO up to 250 ppb. The model is presenting a worst case scenario and the O₃ is titrated as expected with the excess NO hindering the oxidation process.

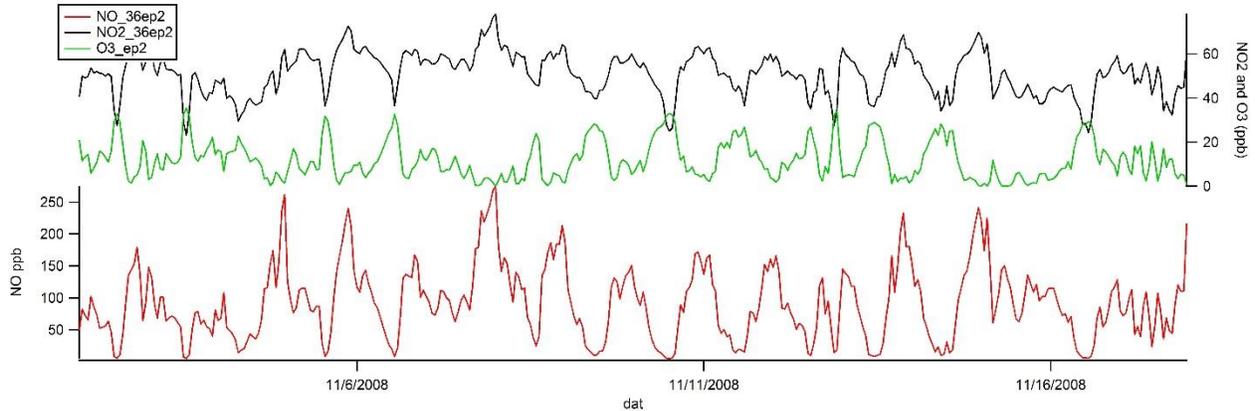


Figure 10 CMAQ modeling output for episode 2 for the NOx sensitivity run, NO (red), NO₂ (black), O₃ (green) all in ppb and wind speed (blue) in m/s.

At night the photolysis of NO_x is not present and to check the model outputs, NO₂ and O₃ are correlated. There should be no concentrations above background ozone (approximately 40 ppb) when there is no photochemistry at night. Therefore NO₂ plus ozone should equal the background as seen in Figure 11. Figure 11 is all daytime and nighttime NO₂ and ozone. There are concentrations about background during the day, this means that most likely there is little photochemistry in the Fairbanks area for NO_x and VOC/NO_x ratios that generally produce photochemical ozone are not applicable under cold, low sunlight conditions. This low photochemical production lead to low OH radical production which forms nitric acid and as reviewed earlier nitric acid forms particle nitrate in PM 2.5 after reacting with water and ammonia gas.

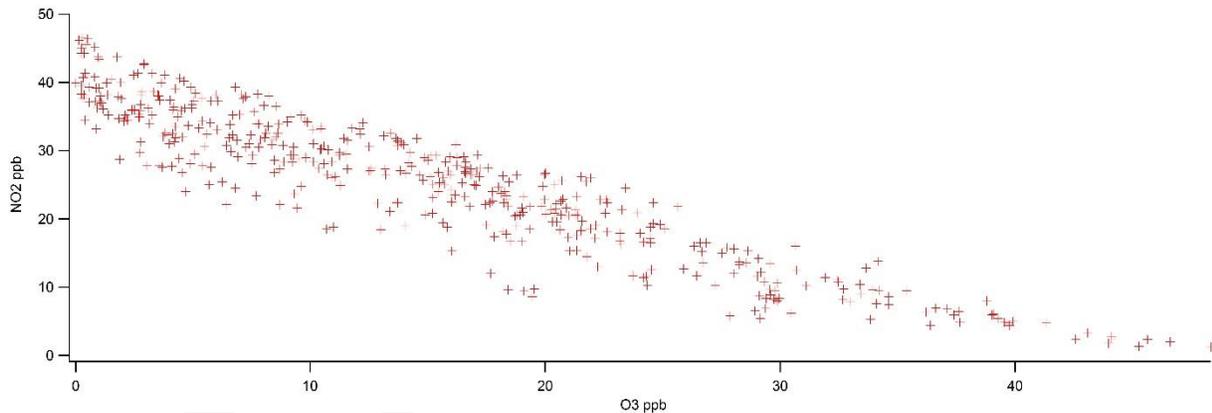


Figure 11. Correlation of hourly NO₂ and O₃ from episode 1.