

**Preliminary Draft  
Precursor Demonstration**

**DRAFT**

**March 22, 2017**

**As part of requirements for subpart 4 Non-Attainment Area (NAA) PM2.5 State Implementation Plan (SIP), all of the precursor gases that contribute to PM2.5 (NO<sub>x</sub>, SO<sub>2</sub>, NH<sub>3</sub> and VOCs) are addressed for potential controls in addition to the primary PM2.5 com.**

## EXECUTIVE SUMMARY

This document serves as a preliminary optional precursor demonstration for the PM<sub>2.5</sub> Serious SIP. Precursor gases include (sulfur dioxide, nitrogen oxides, ammonia, and volatile organic compounds) and contribute to the formation of PM<sub>2.5</sub> 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.<sup>1</sup> This analysis has chosen a threshold of 1.3 µg/m<sup>3</sup> 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<sub>2.5</sub> 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 attain<sup>2</sup>. 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<sub>2.5</sub> 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 implemented<sup>3</sup>.

SO<sub>2</sub>: 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/m<sup>3</sup> in Fairbanks and 4.9 µg/m<sup>3</sup> in North Pole on the average of high concentration days. These values are above the 1.3 µg/m<sup>3</sup> and SO<sub>2</sub> 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 SO<sub>2</sub> precursor emissions are considered significant and any controls deemed feasible for the Fairbanks nonattainment area would be implemented.

NO<sub>x</sub>: Ammonium nitrate is the main particulate compound formed from NO<sub>x</sub> emissions. The underlying chemistry and sensitivity are explained in the following chapter. Concentrations of ammonium nitrate were calculated as 2.4 µg/m<sup>3</sup> in Fairbanks, 2.0 µg/m<sup>3</sup> in North Pole Fire Station, and 1.0 µg/m<sup>3</sup> in North Pole Elementary. The Fairbanks and North Pole Fire Station

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<sup>1</sup> 40 CFR 51.1006 – Optional PM<sub>2.5</sub> precursor demonstrations

<sup>2</sup> <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.

<sup>3</sup> 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<sub>x</sub> from all sources (comprehensive) and from major stationary sources. For the comprehensive demonstration NO<sub>x</sub> passes a 75% sensitivity-based analysis. A separate major stationary source analysis shows that NO<sub>x</sub> passes a zero-out sensitivity-based analysis. Both of these demonstrations and supplemental analysis are provided in this document.

NH<sub>3</sub>: Emitted ammonia is a precursor to the formation of particulate ammonium nitrate and ammonium sulfate. The major contributors to PM<sub>2.5</sub> 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<sub>2.5</sub> while ammonium sulfate does contribute significantly to ambient concentrations of PM<sub>2.5</sub>. Contributions of emitted ammonia to PM<sub>2.5</sub> were calculated as 4.6 µg/m<sup>3</sup> and 4.2 µg/m<sup>3</sup> at the Fairbanks monitors and 4.4 µg/m<sup>3</sup> and 2.1 µg/m<sup>3</sup> 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<sub>2.5</sub> 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<sub>2.5</sub> 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/m<sup>3</sup> at all monitors. For this reason we believe the contribution from VOCs to PM<sub>2.5</sub> are insignificant and do not plan to implement the BACT/BACM and MSM controls for VOCs.

EPA's *Draft PM<sub>2.5</sub> 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<sub>2.5</sub>. 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/m<sup>3</sup> for 24-hour PM<sub>2.5</sub>. 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<sub>2.5</sub>. 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<sub>2.5</sub> 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<sub>x</sub> 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<sub>x</sub> was demonstrated to be insignificant from a 75% sensitivity based analysis. A second NO<sub>x</sub> 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<sub>x</sub> and VOC Precursor Demonstrations**

<b>Precursor</b>	<b>Source(s)</b>	<b>Test Details</b>	<b>Pass</b>
NO <sub>x</sub>	Comprehensive	Sensitivity Based Analysis 75%	Y
NO <sub>x</sub>	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<sub>2.5</sub> requires understanding the Fairbanks and North Pole wintertime characteristics that lead to the formation of PM<sub>2.5</sub> from both direct and secondary formations. Precursor gases form secondary PM<sub>2.5</sub> and this component of PM<sub>2.5</sub> 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

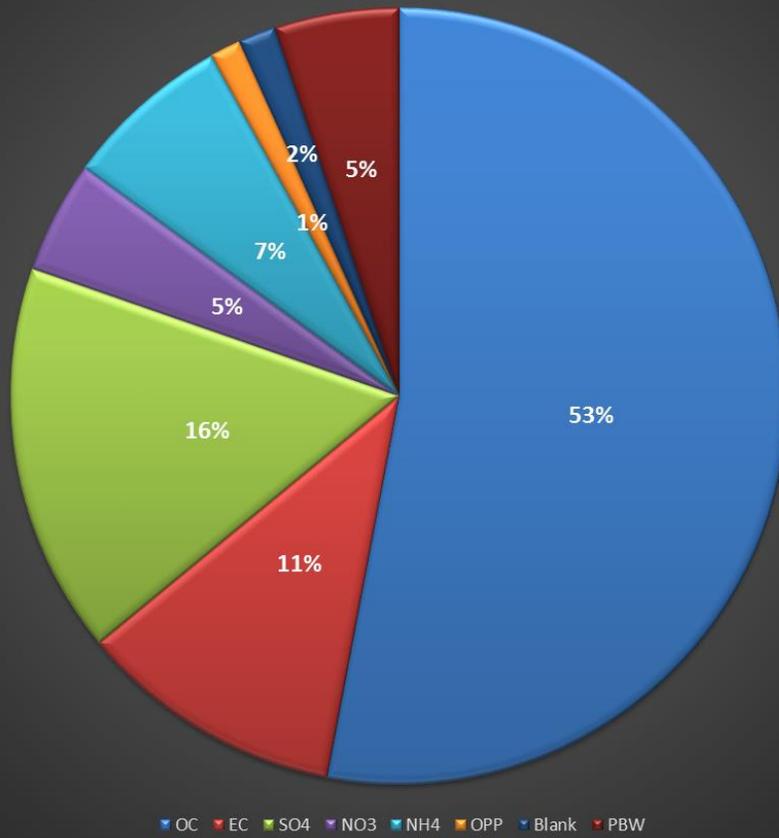


Figure 1: 24-hr average FRM-derived PM<sub>2.5</sub> speciation concentrations based on the design value (DV) of 131.6 µg/m<sup>3</sup> for the high PM<sub>2.5</sub> winter days at North Pole Fire Station

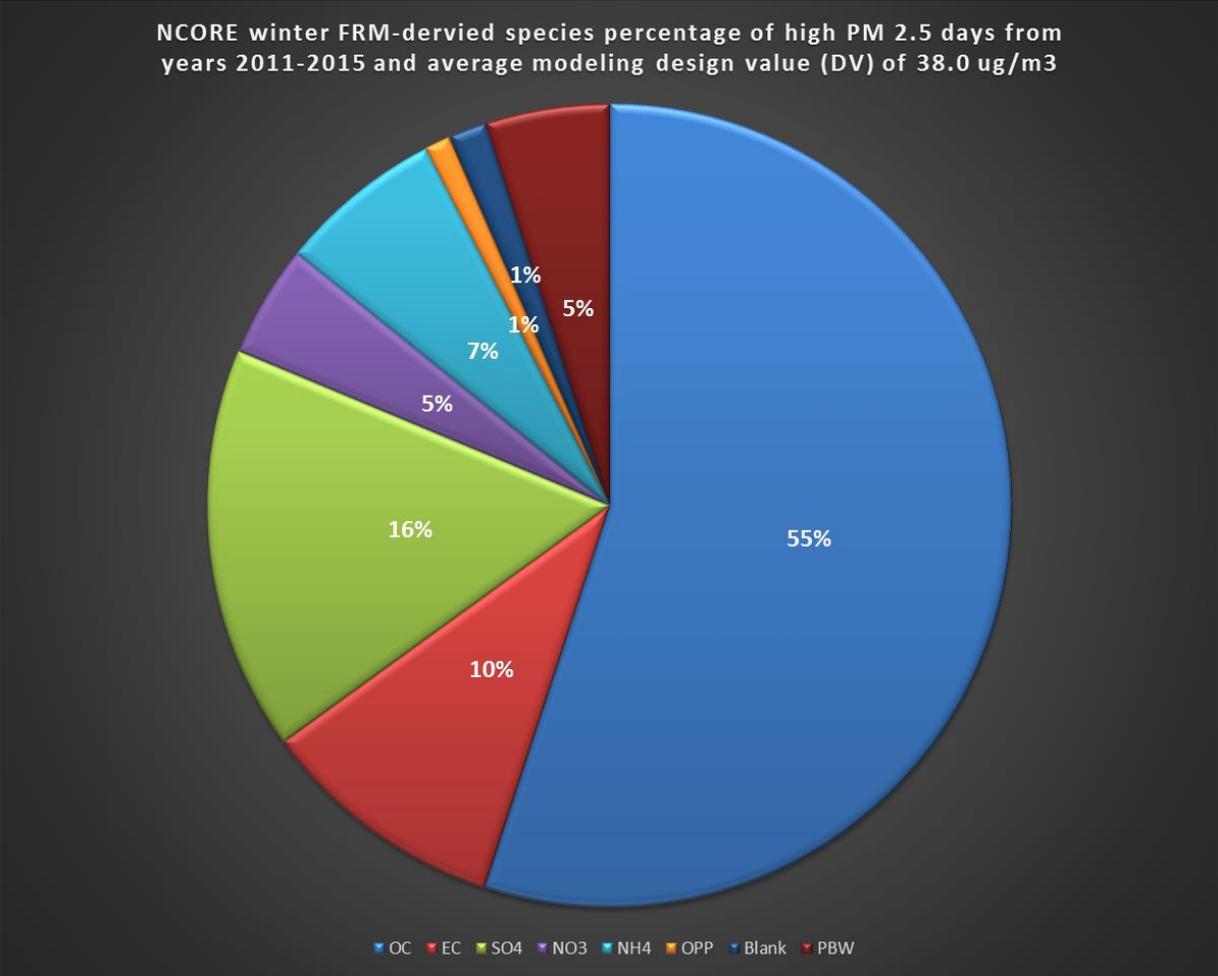


Figure 2: 24-hr average FRM-derived PM<sub>2.5</sub> speciation concentrations based on the design value (DV) of 38.0 μg/m<sup>3</sup> for Fairbanks NCORE Monitor.

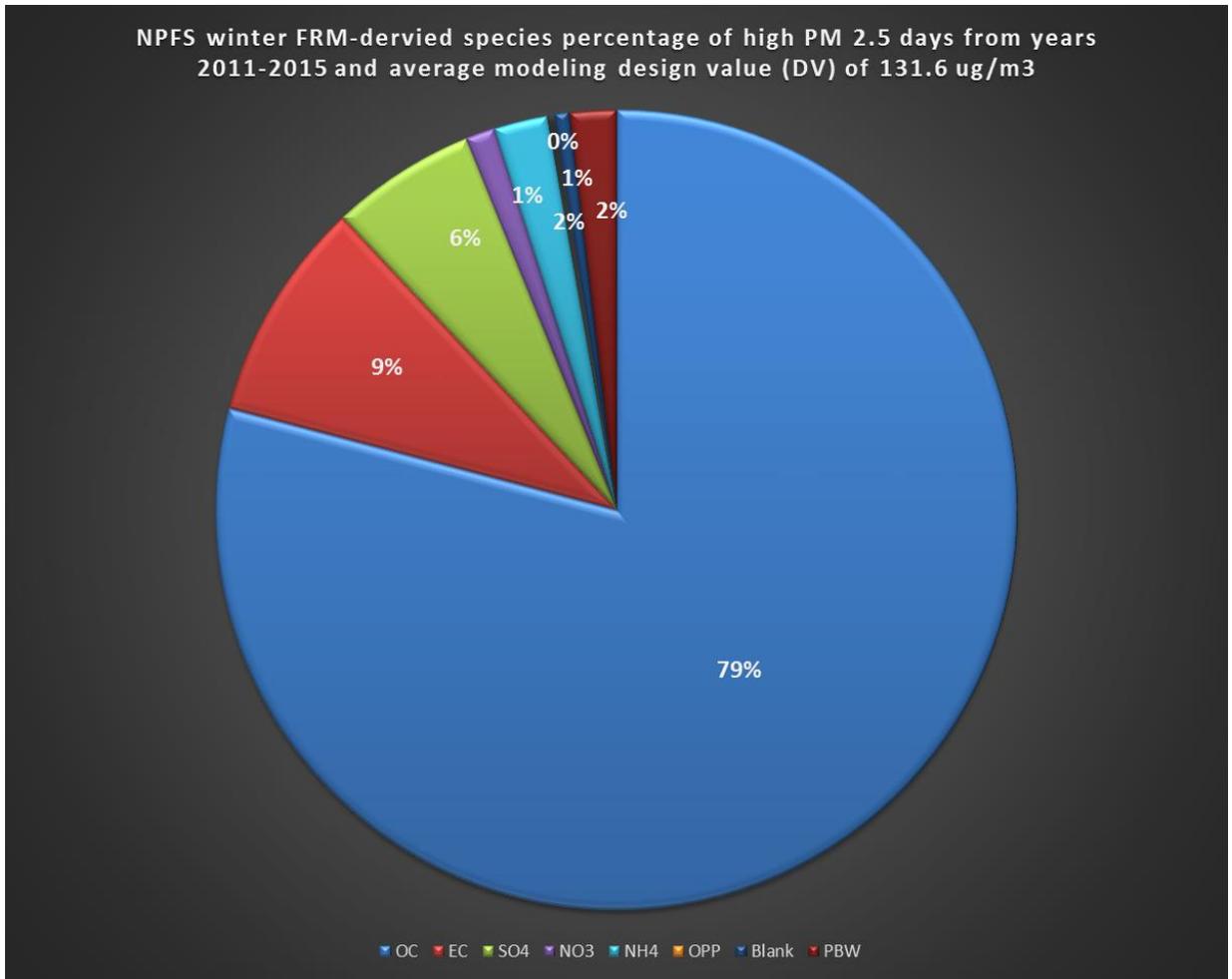


Figure 3: 24-hr average FRM-derived PM<sub>2.5</sub> speciation concentrations based on the design value (DV) of 38.9  $\mu\text{g}/\text{m}^3$  for Fairbanks State Office Building Monitor.

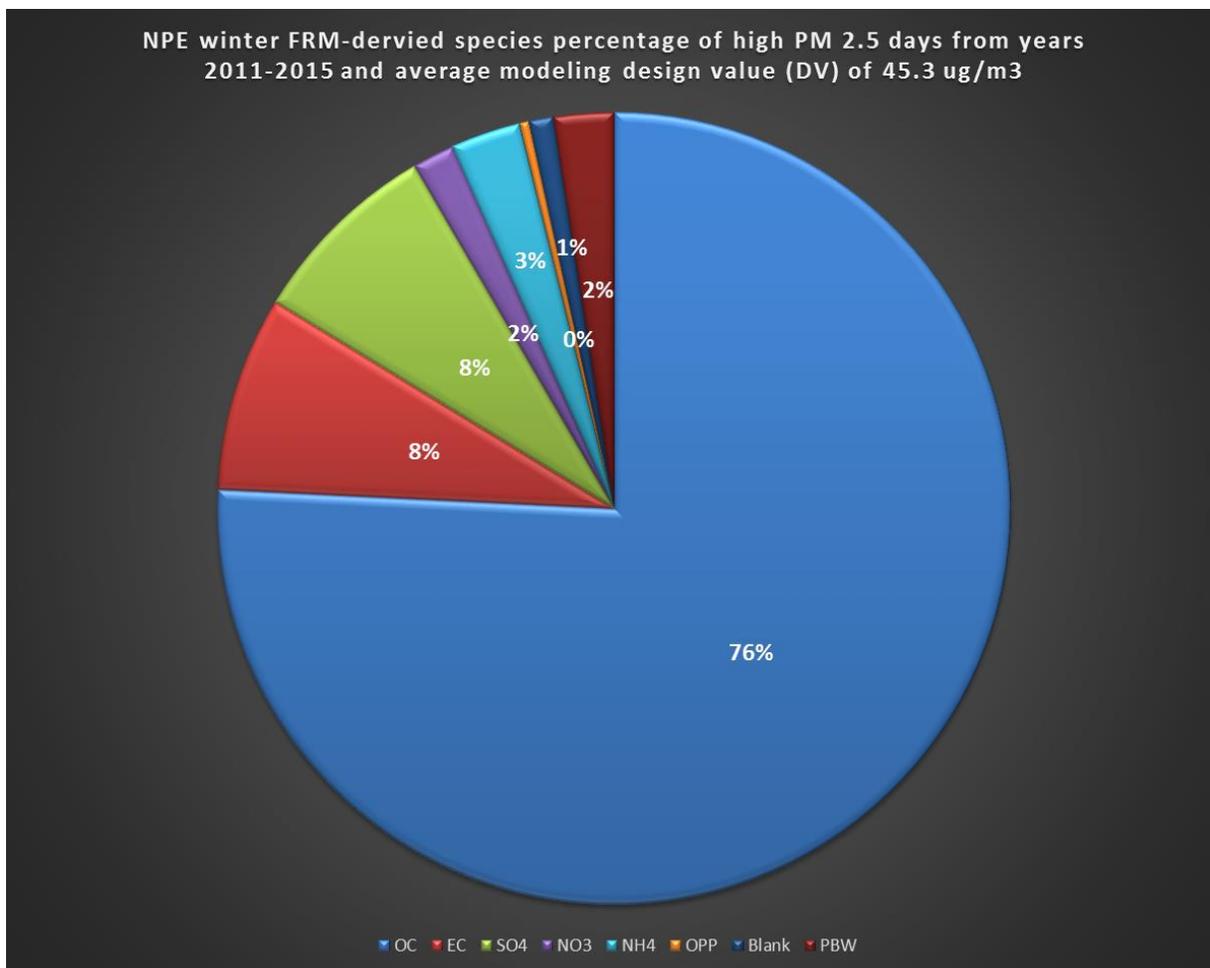


Figure 4: 24-hr average FRM-derived PM<sub>2.5</sub> speciation concentrations based on the design value (DV) of 45.3 μg/m<sup>3</sup> for North Pole Elementary School Monitor.

Particulate Matter (PM<sub>2.5</sub>) 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<sup>-3</sup>), sulfate (SO<sub>2</sub><sup>-4</sup>) and ammonium (NH<sub>4</sub><sup>+</sup>). These species are formed primarily from chemical reactions in the atmosphere involving the gas-phase precursors, nitrogen oxides (NO<sub>x</sub>), sulfur dioxide (SO<sub>2</sub>) and ammonia (NH<sub>3</sub>). The major component of Fairbanks PM<sub>2.5</sub> 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<sub>x</sub> 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<sub>2.5</sub> in the nonattainment area.

Sulfates are a major component of the PM<sub>2.5</sub> mass; estimates show that sulfates comprise approximately 6-16% of the total mass of Fairbanks PM<sub>2.5</sub> (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<sub>2.5</sub> 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<sub>2.5</sub> components (Figure 1) are derived from the high PM<sub>2.5</sub> days from the years 2011-2015. The speciation concentrations that represent the breakdown of the components of PM<sub>2.5</sub> 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<sub>2.5</sub>, we want to compare the components of PM<sub>2.5</sub> measured by the SASS instrument to the FRM measurements that measure total PM<sub>2.5</sub> 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 method<sup>4</sup>. A detailed account of the adjustments made to compare speciation measurements to FRM total PM<sub>2.5</sub> 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<sub>2.5</sub> 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<sub>2.5</sub> reductions will be addressed as part of BACM, which is evaluating controls for all source sectors for PM<sub>2.5</sub> 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<sub>x</sub> (NO<sub>2</sub>+NO), NO and NO<sub>2</sub> with primary emissions coming from combustion processes, home heating, vehicles and industry. Typically, during the day, NO<sub>x</sub> is oxidized by reacting with ozone and OH radical chemistry and forms nitric acid (HNO<sub>3</sub>) and during the night NO<sub>x</sub> is oxidized to form N<sub>2</sub>O<sub>5</sub> (g), which reacts on aerosol surfaces to form HNO<sub>3</sub> (aq) and deposition to snowpack. Particles containing nitrate are neutralized via reaction with ammonia gas (NH<sub>3</sub>) to form ammonium nitrate.

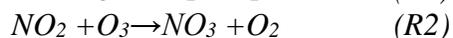
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<sup>4</sup> Frank, N. (2006): Retained nitrate, hydrated sulfates, and carbonaceous mass in Federal Reference Method fine particulate matter for six Eastern U.S. cities. J. Air and Waste Manage. Assoc. 56:500-511.

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 NO<sub>2</sub>. 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 N<sub>2</sub>O<sub>5</sub> is thought to be responsible for 80% of the nitric acid formation at high latitudes<sup>5</sup>, but in polluted areas the fast reaction of excess NO with the nitrate radical, nitric acid formation is hindered at night<sup>6</sup>. 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<sub>x</sub> 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<sub>2.5</sub>. 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 NO<sub>2</sub>, at night NO titrates the ozone removing the main oxidant to form nitrate<sup>7</sup>. During the day the photochemistry is limited by low sunlight and under low wind conditions when PM<sub>2.5</sub> 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<sub>x</sub> 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<sub>2.5</sub> even on the highest days is ammonium nitrate. The modeling outputs were examined for NO, O<sub>3</sub>, and NO<sub>2</sub>. 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<sub>2.5</sub>. 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<sub>2.5</sub> is reduced by the wind. Under the conditions when we have high PM<sub>2.5</sub> (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<sub>x</sub> and reactions with ammonia that produce particle nitrate are hindered (R2).



<sup>5</sup> Dentener, F. J. and Crutzen, P. J.: Reaction of N<sub>2</sub>O<sub>5</sub> on tropospheric aerosols: Impact on the global distributions of NO<sub>x</sub>, O<sub>3</sub>, and OH, J. Geophys. Res., 98, 7149–7163, doi:10.1029/92jd02979, 1993

<sup>6</sup> Seinfeld and Pandis, Atmospheric Chemistry and Physics, 1998

<sup>7</sup> Joyce, P.L., Gasow, R.V., Simpson, W.R., The fate of NO<sub>x</sub> 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.<sup>8</sup>



$N_2O_5$  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)<sup>9</sup> 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.

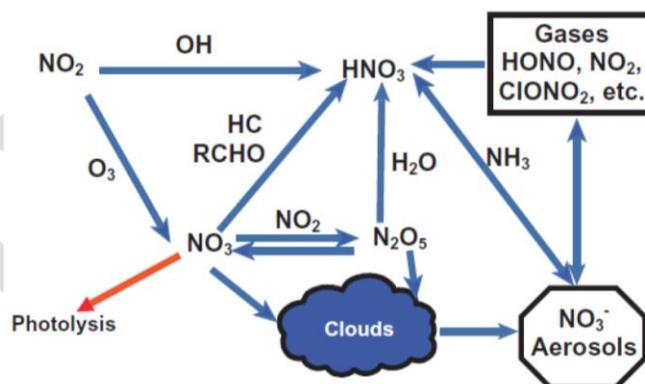


Figure 7. Chemistry processes related to nitrate formation represented in CMAQ<sup>10</sup>

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 nitrate<sup>11</sup>. Parameterization of heterogeneous reactions of  $N_2O_5$  in CMAQ 4.7.1 is based on the method developed by Davis et

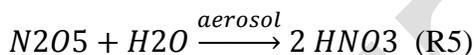
<sup>8</sup> Dentener, F. J. and Crutzen, P. J.: Reaction of  $N_2O_5$  on tropospheric aerosols: Impact on the global distributions of  $NO_x$ ,  $O_3$ , and OH, J. Geophys. Res., 98, 7149–7163, doi:10.1029/92jd02979, 1993

<sup>9</sup> Seinfeld and Pandis, Atmospheric Chemistry and Physics, 1998, pg 283

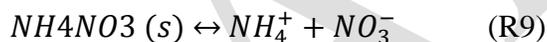
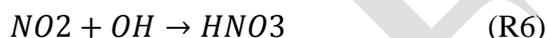
<sup>10</sup> NARSTO 2004. PDF version is available here: <http://www.narsto.org/sites/narsto-dev.ornl.gov/files/Ch3813KB.pdf>

<sup>11</sup> [https://www.atmos.illinois.edu/~nriemer/papers/riemer\\_n2o5\\_2003.pdf](https://www.atmos.illinois.edu/~nriemer/papers/riemer_n2o5_2003.pdf)

al. (2008)<sup>12</sup>, which calculates the N<sub>2</sub>O<sub>5</sub> hydrolysis probability as a function of temperature, relative humidity (RH), inorganic aerosol composition, and phase state. The N<sub>2</sub>O<sub>5</sub> photolysis probability is defined as the fraction of collisions between N<sub>2</sub>O<sub>5</sub> molecules and particle surfaces that lead to the production of HNO<sub>3</sub>. The photolysis probability is higher at lower temperature and higher RH, so nitrate formation through this pathway is more active at nighttime when N<sub>2</sub>O<sub>5</sub> is accumulated and the temperature is low and RH is high. The N<sub>2</sub>O<sub>5</sub> 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 HNO<sub>3</sub>, NH<sub>3</sub>, and aerosols try to reach a thermodynamic equilibrium<sup>13</sup>. The major reactions represented in the model are listed below:



Reaction R6 produces gas phase HNO<sub>3</sub> during daytime. Gas phase HNO<sub>3</sub> and NH<sub>3</sub> react to form NH<sub>4</sub>NO<sub>3</sub> particles. Both gas phase HNO<sub>3</sub> and NH<sub>4</sub>NO<sub>3</sub> 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 SO<sub>2</sub> 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 SO<sub>2</sub> and primary sulfate emissions to ULSD will reduce the SO<sub>2</sub> 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 pathways<sup>14</sup>.

## Ammonia precursor gas and ammonium

Ammonia gas (NH<sub>3</sub>) reacts with acid aerosols containing nitrate (NO<sub>3</sub><sup>-</sup>) and sulfate (SO<sub>4</sub><sup>2-</sup>) to form ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>) and ammonium sulfate ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>). Nitrate is assumed to be

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

<sup>13</sup> [http://nenes.eas.gatech.edu/Preprints/ISORROPIA\\_AGPP.pdf](http://nenes.eas.gatech.edu/Preprints/ISORROPIA_AGPP.pdf)

<sup>14</sup> 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<sub>2.5</sub> 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<sub>2.5</sub> 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<sub>x</sub> and VOCs in the Fairbanks North Star Borough 24-hour PM<sub>2.5</sub> Nonattainment Area. This process is in keeping with EPA's *Draft PM<sub>2.5</sub> Precursor Demonstration Guidance*<sup>15</sup> and 2016 PM<sub>2.5</sub> Implementation rule<sup>16</sup>. 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/m<sup>3</sup> as a starting point for the precursor demonstration for 24-hour PM<sub>2.5</sub><sup>17</sup>. 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.

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<sup>15</sup> *Draft PM<sub>2.5</sub> Precursor Demonstration Guidance*, US EPA Office of Air Quality Planning and Standards, November 17 2016.

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

<sup>17</sup> 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 SANDWICH<sup>18</sup> data processing technique. The ambient dataset is the same that is used in the attainment plan portion of the Serious area plan.

Contributions from  $\text{SO}_2$ ,  $\text{NO}_x$ , and  $\text{NH}_4$  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  $\text{SO}_2$ ,  $\text{NO}_x$ , and  $\text{NH}_3$  below. Contributions for  $\text{SO}_2$  were assessed using the mass of sulfate measured on the filters on the highest concentration days at each monitor site. Contributions for  $\text{NO}_x$  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  $\mu\text{g}/\text{m}^3$ .  $\text{NH}_3$  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 Fairbanks<sup>19</sup>. 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.

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<sup>18</sup> 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.

<sup>19</sup> 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<sub>x</sub> Comprehensive and Major Stationary Precursor Demonstrations Maximum Daily Impacts**

NO <sub>x</sub> Highest Daily Contributions (SMAT µg/m <sup>3</sup> )						
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<sub>2.5</sub> 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.

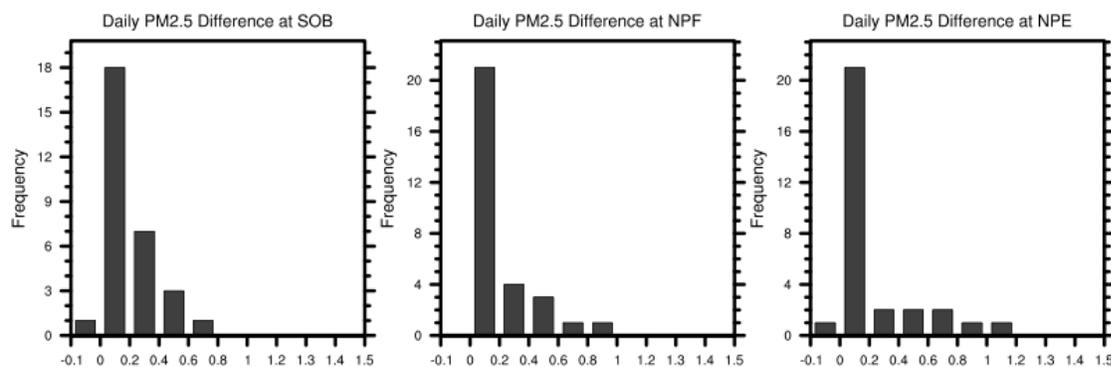


Figure 5. Histograms of the daily PM<sub>2.5</sub> differences at monitor grid cells for the point source NO<sub>x</sub> knock out run (PT0NOX).

For the point stationary source NO<sub>x</sub> zero out case, the reductions in daily PM<sub>2.5</sub> at the three grid cells containing monitored locations are mostly (~20 days) less than 0.2 µg/m<sup>3</sup>. None of the daily differences exceed the 1.3 µg/m<sup>3</sup> 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/m<sup>3</sup>) in daily PM<sub>2.5</sub> when point source NO<sub>x</sub> emissions were removed. The nitrate concentration was decreased for both days, but the other PM<sub>2.5</sub> species were slightly increased due to the removal of point source NO<sub>x</sub> emissions. Both days have a relatively low nitrate concentrations, and it could be that the interaction of various PM<sub>2.5</sub> species on those days is very sensitive to the changes in NO<sub>x</sub> emissions.

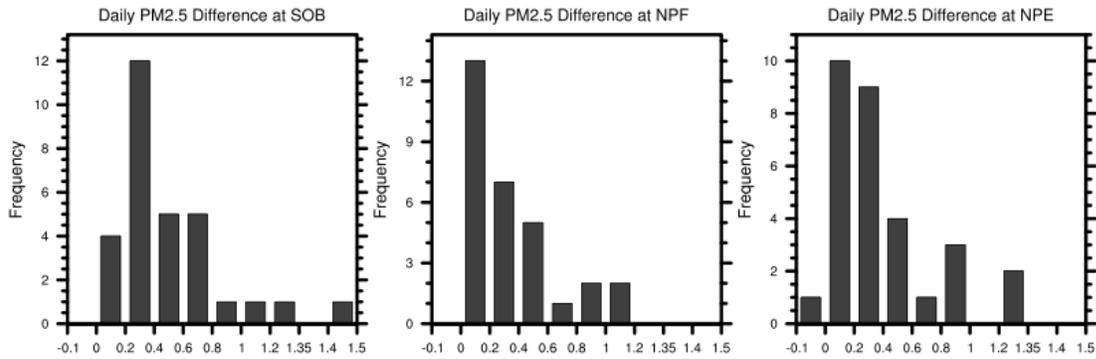


Figure 6. Histograms of the daily PM<sub>2.5</sub> differences at monitor grid cells for the comprehensive NOx 75% off sensitivity run (NOX75OFF).

For the comprehensive NOx 75% off case, most of the days have a reduction of PM<sub>2.5</sub> less than 0.6 μg/m<sup>3</sup>. There is one day at SOB with a reduction slightly larger than 1.3 μg/m<sup>3</sup>. There are two days at NPE that have a reduction above 1.3 μg/m<sup>3</sup>, but below 1.35 μg/m<sup>3</sup>. When rounded to the nearest tenth of a μg/m<sup>3</sup>, these days fall within the threshold value.

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

NOx Episode Average Contributions (SMAT μg/m <sup>3</sup> )						
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 μg/m <sup>3</sup> )						
Test	SOB	NCORE	NCORE BAM	NPFS	NPE	Max Cell

<b>CMAQ Zero-out</b>						
<b>Modeled 75%</b>	0.62	0.58	0.64	0.36	0.22	0.89
<b>Major Stationary Zero-out</b>	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**

<b>NOx Highest Daily Contributions (Unprocessed Modeled <math>\mu\text{g}/\text{m}^3</math>)</b>						
<b>Test</b>	<b>SOB</b>	<b>NCORE</b>	<b>NCORE BAM</b>	<b>NPFS</b>	<b>NPE</b>	<b>Max Cell</b>
<b>CMAQ Zero-out</b>						
<b>Modeled 75%</b>	2.16	2.16	2.16	2.15	2.29	3.13
<b>Major Stationary Zero-out</b>	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<sub>x</sub>.

### Modeled Nitrate Chemistry Investigation

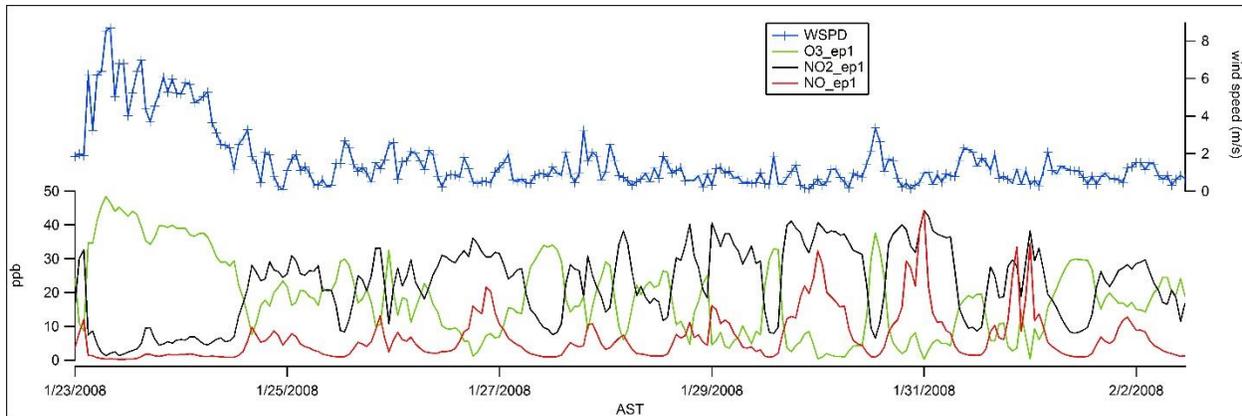


Figure 8 CMAQ modeling output for episode 1 for NO (red), NO<sub>2</sub> (black), O<sub>3</sub> (green) all in ppb and wind speed (blue) in m/s.

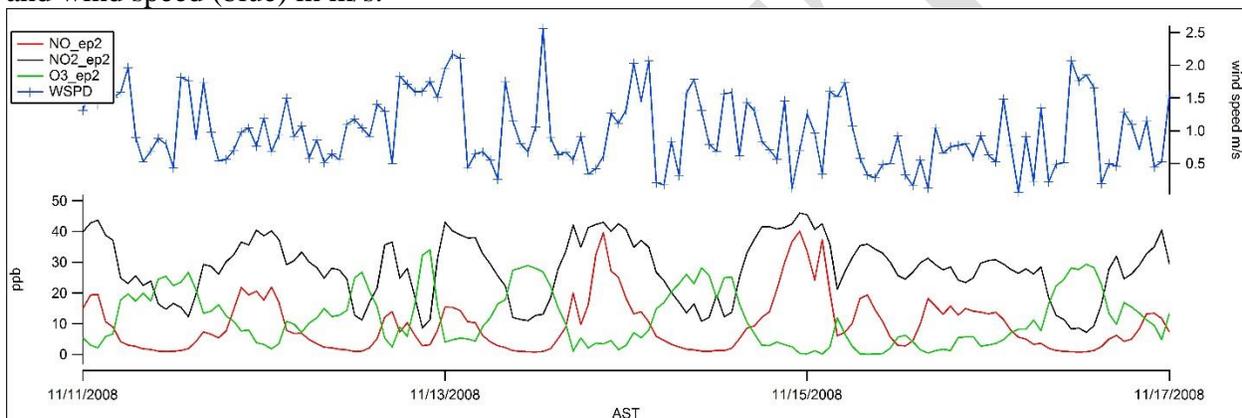


Figure 9 CMAQ modeling output for episode 2 for NO (red), NO<sub>2</sub> (black), O<sub>3</sub> (green) all in ppb and wind speed (blue) in m/s.

The episode average ozone and NO<sub>2</sub> are similar to ambient winter average O<sub>3</sub> and NO<sub>2</sub> 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, NO<sub>2</sub> is 22 ppb and the NO is 35 ppb. In comparison the modeling average hourly data for the episodes is 13 ppb O<sub>3</sub>, 25 ppb of NO<sub>2</sub> 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<sub>x</sub> 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<sub>x</sub> 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 O<sub>3</sub> is titrated as expected with the excess NO hindering the oxidation process.

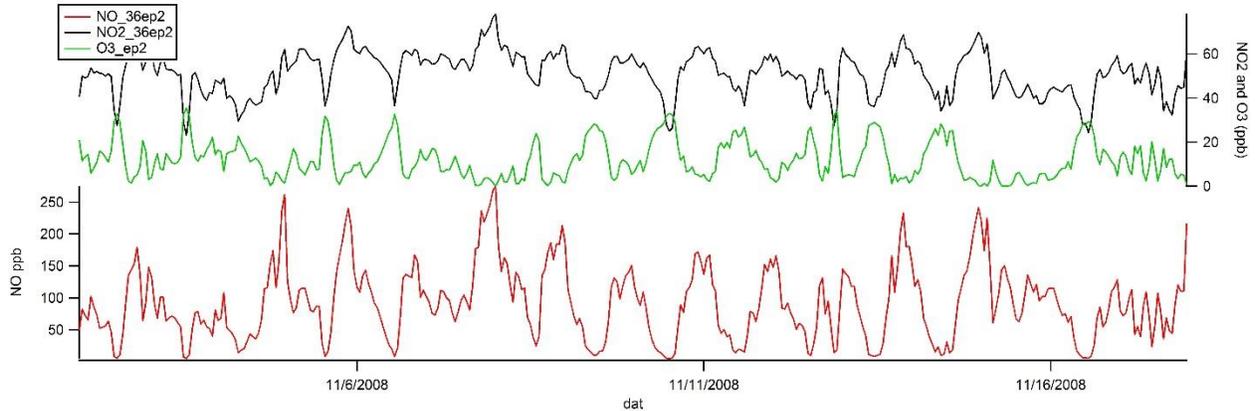


Figure 10 CMAQ modeling output for episode 2 for the NOx sensitivity run, NO (red), NO<sub>2</sub> (black), O<sub>3</sub> (green) all in ppb and wind speed (blue) in m/s.

At night the photolysis of NO<sub>x</sub> is not present and to check the model outputs, NO<sub>2</sub> and O<sub>3</sub> are correlated. There should be no concentrations above background ozone (approximately 40 ppb) when there is no photochemistry at night. Therefore NO<sub>2</sub> plus ozone should equal the background as seen in Figure 11. Figure 11 is all daytime and nighttime NO<sub>2</sub> 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<sub>x</sub> and VOC/NO<sub>x</sub> 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.

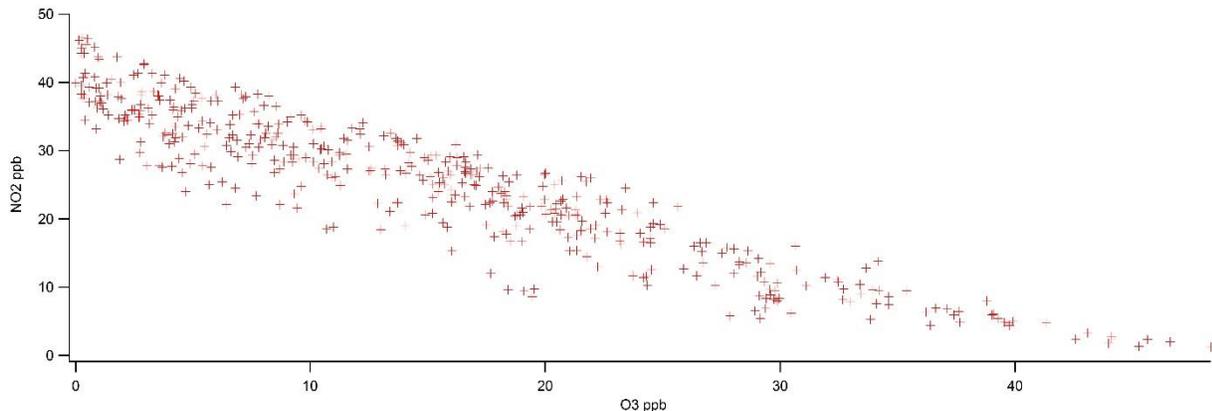


Figure 11. Correlation of hourly NO<sub>2</sub> and O<sub>3</sub> from episode 1.