

Assessing the Emissions from the Oil and Gas Development in the Bakken Formation and Their Impact on Air Quality in National Parks

Summary of the Problem

The rapid expansion of the oil and gas sector in the Bakken formation and the associated population growth and development are causing increased emissions in gaseous, particulate, and hazardous air pollutants (HAPs). These emissions will mix together and can be transported downwind to Theodore Roosevelt National Park (NP), the Fort Union Trading Post National Historic Site (NHS), and the Knife River Indian Villages NHS, all located just tens of miles from active oil and gas development. Theodore Roosevelt NP is also classified as a class I airshed, which provides for the highest level of federal protection of its air quality. At these parks, the increased pollution could lead to

- exceedances of the National Ambient Air Quality Standards (NAAQS), causing adverse human health and welfare effects
- violation of goals of the Regional Haze Rule (degradation rather than improvement of visibility)
- increased reactive nitrogen deposition causing eutrophication of sensitive ecosystems
- “acid” deposition
- HAPs concentrations that affect wildlife and human health
- air toxic deposition in sensitive ecosystems

Current air quality monitoring is insufficient to assess whether or not air quality levels adversely affect these parks and other class I areas in and around the Bakken region. Nor is the impact of the Bakken energy development on the air quality known. However, the rapid energy development will continue and any impacts from this activity are likely to grow in the future.

Most of the development is on private lands, where the current air quality regulatory structure has limited ability at controlling the emissions. This, coupled with the lack of air quality information, presents few options to address the cumulative air quality impacts from the energy development on national parks and other areas. It is critical that this information gap is filled. Specifically,

- Quantify current air quality levels in national parks in the Bakken region
- Assess if the air pollution is due to local or more distant regional sources such as Canadian tar sands development
- Differentiate the contributions from local oil and gas, increasing population centers, and associated mobile sources
- Track the change in air quality in the national parks over time

Air quality models alone are insufficient to accomplish these goals. These models are reliant on emission estimates, but quantifying the emissions from the energy development is problematic due to varying fugitive emissions, changing numbers of flares with different combustion properties, and incomplete information on the population growth and associated activity and development. In addition, air quality models have incomplete formulations of some important atmospheric mechanism. The available air quality data are insufficient to properly evaluate these models and constrain or refine their source attribution results, leading to unknown biases and

errors in the model results. Therefore, a combined monitoring and modeling assessment is needed to fill in these information gaps. The information gained from this assessment would aid the understanding of the impact of existing and planned oil and gas developments in other regions of the country.

Background

The Bakken formation contains billions of barrels of oil and gas trapped in rock and shale in North Dakota, Montana, and Canada (Figure 1). New horizontal drilling and hydraulic fracturing methods have allowed the exploitation of these oil and gas deposits. In 2008 the U.S. Geological Survey (USGS) estimated that there were 3 – 4.3 billion barrels of recoverable oil, making it among the largest oil deposits in the conterminous United States. The USGS estimate is now thought to be a significant underestimate (http://www.eia.gov/pub/oil_gas/natural_gas/feature_articles/2006/ngshock/ngshock.pdf). This has led to an exponential growth in the number of wells and production of oil since 2002 (Figure 2) with most of the activity occurring in North Dakota. In September 2012 there were 7899 active wells in North Dakota, primarily located in the Bakken formation (https://www.dmr.nd.gov/oilgas/mpr/2012_09.pdf). More than 2000 wells are being drilled each year, and the number of wells is expected to grow to more than 40,000. Significant drilling is also occurring in Montana, particularly in the Elm Coulee Field in the Bakken formation (Figure 2).

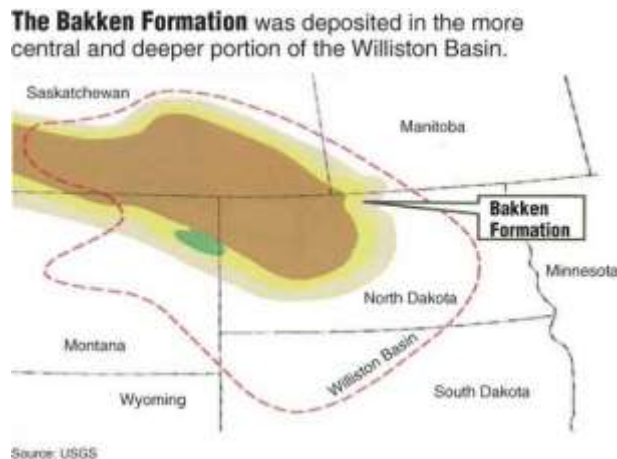


Figure 1. The Bakken formation in the Williston basin.

The natural gas extracted from these wells is primarily methane and other volatile organic compounds (VOC), but it does contain contaminants, with 2% of the gas being hydrogen sulfide (H_2S) and 7% nitrogen (N_2) (Table 1). The Bakken formation is in a relatively remote area without an established infrastructure and pipelines. This complicates the handling of the natural gas, and in North Dakota approximately 30% of the gas is burned off in flares. The flaring readily converts the H_2S and N_2 in the fuel to SO_2 and NO_x , respectively. Due to incomplete combustion, VOCs, hazardous air pollutants (HAPs), carbon monoxide (CO), and particulate elemental and organic carbon are also emitted in the flares. This is evident in Figure 3, where a well gas flare has a brightly colored flame, a sign of incomplete combustion, and black smoke, i.e., EC, is rising from the flame. In the atmosphere, the gaseous SO_2 , NO_x , and VOC emissions are converted to fine particulate sulfates, nitrates, and organics, respectively. This is seen in Figure 4, where the emissions from a well flare accumulated around the well, and the fine particulate matter (PM_{2.5}) created a thick haze near the ground.

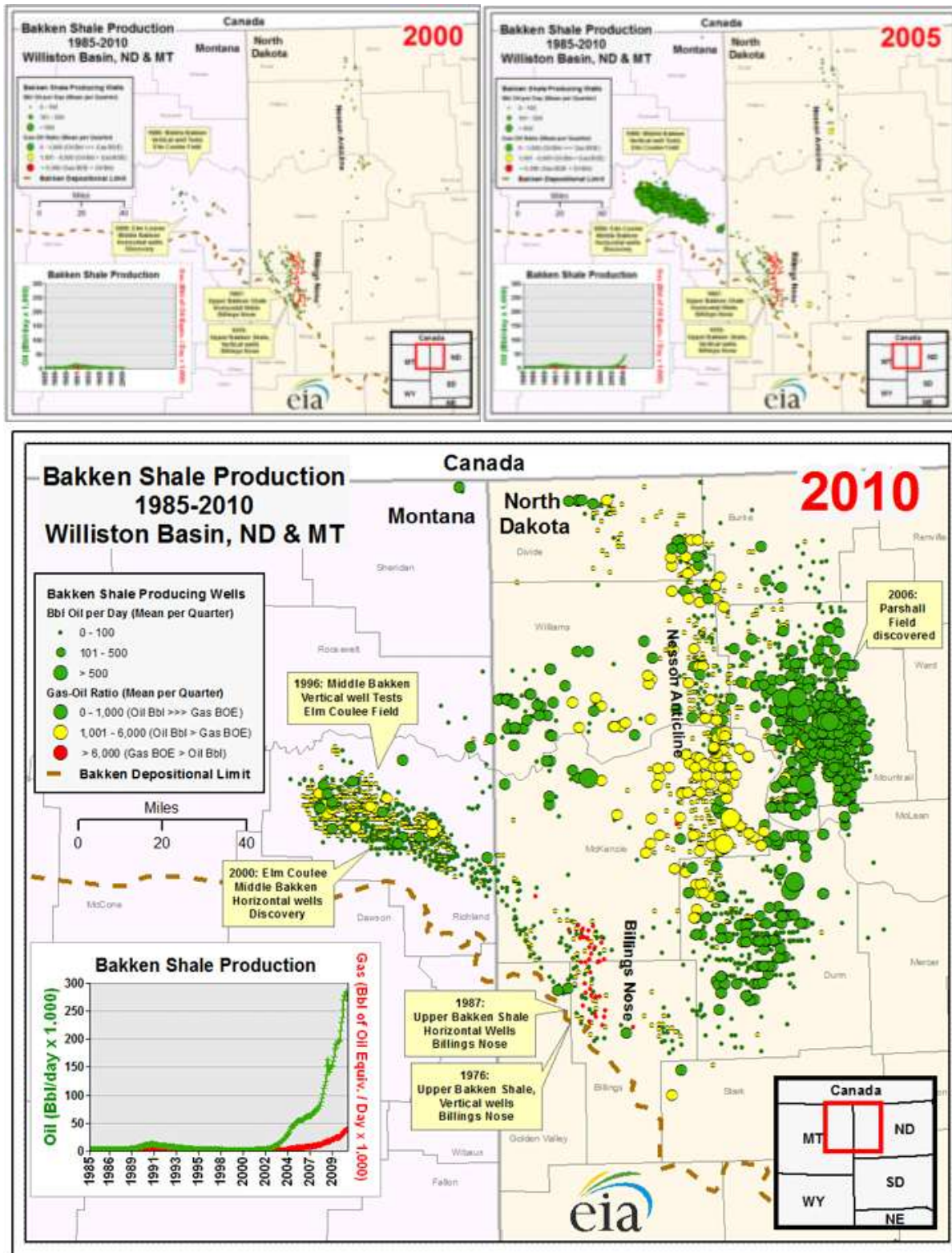


Figure 2. The growth in oil and gas production from 1985 to 2010. (Source: U.S. Energy Information Administration, based on data from HPDI, LLC. <http://www.eia.gov/todayinenergy/detail.cfm?id=3750>)

Table 1. Typical composition of Bakken well natural gas at the well head.

Components	Mol %
H ₂ O	0.29
H ₂ S	2.00
CO ₂	0.51
N ₂	7.10
CH ₄	59.30
Ethane	17.73
Propane	9.42
i-butane	0.70
n-butane	2.03
i-pentane	0.27
n-pentane	0.38
n-hexane	0.16
c-7	0.07
c-8	0.03
c09	0.01
total	100.00



Figure 3. Flaring of natural gas and contaminates at a producing oil and gas well.



Figure 4. Early morning haze caused by the accumulation of primary and secondary PM2.5 from a well flair.

The emissions from the flaring are only part of the problem. There are significant emissions from the support for drilling, operation, and maintenance of active wells. For example, a couple of thousand trucking events and associated diesel emissions are required for each new well drilled; and emissions of VOC and HAPs can occur during the well hydraulic fracturing process. To support the energy development, there has been an influx of people, with the population of Williston and surrounding areas growing by a factor of 4 or 5 over the past seven years. This has led to increased urbanization that significantly adds to pollutant emissions in the region from the increased traffic, construction, cooking, and other human activities. The emissions from the thousands of wells plus the increased human activity mix together and are transported downwind where they can impact national parks and other sensitive areas.

There are three national park units in the path of the oil and gas development: Fort Union Trading Post National Historic Site (NHS) (FOUS), Knife River Indian Villages NHS (KNRI), and the three units of Theodore Roosevelt National Park (NP) (THRO). FOUS and KNRI are class II airsheds while THRO is classified as a class I airshed, which provides for the highest level of federal protection of its air quality. As described by Naylor et al. (2011), the rampant energy development has put these park units “under siege”. Part of the threat is due to the cumulative emissions from all of the oil and gas wells and increased population. The PM_{2.5} directly emitted from the oil and gas activity and formed from the SO₂, VOC, and NO_x precursor species causes haze, degrading the visibility, a protected air quality related value in class I areas. At high concentrations, PM_{2.5} also causes adverse health effects. The NO_x and VOC emissions can combine to form ozone, which can impact human health and is harmful to sensitive vegetation. The reactive nitrogen can deposit in sensitive ecosystems, causing terrestrial and aquatic eutrophication, and in combination with sulfur oxides can cause acidification of terrestrial systems and water bodies.

There is little air quality monitoring in the Bakken region, making any assessments of the current air quality and contributions of the energy development in this region problematic. However, there are some air quality monitors in the area that indicate that the oil and gas development may already be negatively impacting air quality in THRO and the surrounding area. Long-term trends in the annual concentrations of fine particulate sulfate and nitrate are presented in Figure 5. As shown, over the past 10 years there have been steep declines in the sulfate and nitrate concentrations throughout the United States. However, in western North Dakota and eastern Montana, the concentrations have remained flat or increased. In December, starting in 2006, sulfate and nitrate in the Bakken region, as well as to the south, increased significantly (Figure 6). These trends are affecting haze levels in class I areas in this region. As shown in Figure 7, the trends in the 20% worst haze days, i.e., the Regional Haze Rule metric, have remained flat or slightly increased in Bakken region, while outside this region the haze has significantly declined. The role of the energy development in the Bakken formation on these trends relative to other sources, such as increased emissions from the Canadian oil sands, remains an open question.

Current ozone monitoring in the south unit of THRO shows no exceedances of ozone NAAQS health standards. However, no monitoring is available in THRO’s north unit, or in KNRI or FOUS, which are closer to the oil and gas development. Ozone exceedances of the NAAQS have occurred in oil and gas fields in Colorado, Utah, Wyoming, and New Mexico, and even if current concentrations are below the NAAQS, exceedances could occur with continued development and increased emissions.

There is no specific poor air quality season in the Bakken region. Ozone and acid deposition tends to peak in the warm months, but high aerosol concentrations occur all year round (Figure 8). The energy development is expected to contribute to the sulfate, nitrate, carbonaceous, and

dust aerosols. As shown in Figure 8, the highest sulfate and nitrate concentrations occur in the winter months; this is counter to most other regions of the county. During the warmer months, sulfate, organics, and soils are the largest contributors to PM2.5.

The National Park Service (NPS) has a limited ability to address the air quality concerns through the existing regulations. This is summarized in the April 2, 2012, Air Resources Division briefing statement, which states that

“Due to the limited percentage of federal vs. private and state oil and gas ownership coupled with the current air quality regulatory structure (i.e., limited air emission control requirements for the oil and gas sector), few strong handles exist for addressing cumulative air quality concerns. Where federal oil and gas leasing and development is [*sic*] occurring, the NPS does have a handle through the BLM. With regard to nonfederal oil and gas, we are optimistic that some progress could be made to address resource protection concerns through cooperation with the affected states, Tribes, operators and general public.”

The lack of regulatory handles is exacerbated by a lack of monitoring information about current air quality levels in the region and the contribution of the energy and associated development in the region on the air quality. Chemical transport modeling (CTM) of the air quality in this region is also problematic due to the difficulty in quantifying emissions from the energy development and associated human activity and the limitation in current models to simulate many relevant chemical processes. In addition, the available air quality data is inadequate to properly evaluate the models and constrain and refine the CTM source apportionment results. To address the information gaps, an air quality monitoring and modeling assessment study is needed.

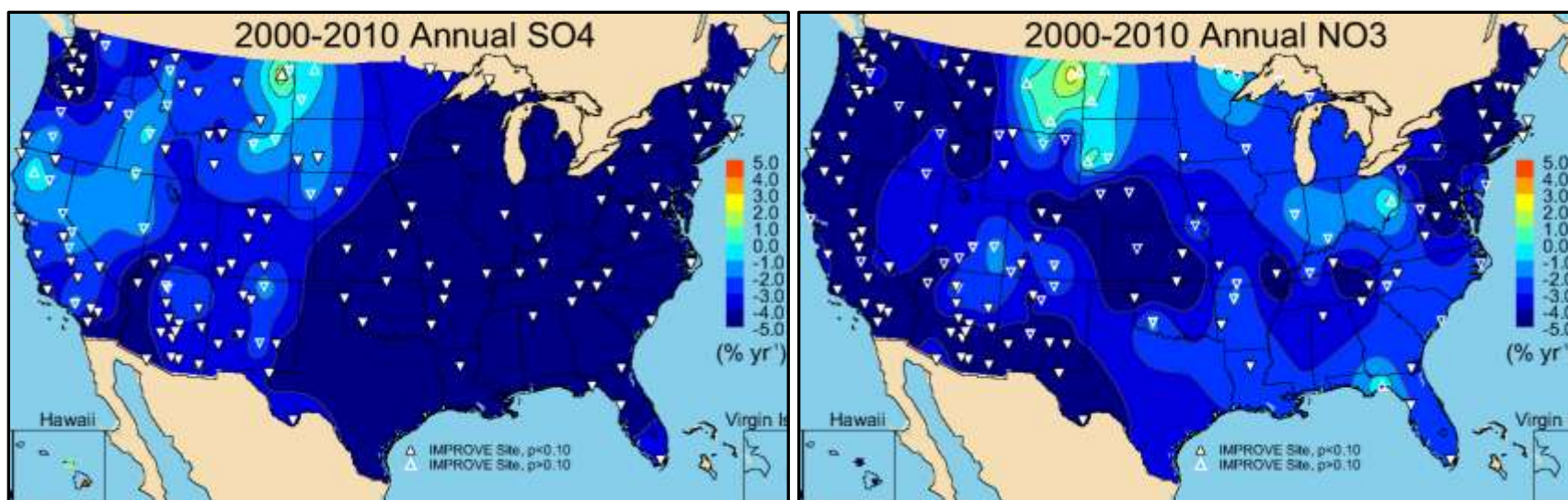


Figure 5. Long-term trends in fine particulate sulfate and nitrate annual concentrations measured at IMPROVE monitoring sites. An IMPROVE monitor is located in the southern unit of Theodore Roosevelt NP, MT.

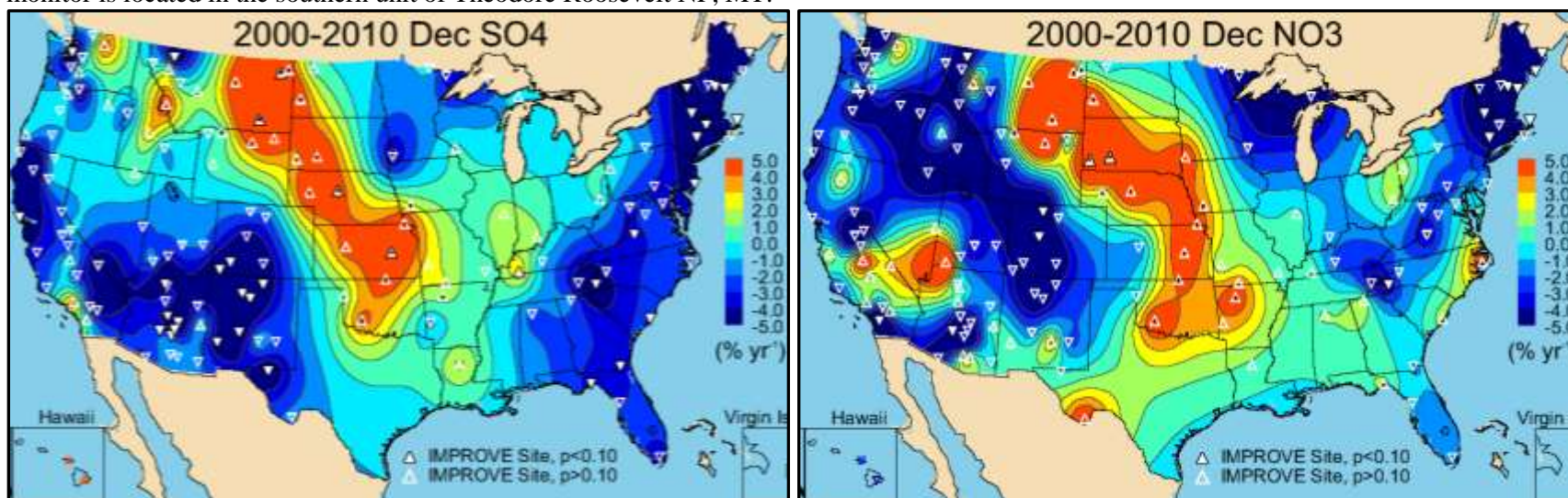


Figure 6. Long-term trends in average December sulfate and nitrate concentrations measured at IMPROVE monitoring sites.

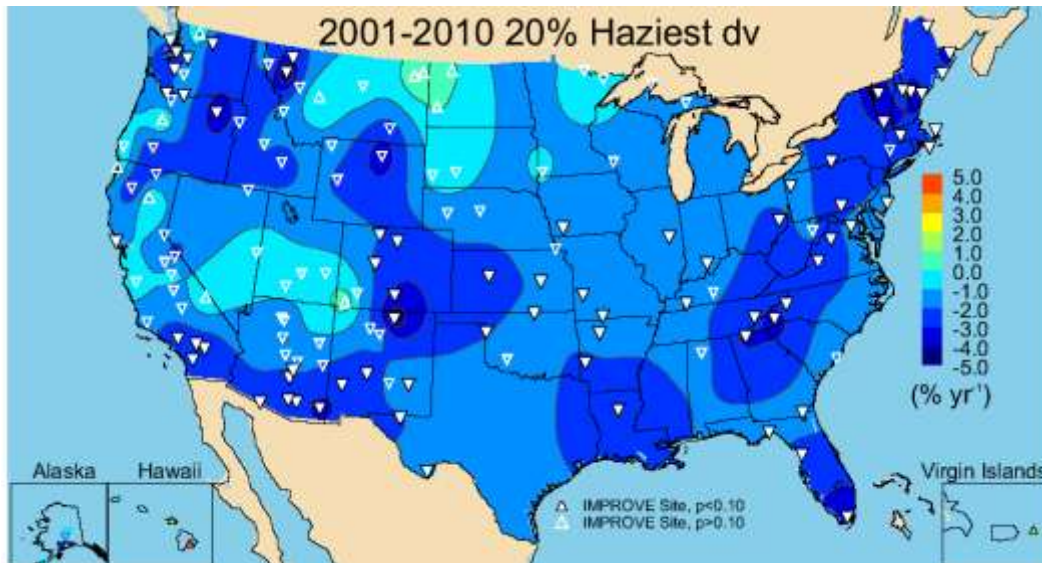


Figure 7. Trends in the annual 20% worst haze days at all IMPROVE monitoring sites from 2001 to 2010.

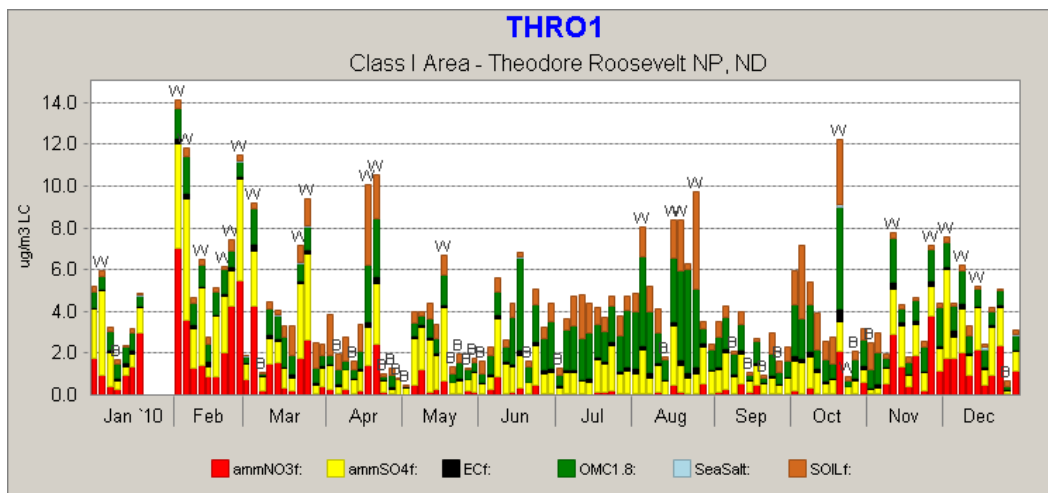


Figure 8. Measured PM_{2.5} concentration and composition at THRO southern unit in 2010. Data are from the IMPROVE monitoring program.

Proposed Assessment Study

The objectives of the proposed study are to characterize the composition and properties of particulate and gaseous pollutants in the three park units and estimate the relative contributions from emission source categories and geographic regions to these pollutants over a period of one year, then establish a long-term monitoring program to track the changes in air quality over time. As stated above, the objectives of the study as well as sub-objectives are to

- quantify current air quality levels in national parks in the Bakken region
 - evaluate the representativeness of the field study period to other years.
- assess if the air pollution is due to local or more distant regional sources such as Canadian tar sands development
 - characterize the meteorological conditions that lead to various atmospheric chemical conditions and source impacts

- differentiate the contributions from local oil and gas, increasing population centers, and associated mobile sources
 - refine emission estimates from the Bakken oil and gas fields and other emission sectors in the Bakken region
- track the change in air quality in the national parks over time
 - develop a protocol and implement long-term monitoring to track the changes in air quality in the national parks due to further energy development in the region

Strategy for Meeting Study Objectives

Due to the complexities of the physicochemical processes and the meteorological patterns that govern the fate of air pollutants, the contribution of a source or source region to ambient concentrations and wet and dry deposition cannot be directly measured. Instead, air quality models capable of simulating the atmospheric physicochemical processes and statistical inference techniques based on physical principles would be used. All models have a number of simplifying assumptions and parameterizations of the relevant atmospheric processes and are often dependent on incomplete and uncertain input information, such as emissions and meteorology, and are thus subject to errors and biases.

To overcome these uncertainties, multiple source apportionment techniques need to be applied and reconciled. The reconciliation process includes a hybrid source apportionment model that merges the results from apportionment estimates and measurements into a statistical model to minimize biases between modeled results and observations, thereby improving the attribution and deposition estimates. These reconciliation models require sets of measurements that are both temporally and spatially intense (high time and spatial density) and would make extensive use of the measured air quality data from the proposed field study.

The focus of the assessment would be on the year of monitoring results. This year may not be representative of other years. Modeling and data analyses for other years would be needed to determine the representativeness of the study period and place the monitoring and analysis time periods into a longer context. In addition, analysis methods could be applied to the long-term monitoring data when available. Finally, the results of this study would be used to develop a conceptual model describing the influential atmospheric processes and emission sources responsible for the air pollution levels and composition at the three NPS park units, as well as the response of the air quality to changes in emissions.

Following is an overview of the monitoring and data and modeling analyses that are needed for a successful study. In addition, what information would be obtained from each analysis, how each analysis would be evaluated, and how similar results would be reconciled and their representativeness to other seasons and years are described. Table 2 summarizes these analyses and what aspect of the source attribution problem and other objectives they address. Figure 9 summarizes the data analyses and the flow of information resulting in the final products and the conceptual model.

Air Quality Monitoring

A one-year, intensive sampling period with a comprehensive suite of measurements is needed to examine the atmospheric loading of key atmospheric species at THRO, FOUS, KNRI, and locations throughout the Bakken oil fields. This intensive monitoring would be followed by

long-term monitoring of routine measurements at the national parks. The network would consist of one core monitoring site, located within the north unit of THRO, and at two secondary sites, one located at FOUS and the second at KNRI. These sites would be instrumented to measure the physical, chemical, and optical properties of aerosols, gaseous species, and wet deposition rates at a high time resolution. Approximately 8–10 satellite sites collecting PM_{2.5} and gases would be deployed from the Canadian border to south of THRO. The intent of the satellite sites is to monitor upwind, downwind, and within the intensive oil and gas activity. The measurement section of the study plan contains a detailed description of the network, pollutants to be measured, and instruments.

Data Analysis

The monitoring data would be extensively analyzed to better understand the concentrations and physical, chemical, and optical properties of the particulate matter and ozone and the aerosol and gaseous nitrogen and sulfur wet-deposition rates. These analyses would include constructing aerosol and extinction budgets that would further our understanding of visibility impairment from aerosols and provide an important check on the quality of the data. Also, nitrogen and sulfur composition budgets would be examined to identify the phase and composition of these compounds and further our understanding of acid deposition.

Receptor Modeling

Data analysis or receptor modeling would be conducted to both qualitatively and quantitatively assess the contributions of source regions and types to air quality at THRO, FOUS, and KNRI.

Spatial and Temporal Analysis. The aerosol, gaseous, and wet-deposition data in the satellite monitoring network would be analyzed for spatial and temporal patterns. The patterns in these data can provide a qualitative assessment of the local versus regional source contributions. For example, if concentrations are relatively homogeneous throughout a region and maxima occur at roughly the same time, then this is indicative of regional distant-source contributions. However, if the concentrations are non-uniform with maxima occurring at different locations and times, then this is indicative of local contributions. In addition, gradients in the concentration fields often point toward source regions. By placing monitors upwind, downwind, and within the Bakken region, a semiquantitative assessment of the additional pollution from the Bakken region to the regional background concentrations can be assessed. This would help to identify an upper bound for some pollutants on the contributions of the energy and associated development to neighboring locations such as THRO. The spatial and temporal analysis would be conducted for all measured species at the satellite sites.

Empirical Orthogonal Function (EOF) Analysis. This is a refinement of the spatial and temporal pattern analysis. EOF distills the large number of spatial patterns into a few simple patterns. These patterns can usually be interpreted in terms of known geographic distributions of emission sources.

Wind Field and Airmass History Analysis. Wind field analyses, e.g., pollution roses, identify wind directions associated with high- and low-pollution concentrations. These methods help to “point” in the direction of potential source regions causing elevated pollutant concentrations. Airmass histories refine the wind field analyses. An airmass history identifies the 2-D or 3-D pathway an airmass took en route to the receptor, a trajectory, and other meteorological parameters along this transport pathway. The implications are that sources, or lack of sources, along the pathway and near the receptor are responsible for the receptor’s air quality. These are

powerful techniques that potentially link source regions to the receptor concentrations. Air mass histories would be examined for all monitoring sites and each sampling day. In addition, ensemble air mass history techniques based upon the residence time analysis would be used to develop statistical relationships between air mass transport pathways and the gaseous and aerosol monitoring data. This information would be used to assess the validity of the quantitative source attribution techniques and would be extensively used in the reconciliation of methods.

Chemical Receptor Models. The chemical mass balance (CMB), UNMIX, and Positive Matrix Factorization (PMF) quantitative receptor models would be used in this study. These models use the detailed speciated aerosol and gaseous data as well as molecular marker species to attribute ambient aerosol and gaseous species to source types, such as oil, gas and mobile and stationary sources. The CMB model can only apportion the primary species but can do this with the temporal resolution of the monitoring data, while UNMIX and PMF can apportion the average contributions of source types to primary and secondary species over an extended time period, such as a month-long sampling period. Neither approach is sufficient since we need to apportion both primary and secondary species on a daily basis and separate contributions from different source regions and source types. These models are also not able to apportion source contributions to ozone. In addition to the source attribution results, these models would be valuable for evaluating the other source attribution results and the emission fields.

Transport Receptor Models. Transport receptor models develop statistical relationships between aerosol and some pollutant concentrations, such as particulate sulfate concentrations, and air mass transport prior to reaching a receptor site such as THRO. From these relationships, the average contribution of source regions throughout North America to the receptor concentration over a period of time can be assessed. Therefore, they can be used to separate out the contributions from the Bakken region from the Canadian oil sands and other regions. These methods would be used to assess the contribution of source regions to aerosol and some gaseous species. However, due to nonlinearities in important atmospheric processes and dependence on multiple pollutants, these methods are not suitable for species such as ozone. Through an examination of the emissions in each source region, these techniques can also provide some indication of the contributions from the various source types.

These methods would be tested by applying them against synthetic data generated by the Comprehensive Air quality Model with extensions (CAMx) model. In the synthetic data, both the receptor concentrations and source contributions are known, so the source attribution results can be evaluated against a known system. However, this evaluation does not incorporate errors due to the input meteorological field used to calculate the air mass transport used in the transport receptor models.

Deterministic Modeling

CAMx would be used to simulate gaseous and particulate pollution within the Bakken region, as well as to estimate the contributions of individual sources, source regions, and source types that contribute to air pollution at the three park units. Source attributions would be estimated using a suite of reactive tracer species within the CAMx PM Source Apportionment Technology (PSAT) module and Ozone Source Apportionment Technology (OSAT) module. Model results would be evaluated by comparing predicted and observed values from the field study and at IMPROVE (Interagency Monitoring of Protected Visual Environments), CASTNet (Clean Air Status and Trends Network), and Environmental Protection Agency monitors, as well as by using probing

tools such as process analysis. This information is vital to understanding what the potential impact of future changes in emissions may be on the fate and origin of the pollutants.

Hybrid (Inversion) Modeling

Air quality simulation and source receptor models each have different strengths and weaknesses. Air quality simulation models can apportion secondary and primary species and identify contributions from individual sources, source regions, and source types. However, the information requirement and chemical mechanism of these models are incomplete, and the results are not constrained by measurements, leading to large errors and biases. On the other hand, the receptor models are constrained by measured data, bounding their errors, but apportioning secondary particulate matter is problematic.

Hybrid source apportionment modeling directly combines measured data with air quality modeling results, ideally preserving the temporal and source-type resolving power of the air quality model, but the results are bounded by the measured data and satisfy the source profiles. In this assessment, we would explore the use of several hybrid models. One would be based on the synthesis inversion method that was first developed for the apportionment of sulfate aerosol at Big Bend NP during the Big Bend Regional Aerosol and Visibility Observational Study (BRAVO). In this approach, the hybrid method starts with the attribution results from the CAMx air quality model and uses a statistical approach to identify multiplicative scaling factors for each source region's attribution and each day that results in a best fit to the measured data. It is based upon the inversion of a linear form of the conservation of mass equation and has been employed in a number of global biogeochemical models to estimate source emission rates.

In theory, the source attribution scaling coefficients are adjustments to the source emission rates. In actuality these coefficients account for systematic biases in the source attribution results due to errors in the emissions, input meteorology, and model formulations. These coefficients provide insights into the biases and errors in the CAMx model. Small coefficients indicate an unbiased model, while large coefficients are an indication of large errors in either the emissions or meteorological input data or the model formulations of important atmospheric mechanisms. In this study, these coefficients would be examined to help assess the CAMx model performance and applicability of CAMx to this study. In addition, explanations would be sought for coefficients significantly different from one. Where it can be shown that errors in emissions are the most likely cause, they would be used to help to refine the emission estimates.

These methods are valid for constituents whose emission/receptor relationship is relatively linear, such as sulfate, $\text{NO}_3 + \text{HNO}_3$, and many primary pollutants. However, they may not be applicable to highly nonlinear constituents such as ozone. For these compounds, alternative inverse models such as adjoint models could be pursued.

Reconciliation

All models and analyses are subjected to varying uncertainties and biases that need to be assessed and understood to generate meaningful and policy-relevant information. This would partly be accomplished in the independent evaluation of each method as well as the application of the synthesis inversion technique to the CAMx model results. In addition, all source attribution methods would be compared to each other and differences reconciled. It is anticipated that the process of understanding the deviation of the methods would require the detailed data analysis, trajectory analysis, and CMB/UNMIX/PMF receptor modeling results. This process would also help to evaluate the source attribution scaling coefficients resulting from

the inversion techniques and whether or not the scaling coefficients reflect errors in the CAMx formulation, meteorological data, or emission data.

As a final product we hope to have a set of source attribution results with a defined level of confidence. In addition, an understanding of the physical and chemical processes and rates responsible for these source attribution results would allow for the assessment of the impact of potential future changes in emissions on the origin and fate of sulfur and nitrogen species. This information would be pulled together to develop a conceptual model describing the causes of air pollutants in the three national park units.

Representativeness

The monitoring and analysis would be focused on the monitoring study year. To determine the utility of the information to other years, it is necessary to assess the representativeness of the study period. This could be done by comparing the meteorological and chemical conditions in northwestern North Dakota to other years. Standard air mass history analyses and air quality data analyses could be used to accomplish this. In addition, if the chemical transport model proves reliable, it could be run for other years.

Conceptual Model

The qualitative and quantitative results would be used to develop a conceptual model describing the causes of air pollutants in the three national park units. Specifically, it would describe the sources and physical and chemical atmospheric processes governing the ambient concentrations of aerosols, sulfur and nitrogen deposition, and ozone, and in addition, how changes in pollutant emissions could impact the ambient concentrations and wet deposition rates. The conceptual model should be a valuable tool in understanding potential benefits and disbenefits of emission changes and help focus future analyses to quantify the impact of emission changes.

Table 2. List of the qualitative and quantitative data analyses and source apportionment analyses and what aspect of the source attribution problem they address.

	Ambient Concentrations (particulate matter, reactive nitrogen, SO ₂ , ozone)										Refine Emissions
	Source Regions	Mobile	Stationary	Agric.	Oil & Gas	Other	Mobile	Stationary	Agric.	Other	
Air Quality Data Analysis											
PM and Best Budgets											
Sulfur and Nitrogen deposition Budgets											
Spatial and temporal analysis of gaseous, particulate and wet deposition data											X
Qualitative Receptor Data Analysis											
Space/Time EOF analysis	X										X
Trajectory Analysis	X										X
Quantitative Receptor Modeling											
Transport (FMBR, TrMB)	X										X
Chemical (CMB, UNMIX, PMF)		X	X	X	X						X
Deterministic Modeling											
CAMx	X	X	X	X	X	X	X	X	X	X	
Hybrid (Inverse) Modeling											
Synthesis Inversion	X	X	X	X	X	X	X	X	X	X	X
Adjoint CMAQ	X	X	X	X	X	X	X	X	X	X	X

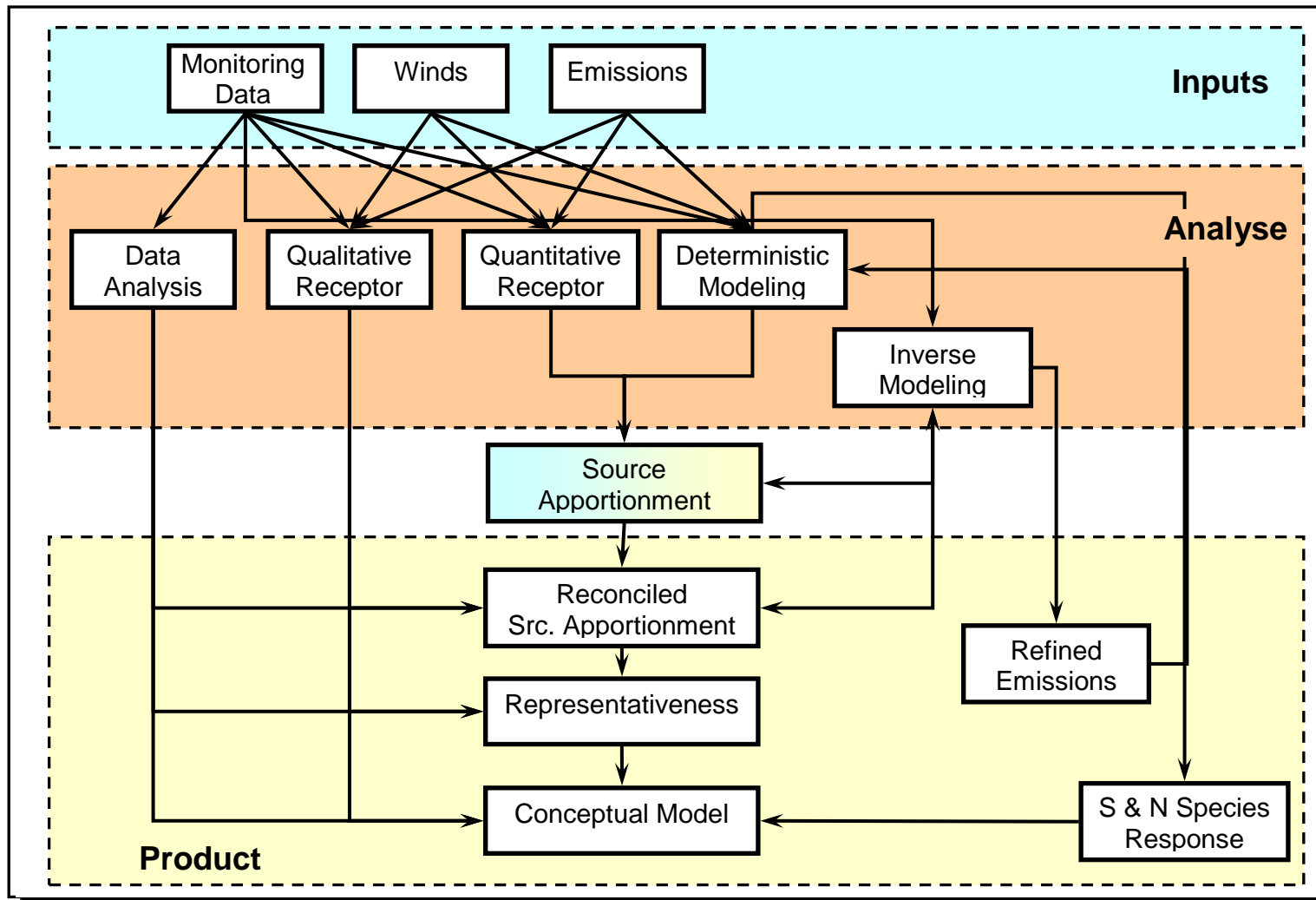


Figure 9. Data flow diagram depicting the various classes of data and model analyses, their inputs and products, and how the analyses would be used to develop the final conceptual model.

Monitoring Required to Meet the Study Goals

A comprehensive suite of measurements is needed to examine the atmospheric loading of key atmospheric species within THRO, FOUS, and KNRI and at locations throughout the Bakken oil fields. A summary of proposed measurements and locations to accomplish this is included in Table 3 and is shown in Figure 10. Measurements would be made at a core site, located within the north unit of THRO, at two secondary sites, one located at FOUS and the second at KNRI, and at an array of approximately 8–10 satellite sites located from the Canadian border to south of THRO.

As shown in Table 2, the most sophisticated suite of measurements and the highest time resolution are needed at the THRO core site. Measurements needed for the THRO site include detailed observations of fine (PM_{2.5}) and coarse (PM₁₀) particle composition, ion size distributions, trace gas concentrations (including SO₂, NO_x, NO_y, NH₃, HNO₃, CO, O₃, and reduced organic nitrogen), wet deposition, particle size distributions, particle light scattering, and meteorology. Both time-integrated and high time resolution (at least hourly) measurements are needed for nearly all measurement parameters at the core site. Measurements at the two secondary sites are focused primarily on concentrations of key particle species, gases, and wet deposition. Measurements at the satellite sites would focus primarily on daily characterizations of key fine particle and trace gas concentrations and composition, in order to help map out concentrations of pollutants throughout the Bakken region under different meteorological scenarios. Brief descriptions of each measurement approach are provided below.

Particle composition. A suite of fine and coarse particle composition measurements is needed as a key component of the study. A variety of techniques and time resolutions are included. Measurements would include both inorganic and organic components of the aerosol. These data are crucial for assessing the impact of the emissions from the Bakken region on visibility, nitrogen and sulfur deposition, and levels and toxicity of PM relative to human health standards. These data would also be used to quantify the contributions of these emissions on the PM loading in the national park units; evaluate emission inventories in the Bakken region; and evaluate chemical transport models.

Fine particle (PM_{2.5}) ions would be characterized through use of filter-pack and particle-into-liquid sampling (PILS) systems. The PILS system activates particles into small droplets by mixing with steam. The droplets formed are then impacted onto a surface over which a liquid film flows. This film carries dissolved ions into two ion chromatographs (ICs) for on-line analysis of anions and cations. Ions to be measured include the main aerosol ion constituents: Cl⁻, NO₂⁻, NO₃⁻, SO₄²⁻, Na⁺, K⁺, NH₄⁺, Mg²⁺, Ca²⁺. These species would be measured both in time-integrated filter-pack samples and at 15-min resolution using PILS. Filter samples would be collected with IMPROVE samplers (24-hr time resolution), URG annular denuder/filter-pack samplers (6- to 24-hr time resolution), and with portable filter-pack samplers (24-hr time resolution). PM₁₀ ions would also be measured at the THRO core site using a PM₁₀ IMPROVE sampler. Size distributions of the same set of ions listed above would also be determined on a 24-hr basis at the core site using a micro-orifice uniform deposit impactor (MOUDI). This device provides concentrations of each ion in 10 particle size intervals extending from approximately 0.06 to 10 μm aerodynamic diameter. Ion concentrations in filter and impactor extracts would be measured using standard techniques of IC.

Other aerosol components that would be measured include organic carbon (OC), elemental carbon (EC), black carbon (BC), trace elements, and organic nitrogen. OC, EC, and trace

elements would be measured on samples collected at 24-hr time resolution using the IMPROVE sampler, following standard IMPROVE protocols. OC and EC would also be measured at the THRO core site at 1-hr time intervals using a Sunset Laboratories semicontinuous carbon analyzer. BC would be measured at 5-min time resolution, utilizing a Magee Scientific 7-wavelength aethalometer. Organic nitrogen (ON), which has been shown to represent a significant portion of the atmospheric nitrogen (non-N₂) load in several locations, would be measured at the core site from aerosol collected on a dedicated filter. The filter samples would be extracted with water and ON would be determined by the difference between the sum of the inorganic nitrogen species (NO₂⁻, NO₃⁻, and NH₄⁺) concentrations before and after strong oxidation by a combustion method.

Trace gas concentrations. Measurements of several key trace gases are important components of the proposed measurement suite. In particular, measurements of NH₃, HNO₃, NO_x, NO_y, and SO₂ are important in determining portions of nitrogen and sulfur atmospheric pollutant loads present in the gas phase. These are also critical for determining total SO_x and NO_x emissions from the Bakken region. All of these species, along with O₃ and CO, would be measured at the THRO core site. Continuous gas analyzers would be utilized for measurements of NH₃, NO_x, NO_y, SO₂, O₃, CO, and a surrogate for reduced organic nitrogen. Additional, denuder-based measurements would be utilized for measurements of NH₃, HNO₃, and SO₂ at 6- to 24-hr time resolution. While the denuder resolution is lower, this technique provides improved detection limits and added confidence in the continuous gas data. Gas measurements at the secondary and satellite sites would be made solely by denuder, and passive samplers would focus on NH₃, HNO₃, and O₃.

Wet deposition. The composition and amount of precipitation, when present, would be measured at the core, secondary, and satellite sites. In contrast to traditional network wet deposition monitoring approaches, at the core and secondary sites we would make these measurements at high time resolution to provide a clearer link between major deposition fluxes and pollutants transport into the study region. This is especially important for comparisons with model simulations. Rain and snow would both be collected in a large (~ 50 cm diameter), thermostated funnel attached to a sample bottle. Rain drains into the bottle. During periods of snow, the heated funnel melts the snow so that it also drains into the collection bottle. A suspended bag sampler (a polyethylene bag attached to a round metal frame (analogous to a windsock)) would also be deployed in periods of snow with high wind to ensure efficient snow collection. The approaches described have been used successfully in several previous studies in the Rocky Mountains and in the Alps. Changes in composition would be measured at approximately half-hour intervals. Such high time resolution is especially important as precipitation chemistry can change rapidly over the course of an event (see, e.g., Collett et al., 1991), due to changes in air masses producing the precipitation (e.g., during frontal passage), changes in cloud/precipitation microphysics, and washout of material from the atmosphere.

Collected precipitation samples would be measured to determine composition and deposition fluxes of water and solutes. Solute species to be measured include major ions (Cl⁻, NO₂⁻, NO₃⁻, SO₄²⁻, Na⁺, K⁺, NH₄⁺, Mg²⁺, Ca²⁺), OC, and ON.

Particle size distributions. Aerosol particle size distributions would be measured at the THRO core site at 15-min time resolution using a suite of three instruments. A TSI differential mobility particle sizing (DMPS) system would be utilized to measure particles over a diameter range from ~ 50 nm to 0.8 μm. A Climet optical particle counter (OPC) would measure particles in the size

range of ~ 0.1–2 µm diameter. Larger particles (~0.5–20 µm diameter) would be measured using a TSI aerodynamic particle sizer. These data would be used to relate particulate matter to light scattering and haze

Particle light scattering. Ambient PM_{2.5} aerosol light scattering would be characterized using a Radiance Research M903 nephelometer. The light scattering measurements would be used in the characterization of visibility reduction.

Meteorological parameters. A complete suite of meteorological instruments including temperature, relative humidity, surface wind speed and direction, solar radiance, barometric pressure, and precipitation would be made at the core site.

Table 3. Proposed measurements.

Measurement	Instrument	Time Resolution	Notes	Core Site	Secondary Site	Satellite Sites
PM _{2.5} inorganic ions	URG annular denuder/filter-pack sampler	6-hr intensives 24-hr routine	Cl ⁻ , NO ₂ ⁻ , NO ₃ ⁻ , SO ₄ ²⁻ , Na ⁺ , K ⁺ , NH ₄ ⁺ , Mg ²⁺ , Ca ²⁺	X	X	
Gaseous NH ₃ , HNO ₃ , and SO ₂	URG annular denuder	6-hr intensives 24-hr routine		X	X	
PM _{2.5} inorganic ions and gases	Filter-pack sampler	24 hr, battery powered	Cl ⁻ , NO ₂ ⁻ , NO ₃ ⁻ , SO ₄ ²⁻ , Na ⁺ , K ⁺ , NH ₄ ⁺ , Mg ²⁺ , Ca ²⁺ , HNO ₃ , NH ₃	X		X
PM _{2.5} inorganic ions	Particle-into-liquid sampler (PILS) – IC	15 min	Cl ⁻ , NO ₂ ⁻ , NO ₃ ⁻ , SO ₄ ²⁻ , Na ⁺ , K ⁺ , NH ₄ ⁺ , Mg ²⁺ , Ca ²⁺	X		
PM _{2.5} OC and EC	Sunset OC/EC analyzer	1 hr	Organic and Elemental Carbon by NIOSH method	X		
BC	Aethalometer	5 min	Measurements of absorbing black carbon at 7 wavelengths	X		
PM _{2.5} mass, ions, elements, H, and OC/EC	IMPROVE sampler	24 hr	Components per IMPROVE protocol	X	X	
PM ₁₀ mass, ions, elements, and OC/EC	IMPROVE sampler	24 hr	Components per IMPROVE protocol	X	X	
Inorganic ion size distributions	MOUDI impactor	24 hr	10 size cuts from ~0.06 to 10 µm aerodynamic diameter; Cl ⁻ , NO ₂ ⁻ , NO ₃ ⁻ , SO ₄ ²⁻ , Na ⁺ , K ⁺ , NH ₄ ⁺ , Mg ²⁺ , Ca ²⁺	X		

Measurement	Instrument	Time Resolution	Notes	Core Site	Secondary Site	Satellite Sites
PM2.5 ON, OC, EC, molecular marker species	Hi-Vol filter sampler	24–72 hr	ON by oxidation	X	X	
SO ₂ , NO _x , NO _y , NH ₃ , CO, O ₃ , reduced ON	Various continuous gas monitors	15 min	NH ₃ detection limit higher than denuder method	X	X	
NH ₃ , HNO ₃ , O ₃ , NO ₂	Passive samplers	week	NH ₃ , HNO ₃ , O ₃ , NO ₂	X	X	X
Wet deposition	Large volume precipitation (rain/snow) sampler	30 min	Cl ⁻ , NO ₂ ⁻ , NO ₃ ⁻ , SO ₄ ²⁻ , Na ⁺ , K ⁺ , NH ₄ ⁺ , Mg ²⁺ , Ca ²⁺ , OC, and ON, PH	X	X	
Wet deposition	Large volume precipitation (rain/snow) sampler	24–72 hr	Cl ⁻ , NO ₂ ⁻ , NO ₃ ⁻ , SO ₄ ²⁻ , Na ⁺ , K ⁺ , NH ₄ ⁺ , Mg ²⁺ , Ca ²⁺ , OC, and ON, PH			X
Meteorological parameters	Met station	2 min	T, RH, WD, WS, precip, SR,BP	X	X	
Particle size distributions	Differential mobility particle sizing (DMPS) system, optical particle counter (OPC), aerodynamic particle sizer (APS)	15 min	0.05–10 μm diameter	X		
Particle light scattering	Nephelometer	2 min	Ambient PM2.5 aerosol	X		
Inorganic and organic aerosol speciation	Aerosol mass spectrometer (AMS)	15 min	Operate for select periods in the year	X		
Speciated volatile organic carbon gases	Proton-transfer-reaction mass spectrometry (PTR-MS)	15 min	Operate for select periods in the year. Can include some HAPs	X		
Speciated volatile organic carbon gases	Canisters	24–72 hr	Canisters of gases taken to lab for analysis	X		

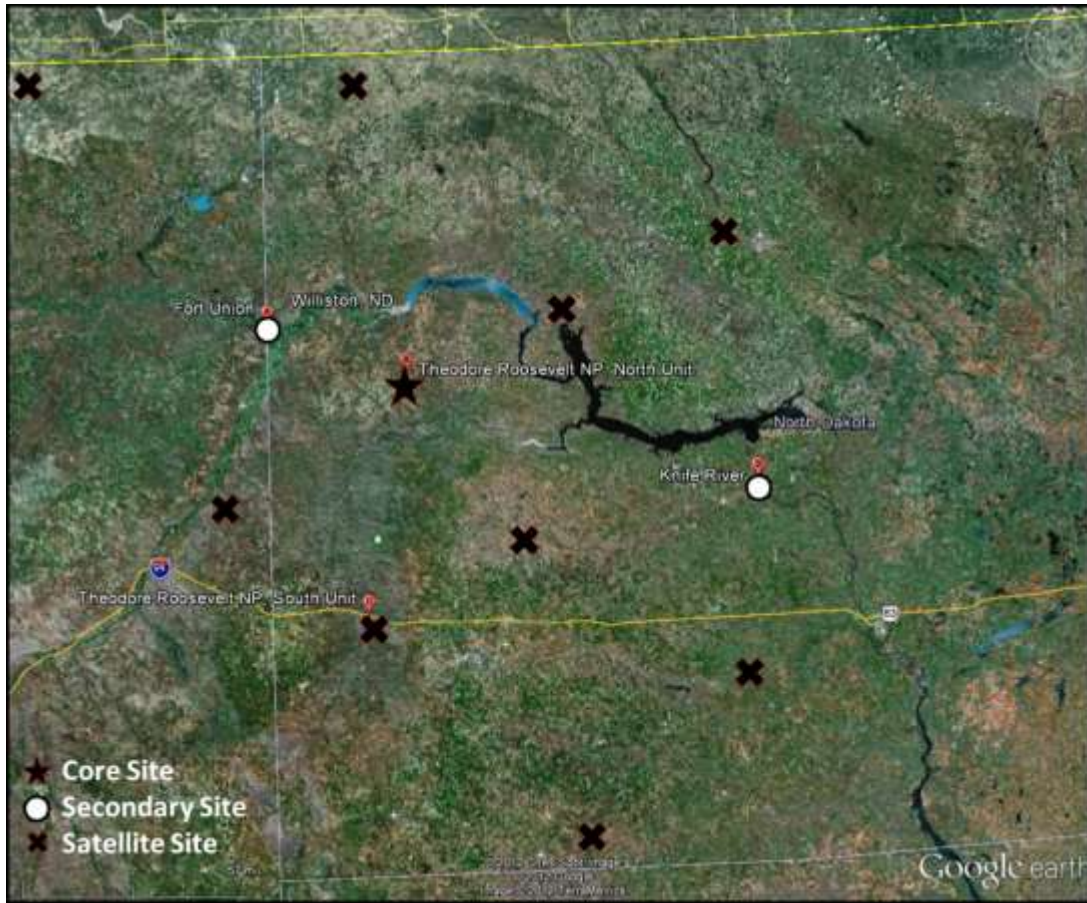


Figure 10. Potential locations for the core, secondary and satellite monitoring sites.