Northern Front Range Air Quality Study

December 1998

Colorado State University

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The Northern Front Range Air Quality Study

A Report to the Governor and General Assembly

December 1998

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Summary

Air pollution along Colorado's Front Range is manifested as visible haze that can range in color from grayish-white to brown. This "brown cloud," caused mainly by airborne particles, is observed most frequently during the winter, when low wind speeds and stagnant conditions accumulate pollutants from diverse sources. During the winter, the brown cloud accumulates in a shallow layer of stagnant air near the South Platte River. To understand the contribution of different pollution sources to the brown cloud, the Colorado General Assembly approved House Bill 1345 in 1995. This legislation established the Northern Front Range Air Quality Study (NFRAQS) to identify sources of air pollution along Colorado's Front Range. The study objectives were reaffirmed in the next session of the General Assembly with passage of HB 96-1179, which expanded the scope of the Study. Nearly 40 government, industry, and research organizations provided funding during the program.

The NFRAQS Technical Advisory Panel (TAP) established three policy-relevant objectives for the Study:

- Identify the sources or contributors to $PM_{2.5}$ (airborne particles less than 2.5 micrometers in diameter)
- Determine the role of gas-phase nitrogen oxides, sulfur dioxide, and ammonia in forming ammonium nitrate and ammonium sulfate constituents of $PM_{2.5}$ particles.
- Identify the sources responsible for forming ammonium nitrate and ammonium sulfate $PM_{2.5}$ particles.

As the House Bill specified, Colorado State University managed the NFRAQS subject to concurrence on plans, selection of research groups and expenditures by the TAP. Fifteen research groups from throughout the United States participated in the three-year study. The NFRAQS program measured $PM_{2.5}$, which causes Denver's brown cloud. Scientists measured ambient meteorology, visibility, and air quality at several locations in the metro Denver area, north to Fort Collins, and along the South Platte River basin northeast to Fort Morgan during three separate periods – Winter 1996, Summer 1996, and Winter 1997.

Key Findings

The NFRAQS was designed to provide information to policy makers in Colorado who are responsible for managing air quality. The following key findings, based mainly on episodic observations made in Winter 1997, are organized by the Study's policy-relevant objectives.

OBJECTIVE 1 – Identify the sources or contributors to $PM_{2.5}$ in the NFRAQS region

During the winter episodes of increased $PM_{2.5}$ concentrations in the metro Denver area, receptor modeling estimated that the most important sources or contributors to $PM_{2.5}$ were:

- Gasoline vehicle and engine $PM_{2.5}$ exhaust, 28%
- Diesel vehicle and engine $PM_{2.5}$ exhaust, 10%
- Dust and debris, 16%
- Wood smoke, 5%
- Meat cooking, 4%
- Directly-emitted $PM_{2.5}$ from coal-fired power stations, 2%
- Particulate ammonium nitrate (formed in the atmosphere from a variety of sources), 25%
- Particulate ammonium sulfate (formed in the atmosphere from a variety of sources), 10%

During the episodes studied, 75% of the directly-emitted $PM_{2.5}$ from mobile sources was produced by gasoline-powered vehicles and engines and 25% of the directly-emitted $PM_{2.5}$ was produced by diesel-powered vehicles and engines. In contrast, in current emission estimates diesel vehicles are projected to produce more $PM_{2.5}$ emissions than gasoline-powered vehicles. High-emitting or smoking gasoline-powered vehicles, which comprise a small fraction of the in-use vehicle fleet, produced nearly one-half of the gasoline exhaust particles. The diesel exhaust particles come from trucks, locomotives, construction equipment and other sources. $PM_{2.5}$ directly emitted from diesel vehicles and engines was one-third of that from gasoline vehicles and engines, even though diesel-powered vehicles comprise only five percent of the regional vehicle miles traveled. Fine particles from road debris and dust, construction activities, and wind-blown sand contributed 16% of the total $PM_{2.5}$, an amount much lower than current emission estimates.

Particulate ammonium nitrate and ammonium sulfate are formed in the atmosphere from gas-phase emissions of ammonia, nitrogen oxides, and sulfur dioxide. These are called secondary particles because they are not emitted directly by pollution sources. Their sources are discussed in Objectives 2 and 3.

OBJECTIVE 2 – Determine the role of gas-phase nitrogen oxides, sulfur dioxide, and ammonia in the formation of ammonium nitrate and ammonium sulfate $PM_{2.5}$ particles

The NFRAQS region is ammonia-rich. Agricultural operations produced most of the ammonia in the Northern Front Range. Current ammonia emissions would have to be reduced 50% to achieve a 15% reduction in particulate ammonium nitrate levels. Further reductions in ammonia emissions would provide proportional decreases in ammonium nitrate concentrations.

OBJECTIVE 3 – Identify the sources responsible for the formation of ammonium nitrate and ammonium sulfate $PM_{2.5}$ particles

Because of limitations in funding, NFRAQS scientists were unable to completely apportion the contributing sources to ammonium nitrate and ammonium sulfate $PM_{2.5}$ particles. Atmospheric models also have not been adequately developed to model the atmospheric formation of particles from their sources. However, the Study found that the majority of nitrogen oxides, and therefore, particulate ammonium nitrate, are produced by mobile sources. The formation of $PM_{2.5}$ nitrate particles is not a linear process. Reductions of nitrogen oxide emissions, the precursor to particulate nitrate, would result in less-than-proportional reductions in $PM_{2.5}$ ammonium nitrate particles. Three-fourths of the sulfur dioxide emissions are produced by coal-fired power plants. Sulfur dioxide is a precursor to particulate ammonium sulfate.

Related Findings

- The 24-hour or 1-hour federal air quality standards for particulate matter were not exceeded at any time during the Study.
- $PM_{2.5}$ episode concentrations have decreased substantially during the last twenty years.
- $PM_{2.5}$ concentrations during the NFRAQS were less than half those reported in 1978. The improvements in air quality are the result of many emission reduction programs, including controls of emissions from mobile sources and industrial sources and reduced street sanding.

In the metropolitan Denver area:

- During the winter, emissions caused by mobile sources (exhaust from cars, trucks, construction equipment and locomotives, and dust from roads and construction activities) produced at least 75% of the $PM_{2.5}$.
- During the winter episodes studied, wood-burning emissions contributed 5% to $PM_{2.5}$. Meat cooking contributed 4% to the total $PM_{2.5}$. About 10 years ago, wintertime wood burning and meat cooking contributed about 35% of the observed $PM_{2.5}$ levels, demonstrating the benefits of the Colorado Department of Public Health and Environment's (CDPHE) program on wood burning restrictions.
- The Denver summer average $PM_{2.5}$ concentration during pollution episodes was 85% as high as during the winter, but its composition was different. Particulate carbon species were dominant in the summer (44% of the total). Dust was more important in the summer than in the winter.
- Fossil fuel combustion produced 75% of the particulate carbon species in the winter and 50% of the particulate carbon species in the summer.
- Less $PM_{2.5}$ ammonium nitrate occurred during the summer (8% of the total) than in the winter (25% of the total), because it evaporates at warm temperatures.
- Ammonium sulfate concentrations were nearly identical in Denver in both summer and winter (10-15% of the total).

In the northern, non-urban locations:

- Although air quality generally was worse in Denver than in other areas, the NFRAQS found that during pollution episodes, $PM_{2.5}$ concentrations sometimes were as high in rural locations northeast of Denver along the South Platte River as they were in downtown Denver. The Study did not determine whether the $PM_{2.5}$

was formed at or near those sites or whether it was transported from Denver, Boulder, Fort Collins, Greeley, or other locations.

- At the rural, northern NFRAQS sampling sites, the average composition of $PM_{2.5}$ during Winter 1997 pollution episodes was different from that in the urban locations, with a smaller fraction from gasoline (5-16%) and diesel emissions (3-7%), and larger portions of particulate ammonium nitrate (34-40%) and ammonium sulfate (11-14%), with 6-27% from dust.

Introduction

In 1995, the Colorado General Assembly approved House Bill 1345 (HB95-1345) that established the Northern Front Range Air Quality Study (NFRAQS). The study was intended to provide important additional scientific information that would aid planning and decision-making for air quality management along Colorado's Northern Front Range. Without more complete information, planning for air quality management would depend upon simulation tools developed with outdated or insufficient data. HB95-1345 stated that "the governor, the private sector, and members of the regulatory community have acknowledged that additional attribution studies must be accomplished in order to fully determine the sources of the visibility pollution along the Northern Front Range." The legislation called for Colorado State University (CSU) to conduct an "independent, objective, scientifically peer-reviewed study . . . to identify and apportion sources of pollution for the Northern Front Range that contribute to Denver urban visibility reduction."

The legislation established Governor Roy Romer, Senate President Tom Norton, and House Speaker Chuck Berry as the Governing Board for the Study. The NFRAQS Technical Advisory Panel (TAP), a twelve-member group, co-chaired by Senator Tom Norton and Representative Shirleen Tucker, was composed of elected officials and representatives of government, industry, citizen, and environmental groups, and reported to the Governing Board (Figure 1). The TAP provided guidance to the NFRAQS through CSU. Additional legislation (HB96-1179) extended the Study period through July 1998 and provided additional funding for the program.

HB95-1345 also called for the creation of a Quality Control Committee (QCC), to provide technical expertise and guidance to the program. The QCC consisted of approximately 75 persons from a variety of government, industry, and environmental groups. The QCC provided technical oversight throughout the Study.

A twelve-member NFRAQS External Peer Review Committee provided independent review of the program. This committee provided review of the science, evaluated proposals, recommended contractors, reviewed statements of work, and reviewed draft reports. In addition, the general public had a six-week period to review the Study's draft reports and to provide comments.

The NFRAQS program began in the fall of 1995 and focused on policy-relevant topics. This summary describes how the scientists designed and conducted the study and it presents the most important NFRAQS findings from technical reports completed through September 1998. See the NFRAQS web site (http://nfraqs.cira.colostate.edu) for all data and technical reports.

NFRAQS Policy-Relevant Objectives

While the Study was being organized, the CSU managers met with elected officials, state, regional, and local policy makers and industry and environmental groups to solicit input. They met with interested citizens to formulate policy-relevant objectives. The TAP and QCC reviewed results from the previous Denver Brown Cloud Studies and the objectives set forth in HB95-1345. Based on all considerations, the Technical Advisory Panel decided to focus on the sampling of $PM_{2.5}$ concentrations and to defer analyses regarding visibility. The TAP approved the following objectives in order of priority:

- Identify the sources or contributors to $PM_{2.5}$ (airborne particles less than 2.5 micrometers in diameter) in the NFRAQS region
- Determine the role and importance of gas-phase nitrogen oxides, sulfur dioxide, and ammonia in the formation of ammonium nitrate and ammonium sulfate $PM_{2.5}$ particles

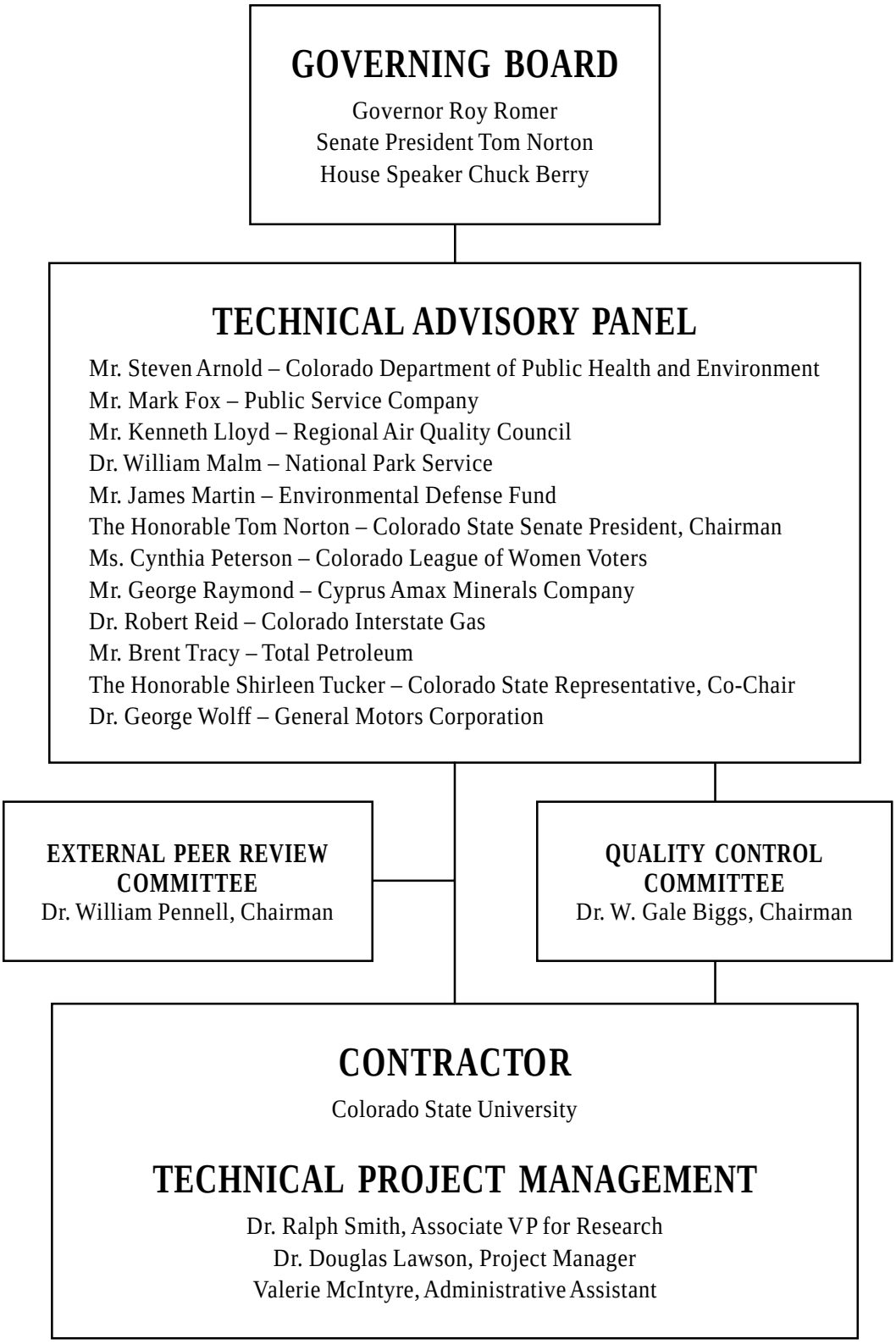


Figure 1. Organization of the Northern Front Range Air Quality Study.

- Identify the sources responsible for the formation of ammonium nitrate and ammonium sulfate $PM_{2.5}$ particles.

Scope of the NFRAQS

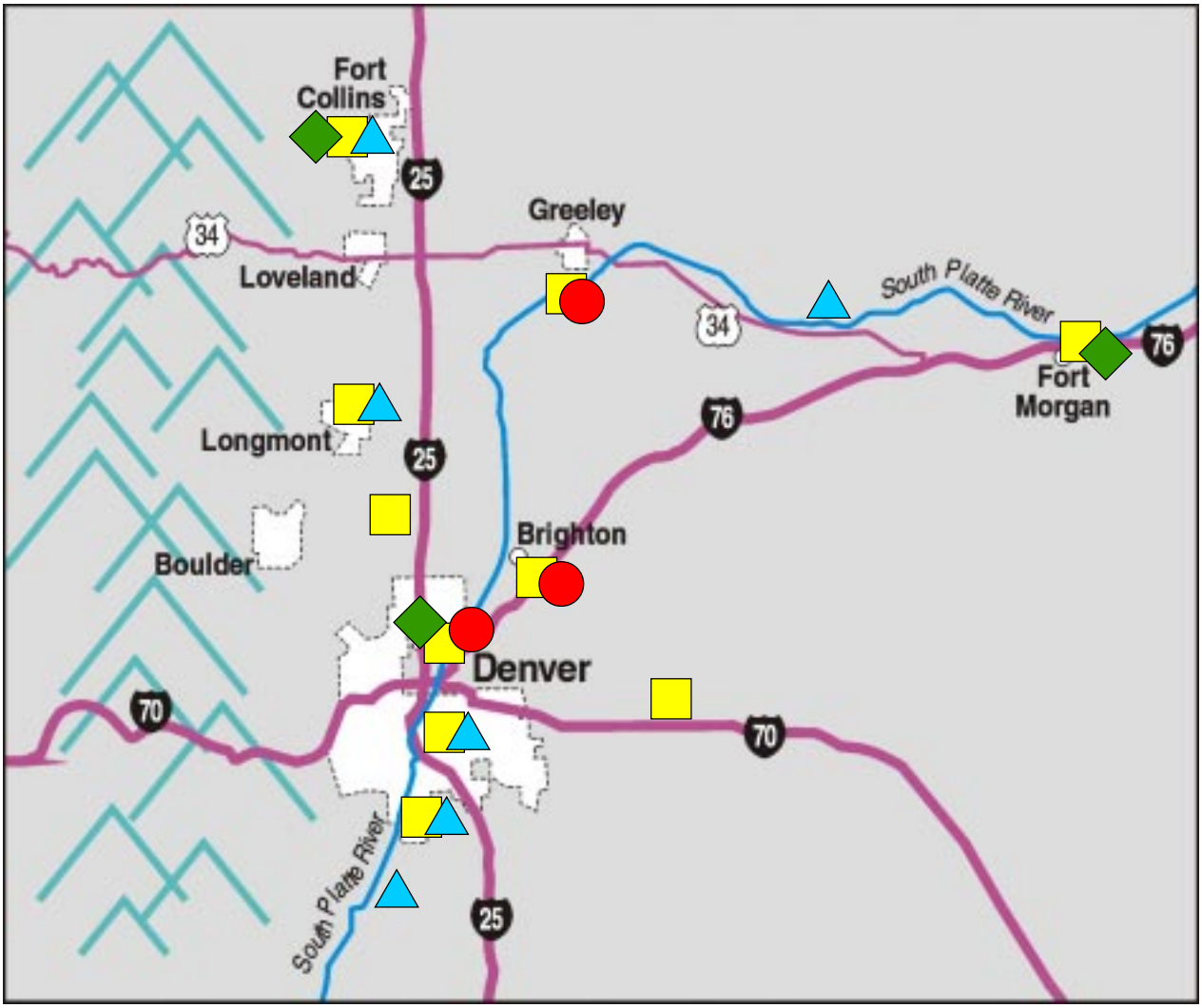
During the three-year program, the NFRAQS scientists conducted comprehensive air quality and meteorological measurements, along with a series of concurrent measurements from the most important pollution sources expected to contribute to $PM_{2.5}$ concentrations during the winter and summer along Colorado's Northern Front Range. Fifteen organizations took part in the Study (see inside front cover of this report) and they acquired millions of air quality and meteorological data points for subsequent analysis. The scientists constructed specialized equipment to measure direct emissions from meat cooking and wood burning. They also used state-of-the-art sampling equipment to measure emissions from nearly 225 gasoline and diesel-powered vehicles. They deployed sophisticated meteorological measurement equipment to characterize air motions and mixing, humidity, and temperature throughout the lower troposphere. The CDPHE provided daily forecasts during the air quality measurement periods, so that sampling could be conducted during episodes of high $PM_{2.5}$ concentrations. The CDPHE also audited air quality measurement sites to determine if measurements were being conducted in accordance with specifications for the Study.

The NFRAQS was carried out in three phases, designated as Winter 96, Summer 96 and Winter 97. Phase I, the Winter 96 study, a pilot project, ran from January 16 to February 29, 1996 when scientists collected samples at Welby in northeast metropolitan Denver (Figure 2). The Winter 96 study provided the opportunity to test sampling equipment for later use in Phases II and III and to gather baseline winter data for comparison with the major study in the winter of 1997. Scientists conducted Phase II, in the summer, from July 16 to August 31, 1996 at Welby, Golden, east of Longmont, and Fort Collins. Phase II provided summer $PM_{2.5}$ samples for comparing the $PM_{2.5}$ characteristics with Winter 96 and Winter 97 data. In Phase III, Winter 97 and the major phase of the NFRAQS, scientists collected samples from December 16, 1996 to February 9, 1997 at three "core" sites (Welby, Brighton, and Evans), and six "satellite" sites (Chatfield Reservoir, Highlands Ranch, downtown Denver, east of Longmont, Fort Collins, and Masters; Figure 2). At each location scientists obtained air quality and meteorological data, and, at some locations, 35 mm slides and time-lapse video recordings. The scientists and QCC members selected measurement methods and the location of the measurement sites that would provide data needed to achieve the Study's objectives.

The NFRAQS emphasized simultaneous collection of $PM_{2.5}$ from pollution sources and ambient air quality samples. The scientists analyzed samples for mass, chemical elements, ions, organic and elemental carbon, many organic compounds, and carbon-14 isotopic abundances. They organized the data, entered it into a documented database (available at the NFRAQS web site), and conducted tests to determine data validity, precision, and accuracy. Where possible, they evaluated sensitivity of conclusions to the range of conditions the data represent, and provided qualifications on the adequacy of the measurements to address each of the Study's objectives.

The Influence of Meteorology on Air Quality in the Front Range Region

Terrain and weather in Colorado's Northern Front Range determine the extent to which emissions accumulate in the atmosphere. The NFRAQS region consists of the eastern part of the Rocky Mountains extending north from the Palmer Divide, which rises to the south of Denver, to the Cheyenne Ridge just north of the Colorado/Wyoming border, and east to the Nebraska border (Figure 2). Within these boundaries, the South Platte River and its tributaries have carved a shallow basin extending to the north and east from the Denver area with the valley becoming wider between Brighton and Fort Morgan. Much of the Front Range urban development lies in or near the low-lying terrain along the South Platte. Normally, the prevailing westerly winds over the Rocky Mountains carry pollutants from these urban areas away to the east. At night, cooling of the earth's surface creates drainage winds that follow the river channels and carry pollutants from higher terrain to low-lying areas where they either pool, typically over agricultural areas of low population density, or exit



Site Type	Location	Symbol
Core	Welby, Brighton, Evans	
Satellite	Chatfield Reservoir, Highlands Ranch, Downtown Denver, Longmont, Fort Collins, Masters	
Video/35mm Slides	Thornton, Fort Morgan, Fort Collins	
Meteorological Measurements	Various	

Figure 2. NFRAQS monitoring sites. The South Platte River is shown as the solid blue line.

the region. Especially during the summer days, the sun heats the earth's surface, causing the pollutants to rise and mix in the heated air, where they are diluted or mixed into the air that passes over the Rocky Mountains.

During the winter, diverse weather conditions trap emissions in a thin layer of cold, surface air that accumulates pollution. Two of the more common conditions are when snow covers the ground and keeps the earth's surface from heating, and when easterly winds trap the cold air in the South Platte River basin and create high pollution periods. When this layer of cold air is shallow and snow covers the ground, pollutants settle in the lower terrain to the north and east of Denver. Occasionally, this polluted air mass sloshes back and forth along the South Platte River Valley, into and out of the Denver area. Under these infrequent winter conditions, the highest concentrations of pollutants occur in low terrain along the South Platte River.

Several different weather conditions cause the easterly winds that trap pollutants along the foothills. Sometimes, a shallow cold, dry air mass plunges southward from the Arctic along the Rocky Mountains creating a strong temperature inversion. At other times weak storm systems push moist, cloudy air from the Great Plains up against the mountains while warmer air blows over the mountains from the west which creates a temperature inversion that can trap pollutants. These different weather conditions allow for both "wet" and "dry" pollution episodes. The "dry" episodes favor accumulation of directly emitted primary particles whereas the "wet" episodes favor creation of secondary ammonium nitrate and ammonium sulfate particles from ammonia, nitrogen oxides and sulfur dioxide. Because Front Range winters vary from wet to dry, the mix and concentration of pollutants vary significantly from winter to winter.

The Emission Inventory

Emission inventories often provide a frame of reference for development of air quality management strategies, because they estimate emissions from different sources. Thus, the inventory must be accurate so policy makers can plan effective programs to reduce emissions. HB95-1345 called for a determination of the sources of air pollution in the NFRAQS region. Table 1, provided by the Regional

Table 1. Direct emissions in percentages from pollution source types in the six-county metro Denver area, winter 1995, as reported by the Regional Air Quality Council ("Blueprint for Clean Air, Phase II Subcommittee Reports," April 24, 1998). Blanks indicate that no value was provided for a given source type and pollutant category. Values given with each pollutant are in tons per day. Total percentages for each pollutant may not equal 100 percent due to rounding.

	Daily Pollutant Emissions, Winter 1995					
Pollution Source Type	**$PM_{2.5}$, 27 tons**	**PM_{10}, 102 tons**	**Nitrogen Oxides, 346 tons**	**Sulfur Dioxide, 85 tons**	**Volatile Organic Compounds 336 tons**	**Carbon Monoxide, 1578 tons**
Gasoline Vehicle Exhaust	6 %	2 %	40 %	4 %	47 %	85 %
Smoking Vehicle Exhaust	<1 %	<1 %				
On-Road Diesel Exhaust	18 %	5 %	10 %	2 %	2 %	2 %
Off-Road Diesel Exhaust	7 %	2 %	8 %	2 %	4 %	7 %
Road Dust & Sand	27 %	50 %				
Unpaved Road Dust	15 %	28 %				
Construction Dust	1 %	2 %				
Wood Burning	7 %	2 %				
Coal-fired Power Stations	3 %	1 %	19 %	73 %		
Restaurant Cooking	5 %	1 %				
Natural Gas	2 %	<1 %	8 %	0 %		
Industrial Sources	10 %	8 %	14 %	20 %	10 %	1 %
Area Sources			<1 %	0 %	27 %	5 %
Biogenic Sources			1 %	0 %	9 %	0 %

Air Quality Council, lists pollutants and their sources for the six-county metro Denver area using methods developed prior to this study. The motor vehicle emission estimates were derived from emission models and factors developed from studies conducted as part of the NFRAQS by the CDPHE and the Colorado School of Mines, along with regional travel estimates.

$PM_{2.5}$ emissions listed in the table are directly emitted particles (called primary particles); they are different from $PM_{2.5}$ particles formed in the atmosphere from gas-phase precursor compounds (called secondary particles). Seventy-seven percent of the directly emitted PM_{10} (all particles having aerodynamic diameters up to 10 mm, including $PM_{2.5}$) is from road dust and sand. Nitrogen oxides (NO_x), sulfur dioxide (SO_2), and ammonia (NH_3) are precursors to the formation of secondary $PM_{2.5}$ ammonium nitrate and ammonium sulfate in the atmosphere. NO_x and gas-phase volatile organic compounds (VOCs) form ozone, and under summertime conditions in the Denver area, VOCs also form secondary organic carbon particles. Carbon monoxide (CO) does not contribute to $PM_{2.5}$ or impairment of visibility.

Table 1 shows what source types are thought to contribute to the each of the pollutants. Wood burning has been reduced substantially during the past ten years because of the CDPHE's wood burning restriction program, and it produces only 7% of the directly-emitted $PM_{2.5}$ (Table 1). Industrial sources are those sources having permits from the Colorado Air Pollution Control Division, such as refineries, print shops, auto body shops, and natural gas compressors. Area sources include vapors from gasoline transfer, paints, degreasers, solvents, and other sources.

According to this inventory, mobile sources produce 58% of the NO_x, 53% of the VOC and 94% of the CO, while power plants produce 73% of the SO_2 emissions. Estimates of ammonia (NH_3) emissions, provided separately by the CDPHE, are for areas outside of the six-county metro Denver area. For the entire NFRAQS region, the CDPHE estimates a total of 114 tons/day of ammonia emissions, of which agricultural operations produce 97 tons, or 85%. Respiration from humans produces the remaining 15%.

Emission inventories are relatively accurate for SO_2 and NO_x, the precursors of secondary $PM_{2.5}$ particles. In other parts of the country VOC emissions from mobile sources are currently underestimated by a factor of two or more. In the NFRAQS, scientists also observed substantial differences between the inventory estimates for $PM_{2.5}$ and the receptor modeling estimates derived from the source and ambient $PM_{2.5}$ data collected during the Study. Additional research is needed to explain this difference.

Study Results

The following section summarizes the key findings of the PM_{10} and $PM_{2.5}$ individual study results and identifies their primary sources.

Summary of PM_{10} Data

As required by legislation, the NFRAQS was to measure PM_{10}, to establish the relationship between $PM_{2.5}$ and PM_{10}. PM_{10} was measured at the Welby site in Winter 96 and Welby, Golden, east of Longmont, and Fort Collins in Summer 96. No PM_{10} concentrations exceeded, or even approached, the 24-hour national ambient air quality standard of 150 $\mu g/m^3$. The maximum PM_{10} reading at any site during the entire program was 56 $\mu g/m^3$.

At Welby, $PM_{2.5}$ concentrations averaged 44 and 48% of the PM_{10} concentrations during the Winter 96 and Summer 96 phases, respectively. Summer 96 data from Fort Collins, Golden, and Longmont sites showed $PM_{2.5}$ averages were 50, 57, and 42%, respectively of the corresponding PM_{10} readings. Although not demonstrated in the NFRAQS, previous Denver area studies have shown that the majority of the PM_{10} mass is composed of geological material, whose origin is reentrained road dust, construction dust, and wind-blown dust.

Summary of $PM_{2.5}$ Data

During the three phases of the NFRAQS, $PM_{2.5}$ levels did not exceed the new national ambient air quality standard at any of the sampling sites; the 24-hour and annual average $PM_{2.5}$ standards are 65 $\mu g/m^3$ and 15 $\mu g/m^3$, respectively. Typical 24-hour average $PM_{2.5}$ values at urban sites during Winter 96 and Summer 96 were 10 to 12 $\mu g/m^3$, well below the national standards. Average $PM_{2.5}$ concentrations

were similar at Welby during the Winter 96 and Winter 97 sampling periods and 13% lower in the summer.

Winter 97 $PM_{2.5}$ Data

The $PM_{2.5}$ had different concentrations and compositions at the nine Winter 97 sampling sites, with carbonaceous particles more important at the urban sites and secondary ammonium nitrate particles more important at the northerly, rural sampling sites. Average $PM_{2.5}$ concentrations on episode days were as high at the northern Evans and Masters sites as they were in downtown Denver, but over the entire sampling periods, the urban Denver sites had consistently higher $PM_{2.5}$ readings.

In the metro Denver area, particles containing carbon species were the largest fraction of $PM_{2.5}$, averaging 53% of the total during both winters. In the winter at the urban Denver sites, three-fourths of the particulate carbon species were produced by fossil fuel combustion from mobile sources. Particulate ammonium nitrate was the second-most abundant species in the wintertime $PM_{2.5}$ in the NFRAQS region. In urban Denver, ammonium nitrate accounted for 21% of the $PM_{2.5}$ mass; at the rural Masters site it accounted for 32% of the $PM_{2.5}$. In the winter, ammonium nitrate was twice as abundant as ammonium sulfate in urban Denver; at the northernmost NFRAQS sites ammonium nitrate was about four times that of ammonium sulfate. Dust accounted for less than 10% of the $PM_{2.5}$ except at Chatfield Reservoir and Masters, where it was 12 and 14% of the total.

The maximum 24-hour average $PM_{2.5}$ concentration of 50 $\mu g/m^3$ was measured at the rural Masters site, with the second-highest value of 43 $\mu g/m^3$ at Evans. The Study did not determine what portion of the $PM_{2.5}$ was formed locally or how much was transported from Denver or the other urban areas along the Northern Front Range. The vast majority of NO_x and SO_2 comes from the urban areas. En route, those $PM_{2.5}$ precursors combine with ammonia from agricultural emissions to form secondary ammonium nitrate and ammonium sulfate particles.

Summer $PM_{2.5}$ Data

During the Summer 96 phase, $PM_{2.5}$ averaged 10-15 $\mu g/m^3$ on the pollution episode days at Welby, Golden, Fort Collins, and the regional site east of Longmont. At Welby, carbon-containing particles were the major contributor to $PM_{2.5}$, averaging 49% of the total. Ammonium nitrate was present in lower concentrations, and it accounted for only 8% of the $PM_{2.5}$ mass, while ammonium sulfate accounted for 13% of the total $PM_{2.5}$. Other components, such as geologic materials, accounted for a greater portion of the $PM_{2.5}$ than in the winter. In the summer, ammonium sulfate was a larger contributor than ammonium nitrate to the ambient $PM_{2.5}$ levels at the urban sites, but at the regional site east of Longmont, ammonium nitrate and ammonium sulfate were present in equal amounts. Geological materials were responsible for about 11% of the $PM_{2.5}$ mass in the summer.

Policy-Relevant Conclusions

The following discussion summarizes the most important conclusions of the three policy-relevant objectives. The NFRAQS scientists assigned each conclusion to one of the following confidence levels according to their judgement:

- High confidence: High certainty in the data or data analysis method, or researchers used multiple, independent data analyses, each of which has moderate uncertainties.
- Medium confidence: Moderate certainty in the data or data analysis approach, and independent analysis approaches were not applied.
- Low confidence: Little certainty in the data or data analysis approach, and researchers did not apply independent analysis approaches or they found the results contradictory.

NFRAQS Policy-Relevant Objective 1. Sources or contributors to observed $PM_{2.5}$ particle concentrations

To achieve Objective 1, scientists estimated the contributions of motor vehicle exhaust, wood smoke, and meat cooking sources to $PM_{2.5}$ at NFRAQS sampling sites using a receptor model with detailed organic chemical analysis in source samples and at ambient sampling sites. See Figure 3 for average 24-hour detailed source contributions to $PM_{2.5}$ at Welby during the episodes analyzed during Winter 1997 phase. See Figure 4 for the estimates of source contributions to $PM_{2.5}$ for 24-hour average samples

for all NFRAQS sites without detailed organic chemical analyses.

Scientists drew the following conclusions about $PM_{2.5}$ in the NFRAQS region:

- Motor vehicle exhaust and road dust were the largest direct $PM_{2.5}$ contributors at the urban NFRAQS sites (High confidence).
- Assuming a direct relationship between NO_x emission sources and their contribution to particulate nitrate, mobile source-related emissions (including $PM_{2.5}$ exhaust and dust from roads and construction activities) could be responsible for at least 75% of the $PM_{2.5}$ in the Denver area (Medium confidence). The contribution of mobile source NO_x emissions to particulate nitrate is discussed in more detail in the conclusions for Objective 3.
- Older technology gasoline-powered cars and trucks have much higher $PM_{2.5}$ exhaust emissions than new vehicles. On average, $PM_{2.5}$ emission rates from smoking vehicles are at least 100 times those from new and well-maintained vehicles (High confidence).
- Motor vehicles produce more $PM_{2.5}$ in cold weather than during warm weather. When the entire fleet of vehicles is started cold in the winter, they produce nearly as much $PM_{2.5}$ as is produced by the few high emitters in the fleet (Medium confidence, see Figure 3).
- When new and well-maintained gasoline-powered vehicles are running under hot, stabilized conditions, their direct $PM_{2.5}$ emissions contribute to only 3% of the $PM_{2.5}$ at Welby (Medium confidence, see Figure 3).
- Light-duty gasoline and heavy-duty diesel vehicles measured in this study produced much higher $PM_{2.5}$ emissions than EPA's mobile source models estimate (High confidence).
- At the urban Denver sites, all gasoline-powered vehicles and engines produced three times the $PM_{2.5}$ as did all diesel vehicles and engines (High confidence).

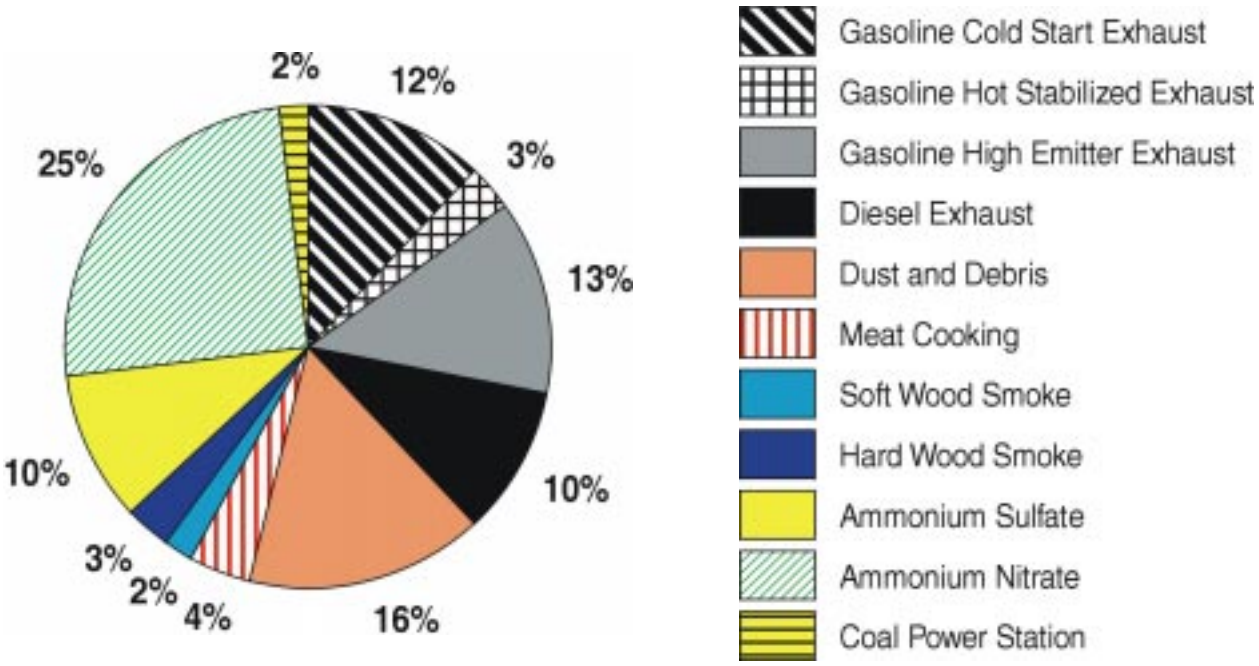


Figure 3. Average source and chemical contributions to the 24-hour average $PM_{2.5}$ concentration at Welby during the Winter 1997 NFRAQS episode periods, using receptor modeling with detailed speciation. Sources of ammonium nitrate and ammonium sulfate were not identified. Average concentrations during the entire winter season are lower than those shown. The day-to-day variability in apportionments is 15-30% with the exception of wood burning, which has greater variation due to burning restrictions. The uncertainty in the apportionments for any single sampling period is larger than 15-30%.

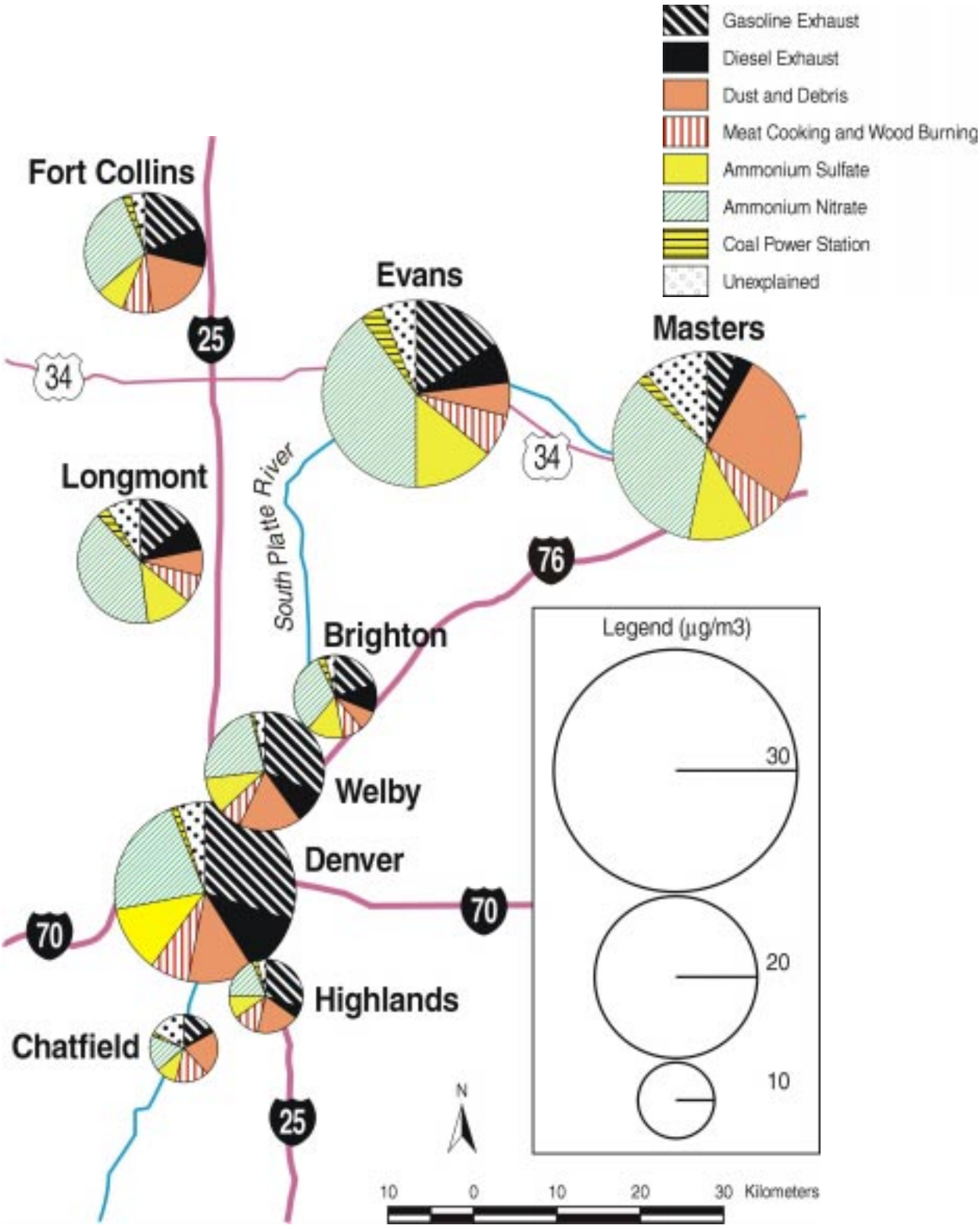


Figure 4. 24-hour average source contributions to $PM_{2.5}$ at all monitoring sites during the Winter 1997 NFRAQS pollution episodes. Sources of ammonium nitrate and ammonium sulfate were not identified. Average concentrations during the entire winter season are lower than those shown. The day-to-day variability in apportionments is 15-30% with the exception of wood burning, which has greater variation due to burning restrictions. The uncertainty in the apportionments for any single sampling period is larger than 15-30%.

- Tire wear from mobile sources was not a significant contributor to $PM_{2.5}$ concentrations (Low confidence).
- Dust and associated debris produced 20-30% of the measured $PM_{2.5}$ at the Denver sites (High confidence). This observation differs from the area's emission inventory estimating that dust from unpaved and paved roads and construction activities accounts for 42% of the directly emitted $PM_{2.5}$.
- On average, meat cooking and wood burning contributed less than 10% of the $PM_{2.5.}$ Large wood burning contributions were observed during some sampling periods, specifically nighttime and morning near the Christmas and New Years holidays and some other days, when contributions were 25-50% of the measured carbonaceous particles. These periods were without burning restrictions (High confidence).
- In the winter, 75% of observed $PM_{2.5}$ carbon species are from fossil fuel combustion; in the summer 50% of the carbonaceous $PM_{2.5}$ is from fossil fuel combustion (High confidence).
- Directly emitted particles from coal-fired power stations contributed 2% of $PM_{2.5}$ in Denver (Medium confidence).

NFRAQS Policy-Relevant Objective 2. Role and importance of gas-phase nitrogen oxides, sulfur dioxide, and ammonia in the formation of ammonium nitrate and ammonium sulfate $PM_{2.5}$ particles

Oxides of nitrogen are emitted, mostly as nitric oxide (NO), that must be oxidized to nitric acid before becoming secondary particulate nitrate. Sulfur emissions are emitted mostly as gas-phase sulfur dioxide (SO_2) and must be oxidized before becoming particulate sulfate. The portions of NO_x and SO_2 that are converted to $PM_{2.5}$ nitrate and sulfate depend upon atmospheric conditions. In winter the atmosphere has limited ability to form nitric acid and particulate ammonium nitrate and ammonium sulfate; the amounts of atmospheric oxidant and water vapor appear to be the controlling factors in secondary particle formation. By contrast, ammonia emissions can participate directly to form $PM_{2.5}$ as ammonium nitrate (reversibly at high temperatures) and ammonium sulfate (irreversibly).

To achieve Objective 2, scientists performed modeling techniques, using winter NFRAQS measurements as model input. Their conclusions are:

- The Northern Front Range is ammonia rich. Sufficient ammonia exists on most winter days to combine with all of the available nitric acid (formed from NO_x emissions), to form $PM_{2.5}$ ammonium nitrate (High confidence).
- A 50% reduction in ammonia concentrations would reduce $PM_{2.5}$ ammonium nitrate by only 15%. After a 50% ammonia reduction, however, scientists expect particulate nitrate to decrease in proportion to reductions in ammonia. Doubling ammonia concentrations would have negligible effect on ammonium nitrate concentrations, because of the excess of ammonia in the atmosphere (High confidence).

NFRAQS Policy-Relevant Objective 3. Contributions of different pollution sources to $PM_{2.5}$ ammonium nitrate and ammonium sulfate

NFRAQS scientists applied dispersion and receptor models, along with other data analysis methods, in an attempt to identify the sources of ammonium nitrate and ammonium sulfate particles. They were able to attribute the majority of $PM_{2.5}$ ammonium nitrate to mobile source emissions, but they were not able to attribute ammonium sulfate to its sources. That said, the scientists made the following conclusions from NFRAQS analyses regarding Objective 3.

Scientists used observational data to suggest that the majority of $PM_{2.5}$ ammonium nitrate was from mobile sources:

- Nitrogen oxides and carbon monoxide concentrations followed the same diurnal patterns, with maximum concentrations during the morning and evening rush hours, consistent with their having a common origin in motor vehicle exhaust (High confidence).
- Ratios of all measured nitrogen and all sulfur species at the monitoring sites showed that emissions from tall stacks at coal-fired power stations could not have contributed more than 10-15% of the ground level oxides of nitrogen and particulate nitrate, with the remainder of the NO_x coming from mobile sources (Medium confidence).

- Less than 10% of the ambient oxides of nitrogen were detected as $PM_{2.5}$ ammonium nitrate during winter. Most emitted NO_x remains in the atmosphere as gas-phase NO and NO_2. Nitrate concentrations increased most rapidly during the day, when photochemical oxidation of NO_2 occurs. The median values for the fraction converted to nitrate were less than 4% at Welby and less than 8% at Brighton (High confidence).
- Current understanding of nitrogen chemistry, derived from knowledge of chemical mechanisms and from modeling studies other than the NFRAQS, suggests that decreases in NO_x emissions would result in less than a proportional decrease in $PM_{2.5}$ nitrate concentrations (Medium confidence).
- Eliminating most NO_x emissions from tall stack emissions, such as those at coal-fired power stations, would decrease surface-level particle nitrate concentrations by less than 10% because insufficient atmospheric oxidants are available to form nitrates (Medium confidence).

Scientists could not attribute $PM_{2.5}$ ammonium sulfate to its sources, but they made the following conclusions regarding the influence of SO_2 emissions on air quality. The attribution of SO_2 to its sources does not necessarily equate to its attribution to $PM_{2.5}$ and particulate sulfate:

- Transport simulations showed that the sulfur with the least dilution originated from the Cherokee power station. Surface sources, including motor vehicle exhaust and low-level point sources, were the next largest contributors in terms of the frequency and intensity with which they arrived at the sampling sites. The Diamond Shamrock and Conoco refineries and the Arapahoe, Valmont, and Trigen coal-fired power stations were moderate to minor contributors, with less frequent impacts at the sampling sites. Using simulations, the scientists found that the Pawnee and Rawhide power stations contributed negligible amounts of sulfur to NFRAQS sites, because winds carried their emissions away from the sampling sites (Moderate confidence).
- Sulfur dioxide measured at the downtown Denver, Welby, Brighton, and Evans sites was highest during midday, when daytime mixing of elevated emissions to ground level occurred (High confidence).
- Receptor modeling estimated that an average of 51% of the sulfur dioxide at Welby and 41% of the SO_2 at Brighton came from coal-fired power generators, based on the apportionment of primary particles from these sources. The modeling estimated the SO_2 contribution from motor vehicle exhaust was 28% of the SO_2 at Welby and 22% of the SO_2 at Brighton (Low confidence).

Recommended Future Work

Budget and time constraints did not permit complete analysis of all the data collected in the NFRAQS. The NFRAQS scientists recommend the following future projects:

- Emission inventory verification work is needed to understand:
  - discrepancies between observed and estimated contributions to $PM_{2.5}$ from gasoline and diesel engines.
  - the relative importance of smoking vehicles, high emitters (not having a visible plume), and "puffing" vehicles (those that emit a puff of smoke when starting cold or when accelerating) to the NFRAQS gasoline vehicle $PM_{2.5}$ apportionment.
  - in-use diesel fleet emissions and the influence of cold temperatures on their emission rates.
  - differences between NFRAQS results and inventory estimates of the contribution of dust to $PM_{2.5}$.
- Limited observations in different parts of Denver suggest that as little as 0.1% or as much as 2.5% of the in-use, light-duty vehicle fleet emits visible particles. Because smoking vehicles have $PM_{2.5}$ emission rates more than 100 times greater than those of new technology vehicles, these observations should be verified. The NFRAQS observation of the significance of high-emitting and smoking vehicles to the "brown cloud" should be investigated.

- Analysis of individual NFRAQS episodes should be performed, to provide additional insight regarding the dynamics of $PM_{2.5}$ formation and the importance of different pollutant source types, such as ground level vs. elevated sources, to observed $PM_{2.5}$ concentrations.
- The reasons for and sources of the relatively high $PM_{2.5}$ concentrations along the South Platte River to the north and east of Denver should be investigated. These concentrations may be confined to the high humidity, stagnant conditions near the River. The Study did not determine the sources of the secondary ammonium nitrate and sulfate particles at the rural sampling sites, so it is not clear whether the NO_x and SO_2 precursors leading to particle formation were produced nearby or whether they were transported from the urban areas.
- The relationships between $PM_{2.5}$ concentrations and visual air quality at NFRAQS sampling sites should be determined, using the high quality chemical and optical data collected during the Study periods.
- The majority of NFRAQS data analysis was performed with data from the Winter 97 study. Additional analysis of data collected during the Summer 96 sampling period should be done.

Acknowledgments

We are grateful for the financial support from the state of Colorado, local, regional, and federal governments, industry, trade groups, and research institutions (listed inside the front cover) that made the Northern Front Range Air Quality Study possible. We also acknowledge the excellent field work and analyses provided by the following research groups (in alphabetical order): Aerosol Dynamics, Inc.; Air Resource Specialists, Inc.; Colorado Department of Public Health and Environment (CDPHE); Colorado School of Mines; Desert Research Institute; ENSR; EPRI; General Motors R&D Center; National Institute of Standards and Technology; National Oceanic and Atmospheric Administration; National Renewable Energy Laboratory; Regional Air Quality Council; Sonoma Technology, Inc.; U.S. Department of Energy; and U.S. Environmental Protection Agency. The CDPHE also provided audits of sampling equipment at the NFRAQS monitoring sites and meteorological forecasts for sampling that took place throughout the entire program. The CDPHE and Regional Air Quality Council provided emission inventory information during the NFRAQS. The technical input from the NFRAQS Quality Control Committee and External Peer Review Group provided guidance to the program and suggested analyses that were conducted as part of the Study.

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Approximately 75 individuals served as members of this committee