

# EXECUTIVE SUMMARY

## Goals and Objectives

The goals of the Northern Front Range Air Quality Study (NFRAQS) are: 1) to attribute the existing air pollution in the Denver urban region to a source or source category; and 2) to collect data necessary to support informed decisions leading to attainment of federal air quality standards. These goals were addressed through a measurement, data analysis, and atmospheric simulation study to address the following policy-relevant objectives: 1) apportion carbonaceous material in airborne particles to sources; 2) determine the extent to which the Denver area is ammonia-rich (or anion-deficient) with regard to the formation of secondary ammonium nitrate and ammonium sulfate; and 3) apportion sources leading to the formation of non-carbonaceous portion of PM<sub>2.5</sub> (particles with aerodynamic diameters < 2.5 µm) with emphasis on nitrate and sulfate.

The major findings and conclusions of the NFRAQS are summarized in this section according to each of the three policy-relevant objectives. Each conclusion is related to the section(s) of the report in which it is treated. Each conclusion is assigned one of the following confidence levels based on the judgement of the principal investigators:

- **High confidence:** There is low uncertainty in the data or data analysis approach or the conclusion is supported by more than one independent analysis approach, each of which has moderate uncertainties.
- **Medium confidence:** There is moderate uncertainty in the data or data analysis approach and independent analysis approaches were not applied.
- **Low confidence:** There is large uncertainty in the data or data analysis approach and independent analysis approaches were not applied or were contradictory.

## NFRAQS Measurements

NFRAQS measurements were acquired for 44 days from 01/16/96 through 02/29/96 (Winter 96), for 45 days from 07/16/96 through and 08/31/96 (Summer 96), and for 60 days from 12/09/96 through 02/07/97 (Winter 97). The Winter 97 monitoring was the most comprehensive, and conclusions related to the three objectives are specific to these data. Conclusions are also presented about how well the Winter 97 measurements represented concentrations measured during Winter 96 and Summer 96, but source attribution was not undertaken for these other periods.

Ambient air and source emissions measurements were taken as part of NFRAQS, as well as acquired from existing meteorological, air quality, and visibility monitoring networks. Ambient and source PM<sub>2.5</sub> samples were acquired and analyzed for mass, chemical elements, ions, organic and elemental carbon, organic compounds, and carbon-14 isotopic abundances. These measurements were organized into a consistent and documented database and subjected to several tests to determine their validity, precision, and accuracy. Validation tests were applied to specify

the observations that could be used to address each objective and the uncertainties that they impart to data analysis and mathematical simulations. Where possible, the sensitivity of NFRAQS conclusions to measurement uncertainties were evaluated, thereby yielding data qualification statements about adequacy of the measurements to address each objective.

### **PM<sub>2.5</sub> Characteristics during Different Measurement Periods**

Measurements during Winter 97 were compared and contrasted with measurements acquired during Summer 96 and Winter 96 to determine the generality of Winter 97 conclusions. The urban Welby site was common to each of these periods. These comparisons showed that none of the samples exceeded the 24-hour PM<sub>2.5</sub> National Ambient Air Quality Standards (NAAQS) of 65 µg/m<sup>3</sup> during any of the three study periods. PM<sub>2.5</sub> constituted 45% to 50% of PM<sub>10</sub> (mass of particles with aerodynamic diameters less than 10 µm), with less variable PM<sub>2.5</sub> to PM<sub>10</sub> ratios during Summer 96 than during Winter 96. Coarse particle (PM<sub>10</sub> minus PM<sub>2.5</sub>) mass was similar for Winter 96 and Summer 96. No PM<sub>10</sub> concentrations exceeded, or even approached, the 24-hour NAAQS of 150 µg/m<sup>3</sup>. Typical PM<sub>2.5</sub> levels at urban sites during Winter 96 and Summer 96 were 10 to 12 µg/m<sup>3</sup>, well below the 24-hour PM<sub>2.5</sub> NAAQS of 65 µg/m<sup>3</sup> and the annual PM<sub>2.5</sub> NAAQS of 15 µg/m<sup>3</sup>.

Twenty-four-hour PM<sub>2.5</sub> concentrations ranged from 12 to 24 µg/m<sup>3</sup> during Winter 96 and from 4 to 26 µg/m<sup>3</sup> during Summer 96. During Winter 97, 24-hour PM<sub>2.5</sub> mass concentrations at the three core sites and six satellite sites ranged from 1 to 51 µg/m<sup>3</sup> depending on the sampling location and time. The highest PM<sub>2.5</sub> concentration of 50.5 ± 2.6 µg/m<sup>3</sup> was found at the Masters site on 01/17/97, with the second-highest being 42.9 ± 2.1 µg/m<sup>3</sup> at the Evans site on the same day. These are both non-urban sites, although they receive pollution generated in urban as well as non-urban areas along the Northern Front Range. PM<sub>2.5</sub> concentrations were also higher than average at the Brighton, Welby, Longmont, CAMP, and Highlands sites on 01/17/97.

Average proportions of PM<sub>2.5</sub> carbon, sulfate, nitrate, ammonium, and geological material in Denver (Welby) were similar to those of 1987-88, but absolute values were half as large. The most abundant PM<sub>2.5</sub> chemical components at the Welby site during Winter 96 were the same as those measured in Winter 97. Carbon, ammonium nitrate, and ammonium sulfate accounted for 82% of the PM<sub>2.5</sub> mass during both Winter 96 and Winter 97. Carbonaceous aerosol constituted 48% of PM<sub>2.5</sub> during Winter 96, while ammonium nitrate and ammonium sulfate constituted 34% of PM<sub>2.5</sub>.

Ammonium nitrate and ammonium sulfate accounted for more than 50% of the PM<sub>2.5</sub> during Winter 97 at the northern, non-urban NFRAQS sites. Carbonaceous aerosol accounted for ~50% of PM<sub>2.5</sub> at urban sites such as Welby and CAMP, but decreased to one-third of PM<sub>2.5</sub> mass with distance along the South Platte River Valley. The highest PM<sub>2.5</sub> concentrations at urban Denver sites contained moderate to large contributions from organic carbon, elemental carbon, nitrate, sulfate, ammonium, and crustal material.

PM<sub>2.5</sub> was often higher at non-urban sites, owing to larger contributions from ammonium nitrate, than at urban sites, even though carbon concentrations were lower and sulfate

concentrations were comparable. Sulfate concentrations were more similar among sites than nitrate concentrations.

Particulate pollution episodes were fewer in number and of shorter duration than those during 1987-88. Snowcover was much less and of shorter duration during winter of 1996-97 than during 1987-88.

### **Source Contributions to Carbon Particles (Objective 1)**

To achieve Objective 1, source contributions to carbon were estimated by the Chemical Mass Balance (CMB) model using enhanced organic speciation in source emissions and at receptors to apportion motor vehicle, wood-burning, and meat cooking contributions. The enhanced organic compound measurements allowed organic, elemental, and total carbon to be apportioned to combine light-duty and heavy-duty diesel exhaust, and three categories of Light Duty Gasoline Vehicle (LDGV) exhaust: 1) hot stabilized operation; 2) cold starts; and 3) high particle emitters.

The relative contributions from these sources were compared with those in a regional inventory and discrepancies were identified. Mass emission rate measurements made in conjunction with the chemical composition sampling during source tests were compared with those used in the inventory to explain these discrepancies. In addition to speciated organic compounds, the isotopic abundance of carbon-14 was measured in source and receptor samples at the urban Welby and non-urban Brighton sites. Carbon-14 is abundant in emissions from recently living material, such as that associated with wood burning or meat cooking, but it is not present in the products of fossil fuel combustion, such as that associated with spark-ignition and diesel exhaust emissions.

Figures ES-1 and ES-2 show average 24-hour contributions to  $PM_{2.5}$  and total, organic and elemental carbon at Brighton and Welby, respectively, during Winter 97. Figures ES-3 and ES-4 show the contributions to  $PM_{2.5}$  and carbon, respectively, for 24-hour average samples for both core and satellite sites using the CMB without detailed organic speciation. Similar source contributions were estimated for the other sites, but the less detailed organic speciation did not permit separation of cooking from wood burning or the different types of gasoline-fueled vehicle exhaust. Off-road diesel contributions (e.g., construction, agriculture, locomotives) could not be distinguished from on-road diesel exhaust contributions.

The following conclusions are applicable to apportionment of  $PM_{2.5}$  carbon in the NFRAQS region.

- Carbon constituted 43% of average  $PM_{2.5}$  at Welby and 34% of average  $PM_{2.5}$  at Brighton for the Winter 97 chemical analysis days. (High confidence based on >20 measured days and moderate measurement precision; Section 6.2.1.1)
- Vehicle exhaust was the largest  $PM_{2.5}$  carbon contributor, constituting ~85% of  $PM_{2.5}$  carbon at sites in the Denver metropolitan area and ~75% of  $PM_{2.5}$  carbon at more

rural sites. This is consistent with carbon-14 measurements that found an average 77% of carbon at Welby and 73% of carbon at Brighton to be of fossil fuel origin. Vehicle exhaust was not the major source of PM<sub>2.5</sub> carbon in the undeveloped area south of Denver and along the northern edge of the study area near the town of Masters, ~120 km northeast of Denver along the South Platte River. (High confidence based on CMB apportionment of enhanced and conventional species measurements, emissions rate estimates, and carbon-14 measurements; Sections 4.3.1, 4.3.1, 7.3 and 7.4).

- Sources with emissions similar to LDGVs contributed about 60% of PM<sub>2.5</sub> carbon at urban Denver sites, and these contributions were 2.5 to 3 times the diesel exhaust contributions. LDGV exhaust contributions were twice diesel exhaust contributions near the town of Evans and were nearly equal near the cities of Brighton, Longmont, and Fort Collins. (High confidence based on comparison of CMB attributions using enhanced and conventional measurements and LDGV emission rate measurements substantially higher than those used to generate emissions inventories; Sections 4.3.1, 4.3.2, 7.3 and 7.4).
- LDGV cold starts and LDGV high particle emitters contributed  $24 \pm 4\%$  and  $28 \pm 5\%$  of PM<sub>2.5</sub> carbon, respectively, at Welby. LDGV high particle emitters were the largest components of PM<sub>2.5</sub> carbon at Brighton, with average 24-hour contributions of  $49 \pm 4\%$ . (High confidence for cold start contributions owing to stability of results with inclusion or exclusion of specific organic compounds from CMB modeling and high measured emission rates. Medium confidence for high particle emitter contributions owing to CMB sensitivity to organic carbon and unknown activity levels for these emissions; Sections 4.4.1, 7.3, 7.4, and C.1.3).
- Hot stabilized emissions from presumably well-maintained vehicles contributed  $6.3 \pm 1.3\%$  of carbon at Welby and  $3.3 \pm 1.0\%$  at Brighton. These vehicles were minor contributors to PM<sub>2.5</sub> carbon and total mass. (High confidence based on low sensitivity of CMB to specific markers and consistent emission rates; Sections 4.3.1, 4.3.2, 7.3, 7.4, and C.1.3).
- Road dust contributed  $4.2 \pm 0.7\%$  and  $3.6 \pm 0.6\%$  to PM<sub>2.5</sub> carbon at Welby and Brighton, respectively. The combined vehicle-related (i.e., exhaust and road dust) contributions to PM<sub>2.5</sub> carbon approached 85% at both Welby and Brighton. (High confidence, based on low sensitivity of CMB to marker species. Sections 7.3 and 7.4).
- Meat cooking contributed moderate amounts of PM<sub>2.5</sub> carbon on some days, but on average these contributions were minor. Average meat cooking contributions at Welby and Brighton were  $6.3 \pm 2.1\%$  and  $2.8 \pm 2.0\%$ , respectively. (High confidence at Welby where carbon-14 and CMB contributions were consistent. Low confidence at Brighton where many cooking marker species were at or near detection limits; Sections 7.3 and 7.4).

- Wood combustion was a moderate contributor, on average, constituting  $8.0 \pm 1.6\%$  of total carbon at Welby and  $3.8 \pm 0.8\%$  at Brighton. Large wood burning contributions were observed for some samples, specifically nighttime and morning near Christmas and New Years holidays and on 12/19 and 1/14, 1/17, and 1/29-30 when contributions were 25% to 50% of carbon. These periods coincided with some of the coldest temperatures during Winter 97 and were without burning restrictions except for 1/17. (High confidence for samples at urban sites based on consistency with burning habits, diurnal cycles, carbon-14 measurements, and stable CMB solutions; Sections 7.3, 7.4, and C.1.3).
- Woodburning contributions during Winter 97 were substantially lower than those measured during the winter of 1987-88, when wood burning contributions at Welby were comparable to those from motor vehicle exhaust. The 1987-88 wood burning contributions were estimated prior to woodburning controls in the Denver metropolitan area. They may also have included meat cooking contributions, as this was not recognized as a potential contributor at the time. (High confidence, based on analyses specified above; Sections 7.3 and 7.4).
- Secondary organic carbon was a small (less than 10%) portion of organic carbon, especially in the urban source areas. (Medium confidence based on organic to elemental carbon ratios that were consistent with those of primary emissions and complete accounting of organic mass by primary sources within measurement uncertainties; Section 6, 7.3 and 7.4).
- Secondary organic aerosol could not be ruled out as a potential contributor to PM<sub>2.5</sub> organic carbon during winter, although primary emissions profiles explained the measured carbon within propagated uncertainty intervals. Concentrations of 2-nitrofluoranthene and 2-nitropyrene, compounds formed by photochemically driven organic gas-to-particle conversion, showed no detectable differences between samples that experienced different levels of solar radiation, but the radiation differences encountered during Winter 97 were not large. (Low confidence based on lack of specific indicators of secondary organic aerosol end-products; Section 7.1).

### **Ammonia Limitations on Nitrate and Sulfate (Objective 2)**

To achieve Objective 2, the equilibrium between ammonium nitrate particles, ammonia gas, and nitric acid gas was simulated by aerosol equilibrium theory (Simulating Composition of Atmospheric Particles at Equilibrium, SCAPE model). These simulations were supplied with measurements of total ammonia (gas and particle), nitrate (gas and particle), sulfate (particle), temperature, and relative humidity at the urban Welby and non-urban Brighton sites. Particulate ammonium nitrate concentrations were simulated for actual NFRAQS conditions and for increases and decreases in ammonia, nitric acid, and sulfate concentrations that might occur because of emissions reduction strategies, urbanization, or growth of farming activities.

The conclusions from these simulations at the Welby and Brighton sites are:

- Sulfate along the Northern Front Range is completely neutralized by available ammonium and is present in the form of ammonium sulfate. (High confidence based on measured ammonium concentrations that are equivalent to those estimated from nitrate and sulfate measurements assuming their presence as ammonium nitrate and ammonium sulfate; Sections A.5.3.4 and A.5.3.5).
- The Northern Front Range is ammonia rich. There was sufficient ammonia, on most days during winter, to completely neutralize available nitric acid. (High confidence based on agreement on phase comparisons between equilibrium model and measurements. Most of the available nitric acid would be neutralized even if ammonia levels were 50% of their current values; Sections 8.2 and C.2.3).
- A 50% reduction in ammonia concentrations would reduce particle nitrate by only 15%. After a 50% ammonia reduction, however, particulate nitrate is expected to decrease in proportion to reductions in ammonia. Doubling ammonia concentrations would have negligible effect on ammonium nitrate concentrations, as there are only minor non-neutralized nitric acid concentrations available for reaction. (High confidence, based on reasons cited above; Section 8.2).
- In a few cases, moderate nitrate concentrations ( $\sim 7 \mu\text{g}/\text{m}^3$ ) were associated with a low molar ratio of total ammonia to total nitrate (1.2). For this infrequent situation, reductions in either ammonia or nitric acid would result in proportional reductions in  $\text{PM}_{2.5}$  ammonium nitrate. (High confidence, based on reasons cited above; Section 8.2).
- Reducing or doubling of sulfate concentrations would have a negligible effect on  $\text{PM}_{2.5}$  nitrate. (High confidence based on measurements showing that there was sufficient free ammonia along the Northern Front Range that the small amount released by removing ammonium sulfate from the atmosphere would have no effect on ammonium nitrate levels; Section 8.2).

### **Source Contributions to $\text{PM}_{2.5}$ (Objective 3)**

To achieve Objective 3, NFRAQS meteorological measurements during Winter 97 were used in transport simulations to determine the probability of sulfur dioxide from tall stacks and surface sources arriving at different receptors. These simulations were evaluated by comparing estimated and measured sulfur concentrations at the Welby and Brighton sites. Simulations were used to determine where and when elevated and surface plumes could have arrived at receptors so that diurnal patterns in observed concentrations of sulfur dioxide, sulfate, nitrogen oxides, and nitrate could be allocated to their possible origins.

$\text{PM}_{2.5}$  mass, sulfur dioxide, and oxides of nitrogen were allocated to sources at the Welby

and Brighton sites by the CMB model. Ratios of total (gas plus particle) sulfur and nitrogen concentrations were compared with each other and to carbon monoxide concentrations and light absorption to estimate the possible range of attributions to coal-burning emissions from tall stacks and from motor vehicle exhaust emitted near ground level. Diurnal cycles of carbon monoxide, light absorption, sulfur dioxide, and nitrogen oxides were examined in conjunction with upper air meteorological measurements to determine where and when ground-level emissions and tall stack emissions arrived at receptors.

Conclusions from these analyses about Objective 3 are:

- Motor vehicle exhaust and geological materials were the largest direct  $PM_{2.5}$  contributors at sites in and near Denver. On average, motor vehicle primary emissions constituted 55% of  $PM_{2.5}$  in Denver. Ammonium nitrate and ammonium sulfate were the largest contributors at non-urban locations in the northern NFRAQS region. (High confidence, based on stability of CMB source attribution; Section 9.2.1).
- Contributions of LDGV cold start emissions were twice as high in the morning and overnight samples than during the afternoon at the Welby site. Contributions of LDGV hot-stabilized emissions, LDGV high particle emitters, and diesel exhaust were lowest during the night. (High confidence based on CMB source attribution stability; Section 9.2.1).
- Meat cooking and wood burning were minor  $PM_{2.5}$  contributors, on average, though there were some samples for which their contributions exceeded 10% of  $PM_{2.5}$ . Meat cooking and wood burning contributions were highest during nighttime samples. (High confidence at Welby but low confidence at Brighton owing to marker concentrations near detection limits; Section 9.2.1).
- Absolute gasoline vehicle exhaust and road dust contributions were twice as high in Denver compared to downwind rural locations (i.e., Longmont, Brighton, and Evans). However, the relative contribution from diesel exhaust was more uniform within the area between Denver and Evans. (High confidence owing to stability of CMB attributions and consistency with emissions measurements; Section 9.2.1).
- Primary particles from coal-fired power stations contributed ~2% of  $PM_{2.5}$  in Denver. (Medium confidence, based on stability of CMB source attributions but high uncertainties owing to ambient measurements near detection limits; Section 9.2.1).
- All of the  $PM_{2.5}$  mass was accounted for by the source contribution estimates, other than coal combustion, within measurement and simulation uncertainties. Point source emitters were negligible contributors to primary  $PM_{2.5}$ . CMB model sensitivity tests showed that brake and tire wear were also negligible contributors to primary  $PM_{2.5}$ . (Medium confidence based on large uncertainties in source profiles and ambient measurements near detection limits for marker species; Section C1).

- Secondary ammonium nitrate and ammonium sulfate contributed more than 50% of the PM<sub>2.5</sub> at the northern non-urban NFRAQS sites. Ammonium nitrate contributions were three to four times the ammonium sulfate contributions in the northern part of the NFRAQS domain and twice the ammonium sulfate contributions in Denver. Diurnal variations in secondary nitrate and sulfate contributions were small at Welby and Brighton with slightly higher values during the afternoon and overnight periods. (High confidence based on high measurement precision; Sections 9.2.1 and A.8).
- The CMB estimated that an average of  $51 \pm 20\%$  of the oxides of nitrogen at Welby and  $73 \pm 24\%$  of the NO<sub>x</sub> at Brighton came from vehicle exhaust, based on the apportionment of primary particles from these sources. The CMB estimated NO<sub>x</sub> contributions from coal-fired power stations of  $7 \pm 3\%$  at Welby and  $9 \pm 4\%$  at Brighton. (Low confidence based on high uncertainties in CMB source attributions of reactive gaseous precursors; Sections 9.2.2 and C.1.3).
- Oxides of nitrogen 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, based on high time resolution and high precision for these measurements; Section 9.3).
- Ratios of all measured nitrogen and all sulfur species concentrations at receptors showed that during more than 90% of the filter sampling periods, contributions from tall stacks at coal-fired power stations could not have contributed more than 10% to 15% of the ground level oxides of nitrogen and particulate nitrate. The atmosphere did not contain the amount of sulfur that would have to exist if these elevated emissions contributed more to ground-level NO<sub>x</sub> and its reaction products. Surface sources emit much less SO<sub>2</sub> in proportion to NO<sub>x</sub> than coal-fired power stations. (Medium confidence, based on correspondence during clearly identifiable meteorological conditions but moderate to large uncertainties in deposition; Section 9.4).
- A small fraction, less than 10%, of the ambient oxides of nitrogen were detected as particle nitrate at the NFRAQS sampling sites during winter. Most emitted NO<sub>x</sub> remains in the atmosphere as NO and NO<sub>2</sub>. Nitrate concentrations increased most rapidly during the day, when photochemical oxidation of NO<sub>2</sub> occurs. The median values for the fraction converted to nitrate were less than 4% at Welby and less than 8% at Brighton. The maximum observed conversion of ambient nitrogen oxides did not exceed 20%. (High confidence, based on high measurement precision; Sections 9.3 and 9.4).
- Current understanding of nitrogen chemistry, derived from our knowledge of chemical mechanisms and from modeling studies other than the NFRAQS, suggests that decreases in NO<sub>x</sub> emissions would result in less than a proportional decrease in particulate nitrate concentrations. (Medium confidence, based on lack of NFRAQS-



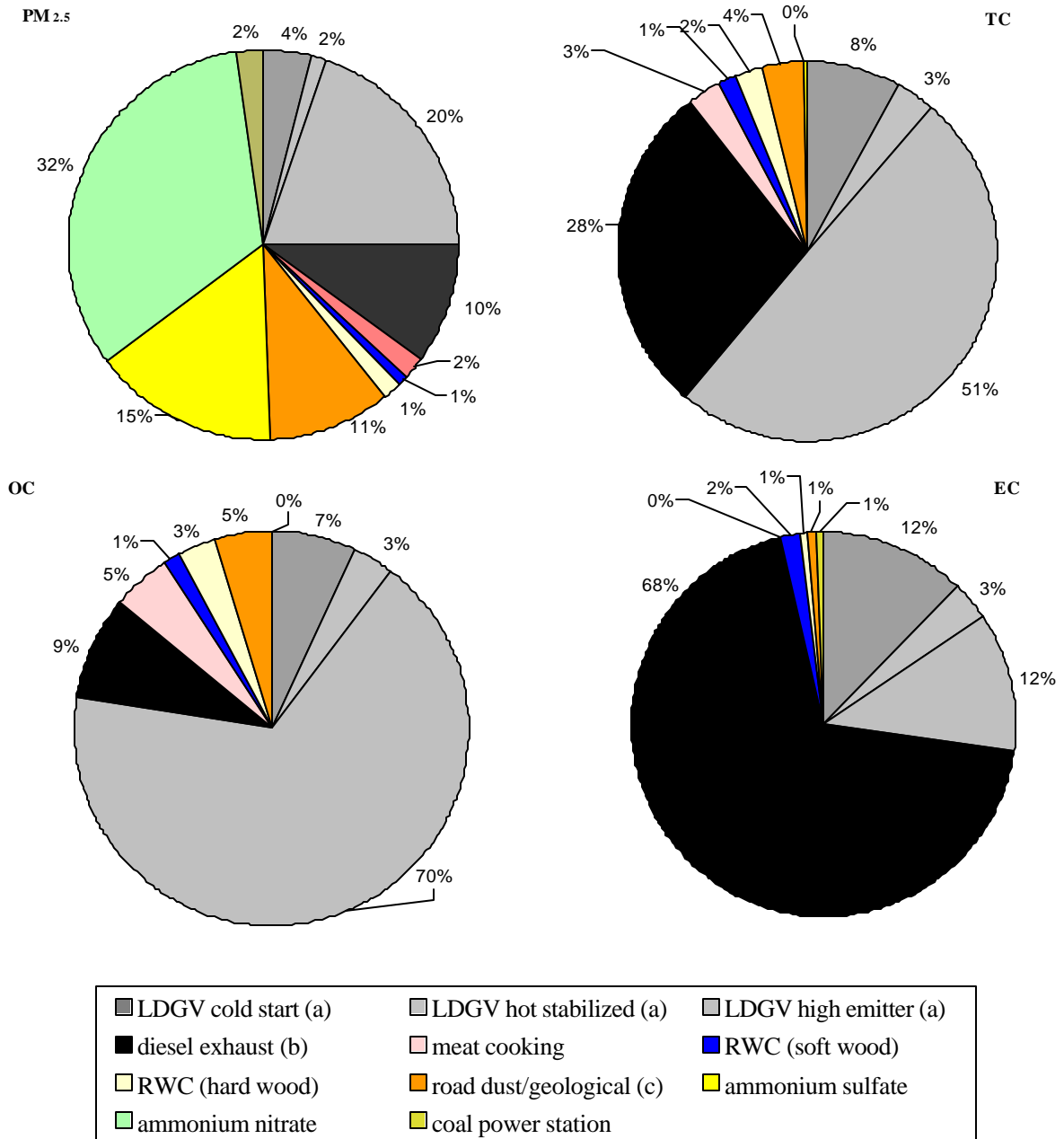
specific application of appropriate chemical mechanisms and insufficient quantification of oxidant availability in the NFRAQS study region; Section 9.4).

- Eliminating most NO<sub>x</sub> emissions from tall stack emissions, such as those at coal-fired power stations, would decrease particle nitrate concentrations measured at surface sites by less than 10%. (Medium confidence, based on contributions to surface oxides of nitrogen during times of day when elevated emissions mix to the surface relative to total contributions throughout the day from all sources; Section 9.4).
- The upper limit on coal-fired power station contributions and the consistent evidence of large oxides of nitrogen contributions from motor vehicle exhaust indicates that vehicle NO<sub>x</sub> is the major contributor to secondary ammonium nitrate along the Northern Front Range. (High confidence, owing trapping of surface emissions within the surface layer and mixing of elevated emissions to the surface only during afternoon; Sections 9.3 and 9.4).
- The CMB estimated that an average of 51 ± 9% of the sulfur dioxide at Welby and 41 ± 9% of the sulfur dioxide at Brighton came from coal-fired power generators, based on the apportionment of primary particles from these sources. The CMB estimated the SO<sub>2</sub> contribution from motor vehicle exhaust was 28 ± 3% of the SO<sub>2</sub> at Welby and 22 ± 2% of the SO<sub>2</sub> at Brighton. (Low confidence, based on high uncertainties in CMB attribution of reactive precursor gases; Section 9.2.2).
- Transport simulations showed that the sulfur emissions that most often encountered the NFRAQS sites 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 receptors. 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 receptors and lower intensities and durations of plume encounters. The Pawnee and Rawhide power stations, and other elevated point sources identified in the emissions inventory, contributed negligible amounts of sulfur to NFRAQS receptors, mostly owing to winds that transported their emissions away from receptors during the simulated episodes. (Moderate confidence, based on moderate uncertainties in wind measurements; Sections 9.1 and C.3.3).
- Sulfur dioxide measured at the CAMP, Welby, Brighton, and Evans sites was highest during midday, when daytime mixing of elevated emissions to ground level occurred. Meteorological analyses indicated that the nighttime plume rise of major point sources is only 250 to 400 m (800 to 1300 ft) above ground level. The nighttime point source emissions are mixed with the prior day's surface emissions that were mixed aloft, and the combined emissions are mixed to the surface together during the following day. (Medium to high confidence, based on low uncertainties in ambient measurement and meteorological data, proximity of the measurement site to emissions sources with little

opportunity for transformation and deposition and no chemical measurements aloft; Section 9.3).

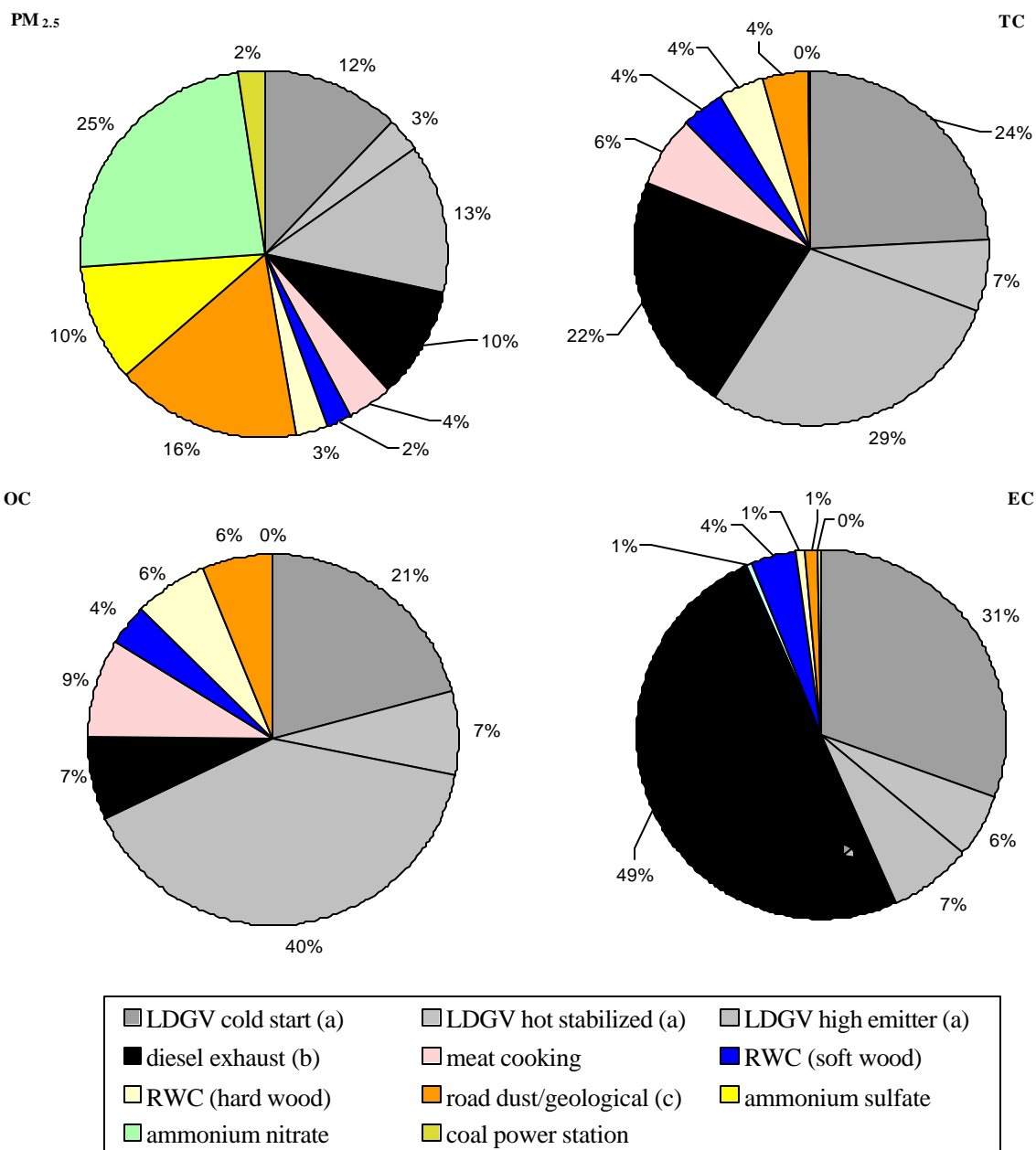
- Sulfur dioxide gas is often either deposited to the ground or oxidized to particulate sulfate, especially in the hours before dawn. Complete loss of SO<sub>2</sub> was observed on more than 25% of the days between the hours of 0200 and 0800 MST at the Welby site and between 1900 and 0900 MST at the Evans site. Complete loss of SO<sub>2</sub> was observed on more than half of the days at 0600 MST at the Welby site and at 0600 and 0700 MST at the Evans site. Complete loss of SO<sub>2</sub> was least common at the Brighton site. (High confidence, based on low uncertainties of ambient measurements; Section 9.4).
- The diurnal sulfate pattern showed little variation, except at Welby where contributions from nearby mobile sources were detected during rush hours. (High confidence, based on low measurement uncertainties and high time resolution corresponding to vertical mixing measurements; Sections 9.3 and 9.4).

### Brighton

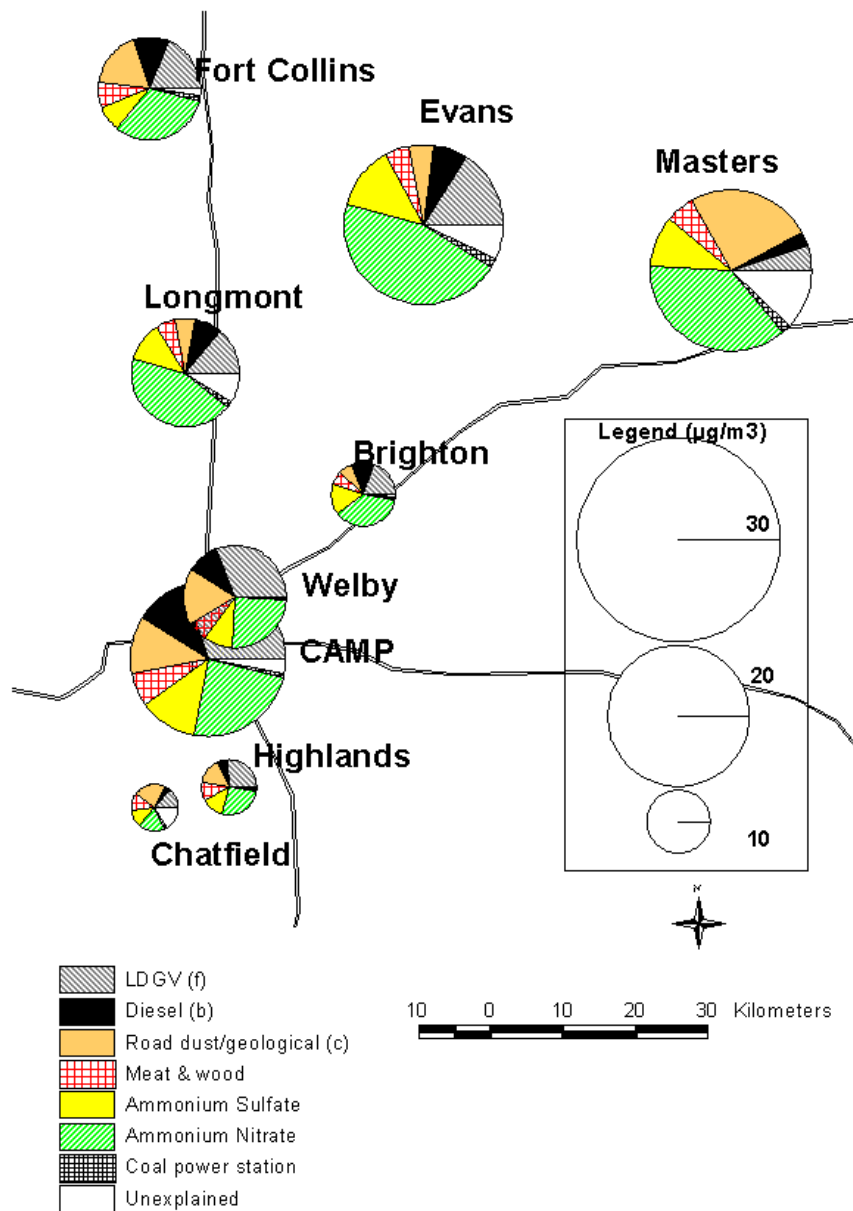


**Figure ES-1.** Average<sup>d</sup> source contributions to PM<sub>2.5</sub> and total, organic and elemental carbon at Brighton during the Winter 1997 NFRAQS. CMB8 with extended species<sup>e</sup> was used to calculate the source contributions. Pie segments are presented in clockwise order beginning at the 12 o'clock position. See explanation to footnotes at the end of this section.

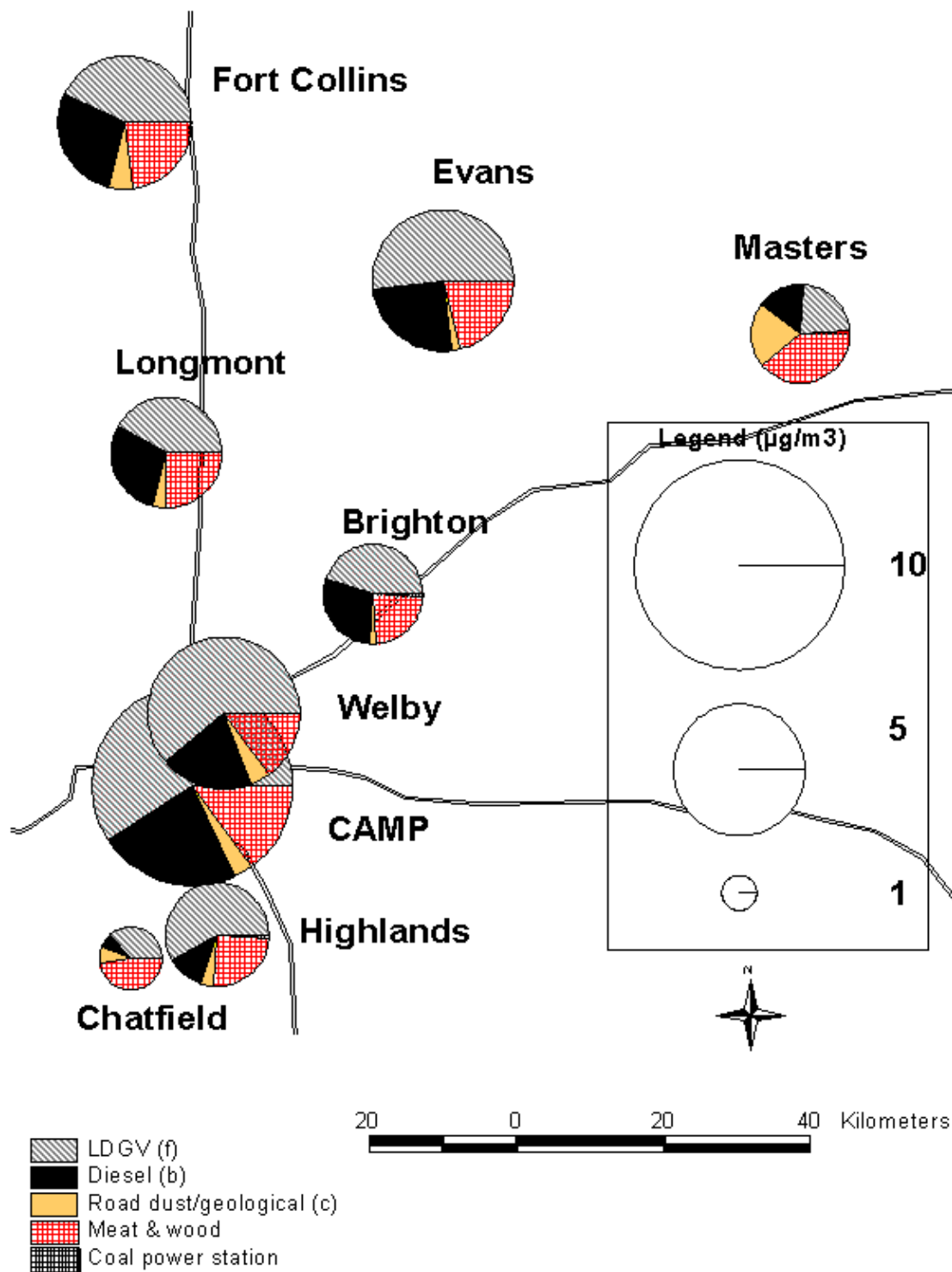
## Welby



**Figure ES-2.** Average<sup>d</sup> source contributions to PM<sub>2.5</sub> and total, organic and elemental carbon at Welby during the Winter 1997 NFRAQS. CMB8 with extended species<sup>e</sup> was used to calculate the source contributions. Pie segments are presented in clockwise order beginning at the 12 o'clock position. See explanation to footnotes at the end of this Section.



**Figure ES-3.** 24-hour average source contributions to PM<sub>2.5</sub> at core and satellite sites during the Winter 1997 NFRAQS using conventional CMB. Pie segments are presented in counter-clockwise order beginning at the 3 o'clock position. See explanation to footnotes at the end of this Section.



**Figure ES-4.** 24-hour average source contributions to PM<sub>2.5</sub> carbon at core and satellite sites during the Winter 1997 NFRAQS using conventional CMB. Pie segments are presented in counter-clockwise order beginning at the 3 o'clock position. See explanation to footnotes at the end of this Section.

Footnotes for Figures ES-1 through ES-4.

- a. Source contributions for light-duty gasoline vehicle exhaust are based on composition profiles that were developed from emissions tests of light-duty gasoline vehicles (LDGV). The composite cold start profile (nvns) was derived from the difference between the phase 1 (cold start) and phase 3 (hot start) portions of the Federal Test Procedure (FTP) driving cycle, and includes low, medium-low, medium, and high particle emitters. The hot stabilized profile (nvns2) was derived from the phase 2 portion of the FTP, and includes low, medium-low, medium and high emitters. The high emitter (nvsm) profile was derived from all phases of the FTP for visibly smoking LDGVs. This profile may include high particle emitters that do emit visible smoke and exhaust emitted during hard accelerations and under heavy loads. The CMB source contribution estimates for one or more of these LDGV profiles could also include heavy-duty gasoline vehicles, off-road gasoline vehicles (e.g., snowmobiles) and gasoline-powered equipment (e.g., snow blowers, chainsaws, etc.)
- b. Source contributions for diesel exhaust are based on composition profiles that were developed from emissions tests of heavy-duty diesel vehicles (nwhdc). The CMB source contribution estimates for this composite profile may include light-duty diesel vehicles, off-road diesel vehicles (e.g., trains and construction equipment) and diesel-powered equipment (e.g., generators).
- c. Source contribution for road dust/geological are based on composition profiles that were derived from a composite of paved road dust samples. The CMB source contribution estimates for this composite profile may include dust from a variety of sources (including wind-blown dust and dust from unpaved roads), tire wear, brake wear, vegetative detritus, and other debris.
- d. Average source contributions are arithmetic means of the relative (%) source contributions for all valid samples collected during six high PM episodes (three samples per day at 0600-1200, 1200-1800, and 1800-0600 on approximately twenty days) during the 60-day study period from 12/9/96 to 2/7/97. These samples include periods of peak PM concentrations as well as the buildup and ventilation periods. The relative source contributions vary with transport trajectory, ambient temperature, and other factors such as day of the week and holiday periods. Thus the average contributions shown in the pie charts do not necessarily correspond to source attributions that would occur during specific diurnal and episodic atmospheric conditions. Nor do they necessarily represent the attributions that would be characteristic of typical winters. However the existing data are suitable for determining the variance in attribution under several meteorological conditions typical of Northern Front Range winters.
- e. Extended species CMB includes speciated organic compounds in the CMB calculation.
- f. The LDGV profile is a composite of the cold start, hot stabilized, and high emitter profiles weighted according to the average relative apportionments of these three categories from the extended CMB.
- g. Average source contributions are arithmetic means of the relative (%) contributions for all 24-hour samples from satellite sites and weighted 24-hour averages of the three period samples from core sites. The caution about application of average contributions in footnote d applies.
- h. Conventional CMB includes only inorganic species and organic and elemental carbon in the CMB calculation.