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ANALYSIS OF PARTICULATE NITRATE AND BLACK CARBON TIME SERIES

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Analysis of Particulate Nitrate and Black Carbon Time Series

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Executive Summary

Objectives. Nitrate and carbon are important constituents of fine particulate matter $(PM_{2.5})$, which is a widespread air pollution problem. The black carbon (BC) or elemental carbon (EC) fraction, also known as soot, is directly emitted from sources such as gasoline and diesel engines and biomass burning. A complementary organic carbon (OC) fraction includes both primary source contributions and secondary organic aerosol. Nitrate in the particle phase is a secondary pollutant that forms from nitrogen oxide (NO_x) emissions that are converted in the atmosphere to nitric acid, which can then react with ammonia to form a condensable product.

The main objective of this research is to describe seasonal, weekly, and diurnal patterns in fine particulate BC and nitrate. Past studies have relied mainly on filter-based PM measurements as the starting point for time series analysis. These studies have focused on spatial and seasonal PM variations. Most of the historical record of speciated PM measurements, typically collected over 24-h sampling periods once every 6th day, is unsuitable for study of diurnal and weekly patterns. In contrast, online measurements of BC/EC and nitrate can provide hourly or better time-resolved data that permit high resolution analyses.

Study of weekly cycles is emphasized in this research, as diesel truck emissions of both BC and NO_x are known to decrease significantly on weekends. Weekly cycles in $PM_{2.5}$ constituents have been considered in a few prior studies. Several groups of investigators have reported lower BC/EC levels on Sundays. There has been less study of weekly cycles in nitrate, and there is disagreement in the literature as to whether weekly cycles are even observed.

Methods. We use data from four measurement sites that were part of the U.S. EPA's Supersite program to study PM. Two of the sites are in California: Fresno in the Central Valley and Claremont in the eastern portion of the Los Angeles air basin. The other sites are Pittsburgh, located in the western part of Pennsylvania and the most affected by

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emissions from coal-fired power plants, and St. Louis, located along the Mississippi River. BC was measured at Fresno from 12/1999-7/2002 and at St. Louis from 1/2003-1/2005. EC was measured at Pittsburgh from 6/2002-7/2002. Nitrate was measured from 9/1999-10/2000, 9/2001-9/2002, 3/2003-5/2005, 6/2001-9/2002, at Fresno, Claremont, St. Louis, and Pittsburgh, respectively.

BC was measured using aethalometers for over a year at both Fresno and St. Louis. The aethalometer is an automated system that measures light transmittance through a quartz filter tape on which sampled particles deposit. BC is assumed to be the only light-absorbing species. Inter-comparisons have shown a high correlation, but consistently lower levels, from the aethalometer relative to thermal-optical methods. EC was measured at Pittsburgh using an online thermal-optical analysis procedure. This method is also automated, provides OC as well as EC, but has lower time resolution compared to the aethalometer. No BC/EC measurements were made at Claremont.

At all four sites nitrate was measured using the integrated collection and vaporization method. Particulate nitrate is collected over 10-minute sampling periods, then volatilized and converted to NO_x , with detection using a standard chemiluminescent analyzer. At Claremont, a custom-built system was used to resolve nitrate into three size fractions: 0.07-0.45, 0.45-1.0, and 1.0-2.5 µm. At the other sites, only a single value for all PM_{2.5} nitrate was measured.

At Pittsburgh, additional measurements from the Pittsburgh Air Quality study included sulfate and precursor gases to both sulfate and nitrate. Additional instruments used at Pittsburgh include a commercial NO_x analyzer as well as a steam sampler with an ion chromatograph combination.

Pollutant concentration data were analyzed in both the time and frequency domains. Time domain analyses were conducted in ways that controlled for the effects of seasonal variations in pollutant concentrations. Periodograms were constructed as the main result

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of frequency domain analysis: these diagrams show the role of different time scales, from seasonal to diurnal, as contributors to variance in pollutant concentrations.

Results. Fresno had the highest BC levels of the 3 sites examined, with peak concentrations observed overnight during the cooler fall and winter months. Emissions from wood burning are a likely major contributor to these overnight peaks. BC/EC levels at both St. Louis and Pittsburgh were higher during warmer months, but showed lower absolute levels and less seasonal variation compared to Fresno. Morning (6-10 AM) peaks are observed at all sites, especially on weekdays. Weekly cycles in BC are present at Fresno and St. Louis, with annual average reductions of 22±6 and 25±5%, respectively, on Sundays relative to moving weekly average values. The amplitude of the weekly cycle at Fresno is larger during summer months. EC data from Pittsburgh suggest a weekly cycle may be present, but we found no statistically significant differences by day of week.

Weekly cycles also appear in the periodograms for all three sites, although the annual cycle is a more important source of variance. The higher time resolution aethalometer data allow for more detailed analysis of the Fresno and St. Louis BC data. At these sites, the periodograms show the importance of diurnal variations. The presence of 2, 3, and 4/day harmonic frequencies indicates the diurnal pattern is not a pure sinusoid. The first harmonic of the weekly cycle is also present in the periodograms for these sites.

Fine particle nitrate levels were higher at the California sites compared to Pittsburgh and St. Louis. Seasonal patterns generally showed lower nitrate levels during warmer months. Claremont was an exception to this rule, with similar peak nitrate levels observed in all seasons. High photochemical formation rates for nitric acid during summer appear to offset much of the effect of warmer temperatures that increase nitrate volatilization. Peak nitrate levels were seen at all sites between 6 AM and noon. Warmer summer temperatures did cause nitrate levels at Claremont to start falling from peak levels earlier in the day than at other times of year.

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Weekly patterns in particulate nitrate were observed at all sites except Pittsburgh. Over the full annual cycle, the lowest ratios relative to a moving weekly average were observed on Mondays. The mean \pm 95% confidence intervals (CI) reductions in nitrate were 29 \pm 23, 23 \pm 12, and 16 \pm 9% at Claremont, Fresno, and St. Louis, respectively, on Mondays relative to weekly average values. No weekly cycle was found at Pittsburgh. At Pittsburgh the weekly reductions in NO_x were not large enough to create statistically significant reductions in particle nitrate. Also, during spring, summer and fall, formation of particle nitrate was limited by ammonia availability and thus weekly NO_x reductions did little to reduce particulate nitrate concentrations. This provides an interesting test case for model-based studies of secondary particle formation: can models reproduce observed pollutant interactions and gas-particle partitioning of nitrate?

Periodograms developed for the nitrate time series show noise in the frequency domain. Although weekly peaks can be located in the periodograms for Fresno, Claremont, and St. Louis, many other nearby frequencies are of similar importance. Further time-domain analysis showed phase shifts in the weekly cycle that depend on season: Monday was the lowest nitrate day during cooler months (October through March), but the weekly minimum shifted to Sunday at Fresno and Tuesday at Claremont during warmer months. A combination of seasonal changes in transport patterns, precursor emissions, and the kinetics of nitric acid formation may alter the timing of atmospheric response to weekly cycles in NOx emissions.

Size-resolved nitrate data from Claremont indicate a predominant 0.45-1.0 μ m mode that accounts for 60% of fine particle nitrate mass during summer months. During winter months the average mass fraction of nitrate in this size range decreases to 40%, and nitrate in the smallest size range (0.07-0.45 μ m) increases from 20 to 40%. Diurnal variations in the fraction of nitrate mass in each size range were minor compared to seasonal variations described above. Times when the smallest size range accounted for >60% of nitrate mass at Claremont were correlated with low humidity northerly flow conditions.

Correlations between nitrate and BC/EC vary by season at all sites. Fresno shows the strongest correlation between these pollutants, with correlation coefficient ranging from 0.89 during the winter to 0.47 during the spring. Correlation coefficients range from 0.03 during the spring to 0.69 during the summer at Pittsburgh, and from 0.13 during the fall to 0.66 during the summer at St. Louis. BC/EC concentrations do not provide a good prediction of nitrate concentrations due to the variability of correlation between these pollutants throughout the year. With the exception of Fresno during the winter, variations in BC/EC concentrations reflect <50% of the nitrate variability.

Conclusions. Weekly cycles in BC/EC were observed at St. Louis and Fresno, as expected based on results of previous research. Fine particulate nitrate concentrations also showed weekly cycles at 3 out of 4 sites examined here, with minima observed on Sunday/Monday, with variations in timing that depended on season.

Recommendations

1. The contribution of wood smoke to carbon particle concentrations at Fresno should be better defined, especially for weekend nights during winter.

2. Further research is recommended to analyze factors that control nitric acid formation and nitrate partitioning between the gas and particle phases.

1. Introduction

Airborne fine particulate matter or $PM_{2.5}$ is a widespread air pollution problem ($PM_{2.5}$ refers to the mass of particles with aerodynamic diameter $D_P < 2.5 \ \mu$ m). In the U.S., annual average $PM_{2.5}$ levels that exceed the national air quality standard of 15 μ g m⁻³ are observed in California and in numerous states east of the Mississippi River (Blanchard, 2004a). Though current air quality standards are defined in terms of total particle mass, to understand $PM_{2.5}$ problems it is helpful to know contributions to the total from key constituents such as carbon, ammonium, nitrate, and sulfate. In the eastern U.S., ammonium sulfate accounts for one quarter to over half of annual average $PM_{2.5}$ mass; sulfate levels are highest in summer months. Carbonaceous particles are also important contributors to $PM_{2.5}$, whereas nitrate levels are relatively low. California, in contrast, typically experiences peak $PM_{2.5}$ concentrations during winter months, with nitrate and carbon dominating fine particle mass (Blanchard, 2004).

The main objective of this research is to analyze time series of measured particle-phase pollutant concentrations to determine if weekly cycles are present in the data. In contrast to past studies that analyzed filter-based PM data, we use data from online measurement methods that provide high time resolution. Our focus is specifically on the black/elemental fraction of carbon particles, and on particulate nitrate. These pollutants are both linked in part to diesel engine emissions, which are known to decrease substantially on weekends (Dreher and Harley, 1998; Chinkin et al., 2003; Harley et al., 2005). Improved understanding of atmospheric responses to emission changes on weekends could help strengthen the technical basis for policy decisions that will reduce emissions on all days of the week in the future.

Previous studies of weekly cycles in PM have been constrained by a sparse data record. The sparse record is due in part to reliance on labor-intensive filter-based PM measurement methods (Chow, 1995). In the past, filter samples were typically collected on a once every 6th day schedule for gravimetric analysis, with only a subset of these samples analyzed for chemical composition. With the implementation in the late 1990s of air quality standards for PM_{2.5}, the sampling frequency has increased to daily at some

sites, or once every 3rd day at others, but again only a subset of filters are analyzed to determine chemical composition of the collected particles. In addition to sparse data, another concern is that standard sampling methods can suffer from negative artifacts due to nitrate volatilization (Hering and Cass, 1999; Ashbaugh and Eldred, 2004).

Black Carbon. Major emission sources of black carbon (BC), also known as soot, include fossil fuel combustion and biomass burning (Novakov et al., 2003; Bond et al., 2004). High soot emission rates are observed from combustion sources where air and fuel are not well mixed, or where the supply of air is inadequate (e.g., diesel engines, residential use of wood or coal for space heating). Particulate carbon is typically measured by thermal analysis of samples collected using quartz filters. Total particulate carbon is divided into elemental carbon (EC, refractory) and organic carbon (OC, volatile) fractions. This split is defined operationally as part of thermal/optical analysis procedures (Chow et al., 1993; Birch and Cary, 1996). There are also semi-continuous techniques for measuring BC (Hansen et al., 1984; Adams et al., 1989; Turpin et al., 1990), and visible light absorption by aerosols (Bond et al., 1999). The size distribution of fresh soot emissions in motor vehicle exhaust is unimodal with a peak around 0.1 µm (Venkataraman et al., 1994). Atmospheric aerosols exhibit a more complex distribution of soot mass, including a predominant mode in the upper submicron size range, in addition to ~0.1 µm and coarse modes (Venkataraman and Friedlander, 1994; Berner et al., 1996).

Various investigators (Allen et al., 1999; Hies et al., 2000; Motallebi et al., 2003; Harley et al., 2005) have reported weekly cycles in BC/EC, with minima observed on Sundays. While this response to a change in primary pollutant emissions is expected, there is uncertainty about the relative importance of diesel exhaust vs. other sources of BC emissions. Further study of weekly cycles in carbon particle concentrations may help to advance understanding of source contributions from diesel vs. gasoline engines, wood burning, etc. A strong weekly BC cycle is expected if diesel exhaust is the dominant source of this pollutant (Harley et al., 2005); seasonal variations in the amplitude of the

weekly cycle may reflect ambient temperature effects on cold start emissions from gasoline engines (Mulawa et al., 1997), and/or variations in the amount of wood-burning.

Weekly cycles in BC may affect photolysis rates and ozone formation through changes in aerosol optical depth and single scattering albedo, which defines the relative amount of light scattering vs. absorption by aerosols (Dickerson et al., 1997; Dreher and Harley, 1998). The effect on ozone of decreasing aerosol optical depth on weekends was found to be small in southern California (Yarwood et al., 2003), as BC does not constitute a large fraction of $PM_{2.5}$ mass. We expect that significant weekend effects on photolysis rates, if any, are more likely to be via the aerosol single scattering albedo and/or effects on fog and low-level clouds. Christoforou et al. (2000) note that between 1982 and 1993 in the Los Angeles area, concentrations of EC and sulfate decreased and were responsible for much of the reduction in $PM_{2.5}$ mass that occurred over that time period. Radiative effects of soot should therefore be decreasing over time, whereas weekday-weekend differences in ozone were observed to be spreading to more locations over the same time period; this is probably due to an increase of regions where ozone production is VOC limited (Marr and Harley, 2002; Fujita et al., 2003).

Particulate Nitrate. Particulate nitrate is formed in the atmosphere through gas-toparticle conversion processes that start with nitrogen oxides (i.e., NO and NO₂), and proceed via formation of nitric acid (HNO₃) as an intermediate step. An important daytime pathway involves reaction of NO₂ with the hydroxyl radical; nighttime formation pathways for nitric acid also exist (Finlayson-Pitts and Pitts, 2000). When sufficient quantities of nitric acid and ammonia are present, their reaction leads to condensation of ammonium nitrate. Conditions that favor particulate nitrate formation include abundant ammonia and nitric acid, low sulfate, low temperature, and high relative humidity (Seinfeld and Pandis, 1998). Studies of the size distribution of inorganic aerosol constituents have revealed a bimodal distribution within the accumulation mode (Hering and Friedlander, 1982; John et al., 1990; Hering et al., 1997). These modes have been linked to particle formation mechanisms: a condensation mode at 0.2 µm related to gasphase oxidation of SO₂ and NO_x, and a droplet mode at 0.6-0.7 µm that implies

involvement of condensed phase processes (e.g., reactions taking place in wet aerosols or fog water). Particulate nitrate can also form by reaction of nitric acid with sea salt particles (Gard et al., 1998). The sodium nitrate generated from sea salt is non-volatile and typically found in a coarse mode that peaks at 4-6 µm (John et al., 1990).

Atmospheric responses to changes in NO_x emissions is a subject of ongoing debate (Croes et al., 2003; Heuss et al., 2003; Lawson, 2003). Counter-intuitive increases in ozone in response to lower NO_x have been observed on weekends, mostly in urban settings where ozone formation is thought to be VOC-sensitive (Cleveland et al., 1974; Altshuler et al., 1995; Marr and Harley, 2002; Fujita et al., 2003; Pun et al., 2003). There is uncertainty about questions such as (1) do factors other than lower NO_x emissions contribute significantly to changes in ozone observed on weekends, (2) what if larger NO_x reductions than those observed on weekends were made, on all days instead of weekends only, and (3) what are the effects of NO_x reductions on other pollutants such as peroxyacetyl nitrate (PAN), nitric acid, and particulate nitrate?

In reviewing ambient concentration data from California, Motallebi et al. (2003) and Blanchard and Tanenbaum (2003) reached different conclusions about whether significant weekly cycles in particulate nitrate were observed. Harley et al. (2005) also reviewed speciated PM_{2.5} data measured in the Los Angeles area during summer and fall of 1995, and found no significant weekly cycle in particulate nitrate. Harley et al. (2005) recommended consideration of newer data sets that provide high time resolution: most past speciated PM_{2.5} measurements were collected at sampling frequencies that were too low to permit detailed study of weekly cycles in the data.

Atmospheric models provide another perspective on the effects of precursor reductions on PM nitrate. A general caveat for the studies cited below is that conclusions are based on model application to short time periods of 2-3 days. Russell et al. (1988) examined effects of controlling mobile and stationary source emissions in Los Angeles. At the most stringent level of control, with 37% reduction in VOC and 61% reduction in NO_x , they reported reductions in particulate nitrate during a summertime air pollution episode that

ranged from 24 to 60% depending on location within the air basin. Lurmann et al. (1997) also applied a three-dimensional air quality model to summertime conditions in the Los Angeles area. They separately considered the effects of 50% reductions in VOC, NO_x, VOC and NO_x, SO₂, NH₃, and primary PM emissions. Reductions in NO_x and ammonia emissions both led to lower PM nitrate; reducing VOC emissions had a smaller but still beneficial effect; reducing SO₂ emissions led to a 7% increase in PM nitrate averaged over all sites that were examined, with no change at the peak site. Separate modeling studies have investigated control of wintertime PM nitrate in California's San Joaquin Valley (Stockwell et al., 2000; Pun and Seigneur, 2001; Kleeman et al., 2005). The first two studies relied on 0-D box models, and reached opposite conclusions about whether VOC vs. NO_x reductions would be preferred for reducing particulate nitrate. Kleeman et al. (2005) used a more realistic 3-D model, and found that 50% reductions in NO_x, VOC, and NH₃ emissions within the San Joaquin Valley led respectively to 25, 17.5, and 10% reductions in particulate nitrate.

In contrast to nitrate which partitions between gas and condensed phases, sulfate formed as a result of SO₂ oxidation is found in condensed phases due to the low vapor pressure of sulfuric acid in the presence of water vapor (Ansari and Pandis, 1998). The most common form is ammonium sulfate, (NH₄)₂SO₄, in which two molecules of ammonia combine with sulfuric acid. If ammonia is scarce, sulfate will remain in more acidic forms such as ammonium bisulfate (NH₄HSO₄) or H₂SO₄. Though ammonia limitations do not affect the fraction of sulfate found in the particle phase, some S(IV) oxidation reactions in the aqueous phase are sensitive to pH and hence ammonia (Seinfeld and Pandis, 1998). A potential interaction among inorganic species is that decreases in sulfate can lead to increased ammonia availability and in some cases, increased particle-phase nitrate (Ansari and Pandis, 1998; Blanchard and Hidy, 2003).

Vehicle Emission Trends. Between 1990 and 2000, there was progress in controlling U.S. motor vehicle emissions, despite growth in the number of vehicles and the amount of driving. Reasons for the emission reductions include reformulated fuels, advances in engine design, and improvements to catalytic converters and other control technology.

For gasoline engines, VOC and CO emissions have been controlled more effectively than NO_x , though all of these pollutants have been reduced (Kean et al., 2002; Parrish et al., 2002). For diesel engines, particulate matter emissions were reduced, but there was little if any change in NO_x emission rates (Yanowitz et al., 2000). Also between 1990 and 2000, on-road use of diesel fuel grew at a rate that was 3 times faster than gasoline (Harley et al., 2005). Therefore the amplitude of the weekly cycle in NO_x emissions increased through the 1990s, as diesels became a more important source in both absolute and relative terms. The weekly NO_x cycle is especially large in California where a high degree of control has been achieved on stationary NO_x sources such as power plants. It is therefore of interest to look for weekly changes in particulate nitrate in relatively recent (i.e., 2000 and later) data sets when the amplitude of weekly variations in NO_x emissions is likely to be larger.

2. Methods

Concentrations of particle-phase pollutants vary on many time scales. Here we study diurnal, weekly, and seasonal patterns in measured concentrations of fine particle nitrate and BC. The sections that follow below describe four PM supersites where speciated $PM_{2.5}$ data were acquired, the measurement methods used at these sites, and time series analysis methods applied to the data as part of this research.

2.1 Field Measurement Sites

Fresno. The city of Fresno is situated near the center of California's San Joaquin Valley. The Valley encompasses nearly 64,000 km², and is bordered by the Coastal Mountains to the west, by the Sierra Nevada Range along the east, and by the Tehachapi Mountains to the south. The metropolitan area of Fresno, with approximately 500,000 inhabitants, is the largest population center within 150 km. Much of the surrounding area is farmland. A major interstate freeway passes along the western edge of the city.

Measurements are taken from the Fresno EPA Super-Site, which shares facilities with a California Air Resources Board monitoring station at 3425 First Street, in the city of Fresno. The station is 5.5 km north-northeast of the downtown commercial district, and is surrounded by commercial establishments, office buildings, churches, schools and single-family homes. Sampling inlets are located on the rooftop of a two-story office building, 10 m above ground level, and 30 m from the street. Measurements of nitrate and BC were taken from 9/1999-10/2000 and 12/1999-7/2002, respectively. Details are given by Watson et al. (2000) who led the measurement effort at this site.

Pittsburgh. The Pittsburgh metropolitan area, with two million inhabitants, is situated in between the Midwest, with its coal-fired electric power generation utilities and agricultural sources, the Eastern Seaboard, with its heavily populated urban centers. The city claims to be within 500 miles of one-half of the country's population.

Data used here are taken from the Pittsburgh Air Quality Study central monitoring site (Wittig et al., 2004a). This was located at Schenley Park, a 456 acre wooded park in the

city of Pittsburgh, near the campus of Carnegie Mellon University. The site is approximately 6 km from downtown and 500 m from the nearest heavily traveled street. Monitoring was conducted from a trailer designed expressly for the study. Inlets were positioned 2 m above the rooftop, or approximately 6 m above the ground. Measurements were made from July 2001 through August 2002.

St. Louis. The city of St. Louis, with a population of approximately 2.7 million, is situated along the Mississippi River. The largest local industry is the manufacture of military aircraft. Data are taken from the core monitoring site of the St. Louis - Midwest Supersite. This was located across the Mississippi River from St. Louis, in the town of East St. Louis, Illinois. The site is a receptor area for the urban area of St. Louis and numerous industrial sources. St. Louis' central business district is 3 km to the west of the site. Other significant point sources are a steel mill 10 km to the north, copper products and zinc processing plants 3 - 4 km SSW of the site, and a lead smelter 40 km to the SSW. Source apportionment analysis shows the influence of these sources, as well as that from gasoline vehicles, diesel trucks, and railroads (Lee et al., 2006).

The core monitoring site measurements were made from two trailers located immediately adjacent to the Illinois EPA compliance monitoring station at S. 13th Street and Tudor Avenue. Inlets were placed 2 m above the trailer roofs. The immediate neighborhood of the site is relatively low density, mixed use residential and light commercial. Monitoring was conducted from April 2001 through June 2003, with a subset of the measurements continuing until June 2005. Turner and coworkers at Washington University led these measurements efforts (Reid et al., 2005).

Claremont. As part of the Southern California Supersite, one year of monitoring was conducted in Claremont, California, a city of approximately 35,000 inhabitants located in the east portion of the Los Angeles Basin. Claremont has no major industrial sources in its immediate vicinity, but is routinely influenced by emissions from the Los Angeles area due to the predominant westerly winds. The sampling site was situated in a residential neighborhood, at the base of the San Gabriel Mountains along the northern

side of town. Measurements were made from the Supersite Aerosol Mobile Laboratory, over a period of one year beginning in September 2001, as described by Fine et al. (2004).

2.2 Measurement Methods

Nitrate. Particle-phase nitrate was measured using the integrated collection and vaporization (ICVC) method of Stolzenburg and Hering (2000). This is an automated, semi-continuous method whereby fine particles are collected by impaction onto a metal surface, and analyzed in place by flash vaporization. The approach is similar to the manual method that has been used for over twenty years to measure the size distribution of sulfate aerosols. The difference is that the particle collection and analysis have been combined into a single cell, allowing the system to be automated. The cycle time is 10 minutes.

At Fresno, a prototype ICVC system was operated from October 1999 through July 2000. In July 2000 the *Rupprecht and Pataschnick* model 8400N, a commercial instrument operating on the same principle, replaced the prototype. Data from this unit is used from July through November 2000. At the Pittsburgh and St. Louis sites, all data were collected using the *Rupprecht and Patashnick* model 8400N. At Claremont, a custom, 3stage cascaded ICVC system was used to provide continuous, automated nitrate in 3 size fractions (Stolzenburg et al., 2003).

The prototype ICVC system used at Fresno has a $PM_{2.5}$ cutpoint impactor to remove coarse particles, followed by an activated carbon denuder, humidifier, and the collection cell. The denuder is used to remove nitric acid and other vapor interferences. The humidifier is used to raise the sample flow humidity to above 65% RH in order to minimize particle rebound from the collection surface. In the collection cell, the humidified particles are deposited onto a bare, 0.025 mm thick stainless steel strip by a single-jet impactor operated at sonic flow. The aerosol sample line is contained within an aspirated sheath line, and the collection system is housed in a ventilated box so as to maintain the sample at near-ambient temperature. Analysis is done by flash-vaporization,

similar to that described by Yamamoto and Kosaka (1994). The particle deposit is heated by capacitor discharge in a nitrogen carrier gas, and the evolved nitrogen oxides are quantified using a *Thermo-Environmental* model 42C chemiluminescent analyzer equipped with a molybdenum catalyst to reduce the higher nitrogen oxides to NO. The flow system is configured such that there are no valves on the aerosol sampling line. The typical collection period is 8 minutes, and the time for analysis is about 90 seconds. The system automatically alternates between collection and analysis to provide on-line values for nitrate every ten minutes.

The commercial units (RP 8400N) employed at Pittsburgh and St. Louis, and for the last three months of the Fresno data set, utilize the same ICVC measurement approach. Particles are denuded, humidified, and collected by impaction as in the prototype unit. Differences are that a sharp-cut cyclone, rather than an impactor provides the precut. The collection is onto a nichrome, rather than a stainless steel strip, and the analysis is done using an API chemiluminscent NO_x monitor (*Advanced Pollution Instruments*). The commercial unit provides for automatic zero and span of the NO_x monitor, a feature not included in the prototype units.

The cascaded ICVC system used at Claremont is based on the prototype ICVC. Instead of a single cell, it has three cells cascaded in series to provide size-resolved nitrate concentrations (Stolzenburg et al., 2003). The three size fractions (0.07-0.45, 0.45-1.0, $1.0-2.5 \mu m$) target the condensation, droplet, and coarse modes of PM_{2.5}. As with the single-stage prototype ICVC described above, the aerosol sample flow passes through a 2.5 μm impactor precut and vapor denuder to remove coarse particles and interfering vapors. The aerosol sample stream then passes through a humidity conditioner, the 1 μm collection cell, the 0.45 μm collection stage, a second humidity conditioner, and the final, 0.07 μm cutpoint collection cell. The first humidity conditioner is designed to provide either drying or humidification as needed to adjust the sample relative humidity to $65\pm2\%$ RH. A target of 65% RH for this first conditioner was chosen to allow for sufficient humidification to prevent bounce, but not so much as to drastically increase particle size. The second humidity conditioner, placed immediately above the final (0.07 µm cutpoint) collection cell, is a simple humidifier designed to raise the relative humidity of the sample stream to above 90%, and thus to enhance the collection efficiency of this final stage. Each of the three collection cells utilizes a single jet impactor collector. The difference in cutpoints is determined by the diameter of the impaction jets, which are 0.99 mm, 0.61 mm, and 0.37 mm, respectively. The sample flow rate of 0.9 L/min is controlled by the final stage, which operates at sonic conditions. The aerosol deposits from each cell are analyzed sequentially, beginning with smallest cutpoint stage, using the procedure similar to that described previously for the single cell ICVC. The sample train, including the preimpactor, denuder, humidifiers, and the three collection-analysis cells are housed in an environmental enclosure that is ventilated with outdoor air by means of an exhaust blower.

Comparison of the continuous nitrate systems to integrated filter-based and impactor methods is given in Table 2.1. At Fresno, comparison is made to 24-hr integrated filter samples collected using the Desert Research Institute (DRI) sequential sampler, which employs a nitric acid denuder, quartz front filter and NaCl impregnated backup filter (Chow et al., 2005). Regression slopes are somewhat higher for the prototype sampler than for the commercial unit. Results are similar for Pittsburgh, which used 24-hr integrated measurements with a denuder and Teflon-nylon filter as reference (Wittig et al., 2004b). At St. Louis, comparison is made to a HEADS sampler, which also employs a sodium carbonate and citric acid denuders followed by Teflon and nylon filters in series. Here the RP8400N deviates from the filter measurements at the higher nitrate concentrations, an effect that is attributed to insufficient reduction of the evolved nitrogen oxides to NO (Reid et al., 2005). For a subset of the data, comparison is made to the onehour average nitrate concentrations obtained by the Particle in Liquid Sampler (PILS), (Weber et al., 2001), which collects particles by condensational growth followed by impaction, with on-line analysis by ion chromatography. For the one-hour comparison, the correlation is high, but the regression slope reflects the lower recovery at higher nitrate concentration seen with the filter measurements. At Claremont, nitrate concentrations from the cascaded ICVC are compared to a denuded filter sample, and with the MOUDI impactor (Fine et al., 2003). On average, the values from the cascaded

ICVC were somewhat lower than the filter measurements, but higher than the impactor. In terms of the analyses presented here, the high correlations indicate that day-to-day variability in nitrate concentrations at each site are well-characterized by the automated nitrate instrument, even though the mean nitrate concentrations may be lower than the filter data at some sites.

Black Carbon. BC data for Fresno and St. Louis were measured using an aethalometer (*Magee Scientific, Berkeley, CA*). As described by Hansen et al. (1984), this instrument measures the change in filter opacity with particle loading. This is done by comparison of the light transmittance at 880 nm between the particle deposit on a quartz filter tape to a clean portion of the same tape. It incorporates an automated system to advance the filter tape when the filter darkness passes a preset threshold, thus keeping the measurements within a linear response range. In urban atmospheres, BC is the dominant light absorbing species, and the aethalometer attributes all of the observed light absorption to BC.

Over the years there have been numerous comparisons of the aethalometer signal to EC or BC as determined by thermal analysis of integrated aerosol samples. Allen et al. (1999) present comparisons to integrated quartz filter samples analyzed by thermal-optical reflectance in Uniontown, PA. Babich et al. (2000) present a similar comparison across seven different US cities. These studies found correlation of the order of $R^2 \sim 0.95$, with slope varying from 0.6 to 0.9. Hansen and McMurry (1990) compared the aethalometer and MOUDI impactor, wherein EC was from the impactor was determined by thermal evolution from aluminum substrates. These studies found correlation of the order of the order of $R^2 \sim 0.95$, with slope varying from 0.6 to 1.0.

Table 2.2 shows the comparison to parallel filter measurements for the data used here. At Fresno, every sixth day sampling on quartz filters was done using the IMPROVE protocol for the thermal optical reflectance method of Chow et al. (1993). Observed concentrations varied from 0.2 to 10 μ g/m³ for 24-hr averaging periods. Regression of the aethalometer against the EC from the FRM sampler operated with a quartz filter,

gives a slope of 0.79 ± 0.03 and $R^2=0.94$, as reported by Watson and Chow (2002). The ratio of mean values is the same as the slope. At St. Louis, the dynamic range in BC concentrations is small, with values of 0.2 to 2 μ g/m³, and the correlation between the aethalometer and filter is correspondingly lower. The regression slope and the ratio of mean values for comparisons to filters analyzed by the IMPROVE protocol are somewhat lower (0.6) than observed at Fresno.

At St. Louis, comparison was made to EC concentrations determined by both the NIOSH and IMPROVE protocols. These protocols differ in the temperature ramp and manner in which the pyrolysis correction is done. As described by Chow et al. (2001; 2004), the methods agree on the value for total carbon concentration, but differ on the split between organic and elemental. At St. Louis, the aethalometer data correlated best with the filters analyzed by the IMPROVE protocol, with R^2 =0.8. On average, the aethalometer BC values are intermediate between the EC reported by the two filter methods.

Elemental Carbon. At the Pittsburgh site, time-resolved measurements for organic and EC were obtained with the Sunset Laboratories aerosol carbon analysis field instrument, an instrument based on the in-situ carbon analyzer of Turpin et al. (1990). With this instrument, aerosol is collected on a quartz filter for a period of 100 to 220 minutes, followed by immediate thermal analysis, as described by Lim and Turpin (2002) and Cabada et al. (2004). The analysis is essentially a two step process in which the filter is incrementally heated to 870°C in a pure helium atmosphere, rapidly cooled to 575°C, and then heated to 910°C in He mixed with 2% O₂. The amount of evolved carbon dioxide is determined by reduction to methane and flame ionization detection. The darkness of the filter is monitored throughout the analysis using a small laser beam to measure the light transmittance through the filter. The filter darkness is observed to first darken while being heated in the pure He atmosphere, and then lighten when heated in the pure He atmosphere, plus that which must be removed during the heating step with O₂ to return the filter to its original darkness. EC is defined as the difference between the total and

organic carbon. At Pittsburgh, all values were corrected for dynamic blanks generated by sampling with a Teflon filter upstream of the filter collectors.

Site	Methods Compared	Dates	Slope/Intercept	R ²	Notes
Fresno	Prototype vs Filter	12/99 – 4/00	0.90 / 0.4	0.97	а
	RP 8400N vs Filter	8/00 – 11/00	0.84/ -0.2	.90	а
Pittsburgh	RP 8400N vs Filter	7/01 – 3/02	0.83 / 0.2	0.84	b
St. Louis	RP 8400N vs Filter RP 8400N vs PILS	2/02 – 5/03 2/02 – 4/02	0.62 / 0.42 0.71 / 0.40	 0.89	c d
Claremont	C-ICVC vs Filter C-ICVC vs MOUDI	9/01 – 2/02 9/01 – 2/02	0.80 1.12	0.79 0.53	е е

Table 2.1	Comparison	of Automated	Nitrate to	o Collocated	Measurements
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a comparison to 24-hr denuded filter measurements, this work

b comparison to 24-hr denuded filter measurements, (Wittig et al., 2004a)

c comparison to 24-hr denuded filters from HEADS sampler, (Reid et al., 2005)

d comparison to hourly nitrate from particle in liquid sampler (PILS), (Reid et al., 2005)

e comparison of cascaded ICVC prototype system (C-ICVC) to 24-hr denuded filters from HEADS, and size resolved measurements from the micro-orifice impactor (MOUDI). Comparison is geometric mean of measurement ratio, (Fine et al., 2004)

Site	Dates	Filter Method	Slope/Intercept	R^2	Ratio of Means	Notes
Fresno	1/00 – 12/00	IMPROVE EC	0.79 / -0.02	0.94	0.79	а
St. Louis	01/03-05/03	IMPROVE EC	0.59 / -0.02	0.77	0.58	b
	01/03-05/03	NIOSH EC		0.61	1.15	b
	01/03-12/03	NIOSH EC			1.04	с
	01/04-12/04	NIOSH EC			1.26	С

a approximately every 6th-day sampling, N=50 data pairs, (Chow et al., 2004)

b for every-day sampling, N=141 data pairs, results from J. R. Turner, private communication

c for 1 in 6 day sampling, N=58 data pairs for 2003, N=53 for 2004, from J.R. Turner

2.3 Data Analysis

Variations in particulate matter concentrations were studied in both the time and frequency domains. In the time domain, we divided and analyzed the data by season: winter (Jan through Mar), spring (Apr through Jun), summer (Jul through Sep) and fall (Oct through Dec). The assessment of weekly cycles in the data considered both 24-h average values and diurnally varying concentration profiles at 1-h time resolution. Daily values were compared by ratio to a moving 7-day average; a pollutant with no weekly cycle would have ratios of ~1 on all days.

Spectral analysis techniques were used to study variance properties in the data as a function of frequency. A key step in this analysis is the calculation of the discrete Fourier transform, which we accomplished using the Fast Fourier Transform (FFT) algorithm included as part of MATLAB. This decomposes an input time series into a sum of sinusoids with different amplitudes, frequencies and phases.

As variance in the data was not stable across seasons, following Hies et al. (2000), a logarithmic transform was applied to the raw data prior to performing the Fourier analysis:

$$C_t' = \log_{10} C_t - \log_{10} C_t$$

 C_t is the measured concentration at time *t*; the term with an overbar indicates subtraction of the annual average of the log-transformed series, resulting in a zero mean for C'_t . For missing data, C_t was filled in by linear interpolation between the two closest recorded values. Longer data gaps present in the Fresno BC time series were filled with $C'_t = 0$.

The periodogram or power spectrum for each pollutant was constructed from the results of a discrete Fourier transform applied to C'_i :

$$X(\mathbf{v}_k) = \frac{1}{\sqrt{N}} \sum_{t=1}^{N} C_t' \exp\left(-2\pi i \mathbf{v}_k t\right)$$

where frequency $v_k = k/N$ for k=0,1,...,N-1. $X(v_k)$ is a complex number that provides both amplitude and phase information for the specified frequency. The periodogram plots spectral power $P(v_k)$ versus frequency, where

$$P(\boldsymbol{v}_k) = \left| X(\boldsymbol{v}_k) \right|^2$$

The periodogram does not include phase information, so it is necessary to perform time domain analyses to determine for example, on which days of the week concentrations are lowest, assuming a weekly cycle is present.

For nitrate at all sites as well as EC at Pittsburgh, we input N=364 (52×7) daily average values in the analysis, and were particularly interested in $v_{52} = 52/364 = 1/7 = 0.14 \text{ d}^{-1}$ which indicates the weekly cycle. For Fresno and St. Louis BC data, hourly values were input with N=8736 (24×364). In this case, the periodogram can be used to identify annual, weekly, diurnal, and other cycles in the data. Note that at least two data points are required within each cycle of the highest frequency signal being studied. It is therefore not possible to use spectral methods to study weekly cycles in most of the available historical record of filter-based particulate matter samples that typically include one 24-h average data point every 6th day. No periodograms were constructed for Claremont, as BC/EC concentrations were not measured at this site, and the particulate nitrate record at this site did not cover a full year.

3. Results for Black/Elemental Carbon

BC was measured continuously using aethalometers for a period of close to two years at both Fresno and St. Louis. Online thermal optical measurements of EC were made for a period of one year at Pittsburgh. BC/EC concentration time series are presented in Figure 3.1. BC concentrations at Fresno were the highest measured, with a peak 24-hour average of ~9 μ g/m³. St. Louis and Pittsburgh both had much lower average carbon concentrations, with maxima of ~3 μ g/m³.

Seasonal and Diurnal Patterns. Figure 3.2 shows diurnal profiles of BC/EC concentrations by site and season. At both St. Louis and Pittsburgh, slightly higher values are seen during summer months. At Fresno, BC concentrations were higher during fall and winter months. The highest average concentration in Fresno occurs during fall and winter months from 7 PM until about midnight. These patterns could be explained by unfavorable dispersion conditions and high woodstove/fireplace emissions during fall and winter evenings. During spring and summer, Fresno BC concentrations peak in the morning hours, from 6 to 9 AM. These morning peaks can also be seen in the cooler months, but the magnitude of the morning peaks is only ~half of the overnight peaks.

BC/EC concentrations at St. Louis and Pittsburgh peak during morning commute hours. At St. Louis, BC concentrations also peak in the evening, but at lower levels than the morning peaks. The evening peaks in St. Louis are unique as they are present through all seasons. At all sites, the timing of high levels of BC in the morning varies slightly with the season; warmer months show earlier morning BC peaks consistent with earlier sunrise times.



Figure 3.1: Time series of fine black/elemental carbon concentrations (daily average values are shown here). Note different scales for each site.





Figure 3.2: Diurnal variation in black/elemental carbon concentrations by season. Note different scales for each site.



Weekly Cycles. Figure 3.3 presents BC/EC concentrations by day of week, normalized to a moving 7-day average. All three sites show weekend days that have ratios of less than one, and Tuesdays through Thursdays with ratios greater than one. St. Louis and Fresno have ratios of ~75% on Sunday, and both values are significantly less than one. In other words, Sunday BC concentrations at these two sites are ~25% less than weekly average concentrations. St. Louis also shows lower Saturday BC concentrations, with a reduction of 13±5% relative to the weekly average.

Figure 3.4 plots diurnal variations in weekday/weekend BC/EC concentrations by season. Weekly cycles are clearly evident across all sites, seasons, and most times of day. The exception is Fresno, where fall and winter weekend averages are higher at early morning hours (midnight to 6 AM) than on weekdays. This pattern points to wood-burning rather than vehicle emissions as the important source. Wood-burning was found to be an important EC source in two California studies (Chow et al., 1995; Schauer and Cass, 2000). Source apportionment using carbon isotope analysis of PM samples from Zurich, Switzerland showed significant wintertime contributions to EC from biomass burning (Szidat et al., 2006).

Variations in BC concentrations at Fresno and St. Louis by day of week are presented in Figure 3.5. St. Louis shows Sunday BC decreases from the weekly average across all seasons ranging from $-38\pm8\%$ to $-17\pm13\%$. Fresno shows Sunday decreases across all seasons ranging from $-33\pm9\%$ to $-13\pm16\%$. All seasons except winter have ratios significantly less than one. This analysis indicates the weekly cycle in BC is not as strong during winter in Fresno compared with the rest of the year.



Figure 3.3: Average (±95% CI) black/elemental carbon concentrations by day of week, normalized to moving seven-day average.



Figure 3.4: Diurnal variation in black/elemental carbon concentrations by season. Solid lines averaged over weekdays, dashed lines averaged over weekend days. Note different scales for each site.



Figure 3.5: Average (±95% CI) black carbon concentrations by day of week and season, normalized to moving seven-day average.

Frequency Domain Analysis. Figure 3.6 shows periodograms for BC or EC time series at each site. For Fresno, one relatively complete year of data was available. For St. Louis, two complete years of data were available to create two periodograms, which were subsequently averaged to reduce the effects of random (white) noise in the data. The Pittsburgh EC time series had lower time resolution than either St. Louis or Fresno, so only daily average values were used to construct the periodogram for that site.

At both Fresno and St. Louis, the four strongest peaks in the periodograms are at periods (inverse of frequency) of a year, week, day, and ½ day. Smaller peaks can be seen at ½ a week, 0.33 day, 0.25 day, and even 0.2 day for Fresno. Harmonics of the daily and weekly cycles are present because the signals for their time periods are not perfectly shaped sine waves. At all sites, the annual cycle is the largest source of variance in the data. At Fresno and St. Louis, the diurnal cycle combined with its first harmonic, followed by the weekly cycle combined with its first harmonic are the next two most important sources of variance in BC. At Fresno the annual cycle accounts for 35% of total variance, while diurnal and weekly cycles account for 6 and 2%, respectively. At St. Louis, however, the annual cycle accounts for only 9%, while diurnal and weekly cycles account for 4 and 3%, respectively. This shows the subsidiary importance of weekly cycles relative to annual and diurnal cycles in affecting ambient BC concentrations.

In the periodogram for EC at Pittsburgh (see Figure 3.6), a peak at the period of 7 days can be seen; however, many other, seemingly randomly distributed peaks of similar magnitude can be seen nearby. The EC data from Pittsburgh are not as complete as BC data from Fresno and St. Louis; data gaps add noise to the periodogram. Similarly, in the preceding time domain analysis, Pittsburgh had much wider confidence intervals than other sites in Figure 3.3. Overall, the evidence from the time domain analyses for Pittsburgh points toward a likely weekly cycle, however this is not clearly evident in the periodogram.



Figure 3.6: Spectral density as estimated by periodograms of daily average black/elemental carbon.
4. Results for Fine Particle Nitrate

Figure 4.1 shows daily average nitrate levels measured at all four sites. All sites have lower nitrate concentrations during summer months. Much higher concentrations of particulate nitrate are observed at the California sites compared to both St. Louis and Pittsburgh. On average, Pittsburgh shows the lowest levels of nitrate. The clearest seasonal changes can be seen at Fresno, where very high nitrate concentrations are observed in December and January. St. Louis and Pittsburgh also show similar periods of increased winter concentrations relative to the warmer seasons. In Claremont, the summer months show slightly lower concentrations than the rest of the year, but no large differences are seen between fall, winter, and spring in average daily nitrate concentrations. The seasonality of nitrate at Claremont differs from the other sites.

Diurnal Patterns. Diurnal variations in nitrate are shown by season in Figure 4.2. The peak nitrate concentration is often observed between 9 AM and noon. At all sites, spring and summer months see peak nitrate earlier in the day compared to the fall and winter months. This may be due to a combination of factors including the temperature dependence of ammonium nitrate dissociation, and the onset of convective mixing in the boundary layer due to earlier summer.

At Claremont, diurnal nitrate profiles do not vary much by season. During fall and winter, nitrate levels remained high through the late morning and early afternoon, while spring and summer days showed a clear peak around 10 AM, with a steady decline through the afternoon as temperatures increase. At all sites except Claremont, increases in nitrate concentrations were observed after 8 PM. At Fresno, nitrate levels increase overnight for October – December, but remain relatively constant at night at other times of year.



Figure 4.1: Time series plots of fine particulate nitrate concentrations (daily average values). Note different scales for each site.



Figure 4.2: Diurnal variation in fine particle nitrate concentrations by season. April – June values not shown for Fresno due to missing data

Weekly Cycles. Day of week variations in nitrate are examined using both average daily values and diurnal patterns. Figure 4.3 presents nitrate concentrations by day of week, normalized to a moving 7-day average. With the exception of Pittsburgh, all sites show significantly lower nitrate concentrations on Mondays relative to the rest of the week. Monday nitrate decreases relative to the weekly average were $29\pm23\%$, $23\pm12\%$, and $16\pm9\%$ at Claremont, Fresno and St. Louis, respectively. Fresno and St. Louis show significantly lower values on Sundays as well, with decreases at $14\pm12\%$, and $21\pm9\%$. A trend seen in these plots is a weekly minimum on Mondays followed by increasing normalized nitrate concentrations through the rest of the week. Pittsburgh does not follow the pattern of the other three sites, and is investigated further in Chapter 5.

Comparing diurnal patterns by day of week (Figure 4.4), lower nitrate levels are seen at all hours on Sunday and Monday compared to Tuesday through Saturday. Pittsburgh, as discussed above, is the exception with higher particulate nitrate levels on Sundays and Mondays during the warmer months. At the other sites, the weekly cycle is most apparent during peak nitrate times: average concentrations on Tuesday through Saturday peak higher than on Sunday and Monday.

Across three of the four sites, lower average nitrate concentrations are observed on Sundays and Mondays. NO_x emissions, a precursor to nitrate, decrease significantly on both Saturdays and Sundays due to less diesel truck traffic (Harley et al., 2005). At Fresno, Watson et al. (2000) reported NO_y concentrations. Analysis of the data indicates decreases of $21\pm8\%$ (mean $\pm95\%$ CI) on Sundays relative to the 7-day moving average. Fujita et al. (2003) report Sunday morning (7-8 AM) decreases in NO_x of ~40% relative to weekdays in Southern California. At Pittsburgh, 24-average NO_x concentrations decreased by $16\pm11\%$ (mean $\pm95\%$ CI) on Sundays. We do not have data on NO_x trends at St. Louis. At Fresno, Claremont and Pittsburgh, NO_x or NO_y concentrations return to weekday levels by Monday, the same day nitrate concentrations reach a weekly minimum. Comparing average weekend to weekday nitrate concentrations would overlook Monday minima; a more detailed analysis of all seven days is required to identify weekly signals in nitrate. If the weekly decrease in particulate nitrate is a result

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Figure 4.3: Average (± 95% CI) fine particle nitrate concentrations by day of week, normalized to moving seven-day average.

Figure 4.4: Diurnal variation in fine particle nitrate concentrations. Solid lines: Tuesday through Saturday. Dashed lines: Sunday and Monday. Red color denotes warmer months of April – September; blue denotes cooler months.



of this decrease in precursors, there appears to be a delay of at least one day for the decrease in precursor emissions to affect nitrate concentrations.

Frequency Domain Analysis. Spectral analysis was used as another approach to study weekly signals in particulate nitrate. Figure 4.5 shows periodograms at each site. If a consistent weekly signal is present, then a peak in the power spectrum would be expected at a frequency of $f = 1/7 = 0.14 d^{-1}$. Small peaks at 0.14 d⁻¹ can be seen in Figure 4.5 for Fresno, Claremont, and St. Louis. The spectral analysis shows other nearby signals, for example, at periods of 5.8, 8.7, and 10.7 days at Fresno. Another important peak is the first harmonic of the weekly cycle, at $f = 1/3.5 = 0.29 d^{-1}$, which is clearly isolated and larger than the surrounding frequencies at Fresno, but not apparent at any of the other sites. It would be appropriate to combine the power of the 3.5-day and 7-day cycles to compare it to the other signals. For Fresno, this makes the weekly cycle substantially more prominent. In general, however, we find that spectral analysis is not identifying clear weekly signals in fine particle nitrate.

The lack of a 7-day cycle in the frequency domain is consistent with a more detailed examination of weekly cycles at each site. Figure 4.6 shows day of the week patterns in nitrate, separated by season. At each site, the day with lowest concentration varies depending on the season. For Fresno, St. Louis, and Claremont, Monday is the lowest nitrate day in winter months. However, during summer months, Sunday and Tuesday are the lowest nitrate days at Fresno and Claremont, respectively. This suggests a shift in the response to lower weekend NO_x that depends on season. Seasonal changes could affect precursor emissions, kinetics of HNO₃ formation, transport times from upwind source regions, and prevailing wind direction/flow patterns. When aggregated over a whole year in the time domain, this subtle shift in the weekly cycle is less apparent. However, in the frequency domain, phase shifts in the weekly cycle by season do not average out.



Figure 4.5: Spectral density as estimated by periodograms of daily average fine particulate nitrate.



Figure 4.6: Average (± 95% CI) fine particle nitrate by day of week and season, normalized to moving seven-day average.







Size Distribution. At Claremont, nitrate measurements were resolved into three size ranges: 0.07-0.45, 0.45-1, and 1-2.5 μ m. No online size-resolved nitrate data are available at the other sites. In Figures 4.7 and 4.8, contributions to total nitrate are shown by size range. Each size range is responsible for a varying fraction of total nitrate mass depending on the day. The distribution of nitrate mass as a function of size appears to vary more by season than it varies within a diurnal cycle for any specific season. The three size ranges track each other closely, with peaks in all size ranges occurring at the same time. Going from winter (January – March) to summer (July – September), the relative importance of the smallest size fraction decreases as a contributor to total PM_{2.5} nitrate.

Table 4.1 compares contributions by size range to total $PM_{2.5}$ nitrate. The fraction of total nitrate in the smallest size range (0.07-0.45 µm) does not vary much by time of day. During summer, the smallest and largest size ranges each hold ~20% of total $PM_{2.5}$ nitrate. In winter, the largest size range comprises ~20% of total nitrate, whereas, the smallest size range doubles in relative importance, accounting for ~40% of the total.

Size Range (µm):		0.07-0.45	0.45-1	1-2.5
Fall	Average:	28%	43%	29%
	Range:	24-33%	40-44%	27-32%
Winter	Average:	37%	42%	21%
	Range:	34-39%	38-45%	18-24%
Spring	Average:	20%	48%	32%
	Range:	19-22%	41-51%	27-38%
Summer	Average:	18%	57%	25%
	Range:	13-25%	48-62%	20-33%

Table 4.1: Fraction of fine particulate nitrate mass by size range.

Prevailing winds at Claremont, Figure 4.9, vary by season. Northwesterly flow dominates during the fall and winter; southwesterly winds (sea breeze effect) dominate in the warmer months. Compared with fall and winter, spring and summer see a higher prevalence of faster (2-3 m/s) wind velocities and a greater proportion of calm hours. Winter wind speeds are consistently slower and less variable in direction.

At Claremont, the times when >60% of total $PM_{2.5}$ nitrate mass was found in the smallest size range were correlated with wind direction, relative humidity and low total nitrate concentrations. Separating these two meteorological effects on nitrate formation is not simple as relative humidity and wind direction are correlated to each other and to total nitrate concentrations.

A wind rose for hours when >60% of total $PM_{2.5}$ nitrate were found in the smallest size range (Figure 4.10) shows a similar pattern to the fall/winter wind rose but with a greater percentage of hours with wind coming from the north and almost no southwesterly flow. Low relative humidity conditions are also correlated with a high fraction of nitrate mass in the smallest size range. Figure 4.10 displays the time distribution of relative humidity. Low (<40%) relative humidity conditions accounted for 21% of the total time during which nitrate measurements were made. However, low relative humidity was observed for more than half of all hours when >60% of total $PM_{2.5}$ nitrate was found in the smallest size range.

The low humidity conditions are consistent with condensation mode formation mechanisms for nitrate (John et al., 1990). The condensation mode results from gas phase reaction products and leads to nitrate formation at the smallest size range measured here. Droplet mode formation, with a size mode at 0.7 μ m, involves fog or aqueous aerosol processes that add nitrate to preexisting wet aerosol. Condensation mode mechanisms were favored at Claremont under dry, northerly flow conditions.



Figure 4.7: Daily average fine particle nitrate concentrations at Claremont, resolved into three size fractions.





Figure 4.9: Distributions of wind speed and direction at Claremont by season.





Figure 4.10: Winds and relative humidity during hours when the 0.07-0.45 µm size range accounted for >60% of total fine particle nitrate at Claremont.



5. Pollutant Interactions

5.1 Correlation between BC/EC and Nitrate

Ambient BC/EC and nitrate concentrations are expected to be correlated as stagnant conditions can lead to higher levels of both pollutants, and because diesel vehicles are an important source of both BC/EC and NO_x . The correlation between pollutants depends on both site and season. At St. Louis and Pittsburgh, BC/EC concentrations peaked during the warmer months, whereas peak nitrate concentrations were observed during winter. At Fresno, both nitrate and BC concentrations were higher during fall and winter.

Figure 5.1 displays scatter-plots of daily averaged concentrations of BC/EC and nitrate by site and season. Seasonal dependence is clear in these plots, with low nitrate concentrations during summer at all sites. The correlation between pollutants depends on site and season as well. Table 5.1 displays correlation coefficients calculated at Fresno, St. Louis, and Pittsburgh. For each city, lag 0 is the correlation between BC/EC and nitrate concentrations measured on the same day and lag 1 is the correlation between one day's average BC/EC and nitrate concentration on the next day. Lag 0 describes the usefulness of either pollutant in capturing variability in measured concentrations of the other pollutant on the same day. Lag 1 describes the usefulness of BC/EC in predicting next day nitrate.

Table 5.1: BC/EC and nitrate cross-correlation coefficient for 24-hour average concentrations.

	Fresno		St. Louis		Pittsburgh	
	Lag 0	Lag 1	Lag 0	Lag 1	Lag 0	Lag 1
Winter	0.89	0.89	0.33	0.22	0.24	0.02
Spring	0.47	0.25	0.16	0.06	0.03	-0.04
Summer	0.77	0.49	0.66	0.59	0.69	0.27
Fall	0.63	0.75	0.13	0.03	0.38	0.00

Fresno has the most highly correlated pollutant time series, especially in winter. During winter at this site, the correlation between BC and either same-day or next-day nitrate is equally strong. In fact BC is a slightly better indicator of next-day nitrate, than nitrate itself is. Summer and fall at Fresno also show higher correlation relative to other sites. At



Figure 5.1: Scatter plots of daily average nitrate vs. BC/EC concentrations.

St. Louis and Pittsburgh, BC/EC and nitrate are well correlated (correlation coefficient >0.50) only during summer months.

Concentrations of both BC and nitrate are higher at Fresno compared with St. Louis and Pittsburgh. The correlation between pollutants is controlled by the larger values. Since there are only a few days at Fresno higher than 5 and 20 μ g/m³ for BC and nitrate, respectively, these few points may unduly influence the correlation. When days with nitrate concentrations above 20 μ g/m³ are excluded, the correlation coefficient during winter at Fresno decreases to 0.61. This correlation is still considerably stronger than the other sites.

Correlations coefficients >0.50 between BC/EC and nitrate are found during parts of the year at all sites. However, the relationship varies by time of year even at Fresno, which is the only site with correlation coefficients >0.50 in more than one season. Therefore, changes in BC do not provide a reliable basis for predicting changes in nitrate throughout the year.

5.2 Nitrate Partitioning and Interactions with Ammonia and Sulfate

Supplemental Measurements at Pittsburgh Supersite. Particle phase nitrate and sulfate plus related pollutants such as NO_x , SO_2 and total nitrate (the sum of gaseous HNO₃ and particle nitrate) and total ammonia (the sum of gaseous NH_3 and NH_4^+ associated with particles) were measured during the Pittsburgh air quality study. These measurements provide a means to answer questions about pollutant interactions among sulfate, nitrate and ammonia, and to study the NO_x /nitrate system at Pittsburgh.

Measurements of total nitrate and ammonia were made using a steam sampler with an ion chromatograph (IC) combination (Khlystov et al., 1995; Slanina et al., 2001). This method uses steam injection to supersaturate the sample, which is collected in a cyclone and analyzed for water-soluble ions by the IC. In this method, gases such as NH_3 and HNO_3 and nitrate and sulfate particles grow to diameters greater than 1 μ m, and are then collected by the cyclone. The time resolution for this instrument varies between 1 to 4

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hours. Measurements in $\mu g/m^3$ were converted to mixing ratios (ppb) using surface temperature measurements taken on site at Pittsburgh.

Measurements of NO_x concentrations were made using a commercial NO_x analyzer, which employs chemiluminescence to measure NO and total NO_x . These measurements are described by Wittig et al., (2004a). The measurements were reported as ten minute averages.

Particulate sulfate concentrations were measured using a flash vaporization cell coupled with a pulsed fluorescence SO₂ analyzer. This instrument follows a similar operating principle to the nitrate instrument of Hering and Stolzenburg; the sulfate instrument is described by Wittig et al. (2004b). Sulfate measurements were reported over 10 minute averaging times. Measurements in μ g/m³ were converted to mixing ratios in ppb units.

Data Analysis and Discussion. Pittsburgh is the only site in this study that did not show a weekly cycle in nitrate. This finding is further studied here by examining patterns of particle nitrate precursors, as well as pollutants such as sulfate that may affect ammonia availability.

 NO_x measured at Pittsburgh shows a weekly pattern throughout the year. As shown in Figure 5.2, NO_x concentrations are lower on Friday through Sunday compared to the rest of the week. The full year data set has more weeks of data and thus narrower 95% confidence intervals. In each season, Friday through Sunday have lower NO_x concentrations relative to the rest of the week; however, only fall and spring have significantly lower values. Figure 5.3 shows variations in NO_x by season and time of day. At almost all times of day, NO_x values are lower on weekends compared to weekdays. The largest weekday/weekend difference in NO_x concentrations is seen from 7-10 AM partially due to the absence of the morning commuter peak on weekends.

Weekend NO_x reductions at Pittsburgh are not clearly reflected in the observed particle phase nitrate concentrations. Examining the sum of gas plus particle nitrate

Figure 5.2: Average (\pm 95% CI) NO_x concentrations at Pittsburgh by day of week, normalized to moving seven-day average. *Shown both by season and over the full span of data (1 year).*



Figure 5.3: Diurnal variations in NO_x by season (fall/winter vs. spring/summer) and time of day.





Figure 5.4: Average (±95% CI) sum of gas and particle nitrate concentrations at Pittsburgh by day of week, normalized to moving seven-day average. Shown both by season and over the full span of data (1 year).

concentrations removes effects of gas-particle partitioning that might obscure a weekly cycle in the nitrate data. The sum of gas and particle phase nitrate concentrations is shown by day of week in Figure 5.4. Over the full annual cycle, Sunday has the lowest concentrations compared to the rest of the week; however, none of the days show statistically significant differences from each other or from the moving weekly average. Dividing the analysis by season creates even wider confidence intervals; no weekly pattern is observed.

Diurnal patterns in the sum of gas plus particle phase nitrate at Pittsburgh by season and day of week are shown in Figure 5.5. While the sum appears to show some hints of a weekly cycle, nitrate in the particle phase alone does not follow this pattern during spring and summer at Pittsburgh, as shown previously in Figure 4.4. This result is examined in more detail below by considering the availability of ammonia and nitric acid.

The diurnal variation in both particle nitrate and the sum of particle and gaseous nitrate is shown in Figure 5.6. Strong seasonal differences can be seen in the fraction of total nitrate present in the particle phase. Summertime afternoons have the highest fraction of gas-phase nitric acid. Almost all the nitrate is in the particle phase at night; this is true for all seasons. From 11 AM to 9 PM, the ratio of gas to particle nitrate is at its highest. This is a time when a weekly cycle is apparent in the sum of gas and particle nitrate (see Figure 5.5). A small change in nitric acid concentrations may not be transferred to the particle phase, as there are high levels of nitric acid compared with ammonia.

During spring, summer, and fall, gas-phase ammonia is at a minimum at midday. Figure 5.7 displays diurnal variation by season of HNO₃ and NH₃ mixing ratios. HNO₃ was calculated as the difference between measured gas plus particle nitrate, and particle nitrate measured separately. Gaseous NH₃ was estimated by subtracting (in molar units) the particle nitrate and twice the sulfate from measured ammonia, both gas and ammonium ion. This assumes two moles of ammonium ion per mole of sulfate. For instances where negative values were encountered, this assumption was invalid and the gas-phase ammonia concentration was set to zero. During all seasons but winter,







Figure 5.6: Diurnal variation in gas and particle nitrate at Pittsburgh by season.





ammonia concentrations are low during daytime hours. This implies that small changes in nitric acid may be unimportant for nitrate particle concentrations compared with changes in ammonia, which appear to be the controlling factor in this case.

Unlike nitrate particles, sulfate particle concentrations are not strongly sensitive to temperature. Thus, sulfate can act as a sink for ammonia, making it unavailable for particle nitrate formation. At Pittsburgh, measured sulfate concentrations show a weekly cycle during spring and summer months (see Figure 5.8). Saturday has lower sulfate concentrations than other days of the week. This pattern raises the possibility of interactive effects with particle nitrate. Lower sulfate could lead to increased ammonia availability and increased particle nitrate formation during the spring and summer.

Figure 5.9 shows diurnal variations of ammonium gas plus particle, sulfate particle, nitrate particle, and predicted ammonium ion concentrations. The ammonium ion prediction makes the assumption that for each mole of nitrate and sulfate measured in the particle phase, there are one and two moles of associated ammonia respectively. During spring and summer afternoons, predicted NH_4^+ levels are higher than the measured sum of gas and particle ammonia. The assumption of 2 moles of NH_4^+ for each mole of sulfate particle cannot hold during these high-sulfate periods. These conditions coincide with measurements of particle nitrate levels close to zero. Reduced levels of particle sulfate on Fridays and Saturdays in the summer do not free more ammonia for interaction with nitrate. Instead, the molar ratio of ammonium to sulfate increases closer to 2, as more of the sulfate is fully neutralized. This can be seen in Figure 5.10, from Sunday to Thursday during summer, the predicted NH_4^+ is higher than measured gas and particle ammonia, while on Friday and Saturday predicted ammonia ion and measured gas and particle ammonia, while on Friday and Saturday predicted ammonia ion and measured gas and particle ammonia, while on Friday and Saturday predicted ammonia ion and measured gas and particle ammonia, while on Friday and Saturday predicted ammonia ion and measured gas and particle ammonia, while on Friday and Saturday predicted ammonia ion and measured gas and particle ammonia, there is no weekly cycle in sulfate during these seasons.

Figure 5.11 shows diurnal variations of gas plus particle ammonium, particle nitrate, and "free" NH₃. Free NH₃ is defined as the difference between the measured sum of $NH_3(g)+NH_4^+$ and two times the measured particulate sulfate. Negative estimates of free

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Figure 5.9: Diurnal variations in nitrate, sulfate, the measured sum of NH_4^+ and NH_3 , and predicted NH_4^+ ($2 \times sulfate + nitrate$) at Pittsburgh.



Figure 5.10: Diurnal variation in predicted NH_4^+ and the measured sum of NH_3 and NH_4^+ at Pittsburgh separated by days of the week.

Figure 5.11: Diurnal variation in gas and particle nitrate, and 'free' ammonia not associated with sulfate ($NH_3 + NH_4^+ - 2 \times sulfate$) at Pittsburgh.



NH₃ were set to zero. Free NH₃ represents all ammonia both in the gas phase and associated with particulate nitrate. Free NH₃ can be limited by low NH₃ emissions and by high sulfate concentrations. Free ammonia provides an upper bound on nitrate particle formation, assuming all sulfate is associated with 2 ammonium ions. During spring and summer, particle nitrate concentrations follow free NH₃ levels closely. Free NH₃ and particle nitrate have similar diurnal profiles, and nitrate particle concentration seems to follow the variation of free NH₃, falling at the same time, and rising after free ammonia levels have grown substantially. During winter, ammonia is not limited and estimated free NH₃ is consistently higher than particulate nitrate. During fall, the assumption of 2 moles ammonium for each mole sulfate fails, as free NH₃ is found to be less than measured particle nitrate for much of the day. In this case, possibly due to the cold temperatures and correspondingly low ammonium nitrate dissociation constant, nitrate particles compete more effectively for ammonium ion with sulfate. During the spring and summer, however, particle nitrate formation at Pittsburgh is clearly limited by ammonia availability.

The weekly cycle in NO_x is not strong enough to create statistically significant weekly cycles in the sum of gas and particle nitrate at Pittsburgh. Even if significant weekly cycles were seen in HNO₃, it is unlikely they would be transferred to particle nitrate because ammonia availability appears to limit nitrate particle formation at this site. The potential for sulfate to affect ammonia availability is high. Weekend reductions in sulfate concentration could lead to increased ammonia availability and thus increase nitrate particle concentrations. In practice this was not observed as days with lower sulfate concentrations often had proportionally more ammonia per mole sulfate in the particle phase.

6. Conclusions & Recommendations

Weekly cycles in BC were expected and observed at St. Louis and Fresno. High nighttime concentrations of BC were observed during fall and winter at Fresno. These nighttime increases were linked to smaller weekly cycles during winter. A likely nighttime source of BC is wood burning, a winter season source that could increase on weekends. Higher weekend BC concentrations were seen at Fresno during winter months between the hours of midnight and 6 AM. These overnight peaks were followed by low daytime concentrations on weekends. Further research to quantify the contribution of woodstove/fireplace emissions to $PM_{2.5}$ and BC at Fresno is recommended.

Past investigations have found little or no evidence of weekly cycles in fine particulate nitrate. Our analysis indicates significant weekly cycles in nitrate at 3 of 4 sites examined. At these sites, Mondays have the lowest nitrate concentrations averaged over a full annual cycle. A delay between decreased weekend precursor emissions and decreased nitrate formation is probably due to the photochemical transformation process. Simply comparing average weekend to average weekday concentrations would overlook Monday minima. More detailed analysis of all seven days is required to identify weekly signals in this secondary pollutant.

Weekly Cycles	BC or EC	Nitrate		
	Sunday/Weekly Average	Monday/Weekly Average		
Fresno	0.78 ± 0.06	0.77±0.12		
Claremont	N/A	0.71±0.23		
St. Louis	0.75±0.05%	0.84±0.09		
Pittsburgh	0.95 ± 0.20	1.01±0.26		

Table 6.1: Annual average ratio (±95% CI) of Sunday BC or EC concentrations and Monday nitrate to 7-day moving average.

Pittsburgh was the only site that did not show evidence of a weekly cycle in nitrate. Investigations of nitrate precursors at Pittsburgh show that weekend NO_x reductions were not large enough to create statistically significant reductions in nitrate. Furthermore, particle nitrate formation at Pittsburgh was limited by ammonia availability and not nitric acid availability during spring, summer, and fall. Nitrate concentrations were sensitive to ammonia availability and relatively insensitive to the effects of the weekly NO_x cycle. Particulate sulfate concentrations were also measured at this site and decreased on weekends. Sulfate reductions and the associated increased ammonia availability may lead to higher particle nitrate concentrations. But this effect was not seen in this case, as sulfate reductions led to more complete neutralization of sulfuric acid rather than increased gas-phase ammonia.

At Claremont, the 0.45-1 μ m size range was the dominant mode for nitrate through all seasons, accounting for 40-60% of the total depending on season. During the winter months, the smallest range (0.07-0.45 μ m) accounted for ~37% of total fine particle nitrate. Instances during which the smallest size range accounted for a majority of total nitrate were correlated with dry northerly flow.

Modeling (specifically conducting sensitivity analysis) would be a useful tool to study factors that influence particle nitrate formation and gas-particle partitioning. Further research, including modeling of secondary fine particle formation for multiple seasons, is recommended to define what controls particle nitrate concentration and the transformation process from precursor emissions to secondary particles.

7. References

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