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Weekly cycles in fine particulate nitrate

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Abstract

Atmospheric responses to changes in emissions are a complex but central issue in control strategy design for pollutants such as ozone and particulate matter. Here, we investigate fine particle nitrate response to weekly cycles in emissions, which includes a large decrease in diesel NO_x emissions among other changes. Nitrate concentrations were measured at 10-min time resolution for a year or longer at four US urban sites: Fresno and Claremont in California, St. Louis, and Pittsburgh. Weekly minima in nitrate concentrations were observed at Fresno, Claremont, and St. Louis, with mean reductions of 21–29% below weekly average values on Sundays or Mondays. The day of week with lowest nitrate varied with site and season. No significant day-of-week variations in nitrate were observed at Pittsburgh. Analysis of ammonium and sulfate measurements at Pittsburgh indicates that weekend sulfate reductions observed at this site during spring/summer months do not increase ammonia availability, but rather lead to more complete neutralization of S(VI). Fine particle nitrate measurements at Claremont were resolved into three size ranges (0.07–0.45, 0.45–1.0, and 1.0–2.5 μm); similar weekly reductions were seen for each size range.

Keywords: Weekend effect; Nitrogen oxides; EPA PM supersites

1. Introduction

Airborne fine particulate matter or $PM_{2.5}$ (particles with aerodynamic diameter $D_P < 2.5\,\mu m$) is a widespread air pollution problem. In the US, annual average $PM_{2.5}$ levels that exceed the national air quality standard of $15\,\mu g\,m^{-3}$ are observed in California and in numerous states east of the Mississippi River (Blanchard, 2004). 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 from key constituents such as carbon, ammonium, nitrate, and sulfate. In the eastern US, 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; Malm et al., 2004).

Particulate nitrate is formed in the atmosphere through gas-to-particle conversion processes that start with nitrogen oxides (i.e., NO and NO_2), and

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proceed via formation of nitric acid as an intermediate step. An important daytime pathway involves reaction of NO_2 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 gas-phase oxidation of SO_2 and NO_x, and a droplet mode at 0.6–0.7 μm that implies involvement of condensed phase processes.

In contrast to nitrate which partitions between gas and condensed phases, sulfate formed as a result of SO_2 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, $(NH_4)_2SO_4$. If ammonia is scarce, sulfate will remain in more acidic forms such as ammonium bisulfate (NH_4HSO_4) or H_2SO_4. 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).

The main objective of this research is to analyze time series of measured particle-phase nitrate concentrations, to determine if weekly cycles are present in the data. Nitrate can be linked in part to diesel engine NO_x emissions, which are known to decrease substantially on weekends (Harley et al., 2005). In reviewing ambient nitrate concentration data, different conclusions have been reached about whether significant weekly cycles in particulate nitrate are observed: Blanchard and Tanenbaum (2003) and Harley et al. (2005) found no weekday–weekend nitrate differences, whereas Motallebi et al. (2003) report small weekend decreases (6% average reduction across the sites they examined).

Previous studies of weekly cycles in PM nitrate concentrations have been constrained by sparse data (until recently PM samples were typically collected only once every 6 days; furthermore only a subset of filter samples are analyzed for chemical composition). The sparse record is due in part to reliance on labor-intensive filter-based PM measurement methods. In addition to sparse data, another concern is that standard sampling methods suffer from negative artifacts due to nitrate volatization (Hering and Cass, 1999). In recent years, a variety of online measurement methods for nitrate and other PM constituents have been developed and applied (Jayne et al., 2000; Stolzenburg and Hering, 2000; Slanina et al., 2001; Weber et al., 2001; Ullah et al., 2006). Here, we use recent yearlong records of nitrate concentrations measured at four US urban sites to study atmospheric responses to weekly cycles in anthropogenic emissions. Other investigators have reported on $PM_{2.5}$ composition and dynamics at individual sites from the EPA Supersites program (Sioutas et al., 2004). In contrast here, our objective is to study patterns in nitrate response to lower weekend NO_x for several of these special study sites.

2. Methods

2.1. Field measurement sites

2.1.1. Fresno

The city of Fresno is situated in California's San Joaquin Valley. A major highway runs by the city, though much of the surrounding area is farmland. Measurements were made at the Fresno air quality monitoring station at 3425 First Street. The station is 5.5 km NNE of downtown and is 10 m above ground on a two-story office building. Details are given by Watson et al. (2000) who led the measurement effort at this site.

2.1.2. Pittsburgh

Data used here are from the Pittsburgh Air Quality Study central monitoring site (Wittig et al., 2004a, b). This site was located at Schenley Park, a 456 acres (185 ha) wooded park near Carnegie Mellon University. The site is ~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 ~6 m above the ground. Measurements were made from July 2001 through August 2002.

2.1.3. St. Louis

Data used here are from the St. Louis-Midwest Supersite (Lee et al., 2006), located across the