Appendix E

Recommended Conversion Factors for Secondary Formation of PM-Nitrate from NO_x Emissions

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Air Resources Board Research Division
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Chemical Formation of Ammonium Nitrate from NO_X Emissions

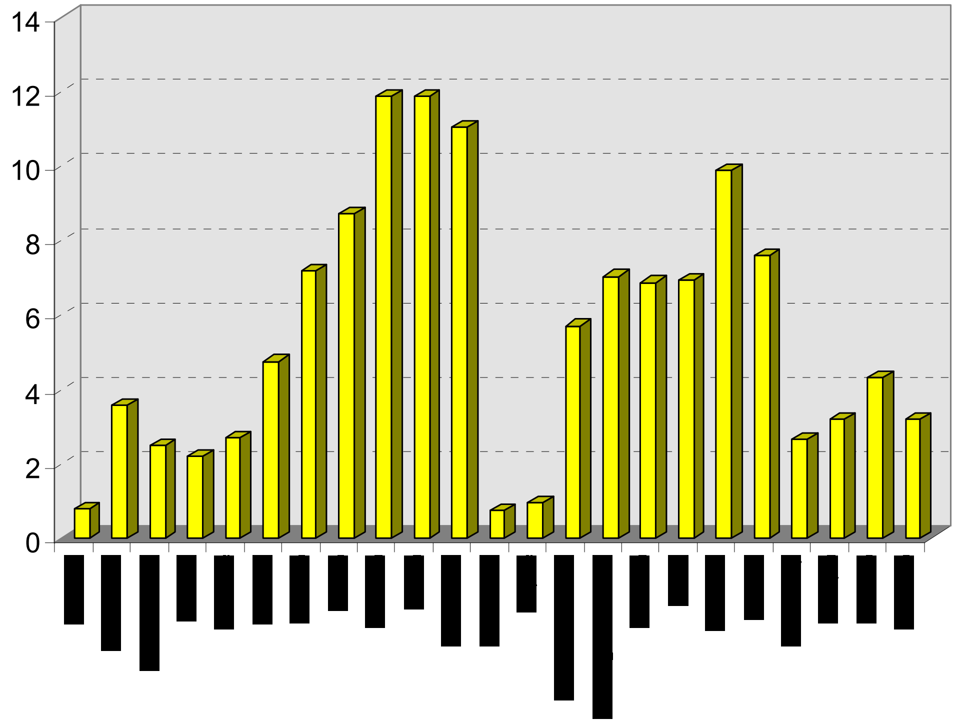
In urban areas of California, nitrate represents a larger fraction of particulate matter (PM) mass compared to the rest of the nation due to wide use of low-sulfur fuels for mobile and stationary sources. For example, electricity generation in California primarily depends on clean-burning natural gas rather than coal or oil, which typically has higher sulfur content. Based on ambient measurements of PM_{10} (particles with an aerodynamic diameter of 10 microns or less), it can be shown that the distribution of PM_{10}-nitrate is different in summer and winter (see Figures 1a and 1b) and can vary significantly between summer and winter at the same site. As is shown in the figures, nitrate predominates in urban areas, particularly during winter, when cool, humid conditions facilitate the formation of ammonium nitrate from ammonia and nitric acid. In the South Coast Air Basin (SoCAB - North Long Beach, Los Angeles, Anaheim, Azusa, Riverside, and Fontana), although nitrate production is greatest during the winter months, the nitrate fraction remains significant during the summer due to extremely high ammonia concentrations from dairy feedlots.

The formation of secondary ammonium nitrate (NH_4NO_3) begins with the oxidation of oxides of nitrogen (NOx) into nitric acid (HNO_3). The nitric acid then reacts with gaseous ammonia to form NH_4NO_3. NOx can be oxidized into nitric acid through both daytime and nighttime reactions involving the hydroxyl radical and ozone respectively. Although volatile organic compounds (VOCs) can play a role in the oxidation of NOx to HNO_3, studies in the San Joaquin Valley have shown that NH_4NO_3 is most responsive to reductions in NOx emissions, with minimal response to changes in VOC emissions.

The sea influences the chemical composition of aerosols in the coastal zone. Sodium chloride (NaCl) is always present in aerosols in the form of large particles originating from seawater. Several studies have indicated the importance of HNO_3 reaction on the sea salt particles, leading to thermally stable sodium nitrate ($NaNO_3$) production in the particle phase accompanied by liberation of gaseous hydrochloric acid (HCl) from the particles. This reaction may be the principal source of coarse (2.5 to 10 µm) nitrate, and plays an important role in atmospheric chemistry because it is a permanent sink for gas-phase nitrogen oxide species.

In a study, a numerical model simulation of marine boundary layer (MBL) was performed to investigate chemical reactions in the gas-phase and aerosol particles in the MBL. Results indicate that under horizontally homogenous conditions with near-neutral stability, transfer of HNO_3 to particle phase to form $NaNO_3$ may decrease the deposition velocity of nitrogen by over 50%, leading to greater horizontal transport prior to deposition to the sea surface. Conversely, for wind speed above 10 m/s, transfer of nitrogen to the particle phase would increase the deposition rate and hence decrease transport prior to sea surface removal. However, several of theoretical studies have stated the need for experimental data to better elucidate the dynamical and chemical process in the marine boundary layer, in particular emission from oceangoing ships in terms of their impact on the chemistry of the marine atmosphere.

Figure 1a. PM10-Nitrate
Winter, Nov-Feb 1998-2000



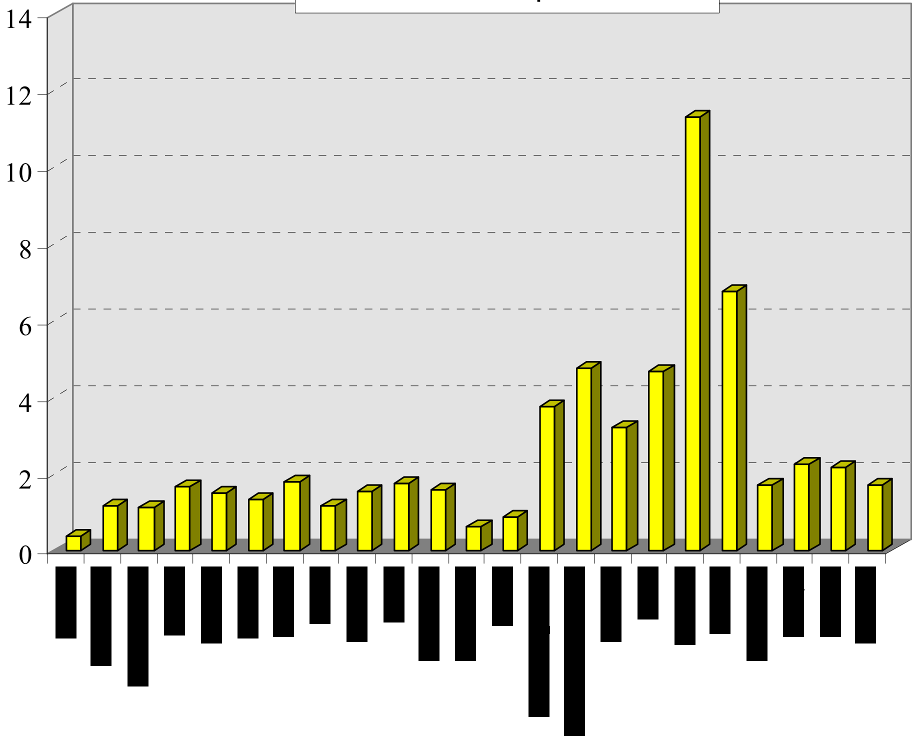


Figure 1b. PM10-Nitrate
Summer, Jun-Sep 1998-2000

To estimate how much of the total PM_{10} nitrate can be attributed to NOx emissions, two parameters need to be considered: (1) the fractional conversion of the total emitted NOx to HNO_3 and (2) the fractional conversion of the HNO_3 to NH_4NO_3 aerosol. It is difficult to determine an accurate estimate of these parameters without performing a comprehensive air quality modeling simulation. Reactions of the precursors with other chemical entities, often formed from photolysis, begin immediately upon the introduction of emissions into ambient air, and depending on emission rate, weather, and air concentration of all reactants, the conversion process may proceed at different rates. Some reactions will take place in minutes, while others in days. In the meantime, the pollutants and their products are being transported, diluted, deposited, and augmented by new emissions. Below ARB staff describes three methodologies that can be used to estimate the conversion rate: the use of photochemical modeling, the analysis of ambient monitoring data, and a simplified box model analysis.

Photochemical Modeling: Dr. Kleeman of the University of California Davis campus, has recently conducted an air quality modeling study in the San Joaquin Valley (SJV). Regional calculations for the SJV based on the IMS95 episode of January 4-6, 1996 show that approximately 13-18% of the reactive nitrogen emissions in the SJV are converted to nitrate at the ground level on a mole basis. Accounting for the difference in molecular weight between NOx and NH_4NO_3, each gram of emitted NOx produces approximately 0.35 - 0.48 grams of NH_4NO_3. [1]

Analysis of Ambient Data: In addition, a simple analysis of ambient concentration data can be performed. Assuming that the sum of the ambient NOx and PM-nitrate concentrations measured at the same place and time represents the emissions that led to the formation of the particles, monthly average conversion factor at several sites in the South Coast Air Basin were calculated. The results show the month-to-month variations in the ambient concentrations and the conversion factors and it generally depicts the increase of the conversion factors in the South Coast Air Basin from the source sites (e.g., Long Beach) to the downwind sites (e.g., Glendora, Upland) to Riverside. This supports the use of a range for the conversion of NO_X to PM nitrate

Box Model: A third estimate of NO_X to nitrate conversion can also be obtained in an air basin considering the air basin as one well-mixed box in which NO_X is being oxidized to nitrate by hydroxyl radical and ozone. The ratio of residence times of the ambient air in an air basin to ambient chemical lifetime of NO_X to nitrate yields conversion factor for secondary formation of PM nitrate from NO_X emissions of about 0.5.

Recommendation

Emissions of NO_X, and ammonia (NH_3) interact in the atmosphere in presence of other ambient air pollutants to form NH_4NO_3 particles. Because this “secondary” particulate matter can constitute a sizable fraction of the total ambient particulate matter measured at air quality monitors, and because emissions of the precursors can vary substantially from source to source, it is important to have at least a simple methodology of the formation of secondary particulate matter from emissions of NOx and NH_3. Unfortunately, but not surprisingly, it is not easy to model secondary aerosol chemistry. Reactions of the precursors with other chemical entities, often formed from photolysis, begin immediately upon the introduction of emissions into ambient air, and depending on emission rate, weather, and air concentration of all reactants, the conversion process may proceed at different rates. Some reactions will take place in minutes, others in days. In the meantime, the pollutants and their products are being transported, diluted, deposited, and augmented by new emissions along their path.

In spite of the complexity of the issue and recognizing the importance of taking secondary PM formation into consideration, we have attempted to construct a quantitative relationship between precursor emissions and secondary ammonium nitrate as described briefly in this document. To estimate the conversion of NOx to PM nitrate, three independent methodologies suggest that the fraction of NOx emissions converted to nitrate ranged from 30 to 50% over entire San Joaquin Valley Air Basin or South Coast Air Basin. Thus, as an approximation, each gram of emitted NOx produces

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[1] Kleeman found that the conversion ratio was highly variable depending on time and location. The 0.35 to 0.48 g of NH_4NO_3 value reported in this study is the average over the entire SJV.

approximately 0.30 - 0.50 grams of secondary PM (i.e., PM-Nitrate). It is important to note that the conversion ratio can be highly variable depending on time and location and that a conversation rate range should be applied.

A strong argument against the application of a single conversion rate is an assumption of linearity as it suggests that decreases and increases in NO_X emissions will lead to proportional reductions and gains in PM-nitrate mass. However, the rate of NO_X oxidation and the branching ratio between inorganic and organic nitrates are known to depend strongly on environmental conditions and reactant concentrations. The partitioning of inorganic nitrate between gaseous nitric acid, ammonium nitrate, and non-volatile nitrate is known to depend in a non-linear manner on a number of factors, such as relative humidity, temperature, and ammonia. Also, the application of a single conversion factor implies that the conversion of NO_X emissions to PM-nitrate is essentially complete. However, this may not be true as some portion of the measured NO_X concentrations are due to “fresh” emissions, which have not had sufficient time to react. This effect can be seen in the SoCAB where detailed air quality models show a change in percent conversion of NO_X to PM-nitrate as one moves from source sites (e.g., Hawthorne, Long Beach, Los Angeles, Burbank), to downwind sites (e.g., Azusa, Upland, Fontana), to Rubidoux, which sits downwind of large ammonia sources.

In addition, it is not recommended to use these conversion factors for emissions that would occur over water such as emissions from oceangoing ships at sea. ARB staff is unable at this time to adequately evaluate the potential for the formation of secondary PM-nitrate at sea due to a lack experimental data under marine conditions, in particular ammonia concentrations and chemical processes. In addition, NO_X loss processes in the marine environment need further investigation as do various aspects of ship plume chemistry.