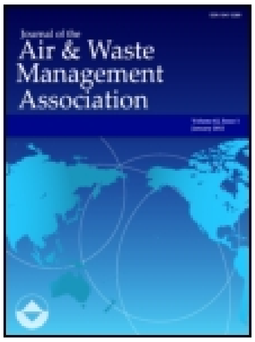

Air & Waste

ISSN: 1073-161X (Print) (Online) Journal homepage: https://www.tandfonline.com/loi/uawm19

Ammonium Nitrate, Nitric Acid, and Ammonia Equilibrium in Wintertime Phoenix, Arizona

John G. Watson , Judith C. Chow , Fred W. Lurmann & Stefan P. Musarra

To cite this article: John G. Watson , Judith C. Chow , Fred W. Lurmann & Stefan P. Musarra (1994) Ammonium Nitrate, Nitric Acid, and Ammonia Equilibrium in Wintertime Phoenix, Arizona, Air & Waste, 44:4, 405-412, DOI: 10.1080/1073161X.1994.10467262

To link to this article: https://doi.org/10.1080/1073161X.1994.10467262

Published online: 05 Mar 2012.

Submit your article to this journal

Article views: 4368

View related articles

Citing articles: 45 View citing articles

Full Terms & Conditions of access and use can be found at
https://www.tandfonline.com/action/journalInformation?journalCode=uawm20

TECHNICAL PAPER

ISSN 1047-3289 *J. Air & Waste Manage. Assoc.* **44:** 405-412

Ammonium Nitrate, Nitric Acid, and Ammonia Equilibrium in Wintertime Phoenix, Arizona

John G. Watson and
Judith C. Chow
Desert Research Institute
Reno, Nevada

Fred W. Lurmann and
Stefan P. Musarra
Sonoma Technology, Inc.
Santa Rosa, California

A secondary aerosol equilibrium model, SEQUILIB, is applied to evaluate the effects of emissions reductions from precursor species on ambient concentrations during the winter in Phoenix, Arizona. The model partitions total nitrate and total ammonia to gas-phase nitric acid and ammonia and to particle-phase ammonium nitrate. Agreement between these partitions and ambient measures of these species was found to be satisfactory. Equilibrium isopleths were generated for various ammonium nitrate concentrations corresponding to high and low humidity periods which occurred during sampling. These diagrams show that ammonia is so abundant in Phoenix that massive reductions in its ambient concentrations would be needed before significant reductions in particulate ammonium nitrate would be observed. When total nitrate is reduced by reductions in its nitrogen oxides precursor, proportional reductions in particulate nitrate are expected. Many of the complex reactions in SEQUILIB do not apply to Phoenix, and its ability to reproduce ambient data in this study does not guarantee that it will be as effective in areas with more complex chemistry. Nevertheless, the nitrate chemistry in SEQUILIB appears to be sound, and it is a useful model for addressing the difficult apportionment of secondary aerosol to its precursors.

PM_{10} (particles with aerodynamic diameters less than or equal to 10 micrometers (μm)) and $PM_{2.5}$ (particles with aerodynamic diameters less than or equal to 2.5 μm) consist of both primary and secondary particles. Primary particles are those which are directly emitted by sources. These particles undergo few changes between source and receptor, and the atmospheric concentrations are, on average, proportional to the quantities which are emitted. Secondary particles are those which form in the atmosphere from gases which are directly emitted by sources. Sulfate, nitrate, ammonium, and hydrogen ions are the most common components of secondary particles in the atmosphere. These particles result from emissions of sulfur dioxide (SO_2), oxides of nitrogen (NO_x), and ammonia (NH_3) gases. The ambient concentrations of these secondary particles are not necessarily proportional to quantities of emissions since the rates at which they form and their gas/particle equilibria may be controlled by factors other than the concentration of the precursor gas. Reactive organic gases are also precursors to secondary particles,[1] though knowledge of these processes is much less than that for inorganic species. This paper limits itself to the inorganic components of secondary aerosol.

Implications

Secondary aerosol ammonium nitrate is often a significant contributor to PM_{10} standard exceedances in urban areas. It is not generally known, however, whether emissions reductions of ammonia or oxides of nitrogen (NO_x) are needed to reduce the ambient concentrations of this compound. The method described here for Phoenix, Arizona, can be applied in other areas to determine which of the precursors limit the formation of ammonium nitrate. Emissions reduction strategies can be better targeted toward ammonia and NO_x sources with this information.

The Chemical Mass Balance (CMB) receptor model[2,3] is commonly used to estimate the contributions of primary particles to their sources and to quantify the chemical compounds which constitute secondary particles (e.g., sulfuric acid, ammonium bisulfate, ammonium sulfate, ammonium nitrate, sodium nitrate). The CMB model, by itself, does not attribute these secondary compounds to sources of their precursor gases. The reason is that compounds such as secondary ammonium nitrate originate from nitrogen oxides (primarily emitted by motor vehicle and stationary combustion sources) and ammonia (primarily emitted by agricultural operations such as fertilizing and animal husbandry). The CMB does not determine which of these precursors needs to be reduced to attain reductions in the particulate nitrate.

While sulfate levels are high in many parts of the eastern U.S., ammonium nitrate has been found to be the major secondary component of suspended particles in urban areas of the western U.S. Gray et al.[4] found ammonium nitrate contributions to PM_{10} as high as 124 μg/m³ at Rubidoux, California during 1986. Chow et al.[5] also found ammonium nitrate contributions exceeding 110 μg/m³ at Rubidoux and neighboring sites in 1988. Chow et al.[6] found region-wide occurrences of ammonium nitrate as high as 79 μg/m³ throughout California's San Joaquin Valley during the winter of 1988-1989. The wintertime 1987-1988 SCENIC Denver[7] visibility study found ammonium nitrate contributions as high as 28 μg/m³ and contributions to light extinction as high as

Copyright 1994 – Air & Waste Management Association

180 Mm^{-1} (a large fraction of total extinction in the Denver Brown Cloud). Ammonium nitrate absorbs water as the relative humidity increases, thereby enhancing its light scattering efficiency.

This paper illustrates a method for estimating the effects of precursor emissions reductions on the secondary ammonium nitrate contribution to PM_{10} calculated by CMB source apportionment. *The Sectional Equilibrium* (SEQUILIB) model of Pilinis and Seinfeld[8] is used to estimate the fractions of total ammonia (gaseous ammonia plus particulate ammonium) and total nitrate (gaseous nitric acid plus particulate nitrate) which are in the gas and particle phases. These fractions are compared with ambient measurements of ammonia, nitric acid, and ammonium nitrate to evaluate the validity of this model for application in Phoenix, Arizona, during the fall and winter of 1989 and 1990. With validity established, isopleths of constant ammonium nitrate concentrations as a function of total ammonia and total nitrate concentrations are generated for typical temperatures and relative humidities. These isopleths can be used to estimate whether reductions in nitrogen oxides (the precursor of nitric acid) or ammonia emissions will be most effective in reducing particulate nitrates.

Characteristics of Phoenix, Arizona

The Phoenix metropolitan area is an inland city in the desert of central Arizona. It covers over 500 square kilometers and has a population exceeding two million people. The urbanized area is surrounded by and interspersed with large tracts of irrigated farmland to the south and west, with desert to the north and east. Large dairy farms are located southwest of the urban area. Phoenix is located in the Salt River Valley at an elevation of 330 m above mean sea level and is bordered on the east and northeast by the McDowell, Goldfield, and Superstition Mountains and on the west and southwest by the Sierra Estrella and White Tank Mountains. The spaces between these ranges are occupied by large, flat desert areas.

Total annual emissions in this area are estimated to be ~45,000 tons/year of PM_{10}, ~55,000 tons/year of nitrogen oxides (NO_x, expressed as equivalent nitrogen dioxide), ~6,000 tons/year of sulfur dioxide, and ~90,000 tons/year of volatile organic compounds (expressed as equivalent methane) during 1989.[9] The major source of sulfur dioxide within the urban area is motor vehicles with about twice as much coming from gasoline-powered vehicles as from diesel-powered vehicles. The major emitters of NO_x are mobile sources with light-duty vehicles being the most abundant contributors. Aircraft and trains are also significant NO_x emitters. Five natural gas-fired power plants account for nearly 20 percent of the total NO_x emissions on an annual basis. Most of these are peaking plants which do not continuously emit NO_x. These plants rarely operate during the winter when energy demands for air conditioning are low.

No estimates of ammonia emissions exist for Phoenix. The Arizona Livestock Board listed 28 licensed feedlots in and around Phoenix with herds ranging from 500 to 10,000 head during 1989. The Arizona Office of the Dairy Commission identifies over 150 dairies located in Maricopa County. Bloyd et al.,[10] in their summary of agricultural statistics in Arizona, show over 200,000 head of cattle, 40,000 sheep, and 11,000 hogs and pigs in Maricopa County during 1988. Adriano et al.[11] estimate an ammonia emissions factor on the order of 40 kg/cow/year. Assuming a 200,000 cow population, this yields annual ammonia emissions on the order of 9,000 tons/year from livestock alone. Ammonia from other sources such as human beings, domestic animals, cultural production, waste water treatment, and fertilizing have not been estimated. This livestock emissions estimate is at least on the same order as the SO_2 and NO_x emissions documented by Chow et al.[9]

There are no major industrial emitters of secondary aerosol precursors in the metropolitan area, although smelter and coal-fired power plants in Arizona are large sulfur dioxide emitters. Watson et al.[12] show average $PM_{2.5}$ sulfate concentrations in downtown Phoenix of ~1.5 $\mu g/m^3$, which are comparable to those found at sampling sites upwind of the city center. Watson et al.[12] also recorded average particulate nitrate concentrations of ~4 $\mu g/m^3$, with maxima of nearly 20 $\mu g/m^3$ during periods of high humidity after rain storms.

Because of the relative simplicity of its sources and the overwhelming importance of nitrate aerosol and its precursors relative to sulfate aerosol and its precursors, Phoenix provides a good test case for the application of newly developed aerosol equilibrium models. If these models cannot explain the gas/particle partitioning in a relatively simple situation such as Phoenix, they should not be expected to succeed in areas which have a complex mixture of acidic sulfates and marine aerosols.

Secondary Particle Formation

Chemical transformation and equilibrium processes for inorganic secondary aerosols are affected by meteorological and chemical variables. Lurmann et al.[13] and Lurmann[14] summarize the different pathways from gas to particle. Calvert and Stockwell[15] have studied the gas-phase chemistry. Stelson and Seinfeld,[16-18] Russell et al.,[19] Russell and Cass,[20,21] Bassett and Seinfeld,[22,23] Saxena et al.,[24] Pilinis and Seinfeld,[8] Wexler et al.,[25,26] Mozukewich,[27] and Tanner and Harrison[28] provide the best explanations of the equilibrium between gas and particle species in polluted environments.

Sulfur dioxide gas changes to particulate sulfate through gas- and aqueous-phase transformation pathways. In the gas-phase pathway, sulfur dioxide reacts with hydroxyl radicals in the atmosphere to form hydrogen sulfite, which in turn reacts rapidly with oxygen and small amounts of water vapor to become sulfuric acid (H_2SO_4) gas. Sulfuric acid gas, which has a low vapor pressure, nucleates in the presence of water vapor to form sulfuric acid droplets. Sulfuric acid gas also condenses on existing particles. These acidic particles are neutralized by ammonia gas to become ammonium bisulfate or ammonium sulfate. Though there are other gas-phase pathways, this one with the hydroxyl radical is usually dominant. Calvert and Stockwell[15] show a wide range of gas-to-particle (SO_2 to $SO_4^=$) transformation rates from less than 0.01 percent/hr to about 5 percent/hr of the sulfur dioxide concentration. The transformation rate appears to be controlled more by the presence or absence of the hydroxyl radical and competing reactions of other gases than by the sulfur dioxide concentration. Hydroxyl radical concentrations are related closely to photochemistry, therefore gas-phase sulfur dioxide transformation rates are highest during daytime and drop to less than 0.1 percent/hr at night.[15]

When fog or clouds are present, sulfur dioxide can be dissolved in a droplet where it experiences aqueous reactions which are much faster than gas-phase reactions. When ozone and hydrogen peroxide are dissolved in the droplet, the sulfur dioxide is quickly oxidized to sulfuric acid. When ammonia is also dissolved in the droplet, the sulfuric acid is neutralized forming ammonium sulfate. As relative humidity decreases below 100 percent (i.e., the fog or cloud evaporates), the sulfate particle consists of a small droplet which includes a portion of liquid water. As the relative humidity further decreases below 70 percent, the droplet evaporates and a small, solid sulfate particle remains. The reactions within the fog droplets occur quickly, and the rate is controlled by the solubility of the precursor gases. Aqueous transformation rates of sulfur dioxide to sulfate are 10 to 100 times faster than gas-phase rates.

Nitrate chemistry is more complicated than sulfate chemistry. The primary emission, nitrogen oxide, converts to nitrogen dioxide, primarily via a reaction with ozone. Nitrogen dioxide is depleted by several pathways: (1) it can change back to nitrogen oxide in the presence of ultraviolet radiation; (2) it can change to short-lived radical species (e.g., O_3, NO_3, N_2O_5); (3) it can form organic nitrates such as peroxyacetyl nitrate (PAN); or (4) it can oxidize to form nitric acid. All of these products are invisible gases which do not affect particulate concentrations or visibility. The major pathway to nitric acid is by reacting with the same hydroxyl radicals which transform sulfur dioxide to sulfuric acid. Nitric acid is deposited from the atmosphere fairly rapidly; but, in the presence of sufficient ammonia, it is neutralized to particulate ammonium nitrate. While ammonium sulfate is a relatively stable compound, ammonium nitrate is not. Its equilibrium with gaseous ammonia and nitric acid is strongly influenced by temperature and relative humidity. Russell et al.[19] show that lower temperatures and higher relative humidities favor the particulate phase of ammonium nitrate. Calvert and Stockwell[15] show a wide range of conversion rates for nitrogen dioxide to nitric acid (NO_2 to NO_3^-), ranging from less than 1 percent/hr to 90 percent/hr. Though they vary throughout a 24-hour period, these rates are significant during both daytime and nighttime hours. This is in contrast to the gas-phase sulfate chemistry which is most active during daylight hours. Nitrate is also formed by aqueous-phase reactions in fogs and clouds. The principal source of aqueous-phase nitrate is dissolved nitric acid and ammonium nitrate aerosol. Though ground fogs were not observed in Phoenix during these experiments, several frontal passages and thunderstorms occurred during which gaseous precursors might be entrained into low-level clouds.

The complexity and uncertainty inherent in these gas-to-particle transformations do not mean that emissions reductions of precursor gases such as sulfur dioxide and nitrogen oxides should be ignored as pollution control measures for PM_{10}. Certainly, if there were no sulfur dioxide or nitrogen oxides in the environment, there would be no ammonium sulfate or ammonium nitrate particles. It is equally true that if there were no ammonia and no hydroxyl radicals, the concentrations of sulfate and nitrate particles would probably be lower (though other pathways not described would surely produce some of these particles). This complexity makes the apportionment to sources of secondary sulfate and nitrate highly imprecise.

SEQUILIB Model

The SEQUILIB model[8] consists of thermodynamic equilibrium relationships which describe the behavior of the nitric acid (HNO_3), nitrate (NO_3^-), ammonia (NH_3), ammonium (NH_4^+), sulfate ($SO_4^=$), chloride (Cl^-), sodium (Na^+), and water chemical system. The version of the model discussed here is that presented by Pilinis and Seinfeld.[8] The SEQUILIB authors have subsequently improved the model formation and input parameters to accommodate a wider range of applications. These changes do not significantly affect the results reported here.

The inputs to the SEQUILIB model are ambient temperature, relative humidity, total nitrate (HNO_3 + NO_3^-), total ammonia (NH_3 + NH_4^+), size-resolved sulfate, and size-resolved chloride ($NaCl+MgCl_2+KCl+CaCl_2$) concentrations. The model outputs are the equilibrium gas-phase concentrations of nitric acid, ammonia, and hydrochloric acid (HCl). Additional outputs are particulate ammonium nitrate (NH_4NO_3), other non-volatile nitrate expressed as sodium nitrate ($NaNO_3$), ammonium, and liquid water concentrations. The model can be used either with or without size-resolved data, and not all of the species included in it are important in every urban area.

The SEQUILIB reactions couple the nitrate/ammonia/sulfate chemical system. Sulfate and nitrate compete for the available ammonia. However, ammonia is preferentially scavenged by sulfate, rather than nitrate, to form ammonium sulfate and ammonium bisulfate. Significant amounts of ammonium nitrate are formed only when the total ammonia exceeds the sulfate by a factor of two or more (on a mole basis). In an ammonia-limited environment, reducing ammonium sulfate concentrations by one molecule might increase ammonium nitrate concentrations up to two molecules. The ammonia that is not scavenged by sulfate is often referred to as "free ammonia."

The most important SEQUILIB component for Phoenix is the combination of nitric acid and ammonia which forms ammonium nitrate. The equilibrium constant for this reaction is both relative humidity (RH) and temperature dependent.[18] Formation of ammonium nitrate is favored under conditions of high relative humidity and low temperature. Aqueous ammonium nitrate forms at or above the relative humidity of deliquescence (RHD) which is above 62 percent at 25°C. Solid ammonium nitrate forms below the relative humidity of deliquescence. The amount of solid ammonium nitrate is determined from the amount above the equilibrium concentration of nitric acid and free ammonia. The relative humidity of deliquescence has an inverse temperature dependence as described by Stelson and Seinfeld.[16] SEQUILIB also includes pathways for the dissolution of nitric acid into the liquid water of wetted aerosols; the direct dissolution of nitric acid is important only at high (>90 percent) relative humidities. High relative humidities are rare in Phoenix, even after rain storms.

Another pathway for the formation of nitrate aerosol consists of the reactions that convert sodium chloride to hydrochloric acid and thermally stable nitrates such as sodium nitrate.[8,20,29,30] These reactions are believed to be the principal source of coarse particle (2.5 to 10 μm) nitrate, and they occur when sodium chloride (from sea salt, road sanding, or dry lake beds) is an abundant atmospheric constituent. Marine air is not present in Phoenix, and Chow et al.[31] showed that sodium concentrations are always at or near detection limits (<0.1 $\mu g/m^3$). This pathway is not significant in Phoenix.

SEQUILIB assumes that sulfuric acid formed in the gas phase rapidly nucleates, condenses on existing aerosol surfaces, and reacts with available ammonia. The model assumes that chemical equilibrium is rapidly established with the existing ammonia, ammonium, nitrate, other salts, and water. The sulfur salts may be in a fully or partially saturated solution, depending on the relative humidity, temperature, and availability of ammonia. Generally, ammonium sulfate and other sulfate end-products are solids below 40 percent relative humidity (at 25°C). These salts exhibit hysteresis wherein an aqueous solution can exist in a supersaturated state below the relative humidity of deliquescence.[32] The sulfate output by SEQUILIB is identical to the input value because under ambient conditions, there is no partitioning between gaseous sulfuric acid and particulate sulfate; the mixture is exclusively sulfate due to the low vapor pressure of sulfuric acid. After a sufficient reaction time, sulfate is always present as a particle of sulfuric acid, ammonium bisulfate (NH_4HSO_4), or completely neutralized ammonium sulfate ($(NH_4)_2SO_4$). Watson et al.[12] show that the sulfate in Phoenix is balanced by the ammonium, so all of the sulfate is in the form of ammonium sulfate. Sulfate levels are low in Phoenix, and much of this sulfate probably originates outside of the urban area and is neutralized en route from the major industrial sulfur emitters in other parts of Arizona. The sulfuric acid and ammonium sulfate chemistry in SEQUILIB are not important to this situation.

Model Input Data

Filter pack samples were obtained from 10/30/89 to 1/21/90 twice per day between 0600 and 1200 (morning sample) and between 1300 and 1900 (afternoon sample) MST. Samples were taken on the roof of the Industrial Commission of Arizona (ICA) Building (40 m above ground level, 370 m above mean sea level) located on 8th Ave. and Washington St. in downtown Phoenix. This site is in the center of the urban area and of the haze cloud as it is seen from locations north and south of the city. Precise locations of this and other sampling sites are specified by Watson et al.[12].

Two sequential filter samples based on the design of Chow et al.[33] were operated side-by-side to obtain measurements of particulate ammonium, sulfate, nitrate, gaseous ammonia, sulfur dioxide, and nitric acid. Each sampler drew a flow rate of 113 l/min through Bendix 240 cyclones (2.5 μm at 50 percent cutpoint) into a plenum where the filter packs were located. Solenoid valves controlled by a timer switched the flow among the filter packs to acquire the morning and afternoon samples at flow rates of 20 l/min. The remaining flow needed to maintain the inlet cutpoint was drawn through a makeup air sampling port.

One sampling system was completely coated with PFA Teflon to minimize the absorption of gaseous nitric acid on sampler surfaces. Two filter packs in this unit simultaneously sampled at flow rates of 20 l/min. One filter pack contained a stack of potassium carbonate and citric acid impregnated cellulose-fiber filters to absorb sulfur dioxide and ammonia gases, respectively. These filters were preceded by a Teflon-coated glass-fiber filter to remove particles. The second pack contained a prewashed nylon filter to collect total nitrate (gaseous nitric acid plus particulate nitrate). The potassium carbonate impregnated filters and nylon filters were extracted and analyzed for sulfate and nitrate by ion chromatography. The citric acid impregnated filters were extracted and analyzed for ammonium by automated colorimetry.

The second sampling system contained oxidized aluminum denuder tubes, after the uncoated inlet, to remove gaseous nitric acid from the air stream. The filter stack consisted of a quartz-fiber filter followed by a nylon filter downstream. The extract from the quartz-fiber filter was submitted to ion chromatographic analysis for chloride, nitrate, and sulfate, and to automated colorimetric analysis for ammonium; the extract from the nylon filter was submitted to ion chromatographic analysis for nitrate. The nylon filter allows the magnitude of volatilized particulate nitrate to be determined and added to the nitrate measurement on the front filter to obtain total particulate nitrate.

Hourly measurements of temperature and relative humidity were also acquired at this site using a Campbell 207 temperature and relative humidity probe interfaced with a Campbell Scientific 21X data logger.

For input to the SEQUILIB model, six-hour average temperature and relative humidity were calculated for the periods corresponding to the filter samples. The model was applied in the "single size cut" mode. The total nitrate inputs to the model were obtained from the non-denuded nylon filter taken from the Teflon-coated sampler. The total ammonia inputs to the model were obtained from the $PM_{2.5}$ ammonium and ammonia gas data and an ammonium equivalent corresponding to the nitrate on the nylon backup filter. The measured $PM_{2.5}$ sulfate and chloride concentrations were also used as model inputs. Sodium concentrations were not measured but were assumed to be zero based on pilot study values measured by Chow et al.[31] The chloride concentrations and the estimated sodium concentrations were low and insignificant with respect to the partitioning of relevant species.

SEQUILIB Comparisons to Measurements

The calculated nitric acid, particulate nitrate, ammonia, and particulate ammonium concentrations are compared with measured values in Figures 1 through 4. As shown in Figures 1 and 2, SEQUILIB estimates average 1 μg/m^3 less than measured concentrations for nitric acid and 1 μg/m^3 more than measured concentrations for particulate nitrate. The average nitric acid concentrations were fairly low (2.7 μg/m^3). In several cases, the calculated nitric acid concentrations were less than the lower quantifiable limits of the measurement system even though the measurements detected nitric acid which exceeded these limits. As shown in Figure 1, the agreement between the measured and calculated nitric acid concentrations is better for the afternoon samples than for the morning samples. The agreement is also better for high values than for low values.

SEQUILIB calculates an average of 5.4 μg/m^3 of particulate nitrate, while an average of 4.3 μg/m^3 was measured. The calculated particulate nitrate values track the measured values reasonably well in Figure 2. With regard to partitioning, the model allots the total nitrate primarily to particulate nitrate (actually, ammonium nitrate), whereas, the measurements show slightly smaller amounts of particulate nitrate and larger amounts of nitric acid.

Average SEQUILIB estimates for ammonia are 8.8 μg/m^3, which compares well with the average measured concentration of 9.1 μg/m^3. Figure 3 shows that the model estimates compare well with the measured ammonia concentrations. The ammonia concentrations at the ICA site were fairly high compared to other

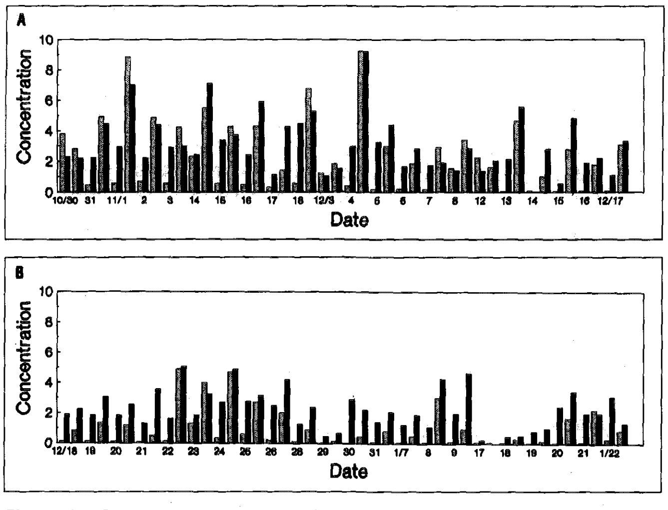

Figure 1. Comparison of calculated (shaded bar) and measured (solid bar) nitric acid concentrations (µg/m^3) in Phoenix from (a) October 30, 1989 to December 17, 1989 and (b) December 18, 1989 to January 22, 1990. The sampling times were 0600 to 1200 MST and 1300 to 1900 MST. The date label is centered under the morning sample.

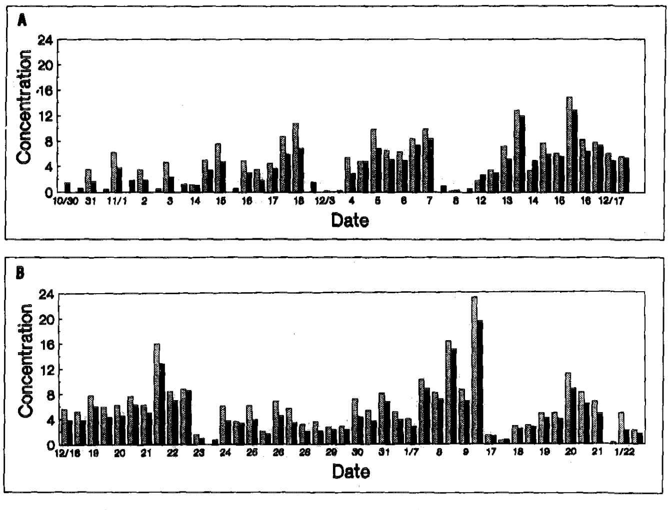

Figure 2. Comparison of calculated (shaded bar) and measured (solid bar) $PM_{2.5}$ nitrate concentrations (µg/m^3) in Phoenix from (a) October 30, 1989 to December 17, 1989 and (b) December 18, 1989 to January 22, 1990. The sampling times were 0600 to 1200 MST and 1300 to 1900 MST. The date label is centered under the morning sample.

urban areas. The measurements and the model show an excess of free ammonia in most cases.

SEQUILIB estimates an average particulate ammonium concentration of 2.0 $\mu g/m^3$, while an average of 1.7 $\mu g/m^3$ was measured. The measured values include the ammonium which is presumed to have evaporated from the front filter, and corresponds to the volatilized nitrate which was captured on the nylon backup filter. The particulate ammonium concentrations are fairly low, about a factor of five lower than the gaseous ammonia concentrations. The average absolute differences between the calculated and measured ammonium and ammonia concentrations are comparable (±0.4 $\mu g/m^3$ on the average); however, the relative percent difference in the ammonium estimates is much larger because the concentrations are much lower.

Figure 5 compares the nitric acid and ammonia concentration product with the theoretical equilibrium constant.[16,17] Since the equilibrium constant for ammonium nitrate is a function of both relative humidity and temperature, Figure 5 compares the observed and theoretical concentration products as a function of inverse temperature for various relative humidity regimes. Most of the measurements were obtained when six-hour average relative humidities were less than 50 percent, and these points (the solid triangles) should correspond to the solid line. Figure 5 shows that few of the products correspond to this line. The observed concentration products range from a factor of 10 below the theoretical values to a factor of 100 greater than the theoretical values. The poorest agreement is for the small number of samples obtained during high relative humidities. The deviation of these products from the theoretical line is much larger than the estimated factor of two for the uncertainty in the equilibrium constant.

A number of researchers have performed similar evaluations of the ammonium nitrate equilibrium constant. Doyle et al.,[34] Grosjean,[35] Harrison and Pio,[36] Hildemann et al.,[37] Chang et al.,[38] and Lewin et al.[39] obtained reasonably good agreement with the theoretical values, while Stelson et al.,[40] Cadle et al.,[41] Tanner,[42] Anlauf et al.,[43] Jacob et al.,[44] and Allen et al.[45] found significant deviations from theoretical estimates and, in some cases, a consistent bias. The amount of scatter in Figure 5 is consistent with that reported by several other studies.[43,45]

The discrepancies could be a result of deficiencies in both the measurements and the model. There are significant variations in the ambient temperature and relative humidity during the six-hour sampling intervals. In Figure 5, a shift of ±0.05 along the horizontal axis corresponds to an average temperature change of ~5°C. Ambient temperatures varied by more than 5°C over each sampling period. The majority of points in Figure 5 lie within ±0.05° of the theoretical line.

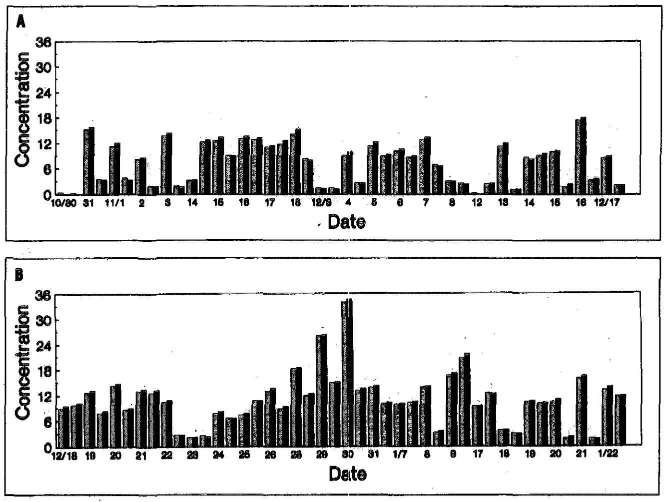

Figure 3. Comparison of calculated (shaded bar) and measured (solid bar) ammonia concentrations ($\mu g/m^3$) in Phoenix from (a) October 30, 1989 to December 17, 1989 and (b) December 18, 1989 to January 22, 1990. The sampling times were 0600 to 1200 MST and 1300 to 1900 MST. The date label is centered under the morning sample.

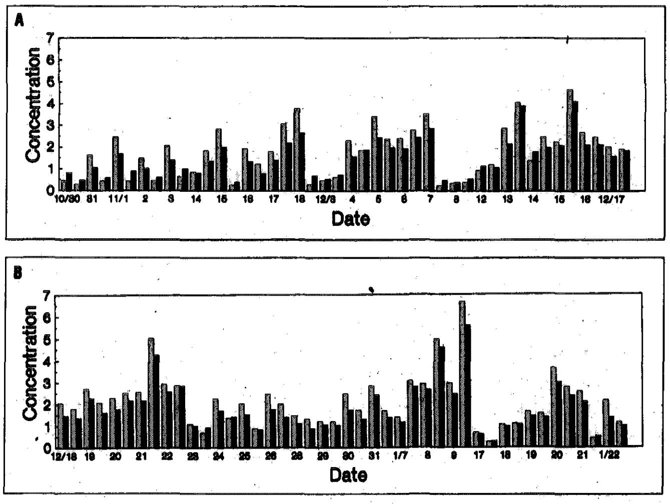

Figure 4. Comparison of calculated (shaded bar) and measured (solid bar) $PM_{2.5}$ ammonium concentrations ($\mu g/m^3$) in Phoenix from (a) October 30, 1989 to December 17, 1989 and (b) December 18, 1989 to January 22, 1990. The sampling times were 0600 to 1200 MST and 1300 to 1900 MST. The date label is centered under the morning sample.

Figures 6 and 7 show how the modeled concentrations for the morning of 12/26/89 (a dry period) and the morning of 12/30/89 (a high humidity period) change with relative humidity and temperature. The SEQUILIB-calculated concentrations of nitrate, ammonia, and ammonium are quite stable with respect to temperature and relative humidity variations. However, the nitric acid and water concentrations change significantly as relative humidity increases, and the nitric acid concentration responds significantly to variations in temperature. Under these conditions, nitric acid is the least abundant species. The large variations in the equilibrium constant and relative humidity are reflected in the sensitivity of the nitric acid concentration to small changes in temperature and relative humidity. There are also 5 to 15 percent uncertainties in the measurements.

Lower bound concentration estimates were calculated using the lowest temperature and relative humidity observed in the sampling period with 90 percent of the observed total nitrate and ammonia, and 110 percent of the observed sulfate. Measurement

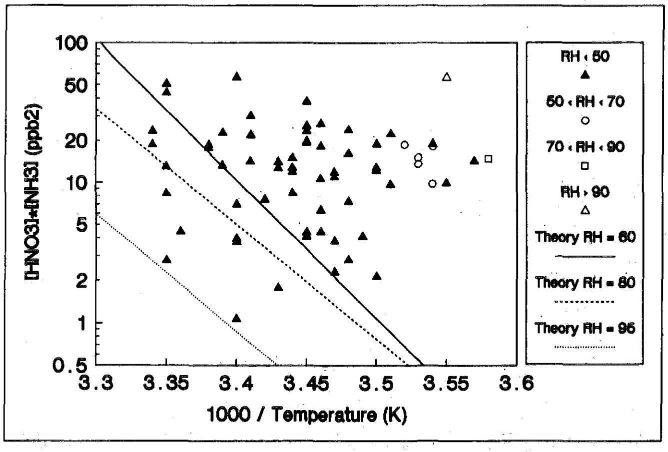

Figure 5. Comparison of theoretical (solid and dashed lines) and measured (triangles and circles) product of nitric acid and ammonia with inverse temperature.

precisions for these species were on the order of ±10 percent. Upper bound concentrations were calculated using the highest temperature and relative humidity observed in the sampling period with 110 percent of the observed total nitrate and ammonia, and 90 percent of the observed sulfate. The conditions on the mornings of 12/26/89 and 12/30/89 were employed because they had comparable nitrate levels yet very different relative humidities (30 percent versus 90 percent).

Under these conditions, the calculated particulate nitrate changes by less than ±10 percent with respect to its mean, while gaseous ammonia changes by slightly greater than ±10 percent with respect to its mean. However, the effect of the same variations in SEQUILIB input data on nitric acid and the [HNO_3][NH_3] product is much larger. For the high relative humidity and ammonia-rich conditions of 12/30/89, the ~10 percent variations in model inputs result in a factor of 450 difference in the [HNO_3][NH_3] product. For the other two cases, the lower and upper bound [HNO_3][NH_3] products differ by a factor of three. The high sensitivity of the [HNO_3][NH_3] product to measurement uncertainty and variations in temperature and relative humidity explains the large amount of scatter exhibited in Figure 5 for these cases. Measurements under these conditions cannot be used to verify the nitrate/ammonia equilibrium constants.

Another uncertainty is associated with coarse-particle nitrate. While the chloride and sodium levels were very low in wintertime Phoenix, there may be some ammonium nitrate on particles larger than 2.5 μm. The measurement approach assumed that the majority of particulate nitrate occurs in the $PM_{2.5}$ size fraction, and particulate nitrate was not measured in the coarse particle fraction. Since the majority of the coarse particle mass was accounted for by primary source contributions,[12] this assumption is probably valid for the purposes of this study. None of the primary source profiles contained more than a few percent abundance for nitrate. However, theory suggests that nitric acid is in equilibrium with all aerosol nitrate, not just the $PM_{2.5}$ portion. The biases between calculated and measured values described earlier might be reduced through measurement of the particulate nitrate in size ranges exceeding 2.5 μm.

As do all models, SEQUILIB makes several assumptions which do not entirely comply with the real world. It assumes the gas, liquid, and solid phases are in perfect chemical equilibrium. Wexler and Seinfeld[46] have shown that at lower temperatures and/or for larger particles, the equilibrium assumption may not hold because the time scales for mass transport are too large for ammonium salts. SEQUILIB assumes values for the relative humidity of deliquescence based on those for the pure salts. There is evidence that the relative humidity of deliquescence of mixed salts may be significantly lower than those for pure salts.[25] SEQUILIB assumes values for a limited number of thermodynamic parameters. The thermodynamics of real atmospheres may require more parameters, and the actual values may differ from those which are assumed.

Effects of Precursor Reductions on Ammonium Nitrate Concentrations

This study was not intended to develop or evaluate models, but to apply them. Although gas/particle conversion and equilibrium theory and modeling are still under development, the SEQUILIB model embodies the essential physics and chemistry of the system being measured in Phoenix. The evaluation of its performance in Phoenix shows that under ammonia-rich conditions, SEQUILIB underestimates gaseous nitric acid and slightly overestimates particulate nitrate and ammonium concentrations. Much of this bias can be attributed to the measurement uncertainty of the input concentrations and to changes in temperature and relative humidity over the six-hour sampling periods. The sample-to-sample calculated partitioning between gaseous nitric acid and ammonia, and particulate ammonium nitrate, follows the measured partitioning quite well even with changes of more than a factor of 10 in concentration from one sample to the next. This gives credence to the use of SEQUILIB calculations for evaluating the effects of ammonia and nitric acid reductions on particulate ammonium nitrate concentrations contributing to the urban haze.

Ambient ammonium nitrate aerosol concentrations can be reduced by decreasing emissions of nitrogen oxides (the major precursor of nitric acid) and/or ammonia. In order to provide guidance for strategy development, nitrate isopleth diagrams were generated using the SEQUILIB model with varying inputs for total nitrate and total ammonia at 0.5 μg/m^3 increments for the conditions on the mornings of 12/26/89 and 12/30/89. The mea-

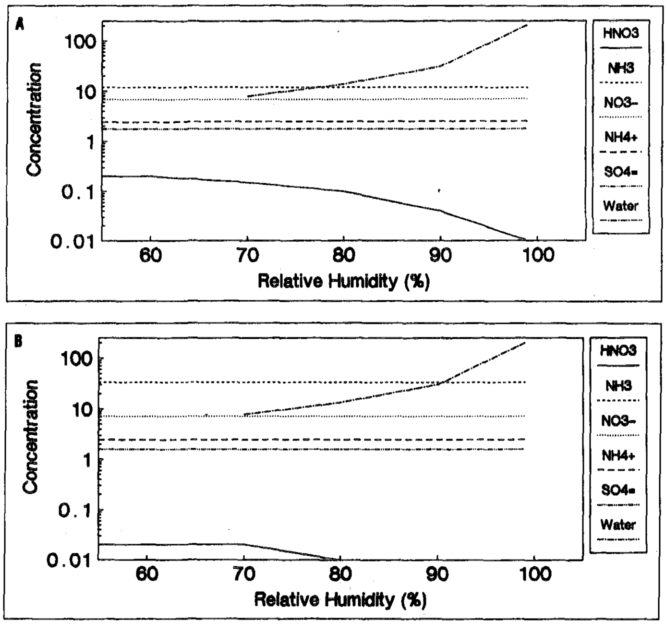

Figure 6. Sensitivity of the calculated gas and aerosol concentrations (μg/m^3) to changes in relative humidity for the conditions observed between 0600 and 1200 MST on (a) December 26, 1989 and (b) December 30, 1989.

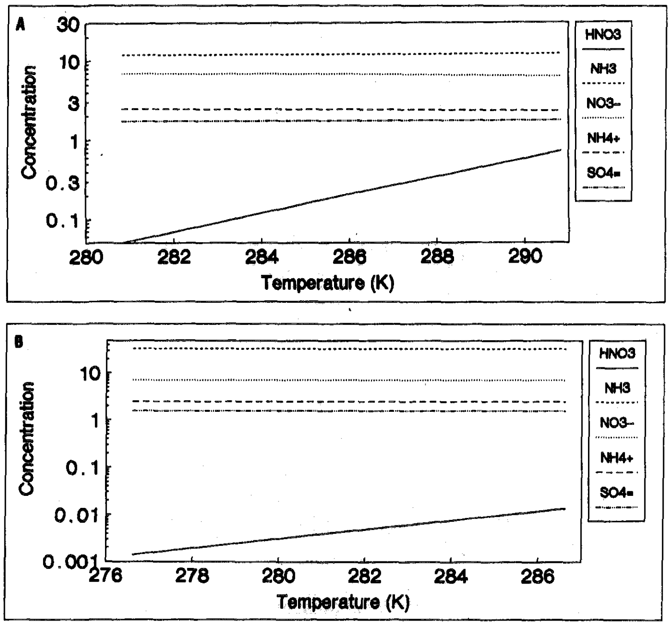

Figure 7. Sensitivity of the calculated gas and aerosol concentrations (μg/m^3) to changes in temperature for the conditions observed between 0600 and 1200 MST on (a) December 26, 1989 and (b) December 30, 1989.

sured sulfate concentrations, nitrate concentrations, temperature, and relative humidity were used for all model runs. The diagrams, shown in Figures 8 and 9, plot model outputs by applying polynomial fits to the model outputs for specific particulate ammonium nitrate concentrations. These figures illustrate how particulate ammonium nitrate concentrations vary with changes in the total nitrate and total ammonia concentrations. The design values on the diagrams correspond to the measured concentrations on these days. The observed total nitrate concentration was about 7 μg/m^3 in both cases, however, the total ammonia was considerably higher for the moist conditions on 12/30/89 (36 μg/m^3) than for the dry conditions on 12/26/89 (14 μg/m^3).

The diagrams can be used to explore the implications of control strategies. For example, what would be the effects of 50 percent reductions in the total nitrate (from nitrogen oxides) and ammonia concentrations? For the dry case, Figure 8 shows that a 50 percent reduction in total nitrate (nitric acid and ammonium nitrate) decreases particulate nitrate by 53 percent. Reducing total ammonia by 50 percent with no concomitant reduction of total nitrate would decrease particulate nitrate by only ~5 percent. Reducing both total nitrate and total ammonia by 50 percent would reduce particulate nitrate by ~50 percent — similar to that of the total nitrate reduction by itself.

For the moist case in Figure 9, a 50 percent reduction in total nitrate would decrease particulate nitrate by ~50 percent. A 50 percent reduction in total ammonia would not detectably change the particulate nitrate concentration. Reducing total nitrate and total ammonia by 50 percent would reduce the particulate nitrate by ~50 percent.

These diagrams show that due to the ammonia-rich conditions at this site, reduction in total nitrate (which results from reducing oxides of nitrogen precursors) is likely to be much more effective in reducing the particulate ammonium nitrate which affects PM_{10} and visibility than equivalent reductions in ammonia.

Although the ammonium nitrate equilibrium constant is not known precisely, and the system may not be in perfect equilibrium, the reactions are sufficiently well-known to characterize the behavior in the ammonia-rich and nitrate-rich conditions. Changes in the scarce reactant will have much more effect on the product species than changes in the abundant reactant. Thus, reductions in oxides of nitrogen emissions that reduce nitric acid formation (which may require corresponding reductions in reactive organic gas emissions taking part in the production of nitric acid) are likely to be effective in reducing the ammonium nitrate levels in the Phoenix area.

Conclusions

This paper has shown how, in a relatively simple situation such as Phoenix, Arizona, a secondary equilibrium aerosol model can be used to evaluate the effects of emissions reductions from precursor species on ambient concentrations. Using this model, it was shown that ammonia was so abundant in Phoenix during the winter of 1989-1990 that massive reductions in its ambient concentrations would be needed before significant reductions in particulate ammonium nitrate would be observed. When total nitrate is reduced, however, by reductions in its oxides of nitrogen precursors, proportional reductions in particulate nitrate are expected.

Many of the complex reactions in the SEQUILIB model[8] do not apply to Phoenix, and its ability to reproduce ambient data in this study does not guarantee that it will be as effective in areas with more complex chemistry. Nevertheless, the nitrate chemistry in SEQUILIB appears to be sound, and it is a useful model for addressing the difficult apportionment of secondary aerosol to its precursors.

Acknowledgments

This work was sponsored by the Arizona Department of Environmental Quality as part of the Phoenix Urban Haze Study. The authors are grateful to Dennis Haase of Visibility Services, Inc. who operated the field sampling site; to Barbara Hinsvark, Sandra Chandra, Bridget Ball, Glenda Hargrove, Cliff Frazier, and Lyle Pritchett for chemical analysis; Kimberly Snow and Dana Dondero for manuscript preparation; and Dr. William Pierson for technical review. The conclusions of this research are those of the authors and do not necessarily reflect the position or policies of the project sponsor.

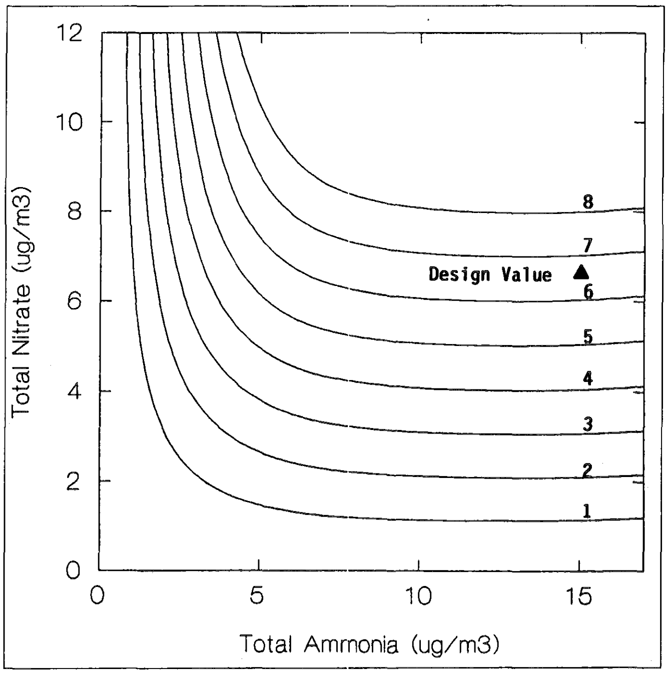

Figure 8. Particulate nitrate isopleths for low relative humidity conditions on the morning of December 26, 1989. The number on each isopleth is the ammonium nitrate concentration in μg/m^3 design value corresponds to the total nitrate and total ammonia measured on this sample.

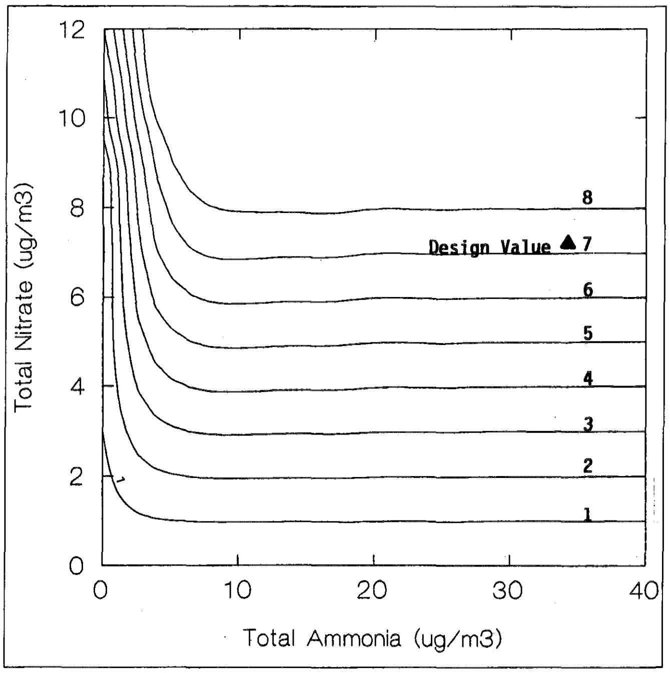

Figure 9. Particulate nitrate isopleths for high relative humidity conditions on the morning of December 30, 1989. The number on each isopleth is the ammonium nitrate concentration in μg/m^3. The design value corresponds to the total nitrate and total ammonia measured on this sample.

References

1. D. Grosjean, "In-situ organic aerosol formation during a smog episode," *Atmos. Environ.* **26A**:953 (1992).
2. J.G. Watson, N.F. Robinson, J.C. Chow, R.C. Henry, B.M. Kim, T.G. Pace, E.L. Meyer, Q. Nguyen, "The USEPA/DRI chemical mass balance receptor model, CMB 7.0," *Environ. Software* **5**:38 (1990).
3. J.G. Watson, J.C. Chow, T.G. Pace, "Chemical Mass Balance," In: *Receptor Models*, P.K. Hopke, Ed., Elsevier Press, New York, NY, pp 83-116, 1991.
4. H.A. Gray, B. Landry, C.S. Liu, R.C. Henry, J.A. Cooper, J.R. Sherman, "Receptor Modeling for PM_{10} Source Apportionment in the South Coast Air Basin of California," In: *Transactions, PM_{10}: Implementation of Standards*, C.V. Mathai and D.H. Stonefield, Eds., Air Pollution Control Association, Pittsburgh, PA, pp 399-418, 1988.
5. J.C. Chow, C.L. Lu, Z. Lu, L.C. Pritchett, "A neighborhood-scale study of PM_{10} source contributions in Rubidoux, California," *Atmos. Environ.* **26A**:693 (1992).
6. J.C. Chow, P.A. Solomon, K. Magliano, S.D. Ziman, L.W. Richards, "PM_{10} source apportionment in California's San Joaquin Valley," *Atmos. Environ.* **26A**:3335 (1992).
7. J.G. Watson, J.C. Chow, L.W. Richards, S.R. Anderson, J.E. Houck, and D.L. Dietrich, *The 1987-88 Metro Denver Brown Cloud Air Pollution Study, Volume III: Data Interpretation,"* DRI Document 8810.1F3, Report prepared for the Greater Denver Chamber of Commerce by Desert Research Institute, Reno, NV, 1988.
8. C. Pilinis, J.H. Seinfeld, "Continued development of a general equilibrium model for inorganic multicomponent atmospheric aerosols," *Atmos. Environ.* **21**:2453 (1987).
9. J.C. Chow, J.G. Watson, L.W. Richards, D.L. Haase, C. McDade, D.L. Dietrich, D. Moon, S. Sloane, *The 1989-90 Phoenix PM_{10} Study. Volume II: Source Apportionment*, DRI Document 8931.6F1, Report prepared for Arizona Department of Environmental Quality by Desert Research Institute, Reno, NV, 1991.
10. B.L. Bloyd, N.W. Bennett, D. Kenerson, C. Fox, B. Roberts, L. Hoffman, E. Dye, A. Bryant, *1988 Arizona Agricultural Statistics*, Bulletin S-24, Arizona Agricultural Statistics Service, Phoenix, AZ, 1989.
11. D.C. Adriano, A.C. Chang, R. Sharpless, "Nitrogen loss from manure as influenced by moisture and temperature," *J. Environ. Qual.* **3**:258 (1974).
12. J.G. Watson, J.C. Chow, L.W. Richards, D.L. Haase, C. McDade, D.L. Dietrich, D. Moon, C. Sloane, *The 1989-90 Phoenix Urban Haze Study, Volume II: The Apportionment of Light Extinction to Sources*, DRI Document 8931.5F1, Report prepared for Arizona Department of Environmental Quality by Desert Research Institute, Reno, NV, 1991.
13. F. Lurmann, J. Collins, J. Coyner, *Development of a Chemical Transformation Submodel for Annual PM_{10} Dispersion Modeling*, Report No. P-#146-002 prepared for the South Coast Air Quality Management District by Environmental Research and Technology, Camarillo, CA, 1988.
14. F. Lurmann, "A Review of PM_{10} Air Quality Models," In: *Transactions, Receptor Models in Air Resources Management*, J.G. Watson, Ed., Air & Waste Management Association, Pittsburgh, PA, pp 461-474, 1989.
15. J.G. Calvert, W.R. Stockwell, "Acid generation in the troposphere by gas-phase chemistry," *Environ. Sci. Technol.* **17**:430A (1983).
16. A.W. Stelson, J.H. Seinfeld, "Relative humidity and temperature dependence of the ammonium nitrate dissociation constant," *Atmos. Environ.* **16**:983 (1982).
17. A.W. Stelson, J.H. Seinfeld, "Relative humidity and pH dependence of the vapor pressure of ammonium nitrate-nitric acid solutions at 25°C," *Atmos. Environ.* **16**:993 (1982).
18. A.W. Stelson, J.H. Seinfeld, "Thermodynamic prediction of the water activity, NH_4NO_3 dissociation constant, density and refractive index for the NH_4NO_3-$(NH_4)_2SO_4$-H_2O system at 25°C," *Atmos. Environ.* **15**:2507 (1982).
19. A.G. Russell, G.J. McRae, G.R. Cass, "Mathematical modeling of the formation and transport of ammonium nitrate aerosol," *Atmos. Environ.* **17**:949 (1983).
20. A.G. Russell, G.R. Cass, "Acquisition of regional air quality model validation data for nitrate, sulfate, ammonium ion and their precursors," *Atmos. Environ.* **18**:1815 (1984).
21. A.G. Russell, G.R. Cass, "Verification of a mathematical model for aerosol nitrate and nitric acid formation and its use for control measure evaluation," *Atmos. Environ.* **20**:2011 (1986).
22. M. Bassett, J.H. Seinfeld, "Atmospheric equilibrium model of sulfate and nitrate aerosols," *Atmos. Environ.* **17**:2237 (1983).
23. M.Bassett, J.H. Seinfeld, "Atmospheric equilibrium model of sulfate and nitrate aerosols — II. Particle size analysis," *Atmos. Environ.* **18**:1163 (1984).
24. P. Saxena, A.B. Hudischewskyj, C. Seigneur, J.H. Seinfeld, "A comparative study of equilibrium approaches to the chemical characterization of secondary aerosols," *Atmos. Environ.* **20**:1471 (1986).
25. A.S. Wexler, J.H. Seinfeld, "Second-generation inorganic aerosol model," *Atmos. Environ.* **25A**:2731 (1991).
26. A.S. Wexler, F. Lurmann, J.H. Seinfeld, "Modelling Condensation and Evapora tion for Atmospheric Aerosols," In: *Transactions, PM_{10} Standards and Nontraditional Particulate Source Controls*, J.C. Chow and D. Ono, Eds., Air & Waste Management Association, Pittsburgh, PA, pp 784-793, 1992.
27. M. Mozurkewich, "The dissociation constant of ammonium nitrate and its dependence on temperature, relative humidity and particle size," *Atmos. Environ.* **27A**:261 (1993).
28. R.L. Tanner and R.M. Harrison, "Acid-Base Equilibria of Aerosols and Gases in the Atmosphere," Chapter 2 In: *Environmental Particles*, Vol. 1, J. Buffle and H.P. van Leeuwen, Eds., Lewis Publishers, Ann Arbor, MI, 1992.
29. Y. Mamane, M. Mehler, "On the nature of nitrate particles in a coastal urban area," *Atmos. Environ.* **21**:1989 (1987).
30. C.A. Pio, R.M. Harrison, "Letter to the editor: equilibrium of ammonium chloride aerosol with gaseous hydrochloric acid and ammonium under tropospheric conditions," *Atmos. Environ.* **21**:1243 (1987).
31. Chow, J.C., J.G. Watson, L. Pritchett, D. Lowenthal, C. Frazier, G. Neuroth, K. Evans, D. Moon, "Wintertime Visibility in Phoenix, Arizona," Paper 90-66.6, presented at the Air & Waste Management Association, 83rd Annual Meeting, Pittsburgh, PA, June 1990.
32. I.N. Tang, "Deliquescence Properties and Particle Size Change of Hygroscopic Aerosols," In: *Generation of Aerosols and Facilities for Exposure Experiments*, K. Willeke, Ed., Chapter 7, pp 153-167, Ann Arbor Science Publishers, Ann Arbor, MI, 1980.
33. J.C. Chow, J.G. Watson, J.L. Bowen, A.W. Gertler, C.F. Frazier, K.K. Fung, L. Ashbaugh, "A Sampling System for Reactive Species in the Western U.S.," In: *ACS Symposium Series*. E. Winegar, Ed. American Chemical Society, Washington, D.C., pp 209-228, 1993.
34. G.J. Doyle, E.C. Tuazon, R.A. Graham, T.M. Mischke, A.M. Winer, J.N. Pitts, "Simultaneous concentrations of ammonia and nitric acid in a polluted atmosphere and their equilibrium relationships to particulate ammonium nitrate," *Environ. Sci. Technol.* **13**:1416 (1979).
35. D. Grosjean, "The stability of particulate nitrate in the Los Angeles atmosphere," *Sci. Total Environ.* **25**:263 (1982).
36. R.M. Harrison, C.A. Pio, "An investigation of the atmospheric HNO_3- NH_3- NH_4NO_3 equilibrium relationship in a cool, humid climate," *Tellus* **35B**:155 (1983).
37. L.M. Hildemann, A.G. Russell, G.R. Cass, "Ammonia and nitric acid concentrations in equilibrium with atmospheric aerosols: experiment vs theory," *Atmos. Environ.* **18**:1737 (1984).
38. Y.S. Chang, G.R. Carmichael, H. Kurita, and H. Ueda, "An investigation of the formation of ambient NH_4NO_3 aerosol," *Atmos. Environ.* **20**:1969 (1986).
39. E.E. Lewin, R.G. dePena, J.P. Shimshock, "Atmospheric gas and particle measurements at a rural northeastern U.S. site," *Atmos. Environ.* **20**(1):59 (1986).
40. P.A. Stelson, S.K. Friedlander, J.H. Seinfeld, "A note on the equilibrium relationship between ammonia and nitric acid and particulate ammonium nitrate," *Atmos. Environ.* **13**:369 (1979).
41. S.H. Cadle, R.J. Countess, N.A. Kelly, "Nitric acid and ammonia in urban and rural locations," *Atmos. Environ.* **16**:2501 (1982).
42. R.L. Tanner, "An ambient experimental study of phase equilibrium in the atmospheric system: H^+, NH_4^+, SO_2^-, NO_3^- - NH_3 (g), HNO_3 (g)," *Atmos. Environ.* **16**:2935 (1982).
43. K.G. Anlauf, J.W. Bottenheim, K.A. Brice, P. Fellin, H.A. Wiebe, "Measurement of atmospheric aerosols and photochemical products at a rural site in SW Ontario," *Atmos. Environ.* **19**:1859 (1985).
44. D.J. Jacob, J.M. Waldman, J.M. Munger, M. Hoffmann, "The H_2SO_4- HNO_3- NH_3 system at high humidities and in fogs. 2. Comparison of field data with thermodynamics calculations," *J. Geophys. Res.* **91**(D1):1089 (1986).
45. A.G. Allen, R.M. Harrison, J.W. Erisman, "Field measurements of the dissociation of ammonium nitrate and ammonium chloride aerosols," *Atmos. Environ.* **23**:1591 (1989).
46. A.S. Wexler, J.H. Seinfeld, "The distribution of ammonium salts among a size and composition dispersed aerosol," *Atmos. Environ.* **24A**:1231 (1990).

About the Authors

J.G. Watson, Ph.D., is a research professor with the Desert Research Institute, 5625 Fox Ave., P.O. Box 60220, Reno, NV 89506. J.C. Chow, Sc.D., is a research professor with the Desert Research Institute, 5625 Fox Ave., P.O. Box 60220, Reno, NV 89506. F.W. Lurmann is the manager of Air Quality Modeling with Sonoma Technology, Inc., 5510 Skylane Blvd., Ste. 101, Santa Rosa, CA 95403. S.P. Musarra, Ph.D., is an air quality scientist with Sonoma Technology, Inc., 5510 Skylane Blvd., Ste. 101, Santa Rosa, CA 95403. This manuscript was submitted for peer review. The final manuscript was received on December 16, 1993.