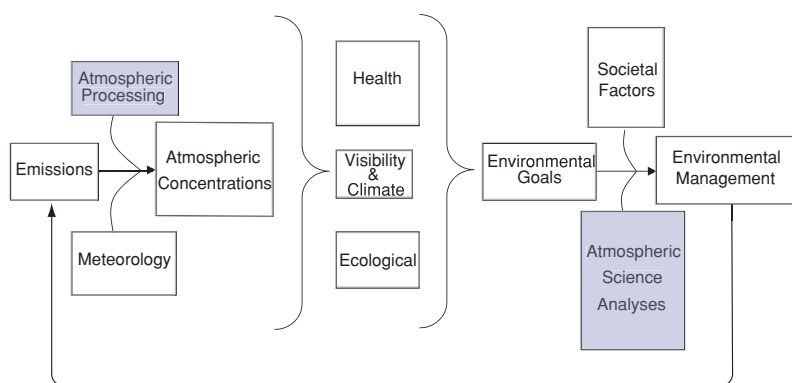


CHAPTER 3

Atmospheric Aerosol Processes

Principal Author: Spyros Pandis



3.1 THE LIFE OF AN ATMOSPHERIC PARTICLE

Atmospheric particles originate either as primary particles - by direct emission from a source or as secondary particles - through in-situ formation from the gas phase (nucleation). Particles vary in size from a few nanometers to tens of micrometers, with their composition reflecting their source. Secondary particles can be created in different parts of the atmosphere, sometimes high near a cloud or even the top of the troposphere and sometimes near the surface of the earth. After entering the lower atmosphere, new particles can exist for several days depending on removal processes. During their lifetime, they are changed by processes such as dilution, dispersion, coagulation, and chemical reaction.

Upon their emission to (or formation in) the atmosphere, particles move under the influence of local air currents, simultaneously diffusing and, possibly, colliding through turbulent and Brownian processes. These processes dilute the particles and mix them with other particles and gaseous compounds (Figure 3.1). Collisions between two or more particles typically result in coagulation, wherein the original particles adhere to form larger particles having the sum of the original masses. Coagulation effectively increases the mass of particles while depleting smaller particles, and often is an important mechanism for shifting the aerosol-size spectrum toward larger particle sizes.

If the particles avoid coagulation, which is relatively rapid near their source, they travel beyond the source

region, interacting with vapors such as H_2SO_4 , organics, HNO_3 , and NH_3 . These semivolatile or reactive vapors, when their concentration exceeds specific thresholds, condense upon available surfaces, including the surfaces of existing particles. Some condensed vapors react with other vapors and attract them to the condensed phase as well. H_2SO_4 reacts with NH_3 , for example, and condensed organic compounds can dissolve other organic vapors. Particles form also as the consequence of gas-phase reactions such as the reaction of NH_3 with HNO_3 to form NH_4NO_3 , thus transferring gaseous material to the particulate phase. Consequently the particles grow in size and contain material derived both from their origin and from the places where they have been. Some of this deposited material may return to the gas phase if the conditions are right. For instance, NH_4NO_3 can volatilize to produce NH_3 and HNO_3 , and organic particles can volatilize to emit organic vapors. Because semivolatile particle components exchange continuously between the gas and condensed phases, it is difficult to measure PM concentrations in the atmosphere and to completely determine aerosol behavior and impact.

During their atmospheric lifetimes particles frequently encounter humidity environments exceeding 70 percent. Under such conditions and depending on their composition, they can absorb water vapor, consequently forming concentrated aqueous solutions. The amounts of water condensed by this process can be quite high, with particle-mass increases amounting to factors of three or four between low (<40 percent) and high (>80 percent) relative humidity. As relative humidity decreases, the water revolatilizes, resulting in particle drying.

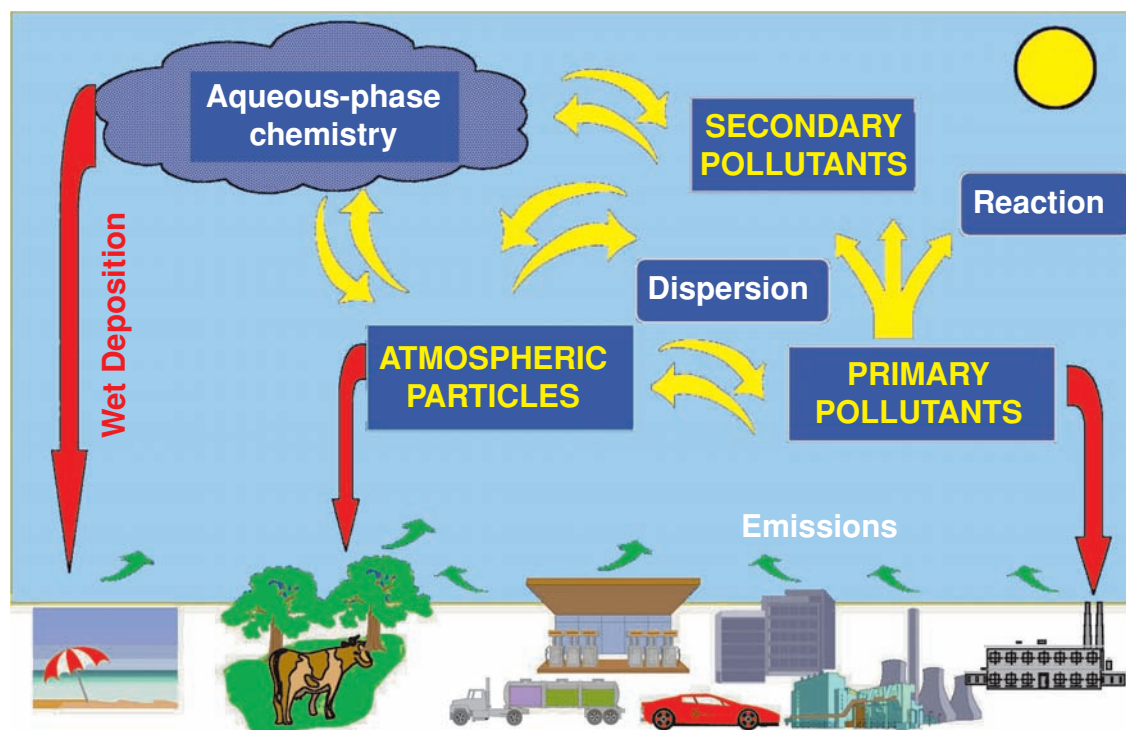


Figure 3.1. Schematic of the life cycle of atmospheric particles and their interactions with the gas and aqueous phases.

Typically, particles are transported extensive distances by the wind as the above-described physicochemical processes occur. At an average wind speed of a few meters per second, particles can travel a few hundred kilometers horizontally, and several kilometers vertically, in a period of one day.

When atmospheric particles experience relative humidities of around 100 percent or higher, they can absorb even larger amounts of water and form cloud droplets. This newly acquired water provides an environment suitable for a new suite of reactions, with the dissolution of SO_2 and its conversion to $\text{SO}_4^{=}$ being a prime example. In a majority of cases the cloud water subsequently re-evaporates, resulting in the re-formation of relatively dry particles. Such condensation-evaporation cycles usually leave their mark, however, with the progressive accumulation of condensed material, such as SO_4^- . Atmospheric particles eventually are removed by wet deposition in rain, snow, or fog water, or by dry deposition at the Earth's surface. Particles transported vertically to extended elevations generally have longer residence times and travel farther than particles at lower elevations.

As a result of particle emission, in-situ formation, and subsequent processes, the atmospheric particle distribution is characterized by a number of modes. The volume or mass distribution is dominated in most areas by two modes (Figure 3.2, lower panel): the accumulation mode (from around 0.1 to around $2\ \mu\text{m}$) and the coarse mode (from around 2 to around $50\ \mu\text{m}$). Accumulation-mode particles result from primary emissions, condensation of secondary sulfates, nitrates, and organics from the gas phase, and coagulation of smaller particles. In a number of cases the accumulation mode consists of two overlapping sub-modes, the condensation and droplet mode (Figure 3.2, lower panel) (John et al., 1990).

The condensation sub-mode results from primary particle emissions and growth of smaller particles by coagulation and vapor condensation. The droplet sub-mode is created during the cloud processing of some of the accumulation-mode particles. Particles in the coarse mode are usually produced by mechanical processes, such as wind or erosion (dust, sea salt, pollens, etc.). Most of the material in the coarse mode is primary, along with some secondary $\text{SO}_4^{=}$ and NO_3^- .

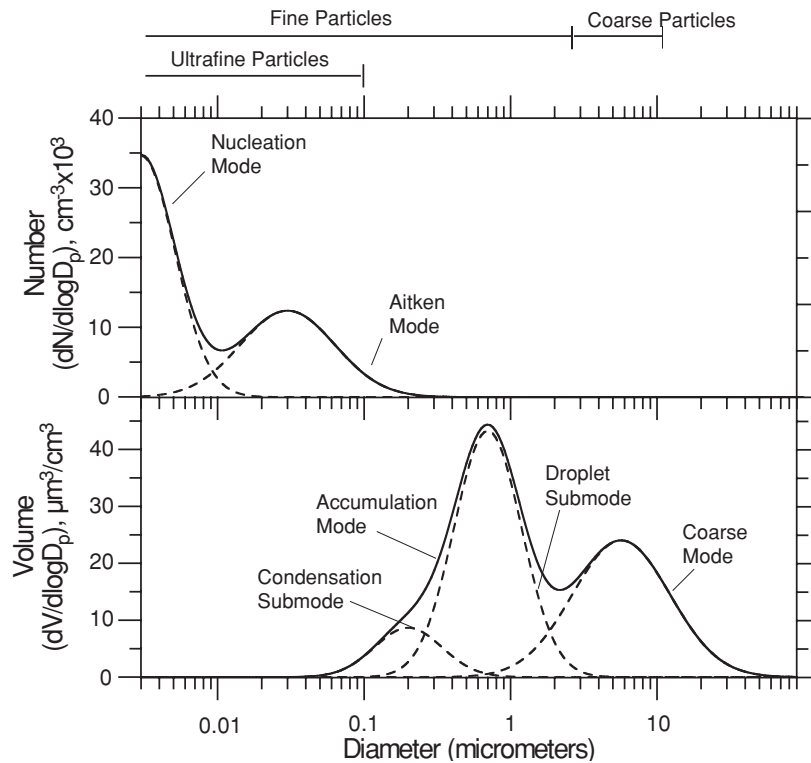


Figure 3.2. Typical number and volume distributions of atmospheric particles with the different modes.

A different picture of the ambient PM distribution is obtained if one focuses on the number of particles instead of their mass (Figure 3.2, upper panel). The particles with diameter larger than 0.1 μm that contribute practically all the PM mass are negligible in number compared to the particles smaller than 0.1 μm . Two modes usually dominate the PM number distribution in urban and rural areas: the nucleation mode (particles smaller than 0.01 μm or so) and the Aitken nucleus mode (particles with diameters between 0.01 μm and 0.1 μm or so). The nucleation-mode particles are usually fresh, created in-situ from the gas phase by nucleation. A nucleation mode may or may not be present in a particular aerosol, depending on the atmospheric conditions. Most of the Aitken nuclei start their atmospheric life as primary particles, and secondary material condenses on them as they are transported through the atmosphere. Nucleation-mode particles have negligible mass (for example 100,000 particles per cubic centimeter with a diameter equal to 0.01 μm have a mass concentration of less than 0.05 $\mu\text{g}/\text{m}^3$) while the larger Aitken nuclei form the accumulation mode in the mass distribution.

The composition of individual particles changes continuously during their atmospheric lifetimes. Near a source, the composition of primary particles is determined by chemical and physical processes that occur within the source. For example, primary particulate emissions from diesel engines include mostly lubricating oil and solid black carbon, while primary particulate emissions from coal-fired power plants include fly ash which consists mostly of oxides and minerals. In the absence of processing, atmospheric particles of a given size would consist of an external mixture of chemically distinct particles emitted by each contributing source type. Atmospheric processing, however, leads to coagulation and the addition of secondary species to preexisting particles, with the result that particles of a given size

become internally mixed and more similar chemically. Atmospheric measurements have shown that particles of a given size often include several chemically distinct types, and particles may include a mixture of compounds. Photographs of particles that were separated according to their tendency to absorb water are shown in Figure 3.3. The non-hygroscopic chain-agglomerate carbon particle shown in Figure 3.3a is similar in composition and morphology to particles emitted by diesel engines, while the hygroscopic particle shown in Figure 3.3b is nearly spherical and includes a mixture of sodium, sulfur, potassium and oxygen. Other work has shown that organics and sulfur are often found together in particles.

As noted in Text Box 1.1, particles with diameters larger than 2.5 μm are operationally identified as coarse particles while those with diameters less than 2.5 μm are called fine particles. The fine-particle category typically includes most of the total number of particles and a large fraction of the mass. Fine particles with diameters smaller than 0.1 μm are often called ultrafine particles.

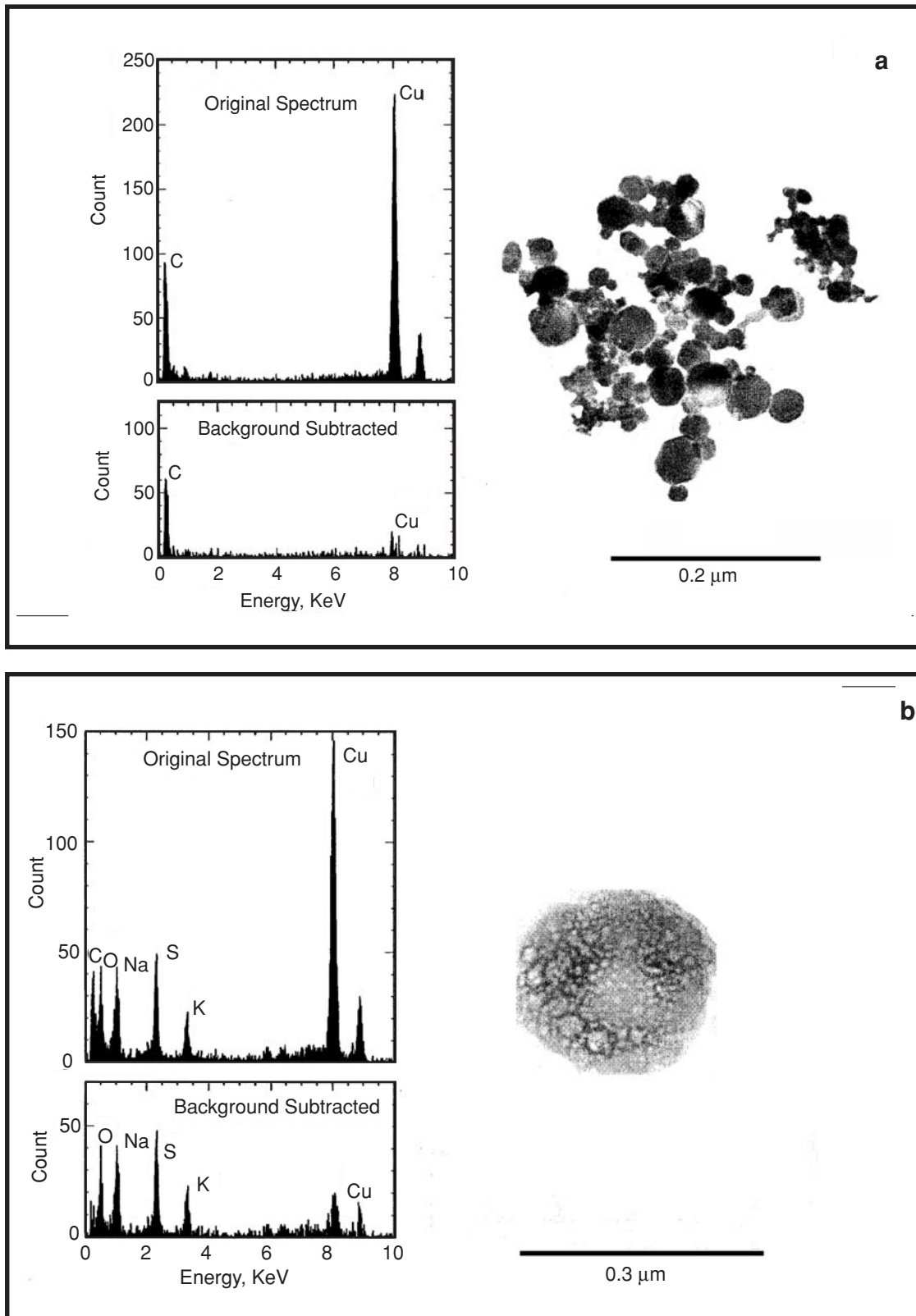


Figure 3.3. Electron micrographs of selected particles: a) carbon agglomerate and b) inorganic composite (McMurry et al., 1996).

3.2 A PARTICLE IS BORN: NUCLEATION

As indicated above, new atmospheric particles can form from gas-phase reactions in a number of different ways, with SO_4^- particle formation being the best-known example. In this process SO_2 reacts with hydroxyl radical forming H_2SO_4 vapor as a product. The H_2SO_4 molecules thus formed either condense on pre-existing particles or combine with each other and form new particles (homogeneous nucleation). The condensation path is by far the easiest if sufficient numbers of pre-existing particles are present (Seinfeld and Pandis, 1998). However, if the quantity of such pre-existing particles is insufficient to accommodate the continuously formed H_2SO_4 , its concentration increases, with the resulting formation of new particles. Water molecules participate in these reactions and it is speculated that NH_3 molecules play a role as well. A quantitative understanding of the role of organics in atmospheric nucleation does not exist even though it is known that they are prominent components of newly formed particles in forested regions. Under the right conditions (high H_2SO_4 production rate, high relative humidity, low temperature, low pre-existing PM concentration), tens of thousands of new particles per cubic centimeter can be formed in a matter of minutes. These particles have diameters of only a few nanometers and their mass is negligible compared to the rest of the particle distribution; however, their numbers can be huge and may dominate the total number concentration. Consequently homogeneous nucleation is not an important process if one is interested in PM_{10} or $\text{PM}_{2.5}$ or even PM_1 mass concentration; but it can be a major contributor to PM number concentration and formation of ultrafine particle mass. The sulfuric acid/water and sulfuric acid/water/ammonia systems are not the only ones of interest in this context. Newly formed organic vapors can also nucleate and form organic particles. These processes have been observed in the laboratory during the oxidation of biogenic hydrocarbons (Griffin et al., 1999) and there is evidence that they also occur near forests

(Kavouras et al., 1998). Nucleation has been shown to be prevalent in the upper troposphere where the conditions (low temperatures, low particle loadings) are favorable. Recent studies have documented nucleation events in major cities like Atlanta, rural polluted areas, and forests (McMurry et al., 2000). Despite this progress, the importance of nucleation as a source of ultrafine particles in urban and rural areas is still not well understood.

Substantial formation of new particles can occur as fresh combustion emissions are entrained into the ambient air, for example near the tailpipes of diesel vehicles (Kittelson et al., 1999). As hot vapors emitted by such sources are cooled, the emitted vapors become supersaturated and new particles form. These ultrafine particles consist largely of organic compounds similar in composition to lubricating oils and fuels (with some sulfates). The numbers of these particles typically increase with increasing fuel sulfur content and decreasing ambient temperature. Concentrations of these ultrafine particles typically follow rush-hour patterns and are quite high near roadways in populated regions. Describing the emissions of these ultrafine particles will be a significant challenge for the next generation of particle emission inventories.

New-particle formation rates can increase if one removes existing particles without removing the corresponding vapors. Technologies that reduce particle emissions without reducing gas-phase precursor emissions have the potential to increase particle number concentrations while decreasing particle diameter and mass. Nucleation is one of the least understood atmospheric aerosol processes. Recent measurements have shown that, during the course of a day, nucleated particles can grow to sizes where they can serve as cloud-condensation nuclei ($\sim 0.05 \mu\text{m}$). Therefore, it is likely that nucleation is significant to climate. Furthermore, if ultrafine particles are found to contribute significantly to health-effect impacts, the understanding of these processes will become critical. *Therefore, the ability to describe the formation of new particles by homogeneous nucleation should be improved.*

3.3 HOW LONG DOES IT TAKE FOR A PARTICLE TO COLLIDE WITH ANOTHER?

Coagulation occurs most efficiently between small particles (a few nanometers) and large ones (a few micrometers). The small particles experience rapid Brownian motion, while large ones provide big collision targets. Therefore, coagulation can be mainly viewed as a process for removing smaller atmospheric particles from the atmosphere. Coagulation has little or no effect on larger particles, because of the addition of a negligible mass to an already big particle. As a result, coagulation is an important process if one is interested in the small particles (or the total particle number) but it has little effect on PM_x mass concentrations with the exception of ultrafine particles. As a process, it is fairly well understood. The evolution of a typical urban particle-size distribution subject to coagulation is shown in Figure 3.4. Most particles with diameters smaller

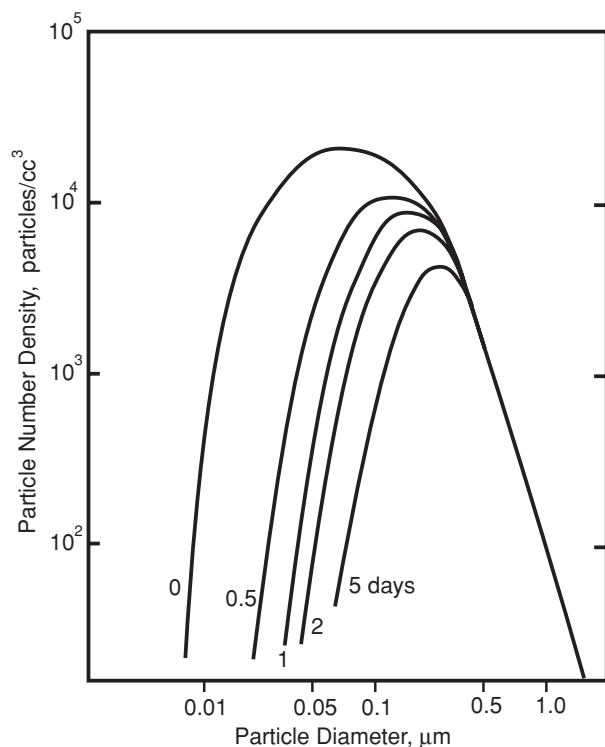


Figure 3.4. Evolution of a typical urban aerosol size distribution subject to coagulation.

than $0.02 \mu\text{m}$ disappear after a few hours as they coagulate into larger particles. After a few days most of the particles with diameters smaller than $0.1 \mu\text{m}$ also disappear. During these few days, coagulation has for all practical purposes no effect on the size distribution of particles with diameters above $0.3 \mu\text{m}$, which are responsible for most of the $PM_{2.5}$ mass concentration. If these particles are in a cleaner environment, at lower overall concentrations, their coagulation becomes less efficient with corresponding increases in particle lifetime (Schutz et al., 1990).

3.4 PARTICLES AND WATER

At very low relative humidity, most inorganic atmospheric particles are solid with the exception of H_2SO_4 . As the ambient relative humidity increases, the particles remain solid until the relative humidity reaches a critical threshold characteristic of the aerosol composition (illustrated as an example for salt, NaCl , in Figure 3.5). At this relative humidity (known as the deliquescence relative humidity), the solid salt particles spontaneously absorb water, producing a saturated aqueous solution. Further increase of the ambient relative humidity leads to additional condensation of water onto the salt solution. On the other hand, as the relative humidity over the wet particle is decreased, evaporation occurs. However, the solution generally does not crystallize at the deliquescence relative humidity, but remains supersaturated until a much lower relative humidity at which crystallization occurs. This hysteresis phenomenon is illustrated in Figure 3.5 for a mixed inorganic ($\text{NaCl}/\text{Na}_2\text{SO}_4$) particle, which deliquesces at 72 percent relative humidity and crystallizes at around 52 percent. For multi-component particles, the behavior becomes more complex but follows the same general principles. The ability of inorganic particles to absorb water is well understood (Figure 3.5), but questions still remain about the crystallization step. Some organic aerosol components are also hygroscopic, and there is growing evidence that organics contribute significantly to water uptake especially at low relative humidities (Saxena et al., 1995). Black carbon and OC are expected to react with OH and other oxidants, becoming hydrophilic; hence particles can absorb

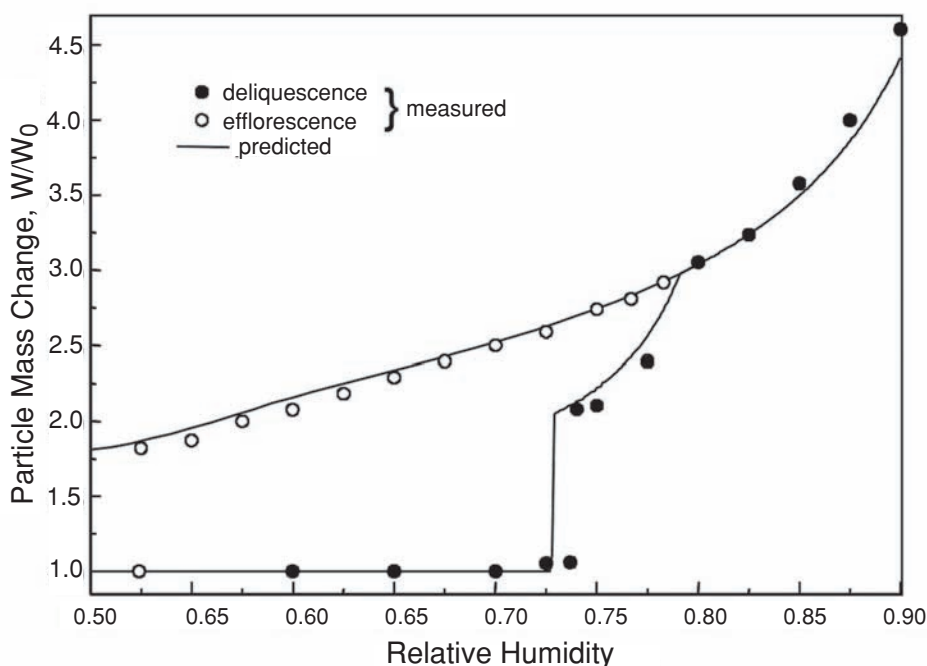


Figure 3.5. Growth (deliquescence) and evaporation (efflorescence) of a $\text{NaCl}/\text{Na}_2\text{SO}_4$ particle with changing relative humidity. The points are the laboratory measurements of Tang (1997) and the line the theoretical predictions of one of the aerosol thermodynamics models (Ansari and Pandis, 1999). The measurements indicate that the particle crystallized at 52 percent relative humidity.

water more efficiently as they age (Bertram et al., 2001). Despite these recent efforts, the effect of the OC fraction on the absorption of water by ambient particles is still not well understood. *More effort is needed to understand the properties of organic particles including factors that govern the hygroscopicity of organic compounds and their gas-particle partitioning.*

As the relative humidity and the water content of the particles change, so does the partitioning of unreactive semivolatile aerosol species. With everything else kept constant (atmospheric composition and temperature), a change in relative humidity changes the water content of atmospheric particles and therefore the preferences of aerosol components like nitrates or organics for the gas versus the condensed phases. Figure 3.6 shows that the NO_3^- concentration in a typical particle population can change from around $2 \mu\text{g}/\text{m}^3$ to $7 \mu\text{g}/\text{m}^3$ as the relative humidity of the environment increases from 30 to 80 percent.

The fact that atmospheric particles can absorb significant amounts of water at higher relative humidity and can retain some water at lower relative humidity creates a number of complications. As the “dry” PM mass (at 20 to 45 percent relative humidity) is the regulated quantity, the existence of water makes the measurement of this “dry” mass challenging. One needs to remove the water from the particles before the measurements. This change in particle composition can change the partitioning of the semivolatile aerosol components (usually

reducing the PM mass because of losses of NO_3^- and organics). At the same time, it is possible that some amount of water may be left in the PM sample during the mass measurement. The discrepancies observed in the northeastern United States between the total PM mass and the sum of the masses of its components could be due to remaining condensed water. This unknown mass is usually reported as “other” in PM measurements. As the airways in the human body are environments of high relative humidity, similar changes happen to the particles during respiration.

3.5 SECONDARY PM FORMATION

Most of the observed ambient $\text{PM}_{2.5}$ mass usually originates as precursor gases (SO_2 , NH_3 , NO_x , VOC) and, through the physicochemical processes noted above, is transferred to the condensed phase. This fraction of the PM mass is called secondary.

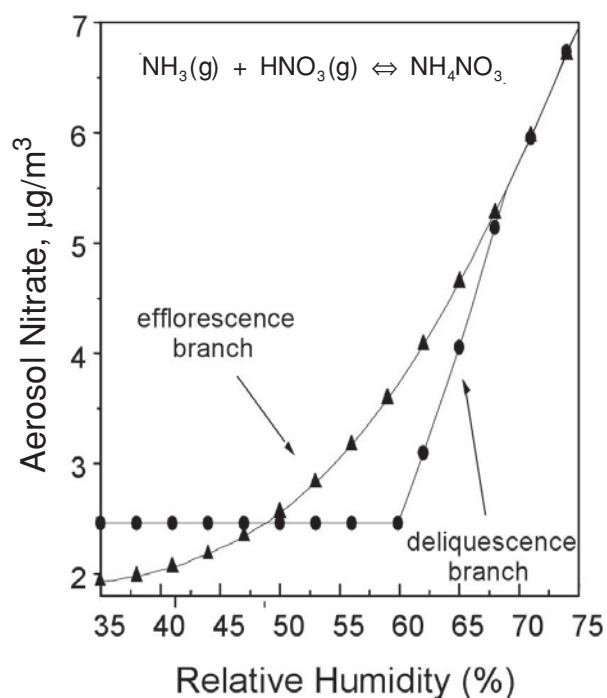


Figure 3.6. Predicted particulate nitrate concentration as a function of relative humidity for a typical environment. The actual value in the atmosphere will depend on the history of the aerosol particles.

3.5.1 Sulfate

The formation of $\text{SO}_4^{=}$ from the oxidation of SO_2 is an important process for most areas in North America. There are three different pathways for this transformation:

1. The oxidation of SO_2 in the gas phase by the hydroxyl radical, OH . This occurs at an average rate of 0.1 percent to 1 percent of SO_2 per hour (with peak rates up to 5 percent per hour) during the daytime. Nighttime conversion via this pathway is essentially negligible.
2. The dissolution of SO_2 in cloud, fog, or rain water and subsequent aqueous-phase oxidation (Figure 3.7). After the cloud evaporates, the $\text{SO}_4^{=}$ remains in the particles and is

eventually deposited to the surface. Aqueous-phase production can be very fast: in some cases all the available SO_2 can be oxidized in less than an hour. Near SO_2 sources the process is usually limited by the availability of oxidants such as hydrogen peroxide, H_2O_2 . An oxidation mechanism that generally takes place more slowly than oxidant-driven transformation of dissolved SO_2 is catalysis by transition heavy metals such as manganese and iron.

3. The oxidation of SO_2 in reactions in the water of the aerosol particles themselves. This process takes place continuously, but only produces appreciable $\text{SO}_4^{=}$ in alkaline (dust, sea salt) coarse particles (Sievering et al., 1992). Oxidation of SO_2 has been also observed on the surfaces of black carbon and metal oxide particles.

During the last twenty years, much progress has been made in understanding the first two major pathways, but some important questions still remain about the smaller third pathway. Models indicate that more than half of the $\text{SO}_4^{=}$ in the eastern United States and the overall atmosphere is produced in clouds (McHenry and Dennis, 1994; Langner and Rodhe, 1991). Processing of SO_2 -rich air masses by clouds or fogs during stagnation periods can lead to elevated concentrations of $\text{SO}_4^{=}$ during specific days both in

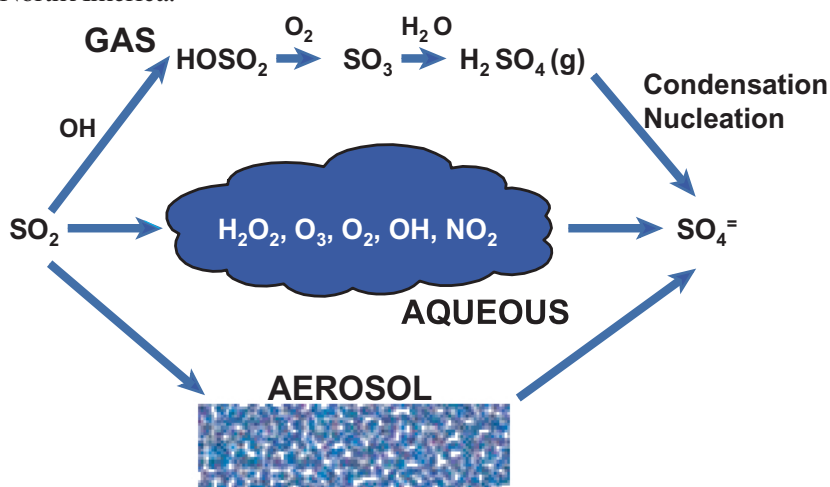


Figure 3.7. Schematic of the three pathways (reaction in the gas, cloud, and condensed phases) for the formation of $\text{SO}_4^{=}$ in the atmosphere. Some of the reactions in the aqueous and condensed phases (e.g., oxidation by oxygen) are catalyzed by trace amounts of metals.

the western (Pandis et al., 1992) and the eastern United States (Stein and Lamb, 2000).

The H_2SO_4 formed from the above pathways reacts readily with NH_3 to form ammonium sulfate, $(\text{NH}_4)_2\text{SO}_4$. If there is insufficient NH_3 present to fully neutralize the available H_2SO_4 (one molecule of H_2SO_4 requires two molecules of NH_3), part of the PM exists as ammonium bisulfate, NH_4HSO_4 (one molecule of H_2SO_4 and one molecule of NH_3) and the associated particles are acidic. In extreme cases, sulfates can exist in particles as H_2SO_4 .

3.5.2 Nitrate

Nitrates are formed from the oxidation of NO and NO_2 (NO_x) either during the daytime (reaction with OH) or during the night (reactions with ozone and water) (Wayne et al., 1991). Nitric acid is continuously transferred between the gas and the condensed phases (condensation and evaporation) in the atmosphere (Figure 3.8). It naturally prefers the gas phase (when left alone), but reactions with gas-phase NH_3 , sea salt, and dust result in its transfer to the condensed phase (Seinfeld and Pandis, 1998). The formation of aerosol NH_4NO_3 is favored by availability of NH_3 , low temperatures, and high relative humidity. The resulting NH_4NO_3 is usually in the sub-micrometer particle range. Reactions with sea salt and dust lead to the formation of NO_3^- in the coarse particles. The availability of significant HNO_3

vapor in an area (even if the particulate NO_3^- concentrations are low or zero) is an indication of the potential for the future formation of NO_3^- -containing particles. Heterogeneous reactions and perhaps photolysis lead to the reduction of particulate NO_3^- and return nitrogen oxides to the gas phase. These reactions are poorly understood but could be important (Honrath et al., 2000).

3.5.3 Secondary Organic Aerosol (SOA) Formation

The organic component of ambient particles is a complex mixture of hundreds or even thousands of organic compounds. These organic compounds are either emitted directly from sources (primary organic aerosol) or can be formed in-situ by condensation of low-volatility hydrocarbon-oxidation products (secondary organic aerosol). As organic gases are oxidized by species such as OH, ozone, and NO_3 , their oxidation products accumulate. Some of these products have low volatilities and condense on available particles (Figure 3.9).

The ability of a given volatile organic compound (VOC) to produce SOA during its atmospheric oxidation depends on four factors: its atmospheric abundance, its chemical reactivity, the availability of oxidants, and the volatility of its products.

Many VOCs do not form PM under atmospheric conditions, owing to the high vapor pressure of their products. These include all alkanes with up to six carbon atoms (from methane to hexane isomers), all alkenes with up to six carbon atoms (from ethane to hexene isomers), benzene and many low molecular-weight carbonyls, chlorinated compounds, and oxygenated solvents (Figure 3.9). This Assessment refers to VOCs that produce SOAs as SOA precursors.

Aromatics are by far the most significant anthropogenic SOA precursors (Grosjean and Seinfeld, 1989). Compounds like toluene, xylenes, trimethyl-benzenes, emitted

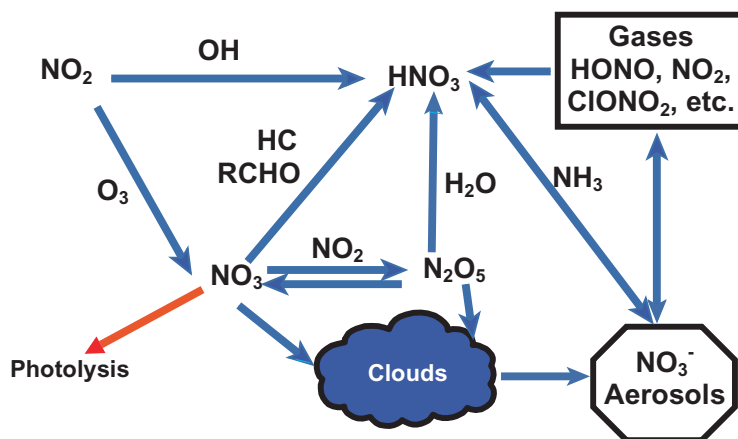


Figure 3.8. Schematic of the formation of HNO_3 and particulate NO_3^- in the atmosphere. Formation of particulate NO_3^- from HNO_3 requires either reaction with NH_3 , sea salt or alkaline dust.

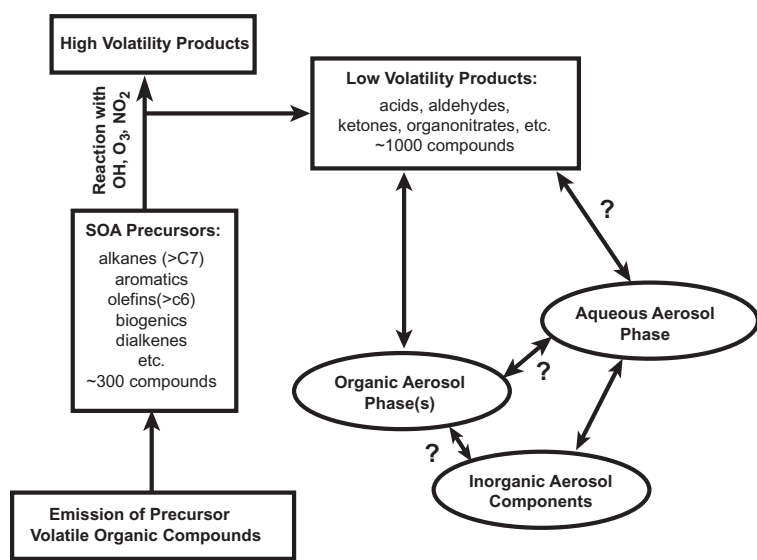


Figure 3.9. Schematic of the formation of secondary organic aerosol in the atmosphere.

by transportation and industrial sources, have been estimated to be responsible for 50 to 70 percent of the SOA. The experimental work of Odum et al. (1997) demonstrates that the SOA-formation potential of gasoline can be accounted for almost totally in terms of its aromatic fraction. Biogenic hydrocarbons emitted by trees are expected to be also an important source of secondary organic PM. Isoprene, an important biogenic VOC, does not form organic aerosol under ambient conditions; but terpenes (α - and β -pinene, limonene, carene, etc.) and the sesquiterpenes are expected to be major contributors to SOA in areas with significant vegetation cover. The rest of the anthropogenic hydrocarbons (higher alkanes, paraffins, etc.) have been estimated to contribute 5 to 20 percent to SOA concentrations, depending on the area.

The contribution of primary and secondary organic aerosol components to measured organic aerosol concentrations remains a controversial issue. Most of the relevant work in this area has been done in Southern and more recently Central California, and relatively little is known about the rest of North America. Early studies suggested that the majority of observed organic PM was secondary in nature. Later investigators focusing on the emissions of primary organic material proposed that 80 percent or so of the organic PM in Southern California on a monthly basis was primary (Hildemann et al., 1993).

More recent studies suggest that the primary and secondary contributions are highly variable. Studies of pollution episodes (Turpin et al., 2000) indicated that the contribution of SOA to the organic PM varied from 20 percent to 80 percent during the same day. The contribution of vegetation to organic PM loadings is expected to depend on spatial vegetation coverage. This issue remains unresolved, and most of the existing estimates are highly uncertain. *The ability to model processes that involve carbonaceous PM should be improved.*

A multiplicative factor of 1.4 is commonly used to estimate organic-particle mass concentrations from raw OC measurements. The value of this factor has been the topic of considerable

debate (Turpin et al., 2000). Turpin and Lim (2001) suggested that while 1.4 is a reasonable estimate of the average organic molecular weight per carbon for an urban aerosol, a ratio of 1.9-2.3 is more accurate for an aged aerosol, and 2.2-2.6 better represents an aerosol heavily impacted by wood smoke.

Despite the significant progress that has been made in understanding the origins and properties of organic PM, it remains the least understood component of $PM_{2.5}$. Its chemical complexity and the difficulty in determining its chemical composition, even by state-of-the-art methods, are limiting progress. The best efforts to unravel the chemical composition of organic PM have quantified the concentrations of hundreds of organic compounds, yet represent only 10 to 20 percent of the total organic aerosol mass (Figure 3.10). *Our understanding of the contributions of primary, secondary, biogenic, and anthropogenic organic PM components should be improved.*

3.5.4 Interactions of Primary and Secondary PM Components

Primary aerosol particles (e.g., BC, organics, dust, sea salt, fly ash) have both direct and indirect roles in the formation of secondary PM. Primary particles can serve as reaction sites for the formation of new

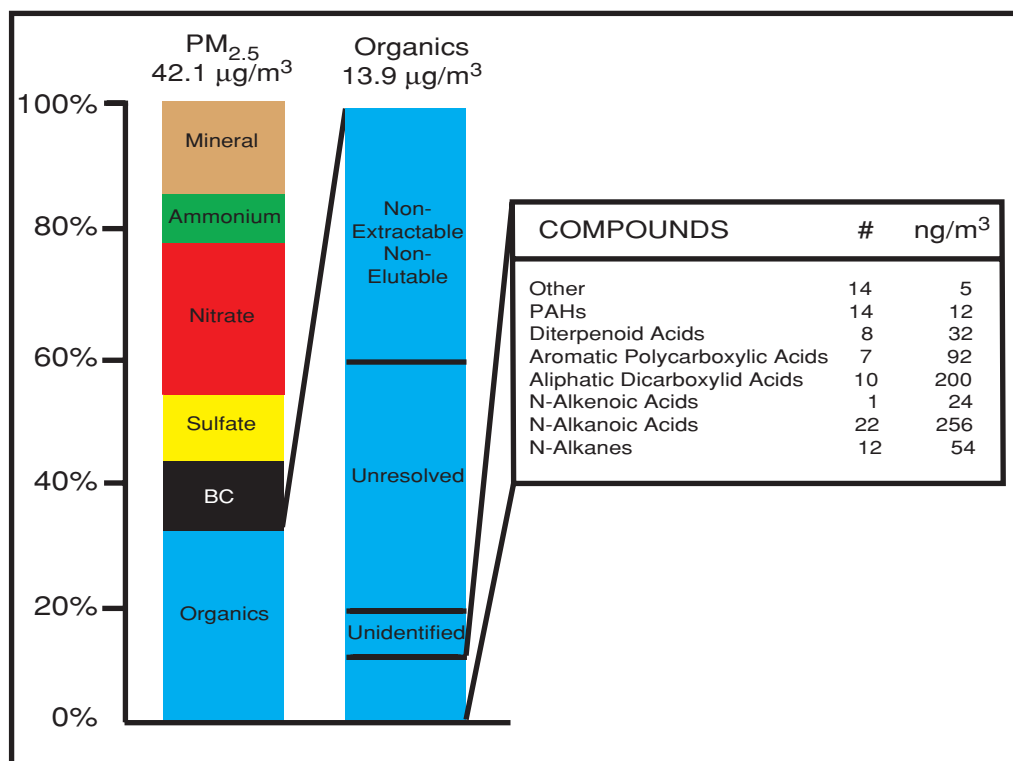


Figure 3.10. Speciation results for organic aerosol in Southern California (Rogge et al., 1993). Even if a hundred or so individual organic compounds are identified and quantified, they represent only 15 percent or so of the total organic mass.

particulate material. The formation of NO_3^- by the reaction of sea salt or alkaline dust with HNO_3 vapor is an example of such reactions (Seinfeld and Pandis, 1998). Other important reactions include the formation of SO_4^{2-} on alkaline particles (discussed previously in Section 3.5.1) and the oxidation of primary organic aerosol compounds to more hydrophilic ones (Zhang et al., 1993). A number of studies have suggested that BC particles react with SO_2 , ozone, and NO_x influencing both the gas- and particle-phase composition (Seinfeld and Pandis, 1998). The strong dependence of the often-conflicting results of these laboratory investigations on the nature of the BC surfaces used has prevented the extrapolation of their results to the atmosphere. As a result, the role of BC particles as sites for the production of SO_4^{2-} or NO_3^- remains not well understood.

3.6 FROM PRECURSOR EMISSIONS TO AEROSOL COMPONENT CONCENTRATION

As noted above, major precursors of secondary PM are SO_2 , NO_x , selected VOCs, and NH_3 . Other precursors like HCl, or dimethyl sulfide (DMS) are of secondary importance for most areas of interest in North America and will not be discussed further. Establishment of the relationship between the emissions of the above precursors and the PM concentrations in a given area is a necessary first step for the design of a $\text{PM}_{2.5}$ control strategy. Calculating the sensitivity of the concentration of $\text{PM}_{2.5}$ in a specific area to a reduction of SO_2 emissions is one example. Precursor emissions exhibit spatial and temporal variability, but for the sake of simplicity, the following discussion focuses on spatially and temporally uniform changes in precursor emissions. The relative contributions of long-range transport and local emissions are discussed in Chapter 8.

3.6.1 Linearity

The change in the emissions of a precursor and the change in the concentrations of its PM product(s), e.g., SO₂ and SO₄⁼, can be related by:

$$\begin{aligned} \text{\% change in PM concentration} \\ \text{of component } i \end{aligned} = \text{(Transfer Coefficient)} \times \left(\begin{aligned} \text{\% change in emission rate} \\ \text{of component } i \end{aligned} \right)$$

This simplified relationship assumes that all of the sources of the precursor are reduced uniformly, and that primary emissions or transport of PM component *i* into the airshed are negligible. The transfer coefficient accounts for the effects of all the atmospheric processes (dispersion, advection, chemical reactions, removal, etc.) affecting the PM component between the source of the precursor and receptor. The value of this coefficient depends not only on the precursor-PM component combination (e.g., SO₂ and SO₄⁼, VOC and SOA, NO_x and NO₃⁻, etc.) but also on the location, season, magnitude of the emissions, averaging time, etc. The above equation can also be written as:

$$\frac{\text{Post-control concentration of component } i}{\text{Pre-control concentration of component } i} = \left(\frac{\text{Post-control precursor emission rate}}{\text{Pre-control precursor emission rate}} \right) \text{Transfer Coefficient}$$

When the transfer coefficient is close to one, then atmospheric concentrations of the secondary PM vary in direct proportion to the emission rates of the precursor gases. In this case the relationship between secondary particles and gas-phase precursors is said to be linear. For nonlinear processes, the transfer coefficient is significantly different from one and is a strong function of the emissions. In such cases percent change in concentrations of secondary particulate matter may exceed or be less than the percent change in precursor-gas emissions.

The above approach is applicable to the direct relationship between precursor and aerosol components (e.g., SO₂ and SO₄⁼ or NO_x and NO₃⁻). However, each precursor may indirectly affect the other aerosol components. For example, changes in

NO_x affect gas-phase chemistry and therefore change the concentrations of OH radical, H₂O₂, ozone, NO₃ radical, etc. These changes result in corresponding changes in SO₄⁼ production rates (both in clean air because of OH and in clouds because of H₂O₂). These indirect effects can be quite significant: they result from complicated interactions and the major issue is not linearity of the corresponding processes (they are rarely linear), but rather their overall significance.

Previous applications of chemical-transport models (see Chapter 8) have exemplified the non-intuitive aspects of PM/precursor relationships. For example, reductions in VOC emissions have been predicted to lead sometimes to increases (Meng et al., 1997; Pai et al., 2000) and sometimes to decreases (Lurmann et al., 1997) in summertime PM_{2.5} concentrations in the Los Angeles Basin, and to decreases in wintertime PM_{2.5} concentrations in the California San Joaquin Valley (Pun and Seigneur, 1999). In addition, one must be aware that an emission-control strategy that is beneficial to ozone concentrations may be counterproductive for PM concentrations. Moreover, an emission-control strategy that benefits one PM component may adversely affect another. A summary of the possible responses of ozone and PM concentrations to changes in emission levels is presented in Section 3.8. Most of these complicated effects can be predicted by state-of-the-art chemical-transport models (see Chapter 8).

One approach that can be used to combine these direct and indirect effects is to examine the overall response of PM_{2.5} concentrations (and not just the effect on one of the PM_{2.5} components) to changes in the emissions of a precursor using the overall transfer coefficient (Seigneur et al., 2000):

$$[\text{Overall Transfer Coefficient}] = [\text{Percent change of total PM}_{2.5}] / [\text{Percent change in source emission strength}]$$

An overall transfer coefficient of unity represents a proportional relationship (e.g., a 50 percent decrease in precursor emissions leads to a 50 percent decrease in PM_{2.5}), an overall transfer coefficient of zero represents no change in PM_{2.5}, and a negative transfer coefficient represents an inverse relationship (i.e., a decrease in precursor emissions leads to an increase in PM_{2.5} concentrations). The overall response of PM_{2.5} to emission controls for a given source (overall transfer coefficient) can be calculated as the sum of

the responses (individual transfer coefficients) of the various $PM_{2.5}$ components weighted by their fractional contribution to the total $PM_{2.5}$.

If the direct relationship of the precursor to the aerosol product is linear (transfer coefficient equal to one) and the precursor has no effect on the other aerosol components (transfer coefficient equal to zero) then the overall transfer coefficient (response of the total aerosol concentration to the emission change) is equal to the fraction of the component of interest in the ambient $PM_{2.5}$.

3.6.2 An Application to Southern California

Most of the available information about these relationships comes from model applications to Southern California. As an example, the transfer coefficients for a summer smog episode in Southern California are given in Table 3.1 (Lurmann et al., 1997). These were calculated for a uniform 50 percent reduction in the corresponding emissions throughout the basin and correspond to the average changes in concentrations in 8 locations. These results are theoretical estimates for a specific area and a given episode, and while by no means general are still instructive. None of the reported transfer coefficients (values in blue in Table 3.1) is equal to one. The reductions in ambient $SO_4^{=}$ concentrations are less than one because of background $SO_4^{=}$ levels and primary $SO_4^{=}$ emissions. The deviation of the transfer coefficients from unity during NO_x and NH_3 emission reductions results from gas- and aerosol-chemistry nonlinearity. Finally, the small sensitivity of organic PM to VOC reductions results from significant primary organic PM sources during that episode. The same study suggests that based on current understanding, a number of the indirect

effects are of secondary importance, at least for this area. For example, the effect of NO_x on $PM_{2.5} SO_4^{=}$ was calculated as -0.04 (a 50 percent reduction in NO_x resulted in a 2 percent increase in $SO_4^{=}$) (see Dennis et al., 2001 for a discussion of this effect for the eastern United States). However, these simulations indicate a number of additional benefits of some controls: VOC reductions in some cases also reduce NH_4NO_3 (sometimes they have the opposite effect). Some of the most counter-intuitive features of the system are also illustrated by this example (values in red in Table 3.1). Emission reductions of some of the precursors can indirectly increase other $PM_{2.5}$ components. In this case SO_2 controls lead to increased NO_3^- levels, and NO_x controls lead to increased OC concentrations. The change in organics is relatively small and results from the change in oxidation rates of the precursors at different VOC/ NO_x ratios (Lurmann et al., 1997).

3.6.3 Effectiveness of SO_2 Emission Reductions

The increase in NO_3^- corresponding to SO_2 emission decreases can be a significant issue for the design of emission-control strategies. When the SO_2 concentrations decrease, then the major product, $SO_4^{=}$, also decreases. However, this $SO_4^{=}$ does not exist alone but is usually in the form of $(NH_4)_2SO_4$. In this case, when the $SO_4^{=}$ is reduced NH_4^+ volatilizes, leading to more NH_3 available in the gas phase. The additional gas-phase NH_3 can react with any available HNO_3 to produce NH_4NO_3 -containing PM. Consequently the system can respond to reductions in $SO_4^{=}$ by substituting it with the available HNO_3 as NO_3^- . This replacement of the “lost $SO_4^{=}$ ” by NO_3^- is expected to happen practically always,

Table 3.1. Predicted changes (percent Concentration Reduction/percent Emission Reduction) in aerosol component concentrations for a uniform 50 percent reduction in precursor emissions for Southern California (June 1987) (Lurmann et al., 1997).

Emission Change	$SO_4^{=}$	NO_3^-	NH_4^+	OC	$PM_{2.5}$
SO_2	0.64	-0.14	0.10	< 0.05	0.06
NO_x	< 0.05	0.40	0.22	-0.08	0.12
NH_3	< 0.05	0.82	0.68	< 0.05	0.42
VOCs	< 0.05	0.16	0.10	0.16	0.08

sometimes with a negligible effect and sometimes to a significant extent. In the extreme case, if all the NH_3 returns to the condensed phase, removal of one $(\text{NH}_4)_2\text{SO}_4$ molecule (molecular weight of 132 g) can result in the formation of two NH_4NO_3 molecules (molecular weight of 80 g). So 132 mass units of PM are replaced by $2 \times 80 = 160$ mass units. In this extreme case, the reduction of SO_2 emissions by 64 g (1 mole) leads to a reduction of $(\text{NH}_4)_2\text{SO}_4$ by 132 g (1 mole) and an increase of NH_4NO_3 by 160 g (2 moles). The transfer coefficient of NH_4NO_3 for an SO_2 emission change therefore can be as low as -2.5 (an increase of NO_3^- 2.5 times the reduction of SO_2), and for the total $\text{PM}_{2.5}$ as low as -0.44 . Obviously, in the other extreme reduction of SO_2 emissions by 1 mole leads to the removal of 1 mole of $(\text{NH}_4)_2\text{SO}_4$ and the transfer coefficient is as much as $+2.06$. These estimates illustrate the importance of NH_3 and its emissions in determining the effectiveness of SO_2 emission reductions.

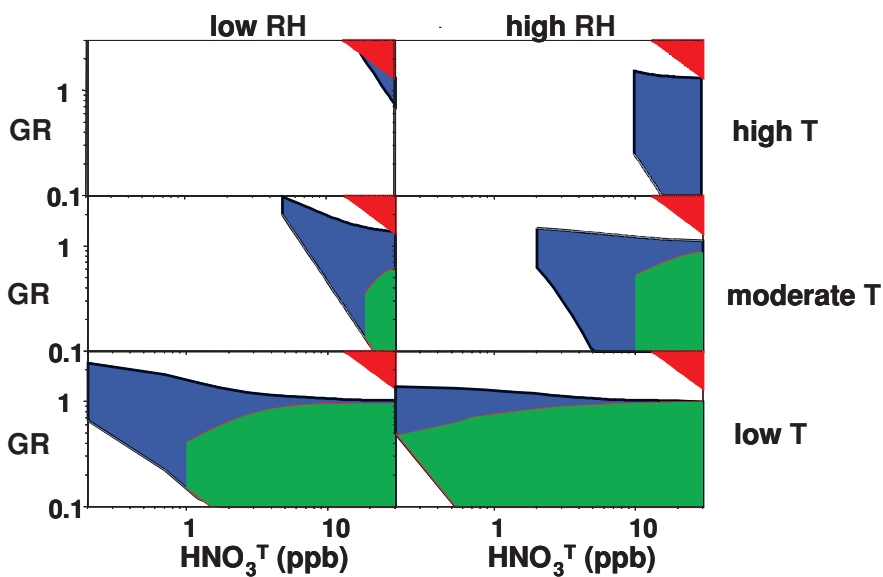
Ansari and Pandis (1998) proposed a method for the quantification of this response for a given area based on measurements of the $\text{SO}_4^{=}$, total nitrate (gas and condensed phases) and total ammonium (gas and condensed phases). The system response, defined as the change in $\text{PM}_{2.5}$ for the change in $\text{SO}_4^{=}$, is shown

in Figure 3.11. The green areas correspond to increases in $\text{PM}_{2.5}$ for reductions of $\text{SO}_4^{=}$, the blue areas correspond to nonlinear behavior of the system (reduction of $0-1 \mu\text{g}$ of $\text{PM}_{2.5}$ for each reduced μg of $\text{SO}_4^{=}$), and the white areas correspond to the near-linear behavior (reduction of $1-1.34 \mu\text{g}$ of $\text{PM}_{2.5}$ for each μg of reduced $\text{SO}_4^{=}$). The areas are defined as a function of the gas ratio:

$$\text{GR} = [\text{NH}_3]^F / [\text{HNO}_3]^T$$

where $[\text{NH}_3]^F$ is the “free” NH_3 , that is NH_3 not associated with $\text{SO}_4^{=}$, and $[\text{HNO}_3]^T$ is the total nitrate (gas and aerosol). The concentration of free NH_3 is calculated by subtracting from the total NH_3 twice the moles of $\text{SO}_4^{=}$. Figure 3.11 indicates that the region of nonlinearity increases at low temperatures (wintertime and during the night) and at high relative humidity. This approach was applied to the eastern United States using data from the EMEFS study (1988-1990) (West et al., 1999). This work indicated that a significant area centered in the Ohio River valley, and extending from western Tennessee to Michigan to New Jersey was in the nonlinear or negative regime during the winter (Figure 3.12). In contrast, no site displayed nonlinearity in the summer, when higher temperatures inhibit the formation of NH_4NO_3 , and the PM is commonly acidic.

The spring and autumn results showed nonlinear responses in the upper Midwest (Ohio, Indiana and Illinois). While the method is general, the data used are dated. Application of such techniques to other areas or periods is currently limited by the lack of appropriate data. It is important to monitor concentrations of gas-phase precursors including NH_3 and HNO_3 as well as PM composition in order to understand the



■ = nonlinear response □ = expected response ■ = negative response ■ = out of range

Figure 3.11. Response of the fine PM mass to changes in $\text{SO}_4^{=}$ concentration as a function of the available HNO_3 , the gas ratio GR, temperature, and relative humidity. The white area (expected response) corresponds to linear behavior.

sensitivity of NH_4NO_3 concentrations to SO_2 emission rates.

SO_2 and $\text{SO}_4^{=}$ reductions correspond to movements vertically in the diagrams of Figure 3.11. Consequently areas currently in the linear regime may be approaching the nonlinear range, while others may be exiting the nonlinear response area and returning to the linear regime.

3.6.4 VOC Emission Reductions and SOA

The response of the organic component of atmospheric PM to emission changes is complicated by its dual origin. The primary component (direct emission of OC from combustion sources, etc.) is expected to respond practically linearly to emission changes. However, the secondary component is linked to VOC and NO_x emissions through strongly nonlinear chemical and thermodynamic processes. Quantification of the primary and secondary components of observed OC is the first task in the design of any OC control strategy. Unfortunately such analyses have been performed primarily for

Southern and Central California, and little is known about OC origins in the rest of North America. Secondary organic PM is expected to respond only weakly to emission changes of the lower molecular-weight VOCs (below than six carbon atoms). As noted previously, these smaller compounds are not important organic PM precursors and therefore influence the organic PM only indirectly by affecting the levels of radicals and ozone. The formation of organic solutions by these compounds suggests that there is a super-linear relationship (the transfer coefficient is more than one) between OC precursors and SOA. Reduction of the emissions of a precursor will reduce not only the concentrations of the products of this precursor in the PM, but also transfer a fraction of the other organic compounds to the gas phase. Even if these processes are qualitatively understood, uncertainties about the details of the chemistry and thermodynamics of SOA do not currently allow the accurate quantification of these relationships. *The ability to model the chemical properties of secondary organic aerosol should be improved.*

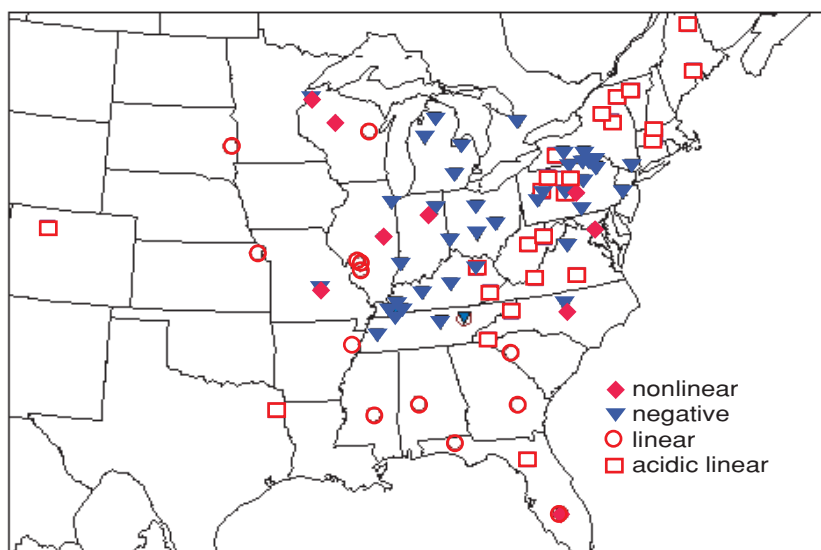


Figure 3.12. Estimated response of fine PM to changes in $\text{SO}_4^{=}$ during the winters of 1988-90 (West et al., 1999). Blue points correspond to increases of the $\text{PM}_{2.5}$ if $\text{SO}_4^{=}$ is reduced, and red points to significant replacement of $\text{SO}_4^{=}$ by NO_3 with a net reduction of $\text{PM}_{2.5}$. The open symbols reflect linear changes (an overall transfer coefficient of 1.0 for “acidic linear”, and 1.34 for “linear”).

3.6.5 Limiting Reactants

A useful concept for the design of control strategies for secondary PM is that of a limiting reactant. For cases where such a reactant exists, the secondary PM component responds readily to concentration changes of this reactant while at the same time it does not respond to changes in the concentrations of other precursors. This is similar in concept to the NO_x - and VOC-limited regimes in ozone formation. Available thermodynamic models can be used to determine if NH_3 , H_2SO_4 , or HNO_3 are limiting the formation of particulate NO_3^- , based on measurements of the availability of the gas and condensed phase

concentrations of these precursors (Blanchard et al., 2000; Watson et al., 1994). Figure 3.13 shows isopleths of particulate NO_3^- concentrations as a function of total HNO_3 and total NH_3 for given concentrations of the remaining aerosol components, temperature, and relative humidity (Blanchard et al., 2000). For a range of temperatures and relative humidities, these isopleths are approximately L-shaped, with a rather sharp transition between the horizontal and vertical segments. Where the isolines are horizontal, PM formation is not limited by NH_3 availability, as all nitrate exists in the condensed phase. The availability of HNO_3 is limiting the formation of particulate NO_3^- . Where the isolines are vertical, particulate NO_3^- formation is NH_3 -limited but not HNO_3 -limited.

Application of all these measurement-based techniques (which do not require emission inventories) is based on measurements of both gas and PM concentrations (NH_3 , NH_4^+ , HNO_3 , NO_3^-). These are not routinely collected. Simpler computational approaches and rules of thumb have been proposed if one wants to avoid the use of an aerosol thermodynamic model (Blanchard et al., 2000). In order to improve the understanding of limiting reagents in NO_3^- formation, sampling networks should include collocated measurements of gas-phase NH_3 and HNO_3 , as well as of particulate composition.

The above illustrative examples are based on numerical models representing the state-of-science in this area. These tools are by no means perfect (see discussion in Chapter 8) and neglect a number of potentially important processes (interactions between organic and inorganic aerosol components, different compositions of particles of the same size, etc.). The models have been able to reproduce daily-average $\text{PM}_{2.5}$ concentrations with errors of 30 to 50 percent, which are probably indicative of predictive ability. Finally, given the complexity of the system, direct extrapolation of these results for specific receptors to other areas in North America should be avoided. Application of the above modeling tools and chemical-transport models in other areas (see Chapter 8) can provide the corresponding insights about the responses of PM to changes in emissions of SO_2 , NO_x , VOCs, and NH_3 .

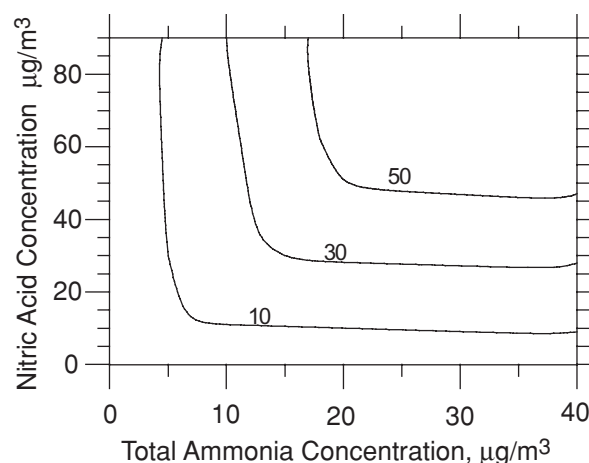


Figure 3.13. Isopleths of predicted particulate NO_3^- concentration ($\mu\text{g}/\text{m}^3$) as a function of total (gaseous + particulate) NH_3 and HNO_3 at 293 K and 80 percent relative humidity. The concentrations of other species were $25 \mu\text{g}/\text{m}^3$ of SO_4^{2-} , and $2 \mu\text{g}/\text{m}^3$ of total chloride (Blanchard et al., 2000).

3.7 REMOVAL AND LONG-RANGE TRANSPORT OF PM

Wet and dry deposition are the ultimate paths by which particles are removed from the atmosphere. Dry deposition is, broadly speaking, the transport of gaseous and particulate species from the atmosphere onto surfaces in the absence of precipitation (including removal by fog deposition). Factors governing the dry deposition of atmospheric particles include the level of atmospheric turbulence, the properties of the particle (size, density, shape, composition), and the nature of the surface itself. The typical lifetimes of the sub-micrometer particles subject only to dry removal are of the order of a few weeks or even months. Particles with diameters in the 0.1 to 1 μm range live the longest because of their slow transfer through the quasi-laminar layer next to the ground. For larger particles, the lifetime, based solely on considerations of dry deposition, is of the order of a few days. While the above values are typical, actual particle lifetimes can be significantly longer or shorter depending on where the particles are emitted (e.g., close to the ground), and on atmospheric conditions.

Figure 3.14 presents a schematic depiction of PM wet-removal processes. It involves first the

transformation of the particle to a new hydrometeor by condensation of water (cloud, rain, fog droplets or ice crystals), or its collision and capture by a pre-existing one, and then its delivery to the earth's surface. Both processes take place inside a cloud, while raindrops collect and remove particles below a raining cloud. The transformation of inorganic particles to cloud droplets (called cloud-droplet nucleation) is relatively well understood, while questions still remain about the ability of organic particles to serve as cloud condensation nuclei. The fundamentals of the removal of particles by the falling rain under a cloud are also relatively well understood (U.S. NAPAP, 1991). Large particles (larger than a few micrometers) are once more collected and removed efficiently by droplets both inside and below the cloud. For particles in the 0.5 to 2.5 μm range, nucleation to cloud droplets during the cloud-formation stage is the most efficient pathway for their incorporation to cloud and then rain droplets. Their composition (inorganic versus organic) is a critical factor for cloud-droplet nucleation and the droplet's subsequent lifetime.

The typical lifetime of a particle in the lower troposphere (Jaenicke, 1993) is shown in Figure 3.15. For particles responsible for most of the $\text{PM}_{2.5}$ mass concentration, the lifetime is estimated to be around a week on average. For individual particles the actual lifetime can vary from seconds to several weeks or months. Wet removal is usually the process that determines these lifetimes. During periods of

frequent rain events, the lifetime of these particles is expected to be shorter than the value indicated in Figure 3.15, while during dryer periods $\text{PM}_{2.5}$ can spend even longer periods in the atmosphere. Particles of diameter less than 0.1 μm have shorter lifetimes because of their higher deposition velocities and also because of their coagulation with larger particles. These coagulation lifetimes are shorter in urban environments (see also Figure 3.4). Particles larger than a few micrometers have shorter residence times in the atmosphere as a result of their larger settling velocities and inertial properties.

Rough estimates of the mean transport distance of atmospheric particles can be obtained by multiplying the transport velocity by the mean atmospheric residence time. The climatologically averaged transport velocity within the mixed layer in North America is a few hundred kilometers per day. Based on an atmospheric lifetime of $\text{PM}_{2.5}$ of the order of a week, some of these particles could easily travel a few thousand kilometers from source to removal.

There is significant evidence that atmospheric particles can be transported over large distances, even intercontinentally under the right conditions. Well-documented examples include the transport of Saharan dust to Europe and North America (Schutz et al., 1990), dust transport from Asia to North America, and the transport of continental pollution to create the Arctic Haze (Barrie, 1986). These events are possible because particles that are transported to

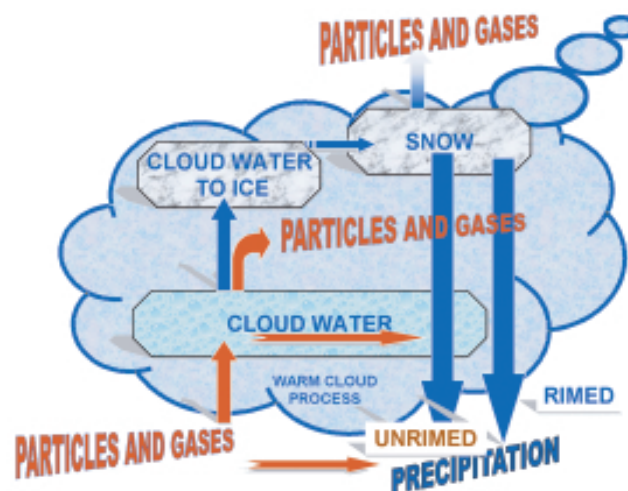


Figure 3.14. Schematic diagram of the processes of in-cloud scavenging of PM and gases from the atmosphere by a precipitating cloud. (adapted from Barrie, 1991).

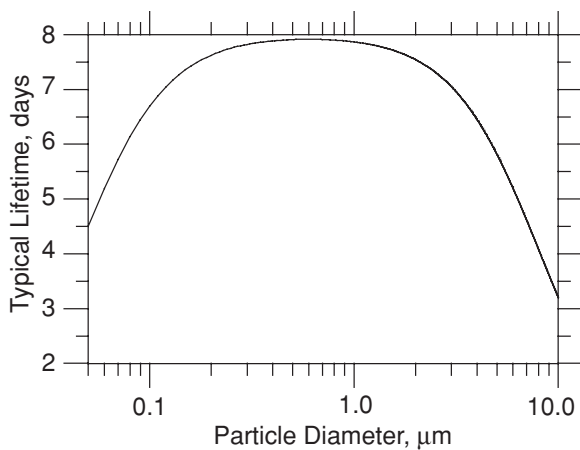


Figure 3.15. Typical lifetime of atmospheric particles in the lower troposphere accounting for losses due to coagulation, dry deposition, and wet removal (Jaenicke, 1993). The actual lifetime can be quite variable depending on the rain frequency, wind speed, concentrations of other particles, point of emission, etc. For areas (e.g., eastern United States) and periods with significant rainfall the lifetimes are shorter.

the free troposphere (above the cloud layer) can live substantially longer than those that remain in the boundary layer. Typical lifetimes of particles in the $PM_{2.5}$ range in the free troposphere are of the order of three weeks; thus intercontinental transport is possible even for large dust particles.

3.8 PM AND OTHER POLLUTANTS

PM, ozone, and other pollutants are related through a complex web of common emissions and precursors, common photochemical production pathways, and meteorological processes (Figure 3.16, Table 3.2). Integrated, multi-pollutant abatement strategies are possible. NO_x and VOCs are precursors of both ozone and of a fraction of atmospheric PM (NO_3^- and secondary organics) while they influence indirectly the formation of the rest of the secondary PM components like SO_4^{2-} .

A number of modeling studies, once more focusing on Southern California, have quantified these effects (for example Meng et al., 1997). These results underline the possibility of counterintuitive interactions, like the increase of $PM_{2.5}$ for reductions

of the VOC emissions in that area. As VOC levels are decreased, the concentration of RCO_3 radicals decreases, and the available NO_2 instead of being converted to PAN is converted to HNO_3 , which reacts with available NH_3 to form NH_4NO_3 . The increase in NH_4NO_3 in that area can exceed the decrease in the SOA concentration, and consequently the total $PM_{2.5}$ may increase even if one of the precursors decreases in concentration. At the same time the ozone concentration is predicted to decrease significantly (Figure 3.17). For example, this study shows that a 25 percent reduction in VOC emissions resulted in a 19 percent reduction of the peak ozone in Riverside California, but an 18 percent increase of the $PM_{2.5}$ concentration. In another test for the same receptor, a 25 percent decrease in NO_x emissions resulted in 3 percent reduction of the peak ozone and a 9 percent decrease of the $PM_{2.5}$ concentrations.

The above illustrates both the potential and also the pitfalls for the design of control strategies caused by the intricate coupling between ozone and PM. Control strategies for VOCs or NO_x that are optimal for ozone controls may even increase $PM_{2.5}$ concentrations. At the same time, careful choices can lead to synergism and reductions of the concentrations of both pollutants.

3.9 POLICY IMPLICATIONS

Particles remain in the atmosphere for days to a few weeks, depending on particle size, the rate at which they are removed by precipitation, etc. It follows that particles detected at a site may have been formed or emitted locally or may have originated at a site located hundreds or even thousands of kilometers away. Particles in the 0.1 to 1.0 μm diameter range have longer lifetimes than smaller or larger particles. *Implication:* Very small ($<0.1 \mu m$) and very large ($>1 \mu m$) particles are more likely to be influenced by local emissions or production than particles in the intermediate size range. This phenomenon is important when evaluating the relative roles of local and upwind sources in the design of compliance strategies.

Primary particle emissions from both anthropogenic and biogenic sources can contribute to PM

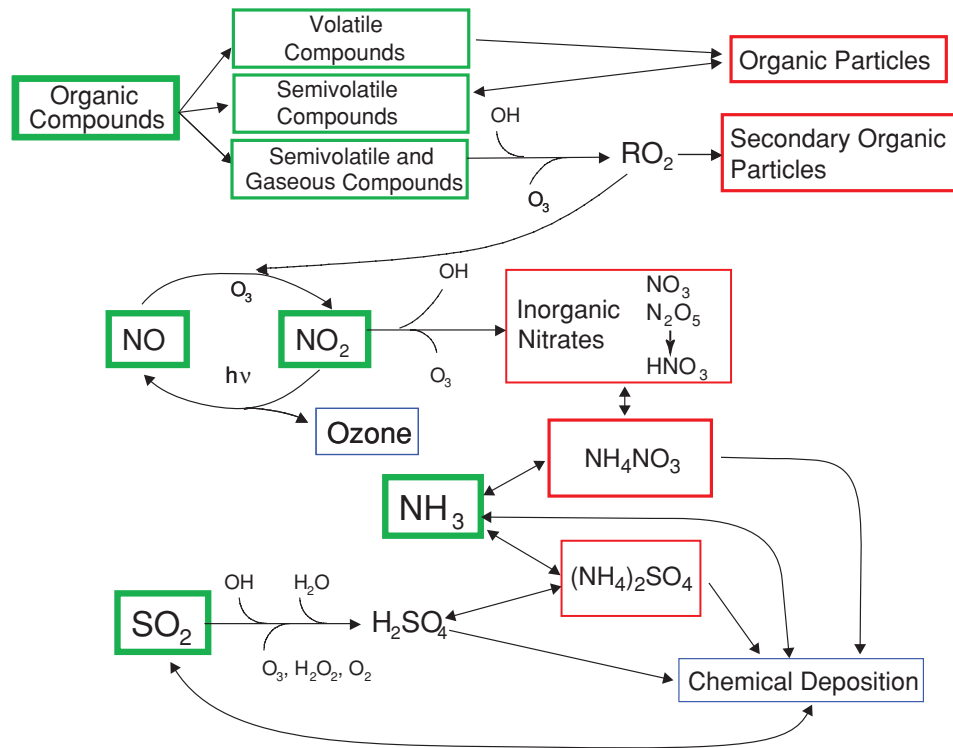


Figure 3.16. Chemical links between ozone and PM formation processes. The major precursors are shown in green squares. The VOC can be gaseous (always in the gas phase), non-volatile (always in the condensed phase), and semivolatile (partitioned between the gas and condensed phases (adapted from MSC, 2001)).

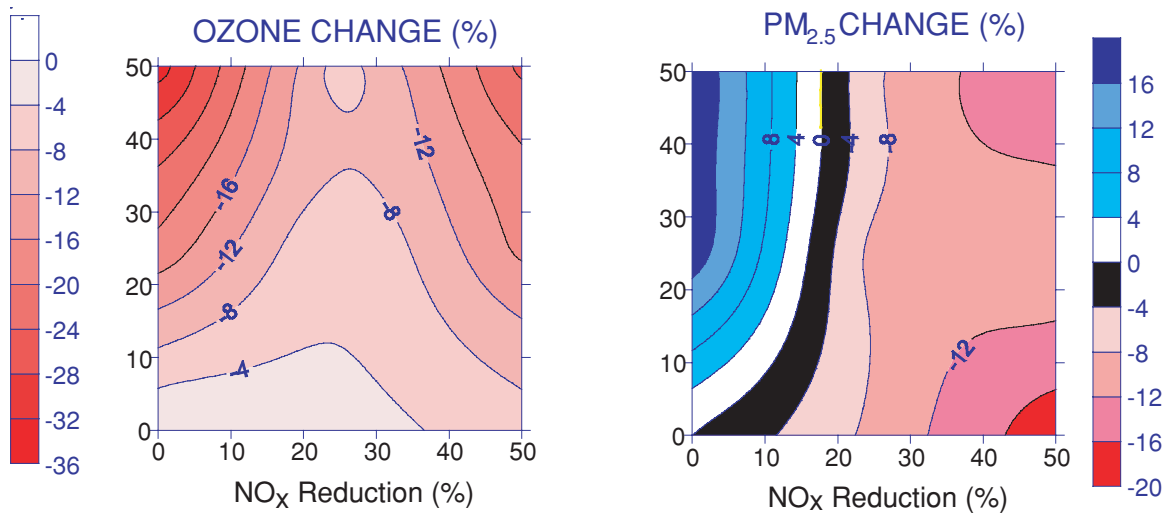


Figure 3.17. Percentage changes of maximum 1-hour average concentrations of ozone and $PM_{2.5}$ simulated at Riverside, California on 28 August 1987 for various combinations of VOC and NO_x emission reductions from base estimated 1987 basin-wide emissions (Meng et al., 1997).

Table 3.2. Typical pollutant / atmospheric issue relationships.^a

Reduction in pollutant emissions	Change in associated pollutant or atmospheric issue					
	Ozone	PM Composition			PM _{2.5} ^(k)	Acid Deposition
		SO ₄ ⁼	NO ₃ ⁻	Organic compounds		
SO ₂		↓	↑ ^(e)		↓	↓
NO _x	↓ ^(a) ↑	↑↓ ^(c)	↓ ^(f)	↓↑ ^(h)	↓↑	↓↑
VOC	↓	↑↓	↓↑ ^(g)	↓ ⁽ⁱ⁾	↓↑	↓↑
NH ₃		↓ ^(d)	↓		↓	↑ ^(l)
Black Carbon	↑ ^(b)			↓ ⁽ⁱ⁾	↓	
Primary Organic Compounds	↑ ^(b)			↓	↓	
Other primary PM (crustal, metals, etc.)	↑ ^(b)				↓	↑ ^(l)

^a Arrow direction denotes increase (↑) or decrease (↓); arrow color denotes undesirable (red) or desirable (blue) response; arrow size signifies magnitude of change. Small arrows signify possible small increase or decrease. Blank entry indicates negligible response.

^b In and downwind of some urban areas that are VOC limited.

^c Effect on daytime ozone due to increase in solar flux and decrease in radical scavenging; effect on nighttime ozone unknown.

^d Due to effect of NO_x on oxidant levels (OH, H₂O₂ and ozone); e.g., see SAMI modeling results.

^e Due to effect of NH₃ on cloud/fog pH.

^f Decrease in sulfate may make more NH₃ available for reaction with HNO₃ to form NH₄NO₃, more important when NH₄NO₃ is NH₃ limited.

^g Decrease except special cases (e.g., SJV); decrease in NO_x may lead to increase in ozone with associated increase in HNO₃ formation.

^h Increase due to less organic nitrate formation and more OH available for reaction with NO₂; decrease due to decrease in oxidant levels.

ⁱ Related to effect of NO_x on oxidant levels (OH, ozone, and NO₃[·]).

^j Decrease of secondary component; magnitude depends on OC fraction that is secondary anthropogenic.

^k Reduction of OC adsorbed or emitted with black carbon.

^l Refers to net acidity atmospheric deposition, not to acidification potential to ecosystem.

concentrations. Furthermore, the size and composition of primary particle emissions vary with the source. Such information can be used to estimate the contributions of various sources to ambient PM. *Implication:* Measurements of size-resolved ambient PM composition should be complemented with measurements of particle composition at both biogenic and manmade sources. Such measurements can help to determine the relative contributions of local anthropogenic emissions, which may be controllable, from biogenic emissions, which may not.

Secondary PM formed in the atmosphere by chemical transformations of reactive gaseous emissions typically constitutes a significant fraction of the PM mass. Most SO₄⁼ and NO₃⁻ are secondary, and a portion of organic PM may be secondary. Both anthropogenic and biogenic sources emit gases that

contribute to the formation of secondary PM, and gaseous emissions from all sources interact as they react to form secondary particles. *Implication:* In designing compliance strategies, it is essential to consider the role of secondary PM and the interactions of emissions from diverse sources in their formation.

Particulate organic compounds typically make up a significant fraction of the PM mass. Organic PM is chemically complex, and its origins and properties are not as well understood those of the inorganic fraction. It is likely that primary sources always contribute significantly to OC, although secondary sources may contribute up to 50 percent in some locations, especially where photochemical transformations of biogenic precursor gases are significant. *Implications:* More research on the sources, composition, and properties of the OC

fraction is needed. The extent to which emission controls of OC and its gas-phase precursors can reduce ambient mass concentrations will likely vary with season and region, and is highly uncertain. Nevertheless, because OC composes such a significant fraction of PM mass, reducing its contributions should be considered when establishing strategies for meeting PM standards.

In some cases it may be possible to define “limiting reagents” for selected components of secondary PM. The mass concentrations of PM will respond readily to changes in the availability of this limiting reagent. *Implication:* Reducing the availability of limiting reagents can be an effective way to control the contributions of that species to PM.

Ammonium nitrate is a semivolatile compound formed by the reaction between HNO_3 and NH_3 . Ammonium nitrate concentrations tend to increase with increasing emissions of NH_3 , photochemical production of HNO_3 (from NO_x), and decreasing temperature. Control measures that lead to decreases in $\text{SO}_4^{=}$ have the potential to lead to increases in NH_4NO_3 . Furthermore, either HNO_3 or NH_3 may be a “limiting reagent” in the formation of NH_4NO_3 . *Implications:* Available modeling tools can be used to estimate the sensitivity of NH_4NO_3 concentrations to local emissions of NH_3 and NO_x , as well as its sensitivity to changes in $\text{SO}_4^{=}$ concentrations. The availability of suitable data on emissions, particle composition, and gas concentrations (especially NH_3 and HNO_3) will help to ensure that model predictions are accurate.

PM, ozone and other pollutants are related through a complex web of common emissions and precursors, photochemical production pathways, and meteorological processes. Therefore, changes in emissions of one pollutant can lead to changes in the concentrations of other pollutants. A variety of approaches can be used to explore such relationships including thermodynamic models, chemical-transport models, and empirical observations. For processes that are well understood, it may be possible to predict these interrelationships with confidence while in other cases one may be limited to “educated guesses.” *Implications:* Interactions between

pollutants need to be considered when making policy decisions. These interactions can be evaluated using available modeling tools.

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CHAPTER 3

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