POLLUTION-CONTROL TECHNOLOGIES IN COAL-FIRED POWER PLANTS
AND THEIR IMPACT ON
AEROSOL NUCLEATION AND GROWTH IN EMISSIONS PLUMES

by

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ABSTRACT

Nucleation and growth of particles in coal-fired power-plant plumes can greatly contribute to particle concentrations near source regions. Pollution-control technologies have been added to coal-fired power plants to reduce emissions of SO_2 and NO_X; however, their cumulative effects may be increasing in-plume particle production. Therefore, a quantitative understanding of in-plume particle production is needed to determine the implications of emission controls on the climate system.

Changes in particle production with changing emissions for coal-fired power plants are simulated using the SAM-TOMAS large-eddy simulation model. For the W.A. Parish power plant, the model predicts increased particle production due to the emissions control technologies. From this, a general understanding of particle production rate changes with NO_X and SO_2 emissions is plotted, and estimates of US coal-fired power plant production rate changes are created. Additional particle production mechanisms are discussed, in particular an exploration of particle production from ammonia slip of NO_X emission controls.

LIST OF ABBREVIATIONS USED

CCN	Cloud Condensation Nuclei
CO	carbon monoxide
DMS	dimethyl sulphide
EPA	U.S. Environmental Protection Agency
EPRI	Electric Power Research Institute
ESP	Electrostatic Precipitator
FGD	Flue Gas Desulphurization
H_2O_2	hydrogen peroxide
H_2SO_4	sulphuric acid
HNO_3	nitric acid
HO_X	$OH + HO_2$
HSO_3^-	hydrogen sulphite
HSO_4^-	hydrogen sulphate
IPCC	Intergovernmental Panel on Climate Change
LES	Large-Eddy Simulation
LTI	Low Turbulence Inlet
NAAQS	National Ambient Air Quality Standards
NARR	North American Regional Reanalysis data
NCAR	National Center for Atmospheric Research
NCEP	National Center for Environmental Prediction
NH_3	ammonia
NH_4^+	ammonium
NO_X	nitrogen oxides ($NO + NO_2 = NO_X$)
NOAA	National Oceanic and Atmospheric Administration
NPC	Net Particle Contribution rate
O_3	ozone
OFA	Over-Fire Air
OH	hydroxyl radical
OPC	Optical Particle Counter
$PM_{2.5}$	particulate matter with diameters less than 2.5 μm
PM_{10}	particulate matter with diameters less than 10 μm
ppb	parts-per-billion
ppt	parts-per-trillion
SAM	System for Atmospheric Modeling
SCR	Selective Catalytic Reduction
SO_2	sulphur dioxide
SO_4^{2-}	sulphate
TOMAS	TwO Moment Aerosol Sectional microphysics
TexAQS	Texas Air Quality Studies
UHSAS	Ultra High Sensitivity Aerosol Spectrometer
VOC	Volatile Organic Compounds

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CHAPTER 1   INTRODUCTION

1.1   Motivation

Atmospheric aerosols are solid or liquid particles suspended in air that affect both climate and human health. Aerosols are characterized into a wide variety of classifications based on their source, concentration, composition and size. They can be directly emitted into the atmosphere via natural or anthropogenic sources (primary aerosols) and can also be formed through gas-phase chemical reactions (secondary aerosols). Some examples of natural primary aerosols include sea salt, volcanic dust and biological debris. Secondary natural aerosols can form from biogenic gases (such as dimethyl sulfide (DMS) from oceanic organisms), volcanic sulphur dioxide (SO_2) that form sulphate, and organic matter from biogenic volatile organic compouds (VOCs). Some examples of primary anthropogenic aerosols include dust and soot from industrial activity, black carbon and organic aerosols. Examples of secondary anthropogenic aerosols are sulphate and nitrate from SO_2 and nitrogen oxides ($NO + NO_2 = NO_X$) formed from combustion processes. Aerosols are deposited out of the atmosphere and down to the earth's surface either by dry deposition or wet deposition when incorporated into cloud droplets.

Aerosols are often distinguished based on their diameters due to size-dependent effects on health and climate. When discussing the impact of aerosols on human health, aerosols are generally defined as either fine (diameters < 2.5 µm, also known as $PM_{2.5}$) or coarse (2.5 µm $<$ diameters < 10 µm) by the National Ambient Air Quality Standards (NAAQS). The sum of fine and coarse particles is known as PM_{10}, and is a concern because these particles can be collected in the lungs and cause respiratory problems. $PM_{2.5}$ is potentially dangerous to humans because of its lung penetrating capabilities, and concentrations greater than ~15 µg m^{-3} are considered particularly dangerous for babies, the elderly and people who have pre-existing respiratory problems (Arya, 1999). Additional health problems associated with PM include cardiovascular diseases

(bronchitis, pulmonary emphysema, lung cancer), eye, nose and throat irritation, and intensification of asthma. PM can also impact the health of natural ecosystems (Arya, 1999).

Along with the coarse and fine size categories designed for aerosol-health impacts, there are four categories of aerosols based on the size and physical processes in the atmosphere that shape them; nucleation, Aitken, accumulation and coarse modes (Seinfeld and Pandis, 2006). The nucleation mode consists of particles generally between 1 and 10 nm in diameter, which are newly formed particles from the condensation of low volatility vapours (nucleation). Aitken-mode aerosols are generally between 10 and 100 nm and contain a combination of primary particles from combustion sources and nucleation-mode particles that have grown into the Aitken mode through condensation of gases. Accumulation-mode aerosols include particles between 100 nm and 1 μm and are formed through primary emissions and condensational growth of smaller particles. Finally, the coarse mode contains particles larger than 1 μm and are mostly created by primary emissions from natural processes such as wind-blown dust and sea spray.

Climate is directly and indirectly affected by aerosols. Atmospheric aerosols directly affect climate by scattering and absorbing incoming solar radiation (direct effect of aerosols on climate). The amount of scattering and absorption per particle depends on the size and chemical composition of that particle.   Depending on how much solar radiation a particle absorbs or scatters, the particle can either heat (absorbed radiation) or cool (scattered radiation) the atmosphere. A common example of the direct effect is the haze that can sometimes be seen, resulting from sunlight scattering off of particles in the atmosphere. Accumulation-mode aerosols most greatly contribute to the direct effect (on a per-mass basis) while smaller aerosols are weaker scatterers/absorbers and larger aerosols have high mass:surface-area ratios. Aerosols indirectly affect climate through their contribution to cloud droplet formation (the indirect effect). Individual cloud drops form on a subset of aerosols known as cloud condensation nuclei (CCN). Without CCN clouds would not be able to form in the atmosphere. Larger and more hydrophilic

aerosols (e.g. sulphate particles larger than 100 nm) are more likely to act as CCN than smaller and hydrophobic aerosols (e.g. 30 nm soot particles) (Seinfeld and Pandis, 2006). In general, accumulation-mode and coarse-mode aerosols contribute to CCN, while the Aitken mode may also contribute under some conditions. Increases in CCN number concentrations cause an increase in cloud droplet concentrations in clouds, which lead to clouds that reflect more sunlight to space thus cooling the earth's surface. This is known as the first indirect effect of aerosols (Twomey, 1974; Albrecht, 1989). The second indirect effect is the ability of aerosols to reduce cloud droplet diameter thereby creating clouds that are less likely to rain. Overall, both the direct and indirect effects are thought to cool the climate system; however, they remain the most uncertain climate forcing as quantified in the most recent Intergovernmental Panel on Climate Change (IPCC) report (IPCC 2007). The uncertainty of CCN contributions from anthropogenic activity is a large contributor to this uncertainty. Due to the strong connection between aerosol size and these climate effects, it is necessary for climate models to accurately predict the size and concentration of aerosols, particularly from anthropogenic sources.

Coal-fired power plants are large sources of the aerosol precursor gas SO_2 (and in some cases primary ash aerosols), particularly in developing nations without modern pollution-control technologies. High emissions of SO_2 in the plumes of these power plants can impact both local and regional areas by increasing local particle number and mass concentrations. However, new-particle formation (aerosol nucleation) within the plumes depends greatly on local conditions (Stevens et al., 2012). Aerosol nucleation in plumes is difficult to represent in regional (e.g. North America) and global models because these models do not spatially resolve the near-source plume. Any uncertainty in power-plant emissions, sub-grid chemistry and physics will lead to an uncertainty in nucleation rates, CCN concentrations and ultimately the radiative forcing of clouds (Pierce and Adams, 2009). This emphasizes the importance of understanding the chemistry and physics within power-plant plumes in order to accurately represent them in large-scale atmospheric models.

Many developed nations have implemented pollution-control technologies on their coal-fired power plants aiming to emit less SO_2 and NO_X. However, unintended additional ultrafine aerosols (with diameters smaller than 100 nm) have been measured in coal-fired power-plant plumes with newly installed pollution controls in Germany, Inner Mongolia and Southern Australia (Junkermann et al., 2011a). The addition of these ultrafine particles could grow to CCN sizes in the atmosphere and alter local cloud and precipitation formation and increase the negative radiative forcing of sulphate, offsetting the positive radiative forcing from CO_2 emissions (Shindell and Faluvegi, 2010; Junkermann et al., 2011a). Thus, it is possible that while reducing SO_2 and NO_X has reduced total PM mass concentrations, the number of Aitken- and accumulation-mode aerosols may have increased, which may have unintended impacts on climate. This project aims to understand how changes in power-plant emissions may affect aerosol nucleation and growth in source plumes.

1.2   Plume chemistry and physics

This subsection provides an overview of the chemistry and physics most relevant to the formation and growth of aerosols in coal-fired power-plant plumes.

1.2.1 SO_2, NO_X and OH in power-plant plumes

Coal-fired power plants are sources of SO_2, NO_X and primary ash particles (Srivastava et al., 2004; Zhao et al., 2008). A product of coal combustion is SO_2, which is oxidized by the hydroxyl radical (OH) in the cloud-free atmosphere, to form sulphuric acid (H_2SO_4) vapour (Seinfeld and Pandis, 2006; Zhau et al., 2011).

$$SO_2 + OH + M \rightarrow HOSO_2 + M \tag{1}$$
$$HOSO_2 + O_2 \rightarrow HO_2 + SO_3 \tag{2}$$
$$SO_3 + H_2O + M \rightarrow H_2SO_4 + M \tag{3}$$

Equation 1 represents the rate-limiting step for this mechanism. Under continental surface conditions, H_2SO_4 vapour will quickly (seconds to minutes) form either new ~1 nm aerosol particles (aerosol nucleation) or condense onto pre-existing particles (Pierce and Adams, 2009b). In clouds, SO_2 will be absorbed into cloud droplets and may be oxidized to H_2SO_4 by aqueous ozone (O_3) or hydrogen peroxide (H_2O_2) when $SO_2 \cdot H_2O$ dissociates to hydrogen sulfite (HSO_3^-) (Zhou et al., 2011). This in-cloud oxidation will increase sulphate aerosol concentrations if the cloud dissipates without removing the aerosols by precipitation. While the in-cloud aerosol-formation mechanism is an important source of aerosol mass, the interaction of aerosols and clouds were not explored in this thesis.

Under mostly sunny conditions, H_2SO_4 vapour concentrations are generally elevated above background levels in the SO_2-rich plumes, and thus power plants may contribute many new particles (Yu, 2010b; Stevens et al., 2012). The rate of SO_2 oxidation (H_2SO_4 formation) depends on the concentration of OH. The formation of OH depends on the amount of incoming solar radiation (hv) and ozone concentrations.

$$O_3 + hv \rightarrow O_2 + O(^1D) \qquad\qquad (4)$$
$$O(^1D) + H_2O \rightarrow 2OH \qquad\qquad (5)$$

O_3 concentrations depend on NO_X and VOC concentrations. Thus, NO_X is an indirect contributor to new particle formation in plumes because it affects the amount of OH available for the $SO_2 \rightarrow H_2SO_4$ reaction. Additionally, at high NO_X concentrations (>30 ppb), the reaction of OH with NO_2 becomes a significant sink for OH, and OH concentrations are reduced with increasing NO_X concentrations.

$$NO_2 + OH + M \rightarrow HNO_3 + M. \qquad\qquad (6)$$

For low NO_X concentrations (<0.5 ppb), the reaction of NO_2 with OH is unimportant, and OH increases with increasing NO_X through the production of additional O_3 (and subsequent OH production through equations 4 and 5).

$$NO_2 + hv \rightarrow NO + O(^3P) \tag{7}$$

$$O(^3P) + O_2 + air \rightarrow O_3 + air \tag{8}$$
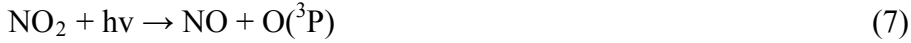
The peak OH concentration occurs in between these ranges at the transition of the two limiting regimes (Fig. 1.1). Thus, OH concentrations may either increase or decrease for decreasing NO_X emissions (due to the addition of control technologies), and gas-phase H_2SO_4 concentrations (and particle formation and growth rates) may subsequently increase or decrease in the plumes.
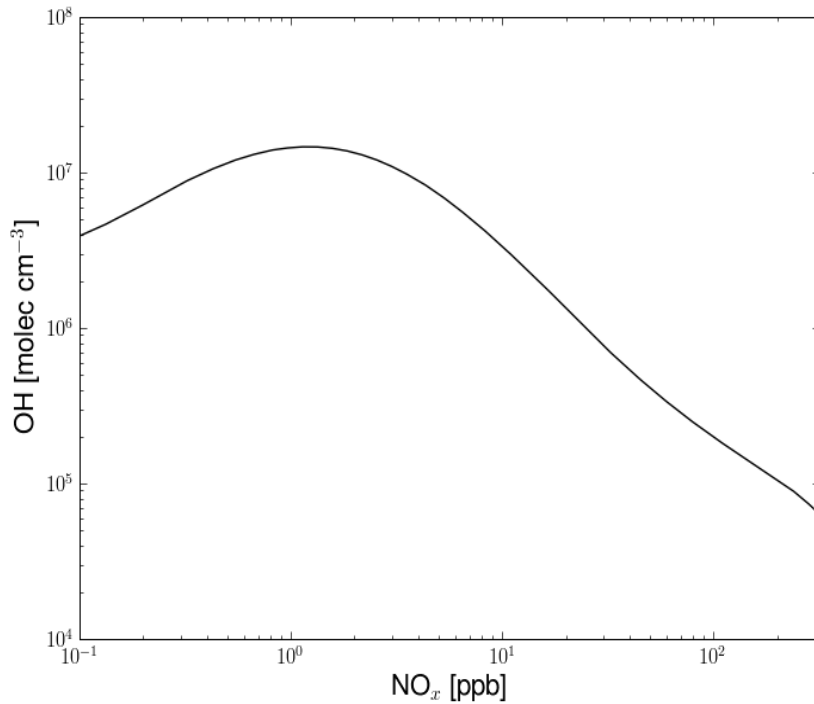
Figure 1.1　　Example of [OH] as a function of [NO_X]. This example is for clear skies, a solar zenith angle of 51.7° and an isoprene (representative VOC) concentration of 150 ppt using the method described in Stevens et al. (2012).

OH concentrations may also be affected by the cycling of the HO_X chemical family ($HO_X = OH + HO_2$). HO_2 can be lost onto the surface of existing aerosols, thereby creating a net OH sink (Thornton et al, 2008). Thornton et al., (2008) found that globally the effect of these reactions on OH concentration was generally small (~1% changes in OH concentrations), but that changes in OH could be larger in regions with high aerosol surface area or aerosols containing copper. In plumes where nucleation is occurring, there is a risk that aerosol surface area may be large; however, the likelihood of an HO_2 molecule that reaches an aerosol being lost by reaction strongly decreases with particle size (Thornton et al, 2008). Thus, new-particle formation in coal-fired power plants is unlikely to strongly contribution to HO_2 loss while particles are still <100 km from the source. The likelihood of this reaction occurring also decreases with increasing acidity, as is the case in plumes with high H_2SO_4 concentrations and low ammonia concentrations. HO_2 will react much more quickly in particles when the particles contain copper; however, we assume that nearly all power-plant particles containing copper are removed via particulate controls installed on the coal-fired power plants. Therefore, although HO_2 loss to particles may be an important oxidizer and OH sink in some parts of the troposphere, it is assumed to be negligible in the case studies presented in this thesis.

1.2.2 Aerosol nucleation and particle growth mechanisms

Aerosol nucleation, or new-particle formation, is the formation of new particles from low-volatility vapours. H_2SO_4 is thought to be involved in all mechanisms of new particle formation in the troposphere (Kulmala and Kerminen, 2008). There are several common nucleation mechanisms that have been speculated to explain the formation of particles in the atmosphere, all containing some combination of species with H_2SO_4. The first nucleation mechanism is that of binary nucleation, which involves water vapour and sulphuric acid vapour forming new particles (Vehkamaki et al., 2002). Because sulphuric acid is a very hygroscopic molecule, the presence of the water vapor decreases the evaporation rate of sulphuric acid from small molecular clusters, which increases the

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likelihood of nucleation (Seinfeld and Pandis, 2006). This nucleation mechanism likely only occurs at lower temperatures in the atmosphere (e.g. upper troposphere). A second mechanism, ternary nucleation, includes a third species in addition to sulphuric acid and water vapour in the newly formed cluster (Napari et al., 2002; Merikanto et al., 2006). This is usually ammonia (NH_3), although in recent studies organic nitrates have been found in newly formed aerosol clusters (Kirkby et al., 2011). These ternary species further reduce the evaporation rates of sulphuric acid from the small molecular clusters. A third type of nucleation includes all previous species with the addition of gas-phase ions that increase the attractive forces of the molecules involved in the new cluster. This is called ion-mediated nucleation and often involves the hydrogen sulphate ion (HSO_4^-) (Yu et al., 2010a).

Because the specific nucleation mechanisms in the atmosphere are not well known or well understood, empirical nucleation schemes that capture much of the variation in nucleation rates are often used in models instead. Cluster-activation nucleation is one of these straight-forward, empirical nucleation schemes. It is a linear function of H_2SO_4 concentrations with an activation constant, A, that is usually between $10^6 - 10^7$ s^{-1} under continental boundary-layer conditions (equation 9)(Kulmala et al., 2006).

$$J = A[H_2SO_4] \qquad\qquad (9)$$

Condensation of vapours onto these freshly nucleated particles will cause these new particles to grow to larger sizes. Common gaseous species for condensational growth include H_2SO_4, HNO_3, NH_3 and secondary organic aerosol. Condensational growth of these new particles is essential for their survival because the small particles are quickly lost by coagulation with large pre-existing particles. Low-volatility gases will condense onto particles if the equilibrium vapour pressure of the gas is less than its ambient vapour pressure, thereby growing the particles and reducing gas-phase concentrations. If high concentrations of particles exist, the fast condensation of H_2SO_4 to these particles will

lower H_2SO_4 vapour concentrations and reduce nucleation rates (Pierce and Adams, 2009b).

Coagulation is the primary loss mechanism for freshly nucleated particles. Coagulation occurs when two suspended particles come into contact with each other (generally through Brownian motion) and stick together to form a new, larger particle equal to the mass of the two smaller particles combined. This process occurs most quickly between a larger particle (with large a surface area) and small particles (that have fast mean speeds, which increase their chance of collision). Thus, tiny freshly nucleated particles are not likely to survive in environments with high concentrations of larger (Aitken, accumulation and coarse mode) particles, and new particles will be less likely to exist in power-plant plumes when the background air is already polluted with many particles. Therefore, high concentrations of pre-existing particles reduce the concentration of nucleated particles through (1) reducing nucleation rates by lowering H_2SO_4 concentration due to fast condensation, and (2) increasing the coagulational loss rates of freshly nucleated particles (Pierce and Adams, 2009b).

The particle formation and growth processes of nucleation, condensation and coagulation are all simultaneously occurring within a power-plant plume. The number of new particles formed in the plume, as well as their size (and ability to act as CCN), will additionally depend on the background conditions (including pre-existing atmospheric particles) as will be discussed in the next sub-section.

1.2.3 Effect of background meteorology and composition

For both particle production and growth, background conditions help determine the final size distribution of aerosols downwind in a source plume. Regarding nucleation, one of the largest controlling factors is that of pre-existing aerosol concentrations (Stevens et al., 2012). As described above, the existence of pre-existing aerosol surface area is a key factor in determining H_2SO_4 concentrations because condensation to pre-existing

aerosols is the dominant sink for H_2SO_4 vapour (even under fast-nucleation conditions). Thus, $[H_2SO_4]$ is approximately inversely proportional to the aerosol surface area (Pierce and Adams, 2009b) and pre-existing particles will decrease new particle formation rates and may even prevent them from forming entirely. Additionally, the pre-existing particles will increase the loss rate of the new particle that form in the plume.

The presence of clouds will also alter growth rates for new particles formed, because of alternative pathways for SO_2 oxidation, as discussed earlier. If precipitation is occurring over the plume, rain drops will collide and coalesce with aerosols in the plume (below-cloud scavenging) and remove them (Arya, 1999). As mentioned earlier, the interaction of in-plume aerosols with clouds or precipitation are not considered in this study as nucleation and growth will be minimal during cloudy conditions. Favourable meteorological conditions for nucleation and growth include the presence of sunlight (to promote photochemistry) and low winds (to prevent dilution with background air). Fast winds and turbulent boundary layer will dilute SO_2 and NO_X emissions and allow for greater influence of pre-existing aerosols.

1.3   Pollution-control technologies

SO_2, NO_X and primary particles are regulated pollutants by the U.S. Environmental Protection Agency's (EPA) NAAQS because of their health and environmental impacts, specifically their capabilities to form acid rain. As a result, coal-fired power plants have implemented pollution-control technologies to reduce emissions. However, because SO_2, NO_X and primary particles each affect particle formation in different ways, it is not clear how pollution controls affect the particle formation within the plumes when multiple technologies are combined.

There are numerous techniques for controlling emissions, and we will review the most common techniques here. For a more extensive discussion of pollution-control strategies,

please refer to Srivastava et al. (2004) and Miller (2011). A common technique to reduce SO_2 emissions is to utilize low-sulphur coal. Low-sulphur coal is desirable as it allows for SO_2 emissions reductions without the need to implement new control systems. Sulphur content in coal varies based on the source of the mined coal. If switching to low-sulphur coal is not available or insufficient for achieving emission standards, another technique utilized is flue gas desulfurization (FGD), otherwise known as scrubbers, which has been in practice since the 1970's with increasing use each year (Miller, 2011). Different classifications of FGD include wet and dry methods. Both techniques typically use lime/limestone as the active alkaline slurry or sorbent to neutralize the acid gas SO_2. Wet techniques remove fly ash before the alkaline slurry is added, and dry techniques add the sorbent followed by fly as removal. Different injection methods of the slurry or sorbent are described in Srivastava and Jozewicz (2001). One disadvantage of FGD includes the additional release of SO_3 or H_2SO_4 in the stack as a by-product of the combustion process, but is also not explored in this paper.

Beginning in the late 1990's, many power plants added some type of NO_X controls in the form of Low NO_X burner technology (LNBT) or over-fire air technique (OFA) or a combination of both. These techniques are currently used in more than 75% of US coal-fired plants. In these techniques, an oxygen-deficient reaction zone is created to allow for the complete combustion of NO_X, but this is often inefficient and allows for only 40-60% NO_X emissions reduction. Selective catalytic reduction technique (SCR) has since been added more recently to many plants to increase removal efficiencies, often in combination with the previous techniques. SCR is a much more efficient technology (> 90% NO_X reductions relative to uncontrolled emissions) but is more expensive. It works by injecting a reductant, NH_3, into the flue gas of a boiler creating a mixture that passes through a catalyst (often tungsten, titanium oxide or other noble metals) to promote the reduction of NO_X by the following reactions;

$$4NO + 4NH_3 + O_2 \rightarrow\ 4N_2 + 6H_2O \qquad\qquad (10)$$
$$2NO_2 + 4NH_3 + O_2 \rightarrow 3N_2 + 6H_2O \qquad\qquad (11)$$
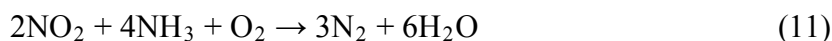
There are a few negative attributes of SCR. A by-product from the catalyst of the SCR reaction can be SO_3, a precursor to H_2SO_4; thus, SCR may have additional impacts on nucleation (Electric Power Research Institute (EPRI), 2008). We will not, however, consider this nucleation pathway in this thesis. Additionally, NH_3 may not react completely with NO_X, and it can become another by-product entering the atmosphere in the gas phase ranging between 0 and 2 ppm for bituminous coal combustion (EPRI, 2008). This process is called ammonia slip and can be somewhat controlled with careful tuning of the SCR system and regular maintenance of the catalysts (Miller, 2011; Gong et al., 2012). Since ammonia is potentially an important enhancer of aerosol nucleation rates (Merikanto et al., 2006), ammonia slip may also affect particle formation and is explored by Gong et al (2012) and discussed in chapter 4.

Technologies to reduce the amount of primary particles emitted from source stacks are currently the most effective control technologies. Nearly all power plants in the US and Canada use baghouse filters or electrostatic precipitators (ESP) with removal efficiencies up to 99.9% (by mass)(Miller, 2011). Baghouse filters contain fibrous materials of various designs and when the flue gas is streamed through it, the fibers catch large particles by inertial and direct impaction (particles > 1µm) and diffusion for smaller particles. The type of material for a filter depends on the desired removal efficiency, operating temperature, and flue gas flow from the power plant. ESP's are able to capture fine particles (0.5 to 200 µm) from large gas streams by delivering a charge to the particles via discharged electrons creating negatively charged ions that collide with the particles. The particles then pass through oppositely charged plates collecting the charged particles before exiting the stack. ESP's, along with the other control-technologies, must be well maintained and cleaned of remnant particles to assure maximum efficiency (Miller, 2011).

In this thesis, the SAM-TOMAS large-eddy simulation model (outlined in chapter 2) was used to explore the possible effects of SO_2 and NO_x controls on the particle formation in

emissions plumes. Model results are explored (chapter 3) as well as the possible effects of NH_3 slip from SCR (chapter 4). The summary, implications and future work of this project are discussed in chapter 5.

CHAPTER 2   METHODS

2.1   SAM-TOMAS

The SAM/TOMAS model was used to explore the dynamics and aerosol microphysics (nucleation, condensation and coagulation) of power-plant plumes (Stevens et al., 2012). The host model was the System for Atmospheric Modeling (SAM), a Large-Eddy Simulation (LES) and cloud-resolving model (Khairoutdinov and Randall, 2003) with a built-in TwO Moment Aerosol Sectional (TOMAS) microphysics algorithm (Stevens et al., 2012). In this paper we used grid-box sizes that were 400 m x 400 m horizontal resolution and two different vertical resolutions of 40 m and 80 m (depending on the boundary layer height) for model runs. The simulations contained the gas-phases species of SO_2, H_2SO_4, NO_X and NH_3.

OH concentrations were parameterized based on NO_X concentrations, incoming solar radiation and an assumed concentration of reactive VOCs. This parameterization is an empirical fit to the photochemical box model of Olson et al., (2006) which successfully simulated tropospheric conditions below 1km over the Eastern US as measured during associated field campaigns. Model results fit the measurements well for low VOC conditions represented by low isoprene concentrations (150 pptv or less), as used in this thesis, with parameters created to represent the OH/NO_X relationship curve (Fig.1.1)(Stevens et al, 2012).

$$x = \log([NOx]) - 0.195 \tag{12}$$

$$y = dswrf/S_0T \tag{13}$$

$$P1 = -0.014x^6 + 0.0027x^5 + 0.1713x^4 - 0.0466x^3 - 0.7893x^2 - 0.1739x + 6.9414 \tag{14}$$

$$P2 = (-1345y^3 + 4002y^2 - 417.8y + 42.72) \cdot 104 \tag{15}$$

$$[OH] = 0.82 \cdot 10^{P1 \cdot \log(P2)/6.8} \tag{16}$$

Where P1 is a polynomial as a function of model estimated NO_X concentrations (x) and estimates the shape of the curve and P2 is a polynomial that shapes the curve as a

function of downward shortwave radiative flux (dswrf)(y) (Stevens et al., (2012)). In order to represent high VOC conditions, higher concentrations of isoprene were used (1.5 ppbv) as well as the addition of a second parameter (defined below) that shifts the peak concentration of OH, as would be the case in higher VOC concentrations (Stevens et al., 2012).

$$x = \log([NOx] \cdot 0.6) - 0.195 \qquad\qquad (17)$$

The number and mass of sulphate aerosol, ammonium and water were tracked in 15 size sections spanning 3 nm to 10 μm using the TOMAS microphysics scheme (Adams and Seinfeld, 2002; Pierce and Adams, 2009a). Power-plant emissions of SO_2 and NO_X were obtained from the Clean Air Market emissions inventory (Clean Air Markets – Data and Maps, 2012) and are discussed further in the next section. Primary-particle emissions were assumed to be negligible in model simulations. Other inputs to the model included background SO_2, NO_X, NH_3 and aerosol size distributions acquired from Texas Air Quality Studies (TexAQS) field campaigns near Houston, Texas during 2000 and 2006 discussed in Section 2.3. The large-scale meteorological forcing of the SAM simulations were provided by vertical profiles of mean winds, temperature and relative humidity and surface sensible heat, latent heat and momentum fluxes from the National Center for Environmental Prediction (NCEP) North American Regional Reanalysis (NARR) data (Mesinger et al., 2006). The reanalysis data were provided by the National Oceanic and Atmospheric Administration (NOAA)/Outstanding Accomplishments in Research (OAR)/Earth System Research Laboratory (ESRL) Physical Sciences Division (PSD), Boulder, Colorado, USA, from their website at http://www.esrl.noaa.gov/psd/. Aerosol nucleation was calculated using the cluster-activation nucleation scheme (Kulmala et al., 2006), with a rate constant of $A=10^{-7}$ s^{-1}. Various nucleation schemes were tested in Stevens et al. (2012), and this nucleation scheme compared best against observations from the TexAQS2006 field campaign. For the work done with the University of Houston Group, the ternary nucleation scheme as described by Napari et al. (2002) and Merikanto et al. (2006) was used in the model to study the effects with NH_3 as the ternary species on in-plume particle formation.

In these simulations, we did not consider the oxidation of SO_2 within clouds (the meteorology on the tested days contained mostly cloud-free boundary layers). Also, the model did not consider the loss of NO_X by OH to form HNO_3. The direct effect of the NO_2 + OH reaction on OH is implicit in the OH parameterization; however, this does not result in the reduction of NO_X concentrations. Early in the plume, the mixing of the plume with background air will dominate the reduction of NO_X concentrations in the plume. Also, NO_X lifetime in high [OH] conditions is only a few hours during the day with the summertime lifetimes being shorter as compared to winter (Beirle et al., 2011). Thus, over-prediction of NO_X concentrations was expected at increasing distances from the source. Primary ash particles were also not considered (because of high removal efficiencies) or particles that may have formed in the stack because of high SO_3 formation from FGD or SCR; however, ammonia slip (from SCR) estimates as explored by Gong et al (2012) were modelled and are discussed in chapter 4.

2.2   Emissions Inventory

Emissions inputs into SAM-TOMAS were acquired from the EPA's Clean Air Markets inventory (Clean Air Markets: Data and Maps, available at: http://camddataandmaps.epa.gov/gdm/). This database is available through their website and includes emissions reports, programs and regulations, allowance summaries and much more information and tools for scientists and the general public about US industrial emissions. More specifically, the "Data and Maps" section provides industrial facility specific information such as energy usage and hourly emission rates. NO_X and SO_2 emissions rates, energy usage were acquired for all of the plants explored in this study. For the W.A. Parish power plant clean technology implementation dates were also acquired. For the pollutants specific to coal-fired plants, continuous emissions records date back to 1997, thus this was the date used to compare to 2010 results. Particulate

emissions rates are not provided due to the assumed high efficiency of removal techniques, and NH_3 emissions were not considered as it is not currently a regulated pollutant under the NAAQS.

2.3   NOAA Aircraft Measurements

Flight measurements are presented as secondary information to test the model's sensitivity to changes in input parameters that represented changing emissions due to pollution-control implementations. Stevens et al., (2012) evaluates the model's capabilities of capturing essential features of the particle size distributions in the plume downwind of the plant is described. In this project the model is evaluated against flight measurements during two aircraft flights; TexAQS2000 flight measurements on 27 August 2000 and TexAQS2006 measurements on 27 September 2006. In general there are not enough available flights through power-plant plumes (that we know of) to assess the effect of pollution-control technologies on aerosol formations in plumes directly or accurately; however these two cases capture plume characteristics before and after extensive emissions reductions. SCR technology to control NO_x emissions was implemented on all four coal-fired units at the W.A. Parish plant by 2004, thus the two dates of the flights are good comparison cases.

During the 2000 campaign on August 27, the NCAR Electra aircraft flew through the W.A. Parish plume at 6 distances from the stack with the plume age ranging from approximately 0.2 to 5.3 hours. Figure 2.1 is presented to give an idea of the flight tracks through the W.A. Parish plume and surrounding Houston area, and describes particle number concentrations and SO_2 sources.

Figure 2.1   A schematic of the flight tracks for the NCAR Electra aircraft through the Houston, TX area during the TexAQS2000 campaign (Brock et al., 2002) with the colours of tracks representing particle concentration (cm^{-3}) ranging from 0 (purple) to 50×10^3 (red) and yellow circles representing SO_2 sources ranging from small to large circles of 5×10^6 and 50×10^6 kg SO_2 yr^{-1} respectively.

Instrumentation on the flights included a five-channel condensation particle counter (CPC) and a LasAir laser optical particle counter (OPC) (Brock et al., 2002). These instruments were used to determine the size-dependent aerosol concentrations. Background information of SO_2, NO_X concentrations and particle size distributions were used as inputs for the model for the 2000 simulations discussed in section 3.3.

During the 2006 campaign on September 27 the NOAA WP-3D aircraft flew through the W.A. Parish plume (Fig. 2.2). Instrumentation on the flight also included a five-channel CPC and an Ultra High Sensitivity Aerosol Spectrometer (UHSAS), and an OPC that

offered better sizing resolution and precision than the LasAir OPC. For both campaigns a low turbulence inlet (LTI) was placed in front of the instruments (Brock et al., 2011). Background information of SO_2, NO_X, NH_3 concentrations and particle size distributions were used from this flight in the model for the 2006 simulations as well as the general calculation of particle formation against SO_2 and NO_X emissions and the calculation of US particle production differences between 1997 and 2010 (also described in chapter 3).
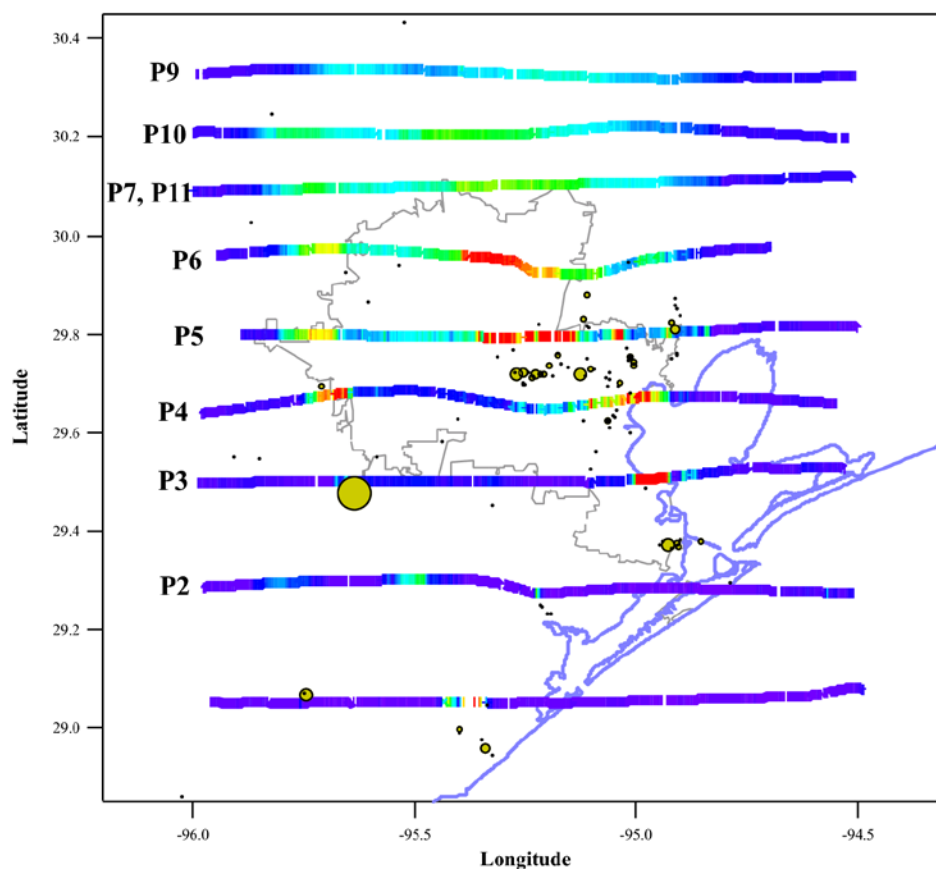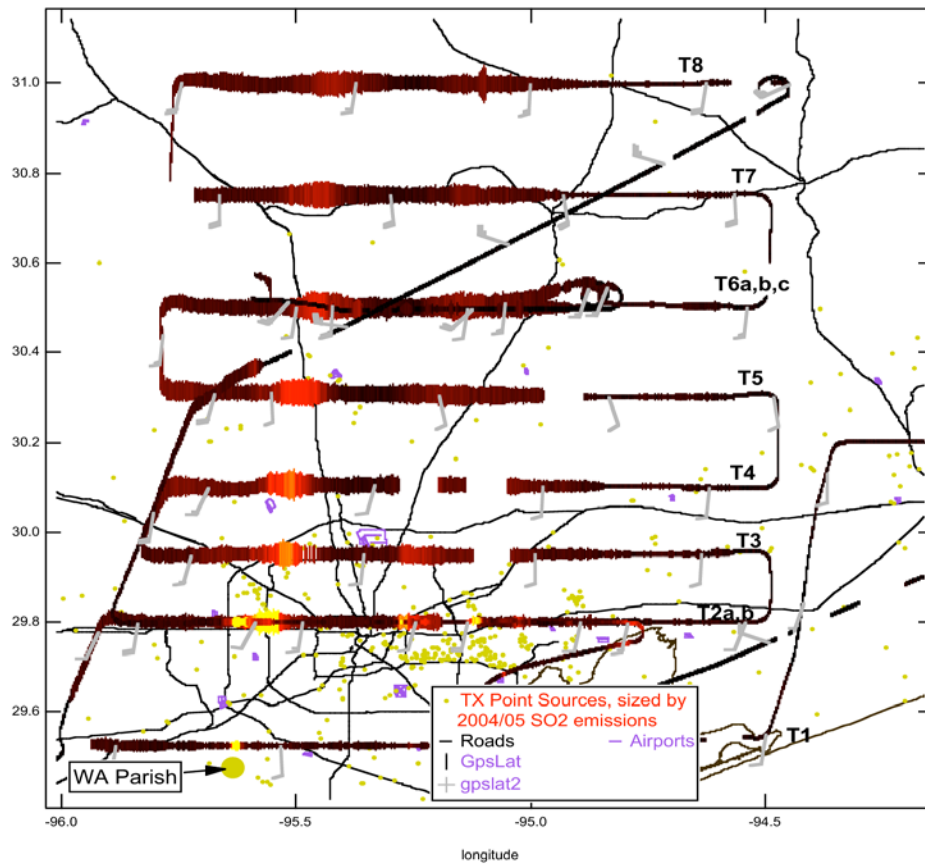

Figure 2.2   A schematic of the flight tracks for the NOAA WP-3D aircraft through the Houston, TX area during the TexAQS2006 campaign on September 27, 2006. The colour and size is proportional to SO_2 concentrations scaled from 0 to 20 ppb.

2.4   University of Houston measurements and model parameters

Work was done with the University of Houston research group regarding ammonia slip assumptions and particle concentrations in the W.A. Parish plume using the SAM-TOMAS model (Gong et al., 2012). My contribution to this paper included the model simulations using their ammonia slip emissions estimates from the power plant to determine particle formation rates. Described in this section are their measurements results and motivation towards our work.

Atmospheric NH_3 was measured on top of the North Moody Tower on the University of Houston campus using an external cavity quantum cascade laser-based sensor
. Aerosol species that were measured using a particle-into-liquid sampler included ammonium (NH_4^+), sodium, potassium, calcium, magnesium, sulphate (SO_4^{2-}) nitrate, nitrite, and chloride with diameters less than 1 μm.

Measurements with elevated NH_3 levels were recorded during mid-day hours of the campaign that corresponded to periods where the wind was blowing from the W.A. Parish power plant. The SAM-TOMAS model was employed to estimate particle production due to the presence of this additional NH_3 assumed to be from ammonia slip of the SCR technology (particle number concentrations were not measured from this site). Unfortunately, NH_3 emissions rates are not recorded by the CAMs database because it is not currently a regulated pollutant under NAAQS. Thus, in order to gain insight on plume development under additional emissions conditions, a range of NH_3 emissions and background estimates as well as two ternary nucleation schemes to estimate the possible range of particle formation in plumes during periods of ammonia slip were used. NH_3 emissions were estimated by the University of Houston Group based on vendor-estimated slip values from SCR technology for high (0.012 kg s^{-1}), medium (0.007 kg s^{-1}) and low (0.0012 kg s^{-1}) emissions slip scenarios. My contribution to the project involved running two nucleation schemes within the model for both high (900 ppt) and low (0 ppt) NH_3 backgrounds. These included the Napari et al., (2002)

(with a nucleation rate scaling factor of 10^{-5}) and Merikanto et al., (2006) ternary ($H2SO_4$ – NH_3 – H_2O) nucleation schemes for a total of twelve model simulations. These results are discussed in chapter 4.

CHAPTER 3 RESULTS

The following chapter is taken from the results section of Lonsdale, C.R., Stevens, R.G., Brock, C.A., Makar, P.A, Knipping, E.M. and Pierce, J.R. submitted to Atmospheric Chemistry and Physics, 2012. As the first author of this paper, I performed all the data analysis, modeling and writing.

3.1   Changes in the W.A. Parish plume between 1997 and 2010

In this section, we discuss the sensitivity of the model to changes in emission input parameters that represent emissions changes due to pollution-controls from the W.A Parish coal-fired power generation facility between 1997 and 2010. First, we discuss the control technologies and changes in the facility during this time period, followed by associated emissions trends. The model's predicted particle production for both years is then discussed.

The annually averaged SO_2 and NO_x emissions from the W.A. Parish power plant from 1997 to 2010 are shown in Fig. 3.1. In 1997, four of the eight total units were coal-fired sources (units 5, 6, 7 and 8). All four of these units contained particle controls in the form of baghouse filters. NO_X controls were installed on unit 5 (LNBT), and unit 8 (OFA) prior to 1997. There is no record of NOX controls on units 6 and 7 in 1997. By 2004 all units contained LNBT with either over-fire air or combinations with SCR, and by 2005 all units contained SCR. For SO_2 controls, only unit 8 is recorded to have Wet Lime FGD for all years, and the other three units have no record of SO_2 controls for any years. From the Clean Air Markets database, it was derived that in 1997 the average NO_X and SO_2 emissions for the W.A. Parish plant were 1.22 kg s^{-1} and 2.24 k g s^{-1}, respectively. In 2010, these emissions were reduced to 0.128 k g s^{-1} and 1.49 kg s^{-1} for NO_X and SO_2, respectively (Fig. 3.1). Even though SO_2 control implementations were not recorded, there is an indication of emissions reduction in the database, and this may

be due to reduced sulfur content in the coal. The emissions of both gaseous species decreased over the 13-year period; however, NO_X rates decreased by ~90% while SO_2 only decreased by ~30%.
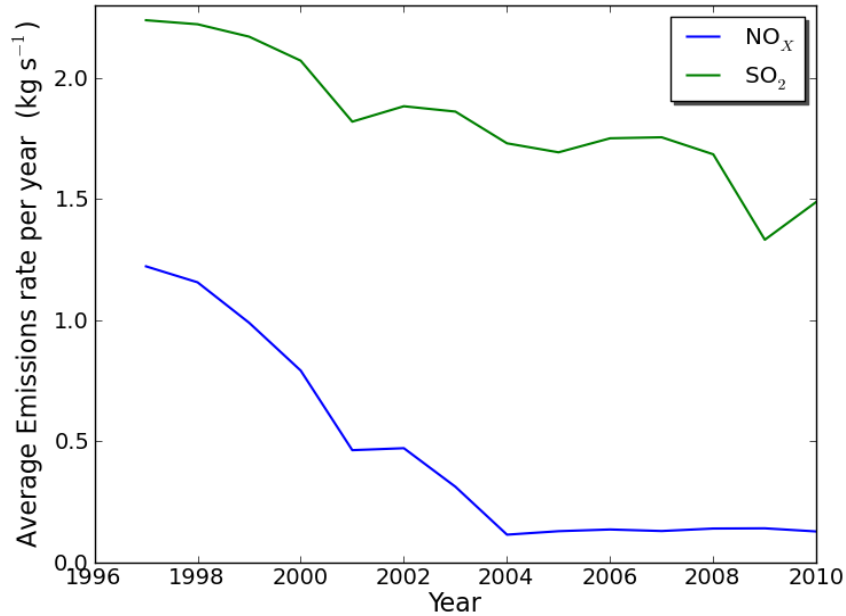
Figure 3.1   The yearly average emissions (kg s^{-1}) of SO_2 (green) and NO_X (blue) from the 4 coal-burning units (summed together) at W.A. Parish power plant.

To estimate how the emissions changes between 1997 and 2010 may have affected particle formation in the plume, we performed two simulations: one with the 1997 emissions and another with the 2010 emissions, each using meteorology and chemical background conditions from 27 September 2006 during the TexAQS2006 field campaign as tested in Stevens et al. (2012). This day had clear skies and a boundary-layer height of 1000 m. The mean boundary-layer winds were northward at 5 m s^{-1} avoiding Houston, Texas with somewhat polluted remote-continental background aerosol concentrations. Figure 3.2 shows the predicted Net Particle Contribution (NPC) rate as a function of distance from the stack.

Figure 3.2   The Net Particle Contribution (NPC) rate at each distance downwind of W.A. Parish Power Plant for the 2010 (blue) and 1997 (red) emissions scenarios. Meteorology and background conditions were the 27 September 2006 conditions for both cases.
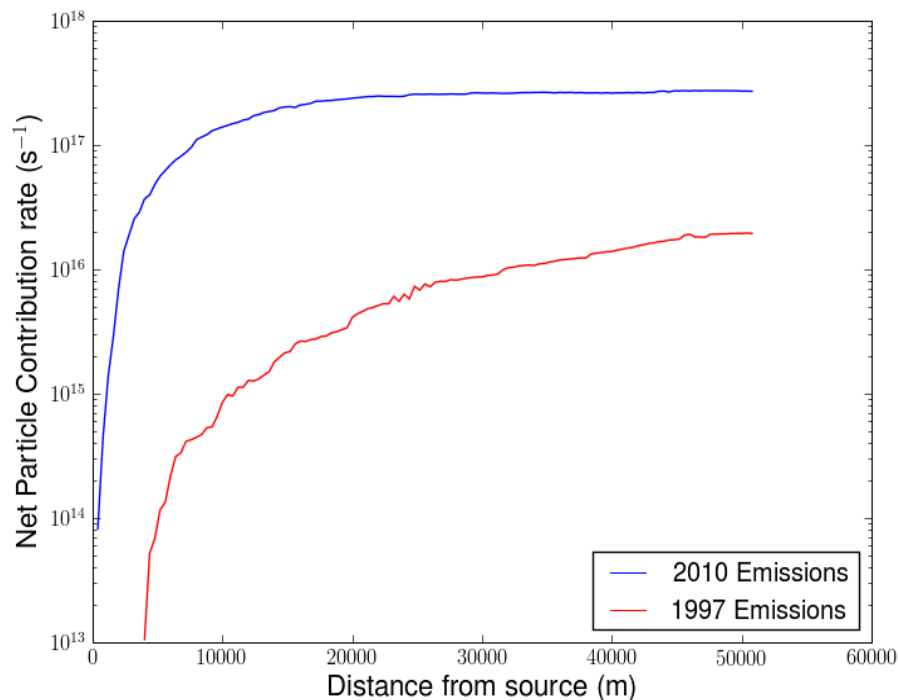
We define the NPC rate as the net number of particles that the power plant has contributed per time at a given distance from the stack accounting for both particle gains by new particle formation and loss by coagulation. The NPC rate is the effective emissions rate of particles from the power plant once chemistry and physics in the plume has been accounted for.   It depends on the distance from the stack because both nucleation and coagulation shape the aerosol distribution as the plume moves further from the stack.

In Figure 3.2, it can be seen that there is over an order of magnitude increase in the predicted NPC rate between 1997 and 2010 (with background conditions fixed). This increase occurs even though SO_2 emissions have decreased by 30%. The increase is due to the large reduction of NO_X emissions that caused an increase in the predicted OH in the plume.

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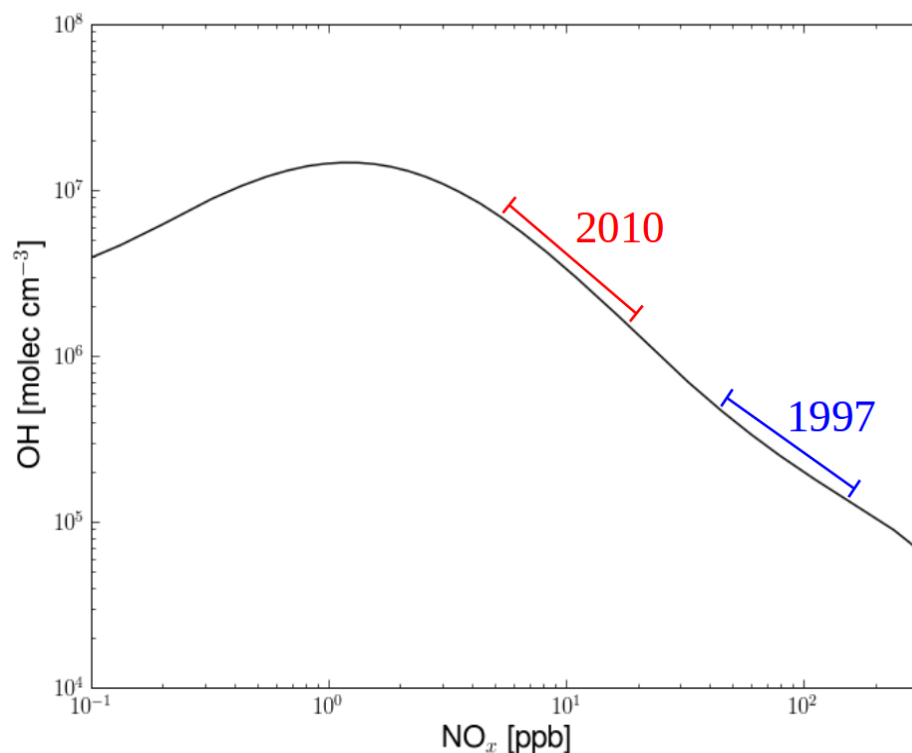
Figure 3.3   [OH] as a function of [NO_X] for the background conditions on September 27, 2006. The red and blue bars show the range of NO_X concentrations found in the first 50 km of the plume for the 2010 and 1997 emissions.

The OH a nd NO_x changes for the corresponding years are shown in Fig. 3.3. T he predicted OH concentrations increase by ~10x in the plume between 1997 and 2010. Thus, SO_2 is oxidized ~10x more quickly in 2010 leading to larger H_2SO_4 concentrations early in the plume even though emissions rates were reduced by ~30%. The predictions shown here are limited to a single set of background conditions. As we will show later (in sub-sect. 3.3), the sensitivity of the NPC rate to changes in emissions depends greatly on the background conditions. In the limit of no or low sunlight (e.g. night) or high background particle concentrations, no nucleation will take place regardless of emissions (Stevens et al., 2012), and the NPC rate will have no sensitivity to emissions (it will be zero).

3.2   Net Particle Contribution rates versus SO_2 and NO_X emissions

To better understand how NPC rates depend on SO_2 and NO_X emissions, Fig. 3.4 shows the NPC rates at 50 km downwind of a source stack against NO_X emissions ranging from 0-1.4 kg s^{-1} and SO_2 emissions ranging from 0-7.5 kg s^{-1} (these ranges encompass most power plants in the US). Similar to Fig. 3.3, the background conditions are set to those for 27 September 2006 at the W.A. Parish power plant. 110 individual SAM/TOMAS simulations were used to populate the figure. The NPC rate ranges from over 10^{17} s^{-1} in high-SO_2 emissions cases to zero particles in very-low-SO_2 emissions cases. Increasing SO_2 emissions rates generally increases the NPC rate. As would be expected based on Fig. 1.1, increasing NO_X emissions leads to an increase in the NPC rate if NO_X emissions are low (OH increases with increasing NO_X), and increasing NO_X emissions leads to a decrease in the NPC rate if NO_X emissions are high (OH decreases with increasing NO_X).
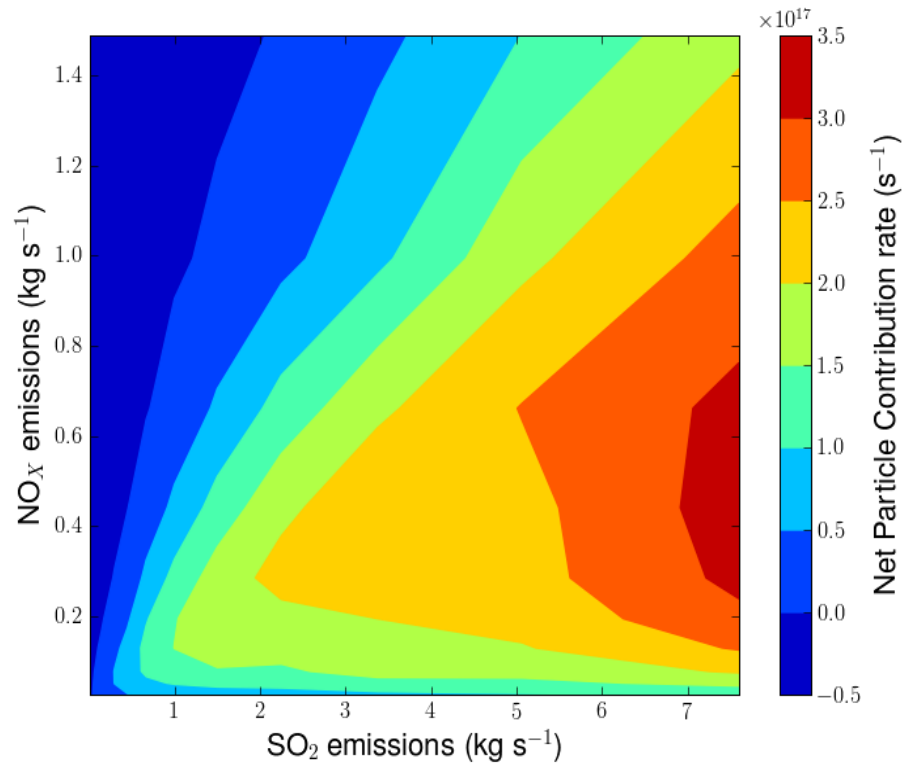
Figure 3.4   Interpolated influence from 110 model simulations of changing NO_X and SO_2 emissions on net particle contribution rate 50 km downwind of the source stack. Meteorology and pre-existing particle background concentrations for all model runs were the 27 September 2006 conditions.

These results indicate that for power plants with high NO_X emissions (> ~ 0.6 kg NO_X s^{-1} according to Fig 3.4.), SO_2 concentrations must be reduced by a larger fractional amount than NO_X in order for particle production in the plume to decrease. Similar to the previous section, these results are only for a single background. The magnitude of the predicted NPC rates will depend greatly on the background concentrations (Stevens et al., 2012), which will be shown in the following section.

3.3 Observational evidence and comparison of model to measurements

Aircraft-based measurements of coal-fired power-plant plumes using the suite of instruments required to set-up and test the model (e.g. SO_2, NO_X, fast aerosol size distribution measurements) are quite sparse. To ideally identify the effect of pollution-control technologies from observations, many aircraft-based measurements of power-plant plumes would be needed both before and after pollution controls were implemented. A large number of measurements would be required in order to average over day-to-day variability in background meteorology and aerosol concentrations. These before/after measurements are even more sparse, though we have found one set of measurements that we will analyze here.

The NCAR Electra aircraft and NOAA P-3 aircraft made transects through the W.A. Parish power plant in the TexAQS2000 and TexAQS2006 field campaigns respectively. For each campaign, we have identified a measurement case where the power-plant plume was able to evolve with minimal additional anthropogenic emissions mixing into the plume (e.g. the plume must avoid the city of Houston). The TexAQS2000 flight measurements were on 27 August 2000 and the TexAQS2006 measurements were on 27 September 2006 (described in section 3.1). There were significant changes in NO_X and SO_2 emissions between these dates (Fig. 3.1). Although the change in emissions is smaller between 2000 and 2006 than it is between 1997 and 2010 (as tested earlier), NO_x emissions were still reduced by 83% and SO_2 emissions were reduced by 15% between 2000 and 2006. The boundary layer height on 27 August 2000 was recorded to have a maximum height of ~2000 m above the surface with northward winds ranging from 3-6 m s^{-1} (Brock et al., 2003). Fair-weather boundary-layer cumulus clouds were occasionally present on this day; however, during the time of flight, low-cloud coverage was less than 10% according to the NCEP North American Regional Reanalysis (NARR). As mentioned earlier, in-cloud oxidation of SO_2 was not included in the

model; however, the reduction of downward short wave radiative flux by the clouds was accounted for in the model inputs.

There was a large difference in the background aerosol size distributions between the campaign days as seen in Fig. 3.5.
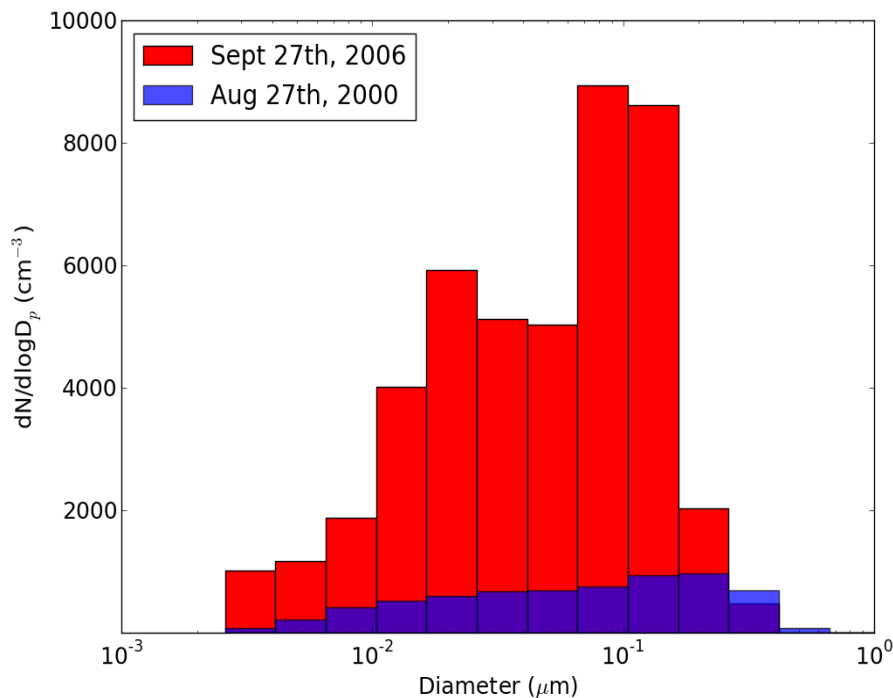
Figure 3.5   The measured background particle size distributions by NOAA P-3 on 27 September 2006 (red) and 27 August 2000 (blue) near the W.A. Parish Power Plant. The condensation/coagulation sink was ~4x larger for the 2006 case.

The condensation/coagulation sink of the background aerosol for the 2000 case was only 0.25 of the 2006 c ase. T hus, we expect the differences in the condensation and coagulation sinks to have a significant effect on the NPC rates, so unfortunately the measured effect of the changes in power-plant emissions between 2000 and 2006 cannot be isolated in the measurements alone.   In this section, we will use the model as a means of interpreting the measured response to the emissions changes by isolating the emissions and background-aerosol changes. W e present 4 simulations: one with 2000 background

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concentrations and meteorology with 2000 e missions, one with 2000 background concentrations and meteorology with 2006 e missions, one with 2006 background concentrations and meteorology with 2000 emissions, and one with 2006 background concentrations and meteorology with 2006 emissions.
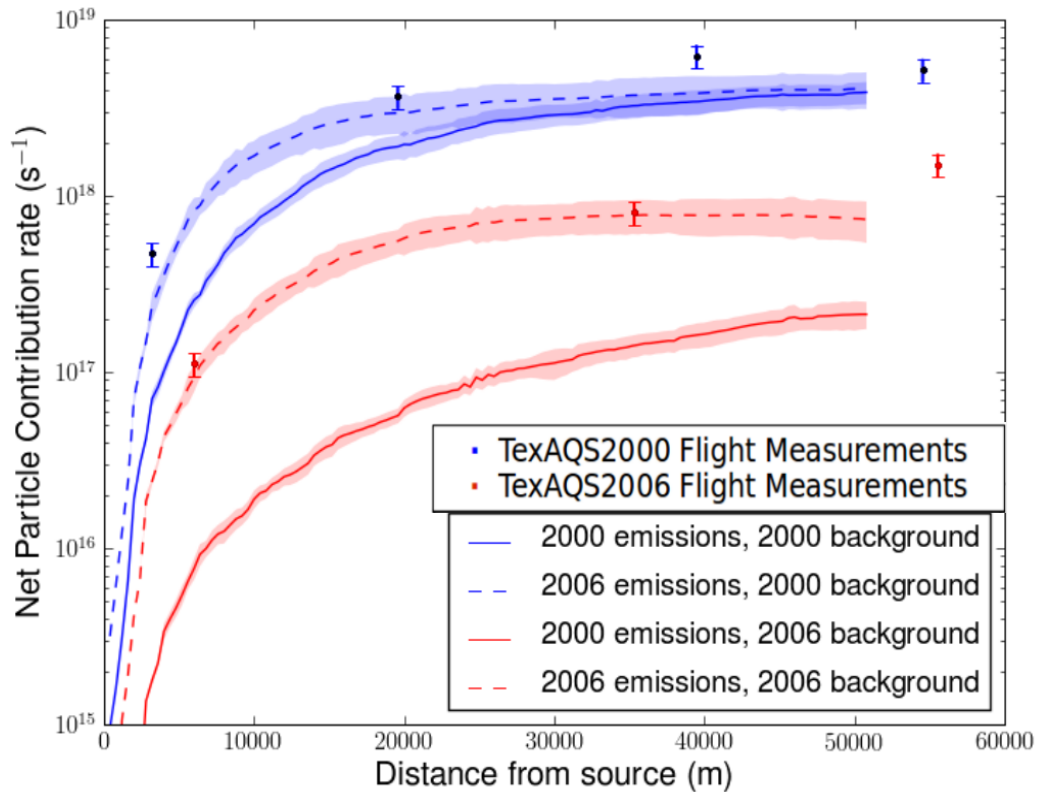
Figure 3.6   Net Particle Contribution rate as a function of distance downwind of the W.A. Parish power plant for the two sets of measurements and the model simulations with the four combinations of emissions and background conditions for the 2000 and 2006 cases.

Figure 3.6 s hows the NPC rate for the four simulations and the measurements. T he simulation with 2006 emissions and 2006 ba ckground matches the 2006 m easurements (red dashed line) considerably better than any other simulation matches the 2006 measurements. O n the other hand, the simulation with 2006 e missions and 2000 background matches the 2000 measurements best (rather than the simulations with 2000 emissions and 2000 b ackground), slightly under predicting the NPC rate for each

transect. However, the difference between this simulation and the simulation with the 2000 emissions and 2000 background is small, particularly farther from the source.

The effect of the background aerosol concentrations on the simulated NPC rate in Fig. 3.6 was significant, consistent with Stevens et al. (2012). The difference between the clean 2000 background cases (blue) and the more-polluted 2006 background cases (red) was about a factor of 10 or higher when the emissions were held fixed. Thus, the differences in background likely contributed significantly to the difference in the measured NPC rates between 2000 and 2006. The model also showed that the difference between the 2000 and 2006 measurements would be even larger if the emissions were held fixed, particularly under the more polluted 2006 background conditions. Thus, if the model-predicted dependence of the NPC rate on the background concentrations is correct, the change in the emissions between 2000 and 2006 resulted in an increase in NPC; however, the change in background between the 2000 and 2006 cases resulted in a decrease in NPC (that is larger in magnitude than the effect of the emissions change).

The model predicts that the sensitivity to changing emissions under fixed background conditions was significantly larger during the more-polluted 2006 conditions (difference between the red lines) than during the less polluted 2000 conditions (difference between the blue lines). Under the cleaner 2000 background conditions, nucleation proceeded quickly in both emissions cases (although more quickly in the case of 2006 emissions). The nucleation mode quickly became the dominant condensation and coagulation sink (the pre-existing particles did not contribute greatly to these sinks). In the 2006 emissions case (with the 2000 background conditions), the condensation and coagulation sink formed in the plume was somewhat larger than the 2000 emissions case (with the 2000 background conditions), and this provided a negative feedback on the NPC rate due to slower nucleation and faster coagulation. Thus, the difference in the NPC rate was small between 2000 and 2006 emissions for the clean 2000 background conditions due to the nucleation mode dominating the condensation/coagulation sink. On the other hand,

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under the more polluted 2006 background conditions, the pre-existing particles continued to be the dominant condensation and coagulation sink throughout the plume. Thus, the total condensation and coagulation sink did not depend greatly on t he SO_2 and NO_X emissions. U nlike the 2000 ba ckground conditions, there was no s trong negative feedback in the 2006 background cases that reduced the new-particle formation rates and increased the coagulation rates for the 2006 emissions case, and this facilitated a large difference in the NPC rate between the 2006 and 2000 e missions cases. Thus, as mentioned earlier, the sensitivity of the NPC rate to emissions is strongly sensitive to the background conditions.

This sensitivity to background conditions is particularly important because power plants may correlate (or anti-correlate) with highly polluted regions. F or example, the power plants in the Ohio River Valley will exist in generally polluted air. T hus, future work will be done using three-dimensional chemical transport models to explore these correlation effects.

3.4   US emissions statistics and estimated particle formation

The increase in particle production of one coal-fired power plant may not be indicative of broader trends in power plants; therefore, we explored how particle production may have changed for each plant in the US based on their SO_2 and NO_X emissions changes. Using the Clean Air Markets' database, the 1997 and 2010 SO_2 and NO_X emissions were found for each of the available 330 coal-fired power plants in the US (with recorded emissions that were operational in each of these years). Figure 3.7 shows the ratio of emissions between 2010 and 1997 for SO_2 and NO_X emissions for these plants. Nearly all power plants show a decrease in both species between 1997 and 2010 with a median ratio of 0.64 and 0.48 for SO_2 and NO_X respectively.
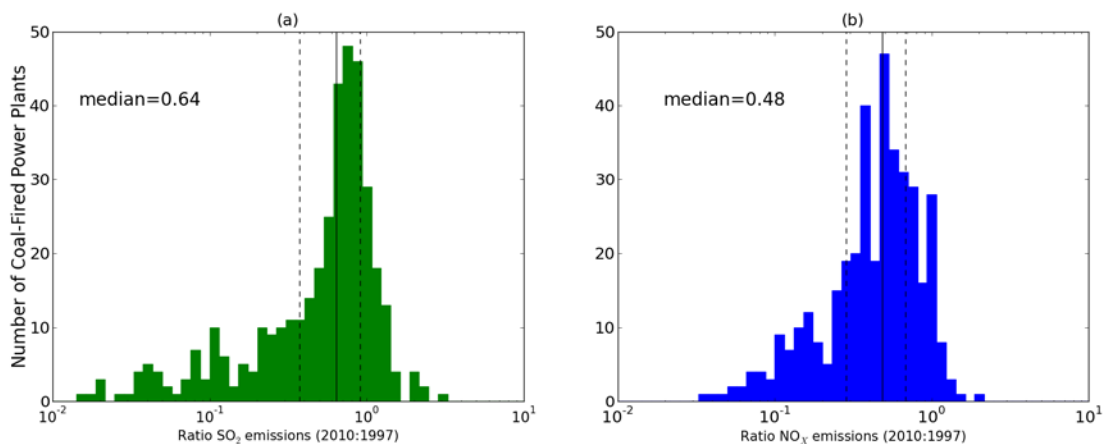
Figure 3.7   Histograms showing the ratio of (a) SO_2 and (b) NO_x emissions changes between 2010 and 1997 for all (330) coal-fired power plants in the US registered to the CAM database. The mean ratio (solid line), 25% and 75% (dashed-lines) quartiles are plotted. There is an overall decrease in emissions with an median ratio of 0.64 SO_2 (green) and 0.45 NO_X (blue) for 2010:1997

In the case of the W.A. Parish power plant explored throughout this paper, NO_X emissions reductions are significantly greater than the SO_2 emissions reductions. Thus, the emissions changes for the W.A. Parish plant were not representative of the general U.S. population of coal-fired power plants. We estimate how the NPC rate from each power plant would change between 1997 and 2010 under the fixed meteorological and background chemical conditions of the W.A. Parish power plant on 27 September 2006 by interpolating the NPC rates in Fig. 3.4. Figure 3.8 shows the ratio of the predicted NPC rate between 2010 and 1997 for the 330 plants under the fixed background conditions. Based on these plants, we estimated that there is a net reduction of particle formation between the two years with a median decrease of 19% when background conditions are held constant. This overall decrease could be due, in part, to NO_X emissions from smaller power plants being low enough such that the plume is not in the high-NO_X regime. For these power plants, reductions in NO_X do not lead to large increases in OH and may even lead to decreases in OH.
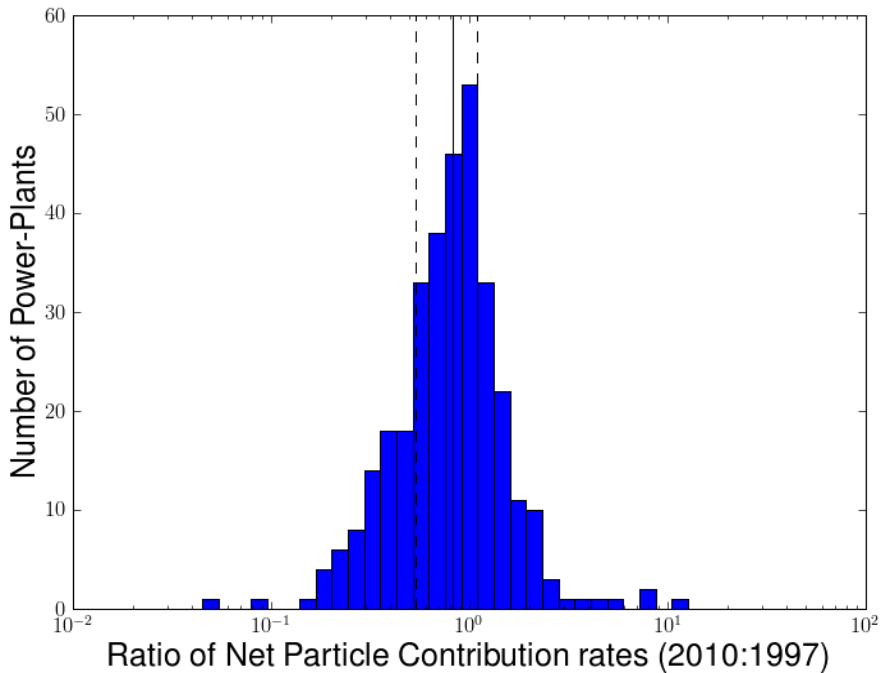
Figure 3.8   Histogram showing the ratio of predicted NPC rates between 2010 and 1997 is shown for all US power plants using the NO_X and SO_2 emissions from each of the years and the predicted NPC rates shown in Fig. 3.4. The NPC rates were calculated for the background conditions of September 27, 2006 and produced a median ratio of 0.81. The solid line represents the median and dashed lines represent the inter-quartile ranges.

It appears that the W.A. Parish power plant investigated throughout this paper may be an extreme case relative to the mean of the US power plants because of its stronger NO_X controls than SO_2 controls. Again, we stress that the results for the sensitivity of NPC rate to emissions changes will depend on the background meteorology and chemistry. However, the results showing that the average change in the NPC rate across the 330 power plants was small. This result is likely robust to changes in background conditions because changes in the background will generally not change the sign of how emissions change the NPC rate. Because the individual 330 plants showed a wide range of increases and decreases in NPC rate that largely cancel out (Fig. 3.8), this cancellation should not change with the background. However, a full analysis of the effect of power-

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plant emissions changes on aerosol concentrations using a regional chemical transport model is planned for future work, which will yield a more comprehensive estimate than provided here.

CHAPTER 4 POTENTIAL EFFECTS OF AMMONIA SLIP ON NEW PARTICLE FORMATION

Gong et al. (2012) measured various gaseous and aerosol species atop their 18-story building at the University of Houston Campus during their August 5 – August 9, 2010 campaign. Winds were light (~4.5 m s^{-1}) coming out of the southwest, the direction of the W.A. Parish power plant. They detected elevated NH_3 gas, and NH_4^+ and SO_4^{2-} aerosol levels when the winds were blowing from the direction of the W.A. Parish power plant. Gong et al. (2012) inferred that the plant was a potential source of ammonia from the SCR technology at the plant, with motor vehicle emissions contributions being unlikely due to lack of carbon monoxide (CO) measurement enhancements. When CO and NH_3 are detected together this is an indicator of the three-way catalytic converter byproducts in vehicle emissions. This is most common and most detected in middle-aged cars (1996-2000)(Kean, 2009).

The SAM-TOMAS model was used to simulate plume evolution, including NH_3 emissions, to estimate possible downwind effects of ammonia slip for the W.A. Parish power plant on aerosol nucleation/growth in the source plume. The importance of NH_3 in particle production is shown in Fig. 4.1 using the Napari et al. (2002) and Merikanto et al. (2006) ternary nucleation schemes and NH_3 as the ternary species. These ternary nucleation schemes did not compare to observations as well as the activation scheme employed earlier (Stevens et al., 2012); however, the ternary schemes were needed to test the effect of ammonia as the empirical activation scheme does not depend on ammonia concentrations.
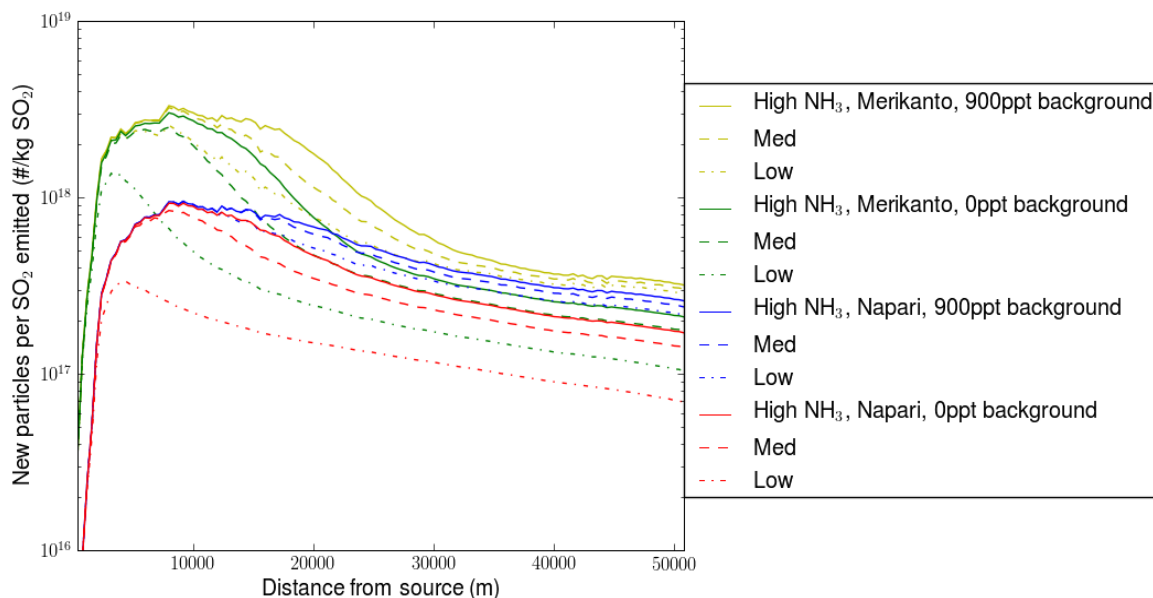
Figure 4.1   The number of particles formed per mass of SO_2 emitted as a function of distance downwind of W.A. Parish for 12 different SAM-TOMAS simulations. Two ternary nucleation schemes include Merikanto (yellow and green) and Napari (blue and red) techniques for high (solid), medium (dashed) and low (fine-dashed) NH_3 emissions under high (yellow and blue) and low (green and red) NH_3 background conditions.

Plotted are the numbers of new particles normalized by the kilograms of SO_2 emitted as a function of distance downwind of the plant. NH_3 emissions were particularly significant under low NH_3 background conditions (variation in green and red lines due to different NH_3 emissions). For higher NH_3 background conditions, nucleation rates were more saturated resulting in small differences between NH_3 emissions cases (variation amongst yellow and blue lines). Overall, however, NH_3 emissions did increase nucleation rates, which emphasizes the impact that ammonia slip from SCR technology could have on in-plume particle production and local particle concentrations.

These predictions are, at best, as good as the Napari et al (2002) and Merikanto et al. (2006) ternary nucleation schemes. Recent experimental results from Kirkby et al. (2011) showed that NH_3 does enhance nucleation rates in warm boundary-layer conditions. However, some organic compounds may preferentially bind with H_2SO_4 in the small nucleating clusters, so in the presence of these organic compounds, the

importance of NH_3 in nucleation is reduced. Even in the absence of the organic compounds, the effect of NH_3 on nucleation begins to saturate above 100 ppt NH_3, though this is somewhat consistent with the Napari et al. (2002) and Merikanto et al. (2006) schemes.

CHAPTER 5 CONCLUSIONS

5.1 Summary

Coal-fired power plants are the number one source of electricity in the world today and if power production rates remain constant coal reserves are estimated to last for more than 100 years (US Energy Information Administration, 2011). Emissions from these coal-fired power plants contain aerosol-precursor gases therefore it is important to understand how these large sources of emissions affect aerosol chemistry and physics within the plumes in order to assess climate and health impacts and accurately represent them in global atmospheric models. Recent policies have addressed the need for emissions reductions, and as a result many power plants have implemented SO_2 and NO_X control-technologies; however, the effect of these technologies on plume chemistry and microphysics are not well understood. This project used the SAM-TOMAS LES model to explore how these pollution-control technologies affect nucleation and growth rates of in-plume particles.

Emissions of SO_2 and NO_x from the W.A. Parish coal-fired power plant decreased by 30% and 90%, respectively, between 1997 and 2010. The effect of these emissions changes on aerosols in the plume were modelled using the meteorology and background conditions from NCEP/NARR datasets and the TexAQS2006 flight track background measurements in the SAM-TOMAS LES model. The decreasing emissions rates were shown to have a significant effect on aerosol formation and growth in the plume. The model showed an increase in net particle contribution (NPC) rate 50 km downwind of the plant between 1997 and 2010 due to decreasing NO_X emissions promoting more available OH to oxidize SO_2 into H_2SO_4. NPC rate is defined as the net number of particles per time at a given distance from the stack that the power plant has contributed and includes both particle gains by new particle formation and loss by coagulation. Two

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aircraft flights through the W.A Parish power plant were examined; one before and one after controls were added. Variation in background aerosol concentrations dominated differences in NPC rates between the flights; however, the emissions changes still likely had a significant effect.

A quantitative representation of emissions ranges was created to show the relationship of SO_2 and NO_X emissions changes to NPC under fixed meteorological/background-aerosol conditions. The range of emissions rates incorporates many coal-fired power plants rates and may serve as a tool for predicting changes in particle production over time due to changing emissions. For high initial NO_x emissions, as NO_X emissions decrease, particle production increases. U.S. yearly averaged emissions statistics from 330 power plants for 1997 and 2010 were then used to estimate the change in NPC rates for each of these plants across this time period. A net reduction of particle formation was estimated between the two years with a median decrease of 19%; however, this is a simplified estimate with background conditions held constant.

5.2 Implications

There has been additional evidence of increased measured particle concentrations in plumes with new pollution control technologies in Germany, Inner Mongolia and Southern Australia. Junkermann et al. (2011) explored these cases and suggest the increase in ultrafine particles could impact local cloud coverage with an overall increase in albedo potentially offsetting the positive radiation forcing from coal-fired power-plant CO_2 emissions. Local precipitation patterns and intensity would also be affected by the addition of ultrafine particles, and the health of local residents could be impacted. The explanation to the addition of particles from Junkermann et al. (2011) differs from this project. Junkermann et al. (2011) attributes the additional ultrafine particles to by-products of the control technologies internal reactions (although there is no direct evidence of this). They explain that SO_3 production within power-plant stacks

contributes to additional sulphuric acid formation. This particular mechanism to particle production was not addressed in this thesis; however, the impacts of additional ultrafine particles formed within the plume, as explored here, may have similar climate and health effects. Additionally, the potential of ammonia slip from Selective Catalytic Reduction (SRC) of NO_x, as explored by Gong et al. (2012) will add to the possible CCN-increasing effects of power-plant controls. In China, energy production from coal-fired power plants has increased by 49% between 2005 and 2007 alone (Wang et al., 2012) and, along with India, is estimated to be responsible for 80% of the growth in coal-fired power facilities over the next few decades (Shindell and Faluvegi, 2010). This will increase coal-fired power-plant emissions globally with power-plant control technologies potentially influencing the resulting particle impacts.

5.3 Future Work

This study has shown that an unintended result of pollution-control technologies may be occurring with the addition of particles produced within power-plant plumes. In order to accurately estimate the cumulative radiative effect of aerosols on climate and health, primary emissions, nucleation and growth of particles in plumes of power plants must be understood. With the continuing construction of coal-fired power plants and the changes in pollution-control technologies, there is a strong need for additional modeling and measurements of power-plant plumes in order to quantify this impact on a global scale. Future work will involve data analysis from additional flight-tracks through power-plant plumes, upon availability, for further testing against model simulations. From this, the impact of power-plant controls on downwind CCN production can be studied using three-dimensional modeling of plume dynamics. A dditionally, a sub-grid plume parameterization is being created as inputs to three-dimensional global models in order to more accurately quantify coal-fired power-plant plumes and their pollution-control technologies' global climate impacts.

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