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The effect of coal-fired power-plant SO$_2$ and NO$_x$ control technologies on aerosol nucleation in the source plumes

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Abstract

Nucleation in coal-fired power-plant plumes can greatly contribute to particle number concentrations near source regions. The changing emissions rates of SO$_2$ and NO$_x$ due to pollution-control technologies over recent decades may have had a significant
[5] effect on aerosol formation and growth in the plumes, with ultimate implications for climate and human health. We use the System for Atmospheric Modeling (SAM) large-eddy simulation model with the TwO-Moment Aerosol Sectional (TOMAS) microphysics algorithm to model the nucleation in plumes of coal-fired plants. We test a range of cases with varying emissions to simulate the implementation of emissions-control tech-
[10] nologies between 1997 and 2010. For the W.A. Parish power plant (near Houston, TX) during this time period, NO$_x$ emissions were reduced by ∼90 %, while SO$_2$ emissions decreased by ∼30 %. Increases in plume OH (due to the reduced NO$_x$) produced enhanced SO$_2$ oxidation and particle nucleation despite the reduction in SO$_2$ emissions. These results suggest that NO$_x$ emissions may strongly regulate particle nucleation
[15] and growth in power-plant plumes. Comparison of model results with airborne measurements made in the W.A. Parish power-plant plume in 2000 and 2006 confirm the importance of NO$_x$ emissions on new particle formation, yet also highlight the substantial effect of background aerosol loadings on this process. A wide range of NO$_x$ and SO$_2$ emissions were modeled to understand how they affect particle formation in
[20] the plume. Particle formation generally increases with SO$_2$ emission, while NO$_x$ shows two different regimes: increasing particle formation with increasing NO$_x$ under low-NO$_x$ emissions and decreasing particle formation with increasing NO$_x$ under high-NO$_x$ emissions. Finally, we calculate emissions statistics of 330 coal-fired power plants in the US in 1997 and 2010, and the model results show a median decrease of 19 % in particle
[25] formation ratesfrom 1997 to 2010 (whereas the W.A. Parish case study showed an increase). These results suggest that there may be important climate implications of power-plant controls due to changes in plume chemistry and microphysics. More ex-

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tensive plume measurements for a range of emissions of SO_2 and NO_x and in varying background aerosol conditions are needed to better quantify these effects.

1   Introduction

Anthropogenic aerosols affect human health and the Earth's climate. High aerosol concentrations are known to cause human health problems such as respiratory and cardiovascular diseases, intensification of asthma, a reduction in physical abilities and an increase in mortality rates (Arya, 1999; Stieb et al., 2002; Peng et al., 2004). Aerosols affect the Earth's radiative properties. The direct effect of aerosols on climate is due to their ability to scatter and absorb incoming solar radiation (Charleson et al., 1992). The indirect effect of aerosols on climate is the change in the radiative properties of clouds from the altering of cloud droplet/crystal size and concentration and potentially precipitation rates by changes in the number of aerosols acting as Cloud Condensation Nuclei (CCN) (Twomey, 1974; Albrecht, 1989). Both the direct and indirect effects of aerosols have large uncertainties associated with them, partly due to uncertainties in primary anthropogenic aerosols and the nucleation of ultrafine aerosols that are initially too small to act as CCN (IPCC 2007; Spracklen et al., 2008; Makkonen et al., 2009; Pierce and Adams, 2009a; Wang and Penner, 2009).

Measurements of high concentrations of ultrafine particles have been found in the plumes of coal-fired power plants despite the reduction of emissions from installed pollution-control technology (Junkermann et al., 2011a,b). Junkermann et al. (2011b) compared the aerosol size distributions measured in plumes from modern power plants with pollution controls to those from older plants without controls. They found the modern plants to have significantly more ultrafine particles (and total particle number) than the older plants. Their hypothesis as to the source of these ultrafine aerosols is explained by in-stack formation from pollution-control technology byproducts (Srivastava et al., 2004). A fraction of these additional ultrafine particles evolve into CCN and may ultimately affect clouds and climate (Adams and Seinfeld, 2003; Pierce and Adams,

2009a; Konwar et al., 2010; Junkermann et al., 2011a, b). Junkermann et al. (2011b) describes how the shift to cleaner power plants may lead to more CCN that can impact climate. Thus, it is important to understand the various processes that affect the net number of particles formed due to power plants that are affected by pollution-control technologies. Along with the in-stack formation of new particles, changes in plume chemistry and microphysics due to the changes in SO_2 and NO_x emissions may also affect the net number of particles contributed by a power plant. This latter effect of SO_2 and NO_x emissions changes has yet to be explored.

Recent pollution-control technologies installed on power plants remove sulfur dioxide (SO_2) and nitrogen oxides ($NO_x = NO + NO_2$). SO_2 may be oxidized in the gas phase via OH to form sulfuric acid (H_2SO_4) vapors that contribute to new-particle formation and growth (Kulmala and Kerminen, 2008). Thus, a reduction in SO_2 alone would result in a reduction of particles formed in power-plant plumes. However, NO_x controls may either increase or decrease OH concentrations in the plume (depending on the environmental conditions). Thus, in many conditions a reduction in NO_x may lead to an increase in the rate at which H_2SO_4 is formed and perhaps an increase in particle formation/growth.

In this paper, we explore the effects of SO_2 and NO_x control technologies on nucleation in the plumes of coal-fired power plants. In Section 2, we review the various chemical and microphysical processes affecting particle formation in plumes. In Section 3, we provide an overview of power-plant control technologies. The methods and the SAM/TOMAS model are described in Sect. 4. Our results, including a detailed case study of the W.A. Parish power plant, a comparison to measurements and an assessment of particle-formation changes from US coal-fired power plants, are given in Sect. 5. In Sect. 6, we present the conclusions.

2 Chemical processes in power-plant plumes

Coal-fired power plants are sources of SO_2, NO_x and primary ash particles (Zhao et al., 2008; Srivastava et al., 2004). However, due to the high efficiency of particulate controls, primary ash emissions in modern coal-fired power plants in developed countries are very low (Miller, 2010). A product of coal combustion is SO_2, which is oxidized in the gas phase by OH to form H_2SO_4 vapor under tropospheric conditions (Seinfeld and Pandis, 2006; Zhao et al., 2011). Under continental surface conditions, H_2SO_4 vapor will quickly (seconds to minutes) form either new $\sim 1\,nm$ aerosol particles (aerosol nucleation) or condense onto pre-existing particles (Pierce and Adams, 2009b). In the presence of clouds, SO_2 is dissolved into cloud or rain droplets and oxidized to sulfate (SO_4^{2-}) by aqueous ozone (O_3) or hydrogen peroxide (H_2O_2), which reduces the H_2SO_4 concentrations in the gas phase (Zhou et al., 2012). Since SO_2 is emitted from power plants, H_2SO_4 vapor concentrations are elevated above background levels in plumes and thus power plants may be a major contributor to nucleated particles in the atmosphere under sunny and clear-sky conditions (Yu, 2010; Stevens et al., 2011). The rate of gas-phase SO_2 oxidation depends on the amount of available OH, which depends on the amount of incoming solar radiation, NO_x concentrations and volatile organic compound (VOCs) concentrations.

NO_x is an indirect contributor to new-particle formation rate because it affects the amount of OH available for the $SO_2 \rightarrow H_2SO_4$ gas-phase reaction (Poppe et al., 1992) (Fig. 1). 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. For low NO_x concentrations (< 0.5 ppb), the reaction of NO_2 with OH is unimportant, and OH increases with increasing NO_x (via photolysis of NO_2, enhanced O_3 formation and increased production of $O(^1D)$, in turn increasing the equilibrium level of OH). The peak OH concentration occurs in between these ranges at the transition of the two limiting regimes. 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.

In addition to H_2SO_4 production contributing to formation and growth (via condensation) rates in the atmosphere, the presence of pre-existing particles also determines if particles will form and survive in a source plume. Condensational growth and coagulation rates depend on the concentration of pre-existing particles (Pierce and Adams, 2007). If a high condensation sink exists (due to a large amount of pre-existing aerosol surface area), H_2SO_4 will condense quickly onto these pre-existing particles, which will lower the H_2SO_4 concentrations and reduce new-particle formation and growth rates. Additionally, freshly nucleated particles are lost through coagulation with the larger pre-existing particles. Thus, large amounts of pre-existing aerosol will reduce the net number of particles formed in a plume both by reducing nucleation and condensational growth rates and by increasing coagulation. Power-plant emissions in polluted-background regions likely generate fewer new particles than in clean regions (Stevens et al., 2012). Although not investigated in this paper, the emissions of primary ash particles by power plants without particulate controls could also provide a large amount of surface area and would also greatly reduce new-particle formation and growth. These primary ash particles may be important in developing countries where particulate controls are not implemented or for historical simulations of periods prior to when these controls were commonplace in developed countries (e.g. the United States before the implementation of the Clean Air Act in 1970 (Miller, 2010)).

Finally, meteorological conditions affect nucleation and growth in the power-plant plumes (Stevens et al., 2012). Both wind and turbulence act to dilute the SO_2 and NO_x emissions from the power plant and thus particle formation. Increased relative humidity will increase the size of hygroscopic aerosols thereby increasing condensation and coagulation rates. Clouds reduce the amount of sunlight for formation of OH. Also, aqueous processes in clouds and raindrops promote the formation of sulfate in the larger, in-cloud aerosols, which reduces the amount of available SO_2 for H_2SO_4 for-

mation and increases the size of the pre-existing particles, which reduces new-particle formation.

3 Clean control technologies in coal-fired power plants

To reduce the anthropogenic impact on the environment by coal-fired power plants, specifically acid rain, PM and tropospheric ozone concentrations (Seinfeld and Pandis, 2006), pollution-control technologies have been implemented to reduce primary-particle, SO_2 and NO_x emissions (EPRI, 2008). 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 (2010).

Technologies to reduce the amount of primary particles emitted from source stacks are currently the most effective of the pollution-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 %. Baghouse filters contain fibrous materials that catch large particles (diameters > 1 µm) by inertial and direct impaction and smaller particles by diffusion (Miller, 2010). ESP involves the charging of the ash particles by corona discharge followed by removal of these charged aerosols by an electric field (Miller, 2010). Because of such high removal efficiencies, emissions rates of primary particles are not included in the EPA's Clean Air Market Database.

Many power plants have switched to burning coal with low sulfur contents to allow for SO_2 emissions reductions without the need to implement new control systems. Another technique to reduce SO_2 emissions includes flue gas desulfurization (FGD, e.g. scrubbers). Different classifications of FGD include wet and dry methods, expressing the production of waste in the form of a wet slurry or dry material, respectively. A disadvantage of FGD includes the sometimes-inefficient removal of sulfur trioxide (SO_3) (which will quickly form H_2SO_4) as a by-product of the scrubbing process, and this

may lead to particle formation in the stack (Junkermann et al., 2011b; Srivastava et al., 2004). However, this particle-formation pathway will not be considered in this paper.

Most coal-burning power plants now contain NO_x controls in the form of Low NO_x Burner Technology (LNBT), the over-fire air technique, or a combination of both. Both of these techniques aim to create combustion conditions that reduce the amount of N_2 (from air) oxidized to NO and generally have an efficiency up to 40–60 % (relative to uncontrolled emissions). An additional technology, selective catalytic reduction (SCR), has more recently been added, often in combination with LNBT or over-fire air, to many plants to increase removal efficiencies (> 90 % NO_x reductions). SCR involves a catalyst and the addition of a reagent, ammonia (NH_3), that promotes the reduction of NO_x to nitrogen and water. A negative attribute of SCR includes an SO_3 by-product that will quickly form H_2SO_4 (Miller, 2010). Thus, similar to FGD, SCR may also lead to particle formation in the power-plant stack (Srivastava et al., 2004; EPRI, 2008). Another disadvantage of SCR is that NH_3 may not react completely with NO_x and may be emitted to the atmosphere (EPRI, 2008; Wang et al., 2012). 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, 2010; Gong et al., 2012). Since NH_3 is potentially an important enhancer of aerosol nucleation rates (Merikanto et al., 2007; Kirkby et al., 2011), this too may affect particle formation. This influence on particle formation is not explored in this paper, but was explored in Gong et al. (2012). Gaseous ammonia may also condense directly onto acidic aerosols (Seinfeld and Pandis, 2006), increasing aerosol mass and size, hence influencing subsequent condensation and coagulation rates.

4 Methods

We use the SAM/TOMAS model to explore the dynamics and aerosol microphysics (nucleation, condensation and coagulation) of power-plant plumes (Stevens et al., 2012). The host model is the System for Atmospheric Modeling (SAM), a Large-Eddy Sim-

ulation (LES) and Cloud Resolving Model (CRM) (Khairoutdinov and Randall, 2003). Stevens et al (2012) evaluated the model's ability to predict nucleation and growth in the sulfur plumes of anthropogenic point sources through testing of several nucleation schemes and varying background conditions. With comparisons to aircraft measurements in two power-plant plumes, the model provided reasonable predictions of in-plume particle number concentration and size at distances 20-100km downwind of the source. In this paper, we use grid-box sizes that are $400\,m \times 400\,m$ horizontal resolution and two different vertical resolutions of $40\,m$ and $80\,m$ (depending on the boundary layer height). The simulations contain the gas-phases species of SO_2, H_2SO_4, NO_x and NH_3. OH concentrations are parametrized based on NO_x concentrations, incoming solar radiation and an assumed concentration of reactive VOCs (Stevens et al., 2012). The number and mass of sulfate aerosol, ammonium and water are tracked in 15 size sections spanning $3\,nm$ to $10\,\mu m$ using the TOMAS microphysics scheme (Adams and Seinfeld, 2002; Pierce and Adams, 2009a). Power-plant emissions of SO_2 and NO_x are obtained from the Clean Air Market emissions inventory (Clean Air Markets – Data and Maps, 2012). Primary-particle emissions are assumed to be negligible in model simulations. Emissions are assumed to be well-mixed in the emissions grid-box. Other inputs to the model include 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. The large-scale meteorological forcing of the SAM simulations are provided by vertical profiles of mean winds, temperature, 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 is calculated using the empirical activation nucleation scheme (Kulmala et al., 2006), where nucleation rates are equal to $A[H_2SO_4]$ and $A = 10^{-7}\,s^{-1}$. Various

nucleation schemes were tested in Stevens et al. (2012), and the activation scheme compared best against observations from the TexAQS2006 field campaign.

In these simulations, we do not consider the oxidation of SO_2 within clouds (the meteorology on the tested days contained cloud-free or nearly cloud-free boundary layers). Also, we do not consider the loss of NO_x by chemical reactions. 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, so the chemical loss of NO_x is less important than later in the plume. 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, we expect to over-predict NO_x concentrations with increasing distances from the source. VOC concentrations were assumed fixed in the OH parameterization in our simulations (150 pptv of isoprene). Changes in VOCs may affect OH concentrations resulting in different SO_2 oxidation rates (Stevens et al., 2012). We also do not consider any primary ash particles (which would result in a decrease in nucleation rates) or particles that may have formed in the stack because of high SO_3 formation from FGD or SCR (which would increase the number of particles in the plumes (Junkermann et al., 2011b)). This formation of SO_3 by the pollution control technologies is an additional way in which pollution controls can lead to increased numbers of ultrafine particles. However, this formation pathway is not explored in this paper.

5 Results

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

We have compared the model to observations (Stevens et al., 2012) and shown that it captures the essential features of aerosol size distributions in anthropogenic plumes. In this section, we discuss the sensitivity of the model to changes in SO_2 and NO_x emis-

sions rates due to pollution-controls from the W.A Parish coal-fired power-generation facility between 1997 and 2010.

The annually averaged SO_2 and NO_x emissions from the W.A. Parish power plant from 1997 to 2010 are shown in Fig. 2. 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 (over-fire air) prior to 1997. There is no record of NO_x 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, we derived that in 1997 the average NO_x and SO_2 emissions for the W.A. Parish power plant were $1.22\,kg\,s^{-1}$ and $2.24\,kg\,s^{-1}$, respectively. In 2010, these emissions were reduced to $0.128\,kg\,s^{-1}$ and $1.49\,kg\,s^{-1}$ for NO_x and SO_2, respectively (Fig. 2). Even though changes in 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-yr period; however, NO_x rates decreased by ~90 % while SO_2 only decreased by ~30 %.

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 (red bars in Fig. 3). Figure 4 shows the predicted Net Particle Contribution (NPC) rate as a function of distance from the stack. 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 Fig. 4, 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 has caused an increase in the predicted OH in the plume. The OH and NO_x changes for the corresponding years are shown in Fig. 1. The predicted OH concentrations have increased by ~10× in the plume between 1997 and 2010. Thus, SO_2 is oxidized ~10× more quickly in 2010 leading to larger H_2SO_4 concentrations early in the plume even though SO_2 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 Sect. 5.3), 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).

5.2 Net Particle Contribution rates versus SO_2 and NO_x

To better understand how NPC rates depend on SO_2 and NO_x emissions, Fig. 5 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. 4, the background conditions are set to those for 27 September 2006 at the W.A. Parish power plant. 110 individual SAM/TOMAS simulations are 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, 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). These results indicate that for power plants with high NO_x emissions ($> \sim 0.6$ kg NO_x s^{-1} according to Fig. 5), SO_2 concentrations must be reduced by a larger fractional amount than NO_x in order for the net 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.

5.3 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 Sect. 5.1). There were significant changes in NO_x and SO_2 emissions between these dates (Fig. 3). Although the change in emissions is

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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 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. 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. The condensation/coagulation sink of the background aerosol for the 2000 case was only 0.25 of the 2006 case. Thus, 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. We present 4 simulations: one with 2000 background concentrations and meteorology with 2000 emissions, one with 2000 background concentrations and meteorology with 2006 emissions, one with 2006 background concentrations and meteorology with 2000 emissions, and one with 2006 background concentrations and meteorology with 2006 emissions.

Figure 6 shows the NPC rate for the four simulations and the measurements. The simulation with 2006 emissions and 2006 background matches the 2006 measurements considerably better than any other simulation matches the 2006 measurements. On the other hand, the simulation with 2006 emissions and 2000 background matches the 2000 measurements best (rather than the simulations with 2000 emissions and 2000 background), slightly under predicting the NPC rate for each transect. However,

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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. 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 is 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 proceeds quickly in both emissions cases (although more quickly in the case of 2006 emissions). The nucleation mode quickly becomes 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 is somewhat larger than the 2000 emissions case (with the 2000 background conditions), and this provides a negative feedback on the NPC rate due to slower nucleation and faster coagulation. Thus, the difference in the NPC rate is 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, under the more polluted 2006 background

conditions, the pre-existing particles continue to be the dominant condensation and coagulation sink throughout the plume. Thus, the total condensation and coagulation sink did not depend greatly on the SO_2 and NO_x emissions. Unlike the 2000 background conditions, there is no strong negative feedback in the 2006 background cases that reduce the new-particle formation rates and increase the coagulation rates for the 2006 emissions case, and this facilitates a large fractional difference in the NPC rate between the 2006 and 2000 emissions 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. For example, the power plants in the Ohio River Valley will exist in generally polluted air. Thus, future work will be done using 3-D chemical transport models to explore these correlation effects.

5.4 US emissions statistics and estimated particle formation

The increase in particle production of a single 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 (that was operational in each of these years). Figure 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 decreases in both species between 1997 and 2010 with a median ratio of 0.64 and 0.48 for SO_2 and NO_x respectively.

In the case of the W.A. Parish plant explored throughout this paper, NO_x emissions reductions are significantly greater than the SO_2 emissions reductions. Thus, the emissions changes for the plant are not representative of the general US 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 con-

ditions of the W.A. Parish power plant on 27 September 2006 by interpolating the NPC rates in Fig. 5. Figure 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 estimate 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.

It appears that the W.A. Parish power plant investigated throughout this paper may be an extreme case relative to the US median of the 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 show that the median change in the NPC rate across the 330 power plants is 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 show a wide range of increases and decreases in NPC rate that largely cancel out (Fig. 8), this cancellation should not change with the background. However, a full analysis of the effect of power-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.

6 Conclusions and discussion

In this paper, we explored how power-plant controls may have affected new-particle formation in coal-fired power-plant plumes. Using the meteorology and background conditions from NCEP/NARR datasets and TexAQS aircraft measurements, we simulated the nucleation of particles at the W.A. Parish coal-fired power plant for 1997 and 2010

emissions with SAM/TOMAS model. The decreasing emissions rates of SO_2 (30 %) and NO_x (90 %) due to pollution-control technologies during this time were simulated, and model results indicated a significant increase in aerosol formation in the plume. The model showed an order-of-magnitude increase in Net Particle Contribution rate (NPC, the effective emissions of ultrafine particles from the plant taking into account formation and coagulation in the plume) 50 km downwind of the plant during this time period. This predicted increase in NPC rate was due to a decreasing in NO_x emissions, which caused an increase in OH and the oxidation rate of SO_2 to H_2SO_4.

Model predictions were compared to aircraft measurements from the TexAQS 2000 and 2006 campaigns. This analysis showed that the change in plume particle concentrations were likely influenced more strongly by differences in the pre-existing particle concentrations between measurement days than by differences in emissions between the years. Meteorological conditions will also have a large influence on the plume microphysics. Thus, it is difficult to quantify the impact of emissions controls on aerosol formation in the plumes from measurements alone without a large number of measurements both before and after the controls were added. In addition, the simulations predict that the sensitivity to changing emissions under fixed background conditions is much larger under more polluted conditions (2006) than during the less polluted conditions (2000).

We determined generally how SO_2 and NO_x emissions changes affect NPC under fixed atmospheric conditions. For power plants with high NO_x emissions, SO_2 concentrations must be reduced by a larger fractional amount than NO_x concentrations in order for particle production to decrease in the plume. Using these results, the US-median NPC rate was estimated to have a 19 % decrease between 1997 and 2010 assuming fixed background conditions. However, the results of this paper are limited by the comparison to only two background conditions, and thus the magnitude of the NPC changes may, on average, be different from these predictions.

Junkermann et al. (2011b) has shown evidence of increased particle concentrations in plumes of coal-fired power plants with new pollution-control technologies measured

in Germany, Inner Mongolia and Southern Australia. They attributed the increased particle concentrations to the in-stack formation of SO_3/H_2SO_4 from Flue Gas Desulfurization and Selective Catalytic Reduction technologies (which may lead to particle formation in/near the stack). They did not investigate the potential for changes in plume chemistry and nucleation as we do here. On the other hand, we did not address the in-stack processes in this paper since emissions data of SO_3, H_2SO_4 or ultrafine particles formed in the stack is not readily available for US power plants. However, the unintended formation of SO_3/H_2SO_4 could cause significant changes in the particle concentrations in plumes of emission-controlled plants and should be investigated in future work. Additionally, NH_3 slip from SCR may lead to increased nucleation rates in a plume. We estimated the possible effects of NH_3 slip in Gong et al. (2012), but do not address this here as NH_3 emission data is also not readily available for US power plants. The aqueous oxidation of particles in clouds was also not considered in this work due to little to no plume/cloud interaction in the test cases. For cases where the plume enters clouds, there would be a decreased NPC rate in the plume due to the aqueous removal of SO_2, additional of sulfate to activated particles, as well as reduced OH because of the reduction in sunlight. Additionally, VOC concentrations were assumed fixed in our simulations, and changes in VOCs may affect OH concentrations resulting in different SO_2 oxidation rates for fixed NO_x emissions and backgrounds.

This study has shown that an unintended result of pollution-control technologies may be occurring with the addition or loss of particles produced within power-plant plumes. In order to accurately estimate the cumulative 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 of particle production as well as the additional investigation of particle growth in plumes.

From this, the impact of power-plant controls on downwind CCN production can be studied using three-dimensional modeling of plume dynamics. Additionally, we are creating a sub-grid plume parameterization for three-dimensional global models to more accurately quantify aerosol microphysics in coal-fired power-plant plumes and the effects of pollution-control technologies.

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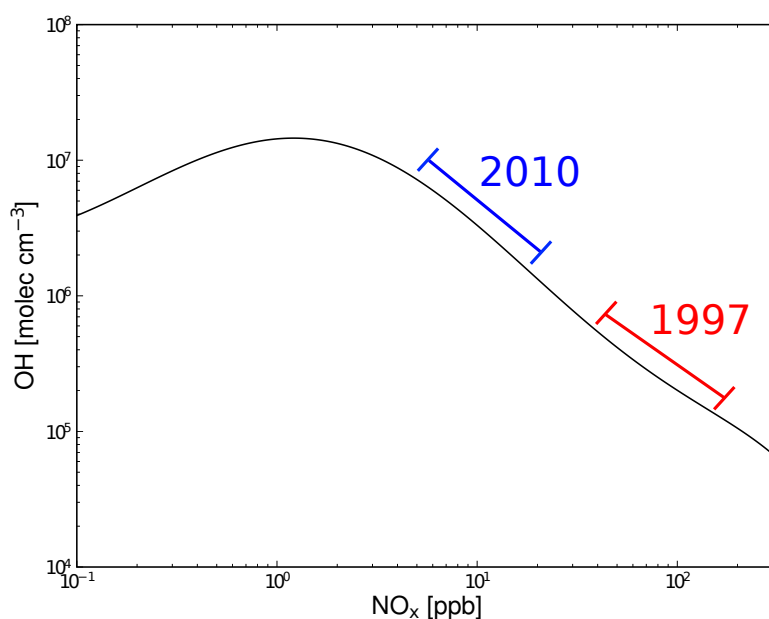
Fig. 1. [OH] as a function of [NO_x] for the background conditions on 27 September 2006. The red and blue bars show the range of NO_x concentrations found in the first 50 km of the plume for the 2010 and 1997 emissions.
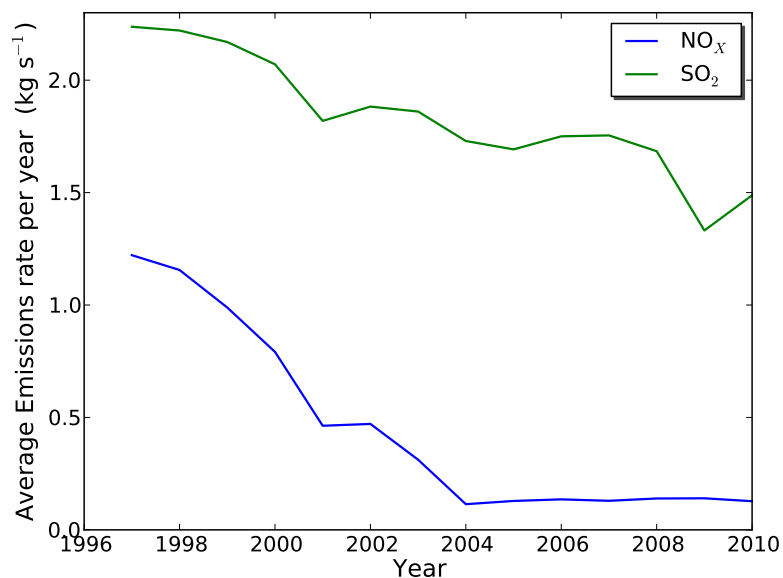
Fig. 2. The yearly average emissions (kg s^{-1}) of SO$_2$ (green) and NO$_x$ (blue) from the 4 coal-burning units (summed together) at the W.A. Parish Power Plant.
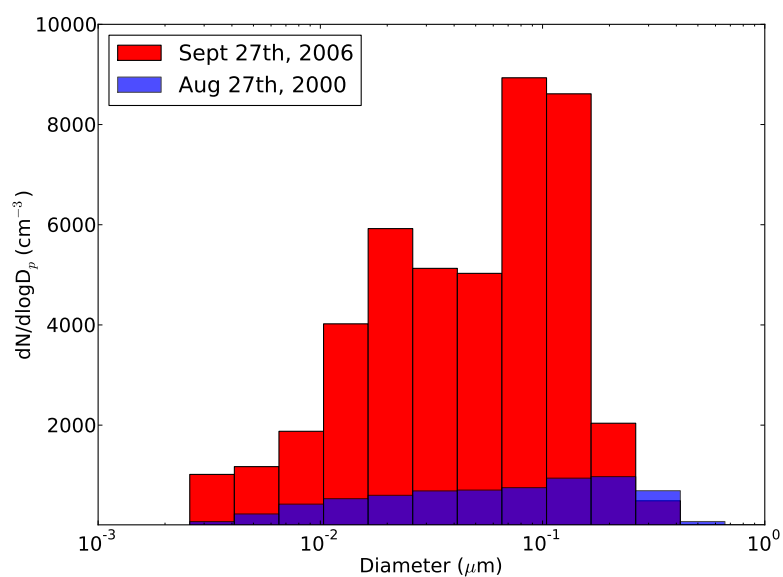
Fig. 3. The measured background particle size distributions by the NOAA P-3 aircraft on 27 September 2006 (red) and the NCAR Electra aircraft 27 August 2000 (blue) near the W.A. Parish Power Plant. The condensation/coagulation sink was ~4× larger for the 2006 case.
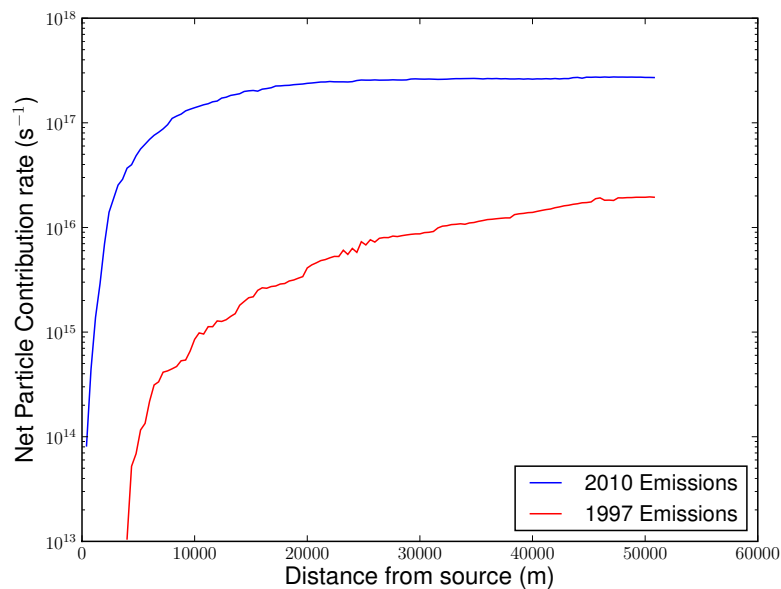
Fig. 4. The Net Particle Contribution (NPC) versus distance downwind of W.A. Parish Power Plant for the 2010 (blue) and 1997 (red) emissions scenarios. Meteorology and background conditions were for 27 September 2006 for both cases.
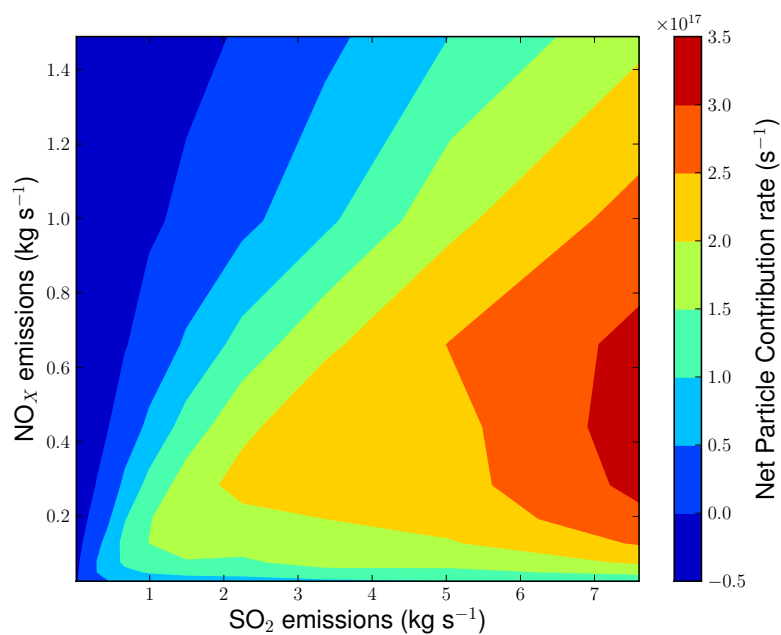
Fig. 5. The interpolated NPC rates (50 km downwind from source) from 110 model simulations versus NO_x and SO_2 emissions. Meteorology and pre-existing particle background concentrations for all model runs were for 27 September 2006 near the W.A. Parish power plant.
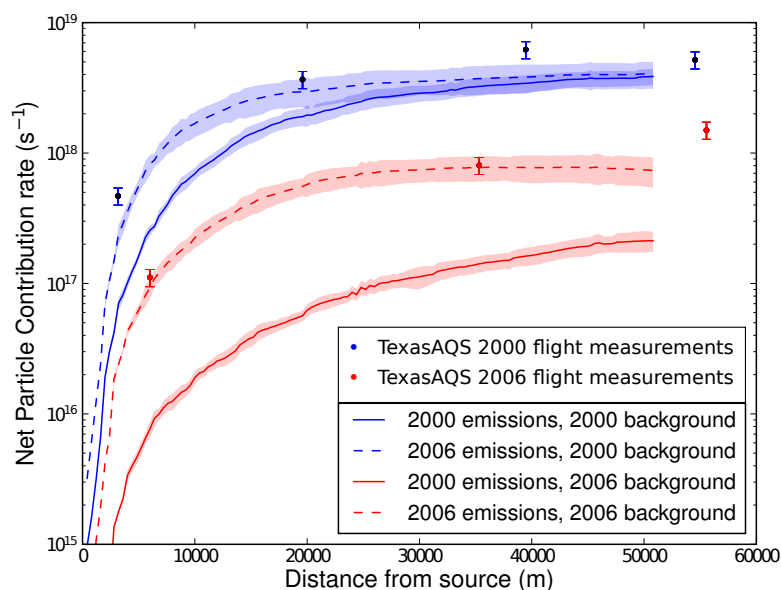
Fig. 6. NPC rate as a function of distance downwind of the W.A. Parish power plant for the two sets of measurements and the model simulations with the four combinations of emissions and background conditions for the 2000 and 2006 cases. The shaded regions correspond to the standard deviation in the model-predicted NPC with time. The error bars correspond to the estimated effect of measurement error (Brock et al., 2002) on the measured NPC rate.
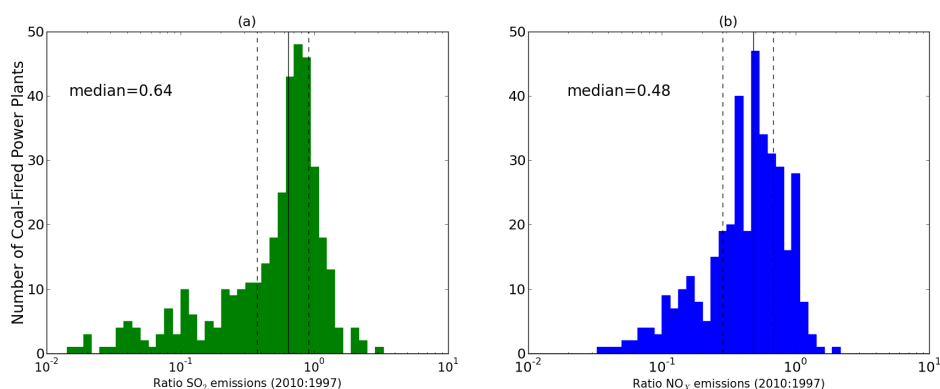
Fig. 7. Histograms showing the ratio of **(a)** SO_2 and **(b)** NO_x emissions changes between 2010 and 1997 for all (330) coal-fired power plants in the US registered to the CAM database. The mean ratio (solid line), 25 % and 75 % (dashed-lines) quartiles are plotted. There is an overall decrease in emissions with a median ratio of 0.64 SO_2 and 0.48 NO_x for 2010:1997.
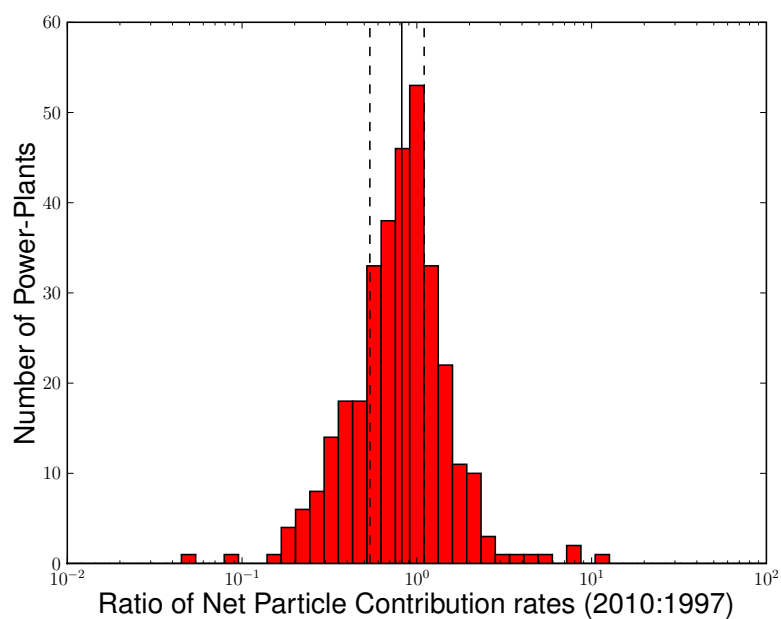
Fig. 8. Histogram showing the ratio of predicted NPC rates between 2010 and 1997 for all US power plants. The plot was made using the NO_x and SO_2 emissions from each of the years and the predicted NPC rates from these emissions shown in Fig. 5. The NPC rates were calculated for the background conditions of 27 September 2006 and produced a median ratio of 0.81. The solid line represents the median and dashed lines represent the inter-quartile ranges.