

# Codependencies of Reactive Air Toxic and Criteria Pollutants on Emission Reductions

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## ABSTRACT

It is important to understand the effects of emission controls on concentrations of ozone, fine particulate matter (PM<sub>2.5</sub>), and hazardous air pollutants (HAPs) simultaneously, to evaluate the full range of health, ecosystem, and economic effects. Until recently, the capability to simultaneously evaluate interrelated atmospheric pollutants ("one atmosphere" analysis) was unavailable to air quality managers. In this work, we use an air quality model to examine the potential effect of three emission reductions on concentrations of ozone, PM<sub>2.5</sub>, and four important HAPs (formaldehyde, acetaldehyde, acrolein, and benzene) over a domain centered on Philadelphia for 12-day episodes in July and January 2001. Although NO<sub>x</sub> controls are predicted to benefit PM<sub>2.5</sub> concentrations and sometimes benefit ozone, they have only a small effect on formaldehyde, slightly increase acetaldehyde and acrolein, and have no effect on benzene in the July episode. Concentrations of all pollutants except benzene increase slightly with NO<sub>x</sub> controls in the January simulation. Volatile organic compound controls alone are found to have a small effect on ozone and PM<sub>2.5</sub>, a less than linear effect on decreasing aldehydes, and an approximately linear effect on acrolein and benzene in summer, but a slightly larger than linear effect on aldehydes and acrolein in winter. These simulations indicate the difficulty in assessing how toxic air pollutants might respond to emission reductions aimed at decreasing criteria pollutants such as ozone and PM<sub>2.5</sub>.

## IMPLICATIONS

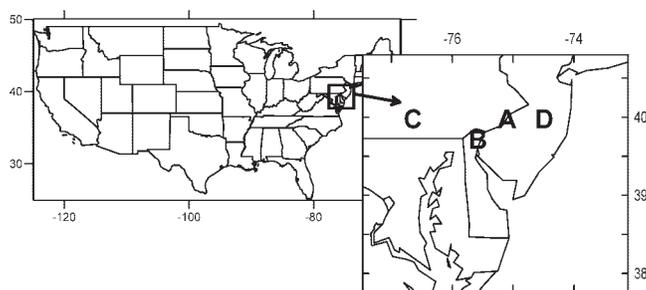
Understanding the overall effect of emission control strategies on important, chemically interrelated atmospheric pollutants is essential for formulating effective and cost-efficient control strategies. This can help avoid strategies that may improve one pollutant but degrade air quality by increasing other pollutants. Emission reductions aimed at reducing ozone concentrations may have different or no effects on concentrations of toxic air pollutants and PM<sub>2.5</sub>. Air planning regulations do not require multipollutant analyses when developing pollutant-specific control strategies. However, by approaching air planning from a "one atmosphere" perspective, we believe that more enlightened planning can be accomplished.

## INTRODUCTION

Many areas in the United States have air quality problems with simultaneously high concentrations of one or more pollutants, including ozone (O<sub>3</sub>), fine particulate matter (PM<sub>2.5</sub>), and/or hazardous air pollutants (HAPs). High O<sub>3</sub> and PM<sub>2.5</sub> concentrations are regulated under the National Ambient Air Quality Standards (NAAQS), but HAPs are controlled through individual source-specific standards for a large number of industrial and area sources, and through non-road diesel and on-road mobile source rules. There is a growing awareness that multipollutant control should be considered because control of volatile organic hydrocarbons (VOCs) and nitrogen oxides (NO<sub>x</sub>) can affect O<sub>3</sub> as well as other oxygenated nitrogen species and secondary organic aerosol.<sup>1-4</sup> Russell et al.<sup>5</sup> modeled reductions of VOC, NO<sub>x</sub>, and ammonia sources in the Los Angeles area and found significant effects on both O<sub>3</sub> and particulate nitrate, but there are few other comprehensive, multipollutant studies, especially those also considering effects on HAPs. O<sub>3</sub> and the secondarily produced portion of PM<sub>2.5</sub> and HAPs are interrelated through complex atmospheric photochemistry. Control strategies for PM<sub>2.5</sub> and O<sub>3</sub> could be expected to also decrease (or increase) HAP concentrations, and vice versa.

In the United States, the Clean Air Act defines 188 compounds as HAPs,<sup>6</sup> also known as toxic air pollutants. Some HAPs are human carcinogens, whereas others can cause neurological, reproductive, respiratory, and other chronic and acute health effects in humans, as well as ecological effects. Many HAPs are affected by atmospheric chemistry, including much of the same photochemistry that controls concentrations of O<sub>3</sub> and secondarily produced PM<sub>2.5</sub>. Ongoing efforts by states and local air pollution control agencies to reduce concentrations of criteria pollutants will affect concentrations of oxidants, radicals, and VOCs. Given the complexity that exists in the cycling of radicals and oxidants, it is not immediately apparent how ambient concentrations of HAPs might be affected by envisioned emission controls.

It is important to understand the effect of emission reductions on all pollutants to calculate the full economic benefit of control strategies or compare alternative strategies. To this end, we use the Community Multi-Scale Air Quality (CMAQ) modeling system to begin to examine the effect of emission reductions on simultaneous concentrations of O<sub>3</sub>, PM<sub>2.5</sub>, and four HAPs: formaldehyde,



**Figure 1.** Large domain and nested smaller domain with location of grids for further examination (A, B, C, and D).

acetaldehyde, acrolein, and benzene. These HAPs have been identified as toxic species of nationwide concern: benzene as a national cancer risk driver, acetaldehyde as a cancer risk contributor, and acrolein as a non-cancer hazard driver.<sup>7</sup> Formaldehyde was identified in earlier assessments as a national cancer risk driver, using the unit risk estimate in the Integrated Risk Information System.<sup>8</sup> The most recent assessment adopted a value reported by the Chemical Industry Institute of Toxicology, which is 0.04% of the previous value, dropping formaldehyde risk to near 0, although the official risk estimate is still being debated. In addition to its potential toxicity, formaldehyde plays a critical role in radical production.

#### ATMOSPHERIC CHEMISTRY OF HAPs

Organic gas-phase HAPs can decay through reaction with the hydroxyl radical (OH). For some longer-lived compounds (such as CCl<sub>4</sub>, CAS no. 56-23-5, half-life of ~40 yr), the reaction rate is so slow that this decay route is insignificant. But for other moderately or highly reactive compounds, reaction with OH controls the chemistry. Some HAPs can also react with O<sub>3</sub> and other radicals and can photolyze.<sup>9</sup> Formaldehyde, acetaldehyde, and acrolein are reactive, whereas benzene has a longer half-life (approximately >6 days).

A few HAPs can be formed in the atmosphere. Both formaldehyde (CAS no. 50-00-0) and acetaldehyde (CAS no. 75-07-0) are directly emitted, e.g. from diesel trucks, and formed through reactions initiated by OH attack on VOCs, including nonhazardous air pollutant VOCs. Acrolein also has a large secondary production, in this case from another HAP: 1,3-butadiene. Previous modeling studies predict that secondary formation accounts for approximately 50 to more than 99% of ambient formaldehyde and acetaldehyde, and approximately 30% of acrolein concentrations.<sup>10</sup> Concentrations of HAPs vary diurnally and seasonally because of variations in temperature, solar radiation, and emission rates.

#### MODEL APPLICATION

##### Model Formulation and Domain

Model simulations were performed on a domain centered on the Philadelphia metropolitan area, with a 4-km horizontal grid size, (76 × 82 cells), and 15 vertical layers (Figure 1). We used CMAQ version 4.5,<sup>11,12</sup> configured with the piecewise parabolic method for transport, multiscale method for horizontal diffusion, and eddy method for vertical diffusion. Continental-scale simulations with

a 36-km horizontal grid resolution provided boundary and initial conditions for the 4-km simulations. Cloud and aerosol processes were included. Emissions were extracted from the 1999 National Emissions Inventory version 3.2, by merging toxic and criteria pollutant inventories. For the immediate Philadelphia area, a refined mobile source inventory was developed based on transportation modeling and the MOBILE6 model. Meteorological fields from the Pennsylvania State/National Center for Atmospheric Research Mesoscale Model (MM5), version 3.6.1,<sup>13</sup> were derived for the 1-mo base-case periods of January and July 2001. We used the SAPRC-99 mechanism,<sup>14</sup> modified to calculate chemistry for 26 additional explicit air toxics.<sup>10</sup>

#### Sensitivity Studies

To examine how criteria and HAP concentrations might be affected differently by an emission reduction, we performed sensitivity studies with across-the-board anthropogenic emission reductions for the periods July 14–25, 2001 and January 10–21, 2001. These across-the-board reductions mimic general potential future emission reductions and their simplicity helps in examining direct and indirect effects on HAP concentrations. The three scenarios are:

- (1) 50% reduction in nitric oxide (NO) and nitrogen dioxide (NO<sub>2</sub>) emissions (NO<sub>x</sub>-only)
- (2) 20% reduction in VOC emissions (VOC-only)
- (3) 50% reduction in NO<sub>x</sub> and a 20% VOC reduction in VOC emissions (NO<sub>x</sub> + VOC)

A significant portion of total VOC emissions are biogenic, so the overall cut in the VOC-only scenario could be less than 20%, especially in non-urban areas. The biogenic contribution to NO<sub>x</sub> is small. To account for reduction of pollutant transport, we reduced concentrations of NO<sub>x</sub> and VOCs at the boundaries by 50 or 20% of the anthropogenic portion. The emissions of all four VOC HAPs are cut in the VOC-only and NO<sub>x</sub> + VOC scenarios

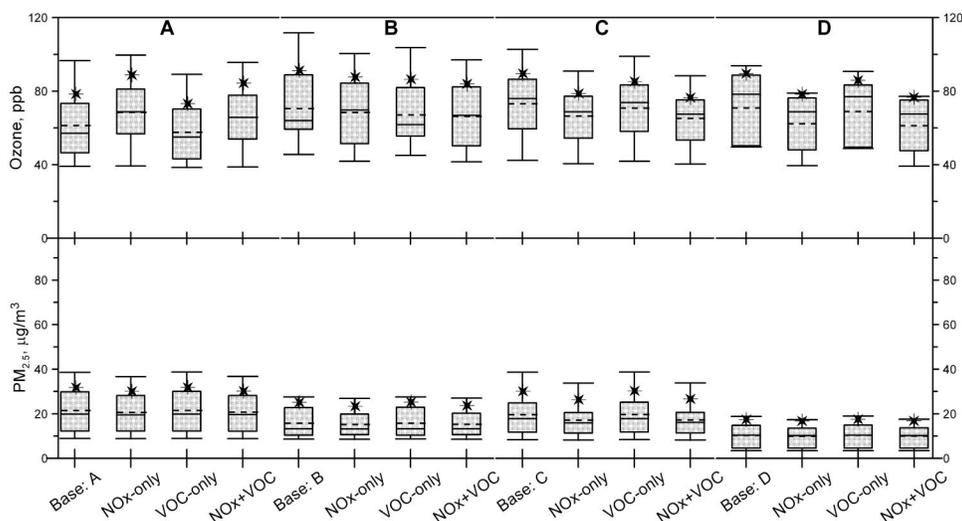
We compared the strategies for overall reductions at four grid points, selected to represent a variety of chemical domains (Figure 1). Grid A is located in urban central Philadelphia, whereas B is slightly southwest and generally upwind of Philadelphia, near Wilmington, DE. Grids C and D are on the same latitude as A, but more rural.

#### RESULTS

##### Effects of Emission Reductions on O<sub>3</sub> and PM<sub>2.5</sub>

**Base Case.** The first bar (Base) in each set of four bars in Figure 2 displays the distribution of daily 8-hr maximum O<sub>3</sub> and 24-hr average PM<sub>2.5</sub> at four grids in this domain for the 12 days of the base-case July simulation. Figure 3 displays the same information for the January simulation. During both July and January episodes, surface winds were primarily calm or light and from the southwest quadrant. The July episode can be characterized as a period of stagnating high pressure typical of a summer high-O<sub>3</sub> event. Although having much stronger upper level winds, the surface winds during the January episode were uncharacteristically light; slightly higher than the wind speeds during the July episode.

CMAQ has been extensively evaluated for its ability to reproduce O<sub>3</sub> and PM throughout the eastern United



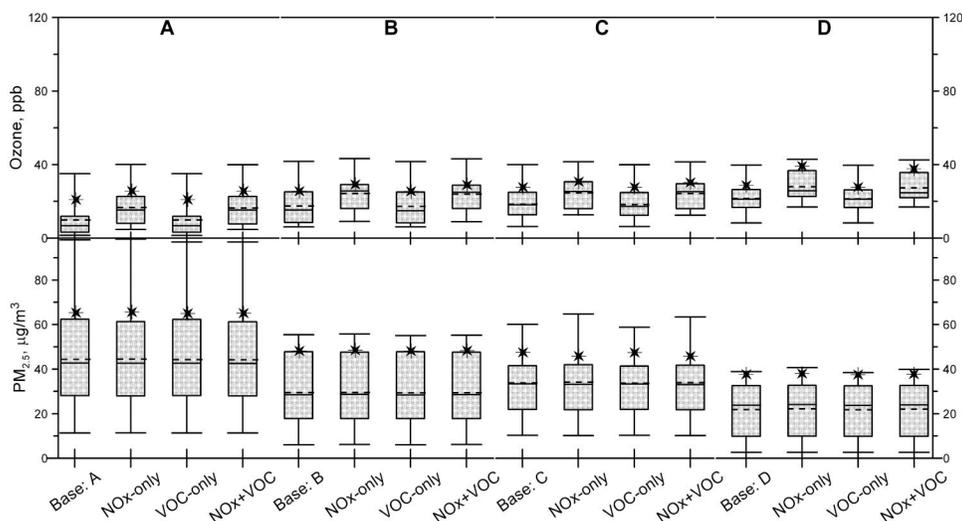
**Figure 2.** Distribution of the July episode daily concentrations of O<sub>3</sub> and PM<sub>2.5</sub> showing the mean (dashed line), median (solid line), 90th percentile (\*), and quartiles of concentrations at four grids for the base case and three control scenarios. O<sub>3</sub> (top) is the daily 8-hr maximum concentrations and PM<sub>2.5</sub> (bottom) is 24-hr average.

States at a 12-km resolution during 2001.<sup>15,16</sup> Although O<sub>3</sub> is typically predicted very well over the eastern United States,<sup>15</sup> the SAPRC-99 mechanism used in this study tends to predict higher O<sub>3</sub> concentrations than other mechanisms.<sup>17</sup> In the 4-km domain used in this study, observations at all sites within the domain<sup>18</sup> show an O<sub>3</sub> overprediction in July with a normalized mean bias (NMB) of 19.1% and normalized mean error of 22.2%, although temporal trends are comparable. Comparisons of PM<sub>2.5</sub> measurements with CMAQ version 4.5 predictions in previous studies have shown good performance in the Northeast in summer, but large overpredictions in winter, although nitrate and sulfate are predicted well.<sup>16</sup> Few observations of PM<sub>2.5</sub> components are available in this 4-km domain during January and July 2001, including only three sites with weekly values. July simulations of PM<sub>2.5</sub> components in this domain show that sulfate and ammonium are predicted well, with NMBs of -6 and

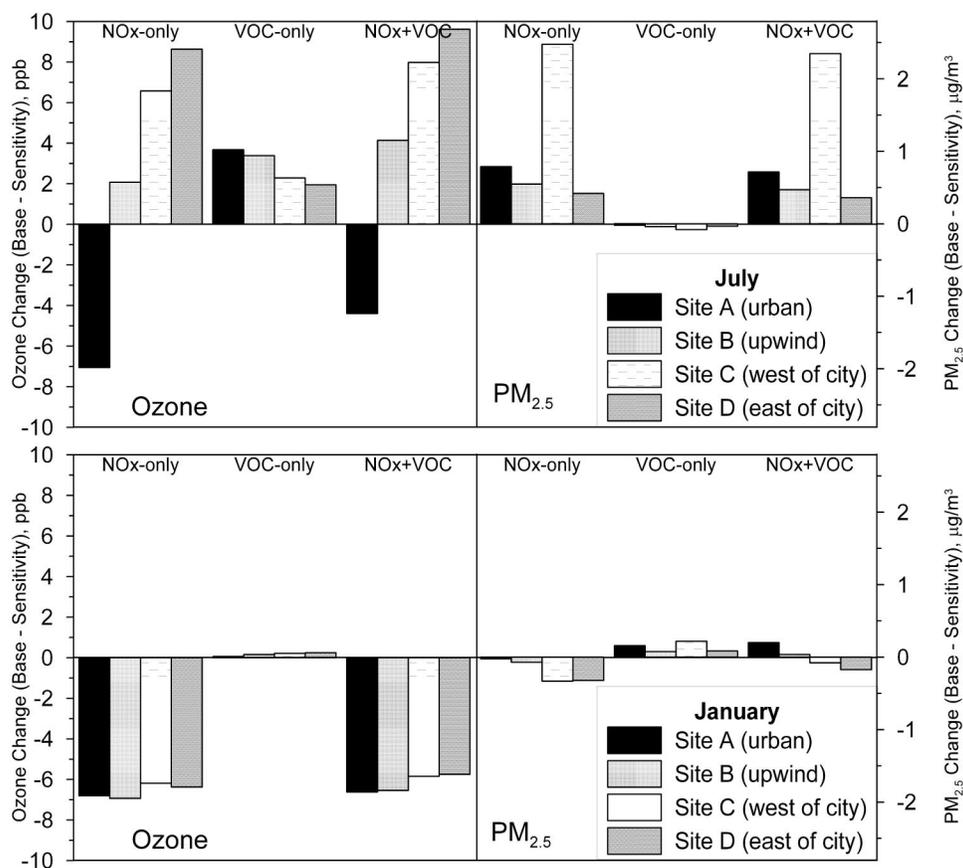
1.9%, respectively. Particulate nitrate is predicted well at the lower values but overpredicted at higher values, with an overall NMB of 26%. In January, nitrate is similarly overpredicted (NMB of 25.8%) although sulfate and ammonium are underpredicted, with NMBs of -18.2 and -39.5%.

**Sensitivity Studies.** Figures 2 and 3 also show daily concentration distributions for each sensitivity study at each grid cell. The largest changes between scenarios occur at higher concentrations, and clear differences can be seen at these upper concentrations. Figure 4 presents the changes in O<sub>3</sub> and PM<sub>2.5</sub> concentrations, defined as (base - sensitivity scenario).

The area encompassed by this domain has an urban corridor, running from the southeast to slightly west of the northeast corner of the domain, with large sources of



**Figure 3.** Distribution of the January episode daily concentrations of O<sub>3</sub> and PM<sub>2.5</sub> showing the mean (dashed line), median (solid line), 90th percentile (\*), and quartiles of concentrations at four grids for the base case and three control scenarios. O<sub>3</sub> (top) is the daily 8-hr maximum concentrations and PM<sub>2.5</sub> (bottom) is 24-hr average.



**Figure 4.** Predicted change in  $O_3$  and  $PM_{2.5}$  at four grids for the July (top) and January (bottom) episodes.  $O_3$  (left axis) is computed as the average of the daily 8-hr maximum concentrations and  $PM_{2.5}$  (right axis) is computed as the 12-day average.

$NO_x$  emissions. This urban area is largely VOC-sensitive whereas surrounding areas are  $NO_x$ -sensitive. The urban core (represented by grid cell A) is predicted to show  $O_3$  increases with  $NO_x$  reductions, whereas other grids show  $O_3$  decreases in July. This behavior is consistent with the expected response to  $O_3$  precursors in these regimes.<sup>1</sup> The VOC-only scenario slightly decreases  $O_3$ , whereas the  $NO_x$  + VOC simulation shows larger benefit and less disbenefit than the  $NO_x$ -only simulation.

The  $NO_x$ -only reductions have a small effect on the  $PM_{2.5}$  concentrations from decreased aerosol nitrate formation. Nitrate comprises a small portion of  $PM_{2.5}$  in this domain (1–17%), so the largest  $PM_{2.5}$  decreases occur where the fraction of nitrate is largest (grid C, with 17% nitrate) and the smallest occurs in grid D, where the nitrate is smallest. Grid C is located in Lancaster county, PA, where ammonia emissions are large, leading to a greater base-case production of ammonium nitrate, and larger response to  $NO_x$  reductions. In the  $NO_x$ -only and  $NO_x$  + VOC scenarios, aerosol ammonia decreases from 4% (grid D) to 18% (grid C). There is also a small contribution from changes in  $O_3$  and OH, which decrease formation of secondary organic aerosol and aerosol sulfate 2–5%. The only  $PM_{2.5}$  components that increase in these scenarios are secondary organic aerosols at grid A (2% increase). The absolute sensitivity of  $PM_{2.5}$  to  $NO_x$  reduction, based on the response of the aerosol nitrate, is not affected by the tendency of CMAQ to overpredict total  $PM_{2.5}$  although the fractional change might be.

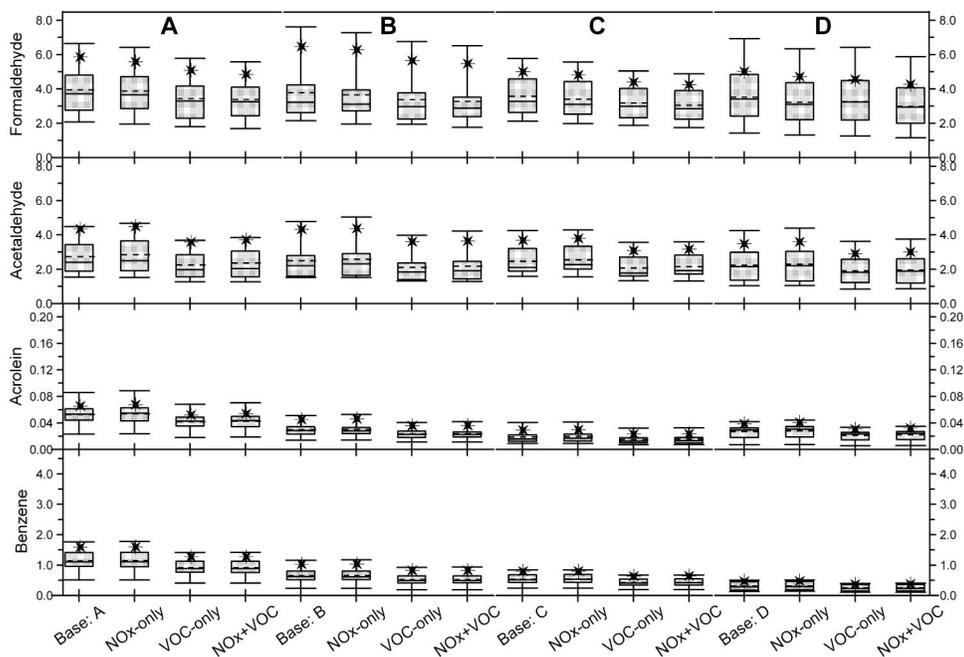
In January,  $O_3$  increases in the  $NO_x$ -only scenario for all grids, slightly less in the  $NO_x$  + VOC scenario (Figure 4, bottom). In winter, biogenic VOC emissions are significantly reduced and the domain becomes more VOC-limited. The  $PM_{2.5}$  changes are small; less than 0.5%.

$O_3$  changes in the  $NO_x$ -only scenario vary slightly for different averaging periods and metrics in the July episode. The benefits of the  $NO_x$ -only reduction are larger for the 8-hr or 1-hr maximum concentrations. This is important from the perspective of the  $O_3$  NAAQS (average of the four highest 8-hr averages in 3 yr) because for shorter averaging times and more extreme events the disbenefits appear to be smallest and the benefits the largest. Similarly, predicted reductions in  $PM_{2.5}$  are also dependent on the averaging metric used. The episode maximum 24-hr value can decrease twice as much as the episode average.

#### Effects of Emission Reductions on HAPs

**Base Case.** Figure 5 shows the base-case, 12-day average concentrations for July (first bar in each set of four bars) at four grids for each HAP. Figure 6 shows concentrations in January.

Although CMAQ has been extensively evaluated for its ability to reproduce  $O_3$  and  $PM_{2.5}$ , the database for evaluation against HAPs is sparse, both temporally and spatially. This model was previously compared with a limited set of HAP observations for 2001 over the continental United States and found to reproduce temporal behavior well, but underpredict concentrations, although

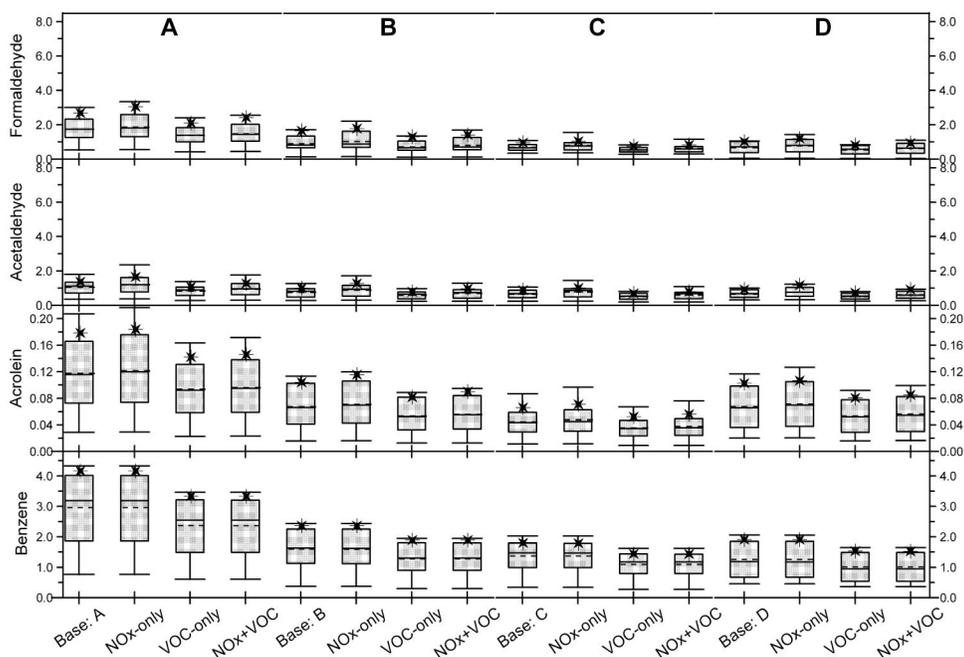


**Figure 5.** Distribution of the July daily concentrations ( $\mu\text{g}/\text{m}^3$ ) of four HAPs showing the mean (dashed line), median (solid line), 90th percentile (\*), and quartiles of concentrations at four grids (A, B, C, and D) for the base case and three control scenarios.

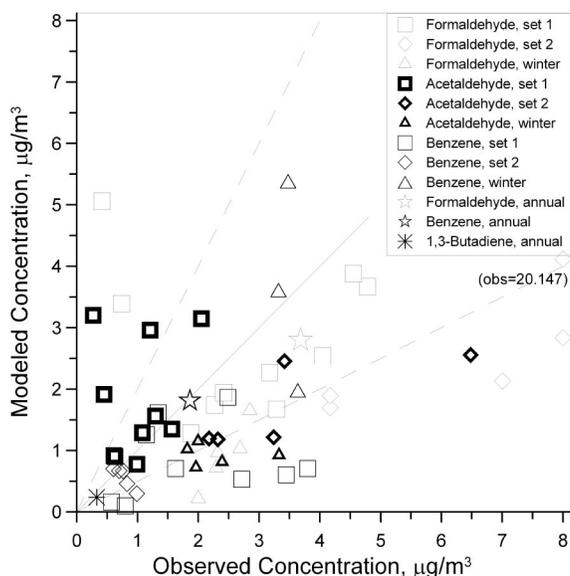
predictions and observations were generally within a factor of 2.<sup>10</sup> Uncertainties in emissions and coarseness of the grid resolution (36 km) were cited as some reasons for differences. For the 4-km domain of this study, four sites in New Jersey were available for comparison,<sup>18</sup> but only a few measurements were made during each month. For January and July 2001, CMAQ tended to underpredict observed concentrations at the 4-km grid, as shown in Figure 7. In this figure, set 1 includes monitors at Camden, Chester, and Elizabeth, NJ, whereas set 2 includes

values at New Brunswick, NJ, only, which were underpredicted more than the other sites. Winter values were available only from Camden and Elizabeth, and also tended more towards underprediction.

Additionally, we compared 2001 annual average predictions of formaldehyde, benzene, and 1,3-butadiene (acrolein precursor) with observations from a monitor within Philadelphia. The last three, "annual" values shown in Figure 7 present these comparisons. Annual 4-km CMAQ predictions were also compared with point



**Figure 6.** Distribution of the January daily concentrations ( $\mu\text{g}/\text{m}^3$ ) of four HAPs showing the mean (dashed line), median (solid line), 90th percentile (\*), and quartiles of concentrations at four grids (A, B, C, and D) for the base case and three control scenarios.



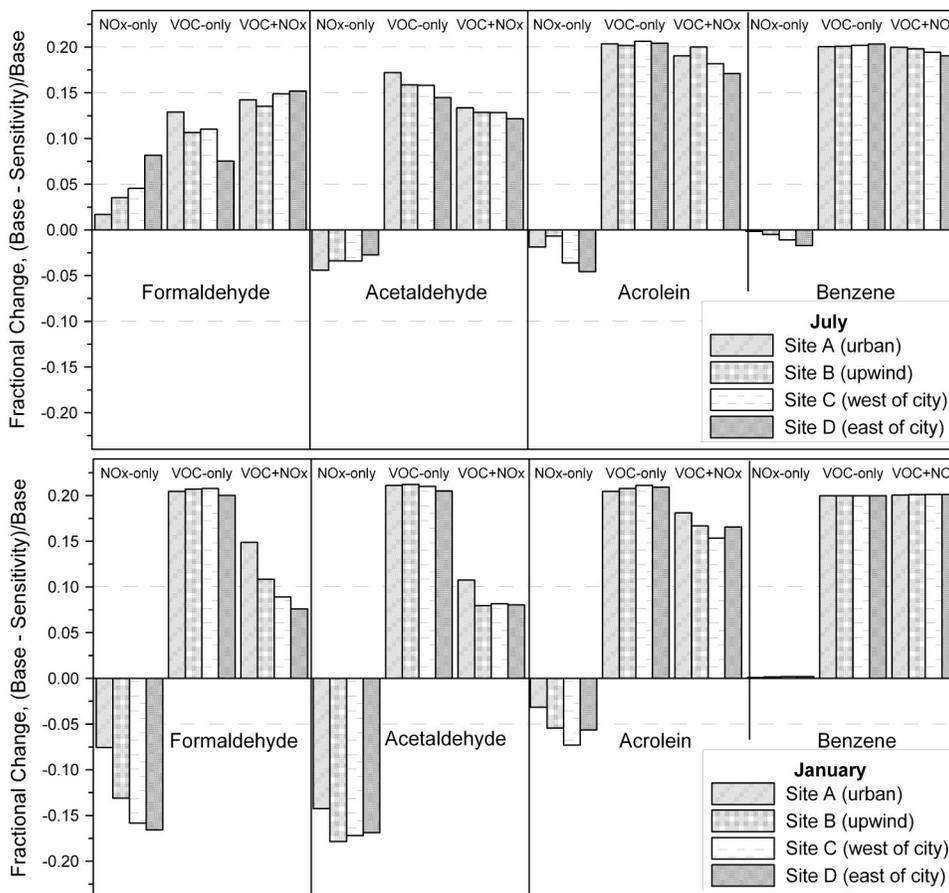
**Figure 7.** Comparison of observed concentrations vs. model predictions for three HAPs. Set 1 consists of monitors at Camden, Chester, and Elizabeth, NJ, whereas set 2 includes values at New Brunswick, NJ. Comparisons with an earlier annual run with a monitor in Philadelphia are also shown.

estimates from the Industrial Source Complex Model (ISCST),<sup>19</sup> which used the same emission inventory and processed surface and upper air observations from the

Philadelphia and Dulles National Weather Service stations, respectively. Both models compared well with observations although CMAQ was slightly closer, with ratios of predicted-to-observed concentrations for formaldehyde, benzene, and 1,3-butadiene of 0.76, 0.96, and 0.74 versus 0.70, 0.77, and 0.67 for ISCST.

It is difficult to make conclusions on goodness-of-fit on the basis of a few data points. However, because the goal of this study is to look at relative changes in concentrations, and not to exactly reproduce observations, the ability to represent the temporal variability and the general ability to model the three New Jersey sites and the Philadelphia data within a factor of 2 gives us confidence that the general transport, reaction, and deposition characteristics are correct.

**Sensitivity Studies.** Figures 5 and 6 also show the distributions of daily HAP concentrations in each of the sensitivity studies and Figure 8 shows fractional changes in the 12-day average concentrations of formaldehyde, acetaldehyde, acrolein, and benzene for each of the emission reduction scenarios, in both July and January, calculated as  $(\text{base} - \text{sensitivity})/(\text{base})$ . Because the VOC-only scenario also cuts VOC HAP emissions, the fractional change allows examination of the linearity of HAP emission reductions on concentrations. The results in Figure 8 are presented as episode averages because risk calculations for HAPs are calculated for long-term exposures.



**Figure 8.** Comparison of fractional reduction in HAP concentrations from three emission reduction scenarios, averaged over the July (top) and January (bottom) episodes.

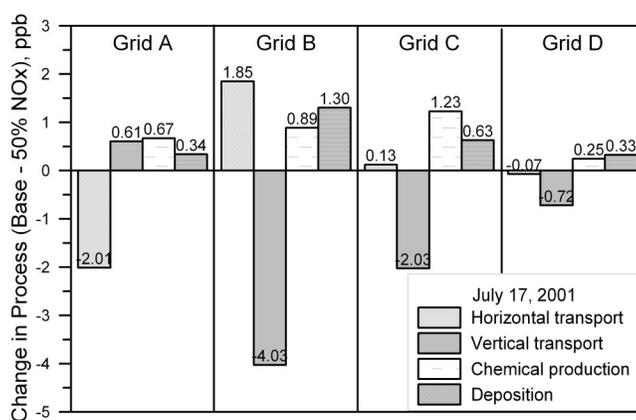
Formaldehyde concentrations are reduced by a small fractional and absolute amount on average when  $\text{NO}_x$  emissions are reduced. Changes in the production of  $\text{O}_3$ , OH, hydroperoxy radical ( $\text{HO}_2$ ) and organic radicals resulting from emission cuts affects concentrations of formaldehyde. Reaction with OH is a major and rapid loss process for formaldehyde, but OH also increases formaldehyde by reacting with other VOCs, which can produce aldehydes.

With the  $\text{NO}_x$ -only cut, less OH is reacting with  $\text{NO}_2$  to form nitric acid, and less  $\text{O}_3$  is being titrated by NO (both reactions decrease by  $\sim 40\text{--}50\%$ ). This causes OH production to increase slightly at grid A (6% increase for the high- $\text{O}_3$  day). These are larger processes in grid A than other grids (10 times larger than at rural grid D) because grid A is VOC-limited and has more scavenging of radicals by  $\text{NO}_x$  than other grids. Increases in  $\text{O}_3$  at grid A also increase the pool of OH. In contrast, the OH decreases by a significant amount (13–18%) at grids B, C, and D. Although  $\text{NO}_x$  reactions with  $\text{O}_3$  and OH are also decreased in the grids, these reactions are less important because the grids tend to be  $\text{NO}_x$ -limited (especially C and D), and the  $\text{NO}_x$  reduction makes them more so, increasing radical-radical reactions forming peroxides and other stable products, with less new OH,  $\text{HO}_2$ , and aldehyde production.

The OH increase in grid A increases the formaldehyde loss and decreases the production through reactions of peroxy radicals with NO. Other sources of formaldehyde increase slightly as represented in SAPRC-99, such as direct production from VOC and OH reactions. This tradeoff is shown by the small size of formaldehyde reduction in grid A relative to other grids. In other grids, reduced OH production reduces initial attack of VOCs, and lower  $\text{NO}_x$  concentrations reduce the subsequent reactions to form alkoxy radicals. Although loss via OH reaction is also reduced, formaldehyde loss through photolysis remains important. The largest change in formaldehyde occurs in rural grid D, which is the most  $\text{NO}_x$ -limited for  $\text{O}_3$  formation.

In contrast, acetaldehyde shows a slight disbenefit in the  $\text{NO}_x$ -only scenario, with concentrations increasing up to 4%. At grid A, where OH and  $\text{O}_3$  are enhanced with the  $\text{NO}_x$  cut, the increased production is less than the increased loss of acetaldehyde with OH, resulting in a small net overall loss of acetaldehyde. In the other three grids, the production decreases to a larger extent than the loss does, also resulting in a net loss. In a few other grids of the domain, there is a net chemical production of acetaldehyde.

Although the net chemical effects of the  $\text{NO}_x$ -only scenario are small or cause a small decrease in acetaldehyde, there is a significant increase in the acetaldehyde from horizontal and vertical transport. An analysis of the integrated process rates, derived from saving the change in species concentrations due to each operator process when integrating the continuity equations, allows us to determine the contribution of physical and chemical processes to the acetaldehyde concentrations.<sup>20</sup> Figure 9 shows the contribution of these processes for a high- $\text{O}_3$  day (July 17, 2001). At elevated layers in the model, acetaldehyde production is increased due to increased  $\text{O}_3$  and

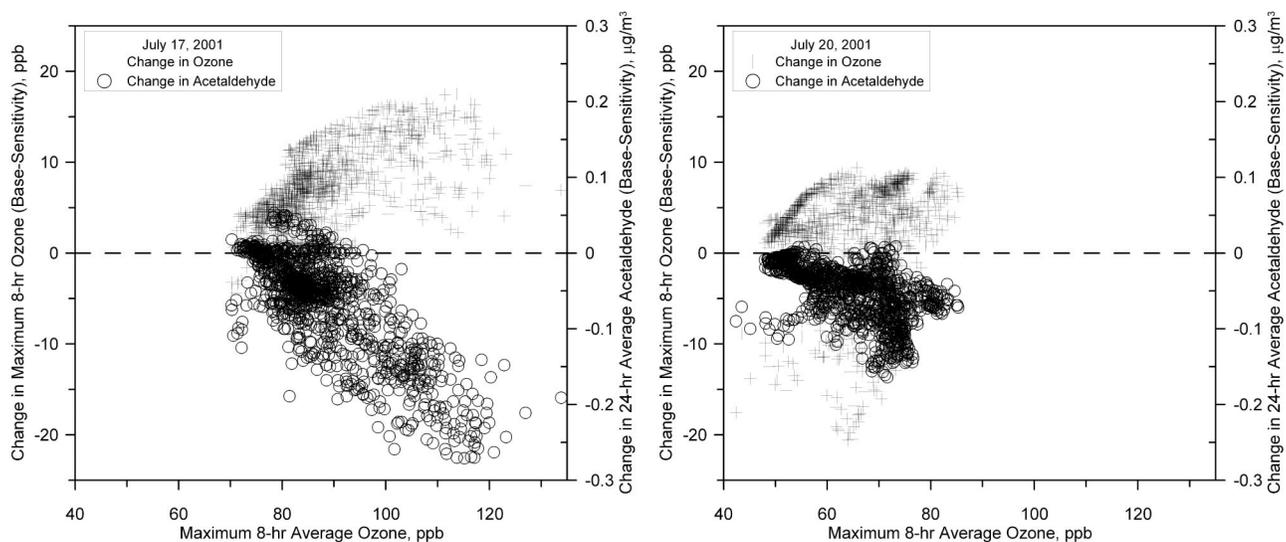


**Figure 9.** Comparison of change in acetaldehyde due to physical and chemical processes for the four grids summed for July 17, 2001.

net dissociation of peroxy propionyl nitrate to acetyl peroxy radicals, which are transported to and from other parts of the domain.

Acetaldehyde disbenefits for the  $\text{NO}_x$ -only scenario are largest on days when  $\text{O}_3$  was highest, which is also when the ozone benefit is greatest. Figure 10 shows the 8-hr maximum  $\text{O}_3$  and the daily average acetaldehyde surface level concentrations at all 6,232 grid cells in the domain, plotted for the high- $\text{O}_3$  day of July 17, 2001 (left side). As the  $\text{O}_3$  concentration increases, the  $\text{O}_3$  benefit and the acetaldehyde disbenefit increase. This does not occur as much on the low- $\text{O}_3$  day, July 20 (Figure 10, right side), where  $\text{O}_3$  disbenefits are largest and the acetaldehyde disbenefits are smallest.

Similarly to acetaldehyde, acrolein shows a slight disbenefit in the  $\text{NO}_x$ -only reduction scenario at all grids. At grid A, this is primarily due to the increase in OH concentration, which increases the production from reaction of 1,3-butadiene with  $\text{O}_3$  and OH. Because acrolein is both lost through reactions with OH and to a smaller extent,  $\text{O}_3$ , and produced from reactions of 1,3-butadiene with OH and  $\text{O}_3$ , the net effect on acrolein depends on the ratio of 1,3-butadiene to acrolein and the relative changes in OH and  $\text{O}_3$ . The yield of acrolein from both the OH and the  $\text{O}_3$  reactions with 1,3-butadiene is approximately 0.5, whereas the rate constant for the reaction of 1,3-butadiene and OH is 3 times larger than the reaction of acrolein and OH. The production of acrolein from 1,3-butadiene and  $\text{O}_3$  is approximately 10 times larger than the loss of acrolein with  $\text{O}_3$ . Where 1,3-butadiene is emitted in larger amounts than acrolein, the production of acrolein outweighs the decay and an increase in OH increases the acrolein concentrations, as seen in grid A, where the ratio of 1,3-butadiene to acrolein is approximately 3. If the ratio remained constant and the OH decreased, the acrolein concentration would also decrease. However, at grids B, C, and D, although the OH and  $\text{O}_3$  decrease, the ratio of 1,3-butadiene to acrolein is also smaller: a value of approximately 0.75 at grid D. This results in a decrease in the secondary production of acrolein but a relatively larger decrease in acrolein decay. The smallest increase in acrolein occurs at grid B, where the ratio of 1,3-butadiene to acrolein is moderate ( $\sim 1.85$ ), the OH change is smallest, and the  $\text{O}_3$  decrease is small.



**Figure 10.** Change in concentrations of O<sub>3</sub> (left axis) and acetaldehyde (right axis) for all grid cells in the domain on a high-O<sub>3</sub> day (July 17, 2001, left) and a low-O<sub>3</sub> day (July 20, 2001, right).

Benzene shows little response to the NO<sub>x</sub> cut. The OH changes have little effect on benzene because it is much less reactive than the other pollutants (half-life of ~6–65 days).

The 20% VOC-only scenario results in only a 7–13% reduction in formaldehyde, with the smallest decreases occurring in grid D where biogenic emissions are largest. Alkenes, including isoprene, are important precursors of formaldehyde, and biogenic sources of alkenes were not reduced in the scenarios. Acetaldehyde shows a larger fractional decrease of 14–16% in the VOC-only scenario. The yields of acetaldehyde from biogenic sources are not as direct or as large as the formaldehyde yields, so acetaldehyde is affected more by the VOC-only cuts. Because both acrolein and 1,3-butadiene are cut in the VOC-only scenario and have no biogenic precursors, the resulting acrolein concentration is a linear decrease of approximately 20%. Similarly, benzene shows a near-20% reduction for VOC cuts.

The NO<sub>x</sub> + VOC scenario combines the effects of both scenarios, thereby moderating the NO<sub>x</sub> disbenefit in grid A. The net reduction in formaldehyde is almost a linear combination of the cuts from VOC-only and NO<sub>x</sub>-only scenarios.

In the January simulation, the 50% NO<sub>x</sub> reduction results in small but visible disbenefits for formaldehyde, acetaldehyde, and acrolein. The aldehydes are lower by about half in winter, so although the disbenefits are large as a fraction of total concentration, they are about equal to those in July on an absolute scale. Concentrations of acrolein are predicted to be larger in January than July, so the absolute disbenefit in January is larger. Ambient O<sub>3</sub> concentrations increase slightly in all grids with the NO<sub>x</sub>-only reduction in January, but the total concentrations are small. Reaction of VOCs with O<sub>3</sub> is more important for aldehyde production in winter because OH concentrations decrease by about a factor of 10 in winter, whereas O<sub>3</sub> decreases by a factor of 2 or less. The increase of O<sub>3</sub> with NO<sub>x</sub> cuts in winter increases formation of aldehydes through reactions of O<sub>3</sub>.

For all three pollutants, the 20% VOC reduction results in a near-20% concentration reduction in the winter. Photochemical reactivity is much smaller, the biogenic portion of emissions is lower in this area in January, and the 20% cut is largely anthropogenic.

## SUMMARY

Modeling studies over the Philadelphia metropolitan area have examined the potential for emission control strategies to affect both criteria pollutants and HAPs, through both direct and indirect effects of emission reductions. Over this domain, for these modeling conditions and control scenarios, a 50% NO<sub>x</sub> reduction in July is found to increase O<sub>3</sub> in the urban core and decrease O<sub>3</sub> outside of the urban core, while decreasing PM<sub>2.5</sub> and formaldehyde, and slightly increasing acetaldehyde and acrolein. In January, NO<sub>x</sub> reductions can increase O<sub>3</sub>, formaldehyde, acetaldehyde, and acrolein. A 20% reduction in VOCs decreases aldehyde concentrations less than 20%, but has little effect on O<sub>3</sub> in this domain. A combination of VOC and NO<sub>x</sub> reductions reflects the cumulative behavior of each of the emission reductions separately and minimizes O<sub>3</sub> and HAP disbenefits.

Even the small changes predicted in this study for all four HAPs are of interest because of the importance of these pollutants. HAPs can be concentrated in areas close to sources, and the effect of pollutant reductions at these hot spots can be larger or smaller than predicted for these grid-averaged concentrations. The fact that some emissions control scenarios for O<sub>3</sub> and PM<sub>2.5</sub> may have no beneficial effect or even a slight disbenefit on HAPs is noteworthy, even if the disbenefit is small. Because of the long-term averaging used in considering risk, potential changes in HAP concentrations are important year-round.

Because changes in secondary HAPs result from a complex series of reactions, the response is dependent on the representation of atmospheric chemistry. The SAPRC-99 chemical mechanism has a long history of use for O<sub>3</sub> modeling, but has not been evaluated as much for ambient aldehyde formation. The mechanism has been

condensed to allow it to work within a three-dimensional air quality model, and the characterization of products and reaction rates of some VOCs has been simplified. Production of formaldehyde and acetaldehyde in the atmosphere and their sensitivity to emissions reductions may differ slightly from model predictions because of errors in this condensation process. Uncertainties in some of the reaction rates and product yields of the VOCs that produce aldehydes may also cause errors in the aldehyde concentrations, as may uncertainties in emissions of HAPs and nonhazardous air pollutant VOCs.

Transport from upper layers and across the boundaries can play a role in the increased HAP concentrations. Although upper air chemistry is often not examined, it can significantly affect chemistry at the surface. In the scenarios studied here, concentrations of VOCs and NO<sub>x</sub> are proportionally reduced at the boundaries, but other oxidized nitrogen species are not. Peroxyacetyl nitrate-type compounds, which act as reservoirs for both NO<sub>x</sub> and acetyl peroxy radicals, can be transported at upper levels and decompose in the central part of the domain, where the reduced NO<sub>x</sub> shifts the equilibrium and the radicals can produce aldehydes.

A better understanding of the overall effect of emissions control strategies on several different types of pollutants will help in formulating optimized emission control strategies. As planning proceeds throughout the United States in support of the PM<sub>2.5</sub> NAAQS and reducing regional haze, we believe that it would be prudent to consider the effect that a control strategy will have on all relevant air pollutants. As we have shown, the complex interrelationships among atmospheric constituents do not allow for easy generalization. An effective control strategy for one area may well be deleterious in another. Because the distribution of atmospheric contaminants varies significantly from place to place, a "one atmosphere" analysis is needed in each area to understand the potentially unique consequences of implementing controls in that area.

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## REFERENCES

1. *Rethinking the Ozone Problem in Urban and Regional Air Pollution*; National Research Council; National Academy: Washington, DC, 1991.

2. Hidy, G.M.; Hales, J.M.; Roth, P.M.; Scheffe, R. Fine Particles and Oxidant Pollution: Developing an Agenda for Cooperative Research; *J. Air & Waste Manage. Assoc.* **2000**, *50*, 613-632.
3. Scheffe, R.; Hubbell, B.; Fox, T.; Rao, V.; Pennell, W. The Rationale for a Multipollutant, Multimedia Air Quality Management Framework; *EM* **2007**, *May*, 14-20.
4. *Air Quality Management in the United States*; National Research Council; National Academies: Washington, DC, 2004.
5. Russell, A.G.; McCue, K.F.; Cass, G.R. Mathematical Modeling of the Formation of Nitrogen-Containing Pollutants. 2. Evaluation of the Effect of Emission Controls; *Environ. Sci. Technol.* **1988**, *22*, 1336-1347.
6. *Clean Air Act Amendments of 1990*; Section 112, 1990; available at <http://www.epa.gov/oar/caa/caa112.txt> (accessed 2007).
7. *1999 National Scale Air Toxics Assessment*, 2006; available at <http://www.epa.gov/ttn/atw/nata1999/nsata99.html> (accessed 2007).
8. *Integrated Risk Information System*, 2007; available at <http://www.epa.gov/iris> (accessed 2007).
9. Atkinson, R. Atmospheric Chemistry of VOCs and NO<sub>x</sub>; *Atmos. Environ.* **2000**, *34*, 2063-2101.
10. Luecken, D.J.; Hutzell, W.T.; Gipson, G. Development and Analysis of Air Quality Modeling Simulations for Hazardous Air Pollutants; *Atmos. Environ.* **2006**, *40*, 5087-5096.
11. Byun, D.; Schere, K.L. Review of the Governing Equations, Computational Algorithms, and Other Components of the Models-3 Community Multiscale Air Quality (CMAQ) Modeling System; *Appl. Mech. Rev.* **2003**, *59*, 51-77.
12. *Community Modeling and Analysis System*, University of North Carolina: Chapel Hill, NC, 2006; available at <http://www.cmaq-model.org> (accessed 2007).
13. *MMS Community Model*, Pennsylvania State University and National Center for Atmospheric Research, 2007; available at <http://box.mmm.ucar.edu/mmm5> (accessed 2007).
14. Carter, W.P.L. *Implementation of the SAPRC-99 Chemical Mechanism into the Models-3 Framework*; Report to the U.S. Environmental Protection Agency, January 29, 2000; available at <http://www.cert.ucr.edu/~carter/absts.htm#s99mod3> (accessed 2007).
15. Appel, K.W.; Gilliland, A.B.; Sarwar, G.; Gilliam, R.C. Evaluation of the Community Multiscale Air Quality (CMAQ) Model Version 4.5: Sensitivities Impacting Model Performance. Part I: Ozone; *Atmos. Environ.* **2007**, *41*, 9603-9615.
16. Appel, K.W.; Bhawe, P.V.; Gilliland, A.B.; Sarwar, G.; Roselle, S.J. Evaluation of the Community Multiscale Air Quality (CMAQ) Model Version 4.5: Sensitivities Impacting Model Performance. Part II: Particulate Matter; *Atmos. Environ.*, doi: 10.1016/j.atmosenv.2008.03.036.
17. Luecken, D.J.; Phillips, S.; Sarwar, G.; Jang, C. Effects of Using the CB05 vs. SAPRC99 vs. CB4 Chemical Mechanism on Model Predictions: Ozone and Gas-Phase Photochemical Precursor Concentrations; *Atmos. Environ.*, in press, doi: 10.1016/j.atmosenv.2007.08.056.
18. *Air Quality System*, 2007; available at <http://www.epa.gov/air/data/aqsdb.html> (accessed 2007).
19. *User's Guide for the Industrial Source Complex (ISC3) Dispersion Models; Volume II: Description of Model Algorithms*; EPA-454/B-95-003b; U.S. Environmental Protection Agency; Office of Air Quality Planning and Standards: Research Triangle Park, NC, 1995.
20. Gipson, G.L. *Process Analysis. Science Algorithms of the EPA Models-3 Community Multiscale Air Quality (CMAQ) Modeling System*; Byun, D.W., Ching, J.K.S., Eds.; EPA-600/R-99/030; U.S. Environmental Protection Agency; Office of Research and Development: Washington DC, 1999.

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