A DETAILED PROCESS-BASED EVALUATION OF VARIOUS ATTEMPTS TO SIMULATE HOUSTON, TX

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1   SUMMARY

This work will present a detailed process-based evaluation of several modeling attempts of the Houston, TX non-attainment area. These modeling attempts include efforts by the Texas state environmental agency, private consultants, and several Universities, resulting in multiple simulations of the same modeling episode and domain. This evaluation will highlight a modeling tool developed at the University of North Carolina at Chapel Hill called `pyPA` (Process Analysis in python). This tool provides a framework for an in-depth analysis of modeling data by quantifying several key chemical parameters such as radical budgets, source and fate of ozone precursors, and the physical processes that affect each species. This key chemical information allowed us to trace the root cause for the model's inability to generate observed levels of ozone. Analysis of the data provided by `pyPA` suggested a lack of organically derived radicals as a possible reason for hindered ozone formation chemistry. This hypothesis was tested by adding a source of organic radicals into the modeling system with subsequent analysis by the `pyPA` tool. We will present the results of this process based analysis of current modeling efforts and our radical sensitivity simulations.

2   INTRODUCTION

Photochemical air quality models, such as the Comprehensive Air Quality Model with Extensions (`CAMx`) and the Community Multiscale Air Quality (`CMAQ`), calculate rates of atmospheric processes that control air pollutant concentrations in the framework of a 3-dimensional grid. These processes include: chemical formation, chemical consumption, advection, diffusion, and deposition. These processes are coupled into a system of mass continuity equations used to predict the species concentrations for each grid cell. Photochemical models, such as `CAMx` and `CMAQ`, output only the spatial and temporal distribution of species concentrations. The rates of the individual processes that lead to these changes in species concentrations are not recorded. With only concentration fields, it is often difficult to infer the reasons why air pollutant concentrations change. A more detailed evaluation of all modeled processes often leads to an increased understanding of the formation processes for pollutants. This reasoning formed the impetus for the development of the `pyPA` tool.

The `pyPA` tool was designed to quantitatively track the individual physical and chemical process that contribute to changing pollutant concentrations for a grid cell or collection of grid cells. The `pyPA` tool provides dynamic information such as: horizontal and vertical pollutant fluxes crossing cell boundaries, chemical production and consumption rates, emission rates, deposition rates, and initial and final concentrations. The advantage of the `pyPA` tool is that it also provides the *separately integrated* rates of individual chemical and physical processes that lead to these concentrations. By assembling these individual integrated rates in different ways in post processing programs it becomes possible to explain exactly how the model achieved its predictions. The tool allows researchers to gain an understanding of the dynamic interaction of the physical and chemical processes operating in the model. Another important advantage of this type of tool is that it allows for a process-based intercomparison of different models or simulation scenarios. This is superior to the traditional approach of comparison where model performance is judged by statistical metrics based solely on model output. By quantifying chemical and physical process rates the user can compare the model on the common processes that all models must possess. This type

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of insight into modeling processes is especially useful when modeling a complex non-linear system such as tropospheric ozone formation or a complex and challenging airshed such as the one found over the Houston Texas non-attainment area.

The American Lung Association's 2004 report ranks the 25 most ozone-polluted cities in the United States. According to the report, Houston, Texas was the fifth most ozone-polluted area in the country. In 1999, Houston exceeded the federal standard for ozone concentrations averaged over one hour (125 ppb) on 52 days. This was the first year that Houston had more days than Los Angeles that exceeded the ozone air quality standard (GHASP, 2005). The U.S. Environmental Protection Agency (EPA) has designated the Houston region as a non-attainment area for the one hour standard and the newly implemented eight hour standard. Ozone is a secondary pollutant; therefore, policy makers must use photochemical models to assess the effectiveness of the proposed emission reduction strategies.

Many of the same issues and challenges posed to air quality modelers and policy makers in Houston are also found in other large urban areas in the United States. Houston, however, is also home to a sizable international port and the largest producer of petroleum products in North America. Anthropogenic emissions from these petrochemical production facilities enter the airshed as massive emissions of reactive industrial products. In addition, Houston's meteorology features slow rotating winds associated with the sea breeze, allowing emitted products to concentrate in the atmosphere. The combinations of these factors produce the conditions favorable for the formation of harmful levels of ozone concentrations. The challenges of the Houston airshed require an unprecedented detailed representation of emissions, meteorology, and ozone chemistry not seen in other non-attainment areas. As a result, considerable research has been focused on developing a sophisticated model that will (1) understand the complex atmospheric conditions present in Houston and (2) be able to predict the impact of proposed control strategies. This investment in Houston has over the last 4 years resulted in nearly $28M in field programs and $12M in modeling and analysis. The field programs in conjunction with the extensive ground monitoring network make the area one of the most data rich areas in the country. The sizable attention toward modeling has yielded a dearth of modeling attempts that include efforts by the Texas state environmental agency, private consultants, and several Universities. The 2000 regulatory episode,

used for the Texas State Implementation Plan (SIP) to attain the eight hour federal O_3 standard, has multiple simulations of the same modeling episode and domain with a variety of meteorological inputs and emission inventories. The `pyPA` tool was used to evaluate this episode developed by the Texas Commission on Environmental Quality (TCEQ).

3 RESULTS

This work will present a process-based evaluation of the several modeling attempts of the Houston, TX non-attainment area. These simulations were performed with both the `CAMx` and `CMAQ` model under a variety of meteorological and emission inputs. At the time of this writing `pyPA` is still in development for the analysis of output generated by `CMAQ`. Instead, this evaluation of model output with the `pyPA` tool will focus solely on the episodes ran with the `CAMx` version 4.2 system (`www.camx.com`). Table 1 lists the simulations that were evaluated with `pyPA` and discussed in this work. Included in this analysis is the episode being used by Texas for the eight hour SIP development and a Houston episode developed by a private contractor, Alpine Geophysics (AG). As an attempt to increase reactivity the TCEQ introduced an imputation of 156 $\frac{tons}{day}$ of VOC causing wide spread model overpredictions of VOC. The AG model does not have this imputation.

Figure 1: Plot of observed and modeled peak ozone concentrations for 20 monitors on 8/25/2000, for TCEQ (b1b) and AG (agb1b2) simulation episodes

The first step of this investigation was a comparison of model output with ambient data. Figure 1 shows the observed and modeled peak ozone concentrations for 20 monitors on 8/25/2000. Although there is an increase in peak ozone concentrations at some monitors due to the large addition of ozone precursors, the levels are still below ambient observations. The TCEQ and AG models both consistently underpredicts observed peak ozone concentrations at most monitors. The TCEQ model has 17 out of 20 monitors that fall below observed levels; the AG model has 19. An

EPISODE DATES	DEVELOPER	EMISSION INVENTORY
8/16 - 9/06, 2000	Texas Commission on Environmental Quality (TCEQ)	Basecase for the 8-hour SIP
	Alpine Geophysics (AG)	AG version of Basecase

Table 1: `CAMx` version 4.2 simulation runs by TCEQ and AG used for this analysis.

examination of the level of agreement between model predictions and observations of ozone concentrations, however, is not a sufficient method to understand the reasons for this inaccuracy. This is especially true in a non-linear feedback system such as ozone formation where the same ozone prediction can be reached through the combination of various physical and chemical processes. The next step of the investigation was an examination of the processes that caused the ozone formation.
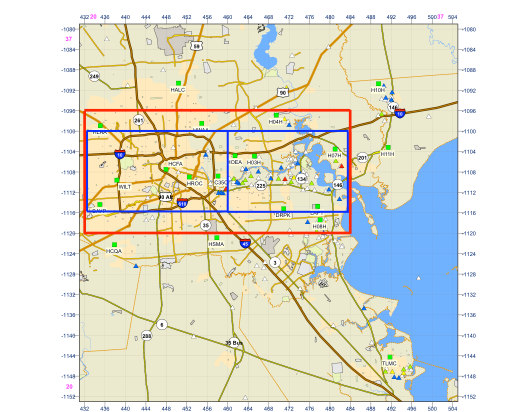
Figure 2: Map of Houston, Texas illustrating the focus analysis areas. The red box shows the analysis area named Central Houston (CHOU). The two blue areas show the location of the analysis areas called East Houston (EHOU) and West Houston (WHOU).

The `pyPA` tool was used to analyze each simulation scenario of the Houston airshed allowing for a process based intercomparison. Figures 2 and 8 show the modeling domains that the `pyPA` focused on initially and the results from the TCEQ and AG modeling episodes. The `pyPA` tool aggregates all the grid cells within a focus area to provide a single averaged process rate. The central Houston focus area, shown in figure 2, was used to try and gain a sense of the aggregated chemical and physical processes occurring throughout the entire city. The city was further divided to focus on the industrial eastern side of the city to the urban dominated west side. An analysis of the radical budget from these three regions revealed a deficient source of organically derived free radicals, HO_2 and OH·, with a range of 16-34 ppb of new OH· radicals. Previous applications of the process analysis method have revealed nearly double these

values (Jeffries *et al.*, 1994). This prompted a more focused investigation of various locations within the modeling domain. The TCEQ episode was used to try to understand radical levels at different parts of the city. Figures 3 and 9 show the focus locations for this part of the analysis and results from the `pyPA` tool. Regions were chosen to reflect conditions in the heavily industrial eastern part of the city and the urban dominated emissions found on the west side. A surprising finding was that regardless of the location of our analysis the radical budgets were similar. The source of new OH· radicals were ~29 ppb with a OH· cycle of ~3.2 resulting in only ~52 ppb of reacted VOC. This means that only 52 ppb of VOC reacted with newly created and recreated OH· regardless of the total level of VOCs available. Although there is an abundant amount of VOC emissions, ~150 ppb, ozone formation is limited not by ozone precursors, but by the radical pool.
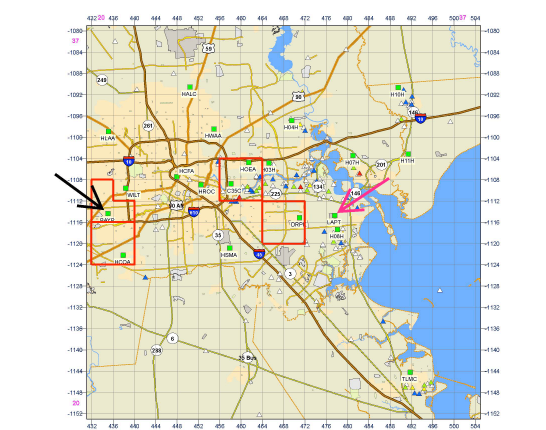
Figure 3: Map of Houston Texas illustrating the focus analysis areas. The red boxes show the 4km grids analyzed, around the monitors of interest. The black arrow is pointing to the Bayland Park (BAYP) monitor.

The `pyPA` tool also has the ability to quantify the source and fate of radical species. Figure 6 shows the fate of OH· radicals in the TCEQ simulation at the Bayland Park monitor on August 25th. This focus area is denoted by an arrow in Figure 3. The pie chart in figure 6 illustrates that nearly half of the available radicals at Bayland Park react with NO_2, CO, and CH_4, while the other half reacts with other VOCs. Similar values were found at nearly every
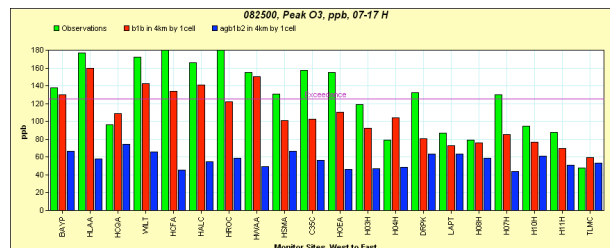
Figure 4: Plot of observed and modeled peak ozone concentrations for 20 monitors on 8/25/2000, for TCEQ (b1b) and UNC1 (b1bFORMeqFLVOC) imputed emissions

Figure 5: Plot of observed and modeled peak ozone concentrations for 20 monitors on 8/25/2000, for TCEQ (b1b) and UNC2 (b1bFORMeq004CO) imputed emissions

focus area. Of the limited amount of radicals that are available nearly a quarter are immediately terminated into nitric acid. The OH· that reacts with CO does not create or terminate OH· but merely propagates it. This high termination rate and lack of OH· sources impairs the systems' ability to generate ozone. In the TCEQ simulation at Bayland Park there was 1.81 NO to NO_2 oxidations per VOC reacted yielding 137.5 ppb of NO_2. Of the NO_2 that was produced approximately 26 ppb are lost by reaction with OH· to make HNO_3, and 51.4 ppb are lost through physical processes, such as deposition. The remaing NO_2 is photolyzed to make ozone. Of that O_3 approximately 21 ppb is photolyzed to make OH· radicals. This is the largest source of radicals in nearly all of the focus areas.

As seen from the data the nitric acid formation pathway is a key competing reaction for OH· radicals. The TCEQ model on 8/25 overpredicts the peak NO_2 concentration at 10 out of 14 monitors, sometimes by a factor of two. The AG model trends in a similar fashion with 11 out of 14 monitors showing an overprediction. This overabundance of NO_2 in the modeling system results in further depleting the limited pool of radicals available for ozone chemistry. In the TCEQ modeling scenario the model is making 87 ppb of ozone by VOC oxidation chemistry. This chemistry is not limited by VOCs, but is limited by radical sources. The photolysis of formaldehyde could be a possible source of missing radical species and the reason for small ozone formation rates. This hypothesis is supported by ambient data revealing a deficiency by the model to predict sufficient levels of formaldehyde at ambient levels on the ground and aloft. Figure 3 shows the location of the LaPorte ground monitoring site (pink arrow). On 8/25/2000 the model underpredicts formaldehyde at that monitor by up to a factor of 2.5. Thus, a possible reason for the model's inability to make ozone could be stemming from a missing direct source of formaldehyde.

Further investigation of this hypothesis was tested by introducing two possible sources of formaldehyde emissions. The incomplete combustion of flares and mobile emissions were tested as two possible sources of formaldehyde that are either underrepresented or omitted from the current inventory. UNC added a total of 172.4 US tons to 13 flares located mainly in the eastern part of Houston; this run will be referred to as UNC1. To represent a missing formaldehyde source from mobile emissions, formaldehyde was scaled to 4% of CO emissions; this run will be referred to as UNC2. This resulted in an increase of a total of 418.15 US tons of formaldehyde. Figures 4 and 5 show an increase in the peak ozone concentrations on August 25th for each sensitivity run. Figure 9 shows a 4% increase in the amount of new OH· radicals for UNC1 and 25% for UNC2 at Deer Park (DRPK). This yielded an increased ozone production rate of 8% and 31% respectively. Figure 7 shows the changes to allocation of OH· radicals for UNC2; UNC1 showed a similar distribution. There is an increase in the total number of OH· reacted and an increases in OH· reactions with VOC. The percentage of OH attack on formaldehyde also increased and there was a decrease in the NO_2 termination pathway. It is clear that the model is sensitive to radical sources and with the proper levels will be able to reproduce ambient levels of ozone formation.

4   REFERENCES

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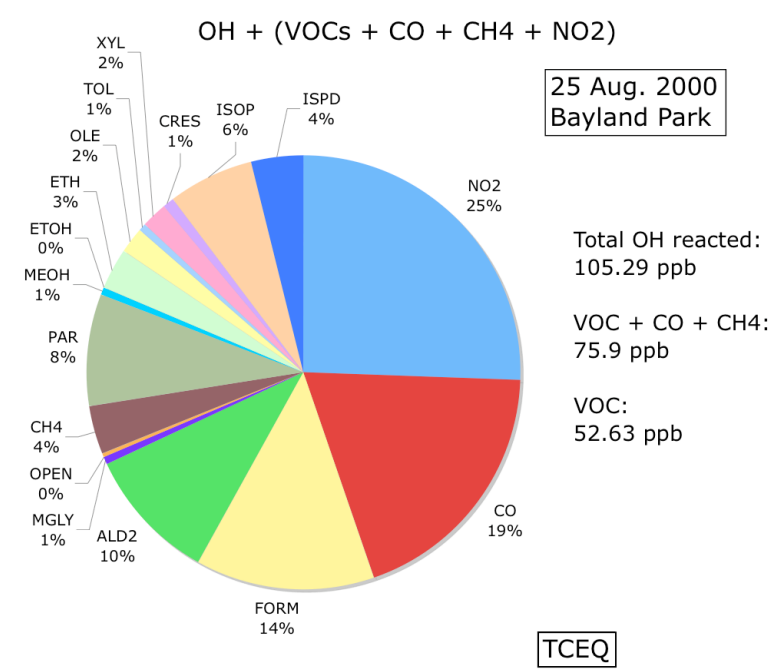
Figure 6: Fate of OH radicals in the TCEQ simulation at Bayland Park monitor (8/25/2000).
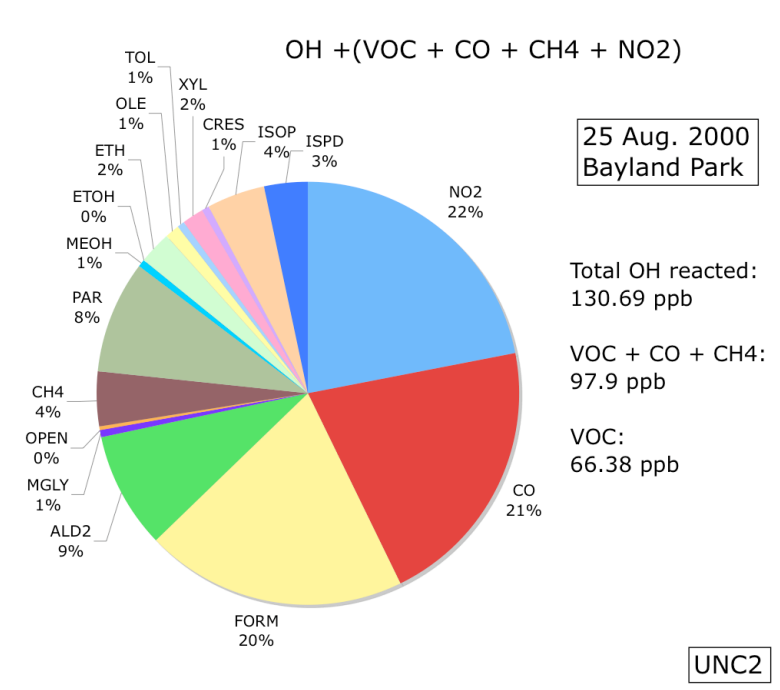

Figure 7: Fate of OH radicals in the UNC2 simulation at Bayland Park monitor (8/25/2000).
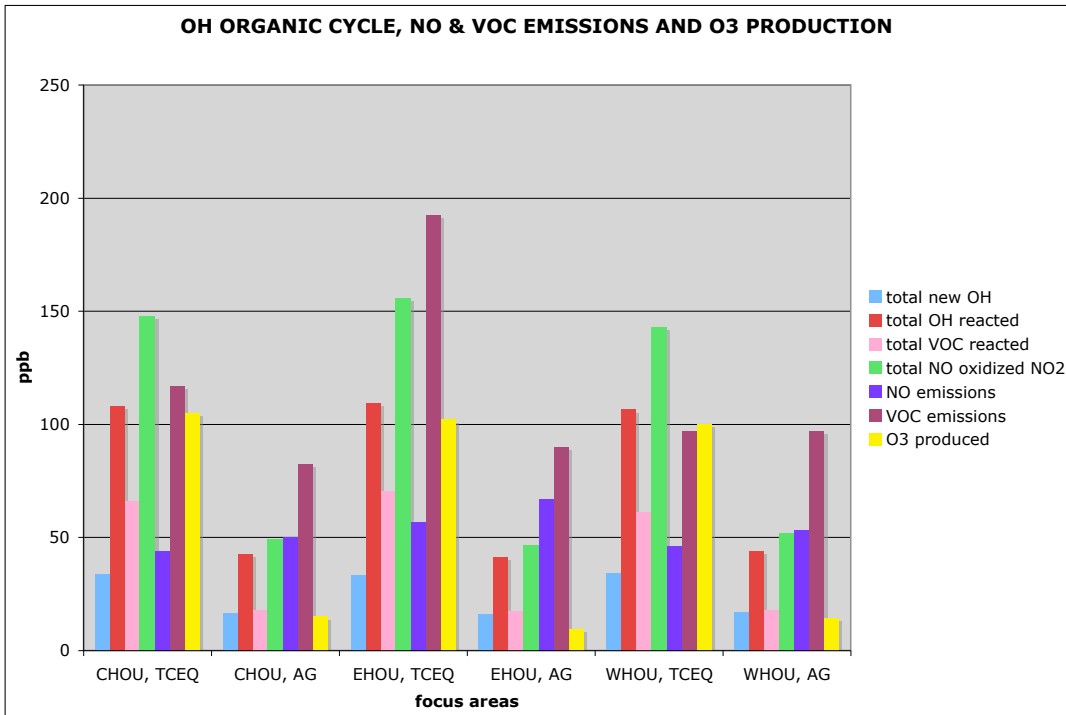
Figure 8: pyPA results from the TCEQ and AG modeling episodes for Central (CHOU), Eastern (EHOU) and Western Houston (WHOU).
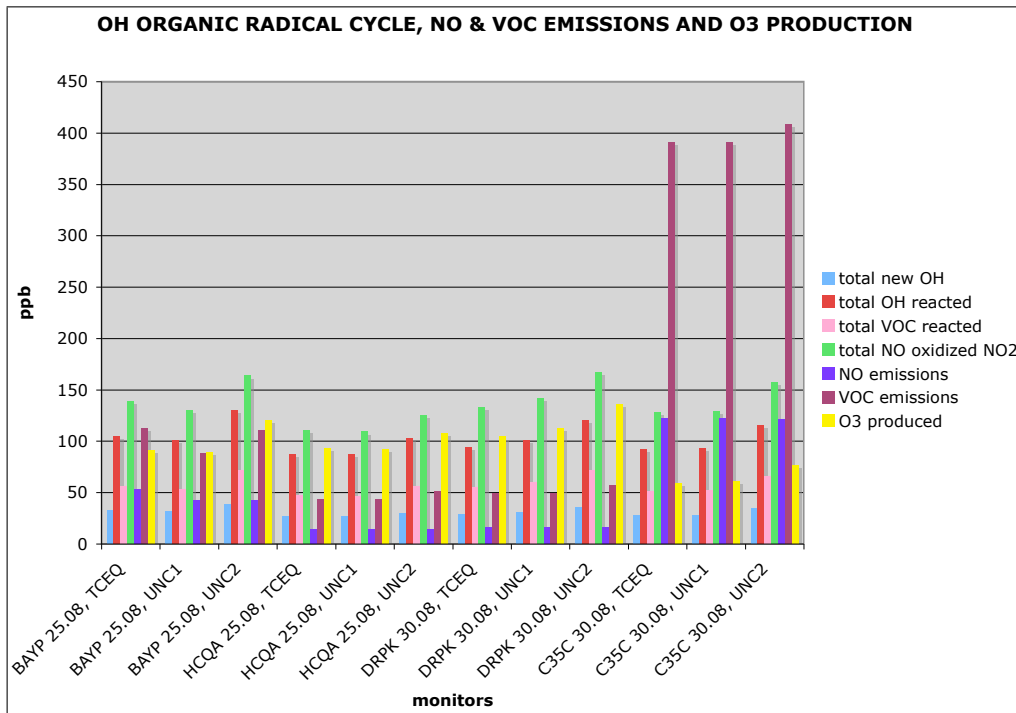

Figure 9: pyPA results from the TCEQ and AG modeling episodes for Bayland Park (BAYP), Croquet (HCQA), Deer Park (DRPK) and Clinton (C35C).