MAQ Lab
Modeling Air Quality Laboratory
UNC-Chapel Hill
Barron Henderson (barronh@unc.edu)

Emission Event Investigation:

Quantifying Impacts with a Detailed Plume Tracking Process Analysis Tool

Barron Henderson[1], Marianthi-Anna Kioumourtzoglou[1], Byeong-Uk Kim[2], William Vizuete[1] and Harvey E. Jeffries[1]

[1] Department of Environmental Sciences & Engineering, University of North Carolina–Chapel Hill [2] Georgia Department of Natural Resources

UNC SCHOOL OF PUBLIC HEALTH
DEPARTMENT OF ENVIRONMENTAL SCIENCES AND ENGINEERING

Summary of Results

This study uses a plume-tracking, dynamic Python based Process Analysis (pyPA) to quantify the impact from physical and chemical processes in a simulation containing two hypothetical industrial releases of highly reactive volatile organic chemicals (HRVOCs). Simulating these industrial releases in a 4-km and 1-km grid resolution produced ozone hourly peak concentrations that differed by as much as 65 ppb. The injection of HRVOCs into a 1-km grid resolution dramatically increased concentrations. The higher concentration of HRVOCs shifted the balance of OH radical reactions and reduced NO_2 termination reactions by as much as 39.9%. The increased percentage of OH attacks on HRVOCs provided a 53.3% average increase of organically derived OH radicals via photolysis of intermediate products. A 29.2% increase in total new OH radicals, primarily organically derived, led to a 27% increase in aggregated focus region peak ozone and a 50.3% individual cell peak ozone.

Background

HRVOC event emissions in Houston result in plumes of high ozone that are typically less than 4 km wide. According to reported data in 2003, a 1,000 lb/hr release occurs 2 to 3 times per week and a 10,000 lb/hr release occurs 2 to 3 times every month.[1] The majority of reported events span one to three hours and are composed of ethylene, propylene, butylenes or 1,3 butadiene.[1] Ambient observations have shown that these releases result in rapid ozone (O_3) formation, which may cause exceedances of the National Ambient Air Quality Standard (NAAQS). UNC investigated the impact this type of event has in 4-km and 1-km domain resolutions.

Methods

Emission Events

These events were located in the industrial ship channel and included one three-hour event totaling 8.73 tons and one two-hour HRVOC event totaling 11.64 tons. To simulate a worst-case scenario the duration and location of the event was chosen to coincide with areas of stagnant wind conditions produced by slow rotating winds associated with the sea breeze. The path of the event plume and timing/location of events are shown in Figure 1. Even with the event emission, the 4-km resolution model was unable to predict within 15% of the highest observed 1-h ozone (ca. 200 ppb)[1]. The 1-km resolution model had a 65 ppb higher ozone peak than the 4-km model and reached 204 ppb. The magnitude and composition of the hypothetical event emission was based on an August 30, 2000 aircraft observation made near a petrochemical facility in the Houston ship channel.[2] The emission events in the model are composed of 17.6% ethylene and 82.4% propylene. On August 30, 2000 there are two emission events whose locations are denoted in Figure 1. Modeled meteorological inputs for August 30, 2000 have winds from the northwest until hour 15 when the wind shifts to come from the southeast. The first event coincides with winds from the northwest, which transport the plume to the second event location. The second event is released at hour 15 when the winds have shifted and the first event is directly above.

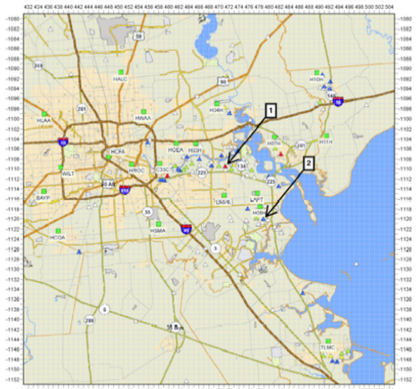


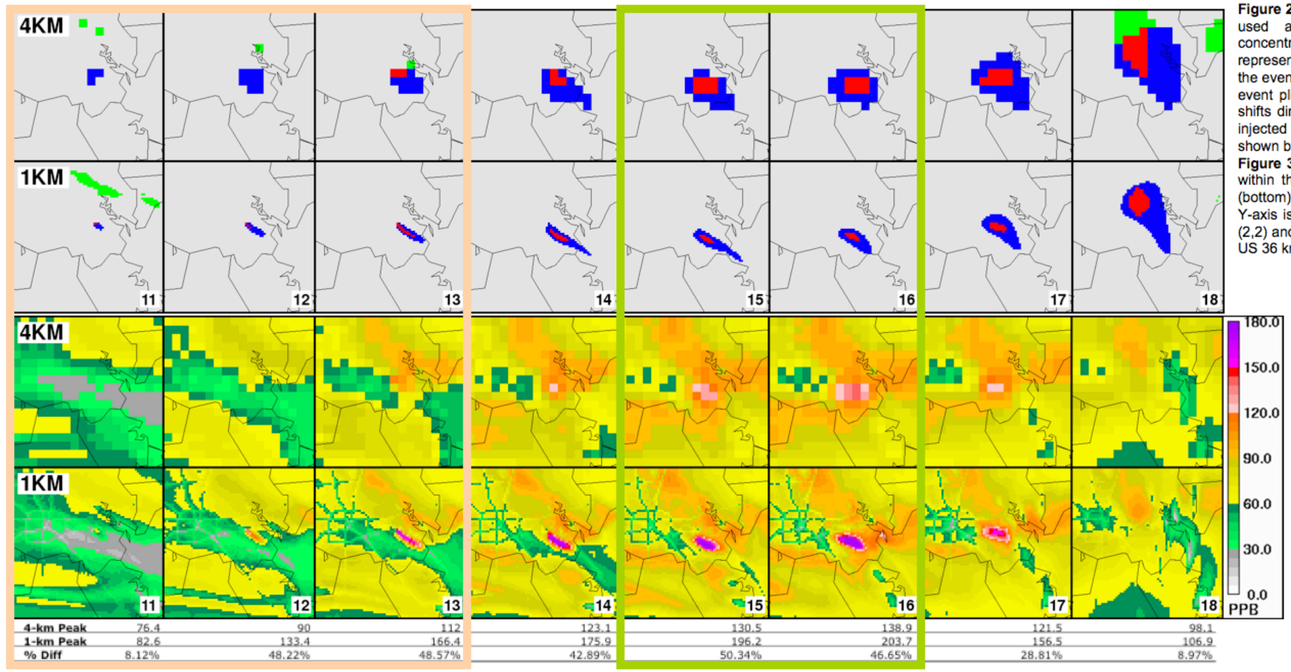
Figure 1: The first event occurs at location 1 and begins at hour 11. This event lasts for 3 hours and releases 8.73 tons of ethylene (ETH) and propylene (OLE + PAR). The second event occurs at location 2 and begins at hour 15. This event lasts for 2 hours and releases 11.64 tons .

Following the Plume

The response of the model's ozone productivity to an emission event was quantified with the process analysis tool. The in-model process analysis algorithm exports hourly averaged cell mass throughputs for physical and chemical pathways. The post processor then aggregates these to create a single focus region for analysis. Our goal was to choose a process analysis focus region that contained only those grid cells that were impacted by the event emission. We used dispersion runs of ETH, OLE and PAR to identify the hourly horizontal expanse of the entire event plume. Using the planetary boundary layer as the height of each grid column we then included columns until 68% of the event plume mass was represented. This horizontal region became the base for our process analysis focus region. Thus, any part of the plume that left the PBL was excluded from this analysis. The resulting horizontal dimensions of the domain are shown in Figure 2 by the blue cells. To confirm the region selection, the domain wide hourly ozone peak (within 10%) is overlaid on the same plot by red inside and by green outside the event plume. In all cases, we found part of the ozone peak was located within the region of the plume. The process analysis shown in this poster is for a full photochemical day: hours 8 to 18. During the hours before the event (8 to 11), the focus region is located at the first hour of event plume. From hour 11 to 15 the focus region moves southeast with the first event plume. At hour 15, the focus region stalls and then reverses direction from hour 15 to 18 following the plume of both event emissions. The peak ozone concentration occurs at hour 16.

Results

The 1-km and 4-km resolution event simulations produced dramatically different ozone peaks as shown in Figure 3. As previously found, ozone peak concentration in the 1-km resolution case is approximately 50% higher than the 4-km. [2] Figure 3 shows the magnitude and location of hourly peaks for the 4-km and a-km resolutions. The peak locations are generally in the same place but occupy different shapes.



4-km Peak	76.4	90	112	123.1	130.5	138.9	121.5	98.1
1-km Peak	82.6	133.4	166.4	175.9	196.2	203.7	156.5	106.9
% Diff	8.12%	48.22%	48.57%	42.89%	50.34%	46.65%	28.81%	8.97%

Figure 2 (left top): The event plume, shown in blue and red, was used as the process analysis focus region. Ozone concentrations within 10% of the domain wide hourly peak are represented by red (inside the event plume) and green (outside the event plume). 1-km resolution is above 4-km resolution. The event plume moves southeast after release. The event plume shifts directions with the sea breeze (typical of Houston) and is injected with more ethylene and propylene. Event hours are shown by the tan and green boxes corresponding to Figure 1.

Figure 3 (left bottom): Ozone concentrations are shown in ppb within the HGMCR 1-km domain for the 1-km (top) and 4-km (bottom) resolution simulations. The X-axis is horizontal and the Y-axis is vertical. Coordinates are given in I and J. Both 1-km (2,2) and 4-km (20,20) start at (432 km, -1152km) of the Eastern US 36 km domain.

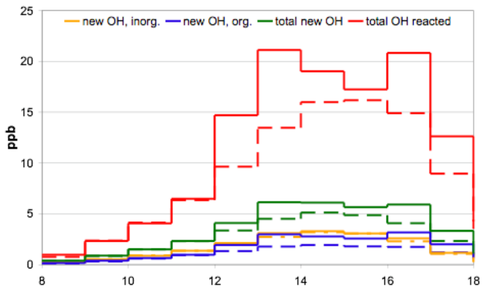
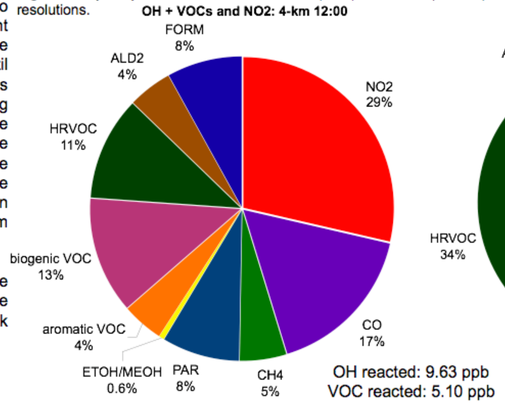


Figure 4: Hydroxyl radical statistics for 1-km (solid) and 4-km (dashed) resolutions.

PARAMETERS	hour of max diff.	4km (ppb/hr) max diff. conc.	4km (ppb/hr) avg.	1km (ppb/hr) max diff. conc.	1km (ppb/hr) avg.	Diff.(%) max	Diff.(%) avg.
net O_3 production	13	12.46	10.48	23.95	15.56	**92.8%**	31.5%
total new OH	16	4.07	3.58	5.90	4.61	45.1%	**29.2%**
OH chain length	12	2.88	3.42	3.60	3.51	24.9%	**3.5%**
new OH, inorg.	13	2.71	2.08	3.09	2.22	14.1%	7.2%
new OH, org.	16	1.74	1.47	3.17	2.30	**82.3%**	53.3%
total OH reacted	13	13.46	11.80	21.11	15.68	**56.9%**	**33.7%**
total new NO	8	15.20	7.52	28.94	9.08	**90.3%**	22.2%
NO chain length	13	1.52	1.70	2.58	2.04	**69.6%**	**26.4%**
NO_2 from NO	13	18.47	16.39	31.65	23.29	**72.4%**	**42.4%**

The concentrations at max difference were calculated for hours 8-18.
The average concentrations were calculated for hours 11-18.

Table 1: Chemical rate statistics for 1-km (solid) and 4-km (dashed) resolutions.



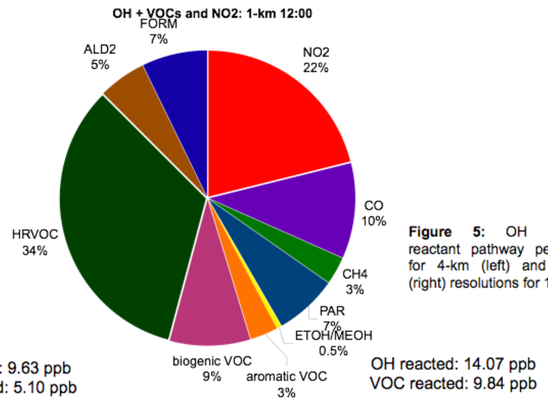


Figure 5: OH radical reactant pathway percents for 4-km (left) and 1-km (right) resolutions for 12:00

Results (cont.)

Chemical Processes:

The 1-km resolution has as much as 92.9% higher hourly net chemical production of ozone from hour 12 to 18. As shown in Figure 4, OH radical production is 29.2% higher for the 1-km resolution from 12 to 18 and chain length, or reuse, is on average 3.6% higher. After hour 11, the total reacted OH is consistently higher, as much as 56.9% higher, in the 1-km resolution. The OH from inorganics is unaffected by resolution, while the OH from organics is 25.1 to 82.3 % higher from hour 12 to 18, converging slightly in 14 and 15. OH from organics is the result of OH+VOC reactions that create intermediates including formaldehyde, which produces more OH. The OH chain length, or number of times each OH radical is reused, is 24.9% and 15.2% higher in the 1-km resolution for the two hours following the first event, but is then comparable and lower for hour 14 and beyond. The 29.2% increase from hour 12 to 18 in new OH radicals combined with the chain length increase of 3.6% resulted in a 33.7% increase in total OH reacted per hour for hours 12 to 18. The 1-km increase of OH reacted also caused more NO to propagate. Figure 5 shows that 34% of OH in the 1-km resolution reacts with HRVOCs, while only 11% do so in the 4-km resolution. More evidence of increased propagation of NO is shown in Table 1 where the NO cycle increased 62.3% in hour 16. Although average new NO mixing ratios in hours 8 to 11 increased in the 1-km resolution by 47.51%, the increased radical source and NO propagation was able to readily oxidize this new NO. For hours 12 and 13, the average amount of NO oxidized to NO_2 increased 71.9%. The average number of times an NO is re-oxidized is 26.4% greater and the average total NO_2 produced is 42.4% greater on average with a peak difference of 72.4%.

Conclusions

Hypothetical industrial releases simulated in a 1-km resolution produced peak ozone concentration 65 ppb higher than the same release in a 4-km resolution model. Comparing chemical and physical process rates demonstrate organically derived OH account for the difference in ozone productivity. The source of organic OH is driven by HRVOC reactions, which are enhanced by resolution. The HRVOC concentration differences result from the difference in grid cell size and potentially dispersion differences in the 4-km and 1-km grid resolutions. OH+VOC reactions reduce NO_2 termination by as much as 39.9% by competing with OH+NO_2 reactions. The shift to OH+VOC reactions and the resultant intermediate product photolysis also increased the average rate of new OH available by 53.3%. The gains in the chemical production of ozone were the result of these 53.3% average (823% max) increases in organically derived OH radicals. A 29.18% increase in new OH radicals resulted in a 27% increase in peak ozone for our aggregated focus region and 50.3% increase in the individual cell peak. This data can be used in future studies to analyze the affect on competition between dispersion and chemistry.

Acknowledgments and References

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2. Allen, D., Murphy, C., Kimura, Y., Vizuete, W., Edgar, T., Jeffries, H.E., Kim, B.-U., Webster, M., and Symons, M. (2004). Final Report Texas Environmental Research Consortium Project H13: Variable Industrial VOC Emissions and their impact on ozone formation in the Houston Galveston Area, UNC-Chapel Hill, UT-Austin.