Reactivity of Volatile Organic Compounds Under Low NO_x Conditions

Final Report

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Overview

A need exists to determine the incremental reactivities of leading pesticide solvent VOC compounds at current NO_x concentrations in the San Joaquin Valley (< 50 ppb). Model simulations and laboratory experiments of these complex mixtures are required to understand the photochemical mechanism governing these aromatic compounds. There are several atmospheric chemical models available for the public; however, this work utilized the SAPRC chemical mechanism due to the fact that CA state agencies utilize this particular chemical mechanism for regulatory work.

During this project, we have set up a laboratory reaction chamber, larger than our previously productive mobile ozone chamber, and developed the apparatus needed to conduct multi-hour experiments under low NO_x conditions – with sufficient quantitative ability to discern increment effects of small concentrations of additional VOCs. Second, we have utilized the complete SAPRC07 modeling approach (on our own computer system) to simulate photochemical formation of ozone, in quantitative agreement with established reactivities. Our three goals for modeling were to (1) evaluate results from ozone forming experiments, (2) guide planning of ozone forming experiments to conditions where mechanism differences may be discerned, and (3) to follow intermediate product species (such as reactive aldehydes) which can reveal strengths and weaknesses of existing models.

Background

PROBLEM

Air quality, including ozone, has been improved dramatically in California generally, but challenges remain. Notably, ozone has decreased much more in urban areas such as Los Angeles (LA) than in less densely populated air basins – especially the San Joaquin Valley (SJV). This is despite large reductions in volatile organic compound (VOC) emissions, and ongoing efforts in NO_x improvement – the two precursors to ground-level ozone. Now, ozone is nearly as high in several areas of the SJV as in LA. For cost-effective ozone reduction, efforts at VOC reduction (for example with past reformulation of gasoline) consider the relative reactivity of VOC ozone precursors. However, there are uncertainties in relative VOC reactivity for lower nitrogen oxides (NO_x) concentration conditions such as currently found in the SJV. Consequently, the relative reactivity of agricultural pesticide product components under rural low NO_x conditions such as the SJV is uncertain. Pesticides are one of the top six contributors to SJV VOCs on a mass basis, but a more accurate evaluation of their actual contribution to ozone will require a better understanding of reactivity under low NO_x conditions typical of rural areas.

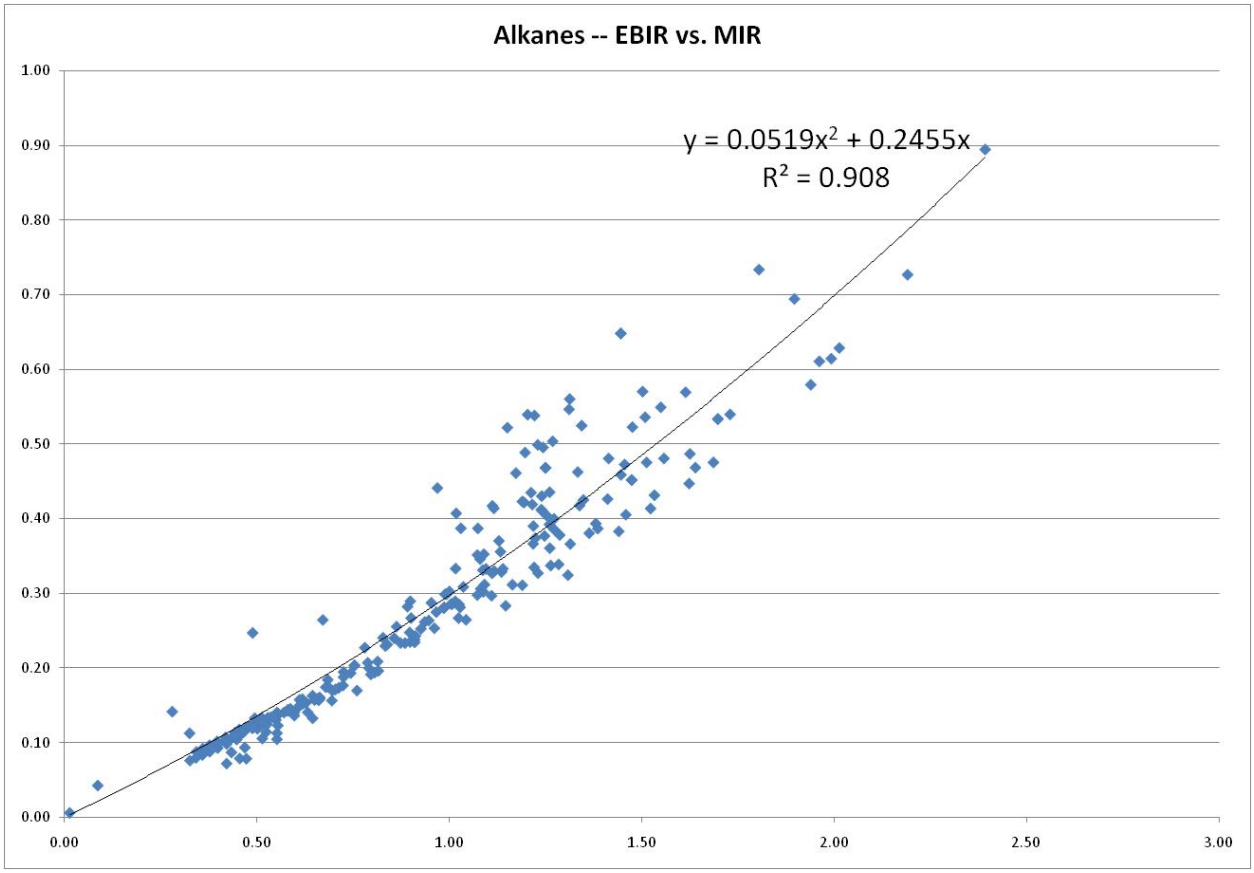
PREVIOUS WORK

Decades of existing research, including smog chamber studies, was performed at NO_x concentrations appropriate for past urban air – understandably where the most people lived, and where the air was worst. Even for studies at "lower NO_x", the levels were much higher (300 ppb, for example) than what now occurs – including during current SJV ozone exceedances (NO_x ~30 to 50 ppb in more urbanized locations such as Fresno, and still lower in outlying locations such as Arvin). Most stimulating in past journal publications (Carter et al. 1997) were observations that some compounds' reactivity decreased sharply at lower NO_x, some decreased modestly, and some increased. So, the relative change to lower NO_x involves a difference of an order of magnitude in ozone formation. That is, the relative contribution towards ozone reduction of one VOC relative to another VOC could be currently unknown by a factor of 10.

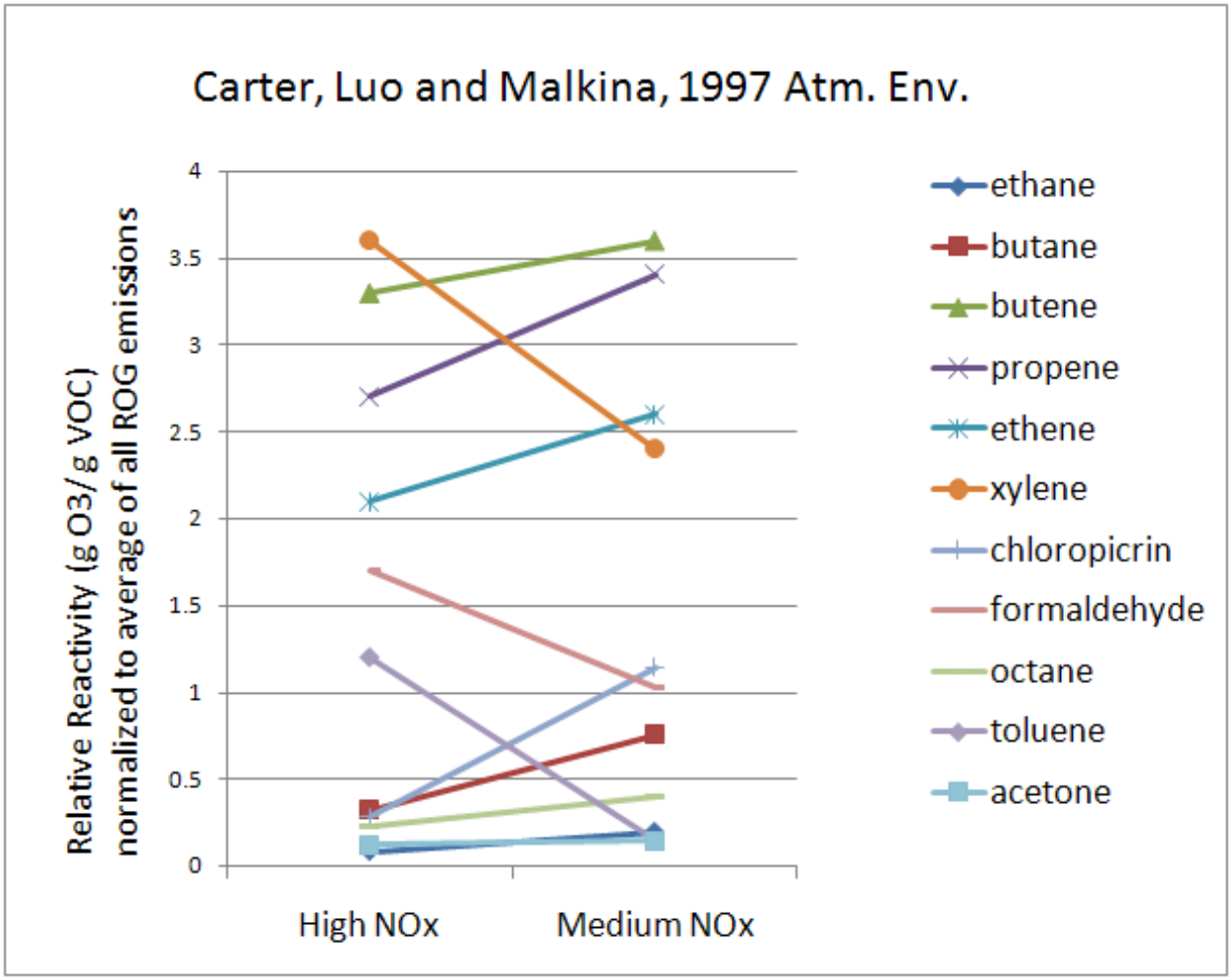
INCREMENTAL REACTIVITY

California's Department of Pesticide Regulation (DPR) uses a mass-based approach to VOC inventory. It has in the past had exploratory consideration of a VOC inventory that weights tabulated emissions on a reactivity basis. In most cases, the required speciation should be straightforward with use of the confidential statements of formula. For highly diverse natural mixtures (for example pesticidal oils and new semi-natural solvent mixtures such as C8-C10 dimethyl amides and C12-C14 methyl esters) it may only be possible to assess ozone formation potential as a bulk sample. So, the main issue is how to characterize the relative reactivity of the different chemical species that are volatilized. In the near term one could use the maximum incremental reactivity (MIR) scale because (1) that scale is widely used, and (2) MIR has much more experimental validation data available. Other scales are highly correlated to the MIR scale. This includes the Equal Benefit Incremental Reactivity Scale (EBIR) which is based on lower NO_x /VOC ratios. However, if one looks at particular examples of VOCs which are important to DPR, one sees there are significant outliers. For example, where most VOCs have a calculated EBIR which has decreased 4-fold to 5-fold from MIR, chloropicrin decreases by only a factor of 1.5, and some aromatics (including both methyl naphthalenes, which constitute 52% of Aromatic

200 solvent) decrease by over 7-fold (see table after the next two figures). These outliers merit further study under appropriate experimental conditions. Chloropicrin is rather unique in having a significant percentage of its own mass being an NO_2 group that is released photochemically.



In the above figure, alkanes (including linear, branched and cyclic compounds – but all fully saturated), have a fairly predictable decrease of incremental reactivity from MIR to EBIR conditions. The same is not true for more diverse types of compounds, as shown below. Though not strictly studying MIR vs. EBIR conditions, the comparison from high NO_x to medium NO_x is illustrative, and includes the types of compounds in this study: aromatics, and the fumigant chloropicrin. It is striking how the relative reactivity of the aromatics declines markedly (as normalized to the average of all VOCs) while the reactivity of chloropicrin increases by the largest relative amount.



The table below provides a selection of reactivities (MIR and EBIR) for a variety of common VOCs of interest. As mentioned, most VOCs have a calculated EBIR which has decreased 4-fold to 5-fold from MIR, chloropicrin decreases by only a factor of 1.5, and some aromatics (including both methyl naphthalenes, which constitute 52% of Aromatic 200 solvent) decrease by over 7-fold.

	MIR	EBIR	ratio
methanol	0.65	0.197	3.30
ethanol	1.45	0.57	2.54
isopropanol	0.59	0.35	1.67
acetone	0.35	0.087	4.02
acetic acid	0.66	0.2	3.30
trimethylamine	6.03	1.9	3.17
isoprene	10.28	2.34	4.39
and some terpenes			
hexane	1.15	0.45	2.56
dodecane	0.5	0.103	4.85
toluene	3.88	0.53	7.32
xylene (p,o,m)	5.69	0.81	7.02
	7.44	1.16	6.41
	9.52	1.49	6.39
ethyl benzene	6.39	0.99	6.45
isopropyl benzene	2.43	0.38	6.39
C10 benzenes	2.27	0.4	5.68
methyl naphthalene	2.96	0.4	7.40
formadehyde	9.24	1.34	6.90
acetaldehyde	6.34	1.61	3.94
chloropicrin	1.8	1.14	1.58
MITC	0.31	0.184	1.68
DCP(cis)	3.61	0.83	4.35
"(trans)	4.19	1.02	4.11
1-octene	3.12	0.78	4.00

For now, however, it is understood that DPR will maintain use of a purely mass-weighted approach to pesticide inventory.

Materials and Methods

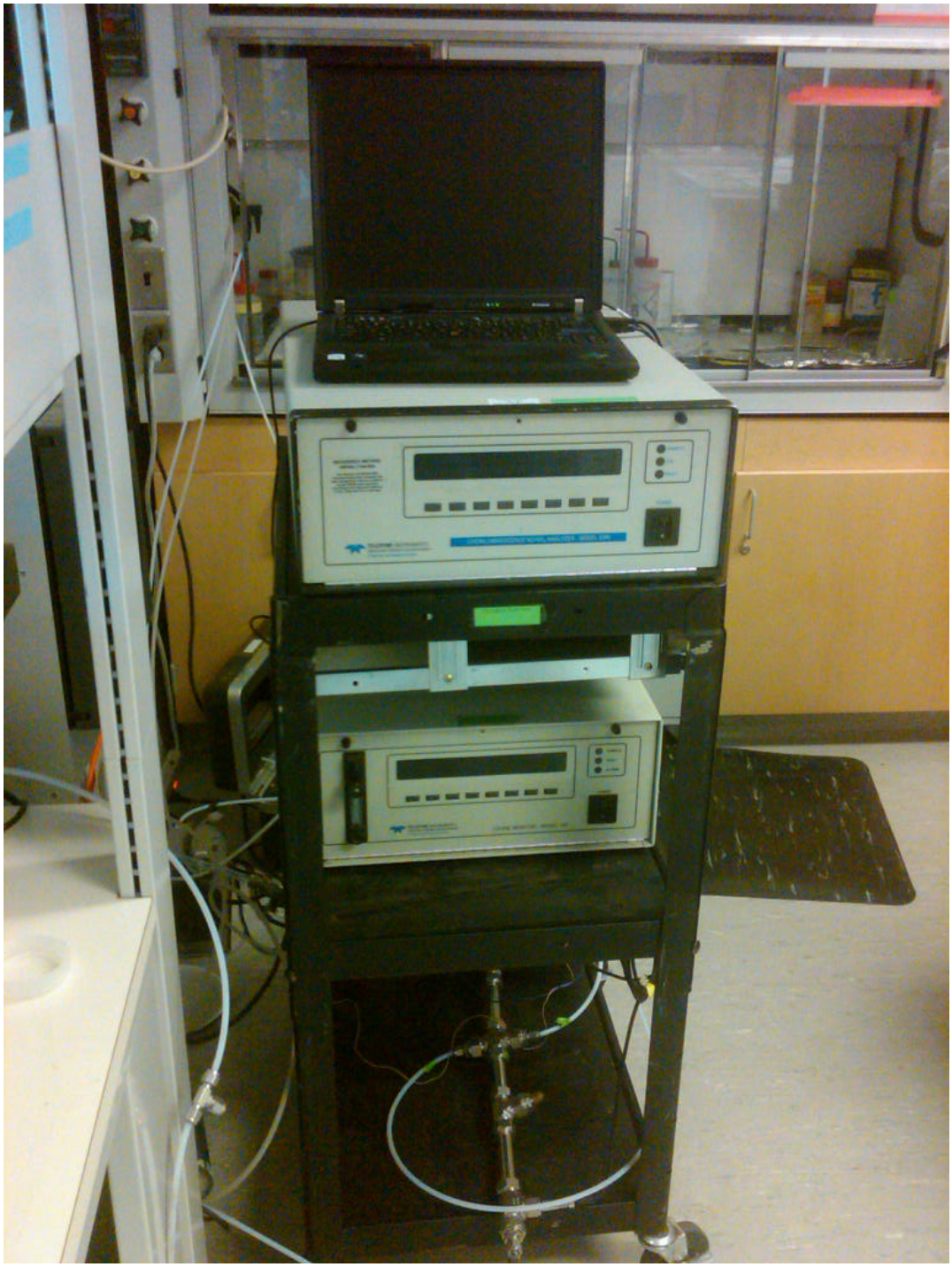
OBJECTIVE:

To determine the reactivity of leading pesticide VOC compounds at what are now the typical NO_x concentrations (less than 50 ppb) during the May to October ozone "season." The short list of VOCs we studied was: isopropyl benzene (cumene, a major component of Aromatic 100, which is still used, particularly in retail product formulations), C10-benzenes (the main constituents of Aromatic 150), methyl naphthalene (most of Aromatic 200). These determinations will provide defensible EBIRs for future use. In doing so, we expected to make progress towards better understanding the photochemical reactions of aromatic compounds under low NO_x conditions. The SAPRC mechanism is the basis for the EBIR calculations, i.e., http://www.engr.ucr.edu/~carter/SAPRC/. In Carter's recommendations section (p. 130, 2009 SAPRC07 document at link above) he states "In addition, the problem of underpredicting O_3 at low ROG/ NO_x ratios and low NO_x levels (as noted by Carter, 2004), which is attributed to problems with the aromatics mechanisms, has not been resolved." We expect that by assessing the reactivity of simpler mixtures (or single compounds), there will be better progress in understanding the aromatic mechanism(s) under low NO_x conditions. In addition, the calculated EBIRs for a variety of aromatics (from simple compounds such as benzene and phenol up to larger disubstituted aromatics) turn out to be negative according to the model.

EXPERIMENTAL

Our 4000 L (4 m^3) Teflon chamber with controlled temperature and illumination was set up in room 2110, Ghausi Hall (formerly Engineering 3), the Department of Civil and Environmental Engineering at UC Davis.

Inside view of reaction chamber.



Instrument package for realtime monitoring: laptop controller, ozone monitor, NO_x monitor (NO_2 and NO).

It has been shown in previous studies that the Teflon chamber may interfere with ozone formation studies. Therefore, it is important to fully characterize the physical and chemical attributes of the reaction chamber. It has been shown that the Teflon chamber may generate a small amount of ozone (<5 ppb) when irradiated with UV for several hours and may also act as a sink for gases to deposit onto during experiments (~10-12% loss / hour of NO_x), thus wall-losses must be taken into account.

These bag effects were quantified during experimental chamber experiments to provide bag interference parameters to the box model. Therefore, this particular box model is able to simulate wall losses to the bag surface as well as ozone generation via Teflon irradiation. To characterize our Teflon chamber, several experiments were conducted. The first set of experiments were conducted by adding zero air to bag, irradiating the bag for 3 hours and measuring ozone formation. This ozone is due to Teflon irradiation as no ozone precursors were added to the bag. The second set of experiments were conducted by adding 40 ppb of NO_x (as NO_2 in zero air) to the chamber (pre-filled with zero air) and examining the NO_x loss rate as a function of time. No irradiation occurred for this experiment. The third set of experiments were conducted by adding NO_x, irradiating the bag, and measuring both the NO_x wall loss rate and chamber ozone generation to examine if NO_x wall losses and Teflon irradiation interfere with each other. An example of the raw data collected from a wall loss / Teflon irradiation experiment is shown in the next section.

MODELING

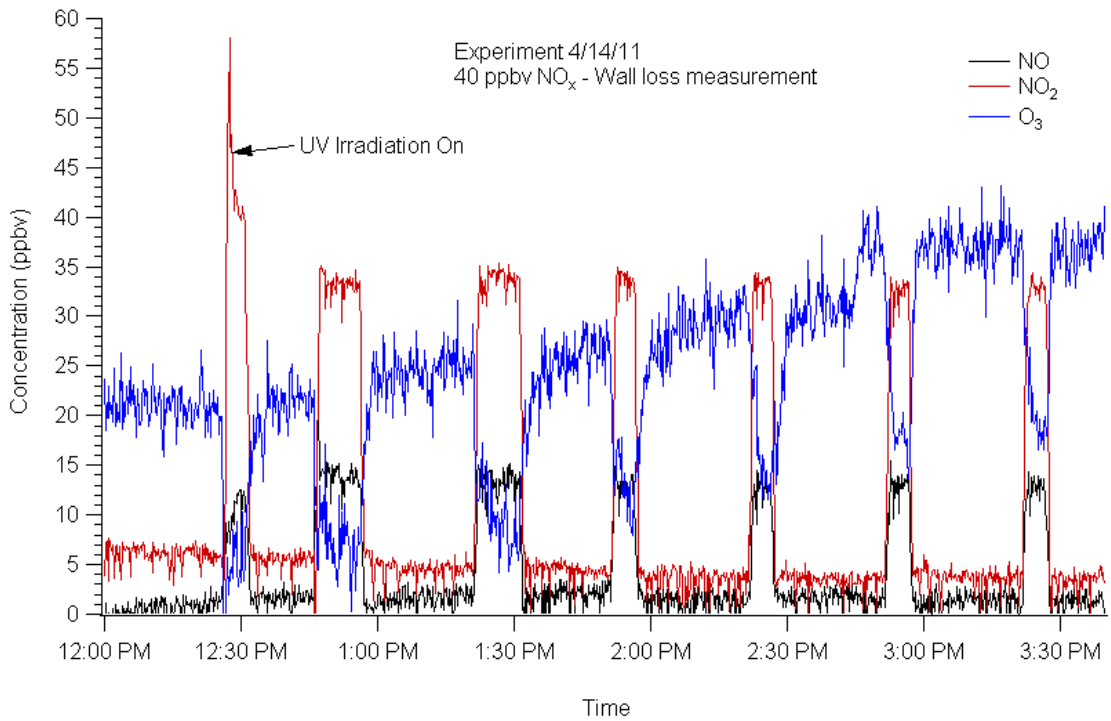
The SAPRC07 atmospheric chemical mechanism was developed by Bill Carter of UC Riverside and is the most recent iteration of the SAPRC ozone chemical mechanism available for public use. SAPRC07 was updated from SAPRC99 to include a number of changes primarily focused on updated rate constants and reactions based on current experimental data to better represent VOC species.

Run Type	Composition
Full Surrogate	n-butane, n-octane, ethene, propene, trans-2-butene, toluene, m-xylene and formaldehyde
Mini Surrogate	ethene, n-hexane, and m-xylene
ARB Average	"HC" - 20 different lumped and individual species
Sacramento, CA	"HC" - includes automobile and biogenic VOCs

HC Composition	Individual Species	Lumped Species
	HCHO	ALK1
	CCHO	ALK2
	RCHO	ALK3
	ACET	ALK4
	MEK	ALK5
	BALD	ARO1
	ETHEN	ARO2
	ISOPR	OLE1
	ACETY	OLE2
	BENZE	
	TERP	

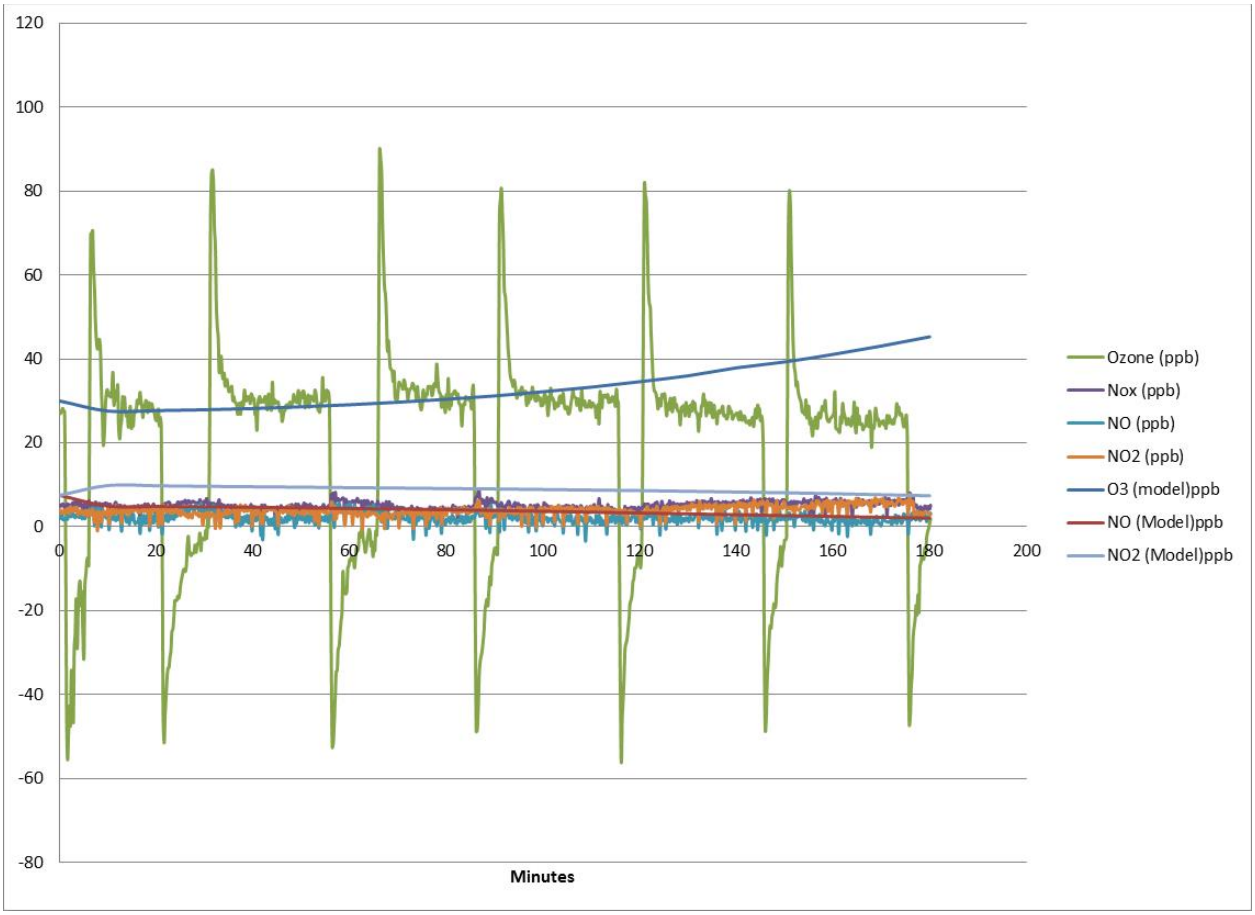
The California Air Resources Board (ARB) currently uses SAPRC99 for ozone simulation studies and it is expected that the ARB will incorporate the SAPRC07 mechanism in the next few years. For this work, the SAPRC07 chemical mechanism was used to predict the ozone formation potential of several pesticide solvents (the main components of the leading commercial solvents sold as aromatic 100, 150 and 200) and compared to experimental chamber studies utilizing pre-determined initial concentrations of NO_x (5-10 ppbv, parts per billion by volume, equal to nL/L, and often simply listed as ppb) and mini-surrogate (VOC).

A box model incorporating the SAPRC07 mechanism was employed to calculate ozone concentrations for various NO_x and VOC concentrations. Two separate models were generated for this work. The first model simulates ozone formation in the free atmosphere whereas the second model simulates ozone formation in a experimental reaction chamber which can then be interpolated to typical atmospheric conditions



Base case experiments are needed to estimate the ozone formation potential, maximum incremental reactivity, and equal benefit reactivity of specific VOCs by calculating ozone concentrations under typical NO_x and VOC concentrations. Base case studies were conducted using NO_x (95% NO_2/5% NO) and a previously established mini-surrogate (55% ethane, 33% n-hexane, 12% xylenes) to represent the background VOC mixture. Once initial NO_x and VOC concentrations were included, the chamber model was run to simulate UV irradiation for 3 hours and final concentrations of ozone, NO, NO_2, and other reaction products were reported. These experiments were conducted for a 16 combinations of initial NO_x and VOC concentrations ranging over 0, 10, 20 and 50 ppb of NO_x and 0, 125, 165 and 300 ppb of VOC to create a baseline ozone isopleth as shown in the next section. In addition, sets of replicate experiments were conducted to assess reproducibility.

At the limit of low concentrations (15 ppb chloropicrin shown here), wall loss of ozone equals (and would eventually exceed) production, as shown below. For these conditions, and to consider lower concentrations, one must rely on the photochemical model calculations.



Results and Comparison Between Model and Experiment

Experimental work progressed nicely with the completion of the reaction chamber. Chamber performance characteristics have been evaluated we were able to account for line losses, NO_x wall losses, and Teflon chamber ozone generation. Because our real-time instruments draw significant volumes of bag air, we collect ~ 5 minute samples every 30 minutes in order to maintain the bag's volume to reduce wall-losses and volume effects. This sampling pattern can be seen in the experimental data below in Figure 4a-f. The uncertainty in the real-time instruments was evaluated by calculating the standard deviation of the baseline noise during the experimental procedure. These performance characteristics are shown below.

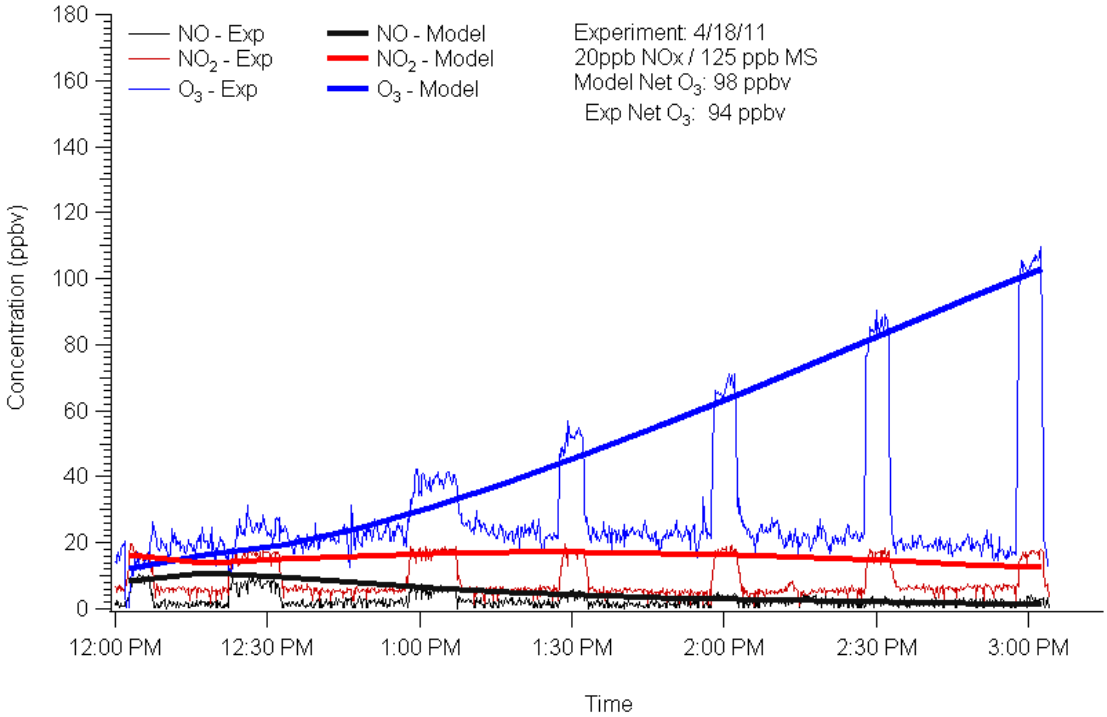
Uncertainty of experimental measurements as limited by baseline noise (ppbv)

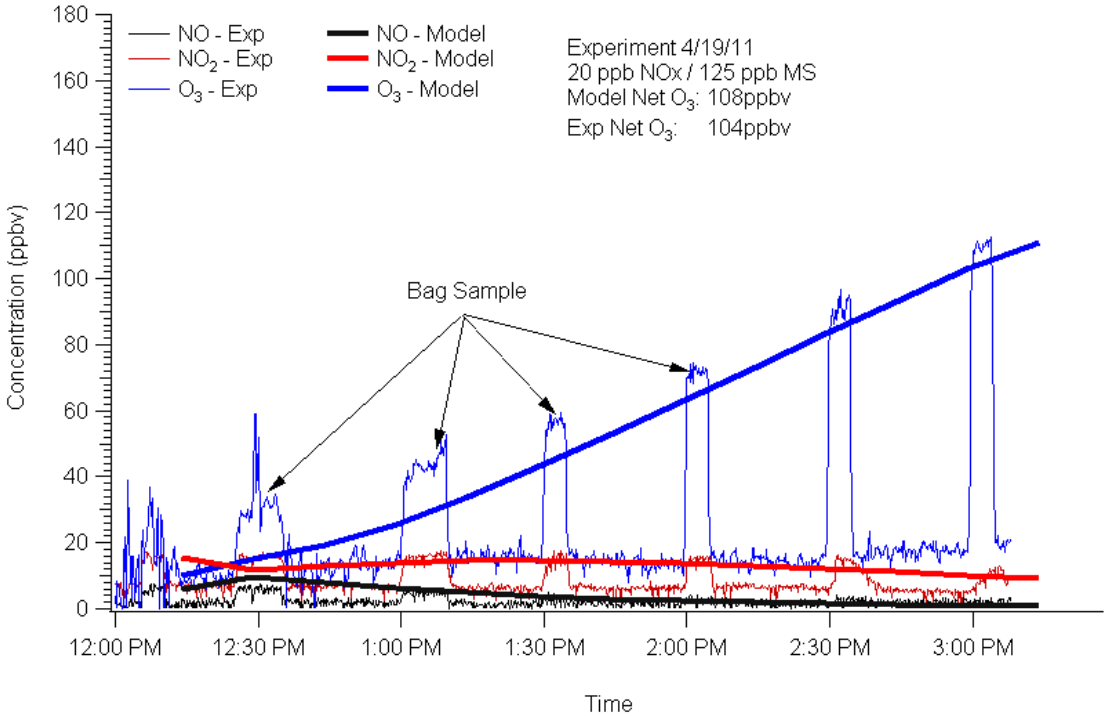
NO_x	NO	NO_2	O_3
0.86	0.99	0.77	1.61

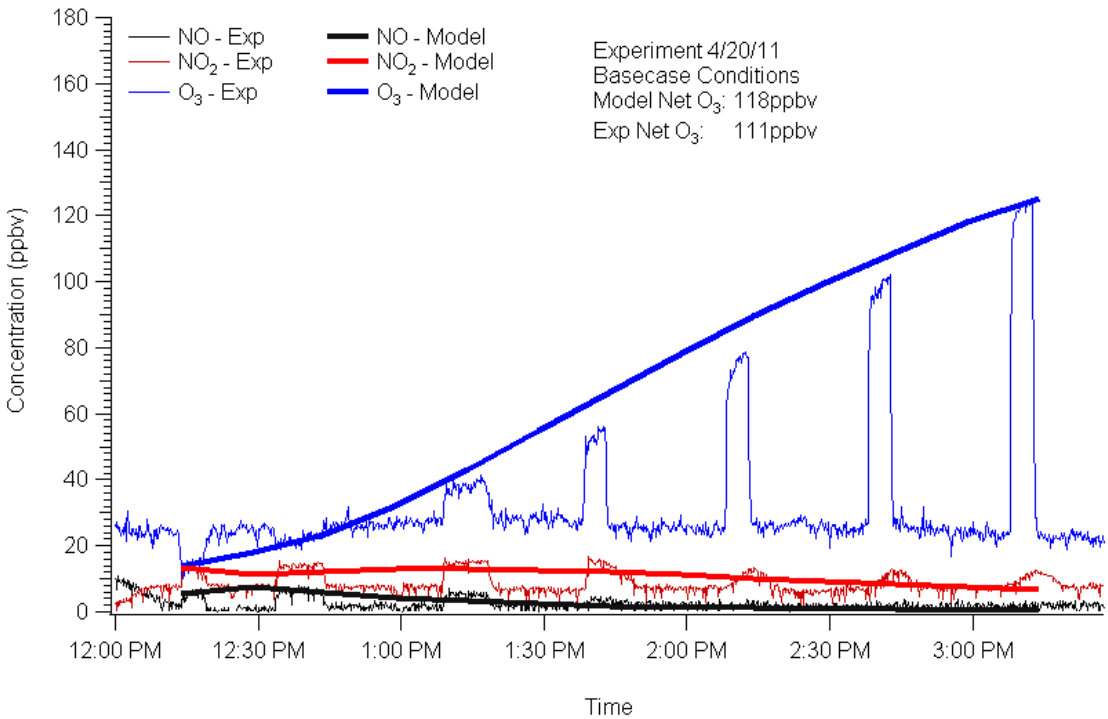
The following plots show experimental data and modeling data for some base case experiments conducted in April 2011. These experiments were conducted at ~20 ppbv NO_x and ~165 ppbv of mini-surrogate. Experiments were conducted by filling the Teflon chamber to half volume with zero air, injecting the designated NO_x and mini-surrogate, and then filling the chamber with zero air. This allows for the NO_x and mini-surrogate to mix uniformly throughout the chamber before UV irradiation. Once the bag is full, UV lights are turned on and sampling begins. The UV light banks were operated in a way to provide uniform coverage with one light bank set at a slightly lower elevation to promote buoyant (thermal convection) mixing of the gases within the reaction chamber.

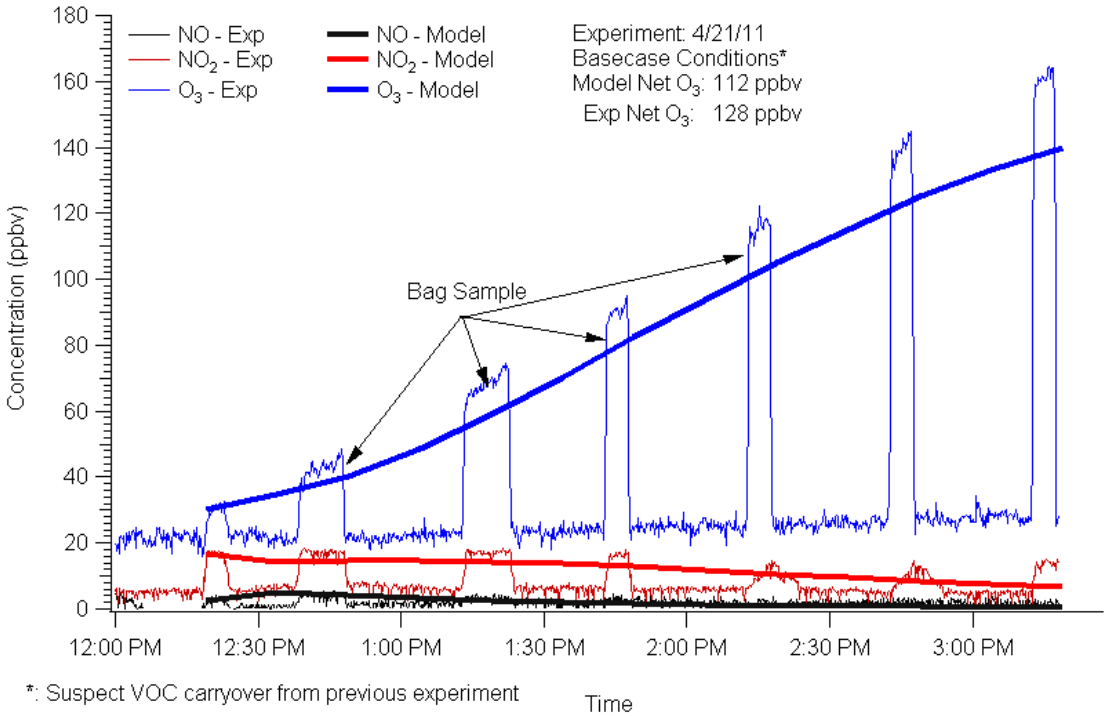
Each experiment was modeled using the SAPRC07 mechanism and compared to experimental laboratory measurements. In general, the model vs experimental data match quite well. The first experiment conducted on 18 April 2011 shows very good agreement between the model and experimental data with 98 vs 94 ppbv of net ozone formed at the end of the experiment. (Agreement at earlier times is difficult to achieve due to transient effects with radical species and the initialization effects of illuminating the chamber walls with UV.) Similarly, the experiment on 19 April 2011 shows similar results with 104 vs 108 ppbv of net ozone formed in both the chamber and the model simulation. The experiment on 21 April 2011 showed that the model underpredicts the amount of ozone in the chamber by ~20 ppb. This was likely due to inadequate cleaning from the previous experiment. VOCs may "stick" to chamber walls and tubing from experiment to experiment; therefore, we increased the amount of flushing between experiments

and also introduced water vapor (at 50% relative humidity) to the flushing gas to remove polar compounds in subsequent experiments.



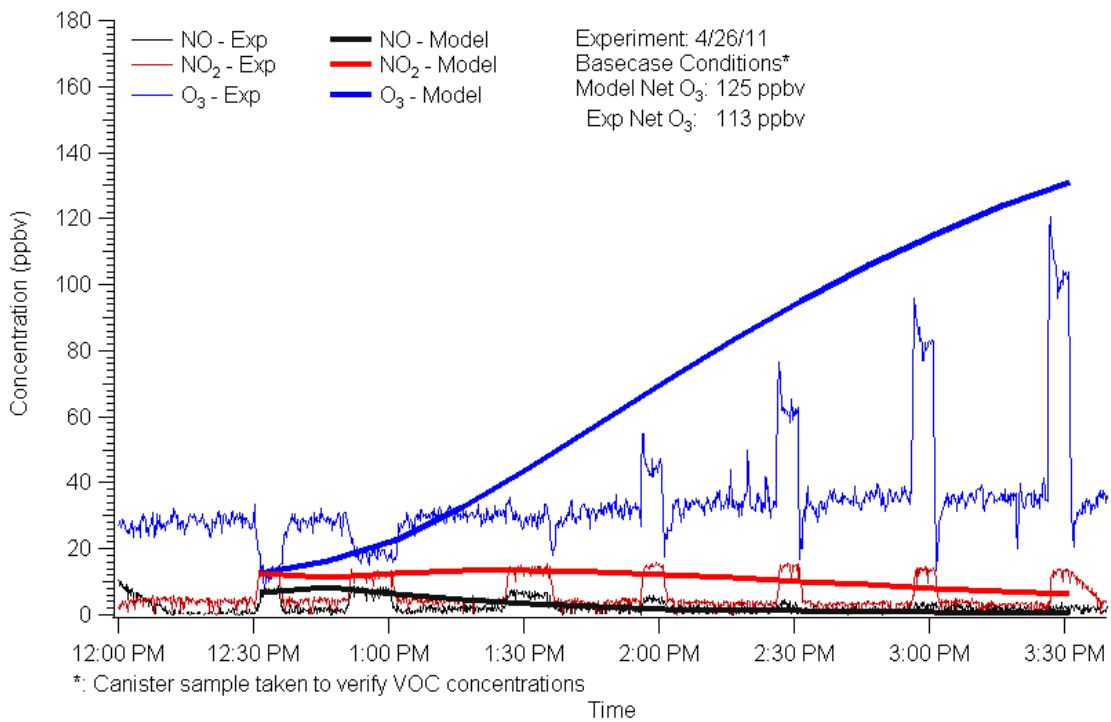




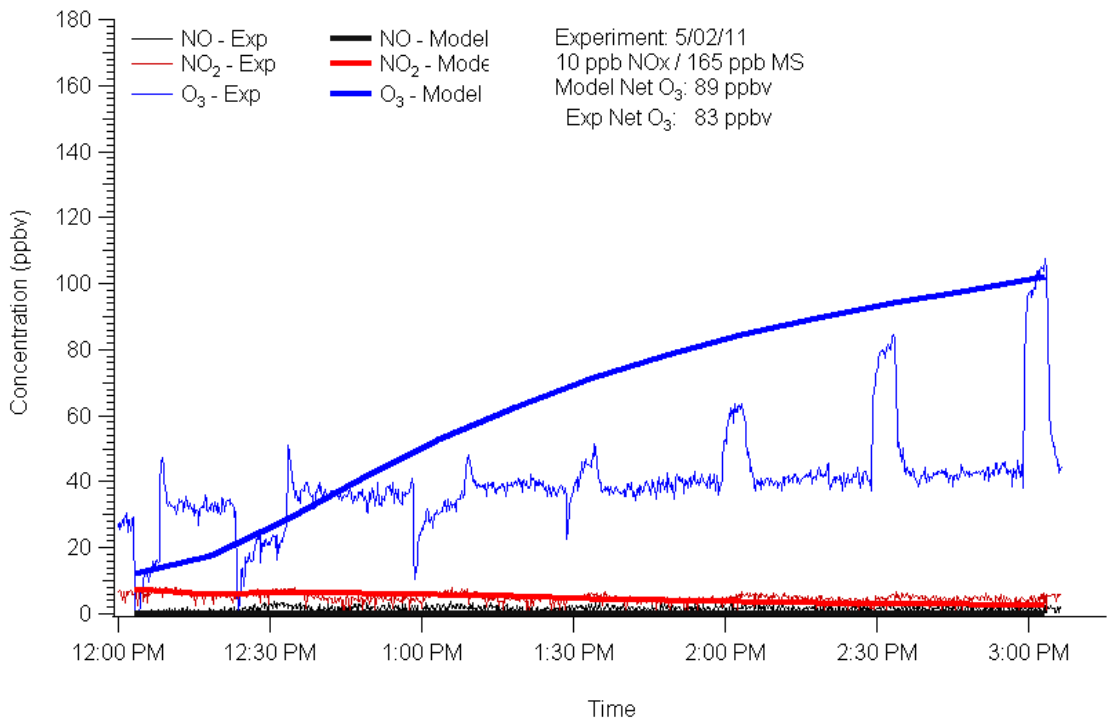


Again, the experiment on 26 April 2011 shows fair model results (125 ppbv vs 113 ppbv) when compared to experimental data. We also collected a SUMMA canister sample and performed GC-MS analysis in order to verify that the correct amount of mini-surrogate was injected into the

chamber. SUMMA canister results show that 13 ppbv (15 ppbv expected) of m-xylene were present in the bag at the start of the experiment. This lower concentration may be due to line losses incurred when injecting gases into the bag. In early trials, we utilized a rotameter to calculate the initial injection volume of mini-surrogate and NO_x into the bag. For later runs, we used a mass flow controller with solenoid valve to more accurately control the concentration of gases injected into the reaction chamber. The flow controller also allowed us to inject additional gases at later time points during experiments.

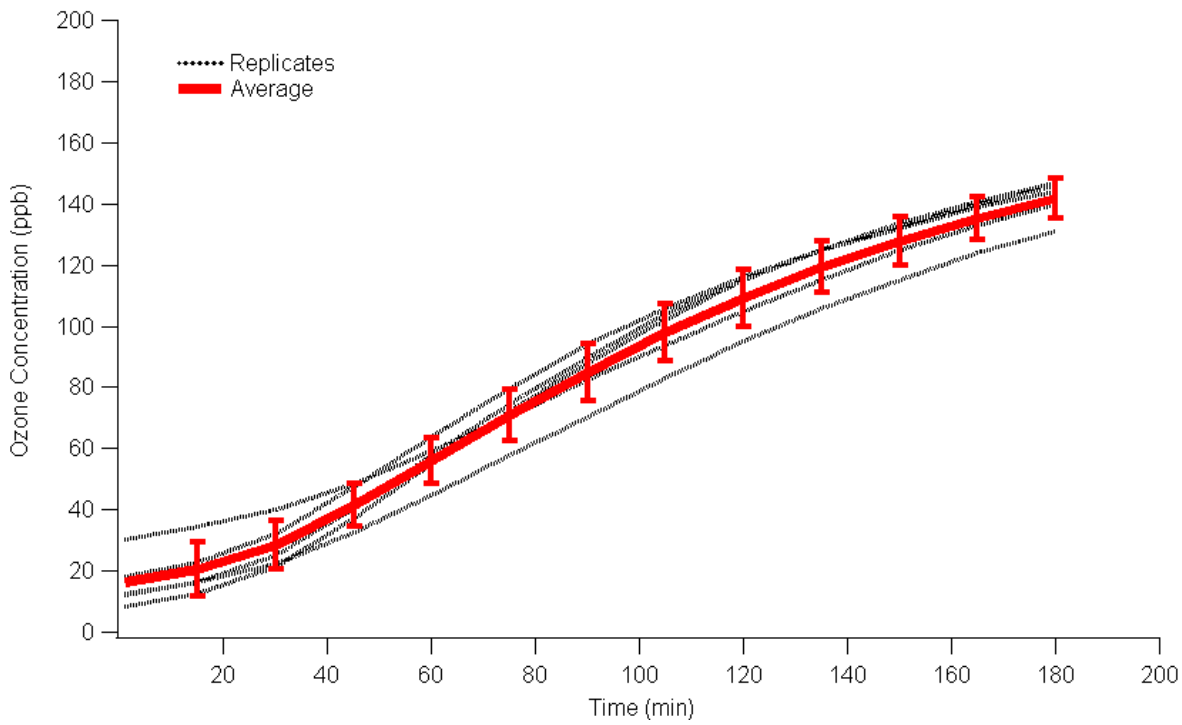


The experiment on 2 May 2011 was the first experiment conducted at 10 ppbv NO_x. The model simulation shows a slight overprediction of net ozone formation though the difference between the experimental and model results is less than 10%.

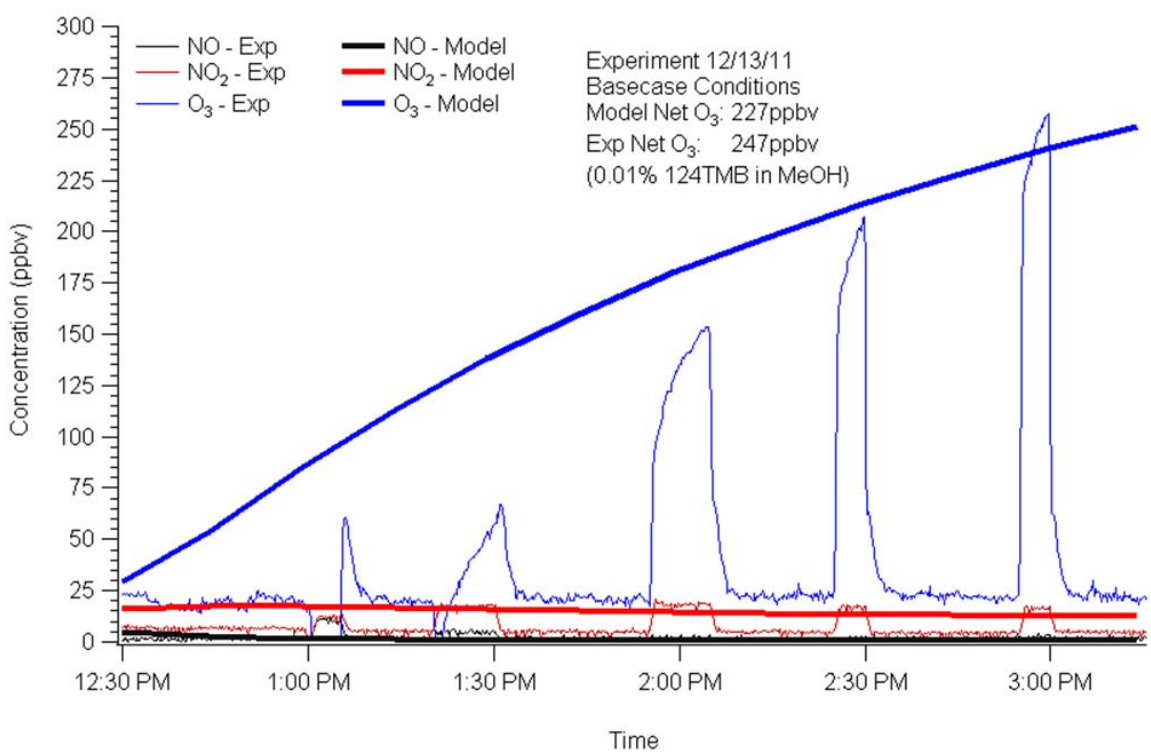


Results Summary

	Initial Reactants			Net Ozone Formation		
Date	NO	NO_2	O_3	Experimental	Model Simulation	Percent Difference
18-Apr	8.27	16.47	12.29	94	98	4.26%
19-Apr	5.88	15.39	9.88	103	108	4.85%
20-Apr	5.46	13.25	13.76	111	118	6.31%
21-Apr	2.56	16.84	29.98	128	112	12.50%
26-Apr	6.87	12.63	12.49	113	125	10.62%
2-May	-0.40	6.39	11.95	83	89	7.23%

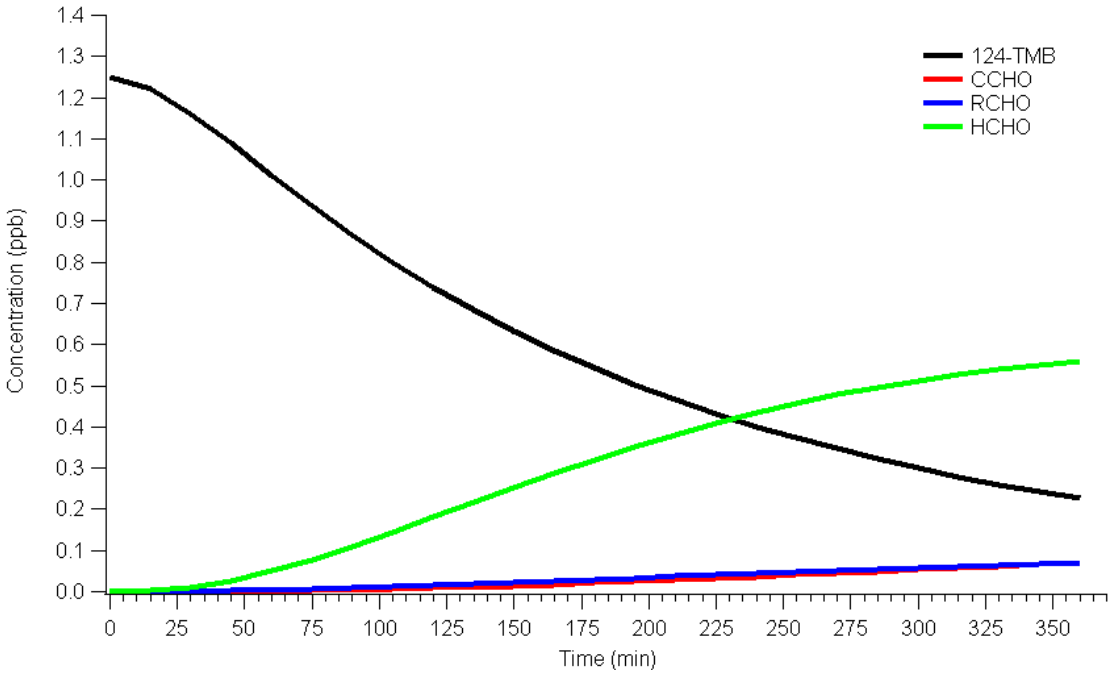


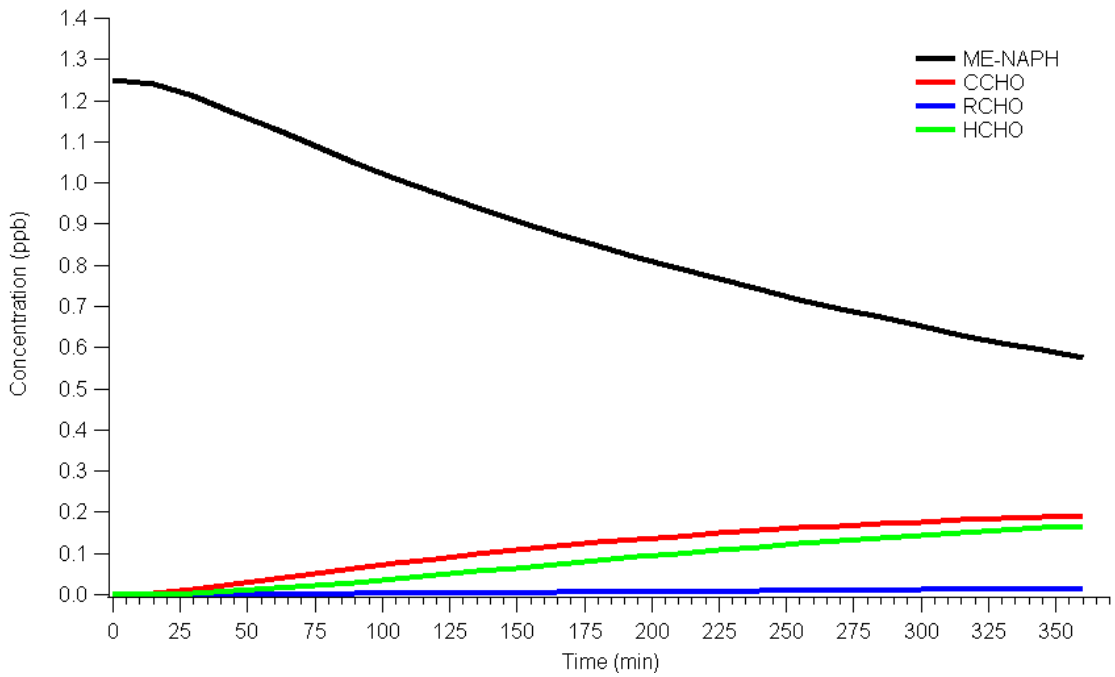
To test reproducibility, the above graph shows repeated experiments, with a cleaning cycle in between, using matched initial concentrations.



The figures above show moderate to high levels of ozone formation and fairly tight reproducibility between replicate experimental runs.

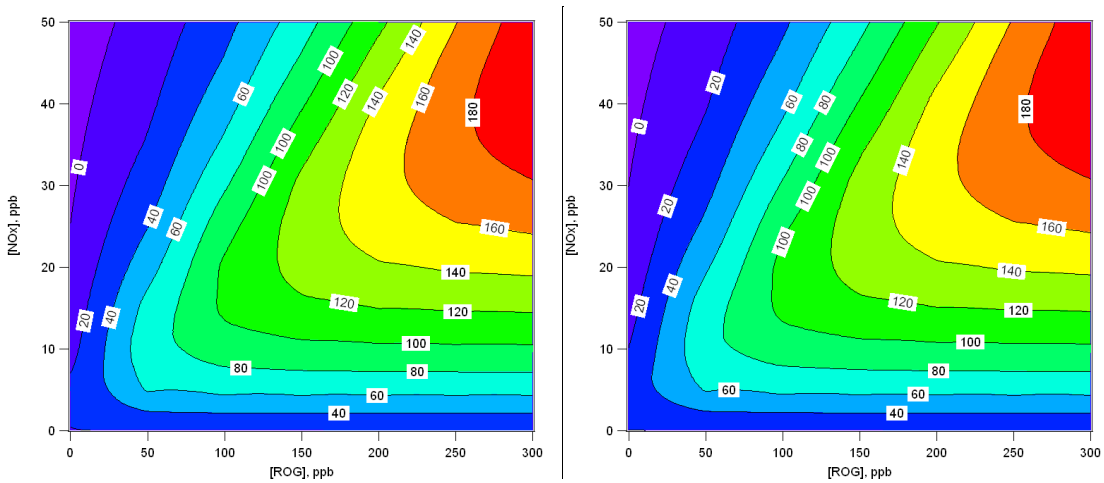
The figures below contain 6 hour SAPRC07 modeling results showing the formation of aldehydes as the VOC of interest is broken down.





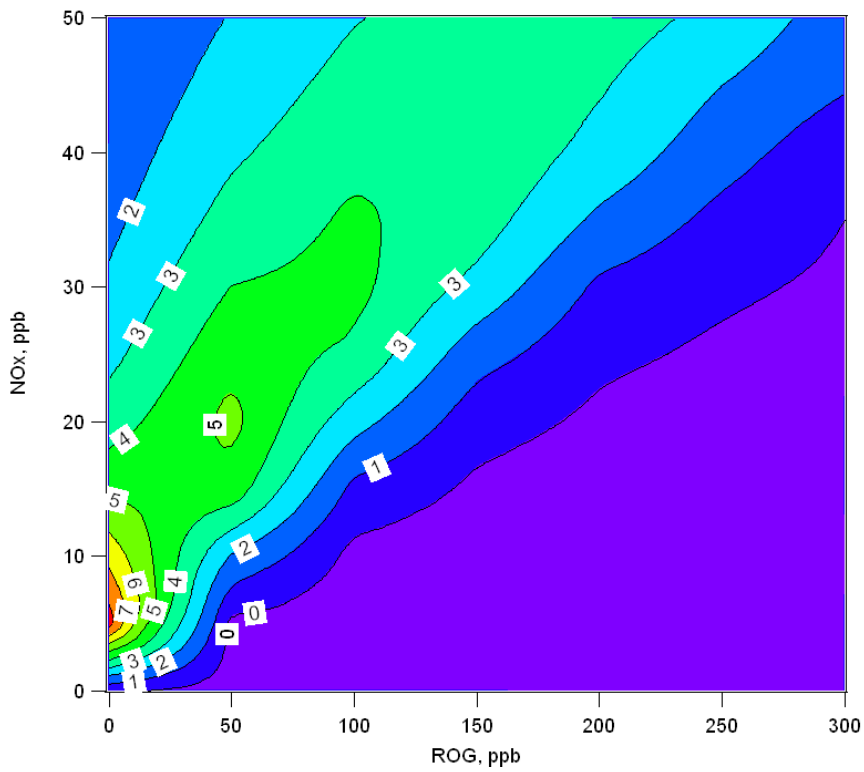
MODELING

The incremental reactivities (excess ozone formed / additional VOC_{test} mass) of individual VOCs were calculated by adding a small amount (1-2 ppb) of a test compound to the mini-surrogate / NO_x mixture in the modeling studies. Adding the test VOC modifies the base case ozone isopleth (left figure) and typically results in increased final ozone concentrations throughout the entire ozone isopleth with some exceptions. The right figure shows the ozone isopleth of the base case condition with an additional 1 ppb of 1, 2, 4-trimethyl benzene. Incremental reactivities for 1,2,4-trimethyl benzene can be calculated by evaluating various points on the ozone isopleth and calculating the slope of the isopleth as ozone concentrations are evaluated at various NO_x and VOC concentrations. All of these plots are based on calculating the ozone formation at 77 different concentrations (7 NO_x times 11 VOC) and then fitting a smooth surface to the results.



Ozone isopleth showing ozone formed as a function of NO_x and VOC concentrations for the base case condition (left) and with the addition of 1 ppb of 1,2,4-trimethyl benzene (right).

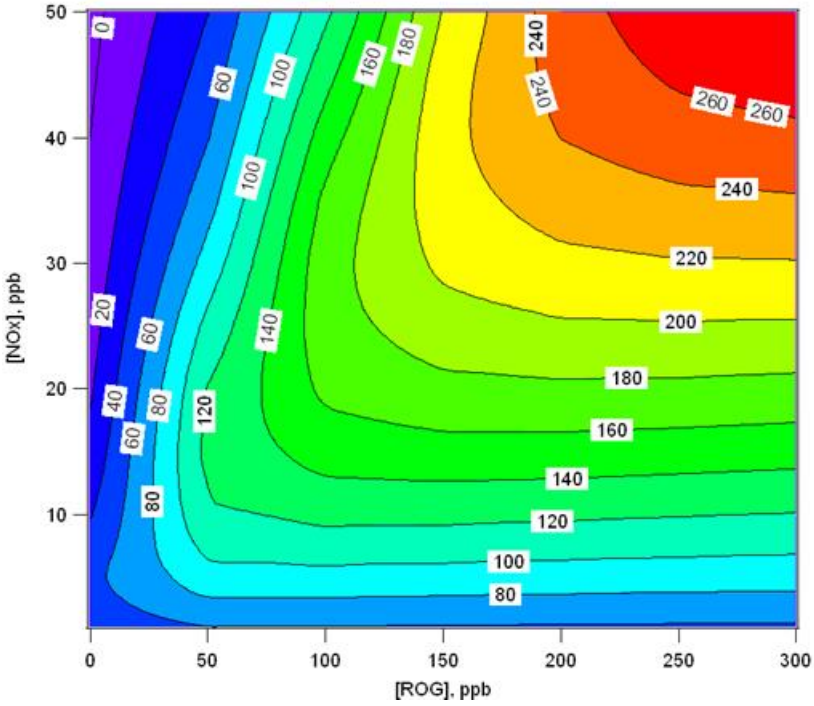
The isopleths appear similar; however, the next figure shows the difference between the above figures. At low NO_x and low ROG concentrations, the simulated (model) addition of 1 ppb of 1, 2, 4-trimethyl benzene can increase ozone concentrations by 2-12 ppb. This is important because ambient air measurements show many days with ozone concentrations only a few ppb below the regulatory criterion. This is because the addition of 1-2 ppb of a test VOC constitutes a significant fraction of the total VOC at low VOC concentrations (<20 ppb VOC total). Having a test VOC account for 5-10% of the total VOC greatly modifies the ozone isopleth and may not be representative of real world conditions. Therefore, incremental reactivity simulations were carried out at low NO_x (5, 10, and 20 ppb) and relatively high VOC concentrations (65 ppb for rural SJV-like conditions and 100-200 ppb for urban environments). As can be seen in the figure below, a 1 ppb increase of 1, 2, 4-trimethyl benzene with NO_x = 20 ppb and VOC = 165 ppb results in no change in ozone concentrations. However, a 4 – 5 ppb increase in O_3 concentrations is observed under rural SJV conditions (NO_x = 20 ppb and VOC = 65 ppb). This suggests that a 1 ppb increase in ambient 1,2,4-trimethyl benzene concentrations will significantly increase O_3 concentrations (from 60 ppb to 65 ppb, ~10% increase) at rural conditions and will not significantly affect ozone concentrations in urban environments. Even though it is only a small change due to one molecule, such an increase may lead ambient air to move from below to above the regulatory limit. Similarly, test VOC isopleth data and VOC_{test}/baseline difference plots may be found in the appendix for methyl naphthalenes and 1,2,4,5-tetramethyl benzene. All three test VOCs exhibit similar trends.



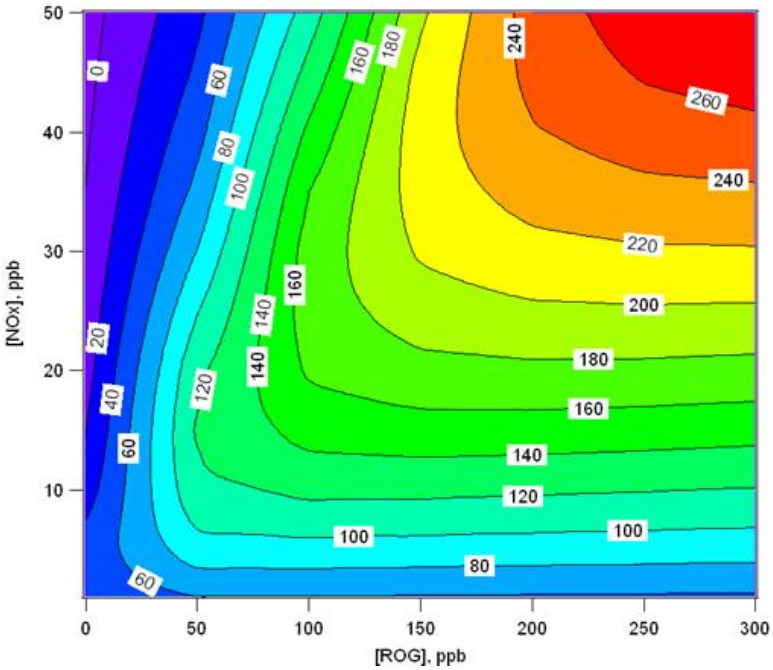
Difference between the ozone isopleths shows the increase of ozone formed with the addition of 1 ppb of 1,2,4-trimethyl benzene.

Incremental Reactivities (IR) were calculated for 1,2,4,5-tetramethyl benzene, methyl naphthalene, and 1,2,4-trimethyl benzene using the above mentioned ozone isopleths. Maximum incremental reactivities (MIR) and equal benefit incremental reactivities (EBIR) were calculated and compared to published data from Carter's established IR values using the SAPRC07 model. MIR is often defined as the incremental reactivity of a compound when NO_x and VOC concentrations have been adjusted to yield the greatest increase in ozone production. This represents relatively high NO_x conditions where ozone formation is most sensitive to changes in VOC concentration. EBIR is defined as scale is derived from scenarios where NO_x inputs are adjusted so that the reduction in O_3 caused by reducing base ROG inputs are the same as those caused by changing total NO_x inputs by the same percentage. This represents the lowest NO_x conditions where controls of VOCs are at least as effective as controlling NO_x; since for lower NO_x levels NO_x controls are always more effective for reducing O_3.

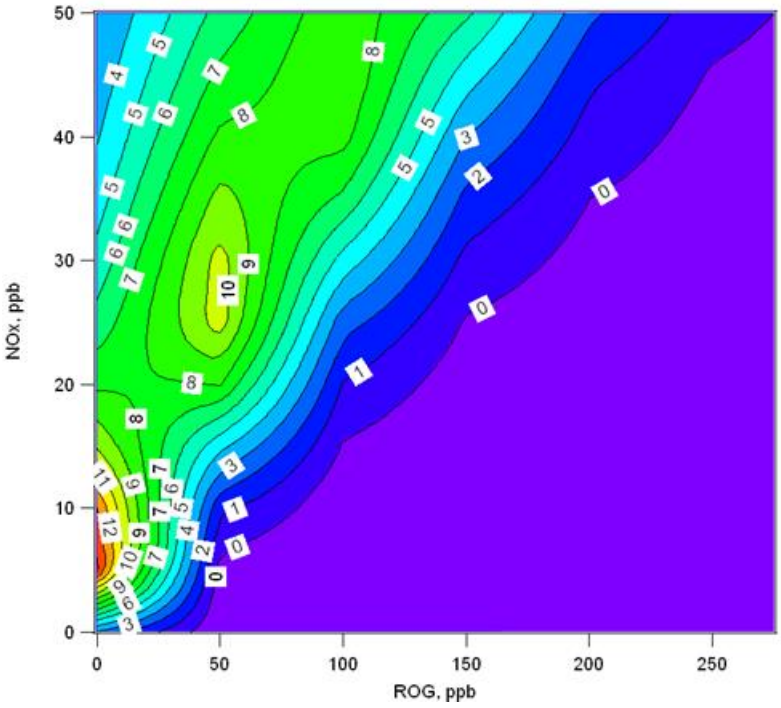
1,2,4,5 TetraMethylBenzene added:



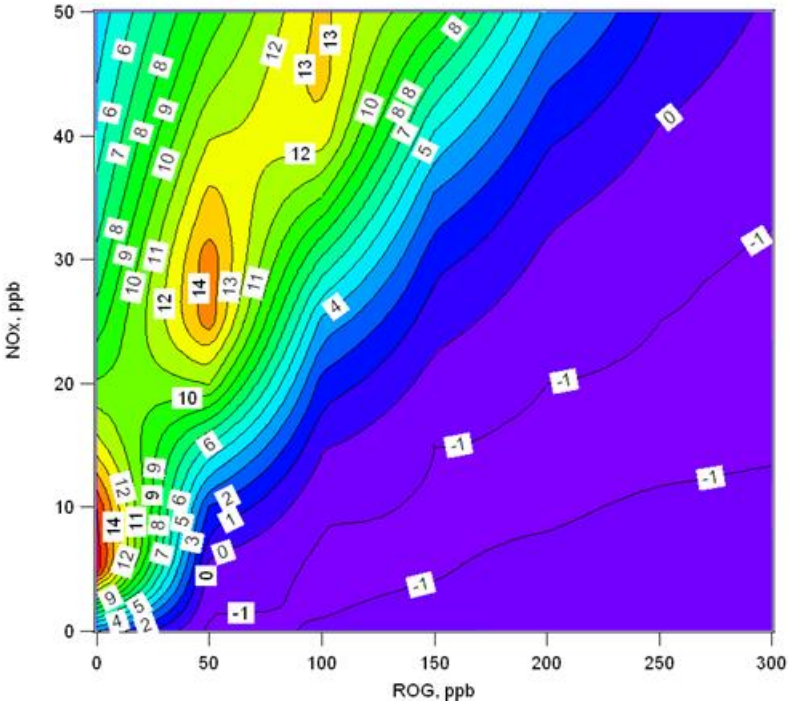
Me-Naphthalene added:



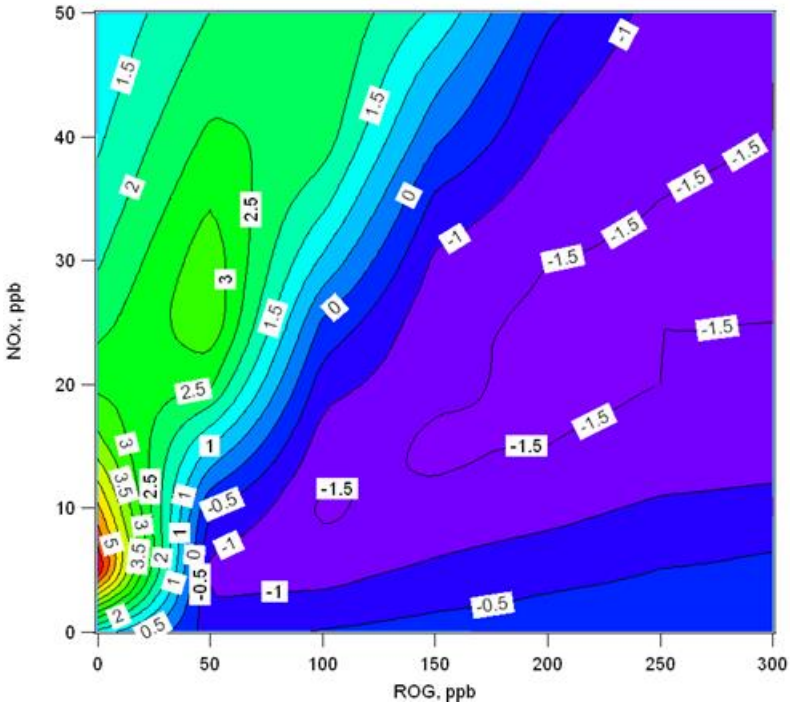
1,2,4-TrMB, incremental (net) ozone:



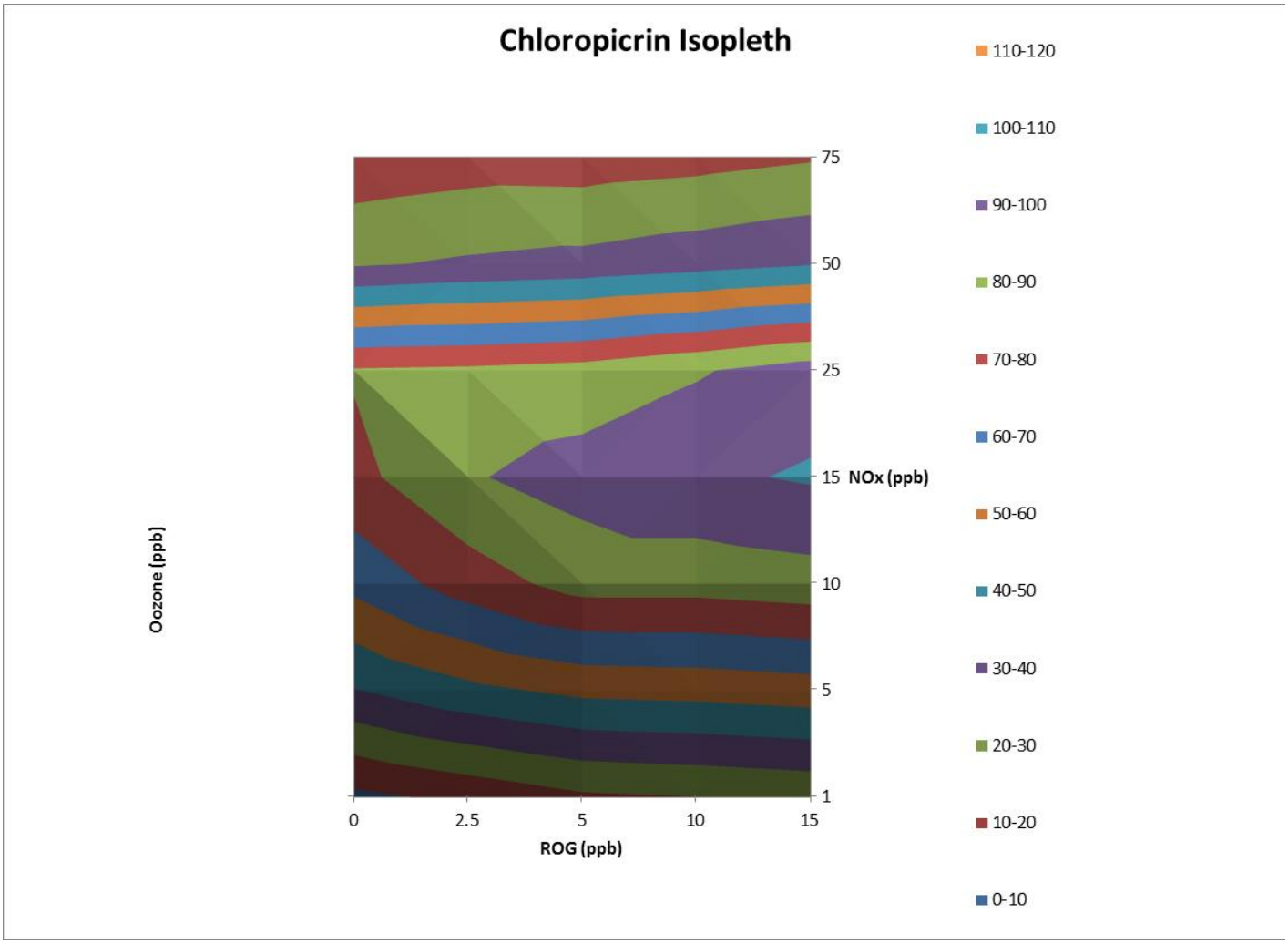
1,2,4,5-TeMB, incremental (net) ozone:



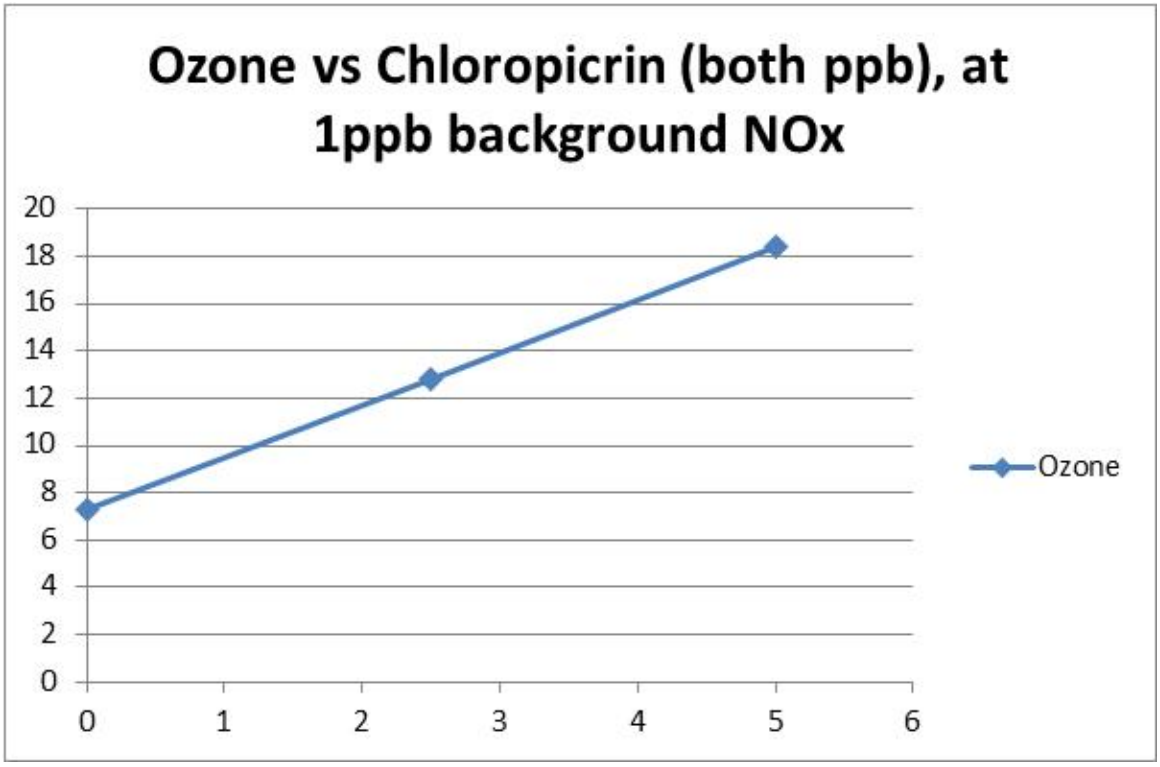
Me-Naph, incremental (net) ozone:



The model calculations for chloropicrin were guided towards the lowest possible background NO_x conditions, where its effect (and atmospheric relevance) was expected to be most important. Indeed, at moderate NO_x levels (above 15-20 ppb) the release of NO_2 from chloropicrin actually leads to depletion of ozone by reaction with it. The isopleth depicts the entire range examined.


Chloropicrin Isopleth
Oozone (ppb)
NOx (ppb)
ROG (ppb)
75
50
25
15
10
5
1
0
2.5
5
10
15
110-120
100-110
90-100
80-90
70-80
60-70
50-60
40-50
30-40
20-30
10-20
0-10

Importantly however, below 15 ppb NO_x, and even down to 1 ppb NO_x, chloropicrin holds a steady production of ozone. In this sense, it acts like a contributor of NO_x.



Data Analyses

MIR and EBIR values were first calculated by using the same EKMA technique that Carter utilizes, with ambient composition data for 39 cities to represent the range of NO_x and VOC conditions present throughout the country. This technique yielded identical incremental reactivities to those derived by Carter. Next, an average ARB VOC profile was obtained for several cities in California as recommended by Bart Croes of the California Air Resources Board. This technique yielded a slightly different value for each IR resulting in slightly greater MIR values and lower EBIR values. The final calculated IR was obtained by using the SAPRC07 box model to simulate experimental chamber studies at NO_x and VOC concentrations relevant to California. All of the model calculations were calculated to be within 10% of the values established by Carter's 39 cities EKMA technique. This suggests that laboratory-generated data should result in IR values within 10% of modeled results as the UCD-model generally agrees with laboratory-generated results.

Calculated MIR Values using SAPRC07

Species	Carter MIR (39 Cities)	UCD MIR EKMA (39 Cities)	UCD ARB Average Profile	UCD Mini-Surrogate MIR
1,2,4,5-tetramethyl benzene*	9.26	9.26	9.53	9.85
methyl naphthalenes	3.06	3.07	3.14	3.03
1,2,4-trimethyl benzene	8.87	8.87	9.13	8.49

* represented by lumped model species

Calculated EBIR Values using SAPRC07

Species	Carter EBIR (39 Cities)	UCD EBIR EKMA (39 Cities)	UCD ARB Average Profile	UCD Mini-Surrogate EBIR
1,2,4,5-tetramethyl benzene*	1.65	1.65	1.66	1.51
methyl naphthalenes	0.42	0.42	0.40	0.42
1,2,4-trimethyl benzene	1.67	1.67	1.62	1.65

* represented by lumped model species

Discussion

Photochemical chamber experiments and model calculations have been completed for three important aromatic compounds, of current concern due to use as solvents for pesticide application. A fourth compound, the unique fumigant chloropicrin was also examined both experimentally and theoretically. We have confirmed that experimental studies in the range of EBIR conditions agree well with the long-established methods based on chemical mechanisms and background atmospheric conditions. There is no evidence for any unexpected atmospheric implications to using calculated reactivities at NO_x levels lower than what is used for the more widely referenced MIR. The three aromatic species show steadily declining reactivities as NO_x decreases. Chloropicrin sustains its reactivity all the way down to 1 ppb NO_x, confirming the idea that it will sufficiently release NO_2 and maintain the reaction pathway for ozone formation.

An important aspect of this discussion is the application to regulatory schemes. At present, ozone-forming VOCs are regulated based on mass, treating all sufficiently reactive compounds equally, and exempting those which react as weakly as, or weaker than, ethane – based on MIR. Better progress would be made improving air quality if priority were given to lowering emissions of the more reactive VOCs. The pilot program by DPR is to compile an inventory where mass is weighted by reactivity. This is a step in the right direction. The question of which reactivity scale to use has been addressed by this project. Current regulations use the MIR scale to determine VOC exemptions, which corresponded to urban conditions of the past, and correspond to experimental conditions used to develop reaction mechanisms for those calculations. This study confirms that EBIR values are observed experimentally. Current conditions in the summer atmosphere for populated regions of California are generally closer to EBIR conditions than MIR.

Conditions vary with weather patterns (temperature, wind, sun…) and it would be possible to assess, in the field, whether conditions are significantly NO_x -limited or VOC-limited. (A proposal to do this has been submitted to ARB recently.) EBIR represents a balance between the two. However, even knowing that conditions vary, and will change in the future, one can state the practical option. NO_x reductions are covered by separate regulations, and are steadily progressing. VOC can be weighted by reactivity, specifically EBIR, with full expectation that ozone production will be lowered as efficiently as can be feasibly planned. Costs for tabulating new EBIRs should be modest. Gains in air quality are hard to estimate, but could be enumerated with a regional air basin modelling study such as those conducted by Prof. Mike Kleeman. That could produce a convincing case for the net value of a changed approach.

It is recommended that DPR proceed with EBIR reactivity-weighted-mass as the basis for lowering VOC emissions. This is compatible with current regulations, so long as total mass is also declining – as required for by the state implementation plan (SIP) for the Clean Air Act. However, when new reductions are triggered by mass-based exceedances, if it is demonstrable

that reactivity-weighted emissions have, in fact, not increased, this could justify delaying or postponing regulatory action.

Conclusions

In planning air quality management for the future, the use of EBIR is validated, where prevailing atmospheric conditions correspond. Morever, at lower NO_x concentrations, the aromatic compounds studied here will steadily become less reactive – as is expected for most VOCs. By contrast, chloropicrin holds reactivity relatively steadily down to the lowest prevailing NO_x conditions. It is recommended that DPR consider EBIR reactivity-weighted-mass as the basis for lowering VOC emissions. This is compatible with current regulations, so long as total mass is also declining.

References

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