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Airshed Calculation of the Sensitivity of Pollutant Formation to Organic Compound Classes and Oxygenates Associated with Alternative Fuels

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In response to the desire to allow the use of cleaner-burning automotive fuels, and at the same time to provide an equitable regulatory framework for comparing specific fuel/vehicle combinations, recent action by the California Air Resources Board proposed a reactivity-weighting for calculating the allowable automobile exhaust mass emission rate of non-methane organic gases. The "ozone-forming potentials" of individual organic compounds, times the mass fraction of those components in the exhaust, are summed to find the net ozone forming potential for a fuel/vehicle combination. In this way, the ozone production potentials of various alternative fuels (and reformulated gasolines) can be directly compared. Currently, the ozone-forming potentials of individual organics are calculated using the results of an average of about 35 episodes simulated with a chemically detailed, 1-dimensional model over short (less than one day) modeling periods. At question is whether using a physically detailed, three-dimensional model and multi-day simulations of a single severe episode gives comparable calculated ozone formation sensitivity, and also what the impact of changing emissions would have on other pollutants such as NO_2, PAN and formaldehyde.

This study uses a 3-D Eulerian photochemical model and an advanced chemical reaction mechanism to evaluate the sensitivity of pollutant levels to changes in emissions. In particular, the ozone forming potentials of classes of organic compounds are calculated, with particular emphasis on oxygenated organics associated with alternative fuels. Methanol, ethanol, MTBE, alkane and toluene emissions were found to add about one-fifth the ozone (on a carbon mass basis) as alkenes, aldehydes, non-toluene aromatics and ethene. On a per-carbon basis, formaldehyde added about ten times as much ozone as the least reactive organics tested. The results of the trajectory model-based study usually compare well with those found here. The pollution formation potentials can now be used in assessing the relative impact of various exhaust gas compositions.

Implications

Use of organic compound reactivities is being promulgated by the California Air Resources Board for providing a level playing field for comparison and taking advantage of the differences between alternative fuels. These regulations are being considered for adoption by other states. This study investigates how results obtained using a comprehensive three-dimensional air quality model compare with species reactivities developed from the EKMA-type model being used in the regulatory process. In general, the results compare well, though some marked differences are apparent.

About one hundred cities in the United States and elsewhere (e.g., Mexico City) experience episodes where ozone concentrations exceed the United States standard of 0.12 ppm. Emissions of reactive organic gases (ROG) are a key precursor to ozone formation in these urban areas, and regulations have targeted reducing the mass emission rates of ROG. However, the same mass emission rate of two organic compounds can contribute very different amounts to the total ozone formation in an urban basin. Reasons for the differences include the individual compound's oxidation rate (particularly the reaction with the hydroxyl radical, OH), the products of the reactions and the prevailing ambient conditions. In an effort to improve air quality in the nation's most polluted cities, regulators and manufacturers are considering taking advantage of the differences in reactivity by using alternative fuels and reformulated gasolines for use in automobiles. These alternative fuels, and the emissions from vehicles using these fuels, are intended to promote less ozone formation than using conventional gasoline. In the near term, these alternatives include methanol, methanol blends, natural gas, ethanol, ethanol blends, and reformulated gasoline, which may contain substantial quantities of oxygenates. A key question arises as to how to compare the relative benefits of the various fuels in terms of their atmospheric impact, and provide a scientifically justified, equitable policy regulating alternatively fueled vehicle (AFV) emissions. While there have been proposals to include the compounds' net reactivity, or "ozone formation potential," to account for reactivity differences, until recently regulations have followed a two-tiered approach classifying organic gases as reactive or unreactive, and if they are reactive they are given equal weighting. Recently, the California Air Resources Board adopted organic gas exhaust emission standards for automobiles with a proposed reactivity-weighting of the emissions. This paper addresses issues associated with reactivity, or "ozone forming potential" of organic gases, and issues associated with the recent California regulations.

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Two directions are available for determining, quantitatively, how fuel changes will improve (or harm) air quality in urban basins. First, the forecast exhaust composition and emission rates from vehicle types [e.g., those running on a methanol-gasoline blend (M85), compressed natural gas (CNG), or reformulated gasoline] may be used with advanced photochemical models to predict what impact using a new fuel in motor vehicles will have on smog formation (see, for example, References 1–3). While this procedure is the most appropriate for determining the effects of the exhaust from the "assumed" vehicle (or vehicle fleet), it suffers from two shortcomings. First, the composition of emissions from future vehicles using different fuels is unknown, and forecasts are debated. A second shortcoming is that this route does not determine the role individual exhaust components have on forming ozone and other pollutants. However, this direct determination does account for the non-linear interactions between the emitted compounds.

A second direction is to test the sensitivity of ozone formation, and other secondary species, to changes in emissions of individual compounds or classes of compounds. This information can then be pieced together to estimate the effects of many of these compounds emitted simultaneously. This route is taken here, and is the motivation of the work of Carter and Atkinson,[4] Carter,[5] and Chang and Rudy.[6] This is also the basis behind recent proposals by the California Air Resources Board[7] for developing reactivity-based standards for mobile source emissions. However, summing individual compound reactivities to estimate the impact of the combined mixture neglects the synergisms between species, and may not fully account for non-linear effects of the chemistry. For small perturbations in emissions, these limitations should be minor, though would be significant for, say, shifting an entire fleet to the use of alternatively-fueled vehicles (AFVs). This paper discusses the use of a 3-D grid-based airshed model to develop a relative reactivity scale for both individual compounds (e.g., methanol, ethene, formaldehyde, etc.), and lumped organic classes (e.g., aromatics, higher aldehydes, alkanes, etc.). This information can be used for regulatory purposes and for comparison with similar calculations conducted using chemically more detailed and physically less complete models.[4–6] Of note is that the reactivity scale currently proposed by the CARB (i.e., developed by Carter[4,5,7]), was derived from a suite of 35 single day, trajectory simulations (effectively less than 18 hours), using a pseudo-1 dimensional model. One question being addressed here is the importance of considering multi-day effects. This is important because most smog episodes are multi-day events, and the carryover of pollutants from one day to the next is critically important. A greater fraction of the less reactive organics will remain on following days. A second issue is if there are significant differences when looking at exposure-based results versus peak ozone formation results.

Methodology

In previous studies[2,8] the 3-dimensional, Eulerian, California/Carnegie Institute of Technology (CIT) photochemical airshed model was used to simulate the evolution of pollutants during a multi-day smog episode in the Los Angeles, California Basin. The period chosen for detailed modeling was August 30 to September 1, 1982, and was selected because:

1. Meteorological conditions present during the three-day period were conducive to forming ozone. By the third day of the 1982 episode, ozone concentrations built up to 0.35 ppm, which is comparable to the highest levels recorded in recent years.
2. The atmosphere prior to the start of the episode was relatively unpolluted. This, and the use of a three-day modeling period, makes predicted pollutant concentrations on the third day relatively insensitive to initial conditions (This was tested, and the results are given elsewhere[8]).
3. Pollutant measurements of trace species, including PAN, HNO_3, aerosol nitrate, and NH_3, were made during the first two days of the period.[9] Along with routine monitoring data, this allowed for extensive model performance testing. Model results for not only O_3 and NO_2, but also trace species such as nitrate and PAN compared well with measurements.[8]
4. Winds during this period were generally westerly from over the Pacific Ocean. Pollutant concentrations over the ocean are low, and if the modeling domain extends sufficiently far out, predicted concentrations in the Basin are relatively independent of boundary conditions.[10]

In this study, the meteorological inputs correspond to the August 30–September 1, 1982 period. Meteorological fields were developed from observations throughout the modeling domain (Figure 1) using objective analysis techniques.[11]

Base case emission inputs used in this study correspond to the year 2010 forecast inventory for the South Coast Air Basin (SoCAB) (Table I). This inventory does not reflect the proposed controls developed as part of the recent Air Quality Management Plan[12] (AQMP), but does reflect more stringent mobile source regulations. The 2010 inventory was chosen for modeling because there is a marked time lag between adopting a source control technique and the time that the control is fully implemented. For example, it takes more than 10 years to turn over the vehicle fleet, and the older vehicles contribute disproportionately to mobile source emissions.

The version of the CIT model used in this study has implemented the Lurmann, Carter Coyner,[13] or "LCC," condensed chemical mechanism. This mechanism was chosen to replace the Caltech mechanism because it represents the state-of-the-art description of atmospheric photochemistry at a level compatible with three-dimensional airshed models. Correct implementation of the LCC mechanism was verified against the supplied test case.[13] In this study, that mechanism was extended to include, explicitly, methanol (METH) and ethanol (ETOH):

$$\mathrm{METH} + \mathrm{OH} \rightarrow \mathrm{HCHO} + \mathrm{HO_2} \qquad K = 1360\ \mathrm{ppm^{-1}\ min^{-1}}$$

$$\mathrm{ETOH} + \mathrm{OH} + 0.1\ \mathrm{NO} \rightarrow 0.922\ \mathrm{ALD2} + 0.156\ \mathrm{HCHO} + 0.1\ \mathrm{NO} + \mathrm{HO_2} \qquad K = 5040\ \mathrm{ppm^{-1}\ min^{-1}}$$

ALD2 is the lumped aldehyde including acetaldehyde. The ETOH chemistry and MTBE oxidation mechanisms taken from Carter[14] were also implemented:

$$\mathrm{MTBE} + \mathrm{OH} \rightarrow 0.98\ \mathrm{RO2R} + 0.37\ \mathrm{R2O2} + 0.02\ \mathrm{RO2N} + 0.41\ \mathrm{MEK} + 0.39\ \mathrm{HCHO} \qquad K = 4130\ \mathrm{ppm^{-1}\ min^{-1}}$$

Emissions were processed to develop a spatially and temporally detailed inventory for use with the LCC chemical mechanism (Table II). This inventory, along with the meteorological and geographical fields, provide the base case predictions of O_3, NO_2, HCHO, PAN and other pollutants.

Local sensitivities to changes in emissions are calculated by perturbing the emission inventory, and re-running the airshed model for the full three-day period. Results from the third day are used to minimize any dependence on initial conditions. In the perturbed simulations, all other inputs, including boundary and initial conditions, were unaltered. The sensitivity to a change in the emissions of

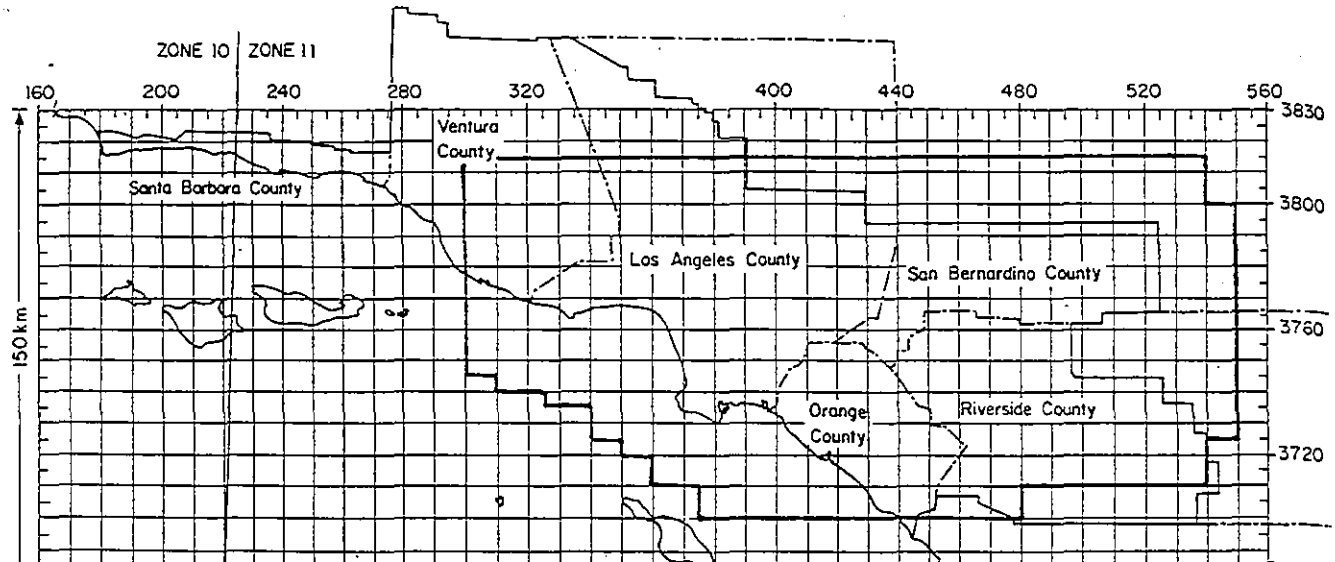

Figure 1. Map of California's South Coast Air Basin (SoCAB), showing the grid system used. The modeling region is denoted by the heavy solid (——) line.

species i, S_i, is then defined as:

$$S_i = \frac{P(E_{pi}) - P(E_b)}{E_{pi} - E_b}$$

where P is the predicted quantity (e.g., peak ozone or ozone exposure), associated with either the i'th perturbed inventory, E_{pi} or the base inventory, E_b. In this study E_{pi} and E_b are measured in moles (or kilograms) carbon of each organic species and CO. The sensitivities are then stated on a per carbon or per gram basis. In most cases, the increase in emissions are allocated with the same spatial and temporal distribution as the original species. Exceptions were made for methanol, ethanol and MTBE, which are currently emitted from relatively few sources. However, if these compounds find greater use in transportation fuels, those emissions could become widespread. For this reason, increases in those emissions were distributed proportionally to the other organics. Emission perturbation levels were chosen to give about a 5 to 10 percent change in peak ozone, but not severely change the total carbon concentrations.

While much concern is devoted to how peak ozone concentrations respond to emission changes, the approach taken here considers a broader range of measures. In addition to the sensitivity of the peak ozone, the sensitivities of the peak HCHO, PAN and NO_2 are also calculated. One advantage of using a three-dimensional airshed model, as compared to a trajectory model, is that the spatial distribution of pollutants is also predicted. These fields can be combined with the forecast population distribution to provide an exposure-based estimate of the impact of raising species emissions. In addition to peak sensitivities, exposure sensitivities are also calculated.

Table I. Forecast 2010 emissions (10^3 kg day).

	CO	NO_x	ROG
On-Road	4274	430	355
Stationary and Off Road	1843	436	1097
Total	6117	866	1452

Results

Predicted peak concentrations and exposures for O_3, HCHO, NO_2 and PAN are given in Table III for the base case. For O_3, exposures are only considered if the predicted concentration is above 0.12 ppm, the national standard. There was a slight change in the predicted concentrations of most species when the chemical mechanism was changed from the Caltech to LCC mechanism, though the relative spatial and temporal distributions were similar. Compared to similar simulations using the CIT model and the Caltech chemistry, the predicted peak ozone in the central portion of the Basin decreased by 9 percent. Exposures responded similarly to the change in mechanism.

Pollutant formation sensitivities to each of the emitted organic classes used in the condensed LCC mechanisms are given in Table IV. In addition, the sensitivities to methanol, ethanol (ETOH) and MTBE are also given. Table V gives the "normalized" sensitivity of peak ozone and exposure, N_i, using the sensitivity of ozone peak and exposure to CO:

$$N_i = \frac{S_i}{S_{co}}$$

This facilitates comparison with the results of different model formulations and sensitivity measures. (It is impractical to try to define an incremental reactivity measure

Table II. Base case emissions by chemical class in moles carbon.

Species	Species description	Emissions (10^3 moles C)
CO	Carbon monoxide	218295
ALD2	Higher aldehydes	850
ALKA	> C_3 alkanes	53601
ALKE	> C_2 alkenes	5890
AROM	Di- and tri-alkyl aromatics	4193
ETHE	Ethene	796
HCHO	Formaldehyde	375
TOLU	Toluene	9353
METH	Methanol	445
MTBE	Methyl t-Butyl ether	0
ETOH	Ethanol	0

Table III. Predicted peak pollutant concentrations for the base case, 2010 simulation.

Pollutant	Predicted peak concentration (ppb)	Exposure (10^3 person-ppm-hours)
O_3	320	10022 (O_3 > 120 ppb)
NO_2	350	22783
PAN	26	900
HCHO	62	6472

similar to that used by Carter and Atkinson[4] because that measure would depend on modeling domain. The peak ozone does not respond equally to emissions in various parts of the Basin.) Similar quantities derived from Carter[5] and those based on the OH-reactivity are also shown for comparison.

Results shown in Tables IV and V can be used to estimate the effectiveness of changing the composition and mass emission rates from sources such as automobiles and solvents. First, it is obvious from this analysis that the pollutant forming potential of a compound is not adequately characterized solely by the mass emission rate or the hydroxyl radical reactivity or a simple combination of the two (e.g., Table V). The limited lifetimes of the highly reactive compounds decrease their impact relative to using the OH-reactivity, over multi-day episodes.

The rank ordering of the species in the per carbon contribution to forming ozone (e.g., exposure) is found to be, in ascending order: CO, MTBE, methanol, ALKA (alkanes), ethanol, toluene, ethene, ALD2 (higher aldehydes), ALKE (alkenes), AROM (di- and tri-alkyl benzenes) and HCHO. (The reason for using a per carbon basis is that the energy content of the organics is more closely associated with the amount of carbon.) On a mass basis, the contribution to forming ozone of the non-aldehyde oxygenates (methanol, ethanol, and MTBE) are similar, and are about one tenth of the higher aldehydes, alkenes, aromatics, HCHO and ethene. (It should be remembered that these classes approximate an average of the reactivities in that class, and individual species may be more or less reactive.)

Table IV. Pollutant sensitivities to individual compounds emissions.

Emitted Compound Class	Pollutant sensitivities* (in per gram of organic compound emitted)			
	Ozone		HCHO	
	Peak ($\times 10^9$)	Exposure ($\times 10^4$)	Peak ($\times 10^9$)	Exposure ($\times 10^4$)
CO	0.95	1.0	0.0	−0.10
Aldehydes	140	92	53	50
Alkanes	49	27	2.6	3.0
Alkenes	190	150	156	85
Aromatics	170	200	43	45
Ethene	190	120	110	110
Formaldehyde	160	180	950	840
Toluene	65	58	17	15
Methanol	18	10	11	10
Ethanol	23	17	7.7	7.0
MTBE	21	13	3.5	3.0
	NO_2		PAN	
	Peak ($\times 10^9$)	Exposure ($\times 10^4$)	Peak ($\times 10^9$)	Exposure ($\times 10^4$)
CO	−1.9	0.53	−0.62	−0.0
Aldehydes	−154	57	22	23
Alkanes	3.6	11	0.43	2.0
Alkenes	168	90	−0.18	27
Aromatics	−163	48	−10	30
Ethene	−20	37	−7.4	9.5
HCHO	92	58	−24	14
Toulene	3.2	13	6.0	8.4
Methanol	7.0	2.6	−0.8	0.56
Ethanol	15	6.7	3.9	3.6
MTBE	11	3.7	−0.3	0.46

*Peak sensitivity is in units of (10^{-9}) ppm per gram organic compound (or CO) emitted, and exposure sensitivity is in units of (10^{-4}) person-ppm-hours per gram. Actual compound molecular weights were used when possible. For lumped species, molecular weight is calculated from average carbon number. Ozone exposure is to concentrations ≥ 0.12 ppm.

Table V. Reactivities of compounds relative to CO (per carbon basis): Comparison of airshed results to EKMA-type model.

	Airshed		$K_{OH}/K_{OH,CO}$		Carter	
	Peak	Exposure	Per molecule	Per carbon	MOR[1]	MIR[2]
CO	1	1	1	1	1	1
ALD2	108	67	65	33[3]	52[4]	71
ALKA	27	14	21	4.9[5]	7[6]	9
ALKE	102	77	178	45[7]	58[8]	63
AROM	87	94	176	23[9]	32[10]	75
ETHE	100	60	35	18	39	67
HCHO	176	188	41	41	63	162
TOLU	32	28	25	4	6	21
METH	21	12	4	4	6	11
Ethanol	20	14	15	8	10	16
MTBE	14	8	12	2.4	6	7

[1] Incremental ozone reactivity at peak ozone predicted as defined by Carter.[14]
[2] Maximum incremental reactivity, as defined by Carter.[14]
[3] Used an average of 2.38 atoms C/molecule.
[4] Used incremental reactivity for acetaldehyde.
[5] An average of 4.27 atoms C/molecule used.
[6] Used 50% C4-C5 alkanes, and 50% C6+ alkanes from Carter.[2]
[7] An average of 3.93 atoms C/molecule used.
[8] Used C4-C5 alkenes from Carter.[2]
[9] An average of 7.8 atoms C/molecule used.
[10] Used equal portions of di- and tri-alkyl benzenes from Carter.[2]

An interesting aspect of using an airshed model in this type of analysis is the ability to compare the exposure-based and peak ozone results. As shown in Tables IV and V, the relative sensitivity of peak ozone and ozone exposure for each species is not identical. This is most striking for AROM and HCHO that have a greater impact on exposure than peak. Their high reactivity leads to rapid ozone formation in the more densely populated, lower ozone regions in the SoCAB. On the other hand, their limited lifetimes and, very importantly, the formation of organic nitrates lead to somewhat smaller impacts in the downwind, peak ozone region. Conversely, the less reactive and longer lived methanol, MTBE and alkanes contribute somewhat more to the downwind peak than to exposure.

Contributions of individual compounds to increasing HCHO, NO_2 and PAN levels do not follow their contribution to forming O_3. For example, CO and methanol (METH) are not precursors to PAN, and substituting those emissions for other compounds can lead to reductions in PAN levels. Not unexpectedly, PAN formation is very sensitive to ALD2, ALKE and AROM. Of the organics tested, METH contributed least to increasing NO_2, and ALKE contributed most. Sensitivity of HCHO formation is smallest for MTBE, CO and alkanes, and the greatest sensitivity is found for increasing HCHO, ALKE and ETHE (ethene) emissions.

Comparison of these results with those of Carter[5] (Table V) shows rather strong agreement in most cases. ALKA, METH and MTBE are more reactive in the airshed analysis. One likely reason for the differences is that these species are less reactive, so a greater fraction can react over three day simulations. Other possibilities include the use of a 3-D model, with greater physical detail (though less detailed chemistry), spatially and temporally explicit emissions, use of a different NO to NO_2 ratio in emissions, the use of a specific meteorological period, or the use of a

lumped mechanism. It is interesting that the ALKA (alkane) results here differ so markedly from those found for the chemically detailed analysis. Reasons for the differences are being explored.

One concern with using this, or the Carter[5]-type of analysis for determining the impact of very large perturbations in the inventory is the non-linearity of the chemistry.[3] The sensitivities developed here are local, and the response will depend not only on the organic emissions, but also on the magnitude of NO_x emissions and the spatial and temporal distribution. Carter and Atkinson[1] show that at very high ROG/NO_x ratios, the ozone reactivity to certain organic compounds may go negative and the relative reactivities change dramatically. However, ROG control will have little effect in those regimes because ozone formation is NO_x-limited.[15] In the base emissions inventory used, the ROG/NO_x ratio is about 5.5 ppmC/ppm NO_x. This leads to an ambient 9:00 am ROG/NO_x ratio of about 8 in dense source regions. Downwind ROG/NO_x ratios are higher, and can exceed 20. Thus, the modeled area spans a wide range of conditions. The predicted peak is in a region with a higher ROG/NO_x ratio, so it is not surprising that the peak sensitivities found correspond more closely with Carter's MOR scale which also is found at higher ratios and is a measure of the peak ozone response. If the relative amounts of ROG and NO_x in the inventory were to change significantly, the sensitivities would likely change.

The seemingly small differences in relative reactivities between Carter's results and these could have major implications for control strategy analysis if the difference leads to a consistent bias in the reactivity of fuel types. The 10 to 20 percent differences found for most species are similar to the reactivity differences between exhaust from some fuels.

Conclusions

A three-dimensional air quality model has been used to provide the relative sensitivities of pollutant formation to changes in organic compound emissions. Results show the benefits of replacing the more reactive aromatic, aldehyde and alkene fractions of emissions with alkanes, methanol, ethanol and MTBE. This is indicative of the benefits of reformulating gasoline to decrease the mass emission rates of the reactive components with alkanes and MTBE (and possibly toluene), and that alternative fuels such as methanol, natural gas and LPG could help decrease ozone concentrations. Lower NO_2, HCHO and PAN concentrations would also result from decreasing the reactivity of the emissions unless ethanol is substituted.

This analysis found important similarities and differences with a similar set of studies by Carter and coworkers[4,5] using an EKMA-type model. The relative reactivity of most compounds compare quite favorably with the EKMA-based results. Toluene, MTBE, and alkanes were found to be relatively more reactive. Further analysis is required to understand all the reasons for these differences.

Reactivities derived by this type of analysis can be used to help guide regulators and manufacturers in improving air quality by looking at the use of cleaner fuels. These results show that the incremental reactivity scale of Carter[5] provides a reasonable first estimate of the relative importance of compounds in forming ozone in an airshed like Los Angeles. This is important given that the reactivity scale used by Carter is for a suite of scenarios, typical of multiple cities. However, the differences can be significant, and warrant the use of more detailed, robust, area specific analysis when possible. Carter's analysis did not provide the sensitivities of other species, such as PAN, NO_2 and HCHO. These species do not respond the same as ozone. Also, airshed analysis provides a measure of pollutant exposure, which as shown does not behave the same as the peak concentrations.

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