

SAPRC-07 Chemical Mechanism Peer Review Comments

Prepared for
California Air Resources Board

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1. Implementation of SAPRC-07 Mechanism in 3-D Airshed Model and Comparison to SAPRC-99

A condensed version of the SAPRC-07 mechanism (Carter, 2008) was implemented in a 3-D air quality model and applied to the Los Angeles area as part of the present review. The CIT airshed model was used; see Martien et al. (2003 and 2006) for description of model input data. The summer 1997 emission inventory was used here. Martien et al. used an extended version of SAPRC-99 that had many individual organic species treated explicitly so that incremental reactivities could be studied; here a more standard version of SAPRC-99 was used, with 5 lumped alkanes, ethene, isoprene, 2 lumped anthropogenic alkenes, lumped terpenes, and 2 lumped aromatics. To help ensure that any differences in model results were due to differences in the descriptions of atmospheric chemistry, the dry deposition calculations were turned off, and secondary aerosol formation was likewise disabled in these 3-D model test runs.

The version of SAPRC-07 used was CS07A without chlorine chemistry. This mechanism uses the same operator species as in the earlier SAPRC-99, and is compatible with existing mechanism preparation software. Airshed model outputs using CS07A were compared against analogous predictions obtained using the older SAPRC-99 mechanism. The emissions in both model runs were identical, except that ALK1, ALK2 and ALK3 were lumped together (with reactivity weighting) in SAPRC-07, and likewise ALK4 and ALK5 were combined (unweighted sum). Also acetone (ACET) and methyl ethyl ketone (MEK) emissions in SAPRC-99 were combined with reactivity weighting and represented using PROD2 in SAPRC-07. The summary table below provides some further details on relevant mechanisms.

	Condensed SAPRC-07 (CS07A)	SAPRC-07 (S07A)	SAPRC-99
# of reactions (no chlorine chemistry)	139	221	210
# of species (excluding constant)	47	74	74

In this test case, airshed model run time decreased by 30% relative to SAPRC-99 when condensed SAPRC-07 (CS07A) was used. This will speed up 3-D air quality models that currently use SAPRC-99: large numbers of computational cells are involved and the numerical integration of stiff systems of differential equations describing atmospheric chemistry can be a major contributor to the overall computational burden.

The speed-up of 30% reported here is in reasonable agreement with the decrease in the number of active chemical species being tracked in CS07A relative to SAPRC-99, as shown above. There is a similar reduction in the number of chemical reactions listed as well. Note that these test runs were deliberately simplified by turning off secondary

aerosol and dry deposition calculations; the speed-up in air quality model calculations from using the condensed SAPRC-07 mechanism could be less than 30% if gas-phase chemistry is not the main determinant of model run times. Nevertheless, the availability of the condensed SAPRC-07 mechanism will be helpful with respect to compute time, memory needs, and file size, as the trend in air quality modeling is to consider larger study domains with increased numbers of computational cells in vertical and horizontal dimensions, and longer simulation periods that extend over whole seasons or even years.

Time series plots of predicted pollutant concentrations are shown below in Figures 1-4 for ozone, nitric acid, formaldehyde, and peroxyacetyl nitrate (PAN). These plots show only model results from the last day of a 2.5-day simulation. Each plot includes predictions obtained using both SAPRC-99 and SAPRC-07 mechanisms, at four sites in the Los Angeles basin starting with Hawthorne near the coast, to Central Los Angeles, Claremont, and Riverside which is the location furthest east (inland) shown here.

The two mechanisms are qualitatively similar in terms of their predicted diurnal patterns of pollutant concentrations. Ozone concentrations are lower using SAPRC-07 versus SAPRC-99. In contrast, predicted nitric acid levels are usually but not always higher (see Figures 1-2). These results are consistent with the 19% increase in OH+NO₂ reaction rate that has been made in SAPRC-07, though there are many other differences between mechanisms, so other factors also contribute to the changes in predicted pollutant concentrations reported here. In contrast to ozone and nitric acid results, there is little change in predicted formaldehyde concentrations between the two mechanisms (Fig. 3). PAN concentrations are lower at all hours at the inland sites (Claremont and Riverside), with larger decreases during the afternoon when temperatures are highest. There are smaller changes in PAN at Central Los Angeles, with increases at most hours except for early afternoon when PAN decreases. Concentrations of this pollutant at the coastal site (Hawthorne) show little change between SAPRC-99 and SAPRC-07. Beyond mechanism changes mentioned above, several key rate coefficients relevant to PAN formation (i.e., peroxyacetyl radical + NO, peroxyacetyl radical + NO₂, and thermal decomposition of PAN itself) were revised in SAPRC-07.

Summary: air quality model results reported here indicate that the condensed version of the SAPRC-07 mechanism will reduce computational burdens in solving gas-phase chemistry in air quality models by about 30%, relative to the currently used SAPRC-99 mechanism. SAPRC-07 shows similar behavior in predictions of key secondary product species of interest in air pollution studies, though predicted ozone levels with SAPRC-07 were lower than SAPRC-99 for the case of a summer high-ozone episode in Los Angeles considered here. The decreases in predicted peak 1-h ozone using SAPRC-07 ranged from 3% (1.6 ppb) at Hawthorne to ~10% (10-15 ppb) at Claremont and Riverside.

Airshed Model Predictions for Ozone
 (SAPRC99 = solid lines; SAPRC07 = dashed lines)

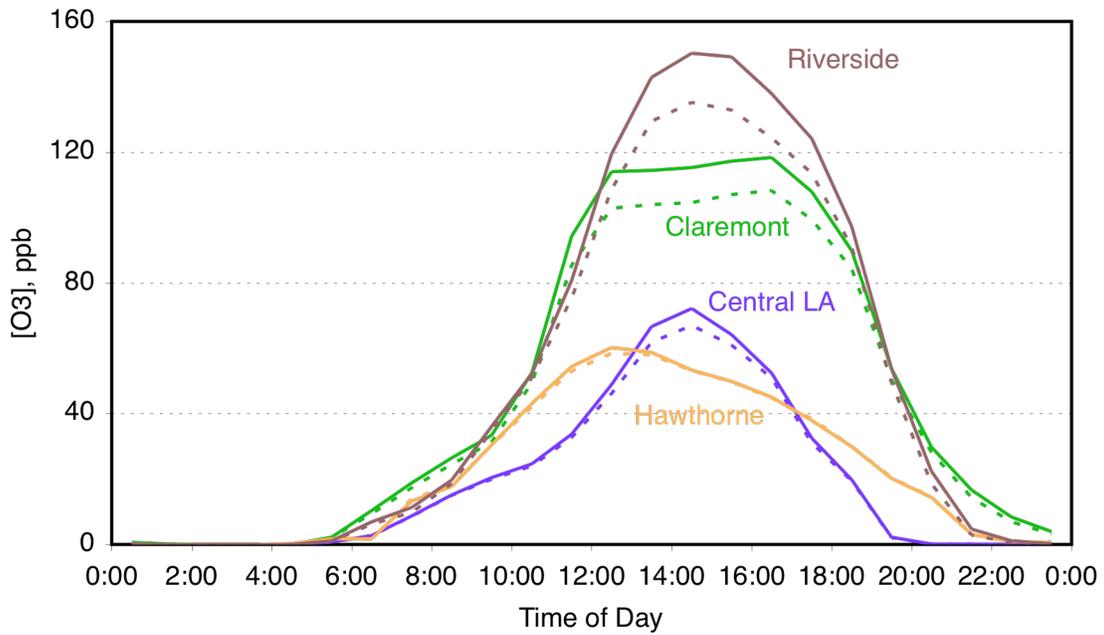


Figure 1. Predicted ozone concentrations using SAPRC-99 and SAPRC-07 mechanisms.

Airshed Model Predictions for Nitric Acid
 (SAPRC99 = solid lines; SAPRC07 = dashed lines)

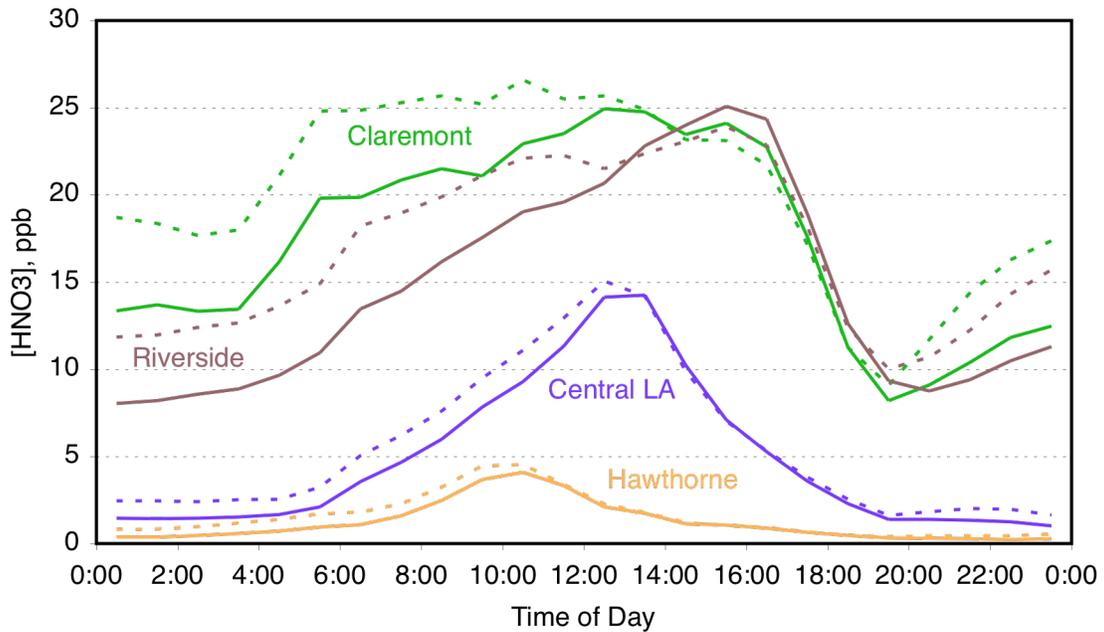


Figure 2. Predicted HNO₃ concentrations using SAPRC-99 and SAPRC-07 mechanisms.

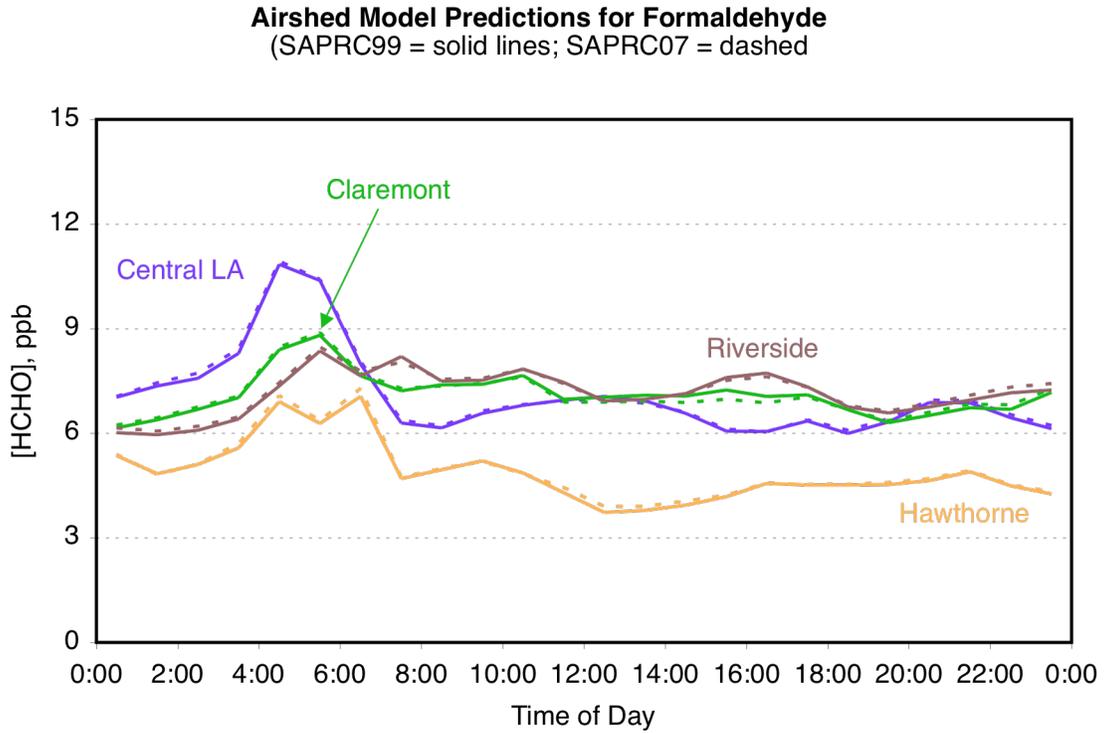


Figure 3. Predicted HCHO concentrations using SAPRC-99 and SAPRC-07 mechanisms.

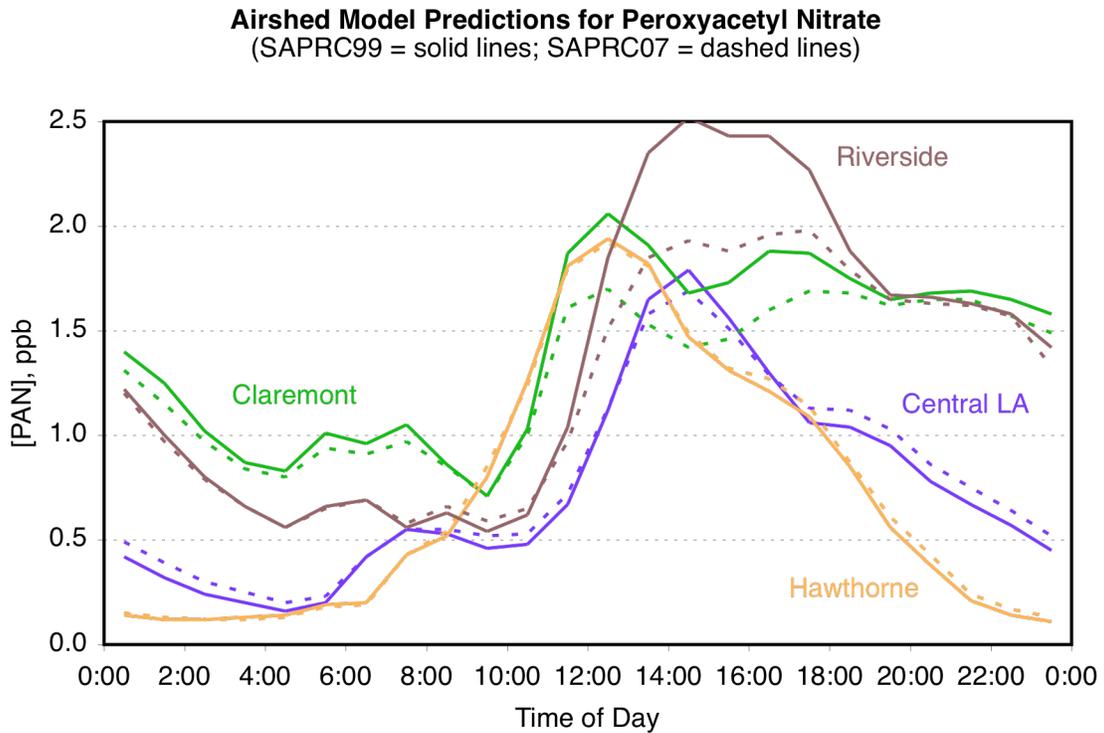


Figure 4. Predicted PAN concentrations using SAPRC-99 and SAPRC-07 mechanisms.

2. Comments on Reaction of Hydroxyl Radical with Nitrogen Dioxide

Martien et al. (2006) and others report that the rate coefficient for the OH+NO₂ reaction forming nitric acid (HONO₂ or HNO₃) is among the most important reactions affecting photochemical air pollution. This reaction serves as a key chain-terminating step, and is a sink for HO_x radicals and NO_x. Table 1 of Carter (2008) indicates a significant increase in SAPRC-07 relative to SAPRC-99: the change is +19% at T=300 K (there appears to be a typo on page 10 of Carter, 2008, where the change is stated as +14% instead of +19%). SAPRC-07 relies on JPL (2006) panel recommendations. IUPAC (2004) recommends an even higher value. Recent advances in understanding of this reaction have identified a second channel that forms an unstable product, peroxyxynitrous acid (HOONO). Okumura, Sander et al. (2005) measured the branching ratio to be 0.11-0.15 at room temperature and pressure, and also constrained the overall reaction rate with better precision using improved measurement methods (pulsed laser photolysis, LP-LIF). Past work that relies solely on measurements of the disappearance of reactants therefore measures the overall rate (both channels), whereas for ozone modeling we only terminate with HONO₂ formation, not HOONO. SAPRC-99 was developed using older values for this important kinetic parameter, as recommended in JPL (2000).

Revisions to the value for k(OH+NO₂) in SAPRC-07 are not easy to implement, because there are other dependent parameters defined in the mechanism. For example, product yields of lumped aromatic and terpene groupings (and perhaps other aspects of the SAPRC-07 mechanism?) are fit to match smog chamber data, so revisions to k(OH+NO₂) imply other revisions need to be made as well. I recommend that the true sensitivity of the mechanism to changes in k(OH+NO₂) should be investigated and further documented.

Summary: I recommend for testing purposes that alternative versions of the SAPRC-07 mechanism (S07A version) be developed based on the following k(OH+NO₂→HONO₂) reaction rates: IUPAC (Atkinson et al., 2004), NASA (JPL, 2006) and Okumura et al. (2005). The temperature dependence of HOONO yield is a remaining uncertainty; Okumura et al. measured the branching ratio at room temperature and over a range of pressures.

IUPAC (Atkinson et al., 2004)	$k = 11.8 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$
JPL (2006)	$k = 10.6 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$
Okumura et al. (2005)	$k = 8.7 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$

3. Comments on Definitions of Lumped Organic Species in SAPRC-07

The SAPRC-07 mechanism includes lumped organic species that are used in 3-D air quality models to reduce the number of individual species that must be tracked separately. The hydrocarbons are lumped using 5 alkane groups, 2 aromatic groups, and 3 alkene groups. Oxygenated species other than aldehydes are assigned to MEK or PROD2 species depending on their reactivity.

OXYGENATES

A comment on Table 17 of Carter (2008) is that the value of k_{OH} used to define the dividing line between oxygenates assigned to MEK versus PROD2 should be stated in the same units used for ALKn, AROn, and OLEn for consistency. The abundance of oxygenates in the base mixture used for incremental reactivity modeling may need to be increased assuming that alcohols, glycols, glycol ethers, esters, etc. are all to be assigned to MEK or PROD2, given increased use of ethanol in fuel and presence of polar organic co-solvents in water-borne (low VOC content) paints.

ALKANES AND AROMATICS

In Table 18 of Carter (2008), the compounds and weighting factors used to derive the parameters for the ALKn and AROn model species in the fixed parameter version of the SAPRC07 mechanism are described. According to Carter (SAPRC-07 report, p. 60), “most [airshed] model applications have used the fixed parameter version of SAPRC-99” rather than deriving lumped organic species oxidation product yields and rate coefficients independently. It is likely that this practice will continue to be the case in the future, so the lumped species definitions used in the fixed parameter version of the mechanism should be reviewed. However, since species assigned to a lumped group are typically already quite similar in terms of atmospheric reaction rates and mechanisms, the effects of updates to the lumped species definitions on modeled ozone are likely to be minor.

The underlying data used to define lumped group composition profiles are measured concentrations of individual hydrocarbons in ambient air – the measurements were made by Lonneman during the 1980s and are now out of date given product and fuel reformulation and implementation of control programs that have affected the composition and relative importance of different VOC emission source categories.

Weighting factors in Table 18 of Carter (2008) were compared with abundances of the same compounds in summer 2006 liquid samples of California gasoline collected in the San Francisco Bay area (Harley, 2008). For the species considered here, relative abundances in liquid gasoline and tailpipe emissions are known to be well-correlated. Products of incomplete combustion that are not represented in the unburned gasoline composition profile include acetylene, ethane, C₂-C₄ alkenes, benzene, and aldehydes.

There are other sources of VOC (e.g., diesel exhaust and petroleum distillates used as solvents) that should also be considered in defining lumped species properties in SAPRC-

07, and further analysis of these contributions is needed. Nevertheless, the comparisons presented here raise questions especially with respect to definitions for the ALK5 and ARO2 lumped groups – these are the most reactive categories of all the ALK_n and ARO_n lumped groups respectively.

A general comment is that some lumped species definitions (especially ALK4, ALK5, ARO1 and ARO2) have become rather long due to inclusion of various minor species below 1 mol% of the total. A justification for including them should be stated if they are truly needed and appropriate, otherwise the lumped group definitions could benefit from some streamlining to improve clarity and facilitate future revisions.

Measurements of ambient hydrocarbon concentrations in Riverside were made by Goldstein and coworkers during the 2005 Study of Organic Aerosols at Riverside (SOAR) using an online GC method that provided semi-continuous data with ~hourly time resolution. The average ratios of n-butane to the sum of n-butane + isobutane during month-long summer and fall season field measurement campaigns were 0.63 and 0.67 respectively. The n-butane fraction was higher later in the year (0.67 vs. 0.63) when vapor pressure limits were relaxed so more n-butane could be blended in gasoline. The definition of the ALK3 lumped group in Table 18 of Carter (2008) is in reasonable agreement with the ambient data: ALK3 is defined as a mix of 68% n-butane and 30% isobutane (one other minor species 2,2-dimethylbutane is also included at 2 mol%).

Table 1a indicates the C₅-C₆ alkanes in gasoline align with the weightings used by Carter to define the ALK4 lumped species properties. While pentanes are lower in liquid gasoline than in ALK4 weightings (see Table 1a), the higher values used by Carter are probably appropriate given that pentanes will be enriched in evaporative (vapor pressure-driven) emissions and in ambient air relative to abundances in unburned liquid gasoline.

Table 1b shows C₇⁺ alkanes in California gasoline and in the definition of the ALK5 lumped species. An important type of hydrocarbons that appear in the gasoline samples are highly branched alkanes such as trimethylpentanes. These alkanes account for ~25 mol% of C₇⁺ alkanes in California gasoline, but appear to be entirely absent from the definition of the ALK5 lumped group. While California uses more alkylate as a gasoline blending component than many other states/countries, this is an area where things may have changed dramatically since the 1980s due to gasoline reformulation. Even in the 1980s there was some (albeit lower) use of alkylate in gasoline, so the absence of trimethylpentanes from the definition of ALK5 is puzzling to me.

The monoalkylbenzenes are dominated by toluene both in California gasoline and in the definition of the ARO1 lumped group. These profiles are in reasonable agreement, as shown in Table 1c. Revisions to the definition of ARO1 are unlikely to have much effect given the dominance of toluene in the mix.

The more reactive aromatics (ARO2) typically have more than one alkyl substituent on the aromatic ring. Here the abundances of individual compounds in California gasoline often do not agree with the definition of the ARO2 lumped group. It is common that meta

& para xylene isomers co-elute in chromatographic analyses; the identical 13% fractions for both these isomers listed in Table 18 may have been obtained by splitting a 26% total into two equal parts. Gasoline analyses where the peaks are resolved separately indicate that m-xylene is more abundant than p-xylene. A further question is whether the abundances of meta vs. para isomers are different in solvents where xylene is used. The distinction is important as the MIR values of these two xylene isomers differ significantly. Also 1,2,4-trimethylbenzene should be more abundant, and the other trimethylbenzene isomers less abundant, in the definition of ARO2.

OLEFINS

Both current and earlier SAPRC mechanisms lump biogenic VOC (i.e., isoprene and terpenes) separately from anthropogenic VOC. This is good practice given that the spatial and temporal distributions of emissions differ for anthropogenic vs. biogenic VOC. If biogenic VOC were lumped together with anthropogenic VOC, it would be difficult to define appropriate reaction rate coefficients and oxidation products yields for the lumped groups, as the mix of individual species present could vary greatly. Recent studies are now addressing another biogenic VOC, methylbutenol, which could be added as an explicit species to the SAPRC-07 mechanism, or perhaps treated more approximately as being similar to isoprene?

A commonly encountered co-elution in GC analyses of emissions and ambient air samples leads to 1-butene and isobutene being reported as a single combined sum. The contributions of the two compounds to the total are not equal, especially when MTBE or 2,2,4-trimethylpentane is present in gasoline, as isobutene is formed from these species as a product of incomplete combustion. I suggest redefining the dividing line between OLE1 and OLE2 to be $k_{OH} = 8 \times 10^4$ instead of $7 \times 10^4 \text{ ppm}^{-1} \text{ min}^{-1}$ so that 1-butene and isobutene are lumped together in OLE1 rather than split between OLE1 and OLE2.

Further work is needed to assess the relative abundances of alkenes used to define the OLE1 and OLE2 lumped groups.

Summary: The most likely areas where improvements could be made to the underlying VOC mixture used to define lumped organic species properties are ALK5 (the most reactive alkane group), ARO2 (the most reactive aromatic group), and OLE1 and OLE2 (lumped olefins). Definitions of ALK3, ALK4, and ARO1 agree with current ambient and gasoline-related composition profiles. Unfortunately refining the definitions of ALK5, ARO2, and the OLE lumped groups will be difficult because the relevant hydrocarbons are very reactive and/or not routinely reported in ambient air samples. A vexing issue for ARO2 is the distinction between meta and para xylene isomers (large difference in reactivity), where analysts often report a single co-eluting peak, and the reported sum gets split 50-50 later by others, whereas in gasoline at least the more reactive meta isomer appears to be more abundant. I recommend moving the k_{OH} dividing line between OLE1 and OLE2 higher so that 1-butene and isobutene are lumped together. The necessity/added value of including minor species at <1 mol% of the total of lumped species definitions should be considered, and some streamlining may be possible.

Table 1a. Most abundant C₅-C₆ alkanes in California phase 3 reformulated gasoline and Carter's ALK4 (all values are in mol%)

Species	California RFG3	Carter ALK4
2-methylbutane	31.9%	43%
2-methylpentane	14.0%	10%
Pentane	9.2%	17%
3-methylpentane	8.5%	7%
methylcyclopentane	8.0%	5%
2,2-dimethylbutane	5.6%	ALK3
Hexane	5.6%	4%
2,3-dimethylbutane	4.6%	3%
Cyclohexane	4.5%	ALK5
Heptane	4.2%	3%
2,4-dimethylpentane	2.2%	5%
Cyclopentane	1.7%	2%

Note: the C₅ alkanes (highlighted in green) are expected to be more abundant in ambient air than in liquid gasoline due to their enrichment in vapor pressure-driven evaporative emissions, relative to abundances in liquid gasoline. So higher values used in the definition of ALK4 for these species may be appropriate.

Table 1b. Most abundant C₇⁺ alkanes in California phase 3 reformulated gasoline and Carter's ALK5 (all values are in mol%)

Species	California RFG3	Carter ALK5
224-triMe-pentane	13.9%	0
3-methylhexane	9.0%	11%
2-methylhexane	7.4%	3%
2,3-dimethylpentane	7.0%	7%
methylcyclohexane	5.9%	4%
234-triMe-pentane	4.6%	0
233-triMe-pentane	4.5%	0
3-methylheptane	3.4%	0
2-methylheptane	3.1%	6%
225-trimethylhexane	3.0%	0

Table 1c. Most abundant monoalkylbenzenes in California phase 3 reformulated gasoline and Carter's ARO1 (all values in mol%)

Species	California RFG3	Carter ARO1
Toluene	79.6%	75%
Ethylbenzene	14.4%	10%
Propylbenzene	3.9%	4%
Cumene	0.8%	2%

Table 1d. Most abundant di/tri-alkylbenzenes in California phase 3 reformulated gasoline and Carter's ARO2 (all values in mol%)

Species	California RFG3	Carter ARO2
m-Xylene	28.2%	13%
o-Xylene	12.9%	11%
124-TriMe-benzene	12.8%	5%
p-Xylene	8.1%	13%
1-Me-3-Et-benzene	8.0%	5%
135-triMe-benzene	4.0%	9%
1-Me-4-Et-benzene	3.5%	5%
123-triMe-benzene	2.8%	9%
1-Me-2-Et-benzene	2.8%	5%
1,2-diethylbenzene	1.5%	2%
1-Me-3-Pr-benzene	1.4%	2%
1,2,4-C10 trisub benzene	3.3%	6%
Indan	1.2%	?

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