

Interactive comment on “Primary and secondary sources of formaldehyde in urban atmospheres: Houston Texas region” by D. D. Parrish et al.

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The authors are grateful to the referees for the time and thought that they put into their reviews and comments regarding our paper [Parrish *et al.*, 2011]. Our responses follow.

Response to Referee 1: Pg. C15214- C15215

We thank the referee for his/her positive comments, and for suggestions of two additional appropriate references to cite. We have included these references within a short additional discussion in our revised manuscript.

Response to Referee 3: Pg. C15407- C15409

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We thank the referee for his/her positive comments, and for suggestions for improving our paper. Those suggestions are addressed below as numbered by the referee. The original referee comment is given in *italics* and our response is given in plain text.

(1) The concept that is used for the estimation of emission and production rates of HCHO is based on various assumptions that introduce uncertainties in the calculated results. The assumptions should be explicitly listed and the related uncertainties quantitatively estimated.

We have modified the paragraph at the end of Section 3.1 to explicitly list the assumptions upon which our concept is based. To the extent possible, we quantitatively estimate the uncertainties involved with each. However, as we describe quantitative estimates are difficult to derive.

For example, a constant yield of HCHO from the oxidation of ethene and propene has been assumed. How much variability is expected for the yield which may depend on solar radiation, NO_x levels etc. How much uncertainty does the assumption of a fixed yield introduce into the estimated secondary production rate?

Actually the yield of HCHO is not expected to vary much. The oxidation mechanism does not depend upon solar radiation, nor on NO_x concentrations, since the oxidation will be at the NO_x saturated limit in the high NO_x environment of Houston. The yield does have a small temperature dependence [see discussion in Orlando *et al.*, 2003], but any uncertainty in the yield of HCHO from OH oxidation of alkenes does not contribute significantly to the overall uncertainty.

On page 32610 (lines 2-4) ozone and nitrate radicals are mentioned as other possible oxidants that degrade alkenes. How large is their likely contribution to the secondary production of HCHO?

This is an excellent question, but an accurate answer would require a full 3-D modeling study of the daytime and nighttime chemistry and transport within the planetary bound-

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ary layer over Houston. In our view such a comprehensive approach is beyond current modeling capabilities of the atmospheric chemistry community. We do present arguments that their contribution is smaller than the contribution from OH. Importantly, we have briefly examined the RACM chemical mechanism [Stockwell *et al.*, 1997] upon which much chemical modeling is based, and find that the oxidation of alkenes by ozone and nitrate radicals also form HCHO with yields not markedly different from the yield from the OH oxidation. Hence, our analysis is relatively insensitive to the fraction of alkenes oxidized by OH.

(2) The estimated uncertainties of the primary emissions (30%; Fig. 4) and the secondary formaldehyde flux (40%; page 32610, line 12) need explanation. How were these values derived?

The estimated uncertainty for the primary emissions is taken from the reference that reported the measurements of the primary emissions. The estimated uncertainty for the secondary formaldehyde flux is our best estimate for the propagation of all errors that enter the analysis.

The percentage contribution of the secondary formaldehyde production to the total rate is given as 95% (Table 4). Why is the uncertainty of this fraction so small (+/-3%)? Is this a typo?

The uncertainty for the percentage contribution of the primary formaldehyde emission is derived from propagation of error techniques, and is relatively large, i.e. 5+/-3%. In our treatment the sum of the primary and secondary percentage contributions must sum to 100%, so the percentage contribution of secondary formaldehyde production must be 95+/-3%. If one attempted to calculate the uncertainty of the relative secondary percentage contribution from propagation of error techniques, one would work with an equation of the form:

$$\% \text{ secondary} = \text{secondary} / (\text{secondary} + \text{primary}) * 100.$$

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Both the numerator and denominator would have large uncertainties, but these uncertainties would be strongly correlated since the numerator and denominator are nearly equal. Hence these uncertainties largely cancel from the propagation of error calculation. The +/-3% is not a typo.

(3) Although it is not the focus of the paper, it would round off the discussion if the authors provide a brief statement how much formaldehyde may be contributed by biogenic VOCs in the Houston Texas region compared to anthropogenic sources.

We prefer to not attempt to provide such a statement, since it would be highly speculative. Hardwood forests with high isoprene emissions lie to the north and east of Houston, so the formaldehyde contribution of biogenic VOCs is a strong function of meteorological conditions. Quantifying this contribution would require 3-D modeling of the daytime chemistry and transport within the planetary boundary layer of eastern Texas. This is well beyond the scope of this paper. Millet *et al.* [2008] discuss some of these issues.

Other comments: - page 32616, line 27: give examples for other possible sources. Do ships play a role?

Ships emit little CH₂O [Williams *et al.*, 2009], so they are unlikely to play a role. The likely source is now indicated in the revised manuscript: "(i.e. transport of petrochemical emission plumes containing secondary CH₂O)"

- Fig. 2: was the intercept of the regression lines constrained to the measured background concentrations of ozone and formaldehyde, or were two parameter fits (slope and intercept) applied to the data pairs?

On pg. 32607 of Parrish *et al.* [2011], we state "In Fig. 2 all linear correlations are required to pass through the estimated background concentrations of CH₂O and O₃ appropriate for that day: 0.5 ppbv CH₂O (the concentration in background air over the Central Gulf of Mexico, Gilman *et al.*, 2009) and 31.7 ppbv O₃ (the O₃ concentration

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at $\text{CH}_2\text{O} = 0.5$ ppbv calculated from the $\text{CH}_2\text{O}-\text{O}_3$ correlation for the farthest upwind transect at 29.0 N)."

Different units (kg/h and kmole/h) are used in the paper. For consistency, I suggest to use only kmole/h throughout the paper. That would make it easier to compare numbers and simplify the tables.

One problem encountered in writing the paper was continual confusion of units. Much of the literature emissions are quantified as kg/h, so where we compare with or discuss literature emissions, we use kg/h for ease of comparison between references. Our analysis approach is most conveniently expressed as kmole/h, and we do prefer that unit, so the final results are given as kmole/h. In the tables we clearly specify the unit used, and in Table 4, which summarizes the final results, we give both units. It does slightly complicate that table, but we believe that the clarity this brings is important.

Tables 1, 3 and 4 are awkward to read. Rates should be given consistently in the same unit (kmole/h).

(See response to preceding comment.)

The meaning of the error bars should be specified in all tables (are these 95% confidence intervals?).

In the revised manuscript, the meaning of the error bars is now specified in all tables.

The percentage values in parentheses (Table 4) need to be explained. I guess these are relative contributions to the total (primary + secondary) rate?

The referee's guess is correct. In the revised manuscript, this is now explicitly stated in the table.

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Interactive comment on *Atmos. Chem. Phys. Discuss.*, 11, 32601, 2011.

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