

***Interactive comment on* “Measurements of OH and HO₂ concentrations during the MCMA-2006 field campaign – Part 1: Deployment of the Indiana University laser-induced fluorescence instrument” by S. Dusanter et al.**

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This paper provides a good description of a new instrument to measure OH and HO₂, including discussion of some of the challenges associated with calibration, interferences, and stability. Not all instrument issues are yet solved but are at least being identified and characterized. A summary of OH and HO₂ measurements made during MILAGRO is presented. These measurements are of great interest, but must be viewed in the context of the experimental uncertainties which remain fairly large. The paper is suitable for publication but some major revision to the text, particularly on

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interpretation, would be beneficial.

MAJOR COMMENTS:

1. The production of O₃ estimated from HO₂ measurements is grossly inconsistent with observed O₃ concentrations. This is shown in Fig. 16: Integrating PO₃ in the morning hours predicts an increase of [O₃] of about 200 ppb by noon, which is more than double the actual observed O₃ concentration. The discrepancy is even worse when RO₂ is considered, and with the correction to Eq. (9) noted in the associated short comment by E. Wood. This discrepancy is not a new find (e.g. Olson et al., J. Geophys. Res., 111, D10301, doi:10.1029/2005JD006617, 2006) but remains largely unresolved. The authors need to acknowledge and discuss this important problem, and specifically whether instrumental problems could have resulted in artificially high HO₂ measurements at high NO_x.

2. In the abstract, throughout the text and in the conclusion, the authors state that OH is highly buffered while HO₂ is highly variable. But very little evidence is presented to support this assertion. In Figs. 9 and 10, excursions in OH seem to be at least as large as those in HO₂. In Fig. 14, the variability in OH seems large compared to its mean value. In Fig. 13, the OH values range from $-5e5$ to $1.2e7$ molec/cm³ regardless of whether NO_x is high or low (HO₂ is not shown). And cursory inspection of Table 1 does not show remarkable consistency in OH, nor unusually high variability in HO₂. If the authors want to insist on this buffering aspect, they should provide solid quantitative statistical evidence for it.

3. The measurements of NO, NO₂, and O₃ concentrations and J(HONO) are not described, although they are used extensively in the interpretation of OH and HO₂ measurements. Were these measurements made by the authors? How? The data are absent from the official MILAGRO archive (NCAR Community Data Portal). Adequate description of these measurements is a sine qua non condition for archival publication in ACP.

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MINOR COMMENTS:

Eq. 5 seems incorrect. The rates (i.e. the inverse of the lifetimes) should be additive: $1/\tau_{\text{tot}} = 1/\tau_{\text{rad}} + \sum k[q]$. In Eq. 5 as written, for zero quencher ($[q] = 0$) the lifetime becomes infinite, which is unreasonable.

The one-photon vs. two-photon argument (p. 13706, and Fig. 6) is not convincing. There are many reasons for which a specific scaling exponent could appear. This is seen in Fig. 6: The unidentified artifact leads to an exponent of 3.8, but certainly the authors would not argue that this results from a four-photon process. It is more likely the net result of complex kinetics involving competing secondary reactions. Of course it is a bit unsettling that as much as 60% correction is required for an unidentified process.

13710/17: The belief that surrounding mountains limit the dispersion of pollutants is a myth which should not be propagated in the MILAGRO special issue. The mountains do contribute to complex local circulations (see de Foy et al., 2007, this issue).

13713/4-23: The discussion of which photolysis frequency provides the best proxy for OH is weak. All of the J values are going to be highly correlated, with only slight deviations due to differences in predominant wavelengths. Furthermore, the effect on OH will be far more sensitive to variations in photolytic precursor concentrations than photolysis frequencies. On lines 12, 13 it is claimed that OH correlates better with J(HONO) than J(O₃->1D), but no evidence is given; the literature cited refers to other locations and to J(NO₂), so it does not provide support for this claim. Speculations, e.g. that the non-zero intercept of Fig. 13 arises from higher morning HONO concentrations (lines 17-20) seem without basis. The buffering argument (lines 20-23) is also suspect, since the variability in OH is so large even at constant J(HONO).

13714/5-16: The normalizations need to be made much more clear. Giving the actual equations may be useful. As currently written, it seems that $\text{OH}(\text{normalized}, t) = \text{OH}(t) * \text{Jave}/\text{J}(t)$ while $\text{HOx}(\text{normalized}, t) = \text{HOx}(t) * \text{HONOave}/\text{HONO}(t)$. However, I think

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the more likely formulation would be: $OH(\text{normalized},t) = OH(t) * R_{ave}/R(t)$ where $R(t) = J(t)*HONO(t)$

13714/16: Is it really as expected? I think model calculations would show a much steeper decrease of HO2 for large NO (e.g. > 30 ppb).

TECHNICAL COMMENTS: 13696/19: allows -> allow 13700/4: exhibit -> exhibits 13700/25: Eqs. 1 and 2 are discussed before being introduced. 13701/23: maximums -> maxima 13702/4: delete 'fraction of' 13705/2: quadratic -> in quadrature 13705/15, 18: spectrums -> spectra 13705/26-29: not clear how this evidence would be assessed. 13693/29: 2002 not 2004 13710/6: insert 'concentration' after 'detectable.' 13710/9: delete 'potential' 13713/5: have -> has

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