Hydroxyl and Hydroperoxy Radical Measurements by Laser-Induced Fluorescence at T0 during the MCMA-2006 Field Campaign

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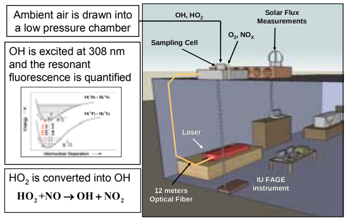
I. Abstract

Atmospheric oxidation processes are driven by a complex chemistry involving the hydroxyl (OH) and hydroperoxy (HO_2) radicals. Comparisons between atmospheric measurements and model predictions can lead to a better understanding of the fast photochemistry in various areas (rural, urban and forested). However, discrepancies are still observed between measured and modeled concentrations of HO_x ($OH + HO_2$) and suggest that there are still gaps in our understanding of HO_x chemistry. The MCMA-2006 campaign was a unique opportunity to collect data in a polluted urban environment where high levels of NO_x and VOCs control the HO_x budget. Our laser-induced fluorescence instrument was deployed at the Instituto Mexicano del Petroleo and data was collected between 14 and 31 March. An overview of the final set of data is shown. The median OH mixing ratios were slightly lower than that observed during MCMA-2003, but the maximum median HO_2 mixing ratios were approximately a factor of 4 lower. Measurements of the HO_2/OH ratio as a function of NO, which provide an insight into the propagation of radicals, are smaller than that measured in 2003 although the slope appears to be similar. Further analysis will provide more details about HO_x production and loss, radical cycling, and instantaneous photochemical O_3 production rates.

II. Indiana University FAGE Instrument

Instrument Description

Figure 1: Schematic diagram of the FAGE apparatus and co-located measurements during MCMA-2006



Ambient air is drawn into a low pressure chamber

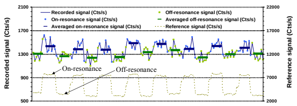
OH is excited at 308 nm and the resonant fluorescence is quantified

HO_2 is converted into OH

$$HO_2 + NO \rightarrow OH + NO_2$$

Measurements were performed from the roof of Building 32 at the Instituto Mexicano del Petroleo (IMP). One detection cell was used to measure successively OH and HO_2 radicals.

Figure 2: Raw signal recorded during OH measurements

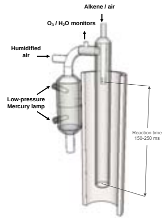


A segment of raw data, recorded on March 15 with a time-resolution of 1-s, is shown in Figure 2. The laser wavelength is alternatively tuned from off-resonance to on-resonance with an OH absorption line.

The net-signal from OH is inferred from the subtraction between the on-resonance signal and the two surrounding off-resonance signals.

The measurement of HO_2 is based on its rapid gas phase reaction with nitric oxide and subsequent detection as OH.

Field and Laboratory Calibrations



Steady state O_3-alkene calibration scheme

$$O_3 + \text{alkene} \xrightarrow{k_1} \alpha\, OH + \text{products}$$
$$OH + \text{alkene} \xrightarrow{k_2} \text{products}$$
$$OH + O_3 \xrightarrow{k_3} HO_2 + O_2$$
$$OH + \text{wall} \xrightarrow{k_w} \text{loss}$$
$$[OH] = \frac{k_1\,\alpha[O_3][\text{alkene}]}{k_2\,[\text{alkene}] + k_3\,[O_3] + K_w}$$

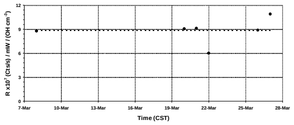
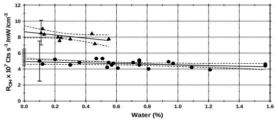


Figure 3: Calibration performed during MCMA-2006

Water-vapor UV-photolysis calibration scheme

$$H_2O + h\nu \rightarrow H + OH$$
$$H + O_2\,(+M) \rightarrow HO_2\,(+M)$$
$$O_2 + h\nu \rightarrow O(^3P) + O(^3P)$$
$$O(^3P) + O_2\,(+M) \rightarrow O_3\,(+M)$$
$$[OH] = [H_2O] \times \sigma_{H_2O,184.9nm} \times \phi_{OH,H,184.9nm} \times F_{184.9nm} \times t_{exposure}$$
$$F_{184.9nm}\ t = \frac{[O_3]}{2\,[O_2]\sigma_{O_2}}$$



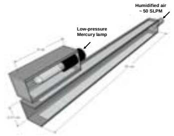


Figure 4: Cross-calibration

The instrumental response towards OH was tracked during the MCMA campaign using a calibration technique based on the generation of a steady-state OH concentration from ozone-alkene reactions in a flow tube reactor at atmospheric pressure. Calibrations performed in the field are displayed in Figure 3, and show good stability during the campaign. A new calibration system was developed in our laboratory after the campaign based on the UV-photolysis of water vapor, and a cross-calibration is presented in Figure 4. The sensitivity derived from the O_3-alkene technique (circles) is systematically lower than the water photolysis technique (triangles) by approximately 40%. Several unknown aspects of the O_3-alkene chemistry make the water photolysis technique more suitable to derive the HO_x concentrations.

III. Field Measurements

Figure 5: OH, HO_2 and J(O¹D) Diurnal profiles between 14 and 31 March

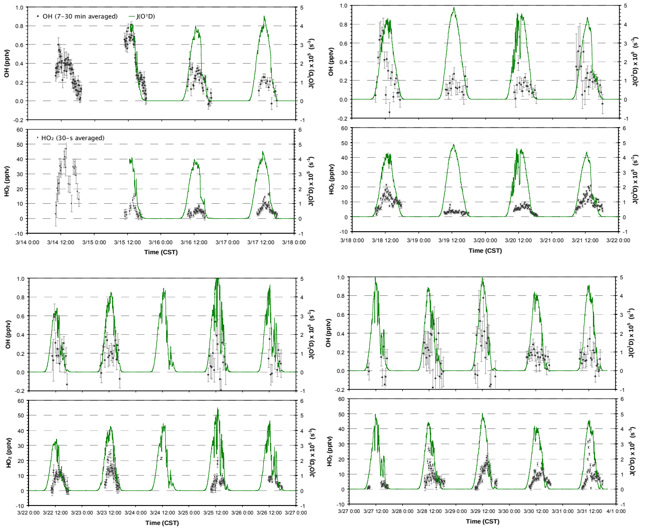


Figure 5: Diurnal profiles of OH and HO_2 recorded on 16 days. Error bars are the precision (1σ). The calibration accuracy (1σ) is 19% for OH and 22% for HO_2. Enhanced levels of OH were observed in the morning on March 18th and 21st, which could suggest an additional HO_X source for the morning hours. Interestingly, these days exhibit the highest HCHO concentrations measured at T0.

Figure 6: Overview of the campaign

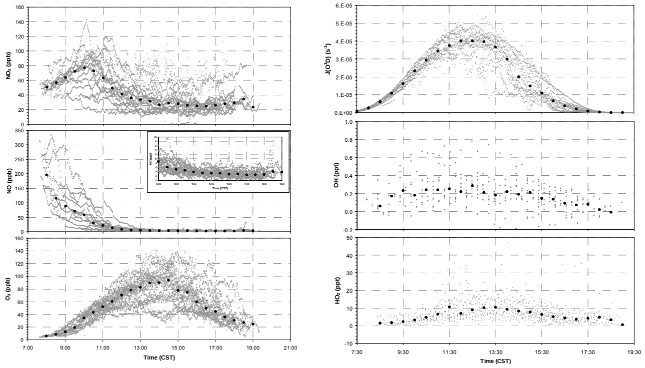


Figure 6: Co-located measurements of NO_x, O_3, J(O¹D) and median OH and HO_2 for the whole campaign. Grey symbols are individual measurements and black symbols are the medians calculated on data binned with a time interval of 10-min. The median OH peaks at 0.29 ppt around 12:30 AM (CST) and is 17% lower than that observed during MCMA-2003. The median HO_2 peaks at 10.4 ppt, 1 hour later than OH and is a factor of 3.6 lower than that measured in 2003.

Figure 7: Measured OH as a function of NO_x. Data have been filtered between 10:00 AM and 2:00 PM (where photolytic OH production is relatively constant) to examine the contribution of NO_x to OH production and loss. Excluding data from 3/15 (orange), measured OH appears to be only weakly dependent on NO_x.

Figure 8: Measured OH as a function of J(O¹D). Grey symbols are individual measurements and black symbols are the median OH calculated on data binned with an intervals of 5 s^{-1}. The correlation between OH and J(O¹D) shows the importance of photolytic processes to OH radical production during MCMA-2006 despite large changes in observed NO_x. The data from 3/15 (orange) exhibits a stronger dependence on J(O¹D) and may indicate the importance of additional photolytic OH sources on this day.

Figure 9: Measured HO_2/OH ratio as a function of NO. Black symbols are individual measurements and orange symbols are the median calculated on binned NO data. The ratio depends strongly on NO_x and VOCs concentrations and decreases with increasing NO because of the fast HO_2 conversion into OH. Measured ratios are smaller than that measured in 2003 (typical ratios of 40 at 10 ppb of NO during MCMA-2003).

Figure 7: Correlation plot between OH and NO_x

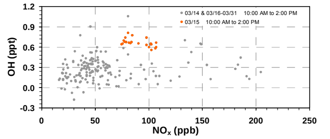


Figure 8: Correlation plot between OH and J(O¹D)

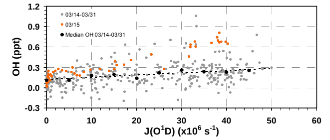
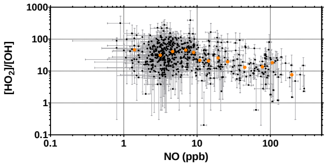


Figure 9: Correlation plot between HO_2/OH and NO



$$\frac{[HO_2]}{[OH]} \approx \frac{\Sigma\, Rate\ of\ reactions(OH \rightarrow HO_2)}{\Sigma\, Rate\ of\ reactions(HO_2 \rightarrow OH)} \approx \frac{k_{OH+VOC}[VOC] + k_{OH+CO}[CO] + k_{OH+O_3}[O_3]}{k_{HO_2+NO}[NO] + k_{HO_2+O_3}[O_3]}$$

IV. Conclusions

The IU-FAGE instrument has been deployed for the first time during MCMA-2006 and has successfully measured OH and HO_2 radical mixing ratios. An unknown source of electronic noise reduced the performance of the instrument in terms of precision and detection limit. As a result, an averaging time of 15-30 min was necessary to achieve a reasonable detection limit. The instrument has been calibrated using two fundamentally different techniques to produce a known concentration of OH. A systematic underestimation of the instrument response towards OH has been observed when calibrating with the O_3-alkene technique. The water photolysis technique appeared to be more reliable and the measurements have been corrected using the cross-calibrations performed after the field campaign.

V. Future Work

The Regional Atmospheric Chemistry Mechanism (RACM) will be use to model the HO_x concentrations measured during the MCMA-2006 field campaign by constraining the model with the sources and sinks of OH and HO_2. A comparison with the MCMA-2003 campaign results would yield interesting information. The Master Chemical Mechanism (MCM) will also be used in collaboration with other groups. These modeling exercises will provide more insight into HO_x production and loss, radical cycling, and instantaneous photochemical O_3 production rates.

Acknowledgements

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