Atmos. Chem. Phys. Discuss., 9, C12493–C12496, 2010
www.atmos-chem-phys-discuss.net/9/C12493/2010/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Atmospheric OH reactivities in the Pearl River Delta – China in summer 2006: measurement and model results" *by* S. Lou et al.

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Received and published: 4 November 2010

Response to Comments by Referee #3

We thank the referee for the valuable and constructive comments.

Comment

The authors measured OH reactivity in the Pearl River Delta (China) using a state of the art instrument, during an intensive field campaign. The authors compared the measured OH reactivity to: (1) the calculated OH reactivity from the reaction of OH with CO, NOx and all the measured VOCs and (2) OH reactivity calculated using a box

model initialized by measured species. The results indicate a difference between measured and calculated OH reactivity, whereas the box model reproduces well observed OH reactivity during daytime. The authors argued that these results suggest that the missing OH reactivity is mainly due unmeasured secondary chemistry products. Direct measurement of OH reactivity is a valuable tool to understand the tropospheric ozone and secondary organic aerosols production as well as the oxidative capacity of the atmosphere. I would like to see this paper published because of the importance of the data.

Comment

1. Pag 17036, lines 12-14. It is a bit surprising that the discrepancy between measured and calculated OH reactivity during daytime is very similar (around a factor of 2) to the nighttime differences even if in the first case the emission are mainly anthropogenic whereas during nighttime they are mainly biogenic.

Response

We agree that this is a surprising observation, given the fact that the explained and the missing reactivity exhibit pronounced diurnal cycles with changing anthropogenic input during day and night.

Comment

2. Pag. 17044, lines 5-10. The ozone (up to 50 ppb) introduced in the reactor to produce OH when ambient ozone concentration is low, could react with the atmospheric sample and modify the atmospheric composition under observation?

Response

Ozone was added when ambient ozone was low or when zero decay measurements were performed in humidified synthetic air. The addition of a small flow that contains ozone has three effects. (1) A marginal dilution (2 %) of the main flow occurs, which is corrected in the evaluation of the measured OH reactivities. (2) The added ozone

can react with OH and thereby increase the reactivity of the sampled gas. This effect is negligibly small (0.1 s^{-1}). (3) The ozone may deplete some of the OH reactants (e.g., NO, NO_2, isoprene, or alkenes) in the flow tube. The corresponding change of reactivity is calculated to be less than 0.1% over the measured lifetimes of OH. We have added an explanation of these influences by ozone in the experimental section 3.1.

Comment

3. Pag. 17048, lines 3-6 Usually the emissions of NOx and CO have a diurnal cycle, why the contribution at the OH reactivity of CO and NOx is flat during the day?

Response

CO and NOx showed pronounced, diurnal cycles with maximum values at nighttime and at early morning, and minimum values during daytime (Fig. 3). As mentioned in the paper (section 6.1), there were few local anthropogenic emissions during daytime (except for the days with biomass combustion), while traffic emissions played a significant role at night. One possible reason were local traffic regulations banning heavy Diesel trucks during daytime from 7:00 to 21:00 in PRD (see also Garland et al., 2008).

Comment

4. Minor points: Pag. 17040, line 14. ". . .if all atmospheric OH reactants are completely measured." and if the relative reaction rate ki are correctly measured.

Response

We have changed the sentence.

Comment

5. Pag. 17046, line 10. Why is 1900 ppb and not 1770 ppb, used as mean CH_4 concentration?

Response

The methane concentration was an assumed value. It is now replaced by the mean value of 2100 ppb which was measured by FTIR (Pinhua Xie, personal communication). The new value makes virtually no difference in the calculated OH reactivities.

References

Garland et al., Aerosol optical properties in a rural environment near the mega-city Guangzhou, China: implications for regional air pollution, radiative forcing and remote sensing, Atmos. Chem. Phys., 8, 5161–5186, 2008.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 17035, 2009.