Atmos. Chem. Phys. Discuss., 6, S5873–S5875, 2007
www.atmos-chem-phys-discuss.net/6/S5873/2007/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "The weekend effect within and downwind of Sacramento: Part 2. Observational evidence for chemical and dynamical contributions" *by* J. G. Murphy et al.

Anonymous Referee #1

Received and published: 2 January 2007

General Comments

This is an interesting paper which uses a variety of field observations for each day of the week, over a significant period, to probe the causes of differences in observed ozone production and other chemical speciation between weekdays and the weekend - for urban (NOx saturated) and rural (NOx limited) sites in and downwind of Sacramento, California. A very simple modelling approach is used to show that there is consistency in the hypotheses put forward to explain the observations. Although the model is very simple, and one would not expect the results to be particularly accurate, the calculations do enable the gross differences in behaviour at weekends and in the week to be

interpreted. The movement of air from the NOx source region from the rural monitoring site in summer time is fairly consistent, aiding the analysis and providing a significant period of data of connected flow. The major conclusions which are of interest to regulators (in particular the California Air Resources Board) are that carryover aloft and NOx dependence of P(O3) explain the higher O3 concentrations on the weekend in urban areas. With this in mind some definite recommendations can be made as to the effect of reducing NOx emissions in Sacramento on the region. The study syntheses a large body of data of several species (NO, NO2, O3, VOCs including biogenis, PAN, HNO3 and alkyl nitrates) made at a significant number of sites in Sacramento, on the Eastern urban fringes and rural sites at higher elevations to the East.

As isoprene has a short lifetime due to reaction with OH then it concentrations from day to day have been used to infer changes in the OH concentration - as complications due to dilution and other transport phenomena can be largely ignored to a first approximation. This is a novel method to infer differences in OH concentrations in the week compared with the weekend, which can then be rationalised by the expected dependence of OH on NOx under NOx limited regimes. The HNO3 concentration is shown to be NOx saturated due to its concentration being dependent upon both OH and NO2, with the former falling away with increasing NO2.

Although some of the reasons put forward to explain the observed data are rather speculative, and the model has to be subject to considerable uncertainties, a consistent picture emerges, given certain assumptions, which on the whole are justified. I therefore recommend publication.

Specific Comments

1. N2O5 hydrolysis is used to explain greater nighttime losses of Ox in urban areas. This will depend upon a NO3 concentrations being significant, which may not be the case if NO levels are elevated at night in the urban area? 2. Equation (3), HO2=RO2, this is true if RO2 is converted to HO2 quantitatively, and if there are no other OH to

ACPD
6, S5873–S5875, 2007

EGU

HO2 processes which do not involve RO2. How is reaction of OH with CO dealt with ? 3. Are the authors the first to develop these expressions? I think this is not the case and therefore some citations are required to work where these expressions were first used for this sort of purpose. 4. The dependence of OH and P(O3) on NOx has been discussed by Poppe et al and again a citation to his work should be given. 5. Is some comment needed on the very wide range of k1[VOC] that is expected for the various species that will be present? Presumably there will be a wide range of values, but from Fig 5 it appears that certain species dominate the weekly behaviour. 6. On page 11985 the production of O3 is modelled in the 4 hours following departure of the airmass from Sacramento, using NOx levels that fall off logarithmically with distance. This gives the chemical production/loss rate of O3, but do mixing effects (e.g. horizontal dilution of NOx, entrainment of O3 from above etc.) need to be taken into account?

Technical corrections

1. Page 11980, line 7, “these data are” 2. Page 11982, line 12, define VOC reactivity here to avoid confusion. 3. Page 11984, line 2, replace “high” by “large” 4. Table 4. Units of rate constant contain s-1. 5. Fig 3., NOx and Ox captions are wrongly given, should be other way around 6. Fig 9. Can uncertainties be given at all?

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 11971, 2006.

ACPD

6, S5873–S5875, 2007