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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Impact of organic nitrates on urban ozone production" *by* D. K. Farmer et al.

D. K. Farmer et al.

delphine.farmer@gmail.com

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We thank the referees for their positive and constructive comments. We will address all the concerns raised in a revised manuscript. In particular, Reviewer 1 (Jochen Rudolph) raised three points:

i) Uncertainty and Range of Validity. The referee pointed out that our approximate equations for deriving OH assumes conditions of 'high NOx when RO2 reacts with NO only', however our figures show low NOx and high VOC reactivity, potentially introducing a bias. We will add text in the revised manuscript noting this effect and giving examples of situations where the approximation begins to fail. We do not believe that breakdown of the approximtaion affects any of the conclusions of this manuscript. We estimate that 25% of RO2 reacts with HO2 when the NO/HO2 ratio is 0.01. For

HO2/RO2 at the high end of urban observations in the range of 100ppt, this corresponds to NO concentrations of 1 ppt. Thus, the assumption that RO2 reacts almost exclusively with NO holds throughout most of the NOx range relevant to urban environments and over the range shown in our figures. The referee points out that the NO to NO2 ratio depends on O3, HO2 and RO2, and thus our assumption that the NO to NO2 ratio is constant is not generally true. We agree that the ratio does vary - however, our algebraic solution is accurate for an instantaneous choice of those variables and the basic conclusions do not depend all that strongly on the ratio. The details of how an integral over space and time would affect a 3-d chemical transport model of ozone would be very interesting, however at the present time the treatment of organic nitrates in most chemical mechanisms is too lumped for a meaningful comparison to our calculation or to calculations constrained by observed VOC. We will highlight this assumption and discuss its effect in more detail in the revised version of the paper.

ii) Relevance of VOC reactivity-branching ratio to real world. The referee raises concerns that the relationship between VOC reactivity and branching ratio in the hypothetical cases outlined in this manuscript are not necessarily relevant in the real world, and suggests that a stronger case is required to suggest that reducing VOC emissions will reduce the branching ratio, α. While we do provide examples in which targeting high-branching ratio compounds (e.g. aromatics and semi-volatiles) would create a situation in which this case holds, we will add additional arguments in the revised manuscript. In particular, Perring et al. (2010, ACP) showed a clear example in which the observed AN branching ratio changed with photochemical age (Figure 6 of that paper), demonstrating that this general concept of shifting branching ratios is observed during the evolution of an anthropogenic plume. As summarized in Perring et al. (2010, ACP), larger branching ratios have been observed in urban locations than in more rural ones, providing further observational evidence that as these VOC mixes transition from anthropogenic to biogenic (either by transport or by changes in emissions), the branching ratio decreases. However, as the referee points out, many of these examples include targeting VOCs that are not dominant ozone producers – but are relevant to air qual-

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ity. Aromatic species are known carcinogens, and the semi-volatile compounds lead to particle formation, and are thus potential targets for air quality improvements. We will reword this section to more clearly state our agreement with the referee that attempts at reducing air pollution (rather than just ozone formation) may result in increased ozone production, and thus decreased air quality. The referee asks the question as to whether our modeled increase in PO3 with decreased VOC reactivity is relevant to real world scenarios. We believe the issues raised in this manuscript do have consequences for urban air quality and that they might alter assessments of the effectiveness of future (or historical) control strategies . Based on our observations in the Mexico City region, we believe that such scenarios are possible, however, our main hope is that this paper will encourage a more thorough and detailed examination of the role of RONO2 by other research groups. The referee also raises the point that regions with ozone control problems are not places that VOC emissions are targeted. We respectfully disagree. In California, for example, VOC controls have been a major target of policy. In many other regions, simultaneous VOC and NOx controls have been implemented.

iii) VOC emission controls & O3 production. We absolutely agree with the reviewer that changes in VOC emission do not directly correspond to changes in VOC concentration or O3 production, and we thank the referee for pointing out the sentences where this could be misunderstood. These sentences will be rewritten in the revised manuscript.

iv) Details. The reviewer noted several technical details that will be corrected in the revised manuscript.

Anonymous Reviewer 2: The second reviewer raised two points: i) the relative amount of organic nitrates present in the particle versus gas phase, and ii) the impact of uncertainties in the observed branching ratio. As described in detail by Rollins et al. (ES&T, 2010), the TD-LIF instrument measures organic nitrates in both particle and gas phases. During the MILAGRO campaign, we did not use filters or other means to derive the partitioning, we make the assumption that any particle-phase organic nitrates were produced in the gas phase, but partitioned into particles based on their

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volatility. If this assumption holds, then the inclusion of particulate organic nitrates does not bias this analysis. We will add a sentence to the revised manuscript pointing out this assumption. The uncertainties in the branching ratio are derived from the slope of Ox versus ΣANs, which has an r2 of 0.5. The slope of this plot is 27.475 +-3.53 (one standard deviation), which translates into a branching ratio range of 0.064 to 0.083 (or 6-8%). While the extremes of this range will alter the plots and numbers slightly, they do not alter the conclusions of the paper. We will include the uncertainty ranges in the revised manuscript.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 23423, 2010.