Atmos. Chem. Phys. Discuss., 12, C8085–C8088, 2012
www.atmos-chem-phys-discuss.net/12/C8085/2012/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Effects of biogenic nitrate chemistry on the NO_x lifetime in remote continental regions" *by* E. C. Browne and R. C. Cohen

Anonymous Referee #2

Received and published: 12 October 2012

Review of "Effects of biogenic nitrate chemistry on the NOx lifetime in remote continental regions" (manuscript acp-2012-478) by E.C. Browne and R.C. Cohen

This manuscript presents a quantification of the reduction of NOx lifetime (and of ozone production efficiency, OPE) that results from the formation of organic nitrates from biogenic volatile organic compounds (BVOCs). This study uses a steady-state box model for daytime and nighttime conditions, and assesses the effects over a range of NOx concentrations and chemical conditions (branching ratios, N2O5 hydrolysis rates, and aldehyde concentrations). The authors conclude that in low-NOx, high BVOC environments (such as found in remote continental boundary layers), organic nitrate

formation provides the major sink for NOx, reducing NOx lifetime and OPE relative to "background" CH4/CO chemistry. The major findings from the box model are confirmed using a 3-D regional CTM.

The topic of BVOC oxidation under low-NOx conditions has received considerable attention recently. As the authors point out, much of this attention has focused on the effects of BVOC chemistry on the HOx budget. Here, the authors turn their attention to the effects on the NOx budget, and find significant effects. The processing (and sequestering) of NOx by BVOC chemistry has important implications for our understanding of the NOx budget and ozone photochemistry. This study makes an important contribution to our understanding of this topic, and suggests future laboratory and field measurements to help constrain the magnitude of this effect. The paper leaves open some important questions and, of necessity, does not span all of parameter space. But, the scope of the paper is suitable and the approximations made are reasonable, so the paper certainly warrants publication in ACP, pending minor revisions as suggested below.

Specific comments

Abstract

The implications of these findings for representation of BVOC chemistry in CTMs and the resulting uncertainty in NOx/O3 chemistry should be mentioned here. How do issues of RONO2 destruction pathways (NOx recycling) influence the interpretation of the findings of this study? Also, what about implications for OPE?

1. Introduction

p.20674 – The first paragraph of this section has insufficient references. For instance, the statement that anthropogenic NOx emissions "contribute directly to ... secondary organic aerosol" needs a reference. So too should the statement about "increasing global background ozone concentration ... making it more difficult for individual cities

to reduce ozone".

p.20674, line 20 – Delete "thus".

p.20675, l.10 – Define "lifetime of NOx" as used in this study.

2. Background

p.20676, l.5 – Do you include loss of HOx through other NOx-related reactions (e.g., organic nitrate production) as part of the "high-NOx" criteria?

3.1 Daytime

p.20679 – Comment on the length of NOx lifetime versus the length of daytime (or nighttime, in section 3.2), and implications for the validity of the steady-state day/night assumptions.

3.2 Nighttime

p.20680, l. 19 – Explain the rationale for splitting alkenes evenly between isoprene (not emitted at night) and alpha-pinene (emitted during day and night).

p.20680, l. 20-21 – Explain what aerosol conditions these N2O5 hydrolysis rates would correspond to.

4.1 Daytime

p.20681, l.24 – Delete "(solid lines) and to HNO3 (dashed lines)".

4.2 Nighttime

p.20684, l.1 – Delete "HNO3 and".

4.3 Twenty-four hour average lifetime

p.20684, l.12-13 – Do you mean that the diurnal average lifetime will be similar to the daytime lifetime *times two* (to account for "much longer" lifetime night)?

p.20684 – How would the added complexity of a realistic diurnal cycle (e.g., driven by constant NOx emissions, resulting in accumulation of NOx to higher concentrations at night) change this estimate of 24-hr average lifetime? Would only a small fraction of RONO2 production occur at night?

5. Ozone production efficiency

p.20684, l.22 – Change "and ozone loss" to "and NOx loss".

p.20685, l. 3-9 – Do alkyl nitrates serve the same reservoir role as peroxy nitrates, or should they be considered as "terminal" sinks for NOx in this context? What are the implications for OPE? (This issue is touched on somewhat in the Discussion section.)

6. Boreal forest

p.20687 – This "net loss" formulation is very sensitive to local conditions, in particular to the local supply of NOx emissions versus the transport of organic nitrates (alkyl and peroxy) from upwind regions.

7. Discussion

p.20689 – What are the key uncertainties in RONO2 chemistry (and biogenic RO2 in general) and how sensitive would the NOx lifetime and OPE results presented here be to these uncertainties? Do the ranges of possibilities considered here (alpha parameter, etc.) span much of the uncertainty in biogenic RO2 chemistry, or are there other significant uncertainties (e.g., current competing understandings of isoprene chemical mechanisms under low-NOx conditions [Peeters et al., Paulot et al., etc.])?

Table 1 – Table footnote "e" seems to be incorrect.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 20673, 2012.