

Interactive comment on “Peroxy radicals and ozone photochemistry in air masses undergoing long-range transport” by A. E. Parker et al.

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Reply to Referees (Referee #2)

The authors are grateful to the referee for the insightful comments that have led to an improvement in the paper.

1. In many places there are lengthy and wordy sentences. This impairs the clarity of the text and makes it difficult for readers to follow. For example, page 18796, line 6-13. These two are long sentences with many folds of meaning. Each can be easily broken into two or more short sentences.

Changed to: “The relevance of ozone and its precursors to atmospheric pollution is well known. Progress has been made in the measurements of many trace gases associated

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with ozone, although there remain key uncertainties in the budgets of these species. Ozone has a lifetime of weeks to several months in the troposphere (Liu et al., 1987) and can be transported great distances in that time. The emission of NO_x and VOCs can lead to further ozone production downstream of the source with subsequent impact on the formulation of local air quality budgets (e.g. (Li et al., 2002)).”

2. Section 2. Since the PERCA instrument has been previously introduced (Green et al. 2003, 2006, as referenced in the paper) and the details of the PERCA measurements is of minor importance to this study, this section can be significantly reduced.

Equations 1 to 7 have been removed, and the rest of the section has been reworked to read:

“Experimental Details The PERCA Instrument The Chemical Amplification technique was introduced by Cantrell in the early 1980’s (Cantrell and Stedman, 1982; Cantrell et al., 1984) and has been widely deployed since then (Cantrell et al., 1993; Mihele and Hastie, 2003; Monks et al., 1998; Zanis et al., 2000; Green et al., 2006), although there is only one previous publication on aircraft measurements using the technique (Green et al., 2003). The PERCA technique utilises the radical catalysed conversion of NO and CO into NO₂ and CO₂ respectively via addition of NO (3 ppmv) and CO (6% v/v) to the inlet region. NO₂ is subsequently detected via aqueous luminol (5-amino-2,3-dihydro-1,4-phthalazinedione) solution chemiluminescence at $\lambda = 424$ nm with an improved LMA-3 detector as described by Green et al (Green et al., 2006).

The yield of NO₂ is equal to $CL * [HO_2 + \sum RiO_2 + \sum RiO + OH]$, where CL is the chain length, i.e. the number of HO₂/OH conversion cycles that occur before termination.

A significant background NO₂ signal is also observed from other sources such as the reaction of ozone with the reagent NO. Consequently, it is necessary to periodically measure only the background NO₂ produced by means other than peroxy radical conversion. This is achieved by injecting CO downstream of the NO injection point. The chain cycle is interrupted and the background NO₂ signal can be measured.

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The sensitivity of the PERCA instrument to humidity is well known (Mihele and Hastie, 1998; Mihele et al., 1999) and consequently a water correction as per Salisbury et al. (Salisbury et al., 2002) has been applied to all data in this study. This correction is relatively small out of the boundary layer as humidity is generally low. The average peroxy radical value increases from 18 – 29 pptv under 2.5 km with the average radical value over 2.5 km only increasing from 35 – 41 pptv when the correction is applied.

Aircraft Inlet System In the previous aircraft deployment of a PERCA instrument (Green et al., 2003), a single inlet was connected to the air sample pipe on the former UK Meteorological Office Hercules C-130, whereas the instrument deployed during ITOP was a dual-channel instrument with the inlets sampling directly through the aircraft wall (for full details see (Green et al., 2006)). The dual-channel inlets directly sampling ambient air avoids two problems previously present in the single-inlet air sample pipe set-up, those of rapidly changing background signal and losses down the air sample pipe. A more in depth discussion of the advantages of a dual-channel system is described elsewhere (Green et al., 2006)."

3. Section 3.1, page 18804-18808. Does the steady state analysis of the production and loss of peroxy radicals basically follow the method introduced in Mihele and Hastie (2003)? If this is the case, it seems to me using $\frac{1}{4}$ of the paper to elaborate on the details of a method that has been published is way too much. Are there any details original in this study (it is not clear from the text)? If not, similar to section 2, this part should also be significantly condensed.

In order to follow the progression of the arguments there is need to understand the analysis the individual terms and there interrelations. The entire section on δ and the enhancement to M&H analysis is new.

4. Air mass identification. On page 18802, line 5-10, the authors mentioned that they classified air masses into marine background air, Alaskan fire plumes and all others using the observed mixing ratios of CO and O₃. Later in the text, the authors

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referred to various long-range transport air-masses from N. America and Asia, e.g. page 18810, line 22-23, "long-range transport air-masses with young east-coast North American air masses, biomass burning, and aged Asian emission signatures". How do you determine it is a mixture of east-coast North American emission or aged Asian emission, or a mixture? Even with the help of back trajectories, it is difficult to pin-point the origin of air mass. Does any information come from the FLEXPART model? Please clarify in the text.

This line is not very clear. It is intended to state that through the course of the campaign we encountered different air masses with different signatures, as classified with a variety of techniques such as Flexpart and back trajectory analyses, and chemical signatures. Where specific events are discussed, the specific evidence is given. It has been clarified as follows:

"different long-range transported air-masses throughout the campaign, such as air-masses with young east-coast North American air masses, biomass burning, and aged Asian emission signatures."

In addition, using CO > 250 ppbv to identify biomass burning plumes is rather crude. I would encourage the authors to explore additional observed species for better identification of fire plumes. For example, HCN, CH₃CN, and fine aerosols are commonly used as biomass burning markers in addition to CO. Are these available during ITOP?

Unfortunately, species such as HCN and CH₃CN are not available. The use of CO > 250 ppbv is backed up by Flexpart analyses. In addition, organic and nitrate aerosol and particle number are enhanced during this period:

median a) Marine Air (O₃ < 40 ppbv, CO < 90 ppbv) b) Alaskan Fire Plume (CO > 250 ppbv) c) All Others

Column 1) is a) column 2) is b) and column 3) is c)

Sulphate $\mu\text{g}/\text{m}^3$ 0.14 0.04 0.08

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Ammonium $\mu\text{g}/\text{m}^3$ 0.09 0.05 0.02

Organic $\mu\text{g}/\text{m}^3$ 0.22 1.66 0.22

Nitrate $\mu\text{g}/\text{m}^3$ 0.01 0.09 0.01

CPC cm-3 709 841 622

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 18793, 2009.

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