

Interactive comment on “Observations of elevated formaldehyde over a forest canopy suggest missing sources from rapid oxidation of arboreal hydrocarbons” by W. Choi et al.

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General comment

The manuscript presents a budget analysis for gaseous formaldehyde in the late period of the BEARPEX campaign of 2007. The topic is within the scope of ACP. The methods and the assumptions in the analysis are clearly outlined but their validity is questioned and the requested changes may make the current conclusions much less robust. In the current analysis the calculations of HCHO sources from BVOC oxidation contain many inaccuracies likely biased towards underestimating the contribution from oxidation of BVOC and of their products. The following changes requested for the analysis could

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well turn out to significantly reduce the missing sources that in the manuscript are estimated to be 0.8-1.3 ppb h^{-1} . If the new analysis will still show a significant missing source for HCHO, the conclusions of the manuscript will be just strengthened by this review.

Major comments

1. Rate constants

In general IUPAC recommendations for rate constants and products yields, if available, should be used. This is not the case for some species considered in the manuscript.

2. HCHO sources

The OH-initiated oxidation and photolysis of glycolaldehyde produce HCHO with a 80% and 90% yield, respectively (Butkovskaya et al., JPC A(2006); Magneron et al., JPC A(2005)). These reactions could be an important source of HCHO. However, it is largely ignored in the manuscript and only implicitly accounted for when it is dealt with ethene oxidation (Orlando et al., JPC A(1998)). Assuming the OH concentration being 5×10^6 molec/cm³, a photolysis frequency of $8 \times 10^{-6} s^{-1}$ and a glycolaldehyde peak mixing ratio of 1.7 nmol/mol as reported by Spaulding et al., JGR(2003) the estimated HCHO production rate would be about 0.24 ppb h^{-1} . The glycolaldehyde contribution needs to be included in the analysis and a fair and easy way would be to assume a constant mixing ratio of 0.69 nmol/mol (average value as given by Spaulding et al(2003)). However, an average diurnal cycle, like the one from Spaulding et al(2003) measured in August-September 2000 at the Blodgett Forest, would be better.

The contribution of MACR oxidation is underestimated. According to Orlando and Tyn dall, GRL(1999), the OH-initiated oxidation of MACR produces 1-methylvinyl radical whose oxidation yields HCHO and HCHO-precursors. The HCHO yield from the OH-addition pathway is equal to the absolute methylglyoxal (CH₃COCHO) yield, 0.08. From the OH-abstraction pathway (45%) the methylvinyl radical decomposition yields 0.65

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$(\text{CH}_3\text{O}_2 + \text{CO} + \text{HCHO})$ and 0.35 $(\text{CH}_3\text{CO}_3 + \text{HCHO})$. Assuming that the peroxy radicals react very quickly, an absolute HCHO-yield of 0.90 is calculated. In total the HCHO yield from MACR oxidation should be 0.98. However, 0.61 is used in (see Table 2). This yield is referred to Paulot et al(2009) which did not deal with the HCHO yield from MACR + OH. The only thing I can think of is that the authors of the present manuscript tried to infer the HCHO yield from the reduced isoprene oxidation mechanism proposed by Paulot et al(2009). In that case the inferred valued is wrong because it is equal to 1.093 $((2 \times 0.53 + 0.47 \times 0.45) \times 0.85 + 0.08 \times 0.15)$.

In the present analysis HCHO production from isoprene oxidation is one of the largest terms. In appendix C1 of the manuscript the correct average HCHO-yield (63%) from high- NO_x isoprene oxidation studies is reported. However, in Table 2 a yield of 55% is written. Which yield was actually used? Moreover, the rate constant for the isoprene + OH reaction is 10% higher than what the IUPAC recommends. The value of 1×10^{-10} $(\text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1})$ should be used.

In Appendix C2 it is stated that the $\text{CH}_3\text{COCHO} + \text{OH}$ reaction is not considered as a source of CH_3CO_3 because the photolysis of CH_3COCHO is 10 times faster. Koch and Moortgat, JPC A(1998) estimated the lifetime of CH_3COCHO against photolysis to be 4.1 h (not 1.7 h!) and against reaction with OH to be 16 h for a OH concentration equal to 1×10^6 molec/cm³. In Fig. 7 of the manuscript OH concentrations as high as 6×10^6 molec/cm³ are reported. It means that the lifetime of CH_3COCHO against reaction with OH can be as low as 3.6 h if the rate constant given by IUPAC is used. Therefore, inclusion of the contribution of the $\text{CH}_3\text{COCHO} + \text{OH}$ reaction to the HCHO production seems to be necessary. LaFranchi et al., ACP(2009) reported mixing ratio peak values of 0.3 ppb and taking $[\text{OH}] = 5 \times 10^6$ molec/cm³ a HCHO production of about 0.07 ppb h⁻¹ is estimated.

LaFranchi et al.(2009) reported mean mixing ratios of biacetyl of 57 ppt that was measured during BEARPEX 2007. The CH_3CO_3 production from biacetyl photolysis, with a yield of 2, is absent in equation C3. LaFranchi et al(2009) showed in Fig. 4 that

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biacetyl photolysis is a significant source of CH_3CO_3 during BEARPEX(2007) and in Tab.4 that it is more important of than that of methylglyoxal.

3. HCHO sinks

In Section 3.1 the rate constant used for the $\text{HCHO} + \text{OH}$ reaction is shown. At 298K it is equal to 9.2×10^{-12} $(\text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1})$, 7% less than the IUPAC recommendations. The the following temperature-dependent expression $5.4 \times 10^{-12} \times \exp(135/\text{temp})$ for this rate constant should be used. From Fig. 12 the HCHO loss due to OH is a major term in the HCHO budget (2-3 ppb h⁻¹) and a 7% change in this term should be significant (0.14-0.21 ppb h⁻¹) when compared to the "missing" sources.

Minor comments

In appendix C1 of the manuscript it is stated that HCHO is formed in the oxidation of C₅-alkyl nitrates but it is neglected because of the "low" nitrate yield (5-7%). I find that statement inaccurate. Paulot et al., ACP(2009) reported an alkyl nitrate yield of 11.7% consistent with most of previous studies (Tuazon and Atkinson, IJCK 1990; Sprengnether et al., JGR(2002)). Only Chen et al., JGR(1998) reported a low yield 4.4%. However, I agree with the authors that the HCHO-yield from the oxidation of alkyl nitrates is likely negligible in the HCHO budget.

In Appendix C1 the authors also state that Isop-O₂ + HO₂ forms HCHO. This is against the experimental evidence that I am aware of. In fact, Dillon and Crowley, ACP(2008) showed that β -hydroxy peroxy radicals in the reaction with HO₂ undergo only (> 94%) the radical terminating channel. Paulot et al., Science(2009) set a 12% OH-yield for the Isop-O₂ + HO₂ reaction in order to account for a small amount of NO_x present initially in the chamber. Therefore, the above mentioned statements should be eliminated or at least reformulated.

In Table 3 and in Section 3.2.2 a 74% HCHO-yield from caryophyllene ozonolysis is

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cited from Lee et al., JGR (2006). The potentials of this reaction in contributing to the HCHO production are also discussed. However, this high HCHO-yield is likely an outlier. Instead, a much lower yield of about 10% (Atkinson and Arey, AE 2003) is consistent with the knowledge of atmospheric organic chemistry. In fact, the double bonds responsible for the fast ozonolysis of sesquiterpenes are internal and highly strained. This has been confirmed by Winterhalter et al., PCCP 2009 that reported a HCHO-yield of 7.7%. The text in Section 3.2.2 and Tab. 2 should be revised accordingly.

p9853 l26,28: it should be "ppb h⁻¹" instead of "h⁻¹"

List of abbreviations

JPC A = Journal of Physical Chemistry A

JGR = Journal of Geophysical Research

ACP = Atmospheric Chemistry and Physics

IJCK = International Journal of Chemical Kinetics

PCCP = Physical Chemistry Chemical Physics

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