

We appreciate your valuable comments concerning rate constants, HCHO yields, and some missing components in the calculations of the production rates. All those comments and suggestions were so helpful to improve the manuscript.

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.

Response: Corrected rate constants according to IUPAC recommendations.

2. HCHO sources

2-1. 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 8×10^{-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.

Response: Glycolaldehyde (GA) is known to be secondarily produced through the oxidation of ethene, MBO, isoprene and other VOCs (Butkovskaya et al., JPC A (2006); Magneron et al., JPC A (2005)). We calculated HCHO production rates from primary

emissions of BVOCs and their overall HCHO yields. HCHO yields used in this study firstly are based on the experimental results reported in the literature, and hence the effects of secondary products on HCHO productions are expected to be incorporated in the HCHO yields somehow if the experimentally obtained HCHO yield was not corrected by bi-product effects. However, Spaulding et al. (JGR, 2003) suggested that only about 30% of GA at Blodgett Forest is attributable to biogenic sources through multiple-regression and factor analysis. Thus, GA effects on HCHO production are worthy of consideration, as pointed out by the reviewer, so we included the HCHO production from GA in the revised manuscript. Unfortunately, GA was not measured during the BEARPEX period, so we used the diurnal profile of GA measured by Spaulding et al. (JGR, 2003) at Blodgett Forest for day 258~259, which is the same period of year as that of HCHO measurements in BEARPEX. The HCHO yield was taken from Butkoviak et al. (JPC, 2006) and Magneron et al. (JPC, 2006) (the mean of 72%) for GA+OH reaction, and from Magneron et al. (JPC, 2006) and Bacher et al. (AC, 2001) (the mean of 59%) for GA photolysis. The HCHO yields of 80% and 90% for photooxidation and photolysis, respectively, that the reviewer mentioned, are the highest values. Magneron et al. (2006) suggested 65% of HCHO yield for OH-initiated oxidation, and discussed that 90% yield from photolysis resulted from the additional production by OH produced as a bi-product. In addition, the experiments conducted in the presence of DNBE gave 54% yield and Bacher et al. (2001) suggested 41% of HCHO yield. The photolysis constant suggested by Magneron et al. (2006) is much higher than that of Bacher et al. (2001) combined with the difference of quantum yields (1.3 vs. 0.75). Thus, here the photolysis constant was calculated from the TUV model. The resultant HCHO production rates from GA decomposition pathways yield 0.09 ppb/h and 0.06 ppb/h for the HCHO High and HCHO Low phase, respectively, and therefore do not significantly alter our previous conclusions.

2-2. The contribution of MACR oxidation is underestimated. According to Orlando and Tyndall, 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 (CH_3COCHO) yield, 0.08. From the OH-abstraction pathway (45%) the methylvinyl

radical decomposition yields 0.65 ($\text{CH}_3\text{O}_2+\text{CO}+\text{HCHO}$) 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. 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 value is wrong because it is equal to $1.093 ((2\times 0.53+0.47\times 0.45)\times 0.85+0.08\times 0.15)$.

Response: Yes, we agree with your absolute HCHO-yield calculation. However, the experiments conducted by Tuazon and Atkinson (IJCK, 1990) show the HCHO yield of 0.5 from OH+MACR reaction. The HCHO yield of 0.5 was also used in Sumner et al. (JGR, 2001). We tried to update this value from the recent study (Table 3. in Paulot et al. (ACP, 2009)). From the table 3 in Paulot et al. (ACP, 2009), the calculated HCHO yield is 0.73 ($0.47\times 0.425+0.53$), because the effect of MCO_3 is additionally considered in the PA calculation. The HCHO-yield from Orlando et al. (GRL, 1999) without considering peroxy radicals is 0.53. Consequently, the mean value of 0.61 was derived from Tuazon and Atkinson (0.5), Orlando et al. (0.53), and Paulot et al. (0.73). The effects of peroxy radicals produced from MACR oxidation are considered in the revised steady state $[\text{CH}_3\text{O}_2]$ estimate.

2-3. 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 $1\times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$) should be used.

Response: We corrected rate constant for isoprene+OH reaction according to the IUPAC recommendation as suggested. The average HCHO-yield from isoprene oxidation of 63% came from high-NO_x conditions. However, NO concentrations estimated from the NO-

NO₂-RO₂-HO₂-O₃ photostationary relations at Blodgett Forest during the BEARPEX 2007 are ~ 100 ppt, which is not exactly "high-NO_x". The HCHO-yield under NO_x-free conditions is 34%. Sumner et al. (JGR, 2001) assumed that HCHO-yield (γ) linearly depends on NO_x abundance factor β . We used the same method to obtain the HCHO-yield at Blodgett Forest. β ranged from 0.59~0.83 and hence corresponding γ was obtained 0.51~0.58. We used the mean HCHO-yield of 0.55 in this study. Dreyfus et al. (JGR, 2002) also used the same method to estimate MVK and MACR yields from isoprene oxidation.

$$\beta = \frac{k_8[NO]}{k_8[NO] + k_9[HO_2] + k_{10}[RO_2]}$$

$$HCHO - yield, \gamma = 0.63\beta + 0.34(1 - \beta)$$

2-4. In Appendix C2 it is stated that the CH₃COCHO+OH reaction is not considered as a source of CH₃CO₃ because the photolysis of CH₃COCHO is 10 times faster. Koch and Moortgat, JPC A (1998) estimated the lifetime of CH₃COCHO against photolysis to be 4.1 h (not 1.7 h!) and against reaction with OH to be 16 h for OH concentration equal to 1×10⁶ molec/cm³. In Fig. 7 of the manuscript OH concentrations as high as 6×10⁶ molec/cm³ are reported. It means that the lifetime of CH₃COCHO 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 CH₃COCHO+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 [OH]= 5×10⁶ molec/cm³ a HCHO production of about 0.07 ppb h⁻¹ is estimated.

LaFranchi et al. (2009) reported mean mixing ratio of biacetyl of 57 ppt that was measured during BEARPEX 2007. The CH₃CO₃ production from biacetyl photolysis, with a yield of 2, is absent in equation C3. LaFranchi et al. (2009) showed in Fig. 4 that biacetyl photolysis is significant source of CH₃CO₃ during PEARPEX (2007) and in Table 4 that it is more important of than that of methylglyoxal.

Response: We modified the equation of the steady-state [PA] (C3) adding the missing contributions mentioned (methylglyoxal+OH reaction, biacetyl photolysis and MACR+OH reaction) according to LaFranchi et al.'s (2009) work.

$$[PA]_{ss} = \frac{\left(k_{12}[CH_3CHO][OH] + 0.72k_{13}[MVK][OH] + k_{14}[PAN] + j_{15}[MeGly] \right) + 0.6k_{16}[MeGly][OH] + 0.35k_{17}[MACO_3][NO] + j_{18}[biacetyl]}{k_{-14}[NO_2] + k_{19}[NO] + k_{20}[HO_2] + k_{21}[RO_2]}$$

LaFranchi et al. (2009) compared the production rates of PA from acetaldehyde, MVK, methyl glyoxal (MeGly), MACR, and biacetyl, assuming the production and loss of PA from PAN reaches an equilibrium. In their calculation, however, the equilibrium concentration of PA between PAN and PA radical accounts for ~75 % of $[PA]_{ss}$ obtained from the steady state calculation including all sources and sinks. Thus the effects of missing contributors on [PA] calculation are less than 15% of total HCHO production rate from PA radical during daytime and ~ 1% at night. If we additionally consider methane oxidation to produce methylperoxy radical, the contributions of biacetyl and MeGly+OH reactions to the total HCHO production rate are much smaller, less than ~6% during daytime and negligible at night, which is considered insignificant.

3. HCHO sinks

In section 3.1 the rate constant used for the HCHO+OH reaction is shown. At 298K it is equal to $9.2 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$, 7% less than the IUPAC recommendations. 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.

Response: We also modified the rate constant according to IUPAC recommendations. The corrected rate constant is about 6% less than that the originally used through the measurement period.

4. Minor comments

4-1. 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.

Response: We corrected the number to 11.7%. Dreyfus et al. (JGR, 2002) assumed a branching ratio of 0.05 for an isoprene-nitrate pathway and referred to Grossenbacher et al. (Suppl. Eos Trans., 81(48), 2000) to discuss that in low-NO_x environments, the ratio may be even smaller. Here we put 10 %, the average value of several studies, which are referred to by Drefus et al. and Paulot et al. However, because we used the experimentally obtained yields from isoprene oxidation both under NO_x-high and NO_x-free conditions, this change does not affect our results.

4-2. 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 b-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.

Response: The discussion concerning Isop-O₂+HO₂ reaction for HCHO formation has been eliminated.

4-3. In Table 3 and in Section 3.2.2 a 74% HCHO-yield from caryophyllene ozonolysis is 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 Table 2 should be revised accordingly.

Response: We mentioned β -caryophyllene as an example of unconsidered reactive species. In fact, the analysis for the effects of very reactive sesquiterpenes performed in Section 5 is based on HCHO yields of 10~50% from sesquiterpene oxidation, and therefore the 70% yield from caryophyllene was not actually used. However, we revised that yield adding other results that suggest a lower yield. In addition, OH-initiated caryophyllene oxidation produces HCHO with a yield of 42 % (Lee et al., JGR, 2006). Considering the reaction rate constant of $1.98 \times 10^{-10} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ (Atkinson and Arey, AE, 2003) and the observed daytime mean [OH] of $6 \times 10^6 \text{ molecule} \cdot \text{cm}^{-3}$ at Blodgett Forest, the lifetime of caryophyllene oxidation by OH is 14 minutes. Combined with the HCHO yield of 42 %, which is 5 times larger than the lower limit of HCHO yield from the ozonolysis, the effects of OH-initiated oxidation on HCHO production is comparable to that of ozonolysis. Therefore we also added the effect of OH-initiated caryophyllene oxidation in the revised manuscript.

4-4. P9853 line 26 and 28: I should be ppb h^{-1} instead of h^{-1} .

Response: It is the first order loss rate constant, and hence it should remain as h^{-1} . The term has been revised.