

1 *Supplement of*

2 **Drivers of biogenic secondary organic aerosol from the past to the future**

3 Yang Shi et al.

4 *Correspondence to:* Yang Shi (yang.shi@pnnl.gov) and Colette L. Heald  
5 (colette.heald@env.ethz.ch)

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## 7 Text S1. Calculation of $f_{RO_2}$

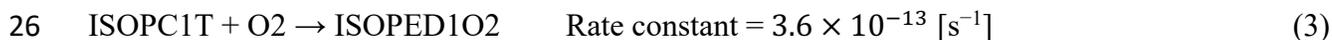
8 In the BASE experiment, the OH oxidation of ISOP, MTERP, and BCARY only produces  
9 one  $RO_2$  species, respectively.  $f_{RO_2}$  for a specific  $RO_2$  reaction is simply calculated as its vertically  
10 integrated reaction rate divided by the sum of the vertically integrated reaction rates of all  $RO_2$   
11 reactions. To determine the globally averaged  $f_{RO_2}$  shown in Figures 2 and 9, we weight the  
12 gridded  $f_{RO_2}$  by the  $RO_2$  concentrations at each grid cell.

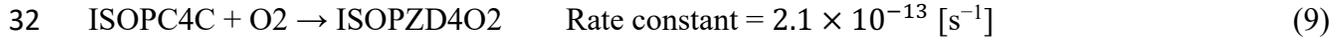
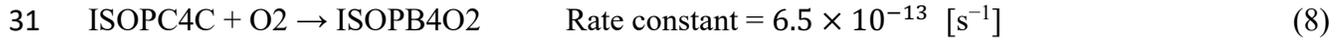
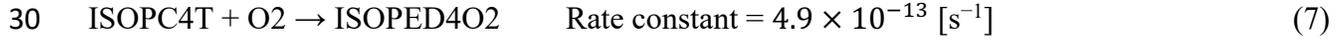
13 In our modified chemistry (i.e., the NEW experiments), the OH oxidation of MTERP  
14 produces two  $RO_2$  species, MTERP- $RO_2$ -1 and MTERP- $RO_2$ -2, with branching ratios of 0.78 and  
15 0.22, respectively. The two  $RO_2$  undergo identical chemistry, except that only MTERP- $RO_2$ -2 can  
16 isomerize. To determine the averaged  $f_{RO_2}$ , we calculate  $f_{RO_2}$  for the two  $RO_2$  species separately  
17 and weight them by their branching ratios. This method ensures reaction fates of each  $RO_2$  species  
18 do not exceed its branching ratio (e.g., the isomerization fate does not exceed 22%). ISOP  
19 oxidation produces six  $RO_2$  species through two-step reactions (Schwantes et al., 2020). Four  
20 isoprene hydroxy alkyl radical isomers (i.e., ISOPC1T, ISOPC1C, ISOPC4T, and ISOPC4C) are  
21 formed through the first-step oxidation:



$$23 \text{ Rate constant} = 2.7 \times 10^{-11} e^{(390/T)} [\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}] \quad (1)$$

24 Then,  $O_2$  radicals attach to these isomers, forming six ISOP- $RO_2$  species:





33 Each alkyl radical isomer forms two types of ISOP-RO<sub>2</sub> at different reaction rates. Therefore, to  
 34 determine the branching ratio of each RO<sub>2</sub> species ( $BR_{RO_2}$ ), we scale the stoichiometric  
 35 coefficients of the alkyl radical isomers (R1) with the corresponding reaction rate constants (R2-  
 36 9):

37 
$$BR_{ISOPB1O_2} = 0.315 * \frac{7.5 \times 10^{-13}}{7.5 \times 10^{-13} + 3.6 \times 10^{-13}} + 0.315 * \frac{7.5 \times 10^{-13}}{7.5 \times 10^{-13} + 1.4 \times 10^{-13}}$$

38 
$$= 0.478$$

39 
$$BR_{ISOPB4O_2} = 0.111 * \frac{6.5 \times 10^{-13}}{6.5 \times 10^{-13} + 4.9 \times 10^{-13}} + 0.259 * \frac{6.5 \times 10^{-13}}{6.5 \times 10^{-13} + 2.1 \times 10^{-13}}$$

40 
$$= 0.259$$

41 
$$BR_{ISOPED1O_2} = 0.315 * \frac{3.6 \times 10^{-13}}{7.5 \times 10^{-13} + 3.6 \times 10^{-13}} = 0.102$$

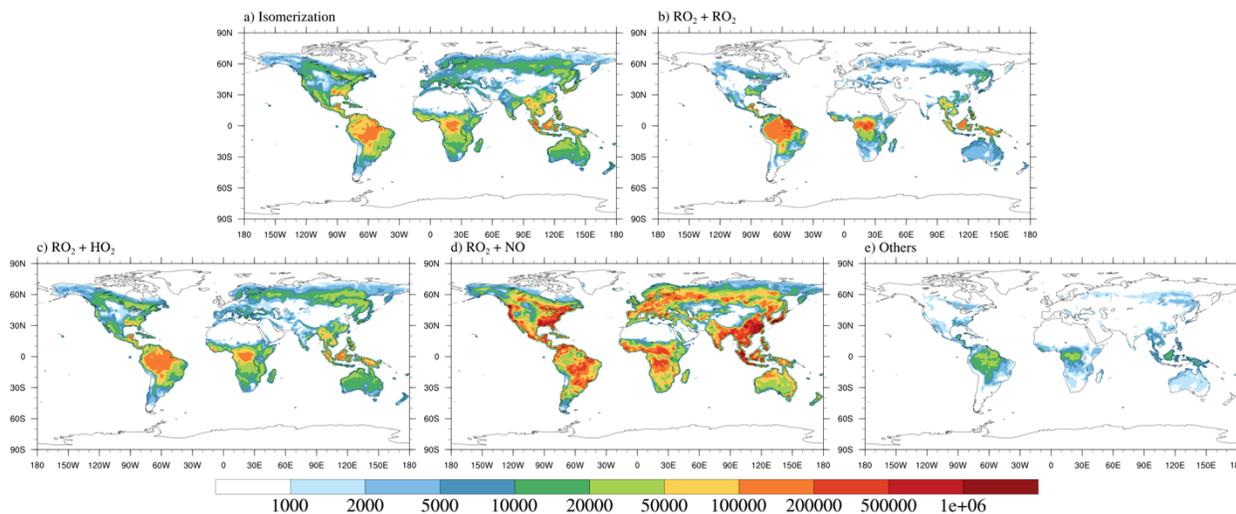
42 
$$BR_{ISOPED4O_2} = 0.111 * \frac{4.9 \times 10^{-13}}{6.5 \times 10^{-13} + 4.9 \times 10^{-13}} = 0.048$$

43 
$$BR_{ISOPZD1O_2} = 0.315 * \frac{1.4 \times 10^{-13}}{7.5 \times 10^{-13} + 1.4 \times 10^{-13}} = 0.050$$

44 
$$BR_{ISOPZD4O_2} = 0.259 * \frac{1.2 \times 10^{-13}}{6.5 \times 10^{-13} + 2.1 \times 10^{-13}} = 0.063$$

45 Similar to MTERP-RO<sub>2</sub>, the averaged fRO<sub>2</sub> for ISOP-RO<sub>2</sub> in the NEW experiments are  
 46 calculated as the fRO<sub>2</sub> of individual RO<sub>2</sub> species weighted by the corresponding branching ratios.  
 47 To determine the globally averaged fRO<sub>2</sub> shown in Figures 2 and 9, we weight the gridded fRO<sub>2</sub>  
 48 by the RO<sub>2</sub> concentrations at each grid cell.

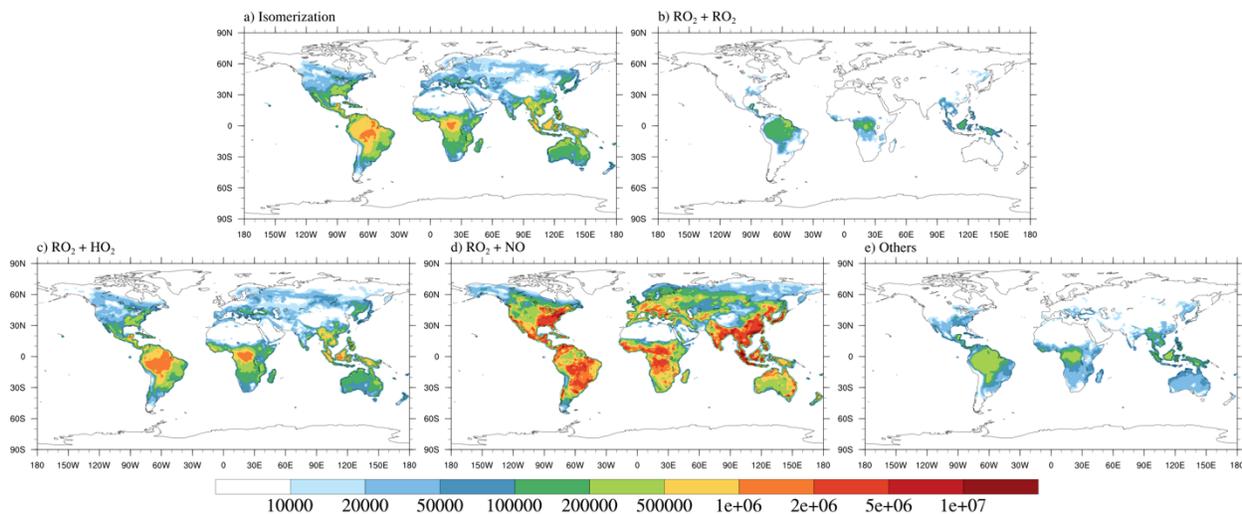
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50

51 **Figure S1.** Annually averaged MTERP-RO<sub>2</sub> reaction rates at the surface from NEW\_slow. The  
 52 reaction rates are the sum of the rates of the corresponding reactions of all RO<sub>2</sub> species, with no  
 53 weight applied. The RO<sub>2</sub> + RO<sub>2</sub> reactions include those between MTERP-RO<sub>2</sub> and ISOP-RO<sub>2</sub>,  
 54 IEPOXOO, MTERP-RO<sub>2</sub> itself, BCARY-RO<sub>2</sub>, and later generations of terpene RO<sub>2</sub> (Table 2,  
 55 part 2), while the reactions with NO<sub>3</sub>, CH<sub>3</sub>O<sub>2</sub>, and CH<sub>3</sub>CO<sub>3</sub> are included in “Others”. Unit:  
 56 molecular/cm<sup>3</sup>/s.

57



58

59 **Figure S2.** Same as Figure S1, except for ISOP-RO<sub>2</sub> reactions. The RO<sub>2</sub>+RO<sub>2</sub> reactions include  
 60 ISOP-RO<sub>2</sub> + MTERP-RO<sub>2</sub> and ISOP-RO<sub>2</sub> + BCARY-RO<sub>2</sub> reactions (Table 2, part 2), while  
 61 “Others” include ISOP-RO<sub>2</sub> decomposition and the reactions with CH<sub>3</sub>O<sub>2</sub> and CH<sub>3</sub>CO<sub>3</sub>.  
 62