

1 *Supplement of*

2 **Competing multiple oxidation pathways shape**
3 **atmospheric limonene-derived organonitrates simulated**
4 **with updated explicit chemical mechanisms**

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Section S1. Sensitivity simulations for limonene-derived ON using box model

A series of sensitivity tests were conducted using chemical box model. The initial concentration for the three oxidants is categorized into low (1.0×10^5 molecules $\cdot$ cm $^{-3}$ for OH, 1.0×10^{11} molecules $\cdot$ cm $^{-3}$ for O $_3$, 1.0×10^9 molecules $\cdot$ cm $^{-3}$ for NO $_3$), medium (1.0×10^{11} molecules $\cdot$ cm $^{-3}$ for OH, 1.0×10^{15} molecules $\cdot$ cm $^{-3}$ for O $_3$, 1.0×10^{13} molecules $\cdot$ cm $^{-3}$ for NO $_3$) and high (1.0×10^{19} molecules $\cdot$ cm $^{-3}$ for OH, 1.0×10^{18} molecules $\cdot$ cm $^{-3}$ for O $_3$, 1.0×10^{17} molecules $\cdot$ cm $^{-3}$ for NO $_3$) levels for analysis in experiments with multiple initial oxidation pathways of limonene.

Sensitivity tests under multiple initial oxidation pathways could be divided into two sets. The first set of simulations was denoted as individual initial oxidation pathway cases, model was performed with only one initial oxidation pathway of limonene (OH-, O $_3$ - or NO $_3$ -initiated oxidation). In the experiments with OH-initiated oxidation pathway, low to high level of initial concentration of OH was added into chemical box model. In the experiments with O $_3$ -initiated oxidation pathway, initial O $_3$ concentration ranging from low to high level was set. Similarly, in the experiments with NO $_3$ -initiated oxidation pathway, low to high level initial concentration of NO $_3$ was set. The second set of simulations was denoted as multiple initial oxidation pathways cases, two and three initial oxidation pathways of limonene were included in chemical box model. These experiments intended to elucidate the synergistic effect of multiple initial oxidation pathways. In the experiments of OH + O $_3$ initiated oxidation pathway, low to high level initial concentrations of OH and O $_3$ were added into chemical box model. In the experiments of OH + NO $_3$ initiated oxidation pathway, additional initial OH and NO $_3$ concentrations ranging from low to high level were set for comparison of an initial concentration of 0 molecules cm $^{-3}$. Similarly, the experiments of O $_3$ + NO $_3$ initiated oxidation pathway with low to high level initial concentrations of O $_3$ and NO $_3$ were performed. Lastly, the experiments of OH + O $_3$ + NO $_3$ initiated oxidation pathway with low to high level initial concentrations of OH, O $_3$ and NO $_3$ were conducted. To ensure adequate intermediate reaction processes during the experiments, the initial concentration of other gaseous species included in chemical mechanism used in experiments were set to high enough. Experiments including OH-initiated oxidation pathway added an additional concentration of NO $_3$, NO and HO $_2$, experiments including O $_3$ -initiated oxidation pathway added an additional concentration of OH, NO $_3$, NO, CO, SO $_2$, HO $_2$ and H $_2$ O and experiments including NO $_3$ -initiated oxidation pathway need to add initial concentrations of OH, NO and HO $_2$. Multiple initial oxidation pathway experiments included

OH-initiated, O₃-initiated or NO₃-initiated oxidation pathways, where the concentration of this oxidant was set according to the three initial concentration gradients mentioned above. The initial concentration of these gaseous species (OH, NO₃, NO, CO, SO₂, HO₂, H₂O) were set to 1.0×10¹⁰, 1.0×10¹², 1.0×10¹², 1.0×10¹⁴, 1.0×10¹⁰, 1.0×10¹¹ and 1.0×10¹⁶ molecules·cm⁻³, respectively.

Section S2. Sensitivity simulations for global atmospheric ON using global model

We conducted sensitivity simulations to evaluate the impacts of oxidation pathways on burden of limonene-derived ON. The base case (Case0) includes all three initial oxidation pathways (OH-, O₃- and NO₃-initiated oxidation) to form limonene-derived ON. The first sensitivity case (Case1) was designed to examine the effects of OH-initiated oxidation pathway on global limonene-derived ON formation. In Case1, the model was run in the same way as Case0 but without OH-initiated oxidation pathway of limonene. The second sensitivity case (Case2) was designed to examine the effects of O₃-initiated oxidation pathway on global limonene-derived ON formation. O₃-initiated oxidation pathway of limonene is not included in Case2 while all the other settings are the same as Case0. The third sensitivity case (Case3) was designed to examine the effects of NO₃-initiated oxidation pathway on global limonene-derived ON formation, whose setup is referred to as the base case (Case0) excluding NO₃-initiated oxidation pathway of limonene. The fourth to sixth sensitivity case (Case4-6) was designed to examine the effects of individual initial oxidation pathway on global limonene-derived ON formation, whose setup is referred to as the base case (Case0) including OH, O₃ or NO₃-initiated oxidation pathway of limonene.

Section S3. Comparison With Measurements

The model's ability to simulate the formation of limonene-derived organonitrates (ON) is evaluated through comparisons with surface measurement data summarized in previous publication with references provided therein.(Li et al., 2023) Given that observational data do not differentiate ON formed specifically from limonene versus other VOC precursors, we compared simulated surface concentrations of ON under two conditions, with and without developed limonene-derived ON formation mechanism in this study, against observations at 33 surface sites (Fig. S5). Global observation of ON concentration ranged from 0.1 to 6.1 $\mu\text{g}\cdot\text{m}^{-3}$. Simulations excluding limonene-derived ON formation largely underestimated the results, which may be due to incomplete consideration of the precursors and formation process of ON in the mechanism. The incorporation of the limonene-derived ON formation mechanism improved global simulation of ON, resulting in increased simulated concentration of ON (0.05-0.50 $\mu\text{g}\cdot\text{m}^{-3}$), which were closer to observations, especially at forest and coastal sites. The simulated ON concentration were within an order of magnitude of most particulate ON observations, though the simulated concentrations were still significantly lower than observed values in some urban and rural sites. It should be noted that this study primarily focused on developing explicit chemical mechanisms for global model to elucidate oxidation pathways of limonene from biogenic emission contributing to ON formation. The large underestimation at urban and suburban sites is likely due to the underestimation of ON generated from anthropogenic VOC emissions in this study, which is needed for further improvements in future research.

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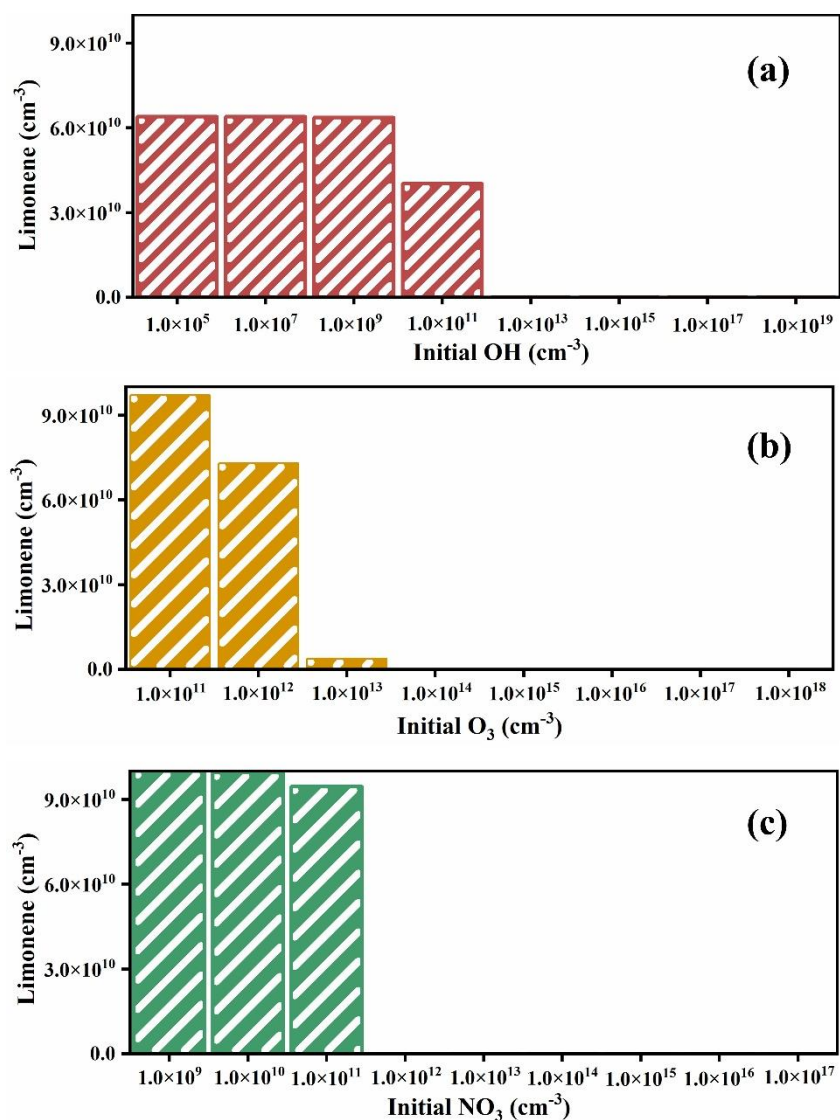


Figure S2. Simulated concentration variations of limonene from individual initial oxidation pathway under different (a) OH (red), (b) O₃ (yellow), (c) NO₃ (green) conditions using chemical box model.

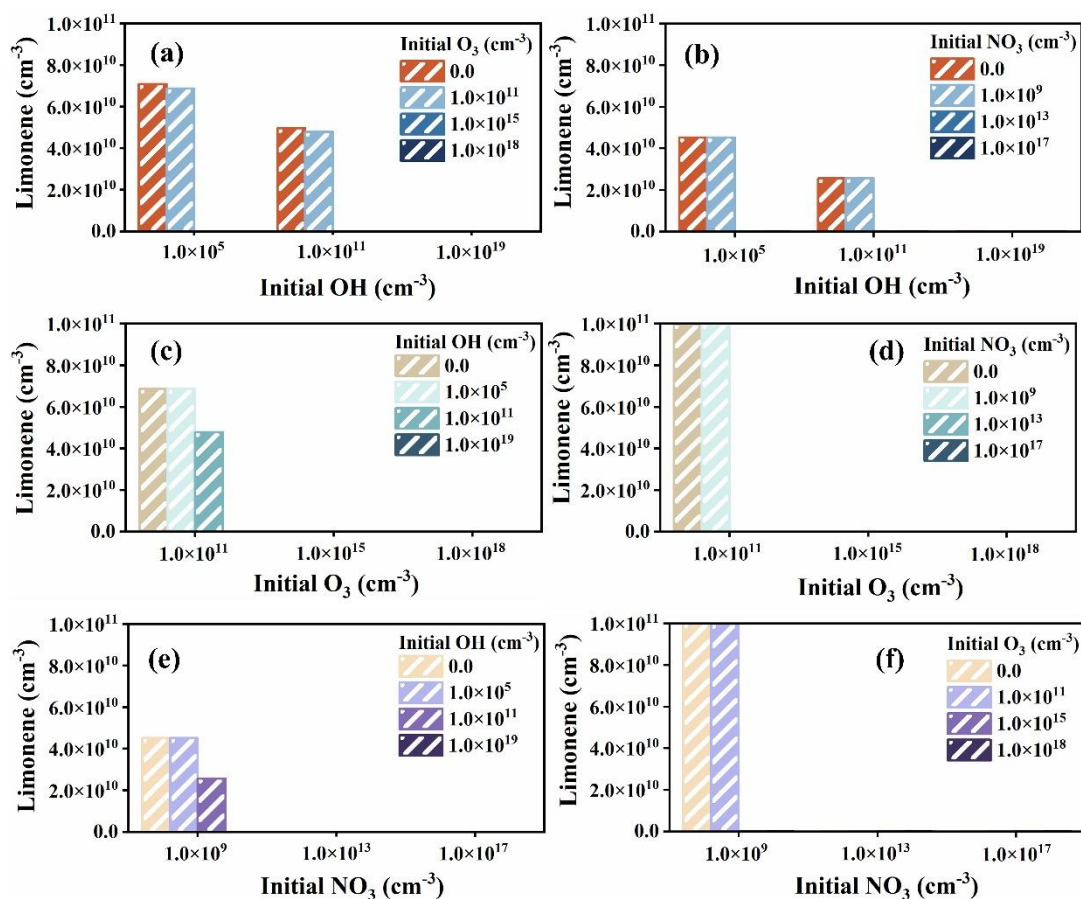


Figure S3. Simulated concentration variations of limonene by adding OH-initiated, O₃-initiated and NO₃-initiated oxidation pathways on the production of limonene-derived ON under different oxidant conditions, including variation of limonene concentration with adding initial OH concentration in the three O₃ levels under (a) low, (b) moderate and (c) high NO₃ levels; variation of limonene concentration with adding initial O₃ concentration in the three OH levels under (d) low, (e) moderate and (f) high NO₃ levels; variation of limonene concentration with adding initial NO₃ concentration in the three OH levels under (d) low, (e) moderate and (f) high O₃ levels.

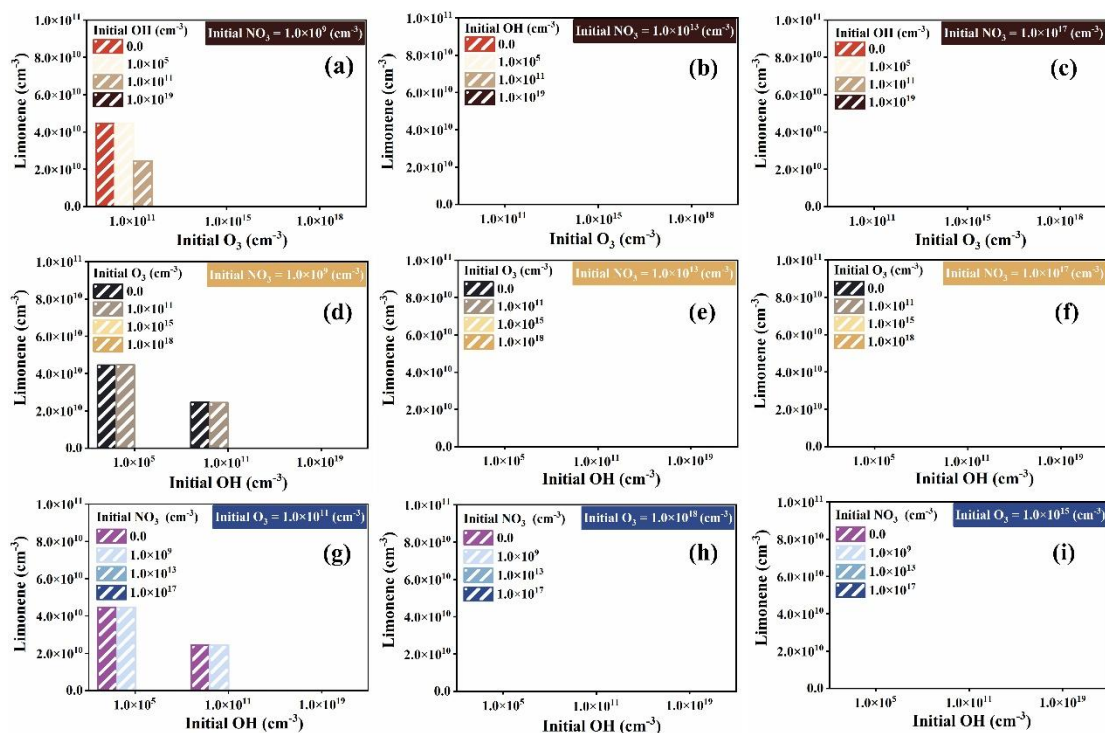


Figure S4. Simulated concentration variations of limonene by adding OH-, O₃- and NO₃-initiated oxidation pathways on the production of limonene-derived ON under different oxidant conditions, including variation of limonene concentration with adding initial OH concentration in the three O₃ levels under (a) low, (b) moderate and (c) high NO₃ levels; variation of limonene concentration with adding initial O₃ concentration in the three OH levels under (d) low, (e) moderate and (f) high NO₃ levels; variation of limonene concentration with adding initial NO₃ concentration in the three OH levels under (d) low, (e) moderate and (f) high O₃ levels.

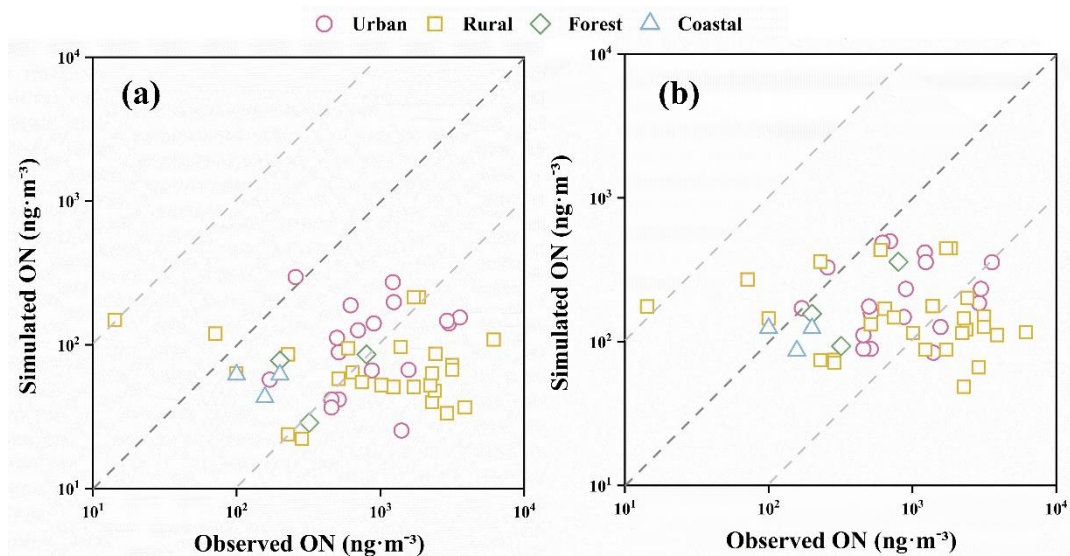


Figure S5. Simulated concentrations of ON and their comparisons against the total observed ON concentrations. (a) simulated ON without limonene-derived ON. (b) simulated ON including limonene-derived ON. Observations shown in colorful symbols: pink circles: urban sites; yellow square: rural sites; green diamond: forest sites; blue triangles: coastal sites. The dark grey dashed line indicates the 1:1 line; the light grey dashed lines indicate one order-of-magnitude differences. Details and references of the observations are shown in Table S9.

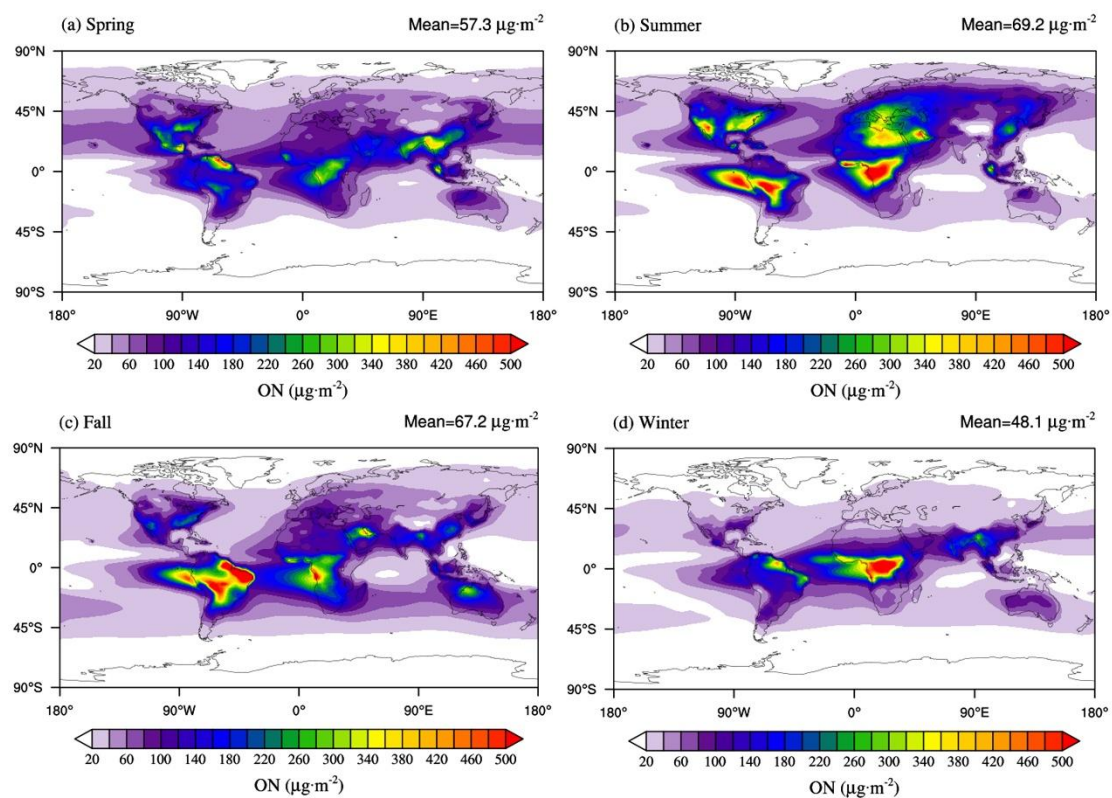


Figure S6. Simulated mean column concentration of limonene-derived ON (Case0) in spring (a), summer (b), fall (c), and winter (d).

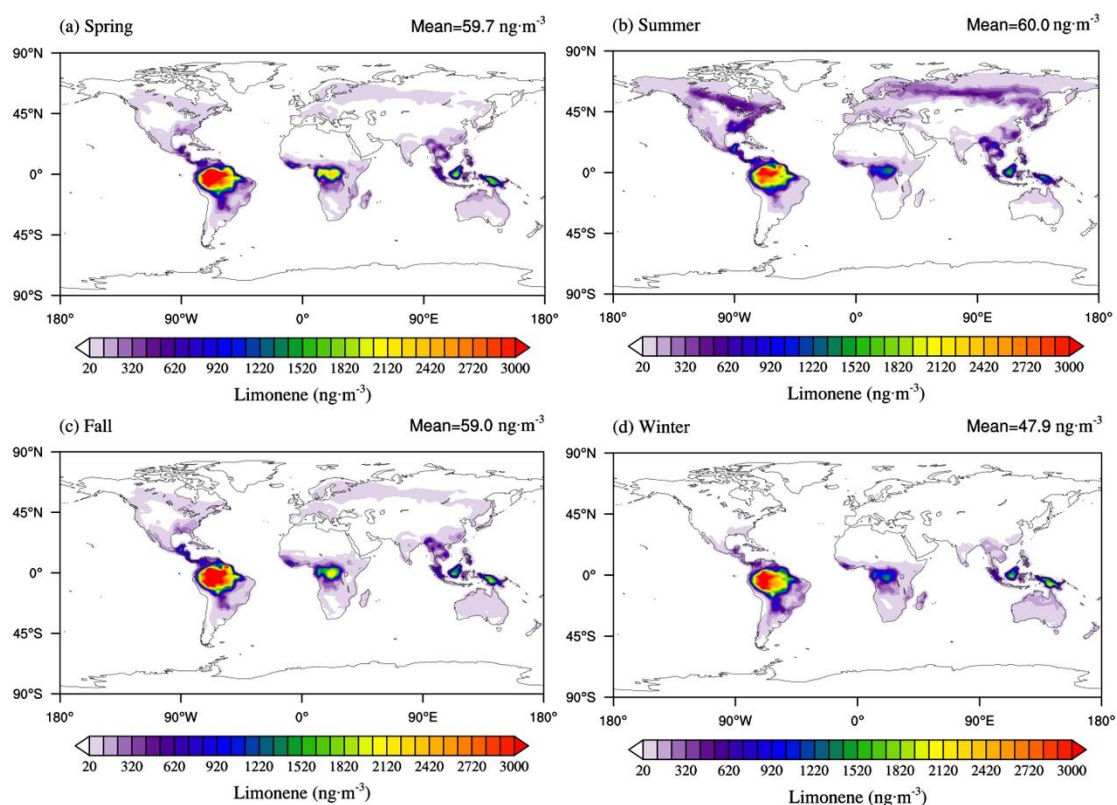


Figure S7. Simulated surface concentration of limonene (Case0) in spring (a), summer (b), fall (c), and winter (d).

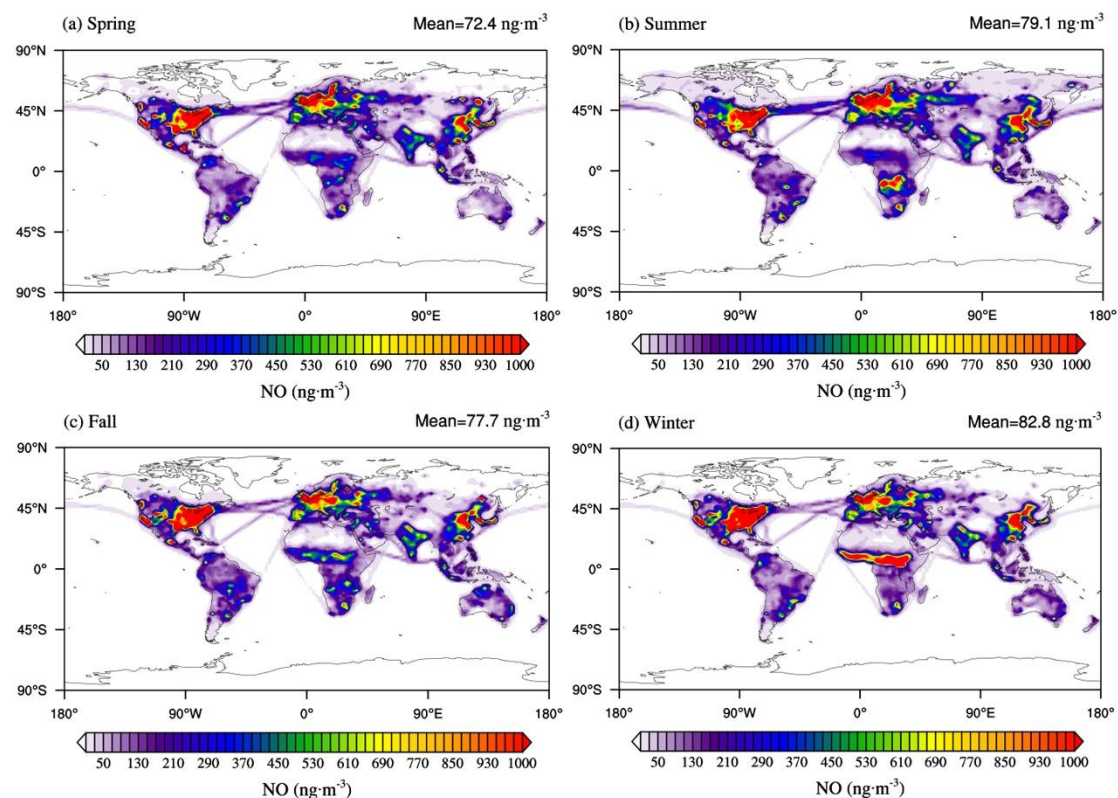


Figure S8. Simulated surface concentration of NO (Case0) in spring (a), summer (b), fall (c), and winter (d).

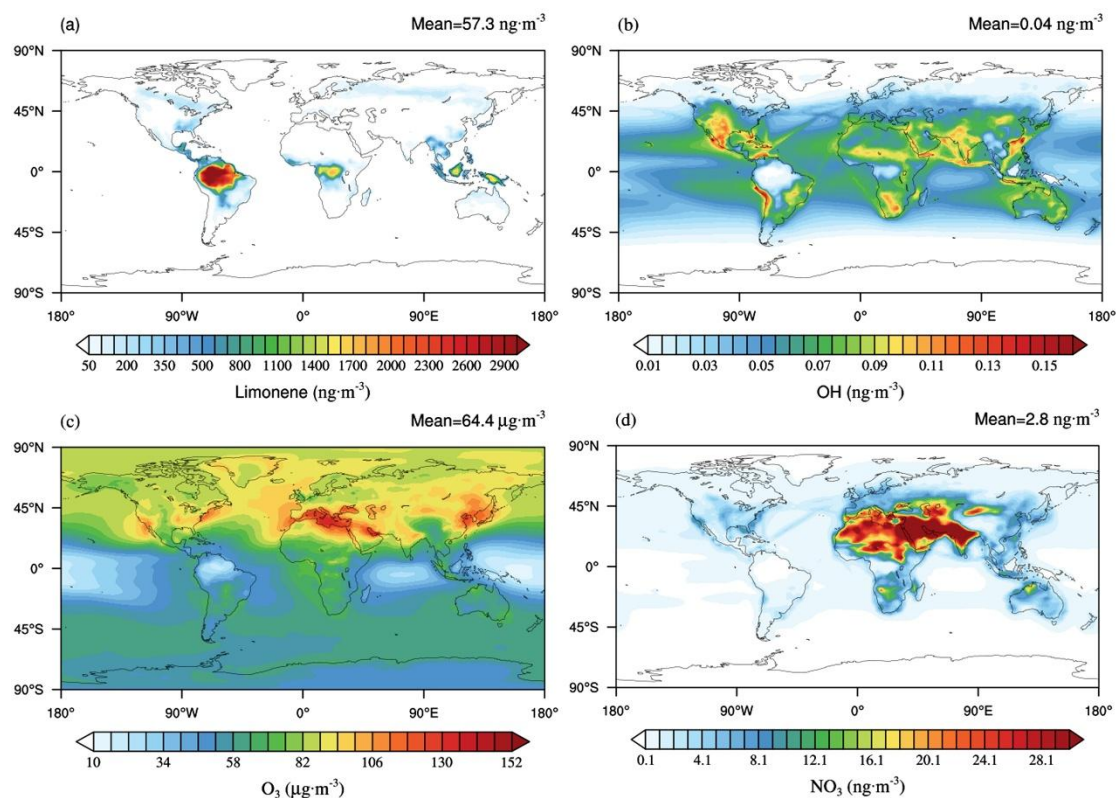


Figure S9. Simulated surface concentration of (a) limonene, (b) OH, (c) O₃ and (d) NO₃ for the Case0.

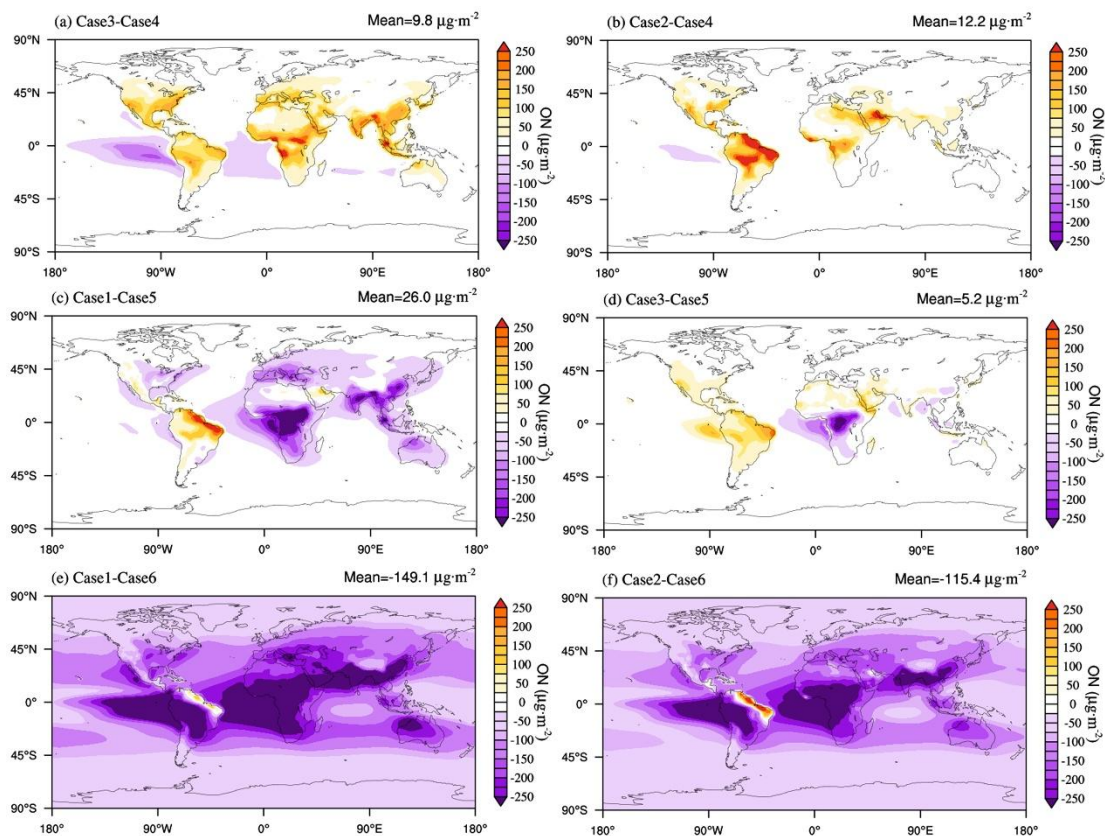


Figure S10. The difference in column concentration of limonene-derived ON between Case3 and Case4 (a), the difference in column concentration of limonene-derived ON between Case2 and Case4 (b), and the difference in column concentration of limonene-derived ON between Case1 and Case5 (c), the difference in column concentration of limonene-derived ON between Case3 and Case5 (d), the difference in column concentration of limonene-derived ON between Case1 and Case6 (e), the difference in column concentration of limonene-derived ON between Case2 and Case6 (f).

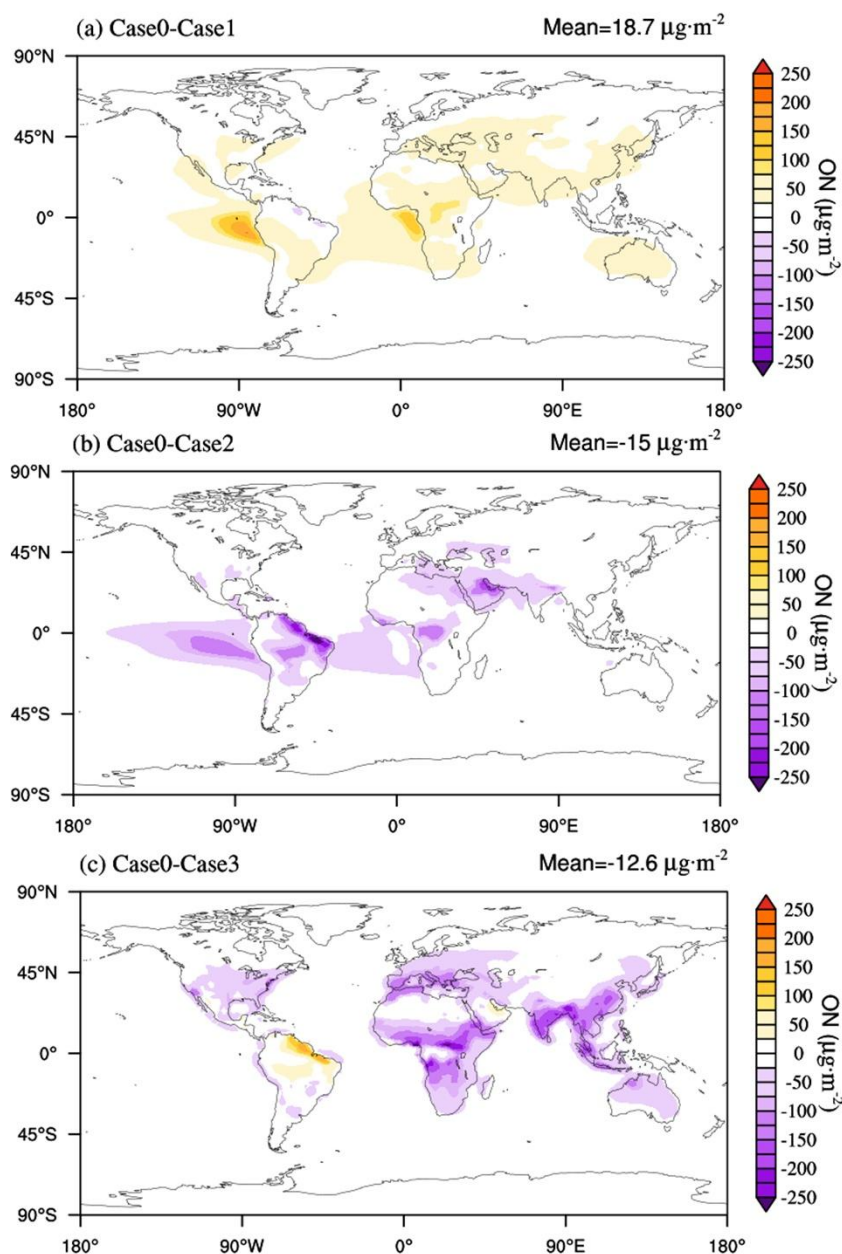


Figure S11. The difference in column concentration of limonene-derived ON between Case0 and Case1 (a), the difference in column concentration of limonene-derived ON between Case0 and Case2 (b), and the difference in column concentration of limonene-derived ON between Case0 and Case3 (c).

272 **Table S1.** Gas-phase species used in the limonene-derived ON formation mechanism

Short name	Chemical formula
LIMO	$\text{CH}_3\text{C}=\text{CHCH}_2\text{CH}(\text{CH}_2\text{CH}_3)\text{C}(\text{=CH}_2)\text{CH}_2$
LIMAO2	$[\text{O}]\text{OC}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_2\text{CHOH})\text{C}(\text{=CH}_2)\text{CH}_3$
LIMBO2	$[\text{O}]\text{OCHCH}_2\text{CH}(\text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)\text{OH})\text{C}(\text{=CH}_2)\text{CH}_3$
LIMAOOH	$\text{HOOC}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_2\text{CHOH})\text{C}(\text{=CH}_2)\text{CH}_3$
LIMBOOH	$\text{HOOCHCH}_2\text{CH}(\text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)\text{OH})\text{C}(\text{=CH}_2)\text{CH}_3$
LIMOOA	$\text{O}=\text{CHCH}_2\text{CH}(\text{CH}_2\text{CH}_2\text{C}(\text{=O})[\text{O}^-])\text{CH}_3\text{C}(\text{=CH}_2)\text{CH}_3$
LIMOOB	$[\text{O}^-][\text{O}^+]=\text{CHCH}_2\text{CH}(\text{CH}_2\text{CH}_2\text{C}(\text{=O})\text{CH}_3)\text{C}(\text{=CH}_2)\text{CH}_3$
NLIMO2	$[\text{O}^-][\text{N}^+](=\text{O})\text{OCHCH}_2\text{CH}(\text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)\text{O}[\text{O}])\text{C}(\text{=CH}_2)\text{CH}_3$
NLIMO2B	$[\text{O}]\text{OCHCH}_2\text{CH}(\text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)\text{O}(\text{=O})[\text{N}^+][\text{O}^-])\text{C}(\text{=CH}_2)\text{CH}_3$
NLIMO2EXO	$\text{CH}_3\text{C}=\text{CHCH}_2\text{CH}(\text{CH}_2\text{CH}_2)\text{C}(\text{CH}_2\text{O}(\text{=O})[\text{N}^+][\text{O}^-])(\text{O}[\text{O}])\text{CH}_3$
NLIMOOH	$[\text{O}^-][\text{N}^+](=\text{O})\text{OCHCH}_2\text{CH}(\text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)\text{OOH})\text{C}(\text{=CH}_2)\text{CH}_3$
NLIMOOHEXO	$\text{CH}_3\text{C}=\text{CHCH}_2\text{CH}(\text{CH}_2\text{CH}_2)\text{C}(\text{CH}_2\text{O}(\text{=O})[\text{N}^+][\text{O}^-])(\text{OOH})\text{CH}_3$
LIMALAO2	$\text{O}=\text{CHCH}_2\text{CH}(\text{CH}_2\text{CH}(\text{O}[\text{O}])\text{C}(\text{=O})\text{CH}_3)\text{C}(\text{=CH}_2)\text{CH}_3$
LIMALBO2	$[\text{O}]\text{OCH}_2\text{C}(\text{=O})\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_2\text{CH}=\text{O})\text{C}(\text{=CH}_2)\text{CH}_3$
LIMANO3	$[\text{O}^-][\text{N}^+](=\text{O})\text{OC}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_2\text{CHOH})\text{C}(\text{=CH}_2)\text{CH}_3$
LIMBNO3	$[\text{O}^-][\text{N}^+](=\text{O})\text{OCHCH}_2\text{CH}(\text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)\text{OH})\text{C}(\text{=CH}_2)\text{CH}_3$
LIMALAOOH	$\text{O}=\text{CHCH}_2\text{CH}(\text{CH}_2\text{CH}(\text{OOH})\text{C}(\text{=O})\text{CH}_3)\text{C}(\text{=CH}_2)\text{CH}_3$
LIMALBOOH	$\text{HOOCH}_2\text{C}(\text{=O})\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_2\text{CH}=\text{O})\text{C}(\text{=CH}_2)\text{CH}_3$
C923CO3H	$\text{HOOC}(\text{=O})\text{CH}_2\text{CH}(\text{CH}_2\text{CH}_2\text{C}(\text{=O})\text{CH}_3)\text{C}(\text{=CH}_2)\text{CH}_3$
LIMBOO	$[\text{O}^-][\text{O}^+]=\text{CHCH}_2\text{CH}(\text{CH}_2\text{CH}_2\text{C}(\text{=O})\text{CH}_3)\text{C}(\text{=CH}_2)\text{CH}_3$
LIMAO	$\text{CH}_3\text{C}(\text{=CH}_2)\text{CHCH}_2\text{CH}_2\text{C}(\text{CH}_3)([\text{O}])\text{CH}(\text{OH})\text{CH}_2$
LIMBO	$\text{CH}_3\text{C}(\text{=CH}_2)\text{CHCH}_2\text{CH}_2\text{C}(\text{CH}_3)(\text{OH})\text{CH}([\text{O}])\text{CH}_2$
NLIMO	$[\text{O}^-][\text{N}^+](=\text{O})\text{OCHCH}_2\text{CH}(\text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)[\text{O}])\text{C}(\text{=CH}_2)\text{CH}_3$
NLIMOEXO	$\text{CH}_3\text{C}=\text{CHCH}_2\text{CH}(\text{CH}_2\text{CH}_2)\text{C}(\text{CH}_2\text{O}(\text{=O})[\text{N}^+][\text{O}^-])([\text{O}])\text{CH}_3$
LIMAL	$\text{O}=\text{CHCH}_2\text{CH}(\text{CH}_2\text{CH}_2\text{C}(\text{=O})\text{CH}_3)\text{C}(\text{=CH}_2)\text{CH}_3$
LIMBCO	$\text{CH}_3\text{C}(\text{=CH}_2)\text{CHCH}_2\text{CH}_2\text{C}(\text{CH}_3)(\text{OH})\text{C}(\text{=O})\text{CH}_2$
LIMALACO	$\text{O}=\text{CHCH}_2\text{CH}(\text{CH}_2\text{C}(\text{=O})\text{C}(\text{=O})\text{CH}_3)\text{C}(\text{=CH}_2)\text{CH}_3$
LIMALBCO	$\text{O}=\text{CHCH}_2\text{CH}(\text{CH}_2\text{CH}_2\text{C}(\text{=O})\text{CH}=\text{O})\text{C}(\text{=CH}_2)\text{CH}_3$

Table S2. Reactions for limonene-derived ON formation mechanism.

Reaction	Rate constant (cm ³ ·molecules ⁻¹ ·s ⁻¹ or s ⁻¹)	Note
LIMO + OH = LIMAO2	$4.3 \times 10^{-11} \times \exp(401/T) \times 0.408$	b
LIMO + OH = LIMBO2	$4.3 \times 10^{-11} \times \exp(401/T) \times 0.222$	b
LIMAO2 + HO2 = LIMAOOH	KRO2HO2×0.914	b
LIMAO2 + NO = LIMANO3	KRO2NO×0.228	b
LIMAO2 + NO = LIMAO + NO2	KRO2NO×0.772	b
LIMAO2 + NO3 = LIMAO + NO2	KRO2NO3	b
LIMAO2 + RO2 = LIMAO	$9.2 \times 10^{-14} \times 0.7$	b
LIMAO2 + RO2 = LIMAOH	$9.2 \times 10^{-14} \times 0.3$	b
LIMBO2 + HO2 = LIMBOOH	KRO2HO2×0.914	b
LIMBO2 + NO = LIMBNO3	KRO2NO×0.228	b
LIMBO2 + NO = LIMBO + NO2	KRO2NO×0.772	b
LIMBO2 + NO3 = LIMBO + NO2	KRO2NO3	b
LIMBO2 + RO2 = LIMBO	$8.8 \times 10^{-13} \times 0.6$	b
LIMBO2 + RO2 = LIMAOH	$8.8 \times 10^{-13} \times 0.2$	b
LIMBO2 + RO2 = LIMBCO	$8.8 \times 10^{-13} \times 0.2$	b
LIMAOOH + OH = LIMAO2	7.4×10^{-11}	b
LIMAOOH + hv = LIMAO + OH	J<41>	b
LIMANO3 + OH = LIMAL + NO2	6.2×10^{-11}	b
LIMAO = LIMAL + HO2	KDEC	b
LIMAOH + OH = LIMBCO + HO2	7.0×10^{-11}	b
LIMBOOH + OH = LIMBCO + OH	1.0×10^{-10}	b
LIMBOOH + hv = LIMBO + OH	J<41>	b
LIMBNO3 + OH = LIMBCO + NO2	5.9×10^{-11}	b
LIMBO = LIMAL + HO2	KDEC	b
LIMO + O3 = LIMOOA	$2.8 \times 10^{-15} \times \exp(-770/T) \times 0.73$	b
LIMO + O3 = LIMOOB	$2.8 \times 10^{-15} \times \exp(-770/T) \times 0.27$	b
LIMOOA = LIMALAO2 + OH	KDEC×0.5	b
LIMOOA = LIMALBO2 + OH	KDEC×0.5	b
LIMOOB = LIMBOO	KDEC×0.5	b
LIMALAO2 + HO2 = LIMALAOOH	KRO2HO2×0.914	b
LIMALAO2 + RO2 = LIMALACO	$8.8 \times 10^{-13} \times 0.2$	b
LIMALAO2 + RO2 = LIMALAOH	$8.8 \times 10^{-13} \times 0.2$	b

LIMALBO2 + HO2 = LIMALBOOH	KRO2HO2×0.914	b
LIMALBO2 + RO2= LIMALBCO	8.8×10 ⁻¹³ ×0.05	b
LIMALBO2 + RO2 = LIMALBOH	8.8×10 ⁻¹³ ×0.05	b
LIMBOO + CO = LIMAL	1.2×10 ⁻¹⁵	b
LIMBOO + NO = LIMAL	1.0×10 ⁻¹⁴	b
LIMBOO + NO2 = LIMAL	1.0×10 ⁻¹⁵	b
LIMBOO + SO2 = LIMAL + SO3	7.0×10 ⁻¹⁴	b
LIMBOO + H2O = LIMAL + H2O2	1.4×10 ⁻¹⁷	b
LIMBOO + H2O = LIMNONIC	2.0×10 ⁻¹⁸	b
LIMO + NO3 = NLIMO2	1.2×10 ⁻¹¹ ×0.63	b
LIMO + NO3 = NLIMO2B	1.2×10 ⁻¹¹ ×0.34	b
LIMO + NO3 = NLIMO2EXO	1.2×10 ⁻¹¹ ×0.03	b
NLIMO2 + HO2 = NLIMOOH	KRO2HO2×0.914	b
NLIMO2 + NO = NLIMO + NO2	KRO2NO	b
NLIMO2 + NO3 = NLIMO + NO2	KRO2NO3	b
NLIMO2 + RO2 => LIMBNO3	9.2×10 ⁻¹⁴ ×0.3	b
NLIMO2 + RO2 = NLIMO	9.2×10 ⁻¹⁴ ×0.7	b
NLIMO2B + HO2 = NLIMOOH	KRO2HO2×0.914	a,b
NLIMO2B + NO = NLIMO + NO2	KRO2NO	a,b
NLIMO2B + NO3 = NLIMO + NO2	KRO2NO3	a,b
NLIMO2B + RO2 = LIMBNO3	8.8×10 ⁻¹³ ×0.2	a,b
NLIMO2B + RO2 = C10H15NO4	8.8×10 ⁻¹³ ×0.2	a,b
NLIMO2B + RO2 = NLIMO	8.8×10 ⁻¹³ ×0.6	a,b
NLIMO2B = C10H16NO7RO2	0.02	a,b
NLIMO2EXO + HO2 = NLIMOOHEXO	KRO2HO2×0.914	a,b
NLIMO2EXO + NO = NLIMOEXO + NO2	KRO2NO	a,b
NLIMO2EXO + NO3 = NLIMOEXO + NO2	KRO2NO3	a,b
NLIMO2EXO + RO2 = NLIMOEXO	9.2×10 ⁻¹⁴ ×0.7	a,b
NLIMO2EXO = C10H16NO7RO2	20	a,c
NLIMOEXO = C10H16NO6RO2	KDEC×0.5	a,b,d
NLIMOOH + OH = NLIMO2	4.3×10 ⁻¹¹	a,b
NLIMOOH + hv = NLIMO + OH	J<41>	a,b
NLIMOOHEXO + OH = NLIMO2EXO	4.3×10 ⁻¹¹	a,b
NLIMOOHEXO + hv = NLIMOEXO + OH	J<41>	a,b
NLIMO = LIMAL + NO2	KDEC×0.92	b

NLIMO = C10H16NO6RO2	KDEC×0.08	b
LIMAL + NO3 = C923CO3 + HNO3	1.1×10 ⁻¹⁰ ×0.092	b
LIMAL + OH = C923CO3	1.1×10 ⁻¹⁰ ×0.288	b
LIMBCO + OH = C923CO3	6.7×10 ⁻¹¹	b
LIMBCO + NO3 = C10H16NO7RO2	2.6×10 ⁻¹³	b
C923CO3 + HO2 = C923CO3H	KAPHO2×0.41	b
C923CO3 + HO2 = LIMNONIC + O3	KAPHO2×0.15	b
C923CO3 + RO2 = LIMNONIC	1.0×10 ⁻¹⁰ ×0.3	b
C923CO3H + NO3 = C10H16NO9RO2	2.6×10 ⁻¹³	b
LIMNONIC + NO3 = C10H16NO8RO2	2.6×10 ⁻¹³	b
LIMALAOH + NO3 = C10H16NO8RO2	2.6×10 ⁻¹³	b
LIMALACO + NO3 => C10H14NO8RO2	2.6×10 ⁻¹³	b
LIMALAOOH + NO3 = C10H16NO9RO2	2.6×10 ⁻¹³	b
LIMALBOH + NO3 = C10H16NO8RO2	2.6×10 ⁻¹³	b
LIMALBCO + NO3 => C10H14NO8RO2	2.6×10 ⁻¹³	b
LIMALBOOH + NO3 = C10H16NO9RO2	2.6×10 ⁻¹³	b
C10H16NO6RO2 + HO2 = C10H17NO6	KRO2HO2×0.914	b
C10H16NO6RO2 + NO = C10H16NO5RO + NO2	KRO2NO	b
C10H16NO6RO2 + NO3 = C10H16NO5RO + NO2	KRO2NO3	b
C10H16NO6RO2 + RO2 = C10H17NO5	5.0×10 ⁻¹³ ×0.25	c
C10H16NO6RO2 + RO2 = C10H15NO5	5.0×10 ⁻¹³ ×0.1	c
C10H16NO6RO2 + RO2 = C10H16NO5RO	5.0×10 ⁻¹³ ×0.65	c
C10H16NO6RO2 = C10H16NO8RO2	0.2	c
C10H16NO8RO2 = C10H15NO7 + OH	0.1	c
C10H16NO5RO = C10H15NO5 + HO2	KDEC×0.1	b,d
C10H16NO5RO = C10H16NO7RO2	KDEC×0.5	b,d
C10H16NO7RO2 + HO2 = C10H17NO7	KRO2HO2×0.914	b
C10H16NO7RO2 + NO = C10H16NO6RO + NO2	KRO2NO	b
C10H16NO7RO2 + NO3 = C10H16NO6RO + NO2	KRO2NO3	b
C10H16NO7RO2 + RO2 = C10H17NO6	5.0×10 ⁻¹³ ×0.25	c
C10H16NO7RO2 + RO2 = C10H15NO6	5.0×10 ⁻¹³ ×0.1	c
C10H16NO7RO2 + RO2 = C10H16NO6RO	5.0×10 ⁻¹³ ×0.65	c
C10H16NO7RO2 = C10H16NO9RO2	0.2	c
C10H16NO6RO = C10H15NO6 + HO2	KDEC×0.1	b,d
C10H16NO6RO = C10H16NO8RO2	KDEC×0.5	b,d

$\text{C}_{10}\text{H}_{16}\text{NO}_9\text{RO}_2 = \text{C}_{10}\text{H}_{15}\text{NO}_8 + \text{OH}$	0.1	c
$\text{C}_{10}\text{H}_{14}\text{NO}_8\text{RO}_2 = \text{C}_{10}\text{H}_{13}\text{NO}_7 + \text{OH}$	0.1	c

^aNew short names are given for species not existing in MCM. ^bRate constants refer to Master Chemical Mechanism (MCM). ^cRate constants refer to recent studies (Mayorga et al., 2022). ^dThe branching ratios are estimated from recent studies (Mayorga et al., 2022).

Table S3. Summary of vapor pressures of highly oxygenated limonene-derived ON calculated by two methods under standard conditions (298 K).

Species	Vapor pressure (atm)	
	EVAPORATION	SIMPOL1
$C_{10}H_{13}NO_7$	1.4×10^{-7}	1.7×10^{-7}
$C_{10}H_{15}NO_4$	1.1×10^{-6}	1.7×10^{-6}
$C_{10}H_{15}NO_5$	2.7×10^{-7}	6.2×10^{-8}
$C_{10}H_{15}NO_6$	3.5×10^{-8}	2.7×10^{-8}
$C_{10}H_{15}NO_7$	2.3×10^{-8}	5.5×10^{-8}
$C_{10}H_{15}NO_8$	7.9×10^{-10}	3.6×10^{-10}
$C_{10}H_{17}NO_5$	1.5×10^{-8}	4.8×10^{-8}
$C_{10}H_{17}NO_6$	6.6×10^{-9}	8.4×10^{-9}
$C_{10}H_{17}NO_7$	2.6×10^{-9}	3.3×10^{-8}

303 **Table S4.** Compilation of experiments in chemical box model.

Scheme	Initial concentration of species (cm ⁻³)									Description
	LIMO	OH	O ₃	NO ₃	NO	CO	SO ₂	HO ₂	H ₂ O	
OH	1.0×10 ¹¹	1.0×10 ⁵ ~1.0×10 ¹⁹	0.0	1.0×10 ¹²	1.0×10 ¹²	0.0	0.0	1.0×10 ¹¹	0.0	Limonene-derived ON formation under individual initial oxidation pathway
O ₃	1.0×10 ¹¹	1.0×10 ¹⁰	1.0×10 ¹¹ ~1.0×10 ¹⁸	1.0×10 ¹²	1.0×10 ¹²	1.0×10 ¹⁴	1.0×10 ¹⁰	1.0×10 ¹¹	1.0×10 ¹⁶	
NO ₃	1.0×10 ¹¹	1.0×10 ¹⁰	0.0	1.0×10 ⁹ ~1.0×10 ¹⁷	1.0×10 ¹²	0.0	0.0	1.0×10 ¹¹	0.0	
OH+O ₃	1.0×10 ¹¹	0.0/1.0×10 ⁵ /1.0×10 ¹¹ /1.0×10 ¹⁹	0.0/1.0×10 ¹¹ /1.0×10 ¹⁵ /1.0×10 ¹⁸	1.0×10 ¹²	1.0×10 ¹²	1.0×10 ¹⁴	1.0×10 ¹⁰	1.0×10 ¹¹	1.0×10 ¹⁶	Limonene-derived ON formation under multiple initial oxidation pathways
OH+NO ₃	1.0×10 ¹¹	0.0/1.0×10 ⁵ /1.0×10 ¹¹ /1.0×10 ¹⁹	0.0	0.0/1.0×10 ⁹ /1.0×10 ¹³ /1.0×10 ¹⁷	1.0×10 ¹²	0.0	0.0	1.0×10 ¹¹	0.0	
O ₃ +NO ₃	1.0×10 ¹¹	1.0×10 ¹⁰	0.0/1.0×10 ¹¹ /1.0×10 ¹⁵ /1.0×10 ¹⁸	0.0/1.0×10 ⁹ /1.0×10 ¹³ /1.0×10 ¹⁷	1.0×10 ¹²	1.0×10 ¹⁴	1.0×10 ¹⁰	1.0×10 ¹¹	1.0×10 ¹⁶	
OH+O ₃ +NO ₃	1.0×10 ¹¹	0.0/1.0×10 ⁵ /1.0×10 ¹¹ /1.0×10 ¹⁹	0.0/1.0×10 ¹¹ /1.0×10 ¹⁵ /1.0×10 ¹⁸	0.0/1.0×10 ⁹ /1.0×10 ¹³ /1.0×10 ¹⁷	1.0×10 ¹²	1.0×10 ¹⁴	1.0×10 ¹⁰	1.0×10 ¹¹	1.0×10 ¹⁶	

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305 **Table S5.** Initial concentrations of species used in chemical box model experiments.

Scheme	Species (cm ⁻³)								
	LIMO	OH	O ₃	NO ₃	NO	CO	SO ₂	HO ₂	H ₂ O
OH	1.0×10 ¹¹	1.0×10 ⁵	0.0	1.0×10 ¹²	1.0×10 ¹²	0.0	0.0	1.0×10 ¹¹	0.0
	1.0×10 ¹¹	1.0×10 ⁷	0.0	1.0×10 ¹²	1.0×10 ¹²	0.0	0.0	1.0×10 ¹¹	0.0
	1.0×10 ¹¹	1.0×10 ⁹	0.0	1.0×10 ¹²	1.0×10 ¹²	0.0	0.0	1.0×10 ¹¹	0.0
	1.0×10 ¹¹	1.0×10 ¹¹	0.0	1.0×10 ¹²	1.0×10 ¹²	0.0	0.0	1.0×10 ¹¹	0.0
	1.0×10 ¹¹	1.0×10 ¹³	0.0	1.0×10 ¹²	1.0×10 ¹²	0.0	0.0	1.0×10 ¹¹	0.0
	1.0×10 ¹¹	1.0×10 ¹⁵	0.0	1.0×10 ¹²	1.0×10 ¹²	0.0	0.0	1.0×10 ¹¹	0.0
	1.0×10 ¹¹	1.0×10 ¹⁷	0.0	1.0×10 ¹²	1.0×10 ¹²	0.0	0.0	1.0×10 ¹¹	0.0
	1.0×10 ¹¹	1.0×10 ¹⁹	0.0	1.0×10 ¹²	1.0×10 ¹²	0.0	0.0	1.0×10 ¹¹	0.0
O ₃	1.0×10 ¹¹	1.0×10 ¹⁰	1.0×10 ¹¹	1.0×10 ¹²	1.0×10 ¹²	1.0×10 ¹⁴	1.0×10 ¹⁰	1.0×10 ¹¹	1.0×10 ¹⁶
	1.0×10 ¹¹	1.0×10 ¹⁰	1.0×10 ¹²	1.0×10 ¹²	1.0×10 ¹²	1.0×10 ¹⁴	1.0×10 ¹⁰	1.0×10 ¹¹	1.0×10 ¹⁶
	1.0×10 ¹¹	1.0×10 ¹⁰	1.0×10 ¹³	1.0×10 ¹²	1.0×10 ¹²	1.0×10 ¹⁴	1.0×10 ¹⁰	1.0×10 ¹¹	1.0×10 ¹⁶
	1.0×10 ¹¹	1.0×10 ¹⁰	1.0×10 ¹⁴	1.0×10 ¹²	1.0×10 ¹²	1.0×10 ¹⁴	1.0×10 ¹⁰	1.0×10 ¹¹	1.0×10 ¹⁶
	1.0×10 ¹¹	1.0×10 ¹⁰	1.0×10 ¹⁵	1.0×10 ¹²	1.0×10 ¹²	1.0×10 ¹⁴	1.0×10 ¹⁰	1.0×10 ¹¹	1.0×10 ¹⁶
	1.0×10 ¹¹	1.0×10 ¹⁰	1.0×10 ¹⁶	1.0×10 ¹²	1.0×10 ¹²	1.0×10 ¹⁴	1.0×10 ¹⁰	1.0×10 ¹¹	1.0×10 ¹⁶
	1.0×10 ¹¹	1.0×10 ¹⁰	1.0×10 ¹⁷	1.0×10 ¹²	1.0×10 ¹²	1.0×10 ¹⁴	1.0×10 ¹⁰	1.0×10 ¹¹	1.0×10 ¹⁶
	1.0×10 ¹¹	1.0×10 ¹⁰	1.0×10 ¹⁸	1.0×10 ¹²	1.0×10 ¹²	1.0×10 ¹⁴	1.0×10 ¹⁰	1.0×10 ¹¹	1.0×10 ¹⁶
NO ₃	1.0×10 ¹¹	1.0×10 ¹⁰	0.0	1.0×10 ⁹	1.0×10 ¹²	0.0	0.0	1.0×10 ¹¹	0.0
	1.0×10 ¹¹	1.0×10 ¹⁰	0.0	1.0×10 ¹⁰	1.0×10 ¹²	0.0	0.0	1.0×10 ¹¹	0.0
	1.0×10 ¹¹	1.0×10 ¹⁰	0.0	1.0×10 ¹¹	1.0×10 ¹²	0.0	0.0	1.0×10 ¹¹	0.0
	1.0×10 ¹¹	1.0×10 ¹⁰	0.0	1.0×10 ¹²	1.0×10 ¹²	0.0	0.0	1.0×10 ¹¹	0.0
	1.0×10 ¹¹	1.0×10 ¹⁰	0.0	1.0×10 ¹³	1.0×10 ¹²	0.0	0.0	1.0×10 ¹¹	0.0
	1.0×10 ¹¹	1.0×10 ¹⁰	0.0	1.0×10 ¹⁴	1.0×10 ¹²	0.0	0.0	1.0×10 ¹¹	0.0
	1.0×10 ¹¹	1.0×10 ¹⁰	0.0	1.0×10 ¹⁵	1.0×10 ¹²	0.0	0.0	1.0×10 ¹¹	0.0
	1.0×10 ¹¹	1.0×10 ¹⁰	0.0	1.0×10 ¹⁶	1.0×10 ¹²	0.0	0.0	1.0×10 ¹¹	0.0
	1.0×10 ¹¹	1.0×10 ¹⁰	0.0	1.0×10 ¹⁷	1.0×10 ¹²	0.0	0.0	1.0×10 ¹¹	0.0
OH + O ₃	1.0×10 ¹¹	1.0×10 ⁵	0.0	1.0×10 ¹²	1.0×10 ¹²	1.0×10 ¹⁴	1.0×10 ¹⁰	1.0×10 ¹¹	1.0×10 ¹⁶
	1.0×10 ¹¹	1.0×10 ¹¹	0.0	1.0×10 ¹²	1.0×10 ¹²	1.0×10 ¹⁴	1.0×10 ¹⁰	1.0×10 ¹¹	1.0×10 ¹⁶

[illegible]

[illegible]

[illegible]

1.0×10^{11}	1.0×10^{19}	1.0×10^{11}	1.0×10^{17}	1.0×10^{12}	1.0×10^{14}	1.0×10^{10}	1.0×10^{11}	1.0×10^{16}
1.0×10^{11}	1.0×10^{19}	1.0×10^{15}	1.0×10^9	1.0×10^{12}	1.0×10^{14}	1.0×10^{10}	1.0×10^{11}	1.0×10^{16}
1.0×10^{11}	1.0×10^{19}	1.0×10^{15}	1.0×10^{13}	1.0×10^{12}	1.0×10^{14}	1.0×10^{10}	1.0×10^{11}	1.0×10^{16}
1.0×10^{11}	1.0×10^{19}	1.0×10^{15}	1.0×10^{17}	1.0×10^{12}	1.0×10^{14}	1.0×10^{10}	1.0×10^{11}	1.0×10^{16}
1.0×10^{11}	1.0×10^{19}	1.0×10^{18}	1.0×10^9	1.0×10^{12}	1.0×10^{14}	1.0×10^{10}	1.0×10^{11}	1.0×10^{16}
1.0×10^{11}	1.0×10^{19}	1.0×10^{18}	1.0×10^{13}	1.0×10^{12}	1.0×10^{14}	1.0×10^{10}	1.0×10^{11}	1.0×10^{16}
1.0×10^{11}	1.0×10^{19}	1.0×10^{18}	1.0×10^{17}	1.0×10^{12}	1.0×10^{14}	1.0×10^{10}	1.0×10^{11}	1.0×10^{16}

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Table S6. Description of global model experiments.

Scheme	Description
Case0	Run with three initial oxidation pathways
Case1	The same as Case0 without OH-initial oxidation pathway
Case2	The same as Case0 without O ₃ -initial oxidation pathway
Case3	The same as Case0 without NO ₃ -initial oxidation pathway
Case4	The same as Case0 without O ₃ and NO ₃ -initial oxidation pathways
Case5	The same as Case0 without OH and NO ₃ -initial oxidation pathways
Case6	The same as Case0 without OH and O ₃ -initial oxidation pathways

Table S7. Estimated reaction rates under two initial oxidation pathway experiments

Test description				Reaction rates ($\text{cm}^{-3}\cdot\text{s}^{-1}$)		
Scheme	Variables (cm^{-3})			R_{OH}	R_{O_3}	R_{NO_3}
	OH	O ₃	NO ₃			
OH + O ₃	1.0×10^5	0.0	/	2.4×10^{10}	4.8×10^4	/
	1.0×10^5	1.0×10^{11}	/	2.3×10^{10}	8.6×10^7	/
	1.0×10^5	1.0×10^{15}	/	1.4×10^{10}	7.9×10^{10}	/
	1.0×10^5	1.0×10^{20}	/	3.2×10^7	1.0×10^{11}	/
	1.0×10^{19}	0.0	/	4.4×10^{10}	1.4×10^5	/
	1.0×10^{19}	1.0×10^{11}	/	4.4×10^{10}	6.3×10^7	/
	1.0×10^{19}	1.0×10^{15}	/	1.9×10^{10}	7.5×10^{10}	/
	1.0×10^{19}	1.0×10^{20}	/	4.1×10^7	1.0×10^{11}	/
	1.0×10^{35}	0.0	/	1.0×10^{11}	3.3×10^6	/
	1.0×10^{35}	1.0×10^{11}	/	1.0×10^{11}	3.3×10^6	/
	1.0×10^{35}	1.0×10^{15}	/	1.0×10^{11}	3.3×10^6	/
	1.0×10^{35}	1.0×10^{20}	/	1.0×10^{11}	7.6×10^6	/
OH + NO ₃	1.0×10^5	/	0.0	5.4×10^{10}	/	2.4×10^5
	1.0×10^5	/	1.0×10^9	5.4×10^{10}	/	2.5×10^7
	1.0×10^5	/	1.0×10^{13}	4.9×10^8	/	9.9×10^{10}
	1.0×10^5	/	1.0×10^{18}	2.0×10^4	/	1.0×10^{11}
	1.0×10^{19}	/	0.0	7.4×10^{10}	/	1.1×10^6
	1.0×10^{19}	/	1.0×10^9	7.4×10^{10}	/	1.7×10^7
	1.0×10^{19}	/	1.0×10^{13}	9.7×10^8	/	9.9×10^{10}
	1.0×10^{19}	/	1.0×10^{18}	3.5×10^4	/	1.0×10^{11}
	1.0×10^{35}	/	0.0	1.0×10^{11}	/	1.5×10^6
	1.0×10^{35}	/	1.0×10^9	1.0×10^{11}	/	1.5×10^6
	1.0×10^{35}	/	1.0×10^{13}	1.0×10^{11}	/	1.5×10^6
	1.0×10^{35}	/	1.0×10^{18}	9.8×10^{10}	/	2.1×10^9
O ₃ + OH	0.0	1.0×10^{11}	/	2.3×10^{10}	8.6×10^7	/
	1.0×10^5	1.0×10^{11}	/	2.3×10^{10}	8.6×10^7	/

	1.0×10^{19}	1.0×10^{11}	/	4.4×10^{10}	6.3×10^7	/
	1.0×10^{35}	1.0×10^{11}	/	1.0×10^{11}	3.3×10^6	/
	0.0	1.0×10^{15}	/	1.4×10^{10}	7.9×10^{10}	/
	1.0×10^5	1.0×10^{15}	/	1.4×10^{10}	7.9×10^{10}	/
	1.0×10^{19}	1.0×10^{15}	/	1.9×10^{10}	7.5×10^{10}	/
	1.0×10^{35}	1.0×10^{15}	/	1.0×10^{11}	3.3×10^6	/
	0.0	1.0×10^{20}	/	3.2×10^7	1.0×10^{11}	/
	1.0×10^5	1.0×10^{20}	/	3.2×10^7	1.0×10^{11}	/
	1.0×10^{19}	1.0×10^{20}	/	4.1×10^7	1.0×10^{11}	/
	1.0×10^{35}	1.0×10^{20}	/	1.0×10^{11}	7.6×10^6	/
O ₃ + NO ₃	/	1.0×10^{11}	0.0	/	7.8×10^7	1.0×10^7
	/	1.0×10^{11}	1.0×10^9	/	7.7×10^7	8.8×10^7
	/	1.0×10^{11}	1.0×10^{13}	/	1.1×10^5	1.0×10^{11}
	/	1.0×10^{11}	1.0×10^{18}	/	3.4×10^2	1.0×10^{11}
	/	1.0×10^{15}	0.0	/	3.3×10^{10}	6.5×10^{10}
	/	1.0×10^{15}	1.0×10^9	/	3.3×10^{10}	6.5×10^{10}
	/	1.0×10^{15}	1.0×10^{13}	/	1.0×10^9	9.9×10^{10}
	/	1.0×10^{15}	1.0×10^{18}	/	1.3×10^6	1.0×10^{11}
	/	1.0×10^{20}	0.0	/	8.4×10^{10}	1.6×10^{10}
	/	1.0×10^{20}	1.0×10^9	/	8.4×10^{10}	1.6×10^{10}
	/	1.0×10^{20}	1.0×10^{13}	/	7.0×10^{10}	3.0×10^{10}
	/	1.0×10^{20}	1.0×10^{18}	/	1.2×10^9	9.9×10^{10}
NO ₃ + OH	0.0	/	1.0×10^9	5.4×10^{10}	/	2.5×10^7
	1.0×10^5	/	1.0×10^9	5.4×10^{10}	/	2.5×10^7
	1.0×10^{19}	/	1.0×10^9	7.4×10^{10}	/	1.7×10^7
	1.0×10^{35}	/	1.0×10^9	1.0×10^{11}	/	1.5×10^6
	0.0	/	1.0×10^{13}	4.9×10^8	/	9.9×10^{10}
	1.0×10^5	/	1.0×10^{13}	4.9×10^8	/	9.9×10^{10}
	1.0×10^{19}	/	1.0×10^{13}	9.7×10^8	/	9.9×10^{10}
	1.0×10^{35}	/	1.0×10^{13}	1.0×10^{11}	/	1.5×10^6

	0.0	/	1.0×10^{18}	2.0×10^4	/	1.0×10^{11}
	1.0×10^5	/	1.0×10^{18}	2.0×10^4	/	1.0×10^{11}
	1.0×10^{19}	/	1.0×10^{18}	3.5×10^4	/	1.0×10^{11}
	1.0×10^{35}	/	1.0×10^{18}	9.8×10^{10}	/	2.0×10^9
NO ₃ + O ₃	/	0.0	1.0×10^9	/	4.2×10^3	8.0×10^7
	/	1.0×10^{11}	1.0×10^9	/	7.7×10^7	8.8×10^7
	/	1.0×10^{15}	1.0×10^9	/	3.3×10^{10}	6.5×10^{10}
	/	1.0×10^{20}	1.0×10^9	/	8.4×10^{10}	1.6×10^{10}
	/	0.0	1.0×10^{13}		1.1×10^3	1.0×10^{11}
	/	1.0×10^{11}	1.0×10^{13}	/	1.1×10^5	1.0×10^{11}
	/	1.0×10^{15}	1.0×10^{13}	/	1.0×10^9	9.9×10^{10}
	/	1.0×10^{20}	1.0×10^{13}	/	7.0×10^{10}	3.0×10^{10}
	/	0.0	1.0×10^{18}	/	1.9×10^{-1}	1.0×10^{11}
	/	1.0×10^{11}	1.0×10^{18}	/	3.4×10^2	1.0×10^{11}
	/	1.0×10^{15}	1.0×10^{18}	/	1.3×10^6	1.0×10^{11}
	/	1.0×10^{20}	1.0×10^{18}	/	1.2×10^9	9.9×10^{10}

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Table S8. Estimated reaction rates under three initial oxidation pathway experiments.

Test description				Reaction rates ($\cdot\text{cm}^{-3}\cdot\text{s}^{-1}$)		
Scheme	Variables (molecum^{-3})			R_{OH}	R_{O_3}	R_{NO_3}
	OH	O_3	NO_3			
The influence of OH-initiated oxidation pathway	0.0	1.0×10^{11}	1.0×10^9	5.2×10^{10}	3.5×10^7	3.7×10^7
	1.0×10^5	1.0×10^{11}	1.0×10^9	5.2×10^{10}	3.5×10^7	3.7×10^7
	1.0×10^{11}	1.0×10^{11}	1.0×10^9	7.0×10^{10}	2.5×10^7	3.6×10^7
	1.0×10^{19}	1.0×10^{11}	1.0×10^9	1.0×10^{11}	3.3×10^6	1.4×10^6
	0.0	1.0×10^{15}	1.0×10^9	2.6×10^9	3.1×10^{10}	6.3×10^{10}
	1.0×10^5	1.0×10^{15}	1.0×10^9	2.6×10^9	3.1×10^{10}	6.3×10^{10}
	1.0×10^{11}	1.0×10^{15}	1.0×10^9	5.0×10^9	3.2×10^{10}	6.1×10^{10}
	1.0×10^{19}	1.0×10^{15}	1.0×10^9	1.0×10^{11}	3.3×10^6	2.6×10^5
	0.0	1.0×10^{18}	1.0×10^9	2.5×10^7	8.5×10^{10}	1.6×10^{10}
	1.0×10^5	1.0×10^{18}	1.0×10^9	2.5×10^7	8.5×10^{10}	1.6×10^{10}
	1.0×10^{11}	1.0×10^{18}	1.0×10^9	3.1×10^7	8.0×10^{10}	2.0×10^{10}
	1.0×10^{19}	1.0×10^{18}	1.0×10^9	1.0×10^{11}	7.6×10^6	1.5×10^6
	0.0	1.0×10^{11}	1.0×10^{13}	4.0×10^8	1.1×10^5	1.0×10^{11}
	1.0×10^5	1.0×10^{11}	1.0×10^{13}	4.0×10^8	1.1×10^5	1.0×10^{11}
	1.0×10^{11}	1.0×10^{11}	1.0×10^{13}	7.2×10^8	1.4×10^5	9.9×10^{10}
	1.0×10^{19}	1.0×10^{11}	1.0×10^{13}	1.0×10^{11}	3.3×10^6	1.4×10^6
	0.0	1.0×10^{15}	1.0×10^{13}	2.9×10^8	9.9×10^8	9.9×10^{10}
	1.0×10^5	1.0×10^{15}	1.0×10^{13}	2.9×10^8	9.9×10^8	9.9×10^{10}
	1.0×10^{11}	1.0×10^{15}	1.0×10^{13}	5.3×10^8	1.4×10^9	9.8×10^{10}
	1.0×10^{19}	1.0×10^{15}	1.0×10^{13}	1.0×10^{11}	3.3×10^6	3.0×10^5
	0.0	1.0×10^{18}	1.0×10^{13}	2.0×10^7	7.0×10^{10}	3.0×10^{10}
	1.0×10^5	1.0×10^{18}	1.0×10^{13}	2.0×10^7	7.0×10^{10}	3.0×10^{10}
	1.0×10^{11}	1.0×10^{18}	1.0×10^{13}	2.7×10^7	7.0×10^{10}	3.0×10^{10}
	1.0×10^{19}	1.0×10^{18}	1.0×10^{13}	1.0×10^{11}	7.6×10^6	1.6×10^6
	0.0	1.0×10^{11}	1.0×10^{17}	2.0×10^4	3.4×10^2	1.0×10^{11}
	1.0×10^5	1.0×10^{11}	1.0×10^{17}	2.0×10^4	3.4×10^2	1.0×10^{11}

		1.0×10^{11}	1.0×10^{11}	1.0×10^{17}	3.5×10^4	3.1×10^2	1.0×10^{11}
		1.0×10^{19}	1.0×10^{11}	1.0×10^{17}	9.8×10^{10}	3.2×10^6	2.0×10^9
		0.0	1.0×10^{15}	1.0×10^{17}	7.7×10^3	1.3×10^6	1.0×10^{11}
		1.0×10^5	1.0×10^{15}	1.0×10^{17}	7.7×10^3	1.3×10^6	1.0×10^{11}
		1.0×10^{11}	1.0×10^{15}	1.0×10^{17}	1.5×10^4	1.3×10^6	1.0×10^{11}
		1.0×10^{19}	1.0×10^{15}	1.0×10^{17}	9.8×10^{10}	3.2×10^6	2.0×10^9
		0.0	1.0×10^{18}	1.0×10^{17}	6.6×10^3	1.2×10^9	9.9×10^{10}
		1.0×10^5	1.0×10^{18}	1.0×10^{17}	6.6×10^3	1.2×10^9	9.9×10^{10}
		1.0×10^{11}	1.0×10^{18}	1.0×10^{17}	1.3×10^4	1.2×10^9	9.9×10^{10}
		1.0×10^{19}	1.0×10^{18}	1.0×10^{17}	9.7×10^{10}	1.4×10^7	2.9×10^9
The influence of O ₃ -initiated oxidation pathway	1.0×10^5	0.0	1.0×10^9	5.2×10^{10}	7.6×10^4	3.3×10^7	
	1.0×10^5	1.0×10^{11}	1.0×10^9	5.2×10^{10}	3.5×10^7	3.7×10^7	
	1.0×10^5	1.0×10^{15}	1.0×10^9	2.6×10^9	3.1×10^{10}	6.3×10^{10}	
	1.0×10^5	1.0×10^{20}	1.0×10^9	2.5×10^7	8.5×10^{10}	1.5×10^{10}	
	1.0×10^{11}	0.0	1.0×10^9	7.0×10^{10}	1.6×10^5	3.3×10^7	
	1.0×10^{11}	1.0×10^{11}	1.0×10^9	7.0×10^{10}	2.5×10^7	3.6×10^7	
	1.0×10^{11}	1.0×10^{15}	1.0×10^9	5.0×10^9	3.2×10^{10}	6.1×10^{10}	
	1.0×10^{11}	1.0×10^{20}	1.0×10^9	3.1×10^7	8.0×10^{10}	2.0×10^{10}	
	1.0×10^{19}	0.0	1.0×10^9	1.0×10^{11}	3.3×10^6	1.5×10^6	
	1.0×10^{19}	1.0×10^{11}	1.0×10^9	1.0×10^{11}	3.3×10^6	1.4×10^6	
	1.0×10^{19}	1.0×10^{15}	1.0×10^9	1.0×10^{11}	3.3×10^6	2.6×10^5	
	1.0×10^{19}	1.0×10^{20}	1.0×10^9	1.0×10^{11}	7.6×10^6	1.5×10^6	
	1.0×10^5	0.0	1.0×10^{13}	3.9×10^8	1.0×10^3	1.0×10^{11}	
	1.0×10^5	1.0×10^{11}	1.0×10^{13}	4.0×10^8	1.1×10^5	1.0×10^{11}	
	1.0×10^5	1.0×10^{15}	1.0×10^{13}	2.9×10^8	9.9×10^8	9.9×10^{10}	
	1.0×10^5	1.0×10^{20}	1.0×10^{13}	2.0×10^7	7.0×10^{10}	3.0×10^{10}	
	1.0×10^{11}	0.0	1.0×10^{13}	7.1×10^8	1.7×10^3	9.9×10^{10}	
	1.0×10^{11}	1.0×10^{11}	1.0×10^{13}	7.2×10^8	1.4×10^5	9.9×10^{10}	
	1.0×10^{11}	1.0×10^{15}	1.0×10^{13}	5.3×10^8	1.4×10^9	9.8×10^{10}	
	1.0×10^{11}	1.0×10^{20}	1.0×10^{13}	2.7×10^7	7.0×10^{10}	3.0×10^{10}	

	1.0×10^{19}	0.0	1.0×10^{13}	1.0×10^{11}	3.3×10^6	1.5×10^6
	1.0×10^{19}	1.0×10^{11}	1.0×10^{13}	1.0×10^{11}	3.3×10^6	1.4×10^6
	1.0×10^{19}	1.0×10^{15}	1.0×10^{13}	1.0×10^{11}	3.3×10^6	3.0×10^5
	1.0×10^{19}	1.0×10^{20}	1.0×10^{13}	1.0×10^{11}	7.6×10^6	1.6×10^6
	1.0×10^5	0.0	1.0×10^{18}	2.0×10^4	1.8×10^{-1}	1.0×10^{11}
	1.0×10^5	1.0×10^{11}	1.0×10^{18}	2.0×10^4	3.4×10^2	1.0×10^{11}
	1.0×10^5	1.0×10^{15}	1.0×10^{18}	7.7×10^3	1.3×10^6	1.0×10^{11}
	1.0×10^5	1.0×10^{20}	1.0×10^{18}	6.6×10^3	1.2×10^9	9.9×10^{10}
	1.0×10^{11}	0.0	1.0×10^{18}	3.5×10^4	2.9×10^{-1}	1.0×10^{11}
	1.0×10^{11}	1.0×10^{11}	1.0×10^{18}	3.5×10^4	3.1×10^2	1.0×10^{11}
	1.0×10^{11}	1.0×10^{15}	1.0×10^{18}	1.5×10^4	1.3×10^6	1.0×10^{11}
	1.0×10^{11}	1.0×10^{20}	1.0×10^{18}	1.3×10^4	1.2×10^9	9.9×10^{10}
	1.0×10^{19}	0.0	1.0×10^{18}	9.8×10^{10}	3.2×10^6	2.0×10^9
	1.0×10^{19}	1.0×10^{11}	1.0×10^{18}	9.8×10^{10}	3.2×10^6	2.0×10^9
	1.0×10^{19}	1.0×10^{15}	1.0×10^{18}	9.8×10^{10}	3.2×10^6	2.0×10^9
	1.0×10^{19}	1.0×10^{20}	1.0×10^{18}	9.7×10^{10}	1.4×10^7	2.9×10^9
The influence of NO ₃ -initiated oxidation pathway	1.0×10^5	1.0×10^{11}	0.0	5.2×10^{10}	3.5×10^7	2.0×10^6
	1.0×10^5	1.0×10^{11}	1.0×10^9	5.2×10^{10}	3.5×10^7	3.7×10^7
	1.0×10^5	1.0×10^{11}	1.0×10^{13}	4.0×10^8	1.1×10^5	1.0×10^{11}
	1.0×10^5	1.0×10^{11}	1.0×10^{18}	2.0×10^4	3.4×10^2	1.0×10^{11}
	1.0×10^{19}	1.0×10^{11}	0.0	7.0×10^{10}	2.5×10^7	5.6×10^6
	1.0×10^{19}	1.0×10^{11}	1.0×10^9	7.0×10^{10}	2.5×10^7	3.6×10^7
	1.0×10^{19}	1.0×10^{11}	1.0×10^{13}	7.2×10^8	1.4×10^5	9.9×10^{10}
	1.0×10^{19}	1.0×10^{11}	1.0×10^{18}	3.5×10^4	3.1×10^2	1.0×10^{11}
	1.0×10^{35}	1.0×10^{11}	0.0	1.0×10^{11}	3.3×10^6	1.4×10^6
	1.0×10^{35}	1.0×10^{11}	1.0×10^9	1.0×10^{11}	3.3×10^6	1.4×10^6
	1.0×10^{35}	1.0×10^{11}	1.0×10^{13}	1.0×10^{11}	3.3×10^6	1.4×10^6
	1.0×10^{35}	1.0×10^{11}	1.0×10^{18}	9.8×10^{10}	3.2×10^6	2.0×10^9
	1.0×10^5	1.0×10^{15}	0.0	2.6×10^9	3.1×10^{10}	6.3×10^{10}
	1.0×10^5	1.0×10^{15}	1.0×10^9	2.6×10^9	3.1×10^{10}	6.3×10^{10}

1.0×10^5	1.0×10^{15}	1.0×10^{13}	2.9×10^8	9.9×10^8	9.9×10^{10}
1.0×10^5	1.0×10^{15}	1.0×10^{18}	7.7×10^3	1.3×10^6	1.0×10^{11}
1.0×10^{19}	1.0×10^{15}	0.0	5.0×10^9	3.2×10^{10}	6.0×10^{10}
1.0×10^{19}	1.0×10^{15}	1.0×10^9	5.0×10^9	3.2×10^{10}	6.1×10^{10}
1.0×10^{19}	1.0×10^{15}	1.0×10^{13}	5.3×10^8	1.4×10^9	9.8×10^{10}
1.0×10^{19}	1.0×10^{15}	1.0×10^{18}	1.5×10^4	1.3×10^6	1.0×10^{11}
1.0×10^{35}	1.0×10^{15}	0.0	1.0×10^{11}	3.3×10^6	2.6×10^5
1.0×10^{35}	1.0×10^{15}	1.0×10^9	1.0×10^{11}	3.3×10^6	2.6×10^5
1.0×10^{35}	1.0×10^{15}	1.0×10^{13}	1.0×10^{11}	3.3×10^6	3.0×10^5
1.0×10^{35}	1.0×10^{15}	1.0×10^{18}	9.8×10^{10}	3.2×10^6	2.0×10^9
1.0×10^5	1.0×10^{20}	0.0	2.5×10^7	8.5×10^{10}	1.5×10^{10}
1.0×10^5	1.0×10^{20}	1.0×10^9	2.5×10^7	8.5×10^{10}	1.5×10^{10}
1.0×10^5	1.0×10^{20}	1.0×10^{13}	2.0×10^7	7.0×10^{10}	3.0×10^{10}
1.0×10^5	1.0×10^{20}	1.0×10^{18}	6.6×10^3	1.2×10^9	9.9×10^{10}
1.0×10^{19}	1.0×10^{20}	0.0	3.1×10^7	8.0×10^{10}	2.0×10^{10}
1.0×10^{19}	1.0×10^{20}	1.0×10^9	3.1×10^7	8.0×10^{10}	2.0×10^{10}
1.0×10^{19}	1.0×10^{20}	1.0×10^{13}	2.7×10^7	7.0×10^{10}	3.0×10^{10}
1.0×10^{19}	1.0×10^{20}	1.0×10^{18}	1.3×10^4	1.2×10^9	9.9×10^{10}
1.0×10^{35}	1.0×10^{20}	0.0	1.0×10^{11}	7.6×10^6	1.5×10^6
1.0×10^{35}	1.0×10^{20}	1.0×10^9	1.0×10^{11}	7.6×10^6	1.5×10^6
1.0×10^{35}	1.0×10^{20}	1.0×10^{13}	1.0×10^{11}	7.6×10^6	1.6×10^6
1.0×10^{35}	1.0×10^{20}	1.0×10^{18}	9.7×10^{10}	1.5×10^7	2.9×10^9

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374 **Table S9.** Published measurements of atmospheric particulate ON concentrations at surface sites.

Area	Site	Observation period	ON ($\mu\text{g}\cdot\text{m}^{-3}$)	Reference
Urban	Bakersfield, California, USA	15 May - 24 Jun 2010	0.51	(Rollins et al., 2012)
Urban	Bakersfield, California, USA	15 May - 24 Jun 2010	0.46	(Rollins et al., 2013)
Urban	Atlanta, Georgia, USA	May 2012 - Feb 2013	0.7	(Xu et al., 2015)
Urban	San Antonio, Texas, USA	May 2 to 26, 2017	0.17	(Guo et al., 2024)
Urban	Ji'nan, China	Apr 2016	0.26	(Li et al., 2018)
Urban	Shenzhen, China	2005 - 2006	0.51	(Yu et al., 2019)
Urban	Shenzhen, China	Spring	0.5	(Yu et al., 2019)
Urban	Shenzhen, China	Summer	1.4	(Yu et al., 2019)
Urban	Shenzhen, China	Autumn	0.87	(Yu et al., 2019)
Urban	Beijing, China	20 May - 23 Jun 2018, 20 Nov - 25 Dec 2018	3	(Xu et al., 2021)
Urban	Beijing, China	20 May - 23 Jun 2018, 20 Nov - 25 Dec 2018	0.9	(Xu et al., 2021)
Urban	Xi'an, China	29 Oct to 19 Nov, 2020	3.57	(Lin et al., 2021)
Urban	Nanjing, China	Apr 2020	1.22	(Ge et al., 2022)
Urban	Nanjing, China	Jul 2019	0.62	(Ge et al., 2022)
Urban	Nanjing, China	Oct 2019	1.24	(Ge et al., 2022)
Urban	Nanjing, China	Dec	2.91	(Ge et al., 2022)
Urban	Barcelona, Spain	1 - 26 Mar 2009	1.57	(Mohr et al., 2012)
Urban	Helsinki, Finland	9 Jan - 13 Mar 2009	0.46	(Carbone et al., 2014)
Rural	Centreville, Alabama, USA	1 Jun - 15 Jul 2013	0.23	(Xu et al., 2015)
Rural	Yorkville, Georgia, USA	26 Jun - 20 Jul 2013	0.6	(Xu et al., 2015)
Rural	Changping, China	15 May - 23 Jun 2016	0.01	(Wang et al., 2018)
Rural	Xianghe, China	25 Dec 2018 - 13 Jan 2019	2.29	(Huang et al., 2021)
Rural	Xianghe, China	9 Jun to 9 Jul 2013	1.86	(Zhu et al., 2021)
Rural	Xianghe, China	9 Jun to 9 Jul 2013	1.71	(Zhu et al., 2021)
Rural	Gucheng, China	10 Dec 2019 - 13 Jan 2020	6.14	(Xu et al., 2021)
Rural	Wanqingsha, China	1 - 30 Sep, 1 - 26 Nov 2010	0.07	(He et al., 2014)
Rural	Cabauw, Netherlands	May 2008	1.71	(Mensah et al., 2012)

Rural	Cabauw, Netherlands	Mar 2009	1.23	(Mensah et al., 2012)
Rural	Jungfrauoch, Switzerland	30 Apr - 29 May 2008	0.1	(Lanz et al., 2010)
Rural	Melpitz, Germany	23 May - 9 Jun 2008	1.01	(Poulain et al., 2011)
Rural	Melpitz, Germany	16 Sep - 3 Nov 2008	2.39	(Poulain et al., 2011)
Rural	Melpitz, Germany	24 Feb - 27 Mar 2009	2.23	(Poulain et al., 2011)
Rural	Payerne, Swiss	Oct 2008	0.64	(Kiendler-Scharr et al., 2016)
Rural	Payerne, Swiss	Mar 2009	2.29	(Kiendler-Scharr et al., 2016)
Rural	Puijo, Finland	Oct 2008	0.23	(Kiendler-Scharr et al., 2016)
Rural	San Pietro Capofiume, Italy	30 Mar - 20 Apr 2008	3.87	(Saarikoski et al., 2012)
Rural	Po Valley, Italy	Oct 2008	2.41	(Kiendler-Scharr et al., 2016)
Rural	Po Valley, Italy	Mar 2009	3.16	(Kiendler-Scharr et al., 2016)
Rural	Harwell HW/GB36	Oct 2008	2.9	(Kiendler-Scharr et al., 2016)
Rural	Hyytiälä, Finland	Oct 2008	0.29	(Kiendler-Scharr et al., 2016)
Rural	Hyytiälä, Finland	Mar 2009	0.29	(Kiendler-Scharr et al., 2016)
Rural	Kpuszta KPO/HU02	Oct 2008	1.39	(Kiendler-Scharr et al., 2016)
Rural	Montseny, Spain	25 Feb - 26 Mar 2009	3.16	(Minguillón et al., 2011)
Rural	Puy de Dome, France	Oct 2008	0.74	(Freney et al., 2011)
Rural	Puy de Dome, France	Mar 2009	0.51	(Freney et al., 2011)
Forest	Woodland Park, Colorado, USA	Jul - Aug 2011	0.2	(Fry et al., 2014)
Forest	Tuscaloosa, Alabama, USA	1 Jun - 15 Jul 2013	0.8	(Ayres et al., 2015)
Forest	Hyytiälä, Finland	Apr 8 and May 4, 2016	0.32	(Graeffe et al., 2023)
Coastal	Connemara, Ireland	May 2008	0.16	(Dall'osto et al., 2010)
Coastal	Finokalia, Crete, Greece	4 May-8 Jun 2008	0.2	(Pikridas et al., 2010)
Coastal	Finokalia, Crete, Greece	25 Feb - 26 Mar 2009	0.1	(Hildebrandt et al., 2011)

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