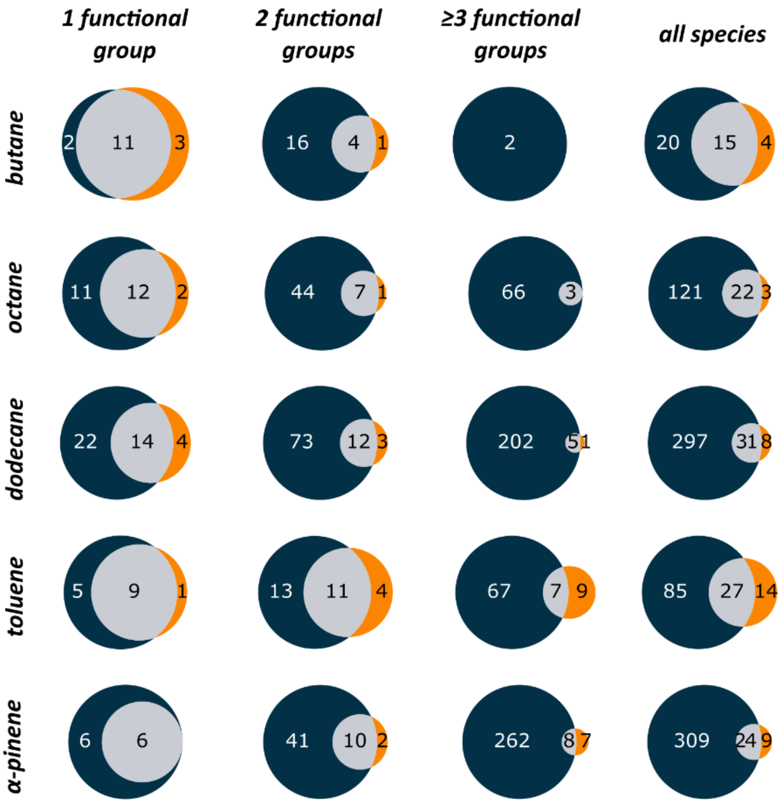

Figure S1: Number of non-radical isomer groups contributing to the carbon budget in the **urban** scenario, partitioned by presence in GECKO-A only, MCM only, or both mechanisms. Left to right panels: monofunctional isomers, bifunctional isomers, polyfunctional isomers (more than two functional groups) and all isomer groups. Top to bottom panels: butane, octane, dodecane, toluene, and α-pinene as parent compounds. Blue: isomer groups present only in GECKO-A; orange: isomer groups present only in MCM; gray: isomer groups common to both mechanisms.

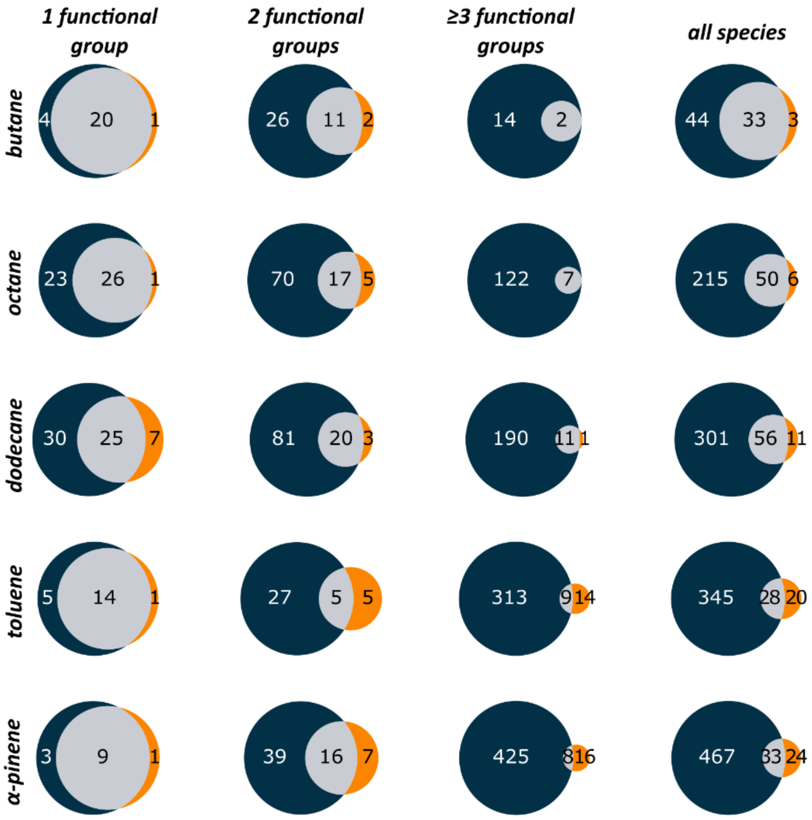

Figure S2: Number of non-radical isomer groups contributing to the carbon budget in the **remote** scenario, partitioned by presence in GECKO-A only, MCM only, or both mechanisms. Left to right panels: monofunctional isomers, bifunctional isomers, polyfunctional isomers (more than two functional groups) and all isomer groups. Top to bottom panels: butane, octane, dodecane, toluene, and α-pinene as parent compounds. Blue: isomer groups present only in GECKO-A; orange: isomer groups present only in MCM; gray: isomer groups common to both mechanisms.

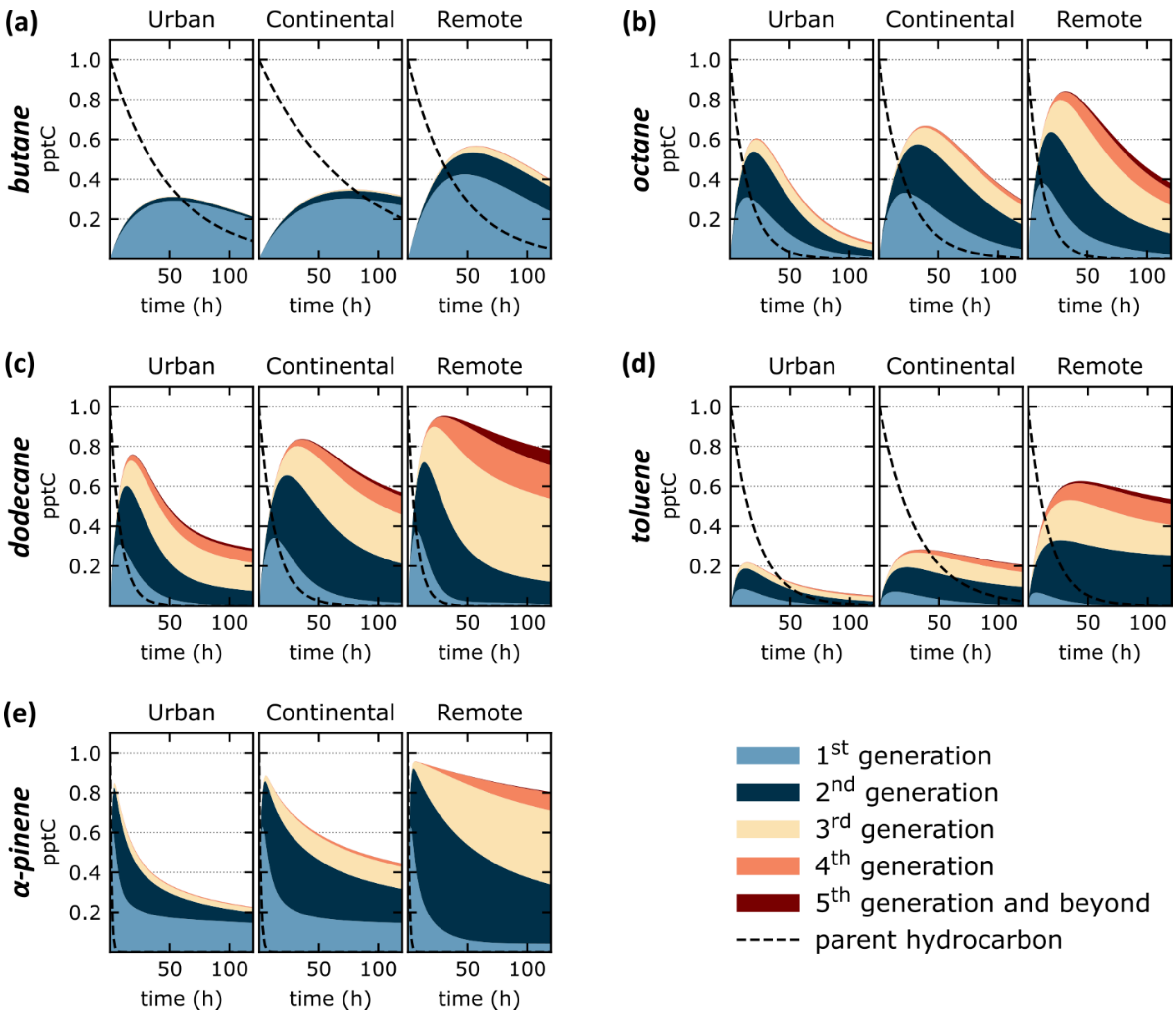

Figure S3: Time evolution of the mixing ratio (pptC) of secondary organic species grouped by generation for various parent hydrocarbons under different environmental scenarios with GECKO-A. Panels (a–e): butane, octane, dodecane, toluene, and α-pinene as parent hydrocarbons, respectively. From left to right in each panel: urban, continental, and remote scenarios. The color indicates the generation of the species.

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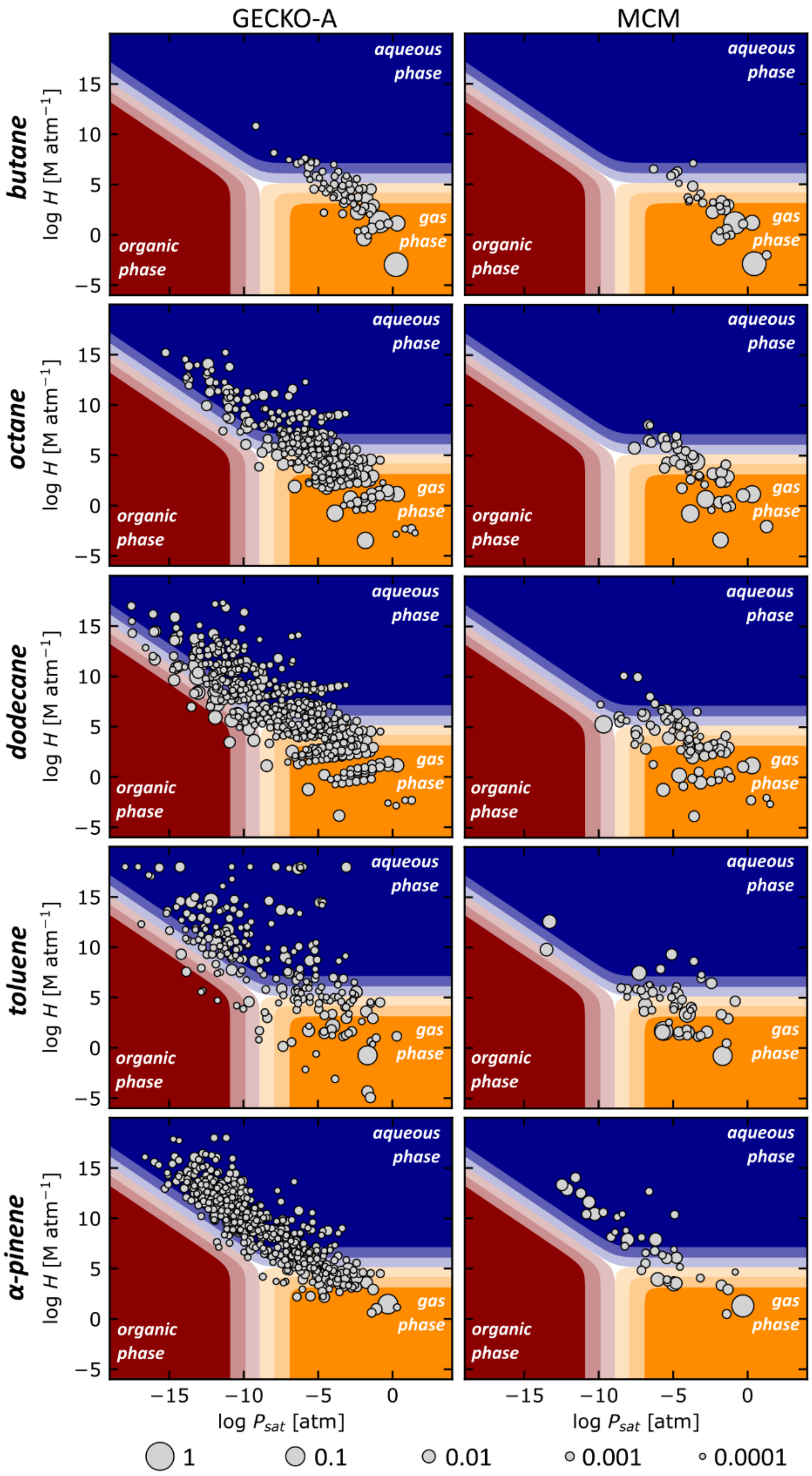

Figure S4: As Figure 15, but for a cloud liquid water environment. Distribution of species from GECKO-A (left column) and MCM (right column) as a function of their saturation vapor pressure and effective Henry's law constant, for the continental scenario after 72 hours of simulation. From top to bottom: butane, octane, dodecane, toluene, and α-pinene as parent compounds. Colored domains indicate the dominant phase of each species at thermodynamic equilibrium: dark, intermediate, and light shades representing partitioning greater than 99%, 90%, and 50% in the respective phase. Domain boundaries are calculated for a mass concentration of 10 µg/m³ in the organic particulate phase and a liquid water mixing ratio $\omega_L = 3 \times 10^{-7}$. Bubble size represents the relative carbon abundance of each species normalized to the initial parent compound.

S5 Thermodynamic phase Partitioning – Boundary lines in the in the phase partitioning space

Let C_g, C_w, and C_o denote the molar concentrations of a species X in the gas phase, aqueous phase, and organic particulate phase, respectively, per liter of air. In what follows, absorption into condensed phases is modeled using a simplified framework: absorption into the organic condensed phase is described by Raoult's law, while absorption into the aqueous phase follows Henry's law. Under these laws, the behavior of species is assumed to be ideal, and the organic and aqueous phases are treated as immiscible.

■ Gas/Aqueous Phase Partitioning

The equilibrium between the gas and aqueous phases for species X is governed by Henry's Law:

$$H = \frac{[X]}{p_X}$$

where H (M.atm^{-1}) is the Henry's law coefficient, $[X]$ is the aqueous-phase concentration of X (in M), p_X is its partial pressure (in atm). Introducing ω_L, the liquid water mixing ratio (volume of liquid water per volume of air), and expressing p_X using the ideal gas law, the phase partitioning ratio is given by:

$$\frac{C_w}{C_g} = HRT\omega_L$$

where R is the ideal gas constant ($R = 0.082$ L atm K^{-1} mol^{-1}).

The Henry's law constant at equipartition ($C_w/C_g = 1$) is:

$$H^{(g:w)} = \frac{1}{RT\omega_L}$$

■ Gas/Organic Particulate Phase Partitioning

The equilibrium between the gas and organic particulate phases follows Raoult's Law:

$$p_X = x_X^o \cdot p_{sat}$$

where x_X^o is the mole fraction of X in the organic phase, and p_{sat} is its saturation vapor pressure. Given C_{OA} as the mass concentration of organic particulate matter (µg/m³) and M_{OA} as the average molar mass (g/mol) of its constituents, the mole fraction is: $x_X^o = 10^{-9}\ C_O(M_{OA}/C_{OA})$ where the factor 10^{-9} accounts for unit conversions. Expressing p_X using the ideal gas law, the phase partitioning ratio is:

$$\frac{C_o}{C_g} = \frac{10^{-9}C_{OA}}{M_{OA}} \cdot \frac{RT}{p_{sat}}$$

The saturation vapor pressure at equipartition ($C_o/C_g = 1$) is:

$$p_{sat}^{(g:o)} = \frac{10^{-9}RT \cdot C_{OA}}{M_{OA}}$$

■ Aqueous/Organic Particulate Phase Partitioning

The equilibrium between the aqueous and organic particulate phases results from the two preceding equilibria. The partitioning ratio is:

$$\frac{C_w}{C_o} = \frac{10^{-9}\omega_L M_{OA}}{C_{OA}} \cdot H \cdot p_{sat}$$

The Henry's law constant at equipartition ($C_w/C_o = 1$) is:

$$H^{(w:o)} = \frac{10^{-9}C_{OA}}{\omega_L M_{OA}} \cdot \frac{1}{p_{sat}}$$

or equivalently:

$$H^{(w:o)} = H^{(g:w)} \cdot p_{sat}^{(g:o)} \cdot \frac{1}{p_{sat}}$$

■ Fraction in the Organic Particulate Phase

Let f_o be the fraction of X in the organic particulate phase:

$$f_o = \frac{C_o}{C_g + C_w + C_o} \Rightarrow \frac{1}{f_o} = 1 + \frac{C_g}{C_o} + \frac{C_w}{C_o}$$

Substituting the partitioning ratios, we obtain:

$$\frac{1}{f_o} = 1 + \frac{M_{OA}RT}{10^{-9}C_{OA}} \cdot p_{sat} \; + \frac{\omega_L M_{OA}}{10^{-9}C_{OA}} \cdot H \cdot p_{sat}$$

$$\frac{1}{f_o} = 1 + \frac{p_{sat}}{p_{sat}^{(g:o)}} + \frac{H \cdot p_{sat}}{H^{(g:w)} \cdot p_{sat}^{(g:o)}}$$

The boundary line $H = f(p_{sat})$ for a fixed f_o in the phase partitioning space is:

$$H = H^{(g:w)} \cdot \frac{(1 - f_o)}{f_o} \cdot \frac{p_{sat}^{(g:o)}}{p_{sat}} - H^{(g:w)}$$

■ Fraction in the Aqueous Phase

Let f_w be the fraction of X in the aqueous phase:

$$f_w = \frac{C_w}{C_g + C_w + C_o} \implies \frac{1}{f_w} = 1 + \frac{C_g}{C_w} + \frac{C_o}{C_w}$$

Substituting the partitioning ratios, we obtain:

$$\frac{1}{f_w} = 1 + \frac{1}{HRT\omega_L} + \frac{C_{OA}}{10^{-9}\omega_L M_{OA}} \cdot \frac{1}{H \cdot p_{sat}}$$

$$\frac{1}{f_w} = 1 + \frac{H^{(g:w)}}{H} + \frac{H^{(g:w)}}{H} \cdot \frac{p_{sat}^{(g:o)}}{p_{sat}}$$

The boundary line $H = f(p_{sat})$ for a fixed f_w is:

$$H = H^{(g:w)} \cdot \frac{f_w}{1 - f_w} \cdot \left(1 + \frac{p_{sat}^{(g:o)}}{p_{sat}}\right)$$

■ Fraction in the Gas Phase

Let f_g be the fraction of X in the gas phase:

$$f_g = \frac{C_g}{C_g + C_w + C_o} \implies \frac{1}{f_g} = 1 + \frac{C_w}{C_g} + \frac{C_o}{C_g}$$

Substituting the partitioning ratios, we obtain:

$$\frac{1}{f_g} = 1 + \frac{H}{H^{(g:w)}} + \frac{p_{sat}^{(g:o)}}{p_{sat}}$$

The boundary line $H = f(p_{sat})$ for a fixed f_g is:

$$H = \frac{1 - f_g}{f_g} \cdot H^{(g:w)} - \frac{p_{sat}^{(g:o)}}{p_{sat}} \cdot H^{(g:w)}$$