Supplementary Information for

Rapid conversion of isoprene photooxidation products in terrestrial plants

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Supplementary Methods – Enclosure Experiment

Experimental Design
The experimental setup is illustrated in Supplementary Figure 1. Gray poplar plants (see Methods - plant material) were placed in an enclosure system consisting of a glass desiccator (Schott Duran ©) of 17.3 L volume turned upside-down. The inner surface of the desiccator was coated with Teflon (PFC 801A, Cytonix, USA) in order to minimize surface deposition of oxidized VOCs (OVOCs). The enclosure was placed on two PTFE ground plates equipped with a groove and tongue and ports for air inlet and air sampling, respectively. The plant stem and a Teflon coated K type thermocouple were fed through a central notch in the plates. Possible leaks were sealed with Teflon tape. A Teflon coated fan (Propeller Stirrer Shaft, 6.5 mm chucking diameter, Bohlender GmbH, Grünsfeld, Germany) connected to a 12 VDC motor was used for turbulent air mixing inside the enclosure. For the entire setup, only chemically inert materials such as PTFE, PFA and PEEK were used. All tubing was light-shielded with pipe insulation to exclude unwanted photolysis of 1,2-ISOPPOOH. The plants were fumigated with synthetic air (5.0 grade, Messer Austria GmbH, Gumpoldskirchen, Austria) that was mixed with CO₂ (4.8 grade, Messer Austria GmbH, Gumpoldskirchen, Austria) resulting in a CO₂ volume mixing ratio of on average ~450 ppm. Before entering the enclosure, the air was flushed through a liquid calibration unit (LCU, see below) (Ionicon Analytik, Innsbruck, Austria) to humidify the air and to add a defined quantity of a solution of a synthetic ISOPPOOH standard (I) in deionized water (2.9 µL ISOPPOOH in 100 mL deionized water (v/v)). The ISOPPOOH standard consisted entirely of the 1,2-ISOPPOOH isomer (kindly provided by the Frank Keutsch group, Harvard University, Boston MA) (I). Air composition at the inlet and outlet of the enclosure was alternately analyzed with the SRI-ToF-MS (see below) and an infrared-gas-analyzer (IRGA, see below).

Characterization of 1,2-ISOPPOOH deposition to the empty enclosure
In order to quantify possible surface deposition and decomposition of 1,2-ISOPPOOH on the Teflon-coated surface of the empty glass enclosure and on Teflon tubing material, we performed 1,2-ISOPPOOH fumigation experiments with the empty enclosure. Before starting the plant fumigation experiments, we fumigated the empty cuvette with 1,2-ISOPPOOH to condition the inner surfaces. Subsequently, the 1,2-ISOPPOOH loss to the surface of the empty enclosure was measured for each individual experiment. The enclosure was flushed with humidified air (RH ~35 %) at room temperature containing 7.8±1.0 ppb 1,2-ISOPPOOH. For an estimation of the 1,2-ISOPPOOH loss to the empty enclosure, we modelled the deposition rate to the surfaces according to (2):

\[ k_{\text{dep,surface}} = \ln \left( \frac{c_{\text{in,ISOPPOOH}}}{c_{\text{out,ISOPPOOH}}} \right) \times \frac{1}{\tau}, \text{[s}^{-1}] \]  

(1)

where \( c_{\text{in,ISOPPOOH}} \) [nmol mol\(^{-1}\)] is the volume mixing ratio (VMR) of 1,2-ISOPPOOH determined in the enclosure inlet air, \( c_{\text{out,ISOPPOOH}} \) [nmol mol\(^{-1}\)] is the VMR of 1,2-ISOPPOOH measured at the enclosure outlet and \( \tau \) [s] represents the residence time for a single exchange of the air in the enclosure (see Supplementary Table 1 and Supplementary Figure 2 for an overview). Under well-mixed conditions, which were achieved with the Teflon fan, the residence time \( \tau \) can be expressed as the ratio of the enclosure volume \( V_{\text{enclosure}} \) to the enclosure inlet gas flow \( F \) (3):
According to (4) it takes $\tau$ to exchange 99% of the air in the enclosure. The residence time in our fumigation experiments was on average 4.5 min, thus requiring 22.5 min to reach 99% air exchange.

Supplementary Figure 2 depicts a typical change in 1,2-ISOPOOH deposition rate $k_{dep, surface}$ over time. At the beginning of the experiment, when surfaces are virtually free of 1,2-ISOPOOH, $k_{dep, surface}$ is $0.25 \text{ molecules s}^{-1}$. Subsequently, the deposition rate decreases exponentially over time. 60 min after starting the 1,2-ISOPOOH fumigation the deposition rate becomes smaller than 0.01 molecules s$^{-1}$ and is neglected for further analysis. The characterization of the empty enclosure system revealed a far slower adaptation to new experimental conditions for highly water-soluble compounds such as 1,2-ISOPOOH compared to more volatile and less soluble compounds. For example, MVK and MEK are typically adjusted after 23 minutes, which is the time required to completely (> 99%) exchange the gas in the enclosure.

We used equation (1) to estimate the time required to reach steady state conditions in our enclosure setup. The 1,2-ISOPOOH deposition rate to the enclosure surface ($k_{dep,wall}$) becomes negligible after 91 min, corresponding to 20 residence times. In the case of MVK this occurs after 23 min (5 residence times). All experiments were performed in such a way that ample time was allowed in order to reach steady-state conditions before analyzing deposition rates of 1,2-ISOPOOH to plants. To minimize the effects of 1,2-ISOPOOH reemission from surfaces due to changes in humidity, only steady-state conditions were considered in each respective step for further analyses.

Photolytic loss of 1,2-ISOPOOH

We tested possible photolysis losses of 1,2-ISOPOOH (caused by irradiation) in the empty enclosure. For this purpose, we fumigated the empty enclosure with 1,2-ISOPOOH in darkness. Once the 1,2-ISOPOOH signals had stabilized after ~120 minutes, the light was switched on. We observed, however, no effect of the radiation on the 1,2-ISOPOOH volume mixing ratios in the enclosure.

Four-step protocol for the 1,2-ISOPOOH fumigation experiment

Each poplar plant was installed in the enclosure system shown in Supplementary Figure 1 several hours before starting an individual experiment, allowing the plant to adapt to the enclosure environment and recover from possible stress during the installation process. Before starting the fumigation run, we measured the “default” emissions of the gray poplars during darkness and illumination. We performed 1,2-ISOPOOH fumigation experiments following a four-step protocol for each plant (Supplementary Table 2). During step (A), 1,2-ISOPOOH from the liquid calibration unit (LCU) was analyzed directly with the SRI-ToF-MS via a bypass system, while the plant enclosure was fumigated with catalytically generated clean air (zero-air, ). During steps (B), (C) and (D), the SRI-ToF-MS sampled air at the enclosure outlet. At step (B), a poplar plant was fumigated with 1,2-ISOPOOH, typically for 9-12 hours, under dark conditions (no light), followed by fumigation of the illuminated plant (step C) for another 9-12 hours. After performing steps (A), (B) and (C), the plant was removed from the enclosure in order to conduct background measurements of the empty enclosure (step D). An asterisk following the step label (e.g. A*) indicates that the air mixture was passed through a 1 m $\times$ ¼
inch (length × diameter) stainless steel tube kept at room temperature before being analyzed by the SRI-ToF-MS. As reported previously (1, 5, 6), under these conditions 1,2-ISOPPOOH is converted efficiently to MVK and C₅-diols. For further analysis, we used the OVOC data averaged over 30-60 min at the end of each experimental step when OVOC signals had reached steady state conditions.

Representative poplar fumigation experiment
Supplementary Figure 3 depicts a typical fumigation cycle for a gray poplar plant, performed according to the four-step protocol. In step A, we enriched the air with 7.8±1.0 ppbv of 1,2-ISOPPOOH across all replicates. The air flow leaving the LCU also contained 2.0±0.4 ppbv MVK and 0.2±0.1 ppbv C₅-diols as contaminants in the 1,2-ISOPPOOH standard. Comparing the 1,2-ISOPPOOH concentration in the outlet air of the fumigated empty enclosure (step D) with the corresponding 1,2-ISOPPOOH values measured in the inlet air before the plant fumigation experiment (step A) revealed only minor (if any) losses to the enclosure system. On average only 6±5% of the input gaseous 1,2-ISOPPOOH was lost to the enclosure surface when equilibration times of more than 2 hours were permitted. Upon starting the fumigation of the plant under dark conditions (step B), the mixing ratio of 1,2-ISOPPOOH increased slowly over the course of several hours, reaching steady state after 8-10 hours. The mixing ratio of MVK reached steady state conditions (equal to the input concentration) after approximately 22 minutes, which is consistent with the time it takes for >99% air exchange of the enclosure (τ ≈ 22 minutes). Instantaneously upon illumination the concentration of 1,2-ISOPPOOH started to decrease. At the same time, the MVK signal showed a slight initial burst, followed by a decrease in emission, which leveled off to a ~1.5-fold increase from the original MVK concentration. MVK emissions were accompanied by a simultaneous increase in the MEK signal. When passing the air flow through metal tubing in steps A*, B*, C* and D*, the MVK and C₅-diol signal increased due to 1,2-ISOPPOOH conversion on metal surfaces, while the MEK signal remained unchanged.

Calculation of emission dynamics
The deposition velocity \( v_d \) (cm s\(^{-1}\)) is commonly used to describe trace gas deposition to vegetation from the atmosphere (7), and is defined as the ratio between the flux \( \Phi_i \) (representing the amount of compound \( i \) deposited to a unit surface area per unit time) and the local concentration \( c_i \).

\[
\Phi_i = -v_d \cdot c_i
\]  

(3)

Similarly, as described in (8), for enclosure measurements the deposition velocity \( v_{d,i} \) for compound \( i \) can be estimated from the flux \( \Phi_i \) to the system (plant + enclosure surface) and the concentrations \( c_{i,\text{out}} \) measured at the enclosure outlet:

\[
v_{d,i} = \frac{-\Phi_i}{c_{i,\text{out}}} \left[ m \text{ s}^{-1} \right]
\]  

(4)

Humidity corrected deposition fluxes \( \Phi_i \) to the plant surfaces inside an enclosure are typically calculated from the difference in trace gas mixing ratios between the inlet (\( c_{\text{in},i} \)) and outlet (\( c_{\text{out},i} \)) in nmol mol\(^{-1}\), taking into account the enclosed single-sided leaf area (\( L_A \), in m\(^2\)) of the plant, the gas flow (\( F \), in mol s\(^{-1}\)) and \( w_i \) and \( w_o \) the mole fraction of water vapor entering and leaving the enclosure, respectively (9, 10):
\[ \Phi_i = \frac{F}{L_A} \cdot (c_{in,i} - \frac{1-w_e \cdot 10^{-3}}{1-w_o \cdot 10^{-3}} c_{out,i}), \text{[nmol m}^{-2} \text{s}^{-1}] \]  

(5)

To take into account possible losses to the enclosure surfaces, we adapted the commonly known formula for emission rates (Equation 5) to the following form (Equation 6) which follows the considerations of (11):

\[ \Phi_i = \frac{F}{L_A} \cdot (c_{out,i,BG} - \frac{1-w_e \cdot 10^{-3}}{1-w_o \cdot 10^{-3}} c_{out,i}), \text{[nmol m}^{-2} \text{s}^{-1}] \]  

(6)

where \( c_{out,i,BG} \) is the volume mixing ratio of substance \( i \) at the enclosure outlet during fumigation of the empty enclosure (step D, see below). Both background and plant experiments were performed under identical conditions in terms of \( 1,2\)-ISOPOOH mixing ratios and relative humidity in the inlet air. This background correction minimizes any potential errors caused by an underestimation of surface sinks.

Liquid Calibration Unit (LCU)

A liquid calibration unit (LCU, Ionicon Analytic GmbH, Innsbruck, Austria) allows quantitative evaporation of liquid standards into a gas stream to generate calibration mixtures. Here an LCU was used to evaporate an aqueous solution of \( 1,2\)-ISOPOOH into a synthetic air stream fed into the plant enclosure. The liquid flow of the \( 1,2\)-ISOPOOH solution was regulated and kept constant at 10 \( \mu \text{L min}^{-1} \). Additionally, 40 \( \mu \text{L min}^{-1} \) of purified water were introduced into the synthetic air stream resulting in a relative humidity of approximately 35% at room temperature. The temperature in the evaporation chamber of the LCU was set to 50°C to avoid thermally-induced dissociation of \( 1,2\)-ISOPOOH.

Infrared gas analyzer (IRGA)

An infrared gas analyzer (LI-840A \( \text{CO}_2/\text{H}_2\text{O} \) Analyzer, LI-COR Inc., Lincoln NE, USA) sampled at 5 min intervals from either the inlet or outlet of the enclosure. \( \text{CO}_2 \) concentrations at the inlet were typically kept constant at 450 ppmv throughout the experiments. Typical relative humidities measured at the cuvette outlet ranged from 35-55 % in darkness to 50-60 % during the illuminated phase. Plants were illuminated by a true light lamp (Dakar, MT/HQI-T/D, Lanzini Illumazione, Brescia, Italy) to provide photosynthetically active radiation (PAR) of 400 \( \mu \text{mol photons m}^{-2} \text{s}^{-1} \) at the canopy level. Infrared light was shielded by a water filter to prevent radiative heating of the enclosure. PAR was measured with a sunshine sensor (Model SQ-326, Apogee Instruments, Logan, UT, USA).

Chemical ionization utilizing SRI-ToF-MS

Chemical ionization of \( 1,2\)-ISOPOOH with \( \text{H}_3\text{O}^+ \) and \( \text{NO}^+ \) leads to strong fragmentation. In contrast, using \( \text{NH}_4^+ \) as reagent ion, \( 1,2\)-ISOPOOH (\( \text{C}_5\text{H}_{10}\text{O}_3 \)) undergoes an association reaction forming \( \text{NH}_4^+ (\text{C}_5\text{H}_{10}\text{O}_3 \)(m/z 136.097) product ions (12). \( 1,2\)-ISOPOOH decomposes at elevated temperatures (e.g., during GC analysis; (11)) or on stainless steel surfaces even at room temperature (6) to MVK and 3-methyl-1-butene-3,4-diol (C₅-diol, (5)). \( \text{NH}_4^+ \) reagent ions also undergo association reactions with these decomposition products of \( 1,2\)-ISOPOOH. MVK is detected as the \( \text{NH}_4^+ (\text{C}_5\text{H}_6\text{O}) \)(m/z 88.07) ion (13) and C₅-diols are found as \( \text{NH}_4^+ (\text{C}_5\text{H}_{10}\text{O}_2) \)(m/z 120.10) product ions. In the \( \text{NH}_4^+ \) reagent ion mode, the MVK and MACR isomers are
both detected as \( \text{NH}_4^+ (C_4H_6O) \) (m/z 88.07) product ions. In order to distinguish between MVK and MACR we used the \( \text{NO}^- \) reagent ion mode, as the ketone MVK undergoes an association reaction forming \( \text{NO}^+ (C_4H_6O) \) (m/z 100.040) ions, while the aldehyde MACR performs hydride ion transfer forming \( C_4H_5O^- \) (m/z 69.034) (14).

To distinguish MEK from isomers such as butanal and 2-methyl propanal, we used the reagent ion \( \text{NO}^- \). Our instrument allows fast switching between different reagent ions. According to (15) the two isomers butanal and 2-methyl propanal undergo hydride abstraction forming the product ion \( C_4H_5O^- \) (m/z 71.05). In contrast, MEK reacts with \( \text{NO}^- \) via an association reaction forming \( C_4H_5O-\text{NO}^- \) (m/z 102.05).

Calibration of the \( \text{NH}_4^+ \)-mode for SRI-ToF-MS

We prepared a quantitative liquid solution of the pure 1,2-ISOPOOH standard with deionized water. The purity of the 1,2-ISOPOOH standard was verified by NMR spectroscopy in Innsbruck (working group Holger Kopacka, Institute of General, Inorganic and Theoretical Chemistry, University of Innsbruck) after shipment from the USA. The liquid solution was evaporated in the LCU into a defined synthetic air stream of 3 slpm. Additionally, we evaporated three different water amounts into the air stream resulting in absolute humidity in the range of 11 - 23 ppth. The sensitivity of 1,2-ISOPOOH at each humidity was then obtained from the slope of a linear fit through a scatter plot of the normalized product ion signals (ncps) vs. the 1,2-ISOPOOH volume mixing ratio. The sensitivity of the C₅-diol was obtained by passing a known amount of 1,2-ISOPOOH in air through stainless steel tubing (1 m length × ¼ inch diameter) kept at room temperature, leading to quantitative conversion of 1,2-ISOPOOH to MVK and C₅-diol. The sensitivity of MVK was obtained from dynamic dilution of a gas standard (Apel-Riemer Inc., Broomfield, USA) in humidified air. Errors were estimated by Gaussian propagation. An overview of the estimated sensitivities is given in Supplementary Table 3.

Impurity determination for fumigation experiments

For all fumigation experiments we used a 12 bottle bundle of synthetic air (5.0 grade). This synthetic air contains < 0.1 ppmv hydrocarbons (as \( \text{CH}_4 \)) and the largest contamination is water vapor (< 5 ppmv). For each plant experiment we conducted a “blank” measurement of the empty enclosure. The SRI-TOF-MS limit of detection (LOD) for MVK and MEK was 0.03 ppbv, while the LOD for 1,2-ISOPOOH was 0.21 ppbv. Blank measurements of the empty enclosure with humidified synthetic air containing 480 ppm CO₂ revealed contaminants at m/z 88.07 (\( C_4H_6O-NH_4^+ \), MVK) and at m/z 90.09 (\( C_4H_8O-NH_4^+ \), MEK) of 0.09 ppbv and 0.07 ppbv, respectively. Contaminants at m/z 136.09 (\( C_5H_{10}O_3-NH_4^+ \), 1,2-ISOPOOH) were below the detection limit. During plant enclosure experiments observed ion signals are substantially higher than these back-ground signals.

Supplementary Methods - Construction of AOR Phylogenetic Trees and AOR Gene Expression Analysis

To detect AOR genes, sequence similarity searches (BLAST; e-value cutoff 1e-4) were conducted against the NCBI nr, dbEST and SRA databases using known amino acid sequences of genes encoding the chloroplast and cytosolic plant AOR proteins. Reciprocal BLAST searches were conducted to ensure that AOR represents the closest homologs to the identified bacterial and Bryophyta sequences in Angiosperms. To recover AOR sequences from Quercus robur and Fagus sylvatica, BLAST searches (e-value threshold 1e-30) were conducted against a local database containing whole genome and predicted protein sequences for these species.
(16, 17). Sequences for *Picea abies* and *Pinus taeda* were obtained from Congenie ([http://congenie.org](http://congenie.org)); *Salix purpurea* AOR sequences were obtained from Phytozome ([https://phytozome.jgi.doe.gov](https://phytozome.jgi.doe.gov)). Multiple sequence alignments containing plant and bacterial (Supplementary Figure 10) and only plant (Figure 3) AOR genes were constructed using MUSCLE (18) and refined manually using Mesquite v. 3.51 (19). Maximum Likelihood (ML) AOR phylogenetic trees were reconstructed using RaxML (20) with bootstrapping (100 bootstrap replicates) and the LG amino acid substitution model. To discriminate between genes encoding cytosolic and plastid-targeted AOR, a targeting peptide prediction was conducted using TargetP 1.1 Server (21).

Expression information for the gray poplar chloroplasic and cytocolic AOR genes was derived from (22). Only samples collected in the light phase from plants maintained under normal control scenarios (AC: ambient CO₂; EC: enhanced CO₂) conditions were considered for analysis.

**Supplementary Methods - Eddy Covariance VOC Flux Measurements**

**Calibration and data analysis of the PTR3**

Isoprene and MEK sensitivities were calibrated as a function of humidity using a gas standard (Apel-Riemer Inc., Broomfield, USA), which was diluted in air with changing humidity. The humidity was varied from dry (synthetic air bottle) to tens of ppth during calibration covering the typical ambient humidity conditions. Water transport in eddies causes the sample humidity to correlate with vertical wind speed. This can induce artifacts in EC measurements if the analyzer shows humidity-dependent sensitivity. In order to accurately calibrate the PTR3-TOF VOC signals, a fast water-sensitive tracer (N₂H⁺), which is produced in the PTR3-TOF, was regularly cross-calibrated against ambient humidity measurements with the IRGA (time resolution of seconds). This calibration of the PTR3-TOF signals was done at 10 Hz, resulting in a fast humidity trace. Data analysis was performed using multi-peak analysis routines (23), which only rely on single-ion counting within specified mass ranges and a subsequent correction of cross talk from neighboring mass peaks. This is important since typical mass spectra show fully developed peak shapes at the 10 Hz acquisition rate that can be peak-fitted. The resulting time-traces were calibrated as described above and used as input for “InnFlux”, an eddy covariance flux routine developed by the group of Thomas Karl at the Faculty of Geo- and Atmospheric Sciences, University of Innsbruck, Austria.

**Statistical analysis**

Biological replication: for enclosure measurements with 1,2-ISOPOOH fumigation we used gas phase data for five biological replicates (for plant details see Supplementary Table 4). For AOR analysis we took samples from seven and five poplars (ISOPOOH and MVK fumigation, respectively). From each extract, three technical replicates were analyzed.
Supplementary Figure 1. Experimental design of enclosure measurements
A poplar plant was placed in the enclosure equipped with a Teflon fan for turbulent mixing. Gas flows of synthetic air and CO₂ were controlled by mass flow controllers (MFC). The liquid calibration unit (LCU) humidified the air stream (RH 35% at room temperature) and added ~7 ppbv 1,2-ISOPPOOH. Switching valves directed the gas stream either before or after the enclosure to the SRI-TOF-MS with or without passing through a metal line. CO₂ and H₂O concentrations were analyzed with an infrared gas analyzer (IRGA) either before or after the enclosure. Plants were illuminated with a true light lamp. Infrared radiation was blocked by a water bath. The enclosure could be flushed with zero air (0-air).
Supplementary Figure 2. Deposition rate to enclosure walls
Deposition rates $k_{\text{dep,wall}}$ for 1,2-ISOPOOH (m/z 136.09) and MVK (m/z 88.07) were obtained by fumigation of the empty enclosure with ~7 ppbv 1,2-ISOPOOH and with ~2 ppbv MVK. Error bars are calculated by Gaussian error propagation.
Supplementary Figure 3. Representative laboratory experimental run

Individual OVOC signals monitored during a representative poplar fumigation experiment. (A) Humidified air containing 7.1 ppbv 1,2-ISOPOOH (m/z 136.09) and 2.5 ppbv MVK (m/z 88.07) was directly analyzed prior to entering the enclosure. (A*) The sample flow was directed through a metal line (indicated by an asterisk) and 1,2-ISOPOOH was converted to MVK and C5 diols (m/z 120.10). During (B), the sample flow was introduced into the enclosure under dark conditions, with the air analyzed at the enclosure exit, showing a rather slow increase in 1,2-ISOPOOH. During B* the remaining 1,2-ISOPOOH (measured after the enclosure) was converted to MVK and C5 diols by passing the flow through the metal line. During (C), the light was switched on thus triggering stomatal opening (CO\textsubscript{2} was taken up; not shown), and 1,2-ISOPOOH decreased to 3 ppbv, while MVK (4.5 ppbv) and MEK (m/z 90.09) (~1.5 ppbv) increased. (D) Removing the plant and fumigating the empty enclosure in the dark led to 1,2-ISOPOOH and MVK signals as measured during (A).
Supplementary Figure 4. Volume mixing ratios (VMR) and fluxes (Φ) of MVK and MEK in MVK fumigation experiments

Box plots of VMR (panels a,b) and deposition/emission fluxes (c,d) are shown for MVK and MEK during MVK fumigation. OVOCs were analyzed at the enclosure inlet and subsequently at the enclosure outlet during fumigation of the empty enclosure (BG) and the darkened/illuminated poplars. On each box, the red line indicates the median, bars show the minimum/maximum, and the blue box indicates the 25th and 75th percentiles of the sample data (N=5). The loss of MVK to the illuminated plant is statistically not significant (Tukey post hoc test). However, the Tukey post hoc test reveals a significant difference in MEK emissions between light and dark conditions (p=0.0001). Increases in both MEK and MVK fluxes under light conditions are statistically significant (p=0.0209 and p=0.0433, respectively).
Supplementary Figure 5. Average net CO\textsubscript{2} assimilation and transpiration rates for 1,2-ISOPOOH fumigated gray poplars

The box plots show the CO\textsubscript{2} assimilation rate A (a) and transpiration rates E (b) among the fumigated gray poplars. Results are shown for both darkened and light conditions. On each box, the red line indicates the median, bars show the minimum/maximum, and the blue box indicates the 25\textsuperscript{th} and 75\textsuperscript{th} percentiles of the sample data (N=5).
Supplementary Figure 6. Stomatal closing under light conditions during a poplar experiment.

Fumigation of a poplar plant with elevated 1,2-ISOPOOH under light conditions for several hours caused plant stress and stomatal closure. The resulting change in stomatal conductance is evident from the ΔH₂O (H₂O mixing ratio difference between inlet and outlet) increase. Stomatal closure was accompanied by an increase in 1,2-ISOPOOH, whereas MVK remained nearly unchanged and MEK levels decreased. These observations support our inference that 1,2-ISOPOOH is converted in the apoplast rather than on plant surfaces.
Supplementary Figure 7. 1,2-ISOPOOH reduction on different metals

1,2-ISOPOOH (m/z 43.02) conversion to MVK (m/z 71.05) on copper (panel a), steel (b) and aluminum (c). The cleaned metal cylinders were placed in the evaporation chamber of the LCU. 1,2-ISOPOOH was measured with the SRI-TOF-MS with H$_3$O$^+$ reagent ions and is detected as a fragment at m/z 43.02. Organic hydroperoxides are inherently unstable species and can undergo decomposition, such as homolytic cleavage of the weak peroxy (O-OH) bond. This reaction is catalyzed by metals. Copper and iron (both transition metals) are known to catalyze Fenton-type reactions of hydrogen peroxide (24). 1,2-ISOPOOH consistently undergoes conversion to MVK while in contact with steel or copper surfaces. Contact of 1,2-ISOPOOH with an aluminum surface results in an initial conversion to MVK followed by a recovery of the 1,2-ISOPOOH signal.
Supplementary Figure 8. MeSA and SQT signals following 1,2-ISOPOOH/MVK fumigation

Methyl salicylate (MeSA) and sesquiterpene (SQT) signals from 1,2-ISOPOOH (panel a, N=5 ± SD) and MVK (panel b, N=5 ± SD) fumigated gray poplars under control conditions and after 20-22h exposure (10-12 h dark conditions, 10-12 h illuminated conditions). As calibration gas standards were not available for MeSA and SQT we present data as relative changes in product ion signals.
Supplementary Figure 9. Kinetic properties of the gray poplar AOR (EC 1.3.1.74, NADPH-dependent alkenal/one oxidoreductase) activity in vitro.
(a) Dependence of AOR activity on NADPH concentration. Insert: Hanes-Woolf diagram for determination of Michaelis constant (Km; indicates substrate concentration at half-maximal enzyme velocity). Km for NADPH 0.49 mM. (b) Dependence of AOR activity on methylvinylketone (MVK) concentration. Insert: Hanes-Woolf diagram with Km for MVK of 14.15 mM. (c) Temperature optimum of apparent in vitro AOR activity in poplar leaf extracts at saturating substrate concentrations. n = 3-6 replicates. The enzyme assays were performed according to (25).
Evolutionary history of genes encoding plastid and cytosolic AOR proteins. The AOR phylogeny was reconstructed using the maximum likelihood (ML) method and LG amino acid substitution model. The bacterial clade (black color) was used as outgroup. Gray coloring of the branch labels indicates genes encoding cytosolic AOR; green coloring indicates genes encoding chloroplast AOR. Numbers at the tree branches indicate node bootstrap support. Basal nodes of the plant AORchl, AORcyt-I and AORcyt-II and bacterial NADPH:quinone reductase ortholog clusters are labeled with solid circles. Scale bar below the tree shows branch length.

This phylogeny implies a bacterial origin of the plant AOR genes and several gene duplication events in Embryophytes. The first duplication event, which gave rise to the chloroplast and cytosolic AOR gene copies, is likely to have occurred during the early evolution of land plants. An additional cytosolic AOR copy has arisen via duplication of the chloroplast AOR copy in Angiosperms.

Supplementary Figure 10. AOR phylogenetic tree
Supplementary Figure 11. *In vitro* AOR activity in fumigated gray poplar leaves

*In vitro* AOR activity in gray poplar leaf protein extracts. (a) Fumigation with 7.1 ppbv 1,2-ISOPOOH; (b) Fumigation with 2.5 ppbv MVK. Gray poplar leaves were sampled before starting fumigation (0 hours), after 24 hours of exposure and after 48 hours (24 hours of exposure followed by 24 hours of recovery). On each box, the red line indicates the median, bars show the minimum and maximum, the blue box indicates the 25th and 75th percentiles of the sample data, and red crosses indicate outliers (N= 7 (1,2-ISOPOOH); N=5 (MVK)).
Supplementary Figure 12. Post-translational modification (PTM) of the *Populus x canescens* AORchl protein.

(a) Schematic representation of the *Populus x canescens* AORchl protein structure with predicted PTM sites. Numbers indicate positions of amino acids in the AORchl peptide sequence that can undergo PTM. (b) Predicted PTM site/locus information. Prediction of the putative tyrosine- and tryptophan-nitration and S-nitrisylation sites was conducted using DeepNitro (26) at medium PTM prediction thresholds.
Supplementary Figure 13. Stomatal fraction of 1,2-ISOPOOH deposition
The stomatal fraction of dry deposited 1,2-ISOPOOH as simulated with the GEOS-Chem base-case run. By default, this approach uses a modified version of the resistance-based scheme from Wesely (27) to calculate dry deposition velocities. Values plotted reflect the stomatal fraction of deposition (i.e., stomatal conductance divided by total surface conductance) as a conductance-weighted mean across all land cover types within each model grid cell.
Supplementary Figure 14. MEK yield as simulated by GEOS-Chem

Global MEK yield expressed as a fraction of isoprene emissions as simulated by GEOS-Chem for 2017. Results shown use our experimentally obtained stomatal uptake values and assume that 100% of dry deposited MVK and 50% of dry deposited 1,2-ISOPOOH is enzymatically converted to MEK in terrestrial plants. Black crosses mark the two EC flux measurement sites (SMEAR II in Finland and PROPHET in US) discussed above. Elevated values are seen where OH is low and isoprene oxidation products undergo proportionately more deposition (e.g., high latitudes), and in low-emission locations subject to deposition from nearby high-emission areas (e.g., western South America).
Supplementary Figure 15. GEOS-Chem run with default dry deposition treatment

GEOS-Chem base-case simulation for 2017 at 2° x 2.5° horizontal resolution. The model uses biogenic emissions from MEGANv2.1. Dry deposition is estimated using a modified version of the Wesely (27) scheme. MEK production in this simulation assumes that 100% of dry deposited MVK and 50% of dry deposited 1,2-ISOPOOH is subject to enzymatic conversion. Relevant parameters include H* values of 1.7x10^6 M atm^-1 for 1,2-ISOPOOH and 44 M atm^-1 for MVK. Reactivity (f0) values for both species are set to 1.0.
Supplementary Figure 16. EC flux measurements of isoprene and MEK at low isoprene emission site

Eddy covariance (EC) flux measurements of isoprene (m/z 69.07) and MEK (m/z 73.065) were performed at the SMEAR II station in Hyytiälä, Finland. During daytime (yellow) the MEK-to-isoprene diurnal flux ratio averages 1.8%. Data are averaged values (+/- SD) over five sunny days in May 2016.
Supplementary Figure 17. EC flux measurements of isoprene and MEK at high isoprene emission site

Diurnal isoprene (panel a) and MEK (panel b) fluxes measured at the PROPHET site in Michigan, US in July 2016. The site is dominated by high isoprene-emitting species. The daytime (yellow shading) MEK-to-isoprene flux ratio averages 0.9%. Error ranges (gray) represent the 95% confidence interval. Data are mean values.
Supplementary Table 1. Wall deposition rates
Averaged wall deposition rates of ISOPOOH to the enclosure walls during fumigation of the empty enclosure across 5 experimental runs.

| Exposure time (min) | $k_{dep,wall}$ (s$^{-1}$) |
|--------------------|--------------------|
| 0                  | 0.23 ± 0.05        |
| 20                 | 0.10 ± 0.03        |
| 40                 | 0.05 ± 0.02        |
| 60                 | 0.03 ± 0.01        |
| 120                | 0.02 ± 0.01        |

Supplementary Table 2. Four-step protocol of the ISOPOOH fumigation experiment
Steps performed during each experimental run of a gray poplar plant.

| Step | Description |
|------|-------------|
| A    | Analyzing air at the enclosure inlet |
| B    | 1,2-ISOPOOH fumigation of the shaded poplar, OVOCs sampled at the enclosure outlet |
| C    | 1,2-ISOPOOH fumigation of the illuminated poplar, OVOCs sampled at the enclosure outlet |
| D    | 1,2-ISOPOOH fumigation of the empty cuvette, OVOCs sampled at the enclosure outlet |
| *    | Sampled air passes through a 1 m long stainless-steel tube before entering the SRI-ToF-MS |

Supplementary Table 3. Sensitivities of the SRI-ToF-MS
Normalized sensitivities of MVK, MEK, acetone, 1,2-ISOPOOH and C$_5$-diol as a function of humidity for NH$_4^+$-mode measurements with the SRI-ToF-MS.

| Humidity (ppth) | LOD (ppbv) | 11 (ncps/ppbv) | 16.8 (ncps/ppbv) | 23.2 (ncps/ppbv) |
|----------------|------------|----------------|------------------|------------------|
| MVK            | 0.03 ± 0.01| 8.5 ± 0.6      | 9.4 ± 0.6        | 10.62 ± 0.6      |
| MEK            | 0.03 ± 0.01| 11.8 ± 0.2     | 12.8 ± 0.6       | 14.06 ± 0.5      |
| Acetone        | 0.04 ± 0.02| 6.6 ± 0.3      | 7.65 ± 0.7       | 9.054 ± 0.7      |
| 1,2-ISOPOOH    | 0.21 ± 0.05| 25.6 ± 6.8     | 21.8 ± 5.9       | 20.26 ± 5.4      |
| C$_5$-diol     | 21.2 ± 9.3 | 20 ± 6.9       | 13.68 ± 7.5      |
**Supplementary Table 4. Plant details**

Leaf areas for the analyzed poplars were calculated by the free tool LeafArea Calculator (https://sites.google.com/site/ptrtof/file-cabinet) which is described in (3).

| Poplar (No.) | Leaf area (cm²) | Fumigation gas | AOR analysis |
|--------------|-----------------|----------------|--------------|
| 1            | 242             | 1,2-ISOPOOH    | -            |
| 2            | 188             | 1,2-ISOPOOH    | -            |
| 3            | 215             | 1,2-ISOPOOH    | -            |
| 4            | 350             | 1,2-ISOPOOH    | -            |
| 5            | 242             | 1,2-ISOPOOH    | -            |
| 6            | 768             | 1,2-ISOPOOH    | X            |
| 7            | 2101            | 1,2-ISOPOOH    | X            |
| 8            | 1983            | 1,2-ISOPOOH    | X            |
| 9            | 1849            | 1,2-ISOPOOH    | X            |
| 10           | 1731            | 1,2-ISOPOOH    | X            |
| 11           | 1629            | 1,2-ISOPOOH    | X            |
| 12           | 1121            | 1,2-ISOPOOH    | X            |
| 13           | 1232            | MVK            | X            |
| 14           | 968             | MVK            | X            |
| 15           | 416             | MVK            | X            |
| 16           | 665             | MVK            | X            |
| 17           | 1121            | MVK            | X            |
Supplementary Table 5. Sequence accession and BVOC emission information
Genes encoding chloroplastic (AORchl) and cytosolic AOR (AORcyt-I and AORcyt-II) proteins in plants emitting different BVOCs.

| Species                      | Database    | Accession nr / genomic coordinates | Gene description                                                         | Plastid-targeting signal (TP) | VOC emission information |
|------------------------------|-------------|------------------------------------|------------------------------------------------------------------------|------------------------------|--------------------------|
| *Arabidopsis thaliana*       | NCBI nr     | OAP18379.1                         | AOR                                                                    | TP                           |                          |
| *Elaeis guineensis*          | NCBI nr     | XP_029123251.1                     | 2-methylene-furan-3-one reductase                                     | noTP                         | isoprene (28)            |
| *Elaeis guineensis*          | NCBI nr     | XP_010925514.1                     | 2-methylene-furan-3-one reductase                                     | TP                           | isoprene (28)            |
| *Eucalyptus grandis*         | NCBI nr     | Eucgr.101800.1.p                   | 2-methylene-furan-3-one reductase                                     | noTP                         | isoprene, monoterpenes   |
| *Eucalyptus grandis*         | NCBI nr     | Eucgr.101801.1.p                   | 2-methylene-furan-3-one reductase                                     | noTP                         | isoprene, monoterpenes   |
| *Eucalyptus grandis*         | NCBI nr     | Eucgr.E01364.1.p                  | 2-methylene-furan-3-one reductase isoform X1                          | noTP                         | isoprene, monoterpenes   |
| *Eucalyptus grandis*         | NCBI nr     | XP_010023565.1                     | PREDICTED: 2-methylene-furan-3-one reductase                          | TP                           | isoprene, monoterpenes   |
| *Fagus sylvatica*            | Beech genome* | FSB010890801                      | 2-methylene-furan-3-one reductase-like/chloroplast stroma;thylakoid | noTP                         | monoterpenes             |
| *Fagus sylvatica*            | Beech genome* | FSB010890501                      | 2-methylene-furan-3-one reductase-like/NADPH:quinone reductase activity | noTP                         | monoterpenes             |
| *Fagus sylvatica*            | Beech genome* | FSB016186801                      | 2-methylene-furan-3-one reductase-like                               | noTP                         | monoterpenes             |
| *Helianthus annuus*          | NCBI nr     | XP_022011957.1                     | 2-methylene-furan-3-one reductase-like                               | TP                           | isoprene, monoterpenes   |
| *Hevea brasiliensis*         | NCBI nr     | XP_021668587.1                     | 2-methylene-furan-3-one reductase-like                               | noTP                         | monoterpenes             |
| *Hevea brasiliensis*         | NCBI nr     | XP_021645268.1                     | 2-methylene-furan-3-one reductase-like                               | TP                           | monoterpenes             |
| *Oryza brachyantha*          | NCBI nr     | XP_006659368.1                     | 2-methylene-furan-3-one reductase                                    | TP                           |                          |
| *NCBI nr                     | XP_015650762.1 | 2-methylene-furan-3-one reductase                                | TP                           |                          |                          |
| *Phoenix dactylifera*        | NCBI nr     | XP_008803292.1                     | 2-methylene-furan-3-one reductase-like                               | noTP                         | isoprene (32)            |
| *Phoenix dactylifera*        | NCBI nr     | XP_008801828.1                     | 1-methylene-furan-3-one reductase                                    | TP                           | isoprene (32)            |
| *Picea abies*                | Congenie    | MA_10433694g0010                   | NA                                                                      | noTP                         | isoprene, monoterpenes   |
| *Picea abies*                | Congenie    | MA_207070g0010                     | NA                                                                      | noTP                         | isoprene, monoterpenes   |

Ref: 28, 29, 30, 31, 32
| Species                   | Source       | Accession/ID | Classification and/or Function | Expression Type | Functional Annotation                      | References |
|--------------------------|--------------|--------------|---------------------------------|-----------------|---------------------------------------------|------------|
| *Picea sitchensis*       | NCBI nr      | ABK24706.1   | unknown                         | noTP            | isoprene, monoterpenes                      | (29)       |
| *Picea sitchensis*       | dbEST        | DR524779.1   | NA                              | noTP            | isoprene, monoterpenes                      | (29)       |
| *Pinus radiata*          | NCBI dbEST   | FE520506.1   | NA                              | noTP            | monoterpenes                                | (29)       |
| *Pinus sylvestris*       | NCBI dbEST   | HE631563, HE627609 | NA                              | noTP            | monoterpenes                                | (29)       |
| *Pinus sylvestris*       | NCBI dbEST   | HE634642,HE629950 | NA                              | noTP            | monoterpenes                                | (29)       |
| *Pinus taeda*            | Congenie     | PITA_000008068 | NA                              | noTP            | monoterpenes                                | (34)       |
| *Pinus taeda*            | Congenie     | PITA_000018354 | NA                              | noTP            | monoterpenes                                | (34)       |
| *Pinus taeda*            | Congenie     | PITA_000018354 | NA                              | noTP            | monoterpenes                                | (34)       |
| *Populus alba*           | NCBI nr      | TKR83752.1   | hypothetical protein D5086 0000265230 | noTP            | isoprene                                    | (33)       |
| *Populus alba*           | NCBI nr      | TKS15680.1   | hypothetical protein             | TP              | isoprene                                    | (33)       |
| *Pinus canescens*        | NCBI SRA     | SRX5822327-SRX5822330 | NA                              | noTP            | isoprene                                    | (33)       |
| *Pinus canescens*        | NCBI SRA     | SRX5820660-SRX5820707 | NA                              | noTP            | isoprene                                    | (33)       |
| *Populus euphratica*     | NCBI nr      | XP_011002607.1 | PREDICTED: 2-methylene-furan-3-one reductase-like | noTP            | monoterpenes                                | (35)       |
| *Populus euphratica*     | NCBI nr      | XP_011029885.1 | PREDICTED: 2-methylene-furan-3-one reductase-like | noTP            | monoterpenes                                | (35)       |
| *Populus trichocarpa*    | NCBI nr      | XP_006379865.2 | 2-methylene-furan-3-one reductase | noTP            | isoprene                                    | (29)       |
| *Populus trichocarpa*    | NCBI nr      | XP_002323668.2 | 2-methylene-furan-3-one reductase | TP              | isoprene                                    | (29)       |
| *Quercus robur*          | Oak genome*  | Qrob_P0187340.2 | 270                              | noTP            | isoprene                                    | (29)       |
| *Quercus robur*          | Oak genome*  | Qrob_P0415420.2 | 285                              | noTP            | isoprene                                    | (29)       |
| *Quercus robur*          | Oak genome*  | Qrob_Chr03:4952 7575-49527850 | NA                              | noTP            | isoprene                                    | (29)       |
| *Quercus suber*          | NCBI nr      | XP_023895222.1 | 2-methylene-furan-3-one reductase-like | noTP            | monoterpenes                                | (36)       |
| *Quercus suber*          | NCBI nr      | XP_023897000.1 | 2-methylene-furan-3-one reductase-like | noTP            | monoterpenes                                | (36)       |
| *Quercus suber*          | NCBI nr      | XP_023917302.1 | 2-methylene-furan-3-one reductase-like | noTP            | monoterpenes                                | (36)       |
| *Salix purpurea*         | Phytozome    | SapurV1A.0580s0100.1.p | quinone oxidoreductase-like protein | noTP            | isoprene                                    | (33)       |
| *Salix purpurea*         | Phytozome    | SapurV1A.0065s0430.1.p | alcohol dehydrogenase and quinone reductase-like medium chain dehydrogenase family/reductase | TP              | isoprene                                    | (33)       |
| *Zea mays*               | NCBI nr      | NP_001151204.1 | quinone oxidoreductase-like protein At1g23740 | TP              | isoprene                                    | (29)       |
* *Fagus sylvatica* (European Beech) genome resource ([http://www.beechgenome.net/](http://www.beechgenome.net/); (17))

** Oak genome sequencing ([http://www.oakgenome.fr/](http://www.oakgenome.fr/); (16))
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