Supporting Information

Multi-stress interaction effects on BVOC emission fingerprints from oak and beech: A cross-investigation using Machine Learning and Positive Matrix Factorization

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Table S1 Gas standard composition used for PTR TOF-MS calibration in this study.

Compound	Protonated mass	Volume mixing ratio (ppb)	Protonated Formula
Methanol	33.0335	1470	CH_5O^+
Acetonitrile	42.0339	1020	$C_2H_4N^+$
Acetaldehyde	45.0335	1100	$C_2H_5O^+$
Ethanol	47.0492	524	$C_2H_7O^+$
DMS	63.0263	1250	DMS
Isoprene	69.0699	1050	$C_5H_9^+$
Methyl vinyl ketone	71.0492	1020	$C_4H_7O^+$
Methyl ethyl ketone	73.0648	945	$C_4H_8OH^+$
Benzene	79.0543	792	$C_6H_7^+$
Toluene	93.0699	1120	$C_7H_9^+$
m-Xylene	107.0856	1210	$C_8H_{11}^+$
1,2,4-Trimethylbenzene	121.1012	1260	$C_9H_{13}^+$
Trifluorobenzene	133.0265	978	TFB
3-Carene	137.1325	1230	$C_{10}H_{17}^+$
1,2,4-Trichlorobenzene	180.9378	1020	TCB
D3	223.06365	980	D3
D4	297.0825	1220	D4
D5	371.1013	1160	D5
Perfluorotributylamine	671.96778	1070	PFB

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Table S2 Compounds used as indicators for different plant biosynthesis pathways, adapted from Fitzky et al. (2023). The LOX, MEP, MVA, and SKM pathways refer to lipoxygenase, methylerythritol phosphate, mevalonic acid, and the shikimate pathway, respectively.

Pathway	Protonated ion	amu	Chemical Formula	Compound Name	Subfamily
LOX	$C_6H_{13}O^+$	101.0961	$C_6H_{13}O$	Hexanal	Carbonyl
LOX	$C_6H_{11}O^+$	99.08044	$C_6H_{11}O$	Cis-3-hexenal	Carbonyl
LOX	$C_6H_{13}^+$	85.10118	C_6H_{13}	1-hexene	Alkene
LOX	$C_8H_{15}O_2^+$	143.1067	$C_8H_{15}O_2$	Hexenyl acetate	CHO
LOX	$C_8H_{17}O_2^+$	145.1223	$C_8H_{17}O_2$	Ethyl hexanoate	CHO
MEP	$C_5H_9^+$	69.06988	C_5H_9	Isoprene	Isoprene
MEP	$C_{10}H_{17}^+$	137.1325	$C_{10}H_{17}$	Monoterpenes	Monoterpenes
MVA	$C_{15}H_{25}^+$	205.1951	$C_{15}H_{25}$	Sesquiterpenes	Alkene
MVA	C_2H_5O+	45.03349	C_2H_5O	Acetaldehyde	Carbonyl
SKM	$C_7H_7O^+$	107.0491	C_7H_7O	Benzaldehyde	Carbonyl
SKM	$C_6H_7^+$	79.05423	C_6H_7	Benzene	Aromatic
SKM	$C_{10}H_{13}O_2^+$	165.091	$C_{10}H_{13}O_2$	Phenethyl acetate	CHO
SKM	$C_8H_9O_3^+$	153.0546	$C_8H_9O_3$	Vanillin	CHO

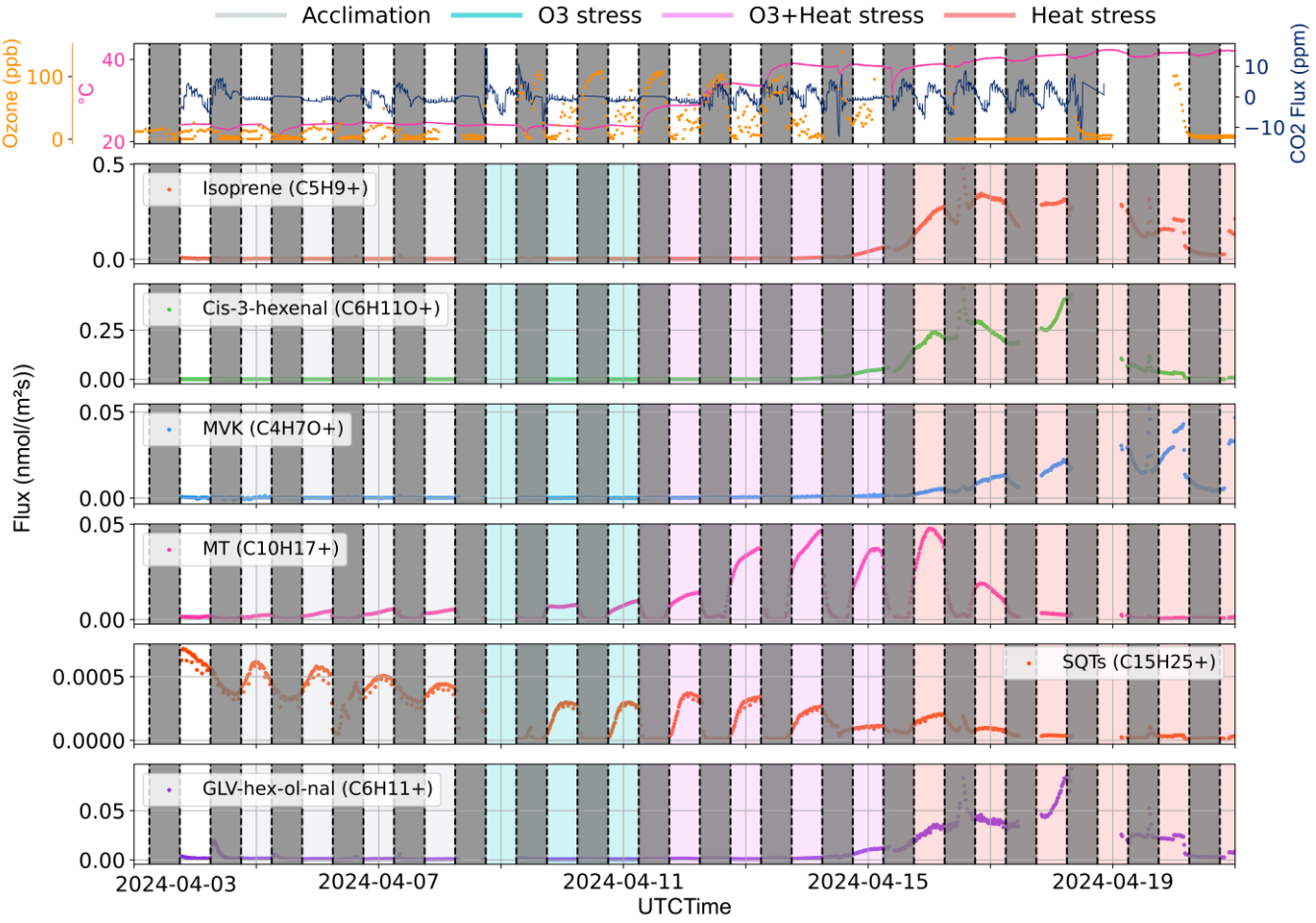

Figure S1 BVOC emission flux overview over the experimental stress period for beech with CO_2 assimilation flux, ozone, and temperature. The dark window represents plants night-time and the light window daytime. Different color shades are for different stress periods. Data shown are 20-minute averages.

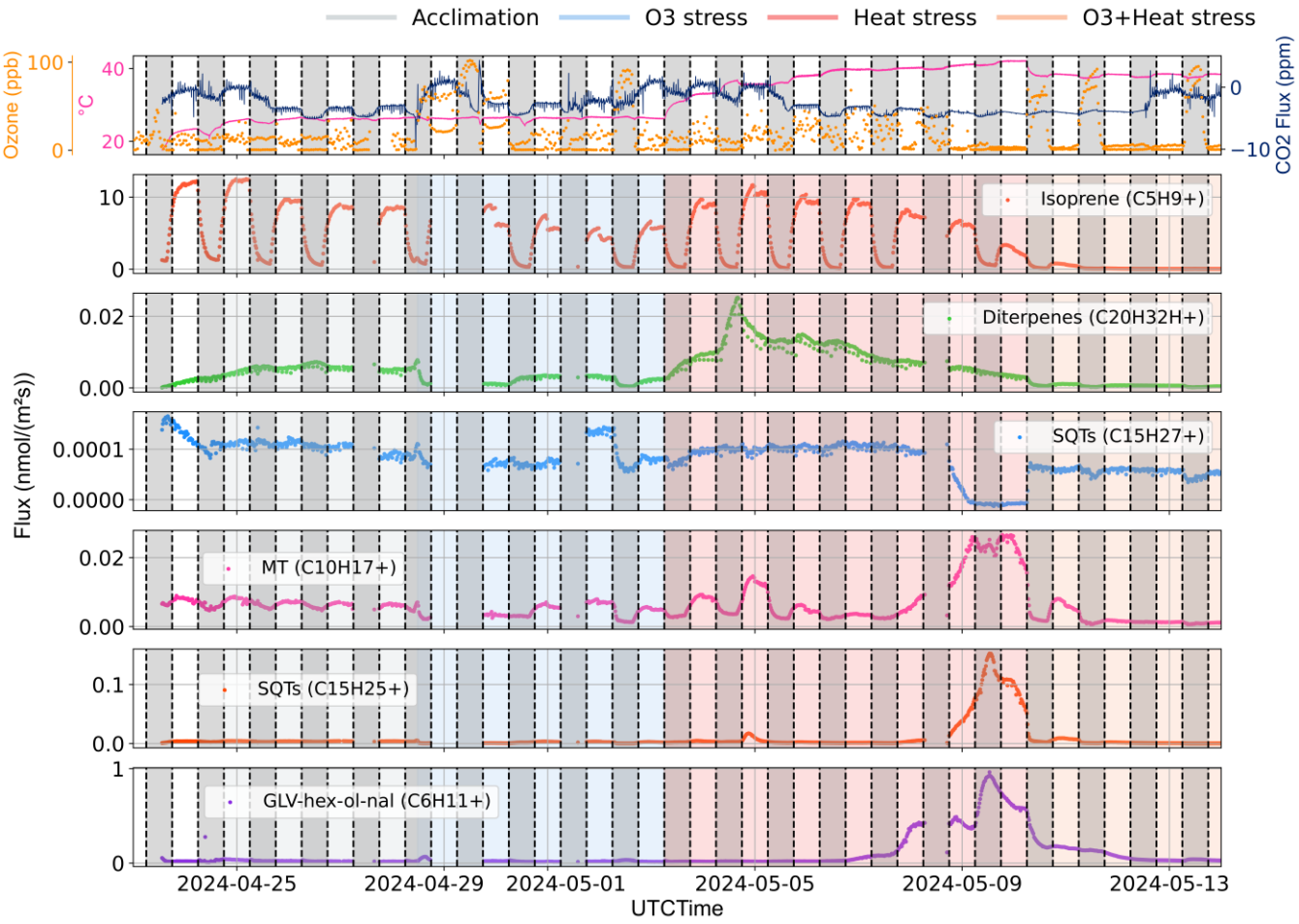

Figure S2 BVOC emission flux overview over the experimental period for oak with CO_2 assimilation flux, ozone, and temperature. The dark window represents plants night-time and the light window daytime. Different color shades are for different stress periods. Data shown are 20-minute averages.

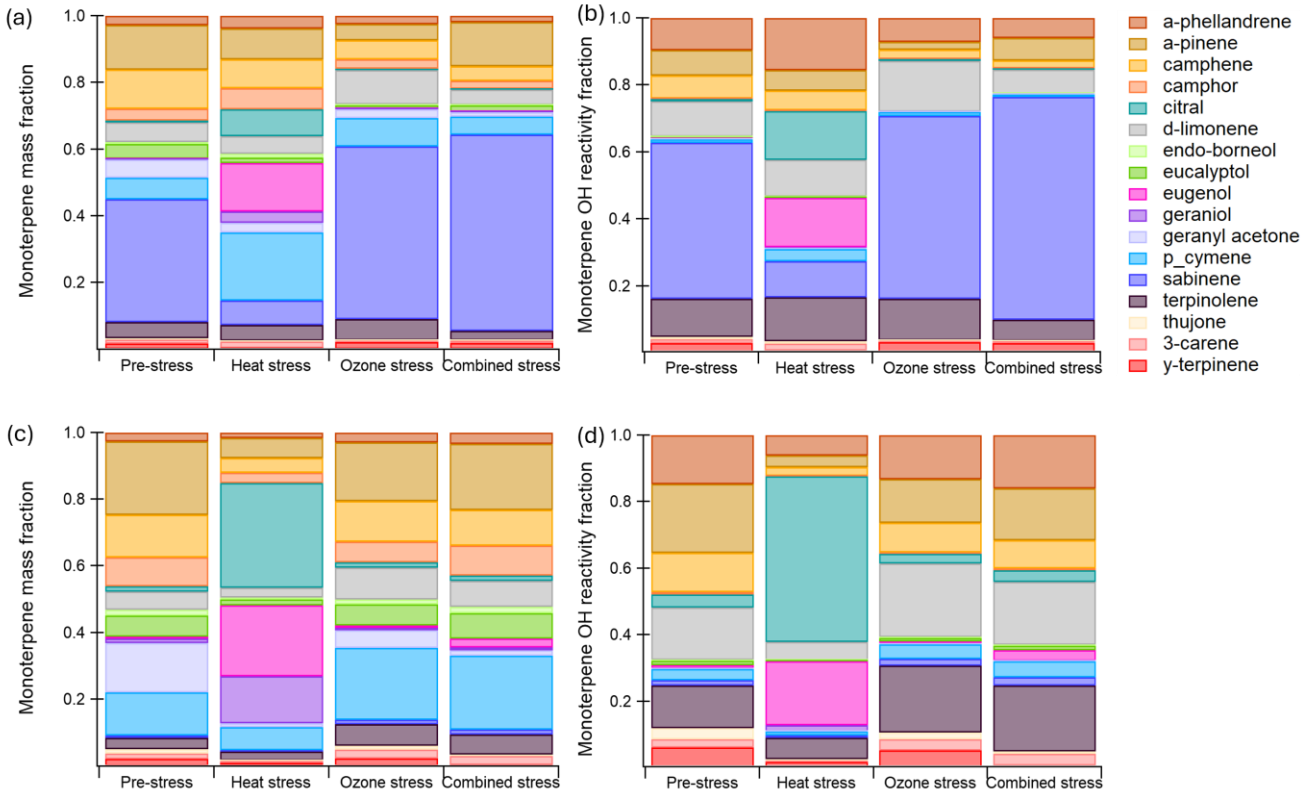

Figure S3. Monoterpene emission composition (a) by mass for beech, (b) by OH reactivity contribution for beech, (c) by mass for oak, (d) by OH reactivity contribution for oak.

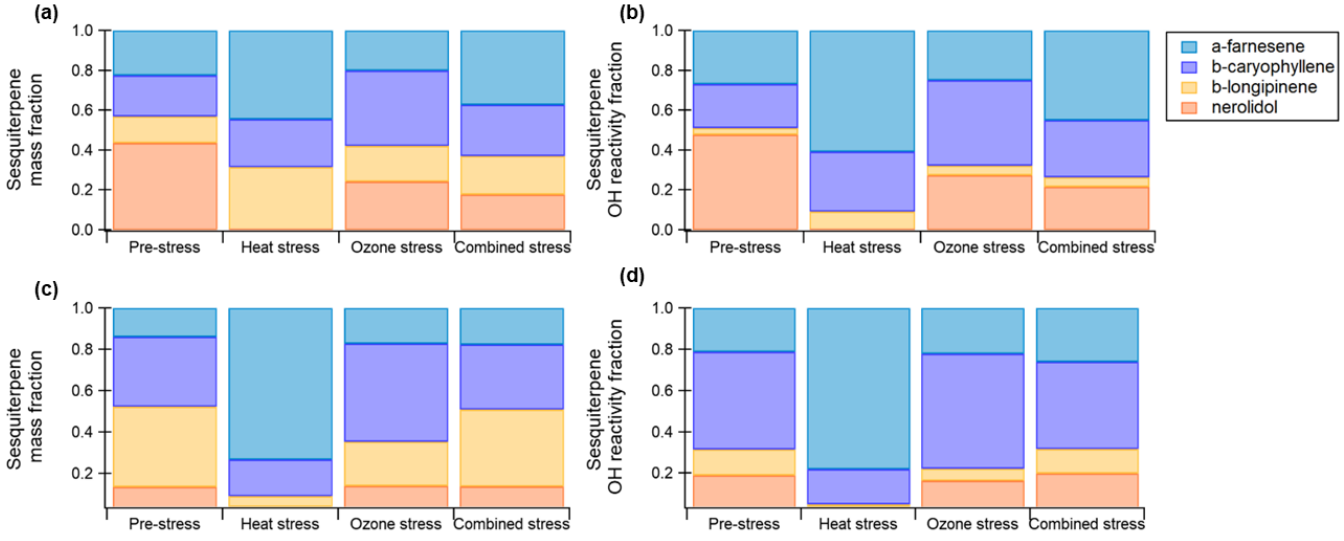

Figure S4. Sesquiterpenes emission composition (a) by mass for beech, (b) by OH reactivity contribution for beech, (c) by mass for oak, (d) by OH reactivity contribution for oak.

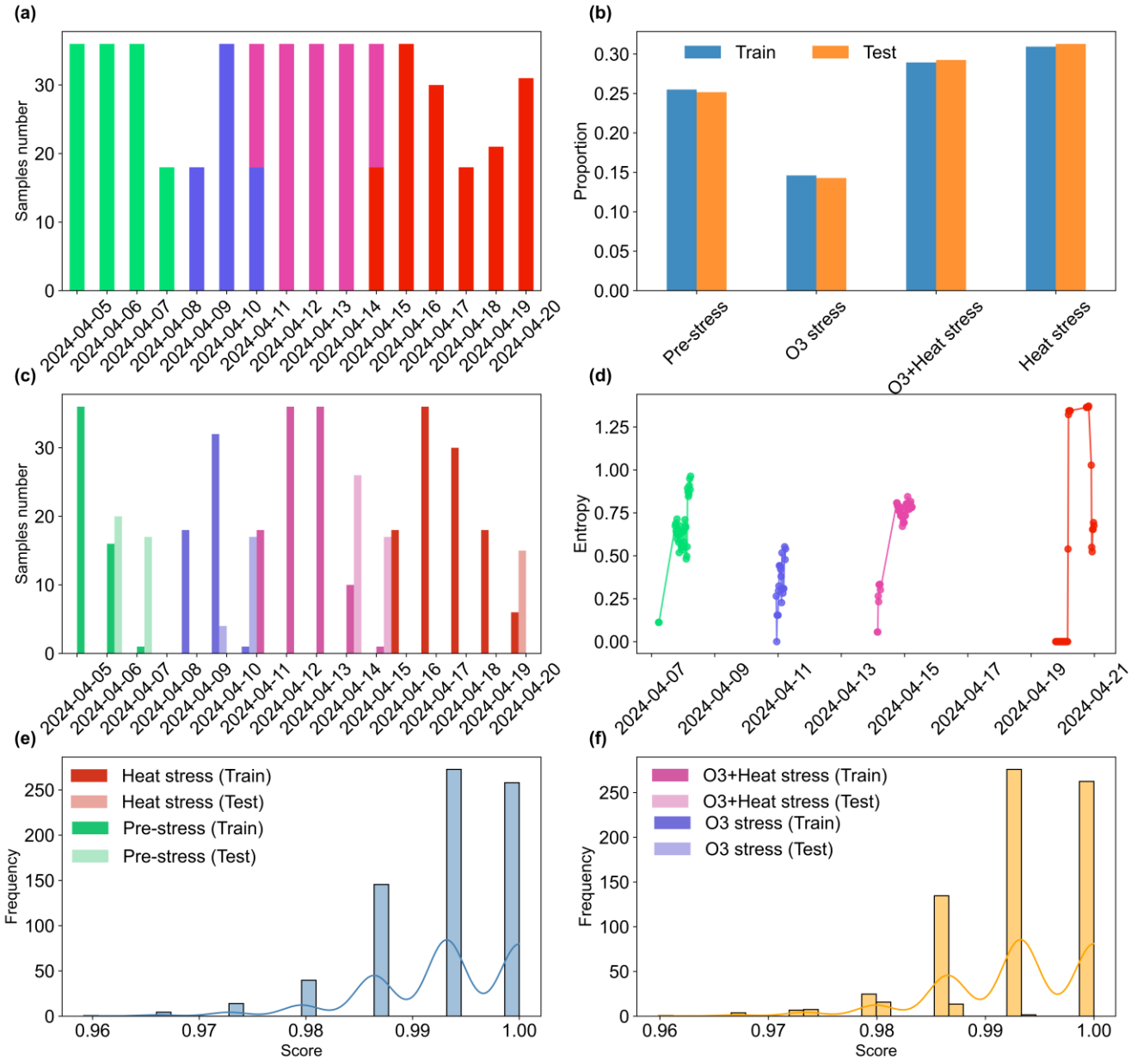

Figure S5 Overview of data distribution, data split strategy, and classification confidence of trained random forest model: Beech. (a) Daily sample counts coloured by stress class, (b) proportional distribution of training and test samples across the four stress classes, (c) training (solid) and test (transparent) temporal data split, (d) Shannon entropy of predicted class probabilities across the stress type for evaluating the trained model's uncertainty, (e–f) frequency distributions of model performance metrics based on 1,000 bootstrap iterations: (e) accuracy and (f) F1 score.

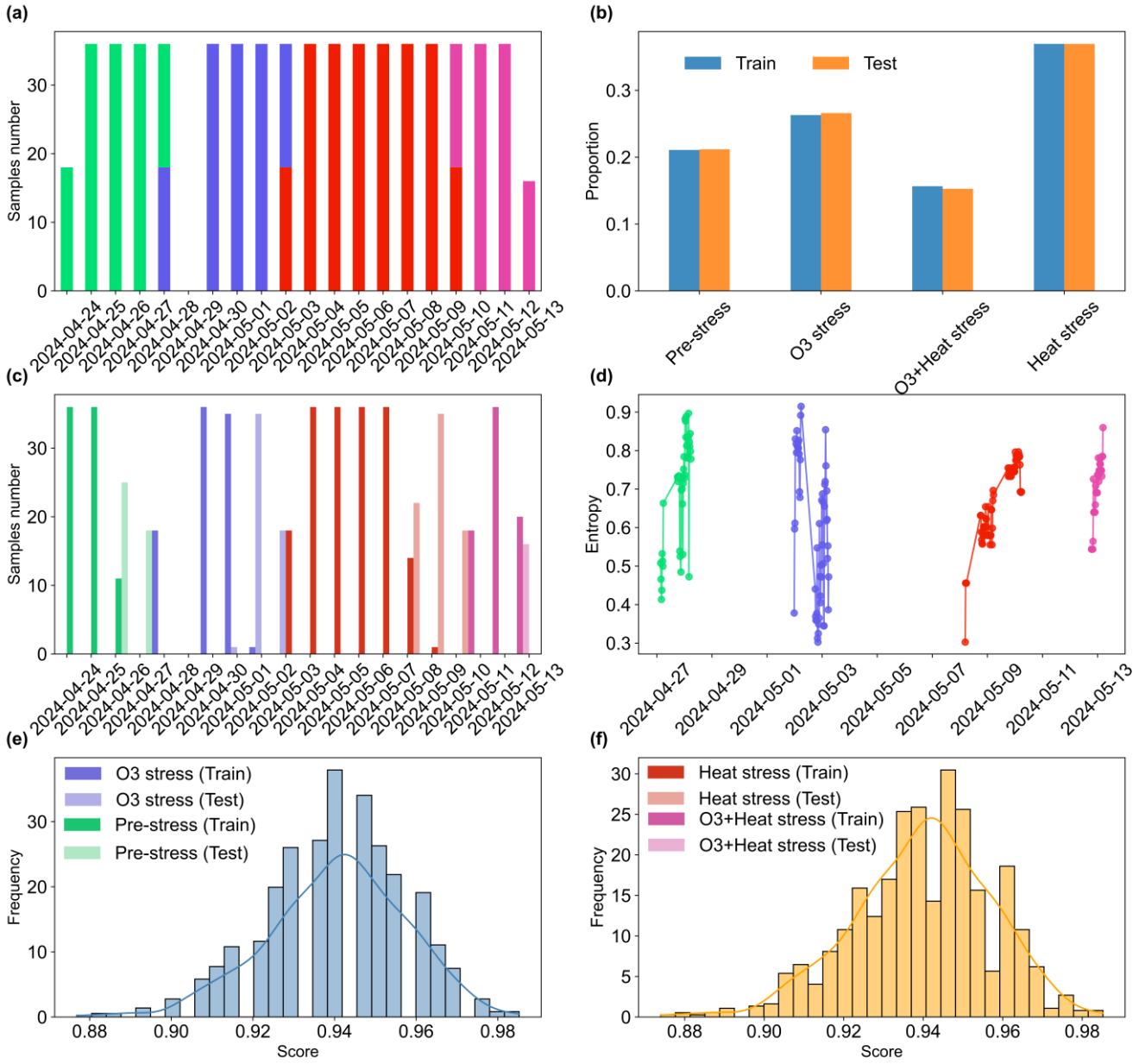

Figure S6 Overview of data distribution, data split strategy, and classification confidence of trained random forest model: Oak. (a) Daily sample counts coloured by stress class, (b) proportional distribution of training and test samples across the four stress classes, (c) training (solid) and test (transparent) temporal data split, (d) Shannon entropy of predicted class probabilities across the stress type for evaluating the trained model's uncertainty, (e–f) frequency distributions of model performance metrics based on 1,000 bootstrap iterations: (e) accuracy and (f) F1 score.

Table S3 Emission overview of stress-specific compounds for beech that are found from positive matrix factorization and machine learning. Median emission fluxes are presented in nmol m^{-2} s^{-1} with standard deviation (median± standard deviation).

Compounds	amu	Tentative name	Pre-stress	O3 stress	O3+Heat stress	Heat stress
CH5O+	33.03349	Methanol	4.01E-01 (± 3.35E-01)	1.04E-01 (± 2.12E-02)	1.03E-01 (± 7.59E-02)	1.64E+00 (± 6.73E-01)
C2H5O+	45.03349	Acetaldehyde	5.48E-02 (± 4.35E-02)	1.45E-02 (± 1.30E-02)	5.43E-02 (± 1.59E-01)	2.86E+00 (± 9.73E-01)
C2H7O+	47.04914	Ethanol	3.01E-03 (± 1.12E-03)	1.16E-03 (± 1.41E-04)	1.85E-03 (± 2.59E-03)	6.39E-02 (± 3.78E-02)
C4H9+	57.06988	Butanol fragments., Butene	8.23E-04 (± 3.15E-03)	6.85E-04 (± 1.80E-04)	2.43E-03 (± 1.96E-03)	1.50E-02 (± 1.08E-02)
C3H7O+	59.04914	Acetone	1.57E-02 (± 3.12E-03)	1.81E-02 (± 2.59E-03)	4.19E-02 (± 9.15E-03)	9.22E-02 (± 6.59E-02)
C3H9O+	61.06479	Propanol	1.65E-03 (± 3.12E-04)	1.16E-03 (± 7.51E-05)	2.39E-03 (± 6.89E-04)	4.54E-03 (± 1.38E-03)
C2H7S+	63.0263	Dimethyl sulfide	9.39E-04 (± 1.49E-04)	9.08E-04 (± 1.08E-04)	5.55E-03 (± 2.50E-02)	2.19E-02 (± 3.56E-02)
C5H9+	69.06988	Isoprene	2.67E-03 (± 5.48E-04)	2.25E-03 (± 8.77E-05)	4.60E-03 (± 1.70E-02)	2.59E-01 (± 8.46E-02)
C4H7O+	71.04914	MVK, MACR	1.95E-04 (± 1.50E-04)	1.06E-04 (± 4.22E-05)	5.35E-04 (± 4.35E-04)	1.28E-02 (± 1.11E-02)
C4H9O+	73.06479	Butanal, MEK	1.23E-02 (± 5.93E-03)	7.75E-03 (± 2.17E-03)	1.05E-02 (± 9.94E-03)	1.49E-01 (± 5.08E-02)
C3H7O2+	75.04406	Propanoic acid	2.59E-03 (± 1.05E-03)	1.09E-03 (± 2.70E-04)	2.85E-03 (± 2.87E-03)	3.54E-02 (± 1.19E-02)
C6H7+	79.05423	Benzenoid fragments	1.12E-03 (± 7.81E-04)	7.24E-04 (± 3.92E-04)	2.56E-03 (± 1.38E-03)	1.76E-02 (± 1.61E-02)
C6H9+	81.06988	MT fragment	2.03E-03 (± 5.05E-04)	3.74E-03 (± 7.65E-04)	1.73E-02 (± 8.19E-03)	6.66E-02 (± 3.02E-02)
C6H11+	83.08553	Cyclohexene	1.03E-03 (± 2.38E-04)	7.38E-04 (± 4.20E-05)	1.38E-03 (± 3.71E-03)	3.32E-02 (± 1.71E-02)
C5H9O+	85.06479	C5H8O	2.00E-04 (± 1.71E-04)	1.34E-04 (± 2.49E-05)	3.21E-04 (± 4.37E-04)	7.97E-03 (± 3.43E-03)
C6H13+	85.10118	Hexanol fr.	7.47E-05 (± 3.70E-05)	6.47E-05 (± 1.37E-05)	1.81E-04 (± 3.68E-04)	2.72E-03 (± 1.66E-03)
C5H11O+	87.08044	C5 carbonyls	1.47E-04 (± 8.71E-05)	1.07E-04 (± 3.28E-05)	3.33E-04 (± 2.93E-03)	4.43E-02 (± 1.66E-02)
C3H5O3+	89.02332	Pyruvic acid	5.46E-05 (± 1.35E-03)	4.40E-05 (± 1.04E-05)	7.85E-04 (± 5.56E-04)	3.10E-03 (± 8.04E-03)
C6H11O+	99.08044	Hexenal	2.42E-04 (± 8.19E-05)	1.60E-04 (± 2.41E-05)	5.16E-04 (± 1.78E-02)	2.14E-01 (± 1.17E-01)
C6H13O+	101.0961	Hexanal	1.05E-04 (± 5.87E-05)	9.23E-05 (± 8.22E-06)	1.78E-04 (± 3.49E-04)	3.99E-03 (± 1.83E-03)
C5H13O2+	105.091	Pentanediol	1.21E-04 (± 4.54E-05)	1.24E-04 (± 1.78E-05)	3.07E-04 (± 2.84E-03)	4.44E-02 (± 1.79E-02)
C7H7O+	107.0491	Benzaldehyde	4.99E-04 (± 3.46E-04)	2.24E-04 (± 1.26E-04)	7.85E-04 (± 6.92E-04)	9.25E-03 (± 3.65E-03)

C7H9O+	109.0648	Methylphenol	3.94E-04 (± 6.98E-05)	3.11E-04 (± 2.46E-05)	6.32E-04 (± 2.57E-04)	1.10E-03 (± 3.72E-04)
C7H13O+	113.0961	C7 unsaturated carbonyls	5.83E-05 (± 2.77E-05)	5.16E-05 (± 7.81E-06)	8.51E-05 (± 2.23E-05)	1.08E-03 (± 1.12E-03)
C6H13O2+	117.091	Ethyl butanoate	1.07E-04 (± 4.84E-05)	6.08E-05 (± 8.71E-06)	2.04E-04 (± 7.10E-03)	7.55E-02 (± 4.11E-02)
C8H9O+	121.0648	Tolualdehyde	1.23E-04 (± 7.05E-05)	7.57E-05 (± 1.08E-05)	2.03E-04 (± 7.17E-04)	8.00E-03 (± 3.71E-03)
C9H13+	121.1012	Trimethylbenzene	5.27E-05 (± 8.89E-05)	5.09E-05 (± 6.10E-06)	1.59E-04 (± 5.89E-05)	4.06E-04 (± 2.06E-03)
C9H15+	123.1168	SQT fragment	8.70E-05 (± 2.37E-05)	5.54E-05 (± 4.14E-06)	1.01E-04 (± 3.25E-05)	1.12E-03 (± 1.15E-03)
C9H12OH+	137.0961	Cumenol	9.68E-06 (± 6.25E-06)	4.75E-06 (± 6.67E-06)	1.16E-05 (± 2.97E-05)	8.04E-04 (± 3.16E-04)
C10H17+	137.1325	Monoterpenes	3.46E-03 (± 1.04E-03)	6.98E-03 (± 1.45E-03)	3.19E-02 (± 1.12E-02)	3.33E-03 (± 1.64E-02)
C8H9O3+	153.0546	Methyl salicylate	3.35E-03 (± 1.02E-03)	4.24E-03 (± 5.63E-04)	1.87E-03 (± 2.62E-03)	2.63E-03 (± 7.89E-03)
C10H13O2+	165.091	Phenethyl acetate	1.53E-05 (± 6.09E-06)	7.35E-06 (± 1.19E-06)	1.91E-05 (± 4.20E-05)	4.92E-03 (± 3.22E-03)
C13H21O+	193.1587	Ionone	7.13E-06 (± 2.99E-06)	4.26E-06 (± 4.57E-07)	1.18E-05 (± 1.63E-04)	2.44E-03 (± 1.37E-03)
C3H8O2H+	77.05971	Propanediol	5.02E-03 (± 1.03E-03)	4.45E-03 (± 4.72E-04)	8.91E-03 (± 1.94E-03)	2.42E-02 (± 2.03E-02)

Table S4 Emission overview of stress-specific compounds for oaks that are found from positive matrix factorization and machine learning. Median emission fluxes are presented in nmol m^{-2} s^{-1} with standard deviation (median± standard deviation).

Compounds	amu	Tentative name	Pre-stress	O3 stress	Heat stress	O3+Heat stress
CH5O+	33.03349	Methanol	1.44E+00 (± 5.45E-01)	1.15E-01 (± 4.31E-01)	8.33E-02 (± 1.15E-01)	1.18E-01 (± 2.04E-02)
C2H5O+	45.03349	Acetaldehyde	1.15E+00 (± 2.09E-01)	4.25E-01 (± 2.23E-01)	3.18E-01 (± 2.63E+00)	1.92E+00 (± 6.03E-01)
CH3O2+	47.01276	Formic acid	5.03E-03 (± 3.02E-03)	1.89E-03 (± 2.27E-03)	1.16E-03 (± 2.35E-03)	7.41E-03 (± 5.98E-04)
C2H7O+	47.04914	Ethanol	1.09E-02 (± 1.60E-03)	7.39E-03 (± 6.83E-03)	3.37E-02 (± 4.51E+00)	3.33E+00 (± 7.09E-01)
C4H9+	57.06988	Butanol fragments, Butene	2.74E-02 (± 3.57E-03)	2.59E-02 (± 6.22E-03)	4.24E-02 (± 1.74E-02)	4.26E-02 (± 5.27E-03)
C3H7O+	59.04914	Acetone	2.02E-01 (± 2.26E-02)	2.38E-01 (± 2.78E-02)	4.38E-01 (± 8.18E-02)	2.82E-01 (± 6.12E-02)
C2H5O2+	61.02841	Acetic acid	1.43E-01 (± 2.79E-02)	1.23E-01 (± 3.71E-02)	1.47E-01 (± 5.02E+00)	3.66E+00 (± 1.12E+00)
C3H9O+	61.06479	Propanol	4.16E-03 (± 4.55E-04)	3.67E-03 (± 2.14E-04)	7.49E-03 (± 2.87E-02)	5.75E-03 (± 7.20E-04)
C2H7S+	63.0263	Dimethyl sulfide	5.52E-03 (± 1.58E-03)	9.05E-03 (± 1.26E-03)	7.44E-02 (± 1.55E-01)	3.16E-04 (± 8.08E-04)
C5H9+	69.06988	Isoprene	8.70E+00 (± 1.63E+00)	6.03E+00 (± 1.87E+00)	8.36E+00 (± 2.45E+00)	9.65E-02 (± 2.78E-01)

C4H7O+	71.04914	MVK, MACR	1.26E-02 (± 4.91E-03)	9.72E-03 (± 1.04E-02)	1.19E-02 (± 3.39E-02)	4.68E-02 (± 1.10E-02)
C4H9O+	73.06479	Butanal, MEK	3.16E-02 (± 6.58E-03)	4.10E-02 (± 9.71E-03)	9.07E-02 (± 1.72E-01)	1.48E-01 (± 1.51E-02)
C3H7O2+	75.04406	Propanoic acid	3.54E-02 (± 3.00E-03)	3.94E-02 (± 4.57E-03)	1.02E-01 (± 6.44E-02)	6.45E-02 (± 3.00E-02)
C6H7+	79.05423	Benzenoid fragments	1.06E-02 (± 2.24E-03)	5.88E-03 (± 1.69E-03)	9.27E-03 (± 1.04E-01)	3.85E-02 (± 1.64E-02)
C6H13+	85.10118	Hexanol fragments	2.08E-03 (± 1.71E-04)	1.99E-03 (± 3.44E-04)	5.30E-03 (± 2.15E-02)	1.04E-02 (± 1.19E-02)
C5H11O+	87.08044	C5 carbonyls	2.16E-03 (± 4.45E-04)	2.21E-03 (± 9.41E-04)	1.40E-02 (± 5.60E-02)	3.24E-02 (± 5.30E-03)
C3H5O3+	89.02332	Pyruvic acid	1.38E-02 (± 2.01E-03)	1.41E-02 (± 2.63E-03)	3.33E-02 (± 4.00E-03)	1.88E-02 (± 4.97E-03)
C6H7O+	95.04914	phenol	8.05E-03 (± 2.98E-03)	6.13E-03 (± 4.60E-03)	1.04E-02 (± 1.48E-02)	1.56E-02 (± 2.89E-03)
C6H11O+	99.08044	Hexenal	4.27E-03 (± 4.48E-04)	4.77E-03 (± 7.87E-04)	6.00E-02 (± 8.50E-01)	2.77E-01 (± 3.08E-01)
C6H13O+	101.0961	Hexanal	4.20E-03 (± 1.17E-03)	4.17E-03 (± 7.85E-04)	7.31E-03 (± 2.03E-02)	1.09E-02 (± 6.61E-03)
C7H7O+	107.0491	Benzaldehyde	3.81E-03 (± 5.99E-04)	3.37E-03 (± 7.91E-04)	8.60E-03 (± 2.82E-02)	2.34E-02 (± 6.21E-03)
C6H7O2+	111.0441	Benzenediol	1.92E-02 (± 3.92E-03)	1.99E-02 (± 5.22E-02)	1.98E-02 (± 4.56E-03)	1.66E-02 (± 1.37E-03)
C6H13O2+	117.091	Ethyl butanoate	2.81E-03 (± 5.30E-04)	3.00E-03 (± 6.62E-04)	2.01E-02 (± 2.70E-01)	1.09E-01 (± 1.19E-01)
C8H9O+	121.0648	Tolualdehyde	9.84E-04 (± 1.73E-04)	1.36E-03 (± 1.12E-03)	1.15E-02 (± 6.42E-02)	3.47E-03 (± 1.55E-03)
C9H12OH+	137.0961	Cumenol	2.08E-04 (± 1.71E-05)	1.88E-04 (± 4.40E-05)	4.12E-04 (± 1.36E-03)	1.30E-03 (± 4.89E-04)
C8H9O3+	153.0546	Methyl salicylate	6.49E-03 (± 3.87E-03)	3.99E-03 (± 1.97E-03)	3.99E-03 (± 4.04E-03)	8.70E-03 (± 3.39E-03)
C10H13O2+	165.091	Phenethyl acetate	1.95E-04 (± 1.79E-05)	1.46E-04 (± 6.42E-04)	3.34E-04 (± 1.56E-02)	6.92E-03 (± 3.82E-03)
C13H21O+	193.1587	Ionone	7.88E-05 (± 8.64E-06)	7.47E-05 (± 1.44E-05)	4.61E-04 (± 2.02E-03)	2.64E-03 (± 2.62E-04)
C15H25+	205.1951	Sesquiterpenes	4.07E-03 (± 2.18E-04)	2.37E-03 (± 1.08E-03)	4.18E-03 (± 3.29E-02)	1.93E-03 (± 3.25E-03)
C5H7+	67.05423	Cyclopentadiene	4.40E-02 (± 6.83E-03)	5.38E-02 (± 9.71E-03)	1.77E-01 (± 3.90E-02)	6.04E-03 (± 9.88E-03)
C3H8O2H+	77.05971	Propanediol	4.55E-02 (± 4.64E-03)	5.81E-02 (± 4.61E-03)	9.81E-02 (± 1.46E-02)	4.16E-02 (± 1.41E-02)

References

Fitzky, A. C., Kaser, L., Peron, A., Karl, T., Graus, M., Tholen, D., Halbwirth, H., Trimmel, H., Pesendorfer, M., Rewald, B., and Sandén, H.: Same, same, but different: Drought and salinity affect BVOC emission rate and alter blend composition of urban trees, Urban For. Urban Green., 80, 0–2, https://doi.org/10.1016/j.ufug.2023.127842, 2023.