Supporting Information

Emissions from heated terpenoids
present in vaporizable cannabis concentrates
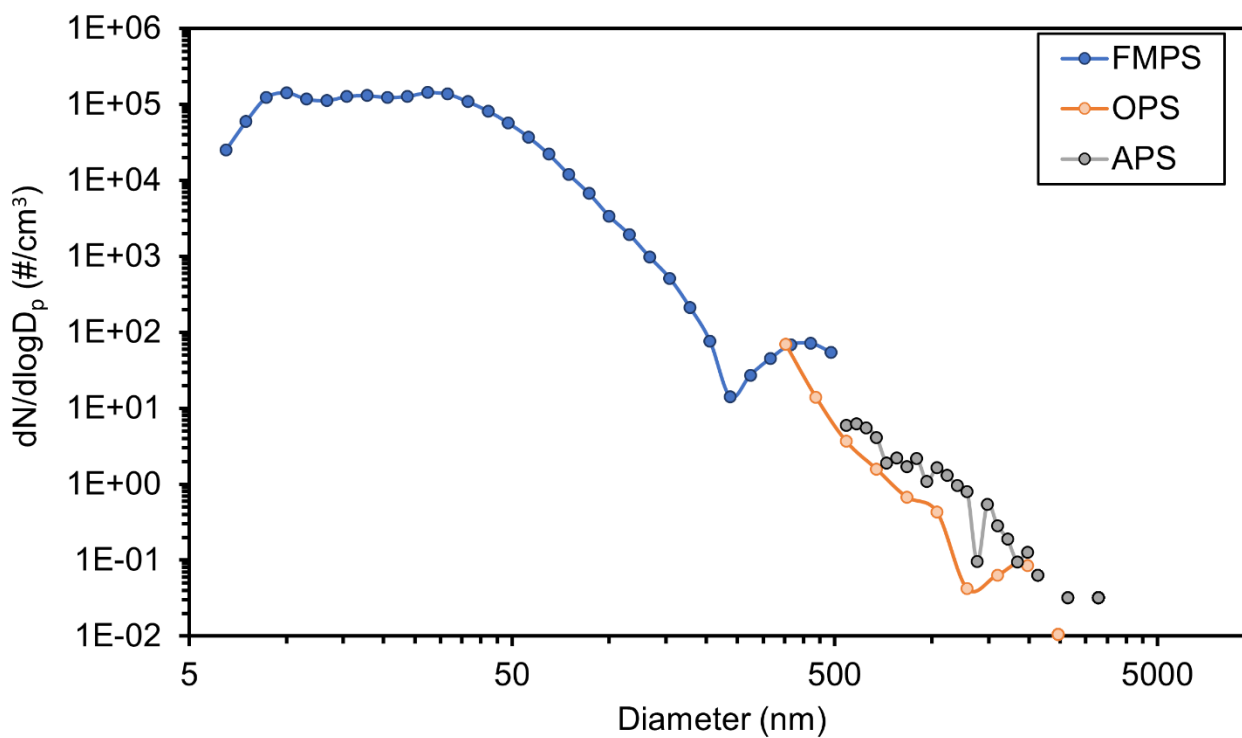
Xiaochen Tang[1,*], Lucia Cancelada[1,2], Vi Rapp[1], Marion L. Russell[1], Randy Maddalena[1],

Marta I. Litter[3], Lara A. Gundel[1], Hugo Destaillats[1,*]

1. Indoor Environment Group, Lawrence Berkeley National Laboratory, 1 Cyclotron Road MS70-108B, Berkeley, California 94720, United States

2. División Química de la Remediación Ambiental, CNEA-CONICET, Avenida Gral. Paz, (1650) San Martín, Buenos Aires, Argentina

3. Instituto de Investigación e Ingeniería Ambiental, UNSAM, CONICET, 3iA, Campus Miguelete, Av. 25 de Mayo y Francia (1650) San Martin, Buenos. Aires, Argentina

*Corresponding authors E-mail: HDestaillats@lbl.gov, XTang@lbl.gov

Number of pages	19
Number of figures	10
Number of tables	4

Light terpenoids

α – Pinene   β – Pinene   β – Myrcene   d-Limonene   Linalool

Heavy terpenoids

β – Caryophyllene   α – Humulene   Cedrol   α – Bisabolol

High MW compounds

Friedelin   Secoisolariciresinol   Quercetin

Figure S1. Molecular structures of studied compounds

Figure S2. Integration of results from three different aerosol instruments to capture the mass range from 5 nm to 5 µm. The figure shows the average particle number concentration measured with FMPS, OPS, and APS within the first minute of an experiment in which the full terpenoid mixture was heated at 500 °C.

Table S1. Mass concentration ($\mu g/m^3$) of gas-phase terpenes measured by GC/MS in chamber air in the blank chamber and from evaporating the full terpenoid mixture at room (~25 °C) and elevated temperatures (100-500 °C). Reported values correspond to the average of duplicate **determinations.**

|	Chamber blank					Full Mixture													
Heating temperature	25 °C #1	25° C #2	400 °C			25 °C	100 °C			250 °C			400 °C			500 °C		
Sample length (min)	180	210	10	20	30	60	10.5	20	30	10	20	30	10	20	30	10	20	30
α-pinene	0.30	0.28	5.3	2.2	1.2	40	52.	48	38	49	43	37	45	41	34	34	30	24
β-pinene	1.14	0.89	ND	ND	ND	65	45	47	59	86	41	51	67	66	56	52	51	48
β-myrcene	0.21	0.16	ND	ND	ND	79	110	95	79	122	91	78	111	95	74	120	103	83
limonene	ND	0.07	ND	ND	ND	45	72	61	46	64	56	44	60	53	42	69	58	47
linalool	ND	1.0	ND	ND	ND	26	20	13	20	22.1	14	11	17	33	21	16	17	23
β-caryophyllene	0.12	0.71	ND	0.5	ND	3.9	27	9.5	9.7*	71*	26	12	37	25*	34	20	26	7.6*
α-humulene	ND	ND	ND	ND	ND	0.2*	25	9.1	18	55*	23	12	39	46	25	16	19	5.6*
cedrol	0.35	0.45	5.4	2.7	1.9	1.7	38	16	14	65	40	16	55	26	12	75	30	9.7
α-bisabolol	ND	0.65	ND	ND	ND	2.6	47	23	17	82	31	20	67	25	15	79	28	14

ND: Not detected

*Determined with a single measurement.

Table S2. Mass concentration ($\mu g/m^3$) of gas-phase terpenes measured by GC/MS in chamber air from heating the complex mixture, light fraction and heavy fraction mixture at 500 °C. Reported values correspond to the average of duplicate determinations.

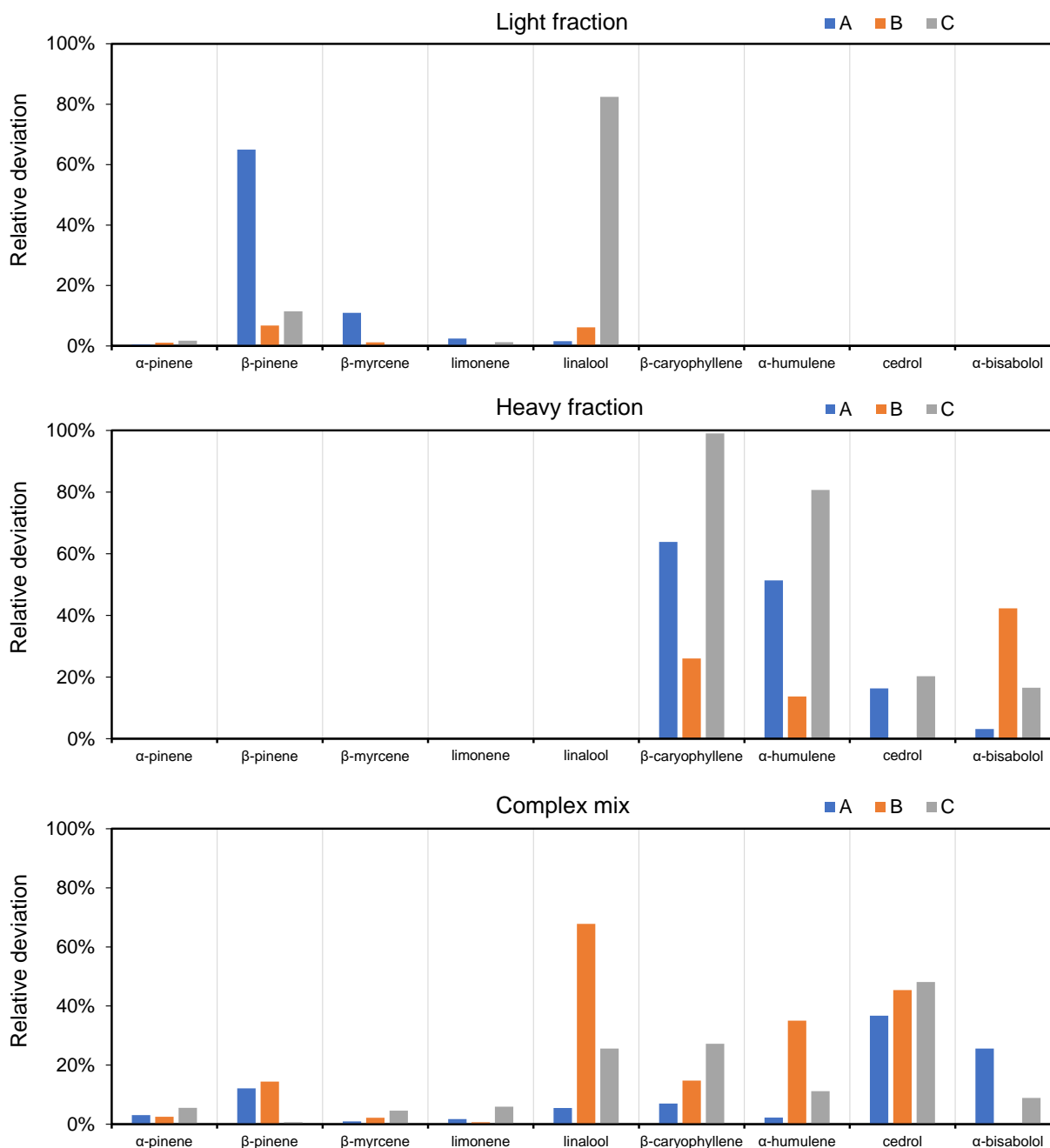|	Complex mixture			Light terpenoid mixture			Heavy terpenoid mixture		
Heating temperature	500 °C			500 °C			500 °C		
Sampling duration (min)	10	17	30	10	20	33	10	20	30
α-pinene	37	33	28	81	68	56	*3.5**	*1.9*	*1.3*
β-pinene	68	59	52	96	128	98	*15*	*7.7*	*5.2*
β-myrcene	120	100	79	220	200	150	*2.4*	*1.3*	*0.9*
limonene	65	56	45	130	110	82	ND	ND	ND
linalool	23	22	20	19	93	54	ND	ND	ND
β-caryophyllene	43	23	19	*0.9*	*1.1*	*1.0*	50	34	26
α-humulene	28	16	10	ND	ND	ND	52	32	21
cedrol	55	26	23	*5.8*	*2.9*	*1.8*	99	11**	14
α-bisabolol	60	25	17	ND	ND	ND	150	48	25

ND: not detected

* Values in italics correspond to concentrations of analytes that were not introduced in the tests, likely present as impurities of the released compounds and/or background chamber levels.

** Determined with a single measurement.
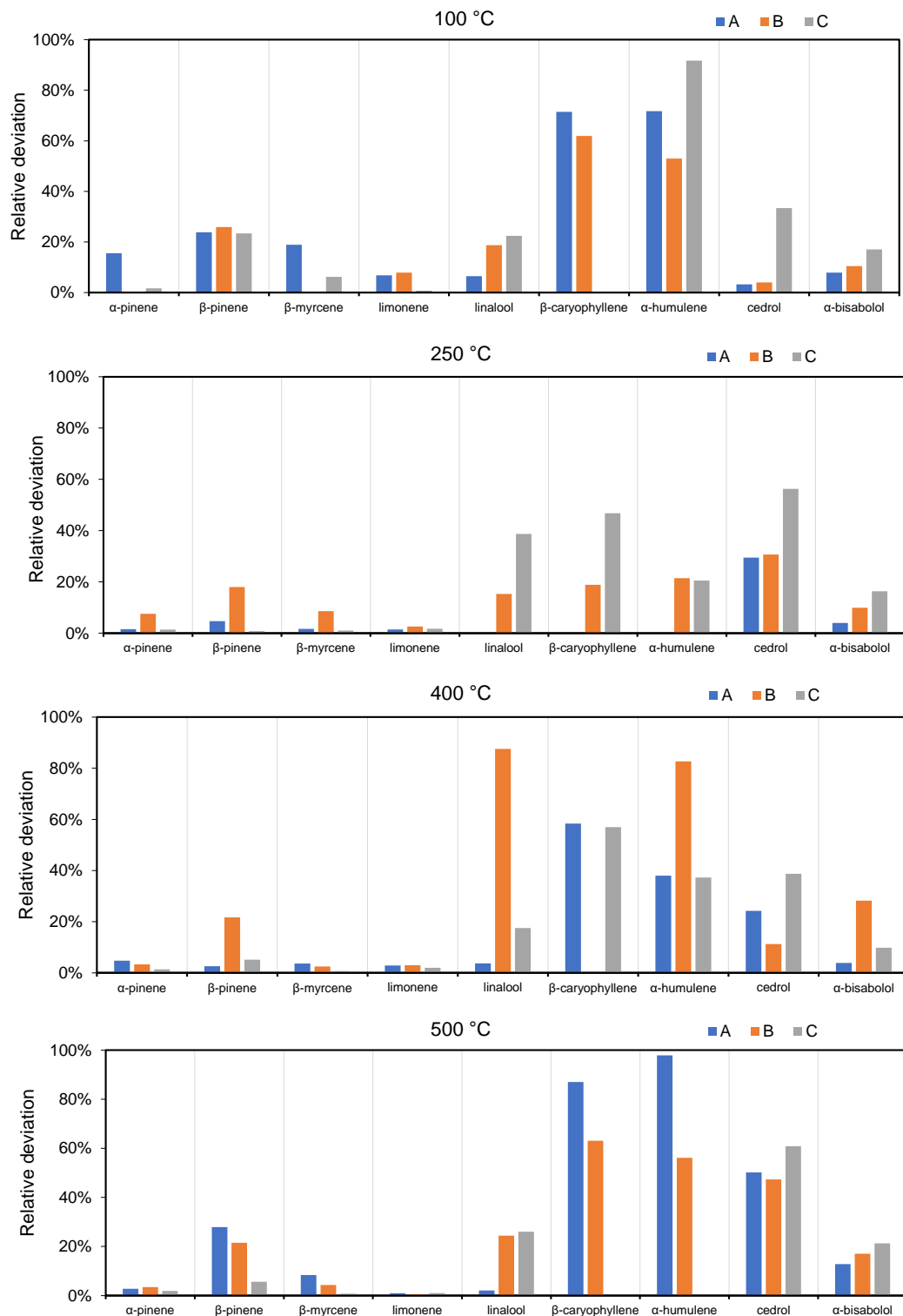
Figure S3. Relative deviation of duplicate GC/MS measurements for each terpenoid in each of the three samples (A, B, and C) collected during experiments conducted at difference temperatures with the full terpenoid mixture. Relative deviation was calculated by dividing the absolute difference of two determinations by their average.

Figure S4. Relative deviation of the duplicate GC/MS measurements for each terpenoid in each of the three samples (A, B, and C) collected during experiments conducted with the complex mixture, light and heavy terpenoid mixtures at 500 °C. Relative deviation is calculated by dividing the absolute difference of the two values by their average.

Table S3. Mass concentrations of degradation byproducts ($\mu g/m^3$) in the chamber blank, and produced upon heating the full terpenoid mixture at different temperatures and heating the complex mix, full mix, light fraction and heavy fraction at 500 °C (blank subtracted). Reported results are the average of two simultaneous determinations, with the difference between those determinations reported in parenthesis.

|	Chamber blank*	Full terpenoid mixture					Complex mixture	Light terpenoid mixture	Heavy terpenoid mixture
Temperature (°C)	**25**	**25**	**100**	**250**	**400**	**500**	**500**	**500**	**500**
Isoprene	0.7 (0.1)	0.9 (0.4)	1.8 (0.5)	2.6 (0.6)	4.1 (<0.1)	12.2 (0.7)	6.5 (0.1)	17 (0.5)	18 (1.4)
2,5-Dihydrotoluene	ND	ND	ND	0.5 (1.0)	0.9 (<0.1)	1.1 (<0.1)	1.0 (<0.1)	1.0 (0.1)	1.1 (0.1)
6-MHO	ND	0.9 (<0.1)	5.7 (0.2)	1.2 (0.3)	ND	1.4 (0.5)	1.7 (0.4)	ND	2.8 (1.6)
Benzene	0.5 (<0.1)	ND	ND	2.3 (0.4)	0.5 (<0.1)	0.4 (<0.1)	2.7 (0.4)	0.8 (<0.1)	0.3 (0.3)
Acrolein	0.2 (<0.1)	ND	3.9 (2.0)	1.6 (0.7)	1.5 (0.4)	1.3 (0.5)	1.6 (1.0)	2.8 (1.2)	1.6 (1.3)
Formaldehyde	4.5 (0.4)	3.5 (0.1)	4.5 (0.5)	2.5 (0.9)	3.1 (0.9)	4.7 (0.1)	2.7 (0.3)	11.0 (0.1)	7.5 (2.0)
Acetaldehyde	2.5 (<0.1)	1.8 (1.5)	1.3 (<0.1)	0.6 (0.2)	2.6 (2.2)	1.3 (0.2)	0.9 (0.2)	5.5 (1.0)	3.5 (0.1)
Acetone	5.4 (0.2)	4.2 (1.7)	3.4 (0.8)	3.0 (0.4)	5.9 (3.5)	10.6 (0.8)	6.7 (0.7)	23 (0.6)	15 (2.1)
Methacrolein	0.2 (<0.1)	ND	ND	ND	ND	2.0 (<0.1)	ND	3.3 (0.2)	2.5 (0.5)
Valeraldehyde	0.2 (<0.1)	8.7 (0.5)	1.9 (0.2)	0.6 (1.2)	ND	1.1 (2.2)	1.9 (0.3)	10 (<0.1)	ND
Hexaldehyde	ND	ND	ND	ND	ND	2.6 (0.3)	ND	ND	ND
2-butanone	0.40 (<0.1)	ND	ND	ND	ND	ND	ND	1.0 (0.5)	0.8 (0.4)

ND: not detected

* Average of two chamber blank measurements
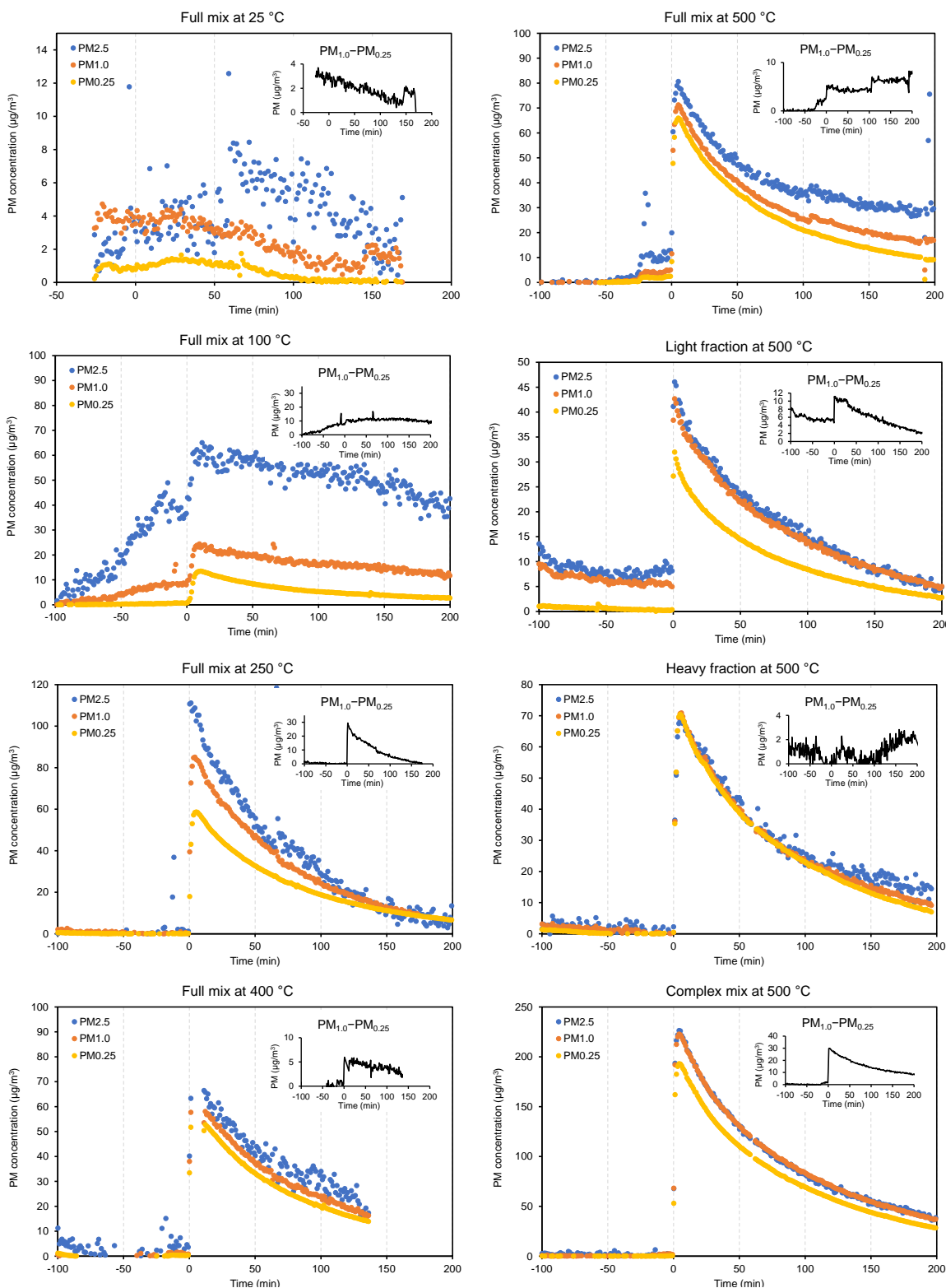
Figure S5. Time series of chamber $PM_{2.5}$, $PM_{1.0}$, and $PM_{0.25}$ mass concentration ($\mu g/m^3$) in all experiments, with the background concentration before the release of terpenoid mixture (time=0) subtracted from the data series. Inserts in the upper right corner show the difference between $PM_{1.0}$ and $PM_{0.25}$ mass concentration.
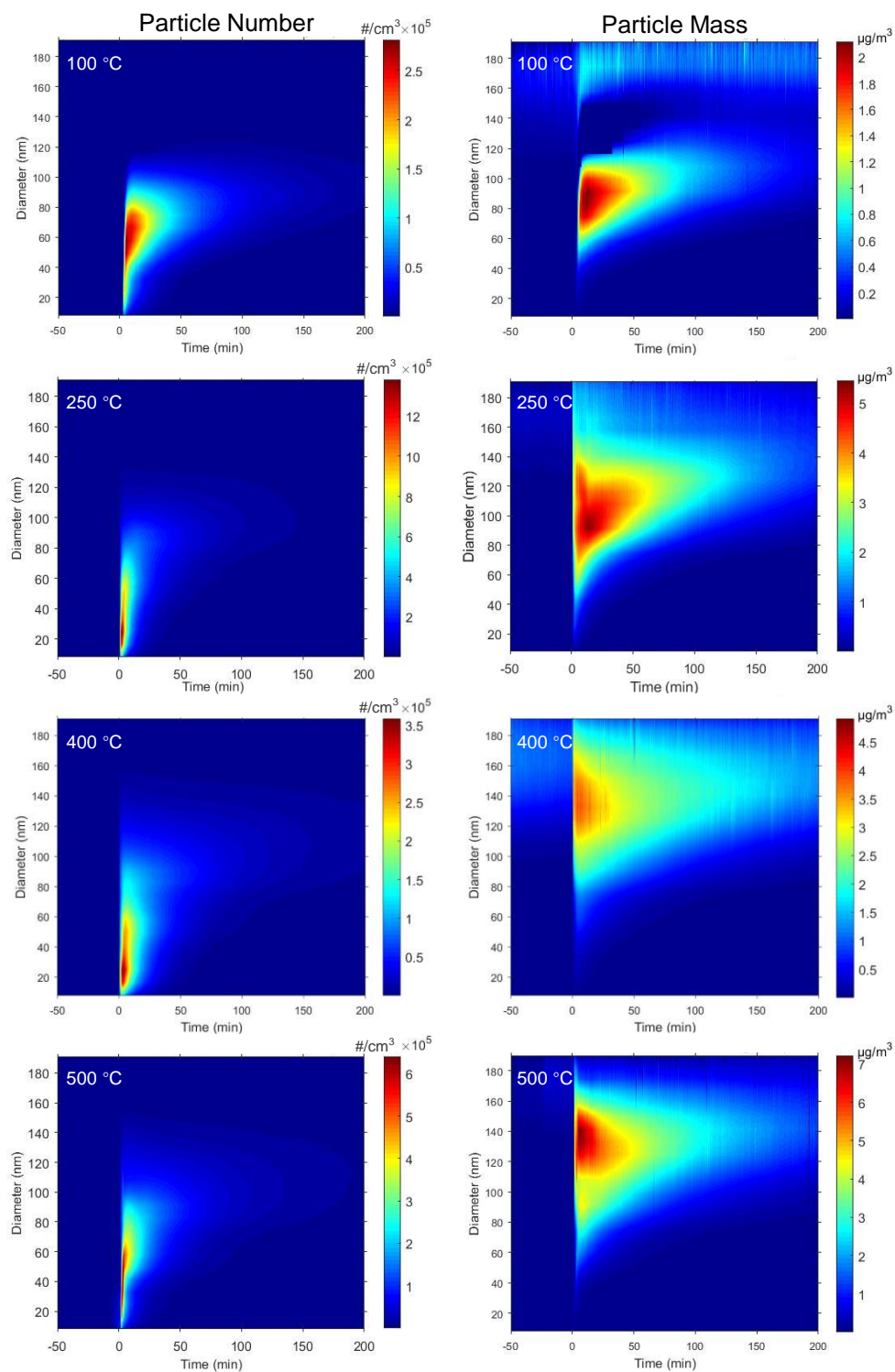
Figure S6. Contour plots of particle number (left) and mass (right) concentration distribution during the first 200 minutes after the full terpenoid mixture was delivered onto the heated surface.
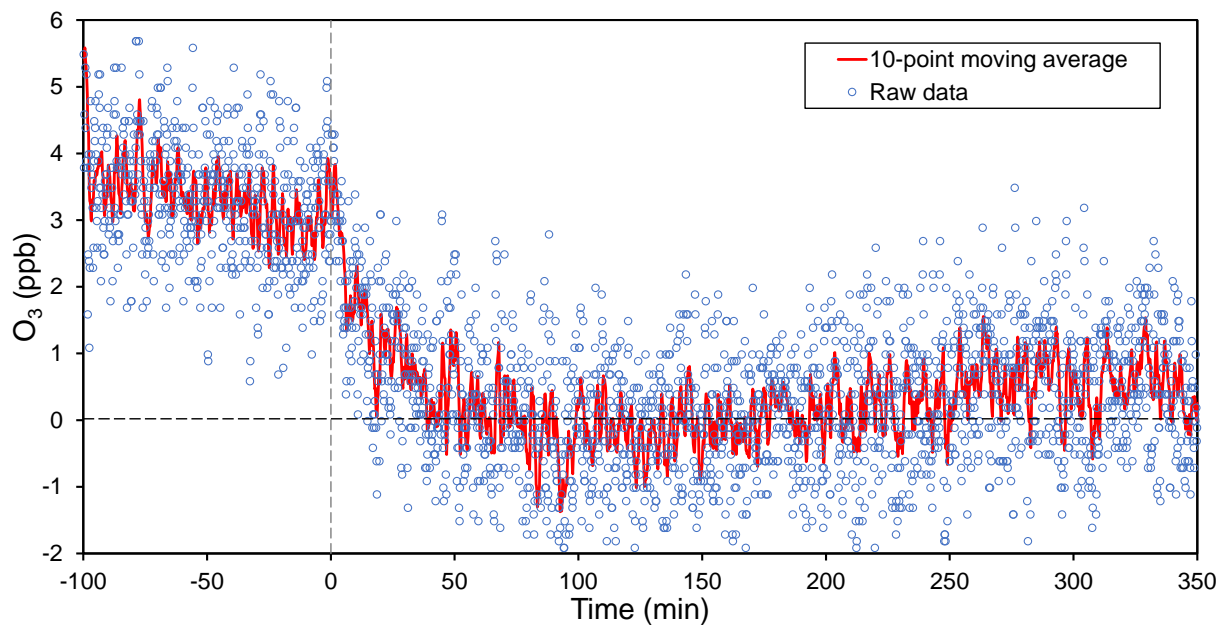
Figure S7. Example of measured chamber O_3 concentration during the experiments, showing a very low level of O_3 present in the chamber before the release of terpenoids.
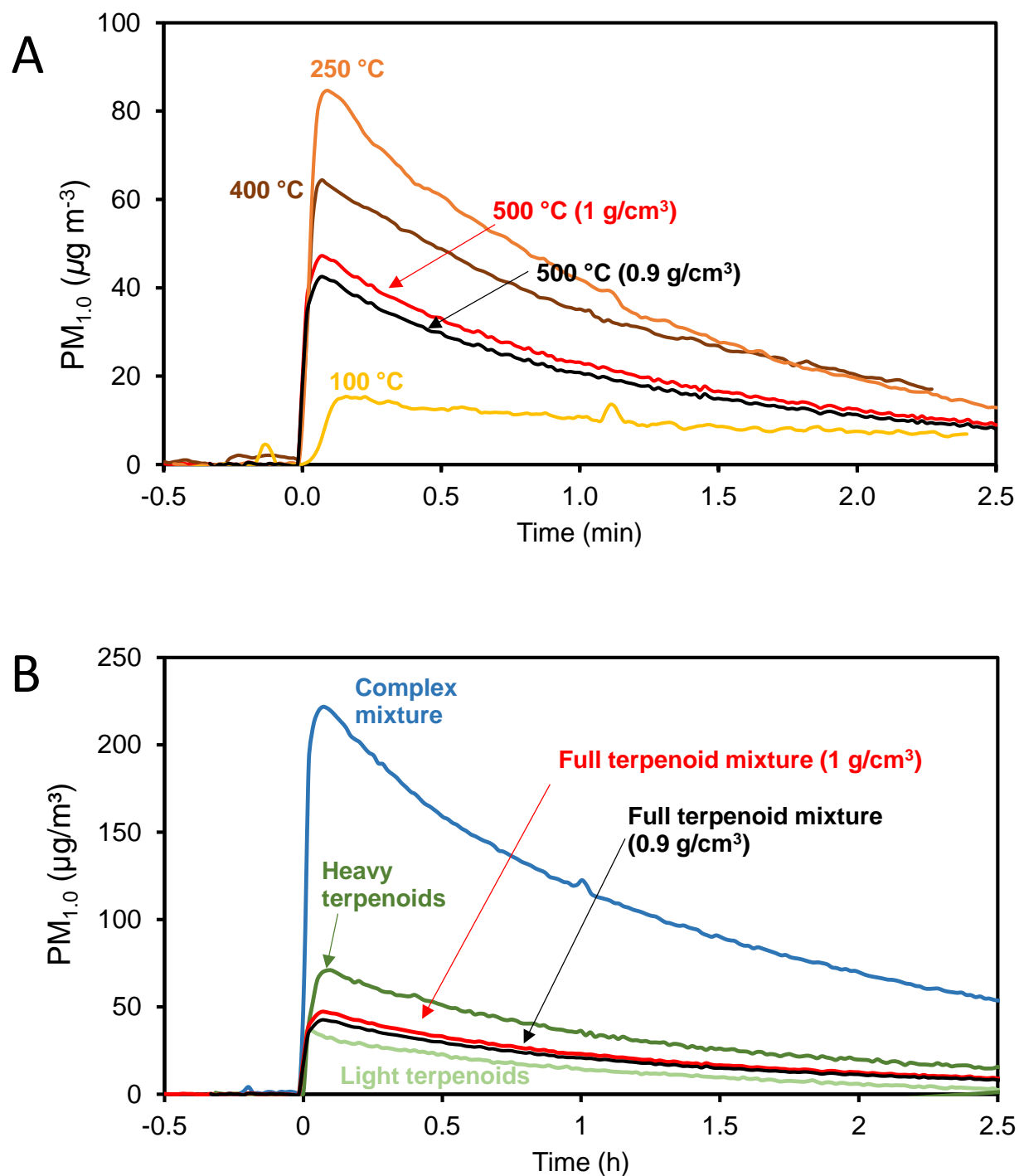
Figure S8. Time series of PM$_1$ mass concentration for aerosols formed from (A) heating the full terpenoid mixture at four different temperatures: 100, 250, 400, and 500 °C, and (B) heating at 500 °C four different mixtures: light fraction, heavy fraction, full mixture, and complex mixture. The plots include two versions of the full terpenoid mixture heated at 500 °C, calculated by assuming a particle density of 1 g/cm^3 and 0.9 g/cm^3, respectively.

A

B
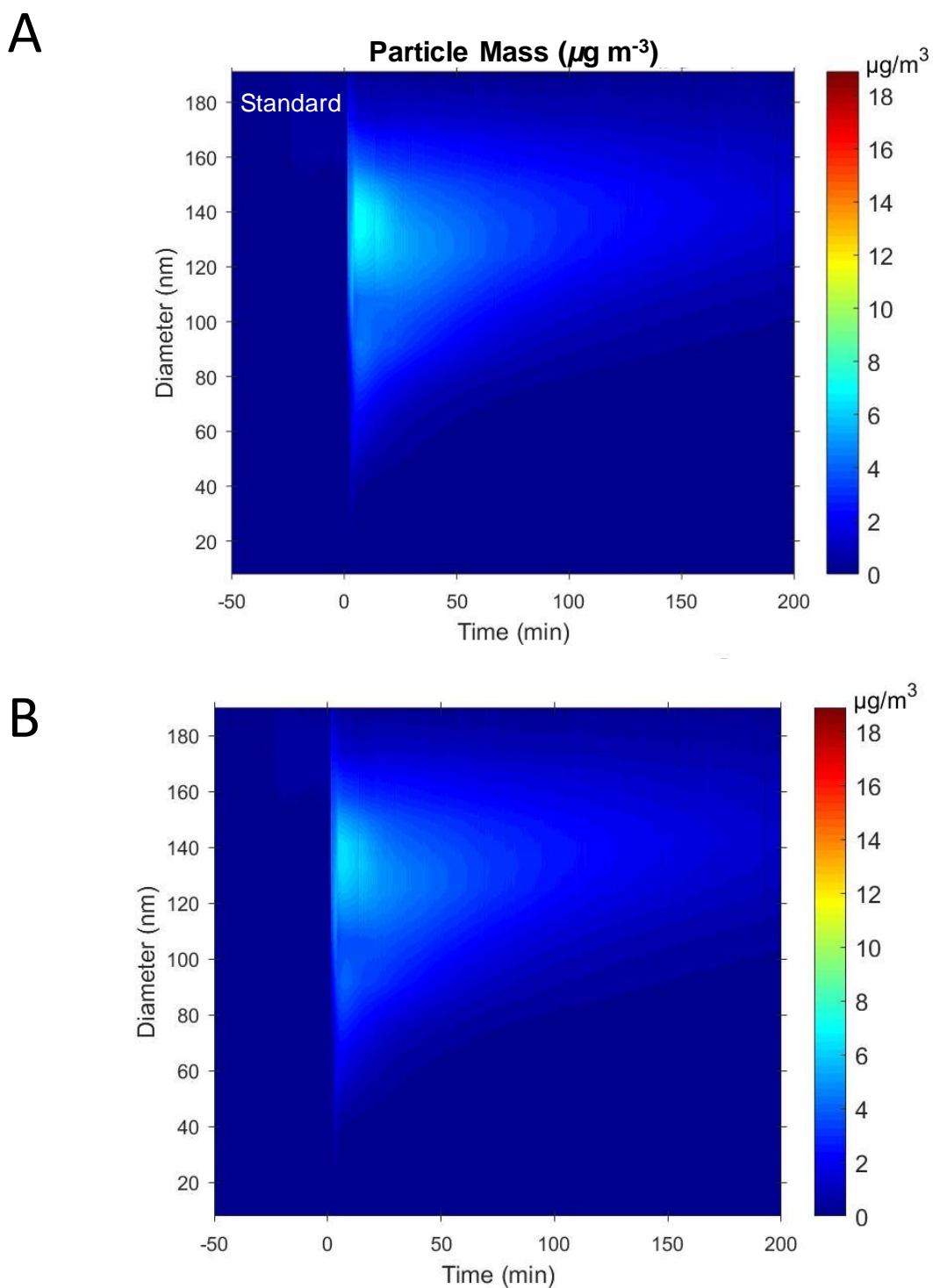
Figure S9. Particle mass concentration of aerosols within 8-200 nm diameter range, formed from heating the full terpenoid mixture at 500 °C. Calculated with (A) a particle density of 1 g/cm^3; and (B) with a particle density of 0.9 g/cm^3.

Calculation of emission rates (E)

The mass of acrolein, methacrolein and $PM_{1.0}$ released into the chamber (m_i), as well as the number of particles (n), were normalized by the mass of terpenoid mixture evaporated in chamber (M_i). The emission rate (E_i) for each contaminant i was determined by multiplying that ratio by the mass of terpenoids released per puff (M_{puff}).

(for acrolein, methacrolein and $PM_{1.0}$) $E_i = \frac{m_i}{M_i} \times M_{puff}$ (1)

(forPN) $E_i = \frac{n}{M_i} \times M_{puff}$ (2)

The amount of terpenoids present in dabbing and vaping formulations, and the amount of VCC consumed per puff were both estimated from values reported in the literature. In the case of vaping, the predicted volume of e-liquid used in a vape-pen cartridge was 1 mL, and the fraction of terpenoids was between 5% and 20%, considering that in some cases terpenoids are not only present in the plant extract but also added as co-solvents.[1] The predicted amount of e-liquid consumed per puff was between 30 and 70 μL. For dabbing, we used a mass of VCC consumed per dab of 40 mg, containing 6% of terpenoids.[2] Consumption patterns change significantly from one device to the next, and also change from one user to another. The terpenoid content can also vary significantly. For these reasons, this approach is applicable to the study of different devices, concentrates and consumption patterns. The emission rates determined with equations S1 and S2 can be adjusted to reflect different product consumption rates and terpenoid compositions.

All calculations were based on chamber concentrations determined upon heating the full terpenoid mixture at 500 °C. Concentrations determined during the first 10 minutes (sample A) were used for this calculation. Dilution from air exchange, at 0.2 h^{-1}, was only 3% during the sampling period. The acrolein chamber concentration (0.4 μg m^{-3}) was comparable to that measured when the mixture was heated at 100, 250 and 400 °C. By contrast, the chamber concentration of methacrolein used in this analysis (2 μg m^{-3}) was achieved after heating the full terpenoid mixture at 500 °C, but the compound was not present in emissions produced at lower temperatures. The PN and $PM_{1.0}$ concentrations were averaged over the first hour after being released to the chamber.

Calculation of daily users' intake

The estimated daily intake for each compound (DI_i) presented in Table 2 was calculated as:

$DI_i = E_i \cdot N \cdot R$ (3)

where N is the number of daily puffs expected for average users, and R is the fraction retained by the user. In this calculation, we used a range of $20 < N < 60$ for vaping, corresponding to a THC dosis equivalent to smoking between 1 and 3 joints per day.[3] In the case of dabbing, it should be noted that on a recent survey of 869 US dab users, only half of respondents reported use frequency equal or higher than once per day. For those cases, we estimated $2 < N < 6$ based on the reported mass of consumed concentrate.[4] It should be noted that the number of daily puffs for cannabis vaping and dabbing was significantly lower than those reported for nicotine/PG/VG e-cigarettes (up to 250 puffs per day) [5] and for conventional (tobacco) cigarettes (180-200 puffs per day for a moderately heavy smoker).[6] In addition, all forms of cannabis consumption are reported with a lower proportion of daily users, compared to tobacco smokers.[7]

Calculation of the increment in pollutant concentrations ($\varDelta C$) in a home

The amount of pollutant i released to the indoor environment per day (P_i) was calculated as

$$P_i = E_i \cdot N \cdot (1 - R) \tag{4}$$

The number of daily puffs (N) and fraction retained (R) were the same as those used to calculate the daily intake. The determined P_i values were used to calculate $\varDelta C$ as the 8-h average concentration in a 50-m^3 room with an air exchange rate of 0.2 h^{-1} following a dabbing or vaping event.

Calculation of the increment in pollutant concentrations ($\varDelta C$) in a public venue

Results reported by Waring and Siegel (2006)[8] of the number of cigarettes smoked per hour by patrons in 17 smoking bars were used to predict the number of puffs per hour in a public venue, assuming comparable occupancy and product use rate. That study reported space volumes between 284 and 2508 m^3, and the number of cigarettes consumed per hour between 40 and 130 units. The average number of cigarettes consumed per hour and per 100 m^3 was 13. This factor was applied to predict the number of puffs per hour for vaping and dabbing in a public venue. In the case of vaping, we predicted 130 puffs per hour per 100 m^3, corresponding to 13 e-cigarettes consumed in that time frame at an average of 10 puffs per e-cigarette. For dabbing, 13 consumers at 2 puffs each were considered to predict a total of 26 puffs per hour per 100 m^3. The amount released per hour and per 100 m^3 in each case was calculated with equation 4, and converted to concentrations in $\mu g\ m^{-3}$ (or to nr. of particles per cm^3, in the case of PN). Table 2 reports $\varDelta C$ as the 8-h average concentration for an air exchange rate of 1 h^{-1}, with vaping or dabbing taking place continuously during that period. The Waring and Siegel study reports a wide range of air exchange rates, between 0.6 and 6.5 h^{-1}. Our chosen value of ACH = 1 h^{-1} represents the low end of that range.

Table S4. PN emission rates plotted in Figure 5

Source	Particle size (nm)	E_{PN} (# min^{-1})	Reference
Heating cannabis terpenoids (vaping)	5 – 50	8 E11 – 1.6 E13	This work
Heating cannabis terpenoids (dabbing)	5 – 50	6 E11 – 1.2 E12	This work
Cooking	2 - 100		9
	7 - 808	3.4E10 – 7.3E11	10
Tobacco smoking	UFP	9 E10 - 3.5 E12	11
	10 - 1000	5.3 E10 – 2.1 E11	12
	5 – 560	1.2 E12 – 1.5 E12	13
Nicotine vaping (solvent: PG/VG)	5 – 560	6.6 E10 – 2.4 E11	13
	10 -1000	9.3 E9 – 1.3 E10	12
Heated tobacco product (IQOS)	5 – 560	1 E11 – 2.6 E11	13
	5 – 560	7.0 E10 – 9.7 E10	14
	10 -1000	2.6 E10 – 8 E10	12
Incense	6 - 560	8.5E10 – 2.4E11	15
Wax/scented candles	20 -100	9E10 – 3.7E11	16
Laser printers	11 – 124	3.4E8 – 1.6E12	17
Cookstoves			18
Ironing	20 – 100	7 E8 – 6 E9	16
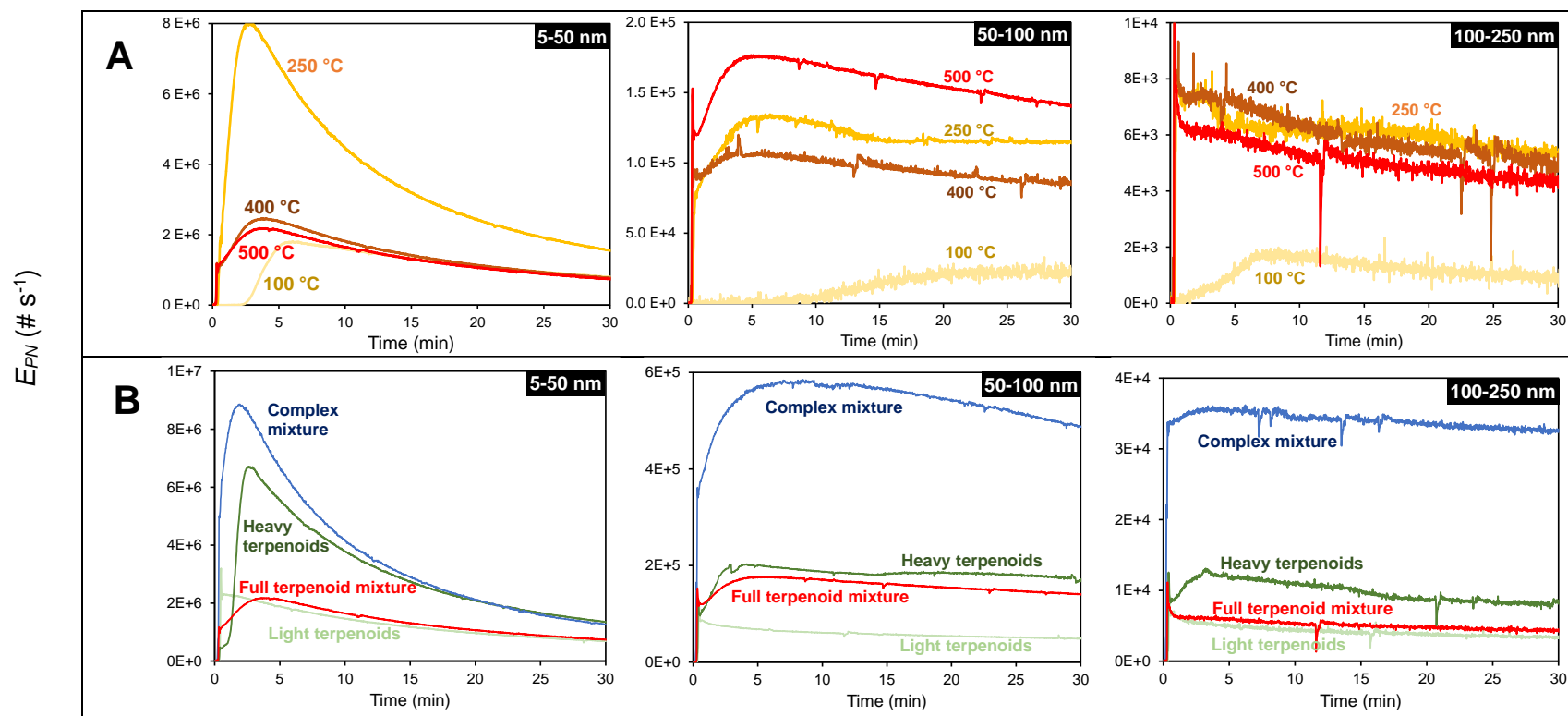
Figure S10. Particle emission rate (E_{PN}) during the first 30 min for three different size bins: 5-50 nm, 50-100nm and 100-250 nm after heating (A) the full terpenoid mixture at different temperatures, and (B) different mixtures at 500 °C.

REFERENCES

1.   Peace, M. R.; Stone, J. W.; Poklis, J. L.; Turner, J. B. M.; Poklis, A., Analysis of a commercial marijuana e-cigarette formulation. *J. Analytical Toxicology* **2016,** *40*, 374-378.

2.   Meehan-Atrash, J.; Luo, W.; Strongin, R. M., Toxicant formation in dabbing: The terpene story. *ACS Omega* **2017,** *2*, 6112-5117.

3.   Meehan-Atrash, J.; Luo, W.; McWhirter, K. J.; Strongin, R. M., Aerosol gas-phase components from cannabis e-cigarettes and dabbing: Mechanistic insight and quantitative risk analysis. *ACS Omega* **2019,** *4*, 16111-16120.

4.   Sagar, K. A.; Lambros, A. M.; Dahlgren, M. K.; Smith, R. T.; Gruber, S. A., Made from concentrate? A national web survey assessing dab use in the United States. *Drug and Alcohol Dependence* **2018,** *190*, 133-142.

5.   Logue, J. M.; Sleiman, M.; Montesinos, V. N.; Russell, M. L.; Litter, M. I.; Benowitz, N. L.; Gundel, L.; Destaillats, H., Emissions from electronic cigarettes: Assessing vapers' intake of toxic compounds, secondhand exposures, and the associated health impacts. *Environ Sci Technol* **2017,** *51*, 9271-9279.

6.   Krebs, N. M.; Chen, A.; Zhu, J.; Sun, D.; Liao, J.; Stennett, A. L.; Muscat, J. E., Comparison of puff volume with cigarettes per day in predicting nicotine uptake among daily smokers. *Amer. J. Epidemiol.* **2016,** *184(1)*, 48-57.

7.   Schauer, G. L.; Njai, R.; Grant-Lenzy, A. M., Modes of marijuana use – smoking, vaping, eating, and dabbing: Results from the 2016 BRFSS in 12 States. *Drug and Alcohol Dependence* **2020,** *209*, 107900.

8.   Waring, M. S.; Siegel, J. A., An evaluation of the indoor air quality in bars before and after a smoking ban in Austin, Texas. *J. Exposure Sci. Environ. Epidemiol.* **2006**, 1-9.

9.   Patel, S.; Sankhyan, S.; Boedicker, E. K.; DeCarlo, P. F.; Farmer, D. K.; Goldstein, A.; Katz, E. F.; Nazaroff, W. W.; Tian, Y.; Vanhanen, J.; Vance, M. E., Indoor particulate matter during HOMEChem: Concentrations, size distributions, and exposures. *Environ Sci Technol* **2020,** *54*, 7107-7116.

10.   He, C.; Morawska, L.; Hitchins, J.; Gilbert, D., Contributions from indoor sources to particle number and mass concentrations in residential houses. *Atmos. Environ.* **2004,** *38*, (21), 3405-3415.

11.	Chen, C.; Zhao, Y.; Zhao, B., Emission rates of ultrafine and fine particles generated from human smoking of Chinese cigarettes. *Atmos. Environ.* **2018,** *194*, 7-13.

12.	Ruprecht, A. A.; De Marco, C.; Saffari, A.; Pozzi, P.; Mazza, R.; Veronese, C.; Angellotti, G.; Muranini, E.; Ogliari, A. C.; Westerdahl, D.; Hasheminassab, S.; Shafer, M. M.; Schauer, J. J.; Repace, J.; Sioutas, C.; Boffi, R., Environmental pollution and emission factors of electronic cigarettes, heat-not-burn tobacco products, and conventional cigarettes. *Aerosol Sci. and Technol.* **2017,** *51*, (6), 674-684.

13.	Protano, C.; Manigrasso, M.; Avino, P.; Vitali, M., Second-hand smoke generated by combustion and electronic smoking devices used in real scenarios: Ultrafine particle pollution and age-related dose assessment. *Environment International* **2017,** *107*, 190-195.

14.	Pacitto, A.; Stabile, L.; Scungio, M.; Rizza, V.; Buonanno, G., Characterization of airborne particles emitted by an electrically heated tobacco smoking system. *Environmental Pollution* **2018,** *240*, 248-254.

15.	See, S. W.; Balasubramanian, R.; Joshi, U. M., Physical characteristics of nanoparticles emitted from incense smoke. *Science and Technology of Advanced Materials* **2007,** *8*, (1-2), 25-32.

16.	Afshari, A.; Matson, U.; Ekberg, L. E., Characterization of indoor sources of fine and ultrafine particles: A study conducted in a full-scale chamber. *Indoor Air* **2005,** *15*, 141-150.

17.	Scungio, M.; Vitanza, T.; Stabile, L.; Buonanno, G.; Morawska, L., Characterization of particle emission from laser printers. *Sci. Total Environ.* **2017,** *586*, 623-630.

18.	Rapp, V. H.; Caubel, J. J.; Wilson, D. L.; Gadgil, A. J., Reducing ultrafine aprticle emissions using air injection in wood-burning cookstoves. *Environ Sci Technol* **2016,** *50*, 8368-8374.