Large-scale reassessment of in-vineyard smoke-taint grapevine protection strategies and the development of predictive off-vine models

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Supplementary Materials.

Table S1. Evaluation of three agro-sprays' ability to influence the adhesiveness of VPs to table grapes.

smoke	treatment[1]	free	concentration (mean ± SEM) of volatile phenols (ng / g)								
			phenol[2],[3]	***o*-cresol**	***p*/*m*-cresol[4]**	**guaiacol**	**4-ethylphenol**	**4-methylguaiacol**	**4-ethylguaiacol**	**syringol**	**eugenol**
-	control	-	5.2 ± 0.21								
+	control	-	291.25 ± 32.34a	47.75 ± 5.95a	135.08 ± 10.31a	157.59 ± 17.92a	12.41 ± 1.29a	112.62 ± 14.92a	17.31 ± 4.14a		9.69 ± 2.36a
-	biofilm	-	5.46 ± 0.46								
+	biofilm	-	851.42 ± 22.22b	157.71 ± 4.06c	395.99 ± 37.31b	554.17 ± 18.28b	32.65 ± 6.83a	475 ± 8.25c	76.43 ± 1.79b	4.05 ± 0.46a	34.46 ± 1.83b
-	oil 1	-	5.02 ± 0.27		1.07 ± 0.04						
+	oil 1	-	479.4 ± 79.64a	90.47 ± 12.67b	188.18 ± 38.85a	274.52 ± 43.4a	15.44 ± 4.38a	228.64 ± 40.6b	34.9 ± 8.37a	2.17 ± 0.31a	17.72 ± 4.23a
-	oil 2	-	3.34 ± 0.45								
+	oil 2	-	433.83 ± 31.89a	85.53 ± 3.89b	184.28 ± 25.09a	255.43 ± 16.04a	15.61 ± 4.74a	223.01 ± 15.03ab	37.84 ± 4.4a	1.59 ± 0.58a	17.83 ± 1.94a
	S x T		****	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	smoke (S)		****	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	treatment (T)		****	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
smoke	**treatment**	**acid**	**phenol**	**o-cresol**	**p-m-cresol**	**guaiacol**	**4-ethylphenol**	**4-methylguaiacol**	**4-ethylguaiacol**	**syringol**	**eugenol**
-	control	+	3.63 ± 0.65	2.74 ± 0.18	2.03 ± 0.11	1.13	3.17 ± 0.58				5.69 ± 1.49
+	control	+	330.15 ± 49.87a	79.09 ± 14.6a	133.19 ± 14.68a	184.69 ± 13.75a	36.97 ± 10.17a	121.25 ± 12.59a	25 ± 4.75a		23.38 ± 4.25a
-	biofilm	+	10.78 ± 0.37		2.68 ± 0.1	1.89 ± 0.17	6.24 ± 0.7		1.44 ± 0.19		7.61 ± 0.38
+	biofilm	+	809.27 ± 27.77b	273.81 ± 19.36b	354.84 ± 20.97b	563.87 ± 27.36b	88.33 ± 15.52a	441.31 ± 30.4b	98.03 ± 1.78b	7.23 ± 0a	65.29 ± 1.42b
-	oil 1	+	15.59 ± 1.75	1.75 ± 0	3.66 ± 0.21	1.79 ± 0.13	6.96 ± 0.8		1.86 ± 0.17		7.62 ± 2.27
+	oil 1	+	436.84 ± 91.02a	134.83 ± 23.84a	172.63 ± 34.11a	270.37 ± 40.15a	40.99 ± 10.17a	212.19 ± 33.5a	43.99 ± 10.56a	3.61 ± 0.76a	36.69 ± 7.64a
-	oil 2	+	22.15 ± 3.36	3.11 ± 0	22 ± 1.76	1.66 ± 0.19	16.64 ± 5.47		3.04 ± 0.44		12.45 ± 2.02
+	oil 2	+	539.43 ± 95.65ab	179.54 ± 23.86ab	1.13 ± 0ab	234.91 ± 17.68a	79.27 ± 16.44a	172.75 ± 11.6a	53.45 ± 6.69a	3.66 ± 0.54a	42.32 ± 5.59ab
	S x T		**	-	****	****	ns	-	-	-	***
	smoke (S)		****	-	****	****	****	-	-	-	****
	treatment (T)		**	-	****	****	*	-	-	-	***

Notes: [1]All treatments are labelled identically to our previous research on the same products. Oil 1 and 2 are briefly described in the materials and methods; further details may be obtained in Favell *et al.* (2019). [2]All averages are reported ± the standard error of the mean of a maximum of three replicates; a pooled sample made from one unique cluster of grapes was considered to be a replicate. No zeros were imputed and blanks indicate that VP was below the method detection limit (MDL) for all three replicates of a particular treatment. Different letters (within columns) indicate a statistically significant difference between means of only the smoked samples for each VP as assessed using a one-way ANOVA followed by a Tukey HSD *post hoc* test ($P < 0.05$). A two-way ANOVA was used to evaluate the interaction between smoke (S) and treatment (T); *, **, *** and **** denote significant differences at $p \leq 0.05$, $p \leq 0.01$, $p \leq 0.001$ and $p \leq 0.0001$, respectively; n.s. = not significant; n.a. = not applicable (due to insufficient replicates). [4]*p*- and *m*-cresol were unresolvable by the GC-MS/MS conditions employed and the sum of these VPs is reported.

Table S2. Evaluation of the impact of washing grapes on VP concentrations[1].

smoke	treatment	wash[2]	concentration (mean ± SEM) of volatile phenols (ng / g)								
			phenol	*o*-cresol	*p*/*m*-cresol	guaiacol	4-ethylphenol	4-methylguaiacol	4-ethylguaiacol	syringol	eugenol
+	control	-	291.2 ± 32.34	47.7 ± 5.95	135.1 ± 10.31	157.6 ± 17.92	12.4 ± 1.29	112.6 ± 14.92	17.3 ± 4.14		9.7 ± 2.36
+	control	+	191.7 ± 21.87****	31.5 ± 2.81ns	91.7 ± 9.87ns	95.3 ± 8.01***	8.2 ± 1.31ns	66.9 ± 6.32ns	8.8 ± 1.32ns		4.1 ± 0.77ns
+	biofilm	-	851.4 ± 22.22	157.7 ± 4.06	396.0 ± 37.31	554.2 ± 18.28	32.6 ± 6.83	475.0 ± 8.25	76.4 ± 1.79	4.1 ± 0.46	34.5 ± 1.83
+	biofilm	+	911.8 ± 65.23ns	162.5 ± 15.57ns	458.5 ± 40.68ns	568.3 ± 53.69ns	46.8 ± 13.75ns	482.8 ± 55.68 ns	81.0 ± 12.98 ns	5.7 ± 0.72 ns	37.8 ± 7.78ns

Notes: [1]Only concentrations of free VPs were recorded. [2] + denotes samples that were washed under cold water for 30 s before processing and VP extraction. The impact of washing was evaluated using an unpaired t-test with the Holm-Sidak method to check for significance; *, **, *** and **** denote significant differences at $p \leq 0.05$, $p \leq 0.01$, $p \leq 0.001$ and $p \leq 0.0001$, respectively; ns = not significant.

Table S3. Concentrations of free and total (*i.e.* acid-labile plus free) VPs in grapes processed 1 and 24 h after smoke-exposure.

hour[1]	treatment	acid	concentration (mean ± SEM) of volatile phenols (ng / g)								
			phenol	*o*-cresol	*p*/*m*-cresol	guaiacol	4-ethylphenol	4-methylguaiacol	4-ethylguaiacol	syringol	eugenol
	smoke										
1	control	-	291.2 ± 32.34	47.7 ± 5.95	135.1 ± 10.31	157.6 ± 17.92	12.4 ± 1.29	112.6 ± 14.92	17.3 ± 4.14		9.7 ± 2.36
24	control	-	42.0 ± 15.20**	2.5 ± 0.28**	12.7 ± 1.61***	2.5 ± 0.71**	1.3 ns	1.8 ± 0.33**			1.3 ns
1	control	+	330.2 ± 49.87	79.1 ± 14.60	133.2 ± 14.68	184.7 ± 13.75	37.0 ± 10.17	121.3 ± 12.59	25.0 ± 4.75		23.4 ± 4.25
24	control	+	292.0 ± 53.44 ns	63.3 ± 17.94 ns	127.2 ± 32.27 ns	114.9 ± 13.60 ns	42.5 ± 18.65 ns	56.9 ± 11.65 ns	9.4 ± 1.54 ns		15.2 ± 4.91 ns
1	bioflim	-	851.4 ± 22.22	157.7 ± 4.06	396.0 ± 37.31	554.2 ± 18.28	32.6 ± 6.83	475.0 ± 8.25	76.4 ± 1.79	4.1 ± 0.46	34.5 ± 1.83
24	bioflim	-	381.2 ± 27.20***	16.1 ± 2.06****	96.3 ± 16.47**	20.8 ± 2.86****	9.4 ± 1.40*	17.4 ± 3.12****	3.1 ± 0.63****		2.2 ± 0.49****
1	bioflim	+	809.3 ± 27.77	273.8 ± 19.36	354.8 ± 20.97	563.9 ± 27.36	88.3 ± 15.52	441.3 ± 30.40	98.0 ± 1.78	7.2	65.3 ± 1.42
24	bioflim	+	801.3 ± 81.56 ns	254.7 ± 57.74 ns	411.8 ± 39.08 ns	504.2 ± 43.32 ns	136.0±30.04 ns	343.7 ± 45.15 ns	56.1 ± 1.37****	8.7 ± 0.37	41.8 ± 3.71 ns
	smoke		**relative concentrations (mean ± SEM) of volatile phenols (% of total)**								
1	control	-	37.2 ± 0.10	6.1 ± 0.14	17.2 ± 1.05	20.1 ± 0.23	1.6 ± 0.15	14.4 ± 0.60	2.2 ± 0.31		1.2 ± 0.18
24	control	-	65.6 ± 12.15	3.8 ± 0.75	19.8 ± 8.85	3.9 ± 0.49	2.0	2.8 ± 0.39			2.0
1	control	+	35.4 ± 0.86	8.5 ± 0.50	14.3 ± 0.39	19.8 ± 1.37	4.0 ± 0.64	13.0 ± 0.40	2.7 ± 0.17		2.5 ± 0.17
24	control	+	40.5 ± 1.46	8.8 ± 0.98	17.6 ± 1.54	15.9 ± 3.31	5.9 ± 1.50	7.9 ± 1.99	1.3 ± 0.19		2.1 ± 0.33
1	bioflim	-	33.0 ± 0.08	6.1 ± 0.88	15.3 ± 0.16	21.5 ± 0.22	1.3 ± 0.46	18.4 ± 0.07	3.0 ± 0.01	0.2 ± 0.06	1.3 ± 0.11
24	bioflim	-	69.8 ± 1.99	2.9 ± 0.11	17.6 ± 1.77	3.8 ± 0.20	1.7 ± 0.15	3.2 ± 0.30	0.6 ± 0.07		0.4 ± 0.06
1	bioflim	+	30.0 ± 0.77	10.1 ± 0.64	13.1 ± 0.58	20.9 ± 1.13	3.3 ± 0.55	16.3 ± 1.20	3.6 ± 0.07	0.3 ± 0.09	2.4 ± 0.04
24	bioflim	+	31.3 ± 1.69	10.0 ± 1.75	16.1 ± 0.87	19.7 ± 2.64	5.3 ± 0.95	13.4 ± 2.39	2.2 ± 0.08	0.3 ± 0.02	1.6 ± 0.07
	no smoke		**relative concentrations (mean ± SEM) of volatile phenols (% of total)**								
1	control	-	100.0 ± 0.00								
1	control	+	19.7 ± 0.65	14.9 ± 0.65	11.0 ± 0.11	6.1	17.2 ± 0.58				31.0 ± 1.42

Notes: [1] Hours post-smoke exposure. The difference in the VP presence over time was also evaluated by **unpaired t-test and the Holm-Sidak** method; **;** *, **, *** and **** denote significant differences at $p \leq 0.05$, $p \leq 0.01$, $p \leq 0.001$ and $p \leq 0.0001$, respectively; ns = not significant.

Table S4. Vineyard 1: Free VP concentrations immediately after (T_1) smoke-exposure and at harvest (T_2).[(1)(2)(3)]

VP	smoke	biofilm application: days before smoke exposure				S x T	smoke (S)	treatment (T)
		control	1	7	14			
time: 1 hour post-smoke exposure (T_1)								
syringol	-							
syringol	+							
phenol	-	2.1 ± 0.51	1.38 ± 0.48	1.54 ± 0.24	1.44 ± 0.16	ns	***	ns
phenol	+	4.22 ± 1.66a	10.58 ± 2.87a	7.56 ± 2.53a	7.35 ± 2.47a			
p/*m*-cresol	-	0.46 ± 0.12	0.3 ± 0.16	0.28 ± 0.12	0.25 ± 0.18	**	****	**
p/*m*-cresol	+	1.69 ± 0.51a	7.98 ± 1.38ab	5.11 ± 0.79ab	4.43 ± 0.74b			
o-cresol	-	1.31 ± 0.38	1.29 ± 0.13	1.47 ± 0.17	1.23 ± 0.32	**	****	**
o-cresol	+	4.81 ± 1.15a	18.08 ± 3ab	12.24 ± 1.75ab	10.06 ± 2.02b			
guaiacol	-							
guaiacol	+	3.91 ± 1.71a	25.15 ± 6.25ab	14.96 ± 4.1ab	10.27 ± 1.87b			
eugenol	-	0.58 ± 0.41	0.74 ± 0.16	1.23 ± 0.7	1.21 ± 0.31	ns	ns	ns
eugenol	+	1.07 ± 0.19a	1.6 ± 0.5a	0.98 ± 0.13a	1.18 ± 0.21a			
4-methylguaiacol	-	0.53 ± 0	0.1 ± 0					
4-methylguaiacol	+	1.06 ± 0.42a	12.07 ± 2.94a	5.78 ± 1.09ab	4.12 ± 0.65b			
4-ethylphenol	-	0.27 ± 0.01	0.25 ± 0.04	0.27 ± 0.03	0.24 ± 0.02	*	****	*
4-ethylphenol	+	0.44 ± 0.03a	0.83 ± 0.12ab	0.65 ± 0.05ab	0.63 ± 0.07b			
4-ethylguaiacol	-							
4-ethylguaiacol	+							
time: harvest (T_2)								
syringol	-							
syringol	+	0.31 ± 0.03a	0.27 ± 0.02a	0.29 ± 0.05a	0.26 ± 0.01a			
phenol	-	11.32 ± 0.91	13.28 ± 0.65	13.14 ± 0.86	13.36 ± 0.49	ns	****	ns
phenol	+	34.42 ± 9.92a	83.91 ± 15.78a	53.73 ± 16.38a	55.96 ± 9.22a			
p/*m*-cresol	-	1.44 ± 0.11	1.85 ± 0.15	1.99 ± 0.09	1.71 ± 0.07	**	****	**
p/*m*-cresol	+	4.93 ± 1.17a	11.17 ± 1.34ab	7.55 ± 1.64b	11.05 ± 1.07b			
o-cresol	-	5.97 ± 1.09	3.57 ± 0.3	5.14 ± 1.27	4.33 ± 0.29	ns	****	ns
o-cresol	+	11.43 ± 3.28a	18.09 ± 1.98a	12.75 ± 2.6a	16.99 ± 1.86a			
guaiacol	-	1.04 ± 0.03	1.3 ± 0.08	1.31 ± 0.04	1.15 ± 0.04	*	****	*
guaiacol	+	6.92 ± 2.5a	20.41 ± 4.11ab	11.68 ± 2.17ab	13.57 ± 1.54b			
eugenol	-	0.15 ± 0	0.41 ± 0.06	0.75 ± 0.62	0.37 ± 0.11	ns	***	ns
eugenol	+	0.85 ± 0.1a	1.17 ± 0.18a	0.92 ± 0.11a	1.44 ± 0.25a			
4-methylguaiacol	-	0.4 ± 0.02	0.42 ± 0.01	0.43 ± 0.02	0.41 ± 0.01	**	****	**
4-methylguaiacol	+	1.36 ± 0.39a	5.2 ± 1.14ab	2.93 ± 0.35ab	3.4 ± 0.37b			
4-ethylphenol	-	1.39 ± 0.07	1.44 ± 0.06	1.59 ± 0.07	1.56 ± 0.04	ns	****	*
4-ethylphenol	+	1.89 ± 0.07a	2.06 ± 0.1a	2.1 ± 0.17a	2.2 ± 0.09a			
4-ethylguaiacol	-	0.19 ± 0.01	0.2 ± 0	0.19 ± 0	0.2 ± 0.02	**	****	**
4-ethylguaiacol	+	0.25 ± 0.02a	0.58 ± 0.11ab	0.36 ± 0.02ab	0.49 ± 0.05b			

Notes: [(1)] Mean VP concentrations ($n = 4$) are recorded in ng/g ± the standard error of the mean (SEM). [(2)] The effects of smoke (S), biofilm treatments (T) and S x T interaction were tested with a two-way ANOVA; *, **, *** and **** denote significant differences of $p \leq 0.05$, $p \leq 0.01$, $p \leq 0.001$ and $p \leq 0.0001$, respectively; ns = not significant ($p \geq 0.05$). [(3)] Different letters (within the rows) indicate the differences in effects of time of biofilm application on the smoked sample only using one-way ANOVA followed by a Tukey's HSD test. Blank cells denote concentrations below the method limit of detection.

Table S5. Vineyard 1: Total (*i.e.* quantitated after acid hydrolysis) VP concentrations immediately after (T_1) smoke-exposure and at harvest (T_2).[(1)(2)]

VP	smoke	biofilm application: days before smoke exposure				S x T	smoke (S)	treatment (T)
		control	1	7	14			
time: 1 hour post-smoke exposure (T_1)								
syringol	-	13.17 ± 1.98	18.21 ± 3.26	11.74 ± 1.77	11.34 ± 1.27	ns	ns	ns
syringol	+	19.64 ± 1.88a	17.99 ± 3.77a	18.21 ± 1.52a	11.46 ± 2.34a			
phenol	-	23.78 ± 2.56	24.25 ± 4.54	21.73 ± 2.3	18.52 ± 1.82	ns	****	*
phenol	+	42.7 ± 8.99a	70.59 ± 7.68a	49.29 ± 10.1a	36.48 ± 9.53a			
p/*m*-cresol	-	4.96 ± 1.3	5.72 ± 0.86	5.88 ± 0.39	5.47 ± 0.45	*	****	**
p/*m*-cresol	+	10.52 ± 1.22a	20.61 ± 2.05a	17.24 ± 2.87a	10.47 ± 2.73a			
o-cresol	-	13.96 ± 5.54	15.57 ± 3.52	13.98 ± 1.14	16.2 ± 2.33	ns	****	ns
o-cresol	+	31.99 ± 3.84a	48.15 ± 7.57a	45.03 ± 8.75a	28.48 ± 5.65a			
guaiacol	-	4.19 ± 0.53	3.08 ± 0.47	2.99 ± 0.31	2.66 ± 0.14	**	****	*
guaiacol	+	12.1 ± 2.84ab	29.24 ± 4.35a	24.31 ± 4.39ab	13.97 ± 3.23b			
eugenol	-	8.16 ± 2.66	7.43 ± 1.79	7.37 ± 2.03	9.5 ± 1.71	ns	ns	ns
eugenol	+	10.52 ± 1.59a	6.28 ± 1.07b	8.03 ± 0.98ab	5.42 ± 0.69ab			
4-methylguaiacol	-	31.92 ± 7.99	44.35 ± 12.76	27.32 ± 6.45	33.87 ± 3.82	ns	ns	ns
4-methylguaiacol	+	50.28 ± 15.72a	57.8 ± 4.88a	41.63 ± 1.45a	27.75 ± 8.62a			
4-ethylphenol	-	6.6 ± 0.33	6.6 ± 1.39	4.58 ± 0.9	4.85 ± 0.29	ns	ns	*
4-ethylphenol	+	6.04 ± 0.42a	7.11 ± 0.21a	5.97 ± 0.53a	5.3 ± 0.6a			
4-ethylguaiacol	-	1.93 ± 0.07	1.46 ± 0.32	1.51 ± 0.12	1.68 ± 0.11	ns	**	ns
4-ethylguaiacol	+	1.97 ± 0.21a	2.35 ± 0.1a	2.16 ± 0.22a	1.76 ± 0.14a			
time: harvest (T_2)								
syringol	-	19.57 ± 2.14	22.38 ± 2.8	18.1 ± 0.75	26.81 ± 12.51	ns	ns	ns
syringol	+	24.28 ± 3.93a	21.31 ± 1.86a	24.92 ± 1.45a	20.98 ± 2.26a			
phenol	-	48.56 ± 7.65	54.58 ± 4.38	40.71 ± 3.25	21.3 ± 7.82	*	****	*
phenol	+	133.02 ± 32.78a	290.43 ± 42.95a	226.6 ± 26.15a	221.16 ± 38.2a			
p/*m*-cresol	-	16.76 ± 4.2	18.83 ± 4.5	12.04 ± 0.64	7.05 ± 2.94	ns	****	ns
p/*m*-cresol	+	44.01 ± 16.42a	74.2 ± 10.06a	68.81 ± 5.08a	74.01 ± 8.82a			
o-cresol	-	77.34 ± 20.71	51.18 ± 8.43	37.54 ± 8.9	22.92 ± 8.89	ns	ns	ns
o-cresol	+	55.51 ± 13.46a	58.7 ± 4.52a	65.76 ± 12.02a	61.2 ± 10.78a			
guaiacol	-	9.59 ± 1.19	9.6 ± 0.87	8.85 ± 0.48	9.05 ± 1.42	*	****	*
guaiacol	+	23.67 ± 7.11a	64.24 ± 11.91ab	47.27 ± 5.22ab	45.96 ± 6.81b			
eugenol	-	4.74 ± 0.97	8.22 ± 1.94	5.31 ± 1.56	6.95 ± 1.11	ns	ns	ns
eugenol	+	4.67 ± 0.66a	6.51 ± 0.89a	7.08 ± 0.35a	8.25 ± 1.18a			
4-methylguaiacol	-	1.08 ± 0.2	0.98 ± 0.23	1.06 ± 0.19	0.98 ± 0.17	**	****	**
4-methylguaiacol	+	5.35 ± 2.4a	23.91 ± 4.95ab	16.21 ± 1.56ab	15.72 ± 3.37b			
4-ethylphenol	-	14.11 ± 3.52	26.02 ± 10.54	10.62 ± 1.29	4.95 ± 2.54	ns	ns	ns
4-ethylphenol	+	11.57 ± 3.35a	15.18 ± 2.15a	13.87 ± 1.17a	15.55 ± 5.94a			
4-ethylguaiacol	-	2.59 ± 0.18	2.92 ± 0.36	2.23 ± 0.16	1.79 ± 0.8	*	****	*
4-ethylguaiacol	+	2.35 ± 0.28a	4.52 ± 0.52b	4.09 ± 0.29b	4.08 ± 0.2b			

Notes: [(1)] Mean VP concentrations ($n = 4$) are recorded in ng/g ± the standard error of the mean (SEM). [(2)] The effects of smoke (S), biofilm treatments (T) and S x T interaction were tested with a two-way ANOVA; *, **, *** and **** denote significant differences of $p \leq 0.05$, $p \leq 0.01$, $p \leq 0.001$ and $p \leq 0.0001$, respectively; ns = not significant ($p \geq 0.05$). [(3)] Different letters (within the rows) indicate the differences in effects of time of biofilm application on the smoked sample only using one-way ANOVA followed by a Tukey's HSD test. Blank cells denote concentrations below the method limit of detection.

Table S6. Vineyard 2: Free VP concentrations immediately after (T_1) smoke-exposure and at harvest (T_2).[(1)(2)]

VP	smoke	biofilm application: days before smoke exposure				S x T	smoke (S)	treatment (T)
		control	1	7	14			
time: 1 hour post-smoke exposure (T_1)								
syringol	-							
syringol	+				0.09 ± 0			
phenol	-	0.15 ± 0	0.32 ± 0.18	1.29 ± 0.81	0.13 ± 0	ns	**	ns
phenol	+	11.83 ± 6.39a	59.06 ± 15a	52.29 ± 14.99a	33.14 ± 9.23a			
p/*m*-cresol	-	0.18 ± 0.15	0.33 ± 0.12	0.41 ± 0.06	0.35 ± 0.17	ns	****	ns
p/*m*-cresol	+	4.54 ± 1.49a	18.23 ± 3.34a	16.86 ± 2.43a	17.36 ± 6.7a			
o-cresol	-	1 ± 0.23	0.82 ± 0.07	0.99 ± 0.13	1.01 ± 0.28	ns	****	ns
o-cresol	+	3.45 ± 1.52a	15.85 ± 3.02a	14.69 ± 2.22a	15.17 ± 5.49a			
guaiacol	-							
guaiacol	+	13.35 ± 3.63a	55.94 ± 13.03a	45.3 ± 4.95a	48.11 ± 18.51a			
eugenol	-	0.41 ± 0.03	0.34 ± 0.27	0.63 ± 0.17	0.44 ± 0.08	ns	ns	ns
eugenol	+	0.2 ± 0.07a	0.92 ± 0.3a	1.01 ± 0.18a	0.61 ± 0.07a			
4-methylguaiacol	-	0.06 ± 0.03	0.25 ± 0.12	0.17 ± 0.08	0.11 ± 0.07	*	****	*
4-methylguaiacol	+	4.19 ± 1.12a	26.21 ± 5.75a	21.44 ± 1.57a	23.43 ± 8.56a			
4-ethylphenol	-	0.64 ± 0.04	0.66 ± 0.04	0.67 ± 0.13	0.67 ± 0.05	ns	****	ns
4-ethylphenol	+	1.34 ± 0.16a	2.71 ± 0.45a	2.55 ± 0.21a	2.72 ± 0.89a			
4-ethylguaiacol	-							
4-ethylguaiacol	+	0.5 ± 0.24a	3.67 ± 0.78a	3.02 ± 0.29a	3.74 ± 1.39a			
time: harvest (T_2)								
syringol	-	1.11 ± 0.18	0.94 ± 0.02	0.92 ± 0.01	0.89 ± 0.01	ns	*	ns
syringol	+	0.89 ± 0.06a	0.8 ± 0.02a	0.83 ± 0.04a	0.8 ± 0.01a			
phenol	-	14.33 ± 3.94	28.78 ± 19.34	28.16 ± 18.74	27.21 ± 10.14	ns	ns	ns
phenol	+	28.42 ± 8.54a	46.68 ± 15.95a	50.75 ± 16.29a	46.43 ± 21.06a			
p/*m*-cresol	-	2.94 ± 0.82	2.11 ± 0.17	7.01 ± 4.79	6.8 ± 2.54	ns	*	ns
p/*m*-cresol	+	5.91 ± 1.88a	11.31 ± 3.68a	10.4 ± 2.95a	11.41 ± 3.97a			
o-cresol	-	13.9 ± 0	27.05 ± 0	33.35 ± 0	13.15 ± 4	*	****	**
o-cresol	+	2.23 ± 0.93a	8.49 ± 2.5a	7.37 ± 0.6a	5.3 ± 2.41a			
guaiacol	-	2.2 ± 0.93	1.38 ± 0.09	5.57 ± 4.18	3.91 ± 1.58	ns	*	ns
guaiacol	+	6.41 ± 2.64a	12.32 ± 5.21a	12.15 ± 5.02a	10.84 ± 5.28a			
eugenol	-	1.86 ± 0.12	2.01 ± 0.26	2.13 ± 0.23	1.98 ± 0.21	ns	*	ns
eugenol	+	1.68 ± 0.21a	1.63 ± 0.06a	1.68 ± 0.17a	1.56 ± 0.15a			
4-methylguaiacol	-	1.1 ± 0.21	2.1 ± 1.23	2.23 ± 1.26	1.61 ± 0.45	ns	ns	ns
4-methylguaiacol	+	1.76 ± 0.69a	3.43 ± 1.15a	2.54 ± 0.82a	2.54 ± 1.06a			
4-ethylphenol	-	2.01 ± 0.09	2.24 ± 0.45	2 ± 0.13	2.17 ± 0.17	ns	ns	ns
4-ethylphenol	+	0.97 ± 0.27a	2.27 ± 0.59a	1.69 ± 0.32a	2.28 ± 0.72a			
4-ethylguaiacol	-	0.68 ± 0.03	0.87 ± 0.21	0.89 ± 0.23	0.76 ± 0.06	ns	**	ns
4-ethylguaiacol	+							

Notes: [(1)] Mean VP concentrations ($n = 4$) are recorded in ng/g ± the standard error of the mean (SEM). [(2)] The effects of smoke (S), biofilm treatments (T) and S x T interaction were tested with a two-way ANOVA; *, **, *** and **** denote significant differences of $p \leq 0.05$, $p \leq 0.01$, $p \leq 0.001$ and $p \leq 0.0001$, respectively; ns = not significant ($p \geq 0.05$). [(3)] Different letters (within the rows) indicate the differences in effects of time of biofilm application on the smoked sample only using one-way ANOVA followed by a Tukey's HSD test. Blank cells denote concentrations below the method limit of detection.

Table S7. Vineyard 2: Total (*i.e.* quantitated after acid hydrolysis) VP concentrations immediately after (T_1) smoke-exposure and at harvest (T_2).[(1)(2)]

VP	smoke	biofilm application: days before smoke exposure				S x T	smoke (S)	treatment (T)
		control	1	7	14			
time: 1 hour post-smoke exposure (T_1)								
syringol	-	8.16 ± 1.82	8.15 ± 0.87	7.01 ± 0.39	6.55 ± 0.84	ns	ns	ns
syringol	+	16.88 ± 7.77a	9.34 ± 0.46a	7.57 ± 1.01a	9.16 ± 1.3a			
phenol	-	27.61 ± 5.75	23.84 ± 2.59	29.62 ± 3.61	22.54 ± 7.82	ns	****	ns
phenol	+	52.88 ± 14.75a	120.72 ± 15.29a	73.85 ± 17.19a	91.11 ± 23.05a			
p/*m*-cresol	-	337.61 ± 76.01	339.31 ± 33.78	426.63 ± 58.74	432.66 ± 211.77	ns	***	ns
p/*m*-cresol	+	90.54 ± 4.65a	97.72 ± 14.87a	68.06 ± 4.41a	98.21 ± 15.95a			
o-cresol	-	3.29 ± 1.65	8.12 ± 3.59	2.35 ± 0.98	6.18 ± 1.52	ns	***	ns
o-cresol	+	13.82 ± 1.26a	44.89 ± 11.72a	32.04 ± 10.22a	58.92 ± 21.86a			
guaiacol	-	3.79 ± 0.32	4.34 ± 0.44	5.15 ± 0.6	3.01 ± 0.62	ns	****	ns
guaiacol	+	17.11 ± 4.41a	72.31 ± 18.81a	41.1 ± 5.79a	59 ± 24.21a			
eugenol	-	3.76 ± 1.23	4.54 ± 0.97	4.31 ± 0.82	3.64 ± 0.4	ns	ns	ns
eugenol	+	3.36 ± 0.81a	4.98 ± 1.21a	3.55 ± 0.57a	4.81 ± 1.6a			
4-methylguaiacol	-		9.79 ± 8.79	4.12 ± 0	8.98 ± 6.07			
4-methylguaiacol	+	7.83 ± 2.4a	26.67 ± 7.92a	9.15 ± 3.2a	27.81 ± 11.47a			
4-ethylphenol	-	15.48 ± 4.92	13.1 ± 1.05	12.1 ± 0.79	12.86 ± 3.26	ns	ns	ns
4-ethylphenol	+	13.59 ± 1.7a	17.51 ± 0.76a	14.59 ± 0.3a	17.95 ± 3.01a			
4-ethylguaiacol	-	2.79 ± 0.32	2.52 ± 0.69	2.38 ± 0.37	1.56 ± 0.24	ns	**	ns
4-ethylguaiacol	+	2.41 ± 0.33a	6.08 ± 1.36a	4.7 ± 0.93a	6.13 ± 2.06a			
time: harvest (T_2)								
syringol	-	16.55 ± 2.53	17.58 ± 1.35	15.58 ± 1.15	11.76 ± 0.74	*	ns	ns
syringol	+	13.8 ± 0.66a	12.46 ± 2.78a	14.87 ± 1.13a	16.06 ± 1.09a			
phenol	-	62.2 ± 21.79	42.16 ± 2.53	52.08 ± 3.87	142.96 ± 59.59	ns	*	ns
phenol	+	144.48 ± 53.4a	189.76 ± 85.61a	122.96 ± 77.35a	260.53 ± 213.48a			
p/*m*-cresol	-	19.86 ± 5.38	38.23 ± 22.87	37.14 ± 18.3	37.98 ± 11.94	ns	****	ns
p/*m*-cresol	+	122.9 ± 16.45a	131.28 ± 37.9a	139.96 ± 14.94a	148.18 ± 18.74a			
o-cresol	-	19.11 ± 7.89	15.1 ± 6.99	33.03 ± 24.43	26.14 ± 2.61	ns	ns	ns
o-cresol	+	17.51 ± 5.52a	29.95 ± 9.29a	36.77 ± 14.54a	76.88 ± 20.91a			
guaiacol	-	14.53 ± 4.15	28.25 ± 15.88	29.3 ± 16.31	21.98 ± 6.46	ns	*	ns
guaiacol	+	28.3 ± 8.03a	51.22 ± 17.55a	48.67 ± 17.85a	46.27 ± 14.93a			
eugenol	-	9.7 ± 1.74	10.57 ± 2.33	9.68 ± 0.87	9.95 ± 1.77	ns	****	ns
eugenol	+	4.15 ± 0.48a	4.04 ± 0.73a	3.12 ± 0.83a	3.68 ± 1.04a			
4-methylguaiacol	-	3.34 ± 1.36	2.25 ± 0.36	8.96 ± 6.5	6.2 ± 2.41	ns	**	ns
4-methylguaiacol	+	13.26 ± 1.02a	43.96 ± 21.13a	24.06 ± 12.37a	17.92 ± 4.75a			
4-ethylphenol	-	12.33 ± 1.52	16.16 ± 3.65	15.49 ± 2.47	15.69 ± 1.45	ns	****	ns
4-ethylphenol	+	28.97 ± 6.22a	29.35 ± 6.15a	31.36 ± 5.31a	39.52 ± 3.91a			
4-ethylguaiacol	-	4.63 ± 0.2	5.09 ± 0.69	5.92 ± 0.87	5.77 ± 0.18	ns	ns	ns
4-ethylguaiacol	+	5.2 ± 0.35a	5.06 ± 0.61a	5.16 ± 0.51a	6.12 ± 0.44a			

Notes: [(1)] Mean VP concentrations ($n = 4$) are recorded in ng/g ± the standard error of the mean (SEM). [(2)] The effects of smoke (S), biofilm treatments (T) and S x T interaction were tested with a two-way ANOVA; *, **, *** and **** denote significant differences of $p \leq 0.05$, $p \leq 0.01$, $p \leq 0.001$ and $p \leq 0.0001$, respectively; ns = not significant ($p \geq 0.05$). [(3)] Different letters (within the rows) indicate the differences in effects of time of biofilm application on the smoked sample only using one-way ANOVA followed by a Tukey's HSD test. Blank cells denote concentrations below the method limit of detection.

Table S8. Vineyard 3: Free VP concentrations immediately after (T_1) smoke-exposure and at harvest (T_2).[1][2]

VP	smoke	biofilm application: days before smoke exposure				S x T	smoke (S)	treatment (T)
		control	1	7	14			
time: 1 hour post-smoke exposure (T_1)								
syringol	-	0.98 ± 0.02	0.97 ± 0.02	0.96 ± 0	1.02 ± 0.04			
syringol	+	1.01 ± 0.05a	0.99 ± 0.03a	1.01 ± 0.05a	1.06 ± 0.03a	ns	ns	ns
phenol	-	2.76 ± 0.33	2.51 ± 0.27	4.91 ± 1.45	2.81 ± 0.19			
phenol	+	21.36 ± 4.69a	34.49 ± 11.71a	27.88 ± 11.05a	26.96 ± 5.55a	ns	****	ns
p/*m*-cresol	-	0.39 ± 0.13	0.42 ± 0.06	1.13 ± 0.41	0.8 ± 0.32			
p/*m*-cresol	+	11.8 ± 0.95a	24.72 ± 4.51a	18.83 ± 1.56a	21.9 ± 3.17a	ns	***	ns
o-cresol	-	11.05 ± 4.34	7.51 ± 1.11	15.2 ± 3.94	7.05 ± 1.63			
o-cresol	+	17.98 ± 3.31a	22.24 ± 5.2a	20.17 ± 1.12a	22.06 ± 2.12a	ns	***	ns
guaiacol	-	0.66 ± 0.15	0.88 ± 0.09	0.59 ± 0.09	0.56 ± 0.12			
guaiacol	+	19.69 ± 3.75a	39.45 ± 9.56a	29.32 ± 2.37a	34.46 ± 8.37a	ns	****	ns
eugenol	-	1.17 ± 0.02	1.1 ± 0.01	1.25 ± 0.02	1.11 ± 0.01			
eugenol	+	1.11 ± 0.01a	1.57 ± 0.12b	1.47 ± 0.07ab	1.55 ± 0.07b	**	****	*
4-methylguaiacol	-	0.11 ± 0.06	0.2 ± 0.05	0.34 ± 0.04				
4-methylguaiacol	+	8.45 ± 2.06a	16.72 ± 3.94a	12.63 ± 2.37a	15.97 ± 4.32a			
4-ethylphenol	-	1.57 ± 0.15	1.51 ± 0.12	1.39 ± 0.05	1.57 ± 0.12			
4-ethylphenol	+	3.7 ± 0.58a	6.45 ± 0.74a	5.07 ± 0.25a	5.96 ± 0.79a	*	****	*
4-ethylguaiacol	-			0.05 ± 0.04				
4-ethylguaiacol	+	1.14 ± 0.38a	2.87 ± 0.68a	1.77 ± 0.23a	2.46 ± 0.68a			
time: harvest (T_2)								
syringol	-					-	-	-
syringol	+	0.08 ± 0.01a	0.08 ± 0.01a	0.14 ± 0ab	0.15 ± 0.03b			
phenol	-	10.31 ± 0.63	9.63 ± 0.35	9.35 ± 0.3	9.36 ± 0.16	*	****	*
phenol	+	58.02 ± 9.2a	65.82 ± 2.96a	83.35 ± 9.25a	90.13 ± 13.89a			
p/*m*-cresol	-	1.39 ± 0.1	1.32 ± 0.05	1.37 ± 0.06	1.27 ± 0.07	ns	****	ns
p/*m*-cresol	+	14.73 ± 2.54a	17.11 ± 1.53a	17.69 ± 1.05a	20.85 ± 2.54a			
o-cresol	-	10.17 ± 1.35	11.22 ± 0.69	10.43 ± 1.13	9.24 ± 0.59	****	****	****
o-cresol	+	10.38 ± 0.64a	12.02 ± 0.8a	22.73 ± 1.37b	30.76 ± 3.84b			
guaiacol	-	0.68 ± 0.04	0.64 ± 0.07	0.52 ± 0.05	0.53 ± 0.03	ns	****	ns
guaiacol	+	9.47 ± 1.35a	14.47 ± 1.73a	12.29 ± 1.44a	12.89 ± 1.94a			
eugenol	-	0.95 ± 0.23	0.6 ± 0.08	0.34 ± 0.1	0.28 ± 0.05	ns	****	***
eugenol	+	0.61 ± 0.06a	0.53 ± 0.04a	1.18 ± 0.05ab	1.45 ± 0.33b			
4-methylguaiacol	-	0.23 ± 0	0.2 ± 0.01	0.17 ± 0.01	0.19 ± 0.01	ns	****	ns
4-methylguaiacol	+	2.84 ± 0.51a	4.25 ± 0.46a	4.06 ± 0.33a	4.25 ± 0.7a			
4-ethylphenol	-	1.15 ± 0.03	1.08 ± 0.02	1.11 ± 0.05	1.04 ± 0.03	ns	**	ns
4-ethylphenol	+	1.94 ± 0.36a	2.37 ± 0.55a	1.17 ± 0.13a	1.61 ± 0.23a			
4-ethylguaiacol	-	0.05 ± 0.01	0.06 ± 0	0.07 ± 0.02	0.06 ± 0.01	*	****	ns
4-ethylguaiacol	+	0.86 ± 0.1a	0.97 ± 0.08a	0.68 ± 0.03a	0.72 ± 0.08a			

Notes: [1] Mean VP concentrations (n = 4) are recorded in ng/g ± the standard error of the mean (SEM). [2] The effects of smoke (S), biofilm treatments (T) and S x T interaction were tested with a two-way ANOVA; *, **, *** and **** denote significant differences of $p \leq 0.05$, $p \leq 0.01$, $p \leq 0.001$ and $p \leq 0.0001$, respectively; ns = not significant ($p \geq 0.05$). [3] Different letters (within the rows) indicate the differences in effects of time of biofilm application on the smoked sample only using one-way ANOVA followed by a Tukey's HSD test. Blank cells denote concentrations below the method limit of detection.

Table S9. Vineyard 3: Total (*i.e.* quantitated after acid hydrolysis) VP concentrations immediately after (T_1) smoke-exposure and at harvest (T_2).[(1)(2)]

VP	smoke	biofilm application: days before smoke exposure				S x T	smoke (S)	treatment (T)
		control	1	7	14			
time: 1 hour post-smoke exposure (T_1)								
syringol	-	7.42 ± 3.65	6.38 ± 0	13.2 ± 0	3.96 ± 1.38	ns	*	ns
syringol	+	6.45 ± 0a	2.72 ± 1.23a	3.18 ± 0.94a	3.03 ± 0.7a			
phenol	-	44.86 ± 2.9	49.56 ± 2.58	47.28 ± 7.05	34.32 ± 6.29	ns	****	ns
phenol	+	112.55 ± 11.27a	141.86 ± 26.2a	119.98 ± 20.8a	114.55 ± 17.94a			
p/*m*-cresol	-	120.98 ± 18.58	81.13 ± 17.83	111.4 ± 12.54	70.95 ± 29.54	ns	ns	ns
p/*m*-cresol	+	133 ± 27.97a	102.11 ± 10.07a	102.73 ± 6.75a	99.8 ± 6.71a			
o-cresol	-	64.52 ± 9.71	75.24 ± 16.71	55.87 ± 16.7	35.25 ± 10.51	ns	ns	*
o-cresol	+	80.23 ± 11.45a	48.98 ± 16.73a	40.11 ± 6.61a	33.09 ± 4.9a			
guaiacol	-	4.73 ± 0.62	4.97 ± 0.13	3.62 ± 0.26	4.87 ± 0.63	ns	****	ns
guaiacol	+	21.45 ± 2.19a	47.71 ± 14.2a	32.05 ± 1.42a	39.67 ± 8.82a			
eugenol	-		0.47 ± 0.37		0.43 ± 0.1			
eugenol	+	0.39 ± 0.00a		0.39 ± 0.32a	0.43			
4-methylguaiacol	-	283.46 ± 72.35	303.72 ± 86.05	102.81 ± 53.03	244.32 ± 78.03	ns	ns	ns
4-methylguaiacol	+	263.82 ± 35.79a	193.35 ± 105.32a	207.18 ± 65.16a	328.56 ± 58.4a			
4-ethylphenol	-	68.1 ± 11.68	59.7 ± 5.12	50.84 ± 17.77	28.17 ± 11.35	ns	ns	ns
4-ethylphenol	+	81.81 ± 20.35a	56.54 ± 9.88a	59.76 ± 7.42a	54.11 ± 6.9a			
4-ethylguaiacol	-	1.74 ± 0.27	2.29 ± 0.18	1.5 ± 0.24	2.43 ± 0.29	ns	****	*
4-ethylguaiacol	+	2.96 ± 0.4a	6.5 ± 1.54a	4.19 ± 0.29a	5.43 ± 0.8a			
time: harvest (T_2)								
syringol	-	11.86 ± 0.24	12.27 ± 1.59	9.65 ± 1.51	9.48 ± 0.53	ns	***	ns
syringol	+	13.8 ± 0.7a	18.77 ± 2.82a	14.34 ± 1.35a	14.17 ± 0.42a			
phenol	-	35.31 ± 2.16	35.14 ± 2.6	34.83 ± 5.09	38.2 ± 2.02	*	****	*
phenol	+	241.46 ± 21.55a	422.92 ± 67.95a	406.36 ± 25.58a	320.43 ± 34.24a			
p/*m*-cresol	-	7.5 ± 0.5	8.93 ± 0.41	8.54 ± 0.65	8.9 ± 0.43	ns	****	ns
p/*m*-cresol	+	65.72 ± 6.97a	109.08 ± 19.71a	108.1 ± 8.21a	89.95 ± 13.34a			
o-cresol	-	65.46 ± 13.25	72.39 ± 24.11	73.46 ± 8.69	64.36 ± 4	ns	***	*
o-cresol	+	76.48 ± 3.24a	151.43 ± 21.73ab	134.71 ± 15.86ab	90.41 ± 9.42b			
guaiacol	-	5.84 ± 0.34	4.89 ± 0.19	6.7 ± 1.49	5.55 ± 0.18	*	****	*
guaiacol	+	41.42 ± 3.57a	57.45 ± 6.76b	57.9 ± 2.04ab	61.91 ± 3.79ab			
eugenol	-	5.57 ± 1.04	4.45 ± 1.23	2.91 ± 0.31	2.84 ± 0.3	*	***	ns
eugenol	+	6.03 ± 0.13a	4.9 ± 0.52a	6.07 ± 0.38a	6.33 ± 0.35a			
4-methylguaiacol	-	0.56 ± 0.08	0.44 ± 0.09	0.41 ± 0.07	0.38 ± 0.02	**	****	**
4-methylguaiacol	+	15.01 ± 1.82a	21.52 ± 2.77b	22.8 ± 0.63ab	25.36 ± 1.95ab			
4-ethylphenol	-	13.34 ± 2.83	13.43 ± 2.45	13.7 ± 2.93	14.88 ± 1.83	*	**	ns
4-ethylphenol	+	14.88 ± 0.69a	26.19 ± 2.29a	23.66 ± 2.08ab	14.83 ± 2.9b			
4-ethylguaiacol	-	3.01 ± 0.26	2.5 ± 0.23	3.35 ± 0.58	2.7 ± 0.28	ns	****	ns
4-ethylguaiacol	+	4.21 ± 0.22a	4.97 ± 0.28a	5.11 ± 0.17a	4.78 ± 0.53a			

Notes: [(1)] Mean VP concentrations ($n = 4$) are recorded in ng/g ± the standard error of the mean (SEM). [(2)] The effects of smoke (S), biofilm treatments (T) and S x T interaction were tested with a two-way ANOVA; *, **, *** and **** denote significant differences of $p \leq 0.05$, $p \leq 0.01$, $p \leq 0.001$ and $p \leq 0.0001$, respectively; ns = not significant ($p \geq 0.05$). [(3)] Different letters (within the rows) indicate the differences in effects of time of biofilm application on the smoked sample only using one-way ANOVA followed by a Tukey's HSD test. Blank cells denote concentrations below the method limit of detection.

Table S10. Meteorological data collected for the vineyards used in biofilm field studies.

vineyard	conditions	date day/month/year	temperature[1,2] (°C)	max. temperature	min. temperature	precipitation (mm)	mean temperature[3]	total precipitation[3]
V1	biofilm; 14 days	29/08/2019	17.2	31.4	8.5	0		
V1	biofilm; seven days	05/09/2019	15.9	27.8	9.6	1.8		
V1	biofilm; one day	11/09/2019	13.9	23.2	12.1	0.6		
V1	smoke exposure (T_1)	12/09/2019	14.2	23.1	9.9	0.4		
V1	harvest (T_2)	30/09/2019	4.5	10.0	1.9	0	15.6	36.4
V2	biofilm; 14 days	23/08/2019	13.1	20.0	9	0.7		
V2	biofilm; seven days	30/08/2019	19.0	30.1	13.9	0		
V2	biofilm; one day	05/09/2019	15.9	27.8	9.6	1.8		
V2	smoke exposure (T_1)	06/09/2019	16.8	28.9	9.6	0		
V2	harvest (T_2)	06/10/2019	3.7	14.2	-0.4	0	14.7	48.3
V3	biofilm; 14 days	03/09/2019	16.1	30.1	8.3	0		
V3	biofilm; seven days	10/09/2019	14.4	21.6	11.1	2.9		
V3	biofilm; one day	16/09/2019	11.6	19.3	10.1	0.2		
V3	smoke exposure (T_1)	17/09/2019	12.8	17.3	8.9	3.6		
V3	harvest (T_2)	26/09/2019	11.6	17.3	6.9	1.5	16.8	41.0
V2[4]	biofilm; seven days	08/24/2018	14.7	29.6	9.2	0		
V2[4]	smoke exposure 1	08/31/2018	13.5	25.5	7.9	0		
V2[4]	smoke exposure 1	09/02/2018	10.8	25.8	8.5	5.4		
V2[4]	harvest	09/14/2018	6.2	12.7	4.6	0.4	15.7	11.6

Notes: [1]All historical weather data collected by the Government of Canada and accessible online at https://climate.weather.gc.ca/historical_data/search_historic_data_e.html; the data obtained were from the Kelowna, BC meteorological station. [2]Temperature at 0700 local time, when vineyard procedures were performed with the exception of sample collection at harvest. [3]Mean temperature and total precipitation between the first spray application (*i.e.* 14-days post smoke-exposure) and harvest. [4]V2 was the site of our initial evaluation of the biofilm spray also using Pinot Noir grapevines as described by Favell *et al.* (2019); biofim and smoke applications were identical although the specific grapevines used differed.

Table S11. Chemical composition of must and wines.

cold soak									
treatment					**parameter**				
smoke	**days post-spray**	**°Brix**	**TA[(1)] (g/L)**	**pH**	**malic acid (g/L)**	**α-amino acids (mg/L)**	**ammonia (mg/L)**	**YAN[(2)] (mg/L)**	**potassium (mg/L)**
-	**control**	20.7	5.0	3.64	3.26	188	61	239	1223
-	**1**	21.8	5.0	3.60	3.23	163	47	201	1210
-	**7**	20.2	4.9	3.58	3.04	157	44	194	1105
-	**14**	20.3	4.9	3.59	3.06	164	50	205	1100
+	**control**	21.5	5.2	3.59	3.24	163	50	204	1148
+	**1**	21.6	4.9	3.60	2.94	153	43	188	1154
+	**7**	21.0	5.2	3.59	2.97	148	42	182	1123
+	**14**	20.8	5.3	3.61	3.26	169	53	212	1176
after alcoholic fermentation									
smoke	**days post-spray**	**alcohol (% v/v)**	**residual sugar (g/L)**	**TA (g/L)**	**pH**	**volatile acidity (g/L)**	**malic acid (g/L)**	**lactic acid (g/L)**	**FC/A_{280}[(3)] (mg/L)**
-	**control**	12.8	0.4	6.0	3.67	0.22	2.62	0.3	44.6
-	**1**	13.5	0.4	6.2	3.67	0.27	2.51	0.3	46.7
-	**7**	12.7	0.3	6.2	3.60	0.20	2.49	0.3	44.2
-	**14**	13.1	0.5	6.0	3.64	0.20	2.49	0.3	46.8
+	**control**	13.4	0.4	6.2	3.65	0.25	2.57	0.3	47.8
+	**1**	13.7	0.4	6.2	3.63	0.26	2.24	0.3	51.6
+	**7**	12.9	0.4	6.2	3.61	0.29	2.45	0.3	44.5
+	**14**	13.0	0.3	6.2	3.65	0.21	2.58	0.3	49.3

Notes:. [(1)]TA = titratable acidity; [(2)]YAN = yeast assimilable nitrogen. (3) FC = Folin-Ciocalteu method for determining total polyphenols; A_{280} = ultraviolet absorbance at 280 nm.

Table S12. Concentration of free VPs in must and wine samples.[1][2]

VP	smoke	biofilm application: days before smoke exposure				S x T	smoke (S)	treatment (T)
		control	1	7	14			
must								
syringol	-	1.18 ± 0			1.27 ± 0			
syringol	+							
phenol	-	1.92 ± 0.46	8.25 ± 0.14	5.96 ± 0.24	8.58 ± 0.49			
phenol	+	22.98 ± 0.97a	26.71 ± 11.16a	20.48 ± 8.66a	35.92 ± 0.36a	ns	****	ns
p/*m*-cresol	-		3.82 ± 1.1	4.34 ± 0.4	5.59 ± 1.67			
p/*m*-cresol	+	5.33 ± 1.8a	9.92 ± 0.81a	6.41 ± 2.28a	11.09 ± 4.78a			
o-cresol	-	3.58 ± 0	10.25 ± 4.22	9.31 ± 1.22	12.3 ± 2.21			
o-cresol	+	6.71 ± 4.61a	5.97 ± 2.22a	6.9 ± 0.76a	7.68 ± 1.15a	ns	ns	ns
guaiacol	-		1.24 ± 0.12	1.15 ± 0				
guaiacol	+	4.09 ± 0.23a	7.12 ± 2.63a	7.83 ± 0.01a	7.52 ± 0.01a			
eugenol	-							
eugenol	+							
4-methylguaiacol	-							
4-methylguaiacol	+		2.32 ± 0.04b	2.19 ± 0.19b	1.52 ± 0.12a			
4-ethylphenol	-							
4-ethylphenol	+			1.36 ± 0				
4-ethylguaiacol	-	1.23 ± 0a	1.82 ± 0.04bc	1.47 ± 0.04ab	1.9 ± 0.12c			
4-ethylguaiacol	+							
wine								
syringol	-	4.2 ± 1.22	4.03 ± 0.6	32.2 ± 28.54	4.51 ± 0.26			
syringol	+	3.46 ± 0.18a	3.69 ± 0.09a	193.29 ± 35.81b	4.29 ± 0.31a	***	**	****
phenol	-	4.89 ± 0.26	7.85 ± 0.65	12.93 ± 0.68	6.07 ± 0.29			
phenol	+	37.18 ± 0.03a	71.39 ± 1.53c	57.44 ± 0.68b	70.45 ± 3.46c	****	****	****
p/*m*-cresol	-		2.53 ± 0.27	3.12 ± 0.17	1.47 ± 0.32			
p/*m*-cresol	+	11.38 ± 0.06a	22.1 ± 0.5a	13.49 ± 5.58a	23.84 ± 0.77a			
o-cresol	-	71.76 ± 8.67	20.45 ± 9.63	3.33 ± 0.14	2.18 ± 0.11			
o-cresol	+	32.26 ± 1.68b	15.57 ± 0.47a	12.57 ± 0.54a	16.85 ± 0.17a	***	ns	****
guaiacol	-		2.2 ± 0.44	1.9 ± 0.27				
guaiacol	+	9.08 ± 0.22a	19.06 ± 0.47c	14.51 ± 0.16b	15.41 ± 0.91b			
eugenol	-	1.38 ± 0.26	1.71 ± 0.01	14.84 ± 13.2	1.5 ± 0.04			
eugenol	+	1.43 ± 0.23a	1.61 ± 0.12a	55.9 ± 23.08a	1.57 ± 0.15a	ns	ns	*
4-methylguaiacol	-			1.74 ± 0				
4-methylguaiacol	+	2.24 ± 0.17a	6.47 ± 0.54b	4.74 ± 0.3b	5.44 ± 0.55b			
4-ethylphenol	-		1.62 ± 0.14	1.18 ± 0				
4-ethylphenol	+	2.59 ± 0.05a	2.77 ± 0.03a	2.6 ± 0.05a	2.82 ± 0.19a			
4-ethylguaiacol	-							
4-ethylguaiacol	+							

Notes: [1] Mean VP concentrations ($n = 4$) are recorded in ng/g ± the standard error of the mean (SEM). (2) The effects of smoke (S), biofilm treatments (T) and S x T interaction were tested with a two-way ANOVA; *, **, *** and **** denote significant differences of $p \leq 0.05$, $p \leq 0.01$, $p \leq 0.001$ and $p \leq 0.0001$, respectively; ns = not significant ($P \geq 0.05$). Different letters (within the rows) indicate the differences in effects of time of biofilm application on the smoked sample only using one-way ANOVA followed by a Tukey's HSD test. Blank cells denote concentrations below the method limit of detection

Table S13. Concentration of total (free plus acid-labile) VPs in must and wine samples.[(1)(2)]

VP	smoke	biofilm application: days before smoke exposure				S x T	smoke (S)	treatment (T)
		control	1	7	14			
				must				
syringol	-	113.01 ± 14.24	26.34 ± 10.7	18.94 ± 4.26	8 ± 0.18			
syringol	+	37.74 ± 25.57a	21.55 ± 3.43a	12.49 ± 3.51a	9.58 ± 1a	*	*	****
phenol	-	39.27 ± 2.64	147.15 ± 85.21	55.3 ± 3.4	63.64 ± 4.47			
phenol	+	156.38 ± 1.31a	195.52 ± 66.97a	151.52 ± 73.55a	202.13 ± 10.12a	ns	**	ns
p/*m*-cresol	-	11.87 ± 0.2	37.13 ± 20.44	8.13 ± 5.86	150.15 ± 142.09			
p/*m*-cresol	+	51.74 ± 2.81a	57.27 ± 19.64a	52.09 ± 12.54a	35.11 ± 1.31a	ns	ns	ns
o-cresol	-	189.3 ± 176.99	46.13 ± 22.23	22.76 ± 3.62	9.91 ± 3.51			
o-cresol	+	39.21 ± 16.85a	66.72 ± 21.91a	167.64 ± 108.43a	57.81 ± 3.35a	ns	ns	ns
guaiacol	-	6.74 ± 0.99	5.33 ± 2.43	1.55 ± 0.1	1.65 ± 0.29			
guaiacol	+	5.89 ± 0.78a	6.82 ± 2.68a	6.22 ± 3.32a	10.97 ± 4.49a	ns	ns	ns
eugenol	-	4.58 ± 0.3	4.77 ± 0.2	4.47 ± 0.12	3.46 ± 0.51			
eugenol	+	4.09 ± 0.19a	4.56 ± 0.24a	3.01 ± 0.56a	4.54 ± 0.18a	*	ns	ns
4-methylguaiacol	-		21.9 ± 19.64					
4-methylguaiacol	+	1.46 ± 0.29a	2.63 ± 0.14a	2.34 ± 1.05a	4.78 ± 0.88a	-	-	-
4-ethylphenol	-	16.02 ± 1.55	21.6 ± 4.83	13.56 ± 6.41	16.25 ± 1.29			
4-ethylphenol	+	16.91 ± 7.15a	23.14 ± 3.13a	10.14 ± 7.2a	16.1 ± 1.77a	ns	**	ns
4-ethylguaiacol	-	2.62 ± 0.63	1.38 ± 0	1.35 ± 0	1.19 ± 0.07			
4-ethylguaiacol	+	2.35 ± 0.14a	1.11 ± 0a	1.7 ± 0a	1.71 ± 0.25a	ns	ns	ns
				wine				
syringol	-	9.16 ± 0.05	4.92 ± 3.41	9.05 ± 0.09	6.57 ± 2.62			
syringol	+	8.38 ± 3.63a	12.34 ± 0.53a	12.32 ± 0a	10.41 ± 0.82a	ns	ns	ns
phenol	-	56.51 ± 4.7	67.57 ± 30.77	106.85 ± 6.65	65.7 ± 5.49			
phenol	+	153.76 ± 70.65a	150.58 ± 108.28a	154.51 ± 117.07a	226.83 ± 99.53a	ns	ns	ns
p/*m*-cresol	-	6.47 ± 0.98	12.85 ± 0.17	14.97 ± 0.37	6.66 ± 2.73			
p/*m*-cresol	+	36.28 ± 2.56a	61.82 ± 2.58a	37.39 ± 15.46a	54.4 ± 4.9a	ns	****	ns
o-cresol	-	12.52 ± 0.65	17 ± 7.62	24.54 ± 1.3	14.98 ± 0.95			
o-cresol	+	46.49 ± 21.69a	117.69 ± 14.61a	101.21 ± 11.78a	96.38 ± 14.49a	ns	****	*
guaiacol	-	15.14 ± 1.1	18.18 ± 8.15	23.84 ± 2.18	15.72 ± 0.82			
guaiacol	+	39.29 ± 4.46b	64.69 ± 4.98a	53.19 ± 5.45ab	52.13 ± 5.22ab	ns	****	*
eugenol	-	2.37 ± 0.51	1.87 ± 0.17	1.82 ± 0.09	2.29 ± 0.06			
eugenol	+	2.02 ± 0.22a	1.88 ± 0.47a	1.83 ± 0.37a	1.95 ± 0.16a	ns	ns	ns
4-methylguaiacol	-	1.85 ± 0	2.07 ± 0.09	2.78 ± 0	1.18 ± 0.06			
4-methylguaiacol	+	4.28 ± 2.59b	19.62 ± 0.97a	16.06 ± 0.28b	17.82 ± 1.05b	**	****	**
4-ethylphenol	-	15.52 ± 3.2	19.63 ± 7.02	19.82 ± 6.65	13.37 ± 5.17			
4-ethylphenol	+	19.71 ± 2.43a	39.46 ± 3.97a	19.54 ± 12.71a	31.8 ± 5.88a	ns	*	ns
4-ethylguaiacol	-	3.38 ± 0.26	3.28 ± 0.53	5.62 ± 0.39	5.11 ± 0.19			
4-ethylguaiacol	+	5.09 ± 0.63a	6.94 ± 0.5a	6.17 ± 0.4a	8.64 ± 1.63a	ns	***	*

Notes: (1) Mean VP concentrations (n = 4) are recorded in ng/g ± the standard error of the mean (SEM). (2) The effects of smoke (S), biofilm treatments (T) and S x T interaction were tested with a two-way ANOVA; *, **, *** and **** denote significant differences of $p \leq 0.05$, $p \leq 0.01$, $p \leq 0.001$ and $p \leq 0.0001$, respectively; ns = not significant ($P \geq 0.05$). Different letters (within the rows) indicate the differences in effects of time of biofilm application on the smoked sample only using one-way ANOVA followed by a Tukey's HSD test. Blank cells denote concentrations below the method limit of detection.

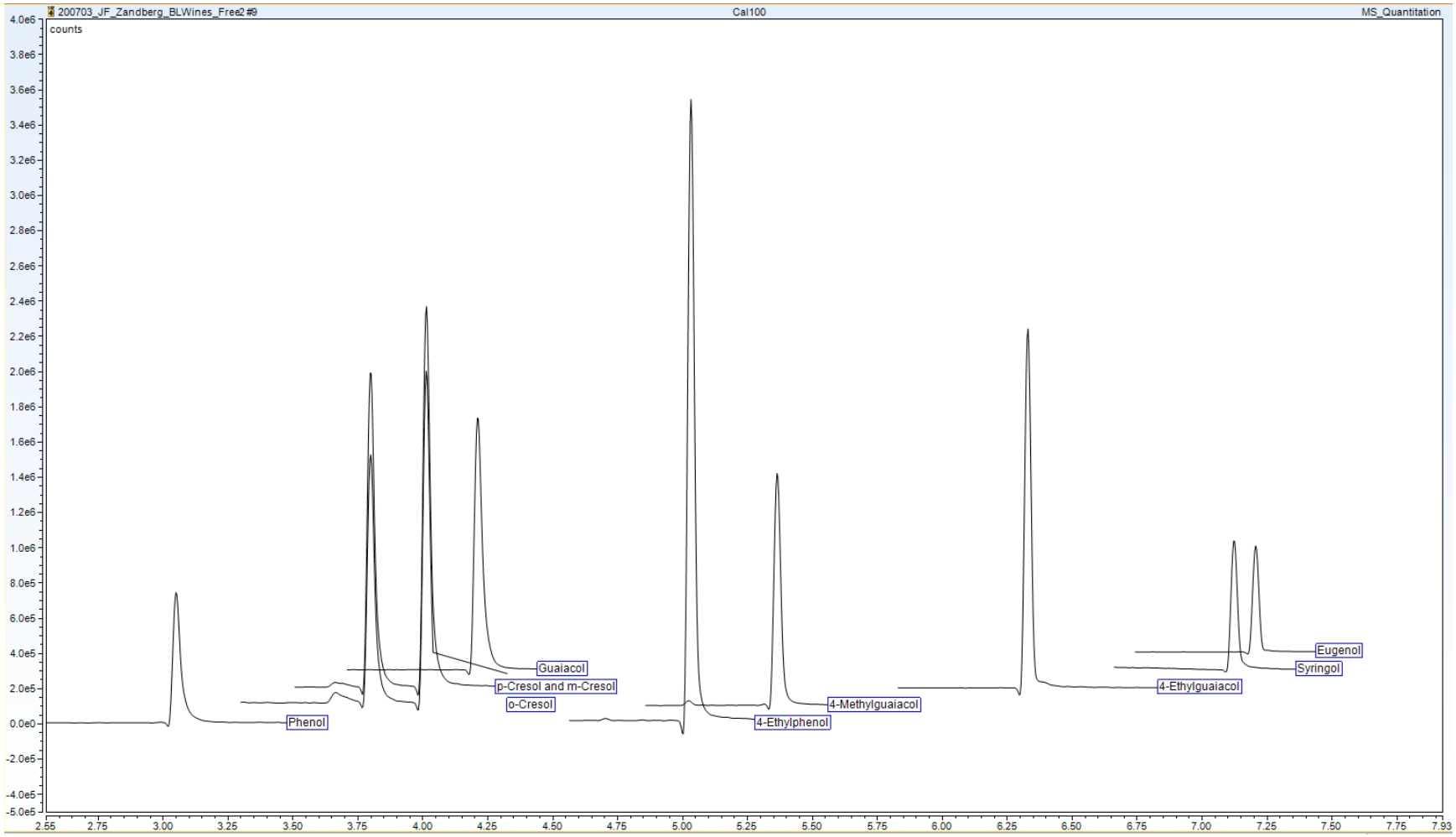

Figure S1. Extracted ion chromatograms for all VPs quantitated.