Supplemental material for “Field measurements of biogenic volatile organic compounds in the atmosphere using solid-phase microextraction Arrow”

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10 **This document contains as supplemental material the figures S1-S11 and tables S1-S3 referred in the manuscript.**

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Figure S1: Home-made dynamic SPME Arrow sampling system developed for the collection of BVOCs from ambient air.

Figure S2: Extraction time profiles obtained for the analytes using SPME fiber and SPME Arrow coated with PDMS/Carbon WR and PDMS/DVB.

Figure S3: Extraction time profiles obtained for the analytes using dynamic SPME Arrow coated with PDMS/Carbon WR.

Figure S4: Comparison of the extraction efficiencies obtained with SPME Arrow and SPME fiber coated with PDMS/Carbon WR and PDMS/DVB.

Figure S5: Comparison between static and dynamic SPME ARROW (PDMS/Carbon WR) collection.

Figure S6: Effect of temperature (°C) on the extraction efficiencies obtained with SPME fiber using PDMS/Carbon WR and PDMS/DVB sorbents.

Figure S7: Effect of relative humidity (%) on the extraction efficiencies obtained with SPME fiber using PDMS/Carbon WR and PDMS/DVB sorbents.

Figure S8: Comparison between the mass of identified monoterpenes (α -pinene, Δ^3 -carene and limonene) and aldehydes (octanal, nonanal and decanal) collected with different SPME devices and sampling modes from ambient air and measured by GC-MS.

Figure S9: Mass of identified monoterpenes (α -pinene, Δ^3 -carene and limonene) and aldehydes (octanal, nonanal and decanal) collected with SPME Arrow (Carbon WR) from ambient air and measured by GC-MS during preliminary tests performed in summer, 2016.

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Figure S10: Comparison between the peak areas of identified monoterpenes (α -pinene, Δ^3 -carene and limonene) collected with different SPME devices and sampling modes from ambient air and measured by GC-MS.

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Figure S11: Effect of temperature (°C), relative humidity (%), photosynthetically active radiation ($\mu\text{mol.m}^{-2}.\text{s}^{-1}$), precipitation (mm), ozone (ppb) and particle number concentration (#.cm^{-3}) on the ratio between the amounts of monoterpenes (grey line) and aldehydes (blue line) sampled with PDMS/Carbon WR and PDMS/DVB and measured by GC-MS.

Table S1: Calibration curves obtained for monoterpene and aldehyde analysis.

Analyte	Equation	R ²	N	Points [ng]	LOD [pg]
α-pinene	1.28E+06-2.01E+05	0.9656	4	0.1, 1, 5, 10	17.7
Δ ³ -carene	1.04E+06-2.80E+05	0.9691	4	0.1, 1, 5, 10	20.1
limonene	6.44E+05-1.57E+05	0.9706	4	0.1, 1, 5, 10	28.0
octanal	2.53E+05-1.54E+05	0.9957	5	0.1, 1, 5, 25, 50	133.8
nonanal	3.86E+05-1.63E+05	0.9949	5	0.1, 1, 5, 25, 50	61.1
decanal	1.95E+05-8.34E+04	0.9941	5	0.1, 1, 5, 25, 50	155.2

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Table S2: GC-MS peak areas obtained for the identified monoterpenes and aldehydes collected from ambient air by using SPME fiber (PDMS/DVB) and SPME Arrows (PDMS/DVB and PDMS/Carbon WR) during the summer campaign, 2017.

Fiber/Arrow	date	α -pinene	Δ^3 -carene	limonene	octanal	nonanal	decanal
fiber PDMS/DVB	11.8.2017 11:12	102155	97019	22933	n.d.	450723	752643
Arrow PDMS/DVB	11.8.2017 11:12	226143	288574	55635	516988	546350	404230
Arrow PDMS/DVB Dynamic	11.8.2017 11:12	194897	397843	131514	590722	1100244	781541
fiber PDMS/DVB	11.8.2017 19:32	193254	186098	63823	n.d.	117173	220635
Arrow PDMS/DVB	11.8.2017 19:32	355427	511758	153227	1109012	2309490	3167716
Arrow PDMS/DVB Dynamic	11.8.2017 19:32	349343	735654	321153	1243202	1745768	2060833
fiber PDMS/DVB	12.8.2017 11:17	221823	216085	48365	n.d.	61163	79964
Arrow PDMS/DVB	12.8.2017 11:17	256924	504716	209916	723429	2217566	3712568
Arrow PDMS/DVB Dynamic	12.8.2017 11:17	399357	524622	149562	740353	1901385	2522420
Arrow PDMS/DVB Dynamic	12.8.2017 13:52	249479	670973	355358	746715	2700469	4262176
Arrow PDMS/DVB	12.8.2017 13:52	407272	740384	234012	577619	1941911	2270098
Arrow PDMS/Carbon WR	12.8.2017 13:52	101526	86947	47265	617677	2037572	2695203
fiber PDMS/DVB	12.8.2017 13:52	344969	376571	106152	n.d.	217925	339500
Arrow PDMS/Carbon WR	12.8.2017 19:37	574053	737382	697334	1895628	5638305	7514517
Arrow PDMS/DVB	12.8.2017 19:37	1069839	1910667	857096	2057784	6265607	8477634
Arrow PDMS/DVB Dynamic	12.8.2017 19:37	1326334	2079328	1254923	2212931	5495153	7318567
fiber PDMS/DVB	13.8.2017 11:02	258150	289284	99815	n.d.	651877	1404529
Arrow PDMS/Carbon WR	13.8.2017 11:02	105350	395029	252311	720631	3028961	1926171
Arrow PDMS/DVB	13.8.2017 11:02	287537	481384	190058	1248222	3547695	4297290
Arrow PDMS/DVB Dynamic	13.8.2017 11:02	313359	580161	344057	1339820	3520847	4107292
fiber PDMS/DVB	13.8.2017 13:32	198712	192090	57882	n.d.	387651	813895
Arrow PDMS/Carbon WR	13.8.2017 13:32	188579	396600	173591	585336	1876372	1760741
Arrow PDMS/DVB	13.8.2017 13:32	280941	461847	140825	840901	4981935	3729651
Arrow PDMS/DVB Dynamic	13.8.2017 13:32	370131	528993	238876	959117	3419215	2928137
fiber PDMS/DVB	13.8.2017 15:57	242118	228838	61816	n.d.	324386	665170
Arrow PDMS/Carbon WR	13.8.2017 15:57	177550	450775	192908	608416	1737199	1397602
Arrow PDMS/DVB Dynamic	13.8.2017 15:57	370746	634574	287238	1090921	4018835	3365609
fiber PDMS/DVB	13.8.2017 18:22	307929	258658	68755	n.d.	291555	455446
Arrow PDMS/Carbon WR	13.8.2017 18:22	279778	643283	223255	812033	1431311	1348124
Arrow PDMS/DVB	13.8.2017 18:22	416906	673481	221152	1370063	2405735	2725082
Arrow PDMS/DVB Dynamic	13.8.2017 18:22	427910	848851	366436	2334492	3264847	3989107
fiber PDMS/DVB	14.8.2017 10:57	199823	179014	49839	n.d.	260991	600882
Arrow PDMS/Carbon WR	14.8.2017 10:57	200146	533570	159586	634837	1897848	2221976
Arrow PDMS/DVB	14.8.2017 10:57	332099	466080	119841	1063327	3180442	3534776
Arrow PDMS/DVB Dynamic	14.8.2017 10:57	419036	580986	189843	1277265	3817540	3523115
fiber PDMS/DVB	14.8.2017 13:17	249223	248007	55845	n.d.	299690	559767
Arrow PDMS/Carbon WR	14.8.2017 13:17	294788	623932	181533	373281	1884908	2387205
Arrow PDMS/DVB	14.8.2017 13:17	339251	545890	110294	1309069	3791981	4900061
Arrow PDMS/DVB Dynamic	14.8.2017 13:17	540446	728189	214357	1399681	5349577	5301776

Table S2: GC-MS peak areas obtained for the identified monoterpenes and aldehydes collected from ambient air by using SPME fiber (PDMS/DVB) and SPME Arrows (PDMS/DVB and PDMS/Carbon WR) during the summer campaign, 2017 (cont.).

Fiber/Arrow	date	α -pinene	Δ^3 -carene	limonene	octanal	nonanal	decanal
fiber PDMS/DVB	14.8.2017 15:47	328463	352382	76114	n.d.	382605	657395
Arrow PDMS/Carbon WR	14.8.2017 15:47	397859	915356	265277	1147707	2024506	2431190
Arrow PDMS/DVB	14.8.2017 15:47	439348	752577	149789	1252703	4188848	4838710
Arrow PDMS/DVB Dynamic	14.8.2017 15:47	560194	980628	291298	1459734	5125966	4752391
fiber PDMS/DVB	14.8.2017 18:07	250763	251820	60596	n.d.	136062	296725
Arrow PDMS/Carbon WR	14.8.2017 18:07	337402	869108	214139	748657	1900288	2179208
Arrow PDMS/DVB	14.8.2017 18:07	567726	828229	171324	1377216	3150688	4726582
Arrow PDMS/DVB Dynamic	14.8.2017 18:07	720812	1151421	313502	1458792	4680225	5108423
fiber PDMS/DVB	15.8.2017 9:42	346637	312672	68476	n.d.	92777	129952
Arrow PDMS/Carbon WR	15.8.2017 9:42	487997	1054949	253687	843865	1433457	1891598
Arrow PDMS/DVB	15.8.2017 9:42	715994	805632	180899	1509715	2675378	3706035
Arrow PDMS/DVB Dynamic	15.8.2017 9:42	720026	1101633	442858	1630498	3326237	3895582
fiber PDMS/DVB	15.8.2017 12:17	263916	264349	49323	n.d.	152241	447283
Arrow PDMS/Carbon WR	15.8.2017 12:17	395541	739588	145130	890742	1888423	1938522
Arrow PDMS/DVB	15.8.2017 12:17	588729	611699	102902	1276479	4163585	6004766
Arrow PDMS/DVB Dynamic	15.8.2017 12:17	559672	787062	217953	1328222	5386943	7381872

Table S3: Meteorological conditions (temperature, relative humidity, precipitation, particle number concentration, ozone and photosynthetically active radiation) registered during the sampling campaign, 2017.

date	temperature [°C]	relative humidity [%]	precipitation [mm]	particle number concentration [#·cm ⁻³]	ozone [ppb]	photosynthetically active radiation [$\mu\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$]
11.8.2017 11:12	20	52	0.000	2704	35	198
11.8.2017 19:32	20	57	0.000	1502	38	10
12.8.2017 11:17	20	61	0.000	1513	40	151
12.8.2017 13:52	20	67	0.002	1944	37	52
12.8.2017 19:37	20	82	0.050	2943	35	2
13.8.2017 11:02	16	79	0.001	983	27	98
13.8.2017 13:32	17	78	0.001	758	24	108
13.8.2017 15:57	17	69	0.048	1543	24	37
13.8.2017 18:22	15	87	0.001	855	17	18
14.8.2017 10:57	17	51	0.000	2295	26	167
14.8.2017 13:17	19	34	0.000	4997	30	398
14.8.2017 15:47	19	38	0.000	5958	29	59
14.8.2017 18:07	17	40	0.000	4812	30	21
15.8.2017 9:42	17	52	0.000	2465	25	149
15.8.2017 12:17	19	45	0.000	3183	32	236