

Supplement to “Wintertime VOC concentration measurements in the Northern traffic supersite demonstrate the strong role of anthropogenic terpene emissions on VOC chemistry”

5 Heidi Hellén¹, Toni Tykkä¹, Elli Suhonen¹, Kimmo Teinilä¹, Teemu Lepistö², Jarkko V. Niemi³, Topi Rönkkö², Hilkkä Timonen¹ and Arnaud P. Praplan¹

¹Finnish Meteorological Institute, P.O. Box 503, FI-00101 Helsinki, Finland
²Aerosol Physics Laboratory, Physics Unit, Faculty of Engineering and Natural Sciences, Tampere University, 33014
10 Tampere, Finland
³Helsinki Region Environmental Services Authority, 00066 Helsinki, Finland

Correspondence to: Heidi Hellén (Heidi.hellen@fmi.fi)

15

Table S1: Concentrations of C₂-C₅ NMHCs during 24-hour canister sampling periods with means of other compounds groups measured with in situ TD-GC-MS for the same measurement periods

ng m-3		Canister1	Canister2	Canister3	Canister4	MEA
			E2		E3	N
Sampling started (UTC+2)		27/01/22	03/02/22	10/02/22	14/02/22	
		10:45	09:51	10:10	10:30	
Sampling stopped (UTC+2)		27/01/22	04/02/22	11/02/22	15/02/22	
		23:37	10:24	10:23	10:11	
Ethane	C2	3497	6552	2822	4190	4265
Ethene	C2	1214	3441	1014	1811	1870
Propane	C3	2216	6854	2002	2740	3453
Propene	C3	419	1123	565	272	595
2-Methylpropane	C4	691	2021	729	798	1060
Butane	C4	1332	3721	1394	1683	2033
Ethyne	C2	865	2734	1003	1570	1543
t-but-2-ene	C4	0	0	0	0	0
but-1-ene	C4	0	0	0	0	0
Cis-but-2-ene	C4	0	0	0	0	0
2-Methylbutane	C5	850	2355	587	941	1183
n-pentane/1,3butadiene	C5	669	2221	503	645	1009

t-pent-2-ene	C5	0	0	0	0	0
Pent-1-ene	C5	0	0	0	0	0
2-Methylpentane	C5	0	808	156	0	241
Other compound groups:						
Terpenes		271	346	116	69	200
C ₆ -C ₁₅ Alkanes		1265	831	961	541	900
C ₆ -C ₉ Aromatic HCs		2416	4829	1996	1681	2730
C ₁₀ -C ₂₀ Aromatic HCs		91	88	92	40	78
Other VOCs		41	27	153	92	78
Gaseous PAHs		38	46	55	64	51

20

Table S2: Mean concentrations of VOCs (ng m⁻³) at Mäkeläncatu traffic supersite, at residential site and at UB supersite (bgr) site 14th -18th February 2022.

ng m ⁻³	Traffic	Residential	Urban background	Traffic/ residential	Traffic/ urban bgr
<u>Terpenes</u>					
α-pinene	50	31	10	1.6	4.9
camphene	12	18	10	0.6	1.2
Myrcene	12	0	6	-	2.0
β-pinene	6	4	2	1.2	2.7
Δ3-carene	23	5	1	4.9	18.6
p-cymene	15	17	12	0.9	1.2
limonene	36	5	3	7.4	13.6
1,8-cineol	12	25	16	0.5	0.7
terpinolene	2	4	2	0.6	1.6
β-caryophyllene	3	0	0	-	-
SUM	169	110	62	1.5	2.7
<u>Aromatic HCs</u>					
benzene	570	1177	1084	0.5	0.5
toluene	662	801	645	0.8	1.0
ethylbenzene	133	185	148	0.7	0.9
p/m-xylene	346	417	375	0.8	0.9
styrene	27	25	16	1.1	1.8
o-xylene	136	175	150	0.8	0.9
propylbenzene	16	30	18	0.5	0.8
3-ethyltoluene	51	65	42	0.8	1.2

4-ethyltoluene	27	24	19	1.1	1.4
135-TMB	23	23	16	1.0	1.5
2-ethyltoluene	20	28	16	0.7	1.2
124-TMB	102	110	77	0.9	1.3
123-TMB	24	28	16	0.9	1.5
13-diethylbenzene	5	13	13	0.4	0.4
14-diethylbenzene	21	19	12	1.1	1.7
2-propyltoluene	4	5	3	0.9	1.7
2-ethyl-p-xylene	7	3	4	2.3	1.9
1245-TMB	5	4	3	1.2	2.0
135-triethylbenzene	1	0	0	-	-
14-dibutylbenzene	1	0	0	-	-
SUM	2182	3132	2656	0.7	0.8
<u>Alkanes</u>					
Hexane	194	504	554	0.4	0.4
Heptane	88	229	209	0.4	0.4
Octane/2-octene	119	86	66	1.4	1.8
Nonane	46	41	42	1.1	1.1
Decane	147	51	66	2.9	2.2
Undecane	56	43	63	1.3	0.9
Dodecane	37	29	46	1.3	0.8
Tridecane	29	21	39	1.4	0.7
Tetradecane	19	16	28	1.2	0.7
Pentadecane	14	9	13	1.6	1.1
SUM	749	1029	1126	0.7	0.7
<u>Others</u>					
Furfural	14	76	27	0.2	0.5
Benzylalcohol	18	31	19	0.6	0.9
o-cresol	5	5	0	1.0	-
p-cresol	6	22	12	0.3	0.5
SUM	43	135	58	0.3	0.7
<u>Gaseous PAHs</u>					
Naphthalene	38	76	54	0.5	0.7
Acenaphthylene	2	0	0	-	-
Acenaphthene	1	0	1	-	1.8
Fluorene	4	3	2	1.5	1.8
Anthracene	5	6	4	0.8	1.3
Phenanthrene	1	1	0	0.9	2.9

Fluoranthene	2	3	1	0.9	1.7
Pyrene	1	1	1	1.0	1.4
SUM	54	91	64	0.6	0.9
<u>Other pollutants</u>					
NO	12	0.7		17	
NO ₂	23	9.2		2.5	
PM _{2.5}	9	14		0.6	

25 **Table S3: Molar mass (M) and reaction rate coefficients of studied compounds for OH-radical (K_{OH}), ozone (K_{O₃}) and nitrate radical (K_{NO₃}) reactions. Coefficients were obtained from Praplan et al. (2017), Hakola et al. (2017), Ng et al. (2017) and NIST chemical kinetics database (<https://kinetics.nist.gov/kinetics/>)**

	M (g/mol)	k _{OH} (cm ³ s ⁻¹)	k _{O₃} (cm ³ s ⁻¹)	k _{NO₃} (cm ³ s ⁻¹)
<u>Terpenes</u>				
α-pinene	136.24	5.25E-11	9.4E-17	6.2E-12
camphene	136.24	7.83E-11	6.8E-19	6.2E-13
Myrcene	136.24	2.13E-10	4.44E-16	
β-pinene	136.24	7.43E-11	1.9E-17	2.5E-12
Δ ³ -carene	136.24	8.8E-11	4.8E-17	9.1E-12
p-cymene	125.24	1.51E-11	5E-20	
limonene	136.24	1.61E-10	2.11E-16	1.2E-11
1,8-cineol	154.24	1.11E-11	1.5E-19	
terpinolene	136.24	2.26E-10	1.6E-15	9.7E-11
β-caryophyllene	204.35	2.01E-10	1.2E-14	1.90E-11
<u>Aromatic HCs</u>				
benzene	78.12	1.32E-12		3.01E-17
toluene	92.15	5.96E-12		6.79E-17
ethylbenzene	106.17	7.1E-12		
p/m-xylene	106.17	1.9E-11		
styrene	104.15	5.8E-11		
o-xylene	106.17	1.37E-11		
propylbenzene	120.16	6E-12		
3-ethyltoluene	120.16	1.92E-11		
4-ethyltoluene	120.16	1.21E-11		
135-TMB	120.16	5.72E-11		
2-ethyltoluene	120.16	1.23E-11		
124-TMB	120.16	3.25E-11		
123-TMB	120.169	3.27E-11		
13-diethylbenzene	134.218	1.42E-11		
14-diethylbenzene	134.22	8.11E-12		
2-propyltoluene	134.218	8.8E-12		
2-ethyl-p-xylene	134.218	1.69E-11		

1245-TMB	134.218	2.05E-11		
135-triethylbenzene	162.271	3.32E-11		
14-dibutylbenzene	190.324	1.37E-11		
<u>C₆-C₁₅ alkanes</u>				
Hexane	86.178	5.61E-12		
Heptane	100.21	7.2E-12		
Octane/2-octene	114.232	8.7E-12		
Nonane	128.2	1.02E-11		
Decane	142.286	1.16E-11		
Undecane	156.31	1.23E-11		
Dodecane	170.33	1.32E-11		
Tridecane	184.4	1.51E-11		
Tetradecane	253.6	1.67E-11		
Pentadecane	270.6	1.81E-11		
<u>Others</u>				
Furfural	96.084	3.74E-11		
Benzylalcohol	108.138	2.61E-11		
o-cresol	108.0575	4.11E-11		
p-cresol	108.138	4.11E-11		
<u>PAHs</u>				
Naphthalene	128.171	2.87E-11		2.00E-11
Acenaphthylene	152.192	7.55E-11	2.52E-16	
Acenaphthene	154.208	6.69E-11		
Fluorene	166.219	8.85E-12		1.52E-14
Anthracene	178.229	4E-11		
Phenanthrene	178.229	1.3E-11		
Fluoranthene	202.251	2.92E-11		
Pyrene	202.251	5E-11		
PAH SUM				
<u>C₂-C₅ NMHCs</u>				
Ethane	30.068	2.57E-13		1E-17
Ethene	28.052	8.52E-12	1.48E-18	2.1E-16
Propane	44.094	1.15E-12		
Propene	42.078	2.63E-11	9.6E-18	9.54E-15
2-Methylpropane	58.12	2.33E-12		
Butane	58.12	2.52E-12		
Ethyne	26.036	8.15E-13		1E-16
but-1-ene	56.104	3.14E-11		
2-Methylbutane	72.15	3.9E-12		
n-pentane	72.146	3.96E-12		
2-Methylpentane	86.17	5.6E-12		

References to Table S3:

Hakola, H., Tarvainen, V., Praplan, A. P., Jaars, K., Hemmilä, M., Kulmala, M., Bäck, J., and Hellén, H.: Terpenoid and carbonyl emissions from Norway spruce in Finland during the growing season, *Atmos. Chem. Phys.*, 17, 3357–3370, <https://doi.org/10.5194/acp-17-3357-2017>, 2017.

35 Ng, N. L., Brown, S. S., Archibald, A. T., Atlas, E., Cohen, R. C., Crowley, J. N., Day, D. A., Donahue, N. M., Fry, J. L., Fuchs, H., Griffin, R. J., Guzman, M. I., Herrmann, H., Hodzic, A., Iinuma, Y., Jimenez, J. L., Kiendler-Scharr, A., Lee, B. H., Luecken, D. J., Mao, J., McLaren, R., Mutzel, A., Osthoff, H. D., Ouyang, B., Picquet-Varraut, B., Platt, U., Pye, H. O. T., Rudich, Y., Schwantes, R. H., Shiraiwa, M., Stutz, J., Thornton, J. A., Tilgner, A., Williams, B. J., and Zaveri, R. A.: Nitrate radicals and biogenic volatile organic compounds: oxidation, mechanisms, and organic aerosol, *Atmos. Chem. Phys.*, 17, 2103–2162, <https://doi.org/10.5194/acp-17-2103-2017>, 2017.

Praplan A. P., Pfannerstill E. Y., Williams J. and Hellén, H: OH reactivity of the urban air in Helsinki, Finland, during winter, *Atmos. Environ.*, 169, 150 - 161, doi: 10.1016/j.atmosenv.2017.09.013, 2017.

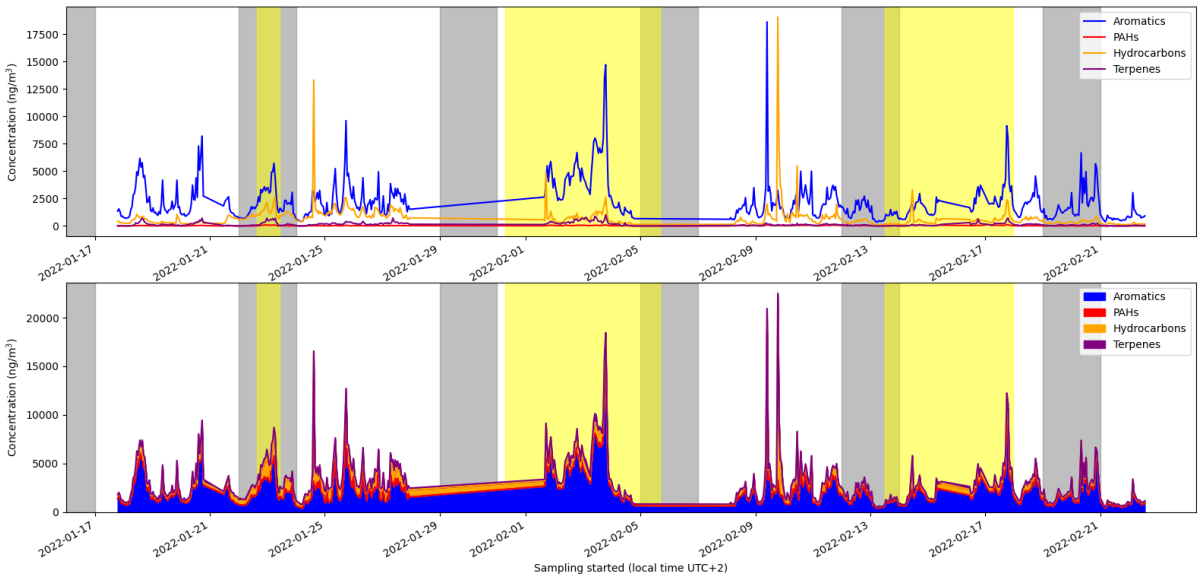


Figure S1: Time series of C₆-C₁₅ compound groups (top) and cumulative contributions (bottom). Grey bars show the weekends and yellow bars show the episodes.