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Volatile organic compound sources and impacts in an urban Mediterranean area (Marseille, France)

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Results of the IVOC Calibration procedure

Figure S1 shows the comparison of the response factor for heavy compounds with the liquid mixture and the standard gas mixture from NPL or theoretical obtained from the octane for compounds not present in the NPL, with the use of the heated calibration solution rig and the figure S2 with the use of the LCU. For each solution, three measurements have been performed and the standard deviation is shown in the figures. The results show that with both evaporation systems, there is no significant differences (<10%) between the response factor of the liquid mixture and the theoretical response factor calculated with the response factor of compounds from the NPL standard gas excepting for the hexadecane (30 % with the heated calibration solution rig and 15% with the LCU). Differences observed can be explained by the reproducibility of the solutions concentrations and random errors in the preparation and injection of the solution into the C6 – C16 TD-GC-FID. Concerning IVOC, they have a low volatility that makes their evaporation from a liquid mixture more difficult than with other VOC.

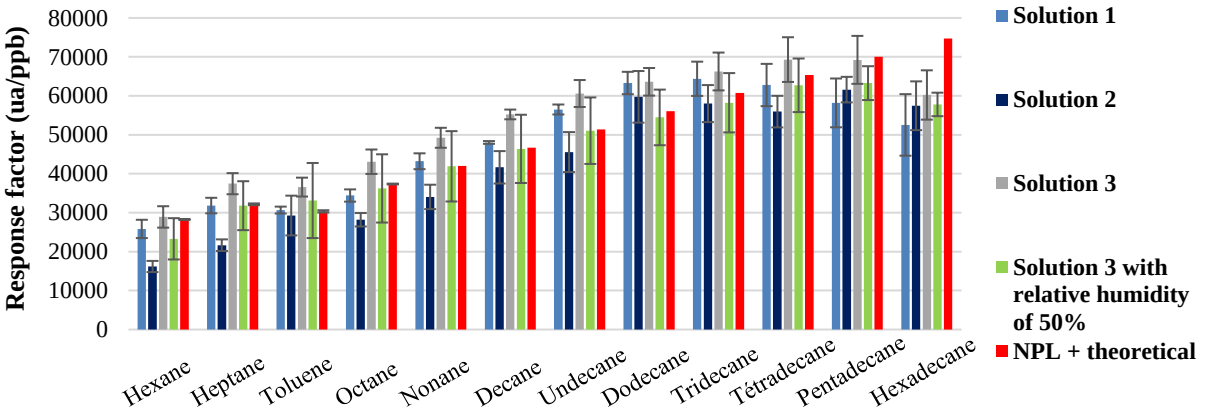

Figure S1: Response factor obtained with the evaporation of a liquid mixture (1 to 3 ppb) via the heated calibration solution rig. Dates correspond to the preparation dates of each liquid mixture. Bars represent standard deviations.

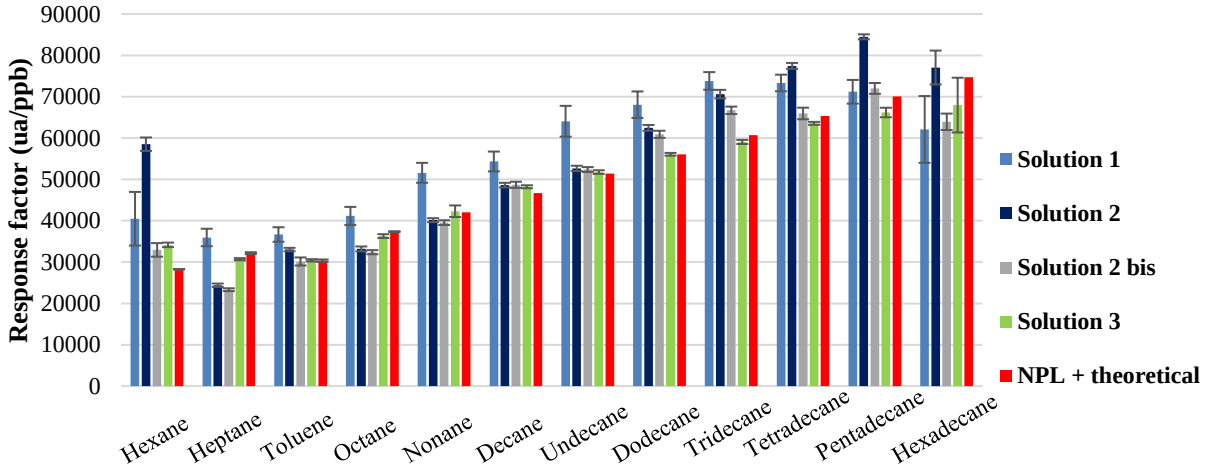

Figure S2: Response factor obtained with the evaporation of a liquid mixture (1 to 3 ppb) via the LCU. Dates correspond to the preparation dates of each mixture. Bars represent standard deviations.

Quality control of data

The first Volatile Organic Compounds – Global Atmosphere Watch (NMHC-GAW) intercomparison points out the importance to harmonize of the NMHC measurement procedures to overcome the high differences obtained with different devices for the same mixture (Rappengluck et al., 2006). During this field campaign, the two instruments installed measured many compounds in common allowing an intercomparison of the data.

Before the deployment on the field, blanks have been done by sampling zero air at a relative humidity of 50 % to determine potential artifacts within both devices. Nevertheless, the intensity of the identified artifacts could change and new ones could appear during a field campaign. Therefore, blank analysis was performed during the campaign. For the TD-GC-2FID the significant artifacts to consider are on the isobutene which is due to the use of a Nafion dryer, isoprene, and n-hexane. During the campaign another artifact has been found for benzene. This could be due to butanol used for SMPS (Scanning Mobility Particle Sizer) by AtmoSud. For the TD-GC-FID significant artifacts have been seen on the n-hexane and on the n-octane, which were considered in the uncertainty estimation.

Quality control of data

The first step in the quality control of our data was the checking of outliers. We applied a log normal law by assuming the logarithm of our measured concentrations is respecting a normal distribution. Then each measurement that is not in the range of the mean ± 4 times the standard deviation is a possible outlier and needs to be verified to determine its reliability.

Beside the use of a log normal law, an intercomparison between isomers like isopentane and pentane or m,p-xylenes and o-xylene is done since these isomers are supposed to have a similar behavior.

For compounds with 6 to 9 carbon atoms the measurement is done by both TD-GC-FID so an intercomparison can be done to see if there is a good agreement between the measurements of the two devices. Figure S3 shows the co-variability of the concentrations of toluene measured by both instruments during the campaign indicating the robust measurement with both instruments.

The Table S1 gives an overview of the results of scatter plots between both GC systems for common compounds. Compounds with a correlation coefficient below 0.7 are the compounds with the lowest concentrations. Concerning the slope, there is a significant difference between both devices for n-hexane and 1,2,3-trimethylbenzene. For n-hexane, the reason could be a bad integration of the artifact on blank measurements that affects the concentration measured. For the 1,2,3-trimethylbenzene the reason could be a co-elution with other compounds. For instance, the limonene which is not measured by the TD-GC-2FID is not well separated from the 1,2,3-trimethylbenzene and can affect the measurement. This

would explain why concentrations measured by the TD-GC-2FID are, in average higher than those measured by the TD-GC-FID.

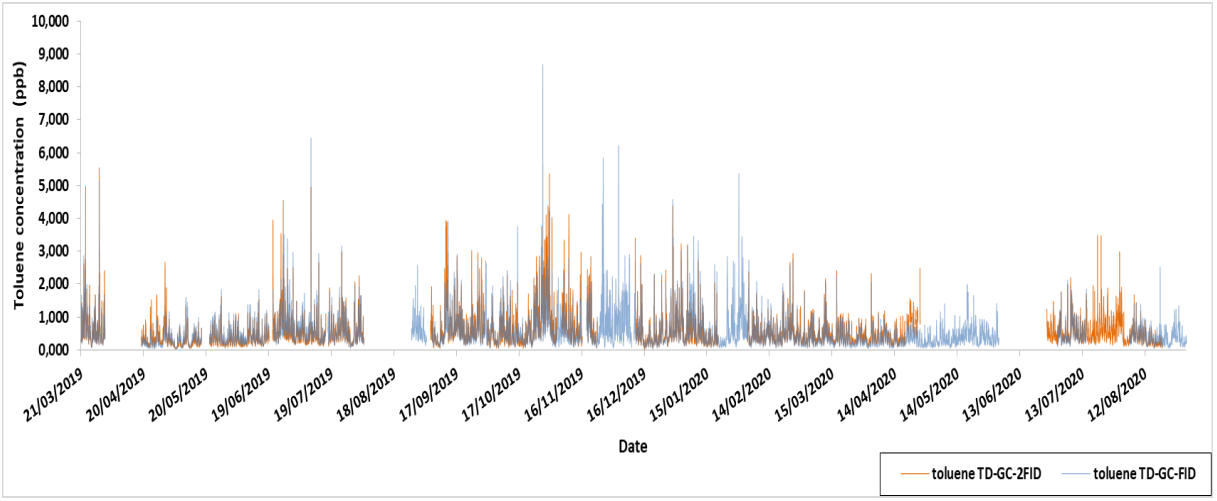

Figure S3: Time series of the toluene concentration measured with the TD-FC-FID Chromatotec and the TD-GC-2FID Perkin-Elmer during the campaign.

Table S1: summary of results of the correlation of compounds in common for both devices with results of the TD-GC-FID as y values and results of the TD-GC-2FID as x values. The intercept is in ppt.

Compounds	Correlation coefficient R	Slope	Intercept
3-methylpentane	0.73	0.43	37
Hexane	0.72	0.52	5
Isooctane	0.61	0.73	10
Heptane	0.78	0.76	24
Toluene	0.82	0.74	130
Ethylbenzene	0.81	0.83	29
m,p-xylenes	0.80	0.77	92
o-xylenes	0.78	0.81	35
Nonane	0.71	0.69	11
1,3,5-trimethylbenzene	0.61	0.89	21
1,2,4-trimethylbenzene	0.74	0.84	27
1,2,3-trimethylbenzene	0.63	0.48	0.005

Table S2: Mean and median concentration and number of measurements below the LoD for all the measured compounds during the whole campaign (the number of measurements below the LoD and the total number of measurements are given in the parenthesis).

Compounds	**Mean concentration (ppt)**	**Median concentration (ppt)**	**Number of measurements below the LoD (%)**
Ethane	2278	1749	0 (2/9675)
Ethene	830	535	3 (244/7177)
Propane	1024	779	1 (53/9675)
Propene	233	156	11 (783/7177)
Isobutane	653	479	0 (8/9675)
Butane	1259	906	0 (6/9675)
Acetylene	483	347	17 (1329/7973)
Trans-2-Butene	67	44	20 (1467/7177)
1-Butene	137	100	10 (696/7177)
Vinyl Chloride	161	59	30 (2945/9675)
Isobutene	311	267	5 (367/7177)
Cis-2-butene	56	38	30 (2155/7177)
Neopentane	13	12	96 (9267/9675)
Isopentane	743	540	0 (6/9675)
Pentane	331	248	0 (10/9417)
Propyne	43	42	99 (9595/9675)
1,3-butadiene	62	22	63 (4538/7177)
3-methylbutene	14	11	90 (6491/7177)
Trans-2-pentene	29	10	56 (4024/7177)
2-methyl-1-butene	38	11	53 (3836/7177)
1-pentene	23	11	76 (5482/7177)
2-methyl-2-butene	31	17	81 (5843/7177)
Cis-2-pentene	17	9	76 (5438/7177)
Butyne	12	9	93 (9036/9675)
Isoprene	343	241	20 (1745/8734)
Cyclopentene	65	27	59 (5289/8905)
Cyclopentane	32	18	75 (6669/8905)
2,2-dimethylbutane	66	53	38 (3373/8905)
2-methylpentane	188	152	0 (0/8905)
3-methylpentane	83	59	1 (54/9826)
1-Hexene	13	4	73 (7200/9826)
Hexane	97	69	3 (256/9826)
2,2-dimethylpentane	78	56	3 (317/9826)

2,4-dimethylpentane	48	34	8 (825/9826)
2,2,3-dimethylbutane	6	6	98 (9643/9826)
Benzene	187	136	0 (3/9826)
3,3-dimethylpentane	15	6	91 (8979/9826)
Cyclohexane	172	112	3 (265/9826)
2-methylhexane	57	36	23 (1529/6787)
2,3-dimethylpentane	31	15	62 (4213/6787)
Trichloroethylene	9	6	100 (9821/9826)
Isooctane	37	23	20 (1931/9826)
Heptane	67	47	6 (586/9826)
Toluene	506	370	0 (3/9826)
Octane	17	8	66 (5701/8602)
Tetrachloroethylene	168	165	99 (8538/8602)
Ethylbenzene	95	69	0 (43/9826)
m,p-xylenes	349	254	0 (18/9826)
Styrene	10	6	39 (3839/9826)
o-xylene	123	86	1 (60/9826)
Nonane	23	17	5 (496/9826)
Isopropylbenzene	5	4	90 (8854/9826)
α-pinene	4	3	88 (8691/9826)
Propylbenzene	12	6	39 (3818/9826)
3-ethyltoluene	39	28	22 (1901/8769)
4-ethyltoluene	53	39	15 (1298/8769)
1,3,5-trimethylbenzene	21	8	61 (5317/8769)
2-ethyltoluene	17	12	39 (3827/9826)
1,2,4-trimethylbenzene	92	68	4 (359/9826)
Decane	38	27	5 (502/9826)
1,2,3-trimethylbenzene	45	29	11 (1093/9826)
Limonene	11	3	59 (5845/9826)
Butylbenzene	5	3	79 (7808/9826)
Undecane	24	20	8 (753/9826)
Dodecane	15	11	29 (2833/9826)
Tridecane	9	6	42 (4112/9826)
Tetradecane	7	2	58 (5694/9826)
Pentadecane	3	2	83 (8142/9826)
Hexadecane	3	2	90 (8865/9826)

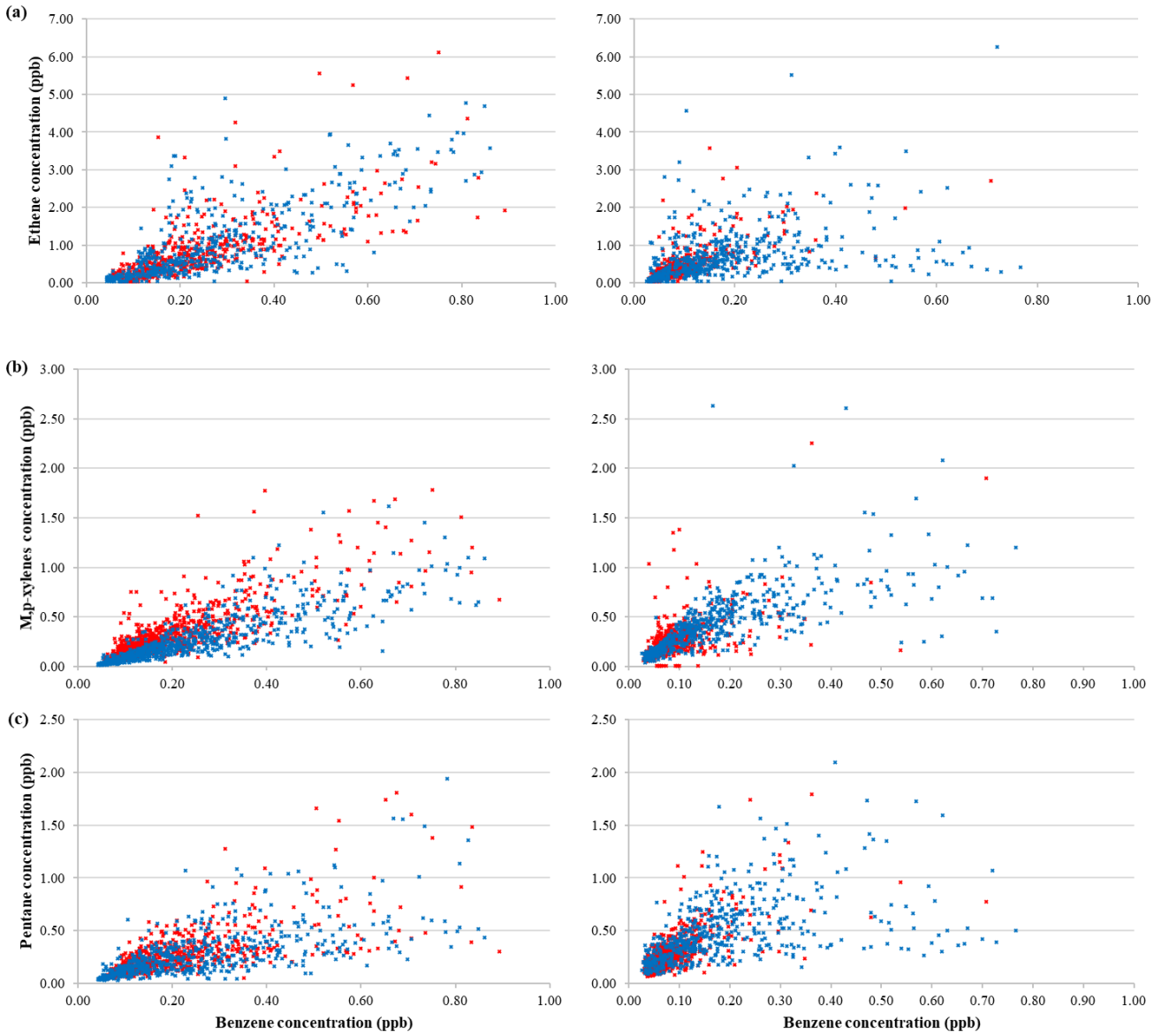

Figure S4: Scatter plot of (a) ethene, (b) m,p-xylene and (c) n-pentane vs. benzene (in ppb) in winter 2020 (left) and summer 2019 (right) during daytime (red) and nighttime (blue).

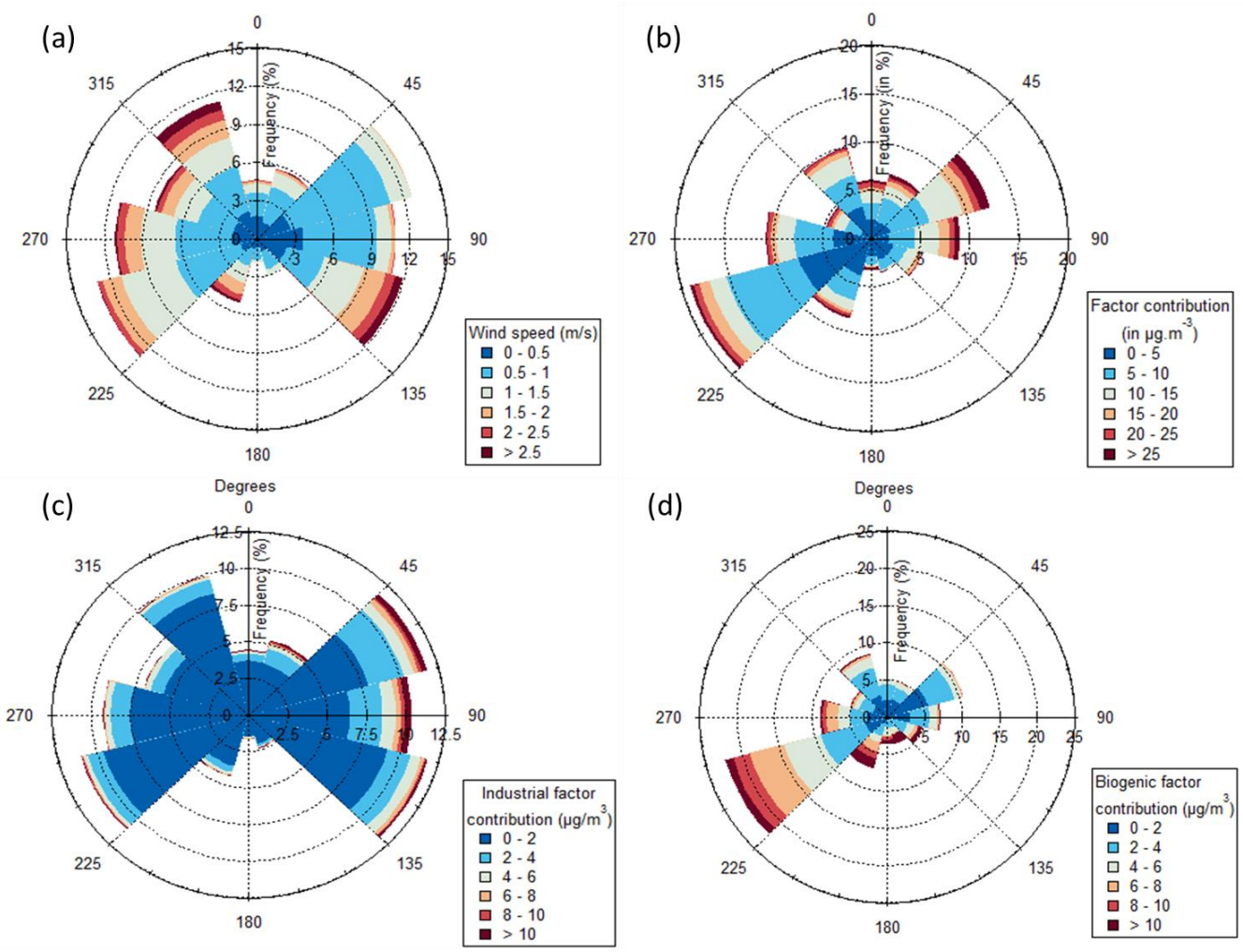

Figure S5: (a) wind rose, (b) pollution rose of the fuel evaporation from traffic factor, (c) pollution rose of the industrial factor and (d) pollution rose of the biogenic factor for the whole campaign.

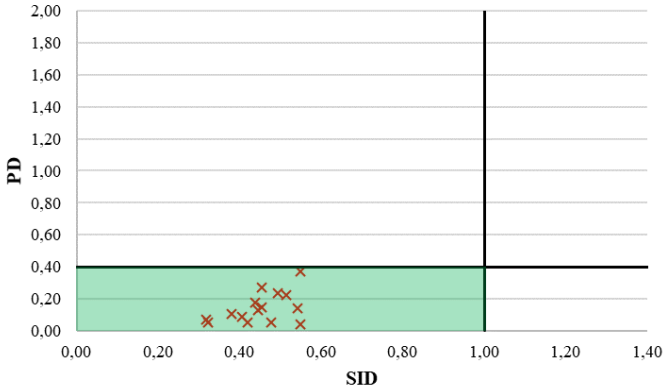

Figure S6: PD-SID for the traffic exhaust factor between each season (red crosses). Horizontal and vertical black lines are the limit acceptable values for PD (0,40) and SID (1,00) respectively. The green area is the acceptance area for both PD and SID.

Table S3: Pearson correlation coefficient and p-value for the traffic exhaust factor with NO and NO_2 for all seasons. * means a p-value < 0.001 %, ** a p-value between 0.001 % and 1 % and * a p-value >1 %.**

		Spring 2019	Summer 2019	Fall 2019	Winter 2020	Spring 2020	Summer 2020
NO_2	**Pearson correlation coefficient**	0.60	0.48	0.54	0.63	0.64	0.49
	p-value (%)	***	***	***	***	***	***
NO	**Pearson correlation coefficient**	0.06	0.09	0.34	0.60	0.07	0.11
	p-value (%)	*	**	***	***	**	**

Table S4: Pearson correlation coefficient and p-value for the fuel evaporation factor with NO and NO_2 for all seasons. * means a p-value < 0.001 %, ** a p-value between 0.001 % and 1 % and * a p-value >1 %.**

		Spring 2019	Summer 2019	Fall 2019	Winter 2020	Spring 2020	Summer 2020
NO_2	**Pearson correlation coefficient**	0.61	0.57	0.48	0.41	0.39	0.46
	p-value (%)	***	***	***	***	***	***
NO	**Pearson correlation coefficient**	0.12	0.12	0.43	0.32	0.01	0.07
	p-value (%)	**	***	***	***	*	*

Table S5: Pearson correlation coefficient and p-value for the heating factor with NO, NO_2 and black carbon from wood burning for all seasons. * means a p-value < 0.001 %, ** a p-value between 0.001 % and 1 % and * a p-value >1 %.**

		Fall 2019	Winter 2020	Spring 2020
NO_2	**Pearson correlation coefficient**	0.48	0.50	0.45
	p-value (%)	***	***	***
NO	**Pearson correlation coefficient**	0.50	0.42	0.13
	p-value (%)	***	***	***
BC_{wb}	**Pearson correlation coefficient**	0.61	0.80	0.78
	p-value (%)	***	***	***

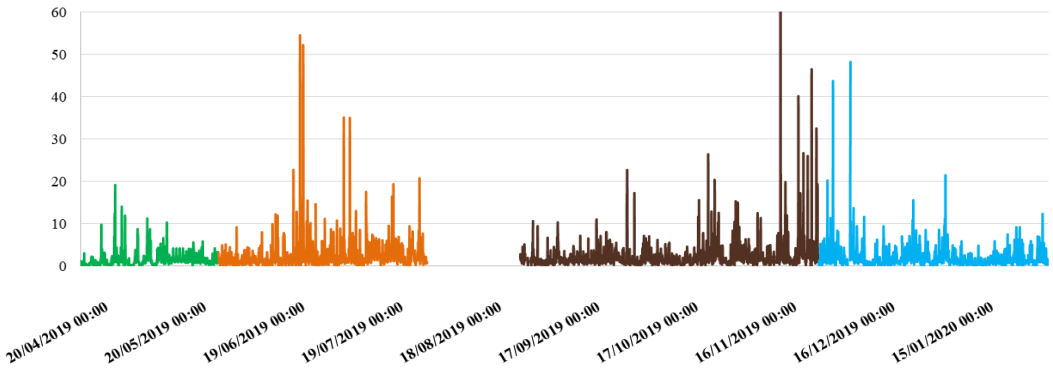

Figure S7: Shipping factor temporal variation from spring 2019 to winter 2020 (in µg/m^3).

Table S6: Pearson correlation coefficient and p-value for the shipping factor with NO_2, NO, traffic-related sources, residential heating and IVOC for all seasons where the factor has been identified. * means a p-value < 0.001 %, ** a p-value between 0.001 % and 1 % and * a p-value >1 %.**

		Spring 2019	Summer 2019	Fall 2019	Winter 2020
NO2	**Pearson correlation coefficient**	0.46	0.41	0.25	0.43
	p-value (%)	***	***	***	***
NO	**Pearson correlation coefficient**	0.08	0.04	0.20	0.28
	p-value (%)	**	*	***	***
Fuel evaporation	**Pearson correlation coefficient**	0.46	0.37	0.32	0.48
	p-value (%)	***	***	***	***
Traffic exhaust	**Pearson correlation coefficient**	0.43	0.56	0.22	0.41
	p-value (%)	***	***	***	***
Residential heating	**Pearson correlation coefficient**	/	/	0.30	0.33
	p-value (%)	/	/	***	***
IVOC	**Pearson correlation coefficient**	0.60	0.31	-0.02	0.53
	p-value (%)	***	***	/	***

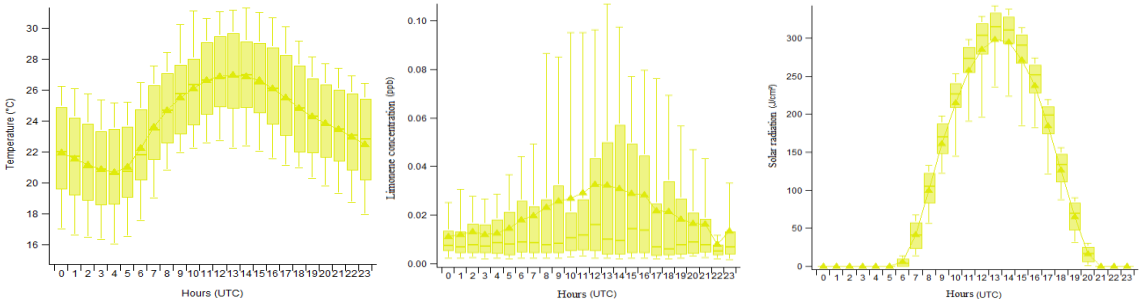

Figure S8: Diurnal profile of the temperature (left), the limonene (middle) and the solar radiation (right) in summer 2019.

Table S7: Pearson correlation coefficient and p-value for the IVOC factor with NO, NO_2, fuel evaporation factor, traffic exhaust factor and residential heating factor for all seasons. * means a p-value < 0.001 %, ** a p-value between 0.001 % and 1 % and * a p-value >1 %.**

		Spring 2019	Summer 2019	Fall 2019	Winter 2020	Spring 2020	Summer 2020
NO_2	**Pearson correlation coefficient**	0.62	0.30	0.04	0.44	-0.03	0.20
	p-value (%)	***	***	*	***	/	***
NO	**Pearson correlation coefficient**	0.18	0.07	-0.02	0.36	-0.02	0.10
	p-value (%)	***	*	/	***	/	**
Fuel evaporation	**Pearson correlation coefficient**	0.54	0.29	-0.02	0.37	-0.11	0.24
	p-value (%)	***	***	/	***	/	**
Traffic exhaust	**Pearson correlation coefficient**	0.40	0.38	0.16	0.47	-0.03	0.18
	p-value (%)	***	***	***	***	/	***
Residential heating	**Pearson correlation coefficient**	/	/	-0.14	0.31	0.02	/
	p-value (%)	/	/	/	***	*	/

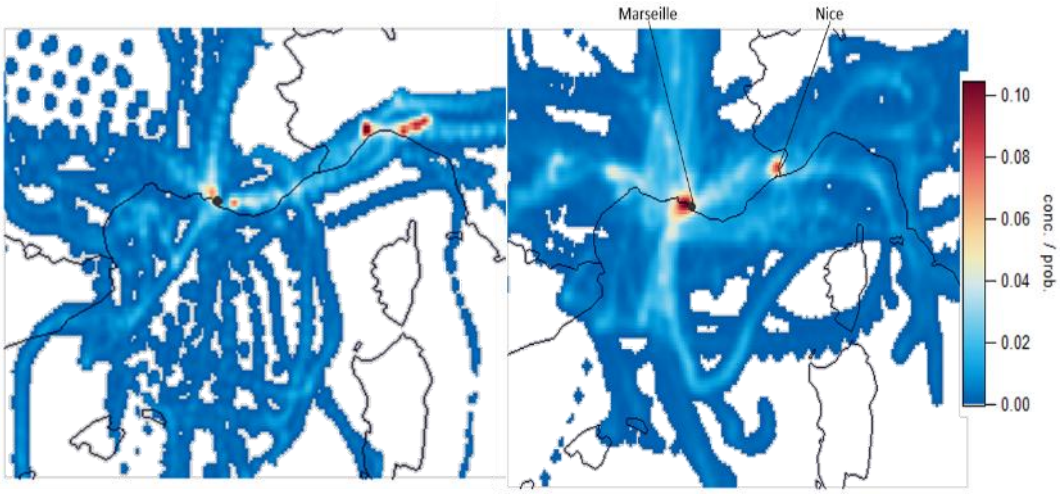

Figure S9: PSCF for background factor contribution in summer 2019 (left) and spring 2020 (right).

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Table S8: List of compounds measured by both devices during the campaign. Co-eluted compounds on the TD-GC-FID are indicated with *.

Compounds	*TD-GC-2FID*	*TD-GC-FID*
Ethane	✓	
Ethene	✓	
Propane	✓	
Propene	✓	
Isobutane	✓	
Butane	✓	
Acetylene	✓	
Trans-2-Butene	✓	
1-Butene	✓	
Vinyl Chloride	✓	
Isobutene	✓	
Cis-2-butene	✓	
Neopentane	✓	
Isopentane	✓	
Pentane	✓	
Propyne	✓	
1,3-butadiene	✓	
3-methylbutene	✓	
Trans-2-pentene	✓	
2-methyl-1-butene	✓	

1-pentene	✓	
2-methyl-2-butene	✓	
Cis-2-pentene	✓	
Butyne	✓	
Isoprene	✓	
Cyclopentene	✓	
Cyclopentane	✓	
2,2-dimethylbutane	✓	✓*
2-methylpentane	✓	
3-methylpentane	✓	✓
1-Hexene	✓	✓
Hexane	✓	✓
2,2-dimethylpentane	✓	✓
2,4-dimethylpentane	✓	✓
2,2,3-dimethylbutane	✓	✓
Benzene	✓	✓
3,3-dimethylpentane	✓	✓*
Cyclohexane	✓	
2-methylhexane	✓	
2,3-dimethylpentane	✓	✓*
Trichloroethylene	✓	✓
Isooctane	✓	✓
Heptane	✓	✓
Toluene	✓	✓
Octane	✓	✓
Tetrachloroethylene	✓	✓
Ethylbenzene	✓	✓
m,p-xylenes	✓	✓
Styrene	✓	✓
O-xylene	✓	✓
Nonane	✓	✓
Isopropylbenzene	✓	✓
α-pinene		✓
β-pinene		✓
Propylbenzene	✓	✓
3-ethyltoluene	✓	✓*
4-ethyltoluene	✓	
1,3,5-trimethylbenzene	✓	✓
2-ethyltoluene	✓	✓
1,2,4-trimethylbenzene	✓	✓

Decane	✓	✓
1,2,3-trimethylbenzene	✓	✓
Limonene		✓
Butylbenzene	✓	✓
Undecane		✓
Dodecane		✓
Tridecane		✓
Tetradecane		✓
Pentadecane		✓
Hexadecane		✓

Table S9: Mean and median expanded relative uncertainties in percentage estimated for both instruments during the campaign.

	C2 – C9 TD-GC-2FID		**C6 – C16 TD-GC-FID**	
	mean	median	mean	median
Ethane	27,6	20,1		
Ethylene	50,7	19,0		
Propane	32,7	22,9		
Propene	60,8	31,1		
Isobutane	17,3	11,1		
Butane	13,8	8,5		
Acetylene	39,2	23,8		
Trans-2-butene	43,3	33,9		
1-butene	26,0	15,6		
Cis-2-butene	38,1	30,5		
Isopentane	12,4	6,9		
Pentane	11,9	8,0		
1,3-butadiene	77,2	42,0		
Trans-2-pentene	>100	70,7		
1-pentene	>100	98,6		
2-methylpentane	64,1	19,8	11,3	7,6
Hexane	30,6	25,2	20,4	14,5
Benzène	30,1	13,9	9,7	8,0
Isooctane	72,1	44,2	46,0	34,6
Heptane	60,4	37,6	26,6	18,7
Toluène	18,0	13,6	5,4	4,4
Octane	>100	81,8	50,5	39,5
Ethylbenzene	48,3	34,8	11,1	8,4
m+p-xylenes	27,0	16,8	5,3	4,0
o-xylene	39,9	25,7	12,8	9,0
1,3,5-trimethylbenzene	>100	75,1	42,9	30,6
1,2,4-trimethylbenzene	54,5	29,4	19,8	11,2
1,2,3-trimethylbenzene	54,0	28,3	59,2	30,3

Table S10: Meteorological conditions during lockdown period in 2020 and the similar period in 2019. Concerning wind speed only speed higher than 0.5 m.s^{-1} are considered and concerning precipitation only hours with at least 1 mm of precipitation are considered.

	Minimal temperature (°C)	Maximal temperature (°C)	Mean temperature (°C)	Minimal wind speed (m.s^{-1})	Maximal wind speed (m.s^{-1})	Mean wind speed (m.s^{-1})	Number of hours under Mistral event	Height of precipitation (mm)	Number of rainy hours
17/03/19 to 10/05/19	6.3	23.2	13.7	0.5	3.8	1.2	267	101	31
17/03/20 to 10/05/20	3.8	24.8	15.0	0.5	2.8	0.9	179	26	17