Supplement material to *VOC sources and impacts at an urban Mediterranean area (Marseille – France)*

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.

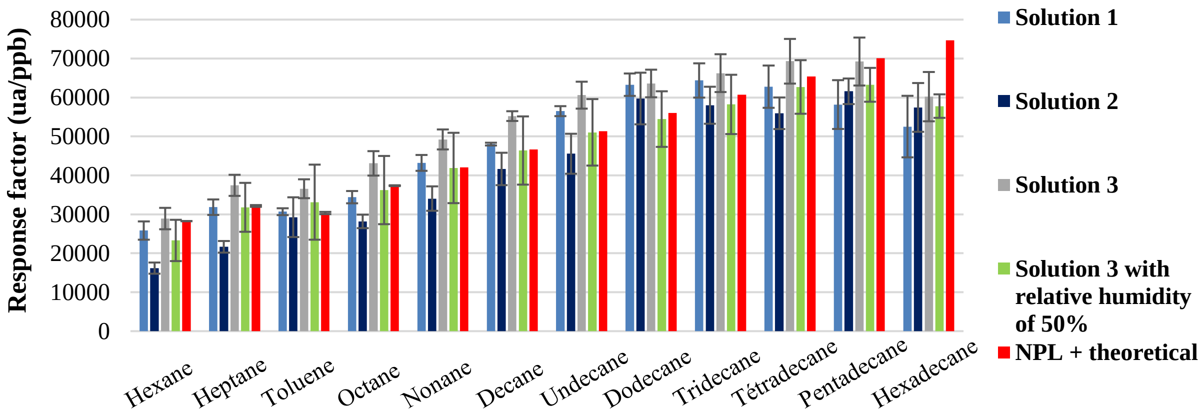

Figure S1: Response factor obtained with the evaporation of a liquid mixture (1 to 3 ppb) via the heated calibration solution rig. Dates correspond to the preparation dates of each liquid mixture. Bars represent standard deviations.

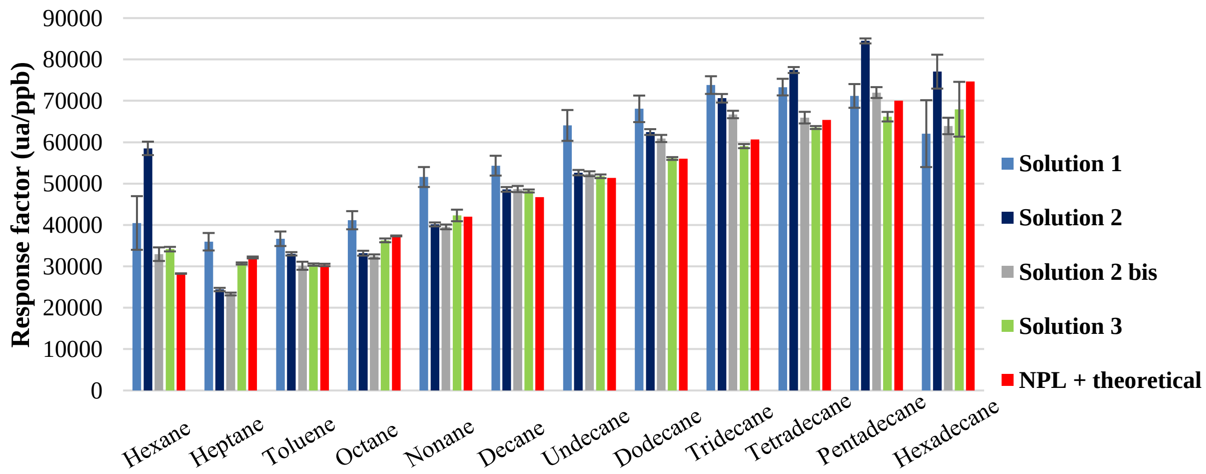

Figure S2: Response factor obtained with the evaporation of a liquid mixture (1 to 3 ppb) via the LCU. Dates correspond to the preparation dates of each mixture. Bars represent standard deviations.

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.

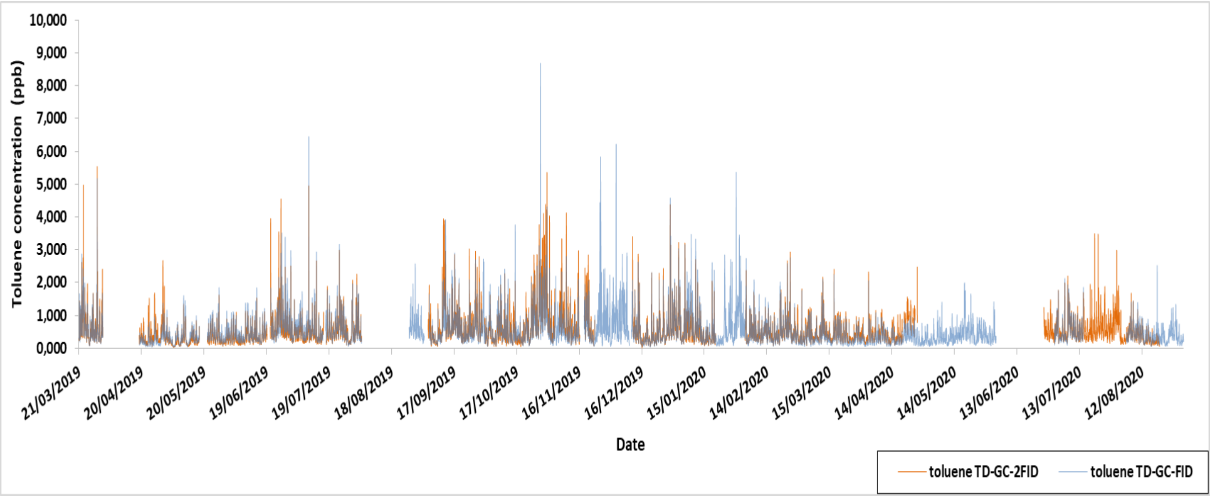

Figure S3: Time series of the toluene concentration measured with the TD-FC-FID Chromatotec and the TD-GC-2FID Perkin-Elmer during the campaign.

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

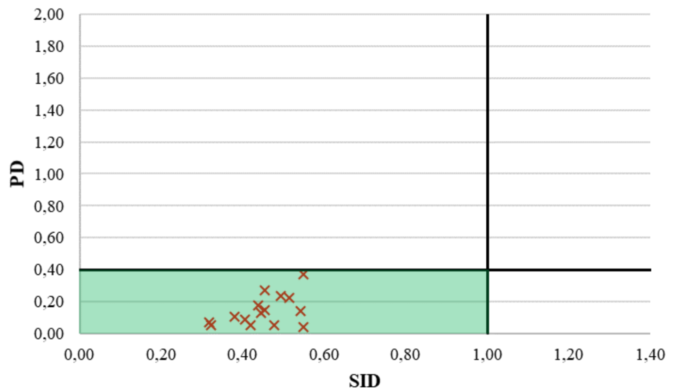

Figure S4: PD-SID for the traffic exhaust factor between each season (red crosses). Horizontal and vertical black lines are the limit acceptable values for PD (0,40) and SID (1,00) respectively. The green area is the acceptance area for both PD and SID.

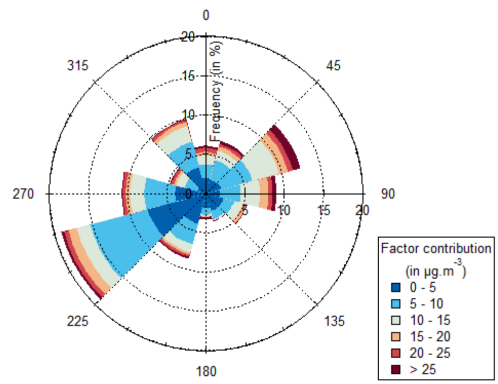

Figure S5: Pollution rose of fuel evaporation during summer 2019.

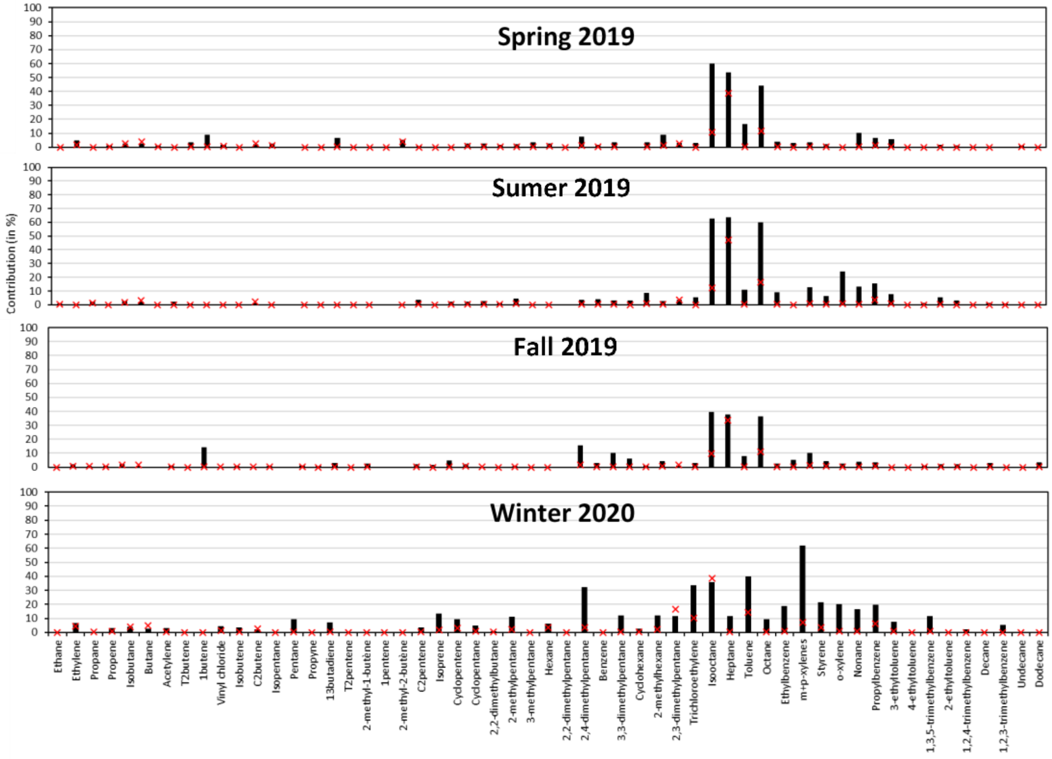

Figure S6: Shipping factor profile during the whole campaign. The black bars are the contribution of the factor to the species concentration and red crosses are the contribution of the species to the factor.

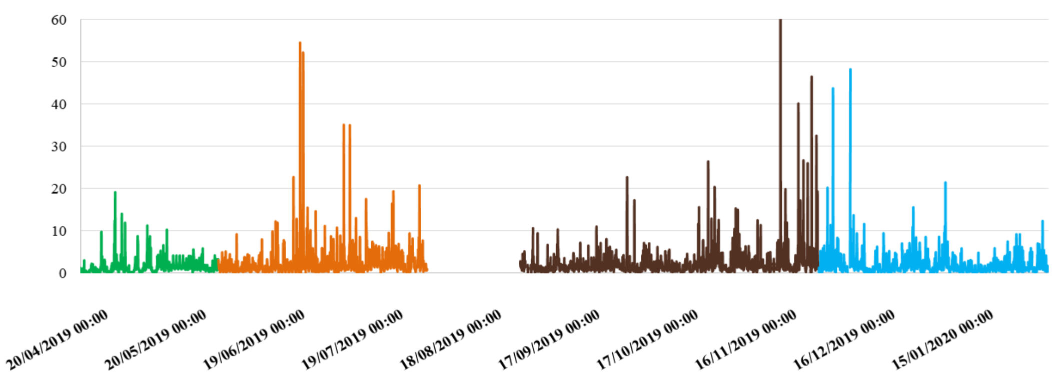

Figure S7: Shipping factor temporal variation from spring 2019 to winter 2020 (in µg/m^3).

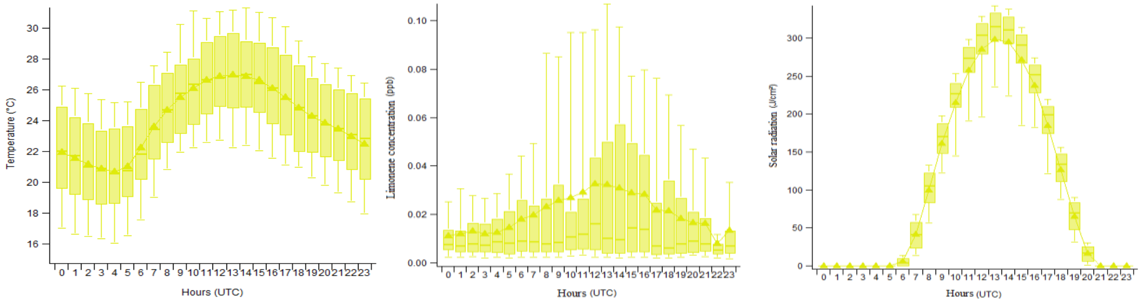

Figure S8: Diurnal profile of the temperature (left), the limonene (middle) and the solar radiation (right) in summer 2019.

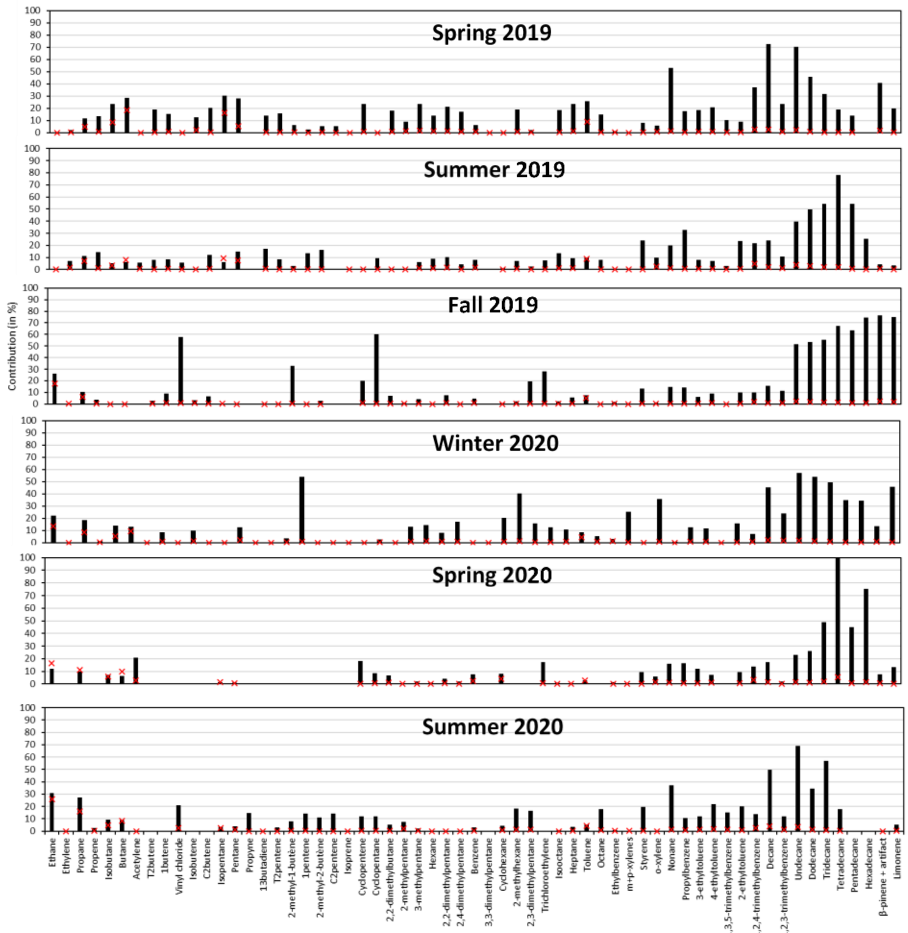

Figure S9: IVOC factor profile during the whole campaign. The black bars are the contribution of the factor to the species concentration and red crosses are the contribution of the species to the factor.

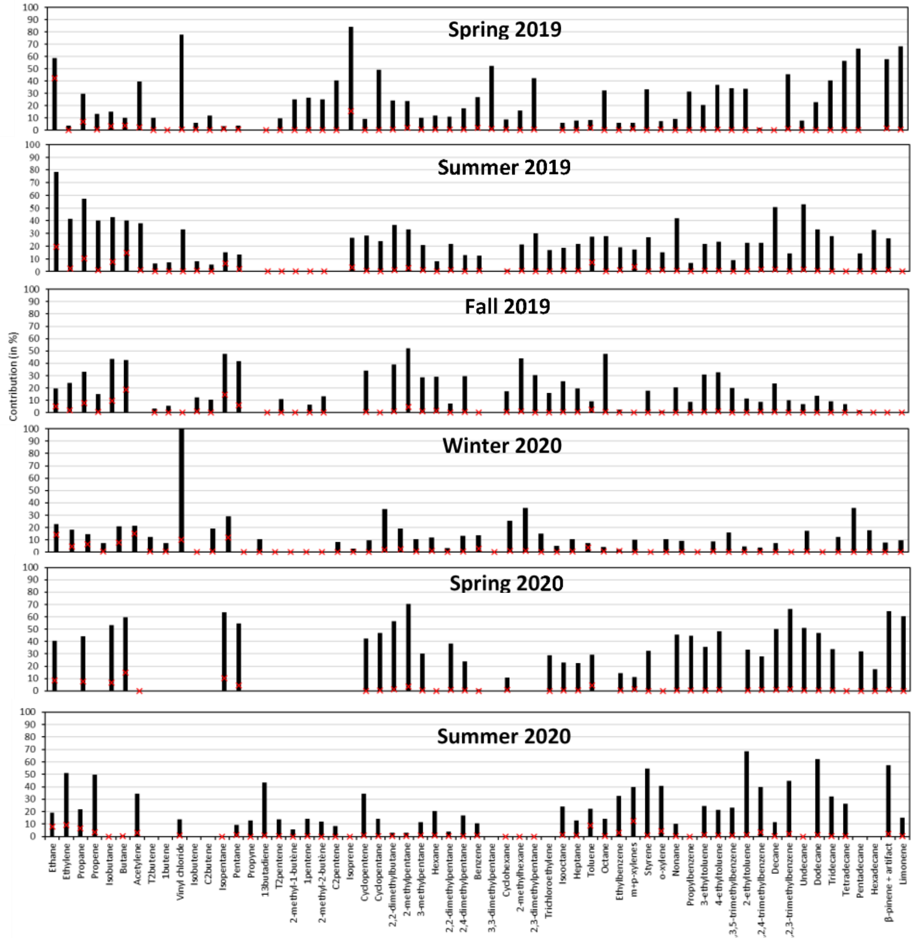

Figure S10: Background factor profile during the whole campaign. The black bars are the contribution of the factor to the species concentration and red crosses are the contribution of the species to the factor.

Table S2: 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 S3: 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 S4: 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 (%)	***	***	/	***