Response to the comments from the first reviewer on essd-2022-406 "Two years of Volatile Organic Compounds online in-situ measurements at SIRTA (Paris region, France) using Proton-Transfer-Reaction Mass Spectrometry"

We thank the reviewer for all the constructive comments. In the following, we provide the response to the reviewer using black for original review comments, green for authors' responses, and *blue italic for changes in the revised version.*

Please note that lines number correspond here to the lines in the preprint and not in the revised version.
The original figures/tables are indicated with their original reference in this document, while the additional figures/tables are referenced here as "Figure/Table R" with a number and their respective reference in the revised paper are indicated in brackets. Example: Table R1 (Table S3 in the revised paper)
For clarity, comments have been numbered.

General comments

Simon and coauthors present a two-year long PTRMS dataset of VOCs in the Paris region. Data was collected across seasons and before and during COVID-19 lockdowns and will be very helpful for models and other interpretations of urban VOC measurements. The authors do a good job of presenting what the dataset is and guide the reader through points of interest and further study in the data set while presenting some of their own conclusions. However, the quality of the dataset is questionable only because a large amount of detail on calibrations and quality control is left out. Major revisions are required to add this detail in and are outlined in the comments below. I have many other minor comments that are needed to communicate some conclusions and for the presentation of this data set.

We thank the reviewer for the valuable comments, which are addressed one by one hereafter.

Specific comments

1) *Line 137-139: I think the kinetic approach needs a little more justification for your system. It's not clear that this will work for your full range of k. This could be a figure of k*(transmission) vs. measured sensitivity in the supplement and then you overlay a few species of estimated sensitivity over a broad k range.*

We are not sure that we have well understood this comment. This kinetic approach is recommended by the PTR-MS and GCU manuals (IONICON, 2010 and 2015) and has been used in many studies (Ghirardo et al., 2020; Li et al., 2019; Zhang et al., 2021). Here, the values used for the k rates were taken from the database provided by Pagonis et al (2019) and from a recent study (Holzinger et al., 2019). In addition, Figure R1 below shows the scatter plot of k*(transmission) vs. measured sensitivity for a few species that have different k rates (methanol, acetonitrile, acetaldehyde, benzene and toluene). The relationship is linear as expected, which indicates that the k rates are appropriate. We hope that this answers your comment.

These sentences are rephrased as: *"Usually, the standard mixture doesn't contain all measured compounds; therefore, another method is applied, the so-called "kinetic approach", where the sensitivity is calculated based on the proton-transfer reaction rate constant and the collision conditions in the drift tube (Yuan et al., 2017; Pagonis et al., 2019; IONICON, 2015). This approach, detailed in Taipale et al. (2008) and summarized in Text S1, consists of calculating a transmission curve using the calibrated compounds' measured sensitivity to retrieve the other compounds' transmission, and determine their sensitivity."*
Moreover, the kinetic approach is further detailed in the Text S1, and the k rates were added in Table 1.
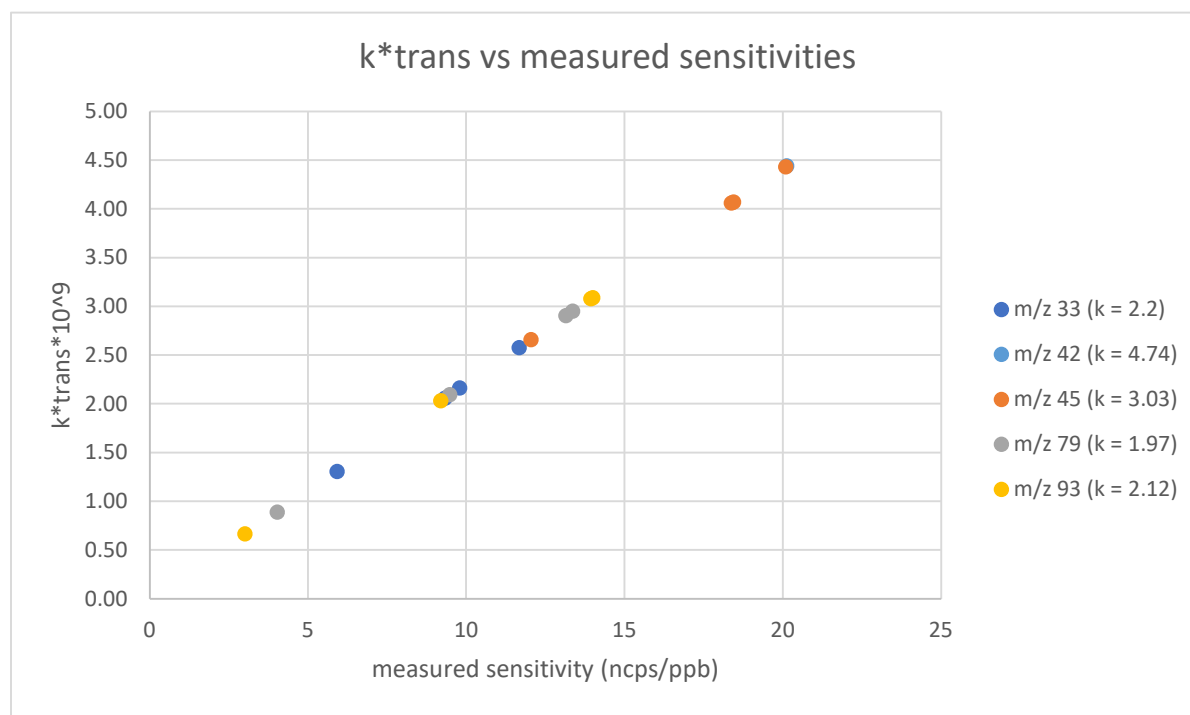

Figure R1: k*transmission vs measured sensitivity for a few species of different k rates

Table 1: List of mass-to-charge ratios measured, their corresponding name in this paper, possible fragmentation (Pagonis et al, 2019), reaction rate constants (Holzinger et al, 2019; Zhao and Zhang, 2004; Španěl et al., 1998 and 2002; Lindinger et al., 1998), their mean detection limit (LOD) and mean uncertainty. Compounds in bold are the ones that are additionally quality checked by ACTRIS.

m/z	Compound(s)	Fragmentation	k rate $(10^{-9}\ cm^3 \cdot s^{-1})$	Mean calib factor (+/- sd) (ncps/ppb)	Mean LOD (ppt)	Mean error (%)
mz_31	Formaldehyde proxy		3.00		58	37
mz_33	**Methanol**		2.20	9 (+/- 2)	221	16
mz_42	**Acetonitrile**		4.74	17 (+/- 4)	9	16
mz_45	**Acetaldehyde**		3.03	16 (+/- 4)	47	18
mz_46	m46		2.10		54	33
mz_47	Ethanol + Formic acid		2.26		67	33
mz_57	**C4H8 + Propenal**		4.20	13 (+/- 5)	23	20
mz_58	Allylamine		3		6	69
mz_59	**Acetone**		3.25	18 (+/- 5)	17	14
mz_60	Trimethylamine	m/z 58 10%	2.40		11	34
mz_61	Acetic acid	m/z 43 40%	3.00		34	31
mz_63	DMS		3		20	41
mz_69	**Isoprene + Furan**	m/z 41 10%	1.85	5 (+/- 2)	37	21
mz_71	**MVK + MACR**		2.72	17 (+/- 3)	10	25
mz_73	**MEK**		3.25	14 (+/- 5)	14	19
mz_75	C3H6O2		2.80		16	33
mz_79	**Benzene**		1.97	7 (+/- 2)	21	19
mz_81	MT's fragments		2.04		8	33
mz_83	Methylfuran + C6H10		3		10	67
mz_85	Methylbutenone		4.60		9	36
mz_87	Butanedione + Methacrylic acid		1.85		40	36
mz_93	**Toluene**		2.12	6 (+/- 3)	24	20
mz_97	Furfural		3.90		11	35
mz_99	Furandione + Furfuryl alcohol		4.20		14	36
mz_107	**C8-aromatics**	m/z 79 < 10%	2.31	5 (+/- 3)	36	23
mz_111	Benzenediol		2.70		30	42
mz_121	C9-aromatics	m/z 93 < 10%	2.40		31	31
mz_137	**Monoterpenes**	m/z 81 35%	2.04	1 (+/- 0.5)	37	34
mz_139	Nopinone	*unknown*	3		24	73
mz_147	Dichlorobenzene	m/z 149	3	1 (+/- 1)	26	43
mz_151	Pinonaldehyde	*unknown*	2.40		46	48

2) *Line 149: You should briefly describe the implications of having a higher humidity in the drift tube.*

This sentence is added: *"Higher humidity implies increased amount of water clusters ($H_2O \cdot H_3O^+$) in the drift tube, which can act as primary ions for the VOCs as well (Blake et al, 2009)."*

3) *Line 157: It is unclear what "sensibility" is used for here.*

This sentence is rephrased as: *"Throughout the measurement period, it was observed that a dwell time of five seconds per mass can result in noisy signals, and so a dwell time of ten seconds was preferred, which would result in a resolution time of 22 minutes."*

4) *Line 159: Explain why it is advantageous to have a cycle of <15 minutes.*

The sentence is completed in the manuscript as: *"In order not to lose the advantage of a resolution time < 15 min, which can be useful for studying specific events at a high time resolution, the m/z selection method was chosen."*

5) *Line 171-175: You should include a supplement table for the sensitivities of select species across the different standards. Also do you propagate this uncertainty into your measurements? If not, you should and state how you do it.*

The Table R1 (Table S3 in the revised paper) summarizes the measured sensitivities across the whole period and is added in the supplementary material. Figure R2 (Figure 2 in the revised paper) represents the temporal evolution of the sensitivities of methanol, acetone and benzene for the different used standards. The most important changes in the sensitivities correspond to maintenances and change of parameters (i.e., detector voltage), whereas standard changes do not lead to significant variations in the sensitivity. The sensitivities can also decrease with the use of the instrument, especially when the ion source gets dirty, as can be seen in the beginning of 2020. This period is followed by a long break during the Covid-19 Spring lockdown, when a maintenance was needed. After this maintenance, the sensitivities are a little higher, and again slowly decrease with the use of the instrument. We note that the change of standard in September 2020 does not lead to a significant change of sensitivity. Another maintenance was performed in early 2021, leading to higher sensitivities. Then, the SEM voltage had to be gradually increased, resulting in higher sensitivities, until the detector was changed in April 2021. A longer maintenance was necessary in summer 2021, following which the sensitivities were stable, even when the standard was changed in early 2022. For the data treatment, the sensitivities are interpolated between each calibration.

Table R1 (Table S3) is added in the supplementary material, while Figure R2 (Figure 2) and its description are added in the main text:

"The obtained sensitivity coefficients are given in Table S3. Figure 2 presents the temporal evolution of these measured sensitivity coefficients for methanol, acetone and benzene shape-coded by the standard reference, as well as the maintenance periods. Here, a sensitivity decrease is observed with the use of the PTR-MS (ie, ion source dirtying, detector aging) while an increase was obtained with detector voltage increase. Therefore, it is important to note that the largest changes of sensitivity were due to instrumental evolution and not to changes of standard."

Time	SEM voltage (V)	Standard	mz_33 Methanol	mz_42 Acetonitrile	mz_45 Acetaldehyde	mz_57 Propenal	mz_59 Acetone	mz_69 Isoprene
1/15/2020	2975	R0904	10.71	19.52	18.97	17.67	21.22	6.55
1/21/2020	2975	R0904	9.43	18.18	17.63	15.81	19.12	5.72
2/25/2020	2975	R0904	9.63	16.23	15.91	13.83	16.47	4.75

Table R1: Sensitivity coefficients (ncps/ppb) throughout the 2020-2021 period

Time	SEM voltage (V)	Standard						
6/11/2020	3100	R0904	11.73	20.13	20.09	18.80	21.90	7.29
7/1/2020	3100	R0904	11.32	20.45	21.37	18.14	22.72	7.24
8/7/2020	3100	R0904	11.97	19.64	19.02	17.97	20.69	6.87
9/10/2020	3050	R0904	11.41	17.01	16.37	14.04	16.86	4.73
10/9/2020	3050	L5387	10.04	17.89			17.15	4.14
11/9/2020	3050	L5387	7.10	17.38			16.91	4.07
12/11/2020	3050	L5387	8.28	16.98			16.96	3.62
1/15/2021	3200	L5387	8.62	21.14			21.32	5.38
1/28/2021	3200	L5387	9.95	21.87			23.14	6.10
2/25/2021	3250	L5387	9.43	22.10			25.41	6.76
4/6/2021	3375	L5387	10.93	24.01			26.82	7.25
4/26/2021	2300	L5387	9.21	18.87			19.19	5.52
5/27/2021	2350	L5387	8.91	19.53			20.04	5.06
8/16/2021	2350	D155286	8.35	14.37	18.72	16.30	21.71	6.46
9/10/2021	2350	D155286	7.87	10.20	12.66	8.58	12.99	3.82
9/20/2021	2350	D155286	7.17	14.19	12.72	8.59	12.12	3.66
10/25/2021	2375	D155286	5.92	10.37	12.05	4.15	10.98	3.31
11/16/2021	2425	D155286	5.43	9.25	11.48	7.99	10.57	2.64
11/16/2021	2425	D155286	5.72	9.50	11.85	8.29	10.71	2.57
12/15/2021	2450	D155286	6.20	10.66	12.25	8.93	11.53	2.84

Time	SEM voltage (V)	Standard	mz_73 MEK	mz_79 Benzene	mz_93 Toluene	mz_107 C8-Aromatics	mz_137 Monoterpenes	mz_147 Dichlorobenzene
1/15/2020	2975	R0904	18.63	8.28	7.95	7.06	1.34	1.65
1/21/2020	2975	R0904	16.39	7.77	7.05	6.03	1.15	1.36
2/25/2020	2975	R0904	13.54	6.12	5.45	4.55	0.84	0.90
6/11/2020	3100	R0904	18.56	9.48	9.20	8.33	1.69	1.94
7/1/2020	3100	R0904	19.75	8.80	8.85	8.01	1.66	1.81
8/7/2020	3100	R0904	17.66	8.37	8.03	7.08	1.39	1.56
9/10/2020	3050	R0904	13.76	5.95	5.43	4.47	0.81	0.94
10/9/2020	3050	L5387		5.31	4.70	3.90		0.84
11/9/2020	3050	L5387		4.99	4.24	3.45		0.80
12/11/2020	3050	L5387		4.52	4.70	3.33		0.68
1/15/2021	3200	L5387		7.68	6.89	6.15		1.52
1/28/2021	3200	L5387		8.23	8.07	6.92		1.75
2/25/2021	3250	L5387		9.72	9.53	8.57		2.08
4/6/2021	3375	L5387		12.23	11.92	10.81		3.26
4/26/2021	2300	L5387		6.81	6.81	4.99		1.42
5/27/2021	2350	L5387		7.28	6.17	4.79		1.32
8/16/2021	2350	D155286	18.65	9.11	8.82	7.76	1.50	1.75

9/10/2021	2350	D155286	10.57	4.35	3.64	2.62	0.44	0.57
9/20/2021	2350	D155286	9.79	4.20	3.31	2.37	0.39	0.45
10/25/2021	2375	D155286	8.63	4.03	3.01	2.10		0.37
11/16/2021	2425	D155286	7.72	3.18	2.45	1.66		0.29
11/16/2021	2425	D155286	7.64	3.37	2.53	1.83		0.29
12/15/2021	2450	D155286	8.57	3.59	2.79	1.97	0.29	0.39

Figure R2: Time series of sensitivities vs time for methanol, acetone and benzene. Standard references are indicated by the shape of the data points (cf Table S2).

6) *Line 174-175: Include the NPL standard species in Table S2.*

This is added in the revised version (see Table S2 below).

Table S2: Standards used for PTR-MS calibrations

Start	End	Standard reference	Species in the standard used for direct calibrations	VMR
18-01-2020	10-09-2020	R0904, Ionicon Analytik	Methanol, Acetonitrile, Acetaldehyde, Acrolein, Acetone, Isoprene, Crotonaldehyde, 2-Butanone, Benzene, Toluene, o-Xylene, α-pinene, 1,2-Dichlorobenzene	1 ppm

10-09-2020	15-06-2020	L5387, Ionicon Analytik	Methanol, Acetonitrile, Acetone, Isoprene, Benzene, Toluene, Xylenes, Trimethylbenzene, 1,2-Dichlorobenzene	100 ppb
01-09-2021	28-04-2022	D155286, SIAD	Methanol, Acetonitrile, Acetaldehyde, Acrolein, Acetone, MEK, Benzene, Toluene, o-Xylene, α-pinene, 1,2-Dichlorobenzene	1 ppm
23-05-2022	current	NPL	Methanol, Acetonitrile, Acetaldehyde, Acetone, Isoprene, Dimethylsulfide, 3-Buten-2-one, 2-Butanone, Benzene, Toluene, m-Xylene, 1,2,4-Trimethylbenzene, 3-Carene	1 ppm

7) *Line 175-177: It is very unclear what this lab test was. What specifically was done to "infer the repeatability of measurements over 3 days"?*

The sentence is completed: *"This standard was also used to infer the repeatability of the measurement at the end of May 2022: it was sampled with the same protocol (same dilution, a blank before and after) over 3 consecutive days, while environmental conditions (i.e., temperature and relative humidity) might vary a little. The obtained coefficients of variation for this test ranged from 1 to 26% (mean value: 7%)."*

8) *Line 177-179: It is surprising that for a quadrupole PTRMS the sensitivities changed on average by 3% from an RH of 30% to 90%. There should be a supplement figure showing sensitivity vs. RH or the ratio of water dimer to monomer for a few ions to support this claim.*

Table R2 (Table S4 in the revised paper) summarizes the sensitivities obtained during this test at different relative humidities, while Figure R2 (Figure S3 in the revised paper) represents these sensitivities vs. RH for some species. These table and figure are added in the supplementary material with the following comment (in the main text):

"In addition, the influence of humidity on the sensitivity was investigated by performing calibrations using the NPL standard at set relative humidities (RH) of 30%, 60% and 90% on August 4th, 2022. Results for these tests are presented in Table S4 and Figure S3, the humidity dependency of the sensitivities for the considered species ranges in 1-7% with an average of 3%. The difference is much lower for the RH range 60-90%, which corresponds to 72% of the data, than for the range 30-60%."

Table R2: Sensitivities (ncps/ppb) obtained for calibrations at various relative humidities

Relative humidity	m/z 33	m/z 42	m/z 45	m/z 59	m/z 69	m/z 71
30 %	8.1	17.0	20.5	22.4	8.6	23.3
60 %	8.1	19.0	18.2	22.1	7.9	21.0
90 %	8.7	19.6	18.8	22.7	8.0	21.9
CV (%)	5	7	6	1	5	5

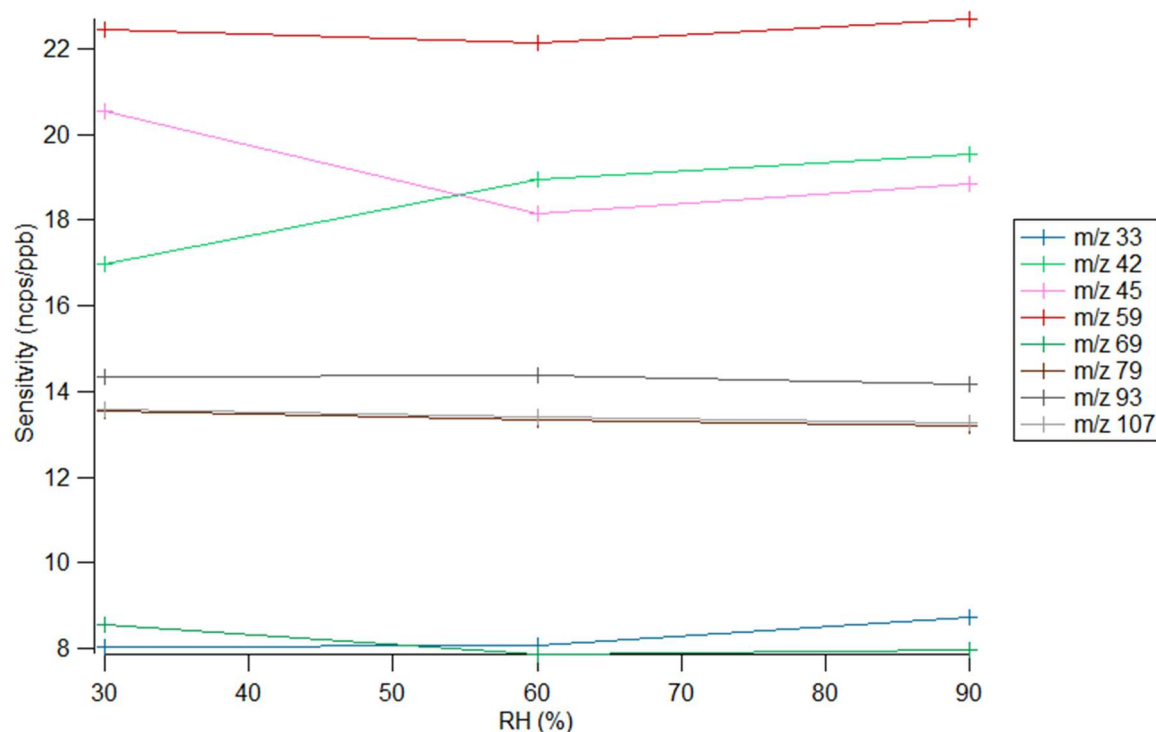| Relative humidity	m/z 73	m/z 79	m/z 93	m/z 107	m/z 121	m/z 137
30 %	21.9	13.6	14.4	13.6	11.1	4.1
60 %	22.2	13.3	14.4	13.4	10.7	4.1
90 %	22.4	13.2	14.2	13.3	10.8	4.2
CV (%)	1	1	1	1	2	2

CV = coefficient of variation

Figure R3: Sensitivities vs RH

9) *Line 180-181: State what reagent ions you are calibrating to and what the normalization factor is. Also there needs to be more detail on how you applied humidity corrections. Did you gather sensitivity vs. humidity curves and then apply them? Which species did you calibrate for/which standard cylinder did you use and what did you do for a humidity correction for species with no standard calibration? The low humidity influence in general is questionable without supporting figures.*

The ambient counts per second (cps) are normalized by primary ions (H_3O^+, m/z 21) and water clusters ($H_2O \cdot H_3O^+$, m/z 37) following equation (1):

$$ncps = \frac{cps \cdot 10^6}{m21 \cdot 500 + X_r \cdot m37} \qquad (1)$$

Initially, a value of 1 was used for the X_r factor to take into account the fluctuations of ambient relative humidity. However, following this comment and the very low humidity dependency observed during the tests (Table R2 and Figure R3), an X_r value of 0 would probably be more accurate and will be considered for the on-going measurements.

Concerning the dataset presented in this paper, we have estimated the uncertainty corresponding to this choice of X_r of 1 instead of 0 by investigating several periods (corresponding to different seasons in 2020 and 2021) and by calculating the impact of this choice on the calculated mixing ratio. The mean value of the difference is 2%, which was considered included in the 5% uncertainty which takes into account humidity changes (see the detailed calculation of uncertainty in our answer to the comment of line 220-221).

Therefore, this sentence is completed as: *"The ambient counts per second (cps) are normalized by primary ions (H_3O^+, m/z 21) and water clusters ($H_2O \cdot H_3O^+$, m/z 37) following equation (1):*

$$ncps = \frac{cps \cdot 10^6}{m21 \cdot 500 + X_r \cdot m37} \tag{1}$$

At the beginning of the measurement period (2020-2021), a value of 1 was chosen for the X_r factor to take into account the fluctuations of ambient relative humidity. The tests of humidity performed afterwards (2022) suggest that a value of X_r of 0 would be more accurate, due to the very low humidity dependency determined. We have estimated the impact of this choice by calculating (on several periods from different seasons in 2020 and 2021) the difference on the mixing ratio when considering $X_r=0$ instead of $X_r=1$. The mean difference being of 2%, the uncertainty associated to this choice was considered included in the 5% uncertainty taken into account for humidity changes (see uncertainty calculation in Section 2.4.4).

The obtained blanks (ncps) and sensitivities (ncps/ppb) are linearly interpolated and are used to retrieve the ambient VMR."

> 10) *Section 2.3.4: To support the quality of this dataset this section needs a lot more detail. In addition to the above comments, you should state in the main text how many species were directly calibrated for and for what fraction of the measurement period (since you changed standards) had direct calibrations. Since you only calibrate once a month you should state how much the sensitivities are changing and include a supplement time series for select species of the sensitivity vs. time. This would also be a good place to overlay calculated sensitivities when cylinders changed.*

The species directly calibrated using the standards are indicated in Table S2. Depending on the periods, it corresponds to 9 to 13 species.

Concerning how the sensitivities change, it is now shown in the Figure R2 presented above that the main changes of sensitivity are due to instrumental evolution and maintenance and not to cylinder changes. Moreover, Table R1 (Table S3 in the paper) summarizes all measured sensitivities and is added in the supplementary material.

In Section 2.3.4, this sentence was rephrased as: *"Different standards were used throughout the study period (see Table S2), allowing to directly calibrate 9 to 13 species, depending on the standard. The obtained sensitivity coefficients are given in Table S3."*

In addition, a new section is added in the results (Section 3.5), where the data for SIRTA is compared with independent measurements using a gas chromatography provided by the regional network for air quality monitoring of the Greater Paris area (AirParif) in the center of Paris. This implies a new co-authorship (Alexia Baudic, AirParif) for the paper.

11) *Line 186-187: Specifically what measurements are you referring to here? Which ions/metrics are you tracking? Are these ions species you would assume are stable over two years in an air cylinder? Also you mention that you check instrument parameters but do not comment on their stability. There needs to be more detail on these tests.*

Table R3 (Table S5 in the revised paper) presents the mean and standard deviation values of the target bottle measurements for all ions which have a signal > 10 ppt. Figure R4 (Figure S4 in the revised paper) presents the temporal evolution of acetone and methanol measurements from the target bottle. Table R3 (Table S5) and Figure R4 (Figure S4) are added in the supplement.

This part is rephrased as: *"The measurements, especially the diagnostic m/z, as well as the instrument parameters (pressures, voltages, source intensity, water flow; Table S1) are checked at least twice a week, in order to diagnose an issue with the PTR-Q-MS. As long as there is no issue in the PTR-MS and for a period with the same set parameters, the drift pressure, the detector pressure, the controlled pressure, the water flow, the drift voltages, the ion source voltage, are stable; their mean coefficient of variation are respectively 0.2%, 1.6%, 0.3%, 0.1%, 0.1%, 0.9%. A decrease of the water bottle flow indicates that it needs to be filled again, a drastic change in the pressures can indicate a leak in the system, and a sudden change in the voltages implies a potential issue with the pumps. A target bottle, containing ambient air, is measured once per week, in order to check that the measurements do not deviate too much from their mean value. The mean and standard deviation values for the target bottle measurements of ions that have a signal > 10 ppt are given in Table S5, and their temporal evolution of these measurements for benzene and acetone is presented in Figure S4."*

Figure R4 (Figure S4) is added in the supplement with a description in the supplement as well: *"Figure S4 shows the temporal evolution of the measurements of acetone and benzene. In 2020 and early 2021, these measurements show small fluctuations but are mainly stable, but by the end of 2021 the VMR of benzene decreases, due to the lower sensitivity (< 5 ncps/ppb). The PTR-MS underwent an important maintenance early 2022 that solved this issue (benzene sensitivity around 13 ncps/ppb)."*

Table R3: Mean and standard deviation values for target bottle measurements

m/z	m/z 33	m/z 42	m/z 45	m/z 46	m/z 57	m/z 59	m/z 60	m/z 61	m/z 69	m/z 71
Mean (ppb)	3.22	0.25	23.68	1.04	1.53	16.58	0.86	0.53	1.82	0.57
Standard deviation	0.72	0.03	2.68	0.57	0.43	0.98	0.16	0.27	0.24	0.17
m/z	m/z 73	m/z 79	m/z 83	m/z 85	m/z 87	m/z 93	m/z 97	m/z 107	m/z 121	

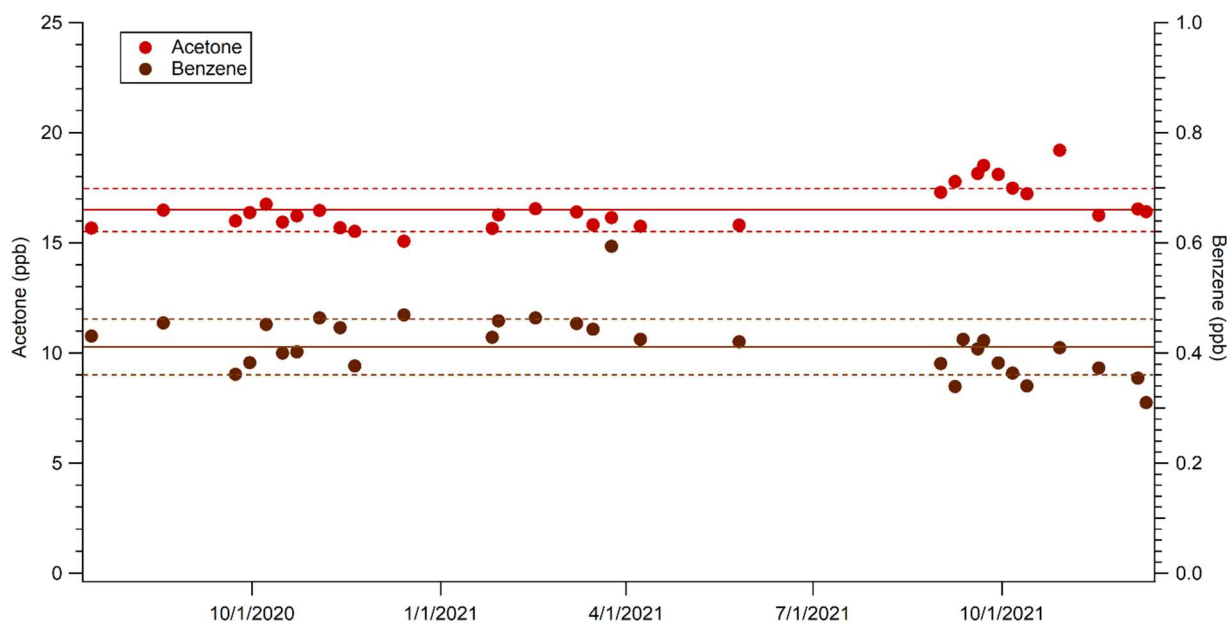|									
Mean (ppb)	1.38	0.41	0.51	0.31	1.90	0.39	0.39	0.59	0.34
Standard deviation	0.18	0.05	0.16	0.16	0.32	0.05	0.16	0.10	0.15

Figure R4: Temporal evolution of acetone and benzene measurements from the target bottle. The lines represent the mean value while the dashed lines represent mean +/- standard deviation.

12) *Line 207: It looks like you could not perform zeros for most of the PTR-ToF measurement time due to lockdowns. Can you show that the zeros are robust over a long period of time? Were you able to calibrate during this time too?*

The blanks that were performed for the PTR-ToF-MS campaigns are shown on Figure R5 for the m/z used for the main isobaric speciation (m/z 46, 47, 57, and 69). Calibrations of the PTR-ToF-MS were performed about once a month during the lockdowns and twice a month in other periods.

Please note that during the periods "spring/summer campaign" and "autumn campaign & lockdown", while there was not a total lockdown like the spring lockdown, it was only possible to come once to twice a week on site.

The Figure R5 (Figure S5) is added to the supplementary material and a short explanation is given in the main text: *"Figure S5 presents the temporal evolution of the obtained blanks where the different periods (i.e., campaigns, lockdowns) are highlighted. Most of these blanks are rather stable, and they are interpolated for the data treatment."*
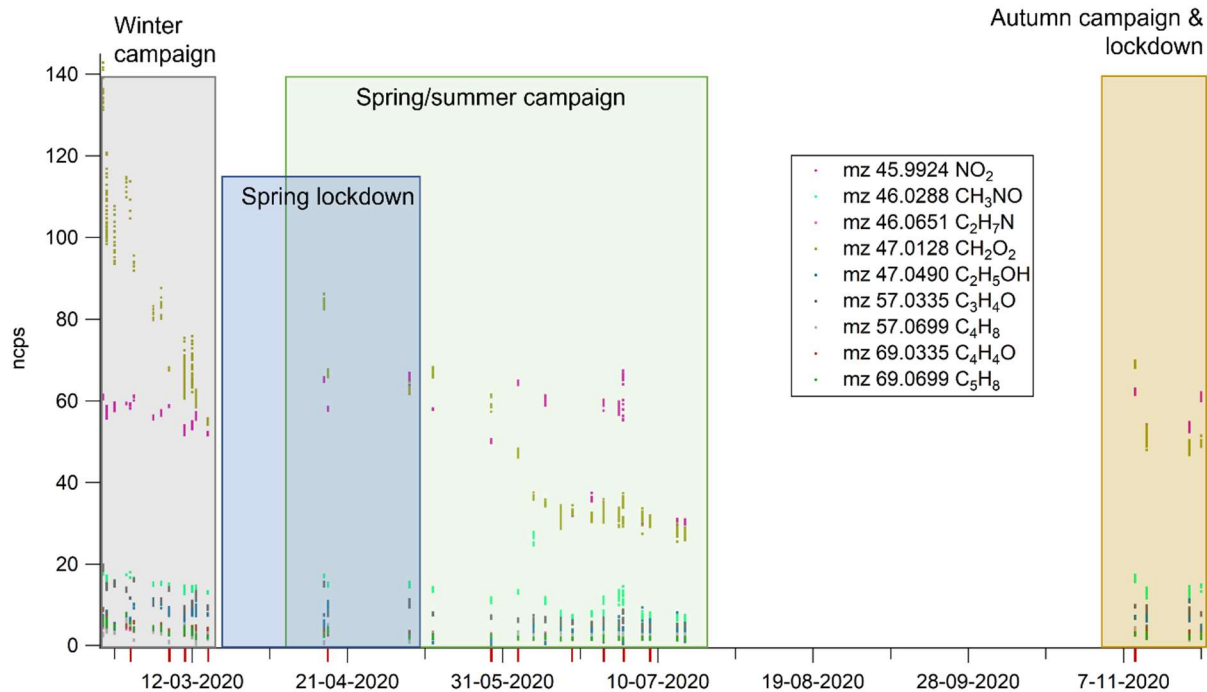
Figure R5: Blanks performed in 2020 for a selection of PTR-ToF-MS m/z. Calibrations are indicated by red sticks.

> *13) Line 208: There needs to be more discussion on how the PTR-ToF is calibrated if you are going to use it for assigning species fractions to isobaric peaks. Is the internal dilution system the calibration system for the PTR-Q-MS or a different one? How frequent were the calibrations and what was in your calibration standard?*

The dilution system is different than the one used for the PTR-Q-MS measurements. For the PTR-Q-MS we use flowmeters inside the GCU system while for the PTR-ToF-MS the dilution system with the flowmeters is inside the instrument. The calibration standards used were a canister (Figure R6) until mid-May 2020 and the standard bottle D155286 (Table S2) from mid-May 2020. The calibrations were performed at least once a month and the temporal evolution of the obtained sensitivities is shown on Figure R7 (Figure S7). The sensitivity decreases gradually with time, as was observed for the PTR-Quad-MS, the long period with no sensitivity measured between April 16th and May 28th corresponds to the lockdown period. An additional calibration was performed on May 13th, but the sensitivities measured were very low due to little gas left in the canister, so this calibration was not considered.

This is rephrased as: *"Calibrations were done about once a month using the internal dilution system (flowmeters located inside the instrument). The calibration standards used were a canister (Figure S6) until mid-May 2020 and the standard bottle D155286 (Table S2) from mid-May 2020. The temporal evolution of the obtained sensitivities is shown on Figure S7. The sensitivity decreases gradually with time with the use of the instrument, as was observed for the PTR-Quad-MS."*

Figure R7 is added to the supplementary material with a short explanation: "Figure S7 presents the temporal evolution of the measured sensitivities for the PTR-ToF-MS. The long period with no sensitivity measured between April 16th and May 28th corresponds to the lockdown period. An additional calibration was performed on May 13th, but the sensitivities measured were very low due to little gas left in the canister, so this calibration was not considered."

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Gas Canister VOC Standard Quality Assurance Certificate

Gas canister serial number: **R2845**

Ionicon guarantees the listed concentrations for a period of 6 months.
Uncertainty is an estimate of a combination of the uncertainties of the original gravimetric preparation and subsequent analysis.

Compound	Volume mixing ratio / ppm	Uncertainty / %
Methanol	0.99	±6
Acetonitrile	0.99	±6
Acetaldehyde	0.95	±5
Ethanol	1.00	±5
Acrolein	1.01	±5
Acetone	0.98	±5
Isoprene	0.95	±5
Crotonaldehyde	1.01	±5
2-Butanone	0.99	±5
Benzene	0.99	±5
Toluene	0.99	±6
o-Xylene	1.02	±6
Chlorobenzene	1.01	±5
a-Pinene	1.01	±5
1,2-Dichlorobenzene	1.02	±5

Gas canisters are filled at a gauge pressure of 2.8 - 3.8 bar and are leak tested for tightness prior to shipping. Should the canister arrive at a pressure lower than the above range, please contact Ionicon immediately; the canister may have developed a leak during transportation and should be returned to Ionicon for refilling.

Jürgen Dunkl
Canister filled by

Signature

10 December 2018
Date   Ionicon Stamp:

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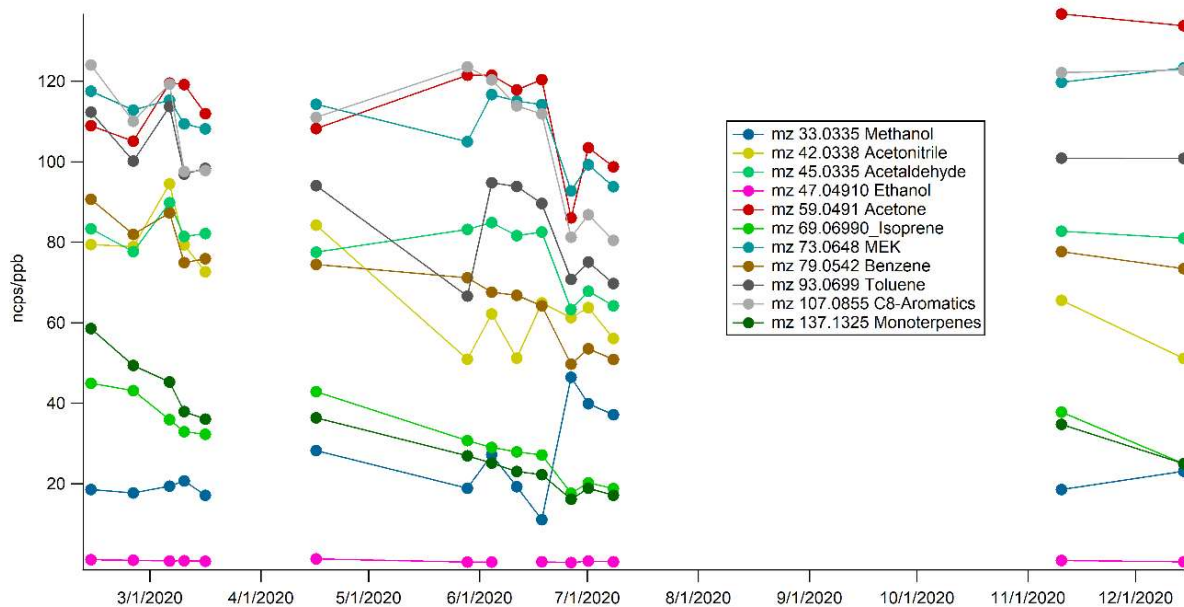*Figure R6: Certificate of the canister R2845 used for PTR-ToF-MS calibrations.*

Figure R7: Temporal evolution of measured sensitivities for the PTR-ToF-MS, the different campaigns are separated by the discontinuity of the line.

14) Line 220-221: These guidelines need to be summarized here. The quality of this data cannot be supported without explaining your detection limit and error determination.

This part is completed in the main text of the revised version as: *"The detection limit (LOD) and the uncertainties for each m/z were calculated using the formulas from the ACTRIS guidelines (in preparation), which are based on de Gouw and Warneke (2006):*

$$LOD = 3 \times \frac{\sqrt{C_{RH^+}^{blank}}}{S_m(RH^+)} \tag{2}$$

With $C_{RH^+}^{blank}$ the ion count per second of the blank signal and $S_m(RH^+)$ the unnormalized sensitivity (cps/ppb).

$$Uncertainty = \sqrt{Precision^2 + Accuracy^2 + 0.05^2} \tag{3}$$

With the precision calculated as the relative standard deviation:

$$RSD = \frac{\sqrt{C_{RH^+}^{ambient} + C_{RH^+}^{blank}}}{C_{RH^+}^{ambient} - C_{RH^+}^{blank}} \tag{4}$$

With $C_{RH^+}^{ambient}$ and $C_{RH^+}^{blank}$ the ion counts for the ambient and blank signals, respectively.

The accuracy corresponds to the quadratic propagation of the error on the GCU and on the standard. The error on the GCU was evaluated to be equal to 10% and the errors on the

standard for each compound are available on its certificate and range from 5 to 10%. Finally, an error of 5% is added to take into account the uncertainty due to humidity changes."

15) Line 223-224: You need to explain what these internal and external quality control checks are.
16) Line 226: define what Ebas is and include a DOI citation for the dataset in the text.

This part is completed as: *"An internal quality check is performed on all m/z, while an external quality control is also performed by ACTRIS on 12 masses corresponding to the following compounds: benzene, propenal+C_4H_8, isoprene+furan, C8-aromatics, monoterpenes, toluene, acetonitrile, acetaldehyde, acetone, MEK, methanol and MVK+MACR. The internal quality control corresponds to carefully verifying each step of the data treatment and the obtained data and deleting erroneous or outlier data points. The external quality check is performed by the Central Facility unit of ACTRIS responsible for VOCs measurements (CiGas). It consists in carefully examining the dataset and performing different figures (e.g., scatter plots, ...) to point out and discuss questionable data (outliers, potential contamination....). These data can then be flagged accordingly (valid but lower than the detection limit, valid but corresponding to a local event, or missing because invalidated). In addition, for long-lived compounds, a comparison with baseline values from other European station is performed to check the consistency of the datasets. Once the submitted data and corresponding flags are compliant and validated by ACTRIS, they are made available on Ebas, which is the ACTRIS open-source database. The 2020-2021 dataset presented here can therefore be found on the corresponding website under https://ebas-data.nilu.no."*

17) Table 1: It is unclear what the mean error is and what quality checked by ACTRIS means.

The mean error is the average value over the 2-year period of the point-by-point uncertainty calculated with Eq. (3). This has now been added in the text. The quality control performed by ACTRIS is explained above.

l. 221-222 is rephrased as: *"Table 1 presents the 2-year-averaged value of the point-by-point calculated LOD and error for all compounds: the detection limit ranged from 6 to 221 ppt and the uncertainties ranged from 14 to 73%."*

The table description is rephrased as: *"List of mass-to-charge ratios measured, their corresponding name in this paper, possible fragmentation (Pagonis et al, 2019), reaction rate constants (Holzinger et al, 2019; Zhao and Zhang, 2004; Španěl et al., 1998 and 2002; Lindinger et al., 1998), mean and standard deviation of measured sensitivities, mean detection limit (LOD) and mean uncertainty. Compounds in bold are the ones that underwent the quality control of ACTRIS."*

18) Line 258: This sentence for isoprene is for global BVOC and you are looking at an urban region. Unless you have literature to support this, it is not necessarily expected that isoprene will be very high in this region relative to monoterpenes. You should remove this or reword it.

In the revised version, this is rephrased as: *"Within the non-aromatic hydrocarbons, monoterpenes have roughly the same boxplot values than isoprene; indeed, monoterpene levels can be as high or higher than isoprene levels in urban regions (Panopoulou et al, 2020), indicating other sources than the biogenic one."*

19) Line 259: Briefly explain what is meant by this. Are you saying the median monoterpene concentration is high because of a wintertime contribution?

This sentence is rephrased as: *"The high median value of m/z 137 could be explained by an important wintertime contribution (Figure 4)."*

20) Line 261-270: The purpose of figure 3 needs to be articulated more or figure 3 should be removed. The supporting paragraph preceding figure 3 does not explain what the figure means but rather states the concentrations of some classes in each bin. Is there some takeaway about sourcing at lower or higher concentrations that uses this figure rather than the other sourcing details later in the paper? There is a brief portion on comparison to particles but no data to compare.

Following the reviewer's suggestion, this figure is removed from the paper.

21) Line 290: How many hours back do the back trajectories go? This would be important for estimating chemical and transport lifetimes. Also are these trajectories sourced and stay near the surface for the duration of the trajectory?

In the present study, 120-h back trajectories were used. Given the reactivity of VOC, this duration is not meant to be representative of their lifetimes within the air mass. A 5-d duration is nevertheless useful for the clustering calculation, providing much more spatial variance. Only latitude and longitude have been taken into account for the clustering, as commonly performed in other studies (e.g., Petit et al., 2021). This analysis is not meant to provide thorough information on the geographical origins of the measured VOCs, but more on the impact of air mass origin on the levels and composition of VOCs. We are going to make that clearer in the text.

This part is completed in the revised paper as: *"This was done using a cluster analysis from ZeFir (Petit et al., 2017), based on the HYSPLIT 120-hour back trajectories reaching SIRTA calculated every 3 hours from January 2020 to December 2021. Only latitude and longitude have been taken into account for the clustering, as commonly performed in other studies (e.g., Petit et al., 2021). This analysis is not meant to provide thorough information on the geographical origins of the measured VOCs, but more on the impact of air mass origin on the levels and composition of VOCs."*

22) *Line 308: is the NO$_2^+$ signal included in your "N-containing" species and if so what fraction does it compose of that class? Since it could be part of reagent ion chemistry I would be cautious of using m/z 46 unless you have a strong calibration and zero to prove that it is not generated in the instrument.*

The NO$_2^+$ signal is 31% of the N-containing class (m/z 46 is 38% of N-containing and NO$_2^+$ is 81% of m/z 46 (TOF measurements, Table 2)). The m/z 46 covaries with NO$_3$ from ACSM measurements (Figure R9) and the corresponding correlation is R^2 = 0.83, while the blank and ambient m/z 46 ncps measurements are shown on Figure R8 and the respective R^2 is 0.51.

This part is completed in the revised paper: *"Another possibility is the formation of alkylnitrates (including PAN) by atmospheric aging of hydrocarbons in the presence of NO, measured as NO$_2^+$ fragment at m/z 46 (Kastler and Ballschmiter, 1998; Müller et al., 2012). It should be noted that this fragment composes 31% of the N-containing class, and although we cannot rule out an instrumental bias, the R^2 correlation of m/z 46 and NO$_3$ being equal to 0.83 suggest that this is an atmospheric signal."*
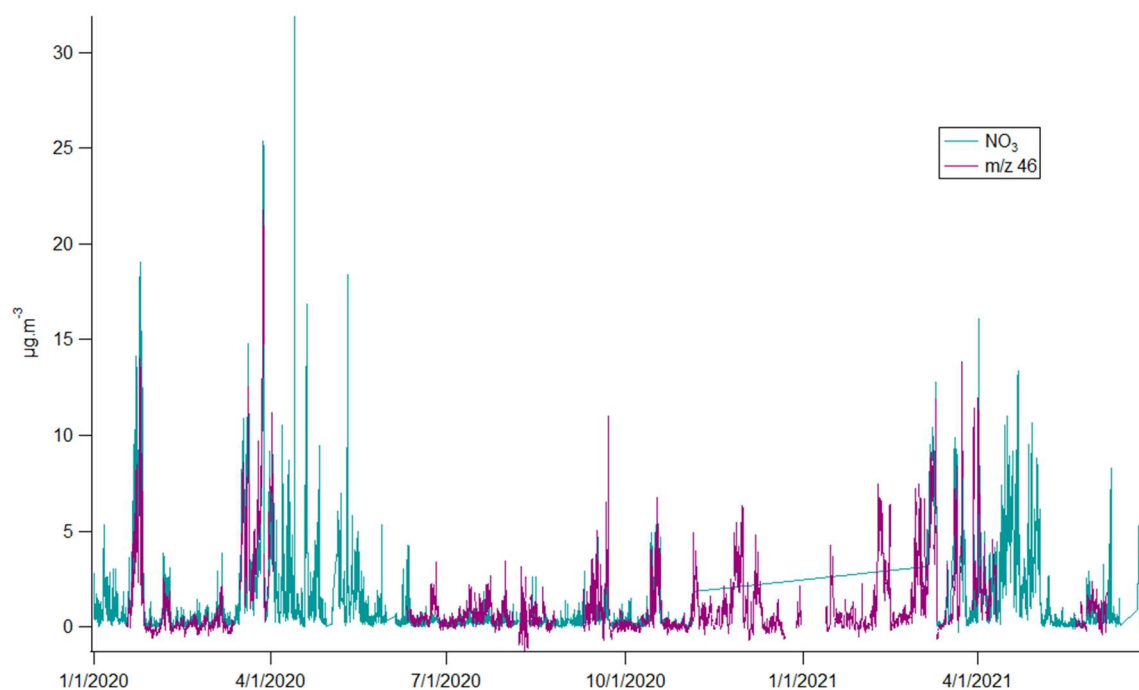

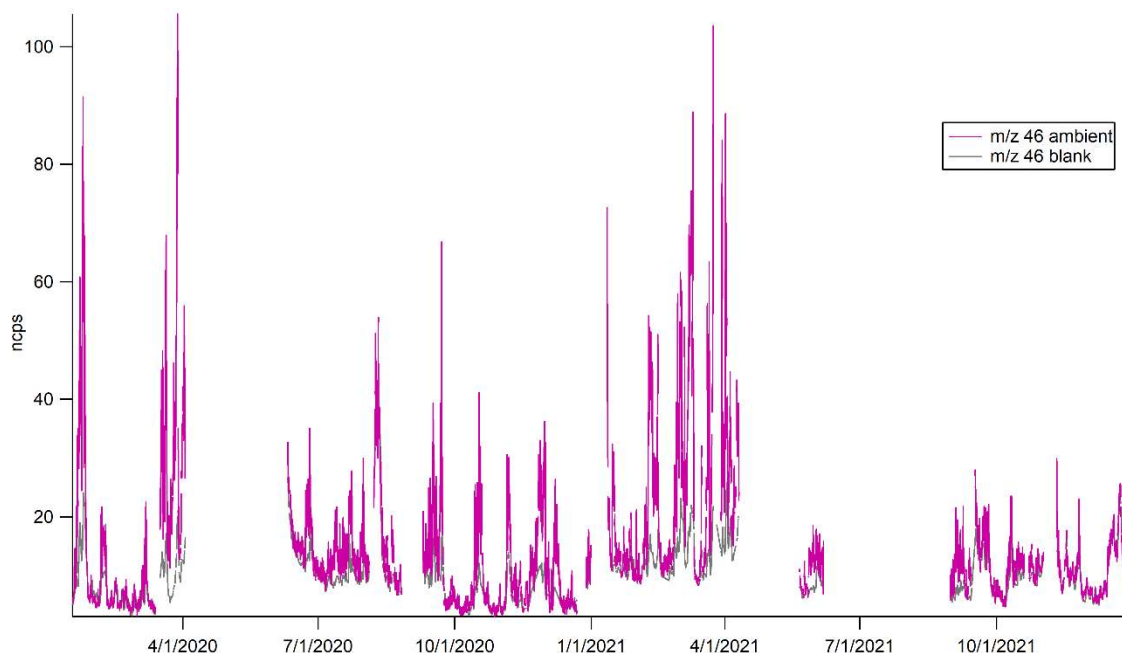*Figure R8: Temporal evolution of m/z 46 and NO3 from ACSM measurements*

Figure R9: Temporal evolution of m/z blank and ambient ncps measurements

> *23) Line 315: How was mixed layer height measured?*

This sentence is added in Section 2.1: *"The mixed layer height is measured by automatic lidar and ceilometer and derived using the CABAM (Characterising the Atmospheric Boundary layer based on ALC Measurements) algorithm (Kotthaus and Grimmond, 2018)."*

> *24) Figure 6: This figure needs more detail in the caption explaining what the distributions are and what the lines are. The title (or legend?) should be consistent with the naming convention in the rest of the paper (N containing instead of n_containing).*

The legend is corrected in the revised paper.

The caption of Figure 6 is corrected as: *"Figure 6: Statistical distribution of N-containing compounds per air mass cluster. Boxes represent 25th and 75th percentiles, the line is the median. Whiskers represent 5th and 95th percentiles and the red dash represents the mean value."*

> *25) Figure 8: A suggestion: I think a comparison of diel cycles during different seasons for select species would be very valuable and support your month average plots of Figure 7 and could be included. For example, your differences in monoterpene concentrations in the summer and autumn could be highlighted in the supplement and could add to your claims of changes in lifetime against oxidation and sourcing across the seasons.*

Thank you for this suggestion, this will be added in the revised paper.

> *26) SI Line 51-53: What fractions of m/z 69 are isoprene and furan?*

This sentence is rephrased as: *"Furan is emitted by biomass-burning activities and has highest contributions in autumn and winter (47-67% of m/z 69, Table 2); while in spring and summer, m/z 69 can be almost exclusively attributed to isoprene (94-96% of m/z 69, Table 2), due to its important biogenic source, although it can also be emitted by anthropogenic sources (Borbon et al., 2001; Wagner and Kuttler, 2014; Panopoulou, 2020)."*

Technical corrections

27) Line 38: secondary organic aerosols and ozone should not be capitalized.

This is done in the revised paper.

28) Line 63-64: non-methane hydrocarbons and oxygenated VOCs should not be capitalized.

This is done in the revised paper.

29) Line 97-98: Is "important" here used to describe the frequency and intensity of traffic? If so, I would suggest replacing "important" with "heavy".

This is done in the revised paper.

30) Figure 1 caption: Change "South-West" to "southwest"

This is done in the revised paper.

31) Line 116: Specify that the AE33 model is an aethalometer. I would just place it in your parenthesis before "Magee Scientific".

This is done in the revised paper.

32) Line 186: You should replace instances of "bottle" with "cylinder" if you are referring to a gas standard. Unless it really is a bottle, then my apologies.

It really is a bottle and not a cylinder.

33) Line 198: "While isoprene is an abundant biogenic VOC…"

This is done in the revised paper.

34) Line 239: VOC has already been defined. You do not have to define it again here.

This is done in the revised paper.

35) Line 262: In general, remove any contractions (e.g., don't) from the text.

This is done in the revised paper.

36) Line 263: use a · instead of . in your units.

This is done in the revised paper.

37) Figure 3: x axis needs units

This figure is deleted in the revised paper.

38) Line 290: define h

This is done in the revised paper.

39) Line 298: Be consistent in naming conventions. Earlier it is "oceanic 1" but here it is "Oceanic 1".

This is done in the revised paper.

40) Line 302: "…Figure 5b." You should use this notation for other instances.

This is done in the revised paper.

41) Line 326: "… to the temperature…"

This is done in the revised paper.

42) Line 361: This variable is defined as B_{ff} earlier on. Stay consistent with names.

This is done in the revised paper.

43) Figure 9: define NR-PM1

The Figure caption is corrected as: *"Figure 9: Time series of VOC, non-refractory submicronic particulate matter (NR-PM$_1$), temperature, wind speed and direction during the month of March 2020. The black dotted line marks the start of the Covid19-induced lockdown in France. Wind roses before (1–13 March) and during (16–31 March) are represented on the figure."*

44) Line 445: remove "seem to have"

This is done in the revised paper.

45) Figure 10: Replace "During" and "Lockdown_2" with "Spring Lockdown" and "Autumn Lockdown", respectively. This is consistent with you caption and text. Also use subscripts with your BC variables to be consistent.

This is done in the revised paper.

46) Should "CRediT" in the authorship statement be "Credit"?

This was written according to the recommendations from Copernicus on the ESSD submission web page: "We recommend using the CRediT contributor roles taxonomy."

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Response to the comments from the second reviewer on essd-2022-406 "Two years of Volatile Organic Compounds online in-situ measurements at SIRTA (Paris region, France) using Proton-Transfer-Reaction Mass Spectrometry"

We thank the reviewer for all the constructive comments. In the following, we provide the response to the reviewer using black for original review comments, green for authors' responses, and *blue italic for changes in the revised version.*

Please note that lines number correspond here to the lines in the preprint and not in the revised version.
The original figures/tables are indicated with their original reference in this document, while the additional figures/tables are referenced here as "Figure/Table R" with a number and their respective reference in the revised paper are indicated in brackets. Example: Table R1 (Table S3 in the revised paper)
For clarity, comments have been numbered.

General comment

This work shows a two year long PTRMS data set in SIRTA, and it is very valuable to the community, particularly modelling community, as it captures COVID 19 lock down as well as other very interesting and contrasting atmospheric chemistry periods. I think it is well written and the paper should be published, but, much more information needs to be provided on data methodology and analysis. Therefore I suggest major revisions mostly on methodological process.

We thank the reviewer for the valuable comments, which are addressed one by one hereafter.

Specific comments

48) 2.1.2. I would remove this section or put it later as this is not your main objective and the data is only for comparison purposes.

Taking into account the reviewer's suggestion, we have deleted the section 2.1.2

49) I also do not see information on temperature, pressure and par measurements which you use for concentration calculations and show it on graphs. I need info on sensors and methodology.

We have added a short description of these additional instruments (including meteorological sensors) in the site description. In consequence, 2.1 is modified as (additions are in bold):

"2.1 Site presentation

The SIRTA (Site Instrumental de Recherche par Télédétection Atmosphérique) observation platform is located 20 km southwest of Paris (France) and is considered as representative of suburban background conditions in the Paris region (Haeffelin et al., 2005; Sciare et al., 2011). It is one of the main ACTRIS national facilities in France. It is composed of a main site (48.718°N, 2.208°E, 156 m above sea level), for monitoring atmospheric meteorological parameters, as well as for aerosols and clouds remote sensing. Dedicated in-situ observations of aerosols and reactive gases are conducted at the Laboratoire des Sciences du Climat et de l'Environnement (LSCE, 48.709° N, 2.159° E, 162 m above sea level), 4 km away from the main SIRTA site.
At the main site, the ambient temperature is measured by a thermometer with a Platinum resistance (PT-100) and the relative humidity is measured by an HMP 110 hygrometer, both at 2 meter high and at a native temporal resolution of 5 seconds (Haeffelin et al., 2005; Chiriaco et al., 2018). The mixed layer height is measured by automatic lidar and ceilometer and derived using the CABAM (Characterising the Atmospheric Boundary layer based on ALC Measurements) algorithm (Kotthaus and Grimmond, 2018).
At SIRTA-LSCE, major submicron aerosol chemical species, i.e organic matter (OM), nitrate, sulfate, ammonium, and chloride, have been measured using a quadrupole Aerosol Chemical Speciation Monitor (Q-ACSM) since 2011 (Petit et al, 2015; Zhang et al, 2019). complementary information on equivalent black carbon (eBC) concentrations and sources is provided by collocated multiwavelength Aethalometer AE33 (Magee Scientific; Petit et al., 2015; Zhang et al., 2019). Therefore, eBC could be discriminated between its two main combustion sources, i.e. fossil-fuel (BC_{ff}) and wood burning emissions (BC_{wb}), using the Aethalometer model (Sandradewi et al., 2008; Favez et al., 2010; Sciare et al., 2011; Drinovec et al., 2015). For these calculations, the absorption Angström exponent values used, in the wavelength range of 470-950 nm, were 0.9 and 1.85 for BC_{ff} and BC_{wb} respectively, based on Petit et al. (2021). Nitrogen monoxide and dioxide (resp. NO and NO_2) have been monitored since 2012 using chemiluminescence $NO_2/NO/NO_X$ analyzer (model T200UP, Teledyne API, USA). More information on these additional gas and particulate measurements are given in Petit et al. (2021).
The Paris region is quite densely populated, local residential areas are situated mainly north and east of the station. Highways with important traffic (A6, A10) connect Paris to other cities

and pass through the east and south of the station, a national road with important traffic (N118) passes to the east. Forests, agricultural and natural areas are located on the west and south of SIRTA, and marine air masses from the Atlantic Ocean can reach the Paris region (Crippa et al., 2013). The station is therefore under different plumes depending on the wind direction, i.e. under regional background and oceanic air masses if the wind comes from the west/southwest, or under Paris and continental plumes if the wind comes from the north/northeast (see Figure 1). In 2020 and 2021, SIRTA was respectively 50% and 36% of the time under oceanic (SW) and continental (NE) plumes.
Throughout this manuscript, results are shown in universal time (UTC), while local time corresponds to CET (UTC+1) from November to March and to CEST (UTC+2) from April to October."

2.3.1.

50) Line 126: Please state the period of PTRMS measurements

This sentence is rephrased as: *"With the aim of characterizing VOC levels on a real-time and long-term basis, a Proton-Transfer-Reaction Quadrupole Mass Spectrometer (PTR-Q-MS, Ionicon Analytik, 2010) has been implemented for continuous measurements at SIRTA from January 17th, 2020 onwards."*

51) Line 134: from where do you get the clean air, how clean is this?

Here, this is a general description, the specificities for the PTR-MS at SIRTA are provided later on. In out setup, the clean air obtained from a GCU equipped with a catalytic VOC scrubber made of Pt/Pd and heated at 350°C.

A sentence is added in the general description: *"These blanks are usually done by passing clean air through the inlet line and conducted ideally every few hours and at least once a day. The clean air is either zero air from a bottle or ambient air that passes through a device which gets rid of the VOC using a scrubber or a catalyzer."*

Moreover, the description of our blank system is completed as:
l. 170: "A Gas Calibration Unit (GCU, IONICON, Austria), equipped with a catalytic VOC scrubber made of Pt/Pd and heated at 350°C, was used for 1-hour blanks every 13 hours 170 and for regular calibrations, about once a month: a VOC standard mixture was injected through the dilution system inside the GCU to perform steps at different volume mixing ratios (VMR, ranging from 1 to 20 ppb)."

52) Lines 137-139: the transmission calculation needs to be better explained. How is the transmission curve? How did you calculate it? How often did you calculate it? How do you interpolate transmission curves over time? Please state k rates for each compound. Why 3 instead of 2 for unknown k rates? Can you provide a reference for this? Which standards you use for transmission, how did you take into account fragmentation of compounds. But to me the most

critical thing is to see if you have calculated several transmission curves or only one (the latter would not be correct then).

The transmission curve was calculated based on the formula from Taipale et al (2008), presented in the supplementary material (Eq S1), using the measured sensitivities, the instrument parameters and the proton transfer reaction rates (now presented in updated Table 1). This transmission is calculated after each calibration, and the obtained coefficients are linearly interpolated to retrieve the sensitivities of the compounds not present in the standards. For unknown compound or rate, a reference of $3 \cdot 10^{-9}$ $cm^3 \cdot s^{-1} \cdot molecule^{-1}$ is used, as usually recommended, because most proton transfer reaction constants range $2\text{-}4 \cdot 10^{-9}$ $cm^3 \cdot s^{-1} \cdot molecule^{-1}$ (ACTRIS guidelines; Holzinger et al, 2015). The standards used for the transmission are the same than for the calibration (because the calibration coefficients are used to calculate the transmission). The compounds that fragment (e.g., isoprene, monoterpenes) are not included for the transmission calculation.

Indeed, several transmission curves were calculated over the 2-year period, two examples of consecutive curves are given in Figure R1 (Figure S2 in the paper).

In Section 2.3.4., the following paragraph is added: *"After each calibration, the transmission is calculated for some of the calibrated compounds (methanol, acetonitrile, acetaldehyde, propenal, benzene, toluene, C8-aromatics, C9-aromatics, dichlorobenzene and trichlorobenzene, when available) using their measured sensitivities (Eq. S1). As an example, two consecutive transmission curves are presented on Figure S2, for 1st July 2020 and 7th August 2020. The transmission coefficients are interpolated linearly over time. The same standards are used for the transmission than the calibration, since we use the measured sensitivities to calculate the transmission. The compounds which could fragment are not included in the calculation of the transmission curve (e.g., isoprene, monoterpenes)."*

In the Text S1, the following part is updated (changes are indicated in bold): *"To obtain the sensitivity (in ncps/ppb) of compounds not present in the calibration standard, first the transmission of compounds present in the standard is calculated, based on the instrument's parameters and following Equation S1 (Taipale et al., 2008):*

$$\frac{T_{RH^+}}{T_{H_3O^+}} = 10^9 \frac{p_{drift}}{I_{norm}p_{norm}} \frac{\mu_0 N_0}{kL} \frac{E}{N^2} S_{norm}$$

*With p_{drift} being the drift pressure, I_{norm} the normalized intensity (equal to 10^6), p_{norm} the normal pressure, μ_0 being the reduced ion mobility of the primary ions and equal to 2.8 $cm^2.V^{-1}.s^{-1}$, N_0 the number density of air standard conditions, **k being the reaction rate constant of the given compound**, L the length of the drift tube, $E = U_{drift}/L$, $N = N_A p_{drift}/(RT_{drift})$, and S_{norm} the normalized sensitivity obtained by a standard calibration.*

The k rates used in this study are summarized in Table 1; for unknown compounds or rates, a value of $3 \cdot 10^{-9}$ $cm^3 \cdot s^{-1} \cdot molecule^{-1}$ is used, as usually recommended, because most proton transfer reaction constants range $2\text{-}4 \cdot 10^{-9}$ $cm^3 \cdot s^{-1} \cdot molecule^{-1}$ (ACTRIS guidelines; Holzinger, 2015)."
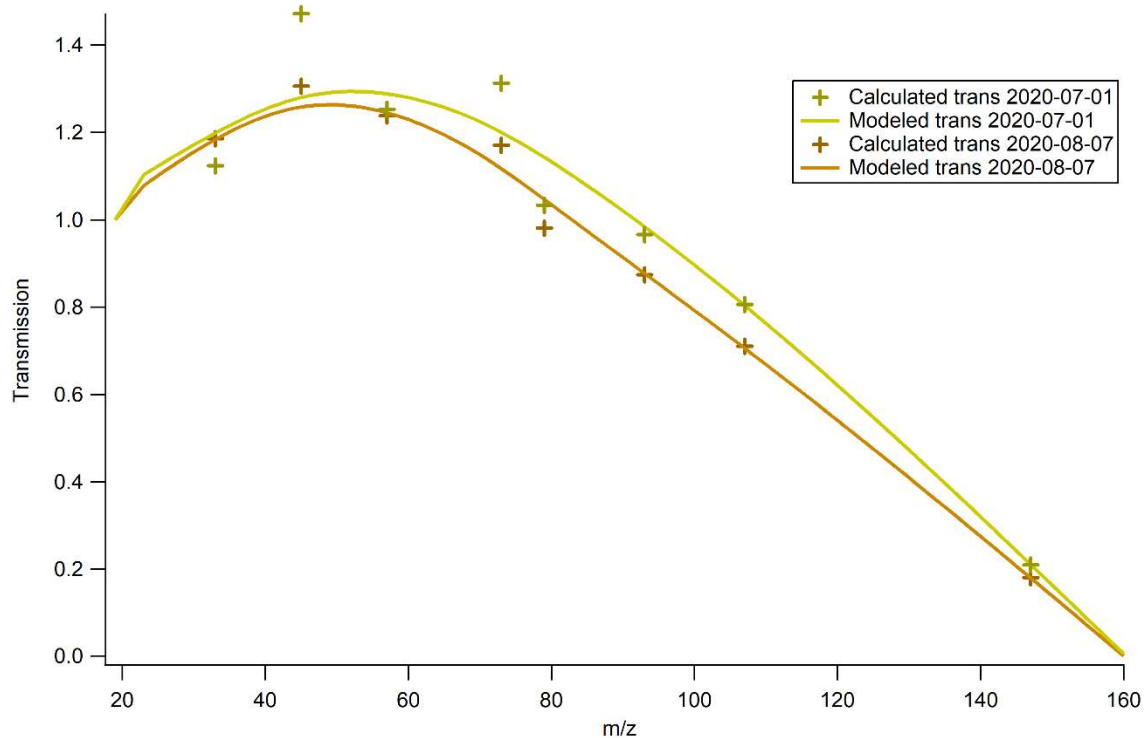
Figure R1: Examples of transmission curves plotted by interpolation of calculated transmissions from the calibrations of 7/1/2020 and 8/7/2020.

53) 2.3. I need a longer explanation on inlet set up. How it is? A picture would be very explanatory. Is the line isolated? How are you heating the line? How tall is the SIRTA station, because 6 m for 15 m above ground is confusing. What is the OD and ID of the PFA lines. How this may be affecting compounds such as dichlorobenzene for stickiness? What is a Valco valve? Explain more on what is this and which material is done, how many connections you have.. etc..

Figure R2 (Figure S1 in the paper) presents the experimental set-up for the PTR-Q-MS measurements at SIRTA. This figure is added in the supplement. The line is isolated and heated using heating wires around the line and with a thermocouple monitoring the temperature. The instrument is located on the second (and last) floor of the building, therefore the line is just connected to the roof. The inner diameter is 9.53 mm, and an outer diameter is 12.7 mm (1/2 inch). This additional information on the line has been added in the text (see below). Although the line was passivated 3 days at the beginning of the measurements, we cannot rule out that some sticky compounds like dichlorobenzene can be affected. We note that this compound (which is not a focus in this study) is associated to a quite large error (43%).

The Section 2.3.1 is completed as: *"The PTR-Q-MS is located on the second and last floor of the building, therefore the sampling line is directly connected to the roof and samples at about 15 m above ground level. The experimental set-up is shown on Figure S1. The sampling line has a total length of 6 metres, with an inner diameter of 9.53 mm, and an outer diameter of 12.7 mm*

(1/2 inch). A pump provides a flow of about 8 L·min^{-1}, thus ensuring a residence time for the air in the tube of about 3 seconds. The sampling line is made of PFA (perfluoroalkoxy). It is isolated and heated with heating wires around the line and with a thermocouple monitoring the temperature at 50°C to avoid condensation. Such a material needs to be passivated at the beginning of the measurement and therefore the first 3 days of measurements were not taken into account. A multiway valve (VALCO, Interchim, France) in stainless steel connects ambient air, blank and standard measurements to the PTR-MS inlet, therefore allowing to automatically switch between them."
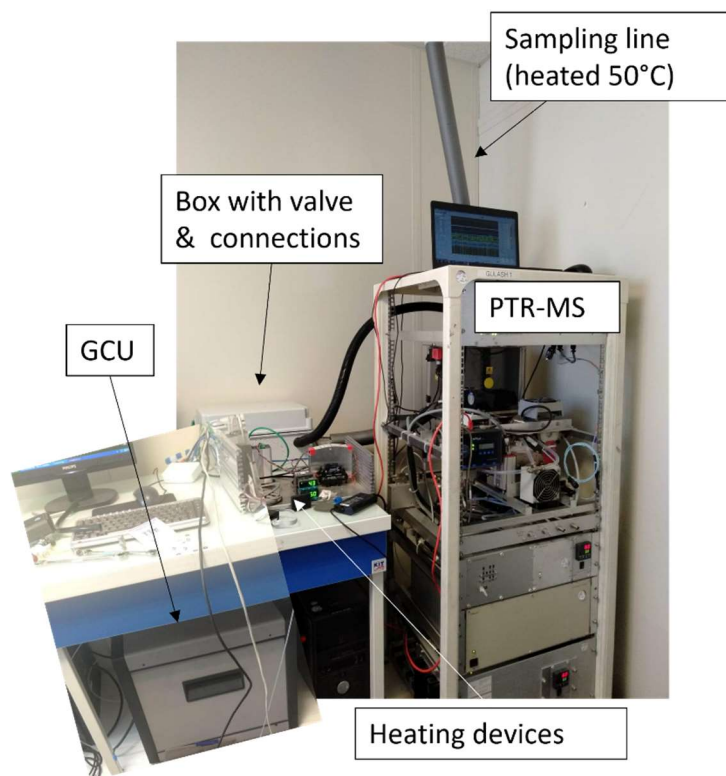

Figure R2: Experimental set-up of the PTR-MS for long-term VOC measurements at SIRTA.

2.3.2.

54) You say tdrift is 60°C in the text but it says 40°C in table S1

Corrected in the Table S1:

Table S1: Instrument parameters throughout the two-year measurement period

Name	Symbol	Value (unit)
Pressure in the drift chamber	P_{drift}	2.2 mbar

Pressure in the detector	P_{detect}	$1.7\text{-}3.3 \cdot 10^{-5}$ mbar
Controlled pressure	$P_{control}$	352-484 mbar
Temperature in the drift chamber	T_{drift}	60 °C
Temperature in the inlet tube	T_{inlet}	60 °C
Voltage in the drift chamber	U_{drift}	600 V
Water flow	F_{H2O}	5–8 mL·min^{-1}
Voltage	U_{SO}	90–130 V
Voltage	U_S	80–120 V
Source intensity	I_{hc}	3–6 mA
Voltage in the SEM	U_{SEM}	2000–3500 V
Drift tube length	L	9.2 cm
Collision energy	E/N	134.4 Td

55) What do you mean by regularly adjusted…. How is this done, how often, do you calibrate for each change? You need to state better how calibrations are done, but we will get there.

These parameters (water flow, ion source current, voltages at the entrance and exit of the drift chamber and detector voltage) are typically adjusted after a maintenance, to have optimized values for the diagnostic m/z (i.e., m/z 30, 32, and 37). The detector voltage is increased if the sensitivity decreases and it is not due to the ion source. Yes, we calibrate after each change in the parameters.

This iss clarified in the text: *"Other parameters such as water flow, ion source current, voltages at the entrance and exit of the drift chamber and detector voltage are adjusted when needed in order to maintain the instrument functioning in an optimized way (See Table S1). For example, if the sensitivity decreases and it is not due to the ion source, the detector voltage is increased; also after a maintenance the drift chamber voltages can be adjusted to keep the amount of m/z 30, 32 and 37 low. A calibration is performed after changes in the parameters."*

2.3.3.

56) Did you have equal dwell time for all compounds? It is not the same to measure acetone and sesquiterpenes for instance, and a dwell time of 10 s for compounds such as acetone, seems too long… although not necessarily wrong. But let me get this straight, you only get a value per compounds every 15 minutes?

This may decrease the power of online measurements… but again not necessarily wrong. I understand calibrations were done with the exact dwell time of measurements, right?

How this lower sensitivity with 5 s has been observed? Can you explain in time when changes were done? Also can you show this decrease in sensitivity?

Also can you explain why a resolution of 15m is better than 22m?

For the sake of simplicity, all compounds have the same dwell time (5 s from January to November 2020; then 10 s) except for diagnostic m/z (21, 25, 30, 32, 37, 55) which have a lower dwell time (100 ms). This results in a resolution time of 2.6 min for 5 seconds per m/z and 5.2 min for 10 seconds per m/z (see lines 166-168). (Please note that sesquiterpenes are not measured here.) The dwell times during the calibrations were not necessarily the same as for the ambient measurements, but since during the calibration it is sampled for a long time, it should not be an issue.

Figure R3 shows the signal in November and December 2020, the dwell time was changed on December 4th from 5s to 10s, which resulted in a less noisy signal. "sensitivity" was not the right word, sorry about that.

We preferred to have a time resolution lower than 15 min (at first 2.6 min then 5.2 min) to be able to study specific events at a high time resolution.

In the main text, it is rephrased as:

l. 156-158: *"Throughout the measurement period, it was observed that a dwell time of five seconds per mass can result in noisy signals, and so a dwell time of ten seconds was preferred, which would result in a resolution time of 22 minutes."*

l. 166-168: *"The dwell time of the first six m/z is set to 100 ms, while the dwell time of all the other m/z was 5 seconds from January to November 2020, on December 4th it was increased to 10 seconds, resulting in a time resolution respectively of 2.6 min from January to November 2020 and 5.2 min from December 2020 on."*
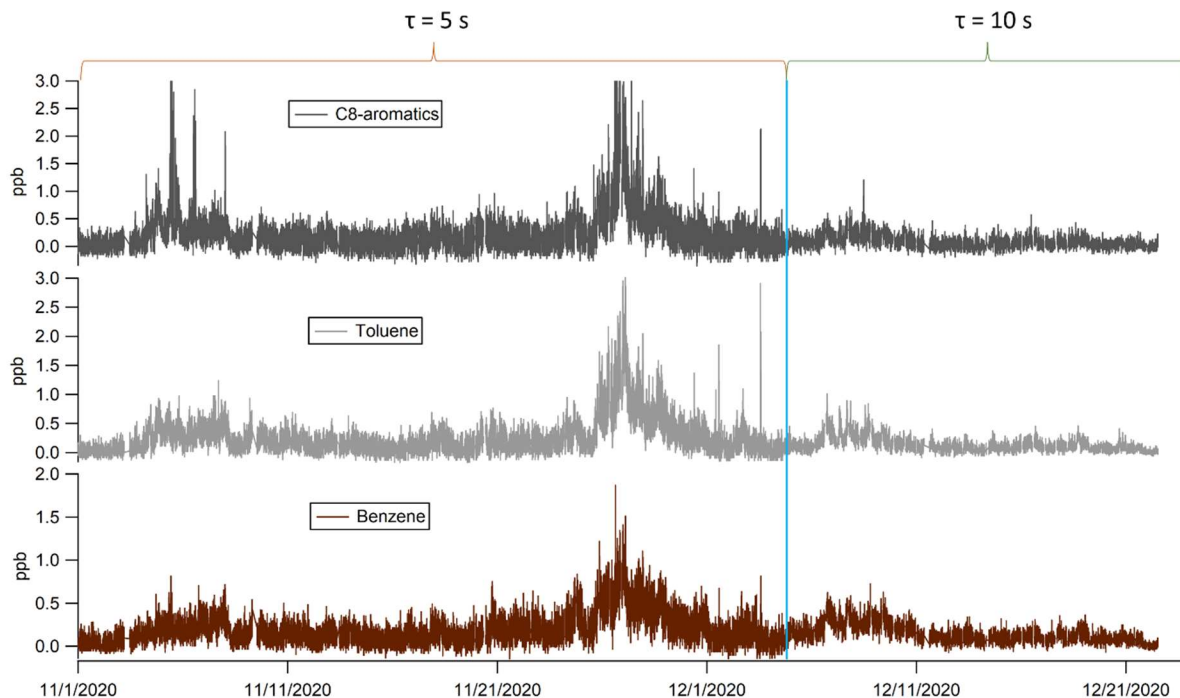
Figure R3: Temporal variability of C8-aromatics, toluene, and benzene in November and December 2020. The blue bar represents the change in the dwell time on December 4th.

57) Line 160: Can you show your scan mode measurements? Which previous studies you used?

Figure R4 shows the mass spectra of mean cps obtained over 5 days of scan mode measurements (from 1/10/2020 to 1/15/2020). The previous studies used are reviews of PTR-MS (de Gouw and Warneke, 2007; Blake et al., 2009; Yuan et al., 2017b) and studies on campaigns in the Paris region (Kammer et al, 2019; and Languille et al, 2020).

This part is rephrased:

"Mass-to-charge ratios were selected based on previous studies: reviews of PTR-MS measurements (de Gouw and Warneke, 2007; Blake et al., 2009; Yuan et al., 2017b), a winter campaign that highlighted markers for the traffic and wood burning source (Languille et al, 2020), and a study on agricultural emissions (Kammer et al, 2019). The scan mode was run for a couple of days before starting the long-term measurements to confirm the selection."
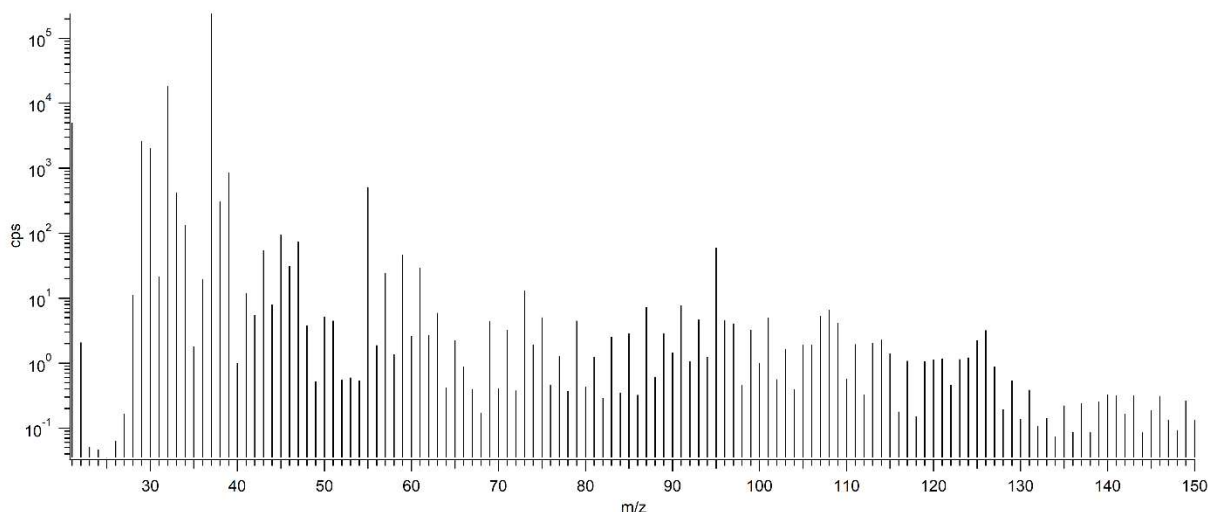
Figure R6: Scan mode measurements from 1/10/2020 to 1/15/2020

58) Line 166-168: This lines seem to contradict what you say in 156-159. Please rephrase and make it consistent.

It is rephrased as: *"This resulted in 37 mass-to-charge ratios measured, the first 6 being for instrumental diagnostic purposes: m/z 21, 25, 30, 32, 37, 55, 31, 33, 42, 45, 46, 47, 57, 58, 59, 60, 61, 63, 69, 71, 73, 75, 79, 81, 83, 85, 87, 93, 97, 99, 107, 111, 121, 137, 139, 147, 151. The dwell time of the first six m/z is set to 100 ms, while the dwell time of all the other m/z was 5 seconds from January to November 2020, on December 4th it was increased to 10 seconds, resulting in a time resolution respectively of 2.6 min from January to November 2020 and 5.2 min from December 2020 on."*

59) I suggest including a table with all monitored masses, compound assignment, possible fragmentation, k rates, calibration factors, LOD and uncertainty……. (basically an updated table 1)

Thank you for this suggestion, Table 1 is updated as follows.

Table 1: List of mass-to-charge ratios measured, their corresponding name in this paper, possible fragmentation (Pagonis et al, 2019), reaction rate constants (Holzinger et al, 2019; Zhao and Zhang, 2004; Španěl et al., 1998 and 2002; Lindinger et al., 1998), mean and standard deviation of measured sensitivities, mean detection limit (LOD) and mean uncertainty. Compounds in bold are the ones that underwent the quality control of ACTRIS.

m/z	Compound(s)	Fragmentation	k rate (10^{-9} cm^3·s^{-1})	Mean calib factor (+/- sd) (ncps/ppb)	Mean LOD (ppt)	Mean error (%)
mz_31	Formaldehyde proxy		3.00		58	37
mz_33	**Methanol**		2.20	9 (+/- 2)	221	16
mz_42	**Acetonitrile**		4.74	17 (+/- 4)	9	16
mz_45	**Acetaldehyde**		3.03	16 (+/- 4)	47	18
mz_46	m46		2.10		54	33
mz_47	Ethanol + Formic acid		2.26		67	33

mz_57	**C4H8 + Propenal**		4.20	13 (+/- 5)	23	20
mz_58	Allylamine		3		6	69
mz_59	**Acetone**		3.25	18 (+/- 5)	17	14
mz_60	Trimethylamine	m/z 58 10%	2.40		11	34
mz_61	Acetic acid	m/z 43 40%	3.00		34	31
mz_63	DMS		3		20	41
mz_69	**Isoprene + Furan**	m/z 41 10%	1.85	5 (+/- 2)	37	21
mz_71	**MVK + MACR**		2.72	17 (+/- 3)	10	25
mz_73	**MEK**		3.25	14 (+/- 5)	14	19
mz_75	C3H6O2		2.80		16	33
mz_79	**Benzene**		1.97	7 (+/- 2)	21	19
mz_81	MT's fragments		2.04		8	33
mz_83	Methylfuran + C6H10		3		10	67
mz_85	Methylbutenone		4.60		9	36
mz_87	Butanedione + Methacrylic acid		1.85		40	36
mz_93	**Toluene**		2.12	6 (+/- 3)	24	20
mz_97	Furfural		3.90		11	35
mz_99	Furandione + Furfuryl alcohol		4.20		14	36
mz_107	**C8-aromatics**	m/z 79 < 10%	2.31	5 (+/- 3)	36	23
mz_111	Benzenediol		2.70		30	42
mz_121	C9-aromatics	m/z 93 < 10%	2.40		31	31
mz_137	**Monoterpenes**	m/z 81 35%	2.04	1 (+/- 0.5)	37	34
mz_139	Nopinone	*unknown*	3		24	73
mz_147	Dichlorobenzene	m/z 149	3	1 (+/- 1)	26	43
mz_151	Pinonaldehyde	*unknown*	2.40		46	48

2.3.4.

This is the most critical part to me

61) How did you perform blanks with the gas calibration unit. Did you have n2? Synthetic air, catalytic converter? If the latter at which temperature? Also how is your blank for compounds such as acetic acid?

The gas calibration unit is equipped with a catalytic VOC scrubber made of Pt/Pd and heated at 350°C. An example of blank and ambient measurements for acetic acid is provided Figure R5.

The description of our blank system has been completed as:
l. 170: "A Gas Calibration Unit (GCU, IONICON, Austria), equipped with a catalytic VOC scrubber made of Pt/Pd and heated at 350°C, was used for 1-hour blanks every 13 hours and for regular calibrations, about once a month: a VOC standard mixture was injected through the dilution system inside the GCU to perform steps at different volume mixing ratios (VMR, ranging from 1 to 20 ppb)."
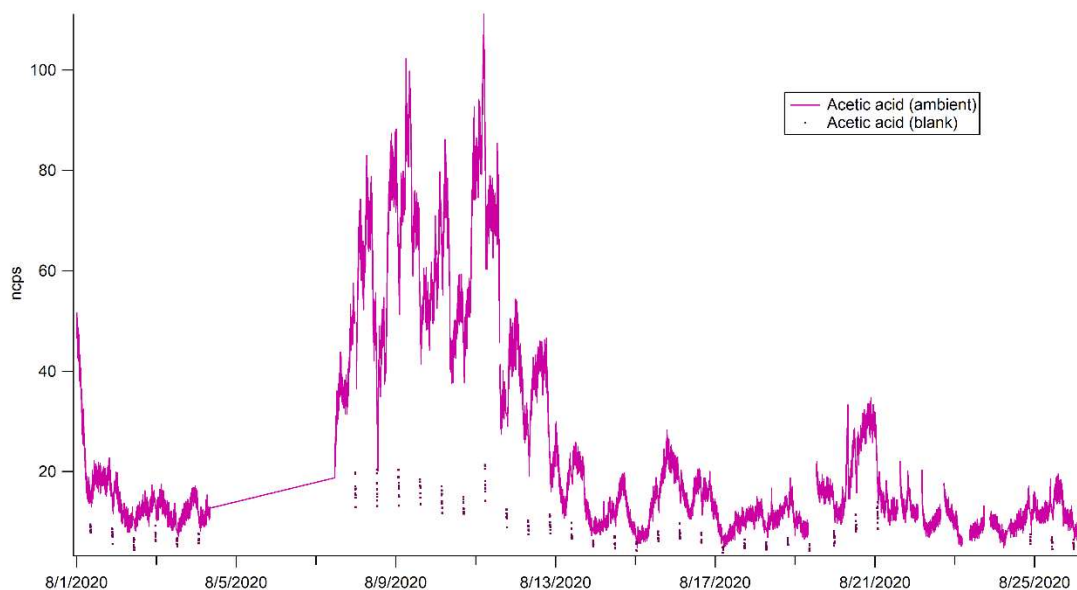
Figure R5: Example of ambient and blank measurements of acetic acid for August 2020

62) Did you find a drift in your calfactors over time? Somehow it may seem one month per doing calibrations is too long. I would like to see a list of calibrations and how these change when ptr parameters are changed.

63) Please show cal factors (ncps/ppbv) per each compound and how they drift with time and with cal gas. This also adds to the comment on transmission. Add the NPL cal gas, and please show how did you account for the variations in calgas. This is very important for the compounds used to calculate the transmission curve. Please also state which compounds are those.

For continuous long-term measurements, Ionicon suggests calibrating approximately once per month (GCU user manual, IONICON, 2010).

Figure R2 (Figure 2 in the revised paper) represents the temporal evolution of the sensitivities of methanol, acetone and benzene for the different used standards. The most important changes in the sensitivities correspond to maintenances and change of parameters (i.e., detector voltage), whereas standard changes do not lead to significant variations in the sensitivity. The sensitivities can also decrease with the use of the instrument, especially when the ion source gets dirty, as can be seen in the beginning of 2020. This period is followed by a long break during the Covid-19 Spring lockdown, when a maintenance was needed. After this maintenance, the sensitivities are a little higher, and again slowly decrease with the use of the instrument. We note that the change of standard in September 2020 does not lead to a significant change of sensitivity. Another maintenance was performed in early 2021, leading to higher sensitivities. Then, the SEM voltage had to be gradually increased, resulting in higher sensitivities, until the detector was changed in April 2021. A longer maintenance was necessary in summer 2021, following which the sensitivities were stable, even when the standard was changed in early 2022. For the data treatment, the sensitivities are interpolated between each calibration.

Table R1 lists all measured sensitivities with the corresponding standard and the SEM voltage and is added in the supplementary material as Table S3.

The compounds used for the transmission curve are methanol, acetonitrile, acetaldehyde, propenal, benzene, toluene, C8-aromatics, C9-aromatics, dichlorobenzene and trichlorobenzene, they are indicated in the revised text.

This is completed and rephrased in the main text as: *"After each calibration, the transmission is calculated for some of the calibrated compounds (methanol, acetonitrile, acetaldehyde, propenal, benzene, toluene, C8-aromatics, C9-aromatics, dichlorobenzene and trichlorobenzene, when available) using their measured sensitivities (Eq. S1). As an example, two consecutive transmission curves are presented on Figure S2, for 1st July 2020 and 7th August 2020. The transmission coefficients are interpolated linearly over time. The same standards are used for the transmission than the calibration, since we use the measured sensitivities to calculate the transmission. The compounds which could fragment are not included in the calculation of the transmission curve (e.g., isoprene, monoterpenes). Different standards were used throughout the study period (see Table S2), allowing to directly calibrate 9 to 13 species, depending on the standard. The obtained sensitivity coefficients are given in Table S3 with the standard used and the detector voltage. Figure 2 presents the temporal evolution of these measured sensitivity coefficients for methanol, acetone and benzene shape-coded by the standard reference, as well as the maintenance periods. Here, a sensitivity decrease is observed with the use of the PTR-MS (i.e., ion source dirtying, detector aging) while an increase was obtained with detector voltage increase. Therefore, it is important to note that the largest changes of sensitivity were due to instrumental evolution and not to changes of standard."*

NPL is added to Table S2:

Table S2: Standards used for PTR-MS calibrations

Start	End	Standard reference	Species in the standard used for direct calibrations	VMR
18-01-2020	10-09-2020	R0904, Ionicon Analytik	Methanol, Acetonitrile, Acetaldehyde, Acrolein, Acetone, Isoprene, Crotonaldehyde, 2-Butanone, Benzene, Toluene, o-Xylene, α-pinene, 1,2-Dichlorobenzene	1 ppm
10-09-2020	15-06-2020	L5387, Ionicon Analytik	Methanol, Acetonitrile, Acetone, Isoprene, Benzene, Toluene, Xylenes, Trimethylbenzene, 1,2-Dichlorobenzene	100 ppb
01-09-2021	28-04-2022	D155286, SIAD	Methanol, Acetonitrile, Acetaldehyde, Acrolein, Acetone, MEK, Benzene, Toluene, o-Xylene, α-pinene, 1,2-Dichlorobenzene	1 ppm
23-05-2022	current	NPL	Methanol, Acetonitrile, Acetaldehyde, Acetone, Isoprene, Dimethylsulfide, 3-Buten-2-one, 2-Butanone, Benzene, Toluene, m-Xylene, 1,2,4-Trimethylbenzene, 3-Carene	1 ppm

Table R1: Sensitivity coefficients (ncps/ppb) throughout the 2020-2021 period

Time	SEM voltage (V)	Standard	mz_33 Methanol	mz_42 Acetonitrile	mz_45 Acetaldehyde	mz_57 Propenal	mz_59 Acetone	mz_69 Isoprene
1/15/2020	2975	R0904	10.71	19.52	18.97	17.67	21.22	6.55
1/21/2020	2975	R0904	9.43	18.18	17.63	15.81	19.12	5.72
2/25/2020	2975	R0904	9.63	16.23	15.91	13.83	16.47	4.75
6/11/2020	3100	R0904	11.73	20.13	20.09	18.80	21.90	7.29
7/1/2020	3100	R0904	11.32	20.45	21.37	18.14	22.72	7.24
8/7/2020	3100	R0904	11.97	19.64	19.02	17.97	20.69	6.87
9/10/2020	3050	R0904	11.41	17.01	16.37	14.04	16.86	4.73
10/9/2020	3050	L5387	10.04	17.89			17.15	4.14
11/9/2020	3050	L5387	7.10	17.38			16.91	4.07
12/11/2020	3050	L5387	8.28	16.98			16.96	3.62
1/15/2021	3200	L5387	8.62	21.14			21.32	5.38
1/28/2021	3200	L5387	9.95	21.87			23.14	6.10
2/25/2021	3250	L5387	9.43	22.10			25.41	6.76
4/6/2021	3375	L5387	10.93	24.01			26.82	7.25
4/26/2021	2300	L5387	9.21	18.87			19.19	5.52
5/27/2021	2350	L5387	8.91	19.53			20.04	5.06
8/16/2021	2350	D155286	8.35	14.37	18.72	16.30	21.71	6.46
9/10/2021	2350	D155286	7.87	10.20	12.66	8.58	12.99	3.82
9/20/2021	2350	D155286	7.17	14.19	12.72	8.59	12.12	3.66
10/25/2021	2375	D155286	5.92	10.37	12.05	4.15	10.98	3.31
11/16/2021	2425	D155286	5.43	9.25	11.48	7.99	10.57	2.64
11/16/2021	2425	D155286	5.72	9.50	11.85	8.29	10.71	2.57
12/15/2021	2450	D155286	6.20	10.66	12.25	8.93	11.53	2.84

Time	SEM voltage (V)	Standard	mz_73 MEK	mz_79 Benzene	mz_93 Toluene	mz_107 C8-Aromatics	mz_137 Monoterpenes	mz_147 Dichlorobenzene
1/15/2020	2975	R0904	18.63	8.28	7.95	7.06	1.34	1.65
1/21/2020	2975	R0904	16.39	7.77	7.05	6.03	1.15	1.36
2/25/2020	2975	R0904	13.54	6.12	5.45	4.55	0.84	0.90
6/11/2020	3100	R0904	18.56	9.48	9.20	8.33	1.69	1.94
7/1/2020	3100	R0904	19.75	8.80	8.85	8.01	1.66	1.81
8/7/2020	3100	R0904	17.66	8.37	8.03	7.08	1.39	1.56
9/10/2020	3050	R0904	13.76	5.95	5.43	4.47	0.81	0.94
10/9/2020	3050	L5387		5.31	4.70	3.90		0.84
11/9/2020	3050	L5387		4.99	4.24	3.45		0.80
12/11/2020	3050	L5387		4.52	4.70	3.33		0.68

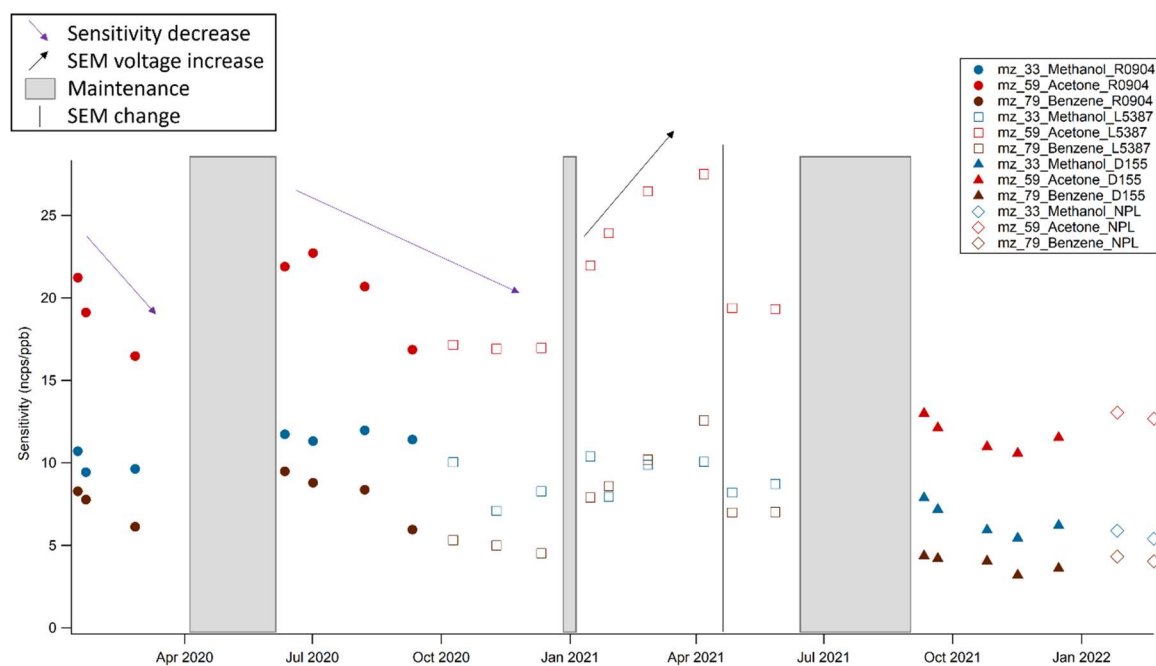|								
1/15/2021	3200	L5387		7.68	6.89	6.15		1.52
1/28/2021	3200	L5387		8.23	8.07	6.92		1.75
2/25/2021	3250	L5387		9.72	9.53	8.57		2.08
4/6/2021	3375	L5387		12.23	11.92	10.81		3.26
4/26/2021	2300	L5387		6.81	6.81	4.99		1.42
5/27/2021	2350	L5387		7.28	6.17	4.79		1.32
8/16/2021	2350	D155286	18.65	9.11	8.82	7.76	1.50	1.75
9/10/2021	2350	D155286	10.57	4.35	3.64	2.62	0.44	0.57
9/20/2021	2350	D155286	9.79	4.20	3.31	2.37	0.39	0.45
10/25/2021	2375	D155286	8.63	4.03	3.01	2.10		0.37
11/16/2021	2425	D155286	7.72	3.18	2.45	1.66		0.29
11/16/2021	2425	D155286	7.64	3.37	2.53	1.83		0.29
12/15/2021	2450	D155286	8.57	3.59	2.79	1.97	0.29	0.39

Figure R7: Time series of sensitivities vs time for methanol, acetone and benzene. Standard references are indicated by the shape of the data points (cf Table S2).

64) Line 175-179: please rephrase…. This is very confusing. When did you do these tests?

These sentences were completed: *"This standard was also used to infer the repeatability of the measurement at the end of May 2022: it was sampled with the same protocol (same dilution, a blank before and after) over 3 consecutive days, while environmental conditions (i.e., temperature and relative humidity) might vary a little. The obtained coefficients of variation for*

65) About humidity in calibrations, did you perform humid calibrations or not? How did you apply this effect?

The calibrations are performed at the ambient humidity since ambient air passes through the scrubber. The humidity tests mentioned above showed a very low humidity dependence (see response to the comment 66 below), so no correction was applied, but it was taken into account in the uncertainty calculation (Section 2.4.4).

66) How did you interpolate sensitivities? Did you interpolate humidity effect over time? Also I guess the impact of humidity is totally different depending the compounds. Please show.

The sensitivities were linearly interpolated. The humidity effect was not interpolated because it was observed to be very low (see Table R2 and Figure R6).

This is added in the revised text: *"In addition, the influence of humidity on the sensitivity was investigated by performing calibrations using the NPL standard at set relative humidities (RH) of 30%, 60% and 90% on August 4th, 2022. Results for these tests are presented in Table S4 and Figure S3, the humidity dependency of the sensitivities for the considered species ranges in 1-7% with an average of 3%. The difference is much lower for the RH range 60-90%, which corresponds to 72% of the data, than for the range 30-60%."*

Table R2: Sensitivities (ncps/ppb) obtained for calibrations at various relative humidities

Relative humidity	m/z 33	m/z 42	m/z 45	m/z 59	m/z 69	m/z 71
30 %	8.1	17.0	20.5	22.4	8.6	23.3
60 %	8.1	19.0	18.2	22.1	7.9	21.0
90 %	8.7	19.6	18.8	22.7	8.0	21.9
CV (%)	5	7	6	1	5	5
Relative humidity	m/z 73	m/z 79	m/z 93	m/z 107	m/z 121	m/z 137
30 %	21.9	13.6	14.4	13.6	11.1	4.1
60 %	22.2	13.3	14.4	13.4	10.7	4.1
90 %	22.4	13.2	14.2	13.3	10.8	4.2
CV (%)	1	1	1	1	2	2

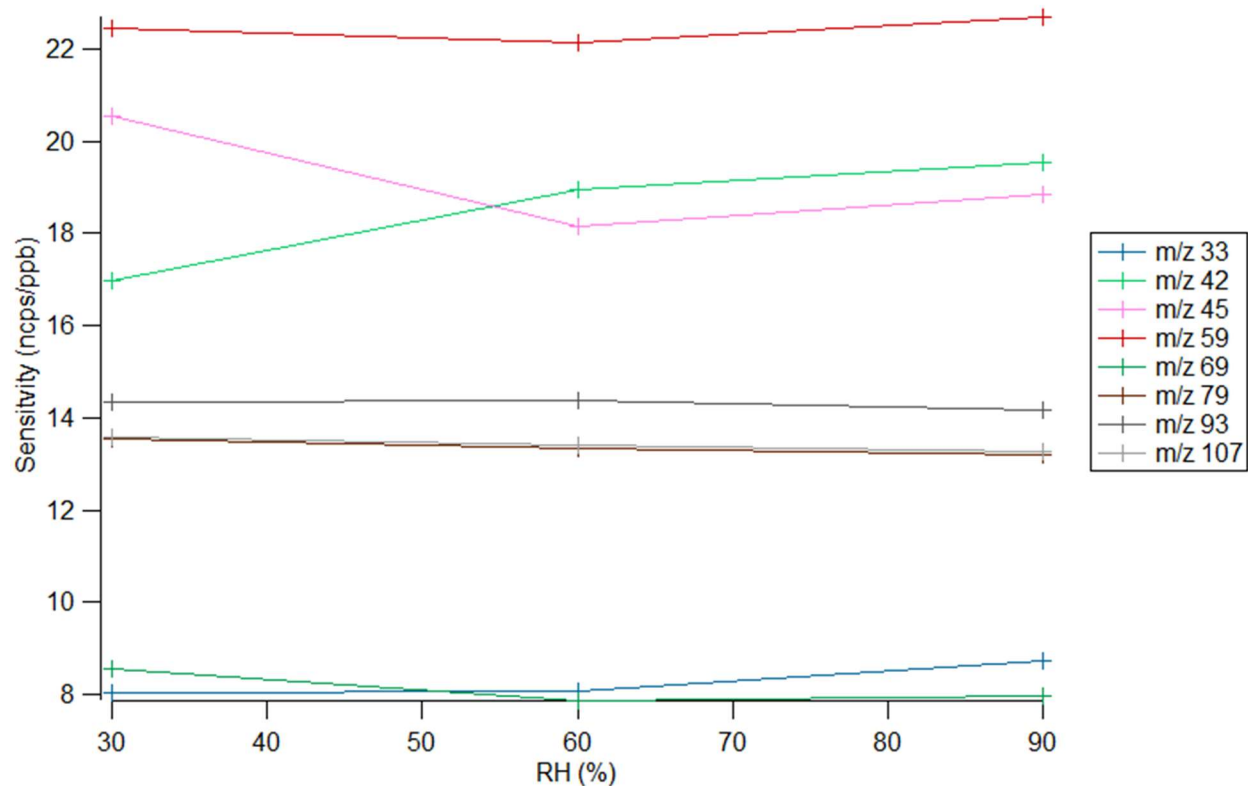*CV = coefficient of variation*

Figure R6: Sensitivities vs RH for methanol, acetonitrile, acetaldehyde, acetone, isoprene + furan, benzene, toluene, C8-aromatics

2.4.1.

67) What is stable ambient air? Can you please rephrase this part? What do you mean check the stability?

Table R3 (Table S5 in the revised paper) presents the mean and standard deviation of the target bottle measurements for species with a signal > 10 ppt, and Figure R7 (Figure S4 in the revised paper) presents the temporal evolution of these measurements for benzene and acetone.

This part is rephrased as: *"A target bottle, containing ambient air, is measured once per week, in order to check that the measurements do not deviate too much from their mean value. The mean and standard deviation values for the target bottle measurements of ions that have a signal > 10 ppt are given in Table S5, and the temporal evolution of these measurements for benzene and acetone is presented in Figure S4."*

Table R3: Mean and standard deviation values for target bottle measurements

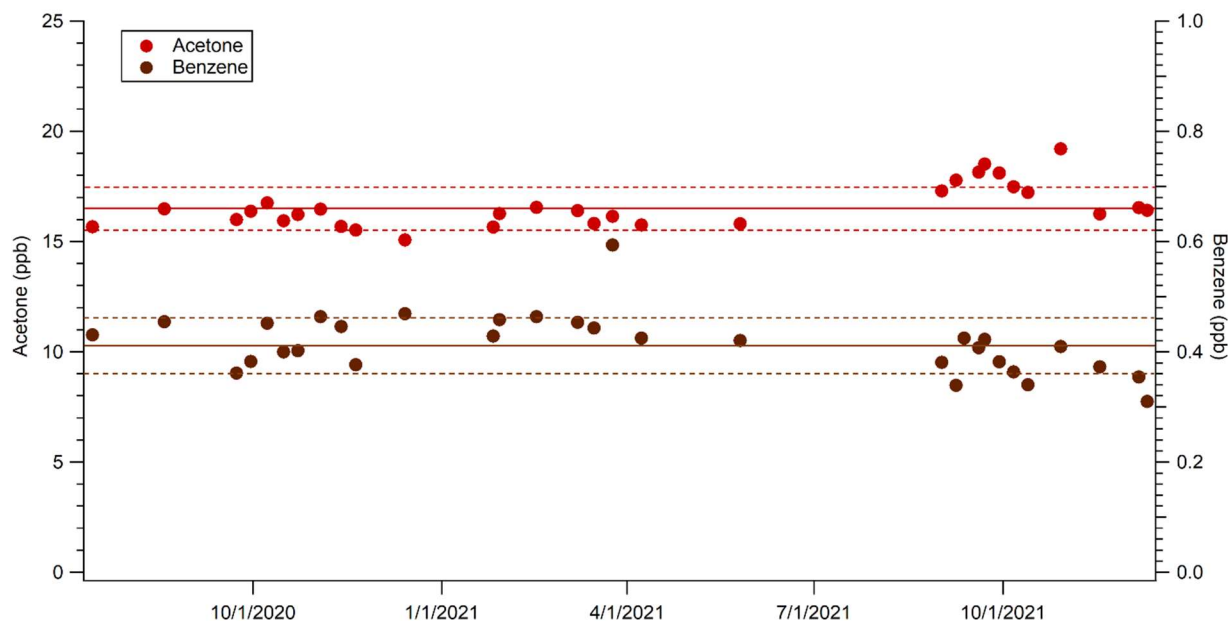| m/z	m/z 33	m/z 42	m/z 45	m/z 46	m/z 57	m/z 59	m/z 60	m/z 61	m/z 69	m/z 71
Mean (ppb)	3.22	0.25	23.68	1.04	1.53	16.58	0.86	0.53	1.82	0.57
Standard deviation	0.72	0.03	2.68	0.57	0.43	0.98	0.16	0.27	0.24	0.17
m/z	m/z 73	m/z 79	m/z 83	m/z 85	m/z 87	m/z 93	m/z 97	m/z 107	m/z 121	
Mean (ppb)	1.38	0.41	0.51	0.31	1.90	0.39	0.39	0.59	0.34	
Standard deviation	0.18	0.05	0.16	0.16	0.32	0.05	0.16	0.10	0.15	

Figure R7: Temporal evolution of acetone and benzene measurements from the target bottle. The lines represent the mean value while the dashed lines represent mean +/- standard deviation.

2.4.2.

68) Line 205: please state inner diameter, as this is the same residence time as expressed in line 143, however with a different flow. Thus Both ptr system sample from different lines? Please restate to make it clear.

The residence time is similar because the pump flow has been increased in order to compensate for the longer line length. Both PTR-MS are not in the same room and do not have the same sampling line.

This part is thus rephrased: *"The PTR-ToF-MS was installed in another room than the PTR-Q-MS, and with a different setup. A second 16-m PFA sampling line with an inner diameter of 9.63 mm, isolated and heated at 50°C was used to sample at the same height as the PTR-Q-MS. A pump provided a flow of 22 L·min^{-1}, thus resulting in a residence time of about 3 seconds."*

69) Line 206 ohh so here is the catalytic converter. Only performed once per two days? This is too long, it changes with time.. even 13hrs may be too long…..

We agree with the reviewer that a higher frequency of blanks would be better. Note that we have increased the frequency of the blank measurements for the PTR-Q-MS in early 2022 to every 6 hours.

The set-up of the PTR-ToF-MS is different than the PTR-Q-MS one, please note that this catalytic converter is not the same as the one in the GCU. Blanks performed during the PTR-ToF-MS campaigns are presented on Figure R8 (Figure S5 in the revised paper), for the m/z used for the main isobaric speciation (m/z 46, 47, 57, and 69).

During the lockdowns, it was not possible to come on site to perform manual blanks (and no automatic method could be setup). Please note that during the periods "spring/summer campaign" and "autumn campaign & lockdown", while there was not a total lockdown like the spring lockdown, it was only possible to come once to twice a week on site.

The Figure R8 is added to the supplementary material and a short explanation is given in the main text: *"Figure S5 presents the temporal evolution of the obtained blanks where the different periods (i.e., campaigns, lockdowns) are highlighted. Most of these blanks are rather stable, and they are interpolated for the data treatment."*
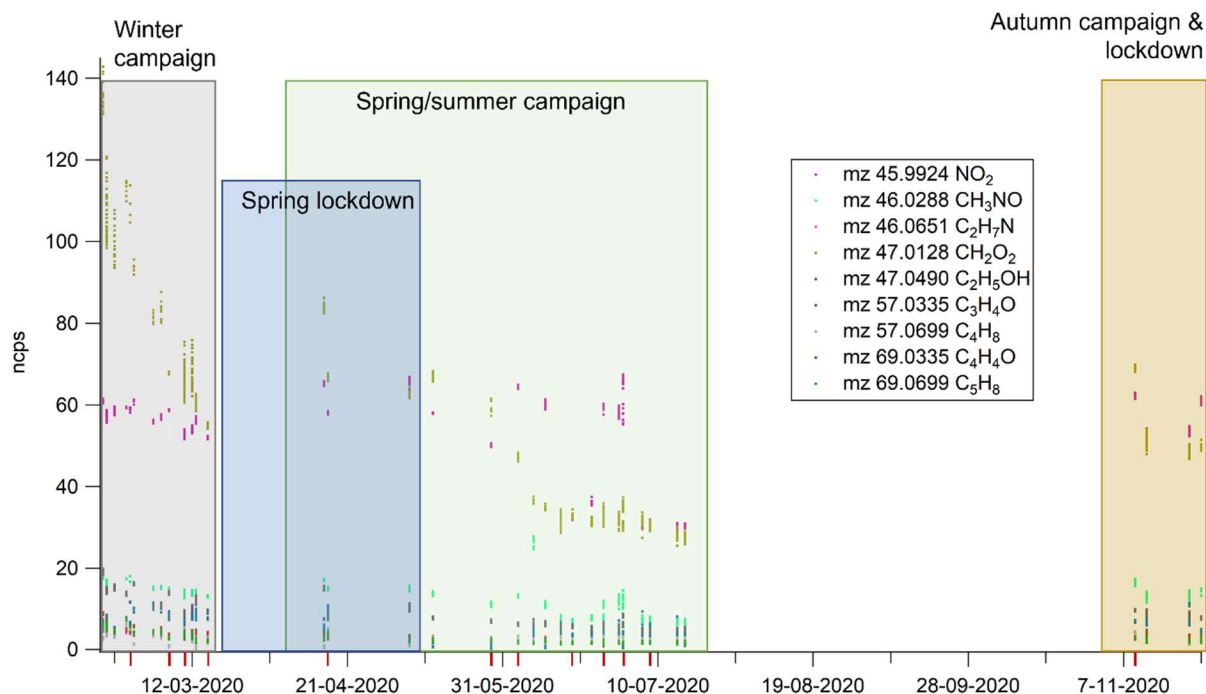

Figure R8: Blanks performed in 2020 for a selection of PTR-ToF-MS m/z. Calibrations are indicated by red sticks.

70) Line 209: how are these calibrations done with the internal standard?

The calibrations are done with an external standard, in a similar way than for the PTR-Q-MS. However, the dilution system is different than the one used for the PTR-Q-MS measurements. For the PTR-Q-MS we use flowmeters inside the GCU system while for the PTR-ToF-MS the dilution system with the flowmeters is inside the instrument. The calibration standards used were a canister (Figure R9) until mid-May 2020 and the standard bottle D155286 (Table S2) from mid-May 2020.

l. 208 is rephrased and completed as: *"Calibrations were done about once a month using the internal dilution system (flowmeters located inside the instrument). The calibration standards used were a canister (Figure S6) until mid-May 2020 and the standard bottle D155286 (Table S2) from mid-May 2020."*

Gas Canister VOC Standard Quality Assurance Certificate

Gas canister serial number: **R2845**

Ionicon guarantees the listed concentrations for a period of 6 months.
Uncertainty is an estimate of a combination of the uncertainties of the original gravimetric
preparation and subsequent analysis.

Compound	Volume mixing ratio / ppm	Uncertainty / %
Methanol	0.99	±6
Acetonitrile	0.99	±6
Acetaldehyde	0.95	±5
Ethanol	1.00	±5
Acrolein	1.01	±5
Acetone	0.98	±5
Isoprene	0.95	±5
Crotonaldehyde	1.01	±5
2-Butanone	0.99	±5
Benzene	0.99	±5
Toluene	0.99	±6
o-Xylene	1.02	±6
Chlorobenzene	1.01	±5
a-Pinene	1.01	±5
1,2-Dichlorobenzene	1.02	±5

Gas canisters are filled at a gauge pressure of 2.8 - 3.8 bar and are leak tested for tightness prior to
shipping. Should the canister arrive at a pressure lower than the above range, please contact Ionicon
immediately; the canister may have developed a leak during transportation and should be returned to
Ionicon for refilling.

Jürgen Dunkl
Canister filled by

Signature

10 December 2018
Date   Ionicon Stamp:

IONICON ANALYTIK
Gesellschaft mbH
**Eduard-Bodem-Gasse 3
6020 Innsbruck, Austria**
Tel.: +43 (0) 512 214 800
Fax: +43 (0) 512 214 800-099
office@i   on.com
w w.IO   ON.com

Doc v.4.3; 01.03.2018

Figure R9: Certificate of the canister R2845 used for PTR-ToF-MS calibrations.

2.4.3.

S3 text

71) If you cant calibrate for formaldehyde, drop it…

As m/z 31 is presented as "formaldehyde proxy", we would like to keep it as it is. In the figures of this paper, m/z 31 is not presented alone, only within the sum of oxygenated, where it constitutes only 2%.

72) The main source for acetaldehyde is not biomass burning (or not only). There is photochemistry and even biogenic. Please rephrase and show references.

Thank you for pointing that out, it was a mistake, biomass burning should have been associated to acetonitrile and not acetaldehyde. Both sentences are rephrased as: *"At m/z 42, CH3CN (acetonitrile) is the main compound measured; interferences from other compounds are negligible (Yuan et al., 2017b). Acetaldehyde is the main component detected at m/z 45 (de Gouw and Warneke, 2006)."*

73) m/z 46 how can you calibrate for them two with transmission only?the same goes for m57

We are not sure what is meant here, nevertheless here are some information about the calibration of m/z 46 and m/z 57. m/z 46 is calibrated by transmission only while m/z 57 is calibrated using a standard containing propenal for most of the periods and using the transmission from October 2020 to June 2021.

74) you say corresponds when I think the word here is we have assigned this mass to this compound. Please change.

Following the reviewer's suggestion, the wording "assigned to" has been used in the revised Text S3 as:

"m/z 31 was assigned to CH_2O (formaldehyde), which cannot be precisely quantified by PTR-MS, due to its proton affinity being too close to that of water, and is thus defined as its proxy. m/z 33 was assigned to CH_3OH (methanol), the main alcohol present in the atmosphere, and is also the most important oxygenated VOC; although at this mass there are interferences from O_2^+, thus resulting in a high background. At m/z 42, CH_3CN (acetonitrile) is the main compound measured; interferences from other compounds are negligible (Yuan et al., 2017b). Acetaldehyde is the main component detected at m/z 45 (de Gouw and Warneke, 2006). m/z 46 can correspond to several compounds: it was mostly identified as CH_3NO and C_2H_7N, respectively formamide and dimethylamine, both compounds emitted by agricultural activities (Yuan et al., 2017a; Kammer et al., 2019). However, a few studies reported this mass as NO_2^+, that would correspond notably to peroxyacetyl nitrate (PAN) fragmentations (Yuan et al., 2017b) or other organic nitrates (Aoki et al., 2007; Duncianu et al., 2017), but cannot be precisely quantify using H_3O^+ ionization. In this study, we will refer to it as m/z 46 (or m46). m/z 47 was assigned to C_2H_6O (ethanol) and CH_2O_2 (formic acid) and will therefore be referred to as their sum, although the sensitivity of ethanol is lower than that of formic acid. Their seasonal contribution can be found in Table 2, and shows that m/z 47 is dominated by formic acid in spring and

summer (> 90%), but in autumn and winter, ethanol contribution becomes significant. This is a similar trend to that of furan's and isoprene's contributions to m/z 69. m/z 57 is usually attributed to propenal (C_3H_4O) (Knighton et al., 2007; Languille et al., 2020), but there are interferences from C_4H_8: butenes or other hydrocarbons' fragmentations, that cannot be precisely quantified but seem to be dominant in our study (Table 2). m/z 58 was assigned to allylamine, a compound emitted by agricultural activities (Kammer et al., 2019). m/z 59 could correspond to C_3H_6O (acetone + propanal), C_4H_{10} (butane) and $C_2H_2O_2$ (glyoxal); PTR-ToF-MS measurements showed that in all seasons, C_3H_6O is dominant by about 97%. de Gouw and Warneke (2007) indicated that propanal is also negligible and m/z 59 can be regarded as acetone only. m/z 60 was assigned to trimethylamine, which is mostly emitted by agricultural activities (Kammer et al., 2019). m/z 61 is attributed to acetic acid, an agricultural and biogenic compound. m/z 63 was assigned to dimethylsulfide, emitted by phytoplanktonic activities in the oceans. m/z 69 was assigned to C_4H_4O: furan and C_5H_8: isoprene and fragments of methylbutenol (MBO), but PTR-ToF-MS measurements showed that MBO is negligible (see discussion of m/z 87). Furan is emitted by biomass-burning activities and has highest contributions in autumn and winter (47-67% of m/z 69, Table 2); while in spring and summer, m/z 69 can be almost exclusively attributed to isoprene (94-96% of m/z 69, Table 2), due to its important biogenic source, although it can also be emitted by anthropogenic sources (Borbon et al., 2001; Wagner and Kuttler, 2014; Panopoulou, 2020). m/z 71 was mainly (by about 85%) attributed to C_4H_6O, the sum of methyl vinyl ketone (MVK), methacrolein (MACR), ISOPOOH, and crotonaldehyde. ISOPOOH are formed from isoprene oxidation under low NO_X conditions (Surratt et al., 2010; Budisulistiorini et al., 2013), and so are expected to be low in a suburban area. In summer, MVK + MACR would be dominant as they are the main isoprene oxidation products, and crotonaldehyde might dominate m/z 71 in winter, due to its wood burning source (Lipari et al., 1984; Languille et al., 2020). Due to its overall higher level in summer, this m/z will be considered as MVK + MACR. m/z 73 was mainly attributed to methyl ethyl ketone (MEK) in ambient air (Yuan et al., 2017b). m/z 75 was identified as $C_3H_6O_2$ (methylacetate, hydroxyacetone, propanoic acid); methylacetate would be a biomass burning compound (Bruns et al., 2017), while hydroxyacetone and propanoic acid are of biogenic origins (Yuan et al., 2017b). It is not possible to separate these compounds because they are isomers, but methylacetate is expected to be the dominant VOC in winter and hydroxyacetone + propanoic acid to be dominant in summer. m/z 79 was assigned to benzene (C_6H_6). m/z 81 was assigned to fragments of monoterpenes (mostly) and of PAHs. m/z 83 was identified as methylfuran (C_5H_6O), that can be found in biomass burning plumes (Bruns et al., 2016), and as a minor oxidation product of isoprene (Kroll et al., 2006; and references therein). This mass was also identified as C_6H_{10}, fragments of hydrocarbons (HC) from gasoline and diesel cars (Gueneron et al., 2015). In winter and autumn, methylfuran is dominant (Table 2) while C_6H_{10} is significant in spring and summer. m/z 85 was mainly assigned to methylbutenone (C_5H_8O), identified as a biomass burning compound by (Bruns et al., 2017) and as a biogenic compound by Kroll et al. (2006). m/z 87 was assigned to $C_4H_6O_2$ (butanedione + methacrylic acid) and $C_5H_{10}O$ (methylbutenol, MBO). Butanedione was found in biomass burning plumes (Bruns et al., 2017), methacrylic acid was identified as an isoprene oxidation product (Williams et al., 2001; Nguyen, 2012) and MBO was shown to be emitted by biogenic sources (Holzinger et al, 2005; Kim et al., 2010). PTR-ToF-MS measurements showed that $C_4H_6O_2$ is dominant (> 80%), thus butanedione would be the main compound in winter and methacrylic acid (MAA) in summer. m/z 93 was assigned to toluene (C_7H_8), a major traffic compound. m/z 97 can be attributed to several compounds such

as C2-substituted furans and furaldehydes (Yuan et al., 2017b), but Bruns et al. (2017) reported this mass as furfural ($C_5H_4O_2$) in biomass-burning influenced regions, and Languille et al. (2020) also defined m/z 97 as furfural in winter at SIRTA. m/z 99 was identified as $C_5H_6O_2$ (furfuryl alcohol) by (Stockwell et al., 2015), and as $C_4H_2O_3$ (furandione) by Bruns et al. (2017), both present in aged biomass burning plumes. In this study, both compounds are present so this mass will be regarded as their sum. m/z 107 was assigned to C_8H_{10} (C8-aromatics: xylenes, ethylbenzene) and C_7H_6O (benzaldehyde); C8-aromatics are dominant by about 80% (Table 2), and thus this mass will be regarded as mainly C8-aromatics. m/z 111 was identified as benzenediol by Bruns et al. (2016) as a biomass burning compound. m/z 121 was assigned to C9-aromatics (trimethylbenzenes), mainly emitted by traffic. m/z 137 was assigned to monoterpenes, for which the main source is supposed to be biogenic, although anthropogenic sources, traffic and wood burning, were identified recently (Panopoulou et al., 2020). m/z 139 was assigned to nopinone, an oxidation product of monoterpenes. m/z 147 was assigned to dichlorobenzene. m/z 151 is identified as $C_9H_{10}O_2$, pinonaldehyde, an alpha-pinene ozonolysis product. Pinonaldehyde is measured at m/z 169 and at m/z 151, which corresponds to pinonaldehyde-H_2O."

2.4.4.

75) Please state how did you calculate the statistical error, the systematic error, and how did you use the theory of error propagation. This information is totally missing. Also how did you calculate the LOD.

76) I think you cant cite ACTRIS guidelines, because they are not ready yet. On the other hand please state which are those guidelines.

This part is completed in the main text of the revised version as: *"The detection limit (LOD) and the uncertainties for each m/z were calculated using the formulas from the ACTRIS guidelines (in preparation), which are based on de Gouw and Warneke (2006):*

$$LOD = 3 \times \frac{\sqrt{C_{RH^+}^{blank}}}{S_m(RH^+)} \tag{1}$$

With $C_{RH^+}^{blank}$ the ion count per second of the blank signal and $S_m(RH^+)$ the unnormalized sensitivity (cps/ppb).

$$Uncertainty = \sqrt{Precision^2 + Accuracy^2 + 0.05^2} \tag{2}$$

With the precision calculated as the relative standard deviation:

$$RSD = \frac{\sqrt{C_{RH^+}^{ambient} + C_{RH^+}^{blank}}}{C_{RH^+}^{ambient} - C_{RH^+}^{blank}} \tag{3}$$

With $C_{RH^+}^{ambient}$ and $C_{RH^+}^{blank}$ the ion counts for the ambient and blank signals, respectively.

The accuracy corresponds to the quadratic propagation of the error on the GCU and on the standard. The error on the GCU was evaluated to be equal to 10% and the errors on the standard for each compound are available on its certificate and range from 5 to 10%. Finally, an error of 5% is added to take into account the uncertainty due to humidity changes."

77) Line 223 what do you mean by internal quality check by carefully verifying? How is the quality check by ACTRIS, please state. What is ebas database, please state.

This part is completed as: *"An internal quality check is performed on all m/z, while an external quality control is also performed by ACTRIS on 12 masses corresponding to the following compounds: benzene, propenal+C4H8, isoprene+furan, C8-aromatics, monoterpenes, toluene, acetonitrile, acetaldehyde, acetone, MEK, methanol and MVK+MACR. The internal quality control corresponds to carefully verifying each step of the data treatment and the obtained data and deleting erroneous or outlier data points. The external quality check is performed by the Central Facility unit of ACTRIS responsible for VOCs measurements (CiGas). It consists in carefully examining the dataset and performing different figures (e.g., scatter plots, ...) to point out and discuss questionable data (outliers, potential contamination....). These data can then be flagged accordingly (valid but lower than the detection limit, valid but corresponding to a local event, or missing because invalidated). In addition, for long-lived compounds, a comparison with baseline values from other European station is performed to check the consistency of the datasets. Once the submitted data and corresponding flags are compliant and validated by ACTRIS, they are made available on Ebas, which is the ACTRIS open-source database. The 2020-2021 dataset presented here can therefore be found on the corresponding website under https://ebas-data.nilu.no."*

78) 3.1 I suggest using statistics (like correlations or heatmap) to group compounds, as in the city you have many different sources, and perhaps what is expected may not be the reality. And also have you considered doing a positive matrix factorization? This could really help on source identification.

The compounds are not grouped by sources here, as these might differ for a single m/z throughout the year. Some correlations are provided in Table S5 for the winter seasons. Preliminary PMF runs were indeed performed but a thorough PMF analysis is beyond the scope of the present paper.

79) Line 242: this statement about methanol and acetone is inconsistence with Figure 4, oxygenated compounds have even higher yaxis.

This sentence is rephrased as: *"Methanol and acetone were separated from the other oxygenated VOC due to their concentration (2-3 times higher than other individual oxygenated compounds) and for the sake of clarity in the next graphs."*

80) Line 246. I really do not understand why you pass to concentrations when comparing ppb across other literarture could be valuable. The only thing I need to know is that you indeed use real temp and atm pressure data to calculate this, per point. Correct?

All figures will be redone with the values in ppb.

81) Line 258: you keep saying isoprene is the most important biogenic compound, and this is not true. It may be the most copiously emitted, but there are species who do not emit isoprene. So rephrase these statements.

In the revised version, this is rephrased as: *"Within the non-aromatic hydrocarbons, monoterpenes have roughly the same boxplot values than isoprene; indeed, monoterpene levels can be as high or higher than isoprene levels in urban regions (Panopoulou et al, 2020), indicating other sources than the biogenic one."*

82) Why are monoterpene concentrations important during winter? And why only in winter, if it is a source from the city, (i.e. perfumery, or cleaning products industry) wouldn't it be all over the year?

This sentence is rephrased as: *"The high median value of m/z 137 could be explained by an important wintertime contribution (Figure 4)."*

83) Despite im not really happy with a figure 2 because it does not give you much info as it is averaged over summer and winter and day and night, so I expect a huge variability, I do not know what is the purpose of figure 3. Please rephrase the purpose of the figure or remove.

Figure 2 gives an overview of the statistical range, while the seasonal and diurnal variabilities are discussed using Figures 4, 7 and 8. Following both reviewers' suggestion, Figure 3 is removed in the revised version.

3.2.

84) Are the trajectories more dominant in particular seasons? Please also state this.

Table R6 (Table S7 in the revised paper) presents the percentage of air mass clusters per season and this sentence is updated in the main text: *"Continental air masses and air masses from the North are more dominant in Spring (around 40%), while the oceanic 1 cluster is more occurrent in Winter (45%, Table S7)."*

Table R4: Percentage of occurrence of air mass clusters per season

%	DJF	MAM	JJA	SON
Continental	21	37	18	23
Anticyclonic	26	20	24	31
Oceanic 1	45	13	23	19
Oceanic 2	26	21	29	24
North 1	13	35	28	24
North 2	16	40	17	27

3.3

85) Line 381:where does the 77% comes from?

This sentence is rephrased as: *"On Figure 8 c, the sum of isoprene and furan shows a more biogenic diurnal cycle because isoprene is dominant (77%, Table 2), with an increasing level in the morning due to enhanced emission with higher temperature and solar radiation."*

4.

86) Explain what flags are

This is explained in Section 2.4.1 (where internal & external quality checks are described), see comment 77.

References

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Response to the comment from the editor on essd-2022-406 "Two years of Volatile Organic Compounds online in-situ measurements at SIRTA (Paris region, France) using Proton-Transfer-Reaction Mass Spectrometry"

Dear Editor,

We thank you for your attention to our manuscript. We responded point by point to the reviewers' comments herewith, and we updated the revised version in order to provide more details on the used quality assurance and quality control procedures, including the description of calibration protocols, supplementary tables and figures evaluating the quality of the data. Furthermore, a new section is added where our dataset for the suburban SIRTA station is compared for some compounds with independent measurements provided by the regional network for air quality monitoring of the Greater Paris area (AirParif) in the center of Paris. This is why a new author (Alexia Baudic from Airparif) is added in the revised manuscript.

Please note that the guidelines for the data treatment and validation from the European infrastructure for aerosols, clouds, and trace gases (ACTRIS) are being finalized and therefore improvements can still be done to reduce the uncertainty; nevertheless, we think that we have produced and presented a robust dataset which can feed a wide user community.

Please also note that we now underline the need of harmonized protocols for PTR-MS long-term measurements in the conclusions, as follows:

"In this paper, we provide the first long-term VOC dataset obtained using PTR-MS measurements at a suburban site in Europe. This two-year dataset contains 31 mass-to-charge ratios (m/z) corresponding to 30+ compounds of interest for atmospheric chemistry research, identified thanks to additional PTR-ToF-MS measurements. Because long-term PTR-MS measurements are still scarce worldwide, we adapted existing recommendations in order to meet the inherent requirements of pluri-annual observations. Data have been carefully inspected following quality control and quality assurance procedures, resulting in a robust dataset. Since long-term PTR-MS measurements are likely to be implemented in a growing number of stations (especially within ACTRIS), harmonized protocols and guidelines are much needed in order to ensure the comparability of the data."