Response to the reviewers' comments 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.
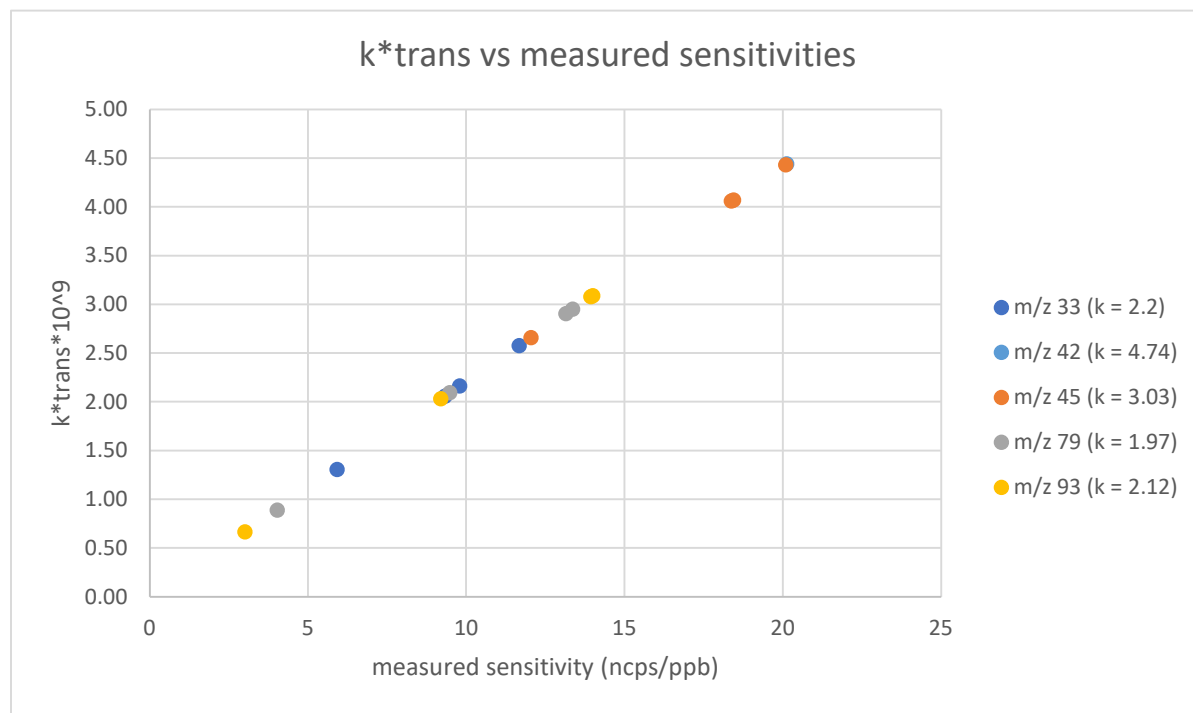
Figure R1: k*transmission vs measured sensitivity for a few species of different k rates

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."

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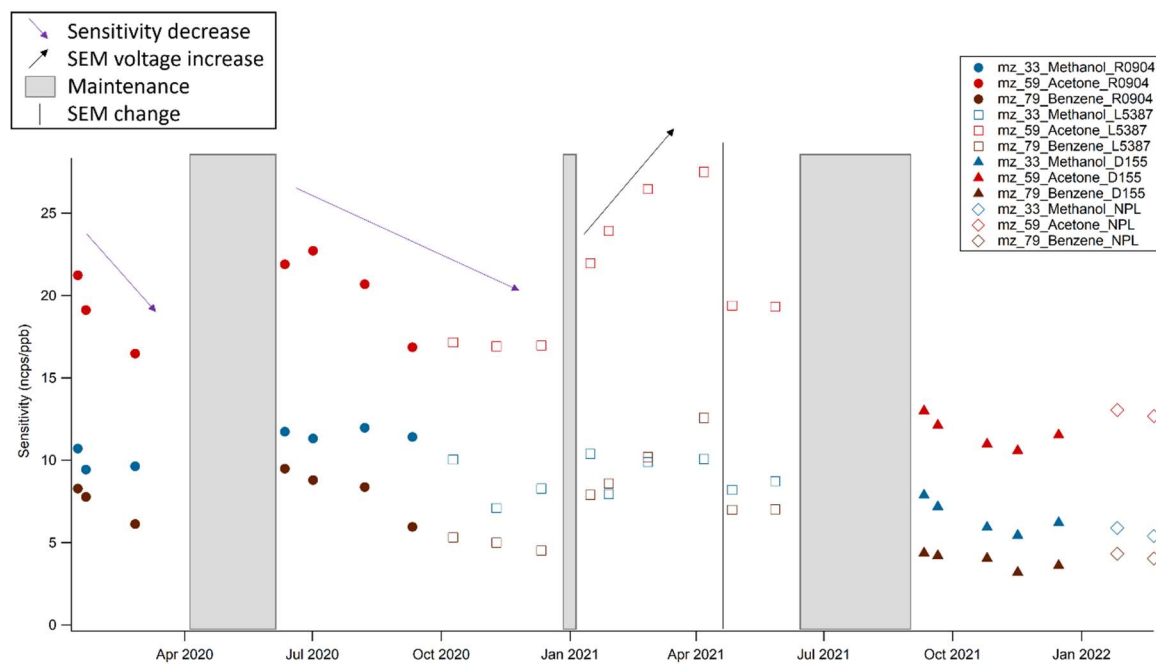
Figure R2: Time series of sensitivities vs time for methanol, acetone and benzene. Standard references are indicated by the shape of the data points (cf Table S2).

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
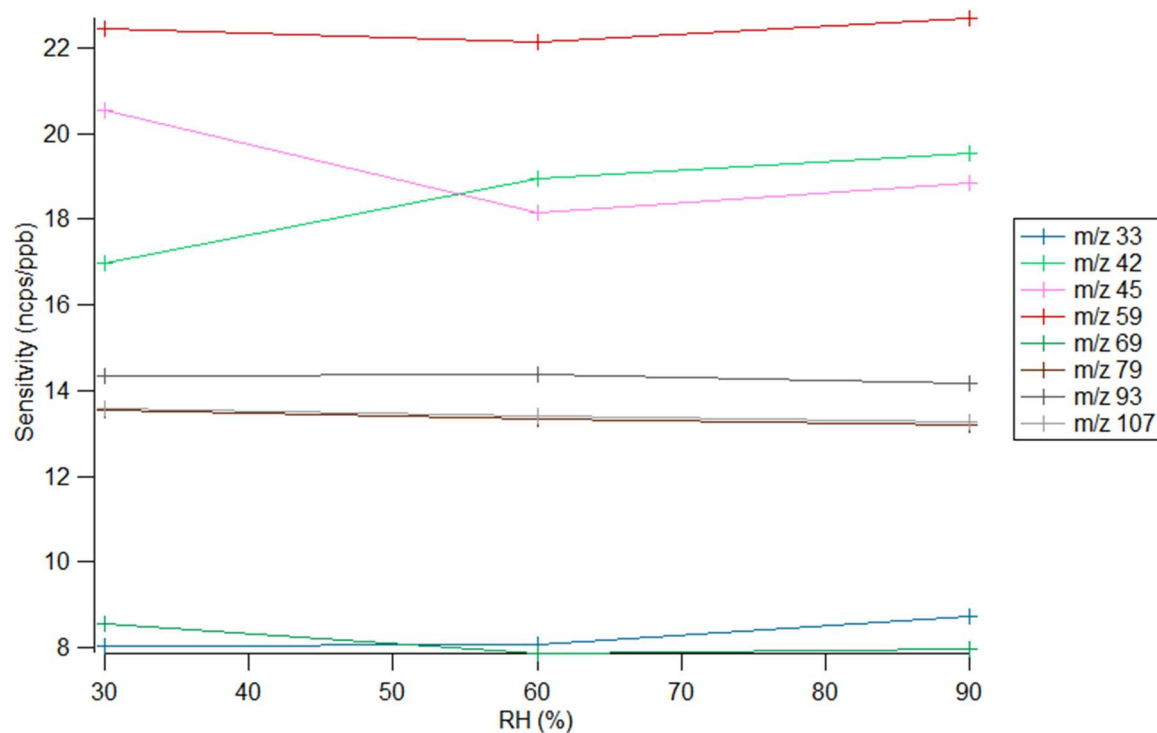
Figure R3: Sensitivities vs RH

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):

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

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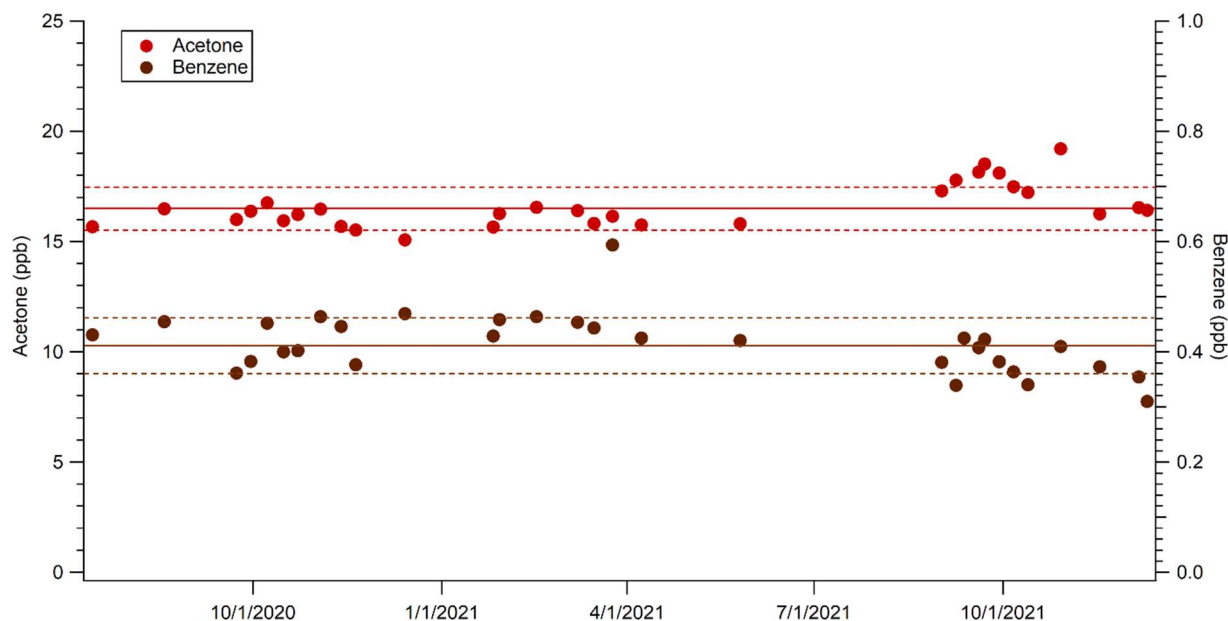
Figure R4: Temporal evolution of acetone and benzene measurements from the target bottle. The lines represent the mean value while the dashed lines represent mean +/- standard deviation.

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."*
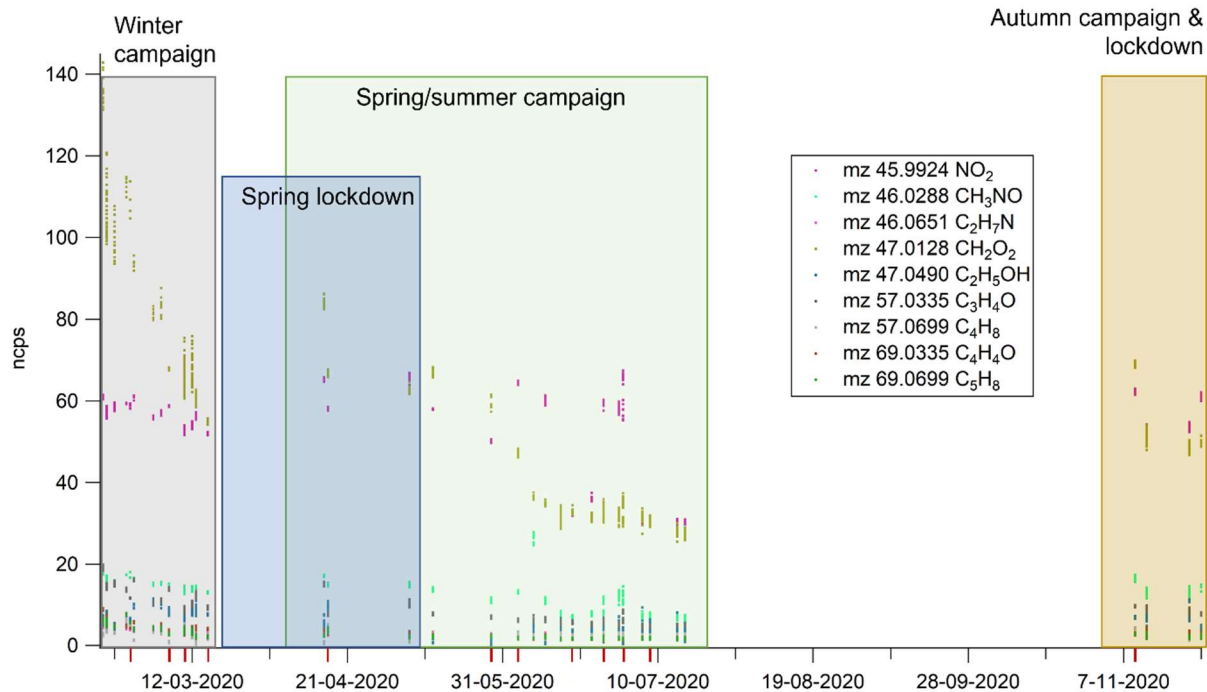
Figure R5: Blanks performed in 2020 for a selection of PTR-ToF-MS m/z. Calibrations are indicated by red sticks.

> *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."

Research & Development
office@ionicon.com

IONICON ANALYTIK GMBH
Eduard-Bodem-Gasse 3
A-6020 Innsbruck
AUSTRIA

Tel: +43 512 214 800
Fax: +43 512 214 800 099
www.ionicon.com

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
α-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@ionicon.com
www.IONICON.com

Doc v.4.3; 01.03.2018

Page 1 of 1

Figure R6: Certificate of the canister R2845 used for PTR-ToF-MS calibrations.
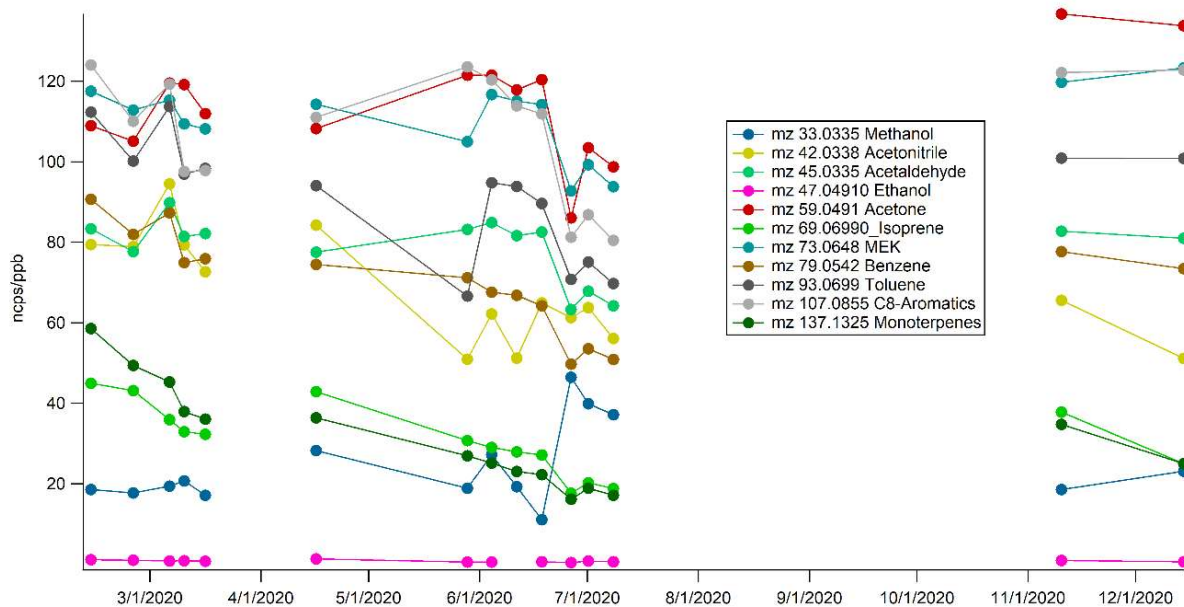
Figure R7: Temporal evolution of measured sensitivities for the PTR-ToF-MS, the different campaigns are separated by the discontinuity of the line.

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):*

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

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

$$Uncertainty = \sqrt{Precision^2 + Accuracy^2 + 0.05^2} \qquad (3)$$

With the precision calculated as the relative standard deviation:

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

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."*
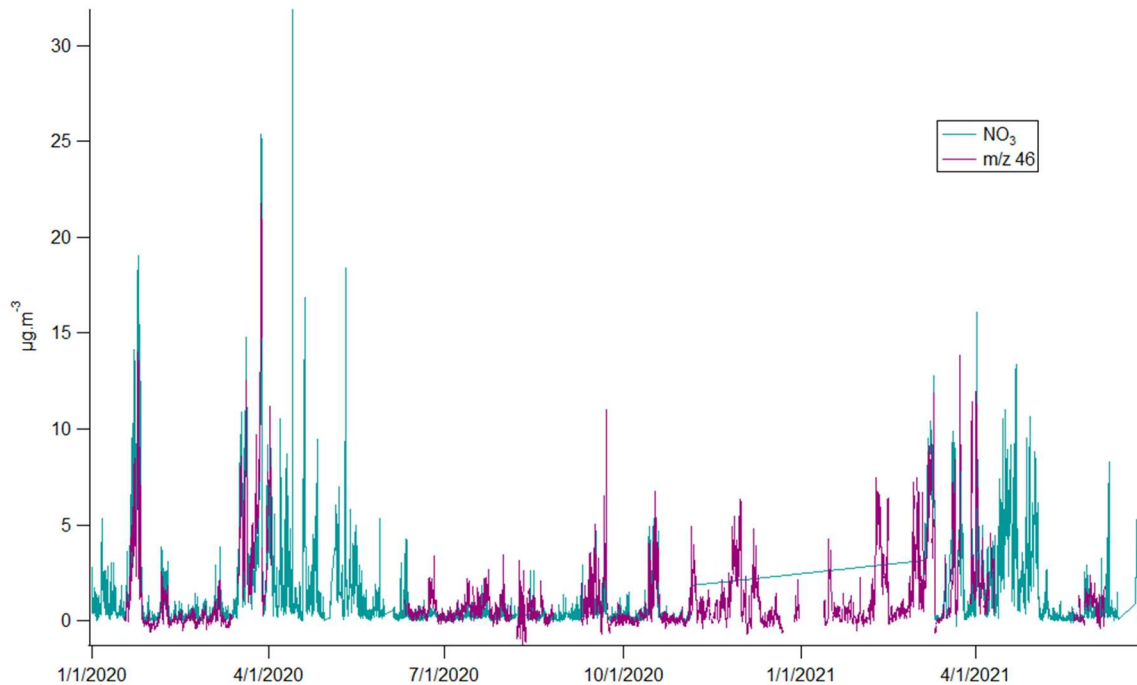
Figure R8: Temporal evolution of m/z 46 and NO3 from ACSM measurements
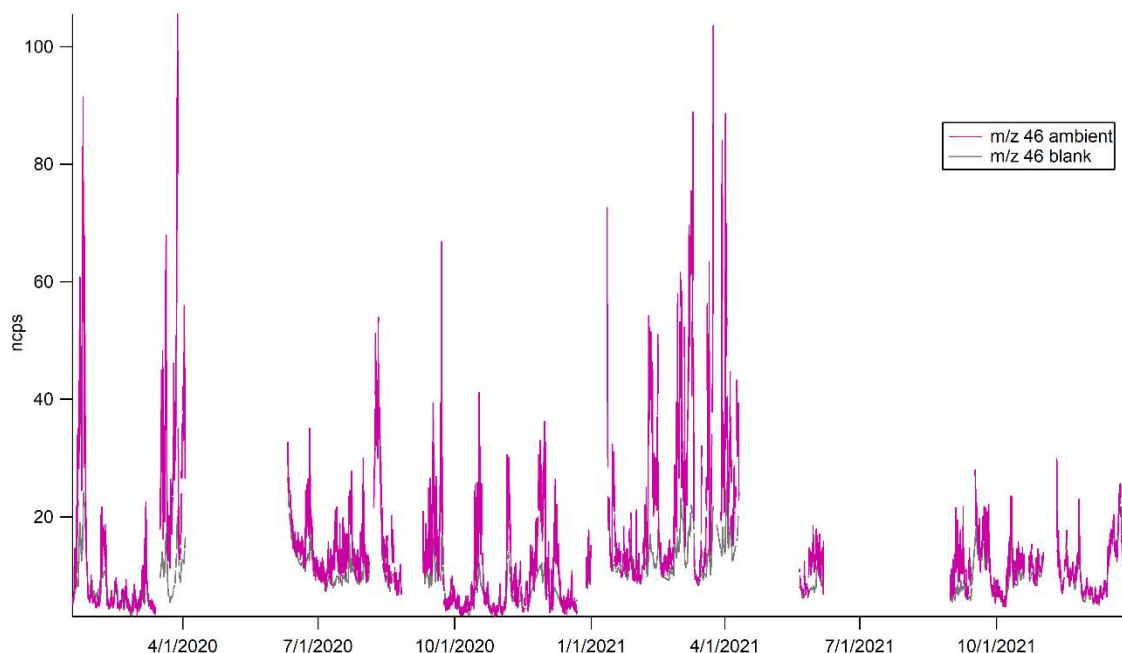
Figure R9: Temporal evolution of m/z blank and ambient ncps measurements

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."

References

Ghirardo, A., Lindstein, F., Koch, K., Buegger, F., Schloter, M., Albert, A., Michelsen, A., Winkler, J. B., Schnitzler, J.-P., and Rinnan, R.: Origin of volatile organic compound emissions from subarctic tundra under global warming, Global Change Biology, 26, 1908–1925, https://doi.org/10.1111/gcb.14935, 2020.

de Gouw, J. and Warneke, C.: Measurements of volatile organic compounds in the earth's atmosphere using proton-transfer-reaction mass spectrometry, Mass Spectrom. Rev., 26, 223–257, https://doi.org/10.1002/mas.20119, 2007.

Holzinger, R., Acton, W. J. F., Bloss, W. J., Breitenlechner, M., Crilley, L. R., Dusanter, S., Gonin, M., Gros, V., Keutsch, F. N., Kiendler-Scharr, A., Kramer, L. J., Krechmer, J. E., Languille, B., Locoge, N., Lopez-Hilfiker, F., Materić, D., Moreno, S., Nemitz, E., Quéléver, L. L. J., Sarda Esteve, R., Sauvage, S., Schallhart, S., Sommariva, R., Tillmann, R., Wedel, S., Worton, D. R., Xu, K., and Zaytsev, A.: Validity and limitations of simple reaction kinetics to calculate concentrations of organic compounds from ion counts in PTR-MS, Atmos. Meas. Tech., 12, 6193–6208, https://doi.org/10.5194/amt-12-6193-2019, 2019.

Kotthaus, S. and Grimmond, C. S. B.: Atmospheric boundary-layer characteristics from ceilometer measurements. Part 1: A new method to track mixed layer height and classify clouds, Quarterly Journal of the Royal Meteorological Society, 144, 1525–1538, https://doi.org/10.1002/qj.3299, 2018.

Li, K., Li, J., Tong, S., Wang, W., Huang, R.-J., and Ge, M.: Characteristics of wintertime VOCs in suburban and urban Beijing: concentrations, emission ratios, and festival effects, Atmospheric Chemistry and Physics, 19, 8021–8036, https://doi.org/10.5194/acp-19-8021-2019, 2019.

Lindinger, W., Jordan, A., and Hansel, A: Proton-transfer-reaction mass spectrometry (PTR–MS): on-line monitoring of volatile organic compounds at pptv levels, Chem. Soc. Rev., 27, 347, https://doi.org/10.1039/a827347z, 1998.

Pagonis, D., Sekimoto, K., and de Gouw, J.: A Library of Proton-Transfer Reactions of H3O+ Ions Used for Trace Gas Detection, J. Am. Soc. Mass Spectrom., 30, 1330–1335, https://doi.org/10.1007/s13361-019-02209-3, 2019.

Panopoulou, A.: Yearlong measurements of monoterpenes and isoprene in a Mediterranean city (Athens): Natural vs anthropogenic origin, Atmospheric Environment, 12, 2020.

Petit, J.-E., Dupont, J.-C., Favez, O., Gros, V., Zhang, Y., Sciare, J., Simon, L., Truong, F., Bonnaire, N., Amodeo, T., Vautard, R., and Haeffelin, M.: Response of atmospheric composition to COVID-19 lockdown measures during spring in the Paris region (France), Atmos. Chem. Phys., 21, 17167–17183, https://doi.org/10.5194/acp-21-17167-2021, 2021.

Španěl, P., Wang, T., and Smith, D.: A selected ion flow tube, SIFT, study of the reactions of H3O+, NO+ and O2+ ions with a series of diols, International Journal of Mass Spectrometry, 218, 227–236, https://doi.org/10.1016/S1387-3806(02)00724-8, 2002.

Yuan, B., Koss, A. R., Warneke, C., Coggon, M., and Sekimoto, K.: Proton-Transfer-Reaction Mass Spectrometry: Applications in Atmospheric Sciences, Chem. Rev., 43, 2017.

Zhang, H., Chen, C., Yan, W., Wu, N., Bo, Y., Zhang, Q., and He, K.: Characteristics and sources of non-methane VOCs and their roles in SOA formation during autumn in a central Chinese city, Science of The Total Environment, 782, 146802, https://doi.org/10.1016/j.scitotenv.2021.146802, 2021.

Zhao, J. and Zhang, R.: Proton transfer reaction rate constants between hydronium ion (H3O+) and volatile organic compounds, Atmospheric Environment, 38, 2177–2185, https://doi.org/10.1016/j.atmosenv.2004.01.019, 2004.