Point-to-point response to Referee #1 (RC1)

We are grateful for yours comments on how to strengthen our manuscript. Please find attached revised manuscript and see our point-to-point response to your comments below:

1. **As mentioned on the Title, page 1 line 16, page 4 line 1 and elsewhere the authors state that this is a new or newly developed method. Nevertheless, a method bearing great similarities has been already described in the past (Bauer et al, 2009 and references therein). The paper describes an analyser of a different manufacturer that "also determines optical OC and optical EC by monitoring the laser transmission data through the quartz filter", "Total carbon (TC) is determined using the thermal-optical method, and then optical OC is deduced by subtracting optical EC from TC (optical OC =TC -optical EC)".Where optical OC and EC would be simply a different terminology given for eOC and eEC used in the current paper. How would the authors comment on the method similarities of the two studies and the suitability of the description "new" for the method?**

There are conceptual similarities between method mentioned above (Bauer et al., 2009) and TC- BC method developed in this study: the new method takes the advantage of decoupling thermal and optical method into two separate instruments, both dedicated for different measurements. With this, the new method has higher time resolution, no dead time, online loading compensation for eBC measurements and is more convenient for field measurements as the thermal measurement is done without fragile quartz cross oven, high purity gases and catalyst. The main difference are listed and described in details below:

- The optical EC in semi continuous Sunset instrument is a measurement of transmittance through the filter at a wavelength of 660 nm prior to the thermal analysis, while the equivalent eEC is an equivalent BC measurement with AE33 at 880 nm, then multiplied by a proportionality factor b (eEC = bBC). Contribution of light absorbing organics is higher at 660 nm.
- Light source used in AE33 is non-coherent set of light emitting diodes (LEDs) with diffuser-like optics (BC6 is measured at 880 nm), while the semi continuous Sunset instrument uses diode laser at 660 nm. Distorted wave fronts of LEDs produce homogeneous signal on the exposed filter area and the transmittance signal has no speckle/interference noise, making the LED light source far more convenient for filter attenuation (ATN) measurements.
- The presence of the loading effect in filter-based absorption photometers causes an ATN-dependent change in the instrumental sensitivity. The Aethalometer model AE33 performs real time compensation for this nonlinearity using patented dual spot algorithm.
- ATN in AE33 is determined more precisely as detector intensity signal for the measurement spot I and detector signal for the reference spot I_o are measured concurrently. Any drift in LED light intensity due to temperature and other changes are compensated in real time. While the stabilization of laser source is possible but there are no publication describing this process for Sunset semi-continuous instrument.
- When the attenuation reaches a certain threshold, a tape advance is induced so that measurements starts on a clean spot. Significant buildup of refractory substances on

the filter in the semi continuous Sunset instrument will reduce initial intensity and introduce higher signal to noise ratio at each subsequent optical analysis. Two dedicated instruments are better for this purpose.

A short paragraph was added to the manuscript (Chapter: 2.1 TC-BC method for online high time resolved OC-EC measurements, p. 4, lines 17-21:

- Although one can find conceptual similarities between method presented in Bauer et al., 2009 (and references therein) and TC- BC method presented in this study, the new method takes the advantage of decoupling thermal and optical method into two separate instruments, both dedicated for different measurements. With this, the new method has higher time resolution, no sampling dead time, online loading nonlinearity compensation for eBC measurements (Drinovec et al., 2017) and is more convenient for field measurements as the thermal measurement is done without fragile quartz cross oven, high purity gases and catalyst.

Two references were added to the manuscript:

- Bauer, J. J., Yu, X.-Y., Cary, R., Laulainen, N., and Berkowitz, C.: Characterization of the Sunset Semi-Continuous Carbon Aerosol Analyzer, J. Air Waste Manag. Assoc., 59(7), 826–833, doi:10.3155/1047-3289.59.7.826, 2009.

- Drinovec, L., Gregorič, A., Zotter, P., Wolf, R., Bruns, E. A., Prévôt, A. S. H., Petit, J.-E., Favez, O., Sciare, J., Arnold, I. J., Chakrabarty, R. K., Moosmüller, H., Filep, A., and Močnik, G.: The filter-loading effect by ambient aerosols in filter absorption photometers depends on the coating of the sampled particles, Atm. Meas. Tech., 10(3), 1043–1059, doi:10.5194/amt-10-1043-2017, 2017.

2. **While the terms of OC, EC and eOC, eEC are clearly defined, their use in the text overlaps and is occasionally confused. Proper terminology should be consistently used in order to avoid any misinterpretations by readers. For example, the abstract mentions in lines 22-23 that this new application can result in high time resolution determination of organic and elemental carbon while in reality it provides an estimation of eOC and eEC values. Another example would be in section 3.6: eOC and eEC should be used instead of OC and EC. Also applicable in all graphs.**

Terms OC, EC and eOC and eEC where changed throughout the manuscript using proper terminology as follows:
- Page 1, line 20: The concentration of particulate equivalent organic carbon (eOC) is determined by subtracting black carbon concentration, concurrently measured optically by an Aethalometer®, from the total carbon concentration measured by the TCA08.
- Page 1, line 23: The combination of TCA08 and Aethalometer (AE33) is an easy-to-deploy and low maintenance continuous measurement technique for the high time resolution determination of equivalent organic and elemental carbon (eEC) in different particulate matter size fractions, which avoids pyrolytic correction and need for high purity compressed gases.
- Page 9, Table 2:

| OC (see Eq.7) | eOC | 31 | 0.94 | 0.99 ± 0.02 | 0.98 | 0.86 ± 0.02 | 1.33 ± 0.18 |
| eOC | OM$_{ACSM}$ | 300 | 0.96 | 1.82 ± 0.01 | 0.97 | 2.05 ± 0.02 | -2.45 ± 0.20 |

Table 2: Summarized comparison results between off-line filter measurements and 24 h average values of high-time resolution measurements of TC, BC, eOC and OM; and between high time resolution measurements (3h) of eOC and OMACSM measurements.

- Page 16, line 15: 3.5Comparison of online eOC measurements from TCA with offline OC filter analyses.
- Page 16, line 16: Online eOC measurements can be derived using the above EC-BC correlation plot to assign the appropriate operational value of the parameter *b*; the online BC data; and the online TCA data.
- Page 16, line 19: These results show that when using an appropriate value of *b*, the "TC – BC Method" yields online data for the eOC content of ambient aerosols that agree very well with conventional offline thermal analyses.
- Page 16, line 23: The in-depth analysis of the relative difference between OC from 24 h filters and eOC determined by online measurement as TC-*b*BC shown in Fig. 9 reveals that the positive artefact can be the dominant apparent source of OC for days with very low OC concentrations ($< 5\ \mu g/m^3$) in comparison to offline 24 h filters, for which also negative artefact (desorption of VOCs) can occur.
- Page 17, Figure 8. eOC on y-axis
- Page 18, Figure 9. eOC and eEC on y-axis.
- Page 18, line 8: 3.6 Comparison of OM online measurements from ACSM with offline OC from filter sampling and online eOC
- Page 18, line 9: The data from an AE33 and TCA08 can be combined with an operational timebase of 1 hour, yielding eOC and eEC data with much greater time resolution than what can be achieved by the analysis of filter samples.
- Page 20, Figure 11: eOC on x-axis.
- Page 20, Line 10: (b) Comparison of 3h eOC data derived as eOC = TC - bBC, to OM data measured by ACSM.
- Page 21, line 6: The diurnal variation of eOC and eEC for this urban background environment is strongly influenced by the temporal patterns of emissions from traffic and biomass burning (domestic heating) during wintertime.
- Page 21, line 9: When the TCA08 is combined with an AE33Aethalometer, the TC-BC method yields eOC-eEC data with much greater time resolution than that offered by the analysis of filter-based samples.

3. **NDIR detectors, similarly to the one in the current application, may deteriorate in performance in long term and show a drift in their baseline. Since there is no application of an internal standard calibration or a span check, have the authors evaluated how often would an external standard calibration be required? Would there be any NDIR detector related maintenance needs, e.g. source replacement, and in what frequency would that be required?**

Light source life in Licor 840A NDIR detector is estimated to be 18000 hours. When light source fails the TCA instrument detects it, stops the measurements and displays Licor CO2 Error status.

Total Carbon content of the sample measured by TCA08 is a function of a CO2 difference between signal and background values and thus not directly connected to absolute value of CO2 (Eq. 4). That is why the TC result is less dependent on the light source drift in the NDIR

detector than if the absolute value is used in the calculations. Additionally, the drift of the dual wavelength light source in the NDIR detector used in TCA08 is compensated online. Concentration measurements of CO_2 are based on the difference ratio in IR absorption between sample and reference signal. The CO_2 sample uses an optical filter centred at wavelength of 4.26 μm corresponding to an absorption band for CO2. The reference channel for CO2 has an optical filter centered at 3.95 μm, which has no absorption due to CO2.

During NDIR detector lifetime there is no need to preform internal standard calibration and span check for TC measurements, as the whole system (NDIR detector + TCA analytic chamber) can be calibrated or validated with Carbon Calibration and Carbon Validation procedure for TCA08. This the great benefit of this instrument. Both procedures are described in TCA08 User Manual (TCA08, 2019). Carbon calibration of TCA08 should be done once per year or after any major maintenance or modification of the system.

A short paragraph was added to the manuscript (p. 6, lines: 11-20):

- Light source life in LI-840A CO2/H2O Analyser is estimated to be 18000 hours. When light source fails the TCA instrument detects it, stops the measurements and displays Licor CO_2 error status. Total Carbon content of the sample measured by TCA08 is a function of a CO_2 difference between signal and background values and thus not directly connected to absolute value of CO_2 (Eq. 4). This is why the TC result is less dependent on the light source drift in the NDIR detector than if the absolute value is used in the calculations. During light source lifetime there is no need to preform internal standard calibration and span check for NDIR detector, as the whole system (NDIR detector + TCA08 analytic chamber) can be calibrated or validated with Carbon Calibration and Carbon Validation procedure for TCA08, which is the great benefit of this instrument. Both procedures are described in TCA08 User Manual (TCA08, 2019). Carbon calibration of TCA08 should be done once per year or after any major maintenance or modification of the system.

4. **The last paragraph of section 2.3 describes tests performed on the denuder efficiency but it seems that results are not included in the paper. Page 7, line 21 also refers to TC data "(see below", which are not presented later on in the text. Related to the denuder efficiency, there is clear evidence of a positive artefact for eOC concentrations below 8µg/m3, visible in Figure 8 (OC vs eOC) as well as in Figure 11 (b) (OM vs eOC). Further there are signs of a negative artefact for higher concentrations, based on the same graphs, suggesting reduced combustion efficiency. The later would be more profound if there would be an addition of second denuder monolith as suggested in page 12 lines 25-27 or if a correction for the positive artefact would be applied. Should the user then consider the use of 2 correction factors (b) related to the concentration levels measured? Or would there be any other suggestion to overcome these issues?**

As we noted in the first paragraph of chapter 2.3 the measurement of carbonaceous aerosols using quartz-fiber filters is always very challenging because of the possibility of positive and negative sampling artifacts which are hard to quantify. The TCA08 instrument was developed in a way, that sampling face velocity was similar to the one of high volume samplers for offline analysis for easier comparison. With shorter sample time basis the positive artefact is much more pronounced and negative artefact can be neglected.

We believe that TCA08 with its denuder efficiency procedure is a great tool to investigate (1) denuder efficiency and (2) temporally variations of positive/negative artefact. In our current study (Gregorič et al., 2019, 2020), positive and negative artefact on quartz filters depending on sample time base, face velocity, number of denuders, chemical deposition of aerosol is investigated in details. When investigating dependence on sample time base, we found out that adsorption of organic vapors in TCA08 can be described with a sum of two exponential functions with $a_1*(1 - Exp[-x/\tau_1]) + a_2*(1 - Exp[-x/\tau_2]$ with a fast and slow time constants τ_1 and τ_2. Slow time constants are around 15-60 minutes, indicating that positive artefact prevails for sampling times up to 2 hours.

Nevertheless, high VOC concentrations are usually connected to high OC concentrations as well. We believe that negative artefact due to combustion efficiency mentioned by reviewer is not the reason for lower slope. External calibration of TCA shows that combustion efficiency does not reduce with higher TC, OC or EC concentrations (see Figure 1), therefore, two correction factors are not needed. Users should use appropriate number of denuders and choose appropriate sampling timebase according to denuder efficiency test and ambient TC and OC concentrations. In our next publication guidelines and recommendations on how to asses positive/negative artefact with TCA08 and how to use this knowledge for more quality measurement data will be described.
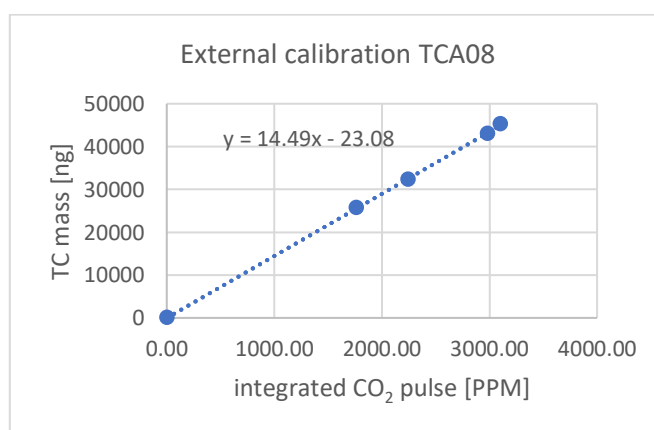

Figure 1 External calibration of TCA08 - TC mass calibration range

The last paragraph in section 2.3 was changed accordingly:
- We developed these routines during the instrument design and performed the measurements as part of the field campaign (see Section 3). After five weeks of continuous operation with consistent TC data (see below), the measured denuder efficiency was 74%. We recommend that the denuder should be replaced or regenerated when its efficiency drops below 70% (Ania et al., 2005; Bhagawan et al., 2015; Gao et al., 2014). The Standard Operating Procedure for routine use of the TCA08 instrument recommends replacement or regeneration of the denuder honeycomb element once per month. Further, in environments with high VOC concentrations, two denuder honeycombs in series are recommended (Gregorič et al., 2020).

5. **Section 3 refers to EN 16450:2017 regarding the orthogonal regression analysis on the 31 daily measurements between the new instrument (candidate method) and 2 independent laboratories (reference method). A proper application of EN16450:2017 would require a minimum of 40 valid data pairs with the further requirement of 2 candidate applications for each type testing application. EN16450:2017 further describes requirements related to the number of locations and the concentration range of data points. The use of just one candidate method limits the conclusions on performance consistency between identical instruments and restricts the candidate method uncertainty calculations. It seems that quite a significant part of section 3 discusses the comparability between the two reference method applications, which is a topic thoroughly documented elsewhere in the literature (Intercomparison exercises publications are included in the reference list of the current paper). A more relevant approach would have included and compared two new instruments in parallel measurements. How would the authors comment on the approach applied and the data suitability?**

We agree with reviewer that equivalence comparison was not done exactly according to standard EN 16450:2017, but it is our best attempt to do it so. As there is no standard for reference method for online measurement of OC and EC concentrations available at the time of the writing of this manuscript, we followed EN16450:2017 and choose EN 16909:2017, 2017 as the reference method. The comparison was done on the available data (31 daily filters - limitations of DIGITEL high volume sampler availability). Furthermore, we used only one set of instrument for the candidate method comparison, as they are both compared to the reference set of instruments after their assembly (in-house defined requirements for successful intercomparing test are: 1. TCA08: TC concentration range up to 75.000 ng/m^3, slope between 0.97-1.03, R^2 above 0.98 ; 2. AE33: eBC concentrations up to 30.000 ng/m^3; slope between 0.97-1.03, R^2 above 0.98). Table below (Table 1) shows results of such comparison for TCA08 instrument.

	Instruments serial number	Slope	R^2	N	TC value max (ng)	TC value min (ng)
1	TCA08-S00-0131	1.0216	0.9975	65	45856	2732
2	TCA08-S00-0132	1.0098	0.9992	65	45803	2732
3	TCA08-S00-0133	1.0041	0.9993	19	67274	6286
4	TCA08-S00-0134	0.9987	0.9989	19	67274	6286
5	TCA08-S00-0135	0.9967	0.9994	19	67274	6286
6	TCA08-S00-0136	0.9874	0.9992	139	76684	2498
7	TCA08-S00-0137	0.9964	0.9987	65	51119	2592
8	TCA08-S00-0138	0.9867	0.9993	65	51119	2592
9	TCA08-S00-0139	0.9605	0.9988	65	51119	2592
10	TCA08-S00-0140	1.0168	0.999	62	73190	2644
11	TCA08-S00-0141	0.9974	0.9998	22	64579	3336
12	TCA08-S00-0142	1.0057	0.998	136	76466	2823
13	TCA08-S00-0143	0.9967	0.9989	22	64579	3336
14	TCA08-S00-0144	0.9972	0.9993	22	64609	3336
15	TCA08-S00-0145	0.9699	0.9978	137	72992	2823

Following paragraph was added to the manuscript (page 9, lines: 12-21):

- As there is no standard for reference method for online measurement of OC and EC concentrations available at the time of the writing of this manuscript, we followed EN16450:2017 and choose EN 16909:2017 as the reference method. Nevertheless, a proper application of EN16450:2017 would require a minimum of 40 valid data pairs with the further requirement of two candidate applications for each type testing application. Additionally, the same standard further describes requirements related to the number of locations and the concentration range of data points. The results and discussion in this chapter is our best attempt of equivalence comparison on the available data (31 daily filters due to the limited access to the DIGITEL high volume sampler). Furthermore, we used only one set of instrument for the candidate method comparison, as they are both compared to the reference set of instruments after their assembly as one of the tests during final inspection procedure (in-house defined requirements for successful intercomparison test are: 1. TCA08: TC concentration range up to 75.000 ng/m3, slope between 0.95-1.05, R2 above 0.98 ; 2. AE33: eBC concentrations up to 20.000 ng/m3; slope between 0.95-1.05, R2 above 0.98).

6. **The uncertainty limit value of 2.00 µg/m$_3$ mentioned in page 10 line 13 originates from calculations of PM reference methods where limit values of 30µg/m$_2$ or more apply. Would that be directly applicable for TC method and concentrations? Further section 3.3 describes method uncertainty calculations based on the NDIR detector response. Have the authors considered additional sources of uncertainty to be included in the uncertainty budget, e.g. use of denuder, zero air carrier gas, ambient temperature and pressure variations?**

Carbonaceous aerosols frequently account for a large and often dominant fraction of fine particulate matter (PM2.5) mass in polluted atmospheres. Total carbon mass concentrations can contribute up to 50% of PM2.5 mass in special pollution events, which justify the use of uncertainty limit value of 2.00 µg/m^3 for TC concentrations.

Temperature and pressure variations during sampling are measured with meteorological sensor and are included into calculations as the volumetric sample flow is used for concentration calculations. During analysis temperature and pressure of the analytic stream are measured within NDIR sensor and are included in CO_2 concentration determination.

Uncertainty due to variations in zero carrier (analytic) gas during thermal analysis was tested by measuring replicates of blank samples. This approach is also used for Limit of Detection determination, which is 0.3 µg of TC for TCA08. Again, before entering the chamber, the analytic air passes through a 10-liter buffer volume for ambient CO_2 fluctuation averaging and a capsule filter filled with activated carbon and pleated glass fiber filter, which removes organic gases and particles from the stream.

An example of such LoD determination for TCA08-S00-00103 is shown in table below (Table 2)

Blank measurement	TC counts (ppm)	TC (ng)
1	11.8427	186.4
2	1.3997	23.22
3	0.5914	9.31
4	2.4629	40.86
5	7.7607	122.15
6	9.803	162.63
7	0.0469	0.74
8	3.2019	53.12
9	-0.7977	-12.56
10	8.2248	136.45
11	-5.9253	-93.26
12	12.3681	205.19
13	-9.4706	-149.07
14	17.5429	291.04
15	9.1144	143.46
16	4.7438	78.7
17	1.0516	16.55
18	-2.4038	-37.84
19	6.3558	105.44
20	12.1225	201.11
21	10.3992	163.68
22	5.6442	88.84
23	-3.9845	-62.72

Table 2 Measurements of replicates of blank samples in order to determine Limit od detection (LoD). LoD = mean + 2 SD = 300 ng of TC

We did not include positive artefact and denuder efficiency in the uncertainty budget, as they are also not considered in the uncertainty budget in standards EN 12341:2014 and EN 16909:2017:

- **EN 12341:2014, Chapter 9.3.2.11:** Artefacts due to interactions between the filter material and gasses: In addition to water, filter materials my adsorb volatile compounds presented in the sampled air. Examples hereof are ammonia, nitrogen dioxide and organic gases. Contributions to the filter mass will vary with concentration of the gases and the chemical nature of the filter material. Adsorption may even lead to a reduction of losses of semi-volatile constituents of PM (9.3.2.4). Consequently, the magnitude of the effects of adsorption of gases cannot be quantified. For the purpose of application of this European Standard the phenomenon is recognized but not considered in the uncertainty budget.
- **EN 16909:2017, Chapter 9.2**: All sampling artefacts are inherent by convention and part of the EC and OC values according to this standard. Sampling artefacts are mainly to be expected for OC and they can be significant (Chow et al. [12]).

A following sentences were added to the manuscript:

- (page 11, lines 12-13):
  The uncertainty u_{RM} between the reference methods for TC

$$u_{\text{RM}}^2 = \frac{1}{2n}\sum_{i=1}^{n}\left(TC_{i,\text{ARSO}} - TC_{i,\text{IGE}}\right)^2 \qquad (6)$$

  is 0.43 µg/m³ which is well below the limit of 2.00 µg/m³ requested for reference methods for PM mass concentration measurements (EN 16450:2017, 2017).
- (page 14, lines 15-22):
  where LoD is the limit of detection of the TCA08 at a sample flowrate of 16.7 LPM and sample timebase of 1h. In the uncertainty budget of TC measurement with the TCA08 the following sources of uncertainties were not included: (1) Temperature and pressure variations in the sample flow as they are measured by meteorological sensor and included in TC concentration calculations. (2) Temperature and pressure variations in analytical flow as both parameters are measured within NDIR Licor sensor and included in CO_2 concentration determination. (3) Sampling artefacts and denuder efficiency: positive/negative artefact phenomenon is recognized by standards EN 12341:2014 and EN 16909:2017, but, as the magnitude of these effects cannot be quantified precisely, they are not considered in the uncertainty budget.

7. High volume samples were collected for analysis by the two laboratories. Is there information available on the type of the filters used? Was the homogeneity of the samples estimated for this study? Did the laboratories analyze the samples in triplicate or duplicate and were there standard external solutions analyzed like in most of the comparison exercises referenced in the text? Standard solutions may provide an insight if the difference between the TC results of the 2 laboratories was a result of calibration deviations.

The filters used for offline sample are 150 mm Tissuquartz 2500 Qat-Up produced by Pall Corporation. The homogeneity of samples was tested by ARSO laboratory for 5 random filters from the campaign. In the table (Table 3) below results of the homogeneity test are shown:

Date	OC [1 st] µg/cm2	EC [1 st] µg/cm2	TC [1 st] µg/cm2	OC [2nd] µg/cm2	EC [2nd] µg/cm2	TC [2nd] µg/cm2	ABS DIFF OC µg/cm2	ABS DIFF EC µg/cm2	ABS DIFF TC µg/cm2
18/02/2017	27.34	4.11	31.45	27.18	4.34	31.52	0.15	0.23	0.07
03/03/2017	29.15	8.22	37.37	29.77	9.96	39.73	0.62	1.74	2.37
08/03/2017	17.50	7.78	25.28	17.75	7.91	25.66	0.25	0.12	0.37
09/03/2017	32.07	10.21	42.29	31.82	11.02	42.85	0.25	0.81	0.56
10/03/2017	19.78	5.82	25.60	18.51	5.69	24.20	1.27	0.13	1.40

Table 4 Results of homogeneity test for 5 different filters from the measurement campaign

Both laboratories use standard calibration solutions and quality control procedures according to standard EN 16909. Additionally, both laboratories were part of ACTRIS exercises and follow ACTRIS guidelines and recommended practices:
- IGE laboratory (Inter-laboratory comparison 2016 and 2017, contact person: Jean Luc Jaffrezo), (ACTRIS, 2016, 2017)

- ARSO laboratory (inter-laboratory comparison 2018, contact person: Judita Burger), (ACTRIS, 2018)

8. **A common practice in comparison exercises is following identical procedures on filter handling, transport and storage for all participants. In the current case filters were first analyzed by the ARSO laboratory and then shipped to IGE for further analysis. Even though the authors mention that "sampling, transport and storage of the filters was done according to the EN 16909:2017" IGE received the filters for analysis at a later period, after additional transport, handling and storage. Could that have contributed to the small uncertainty observed between the reference methods? Wouldn't an approach of dividing the samples and shipping in both labs in parallel have resulted in improved comparability of the two laboratories?**

We agree with the reviewer, it would be better to wait for the end of the campaign, than divide the filters and afterwards analyze them in both laboratories. Nevertheless, all measures were taken to assure that shipped samples to IGE were not contaminated. The measurement campaign was conducted between 7 February and 10 March 2017 at the urban background air quality monitoring station of the Slovenian Environmental Agency (ARSO). After the cartridge with 14 sampled filters was replaced by a cartridge with fresh filters, the sampled filters were stored at ARSO storage facility according to EN 169090:2017. They were analyzed in order by date in three days: 20 Feb 2017, 8 March 2017 and 21 March 2017. Afterwards, approx. 40 mm punches of these filters were stored in sealed petri dishes in shipped to IGE laboratory by express postal service. During shipment the petri dishes containing the filter punches were stored in cooled portable freezer box with temperatures between 5-15 $^\circ$C.

9. **Table 3 provides with a wide range of b factors and the recommendation right above is: "the determination needs to be performed for each location and with filters sampled over the time-period of interest". Considering that the b factor is location and season specific, could the authors suggest a typical coverage period range with OC/EC offline analysis in parallel? How often would the b factor have to be re-evaluated per location?**

The proportionality parameter *b* is an effective value with a local and regional component. Usually, the local contribution to concentrations is dominant and the local BC and EC contributions dominate the relationship. The differences in *b* values presented in Table 3 show, that there is a big variation between different rural/regional background sites, and also between the urban sites. This is the reason why similar offline-to-online intercomparison is recommended for every new background site or site with strong mixture of local and regional contribution. The time period of intercomparison should cover seasonal variations in *b* values, for example 2-3 weeks each season. The re-evaluation intercomparison campaign for the certain location should be done if significant changes in the BC emission inventory is expected (traffic or wood burning restrictions, *etc.*). For sites with dominant traffic contribution, where the *b* factor mostly depends on the properties of the vehicle in the fleet, the intercomparison measurements will result in similar *b* values unless a significant fleet change occurs.

Following sentences were added to the manuscript:

- (page 15., lines 11-18)

The proportionality parameter *b* (Eq. 3) is compared with values taken from the literature in Table 3. These values depend on the location, the nature of the aerosol, and the thermal protocol used for analysis. The value of 0.44 which we determined in this study for an urban background site is slightly lower than values for other urban and urban background sites using EUSAAR 2 thermal protocol, and considerably lower than the values for rural sites. The proportionality parameter *b* is an effective value that features a local and a regional contribution of BC and EC. Usually, the local contribution to concentrations is dominant and the local BC and EC contributions dominate the relationship. The differences in *b* values presented in Table 3 show, that there is a big variation between different rural/regional background sites, and also between the urban sites. This is the reason why similar offline-to-online intercomparison is recommended for every new background site or site with strong mixture of local and regional contribution. The time period of the intercomparison should cover seasonal variations in *b* values, for example 2-3 weeks each season. The re-evaluation intercomparison campaign for the certain location should be done if significant changes in the BC emission inventory is expected (traffic or wood burning restrictions, *etc.*) For sites with dominant traffic contribution, where the b factor mostly depends on the properties of the vehicle in the fleet, the intercomparison measurements will result in similar *b* values unless a significant fleet change occurs.

10. **The calculated b factor for this study (0.44) is the lowest among EUSAAR_2 users of the literature listed in Table 3. Further the slope from the OM – eOC comparison of (Figure 11,(b)) is 1.82, and would have been even higher when considering the high negative intercept. Following the ranges provided by the literature in page 17, lines 14-15, these slopes fit better a rural site rather than an urban environment. This comes in contradiction with the characteristics of the selected site which is influenced from traffic emissions. If the estimated b factor was within the literature range that would have further resulted in a lower OM - eOC slope and would fit the literature range better. How would the authors comment on these observed differences compared to the literature?**

There is a big variation between different rural/regional background sites, and also between the urban sites. These differences show that a site and season specific factor *b* needs to be assessed. The obtained OM/OC of 1.82 indicates on mixture of traffic and biomass emissions which agrees with other studies done in Ljubljana (Gjerek et al., 2018; Ogrin et al., 2016). Ljubljana is located in a subalpine basin surrounded by hills. Large forest areas provide a cheap heating source, which represents a government promoted alternative to the use of fossil fuel. While the measurement of black carbon in Ljubljana apportioned to traffic show great variability in concentrations among measurement sites, the contribution of biomass burning is spatially distributed much more homogeneously across wider area in Ljubljana. In winter 2013/14 campaign at 2 urban background measuring sites, study showed averaged value of BC from traffic of 2.5 ± 1.8 µg/m^3, while from biomass burning contribution of 1 ± 0.7 µg/m^3 (Ogrin et al., 2016).

11. **Following Graph 7, it seems that in the first half of the campaign BC is overestimated while on the second half underestimated, compared to EC. Would there be any interpretations for this observation? Further, around the 5th of March eOC and TC from the TCA08 configuration**

are overestimated and bBC is underestimated, significantly more from the rest of the data points. Would there be any justification by the authors?

Detailed analysis of the EC and BC data does not reveal any new interpretation of this observation. Analysis of the 24 h averaged values of the loading compensation parameter k6 and eEC concentrations shown in Figure 2 does not show any significant change of the coating of the BC particles during measurement campaign that could have an effect on the measured eEC concentrations (Drinovec et al., 2017).
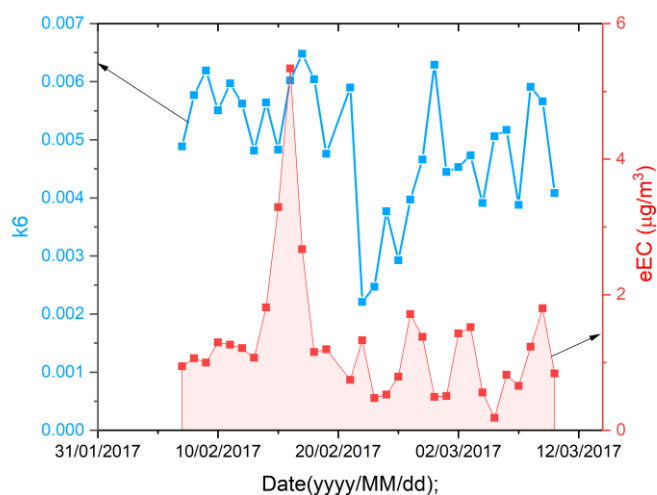

Figure 2 Loading compensation parameter k6 and eEC concentrations during measurement campaign

Similary, the comparison of the offline analysis for EC on filter by sampling date (Figure 3) or by date of the analysis at the ARSO laboratory (Figure 4) does not show any significant descripancies. At the moment, the temporal variations of descripancy between eEC and offline EC values is unknown.
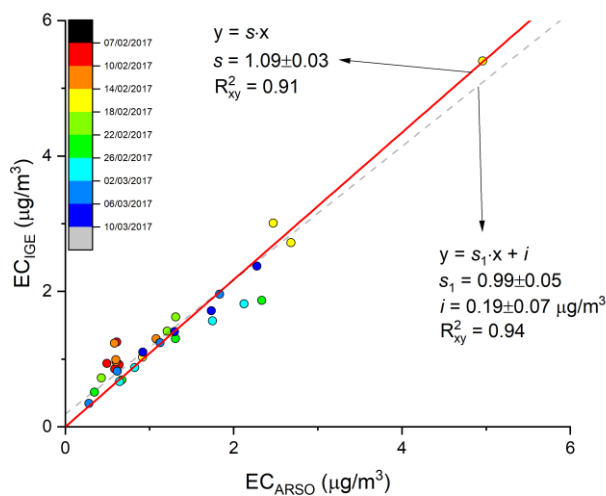

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Figure 3 Comparison of offline EC analysis between ARSO and IGE laboratories sorted by sampling date.
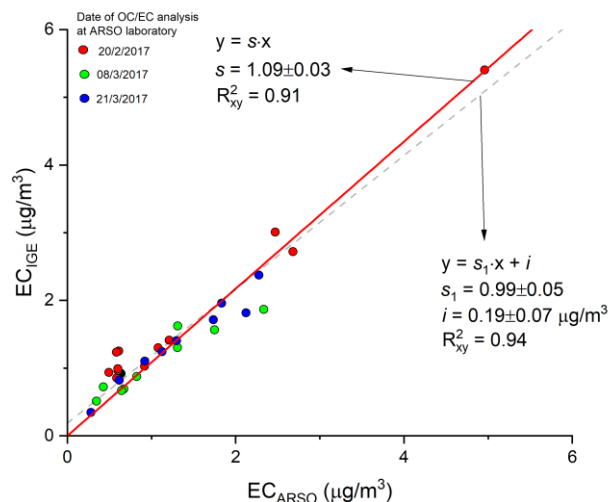
Figure 4 Comparison of offline EC analysis between ARSO and IGE laboratories sorted by the date of analysis by ARSO laboratory.

12. Page 15, lines 19-21, suggest that the intercept due to the eOC positive artefact can be neglected based on the comparability with the OC intercept of the two independent laboratory measurements. Nevertheless, as discussed earlier in the text, the eOC intercept is systematic and attributed to the denuder performance. It should also be noted that the eOC concentrations are compared to the average values between the two laboratories. It would be more appropriate if the artefacts observed for a new instrument would not be overlooked but rather investigated further and be dealt with. The use of two candidate method analyzers and an extended data set would be required for in-depth analysis. The above comes also in contradiction with the conclusion of page 20, line 12: "the correlation analysis showed very high agreement between eOC and eEC to the EC and OC". It seems that there is room for improvement in agreement once the artefact issues are resolved.

We agree with the reviewer. We are aware of the importance of OC positive/negative artefact when comparing online OC/EC instruments to analysis of the 24h filters. In our current study (Gregorič et al., 2020), positive and negative artefact on quartz filters depending on sample time base, face velocity, number of denuders, chemical deposition of aerosol is investigated in details in order to quantify the magnitude of these effects. In this publication guidelines and recommendations on how to asses positive/negative artefact with TCA08 and how to use this knowledge for more quality measurement data will be described. Again, positive artefact and denuder efficiency is recognized by standards EN 12341:2014 and EN 16909:2017: but not included in the uncertainty budget.

Please refer to points 4, 5, and 6 for details.

13. Technical corrections:
Page 2, line 26: tTe.
- The amount of OC converted into PC during the analysis depends on many factors, including the amount and type of organic compounds, the sources of air pollution,

temperature steps in the analysis, the residence time at each temperature step, and the presence of certain inorganic constituents (Yu et al., 2002).

Page 15, line 4: It is not clear on which comparison the authors refer.

- The EC data determined by offline OC/EC analysis used in the comparison depends greatly on the thermal protocol used (Karanasiou et al., 2015).

Page 17, line 21: Fig 10(b) to Fig 11(b).

- The negative offset in the regression model with intercept (Fig. 11 (b)) again reveals the pronounced positive sampling artefact due to adsorption of organics on quartz fiber filters for short sampling times in TCA08 method.

Page 18: Figure 11 (a) misses the dashed trendline.

- Figure 11: (a) Comparison of offline measurements of OC (laboratory filter analysis) using the EUSAAR_2 thermal protocol, to the 24-hour average of online measurement of OM data taken by the ACSM. A total of 31 filter samples were collected for analysis during the campaign. Please note that red trendline completely covers dashed trendline (s=s1). (b) Comparison of 3h eOC data derived as eOC = TC - bBC, to OM data measured by ACSM. Linear orthogonal regression results are shown with s as the slope (red line) for the model without an intercept and with s1 as slope and i as intercept (dashed gray line) for the model with a intercept. R2xy is the square of the Pearson correlation coefficient. 300 data points are used in the regression analysis.

References:

ACTRIS: Results of the inter-laboratory comparison exercise for TC and EC measurements. [online] Available from: https://www.actris-ecac.eu/files/ECAC-report-OCEC-2016-1.pdf, 2016.

ACTRIS: Results of the inter-laboratory comparison exercise for TC and EC measurements. [online] Available from: https://www.actris-ecac.eu/files/ECAC-report-OCEC-2017-1.pdf, 2017.

ACTRIS: Results of the inter-laboratory comparison exercise for TC and EC measurements. [online] Available from: https://www.actris-ecac.eu/files/ECAC-report-OCEC-2018-1.pdf, 2018.

Ania, C. O., Parra, J. B., Menendez, J. A. and Pis, J. J.: Effect of microwave and conventional regeneration on the microporous and mesoporous network and on the adsorptive capacity of activated carbons, Microporous Mesoporous Mater., 85(1), 7–15, 2005.

Bauer, J. J., Yu, X.-Y., Cary, R., Laulainen, N. and Berkowitz, C.: Characterization of the Sunset Semi-Continuous Carbon Aerosol Analyzer, J. Air Waste Manag. Assoc., 59(7), 826–833, doi:10.3155/1047-3289.59.7.826, 2009.

Bhagawan, D., Poodari, S., Ravi kumar, G., Golla, S., Anand, Ch., Banda, K. S., Himabindu, V. and Vidyavathi, S.: Reactivation and recycling of spent carbon using solvent desorption followed by thermal treatment (TR), J. Mater. Cycles Waste Manag., 17(1), 185–193, doi:10.1007/s10163-014-0237-y, 2015.

Drinovec, L., Gregorič, A., Zotter, P., Wolf, R., Bruns, E. A., Prévôt, A. S. H., Petit, J.-E., Favez, O., Sciare, J., Arnold, I. J., Chakrabarty, R. K., Moosmüller, H., Filep, A. and Močnik, G.: The filter-loading effect by ambient aerosols in filter absorption photometers depends on the coating of the sampled particles, Atmospheric Meas. Tech., 10(3), 1043–1059, doi:10.5194/amt-10-1043-2017, 2017.

EN 12341:2014: Ambient air - Standard gravimetric measurement method for the determination of the PM10 or PM2,5 mass concetration of suspended particulate matter, EN 123412014, 2014.

EN 16450:2017: Ambient air - Automated measuring systems for the measurement of concentration of particulate matter (PM10; PM2.5), EN 164502017, 2017.

EN 16909:2017: Ambient air - Measurement of elemental carbon (EC) and organic carbon (OC) collected on filters, , EN 16909:2017, 2017.

Gao, Y., Zhong, D., Zhang, D., Pu, X., Shao, X., Su, C., Yao, X. and Li, S.: Thermal regeneration of recyclable reduced graphene oxide/Fe$_3$O$_4$ composites with improved adsorption properties: Thermal regeneration of recyclable RGO/Fe$_3$O$_4$ composites, J. Chem. Technol. Biotechnol., 89(12), 1859–1865, doi:10.1002/jctb.4268, 2014.

Gjerek, M., Koleša, T., Logar, M., Matavž, L., Murovec, M., Rus, M. and Žabkar, R.: Air qualitiy in Slovenia 2017, 2018.

Gregorič, A., Lavrič, G., Drinovec, L., Močnik, G. and Rigler, M.: VOC Denuder Efficiency and Positive Sampling Artefact Evaluation Using the Total Carbon Analyzer (TCA 08), Prep., 2020.

Ogrin, M., Vintar Mally, K., Planinšek, A., Gregorič, A., Drinovec, L. and Močnik, G.: Nitrogen Dioxide and Black Carbon Concentrations in Ljubljana, 1st ed., Ljubljana University Press, Faculty of Arts, Ljubljana., 2016.

TCA08: Total Carbon Analyzer TCA 08 - User's Manual, 2019.

Yu, J. Z., Xu, J. and Yang, H.: Charring Characteristics of Atmospheric Organic Particulate Matter in Thermal Analysis, Environ. Sci. Technol., 36(4), 754–761, doi:10.1021/es015540q, 2002.