Author Comment with regard to:

"Estimation of atmospheric total organic carbon (TOC) – paving the path towards carbon budget closure"

by M. Yang and Z. Fleming

Many thanks for the thorough *comments and suggestions from Anonymous Referee #2*. We are very glad to hear that the referee found our contribution interesting. Below are our replies to the referee's comments, which are in *italic*.

Anonymous Referee #2

Summary:

The authors measured total organic carbon using a Picarro CH4/CO2 analyzer in combination with a platinum catalyst in an urban area in the UK for one month. The total organic carbon was compared to speciated VOC from PTR-MS. A weekday/weekend effect was discovered. The sum of speciated PTR VOCs accounted for about 60% of measured TOC. The missing species are suggested.

Total Organic Carbon is an interesting and worthwhile measurement target and I think the approach the authors have taken here is reasonable. The analysis of the data is clear and appropriate. The close value of the overall total OC in marine air to other values reported in the literature is an interesting result.

Major questions

The authors are attempting to measure a small value (~10ppb of "missing" carbon) on top of a large, imprecise background (400 ppm of atmospheric CO2 with a precision of 100 ppb). I think this is possible with a lot of time-averaging over a period with stable concentrations. However there is very little recognition and discussion of the difficulties associated with making a highly precise measurement atop a large background. For example, it is stated that methane is combusted with 98.7% efficiency; however, at typical atmospheric mixing ratios this corresponds to 40-50ppb which is much larger than the target VOC concentrations. CO was not measured, and the uncertainty in the reconstructed CO (~6-8ppb) is on the same order as the suggested missing VOC.

The large backgrounds in the major gases (especially CO2) are definitely the most important sources of random uncertainty in the TOC measurement. The very high precision/stability of the CO2/CH4 instrument and the frequent alternation between the ambient air and catalyst-scrubbed air measurement (enabling further averaging) help to largely overcome these challenges.

We note that in equation 1:

$$TOC + CO = CO2^* + CH4^* - CO2 - CH4$$

The small amount (1.3%) of yet-to-be oxidized CH4 is accounted for in the CH4* term. Furthermore, any errors in the 'zeros' of the CO2 and CH4 measurements should be canceled out in the equation above.

That CO was not measured at the time of the TOC+CO/PTRMS measurements is a shortcoming of this dataset. Appropriately, we do not claim to have closed the organic carbon budget in the title, abstract or conclusion. Rather, we mostly focus on presenting a new way to quantify TOC.

Additionally, the authors need to much more clearly state the time-averaging period of not just the new instrument presented here but also of the component instruments, and the previous TOC instruments cited from the literature. Otherwise it is not possible to assess and compare the various detection limits. For instance, the precision of the TOC measurement, which involves subtracting total atmospheric CO2 and CH4, can only be as precise as the precision of the direct CO2 and CH4 measurements. The CO2 measurement has a precision of 100 ppb at 2Hz. A best-case hourly precision of 8 ppb is stated, are the data presented hourly data? I understand the actual hourly precision was 30 ppb, is an 8ppb difference in speciated VOC compared to measured TOC significant with this precision? Does the calculation of the hourly precision take into account the instrument duty cycle (2 minutes ambient followed by 1 minute catalyst)?

Yes we have accounted for the instrument duty cycle in the hourly precision calculation. Specifically, consecutive ambient air (last 5 seconds of 2 minutes) & catalyst (last 25 seconds out of 1 minute) are treated together as a measurement pair. Random uncertainty scales with sqrt(N), where N = number of measurements. Thus starting from a precision of 100 ppb at 2Hz for CO2, we get sqrt((100 ppb/sqrt(10))^2+(100 ppb/sqrt(50))^2) = 34.6 ppb for each pair of measurement. There are 20 measurement pairs in an hour, and so the hourly precision becomes 34.6 ppb/sqrt(20)= 7.7 ppb (see also line 151). The precision of CH4 measurements contributes negligibly to the uncertainty of the TOC measurement.

However, the above calculation represents a best-case scenario because it assumes that the major gases (mostly CO2) are invariable. When these major gases are changing rapidly, the calculation of CO2* + CH4* - CO2 – CH4 will natural yield highly variable TOC + CO estimates. The 30 ppb mentioned on line 155 is not a precision; it's the actual standard deviation in a subset of the measurements and an indication that the major gases at this semi-polluted coastal city were never especially constant. The comparison between the estimated TOC and Sum(VOC) is made in the mean for all Atlantic-dominated airmasses (142 hours total), and not on an hour-by-hour basis.

Finally, previous TOC measurements were based on GC analyses and have a cycle time of tens of minutes.

Specific comments

32 - This is actually an estimate of the total number of species that have been measured. The extant number of species in the atmosphere is higher.

We will revise the sentence to "The total number of measured organic carbon species…"

53 - the VOC relationship to ozone and organic aerosol (both climate forcers) is another important climate-related consideration.

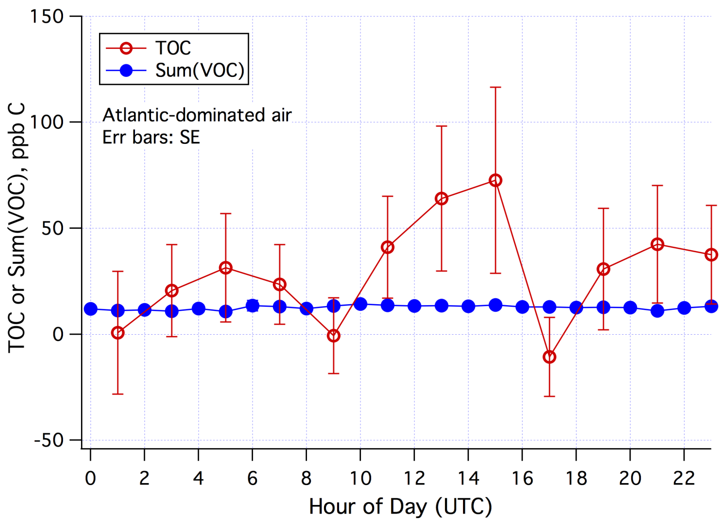
Suggestion accepted.

127 The VOC concentrations in various analytical standards are exceedingly high compared to the range of VOC measured, and the suggested amount of "missing" carbon.
Gas standard: 1295 ppb; instrument measures 63ppbv lower
Background: 39 ppb
Typical total OC: 19 ppb
Why were such high values of calibration standard concentration chosen? I strongly suggest that the instrument is re-calibrated in a more appropriate range.
We note that there is an uncertainty in the diluted gas standard (up to 78 ppb), which mostly comes from the certified certainty of the standard itself (from Apel-Riemer Environmental). The measurement of TOC system agrees with the gas standard concentration within the uncertainties. We purposely used a high standard concentration because if all the VOCs are fully oxidized at concentrations 1-2 orders of magnitude higher than ambient, we would expect these VOCs in ambient air to fully oxidize too.

151 Can you please show more clearly how these two values were calculated (35ppb and 8ppb).
See detailed derivations above.

Fig 2 It would be useful to have a figure that shows the measured TOC compared to known TOC, for the multiple-step calibration with the 6-component calibration standard shown in Figure 2.
Perhaps this was not very clear in the text, but the measurements of the oxidized gas standard by the TOC system and by the PTRMS were done separately. To measure this oxidized standard with both systems at the same time would require an approximate doubling of the gas flow rate through the catalyst, which will probably reduce the oxidation efficiency.

Figures The paper is missing a figure showing a time series or diurnal cycle of total measured OC, minus CO, on the same scale and the same plot as total measured speciated VOC. As the difference between these two measurements is a major result of the paper, this plot needs to be shown.
We have produced a plot showing the diurnal cycles of the estimated TOC and Sum(VOC) on the same scale (see below). We limited this comparison to a) Atlantic dominated airmasses only (so that we could use the CO concentration measured from Cardiff), and b) for weekends only (to reduce the effect of location pollution). We see that in this subset of data (about 200 hrs total), Sum(VOC) shows essentially no diurnal variability. The TOC estimate is noisier, with a suggestion of higher concentrations in the early afternoon. The minima in TOC at around 0900 and 1700 UTC are most likely artifacts – due to residual traffic signals in the Cardiff CO data despite the airmass selection. Having an in situ measurement of CO and a longer overlap between the measurement systems would lead to a more insightful comparison. We don't think this figure provides a lot of additional insight but can include it in the paper or in a supplementary if the referee/editor deems it necessary.



TOC
Sum(VOC)
Atlantic-dominated air
Err bars: SE
TOC or Sum(VOC), ppb C
150
100
50
0
-50
0
2
4
6
8
10
12
14
16
18
20
22
Hour of Day (UTC)