

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

Yang and Fleming, 2018

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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.

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)?

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

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