

Dear editor:

Thank you for your efforts in coordinating the reviews for “Estimation of atmospheric total organic carbon (TOC) – paving the path towards carbon budget closure.” Please find below our point-by-point replies to the referee’s comments, which are in *italic*.

**Anonymous Referee #1**

*1. Given the novel measurement approach it seems this should be described in the abstract (brief description, precision, comment on whether all species are comprehensively detected – see comment #2).*

Thanks for the suggestions. We will add the following sentences to the abstract (after the first sentence, line 13).

“Here we present a novel and simple approach to measure atmospheric non-methane total organic carbon (TOC) based on catalytic oxidation of organics in bulk air to carbon dioxide. This method shows little sensitivity towards humidity and near 100% oxidation efficiencies for all VOCs tested. We estimate a best-case hourly precision of 8 ppb C during times of low ambient variability in carbon dioxide, methane, and carbon monoxide (CO). As proof of concept of this approach, we show measurements of TOC+CO during August-September 2016 from a coastal city in the southwest United Kingdom.”

We have added this sentence to the second to last line of the abstract:

“Finally, we note that the use of a short, heated sample tube can improve the transmission of organics to the analyzer, while operating our system alternately with and without a particle filter should enable a better separation of semi-volatile and particulate organics from the VOCs within the TOC budget.”

*2. Section 2: The authors mention the inlet and briefly allude to SV/IVOCs and aerosols in the text (lines 100, 123-126). The manuscript would benefit from more discussion of this, but most importantly, the authors should reiterate these gaps in the conclusions and abstract. Ultimately the reported TOC is not comprehensive and this should be made clear to the reader, with appropriate suggestions for assessing the degree of comprehensiveness and/or improving the instrumentation in the future (as given on lines 308-309).*

See above. Also, we have added the following sentence to line 308:

“Due to the use of a long, unheated Teflon inlet tube, the semi-volatile and particulate organics were likely not well represented in the measurements presented here. A simple improvement to this measurement system would be to minimize the length of the inlet tube before the catalyst.”

*3. Section 2.1: There is some ambiguity of units in this section between ppb and ppbC and it would be useful for the units of all quantities to be carefully defined (line 115). I believe that some quantities are incorrectly given as ppb instead of ppbC (line 131, 135, 141, 145, 148, 151, 155), though it's not always clear from the text. Please correct as necessary.*

We apologize for the ambiguity. The units are:

Line 115: ppb C and ppb are equivalent here

Line 131, 135, 141, 145, 151, 155: ppb C

Line 148: ppb C and ppb are equivalent here

These units are specified in the revision.

*4. line 84: I suggest you place “e.g” in front of the Nolscher et al. reference since many studies have discussed the “missing OH reactivity”*

Suggestion accepted.

*5. line 194: September 8-10 also looks windy and rainy from the plots. Why aren't these dates included here?*

These dates have been added to this sentence in the revision.

*6. Figure captions: I recommend adding the measurement location to the captions so that the casual reader is clear that these represent field measurements at a given site.*

Suggestion accepted.

*7. Figure 7, Figure 9, and lines 225-226, 250, 263: These scatter plots show some relationships, but the correlation appears quite weak. Please include the R2 on the figures and temper the text accordingly.*

The correlations in the scatter plots are heavily influenced by the random noise in the measurement. Take Figure 9, for example, (TOC+CO vs. Sum(VOC)). The  $r^2$  value is 0.12 for the hourly average (N=299), 0.20 for the 6-hr average (N=61), and 0.91 for the bin average shown in Figure 9 (N=6). All of these correlations are highly significant at the 95% confidence level according

to a t-test. The purpose of bin-averaging is to remove most of the random noise in order to more clearly demonstrate the mean relationship. We have added this information to the revision.

#### **Anonymous Referee #2**

*The authors are attempting to measure a small value (~10ppb of “missing” carbon) on top of a large, imprecise background (400 ppm of atmospheric CO<sub>2</sub> 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 CO<sub>2</sub>) are definitely the most important sources of random uncertainty in the TOC measurement. The very high precision/stability of the CO<sub>2</sub>/CH<sub>4</sub> 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:

$$\text{TOC} + \text{CO} = \text{CO}_2^* + \text{CH}_4^* - \text{CO}_2 - \text{CH}_4$$

The small amount (1.3%) of yet-to-be oxidized CH<sub>4</sub> is accounted for in the CH<sub>4</sub>\* term. Furthermore, any errors in the ‘zeros’ of the CO<sub>2</sub> and CH<sub>4</sub> 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 CO<sub>2</sub> and CH<sub>4</sub>, can only be as precise as the precision of the direct CO<sub>2</sub> and CH<sub>4</sub> measurements. The CO<sub>2</sub> 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 CO<sub>2</sub>, we get  $\sqrt{(100 \text{ ppb}/\sqrt{10})^2 + (100 \text{ ppb}/\sqrt{50})^2}$  = 34.6 ppb for each pair of measurement. There are 20 measurement pairs in an hour, and so the hourly precision becomes  $34.6 \text{ ppb}/\sqrt{20}$  = 7.7 ppb (see also line 151). The precision of CH<sub>4</sub> 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 CO<sub>2</sub>) are invariable. When these major gases are changing rapidly, the calculation of CO<sub>2</sub>\* + CH<sub>4</sub>\* - CO<sub>2</sub> - CH<sub>4</sub> 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. We have added the above information in the revised manuscript.

#### **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 have revised 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).

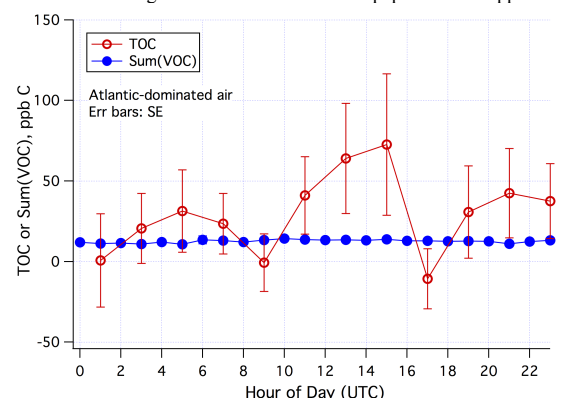
See detailed derivations above.

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.



Other changes in the revision include:

- a slight re-organization of section 2.1 (moving the discussions on particulate and semi-volatile organics to the end of the section)
- additions of references suggested by James Roberts

The revised manuscript is attached below.

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

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165 & Now at Center for Climate and Resilience Research (CR2), Departamento de Geofísica, Universidad de Chile, Santiago, Chile

**Abstract.** The atmosphere contains a rich variety of reactive organic compounds, including gaseous volatile organic carbon

(VOCs), carbonaceous aerosols, and other organic compounds at varying volatility. Here we present a novel and simple

170 approach to measure atmospheric non-methane total organic carbon (TOC) based on catalytic oxidation of organics in bulk air to carbon dioxide. This method shows little sensitivity towards humidity and near 100% oxidation efficiencies for all VOCs tested.

We estimate a best-case hourly precision of 8 ppb C during times of low ambient variability in carbon dioxide, methane, and carbon monoxide (CO). As proof of concept of this approach, we show measurements of TOC+CO during August-September

175 2016 from a coastal city in the southwest United Kingdom. TOC+CO was substantially elevated during the day on weekdays

(occasionally over 2 ppm C) as a result of local anthropogenic activity. On weekends and holidays, with a mean (standard error)

of 102 (8) ppb C, TOC+CO was lower and showed much less diurnal variability. TOC+CO was significantly lower when winds

were coming off the Atlantic Ocean than when winds were coming off land if we exclude the weekday daytime. By subtracting

the estimated CO from TOC+CO, we constrain the mean (uncertainty) TOC in marine air to be around 19 ( $\pm 8$ ) ppb C during

this period. A proton-transfer-reaction mass spectrometer (PTR-MS) was deployed at the same time, detecting a large range of

180 organic compounds (oxygenated VOCs, biogenic VOCs, aromatics, dimethyl sulfide). The total speciated VOCs from the PTR-

MS, denoted here as Sum(VOC), amounted to a mean (uncertainty) of 11 ( $\pm 3$ ) ppb C in marine air. Possible contributions from

a number of known organic compounds present in marine air that were not detected by the PTR-MS are assessed within the

context of the TOC budget. Finally, we note that the use of a short, heated sample tube can improve the transmission of organics to the analyzer, while operating our system alternately with and without a particle filter should enable a better separation of semi-

185 volatile and particulate organics from the VOCs within the TOC budget. Future concurrent measurements of TOC, CO, and a

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more comprehensive range of speciated VOCs would enable a better characterization and understanding of atmospheric organic carbon budget.

## 1 Background

The atmosphere hosts a rich variety of organic carbon, including volatile organic compounds (VOCs) such as hydrocarbons, alcohols, carbonyls, aromatics, ethers, etc, as well as lower-volatility compounds and aerosols. Some organic species contain other functional groups, such as organosulfurs, organonitrogens, and organohalogens. Many VOCs are reactive and affect the atmospheric oxidative capacity, while organic aerosols are important for air quality, human respiratory health, and potentially cloud formation. The total number of [measured](#) organic carbon species in the atmosphere is estimated to be on the order of  $10^4$  –  $10^5$  (Goldstein and Galbally, 2007). Both the abundance and cycling of total non-methane organic carbon (here abbreviated as TOC) are not well known. The total reservoir of TOC in the atmosphere is recently modeled to be about 16 Tg C (Safieddine et al., 2017), with large variability in both space and time. Emissions of the initially reduced biogenic VOCs (including isoprene and terpenes), estimated to be on the order of  $1000 \text{ Tg yr}^{-1}$ , are by far the largest terrestrial source of TOC to the atmosphere (Guenther et al., 2012). Anthropogenic emissions of mostly hydrocarbons and biomass burning are also important sources of TOC (Andreae et al., 2001). The large emissions of non-methane organic carbon relative to their relatively modest atmospheric burden imply rapid turnover of these compounds.

Once emitted into the atmosphere, organic compounds undergo chemical reactions (gas phase and heterogeneous oxidations, fragmentation and oligomerization, hydration and dehydration, etc) as well as physical transformations (e.g. condensation into the aerosol phase). Atmospheric organics are terminally removed by conversion to carbon monoxide (CO) and carbon dioxide (CO<sub>2</sub>), or wet and dry deposition to the surface as aerosols or gases (Goldstein and Galbally, 2007). In the gas phase, organic compounds can be photolyzed or react with oxidants such as the hydroxyl radical (OH), nitrate radical (NO<sub>3</sub>), halogen radicals, and ozone (O<sub>3</sub>) at vastly different reaction rates and through distinct mechanisms. Over periods of hours to weeks, these compounds become progressively more oxidized in the atmosphere, yielding a wide variety of more oxygenated compounds (Kroll et al., 2011). Lewis et al. (2005) found that under maritime conditions at Mace Head (a coastal site in the North Atlantic), oxygenated volatile organic compounds (OVOCs) including methanol, acetaldehyde, and acetone together contributed up to 85% of the observed non-methane organic carbon and explained 80% of the estimated [organic](#) OH radical sink. Read et al. (2012) found that compared to the no OVOC case, the inclusion of these OVOCs led to a ~40% reduction in the modeled OH radical concentration in the Eastern Tropical Atlantic. Depending on levels of nitrogen oxides (e.g. NO and NO<sub>2</sub>), VOCs may be responsible for either the production or consumption of O<sub>3</sub>, a harmful pollutant at high concentrations (Seinfeld

215 and Pandis, 2006). Through affecting the cycling of the OH radical (the principal sink of the Greenhouse Gas methane), O<sub>3</sub>, and aerosols, organic compounds are important for climate.

The relative importance of oxidation vs. deposition as terminal sinks of atmospheric organics is poorly quantified. Jurado et al. (2008) estimated the global dry and wet depositions of organic aerosols to be 11 and 47 Tg C yr<sup>-1</sup>, and wet deposition of organic gases to be 187 Tg C yr<sup>-1</sup>. The ocean is found to be a source of organic gases such as dimethyl sulfide (DMS, e.g. Lana et al. 2011), OVOCs (e.g. Yang et al. 2014; Schlundt et al. 2017), isoprene (e.g. Hackenberg et al. 2017), methane (CH<sub>4</sub>, e.g. Forster et al. 2009), and halocarbons (Yokouchi et al., 2013), with annual fluxes of tens of Tg C yr<sup>-1</sup> or less. Thus far, the few estimates on atmosphere-ocean diffusive total organic gas transport (Dachs et al. 2005; Ruiz-Halpern et al. 2010; Hauser et al. 2013; Ruiz-Halpern et al. 2014) have yielded net deposition and emission fluxes that are more than an order of magnitude greater than the fluxes above, illustrating the substantial uncertainty in the role of the ocean on the atmospheric TOC budget.

Simultaneous quantification of all atmospheric organic species individually is essentially impossible (or not always desirable), hence the need to measure total organic carbon as a single parameter (Heald et al. 2008). Several commercially available methods have been developed to measure total gaseous non-methane hydrocarbon concentrations in relatively polluted environments. However, these methods have large uncertainties and/or poor precision. Direct gas chromatography/flame ionization detection (GC/FID), photoacoustic infrared (PA-IR), and photoionization detector (PID) techniques all suffer from variable instrumental response towards different organic compounds. Thus, without prior knowledge of the atmospheric composition, accurate quantification of the total organic carbon with these methods is impossible.

To achieve equal instrument response regardless of the compound type, organic carbon may be oxidized and detected as CO<sub>2</sub> (analogous to measurement of dissolved organic carbon in water). Roberts et al. (1998) developed a technique based on cryogenic trapping of TOC, pre-separation of the major background gases (CO<sub>2</sub>, CH<sub>4</sub>, and CO) from TOC by a GC column, thermal desorption and catalytic conversion of TOC first to CO<sub>2</sub> and then to CH<sub>4</sub>, and finally detection by flame ionization detection. The GC based system had a cycle time of ten minutes or more. As cryogenic trapping retains moisture, sensitivity towards changing ambient humidity and variability in pre-separation/desorption contribute to uncertainties in their system (on the order of 10 ppb C). A similar method was developed by the group of Paulson et al. (2002), Maris et al. (2003), and Chung et al. (2003), with a detection limit of 35 ppb C.

Efforts trying to close the atmospheric organic carbon budget have often yielded significant fractions of 'missing', or unidentified carbon. Roberts et al. (1998) reported TOC concentrations from a remote site in Nova Scotia, Canada that were typically ~30% higher than the sum of the speciated compounds. In air quality studies in California, Chung et al. (2003) found that measurements of total non-methane organic carbon and speciated VOCs by standard GC/FID agreed well near primary

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245 pollution sources. However, in aged air masses the total non-methane organic carbon was in excess by up to 45%. Similarly,  
observations of total OH reactivity when evaluated with speciated organic concentrations often suggest that a large fraction of  
OH reactivity is unexplained, e.g. a portion of the total organic carbon is not detected by speciated measurements (e.g. Nolscher  
et al., 2016).

Hunter et al. (2017) attempted to close the atmospheric organic carbon budget at a forested site by simultaneously  
250 deploying five mass spectrometers, a Herculean undertaking. They found that previously unmeasured species such as  
semivoltatiles and intermediate-volatility organics accounted for a third of the sum of observed organic carbon. Isaacman-  
VanWertz et al. (2018) used the same set of techniques to track the oxidation chemistry of a monoterpene over multiple  
generations in the laboratory. They found that after a day of atmospheric ageing, most of the organic carbon ends up as either  
VOCs or organic aerosols. Safieddine et al. (2017) modeled the global atmospheric TOC budget, and found it to be dominated by  
255 ketones, alkanes, alkenes, and aromatics. Both comprehensive speciated measurements as well as modeling studies of  
atmospheric organic carbon budget can benefit from in situ measurements of TOC, which are to date extremely scarce. In this  
paper, we describe a simple and robust method of quantifying TOC, and show how TOC observations from a coastal site varied  
with concurrent speciated VOC measurements and other environmental variables.

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## 260 2 Experimental

Observations of total and speciated organic carbon were made from the rooftop of Plymouth Marine Laboratory (PML, ~45 m  
above mean sea level, ~300 m from waters edge) during August-September 2016. Similar to the setup used by Yang et al.  
(2013), ambient, unfiltered air was pulled from an inlet on the rooftop via 25 m of unheated perfluoroalkoxy (Teflon PFA) tubing  
(6.4 mm inner diameter, ID) at a flow rate of ~30 L min<sup>-1</sup>. TOC system and the proton-transfer-reaction mass spectrometer  
265 (PTR-MS) subsampled from this main flow at a flow rate of ca. 140 and 120 mL min<sup>-1</sup>, respectively. The TOC system was  
operated continuously during this five-week campaign. The PTR-MS measurements were made primarily after working hours  
and on weekends, as the instrument was needed by other projects during the working hours.

### 2.1 The TOC System

270 TOC was quantified in a simple fashion – via catalytic oxidation of organics in bulk air to CO<sub>2</sub>. Ambient air was directed  
through a platinum catalyst periodically (typically 2 minutes of ambient air followed by 1 minute of catalyst air) via a 3-way  
polyterafluoroethylene (PTFE) solenoid valve (Takasago Electric, Inc.). Platinum on glass wool (Shimazu) was packed in a 13  
mm diameter stainless steel tube and heated to 450°C. Dry CO<sub>2</sub> and CH<sub>4</sub> mixing ratios were continuously monitored at a

frequency of ~2 Hz by a Picarro G2311f CO<sub>2</sub>/CH<sub>4</sub>/H<sub>2</sub>O analyzer (in high precision mode). The Picarro instrument was calibrated against NOAA CO<sub>2</sub> and CH<sub>4</sub> standards.

From each pair of ambient and catalyst measurements, the sum of TOC and CO is derived semi-continuously in mixing ratio of carbon (ppb C):

$$\text{TOC} + \text{CO} = \text{CO}_2^* + \text{CH}_4^* - \text{CO}_2 - \text{CH}_4 \quad (1)$$

Here CO<sub>2</sub> and CH<sub>4</sub> represent the dry mixing ratios in ambient air (averaged from the last 5 seconds before switching to measuring catalyst air). The asterisks of CO<sub>2</sub>\* and CH<sub>4</sub>\* indicate dry mixing ratios when air is directed through the catalyst (averaged from the last 25 seconds of the catalyst phase). Any errors in the 'zeros' of the CO<sub>2</sub> and CH<sub>4</sub> measurements should be canceled out in Equation 1. The monitoring of CH<sub>4</sub> enables the continuous assessment of the efficiency of the catalytic

conversion (computed as [CH<sub>4</sub> - CH<sub>4</sub>\*]/CH<sub>4</sub>). At the flow and temperature used, oxidation of CH<sub>4</sub> was highly efficient (98.7-98.9%) and largely insensitive towards humidity during this campaign (Figure 1). CH<sub>4</sub> is thermodynamically one of the most reduced and stable compounds. Thus its rapid and near complete removal by the catalyst suggests ~100% oxidation of other

VOCs as well as CO to CO<sub>2</sub>, which is confirmed by laboratory tests as discussed below. We note that based on previous work using platinum catalytic converters (Veres et al. 2010; Stockwell et al. 2018), it is likely that the oxidation efficiency of this system will be lower at a much higher flow rate.

To verify the TOC system, we measured a diluted VOC gas mix. A multi-species gas standard consisting of methanol, acetaldehyde, acetone, DMS, benzene, and toluene (nominal mixing ratio of 500 ppb for each VOC balanced in nitrogen, Apel-Riemer Environmental, Inc, USA) was diluted by a factor of 10 with zero air. The zero air was generated by pre-scrubbing a low-VOC synthetic air (BOC BTCA 178, containing 20% oxygen) with a second 450°C platinum catalyst.

The expected total ppb of carbon in this diluted standard ( $1295 \pm \leq 78$  ppb C) is computed as follows:

$$\text{Sum}(\text{VOC}) = \sum \text{VOC} \cdot N_c \quad (2)$$

Here  $N_c$  is the number of carbon in each speciated VOC. The total uncertainty in this Sum(VOC) is propagated from the accuracies of the VOC standard concentrations and from the uncertainties in the dilution. We measured a difference in TOC + CO between the diluted VOC standard and zero air alone of 1232 ( $\pm 1$  standard error of 21) ppb C. Assuming negligible CO in the zero air as well as in the VOC standard, TOC + CO here can simply be equated to TOC. In this case TOC and Sum(VOC) agree well within the experimental uncertainties. Here, we have purposely chosen a high VOC standard concentration because if all the VOCs are fully oxidized at concentrations 1 to 2 orders of magnitude higher than in ambient air, we would expect these VOCs at ambient levels to fully oxidize as well.

Because the catalyst (made up of platinum, glass wool, and stainless steel) does not contain any carbonaceous components, we expected the instrument background in TOC + CO (i.e. when measuring air that is free of organics and CO) to

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be zero. However, post-campaign measurements of zero air (see above) yielded a TOC + CO background of 39 ( $\pm 1$  standard error of 3) ppb C. The reason for this small but significantly positive background is unclear. It could be that some particulate organic carbon either preexisting in the atmosphere or formed via charring to 450°C is captured by the glass wool, and then slowly oxidized to CO<sub>2</sub> over time. We note that the Sunset Laboratory's OCEC (Organic Carbon Elemental Carbon) analyzer heats to 850°C (over manganese dioxide) for complete desorption and conversion of refractory organics (e.g. soot) to CO<sub>2</sub>. We subtracted the background value of 39 ppb C from the TOC + CO measurements during the 2016 campaign. However, the fact that the background measurement was not made at the time of the campaign is a source of potential bias in this dataset.

Measurement of TOC+CO by our approach is made possible thanks to the very high precision of the Picarro G2311f instrument (~100 and 0.4 ppb for CO<sub>2</sub> and CH<sub>4</sub> at 2 Hz, respectively). Scatter in TOC+CO depends on random noise as well as ambient variability in the CO<sub>2</sub>/CH<sub>4</sub>/CO mixing ratios, with CO<sub>2</sub> being the most critical. The measurement precision is significantly improved through averaging, as random noise scales with  $N^{1/2}$  (N being the number of measurement). In the limit of no ambient variability in CO<sub>2</sub>/CH<sub>4</sub>/CO, each pair of CO<sub>2</sub>\*/CH<sub>4</sub>\* and CO<sub>2</sub>/CH<sub>4</sub> measurements has a propagated precision of 35 ppb C (= ((100 ppb/N<sup>1/2</sup>)<sup>2</sup> + (100 ppb/N<sup>1/2</sup>)<sup>2</sup>)<sup>1/2</sup>) in our setup. Since there are nominally 20 measurements per hour, this implies a best-case hourly precision of 8 ppb C (=35 ppb C/20<sup>1/2</sup>) for TOC + CO. While not substantially more precise than earlier methods, the technique described here is robust in that it avoids many of the uncertainties and complexities associated with trapping and desorption (e.g. Roberts et al. 1998). The precision estimate above may be appropriate for parts of the remote marine atmosphere (i.e. very low variability in CO<sub>2</sub>/CH<sub>4</sub>/CO). Closer to emission sources, the greater variability in these major gases is expected to significantly increase the scatter in TOC + CO. At our polluted coastal environment where the major gases were generally not very constant, the standard deviation in the hourly mean TOC + CO was about 30 ppb C during periods of fairly low ambient CO<sub>2</sub> variability (1 standard deviation of ~0.2 ppm).

In addition to gases, ambient TOC measured with this method likely includes some aerosols and low/moderate-volatility compounds, which can reversibly partition onto the inlet tube surface and lengthen the measurement response time. The contribution of these particulate and semi-volatile organics towards TOC depends on their transmission through the inlet tube as well as on their oxidation efficiency in the catalyst. We did not explicitly test these aspects as organic aerosol mass is already quantifiable using aerosol mass spectrometry as well as thermal methods (e.g. Sunset Laboratory's OCEC analyzer).

## 2.2 Speciated VOC measurements

Speciated organic gases were quantified using a PTR-MS, which was freshly serviced and calibrated by Ionicon. The PTR-MS settings were essentially the same as those used by Yang et al. (2013; 2014), except for a lower drift tube pressure (2.25 mbars). The monitored masses (m/z) with a H<sub>3</sub>O<sup>+</sup> source were attributed to the following compounds: m/z 33 (methanol), 42

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335 (acetonitrile), 43 (fragmented ~~propanol or acetic acid~~), 45 (acetaldehyde), 47 (ethanol), 59 (acetone), 61 (~~propanol or acetic acid~~), 63 (DMS), 69 (isoprene), 79 (benzene), 91 (toluene), 107 (xylene), 137 (monoterpenes). The total speciated VOCs from the PTR-MS is computed following Equation 2. The same VOC gas standard as above (containing methanol, acetaldehyde, acetone, DMS, benzene, and toluene) diluted in synthetic air (BOC BTCA 178) was used for 1) calibration of the PTR-MS, and 2) further demonstration of the oxidation efficiency of the platinum catalyst. For detected VOCs that were not directly calibrated, recommended kinetic reaction rates from Zhao and Zhang (2004) were used to compute the mixing ratios from the PTR-MS raw counts.

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340 The oxidation of all VOCs in the platinum catalyst tested here appears to be immediate, complete, and independent of the amount of VOCs present as well as the humidity (within the test range). Figure 2 shows a time series of raw VOC mixing ratios from such a laboratory experiment. The flow of the VOC gas standard was increased stage-wise, resulting in greater measured VOCs from about 3000 to 11500 seconds. The differences in the amplitudes of the different raw VOC mixing ratios are primarily due to their different kinetic reaction rates and transmission efficiencies within the PTR-MS, which are corrected for in the final dataset. For the second half of each stage of dilution, the VOC containing air was directed through the platinum catalyst. With increasing amount of VOCs added, VOC measurements during the catalyst section remained constant and equal to (or slightly less than) measurements of synthetic air alone (after ~12200 seconds), demonstrating 100% oxidation efficiency. In a separate experiment, synthetic air was moistened to an absolute humidity of 12.8 g kg<sup>-1</sup> before the addition of the VOC standard. The higher humidity in the sample air did not affect the oxidation efficiency of these VOCs.

350 Within the range of ambient humidity during this campaign and under the PTR-MS setting used, the only VOC measurements with noticeable humidity-sensitivity were isoprene and monoterpenes. Calibrations and air scans show that these two VOCs were partially fragmented into m/z of 41 and 81, respectively, consistent with previous findings (e.g. Schwarz et al. 2009; Tani et al. 2004). The fragmentation tended to be more severe at a lower ambient humidity and these daughter fragments are accounted for in the budgets of biogenic VOCs and Sum(VOC). We show in Section 5 that Sum(VOC) was dominated by OVOCs during this campaign and these gases were well calibrated. Biogenic VOCs accounted for only a small fraction of Sum(VOC), such that any uncertainty from the humidity-dependence in these fragmentations likely contributed little to Sum(VOC). In total we expect the accuracy in Sum(VOC) during our campaign to be at worst 25%.

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### 360 3 Variability in TOC+CO

The period of 4<sup>th</sup> August to 22<sup>nd</sup> September 2017 was mostly sunny (noontime shortwave irradiance of 600-700 W m<sup>-2</sup>) and calm (mean wind speed ~4 m s<sup>-1</sup>). Figure 3A shows the time series of hourly averaged TOC+CO from the entire measurement period. Large variability was observed in TOC+CO on weekdays, with values occasionally exceeding 2 ppm C. In contrast, TOC+CO

365 | was significantly lower and less variable on weekends and holidays. Stronger winds ~~over~~ <sup>1.0</sup> m s<sup>-1</sup> from the southwest came through between 19<sup>th</sup> and 22<sup>nd</sup> August and on 3<sup>rd</sup> ~~and~~ <sup>9</sup><sup>th</sup> September, carrying along rainfall (Figure 3B). Relative low and consistent TOC+CO were observed during these periods.

The hourly TOC+CO data were clearly noisier in the first week, when the measurement frequency was lower (5 minutes of ambient air followed by 2 minutes of catalyst air). Increasing the measurement frequency subsequently (2 minutes of ambient air followed by 1 minute of catalyst air) reduced the noise in the hourly averaged TOC+CO by about 50%. Scatter in the hourly  
370 | TOC+CO (and some of the negative values), largely a result of highly variable ambient CO<sub>2</sub> mixing ratios, is greatly reduced in the 6-hour mean and median. This further confirms that our TOC + CO measurement is precision-limited.

Averaged over the entire campaign, TOC+CO was much higher (exceeding 1 ppm C) during the day than at night (~0.15 ppm C) on weekdays (Figure 4A). Typical of urban air pollutants, two peaks were observed in the weekday data, one around the morning rush hour traffic, and the second one around the late afternoon rush hour traffic. Less diurnal variability was  
375 | apparent on weekends and holidays, with mean (standard error) TOC+CO of 102 (8) ppb C. Higher ambient CO<sub>2</sub> mixing ratio was also generally observed on weekdays than on weekends and holidays during the daytime (Figure 4B). This suggests that the elevated TOC+CO levels during the weekday daytime were largely due to local anthropogenic activities. In particular, demolition of a large building with heavy machinery took place south of the PML building during the working hours of this period.

380 | We estimate the emission factor of TOC+CO from local anthropogenic sources. The difference in TOC+CO between weekdays and weekends/holidays is plotted against that of CO<sub>2</sub> in Figure 5. A positive correlation is evident, with a dimensionless ratio of roughly 0.1 (largely between 0.05 and 0.2). This is on the higher end of previously reported CO:CO<sub>2</sub> emission ratios from urban environments (e.g. Wang et al., 2010; Ammoura et al., 2014), probably in part due to the inclusion of VOCs.

385 | For the rest of this paper, we focus on data from weekends/holidays and weekday nighttime only in order to minimize the effects of local pollution. TOC+CO and CO<sub>2</sub> are averaged in wind direction bins in Figure 6A. Both variables show qualitatively similar patterns, with lower values when winds were from the sea (southwest, here 180-270°) than when winds were from land (north to southeast, here 330-120°). Comparing the difference between land air and marine air in TOC+CO (0.247 –  
390 | 0.079 ppm C) vs. that in CO<sub>2</sub> (421.0 – 396.4 ppm), we get a dimensionless ratio of approximately 0.0068. This ratio is ~~roughly~~ an order of magnitude lower than the slope derived from local pollution (Figure 5) for probably multiple reasons. Unlike local pollution, TOC+CO in marine air is likely less coupled to CO<sub>2</sub> emissions. Due to the shorter lifetimes of organics, we also expect a far more rapid degradation of TOC further away from the emission sources than CO<sub>2</sub>.

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A fraction of TOC measured at PML appeared to be highly soluble and readily removed by wet deposition. The mean

(SE) TOC+CO during non-raining periods was 0.136 (0.008) ppm C, while that during rain events (65 hours total over the campaign) was 0.071 (0.002) ppb C. Though part of this difference could be due to the greater occurrence of rain when winds were from the southwest (off the Atlantic Ocean). TOC+CO correlated in the mean with CO<sub>2</sub> (Figure 7A) and also with O<sub>3</sub> (Figure 7B) from the Penlee Point Atmospheric Observatory (PPAO) 6 km to the south of PML (Yang et al., 2016), similar to observations from Roberts et al. (1998). For reference, mean CO<sub>2</sub> and O<sub>3</sub> were about 395 ppm and 18 ppb when winds came from the southwest during this campaign. In the following sections, we constrain the magnitude of TOC in marine air and compare it against speciated organic carbon measurements from the PTR-MS as well as against previous observations.

#### 4 Constraining the magnitude of TOC

Accurately determining TOC requires the concurrent measurement of CO, which was unfortunately not available during this period. CO was measured at PML during May-July 2017 using a combination of gas chromatography and chemical sensors by the University of York. Averaged to daily bins, these measurements agreed within ~10% in the mean with CO measured from the Defra Air Quality monitoring station in Cardiff during the same period when winds were from the southwest (Katie Read, personal communications in 2018). Furthermore, the Copernicus Atmospheric Monitoring Service (CAMS) analysis of CO (Inness et al., 2015), constrained by satellite column as well as in situ CO measurements, generally do not show a large difference in surface CO mixing ratio between Plymouth and Cardiff. This is not surprising because these two maritime cities both face the Atlantic to the southwest and are only about 150 km apart.

We subtract CO measured at Cardiff during August-September 2016 from TOC+CO to yield TOC. Doing so is likely only reasonable during southwesterly conditions. TOC + CO from this ocean sector had a mean (SE) of 79 (7) ppb in our measurements, while CO at Cardiff during these conditions averaged 60.3 (SE of 1.5) ppb. This implies in a mean TOC mixing ratio of about 19 ppb C in marine air (with a minimum uncertainty of 8 ppb). Our estimate is within the range of previous observations. Roberts et al. (1998) reported a median TOC mixing ratio of 55 ppb C from the city of Boulder, Colorado and 11 ppb C from the remote Chebogue Point, Nova Scotia. Chung et al. (2003) measured TOC mixing ratios of several hundred ppb C from polluted areas of California.

To minimize local land influence, we focus on airmasses coming off the Atlantic Ocean. The UK Met Office's NAME dispersion model (Jones et al., 2007) was used to produce a footprint of the air arriving at the station every 3 hours. The residence time over the 5-day journey of airmasses over a series of geographical regions were calculated, and then converted into % relative residence times out of the whole domain. As shown in Figure 7C, TOC+CO decreased with increasing Atlantic influence in the mean. In Atlantic-dominated (>80% relative residence time) airmasses, TOC + CO had a mean (median) of 81

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(65) ppb C, in agreement with the statistics selected by the southwest wind sector. This again implies that TOC in Atlantic-dominated airmasses averaged about 20 ppb C. In contrast, in airmasses dominated by mainland Europe and the English Channel (>50% relative residence time), TOC+CO had a mean (median) of 198 (191) ppb C (Figure 7D). Examples of these two types of airmasses as well as the regional map used for the airmass classification are shown in Figures S1-S3.

## 5 Attempting a TOC budget closure

During the 1.5 months study, the PTR-MS was used to measure a large range of organic gases over 22 days. The total mixing ratio of speciated organic carbon, Sum(VOC), is shown in Figure 8, which averaged 15 ppb C. Sum(VOC) was higher during weekdays (mean  $\pm$  standard error of  $16.0 \pm 0.4$  ppb C) than on weekends (mean  $\pm$  standard error of  $14.3 \pm 0.4$  ppb C), but this difference is much less drastic than in the case of TOC+CO. This suggests that the significantly elevated TOC + CO during the weekday daytime was largely due to compounds that were not measured by the PTR-MS (e.g. CO, small alkanes, or alkenes).

Sum(VOC) was dominated by OVOCs (here methanol, acetone, acetaldehyde, ethanol, propanol/acid acid), consistent with Lewis et al. (2005) and Heald et al. (2008) (Figure 6B). Aromatic compounds (benzene, toluene, xylenes) were more abundant when winds were from land (northwest to northeast), as expected from anthropogenic emissions. Similarly, mixing ratios of biogenic VOCs (isoprene and monoterpenes) were higher when winds were from northwest to northeast in comparison to south and southwest. Among detected VOCs, only DMS mixing ratio was higher in marine air than in continental air. Similar to TOC+CO, Sum(VOC) showed the lowest value when winds were from the sea (~11 ppb C during southwesterly conditions). In comparison, in the synthesis by Heald et al. (2008) the sum of speciated organic compounds was about 8, 14, and 18 ppb C at Trinidad Head (California), Azores, and Chebogue Point (2004 measurements), respectively. Our mean Sum(VOC) is within the range of those coastal observations, which were generally more comprehensive than just the PTR-MS measurements here.

Interestingly, the approximate carbon fraction of total VOCs (i.e. carbon mass : total mass) was also the lowest when winds were from the sea. This indicates that VOCs in marine air on average contain more non-carbon functional groups (e.g. nitrogen, sulfur).

Sum(VOC) correlated positively with TOC+CO in the mean (Figure 9) when limiting data to weekends and weekday nights only. Similar to Figure 7, the degree of correlation here is heavily influenced by the random noise in the TOC+CO measurement. The  $r^2$  value between TOC+CO and Sum(VOC) is 0.12 for the hourly average (N=299), 0.20 for the 6-hr average (N=61), and 0.91 for the bin average as shown in Figure 9 (N=6). All of these correlations are highly significant at the 95% confidence level according to a t-test. Bin-averaging helps to remove most of the random noise in order to more clearly demonstrate the mean relationship.

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We see that TOC ( $19 \pm 8$  ppb C, estimated by subtracting CO from TOC+CO) is  $\sim 70\%$  higher than Sum(VOC) when winds were from the southwest but the difference is within the measurement uncertainties. Comparing TOC with Sum(VOC) in background marine air, **partly** necessitated here by our lack of in situ CO observations, challenges the signal to noise of the TOC measurement. We expect such a comparison to be more insightful in environments with a higher TOC burden. Nevertheless, we know that the PTR-MS with hydronium ion source is not suitable for detecting many VOCs, such as low molecular weight hydrocarbons that are expected to make up most of the primary anthropogenic organic emissions. Below we examine the

magnitudes of some nominally abundant VOCs in marine air that were not measured by the PTR-MS. Formaldehyde (HCHO), the most abundant aldehyde in the atmosphere, was measured at **PML's** PPAO from the spring of 2015 to the beginning of 2016 using **multi-axes differential optical absorption spectroscopy (MAX-DOAS)**. During southwesterly conditions the surface mixing ratio of HCHO was about 0.5 ppb C (Johannes Lampel, personal communication in 2016). Non-methane hydrocarbons, such as alkanes, have large seasonal variability in temperate regions, with significantly lower abundance in the summer time due to greater OH destruction. Grant et al. (2011) reported long-term time series measurements of hydrocarbons from Mace Head. For the months of August and September from 2005 to 2009, the mean mixing ratio of ethane and propane were about 2 and  $<0.3$  ppb C during maritime conditions, respectively. Grant et al. (2011) also measured (i- and n-) butane and (i- and n-) pentane, which were of even lower abundance. Salisbury et al. (2001) reported the mixing ratios of a large range of alkenes from Mace Head. The most abundant alkenes, ethene and propene, had mean mixing ratios of about 0.05 and 0.06 ppb C, respectively. Acetylene, the simplest alkyne, has a mixing ratio of  $\sim 0.5$  ppb C over the Atlantic (Xiao et al., 2007). The ocean is a source of a host of halocarbons. Among these chloromethane ( $\text{CH}_3\text{Cl}$ ) is the most abundant, with a mixing ratio of the order of 0.5 ppb C in the marine boundary layer (Yokouchi et al., 2013). Together these organic gases make up to approximately 5 ppb C.

Because of the high temperature and oxidative conditions in the catalyst, we expect some organic aerosols and semi-volatile species to be oxidized and detected as  $\text{CO}_2$ . Particulate matter less than  $2.5 \mu\text{m}$  ( $\text{PM}_{2.5}$ ) in the City Center of Plymouth, also from the Defra Air Quality Monitoring station, was about  $6 \mu\text{g m}^{-3}$  during this period when winds were from the southwest. If we assume that half of the  $\text{PM}_{2.5}$  was made up of carbon by mass (most likely an overestimate for this region, e.g. Morgan et al., 2010), the aerosol contribution to TOC could be up to 6 ppb C (or a third of TOC). Heald et al. (2008) reported that organic aerosols only accounted for 4-16% of total speciated organics (gases **plus** aerosols) in the marine atmosphere. Overall, considering the aforementioned VOCs and organic aerosols that were not detected by the PTR-MS, there does not appear to be a substantial 'missing' term in the TOC mass budget.

## 6 Concluding remarks

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In this paper we report a relatively novel and simple method to measure the mixing ratios of total organic carbon (TOC) and carbon monoxide in the atmosphere at a high frequency. Based on essentially complete oxidation of organics in bulk air to CO<sub>2</sub> in a platinum catalyst, our method shows very low sensitivity towards ambient humidity, avoids the complexities associated with trapping and desorption, and has an hourly precision of as low as 8 ppb C. Due to the use of a long, unheated Teflon inlet tube, the semi-volatile and particulate organics were likely not well represented in the measurements presented here. A simple improvement to this measurement system would be to minimize the length of the inlet tube before the catalyst. Future measurements with and without an aerosol filter and a heated inlet should enable the semi-volatile and particulate fractions of TOC to be better separated from the VOCs.

The estimated TOC from a polluted marine environment is compared to the sum of speciated VOCs here. Accounting for literature values of unmeasured VOCs and organic aerosols, there does not appear to be a significant undetected fraction of organics in marine air. A more rigorous examination of the atmospheric organic carbon closure requires concurrent measurements of TOC, CO, and a comprehensive range of speciated organic compounds. Additional measurements of total OH reactivity would bridge the gap between organic burden and composition with oxidative capacity. With recent advances in mass spectrometry that are able to resolve ever more organic species (Hunter et al., 2017) as well as in chemical transport modeling (Safieddine et al., 2017), the stage seems set for closing the atmospheric organic budget.

### Acknowledgment

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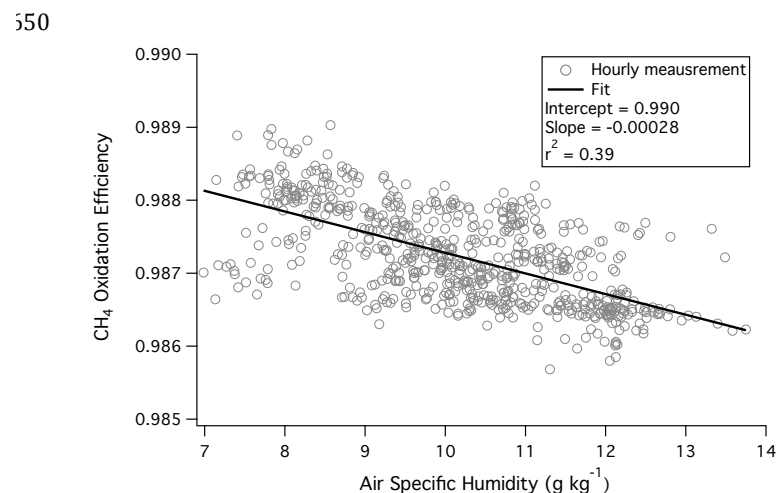


Figure 1. Oxidation efficiency of  $\text{CH}_4$  by the platinum catalyst was nearly 99% and demonstrated only a weak dependence on ambient humidity [during the 1.5-month measurement campaign from the rooftop of Plymouth Marine Laboratory](#).

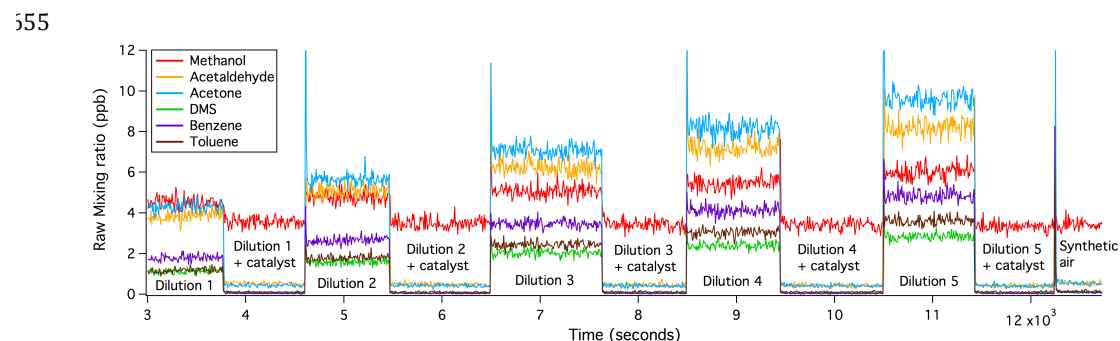


Figure 2. Catalytic oxidations of VOCs were complete, immediate, and independent of the VOC input within the range tested.

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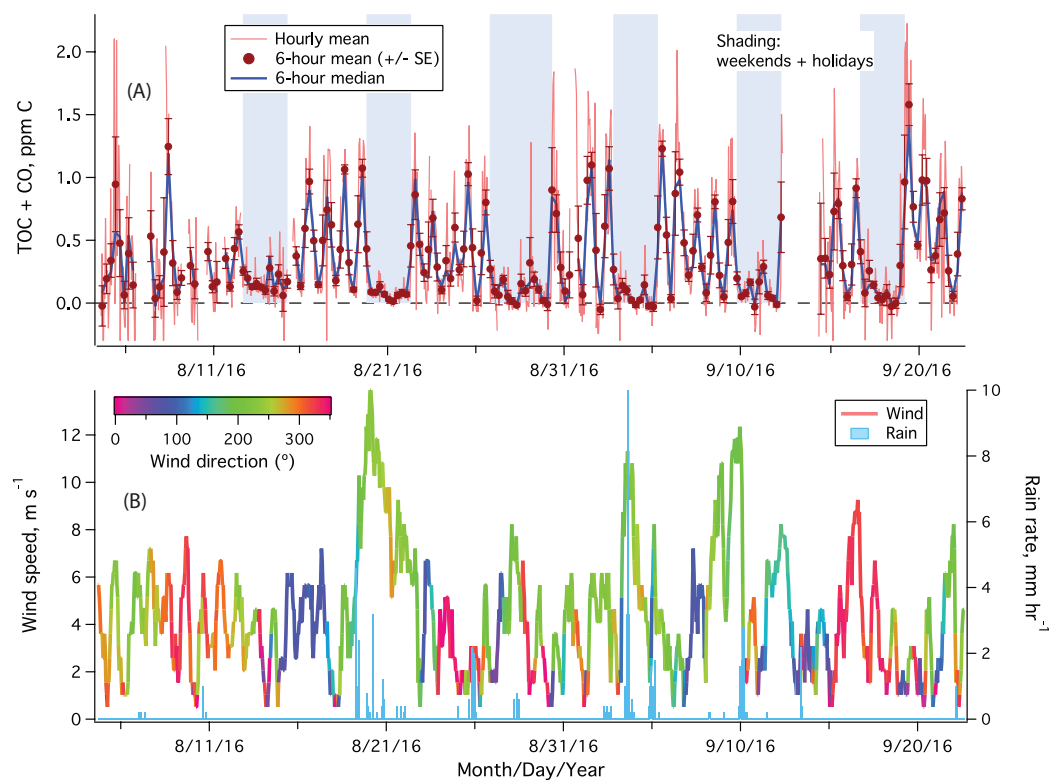


Figure 3. (A) Time series of TOC+CO in units of ppm C [from the rooftop of Plymouth Marine Laboratory](#). Error bars on 6-hr means indicate standard errors; (B) wind speed (color-coded by wind direction) and rain rate.

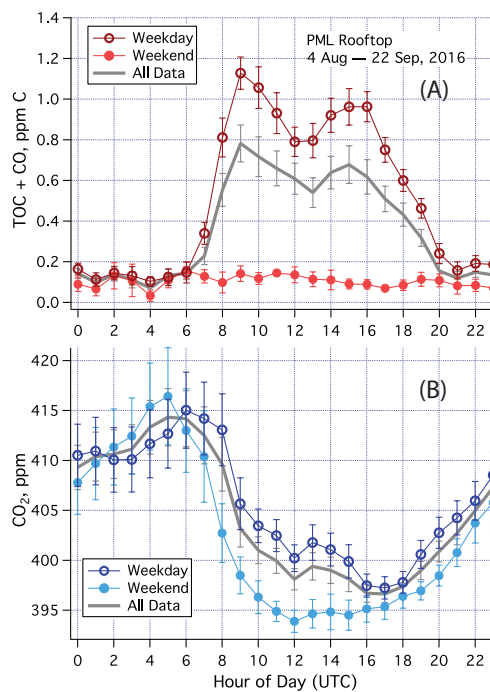


Figure 4. (A) Averaged diurnal cycle in TOC+CO, and (B) CO<sub>2</sub> for weekdays, weekends/holidays, and all data during the 1.5-month measurement campaign from the rooftop of Plymouth Marine Laboratory. Error bars indicate standard errors. TOC+CO were much higher during weekdays than weekends, especially in the daytime. Limited diel variability in TOC+CO was observed in the weekend data. CO<sub>2</sub> was also higher in the daytime during weekdays than weekends. UTC here is one hour behind local time.

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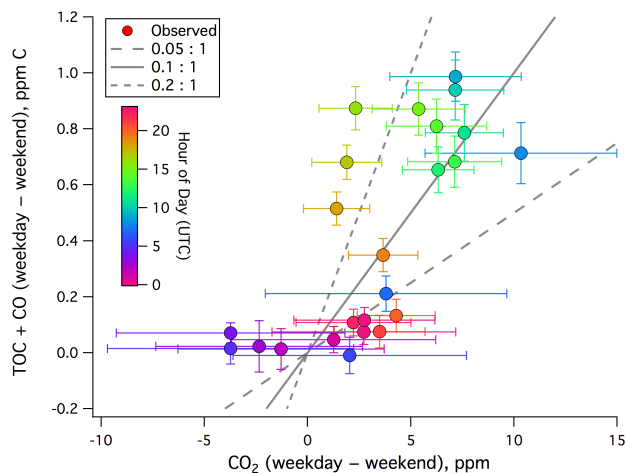


Figure 5. Weekday-weekend difference in TOC+CO (ppm C) vs. weekday-weekend difference in CO<sub>2</sub> from the rooftop of Plymouth Marine Laboratory. A positive correlation is observed, with a dimensionless ratio ranging from mostly less than 0.05:1 to over 0.2:1.

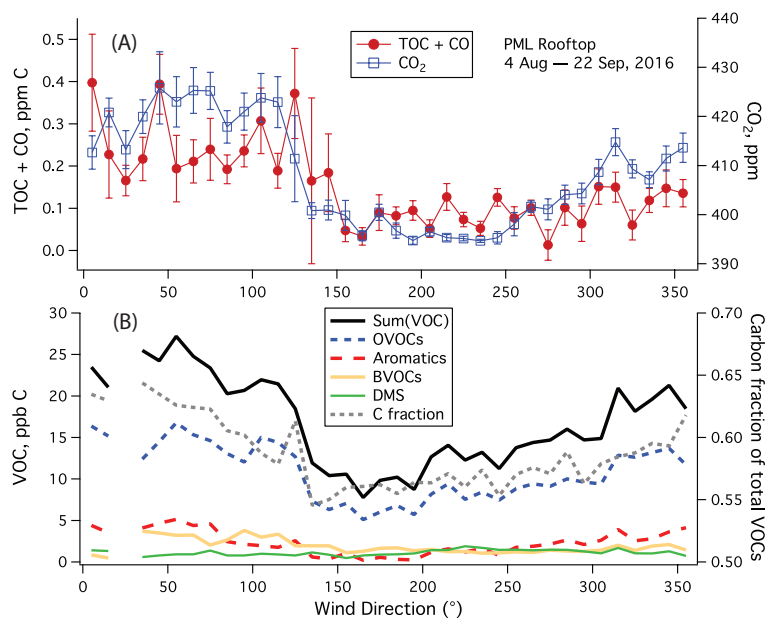


Figure 6. (A) TOC+CO and CO<sub>2</sub>, and (B) Sum(VOC) and speciated VOC averaged to 10-deg wind direction bins. Error bars indicate standard errors. TOC+CO, CO<sub>2</sub>, and Sum(VOC) showed higher values when winds were from land (north to southeast) than winds were from the ocean (southwest). Most VOCs had lower mixing ratio in marine air than in air from land except for DMS. Amongst speciated VOCs measured by the PTR-MS, OVOCs dominated in terms of carbon mass. The fraction of carbon in the total speciated VOC mass was also lower in marine air.

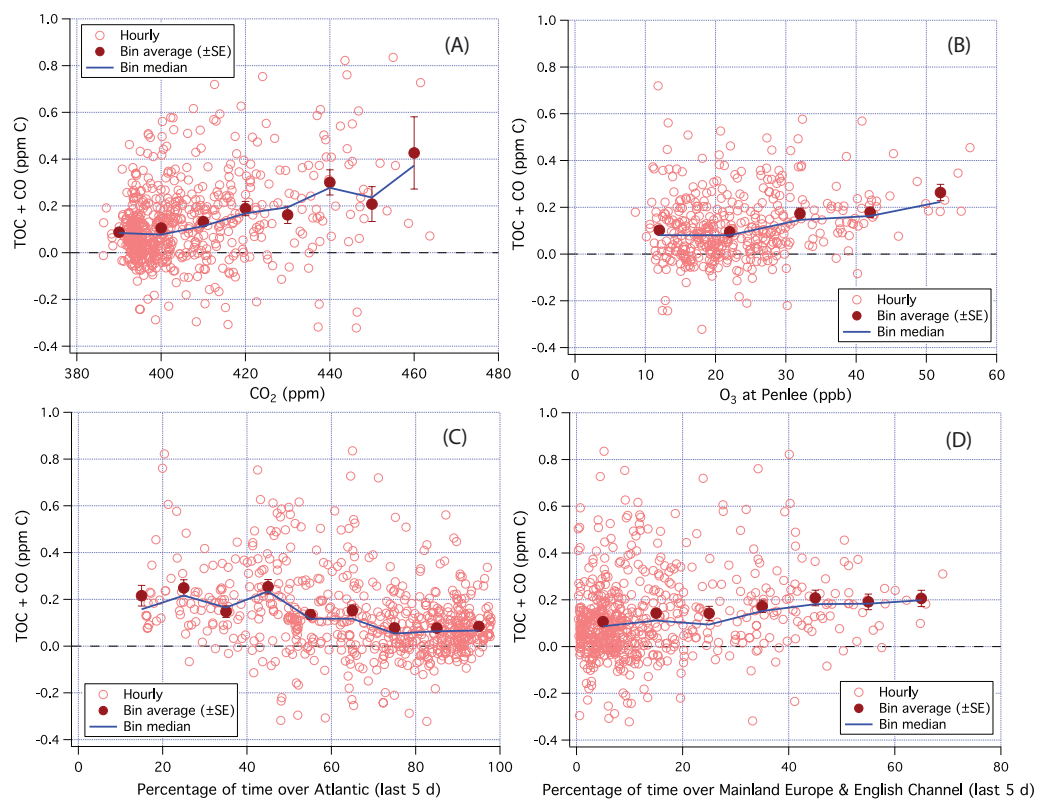


Figure 7. Relationship between TOC+CO with (A)  $CO_2$ ; (B)  $O_3$ ; (C) percentage of time that the air mass was over the Atlantic ocean over the last 5 days; and (D) percentage of time that the air mass was over Mainland Europe and the English Channel over the last 5 days. Hourly data limited to weekends & weekday nights only.

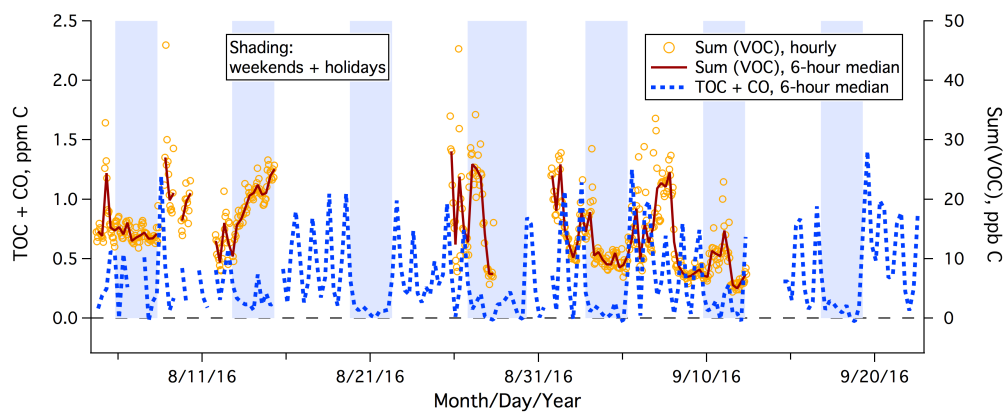


Figure 8. Time series of TOC + CO and Sum(VOC) from the rooftop of Plymouth Marine Laboratory. Sum(VOC) is shown as hourly mean and 6-hour median, while for clarity TOC + CO is shown as 6-hour median only.

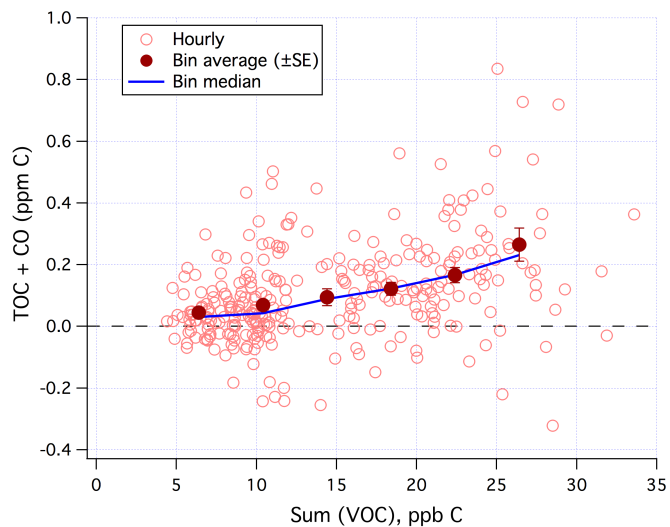


Figure 9. TOC+CO correlated positively with Sum(VOC). Hourly data limited to weekends & weekday nights only.