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Atmospheric Chemistry and Physics

# Total observed organic carbon (TOOC) in the atmosphere: a synthesis of North American observations

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**Abstract.** Measurements of organic carbon compounds in both the gas and particle phases made upwind, over and downwind of North America are synthesized to examine the total observed organic carbon (TOOC) in the atmosphere over this region. These include measurements made aboard the NOAA WP-3 and BAe-146 aircraft, the NOAA research vessel Ronald H. Brown, and at the Thompson Farm and Chebogue Point surface sites during the summer 2004 ICARTT campaign. Both winter and summer 2002 measurements during the Pittsburgh Air Quality Study are also included. Lastly, the spring 2002 observations at Trinidad Head, CA, surface measurements made in March 2006 in Mexico City and coincidentally aboard the C-130 aircraft during the MILAGRO campaign and later during the IMPEX campaign off the northwestern United States are

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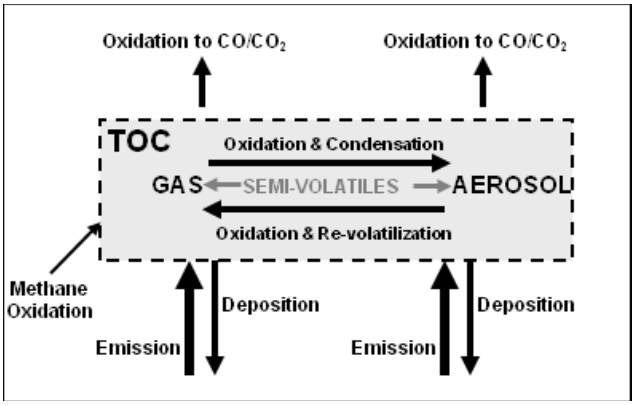


**Fig. 1.** Conceptual framework for total organic carbon (TOC).

incorporated. Concentrations of TOOC in these datasets span more than two orders of magnitude. The daytime mean TOOC ranges from 4.0 to 456 $\mu$gC m$^{-3}$ from the cleanest site (Trinidad Head) to the most polluted (Mexico City). Organic aerosol makes up 3–17% of this mean TOOC, with highest fractions reported over the northeastern United States, where organic aerosol can comprise up to 50% of TOOC. Carbon monoxide concentrations explain 46 to 86% of the variability in TOOC, with highest TOOC/CO slopes in regions with fresh anthropogenic influence, where we also expect the highest degree of mass closure for TOOC. Correlation with isoprene, formaldehyde, methyl vinyl ketone and methacrolein also indicates that biogenic activity contributes substantially to the variability of TOOC, yet these tracers of biogenic oxidation sources do not explain the variability in organic aerosol observed over North America. We highlight the critical need to develop measurement techniques to routinely detect total gas phase VOCs, and to deploy comprehensive suites of TOOC instruments in diverse environments to quantify the ambient evolution of organic carbon from source to sink.

## 1 Introduction

We introduce here a new paradigm for holistic consideration of the total organic carbon (TOC) budget. Similar budget approaches are routinely used for nitrogen oxides and sulfur in the atmosphere, and rapidly improving measurement techniques are beginning to make this possible for organic carbon. Despite these advances, complete TOC closure in the atmosphere is not yet possible. We therefore focus here on the total observed organic carbon (TOOC) budget (excluding methane), which reflects the subset of compounds currently measured in the ambient atmosphere.

Carbon in the atmosphere is dominated by its inorganic forms, particularly, carbon dioxide ($CO_2$), the global annual average concentrations of which reached 385 ppm in 2006 (equivalent to a global burden of 820 PgC) (IPCC, 2007). The most abundant organic gas in the troposphere is methane, with a current global annual mean concentrations of ∼1751 ppb (equivalent to ∼4 PgC) (Dlugokencky et al., 2003). While methane is an important greenhouse gas, it is long lived (lifetime ∼10 years) and has a comparatively well understood life cycle in the troposphere. Therefore, it will be excluded from the organic carbon budget discussed here. Organic carbon in the atmosphere, excluding methane, is a much smaller carbon reservoir (estimates range in the ∼10 s TgC) (IPCC, 2007). However, these compounds play an important role in the chemistry of the troposphere, and in aerosol form, as a climate forcing agent. The organic carbon budget includes a large suite of compounds, with many that are likely to contribute (based on laboratory studies or theory) not having been observed under ambient conditions (Goldstein and Galbally, 2007), with varying sources, lifetimes and properties in the atmosphere. Measurements of TOC are difficult, thus the organic carbon budget in the atmosphere remains poorly quantified. Organic carbon is lost from the atmosphere via multiple gas-phase oxidation steps to CO and $CO_2$ or wet and dry deposition to the surface. Recent studies suggest that organic carbon may undergo chemically mediated phase changes under ambient conditions (Kwan et al., 2006; Molina et al., 2004; George et al., 2007), suggesting a "fluid" organic carbon pool in the atmosphere (Fig. 1).

Organic carbon in the atmosphere includes hydrocarbons, oxygenated or halogenated compounds and multifunctional compounds, as well as particulate matter. Dominant and well-studied organic constituents of the atmosphere include alkanes and alkenes (Harley et al., 1993; Goldstein et al., 1996), formaldehyde (Singh et al., 1995;Chance et al., 2000), acetone (Jacob et al., 2002), methanol (Jacob et al., 2005; Galbally and Kirstine, 2002), and isoprene (Guenther et al., 1995), which originate from a range of anthropogenic and natural sources, and both primary and secondary processes. An additional source of TOOC, as defined here, is the oxidation of methane to formaldehyde. Particle organic carbon can be directly emitted from combustion and other sources or formed in the atmosphere from oxidation of both biogenic and anthropogenic volatile organic compounds (VOCs). These aerosol classes are referred to as primary organic aerosol (POA) and secondary organic aerosol (SOA) respectively (Seinfeld and Pankow, 2003).

The number of organic compounds in the atmosphere far exceeds the number of measured species. In 1986, Graedel et al. (1986) identified 2857 organic compounds in the atmosphere and current estimates of identified compounds exceed $10^4$(Goldstein and Galbally, 2007). A suite of hydrocarbons and VOCs are routinely detected using Gas Chromatography (GC) (Blake et al., 1992; Lamanna and Goldstein, 1999) and Proton Transfer Reaction Mass Spectrometry (PTR-MS) techniques (Lindinger et al., 1998; de Gouw et al., 2003). The number of reported compounds for a typical

field campaign ranges from 30 to 100. Instruments designed to measure "total VOCs" in the gas-phase suggest that the VOC mass reported by these speciated techniques account for 55–85% of the total VOC mass, with a growing unidentified fraction as air masses age (Chung et al., 2003). However, Roberts et al. (1998) achieved closure (to measurement precision) between total non-methane organic carbon and the sum of $C_2$–$C_7$ hydrocarbons and carbonyls measured in Chebogue Point, Nova Scotia. Additional total VOC measurements are needed to clarify the conditions necessary for gas phase organic carbon mass closure.

Limitations of current measurement techniques dictate that semi-volatile compounds and particularly those with multiple functional groups typically are not measured. Individually these compounds are expected to be present at low concentrations, but the cumulative contribution of all of these compounds and their isomers may be large (Goldstein and Galbally, 2007). Box models of oxidation predict that even after several days, the bulk of oxidized mass exists as highly functionalized organics in the atmosphere (Aumont et al., 2005). In particular, large semi-volatile compounds may contribute disproportionately to SOA formation (Robinson et al., 2007).

Organic aerosol traditionally has been sampled on filters and thermally separated and detected off-line after collection (Watson and Chow, 2002). Recent on-line instruments, such as the Aerosol Mass Spectrometer (AMS) (Canagaratna et al., 2007), the Sunset Labs OC/EC (elemental carbon) analyzer (Lim et al., 2003) and water-soluble organic carbon (WSOC) particle-into-liquid sampler (PILS) instrument (Sullivan et al., 2004), provide higher time-resolution measurements of organic matter in particles. The organic aerosol concentrations reported by these techniques may differ due to operational definitions and collection efficiencies. Some chemical information on the types of species present can be extracted from the AMS spectra (Zhang et al., 2005). FTIR and NMR spectroscopies have been used to identify and quantify the relative contributions of organic functional groups within aerosol samples (Gilardoni et al., 2007; Decesari et al., 2007). Highly speciated organic aerosol measurements can be made using multi-dimensional chromatography (GCxGC) which differentiates compounds based on both volatility and polarity (Lewis, 2000). Using this technique a single organic aerosol filter sample from London, England was found to contain over 10 000 individual compounds (Hamilton et al., 2004). Analysis of GCxGC measurements is onerous; therefore, the record of ambient speciated organic aerosol composition measured by this technique is sparse. In addition, some compounds can decompose upon heating in the GC injector and column (Tobias et al., 2000), and traditional GC analyses using non-polar columns discriminate against compounds that comprise oxygenated organic aerosols (Huffmann et al., 2007[1]) which represents the largest fraction of organic aerosol mass in the atmosphere (Zhang et al., 2007a). Alternative techniques of organic speciation that do not require chromatographic separation are under development. However, species identification remains difficult, and few ambient results have been reported to date (Hearn and Smith, 2006; Oktem et al., 2004).

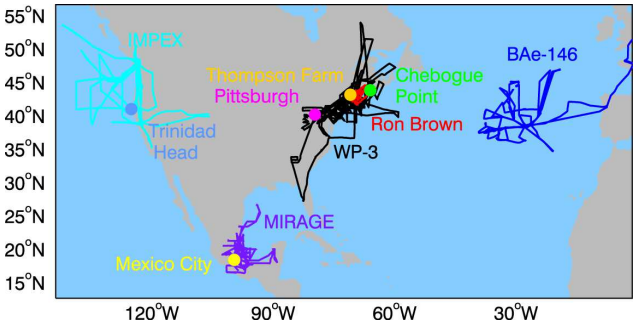


**Fig. 2.** Flight tracks, ship tracks and field site locations for observation platforms.

De Gouw et al. (2005) first used ambient measurements to examine how the relationship between gas and aerosol organic carbon evolves in anthropogenic plumes. We present here a synthesis of organic carbon compound data in both the gas and particle phases measured over and downwind of North America and the first attempt to assess the mean TOOC budget over this region. Variability of TOOC on this scale as well as future directions are also discussed.

## 2 Mean TOOC over North America

Coincident observations of both aerosol and speciated gas-phase organics are rare. Therefore, we focus here on North America (and upwind/downwind), a region with comprehensive measurements from numerous measurement campaigns.

Both gas and particle phase organic carbon were measured during the International Consortium for Atmospheric Research on Transport and Transformation (ICARTT) campaign of the summer 2004 on multiple platforms (Fehsenfeld et al., 2006). These include the NOAA WP-3 aircraft which surveyed northeastern North America focusing on urban plumes, the FAAM BAe-146 aircraft based in the Azores in the mid-Atlantic (Lewis et al., 2007), the NOAA Research Vessel *Ronald H. Brown* (RHB) in the Gulf of Maine, the University of New Hampshire Observing Station at Thompson Farm (TF, 43.11° N, 70.95° W, elevation 24 m) located in the southeastern, rural area of Durham, NH, and the NOAA Chebogue Point (CHB, 43.75° N, 66.12° W, elevation 15 m)

[1]Huffman, J. A., Aiken, A. C., Docherty K. S., et al.: Volatility of primary and secondary organic aerosol in the field contradicts current model representations, Geophys. Res. Lett., submitted, 2007.

field site in Nova Scotia, Canada (Millet et al., 2006). In the spring of 2006 the NSF/NCAR C-130 aircraft sampled over the Mexico City region during the March MIRAGE campaign (MEX) (DeCarlo et al., 2007[2]), where continuous measurements were also made at the T0 surface site (Instituto Mexicano del Petroleo) within the Metropolitan Area of Mexico City (19.49° N, 99.15° W, elevation 2240 m). In the spring of 2006 this aircraft also sampled over the western United States and eastern Pacific during the April–May INTEX-B/IMPEX campaign (IPX) (Dunlea et al., 2008[3]). We add to these observations the urban sampling from the 2001–2002 Pittsburgh Air Quality Study (PAQS) (Wittig et al., 2004), from the winter and summer only when extensive VOC measurements were made as well as the ground site at Trinidad Head, CA (THD, 41.05° N, 124.15° W, 107 m elevation) in spring 2002 during the ITCT-2K2 campaign (Goldstein et al., 2004). Sampling locations for all these sites and platforms are shown in Fig. 2. Note that each mobile platform pursued specific air masses and plumes depending on the scientific objectives of the campaigns and also sampled different amounts of clear air (with a variety of aged air masses and mixing histories) depending on the distance between bases of operation and locations of interest for sampling. The comparisons between campaigns and platforms shown here provide a large-scale overview of organic carbon in the atmosphere, but as the data for each campaign have not been broken up by air mass type, the quantitative concentration comparisons should not be over interpreted.

Organic carbon species measured with less than 30% uncertainty are listed in Table 1 for each platform along with the corresponding measurement technique (a total of 139 compounds). Concentrations of each compound are converted to units of carbon mass concentration ($\mu$g C m$^{-3}$) at standard temperature and pressure conditions (STP, 273 K, 1013.25 hPa) to compile the TOOC budget (excluding methane, by definition). Organic aerosol concentrations are measured by AMS instruments for eight of the eleven datasets examined here. The organic aerosol observations included are accumulation mode measurements, all reporting sub-micron aerosol mass ($PM_1$), with the exception of the PAQS filter observations which represent $PM_{2.5}$. With the exception of large primary non-volatile biological particles, the sub-micron size range comprises the bulk of organic particulate mass (Kanakidou et al., 2005). A factor of 1.81 is applied to the measurements of water soluble organic carbon made aboard the WP-3 aircraft to account for non-soluble carbon (de Gouw et al., 2007). The average ratio of particulate organic matter to organic carbon aerosol aboard the Ron Brown was determined to be 1.9 (Quinn et al., 2006). Organic elemental analysis using high-resolution AMS data analysis (Aiken et al., 2007) suggests that a similar factor is appropriate for Mexico City and IMPEX. We therefore use a factor of 0.5 to convert particulate organic matter to organic carbon aerosol for all platforms, with the exception of Pittsburgh, where a mean factor of 0.56 is appropriate for less aged aerosol (Zhang et al., 2005; Polidori et al., 2007[4]). Turpin and Lim (2001) suggest that the carbon weight per organic molecular weight can vary from 0.48 to 0.63; our use of a single conversion factor may therefore imply up to 25% error in individual observations of organic carbon in particle phase.

Mean daytime concentrations of TOOC and the contributions of several dominant species/classes (highlighted in yellow in Table 1) are shown in Fig. 3 (with mean values listed in Table 2). The local 06:00 a.m.–06:00 p.m. average for each location synthesizes only measurement times where all the dominant species are reported. These "dominant" species account for 73–96% of TOOC. Compounds highlighted in grey in Table 1 contribute less than 1% of mean TOOC across all platforms. The details of these measurements and the concentrations of individual species can be found in the appropriate mission references cited in Table 1. The bars in Fig. 3 denote the interval of $\pm$ one standard deviation on the mean TOOC. We aim here to characterize the typical TOOC budget and therefore exclude biomass burning plumes from the Alaskan fires of 2004 based on acetonitrile concentrations (Heald et al., 2006) and in the Mexico City region based on HCN concentrations (DeCarlo et al., 2007[2]) throughout this analysis. We show for comparison in Fig. 3 the TOOC budget in the fire plumes measured aboard the WP-3 aircraft northeastern North America. These plumes represent atypical air masses and will be discussed separately at the end of this section. The North American TOOC concentrations shown in Fig. 3 are separated into surface and aircraft measurements and then ordered generally by distance from anthropogenic sources. Comparing between datasets there is a clear decline of TOOC with "age" from sources, as expected from removal of organic carbon via deposition, oxidation to CO and $CO_2$ and dilution. However, we also expect that multiple generations of oxidation produces a suite of highly functionalized gas phase compounds which are not detected in the gas phase, and thus that some proportion of this decline may be attributed to deteriorating total mass closure. When interpreting this figure it is essential to acknowledge that the

[2]DeCarlo, P. F., Dunlea, E. J., Kimmel, J. R., et al.: Fast Airborne Aerosol Size and Chemistry Measurements with the High Resolution Aerosol Mass Spectrometer during the MILAGRO Campaign, Atmos. Chem. Phys. Discuss., submitted, 2007.

[3]Dunlea, E. J., DeCarlo, P. F., Aiken, A. C., et al.: Observations of Processed Asian Pollution with a High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS) from the C-130 Aircraft During the INTEX B Field Campaign, in preparation, 2008.

[4]Polidori, A., Turpin, B. J., Davidson, C., Rodenburg, L. A., and Maimone, F.: Organic $PM_{2.5}$: Fractionation by Polarity, FTIR Spectroscopy, and OM/OC for the Pittsburgh aerosol, Aerosol Sci. Tech., submitted, 2007.

**Table 1.** Organic compounds measured at each field location included in this analysis. Species highlighted in yellow are tracked as dominant compounds, species highlighted in grey make up than less than 1% of observed total organic carbon measured across all platforms. Species highlighted in light yellow make up less than 1% of TOOC across all platforms, but are part of a dominant compound class. Compounds measured for each platform are denoted with a symbol; measurement techniques are as follows: Gas Chromatography Mass Spectrometry (GC-MS, •), Proton Transfer Mass Spectrometry (PTR-MS, ∘ ),Hantzsch fluorometric (♦), Difference Frequency Generation-Tunable Diode Laser (DFG-TDL, ◇), Tunable Diode Laser Absorption Spectroscopy (TD-LAS, ▲), Trace Organic Gas Analyzer Mass Spectrometry (TOGA-MS, ▼), Electron Capture mine Gas Chromatography (GC-ECD, ▶), Chemical Ionization Mass Spectrometry (CIMS, —), Particle into Liquid Sampler (PILS, ◘), Aerosol Mass Spectrometry (AMS, □), Filter sample (■). Species measured only for the summertime PAQS sampling are noted with an "**S**". Compounds which were not observed above detection limits are noted with these limits. See footnotes for individual measurement references.

| | Species | Chemical Formula | T0[a] | PAQS[b] | RHB[c] | TF[d] | CHB[e] | THD[f] | MEX/ IPX[g] | WP3[h] | BAE[i] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Ethane | C2H6 | • | | • | • | | | • | • | • |
| 2 | Ethene | C2H4 | • | | • | • | | | • | • | • |
| 3 | Acetylene | C2H2 | • | | • | • | | | • | • | • |
| 4 | Propane | C3H8 | • | • | • | • | • | • | • | • | • |
| 5 | Propene | C3H6 | • | • | • | • | • | • | • | • | • |
| 6 | 2-methyl-propene | C4H8 | | • | | | | | | | •<1ppt |
| 7 | Propadiene | C3H4 | | | | | | | | | • |
| 8 | Propyne | C3H4 | | • | | | • | • | | | • |
| 9 | Butane | C4H10 | • | • | • | • | • | • | •▼ | • | • |
| 10 | Isobutane | C4H10 | • | • | • | • | • | | •▼ | • | • |
| 11 | 2,2-dimethylbutane | C6H14 | | | • | | | | | | • |
| 12 | 2,3-dimethylbutane | C6H14 | | | • | | | | | | •<1ppt |
| 13 | 2,2,3-trimethylbutane | C7H16 | | | • | | | | | | •<1ppt |
| 14 | Isobutene | C4H8 | | | | | | | | | • |
| 15 | 1-butene | C4H8 | | • | • | • | • | • | • | | • |
| 16 | t-2-butene | C4H8 | | • | • | • | • | • | • | | • |
| 17 | c-2-butene | C4H8 | | • | • | • | | | • | | • |
| 18 | 3-methyl-1-butene | C5H10 | | • | • | | • | | | | •<1ppt |
| 19 | 2-methyl-1-butene | C5H10 | | • | • | • | | | | | • |
| 20 | 2-methyl-2-butene | C5H10 | | | | | | | | | • |
| 21 | 1,2-butadiene | C4H6 | | | | | | | | | • |
| 22 | 1,3-butadiene | C4H6 | | | | | | | • | | • |

number of compounds measured is not consistent across all platforms, however the trend in decreasing TOOC cannot be attributed to these sampling differences. The trend in aerosol mass with distance from anthropogenic source regions is less distinct (Fig. 4), indicative of the more complex balance between aerosol formation and loss.

The mean TOOC ranges from 4.0 $\mu$gC m$^{-3}$ measured at the coastal surface site at Trinidad Head to 455.3 $\mu$gC m$^{-3}$ measured at the most polluted site (Mexico City, note concentrations in Fig. 3 are scaled down by a factor of 8 for this site). Trinidad Head was subjected to consistent daytime flow from the northwest, and thus represents clean marine boundary layer concentrations, with rare Asian influence (Goldstein et al., 2004); for those compounds measured, concentrations are consistently lower than at the other sites, with the exception of propane and aromatics, which we attribute to local emissions. TOOC aboard the BAe-146 aircraft over the Azores was also low relative to the other platforms (mean of 6.6 $\mu$gC m$^{-3}$) as air masses were depleted of a number of key species (monoterpenes, ethanol, methacrolein, methyl vinyl ketone), concentrations of which never exceeded detection limits (see Table 1). A notable exception to this are the elevated levels of acetaldehyde reported, but those may be produced during canister storage (Lewis et al., 2007). Air masses sampled in the Azores region are far from continental sources and are therefore deficient in organic compounds which are removed (by precipitation and oxidation) during transport (Lewis et al., 2007). In addition, many oxidized VOCs are multi-functional and may not be detected (Goldstein and Galbally, 2007). Concentrations of TOOC reported for the IMPEX campaign over the western US and eastern Pacific are similarly low (mean of 8.6 $\mu$gC m$^{-3}$). However, both Central Valley pollution and Asian plumes were mixed with the pristine Pacific air sampled during this mission, raising hydrocarbon concentrations, particularly when compared to measurements taken near the Azores. These three datasets are significantly influenced by clean marine conditions and are denoted with shades of blue in Fig. 2 as well as in Figs. 5–7 that will be discussed subsequently. Neither ethane nor formaldehyde were measured at Trinidad Head, inclusion of which would likely elevate mean TOOC at this site to ∼6 $\mu$gC m$^{-3}$. This value, when compared with the concentrations measured over the Azores and during the IMPEX campaign can be taken as a lower limit for mean TOOC in the temperate Northern Hemisphere during spring/summer.

**Table 1.** Continued.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 25 | Cyclopentane | C5H10 | | ● | ● | ● | | | | | ● |
| 26 | Methyl cyclopentane | C6H12 | | | ● | ● | | | | | ●<1ppt |
| 27 | 2- and 3-methylpentane | C6H14 | | ● | ● | | ● | ● | ● | | ● |
| 28 | 2,3-dimethylpentane | C7H16 | | | ● | | | | | | ●<1ppt |
| 29 | 2,4-dimethylpentane | C7H16 | | | ● | | | | | | ●<1ppt |
| 30 | 2,2,4-trimethylpentane | C8H18 | | | ● | ● | | | | | ●<1ppt |
| 31 | 2,3,4-trimethylpentane | C8H18 | | | ● | ● | | | | | ●<1ppt |
| 32 | 2,3,3-trimethylpentane | C8H18 | | | ● | | | | | | ●<1ppt |
| 33 | 1-pentene | C5H10 | | ● | ● | ● | ● | ● | | | ●<1ppt |
| 34 | t-2-pentene | C5H10 | | ● | ● | ● | ● | ● | | | ● |
| 35 | c-2-pentene | C5H10 | | | ● | ● | ● | ● | | | ● |
| 36 | 1-methyl-cyclopentene | C6H10 | | ●S | | | | | | | ●<1ppt |
| 37 | Hexane | C6H14 | ● | ● | ● | ● | ● | ● | ● | | ● |
| 38 | 2-methylhexane | C7H16 | | | ● | | | | | | ●<1ppt |
| 39 | 3-methylhexane | C7H16 | | | ● | | | | | | ●<1ppt |
| 40 | Cyclohexane | C6H12 | | | ● | ● | | | | | ● |
| 41 | Methyl cyclohexane | C7H14 | | | ● | ● | | | | | ●<1ppt |
| 42 | Heptane | C7H16 | | | ● | ● | ● | | ● | | ● |
| 43 | 2-methylheptane | C8H18 | | | ● | ● | | | | | ●<1ppt |
| 44 | 3-methylheptane | C8H18 | | | ● | | | | | | ●<1ppt |
| 45 | Octane | C8H18 | | | ● | ● | | | | | ● |
| 46 | Decane | C10H22 | | | ● | ● | | | | | ●<1ppt |
| 47 | Isoprene | C5H8 | ○ | ●S | ●○ | ●○ | ●○ | ● | ●▼ | ●○ | ● |
| 48 | Benzene | C6H6 | ●○ | ● | ● | ●○ | ●○ | ● | ●▼ | ●○ | ● |
| 49 | Ethylbenzene | C8H10 | ● | ● | ●○ | ● | ● | ● | ●▼ | ●○ | ● |
| 50 | Propylbenzene | C9H12 | | | ●○ | | | | ● | ○ | ●<2ppt |
| 51 | Isopropylbenzene | C9H12 | | | ●○ | | | | ● | ●○ | |
| 52 | 1,3,5-trimethylbenzene | C9H12 | | | ●○ | ● | | | ● | ●○ | ●<2ppt |
| 53 | 1,2,4-trimethylbenzene | C9H12 | | | ●○ | ● | | | ● | ●○ | ●<2ppt |
| 54 | 1,2,3-trimethylbenzene | C9H12 | | | ●○ | ● | | | | ●○ | |
| 55 | Styrene | C8H8 | ○ | | ● | ● | ● | | | | ●<2ppt |
| 56 | Toluene | C7H8 | ●○ | ● | ●○ | ●○ | ● | ● | ●▼ | ●○ | ● |
| 57 | 2-ethyl-toluene | C9H12 | | | ●○ | ● | | | | ●○ | |
| 58 | 3-ethyl-toluene | C9H12 | | | ●○ | ● | | | ● | ●○ | |
| 59 | 4-ethyl-toluene | C9H12 | | | ●○ | ● | | | ● | ●○ | |
| 60 | p-xylene | C8H10 | | ● | ●○ | ● | ● | ● | ●▼ | ●○ | ● |
| 61 | m-xylene | C8H10 | | ● | ●○ | ● | ● | ● | ●▼ | ●○ | ● |
| 62 | o-xylene | C8H10 | ● | ● | ●○ | ● | ● | ● | ●▼ | ●○ | ● |
| 63 | Alpha-pinene | C10H16 | ○ | ● | ●○ | ●○ | ●○ | ● | | ●○ | ●<2ppt |
| 64 | Beta-pinene | C10H16 | ○ | | ●○ | ●○ | ●○ | | | ●○ | ●<2ppt |
| 65 | Camphene | C10H16 | | | ○ | ● | | | | ○ | ●<2ppt |
| 66 | Limonene | C10H16 | | | ●○ | ● | | | | ●○ | ●<2ppt |
| 67 | Carene | C10H16 | | | ○ | | ● | | | ○ | ●<2ppt |
| 68 | Methyl t-butyl ether (MTBE) | C5H12O | | ● | ●○ | | ● | ● | ▼ | ● | |
| 69 | Methanol | CH3OH | | ● | ●○ | ○ | ●○ | ● | ▼ | ○ | ● |
| 70 | Ethanol | C2H5OH | | ● | ● | | ● | ● | ▼ | | ●<20ppt |
| 71 | Isopropanol | C3H7OH | | ● | ● | | ● | ● | | | |
| 72 | Phenol | C6H5OH | ○ | | | | | | | | |
| 73 | Formic Acid | HCOOH | ○ | | | | | | — | | |
| 74 | Acetic Acid | CH3COOH | ○ | | ○ | ○ | ○ | | — | ○ | |
| 75 | Peroxyacetic Acid | CH3COOOH | | | | | | | — | | |
| 76 | Propanoic Acid | C2H6COOH | | | | | | | — | | |
| 77 | Formaldehyde | HCHO | ♦ | | | | ○ | | ◊ | ▲ | ♦ |

**Table 1.** Continued.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 78 | Acetaldehyde | CH3CHO | ○ | ● | ●○ | ○ | ●○ | ● | ▼ | ○ | ● |
| 79 | Methacrolein | C4H6O | ○ | ●S | ●○ | ○ | ●○ | ● | | ●○ | ●<15ppt |
| 80 | Propanal | C3H6O | | | ● | | ● | | ▼ | | ●<20ppt |
| 81 | 2-methyl-propanal | C4H8O | | | | | ● | | | | |
| 82 | Butanal | C4H8O | | ● | ● | | ● | ● | ▼ | | ●<20ppt |
| 83 | 2-methyl butenol (MBO) | C5H9OH | | | | | ● | ● | | | |
| 84 | Pentanal | C5H10O | | ●S | ● | | ● | | ▼ | | |
| 85 | Hexanal | C6H12O | | ● | ● | | | | ▼ | | |
| 86 | Heptanal | C7H14O | | | ● | | | | | | |
| 87 | Acetone | C3H6O | ○ | ● | ●○ | ○ | ●○ | ● | ▼ | ○ | ● |
| 88 | Hydroxyacetone | C3H5OHO | | | | | ○ | | | | |
| 89 | Methyl vinyl ketone (MVK) | C4H6O | ○ | ● | ●○ | ○ | ●○ | ● | | ●○ | ●<10ppt |
| 90 | Methyl ethyl ketone (MEK) | C4H8O | ○ | ● | ●○ | ○ | ●○ | ● | ▼ | ●○ | ●<15ppt |
| 91 | Methyl butanone | C5H10O | | | | | ● | | | | |
| 92 | 2-pentanone | C5H10O | | | | | ● | | ▼ | | |
| 93 | 3-pentanone | C5H10O | | | | | ● | | ▼ | | |
| 94 | 2-hexanone | C6H12O | | | | | | | ▼ | | |
| 95 | 3-hexanone | C6H12O | | | | | | | ▼ | | |
| 96 | 3-methylfuran | C5H6O | | ●S | | | ● | | | ● | |
| 97 | Nopinone | C9H14O | | | | | ○ | | | | |
| 98 | Pinonaldehyde | C10H16O4 | | | | | ○ | | | | |
| 99 | Methylene chloride | CH2Cl2 | | ●S | ● | | ● | | ●▼ | ● | |
| 100 | Methyl chloride | CH3Cl | | | | | ● | | ●▼ | ● | |
| 101 | Methyl iodide | CH3I | | | | ● | ● | ● | ●▼ | ● | |
| 102 | Methyl bromide | CH3Br | | | | ● | | | ● | ● | |
| 103 | Methylene bromide | CH2Br2 | | | | ● | | | ● | ● | |
| 104 | Bromoform | CHBr3 | | | | ● | | | ● | ● | |
| 105 | Chloroform | CHCl3 | ● | ● | ● | | ● | ● | ●▼ | ● | |
| 106 | Dibromochloromethane | CHClBr2 | | | | | | | ● | ● | |
| 107 | Bromodichloromethane | CHBrCl2 | | | | | | | ● | | |
| 108 | Methylchloroform | CH3CCl3 | | | | | | | | ● | |
| 109 | Trichloroethane | C2H3Cl3 | | | ● | | | | ▼ | ● | |
| 110 | Trichloroethylene | C2HCl3 | | | | ● | ● | | ● | ● | |
| 111 | 1,2-Dichloroethane | C2H4Cl2 | | | | | | | ● | ● | |
| 112 | Ethylchloride | C2H5Cl | | | | | | | ● | | |
| 113 | 2-Bromapropane | C3H7Br | | | | | | | | ● | |
| 114 | HFC-134a | C2H2F4 | | | | | | | ● | ● | |
| 115 | HCFC-21 | CHFCl2 | | | | | | | | ● | |
| 116 | HCFC-22 | CHClF2 | | | | | | | ● | ● | |
| 117 | HCFC-123 | C2HCl2F3 | | | | | | | | ● | |
| 118 | HCFC-124 | C2HClF4 | | | | | | | | ● | |
| 119 | HCFC-141b | C2H3Cl2F | | | | | | | ● | ● | |
| 120 | HCFC-142b | C2H3ClF2 | | | | | | | ● | ● | |
| 121 | Dimethylsulfide (DMS) | C2H6S | ○ | ●S | ●○ | ○ | ●○ | ● | ●▼ | ●○ | ● |
| 122 | Acetonitrile | CH3CN | ○ | ●S | ●○ | ○ | ●○ | ● | ▼ | ○ | |
| 123 | Hydrogen cyanide | HCN | | | | | | | — | | |
| 124 | Methyl nitrate | CH3NO3 | | | ● | ● | ● | | ● | ● | ● |
| 125 | Ethyl nitrate | C2H5NO3 | | | ● | ● | ● | | ● | ● | ● |
| 126 | Isopropyl nitrate | C3H7NO3 | | | ● | ● | ● | | ● | ● | |
| 127 | Propyl nitrate | C3H7NO3 | | | ● | ● | ● | | ● | ● | ● |
| 128 | Butyl nitrate | C4H9NO3 | | | ● | ● | ● | | ● | ● | |
| 129 | 3-methyl-2-butyl | C5H12NO3 | | | | | | | ● | ● | ● |

**Table 1.** Continued.

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | nitrate | | | | | | | | | | | |
| 130 | 2-pentyl nitrate | C5H11NO3 | | | | ● | | | ● | ● | ● |
| 131 | 3-pentyl nitrate | C5H11NO3 | | | | ● | | | ● | ● | ● |
| 132 | PAN | C2H3NO5 | | | ▶ | ▶ | ▬ | | ▬ | ▬ | ▶ |
| 133 | PPN | C3H5NO5 | | | ▶ | | ▬ | | ▬ | ▬ | |
| 134 | PBN | C4H7NO5 | | | | | | | ▬ | ▬ | |
| 135 | PBzN | C7H5NO5 | | | | | | | | ▬ | |
| 136 | APAN | C3H3NO5 | | | | | | | ▬ | ▬ | |
| 137 | MoPAN | C3H5ONO5 | | | | | | | ▬ | ▬ | |
| 138 | MPAN | C4H5NO5 | | | ▶ | | | | ▬ | ▬ | |
| 139 | Aerosol organic carbon | | □ | ■ | □ | □ | □ | □ | □ | ◘ | □ |

[a] (Aiken et al., 2007)
[b] (Millet et al., 2005; Polidori et al., 2006)
[c] (Goldan et al., 2004; Flocke et al., 2005; Warneke et al., 2005; Quinn et al., 2006)
[d] (Flocke et al., 2005; Sive et al., 2005; Zhou et al., 2005; Cottrell et al., 2007)
[e] (Millet et al., 2006; Holzinger et al., 2007; Allan et al., 2007)
[f] (Allan et al., 2004; Millet et al., 2004)
[g] (Dunlea et al., 20083; DeCarlo et al., 20072)
[h] (Schauffler et al., 1999; de Gouw et al., 2006; Sullivan et al., 2006)
[i] (Hopkins et al., 2003; Jayne et al., 2000)

**Table 2.** Mean concentrations of TOOC dominant organic carbon compounds for each platform in units of $\mu$gC m$^{-3}$ (as ordered in Fig. 3). Please refer to Table 1 for measurement techniques.

| | T0 | PAQS S | PAQS W | RHB | TF | CHB | THD | MEX | WP3 | IPX | BAE |
|---|---|---|---|---|---|---|---|---|---|---|---|
| OC aerosol | 12.08 | 5.16 | 2.35 | 2.71 | 2.77 | 1.40 | 0.20 | 1.57 | 2.73 | 0.33 | 0.30 |
| Ethane | 5.22 | | | 1.47 | 1.12 | | | 0.88 | 1.35 | 1.38 | 0.98 |
| Propane | 51.89 | 2.92 | 4.95 | 0.89 | 0.58 | 0.38 | 0.57 | 1.20 | 0.65 | 0.62 | 0.17 |
| Butane | 125.35 | 2.00 | 4.46 | 0.48 | 0.24 | 0.18 | 0.10 | 0.86 | 0.32 | 0.19 | 0.07 |
| Acetone | 25.92 | 6.89 | 1.72 | 2.43 | 3.57 | 1.52 | 1.04 | 2.33 | 3.17 | 1.82 | 1.92 |
| Methanol | | 6.05 | 2.46 | 1.14 | 1.78 | 0.89 | 0.48 | 2.04 | 1.18 | 1.23 | 0.46 |
| Ethanol | | | 1.70 | 0.28 | | 0.25 | 0.21 | 0.35 | | 0.13 | 0.00 |
| Acetic Acid | 5.03 | | | 0.41 | 0.74 | 0.62 | | 1.04 | 0.78 | 0.20 | |
| Formic Acid | 2.64 | | | | | | | 0.76 | | 0.17 | |
| Acetaldehyde | 6.86 | 2.17 | 0.67 | 0.53 | 0.39 | 0.23 | 0.26 | 0.54 | 0.52 | 0.16 | 1.80 |
| Formaldehyde | 5.29 | | | | | 1.06 | | 0.49 | 1.17 | 0.10 | 0.33 |
| Monoterpenes | 0.28 | 0.10 | 0.03 | 0.46 | 0.64 | 0.14 | 0.13 | | 0.01 | | 0.00 |
| Isoprene | 1.25 | 4.53 | | 0.28 | 1.54 | 0.12 | 0.01 | 0.11 | 0.32 | 0.05 | 0.01 |
| MVK+MACR | 40.45 | 0.67 | | 0.27 | 1.37 | 0.12 | 0.05 | | 0.52 | | 0.00 |
| Aromatics | 71.08 | 3.27 | 2.84 | 0.57 | 1.10 | 0.23 | 0.34 | 0.46 | 0.10 | 0.22 | 0.18 |
| PANs | | | | 1.11 | 0.32 | 0.18 | | 0.72 | 0.59 | 0.33 | |
| Halogens | | 0.10 | 0.04 | 0.06 | 0.02 | 0.36 | 0.01 | 0.55 | 0.29 | 0.53 | 0.00 |
| Other | 101.97 | 12.75 | 7.70 | 3.46 | 2.28 | 1.15 | 0.63 | 2.91 | 2.16 | 1.19 | 0.43 |
| TOOC | 455.31 | 45.12 | 28.91 | 16.54 | 18.47 | 8.83 | 4.04 | 16.80 | 15.87 | 8.65 | 6.65 |

TOOC concentrations in Mexico City, North America's most populous (over 20 million inhabitants), and most polluted city (Molina et al., 2007), represent a stark contrast to remote sampling and also to a US urban area (Pittsburgh). Mean TOOC concentrations are at least 10 times greater than at any other site. The proximity to large emission sources and particularly fresh hydrocarbon emissions results in high daytime mean TOOC concentrations. Over half of the TOOC consists of hydrocarbons (alkanes and alkenes make up the majority of the large "other" contribution to TOOC at this site), which can be attributed to large vehicular and liquefied petroleum gas (LPG) emissions (Velasco et al., 2007). Concentrations of primary biogenic species are similar to concentrations reported at other sites in North America. The TOOC at this site is likely to be the most comprehensive in terms of carbon closure, due to the short interval between emission and sampling, leading to a relatively smaller fraction of gas phase secondary compounds.

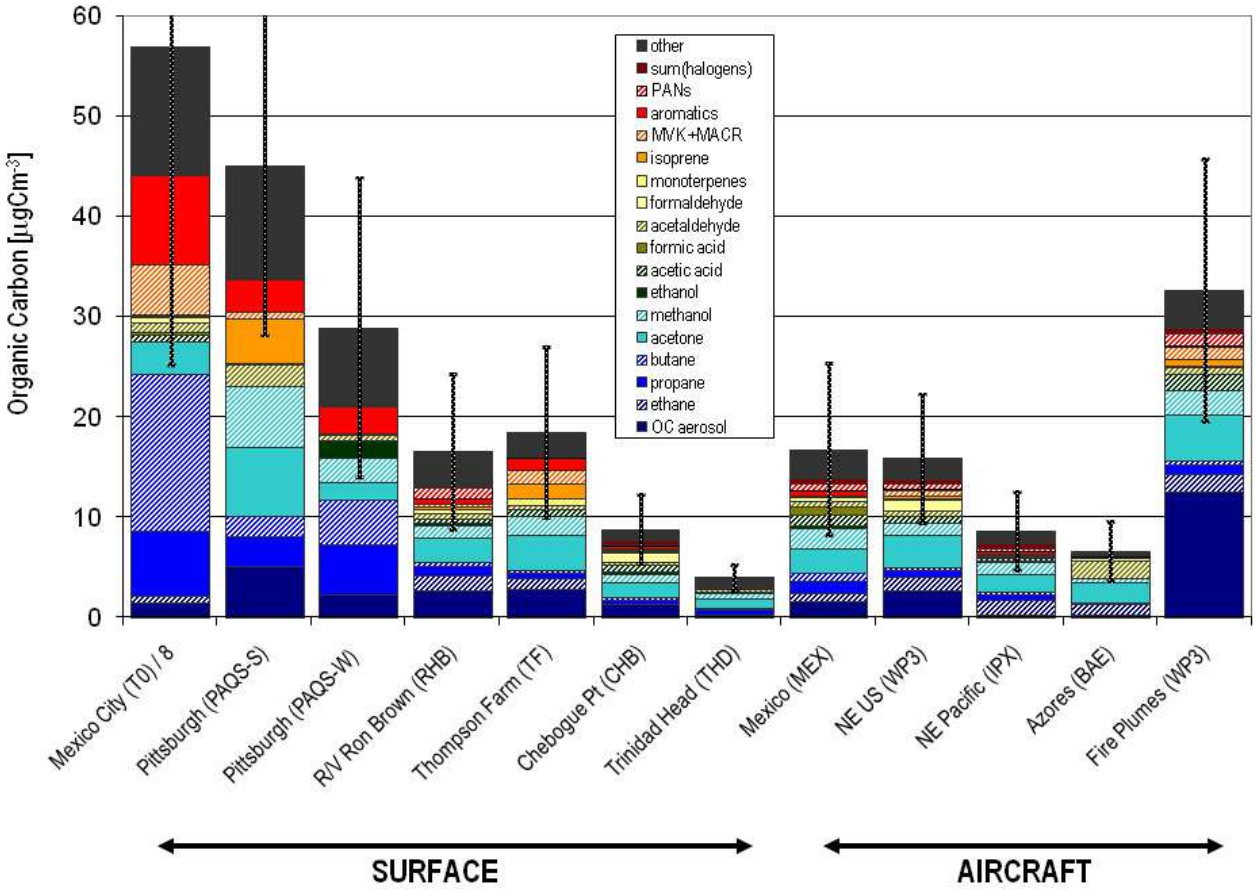


**Fig. 3.** Mean daytime organic carbon concentrations for ICARTT platforms (NOAA WP-3 aircraft, UK BAe-146 aircraft, NOAA R/V Ron Brown, AIRMAP Thompson Farm site, NOAA Chebogue Point site) during July–August 2004, for the Trinidad Head site in April–May 2002, for the Pittsburg Air Quality Study in January–February 2002 (W) and July–August 2002 (S), for the NSF/NCAR C-130 aircraft during MIRAGE in March 2006 and IMPEX in April–May 2006 and the T0 Mexico City surface site in March 2006. Also shown are the mean TOOC concentrations measured in these fire plumes aboard the NOAA WP-3 aircraft during ICARTT. Organic carbon concentrations at the Mexico City site are divided by a factor of 8. The grey bars denote the standard deviation of the TOOC concentrations reported for each platform. See text for details.

Typical urban conditions in North America are represented by the Pittsburgh site. Mean TOOC concentrations here in summer (45.1 $\mu$gC m$^{-3}$) are greater than twice the concentrations reported at other North American sites, with the exception of Mexico City. As seen in Mexico City, alkanes and alkenes are elevated at this site and contribute approximately half of total TOOC. Elevated propane and butane concentrations are attributed to nearby fuel and natural gas sources (Millet et al., 2005).

Mean TOOC concentrations reported by aircraft sampling outflow from the northeastern US (WP-3) and Mexico (C-130) are similar (means of 15.9 $\mu$gC m$^{-3}$ and 16.8 $\mu$gC m$^{-3}$). During MIRAGE (Mexico City), mean concentrations of isoprene and oxidation products (including formaldehyde) are less than half of those measured over the northeastern US. However the MIRAGE observations during early spring do not represent the same peak in biogenic activity as the summertime sampling of the WP-3. Over Mexico City, anthropogenic compounds such as aromatics and halogens are present at over twice the mean concentration observed over the northeastern US (WP-3), and both particulate OC and methanol concentrations are also elevated.

The largest contributors to gas-phase OC across platforms are acetone (1.0–25.9 $\mu$gC m$^{-3}$), methanol (0.5–6.0 $\mu$gC m$^{-3}$) and ethane (0.5–5.2 $\mu$gC m$^{-3}$). The relatively long lifetimes of acetone and methanol (7–14 days) explain the prevalence of these compounds throughout the troposphere. Jacob et al. (2002, 2005) suggest a similar global atmospheric burden of 4 Tg for these two compounds; in terms of carbon this is equivalent to a factor of two more acetone than methanol, generally consistent with mean concentrations observed here. Ethane is relatively well-mixed in each hemisphere with a lifetime of months (Rudolph, 1995; Goldstein et al., 1995).

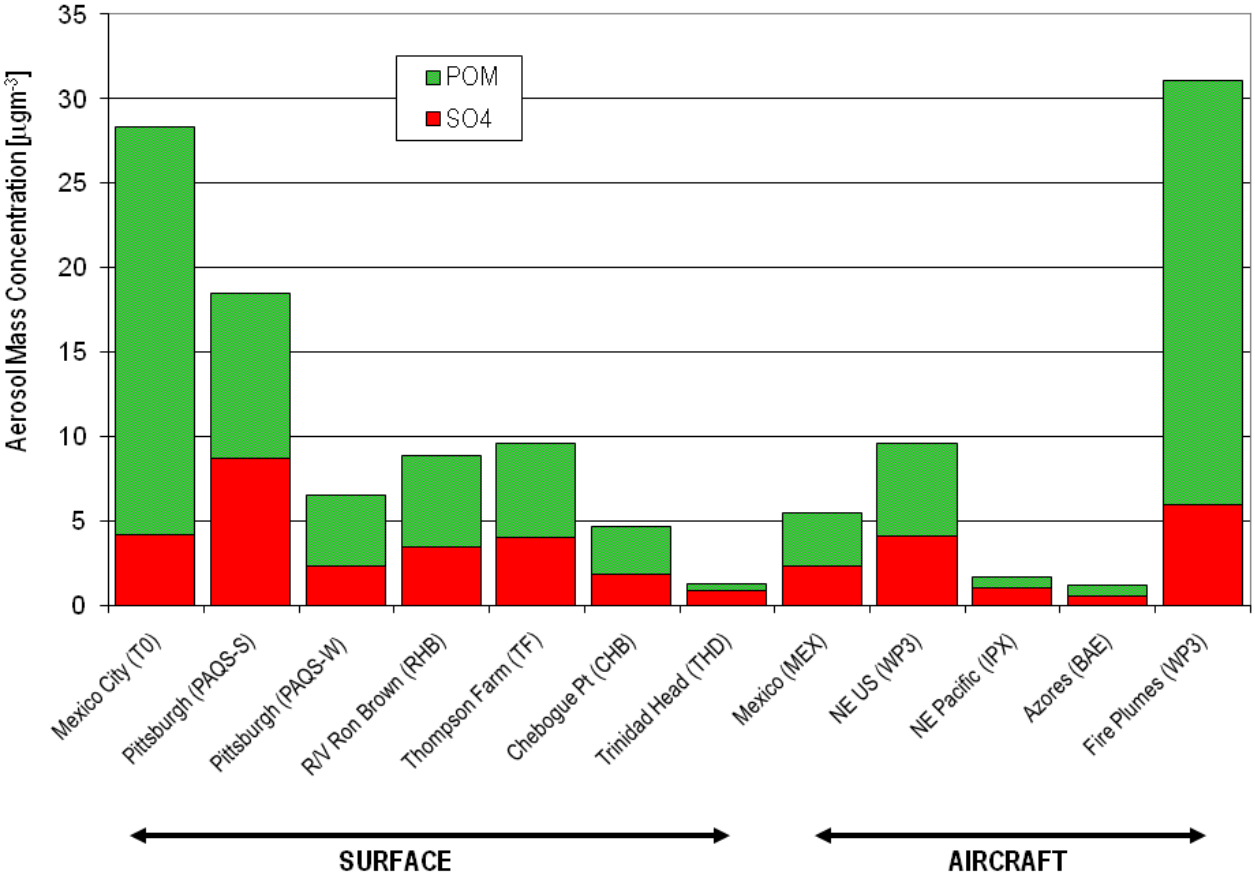


**Fig. 4.** Mean daytime sulfate and particulate organic matter concentrations for the same platforms and time periods as Fig. 3. See text for details.

Formaldehyde concentrations reported here make up a significant fraction of the gas-phase TOOC, with the exception of the measurements over the northeastern Pacific. Formaldehyde is produced in the atmosphere by the oxidation of VOCs. The oxidation of methane provides a large global background of formaldehyde with major local enhancements resulting from rapid oxidation of biogenic and anthropogenic VOC sources. In situ measurements of formaldehyde over North America, primarily in forested regions, in the summer-fall range from 0.5–7.5 $\mu$gC m$^{-3}$ (Palmer et al., 2003). Measurements of formaldehyde mixing ratios were not available at Thompson Farm, which is located in a mixed hardwood forest in New Hampshire and generally receives unpolluted airflow from the west (Talbot et al., 2005). Biogenic VOCs (monoterpenes, isoprene and its oxidation products methacrolein and methyl vinyl ketone) at Thompson Farm make up the largest fraction of the TOOC budget among all the datasets reported here (White et al., 2007[5]). Formaldehyde concentrations of 1.1–4.3 ppb (0.5–2.1 $\mu$gC m$^{-3}$) were observed over the region in low-altitude flights of the DC-8 in summer 2004 (Fried et al., 2007[6].) This suggests that formaldehyde from biogenic oxidation could be an important additional component to the organic carbon budget at the Thompson Farm site.

Organic carbon in the particle phase makes up 3–17% of the TOOC budget shown in Fig. 3. The highest mean concentration (12.1 $\mu$gC m$^{-3}$) is reported in Mexico City, but makes up the smallest fractional contribution to TOOC at this site. The largest proportion of TOOC in aerosol (15–17%) is found over northeastern North America (WP3, RHB, TF and CHB). These sites and platforms are downwind of the Boston-New York corridor and the Ohio River Valley, but are also influenced by airflow from rural northeastern US and

[5]White, M. L., Russo, R. S., Zhou, Y., Mao, H., Varner, R. K., Ambrose, J., Veres, P., Wingenter, O. W., Haase, K., Talbot, R., and Sive, B. C.: Volatile Organic Compounds in Northern New England Marine and Continental Environments during the ICARTT 2004 Campaign, J. Geophys. Res., submitted, 2007.

[6]Fried, A., Walega, J. C., Olsen, J. R., et al.: Formaldehyde over North America and the North Atlantic during the Summer 2004 INTEX Campaign: Methods, Observed Distributions, and Measurement Box Model Comparisons, J. Geophys. Res., submitted, 2007.

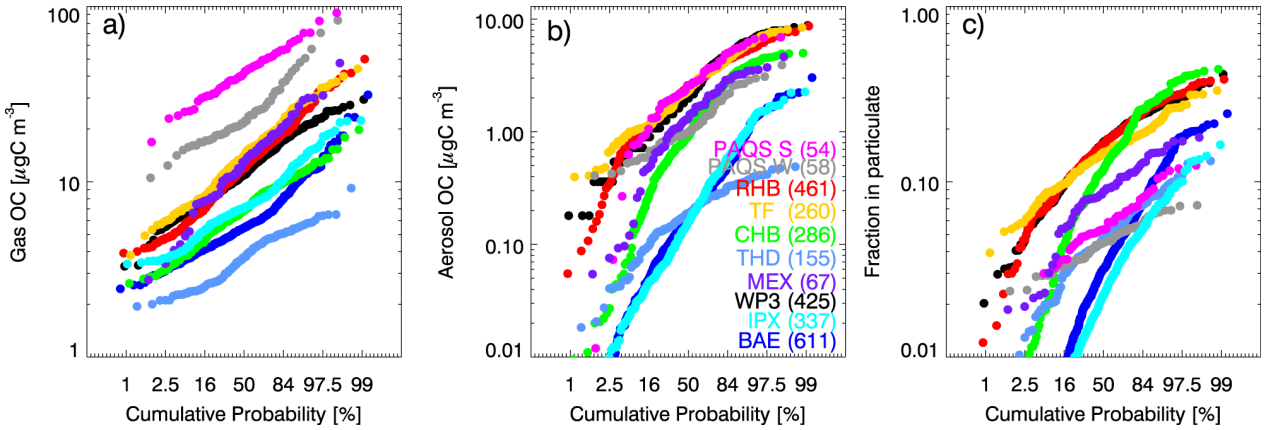


**Fig. 5.** Cumulative probability distribution of observed **(a)** gas-phase organic carbon mass concentrations **(b)** particle-phase organic carbon mass concentrations **(c)** the fraction of TOOC in particle phase. Abbreviations for each measurement platform are given in the center panel with the number of observations. Colors correspond to measurement locations in Fig. 2. Each data point represents 1 min merged data for the aircraft (WP3, BAE), 30 min merged data aboard the ship (RHB) and at Thompson Farm (TF), hourly means at Chebogue Point (CHB), and 3 min merged data for MIRAGE (MEX) and IMPEX (IPX), with coincident "dominant" species measurements during the day only (see Table 1). Note that detection limits for aerosol measurements vary with platform. The 1-min WP-3 observations here do not include HCHO (5-min averaging necessary to overcome noise).

Canada (Millet et al., 2006; Quinn et al., 2006; Sullivan et al., 2006). The observed aerosol OC includes POA from urban emissions but is dominated by SOA from both anthropogenic and biogenic oxidation (de Gouw et al., 2005; Williams et al., 2007; Zhang et al., 2007a). In general, the OC aerosol measured aboard the Ron Brown and at Chebogue Point is more oxidized than at other continental sites (Zhang et al., 2007a; Williams et al., 2007). Approximately 90% of the TOOC in Pittsburgh is in the gas-phase throughout the year, although the absolute concentrations of aerosol OC doubles in the summertime due to secondary production (Millet et al., 2005; Zhang et al., 2005). Air masses sampled at Trinidad Head in coastal California, by the BAe-146 near the Azores, and by the C-130 over the northeastern Pacific include non-negligible amounts of organic carbon in aerosol form (mean 0.2–0.4 $\mu$gC m$^{-3}$, equivalent to ~5% of TOOC) despite the distance from continental emissions.

Particulate organic matter makes up 25–54% of the total mean aerosol mass observed in the studies summarized here, often in excess of sulfate (Fig. 4), a pattern that extends to most of the polluted regions of the Northern Hemisphere (Zhang et al., 2007a). Vertical profiles of aerosol concentrations off of eastern North America show an increase in the mean particulate organic matter to sulfate mass ratio with altitude, from 0.5 in the boundary layer up to factors of 3–4 in the mid-upper troposphere (Peltier et al., 2007a), similar to observations off of Asia (Heald et al., 2005) and the southern United States and Costa Rica (Murphy et al., 2006). However, aerosol profiles over Mexico City and off of the western US show greater sulfate aloft and do not exhibit this same shift in composition with altitude (Peltier et al., 2007[7]). Higher OC aerosol concentrations aloft in continental outflow regions may be the result of lofting of insoluble SOA precursors and continuous aerosol production with aging.

The surface TOOC observations within the Metropolitan Area of Mexico City (T0) are substantially elevated (by over a factor of 25 in the mean) compared to the regional aircraft sampling of the C-130 aircraft during the MILAGRO campaign (MEX). These differences are dominated by the high concentrations of short-lived hydrocarbon and aromatics measured within the source region. Mean daytime OC aerosol concentrations are eight times higher at the T0 surface site than aboard the aircraft. However, when coincident sampling periods are selected this difference is reduced to less than a factor of two. Stone et al. (2007) also report a factor of two decrease in OC aerosol concentrations when moving from the urban T0 site to the peripheral T1 site in Mexico City. We attribute the reduced mean TOOC reported aboard the aircraft to both the dilution of the Mexico City outflow and the mixed regional sampling (including clean air masses) compared to the concentrated source signature reported at the surface.

Figure 3 compares the mean TOOC budget within air influenced by the 2004 Alaskan fires measured aboard the WP-3 aircraft, to non-fire influenced conditions. Concentrations of the dominant gas-phase species are elevated by 30–110% in the fire plumes, accompanied by an increase of over a factor of four in OC aerosol concentrations. Particulate organic

[7]Peltier, R. E., Hecobian, A. H., Weber, R. J., et al.: Water-Soluble Organic and Inorganic $PM_{1.0}$ Bulk Composition from Asia: Results from IMPEX-B Field Campaign, in preparation, 2007.

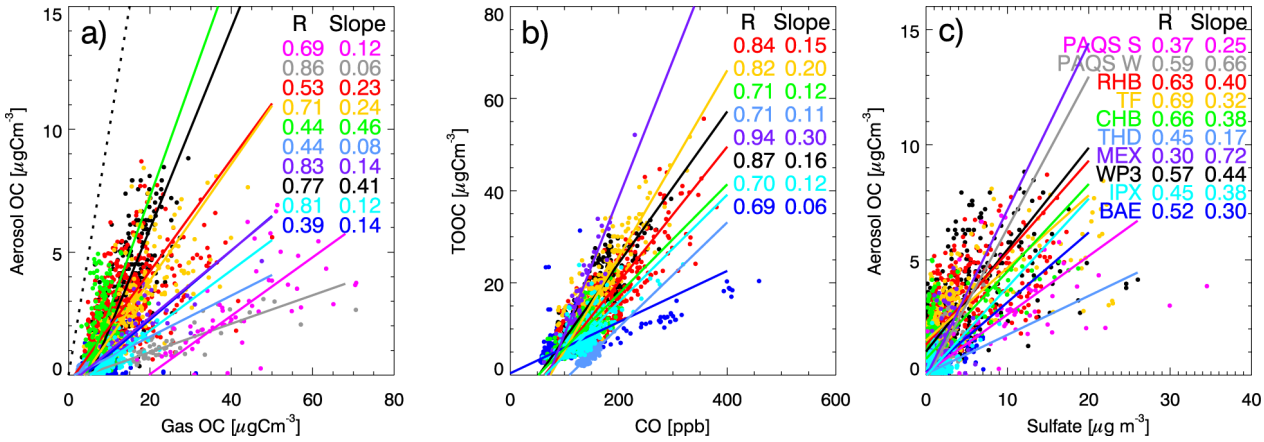


**Fig. 6.** Relationship between observed day-time concentrations of **(a)** aerosol OC and gas-phase OC **(b)** total observed organic carbon (TOOC) and carbon monoxide (CO) **(c)** aerosol OC and sulfate. Colors correspond to measurement platforms in Fig. 2. Regression lines are computed using the reduced major axis method (Hirsch and Gilroy, 1984), with the correlation coefficient (R) and slope for each platform shown in insets. Abbreviations for each measurement platform are given in the right-most panel. Data details are as in Fig. 5.

matter contributes over 70% of the aerosol mass observed in these biomass burning events (Fig. 4). Biomass burning represents the bulk of global primary emissions of organic carbon aerosol (IPCC, 2007), and this highly variable source can produce large increases in TOOC, both locally and downwind (Lewis et al., 2007; Heald et al., 2006).

In addition to those compounds reported here, a number of lower molecular weight organic carbon compounds have been detected in the ambient atmosphere. These include glyoxal, methylglyoxal, and carboxylic acids. Typical glyoxal concentrations of 0.02–0.1 ppb (Liggio et al., 2005) are a minor contributor to the organic carbon budget, although may be more important in urban regions with photochemical smog (Volkamer et al., 2006) and may be responsible for a significant fraction of urban SOA formation (Volkamer et al., 2007). Methylglyoxal has similarly been detected at low atmospheric concentrations (Munger et al., 1995; Spaulding et al., 2003). For most of the datasets here, acetic acid (ranging from 0.2–1.0 $\mu$gC m$^{-3}$) is the only carboxylic acid measured. The C-130 observations alone include a suite of carboxylic acid measurements ($C_1$-$C_3$), with mean total concentrations of over 2 $\mu$gC m$^{-3}$ during MIRAGE and 0.4 $\mu$gC m$^{-3}$ during IMPEX. Tanner and Law (2003) summarize the range of ambient formic acid (0.04–7.2 $\mu$gC m$^{-3}$) observations for remote to urban conditions. The additional mass inferred for these unmeasured compounds is in line with the 55–85% VOC mass closure estimates of Chung et al. (2003).

## 3 Variability of TOOC over North America

Figure 5 shows that there is large variability in the concentration and phase of TOOC. The cumulative probability distribution is shown to emphasize the "tails" of the frequency distribution, with the median observations shown at 50%. We note here that not all datasets include the same compounds (see Table 1). We do not include surface observations at Mexico City (T0) in the analysis of this section due to the limited number of whole air sample measurements at this site. Both gas-phase and particle-phase organic carbon observations in Fig. 5 span two orders of magnitude. Total gas-phase organic carbon is never observed below concentrations of 2 $\mu$gC m$^{-3}$ at any location, and at Pittsburgh minimum concentrations are five times as high. Aerosol concentrations range from detection limits up to 10 $\mu$gC m$^{-3}$. The maximum observed fraction of TOOC in the particle phase for an individual observation is 50%. Previous reported measurements of total non-methane organic carbon in the gas phase at Chebogue Point in Fall 1993 ranged from detection limits to 87 $\mu$gC m$^{-3}$, with a mean of $\sim$7 $\mu$gC m$^{-3}$ (Roberts et al., 1998). While the mean agrees well with TOOC concentrations reported here, the range of concentrations measured in 2004 appears smaller. The larger values in 1993 were attributed to plumes and our longer measurement averaging times (1 h) mute this effect here. In addition, emission inventories from the EPA suggest that VOC emissions in the northeastern United States, particularly vehicular emissions, have declined substantially in the past 11 years (Parrish, 2006); thus plumes are expected to be less concentrated in 2004. We also note that the measurements in 2004 did not include $C_2$ hydrocarbons which were estimated to contribute 2 to 5 $\mu$gC m$^{-3}$ to the organic carbon measured at Chebogue Point in 1993 (Roberts et al., 1998). The range of organic carbon concentrations, as well as the mean phase distribution (Fig. 3) is similar at Thompson Farm and aboard the Ron Brown. These two sites also have the highest proportion of organic carbon in the particle phase (Fig. 5c). Together, they suggest a rather homogeneous character to surface organic

carbon over New England (outside of urban areas). The aircraft observations provide a clear contrast between outflow conditions (WP-3 over the northeastern US) and remote sampling (BAe-146 over the Azores), with smaller concentrations overall measured at the Azores. The TOOC observations from the IMPEX campaign over the eastern Pacific are very similar to those in the "clean" conditions sampled over the Atlantic by the BAe-146, but with a smaller maximum fraction in aerosol form. TOOC concentrations at the similarly remote Trinidad Head site in coastal California are both smaller and less variable, and thus appear to be less influenced by anthropogenic plumes. TOOC variability is also small at the Pittsburgh site due to the lack of very clean periods because of the consistent influence of primary gases and aerosols in urban areas.

Previous studies have used photochemical "clocks", defined by contrasting rates of hydrocarbon oxidation, to characterize the evolution of air masses in the atmosphere (Roberts et al., 1984). De Gouw et al. (2005) successfully used these clocks on observations of anthropogenic plumes from coastal New England in 2002 to demonstrate the increase of organic aerosol concentrations over time. We find here that while a photochemical clock defined by the toluene:benzene ratio robustly predicts the mass loading of organic carbon aerosol over the Gulf of Maine ($R$=0.77), as shown by de Gouw et al. (2005), this does not appear to be a widespread trend across the measurement platforms examined here. For measurements at large distances from the emission sources (Trinidad Head, BAE aircraft in the Azores, IMPEX) this is not surprising given the small concentrations of particle phase OC observed. The measurements of organic carbon aerosol reported here represent a wide range of sampling conditions, including observations from mixed sources and aged air masses which may limit the robustness of the photochemical clock calculation (McKeen et al., 1996; Parrish et al., 2007). Consequently, the photochemical clock cannot be used to robustly characterize the evolution of the organic aerosol over North America.

Figure 6 illustrates some robust relationships seen across all platforms. Concentrations of gas-phase and particle-phase organic carbon are correlated (Fig. 6a). Air masses are rarely dominated by one phase, and comparison with the 1-to-1 line shows that there are no sites or platforms where the majority of TOOC is in particle phase. The slopes here confirm that the observations in the northeastern United States have the highest proportion of TOOC in the particle phase. The lowest fraction of particulate OC is seen at Pittsburgh and the remote sites; the former is likely a result of proximity to sources and insufficient time for secondary production and the later results from preferential wet removal during transport.

Figure 6b shows that carbon monoxide (CO), traditionally viewed as a tracer of combustion sources, is a good predictor for TOOC concentrations, explaining 46–86% of the variability. This indicates that the factors which control

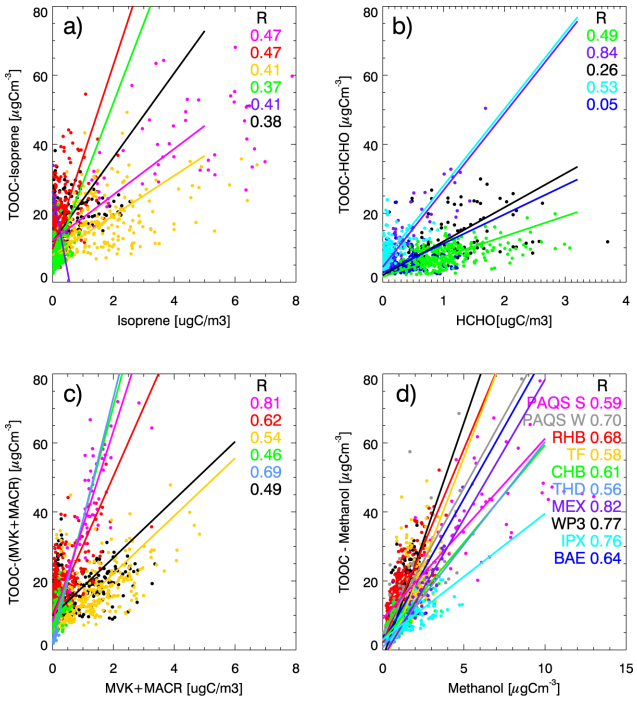


**Fig. 7.** Relationship between observed day-time concentrations of biogenic tracers and TOOC-biogenic tracers: **(a)** Isoprene **(b)** Formaldehyde (HCHO) **(c)** methyl vinyl ketone (MVK) and methacrolein (MACR) **(d)** methanol. Colors correspond to measurement platforms in Fig. 2. Regression lines are computed using the reduced major axis method Hirsch and Gilroy, 1984), with the correlation coefficient (R) for each platform shown in insets. Abbreviations for each measurement platform are given in the right-most panel. Data details are as in Fig. 5.

CO concentrations, either sources or plume dilution/mixing, strongly influence TOOC. Recent evidence has shown that biogenic sources of secondary CO may be larger than anthropogenic sources in the United States during the summer (Hudman et al., 2008), therefore this relationship does not provide unambiguous evidence of source type for TOOC away from large anthropogenic plumes. The lack of correlation (not shown) between TOOC and sulfur dioxide ($SO_2$) concentrations (with the exception of Asian plumes observed during IMPEX) does suggest that variability in this source is unlikely to be dominated by power generation. The six datasets which include measurements of acetylene, an unambiguous tracer of pollution and fire influence (Xiao et al., 2007), show strong correlations between this tracer and TOOC (not shown). Sites and platforms with anthropogenic influence exhibit the largest TOOC/CO slopes (highest values reported near Mexico City); however the routine VOC measurements included in these datasets are also most likely to approach total mass closure in fresh air masses. The variability of TOOC at remote sites is not as well predicted by CO and the TOOC/CO slope is systematically lower. CO

is well correlated with both the gas-phase and particle-phase OC across all platforms, but correlation coefficients are highest when the total observed OC budget (TOOC) is considered. This result suggests that the TOOC "family" may be a useful concept for understanding large scale variability in the organic carbon budget.

Organic carbon aerosol concentrations are also correlated with sulfate but to a lesser degree (Fig. 6c). Several factors may contribute to this: common anthropogenic sources or source regions, similar formation mechanisms, shared removal processes and synoptic changes in meteorology. At both Thompson Farm and in Pittsburgh, sulfate is better correlated ($R>0.8$) with the oxygenated component of organic aerosol than with total organic aerosol concentrations, suggesting that the relationship between sulfate and organic aerosol is not solely driven by primary anthropogenic emissions (Zhang et al., 2005). Sullivan et al. (2006) suggest that the organic carbon aerosol observed in the boundary layer aboard the WP-3 is of secondary anthropogenic origin. Recent laboratory studies (Ng et al., 2007) have demonstrated high SOA yields (30–37%) from anthropogenic aromatic precursors under low $NO_x$ conditions, which could contribute to concentrations downwind of urban regions. Alternatively, the correlation may be driven by similar formation mechanisms for SOA and sulfate, such as aqueous-phase chemistry (Carlton et al., 2006), shared oxidants, or the co-condensation of secondary inorganic and organic aerosols. Acid catalysed formation is unlikely to explain these correlations (Zhang et al., 2007b; Peltier et al., 2007b). Finally, both organic carbon aerosol and sulfate are subject to wet removal from the atmosphere. The OC/sulfate slopes here are again highest at anthropogenically influenced locations, with the notable exception of summertime sampling during the Pittsburgh Air Quality Study. This is likely due to the generally segregated influences of primary emission and secondary formation at this site, resulting in the least coherent relationship between OC and sulfate across all platforms. The correlation between the aerosol organic and sulfur compounds does not extend to the total gas+aerosol concentrations (TOOC vs. $SO_x \equiv SO_2$+sulfate). This suggests that the relationship between sulfate and OC aerosol is not controlled by common emission sources.

Figure 7 shows a series of biogenic tracers as predictors for TOOC concentrations. Methanol as well as isoprene and its oxidation products, formaldehyde (HCHO), methyl vinyl ketone (MVK) and methacrolein (MACR) are important components of the TOOC budget. Therefore to ensure that these relationships are not dominated by self-correlation, we remove the concentration of each compound from TOOC in Fig. 7. These species are not measured at all sites (we do not show isoprene for the remote/marine sites where concentrations never exceed 40 ppt and are therefore close to detection limits), and correlations are weaker than the relationships of Fig. 6; nevertheless, these measurements do support a biogenic variability to TOOC and can explain up to 67% of the observed variance. Correlations between TOOC and the biogenic tracers are higher than these same tracers and CO by 0.1-0.3 indicating that the shared variability between TOOC and biogenics goes beyond common mixing and dilution processes. Correlations are highest with the longest-lived tracer, methanol, whose estimated tropospheric lifetime ($\sim$7 days) is comparable to the lifetime of organic aerosol (Jacob et al., 2005). Despite low overall concentrations of methacrolein and MVK at Pittsburgh in summertime, the strong relationship with TOOC indicates the importance of secondary biogenic oxidation at this location (Fig. 7c), where isoprene is also elevated (Fig. 3).

The anthropogenic sources of methanol (biomass burning, vehicles, solvents and manufacturing) and formaldehyde (anthropogenic VOC oxidation, small primary emissions) complicate their interpretation as indicators of biogenic origin. TOOC is best correlated with methanol for several of the more urban environments, and datasets which may include background fire influence, despite the filtering of strong fire plumes (Fig. 7d). In particular, we do not expect biogenic activity to be a significant contributor to TOOC in Mexico City, and especially not so in springtime. Accordingly, TOOC is anti-correlated with isoprene at this location, where isoprene is elevated in remote regions away from urban influence and oxidized in polluted plumes. We attribute the high correlation seen between TOOC and HCHO near Mexico City to secondary anthropogenic oxidation, and mobile source emissions (Garcia et al., 2006).

Holzinger et al. (2007) found that a subset of aged biogenic air masses (characterized by secondary biogenic oxidation products) were associated with coastal aerosol growth at Chebogue Point. While such select conditions are characterized by a strong relationship between organic aerosol and biogenic oxidation tracers, the short-lived biogenic oxidation products in this dataset can explain at most 30% (and generally less than 10%) of the variability of organic aerosol over the range of conditions observed. Organic aerosol is well-correlated (not shown) with methanol for the suite of datasets with consistent urban influence (MEX, PAQS, WP3), but explains only 2–32% of the variability of organic aerosol in the more rural environments (CHB, TF, THD, BAE). These datasets therefore suggest that while biogenic activity contributes to the variability of TOOC, there is no evidence that the dominant variability in organic aerosol observed over North America can be explained by biogenic oxidation sources. This may be due to the relatively short lifetimes of the biogenic tracers measured in these datasets, or it may indicate that the variability of observed organic aerosol is dominated by the loss processes and not the source. We cannot preclude a biogenic source for these aerosols; indeed $^{14}C$ observations suggest that modern carbon makes up the majority of organic carbon aerosol throughout the rural US (Bench et al., 2007). Weber et al. (2007) have also noted this apparent inconsistency between the high modern fraction and correlation with anthropogenic tracers of OC aerosol. It may be,

however, that anthropogenic pollution in the form of elevated $NO_x$ or enhanced oxidation chemistry, may be a pre-requisite for secondary aerosol formation. Further time-resolved measurements of $^{14}C$ with coincident gas-phase measurements are clearly required to resolve this incongruity.

## 4 Future directions

The integration of this set of measurements represents the first attempt to broadly and observationally quantify the organic carbon budget of the troposphere. The prevalence of TOOC across these environments and throughout the depth of the troposphere, as shown here, highlights the need to understand the climate impact of these compounds in particle form (i.e., composition, cloud nucleating, and optical properties) and the relative importance of natural versus anthropogenic sources.

Two key questions arise from this analysis. First, how much of the TOC is accounted for in the TOOC? Secondly, how representative are these observations of the global composition of the atmosphere? A complete description of the ambient evolution of organic carbon from source to sink (and between phases) requires carbon mass closure in the gas and particle phases. There is a critical and urgent need to develop measurement techniques to routinely detect total gas phase VOCs (or total gas plus particle phase OC), the dominant constituents of oxidized gas-phase organic carbon, and semi-volatile species that partition between both phases. The assessment of how successfully TOOC, as determined by the total of currently measured speciated compounds, captures the total organic carbon budget will remain unanswered until TOC measurements can be achieved. As we have highlighted here, the TOOC-TOC gap may grow with distance from emission sources as the contribution from unmeasured secondary organic compounds grows. This presents a particular challenge for quantifying the organic carbon budget over remote regions. Furthermore, the degrading closure between TOOC and TOC complicates any interpretation of the evolution of the organic carbon budget.

Organic carbon variability in the atmosphere is driven largely by local sources and the photochemical age and deposition lifetime of air masses, the combination of which characterizes diverse observational environments. The observations selected here represent a wide range of sampling conditions. However, the geographical domain of these observations is limited, and additional sampling in the Southern Hemisphere and over significantly different continental environments (for example: Asia, the tropics, the polar regions) is required to present a truly global picture of organic carbon in the atmosphere. Further assessment of the TOOC budget requires a broad and comprehensive suite of measurements from large-scale field campaigns. It is essential that the main fixed sites or mobile platforms of future field campaigns include as comprehensive as possible suite of organic measurements in order to minimize the gap between total observed organic carbon (TOOC) and total organic carbon (TOC), and to further characterize the role of various species in the TOOC budget.

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