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To cite this version:
C. L. Heald, A. H. Goldstein, J. D. Allan, A. C. Aiken, E. Apel, et al.. Total observed organic carbon (TOOC) in the atmosphere: a synthesis of North American observations. Atmospheric Chemistry and Physics, 2008, 8 (7), pp.2007-2025. hal-00296519

HAL Id: hal-00296519
https://hal.science/hal-00296519v1
Submitted on 18 Jun 2008

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

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Received: 26 October 2007 – Published in Atmos. Chem. Phys. Discuss.: 13 December 2007
Revised: 7 March 2008 – Accepted: 25 March 2008 – Published: 8 April 2008

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
nual average concentrations of which reached 385 ppm in forms, particularly, carbon dioxide (CO$_2$) measured in the ambient atmosphere. Methane), which reflects the subset of compounds currently incorporated. Concentrations of TOOC in these datasets span more than two orders of magnitude. The daytime mean TOOC ranges from 4.0 to 456 µgC 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 $\sim$1751 ppb (equivalent to $\sim$4 PgC) (Dlugokencky et al., 2003). While methane is an important greenhouse gas, it is long lived (lifetime $\sim$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 $\sim$10 s TgC) (IPCC, 2007). However, these compounds play an important role in the chemistry of the troposphere, and in aerosol form, as a climate forcing agent. The organic carbon budget includes a large suite of compounds, with many that are likely to contribute (based on laboratory studies or theory) not having been observed under ambient conditions (Goldstein and Galbally, 2007), with varying sources, lifetimes and properties in the atmosphere. Measurements of TOC are difficult, thus the organic carbon budget in the atmosphere remains poorly quantified. Organic carbon is lost from the atmosphere via multiple gas-phase oxidation steps to CO and CO$_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$^5$ (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 (Gilarondi 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 10000 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 (Huffman et al., 2007) 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).

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) of primary and secondary organic aerosol in the field contradicts current model representations, Geophys. Res. Lett., submitted, 2007.

1Huffman, J. A., Aiken, A. C., Docherty K. S., et al.: Volatility
of Mexico City (19.49°N, 99.15°W, elevation 2240 m). In
the spring of 2006 this aircraft also sampled over the west-
ern United States and eastern Pacific during the April–May
INTEX-B/IMPEX campaign (IPX) (Dunlea et al., 2008).
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 ele-
vation) in spring 2002 during the ITCT-2K2 campaign (Gold-
stein 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 sam-
ples 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 sam-
ping. 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 concentra-
tion comparisons should not be over interpreted.

Organic carbon species measured with less than 30% un-
certainty 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 (µg C
m⁻³) at standard temperature and pressure conditions (STP,
273 K, 1013.25 hPa) to compile the TOOC budget (exclud-
ing 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 report-
ing sub-micron aerosol mass (PM1), with the exception of
the PAQS filter observations which represent PM2.5. With
the exception of large primary non-volatile biological parti-
cles, 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

\(^2\)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.: Observa-
tions 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.

made aboard the WP-3 aircraft to account for non-soluble
carbon (de Gouw et al., 2007). The average ratio of par-
ticular 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 or-
ganic 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).
Turpin and Lim (2001) suggest that the carbon weight per or-
ganic 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 contribu-
tions of several dominant species/classes (highlighted in yel-
low 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 ac-
count 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 con-
centrations of individual species can be found in the appro-
priate mission references cited in Table 1. The bars in Fig. 3
denote the interval of ± one standard deviation on the mean
TOOC. We aim here to characterize the typical TOOC bud-
get 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) 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 atyp-
ical 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 mea-
surements and then ordered generally by distance from an-
thropogenic 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 CO₂ 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

\(^4\)Polidori, A., Turpin, B. J., Davidson, C., Rodenburg, L. A.,
and Maimone, F.: Organic PM2.5: Fractionation by Polarity, FTIR
Spectroscopy, and OM/OC for the Pittsburgh aerosol, Aerosol Sci.
Tech., submitted, 2007.
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 \( \mu \text{gC m}^{-3} \) measured at the coastal surface site at Trinidad Head to 455.3 \( \mu \text{gC m}^{-3} \) 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 8.6 \( \mu \text{gC m}^{-3} \)). 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 \( \sim 6 \mu \text{gC m}^{-3} \). 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. 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 less than 1% of TOOC 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, ▼), Capture Electon 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 | T0a | PAQSb | RHBc | TFd | CHBe | THDf | MEX/ IPXg | WP3b | BAEh |
|-----------------|------------------|-----|-------|------|-----|------|------|-----------|------|------|
| 1 Ethane        | C2H6             | ●   | ●     | ●    | ●   | ●    | ●    | ●         | ●    | ●    |
| 2 Ethene        | C2H4             | ●   | ●     | ●    | ●   | ●    | ●    | ●         | ●    | ●    |
| 3 Acetylene     | C2H2             | ●   | ●     | ●    | ●   | ●    | ●    | ●         | ●    | ●    |
| 4 Propane       | C3H8             | ●   | ●     | ●    | ●   | ●    | ●    | ●         | ●    | ●    |
| 5 Propene       | C3H6             | ●   | ●     | ●    | ●   | ●    | ●    | ●         | ●    | ●    |
| 6 2-methyl-propene | C4H8         | ●   | ●     | ●    | ●   | ●    | ●    | ●         | ●    | ●    |
| 7 Propadiene    | C3H4             | ●   | ●     | ●    | ●   | ●    | ●    | ●         | ●    | ●    |
| 8 Propyne       | C3H4             | ●   | ●     | ●    | ●   | ●    | ●    | ●         | ●    | ●    |
| 9 Butane        | C4H10            | ●   | ●     | ●    | ●   | ●    | ●    | ●         | ●    | ●    |
| 10 Isobutane    | C4H10            | ●   | ●     | ●    | ●   | ●    | ●    | ●         | ●    | ●    |
| 11 2,2-dimethylbutane | C6H14       | ●   | ●     | ●    | ●   | ●    | ●    | ●         | ●    | ●    |
| 12 2,3-dimethylbutane | C6H14       | ●   | ●     | ●    | ●   | ●    | ●    | ●         | ●    | ●    |
| 13 2,2,3-trimethylbutane | C7H16       | ●   | ●     | ●    | ●   | ●    | ●    | ●         | ●    | ●    |
| 14 Isobutene    | C4H8             | ●   | ●     | ●    | ●   | ●    | ●    | ●         | ●    | ●    |
| 15 1-butene     | C4H8             | ●   | ●     | ●    | ●   | ●    | ●    | ●         | ●    | ●    |
| 16 t-2-butene   | C4H8             | ●   | ●     | ●    | ●   | ●    | ●    | ●         | ●    | ●    |
| 17 c-2-butene   | C4H8             | ●   | ●     | ●    | ●   | ●    | ●    | ●         | ●    | ●    |
| 18 3-methyl-1-butene | C5H10      | ●   | ●     | ●    | ●   | ●    | ●    | ●         | ●    | ●    |
| 19 2-methyl-1-butene | C5H10      | ●   | ●     | ●    | ●   | ●    | ●    | ●         | ●    | ●    |
| 20 2-methyl-2-butene | C5H10      | ●   | ●     | ●    | ●   | ●    | ●    | ●         | ●    | ●    |
| 21 1,2-butadiene| C4H6             | ●   | ●     | ●    | ●   | ●    | ●    | ●         | ●    | ●    |
| 22 1,3-butadiene| C4H6             | ●   | ●     | ●    | ●   | ●    | ●    | ●         | ●    | ●    |

www.atmos-chem-phys.net/8/2007/2008/ Atmos. Chem. Phys., 8, 2007–2025, 2008
Table 1. Continued.

| No. | Compound                        | Formula   | Concentration |
|-----|---------------------------------|-----------|---------------|
| 25  | Cyclopentane                    | C5H10     |               |
| 26  | Methyl cyclopentane             | C6H12     |               |
| 27  | 2- and 3- methylpentane         | C6H14     |               |
| 28  | 2,3-dimethylpentane             | C7H16     | <1 ppt        |
| 29  | 2,4-dimethylpentane             | C7H16     | <1 ppt        |
| 30  | 2,2,4-trimethylpentane          | C8H18     | <1 ppt        |
| 31  | 2,3,4-trimethylpentane          | C8H18     | <1 ppt        |
| 32  | 2,2,3-trimethylpentane          | C8H18     | <1 ppt        |
| 33  | 1-pentene                       | C5H10     |               |
| 34  | t-2-pentene                     | C5H10     |               |
| 35  | c-2-pentene                     | C5H10     |               |
| 36  | 1-methyl-cyclopentene           | C6H10     | S <1 ppt      |
| 37  | Hexane                          | C6H14     |               |
| 38  | 2-methylhexane                  | C7H16     |               |
| 39  | 3-methylhexane                  | C7H16     |               |
| 40  | Cyclohexane                     | C6H12     |               |
| 41  | Methyl cyclohexane              | C7H14     |               |
| 42  | Heptane                         | C7H16     |               |
| 43  | 2-methylheptane                 | C8H18     | <1 ppt        |
| 44  | 3-methylheptane                 | C8H18     | <1 ppt        |
| 45  | Octane                          | C8H18     |               |
| 46  | Decane                          | C10H22    |               |
| 47  | Isoprene                        | C5H8      | o S <1 ppt    |
| 48  | Benzene                         | C6H6      |               |
| 49  | Ethylbenzene                    | C8H10     |               |
| 50  | Propylbenzene                   | C9H12     |               |
| 51  | Isopropylbenzene                | C9H12     |               |
| 52  | 1,3,5-trimethylbenzene          | C9H12     |               |
| 53  | 1,2,4-trimethylbenzene          | C9H12     |               |
| 54  | 1,2,3-trimethylbenzene          | C9H12     |               |
| 55  | Styrene                         | C8H8      | o             |
| 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    |               |
| 64  | Beta-pinene                     | C10H16    |               |
| 65  | Camphene                        | C10H16    |               |
| 66  | Limonene                        | C10H16    |               |
| 67  | Carene                          | C10H16    |               |
| 68  | Methyl t-butyl ether (MTBE)      | C5H12O    |               |
| 69  | Methanol                        | C3H8OH    |               |
| 70  | Ethanol                         | C2H5OH    |               |
| 71  | Isopropanol                     | C3H7OH    |               |
| 72  | Phenol                          | C6H5OH    |               |
| 73  | Formic Acid                     | HCOOH     |               |
| 74  | Acetic Acid                     | CH3COOH   |               |
| 75  | Peroxyacetic Acid               | CH3COOCH   |               |
| 76  | Propanoic Acid                  | C2H6COOH  |               |
| 77  | Formaldehyde                    | HCHO      |               |
|    | Chemical          | Abbreviation | Concentration |
|----|-------------------|--------------|---------------|
| 78 | Acetaldehyde      | CH3CHO       |               |
| 79 | Methacrolein      | C4H6O        | ○ ● ○ ● ○ ● ▼ | ○ ● ●<20ppt |
| 80 | Propanal          | C3H6O        | ●              |                |
| 81 | 2-methyl-propanal | C4H8O        | ●              |                |
| 82 | Butanal           | C4H8O        | ● ● ● ● ● ▼    | ●<20ppt       |
| 83 | 2-methyl butenol  | C5H9O        | ●              |                |
| 84 | Pentanal          | C5H10O       | ● ● ○ ● ○ ● ▼ | ○ ● ●          |
| 85 | Hexanal           | C6H12O       | ● ●           |                |
| 86 | Heptanal          | C7H14O       | ●              |                |
| 87 | Acetone           | C3H6O        | ○ ● ○ ○ ○ ● ▼ | ○ ● ●          |
| 88 | Hydroxyacetone    | C3H5OHO      | ○              |                |
| 89 | Methyl vinyl ketone | C4H6O     | ○ ● ○ ○ ○ ● ▼ | ○ ● ●<10ppt   |
| 90 | Methyl ethyl ketone | 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| Methylene 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-Bromopropane    | 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         | C2H3Cl2F     | ● ● ● ● ● ▼    | ●              |
| 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    | CH3NO3       | ● ● ● ● ● ▼    | ●              |
| 128| Butyl nitrate     | C4H9NO3      | ● ● ● ● ● ▼    | ●              |
| 129| 3-methyl-2-butyl  | C5H12NO3     | ● ● ● ● ● ▼    | ●              |
Table 1. Continued.

| Substance | Structure | Measurement Techniques |
|-----------|-----------|------------------------|
| Nitrate   | C5H11NO3  | •                      |
| 2-Pentyl Nitrate | C5H11NO3 | •                      |
| 3-Pentyl Nitrate | C5H11NO3 | •                      |
| PAN       | C2H3NO5   | • ▼ ▼ ▼ ▼ ▼          |
| FPN       | C3H5NO5   | ▼ ▼ ▼ ▼ ▼            |
| PBN       | C4H7NO5   | ▼ ▼ ▼ ▼              |
| PBzN      | C7H5NO5   | ▼ ▼ ▼ ▼              |
| APAN      | C3H3NO5   | ▼ ▼ ▼ ▼ ▼ ▼ ▼      |
| MoPAN     | C3H5ONO5  | ▼ ▼ ▼ ▼ ▼ ▼ ▼ ▼ ▼ ▼ ▼ |
| MPAN      | C4H5NO5   | ▼ ▼ ▼ ▼ ▼ ▼ ▼ ▼ ▼ ▼ ▼ |
| Aerosol organic carbon | C4H5NO5 | ▼ ▼ ▼ ▼ ▼ ▼ ▼ ▼ ▼ ▼ ▼ |

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)

Table 2. Mean concentrations of TOOC dominant organic carbon compounds for each platform in units of µgC m⁻³ (as ordered in Fig. 3). Please refer to Table 1 for measurement techniques.

| Substance | 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|
| Ethane    | 5.22   | 1.47   | 1.12|     |     |     | 1.57| 0.45| 0.33| 0.38|
| Propane   | 51.89  | 2.92   | 4.95| 0.89| 0.89| 0.38| 0.57| 1.20| 0.65| 0.38|
| Butane    | 125.35 | 2.00   | 4.46| 0.48| 0.24| 0.18| 0.10| 0.86| 0.32| 0.19|
| Acetone   | 25.92  | 6.80   | 1.72| 2.43| 3.57| 1.52| 1.04| 3.23| 3.71| 1.82|
| 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   |     |     |     |     |     |     |     |     |
| Acetaldehyde | 6.86   | 2.17   | 0.67| 0.53| 0.39| 0.23| 0.26| 0.54| 0.52| 0.16|
| Formaldehyde | 5.29   | 1.06   |     |     |     |     |     |     |     |     |
| Monoterpenes | 0.28   | 0.10   | 0.03| 0.46| 0.64| 0.14| 0.13| 0.01| 0.01| 0.00|
| Isoprene  | 1.25   | 4.53   |     |     |     |     |     |     |     |     |
| MVK+MACR | 40.45  | 0.67   | 0.27| 1.37| 0.12| 0.05| 0.52| 0.00| 0.00|     |
| Aromatics | 71.08  | 3.27   | 2.84| 0.57| 0.10| 0.23| 0.34| 0.46| 0.10| 0.22|
| PANs     | 1.11   | 0.32   | 0.18| 0.37| 0.18| 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|
| TOOC     | 455.31 | 45.12  | 28.91| 16.54| 18.47| 8.83| 4.04| 16.80| 15.87| 8.65|

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.
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).
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 µgC 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 µgC 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 µgC 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 England Marine and Continental Environments during the ICARTT 2004 Campaign, J. Geophys. Res., submitted, 2007.

\(^5\)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

\(^6\)Fried, A., Walega, J. C., Olsen, J. R., et al.: Formaldehyde over North America and the North Atlantic during the Summer 2004 IN-TEX Campaign: Methods, Observed Distributions, and Measurement Box Model Comparisons, J. Geophys. Res., submitted, 2007.
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 µgC 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). 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

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7Peltier, R. E., Hecobian, A. H., Weber, R. J., et al.: Water-Soluble Organic and Inorganic PM1.0 Bulk Composition from Asia: Results from IMPEx-B Field Campaign, in preparation, 2007.
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 \( \mu \text{gC m}^{-3} \)) 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 \( \mu \text{gC m}^{-3} \) during MIRAGE and 0.4 \( \mu \text{gC m}^{-3} \) during IMPEX. Tanner and Law (2003) summarize the range of ambient formic acid (0.04–7.2 \( \mu \text{gC m}^{-3} \)) 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 \( \mu \text{gC m}^{-3} \) at any location, and at Pittsburgh minimum concentrations are five times as high. Aerosol concentrations range from detection limits up to 10 \( \mu \text{gC m}^{-3} \). 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 \( \mu \text{gC m}^{-3} \), with a mean of \( \sim 7 \mu \text{gC m}^{-3} \) (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 \( \mu \text{gC m}^{-3} \) 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.
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 particulate-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 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 \((\text{SO}_2)\) 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.
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 NOx conditions, which could contribute to concentrations downwind of urban areas. 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. $SOX=SO2+sulfate$). 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 (∼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 NOx 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.

Acknowledgements. This work was supported by the NOAA Postdoctoral Program in Climate and Global Change, administered by the University Corporation for Atmospheric Research. Field measurements were supported by NOAA (under grants RA133R05SE4459, RA133R04SE0368, NA17R02632, NA03OAR4600122, NA04OAR4600154 and NA05OAR4600189) NSF (under grants ATM-0449815 and ATM-0513116) and NASA (under grant NNG06GB03G). We thank B. Lerner for providing the CO observations aboard the R/V R. Brown, M. Evans for providing the BAE-146 merged data, R. Cohen, D. Farmer, and J. Fry for useful discussions and gratefully acknowledge core data from the BAE 146 aircraft provided by the UK Facility for airborne Atmospheric Measurements.

Edited by: A. Hofzumahus

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