Climatology of PM2.5 Organic Carbon
Concentrations from a Review of
Ground-Based Atmospheric Measurements by
Evolved Gas Analysis

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Abstract

In this work we have compared ground-based measurements of organic carbon (OC) in the fine aerosol (PM2.5) fraction that are reported in peer-reviewed publications as part of both short campaigns and continuous monitoring networks. The comparison provides a quantitative review of global OC measurements for the purpose of establishing the extent to which organic aerosol concentrations are known with sufficient geographic and historical resolution to constrain global climate models. Only North America has sufficient measurements to provide meaningful spatial and temporal trends, although available measurements from China and Japan indicate that the Asian region is most polluted with OC concentrations of approximately 10 µg m⁻³. These measurements have a low spatial resolution, with most sites located in highly urban areas within a small geographic region. OC concentrations in North America are approximately 1 µg m⁻³ and are better characterized spatially, temporally, and historically by continuous monitoring networks established decades ago. OC concentration shows a weakly increasing trend in some regions from 1997-2006,
although in most regions it has remained effectively constant over the last ten years. Eastern U.S. sites show maximum OC in the winter and western U.S. sites show maximum OC in the summer. There is no correlation at U. S. sites between OC concentration and sulfate, nitrate, or ammonium ions, with $R^2 < 0.1$ in each case.

Key words: Organic Carbon, Aerosol composition

1 Introduction

Aerosols absorb and scatter solar radiation, changing the energy balance of the Earth-atmosphere system (Charlson et al., 1992; Haywood and Shine, 1995). Carbonaceous particles are a complex mixture of chemical compounds that comprise a significant fraction of atmospheric aerosols and are usually divided into two major fractions. Elemental carbon (EC) originates from combustion of carbonaceous matter and absorbs incoming solar radiation, resulting in additional heating of the atmosphere. Organic carbon (OC) is both directly emitted from combustion and natural sources (known as primary organic aerosol, or POA) and formed from the oxidation products of volatile organic compounds condensing on preexisting aerosol (secondary organic aerosol, or SOA). Organic carbon has been shown to play an important role in both direct and indirect aerosol forcing (Lioussse et al., 1996; Cooke et al., 1999; Hansen et al., 1997; Penner et al., 1998; Lohmann et al., 2000; Jacobson, 2001; Chung and Seinfeld, 2002). Increased scatter of solar radiation back to space due to atmospheric OC particles results in a cooling of the atmosphere. Hygroscopically active OC particles form cloud condensation nuclei (CCN) resulting in a modification of

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cloud formation, coverage, and lifetimes (Twomey, 1977; Albrecht, 1989; Jones et al., 1994).

Although these qualitative climate effects of OC aerosols are understood, there exists significant uncertainty between 100 and 200% in their quantitative radiative forcing (Chung and Seinfeld, 2002; Maria et al., 2004). Kanakidou and coworkers (Kanakidou et al., 2005) presented a review of the organic aerosols important to climate models indicating uncertainties in both current OC emission estimates and large uncertainties due to OC measurement artifacts. It was estimated that the net global emission estimates of OC vary by a factor of 2-5 and have a strong regional dependence. There exists a further uncertainty in the defined separation between OC and EC, with an empirical OC/EC ratio between 1.2-1.7 adopted in climate models. The uncertainty in OC/EC ratio can possibly be resolved using detailed chemical speciation and characterization of organic compounds by functional groups (Kanakidou et al., 2005).

Another possible approach is the use of closure studies based on comparison of two or more independent methods of OC measurement to identify the method that best reduces the uncertainty (Bates et al., 2005). A global model simulation (GISS GCM II prime) by Chung and Seinfeld (2002) estimating climate forcing by carbonaceous aerosol (both anthropogenic and biogenic) under-predicted observed OC concentrations at worldwide rural, remote, and marine sites by factors of more than 3. These large uncertainties in regional OC concentration lead to further uncertainty in the total column-integrated atmospheric burden and the extinction resulting from absorption or scattering of radiation by aerosol. In this work we assess the extent to which existing measurements are sufficient to reduce some of this uncertainty.

An increase in worldwide measurement campaigns and the establishment of
continuous monitoring networks over the last two decades has resulted in a large amount of aerosol size and chemical composition information. The wealth of measurements should be applied to reducing the uncertainty in the total aerosol burden by quantifying trends in spatial and temporal distributions. We have compiled measured atmospheric OC concentrations from various parts of the world with the following objectives - to characterize OC concentrations over different geographic regions, to identify the long term and seasonal variation in OC, to identify regions representing different environments based on demographics, and to examine correlations of OC with chemically speciated co-pollutants. The availability and quality of OC measurements is examined in Section 2, multi-year and annual trends in OC concentration for different geographic regions are described in Sections 4 through 6, and the correlations between OC and inorganic ions in the United States are in Section 7.

2 Global availability of OC measurements

The number of OC measurement sites (from both continuous monitoring networks and journal publications) around the world is illustrated in Figure 1, and the corresponding total number of measurements in Figure 2. The majority of measurements shown have been compiled by continuous monitoring networks including the Interagency Monitoring of Protected Visual Environments (IMPROVE), the Speciated Trends Network (STN) administered by the Environmental Protection Agency (EPA), California Regional PM10/PM2.5 Air Quality Study (CRPAQS) (Chow et al., 2006), North American Research Strategy for Tropospheric Ozone (NARSTO), New England Air Quality Study (NEAQS), Tropospheric Aerosol Radiative forcing Observational Experiment (TARFOX), Southeastern Aerosol Research and Char-
acterization Study (SEARCH) (Hansen et al., 2003), European Monitoring and Evaluation Programme (EMEP), the Construction, Use and Delivery of a European Aerosol Database (CREATE), and the Hong Kong Environmental Protection Agency. Individual small-scale regional studies (Gray et al., 1986; Bae et al., 2006; Nunes and Pio, 1993; Castro et al., 1999; Dan et al., 2004; Kim et al., 2000; Mayol-Bracero et al., 2002; Smith et al., 1996; Salam et al., 2003a,b; Fuzzi et al., 2007; Gatari and Boman, 2003) provide measurements prior to the establishment of the networks, and in regions where continuous monitoring has not yet been implemented. Most of the measurements have been compiled in the North American region at 1118 different sites comprising more than 50 measurement campaigns in the United States (Cadle and Dasch, 1988; Chow et al., 1993a; Fraser et al., 2002), Canada (NARSTO), and Mexico (Chow et al., 2002). OC measurement sites in Asia are predominantly located in China with approximately 70 (Cao et al., 2003; He et al., 2004; Dan et al., 2004; Duan et al., 2006; Yang et al., 2005a,b; Zhang et al., 2005) and in Japan with 10 (Ohta and Okita, 1990; Kadowaki, 1990; Ohta et al., 1998; Holler et al., 2002; Minoura et al., 2006; Miyazaki et al., 2006). Measurements are also available from Korea (Kang et al., 2006; Kim et al., 1999, 2000; Lee and Kang, 2001; Park et al., 2001, 2002), India (Chowdhury et al., 2001; Venkataraman et al., 2002; Mayol-Bracero et al., 2002; Ball et al., 2003), Pakistan (Smith et al., 1996), and Bangladesh (Salam et al., 2003a,b) with less than 10 sites each. The European continent has 28 measurement sites spread across Ireland, Portugal, France, Austria, Switzerland, Italy, Spain, Finland, Norway, the Czech Republic, the Netherlands, Greece, Belgium, the United Kingdom, Germany, and Slovakia (Castro et al., 1999; Roosli et al., 2001; Putaud et al., 2004; Sillanpaa et al., 2005; Viana et al., 2007). Very limited measurements are available for the rest of the world including South Amer-
ica (Fuzzi et al., 2007) and Africa (Formenti et al., 2003; Gatari and Boman, 2003). Regionally, OC levels can be best characterized over North America, Western Europe and parts of Asia, but there are still large gaps in information in the Southern hemisphere and in many populous regions in southern Asia. A global representation of OC concentration for use in climate models is likely to have poor spatial resolution, explaining in part the discrepancy in the modeled organic aerosol forcing (Chung and Seinfeld, 2002).

OC measurements are reported for different averaging periods including hourly, daily, weekly, monthly, seasonal, and annual as shown in Table 1. Most of the measurements consist of samples collected for a period of one day between three and seven times a week. The total number of individual OC measurements between the years 1977 and 2007 varies from a maximum of 430,000 for North America to a minimum of 2 for Bangladesh. The wealth of higher time-resolution measurements can be directly attributed to the establishment of the continuous monitoring networks. As an example, the start of IMPROVE in 1988 increased the number of available daily measurements in North America from approximately 10 to 1000 per year. The Speciated trends network established by the EPA since 2000 has contributed to a further sharp increase to between 10,000-100,000 measurements per year for this region. Atmospheric monitoring is carried out by several local agencies in representative urban areas and the measurements are made available in the public domain through the Air Quality System (AQSEPA) data repository.

Table 2 summarizes protocols used in determining reported OC concentrations and associated uncertainties from several key literature sources. These protocols have been adapted for OC concentration determination and are in wide use. Table 2 also includes examples of subsequent work utilizing these
central protocols. OC concentrations documented in this work are obtained from the evolved gas analysis (EGA) method based on thermal evolution of organic and elemental carbon in a Helium or Helium/Oxygen environment. Aerosol particles collected on quartz fiber filters are oxidized to CO$_2$, followed by a reduction to methane gas, and subsequent detection of total carbon mass through flame ionization (Birch and Cary, 1996). The distinctions in the various protocols are based largely upon the temperature at which various fractions of carbon are volatalized, the duration of exposure at each temperature, and the rate of temperature increase (Chow et al., 1993b). These differences in protocol have a minor effect on the total carbon mass measured, but have a significant impact on the delineation between organic carbon and elemental carbon, contributing to some uncertainty in OC mass. The quartz filters used for particle collection are prone to artifacts that result in erroneous measurements of particles (Turpin et al., 1994). Possible adsorption of gas phase OC onto the filter results in an overestimation of the total (a positive artifact), and volatilization of collected particulate matter from the filter results in an underestimation (a negative artifact) (Turpin et al., 2000). Estimates of the OC artifact range from a positive artifact between 15% and 50% of the total OC (Chen et al., 2002; Kirchstetter et al., 2001; Turpin et al., 1994) and a negative artifact up to 80% (Eatough et al., 1993; Ding et al., 2002a,b). The magnitude of the artifact is dependent on factors such as sampler configuration, face velocity, sampling duration, and location (McDow and Huntzicker, 1990; Turpin et al., 1994). Corrections for the positive artifact have been estimated in limited studies by the inclusion of a quartz after-filter designed to sample gas phase OC after the particulate matter has been removed (Watson, 2002; Fung et al., 2002). There is no documented protocol for the correction of the negative artifact though it may exceed the positive artifact under certain
conditions (Lewtas et al., 2001). Sampling artifacts can be significant and may explain a portion of the discrepancy between measurements and models. Since relatively few studies have reported the artifact correction, the magnitude of these corrections for the majority of OC measurements is not documented in the literature (Chow et al., 1993b).

OC measurements from EGA techniques have reported or inferred uncertainty of up to 100% and a minimum detection limit of 0.05 µg m\(^{-3}\). Moreover the strong temperature dependence of both SOA and POA partitioning to the particle phase has significant implications for interpreting OC concentrations (Donahue et al., 2006; Greishop et al., 2007). Despite the high uncertainties, there are sufficient data to assess long-term trends and annual variability in organic carbon concentrations as shown in sections 4 and 6.

3 Mobile platforms

To identify different sources and climate effects of aerosol particles in polluted continental environments and marine environments, mobile platforms (ships and aircraft) have been used (Heald et al., 2005; Quinn and Bates, 2005; Zhang et al., 2007; Shiobara et al., 2007) in conjunction with fixed ground-based monitoring stations for atmospheric aerosol characterization. These measurements are especially important in marine environments, where anthropogenic sources are mixed with natural sea salt particles (Neussus et al., 2002). The comparison between fixed and mobile platform measurements shows the differences between the long-term trend evident in multi-year ground-based studies and process-focused intensive studies. Ship-based and aircraft-based measurements of atmospheric OC concentration are limited by cost and other
sampling constraints. Most mobile studies to date have reported OC for sub-micron particles rather than the PM2.5 used in ground sites. Tables 3 and 4 summarize the availability of OC concentrations from major field campaigns. Several of these campaigns have been reviewed in recent publications (Quinn and Bates, 2005; Heald et al., 2008). OC concentrations in coastal and remote marine regions are largely consistent and range from 0-2 $\mu g \ m^{-3}$, showing less variability compared to continental measurements. OC concentrations from aircraft measurements are higher near the surface (4 $\mu g \ m^{-3}$ in the United States) but drop off at higher altitudes due to mixing with cleaner stratospheric air. These measurements are typically carried out in pollution plumes, resulting in a bias towards higher organic concentrations.

### 4 Multi-year trends

OC Measurements prior to 1988 are only available from small-scale studies, most of which were conducted in North America. These studies do not reflect long term trends, but provide significant insight into local influences. In 1977 relatively high median OC concentrations (9.8 $\mu g \ m^{-3}$) are reported for urban sites in California, and in 1978 (9.7 $\mu g \ m^{-3}$) for New York and Colorado (Rosen and Hofmann, 1981). Lower annual median OC concentrations are reported for 1979, corresponding to sites in Illinois and Maryland (Rosen and Hofmann, 1981). In 1982 high annual average OC concentrations are reported for California (Gray et al., 1986) and New Jersey (Gaffney et al., 1984), with lower concentrations for rural sites in Pennsylvania and Michigan (Cadle and Dasch, 1988), and Bermuda (Wolff et al., 1986). These strong trends suggest that atmospheric OC levels may be strongly influenced by land use patterns. Many of these measurements were performed close to localized anthropogenic...
OC sources such as automobiles, power plants, wood smoke, incinerators, and agriculture and do not represent larger-scale regional atmospheric levels. These studies were also conducted before the institution of standardized measuring protocols (Chow et al., 1993a) and may suffer from high sampling artifacts. Though we include these pioneering examples of atmospheric monitoring, we have omitted these sparse early data sets in the comparative analyses in the remainder of this work.

As shown in Table 1, OC measurements are typically available as daily averages which can be used to determine annual averages for the purpose of analyzing the long-term evolution of OC concentrations. Figure 3 illustrates annual averages of the OC concentration for North America, Europe, China, and Japan for the last ten years (1997-2006). There are no significant measurements outside the United States from 1988-1997 and this time period is not illustrated. Since the mean of data sets with high scatter can be dominated by occasional extreme values, the median values are used here to reflect time-averaged OC concentration for each location. The measurements are illustrated using box-and-whisker plots which show the median, 25th-75th percentile values (within the box), and 10th-90th percentile values (the whisker length), and individual outliers. The median value then represents average OC level, and the box size (50% of all measurements) and whisker length (80% of all measurements) represent the magnitude of the variability. Although measurements outside the whisker length are indicators of extreme variability in the OC, they comprise less than 10 % of the available measured values and should not be considered a very significant factor. The median concentrations in the United States lie between 0.9 and 2.6 µg m$^{-3}$, with corresponding ranges of 1.6-5.6 µg m$^{-3}$ for Europe, 2.5-5.0 µg m$^{-3}$ for Japan, and 10-20 µg m$^{-3}$ for mainland China.
Median OC concentration in North America shows a slow increase from 0.9 µg m\(^{-3}\) in 1997 to 2.6 µg m\(^{-3}\) in 2007 at the rate of approximately 0.1 µg m\(^{-3}\) per year. The overall trend from 1997 to 2004 in Europe is a decrease of about 0.3 µg m\(^{-3}\) per year, but this analysis is limited by the small number of sporadic OC measurements. European site locations varied annually, increasing the spatial variability of OC measurements. Similarly, an increase in median OC concentration in 1999 and a decrease in 2004 is observed in China. In Japan, OC median concentrations are relatively higher from 1996-1998 (3.0 µg m\(^{-3}\), with an observable decrease from 1999 to 2003 and an increase in 2004. The apparent increase in 2004 may be a consequence of a bias introduced due to a large number of measurements in the relatively polluted Tokyo region (Miyazaki et al., 2006).

5 Contribution to OC from population density

Average OC concentrations are strongly influenced by local land use and emission patterns (Chow et al., 1996). The significant differences between North American and Asian OC concentrations seen in Figure 3 may reflect the differences in population density on these two continents, since many emissions increase with population. To assess these differences, monitoring sites can be characterized using local demographics to classify the region as urban, rural, and remote. Extending these classifications to different parts of the world results in some ambiguity. For example, a “rural” site in Asia is likely to have differing demographics and land use than a “rural site” in North America. A quantitative approach to classifying local emission sources based on population is using the average population density at the site location. Figure 4 shows a comparison of the measured OC and local population density. OC
concentrations from North America, Asia and Europe are included on the plot. The population density used is from year 2000, with a 0.25°x0.25° resolution for the grid. The Asian sites have both the highest population densities (ranging between 300 and 8000 km$^{-2}$) and mean OC (ranging between 0.1 and 40 µg m$^{-3}$). European sites show intermediate values for the population density (100-1000 km$^{-2}$) and OC (0.1-5 µg m$^{-3}$) with North American sites comprising the lower range of values (population densities from 1-200 km$^{-2}$ and OC from 0.01-10 µg m$^{-3}$). Notable exceptions to this general trend in North America are Mexico City (10,000 km$^{-2}$), New York City (7000 km$^{-2}$) and Chicago (5000 km$^{-2}$), which have significantly higher population densities that are comparable to Asia. The use of a uniform grid to estimate population density may introduce certain biases in the analysis - for example sparsely populated regions upwind of major urban areas (emission sources) may have a high population density but low OC concentration.

While there really is no significant correlation between OC and population density for North America, Figure 4 does illustrate the overall trend between North America (at a lower OC and population density) and Asia (at a higher average OC and population density) for the measured regions. However the North American measurements span a wide range of population density and a narrow range of OC concentration and the Asian measurements span a large range of OC concentrations and a narrow band of population density. The trend is weighted by the larger number of North American sites and the paucity of measurements in non-urban Asian sites. The extremely poor correlation between OC and population density in North America indicates that anthropogenic sources of OC that scale with population are not the single dominant contributor to average concentrations. Significant contributions from medium or long-range transport, and biogenic or other natural OC sources would ex-
plain this lack of correlation to population density, although the latter two
better explain the lack of growth in median OC concentrations in the last 10
years (Figure 3). A large number of measurements in the United States are
from the IMPROVE network which is designed to sample regions not directly
influenced by anthropogenic emissions. Another possible explanation of this
weak correlation is the formation of secondary aerosols from semi-volatile OC
(Robinson et al., 2007) far from emission sources.

The existence of a weak correlation to population density for the larger global
measurement set suggests that anthropogenic contributions to OC may begin
to dominate biogenic sources for the more densely populated and less-forested
regions in Asia. The smaller number of measurements outside the United
States provides a very incomplete picture. While many factors contribute to
OC emissions in populated regions - including environmental regulations on
combustion emissions and implementation of combustion technologies - many
of these factors tend to co-vary with population density. More complete source
inventories are needed to evaluate the factors that control OC concentrations
(Bond et al., 1998; Koch et al., 2007), especially in countries outside North
America that have not been adequately sampled.

6 Annual Trends

Spatial and seasonal patterns in aerosol measurements from the IMPROVE
network have been published in a series of three year reports (Sisler et al.,
1993; Sisler, 1996; Malm, 2000; Debell et al., 2006) and key journal articles
(Malm et al., 1994, 2004). In this section we examine similar trends in OC
concentration in the relatively large amount of OC measurements available
for North America. Figure 5 illustrates monthly OC averages during a year for nine American states - Washington, Oregon, and California on the Pacific coast, Minnesota, Ohio, and Texas in the central U.S., and New Hampshire, New Jersey, and Georgia on the Atlantic coast. The measurement sites from the IMPROVE network and STN database are separated since they represent remote and urban regions respectively. Despite the large scatter, consistent annual trends are observed at each measuring station in both networks. Organic carbon levels from the IMPROVE network reach a maximum in the late summer months (August and September) across the United States, although some reports suggest this may be associated with sample storage protocol (Subramanian et al., 1994). STN measurements show a maximum in the winter (December and January) on the Pacific coast and a summer maximum elsewhere. The maximum in the monthly STN averages is approximately double the median, for example the winter maximum in California is 10 µg m$^{-3}$ compared to the annual median of 5 µg m$^{-3}$, and 6 µg m$^{-3}$ for the summer compared to the annual median of 3.5 µg m$^{-3}$ in New Jersey. The peaks in the IMPROVE measurements are less pronounced with an average maximum value of approximately 1.5 µg m$^{-3}$ compared to the mean value of 1.0 µg m$^{-3}$ in each case. Since the STN sites are located in urban areas, the amplitude of the annual cycle is probably driven by human activities such as fossil fuel combustion for wintertime heating.

A corresponding seasonal analysis for select regions from the rest of the world is illustrated in Figure 6. Urban sites in China show a strong winter maximum. The observed December and July means are 35 µg m$^{-3}$ and 15 µg m$^{-3}$ respectively in Beijing, and 13 µg m$^{-3}$ and 5 µg m$^{-3}$ in Hong Kong. Though the majority of measurement sites in Japan are located in the Tokyo urban area, no corresponding seasonal trend is observed. The OC measurement sites
in Europe are located in largely rural areas which do not exhibit an observable seasonal trend. The limited number of measurements outside of North America are insufficient to fully identify seasonal patterns in these regions.

The observed summer maxima in non-urban areas may be related to increased biogenic emissions in the spring and summer months (in the northern hemisphere) and a corresponding increase in the formation of secondary organic aerosol solar oxidation of VOC. The winter maxima on the North American west coast and urban Asian sites may be related to increased fuel usage, biomass burning, and other anthropogenic activities. The winter maximum may also be caused by lower mixing heights at lower temperatures.

The observed annual trends in North America can be compared with a functional fit to available OC measurements. A modulated sinusoidal function provides a representation of the primary cycles observed in OC concentrations. The functional form is

\[
\log_{10} C = a_0 + a_1 t + a_2 \sin (2\pi \nu t + \phi),
\]

where \(C\) is the measured concentration and \(t\) is elapsed time from an arbitrary reference date. The logarithm of the concentration is used to accommodate the observed variability, which exceeds 2 orders of magnitudes. In Equation 1, \(a_0\) are the average OC levels (which are higher than the median due to outliers, but directly co-vary), \(a_1\) is the multi-year rate of increase in the background level, \(a_2\) represents the amplitude of the seasonal variability, and \(\nu\) is the frequency of the seasonal cycles. The offset \(\phi\) relates the period of measurement to the reference date chosen. Fits performed for individual measurement sites are illustrated in Figure 7. The fit replicates the median OC value and seasonal
frequencies, but is less successful in capturing the amplitude of variability due to the presence of multiple outliers.

Histograms of the fit parameters of Equation 1 are illustrated in Figure 8 separated by geographical region for the IMPROVE and STN sites in North America. A small number of fits (less than 5) failed to converge due to exceptionally high scatter. The value of \(a_0\) (background level) for remote sites lies between 0-3 \(\mu g\) \(m^{-3}\) (with a few outliers) in North America. The corresponding value for urban sites also lies between 0-5 \(\mu g\) \(m^{-3}\) but has both a wider distribution and a larger number of concentrations at higher values, indicating a greater degree of pollution. The \(a_0\) parameter in Europe (1-5) and Asia (15-20) reflects regional OC levels. The value of \(a_1\) (annual rate of increase) is insignificant (and in a few cases less than 0) for the majority of North American and European sites, since there is only a very minor increase (or decrease) in median OC levels during the last 10 years. Urban measurement sites have a higher rate of increase than remote sites. Asian sites show divergent behavior with \(a_1\) between 0.2-0.4, which corresponds to an annual rate of increase as high as 50%. The \(a_2\) parameter for non-Asian sites is approximately 1 \(\mu g\) \(m^{-3}\) and shows a similar spread for both urban and remote sites. The absolute values for Asian sites are again higher at 2 \(\mu g\) \(m^{-3}\), however these values correspond to a smaller seasonal variability due to the higher mean. As illustrated in Figure 7 the fit values of \(a_2\) do not sufficiently capture the entire range of variability in the OC measurements which span more than an order of magnitude. The frequency parameter for all sites is approximately 1 per year. This agrees well with the observed trends of a single summer or winter maximum.
7 Correlations to inorganic ions

In addition to PM2.5 OC, concentrations of the primary inorganic components of atmospheric aerosols, i.e. ammonium, nitrate, and sulfate, are available for the IMPROVE and STN sites in North America. These components have been shown to occur simultaneously in primary emission aerosols. We examine the correlations between concentrations of these components with organic carbon, as such correlations may indicate which pollutants are co-emitted or co-processed. Sulfate, nitrate, and ammonium concentrations show a very weak correlation to the OC. The $R^2$ is 0.09 for a linear regression fit between sulfate and OC and 0.03 between nitrate and OC. A more regional comparison (at the state level) does not show improvement over the nationwide correlation. The poor correlations for both individual measurements and long term trends reflect that organic carbon has different emission sources than nitrate, sulfate, or ammonium.

8 Conclusions

Ground based measurements of OC in the aerosol phase from continuous monitoring networks and field campaigns have been compiled and compared for the purpose of better constraining worldwide OC concentrations for use in climate models. The OC concentration is known with a high spatial resolution over the United States, Japan, parts of Europe, and eastern China from the large number of measurements available with daily resolution. Few measurements exist for the rest of the world and a complete global picture can not be constructed in the absence of further OC monitoring. The differences in median OC concentration (for example, $2 \mu g \ m^{-3}$ in North America compared

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to 10.2 µg m$^{-3}$ in China) indicates a strong regional variation reinforcing the need for further measurements. There is significant variability in available OC concentrations (up to a factor of 100) which is larger than the uncertainty in individual measurements (up to a factor of 2) in all regions where extensive measurements have been conducted.

Multi-year trends in OC do not show a significant increase in background median levels from 1997-2006 in any geographic region. Annual trends in North America show a strong seasonal variation, with observable summer maxima over much of the landmass and winter maxima on the west coast. The total organic carbon shows a very poor correlation with sulfate, nitrate and ammonium concentrations in the fine aerosol phase ($R^2 < 0.1$) indicating that OC variability cannot be explained by trends in nitrate, sulfate, or ammonium emissions.

**Acknowledgements**

This research was supported by a grant from British Petroleum. The opinions, findings, and conclusions and recommendations are those of the authors and do not necessarily reflect the views of British Petroleum. We appreciate the many years of dedicated measurements by the researchers whose OC measurements were used in this study, including Mika Silanpää, Yuzo Miyazaki, Judy Chow, and Robert Watson. We also thank Satoshi Takahama for his suggestions and advice.
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Table 1

Global inventory of individual organic carbon measurements. Sampling durations range between one hour and one year. Ground based field campaigns (excluding large scale monitoring) from each region are listed in the footnotes.

\(^a\) Includes: Rosen and Hofmann (1981); Gaffney et al. (1984); Gray et al. (1986); Wolff et al. (1986); Cadle and Dasch (1988); McDow and Huntzicker (1990); Chow et al. (1993a); Turpin et al. (1994); Chow et al. (1996); Novakov et al. (1997); Tolocka et al. (2001); Cabada et al. (2002); Chen et al. (2002); Chow et al. (2002); Fraser et al. (2002); Lim and Turpin (2002); Butler et al. (2003); Hansen et al. (2003); Lim et al. (2003); Solomon et al. (2003); Bae et al. (2004); Held et al. (2004); Schwab et al. (2004); Tanner et al. (2004); Bates et al. (2005); Bae et al. (2006)

\(^b\) Includes: Castro et al. (1999); Roosli et al. (2001); Putaud et al. (2004); Sillanpaa et al. (2005); Viana et al. (2007)

\(^c\) Includes: Ohta and Okita (1990); Kadowaki (1990); Smith et al. (1996); Ohta et al. (1998); Kim et al. (1999, 2000); Chowdhury et al. (2001); Lee and Kang (2001); Park et al. (2001); Holler et al. (2002); Mayol-Bracero et al. (2002); Park et al. (2002); Venkataraman et al. (2002); Ball et al. (2003); Cao et al. (2003); Salam et al. (2003a,b); He et al. (2004); Dan et al. (2004); Yang et al. (2005a,b); Duan et al. (2006); Kang et al. (2006); Minoura et al. (2006); Miyazaki et al. (2006)

\(^d\) Includes: Formenti et al. (2003); Gatari and Boman (2003)
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<th>Uncertainty</th>
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<td>Huntzicker et al. (1982)(^a)</td>
<td>Thermal/Optical</td>
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<td>Cachier et al. (1986)(^b)</td>
<td>Thermal/Optical</td>
<td>0.03</td>
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<td>Chow et al. (1993)(^c)</td>
<td>Thermal/Optical</td>
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<td>5%</td>
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<td>Birch and Cary (1996)(^d)</td>
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<td>Novakov et al. (1997)(^e)</td>
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<td>10%</td>
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Table 2
Methods for determination of OC concentration
\(^a\) Cited : Gray et al. (1986); McDow and Huntzicker (1990); Hildemann et al. (1994); Saxena and Hildemann (1996); Castro et al. (1999); Hitzenberger et al. (2000); Chowdhury et al. (2001); He et al. (2001, 2004)
\(^b\) Cited : Nunes and Pio (1993); Neususs et al. (2002); Quinn et al. (2002); Salam et al. (2003a); Ball et al. (2003); Sillanpaa et al. (2005); Duan et al. (2006)
\(^c\) Cited : Saxena and Hildemann (1996); Kim et al. (2000); He et al. (2001); Tolocka et al. (2001); Cabada et al. (2002); Fraser et al. (2002); Chen et al. (2002); Cao et al. (2003); Hansen et al. (2003); Ho et al. (2003); Ye et al. (2003); Bae et al. (2004); Ma et al. (2004); Tanner et al. (2004); Kang et al. (2004); Bates et al. (2005); Chow et al. (2005); Louie et al. (2005); Yang et al. (2005a); Zhang et al. (2005); Kang et al. (2006); Cao et al. (2006); Minoura et al. (2006); Ho et al. (2006); Lee et al. (2006)
\(^d\) Cited : Birch (1998); Chowdhury et al. (2001); Bergin et al. (2001); Xu et al. (2002); Viidanoja et al. (2002); Venkataraman et al. (2002); Maria et al. (2002, 2003); Butler et al. (2003); Formenti et al. (2003); Schwab et al. (2004); Quinn et al. (2004); Yu et al. (2004); Duan et al. (2006); Feng et al. (2006); Zheng et al. (2006); Viana et al. (2007)
\(^e\) Cited : Kadowaki (1990); Hegg and Kaufman (1998); Hitzenberger et al. (2000); Mayol-Bracero et al. (2002); Novakov et al. (2005)
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<th>Dates</th>
<th>Reference</th>
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<td>SAGA2</td>
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<td>May-July 1987</td>
<td>Rau and Khalil (1993)</td>
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<td>ACE2</td>
<td>North Eastern Atlantic</td>
<td>June-July 1997</td>
<td>Quinn et al. (2000)</td>
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<td>INDOEX</td>
<td>Northern Indian Ocean</td>
<td>January-March 1999</td>
<td>Ramanathan et al. (2001)</td>
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<td>US Eastern Seaboard</td>
<td>July-August 2002</td>
<td>Bates et al. (2005)</td>
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<td>TEXAQS</td>
<td>Houston Shipping Channel</td>
<td>August 2006</td>
<td>Quinn et al. (2008)</td>
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Table 3
Summary of Ship-based measurements of OC concentration
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<th>Reference</th>
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<td>TARFOX</td>
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<td>Novakov et al. (1997)</td>
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<td>EXPRESSO</td>
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<td>November 1996</td>
<td>Ruellan et al. (1999)</td>
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<td>Heald et al. (2005)</td>
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<td>SAFARI</td>
<td>Namibia</td>
<td>November 2002</td>
<td>Haywood et al. (2003)</td>
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<td>ICARTT</td>
<td>US Eastern urban plume</td>
<td>July 2004</td>
<td>Heald et al. (2008)</td>
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<td>Several flights</td>
<td>Inland China</td>
<td>2002-2004</td>
<td>Wang et al. (2007)</td>
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Table 4
Summary of Aircraft-based measurements of OC concentration
Fig. 1. Worldwide Organic carbon measurements. Circles represents one ground measurement site and indicate average PM2.5 concentration. Ship and flight tracks from major campaigns have been shown as dotted lines, with markers corresponding to individual submicron OC measurements.
Fig. 2. Total number of organic carbon measurements available per year. Different geographical regions are separated with the height of bars indicating number of individual measurements. The orange line indicates the total worldwide.
Fig. 3. OC measurements in the 1997-2006 time period. Measurements are from (a) the United States, (b) China, (c) Europe, and (d) Japan. Center point of the boxes indicates median value, boxes indicate values between the 25th and 75th percentile, whiskers indicate values between the 10th and 90th percentile, and circles are outliers.
Fig. 4. Trend between mean OC concentration and local population density. Markers represent individual measurement sites. Red markers are in Asia, blue in Europe, and black in North America.
Fig. 5. Monthly averages of organic carbon measurements in the United States. Measurements from Washington (WA), Oregon (OR), California (CA), Minnesota (MN), Ohio (OH), Texas (TX), New Hampshire (NH), New Jersey (NJ), and Georgia (GA) are illustrated. Blue lines show measurements from the STN sites, red lines show measurements from the IMPROVE network. Error bars indicate standard deviation in the mean value.
Fig. 6. Monthly OC averages in select regions. Measurements from China - Beijing region (CH), Hong Kong (HK), and Japan (JA) in Asia, and Germany (GE), Finland (FI), and Slovakia (SV) in Europe are illustrated.
Fig. 7. Examples of sinusoidal fits for OC daily averages from the IMPROVE network. Markers are individual measurements and the black line shows the best fit to Equation 1.
Fig. 8. Histograms of the fit parameters in Eq. 1. (a) Median OC concentration, (b) rate of annual increase, (c) amplitude in variability, and (d) frequency of seasonal oscillations. Red bars correspond to measurement sites in the IMPROVE network, blue bars correspond to the STN sites, green bars correspond to Asian sites and brown bars to European sites.