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Spatially and seasonally resolved estimate of the ratio of organic mass to organic carbon

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HIGHLIGHTS

- Simple method to estimate spatially and seasonally resolved OM/OC.
- The OM/OC ratio can be estimated from satellite-derived NO_2 concentrations.
- Parameterization developed from Aerosol Mass Spectrometer measurements.
- OM/OC is lower in urban areas and higher in rural areas.
- OM/OC is lower in winter and higher in summer.

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ABSTRACT

Particulate organic matter is of interest for air quality and climate research, but the relationship between ambient organic mass (OM) and organic carbon (OC) remains ambiguous both in measurements and in modeling. We present a simple method to derive an estimate of the spatially and seasonally resolved global, lower tropospheric, ratio between OM and OC. We assume ambient NO_2 concentrations as a surrogate for fresh emission which mostly determines the continental scale OM/OC ratio. For this, we first develop a parameterization for the OM/OC ratio using the primary organic aerosol (POA) fraction of total OM estimated globally from Aerosol Mass Spectrometer (AMS) measurements, and evaluate it with high mass resolution AMS data. Second, we explore the ability of ground-level NO_2 concentrations derived from the OMI satellite sensor to serve as a proxy for fresh emissions that have a high POA fraction, and apply NO_2 data to derive ambient POA fraction. The combination of these two methods yields an estimate of OM/OC from NO_2 measurements. Although this method has inherent deficiencies over biomass burning, free-tropospheric, and marine environments, elsewhere it offers more information than the currently used global-mean OM/OC ratios. The OMI-derived global OM/OC ratio ranges from 1.3 to 2.1 (µg/µgC), with distinct spatial variation between urban and rural regions. The seasonal OM/OC ratio has a summer maximum and a winter minimum over regions dominated by combustion emissions. This dataset serves as a tool for interpreting organic carbon measurements, and for evaluating modeling of atmospheric organics. We also develop an additional parameterization for models to estimate the ratio of primary OM to OC from simulated NO_x concentrations.

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1. Introduction

Organic aerosols (OA) are a major constituent of fine particulate mass which affects air quality, visibility, and climate. Primary OA

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(POA) are mostly produced by combustion sources, while secondary OA (SOA) form through oxidation and partitioning of volatile organic compounds from anthropogenic and biogenic sources. Ambient OA is a complex mix of thousands of different organic molecules that introduces difficulties in analytical measurements, leaving large measurement uncertainty (e.g., Kanakidou et al., 2005; Jimenez et al., 2009). OA contains organic carbon (OC) as its major constituent and other elements such as oxygen, hydrogen and nitrogen, which together with OC constitute the total organic aerosol mass. Characterization of OA requires spatially and seasonally resolved information about the ratio of OA with OC (OA/OC, also commonly written as OM/OC, where OM is "organic mass", a synonym of OA).

Traditional ground-based impaction or filter-based instruments routinely measure OC using different analytic methods (e.g., Hand et al., 2012), but not OM due to difficulties in characterizing different components of OM. Other specific techniques that measure OM directly, such as Fourier Transform Infrared spectroscopy (FTIR) (Russell et al., 2009) and solvent extraction techniques (El-Zanan et al., 2005), are not used extensively. A wide range of literature is available on the methods to determine the OM/OC ratio, and it is a broadly debated issue. A common practice to interpret OC measurements is through the use of a continental mean value for the OM/OC ratio (such as 1.4 (Grosjean and Friedlander, 1975; White and Roberts, 1977), 1.6 (Malm et al., 1994), 1.4–2.1 (Turpin and Lim, 2001), and 1.8 (Hand et al., 2012) for North America). The spatial and seasonal variation in the OM/OC ratio is often neglected in the interpretation of measurement data due to insufficient information (e.g., Hand et al., 2012).

These global-mean values are frequently used in aerosol models to convert between POA and OM (e.g., Park et al., 2003). This is because most global and regional models simulate POA as OC. Despite notable developments for simulating the oxidative aging of OM (Simon and Bhave, 2012), most models do not yet readily predict the OM/OC ratio. A spatially and seasonally varying estimate of the OM/OC ratio should help interpret simulated organic aerosols.

The OM/OC ratio is directly related to the O/C ratio in the organic mass, since the contribution of non-oxygen elements to the OM/OC ratio is generally small, and both ratios increase with chemical aging of OA (Aiken et al., 2008; Pang et al., 2006). OM/OC has seasonal and spatial variation depending on the sources of POA and SOA and their degree of aging. The Aerosol Mass Spectrometer (AMS) offers quantitative determination of the size-resolved submicron OM at high temporal resolution through mass spectrometry (Jimenez et al., 2003; Canagaratna et al., 2007). Factor analysis of the AMS spectra can differentiate POA such as hydrocarbon-like OA (HOA) and several types of oxygenated OA (OOA) (Zhang et al., 2005a) that are typically SOA surrogates (Zhang et al., 2007, 2011). POA has lower OM/OC than SOA, and fresh SOA has lower OM/OC than aged SOA (Aiken et al., 2008).

The oxidative aging of organics may be indirectly estimated through different proxies. Both NO_x and submicron POA are mainly emitted from combustion processes. NO_x is oxidized in the atmosphere with a timescale of about a day. Over regional scales OA is dominated by SOA, and anthropogenic SOA is also formed with a timescale of about a day and in amounts much larger than the originally emitted POA (DeCarlo et al., 2010). Globally most SOA may be due to anthropogenic enhancement of biogenic SOA, which is also thought to have a similar timescale of formation (Goldstein et al., 2009; Spracklen et al., 2011). Once formed, all types of SOA appear to age with a characteristic timescale of about 1–2 days, increasing the OM/OC ratio (Jimenez et al., 2009). Given the similar spatial emission patterns and timescales, we explore ambient NO_2 concentrations as a surrogate for the POA/OA fraction and thus OM/OC ratios.

Here, we introduce a parameterization for OM/OC based on the POA fraction estimated from AMS measurements (Section 2.1), test global ground-level NO_2 and NO_x concentrations as a proxy for POA and thus OM/OC (Sections 2.2 and 2.3), and develop a gridded dataset of the seasonally varying OM/OC ratio (Section 2.4). We describe the spatially and seasonally varying satellite-derived OM/OC in Section 3.

2. Materials and methods

2.1. Primary OA fraction of the AMS data to predict OM/OC

We first explore a method to derive OM/OC. For this, we use the POA fraction of the AMS data as a proxy for combustion emissions (where combustion emissions can then be determined from the measurements of co-emitted species such as NO_x). Aiken et al. (2008) demonstrate a method to use high-resolution time-of-flight AMS ambient OA measurements to directly quantify the OM/OC ratio. Aiken et al. (2008) report a high correlation for OM/OC versus O/C ($r = 0.998$), quantify the OM/OC ratio for urban POA as ~1.3, and find that for OOA the OM/OC ratio varies from 1.9 to 2.4. Per the timescale discussion above, f_{POA} (the ratio of POA, determined from factor analysis of AMS spectra (Zhang et al., 2011), to the total measured OA) is expected to be inversely related to OM/OC. Therefore, we parameterize OM/OC from AMS using f_{POA},

$$OM/OC = 1.3 \times f_{POA} + 2.1 \times (1 - f_{POA}) \tag{1}$$

This method assumes that POA has an OM/OC ratio of 1.3 and OOA has a value of 2.1. However it should be noted that the OM/OC values for OOA can range from 1.9 to 2.4, and therefore our assumption introduces an uncertainty to the OM/OC estimates from the equation (1). An independent evaluation with direct OM/OC estimates from the AMS quantifies this uncertainty (± 0.2 μg/μgC) as described below. We collected nine published high mass resolution campaign-mean AMS-estimated f_{POA} and AMS-measured OM/OC data from field campaigns to evaluate this parameterization. Fig. 1 shows the scatter plot of AMS OM/OC and f_{POA}. It includes a representation of a typical urban POA with OM/OC ratio of 1.3 ($f_{POA} = 1$). We plotted equation (1) over this scatter plot
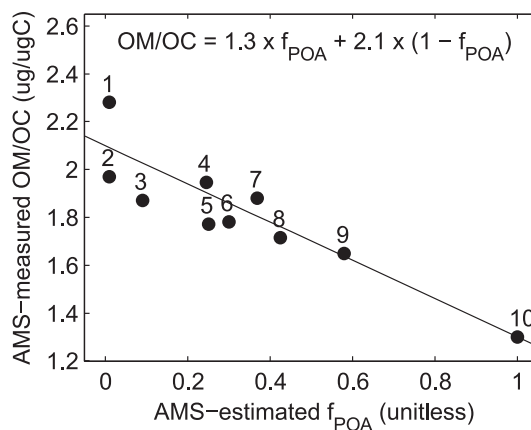

Fig. 1. Scatter plot of Aerosol Mass Spectrometer (AMS) measured OM/OC ratio, and the corresponding estimated primary organic aerosol fraction (f_{POA}) from several field campaigns around the globe. The dots and the corresponding numbers on the plot represent AMS field campaign-mean values for (1) Whistler, Canada (Sun et al., 2009); (2) Long Island (Personal communication from Qi Zhang); (3) CARES T1 (Setyan et al., 2012); (4) Pearl River Delta, China (Huang et al., 2011); (5) SOAR 1 (Docherty et al., 2011); (6) New York City (Sun et al., 2011); (7) CalNex, Los Angeles (Hayes et al., 2013); (8) Beijing, China (Huang et al., 2010); (9) Fresno, California (Ge et al., 2012); and (10) typical urban POA (Jimenez et al., 2009). The solid black line is equation (1) (also in inset).