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Y. Pang,[1] B.J. Turpin,[2] and L.A. Gundel[1]

[1]Lawrence Berkeley National Laboratory
Environmental Energy Technologies Division
Indoor Environment Department
University of California, Berkeley, CA 94720

[2]Department of Environmental Sciences
Rutgers University
New Jersey

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Y. Pang,[1#] B.J. Turpin,[2] and L.A. Gundel[1]

[1]E.O. Lawrence Berkeley National Laboratory, Environmental Energy Technologies

Division, University of California, Berkeley, CA 94720

[2]Department of Environmental Sciences, Rutgers University, NJ

ABSTRACT

This study shows how aerosol organic oxygen data could provide new information about organic aerosol mass, aqueous solubility of organic aerosols, formation of secondary organic aerosol (SOA) and the relative contributions of anthropogenic and biogenic sources. For more than two decades atmospheric aerosol organic mass (OM) concentration has been estimated by multiplying the measured carbon content by an assumed (OM)-to-organic carbon (OC) factor, usually 1.4. However, this factor can vary from 1.0 to 2.5 depending on location. This large uncertainty about aerosol organic mass limits our understanding of the influence of organic aerosol on climate, visibility and health.

New examination of organic aerosol speciation data shows that the oxygen content is responsible for the observed range in the OM-to-OC factor. When organic oxygen content is excluded, the ratio of non-oxygen organic mass to carbon mass varies very little across different environments (1.12 to 1.14). The non-oxygen-OM-to-OC factor for all studied sites (urban and non-urban) averaged 1.13. The uncertainty becomes an order of magnitude smaller than the uncertainty in the best current estimates of organic mass to organic carbon ratios (1.6± 0.2 for urban and 2.1± 0.2 for non-urban areas). This analysis suggests that, when aerosol organic oxygen data become available, organic aerosol mass can be quite accurately estimated using just OC and organic oxygen (OO) without the need to know whether the aerosol is fresh or aged. In addition, aerosol organic oxygen data will aid prediction of water solubility since compounds with OO-to-OC higher than 0.4 have water solubilities higher than 1 g per 100 g water.

INTRODUCTION

The organic constituents of airborne particles influence the behavior and impacts of particulate matter (PM) on human health, regional visibility and global climate (Novakov and Penner 1993; NRC 1999; IPCC 2001). Organic PM consists of hundreds of compounds from many chemical classes that differ widely in polarity and aqueous solubility. Improved understanding of the roles played by aerosol organics in atmospheric processing depends on knowledge of their aggregate polarity and aqueous solubility. One approach is detailed chemical characterization through identification and quantification of individual constituents by gas or liquid chromatography coupled with mass spectrometry (GC-MS and LC-MS, respectively).

The determination of organic compounds by GC-MS or LC-MS generally involves high volume sampling, complex sample preparation (e.g., solvent extraction, evaporation and derivatization), sample analysis, and data reduction. The complexity and limits of detection of these methods currently limit their widespread use, although they have been utilized to identify extractable organic compounds in organic aerosols at various locations (Alves et al., 2002; Edney et al., 2003; Kubatova et al., 2002; Mochida et al., 2003; Rogge et al., 1993; Zheng et al., 2002). However, these approaches have typically identified less than 30% of total organic mass in ambient aerosols. Even though molecular-level analyses are extremely valuable, simpler thermal methods (Ellis et al., 1984; Chow et al., 1993; Birch and Cary, 1996) are more widely used to characterize the carbonaceous components of PM by determining organic and elemental (black) carbon (OC and EC, respectively). Such bulk analyses could provide sufficient high quality data to characterize spatial and temporal distributions of organic PM and estimate organic PM mass concentrations, if the relationship between OC and organic mass (OM) could be established accurately.

However, because of the complexity of organic aerosols, obtaining accurate estimates of organic PM mass concentrations from OC remains a challenge. For 25 years aerosol organic mass estimates have been obtained by multiplying measured OC mass by an assumed OM-to-OC ratio of 1.4 (Turpin and Lim, 2001). This ratio represents an average organic molecular weight per carbon that was calculated from speciation data measured on two days in Pasadena, CA in 1970s (White and Roberts, 1977). Values of OM-to-OC factor from 0.9 to 2.5 have been reported in the literature (Putaud et al., 2000; Russell, 2003; Turpin and Lim, 2001) although ratios less than 1.0 are not physically meaningful. Turpin and Lim (2001) predicted that the OM-to-OC ratio will see increasing use in the current decade as a practical tool for the development of control strategies for fine particles, in spite of large uncertainty. Based upon review and analysis of current speciation data for organic aerosols, they recommended ratios of 1.6±0.2 for urban fresh and 2.1±0.2 for non-urban aged aerosols. As an alternative approach, Russell (2003) computed the OM-to-OC ratio from infrared spectroscopic measurements of organic functional groups. This approach requires functional group standards of absorptivity of the mix of organic compounds in ambient PM (for example, alkanes, aromatics, carbonyls, alcohols and organic acids). Overlapping peaks also complicate quantitation. Single particle mass spectrometer data may provide an alternative approach (Zhang et al 2005).

Recent reviews (Jacobson et al., 2000; Seinfeld and Pankow, 2003; Huebert and Charlson, 2000) show that the past 30 years of investigation of organic aerosol concentrations and properties have relied heavily on organic carbon measurement. Aerosol organic oxygen (OO) has received little attention, although oxygen, by mass, is second only to carbon in organic PM. The primary objective of this investigation is to use currently available data for aerosol organic composition to evaluate the importance of determination of organic oxygen for accurate estimation of organic PM mass and prediction of organic aerosol solubility and density. The approach is to start with the framework of Turpin and Lim (2001) and show how uncertainties in estimation of organic mass change when both organic carbon and organic oxygen data are available. The long range objective of this investigation is to provide motivation and justification for updating tools for aerosol organic oxygen so that it can be determined as routinely as OC.

DATA ANALYSIS

OM-to-OC and non-oxygen-OM-to-OC ratios

Below we show that the amount of oxygen is the main factor causing the large variations in OM-to-OC ratios among samples from different sources and locations (Putaud et al., 2000; Russell, 2003; Turpin and Lim, 2001). Since the possible range of C to H molar ratios in organic compounds is quite narrow (1 to 1.4), and aerosol organic nitrogen is expected to be much less prevalent than OO, excluding oxygen from the calculation of aerosol OM-to-OC ratios should also narrow possible range of values. Therefore, the ratio that we define as *non-oxygen organic mass to organic carbon (non-oxygen-OM-to-OC)* should have lower uncertainty than the OM-to-OC ratio in atmospheric aerosols.

The second column of Table 1 shows the OM-to-OC ratios for compound classes that have been found in ambient aerosols (Turpin and Lim 2001) and the ratios of non-oxygen-OM-to-OC for the same classes. Indeed, the non-oxygen OM-to-OC ratios have a much narrower range (1.0 to 1.3) than OM-to-OC ratios (1.0 to 3.8). Acids have the highest OM-to-OC ratios, for which the amount of oxygen is the main contributor to the variation. For example, the OM-to-OC ratios of oxalic acid (HOOCCOOH) and nonanedioic acid ($HOOC(CH_2)_7COOH$) are 3.8 and 1.7, respectively. When oxygen is excluded, the non-oxygen-OM-to-OC ratios of oxalic acid and nonanedioic acid are very similar (1.1 and 1.2, respectively). A recent study indicates that oligomers may contribute significantly to organic aerosols (Kalberer et al., 2004), and Table 1 shows that non-oxygen-OM-to-OC ratios are very similar (1.1) for the candidate oligomers.

Table 1. Organic mass to organic carbon ratios, with and without oxygen, for classes of particle-phase organic compounds found in urban air (Rogge et al., 1993; Schauer, 1998).

Compound class	OM-to-OC[a]	Non-oxygen OM-to-OC[b]	Oxygen-to-Carbon
Low Aqueous Solubility[c]			
n-Alkanes	1.2	1.2	0
n-Alkanoic acids (C_9–C_{30})	1.3–1.5	1.2	0.1-0.3
Polycyclic aromatic hydrocarbons (C_{16}–C_{24})	1.1	1.1	0
Polycyclic aromatic ketones and quinones (C_{17}–C_{19})	1.1-1.2	1.0-1.1	0
Soluble in Water[c]			
Aliphatic dicarboxylic acids (C_2–C_6)	2.0–3.8	1.1-1.2	0.9-1.8
Glyoxal (C_2)	2.4	1.1	1.3
Ketoacids (C_2–C_5)	1.9–3.1	1.1	1.0-2.0
Polyols (C_2–C_7)	1.5-2.6	1.1	0.4-1.3
p-Nitrophenol (C_6)	1.9	1.3	0.7
Amines and amino acids	2.4–3.6	1.4-1.9	0.0-1.3 (0.4-1.3 without amines)
Misc. multifunctional (C_3–C_6)	2.4–3.1	1.1-1.2	1.3-2.0
Other Compounds[c]			
n-Alkanols (C_{25}–C_{32})	1.2	1.2	0.1
n-Alkanals (C_9, C_{26}–C_{32})	1.2–1.3	1.2	0.1
Aliphatic dicarboxylic acids (C_7–C_9)	1.7-1.9	1.1-1.2	0.6-0.8
n-Alkenoic acids (C_{17}–C_{18})	1.3–1.5	1.2	0.2
Aromatic polycarboxylic acids (C_8–C_{10})	1.7–2.1	1.1	0.7-1.1
Steroids (Cholesterol, C_{27})	1.2	1.2	0.1
Nitrogen-containing compounds (C_6–C_{10})	1.2–1.9	1.2-1.3	0.0-0.3
Phenol and substituted phenols (C_6–C_7)	1.5	1.1	0.4
Guaiacol and substituted guaiacols (C_7–C_{11})	1.4–1.6	1.1	0.3-0.5
Syringol and substituted syringols (C_8–C_{12})	1.4–1.7	1.1	0.4-0.6
Mono-, sesqui-, and triterpenoids (C_{10}–C_{12}, C_{30})	1.3	1.1-1.2	0.1-0.2
Sugars (levoglucosan, C_6)	2.3	1.1	1.1
Oligomers[d]	1.5-2.1	1.1	0.4-1.0

[a] *From Turpin and Lim, 2001.*

[b] *This work.*

[c] *Soluble (>100 g solute per 100 g water) and insoluble (<100 gsolute per 100 g water) compounds are classified based on criteria used by Saxena and Hildemann (1996) and Turpin and Lim (2001). These authors did not cite solubility data for the classes grouped here as 'Other Compounds.'*

[d] *From Fig. 3 of Kalberer et al., 2004, assuming three routes for polymer formation.*

Table 2 shows what happens when non-oxygen OM-to-OC ratios of Table 1 are used with available data for concentrations of aerosol organic compounds at urban and non-urban California sites (Rogge et al., 1993; Schauer, 1998).

The range of non-oxygen OM-to-OC for all sites was very small (1.11 – 1.14). The average was 1.13± 0.02 for measured organic compounds for all sites (urban and non-urban). For consistency and direct comparison with published OM-to-OC ratios, we used the same approach to calculate average non-oxygen-OM-to-OC ratios as Turpin and Lim (2001) used for OM to OC ratios, giving all data for each site equal weight even though data for some sites (Los Angeles Basin) are annual averages while data for other sites (San Joaquin Valley) are two-day averages.

Table 2. Average OM-to-OC and non-oxygen-OM-to-OC ratios calculated as mass-weighted averages, based on ambient organic speciation data and Table 1.

Location	OM-to-OC ratio	non-Oxygen-OM -to- OC	% mass[a]	Reference
Los Angeles Basin (Annual avg.)			7-15%	Rogge et al., 1993
Downtown	1.65	1.11		
West LA	1.63	1.12		
Rubidoux	1.77	1.11		
San Nicolas Island[b]	1.29	1.14		
San Joaquin Valley (Dec 26, 1995; Jan 4, 1996)				Schauer, 1998
Fresno	2.54[c]; 2.24[d]	1.14[c] 1.14[d]	5–10%	
Bakersfield	2.52; 2.58	1.14;1.14	5–10%	
Kern Refuge	1.82; 3.04	1.14;1.14	<1%	

[a] % mass is the percentage of the organic mass identified at the molecular level and used in the ratio.

[b] Numerous compounds were below detection limits at this background site.

[c] for Dec 26 1995

[d] for Jan 4, 1996

Large uncertainties exist in the OM-to-OC molecular weight ratio for organic aerosol PM because of the lack of information about polar organic PM components. Turpin and Lim (2001) suggested that current analytical limitations result in underestimation of the polar organic constituents in PM and OM-to-OC ratios that are based on molecular level analysis. Because polar organics have more oxygen than non-polar organics, analytical limitations have more influence on OM-to-OC than non-oxygen-OM-to-OC ratios.

Solubility of organic aerosols

The aqueous solubility of the complex mixture of organic species in PM can influence chemical and physical transformation of atmospheric aerosols. For example, modeling results suggest that water soluble organics in aerosols influence the number and size of droplets by increasing the droplets' solute mass and reducing both the surface tension and the critical supersaturation ratio for droplet activation (Anttila and Kerminen, 2002). Water soluble organics are thought to have more significant effects on climate than insoluble organics (Swietlicki et al., 1999; Anttila and Kerminen, 2002; Chung and Seinfeld, 2002; Shantz et al., 2003). After surveying the literature, Saxena and Hildemann (1996) concluded that 20-70% of the organic aerosol mass consists of water-soluble organics (>100 g solute per 100 g water). Tables 1 shows OM-to-OC, non-oxygen OM-to-OC and oxygen-to-carbon ratios for organic compounds with low and high aqueous solubilities, respectively, for species included in the review by Saxena and Hildemann (1996). We included aromatic polycarboxylic acids in Tables 1 in the category of *Other Compounds* rather than as soluble compounds because their water solubility varies from 0 to 3 g solute per 100 g water, bridging both categories.

Table 1 shows that most of the less soluble organic compounds have oxygen-to-carbon-mass ratios from 0.0 to 0.3. In contrast, the oxygen-to-carbon ratios for water-soluble organics are larger, 0.4- 2.0, except for amines that comprise a very small part of the total aerosol organic mass.

Organic aerosol density

Table 3 compares the O:C ratios with the densities of aerosol organic compounds, as measured or estimated for 20 °C and 1 atm (from Howard and Neal, 1992; Immirzi and Perini, 1977; Lang, 1973; Lide, 1994, as identified by Rogge et al., 1993 or Sempere and Kawamura, 1994). When the mass ratios of oxygen-to-carbon are higher than 0.5, the densities are higher than 1.0 g cm^{-3}, except for PAHs.

Table 3. Densities of particle-phase organic compounds and oxygen-to-carbon mass ratios.

Compound class	Density Range g cm^{-3}	Density Avg. g cm^{-3}	Oxygen-to-Carbon
n-Alkanes (C_{23}–C_{34})	0.77–0.81	0.79 ± 0.01	0.0
n-Alkanoic acids (C_9–C_{30})	0.81–0.99	0.89 ± 0.07	0.1-0.3
n-Alkanals (C_9)	0.83	0.83	0.2
Aliphatic dicarboxylic acids (C_2–C_9)	1.03–1.90	1.46 ± 0.23	0.6-1.8
Ketocarboxylic acids (C_2–C_3)	1.1–1.27	1.18 ± 0.12	1.0-2.0
Aromatic polycarboxylic acids (C_8–C_{10})	1.39–1.60	1.49 ± 0.08	0.6-1.1
Polycyclic aromatic hydrocarbons (C_{16}–C_{24})	1.10–1.55	1.28 ± 0.12	0.0
Polycyclic aromatic ketones and quinones (C_{17}, C_{18})	1.16–1.22	1.19	0.1
Steroids (Cholesterol, C_{27})	1.07	1.07	0.05
Nitrogen-containing compounds (C_6–C_{10})	1.08–1.19	1.11 ± 0.05	0.0-0.3
Polyols (C_2–C_8)	0.93–1.26	1.04 ± 0.13	0.4-1.3
Amino acids (C_2–C_6)	1.01–1.60	1.42 ± 0.21	0.4-1.3

DISCUSSION

Turpin and Lim (2001) found that OM-to-OC ratios vary considerably across the classes of compounds found in PM. Using the available data for speciated ambient PM, they found large differences between rural and urban locations, presumably because of increased oxidation with regional transport, as well as differences in emission sources. In contrast, Table 2 shows that the non-oxygen-OM-to-OC ratios derived from the same samples varied little (from 1.11 to 1.14 with 1.13 mean ± 0.02). For Kern Refuge, the OM-to-OC ratios were quite different for Dec 1995 and Jan 1996 (1.82 and 3.04 respectively). However, the non-oxygen-OM-to-OC ratios were the same. For San Nicolas Island the OM-to-OC ratio was lower than that expected for a non-urban area, but many samples from San Nicolas Island had organic concentrations below detection limits. In spite of this, the non-oxygen-OM-to-OC ratio at this site was closer to the ratio for non-urban areas (e.g., Fresno, Kern Refuge, 1.14) than for urban areas (e.g., LA Downtown, West LA, 1.11).

The degree of saturation of carbon bonds increases during oxidation of both polar and non-polar organic compounds. Saturated organic compounds generally have more hydrogen bonded to carbon. Furthermore, high molecular weight polar compounds are generally more difficult to identify and yet may account for a large fraction of organic aerosol mass. The unidentified polar organic compounds will certainly influence the true OM-to-OC ratios, but the non-oxygen-OM-to-OC ratios are much less affected. This may explain why the non-oxygen-OM-to-OC ratio of San Nicolas with more aged secondary organic aerosol (SOA) was different from that of downtown LA with more primary organic aerosols even though fewer organic compounds were identified.

The uncertainty in the non-oxygen-OM-to-OC ratio (1.13± 0.02) is an order of magnitude smaller than the uncertainty in the best current estimates of total organic mass to the organic carbon ratios (1.6± 0.2 for urban and 2.1± 0.2 for non-urban areas). Since 1.13 was estimated from limited data for organic species in ambient PM (7 sites in California), more studies should be done to refine this new parameter for aerosol characterization. The non-oxygen-OM-to-OC ratio will be more useful when aerosol organic oxygen concentrations can be determined directly from ambient samples. As long as sampling and measurement uncertainties are reasonable (~15% or less) the sum of aerosol organic oxygen mass and non-oxygen organic mass calculated from OC data will provide much more accurate estimates of aerosol organic mass than are now possible. Compared with determination of all organic compounds or functional groups in aerosols, determination of aerosol organic oxygen mass is likely to be easier and more cost-efficient when a method exists that is a straightforward as OC-EC analysis is today and each sample can be analyzed in 20 min. Benner and Hansen (1984) developed a thermal method for aerosol oxygen and demonstrated its usefulness for characterization of urban PM (Benner et al., 1984). Although their method has not been widely used, efforts have begun to update and optimize it for routine measurements of aerosol organic oxygen (Cary et al. 2003). It may also be possible to extract organic oxygen concentrations from single particle mass spectrometer data (Zhang et al 2005).

The data of Table 1 indicate that oxygen is the main factor contributing to the variation of OM-to-OC ratios among the compound classes that have been quantified in ambient PM. Table 2 strongly suggests that variation in organic oxygen is largely responsible for the range of OM-to-OC ratios found in ambient aerosols. Therefore, monitoring aerosol organic oxygen concentrations may provide useful information for source apportionment, investigations of aerosol processing, and prediction of effects.

Identification of the relative contribution of anthropogenic and biogenic sources is critical for policy makers. From data for fireplace combustion of pine, oak, and eucalyptus wood (Schauer, 1998) we calculate that the ratios of concentration-weighted aerosol organic oxygen mass to carbon mass were 0.77, 0.81, and 0.96, respectively, and averaged 0.85. This is much higher than we calculate from the data of Schauer et al. (2002) for fossil fuel combustion for which emissions were dominated by hydrocarbons. The concentration-weighted oxygen-to-carbon ratio was 0.1 for catalyst-equipped gasoline-powered motor vehicle engines. This example suggests that the ratio of aerosol organic oxygen mass to organic carbon mass might also provide insights about the relative contribution of biogenic and anthropogenic sources to organic aerosols.

The degree of oxidation, inferred from the amount of organic oxygen in aerosol organics, is also an indicator of SOA formation because SOA consists of the oxidized products of reactions of primary organic compounds with photochemically generated oxidants (e.g., ozone and OH). Three methods are used currently to estimate SOA concentrations in the atmosphere (Seinfeld and Pankow, 2003): the EC tracer method, detailed speciation and quantification of members of organic compound classes, and determination of concentrations of molecular tracers to assess the role of individual hydrocarbon precursors in SOA formation. Seinfeld and Pankow (2003) concluded that the EC tracer method will continue in common use because better methods are currently lacking, even though the estimates of SOA formation from OC and EC data have large uncertainties. Measurements of aerosol organic oxygen (OO), used with OC and EC data, might reduce EC tracer method uncertainties because increases in OO are likely to track atmospheric oxidation processes. OO measurements can provide a new tool to monitor formation of SOA and subsequent atmospheric reactions. Adding OO characterization to OC-EC measurements could also improve source apportionment of ambient PM. OO along with OC-EC data may help in distinguishing oxygen-rich primary biogenic aerosol from SOA produced from both anthropogenic and biogenic sources.

To our knowledge, no methods can estimate the solubility of aggregated organic aerosols. Table 1 suggests that aerosol organic oxygen could aid the prediction of organic aerosol water solubility when OC-EC data are also available. Such data could contribute to improved understanding of the effects of organic aerosol constituents on climate, visibility and dosimetry.

In conclusion, aerosol OO data could provide new and independent information about organic aerosols and new tools to understand several properties of organic aerosols. Organic oxygen data could lead to better estimation of aerosol organic mass and aqueous solubility, as well as better apportionment of the contributions of anthropogenic, biogenic sources and secondary organic aerosol to PM. We recommend the use of a non-oxygen-organic mass-to-organic carbon ratio 1.13±0.02 for organic aerosol mass estimation, as well as development of methods for determining aerosol organic oxygen. This approach will decrease uncertainties in organic PM mass estimates and improve our understanding of effects of organic aerosols on health, visibility, and climate.

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