# Mass reconstruction methods for $\mathbf{P M}_{2.5}$ : a review 

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Received: 18 February 2015 / Accepted: 17 March 2015 /Published online: 7 May 2015
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#### Abstract

Major components of suspended particulate matter (PM) are inorganic ions, organic matter (OM), elemental carbon (EC), geological minerals, salt, non-mineral elements, and water. Since oxygen $(\mathrm{O})$ and hydrogen $(\mathrm{H})$ are not directly measured in chemical speciation networks, more than ten weighting equations have been applied to account for their presence, thereby approximating gravimetric mass. Assumptions for these weights are not the same under all circumstances. OM is estimated from an organic carbon (OC) multiplier $(f)$ that ranges from 1.4 to 1.8 in most studies, but $f$ can be larger for highly polar compounds from biomass burning and secondary organic aerosols. The mineral content of fugitive dust is estimated from elemental markers, while the water-soluble content is accounted for as inorganic ions or salt. Part of the discrepancy between measured and reconstructed PM mass is due to the measurement process, including: (1) organic vapors adsorbed on quartz-fiber filters; (2) evaporation of volatile ammonium nitrate and OM between the weighed Teflon-membrane filter and the nylon-membrane and/or quartz-fiber filters on which ions and carbon are


Electronic supplementary material The online version of this article (doi:10.1007/s11869-015-0338-3) contains supplementary material, which is available to authorized users.

[^0]measured; and (3) liquid water retained on soluble constituents during filter weighing. The widely used IMPROVE equations were developed to characterize particle light extinction in U.S. national parks, and variants of this approach have been tested in a large variety of environments. Important factors for improving agreement between measured and reconstructed PM mass are the $f$ multiplier for converting OC to OM and accounting for OC sampling artifacts.

Keywords $\mathrm{PM}_{2.5}$ - Mass closure • Chemical speciation . Organic matter $\cdot$ Sampling artifact

## Introduction

Particles with aerodynamic diameters $<2.5 \mu \mathrm{~m}\left(\mathrm{PM}_{2.5}\right)$ and $10 \mu \mathrm{~m}\left(\mathrm{PM}_{10}\right)$ mass concentrations are regulated by the National Ambient Air Quality Standards (NAAQS; Bachmann 2007; Chow et al. 2007a) in the USA, with variations being adopted in other countries (Cao et al. 2013). For compliance monitoring, ambient particles are collected over 24-h durations onto filters that are weighed before and after sampling (Chow 1995; Watson and Chow 2011). Chemically speciated PM is needed to better understand pollution sources, atmospheric processing (e.g., transport and transformation), temporal and spatial variations and long-term trends, as well as adverse health and environmental consequences. $\mathrm{PM}_{2.5}$ mass and chemical components (i.e., ions, elements, and carbon) have been acquired in the National Park Service (NPS) Interagency Monitoring of Protected Visual Environments (IMPROVE) non-urban network, and the US Environmental Protection Agency (EPA) urban Chemical Speciation Network (CSN; Solomon et al. 2014; USEPA 2015) on an every-third- or sixth-day schedule since 1987/1988 and 1999/2000, respectively. Measurement
protocols for the US $\mathrm{PM}_{2.5}$ networks are documented by Chow et al. (2010) and Solomon et al. (2014). Sampling and chemical analysis methods vary in these and other long-term networks and in special studies from the USA and elsewhere (e.g., Dabek-Zlotorzynska et al. 2011; Zhang et al. 2012).

Chow and Watson (2013) summarize different PM chemical analysis methods. The major PM components measured to explain gravimetric mass include: (1) anions (e.g., chloride $\left(\mathrm{Cl}^{-}\right)$, nitrate $\left(\mathrm{NO}_{3}{ }^{-}\right)$, and sulfate $\left.\left(\mathrm{SO}_{4}{ }^{-}\right)\right)$and cations (e.g., water-soluble sodium $\left(\mathrm{Na}^{+}\right)$, potassium $\left(\mathrm{K}^{+}\right)$, and ammonium $\left(\mathrm{NH}_{4}{ }^{+}\right)$); (2) elements, including metals (up to 51 elements from sodium ( Na ) to uranium (U)); and (3) organic carbon (OC) and elemental carbon (EC) and their carbon fractions. To accommodate chemical speciation, at least two types of sampling substrates (i.e., Teflon-membrane and quartz-fiber filters) are needed (Chow 1995). IMPROVE and CSN use three parallel channels, in which mass by gravimetry and elements by X-ray fluorescence (XRF; Watson et al. 1999) are measured on Teflon-membrane filters; ions by ion chromatography (IC; Chow and Watson 1999) are measured on nylonmembrane filters preceded by a sodium carbonate $\left(\mathrm{Na}_{2} \mathrm{CO}_{3}\right)$ denuder (Ashbaugh and Eldred 2004) to remove nitric acid $\left(\mathrm{HNO}_{3}\right)$; and OC and EC by thermal/optical carbon analysis (Chow et al. 1993, 2007a, 2011) are measured on quartz-fiber filters. PM components include carbon (C), hydrogen (H), nitrogen $(\mathrm{N})$, sulfur $(\mathrm{S})$, oxygen $(\mathrm{O})$, and a wide variety of other elements. Owing to practical analytical limitations (Chow and Watson 2013), most networks do not measure H and O associated with OC, geological minerals, and liquid water-with the exception of the IMPROVE network, where $H$ was quantified from 1988 to 2010 (Nejedly et al. 1997). As a result, the sum of the measured species is often lower than the gravimetric mass. Watson (2004) specifies a percent mass explained of $100 \pm 20 \%$ for source apportionment models, and this is a reasonably good criteria for mass reconstruction.

PM mass reconstruction (also called mass closure or material balance) applies multipliers to several of the measured species to estimate unmeasured components. Mass reconstruction is used to: (1) identify and correct potential measurement errors as part of data validation efforts (Chow et al. 1994a; Malm et al. 2011; Watson et al. 2001); (2) understand temporal and spatial variations of chemical composition (Hand et al. 2014; Malm et al. 2011); and (3) estimate source contributions to PM and light extinction (Chow and Watson 2013; Watson 2002). Mass reconstruction attempts to achieve closure between gravimetric mass and the sum of major components with assumptions to account for unmeasured species, but without double counting. For example, when $\mathrm{SO}_{4}{ }^{=}$is included, elemental S is omitted; inclusion of elemental chlorine ( Cl ) excludes water-soluble $\mathrm{Cl}^{-}$; and the same applies for elemental potassium (K) and water-soluble potassium $\left(\mathrm{K}^{+}\right)$ (Chow et al. 1994a). Although this review focuses on $\mathrm{PM}_{2.5}$, a similar approach is applicable for $\mathrm{PM}_{10}$. As $\mathrm{PM}_{2.5}$ is part of
$\mathrm{PM}_{10}$, mass reconstruction should be conducted for both $\mathrm{PM}_{2.5}$ and $\mathrm{PM}_{\text {coarse }}$ (i.e., $\mathrm{PM}_{10-2.5}$ ) when $\mathrm{PM}_{10}$ speciation is available (e.g., Chow et al. 2002a).

Various approaches have been taken for PM mass reconstruction (e.g., Frank 2006; Hand et al. 2011; Malm et al. 2011)-the widely used 11 equations are documented in "Commonly applied reconstructed mass equations." Applications of these equations to past studies (summarized in the supplemental material) are enumerated in "Applications of mass reconstruction equations to special studies." To provide a perspective on the fraction of mass explained, examples of mass reconstruction applications for the long-term US IMPROVE network are given in "Evaluation of mass reconstruction through analysis of large data sets." Various regression techniques have been used to derive multipliers for major PM components and to examine the adequacy of using the IMPROVE equations for mass reconstruction. Major factors that bias mass reconstruction (e.g., the use of an OC multiplier to estimate organic matter (OM), carbon sampling and analysis artifact, ammonium and nitrate volatilization, and particlebound water on Teflon-membrane filters) are discussed in "Major factors influencing mass reconstruction." This review examined hundreds of prior studies and intends to: (1) track the evolution and approaches for mass reconstruction; (2) discuss the adequacy of each approach; and (3) address major PM sampling and analysis issues that influence mass reconstruction.

## Commonly applied reconstructed mass equations

Table 1 summarizes 11 PM mass reconstruction methods (i.e., Eqs. 1 to 11, sequence in chronological order of publication) that have been applied to data acquired since the late 1970s. Some variations from other studies are referenced. Reconstructed mass (RM) is expressed as the sum of its seven representative chemical components, including: (1) inorganic ions; (2) OM or OC; (3) EC, also referred to as "black carbon" (BC), "soot," or light absorbing carbon (LAC); (4) geological minerals (or materials), often referred to as "dust," "soil," or "crustal material;" (5) salt (sea salt near oceans and inland seas, but also deriving from wintertime de-icing material and desert playas); (6) trace elements (other elements that are not accounted for as minerals, as from fly ash); and (7) "others," or "remaining mass," representing other unaccounted or unidentified components. As such, RM equations take the following form:

$$
\begin{align*}
\mathrm{RM}= & \text { Inorganic ions }+\mathrm{OM}+\mathrm{EC} \\
& + \text { Geological minerals }+ \text { Salts } \\
& + \text { Trace elements }+ \text { Others } \tag{A}
\end{align*}
$$

Each of these components can derive from a variety of sources, though they are often dominated by a few sources.
Table 1 Summary of the 11 mass reconstruction equations and their major chemical components

| Equation No. (reference)/study area | Inorganic ions | Organic mass/organic carbon (OM/OC) ratio | Elemental carbon (EC) | Geological minerals ${ }^{\text {a }}$ | Salt ${ }^{\text {b }}$ | Trace elements ${ }^{\text {c }}$ | Others |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Equation 1 (Macias et <br> al. 1981)/Page, AZ | $\left(\mathrm{NH}_{4}\right)_{2} \mathrm{SO}_{4}+\mathrm{NH}_{4} \mathrm{NO}_{3}$ | $1.5{ }^{\text {d }}$ | Yes | $\begin{gathered} 1.89 \mathrm{Al}+2.14 \mathrm{Si}+1.4 \mathrm{Ca}+1.2 \mathrm{~K}+ \\ 1.43 \mathrm{Fe}\left(\text { assuming } \mathrm{Al}_{2} \mathrm{O}_{3},\right. \\ \mathrm{SiO}_{2}, \mathrm{CaO}, \mathrm{~K}_{2} \mathrm{O}, \text { and } \mathrm{Fe}_{2} \mathrm{O}_{3} \text { ) } \end{gathered}$ | None | $\begin{aligned} & 1.25 \mathrm{Cu}+1.24 \mathrm{Zn}+1.08 \mathrm{~Pb} \text { (assuming } \\ & \mathrm{CuO}, \mathrm{ZnO} \text {, and } \mathrm{PbO} \text { ) } \end{aligned}$ | None |
| Equation 2 (Solomon et al. 1989)/Los Angeles, CA | $\mathrm{SO}_{4}{ }^{=}+\mathrm{NO}_{3}{ }^{-}+\mathrm{NH}_{4}^{+}$ | 1.4 | Yes | $1.89 \mathrm{Al}+2.14 \mathrm{Si}+1.4 \mathrm{Ca}+1.43 \mathrm{Fe}$ (no oxides were specified) | None | Sum of all species measured by XRF (excluding $\mathrm{S}, \mathrm{Al}, \mathrm{Si}, \mathrm{Ca}$, and Fe ) plus $\mathrm{Na}^{+}$and $\mathrm{Mg}^{++}$measured by AAS | None |
| Equation 3 (Chow et al. 1994b)/Los Angeles, CA | $\mathrm{SO}_{4}{ }^{+}+\mathrm{NO}_{3}{ }^{-}+\mathrm{NH}_{4}^{+}$ | 1.4 | Yes | As in Eq. 2 (assuming $\mathrm{Al}_{2} \mathrm{O}_{3}$, $\mathrm{SiO}_{2}, \mathrm{CaO}$, and $\mathrm{Fe}_{2} \mathrm{O}_{3}$ ) | None | Sum of 40 elements ( Na to U ) by XRF excluding $\mathrm{S}, \mathrm{Al}, \mathrm{Si}, \mathrm{Ca}$, and Fe | None |
| Equation 4 (Malm et al. 1994)/IMPROVE network | 4.125 S as $\left(\mathrm{NH}_{4}\right)_{2} \mathrm{SO}_{4}$ $\mathrm{NO}_{3}{ }^{-}$was excluded due to the concern that $\mathrm{NO}_{3}{ }^{-}$can volatilize from the Teflonmembrane filters but not from the Nylon filter | 1.4 | Yes | $2.2 \mathrm{Al}+2.49 \mathrm{Si}+1.63 \mathrm{Ca}+1.94 \mathrm{Ti}+$ <br> 2.42Fe (assuming $\mathrm{Al}_{2} \mathrm{O}_{3}, \mathrm{SiO}_{2}$, $\mathrm{CaO}, \mathrm{Fe}_{2} \mathrm{O}_{3}$, and FeO (in equal amounts), $\mathrm{TiO}_{2}$, and $\mathrm{K}_{2} \mathrm{O}$ (assuming that soil K is 0.6 Fe ), with all oxide multipliers by 1.16 to account for other missing compounds) | None | None | None |
| Equation 5 (Chow et al. 1996)/ San Joaquin Valley, CA | $\mathrm{SO}_{4}{ }^{+}+\mathrm{NO}_{3}{ }^{-}+\mathrm{NH}_{4}^{+}$ | 1.4 | Yes | As in Eq. 2 | $\mathrm{Na}^{+}+\mathrm{Cl}^{-}$ | As in Eq. 2: also excluding $\mathrm{Na}^{+}, \mathrm{K}^{+}$, and $\mathrm{Cl}^{-}$ | None |
| Equation 6 (Andrews et al. 2000)/Great Smoky Mountains National Park, TN | $\mathrm{SO}_{4}{ }^{=}+\mathrm{NO}_{3}{ }^{-}+\mathrm{NH}_{4}{ }^{+}$ <br> (MOUDI sampler $\mathrm{NH}_{4}{ }^{+}$was estimated by HEADS $\mathrm{SO}_{4}{ }^{-} / \mathrm{NH}_{4}{ }^{+}$ratio) | 1.4 | Yes | As in Eq. 2 plus 1.67 Ti (assuming $\mathrm{Al}_{2} \mathrm{O}_{3}, \mathrm{SiO}_{2}, \mathrm{CaO}, \mathrm{K}_{2} \mathrm{O}, \mathrm{TiO}_{2}$, and $\mathrm{Fe}_{2} \mathrm{O}_{3}$ ) | None | Sum of remaining species (excluding S, Al, Si, Fe, Ti, Ca, and K; see Table S-1 of Andrews et al. 2000) | None |
| Equation 7 (Malm et al. 2000); original IMPROVE Eq.)/ IMPROVE network | $\begin{aligned} & 4.125 \mathrm{~S}\left(\text { as }\left(\mathrm{NH}_{4}\right)_{2} \mathrm{SO}_{4}\right)+ \\ & \quad 1.29 \mathrm{NO}_{3}^{-}\left(\text {as } \mathrm{NH}_{4} \mathrm{NO}_{3}\right) \end{aligned}$ | 1.4 | Yes | As in Eq. 4 | None | None | None |
| Equation 8 (Maenhaut et al. 2002)/Melpitz, Germany | $\mathrm{SO}_{4}{ }^{+}+\mathrm{NO}_{3}{ }^{-}+\mathrm{NH}_{4}^{+}$ | 1.4 | Yes | As in Eq. 4 | $\mathrm{Cl}+1.4486 \mathrm{Na}$ | Sum of all non-sea salt and non-crustal elements, excluding S and K . | Non-crustal K ( $\mathrm{K}-0.6 \mathrm{Fe}$ ) |
| Equation 9 (DeBell et al. 2006)/IMPROVE network | $\begin{aligned} & 4.125 \mathrm{~S}\left(\text { as }\left(\mathrm{NH}_{4}\right)_{2} \mathrm{SO}_{4}\right)+ \\ & \quad 1.29 \mathrm{NO}_{3}^{-}\left(\text {as } \mathrm{NH}_{4} \mathrm{NO}_{3}\right) \end{aligned}$ | 1.8 | Yes | As in Eq. 4 | None | None | None |
| Equation 10 (Hand et al. 2011; revised IMPROVE <br> Eq.)/IMPROVE network | $\begin{gathered} 1.375 \mathrm{SO}_{4}{ }^{-}\left(\text {as }\left(\mathrm{NH}_{4}\right)_{2} \mathrm{SO}_{4}\right)^{\mathrm{e}}+ \\ 1.29 \mathrm{NO}_{3}{ }^{-}\left(\text {as } \mathrm{NH}_{4} \mathrm{NO}_{3}\right) \end{gathered}$ | 1.8 | Yes | As in Eq. 4 | $1.8 \mathrm{Cl}^{-}$ | None | None |
| Equation 11 (Simon et al. 2011)/IMPROVE network | $\left(\mathrm{NH}_{4}\right)_{2} \mathrm{SO}_{4}+\mathrm{NH}_{4} \mathrm{NO}_{3}$ | 1.8 | Yes | $3.48 \mathrm{Si}+1.63 \mathrm{Ca}+2.42 \mathrm{Fe}+1.94 \mathrm{Ti}$ | $1.8 \mathrm{Cl}^{-}$ | None | $\begin{aligned} & \text { Non-crustal } \\ & \mathrm{K}=1.2 \times \\ & (\mathrm{K}-0.6 \mathrm{Fe}) \end{aligned}$ |

 Denuder System
 oxide $\left(\mathrm{TiO}_{2}\right)$, iron ( Fe$)$, ferric oxide $(\mathrm{FeO})$, and ferrous oxide $\left(\mathrm{Fe}_{2} \mathrm{O}_{3}\right)$ ${ }^{\mathrm{b}}$ Salt includes: sea salt, chloride $\left(\mathrm{Cl}^{-}\right)$, potassium ion $\left(\mathrm{K}^{+}\right)$, and sodium ion $\left(\mathrm{Na}^{+}\right)$
 fluorescence (XRF) and atomic absorption spectroscopy (AAS)
${ }^{d}$ Based on assumed organic compound composition proportional to $\mathrm{CH}_{2} \mathrm{O}_{0.25}$
${ }^{\mathrm{e}}$ Hand et al. (2011) estimated $\left(\mathrm{NH}_{4}\right)_{2} \mathrm{SO}_{4}$ from the $\mathrm{SO}_{4}{ }^{=}$concentration as $1.375 \times \mathrm{SO}_{4}{ }^{=}$to account for unmeasured $\mathrm{NH}_{4}{ }^{+}$

Minerals, for example, do not include OM that might be associated with engine exhaust or bioaerosols deposited onto roadways or agricultural soils. These would be included in the OM fraction. Similarly, some fugitive dust sources include salts, but these would be accounted for in the salt fraction; sulfates and nitrates that react with salt (Hoffman et al. 2004) would be accounted for in the inorganic ion fraction. The background and assumptions related to these RM components are described in the following subsections.

## Inorganic ions

In addition to commonly measured anions and cations by IC, automated colorimetric (AC), atomic absorption spectroscopy (AAS), and inductively coupled plasma-atomic emissions spectroscopy (ICP-AES) have also been applied for ionic speciation (Chow and Watson 2013). Depending on the measurements available, the following methods are used to determine their mass contributions:

- In the absence of $\mathrm{NH}_{4}{ }^{+}$measurement, $\mathrm{SO}_{4}{ }^{=}$and $\mathrm{NO}_{3}{ }^{-}$are assumed to be neutralized to ammonium sulfate $\left(\left(\mathrm{NH}_{4}\right)_{2} \mathrm{SO}_{4}\right)$ and ammonium nitrate $\left(\mathrm{NH}_{4} \mathrm{NO}_{3}\right)$, with the $\mathrm{NH}_{4}{ }^{+}$fraction accounted for by stoichiometric multipliers: $1.375 \mathrm{SO}_{4}{ }^{=}$and $1.29 \mathrm{NO}_{3}{ }^{-}$, respectively (i.e., Eqs. 1, 10, and 11 in Table 1). An ion balance based on molar equivalence between the measured anions and cations should be applied to verify the extent of neutralization (Chow et al. 1994b).
- $\mathrm{SO}_{4}{ }^{=}, \mathrm{NO}_{3}{ }^{-}$, and $\mathrm{NH}_{4}{ }^{+}$are summed without weighting factors (i.e., Eqs. 2, 3, 5, 6, and 8). This does not account for H when $\mathrm{SO}_{4}{ }^{=}$is incompletely neutralized by $\mathrm{NH}_{4}{ }^{+}$as in sulfuric acid $\left(\mathrm{H}_{2} \mathrm{SO}_{4}\right)$, ammonium bisulfate $\left(\mathrm{NH}_{4} \mathrm{HSO}_{4}\right)$, or letovicite $\left(\left(\mathrm{NH}_{4}\right)_{3} \mathrm{H}\left(\mathrm{SO}_{4}\right)_{2}\right)$.
- When only S is measured, it is assumed to be neutralized $\left(\mathrm{NH}_{4}\right)_{2} \mathrm{SO}_{4}$ (i.e., 4.125 S in Eqs. 7 and 9) and summed with either $\mathrm{NO}_{3}{ }^{-}$(Landis et al. 2001) or $\mathrm{NH}_{4} \mathrm{NO}_{3}\left(1.29 \mathrm{NO}_{3}{ }^{-}\right.$in Eqs. 7 and 9). If $\mathrm{NO}_{3}{ }^{-}$is not measured, $\mathrm{NH}_{4} \mathrm{NO}_{3}$ is assumed to be negligible (Malm et al. 1994, Eq. 4). This assumption is valid only when the $\mathrm{NO}_{3}{ }^{-}$concentration is low, as it is for some non-urban, eastern US IMPROVE sites but not for others (Pitchford et al. 2009). Abundant $\mathrm{NO}_{3}{ }^{-}$has been found in several urban areas, especially during fall and winter (Green et al. 2015).

Assuming $1.29 \mathrm{NO}_{3}{ }^{-}$for $\mathrm{NH}_{4} \mathrm{NO}_{3}$ may not be valid when $\mathrm{HNO}_{3}$ reacts with suspended dust to form calcium nitrate $\left(\mathrm{Ca}\left(\mathrm{NO}_{3}\right)_{2}\right)$ or when it reacts with sodium chloride $(\mathrm{NaCl})$ from a marine intrusion or suspension from an alkaline playa to form sodium nitrate $\left(\mathrm{NaNO}_{3}\right)$ (Hoffman et al. 2004). Lee et al. (2008) noted the presence of $\mathrm{PM}_{2.5} \mathrm{Ca}\left(\mathrm{NO}_{3}\right)_{2}$ at several IMPROVE sites owing to a coarse particle $\mathrm{NO}_{3}{ }^{-}$tail that extended below $2.5 \mu \mathrm{~m}$. Harrison et al. (2003) applied Eq. 7
for $\mathrm{PM}_{2.5}$ ions and added $\mathrm{NaNO}_{3}$ for $\mathrm{PM}_{10-2.5}$. Several studies used front filter $\mathrm{NO}_{3}{ }^{-}$(i.e., non-volatilized $\mathrm{NO}_{3}{ }^{-}$from Teflonmembrane or quartz-fiber filters), as volatilized $\mathrm{NO}_{3}{ }^{-}$is not part of the gravimetric mass (Chow et al. 2002a). Ma et al. (2001) estimated $\mathrm{NH}_{4} \mathrm{NO}_{3}$ as 2.857 N , with N measured by an elemental analyzer, which is commonly applied to fuel assays. The presence of ammonium chloride $\left(\mathrm{NH}_{4} \mathrm{Cl}\right)$ in $\mathrm{PM}_{2.5}$ was noted by Kelly et al. (2013) for Utah's Salt Lake valley; by Pant et al. (2015) in New Delhi, India, where there is abundant trash burning; and by Levin et al. (2010) for biomass burning samples.

Elemental S has been commonly measured by XRF or proton-induced X-ray emission (PIXE) analyses (Watson et al. 1999). Based on molecular weight, 3S can be used to estimate $\mathrm{SO}_{4}{ }^{=}$, assuming that all S is water-soluble $\mathrm{SO}_{4}{ }^{=}$. This is not the case when: (1) S is associated with insoluble organic compounds such as mercaptans; (2) S is not completely watersoluble, as is the case for minerals such as gypsum $\left(\mathrm{CaSO}_{4}\right.$. $2 \mathrm{H}_{2} \mathrm{O}$ ) and pyrite $\left(\mathrm{FeS}_{2}\right)$; or (3) S consists of sulfur dioxide $\left(\mathrm{SO}_{2}\right)$ adsorbed onto soot or other particles (Watson 2002).

For coastal environments, non-sea-salt sulfate (i.e., nssSO ${ }_{4}{ }^{=}=\mathrm{SO}_{4}{ }^{=}-0.252 \mathrm{Na}^{+}$, based on $\mathrm{SO}_{4}{ }^{=} / \mathrm{Na}^{+}$molar ratio in sea water) can be estimated (Sciare et al. 2003). Summed $\mathrm{nssSO}_{4}{ }^{=}+\mathrm{NO}_{3}{ }^{-}+\mathrm{NH}_{4}{ }^{+}$has been applied to estimate contributions from inorganic ions (Cheung et al. 2011; Maenhaut et al. 2008; Mkoma et al. 2009; Querol et al. 2001; Terzi et al. 2010). Zhang et al. (2013) also included $\mathrm{K}^{+}$(a marker for biomass burning) as an additional inorganic ion.

Since $\mathrm{NH}_{4}{ }^{+}$is not quantified in the IMPROVE network, $\left(\mathrm{NH}_{4}\right)_{2} \mathrm{SO}_{4}$ is estimated by 4.125 S (Eq. 7). Due to variations between $\mathrm{SO}_{4}{ }^{=}$(by IC) and S (by XRF) ratios, Hand et al. (2011) used $1.375 \mathrm{SO}_{4}{ }^{=}$(Eq. 10). Both the original (Eq. 7) and the revised (Eq. 10) IMPROVE equations have been the foundation for reconstructing light extinction in the USA under the Regional Haze Rule (now termed the Clean Air Visibility Rule; Pitchford et al. 2007; USEPA 2001; Watson 2002).

## Organic mass/organic carbon (OM/OC)

To account for the unmeasured $\mathrm{H}, \mathrm{O}, \mathrm{N}$, and S in organic compounds, a conversion factor (or multiplier) is used to transform OC to OM, i.e.,
$\mathrm{OM}=f \times \mathrm{OC}$
The $f$ multipliers of 1.4 and 1.8 in Table 1 are not site or time specific. Depending on the extent of OM oxidation and secondary organic aerosol (SOA) formation, values for $f$ vary from 1.2 for fresh aerosol in urban areas (Chow et al. 2002a, b) to 2.6 for aged aerosol (Countess et al. 1980; Robinson et al. 2007, 2010; Roy et al. 2011; Turpin and Lim 2001). For example, benzo(a)pyrene $\left(\mathrm{C}_{20} \mathrm{H}_{12}\right)$, an indicator of incomplete fuel combustion found in engine exhaust (Lowenthal et al.
1994) has an $f=1.05$; whereas cellulose $\left(\mathrm{C}_{6} \mathrm{H}_{10} \mathrm{O}_{5}\right)_{n}$, a major component of unburned biological material, has an $f=2.25$ (Cerqueira et al. 2010; Puxbaum and Tenze-Kunit 2003; Sanchez-Ochoa et al. 2007).

The origins for $f=1.2-1.5$ result from circular reasoning with limited measurements. Macias et al. (1981, Eq. 1) used 1.5 based on an assumed organic composition proportional to $\mathrm{CH}_{2} \mathrm{O}_{0.25}$. Solomon et al. (1989, Eq. 2) used 1.4, citing Gray et al. (1986), who used both 1.2 and 1.4 for studies in California's South Coast Air Basin (SoCAB). The $f=1.2$ originated from Countess et al. (1980), based on the analysis of ambient carboxylic acid $\left(\mathrm{C}_{16}:(\mathrm{C}+\mathrm{H}+\mathrm{O}) / \mathrm{C}=1.3\right)$, polynuclear aromatic $((\mathrm{C}+\mathrm{H}) / \mathrm{C}=1.08)$, and aliphatic compounds $((\mathrm{C}+\mathrm{H}) /$ $\mathrm{C}=1.17$ ) (van Vaeck and van Cauwenberghe 1978) in Denver, CO. Ma et al. (2001) used 1.4 but cited Countess et al. (1980). As noted by Andrews et al. (2000) and Watson (2002), the 1.4 derives from Grosjean and Friedlander (1975), based on two Los Angeles total suspended particle (TSP) samples. The ratios of C to the sum of $\mathrm{C}, \mathrm{H}, \mathrm{N}$, and O was 0.66 for oxygenated organics and 0.86 for aliphatics; the inverses are 1.5 and 1.2 , respectively. Gray et al. (1986) referred to White and Roberts (1977), who used $f=1.4$ to construct a chemical light extinction budget based on Grosjean and Friedlander (1975). Harrison et al. (2003) used 1.4 for urban background sites in Birmingham, UK, and 1.3 for roadside sites in London, UK, citing Russell (2003).

Chow et al. (1994b; 1996, Eqs. 3 and 5, respectively) used 1.4, citing Solomon et al. (1989). Andrews et al. (2000, Eq. 6) also used 1.4, citing both White and Roberts (1977) and Grosjean and Friedlander (1975). Maenhaut et al. (2002, Eq. 8) used 1.4 for samples from Melpitz, Germany, citing Turpin et al. (2000). DeBell et al. (2006, Eq. 9) and Hand et al. (2011, Eq. 10) increased the $f$ from 1.4 to 1.8 for the revised IMPROVE equation (Eq. 10) based on non-urban aerosols (e.g., El-Zanan et al. 2005) and regression analysis by Malm and Hand (2007). The average regression coefficient was 1.7 for OC across all IMPROVE sites for years 19882003. This is similar to the $f=1.8$ used by Maenhaut et al. (2008) for samples from K-puszta, an EUSAAR station in Hungary, and by Mkoma et al. (2009) for a rural site in East Africa.

Several studies (e.g., Mkoma et al. 2009; Ni et al. 2013; Remoundaki et al. 2013; Terzi et al. 2010; Vecchi et al. 2008; Viana et al. 2007) used an $f$ multiplier of 1.6 , whereas $f=1.7$ was reported by others (e.g., Guinot et al. 2007; Putaud et al. 2000; Rees et al. 2004). The value of the $f$ multiplier under different situations remains the subject of current research. Biomass burning (especially during the smoldering phase) may require a higher $f$ multiplier as it contains many oxygenated organic compounds (Chen et al. 2010; Chow et al. 2007b), such as levoglucosan $\left(\mathrm{C}_{6} \mathrm{H}_{10} \mathrm{O}_{5}\right)$, a wood smoke marker (Simoneit et al. 1999) with the same chemical formula but a structure that differs from cellulose. For laboratory-
generated vegetative burning, Levin et al. (2010) reported $f=$ 1.55 , consistent with a finding of $f=\sim 1.5$ by Reid et al. (2005). Aiken et al. (2008) reported $f=1.55-1.7$ for primary biomass combustion emissions in Mexico City, lower than 1.9-2.1 found by Polidori et al. (2008) in Pittsburgh, PA, during winter and 2.2-2.6 suggested by Turpin and Lim (2001).

## Elemental carbon

The RM equation in Table 1 contain EC without any multiplier. Since OC and EC are operationally defined, absolute OC and EC concentrations and the ratio of OC to EC vary by carbon analysis method (Watson et al. 2005).

## Geological minerals

Geological "minerals" might better represent geological "material," as only assumed oxides of mineral elements (e.g., aluminum $(\mathrm{Al})$, silicon $(\mathrm{Si})$, calcium $(\mathrm{Ca}), \mathrm{K}$, titanium ( Ti ), and iron ( Fe ) ) are included to calculate geological mass. These elements have been measured by XRF, PIXE (e.g., Maenhaut et al. 2008), and, in some cases, instrumental neutron activation analysis (INAA; Maenhaut et al. 2001; Siddique and Waheed 2014) or ICP-mass spectrometry (ICP-MS). Most researchers use one of the five soil formulae listed in Table 1. Macias et al. (1981, Eq. 1) expressed minerals as the sum of the oxides of $\mathrm{Al}, \mathrm{Si}, \mathrm{Ca}, \mathrm{K}$, and Fe assuming the common oxide forms of $\mathrm{Al}_{2} \mathrm{O}_{3}, \mathrm{SiO}_{2}, \mathrm{CaO}, \mathrm{K}_{2} \mathrm{O}$, and $\mathrm{Fe}_{2} \mathrm{O}_{3}$, respectively (Pettijohn 1975). Several studies eliminated the 1.2 K (Eq. 2), except for Andrews et al. (2000, Eq. 6), Kleindienst et al. (2010), and Ni et al. (2013), which also included 1.67 Ti . A higher value $(1.95 \mathrm{Ca})$ was used by Terzi et al. (2010) and Remoundaki et al. (2013) to account for both CaO and $\mathrm{CaCO}_{3}$.

The IMPROVE "soil" formula (Malm et al. 1994, Eq. 4), applied in Eqs. 7-10, follows Macias et al. (1981, Eq. 1) with the following modifications: (1) iron oxides are equally divided between $\mathrm{Fe}_{2} \mathrm{O}_{3}$ and FeO ; (2) K in soil is estimated as 0.6 Fe , based on the composition of coarse particles (Cahill et al. 1986), because some $\mathrm{PM}_{2.5} \mathrm{~K}$ is emitted by biomass burning; and (3) titanium dioxide $\left(\mathrm{TiO}_{2}\right)$ is included. All of the initial element coefficients are then multiplied by 1.16 to account for unmeasured O , therefore:

$$
\begin{align*}
\text { Geological minerals }= & 2.2 \mathrm{Al}+2.49 \mathrm{Si}+1.63 \mathrm{Ca} \\
& +1.94 \mathrm{Ti}+2.42 \mathrm{Fe} \tag{C}
\end{align*}
$$

The IMPROVE "soil" formula (Eq. C) has been applied in several other studies (e.g., Chan et al. 1997; Pant et al. 2015). Rogula-Kozlowska et al. (2012) applied Eq. C but supplemented with 2.4 K based on the stoichiometric concentration of $\mathrm{K}_{2} \mathrm{O}$. Due to the uncertainties associated with Al by XRF
(McDade 2008), Simon et al. (2011, Eq. 11) eliminated Al and used 3.48 Si , based on the Al to Si ratio (0.46) in IMPROVE samples. Landis et al. (2001) also eliminated Al but used 3.79 Si , citing uncertainties in quantifying Al by energydispersive XRF. Hueglin et al. (2005) estimated Si in Eq. 1 as 3.41 Al (Mason 1966) and also included 1.66 Mg .

Single crustal elements have also been used to estimate the geological mineral contribution to PM mass. Si is the most abundant element ( $10-20 \%$ ) in the earth's crust besides O (Chow et al. 2003; Houck et al. 1989). Countess et al. (1980) used 3.5 Si , and Ma et al. (2001) used 4.807 Si (assuming 20.8 \% Si in soil; Scheff and Valiozis 1990). Using Al as a soil marker (Duce et al. 1980), Ho et al. (2006) used 13.77Al, Hsu et al. (2008) used 12.5Al, and Zhang et al. (2013) used 14.29Al. Besides 4.3Ca (from gypsum), Harrison et al. (2003) used the sum of 9 Fe for background and 3.5 Fe to 5.5 Fe for roadside sites, assuming $11-29 \%$ of Fe in fugitive dust. Putaud et al. (2000) summed non-sea-salt (nss) $\mathrm{K}^{+}$, $\mathrm{nssCa}^{++}$, and gravimetric analyses of water insoluble species as residues $\left(600{ }^{\circ} \mathrm{C}\right.$ for 8 h$)$ to estimate minerals. Since geological minerals are not a major component of $\mathrm{PM}_{2.5}$, variations in the assumptions regarding metal oxides or multipliers do not contribute to large variations in RM.

## Salt

Chow et al. (1996, Eq. 5) and Rogula-Kozlowska et al. (2012) used the sum of $\mathrm{Na}^{+}$and $\mathrm{Cl}^{-}$to track summertime transport of marine aerosol in California. Others (e.g., Maenhaut et al. 2002, Eq. 8, 2008; Mkoma et al. 2009; Viana et al. 2007) used $\mathrm{Cl}+1.4486 \mathrm{Na}$, based on the ratio of the sum of all elements (except Cl ) to Na in sea water (Riley and Chester 1971). Ohta and Okita (1994) used $3.27 \mathrm{Na}^{+}$, and others (e.g., Chan et al. 1997; Chow et al. 2007a; Ho et al. 2006; Siddique and Waheed 2014; Yan et al. 2012) used $2.54 \mathrm{Na}^{+}$, whereas Harrison et al. (2003) and Joseph et al. (2012) used $1.65 \mathrm{Cl}^{-}$ to represent salt content.
$\mathrm{PM}_{2.5} \mathrm{Na}$ is a conservative marker for salt (Lowenthal and Kumar 2006; White 2008), but it suffers self-absorption interferences by XRF (Dzubay and Nelson 1975; Formenti et al. 2010; Watson et al. 1999). Therefore, $1.8 \mathrm{Cl}^{-}$, based on the abundance of $\mathrm{Cl}^{-}$in sea water (White 2008), is used in the revised IMPROVE equation (Eq. 10). This approach is reasonable when: (1) there is no depletion of $\mathrm{Cl}^{-}$in salt aerosols from reaction with $\mathrm{H}_{2} \mathrm{SO}_{4}$ or $\mathrm{HNO}_{3}$; (2) hydrochloride acid $(\mathrm{HCl})$ is retained on the nylonmembrane filter, i.e., the preceding $\mathrm{Na}_{2} \mathrm{CO}_{3}$ denuder to remove $\mathrm{HNO}_{3}$ (Channel 2 of the IMPROVE sampler) does not remove any HCl ; and (3) HCl only originated from reactions of acids with salt particles. In any case, $1.8 \mathrm{Cl}^{-}$is a lower limit to estimate salt, assuming that $\mathrm{Cl}^{-}$is measured accurately by IC (Chow and Watson 1999). With advances in chromatographic techniques, the $\mathrm{Cl}^{-}$signal in the chromatogram no
longer overlaps the deionized distilled water dip and can be determined quantitatively. As Cl may be depleted under vacuum by XRF analysis, $\mathrm{Cl}^{-}$is a logical choice to estimate salt concentration. More water-soluble species in salt sources (e.g., sea water; Pytkowicz and Kester 1971) could be measured to reduce the uncertainty.

Depletion of $\mathrm{Cl}^{-}$occurs as $\mathrm{H}_{2} \mathrm{SO}_{4}$ or $\mathrm{HNO}_{3}$ reacts with sea salt, which exchanges $\mathrm{Cl}^{-}$for $\mathrm{SO}_{4}{ }^{-}$or $\mathrm{NO}_{3}{ }^{-}$, respectively. This will increase the sea salt mass as $\mathrm{SO}_{4}{ }^{-}(\mathrm{MW}=96)$ and $\mathrm{NO}_{3}{ }^{-}(\mathrm{MW}=62)$ are heavier than $\mathrm{Cl}^{-}(\mathrm{MW}=35)$ (Bardouki et al. 2003). For coastal samples from Canada, Yao and Zhang (2012) hypothesized $\mathrm{Cl}^{-}$replacement with di-nitrogen pentoxide $\left(\mathrm{N}_{2} \mathrm{O}_{5}\right)$, instead of $\mathrm{HNO}_{3}$, and that $\mathrm{SO}_{4}{ }^{=}$may be associated with $\mathrm{Cl}^{-}$depletion under acidic conditions. Sciare et al. (2003) defined sea salt (ss) as the sum of $\mathrm{Na}^{+}, \mathrm{Cl}^{-}, \mathrm{ssCa}^{++}$, $\mathrm{ssK}^{+}$, water-soluble magnesium $\left(\mathrm{Mg}^{++}\right)$, and $\mathrm{ssSO}_{4}{ }^{=}$; Zhang et al. (2013) substituted ssMg ${ }^{++}$for $\mathrm{Mg}^{++}$, whereas Hsu et al. (2010) used the sum of $\mathrm{Na}^{+}, \mathrm{Cl}^{-}$, and $\mathrm{Mg}^{++}$.

## Trace elements

Minor or trace elements, excluding geological species, can be added to the RM. Macias et al. (1981, Eq. 1) summed the trace elements in the form of $\mathrm{CuO}, \mathrm{ZnO}$, and PbO . Other studies (i.e., Eqs. 3, 5, 6, and 8) summed remaining elements by XRF, excluding $S$ and the geological elements, with the exception of Solomon et al. (1989, Eq. 2), who also included $\mathrm{Na}^{+}$and $\mathrm{Mg}^{++}$. Trace elements are more pronounced in coarse particles or at sampling sites near industrial facilities contaminated with toxic metals (Chow et al. 2002b) when some elements are not accounted for by the mineral formulae in Table 1. More complicated trace element oxides (TEOs; sum of oxides for vanadium (V), manganese (Mn), nickel (Ni), copper $(\mathrm{Cu})$, zinc $(\mathrm{Zn})$, arsenic $(\mathrm{As})$, lead $(\mathrm{Pb})$, selenium $(\mathrm{Se})$, strontium $(\mathrm{Sr})$, phosphorus ( P ), chromium ( Cr ), and K ) were used by Landis et al. (2001) and Zhang et al. (2013), but this component accounted for a small fraction ( $0.5-1.6 \%$ ) of $\mathrm{PM}_{2.5}$ mass. Therefore, summing the remaining elements may be sufficient.

## Others

The remaining mass may be attributed to measurement errors, improper multiplier(s), missing source(s), and/or particle-bound water (e.g., Frank 2006; Malm et al. 2011). This component could represent negative mass if RM overestimates gravimetric mass.

Non-crustal K was estimated as "Others" by Maenhaut et al. (2002), Simon et al. (2011), and Yan et al. (2012) based on either $\mathrm{K}-0.6 \mathrm{Fe}$ (Eq. 8 ) or $1.2 \times(\mathrm{K}-0.6 \mathrm{Fe}$ ) (Eq. 11), respectively. Organic acids (sum of acetate, fomite, methane sulfonate, pyruvate, and oxalate) were added to RM by Putaud et al. (2000).

## Applications of mass reconstruction equations to special studies

Supplemental Table S-1 summarizes previous studies which give rise to the 11 RM equations in Table 1. Only a subset of equations (i.e., Eqs. 1, 2, 3, 5, and 8) are applied in these shortterm special studies. Concerns over visibility degradation in the southwestern USA prompted the establishment of the Western Fine Particle Network that measured size segregated mass and elements during 1977-1981 (Flocchini et al. 1981). As part of the Denver Winter Haze Study and Project VIST TA, Countess et al. (1980) and Macias et al. (1981) started using RM to determine sources of haze-causing aerosol in uban Denver and non-urban Grand Canyon areas, respectively. Equation 1 was developed by Macias et al. (1981) for PM samples at two remote desert sites near Page, $\mathrm{AZ} . \mathrm{SO}_{4}{ }^{=}$was not completely neutralized based on the molar ratio of $\mathrm{NH}_{4}{ }^{+}$to $\mathrm{SO}_{4}{ }^{=}$(1.65 instead of 2.0). RM accounted for 75-93 \% of $\mathrm{PM}_{2.5}$ and 50-69 \% of $\mathrm{PM}_{15-2.5}$. Low $\mathrm{PM}_{15-2.5}$ RMs were attributed to the absence of carbon measurements.

For nine sites in the SoCAB (Solomon et al. 1989, Eq. 2), RM accounted for 86-94 \% (averaging $92 \%$ ) of annual $\mathrm{PM}_{10}$. Average measured $\mathrm{NH}_{4}{ }^{+}$concentrations were $17 \%$ lower than those estimated from $\left(\mathrm{NH}_{4}\right)_{2} \mathrm{SO}_{4}$ and $\mathrm{NH}_{4} \mathrm{NO}_{3}$, consistent with sulfates being slightly acidic or some of the nitrates being present as $\mathrm{NaNO}_{3}$. In another SoCAB study (Chow et al. 1994b, Eq. 3), RM accounted for $70-80 \%$ of $\mathrm{PM}_{2.5}$ and $80-85 \%$ of $\mathrm{PM}_{10}$ at nine sites during summer; unexplained mass was $5 \%$ lower at six sites during fall. Chow et al. (1994b) measured OC on tandem quartz-fiber filter packs (i.e., OC on quartz-fiber front filter as $\mathrm{OC}_{\mathrm{QF}}$, followed by a quartz-fiber backup filter as $\mathrm{OC}_{\mathrm{QBQ}}$ ) to estimate adsorption of volatile organic compounds (VOCs; Chow et al. 2006a; Subramanian et al. 2004; Turpin et al. 1994), but large variations were found in $\mathrm{OC}_{\mathrm{QBQ}}$. Average OC field blanks $\left(\mathrm{OC}_{\mathrm{FB}}\right)$ are commonly subtracted from $\mathrm{OC}_{\mathrm{QF}}$ (Chow et al. 2010; Watson et al. 2009). In such cases, RM uses blank subtracted values.

In central California (Chow et al. 1996, Eq. 5), RM accounted for $>90 \%$ of $\mathrm{PM}_{2.5}$ and $\mathrm{PM}_{10}$ at ten sites. At PM concentrations $<30 \mu \mathrm{~g} / \mathrm{m}^{3}$, the RM often exceeded the measured PM mass. This was in part attributed to $\mathrm{OC}_{\mathrm{QF}}$ that was not blank-corrected as $\mathrm{OC}_{\mathrm{QBQ}}>\mathrm{OC}_{\mathrm{QF}}$ in 168 out of 584 ( 29 \%) samples during ozone episodes. Uncorrected $\mathrm{OC}_{\mathrm{QF}}$ may be affected by a combination of positive (adsorption) and negative (volatilization) biases (Chow et al. 2010; Watson et al. 2009).

In Melpitz, Germany, RM accounted for $86 \%$ of $\mathrm{PM}_{2}$ and $116 \%$ of $\mathrm{PM}_{10-2}$ (Maenhaut et al. 2002, Eq. 8). OC was overestimated owing to adsorption of VOCs on quartz-fiber filters, as PM mass was $21 \%$ higher from the quartz-fiber than the collocated Nuclepore-membrane filters. Water associated with hygroscopic species was not accounted for by gravimetry.

Considering that the sum of inorganic ions accounted for $34 \%$ of the $\mathrm{PM}_{10-2}$, the associated water at $50 \%$ filter equilibration RH could have accounted for the overestimation of $\mathrm{PM}_{10-2}$ mass.

## Evaluation of mass reconstruction through analysis of large data sets

Several studies have evaluated RM in the IMPROVE network (see Eqs. 4, 6, 7, and 9-11 in Table 1), the largest and most consistently acquired chemical speciation data set in the world. Malm et al. (1994, Eq. 4) first applied the IMPROVE "soil" formula (Eq. C) to 36 sites, and RM accounted for 75$80 \%$ of $\mathrm{PM}_{2.5}$, consistent with an OM underestimation using $1.40 C$. Andrews et al. (2000, Eq. 6) reported low RM (58$67 \%$ of $\mathrm{PM}_{2.1}$ ) among four different types of samplers at Great Smoky Mountains National Park. Replacing $\mathrm{SO}_{4}{ }^{=}$with $\left(\mathrm{NH}_{4}\right)_{2} \mathrm{SO}_{4}$ increased RM by $6 \%$. The corresponding IMPROVE samples yielded RM as $83 \%$ of measured mass. Andrews et al. (2000) attributed the mass deficit to: (1) underestimation of geological minerals; (2) water retention on the Teflon-membrane filter deposit; and (3) underestimation of OM. However, the mineral contribution was too small to account for the deficit. The RM deficiency was reduced to $15-$ $23 \%$ after estimating water content; hygroscopic organics may result in additional particle-bound water (Saxena and Hildemann 1996). In addition to the low OM (1.4OC) estimate, subtracting $\mathrm{OC}_{\mathrm{QBQ}}$ over-corrected for organic vapor adsorption (Andrews et al. 2000).

Lowenthal and Kumar (2003) applied Eq. 7 to 59 IMPROVE sites from 1988 to 1999. RM averaged 88 \%, ranging 61-98 \% of $\mathrm{PM}_{2.5}$. Incorporating $\mathrm{Na}, \mathrm{Cl}$, and trace elements increased RM by $30 \%$ at the coastal Point Reyes site but had a small effect ( $\sim 3 \%$ ) at other sites. RM accounted for a larger fraction during winter than summer at 51 of 59 sites.

At $\sim 40 \%$ RH (i.e., IMPROVE filter equilibration conditions for gravimetric analysis), $\left(\mathrm{NH}_{4}\right)_{2} \mathrm{SO}_{4}$ and $\mathrm{NH}_{4} \mathrm{NO}_{3}$ (Eq. 7) absorb about 0.3 and 0.2 g of water/g of dry compound, respectively, assuming supersaturated $\left(\mathrm{NH}_{4}\right)_{2} \mathrm{SO}_{4}$ (Chan et al. 1992; Tang and Munkelwitz 1994). The addition of water would increase RM by $11 \%$ in summer and $12 \%$ in winter. A more hygroscopic form of $\mathrm{SO}_{4}{ }^{=}$or $\mathrm{H}_{2} \mathrm{SO}_{4}$ is needed during summer to account for the observed seasonal differences. However, this assumption cannot be tested without measured $\mathrm{NH}_{4}^{+}$or $\mathrm{H}^{+}$and would not explain the discrepancies when $\mathrm{SO}_{4}{ }^{=}$levels are low.

Using 2.1OC (Turpin and Lim 2001) increased RM by $14 \%$ in summer and $16 \%$ in winter (which overestimated measured $\mathrm{PM}_{2.5}$ ). A lower $f$ may be applicable in winter due to lower photochemical activity (i.e., less unmeasured O in OM ). For IMPROVE sites, monthly median $\mathrm{OC}_{\mathrm{QBQ}}$ (acquired at $\sim 5 \%$ of IMPROVE sites) was used for blank subtraction,
assuming VOCs adsorbed on both QF and QBQ became saturated (Watson et al. 2009). During 1990-1999, monthly median $\mathrm{OC}_{\mathrm{QBQ}}$ in summer were $0.155 \mu \mathrm{~g} / \mathrm{m}^{3}\left(\sim 3 \%\right.$ of $\left.\mathrm{PM}_{2.5}\right)$ higher than winter. Gaseous organic adsorption and seasonal effects in the OC multiplier, evaluated by Lowenthal and Kumar (2003), narrowed the seasonal RM deficit.
$\mathrm{PM}_{2.5}$ sampling methods in both the IMPROVE network and CSN result in artifacts for RM (DeBell et al. 2006, Eq. 9; Hand et al. 2011, Eq. 10). Malm et al. (2011) addressed the uncertainties in $\mathrm{PM}_{2.5}$ gravimetric and speciation measurements. $\mathrm{PM}_{2.5}$ ions (e.g., $\mathrm{Cl}^{-}, \mathrm{NO}_{3}{ }^{-}$, and $\mathrm{SO}_{4}{ }^{=}$) are measured on a nylon-membrane filter after a denuder to remove $\mathrm{HNO}_{3}$, which captures both non-volatilized and volatilized $\mathrm{NO}_{3}{ }^{-}$. Particulate $\mathrm{NH}_{4} \mathrm{NO}_{3}$ exists in equilibrium with gaseous $\mathrm{HNO}_{3}$ and ammonia $\left(\mathrm{NH}_{3}\right)$ (Hering and Cass 1999) depending on temperature, pressure, and RH. During sampling, $\mathrm{NO}_{3}{ }^{-}$ can evaporate as $\mathrm{HNO}_{3}$ due to the pressure drop across the filter and be re-absorbed as volatilized $\mathrm{NO}_{3}{ }^{-}$. However, volatilized $\mathrm{NO}_{3}{ }^{-}$is not part of the gravimetric mass, resulting in a negative artifact, which is most prominent during summer. The uptake of water by sulfates, nitrates, and organics during weighing (at $\sim 40 \% \mathrm{RH}$ ) counterbalances $\mathrm{NO}_{3}{ }^{-}$volatilization from the Teflon-membrane filter (Chow et al. 2005).

Blank subtraction is applied to $\mathrm{OC}_{\mathrm{QF}}$ for IMPROVE samples but not for CSN samples (Chow et al. 2010; Watson et al. 2009). For the period prior to $2007 / 2008$, carbon analysis followed the STN_TOT protocol in CSN (thermal/optical transmittance; Peterson and Richards 2002) and the IMPROVE_TOR protocol in IMPROVE (thermal/optical reflectance; Chow et al. 1993). Although total carbon (TC= OC +EC ) is comparable, STN_TOT reports higher OC and lower EC than the IMPROVE_A_TOR protocol (Chow et al. 2007c). Malm et al. (2011) used collocated measurements in order to relate CSN to IMPROVE carbon concentrations using ordinary least squares (OLS; unweighted) regression:

$$
\begin{align*}
\mathrm{PM}_{2.5}= & \mathrm{a} 1 \times 1.375 \mathrm{SO}_{4}^{=}+\mathrm{a} 2 \times 1.29 \mathrm{NO}_{3}^{-}+\mathrm{a} 3 \\
& \times \mathrm{OC}+\mathrm{a} 4 \times \text { Other } \tag{D}
\end{align*}
$$

where "Other" is the sum of EC, geological minerals, and salt (DeBell et al. 2006, Eq. 9). The two regression coefficients, al and a2, should equal unity if $\mathrm{SO}_{4}{ }^{=}$and $\mathrm{NO}_{3}{ }^{-}$ are present as $\left(\mathrm{NH}_{4}\right)_{2} \mathrm{SO}_{4}$ and $\mathrm{NH}_{4} \mathrm{NO}_{3}$, respectively. Equation D assumes no water uptake at weighing equilibration conditions and no $\mathrm{NH}_{4} \mathrm{NO}_{3}$ evaporation during sampling. a3 is the OC multiplier $(f)$ and $a 4=1$ if the weighting factors for geological minerals and salt are correct. For 168 IMPROVE sites during 1988-2008, average a1, a2, a3, and a4 values were $1.12,0.75,1.60$, and 1.06 , respectively. This implies a $12 \%$ contribution from water mass associated with $\left(\mathrm{NH}_{4}\right)_{2} \mathrm{SO}_{4}$ during weighing, a net loss of $25 \% \mathrm{NH}_{4} \mathrm{NO}_{3}$ during sampling, and an OC
multiplier of 1.6 with $6 \%$ more EC, geological minerals, and salt. A higher a3 for OC was found during summer $(f=1.7)$ than winter $(f=1.42)$, with a lower a2 during summer showing more $\mathrm{NH}_{4} \mathrm{NO}_{3}$ evaporation, as expected.

Different regression analyses were conducted for 708 IMPROVE samples at the urban Fresno Supersite (Watson et al. 2000) from 2004 to 2010, as shown in Table 2. Ordinary weighted least squares (OWLS) regression takes into account the measurement uncertainty of the independent variable (i.e., $\mathrm{PM}_{2.5}$ ), while effective variance (EV) regression takes into account the uncertainties of both the independent and dependent variables and should provide the most realistic results. Table 2 shows that average $\mathrm{PM}_{2.5} \mathrm{NO}_{3}{ }^{-}$(3.9士 $\left.4.9 \mu \mathrm{~g} / \mathrm{m}^{3}\right)$ and OC $\left(3.2 \pm 2.5 \mu \mathrm{~g} / \mathrm{m}^{3}\right)$ were the major components, with $1.33 \pm 1.26 \mu \mathrm{~g} / \mathrm{m}^{3}$ for $\mathrm{SO}_{4}{ }^{=}$. The average EC, geological minerals, and salt concentrations were $0.93,1.42$, and $0.27 \mu \mathrm{~g} / \mathrm{m}^{3}$, respectively. Without accounting for measurement uncertainties, a large OLS a1 of 1.61 for $\mathrm{SO}_{4}{ }^{=}$yields an increment $(1.61-1.00=0.61)$ five times higher than the 0.12 increment (i.e., regression coefficient of 1.12) from Malm et al. (2011)-this is inconsistent with 30-40 \% RH weighing conditions. The $8 \% \mathrm{NO}_{3}{ }^{-}$volatilization (i.e., a $2=$ 0.92 ) and an OC multiplier (a3) of 1.67 in Table 2 seem reasonable for typical ion concentrations. The geological mineral mass is overestimated $(a 4=0.59)$ by the IMPROVE "soil" formula (Eq. C).

Table 2 shows a $1 \leq 1(0.90-0.93)$ by OWLS and EV regression methods, implying $\mathrm{SO}_{4}{ }^{=}$is somewhat acidic in Fresno, which is probably not the case. $\mathrm{NH}_{3}$ is abundant in this agricultural region (e.g., Chow et al. 1998, 1999, 2006b). The a2 of $0.85-0.88$ is slightly lower than 0.92 in OLS, but it is consistent with $\mathrm{NO}_{3}{ }^{-}$volatilization. The a3 is $2-4 \%$ higher in OWLS (1.74) and EV (1.71) than OLS (1.67), but a4 (0.78) is $\sim 30 \%$ higher than OLS (0.59). The high a1 and low a4 in the OLS regression are not realistic. However, the regressions in all cases are statistically significant and the squared multiple correlations ( $r^{2}$ ) are 0.98 or 0.99 . Hand et al. (2011) and Malm et al. (2011) provide insights into sampling and analytical artifacts in long-term $\mathrm{PM}_{2.5}$ networks. However, the example illustrated for Fresno indicates limitations on generalizing from a single dataset and one statistical approach.

Simon et al. (2011, Eq. 11) employed data screening procedures to eliminate suspect or physically unreasonable concentrations. Data sets with correlation coefficients ( $r$ ) among explanatory variables greater than the absolute value of 0.85 were eliminated; whereas EC was removed due to correlations with OC. However, the effects of collinearity fell along a continuum, and selecting the level of correlation that can be tolerated is subjective. OLS regression was found to produce more bias in regression coefficients than OWLS or EV. Overall, the estimated median OC multipliers (a3) at the 50th percentile were lower for winter $(f=1.39)$ and fall $(f=$ 1.59 ) and comparable between spring $(f=1.83)$ and summer

Table 2 Regression coefficients for mass reconstruction (Eq. D) using various regression methods for Interagency Monitoring of Protected Visual Environments (IMPROVE) network samples collected at urban Fresno supersite in CA from 3 September 2004 to 31 December 2010

|  | OLS $^{\mathrm{b}}$ | OWLS $^{\mathrm{c}}$ | $\mathrm{EV}^{\mathrm{d}}$ | Average standard deviation $^{\mathrm{e}}$ | Minimum-maximum |
| :--- | :--- | :--- | :--- | :--- | :--- |
| Category ${ }^{\mathrm{a}}$ |  |  |  |  |  |
| Coefficient a1 $\left(\mathrm{SO}_{4}{ }^{-}\right)$ | 1.61 | 0.90 | 0.93 |  |  |
| Coefficient a2 $\left(\mathrm{NO}_{3}\right)$ | 0.92 | 0.85 | 0.88 |  |  |
| Coefficient a3 $(\mathrm{OC})$ | 1.67 | 1.74 | 1.71 |  | $0.079-25$ |
| Coefficient a4 (Other) | 0.59 | 0.78 | 0.78 |  | $0.138-38$ |
| Species |  |  |  |  | $0.54-24$ |
| Avg. $\mathrm{SO}_{4}{ }^{=}\left(\mu \mathrm{g} / \mathrm{m}^{3}\right)$ |  |  |  | $1.33 \pm 1.26$ | $0.9 \pm 4.9$ |
| Avg. $\mathrm{NO}_{3}{ }^{-}\left(\mu \mathrm{g} / \mathrm{m}^{3}\right)$ |  |  |  | $3.2 \pm 2.5$ | $0.53-26$ |
| Avg. OC $\left(\mu \mathrm{g} / \mathrm{m}^{3}\right)$ |  |  |  | $2.6 \pm 1.8$ |  |
| Avg. Other $\left(\mu / \mathrm{m}^{3}\right)$ |  |  |  |  |  |

${ }^{\mathrm{a}} \mathrm{http}: / / v i e w s . c i r a . c o l o s t a t e . e d u / w e b /$. To ensure data quality, only samples with species concentrations exceeding their uncertainties were included for regression analyses
${ }^{\mathrm{b}}$ Ordinary least squares-no weighting
${ }^{c}$ Ordinary weighted least squares-weighting depends on uncertainty of independent variable
${ }^{\mathrm{d}}$ Effective variance least squares-weighting depends on uncertainties of both the independent (i.e., $\mathrm{SO}_{4}{ }^{=}$, $\mathrm{NO}_{3}{ }^{-}$, OC, and Other) and dependent variables (Watson et al. 1984)
${ }^{\mathrm{e}}$ Average and calculated ranges are as follows (number of samples in all averages $=708$ )
$(f=1.81)$. The lowest median a3 $(f=1.29)$ was estimated at western sites during winter. Simon et al. (2011) concluded that more realistic and unbiased estimates of the OC multiplier were obtained using an "error in variables" regression and eliminating EC.

## Major factors influencing mass reconstruction

The key factors affecting RM are examined for: (1) the OC multiplier ( $f$ ); (2) sampling artifacts; (3) carbon analysis methods; (4) ammonium and nitrate volatilization; and (5) water uptake on Teflon-membrane filter deposits at different equilibration RHs.

## Measurement of the OC multiplier ( $f$ ) to estimate OM

Several aerosol extraction (a combination of water, organic solvents, and/or solid-phase extraction) and analytical methods (e.g., elemental analysis, Fourier-transform infrared (FTIR) spectroscopy, quadrupole-aerosol mass spectrometer (Q-AMS), etc.) have been applied to estimate the $f$ multiplier (i.e., the OM/OC ratio). As shown in Table 3, the results from these direct measurements are variable with $f=1.27-2.2$. Aircraft sampling with FTIR often yielded $f=\sim 1.3-1.4$ (Gilardoni et al. 2007; Maria et al. 2002; Russell 2003) with a higher $f$ multiplier (1.6-1.8) found by Takahama et al. (2011). Lower $f$ values ( $\sim 1.4$ ) were also found for personal and indoor sampling (Reff et al. 2007), for ship emissions ( $\sim 1.6$ by Gilardoni et al. 2007), and for urban areas ( $\sim 1.6$ by Day et al. 2010; Hawkins and Russell 2010; Ruthenburg et al. 2014). Higher $f$ values ( $\sim 2.0$ to 2.2 ) were typically found for
aged aerosols sampled in remote areas (e.g., Gilardoni et al. 2007; Takahama et al. 2011).

Weighing samples before and after solvent extraction (Japar et al. 1984) resulted in $f=1.4$ for diesel exhaust samples. In Pittsburgh, PA, Polidori et al. (2008) found that $f$ increased with increasing polarity with $f$ higher in summer (June and July) and winter (December and January) than in spring (March) and fall (October and November). High summer and winter values $(f=2.08-2.11)$ were attributed to biomass burning and residential wood combustion (RWC), respectively. Accounting for both solvent extractable and nonextractable material, the annual average $f$ was estimated to be $2.05 \pm 0.18$.

Based on AMS measurements and multivariate analyses (e.g., principle component analysis (PCA), regression analysis, and positive matrix factorization (PMF)), Zhang et al. (2005) and Aiken et al (2008) reported average $f=1.7-1.8$ with $f=1.2-1.3$ for hydrocarbon-like organic aerosols (HOAs) and $f=1.9-2.5$ for oxygenated OA (OOA). Aiken et al. (2008) also reported $f=1.6-1.7$ for biomass burning $\mathrm{OA}(\mathrm{BBOA})$. Based on a series of field studies, Philip et al. (2014) parameterize OM/OC from AMS measurements using $f=1.3$ for primary organic aerosol and $f=2.1$ for OOA. The OM/OC ratio is determined as $1.3\left(f_{\mathrm{POA}}\right)+2.1\left(1-f_{\mathrm{POA}}\right)$, where $f_{\mathrm{POA}}$ is the primary organic aerosol (POA) fraction of the AMS data, a proxy for combustion emissions (derived from ambient $\mathrm{NO}_{2}$ measurements). The $\mathrm{OM} / \mathrm{OC}$ ratios ranged from 1.7 to 2.1.

The $f$ multiplier is expected to be higher in rural than in urban areas due to oxidation and/or addition of SOA during transport. However, the results in Table 3 do not show systematic variations. Organic compounds vary by location, season, and time of day. Site-specific $f$ values need to be measured.
Table 3 Examples of OM/OC ratio determined in various studies at urban and remote locations

| Study | Particle size | Method/description ${ }^{\text {a }}$ | OM/OC (ratio) |  | Location | Season <br> (sampling period) |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  | Urban/sub-urban | Remote |  |  |
| Krivacsy et al. (2001) | $\mathrm{PM}_{2.5}$ | Used total organic carbon (TOC) analyzer to determine TC and WSOC <br> Used solid-phase extraction on a copolymer sorbent <br> Analyzed C, H, N, and S of OM by elemental analyzer with estimated O <br> Determined OM mass by gravimetry |  | 1.9 | High alpine research station, Jungfraujoch, Switzerland (in the Swiss alps; elevation 3580 m above sea level (asl)) | July to August 1998 |
| Kisset al. (2002) | $\mathrm{PM}_{1.5}$ | Used total organic carbon (TOC) analyzer to determine TC and WSOC <br> Used solid-phase extraction on a copolymer sorbent <br> Analyzed C, H, N, and S of OM by elemental analyzer with estimated O <br> Determined OM mass by gravimetry |  | $\begin{aligned} & 1.93 \pm 0.038 \text { (ranged } \\ & \text { from } 1.9 \text { to } 2.0 \text { ) } \end{aligned}$ | Rural K-puszta site with mixed forest, Hungary | January to September 2000 |
| Maria et al. $(2002,2003)$ | $\mathrm{PM}_{1}$ | Calculated OC and OM from FTIR and compare with thermal/optical OC <br> A 4-solvent rinsing procedure was used to separate functional groups into fractions of increasing hygroscopicity Used carbon monoxide (CO) vs. FTIR OC ratios to classify back trajectory clusters into 10 groups |  | $1.27 \pm 0.02$ to $1.49 \pm 0.28$ | Aircraft sampling over northeast Asia during the ACE-Asia Campaign | April and May 2001 |
| Russell (2003) | Submicron PM | FTIR, estimated OC from the number of carbon bonds and OM from the molecular mass of each functional group |  | $1.36 \pm 0.13$ (1.2-1.6) | Aircraft and ship-based sampling in the Caribbean and northeastern Asia ${ }^{\text {b }}$ | March to April and July 2001 |
| $\begin{aligned} & \text { El-Zanan et al. } \\ & (2005) \end{aligned}$ | $\mathrm{PM}_{2.5}$ | After sequential solvent extraction with dichloromethane, acetone, and water, the dried residue was weighed for OM and analyzed for OC by TOR OC. The water extracts were also analyzed for ions ( $\mathrm{Cl}^{-}, \mathrm{NO}_{3}{ }^{-}, \mathrm{SO}_{4}{ }^{=}, \mathrm{Na}^{+}, \mathrm{K}^{+}$, and $\mathrm{NH}_{4}{ }^{+}$) to subtract inorganic ion mass. |  | $\begin{aligned} & 1.92 \pm 0.40(1.58-2.58) \\ & 2.07 \text { by mass balance } \end{aligned}$ | U.S. National Parks (5 sites) ${ }^{\text {c }}$ | Annual (1988-2003) |
| Zhang et al. (2005) | $\mathrm{PM}_{1}$ | Inorganic ions (e.g., sulfates, nitrates, ammonium) and organics by AMS, followed by deconvolution of AMS mass spectrum to identify HOAs and OOAs. | Averaged 1.8 with 1.2 for HOA and 2.2 for OOA |  | Pittsburgh, PA | September 2002 |
| Yu et al. $(2005 \mathrm{a}, \mathrm{~b})$ | $\mathrm{PM}_{1.5}$ | Used water and solvent extraction followed by GC/MS analysis for WSOC and solvent-soluble OC |  | $\begin{aligned} & \text { Daytime } 2.0 \pm 0.3 \\ & \text { (1.4-2.5). Nighttime } \\ & 1.8 \pm 0.2 \text { (1.3-2.0) } \end{aligned}$ | Great Smoky Mountains National Park, TN | July to August 2005 |

Table 3 (continued)

| Study | Particle size | Method/description ${ }^{\text {a }}$ | OM/OC (ratio) |  | Location | Season <br> (sampling period) |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  | Urban/sub-urban | Remote |  |  |
| $\begin{aligned} & \text { Chen and Yu } \\ & (2007) \end{aligned}$ | $\mathrm{PM}_{2.5}$ | Determined OM by combining heating, gravimetric, and chemical constituents | $2.1 \pm 0.3$ |  | Sub-urban site at Clearwater, Hong Kong | October 2003 to June 2005 |
| Gilardoni et al. (2007) | $\mathrm{PM}_{1}$ | FTIR and comparison with IC-PILS for speciated carboxylic acids |  | $\begin{aligned} & 1.4 \pm 0.12 \\ & 1.6 \pm 0.4 \\ & 1.5 \pm 0.16 \\ & 1.6 \pm 0.14 \end{aligned}$ | Aircraft sampling of Ohio power plant emissions and regional background (12 flights) <br> Ship sampling in the Gulf of Maine <br> Appldore Island, ME <br> Chebogue Point, Nova Scotia, Canada | Summer 2004 |
| Reff et al. (2007) | $\mathrm{PM}_{2.5}$ | FTIR for aliphatic (CH) and carbonyl $(\mathrm{C}=\mathrm{O}$ and $[(\mathrm{C}=\mathrm{O})-\mathrm{OH}]$ by partial least squares (PLS) equation | Outdoor 1.7-2.6 <br> Indoor 1.3-1.7 (average $1.45 \pm 0.17$ ) <br> Personal 1.3-1.6 (average $1.4 \pm 0.11$ ) |  | 219 non-smoking homes in LA county, CA, Elizabeth, NJ, and Houston, TX | Summer 1999 to Spring 2001 |
| Aiken et al. (2008) | $\mathrm{PM}_{1}$ | Elemental analysis by AMS | Average 1.71 with $1.2-1.3$ for HOA, $1.85-2.45$ for OOA; and 1.6-1.7 for BBOA |  | Mexico City, Mexico ${ }^{\text {d }}$ | March 2006 |
| Cozic et al. (2008) | $\mathrm{PM}_{1}$ | OM by Q-AMS, normalized to OC by OC/EC TOT carbon analyzer |  | 1.84 | Jungfraujoch, Switzerland | February and March 2005 |
| Polidori et al. (2008) | $\mathrm{PM}_{2.5}$ | Used a combination of polarity-based extraction/fractionation method, determine OM by gravimetry and OC by thermal/optical analysis (polarity generally increases as organic oxygen content increases) | OM/OC ratios increase with increasing polarity: 1.37 for hexane, 1.66 for dichloromethane, 1.89 for ethyl acetate, 2.11 for acetone, and 2.25 for methanol extractions. Annual average ratios with $\left(\mathrm{OM} / \mathrm{OC}_{\text {total }}\right)$ and without ( $\mathrm{OM} / \mathrm{OC}_{\text {extract }}$ ) non-extractable material were $2.05 \pm 0.18$ and $1.91 \pm 0.24$, respectively |  | Pittsburgh, PA | $\begin{aligned} & \text { Annual (July } \\ & \text { 2001-July 2002) } \end{aligned}$ |
| Gilardoni et al. (2009) | $\mathrm{PM}_{1}$ | FTIR | 1.8 | 2.0 | Mexico City, Mexico <br> Altzomoni ( 60 km SE of <br> Mexico City, Mexico) | March 2006 |
| Day et al. (2010) | $\mathrm{PM}_{1}$ | FTIR and comparison of OM with Q-AMS | $1.66{ }^{\text {e }}$ |  | La Jolla, CA | February and March 2009 |
| Hawkins and Russell (2010) | $\mathrm{PM}_{1}$ | FTIR and comparison with Q-AMS | $1.55 \pm 0.17$ |  | La Jolla, CA | June to September 2008 |
| Takahama et al. (2011) | Submicron PM | FTIR and comparison with ACSM |  | $\begin{aligned} & 2.0-2.2 \\ & 1.6-1.8 \end{aligned}$ | Whistler Mountain, BC, Canada <br> Aircraft sampling over Mexico and the Gulf of Mexico coast (12 flights) | March and April 2009 <br> May to September 2009 |

Table 3 (continued)

| Study | Particle size | Method/description ${ }^{\text {a }}$ | OM/OC (ratio) |  | Location | Season <br> (sampling period) |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  | Urban/sub-urban | Remote |  |  |
| Ruthenburg <br> et al. (2014) | $\mathrm{PM}_{2.5}$ | FTIR |  | $\begin{aligned} & 1.83 \\ & 1.79 \end{aligned}$ | Mesa Verde, CO Olympia, WA | Annual (2011) at seven IMPROVE sites |
|  |  |  |  | 1.78 | Proctor Maple R.F., VT |  |
|  |  |  |  | 1.71 | St. Marks, FL |  |
|  |  |  |  | 1.73 | Trapper Creek, AK |  |
|  |  |  | 1.56 |  | Phoenix, AZ |  |

$P M$ particulate matter, $P M_{x}$ PM with diameter smaller than $x$ micrometers at $50 \%$ cut-point, $H O A$ hydrocarbon-like organic aerosol (represent gasoline and diesel engine exhaust emissions), $O O A$ oxygenated organic aerosol (contains more oxygen atoms than HOAs, resemble humic-like substance, and have been associated with secondary organic aerosol), BBOA biomass burning organic aerosol ${ }^{\text {a }}$ Measurement methods include aerosol chemical speciation monitor (ACSM), aerodyne aerosol mass spectrometer (AMS), quadrupole-aerosol mass spectrometer (Q-AMS), ion chromatography-particle into liquid sampler (IC-PILS), Fourier transform infrared analysis (FTIR), total carbon (TC), thermal/optical reflectance (TOR), thermal/optical transmittance (TOT), water-soluble organic carbon (WSOC), ${ }^{\mathrm{b}}$ During the aerosol characterization experiment (ACE)-Asia study in the western Pacific and the Passing Efficiency of the Low Turbulence Inlet Experiment (PELTI) study in the Caribbean ${ }^{\text {c }}$ Sites are Acadia, ME; Great Smoky Mountains, TN; Big Bend, TN; Indian Gardens, Grand Canyon, AZ; and Mount Rainier, WA
${ }^{\mathrm{d}}$ During the Megacity Initiative: Local and Global Research Observations (MILAGRO) field campaign, ground-based sampling was done at the T0 Supersite at the Instituto Mexicano del Petróleo (IMP) and aircraft data were collected aboard the NCAR C-130 aircraft over the city
${ }^{\mathrm{e}}$ Estimated based on the sum of carbon mass in the functional groups (Russel 2003)

## Sampling and analysis artifacts

Different approaches to sampling and analysis introduce uncertainties and systematic biases, including carbon sampling artifacts, thermally evolved carbon analysis methods, ammonium and nitrate volatilization, and particle-bound water on Teflon-membrane filters. The following subsections address these measurement uncertainties.

## Carbon sampling artifacts and carbon analysis by thermal evolution

As noted, $\mathrm{PM}_{2.5}$ sampling onto quartz-fiber filters is accompanied by positive (e.g., VOC adsorption) and negative (e.g., volatilization during and after sample collection) OC artifacts (Chow et al. 2010; Putaud et al. 2000; Turpin et al. 1994; Watson et al. 2009). Positive artifacts (e.g., estimated by field blank $\left(\mathrm{OC}_{\mathrm{FB}}\right)$, backup filter $\left(\mathrm{OC}_{\mathrm{QBQ}}\right)$, preceding organic denuders, and regression analyses) often exceed negative artifacts (ten Brink 2004; Watson et al. 2009). OC artifacts may bias EC values by as much as $\sim 50 \%$, especially by TOT, as light attenuation due to charring of the adsorbed organics within the filter has greater influence than charring of the surface particle deposit in TOR (Chen et al. 2004; Chow et al. 2004).

In a review of carbon comparison studies, Watson et al. (2005) found EC differed by up to a factor of seven (Schmidt et al. 2001) among 19 thermal evolution methods. Table 4 summarizes the three most widely applied thermal/ optical carbon analysis protocols (i.e., IMPROVE_A_TOR, STN_TOT, and EUSAAR_2_TOT). The US long-term networks (e.g., IMPROVE and CSN) apply the IMPROVE_A_TOR protocol (USEPA 2006). The European Union EUSAAR-2 protocol (Cavalli et al. 2010; Panteliadis et al. 2015) is similar to the IMPROVE_A temperature protocol with variations in selected temperature plateaus and shorter ( $70-180 \mathrm{~s}$ ) residence times. Higher OC values in TOT can result in lower OM/OC ratios and might bias RM.

## Ammonium and nitrate volatilization

Compared with total particulate $\mathrm{NO}_{3}{ }^{-}$, Chow et al. (2005) found volatilized $\mathrm{NO}_{3}{ }^{-}$losses ranging from $<10 \%$ during cold months to $>80 \%$ during warm months (from the front quartz-fiber filter) for urban and non-urban sites. The amount of $\mathrm{NH}_{4} \mathrm{NO}_{3}$ volatilization from the Teflon-membrane filter can be estimated by a thermodynamic model (Hering and Cass 1999; Mozurkewich 1993), but this is only possible when gaseous $\mathrm{HNO}_{3}$ and $\mathrm{NH}_{3}$, total particle $\mathrm{NO}_{3}{ }^{-}$, temperature, and RH are known (Chow et al. 2005; Stelson et al.

Table 4 Comparison of common thermal/optical protocols: IMPROVE_A, STN, and EUSAAR_2

| Carbon fraction | Atmosphere ${ }^{\text {d }}$ | IMPROVE_A_TOR ${ }^{\text {a }}$ |  | STN_TOT ${ }^{\text {b }}$ |  | EUSAAR_2_TOT ${ }^{\text {c }}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | Temp. $\left({ }^{\circ} \mathrm{C}\right)$ | Residence time (s) ${ }^{\text {e }}$ | Temp. $\left({ }^{\circ} \mathrm{C}\right)$ | Residence time (s) | Temp. $\left({ }^{\circ} \mathrm{C}\right)$ | Residence time (s) |
| OC1 | Inert | 140 | 80-580 | 310 | 60 | 200 | 120 |
| OC2 | Inert | 280 | 80-580 | 480 | 60 | 300 | 150 |
| OC3 | Inert | 480 | 80-580 | 615 | 60 | 450 | 180 |
| OC4 | Inert | 580 | 80-580 | 900 | 90 | 650 | 180 |
|  | Oven cooling ${ }^{\text {f }}$ | NA | NA | NA | 30 | NA | 30 |
| EC1 | Oxidizing | 580 | 80-580 | 600 | 45 | 500 | 120 |
| EC2 | Oxidizing | 740 | 80-580 | 675 | 45 | 550 | 120 |
| EC3 | Oxidizing | 840 | 80-580 | 750 | 45 | 700 | 70 |
| EC4 | Oxidizing | NA | NA | 825 | 45 | 850 | 80 |
| EC5 | Oxidizing | NA | NA | 920 | 120 | NA | NA |

[^1]1979). Volatilized $\mathrm{NO}_{3}{ }^{-}$is not considered in the USEPA's (1997) PM $_{2.5}$ Federal Reference Method (FRM) for compliance monitoring. However, for evaluating light extinction or health effects, it is necessary to account for $\mathrm{NO}_{3}{ }^{-}$volatilization during sampling.

Yu et al. (2005c) noted that gaseous $\mathrm{HNO}_{3}$ interacts with nylon filters and retains $\mathrm{HNO}_{3}$ that volatilized from $\mathrm{NH}_{4} \mathrm{NO}_{3}$. However, losses of $\mathrm{NH}_{4}^{+}$(i.e., gaseous $\mathrm{NH}_{3}$ ) from nylon filters after a $\mathrm{Na}_{2} \mathrm{CO}_{3}$ denuder for the selected six IMPROVE sites ranged from 10 to $28 \%$ (monthly average) during summer. Yu et al (2006) found that, for individual samples, the $\mathrm{NH}_{4}^{+}$losses spread between 1 and $65 \% . \mathrm{NH}_{4}^{+}$ volatilization is enhanced by increasing temperature and RH , and with the fraction of total $\mathrm{NH}_{x}$ (sum of $\mathrm{NH}_{3}$ and $\mathrm{NH}_{4}{ }^{+}$) present as $\mathrm{NH}_{3}$ (Chen et al. 2014).

Losses of $\mathrm{NH}_{4}{ }^{+}$after sampling need to be investigated. Non-volatilized $\mathrm{NH}_{4}{ }^{+}$can be acquired on Teflon-membrane or quartz-fiber filters without preceding denuders. Ideally, both non-volatilized and volatilized $\mathrm{NH}_{4}{ }^{+}$should be acquired on a parallel channel, using a preceding citric acid denuder to remove $\mathrm{NH}_{3}$, followed by a quartz-fiber filter with a citric acid impregnated cellulose-fiber backup filter (e.g., Chow 1995; Chow et al. 1998).

## Particle-bound water on the Teflon-membrane filter

The influence of particle-bound and particle-adsorbed water on PM has been explored in several studies (e.g., Frank 2006; Malm et al. 2011; Malm and Day 2001; Perrino et al. 2013; Rees et al. 2004; Temesi et al. 2001). Water associated with PM was estimated by Harrison et al. (2003) by applying 1.29 to the sum of $\left(\mathrm{NH}_{4}\right)_{2} \mathrm{SO}_{4}$ and $\mathrm{NH}_{4} \mathrm{NO}_{3}$ concentrations and in others (e.g., Murillo et al. 2012; Siddique and Waheed 2014) by multiplying 0.32 to the sum of $\mathrm{NH}_{4}^{+}$and $\mathrm{SO}_{4}{ }^{=}$.

Hygroscopic salts (e.g., $\left(\mathrm{NH}_{4}\right)_{2} \mathrm{SO}_{4}, \mathrm{NH}_{4} \mathrm{NO}_{3}$, and NaCl ) absorb water as a function of RH (Chan et al. 1992; Tang and Munkelwitz 1994). At the deliquescence RH (DRH; ~80 \%), dry $\left(\mathrm{NH}_{4}\right)_{2} \mathrm{SO}_{4}$ particles start to absorb water and the amount rises with increasing RH . The hydrated particle retains water below the DRH until it re-crystallizes at the efflorescence RH (ERH) of $\sim 30-40 \%$, the hysteresis effect (e.g., Han and Martin 1999). Acidic $\mathrm{H}_{2} \mathrm{SO}_{4}$ absorbs and desorbs water continuously with changes in RH , without exhibiting deliquescence or efflorescence. The DRH and ERH of pure $\mathrm{NH}_{4} \mathrm{NO}_{3}$ are 62 and $32 \%$, respectively. Tang et al. (1997) found that sea salt begins to deliquesce at low RH in the presence of $\mathrm{Mg}^{++}$ and $\mathrm{Ca}^{++}$, but that most of the material deliquesces between 70 and $74 \%$, the DRH of NaCl . Day et al. (2000) and Malm et al. (2003) found little evidence for deliquescence or efflorescence in ambient aerosols at the IMPROVE sites.

At RH $>80 \%$, water may constitute more than $50 \%$ of $\mathrm{PM}_{2.5}$ mass (Chen et al. 2003; McMurry 2000). If particles were hydrated during sample collection, the sample filters
may retain water for weighing (equilibration of RH 3040 \%; USEPA 1997), unless they were dried below ERH between sample collection and weighing. Based on theoretical thermaldynamic modeling of salt mixtures, Pilinis et al. (1989) found that aerosol may contain up to $30 \%$ water for $\mathrm{RH}=\sim 20-50 \%$. McInnes et al. (1996) observed that water associated with sea salt particles contributed $26 \%$ of the mass at $40 \%$ RH. Speer et al. (2003) measured changes in $\mathrm{PM}_{2.5}$ mass as a function of RH in a humidity-controlled chamber (increased from 4 to $94 \%$ in $5 \%$ increments and then decreased similarly to $12 \%$ ) using a beta attenuation monitor (BAM) on Teflon-membrane filters. For samples collected at Research Triangle Park, NC, Speer et al (2003) observed hysteresis in most cases.

The water-soluble organic carbon (WSOC) portion of OM can enhance or inhibit water absorption by inorganic salts (Facchini et al. 1999; Mircea et al. 2002; Saxena et al. 1995; Saxena and Hildemann 1997). At Great Smoky Mountains National Park during the summer of 2006, Lowenthal et al. (2009) reported the water uptake as $5 \% \mathrm{PM}_{2.5}$ WSOC at $45 \%$ RH and $33 \%$ at $80 \%$ RH. Based on thermodynamic modeling (Chen et al. 2003; Clegg et al. 1998; Tang and Munkelwitz 1994), $\sim 80 \%$ of the measured water can be associated with $\mathrm{SO}_{4}{ }^{=}$and $\mathrm{NO}_{3}{ }^{-}$. Speer et al. (2003) attributed the $\sim 20 \%$ "residual water" to organics; the amount of water per unit mass of organics was $\sim 50 \%$ of that associated with $\left(\mathrm{NH}_{4}\right)_{2} \mathrm{SO}_{4}$ (per unit mass) at 60-80 \% RH. Conversely, Engelhart et al. (2011) determined that water growth of aerosols in Crete, Greece, was consistent with thermodynamic modeling based on inorganic constituents alone. Water mass on the Teflon-membrane filter can be determined by weighing the filter under equilibrium conditions ( $30-40 \% \mathrm{RH}$ ), drying the filter completely in a desiccator, and then rapidly re-weighing.

Recent advances in thermodynamic models have incorporated some organic compounds to estimate the associated water activity (Clegg et al. 2001, 2008; Clegg and Seinfeld 2006). However, most of the organic species have not been identified, and their thermodynamic properties are uncertain (Saxena and Hildemann 1996; Sempéré and Kawamura 1994). While thermodynamic modeling may provide insights on particle-bound water, the most straightforward means is through direct gravimetric analysis over a range of RHs.

## Summary and conclusions

As $\mathrm{PM}_{2.5}$ mass concentration has been regulated in NAAQS to protect public health and welfare, it is important to understand the particle composition in order to: (1) examine the causes of elevated concentrations; (2) attribute ambient concentrations to air pollution sources; (3) relate toxic components to public health and ecosystems; and (4) associate particle scattering and absorption properties with visibility
impairment, the Earth's radiation balance, and climate change. With advances in sampling and analysis techniques, the demand for characterizing the chemical, physical, and optical properties of atmospheric aerosol is increasing worldwide. The validity of mass and chemical measurements needs to be examined prior to or in conjunction with air-quality modeling to develop pollution control strategies and reduce human exposure to hazardous pollutants.

Mass reconstruction is a simple and useful tool for validating the consistencies and addressing uncertainties among mass and chemical measurements. The reconstruction of measured mass was started by Countess et al. (1980) and Macias et al. (1981) as PM chemical speciation for ions, carbon, and elements became available. The 11 reconstructed mass (RM) equations examined here provide history and insight into the evolution of RM. Major PM components include: (1) major inorganic ions (e.g., $\mathrm{SO}_{4}{ }^{=}, \mathrm{NO}_{3}{ }^{-}$, and $\mathrm{NH}_{4}{ }^{+}$); (2) OC and its multiplier $(f)$ to estimate $\mathrm{OM},(3) \mathrm{EC}$, (4) geological minerals (based on estimated metal oxides), (5) salt, (6) trace elements (excluding double counting of ions and crustal components in geological minerals), and (7) others (as remaining mass including particle-bound water). The remaining mass can be negative when RM overestimates the gravimetric mass.

For inorganic ions, either the sum of $\left(\mathrm{NH}_{4}\right)_{2} \mathrm{SO}_{4}$ and $\mathrm{NH}_{4} \mathrm{NO}_{3}$ (calculated by their respective stoichiometric multiplier as $1.375 \mathrm{SO}_{4}$ and $1.29 \mathrm{NO}_{3}{ }^{-}$) or the sum of $\mathrm{SO}_{4}{ }^{=}, \mathrm{NO}_{3}{ }^{-}$, and $\mathrm{NH}_{4}^{+}$is most commonly applied. For coastal environments, variations account for non-sea salt $\mathrm{SO}_{4}{ }^{=}\left(\mathrm{nssSO}_{4}\right)$, $\mathrm{CaSO}_{4}, \mathrm{Na}\left(\mathrm{NO}_{3}\right)_{2}$, and $\mathrm{NH}_{4} \mathrm{Cl}$. The assumption that $\mathrm{SO}_{4}{ }^{=}$is completely neutralized as $\left(\mathrm{NH}_{4}\right)_{2} \mathrm{SO}_{4}$ overestimates $\mathrm{SO}_{4}{ }^{=}$ mass when non-neutralized (acidic) sulfates are present. Summing of $\mathrm{SO}_{4}{ }^{-}, \mathrm{NO}_{3}{ }^{-}$, and $\mathrm{NH}_{4}^{+}$will not account for H associated with partially neutralized $\mathrm{SO}_{4}{ }^{=}$(e.g., $\mathrm{NH}_{4} \mathrm{HSO}_{4}$ ). Ion balances should be applied to ensure the molar equivalence between the measured anions and cations and to justify the degree of neutralization. $\mathrm{NH}_{4}{ }^{+}$measurements should be included in routine monitoring networks and special studies, preferably on a quartz-fiber filter or with preceding citric acid denuder and citric acid impregnated backup filter that can capture both non-volatilized and volatilized $\mathrm{NH}_{4}{ }^{+}$, respectively.
$\mathrm{PM}_{2.5} \mathrm{NH}_{4} \mathrm{NO}_{3}$ may evaporate from Teflon-membrane and quartz-fiber filters during warm, non-winter periods, but its contribution to RM is expected to be highest during winter when low temperatures and high RH favor the particle phase. Ammonium and nitrate volatilization during sampling does not affect mass reconstruction. However, positive bias in RM is expected for CSN and the IMPROVE network where total particulate $\mathrm{NO}_{3}{ }^{-}$measured on a nylon-membrane filter includes volatilized $\mathrm{NO}_{3}{ }^{-}$that is not part of the gravimetric mass on Teflon-membrane filters. To account for this bias, gaseous $\mathrm{HNO}_{3}$ can be removed with a preceding denuder and volatilized $\mathrm{NO}_{3}{ }^{-}$can be collected on a nylon filter or salt-impregnated filter behind one of the filters.

The OC multiplier $(f)$ ranges from 1.2 to 2.6 , depending on the extent of OM oxidation. The most commonly applied multipliers are 1.4 for urban and 1.8 for non-urban sites. The $f$ multiplier is expected to be highest in non-urban areas due to oxidation and/or addition of secondary organic compounds during transport. Organic compounds vary by location, season, and time of day. Site-specific $f$ values need to be measured. Future studies should focus on direct measurement of the OM/OC ratio at urban and remote locations with sampling periods covering warm and cold seasons.

Organic sampling artifacts need to be quantified using preceding carbon denuders, field blanks, and/or backup filters. Subtracting averaged field blanks from OC is the most convenient way to remove passive organic adsorption. Different thermal/optical carbon analysis protocols may result in additional uncertainties. The analysis protocol used in the CSN prior to 2007/2008 overestimated OC and consistently led to high-biased RM. Consistent carbon analysis protocol should be applied nationwide and internationally. Among the seven $\mathrm{PM}_{2.5}$ components, EC is the most straightforward as a single component without any multiplier. However, the abundance of EC is method dependent as OC and EC are operationally defined.

For geological minerals containing $\mathrm{Al}, \mathrm{Si}, \mathrm{Ca}$, and Fe , compounds are assumed to be $\mathrm{Al}_{2} \mathrm{O}_{3}, \mathrm{SiO}_{2}, \mathrm{CaO}$, and $\mathrm{Fe}_{2} \mathrm{O}_{3}$, respectively, with variations including or excluding FeO , $\mathrm{K}_{2} \mathrm{O}$, and $\mathrm{TiO}_{2}$. The IMPROVE "soil" formula applies a factor of 1.16 to account for unmeasured compounds and tends to overestimate geological minerals. This can be examined empirically by measuring the chemical composition of local geological samples after subtracting OM and ionic concentrations. Since geological minerals are not a major component of $\mathrm{PM}_{2.5}$, variations in the assumptions regarding metal oxides or multipliers do not contribute to large variations in RM, but they are important for $\mathrm{PM}_{10-2.5}$ and $\mathrm{PM}_{10}$ RMs. Trace elements as a sum of remaining elements by XRF (excluding S and geological elements) or as complicated trace element oxides only account for a small fraction (0.5-1.6 \%) of $\mathrm{PM}_{2.5}$ mass.

There is no standard method to estimate salt. It is mainly based on: (1) the sum of elements (excluding $\mathrm{Cl}^{(1)}$ and $\mathrm{Cl}^{-}$) to Na or $\mathrm{Na}^{+}$ratio in seawater; (2) straight sum of $\mathrm{Na}^{+}$and $\mathrm{Cl}^{-}$; or (3) estimated as $1.8 \mathrm{Cl}^{-}$as in the revised IMPROVE equation. Depletion of $\mathrm{Cl}^{-}$by reaction with sea salt particles with a strong acid (e.g., $\mathrm{H}_{2} \mathrm{SO}_{4}$ and $\mathrm{HNO}_{3}$ ) is difficult to estimate without additional measurement. However, the salt component should be accounted for at sampling sites near coastal areas, salt lakes, or desert playas, as it may comprise up to $20-30 \%$ of $\mathrm{PM}_{2.5}$ mass.

Potential bias in measured mass due to the absorption of water by hygroscopic species on the Teflon-membrane filter from which $\mathrm{PM}_{2.5}$ mass is determined can be estimated theoretically from concentrations of water-soluble species
measured on nylon-membrane or quartz-fiber filters using a thermodynamic model.

In conclusion, the principal sources of uncertainty are: (1) ammonium and nitrate volatilization and inconsistency between total particulate $\mathrm{NO}_{3}{ }^{-}$on nylon-membrane filters and non-volatilized $\mathrm{NO}_{3}{ }^{-}$on Teflon-membrane filters; (2) unknown OC multipliers $(f)$ to estimate OM; (3) inaccurately accounting for OC sampling artifacts; (4) differences among OC and EC analytical protocols; (5) inaccurate conversion of crustal element concentrations to geological minerals; (6) various degrees of $\mathrm{Cl}^{-}$depletion at coastal locations; and (7) particle-bound water on the Teflon-membrane filter deposits. Reasonably accurate $\mathrm{PM}_{2.5}$ mass reconstruction can be accomplished by minimizing sampling artifacts and conducting comprehensive chemical analyses to ensure mass closure.

Acknowledgments This work was jointly sponsored by the National Park Service (NPS) IMPROVE Contract No. P11PC00036, the National Science Foundation (CHE-1214163), and the San Joaquin Valley Air Pollution Control District (Contract No. 11-10 PM). The authors wish to thank Miss Iris Saltus for her help in assembling and editing the manuscript.

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[^1]:    NA not applicable
    ${ }^{\text {a }}$ The non-urban Interagency Monitoring of Protected Visual Environments (IMPROVE) network and urban Chemical Speciation Network (CSN), measures and reports both thermal/optical reflectance (TOR), and thermal/optical transmittance (TOT), following the IMPROVE_A_TOR protocol (Chow et al. 2007b, 2011)
    ${ }^{\mathrm{b}}$ Speciation Trends Network (STN), also called NIOSH-like protocol (Peterson and Richards 2002)
    ${ }^{\text {c }}$ European Supersites for Atmospheric Aerosol Research, EUSAAR_2, protocol (Cavalli et al. 2010)
    ${ }^{d}$ Inert atmosphere ultra-high purity (UHP) helium (He) for OC analysis. Oxidizing atmosphere $98 \% \mathrm{He} / 2 \%$ oxygen $\left(\mathrm{O}_{2}\right)$ for all protocols
    ${ }^{\mathrm{e}}$ Ramping to the next temperature or atmosphere begins when the flame ionization detector (FID) response returns to either baseline or a constant value; these times represent minimum and maximum times to be spent in any segment, respectively
    ${ }^{\mathrm{f}}$ At the end of OC analysis, a cooling blower turns on for $\sim 30 \mathrm{~s}$. EC analysis starts $\sim 10 \mathrm{~s}$ after the introduction of $98 \% \mathrm{He} / 2 \% \mathrm{O}_{2}$

