STANDARD OPERATING PROCEDURES

Reconstructing Fine Particulate Matter Mass from Measured Chemical Components

Dalhousie University
Halifax, Nova Scotia, Canada

Prepared by: Crystal Weagle, Xuan Liu
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1.0 SCOPE AND APPLICATION

This SOP describes the method used by SPARTAN to reconstruct the fine particulate matter ($PM_{2.5}$) mass measured on sampled PTFE® filters. Chemical constituents measured through ion chromatography, sulfate (SO_4^{2-}), nitrate (NO_3^-), ammonium (NH_4^+), and sodium (Na^+), are used along with measured trace element concentrations to infer major constituent such as ammonium nitrate and crustal material (CM). Equivalent black carbon (EBC) is determined as described in SPARTAN SOP EBC SSR Revision 2.0. The particle-bound water in the total $PM_{2.5}$ is estimated based on the chemical constituent concentrations using κ-Kohler theory and described herein. The inferred residual matter (RM), taken as the difference between the total $PM_{2.5}$ and the sum of measured components, is used as a surrogate for organic matter that is not yet directly measured by SPARTAN.

REVISION HISTORY			
Revision No.	Change Description	Date	Authorization
2.0	General reorganization and clarification; update to CM calculation and RM mass growth factors	August 20, 2018	Crystal Weagle
3.0	Transition of trace metals calculated from ICP-MS to XRF measurements; inclusion of sea salt concentration threshold and update to TEO calculation	April 15, 2020	Brenna Walsh Crystal Weagle
3.1	Update of elements used in CM and TEO calculations	June 22, 2022	Xuan Liu

2.0 RECONSTRUCTING WATER-SOLUBLE CONSTITUENTS

2.1 Dry inorganic species from water-soluble ions

As described in SPARTAN SOP Anion/Cation Revision 3.0, there are seven anions and six cations quantified by ion chromatography from SPARTAN filters. The determined amount of individual water-soluble ions is used to infer the concentrations of ammonium nitrate, sea salt, sodium sulfate, and ammoniated sulfate contained in the measured $PM_{2.5}$ mass. References for each method are provided in Table 1 in section 5.0. Here, the term “dry” refers to components with no associated water (0 % relative humidity). The term “wet” refers to components with associated water at the humidity of weighing conditions, assumed to be 35 % relative humidity.

To account for the sodium associated with crustal material, 10 % of measured aluminum is taken to be associated with sodium and removed from the total sodium concentration. To account

for the associated Cl, the dry sea salt concentration is represented as $2.54[Na^+]_{SS}$, based on the 1:1 molar ratio of Na^+:Cl^-. Due to the possibility of Na contamination on PTFE® filters, a threshold of 2 µg/m^3 for wet sea salt concentration has been implemented. Calculated wet sea salt concentrations exceeding this concentration are set to the site average sea salt concentration, excluding values above the threshold. The corresponding dry sea salt and Na concentrations are subsequently adjusted to reflect this change.

Sodium sulfate is calculated as a fraction of the measured sodium, $0.18[Na^+]_{SS}$. To account for sulfate in the form of sodium sulfate, 12 % of the measured sodium concentration is removed from the total measured sulfate. Nonetheless, sodium sulfate is found to contribute negligibly to the total $PM_{2.5}$ mass (< 0.1 %) at all sampling sites and is not included in the reconstructed mass.

All measured nitrate is treated as neutralized by ammonium to form ammonium nitrate when in the aerosol form. The corresponding mass of dry ammonium nitrate is defined as $1.29[NO_3^-]$ based on the 1:1 molar ratio of NH_4^+:NO_3^-. Ammonium that is not in the form of ammonium nitrate, and sulfate that is not in the form of sodium sulfate are assumed to be a mixture of ammonium bisulfate and ammonium sulfate. Thus, this mixture is referred to as ammoniated sulfate (ASO_4, dry). The sum of dry ammonium nitrate and dry ammoniated sulfate is equal to the sum of measured sulfate, nitrate, and ammonium.

2.2 Accounting for water associated with inorganic species

Under the weighing conditions used, where the relative humidity is between 34 and 36 %, there is water associated with the inorganic species. This particle-bound water (PBW) contributes to the total $PM_{2.5}$ mass and must be accounted for. The PBW is estimated based on the mass of the chemical component *X*, as:

$$PBW_X = [X]\kappa_{m,X}\frac{RH}{100 - RH} \quad (1)$$

where [X] is the concentration of the chemical component, $\kappa_{m,X}$ is the mass growth factor for the chemical component, and RH is the relative humidity of the weighing conditions. Since the RH of the clean room during weighing is 34 and 36 %, an RH of 35 % is used for PBW calculations. The estimated mass growth factors for the three relevant inorganic species are estimated based on the volume growth factors and densities of the species:

$\kappa_{m,NH4NO3} = \kappa_{v,NH4NO3}/\rho_{NH4NO3} = 0.67/1.72 = 0.39$
$\kappa_{m,ASO4} = \kappa_{v,ASO4}/\rho_{ASO4} = 0.53/1.77 = 0.30$
$\kappa_{m,NaCl} = \kappa_{v,NaCl}/\rho_{NaCl} = 1.12/2.17 = 0.52$

To obtain the concentration of a component at 35 % RH:

$$[X]_{35\%} = [X]_{dry}\left(1 + \kappa_{m,X}\frac{RH}{100 - RH}\right) \quad (2)$$

The total PBW associated with inorganic components, PBW_{IN_mass}, can be calculated as the sum of the difference between the $[X]_{35\%}$ and $[X]_{dry}$ terms of all inorganic components. The EBC determined as described in SPARTAN SOP EBC SSR Revision 2.0 is assumed to be hydrophobic and have no associated water.

3.0 ADDITIONAL CONSTITUENTS FROM TRACE ELEMENTS

As described in SPARTAN SOP Trace Metals XRF Revision 2.1, there are over 20 elements that are quantified by X-ray fluorescence (XRF). The concentrations of elements determined through this method are used to estimate contribution of crustal material and trace element oxides to total $PM_{2.5}$. The water uptake of crustal material and trace element oxides is treated as negligible.

Concentrations of elements Al, Si, Ca, Fe, and Ti are used to estimate the crustal material component of $PM_{2.5}$ mass. Crustal material (CM) consists of resuspended road dust, desert dust, soil, and sand. The global dust equation developed by Liu et al. (2022) is employed to represent the CM concentration as follows:

$$[\mathrm{CM}] = \{\, 1.89[\mathrm{Al}] \times (1 + \mathrm{MAL}) + 2.14[\mathrm{Si}] + 1.40[\mathrm{Ca}] + 1.36[\mathrm{Fe}] + 1.67[\mathrm{Ti}] \,\} \times \mathrm{CF} \quad (3)$$

The coefficients MAL and CF depend on the region where each site is located. For sites in the Middle East, MAL = 0.72, CF = 1.14; For sites in Sahel, MAL = 0.27, CF = 1.05; For sites in East Asia, MAL = 0.59, CF = 1.11; For sites in Australia, MAL = 0.24, CF = 1.05; For sites in Eastern US, MAL = 0.27, CF = 1.05; For sites in Western US, MAL = 0.66, CF = 1.14; For other sites, MAL = 0.62, CF = 1.02.

Trace elemental oxides (TEO) are the sum of the masses of trace elements measured by XRF, less those used in other calculations, in their oxide form. TEO concentrations are a function of the measured elemental mass and typical oxides of that element found in nature. The total mass contributed from TEO is calculated as follows:

$$[\mathrm{TEO}] = 1.79[\mathrm{V}] + 1.69[\mathrm{Cr}] + 1.63[\mathrm{Mn}] + 1.34[\mathrm{Co}] + 1.27[\mathrm{Ni}] + 1.25[\mathrm{Cu}] + 1.24[\mathrm{Zn}] + 1.43[\mathrm{As}] + 1.41[\mathrm{Se}] + 1.09[\mathrm{Rb}] + 1.18[\mathrm{Sr}] + 1.14[\mathrm{Cd}] + 1.20[\mathrm{Sn}] + 1.26[\mathrm{Sb}] + 1.20[\mathrm{Ce}] + 1.12[\mathrm{Pb}] \quad (4)$$

4.0 CALCULATION OF RESIDUAL MATTER

Currently the organic components of the collected $PM_{2.5}$ is not directly measured by SPARTAN. However, the residual matter (RM) component is assumed to be predominately organics based on comparison with independent measurements as reported by Snider et al. (2016). The RM component at 35 % RH is calculated via mass balance by subtracting the total of

the measured inorganic chemical components ($IN_{mass,dry}$) and associated water (PBW_{IN_mass}) from the total $PM_{2.5}$ mass:

$$RM_{35\%} = PM_{2.5,35\%} - \left[IN_{mass,dry}\right] - \left[PBW_{IN_mass}\right] \quad (5)$$

where $\left[IN_{mass,dry}\right] = ([NH_4NO_3]_{dry} + [ASO_4]_{dry} + [NaCl]_{dry} + [CM] + [TEO] + [EBC] + [Na_2SO_4]_{dry})$

Negative $RM_{35\%}$ values are retained if $RM_{35\%}$ exceeds the total $PM_{2.5}$ mass by less than 10 %, otherwise values are flagged as invalid and not reported. Invalid negative $RM_{35\%}$ values may result from an overestimation of an inorganic component. Thus, reconstructing $PM_{2.5}$ mass acts as a Level 2 data validation of other analysis methods by leading to investigation of obtained values.

Identifying a representative organic hygroscopic parameter is challenging, as many are available from laboratory studies and field campaigns which vary by site and season. Value of κ_v for organic matter ($\kappa_{v,OM}$) range from 0 to 0.2, thus a single $\kappa_{v,OM}$ value of 0.1 is chosen based on an O:C ratio of 0.5 to represent the urban, populated nature of SPARTAN sites. Therefore, following the calculation of the RM contribution at 35 % RH, the dry RM concentration can be determined following the method outlined in section 2.2 using an estimated mass growth factor as follows:

$$\kappa_{m,RM} = \kappa_{v,OM}/\rho_{OM} = 0.1/1.4 = 0.07$$

5.0 SUMMARY OF SPECIATION DEFINITIONS

Table 1 provides a summary of the speciation definitions used to reconstruct $PM_{2.5}$ mass, the measurement method used to obtain relevant species, and the reference used to inform component definitions.

Table 1. Summary of speciation definitions and associated references

Species	Method	Species mass (μg)	Reference
SS	IC + XRF	$2.54[Na^+]_{SS}$, where $[Na^+]_{SS} = [Na^+]_{total} - 0.1[Al]$	Malm et al., 1994; Remoundaki et al., 2013
NH_4NO_3	IC	$1.29[NO_3^-]$	Malm et al., 1994
ASO_4	IC	$[SO_4^{2-}]_{non\text{-}SS} + [NH_4^+] - 0.29[NO_3^-]$, where $[SO_4^{2-}]_{non\text{-}SS} = [SO_4^{2-}]_{total} - 0.12[Na^+]$	Dabek-Zlotorzynska et al., 2011; Henning, 2003
Na_2SO_4	IC	$0.18[Na^+]_{SS}$	Dabek-Zlotorzynska et al., 2011; Henning, 2003
CM	XRF	CM = { 1.89[AL] x (1+MAL) +2.14[Si]+1.40[Ca]+1.36[Fe]+1.67[Ti]} x CF where MAL and CF are regionally dependent, Middle East: MAL = 0.72, CF = 1.14 Sahel: MAL = 0.27, CF = 1.05 East Asia: MAL = 0.59, CF = 1.11 Australia: MAL = 0.24, CF = 1.05 Eastern US: MAL = 0.27, CF = 1.05 Western US: MAL = 0.66, CF = 1.14 All other regions: MAL = 0.62, CF = 1.02	Liu et al., 2022
EBC	SSR	$20.7 \times \ln(R/R_o)$	Taha et al., 2007
TEO	XRF	1.79[V] + 1.69[Cr] + 1.63[Mn] + 1.34[Co] + 1.27[Ni] + 1.25[Cu] + 1.24[Zn] + 1.43[As] + 1.41[Se] + 1.09[Rb] + 1.18[Sr] + 1.14[Cd] + 1.20[Sn] + 1.26[Sb] + 1.20[Ce] + 1.12[Pb]	Reff et al., 2009
PBW_{IN_mass}	$\kappa_{m,X}$	$\sum_X [f_{m,X}(RH) - 1][X]$	Kreidenweis et al., 2008
PBW_{RM}	$\kappa_{m,OM}$	$RM\,(1 - 1/f_{m,RM})$	Jimenez et al., 2009
RM (35 % RH)	Mass balance	$[PM_{2.5}] - \{ [EBC] + [CM] + [TEO] + [NH_4NO_3] + [SS] + [ASO_4] + [Na_2SO_4] + [PBW_{IN_mass}] \}$	This study
RM (0 % RH)	Mass balance, $\kappa_{m,OM} = 0.07$	$RM(35\ \%) - PBW_{RM}$	Jimenez et al., 2009; Sun et al., 2011

Measurement methods: IC = Ion Chromatography, XRF = X-ray Fluorescence, SSR = Smoke Stain Reflectometer, κ = κ-Kohler hygroscopicity theory

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