

SOP # 10

Reconstructing Fine Mass

General Summary: In this section we explain how we account for water retained in post-weighed filters (via κ -Kohler theory), and definitions for major aerosol constituents: soil, ammonium sulfate/nitrate, trace metals oxides, sea salt, black carbon, and residue matter (a surrogate for organic matter).

REVISION HISTORY			
Revision No.	Change Description	Date	Authorization
2.0	Update of Soil equation	July 20, 2018	Paul Bissonnette

Summary definitions of inorganic aerosol constituents:

Both $PM_{2.5}$ and PM_{10} are collected on separate Teflon filters in a given cartridge. Ambient concentrations are determined by dividing the gravimetrically determined mass by the volume of air sampled, as described in SOP #3:

$$[PM] = (\text{Post-weighed filter mass} - \text{Pre-weighed filter mass})/V$$

We are only able to reconstruct PM mass of inorganic components $[IN_{tot}]$. Gathering the most abundant ions and metals we have:

$$[IN_{tot}] = [ASO_4] + [ANO_3] + [NaCl] + [PBW] + [SOIL] + [TEO] + [EBC]$$

Where

$[ASO_4]$ = Ammonium sulfate $(NH_4)_2SO_4$

$[ANO_3]$ = Ammonium nitrate NH_4NO_3

$[RM]$ = Residue Mass (assumed to be comprised mainly of Organic Matter, OM)

$[EBC]$ = Effective black carbon ($\sim [BC]$)

$[SOIL]$ = Fine soil /dust

$[TEO]$ = Trace Element Oxides

$[NaCl]$ = Sea salt

$[PBW]$ = Particle-bound water

We cannot include organic components directly, but they are inferred by

$$[\mathbf{RM}] = [\mathbf{PM}] - [\mathbf{IN}_{\text{tot}}]$$

Total inorganic mass is based on the IMPROVE equations as outlined below and (Dabek-Zlotorzynska et al., 2011) as well as (Okuda et al., 2004) and (Hueglin et al., 2005). We reconstruct residual mass by subtracting all other masses from measured PM. In the past, direct measurement of the organic fraction of PM has not been possible under the sampling conditions used, leading to the use residual mass as a proxy. Below are details on inorganic mass reconstruction.

IC-Reconstructed Mass (IC-RM):

We determine the ion-chromatography compounds by combining sea salt, ammonium nitrate, non-sea salt ammonium sulfate, and particle-bound water.

$$[\mathbf{ICM}] = [\mathbf{ASO}_4] + [\mathbf{ANO}_3] + [\mathbf{PBW}] + [\mathbf{NaCl}]$$

where:

$$[\mathbf{SO}_4^{2-}(\text{NSS})] = [\mathbf{SO}_4^{2-}(\text{tot})] - 0.12*[\mathbf{Na}^+] - 0.175*[\mathbf{Ca}^{2+}] \quad (\text{Henning et al., 2003})$$

(NSS = non sea salt. We ignore the $[\mathbf{Ca}^{2+}]$ subtraction as IC-derived calcium is sometimes overestimated, possibly due to water contamination)

$$[\mathbf{ANO}_3(\text{dry})] = [\mathbf{NO}_3^-] + (18/62*[\mathbf{NO}_3^-]) = 1.29*[\mathbf{NO}_3^-] \quad (\text{assume all nitrate exists as ammonium nitrate})$$

$$[\mathbf{ASO}_4(\text{dry})] = [\mathbf{SO}_4^{2-}(\text{NSS})] + [\mathbf{NH}_4^+] - (18/62*[\mathbf{NO}_3^-]) \quad (\text{assume all remaining ammonium and sulfate bind together and that ASO}_4 \text{ includes } [(\mathbf{NH}_4)_2\mathbf{SO}_4 + \mathbf{NH}_4\mathbf{HSO}_4 + (\mathbf{NH}_4)_3\mathbf{H}(\mathbf{SO}_4)_2] \text{ (Dabek-Zlotorzynska et al., 2011)})$$

Note that $[\mathbf{ANO}_3(\text{dry})] + [\mathbf{ASO}_4(\text{dry})] = [\mathbf{SO}_4(\text{dry})] + [\mathbf{NO}_3(\text{dry})] + [\mathbf{NH}_4(\text{dry})]$.

$$[\text{NaCl (dry)}] = 2.54 \times [\text{Na}^+] \text{ (assume Na is 1:1 molar with Cl (mass: } 35.5/23.0 + 1 = 2.54))$$

Adding moisture to mass of dry particles:

$$[\text{ANO}_3(\text{wet})] = [\text{ANO}_3(\text{dry})] \times (1 + \kappa_{m,\text{ANO}_3} \times \text{RH}_{\text{dry}} / (1 - \text{RH}_{\text{dry}}))$$

$$[\text{ASO}_4(\text{wet})] = [\text{ASO}_4(\text{dry})] \times (1 + \kappa_{m,\text{ASO}_4} \times \text{RH}_{\text{dry}} / (1 - \text{RH}_{\text{dry}}))$$

$$[\text{NaCl (wet)}] = [\text{NaCl (dry)}] \times (1 + \kappa_{m,\text{NaCl}} \times \text{RH}_{\text{dry}} / (1 - \text{RH}_{\text{dry}}))$$

$$[\text{OM (wet)}] = [\text{OM (dry)}] \times (1 + \kappa_{m,\text{OM}} \times \text{RH}_{\text{dry}} / (1 - \text{RH}_{\text{dry}}))$$

for $\text{RH}_{\text{dry}} = 0.35$ (the RH used in our laboratory weighing), $\text{RH}_{\text{dry}} / (1 - \text{RH}_{\text{dry}}) = 0.538$

Estimated mass growth factors (here assuming RM = OM):

$$\kappa_{m,\text{ANO}_3} = \kappa_{v,\text{ANO}_3} / \rho_{\text{ANO}_3} = 0.67 / 1.72 = 0.39$$

$$\kappa_{m,\text{ASO}_4} = \kappa_{v,\text{ASO}_4} / \rho_{\text{ASO}_4} = 0.53 / 1.77 = 0.30$$

$$\kappa_{m,\text{NaCl}} = \kappa_{v,\text{NaCl}} / \rho_{\text{NaCl}} = 1.12 / 2.17 = 0.52$$

$$\kappa_{m,\text{RM}} = \kappa_{v,\text{OM}} / \rho_{\text{OM}} = 0.05 / 1.4 = 0.035$$

Particle-bound water is the summation of difference of $[X]_{\text{wet}} - [X]_{\text{dry}}$ terms, hence

$$\text{PBW}(35\%) = \sum_i [X_i]_{\text{wet}} - [X_i]_{\text{dry}} = \sum_i [X_i]_{\text{dry}} \kappa_{m,i} \frac{\text{RH}}{1 - \text{RH}}$$

$$[\text{PBW}] = 0.21[\text{ANO}_3]_{\text{dry}} + 0.16[\text{ASO}_4]_{\text{dry}} + 0.52[\text{NaCl}]_{\text{dry}} + 0.019[\text{RM}]_{\text{dry}}$$

Hence the 'dry' particle-bound water is a linear function of the four compounds that are known to adsorb water. Depending on the site all four may be relevant.

ICP-Reconstructed Mass (ICPM):

With the ICP we can obtain [TEO], and combined with IC we can obtain [SOIL].

For soil estimates use the most reliable among elements {K,Mg,Ca,Al,Si,Ti,Fe}

For trace oxidized elements use all remaining reliable elements (not already used for previous summations).

If iron is found to be uncontaminated and silicon is known, then:

$$[\text{SOIL}] = 3.48[\text{Si}] + 1.21[\text{K}] + 1.66[\text{Mg}] + 1.63[\text{Ca}] + 1.94[\text{Ti}] + 2.42[\text{Fe}]$$

However, iron concentrations are sometimes biased by contamination and silicon is rarely available, additionally calcium also often suffer from contamination. Ratios of elements are used to complete the soil equation when lack of certain elements would make it otherwise impossible to calculate. The following ratios are used: $[\text{Si}]/[\text{Al}] = 2.9$, $[\text{Fe}]/[\text{Ti}] = 30$, and $[\text{Ca}]/[\text{Mg}] = 7$. These ratios are used to produce the equations below, which ascribe 10% of soil mass to be contributed from the sum of the three selected elements.

If Fe shows no signs of contamination:

$$[\text{SOIL}] = 10 * ([\text{Al}] + [\text{Fe}] + [\text{Mg}])$$

If Fe cannot be used due to contamination:

$$[\text{SOIL}] = 10 * ([\text{Al}] + 30 * [\text{Ti}] + [\text{Mg}])$$

Trace element oxides are a function of elemental mass and typical oxides of that element found in nature. For instance, there are many oxides of vanadium (V_2O_5 , V_3O_7 , etc.), but V_2O_3 is found to be representative. We sum over all the trace metal ion masses available to us (13 in all, removing those doubly counted in soil and salt).

$$[\text{TEO}] = 3.07[\text{P}] + 1.47[\text{V}] + 1.27[\text{Ni}] + 1.25[\text{Cu}] + 1.24[\text{Zn}] + 1.32[\text{As}] + 1.2[\text{Se}] + 1.07[\text{Ag}] + 1.14[\text{Cd}] + 1.2[\text{Sb}] + 1.12[\text{Ba}] + 1.23[\text{Ce}] + 1.08[\text{Pb}]$$

Total mass contributed to the sum of TEO is small, typically only a few percent. Trace elements can also be used for source apportionment with emission trends.

Effective Black Carbon (EBC):

Effective black carbon is obtained by a normalized calibration plot of total light reflectance of filters measured against a blank filter (**Section 6**). We use Diffusion Systems EEL 43M SSR, which measures EBC, which is in turn a proxy for elemental carbon (EC). Quartz filters and an OC/EC analyzer are the only way to obtain EC, and for SPARTAN are only available during the 3-week Harvard Impactor collocation period of daily sampling.

From Section 6 the equation below relates absorption coefficient σ , surface reflectance R , total air sample volume V , and filter area A to the original air concentration of black carbon:

$$[\text{EBC}] = \frac{A}{2V\sigma} \ln\left(\frac{R_0}{R}\right)$$

Given $A/2 = 1.57 \text{ cm}^2$ and $R_0 = 100$, and $\sigma = 0.1 \text{ cm}^2/\mu\text{g}$, then:

$$[\text{EBC}] = \frac{15.7 \text{ } \mu\text{g}}{V \text{ m}^3} \ln\left(\frac{100}{R}\right)$$

Sample volume (V, m^3) varies per sample site while R determines the reflectance (the smaller the value of R , the larger EBC).

EBC cannot be determined for nuclepore filters, hence the reconstructed coarse mass must omit EBC. Therefore RM for coarse reconstruction is a function of both total OC and EC.

Combining EC, IC, and ICP fractions

Once EC, IC and ICP work are compiled separately, the *inorganic* mass reconstruction is:

$$[\text{IN-tot}] = [\text{ICM}] + [\text{ICPM}] + [\text{EBC}]$$

Residue Mass (assumed associated with organic matter) in $\text{PM}_{2.5}$ can therefore be estimated as:

$$[\text{RM}] = [\text{PM}] - [\text{IN-tot}]$$

The final results can be seen in the example figures below.

Table 9.1: Summary speciation definitions

Species	Measurement Instrument	Species Mass (μg)	Reference
E-BC	SSR	$15.7 \times \ln(100/R)$	(Taha et al., 2007)
Soil/crustal*	ICP-MS & IC	$10^* ([\text{Al}] + [\text{Fe}] + [\text{Mg}])$	Based on (Dabek-Zlotorzynska et al., 2011)
TEO	ICP-MS	$3.07[\text{P}] + 1.47[\text{V}] + 1.27[\text{Ni}] + 1.25[\text{Cu}] + 1.24[\text{Zn}] + 1.32[\text{As}] + 1.2[\text{Se}] + 1.07[\text{Ag}] + 1.14[\text{Cd}] + 1.2[\text{Sb}] + 1.12[\text{Ba}] + 1.23[\text{Ce}] + 1.08[\text{Pb}]$	Based on (Dabek-Zlotorzynska et al., 2011)
ANO ₃	IC	$1.29[\text{NO}_3^-]$	
NaCl	IC	$2.54[\text{Na}^+]$ (Cl- not reliable)	
ASO ₄	IC	$[\text{SO}_4^{2-}]_{\text{non-salt}} + [\text{NH}_4^+] - 0.29[\text{NO}_3^-]$ where $[\text{SO}_4^{2-}]_{\text{non-salt}} = [\text{SO}_4^{2-}]_{\text{total}} - 0.12[\text{Na}^+]$	(Dabek-Zlotorzynska et al., 2011; Henning et al., 2003)
Na ₂ SO ₄	IC	$0.18[\text{Na}^+]$	
PBW _{inorg}	κ -Kohler	$\sum_X [f_{m,X}(RH) - 1][X]$	(Kreidenweis et al., 2008)
PBW _{RM}		$\text{RM}_{\text{wet}}(1 - 1/f_{m,\text{RM}})$	
RM _{wet}	Mass balance	$[\text{PM}_{2.5}] - \{[\text{E-BC}] + [\text{Soil}] + [\text{TEO}] + [\text{ANO}_3] + [\text{NaCl}] + [\text{ASO}_4] + [\text{Na}_2\text{SO}_4] + [\text{PBW}]\}$	

Species: E-BC = Equivalent black carbon, TEO = Trace metal oxides, ANO₃ = Ammonium nitrate, ASO₄ = Ammonium sulfate, PBW = particle-bound water, RM = residue matter (assumed representative of organic matter). **Measurement Instrument:** IC = Ion Chromatography, ICP-MS Inductively coupled plasma mass spectrometry, κ -Kohler = hygroscopicity theory, *Silicon is not reliably measured in our ICP samples therefore we assume $[\text{Si}]/[\text{Al}] = 2.9$ (by mass)

References

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