

Responses to Referee #1 comments ACP-2012-816

Comment #1: *My main criticism is related to the choice of parameters (chemical markers or compounds) used for PMF analysis. Although the use of different form of the same elements (or compounds) sometime could give a best source fingerprint, in the paper some parameters are redundant in the PMF analysis. In particular, I understand the use of both K and K+ in the PMF analysis because K (total content) is more related to crustal source, conversely K+ is more specific for biomass burning source (and primary marine). I'm less convinced about the use of both S and SO₄, actually S comprise also methane sulfonate (MS) from atmospheric oxidation of biogenic dimethylsulfide, but at this site MS have to be negligible because the SO₄/S ratio is higher than 3 (line 13 page 836) likely due to underestimation of S and absence of MS. I disagree to the use of OC1, OC2, OC3 and OC4 together with total OC. The use of more specific fraction of OC makes unnecessary insert total OC in the PMF. Besides, in quantification procedure by PMF all these parameters (K - K+, S-SO₄, OC1, OC2, OC3, OC4 –OC), representing more or less the same amount, give an overestimation of the contribution of the source. May be the authors exclude the double parameters from source quantification, but this is not reported in the text; please the authors better explain their approach.*

Response: The inclusion of both S and OC may, mathematically, result in the overestimation of the source contributions. However, by comparing the contribution of aerosol sources to PM_{2.5} mass (Table 2) against the types of aerosol particles (Table 1), we observed that: (i) the predicted (by PMF) PM_{2.5} concentration was lower than the measured PM_{2.5} mass; (ii) the amount of organic mass was higher than the sum of biomass+traffic+diesel+aged sea salt (lets define the difference as “OC-other”); and (iii) the amount of ammonium sulfate was slightly lower than the contribution of secondary sulfate source (actually the difference is comparable to the “OC-other” (and there was a correlation of OC and its fraction with the secondary sulfate source). These results clearly demonstrated that the inclusion of S and OC did not have an effect on the qualitative and quantitative outcomes of the analysis.

Comment #2: *Sampling site and measurements: analytical procedures are simply listed (line 11-14 page 831) and no references to find further information are reported. In particular, what procedures for extraction were used for ICP and ICP-MS analysis? Total or the soluble content is achieved? If soluble content is determined, in which condition? What ICP-MS is used? What resolution is used?*

Response: The collection and chemical analysis of aerosol filters is done by EPA's affiliated and/or contracted laboratories following specific protocols that apply for all NCore and IMPROVE sites in the US. The experimental section is updated to include the link to the Standard Operating Procedures of the laboratory methods.

Comment #3: *Page 837 formula (9). Why for the calculation of secondary species coefficients are applied to NO₃⁻, NH₄⁺ and SO₄²⁻? In my opinion only the secondary species: NO₃⁻, NH₄⁺ and SO₄²⁻ have to be considered in this specific class of particles. Only NO₃⁻, NH₄⁺ and SO₄²⁻ have a secondary source from oxidation processes in the atmosphere and/or gas to particle conversion, counter ions have not to be included here. At line 11-13 Authors state that “Nitrate may also be associated with coarse particles from neutralization of nitric acid with sea salt or calcium carbonate” this is right but Na or Ca have not be included in secondary species even if chemically link to secondary species. Besides, if they are included in “secondary species” they will be considered two times in reconstructed PM. For instance Ca is reported both in “soil” and in “secondary species”. Please change this section in accord to these suggestions. Page 837 line 13. I suppose the conversion factor 1.6 is related to OC – OM conversion but is not clear in the sentence put just after nitrate neutralization.*

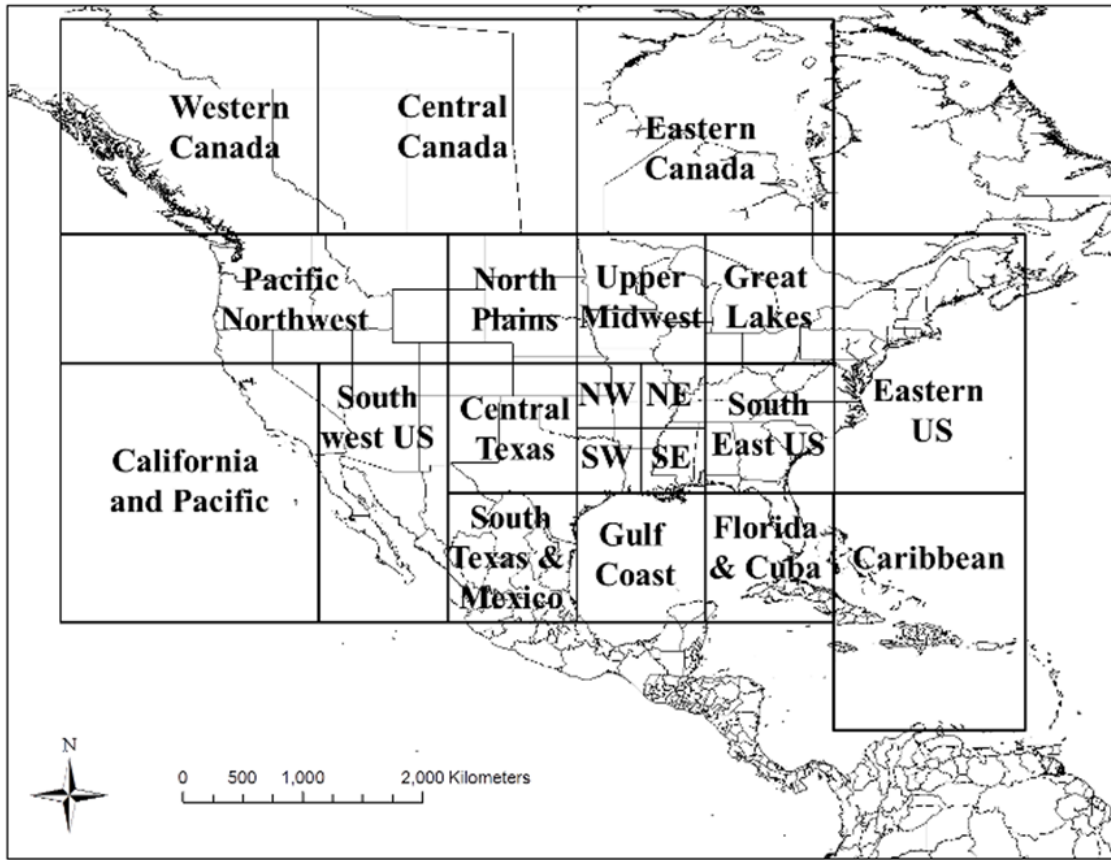
Response: The equation (9) calculates the concentrations of dry ammoniated sulfate and nitrate when sulfate, nitrate and ammonium are measured. This equation is applied to analysis of IMPROVE and EPA PM_{2.5} speciation networks. Detailed description is given in Sisler, 2000. To clarify this issue, we cited the reference Sisler, 2000. Malm et al. (2007) previously

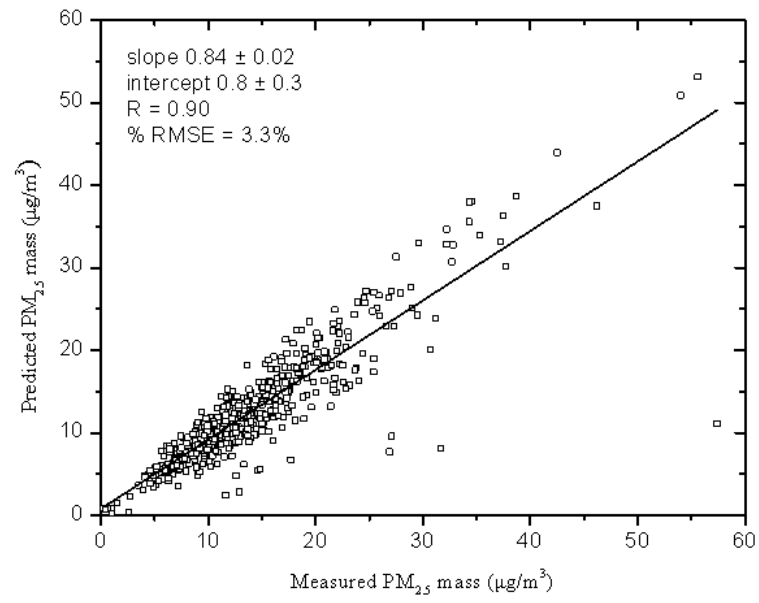
showed that coarse nitrate was associated with Ca and Na (particles with aerodynamic diameter between 2.5 and 10 μm). This was mostly observed in the western US where ammonium levels are not sufficient to neutralize sulfate and nitrate and there are plenty of mineral particles. In this study, chemical speciation measurements were only available for fine particles, so the neutralization of nitrate by Ca and Na was not considered. Previous studies showed that sulfate and nitrate in Midwest and eastern US were predominantly neutralized by ammonium. To clarify this issue, we modified the statement as follows: **“Nitrate may also be associated with coarse particles from neutralization of gas phase nitric acid with sea salt or calcium carbonate. This was typically observed in western US (Malm et al., 2007).”**

We modified the statement as follows: **“Organic carbon to organic mass (OC-to-OM) conversion factors varied from 1.7 ± 0.2 in IMPROVE background sites to 2.1 ± 0.2 for rural $\text{PM}_{2.5}$ aerosol to reflect the presence of oxygenated functional organic compounds formed during transport (Turpin and Lim, 2001; Malm and Hand, 2007). We assumed an OC-to-OM conversion factor of 1.6 which is typically used for urban $\text{PM}_{2.5}$ atmospheric aerosol (Turpin and Lim, 2001)”**

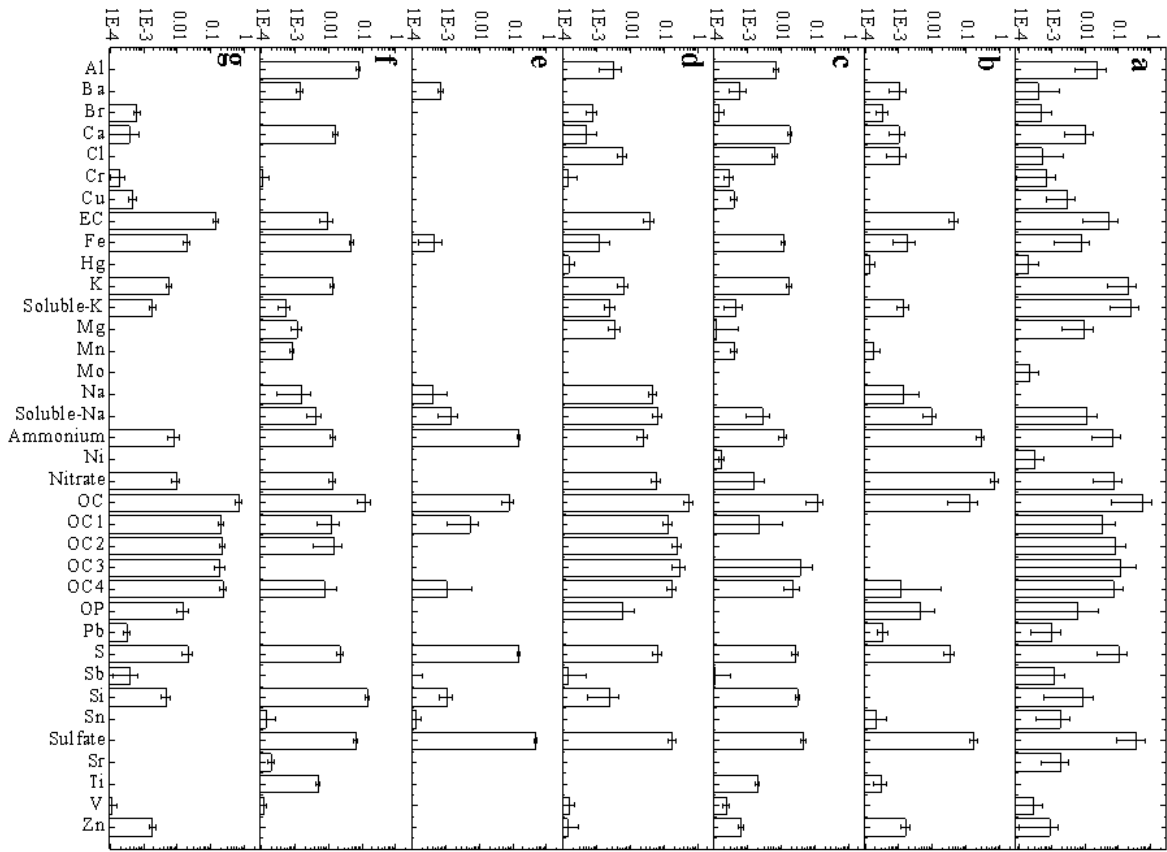
Comment #4: *Labels in the figures often are not visible, please use larger size font. Line 12 page 829: “. . .mass concentrations decreased from 24% to 28%...” I suppose “increases” is the right word. Please specify the acronyms PIXE, ICP, ICP-MS at lines 11-12 and Lat (_N) and Long (_E) at line 4 page 831*

Response: The font sizes in labels and legends are increased and the quality (resolution) of the figures is increased (see below). The statement in Line 12 (page 829) is modified as follows: **“In the US, $\text{PM}_{2.5}$ (particles with aerodynamic diameter less than 2.5 μm) mass concentrations decreased by 27% between 2001 and 2010 (US EPA, 2012a)”**. The acronyms and coordinates are also corrected.





Fine particle (ng/ng)



PM_{2.5} mass concentration ($\mu\text{g m}^{-3}$)

