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Interactive comment on "Processing of biomass burning aerosol in the Eastern Mediterranean during summertime" *by* A. Bougiatioti et al.

A. Bougiatioti et al.

kbougiatioti@gmail.com

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The paper of Bougiatioti et al. provides evidence of significant atmospheric processing of biomass burning aerosol in Eastern Mediterranean during summer time leading to significant underestimation of the biomass burning source based on traditional PMF source apportionment. While atmospheric processing of biomass burning aerosol has been established few studies exist about the implications of the processing using traditional source apportionment techniques. Having said that, the quantitative assessment of the processed BBOA aerosol needs a better reasoning and more thorough discussion or some of the conclusions should be played down mainly due to the fact that the aerosol chemical speciation monitor was designed mainly for monitoring purposes rather than being a truly scientific instrument. There is simply too much information lacking - high resolution fragmentation pattern, mass size distribution, inference of mixing state – to make the unambiguous conclusions. My biggest concern is the claim that almost half of OA can be attributed to biomass burning. While that may be true in particular region and particular air masses, especially the ones associated with fire plumes, the conclusion is clearly overblown out of proportions. Other than that the paper is pretty well written and easy to follow though there were many details lacking as well. The paper can be recommended for publication after addressing the above major and many minor comments below.

Response: We would like to thank the reviewer for all these constructive comments and suggestions. We do think that our analysis and its conclusions are robust despite the limitations of the ACSM In the publication introducing the ACSM, Ng et al (2011) compared the results obtained by the ACSM with an Aerodyne high-resolution time-of-flight Aerosol Mass Spectrometer (HR-ToF-AMS). The corresponding PM component concentrations, aerosol mass spectra and factors from PMF were in good agreement. Based on the conclusions of that study performing PMF analysis on ACSM data is absolutely feasible. While analysis of high resolution AMS data can sometimes give improved results in a number of cases the corresponding improvement is small. Furthermore, in ACTRIS project, a large number of ACSM instruments deployed in different countries in Europe both to monitor fine PM composition but also to obtain OA source information using PMF. We consider that our analysis is not weighed down by the fact that the ACSM does not provide a high resolution fragmentation pattern and a mass size distribution. The statement which the reviewer is referring to was indeed confusing and has been rewritten to avoid misunderstandings (this point was also raised by Reviewer #3). It refers to the periods during which the area was affected by biomass burning plumes and it is an upper limit. As it is also illustrated in the Minor Comments section by providing FIRMS maps for the years 2008-2013 and for July-September, the frequency of fire events in the area during this period is clearly high. We have revisited the corresponding statement to clarify the periods to which it refers.

The main argument in the paper for the existence of OOA-BB factor is a 3 factor solution and consideration of Sicilian fires lacking direct biomass burning traces. It may look statistically correct, but there are few important questions remaining before the OOA-BB factor can be considered established and quantified. BBOA and OOA factors are indeed pretty obvious; the former associated with fire plumes and the other correlating with sulphate and processed down to m/z 44 mainly. It does not mean, however, that OOA factor has one source origin, but rather it has been processed to the highest degree of oxygenation becoming an end product of atmospheric transformation of organic matter. Naturally, OOA-BB factor looks like an intermediate product, but the details are ambiguous. For instance, why BBOA and OOA-BB should be correlating with nitrate? Is nitrate and not sulphate produced in biomass burning plumes? Or is it a regional phenomenon, but then both nitrate and sulphate should be equally present in internally mixed aerosol? Moreover, why OOA-BB is poorly correlating with BC if atmospheric processing is supposedly processing OA, but not splitting with BC? In the absence of wet scavenging, atmospheric processing alone should not break the correlation between BBOA and BC. Even considering OOA-BB coming from multiple diffused fire plumes it should still be correlating with the originally present BC. The breakdown of correlation suggests to me that the OOA-BB factor is not unique and is a combination of additional factor even if processed BBOA is dominating OOA-BB factor. Based on purely statistical terms, R square value is not a correlation (r is the correlation), but rather the variance which shows a fraction of the total variance of the two variables explained by the common source. Hence, R2=0.48 of OOA-BB and BC suggests that biomass burning can explain 48% of the variance with the rest of the variation due to other sources or reasons. Even BBOA and BC have 62% of the common variance which is large, but not overwhelming.

Response: Our choice of the 3 factor PMF solution of the analysis was based on all relevant parameters, including the different time series and diurnal variability of the factors. Also the comparison between the mass spectra of OOA-BB and OOA gave a value of theta angle of almost 20 degrees, which means that there is a similarity between the 2 spectra, but there are also considerable differences. Furthermore the fact that OOA-BB peaks during the same periods as BBOA shows that there is a strong link between the 2 factors and that OOA-BB is most probably processed OOA from BBOA after atmospheric processes. We do agree that the results of one study are not sufficient to consider such a factor established. As with all other AMS factors additional studies in other areas will be needed to confirm such a finding. Clearly the OOA factor has multiple source origins and it is not only the result of processing of biomass burning OA. However, our results strongly support that it is also a product of BBOA chemical processing in the atmosphere. This fact is clearly demonstrated in Fig. 5a, where it can be seen that concurrently with the peaks in BBOA and OOA-BB, there is also a peak in the OOA. As also stated in the manuscript, this is also consistent with the observation of aging of fresh biomass burning OA in plumes over Canada only within a few hours after emission (Lathem et al., 2013). The correlation with nitrate can be explained in a number of ways in this case. The nitrate correlation with the BBOA and OOA-BB is probably an indication of the semi-volatile character of all those components. Traditionally, nitrate is correlated with semi-volatile oxygenated organic aerosol (SVOOA) and sulfate with low-volatility oxygenated organic aerosol (LVOOA). Furthermore, probably both nitrate and sulfate are produced by fires, but for nitrate the fires is a much more important source compared to sulfate, which has other mass sources in the area. For instance, when the site is not affected by biomass burning plumes during summertime, fine mode nitrate is usually below the detection limit while sulfate presents its maximum with values up to 6-8 μg m-3. The correlation between the OOA-BB and BC does indeed deserve additional discussion. The R2=0.48 refers to all the study period. If one focuses on the specific periods during which the site was affected by the fire plumes the respective R2 between OOA-BB and BC is 0.74, 0.59, 0.71, 0.53 and 0.45. This is also the case for BBOA and BC for the separate events, with R2 equal to 0.85, 0.65, 0.8, 0.76 and 0.48. Considering the fact that the OOA-BB concentration is affected both by chemical processes (its production from BBOA and its conversion to OOA) and physical ones (partitioning between the gas and the particulate phases) plus that there are also other sources of BC the above variances are quite high. We believe that the results of this statistical analysis support our conclusion about the OOA-BB. We have added text to the revised paper addressing the points above and also presenting the additional statistical analysis for the specific biomass burning periods. Moreover, the comparison between the BBOA and OOA-BB from the whole time period with the estimated BC coming from wood burning also shows significant correlation (R_pearson=0.81 and 0.69 respectively). This indicates that indeed biomass burning contributes significantly in the area during the specific time period.

The diurnal patterns presented in Figure 5c need more thorough consideration. Why OOA has peculiar diurnal pattern if this type of OM should be already processed to the highest possible degree and no photochemical activity can enhance the concentration in the afternoon? What was the diurnal pattern of sulphate? Typically, factors representing regional sources (background) do not exhibit diurnal patterns except the ones related to boundary layer dynamics. Possibly the factor is not unique either. Quite contrary, OOA-BB doesn't show any pronounced diurnal pattern with only a small peak coinciding with the morning BBOA peak. Also, why would BBOA peak in the morning? It must be due to specific transport time as biomass fires typically burn day and night. Authors should try estimating transport time from identified fires by backward trajectories to check for the consistency. Based on the above it can be argued that in absolute terms processed BBOA amounts to the difference between the background OOA-BB and the morning peak concentration (_0.2-0.3 ug/m3) limiting its significance.

Response: We have followed the reviewer's suggestion and compared the average diurnal pattern of OOA and sulfate during the study period. As it can be seen in the attached Figure 1, sulfate and OOA have the same diurnal pattern, something consistent with their good correlation. These results do suggest that there is chemistry and production of both sulfate and OOA near the site and that the corresponding conversion of sulfur dioxide to sulfate and organic compounds and OA to OOA has not

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been completed. This chemical processing (e.g. conversion of BBOA and OOA-BB to OOA) together with vertical exchange processes could explain the observed average variability. A similar behavior (with a weaker diurnal variation) has been reported by Hildebrandt et al. (2010) in an earlier study in the same area during similar time period using a Q-AMS. Hildebrandt et al. (2010) show in their Fig. 12b that OOA-1, which is the more oxidized identified organic component had the same behavior as the OOA of this current publication. Furthermore, when comparing the mass spectra of these two factors, they have a theta angle of 11 degrees, value that represents a significant similarity between the two spectra. We agree that the diurnal profile of OOA-BB is not very pronounced (this was pointed out also by Referee 2), nevertheless there is increase in the OOA-BB concentrations between 5 and 10 am. The arrival of the biomass burning laden air masses is the reason for the variability of the OOA-BB levels during this early morning period. Based on the back-trajectory analysis performed for each fire event, three out of the five plumes arrived in the early morning hours: Chios (around 7 am), Euboea (around 5 am) and Andros with two plumes (one around 11 pm and one the following morning around 9 am). For the Croatian fires, there were two different plumes, one arrived at around 1 pm (27/08) and one the next day (around 6 am). Finally the plume from Sicily arrived at the site around 1 pm. The fire events with the highest loadings (Chios and Euboea) are the ones that contribute the most in the observed diurnal variability (Figure 5c), which exhibits higher concentrations during early morning hours. So there was some variability in the time of arrival of these fires. It is possible that some of these plumes were aloft (above the nighttime mixing layer) and they were mixed downwards reaching the site in the morning. The estimated transport times for each plume are shown in Table 1. A brief discussion of the above has been added in Section 3.2 of the manuscript.

Biomass burning fires in Sicily need much better reasoning as they constitute the concluding argument in favour of significant OOA-BB. The associated evidence of fires in Sicily is rather loose and ambiguous (lines 12-14, page 25978; was it a fire or not a fire event?). As already noted above, the heavy processing of BBOA originating in Sicily should not break correlation with BC. Air mass back trajectories including their vertical evolution should be presented and discussed.

Response: Fires that took place in Sicily during 18-21 September influenced our site on 21 September as a result of travel time and wind direction. The discussion in page 25978 (lines 12-14) is about the 24-30 September period where there also relatively high BC levels but are not related to a fire event in the area. We are afraid that this discussion was confusing and has been rewritten. This is a totally different case than Sicily and is not part of OOA-BB related analysis.

Minor comments

P25972, line 11-14. The PMF factor analysis is primarily based on temporal variation of all the fragments included, not just 44 and 43. Have authors tried to assign different weighting to the dominant m/z, especially m/z 44?

Response: For the PMF analysis we used the proposed configuration and parameters for the Multilinear Solver (ME-2) developed at the Paul Scherrer Institute (Canonaco et al., 2013). The matrices used for the PMF analysis are directly derived from the ACSM software. This point is mentioned in the manuscript.

P25974, line 3. Authors clearly state they focus on specific clearly identified fires, but the main conclusion refers to the overall Eastern Mediterranean region. I would like to note that the measurements only covered two month of a single year.

Response: The main conclusion refers to the overall Eastern Mediterranean region, for the specific time period which is summertime. FIRMS maps for the years 2008-2013shown in the attached Figure2 for July-September clearly demonstrate that the frequency of fire events in the area is extremely high. The significant influence of biomass burning in the area during this period has also been demonstrated in a long-term (5-year) study of Sciare et al. (2008), originating from long-range transport.

Line 12. Spell ACSM for the first time and then use the acronym. Response: Done

Line 16. Correct to “particle flash vaporisation in high vacuum”. Response: Done

Line 19. How relevant is the referral to PM10 inlet if ACSM aerodynamic lens limit particle transmission to PM1 – misleading information to uninformed reader.

Response: This is a valid point. In the revised version of the manuscript we clarify that the particle lens of the ACSM focuses submicron aerosol of ∼40-1000 nm aerodynamic diameter. Nevertheless the PM10 inlet removes particles above 10 micrometers which could cause problems for the ACSM inlet system e.g. clogging of the pin hole.

Line 22. Different collection efficiency for sulphate is wrong. Authors possibly refer to relative ionisation efficiency (REI) which was not estimated by calibration. Or was it? Otherwise I don’t understand applying arbitrary CE for sulphate and only then comparing to filter measurements.

Response: The issue with using a different collection efficiency for sulfate was also raised by Referee #2. As RIE of sulfate we use the nominal 1.15 proposed by Ng et al. (2011). The value of 0.25 as CE for sulfate was based on concurrent PM1 filter analysis for the time period of June-September 2012, the daily averaged ACSM concentrations were one quarter of those determined by ion chromatography of the daily filters, as demonstrated in the attached Figure3. Furthermore, upon arrival of the ACSM instrument in Greece, it first ran concurrently with a High-Resolution Time of Flight Aerosol Mass Spectrometer in the Laboratory of Air Quality Studies(LAQS) in Patras, Greece for a week and based on the intercomparison of the concentrations the ACSM sulfate concentrations were qualitatively half of those measured by the High-Res while the rest of the species were in very good agreement. Based on these observations we have used a CE for sulfate of 0.25. This point is explained in the revised paper.

P25975, line 6. Spell oxalate for the first time. Response: Done

Line 19. If acronym is ME, spelling should be multilinear engine, not solver. Response: Done

Line 25. Statistical tool is not a model, better use “mathematically extracted” instead of “modelled”.

Response: Done

P25976, line 10. Discrepancies can also be attributed to different sampling devices because 1μm cut off function is slightly different in aerodynamic lens compared to atmospheric sampling devices.

Response: This could also contribute to the difference and has been added as an explanation to the revised manuscript.

Line 11. Sentence about parameterisation is awkward and sounds out of context.

Response: The parameterization proposed by Middlebrook et al. (2012) was used to show that the sampled aerosol had acidic behavior, as based on this publication the effect of both elevated aerosol acidity, but high relative humidity (RH) as well may influence the CE of AMS species. This has been put into context in the revised version of the manuscript.

Line 23, 26. SMPS and gravimetric measurements were not introduced in Experimental section.

Response: The lack of this information was also pointed out by Referee#3 and has been added in the revised version of the manuscript.

Line 24. Density of particles is very low considering densities of sulphate/nitrate (∼1.7), organics (1.4) and any dust (∼1.8-2.0). My guess is that the density estimated in referenced paper included water. By the way, was SMPS fully dried (often SMPS systems run at around 40% RH which is not low enough to evaporate water completely)? Hence, the density of 1.35 could have worked because SMPS was not completely dried.

Response: The value of 1.35 g cm-3 refers to the average organic aerosol density (not the overall particle density), derived from the Lee et al. (2010) paper for the same site

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during late spring of 2008. This value, combined with the 1.77 g cm-3 for ammonium sulfate and the respective mass fractions was used to estimate the mass from the SMPS volume. The used SMPS system runs with a nafion dryer that lowers RH to ∼30% therefore can be considered as mostly dry. This was clarified in the paper to avoid confusion.

P25977, line 10. Wrong expression “at the expense of sulphate”, otherwise explain how sulphate may be substituted/replaced.

Response: This expression has been rephrased.

P25978, line 12-16. I am confused about the second period of 25-30 of September. What for was it mentioned? I am confused whether Sicilian biomass burning events were fires or not.

Response: As aforementioned, lines 12-14, p.25978 is our explanation why the higher BC concentrations during 25-30 September are not related to a biomass burning event. This is a totally different case than the Sicilian biomass burning events. We have clarified this point in the revised version of the manuscript.

Section 3.3. Conclusions based on O/C ratio are overstated considering very indirect estimation of the ratios based on studies from often different continents. To me 2 decimal places of the estimated O/C ratios are not justified based on the above uncertainty. I suggest stating uncertainties after introducing the calculations and then presenting and discussing ratios with a single decimal point without error.

Response: We agree with this point. We present and discuss the ratios with a single decimal point in the revised version of the manuscript, after introducing the calculations and stating the uncertainties.

P25980, line 2. It should be noted that PMF was run on OM mass spectra only. There are studies when PMF was run on all fragments.

Response: Corrected

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Line 3. 1 factor solution is not a solution – it's the total OM. Discussion should start from 2 factor solution.

Response: Corrected

Line 10. Provide number for "relatively well".

Response: Added

Line 12-13. Replace "splitting behaviour" to "split factors".

Response: Corrected

Line 13. "new factor profile" to "unique factor profile".

Response: Changed

Table 1. 2 decimal places are optimal considering precision. Make numbers uniform.

Response: Done

Figure 2. Daily filter measurements should be presented as a step line, not a point. A step line will make it clearer for the visual agreement/disagreement.

Response: The figure has been redrawn.

Figure 5c. Make order of factors from top to bottom same as in 5b.

Response: Corrected

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 25969, 2013.

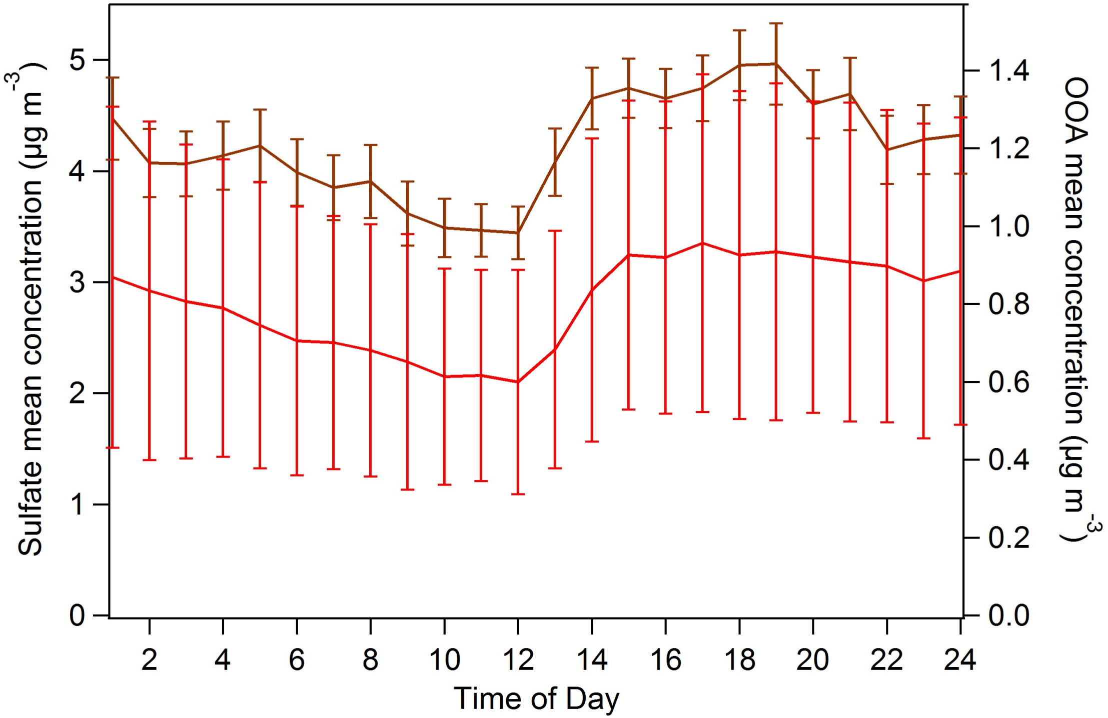
Sulfate mean concentration (µg m^{-3})
0
1
2
3
4
5
OOA mean concentration (µg m^{-3})
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
2
4
6
8
10
12
14
16
18
20
22
24
Time of Day

Fig. 1.

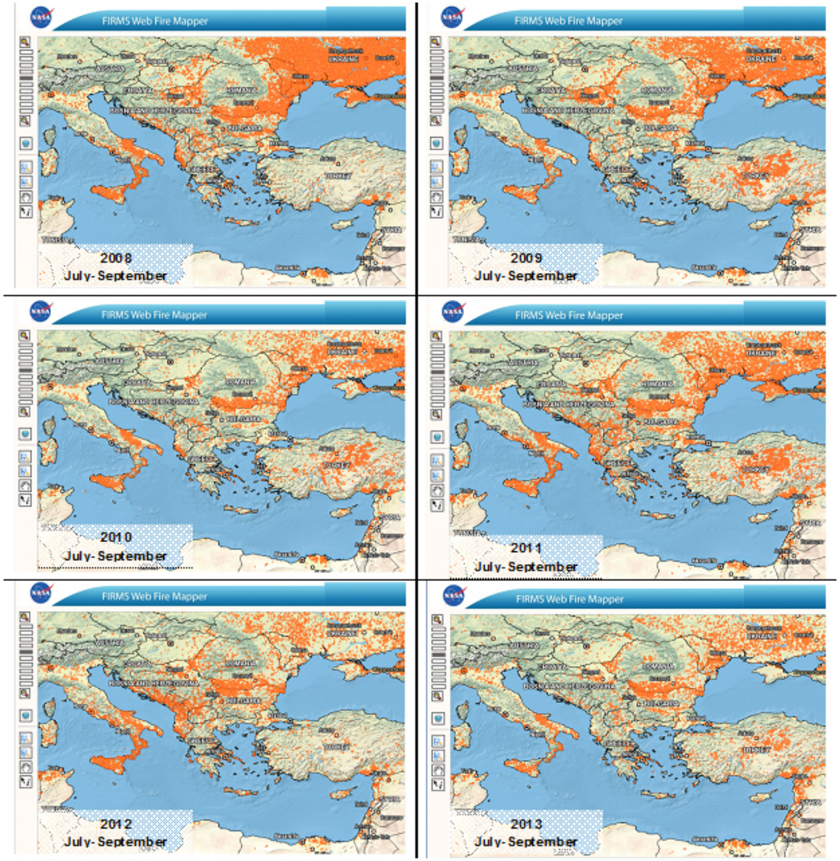

Fig. 2.

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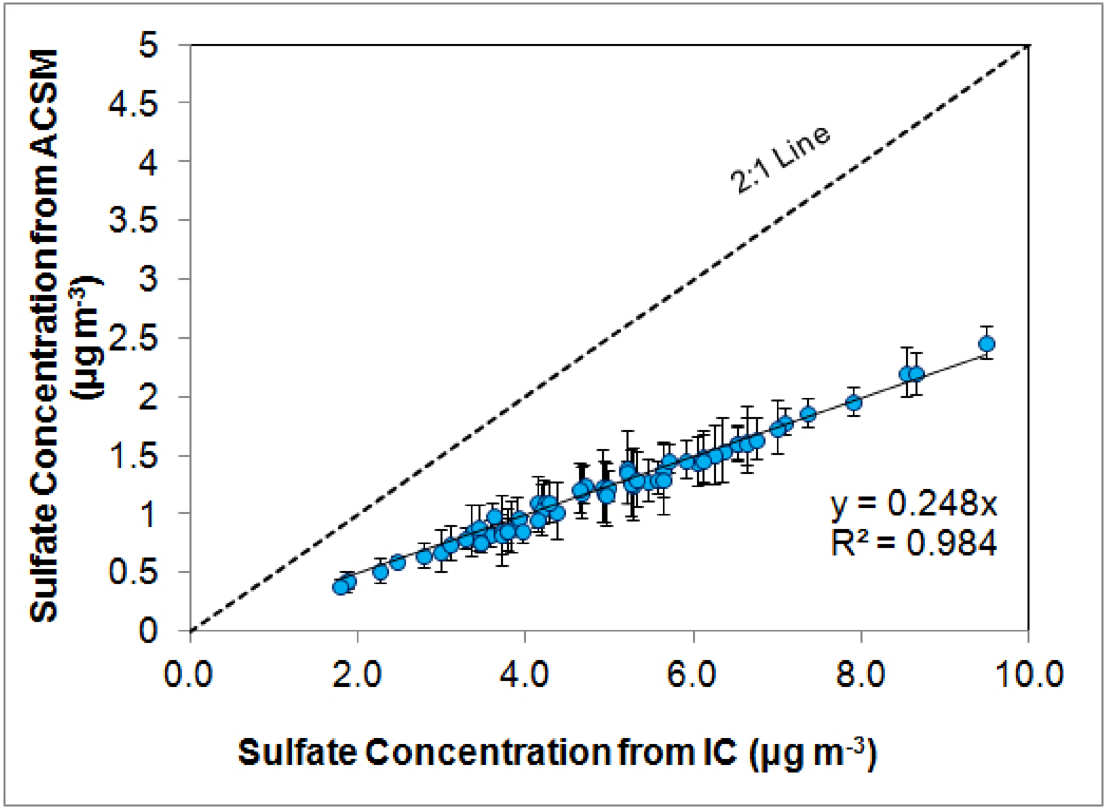
Sulfate Concentration from ACSM (μg m^{-3})
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
0.0
2.0
4.0
6.0
8.0
10.0
Sulfate Concentration from IC (μg m^{-3})
2:1 Line
y = 0.248x
R² = 0.984

Fig. 3.