Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on "Source apportionment of atmospheric aerosol in a marine dusty environment by Ionic/composition Mass Balance (IMB)" *by* João Cardoso et al.

João Cardoso et al.

casimiro@ua.pt

Received and published: 30 April 2018

Interactive comment on "Source apportionment of atmospheric aerosol in a marine dusty environment by Ionic/composition Mass Balance (IMB)" by João Cardoso et al.

These authors answers, together with changes added to the initial manuscript are also present in the annexed pdf file.

Anonymous Referee #1 Received and published: 2 April 2018

This study applied a method called IMB for source apportionment in Cape Verde, and compared the results with those from PMF. Essentially, the IMB method is nothing more

than linear combinations of weighted concentrations of PM components. It might be acceptable to identify some factors with known and relatively ïňĄxed ratios between species, e.g. Na and Cl in sea spray and metals and oxygen in dust, however, it is of limited use when handling sources with similar components but varied weights.

Answer: We do not agree with the referee. Of course that the IMB is not a full solution to Source Apportion the atmospheric aerosol. However, partial mass balance has been used in the past in a multitude of situations to partially apportion the atmospheric aerosol with success. Here we extend this methodology further in order to apportion the totality of the aerosol mass, obtaining aerosol fractions that fit completely in the total PM mass and that give interesting and important information concerning sources and formation processes. This information is complementary to information obtained from PMF and is quite useful to test the accuracy of the PMF obtained solution. The "European Guide on Air Pollution Source Apportionment with Receptor Models" (http://publications.jrc.ec.europa.eu/repository/bitstream/JRC83309/lb-na-26-080-en-n.pdf) clearly alleged in page 19 that "Receptor Models can be used in combination with independent methodologies (e.g. emission inventories, chemical transport models (CTMs)) to achieve more robust estimations by mutual validation of the outputs". In this paper we wanted to show that IMB may help in the obtaining of a more real and accurate solution than that the one obtained only with PMF. This will be especially important when the various source emission impacts in the receptor covary in time, situation in which methodologies such as PMF are unable of completely separating the different sources of Secondary Inorganic Aerosol (SIA), as it was the present case. We would like to emphasize that in the review of ambient particulate matter source apportionment results obtained using receptor models achieved by Belis et al. (Atmospheric Environment 69 (2013), 94-108) it was stressed that "SIA" was the strongest source for PM mass concentrations over Europe. These authors also declared that "SIA" contributions increased significantly when PM10 and PM2.5 concentrations, respectively were above the normative limit values. However, in most of the studies that were reviewed "SIA" was mainly composed of ammonium- sulphate and nitrate

and only one third of them reported sulphate and nitrate contributions separately. It should also be noted that SIA levels thus determined could be underestimated since other secondary inorganic contributions were included in the classical "Sea/Road Salt" and the "Crustal/Mineral Dust" categories (Belis et al., Atmospheric Environment 69 (2013), 94-108; Atmospheric Environment 85 (2014), 275-276). From these results it can be concluded that in general terms RMs currently used were not able to provide a rather-full discrimination of different secondary inorganic contributions to the PM mass registered at a given receptor site.

The factor of "noncarbonate Carbonaceous elemental and organic matter" showed exactly the limitation of this IMB method, as OC and EC may come from multiple anthropogenic sources but this method failed to separate them. OC is additionally contributed by secondary process which was also not able to identify by IMB. If performing well, PMF should be able C1to identify the multiple sources for OC and EC, as evidenced in many other places in the world.

Answer: We agree with the referee in relation to the limitations of the IMB method to completely separate and identify all the sources responsible for the carbonaceous matter, because these sources contain other substances besides carbonaceous material. But we continue to disagree with the referee about the capability of the IMB method to provide useful information concerning carbonaceous sources and formation processes. In the present case we did not invest much in separating the non-carbonated, carbonaceous component into fractions, because concentrations are quite low and, for EC, very near the limit of detection of the system analysis capabilities (very low concentrations of EC in a matrix with quite high concentrations of interfering colored dust). In the present case, the total contribution of non-carbonate carbonaceous matter to PM10 is only of the order of 2%. However in another situation where we are applying IMB (concerning urban pollution), where contribution of carbonaceous mater is of the order of 50%, we could separate the carbonaceous matter into biomass burning, primary fossil fuel emission by cars and secondary formation processes. For that, we

used levoglucosan measurements, edge lines for EC, versus OC versus fine K, versus levoglucosan and known ratios taken from specialized literature. In this urban data the biomass burning mass contribution compared very well between IMB and PMF (results to be submitted for publication, soon). This is a demonstration of the capabilities of IMB in "more complex" situations.

The fact that the IBM results happen to be consistent with PMF ones is that the PM contributing sources in Cape Verde is quite simple, which cannot sufïňĄciently justify that this method is also applicable in other places with complicated contributing sources. In contrast, PMF has seen successful applications around the world with distinct environmental conditions. Therefore, I consider the approach applied in this study had signiïňĄcant drawback, and the limited scientiïňĄc signiïňĄcance of this study does not meet the standard of Atmospheric Chemistry and Physics.

Answer: Part of the answer to this commentary has been given in the two previous answers. Here we will only complement the previous exposition. First, we want to stress that we do not have the intention of showing that the IMB should substitute the PMF, neither that it is better. We defend that IMB is a good methodology that extends and deepens frequently used methodologies in the past, which by being able of explaining the total PM mass is therefore more constrained and secured than previous incomplete attempts and that is complementary and useful to evaluate PM sources and formation processes in conjunction with other employed methods, such as PMF. The present evaluated aerosol is simple in what concerns the number of source contributions, taking into account classic air pollution considerations. But it is complex in which concerns collinearity of concentration variations because anthropogenic industrial and transport pollution are originated from the same directions than the sources of dust. Also, dust is emitted with different compositions in different parts of Africa and is important to know the dust contributions from each region. For telling the truth, neither the IMB, nor the PMF, were capable of fully discriminating the regional origins and contributions of the African dust. As demonstrated in the text now added to the manuscript, in the present

situation the PMF could not completely separate even sources such as Sea-salt and Dust, because of the common composition of dust and sea salt, concerning major ions. In many occasions PMF calculated zero sea salt contribution (impossible for a place in the middle of the ocean); in other occasions PMF considered important contributions of Al and Si in the sea salt component. So, this is not a "quite simple" situation.

Anonymous Referee #2 Received and published: 19 March 2018

Some improvements have been made in this revised version and I recommend publication in ACP. The paper reported the development of mass balance models for source apportionment of aerosol particles and the models were compared with PMF model. Results showed good agreements between the two models. I have following questions about the ionic mass balance (IMB) model as highlighted below. (1) Is that possible to compare the mass balanced model developed in the present study with previous works, such as Malm et al., 1994 (JGR, 99, 1347), and other mass balance model thereby to further demonstrate the usefulness of new model.

Answer: The reference in consideration was added to the paper and several sentences were added to the text comparing IMB with previously published Mass Balance attempts.

(2) I would suggest to add some discussions about the robustness of the new IMB model C1as compared with PMF.

Answer: Text is added to the manuscript where the subject is discussed.

(3) Authors mentioned uncertainties in multivariate methods, such as PMF, are there any uncertainties in IMB model developed and applied in this study?

Answer: We have added a subsection in the manuscript where uncertainties for the IMB method are presented and discussed.

Anonymous Referee #3 Received and published: 28 March 2018

This paper analyzed elemental and some ion data in PM10 acquired from Cape Verde, an island west of the African Continent, with the attempt to determine the contributions from Saharan dust, sea salt, and their derivatives due to atmospheric transformation. Their approach is mainly based on ion balance, assuming known crustal and sea water chemical composition and the sequence of cation/anion neutralization. The mass and ion closure result from the approach generally make sense, especially when accounting for the residual water content. However, uncertainties were not provided for each contribution estimate, as PMF and other receptor models usually did. In many cases, the authors picked a middle value from a range of possible ratios, such as the water/soluble dust ratio, Fe/Na+ ratio, Mg2+ss/Na+ss, ratio, etc. to carry out their cal culation. Is it possible to propagate uncertainties in these assumptions throughout the calculation and give an overall uncertainty estimate in Table 3? The uncertainties should be compared with those from PMF based on the bootstrapping or DISP methods. Answer: We have added a subsection in the manuscript where uncertainties for the IMB method are presented and discussed.

In fact, the dust Fe/Na+ ratio (3.7) determined from the edge line (Figure 2) is based on only 3 points and the ratio falls at the low end of possible range of Fe/Na ratio for Sahara dust. It is nearly impossible to iňĄnd a period with zero sea salt contribution at the island, and therefore using the edge line to determine the dust Na+ fraction is risky. At the very least, uncertainty in this method should be given and propagated into all subsequent calculations.

Answer- In this point we do not agree with the referee. This methodology is much better than the known alternative, which is to attribute all Na+ to sea salt production. In reality the edge line is not based in 3 points only (see Figure presented in the annexed pdf file). If we use an estimation taking into account predicable measuring analytical errors, the Fe/Na+ edge ratio is based in 10 points. As important, the edge line intercepts the x axe at Na+ levels within the range of values (represented by the blue rectangle) referring to periods without significant dust intrusions, in accordance with the fact that there is

always sea salt spray in this marine atmosphere (The subject is further discussed in the new added sub-section 4.5).

When the authors compare IMB and PMF source contribution, they only compare the average contributions for the three periods. It is also meaningful to compare: 1) correlation of respective source contributions determined by the two methods across individual samples and 2) chemical composition of corresponding sources/classes, particularly the sea salt and dust sources, to examine whether the authors' assumptions in IMB, such as the aforementioned $Fe/Na+$ ratio, are consistent with PMF. These comparisons should be presented and discussed explicitly.

Answer: New figures with individual comparisons between IMB and PMF (Figure 6a, b, c and d): Comparisons were discussed in added text, showing the capabilities of IMB to source apportion the aerosol.

Additional comments:

Page 10, Line 16. What is the range of this F factor? Can this be propagated into the uncertainty estimate?

Answer: The subject is discussed in new sub-section 4.5 (see annexed file).

Page 10, Line 33. Does $K+$ (and perhaps $Cl-$) generated from biomass burning need to be considered in the IMB for the region?

Answer: The amounts of possible bio-mass burning material are so small by comparison with other sources that any tentative to detail this source is mostly speculative.

Page 13, Line 12-19. How does the assumption of average inorganic and organic water growth factor inïňĆuence the mass closure, and the contribution of each source to PM10? Can the range be estimated?

Answer: The subject is discussed in new added 4.5 sub-section (see annexed file).

Please also note the supplement to this comment:
https://www.atmos-chem-phys-discuss.net/acp-2018-10/acp-2018-10-AC1-supplement.pdf