

Interactive comment on “Geochemical perspectives from a new Aerosol chemical mass closure” by B. Guinot et al.

B. Guinot et al.

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Dear Editor,

We thank Anonymous Referee # 1 for the fast and complete review. Please find below the answers which are embedded in the AR#1's text review below. Manuscript will be corrected accordingly.

Anonymous Referee #1 Received and published: 6 December 2006

General Comments: The paper presents a novel approach to mass closure which could be used when no elemental analysis is available. The paper is well written in English but some errors are present in the text (see technical corrections), methods and assumptions are clearly described and an evaluation of uncertainties is also given.

A major criticism about this work relies on its “self-consistency”. To be proposed as a valuable and robust alternative method, the comparability of its results should be proved against those given by more traditional approaches for mineral dust assessment.

The method presented here provides arguments to retrieve the mineral dust and the POM contents of aerosols. The reviewer concern is actually about the self consistency of dust retrievals and we are able to answer this important point.

Traditional methods are based on a “mean desert composition” and rely on the multi-analysis of dust metals and subsequent linear correlations (accounting for oxygen and hetero-atoms) such as:

$$\text{Mineral dust content} = 2.20[\text{Al}] + 2.49[\text{Si}] + 1.63[\text{Ca}] + 1.42[\text{Fe}] + 1.94[\text{Ti}] \text{ [E1]}$$

(from: Pettijohn F.J. . In : “ Sedimentary Rocks ”, “ Earth data ”, (NY, Harper and Row), 1975)

We cannot offer to make such calculations based on our own measurements due to lack of elemental data. However literature data on Beijing aerosols provide metal content of dust and we are able to provide a comparison between the two approaches. Table T1 presents our f ratios in Beijing city compared to calcium-to-mineral dust ratios (similar to f by definition) estimated from the elemental analysis results obtained in Beijing by He et al. (2001) and Sun et al. (2004). The f ratios calculated from both methods are indeed found highly comparable - and sometimes even identical like in winter 2003. These results thus support our simple method as a valuable and robust alternative to assess mineral dust content in aerosols.

We would like to emphasize that our method is simple and has moderate costs regarding time and man-power demands and analytical costs (12028 from line 8). Furthermore, whereas traditional methods for dust content evaluation have limitations, our method is based on experimental data obtained at the

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given site of interest. Indeed, it may be recalled that dust has not a single composition and a relationship such as E1 should be adapted to each situation (Elred, 2003)* which by far is not the case. *Elred Bob, “ Evaluation of the equation for Soil Composite ” Internal memo to IMPROVE Staff , 2003. http://vista.cira.colostate.edu/improve/Publications/GrayLit/023_SoilEquation/Soil_Eq_Evaluation.pdf

According to the referee’s opinion the title is a little bit confounding (especially the words “geochemical perspectives”) and it could be simply changed in “A new approach for aerosol chemical mass closure”.

Regarding this point in particular, we believe that our method which is based on data obtained at the site definitely brings interesting geochemical insights on dust sources from the consistency of f values and their small variations. As an example, different f values obtained at different sites in Beijing region (suburbs and downtown) suggest different origins and results are consistent for the 3 experiments.

Table S1. Comparison of urban f ratio obtained in Beijing by our study and by dust metal analysis (data presented for f ratio coarse // f ratio fine)

This work: Winter 2003: 0.07 // 0.07 Summer 2003: 0.12 // 0.12 Summer 2004: 0.09 // 0.09 Sun et al. 2004: Winter 2003: 0.07 // 0.09 Summer 2002: 0.10 // 0.08 He et al. 2001: Year 1999-2000: nd // 0.10

Specific Comments:

In table 1 the worst results are for Florence monitoring station: have any explanation for this? As regards to Florence results, in page 12039 lines 17-19 the contribution from biomass burning is intended to be wood burning for domestic heating? If it is the case, differences between the wintertime vs. summertime results would help in the identification of the real cause of differences between Paris and Florence. On the other hand, if you mean biofuels instead of biomass burning you should specify it.

Biomass burning in Florence can explain the poor correlation between BC results from

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the two thermal and thermal-optical methods. Indeed, the residential use of wood is one of the main contributors to BC concentrations in Florence in winter, along with a complex emission pattern from traffic (Cachier et al., 2004). But distinguishing the wintertime results from summertime to identify the real cause of differences between Paris and Florence would not help significantly, since higher summer temperatures in Florence result in higher photochemical transformations, which thus sustains a higher k value all the year long (1.5 compared to 1.4 in Paris).

Page 12026 from line 27: The “burning procedure” that you cite, apart from differences in temperatures, is what is usually called “pre-firing” to obtain low blank values? How the pre-firing of the blank filter can influence and minimize sampling artifacts? Moreover, how can you get rid of negative artifacts heating the samples prior to analysis? Please specify.

The “burning procedure” mentioned will be changed in “pre-firing procedure” in the final version. Pre-firing blank filters at high temperatures (600 to 900°C) for several hours activates the filter surface matrix enhancing the potential capture of VOC during sampling. We checked that filter pre-firing at 400°C during 48hr is a valuable alternative (blanks of the same order and VOC capture minimized as shown by filter blank value evolution).

We apologize for mentioning negative artefacts which is not true (page 12027 line 5), since only positive artefacts are get rid when heating samples at 60°C for 15 min prior to analysis. This will be discarded in the final version.

Page 12030 and Figures 1a, 1b: the problem due to heated inlets for TEOM is well known and here it is not clear the relevance of this observation. Both the text and the figures could be eliminated.

The results presented in this paragraph intend to show that, at present, chemical mass closure can only be attempted using weighed filters, or TEOM data obtained in summer only. They also underline the particular conditions met in Florence atmosphere

where semi-volatile VOC's much more than ammonium nitrate are the main agents for this artifact. This subsequently supports the earlier remark regarding the differences between Florence and Paris k results. A sentence will be added in the final version to better precise the site specificity.

Page 12039 line 1: what the authors mean exactly with the sentence “photochemistry giving a more important abundance in summer than in winter for nitrates” ? Generally, low temperatures and low mixing layer heights favour nitrate particulate phase during winter periods.

Yes we were not clear enough. The nitrate capture mentioned in the text refers to the capture of gaseous (acidic) HNO_3 by basic mineral dust. A sentence will be added to make it clearer.

Page 12040 paragraph 5.3: why these results should give consistency to your protocol? Please clarify what you mean exactly. In table 4 the choice of different stages appear to be a little bit “subjective”

The chemical characterisation performed on cascade impactor should allow to attempt chemical mass closure on each stage. However, as the different modes overlap for some bins, we preferentially worked out the chemical mass closure at stages where this problem is not encountered. The similarity, at both modes, between the f and k results obtained from this single-sample analysis on impactors and the mean campaign results obtained from SFU samplings, suggests that our method may consistently apply to different sampling procedures. This is the purpose of this paragraph 5.3 as it will be clarified in its last sentence.

Page 12030 lines 10-12 and page 12031 lines 28-29: why in Paris the unbalanced Ca^{2+} is only considered as carbonate? How can you exclude the presence in the coarse mode of compounds similar to those found in Beijing? Finally, it is not always clear if you consider the carbonate a soluble or insoluble species.

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As coarse NO_3^- and SO_4^{2-} concentrations are relatively lower in Paris than in Beijing, this result suggests that Ca^{2+} may be largely neutralised by carbonate in Paris. However, we agree that it does not constitute a systematic argument to assess the presence or not of carbonate. In this regard, the sentence about Paris (Page 12030 line 9) will be removed, while the general final sentence (Page 12032 line 1) will be modified as “It is not excluded that a significant portion of Ca^{2+} is possibly present as CaSO_4 or $\text{Ca}(\text{NO}_3)_2$ ”.

Page 12040 line 8: the ratio is BC/CO or BC/OC?

In the ratio BC/CO, CO refers to carbon monoxide.

Technical corrections: We are grateful to AR#1 for the technical corrections notified, which will all be taken into account in the final version.

All references reported in the text should be carefully checked as they present a lot of errors (many differences in years between references in the text and those in the “reference” section; moreover, Guinot et al. 2006 is not reported). Page 12025 line 1: SFU is “stacked filter unit” Figure 3a: the caption left/right should be changed in top/bottom Page 12027, line 17: the Birch & Cary protocol is generally referred to as NIOSH 5040 and not NIOSH 5054, please check it. Figure legends and axes are difficult to read. Figure 3b and 3c are identical despite the description in the caption !

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 12021, 2006.

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