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Atmospheric
Chemistry
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Discussions

Interactive comment on "Organic functional groups in aerosol particles from burning and non-burning forest emissions at a high-elevation mountain site" *by* S. Takahama et al.

Anonymous Referee #1

Received and published: 21 March 2011

The submitted manuscript presents a 6 months time series of organic functional groups (OFG) measurements using FTIR performed at a high elevation mountain site in Canada (Whistler Peak, 2182 masl). This long observation period were characterized by frequent inputs of biomass burning aerosol. Statistical analysis (PMF and hierarchical clustering analysis) were carefully performed in order to quantify the major sources of the observed organic aerosol and to establish OFG composition of these sources. The results presented here are very interesting and I recommend their publication in ACP. Nevertheless the manuscript is particularly unclear. This is mostly due to a lack of structure (10 pages for section 3.3 without clear subsections, no subsection for section 2) and a quite "anarchic" mix of the results obtained here and results previously

published (section 3.3). This is also difficult to identify the real focus and the "take home messages" of the paper. The abstract illustrates well this lack of focus. I am not sure that the main conclusion of the paper is a comparison with results obtained 1 year before and 1000 m below. This part (section 3.4) is from my point of view useless. Therefore the manuscript needs some clarifications and improvements before publication in ACP.

General comments

1/ The introduction is too broad and leaves little indication as to what the rest of the paper covers exactly. Why OFG measurements are important for assessing radiative impacts of aerosol particles? More generally why OFG characterization is important in aerosol science? Also I would have like to read a short synthesis of previous works regarding chemical characterization of wood burning and the influence of aging on this chemical composition in terms of functional groups composition or overall chemical composition(typically AMS results as AMS results are used in this study).

2/ The section 2 (Methods) is particularly difficult to read. Please make subsections (ie sampling site and particles collection, Organic functional groups analysis, AMS etc..) and reorganized the text. Some parts can be shortened and simplified (ie sample collection). In this section a lot of analytical approaches or instrumentations are described but their results are barely used in the discussion (ie SMPS, UCPC, XRF). Some of these descriptions can be moved in Supporting Information.

3/ As OFG is the central point of the results discussed in the paper I would have like to read more information's about this analytical approach... I am aware that this method has already been described by Russell et al 2009, but in this paper the authors have to describe this method more carefully. How the method is calibrated (one compounds per function, or a mixture, ..) ? What are the detection limits ? What are the uncertainties associated with your OFG concentrations? Is there any shortcomings or biases? Due to this lack of details, I have several issues regarding the significance of the results.

3.1. All the concentrations are given in μg/m3. But what does the mass exactly represent? This point is not clear. For hydroxyl groups, does the mass represent the OH or C-OH mass? The same for non acidic carbonyl (O or C=O)? This issue is particularly important for alkanes. Does the mass correspond to all the C-H (even C-H associated with primary or secondary alcohols or aromatic compounds) or only C-H from aliphatic compounds? In such conditions, isn't it easier to discuss the results in mole of function/m3? 3.2. This issue is directly linked to the previous one. The % of functions given in the results section do not correspond to functionnalization rates as calculated by Dron et al, ACP, 2010 (for example). From my point of view, functionnalization rates are the most interesting information provided by OFG analysis. Is it possible to assess such functionnalization rates with your results? (you need OC concentrations in order to calculate the total molar concentration of Carbon, do you measure OC/EC in your study?) 3.3. Black Carbon (or Elemental Carbon) contains a lot of C-H functions associated with aromatic rings. Is there any biases induced by this specific organic fraction on your results related to OM? 3.4. Page 2658 line 14 you state that FTIR provides concentrations of aromatic groups. Why aromatic concentrations are not presented in the manuscript? Considering the abundance of aromatic compounds in biomass burning aerosol (methoxy-phenols, PAHs, ..) I am pretty sure that it is not a problem of detection limit. 3.3. I suppose that OM concentrations discussed in the text correspond to the sum of individual functional group concentrations calculated in your samples. Please specify this in the text. Also as aromatics are not measured here, as well as the ether or alkene functions, OM concentrations are potentially under evaluated. Do you have an idea of the magnitude of this bias? And more generally the uncertainties associated with these OM values (at least the sum of all uncertainties associated with each functional group quantified)?

4. You observed a strong biomass burning event between July 28 and August 8. Considering fig 2, there are very little differences of the OFG relative contributions with the other periods. You suggest that this uniformity of the OFG fingerprints along the campaign can be explained by chemical aging of the OM. I globally agree with this assumption, especially for BB aerosol. On the other hand, I believe (maybe I am wrong) that OFG of the total OM are mainly driven by HULIS functionalization. If true these observations suggest that HULIS are reactive.. What is your feeling on this issue?

5. I do not understand very well the complementarity of hierarchical clustering and the PMF analyses. In other words, PMF analysis was not sufficient? (This section is also particularly difficult to read, please try to simplify)

6. I am very surprised by the OFG fingerprint of BB inferred by PMF (fig 11 and 12). BB OFG exhibits a huge contribution of alkanes ($\sim$40%) and a very small contribution of hydroxyl group ($\sim$5%) (even smaller than that reported for fossil fuel combustion aerosol !). Biomass burning aerosol particles are however associated with the huge amounts of levoglucosan (C6 compound bearing 3 OH groups) plus other sugars and of methoxy-phenols (guaiacyl and syringyl derivatives), but are not known to contain a lot of alkanes (see for example Fine et al, EST, 2002). Can you discuss this issue?

7. Amine concentrations are not discussed in the manuscript. Do you think that primary marine aerosol can contribute to the total amine concentrations observed in your study?

8. Why PMF analysis has not been performed with the AMS dataset? It would have been very relevant to combine AMS/PMF and OFG analyses.

Specific comments

P2656 line 10 : "Ketone".. All along the text non acidic carbonyl function is called carbonyl or ketone or non acidic carbonyl. Please choose a denomination, and clearly define it in the method section.

P2656 line 10 : what do you mean by "forest aerosol"?

P2659 line 23 : "Sizer" instead of "System". P2660 line 21 : What do you mean by 'nearly monodisperse aerosol"? P2661 line 1 : A Single Particle Soot photometer (SP2, Droplet Measurement Technologies, Inc) P2661 line 18 : 120 L m-3 P2664 line 11-12

: Please explain the method used (shortly). What are the implications of the result obtained (slope 1.25). I suppose that you compare your OFG results (OM) obtained in the submicron fraction with the ACMS results. Please specify.

P2664 line 20, 21, 28, 29 : (r=X, n=??) P2666 line 14-16 and line 28. BB is also a combustion. P2667 line 3 : Org/(org+sulfates) ? Not shown in fig 7a. P2668 line 26-27 : Biogenic Part 3, Biogenic Part 1?? Please explain. P2671 : For fig 11, report Fig11A or E instead of fig11a or e P2675 and 2676 : Section 3.4 is useless.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 2655, 2011.