

Interactive comment on “Chemical composition, main sources and temporal variability of PM₁ aerosols in southern African grassland” by P. Tiitta et al.

Anonymous Referee #1

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The paper is a valuable contribution to the body of knowledge of aerosol chemical composition in poorly characterised regions like South Africa or African continent in general, however, geographical aspect of the paper is probably the most valuable one. A validation of the usefulness of ACSM is indeed essential to the aerosol community, but that is rather a technical issue, not scientific. The paper is well written and data analysis is largely correct, but provides limited scientific results and, therefore, leaves me wondering if ACP is the appropriate journal for this paper without demonstrating a significant advancement in the field of atmospheric chemistry and physics. I am not objecting the publication of the paper in ACP given a positive opinion of the editor and

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other reviewers, but rather express my concerns. In any event, I believe my comments will help to improve the paper before it can be accepted for publication in ACP or other journal. The paper is well written overall and all the methods and instrument used appropriately, however, there were three major problems:

1. The authors invoke the process of free troposphere entrainment when it suits their argument and tend to dismiss when it does not. While the entrainment is a well known phenomenon and may contribute significantly to the particle population (number) its effect on particulate matter mass is limited due to several reasons:

a) new particle formation from SO₂ oxidation in the upper troposphere produces many secondary particles but they are generally small in size (mainly Aitken mode at best) and, therefore, their contribution to the particulate mass is small.

b) the entrained particles undergo large scale dilution in the boundary layer (at least 5 times or more depending on the boundary layer height and structure) further diminishing their contribution to particulate mass. Considering dilution effect the particulate sulphate mass in the upper troposphere must be an order of magnitude higher than in the boundary layer to account for the observed effects, however, that was not regularly observed on a systematic basis.

2. Quite contrary, in-cloud aqueous phase oxidation of SO₂ can produce copious amounts of particulate sulphate (and other compounds as well), especially that ozone concentration is not a limiting factor outside urban environment. Evaporated cloud droplet residues (even relatively few) will greatly contribute to accumulation mode particle number and particulate mass due to the cubic effect between particle size and volume (cloud residues are at least 2-3 times as big as Aitken mode particles in the upper troposphere making their volume 8-27 times as big). The effect of in-cloud oxidation will be highlighted in minor comments.

3. The significance of the paper would be greatly enhanced if it tried to highlight and quantify secondary biogenic particles. I understand the difficulties having a techni-

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cally limited ACSM, but nevertheless an attempt should be made. Moreover, this result would be of great interest to the modelling community providing an estimate of such an important source. I may suggest two ways of approaching this problem: a) try to focus on SV-OOA in distinctly different air masses – regional (interior Africa) versus the industrial (megacity and various industries) paying attention to correlating species like nitrate. b) possibly PMF can be performed including other than organic fragments which may help splitting contribution of nitrate and sulphate. Supposedly, SV-OOA from continental biogenic sources (excluding biomass burning) should be accompanied by limited nitrate and sulphate. I understand that there were few efforts in running a combined PMF analysis (I am aware of the reasons behind), but there were few studies (e.g. Chang et al. 2011, ACP) with interesting results.

Minor comments

Abstract

How can authors explain BBOA peaking in air masses passed over industrialised areas? Not only it should be better explained in the text, but such statement is confusing in the abstract.

Introduction

P15520, line 6. Be specific about “effect and drivers”.

P15520, line 11. A substantial fraction of petrol in South Africa produced not only from coal, but equally from natural gas as well.

P15521, line 15. Ambient observation data more often used for model validation, not just inputs.

Methods

P15523, line 24. Wrong wording. What is meant by regional background over which air masses pass?

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P15525, line 16. Rephrase “50% transmission range of 75-650nm). 75 and 650 nm are the D50 limits of the lenses.

P15526, line 10-20. My knowledge is that CE is largely determined by chemical composition which affects aerodynamic focusing of particles (due to shape) and flash evaporation (including bouncing). Should be rephrased.

P15527, line 11. Density looks high considering chemical composition observed. The reason behind may be particulate monitor which does not dry particles efficiently and particle bound water artificially increases the derived density. Try to estimate particle bound water content by E-AIM (Extended Aerosol Inorganics Model) model (<http://www.aim.env.uea.ac.uk/aim/aim.php>) developed by the University of East Anglia. OM bound water can be arbitrarily estimated as well.

P15527, line 14-17. Let's start being more specific about species detectable/non-detectable by AMS. Some metal salts (Pb(NO₃)₂) can be quantified (Salcedo et al., 2010), especially that plenty of nitric and hydrochloric acids must have been present in the particle phase due to limited ammonium in this study. Sea salt quantitative detection by AMS has been recently demonstrated as well (Ovadnevaite et al., 2012). Why potassium chloride was singled out, but non-volatile organics was not?

P15527, line 20. Revisit the equation and coefficient of 0.84 after taking into account particle bound water.

Results

P15531, line 13. Consider replacing “arrival of clean background air masses” by “frontal systems”.

P15531, line 17. Not sure about comparing the rural savannah site of this study to Mexico or Beijing megacities.

P15532, line 4. Revisit refractory mass estimation after particle bound water has been estimated.

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P15532, line 26. Consider rephrasing SO₂ to SO₄ conversion by “in-cloud aqueous phase oxidation”.

P15533, line 3-14. Rewrite after considering major comment. Increase in sulphate mass in afternoon can be due to partial evaporation of clouds at higher daytime temperature and convection.

P15534, line 20-23. There was high chance that nitrate and chloride were in the form of nitric and hydrochloric acid, respectively, which could then react with metal oxides.

P15535, line 16. Try to avoid expression of “SO₂ to SO₄ conversion”.

P15539, line 4-5. Consider dilution effect and major comment.

P15539, line 28. Hydrocarbons were diluted with respect to what?

P15540, line 16-17. I am not sure you can claim the difference of 1-2% as statistically significant. Otherwise prove it by standard error.

P15541, line 3. BVOC must have regional source not local. Explain. Be more specific about local household combustion – what kind of fuel was that?

P15542, line 1-8. Rewrite considering major comment. Here you suggest that SV-OOA was from secondary biogenic sources, however, in P15539 you implied combustion source due to correlation with nitrate, BC and CO.

Conclusions

P15543, line 2. Is the difference between 0.8 and 0.7 statistically significant? If yes, prove it.

Figures

I suggest splitting Figure 9 into wet and dry season as it was done in Figure 4 and discuss differences/similarities.

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Interactive comment on Atmos. Chem. Phys. Discuss., 13, 15517, 2013.

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