

We thank the referee for a detailed review of our manuscript. The referee comments were very valuable and we believe that addressing the issues raised by the referee will considerably improve the manuscript.

Referee 1: Major comments 1 and 2 together:

We fully agree about the dilution problem raised by the reviewer, as well as about the plausible contribution of in-cloud oxidation to high sulfate concentrations. We had mistakenly referred to “upper free troposphere” when actually meaning the region above the surface mixed layer affected directly by the local and nearby surface emissions. Clearly, the presence of clouds matters during the wet season, and the vertical layering of pollutants coming from local vs. more distant sources matters in general. Unfortunately, we do not have data above the surface to make quantitative statements. To address the main critics by the reviewer, we modified the lines 6-13 in the first paragraph on page 15533 as follows:

“The most likely explanation for this was the breakup of the inversion layer(s) during daytime, which increased the height of the surface mixed layer and entrainment of air from above. In this way, the high-stack emitted SO_2 and its oxidation product SO_4^{2-} could be brought more efficiently down to the surface. The more efficient mixing during the daytime may also have accelerated the oxidation of SO_2 to SO_4^{2-} by more efficient in-cloud processing of the air, but this phenomenon cannot be verified with our surface measurements. During the dry season, ... “

Referee 1: Major comment 3 a and b together:

We agree with the reviewer that the paper would be improved if secondary biogenic particle could be investigated in more detail. However, it is very difficult to make this assessment of biogenic contribution; even with HR-ToF-AMS data it is not straightforward, unless there are distinct air masses with biogenic sources from different directions. For this dataset, there is not a specific source of BVOC from any specific air mass, but rather there's the homogeneous BVOC source. Therefore we couldn't separate the biogenic factor by PMF.

As the reviewer requested, we calculated SV-OOA correlation coefficients (R) with nitrate for the different source regions, i.e. 0.39, 0.43, 0.53, 0.92 for ACBIC, BG, iHV and VT regions, respectively. Therefore, the SV-OOA factor correlates with nitrate in industrial regions, which could indicate the anthropogenic nature of this factor. It has to be noted that the industrial regions in SA are also located in the areas for which higher biogenic emissions are expected (e.g. savannah and grassland biomes) in the wet season, if compared to the BG (e.g. Kalahari and Karoo biomes). When we study SV-OOA in the f_{44} vs. f_{43} space (Fig.10b), it looks quite similar to PMF factors with “components with biogenic influences” (Ng et al., 2010, Fig 4). Also high BG conc. and moderate conc. differences between the different regions (Fig 11a) support biogenic nature of this factor.

It seems that our SV-OOA is a factor from a variety of mixed sources that are semi-volatile, including at least HOA and biogenic OOA so that a diurnal trend dominated by temperature dependent volatility behaviour as

is the case for NO_3^- . The SV-OOA factor correlates much better with standard SV-OOA ($R=0.83$) than standard HOA ($R=0.51$) (Ng et al., 2011b).

We modified the lines 2-6 in the first paragraph on page 15542 as follows:

“The concentration of SV-OOA (Fig. 11a) showed only moderate differences between the different regions suggesting that major point sources don’t have a large influence to SV-OOA factor. This factor correlates with nitrate in industrial regions and secondly it is quite similar to biogenic SV-OOA in Ng et al., 2010. It has to be noted that the industrial regions in SA are located in the areas for which higher biogenic emissions are expected (e.g. savannah and grassland biomes) in the wet season, if compared to the BG (e.g. Kalahari and Karoo biomes). Overall SV-OOA seems to be a factor from a variety of mixed sources that are semi-volatile so that a diurnal trend dominated by temperature dependent volatility behaviour is observed, similar to NO_3^- . In the dry season, ... “

Spatial variability of OA, sulfate, nitrate, ammonium, BC and chloride concentrations in both the dry and the wet seasons were calculated to clarify differences between the source regions, and added to supplementary material (see plots in the end of text).

Here are the referee minor comments followed by replies:

Abstract

The Industrial Highveld (iHV) source region is a large area including the Johannesburg–Pretoria megacity region with more than 10 million inhabitants. Previous studies have showed that domestic burning for heating and cooking (e.g. Hirsikko et al., 2012) is a significant aerosol source in the industrial regions. Incomplete combustion of coal and wood in ineffective appliances for household heating and cooking are common occurrences in the semi-formal and informal settlements (Venter et al., 2012). Therefore the high quantity of domestic burning and cooking in the megacity region together with grassland fires enhance BBOA factor concentration in the iHV region.

P15520, line 11: This line was corrected to “..substantial fraction of petrol is distilled from coal, as well as obtained from natural gas.”

P15521, line 15: The reviewer is correct that ambient observation data are also used for model validation. The text was modified to read “However, this station is not representative of the inland/sub-continental southern Africa, especially for modeling validation or inputs, since the dominant wind direction is from the open sea.”

P15523, line 24: The regional background (BG) is explained in detailed in Paragraph 2.5.

P15525, line 16. This line was corrected and now reads that 75 and 650 nm are the D_{50} limits of the lenses.

P15526, line 10-20. The effect of particle composition on CE is mentioned later in lines 19-21 (P15526).

P15527, line 11. As the reviewer correctly pointed out, calculated average aerosol density is high. We think that the high density of the aerosols is due to location of Welgegund measurements station: 1) Average oxidation level of organics is high in this study (P15541, lines 23-26) and previous studies have shown that the density of organic aerosol increase with increasing oxidation (e.g. Hallquist et al., 2009), 2) Welgegund station is located quite near the Bushveld Igneous Complex (BIC) that is well known as a highly industrialized area with numerous mining and metallurgical operations (Beukes et al, 2010). This type of industry increase metal aerosols with high density in the sampled aerosols. Density calculation was conducted using SHARP and DMPS PM₁ data including refractory material.

The sampled air was dried so water content was low.

P15527, line 14-15 The sum of the total ACSM mass and BC concentration correlated well with the mass concentration calculated from the DMPS measurements with a correlation coefficient of 0.94. The operating protocol of ACSM during this campaign (RGA type analyzer, oven temperature of 600 °C, sample-filter switching time of 30 s) did not allow for quantitative detection of refractory, crustal and other slowly vaporizing species including non-volatile organics.

P15527, line 20. As mentioned before, RH of sampled air was low, so particle bound water should not effect on results.

P15531, line 13: The text was modified to read "... followed by quick drops in the PM₁ mass concentration associated with heavy rains and/or frontal systems from the west that are associated with relatively clean air masses."

P15531, line 17: We agree with the reviewer that this measurement site cannot be compared directly with megacities, but we wanted to contextualise the results globally because this was the first aerosol mass spectrometer campaign in southern Africa.

P15532, line 4. The RH of sampled air was low as mentioned already before.

P15532, line 26: We rewrote the two sentences in lines 23-26 into the following form: "At least two factors contributed to the high SO₄²⁻ concentrations during the wet season: the more frequent exposure to easterly air masses affected by the IHV area with high SO₂ emissions and the frequent presence of clouds which tends to enhance SO₄²⁻ formation by in-cloud SO₂ oxidation (Shen et al. 2012)."

P15533, lines 3-14: This paragraph was rewritten as explained above in our response to the major comments 1 and 2.

P15534, line 20-23: We agree with the reviewer that there were chance that fraction of NO_3^- and Cl^- were in the form of nitric and hydrochloric acid which could then react with metal oxides. However, it was not possible to detect metals by ACSM so only NO_3^- and Cl^- ions that vaporized at temperature of 600°C were considered. Refractory material including metals was estimated to be 13% of total PM_{10} .

P15535, line 16: We modified this sentence into the following form: "...also due to other factors like the in-cloud oxidation of SO_2 to SO_4^{2-} discussed earlier."

P15539, lines 4-5: We modified the sentence as "...transported from above the surface mixed layer."

P15539, line 28: We modified the sentence as "It is worth noting that most of the hydrocarbons were diluted by mixing of the surface mixing layer and oxidized before arriving at the site"

P15540, line 16-17: Equation 5 was derived from the ambient measurements conducted in Mexico City and provide an estimation of the O:C ratio of the average OA because O/C ratios cannot be directly determined from the unit mass resolution spectra obtained with the ACSM. Relatively large dataset was applied to decreased statistical uncertainty in this work. We therefore think that the biggest uncertainty of O:C values is due to the applicability of Eq. 5 and not statistical significance.

P15541, line 3: Wood and relatively cheap low grade coal are the most common fuels used in household combustion for space heating and cooking in informal and semi-formal settlements (Venter et al., 2012). The formal housing community do not use household combustion to any significant extent in South Africa.

P15542, line 1-8: This paragraph was rewritten as explained above in our response to the major comment 3.

Conclusions

The statistically significant of O:C ratio is already discussed earlier.

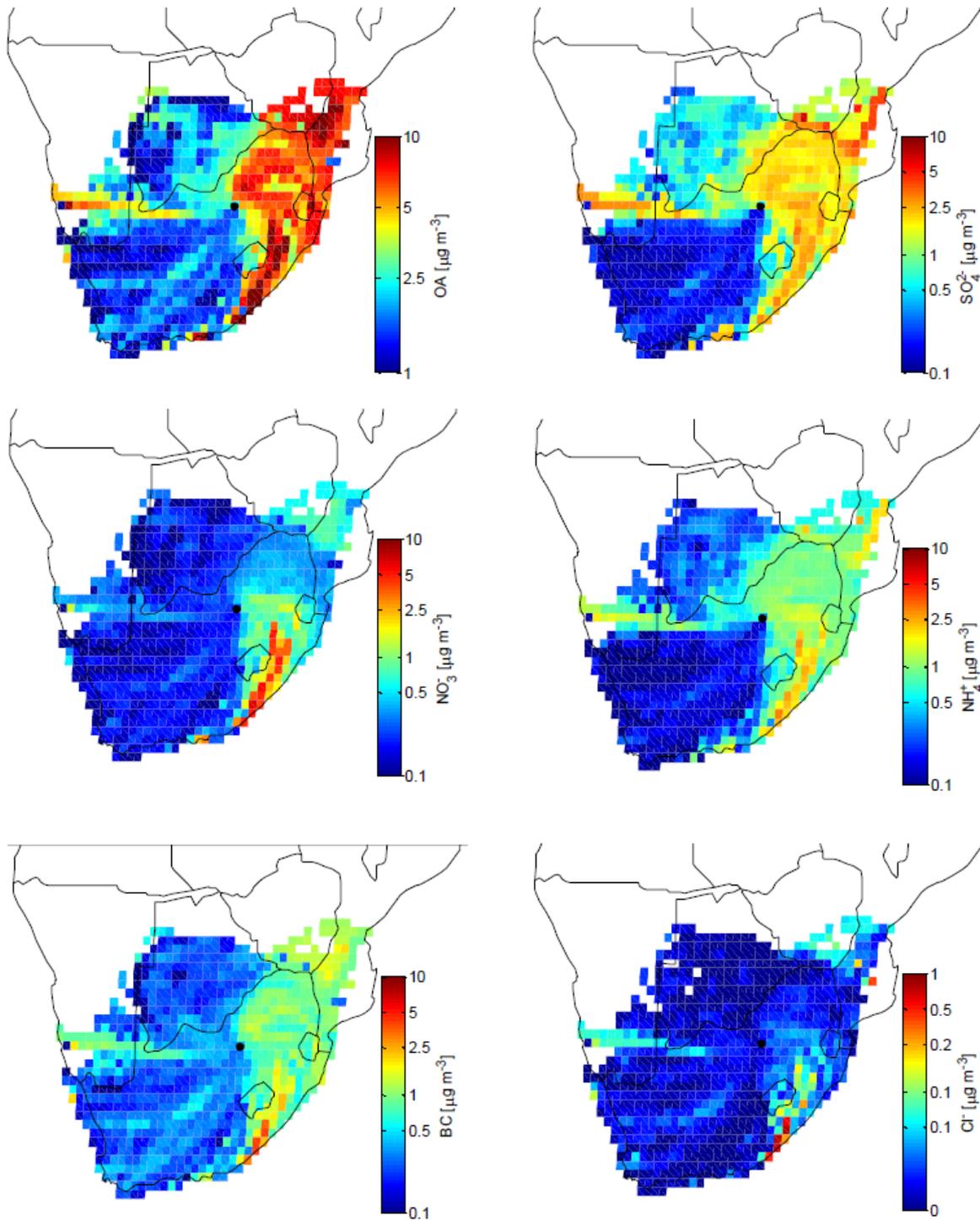
Figures

SV-OOA / LV-OOA factors are already calculated from wet season data and BBOA / OOA factors from dry season data in Fig 9.

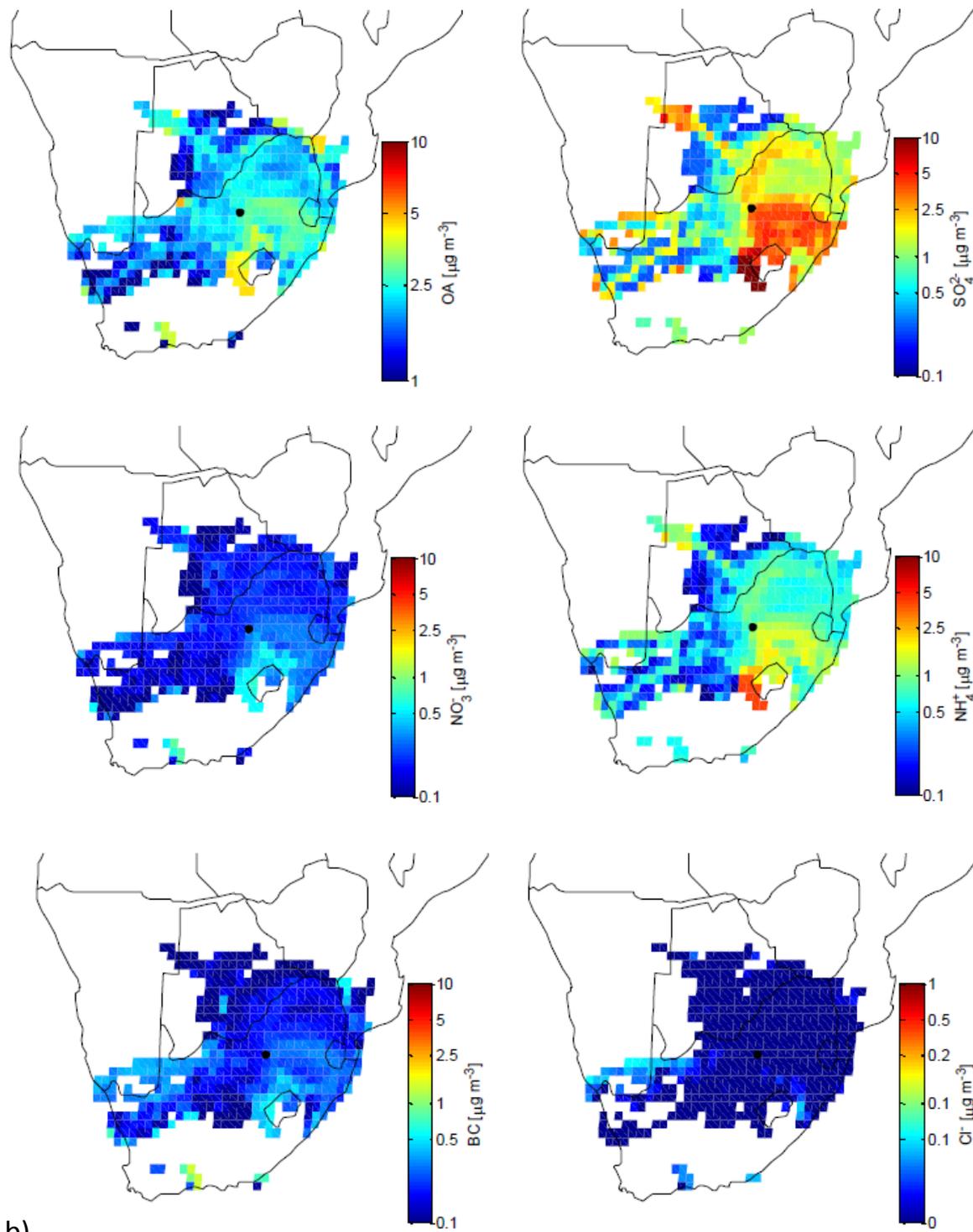
Reference

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D., Szmigielski, R., and Wildt, J.: The formation, properties and impact of secondary organic aerosol: current and emerging issues, *Atmos. Chem. Phys.*, 9, 5155–5236, doi:10.5194/acp-9-5155-2009, 2009.



a)



b)

The spatial variability of OA, sulfate, nitrate, ammonium, BC and chloride concentrations (median values). Concentrations were calculated applying air mass history from back-trajectories similarly to Vakkari et al. (2011) and (2013) in both the dry (a) and the wet (b) seasons.