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Interactive comment on “Measurements of the aerosol chemical composition and mixing state in the Po Valley using multiple spectroscopic techniques” by S. Decesari et al.

Anonymous Referee #1

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Decesari and co-authors describe the detailed composition and chemical mixing state of aerosol detected in the Po Valley, Italy in summer 2009 in the context of meteorology and transport. An impressive variety of off-line and on-line techniques have been employed to investigate the impact of meteorology and atmospheric processing upon the composition of particles detected at the receptor site. Aerosol mass spectrometry (HR-ToF-AMS and SP-AMS) is used to measure submicron aerosol chemical composition and black carbon (BC) coatings. Single particle mass spectrometry is employed to assess the chemical mixing state of BC, and NMR is used off-line for bulk organic aerosol speciation. Inorganic and organic gas phase aerosol precursor measurements

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are also reported using a CIMS instrument. Organic aerosol apportionment is described in terms of the AMS and NMR results and attempts are made to link changes in BC mixing state with meteorology, boundary layer height and mixing. Overall, some interesting data are presented but conclusions are unfortunately drawn based on speculation, in particular with respect to aerosol mixing state as discussed below. Provided that speculative issues are addressed, and conclusions are related to the data more coherently, this article should be suitable for publication subject to the following major revisions.

General comments

While the breadth of analytical techniques employed is certainly impressive, the synthesis of the separate analyses to create a coherent narrative is less so. In its current form the manuscript is simply too long, and the disparate conclusions drawn from the separate analytical techniques need to be interpreted with more care. The reader is referred to the wrong figure in several places, and naming conventions for particle types are confusingly interchanged throughout the discussion. Crucially, conclusions drawn regarding aerosol mixing state using the reported data are highly speculative at times as discussed below. A stronger emphasis should be placed either on the impact of meteorology upon regional air quality in this remote environment (the mixing down of the residual layer aerosol is interesting), or on source apportionment of organic aerosol at this site (the described comparison of NMR and AMS OA PMF certainly has potential), or upon the complementary nature of the aerosol mass spectrometers used and how this helps to determine aerosol mixing state more effectively (as implied by the title). In attempting to address all three of these points none are managed effectively. There are certainly data of significant value here, however, and streamlining the article significantly would make it far more accessible. Assessing detailed aerosol composition and mixing state comprehensively using these complementary tools is a worthwhile undertaking.

Specific comments:

The abstract is overly long and contains some content better suited to an introduction. Streamlining the manuscript would make the content more accessible. In the main manuscript, the laborious description of air mass types is unnecessarily long, involves too many subcategories and therefore cannot be followed when referred to later with respect to aerosol composition. Furthermore, can these features really be described as representative of all other “heavily populated areas... of Eurasia and North America” that exhibit “complex orography”? Meteorology in the Po Valley is not necessarily transferrable to other sites/continents.

Descriptions of gas-phase precursors are also too long and detract from the focus on aerosol composition. It should be reduced down to a brief discussion of the main points- knowledge of gas phase nitric acid and SO₂ mixing ratios and hydroxyl radical concentrations, and how these are related to changes in aerosol chemical composition. The organic gas phase data from the TAG instrument should also be reduced in length with brief reference to aerosol composition where appropriate. Using alkanes to support traffic emissions and benzoic acid to support SOA formation is suitable, but the length should be reduced.

With respect to amines, why is only TMA observed in the ATOFMS data when DEA and TEA are also observed in the NMR OA results? Is there a sensitivity issue? Amine mixing state is mentioned in the abstract but is not described further in the manuscript.

The separation of LVOOA into two factors is also not convincing, and is validated/constrained through a separate instrument that broadly measures aerosol mixing state, not organic aerosol composition. The mass spectra of both factors are almost identical (Fig S7), and the zoomed region of the MS that is referred to in the text is not included. Also, in the main text the splitting of the LVOOA factor is supported through reference to Fig. 10C which does not actually show this data. The middle panel does show benzoic acid vs the LV-OOA-MO factor but LV-OOA-LO is not included for comparison.

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The SP-AMS data are uncalibrated and it is stated that the temporal trends for OA, inorganics and BC are representative of changes in mass concentration. The temporality may be relevant for the individual species, however, in the absence of calibrated RIE values for BC relative to the other species, how can a pie chart such as that shown in Fig. 5 (bottom) be reliable or meaningful? This has implications for the interpretation of BC mixing state too. Why was the SP-AMS not operated alternately in SP laser on/off modes to assess BC associated material vs externally mixed material? Instead the separate HR-ToF-AMS instrument is used for comparison. Thus, knowledge of accurate collection efficiencies and relative ionization efficiencies are important here. Was the thermal vaporizer removed from the SP-AMS completely?

A collection efficiency of 0.5 was applied for the HR-ToF-AMS, and this is stated to be in line with Middlebrook et al (2012), when in fact that study describes that the collection efficiency can be calculated more accurately by considering aerosol composition than using a fixed value of 0.5.

In section 3.5/3.6 why are chemical processes observed in London used to explain aerosol processing at this site? Are the sources expected to be similar? Condensation of nitrate at high relative humidity and low temperature is not specific to London.

Why was a MAC value of 10 m² g⁻¹ chosen for the PSAP absorption conversion to mass concentration?

The description of single particle types is also overly long and could be reduced to simply support the mixing state conclusions regarding BC drawn from the SP-AMS measurements. Why are 8 particle types shown when 12 are identified? Furthermore, the names of these classes change around during the manuscript and do not always match the figures, and therefore this section becomes very difficult to interpret. There are also unsupported claims regarding mixing state. For the EC type, how can an EC core be effectively vaporized while coating material is not? And in the absence of signal for any secondary material how can a regional source be applied here? An isobaric

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interference for OA and potassium is referred to but not assessed. How does the local source of K particles in London inform their apportionment as local here? Where is EC-SUL in the graph? Names change around here and cannot be followed. The ATOFMS data should be connected to the SP-AMS findings more explicitly.

Correlation coefficients are used selectively throughout the manuscript. Why provide this value for LVOOA-MO relative to existing LVOOA datasets but not provide it for LVOOA-LO, for example? Are these very different? The fact that the factors need to be recombined to match the NMR HULIS factors also suggests that they should not be split in the first place. And what is OOA regional? Why is temporality of the SPAMS factors not included in the supplement?

In section 3.7.2 HOA is described as internally mixed with BC. All non-refractory species detected using the SP-AMS in SP mode must be associated with BC to be detected in the first place. The fact that fewer SP-AMS OA factors are resolved than HR-ToF-AMS factors may also be due to the presence of externally mixed OA containing no BC. This would be consistent with the cooking particle type and the rest of the discussion. The end of this section regarding RIE and detection efficiency issues is highly speculative and misleading, with no supporting evidence.

The start of Section 3.8 belongs in the Method section.

Section 4.1 is very speculative, as is Fig. 13. This is unfortunate because this may be the most interesting aspect of the manuscript. There needs to be a clear distinction drawn between what the aerosol mass spectrometers can and cannot confirm regarding this schematic. Conclusions drawn based on speculation are expressed as fact in several places. It is stated that particles exist that contain an EC-sulphate core that is not detected by the ATOFMS when these particles are coated with ammonium nitrate. While partial ablation of a particle is certainly possible, why would ammonium nitrate and sulphate not be mixed, especially under humid conditions, and detected simultaneously in the coating? The core-shell-shell arrangement depicted for these particles

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in the bottom-left of Fig. 13 is misleading as there is no evidence to support that this structure exists. Furthermore, it is stated that “the ATOFMS is probably insensitive to changes in coatings of particles very rich in BC”, but there is no evidence for this. In fact, the reverse has been demonstrated; partial ablation is more likely to highlight changes in coating composition than to result in vaporization of the refractory core only. See depth profiling work by Zelenyuk (2008) and thermodenuder single particle work by Pratt (2009).

Why would the SPAMS sensitivity for coated BC decrease to the extent where these particles are not observed? If anything, coated BC is focused more effectively during transmission through the sizing region and therefore should be detected with greater efficiency than fresh fractal BC, which may diverge from the particle beam (Onasch 2012). Furthermore, if both instruments really were subject to these significant effects, could any solid conclusions be drawn regarding BC mixing state here at all? The final sentence is highly speculative: “The behaviour of these metrics for aerosol mixing state becomes more confused in the afternoon/evening, possibly because of the insensitivity of ATOFMS to some types of organic coatings on the large EC particles”. Again, ablating the EC core should result in detection of the coating material. Selectivity of the desorption/ionization laser for BC-containing particles is more likely to manifest as an overprediction in the fraction of BC-containing particles present in the total population, rather than as a reduction in sensitivity for coating materials.

Discussion of chloride displacement with nitrate for single sea salt particles should refer to Gard et al 1998.

The authors pose questions to the reader at times during the manuscript, which should be avoided.

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