Dear Referee #2,

Please find below your comments in blue and the authors' responses in black.

This manuscript reports results obtained with an Aerodyne Aerosol Chemical Speciation Monitor (ACSM) during a long-term measurement period (1 year) in the Po Valley (Italy). The authors investigated the chemical composition of non-refractory submicron PM (NR-PM1) with a time-resolution of 30 minutes and identified of the main components of the organic fraction. In addition, the parallel multiple off-line analyses were carried out to assess the performance of the ACSM in the determination of PM chemical species regulated by Air Quality Directives. This work is meaningful, and the workload is very large. The observed results are representative because they have been measured for almost one year. It is completely within the scope of Atmospheric Chemistry and Physics. However, the results presented here are a little superficial, and a more deeply analyses on these observation results is necessary. Therefore, I recommend its publication after a major revision.

Specific Comments

Abstract

Although the abstract has summarized the main contents of the text, it is still lack of some points to attract readers. I think the authors have done a lot of works, but they do not have an in-depth analysis on their results. For example, the author did not find the BBOA in summer. While, they only showed the average results in this part and main text. Then some interesting information was averaged and masked. Therefore, I believe other more meaningful results could be found after a more in-depth analysis.

After the comments of referee #2 on 16/09/2015, the abstract has been fully reworded to better highlight innovative results and therefore attract readers. The absence of BBOA in summer is mentioned in the main text (l. 282-283), and further discussed in the supplementary material (l. 68-88; l. 103-117). We believe it has been the subject of an in-depth analysis. In this manuscript, we chose to present results which are representative of a given time-period (e.g. daily cycles, seasonal averages, etc.), in order to recommend PM abatement strategies. Specific pollution events or phenomena are therefore not presented here by choice.

Introduction

Please add a simple introduction on the previous ACSM and AMS research results in this area. Then discuss the innovation of your research is more appropriate.

A simple introduction on the previous ACSM and AMS research results in this area is added accordingly: l.73-76: "In addition, studies based on aerosol mass spectrometer measurements have been conducted in the Po valley, with the aim of characterizing specific phenomena (e.g. fog events, cooking aerosols) or seasons (Dall'Osto et al., 2015; Decesari et al., 2014; Gilardoni et al., 2014; Saarikoski et al., 2012)".

About the article structure.

Section 3 (results) contains : (1) discussion on consistency of ACSM measurements; (2) discussion on organic apportionment quality control. Meanwhile, some content looks like a introduction of analysis method. I think these contents are more like a discussion part not results. On the contrary, the author showed a lot of experimental results in section 4 (discussion). Therefore, I suggest that the author reconsider the article structure carefully and some discussion content could be put in the supplementary material.

The titles of Sect. 3, 3.1, 3.2 and 4 have been reconsidered. The new titles are: Sect. 3 "Quality assurance / quality control", Sect. 3.1. "Quality assurance / quality control of ACSM measurements", Sect. 3.2. "Quality assurance / quality control of organic source apportionment", and Sect. 4 "Results and discussion".

About the language: Some sentences are not easy to understand. While high quality language expression is very important for a high quality article. Therefore, please improve the language after this modification.
We did go through the manuscript and corrected language issues where we found them. In addition the publication shall be proof-read by the editorial office of ACP.

At the beginning of section 4.3, the variations of NR-PM1 chemical composition and OA factors' contributions as a function of total NR-PM1 mass are examined. However, these analysis is not deep enough. According to the results mentioned above, the contribution of every NR-PM1 and OA species to the total is different in four seasons. It means that the pollution characteristics in four seasons may be different. Therefore, I strongly recommend the author to discuss the variation of every species with the change of total NR-PM1 mass for different seasons. Then some common features for four seasons and some unique characteristics for one season could be found. These results are more interesting than that provided now.
The variation of every species with the change of total NR-PM_1 mass has been investigated for different seasons accordingly (Fig. S9, Sect. S4). The following text has been added in the manuscript:

l. 496-499: "In order to investigate the characteristics of fine aerosol pollution events, the variations of NR-PM1 chemical composition and OA factors' contributions as a function of total NR-PM1 mass are examined. This investigation is made on the annual (Fig. 8, discussion below) and seasonal scales (Fig. S9, discussion in Sect. S4)."
Supplementary material: Sect. S4 has been added as follows:
l. 131-142: "The seasonal variations of NR-PM_1 chemical composition and OA factors' contributions as a function of total NR-PM_1 mass is shown in Fig. S9. During spring and autumn, the characteristics of submicron aerosol pollution events are similar to what is described on the annual scale (Sect. 4.3). Nitrate and BBOA are the main responsible for NR-PM_1 concentrations increase. Specific patterns are observed during summer, with i) fairly stable contributions of OA sources irrespective of NR-PM_1 levels, and ii) noticeable proportions of sulfate (~20%). Sulfate is nevertheless not responsible for the increase of NR-PM_1 concentrations. Note that the intensity and frequency of NR-PM_1 pollution events are lower during summer compared to other seasons. Finally, the importance of BBOA in submicron aerosol pollution events is highlighted during winter ([BBOA]~40% of [OA], when [NR-PM_1]> 30 µg/m^3). An increase of HOA is for the first time observed during this season, which indicates that primary sources largely contribute to high NR-PM_1 concentrations during winter."

Figure 3:
(1) "Left, bottom, top right, bottom right" is not clear enough. Figure 3a, b, c, d is better. I suggest the author do the modification in this and other figures.
Figure 3 has been modified accordingly (Fig. 3 a, b, c, d).
Figure 5 has been modified similarly.

(2) This figure looks not every clear.
For example:
The following figure is a part of the relative chemical composition of all NR-PM1 species. I found that the contribution of organic in spring (March-April-May) is lower than 50% (red line) in most of time, and frequently lower than 40%. However, the average contribution reached to 52% in the main text. It looks very strange.
In addition, according to the relative chemical composition figure, it seems that the contribution of organic was 0 some time. However, the mass concentration of organic looks always higher than 0. The same phenomenon also appeared in Figure 5. Please see the following figure: It can be found that the contribution of HOA is almost always higher than 10% (red line), even frequently higher than 30%. However, the average contribution was only 11%.

Referee#2 is thanked for pointing out this issue. There were indeed problems with Fig. 3 and 5 exhibiting the relative contributions of chemical species and OA factors with 30 min time-resolution. These figures have been updated. We confirm that the average contributions mentioned in the text, on the seasonal and annual scales, were correct.

Other comments:

Abstract.

Line 31-33. A detail comparison with other study results is not necessary in abstract. I don't recommend to cite the detailed data results.

Detailed data results - i.e. "(USA, 14.2 µg/m^3)" and "(Japan, 12-15 µg/m^3)" - have been removed accordingly.

Introduction.

Line 50 Please provide the annual PM2.5 mean concentration value. That could make this sentence more convincing.

PM2.5 mean concentration values are provided in this sentence for an urban (l. 52) and a regional background site (l. 53).

Line 69 "2008/50/EC" is a reference or other standard ? It is not easy to understand.

"2008/50/EC" refers to the European Directive mentioned in this sentence. For clarity, this has been replaced by a reference in the text: "(EU, 2008)" (please see references at the end of our responses).

Section 2.1 I suggest the author add a sampling site map in main text or supplement material.

A sampling site map has been added in the supplement material accordingly (Fig. S1, reference in the main text l. 111).

Line 205 Please check the format.

Format modified accordingly.

Line 219 What is the reason for the poor correlation and results difference of chloride ?

Chloride quantification suffers from high uncertainties, both from ion chromatography analyses (l. 248) and from the ACSM (Crenn et al., 2015).

Section 3.2.3 Although the author explained the reasons for HOA was not well correlated with BC, CO and NOx, I still feel confused. What are the main sources of BC, CO, and NOx in the study site ? It looks BBOA has a very big impact on them. In addition, chloride is also an important tracer for BBOA, did you have an analysis of their relationship ?

The main sources of BC, CO and NOx at the study site are fossil fuel and biomass burning. BBOA indeed has a very big impact on them. For example, during winter, Gilardoni et al. (2011) estimated that fossil fuel and biomass burning sources contribute to 51 and 49%, respectively, of Elemental Carbon concentrations at the study site during winter. Gaeggeler et al. (2008) also report high correlations between CO and BC stemming from biomass burning in the alpine valleys.

Chloride in the form of potassium chloride is indeed an important tracer for BBOA. The ACSM analyses non-refractory (NR-) chloride i.e. mostly ammonium chloride (Huang et al., 2010). We thus do not expect to have correlations between BBOA and NR-Chloride here because biomass burning related chloride would be mostly in the form of KCl. As mentioned before, high uncertainties are associated with chloride quantification from ion chromatography (IC) analyses, preventing us from making comparisons between BBOA and IC-Chloride.

Line 376-378 Pleases add the values of the highest NR-PM1 levels reported at rural and urban …….

The highest NR-PM$_1$ level reported i) in Europe (Crippa et al., 2014) is 16.4 µg/m^3 in Barcelona (Spain), ii) in the world (Jimenez et al., 2009; Zhang et al., 2007, 2011) is 63 µg/m^3 in Beijing (China). We found

misleading to mention only the maximum NR-PM_1 levels reported in the previous studies, since it is stated that: "the annual averaged NR-PM_1 mass reported here (14.2 μg/m^3) ranges amongst the highest NR-PM_1 levels reported at rural and urban downwind sites in Europe (Crippa et al., 2014) and worldwide (Jimenez et al., 2009; Zhang et al., 2007, 2011)". We have nonetheless reported that our site has the 7th highest NR-PM1 levels out of 41 sites compared in the aforementioned studies. We also have mentioned that these previous studies are based on typically one month of measurements in different seasons.

Line 385-386 Please add "(Fig. 3)" to the back of this sentence.
"(Fig. 3)" is added to the back of this sentence accordingly.

Line 393 Did you measured the BLH in different seasons ? A comparison on measurement results is more useful.
BLH were not measured in different seasons during the campaign. The fact that BLH are lower during cold months in the Po Valley is well documented in the literature (e.g. Vecchi et al., 2004).

Figure 1 and 2. These figures are very difficult to see clearly due to the too small words. It is necessary to enlarge the font size in the two figures.
The font size has been enlarged in Fig. 1 and Fig. 2 accordingly.

Figure 6. It is not very clear and the font is too small. I suggest that all the figures are divided into two lines. Then the figures will not too narrow.
Figure 6 has been divided into two lines accordingly.

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