Anonymous Referee #1

Received and published: 8 March 2016

In this study, the results from a field campaign in Barcelona (Spain) in which for the first time two ATOFMS were concurrently deployed in a urban background site and a roadside site are presented. The two instruments had different inlet configurations. Although this may have hampered a direct comparison between the two sites, it was useful to be able to detect more efficiently different characteristic particle types that are likely to be anyway rather unique to the specific site. In my opinion the manuscript present interesting new insights into single particle composition and atmospheric processing and it is suitable for publication in ACP after addressing the comments that follow.

We thank reviewer_1 for enjoying the paper, comments are address below.

Page 7, lines7-8: Please specify how air was dried (e.g. Nafion® tube or silica drier) and what the RH downstream was. How often was the drier regenerated to maintain the same RH during the sampling campaign?

The sample air was dried (through a Nafion dryer, Perma-Pure, length 100 cm, RH <40%) before arriving at the instruments. Standard procedures were used to dry aerosols for other instruments including the HR-ToF-AMS, as described in the SAPUSS overview paper (Dall´Osto et al. 2013).

Directions of air masses are often discussed in the text. Please add details on how they were obtained and please show (in the SI) the examples that are discussed, like NAF_W, NAF_E, and regional transport vs. long range, air masses from Europe. Please define NAF_E the first time that it is mentioned.

The air masses have been described in detail in the SAPUSS overview paper (Dall´Osto et al. 2013). Nevertheless, to aid the reader of this article, we have inserted a short section (section 2.3) that provides a brief summary of the air mass origins and the nomenclature used.

Page 12, line 6. Please add correlation coefficient. Is the anticorrelation between LRTNIT and LRT-SUL affected by the "rainy periods" mentioned a few lines after? Does the correlation change if we exclude those periods? I suggest showing rainfall on the timeseries of these two clusters in Figure S1. Why are these two particle types more abundant in the roadside site rather than in the urban background site if they come from long range transport? Does it depend on inlet configuration of the two instruments?

Since the correlations were already reported in previous studies, we have edited the text thus: "The LRT-SUL and LRT-NIT diurnal trends are anti-correlated, as previously described elsewhere (Dall´Osto et al., 2009; Decesari et al., 2014), with LRT-SUL concentrations peaking in the afternoon hours." Additionally, we added suggestions:

" These two particle types were more abundant at the RS site, likely because of the improved focussing of smaller particles provided by the aerodynamic lens inlet " We have also modified Figure S1b as suggested by the reviewer.

In general, are diurnal profiles of particle types detected at the roadside site affected by wind speed and direction considering that the site is closed to a street canyon and therefore wind direction can be a key parameter for transporting pollutants from the street to the sampling site?

The following text has been added to the mansuscript:
"Overall, we did not find major differences in the diurnal profiles of similar particle types detected simultaneously at the UB site and RS site. In other words, there were not major differences that could have been affected by wind speed and direction considering that the RS site is close to a large street canyon."
Further information on meteorological conditions during SAPUSS can be found in Dall´Osto et al 2013).

Page 20-21. I do not find convincing the argument around the Amine (ETS 84) being from tobacco smoke. The diurnal trend itself does not seem to suggest that. Are there any concurrent data that can support this conclusion like gas phase concentration of nicotine or other cigarette smoke markers? Does Amine (ETS 84) correlate with gas phase nicotine in either a direct or time-dependent way? Also, the authors compare the mass spectrum of Amine (ETS 84) with the mass spectrum of a particle type previously reported in Athens. The comparison is done with an analysis of the correlation using r2 but this assumes that data are normally distributed which is very unlikely for a mass spectrum where the multiple null values will definitely cause a skewed distribution. From a qualitative point of view, the mass spectra look actually different in the sense that signals of CN-/CNO- are missing in Amine (ETS 84) which are expected from a combustion source and they were main peaks reported in the cited study in Athens. I suggest being more cautious in relating the observed particle type to tobacco smoke unless additional data are available and reported to confirm this hypothesis.

The following text has been added to the manuscript to address this point:
The ATOFMS cluster Amine (ETS 84) attributed to tobacco smoke was compared to the measured nicotine value described in Alier et al (2013). Briefly, much higher nicotine concentrations (58 ngm^{-3}) were observed at the RS site than at UB site (7 ngm^{-3}). This eight-fold difference pointed to a very high level of outdoor cigarette consumption near the RS site, which is situated next to a busy street and an exit of an underground metro station (Alier et al., 2013). Moreover, nicotine concentrations were more affected by daytime working activities during weekdays rather than during the weekends. ATOFMS cluster Amine (ETS 84) was temporally correlated with nicotine concentrations available at 12 hours resolution, and an R^2 of 0.65 was found, confirming the tobacco smoke source suggested.
Page 23, lines 10-11: The authors suggest that m/z 118 could not be associated to secondary processes as they have found it in two particle types that they relate to fresh emissions. Oxidation processes can occur on a very short time scale and the fact that Amine 58 shows diurnal peaks with 1-h delay respect with rush hours seem to point out that atmospheric processing is occurring on the particles. It would be interesting to show correlations with RH, T and irradiation since, for example, particle

phase oxidation is limited by uptake of oxidants on the particles which is favoured at high RH (Bedjanian, et al. Atmos. Environ. 2010, 44, 1754−1760; Slade, et al. Geophys. Res. Lett. 2014, 41, 5297−5306).

The analysis of the ATOFMS dataset for the RS site shows that the majority (about 80%) of amine particle mass spectra containing a peak at m/z 118 were found in the tobacco related ATOFMS Amine (ETS 84) class. ATOFMS cluster Amine (ETS 84) was temporally correlated with nicotine concentrations available at 12 hours resolution, and an R^2 of 0.65 was found, confirming the tobacco smoke source suggested. We are thus confident in assigning this peak to fresh tobacco emissions.

Page 26, lines 1-3. OC-CHO seems to be associated with oxidation of aromatics by OH radical which is reported also in a previous study from the same authors among other studies (Giorio, et al. Envrion. Sci. Technol. 2015, 49, 3330-3340; Bedjanian, et al. Atmos. Environ. 2010, 44, 1754−1760 ; Platt, et al. Atmos. Chem. Phys. 2013, 13, 9141-9158).

Thanks for pointing this out. The following sentence has been added:
"Cluster OC-CHO could also be associated with oxidation of aromatics by the OH radical (Platt et al., 2013; Giorio et al., 2015)".

Page 26, lines 5-9. I found this part very interesting and I think that more discussion is worthwhile to add about the atmospheric processing at different times during the day.

Given the qualitative aspect of any ATOFMS study, we prefer not to speculate too much. However, the following sentence has been added:
"This is likely to be governed by a combination of emissions from local sources during rush hour periods, as well as by meteorological parameters such as atmospheric wind speed, wind direction, relative humidity and temperature."

Page 29, line 21. Authors suggest that concentrations of ammonia are higher at the roadside site. Emissions of ammonia from vehicular traffic have been widely reported and they are likely to increase in the future because it is not a regulated pollutant (Suarez-Bertoa, et al. Environ. Sci. Pollut. Res. 2015, 22, 7450-7460).

We have added the following text to address this point:
"Emissions of ammonia from vehicular traffic have been widely reported and they may increase in the future because it is not a regulated pollutant (Suarez-Bertoa et al., 2015)."

Page 30, lines 18 to 23. I do not fully understand this paragraph. May you clarify the discussion around the different amine types and different formation processes and how these are linked to the observations? There is a lot of information but I am not sure I can follow the flow and perhaps other readers may find this part confusing too.

We have edited and better explained this section thus:

„Previous ATOFMS studies reported that most of the amines volatilised during cold seasons, whereas during summer most were in the form of low-volatility aminium nitrate and sulfate salts when particle acidity was higher (Pratt et al., 2009). This observation supports previous laboratory studies which reportedthat aerosol containing non-salt organic amines are more stable and less volatile than nitrate salts (Murphy et al., 2007). „

Page 31, lines 1-3. High RH favours aqueous processing in general because aerosol is more likely to be in a deliquescent or partly deliquescent form (Saukko, et al. Aerosol Sci. Technol. 2015, 49, 531-537).

Good point. The following text has been added:
"High RH favours aqueous processing in general because aerosol is more likely to be in a deliquescent or partly deliquescent form (Saukko et al., 2015)"

Page 31, lines 16-18. Could OC-Aro-NIT be associated with reactions between aromatics and NO3 radical?

It could, given the fact most of the OC-Aro-NIT was detected during night time. The following text has been added:
"Part of the OC-Aro-NIT could be associated with products from the reaction of aromatic components with NO_3 radicals (Atkinson, 2000; Benton et al., 2010)".

Anonymous Referee #2

Received and published: 10 March 2016

This paper presents measurements of single particles at a urban background site and a roadside site in the city of Barcelona (Spain) using two ATOFMS with different inlet configurations. While I do not detect major flaws in the paper, I have just concerns whether the different instrument configurations have an impact on the observed particle types at the two sites, and what are the new points obtained on atmospheric processes by simultaneous deployment of two ATOFMS at two sites.

We thank reviewer_2 for reviewing the current manuscript, comments are address below.

Much of the paper discusses the characteristics of the particle types at the two sites. A natural question to the study would be what causes the differences between these two sites to exhibit different particle types and mixing state. Unfortunately, this paper does not seem to explain them. Additionally, I echo the concern raised by Referee #1 that the authors have gone to draw too many speculative. I believe that with some major modifications suggested here and as pointed out by Referee #1 manuscript may achieve the adequate standards of ACP for publication.

We have edited all comments raised by Referee_1, and we believe the manuscript has improved. Please find answers to referee_1 above. Answers to reviewer_2 are below.

Specific comments: I use the abstract to illustrate my main concerns of the paper. The authors state in the abstract: . . .. . .The different instrument configurations had an impact on the observed particle types at the two sites. . .. . .This ATOFMS study clearly shows that the composition of atmospheric fine particles in Barcelona, and likely other Mediterranean urban areas, is complex, with a wide range of local and regional sources combining with chemical processing to produce at least twenty-two different particle types exhibiting different temporal behaviour. The advantage of using two ATOFMS instruments is also demonstrated, with the nozzle-skimmer configuration enabling detection of coarse dust particles and the aerodynamic lens configuration allowing better identification of particles rich in organic carbon and amines.

Briefly, we have added a section in the manuscript where we state the limitations of this study. The ATOFMS cannot provide direct quantitative information, therefore any attempt at describing different percentages of different particle types detected at both sites would be speculative. Additionally, the fact we used two different ATOFMS inlets (for finer aerosol at the RS, and coarser aerosol at the UB site) makes it even harder. Nevertheless, the ATOFMS was never deployed before in Spain, and to our knowledge this is the first time two ATOFMS have been deployed in the same urban site. We have edited the manuscript, and stressed the limitation of the study. We have also tried to further stress the results in the abstract and in the conclusion. More specific comments can be found below.

Since the different instrument configurations have an impact on the particle types, then clarify what impact? The highlighted results above are not really exciting. Given a complex environment in an urban environment like Barcelona, it is not surprised to observe the complex composition of atmospheric fine particles there. In fact, many researches have reported these complexities already.

We state it in the abstract: "The different instrument configurations had an impact on the observed particle types at the two sites." We recognise that a number of previous studies have highlighted the complexity of the particle composition and sources in urban areas. However, the current study is novel because provides information on the mixing state of the particles, e.g. it identifies the other chemical components that nitrate-containing particles are mixed with. No other techniques can provide this type of information. In order to help address this point we have the following text in section 4:
"European Union (EU) abatement of traffic related NOx levels is still required to maintain levels within international standards (EEA 2007). Higher NOx levels (due to the high vehicle density and the high percentage of diesel vehicles) are often seen in urban background locations in Barcelona (and southern Europe) relative to other northern and central European cities (Eeftens et al., 2012). Latitude variations within Europe influence secondary nitrate aerosol formation (Revuelta et al., 2012). Organic nitrogen speciesrepresent a considerable fraction of fine particulate matter (Kiendler-Scharr et al., 2016). The present work shows a number of unique particle types detected mainly at the traffic-dominated RS site containing organic nitrogen and presenting different diurnal profiles, likely originating from different sources and

different processes. Further studies are needed at high time resolution, emphasizing the need to better understand the sources and properties of particulate organic nitrogen. "

For the advantage of using the two ATOFMS instruments, they have been well known. I suggest the authors to focus on the more conclusive findings of this study.

To the best of our knowledge, there are no studies in the literature reporting the simultaneous deployment of two ATOFMS in the same location. One study was carried out in San Diego (PhD thesis of Dr. David A. Sodeman) but was never published in peer review journals.

Page 6: Authors have not detailed the issues related with the potential local sources at the two sampling sites. Is there any difference for the local sources between the two sites?
The following text has been added to address this point:
"The two sites were about 2 km from each other (Dall'Osto et al., 2013a). While the UB site was open to wind from all directions, the wind flow and turbulence at the RS site were partially affected by the nearby street canyons and vehicular traffic. Previous reports from the SAPUSS campaign, based on measurements of organic and elemental components of the aerosol, indicate that the particle composition and thus sources are similar at both sites (Dall´Osto et al., 2013b; Alier et al., 2013). Specifically, six organic aerosol (OA) components were identified at both sites: two of primary anthropogenic origin, three of secondary origin and one whose soure was not clearly defined (Alier et al., 2013). –Elemental analysis provided by Particle Induced X-ray Emission (PIXE) –enabled identification of nine different aerosol sources at both sites: three of regional origin, three types of dust aerosols and three types of industrial aerosols (Dall´Osto et al., 2013b)."

Page 7, Line 7: It is probably not dry but relatively less humid. Page 7, Lines 16-19:
This has been clarified in the text:
"The sample air was dried (through a Nafion dryer, Perma-Pure, length 100 cm, RH<40%) before arriving at the instruments."

The different instrument configurations are used, and the particle sizes do not have complete overlap for the two instruments. Then how does that affect the unique particle types to the specific site?

The following passages of text have been added to address this point:

"The instrument deployed at the RS site was an ATOFMS TSI model 3800-100, in which particles are sampled through an orifice and accelerated through an aerodynamic lens to the sizing region of the instrument (Su et al. 2004). By contrast, the instrument at the UB site was an ATOFMS TSI Model 3800 that utilized a converging nozzle inlet (Gard et al. 1997). Both instruments provide the aerodynamic diameter of particles sizes between about 100 nm and 3 μm by calculating their time of flight between two orthogonally positioned continuous wave lasers (λ = 532 nm). However, the transmission efficiencies of the two instruments are quite different. While the aerodynamic lens affords a much higher transmission efficiency for

particles with diameters less than about 1 μm, its performance for larger particles is not as good as the converging nozzle inlet."
"The two different inlet configurations (aerodynamic lens and nozzle-skimmer) strongly affect the size distributions of the detected particles and the overall aerosol population (Gard et al., 1997; Su et al., 2004). Hence, only a qualitative description of the detected particles is presented in this study. Furthermore, the ATOFMS mass spectrum is qualitative in that the intensities of the mass spectral peaks are not directly proportional to the component mass but are dependent on the particle matrix, the coupling between the laser and the particle, as well as the shot to shot variability of the laser (Dall´Osto and Harrison, 2012). Recent studies (Jeong et al., 2011) report excellent correlations for inorganic species (sulfate, nitrate and ammonium) but weaker ones between total organic and elemental carbon detected with ATOFMS and other instruments (Jeong et al., 2011). However, the ATOFMS can provide quantitative information on particle number as a function of composition; providing a measure of all particle components and can be used to assess mixing state."
Page 9: Please clarify how to define the local and regional particle types and the principle of particle classification in the main text. Page 9, Lines 19-20: Fig. SI1 presents the temporal trends of ATOFMS particle types. The size distribution of EC particles is given in Fig SI 2 not SI 1.

Explained and edited

Page 10, Lines 2-8: The EC signals in the positive mass spectra and near-total absence in the negative mass spectra suggests not freshly emitted. Is that true? References would be helpful. In my opinion, the chemical composition affects the ionization and fragmentation pattern of EC, thus fresh EC particles emitted various sources might exhibit different mass spectra. Actually, the EC signals in the positive and negative mass spectra are observed in fresh particles (Environ. Sci. Technol. 2005, 39, 4569-4580; Atmos. Environ. 2007, 41, 3841-3852).

We did cite a paper that explains and shows that EC signals in the positive mass spectra and near-total absence in the negative mass spectra suggests not freshly emitted. "Indeed, Giorio et al. (2012) reported for a regional background site that strong EC peaks in the negative ion mass spectrum are more indicative of fresh emissions while strong EC peaks in the positive mode represent aged elemental carbon. This is consistent with observations which indicate that particle composition affects the ionization and fragmentation pattern of EC (Reinard and Johnson, 2008)."

The reference is used already in other papers. For example: Giorio et al. 2012 reported for the first time at a regional background site that EC- is related to fresh emissions while EC+ represents aged elemental carbon as an effect of particle composition which affects the ionization and fragmentation pattern of EC. (Giorio et al., 2015, Environ. Sci. Technol., 2015, 49 (6), pp 3330–3340, DOI: 10.1021/es506249)

Page 11, Line 18: LRT-NIT has been defined in Line 9.

Removed

Page 13, Line 5: A reference would be helpful. Page 13, Line 18: Two sea salt particle

types account for 9.4% and 18.3% of the total particles sampled at RS and UB. The instrument configurations should have an impact on this type particles since the two sampling sites are only 2 km from each other.

Indeed. The following text has been added:
"The higher percentage detected at the UB is likely due to the instrument configuration, given that the nozzle inlet enables more efficient detection of coarser particles."

Page 15 Lines 13-16: Pb particle type with a large mode (700-900 nm) is likely related to local combustion without any substantial evidence. The temporal trend and the diurnal profile of the particle types could identify the local and regional particles, please clarify how to identify? I wonder if the regional particles could also show the diurnal variation. It is not clear to me.
This Pb particle type was discussed in a previous paper (Dall´Osto et al., 2013b) where a unique local source of Pb-Cl (associated with combustion emissions) was found to be the major (82 %) source of fine Cl in the urban agglomerate. The Pb particle type shows spikes typical of nearby sources. This is clarified in the following sentence:
"Further information can be found in Dall´Osto et al (2013b), where this ATOFMS particle type was found highly correlated with hourly elemental concentrations determined by PIXE analysis (Dall´Osto et al., 2013b), showing that this source of Pb-Cl is a major (82%) source of fine Cl in the urban agglomerate of Barcelona."

The temporal trend and diurnal profile for regional Fe particle types are discussed in the literature. The following sentence has been added to this effect:
"The flat diurnal profile for the Fe particle type (Fig. 3) also suggests a regional origin. The long range transport of fine Fe-containing particles (internally mixed with nitrate) is discussed further elsewhere (Dall´Osto et al., 2016)."

Pages 17-18: Saharan dust particles are only detected at UB, why not at RS? The authors attribute it to the different instrument inlet. However, sea salt particles also show a big size distribution above 1 um, they can be detected at both sites.

The Saharan dust was a very minor particle type (1.3% of the population), whereas the sea salt particles were about 10% in both sites. It is likely that Art-2a did not apportion this minor particle type of regional origin in the RS site. A sentence to this effect has been added.

Page 21, Line 18: "Zhuang et al., 2012" is not listed in the References.

Deleted

Page 23: The authors suggest that m/z 118 could not be associated to secondary processes and peaks at m/z 74, 88, 104 and 191 are attributed to organic nitrate. Actually, these peaks could also be attributed oxidized organics.

Previous studies have focused on the occurrence of these specific peaks in the same mass spectrum, see for example the work of Angelino et al. (2001). Clearly, m/z 74 for

example can be associated with a CxHy fragment, but the the combined presence of strong signals at m/z 74, 88, 104 and 191 is usually attributed organic nitrogen peaks.

Pages 15-26: It is also a good idea to discuss the influence of meteorological condition such as T, RH, wind direction, rain, air masses, for example, on the particle types. I recommend the authors obtaining such kind of information to provide in-depth insights into the unique particle types.

The ATOFMS data can only give qualitative data, and such data were compared where possible with meteorological data and air mass trajectories, but unfortunately did not allow us to give further insights.

Technical corrections: The numbers and captions of the figures are too small to read and should be increased.

Formats used in previous ACP papers. Edited and made them bigger.