Reeree #1

GENERAL COMMENT: The manuscript by Querol et al. presents long-term measurements of different fractions/ metrics of carbonaceous aerosol associated with different fractions of particulate matter from different monitoring sites using different (and occasionally indirect) analytical methods. Because of the large variability (sampling, analytical) individual measurements are associated with substantially different uncertainties; however, these are not mentioned in the manuscript or supplementary material. The most significant issue of the manuscript is associated with the overall effect of the limitations.
REPLY: We regret that the referee did not find significant contributions in our manuscript as found by referees #2 and #3. In any case we appreciate very much the comments supplied because we believe these contribute to significantly improve the presentation of our results.

As stated in a specific section of our paper we are aware of the limitations. However we also would like to note that the relatively good fitting of the correlation of OC and EC data obtained from different sites and OC and EC protocols in our study and from studies carried out around Europe, as well as the clear gradients found for different environments for OC, EC, OC/EC and nmC, point that the analytical limitations do not prevent us from obtaining general conclusions. In the US there is a very well established PM speciation network with very well defined analytical protocols. In Europe such network does not exists and this study has made a huge effort in compiling annual data of nmC, OC and EC from 78 sites of Spain obtained with 'similar' protocols (European EUSAAR2 protocols or similar to these) and at the end compared with published individual or collective studies from other sites of Europe. We have tried to better address the issue of limitations in the new version, at least by discussing EUSAAR/NIOSH comparison to show that EUSAAR may slightly underdetermine EC data.

1/ The authors outlined the potential limitations, however, they failed to provide how they will bias their findings. At its simplest form, this could be an overestimate/underestimate evaluation (I think the magnitude should also be discussed). For example, if all limitations lead to an underestimation, then, the conclusions represent a conservative estimate. This is a critical point because of the many-many limitations of the datasets and the suggestions for air quality policy with data that, after all, may be not that different.
REPLY: As you may see in the revised version, we completely modified the introduction and the section on limitations of the methods. We removed all issues related to analytical issues in the introductory section and we added and expanded them in a specific section dedicated to explain the analytical protocols and the limitations, in the methodology section. We agree with referee # 3 that although we reported here few insights on possible uncertainty ranges for results presented, a solid uncertainty calculation seems hardly feasible in the context of such high and unknown artifact influences and the use of different OC&EC analysis protocols. However, we may probably have underestimate in this study EC levels (not nmC or OC+EC) with respect to the use of NIOSH OC/EC protocol since prior studies evidenced that EUSAAR2 protocol may underestimate EC yield by 9-31% with respect this US protocol (Maenhaut et al., 2012). We included this text in the revised version.

2/My second concern is associated with the potential implication for air quality policy and the suggestions to include metrics of carbonaceous aerosol. It is not clear whether authors propose to monitor carbonaceous aerosol because of their potential health effects or as an alternative to existing particle mass measurements. If the former, then, at this point, there is no sufficient, statistically-significant and consistent evidence (strong indications, yes) that carbonaceous aerosol are associated with adverse short- and long term health effects (see the Integrated science assessment on PM2.5 done during the last revision of PM2.5 standards,

available at www.epa.gov). The large variability in chemical composition, large sampling/analytical errors are also limiting factors. If the latter, then this is not a valid suggestion because other non-carbonaceous aerosol species showed stronger health effects than carbonaceous (e.g. iron has a stronger potential to form ROS than organic compounds; Ca has a higher risk for respiratory symptoms than BC/EC or OC, etc). With respect to continuous EBC, this is practically continuous measurements of soot carbon (initial air quality measurements before the use of PM10 and PM2.5 mass) which has been rejected in the past because of the inability to account for other types of sources and pollutants as well as changes in traffic emissions (for BC to SOA/NOx-rich emissions). My suggestion here is to exclude this section because it does not rely on the data of the manuscript, it does not include a detailed review of existing health literature (other than one report and one paper) and it is highly speculative.

REPLY:

2.1. We, and the other 2 referees, do not consider this section irrelevant. Our suggestion is to add BC to the existing PM10 and PM2.5 regulated metrics, not to replace them. Then the second and third parts of your discussion on this issue are not applying here. We have clarified the text in this sense.

2.2. In several parts of Europe we have a large proportion of diesel cars in our fleets. We measure by law in traffic hotspots in addition to urban background. It is in these traffic hotspots where most of the PM10 exceedances are recorded, and where BC and nmC are high, in addition of specific biomass burning hotspots. Here we record also the highest PaH levels. The monitoring of BC or nmC may have not only health relevance but it is a good tool to evidence effects of measures taken to abate emission from road traffic, main cause of exceedance of PM limit values in Europe, and one of the main causes of health outcomes of PM in Europe as reported by the REVIHAAP WHO's report in January 2013.

2.3. We are aware of the Integrated science assessment on PM2.5 done during the last revision of PM2.5 standards, available at www.epa.gov, but we are also aware of the recent WHO reports on health effects of BC (not probably per se but, due to carrier role for health relevant substances such as PaH) in 2012 and REVIHAAP in 2013, pointing to health evidences supported by both EU and US scientific community.

2.4. We did not mention in any place that BC is the solely PM component with health effects. Of course we are aware of the effects of metals and other components. We have clarified these issues in the new version to avoid confusions.

2.5. Yes we refer only one report and one paper but the report summarizes the most updated scientific information on health effects of BC by WHO 2012 and the REVIHAAP WHO's report in 2013.

2.6. We have already clarified these issues in the manuscript.

3/ One important limitation is the absence of comparison of EC/BC, OC and nmC measurements to PMx. It is important to know the percentage contribution of these components to mass.

REPLY: As stated in the manuscript, we have published this information in previous works (Querol et al., 2008) and summarized at the beginning, in the introductory section. In any case we have highlighted this description in the introduction to include your suggestions.

4/ Page 6996 lines 5-10. Discussion about the equation OC/EC=aECˆb. I do not understand the practicality of this equation as compared to OC=aECˆb. Why? It is basically y=axˆb with y=f(x) so, f(x)=axˆb or z/x= axˆb which leads to z= axˆ(b+1).

REPLY: As suggested by the referee we excluded the OC/EC- EC regression equations from figure and text and we have focused only in the simplest one (OC-EC).

Referee #2.

GENERAL COMMENT: This paper presents a very impressive and interesting data set on carbonaceous aerosol compiled since the last 12 years in 78 locations over Spain. Considering the quality of the dataset and of the results presented in the paper I recommend the publication to ACP.
REPLY: We do thank the favorable comments from the referee, but also, and specially, the detailed review done and the very constructive criticism and key suggestions given that in our opinion have improved the quality of our presentation. As we report below we took into account all suggestions given.

1/ Implications of the results presented here are important for air quality policy issues (as discussed in the manuscript), but also (and mainly, in my opinion) for the scientific community. This kind of dataset allows pointing out the most relevant research activities that need to be conducted in the next years. This aspect of the discussion/conclusion is not developed (or scarcely) in the paper. I will have preferred a specific section on this point rather than the general discussion on the implication in terms of air quality policy (section 5.1). This last section, mostly discussing the recent WHO report on health effect of BC, should be incorporated in the introduction (see next comment).
REPLY: We have changed the name of this section and included as requested 'pointing out the most relevant research activities that need to be conducted in the next years'. We have included new paragraphs for scientific and scientific-policy issues.

2/ Introduction. This section needs to be reorganized. Overall it is too technical and many aspects should be moved to the experimental section (description of the methodologies used to measure OC/EC, BC, nmC ; artifacts). From my point of view, the introduction should focus on carbonaceous aerosol (concentrations in different locations in Europe, trends –paper of Pio et al 2011-), health impact (why the WHO report on BC is only discussed in the final section of the paper?), trends of other pollutants (especially PM ; Querol et al, 2008) . In other terms, provide information to the reader in order to contextualize this work in a more precise way.
REPLY: As you may see in the revised version, we completely modified this section according your suggestion. We added the discussion requested and moved the issues of analysis to the methodology section.

3/ You clearly state (p6981, line 15) that "The assessment of the comparability between the different thermal protocols used is not the objective of the present work". I agree with that point but as your conclusions can be greatly affected by these methodological issues (sampling artifact included), I suggest that you add a specific section in order to discuss these aspects (in addition to the section 2.5). In the current version of the manuscript, all the elements of comparison (or all the elements available) are discussed but in different part of the manuscript. I think that it will be clearer for the reader to discuss these aspects in one dedicated section. Also, as many methodologies are used to measure OC/EC, BC, nmC, I suggest that you add at the beginning of the experimental part, a specific section discussing of some fundamental aspects of the measurements of these still mysterious fractions. Because, conceptually, OC/EC and BC are mostly defined by the methodology used to measure it. Once again the aim of this comment is to clarify the manuscript. I'm totally aware that these methodological issues are a no end story.
REPLY: As you may see in the revised version, we completely modified this section according your suggestion. We removed all issues related to analytical issues in the introductory section and we added and expanded them in a specific section dedicated to explain the analytical protocols and the limitations, in the methodology section.

4/ Inter annual trends of EC (/BC) are very interesting. Unfortunately no data on the evolution of the vehicular fleet in Spain is shown in the manuscript. Considering the statistic provided by the European automobile manufacturer association it seems that the fraction of diesel in Spain increases from 50.6% in 1999 to 70,1% in 2009. Can these trends of EC (/BC) be discussed in the light of more official statistics of the evolution of the vehicular fleet in Spain?
REPLY: To consider your suggestion we added in the discussion section the following text: *The Spanish vehicle fleet underwent an intense dieselization since the 1990s. This resulted in a proportion of diesel vehicles reaching 10% in 1991 that markedly increased to 55% in 2010, with annual sales of diesel vehicles reaching 70%. This increase has probably caused a marked increase of EC and OC emissions from road transport. However, the effort done by car manufacturers to meet Euro 4 (since 2004) and Euro 5 (since 2009) PM emission standards may have had an important impact in reducing ambient mass concentrations of carbonaceous aerosols in urban areas.*

Specific comments

a) p6973 line 26 : NO2/(OC+EC): REPLY: Changed
b) p6974, line 10 “transferred” instead of “formed” REPLY: Changed
c) p6974, line 15-19. Be more quantitative. REPLY: As stated in text quantitative proportions depend on the environment that is monitored. We have rephrased the text to be clearer.
d) p6975, line 1-5 : Develop this aspect (WHO report etc..). REPLY: done a few lines below in the introduction.
e) p6976, line 9-12 : not here : Reply: now moved with all analytical discussions to methodology.
f) p6976, line 13-16 : develop this section. Reply: Done as you proposed before
g) p6976, line 18-20. Be more specific. What kind of “state of the art techniques”? what type of organic species? In a more general point of view, is this paragraph useful? REPLY: We agree with you, not very useful, and consequently we have deleted it in the revised version
h) p 6977 , sampling section. Information regarding the site typologies and classification would be more useful here than in S1 REPLY: It was there before the ACPD quick review process. Now we moved it back again to the methodology.
i) P6979, line 3 : be more specific. What are the LOD of elemental analyzers? REPLY: Added
j) p6986, line 19 : 5 µg m-3 Reply: Changed
k) p6987, section 3.1 and 3.2: How are defined : small, midsized and large cities? Can you compare these results with other locations in Europe? From my experience the concentrations of EC and OC seems quite low, especially in urban environnement. REPLY: We reported now in the revised version the inhabitants for each size bin. Concerning the comparison with other cities of Europe this is done in the discussion.
l) p6990 line 11: rate of 0.3 yr-1 REPLY: Corrected
m) p6990 line 18 : R2 of 0.99, n=? REPLY: Added.
n) p6990 line 22 : µg m-3 REPLY: Corrected
o) p6991 line 5-15 : Considering the results previously presented, this first paragraph of the discussion is very speculative. For the traffic sites, the ratios OC/EC observed here (1.6-1.7) are too high to state that OC is mainly from primary vehicular exhaust, especially considering a vehicular fleet largely dominated by diesel vehicles. Typically the ratio OC/EC is lower than 0.5 for diesel emissions (for example: Zielinska et al, 2004 or El Haddad et al, 2009). Thus, in the traffic sites discussed in the paper, We can consider that _75% of the OC is not from diesel exhaust. Considering that 70% of the

vehicle fleet is diesel (with respect to the statistic of the European automobile manufacturer association) and EF of gasoline cars, primary gasoline emissions can not explain the OC concentrations observed. REPLY: Useful observation. The diesel share is 55%, what is 70 is the annual sales. We modified the paragraph and added the references*: Typically the ratio OC/EC is lower than 0.5 for diesel emissions (Zielinska et al, 2004; El Haddad et al, 2009). Pio et al. (2011) found minimum OC/EC ratios (attributed to primary traffic contributions) at urban background sites in Europe to be around 0.7 in $PM_{2.5}$ and 1.0 in PM_{10}. If we consider an OC/EC ratio for traffic sites close to 1.6-1.7, and we have into account that 55% of the fleet are made of diesel cars, it is clear that even at traffic sites the contribution of SOA (from gasoline, biogenic or other sources) to OC is very relevant. The above primary OC/EC ratios are closer to the ones determined at the Atlantic island site of Santa Cruz de Tenerife (0.8), where probably both biogenic and anthropogenic SOA formation has a lower contribution on OC levels.*

p) p6991, line 20 : "biomass burning is probably causing an increase of 1µg/m3 in. ." how this value is estimated? Reply: This is deduced from the difference on nmC concentrations from most regional background sites in this study (1.8-2.6 µg m^{-3}) and the concentration recorded at the regional site of Bemantes (3.5 µg m^{-3}), highly influenced by biomass burning emissions in the region. We added this explanation (that was already given in the results section).

q) p 6991, line 25 : 1.0 or 1.6 for the lower OC/EC ratio in traffic sites? Reply: Corrected

r) p6993, line 9 : OC/EC ratio is also very high for gasoline exhaust (typically 5-10): REPLY: We added: *Primary gasoline exhaust emission have also high OC/EC ratios but their emission levels in absolute values are small compared with the diesel primary exhaust emissions, at least for Euro 3 diesel cars and older.*

s) Fig 3. Years of works have been necessary to obtain the data presented in this figure. All this work is not emphasized by the figure.

t) Fig 6 : Personal curiosity.. A intense peak of OC and EC is observed in Barcelona during winter 2008. Do you have an explanation of this increase of the concentrations at this period? REPLY: We believe this is due to: a) Intense anticyclonic episodes in November 2007 and b) During January and February 2008 the works done to build a tunnel for the subway system in the vicinity (200 m) of the monitoring site. We had an incredible number of trucks transporting the sediments from the tunnel to land disposal.

Referee #3, Dr O. Favez.

GENERAL COMMENT: This manuscript presents a comprehensive phenomenology of non-mineral PM carbonaceous fractions in Spain over the last decade. This subject is of prime interest for the scientific community as well as for decision makers since organic matter is one of the top major PM species and a better knowledge of its main emission sources and (trans-) formation processes in the atmosphere is strongly needed for the elaboration of efficient PM reduction action plans. Moreover elemental carbon (EC), which presents much lower concentrations, is gaining more and more attention from decision makers due to its climatic relevance as well as its potential use as an indicator of PM health effect.

Authors proposed a clear, concise and well-written manuscript. It also provides valuable information that could be extrapolated elsewhere.

It is to note that the used database is composed of results obtained from very different sites, at different periods and using different analytical approaches. Moreover, the latter analytical methods are known to be subject to various artifacts, some of them probably still to be discovered. This induces large limitations to the study. Nevertheless, authors extensively describe and discuss these limitations. They also propose few insights on possible uncertainty ranges for results presented here, while a solid uncertainty calculation seems hardly feasible in the context of such high and unknown artifact influences.

It thus comes that the present manuscript could be considered as a call for standardisation of carbonaceous PM sampling and analysis, which authors do not really insist on. Given these issues, authors decided to mainly discuss inter-annual trends based on nmC (OC+EC) concentrations, which to my opinion sounds very appropriate.

They also conclude the manuscript considering the need to develop EBC monitoring. Authors could then be asked to clearly precise their opinion on a what kind of strategy should be chosen for the monitoring of carbonaceous aerosols (if any): for instance, would this strategy rely on collocated nmC and EBC measurements, and then the estimation of OC from the difference of these two parameters (disregarding OC and EC thermo-optical measurements)?

Besides these technical points, data treatments presented are scientifcally-sound and well presented. Overall, I would recommend the publication of this manuscript within ACP. However, would have three main concerns that should be answered before publication (see below).

REPLY: We thank a lot the favorable comments from Dr Favez, but also, and specially the detailed review done and the very constructive criticism and key suggestions given that in our opinion improved a lot the quality of our presentation. As we report below we took in to account all suggestions given, especially the text underlined above and the specific comments below.
As you may see in the revised version, we completely modified the introduction and the section on limitations of the methods. We removed all issues related to analytical issues in the introductory section and we added and expanded them in a specific section dedicated to explain the analytical protocols and the limitations, in the methodology section. We added your statement: Although we reported here few insights on possible uncertainty ranges for results presented , a solid uncertainty calculation seems hardly feasible in the context of such high and unknown artifact influences. However, we probably slightly underestimate in this study EC levels (not nmC or OC+EC) with respect the use of NIOSH OC/EC protocol due to the

fact that prior studies evidenced that EUSAAR2 protocol may underestimate EC yield by 9-31% with respect this US protocol (Maenhaut et al., 2012).

1/ The quality of figures is rather low, especially Figure 8 (hazy; X-axis: L = "July" ?; Y-axis not readable). REPLY: Modified

2/ Apparent fluctuations within long-term trends (when looked from far away).
REPLY: Yes, but we have indicated when the trends are statistically significant.

3/ Inter-annual trends presented in Figure 6 for long-term datasets globally seem to correspond to two different trends (significant decrease before about 2008, but low decrease, if any, afterwards). This would also be in line with statements repeated in the paper that short database (<5y) do not show such obvious decreasing trend than longer database. If true, what would be the impact of such a decrease of the decreasing trends on proposed explanations related to the influence of traffic EURO regulations?
REPLY: It is true that for some sites, such as Barcelona and Montseny, the decreasing trend for OC is not very clear after 2008. Nevertheless, EC shows a clear decreasing trend after 2008 at Barcelona (not shown in MSY) and the minimum nmC in BCN was detected in 2010. In the other sites also minimum values were obtained for EC and OC after 2008. Therefore, it is difficult to evidence two different trends and to relate these with the EURO regulations. Nevertheless, following your observations, we have indicated this difference in the trend of OC in Montseny and Barcelona in the text.
"*However, the decreasing trend was already evident before 2008 when the crisis started, and it was even more marked before this year for OC at some sites, such as Barcelona and Montseny (Figure 6). Although in some cases we may find a lower decreasing trend for OC levels since 2008, nmC trends tend to evidence minimum values around 2010 coinciding with the low PM levels recorded in the Western Mediterranean with the most negative North Atlantic Oscillation Index in the last century (Cusack et al., 2012).*"

4/ The ambiguity on the real impact of biomass burning on total organic matter concentrations as presented by authors. Indeed, it is stated P. 6991 L. 5-9 that "The spatial variability of nmC across different atmospheric environments in this study shows that anthropogenic carbonaceous aerosols in Spain within the period 1999–2010 mainly originated from road traffic and in a minor proportion from biomass burning ...". The way this statement can be done would certainly need to be precised and detailed a little bit more. This statement is also rather vague, as no numerical values are proposed. This issue actually concerns the whole manuscript, which globally point out traffic emissions as the very major sources of nmC in Spain (which I could believe), but also frequently indicate significant influences of biomass burning emissions (e.g.P. 6991 L. 19-22: "biomass burning (domestic, agricultural and forest fires) is probably causing an increase of around 1 ugm-3 in the annual nmC mean at regional background sites in northern Spain with respect to the rest of the Spanish territory.": this extra ug/m3 on a yearly basis may represent up to 50% or more during burning periods, isn't?). Could authors please try to precise the impact of biomass burning on carbonaceous matter in Spain? and more extensively compare this impact to the ones in the rest of Europe? Given the elevated influence reported for biomass burning emissions on air quality within other European countries, these clarifications would seem to remain within the scope of the manuscript, which also attempt to indirectly elucidate major carbonaceous matter sources.
REPLY: The following text has been added to the manuscript: *Biomass burning contributions may have an impact in rural areas but have little impact on air quality in urban areas. In Barcelona, three studies (Minguillón et al., 2011; Reche et al., 2012; Viana et al., 2013) quantified these contributions as 3% of PM_{10} and $PM_{2.5}$ (annual mean), while this percentage increased up to 5% of PM_{1}. Annually, biomass burning emissions accounted for 19%–21% of*

total OC levels in PM10, PM2.5 and PM1. Absolute contributions of biomass burning were higher in winter at urban and regional sites.

We also added a text to justify the 1ug/m3 increase caused by BB: *This is deduced from the difference on nmC concentrations from most regional background sites in this study (1.8-2.6 µg m^{-3}) and the concentration recorded at the regional site of Bemantes (3.5 µg m^{-3}), highly influenced by biomass burning emissions in the region.*

We appreciate the reviewer's comment, but think that adding a comparison between biomass burning contributions to PM in Spain and Europe would need to be quite extensive to make it comprehensive, and this would be an excessive for the manuscript. Therefore, we have preferred to add the previous discussion to the text.

5/ Para. 2.2: could be precised as soon as here than Ca and Mg may have different origins than mineral dust aerosols.
REPLY: We include in this section the paragraph from section 2.5: *Ca and Mg may be present in mineral dust in forms other than calcite and dolomite, e.g., a small fraction of Ca in soils may be present in aluminium-silicates, such as anorthite (not as carbonate species) and Mg can have a minor sea salt origin and may be supplied also by some clay minerals. But in both cases these contributions are lower than the one from carbonate minerals. Furthermore, even in case that dust soil particles are emitted as carbonates, inter-reaction in the atmosphere with SO_2, H_2SO_4 and HNO_3 has a tendency to transform those into sulfate and nitrate species. Therefore, the use of Ca and Mg as tracers may result in an underestimation of nmC levels, but in any case calculated CC concentrations are low when compared with nmC (e.g., 2%-9% of total C in Barcelona).*

6/ P. 6692: What about the seasonal variations of non-fossil vs. fossil OC ? Does it tell something about sources?
REPLY: The following text has been added to the manuscript: *Minguillón et al. 2011 has evidenced that absolute concentrations of fossil OC were also higher in winter than in summer at Barcelona due to stronger accumulation of pollutants during the cold season with lower atmospheric dispersion, and probably to higher fossil combustion for residential heating. Concentrations of non-fossil OC and non-fossil EC at Barcelona were twice as high in winter than in summer, probably due to a higher contribution of biomass burning and reduced mixing in winter.*

7/ At MSY, non fossil OC was similar in summer and winter, despite the lower biomass burning contribution in summer as evidenced by the lower non fossil EC. These authors estimated biomass burning OC to account for 30–35 % of the non fossil OC at both sites and seasons (17–21 % of total OC), with the exception of MSY in summer, where it only accounted for 12 % of total OC. This can likely be explained by a higher contribution of biogenic SOA in summer, due to higher biogenic emissions and enhanced photochemistry. P. 6692: Is cooking expected to be a possible major source at every sites (in particular rural and remote ones)?
REPLY: Recently, a number of papers based on AMS online measurements have evidenced the importance of cooking activities as a major contributor to urban aerosol loadings (Allan et al., 2010; Mohr et al., 2012).

The following text was modified: *Other contributions to modern OC, such as the contribution of cooking aerosols (COA) identified in Barcelona by Mohr et al. (2012), cannot be discarded for urban areas. However, their mass contribution is still unclear. Mohr et al. (2012) estimated COA contributing to 17% of OA in Barcelona, but it is clear that at remote and regional background sites this contribution will be much lower, probably negligible.*