RESPONSE TO THE REVIEWERS FOR MANUSCRIPT ACP-2012-735

Volatile Organic Compounds in the Western Mediterranean Basin: urban and rural winter measurements during the DAURE campaign

We are very grateful to the reviewers for their comments and for their careful reading of the paper. We have addressed each one of the points raised, and have altered text, figures and tables wherever appropriate to address the concerns raised. We believe that this has improved the paper, and thank the reviewers for their time and effort in pointing out where improvements could be made.
We look forward to having the editor's approval to submit a revised manuscript to be considered for final publication in ACP.

The referees' comments followed by our responses (R) are below.

REFEREE #1

This is an excellent paper showing important measurements and analysis of VOC concentrations at two different locations differing in anthropogenic influences and with the focus on winter period. The story fits well with the other papers from the DAURE campaign. I would just have a few comments to be addressed and then I would like to recommend the article for publication in ACP.
R: We thank the encouraging opinion of the reviewer.

1) Heights/elevations. Since the paper discusses the concentrations (rather than the fluxes), my suggestion is to be more clear about the heights and their possible effects on concentrations. For a constant flux (assuming there is no flux divergence), larger turbulent eddies at higher altitudes generally lead to lower concentrations. The sites were located at different heights a.s.l., 80 and 720 m. Would different elevations have any impact on the observed differences in the concentrations? From p. 30915 l.12 it seems that the inlets were at 3 m at both sites. Please make it clear in the text above what (ground, vegetation, roof)?
R: In our paper the gaseous quantities are expressed as mixing ratios (ppbv = parts per billion by volume). This means that the ppbv represent the ratio between the number of molecules of the species of interest and all other molecules present in the air. At different elevations the atmospheric pressure varies and hence for the same mixing ratio, different concentrations (expressed as molecules per cubic centimeter for example) can be found at different altitudes. A quick calculation based on the atmospheric pressures at both sites suggests that a 8% difference is plausible. In our paper, though, since VOC quantities are expressed in mixing ratios, both BCN and MSY can be compared without regard to height. Nevertheless, we have now included a note at the end of section 2.2 to made it clear to the reader that the VOC numbers are expressed as mixing ratios (ppbv).

We have now modified the sentence about the location of the inlet lines. It now reads:

> Both PTR–MS setups sampled ambient air through a heated inlet line (4 m long), made either of deactivated Sulfinert (MSY) or teflon (BCN) tubes, installed at heights of 3 m above the ground on the front of the house (MSY) or cabin (BCN) where each PRT-MS was installed.

2) Lifetimes. Although reactive compounds such as isoprene are characterized by a relatively small concentration footprint, methanol and compounds with long atmospheric life times may have remote sources. It might be worth discussing potential effects of the lifetimes on the interpretation of the results.
R: Thanks for pointing this out. We have now included comments in the text about the implications of lifetimes of VOCs on their average diurnal cycles and their transport from BCN to MSY in section 3.3.1. For example we have now added the following text:

> “Despite acetonitrile’s long atmospheric lifetime that allows its long range transport and may dampen its atmospheric concentration fluctuations, our data show clear peaks during rush hours, especially in the morning, which suggest its main emission source at BCN are vehicle exhausts.”

3) Acetic acid (MSY). This reviewer has a reservation to the quantification method of acetic acid from the PTR-ToF-MS. Table 1 footnote b: “These sensitivities were not measured in calibrations, and acetone sensitivity was used instead (divided by 2 in the case of acetic acid because of the fragmentation on m/z 43.02, see Langebner et al., 2012).” The approach taken from the cited paper in preparation might be of concern. I refer the authors to Haase et al., 2012 who reviewed and showed that the sensitivity ratios of the parent ion (m/z+ 61) and dehydrated CH_3CO^+ (m/z+ 43) in acetic acid calibrations ranged from 0.04 to 7.6 in various studies. Does the factor 2 come from the calibration on the same instrument? Therefore, I guess the reported concentrations at the MSY site may have been different at the two sites. Given such a high uncertainty, it is suggested to either conduct a lab calibration at the same drift-tube conditions and humidity, or omit acetic acid results from the MSY site.

R: We understand the concern of the reviewer. But we must say that the TOF instrument used in the paper by Langebner et al is the same as the one used in this study and the authors are pretty confident that the estimated sensitivity for acetic acid is good enough.

4) Ethanol (BCN). This reviewer is surprised with the high sensitivity for ethanol (10.9 ncps/ppbv) and low detection limit (79 ppt) for such a high E/N ratio (140 Td). Lab studies suggest optimal sensitivity for ethanol at 90 Td (e.g., slide 8 in Galbally et al., 2010). At 140 Td the sensitivity can be one order of magnitude lower possibly due to fragmentation into H_3O^+. Therefore, the sensitivities closer to those reported for the PTR-ToF instrument at the MSY site would be expected. For the sake of data quality, it is strongly recommended to either use the calibrated sensitivity from this instrument at the same E/N ratio or to use another approach which accounts for fragmentation. Otherwise, quantification of ethanol should be omitted from the BCN site.

R: We agree with the referee that the quantification of ethanol is tricky with a PTR-MS without proper calibration. That is why we had previously included a paragraph on section 2.2 to make the reader aware of this issue. Now, following the reviewer suggestion, we have omitted all the ethanol/formic acid data from the BCN site in the revised version of the manuscript.

5) Uncertainties. Please either add a note or reference on estimated uncertainties, or/and add error bars to the figures. Concentrations of compounds derived from calibration and transmission may have different uncertainties.

R: We have now added information about the estimated uncertainties of the measurements. The text fragment now reads:

> The uncertainty of the measurements made with the PTR-Quad-MS was estimated to be 14% for calibrated compounds and 25% for compounds not present in the calibration standard. In the case of the TOF, uncertainties were estimated to be 13% and 24% for calibrated and uncalibrated VOCs, respectively.

6) Scenarios. This reviewer likes the identified atmospheric scenarios and their discussions. Please revise acetic acid and ethanol though, with respect to 3) and 4).

R: We thank the favorable comment of the reviewer about the atmospheric scenarios. As stated before, in questions 3 and 4, we have kept the acetic acid data and have omitted the BCN ethanol/formic acid data in the revised version of the manuscript.

technical:
7) p.30914 l.2 change “measuring” to “measurements”

R: This has been changed as the referee suggested.

8) P.30914 l.15 replace “We here” with “Here, we”

R: This has been changed too.

REFEREE #2

This paper provides new data on daily mixing ratios, close to ground-level, of a range of VOCs, measured simultaneously both in Mediterranean urban and natural environments, using the PTR-MS system during the DAURE winter field campaign.
The authors explain the observed hourly VOC mixing ratios of both sites as affected mainly by changes in wind regimes, emissions from local or distant sources advected to the site by long-range transported air masses, as well as by vertical meteorological conditions and photochemical reactions. At the urban location, vehicular traffic proved to be the main local contributors, governing the diurnal cycle of the VOCs and inorganic gaseous pollutants such as NOx and O3, showing a typical urban profile with a bimodal structure. At the rural location the VOCs levels are mainly driven by meteorological processes (sea breeze transporting compounds from the upwind urban area) and/or originated from local biogenic emission sources. Moreover, the authors identify different atmospheric scenarios and provide explanations of their influence on the VOC mixing ratios measured at both sites.
Overall, the scientific quality of the manuscript is good and this is the first attempt to conduct these concurrent measurements of VOCs mixing ratios in both a natural and an urban environment in the Mediterranean region during the winter season. Taking into account that the WMB presents unique atmospheric dynamics regulated by complex climatic and orographic effects, this paper, through chemical speciation of VOCs, gives valuable insight on the formation and transport mechanisms for photochemical smog in urban and downwind rural areas in this region. The comparison of already published VOCs measurements, carried out in a natural environment, with new parallel data from the urban site in BCN is interesting, providing more in depth information on the major atmospheric processes and sources affecting the hourly evolution of VOC mixing ratios with special emphasis on the biogenic compounds. As there are many studies on aromatic hydrocarbons and other anthropogenic VOCs in urban environment, while studies on biogenic VOCs, in particular isoprenoids, are scarce, the presented paper addressing an interesting dataset make an important contribution to this topic. Thus, I recommend for publication after considering the following listed comments and questions which are intended in order to allow any reader to gain the highest information possible from the presented data.
R: We thank the favorable comments of the reviewer regarding our manuscript.

Although one of the advantages of the PTR-MS technique, applied by the authors to measure ambient VOCs mixing ratios, is to provide chemical speciation of the measured VOCs, the authors describe and discuss the observed mixing ratios of VOCs mainly in the form of chemical classes. In particular, VOCs data measured at the BCN site are investigated grouping them in different categories, and VOCs mixing ratios observed at the MSY site are basically discussed as full VOC data, except the isoprenoids. In addition, when the authors describe and compare mixing ratios for single compounds such as acetone or ethanol at the two site, they do not provide any related explanation for the observed differences or similarities. Although I recognize that different VOC species show similar behavior separately, more detailed information on individual chemical species should be given to better understand the differences and relationships in mixing ratios between urban and rural areas, and thus extract conclusions about the source of these compounds.
R: We described the observed mixing ratios as chemical classes to point out that those VOCs possibly share sources or processes in the atmosphere. Since almost all VOCs showed a similar daily profile at each site, with our data it is very difficult to tell if there was more than one source for VOCs. In the case of MSY, almost all the VOCs rise with the advection of the air mass coming from the industrialized plains below. For MSY, full VOC data was used because a more detailed description is available at the already published paper comparing winter and summer mixing ratios. Furthermore, here we described the isoprenoids at MSY in more detail because it may be surprising that the mixing ratios of these VOCs were higher at BCN. The explanation of why this could happen is now richer in the new version of the manuscript with the inclusion in the discussion of references suggested by this referee (e.g. Hellen et al 2012) and the inclusion of information suggested by both referees.

Closely connected to this issue, I wonder if the authors took into account the different reactivity characteristics of the individual chemical species in order to investigate more in depth the formation and transport mechanisms for ozone and its precursors at the urban and rural areas.

Moreover, I also suggest to compare the VOC composition (in term of relative percentage of each individual VOC on the total VOC amount) between urban and rural areas to clarify the nature of emission sources across the two sites, e.g. discriminating between local emission and photochemical reactions during transport.

R: This is a very good point. In order to avoid over-complicating the manuscript, we included information relative to these topics in the new Supplementary material of the article. In the Supplement the reader will find some graphs and explanations about the percentage that each VOC mixing ratio represents relative to the total VOCs mixing ratio at each site (taking only into account the VOCs measured with the PTRMS during this campaign, not *all* the VOCs present in the atmosphere, which we did not measure). Also, using reactivity scales for ozone formation (e.g. MIR and MOIR reactivity scales from Carter 2010) we estimated the potential contribution of each VOC species to ozone formation at each site.

Investigation of the relationships between VOCs and the meteorological parameters, and between the different VOC chemical species by appropriate statistical analysis would provide better insight of the ozone formation mechanisms, more information about the emission sources as well support the argument that the observed VOC mixing ratios at the rural site were advected by the wind from the urban location. The suggested statistical analysis to investigate the relationships between variables could be provided in the supplementary material as done for Seco et al., 2011b.

R: As the reviewer suggests we have prepared a new Supplementary material that includes a Table that shows the correlation coefficients between different VOCs and between VOCs and meteorological parameters, similar to that of Seco et al 2011b.

Another approach that may be worth to try is calculating the BTEX (benzene: toluene: ethylbenzene: xylene) concentration ratios and verifying the correlations between different BTEX at the rural area to compare the VOC emission sources (local or far from the sampling location) between the two locations and, thus, confirming the possible origin of these compounds from similar sources (see Khoder et al., 2007). The ratios of aromatics are highly informative of the contribution of the vehicular source to the VOC background air profile (Kupiszewska and Pilling 1994) and they would be very informative when comparing the urban ambient VOC mixing ratios of BCN with those of many polluted cities in the world.

R: We agree with the reviewer that these aromatic VOC ratios do help understanding the vehicular source and photochemical processing of the air masses. This is the reason why we already included the benzene:toluene ratios for this study in section 3.3.3 of the previous version of the manuscript. Unfortunately, the PTR-MS technique does not allow to separate isobaric compounds like *m*-xylene, *p*-xylene or ethylbenzene (all of them detected on *m/z* 107 and reported together as C8-aromatics). Because of this, we cannot calculate the BTEX ratios reported in the paper by Khoder et al (2007), such as (*m*,*p*)-xylene:benzene, the *o*-xylene:benzene, the (*m*,*p*)-xylene:ethylbenzene or the benzene:toluene:ethylbenzene:xylenes. These ratios would enable to comparison to that paper and others using the same ratios.We report, however, the benzene:toluene ratio that enables the comparion to almost all papers reporting these two aromatic species, which include most studies involving the use of PTR-MS for ambient air measurements.

The authors explain the low mixing ratios of monoterpenes detected at MSY as due to the low leaf-level oak emission rates during the winter period. Although this justifies the isoprenoid mixing ratios found in MSY, it does not explain the lower mixing ratios detected in MSY as compared to those measured in BCN. Can this discrepancy of monoterpenes at the two sites be attributed to local anthropogenic sources of monoterpenes at the urban site? Although the monoterpenes are not usually considered to be emitted from traffic, the study by Hellen et al. (2012), who found higher isoprene and monoterpenes concentrations at an urban site as compared to a forested one during winter, suggests the contribution of anthropogenic sources for both isoprenoids in urban air especially during this period.
Moreover, episodes of parallel increase of monoterpenes accompanied with increased NOx concentrations have also been described by Hellen et al., (2012) to prove the anthropogenic origin of monoterpenes. Although I acknowledge that during winter low monoterpene mixing ratios at both sites

could be due to low biogenic input, an anthropogenic source could be as well contemplated during winter, even if possibly minimized by the natural location at MSY.

R: Thanks for pointing out this possibility and the reference of Hellén et al. 2012. The discussion about isoprenoids is now much more complete in section 3.3.1 (BCN urban site) and reads:

> Among the isoprenoids, usually considered to be of mainly biogenic origin, isoprene also has known anthropic sources, e.g. automobile exhaust, which can be important in urban areas such as BCN, especially in winter (Borbon et al 2001; Barletta et al 2005; Hellén et al. 2012). As shown in Fig. 3, maximum mixing ratios of isoprene happen during rush hours. This fact suggests that most of the isoprene detected at BCN is of anthropic origin too. A similar case is that of monoterpenes, usually considered biogenic-only VOCs. Traffic-related origin of monoterpenes has been proposed by a study in northern Europe (Hellén et al. 2012), based on the fact that the diurnal cycle of monoterpenes resembled that of aromatics. In our study, we also observed an increase during rush hours, which suggests a traffic origin. However, the mixing ratios did not decrease after the evening rush hour, and the highest mixing ratios of monoterpenes at BCN occurred at night (Fig. 3). This observation suggests that the lowering of the PBL, the cessation of photochemical destruction and the dropping sea breezes could favor the accumulation of monoterpenes at night. Obviously, other biogenic sources for monoterpenes cannot be ruled out. The trees, which included pines, of the small urban park where the measuring station was installed may have been the source of these monoterpenes. Also, air masses are transported during the night from the nearby Collserola mountains (located only about 1 km away), that have important stands of pine (Pinus halepensis Mill. and P. pinea L.) forests. Pines emit monoterpenes not only in response to light but also to temperature (Peñuelas et al. 2001), and nocturnal temperature-dependent emissions of stored monoterpenes from pine forests have previously been described at Mediterranean locations (Davison et al. 2009).

We have also modified the discussion of section 3.3.2 (MSY rural site) to include reference to the work by Hellén et al. 2012.

During winter, even if the biogenic emissions are not as high as later in spring or in summer, their influence on local photochemistry has been found to be almost as high as the one of aromatic hydrocarbons, thus playing a relevant role on the OH radical reactivity and contribute to local ozone formation (Hellen et al., 2012). Based on this, what about OH measurements by PTR-MS? Taking into account that for both monoterpenes and isoprene the OH radical reactions are important even during winter, are the authors able to calculate the contribution of OH radicals at the two sites? The calculation of OH radical mixing ratios can also be attained through the relationship between isoprene and its oxidation products (Liu et al., 2009), all of them measured by the authors.

R: .This would be very interesting to calculate. Unfortunately, we do not have information about the OH radical mixing ratios during this campaign. Furthermore, the calculations used in Liu et al. (2009) to attain the OH radical mixing ratios involve knowing the concentration of the isoprene reaction products methacrolein (MACR) and methyl vinyl ketone (MVK) separately. However, one of the limitations of the PTR-MS technique is that it does not allow for the separation of these two isomers and both are detected at the same *m/z* (71 for the Quad and 71.09 for the ToF, see Table 1 of the manuscript). We have now included a reminder of the fact that MVK and MACR isomers are detected at the same *m/z* in section 2.2 of the manuscript.

The temperature-dependent mechanism used by the authors to explain a significant part of the high value of nocturnal monoterpene mixing ratios is reasonable, provided temperatures remain sufficiently high during the night (Owen et al., 1997; Staudt et al., 1997). Considering the temperature range of winter DAURE field campaign, night-time emissions from storage in this species are expected to be low, while a decreased vertical mixing and lower photochemical reaction might explain the observed high monoterpene mixing ratios. These factors would also help to explain the fall of monoterpene mixing ratios in the middle of the day. Indeed, although the emissions from pine trees at the BCN site are expected to be higher during the day, the lowest ambient air mixing ratios combined with fast photochemical reactions might explain the observed monoterpene mixing ratios. I suggest to consider the following references which explore the urban and rural influence on atmospheric VOC mixing ratios under different atmospheric conditions and provide support to the author findings.

Monteiro et al., (2012) analyzed high O3 episodes by a statistical technique and modeling approach at a mountain site in the Mediterranean region, reporting transport of O3 and its precursors by local mountain breezes and sea breeze circulation as mainly responsible for the high O3 concentrations.
Guo et al., (2012) is still available as open discussion in ACPD and it provides measurements of air pollutants at an urban and rural site, the latter located on the mountain. They described the observed levels of pollutants as due to the combination effects of different factors: NO titration, vertical meteorological conditions, regional transport and mesoscale circulations.
Tsai et al., (2008) carried out measurements in central Taiwan showing similar diurnal pattern of inorganic gaseous pollutants, ozone and VOCs mixing ratios produced in large urban areas along the sea cost and transported by air circulation (sea-breeze regime) towards rural areas.

R: We appreciate the suggestion of these references. They have now been added at the end of section 3.1 and now the revised text reads:

> The importance of mesoscale circulation (i.e. mountain and sea breezes) in the transport of ozone and photochemical precursors (VOCs and NO_x) between urban areas and nearby mountainous rural areas, as highlighted by this study, has been confirmed in several other locations worldwide, such as for example Portugal (Monteiro et al., 2012), Taiwan (Tsai et al., 2008) and Hong Kong (Guo et al., 2012).

Specific comments
1.PAGE 30911 the abstract should include shortly the methodological PTR-MS approach.

R: A mention in the abstract to the PTR-MS used during the campaign has now been included. The text now reads:

> We measured VOC mixing ratios concurrently at an urban and a rural site during the winter DAURE campaign in the northeastern Iberian Peninsula, by means of PTR-MS at both locations: a PTR-Quad-MS at the urban site and a PTR-ToF-MS at the rural site.

2.In Introduction and Methods provide the specific period (month and year) during which the measurements were done.

R: We have now included the period (February-March 2009) at the end of the Introduction, just before the Methods, where the content of the manuscript is presented.

3.PAGE 30918 L13 I couldn't find Jorba et al., 2011 in ACPD. Please check carefully if it is still available in the open discussion stage of ACPD.

R: This manuscript is available in the ACPD archives, although not in the open discussion stage any more. It can be found at http://dx.doi.org/10.5194/acpd-11-4953-2011 .

4.PAGE 30920 L5-L12 in the first two sentences the authors discuss nitrogen oxides data in the form of NO2 and NO, while in the third sentence they refer to NOx only in the form of NO2. What about NO at the rural area? Please uniform it, and provide the same detailed information for both sites.

R: What happened is that the NO concentrations in the rural area were usually below the limit of detection of the instrument setup that the government air monitoring agency deployed there. Basically, the reason for this is that, up to the moment that our measurement campaign was held, this agency had only used these type of analyzers in urban areas to check for pollutants being higher than the legal limits. So the software that recorded the half hour averages of the data was only prepared to store "high concentration" numbers, the kind of "high concentration" numbers measured for example in a polluted city like the BCN site. The measuring campaign reported here served to the monitoring agency managers to realize that, for more remote areas as MSY, they should change the software in the near future. But unfortunately more accurate data was not available for us in this campaign.

We have now added a clarification for this in section 2.3 of the manuscript.

5.PAGE 30920 L13 how is the shape of the ozone diurnal cycle pattern? please describe it.

R: The description of ozone diurnal pattern has now been expanded, also describing its relationship to NO_x. This section now reads:

> Ozone showed a similar diurnal cycle at both sites, having the maximum mixing ratios (of about 32 ppbv for BCN and 44 ppbv for MSY) during the central part of the day (Fig. 2). Especially at BCN, when NO_x mixing ratios increased due to traffic-related emission, ozone mixing ratios dropped in clear indication of NO titration.

6.PAGE 30920 L19-L22 in order to provide better understanding of the relative importance of VOCs on photochemical O3 formation at the two sites, it would be helpful if the authors could provide data on the VOC/NOX ratios, which is the most important parameter driving the O3 formation. Calculation of this ratio would be useful to better explain differences in O3 levels between rural and urban areas, and it would also reveal more detailed mechanisms such as investigation of the role of higher NOx in the urban areas in suppression of ozone by NO titration as compared to the rural site.

R: We have now added a new supplementary material that includes a figure showing the diurnal cycle of the VOC to NO_x ratios for both sites. BCN, with high emissions of NO_x, presented VOC-sensitive conditions all day long, while MSY, farther away from the NO_x sources, showed VOC to NO_x ratios more prone to ozone formation.

7.PAGE 30920 L23-L25 consider the study by Guo et al., 2012 available in the open discussion stage of ACPD.

R: The reference to the work of Guo et al 2012 has now been included in this section.

8.PAGE 30921 L20 as Kristensson et al., (2004) restrict the origin of aromatics only to the subcategory of polycyclic aromatic compounds, I suggest to consider and add Hsieh et al., (1999) and Yamamoto et al., (2000).

R: We have replaced the reference of Kristensson et al 2004 with those suggested by the reviewer.

9.PAGE 30922 L4-19 the characteristic diurnal pattern of isoprene and monoterpenes is not well described. Please integrate and explain it.

R: An explanation of the diurnal pattern of isoprenoids in BCN has been now included in the description.

10.PAGE 30922 L20-L27 the authors provide a description of the comparison between their data on daily mixing ratios of VOCs data with those of previous studies carried out in different cities, but there is no discussion. What does it mean and how informative could be? The authors report that the concentration of these compounds in some cases fall in the range of VOC measurements reported in previous studies of other urban locations. Does it mean that all the locations have similar emission sources or meteorological conditions? Can the authors comment on this?

R: Our intention was not to compare emission sources or imply that the sources in those cities were similar to the sources in BCN. The data of other cities was included in the manuscript to give some context to our measurements, so the reader could have an idea of what range of mixing ratios have been reported in other urban areas around the world. For a comparison of the VOC mixing ratios in MSY with other rural areas, the reader is referred to Seco et al (2011b).

11.PAGE 30942 I would say "Location" instead of "City" as not all the evaluated urban areas are referred to a specific city.

R: This has been changed following the reviewer's suggestion.

12.PAGE 30944 I would change "gases" with inorganic gaseous pollutants".

R: This has been changed following the reviewer's suggestion.