Atmos. Chem. Phys. Discuss., 12, C10818–C10824, 2012
www.atmos-chem-phys-discuss.net/12/C10818/2012/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Volatile organic compounds in the Western Mediterranean Basin: urban and rural winter measurements during the DAURE campaign" *by* R. Seco et al.

Anonymous Referee #2

Received and published: 20 December 2012

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.

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 iso-

ACPD
12, C10818–C10824, 2012

prenoids. 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.

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.

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.

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

ACPD
12, C10818–C10824, 2012

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.

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.

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

ACPD

12, C10818–C10824, 2012

between isoprene and its oxidation products (Liu et al., 2009), all of them measured by the authors.

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

ACPD

12, C10818–C10824, 2012

large urban areas along the sea cost and transported by air circulation (sea-breeze regime) towards rural areas.

Specific comments

1.PAGE 20911 the abstract should include shortly the methodological PTR-MS approach.

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

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.

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.

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

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.

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

8.PAGE 30921 L20 as Kristensson et al., (2004) restrict the origin of aromatics only

ACPD

12, C10818–C10824, 2012

to the subcategory of polycyclic aromatic compounds, I suggest to consider and add Hsieh et al., (1999) and Yamamoto et al., (2000).

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

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?

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

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

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 30909, 2012.