

# Interactive comment on “Meteorology during the DOMINO campaign and its connection with trace gases and aerosols” by J. A. Adame et al.

## Anonymous Referee #1

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We thank Referee 1 for the detailed reading and analysis performed with our paper. We have tried to reply to all comments and questions. The responses in this document are shown in blue print.

General comments.

This work by Adame et al., presents the weather conditions, air mass circulation, and observed behaviors of a number of atmospheric compounds (O<sub>3</sub>, NO, NO<sub>2</sub>, SO<sub>2</sub>, particle number, benzene, isoprene), chemical properties (OH reactivity) and aerosol chemistry during the DOMINO campaign which took place from 21 November to 8 December 2008 at the El Arenosillo observatory (South- West of Spain).

The paper is well written, even if some Section appears redundant to me (ex. Section 2.2). However, my principal concern about this paper is the lacking of a clear/strong scientific goal. Moreover, I did not think that substantial conclusions have been reached. The authors stated that the goal of the paper is to “investigate weather conditions during the DOMINO campaign, emission sources and land uses, to identify air masses of different origins and to analyse trace gases and particles in the air-masses, in the south-west of the Iberian peninsula during late-autumn”.

At the end of the Introduction we state: “The aim of this paper is to carry out a detailed analysis of the weather conditions during the campaign, to identify distinct air mass characteristics (urban, industrial and natural with continental and marine influences), to determine the meteorological conditions associated with these regimes and to investigate their influence on the behaviour of O<sub>3</sub>, NO, NO<sub>2</sub>, SO<sub>2</sub>, OH reactivity, isoprene, benzene, particles and aerosol chemical composition.”

We feel the scientific goal of this paper is clearly stated in this paragraph.

Even if of some importance in the framework of the DOMINO campaign data interpretation, I do not think that the analysis presented in this work represents a serious advance in the scientific knowledge, as requested by ACP for publication.

Our study is a first in many aspects, namely in the application to this specific geographic region: The relation of sources and land uses with the chemical species occurring in this area; the analysis of air mass origin variation with altitude, using HYSPLIT and meteorological files of high spatial resolution (ECMWF); the use of data from a 100 m meteorological tower to estimate the atmospheric stability and its impact on local air chemistry. It is also the first time the daily cycle of a whole suite of chemical species and measurements in different air masses, classified for their origin and distinct sources of pollution, is presented for the atmospheric observatory of El Arenosillo, allowing for chemical characterisation of urban air after transport of a few hours (from Huelva) and several hours (from Seville) as well as marine and rural air.

In particular, also considering the relatively short time period of the campaign as well as the fact that, as stated by the authors, the investigated period was characterized by anomalous atmospheric circulation in respect to the previous 14 yr which partially prevents a generalization of the results.

As the Referee 1 knows this sort of campaign can have a variable duration, one week to a few months. In our case this campaign was of approximately one month, time sufficient to collect the main wintertime scenarios in this area. As it has been commented by the Referee 1 below "*The data set of the DOMINO campaign is certainly of high value...*", others papers using data in the same period from this campaign have been published.

Moreover, a number of paper describing the DOMINO results as well as the long-time measurements at El Arenosillo were already published, and similar analysis presented in this work by Adame et al., were already presented (e.g. Diesch et al., 2012; van Stratum et al., 2012; Sinha et al., 2012; Sorribast et al., 2013; Notario et al., 2013; Adame et al., 2010). So what's new with this paper? This should appear more clearly before the paper can be accepted for publication. The data set of the DOMINO campaign is certainly of high value (as demonstrated by the publications already present in the special issue).

The papers mentioned by the Referee present different aspects of the DOMINO campaign and other topics. Specifically, in Notario et al. (2013) an OX analysis is presented and in Adame et al. (2010) the ozone variation due to mesoscale processes. In this work these issues have not been studied, instead our study is a detailed analysis of the meteorology during the DOMINO campaign that cannot be found in any other DOMINO paper, but can be useful to further evaluate the results shown there. In addition a characterization of the chemistry in dependence of distinct air sources has been performed using a whole suite of atmospheric measurements, which is unique for this region of Europe.

So my suggestion for the authors is to find an original/novel topic and try to better focus the paper on that (maybe the contribution from ship emissions can represent an interesting point to be better exploited? Or the relative contribution of mesoscale dynamic vs synoptic-scale circulation?).

The influence of ship emissions at El Arenosillo is an interesting topic but not the aim of our current study. For this we would need more data with wind from the ocean to compare situations of varying marine traffic, as well as data from the ships.

As mentioned in the manuscript and above, during DOMINO period the lower atmosphere was governed by synoptic scale processes. Then, how can we study the contribution of the mesoscale vs. synoptic scale in this period?

Below my specific comments are reported.

Specific comments Section 2.2 I do not think that this detailed description of the emission data-base is really necessary. This also considering that the list of number here presented were not specifically used/cited in the following of the paper: : Moreover, it looks to me that some large differences existed between the two cited data-bases (EPER vs CMAJA), e.g. SO<sub>2</sub> for industry at Huelva. You can simply indicate what are the major emission sectors for each regions as a function of atmospheric compound.

It is true that there are differences between the emission inventories. We agree that this section might be shortened.

Suggestion for the paper: can your data be used to verify the goodness of these emission inventories (maybe also using long-term measurements)?

In our opinion it is not easy but could be possible using long-term observation data from the monitoring station, applying mesoscale dispersion models. In function of the concentrations measured at El Arenosillo these models could be used to estimate the source location and emissions contribution in kg per hour. We thank Referee 1 for this idea. However, we believe it amply surpasses the scope of our current study.

Section 2.3 A table reporting all the available measurements with details on instrumentation and location can be useful for the reader! Can you provide a combined uncertainty for O<sub>3</sub> measurements?

Following this suggestion, in the next manuscript version a new Table with the instrumentation will be added.

It is unclear to us what the referee means with a combined uncertainty for O<sub>3</sub> measurements. As stated in the manuscript, "The precision and the detection limit were 1 ppb", respectively.

Section 3.1.1 Which was the advantage of using ERA interim fields? Are the obtained results significantly different from that calculated using the 1deg X 1 deg meteorological files? How about representation of topography? In naming the air-mass circulation classes you completely forgive the "long-range" origin of air-masses. Thus, only the local/regional emissions are important for El Arenosillo atmospheric composition?

To compute back trajectories with HYSPLIT we have as base the files provide by NOAA, from surface to 500 mb 14 vertical levels and 1° spatial resolution. They are available from NOAA servers. Using ECMWF you can build your files, download the grib files with the meteorological fields necessary from the MARS (Meteorological Archival and Retrieval System)-ECMWF server and later to convert these files to ARL format which are used by HYSPLIT model. As mentioned in the section 3.1.1 we have created files with 16 vertical levels from surface to 500mb and 0.25° spatial resolution. The advantage is a better representation of the meteorological conditions. In a 1° file you have meteorological data every 1° and with the 0.25° files you have four meteorological data sets in 1°, allowing the computation of the trajectory to be more reliable.

In general, under synoptic conditions the difference obtained with files of 1° and 0.25° may not be large, but depend on specific weather conditions and area.

The topography is one of the parameters in the input file. When you export the information from MARS, in your script you can define the topography, hence this information is from ECMWF.

Although in previous studies carried out in this area the air mass trajectories have been computed with a duration of 120 hours, we have decided to use 48 hours. You can see in Fig. 2 and 4 that the back trajectories calculated collect the transport over a few thousand km, covering the whole Iberian Peninsula and the North Atlantic Ocean. Considering the lifetimes of only a few days of many of the chemical species measured in DOMINO, this transport range is sufficient. Though the trajectories take into account such a wide area, due to the limited lifetime of the reactive species observed during DOMINO, the measurements can be expected to be affected predominantly by local emissions (sources in a range of about 100 km).

Section 3.3 The general implication of the observed variability (especially for OH reactivity) should be better addressed here or in the Discussion section! Here, I have serious concerns about the robustness of the depicted diurnal cycles. Looking at the table 2, each mean cycle is resulting from averaging a maximum of about 4 days (92 hours for Huelva-Portugal air-masses) to a minimum about 1.5 days (35 hours for Marine air-masses). This is evident looking at the plots, where very noisy behaviors can be seen (especially for NO<sub>2</sub>, SO<sub>2</sub>, VOCs). I suggest to the authors to simply calculate night-time/day-time average values (with a proper interval of confidence) and put them in a Table for the different parameters and air-masses and then discuss it. Other way can be to discuss representative case studies: : :

It is true that the mean cycles of pure air flows are obtained with data from between 4 and 1.5 days, but these periods have been filtered for distinct air origins without mixing with other sources. We feel it is easier to visualize these data in graphical form than in a table. In addition we compare several species with

very different diel behaviour, therefore we settled for diurnal cycle plots. The noise in the graphs also gives a better impression of the variability of the data and the robustness of the conclusions than a table would. To study representative cases would be almost the same, only with even less data.

Row 11, pag 19258: “no significant photochemical production in more polluted air”. I do not think that photochemical production can be neglected in explaining the O<sub>3</sub> diurnal variability (especially for Seville air-masses: : :), see also Diesch et al., 2012.

The values observed during the DOMINO campaign in November-December, are the lowest ozone values of the year. In spring and summer, when ozone production is significant, the ozone values can be doubled, ~70-80 ppb. The highest values obtained during DOMINO were in relatively clean maritime air masses, i.e. more polluted air from other direction did not show any additional photochemical production. Instead, nighttime ozone in more polluted air masses was lower, indicating a stronger ozone destruction. The air mass classification carried out in Diesch et al. (2012) is different, which is a main reason for apparently different conclusions.

Row 13, pag 19262: Do you have a very small number of filter samplings. How about their representativeness? I do not think that you can use these info for generalizing, but just as “ancillary” information to reinforce the discussion: : :

We use the data for a direct comparison of the observed chemistry in air from different sources, with a focus on separating clearly between areas of different sources and avoiding air masses with mixed origin. This is especially important for the filters. The statistics are obviously limited by the amount of data obtainable during the duration of the campaign. However each filter used in our study integrates 12 hours of air from a well-defined source region, thus should be representative for this source region.

4. Discussion In general this section relies too strongly on the description of the diurnal cycles depicted by Fig. 8 for which I have serious doubts about robustness. E.g.: row 18, pag 19266: “from this time to midnight daily maxima of No<sub>2</sub>, benzene, and isoprene appears”: actually they are just single peaks (probably related to specific events).

We show the daily variation of the chemical species under pure flows, and again the robustness of this information is the selection of pure flows and not in the number of days used. In an experimental campaign of one month, it is not possible to have many days with the same conditions. Maybe, in continental areas governed by the same weather conditions during long time. In fact, the strength the campaign in this area was to try to collect the atmospheric chemical composition under different scenarios.

Row 23, pag 19263: “transport for Huelva: : :..in less than 3 h”. How did you calculate the transport time?

We know that in this area and under synoptic flows the wind speed is homogeneous. Then, we assume a similar wind field (in direction and speed) from Huelva to DOMINO area, and with the wind speed measured at El Arenosillo we can obtain the transport time. Pag. 19263, Rows 23-24: “*The wind speed of ~ 2.5ms<sup>-1</sup> and the distance of 25 km, favour the arrival of the air pollutants before they are removed by chemical or deposition processes*”.

Row 26, pag 19267: Actually the OH reactivity and NO<sub>2</sub> decreases appeared to be related with a decrease of wind speed (not an increase), at least looking at Fig. 8 and Fig. 6.

This section corresponds to the analysis of Seville-Guadalquivir sector. You can see in the Fig. 6, in the daily cycle of the wind speed, a clear increase from midnight to 9:00 UTC (red line). It is the highest nocturnal wind speed collected during the campaign. For this reason, we suppose that due to this dispersion situation the values of these species decrease.

Row 20, pag 19268: you should see more in details to the actual weather/transport conditions which promoted these NO<sub>x</sub> and O<sub>3</sub> peaks for trying an attribution.

Thank to previous studies in this area, we know that under synoptic flows the wind field is similar. If we assume a same wind field, then we can calculate this time transport and to look for an explanation to the origin of this behaviour. Pag. 19268, rows 19-23: *"The wind speed at this time 20 was ~3ms<sup>-1</sup>, i.e. transport from Seville needed 7 h assuming a constant velocity. The peaks in NO<sub>x</sub> and ozone must be therefore due to a peak in NO<sub>x</sub> emissions in Seville in the early afternoon, which seems unlikely since the peak of urban NO<sub>x</sub> emissions is usually during rush hours in the morning and evening, or to sources closer to the site."*

Row 24, pag 19628: please, consider that you have only one filter for this air-mass class: avoid generalization!

You refer to this sentence *"On the other hand, the lowest PM<sub>10</sub> and PM<sub>10-2.5</sub> concentrations are also found in air from this sector with 4.9 µgm<sup>-3</sup> and 1.4 µgm<sup>-3</sup>, respectively."* We compare the values obtained in this sector with the measured under pure flows from other sectors during the campaign.

Section 4.4 Sinha et al., reported significant SO<sub>2</sub> mixing ratios in marine air-masses (see their Fig. 4). Please can you comment this discrepancy with your results? Significant difference appears also comparing NO<sub>2</sub> diurnal cycle (Fig. 5 by Sinha et al.).

We agree with you about the discrepancies obtained with the work stated by Sinha et al. (2012). In this work has been applied a classification based in the wind sectors and back trajectories computed at 20, 100 and 500 m; to conclude three air flows types. According with the type of study to perform it is possible to use different air masses classifications. If the classification is different the number of hours in each sector (moreover the number of sectors is not the same) can be different and then the results can show differences. Taking into account that we have selected only pure air flows and four sectors, therefore our study is more restrictive and will show differences regard to Sinha et al. (2012).

Row 21, pag 19269: I think it is important to consider air-mass back-trajectories longer than 48 hours, especially for ozone variability.

We agree with this comment of the Referee 1. For other species different to ozone, we think that 48 hours is sufficient to know the influence of emission sources, as it has been commented previously in this response. However, for ozone under specific weather conditions could be not sufficient. For this reason we performed a study to know the ozone transport in the Atlantic Ocean and cited in the Page 9269, rows 23-28: *"...it is aged ozone with origin probably associated to long-range transport which has travelled over the Ocean reaching the measurement area through the marine boundary layer. In order to follow the long-range transport under these conditions, back trajectories for the previous 10 days (data not shown) have been computed."*

Conclusions Row: 25, pag 19270: "long-range transport: : :on local chemistry". You should try to better quantify this contribution.

*We take into account this suggestion.*

Row 1. Pag 19271: I do not think that these conclusions are really substantial!

With this paragraph *“This study illustrates the importance of both chemistry and dynamics for atmospheric composition of a rural site surrounded by sources of diverse nature, as are most rural sites. It is also meant to be a reference for all future studies with the data from the DOMINO campaign”* we want to highlight the importance of atmospheric dynamic in the chemistry. Sometimes, the chemical composition is analysed without the weather conditions, and this work presents the importance to study these two issues jointly. In the framework of DOMINO campaign we consider that this work could be reference for future studies. For these reasons, we think the conclusion must be maintained.

We are currently working on our reply to the referee’s specific comments, which we intend to submit shortly together with further improvements of our manuscript.