Atmos. Chem. Phys. Discuss., 11, C15632–C15641, 2012
www.atmos-chem-phys-discuss.net/11/C15632/2012/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Variability of aerosol, gaseous pollutants and meteorological characteristics associated with continental, urban and marine air masses at the SW Atlantic coast of Iberia" *by* J.-M. Diesch et al.

J.-M. Diesch et al.

j.diesch@mpic.de

Received and published: 24 February 2012

General comments

This paper presents the results obtained during a field campaign carried out in south-western Span during a three weeks period in winter 2008. Authors obtained a large set of data by means of a combination of instruments (HR-ToF-AMS, FMPS, CPC, OPC, MAAP, APS; among others); the paper is mainly based on the interpretation of the AMS data as a function of the origin of air masses determined by the application of the HYS-

Full Screen / Esc
Printer-friendly Version
Interactive Discussion
Discussion Paper

PLIT model. A major concern is the limitation of the methodology used to interpret the origin of the air masses with influence on the levels of pollutants, and consequently the variability of aerosols in the area. This limitation is mainly related to the meteorology and to the frequent impact of emissions from the close Huelva industrial states (20 km distant) in the Arenosillo. Interpretation of this vast amount of data obtained at high time resolution may not be accomplish by applying a low spatial resolution model. In addition, the sampling period is too short in order to describe the variability of aerosols in this complex area. Consequently I recommend rejecting this paper in the present form.

Author: We agree with Reviewer #2 that a three-week field campaign is not sufficient to describe the typical features for a certain site as they are experienced over the year or even over a typical year. However, we do not claim to do this within this manuscript. The manuscript presents an overview over the multiple measured data within this field campaign and how they vary over time and as function of air mass source. And for this purpose the manuscript is very valuable to the community, which is shown by already three papers by other authors in press or published and additional papers in preparation which cite this work and used this data set for further analysis. To make this clearer we reworded the title of the manuscript to: “Variability of aerosol, gaseous pollutants and meteorological characteristics associated with changes in air mass origin at the SW Atlantic coast of Iberia”. We agree with Referee #2 that HYSPLIT is a low spatial resolution model that is not capable of modeling local features of atmospheric transport, especially when they are caused by mesoscale processes or by local topography. However, during the DOMINO field campaign atmospheric transport was dominated by synoptic large-scale processes which are well modeled by the HYSPLIT model. This fact was also pointed out by J.A. Adame Carnero in the interactive comment during the open discussion phase of this manuscript (J.A. Adame Carnero, Atmos. Chem. Phys. Discuss. Interactive comment, 11, C14767-C14769, 2012). J.A. Adame Carnero is an experienced atmospheric scientist with many years research experience in the area where the DOMINO campaign was performed. He has performed a systematic study

ACPD

11, C15632–C15641, 2012

for the campaign period which showed that the HYSPLIT backtrajectories that were used within our manuscript to determine the air mass origins are representative for the respective time intervals (presented on AGU 2011, manuscript in preparation). Last, but not least, the separation of different types of particle formation events during this field campaign, presented in a paper by some of the authors of this paper and submitted to ACP recently, shows very clear indications that the separation of air masses into the source categories is valid as presented in this manuscript. The close proximity of urban sources in the Huelva area are not a limiting issue in the association of measurement data with source regions because we only used data measured within extended time intervals of similar transport patterns over at least several hours and in addition we compared local wind direction measurements with back-trajectory analyses to assure that the results of both are reasonable. Both is presented in the manuscript. We are slightly confused by the fact that one of the reviewers stated in the quick review before publication of the paper in ACPD regarding the limitations of HYSPLIT and the short sampling period: "This could be not an inconvenience for publishing but first a number of issues should be addressed." All issues brought up by this reviewer were addressed in the current manuscript, e.g. we added Figure 4 with time series for various parameters to show that all categories were measured continuously over relatively long time periods and beside the "Portugal+Huelva" one, all categories were measured during different days so that the influx from other source regions as mentioned by the reviewer is very unlikely. Additionally, the DOMINO objectives were further explained in the manuscript as requested by the reviewer.

Specific comments

Meteorology in the area is complex and difficult to model with HYSPLIT in order to interpret high time resolution measurements. Meteorology in the area is significantly influenced by thermally originated local circulations, especially in summer, favored by the regional orographic features (with a high influence of the rivers Tinto and Odiel, channeling the transport of polluted air masses). This results in the persistent formation

ACPD

11, C15632–C15641, 2012

of daily cycles, characterized by a limited spatial development with return circulation at high levels, giving rise to the transport of the air masses in relative small volumes; change of wind direction along the day with an opposite direction day/night resulting in a poorest renovation of air masses and in the dispersion of pollutants over a wide and extended area.In winter, anticyclonic situations favored the nocturnal accumulation of the industrial emissions form Huelva, increasing levels of aerosols and gases in the area. Slightly reinforced winds during the day may spread these pollutants over the area. This situation is similar to that recorded in the first week of the campaign. The variability of aerosols at the site of Arenosillo is strongly influenced by the proximity of the highly industrialized city of Huelva, located 20 km WNW of the site. The town is surrounded by three industrial estates with different industrial emissions. Among others, the industrial activities are: production of phosphate derivatives, Cu beneficiation from sulfides and sulfuric acid production, petrochemical, TiO2 production, power generation, chloride and sodium hydroxide and cellulose paste. This industrial complex results in high emission of gases and particulate pollutants. A characterization of the emission profiles of these industries is available in Alastuey et al. 2006. Of special interests are the emissions of Cu beneficiation plant characterized by SO2, -rapidly converted to H2SO4, and As. Although long rang transport may influence this area iin southwestern Spain, location of the industrial states together with the meteorology may result in the frequent impact of the industrial pollutants in the Arenosillo site. Therefore, interpretation of the air mass origin based on the calculation of 48h back trajectories may be not adequate to separate the external from the local (from Huelva, only 20 km distant) contributions, and consequently to interpret the variability of aerosols as a function of their origin. Impact of both long range transport and local industrial emissions from Huelva in the Arenosillo sites is well documented (Pey et al 2008, de la Rosa et al, 2010). Pey et al 2008, by applying high h spatial resolution modeling combined with PM chemistry identified a long-range transport episode from Western Iberia, recalculating the air masses through the Gulf of Cadiz and the Straits of Gibraltar towards the study area. They also identified the impact of Huelva emission based on the levels of

ACPD

11, C15632–C15641, 2012

trace metals (As, Cu, among others). This industrial impact is also demonstrated by de la Rosa et al., 2010 determines annual average levels of As in Arenosillo of 5 ng m-3, very similar to those obtained at Huelva background sites (6 ng m-3) and clearly higher than levels usually determined at urban and rural sites, indicating a clear impact of the Cu smelter plant. These local/industrial and long range transports (with recirculation of air masses from western Iberia –Portugal- passing through the Strait of Gibraltar) cannot be identified by the application of HYSPLIT.

Author: As detailed above, we agree that HYSPLIT is not capable of modeling the transport of a certain emission source within the Huelva industrial area to our measurement site. However, this is not what we claim. The reviewer describes in detail the various sources and related emissions in the Huelva industrial area. This is also described in our manuscript with some detail. As the reviewer states in his comment many of the local effects are not very pronounced during winter, where the campaign was performed. Therefore, and since we do not want to identify individual plumes from Huelva at our site and since further research (see above, research by J.A. Adame Carnero et al.) has shown that during the DOMINO campaign synoptic transport processes dominated we are confident that our HYSPLIT calculations provide reasonable transport patterns and therefore allow the discrimination of different air mass source regions for the data.

Authors discussed (page 31595) about the differences between wind directions measured locally and HYSPLIT back trajectories. It is true that HYSPLIT may give more information about long range and regional transport, but given the high spatial resolution of the model (45 km) it does not permit to identify the impact of the emissions of the industrial estates of Huelva (only 20 km distant). It is also difficult to reproduce the local effects of the orography (channeling in the Tinto and Odiel river valleys). To this end the interpretation of local winds may be more useful. Complementary a higher resolution model could be useful for the interpretation of the origin of the air masses (see Pey et al, 2008). In Figure 4, peaks of BC and PM are usually registered simulta-

ACPD
11, C15632–C15641, 2012

neously with peaks of SO2 and NOx, and coincide with the increase of levels of sulfate. It should be noticed that the highest pollution episodes were registered at the beginning of the campaign, during periods that were not clas- sified according to their origin and therefore were not considered for the interpretation of the variability of aerosols in this manuscript. These periods coincide with the anticyclonic pollution episode mentioned in the manuscript, and reflect the impact of the Huelva industrial emission in the Arenosillo. Therefore, the present investigation does not permit to interpret the variability of aerosol in Arenosillo during the highest pollution episodes recorded during the campaign. Similarly, during other episodes, labeled as "Marine+Huelva" "Portugal +Huelva" and "Seville", PM peaks are simultaneous with SO2 and/or NOx episodes, suggesting the impact of the Huelva industrial emissions. As deduced from the wind directions, these short episodes s were possibly recorded during transitory hours when the land-sea breeze changes, transporting polluted air masses from the Huelva industrial areas. Therefore, I think that impact of emissions from the Huelva industrial state in the Arenosillo site is not sufficiently identified by the methodology used in this paper. Limitations of using HYSPLIT at 45 km resolution should be clearly stated. Some of the air mass origins defined (mainly the Huelva+marine, Portugal + marine, and continental) mainly reflects the impact of the Huelva industrial emissions.

Author: As suggested by the reviewer we added information on the limitations of using HYSPLIT to model the regional air transport to the manuscript: "HYSPLIT is intended for transport processes on larger spatial scales due to its relatively low grid resolution. Especially for lower backtrajectory altitudes the model suffers from severe limitations. Therefore, under the influence of mesoscale processes, HYSPLIT is not able to reproduce local meteorology adequately. However, during the DOMINO campaign synoptic conditions dominated also regional transport which can therefore be reproduced sufficiently accurate down to the lower boundary layer by HYSPLIT calculations as was shown by thorough sensitivity analyses and comparison to measurement data (personal communication, J. A. Adame Carnero)". Regarding the local wind direction measurements: We agree with the reviewer in the statement that for some transport

ACPD

11, C15632–C15641, 2012

features locally measured wind directions might provide better information on the transport characteristics while for others are better represented by the back trajectory calculations. This is exactly the reason why we included the comparison of trajectory-based and wind direction-based classification of air masses in the manuscript. Actually this comparison shows that both approaches generally result in similar classifications with the back-trajectory-based classification allowing additional separation. Regarding the pollution episodes during the campaign which were not classified: It would have been nice to include such periods in the overall classification of air masses and identify the source areas of the increased pollution levels. However, these events with high pollution levels occurred during times when the trajectories showed a strong transition, e.g. from continental origin without Huelva-related influence over Huelva to marine air masses. Since such transitions can only be classified as being associated with a certain source region with very large uncertainty, we decided not to classify such episodes. This also shows that we did not apply our classification method with levity to the data but only when we had a certain degree of confidence into the classification – even though the data might have suggested a certain association to a source region.

Pages 31597-31600 The increase of sulfate may be related to the impact of the industrial emissions from Huelva and may be related to the emissions of the Cu beneficiation and the sulphuric acid plants. Other sources such as shipping emissions and long range transport cannot be discarded. However, the methodology used does not permit the identification of the origin.

Author: We see an increase of sulfate when sampling the urban source categories and the marine source category. As the reviewer correctly states, we cannot distinguish single point sources like for example individual plants and we do not claim this. In addition we mentioned in the manuscript that we think such increased sulfate levels could be the result from shipping emissions in the marine category, for example.

Organic particulates increased during the Continental air masses. It should be of interest to investigate if there is a relationship between these organic episodes and the im-

ACPD

11, C15632–C15641, 2012

pact of the cellulose paste plant, located north east of Huelva, and north of Arenosillo.

Author: As detailed in the manuscript “Continental” air masses are sampled for a very large wind direction (or trajectory) sector ranging from approximately NW to NE. Of course all point sources at all distances within this sector are sampled as part of this category – including the cellulose paste plant mentioned by the reviewer. This plant is located NE of Huelva and N of Arenosillo, therefore it has a distance of at least 30 km from the sampling location. As stated above we cannot – and do not intend to – identify and separate individual point sources within the sectors. However, it is extremely unlikely that a single plant can be detected at such a distance from the source if not very specific markers are used for identification. For example measurements in the vicinity of large integrated steel plants showed that the emission plume is already diluted almost down to background levels already approximately 15-20 km from the source. Therefore we definitely measured the emissions from this single source within the continental sector as well as those of all other sources within this sector however, it cannot be separated from the sector ‘baseline’. More likely these organic episodes are caused by particle formation and growth as a consequence of photochemical processing of precursor species.

Particle number: authors should refer to a recent paper by Fernandez Camacho et al. 2010b This paper demonstrated the importance of photochemical nucleation in Huelva, favored by the high SO2 industrial emissions. In the present paper production of fresh particles is deduced for Marine+ Huelva air masses; from Figure 6 it can be deduced that this process is also important for Continental and Portugal + Marine

Author: We discussed in the paper that particle nucleation occurred for the “Continental” and “Marine+Huelva” categories (also shown in Fig. 7), not as mentioned by the reviewer for “Marine+Huelva” only. For these both categories we analyzed new particle formation events in detail in a second manuscript that was recently submitted to ACP. “For the “Portugal+Marine” category we also observed a mode around 10 nm but we could neither identify nor exclude new particle formation events for this category as

ACPD
11, C15632–C15641, 2012

now stated in the manuscript. However, since our focus within this manuscript is on the general characteristics of the various air masses and since the manuscript is already too long, we did not add the publication and its discussion in the manuscript.

Page 31610 (and page 31617). About WBOA; wood combustion domestic heating is not frequent in the area. Biomass burns may be significant in winter but are mainly during the day. Could the WBOA be related to the influence of the cellulose plant? It would be interesting to investigate the influence of the organic industrial emissions in the area (petrochemical, cellulose plants,..) with the organic aerosol components identified.

Author: Thank you for this information that domestic heating using wood combustion is not frequent in this area. We have added this in the manuscript. However, we cannot investigate the impact of single point sources like for example the cellulose paste plant or other point sources within the Huelva industrial area. Additionally, one individual point source would produce a more peak-like signature in the time series of certain parameters what we do not observe. For this reason, we think WBOA mainly originates from wood combustion and the diurnal cycle originates from the evolution of the boundary layer height.

Page 3612. It should be stated that the articles cited (Adame et al 2010 and Carnero et al 2010) were carried out at Arenosillo. This section on ozone variability could be deleted: does not contribute to the discussion and it is not a significant input with respect the cited papers.

Author: The information that the work for the mentioned articles were carried out in El Arenosillo was added into the manuscript. However, as our manuscript is also intended to be a paper that presents an overview over our particle and gas phase measurements during the DOMINO project, with our data being used and the manuscript being cited already by 2 printed papers and by additional papers which are in ACPD now or in preparation, we did not remove the ozone discussion from our manuscript.

ACPD

11, C15632–C15641, 2012

Other comments

Page 31590: Please indicate size range for CPC 3786

Author: The size range was already stated in Table 1. But we did additionally add the CPC size range in the text now.

Page 31593:please check the wind direction for Seville, P+H, and M+H-, it seems these are different to those depicted in Figure 3.

Author: The denoted wind direction ranges are right but sorry for the misunderstanding. On page 31593 the wind direction range was obtained from the boundaries of the trajectory arrival directions. Figure 3 was obtained by using the locally measured wind directions corresponding to times where the back trajectories were used for classifying the different categories as also mentioned in the manuscript. However, due to this misunderstanding we tried to express this now in the text more clearly (see reply below).

Page 31612: last line: Figs 10c instead of 9c. and Page 31641. Caption Fig. 10. Please add (b) in caption

Author: Corrected, thank you.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 31585, 2011.

ACPD

11, C15632–C15641, 2012

Interactive Comment