Atmos. Chem. Phys. Discuss., 11, C14735–C14739, 2012
www.atmos-chem-phys-discuss.net/11/C14735/2012/

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.

Anonymous Referee #2

Received and published: 26 January 2012

General comments This paper presents the results obtained during a field campaign carried out in southwestern 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 Hysplit 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.

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 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 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. 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 simultaneously 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.

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

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. 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.

Other comments Page 31590: Please indicate size range for CPC 3786 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. Page 31612: last line: Figs 10c instead of 9c. Page 31641. Caption Fig. 10. Please add (b) in caption

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