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Atmospheric Chemistry and Physics Discussions

Meteorology during the DOMINO campaign and its connection with trace gases and aerosols

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Abstract

The DOMINO (Diel Oxidant Mechanisms in relation to Nitrogen Oxides) campaign was carried out from 21 November to 8 December 2008 at El Arenosillo station (SW of Spain) in a coastal-rural background environment. The main weather conditions are analysed using local meteorological variables, meteorological soundings, synoptic maps, as well as back trajectories of the air masses using the HYSPLIT model and high spatial resolution of meteorological fields. Measurements of the main meteorological parameters were collected both on the surface and on a tall tower. A detailed land use analysis was performed on a 80 km scale showing the main vegetation types. Also the main anthropogenic atmospheric emission sources both industrial-urban from Huelva and from the urban Seville area are shown. A study to identify air mass origins and their variation with height was carried out. In this intensive campaign air masses coming from different areas with different emission sources were observed: from the NW, with a highly industrial-urban character; continental flows from northerly directions; from the NE, with pathway, first, over the Seville metropolitan area and, then, over the Doñana National Park; and maritime air masses coming from the Atlantic Ocean. To study the chemistry in the four atmospheric scenarios identified, gas phase measurements of primary and secondary species such as ozone, NO, NO_2 and SO_2, biogenic and anthropogenic VOCs like benzene and isoprene, as well as total particles concentration and chemical composition of the aerosols are compared and discussed. The highest levels for total particle concentration, NO, NO_2, SO_2, benzene, PM_{10}, $PM_{2.5}$ and chemical elements such as As or Cu were found under flows associated with industrial-urban emissions from the Huelva-Portugal sector which are transported to the site before significant removal by chemical or deposition mechanism can occur. The air masses from the north were affected mainly by crustal elements and biogenic sources, the latter being exemplified by the biogenic species such as isoprene, particularly in the first part of the campaign. The urban air from the Seville area, before arriving at El Arenosillo traverses the Doñana National Park and therefore, was affected

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by industrial-urban and biogenic emissions. This air can transport low levels of NO_x , total particle concentration and SO_2 with aged ozone and some isoprene. Marine air masses from the Atlantic Ocean influence El Arenosillo frequently. Under these conditions the lowest levels of almost all the species were measured with the exception of ozone levels associated to long-range transport.

1 Introduction

Regional atmospheric physics and chemistry over a region can be characterized through measurements either routinely carried out at atmospheric observatories or sporadically within the frame of intensive measurement campaigns. The latter typically involve a larger number of specialized instruments, deployed together at the surface or on aircraft measuring many atmospheric parameters simultaneously (Geyer et al., 2003; Molina et al., 2010; Royer et al., 2011), sometimes at remote sites where permanent measurements do not exist and would be difficult to set up (Martinez et al., 2010; Williams et al., 2011). Atmospheric observatories on the other hand have the advantage of producing long-time data series which are needed for the characterization of seasonal dependencies and detection of long-term trends in air quality and even climate studies (Toledano et al., 2007; Cristofanelli et al., 2009; Sorribas et al., 2011).

El Arenosillo, located in the South-western of Europe, is an observatory with various atmospheric instrumentation measuring total ozone, ultraviolet radiation, surface gases (ozone and NO_x) and aerosols, among others. Due to the different atmospheric emission sources (biogenic and anthropogenic) surrounding this site and the orography features of this region, levels of atmospheric chemical species depend strongly on the air mass origin.

The diversity of source regions impacting the site, in addition to photochemical activity even in wintertime, together with the permanent instrumentation and long-time database available at this observatory, made El Arenosillo the site of choice for the DOMINO campaign. DOMINO (Diel Oxidant Mechanisms in relation to Nitrogen Ox-

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ides) aimed to close the radical budget in a variety of air masses, and to study the processing of anthropogenic pollution in an environment with both anthropogenic and biogenic VOCs. Many atmospheric variables were measured during the campaign, including meteorological (at the surface, at different altitudes on a tower and also using balloon soundings), trace gases (NO, NO_2, O_3, SO_2, N_2O_5, HONO, VOCs, etc.) including radicals (OH, HO_2, RO_2, NO_3) and aerosols (particle concentration, chemical composition, particle size distribution, etc).

The database generated in the campaign has been used by several studies so far. A study in order to identify HONO sources has been performed by Sörgel et al. (2011); nighttime mixing ratios of boundary layer N_2O_5 and NO_3 lifetimes depending on the type of air masses have been studied by Crowley et al. (2011); a general overview of the VOCs measured in the campaign, both biogenic such as monoterpernes and isoprenes and anthropogenic such as benzene or toluene has been published by Song et al. (2011); aerosol number and mass, polycyclic aromatic hydrocarbons and black carbon concentrations, among others, have been analysed by Diesch et al. (2012); OH reactivity as well as ozone production rates and regimes have been determined by Sinha et al. (2012); a study devoted to investigate the interactions between atmospheric boundary layer (ABL) dynamics and atmospheric chemistry using a mixed-layer model coupled to chemical reaction schemes has been performed by van Stratum et al. (2012).

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_3, NO, NO_2, SO_2, OH reactivity, isoprene, benzene, particles and aerosol chemical composition. Therefore, this work aims be complementary and an extension of the studies started by Diesch et al. (2012), Sinha et al., (2012) and van Stratum et al. (2012).

A review of the emissions sources in this region and instrumentation is presented in Sect. 2. A method for classification of the air masses is presented in Sect. 3.1 and

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applied to the data from the campaign together with a detailed analysis of land use around the site. Section 3.2 is devoted to an overview of the meteorological conditions considered as a whole and as a function of the air flow type. The levels and variations of the chemical species are presented in Sect. 3.3. The results are discussed in Sect. 4.

2 Campaign framework, area description, emission sources, instrumentation and data

2.1 Campaign framework and area description

The DOMINO (Diel Oxidant Mechanisms in relation to Nitrogen Oxides) campaign was promoted by the Max Plank Institute for Chemistry in Mainz – Germany (MPICH) and performed in cooperation between the MPICH and the National Institute for Aerospace Technology (INTA). The measurements took place at El Arenosillo (37.1° N, 6.7° W, 40 m a.s.l.) from 21 November to 8 December 2008.

At the Atmospheric Sounding Station – El Arenosillo (ESAt) several atmospheric parameters are monitored routinely. Measurements of the atmospheric total ozone column at this site started in 1980, surface meteorology in 1994, ultraviolet radiation in 1997 (Antón et al., 2012), total aerosol in 2000 (Toledano et al., 2007), surface ozone in 2000 (Adame et al., 2010a, b), aerosol size distribution in 2004 (Sorribas et al., 2011), aerosol scattering and back-scattering coefficients in 2006 (Sorribas et al., 2013), surface NO and NO_2 in 2007 (Notario et al., 2013) and aerosol absorption coefficient in 2012.

El Arenosillo is located in the Doñana National Park in the SW of the Iberian Peninsula, close to the Atlantic coastline (Fig. 1). The nearest town is Mazagón at 9 km towards the WNW, with a population of less than 4000 inhabitants. The city of Huelva with a population of 150 thousand inhabitants (INE, 2009) is situated 26 km to the NW. Close to Huelva city there are three industrial complexes with chemical and petrochemical activities.

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In S–SW direction of El Arenosillo is the Atlantic Ocean, which is the origin of frequent maritime air masses which are channelled inland from the Gulf of Cadiz through the Guadalquivir valley. Air masses originating in the Saharan desert also arrive occasionally from this direction, though not during the period of the campaign. Along the coast there is continuous maritime traffic of ships traveling to or from the port of Huelva.

At 75 km from the coastline of El Arenosillo in the NE direction lies the Seville metropolitan area with a population of more than 1.5 million inhabitants, being the most densely populated urban area in the south of the Iberian Peninsula. In addition to important traffic emissions there also are some industrial factories whose atmospheric emissions are commented in detail in the next section.

The emissions of the industrial activities in Huelva affect the DOMINO site when the wind blows from the WNW-NNW sector. In November and December this situation occurs with an occurrence fraction between 5 and 10 %, similar to the annual mean of 4–10 % obtained from the historical series from 1994–2007. On the other hand, emissions from the area of Seville can also affect El Arenosillo when the wind comes from the NE–ESE sector, which occurs between 20 and 25 % of the time during the November–December months and with a 10 % occurrence annually.

2.2 Emission sources

The measurement area is regularly influenced by emission sources both of biogenic and anthropogenic origin. Due to its location in the Doñana National Park and the low traffic and population in the area during winter, there were no important anthropogenic emission sources in the direct vicinity of the measurement site other than occasional traffic on the road passing the site and the traffic to and from El Arenosillo. The closest relevant anthropogenic emission sources that can affect the measurement site are located in the Huelva and Seville cities.

Industrial complexes close to Huelva city are the main sources of NO_x, SO_2, PM_{10} and benzene in the Huelva province. The Spanish Register of Emission and Pollutant Sources (EPER) (http://www.en.prtr-es.es) gives detailed information on the emissions

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in 2008 and more compounds are included than in the Andalusia Government inventory. According to the EPER inventory 8824 t of SO_2, 7615 t of NO_x, 8824 t of PM_{10}, 1498 t of NMVOC and 5.14 t of benzene were emitted from these industrial areas in 2008. In addition, elevated levels of metals such as 1.71 t of As, 0.171 t of Cd, 10.7 t of Cu, 0.173 t of Hg, 3.864 t of Ni, 5.63 t of Pb and 7.035 t of Zn were released.

According to the Andalusian Government inventory (CMAJA, 2005), the NO_x emissions in the province of Huelva associated to the vehicle traffic account for only 30 % (8670 $t\,yr^{-1}$) and industrial activities account for 48 %. In the province of Seville the vehicle traffic contribution is comparatively larger reaching 53 % (16 259 $t\,yr^{-1}$) while industrial emissions cause a mere 16 %.

SO_2 emissions in Huelva are 96 % industrial (15 348 $t\,yr^{-1}$) mainly from the chemical and petrochemical sectors, while 1.5 % is associated to the maritime traffic. In Seville the emissions of these species are related to the industry for 55 % (1254 $t\,yr^{-1}$) and 29 % come from other activities such as the commercial sector; however, total emissions are much lower than in Huelva.

The PM_{10} emitted by vehicle traffic accounts for 14.7 % in Huelva while industry emits 48 % (1236 $t\,yr^{-1}$). In Seville the traffic is the most important PM_{10} source with 25 % (1291 $t\,yr^{-1}$) and agricultural activities come second with 20 % while industrial emissions in this province contributes with a percentage lower than 10 %.

In Huelva 84 % of benzene (96.3 $t\,yr^{-1}$) is emitted by the petrochemical industries while 16 % is emitted by the paper industry. The industry in Seville contributes to benzene emissions in a similar proportion, accounting for 85 % (2×10^{-3} $t\,yr^{-1}$) of the total emissions in the province, although the absolute levels are lower than in Huelva.

VOCs (non-methane volatile organic compounds) are mainly from biogenic origin in Huelva with 74 % (61 538 $t\,yr^{-1}$) while the industry emits 10.3 % and traffic 2.5 %. In Seville biogenic emissions also are the main source of VOCs with 31.5 % (23 267 $t\,yr^{-1}$) from natural emissions followed by agriculture with 23.5 %.

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2.3 Instrumentation and data

The Atmospheric Sounding Station (ESAt) is located at less than 1000 m distance from the coastline, and hosts the atmospheric monitoring instrumentation continuously deployed by this observatory. Most of the instrumentation deployed for the DOMINO campaign, however, was placed at a site in between the ESAt and the coast, at about 100 m from the coastline, although several of the ESAt's instruments remained in the ESAt. The equipment on the main measurement site was distributed in four containers and the sampling inlets were installed on top of a structure of 10 m height (see image in Fig. 1).

Ozone measurements were based on the absorption of ultraviolet radiation by ozone at 254 nm. The ozone analyser, using a flow rate of 2 L min^{-1}, was checked daily and calibrated before and after the campaign. The precision and the detection limit were 1 ppb.

NO_x data was collected with a high resolution and high sensitivity chemiluminescence detector (ECOPhysics CLD 790 SR, ECO-Physics, Dürnten, Switzerland) which carries out simultaneous in situ measurements of NO and NO_2. While NO is measured directly, NO_2 is measured indirectly after conversion to NO using a blue light converter which is a solid state photolytic converter (Droplet Measurement Technologies, Boulder, Co, USA). A detailed description of the instrument, the calibration techniques and the error calculation has been given by Hosaynali-Beygi et al. (2011). SO_2 was monitored using an Airpointer (Recordum GmbH) with a detection limit of 1 ppb and calibrated periodically during the campaign.

An on-line sampling TD-GC-MSD measurement system was used for the in situ observation of benzene and isoprene. The system consists of a flow controller and a thermal desorber (Markes International, Pontyclin, UK) connected to a gas chromatograph (GC 6890, Agilent, Wilmington, CA, USA), equipped with a Mass Selective Detector (MSD 5973 inert) from the same company. This experimental set-up allowed the mea-

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surement of anthropogenic VOCs such as benzene as well as biogenic species such as isoprene.

The air sampling line was fitted with a Teflon filter to prevent particles from entering the inlet line. Ambient air was drawn continuously through a main sample line at about 10 L min^{-1} by a high volume pump. The residence time of air in the inlet line was approximately 12 s.

OH reactivity was measured using the comparative reactivity method which employs an in situ competitive kinetics experiment in which a proton transfer reaction mass spectrometer (PTR-MS) is coupled to a turbulent flow glass reactor. Pyrrole (C_4H_5N) is introduced into the reactor and its concentration $C1$ is monitored with a PTR-MS, in the air exiting the reactor (Sinha et al., 2008, 2010). Then, synthetically generated OH radicals ([OH] < [Pyrrole]) are introduced into the reactor at a constant rate to react with pyrrole. This causes $C1$ to decrease to concentration $C2$. When ambient air is introduced into the reactor, the various species present in it compete with pyrrole for the available OH, so that the concentration of pyrrole increases to $C3$. The comparison of the amount of pyrrole exiting the reactor in the zero air ($C2$) and ambient air ($C3$), allows the introduced air sample's OH reactivity to be determined, provided the system is suitably calibrated for pyrrole (Sinha et al., 2009).

Total concentration for particles larger than 2.5 nm was measured by an Ultrafine Condensation Particle Counter (UCPC) (TSI Model 3776) operating at high flow and with 1 min time resolution. AIM software (version 8.0.0, TSI INC, St. Paul, MN, USA) was used for data reduction of the UCPC outputs. The accuracy of the system is about 10 %. A description of the sampling system to transport the sampled aerosol into the UCPC can be found in Sorribas et al. (2011).

Simultaneous PM_{10} and $PM_{2.5}$ concentrations were sampled using two high-volume captors (CAVF-PM1025, 30 m^3 h^{-1}), equipped with MCV PM_{10} and $PM_{2.5}$ inlets and quartz micro-fibre filters. The time resolution was one filter every day with sampling duration of 24 h. Filters were weighed before and after sampling. PM_{10} filters were sent to Actlabs Company (in Canada) to provide an analytical analysis to completely charac-

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terize metals. Techniques for determination of the concentration of major and trace elements were (1) inductively coupled plasma atomic emission spectrometry (ICP-AES) and (2) inductively coupled plasma mass spectrometry (ICP-MS), respectively.

Local weather conditions were measured using commercial instruments, Vaisala 520WXT. Temperature, relative humidity, pressure, rainfall, wind speed and direction data were collected. This sensor was used both on top of the structure and on a 100 m tower between the DOMINO measurement site and the ESAt building. To measure ultraviolet radiation a Brewer MK-III spectroradiometer was used which has been monitoring this parameter since 1997 on the roof of the ESAt.

Meteorological soundings were performed at the main DOMINO measurement site. Normally, two balloons were launched per day: One in the morning (around 10:00–11:00 UTC) and one in the afternoon (around 16:00–17:00 UTC). On selected intensive days, however, a sonde was launched every hour. Meteorological data were obtained with GRAW DFM-06 radiosondes which measured temperature, relative humidity, and location (differential GPS). The measurement accuracy for temperature is $< 0.2\,^{\circ}\mathrm{C}$ at a resolution of $0.1\,^{\circ}\mathrm{C}$. Relative humidity is measured with an accuracy of $< 5\,\%$ and a resolution of 1 %. Through the change in GPS position, wind speed ($< 0.2\,\mathrm{m\,s^{-1}}$ accuracy), wind direction, and updraft were calculated. Using surface pressure as additional input, the vertical profile of pressure (< 1 hPa accuracy) was obtained.

NO, NO_2, isoprene, benzene, OH reactivity and the meteorological parameters were measured on the top of the mentioned structure, O_3 and SO_2 were measured in a mobile laboratory (Drewnick et al., 2012) with the inlet at the same height as those on the structure and meteorological soundings were launched at the main DOMINO measurement site. Total particles, aerosol chemical and the ultraviolet radiation data were collected at the ESAt building. Finally, the 100 m tower was used to measure meteorological variables at the 50 m level. All the data were recorded with a time resolution of 10 min or less with the exception of the VOCs, which had a sampling time of 60 min.

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3 Results

3.1 Air masses study

3.1.1 HYSPLIT model

The trajectories followed by the air masses before reaching El Arenosillo were calculated using the HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) model, developed by the NOAA's Air Resources Laboratory (ARL) (Draxler et al., 2011). Several studies have been carried out at El Arenosillo in the past to study air masses in this region, including an analysis with five years of daily back trajectories and their relation with the aerosol optical properties (Toledano et al., 2007), two years of six back trajectories per day and their relation with the sub-micron particle size distribution (Sorribas et al., 2011) and a study with ten-years of back trajectories to identify clusters of trajectories, their seasonal variation and dependence on altitude and on various features of the local meteorology (Hernández-Ceballos et al., 2013).

These studies are based on back trajectories computed once per day with a previous pathway of 120 h and using input meteorological files with a horizontal resolution of $1^{\circ} \times 1^{\circ}$. In the framework of the DOMINO campaign, air masses trajectories have been calculated using HYSPLIT and meteorological fields of low resolution. Diesch et al. (2012) calculated back trajectories at 10 m arrival height every 2 h during the whole campaign period; Sinha et al. (2012) computed back trajectories at 20, 100 and 500 m; in van Stratum et al. (2012) the forward trajectories for a specific day at 100 and 2000 m were shown.

In this work a new and detailed back trajectory analysis with a higher resolution both temporal and spatial has been performed. The input meteorological files used in this study were the ERA Interim from the global model ECMWF (European Centre for Medium Range Weather Forecasts). The files downloaded from ECMWF and converted to a format compatible with HYSPLIT have a spatial resolution of $0.25^{\circ} \times 0.25^{\circ}$ (approximately 27 km), 16 vertical levels from surface to 500 mb and 6 h of tempo-

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ral resolution. 3-D kinematic back trajectories have been calculated using the vertical wind component given by the ERA Interim meteorological fields. 48 h back trajectories from El Arenosillo station have been simulated to analyze the origin and pathway of air masses. Hourly back trajectories were computed for the whole period of DOMINO, approximately 445 back trajectories at each altitude.

3.1.2 Variation of the air mass trajectory with altitude

Hourly back trajectories at five altitudes have been computed inside the atmospheric boundary layer (ABL) at 100, 250, 500, 750 and 1000 m arrival height in order to know the variation, origin and pathways of the air masses that reached El Arenosillo during DOMINO. The HYSPLIT model has a tool which allows the grouping of back trajectories into clusters. Using the TSV (minimum increase in total spatial variance between clusters) and the SPVAR (minimum increase of spatial variance between cluster components), the HYSPLIT model can calculate the optimal number of clusters (Stunder, 1996). This clustering tool has been applied to the back trajectories set obtained for each altitude and has resulted in an optimal number of four clusters. The results obtained in the five altitudes calculated are very similar, in Fig. 2 the cluster means at 100 and 1000 m are shown. Independently of the altitude analysed, two clusters show a strong maritime influence, originating over the Atlantic Ocean, while the other two have a more continental character with a track over the Iberian Peninsula. The most frequent is the marine cluster *C*4 with an occurrence between 32 % and 36 % at all altitudes. The other mostly maritime cluster *C*3 is the next most frequent oscillating between 24 to 25 % at different altitudes, with a longer pathway and originating at higher latitudes than *C*4.

The continental clusters (*C*1 and *C*2) occurred less frequently than the marine clusters with an occurrence ratio of between 17 and 26 %. These clusters show travel times of 24–36 h over the Iberian Peninsula before arrival at the DOMINO area. *C*1 has its origin in the SE of the Iberian Peninsula and the Guadalquivir valley and could be affected by the Mediterranean area while *C*2 represents pathways from north to south

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crossing the Iberian Peninsula through the centre and the west of Spain. In general, all the clusters show little variation with altitude.

Continental clusters seem to be more influenced by vertical mixing processes, as shown by altitude variations along the trajectories and higher levels at the origin than at the arrival point. Marine clusters in contrast show little variation in altitude along the trajectories, indicating a more stable atmospheric layering over the ocean.

The low variability with the height of the air masses during the DOMINO campaign at 5 different arrival altitudes up to 1000 m shows that the boundary layer is generally well mixed. Also van Stratum et al. (2012) obtained a similar atmospheric transport at 100 and 2000 m using trajectories for a specific day (23 November) and meteorological fields of lower spatial resolution. In the following sections the back trajectories obtained for the lowest altitude of 100 m will be used to discuss the measurement data taken close to the ground.

3.1.3 Land use and definition of sectors

Land use analysis has been demonstrated to be a powerful tool to understand the contribution of human activities as well as biogenic sources when interpreting local measurements of an atmospheric parameter (Williams et al., 2011). Potential local and regional influences on measurements during the campaign were assessed within an 80 km radius of the site using the Corine land cover database. These data were edited using the ArcGis 10 (Esri©) Geographic Information Systems (GIS) software. The radius was chosen in order to include the city of Seville, which is the most populated area in the surroundings of the sampling site.

As described in Sect. 2.1, there are two significant urban centres, Huelva and Seville, within 80 km of the sampling site. Most anthropogenic emissions are supposed to come from these areas with their industrial and commercial units (in red in Fig. 3). Apart from those urban areas, other characteristic land uses will be described on the base of the different back trajectories defined by the HYSPLIT model.

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According to the different land use surrounding the measurement site, four different sectors can be defined influencing the measurement area with distinct anthropogenic and biogenic emissions. The sector between W and NNW, affected mainly by emissions from urban and industrial activities of Huelva, is further named the Huelva-Portugal sector. From the north, between NNW and NE, air masses from the central Iberian Peninsula arrived, containing mostly rural emissions and possibly also aged pollution from distant urban sources. This sector is further identified as Continental-North. The sectors defined in this work as Continental-North, Marine and Seville present a good agreement with the classification shown in Diesch et al. (2012). However, the Huelva-Portugal sector from this study is divided into three sectors in their work which are useful for the interpretation of the aerosol chemical composition shown in Diesch et al. (2012). In the investigation carried out by Sinha et al. (2012) three sectors were defined, based on wind measurements and back trajectories. The Marine and Huelva sectors are similar while the Continental sector defined in Sinha et al. (2012) is divided in our work into Continental-North and Seville.

From wind directions between NE and ESE arrive flows coming from the Guadalquivir valley that have crossed the Seville metropolitan area and the Doñana National Park, therefore this sector has been classified as Seville-Guadalquivir valley. Finally, the air masses coming from between ESE and W from the Atlantic Ocean have been identified as Marine.

The Atlantic Ocean covers approximately 40 % of the area around the site. A semi-quantitative analysis of the land use map in Fig. 3 is given in Table 1. The most significant land use is forests and cultivations. Arable land, woody crops and other cultivated areas reach near to 25 % of the land use. The National and Natural Parks of Doñana surrounding the sampling site are among Europe's most relevant protected areas due to their populations of migratory birds and sandy landscapes. Nevertheless, many natural or semi-natural forested areas are also frequent (13.2 % including broadleaved and coniferous forest and agroforestry areas). Those areas identified as coniferous forests

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were found to be Stone Pine (*Pinus pinea L.*) which has been identified previously as strong terpene emitter in summer (Song et al., 2011).

These forests are abundant to the north of the site in the immediate vicinity of the sampling site. Other coniferous formations of this species are located further away to the east of the sampling site. Broadleaved forests are found throughout the landscape and these are the original vegetation of this area before its intensive transformation by human activity. These original forests are called Mediterranean forest in which holm oak (*Quercus ilex*) and cork oak (*Quercus suber*) are the most relevant tree species. In general, many species of Mediterranean vegetation are frequently described as potential emitters of isoprene (Schurgers et al., 2009). It is interesting to point out the large extension of salt marshes in the surroundings. To the northwest the Protected Spot called Marismas del Odiel is located. More extended salt marshes of the National Park of Doñana are southeast of the site.

3.1.4 Air mass classification according to source regions

One of the goals of the DOMINO campaign was to analyze atmospheric chemistry in air masses of different origins and with distinctively different types of emissions. In order to distinguish between emission loadings of air masses, the hourly back trajectories computed for an altitude of 100 m at arrival were viewed, selected and were grouped according to their origin from the sectors defined in the last section, rejecting those trajectories that crossed more than one sector before reaching El Arenosillo. The back trajectories grouped for each sector are shown in Fig. 4. The local wind direction agreed with the direction of the trajectories in > 80 % of all cases.

Air masses with recent anthropogenic emissions including a strong industrial component coming from Huelva, after crossing the south of Portugal were found in a total of 65 h (Table 2). Air masses with continental air, from the western and central parts of the Iberian Peninsula affected both by biogenic emissions and by moderate anthropogenic emissions from roads and smaller settlements, possibly also by long-range transport of aged pollutants from larger cities like Madrid were identified in a total of 42 h.

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Air masses with anthropogenic urban pollution from the Guadalquivir valley, affected by the emissions of the Seville metropolitan area within the last 12 h of transportation were detected in 41 h. Finally, Atlantic air masses without continental influence during the last 48 h before reaching El Arenosillo were observed in 35 h.

3.2 Overview of the meteorological conditions

The characterization of weather conditions during the DOMINO campaign is based on local measurements of surface temperature, potential temperature difference between 50 and 10 m, relative and specific humidity, wind direction and speed, ultraviolet radiation, pressure, rainfall and the height of the atmospheric boundary layer (ABL) (Fig. 5). Profiles of potential temperature, specific humidity and wind have been plotted to obtain the structure of the ABL (Seibert et al., 2000), both in stable and unstable (i.e. mixing layer) conditions. The meteorology was further studied on a synoptic level analyzing the surface pressure maps and the back trajectories (shown in the last section). Although in this coastal area both synoptic and mesoscale processes can be developed (Adame et al., 2010a), during the whole campaign the weather conditions were governed by synoptic scale motions.

During the first three days of the campaign the air was coming from the Seville-Guadalquivir valley and Continental-North sectors, caused by a high pressure system located in the Atlantic Ocean which influenced the Iberian Peninsula. The air masses arriving at the site started 48 h before in the SE or centre of the Iberian Peninsula and travelled through the Guadalquivir valley. The days were sunny as can be observed in the smooth ultraviolet radiation daily cycles uninterrupted by cloud. Maximum daily temperatures higher than 20 °C were reached and well defined daily temperature cycles were observed; moreover, relative humidity changes between minimum ∼ 35 % and maximum ∼ 70 % were also observed. The specific humidity in these continental flows was almost constant with values of around 6–7 g kg^{-1}. The mixing layer reached maximum heights > 1000 m around the evening hours and during nighttime strong in-

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versions built up, with potential temperature differences > 4 °C, the highest of the campaign.

In the late hours of 23 November the synoptic flows were modified due to the displacement from Greenland to the British isles of a low pressure centre (989 hPa) with a high isobaric gradient. In this new situation the low pressure centre governed the weather in all of Western Europe. From late 23 November to midday 25 November local air flows at El Arenosillo were from W–N. The air masses crossed the Iberian Peninsula from north to south at first, later coming from the Atlantic Ocean through Portugal and crossing Huelva before reaching El Arenosillo.

Under this new situation, the temperature decreased to daily maxima of 15–18 °C and minima of 6–8 °C. Associated with maritime flows, the relative humidity was higher than the previous days, while the specific humidity remained similar. The cloudiness these days increased. During the night of 24 November no significant nocturnal inversion was built up. The low pressure system continued moving towards the north of Europe and, by late 25 November, it had lost its influence in the SW of Europe.

Another high pressure system now affected the Iberian Peninsula. Flows from NE–E occurred, similar to the first days of the campaign, since late 25 November to approximately midday on 27 November. The air masses travelled from the centre of the Iberian Peninsula and later from the SW along the Guadalquivir valley. The maximum daily temperatures were lower than on the previous days. A decrease in the relative humidity was also observed with maximum values ranging between 75 and 85 % simultaneously with a decrease of the specific humidity, with mean daily values of 3–4 $g\,kg^{-1}$, the lowest detected during the campaign.

At high latitudes of the Atlantic Ocean, between Great Britain and Greenland, a new low pressure system was generated, located at the north of the high pressure system. This new isobaric configuration started to move towards the European continent.

The Iberian Peninsula was left under a weak isobaric gradient and El Arenosillo received wind from variable directions, blowing mainly from SSE–WNW–N, from midday 27 November to approximately 28 November at 08:00 UTC. Other surface meteorolog-

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ical parameters did not change. 28 November marked a clear transition, with the wind veering from NW to SW the origin of air masses changed. Early on 28 November the air was coming from the Iberian Peninsula crossing it from north to south, i.e. the north-continental sector. Later the air arriving at El Arenosillo had an increasing maritime influence, with wind from the Atlantic Ocean at the end of the day. Both relative and specific humidity increased during the day with maximum values of 94 % and 9 g kg^{-1} respectively. A decrease in pressure was observed, reaching the lowest values of the campaign, associated with an enhancement in cloudiness and rainfall in the following night.

The marine influence continued throughout 29 November. The temperature decreased continuously from 14 to 11 °C throughout the day without any diurnal maximum. Relative humidity increased up to 90 % while the specific humidity remained similar to the previous day.

On 30 November the low pressure system started to move away from the Iberian Peninsula through the SW of France, leading to an increase in pressure. This situation remained for the next four days until the late 3 December. Local wind was variable, blowing from southwesterly to northwesterly directions. In agreement with the change in the wind direction maritime air masses were later replaced by air from Portugal and finally from the north of the Iberian Peninsula. Temperature and relative humidity showed well defined daily cycles with maxima of 12–14 °C and of up to 90 % respectively. The specific humidity decreased and cloudiness was low. The evening mixing layer height on 29 and 30 November was significantly lower than on the previous days.

The displacement of the low pressure system towards the European continent favored the influence of a new high pressure centre, leading to local winds from the NW, Huelva-Portugal sector. On 4 December the synoptic meteorology over the Iberian Peninsula was characterized by a weak isobaric gradient with low wind speeds. Starting 5 December, the Atlantic anticyclone moved to lower latitudes and the northern part of the Iberian Peninsula was affected by a strong low pressure system (972 hPa) located in the north of the British isles. Due to these conditions, during the last four

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days of the DOMINO campaign the wind direction was variable blowing from the NNW and veering to the W–SW bringing maritime air masses. On 3 December air masses travelled through the south of Portugal and reached El Arenosillo from the NW. With the change in the wind direction to the west, the air showed a strong maritime character, which remained for the last days of the campaign. Weak temperature, relative and specific humidity daily cycles were observed. The temperature changed between 13 and 17 °C, the relative humidity between 75 and 95 %, while the specific humidity reached the highest values of the campaign oscillating between 8 and 10 g kg^{-1}. There was an increase in cloudiness and in the last hours of 7 December rainfall occurred. Throughout these days, the potential temperature difference between 50 and 10 m altitude was mostly negative, i.e. without significant nocturnal inversions. In the evening hours the mixing layer hardly reached 750 m and even atmospheric stable stratification was sometimes observed, as would be expected for a marine boundary layer.

Summarizing, air masses from the Huelva-Portugal, Continental-North, Seville-Guadalquivir valley and Marine sectors were observed with an occurrence frequency of 42 %, 30 %, 7 % and 21 %, respectively. Nevertheless, according to the historical data series the dominant wind direction at this time the year is from the Seville-Guadalquivir and Continental-North sectors with an incidence > 40 % each. These air masses are advected from the centre of the Iberian Peninsula or the European continent. Therefore, the wind regime in November and December 2008 was anomalous with respect to the previous 14 yr.

Using only air masses with trajectories completely within one of the four sectors defined in Sect. 3.1.4, average diel profiles for temperature, potential temperature difference, specific and relative humidity and wind speed have been calculated for each sector (Fig. 6); in addition, potential temperature and specific humidity vertical profiles are also shown in the same figure.

The meteorological features from the four sectors are quite different. Nighttime temperatures differ by up to 6 °C while daytime average temperatures agree within 2.5 °C. Air from the marine sector showed little diel temperature variation, since the tempera-

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ture of the air over the ocean is less affected by diurnal heating and nocturnal cooling. In contrast, air with continental influence, i.e. Continental-North and Seville-Guadalquivir, shows a clear diel cycle.

Similarly the potential temperature in marine air was almost equal at 10 and 50 m altitude both during day and night, whereas air from all other three sectors showed temperature decreasing with altitude by close to 1 °C in the lowest 50 m during daytime. The largest vertical potential temperature differences are found in nocturnal stable conditions, with values of up to 5 °C for the Continental-North sector.

The humidity (specific and relative) was relatively low under continental influence (Continental-North and Seville-Guadalquivir) and high under Marine conditions. Intermediate values were observed in air from the Huelva-Portugal sector. The highest wind speeds were associated with trajectories from the Seville-Guadalquivir sector, probably due to the channeling effect of the Guadalquivir valley. For the Continental-North and Huelva-Portugal sectors wind speeds were similar and the lowest wind speeds occurred under marine conditions, usually being less dispersive.

The atmospheric boundary layer height for air from the Continental-North and Seville-Guadalquivir sectors is similar and the effect of continental conditions while in air from the Marine sector it is a typical marine boundary layer. In air masses coming from Huelva-Portugal both marine and continental influences can be expected.

3.3 Levels and variation according to the air flow types for O_3, NO_2, SO_2, OH reactivity, isoprene, benzene, particles and aerosol chemical composition

An overview of the mixing ratios of chemical trace gases such as ozone, NO, NO_2, SO_2, isoprene and benzene as well as the total OH reactivity, the number of particles and the aerosol chemical composition measured during DOMINO is given in this section. The whole data series of these species are shown in Fig. 7 and Table 3. The average daily evolution for air of different origin is shown in Fig. 8 and the daily average for the aerosol chemical composition is displayed in Table 4.

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Surface ozone at El Arenosillo has been monitored since the year 2000 and was used in several studies on ozone under different weather conditions (Adame et al., 2010a, b). During the DOMINO campaign the 10 min ozone data varied between 46 and 11 ppb. The long-term averages for November and December obtained from the historical data series are 30 ± 2 ppb and 26 ± 2 ppb respectively, being the lowest of the year. The average for DOMINO was a little higher with 31 ± 7 ppb. Throughout the campaign a clear daily cycle was observed for ozone with maximum values of up to 35 ppb in the afternoon, approximately 1–1.5 h later than the maximum solar radiation. An exception to this was the period from 28 to 30 November, when ozone remained almost constant for over 36 h.

Average diel ozone profiles were quite similar for all air mass origins during daytime, indicating no significant photochemical production in more polluted air. Significant differences were found mostly during nighttime, indicating different levels of ozone destruction. The highest values were recorded in the relatively clean marine air, the lowest in continental air coming from Continental-North and Seville-Guadalquivir sectors.

The total particle concentration greater than 2.5 nm diameter measured with 10 min time resolution reached a mean value of $(11 \pm 16) \times 10^3$ particles cm^{-3} during the DOMINO campaign. The total particle concentration with diameters within 14–675 nm is also being routinely measured at El Arenosillo, showing an annual mean level of $(8.6 \pm 6.7) \times 10^3$ cm^{-3} (Sorribas et al., 2011). The differences between the mean total particle concentration reported in Sorribas et al. (2011) and during DOMINO could be due the different particle size ranges used for the two studies. The highest particle concentrations are observed close to noon, the lowest during nighttime. At El Arenosillo, the diurnal maximum could be attributed to the new particle formation events. Diel profiles for the different air mass origins show that the total particle concentrations during nighttime are similarly low for air from all sectors. However, during daytime the total particle concentration is highly variable. Air masses coming from the marine and the Seville-Guadalquivir sectors did not show maxima at noon, indicating that no nucleation events occurred during transport from these sectors. Particle levels were very

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different with an average of 1652 particles cm^{-3} for marine and 7104 particles cm^{-3} for Seville-Guadalquivir sectors. For the particle concentration the Continental-North sector shows the typical diel profile of a nucleation event. During sunrise, new particles were formed by photochemical processes and the total particle concentration increased around 10:00 UTC. From 10:00 UTC to 11:00 UTC, the mixing processes start increasing the height of the boundary layer and decreasing its particle concentration. When the nucleation velocity becomes higher than the dilution velocity, the particle concentration increases again at around 12:00 UTC. During the evening, the particle coagulation and condensation processes produce a slow decrease of the particle concentration within the size range measured by the UCPC. The highest noon levels were measured in air masses coming from the Huelva-Portugal sector, and are likely due to secondary particle formation from emissions of the industrial areas situated around Huelva city.

Since El Arenosillo is a rural-background environment without NO_x emission sources nearby, average mixing ratios measured of NO and NO_2 were relatively low (0.21 ± 0.51 ppb and 1.90 ± 1.89 ppb respectively). The NO levels are close to zero during the night time, due to titration with O_3 forming NO_2.

During nighttimes, the highest NO_2 mixing ratios were observed in air from the Continental-North, indicating important sources to the north of El Arenosillo, likely from the industrial emissions. Daily maximum NO mixing ratios during daytime exceeded 4 ppb and were observed in air from the Huelva-Portugal sector. A rapid increase is observed in the early morning, when the daily maximum is reached, coinciding with the maximum mixing ratios of 9 ppb NO_2, likely due to accumulation in the stable nocturnal residual layer, mixing down to the ground with the breaking of the inversion layer. NO_2 mixing ratios were about 50 % higher in air from Huelva-Portugal than in air from the other inshore sectors. During daytime air passing Seville-Guadalquivir has similar NO_2 loadings as air from more northerly sectors. The lowest NO_2 was recorded in Marine air, a few 100 ppt during daytime and around 1 ppb during nighttime.

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The variability of SO_2 during the campaign is associated with the arrival of air masses loaded with SO_2 and showed no diel cycles. Mixing ratios varied between the limit of detection (1 ppb) and a maximum of 23 ppb, 1.02 ± 2.13 ppb in average. SO_2 shows very elevated values in Huelva-Portugal air compared to air from other sectors, except during nighttime between 01:00 and 08:00 UTC. The origin of these mixing ratios could be attributed to industrial emissions. The lowest values were observed in Seville-Guadalquivir air, reflecting lowest influence of local industrial pollution in this sector. The Continental-North sector has some mixing in of Huelva industrial air during nighttime, evidenced by elevated SO_2 around midnight and due to the strong vertical stability observed in nocturnal air from this sector. Marine air also has more SO_2 than Seville air, more likely due to ship emissions than to influence by local industrial pollution, since nighttime values after 01:00 UTC are often higher in marine air than in Huelva air.

During the campaign OH reactivity was measured by Sinha et al. (2012), ranging from below limit of detection ($3.5\,s^{-1}$) to $76\,s^{-1}$ with a mean value during the campaign of $18 \pm 15\,s^{-1}$. The highest values were observed in air from northerly directions during nighttime. Although Huelva-Portugal air reaches similarly high values in the afternoon, when vertical mixing is highest, values are lower at all other times, indicating that Huelva sources play a smaller role than long-range transported species for OH reactivity. Air masses from the Seville-Guadalquivir sector also show lower OH reactivities than continental air from northerly directions. Marine air shows by far the lowest OH reactivities.

Although an overview of the VOC measurements during the campaign was published by Song et al. (2011), in this work benzene and isoprene have been selected as representative of anthropogenic (urban-industrial emissions) and biogenic VOCs respectively. Benzene was measured with an average mixing ratio of 179 ± 285 ppt during the campaign and maximum and minimum mixing ratios of 3461 and 12 ppt. Isoprene displayed a mean mixing ratio of 15 ± 17 ppt, and maximum and minimum values of 137 and 2 ppt respectively. Both benzene and isoprene were strongly affected by air mass origin. As VOC mixing ratios are generally low in marine air, little isoprene and benzene

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were found in air from this sector, Benzene in air coming from Huelva-Portugal sector is about double that in air from the Continental-North, being the Huelva-Portugal sector being the main source of this emission. Air masses from Seville-Guadalquivir show mixing ratios in between those two sectors. Isoprene (biogenic) has a maximum in the afternoon, due to the diurnal cycle of biogenic emissions. Isoprene mixing ratios are highest in the Continental-North (the main source of biogenic emissions) and lowest in the Huelva-Portugal sector. Air from Seville again shows values in between the other two inshore sectors. This indicates a larger role of biogenic VOCs for OH reactivity than from recent anthropogenic VOC emissions.

Aerosol chemical composition was analysed thanks to samples collected on filters each 24 h. Laboratory analysis was used to obtain the daily levels of PM_{10}, $PM_{2.5}$, $PM_{10-2.5}$ and the major and trace element components for PM_{10} measured during DOMINO. Table 3 gives the mean values, standard deviations, maximum and minimum daily values for each parameter. A particle-size prevalence was not observed given that mean $PM_{2.5}$ was 55 % of the mean PM_{10} fraction (16 $\mu g\,m^{-3}$ for PM_{10} and 9 $\mu g\,m^{-3}$ for $PM_{2.5}$). These results agree with the ranges of mean annual values across Spanish background sites for PM_{10} and $PM_{2.5}$, though it is lower than mean annual values for southern Spain (Querol et al., 2002, 2008; Sánchez de la Campa et al., 2009). This is related to the season when the DOMINO campaign took place, without impact of desert dust aerosol which usually increases PM_{10} and $PM_{2.5}$ levels across the south of Spain.

Concentrations of major components highlight Na and K since they exhibit the highest levels in comparison to previous analysis in the south of Spain (De la Rosa et al., 2010), with 2.66 $\mu g\,m^{-3}$ and 1.08 $\mu g\,m^{-3}$, respectively. Both components show a moderate correlation with Zn concentrations (r = 0.54 and 0.60 respectively), which could be due to the presence of marine air masses during DOMINO campaign.

The K compound could be also related to the industrial activities around Huelva city. Fe, Si and Mn are natural crustal elements associated with continental air masses.

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Additionally, high particle concentration levels of As and Cu were found compared to other sampling sites in southern Spain. However, even under the unusual contribution from the Huelva-Portugal sector that occurred during the DOMINO campaign, As and Cu concentrations are lower than and similar to, respectively, the annual mean measured in this area in previous studies (De la Rosa et al., 2010). Arsenic levels presented a high correlation with Pb (r = 0.93), Cu (r = 0.86), Cd (r = 0.87) and moderate correlation with P (r = 0.70) and Se (r = 0.65).

In order to perform a study for the different sectors of air mass origin defined above, clustering of the data for mass concentration and chemical composition has been carried out. For each filter the fraction of time with air masses coming from each sector was calculated. If the fraction for a given sector was higher than 60 %, the sampled filter was considered as representative of this sector.

Applying this methodology two filters were considered as representative of the Huelva-Portugal sector, measured on 24 November and 08 December; the filter corresponding to 22 November as Continental-North, one filter as belonging to the Seville-Guadalquivir sector on 26 November and one representative of the Marine sector on 7 December. Table 4 shows the daily levels of PM_{10}, $PM_{2.5}$, $PM_{10-2.5}$ and major and trace elements components for PM_{10} by sectors.

Mean PM_{10} concentrations ranged from 5 $\mu g\,m^{-3}$ for the Seville-Guadalquivir sector to 22 $\mu g\,m^{-3}$ for the Huelva-Portugal sector and equivalent results have been found for $PM_{2.5}$. The high PM_{10} and $PM_{2.5}$ concentrations in the Huelva sector are most likely due to the particle contributions of the industrial activities around Huelva City.

Natural crustal elements (Fe, Mn and Si) from the ground were detected mostly for the Continental-North and Seville-Guadalquivir sectors due to the continental influence (Kothai et al., 2011), while the highest values of Na and K were detected in air from the Marine sector.

The group of trace elements which are considered to be main components of natural marine emissions in the gas phase (e.g. S and As) and sea-salt particles have been found mainly in air from the Marine sector (e.g. Cu, Ni, Pb and Zn).

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4 Discussion

Derived from a study of the weather conditions during the campaign, using observational data (from the surface, elevated height and soundings) and modelling tools to calculate the air masses back trajectories as well as a land use map, we are able to distinguish four sectors of air mass origin with distinct sources: Huelva-Portugal, Continental-North, Seville-Guadalquivir and Marine. Together with an overview of the chemical species for the entire campaign, the analysis of the different air masses according to their sector of origin is of special interest, evidencing distinct atmospheric and chemical features.

4.1 Huelva-Portugal sector

Air masses from the urban-industrial area of Huelva, after coming from the Atlantic Ocean and across the south of Portugal, were the most frequent during the campaign. Nevertheless, this air flow is unusual for this time of year. Air from this sector showed the lowest temperatures both during day and night, intermediate values of humidity (relative and specific), and relatively constant wind speeds throughout the day, with a slight decrease in the afternoon. From midnight to sunrise inversion layers developed with similar intensity as in air from the Seville-Guadalquivir sector but lower than in air from the Continental-North. Unstable conditions developed during the approximately 8 daylight hours, with a mixing layer height in the afternoon of around 1000 m. These atmospheric features are associated with both maritime and continental influences.

From midnight to sunrise, under more stable atmospheric conditions, horizontal transport from the Huelva industrial area reached the measurement area in less than 3 h. The wind speed of $\sim 2.5\,m\,s^{-1}$ and the distance of 25 km, favour the arrival of the air pollutants before they are removed by chemical or deposition processes. Under these air flows and during this nocturnal period, the highest mixing ratios of benzene, SO_2 and NO_2, and the lowest of ozone were measured. The sunrise brings the breaking of the inversion layer and the formation of the mixing layer. Between 08:00 to 10:00 UTC

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a marked decrease in the values of ozone and OH reactivity was observed, while SO_2, total particles concentrations, NO, NO_2 and benzene exhibited daily peaks. The values measured can have a double origin: fresh emissions released 2 h before by the industry and transported horizontally in the still shallow and undiluted boundary layer, together with aged pollutants accumulated in upper residual layers being mixed down as the nighttime inversion breaks up in the morning. Under unstable boundary layer conditions (i.e. during daytime) the highest values of the campaign for total particle concentration, NO, NO_2, SO_2, OH reactivity and benzene were found. The air pollutants emitted in the industrial area reached El Arenosillo in less than 3 h. Ozone mixing ratios were similar to those in air from other sectors. Isoprene values were more or less constant throughout the day with maximum mixing ratios < 20 ppt. Between Huelva and El Arenosillo there are many agro-forestry and cultivated areas, coniferous and Mediterranean forest being irrelevant in comparison to other sectors. This explains the lower values of isoprene when wind came from this sector.

In the last hours of the day, between 20:00 and midnight, under stable-neutral conditions and a slight increase in the wind speed, i.e. favouring the air pollutant accumulation close to the ground, a rise of ozone, NO_2, SO_2 (daily peak), OH reactivity and benzene (daily peak) was detected while the total particle concentration remained low.

The chemical composition indicates metallurgical activities for Cu production (mainly As, Cd, Cu, Zn, Ni and Pb), a power plant (mainly As, Cd, Ni and Zn) and industrial activities based on the production of phosphate products and phosphoric acid (mainly P). Also typical tracers of combustion emissions (S, V and Se) were observed (Grahame and Hidy, 2004; Frossard et al., 2011).

Although air masses coming from the sector identified as Huelva-Portugal can have contributions from Portugal or even marine, this is not evident in our results. The elevated levels of species such as SO_2, NO_2, benzene, total particle concentration, As, Cu, etc., recorded during DOMINO under this atmospheric regime are clearly associated with the industrial emissions since the emission inventory includes these same species. High local emissions, at distances too short from the sources to produce sig-

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nificant dispersion or elimination, combined with the atmospheric neutral-stable conditions are the main factors leading to these elevated concentrations. Also the highest PM_{10} and $PM_{10-2.5}$ concentrations are found in this sector with 21.9 $\mu g\,m^{-3}$ and 10.5 $\mu g\,m^{-3}$, respectively.

4.2 Continental-North sector

Air reaching El Arenosillo from the Continental-North sector is not affected by the urban-industrial area of Huelva. The structure of the lower atmosphere is strongly affected by the thermal contrast between day and night, showing a structure typical of the PBL. The daily temperature cycles are very marked with thermal amplitudes of up to 8 °C; the humidity levels are the lowest together with those in the Seville-Guadalquivir air. During the night the highest thermal inversions of the whole campaign where observed, likewise, under unstable vertical conditions during daytime, the mixing layer height in the afternoon was close to 1000 m, similar to the Huelva-Portugal sector.

From midnight to sunrise low values of total particle concentration, NO_2, SO_2 and benzene where detected, whereas OH reactivity shows a decreasing trend. The nocturnal ozone under these conditions is constant at high levels, lower only than ozone from the Marine sector, due to the strong thermal inversion and the relatively absence of low anthropogenic emissions. After sunrise, between 09:00 to 10:00 UTC the nocturnal stable boundary layer breaks up and an increase of ozone, NO, benzene, isoprene and even the total particle concentration are observed. In this sector the emission sources have mainly a biogenic origin. According to our land use analysis, the main land use in the north of El Arenosillo is natural and semi-natural vegetation. Wide extents of transitional woodland shrubs, sclerophyllous vegetation and Mediterranean forest play an important role in the dynamics of biogenic emissions in the vicinity of sampling site, particularly in summer. Possible anthropogenic sources which could affect air from this sector are the motorway Huelva-Seville and a cement industry located at 30 km distance. Assuming that the particles origin was the anthropogenic emissions and using the wind speeds recorded, the emissions would have occurred 3 h before (around 06:00

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and 08:00 UTC). However, during the night and under the same conditions of horizontal transport, much lower mixing ratios were measured, hence is unlikely that these are the main sources of the morning increase. Like for the air coming from Huelva and under the influence of even stronger nocturnal atmospheric stability, residual layers developed which were mixed into the boundary layer in the early morning, leading to an increase of aged air pollutants and particles at ground level. This is also supported by the isoprene increase, since the first peak in isoprene occurred too close to sunrise for the vegetation emitting isoprene to triple the concentrations of the previous hours. The increase of the total particle concentration could be due to new particle formation by photochemical reactions of precursor gases such as isoprene. Between 10:00 to 11:00 UTC particle concentrations decrease likely due to dilution in an increasing mixing layer, until around 12:00 UTC, the total particle concentration increases again dominated by nucleation events.

In the afternoon, starting around 14:00 UTC, NO_x and OH reactivity increase again. The continuing low values of SO_2 indicate that in air from this sector the influence of the local urban-industrial area is minimal.

After 17:00 UTC rapidly a strong inversion layer developed, moreover associated with an increase in the horizontal advection. From this time to midnight daily maxima of NO_2, benzene and isoprene appeared. Isoprene emitted by biogenic sources located 70–80 km away from the sampling site in the early afternoon reaches the site 8 h later. The Natural Park of Sierra de Aracena is an important site of natural vegetation, with holm- and cork-oak trees, potential sources of terpenes, widely spread in this Park. Therefore, the species of biogenic origin are likely emitted at distances of 70–80 km, while anthropogenic species may have their origin at closer sources around 30 km away being accumulated in the nocturnal boundary layer.

Fe, Mn and Si reached higher levels than in air from other sectors since these compounds are natural crustal elements from the ground. Similar levels were also measured in air from the Seville-Guadalquivir sector. On the other hand, this sector shows the absence of K, Na, As, Cd, Co, Sc, Se and Zn.

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4.3 Seville-Guadalquivir sector

The city of Seville is the most populated urban area in the south of Spain and air from the Seville-Guadalquivir sector is likely to carry emissions from Seville. Before arriving to Seville the air masses are likely to move along the Guadalquivir valley. From Seville to El Arenosillo the air crosses the Doñana National Park. Accordingly, air from the Seville-Guadalquivir sector has travelled through industrial-urban and biogenic emissions sources.

These air masses present a clear continental influence, characterized by diurnal heating and nocturnal cooling, with the highest temperatures and thermal amplitudes observed during the campaign as well as the lowest values of humidity. Mixing layer heights in the afternoon reached ~1500 m. Despite development of stable nocturnal boundary layers for up to 12 h, the differences observed in the potential temperature between 10 and 50 m were not high and similar to those observed in air from the Huelva-Portugal sector. The highest wind speed was recorded in air from this sector likely due to the channelling effect of the Guadalquivir valley. OH reactivity was highest during nighttime, which could be attributed to the nocturnal atmospheric stability favouring horizontal advection whereas unstable conditions inhibit the horizontal transport and wind speeds were lower.

SO_2 shows low levels, and neither major nor trace particle component such as K, Na, As, Cd, Co, Sc and Se were measured in air from this sector, thereupon Seville industrial-urban emissions of these substances did not reach El Arenosillo. In nocturnal stable conditions the values of O_3, total particles concentration, benzene and isoprene did not change. An increase in the wind speed over the night, i.e. under suitable dispersion conditions, did not produce variations in these species. However, a decrease in NO_2 and OH reactivity was observed, probably associated with dispersion and elimination processes.

In the early morning, around 09:00 to 11:00 UTC, the mixing processes started leading to increases in observed ozone, NO_x and also isoprene. This increment could be

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mostly due to the vertical transport of aged pollutants from the residual layer; SO_2 and total particle concentration remained constant. In the afternoon, 14:00–16:00 UTC, with temperatures up to 16 °C and a well established mixing layer, ozone and NO_2 reach the daily maximum; isoprene follows an increasing trend. Taking into account the wind speed, the species measured at El Arenosillo at this time needed 8 h from Seville, i.e. would have been in the metropolitan area at around 06:00–08:00 UTC. Assuming that the photochemical activity started ~ 10:00 UTC and using the wind speed recorded at this time, the isoprene emissions would have started 35 km away from El Arenosillo where coniferous forests are widely spread in the National Park of Doñana in the direction of Seville. Ozone could be formed from NO_x emitted in Seville, however mixing ratios at El Arenosillo are not higher than in air from other sectors, thus secondary production of ozone in this season is not enhanced by Seville urban emissions. Around 17:00–18:00 UTC the ground starts to cool and the inversion layer begins to develop. Simultaneously an increase in the benzene, isoprene and total particle concentrations was observed, likely due to less dilution in the shallowing mixing layer.

Between 18:00 and 21:00 UTC the wind speed increased while the difference of potential temperature shows the development of an intense inversion layer, simultaneously a peak in ozone, NO_2 and OH reactivity was observed, while benzene values remained almost constant and isoprene decreased. The wind speed at this time was ~3 $m\,s^{-1}$, i.e. transport from Seville needed 7 h assuming a constant velocity. The peaks in NO_x and ozone must be therefore due to a peak in NO_x emissions in Seville in the early afternoon, which seems unlikely since the peak of urban NO_x emissions is usually during rush hours in the morning and evening, or to sources closer to the site.

On the other hand, the lowest PM_{10} and $PM_{10-2.5}$ concentrations are also found in air from this sector with 4.9 $\mu g\,m^{-3}$ and 1.4 $\mu g\,m^{-3}$, respectively. The main chemical compounds were Fe, Mn and Si, as was presented previously in sector Continental-North since they are natural crustal elements from the ground.

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4.4 Marine sector

Air from the Atlantic sector is observed at the site with a high frequency throughout the year and also occurred during the campaign. As was expected, the highest relative and specific humidity were encountered in air from this sector, as well as the lowest values for wind speed and the highest temperature, although the daily amplitude was minimal. The diurnal variability of the difference of potential temperatures showed values close to zero, i.e. neutral conditions, and the mixing layer height is the lowest with 150–300 m in the afternoon, characteristic for a marine boundary layer. The trajectories calculated for 100 m altitude are close to the Ocean surface without experiencing much vertical mixing.

Atlantic air masses transported little primary pollution, and the lowest levels of all the species analyzed with the exception of ozone were observed in air from this sector. It is well know that Ocean is not a source of SO_2, benzene, isoprene or NO_2, however measurable concentrations of these species were found. These substances are likely associated with maritime traffic, arrival and departure from the Huelva port. According to the emission inventory an emission by ships of 243 and 330 t yr^{-1} for SO_2 and NO_2 occurs.

Concentrations of trace components such as S, As, Cu, Ni, Pb and Zn are typical for marine air. And major sea salt components like Na are only observed within this sector while K reached its highest levels.

Under this atmospheric pattern the highest ozone mixing ratios of the campaign have been observed, between 35 to 40 ppb throughout the day. There is no diurnal formation or nocturnal destruction; 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. The air had its origin in latitudes higher than 60° N, moving over the North Atlantic from north to south between two low pressure systems located to

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the north and south of the British isles and a high pressure system located in the west at latitudes < 45° N. Therefore, measurements from the Marine sector typically reflect long-range transport of clean atmospheric background air.

5 Conclusions

The main goal of this work was to investigate the weather conditions during the DOMINO campaign, the emission sources and land uses, to identify distinct air masses of different origins, and to analyse trace gases and particles in these air masses, in the southwest of the Iberian Peninsula during late-autumn, when heat-driven turbulence and synoptic are low. The Mediterranean climate and a moderate solar radiation still allow a relatively high rate of photochemical activity compared to the rest of Europe. Coniferous and Mediterranean forests in the surrounding of sampling site are not covered by snow. The site is also close to the Atlantic Ocean. Therefore, a range of primary and secondary species of diverse origins could be used for our study. Distinct air mass characteristics dependent on the origin of the air measured at El Arenosillo station were classified into four sectors of air mass origin with distinct emissions of anthropogenic urban and industrial as well as biogenic sources. The influence of boundary layer conditions under continental and marine influences was also taken into account in order to analyse the measured mixing ratios of primary and secondary gas-phase pollutants and particles. Though the site is complex and many parameters interact with each other to influence the measured mixing ratios and concentrations, the use of land use maps together with back-trajectory calculations has permitted to identify air masses with distinct chemistry and to discuss anthropogenic as well as biogenic emissions and their effect on the local composition of the air. Biogenic species in late autumn play a minor role in southern Spain, though they are still present in measurable concentrations. Long-range transport of anthropogenic as well as biogenic pollutants has measurable effects on local chemistry. Particle composition even allows the identification of industrial sources at several tens of km distance.

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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.

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Table 1. Land use, total and by sectors of air mass origin. The analysis was carried out in a radius of 80 km from the sampling site. Each column shows the area (km^2) of each land use and the percentage of total surface.

Land use	80 km radius	%	Seville-Gudadalquivir	%	Continental-North	%	Huelva-Portugal	%	Marine	%
Urban fabric	2 611 517	1.29	1 004 124	3.99	148 651	0.59	357 638	1.43	–	–
Industrial and comercial units	564 649	0.28	157 043	0.62	8538	0.03	131 300	0.52	–	–
Road and rail networks	25 523	0.01	16 723	0.07		–	2933	0.01	–	–
Portareas	121 326	0.06	28 443	0.11		–	2845	0.01	–	–
Airports	40 181	0.02		–		–		–	–	–
Mineral extraction sites	602 363	0.30	129 246	0.51	331 684	1.32	81 302	0.32	–	–
Dump sites	131 269	0.07	29 635	0.12	27 667	0.11	55 578	0.22	–	–
Green urban areas and sport facilites	244 475	0.13	98 726	0.39	1556	0.01	4580	0.02	–	–
Irrigated and non irrigated arable land	29 802 270	14.82	6 847 389	27.25	2 418 222	9.62	2 201 235	8.76	–	–
Rice fields	3 983 986	1.98		–		–		–	–	–
Vineyards, olives and fruit trees	8 228 727	4.10	3 980 340	15.84	809 808	3.22	1 290 941	5.14	–	–
Complex cultivation patterns	9 307 662	4.63	2 279 322	9.08	1 493 728	5.95	1 940 301	7.73	–	–
Agroforestry areas	7 641 427	3.80	1 832 481	7.29	2 043 823	8.13	3 741 862	14.89	–	–
Broadleaved forest	12 152 093	6.04	1 812 897	7.21	5 529 001	22.00	2 917 942	11.61	–	–
Coniferous forest	6 797 579	3.38	1 582 453	6.30	1 578 989	6.29	1 973 859	7.85	–	–
Mixed forest	1 632 397	0.81	326 013	1.30	947 933	3.77	187 012	0.74	–	–
Natural grasslands	4 323 052	2.15	412 905	1.64	547 161	2.18	1 750 986	6.97	–	–
Sclerophyllous vegetation	7 943 038	3.95	987 026	3.93	2 619 577	10.43	2 448 070	9.74	–	–
Transitional woodlandshrub	16 023 773	7.97	3 502 676	13.94	6 529 894	25.97	4 178 086	16.62	–	–
Inland and salt marshes, salines	6 088 301	3.03		–		–	863 471	3.44	–	–
Beaches, dunes, sands and intertidal flats	598 384	0.29		–		–	73 459	0.29	–	–
Water courses, water bodies, lagoons and estuaries	2 264 036	1.13	105 275	0.41	96 510	0.38	535 526	2.12	–	–
Sea and ocean	79 933 903	39.76		–		–	393 815	1.57	25 132 741	100.00
Total	201 061 930	100	25 132 716	100	25 132 741	100	25 132 741	100	25 132 741	100

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Table 2. Periods identified as representative for different air mass source regions (time in UTC).

Air mass types	From	To	Hours
Huelva-Portugal	24 Nov 2008 at 06:00	25 Nov 2008 at 06:00	25
	3 Dec 2008 at 02:00	3 Dec 2008 at 04:00	3
	3 Dec 2008 at 23:00	4 Dec 2008 at 19:00	21
	8 Dec 2008 at 09:00	8 Dec 2008 at 24:00	16
Continental-North	22 Nov 2008 at 06:00	23 Nov 2008 at 06:00	25
	25 Nov 2008 at 13:00	25 Nov 2008 at 19:00	7
	2 Dec 2008 at 10:00	2 Dec 2008 at 15:00	6
	2 Dec 2008 at 19:00	2 Dec 2008 at 22:00	4
Seville-Guadalquivir valley	21 Nov 2008 at 01:00	21 Nov 2008 at 17:00	17
	26 Nov 2008 at 18:00	27 Nov 2008 at 17:00	24
Marine	28 Nov 2008 at 18:00	29 Nov 2008 at 01:00	8
	6 Dec 2008 at 23:00	8 Dec 2008 at 24:00	27

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Table 3. Mean, standard deviation (STD), maximum (Max) and minimum (Min) daily levels of PM_{10}, $PM_{2.5}$, $PM_{10-2.5}$ and major (in $\mu g\,m^{-3}$) and trace components (in $ng\,m^{-3}$) for PM_{10} measured during DOMINO.

Major components (in $\mu g\,m^{-3}$)					Trace components (in $ng\,m^{-3}$)					Trace components (in $ng\,m^{-3}$)				
	Mean	STD	Max	Min		Mean	STD	Max	Min		Mean	STD	Max	Min
PM_{10}	16.16	7.07	32.12	4.89	As	4.00	4.15	12.77	< 0.10	S	437.31	152.80	741.62	261.11
$PM_{2.5}$	8.74	3.17	15.88	3.48	Cd	0.19	0.35	1.24	< 0.10	Sc	0.02	0.09	0.37	< 0.10
$PM_{10-2.5}$	7.42	6.65	24.59	< 0.10	Co	0.10	0.17	0.55	< 0.10	Se	0.49	1.22	4.80	< 0.10
Ca	0.12	0.09	0.37	< 0.10	Cu	15.42	9.02	36.08	3.69	Si	62.38	61.90	167.92	< 0.10
Fe	0.31	0.21	0.64	0.07	Mn	5.25	2.15	9.34	2.07	Sn	1.58	0.74	2.81	< 0.10
K	1.08	1.26	3.48	< 0.10	Ni	3.97	1.01	6.39	2.73	Sr	1.22	1.05	4.11	< 0.10
Mg	0.11	0.08	0.26	0.02	P	20.05	8.90	42.41	10.81	Ti	28.80	14.12	58.30	7.23
Na	2.66	4.23	12.50	0.00	Pb	7.11	4.40	17.18	< 0.10	V	2.46	1.22	5.07	0.92
										Zn	21.15	39.25	154.70	< 0.10

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Table 4. Daily levels of PM_{10}, $PM_{2.5}$, $PM_{10-2.5}$ and major ($\mu g\,m^{-3}$) and trace components (in $ng\,m^{-3}$) for PM_{10} in the Huelva-Portugal (H-P), Continental-North (C-N), Seville-Guadalquivir (S-G) and Marine (M) sectors.

Major components (in $\mu g\,m^{-3}$)	H-P	C-N	S-G	M	Trace components (in $ng\,m^{-3}$)	H-P	C-N	S-G	M	Trace components (in $ng\,m^{-3}$)	H-P	C-N	S-G	M
PM_{10}	21.87	10.85	4.89	13.06	As	7.63	0.00	0.00	5.65	S	609.62	291.72	272.73	418.81
$PM_{2.5}$	11.38	8.21	3.48	10.49	Cd	0.28	0.00	0.00	0.00	Sc	0.00	0.00	0.00	0.00
$PM_{10-2.5}$	10.49	2.64	1.41	2.57	Co	0.27	0.00	0.00	0.00	Se	0.72	0.00	0.00	0.00
Ca	0.05	0.23	0.15	0.052	Cu	18.47	10.37	3.69	14.20	Si	83.96	114.62	122.97	0.00
Fe	0.39	0.42	0.43	0.100	Mn	5.55	7.64	6.05	2.64	Sn	1.41	1.97	1.60	1.95
K	1.38	0.00	0.00	3.48	Ni	4.96	4.53	3.14	3.01	Sr	0.90	0.00	0.05	1.30
Mg	0.14	0.02	0.02	0.10	P	21.67	18.05	16.65	11.81	Ti	36.42	21.64	16.69	37.77
Na	0.00	0.00	0.00	8.50	Pb	9.71	5.14	3.47	7.33	V	3.00	0.92	1.24	2.09
										Zn	17.67	0.00	0.00	154.70

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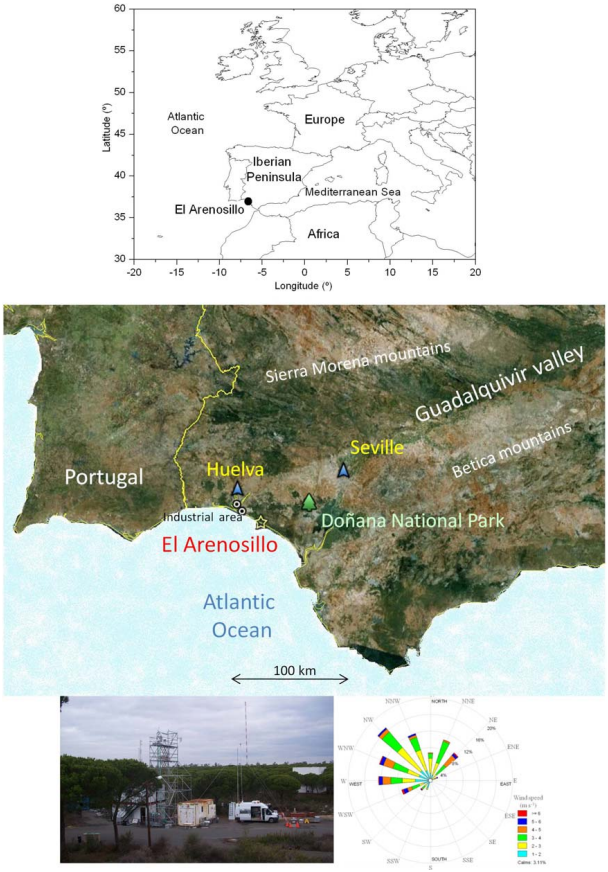

Fig. 1. Location of El Arenosillo in Europe, in the coast and in the Guadalquivir valley, infrastructure installed for DOMINO campaign, wind rose in the measurement period.

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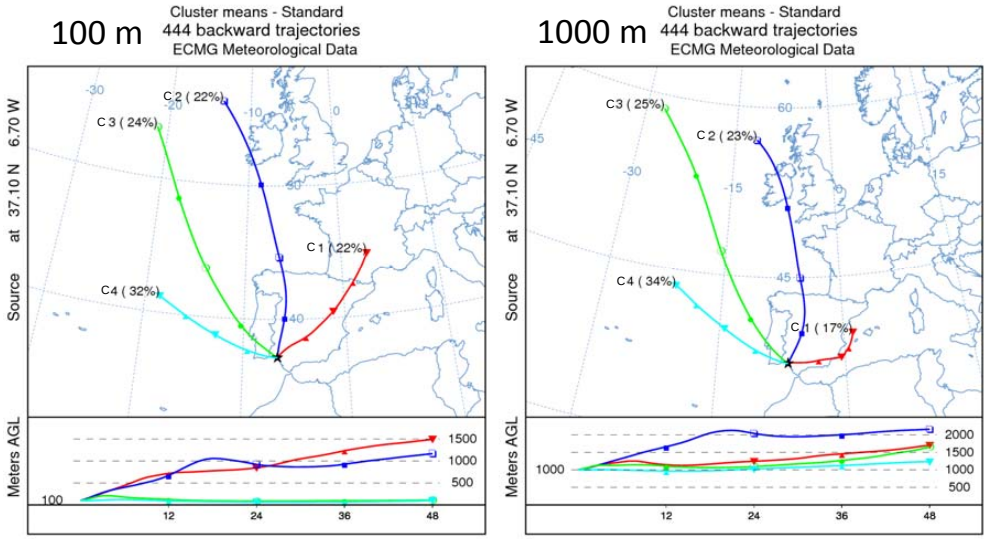

Fig. 2. Back trajectory clusters obtained from hourly trajectories with a pathway of 48 h at 100 and 1000 m.

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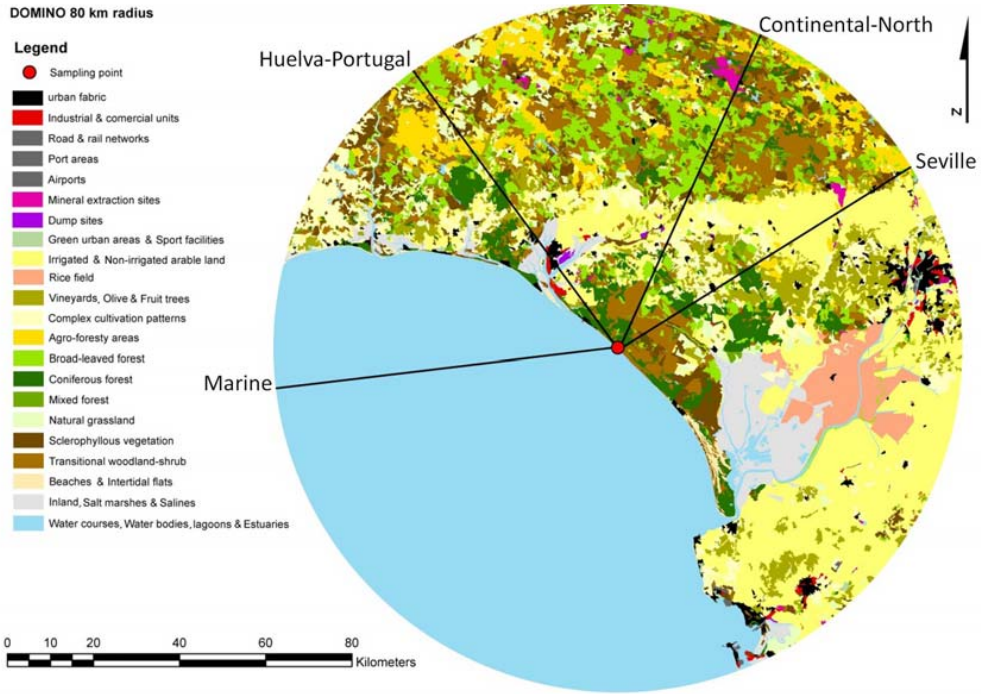

Fig. 3. Distribution of land use within 80 km of the measurement site. Black lines indicate the last part of the back trajectories cluster means at 100 m.

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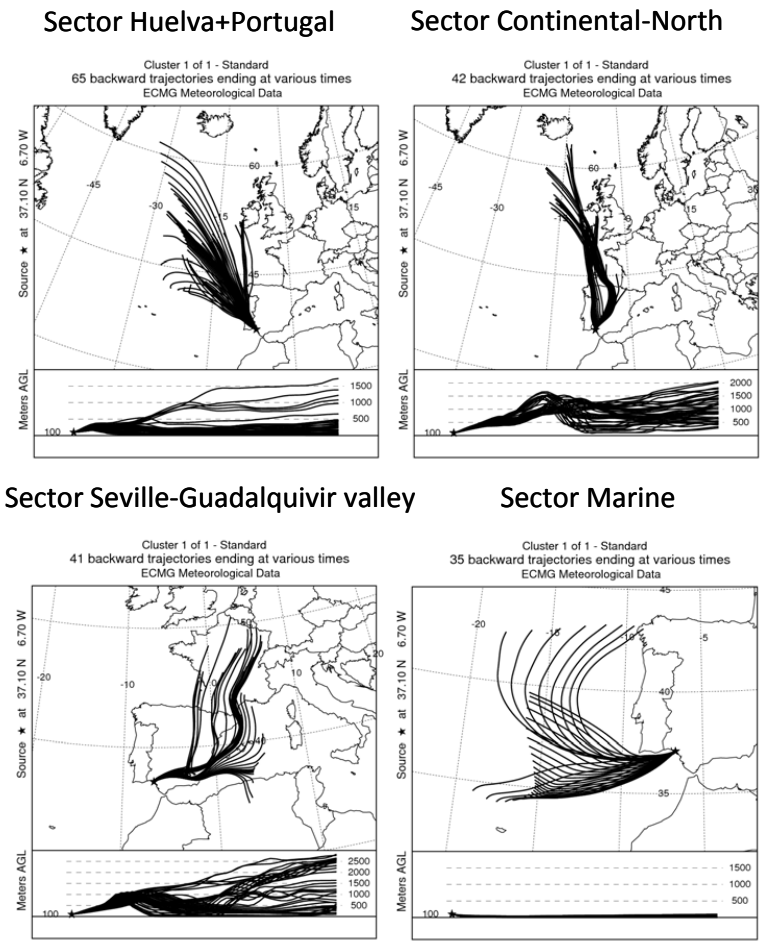

Fig. 4. Back trajectories of 48 h computed for 100 m arrival at El Arenosillo representative of the flows from Huelva-Portugal, Continental-North, Seville-Guadalquivir valley and Marine.

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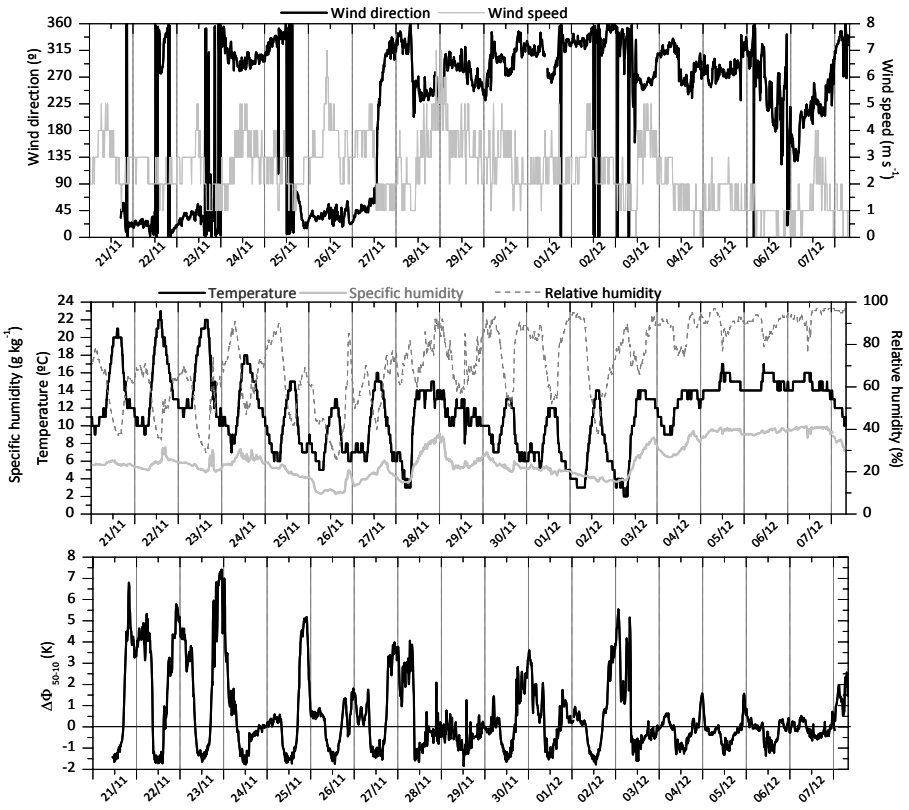

Fig. 5a. Temporal evolution of the wind direction and speed, temperature, relative humidity, specific humidity and potential temperature difference (between 50 and 10 m) using 10 min averages from the whole DOMINO campaign.

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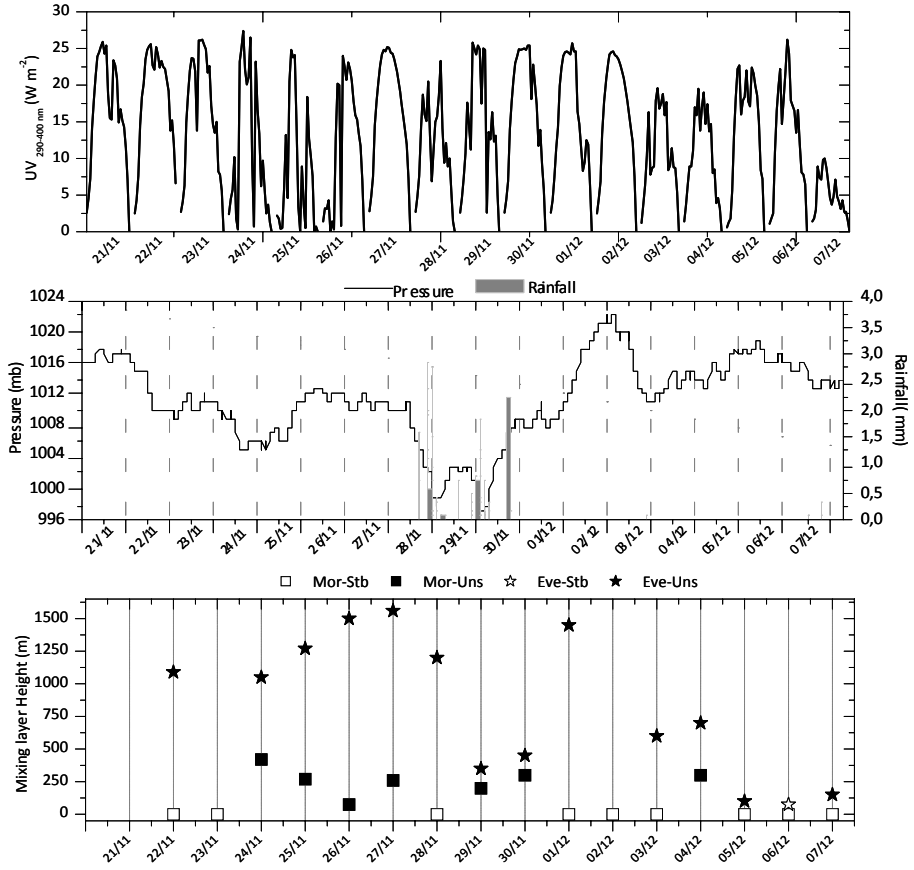

Fig. 5b. Temporal evolution of ultraviolet radiation, pressure, rainfall using 10 min averages and mixing layer height obtained from soundings (Mor-Stb: morning sounding with stable conditions, Mor-Uns: morning sounding with unstable conditions, Eve-Stb: evening sounding with stable conditions and Eve-Uns: evening sounding with unstable conditions) during the whole DOMINO campaign.

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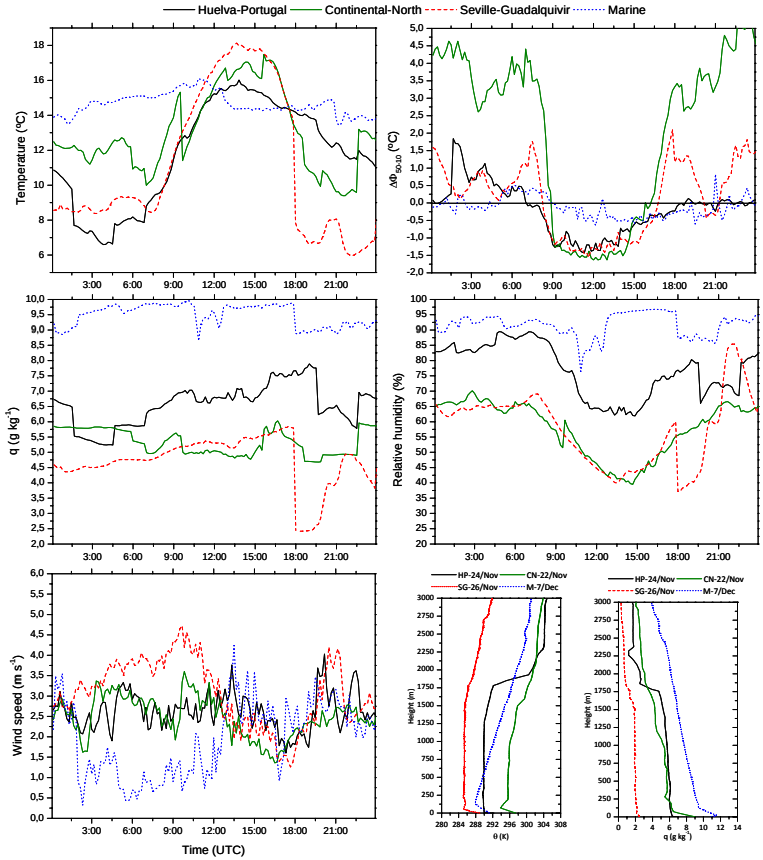

Fig. 6. Average diel profiles for temperature, potential temperature difference, specific and relative humidity and wind speed from the four sectors of origin. Vertical profiles of potential temperature and specific humidity obtained in the afternoon soundings under Huelva-Portugal (H-P on 24 November), Continental-North (C-N on 22 November), Seville-Guadalquivir (SG on 26 November) and Marine (M on 7 December) flows.

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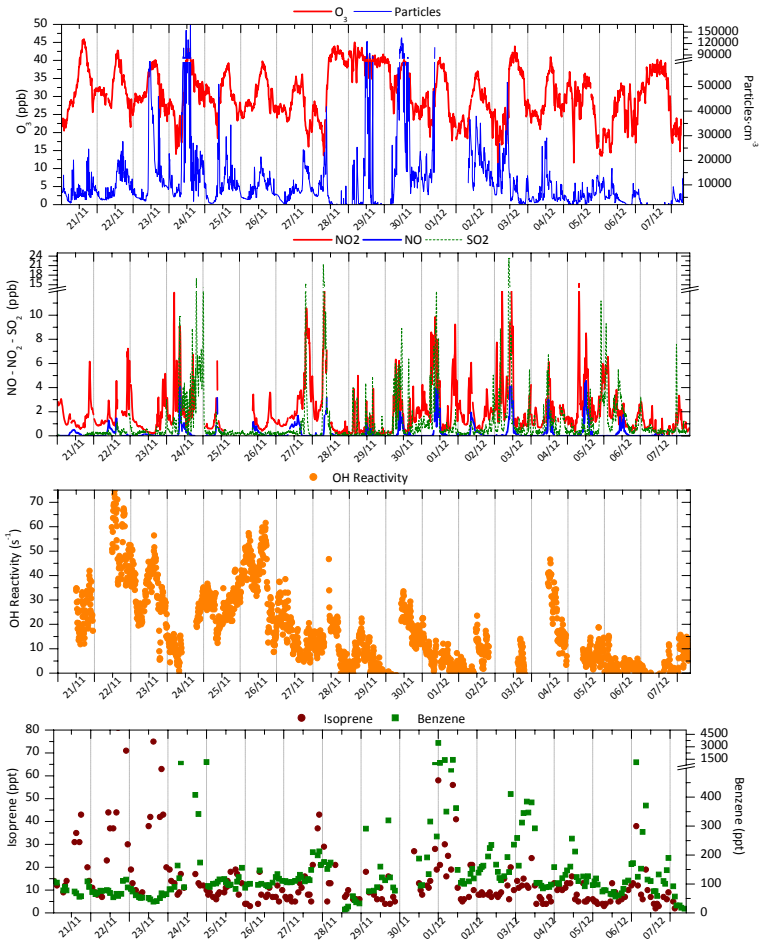

Fig. 7. Mixing ratios of ozone, NO, NO_2, SO_2, particle concentrations, total OH reactivity (10 min data), isoprene and benzene mixing ratios (hourly data) throughout the DOMINO campaign.

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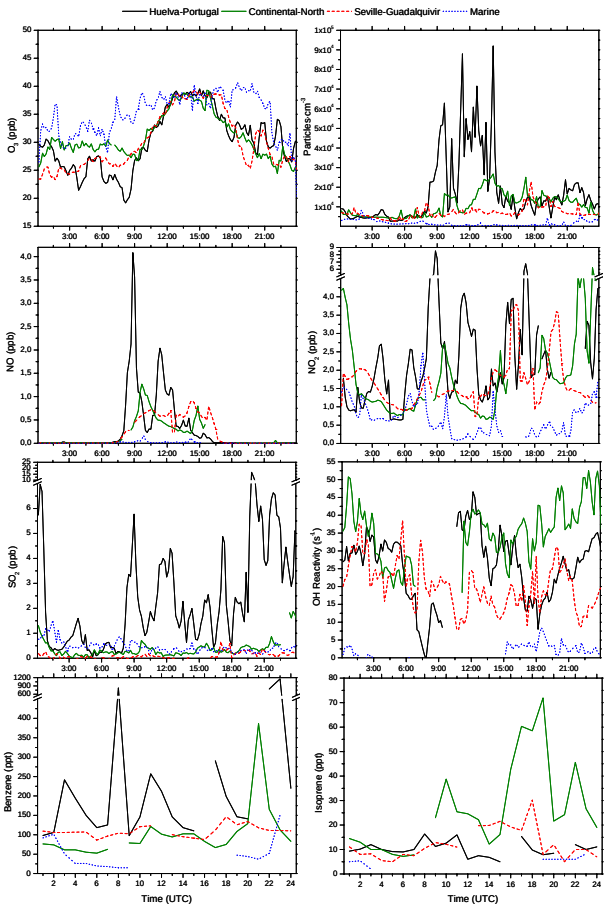

Fig. 8. Mean diel variation for ozone, particles with $D > 2.5$ nm, NO, NO_2, SO_2, total OH reactivity, isoprene and benzene for air with different origin.

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