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Ozone over the Western Mediterranean Sea – results from two years of shipborne measurements

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Abstract

Ozone, along with other air pollutants, has been measured for two years from a monitoring station placed on a cruise ship that follows a regular track in the Western Mediterranean between April and October. Conditions favoring high ozone levels have been studied by analysis of weather maps and back trajectories. This analysis was focused on a transect over the open sea in the South Western Mediterranean between Tunis and Palma de Mallorca. High ozone levels were found in situations with an anticyclonic circulation over the Western Mediterranean when subsidence brings air masses down from altitudes between 1000 and 3500 m a.s.l. Analysis of composite meteorological maps suggest a relevant contribution of breeze circulation to subsidence during events with high surface ozone concentrations; this points to an important contribution from local ozone formation. A detailed back trajectory analysis of the origin of air masses with high ozone concentrations was carried out for two "hot spots" for ozone pollution, found along the coast south of Genova and between Napoli and Palermo, respectively. While it was found that the influence of plumes from areas with high pollutant levels might explain most episodes in the Northwestern transect, such "local" influences appeared to be of minor importance within the Napoli-Palermo transect.

1 Introduction

Ozone (O_3), along with water vapour (H_2O), carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O), is a greenhouse gas that changes the radiative balance of the Earth's surface and contributes to climate change; it ranks as the fourth most important contributor to global warming (IPCC, 2007). Moreover, ozone is a strong oxidant with harmful effects on plants, animals and humans. Although emissions of ozone precursor gases decreased substantially in Europe, both annual and eight-hourly average ground-level ozone concentrations relevant to EU limit values did not show a decrease (EEA, 2007).

Data from monitoring stations as well as results of measurement campaigns show that ozone concentrations in the Mediterranean Basin appear to be relatively high: Lelieveld et al., (2002), found summer O_3 concentrations over the Mediterranean a factor of 2.5–3 higher than in the hemispheric background troposphere in the boundary layer and up to 4 km altitude. Rural stations in continental Greece, Italy and eastern Spain report summer average ozone values of about 60–70 ppbv, significantly higher than values in Northern and Western Europe (Kalabokas and Repapis, 2004; Paoletti, 2006; Millan et al., 2000). Observations at the islands of Gozo (Malta), Crete (Greece) and Cyprus indicate also high ozone values; monthly averages of ozone mixing ratios at Gozo are among the highest found worldwide for low altitude stations, with maximum values on average of 56 ppbv in spring and minimum average values for the winter months of 44 ppbv (Nolle et al., 2002), a value that is approximately twice as high as on the European continent. Thus, available nowadays ozone measurements suggest that the entire Mediterranean region is characterised not only by photochemical episodes in urban areas, but also by high background ozone concentrations. Results from a 3-D chemistry transport model also suggest that ozone concentrations over the Mediterranean Sea are higher than for the rest of Europe (e.g. Johnson et al., 2001). A major question is to what extend this background ozone is related to sources within the Mediterranean Basin and how much it results from long range transport of ozone and precursors emitted outside the Basin.

High ozone values are typical not only for ground level measurements in the Mediterranean, but in the entire boundary layer. Vertical ozone profiles provided by 77 MOZAIC flights revealed significantly enhanced (20–40%) ozone levels in the 1000 hPa–900 hPa layer of the Eastern Mediterranean with respect to Central Europe (Kalabokas et al., 2007). In the western part, along the Spanish coast in summer, the presence of stacked ozone layers reaching 2–3 km in height and extending more than 300 km out to sea have been reported by Millan et al. (1997, 2000, 2005).

The ozone behaviour and distribution in the Mediterranean region are closely related to the unique geographical characteristics and specific weather conditions. During the summer period, the Mediterranean area is directly under the descending branch of the Hadley circulation, caused by deep convection in the tropics (Lelieveld, 2009). The region incorporates the world's largest inland sea, which is surrounded by relatively high mountain ridges on almost every side; its climate is in general warm and dry (Bolle, 2003). The Mediterranean summers, connected with high pressure situations leading to subsidence, stability, clear sky and high solar radiation intensity enhance photochemical processes and emissions of biogenic volatile organic compounds to the atmosphere (Millan et al., 2002). In the mid-troposphere also transport of pollutants across the Atlantic is of relevance (Lelieveld et al., 2002).

However, the physical and chemical processes leading to O_3 formation appear to vary greatly within the Mediterranean basins: In the Western Mediterranean, the complex layout of the coasts and surrounding mountains favours the development of combined sea breeze – upslope winds and the evolution of return flows with several layers of pollutants and subsidence over the coast and the sea during daytime in summer. At night, land breezes can store polluted air masses above the maritime boundary layer and thus build reservoirs of aged polluted air that may return onshore on the following day (Gangoiti et al., 2001; Ancellet and Ravetta, 2005). A recent modeling study concerning the northwestern Mediterranean basin finds that local recirculation is of key importance for the surface concentration of ozone (Jiménez, 2006). Similar processes have been documented for the Central Mediterranean (Georgiadis et al., 1994) and for the Tunisian Coast (Bouchlaghem et al., 2008).

The sea-breeze recirculation is common in many locations, so that air can remain within a region for a prolonged period, and thus ozone formation due to local and regional sources is expected to be more important than in Central and Northern Europe (Beck et al., 1999). However, based on observational and modelling data, also long-range transport of European air toward the Mediterranean Basin has been claimed to be a main cause of elevated ozone concentrations in the Western Mediterranean area (Lelieveld et al., 2002).

The Eastern Mediterranean in summer is affected by semi-persistent strong northerly winds (Etesian winds), the development of recirculations is largely inhibited and high levels of lower tropospheric ozone are associated with transport of polluted air from the Balkans and Eastern Europe (Ziomas et al, 1998; Zerefos et al., 2001; Kalabokas et al., 2007, 2008).

Background ozone data for the Mediterranean basin are provided by the EMEP stations on a regular basis. However, only a few of these stations are located close to the sea and they do not cover the whole area. Additionally, various measurement campaigns have been conducted, particularly at the Spanish East coast, in Southern France and at the Aegean Sea. Some campaigns included ozonesonde and/or flight data, and shipborne observations besides ground based measurements, however they do not provide continuous observations over the open sea. Such measurements are particularly needed to assess the regional climate effects of ozone.

In an attempt to fill in the gap of observations in the Mediterranean basin and to gain more insight into the atmospheric dynamical and chemical mechanisms leading to high surface ozone levels, the Joint Research Centre of the European Commission (JRC, EC) has started regular ship borne measurements over the Mediterranean Sea. In 2005 a collaboration has been established between JRC-EC and the Italian cruise line Costa Crociere. In this context a monitoring station for ozone and black carbon aerosols (BC) was installed on board of the cruise ship Costa Fortuna, which had a regular weekly route in the Western Mediterranean during spring, summer and autumn for two years (2006 and 2007) and in the Eastern Mediterranean in winter 2006.

These measurements are planned to be continued for a longer period in order to contribute to capture trends in pollution levels. Such trends will depend on changes in emissions related to economic and technological development as well as new regulations (e.g. regarding shipping). They may also be influenced by climatic changes: it is expected that the Mediterranean climate will become increasingly warm and dry in the coming decades. Some model simulations also suggest that there will be less Mediterranean cyclones and that windspeeds on average will be reduced in this area

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(IPCC 2007).

The main purpose of this paper is to present the ozone data collected during 2006–2007 on board of Costa Fortuna and to characterize the specific meteorological conditions leading to high ozone levels. The analysis, that relates ozone concentrations to synoptical situations and calculated back-trajectories, contributes to understanding the causes of ozone pollution in the area. A good understanding of the links between meteorology and ozone levels is needed to evaluate the likely effects of climatic changes on ozone levels in this area. Ozone and black carbon observations from the Costa Crociere cruise ship in the Eastern and Western Mediterranean have been used to verify ship emission inventories in a recent publication (Marmer et al., 2009). In the present paper we will focus on the ozone observations in the Western Mediterranean where we have the most comprehensive set of measurements available. BC measurements will here only be discussed qualitatively in relation to correlations between BC and ozone.

2 Methods

2.1 Set-up of on-board monitoring station

The automatic monitoring station, installed on board of Costa Fortuna, contained the following measurement equipment:

- UV Photometric Ozone Analyzer (Model C49 Thermo Electron Instruments Inc., USA),
- Aerosol Black Carbon Analyzer (Aethalometer, AE 21, 2 wavelengths, Magee Scientific, USA)
- Optical Aerosol Spectrometer (GRIMM Model 1.109, GRIMM Aerosol Technik GmbH, Germany),

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The raw data are averaged over a 10 min interval and stored in a computer.

The ozone analyzer uses a dual cell measurement system, where ozone has been removed by a scrubber from the air going into one of them; this allows to eliminate potential interferences. The stated precision is 1 ppbv, the observed zero-drift between calibrations was ≤1 ppbv, the span-drift was between 0 and 3%. Calibrations were performed by comparison to a portable primary standard (Thermo Electron 49C PS).

Information about the ships position, speed and sailing direction were received together with meteorological parameters (wind speed and direction, temperature, humidity) every 15 min.

2.2 Selection of location for monitoring station on the ship

The ideal location for the installation of devices measuring various gas concentrations and especially aerosol particles appears to be the frontal part, at the prow of the ship at Deck 4 (Fig. 1), 16 m a.s.l. However, as this part of the ship was unavailable a site at the front of the top deck (Deck 14, 47 m a.s.l.) was chosen. In order to assure that the two measurement points were equivalent and not influenced by different aerodynamic conditions, comparative measurements have been carried out. Two identical racks, including ozone analyser, aerosol counter, pumps and flowmeters were used, the two racks were operating for 24 h at the prow of the ship, and then one was moved to Deck 14. Simultaneous measurements have been performed for one week in July 2005 during a regular ship cruise along the track Savona – Napoli – Palermo – Tunis – Palma de Mallorca – Barcelona – Marseille – Savona. The difference between the ozone values measured at Deck 4 and Deck 14 are small and within the error interval for such type of measurements, apart from some occasions in harbours with strong local emission sources and during a fog episode in the Gulf of Lion, where the height difference between the two stations is likely to be important.

Further in our analysis we will use the data obtained at Deck 14 during the period April–October in 2006 and 2007.

2.3 Filtering of data

The observations used for the analysis of ozone concentrations over the open sea, discussed in the following, have been filtered in the following way:

- measurements done in harbours and their nearest surroundings (the last two hours before arrival and the first two hours after departure) have been excluded

- measurements where a comparison of wind speed and direction with the speed and course of the ship showed that smoke from the stack of the ship might reach the monitoring station (ship speed smaller than wind speed, difference between wind direction and course of ship less than 30°) have been excluded as well.

Measurements done in harbours are treated separately.

3 Results and discussion

3.1 Overview of the data – Western Mediterranean

The summer route of Costa Fortuna in the Mediterranean Sea is shown on Fig. 2. In most cases the ship arrives in a port in the morning (7:00–9:00 LT) and leaves in the late afternoon/early evening (17:00–19:00 LT); thus the ship sails mainly during the night. The only exeptions are the two longest legs: Savona-Napoli (departure 17:00 LT, arrival 13:00 LT next day) and Tunis-Palma de Mallorca (departure 13:00 LT, arrival 14:00 LT next day). Local time (LT) is for all data shown UT plus two hours.

The measurements of ozone and BC performed during the summer periods (April–October) of 2006 and 2007 are shown in Fig. 3. The figure shows all measurements, including harbours; in the harbours a strong anticorrelation between BC and ozone is found, as expected, because the high BC levels in harbours are caused by local combustion sources that also emit NO that destroys ozone by a fast "titration" reaction. The seasonally averaged measurements are shown in Fig. 4, plotted on a grid scale of $1° \times 1°$.

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The patterns of measurements show a remarkable similarity between the average weekly concentration profiles observed during the two years. This similarity is not only caused by the impact of harbours, causing ozone minima at these points both years; there is also a very similar behaviour of the measurements over the sea for the two years. This may be explained by the fact that high (and to some extent also low) ozone concentrations are found in situations with a characteristic type of air circulation, as discussed in the following, and thus tend to show a similar geographical distribution of the ozone concentration levels. Also the impact of "titration" by NO from local sources seems to play a role, most evidently in the concentration "dip" found between Savona and Naples, observed in the vicinity of the Rome area.

Although the measurements show similar variations along the track both years with the highest values in the same areas, there is a difference between the absolute concentration levels in the summer of 2006 and that of 2007, the latter being significantly lower. For example, over the long leg between Tunis and La Palma, the average ozone in June–July–August 2006 was 51 ppbv while it was 46 ppbv for the same period in 2007; looking at July only, the difference between the two years was as large as 55 ppbv compared to 41 ppbv.

In Chapter 4 we will focus the discussion of the data on understanding the causes of elevated ozone concentrations through characterisation of the source regions by trajectory analysis and analysis of the synoptical situations and their relation to ozone levels in this area.

3.2 Diurnal variations

The fact that most of the measurements over the open sea are performed during night time must be taken into account when evaluating the data. Ground level ozone shows a diurnal variation caused by the balance between transport, sinks and the photochemical sources, usually with a maximum during the daytime. However, over the open sea both sources and sinks are likely to be relatively small. Deposition of ozone on water is slow and also the photochemical formation of ozone is slow due to the low precursor concentrations, so diurnal variations are expected to be small.

An estimate of the amplitude of the diurnal cycle of ozone over the sea can be made by looking at observations made on islands in the area. The observations made at two EMEP stations located at the islands of Malta and Crete are shown in Fig. 5. The data have been obtained from the EMEP website (EMEP 2009).

The most notable feature of the monthly averaged daily ozone cycle at these stations is the low amplitude, not exceeding 7–8% with respect to the means of the diurnal values. Long term measurements at Gozo, Malta confirm this diurnal behaviour (Nolle et al, 2002). For the Eastern Mediterranean, at Finokalia, Crete, Kouvarakis et al. (2002) report an amplitude of 8% for the diurnal ozone variation and note that this is in agreement with diurnal amplitudes observed in remote marine locations.

Based on the ozone data for the islands we assume that the diurnal variation of ozone over open sea should be small (+/−2.5 ppbv), impying that our onboard night-time ozone measurements over the open sea could be treated as representative also for the day-time.

This diurnal behavior is not typical for land stations, were the ozone amplitude is strongly related not only to the solar radiation, but also to the topographic location of the observing station, the atmospheric circulations, local emissions, and the chemical processes involved and the higher ozone deposition velocities over land (Millan et al., 2000).

The concentrations measured in harbours show a completely different behaviour, as they are subject to local sources and coastal meteorology. The observations clearly show the influence of seabreeze circulation on the profiles of ozone and BC concentrations in some harbours as illustrated in Fig. 6, where also the change in wind direction for a typical day with sea breeze is shown. At these harbours the vessel arrives before the onset of the sea breeze and departures around 17:00–19:00 local time. For each harbour the days with well expressed sea breeze circulation have been selected on the basis of data provided by the ship's automatic meteorological station: 24 cases for Palermo, 19 for Barcelona, 17 for Marseille and 17 for Savona. The minimum ozone

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values correspond to maximum values of black carbon. This generally happens at around 07:00 LT, a period characterized by windless conditions as the sea breeze has not yet begun. For these transition hours the measurements show a build-up of BC while ozone is titrated away by the reaction with NO.

Two to three hours after the onset of the sea breeze regime, the wind speed and wind direction were nearly constant, as it was evident from the meteorological observations. However, the ozone concentrations continued to increase to reach maximum values in the afternoon.

This behaviour may be explained the following way: In the first hours the breeze circulation (breeze cell) has a small horizontal and vertical extension and titration of ozone by NO is important. With increasing solar radiation, the dimensions of the breeze cell grow and the local NO emissions are mixed into a larger volume of air. This is accompanied by transport of ozone from the open sea and photochemical formation of ozone.

4 Data analysis: Ozone over the open sea, Tunis – Palma de Mallorca

4.1 Relation between ozone levels and synoptical situation

We will focus here on the ozone data for this part of the Mediterranean Sea because only for this leg there are 24 h of continuous measurements above the sea and the vessel covers a distance of about 800 km, as illustrated in Fig. 2.

For the spring – summer period of 2006 and 2007 ozone has been successfully measured on Costa Fortuna along the transect Tunis – Palma de Mallorca 42 times. The measured ozone concentrations in these 42 study cases have been classified into 3 groups (see Table 1) in order to analyse the influence of the synoptical situation:

- The first group (8 cases) is characterized by high ozone concentrations – around or above 60 ppbv observed for over one hour.

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– The second group includes 9 cases with relatively low ozone concentrations – below 40 ppbv, observed for over one hour.

– The third group includes the remaining 25 cases with intermediate mean ozone values of 40–60 ppbv.

60 ppbv is the 8-hours EU air quality standard while 40 ppbv corresponds to reported values for clean marine air (Anderson et al, 1993) and is regarded as representative for clean marine air levels of ozone in the Eastern Mediterranean (Kourtidis et al., 2002).

In general the ozone concentrations show fluctuations and variability related to the complex pattern of the synoptic situation, peripheral parts of cyclones, strong surface winds, passage of atmospheric fronts etc., most of which are difficult to categorize. However, the analysis of synoptic charts for the relative dates has revealed some common features for the cases inside a given group:

The High Ozone group is characterized by an anticyclone pressure centre situated above the Mediterranean Sea, typical for the spring or early summer. The common feature for the group is the anticyclonic circulation at the time of the ship's movement along the track, or immediately before, with isobars following to a great extent the curvature of the sea coast. The individual features of particular days in the group are related to the type of anticyclone: a synoptic (general) high pressure system or large mesoscale anticyclonic circulation developed by thermal factors, connected to the breeze circulation and the large-scale pressure centers in the surroundings.

The Low Ozone group is strongly associated with the presence of a low pressure system (cyclone) located near the ship route. The synoptic features are more complex and measured ozone concentrations seem to be dependant on the frontal position and the related wind and precipitation phenomena.

The "in between" group has not been analyzed in detail. It may well contain days with synoptical situations similar to either the "High" or the "Low" ozone groups but where the duration of this situation has been too short to reach the upper or lower concentration levels.

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In order to gain more insight into the atmospheric processes in the lower troposphere over the Mediterranean and their relationship to the ozone concentrations in the "High" and "Low" ozone groups we have further analyzed composite weather maps, constructed from the NCEP/NCAR reanalysis following the procedure of Kalnay et al., (1996). These maps provide a picture of the average meteorological conditions found during all of the observed episodes with high and low ozone levels.

The composite maps for the geopotential heights at different isobaric levels (Fig. 7a, b) show that differences for the two groups are noted not only at surface level, but also aloft. At about 1500 m a.s.l. (850 hPa), the ridge of high pressure for the High group extends from North Africa over the Western Mediterranean Sea towards Southern Central and Southeastern Europe, while for the Low group this ridge is not so well expressed and is moreover displaced towards east. At about 3000 m a.s.l. (700 hPa) the pressure distribution maintains this pattern, while at 500 hPa (about 5000 m a.s.l.) the differences are smoothed.

The composite maps for the wind field in both groups (not shown) are characterized by low wind velocities up to about 1500 m a.s.l. (850 hPa), typical for anticyclonic conditions with very low pressure gradients. However, the wind speeds aloft are higher for the Low than for the High group (approximately by a factor of two), particularly over the southern part of the Western Mediterranean Sea.

It should be noted that the composite maps are obtained with a coarse resolution model ($2.5\times2.5^{\circ}$), but we find that for the qualitative analysis we are presenting for the Western Mediterranean these maps are informative.

The composite maps for the vertical velocity (Fig. 8) are of particular interest, since vertical transport is associated with subsidence in the typical summer anticyclonic circulation. Widespread subsidence can enhance surface ozone by bringing higher levels of ozone down from the upper troposphere (e.g. Fishman et al, 2005). Previous studies of the summer circulation in the Western Mediterranean basin (Gangoiti et al., 2001; Millan et al., 1997, 2000, 2002) bring evidence that within the general subsidence due to the Azores anticyclone, a compensatory subsidence occurs in response to the development of the sea breeze circulation and the Iberian Thermal Low.

Composite maps of vertical velocities in a south-to-north vertical cross section across the track of the ship (longitude 7E) are displayed in Fig. 9 in order to illustrate the atmospheric circulation over the region. For the "High group" an intense sinking can be noticed over the sea while upward motions above the land are evident. The maximum downward velocities are at about 900 hPa, which corresponds approximately to 1000 m a.s.l. At the same height Kalabokas et al. (2007) report maximum ozone concentrations for the Eastern Mediterranean. As can be seen on Fig. 9, this circulation pattern has a horizontal dimension of about 700 km and vertical extension of about 3 km.

Previous studies of the summer circulation in the Western Mediterranean basin (Millan et al., 1996, 1997, 2000, 2002) bring evidence that within the general subsidence due to the Azores anticyclone, a compensatory subsidence occurs in response to the development of the sea breeze cycles and the Iberian Thermal Low. In an attempt to see how these thermal circulation effects can influence the ozone levels also in the region between Tunis and Palma de Mallorca we have analysed composite weather maps of the vertical velocity in south-to-north vertical cross section in different synoptic situations (Fig. 10).

At 18:00 UTC the sea breeze circulation is still well developed, although the land surface begins to cool. At 00:00 UTC the temperatures on the European coast are lower than the temperatures over the open sea, and land breeze develops. Due to higher temperatures on the African coast the situation there is opposite and the circulation remains as during the day (sea breeze). At 06:00 UTC a convergence and respective upward motions over the open sea are noticeable. It should be stressed, that the breeze effects are only at the peripheries of the larger circulation centered over open sea and extending over 700 km in the horizontal direction. The above figures suggest, however, that these peripheral diurnal cycles, can affect the intensity and the vertical extent of the subsidence and the circulation over the sea.

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Figure 8 also illustrates the fact that the nocturnal (land breeze) velocities are with lower intensities than the diurnal (sea breeze) ones. Recalling that the nocturnal processes at these latitudes have shorter duration than the diurnal, it is clear that the nighttime atmospheric circulation is not equivalent to the daytime circulation. As a result, the daytime subsidence prevails and ozone from higher levels can be transported down to the sea. This appears to be a main reason for the relatively high ozone concentrations above the sea, observed in this part of the Mediterranean.

4.2 Backward trajectories

Ground level ozone in the Mediterranean Basin is controlled not only by internal formation and loss processes, but also by ozone imported into the Basin and influenced by changes in the background ozone concentrations. Since its photochemical lifetime is about 1–4 weeks above the well mixed boundary layer, ozone has the potential to be transported and mixed over larger scales (EMEP Report, 2005).

To investigate the relationship between ozone concentrations observed on Costa Fortuna along the track Tunis-Palma de Mallorca and the origin of the air masses arriving there, 5-day backward trajectories have been computed for the episodes with persistent high or low ozone concentrations (see Sect. 4.1).

The trajectories were calculated using the BADC trajectory service (BADC, 2007) with 1.125×1.125 degree resolution ECWMF archived data (91 vertical layers). The same calculations were performed using the US NOAA Hysplit website (HYSPLIT, 2007) with GDAS meteorological data ($1\times1^{\circ}$ horizontal resolution, 23 vertical layers); although minor differences between the two sets of calculations were found, the qualitative picture they provided were the same.

These trajectory calculations showed that high ozone levels are associated with air masses originating from the sector north to east-southeast (Central and South Europe) and their shape typically reflect the anticyclonic circulation around a pressure centre situated over the Mediterranean Sea. Four episodes with high ozone concentrations are shown in Fig. 11. These include typical mesoscale anticyclone situations (like a and c), but also weather conditions determined by a synoptic cyclone (b) and a more complex pattern (d). The Figure indicates that the air masses are brought down over Costa Fortuna from altitudes about 1000 to 3500 m due to the widespread subsidence in an anticyclone located over the Mediterranean Sea and Central Europe. This behaviour was found in 7 out of the 8 cases of high ozone levels.

Our measurements show that the highest ozone concentrations have been observed in cases when the "regional summer anticyclone" is embedded in a synoptic scale high pressure system coming towards the Mediterranean. An example for the trajectories in this case is given in Fig. 11 (a and c), when the large scale anticyclone is approaching the region from the North and finds the "regional summer anticyclone". Under such conditions, the high ozone concentrations are found in the air masses that have been brought down to the sea level from higher altitudes. We have observed high ozone concentrations also under low pressure conditions over the Mediterranean. This happens when the "regional summer anticyclone" is in the periphery of a synoptic cyclone or within a large-scale weak (low gradient) depression (e.g. as in the case of trajectory b in Fig. 11). Of importance is the intensity of the low pressure systems and their speed. When the cyclones are moving slowly towards the region of high pressure, the breeze cell circulation can adapt to the changing ambient pressure and despite some disturbances like cloudiness, changes in the prevailing winds and pressure decrease, the breeze cell still exists. In this case the large scale depressions "see" the "regional summer anticyclone" as an obstacle and can pass around it.

Back trajectories for the low ozone episodes ("Low"-group) could be divided into 3 classes after analysis of the corresponding synoptic charts for the previous 5 days. These classes are characterized by respectively

1. dominant westerly flow for the last 5 days, which is part of cyclones with diverse intensity,

2. dominant north-westerly flow,

3. unclear trajectories in complex situations (low baric gradients during transition

from anticyclonic to cyclonic circulation over the sea).

Low ozone concentrations are related to processes leading to destruction of the breeze circulation and thus to destruction or weakening of the "regional summer anticyclone". In the majority of our cases these processes have been observed in situations of moving atmospheric fronts accompanied by strong winds and precipitations. This happens when the weather changes due to low pressure systems approaching the Western Mediterranean basin. Low ozone days are associated with cyclonic curvature of the isobars and relatively weak pressure gradients. Deep cyclones approaching the Iberian Peninsula from the Atlantic can lead to occurrence of a low pressure center over the sea due to orographic reasons, or contribute to the development of a low pressure trough. In such cases the ozone data over the sea are characterized by low values (40 ppbv and below).

It should be mentioned that there are relevant uncertainties in the calculated back trajectories caused by errors in the input data, model assumptions and resolution. Stohl (1998) estimates the accuracy of computed trajectories with position errors of up to 20% of the travel distance. However, the results for the High and Low ozone episodes demonstrate substantial differences and provide evidence for the effect of long range transport on ground level ozone concentrations observed along the track Tunis – Palma de Mallorca.

The small number of episodes included in the groups does not allow a more detailed study for clustering and characterization of the trajectories origin. Nevertheless, we consider the qualitative conclusions above as a general indication for the influence of the large scale flow on the measured ozone concentrations in this part of the Mediterranean Sea.

4.3 Trajectory analysis of two ozone "hot spots"

The maps of seasonally averaged ozone concentrations (Fig. 4) show some areas with particularly high concentrations of ozone; the largest of these "hot spots" is found along

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the first part of the track between Savona and Napoli, approximately down to the island of Corse, in the spring and summer months. The red colour spots on these maps are characterized by ozone concentrations of above 60 ppbv. In order to understand the origin of the air masses bringing high ozone concentrations to these areas, back trajectories have been calculated for all episodes where ozone levels above 60 ppbv have been measured using the Hysplit website as previously described.

During the periods from June to August 2006 and from March to May 2007, ozone measurements along the leg Savona-Naples are available for 19 cruises, out of which 12 show values above 60 ppbv in the part of the cruise indicated in red in Fig. 4. The "High Ozone" trajectories for June–August 2006 are shown in Fig. 12. The 12 trajectories were characterized according to their origin. Concerning the ground level trajectories, three came from the East (Po Valley), four from the West, passing over the southern coast of France, two came from North-North West. Thus transport of pollutants from the highly urbanized coastal areas or from the Po Valley appeared likely to give an important contribution to the high ozone levels observed. However, high ozone concentrations were also measured in a case where the ground level trajectory was entirely over the sea for the last 5 days and in two cases where the trajectories were entirely over the sea apart from a passage over the island of Corse. Subsidence of air masses along the trajectories was observed, but the tendency was less pronounced than what was found for the leg Tunis – La Palma: Subsidence moving air masses down from 1000 m or more were observed in five cases.

A similar backtrajectory analysis (same period, same criterion) was carried out of the elevated ozone concentrations in the transect Naples-Palermo. 11 episodes with high ozone (above 60 ppbv) were observed and back trajectories were calculated for these episodes. Four trajectories brought air from North or North East, four came from North West (in three cases reaching France), one from south East (Calabria/Eastern Mediterranean) and two from West. In four cases, an impact of the plumes of either Napoli or Rome appeared likely. Sinking of air masses from 1000 m or more to ground level was observed in four cases. Two ground level back trajectories had remained over

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the sea for all of the five days.

Ship emissions are gaining increasing importance as sources of both NO_x and VOCs, and they might be one of the explanations for high ozone concentrations in air with trajectories of marine origin. However, the present study does not allow drawing conclusions about this impact. The recent modelling study by Marmer et al., (2009) finds that the average impact of ship emissions on ozone along the route of Costa Fortuna in the Western Mediterranean is relatively small (a few ppbv).

5 Conclusions

These ship borne measurements have the advantage of providing regular observations from an area with a relatively large geographical extension. The disadvantage, when compared to a measurement station at a fixed site such as an island, is a lower measurement frequency at each location. The choice of performing measurements along a cruise track seems to be justified by the fact that seasonally averaged concentrations of ozone over the sea show a relatively large geographical variation (Fig. 4) which measurements at one or a few fixed observational sites might not have revealed.

The measurements show that high ozone levels over the open sea along the transect Tunis – La Palma are mainly found in situations with an anticyclonic circulation over the Western Mediterranean. During summer, it appears that a well developed sea breeze regime induces an anticyclonic circulation over the whole region with subsidence over the sea. This finding is consistent with a number of comprehensive studies for the Western Mediterranean Basin performed by Millan et al., (1992, 1996, 1997, 2000, 2002, 2005). This regional, thermal type of anticyclone can be easily embedded into a synoptic scale high pressure system and thus intensify the general subsidence. At surface level the breeze regime is then manifested as a ridge of high pressure over the sea. The anticyclonic conditions in the Western Mediterranean can persist in some cases even when they are embedded into a larger synoptical low pressure system. High ozone concentrations in this part of the Mediterranean are most often found in air masses brought down from aloft; thus the subsidence in this “regional summer anticyclone” appears to be a main reason for the high ozone levels, with the main sources of precursors likely to be found inside this area.

The origin of air masses causing high ozone concentrations in the transect along the coast from the Gulf of Genova down to the latitude of the island of Corse was studied by back-trajectory calculations. A similar analysis was made for the transect Napoli-Palermo. While it was found that plumes from areas with high pollutant levels (urban areas, Po Valley) might explain most episodes in the Northwestern transect, such “local” influences appeared to be of minor importance within the Napoli-Palermo transect. In four cases the “High Ozone” backtrajectories were entirely over the sea for the last five days, thus providing evidence of a long atmospheric lifetime of ozone over the sea.

Climate models predict that Mediterranean summers will be increasingly characterized by warm, dry weather with calm winds (IPCC, 2007). Thus it seems that the conditions that favour high ozone levels over the sea and along the coasts are likely to become more frequent in the coming years and the conditions that favour the build-up of ozone will presumably also promote the build-up of other secondary air pollutants, e.g. particles. Long term monitoring is needed to establish the actual trends in air pollution over the Mediterranean Sea; platforms on ships like the one reported in the present paper appear to offer an interesting possibility of providing such data.

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Table 1. Grouping of measurement periods according to measured ozone concentrations (see text).

	2006	2007
Group 1 High ozone concentrations	7–8 June, 21–22 June, 12–13 July, 6–7 September	25–26 April, 9–10 May, 13–14 June, 18 July
Group 2 Low ozone concentrations	28–29 June, 5–6 July, 27–28 September, 4–5 October, 18–19 October	2–3 May, 20–21, 27–28 June, 19 July
Group 3 Intermediate ozone concentrations	26–27 April, 3–4, 10–11, 24–25 May, 31 May–1 June, 14–15 June, 5–6, 19–20, 26–27 July, 2–3, 9–10, 16–17, 23–24, 30–31 August, 13–14, 20–21 September, 11–12 October	16–17 May, 6–7 June, 4–5, 11–12 July, 22–23 August, 5–6, 12–13, 19–20 September

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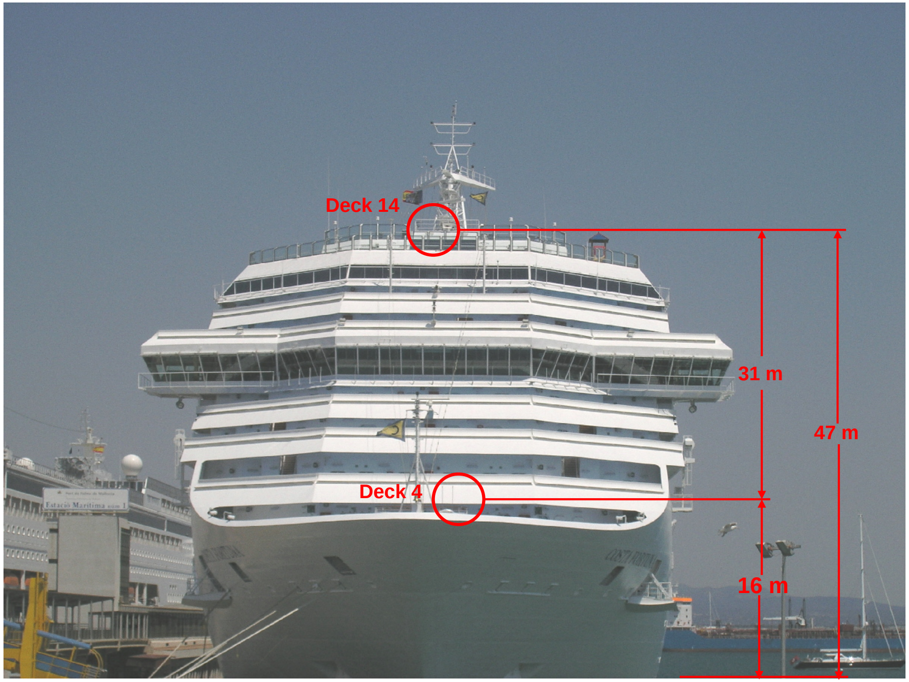

Fig. 1. Frontal view of Costa Fortuna with the locations for the instrumental set-up.

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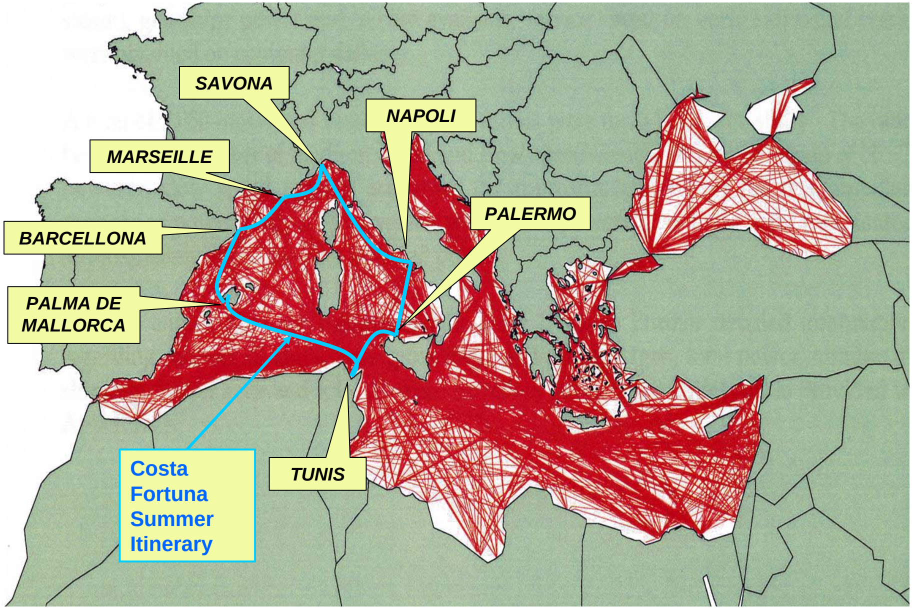

Fig. 2. The route of Cost Fortuna during the period April–October 2006 and 2007. The red lines indicate ship trajectories in the Mediterranean (adapted from the Lloyd Register Report 99/EE/7044, Lavander, 2001).

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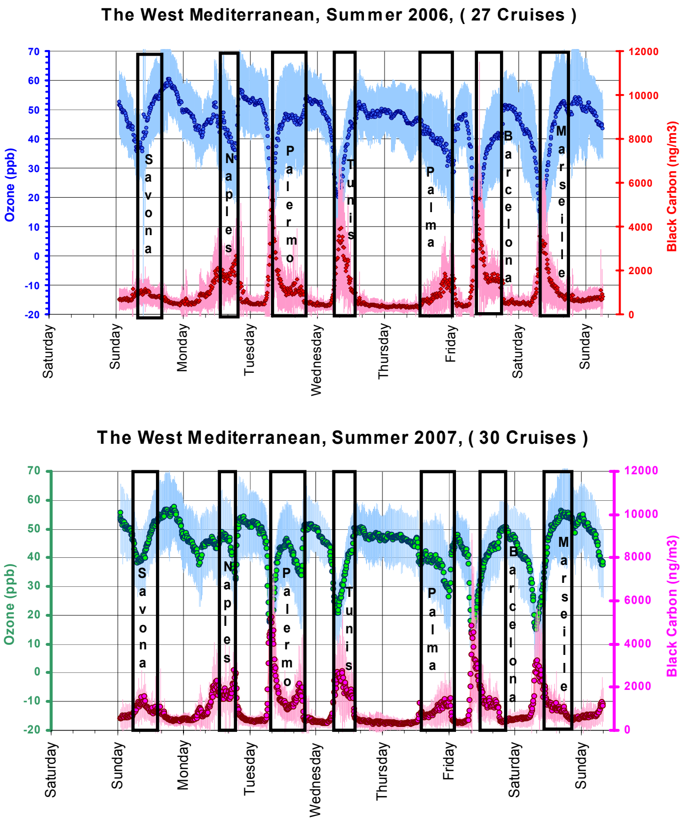

Fig. 3. Ozone and black carbon concentrations in the Western Mediterranean as measured along the cruise track. The figure shows average values with standard deviation for the periods April–October 2006 and 2007. The black columns show the periods where Costa Fortuna is at berth in ports.

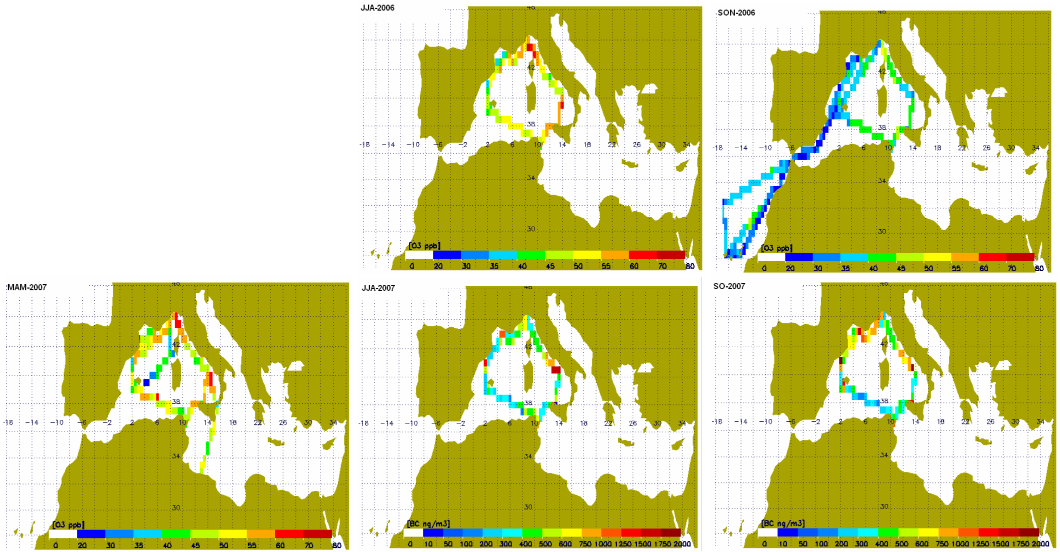

Fig. 4. Plots of averaged measured concentrations of ozone during spring (March, April, May), summer (June, July, August) and autumn (September, October, November) for the years 2006 and 2007. The data have been filtered as described above. Although measurements were performed also during the period March, April and May 2006 these data are not included because of missing data regarding the ships position.

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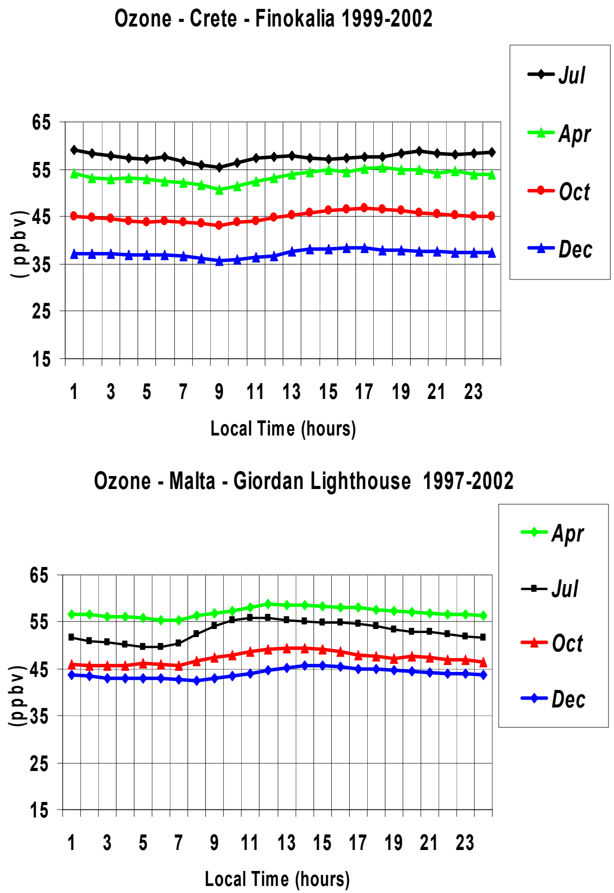

Fig. 5. Monthly averaged diurnal variations of ozone measured at the EMEP stations: Finokalia, Crete (upper panel) and Giordan Lighthouse, Malta (lower panel).

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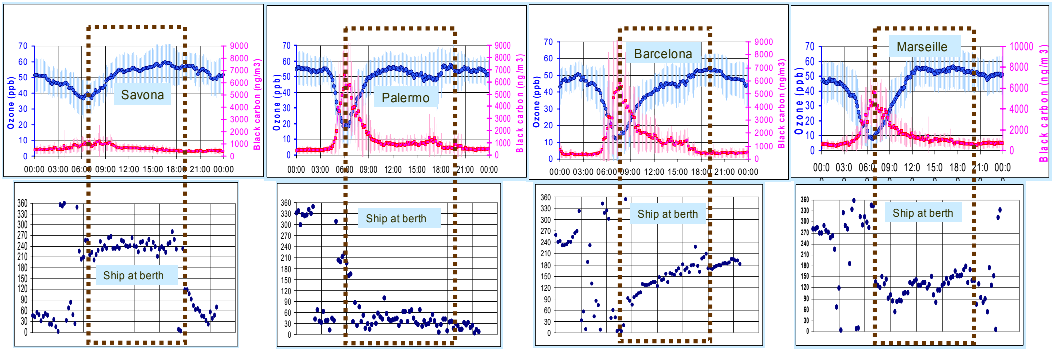

Fig. 6. The averaged diurnal variation of O_3 and BC concentrations (upper figures) at the ports of Savona, Palermo, Barcelona and Marseille, together with the change in the wind direction for a typical day with sea breeze (lower figures) for days with sea breeze circulation.

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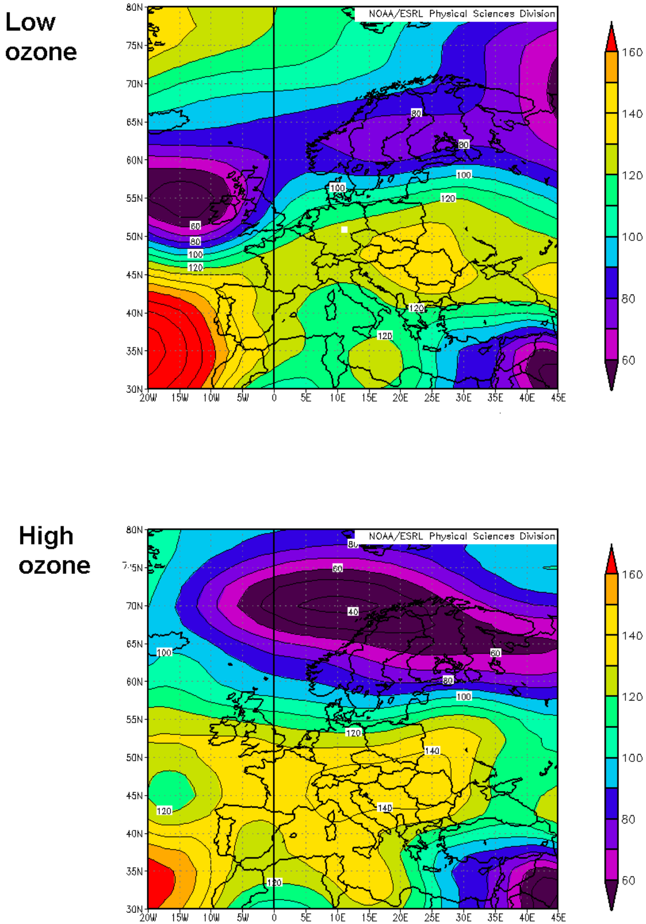

Fig. 7. a) Composite maps of the geopotential height for the "High" (lower) and "Low" (upper) ozone episodes at 1000 hPa.

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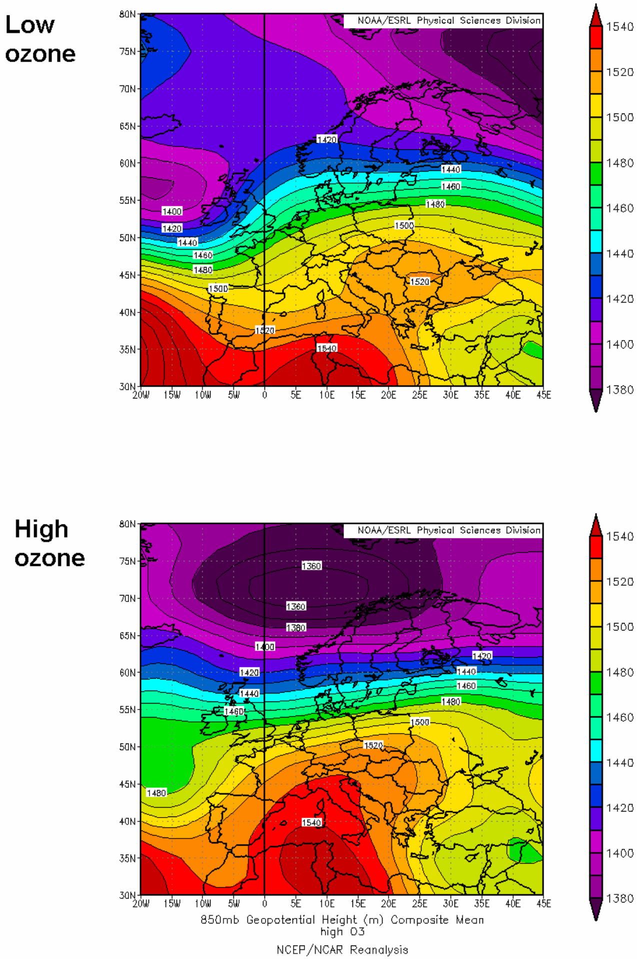

Fig. 7. b) Composite maps of the geopotential height for the “High” and “Low” ozone episodes at 850 hPa.

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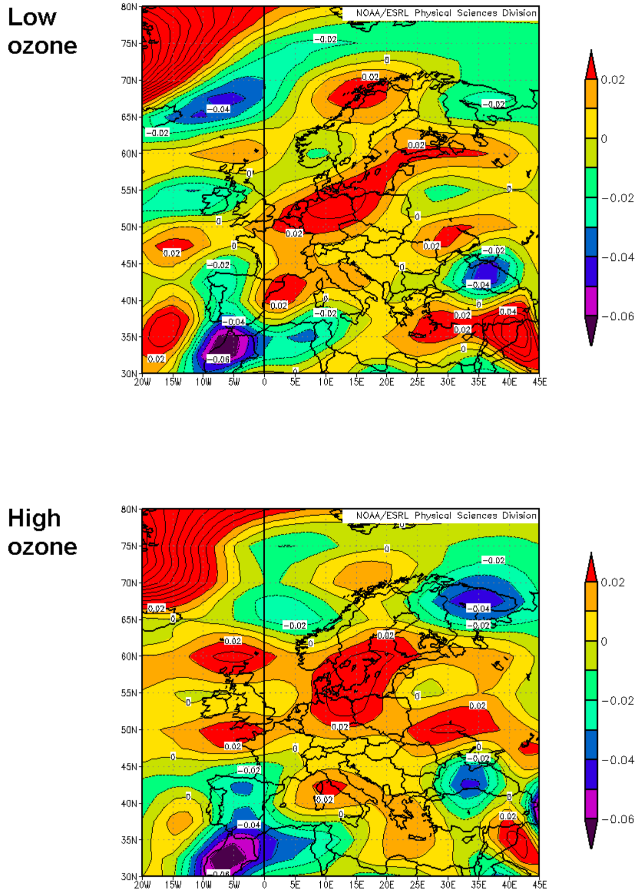

Fig. 8. Composite maps of the vertical velocity (omega) in Pa/s for the "High" and "Low" O_3 episodes at 1000 hPa.

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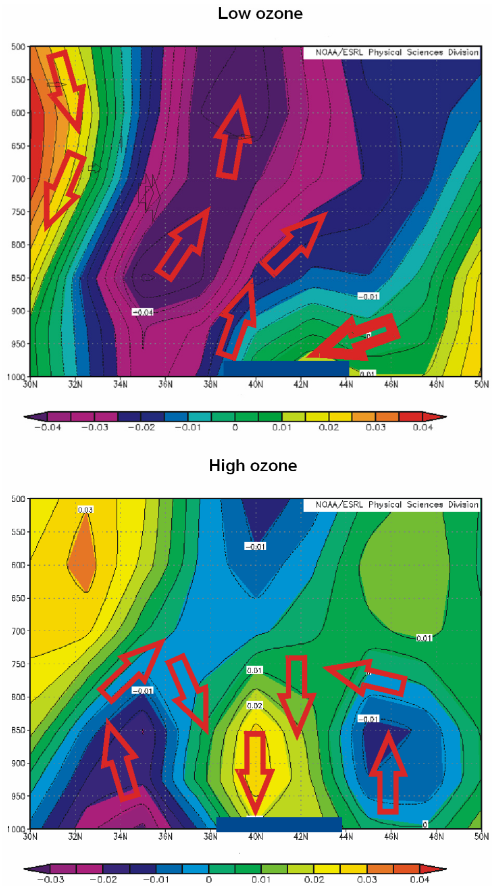

Fig. 9. Composite maps for the vertical velocity (omega) in Pa/s – south-to-north vertical cross section at longitude of 7° E for the "High" and the "Low" ozone groups. The sea is marked by the thick blue line; red arrows indicate direction of the air motions.

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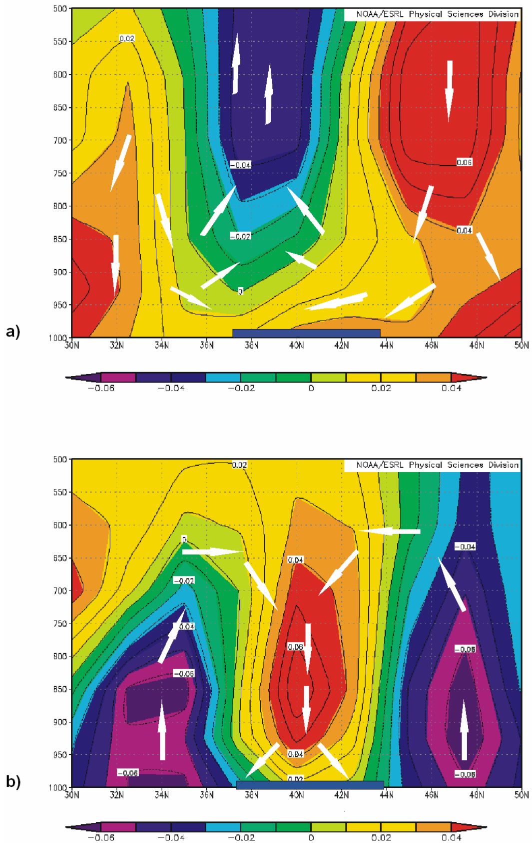

Fig. 10. Composite maps for the vertical velocity (omega) in Pa/s along the south-to-north vertical cross section at longitude of 7° E for the "High Ozone" group: **(a)** 06:00 UTC **(b)** 18:00 UTC. The sea is marked by the thick blue line; arrows indicate direction of the air motions.

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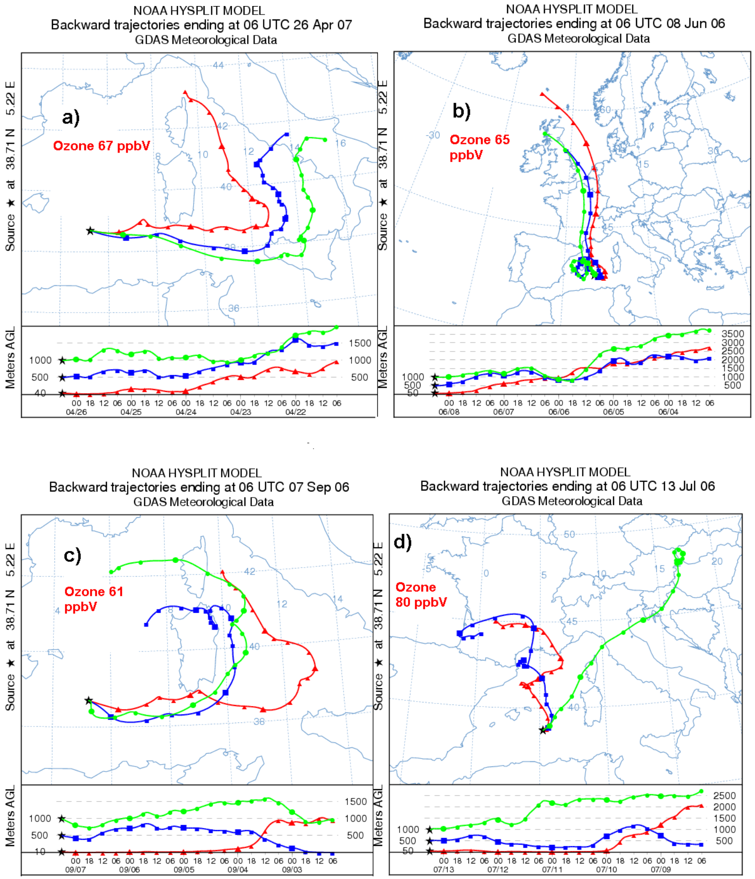

Fig. 11. 5-day back trajectories arriving at Costa Fortuna on the route between Tunis and Palma de Mallorca, arriving at 50 m, 500 m and 1000 m above sea level for four "High Ozone" episodes.

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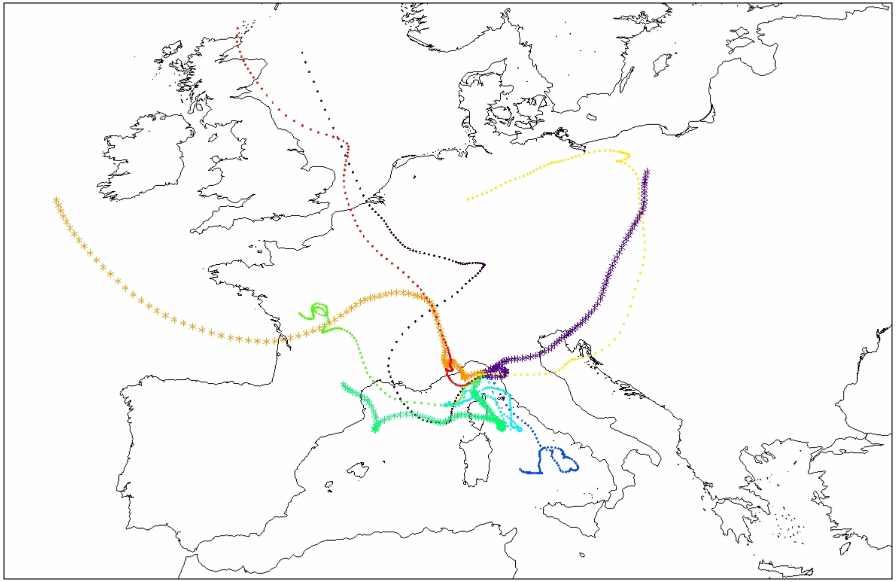

Fig. 12. Backtrajectories for ozone levels higher than 60 ppbV, summer 2006, at the "hot spot" after Savona (see discussion in text). The three trajectories in larger characters are for ozone levels higher than 80 ppbV.

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