Photooxidant dynamics in the Mediterranean basin in summer: Results from European research projects

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Abstract. Most of the Mediterranean Sea is surrounded by mountains 1500 m or higher. Their east and south facing slopes favor the early formation of upslope winds, reinforcing the sea breezes. These slopes also act as orographic chimneys which link the surface winds directly with their return flows aloft, creating recirculations. To characterize the dynamics of pollutants in the Mediterranean basin and to compose a mosaic of the atmospheric circulations involved, the European Commission (EC) supported the following projects: (1) meso-meteorological cycles of air pollution in the Iberian Peninsula (MECAPIP), 1988–1991, intended to document the atmospheric circulations over the Iberian Peninsula; (2) regional cycles of air pollution in the west central Mediterranean area (RECAPMA), 1990–1995, which extended the characterization from the Atlantic coast of Portugal to Italy; and (3) south European cycles of air pollution (SECAP), 1992–1995, for the whole of the basin. The level of interpretation of the data and the elaboration and validation of working hypotheses across the basin have followed, in turn, with the corresponding lags in space and time. The purpose of this paper is to present a summary (to 1995) of the documented, as well as the postulated, processes involved. The MECPAPI and RECAPMA projects have shown that stacked layer systems form along the Spanish Mediterranean coasts, 2–3 km deep and more than 300 km wide, with the most recent layers at the top and the older ones near the sea. These act as a reservoir for aged pollutants to recenter land the next day, and tracer experiments have shown that turnover times are from 2 to 3 days. During the night, part of this system drifts along the coast. Under strong insolation these circulations become “large natural photochemical reactors,” where most of the NO, emissions and other precursors are transformed into oxidants, acidic compounds, aerosols, and O₃ (exceeding some EC directives for several months). Finally, the preliminary analysis of the data obtained in the SECAP project supports the hypothesis that pollutants emitted in the Mediterranean basin could be transported toward the Intertropical Convergence Zone, located along northern Africa in summer, and pumped directly into the upper troposphere. If this is verified, the Mediterranean basin could be one place where all the links from the local to the global scales could be identified and documented.

Introduction and Background

Meteorological processes across the entire Mediterranean in summer are dominated by two large, semipermanent weather systems located at each end of the basin, as illustrated in Figure 1. At the western edge is the Azores anticyclone, and over the eastern borders is the low-pressure system which extends from the Middle East to the whole of southwestern Asia (i.e., the monsoon system). As a result of this large-scale pressure configuration, pressure differences of up to ~30–40 hPa can develop between the Atlantic coast, west of Portugal, and the Arabian Peninsula [Meteorological Office, 1962]. “Classic” frontal systems approaching from the Atlantic travel mainly north of the Alps. Approximately midway between the two major weather systems, the “average flow” is diverted southward over the Great Hungarian Plain and farther south, onto North Africa via the Adriatic and Ionian Seas and/or the Black Sea, Aegean Sea, and the Levantine basin.

The weather, the surface properties, and the mountain ranges which surround the basin create the development of strong sea breezes, upslope winds, or combinations of these, depending on the mountain-coast geometry. The development of “mountain gap winds,” as a result of either “subsidence aided” drainage flows and/or large-scale channeling [Scoiter, 1952], is also a fact in the entire region. Finally, the same conditions also favor the formation of extensive and deep convective cells and/or thermal lows over the major landmasses. Thus subordinate to the larger structures, other mesoscale systems develop during the day with important compensatory subsidencies, that is, the Iberian, Italian, and Anatolian thermal low systems, which can strongly modify the regional flows during the day. As an example, Figure 2 illustrates the development of the thermal low over the Iberian Peninsula on a summer day.

The thermally driven mesoscale processes become semiper-
Plate 1. (top) Vertical ozone distribution and (bottom) wind field along the transect (H→G) as documented by an instrumented aircraft in the afternoon of July 24, 1989. The actual aircraft path is shown by a dotted line, and the ground track appears in the maps at the left. At the time of the flight presented, the coastal cell has reached ~100 km inland with ozone mixing ratios of more than 90 parts per billion by volume (ppbv) over the coastal mountains. Two return layers can be identified over the coast, and the O₃ injection probably reached elevations higher than 2500 m (see Plate 2). A column with lower O₃ values can be observed separating the coastal and central convective cells (Figure 5).
manent with marked diurnal cycles at both ends of the Mediterranean basin, where the dominance of the two major pressure systems is well established. This behavior occurs for the Anatolian and Iberian thermal lows. However, the central basin, including the Italian and to some extent the Hellenic regions, can be considered as the natural boundary between the Azores high-pressure systems and the monsoon low-pressure systems and their induced effects. For all intending purposes this basin is located in the corridor between the "cogwheels" of the major weather systems. Thus any change in the pressure patterns associated with these could significantly, and abruptly, shift the balance between the prevailing mesoscale processes over the whole of the central Mediterranean basin. It could also determine whether the thermally induced local flows develop or are overridden by synoptic processes.

In southern Europe the experimental evidence accumulated to 1986 had shown that air quality problems were governed by meso-meteorological processes with marked diurnal cycles and space scales of tens of kilometers [Lalas et al., 1983; Millán et al., 1984, 1987]. Starting in 1979, correlation spectrometer (COSPEC) tracking of SO$_2$ plumes from tall stacks in several regions of Spain in summer had also indicated that the formation of thermal lows was associated with the convergence of surface winds from the coasts toward the interior of the peninsula and with high levels of O$_3$ along the Spanish Mediterranean coast [Martin et al., 1991; Millán et al., 1991]. Those observations also raised the prospects of large-scale (deep) convection over the central plateau and compensatory subsidence over the surrounding seas. Analysis of the available data also confirmed the diurnal period of the processes involved and extended the awareness of their spatial scales from tens to a few hundred kilometers or more.

This evidence also formed the basis for the first European Commission (EC) scientific efforts focused on Mediterranean air pollution dynamics. The project meso-meteorological cycles of air pollution in the Iberian Peninsula (MECAPIP), 1988–1992, was aimed at studying the origin and evolution of the atmospheric circulations responsible for the observed behavior over the Iberian Peninsula [Millán et al., 1992]. The projects regional cycles of air pollution in the west central Mediterranean area (RECAPMA), 1990–1992, and south European cycles of air pollution (SFCAP), 1992–1995, followed to characterize the continuity of those processes over the western Mediterranean and Atlantic seaboard and over the whole Mediterranean basin, respectively. The purpose of this paper is to review some of the findings through 1995.

Figure 2. Surface pressure maps for July 25, 1989, illustrating the development of the Iberian thermal low at the synoptic scale.
Results From the MECAPIP Project: Effects of the Iberian Thermal Low

The field deployment area and flight tracks for the MECAPIP project are shown in Figure 3. The following processes were documented over the Iberian Peninsula in summer:

1. During the day the sea breezes combine with upslope winds to transport coastal pollutants inland (up to $\sim 60$ 100 km on the east coast), while at the leading edge of the breeze front a large fraction of these pollutants are injected in their return flows aloft (Plate 1) at heights ranging from 2 to 3 km.

2. Once in these upper layers the pollutants move back toward the sea, and the compensatory subsidence creates "stratified reservoir layers" of aged pollutants, stacked up to $\sim 2$-3 km high, along the coast over the sea (Plate 2).

3. These layers act as reservoirs and retain ozone from one day to the following days. The next morning the lowermost layers are drawn inland by the sea breeze, and the aged pollutants can react with new coastal emissions.

4. Tracer experiments indicate that the recirculation times from first emission on the coast, during the sea breeze, to their reappearance with the sea breeze (i.e., as if originating from the sea), are of the order of 2-3 days [Millán et al., 1992].

5. All together, these mechanisms can be considered to form "a large photochemical reactor" which operates along the coasts almost every day from spring to fall. For periods of several months it can generate ozone levels 2-3 times higher than EU directives for damages to vegetation (Figure 4).

6. In these processes some of the coastal pollutants are also carried farther inland along the natural passes that connect the coasts with the central plateaus.

7. Over the central plateau(s) one or various deep convective cells develop, easily reaching 3.5-6 km in height, and inject aged pollutants, from either the Madrid area and/or those transported previously from the coastal areas, directly into the middle troposphere [Millán et al., 1996].

Deduced and Modeled Structure Within the Iberian Thermal Low

In the planning stages of the MECAPIP project it was assumed that the wind field within the thermal low would consist of a combination of several thermal circulatory cells which blended into an "organized" circulation at the peninsular scale during the day. Because the sea surface temperature is the least affected by the diurnal cycle of solar heating, it provides the most stationary energy sink for the overall process. As a result, the circulations which govern the growth of the whole system are the sea breezes. These were expected to grow in intensity and extension at the expense of upslope winds and other weaker, land-based circulatory cells, which would become incorporated into an ever growing circulatory system.

Surface and airborne data show that by late afternoon the E-W cross section of the Iberian thermal low system may consist of several circulatory cells. In the east a coastal cell combines the sea breezec and upslope winds, reaches depths of up to $\sim 3$ km, and extends $\sim 80$-100 km inland (Plate 1). A second cell forms over the central plateau and Madrid area, sheltered by the south facing slopes of the central range, and its convective activity reaches depths of $\sim 3.5$-5 km. Finally, another coastal cell could be expected to develop over Portugal and the Atlantic coast. Compensatory subsidence occurs between the main convective cells, as shown in Plate 1 and illustrated with modeling results in Figure 5. These results are summarized in Plate 3, which shows an idealized two dimensional section of those circulations.

Modeling of these processes has been initiated within the SECAP project using the regional atmospheric modeling system (RAMS) [Pielke et al., 1992]. Although the synoptic maps may show a closed loop of low pressure, the structure within the Iberian thermal low cannot be contemplated in the classic context of a meteorological low-pressure area. Figure 6 shows the results of the simulation for July 20, 1989. The structure is
Plate 2. Vertical ozone distribution along 450 km of the Spanish east coast as documented by an instrumented aircraft in the early morning of July 25, 1989. (top) Outgoing flight between 0410 and 0511 UTC, over the sea. (bottom) Return flight between 0518 and 0623 UTC, over the coastal plains. The separation between the two flight tracks was, on the average, ~50 km. The observed ozone distribution results from the injection of pollutants in the return layers of the breezes the previous day (Plate 1). At ~300 km from the origin of the flight the venting of cleaner continental air via the Ebro valley appears as a hole in the O₃ distribution.
Figure 4. Average ozone concentrations (24 hours) at two inland stations (Morella ~100 km, Corachar ~80 km) on the Spanish east coast. The European Commission Directive for phytotoxicity to plants (65 µg m⁻³, 24 hour average) is exceeded for 6–7 months in the year, and by a factor of nearly two during June and July.

Plate 3. Schematic cross section of the Iberian thermal low circulations as deduced from the meteorological and air quality observations.
important factor in the development of these thermal circulations and their asymmetry, is that the Azores anticyclonic subsidence becomes weaker (uncompensated) across the Iberian Peninsula from the Atlantic to the Mediterranean. Solar heating and the formation of the thermal low further weaken the processes of general subsidence over the Iberian Peninsula during the day and produce a dynamic compensation over the Mediterranean and Atlantic, which intensifies the sinking process over the colder waters.

Over the Portuguese seaboard and northern Spanish coast the sea surface temperature is cooler, and a strong dynamically compensated anticyclonic inversion dominates. Subsidence compensatory to the Iberian thermal low further increases the observed inversion strength and its rate of sinking during the day, as shown in Figure 9. This is accompanied by an increase in surface wind speed, and it is not yet known whether layers of aged pollutants form along the Portuguese coast. A transition region between the dynamically compensated and uncompensated subsidence appears to exist over the south of Portugal and Gibraltar area. As Figures 6, 7, and 8 also show, processes in this region could be instrumental for the venting onto the central Atlantic of photooxidants generated in the western Mediterranean basin.

A similar compensating situation occurs over the warmer waters of the Mediterranean Sea, as also shown in Figure 9. In this region the anticyclonic subsidence is weaker than over the Atlantic, and during the night an inversion of \( \approx 4^\circ \) at \( \approx 1500 \) m builds up over the main plateau and coastal plains. This subsidence inversion is easily and rapidly destroyed by solar heating during the day [Millán et al., 1992, Figure 13b] along with the development of the layering and injection mechanisms described.

To document the continuity of the layers over the western Mediterranean, aircraft profiling above the Balearic basin was conducted during the SECAPMA project in 1991. Figure 10 shows the general deployment area for this project, the aircraft flight track, and one of the profiles obtained south of Majorca, \( \approx 300 \) km off the Spanish east coast. These aircraft profiles documented strong levels of subsidence, that is, sinking speeds of 10–15 cm s\(^{-1}\) lasting several hours in the afternoon. This also suggests that compensatory subsidence in most coastal circulations around the western Mediterranean could extend to the whole of the basin.

**Long-Range Transport Scenarios, the Initial Mosaic Results From the SECAP Project**

For each of the main Mediterranean basins the following interregional and long-range transport scenarios have now been identified.

**Western Mediterranean Basin and Atlantic Seaboard**

Two scenarios have been identified for the transport of photooxidants and other pollutants within and out of the western Mediterranean basin. The most significant aspects are that the resulting transport takes place at different heights and in almost opposite directions and that the resulting tropospheric O\(_3\) anomalies, as shown in Plate 1, can be detected by satellite [Fishman et al., 1990].

The first scenario involves the pollutants injected 3–5 km
over the Spanish central plateau directly into the middle troposphere. For example, Figure 10 (bottom) shows $O_3$ layers at or above $\sim 3.5$ km, and the winds at the time and height indicate that the $O_3$ had been injected over the Spanish central plateau the previous day. On the basis of prevailing winds at those heights the pollutants can move off within the sector which covers an area from the SE to the NE of Spain. These could be responsible for the long-range transport of photooxidants toward central Europe and explain the recent trends in high $O_3$ values recorded at high observing stations in the Alps on summer nights [Sandroni et al., 1994], not easily ascribed to upslope transport from the surface layer.

The strong levels of subsidence documented over the Balearic basin also raise some questions about the continuity and long-range transport of the upper layers when they drift over the Balearic basin, since at those sinking speeds they could be brought down within the reach of the coastal recirculations of any downwind land masses (Italy and possibly North Africa), 2-3 days later. The ultimate fate or continuity of the upper layers, whether they move toward the Alps in the NE direction or drift toward the east to SE and become recirculated within the Balearic basin must still be determined.

The second scenario involves the “reservoir layers” created along the Mediterranean coast. The key components are the semipermanent high(s) pressure area over the colder waters in the Gulf of Lions, the mountain ranges which surround it, and the coastal processes.

During the day the return flows to the coastal circulations renovate the upper reservoir layers, while the lower ones are drawn inland with the sea breeze. Thus the effective flow near the surface is mostly perpendicular to the coast. During the night, however, anticyclonic subsidence within the orographically confined western Mediterranean basin generates surface winds (up to a depth of $\sim 700-1000$ m) which are forced to flow along the Spanish Mediterranean coast. This produces strong mountain gap winds at the Strait of Gibraltar, that is, the Tarifa winds [Soreer, 1952]. The reservoir layers formed during the day move along with this flow and can reach the Atlantic after several cycles of recency and layering during the day, followed by nocturnal transport along the coast.

By the time the layer system reaches Gibraltar, part of the pollutants could be above the trade winds at or above the main subsidence level of the Azores high. These processes could be favored by a higher orographic injection level provided by the south facing slopes of the Sierra Nevada range (3000–3482 m

Figure 6. (top) Synoptic surface pressure map and (bottom) modeled (near) surface streamlines for July 20, 1989, at 1300 UTC. The resulting flow is dominated by a series of convergence lines with an almost closed structure, following the major mountain ranges. Venting of the Mediterranean onto the Atlantic via the Strait of Gibraltar is weak.

Figure 7. (top) Synoptic surface pressure map and (bottom) modeled (near) surface streamlines for July 25, 1989, at 1800 UTC. The resulting flow appears to be dominated by a line of intense convergence in the shape of a “U,” and evening storms developed along the bottom part of the U. On this day the venting of the Mediterranean onto the Atlantic via Gibraltar is also weak.
peaks) in southern Spain. This transport mechanism, if verified, could explain some of the high $O_3$ levels at the Izaña background station in the Canary Islands in summer (see below), not easily attributed to tropopause folding over the Atlantic. The pollutants remaining in the lower layers could also travel along the African coast with the trade winds. This scenario is presently being modeled, however, and has yet to be verified experimentally.

Finally, transport of $O_3$ from other European regions, via France at heights between 1500 and 2000 m, was also documented over the northern coast of Spain during the MECAPIP project. These data are presently being analyzed (G. Gangolli, personal communication, 1990). It could imply that some of the pollutants convectively injected over France, the Low Countries, and part of Germany, could be also transported along the northern Spanish and Portuguese coasts toward the central Atlantic. As Figures 7, 8, and 9 show, these air masses sink as they move along the Portuguese seaboard during the day. On their way to Izaña and farther along the African coast, these air masses could join others vented out of the Mediterranean basin.

Central and Levantine Mediterranean Basins

Over the Italian Peninsula, storms develop almost every evening along the Apennines in summer. These appear to result from the convergence of the sea breezes from the Adriatic and Tyrrhenian Seas [Cantini and Gandino, 1977]. The transport of photooxidants inland from the coast, past Rome and farther inland, has also been documented during the RECAPMA and SECAP projects, and layer-forming mechanisms along the Italian coasts, involving sea breezes, upslope winds, and their compensating flows are also likely. Their overall displacement along the coast, as a result of the prevailing pressure gradient, is expected to be to the southeast. However, no experimental data exist to verify this. Information is also lacking to document any pollutant behavior during the transition from the regime dominated by the sea breeze and upslope winds to the evening storm cycle.

Figure 8. (top) Synoptic surface pressure map and (bottom) modeled surface streamlines for July 26, 1989, at 1800 UTC. Although the synoptic pressure field seems very similar to Figure 7, the resulting flow is dominated by a series of convergence lines without a clearly recognizable structure. This may be a result of wetter ground in the areas where it rained the previous day. In this occasion, venting of the Mediterranean onto the Atlantic via Gibraltar is very strong.

Figure 9. Atmospheric temperature and wind soundings over the Atlantic (Sines, Portugal) and the Mediterranean coast (Castellón, Spain) on July 23, 1990, showing subsidence compensatory to the Iberian thermal low during the day.
Finally, within the AVICENE project “Transport and Transformation of Air Pollutants From Europe to the Eastern Mediterranean,” and during the SECAPs 1994 summer campaign, an instrumented aircraft tracked the Athens plume moving in a general southerly direction toward the Libyan coast under the influence of strong Aeolian winds [Kilos, 1995]. In a way similar to the winds at Tarifa these are generated by venting of the Black Sea along the Bosporus and Danianelles straits. This process also appears to be a combination of channeling along the Bosporus, reinforced during the day by the compensatory subsidence to the Anatolian thermal low over the Black Sea. Figure 11 shows modeling results obtained by the same team of the surface wind fields over the entire Mediterranean basin for a typical summer day (July 2, 1994, 1200 UTC).

**Additional Considerations Concerning Long-Range Transport Mechanisms on the Mediterranean Basin in Summer**

Regarding the long-range transport of aged air masses within and out of the entire Mediterranean basin, it is important to emphasize the following: (1) during the summer the sea surface temperature (SST) is warmer over the Mediterranean but significantly lower than over the surrounding land areas during the day; (2) the convective and orographic processes that were mentioned occur during the warmer part of the day; (3) all of those processes lead to layering of the aged pollutants, that is, being trapped in strata which are essentially uncoupled from each other and from the surface; and (4) over the Mediterranean basin most of these layers are generated directly along the coastal mountain ranges and/or are advected toward the sea if originated farther inland. From point 4, it follows that (1) the potential temperature of these layers is higher than the SST; and thus any further compensatory subsidence of these layers over the sea, simply increases their stratification, and (2) the transport in stratified layers over the sea is essentially frictionless and unimpeded during the day or night until reaching any strong convective activity over a warm (er) surface.

It should also be recalled that the prevailing winds in the stratum from 1500 to 2000 m altitude can range from 10 to 20 m s$^{-1}$ at this time of year and that the average N-S extent of the Mediterranean Sea is $\approx 800$ km. It follows that the transport during one night at that height, although not necessarily in the N-S direction, is of the same order of magnitude as the N-S distance across the Mediterranean basin.

**Summary of Middle to Upper Tropospheric Injection Mechanisms in the Mediterranean Basin**

On the basis of the available evidence and the postulated processes, Plate 5 shows a schematic of the proposed circulations for the whole Mediterranean basin in summer. The following mechanisms can be considered.

**Reservoir/Transport Layers in the Lower to Middle Troposphere (to $\approx 2.5$ km)**

Experimentally documented along the Spanish east coast, these layers are produced by thermally driven land-sea processes and their return flows. These processes are favored by the existence of coastal mountains with slopes oriented east and south, which act as orographic chimneys. During the day the layers are convectively unstable over the coastal areas with turnover times of the order of 2-3 days. During the night the layers travel along the coast uncoupled from the surface until the following day. These processes are favored along the east and south Spanish coasts, Italian coasts, south Turkish coasts, and the Lebanon and Israeli coasts, they could occur also over the northwestern African coast.

**Direct Middle Troposphere Injection (Up to $\approx 5$ km)**

Experimentally documented over the Spanish central plateau and their continuity over the western Mediterranean, injection can result from diurnal convective cycles over the larger and dryer land areas and/or from orographic injection, that is, the South facing slopes of mountain ranges higher than 3000 m. It can be more important over the drier slopes in late summer and can trigger storms. If condensation occurs, heterogeneous chemistry would become important. The stratified layers move away with the synoptic flow at their height, mainly during the night. Large-scale subsidence is likely if they drift...
over the Mediterranean Sea. These processes are favored over the Alps, along the Apennines, and over the Spanish and Turkish Plateaus. It could also occur over the Atlas Mountains and over other regions inland of and along the African coast.

Direct Upper Troposphere/Lower Stratosphere Injection (Up to \( \sim 10-14 \) km)

At the working hypothesis level, injection could occur as a result of convective pumping with cumulus congestus developing in the late afternoon; if rain storms develop, some pollutants may be rained out. In any case, heterogeneous chemistry will be important in these processes. The injected fraction drifts away with the upper flow. In some areas the development of evening storms may be an integral part of a sea breeze and/or upslope wind system; for example, in the case of the Apennines in central Italy, they may occur almost everyday. They also tend to be landlocked to specific land features. In the case of the Atlas Mountains and inland from the Egyptian and Libyan coasts, the sea breezes, aided by the overall synoptic conditions, may flow toward the Intertropical Convergence Zone and pump the aged pollutants directly into the upper troposphere.

Plate 4. Average integrated tropospheric ozone as deduced from satellite measurements for the June to August period [Fishman et al., 1990].

Plate 5. Schematic summary of the observed and postulated circulations for the whole Mediterranean basin in summer.
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