OZONE FORMATION DOWNWIND AN INDUSTRIAL COMPLEX IN THE WESTERN MEDITERRANEAN

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ABSTRACT

It is widely known that the formation of ozone (O_3) is chemically linked to the emissions of nitrogen oxides (NOx) and volatile organic compounds (VOC). This chemical interdependence is highly complex and gives rise to non-linear and coupled pollutant formation processes. In the present study, airborne measurements of sulfur dioxide (SO_2), NO_x, total reactive oxides of nitrogen (NOy), and O_3 taken from an instrumented aircraft (IFU HS-125) within MECAPIP-1989 project are presented and analyzed. The experiment was carried out in the Castellón industrial area, located on the Mediterranean coast of the Iberian Peninsula. Morning near field transects show a strong ozone titration effect downwind the photochemical plume. Moreover, while afternoon measurements still depict ozone consumption near the emissions area, ozone net formation is observed in the mid-field of the Castellón industrial complex. Ozone production efficiencies are derived from the aircraft measurements. This analysis shows a nearly constant ozone production with increasing distance from the industrial area for the morning period. On the other hand, O_3 formation reaches a maximum downwind the emissions complex for the afternoon hours. The marked coastal distribution of the emissions within this area, in addition to the atmospheric dynamics, dominated by coastal-valley mesoescale circulation systems, combine in a way that favors the formation of photochemical pollutants. Furthermore, due to the dynamically driven enhancement of air mass residence times, this particular location offers the unique possibility for studying the influence that local conditions have on the way oxidant production occurs.

INTRODUCTION

The formation of ozone is chemically linked to the emissions of nitrogen oxides (NOx) through oxidation of gaseous precursors such as nitrogen dioxide (NO_2) and volatile organic compounds (VOC). Once released into the atmosphere, the NOx compounds undergo a series of photochemical transformations involving VOC that form a variety of oxidants (e.g., hydroxyl radical, OH). These oxidants react with NO_x, and VOC and ultimately lead to the formation of ozone and particulates. This chemical interdependence reveals some of the complexity of the photochemical system that gives rise to highly non-linear and coupled pollutant formation processes.

We will focus our study on the western Mediterranean coast, particularly on the Castellón coastal area on the Mediterranean coast of the Iberian Peninsula as a typical representative location of the Western Basin. This location is surrounded by a variety of mixed industries and encompasses an increasingly growing number of transport vehicles, showing features of an urban-industrial environment. The marked coastal distribution of these emissions in addition to the atmospheric dynamics, leading to residence times of the

order of a week to ten days, combine in a way that favors the formation of photochemical pollutants. Furthermore, due to this enhancement of air mass residence times, this particular location offers the unique possibility of studying the influence that local conditions have on the way oxidant production occurs.

In this work we analyze and interpret airborne measurements of key pollutants such as ozone (O_3), total nitrogen oxides (NOy) and sulfur dioxide (SO_2) that have been performed within the framework of the Mesometeorological Cycles of Air Pollution in the Iberian Peninsula (MECAPIP) project. This project revealed some key issues regarding the transport and dispersion of air pollution in Spain during summertime [1]. The role of the Iberian Thermal Low on the reinforcement of the sea breeze and the subsequent transport of polluted air masses from coastal to inland areas with significant injection of contaminant into return flows has been verified. Furthermore, once injected into the return flows of the combined sea breeze and up-slope winds, the air masses drift back towards the sea forming stratified layers at different heights. Moreover, the MECAPIP project providing measurements of fundamental photochemical contaminants allows the study not only of the transport and dispersion but also of the chemical processes that give rise to the formation of pollutants in coastal areas of the western Mediterranean as presented in this paper.

METHODOLOGY

Meteorological and chemical data have been measured from an instrumented aircraft (Hawker Siddeley 125 F400B (HS-125)). Two windows of the airplane have been replaced with plates equipped with four air inlets to perform the air sampling. Navigational parameters such as the position information have been acquired by the navigation system and directly stored whereas the speed data have been fed to the on-line calculation algorithm from the horizontal wind vector. Moreover, static temperature, relative humidity and horizontal wind vector have been continuously measured aboard the aircraft.

All instruments sample air from a pressure-controlled manifold supplied by one of the air inlets. The pressure in the manifold was held constant to 600 hPa, giving a flow of 50 L (STP) min^{-1}. The chemical instrumentation is described in Table 1. The calibrations of the chemical monitors have been carried out with the aircraft on the ground. Most of the calibrations are multipoint calibrations using permeation devices and flow-controlled diluted calibration gas mixtures. For the SO_2, O_3, NO, and NOy monitors the calibration has been based on the linear slope of the corresponding calibration plot. On the other hand, the signal from the fast chemiluminiscence ozone instrument has been normalized to the concentrations determined by the UV photometer during the flight.

On July 27, 1989 two instrumented flights took place around the Castellón industrial area, located on the Mediterranean coast of the Iberian Peninsula. The first flight covered the near field of the industrial complex (Figure 1a) and lasted from 11:42 to 12:23 UTC while the second one comprehended the midfield of the industrial complex (Figure 1b) and continued from 15:09 to 15:55 UTC. The aircraft followed a zipper pattern roughly following the terrain, the height above the surface was maintained between 400 and 500 m, increasing this altitude when reaching the edge of the mountains. Airborne measurements of tracers, originally injected into the 150-meter Castellón power plant stack, using grab samples ensured that these flight patterns included and followed up the geographical evolution of air pollutants released from the industrial complex.

Species	Record	Method	Detection Limit	Accuracy [%]	Precision [%]	Time Resolution [s]
NO	Cont.	Chemilumin.	20 pptv	15	5 %	1
NOy	Cont.	Chemilumin.	40 pptv	15	5 %	1
O_3	Cont.	Chemilumin.	2 ppbv	10	5 %	1
O_3	Cont.	UV- absorpt.	2 ppbv	10	5 %	30
SO_2	Cont.	UV-fluor.	0.1 ppbv	10	5 %	5

Table 1: Description of the chemical instrumentation

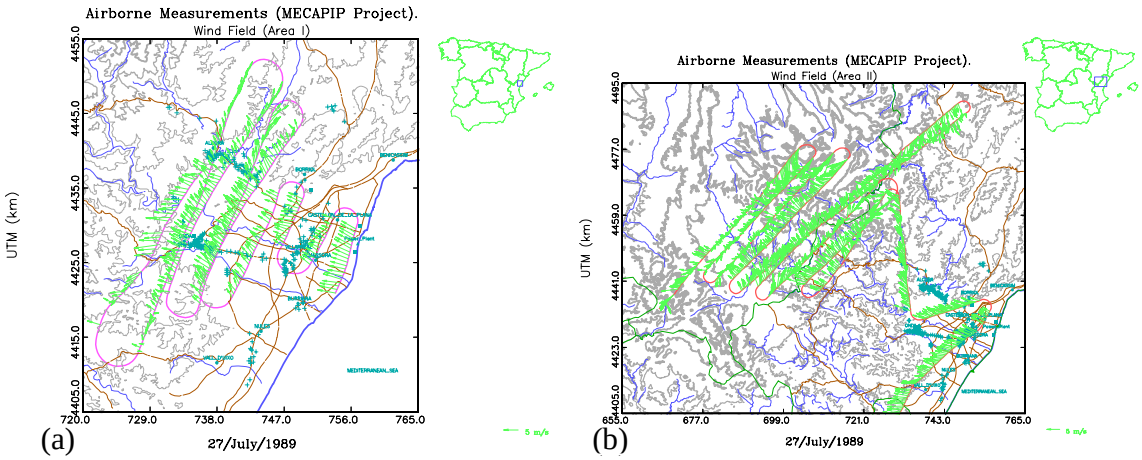


Figure 1: Flight pattern and wind vectors for near field (a) and midfield (b) regions downwind Castellón. The map of Spain on the sides shows the areas covered by the flights.

METEOROLOGICAL CONDITIONS

Airborne measurements have been carried out under summertime atmospheric conditions, associated to the presence of an Atlantic high-pressure system, well established at mid-latitudes and extending to central Europe and the Western Mediterranean. Moreover, a high-level pressure ridge reinforces this system. Throughout the day, thermally driven low pressure develops over the Iberian Peninsula giving rise to a southerly gradient over the Eastern shore of Spain. Under these conditions of atmospheric stability, local mesoscale circulations determine the surface level wind and limit the vertical diffusion.

The early morning vertical profile taken over the coast near Castellón evidences a strongly stratified feature with a weak drainage flow confined to the first 40-50 meters. Three layers are present above it (within the measured 800 m), with stratified layers traveling uncoupled along slightly different directions but generally blowing from the third quadrant. As daytime evolves, the well-developed sea breeze enters further inland, reaching a maximum height of 750 m (13 UTM sounding) with all its stratified layers coupled and veering from easterly to southeasterly. Moreover, the mixing height increases from 200 m at 10 UTM to about 350 m at 13 UTM and falls in the late afternoon, recovering its highly decoupled vertical structure.

Under these conditions, the pollutants measured during the flights have been emitted into an atmosphere relatively confined by the presence of at least one inversion layer. This coastal thin layer extends to about 800 m at its maximum development stage. It is expected, however, to grow higher inland. During the airborne sampling, the wind field

pattern shows a well-defined easterly circulation along with channeling of the flow thought the Mijares river and Rambla de la Viuda basins. The sea breeze front is evident over the mountain slopes and a convergence line is developing at about 30 km onshore. Nevertheless, this wind field distribution, being strongly conditioned by the orographic features of the basin and evolving throughout the day, is not uniform or stationary [1].

RESULTS AND DISCUSSION

Figure 2 shows the observed SO_2, NOy and O_3 mixing ratios corresponding to the near field of the industrial area. The SO_2 plume shows a decrease in peak values and a widening effect as a function of distance from the source (Figure 2a). This is mainly attributed to a combination of dispersion, chemical conversion to sulfate and dry deposition. NOy shows a similar shape to that of SO_2, however NOy undergoes solely dry deposition and dispersion (Figure 2b). On the other hand, a strong titration effect is evident from the decrease in O_3 levels downwind of the emissions complex as depicted in Figure 2c. Afternoon measurements show similar patters as those observed for noon near field data for SO_2 and NOy (Figures 2 d and e). However, while afternoon measurements still depict ozone consumption near the emissions area, O_3 net formation is observed in the mid-field of the Castellón industrial complex (Figure 2f).

In order to describe the formation of ozone downwind the urban-industrial area the concept of ozone production efficiency (OPE) ([2]; [3]) have been utilized. The OPE represents the number of molecules of ozone produced per NOx emitted, as represented by the measured NOy. This quantity has been determined as the slope from an O_3-NOy linear regression. This approach gives an upper limit to the OPE mainly due to the differential loss of NOy with respect to O_3 [4]. Figure 3 represents the O_3 concentrations as a function of NOy for selected portions of the measured data. The selection criterion has been based on the SO_2 measurements to include only portions of the plume that were not affected by sources other than those of the industrial area. As can be inferred from the figure, ozone shows a good correlation with NOy. A negative correlation is observed for the noon flight reflecting the net consumption of ozone in the near field of the source area (Figure 3a). On the other hand, values for OPE range from 5-10 and O_3 molecules per NOy for the afternoon flight. These values are well within those found in the literature for areas downwind urban-industrial areas such as the one under study ([5];[6];[7]). The OPE increases as a function of distance from the sources reaching a peak downwind the sources (Figure 3b, Table 2). This feature has also been described elsewhere ([8]; [3]). In the vicinity of the source, ozone formation is dominated by slow inorganic reactions yielding a low OPE. Further downwind, when dilution and entrainment of biogenic hydrocarbons takes place the O_3 production increases. In this stage NOx is acting as a catalyst for the degradation of volatile organic compounds while actively participating in ozone formation. The last stage is characterized by a decrease in OPE due to the exhaustion of nitrogen oxides and further dilution within the pollution plume. On the other hand, following the approach described in [8], an attempt to take into account the differential loss in NOy with respect to O_3 when calculating the OPE has produced lower values of these quantities (on the order of 4-8). However, this result has not altered the main features of the variation of OPE observed downwind the Castellón industrial complex.

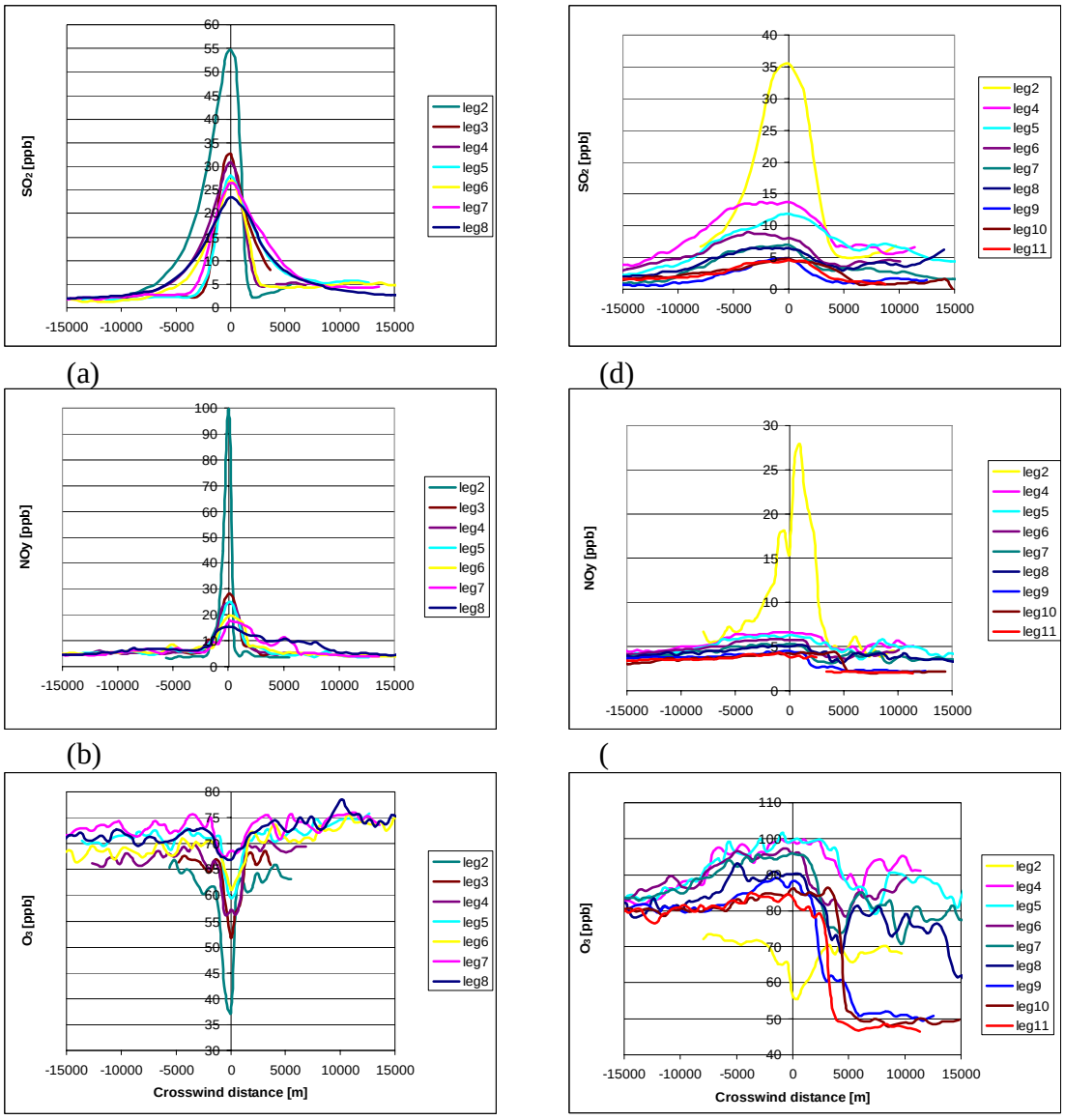
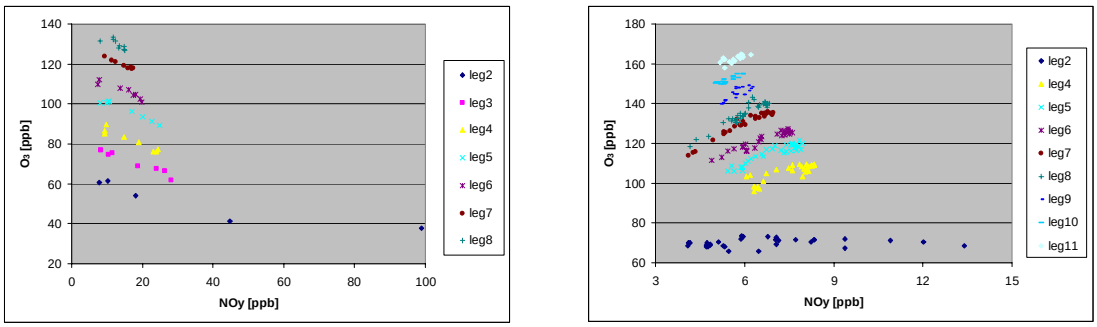


Figure 2: (a) / (d) SO_2, (b) / (e) NOy, and (c) / (f) O_3 crosswind mixing ratios for noon / afternoon flights covering the near field / midfield of the Castellón industrial complex.

Near field flight (noon)		Midfield flight (afternoon)	
Leg #	**OPE**	**Leg #**	**OPE**
2	-0.26 ± 0.07	4	5.5 ± 0.7
3	-0.66 ± 0.06	5	6.9 ± 0.4
4	-0.73 ± 0.09	6	6.8 ±0.4
5	-0.73 ± 0.05	7	9.5 ± 0.4
6	-0.7 ± 0.1	8	10.6 ± 0.7
7	-0.74 ± 0.05	9	10 ± 2
8	-0.8 ± 0.3	10	7 ± 1
		11	6 ± 1

Table 2: OPE values derived from the slope from the O3-NOy linear regressions.



(a) (b)

Figure 3: O_3 vs NOy for each flight leg. Data from legs 3 through 11 are offset 10 ppb from the previous leg value along the vertical axis for clarity.

CONCLUSIONS

Airborne measurements of key photochemical species have been carried out around the area of Castellón, on the East coast of Spain. Ozone production efficiencies have been derived from O_3 and NOy data. The noon near field flight depicts a strong titration effect arising from NO emission sources that inhibit the formation of ozone, as reflected in the negative estimated OPEs. On the other hand, the afternoon midfield sampling shows an increase in OPE with distance from the emissions reaching a maximum downwind of the sources. The high ozone formation efficiencies derived for the afternoon hours evidence the influence of hydrocarbons, of urban or of biogenic origin, over this region. On the other hand, the repetitive atmospheric circulation patterns present in this area facilitate the determination of the transport paths the pollutants emitted at the coast follow and their further downwind detection. Therefore, this particular location offers a unique possibility for studying the influence that local conditions have on the way oxidant production occurs.

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